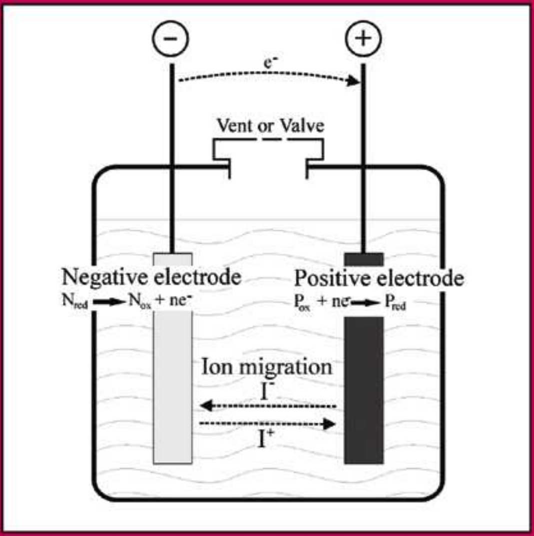

BATTERY TECHNOLOGY HANDBOOK

Second Edition

edited by

H. A. KIEHNE

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Additional Volumes in Preparation

Preface to the Second Edition

There have been many changes since the first edition of the *Battery Technology Handbook*, such as technical progress, worldwide changes in the ownership of the battery companies, and the merging of companies into conglomerates. There were also changes in the group of contributors of this book. Some former contributors are no longer with us, while others retired and were replaced by younger experts. All the chapters have been revised, and some chapters are completely new.

Chapter 1, "Electrochemical Energy Storage," has been revised and expanded by D. Berndt, one of the leading battery experts. Completely revised is Chapter 5, "Battery-Powered Traction: The User's Point of View," by a new author, W. König. Also new is Chapter 8, "The Operation of Batteries," written by U.-C. Stahl. Chapter 9, "Motor Vehicle Starter Batteries," has been revised by, G. Sassmanhausen and E. Nann, describing the coming 48-volt technology for cars. Chapter 10, "High Energy Batteries," is now nearly completely new and was revised by C.-H. Dustmann, based on the former chapter by W. Fischer. Chapter 15, "Batteries, an Overview and Outlook" has been revised by H. A. Kiehne, as has Chapter 16, "Feasibility Study for Appliances" based on the former chapter by W. Raudzsus. Chapter 17, "Maintenance-Free Lead Batteries with Immobilized Electrolyte" is completely new and was written by H. Tuphorn, a well-known expert in the field of valve-regulated lead batteries. A new author and an expert on lithium battery technology, W. Jacobi, has entirely rewritten Chapter 18, "Lithium Batteries: The Latest Variant of Portable Electrical Energy." Following the demand for information on the actual situation in the disposal and recycling of used batteries, the two authors J. L. Fricke and N. Knudsen give an exciting report in Chapter 19, "The Disposal of Portable Batteries."

The book is not meant to be a scientific report on brand new developments, which is the task of events such as scientific conferences and their proceedings, but delivers basic information and instructions on how batteries work.

I thank all the authors for their contributions, and the patience of the publishers, Expert Verlag and Marcel Dekker, Inc., in the completion of the manuscripts. I also thank my wife, Renate Kiehne, who assisted me in correcting the translation of the original German manuscripts.

H. A. Kiehne

Preface to the First Edition

Batteries in various applications as rechargeable secondary batteries or as non-rechargeable primary batteries have to be adapted to steadily changing demands. Improvements to the existing and well-established systems, e.g., the lead-acid battery, the nickel-cadmium battery, and the well-known primary battery systems, have been made in recent years. Increased energy density and maintenance-free operation, as well as an extended temperature range, are the main aims of development. At the same time, research and development on new systems, e.g., fuel cells and high-temperature batteries, are needed for coming applications as battery-powered road vehicles with a wider range are already being demonstrated with the existing types of batteries. Furthermore, miniaturized batteries, such as lithium batteries, are needed as power sources for appliances and electronic watches.

The origins of this book go back to two-day seminars on batteries taught at the Technical Academy of Esslingen. In 1980, Expert Verlag published the first edition of *Batteries*. By 1983, a revised second edition was necessary. The chapters dealing with primary batteries and small rechargeable batteries (lead-acid and nickel-cadmium batteries) were published at the same time as a separate book, *Portable Batteries*, which now constitutes the second half of this volume.

Updated editions of *Batteries* and *Portable Batteries* appeared in 1988. It is hoped that this present English edition will be of help to those who want an extensive survey on the technical level of commercial batteries as well as insight into their emerging applications.

I would like to thank all the contributors and the translator for their cooperation and the Technical Academy of Esslingen for lecture materials. My thanks also to Expert Verlag, the original publisher.

H. A. Kiehne

Contents

I. Fundamentals and Theory, Running Techniques, Applications, and Outlook: Traction Batteries, Stationary Batteries, and Charging Methods

12 Charging Methods and Techniques: General Requirements and Selection of Chargers

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1

Electrochemical Energy Storage

D. BERNDT

1.1 INTRODUCTION

Electrical energy plays an important role in our daily life. It can universally be applied and easily be converted into light, heat or mechanical energy. A general problem, however, is that electrical energy can hardly be stored. Capacitors allow its direct storage, but the quantities are small, compared to the demand of most applications. In general, the storage of electrical energy requires its conversion into another form of energy. In batteries the energy of chemical compounds acts as storage medium, and during discharge, a chemical process occurs that generates energy which can be drawn from the battery in form of an electric current at a certain voltage.

For a number of battery systems this process can be reversed and the battery recharged, i.e. the intake of electric energy can restore the chemical composition that contains higher energy and can closely reestablish the original structures within the battery.

As a consequence, two different battery systems exist:

- Primary batteries that are designed to convert their chemical energy into electrical energy only once.
- Secondary batteries that are reversible energy converters and designed for repeated discharges and charges. They are genuine electrochemical storage systems.

There is no clear border between them, and some primary battery systems permit charging under certain conditions. Usually, however, their rechargeability is limited.

The first part of this book (Chapters 2 to 14) concerns batteries of larger capacities that are employed as standby batteries in stationary applications, provide energy in vehicles like forklift trucks, or stabilize an electrical network like the starter battery in motor cars. Rechargeable batteries usually are the choice in such applications, since primary batteries would be too expensive for the required rather high capacity. The second part (Chapters 15 to 19) regards batteries mainly in portable applications and concerns smaller capacities. In this field primary as well as secondary batteries are employed.

1.2 THE ELECTROCHEMICAL CELL AND THE CELL REACTION

The cell reaction is a chemical reaction that characterizes the battery. When the battery is discharged, chemical compounds of higher energy content are converted by this reaction into compounds of lower energy content. Usually the released energy would be observed as heat. But in a battery, the cell reaction is divided into two electrode reactions, one that releases electrons and the other one that absorbs electrons, and this flow of electrons forms the current that can be drawn from the battery. Thus the generation or consumption of energy that is connected to the cell reaction is directly converted into an electric current. This is achieved in the electrochemical cell, sketched in Fig. 1.1.

A positive and a negative electrode are immersed in the electrolyte and the reacting substances (the active material) usually are stored within the electrodes, sometimes also in the electrolyte, if it participates in the overall reaction. During discharge, as shown in Fig. 1.1, the negative electrode contains the substance that is oxidized (i.e. releases electrons), while the positive electrode contains the oxidizing substance that is reduced (i.e. accepts electrons).

Thus at the negative electrode oxidation of $S(N)_{red}$ occurs according to

$$S(N)_{red} \Rightarrow S(N)_{ox} + n \cdot e^- \tag{1a}$$

while $S(P)_{ox}$ is reduced at the positive electrode

$$S(P)_{ox} + n \cdot e^- \Rightarrow S(P)_{red} \tag{1b}$$

Both together form the cell reaction

$$S(N)_{red} + S(P)_{ox} \Rightarrow S(N)_{ox} + S(P)_{red} + \text{energy} \tag{1}$$

When the battery belongs to the secondary type and is charged, this reaction is reversed and a corresponding amount of energy has to be supplied to the cell.

The difference of the bonding energy between the composition at the starting point of the cell reaction ($S(N)_{red} + S(P)_{ox}$) and its final state ($S(N)_{ox} + S(P)_{red}$) represents the energy that can be drawn from the cell as a current (except the reversible heat (Section 1.4.1) that is lost as heat or gained as additional energy and except other losses that produce Joule heating (Section 1.4.2)). This direct conversion of the current into chemical energy characterizes batteries and fuel cells. Other systems, like combustion engines, use also a chemical reaction where a ‘fuel’ is oxidized, but in these devices the energy is generated as heat and has to be converted by further processes into mechanical or electrical energy. The advantage of the direct energy conversion is its high efficiency.

Examples of such cell reactions are

$$Zn + 2MnO_2 \Rightarrow ZnO + Mn_2O_3 \tag{2}$$

for a primary battery (Leclanché battery), where zinc (Zn) and manganese dioxide (MnO_2) are the compounds of higher energy content and

$$Cd + 2Ni(OOH) + H_2O \Rightarrow 2Ni(OH)_2Cd(OH)_2 \tag{3}$$

as the (simplified) cell reaction of the rechargeable nickel/cadmium battery. In this case cadmium (Cd) and nickel hydroxide (Ni(OOH)), which contains Ni^{3+} ions, are the reactants of higher energy content.

Mostly in batteries the reacting substances are stored within the electrodes (the 'active material'), but there are also systems where the electrolyte participates, as in lead-acid batteries, or where the reacting substances are stored in separate tanks, e.g. Zn/Cl, Zn/Br, and vanadium redox batteries (Section 1.8.5), or as a gas in the container of nickel-hydrogen batteries (Section 1.8.3).

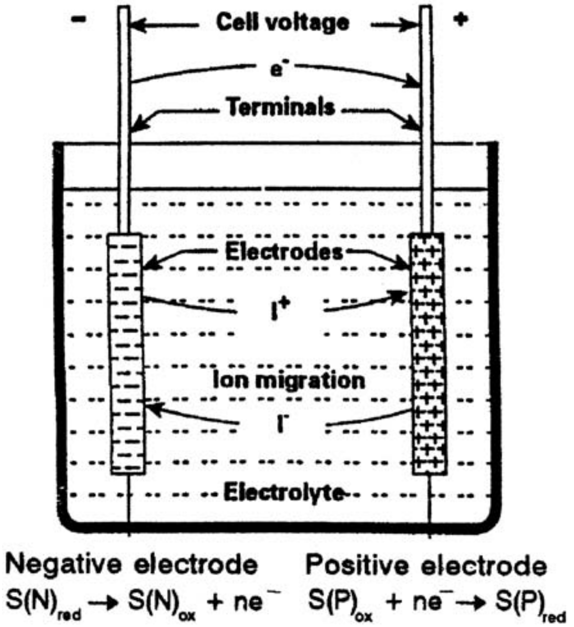

Figure 1.1 The electrochemical cell and the split up of the cell reaction. $S(N)_{red}$ and $S(P)_{ox}$ are the components of the negative and the positive electrode respectively. They are oxidized into $S(N)_{ox}$ at the negative and reduced into $S(P)_{red}$ at the positive electrode, when the battery is discharged as indicated in the figure.

According to the definition of the terms 'anodic' and 'cathodic', given in Section 1.5.1, in the situation shown, the positive electrode is the 'cathode' and the negative electrode the 'anode'.

Fuel cells are also based on an electrochemical cell as shown in Fig. 1.1, but in fuel cells the reacting substances are supplied from outside, and the electrodes only provide the surface for the reaction and the connection to current flow. For this reason, fuel cells do not store electric energy, but are converters of energy, and storage parameters, like Wh/kg or Wh/L, have no relevance for them. Therefore, fuel cells cannot directly be compared with batteries.

Note: *The arrangement shown in Fig. 1.1 resembles an electrolytic capacitor where also two electrodes are separated by the electrolyte. However, charging and discharging of such a capacitor means only charge shifting within the double layer at the electrode/electrolyte interface. Chemical reactions do not occur and the physical structure of the electrodes is not affected. Since mass transport does not occur, charge and discharge of a capacitor are extremely fast, and a nearly unlimited number of charge/discharge cycles is possible. But the amount of stored energy per weight or volume is comparatively small.*

In batteries such a double layer also exists, and the large surface area of the active material gives rise to a high double layer capacitance when impedance measurements are made. The real battery capacity, however, is much higher and based on chemical reactions. As a consequence, each charge/discharge cycle changes the physical structure of the electrodes, and these changes inevitably cause an aging process. For this reason, with batteries the number of possible charge/discharge cycles is limited, and performance changes over service life are unavoidable.

1.3 FUNDAMENTAL LAWS

The fundamental parameters that describe a battery system concern the cell reaction. In the following, a brief survey is given of the most important rules. For details and derivations, the reader is referred to textbooks of electrochemistry or fundamental books on batteries (e.g. Ref. 1).

1.3.1 Parameters that Influence the Cell Reaction

There are two groups of parameters that have to be considered:

1. Thermodynamic or equilibrium parameters describe the system in equilibrium, when all reactions are balanced. In the electrochemical cell this applies when no current flow exists. This means that these parameters represent maximum values that only can be reached under equilibrium.
2. Kinetic parameters appear when the reaction occurs. These parameters are connected to current flow and they always aggravate the values given by the thermodynamic data. Kinetic parameters include mass transport by migration or diffusion that is required to bring the reacting substances to the surface of the electrode. Furthermore, the voltage drop, caused by current flow in electron or ion conductors, is included in kinetic parameters. Kinetic parameters are influenced by design parameters of the cell, like thickness and spacing of the electrodes.

1.3.2 Equilibrium or Thermodynamic Parameters

The laws of thermodynamics generally apply to the state of equilibrium, and on account of this balance, the thermodynamic parameters do not depend on the reaction path, but depend only on the different energy levels between the final and initial components (the 'products' and the 'reactants' of the electrochemical reaction). The thermodynamic parameters describe the possible upper limit of performance data. As soon as current flows through the cell, these data are reduced by the influence of kinetic parameters.

The thermodynamic parameters of an electrochemical reaction are

1. Enthalpy of reaction ΔH represents the amount of energy released or absorbed. ΔH describes the maximum heat generation, provided that the chemical energy is converted into heat by 100%.
2. Free enthalpy of reaction ΔG, also called change of Gibb's free energy ΔG, describes the (maximum) amount of chemical energy that can be converted into electrical energy and vice versa.
3. Entropy of reaction ΔS characterizes the reversible energy loss or gain connected with the chemical or electrochemical process.

Important relations between the three parameters are

$$\Delta G = \Delta H - T \cdot \Delta S \qquad \text{or} \qquad \Delta H - \Delta G = T \cdot \Delta S \tag{4}$$

with T: temperature in K.

The difference between ΔH and ΔG, the product $T \cdot \Delta S$, is called reversible heat effect. It represents the heat exchange with the surroundings when the process occurs 'reversibly', which means that all equilibria are balanced. $T \cdot \Delta S$ can be positive or negative. In the first case additional energy is generated by cooling of the environment (Peltier or heat pump effect). Otherwise, $T \cdot \Delta S$ contributes additional heat (cf. also Section 1.4.1).

The equilibrium cell voltage $U^o(V)$ is given by

$$U^o = -\frac{\Delta G}{n \cdot F} \tag{5}$$

with n: number of exchanged electronic charges; F: Faraday constant, equivalent to 96485 As/equiv.; $n \cdot F$ means the amount of electrical charge connected with the reaction ($1 \cdot F = 26.802\,\text{Ah/equiv.}; 2 \cdot F = 53.604\,\text{Ah/equiv.}$); $n \cdot F \cdot U^o$ describes the generated electrical energy (kJ).

Thermodynamic parameters describe the fundamental values of a battery, like the equilibrium voltage and the storage capability. Some examples are listed in Table 1.1. Column 7 shows the 'nominal voltage', which approximates the value given by Eq. (5) (cf. Section 1.6.1).

Thermodynamic quantities like ΔH and ΔG depend on the concentrations (or more accurately *activities*) of the reacting components, as far as these components are dissolved. The corresponding relation is

$$\Delta G = \Delta G_s + R \cdot T \cdot \left(\sum \ln\left[(a_i)^{j_i}\right]_{prod} - \sum \ln\left[(a_i)^{j_i}\right]_{react} \right) \tag{6}$$

Table 1.1 Thermodynamic data, electrodes, electrolyte, cell reaction, equilibrium cell voltage, and specific energy of some customary primary- and secondary-battery systems. The theoretical specific energy, listed in Column 8 results from division of ΔG by the weight of the reacting components. The difference between these values and those observed in practice (Column 9) is caused by kinetic parameters.

1	2	3	4	5	6	7	8	9
		Electrode material					Specific energy Wh/kg	
	Battery system	Positive	Negative	Electrolyte	Cell reaction	U^{oa} Volt	Theoretical	Practice[c]
Primary batteries								
1	Leclanché	MnO_2	Zn	Slightly acidic	$Zn + 2 \cdot MnO_2 + 2NH_4Cl \Rightarrow ZnNH_3Cl_2 + Mn_2O_3$	1.5	222	≈ 120
2	Manganese alkaline	MnO_2	Zn	Diluted KOH	$Zn + 2 \cdot MnO_2 + 2 \cdot H_2O \Rightarrow ZnO + Mn_2O_3$	1.5	272	≈ 170
3	Silver oxide/zinc	Ag_2O	Zn	Diluted KOH	$Zn + Ag_2O + H_2O \Rightarrow Zn(OH)_2 + 2Ag$	1.6	350	≈ 250
4	Air/zinc (alkaline)	O_2 (air)	Zn	Diluted KOH	$Zn + 1/2O_2 \Rightarrow ZnO$		1.45	1086
≈ 350								
5	Lithium/ manganese dioxide	MnO_2	Li	Organ.	$Li + Mn^{(+4)}O_2 \Rightarrow Mn^{(+3)}O_2 (Li^+)$	3.5	1005	≈ 300
6	Thionyl chloride	$SOCl_2$[d]	Li	$SOCL_2$	$4Li + 2SOCl_2 \Rightarrow 4LiCl + S + SO_2$	3.9	1470	≈ 450

Secondary batteries								
7	Lead-acid	PbO_2	Pb	Diluted H_2SO_4	$Pb + PbO_2 + 2 \cdot H_2SO_4 \Leftrightarrow 2 \cdot PbSO_4 + 2 \cdot H_2O$	2[b]	161	20–50
8	Nickel/cadmium	NiOOH	Cd	KOH	$Cd + 2NiOOH + 2 \cdot H_2O \Leftrightarrow 2Ni(OH)_2 + Cd(OH)_2$	1.3[e]	240[e]	20–55
9	Nickel/metal hydride	NiOOH	H_2[f]	KOH	$H_2 + 2NiOOH \Leftrightarrow 2Ni(OH)_2$	1.3[e]	≈ 300[g]	50–80
10	Lithium-ion	$Li_{(1-x)}MnO_2$	Li_xC	Organ.	$Li_xC_6 + Li_{(1-x)}Mn_2O_4 \Leftrightarrow C_6 + Li_xMn_2O_4$	3.6	> 450	≈ 100
Special battery systems								
11	Sodium/sulfur[h]	S	Na	Solid	$2Na + 3S \Leftrightarrow Na_2S_3$	2.1	795	90–120
12	Sodium/nickel chloride[h]	$NiCl_2$	Na	Solid	$2Na + NiCl_2 \Leftrightarrow 2NaCl + Ni$	2.6	719	90–100
13	Zinc/bromine	Br_2	Zn	$ZnBr_2$	$Zn + Br_2 \Leftrightarrow Zn/Br_2$	1.4	435	≈ 70[i]

[a] Nominal voltage that with many systems cannot exactly be measured.

[b] Depends on acid concentration (cf. Eq. (11)).

[c] Values depend on cell design and discharge parameters.

[d] Thionyl chloride ($SOCl_2$) simultaneously represents the electrolyte and the active material of the positive electrode.

[e] Only approximated data that depend on the oxidation state of the nickel hydroxide.

[f] Hydrogen is absorbed by special alloys.

[g] Depends on the alloy, used for hydrogen storage.

[h] Operating temperature 300 to 400 °C.

[i] Value depends on the size of the separate tanks for the active material.

with a_i: activity of the reacting component i (approximately the concentration) ($\text{mole} \cdot \text{cm}^{-3}$); j_i: number of equivalents of this component that take part in the reaction; R: molar gas constant for an ideal gas ($R = 8.3145 \text{J} \cdot \text{K}^{-1} \cdot \text{mole}^{-1}$); T: temperature (K); $\Delta G^{o,s}$: standard value when all activities are unity; *react* and *prod*: reactants and products when the reaction equation is written so that it occurs spontaneously.

Combination of Eq. (5) and Eq. (6) results in the so-called 'Nernst Equation':

$$U^o = U^{o,s} - \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{\prod (a_i)^j_{react}}{\prod (a_i)^j_{prod}} \tag{7}$$

which is simplified for 25 °C (298.2 K) to

$$U^o = U^{o,s} - \frac{0.0592}{n} \cdot \log \frac{\prod (a_i)^j_{react}}{\prod (a_i)^j_{prod}} \quad V \tag{8}$$

under consideration that $\ln(..) = 2.303 \log(..)$; $R = 8.3145 \text{J}/(\text{K} \cdot \text{mole})$; $F = 8.3145 \text{Ws}/(\text{K} \cdot \text{mole})$, $F = 96485 \text{As/equiv.}$; thus $R/F = 0.02569 \text{V} \cdot \text{equiv.} \cdot \text{mole}^{-1}$.

The lead-acid battery may be taken as an example: In the usually applied concentration range, diluted H_2SO_4 is dissociated mainly into H^+ and HSO_4^- ions. Only about 1% of the H_2SO_4 molecules dissociate into $2 \cdot H^+$ and SO_4^{2-}. In consideration of the actual state of dissociation, the cell reaction can be written

$$Pb + PbO_2 + 2 \cdot H^+ + 2 \cdot HSO_4^- \Leftrightarrow 2 \cdot PbSO_4 + 2 \cdot H_2O \tag{9}$$

The free enthalpy of this reaction is $\Delta G = -372.6 \text{kJ}$. When this value is inserted into Eq. (5) the standard value of the equilibrium voltage results:

$$U^{o,s} = 1.931 \text{V} \tag{10}$$

which applies for a_{H^+}, a_{HSO_4}, and $a_{H_2O} = 1 \text{mole/L}$ and is approached by an acid of the density 1.066g/cm^3 or a concentration of about 1.083 mole/L ($\approx 10 \text{wt\%}$).

Table 1.1 shows battery systems, their cell reaction, nominal voltage U^o and theoretical specific energy that is derived by the above thermodynamic laws, and in Column 9 the actually reached specific energy. The special battery systems, listed in the lines 11 and 12 in Table 1.1, will be treated in Chapter 10, the zinc/bromine system in Section 1.8.5.

The dependence of the equilibrium voltage on the concentration of dissolved components is given by the Nernst equation (Eq. (8)), and reads for the lead-acid battery as an example:

$$U^o = 1.931 + 0.0592 \cdot \log \frac{a_{H^+} \cdot a_{HSO_4^-}}{a_{H_2O}} V \tag{11}$$

Equation (11) shows that the equilibrium cell voltage depends only on the acid concentration. It is independent of the present amount of lead, lead dioxide or lead sulfate, as long as all three substances are available in the electrode. (They are in solid state and per definition their activity is 1 mole/L.) The result of this equation is plotted in Fig. 1.2.

In battery practice, mostly the approximation is used:

$$\text{Equilibrium cell voltage} = \text{acid density (in g/cm}^3 \text{ or kg/dm}^3) + 0.84 \qquad (12)$$

Fig. 1.2 shows that the calculated curve and the approximate formula coincide quite well.

Note: *Actually not the true equilibrium voltage but only the open circuit voltage can be measured with lead-acid batteries. Due to the unavoidable secondary reactions of hydrogen and oxygen evolution and grid corrosion, mixed potentials are established at both electrodes, which are a little different from the true equilibrium potentials (cf. Fig. 1.18). But the differences are small and can be ignored.*

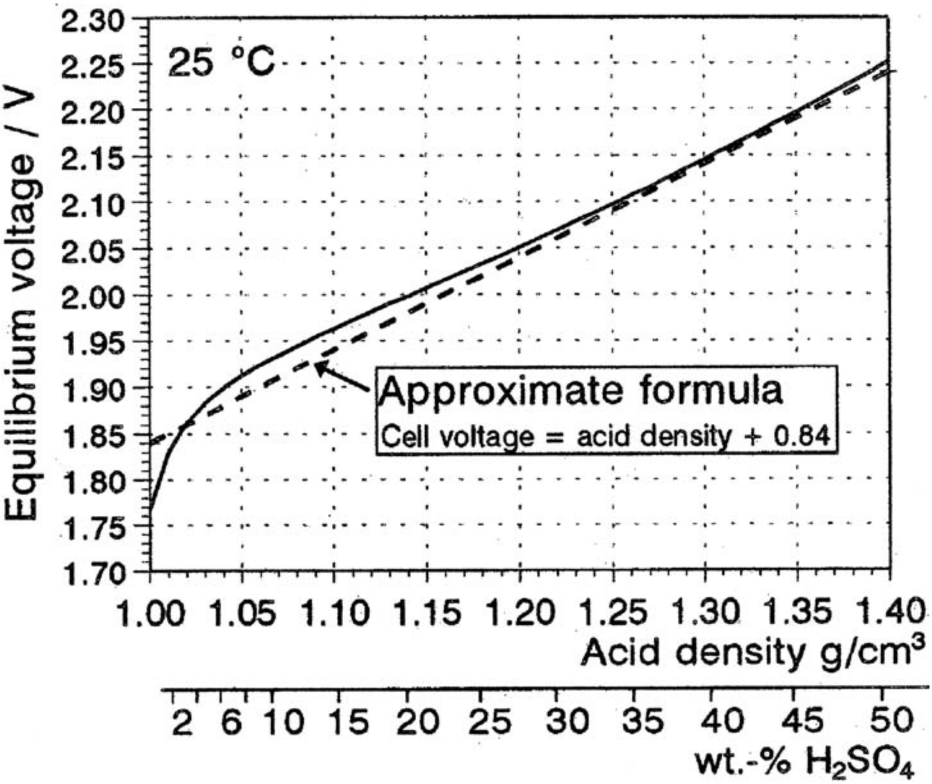

Figure 1.2 Equilibrium cell voltage of the lead-acid battery referred to, acid density, and acid concentration in wt% H_2SO_4.

The thermodynamic data also determine the temperature coefficient of the equilibrium cell voltage or electrode potential according to the relation

$$\frac{dU^o}{dT} = -\frac{\Delta S}{n \cdot F} \tag{13}$$

In battery practice this coefficient usually can be neglected, since it is small and concealed by other effects that far more strongly depend on temperature.

The specific energy (Column 8 in Table 1.1) results from division of the energy that can be drawn from the cell ($U^o \cdot n \cdot F$) by the weight of the reacting components. The discrepancy between the theoretical value and that in practice (Column 9) is caused by all the passive components that are required in an actual cell or battery.

1.3.2.1 Single Electrode Potential

Thermodynamic calculations are always based on an electrochemical cell reaction, and the derived voltage means the voltage difference between two electrodes. The voltage difference between the electrode and the electrolyte, the 'absolute potential', cannot exactly be measured, since potential differences can only be measured between two electronic conductors (2). 'Single electrode potential' always means the cell voltage between this electrode and a reference electrode. To get a basis for the electrode-potential scale, the zero point was arbitrarily equated with the potential of the standard hydrogen electrode (SHE), a hydrogen electrode under specified conditions at 25 °C (cf. Ref. 3).

In battery practice, hydrogen reference electrodes are not used. They are not only difficult to handle, but include in addition the risk of contamination of the battery's electrodes by noble metals like platinum or palladium (4). Instead, a number of reference electrodes are used, e.g. the mercury/mercurous sulfate reference electrode (Hg/Hg_2SO_4) in lead-acid batteries, and the mercury/mercuric oxide reference electrode (Hg/HgO) in alkaline solutions (e.g. Ref. 5). In lithium ion batteries with organic electrolyte the electrode potential is mostly referred to that of the lithium electrode (cf. Chapter 18).

1.3.3 Current Flow, Kinetic Parameters, and Polarization

When current flows, the cell reaction must occur at a corresponding rate. This means that electron transfer has to be forced into the desired direction, and mass transport is required to bring the reacting substances to the electrode surface or carry them away. To achieve this current flow, additional energy is required. It finds its expression in overvoltages, i.e. deviations from the equilibrium voltage (sometimes denoted as 'irreversible entropy loss' $T \cdot \Delta S_{irr}$). Furthermore, current flow through conducting elements causes ohmic voltage drops. Both mean irreversible energy loss and corresponding heat generation, caused by current flow.

As a result, the voltage U under current flow is reduced on discharge or increased secondary cell on charge compared to the equilibrium value U^o. The difference $U - U^o$, when measured as deviation from cell voltage, comprises:

1. The overvoltage, caused by electrochemical reactions and concentration deviations on account of transport phenomena.

2. The ohmic voltage drops, caused by the electronic as well as the ionic currents in the conducting parts including the electrolyte.

The sum of both is called polarization, i.e.

$$\text{polarization} = \text{overvoltage} + \text{ohmic voltage drops} \tag{14}$$

The quantity determined in practice is always polarization. Overvoltage can only be separated by special electrochemical methods.

1.3.3.1 Courses of the Reaction

Various possibilities exist for the combination of reaction steps, and only some of them will briefly be described. Usually the reaction path consists of a number of reaction steps that precede or follow the actual charge transfer step as indicated in Fig. 1.3. The slowest partial step of this chain is decisive for the rate of the overall reaction. As a consequence, overvoltages, or even limitations of the reaction rate, often are not caused by the electron-transfer step itself, but by preceding or following steps.

Some of these steps include mass transport, since the reaction would soon come to a standstill, if ions would no longer be available at the surface of the electrode or if reaction products would not be cleared away and would block the reacting surface. For this reason, migration and diffusion influence the kinetic parameters.

In a number of electrode reactions, the reaction product is dissolved. This applies, for example, to some metal electrodes, like zinc, lithium, cadmium, and also to lead. For the latter two, the low solubility of cadmium hydroxide ($Cd(OH)_2$) and

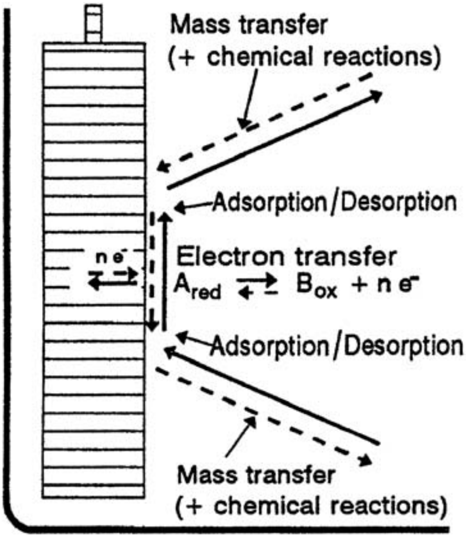

Figure 1.3 Course of an electrochemical reaction. Charge transfer often can only occur with adsorbed species, then adsorption/desorption steps are included. Furthermore, chemical reactions may precede or follow the electron transfer step.

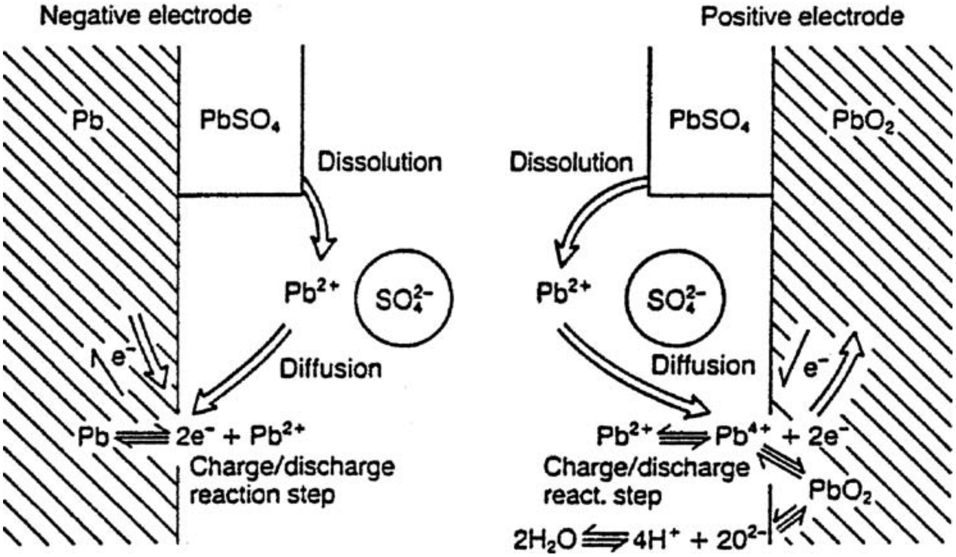

Figure 1.4 Reaction steps in the lead-acid battery. Double-lined arrows mark the charging reaction.

lead sulfate ($PbSO_4$) causes precipitation of the formed new compound, as illustrated for the lead-acid system in Fig. 1.4.

During discharge, lead ions (Pb^{2+}) are dissolved at the negative electrode. A corresponding number of electrons is removed from the electrode as negative charge. The solubility of the Pb^{2+} ions is, however, limited to about 10^{-6} mole/dm^3 in the presence of HSO_4^- or SO_4^{2-} ions (sulfuric acid, cf. Eq. (10)). As a consequence, the dissolved Pb^{2+} ions form lead sulfate ($PbSO_4$) on the electrode surface immediately after the dissolution process, mostly within the pore system of the active material.

The discharging reaction at the positive electrode proceeds in a similar manner: bivalent lead ions (Pb^{2+}) are formed by the reduction of tetravalent lead ions (Pb^{4+}) acquiring two electrons. The Pb^{2+} ions also dissolve and immediately form lead sulfate ($PbSO_4$). In addition, water is formed at the positive electrode during discharging, because oxygen ions (O^{2-}) are also released from the lead dioxide (PbO_2) that combine with the protons (H^+) of the dilute sulfuric acid to H_2O molecules.

During charging of the battery, these reactions occur in the opposite direction, as indicated by the double-line arrows in Fig. 1.4. Lead (Pb) and lead dioxide (PbO_2) are formed from lead sulfate ($PbSO_4$).

The electrochemical reaction, the transfer step, can only take place where electrons can be supplied or removed, which means that this conversion is not possible on the surface of the lead sulfate, as lead sulfate does not conduct electric current. For this reason, the Pb^{2+} ions must be dissolved and transported by migration or diffusion to the conductive electrode surface (lead or lead dioxide).

The solubility of the reaction products is a very important parameter for electrode reactions that occur via dissolution of the reactants, as the example shown

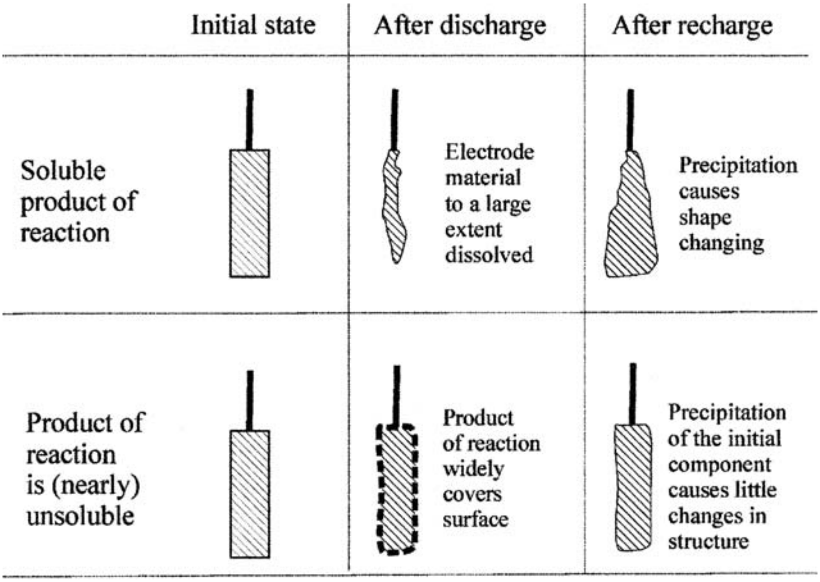

Figure 1.5 Effect of the solubility of the reaction products on electrode structure when the discharging/charging mechanism occurs via the dissolved state.

in Fig. 1.4. If the product of the discharge is highly soluble, during discharge the electrode will to a large extent be dissolved and will lose its initial structure. This leads to problems during recharge because the redeposition of the material is favored where the concentration of the solution has its highest value. As a consequence, the structure of the electrode will be changed as demonstrated in the upper row of Fig. 1.5.

Connected to the shape change is a further drawback of the high solubility, namely the tendency that during recharging the precipitated material forms dendrites that may penetrate the separator and reach the opposite electrode, thus gradually establishing a short circuit.

A typical example of this situation is the zinc electrode, which allows only limited discharge/charge cycles. Zinc electrodes are therefore not used in commercial secondary batteries, with the exception of the rechargeable alkaline zinc manganese dioxide battery (RAM) (6) which is a battery of low initial cost, but also limited cycle life.

The metallic lithium electrode is another example where cycling causes problems due to its high solubility that causes shape change (cf. Chapter 18 and the lithium-ion system in Fig. 1.7).

Extremely low solubility of the reaction products leads to a more or less dense covering layer (lower row in Fig. 1.5), and when the formed substances do not conduct electrons, like the $PbSO_4$ in Fig. 1.4, the discharge reaction comes to a halt as soon as the passivating layer is completed. Thus only a thin layer of the active material reacts. To encounter such a passivation, the active material in technical electrodes, e.g. lead and cadmium electrodes, are used as a spongy structure that has

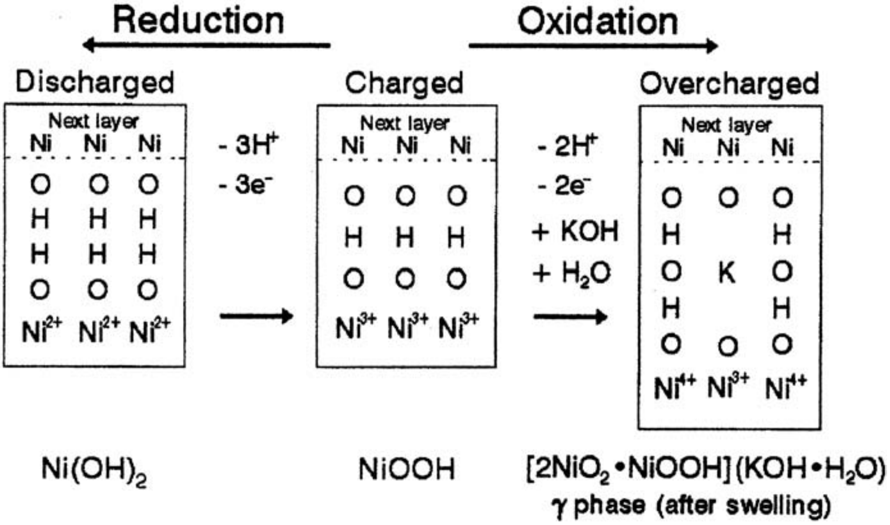

Figure 1.6 Simplified charge and discharge mechanism of the nickel-hydroxide electrode with simultaneous release and absorption of protons (H^+ ions) and incorporation of a small amount of potassium ions (K^+).

a large surface area on the order of m^2/g. The advantage of the low solubility is that the products of the reaction are precipitated within the pores of the active material, close to the place of their origin, and the structure of the electrode remains nearly stable. Nevertheless, a gradual disintegration of the active material is observed after a certain number of charge/discharge cycles.

A quite different course takes the reaction in the nickel-hydroxide electrode that is employed in nickel/cadmium, nickel/hydrogen, and nickel/metal hydride batteries as the positive one. This mechanism is illustrated in Fig. 1.6. Here the reaction product is not dissolved, but the nickel ions are oxidized or reduced while they remain in their crystalline structure (that of course undergoes certain changes). To preserve electrical neutrality, a corresponding number of H^+ ions (protons) must migrate into the crystal lattice during the discharge, which means reduction of Ni^{3+} or Ni^{4+} ions into Ni^{2+} ions. When the nickel electrode is charged (oxidized), these protons have to leave the crystal lattice. Otherwise, local space charges would immediately bring the reaction to a standstill. The comparatively high mobility of the small H^+ ions allows such migration, but requires a large surface area of the active material to keep the penetration distance low.

Here oxidation and reduction occur within the solid state, and it depends on the potential of the electrode how far the material is oxidized. A consequence in battery practice is that full capacity of this electrode is only reached at a sufficient high end of charge voltage. Float charging at a comparatively low voltage, as it is normal for standby applications, does not preserve full capacity and requires regular equalizing charges or corresponding oversizing of the battery.

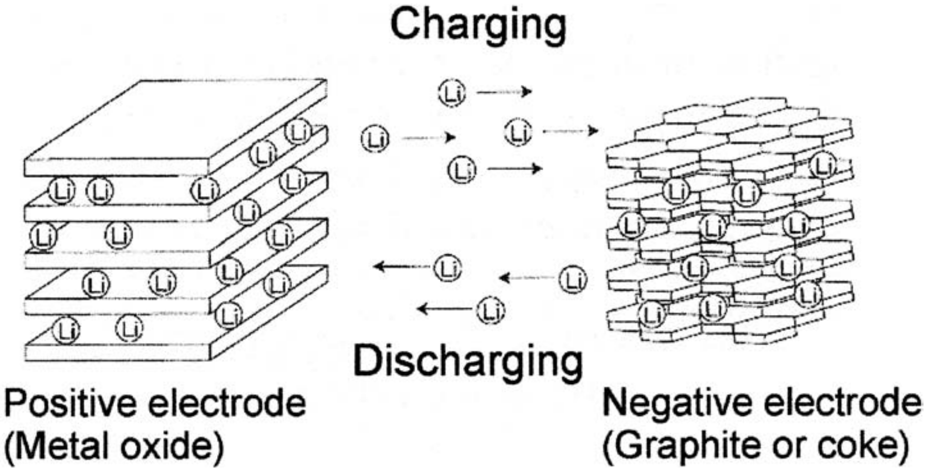

Figure 1.7 Charging/discharging of lithium-ion batteries. In the charged state, the carbon electrode is filled with lithium. During discharge, lithium ions are intercalated into the oxide (from Ref. 7).

Another reaction mechanism that in a certain aspect resembles to the above one characterizes lithium-ion batteries (cf. Chapter 18). The course of the cell reaction is illustrated in Fig. 1.7

In such a battery, a carbon electrode that forms layers and allows intercalation of Li ions is combined with a positive electrode of a metal oxide that also intercalates the small Li^+ ions into a layered structure (mainly Li_xCO_2, Li_xNiO_2, or $Li_xMn_2O_4$). These positive electrodes intercalate the lithium when discharged, i.e. the lithium-filled material characterizes the discharged state of the positive electrode, and the Li^+ ions compensate for a corresponding reduction of the metal ions ($Me^{4+} + x \cdot e^- \Rightarrow Me^{(4-x)+}$). The (simplified) cell reaction is

$$\text{nC} + \text{Li}_x\text{MeO} \underset{\leftarrow\text{Discharging}}{\overset{\text{Charging}\rightarrow}{\Leftrightarrow}} \text{MeO} + \text{Li}_x\text{C}_n \tag{15}$$

In both electrodes, the host material and its structure remains (nearly) unchanged, and only the Li^+ ions swing between the positive and negative electrode. This gave the battery the sometimes used name 'rocking chair battery'. As a consequence, the problems caused by solution of a metallic lithium electrode as indicated in Fig. 1.5 are no longer relevant, and a great number of discharge/charge cycles is possible without losing the structure of the electrodes.

Electron Transfer

The electron transfer reaction denotes the central reaction step where the electrical charge is exchanged (cf. Fig. 1.3). Current flow affords additional forces because of an energy barrier that has to be surmounted by electrons. The required additional energy is called 'activation energy' and the dependence of reaction rates is expressed by the Arrhenius equation, which reads

$$k = k_o \cdot \exp\left(-\frac{E_A}{R \cdot T}\right) \tag{16}$$

with k: reaction constant; E_A: activation energy ($J \cdot mole^{-1}$); R: molar gas constant ($8.3143\, J \cdot mole^{-1} \cdot K^{-1}$).

E_A actually depends on temperature, but often can approximately be treated like a constant.

In electrode reactions, $n \cdot U \cdot F$ is the driving force, and the corresponding relation is

$$i = k' \cdot c_j \cdot \exp\left(\frac{n \cdot F}{R \cdot T} U\right) \tag{17}$$

k' includes the 'equivalence factor' $n \cdot F$ between mass transport and current i; U is the electrode potential; and c_j the concentration of the reacting substance that releases or absorbs electrons.

Electron transfer, however, does not occur in only one direction: the reverse reaction is possible as well, and the balance between both depends on electrode potential. Thus, Eq. (17) has to be completed into

$$i = k_+ \cdot c_{red} \cdot \exp\left(\frac{\alpha \cdot n \cdot F}{R \cdot T} U\right) - k_- \cdot c_{ox} \cdot \exp\left(-\frac{(1-\alpha) \cdot n \cdot F}{R \cdot T} U\right) \tag{18}$$

where addend 1 describes the anodic reaction (e.g. $Pb \Rightarrow Pb^{2+} + 2 \cdot e^-$); addend 2 its reversal; α denotes the transference factor (usually close to 0.5) that denotes how symmetrically the reaction and its reversal depend on electrode potential (difference in activation energies); n is the number of charges; and c_{red}, c_{ox} are the concentration in mole/dm^3 of the reduced and oxidized states of the reactants.

Electron transfer according to Eq. (18) occurs also at an open circuit when no current flow is observed through the electrode. The electrode then automatically attains a potential that is characterized by equal rates of the reaction in both directions as a dynamic equilibrium, and this equilibrium voltage (U^o) is determined by the point at which the forward and reverse reaction rates are equal. Then the current flow in both directions is balanced which means $i_+(0) = -i_-(0) = i_o$. This balancing current is called exchange current density (necessarily it is related to the surface area, therefore it is a current density given, for example, in units of mA/cm^2).

Often the current/voltage curves are related to the deviation from the equilibrium potential, the overvoltage $\eta = U - U^o$. This leads to the usual form of Eq. (18):

$$i = i_o \left[\exp\left(\frac{\alpha \cdot n \cdot F}{R \cdot T} \eta\right) - \exp\left(-\frac{(1-\alpha) \cdot n \cdot F}{R \cdot T} \eta\right)\right] \tag{19}$$

where i_o is the exchange current density that characterizes the dynamic equilibrium, as shown in Fig. 1.8. The resulting current is represented in Fig. 1.8 by the solid curve as the combination of anodic and cathodic current/voltage curves.

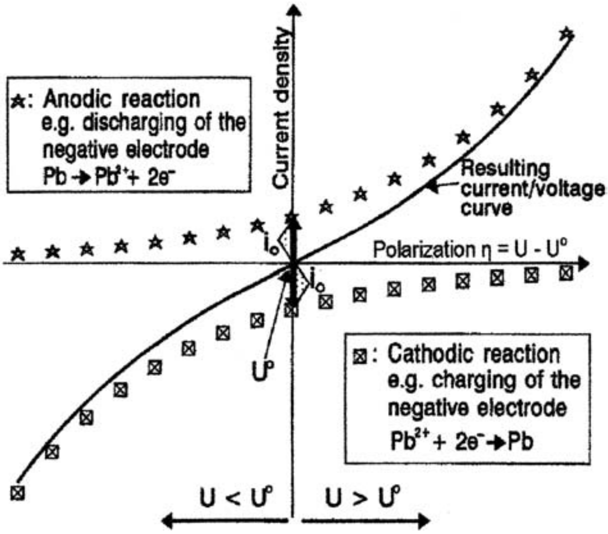

Figure 1.8 The current/voltage curve. The horizontal axis (abscissa) represents polarization $\eta = \mathrm{U} - \mathrm{U}^{\mathrm{o}}$, the vertical axis (ordinate) current density i, which is synonymous to the reaction rate. $\mathrm{i_o}$ is the exchange current density that characterizes the dynamic equilibrium. According to Eq. (14), polarization is the sum of overvoltage and ohmic voltage drop. In practice polarization is always determined. The reaction of the lead electrode is inserted as an example.

Electrode Polarization

Polarization has been introduced as the deviation of the actual voltage from equilibrium by Eq. (14). It is also an important parameter for the single electrode potential, given by the relations

$$\eta_+ = \mathrm{U}_+ - \mathrm{U}^{\mathrm{o}}_+ \quad \text{or} \quad \eta_- = \mathrm{U}_- - \mathrm{U}^{\mathrm{o}}_- \tag{20}$$

with η_+ and η_-: polarization of positive and negative electrodes respectively; U_+ and U_-: actual potential; $\mathrm{U}^{\mathrm{o}}_+$ and $\mathrm{U}^{\mathrm{o}}_-$: equilibrium potential of positive and negative electrodes, respectively.

The cell voltage, as the difference U_+ minus U_-, is given by

$$\mathrm{U} = \mathrm{U}^{\mathrm{o}} + \eta_+ - \eta_- \tag{21}$$

with U^{o}: equilibrium or open circuit voltage of the cell; η^+ and η^-: polarization of the positive and negative electrode, respectively.

According to this definition, the polarization of the negative electrode has the negative sign when the electrode potential is below its equilibrium value. If only the cell voltage is considered, η_+ and η_- are summed up to η.

Polarization of the single electrode in a battery is a very important parameter. The negative electrode is only kept fully charged when its polarization is negative or zero ($\eta_- \leqslant 0$) while for a charged positive electrode a positive polarization is required ($\eta_+ \geqslant 0$).

Tafel Lines

If the potential is shifted far enough from the equilibrium value, in Eq. (19) the reverse reaction can be neglected. Then the resulting current/voltage curve in Fig. 1.8 becomes a simple exponential function

$$i = i_o \cdot \exp\left[\frac{\alpha \cdot n \cdot F}{R \cdot T} \cdot \eta\right] \tag{22}$$

This equation can be rearranged into

$$\eta = \frac{R \cdot T}{\alpha \cdot n \cdot F} \cdot \ln(|i|) - \frac{R \cdot T}{\alpha \cdot n \cdot F} \cdot \ln(|i_0|) \tag{23}$$

that can be written in a form known as the Tafel equation (J. Tafel was the first to describe this relation in connection with hydrogen overvoltage measurements on noble metals (8)):

$$\eta = a + b \cdot \log(|i|) \tag{24}$$

The curves represented by Eq. (24) are linearized when plotted semilogarithmically and are called Tafel lines. The constant b represents the slope of the Tafel line and means the potential difference that causes a current increase of one decade. Tafel lines are important tools when reactions are considered that occur at high overvoltages, since such a linearization allows quantitative considerations. They are often used with lead-acid batteries, since polarization of the secondary reactions hydrogen evolution and oxygen evolution is very high in this system (cf., Fig. 1.24).

Influence of Temperature

The kinetic parameters depend on temperature as do the rates of chemical reactions. This dependence is described by the Arrhenius equation, which already has been introduced as Eq. (16) in connection with the term ‘activation energy’.

The logarithmic form of Eq. (16) reads

$$\ln(k) = -\frac{E_A}{R \cdot T} + \ln(k_o) \quad \text{or} \quad \ln(k) = -\frac{E_A}{R} \cdot \frac{1}{T} + \ln(k_o) \tag{25}$$

On account of this relation, the temperature dependence of kinetic parameters can often be linearized, when the logarithm of the reaction rate is plotted against 1/T, which is often called an Arrhenius plot (for examples, cf. p. 556 in Ref. 9).

Very often the approximation holds true that a temperature increase of 10 K (or 10° C) doubles the reaction rate. In electrochemical reactions, this means that the equivalent currents are doubled, which denotes a quite strong temperature dependence. A temperature increase of 20 K means a current increase by a factor of 4; a rise in temperature of 30 K corresponds to a factor of 8. This relation can be expressed by

$$\frac{k(T + \Delta T)}{k(T)} = 2^{(\Delta T/10)} \tag{26}$$

with k: reaction rate (mole/sec) which might be expressed as a current; T: temperature in K.

1.3.3.2 Diffusion and Migration

Figure 1.3 shows that mass transport concerns various steps within the reaction chain that forms the cell reaction. Transport of the reacting species is achieved by two mechanisms: diffusion that is caused by the concentration gradient of the concerned species and migration of ions caused by the current. When only one-dimensional transport is assumed, the sum of both is given by

$$N_j = \frac{i_j}{n \cdot F} = -D_j \frac{\partial c_j}{\partial \xi} + \frac{i \cdot t_j}{z_j \cdot F} \tag{27}$$

with Nj: flux of species j in $\text{mole} \cdot \text{cm}^{-2}$; i_j/nF: current equivalent; c_j: concentration of species j in $\text{mole} \cdot \text{cm}^{-3}$; $\partial c_j/\partial \xi$: concentration gradient in $\text{mole} \cdot \text{cm}^{-4}$; D: diffusion coefficient in $\text{cm}^2 \cdot \text{s}^{-1}$; t: transference number; z_j: valence number (charges per ion i); ξ: diffusion direction in cm.

Addend 1 of the right-hand part of this equation describes transport by diffusion that always equalizes concentration differences. It is independent of the electric field that drives ions. When as an approximation a linear concentration gradient $\partial c_j/\partial \xi$ across the distance d is assumed, this expression can be written

$$\frac{i_j}{n \cdot F} = -D_j \frac{c_{j,o} - c_j}{d} \tag{28}$$

with $c_{j,o}$: initial concentration of the reacting substance (mole/L); c_j: concentration at the electrode surface; d: thickness of the diffusion layer.

When transport by diffusion of reacting neutral particles (like that of O_2 in the internal oxygen cycle (Fig. 1.25)) precedes the transfer reaction, the actual concentration is reduced with increasing current. If c_j reaches zero, a further increase of the current is not possible. Such a situation is called a (diffusion) limiting current, which according to Eq. (28) is given by

$$i_{d,j} = -D_j \frac{n \cdot F}{d} \cdot c_{j,o} \tag{29}$$

Then the current no longer depends on electrode potential, as shown by the horizontal curve for oxygen reduction in Fig. 1.19.

Addend 2 in the right-hand part of Eq. (27) denotes the share of the total current that is carried by the corresponding ionic species by migration. It is characterized by the transference number. In a binary electrolyte, dissociated into A^+ and B^-, the transference numbers are connected by the relation

$$t_+ + t_- = 1 \tag{30}$$

Transference numbers depend on concentration of the ions and on temperature. In binary salt solutions they are fairly close to 0.5, which means that both ion species more or less equally share in ion conductivity. Larger deviations are observed in acids and bases on account of the much higher ion mobility of H^+ and OH^- ions. The values for the battery electrolytes sulfuric acid (dissociated into H^+ and HSO_4^-) and potassium hydroxide are given in Table 1.2.

Table 1.2 Transference numbers in sulfuric acid and potassium hydroxide at room temperature. For diluted solutions of sulfuric acid given in Ref. 10, but also true for concentrations used in batteries. For potassium hydroxide true for a wide concentration range given in Ref. 11.

Sulfuric acid	$t_+ = t_{H^+} = 0.9$	$t_- = t_{HSO_4^-} = 0.1$
Potassium hydroxide	$t_+ = t_{K^+} = 0.22$	$t_- = t_{OH^-} = 0.78$

The transference number indicates how much the concentration of the concerned ion is changed by migration due to the current flow. The small value of the HSO_4^- ion means that its concentration is only slightly influenced by migration. In lithium-ion batteries, where lithium ions (Li^+) swing between the negative and the positive electrode, the transference number $t_{Li} = 1$ would be desirable, since then a constant concentration profile would be maintained during discharging and charging. This is one reason to aim at conducting salts with large anions (cf., e.g. p. 462 in Ref. 7).

1.3.3.3 Lead-Acid Discharge Curves as Examples

To illustrate the influence of kinetic parameters, discharge curves of a lead-acid battery are compared to the equilibrium voltage in Fig. 1.9. The figure shows

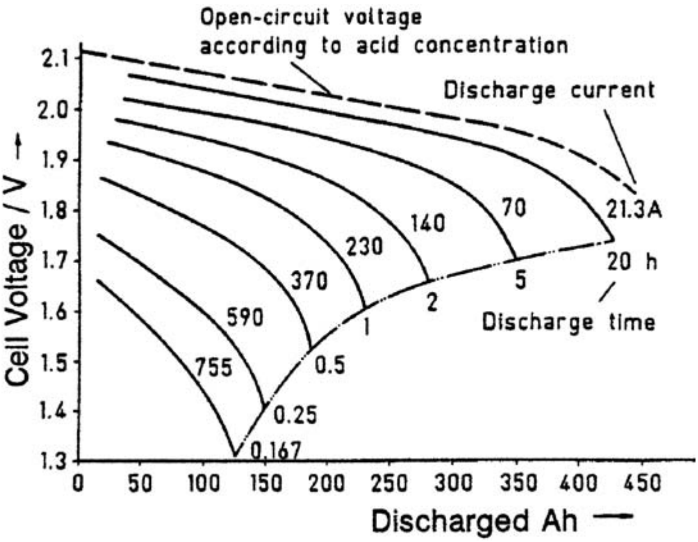

Figure 1.9 Discharge curves relative to the drawn amount of Ah. The dashed curve shows the equilibrium voltage according to the Nernst equation. It reflects the dilution of the acid with progressing discharge (cf. Fig. 1.2).

Flooded traction cell with tubular plates (350 Ah at 5-hour rate).

discharge curves at various loads relative to the amount of Ah drawn from the battery. The dashed curve at the top represents the changing equilibrium voltage due to the gradually decreasing acid concentration, according to the Nernst equation (Eq. (11), Fig. 1.2). If all the partial-reaction steps were fast enough, i.e. if no kinetic hindrance occurred, the increased discharge rate would cause only a voltage drop that would shift the dashed line in parallel to lower voltages.

Figure 1.9 shows that not only a considerable voltage drop can be observed with increasing discharge current, but also a growing decline of the curves. So, with increasing load, the dischargeable share of the capacity is more and more reduced by the impact of kinetic parameters, and the current amount that can be drawn from the battery is markedly reduced, although the end-of-discharge voltage is lowered with increased load. Mainly acid depletion at the electrode surface reduces the rate of the reaction. Furthermore, some of the undischarged material may be buried underneath the growing $PbSO_4$ layer. This layer grows very fast at high loads, resulting in a thin but compact covering layer that prevents further discharge very early.

1.4 HEAT EFFECTS

Electrochemical reactions, like chemical reactions, are always connected with heat effects, determined by the (positive of negative) reversible heat effect, already mentioned in Eq. (4). When current flows through the cell, additional heat is generated by ohmic resistances in the electrodes and the electrolyte, but also by polarization effects, which together cause 'Joule heating'.

1.4.1 The Reversible Heat Effect

The reversible heat effect

$$Q_{rev} = T \cdot \Delta S \qquad (31)$$

represents the unavoidable heat absorption or heat emission connected with electrochemical reactions. It is related to the thermodynamic (equilibrium) parameters of the concerned reaction, and is strictly connected with the amount of material (in electrochemical equivalents) that reacts. Thus, the reversible heat effect does not depend on discharge or recharge rates. When the cell reaction is reversed, the reversible heat effect is reversed too, which means it gets the opposite sign. Thus, energy loss in one direction means energy gain when the reaction is reversed, i.e. the effect is 'reversible'.

The reversible heat effect per time unit can be related to current flow, because each multiple of the cell reaction requires the current amount $n \cdot F$:

$$\frac{dQ_{rev}}{dt} = \frac{Q_{rev}}{n \cdot F} \cdot i \qquad \mathrm{W} \qquad (32)$$

with n: number of exchanged electrons; F: Faraday constant (= 96485 As/equivalent); i: current in A.

Q_{rev}/nF has the dimension V. So it is equivalent to a voltage, although it is not a voltage that can be measured, but for caloric evaluations it is convenient to use the difference

$$U_{cal} = U^o - \frac{Q_{rev}}{n \cdot F} \qquad V \tag{33}$$

as 'calorific voltage' (or thermoneutral potential E_{tp} (12)). U_{cal} is a hypothetical voltage that includes the reversible heat effect, and is used instead of the equilibrium voltage for caloric calculations.

Combination with Eqs. (31) and (32) shows that U_{cal} also can be written

$$U_{cal} = -\frac{\Delta H}{n \cdot F} \tag{34}$$

U_{cal} is a fictive equilibrium voltage that includes the reversible heat effect and is convenient with heat calculations (cf., e.g. Eq. (41)).

1.4.2 Current Related Heat Effects (Joule Heating)

Current flow through any conducting object generates heat proportional to the voltage drop caused by the current itself according to

$$dQ_{Joule}/dt = \Delta U \cdot i \tag{35}$$

with Q_j: generated heat (Joule effect) (J); t: time (s); ΔU: voltage drop caused by the current (V); i: current (A). This heat is called the Joule effect; it always means loss of energy.

Note: *Strictly speaking, the negative absolute value should be used in Eq. (35) for consistency with the arithmetical sign of the thermodynamic parameters (lost energy always has the negative sign).*

In an electrochemical cell, the voltage drop caused by the current is represented by the difference between the cell voltage under current flow (U) and the open circuit cell voltage (U^o). Then the Joule effect reads according to Eq. (35):

$$dQ_{Joule}/dt = (U - U^o) \cdot i \qquad /W \tag{36}$$

or its integrated form for a period t (in hours):

$$Q_{Joule} = \int_0^t \{(U - U^o) \cdot i\} dt \qquad /Wh \tag{37}$$

Note: *$U - U^o$ means polarization. It includes the voltage drop caused be current flow through electronic resistance as well as the electrolyte, but also overvoltage caused by kinetic hindrance of the reaction. For heat effects this is not relevant, since heat generation is proportional to polarization.* $U - U^o$ *does not remain constant during charging or discharging, because it is related to the internal resistance, which usually increases with proceeding discharge, because of the lower conductivity of the discharged products.*

1.4.3 Heat Generation in Total

Summation of the Joule effect and the reversible heat effect gives the total heat generated in the cell or the battery, which means

$$Q_{total} = Q_{Joule} + Q_{rev} \qquad /\mathrm{Wh} \tag{38}$$

as energy, e.g. Wh, or as work per time unit:

$$\frac{dQ_{total}}{dt} = \frac{dQ_{Joule}}{dt} + \frac{dQ_{rev}}{dt} \qquad /\mathrm{W} \tag{39}$$

Depending on the sign of dQ_{rev}/dt, the total energy generation may be larger or smaller than the Joule effect.

According to Eq. (36), dQ_{Joule}/dt can be substituted by $(U - U^o) \cdot i$ and gives

$$\frac{dQ_{total}}{dt} = -(U - U_o) \cdot i + \frac{dQ_{rev}}{dt} \tag{40}$$

Substitution of dQ_{rev}/dt through Eq. (32) and application of Eq. (33) results in the simple relation that is convenient for heat calculations:

$$\frac{dQ_{total}}{dt} = (U - U_{cal}) \cdot i \tag{41}$$

Note: *Strictly speaking, Eq. (41) should have the negative sign according to thermodynamic parameters, since the Joule effect is always lost energy, as mentioned in connection with Eq. (35). To overcome this difficulty,* $Q_{gen} = -Q_{total}$ *is introduced in Section 1.4.5.*

1.4.4 Examples for Heat Generation in Batteries

To illustrate the possibility of heat calculations, four examples will be shown in this section, concerning lead-acid and nickel/cadmium batteries. The thermodynamic data that determine the equilibrium values are listed in Table 1.3. The table also

Table 1.3 Thermodynamic data of lead-acid and nickel/cadmium batteries and water decomposition.

	1	2	3	4	5
1	System		Lead-acid battery	Ni/Cd battery[a]	Water decomposition
2	Cell reaction		$Pb + PbO_2 + 2 \cdot H_2SO_4 \Rightarrow$ $2 \cdot PbSO_4 + 2 \cdot H_2O$	$NiOOH + Cd \Rightarrow$ $Ni(OH)_2 + Cd(OH)_2$	$H_2O \Rightarrow H_2 + 1/2O_2$
3	ΔH_s	Eq. (4)	– 359.4 kJ	≈ – 282 kJ	285.8 kJ
4	ΔG_s	Eq. (4)	– 372.6 kJ	≈ – 255 kJ	237.2 kJ
5	$T\Delta S_s = Q_{rev}$	Eqs. (4), (31)	13.2 kJ	≈ – 27 kJ	48.6 kJ
6	$U^{o,s}$	Eq. (5)	1.931 V	≈ 1.3 V	1.227 V
7	$Q_{rev}/\Delta G_s$		– 3.5%	≈ 11%	20.5%
8	U_{cal}	Eqs. (33), (34)	$U_o - 0.068V$	≈ 1.44 V	1.48 V

[a] Actually these reactions are much more complex, and exact values of the thermodynamic data are not available (cf., e.g. Section 5.2.2.1 in Ref. 5).

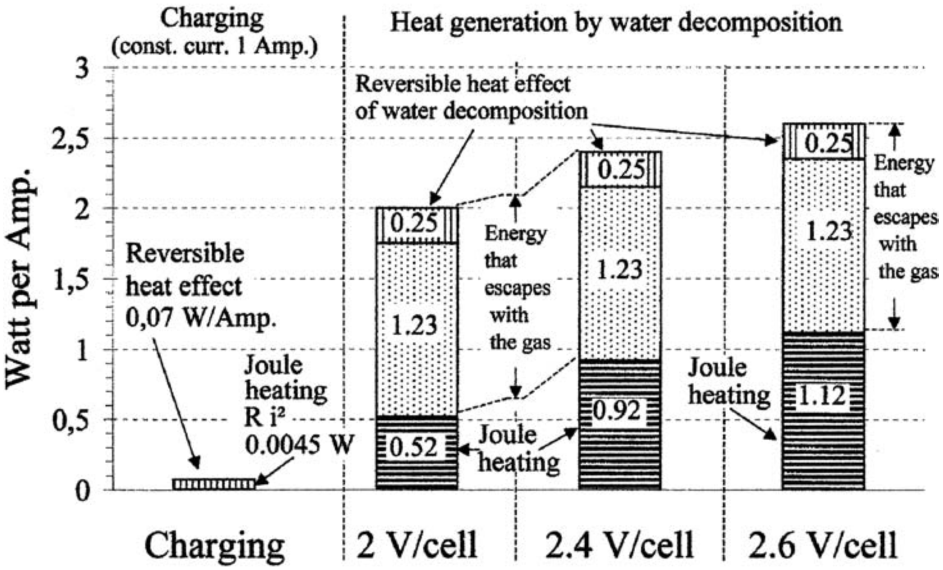

Figure 1.10 Heat generation in a vented lead-acid battery by the charging reaction and by water decomposition, relative to a current of 1 A. Assumed internal resistance 4.5 mΩ per 100 Ah of nominal capacity as in Fig. 1.11.

shows corresponding data of water decomposition that always occurs in batteries with aqueous electrolyte as an unavoidable secondary reaction when the voltage of 1.227 V is exceeded. In valve-regulated lead-acid and sealed nickel/cadmium batteries, instead of water decomposition the internal oxygen cycle is the important reaction that carries most of the overcharging current (cf. Sections 1.8.1.5.2, 1.8.3.2 and 1.8.5.2.6).

Heat generation in a battery is decisively affected by the distribution of the charging current between the various reactions, because of their specific heat generation. This is illustrated in Fig. 1.10.

In a vented lead-acid battery heat effects during charging are caused by the charging reaction itself and by water decomposition that accompanies the charging process at an increasing rate with increasing cell voltage. The charging reaction is a very fast one which means that overvoltage is small. At an assumed internal resistance of 4.5 mV/100 Ah, a charging current of 1 A causes polarization of only 4.5 mV and the resulting heat generation would be $\Delta U \cdot i = R \cdot i^2 = 4.5\text{mW}$, which is represented only as a line at the bottom of the left column in Fig. 1.10. The reversible heat effect, on the other hand, is determined by the amount of converted material (formula mass that is proportional to current) and amounts to 0.07 W/A.

Most of the energy that is employed for water decomposition escapes from the cell as energy content of the generated gases. This energy consists of the two components:

1. The 'decomposition energy of water', which means the product current times 1.23 V.

2. The reversible heat effect, which amounts to about 20% of the converted energy and means cooling of the cell during electrolysis (Column 5 in Table 1.3), and a corresponding increase of the energy content of the gas.

Both shares are proportional to the amount of decomposed water, which again is only determined by the current i as the product $U_{cal} \cdot i = 1.48\,Wh/A$.

The portion of heat that remains within the cell is generated by Joule heating and determined by polarization of the water-decomposition reaction, i.e. by $(U - 1.48) \cdot i\,(Wh)$ and increases with cell voltage as shown in Fig. 1.10.

As an example Fig. 1.11 shows current distribution and heat generation in the course of a charging/discharging cycle as it is customary for vented lead-acid batteries in traction applications.

The voltage curve is shown at the top of the figure. The current-limited initial step of charging is followed by a constant-voltage period at 2.4 V/cell. Equalizing charging up to 2.65 V/cell is the final step of the charging schedule. Discharge is assumed at constant current ($I_5 = 20$ A/100 Ah). The broken line represents the calorific voltage U_{cal}, the full line the actual discharge voltage U.

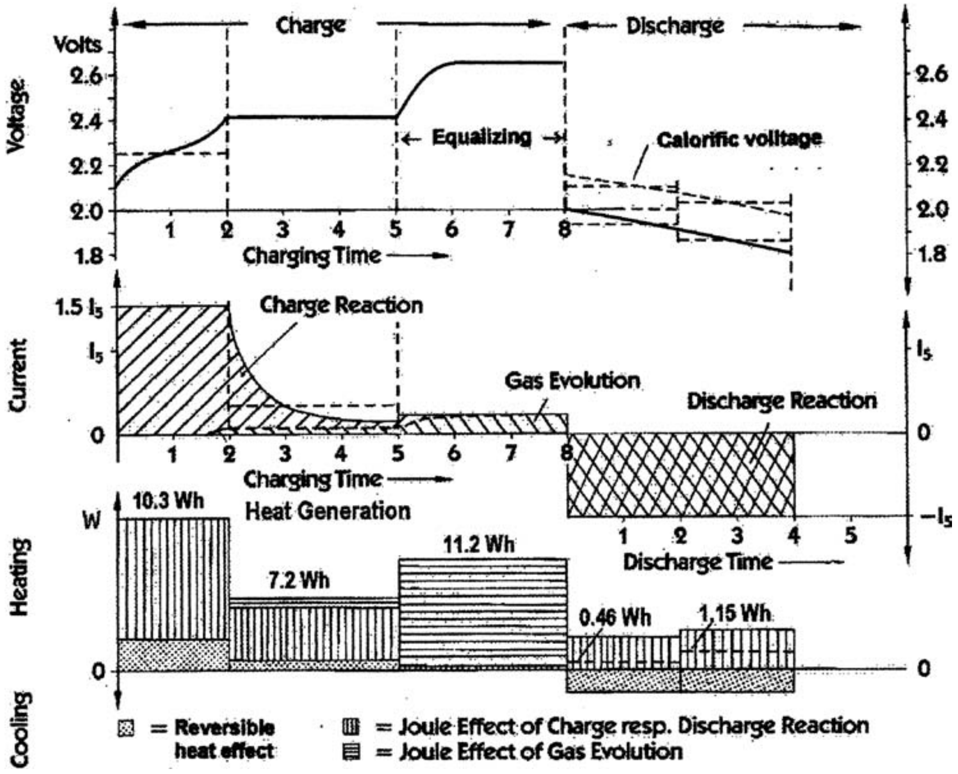

Figure 1.11 Charging/discharging cycle of a vented traction battery.

Lead-acid with tubular positive plates (Varta PzS), 500 Ah. Heat-generation values referred to 100 Ah of nominal capacity. The figures in the bottom part represent heat generation in total. The sum of the whole charging period amounts to 28.7 Wh/100 Ah. Internal resistance 4.5 mΩ per 100 Ah of nominal capacity.

The center part of Fig. 1.11 shows how the current is distributed to charging, water decomposition, and discharging. During the initial stage, practically only charging occurs; water decomposition can be neglected on account of the flat current voltage curves for gas generation (cf. Fig. 1.19). Only when the voltage approaches the 2.4 V level, the onset of water decomposition becomes noticeable. The broken horizontal line marks the average voltage during this initial step. When subsequently the cell voltage remains at 2.4 V, gas evolution is maintained at a roughly constant rate (assuming that the potentials of the positive and negative electrodes do not change too much). During the equalizing step, nearly all the current is used for water decomposition on account of the progressively reduced charge acceptance. During discharge, water decomposition again can be neglected because of the reduced cell voltage.

At the bottom of Fig. 1.11, the heat generation is drawn as blocks that represent average values for the corresponding sections of the charging/discharging process. The distribution between reversible heat effect, charging, and water decomposition is marked by different patterns of the areas concerned. The value above each block is the total heat generation in Wh.

During the first stage of the charging process, gas evolution can be neglected. The heat is mainly generated by the Joule effect, on account of the high current and the rather high internal resistance of 4.5 mΩ assumed for this example, which corresponds to a battery with widely spaced tubular plates and causes a voltage drop (polarization) of 180 mV. But the reversible heat effect also contributes noticeably to heat generation, on account of the converted active material. (40Ah ≈ 85 Wh is

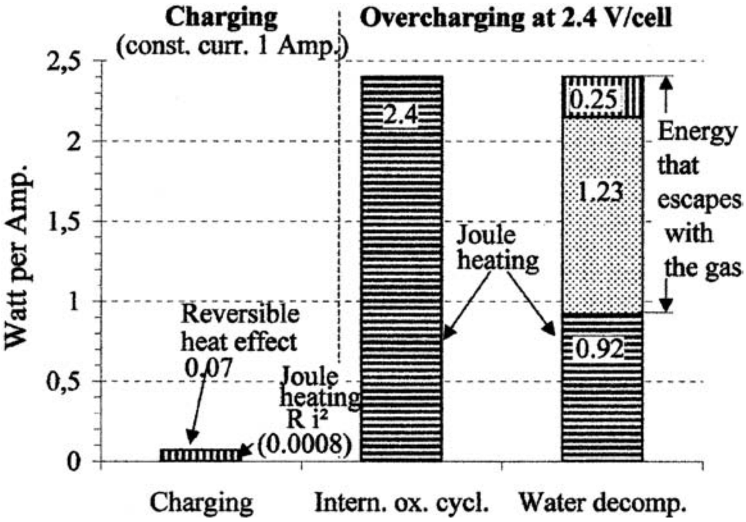

Figure 1.12 Heat generation in valve-regulated lead-acid batteries by charging and overcharging, referred to a current of 1 A.

When the internal oxygen cycle is established, almost all the overcharging current is consumed by the internal oxygen cycle (center bar in the graph). The bar on the right corresponds to a vented battery. Internal resistance assumed as 0.8 mΩ per 100 Ah of nominal capacity, as in Fig. 1.13.

charged during this period, which means a reversible heat effect of about 3 Wh = 11 kJ.)

When 2.4 V is reached, the current is reduced and, as a consequence, Joule heating and the reversible heat effect caused by the charging reaction are reduced too. But now the approximately constant gas evolution causes most of the generated heat $((U - 1.48) \cdot i)$.

During the equalizing step, gas evolution (required for mixing of the electrolyte) dominates. On account of the large difference between the actual charging voltage and the calorific voltage of water decomposition, heat generation is considerable, although the current is rather small (cf. Fig. 1.10).

During discharge, due to the small overvoltage, heat generation is also small, and further reduced by the reversible heat effect that now causes cooling.

Heat generation in a valve-regulated lead-acid battery (VRLA battery) is mainly determined by the internal oxygen cycle that characterizes this design. It means that the overcharging current is almost completely consumed by the internal oxygen cycle formed by oxygen evolution at the positive electrode and its subsequent reduction at the negative electrode (cf. Section 1.8.1.5A)

The reversible heat effect equals that in Fig. 1.10, but Joule heating is much smaller because of the lower internal resistance assumed in this example, which corresponds to a modern valve-regulated lead-acid battery designed for high loads. The most effective heat source is the internal oxygen cycle, since it converts all the electrical energy employed for overcharging into heat within the cell, because the reaction at the positive electrode is reversed at the negative one, and thus the equilibrium voltage of this ‘cell’ would be zero. As a consequence, the cell voltage in total means polarization that produces heat. For this reason, overcharging of valve-regulated lead-acid batteries must be controlled much stronger than that of vented ones to avoid thermal problems.

The charging behavior of a valve-regulated type is shown in Fig. 1.13 that corresponds to Fig. 1.11. The calculation assumes an initial charging period at constant current of 40 A/100 Ah ($2 \times I_5$; voltage drop 32 mV), limited by the charging device, and subsequent charging at 2.4 V per cell. As an ‘equalizing step’, overcharging for 1.5 hours at 2.5 V at a maximum current of 5 A/100 Ah is assumed, which corresponds to the usual operation of a cycle regime of valve-regulated lead-acid batteries.

In the center of Fig. 1.13 the distribution of the current between charging and internal oxygen cycle is shown. The current share, consumed by the internal oxygen cycle is magnified by 10 during the initial phase and by two during equalizing. The sum of charging current and internal oxygen cycle represents the charging current (hydrogen evolution and grid corrosion equivalents are not considered, since they are two orders of magnitude smaller than that of the internal oxygen cycle). Actually, the current would slightly be increased by heating of the battery. This increase also is not considered in Fig. 1.13.

The bottom part of Fig. 1.13 shows the heat generation by the various processes. At the beginning, the reversible heat effect dominates heat generation due to the high amount of material that is converted. Joule heating is proportional to the voltage drop, caused by the current flow. The relation between the reversible heat effect and Joule heating is determined by the internal resistance of the battery. With batteries of higher internal resistance, Joule heating would dominate during this

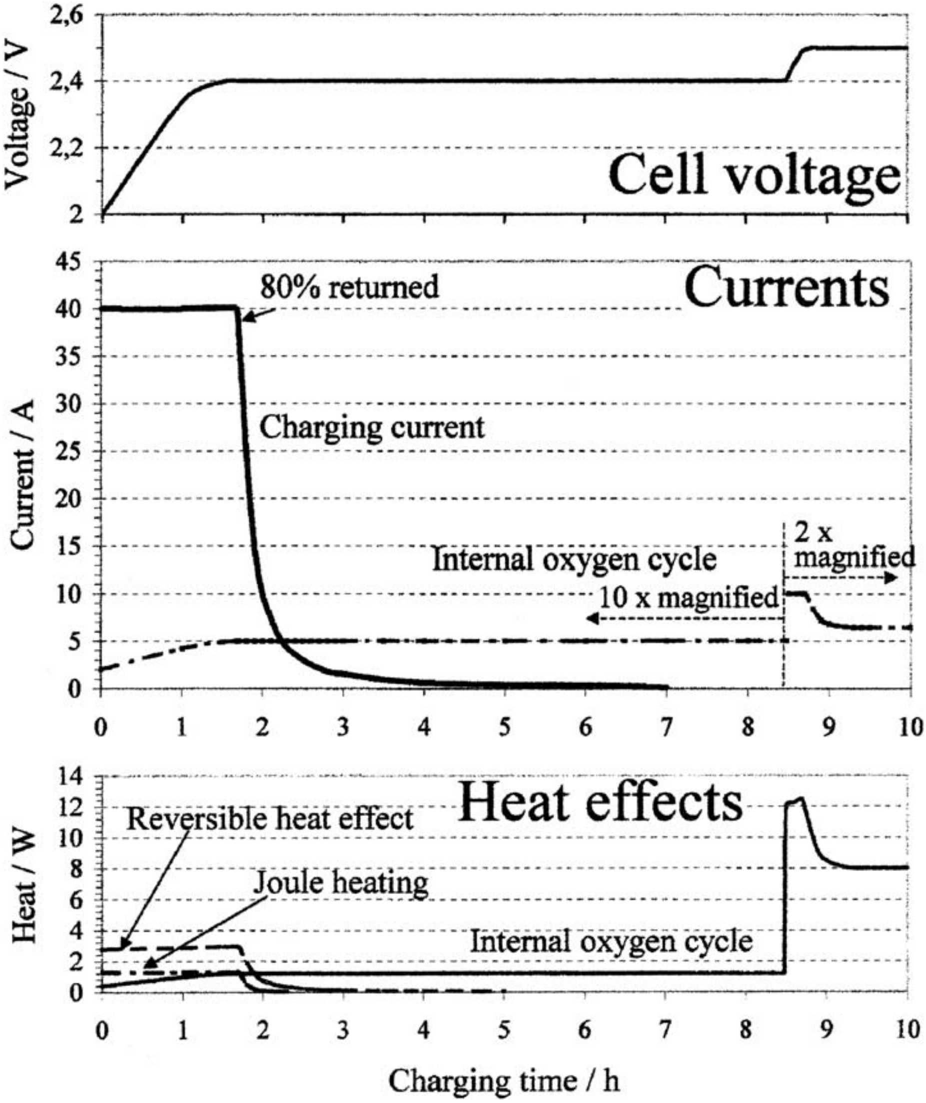

Figure 1.13 Charging of a VRLA battery at 2.4 V/cell, calculated curves, constant temperature, and 100% of recombination efficiency assumed. Internal resistance 0.8 mΩ (single cell). 1.5 hours equalizing at 2.5 V/cell at a current limit of 5 A. Heating of the battery during charging is not considered. Heat generation: reversible heat effect 5.7 Wh; Joule heating 2.3 Wh; internal oxygen cycle 23.2 Wh; in total: 31.2 Wh.

initial stage of the charging process. This applies, for example, to Fig. 1.11 where the calculation is based on an internal resistance of 4.5 mΩ/100 Ah, corresponding to a larger traction battery with tubular plates.

When the charging voltage is reached, the current decreases and this applies also to heat generation due to the reversible heat effect and Joule heating, while heat generation by the internal oxygen cycle remains constant, according to the constant cell voltage (which actually would slightly be increased by heating up).

Figure 1.13 shows the strong heating effect caused by the internal oxygen cycle. The current share consumed by this reaction is very small and had to be magnified to be recognized in the current comparison. But the total heat generation is largely determined by the internal oxygen cycle, especially during the equalizing step that in Fig. 1.13 causes 13.5 Wh of heat, and so nearly half of the heat generated in total. Actually, an even larger heat generation is to be expected, since, as already mentioned, the calculation did not consider the heat increase within the cell during charging that again would increase the rate of the internal oxygen cycle.

In nickel/cadmium batteries the reversible heat effect is larger than that in lead-acid batteries and has the opposite sign, i.e. it acts as a cooling effect during charging and contributes additional heat during discharge (cf. Table 1.3). As a consequence, vented nickel/cadmium batteries are more in danger of being overheated during discharging than during charging. This is different for sealed nickel/cadmium batteries where the internal oxygen cycle is a most effective heat source when the battery is overcharged (cf. Fig. 1.15).

Figure 1.14 shows heat generation in a vented nickel/cadmium battery when charged and discharged with a constant current (5 hour rate) and the charging voltage is limited to 1.65 V/cell. The calculation is based on the equilibrium voltage $U^o = 1.3$ V (Table 1.1) and the calorific voltage $U_{cal} = 1.44$ V (Table 1.3). Due to the uncertain thermodynamic data, these calculations are only rough approximations, but correspond with practical experience.

During the initial two sections of the charging period, slight cooling is observed on account of the reversible heat effect that consumes heat at a constant rate proportional to the current. With increasing cell voltage, Joule heating is increased, and when the charging voltage exceeds 1.48 V/cell, water decomposition contributes an increasing amount of heat, since its calorific voltage is exceeded (Column 5, Line 8 in Table 1.3 and Fig. 1.10). Thus, during the final sections of the charging period, a growing amount of heat is generated.

In total 12.3 Wh were generated during discharging, while heat generation during charging only amounted to 9.25 Wh. The main reason is that the reversible heat effect generates additional heat during discharge, while it compensates for heat generation during charging.

The situation is different for sealed nickel/cadmium batteries, due to the internal oxygen cycle. Figure 1.15 illustrates the heat evolution of a sealed nickel/cadmium battery during constant-current charging with a charge factor of 1.4 (such an amount of overcharge is usual for conventional charging methods but can only be applied to comparably small batteries < 10 Ah).

- The voltage curve at the top shows the gradual increase of charging voltage with charging time. The generated heat is calculated as an average value for different sections of this curve. The numbers beside the charging curve are the average voltages (V per cell) for the corresponding section.
- The middle figure shows the (constant) current and its distribution between charging process and internal oxygen cycle.
- The bottom figure shows the heat generation as average value for the different sections. The numbers are the heat in kJ (for comparison, converted to 100 Ah of nominal capicity). During the first 2 hours, the

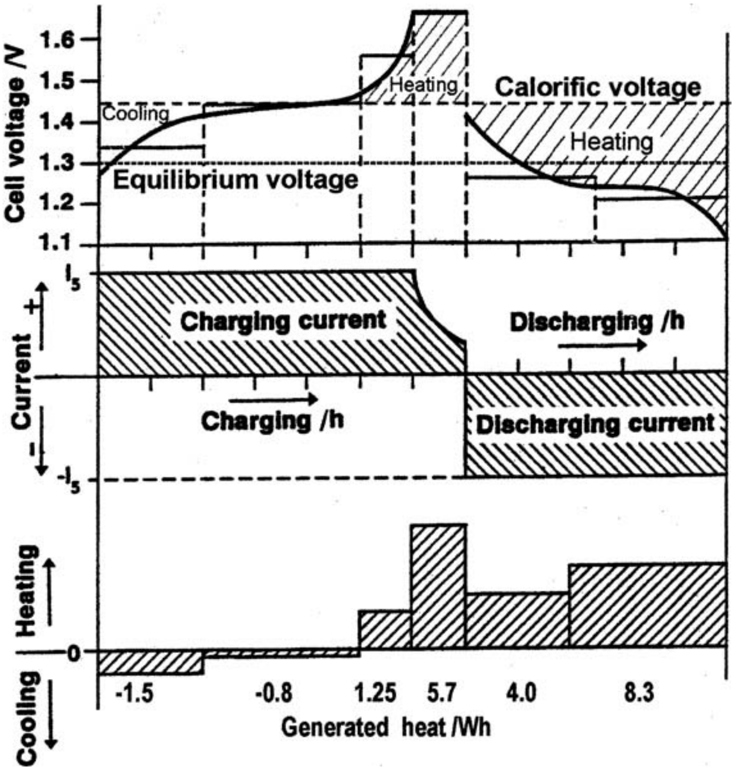

Figure 1.14 Heat generation during charge and discharge of a vented nickel/cadmium battery. Charging with constant current I_5 (5 hour rate) until 1.65 V/cell is reached. Discharge also with I_5.

In the top part, sections are shown that were used to calculate the average heat generation, shown in the bottom part. The calorific voltage of 1.44 V is shown as the broken line. The difference $U - U_{cal}$ determines the effect of heating or cooling. (Calculation based on $U^o = 1.3$ V; $U_{cal} = 1.44$ V.) VARTA TS-type values referred to 100 Ah of nominal capacity.

> reversible heat effect exceeds the Joule effect and cooling is observed. So the number for this section is written below the zero line.

When the charging process approaches completion, nearly all the current is used for the internal oxygen cycle, which causes much heat generation.

Battery manufacturers usually strongly advise the customer not to charge sealed nickel/cadmium batteries at constant voltage without monitoring, because of this heat generation on account of the internal oxygen cycle. Since this cycle can attain extremely fast rates, the situation is very dangerous in regard to thermal runaway.

Altogether 264.7 kJ = 73.53 Wh of heat are generated, referred to a nominal capacity of 100 Ah. These figures are much larger than the 31.2 Wh/100 Ah of the valve-regulated lead-acid battery in Fig. 1.13. The main reason for the high heat generation of the sealed nickel/cadmium battery in Fig. 1.15 is the high charge factor of 1.4. The charging factor for the lead-acid battery in Fig. 1.13 is only about 1.10.

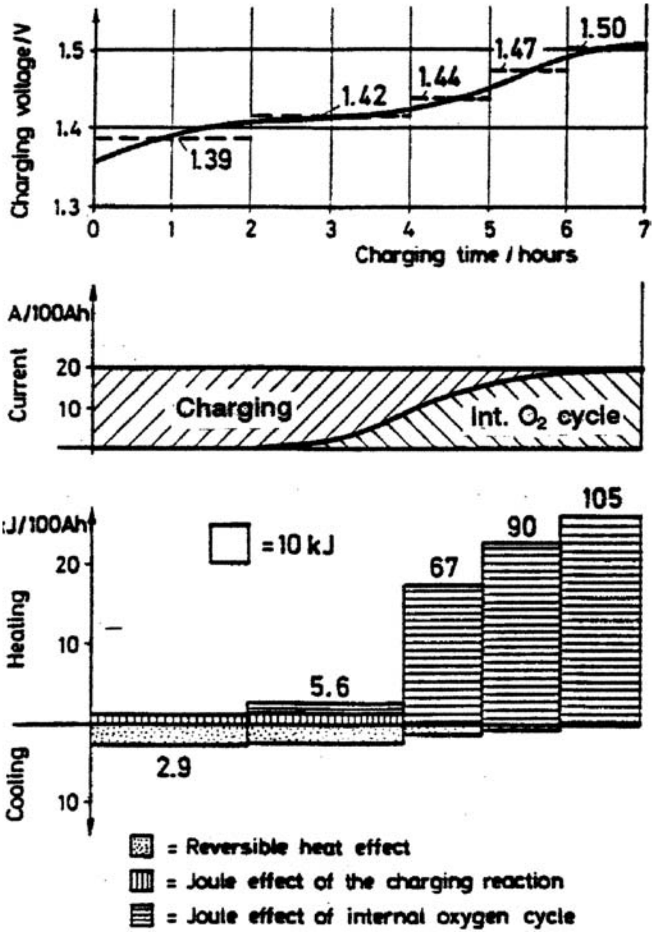

Figure 1.15 Charging of a sealed nickel/cadmium battery with constant current 0.2 C(A). During 7 hours 140% of the nominal capacity are recharged, which corresponds with a charge factor 1.4. For comparison, all values are converted to 100 Ah of nominal capacity. Actually, batteries of this type and for such a charging schedule are only available in sizes < 10 Ah.

Middle: current distribution between charging and internal oxygen cycle.

Bottom: heat generation as an average of the different sections (slight cooling during the first 2 hours).

This indicates the strong influence of overcharging on heat generation in sealed or valve-regulated batteries caused by the internal oxygen cycle.

Figure 1.15 shows that this heat is generated practically during the last 3 hours of the charging process, and means an average heat generation of 24.51 W/100 Ah for these 3 hours. The conclusion can be drawn that sealed nickel/cadmium batteries can be charged at a high rate as long as the current is actually used for charging and not for the internal oxygen cycle. Rapid charging methods, as described in Section 13, are always based on this principle.

1.4.5 Heating of the Battery and Heat Capacity

While a battery is being charged or discharged, the heat generation caused by the flowing current raises the temperature until balance is achieved between heat generation in the cell and heat dissipation to the environment. Thus the two parameters heat generation within the battery and heat dissipation from the battery determine the temperature changes of the battery according to the formula

$$\frac{dT}{dt} = \frac{1}{C_{Batt}} \cdot \left(\frac{dQ_{gen}}{dt} - \frac{dQ_{diss}}{dt} \right) \tag{42}$$

with dQ_{gen}/dt: generated energy per unit of time; dQ_{diss}/dt: dissipated energy per unit of time; Q_{gen} is positive, when energy is generated $= Q_{total}$ in Eq. (38).

Equation (42) points out that heat generation and heat dissipation are parameters of equal weight, which means that possibilities to dissipate heat are to be considered as thoroughly as the problem of heat generation. The rate of the temperature change is determined by the heat capacity of the battery C_{Batt}. (in$\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) defined by

$$\sum \left[m(i) \cdot C_p(i) \right] = C_{Batt}. \tag{43}$$

with m(i): component i in kg; (i): the components in the battery; Cp(i): specific heat of component (i) in $\text{kJ}/(\text{kg} \cdot \text{K})$.

The specific heat C_{Batt} of a battery depends on its specific design, but the different systems do not vary too much. In batteries with aqueous electrolyte, the content of water is of great importance due to its high specific heat. The specific heat of customary vented lead-acid batteries is slightly above $1\,\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$, while the corresponding value of VRLA batteries is in the range of 0.7 to $0.9\,\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$. As the specific heat of a vented nickel/cadmium battery with sintered electrodes the value $1.25\,\text{J}\ \text{kg}^{-1}\text{K}^{-1}$ is reported (9), while that of the sealed version is correspondingly lower. For lithium/thionyl chloride and lithium-ion batteries values of 0.863 and $1.052\,\text{J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$ are reported (13).

Heat dissipation increases with a growing temperature difference ΔT between the battery and its surroundings, and a stable temperature of the battery is reached at a certain ΔT when heat generation balances heat dissipation, i.e. when $dQ_{gen}/dt = dQ_{diss}/dt$.

If heat generation within the battery increases faster with increasing battery temperature than heat dissipation, such a thermal balance is not reached and temperature increase continues unlimited. This situation is called ‘thermal runaway’.

If heat dissipation dQ_{diss}/dt is zero (adiabatic situation where heat dissipation is not possible), it is only a question of time, until the battery will exceed any temperature limit, even at a very small heat generation.

1.4.6 Heat Dissipation

Heat exchange of a battery with its surroundings proceeds in various ways. For the emission of heat these ways are sketched in Fig. 1.16. A corresponding situation with all the arrows reversed would apply for heat absorption from a warmer surroundings.

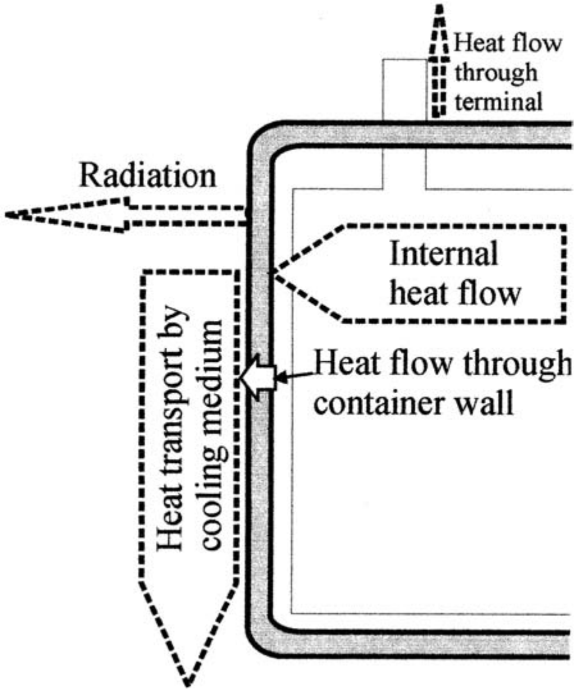

Figure 1.16 The various ways of heat escape from the battery.

Three mechanisms are involved in this heat exchange:

1. Heat radiation.
2. Heat flow by thermal conduction, e.g. through the components of the battery and the container wall.
3. Heat transport by a cooling or heating medium.

Usually they occur in combination.

Figure 1.16 indicates that cooling of batteries mostly occurs via their side walls. The bottom surface usually is in contact with the basis that attains the same temperature as the battery itself, except the battery is equipped with cooling channels in the bottom. The upper surface usually is of little importance for heat exchange, since the lid has no direct contact to the electrolyte, and the intermediate layer of gas hinders heat exchange because of its low heat conductivity (cf. Table 1.5). Moreover, in monobloc batteries the cover often consists of more than one layer. Heat flow through the terminal normally can also be neglected, since the distance to the electrodes is rather long and often the terminals are covered by plastic caps. (Cooling through the terminal occasionally has been applied with submarine batteries which are equipped with massive copper terminals (14).)

1.4.6.1 Heat Radiation

Heat radiation occurs according to the law of Stefan-Boltzmann:

$$dQ/dt = \varepsilon \cdot \sigma \cdot T^4 \qquad W/m^2 \tag{44}$$

with ε: Stefan-Boltzmann constant ($5.67 \cdot 10^{-8}\, W \cdot m^{-2} \cdot K^{-4}$); σ: emission ratio of the material with respect to an ideal emitter (ca. 0.95 for usual plastic materials that are used for battery containers); T: absolute temperature in K.

The fourth power of T in Eq. (44) means a very strong dependence on temperature. Heat radiation always happens from the warmer to the colder part, and there is no heat flow between elements having the same temperature.

The heat flow by radiation between two elements A, B is

$$dQ/dt = \varepsilon \cdot \sigma \cdot (T(A)^4 - T(B)^4) \qquad W/m^2 \tag{45}$$

This also applies when one of these elements is the surroundings.

For comparatively small temperature differences against the environment, heat dissipation by radiation amounts to

$$dQ/dt \approx 5 - 6\ W \cdot m^{-2} \cdot K^{-1} \tag{46}$$

which means that a battery emits by radiation about 5-6 W/m^2 of its exposed surface for each K (or °C) of difference between its container surface and a lower environmental temperature. If the temperature of the surroundings is higher, a corresponding amount of heat would be absorbed. The size of the exposed surface referred to capacity depends largely on size and design of the battery. Some rough figures for lead-acid batteries are listed in Table 1.4. Corresponding values of nickel/cadmium and nickel/metal hydride batteries are slightly smaller because of the higher energy density that is reached by these systems, but the difference is fairly small.

According to these values, heat dissipation by radiation can be expected in the

Table 1.4 Specific surface area of prismatic cells in lead-acid batteries (rough approximations that just show the order of magnitude).

Single cells	
Large cells	≈0.04 m^2/100 Ah
Medium cells	≈0.1 m^2/100 Ah
Small cells	≈0.3 m^2/100 Ah
Cells in monoblocs	
Average per block	0.06 m^2/100 Ah
Center cells	0.04 m^2/100 Ah

Source: Ref. 5.

range of 0.2 to 1.5 W/100 Ah per K of temperature difference against the surroundings when 5 W/m^2 of radiation is assumed, according to Eq. (46). The estimation shows that radiation alone would be sufficient to dissipate the heat that is generated in lead-acid batteries under normal float conditions which hardly will exceed the current of 100 mA/100 Ah that means 0.2 W/100 Ah of generated energy per cell. But the estimation shows that radiation is fairly effective and thus a hot surface in its neighborhood will considerably heat up a battery.

1.4.6.2 Heat Flow by Thermal Conduction

Heat flow through a medium is determined by its heat conductivity and by the distance that has to be passed. It is described by

$$\frac{dQ}{dt} = f \cdot \lambda \cdot \frac{\Delta T}{d} \quad W/m^2 \tag{47}$$

with f: surface area in m^2; λ: specific heat conductance ($J \cdot s^{-1} \cdot m^{-1} \cdot K^{-1}$); d: thickness of the medium (e.g. the container wall) in m.

The specific heat conductance of some materials that are of interest in connection with batteries or their surroundings are compiled in Table 1.5. It shows that heat conductivity is fairly high for materials that are used within the battery, like the various metals or water. As a consequence, the internal heat flow widely equalizes the temperature within the battery.

When metal is used as container, the temperature drop across its wall can be neglected. For plastic materials λ is in the order of $0.2\,W \cdot m^{-1} \cdot K^{-1}$. Thus heat conduction through the container wall can be approximated

$$dQ/dt = 200\,\Delta T/d \quad W/m^2 \text{per K for d mm of wall thickness} \tag{48}$$

which means for a wall thickness of 4 mm

$$dQ/dt \approx 50\,W \cdot m^{-2} \cdot K^{-1} \tag{49}$$

Table 1.5 Heat conductance (λ in Eq. (47)) of some materials at room temperature.

Material	Heat conductance $W \cdot m^{-1} \cdot K^{-1}$
Lead	35
Iron	80
Copper	400
Nickel	91
Water	17
SAN	0.17
PVC	0.16
Polypropylene (PP)	0.22
Hydrogen	$10.5 \cdot 10^{-5}$
Air	$1.5 \cdot 10^{-5}$

or ten times that of radiation (Eq. (46)). Thus heat conductivity even through a plastic container wall is fairly high, and the temperature measured at the sidewall usually represents a good approximation of the average cell temperature. This is no longer true at very high loads. For example, during high rate discharges (about 6 minutes of discharge duration), temperature differences up to 15 K have been observed between the center and the surface in 155 Ah monoblocs of lead-acid batteries (15).

1.4.6.3 Heat Transport by Coolants

The most simple way of cooling by heat transport is free convection of air at the outer vertical surfaces which usually is applied to stationary batteries. It depends on the height of the cells or monoblocs and amounts for small differences ΔT to

$$dQ/dt \approx 2 - 4\,W \cdot m^{-2} \cdot K^{-1} \qquad (50)$$

These figures hold only for free air convection, which requires a minimum distance of about 1 cm between facing walls (cf., e.g. Ref. 5, p. 39). Corresponding spacing of battery blocks should always be observed.

Comparison between Eq. (46) and Eq. (50) indicates the importance of energy dissipation by radiation even at room temperature (which often is underestimated). Consequently, uniform radiation conditions should be observed when a battery is installed. Heated surfaces in the neighborhood (e.g. from rectifiers) must be well shielded.

Forced Cooling and Heat Management

Proper heat management of a battery is not only intended to avoid a too high temperature, rather it is of the same importance to keep all cells of a battery within a range of temperatures that is as small as possible. Otherwise, the strong influence of the temperature on aging would cause different states of the individual cells (state of charge (SOC) as well as state of health (SOH)), depending on their location within the battery. Then charging and discharging performance of the individual cells would no longer be uniform, and premature failure of the cells that are in an unfavorable location might cause premature failure of the whole battery.

With many applications, especially in the field of stationary batteries, ‘natural’ cooling is sufficient as long as all the cells or monoblocs operate under similar thermal conditions. Forced cooling, however, is required for large and compact batteries, especially when they are loaded heavily or cycled. Therefore, forced cooling systems have mainly been developed for electric vehicles, to prevent overheating and to attain uniform temperature in the inner and outer cells in larger batteries (16). For comparison, some figures of the efficiency of cooling methods are listed in Table 1.6.

The most simple method of forced cooling is forced airflow, listed in Line 4 of the table. It uses air as coolant that is blown by a fan through channels formed by the spacing of the cells or monoblocs within the battery. The low specific heat of air and its low specific heat conductance, however, limit this method. More effective coolants are mineral oil and water. The first has the advantage that it cannot cause short circuits, but its specific heat content is rather low, at least compared to water, which proves to be most effective.

Table 1.6 Heat dissipation by various mechanisms. Especially the figures for forced flow depend on a large number of parameters, e.g. design of the cooling system, flow rate, etc., and the listed values can only be considered as a rough comparison gained by a particular experiment.

	Heat dissipation process	Heat dissipation	Sources
		$W \cdot m^{-2} \cdot K^{-1}$	
1	Radiation	5–6	Eq. (46)
2	Heat flow through a plastic wall of thickness d (mm)[a]	200/d	Eq. (48)
3	Heat transport by vertical free air convection[b]	2–4	Eq. (20)
4	Forced airflow	25	[c]
5	Forced flow of mineral oil	57	[c]
6	Forced flow of water	390	[c]

[a] Heat flow through metallic containers or troughs is by orders of magnitude faster (Table 1.5).

[b] Sufficient spacing of the cells must be provided.

[c] Measured with an Optima battery for a uniform mass flow of the cooling media of 50 g/s (16).

A widespread method for forced cooling uses pockets of plastic material that are arranged between the cells or blocks (along the sidewalls) and are passed by the cooling medium, usually water. Other battery designs provide special passages for the coolant within the cells or monoblocs. A system that was applied in the 1970s to power large busses by lead-acid batteries used spirally wound tubes through which the coolant flowed (cf. Fig. 4.8).

1.5 GENERAL TERMS AND CHARACTERISTICS

In the following some terms and definitions will be described that are in general use. It has, however, to be considered that in the different fields of battery application the meaning of these terms may vary, and that, furthermore, such terms are subject to historical development. Thus deviations from the given definitions occasionally may be observed, despite great efforts of various international committees to standardize them.

1.5.1 Cathodic/Anodic

Figure 1.1 shows the basic design of a single cell. When the battery is discharged, the active material in the positive electrode is reduced ($S(P)_{ox} + n \cdot e^- \Rightarrow S(P)_{red}$), i.e. a negative current flows from the electrode into the electrolyte. Such a reducing current flow is called cathodic. In the negative electrode, the active material is oxidized ($S(N)_{red} \Rightarrow S(N)_{ox} + n \cdot e^-$) by an anodic current. The terms cathodic and anodic are strictly connected to the direction of current flow. Cathodic means that a negative current flows from the cathode into the anode via the electrolyte; anodic means a positive current flowing from the anode to the cathode via the electrolyte, i.e. in opposite direction. In accordance with these terms, in the field of primary batteries the positive electrode is usually called cathode since the positive electrode is discharged by a cathodic current, while the negative electrode is called anode, and this is unambiguous, since only discharge occurs.

In secondary batteries, it depends on charge or discharge which of the two electrodes is the anode or cathode. Thus, in lead-acid batteries, the negative is the anode during discharging ($\mathrm{Pb} \Rightarrow \mathrm{Pb}^{2+} + 2 \cdot \mathrm{e}^-$), but the cathode during charging. The opposite applies to the positive electrode: $\mathrm{Pb}^{4+} + 2 \cdot \mathrm{e}- \Rightarrow \mathrm{Pb}^{2+}$ is a cathodic reaction, and the PbO_2 electrode is the cathode during discharging but the anode during charging. Because of this ambiguity, the terms ‘positive electrode’ and ‘negative electrode’ are preferred for secondary batteries. However, with lithium-ion batteries that partially have been developed commonly with primary lithium batteries, the terms cathode and anode have become customary also in the field of rechargeable batteries. And a similar use is observed with nickel/metal hydride batteries. When used with secondary batteries, the terms anode and cathode always apply to the discharging situation.

1.5.2 Cell/Battery

The basic element of each battery is the cell, corresponding to Fig. 1.1. The term ‘battery’ often refers to several cells being connected in series or in parallel, but sometimes also single cells are called ‘batteries’. The International Electrotechnical Commission (IEC) has meanwhile decided that officially the term *battery* also includes single cells if they have terminal arrangements such that they can be placed into a battery compartment. Furthermore such a ‘battery’ must carry markings as required by the IEC standard (17,18). According to IEC the term ‘cell’ still applies when referring to the component cells inside of a multicell battery.

Sometimes single-cell batteries are also called ‘monocells’, while batteries formed by a number of cells within a common container are known as ‘monoblocs’, especially in the field of lead-acid batteries. Multicell nickel/cadmium and nickel/metal hydride batteries are used as battery packs also called power packs, that combine a number of cells within a common housing. The cells in such a pack are often selected to have uniform capacity to prevent premature failure by deep discharging of single cells. Battery packs, in the field of lithium-ion batteries, and single cells are often equipped with safety devices, like temperature sensors, thermal fuses, or devices that increase the internal resistance when a specified temperature is exceeded. ‘Smart batteries’ have an incorporated controlling system, based on a processor that provides information in regard to capacity and aging of the battery, and, furthermore, controls proper charging and prevents overdischarge.

1.5.3 Active Material and Change of Volume

The term ‘active material’ means the components of the cell reaction. This term usually concerns materials in the positive and negative electrode, but may also include certain components of the electrolyte, like sulfuric acid in lead-acid batteries. Furthermore, some battery systems exist where the battery is stored separately (cf. Section 1.8.5).

The active material suffers chemical conversion on charge and discharge, and thereby often changes its volume. This may require special design features: Volume for expansion must be provided when the volume of the active material grows. Reduction in volume, on the other hand, can cause contact problems that require mechanical components like springs or ribbons that provide pressing forces within the electrode/separator couple and to the current-connecting elements.

The influence of the solubility of the reaction products has been considered in Fig. 1.5.

1.5.4 Nonactive Components

The split up of the cell reaction into two electrode reactions as indicated in Fig. 1.1 requires also a number of nonactive components. They can be classified into conducting and nonconducting components.

1.5.4.1 Conducting Components

The current has to be collected from the active material and conducted to the terminals. Often the current conductor simultaneously acts as a support for the active material. In some systems the container of the cell is made of metal and often simultaneously acts as terminal. In Leclanché cells (or zinc/carbon cells) the can of zinc simultaneously represents the active material of the negative electrode. When a number of electrodes are connected in parallel within the cell, corresponding connecting parts like pole bridges are required.

Additives, like carbon or metal powder, sometimes are required to improve the conductivity within the active material, especially in thick layers.

1.5.4.2 Separators

Separation of the two electrode reactions, as indicated in Fig. 1.1, requires that any electronic contact between positive and negative electrodes has to be strictly prevented. Otherwise, a short circuit is formed that discharges the battery. On the other hand, the ionic current through the electrolyte should be hindered as little as possible. In the early days, the widely spaced electrodes in lead-acid and nickel/iron or nickel/cadmium batteries were only separated by rods of glass or rubber. In modern batteries, thin plastic sheets are used with pores in the micrometer range that provide more than 80% of open volume, or layers of correspondingly fine plastic or glass fibers. The latter are applied in valve-regulated lead-acid batteries (VRLA batteries) and are known by the name AGM (absorbing glass mat).

In batteries with the internal oxygen cycle, like sealed nickel/cadmium, nickel/metal hydrid, or VRLA batteries, the felt not only separates the electrodes, but also stores the electrolyte while the large pores stay open for fast oxygen transport through the gaseous phase (Sections 1.8.1.5 and 1.8.2.2).

In narrowly spaced vented nickel/cadmium batteries, cellophane occasionally is used as an ion-conducting foil to prevent direct gas flow between the electrodes.

Polymer electrolytes can also be regarded as ion-conducting separators. A semipermeable membrane that only allows the permeation of sodium ions (Na^+) is the β alumina that simultaneously acts as separator and electrolyte in sodium/sulfur or sodium/nickel chloride batteries (Chapter 10).

1.5.4.3 Containers

Various types of plastic materials are used in the different systems. In lead-acid batteries it is a must to use glass, rubber, or plastics on account of the high cell voltage that would destroy all metals. The advantage of a plastic container is that no insulation is required between adjacent cells. A general drawback of plastic materials is their permeability for gasses, water vapor, and volatile substances. Therefore, with sealed nickel/cadmium batteries and also nickel/metal hydride batteries metal is used as container material.

1.5.4.4 Terminal Seals

The seal of the terminals is a critical element. In vented batteries with liquid electrolyte it has to prevent creeping of the electrolyte, which especially is observed for batteries with alkaline electrolyte. With sealed batteries, the post seal, furthermore, has to prevent the escape of hydrogen, and also has to prevent the intake of oxygen from the surroundings. Special techniques have been developed for the different battery systems. Premium cells for spacecraft applications, but also lithium batteries for long service life, often are equipped with metal/glass/metal seals that prevent any transport phenomena through its glass body.

1.5.4.5 Vents and Valves

Vent plugs are required with a number of battery systems because of secondary reactions that generate gases which must escape. Vents, as used for some rechargeable batteries, are simple openings that allow gas flow in both directions, i.e. out of the battery but also vice versa. The openings in such vent plugs are small to minimize water loss by diffusion of the water vapor. In modem batteries, such vents mostly are equipped with porous disks that prevent ignition sparks or flames from entering the cell and hinder the escape of electrolyte fumes from the cell.

Valves allow only the escape of gas and are required in valve-regulated lead-acid batteries for the escape of hydrogen, but are also used in most other sealed batteries to prevent damage of the cell in the case of a too high internal pressure when the battery is abused, e.g. overcharged at a too high current rate or reversed.

Rechargeable button cells in general have a rupture vent (breaking point) embossed into their metallic cell container that opens on a preset overpressure before the cell explodes.

Safety features that prevent overpressure sometimes are also employed in primary batteries.

1.6 BATTERY PARAMETERS

The discharging/charging behavior of a battery depends on a number of parameters, like current, voltage, and temperature. These parameters have to be specified when such data are compared.

1.6.1 Voltage

In the case of reversible systems the cell voltage may be derived from the thermodynamic data of the cell reactions according to Eq. (5). But often this equilibrium voltage cannot exactly be measured (even not at an open circuit), since the electrode process is not quite reversible, as in the case of the nickel electrode or since secondary reactions cause a slight deviation (cf. Fig. 1.18). Then the open cell voltage (OCV) actually is measured.

In some battery systems, like lead-acid, the OCV can be used for a rough determination of the state of charge. Other systems again, e.g. some primary lithium systems, offer a rather high initial open circuit voltage obviously due to higher valence oxides, which collapses by several hundred millivolts on the slightest load and never recovers to its initial value.

The cell voltage under load, the closed circuit voltage (CCV), depends on the current, the state of charge, and on the cell's history, like its lifetime or storage period.

A further term is the nominal voltage of a cell or battery that approximates the voltage of a system for its characterization (cf. Table 1.1). The nominal voltage is a specified value that experimentally may not be verifiable.

The coup de fouet, or initial voltage minimum, is a voltage minimum in the range of 20 mV/cell that is observed at the beginning discharge of fully charged lead-acid batteries (cf. Fig. 1.17). It is caused by the positive electrode, and can be ascribed to crystallization overvoltage (19). Initial voltage minima are also known

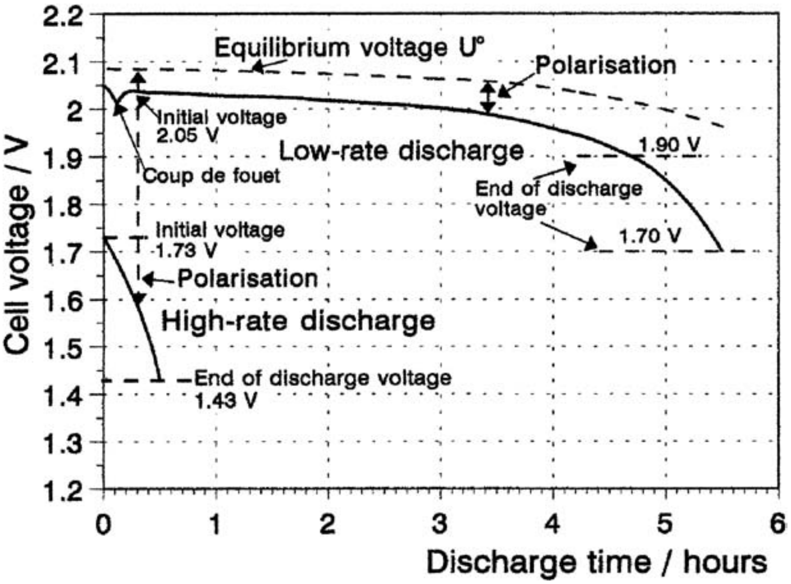

Figure 1.17 Typical low-rate discharge and high-rate discharge curves of a lead-acid battery and the main discharge parameters. The broken curve denotes the equilibrium or open circuit voltage.

The influence of the discharge current is also shown in Fig. 1.9.

for lithium batteries. They are referred to as initial voltage delay and are caused by protecting layers at the negative electrode.

1.6.2 Capacity

The capacity of a battery is defined by international convention as the electrical charge in units of Ah that can be drawn from the battery. When the battery is discharged with a constant current, its capacity is given by the relation

$$C_{Ah} = I \cdot \Delta t \quad /Ah \tag{51}$$

A more general definition would be

$$C_{Ah} = \int_0^t I(t) \cdot dt \qquad /Ah \tag{52}$$

The discharge parameters that beside the design of a battery mainly influence the capacity are

- Discharge current.
- Voltage limit, i.e. the final, the end point, the cut-off, or end-of-discharge voltage (EOD), that has to be specified.
- Temperature.

Further parameters that also influence the capacity, are the state of charge and the history of the battery, e.g. the preceding storage period. Any comparison of capacity data must always consider these parameters.

Figure 1.17 shows an example of two typical discharge curves of a lead-acid battery. The upper curve represents a low-rate discharge; the lower curve stands for a high-rate discharge. The broken curve in Fig. 1.17 represents the equilibrium voltage that for a lead-acid battery gradually decreases with progressing discharge on account of acid dilution (cf. Fig. 1.2). In other systems, where the electrolyte is not involved in the cell reaction, e.g. nickel/cadmium or nickel/metal hydride batteries, U^o remains approximately constant. The difference between the actual discharge curves and U^o means polarization according to Eq. (14). This difference usually increases with progressing discharge on account of the gradual increase of the internal resistance.

The depth of discharge (DOD) is an important parameter in regard to the number of cycles that can be reached with rechargeable batteries. For lead-acid batteries, deep discharges that are continued beyond the recommended maximum DOD can reduce the service life dramatically (cf. Section 4.3 of Ref. 5).

The nominal or rated capacity of a battery is specified by its manufacturer as the standard value that characterizes this battery. Usually it is specified for a constant current discharge at 20 °C or for room temperature. For various applications, nominal or rated capacities are often referred to different discharge durations, termed as C_{20}, C_{10}, or C_5.

1.6.2.1 Specification of Charging/Discharging Currents

In the field of conventional lead-acid batteries the designation of discharging/charging currents expresses the duration of discharge. So I_{10} and I_5 mean the current that results in ten and five hours duration of discharge, respectively. These discharge currents are specified for the various types.

Capacity ratings based on currents as multiples of the nominal capacity were initially used for nickel/cadmium batteries. But they soon became common practice also with lead-acid batteries and other rechargeable battery systems. In this case the discharge current is written

$$i = m \cdot C_r \tag{53}$$

with i: current in A; m: number that indicates multiple or fraction of C_r; C_r: rated or nominal capacity in Ah, but expressed in A; r: discharge period in hours that the capacity is rated to.

Note: *The factor m has no relation to discharge time; m is a pure number. For this reason, discharge rates in terms of multiples of the capacity cannot be converted into discharge duration. To evaluate the discharge duration, the discharge curves must be known.*

To indicate that the current is expressed as a multiple of the capacity, it is often written as 'CA' or 'C(A)', to indicate that 'C' does not mean a capacity in Ah but a corresponding current in A. In regard to the dimensions, Eq. (53) is not correct, since it mixes quantities with units (i in A, C_r in Ah, m without dimensions). But in the battery field, this description of discharging and charging currents is well established and understood. It is also used in the IEC standard for secondary cells and batteries containing alkaline or other nonacid electrolytes (20).

For primary batteries two discharge methods are in use:

1. Constant current discharge,
2. Constant resistance discharge.

Some test houses prefer method 1. By far prevailing is, however, method 2, as is evident from manufacturer's technical handbooks. Method 2 prevails also in the IEC standard for primary batteries.

Depending on manufacturer, the capacity of primary batteries may be given in terms of a service output duration that is gained by a test that simulates the concerned application (e.g. transistor radio test, portable lighting test, toy test, etc.). This duration (in hours or days) is proportional to the available capacity under these conditions. An exception are button cells to operate, for example, wristwatches. Their capacity is given in mAh.

The IEC standard for primary batteries, which so far has proposed most of the existing application tests, quotes 'minimum average duration values' instead of capacities in order to describe battery performance (21).

1.6.3 Energy Content

In general form, the energy E in Wh that can be drawn from the battery is represented by the product

$$E = \int_0^t U(t) \cdot I(t) \cdot dt \quad \text{Wh} \tag{54}$$

with U = voltage (V); I = discharge current (A); t = discharge period (hours).

Capacity measurements often are carried out at a constant-current load, and the energy output is calculated by multiplying the measured capacity with the discharge voltage. Therefore either the exact integration according to Eq. (54) is formed, or average voltages are used. Corresponding terms are

- Initial discharge voltage: voltage at the moment the load is applied.
- Average discharge voltage or mean discharge voltage: approximate average of the voltage during the whole discharge period).
- Midpoint discharge voltage: voltage after 50% of the capacity has been discharged ($\approx$ average voltage).

For constant resistance discharge as normally carried out for primary batteries, with R(Ω) = constant as resistive load, the following relation applies

$$E = \frac{1}{R} \int_0^t U(t)^2 dt \tag{55}$$

1.6.4 Specific Energy and Energy Density

For system comparison it has become common practice to relate the energy content of a given battery either to its weight or to its volume. The weight-related energy in Wh/kg is the specific energy. (In the negligent use of such terms it is often also called energy density or gravimetric density, although a density should always be referred to a volume.) A typical value for the specific energy of a lead-acid traction battery is 25 Wh/kg. For comparison, a modern lithium-ion battery offers approximately 125 Wh/kg.

The volume-related energy density is given in units of Wh/L or Wh/cm^3. The energy density is of special interest for batteries designed to power portable equipment. In such applications the size of the battery is in general of a higher priority than its weight. Present systems cover a range of 150 mWh/cm^3 (zinc/carbon) up to 1.2 Wh/cm^3 (alkaline zinc/air).

1.6.5 Internal Resistance

The internal resistance characterizes the capability of the battery to handle a certain load. It determines the battery's power output, and a general requirement is that the internal DC resistance must be significantly below that of the appliance (1/10 and less), otherwise the voltage drop caused by the current demand of the consuming device would limit the battery's service output duration too early.

The meaning of the term 'internal resistance' has to be considered with some caution, because it is not a simple ohmic resistance and depends on the way that it is used for its determination and also on the state of charge of the battery. With most battery systems the internal resistance increases when the end of discharge is approached, because of reduced conductivity of the formed compounds.

Mostly the direct-current method is applied, where the terminal voltage is compared at two different loads. The battery is loaded with the current i_1 for a few seconds and the voltage U_1 results. Then the current is increased to the value i_2 and the battery voltage is reduced to the value U_2, and the internal resistance R_i is calculated according to

$$R_i = \frac{U_1 - U_2}{i_2 - i_1} = \frac{\Delta U}{\Delta i} \tag{56}$$

The so-determined R_i comprises ohmic resistance within the electrodes and the electrolyte as well as overvoltage at the phase boundaries between the electrodes and the electrolyte. Equation (56) implies that the overvoltage is comparatively small compared to the ohmic voltage drop. To ensure a certain comparability, the tests are specified for many types of batteries and cell sizes (examples in Ref. 5).

For batteries with aqueous electrolyte the internal resistance can be determined by this method only for the discharge, but not during charging because of the high overvoltage of the gassing reactions.

When a preceding diffusion process limits the transport of reacting particles and a limiting current according to Eq. (29) is formed, voltage increase can no longer increase the current. Equation (56) would then lead to the $R_i \rightarrow \infty$. An example for such a behavior is the air/zinc system: with increasing current i the transport of oxygen, determined by the diffusion rate of oxygen becomes finally rate determining, and the voltage under a higher load collapses.

The short-circuit current is of interest especially for larger stationary batteries, since it stands for the maximum current that could be supplied by the battery for a short period of time. Its value helps in estimating the size of a fuse that might operate with the battery. The short-circuit current is determined according to Eq. (56) by extrapolating the resulting line to the voltage zero. It represents a dynamic parameter that decreases quickly with proceeding discharge. Published values always refer to the charged battery, if not specified otherwise.

The AC internal resistance of a battery is a complex parameter and difficult to interpret, since the AC behavior of a battery can only be approximated by an equivalent circuit of many components. During the last decades, the ohmic part of the impedance gained importance as a possibility to check the situation of valve-regulated lead-acid batteries that otherwise could be determined only by discharging. The impedance is mostly measured at a frequency of 1000 Hz. At such a high frequency it does not give any information on the battery's electrochemistry but only on its ohmic components, including the electrolyte. The resulting values are only used for comparison to detect faulty cells within a string. Established methods and devices are on the market.

1.6.6 Self-Discharge

Self-discharge means gradual loss of charge in the positive and/or negative electrode, when the battery is idle at open circuit. One reason can be the gradual reduction of the oxidation state in the positive electrode, e.g. the loss of oxygen in nickel hydroxide electrodes.

1.6.6.1 Mixed Potential

Secondary reactions can also cause self-discharge when, according to the thermodynamic data, they are possible at the equilibrium potential of the concerned electrode. Then the secondary reaction and the discharge reaction form a 'mixed potential', as shown in Fig. 1.18. The two electrochemical reactions compensate each other, and gradual discharge is the consequence.

The fairly steep current/voltage curve pointing upwards, represents the discharge of the lead electrode. The fast rise of this curve indicates the low overvoltage that characterizes this reaction. It means that high discharge rates can be achieved at low overvoltage or polarization values. The high overvoltage, marking the hydrogen evolution reaction, is expressed by the gradual rise of the corresponding current curve. At open circuit voltage, discharge reaction and hydrogen evolution have to balance each other, because no current flows through the electrode. The result of this balance is the mixed potential U_M in Fig. 1.18. As typical for an equilibrium potential, no external current appears. But the mixed potential is

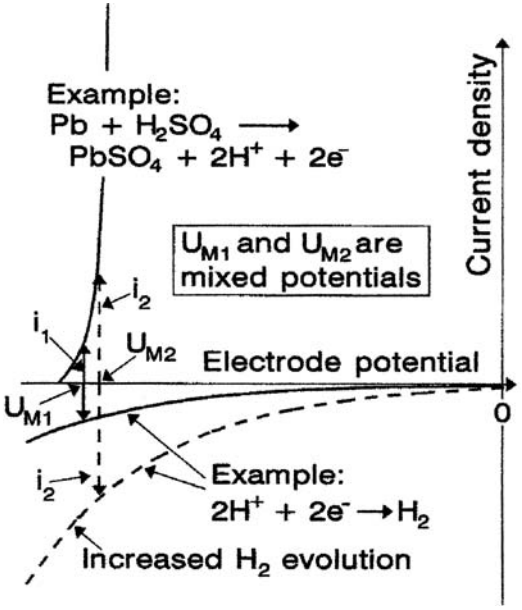

Figure 1.18 Mixed potential between discharge of the lead electrode and hydrogen evolution with the result of self-discharge. The dashed curve represents reduced hydrogen overvoltage. U_M: mixed potential. i_1, i_2: rate of self-discharge

not an equilibrium potential, because two different reactions occur, and gradual discharge of the negative electrode is the result.

The position of the mixed potential is largely determined by the faster one of the two reactions, while the rate of the reaction, the self-discharge in this example, is determined by the slower reaction. This is illustrated by comparison of the continuous and broken curves in Fig. 1.18. The continuous curve represents a fairly high hydrogen overvoltage; the broken curve depicts the case when hydrogen can be evolved more easily. The position of U_M is only slightly changed between the two examples, but the rate of the self-discharge, the current i_2, grows to a multiple of i_1 in the second case.

1.6.6.2 Further Self-Discharge Mechanisms

Self-discharge can also be caused by oxidizable or reducible substances in the electrolyte, when they reach the positive or negative electrode, respectively.

Such an effect is called a ‘shuttle’. It can, for example, be caused by iron ions in nickel/cadmium batteries which are reduced at the negative electrode according to

$$Fe^{3+} + e^- \Leftrightarrow Fe^{2+} \tag{57}$$

The Fe^{2+} ions migrate to the positive electrode, where they are oxidized by the reverse reaction. The process is repeated, when the so-formed Fe^{3+} ions again reach the negative electrode. In this way both electrodes are gradually discharged.

Another well-known shuttle is the ‘nitrate shuttle’ in nickel/cadmium batteries caused by relics of nitrate (NO_3^-) that have been left from the manufacturing process and are reduced to NH_4^+ at the negative electrode and subsequently again oxidized to NO_2^- at the positive electrode, and so form a shuttle.

The formation of electron conducting bridges is another mechanism that may establish a self-discharge, e.g. the formation of ZnO dendrites penetrating the separator system and getting in touch with the cathode, e.g. Ag_2O. The cathode material itself, if soluble to a certain extent like Ag_2O, may also lead to the formation of electron conducting Ag bridges if reduced by cell components, like an unsuitable separator (22).

1.6.6.3 Apparent Self-Discharge

After prolonged storage of primary cells, their increased internal resistance is often misinterpreted as self-discharge. Then the delivered capacity is reduced by an increased voltage drop, although the electrodes are still fully charged, i.e. at a reduced load the battery’s full capacity may still be obtained.

1.6.6.4 Capacity Loss During Storage

For reasons as given above, a battery loses capacity during storage. The extent of this loss depends on system, construction, and storage conditions, like temperature. In general, there is a distinct difference in capacity loss during storage between primary batteries and secondary batteries. The latter usually suffer faster self-discharge. For a given system, self-discharge mostly correlates roughly with the specific power output, i.e. the higher the specific power output, the higher the capacity loss during storage and vice versa.

Practical values for primary batteries at ambient temperature, that also include the apparent self-discharge, are in the range of 0.5% (and less) to 20% per year. The low value applies, for example, to lithium batteries with a high-quality seal. The 20% value is considered to be a maximum value for low-cost zinc carbon batteries, which is, however, mostly determined by the 'apparent self-discharge' that actually is caused by an increased internal resistance which actually only reduces the voltage under load so indicates an only apparent self-discharge. The true chemical or electrochemical self-discharge is much smaller.

Also secondary battery systems exhibit a broad range of different rates of self-discharge. Their values, however, are based on a 1-month period in contrast to primary systems (1-year period). Depending on system and construction typical values vary between 2% and 30% per month at ambient temperature. For the lead-acid system the values vary between 2% and 20% per month depending on antimony content and age. The lithium-ion system offers about 5% to 10% per month. Values in the range of 20% to 30% per month are observed for the nickel cadmium and the nickel metal hydride system.

In addition to the term capacity loss ΔC_S the term capacity retention ΔC_R is also in use. The capacity retention is defined by $\Delta C_R/C = 1 - \Delta C_S/C$, with C being the initial capacity of the fresh (and charged) battery.

1.7 GENERAL ASPECTS OF ELECTROCHEMICAL ENERGY STORAGE

According to the fundamental rules, the choice of a battery of a high specific storage capability should be guided by two aspects:

1. The free enthalpy ΔG should be large to achieve a high cell voltage (Eq. (5)).
2. The equivalent weight (mole weight per exchanged electron) of the reacting components should be as low as possible to gain a high energy output per weight.

According to these two criteria, favorites would be combinations of the light elements that are very distant in the periodic system of elements and thus have great chemical affinity to each other. Some examples of such a choice are listed in the matrix of Table 1.7

The combination lithium and fluorine according to the cell reaction

$$2Li + F_2 \Rightarrow 2LiF \tag{58}$$

offers the highest specific energy of all imaginable electrochemical systems. Its specific energy of more than 6 kWh/kg comes quite close to that of liquid fuels like gasoline that delivers about 10 kWh/kg (as ΔH). However, Eq. (58) would not be a cell reaction that could be handled in an electrochemical cell as shown in Fig. 1.1. Comparison of this value with the two last columns in Table 1.1 indicates how large the gap is between this hypothetical systems and corresponding values of actual batteries.

The decrease of the specific energy with increasing mole weight of the reacting components is indicated in the two lines for the halogens chlorine (Cl_2) and bromine

Table 1.7 Hypothetical electrode couples and their theoretical specific energy and cell voltage on the basis of thermodynamic data.

Positive electrode	Negative electrode H_2	 Li	 Na	 Mg
F_2	4100 Wh/kg 3.06 V	6270 Wh/kg 6.07 V	3588 Wh/kg 5.62 V	4690 Wh/kg 5.45 V
Cl_2	1000 Wh/kg 1.36 V	2520 Wh/kg 3.99 V	1830 Wh/kg 3.99 V	1732 Wh/kg 3.08 V
Br_2	354 Wh/kg 1.07 V	1116 Wh/kg 3.62 V	941 Wh/kg 3.61 V	755 Wh/kg 2.59 V

(Br_2) in Table 1.7 and their combinations with lithium (Li), sodium (Na), and magnesium (Mg). The halogens F_2, Cl_2, and Br_2 are of similar chemical affinity for these three negative electrode materials, but their mole weight is 19, 35.5, and 79.9 g/mole, respectively. Thus the cell voltage for the corresponding combination is very similar, but the specific energy is reduced in the ratio of the mole weight.

1.7.1 Electrolytes

The electrolyte is an important component of the cell. Often it is only the medium for electrode reactions and ionic conductivity and does not appear in the cell reaction (e.g., in nickel/cadmium and nickel/hydrogen batteries), sometimes as in lead-acid batteries, it is also a component of the cell reaction. A certain interaction, however, between the electrolyte and the active material usually cannot be prevented and often influences aging of the battery.

A great number of battery systems employ aqueous electrolyte, like the primary systems in Lines 1 to 4 in Table 1.1 and the secondary batteries in Lines 7 to 9 and 13 in this table. Their advantage is a high conductivity of acid and alkaline solutions at room temperature, and, furthermore, that quite a number of suitable electrode reactions occur in such solutions. The disadvantage of aqueous electrolytes is the comparatively low decomposition voltage of the water that amounts to 1.23 V and often gives rise to unwanted secondary reactions (Section 1.8.1).

Lithium as active material would heavily react with water. Batteries with lithium electrodes therefore have to use nonaqueous inorganic electrolytes, like thionyl chloride (Line 6 in Table 1.1) or organic electrolytes (Lines 5 and 10 in Table 1.1). A general disadvantage of organic electrolytes is the conductivity that at least is one order of magnitude below that of aqueous electrolytes. It must be compensated by narrow spacing of thin electrodes. Furthermore, interaction between the electrolyte and the active material is unavoidable at the high cell voltage as will be shown in Chapter 18.

Solid state electrolytes are also used, mainly in special long lasting batteries for extremely low loads, like lithium/LiJ/iodine batteries that are applied in pacemakers. High load batteries are the two examples, in Lines 11 and 12 of Table 1.1, based on sodium as active material in the negative electrodes. Both have been developed mainly to power electric vehicles (cf. Chapter 10). They have to be operated at temperatures of 300 to 400 °C to achieve sufficient conductivity of the electrolyte.

1.8 FUNDAMENTAL ASPECTS OF EXISTING BATTERY SYSTEMS

The large gap between the hypothetical storage data in Table 1.7 and those of existing batteries in Table 1.1 indicates that a great number of influences are to be considered in practical systems. A number of such basic influences will be illustrated in the following sections using some of our familiar battery systems as examples. Technical details of these batteries and their application, however, are subjects of later chapters.

1.8.1 Lead-Acid Batteries

The lead-acid battery (Line 7 in Table 1.1) has repeatedly been mentioned. It is the oldest secondary system, widely used, and well known. It is characterized by the fact that lead is used in both electrodes as the active material. In the negative electrode, lead (Pb) is oxidized by discharging into the divalent ion Pb^{2+} that in the diluted electrolyte of sulfuric acid forms lead sulfate $PbSO_4$ (as mentioned in connection with Fig. 1.5). In the positive electrode, the charged active material is based on four-valent ions (Pb^{4+}), which by discharging are also reduced to Pb^{2+}. The discharging/charging reactions can be written:

$$\text{Charging} \Leftrightarrow \text{Discharging}$$

$$\text{Positive electrode} \quad PbO_2 + H_2SO_4 + 2 \cdot H^+ + 2 \cdot e^- \Leftrightarrow PbSO_4 + 2 \cdot H_2O \quad (59a)$$

$$\text{Negative electrode} \quad Pb + H_2SO_4 \Leftrightarrow PbSO_4 + 2 \cdot H^+ + 2 \cdot e^- \quad (59b)$$

$$\text{Cell reaction} \quad Pb + PbO_2 + 2 \cdot H_2SO_4 \Leftrightarrow 2 \cdot PbSO_4 + 2 \cdot H_2O \quad (59)$$

The nominal equilibrium voltage amounts to $U^o = 2.0\,V$ as the difference between the equilibrium values of the electrode reactions $U^o_{PbO_2/PbSO_4} = 1.7\,V$ and $U^o_{Pb/PbSO_4} = -0.3\,V$ (referred to standard hydrogen electrode). These values depend on acid concentration (cf. Fig. 1.2; detailed table in Ref. 5; and the actual value at certain activities in Eq. (10)).

The comparatively high cell voltage, as a result of the high potential of the positive electrode and the low potential of the negative electrode, gives rise to a number secondary reactions that occur at electrode potentials within the cell voltage.

$$\text{Oxygen evolution at the positive electrode} \quad 2 \cdot H_2O \Rightarrow O_2 + 4 \cdot H^+ + 4 \cdot e^- \quad (60a)$$

$$\text{Hydrogen evolution at the negative electrode} \quad 4 \cdot H^+ + 4 \cdot e^- \Rightarrow 2 \cdot H_2 \quad (60a)$$

$$\text{Both together mean water decomposition} \quad 2 \cdot H_2O \Rightarrow O_2 + 2 \cdot H_2 \quad (60)$$

The equilibrium voltage of this reaction is $U^o = 1.23\,V$ (the difference $U^o_{H_2O/O_2} = 1.23\,V - U^0_{H^+/H_2} = 0\,V$) and is much smaller than the nominal voltage of the lead-acid battery.

Furthermore, at an electrode potential below 1.23 V, the reversal of Eq. (60a) is possible, according to

$$O_2 + 4 \cdot H^+ + 4 \cdot e^- \Rightarrow 2 \cdot H_2O \tag{61}$$

which means that reduction of oxygen always is to be expected at the negative electrode.

As a further problem, at the high potential of the positive electrode all metals are destroyed by oxidation. This applies also for lead that in principle starts to corrode at the potential of the negative electrode in the form of the discharge reaction $Pb \Rightarrow PbSO_4$. At the potential of the positive electrode, lead is further oxidized to lead dioxide (PbO_2) that forms a protecting layer according to

$$Pb + 2 \cdot H_2O \Rightarrow PbO_2 + 4 \cdot H^+ + 4 \cdot e^- \tag{62}$$

But this layer is not quite stable, and a certain corrosion remains (cf. Section 1.8.1.4).

As a consequence, the following unwanted reactions are always present in a lead-acid battery:

1. Oxygen evolution at the positive electrode.
2. Oxygen reduction at the negative electrode.
3. Hydrogen evolution at the negative electrode.
4. Grid corrosion.

Figure 1.19 illustrates the situation. The horizontal axis shows the potential scale referred to the standard hydrogen electrode, the range of the negative electrode on the left, the range of the positive electrode on the right. In the center, a range of about 1.2 V is omitted to stretch the scale. The rates of the various reactions are represented by current/voltage curves that indicate how the rate of the concerned reaction, expressed as current equivalent, depends on polarization (cf. Fig. 1.8).

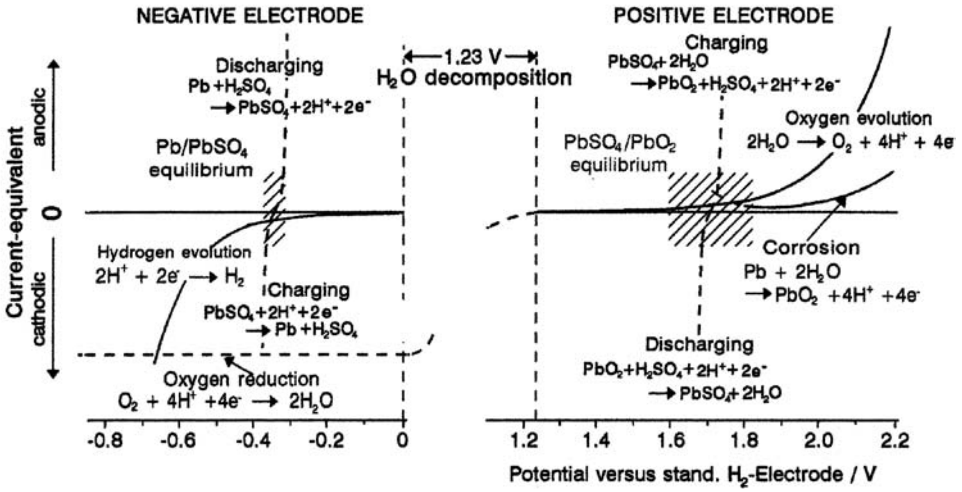

Figure 1.19 Reactions that occur in lead-acid batteries plotted vs. electrode potential. The rates of these reactions are indicated by current potential curves.

The two hatched columns represent the equilibrium potentials of the negative and positive electrodes. Their dependence on acid concentration is indicated by the width of these columns. The charging and discharging reactions are represented by the broken curves. They are very steep, since these reactions are fast, and occur at a high rate even at a small deviation from the equilibrium potential.

Figure 1.19 shows that hydrogen and oxygen evolution already occur at the open circuit potential of the negative and positive electrodes, respectively. The gradual increase of the corresponding curves at their beginning indicates that these reactions occur slowly, as long as the potential difference relative to their origin, the 'polarization' or 'overvoltage', remains fairly small. When, however, this deviation from the equilibrium potential exceeds a certain value, the two curves show a steep increase. This means that hydrogen as well as oxygen generation gain in volume enormously at correspondingly low and high polarization.

Figure 1.19 indicates a slight minimum of the corrosion reaction at about 40 to 80 mV above the $PbSO_4/PbO_2$ potential that always is observed. At an electrode potential below this minimum, corrosion increases due to destabilization of the protecting layer. Above this minimum, the corrosion rate follows the usual exponential increase with increasing electrode potential.

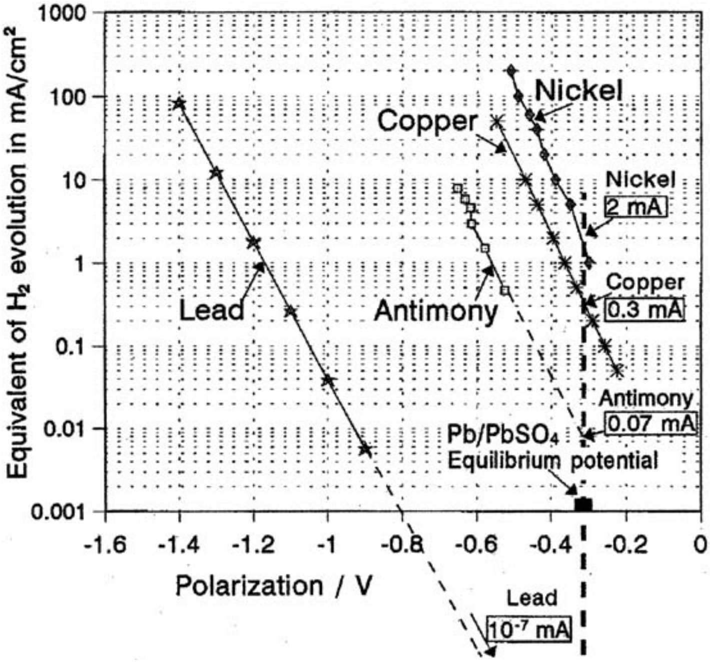

Figure 1.20 Hydrogen evolution in sulfuric acid at various metal surfaces in a semilogarithmic plot versus electrode potential (polarization). The origin of the horizontal scale is the equilibrium potential of the hydrogen electrode. The enframed figures represent the gassing rates at the open circuit potential of the lead electrode. [Data: lead (23); antimony (24), copper (25), nickel (26).]

The rate of oxygen reduction (according to Eq. (61)) is largely determined by the rate of oxygen transport and therefore does not depend on the potential of the negative electrode. It is characterized as a 'limiting current' (cf. Eq. (29)) by the horizontal curve in Fig. 1.19. In conventional batteries with liquid electrolyte, this limiting current is very small, since the diffusion rate of dissolved oxygen is very slow and its solubility is small. As a consequence the equivalent of oxygen reduction is limited to a few mA per 100 Ah of nominal capacity and thus is hardly noticed in battery practice. But in valve-regulated lead-acid batteries it is a fast reaction that characterizes overcharging (cf. Section 1.8.1.5).

1.8.1.1 Hydrogen Evolution

Hydrogen evolution, already mentioned as Eq. (60b),

$$2 \cdot H^+ + 2e \Rightarrow H_2 \qquad (63)$$

is one of the unwanted secondary reactions that fortunately are hindered for kinetic reasons and therefore are comparatively slow, even at an increased polarization. But hydrogen evolution is unavoidable, since its equilibrium potential is about 320 mV more positive than that of the negative electrode. For this reason, hydrogen evolution always occurs, even at the open circuit voltage, and a mixed potential is formed according to Fig. 1.18 that causes gradual discharge of the negative electrode according to

$$\begin{array}{lll} \text{Discharge} & Pb + H_2SO_4 \Rightarrow PbSO_4 + 2 \cdot H^+ + 2 \cdot e^- & (64a) \\ \text{Hydrogen evolution} & 2 \cdot H^+ + 2e \Rightarrow H_2 & (64b) \\ \hline \text{In total} & Pb + H_2SO_4 \Rightarrow PbSO_4 + H_2 & (64) \end{array}$$

This self-discharge at open circuit voltage represents the lowest hydrogen evolution rate of the charged negative electrode. When the electrode is polarized to more negative values, hydrogen evolution is increased according to the curves shown in Fig. 1.18. Polarization to more positive values than the equilibrium potential reduces hydrogen evolution, but simultaneously means discharge of the electrode.

Note: *In flooded batteries, self-discharge of the negative electrode usually is equated with Eq. (64), since other reactions can be neglected. In valve-regulated lead-acid batteries (cf. Section 1.8.1.5), however, oxygen intake can also cause considerable self-discharge of the negative electrode due to the easy access of oxygen to the electrode surface. In the mixed potential of Fig. 1.18, oxygen reduction then would form an additional discharging current.*

Hydrogen evolution is extremely hindered at the lead surface. This is pointed out in Fig. 1.20, where the hydrogen evolution rate as a function of the electrode potential is compared for several metals.

In this semilogarithmic plot, the hydrogen evolution curves represent Tafel lines (Section 1.3.3.1). Figure 1.20 indicates the outstanding situation of lead. The position of its Tafel line is far to the left, and hydrogen evolution at a faster rate than 0.001 mA/cm^2, the beginning of the current scale in this figure, is only possible at a polarization more negative than 0.8 V referred to the standard hydrogen electrode or -0.5 V compared to the open circuit potential of the negative electrode (the

$Pb/PbSO_4$ equilibrium potential). (Of all metals only mercury shows a similar hindrance of hydrogen evolution.) This is emphasized by the enframed figures for hydrogen evolution at the equilibrium potential of the lead electrode (in equivalents (mA/cm^2)). At nickel, copper, and antimony, hydrogen is evolved at the rate of 2, 0.3, and 0.07 mA/cm^2, respectively. At the lead surface, this value that approximately corresponds to the rate of self-discharge at open-circuit voltage is about six orders of magnitude smaller compared to hydrogen evolution at the other metals. Self-discharge by hydrogen evolution is noticed in the lead-acid battery despite of this small rate only because of the large surface area of the active material of about 500 m^2 per 100 Ah of nominal capacity. Multiplied by this surface area, the 10^{-7} mA/cm^2 in Fig. 1.20 correspond to 0.5 mA/100 Ah as a reference figure for self-discharge of pure lead.

Extreme hindrance of an electrochemical reaction is always endangered to be released by contaminants. Thus hydrogen evolution on the lead surface would enormously be increased by the precipitation of traces of other metals, like those shown in Fig. 1.20. Such a contamination shifts the Tafel line more to the right and annuls or at least aggravates the exceptional situation of lead.

Consequently, a low hydrogen evolution rate can only be achieved by the use of extremely purified lead and stable materials in the other components. This concerns mainly the active material and the grid in the negative electrode, but also all the other components of the cell, since critical substances may be leached out and migrate to the negative electrode where they are precipitated when their equilibrium potential is more positive than that of lead. The demand on highly purified materials, however, contrasts with the price that considerably grows with increasing purity. In the near future, this question may gain in importance, since due to the growing recycling efforts of all materials, secondary lead has increasingly to be used also for the active material in batteries. In the United States currently 75% of the lead on the market is secondary lead with a slightly increasing tendency (27). Secondary lead, however, may contain quite a number of additives which in their entirety determine the hydrogen evolution rate (28), and it is an economical question how far the various smelters can purify the lead at an acceptable price. Thus it may get more and more expensive to purchase ‘highly purified lead’. (According to practical experience, hydrogen gassing of the negative active material should be below 12 mL per 100 Ah per day to achieve a ‘balanced cell’ (29) (cf. Section 1.8.1.5). This corresponds to 1.09 mA/100 Ah and comes very close to the above value for pure lead).

Additives like organic expanders are often considered as a possibility to increase hydrogen over-voltage and reduce so hydrogen evolution. However, the intrinsic extraordinarily strong hindrance of hydrogen evolution at the lead surface makes it unlikely to find substances that further increase this effect without simultaneously blocking the charging/discharging reactions.

1.8.1.2 Oxygen Evolution

Oxygen evolution starts at 1.23 V (referred to SHE) and thus is always present as a secondary reaction at the positive electrode. The corresponding reaction, already mentioned as Eq. (60a), is

$$H_2O \Rightarrow 1/2 \cdot O_2 + 2 \cdot H^+ + 2 \cdot e^- \qquad (65)$$

Oxygen evolution and the discharge reaction of the positive electrode also form a mixed potential, similar to the situation of the negative electrode shown in Fig. 1.18. But oxygen evolution at the open circuit potential is small and therefore self-discharge due to oxygen evolution usually is not noticed. But oxygen evolution increases more rapidly with increasing potential than hydrogen evolution, and the slope of the corresponding Tafel line is steeper. For this reason, considerable rates of oxygen evolution are observed at a higher potential of the positive electrode. This is important, since oxygen evolution determines the rate of the internal oxygen cycle in valve-regulated lead-acid batteries which again is decisive for the rate of the float current as shown in Section 1.8.1.5.

1.8.1.3 Oxygen Reduction

Oxygen reduction is the reversal of oxygen evolution described by Eq. (65). It occurs according to

$$1/2 \cdot O_2 + 2 \cdot H^+ + 2 \cdot e^- \Rightarrow H_2O \tag{66}$$

at an electrode potential below 1.23 V vs. SHE (in the acid solution). Thus it is always possible at the negative electrode, and oxygen is immediately reduced when it reaches the surface of the negative electrode. Thus the rate of this reaction is largely determined by the rate of oxygen transport to the negative electrode surface, and forms a limiting current according to Eq. (29), represented by the horizontal line in Fig. 1.19.

Data that determine this transport are shown in Table 1.8. The transport rate of the oxygen in air is proportional to the diffusion coefficient, while that in the liquid is proportional to the product of solubility and diffusion coefficient. The resulting ratio is

$$\frac{\text{Transport rate in the air}}{\text{Transport rate in the liquid}} = \frac{0.18}{0.02 \cdot 2 \cdot 10^{-5}} = 4.5 \cdot 10^5 \tag{67}$$

Thus oxygen transport is about half a million times faster in the gaseous phase than in the liquid.

This great difference between the transport rates explains why oxygen reduction is hardly noticed at a charged negative plate that is submerged into water or acid, while a moist charged plate heavily reacts with oxygen according to $Pb + 1/2O_2 \Rightarrow PbO$ when exposed to the air ('burning' of the plate). In the latter case, oxygen has to permeate in the dissolved state only the thin wetting layer on the surface.

Table 1.8 Diffusion coefficient and solubility of oxygen at room temperature.

Diffusion coefficient of oxygen in air	$D_{air} = 0.18 \cdot cm^2 \cdot s^{-1}$
Diffusion coefficient of oxygen in 20% H_2SO_4	$D_{liq} = 2 \cdot 10^{-5}\ cm^2 \cdot s^{-1}$
Solubility in sulfuric acid (Bunsen coefficient)	$\alpha = 0.02$

1.8.1.4 Corrosion

Corrosion of lead in principle starts at the equilibrium potential of the negative electrode. At a more positive potential lead (Pb) is no longer stable as a metal but is converted into the divalent Pb^{2+}that forms lead sulfate ($PbSO_4$) according to

$$Pb + H_2SO_4 \Rightarrow PbSO_4 + 2 \cdot H^+ + 2 \cdot e^- \quad (68)$$

which equals the discharge reaction of the negative electrode, and its equilibrium potential is $U^o_{Pb/PbSO_4} = -0.3\,V$, as already mentioned in connection with Eq. (59).

During charging or float charging, the potential of the negative electrode is below this value and corrosion according to Eq. (68) is not possible. This applies not only to the grid, but also to the conducting elements as long as they are connected with the electrolyte (‘cathodic corrosion protection’). This usually is true in flooded batteries, where the conducting elements are submerged into the electrolyte or covered by a wetting layer of acid that continuously is reconcentrated by acid fumes and remains connected to the electrolyte by ionic conductivity. In valve-regulated lead-acid batteries, however, due to the immobilized electrolyte, the plate lugs and the other conducting elements cannot be submerged into the electrolyte and the wetting film is diluted by the formation of water according to Eq. (66) (cf. Section 1.8.1.5). Then the potential of the wetting layer may be shifted to more positive values and the cathodic corrosion protection may be lost and corrosion occur as indicated in Fig. 1.21.

The continual oxygen reduction at the wetted lead parts has the following results:

- Oxygen reduction on the lugs and the connecting bus bar consumes H^+ ions and causes a current along the wetting film, and thus a voltage drop along the wetting film that displaces the potential in the upper part of the film to more negative values.
- The potential of the metallic parts is uniform. On account of the potential shift along the wetting film, the potential between that film and the metallic surface is increased with the distance from the electrolyte surface (an increase of as much as 200 mV has been observed (31)). Referred to its wetting film, the potential of metal gets more and more positive, and at a given distance it reaches and even exceeds the $Pb/PbSO_4$ equilibrium value (Zone 2 in Fig. 1.21).

As a result, three different zones can be observed:

- **Zone 1:** The potential of the metal versus its electrolyte film is below the $Pb/PbSO_4$ equilibrium potential, Lead is stable and reduction of oxygen is neutralized by recombination with H^+ ions to H_2O.
- **Zone 2:** When the potential difference between the metal and its wetting layer reaches the $Pb/PbSO_4$ equilibrium potential or is more positive, Pb^{2+} ions are formed, and oxygen reduction is balanced by $PbSO_4$ formation. The situation is aggravated as the acid in the wetting layer at lug and group bar becomes diluted by the generated water. This dilution decreases the

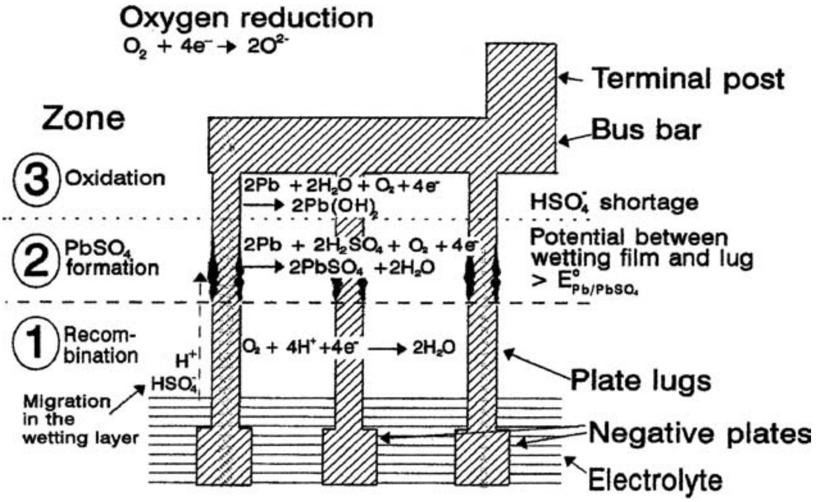

Figure 1.21 Corrosion at negative plate lugs that occasionally is observed. Current flow along the wetting layer of the nonimmersed parts causes a potential shift within that layer. Thus, 'cathodic corrosion protection' may no longer exist above a certain distance from the electrolyte level. The situation is influenced by the alloys used in the parts and for welding (corresponds to Fig. 4.30 in Ref. 5 partly based on results in Ref. 30).

conductivity of the wetting layer and increases the voltage drop along the layer. Furthermore, corrosion roughens the surface and that again increases current and voltage drop. Thus the progressing corrosion accelerates the process.

- **Zone 3** in Fig. 1.21 is characterized by lack of HSO_4^- ions that are required for the formation of lead sulfate. So lead can only be oxidized. Because of the higher vapor pressure of this nearly neutral region compared to the acid electrolyte, drying converts the $Pb(OH)_2$ into PbO and finally stops further oxidation.

It depends mainly on the used alloys whether serious corrosion actually occurs in Zone 2. As a remedy, bus bars can be wrapped by glass felt to preserve the contact with the electrolyte and so preserve the 'cathodic corrosion protection'. The selection of welding alloys is also important.

Corrosion Effects at the Positive Electrode

Above the potential of the positive electrode, the four-valent ion (Pb^4+) is the stable state that forms lead dioxide (PbO_2). Thus grid corrosion in the positive electrode means the conversion of lead (Pb) into lead dioxide (PbO_2) according to

$$Pb + 2 \cdot H_2O \Rightarrow PbO_2 + 4 \cdot H^+ + 4 \cdot e^- \qquad (69)$$

The so-produced lead dioxide forms a rather dense layer that protects the underlying lead from further corrosion. The situation at the phase boundary lead/lead dioxide, however, is not stable as indicated in Fig. 1.22.

In Fig. 1.22 the area on the left represents the grid while the active material is shown on the right. Underneath the porous lead dioxide that constitutes the active material, a dense layer, also of lead dioxide, covers the grid surface. This layer is formed by corrosion and protects the grid. However, lead dioxide and lead cannot exist beside each other for thermodynamic reasons, and a thin layer of less oxidized material (PbO_x) is always formed between the grid and the lead dioxide. The existence of lead oxide PbO in this layer has been determined; the existence of higher oxidized species is assumed, but their structure is not yet known exactly. (This intermediate layer is the main reason why periodical charges are required with lead-acid batteries during prolonged storage periods, since at open circuit this layer gradually grows by further oxidation of the lead, while PbO_2 is reduced. Thus the result would be

$$Pb + PbO_2 \Rightarrow 2PbO \tag{70}$$

and the protection of the grid against corrosion would be lost when the (unstable) PbO layer comes in contact with the acid and forms $PbSO_4$).

The PbO_2/PbO_x layer gradually penetrates into the grid, as indicated in Fig. 1.22 by the arrow, although at a very slow rate as a solid state reaction. But cracks are formed when the oxide layer exceeds a given thickness, on account of the growth in volume when lead becomes converted into lead dioxide. Underneath the cracks, the corrosion process starts again and again. As a result, under the usual float conditions the corrosion proceeds at a fairly constant rate between 0.005 and 0.05 mm per year and never comes to a standstill, and a continually flowing anodic current, the corrosion current, is required to re-establish the corrosion layer.

Figure 1.23 illustrates the consequences for battery practice. An assumed penetration rate of 0.03 mm/year would reduce the cross-section of a grid spine in a tubular electrode by about 50% within the usual service life of 15 years. This result is confirmed by field experience and shows that long-life batteries must have a corresponding ‘corrosion reserve’ in their positive grids.

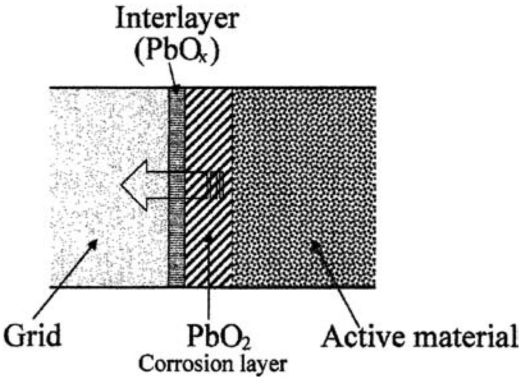

Figure 1.22 Structure of the corrosion layer at the surface of the positive grid.

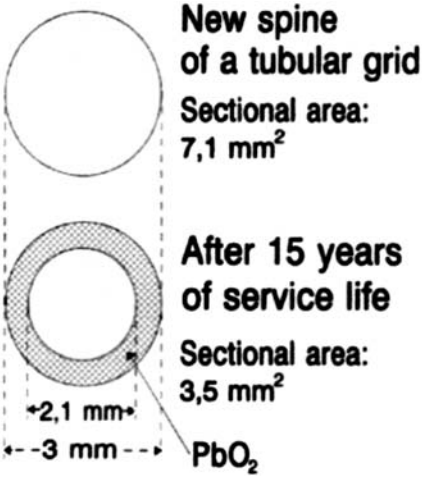

Figure 1.23 Conversion of grid material into lead dioxide by corrosion at a corrosion rate of 0.03 mm/year which corresponds to experience with 1.6% antimony grid alloys. Spine of a positive tubular plate. New plate: 3 mm diameter means 7.1 mm_2 cross-section (πr^2 with $r = 1.5$ mm). Aged plate: reduction of r by $0.03 \times 15 = 0.45$ mm means $\pi r^2 = 3.5$ mm^2.

Since grid material is converted into lead dioxide, a slight increase of the actual capacity is often observed. The reduced cross-section in Fig. 1.23 does not affect the performance of such batteries that normally are used for discharge duration on the order of 1 hour or more. Attention must, however, be paid to batteries that are loaded with high currents, because the conductivity of the grid gains importance with increased current flow. Advanced corrosion of the grid can cause an intolerable voltage drop at high discharge rates.

General parameters that determine this corrosion current are

- Electrode potential.
- Temperature.

Two further parameters, specific to the concerned battery, are

- Specific corrosion rate of the employed alloy.
- Surface area of the grid.

The specific corrosion rate is a complex quantity that is not only influenced by the composition of the alloy, but also by a number of further parameters, like its metallographic structure. In general, pure lead has the lowest corrosion rate. A survey of alloys that especially are applied in valve-regulated lead-acid batteries is given in Ref. 32.

The grid surface that is exposed to the active material and thereby to the electrolyte can vary between about 800 cm^2 in a tubular electrode and about 4000 cm^2 per 100 Ah of nominal capacity in a thin punched grid as are used in cylindrical VRLA batteries.

Based on these values, currents between 0.3 and 10 mA/100 Ah are to be expected as corrosion currents that are required to continuously re-establish the protecting layer of PbO_2 and thereby keep the situation at the grid surface stable (cf. Table 4 in Ref. 33).

Types of Alloys

The unavoidable corrosion of the positive grid and other parts of conducting material has far-reaching consequences for the lead-acid battery, and is the reason that alloys play such an important role:

- Grid corrosion finally limits service life of every lead-acid battery, unless other failures occur earlier. A long service life battery must be equipped with a corresponding 'corrosion reserve' of the positive grid, which causes additional weight.
- Grid corrosion also is a water-consuming reaction which is of great importance in valve-regulated lead-acid batteries (cf. Section 1.8.1.5).
- The rate of grid corrosion is influenced by the composition of the grid alloy and the manufacturing process. Selection of appropriate alloying additives is important to reach the desired service life.
- Alloying constituents are released when the grid material is transformed into lead dioxide. If not absorbed by the active material, they are leached out of the positive plate and can reach the negative electrode by diffusion.

The selection of grid alloys must not only consider fabrication requirements (to produce flawless grids), mechanical strength (for handling during production), creep strength (to resist growth during service), and corrosion resistance, but also pay attention to the fact that the alloy and the alloying constituents may cause electrochemical problems, like increased water decomposition or premature loss of capacity due to passivation effects at the positive grid surface. As it is not possible to match all these requirements at their optimum with one alloy, a number of different grid alloys are in use. (A survey on metallurgical properties of lead alloys for batteries is given in Ref. 34). In Table 1.9, examples of alloys employed in lead-acid batteries and their characteristic constituents are compiled.

Standard antimony alloys contain 6 to 12% antimony. The composition of these alloys is rather close to the eutectic mixture (11% Sb), which is easy to cast and results in strong grids. Furthermore, a high antimony content stabilizes the active material in the positive electrode and improves the cycle performance of the battery. For this reason, most traction batteries today contain positive grids with antimony contents between 4 and 11%.

The disadvantage of a high antimony content is the increase of water-decomposition rate with service time, caused by antimony released from the positive grid by corrosion and precipitated on the surface of the negative electrode. Hydrogen can be evolved much more easily at the antimony-contaminated lead surface as indicated in Fig. 1.20.

Low antimony alloys constitute a possibility to diminish the disadvantages of antimony by a reduction of its content in the positive grid below 2%. Such reduction became possible only when grain refining additives were developed. Copper and sulfur are such additives. The most effective additive is selenium. It was introduced for submarine batteries in 1949 (35) and its widespread use for stationary and car

Table 1.9 Grid alloys for lead-acid batteries, their characteristic additives, and fields of application.

Kind of alloy	Additives	Field of applications
Standard antimony	4–11% Sb, As, Sn, Cu (Ag)	Traction
Low antimony	0.5–3.5% Sb Se, Te, S, Cu[a] As, Sn(Ag)	Low maintenance (stationary, traction) SLI[b] batteries
Standard calcium	0.06–0.12% Ca 0 to 3% Sn, Al	Stationary, vented, and VRLA batteries, SLI[b] batteries
Low calcium	0.02–0.05% Ca 0.3–3% Sn, Ag 0.008–0.012% Al	Valve-regulated, SLI[b] batteries (continuous grid manufacturing)
Lead/tin	0.2–2% Sn	Valve-regulated batteries, conducting elements
Pure lead		Planté plates, Bell Systems round cell (Bell Linage 2000)
ASTAG,	0.009% As, 0.065 Te, 0.08% Ag	Submarine batteries, stationary batteries (Scandinavia, Italy)
ASTATIN[c]	Sn (ASTATIN)	
Antimony/cadmium[d]	1.5% Sb; 1.5% Cd	Valve-regulated

[a] Se, Te, S, and Cu are added as 'grain refiners'.
[b] Starting, lighting, ignition (SLI) means starter battery for motor cars.
[c] Alloys used by the Tudor Group in Scandinavia.
[d] Used under the trade name MFX alloy only by GNB, now Exide.

batteries initiated by Varta in the early 1970s (36). Nowadays (2002), these alloys are used for vented SLI and stationary batteries and partly also for low maintenance traction batteries, in the latter with contents below 1%. In valve-regulated lead-acid batteries they are substituted by antimony-free alloys.

The introduction of lead-calcium alloys started in the United States in the 1930s (37) and was specified for standby batteries in the Bell telephone service in 1951 (38). Corrosion of the lead-calcium alloy does not affect the electrochemistry of the battery, because calcium is not precipitated at the negative electrode but remains as Ca^{2+} ion in the electrolyte. As a consequence, the hydrogen evolution rate is low and remains practically unaltered during the whole service life of the battery.

One disadvantage of lead-calcium alloys is their tendency to grid growth, a further demerit of the reduced stability of the capacity, especially when deep discharge cycles are performed (39). A passivating layer of lead sulfate was often observed between the grid and the active material, and was assumed to be the reason for capacity loss. More recent investigations (40) showed that this capacity loss is a much more general problem, mainly obvious in batteries with antimony-free grid alloys, but depends also on a number of other parameters like the charge current rate and the history of the battery (41).

Tin additions are used in a wide range between 0.02 and 1.2 wt% for lead-calcium alloys applied for positive grids.

Low calcium alloys have been introduced during recent years. Their main advantage is reduced corrosion attack, and thereby reduced grid growth. Silver addition is claimed to increase the creep resistance and improve the corrosion behavior (42).

A disadvantage of these alloys is their softness. So they cannot be manufactured by the conventional casting process, because they could not be handled in the usual equipment, like pasting machines. Rather they depend on continuous processes that combine grid manufacture with pasting.

Lead-tin alloys gained much importance as a remedy against corrosion problems of the conducting elements in valve-regulated lead-acid batteries. But they are also applied for grids, where a tin addition of 0.6 wt% proved to be the optimum (43). Lead-tin alloys for conducting elements like the pole bridge may contain fairly high tin additions of up to 3 wt%.

Pure lead is used for positive Planté plates and the grids in the Bell System vented round cell. Cylindrical cells of valve-regulated design (Gates, now Hawker) with punched grids employ lead for both grids with a small tin addition (44).

Table 1.9 contains a further alloy, Astag, used to a small extent for stationary batteries in Scandinavia, where it was introduced by Tudor Sweden, originally for submarine application. A similar alloy, basically corresponding the Astag alloy, but using tin as a further additive, is applied under the name Astatin (45).

The antimony-cadmium alloy is used under the name MFX alloy exclusively by GNB (now Exide) for the Absolyte Battery. It contains 1.5% antimony and 1.5% cadmium. With this alloy, cycling is possible owing to the antimony content. On the other hand, antimony release is rather low because the intermetallic compound SbCd is formed between antimony and cadmium that keeps antimony within the positive plate. A disadvantage of this alloy is its high cadmium content, because of the toxicity of cadmium. This does not concern the battery, but might cause problems for remelting of these batteries when they are recycled after service.

1.8.1.5 Electrochemical Consequences

To gain insight into the mutual dependence of the involved reactions, their characteristics have to be considered which are described by the corresponding current/voltage curves.

Charge/discharge, hydrogen and oxygen evolution, and also grid corrosion occur independently from one another, and their rates are only determined by the potential of the concerned electrode.

For oxygen reduction the situation is different:

- In flooded or vented lead-acid batteries, the slow transport of the oxygen limits oxygen reduction to a small current equivalent that usually can be neglected.
- In valve-regulated lead-acid batteries, oxygen transport occurs through the gaseous phase and is very fast (cf. Eq. (67)). Due to the high transport rate, a high efficiency of the internal oxygen cycle usually is achieved, and the amount of reduced oxygen closely corresponds to the rate of oxygen evolution at the positive electrode (provided that oxygen intake from the

surroundings is precluded by proper sealings and a properly operating valve).

A strong relation between these reactions is given by the primary rule:

The same current must flow through both electrodes as soon as the charging or discharging current circuit is closed.

Vented Lead-Acid Batteries

Charging curves of lead-acid batteries have been shown in Fig. 1.11 and 1.12 for a vented and a valve-regulated lead-acid battery, respectively. Charging itself shows no differences for both designs: At the beginning, charge acceptance is high and the charging process is automatically limited by the charging device. Later charge acceptance is reduced more and more, and with increasing cell voltage, secondary reactions gain in importance.

When the battery approaches the state of full charge, the charging reaction diminishes, and finally the secondary reactions are the only ones that remain when the battery is overcharged or kept at a comparatively low float voltage in standby operation.

Figure 1.24 illustrates the resulting situation of a flooded cell that is overcharged at 2.35 V/cell or float charged at 2.27 V/cell. The figure corresponds to Fig. 1.19, but the horizontal axis now shows the polarization of the positive and negative electrodes referred to their open-circuit values. Thus the zero point of the horizontal axis is the open circuit voltage of the cell, i.e. zero polarization of positive and negative electrodes. Furthermore, the current now is plotted in a logarithmic scale, and the current voltage curves of oxygen and hydrogen evolution are represented by Tafel lines according to Section 1.3.3.1. The values are based on model calculations by U. Teutsch (46, 47).

Figure 1.24 shows the typical slopes per decade of current increase of – 120 mV and + 80 mV for hydrogen and oxygen generation, respectively. At open circuit, i.e. zero polarization, oxygen and hydrogen evolution in this example correspond to 1 mA/100 Ah and 2 mA/100 Ah, respectively. The latter would be equivalent to a self-discharge of the negative of 1.44 Ah/month or 1.44% per month.

The corrosion behavior is represented in Fig. 1.24 by the combination of two Tafel lines. This is a rough approximation, but it corresponds to the practical experience and describes the always observed minimum of corrosion at 40 to 80 mV above the open-circuit potential of the positive electrode. At lower potentials the protecting layer of PbO_2 is destabilized. At polarization values more positive than this minimum, the corrosion rate increases also exponentially in respect to polarization. The slope of this Tafel line is 240 mV per decade, which is in accordance with the general experience in practice.

Oxygen reduction is limited by the slow transport rate. In Fig. 1.24 this limitation is assumed at an equivalent to 2 mA/100 Ah. It is expressed by a horizontal line, which means that the oxygen reduction rate is independent from the potential of the negative electrode. At a very small polarization, which corresponds to a correspondingly low cell voltage, decrease of this reaction is to be expected, due to the reduced oxygen evolution at the positive electrode, as indicated by the broken curve.

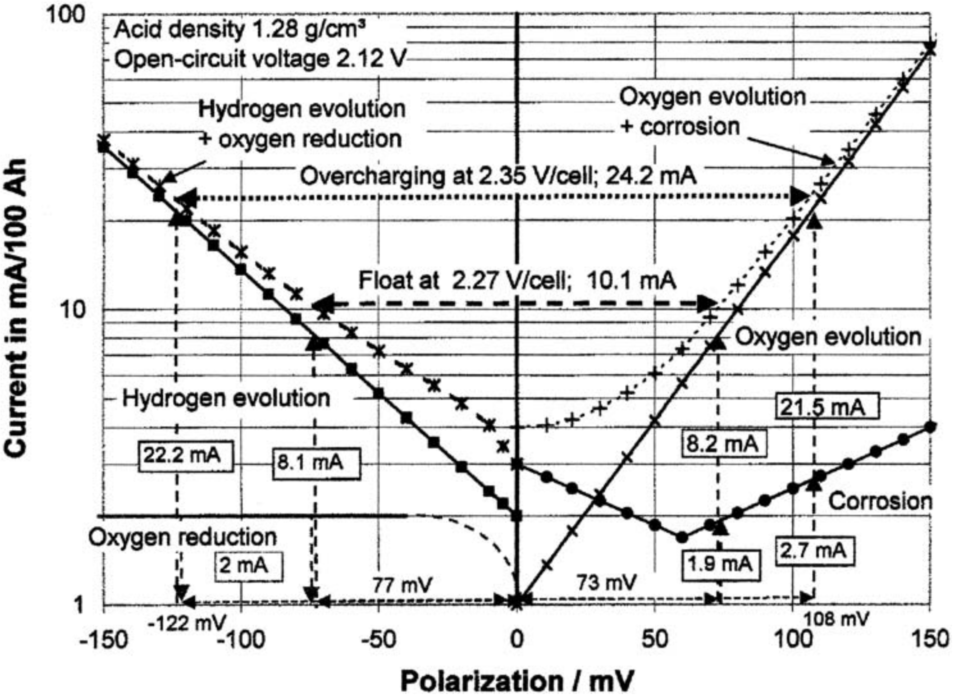

Figure 1.24 Overcharging and float charging of a flooded battery. Current voltage curves as current equivalents in a semilogarithmic scale versus polarization, referred to the open circuit potential of the negative and positive electrodes. Values based on generalized data. Actually they depend on the specific parameters of the concerned battery. The curves for charge and discharge are not drawn, since they would be represented by nearly vertical lines due to their low polarization.

The inserted double arrows show the situation that results at a voltage of 2.35 and 2.27 V/cell, which means a polarization of 230 and 150 mV, respectively, referred to the open circuit voltage of 2.12 V. The above-mentioned demand, that the sum of hydrogen evolution and oxygen reduction at the negative electrode (in electrochemical equivalents) must equal the sum of oxygen evolution and grid corrosion at the positive electrode, is only fulfilled at a certain polarization, and there exists only one solution for this current balance.

Overcharging at 2.35 V/cell causes a polarization of + 108 mV and – 122 mV of the positive and the negative electrodes, respectively. At the positive electrode, such a polarization causes oxygen evolution equivalent to a current of 21.5 mA and corrosion equivalent to 2.7 mA (always referred to 100 Ah). Both together form the total float current of 24.2 mA. At the negative electrode oxygen reduction at a rate of 2 mA/100 Ah forms a limiting current due to the slow diffusion rate, and therefore does not depend on electrode polarization. Together with hydrogen evolution equivalent to 22.2 mA it forms the overcharging current of 24.2 mA/100 Ah.

At the lower float voltage of 2.27 V/cell, polarization of + 73 mV and – 77 mV of the positive and the negative electrodes, respectively, fulfills the required condition. At the positive electrode it causes oxygen evolution equivalent to a current of 8.2 mA and corrosion equivalent to 1.9 mA (always referred to 100 Ah). Both together form the total float current of 10.1 mA. At the negative electrode oxygen reduction (2 mA) and hydrogen evolution (8.1 mA) cause the corresponding result.

Oxygen and hydrogen evolution are the main overcharging reactions, and both electrodes are polarized so that hydrogen and oxygen are generated (nearly) equivalent to the float current at the negative and positive electrodes, respectively. A (nearly) stoichiometric ratio of hydrogen and oxygen escapes from the cell, and a corresponding water loss is observed (The deviation from stoichiometry is caused by corrosion and oxygen reduction.) The equivalent currents of oxygen reduction and grid corrosion are comparatively small compared to the float current.

The float charging situation depends, as mentioned with the figure, on the specific parameters of the individual battery. When, for example, hydrogen evolution is more hindered, the corresponding Tafel line is shifted downwards, and polarization of both electrodes also would be shifted to more negative values. This would, for example, apply to a flooded stationary battery with comparatively thick plates based on grids made from lead-calcium alloys or pure lead. Then polarization of the positive electrode might be reduced too far and proper charging no longer be possible under float conditions.

Such a behavior has been observed in practice, and as a remedy it is a well known practice in the United States to add traces of palladium to flooded batteries that are float charged at a very low voltage. Such an addition increases the hydrogen evolution rate and shifts the polarization of both electrodes to more positive values. Furthermore, at such a low voltage a perceivable portion of the small amount of generated oxygen is recombined, although the cell is flooded, and varying efficiency of the internal oxygen cycle in the individual cells can split the battery into groups of deviating float voltages (48).

Valve-Regulated Batteries

In valve-regulated lead-acid batteries (VRLA batteries), the limiting situation no longer exists for oxygen reduction, since the electrolyte is immobilized (next section) and fast transport of oxygen occurs via the gaseous phase (cf. Eq. (67)). Furthermore, the cell is closed by the valve. As a consequence, the internal oxygen cycle characterizes the overcharging situation, i.e. the oxygen, generated at the positive electrode according to Eq. (65), does not escape from the cell, but is reduced at the negative electrode (Eq. (66)). Since the transport of oxygen and its reduction are fast, the partial pressure of oxygen is kept fairly low. The reaction at the positive electrode is thus reversed at the negative electrode. This internal oxygen cycle is the same principle that characterizes the sealed nickel/cadmium battery. In lead-acid batteries, however, it can only be approximated, since hydrogen evolution at the negative electrode and also grid corrosion at the positive electrode are always present as secondary reactions at a certain rate. (cf. Fig. 1.19).

Hydrogen that is generated at the negative electrode must escape from the battery. An ‘internal hydrogen cycle’ is not established, since hydrogen oxidation at the positive electrode is an extremely hindered reaction. For this reason, a lead-acid battery cannot be sealed hermetically but must have a valve that opens from time to

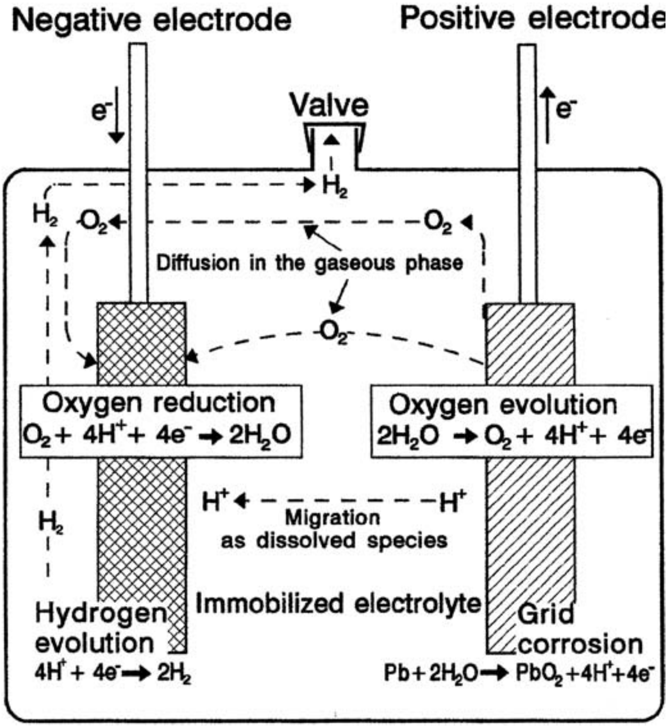

Figure 1.25 Internal oxygen cycle in a valve-regulated lead-acid battery (VRLA battery).

In sealed nickel/cadmium batteries, oxygen evolution and oxygen reduction that form the internal oxygen cycle are the only reactions during overcharging (cf. Section 1.8.2.2).

In lead-acid batteries, however, this cycle is unavoidably accompanied by hydrogen evolution and corrosion of the positive grid. Hydrogen is not oxidized within the cell, but has to escape through the valve. Corrosion consumes oxygen that remains in the cell as PbO_2.

time for gas escape, even under normal operational conditions, as indicated in Fig. 1.25.

Hydrogen evolution and grid corrosion cause water loss, since the sum of both reactions is

$$\begin{array}{ll} \text{Hydrogen evolution} & 4\cdot H^+ + 4\cdot e^- \Rightarrow 2\cdot H_2 \\ \text{Grid corrosion(Eq.(6))} & Pb + 2\cdot H_2O \Rightarrow PbO_2 + 4\cdot H^+ + 4\cdot e^- \\ \hline \text{In total} & Pb + 2\cdot H_2O \Rightarrow PbO_2 + 2\cdot H_2 \end{array} \qquad (71)$$

Immobilized Electrolyte

The internal oxygen cycle requires fast oxygen transport that only can be achieved by diffusion in the gaseous phase, as indicated by the ratio shown in Eq. (67). To provide void volume for such a fast transport, the electrolyte must be “immobilized”. This can be achieved by two methods:

1. Addition of about 6 wt% of silica (SiO_2) that converts the acid into a stiff gel.
2. Application of absorbent-glass-mat separators (AGM) that are soaked by the acid so that liquid acid is not left within the cell. In alkaline electrolyte, polyamide or polypropylene fibers form corresponding mats that are used, for example, in sealed nickel/cadmium batteries (Section 1.8.2.2).

When the gel is formed, a certain amount of acid is released on account of shrinkage during the solidification process. This liquid can be removed or is lost according to Eq. (71), and void cracks remain within the gel that allow fast gas transport.

In glass-mat separators, the capillary forces fill the smaller pores while the larger ones remain void for gas transport. Such separators usually are mixtures of ‘coarser’ types of fibers with diameters slightly above 1 μm and ‘fine’ types with a diameter of about 0.5 μm, to achieve both sufficient stiffness and absorptive capacity. ‘Hybrid separators’ contain plastic fibers to increase stiffness and effectuate a certain void pore volume by ‘controlled wetting’ (49). Separators that consist of two or more layers of different fibers are also on the market (a survey is given in Ref. 50). Such layered separators offer advantages for special applications, and they can also be helpful for the filling process, since layers of coarse fibers are more quickly soaked. On the other hand, mats of fine fibers are superior in regard to the wicking height, which is advantageous in tall cells and also reduces stratification effects in cycling applications (51) (cf. also the following section).

In both versions of immobilization, sufficient void space is left that allows fast diffusion of oxygen through the gaseous phase. Only a thin wetting layer at the negative electrode surface has to be permeated by dissolved oxygen, and the efficiency of the internal oxygen cycle comes close to 100%. Even when a battery initially contains too much liquid that hinders fast oxygen transport, increased water loss of such ‘wet’ cells finally yields an efficient internal oxygen cycle.

For most applications, the differences between the two immobilization methods are marginal. When batteries of the same size and design are compared, the internal resistance of the gel battery is slightly higher, mainly due to the conventional separator that is required with gelled electrolyte, since the gel itself does not prevent the penetration of lead dendrites that can cause short circuits between the electrodes. As a consequence, AGM batteries are preferred for high load applications, because of the possibility to achieve a very low internal resistance. In gelled electrolyte, on the other hand, the acid is more strongly fixed and therefore the influence of gravity is almost neglectable. Thus gel batteries do not show acid stratification. In general they are superior in cycle applications, and tall gel cells can be operated also in upright position, while with tall AGM batteries, operation in horizontal position usually is recommended to limit the height of the separator to about 30 cm.

In gelled electrolyte, most of the oxygen must surround the separator. This is one of the reasons that the maximum rate of the internal oxygen cycle is lower in gel cells. Another reason may be that a certain portion of the surface is masked by the gel. Rough figures of this maximum rate are 10 A/100 Ah in AGM batteries and 1.5 A/100 Ah in gel batteries. A charging current that exceeds this maximum causes gas escape as in a vented battery. But this limitation normally does not influence charging or float behavior, since lead-acid batteries are charged at a constant voltage, and overcharging rates are far below 1 A/100 Ah, even at 2.4 V/cell. The more limited maximum rate of the internal oxygen cycle in gel batteries even offers the advantage that gel batteries are less sensitive to thermal runaway when overcharged at a too high voltage.

ACID STRATIFICATION. The immobilization of the electrolyte has a side-effect of enormous practical importance: it eliminates stratification of the electrolyte, at least to a large extent. This stratification is caused by the peculiar situation of the lead-acid battery that the sulfuric acid in the electrolyte participates in the electrode reaction. The thereby evoked stratification of the electrolyte is illustrated in Fig. 1.26.

When the battery is discharged, the concentration of the acid is reduced, since SO_4^{2-} ions are absorbed by both electrodes according to Eq. (59a) and (59b), and at the positive electrode in addition water is generated according to Eq. (59a), as indicated in the left-hand part of Fig. 1.26. Acid consumption occurs in the pores of the active material, and thus reduces the specific weight close to the electrode surface. This evokes an upward flow that mixes the bulk of the electrolyte between and above the electrodes. At the end of discharge, the concentration of the acid is lower, but more-or-less uniform, except the share localized below the electrodes that had not been included into the convection due to its higher density. Complete uniformity of all the acid would be reached only after a prolonged period of time by diffusion.

When the battery is recharged, SO_4^{2-} ions are released from the electrodes, and by the positive electrode, furthermore, water is consumed. Thus the acid concentration in a layer close to the surface of the electrodes is increased, especially at the positive electrode, and its higher specific density initiates a downward movement. Thus the acid at the bottom becomes increasingly concentrated, and when such partly discharging/charging cycles are repeated without acid mixing, the acid at the top is more and more diluted, while at the bottom the concentration

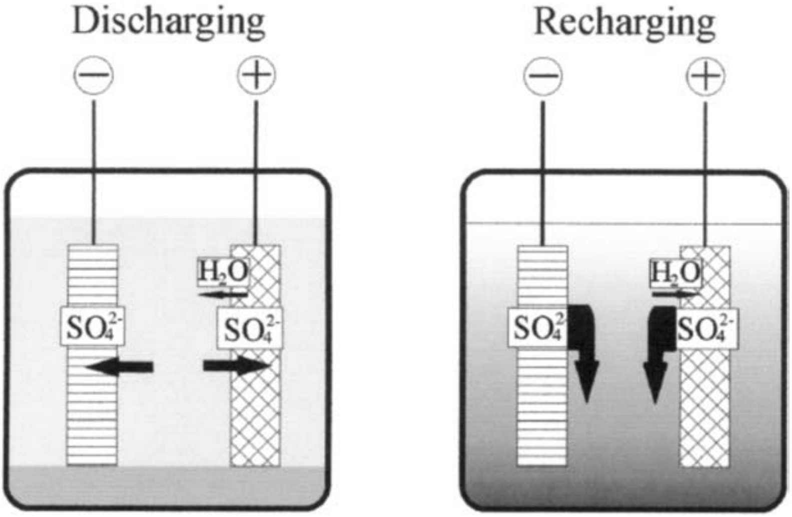

Figure 1.26 The emergence of acid stratification in lead-acid batteries with liquid electrolyte.

significantly may exceed the initially specified value, as indicated in the right-hand part in Fig. 1.26. The consequence of such a stratification is that in the upper part of the electrodes the active material is only partly utilized due to lack of acid, while it is overstressed in the bottom zone of both electrodes. Thus in the bottom part disintegration of the active material in the positive electrode and its sulfatation in the negative electrode are results that will cause premature failure of the battery.

For this reason, vented lead-acid batteries with liquid electrolyte are not suited for such partly discharging/charging schedules, rather they have regularly to be overcharged by about 115% to eliminate acid stratification. During such overcharging periods the heavy gassing produces bubbles that ascend within the electrolyte and so cause mixing. More effective mixing is achieved by forced acid agitation with the aid of inserted air-lift pumps. For such batteries an overcharge factor of 104% is sufficient (cf. Ref. 5).

In VRLA batteries, the immobilized electrolyte greatly hinders the vertical flow of the acid, and this applies the more, the more the electrolyte is fixed. (This is one reason to use very fine fibers for AGM separators that form correspondingly fine pore systems with high capillary forces (52)). As a consequence, only very small stratification effects are observed in AGM felts, and the strong bond of the acid in the gelled electrolyte means that such batteries do not show any stratification effects. The so-reduced or even eliminated stratification allows the use of VRLA batteries in the mentioned applications where acid mixing by overcharging cannot be achieved, and where conventional lead-acid batteries suffer premature failure due to acid stratification. Such applications are automatic guided transport vehicles where only intermediate boost charges are possible that do not fully recharge the battery. Batteries in taxicabs also show a significantly improved service life in the VRLA version, since during the standstills of the car they are cycled to a certain extent, and are only partly recharged because of the limited driving ranges. In stationary applications, VRLA batteries perform superior as standby batteries for wind and solar energy generation. These batteries cannot be recharged regularly and properly, since the required energy often is not available. Recently, VRLA batteries with AGM separators have been reported to operate also properly in 'peak shaving' applications where the battery is continuously partly discharged and recharged at an average state of charge of about 80% (53).

Overcharging Behavior of VRLA Batteries

Figure 1.27 illustrates the situation of a valve-regulated cell that is overcharged at 2.27 V/cell. The figure corresponds to Fig. 1.24, and the characteristics of hydrogen evolution, oxygen evolution, and grid corrosion are identical to those in Fig. 1.24, and also the same float voltage is assumed. The important difference between the figures is the fact that in the valve-regulated version oxygen does not escape but is reduced at the negative electrode. As a consequence, the main secondary reaction at the negative electrode is oxygen reduction, and the equivalent of hydrogen evolution is small compared to the float current.

In this example, 100% of recombination efficiency is assumed, i.e. all the oxygen (O_2) that is evolved at the positive electrode subsequently is reduced at the negative. Thus oxygen evolution is completely compensated for by oxygen reduction, and the current equivalents for oxygen evolution and oxygen reduction equal each other. As a consequence, also the current equivalents of hydrogen evolution and grid

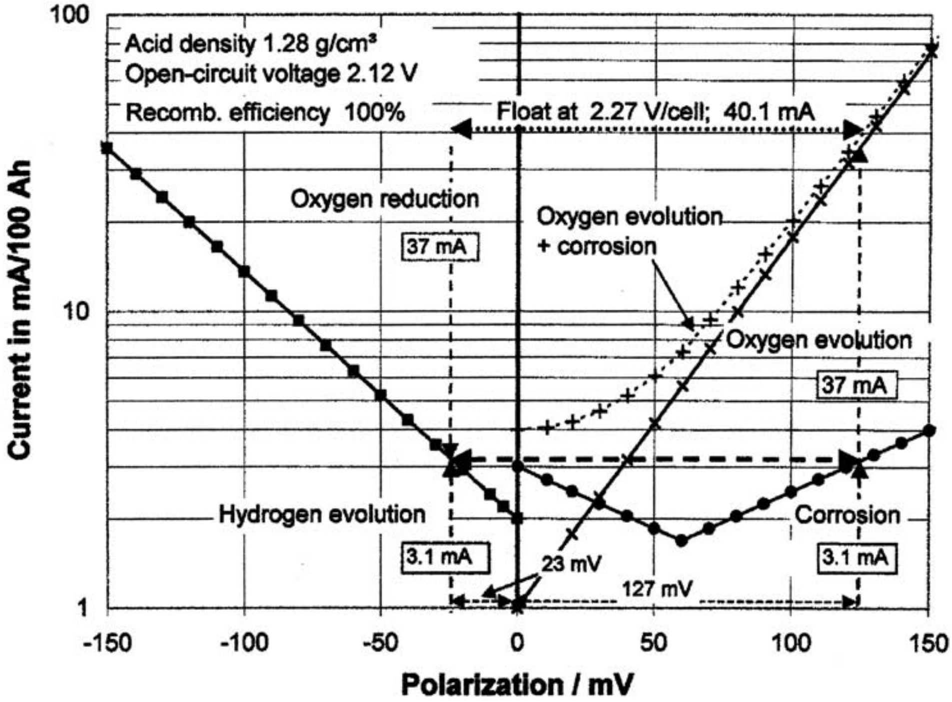

Figure 1.27 The float-charging situation of a VRLA battery. Current voltage curves as in Fig. 1.23, but at 100% of recombination efficiency of the internal oxygen cycle.

corrosion must equal each other, since they are the required supplements for the current in total. This is indicated by the lower double arrow in Fig. 1.26. (In practice, 100% of recombination efficiency can only be approximated, since a small partial pressure of oxygen always exists within the cell and a corresponding small portion of oxygen is lost together with the escaping hydrogen.)

Also in the valve-regulated design, the sum of hydrogen evolution and oxygen reduction at the negative electrode (in electrochemical equivalents) must equal the sum of oxygen evolution and grid corrosion at the positive electrode, and in the example of Fig. 1.27 this demand is only fulfilled at a polarization of $+127\,\text{mV}$ and $-23\,\text{mV}$ of the positive and the negative electrodes, respectively. At the positive electrode, such a polarization causes oxygen evolution equivalent to a current of 37 mA and corrosion equivalent to 3.1 mA (always referred to 100 Ah). Both together form the total float current of 40.1 mA. At the negative electrode oxygen reduction (37 mA) and hydrogen evolution (3.1 mA) cause the corresponding result.

The result, shown in Fig. 1.26, is typical for most VRLA batteries: The polarization of the negative electrode is small and the hydrogen evolution rate is close to the self-discharge rate at open circuit. (Compared to the vented design in Fig. 1.23 it is reduced to about one-third.) This is a question of balance between hydrogen evolution and grid corrosion. When hydrogen evolution is higher compared to grid corrosion, balance will be achieved at a more positive polarization of both electrodes and a correspondingly increased float current and also increased hydrogen evolution would result (cf. Fig. 1.28).

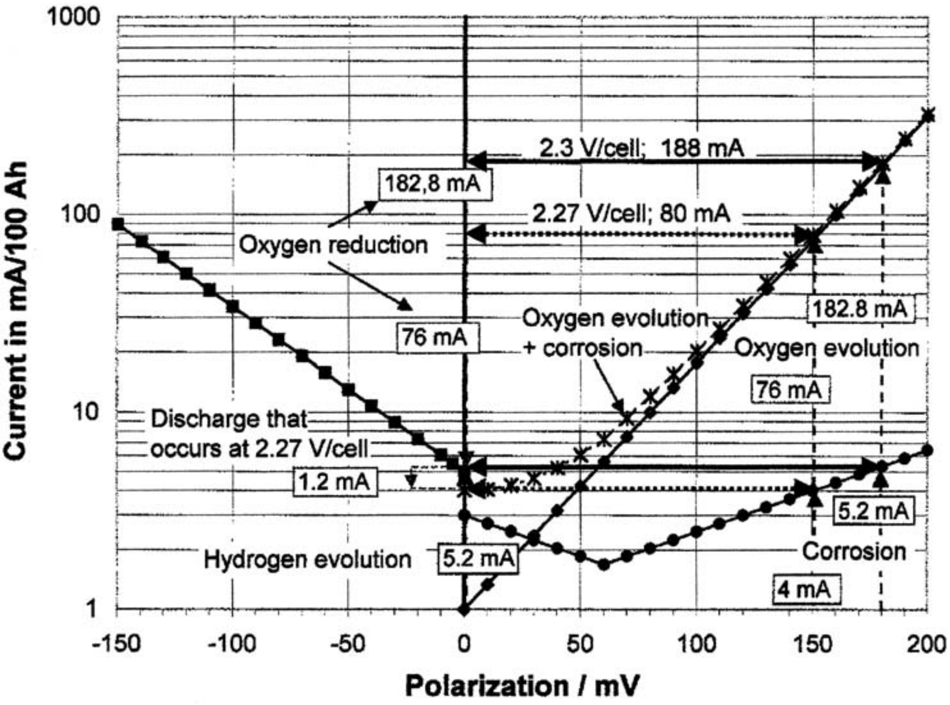

Figure 1.28 Overcharging of a VRLA battery. Characteristics as in Fig. 1.27, except an increased hydrogen evolution by the factor 2.5. 100% of recombination efficiency. (Zero point of polarization: $E_o = 2.12\,V$ i.e. acid density $1.28\,g/cm^3$).

Three important statements can be derived from Fig. 1.26:

1. The polarization of the negative and positive electrodes is determined by the balance between hydrogen evolution and grid corrosion, expressed in current equivalents.
2. Water loss is equivalent to the hydrogen evolution rate, which together with corrosion results in $2 \cdot H_2O + Pb \Rightarrow 2 \cdot H_2 + PbO_2$ (Eq. (71)).
3. The float current is determined by the sum of the internal oxygen cycle and grid corrosion and has no direct relation to water loss.

Strictly speaking these relations are valid only at 100% of efficiency of the internal oxygen cycle. But they can be transferred to most VRLA batteries, since usually such a high efficiency is closely approached.

Note: *In regard to water loss, attention has to be drawn to the fact that water loss in VRLA batteries can only be determined by measurement of the escaped hydrogen. Due to the fugazity of hydrogen such measurements have to be carried out very thoroughly and it has to be observed that only suitable tubing and sealing materials are used. Otherwise, the permeation of hydrogen disturbs the results too much. Water loss cannot be determined by loss of weight, since oxygen that is consumed by corrosion remains in the cell, and only the low-weight hydrogen escapes.*

Balance Between Hydrogen Evolution and Grid Corrosion

Standby batteries in stationary applications are continuously overcharged at a comparatively low voltage for two reasons:

1. The overcharging current should be as low as possible to minimize hydrogen evolution and corrosion and thus water loss.
2. The gap between charging and discharging voltage should be as small as possible to allow uninterrupted power supply without additional switching equipment.

Under such conditions, balance between hydrogen evolution and grid corrosion is important to ensure sufficient polarization of both electrodes. To emphasize the problem that may arise, in Fig. 1.28 the hydrogen evolution rate is assumed 2.5 times higher compared to Fig. 1.27, expressed by a corresponding shift of the Tafel line in vertical direction. As a consequence, the ratio between hydrogen evolution and grid corrosion is shifted correspondingly.

At 2.3 V/cell, the required equal current flow through both electrodes is achieved only at +180 mV of polarization of the positive electrode. But then the polarization of the cell (2.3 – 2.12 V) is completely required for the positive electrode, while the polarization of the negative electrode is reduced to zero. The float current that mainly is determined by oxygen evolution amounts now to 188 mA/100 Ah and is composed at the positive electrode of 182.8 mA for oxygen evolution and 5.2 mA for grid corrosion and is balanced at the negative electrode by the sum of 182.8 mA for oxygen reduction and 5.2 mA for hydrogen evolution. This, however, represents a very critical situation of the negative electrode, since the slightest further increase of hydrogen evolution or a reduction of the cell voltage would cause positive polarization and this means discharge of the negative electrode.

This is clearly to be seen at the lower overcharging voltage of 2.27 V/cell which means a reduction of the cell polarization to 150 mV (dotted double arrows in Fig. 1.28). At this overcharging voltage, balance between hydrogen evolution and grid corrosion can no longer be achieved, since the self-discharge rate of the negative electrode at zero polarization exceeds grid corrosion at 150 mV of positive polarization. As a consequence, the polarization of the negative electrode is shifted to a positive value. This evokes discharge of the negative electrode as an additional (anodic) reaction that fills the gap between hydrogen evolution and grid corrosion. Only a few millivolts of positive polarization would be sufficient, since discharge is a very fast reaction. Thus the surplus of hydrogen evolution is compensated by a self-discharge current equivalent to 1.2 mA/100 Ah in this example, and the resulting difference 5.2 mA – 1.2 mA = 4 mA balances grid corrosion.

The discharge of the negative electrode equivalent to 1.2 mA/100 Ah means a loss of capacity of 0.9 Ah per month or about 10% per year. After floating for three years under these conditions, the battery would have lost about 30% of its capacity, and that would not have been realized by voltage readings, since the battery is floated at the correct voltage. Even the open circuit voltage would hardly give an indication, since its decay is much lower, compared to the figures often published as a possibility for a rough determination of the state of charge (cf. (54)), since under the conditions shown in Fig. 1.28 only the negative electrode is discharged according to Eq. (59b), and acid dilution amounts to less than a half of the dilution that would be caused by discharge of both electrodes (Eq. (59)), as shown in Fig. 1.29.

For this reason, it is rather difficult to detect an unbalanced cell under float conditions, except by capacity tests.

OXYGEN INTAKE. The balance between hydrogen evolution and grid corrosion can also be disturbed by the intake of oxygen which may be caused by a not properly closing valve or a leakage in the sealings of the container. Due to its easy access to the negative electrode, oxygen would be reduced and form an additional (anodic) current with the consequence that the potential of the negative electrode is shifted to more positive values. When the amount of oxygen exceeds a certain limit, the potential of the negative electrode will even be shifted to positive values and its gradual discharge would be the result, as described in the preceding section for the unbalanced cell.

CATALYSTS IN VALVE-REGULATED LEAD-ACID BATTERIES. The problem of discharged negative electrodes has repeatedly been reported in the United States, and it mainly appeared with batteries designed for long service life (cf. Ref. 55). The reason may be that in such batteries highly corrosion-resistant alloys are combined with negative electrodes that evolve too much hydrogen.

As mentioned in Section 1.8.1.1, the required high purity level of lead may not always be available, and a number of remedies to avoid discharge of the negative electrodes have been proposed and are in use, like regularly repeated boost charges. One possibility is the installation of a small catalyst within the cell (56). The effect of such a catalyst is illustrated in Fig. 1.30. Its principle is that the direct recombination

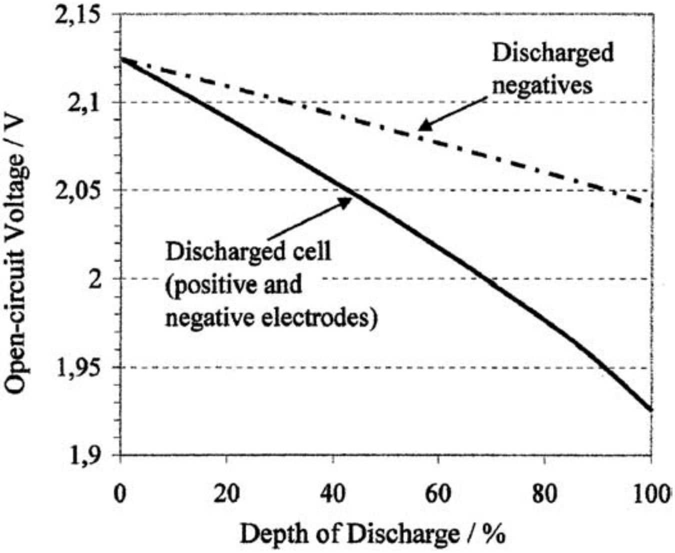

Figure 1.29 Open circuit voltage vs. depth of discharge (DOD), caused by acid dilution (cf. Fig. 1.2). The continuous line indicates the relation when both electrodes are discharged according to Eq. (59). The broken line represents the relation when only the negative electrode is discharged (Eq. (59b)).

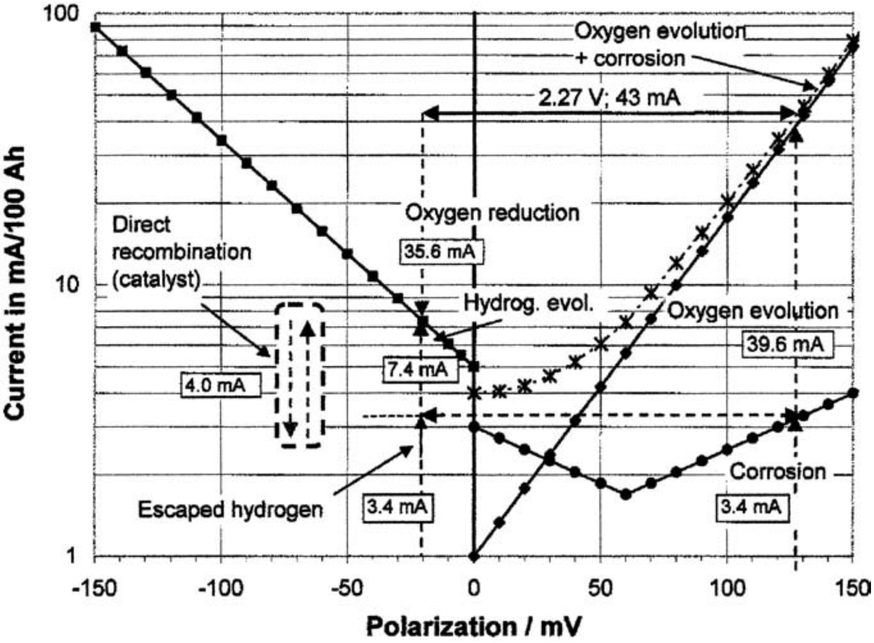

Figure 1.30 Effect of a catalyst. Characteristic data as in Fig. 1.28. Efficiency of the catalyst is 4.0 mA or 10% of the internal oxygen cycle. The efficiency of the internal oxygen cycle is thereby reduced to 90%.

of hydrogen and oxygen reduces the efficiency of the internal oxygen cycle, since a certain amount of the evolved oxygen does not reach the negative electrode. This ‘missing amount’ of oxygen is directly recombined with hydrogen by the catalyst and forms water vapor that subsequently is condensed to water within the cell. The electrochemical equivalent of this ‘lost’ oxygen cannot be recombined at the negative electrode and a corresponding increased equivalent of hydrogen must be evolved to achieve the required current balance, and this means increased polarization of the negative electrode.

In Fig. 1.30 the basic situation corresponds to that in Fig. 1.28, but now the direct recombination of oxygen by the catalyst, equivalent to 4 mA, causes a deficit of oxygen, and requires a corresponding increase of hydrogen evolution. For this reason, now the negative electrode is polarized by – 20 mV, which again reduces the polarization of the positive electrode correspondingly. Thus the corrosion rate is also slightly reduced, and the amount of hydrogen that must escape from the cell equals this reduced corrosion rate.

Thus the catalyst is effective in several aspects:

- It stabilizes the potential of the negative electrode at a more negative polarization.
- Since the potential of the positive electrode is equally reduced, a corresponding (slight) reduction of the rate of corrosion and the float current is observed.

- Water loss is reduced to the rate of the (reduced) corrosion, since oxygen and hydrogen that directly are recombined remain as water in the cell.

Such catalysts have been in practical use since 1998 and experience has proved the above statements (57).

Note: *The situation of such a catalyst is absolutely different from those in 'recombination plugs' that are known for vented lead-acid batteries (cf. Ref. 5, p. 259). Such recombination plugs are aimed to recombine as much as possible of the generated hydrogen and oxygen gases to reduce water loss. High recombination rates are required and thermal problems are the main concern, since the recombination generates much heat. The here described catalyst in the VRLA battery has only to disturb the internal oxygen cycle and cause a small gap between oxygen evolution and the amount of oxygen that reaches the negative electrode. The efficiency of this catalyst can be very limited and this implies that heat problems are not evoked.*

1.8.2 Nickel/Cadmium Batteries

Nickel/cadmium batteries (line 8 in Table 1.1) have been in technical use nearly as long as lead-acid batteries. They belong to a whole family of secondary batteries that are based on aqueous, but alkaline electrolyte, usually diluted potassium hydroxide. Nickel/cadmium, nickel/hydrogen, and nickel/metal hydride batteries are the most important members of this group. A further common feature of these battery systems is that they employ the nickel-hydroxide electrode as the positive one. Some of their basic features will be described in the following.

The development of nickel/cadmium batteries started in the beginning of the twentieth century in parallel to that of the nickel/iron battery. The latter played an important role mainly as a sturdy traction battery that reached many charge/discharge cycles. But after World War II it gradually lost its market, mainly because of the high hydrogen evolution rate and comparatively low power efficiency. The nickel/cadmium battery, however, still has a strong market position, mainly in its sealed version as a portable power source, but also as a flooded battery in traction and stationary applications.

The positive electrode, the nickel-hydroxide electrode, already has been mentioned and its reaction mechanism sketched in Fig. 1.6. When it is discharged, Ni^{3+} ions are reduced to Ni^{2+} according to the (simplified) equation

$$\mathrm{NiOOH} + \mathrm{H_2O} + e^- \Rightarrow \mathrm{Ni(OH)_2} + \mathrm{OH^-} \tag{72}$$

In the nickel/cadmium battery it is combined with the cadmium electrode that reacts via the solution similar to the lead electrode (Fig. 1.4) and is discharged according to

$$\mathrm{Cd} + 2\cdot\mathrm{OH^-} \Rightarrow \mathrm{Cd(OH)_2} + 2\cdot e^- \tag{73}$$

As the sum of both equations, the cell reaction during discharge results that formally can be written

$$2\cdot\mathrm{Ni(OOH)} + 2\cdot\mathrm{H_2O} + \mathrm{Cd} \Rightarrow 2\cdot\mathrm{Ni(OH)_2} + \mathrm{Cd(OH)_2} \tag{74}$$

When the battery is recharged, this reaction is reversed.

For the positive electrode, the reaction actually is more complicated. Nickel hydroxide is not an exactly defined chemical compound, and not only trivalent nickel ions are present in the charged material, but it can be a mixture between Ni^{2+}, Ni^{3+}, and Ni^{4+} (cf. Fig. 1.6). Thus $2 \cdot NiOOH$ as the charged state more precisely should be written

$$u \cdot NiO_2 v \cdot NiOOH w \cdot H_2O \tag{75}$$

where u, v, and w are factors that describe the share of the three components (58). As a consequence of its complex reaction, the nickel-hydroxide electrode is not quite reversible, and does not attain a true equilibrium potential, and thermodynamic data and values are only approximate.

A remarkable feature of the charge/discharge reaction is that neither potassium hydroxide (KOH) nor potassium appear in Eq. (74) or in one of the electrode reactions (except small amounts of K^+ ions that are incorporated into the nickel-hydroxide electrode, as indicated in Fig. 1.6. They, however, are so small that they do not have any influence on potassium concentration). Only H_2O and OH^- ions as its dissociation product take part in these reactions. Water, however, is the predominant portion of the electrolyte, because the usually applied concentrations of KOH are in the range between 20 and 32 wt% (densities at 20 °C between 1.19 and 1.30 g/cm^3). From the discharge equation can be deduced that 0.67 g of water are required per Ah of discharge (36 g per 53.6 Ah). Since in vented nickel/cadmium batteries, 10 g of electrolyte at minimum is contained per Ah of nominal capacity, the change in density is smaller than 0.015 g/cm^3, which will not be noticed in practice. In sealed batteries, despite their lower content of electrolyte, the density change caused by discharge does not exceed 0.02 g/cm^3 and can also be neglected. Thus a concentration change with progressing discharge as shown in Fig. 1.9 for lead-acid batteries is not observed with nickel/cadmium batteries, and furthermore the amount of electrolyte can be very small and the electrodes narrowly spaced.

1.8.2.1 Equilibrium or Open Circuit Voltage

The free enthalpy of the discharge reaction (Eq. (74)) is

$$\Delta G = \approx -256\,\text{kJ} \tag{76}$$

Inserting this value into Eq. (5) results in the equilibrium or open circuit voltage:

$$U^o \approx 1.32\,\text{V} \quad \text{in practice } U^o \approx 1.3\,\text{V} \tag{77}$$

The sign '≈' expresses that this potential does not represent a true equilibrium potential and that this value can only be approximated, as already has been indicated above and also in Table 1.1. Actually, after charging, values between 1.3 and 1.4 V are observed, depending on the previous treatment of the battery. But on open circuit the cell voltage decreases to less than 1.3 V within a few days (59).

1.8.2.2 The Temperature Coefficient of the Equilibrium Voltage

The temperature coefficient of the equilibrium voltage is also determined by thermodynamic parameters according to Eq. (13) and results in

$$\frac{dU^o}{dT} \approx -0.45\,\mathrm{mV/K} \tag{78}$$

This decrease of the equilibrium voltage of about 0.5 millivolt per degree can usually be neglected in battery practice.

1.8.2.3 The Reversible Heat Effect and Calorific Voltage

The reversible heat effect of the discharge reaction is

$$Q_{rev} = T \cdot \Delta S \approx -26\,\mathrm{kJ} \tag{79}$$

per multiple of the cell reaction. Comparison with the value of ΔG shows that the reversible heat effect amounts to 10.5% of the converted energy when the nickel/cadmium battery is discharged or charged, and the negative sign means that additional heat is generated during discharge, while a cooling effect is observed during charging, as shown in Fig. 1.14 and Fig. 1.15.

During charging, water decomposition can only be critical as a heat source, when the cell voltage considerably exceeds 1.48 V (= U_{cal} for water decomposition). As a result, vented nickel/cadmium batteries can be charged at quite high rates without suffering heat problems. But in the sealed version, the internal oxygen cycle can cause serious thermal problems (cf. Fig. 1.15).

1.8.2.4 Secondary Reactions

Figure 1.31 shows the charge/discharge and secondary reactions and their dependence on electrode potential. The drawing corresponds to Fig. 1.19, but for the x-axis two scales are employed: The upper one represents the potential referred to the hydrogen electrode in the same solution (HESS). This scale is independent of the electrolyte concentration, since the equilibrium potentials for all the reactions are shifted in the same manner with changing pH value, namely −0.059 V/pH. The lower scale represents the electrode potential referred to the standard hydrogen electrode (SHE). The electrolyte density has to be considered in this case, since all potentials in the figure are shifted with KOH concentration as mentioned above.

The equilibrium potential of the cadmium electrode is about 20 mV more positive than that of the hydrogen electrode. As a consequence, self-discharge by hydrogen evolution, as described for the lead electrode in Fig. 1.18, does not occur with the cadmium electrode.

The equilibrium potential of the nickel-hydroxide electrode is slightly above that of water decomposition. In this respect the situation resembles that of the lead-dioxide electrode, but the much lower value of this potential allows the use of nickel as conducting element, since corrosion of this metal can be neglected, at least under normal conditions. For this reason, corrosion is not shown in Fig. 1.31. (Only in foam electrodes with an extremely large surface area of the substrate, nickel corrosion may slightly disturb the current balance in sealed cells.)

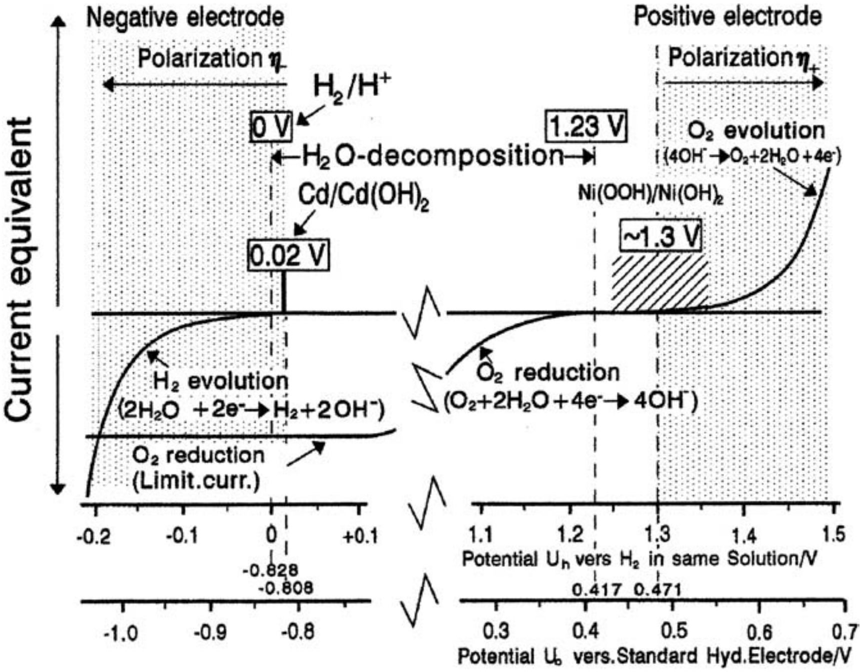

Figure 1.31 Equilibrium potentials of the negative and positive electrodes in a nickel/cadmium battery, and current/voltage curves for O_2 and H_2 evolution and O_2 reduction.

For the x-axis, i.e. the electrode potential, two scales are employed:

The upper one represents the potential U_h referred to the hydrogen electrode in the same solution (HESS); the lower scale U_o is referred to the standard hydrogen electrode (SHE) for 1.250 g/cm^3 density of the KOH solution at 25 °C.

Compared to the situation of the lead-acid battery, illustrated in Fig. 1.19, the situation in the nickel/cadmium battery shows similarities, but also important differences:

- As in lead-acid batteries, oxygen evolution cannot be avoided at the positive electrode, it already occurs at open circuit and is increased with a more positive polarization of the positive electrode.
- Oxygen reduction at the negative electrode in nickel/cadmium batteries is also limited by the transport rate of oxygen. The reduction itself at the nickel substrate of the cadmium electrode is faster than in lead-acid batteries. In flooded batteries this limiting current is as low as that in vented lead-acid batteries. In sealed nickel/cadmium batteries, oxygen transport rates can be quite high, and the internal oxygen cycle correspondingly fast due to void volume within the separator and narrow spacing of the electrodes (cf. heat generation in Fig. 1.15).
- Hydrogen evolution starts below the equilibrium potential of the negative electrode and can completely be avoided, if the (negative) polarization of the cadmium electrode during charging is kept so small that the hydrogen

equilibrium potential is not reached. In practice, overcharging at the 5 hour rate is possible for many of the sealed designs without hydrogen evolution. As already mentioned, self-discharge of the cadmium electrode caused by hydrogen evolution does not occur.

- Corrosion of the nickel substrate in the positive electrode is negligible, and thus not shown in Fig. 1.31.

1.8.2.5 The Sealed Nickel/Cadmium Battery

The internal oxygen cycle, formed by oxygen evolution at the nickel-hydroxide electrode and its subsequent reduction at the cadmium electrode, was already detected in the 1940s as a possibility to avoid gas escape during overcharging, and the sealed nickel/cadmium battery appeared on the market in the 1950s. Immobilization of the alkaline electrolyte is achieved by absorption in mats of fibers of polyamide or polypropylene. Formation of a gel, as described in Section 1.8.1.5 for lead-acid batteries, is not possible with alkaline electrolyte. As mentioned above, corrosion (almost) does not occur in the nickel-hydroxide electrode and its current connectors, and at the cadmium electrode hydrogen evolution can be avoided. As a consequence, the internal oxygen cycle is not disturbed by secondary reactions, and the nickel/cadmium battery can virtually be sealed, provided that oxygen transport from the positive to the negative electrode is fast enough to keep the internal pressure of oxygen during overcharging below a critical value. The overcharging situation corresponds to that shown in Fig. 1.25, but without the two unwanted side reactions 'grid corrosion' and 'hydrogen evolution'. Thus only the internal oxygen cycle is left, and the battery does not need a valve. (Actually, also nickel/cadmium batteries, except of button cells, are equipped with a valve, but this only opens in an emergency when the internal pressure exceeds its upper limit, usually caused by overcharging at a too high rate or when the cell is reversed.)

Hydrogen oxidation at the nickel-hydroxide electrode occurs faster compared to the reaction rate at a lead-dioxide surface in acid electrolyte, but it is still a very slow reaction, and thus an internal hydrogen cycle of an acceptable rate is not established. Hydrogen gas, if formed at the negative electrode, increases the internal pressure until the valve opens or the cell bursts. Hydrogen, however, cannot be generated as long as the negative electrode retains its potential above the hydrogen-equilibrium potential, which means that the potential of the negative electrode has to be kept quite close to its equilibrium value (c.f. Fig. 1.31). Two conditions must be fulfilled to achieve this:

- The potential of the negative electrode must be stable, i.e. charged material (Cd) as well as discharged material ($Cd(OH)_2$) must be present to maintain the equilibrium potential.
- The overcharge current must not exceed the maximum oxygen transport rate, so that all the oxygen that has been generated at the positive electrode reaches the negative electrode fast enough to be reduced.

The first point is achieved by oversizing the cadmium electrode, as shown in Fig. 1.32. The dotted blocks in the figure indicate the shares of capacity that actually can be utilized. The upper one represents the electricity that can be drawn from the

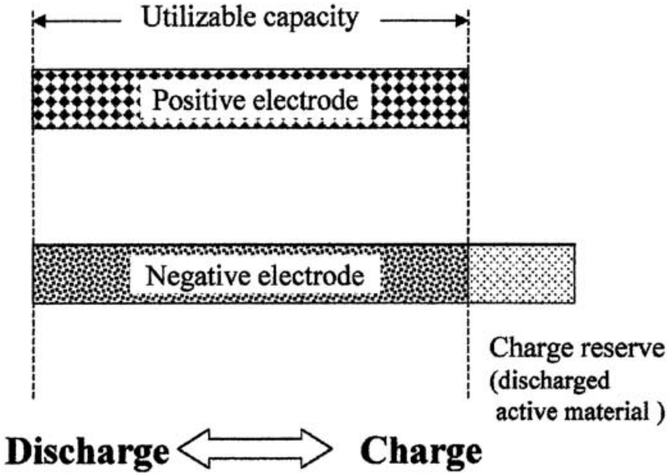

Figure 1.32 Cell balance of a sealed nickel/cadmium battery.

positive electrode and recharged again. This utilizable capacity of the positive electrode is synonymous with the capacity of the cell.

The capacity of the negative electrode is represented by the lower block. Its capacity is oversized, compared to the positive electrode. To match the design conditions shown in Fig. 1.32, the two electrodes must be assembled in a definite state of charge. Some of the active material in the negative electrode must remain discharged (as $Cd(OH)_2$) when the positive electrode is fully charged and the cell is sealed. This share of capacity is called charge reserve. To achieve this layout, the negative electrode is discharged to a definite extent before it is assembled with a fully charged positive electrode. After the battery cell is sealed, this layout remains largely unchanged under normal operating conditions.

The charge reserve in the negative electrode complies with the first of the two above conditions; it stabilizes the potential of the negative electrode. When the battery is charged, the two dotted blocks in Fig. 1.32 are converted from the discharged into the charged state at a uniform rate. When the positive electrode reaches the state of full charge, oxygen evolution occurs instead of the charging reaction, and this oxygen is transported to the negative electrode and reduced. When the overcharging current only generates oxygen at the positive electrode that subsequently is reduced at the negative electrode, no current is left for further charging of the negative electrode. Thus, the charge reserve remains in its discharged state for an unlimited period of overcharge. The charge reserve acts as a ‘potentiostat’ to prevent the negative electrode from becoming polarized to a more negative potential which would cause hydrogen evolution. Such a charge reserve would not make sense in a valve-regulated lead-acid battery, since it would increase the rate of the inherent hydrogen evolution and so even aggravate the situation and further disturb the balance, described in Section 1.8.1.5.

To fulfill the second of the above-mentioned conditions, oxygen transport from the positive to the negative electrode must be fast enough. This is achieved by sufficient void space in the separator (cf. Section 1.8.1.5), and it is favored by the narrow spacing between the electrodes in nickel/cadmium batteries.

1.8.2.6 Comparison Between Ni/Cd and Lead-Acid Batteries

The above-shown basic characteristics that can be derived from the reaction equations cause differences between nickel/cadmium and lead-acid batteries that are of great influence on battery practice:

- The electrolyte does not participate in the cell reaction of nickel/cadmium batteries; it acts only as ion conducting medium. Therefore a certain amount of electrolyte is not required between the electrodes, rather they can be narrowly spaced. The internal resistance can so be minimized which makes nickel/cadmium batteries suited for extremely high loads.
- For the same reason, dilution of the electrolyte, as described by Fig. 1.2 for lead-acid batteries, does not occur in nickel/cadmium batteries. Thus the freezing point of about – 60° C remains also in the discharged battery, and there is no danger of ice formation. This makes nickel/cadmium batteries especially well suited for applications at extremely low temperature.
- Corrosion of nickel used for plate substrates and conducting elements can be neglected, and thus very thin nickel layers are sufficient as current conductors. Various types of substrates (sintered, foamlike) are in use that allow high utilization of the active material.
- Hydrogen evolution can also be prevented, and thus the unwanted secondary reactions hydrogen evolution and grid corrosion that disturb the internal oxygen cycle in lead-acid batteries, as shown in Fig. 1.25, are not present in nickel/cadmium batteries, which therefore can be hermetically sealed so that neither vapor or gas escapes from the battery. This is the reason for the market success of these batteries in the field of portable applications.

1.8.3 Nickel/Hydrogen Batteries

Nickel/hydrogen batteries are closely related to the nickel/cadmium battery, since they employ the same positive electrode and the same electrolyte. They have been developed for aerospace applications and are still the number one energy storage system in many satellite projects 60.

For the negative electrode, hydrogen is used as active material instead of cadmium. Furthermore, the negative electrode is different from a conventional battery electrode and corresponds to a fuel cell electrode. The electrode material is not transformed, but acts only as a catalytic surface that provides or absorbs electrons. Hydrogen is not stored in the electrode. In the charged state, it remains as gaseous hydrogen within the cell. The container therefore has to withstand pressures up to about $7 \cdot 10^6$Pa (70 bar). On account of the hydrogen storage, nickel/hydrogen batteries must be hermetically sealed. In the discharged state, hydrogen is absorbed by the nickel hydroxide.

Note: *The catalytic effect of the negative electrode is not a pure surface effect, it rather includes absorption and the formation of metal hydrides. But the amount of platinum or* *palladium used in such batteries is so small that the storage capacity of the electrode has no relevance.*

Figure 1.33 shows a sectional view. The electrodes are arranged as a stack in the center; the immobilized electrolyte is soaked by the separator; and the edges of the electrodes are sealed to prevent short circuits around the separator.

In the hydrogen electrode, usually platinum is applied as electrode material on account of its outstanding catalytic capabilities and its chemical stability. It mostly is Teflon bonded or covered by microporous Teflon membranes (plastic net in Fig. 1.33) to make the surface hydrophobic and so prevent the formation of thicker layers of water that would hinder gas access. The electrolyte is immobilized by soaking fiber felts or knitted textiles of mineral fibers (fuel-cell-grade asbestos paper) or zircon fibers stabilized with yttrium (Zircar cloth). They provide high temperature resistance and chemical resistance for long-life batteries.

The generation of gaseous hydrogen during charging and its consumption during discharging means that the internal gas pressure is proportional to the state of charge. This offers the possibility to check the state of charge by measurement of the internal cell pressure.

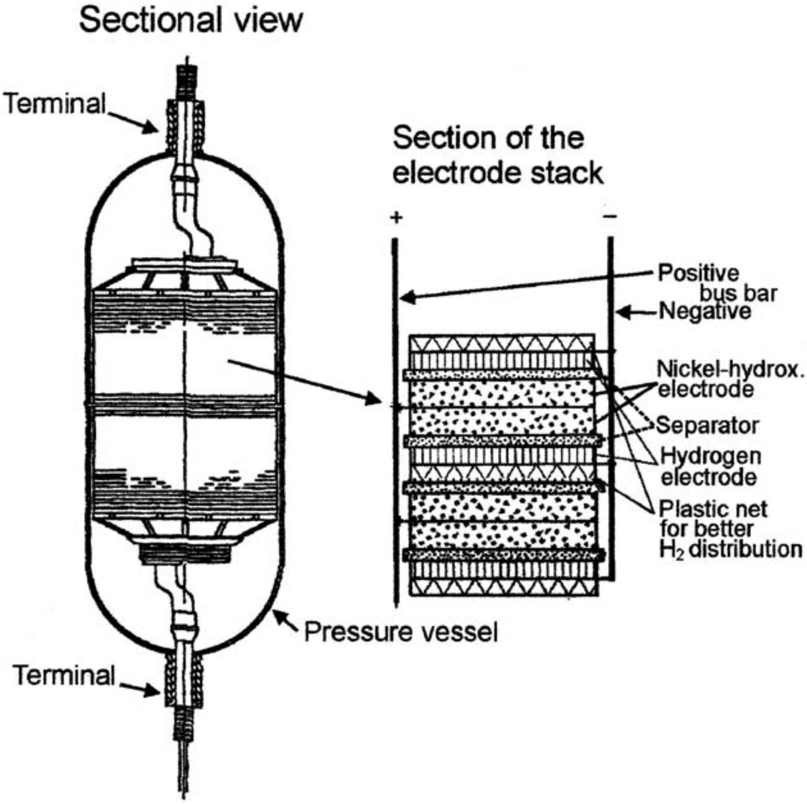

Figure 1.33 Sectional view of a nickel/hydrogen cell and details of the electrode stack.

1.8.3.1 Thermodynamic Situation

The discharge reaction of the negative electrode is

$$H_2 + 2 \cdot OH^- \Rightarrow 2 \cdot H_2O + 2 \cdot e^- \tag{80}$$

Its reversal (from right to left) represents charging. Combination with the reaction of the nickel electrode (Eq. (72)) leads to the cell reaction (discharge from left to right)

$$2 \cdot NiOOH + H_2 \Leftrightarrow 2 \cdot Ni(OH)_2 \tag{81}$$

During discharge, NiOOH is reduced to $Ni(OH)_2$ and hydrogen is consumed. During charge, this equation is reversed, and the released hydrogen (H_2) stored as a gas in each cell.

The free enthalpy of reaction ΔG and the reversible heat effect $T \cdot \Delta S$ are

$$\Delta G = -259 kJ \qquad \text{and} \qquad Q_{rev} = T \cdot \Delta S = -36\,kJ$$

and, according to Eq. (5), ΔG leads to the equilibrium cell voltage:

$$U^o = 1.34 V$$

which is very close to that of the nickel/cadmium battery, and due to the uncertainties connected to the nickel-hydroxide electrode mentioned above, the same value results for the nominal voltage of both battery systems:

$$U^o \approx 1.3\,V \tag{83}$$

The reversible heat effect is slightly higher in nickel/hydrogen batteries, which means that cooling during charging is slightly more expressed compared to the corresponding effect with nickel/cadmium batteries described above.

Also the closely related temperature coefficient of the equilibrium cell voltage is slightly higher and results according to Eq. (13) to

$$U^o/dT \approx -0.6\,mV/K \tag{84}$$

As with nickel/cadmium batteries, it can be neglected in practice.

1.8.3.2 Secondary Reactions

The situation with respect to secondary reactions is shown in Fig. 1.34. It is similar to that in the nickel/cadmium battery shown in Fig. 1.32 as far as the positive electrode is concerned. Different is the situation at the negative electrode. The electrode potential is nearly the same, since the equilibrium potential of the hydrogen electrode is only about 20 mV below that of the cadmium electrode. But now hydrogen is used as active material instead of cadmium, and hydrogen evolution as well as hydrogen oxidation are fast reactions, since both are catalyzed by the platinum surface of the negative electrode.

Oxygen evolution, oxygen reduction, and the internal oxygen cycle occur as in nickel/cadmium batteries. If no current flows through the cell, any oxygen that had been generated within the cell is removed by direct catalytic reaction (recombination of oxygen and hydrogen), because the negative electrode acts like a recombination device.

Hydrogen oxidation occurs as the discharge reaction at the negative electrode. But due to its high pressure, hydrogen is also oxidized at a perceivable rate at the

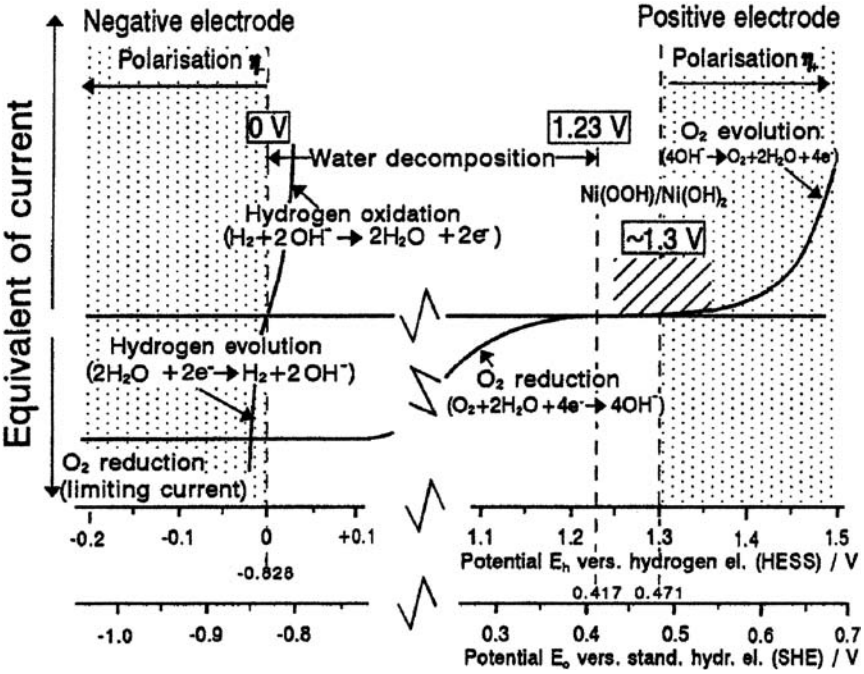

Figure 1.34 Equilibrium potentials and current/voltage curves in a nickel/hydrogen or a nickel/metal hydride battery. Current/voltage curves for O_2 evolution and reduction and for H_2 evolution and oxidation. For the x-axis, the electrode potential, two scales are employed as in Fig. 1.31.

positive electrode as an unwanted secondary reaction. At open circuit, reduction of the nickel hydroxide is the counter reaction; and self-discharge according to

$$2 \cdot \mathrm{NiOOH} + H_2 \Rightarrow 2 \cdot \mathrm{Ni(OH)_2} \tag{85}$$

is the result. In the charged battery, this direct reaction between H_2 and Ni(OOH) causes the considerable self-discharge rate of nickel/hydrogen batteries, especially when the H_2 pressure is high in the fully charged battery, and this rate strongly depends on temperature and can reach more than 50% per week at temperatures above 30° C (cf. Figures 32.15 and 32.16 in Ref. 1).

An internal hydrogen cycle is established when the battery is discharged so deeply that hydrogen is evolved at the reversed nickel-hydroxide electrode. This hydrogen subsequently is oxidized at the negative electrode according to the normal discharge reaction. So, the negative electrode is not reversed, but remains at its normal discharge potential, while hydrogen (H_2) is now supplied by the reversed positive electrode. This internal hydrogen allows deep discharges that include the reversal of positive electrodes without damage of the battery.

Advantages of the nickel/hydrogen battery system are

- A fairly high specific energy of 50 to 60 Wh/kg depending on design and size.
- The ability to withstand a great number of discharges (about 40,000 cycles at 40% DOD).
- A calendar life of about 15 years.
- The battery can be deep discharged and single cells reversed without damage.
- The state of charge can easily be controlled by measurement of the internal H_2 pressure.
- Each cell is hermetically sealed. No maintenance is required.

Disadvantages are

- Its high price which limits the application more or less to aerospace projects.
- High self-discharge rate due to direct reaction between hydrogen and nickel as mentioned above.
- The energy density amounts to only 20 to 40 Wh/dm^3, because of the volume required for gas storage and the shape of the pressure vessel.

The above listed advantages explain the widespread use in the aerospace field. Especially the high number of possible cycles and the capability to stand deep discharges are important. The high self-discharge rate can also be accepted in space applications, since most satellites perform a number of orbits per day and are correspondingly often recharged.

Figure 1.35 shows as an example one 'half-battery' of the International Space Station Alpha (ISS).

A modified version of this system is the low pressure nickel/hydrogen battery. It is in principle the same design, but the hydrogen (H_2) is stored as a metal hydride in alloys as they are used in nickel/metal hydride batteries. The advantages are that the container must not withstand high pressure and the rate of self-discharge is lower. This system, however, did not achieve a significant market position.

1.8.4 Nickel/Metal Hydride Batteries

Nickel/metal hydride batteries are based on the same reactions as the nickel/hydrogen batteries. However, hydrogen is not stored as a gas, but during charging it is absorbed by the negative electrode material and desorbed during discharging, and both occur at a low hydrogen pressure. This is achieved by special alloys that act as the catalytic electrode surface and simultaneously absorb the hydrogen (H_2) by forming metal hydrides. Thus the negative electrode material catalyzes the reaction according to Eq. (80) and simultaneously stores the hydrogen that is formed during charging. Due to the low internal pressure, nickel/metal hydride batteries do not require a cell container that can withstand high pressures, but they can be encapsulated like sealed nickel/cadmium batteries.

1.8.4.1 Thermodynamic Parameters

The thermodynamic parameters are identical to those of the nickel/hydrogen battery, and the nominal cell voltage is also 1.3 V. This has the very important

Figure 1.35 A module of 38 cells of a nickel/hydrogen battery that forms one-half of a 76 cell battery (≈ 100V). 24 of such batteries will power the International Space Station (ISS). Cell capacity 85 Ah; stored energy ≈ 8 kWh per battery (from Ref. 61).

consequence that nickel/metal hydride batteries can substitute nickel/cadmium batteries.

The temperature behavior of nickel/metal hydride batteries is slightly different from that of nickel/cadmium batteries, since hydrogen absorption and desorption contribute heat effects. Hydrogen absorption is an exothermic reaction and generates additional heat during charging, while a (nearly) corresponding cooling effect is observed when hydrogen is desorbed. This effect is not quite reversible (cf. Fig. 1.36), and its quantity depends on the alloy applied for hydrogen storage. It might compensate or even overcompensate the reversible heat effect. For this reason, the characteristic feature of nickel/cadmium batteries that the charging reaction causes cooling, as shown in Figs. 1.14 and 1.15, does not apply for nickel/metal hydride batteries.

1.8.4.2 Self-Discharge

Self-discharge in nickel/metal hydride batteries is based on hydrogen oxidation as has been described for nickel/hydrogen batteries above. But, due to the low hydrogen equilibrium pressure, the rate of self-discharge is reduced so far that it only attains rates known for nickel/cadmium batteries ($< 20\%$ per month).

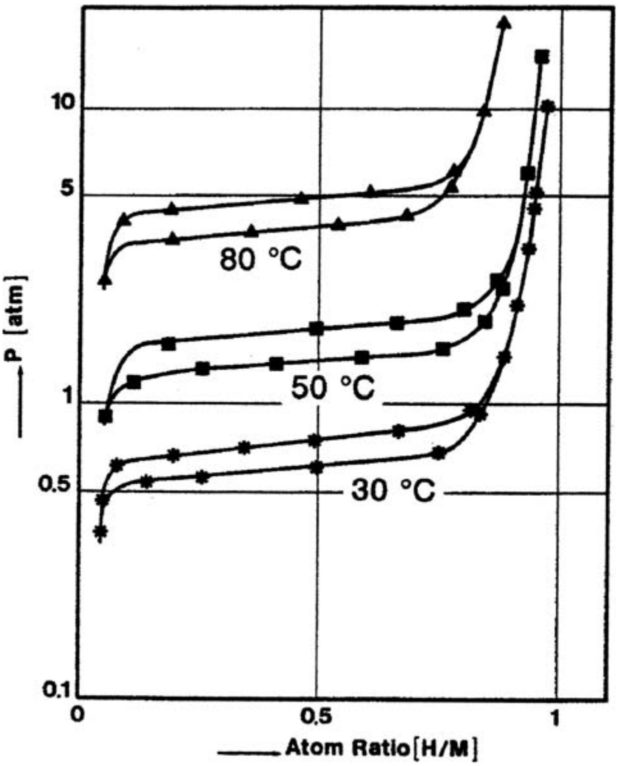

Figure 1.36 Pressure composition isotherms (PCI curves) of an AB_5 alloy with nickel partly substituted by aluminum ($LaNi_{4.7}Al_{0.3}$) vs. hydrogen content (from Ref. 72).

1.8.4.3 Hydrogen-Absorbing Alloys

An important prerequisite for nickel/metal hydride batteries was the development of alloys that absorb and desrob hydrogen at a suitable pressure and simultaneously can act as a catalytic surface. The possibility to store hydrogen is known for a number of metals. Palladium, for example, absorbs between 0.4 and 2 wt% of hydrogen. This means that 1 cm^3 palladium is able to store up to 0.24 g of H_2, which corresponds to 2800 cm^3 of gaseous H_2 at 25 °C and 1 atm. This demonstrates the enormous hydrogen storage capability of such metals.

Less noble metals are also able to store considerable amounts of hydrogen, and a great variety of elemental hydrides exists. But little practical use was possible, since only a few offer a reasonable hydrogen equilibrium pressure at room temperature. This situation has changed since intermetallic compounds have been developed that combine strong-hydride forming elements with those that form weak hydrides. An appropriate ratio between both components can be used to tailor metal hydrides of the desired decomposition pressure.

The variety of such compounds is nearly unlimited, and a great number of alloys has been discovered or developed that form metal hydrides (62), providing hydrogen storage in a suitable range of pressure and temperature (surveys are given in Ref. 63). They are divided into groups A_uB_v, based on composition and crystal structure. 'A' represents a strong-hydride forming element and 'B' the weak-hydride forming component. For practical purposes and to reduce the price of the product, A and B are often combinations of various elements.

Combinations that proved to be suited for hydrogen storage in batteries are known as AB, AB_2, A_2B, and AB_5 (cf., e.g. Ref. 64). Table 1.10 shows examples of characteristic composition and some of their features.

AB_5 alloys are now mainly used for nickel/metal hydride batteries. Mischmetals, which are unrefined mixtures of rarc carths, are mostly substituted instead of lanthanum, mainly because they are less expensive than pure La. But such substitutions also are required to stabilize the alloy and prevent its premature degradation.

The AB_2 type in Line 2 of Table 1.10 is based on vanadium, titanium, zirconium, and nickel. Especially for these intermetallic compounds the stoichiometry is not well defined. So some alloys ascribed to this group may be named A_2B or AB as well.

Titanium/nickel intermetallic phases (A_2B and AB type) were developed in the 1970s with great assiduity when the aim was hydrogen storage for road vehicles with hydrogen combustion engines (70).

Hydrogen storing alloys as shown in Table 1.10 are not manufactured in battery plants, but are provided by specialized suppliers (some references are given in Section 2.5 of Ref. 72). Selection of the raw materials and preparation of the hydrogen absorbing alloy are most important, because not only its composition, but also its structure and the distribution of the alloying elements are decisive for capacity and service life (71).

Figure 1.36 shows as an example pressure isotherms of an AB_5 alloy versus their hydrogen content at various temperatures. For each temperature the upper and lower curves denote absorption and desorption, respectively. The nearly horizontal sections of the curves indicate that in a narrow pressure range nearly all of the

Table 1.10 Classes of intermetallic compounds that are used for negative electrodes of nickel/hydride batteries. Alloys corresponding to Lines 1 and 2 are nowadays mainly applied.

	A_uB_v class (basis)	Actual components	Storage capability (Ah/kg)	Remarks
1	AB_5 ($LaNi_5$)	**A**: Misch metal[a], La, Ce, Ti **B**: Ni, Co, Mn, Al	≈300 at max. (65)	At present, most used alloy group
2	AB_2 ($TiNi_2$)	**A**: V, Ti **B**: Zr, Ni (+Cr, Co, Fe, Mn)	≈400 at max. (66)	Basis of multi-component alloys (67)
3	AB (ZrNi)	**A**: Zr, Ti **B**: Ni, Fe, Cr, V		Initially used for hydrogen storage in cars and as electrodes (68)
4	A_2B (Ti_2Ni)	**A**: Mg, Ti **B**: Ni		

[a] Mischmetal (mm) is an unrefined rare earth mixture (mainly Ce, La, Nd, and Pr). Its composition depends on the ore (64), but "synthetic misch metals" are also known (69).

hydrogen is desorbed during discharging or absorbed during charging, and at 50 °C this pressure is close to 1 atm.

Initially hydrogen is absorbed with increasing pressure, until the formation of the MH_n phase starts. Then the pressure remains approximately constant, until the metallic phase is converted into hydride. Desorption of hydrogen occurs at lower pressure and the hysteresis between absorption and desorption pressure indicates the energy loss between absorption and desorption, which causes additional heat effects. The horizontal axis is given in moles hydrogen per moles metal. So the ratio 1 means $6 \cdot H$ per alloy formula AB_5, or with the mole weights of La, Ni, and Al = 138,59, and 27, respectively, 6 g hydrogen per 423 g of alloy. This means a storage capability of about 1.4 wt%.

In the battery, the hydrogen storing alloy is in direct contact with the electrolyte and acts as the electrode as well. So an interface layer is formed that has to resist corrosion and oxidation attacks and may undergo significant structural and compositional changes (73). This layer plays an important role: While the bulk of the electrode material determines the capability for hydrogen absorption and so the capacity, the interface layer is decisive for most performance data. High rate discharge capability and cycle life are such parameters.

1.8.4.4 Cell Balance

Cell balance, as described in Fig. 1.32 for nickel/cadmium batteries, is also required in nickel/metal hydride batteries. Different from nickel/cadmium batteries, hydrogen evolution cannot be suppressed in nickel/hydrogen and nickel/metal hydride batteries, since it is the charging reaction of the negative electrode. But enough storage capacity must be available in the negative electrode to prevent an intolerable increase of the internal pressure when the battery is overcharged. On the other hand, it must be prevented that the negative electrode is reversed when the battery is deep discharged, otherwise the storage alloy would be damaged by oxidation due to the then reached positive potential. Both are achieved by the balance between positive and negative electrode, shown in Fig. 1.37.

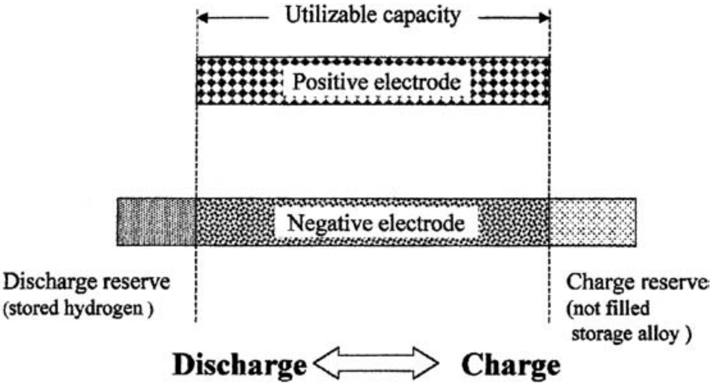

Figure 1.37 Balance of electrode capacities (cell balance) in a nickel/metal hydride battery by means of charge reserve and discharge reserve.

The ‘charge reserve’ acts in a similar way as described in Fig. 1.32 for nickel/cadmium batteries, but now it does not prevent hydrogen evolution, but keeps the hydrogen pressure low when the cell is overcharged, until the positive electrode is fully charged and only generates oxygen that is reduced at the negative electrode. Then the current in total is consumed by the internal oxygen cycle, and no current is left for further hydrogen evolution, and so the charge reserve remains unchanged.

The ‘discharge reserve’ in Fig. 1.37 ensures that the negative electrode is still partly charged when the positive electrode is completely discharged and so prevents reversal of the negative electrode that would cause damage to the alloy by oxidation. At the reversed positive electrode, hydrogen is evolved according to

$$2 \cdot H_2O + 2 \cdot e^- \Rightarrow H_2 + 2 \cdot OH^- \tag{86}$$

which is oxidized at the negative electrode according to its normal discharge reaction (Eq. (80)):

$$H_2 + 2 \cdot OH^- \Rightarrow 2 \cdot H_2O + 2 \cdot e^- \tag{87}$$

As a result, the negative electrode is not further discharged. It remains at its normal discharge potential, and the combination of Eqs. (86) and (87) forms an internal hydrogen cycle. This cycle causes a stable state of the overdischarged cell where the positive electrode is reversed, while the negative electrode remains at its potential.

1.8.4.5 Comparison the Nickel/Cadmium and Nickel/Metal Hydride Battery

The characteristics of nickel/metal hydride batteries are very similar to those of sealed nickel/cadmium batteries. The cell voltage differs by only 20 mV, and charging as well as discharging performance are so alike that both battery systems can be replaced by each other in all normal applications. The discharge curves in Fig. 1.38 confirm this.

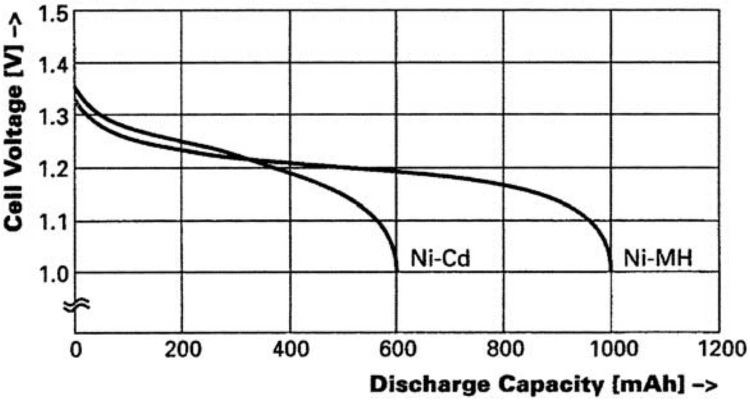

Figure 1.38 Comparison of discharge voltage and capacity between nickel/cadmium and nickel/metal hydride batteries of the same size. Cylindrical cells, AA type, discharging current 0.2 CA (≈5 hours) (from Ref. 74).

Figure 1.38 clearly shows the superiority of the nickel/metal hydride system and explains the enormous success of this system on the market. Its development was initiated by the wish to substitute the toxic cadmium which causes problems when used nickel/cadmium batteries are disposed into the usual household garbage and so might be incinerated. The higher storage capability, however, turned the nickel/metal hydride battery to more than only a substitute and opened many applications for the new battery system, although its price is higher compared to that of nickel/cadmium batteries.

Two disadvantages compared to nickel/cadmium batteries may be mentioned which are caused by the basic parameters of the system:

1. At low temperatures and at high loads the desorption rate of the hydrogen can be limiting. For this reason, nickel/cadmium batteries may be preferred in such applications.

   In practice, however, discharge performance under these conditions is mainly a question of electrode thickness. Thus, such a comparison depends largely on the special battery design, and nickel/metal hydride batteries with thin electrodes can give a better performance at low temperatures than nickel/cadmium batteries with thicker electrodes.
2. Hydrogen absorption and desorption by the storing alloy are not completely reversible (Fig. 1.36), and in total contribute additional heat when a whole charge/discharge cycle is considered. For this reason, nickel/metal hydride batteries are stronger heated up compared to nickel/cadmium batteries, when used in a heavy cycling schedule as occurs in tools like drilling machines under professional operation. As a consequence, nickel/cadmium batteries are often preferred in such applications.

1.8.5 Batteries of Particular Design

In the classical design of a battery according to Fig. 1.1, the reacting substances are stored as active material in the electrodes. An already described exception is the nickel/hydrogen battery (Section 1.8.3), where the active material of the negative electrode, the hydrogen, in its charged state is stored as a gas under high pressure not in the electrodes but in the container of each cell. Further possibilities are to store the active material outside the cells in separate tanks, or to take oxygen from the surrounding atmosphere as active material of the positive electrode. To some extent such batteries are hybrids of batteries and fuel cells. Their technical development was mainly initiated by the desire to increase the storage capability by enlarging not the whole cell but exclusively extending the volume of the active material, or taking the active material of the positive electrode as air from the surrounding and saving so space and weight. Some examples are described in this section.

In zinc/chlorine and zinc/bromine batteries, the active material is partially stored outside the electrodes in separate tanks which in parallel supply all cells of the battery.

The vanadium redox battery stands for a whole family of batteries in which the active material is exclusively stored in the electrolyte. The electrode material does not participate in the electrochemical reactions but only acts as acceptor or donator of electrons. The capacity of such a battery is determined by the amount of electrolyte that is stored in the tanks.

Zinc/air and metal/air batteries take the active material of the positive electrode, the oxygen, from the surrounding atmosphere. So the positive electrode does not contain active material, but only delivers electrons for the reduction of oxygen ($O_2 + 4 \cdot e^- \Rightarrow 2 \cdot O^{2-}$). Occasionally they are called metal/fuel cells (75) although they are predominantly used as primary batteries, and the capacity of their negative electrodes is limited by the amount of zinc that forms the active material.

Such batteries are in widespread use as button cells based on alkaline electrolyte, as mentioned in Table 1.11, as power sources in hearing aids, but also as larger cells with slightly acid electrolyte, e.g. in warning lights at road construction sites. They are described in Chapter 15 to some detail.

The advantage is obvious, when the air in the surrounding atmosphere is used as positive active material, weight and volume of the battery can be reduced and capacity correspondingly be increased. Problems to recharge a soluble metal electrode as described in Fig. 1.5, however, conflict with the possibility to repeat charge/discharge cycles. For this reason, secondary metal/air batteries always include the substitution of the discharged negative electrode by a new one after each cycle or after a small number of cycles.

Table 1.11 shows characteristic data of some batteries that belong to these systems of special design. These figures, however, can only be considered as a rough comparison, since such performance data strongly depend on the special design parameters.

Table 1.11 Battery systems of special design.

		Equilibrium voltage	Stored energy		
				Practice	
	System	V/cell	Theory Wh/kg	Wh/kg	Wh/dm^3
1a	Zinc/chlorine	2.12	$\approx$500[a]	$\approx$110	$\approx$130
1b	Zinc/bromine	1.8	438	65 to 70[b]	max. 70[b]
2	Vanadium redox	1.6[c]	$\approx$40[d]	20–30	20–40
3a	Zinc/air (primary)[e]	1.65[g]	1320[h]	$\approx$290[i]	$\approx$900[j]
3b	Zinc/air (secondary)[f]	1.65[g]	1320[h]	$\approx$170[j]	$\approx$200

[a] Assuming that chlorine is stored as [$Cl_2 \cdot 7H_2O$].

[b] Whole battery, depending on the size of the electrolyte tanks.

[c] When fully charged. At standard concentrations 1.26 V/cell.

[d] When the vanadium solution alone is considered.

[e] Primary version with alkaline electrolyte.

[f] Rechargeable by replacing the negative electrodes after discharge.

[g] Open circuit voltage in practice $\approx$ 1.4 V/cell.

[h] Referred to pure zinc as negative electrode and to the charged state: oxygen intake during discharge reduces the figure to 1211 Wh/kg.

[i] Button cells.

[j] Referred to the weight of the charged state.

1.8.5.1 Zinc/Chlorine and Zinc/Bromine Batteries

The zinc/chlorine battery was a predecessor of the zinc/bromine battery. It had been developed in the 1960s and 1970s for vehicle application (cf., e.g. Ref. 76, p. 302). It is based on the cell reaction

$$\begin{aligned}&\text{Charging} \Leftrightarrow \text{Discharging}\\ &\mathrm{Zn} + \mathrm{Cl_2} \Leftrightarrow \mathrm{ZnCl_2}\end{aligned} \qquad (88)$$

The design uses a cell stack similar to that shown in Fig. 1.39 for the zinc/bromine battery and also separate tanks to store electrolyte and the partly dissolved active material. The electrolyte is also pumped through the cell stack. Chlorine (Cl_2), generated during charging, is precipitated and stored as solid chlorine hydrate ($Cl_2 \cdot xH_2O; 6 \leqslant x \leqslant 8$). This hydrate is stable at temperatures below 10 °C. Therefore, adequate cooling of the storage tank is required during charging. During discharge, the electrolyte has to be warmed up and then releases the required chlorine.

Although according to the theory the considerable specific energy density of 500 Wh/kg (Table 1.11) should be possible, the development was not continued due to technological problems.

The zinc/bromine system was pioneered by Exxon and Gould in the United States. The development was mainly continued by SEA in Austria. Prototypes of this battery system have been built. A great number of tests has been carried out in electric vehicles, and also stationary applications, like load leveling, have been included (77)

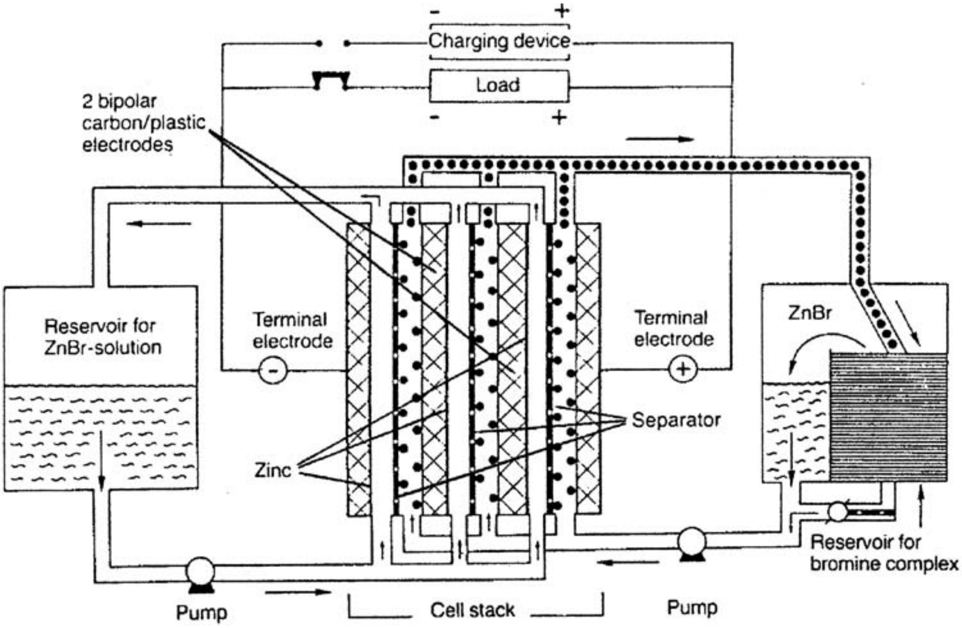

Figure 1.39 Zinc bromine battery (from Ref. 77).

This battery uses zinc and bromine as active materials. The reactions are:

$$\text{Charging} \Leftrightarrow \text{Discharging}$$

$$\text{Positive electrode}\quad Br_2 + 2 \cdot e^- \Leftrightarrow 2 \cdot Br^- \tag{89a}$$

$$\text{Negative electrode}\quad Zn \Leftrightarrow Zn^{2+} + 2 \cdot e^- \tag{89b}$$

$$\text{Cell reaction}\quad Br_2 + Zn \Leftrightarrow ZnBr_2 \tag{89}$$

During charging, Zinc (Zn) is precipitated as a solid metal, that is dissolved as zinc bromide ($ZnBr_2$) during discharge. At the positive electrode, the charged material is bromine (Br_2) that together with organic substances forms a polybromide oil that does not mix with the aqueous electrolyte and easily can be separated from the electrolyte. Since most of the bromine thus is stored separately, only a small portion can diffuse through the separator, and self-discharge of the battery is low. The formation of the bromine complex furthermore prevents the escape of bromine from the battery. The conductivity of the electrolyte is enhanced by the addition of potassium or ammonium chloride (KCl or NH_4Cl).

A general problem of such cell-stack designs are shunt losses, caused by connection of the electrodes at different voltages via the electrolyte. Special design of the electrolyte channels can reduce the shunt loss to about 3% of the discharged energy.

Figure 1.39 shows the principle of the zinc/bromine battery. In Fig. 1.39, the cell stack consists of only three cells. Actual batteries contain stacks of 50 or more cells. Except the two end plates, all electrodes are bipolar. They consist of an electron-conducting plate of carbon plastic enframed by insulating plastic. On the positive side, a porous layer of carbon increases the surface to increase the reaction rate of bromine. In the center of each cell, a microporous separator is positioned as used in lead-acid batteries (e.g. Daramic™) to suppress the direct contact between bromine and zinc as far as possible.

The electrolyte forms two circuits: one that flows in parallel through the compartments formed between negative electrodes and separators and through the tank, on the left in Fig. 1.39, and a second circuit along the positive electrodes and through the tank, on the right in the figure.

On charging, zinc is deposited at the negative electrodes, and shape changing problems (cf. Fig. 1.5) or the formation of zinc dendrites are not relevant, since the precipitation occurs from the fast streaming electrolyte. When the battery is discharged, the zinc bromine ($ZnBr_2$) concentration is correspondingly increased.

At the positive electrode, bromine (Br_2) is formed during charging. The tendency of bromide to form complex compounds is used by the addition of two corresponding substances to the electrolyte: pyrrolidinium bromide (MEP) and morpholinium bromide (MEM) (78). They form droplets of non-aqueous complexes with the generated Br_2 that easily can be separated from the electrolyte as indicated in the tank on the right in Fig. 1.39. When the battery is discharged, the bromine complex is added to the streaming electrolyte and bromine (Br_2) is released.

Figure 1.40 shows as an example the prototype of a rather small zinc/bromine battery.

Figure 1.40 Prototype of a Zn/Br battery, 48 V, 5 kW. The cell stack is arranged in the center seen in the upper part. The pumps are to be seen below the cell stack. The storage tanks enframe both on the left- and on the right-hand side (from Ref. 79).

1.8.5.2 The Vanadium Redox Battery

The vanadium redox battery uses also a cell stack of bipolar plates and separate tanks for the positive and the negative electrolytes, similar to the design of Fig. 1.39. (cf., e.g. Fig. 7.9 in Ref. 76). An ion exchange membrane is used as separator in each cell.

This system makes use of the different states of oxidation that are characteristic for vanadium. The V^{5+}/V^{4+} equilibrium and the V^{3+}/V^{2+} equilibrium are used at the negative and positive electrode, respectively. The corresponding reactions are:

$$\text{Charging} \Leftrightarrow \text{Discharging}$$

$$\text{Positive electrode} \quad V^{5+} + e^- \Leftrightarrow V^{4+} \tag{90a}$$

$$\text{Negative electrode} \quad V^{2+} \Leftrightarrow V^{3+} + e^- \tag{90b}$$

$$\text{Cell reaction} \quad V^{5+} + V^{2+} \Leftrightarrow V^{4+} + V^{3+} \tag{90}$$

The electrolyte is a mixture of 2 mole/L vanadium sulfate and 20 wt% sulfuric acid.

Figure 1.41 shows charge/discharge curves of a cell stack. A main advantage of such a redox system is that the electrode reactions do not involve solid phase changes or precipitation mechanisms. As a consequence, a large number of cycles can be reached, and deep discharges are not critical.

Most striking disadvantages are the comparatively low values of specific energy (Wh/kg) and energy density (Wh/dm^3), shown in Table 1.11. They are caused by the

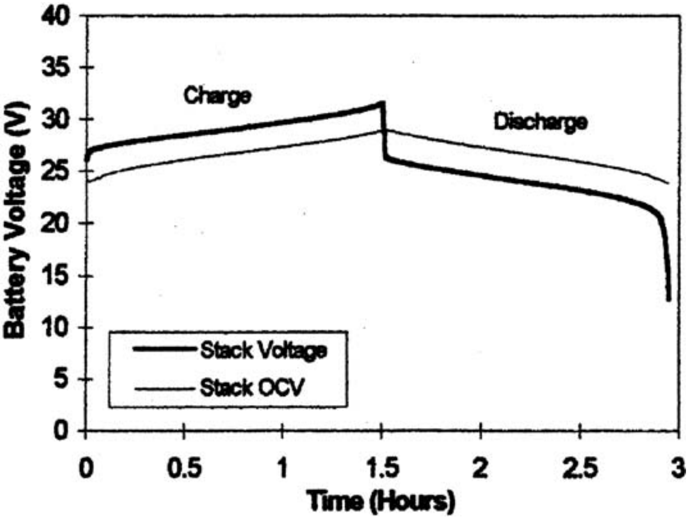

Figure 1.41 Charge/discharge curves of a vanadium redox battery. The cell stack consisted of 17 cells. Constant current of 100 Ah for charging and discharging (from Ref. 80).

low concentration of the reacting species on account of limited solubility. The specific power (W/kg) is limited for the same reason.

A further disadvantage is a certain transient of the positive vanadium ions from the compartment of the positive electrode to that of the negative electrode, caused by migration (cf. Section 1.3.3.2). It results in gradual concentration increase in the compartments of the negative electrodes and requires occasional remix of the two electrolytes.

Shunt currents, as mentioned with the zinc/bromine system are also in this system unavoidable. To keep these parasitic currents low, the connecting tubes must be small, but this simultaneously limits the high rate performance.

1.8.5.3 Rechargeable Zinc/Air Batteries

The main advantages of zinc/air batteries are the high values of specific energy and specific density shown in Table 1.11. This is partly due to the fact that the active material of the positive electrode is not contained in the battery when charged. Furthermore zinc is an element of low weight and offers a very negative equilibrium potential when used as an electrode.

The (simplified) electrode reactions are

$$\text{Charging} \Leftrightarrow \text{Discharging}$$

$$\text{Positive electrode} \quad 1/2O_2 + H_2O \Leftrightarrow 2OH^- \tag{91a}$$

$$\text{Negative electrode} \quad Zn + 2OH^- \Leftrightarrow ZnO + H_2O \tag{91b}$$

$$\text{Cell reaction} \quad Zn + 1/2O_2 \Leftrightarrow ZnO \tag{91}$$

Two problems arise in respect to recharging:

- The high solubility of zinc causes shape change, as indicated in Fig. 1.5.
- Intensive oxygen evolution that occurs during charge may harm the positive electrode.

A result of the first item is that in general zinc electrodes can stand only a very limited number of cycles. One possibility to overcome this problem is to replace the used zinc electrodes after each discharge by new ones ('mechanical recharge'). The zinc oxide of the removed negative electrodes is regenerated in a central electrolysis unit that operates for a whole fleet of cars, equipped with such zinc/air batteries (81).

Another approach applies a small number (< 10) recharges within the cell before the zinc electrode is replaced (82). When the negative electrodes are recharged within the battery, auxiliary electrodes are used as positives.

1.8.5.4 Rechargeable Aluminum/Air Batteries

The above described principle of the zinc/air battery is not limited to zinc as negative electrode material. Under the name metal/air fuel cell the aluminum/air battery is claimed as a superior solution with an output of 320 to 400 Wh/kg (75). This means a considerable increase compared to the rechargeable zinc/air system (Line 3b in Table 1.11).

1.9 FINAL REMARKS

The examples in Section 1.8.1 to 1.8.3 show the complex concurrence of the cell reaction and secondary reactions that often characterizes a battery, since electrochemical reactions are independent from each other and only the electrode potential determines whether they occur or not. As a consequence, the cell reaction and its parameters are not sufficient to describe the behavior of a battery system; instead many further parameters influence parameters influence its performance.

In battery systems based on aqueous electrolyte, water decomposition, which occurs above a cell voltage of 1.23 V, is such an unavoidable secondary reaction. But under certain conditions the resulting water loss can be avoided, and the system is used as a sealed one, as achieved with sealed nickel/cadmium, nickel/hydrogen, and nickel/metal hydride batteries. In lead-acid batteries corrosion is an additional unwanted secondary reaction with the consequence that lead-acid batteries cannot be made virtually sealed, but must have a valve, and a certain water loss cannot be prevented.

The complex concurrence of main and secondary reactions makes a general comparison of the various battery systems impossible, since the suitability of a battery depends not only on its system and the special design, but also on the mode of application and the required performance data. As a consequence, the 'superbattery' that outmatches all others does not exist. Rather the choice of a battery has to select the system and type that matches the application.

The special systems described in Section 1.8.5 indicate how difficult it is to exceed the limited storage capability of batteries beyond that of the 'classic' systems. Advantageous aspects of these systems are restricted by a number of additional parameters that hitherto prevented a larger success of such systems in the market.

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2

Batteries for Electrically Powered Industrial Trucks

H. A. KIEHNE

2.1 INTRODUCTION

Electrically powered road vehicles are currently more and more debated and many new prototypes of vehicles and batteries have been presented, e.g. at the 18th International Battery, Hybrid and Fuel Cell Electric Vehicle Symposium and Exhibition in October 2001 in Berlin, Germany, the world's largest event on this topic under the motto "*Clean and efficient mobility for the millennium*". While for materials handling battery-powered trucks, elevating trucks, forklifts, and other vehicles for internal factory transportation have been used for decades, today the market for electric road vehicles seems to be open only in some niches, because of the relative higher initial costs. As environmental laws tighten and oil and gasoline become more expensive, battery-powered machinery gains importance in more than one regard. Table 2.1 gives a view of the variety of battery electric powered vehicles. For more on electric road vehicles see Chapter 4.

2.2 DEMANDS OF THE MARKET

The demands concerning batteries can be listed in short as follows:

- Easy service, long service intervals, maintenance freedom, highest possible performance at unchanged weight and size. All of the above are expected in connection with optimized service life.

Table 2.1 Battery powered vehicles.

	Traffic range					
Type of vehicle	Rooms in buildings	Outdoor	Roads and streets	Rails	Water	Air
Land operating vehicles						
Materials handling trucks	●	●	(●)			
– Forklift trucks	●	●	(●)			
– Pedestrian and pallet trucks	●	●				
– Tow tractors	●	●	(●)			
– AGVs	●	(●)				
Special operating machines	●	●	●			
– Cleaning machines	●	●	●			
Rail vehicles				●		
– Locomotives				●		
– Mining locomotives				●		
– Railway coaches				●		
Electric road vehicles		●	●			
– Bicycles, motorcycles		●	●			
– Wheelchairs	●	●	●			
– Passenger cars	●	●	●			
– Vans		●	●			
– Lorries, trucks		●	●			
– Motor coaches, buses		(●)	●			
Ships					●	
Aircrafts						●

- The vehicles must be of rugged design; the same goes for the batteries powering them; they should be indifferent to exhaustive discharge and low temperatures. On top of all that there is the demand for economy in comparison with other energy sources or powering systems.

This package of demands is presently almost fulfilled.

Sophisticated battery systems do already exist, such as the battery of a MAN-bus, which continuously checks its state by a number of well-tested peripheral devices, such as a centralized water refilling system, a centralized gas disposal, a temperature-controlling device, and a discharge/charge surveying apparatus.

In the German city of Düsseldorf buses powered by such batteries have covered in 16-hours-per-day regular service more than 140,000 km per battery before the end of service life.

Battery systems are presently available for industrial trucks, easily recharged by new-generation control circuits that also permanently survey the batteries' state of charge.

All these batteries are of tubular cell design, commonly employed in industrial trucks throughout Europe. Three reasons for this are: their overwhelming life expectancy, which has been practically determined to be greater than 5 years; their low weight/power ratio and high power density; and last but not least their favorable lifetime/costs ratio and the experienced economy. Only smaller, especially hand-directed vehicles are preferably fitted with monobloc batteries or grid-type plate cells.

Apart from the standardized battery sizes there are innumerable battery designs due to the variety of industrial trucks being in action, that differ only in small details such as lifting eyelets, terminals, and locking catches for fixing in the truck.

Not only experts, but also the users of the manifold types of battery vehicles know that this is a simpler system compared to vehicles powered by internal combustion engines. This means battery/electric materials handling is highly economic and avoids pollution in the surroundings where exhausted gasses and noise cannot be tolerated, e.g. in warehouses, food markets, and factories where workers want a healthy atmosphere.

2.3 STANDARDIZED DESIGNS

As it is important for the applicant to know the present situation of the standards, a survey of the presently standardized cells and batteries shall be given.

DIN (Deutsche Industrie Normen) and VDE standards (Verein Deutscher Elektriker) are valid only inside national borders; more and more they are substituted by European Norm (EN) Standards and international standards, the IEC Standards (International Electrotechnical Commission) and ISO standards (International Standardization Organization), as for instance for battery voltages. Generally all batteries must be designed and manufactured in accordance with the VDE directions (VDE 0501/.1.77). See, for example, Table 2.2.

These directions for instance cover the classification and the consistency of the electrolyte and of refill water and how batteries must be fitted in containers for safety reasons (VDE 0510 is at present time under revision). See also Chapter 6 and 14.

Concerning the single-cell designs of tubular plate cells two standards sheets inform of nominal capacities and main dimensions:

1. DIN 43 595: Tubular plate cells for land- and water-bound vehicles, low maintenance type.
2. DIN 43 567 part 2: Tubular plate cells for land- and water-bound vehicles.

DIN 43 595 concerns cells of the low maintenance type with compound sealed or welded cell lids. The connector bars are permanently attached to the terminals by means of welding or crimping on. The main dimensions only vary slightly from the earlier DIN 43 567. DIN 43 595 recently has been drawn back, while the dimensions are still valid and conform to the international standard IEC 60 254-2. New types with higher capacities will be listed in a new standard, having the same dimensions (see Table 2.3).

DIN 43 567 concerns tubular plate cells with bolted connectors, with flat terminals and with conical terminals for the ex types up to VDE 0170/0171 for explosion-safe types. The lids of these types can be removed and are sealed by a flexible rubber seal.

The overall dimensions of these tubular plate-type cells also accord to the IEC Standard 60 254-2, “Lead-acid traction batteries, part 2, cell dimensions for traction batteries”.

Table 2.2 Survey of the PzS standard cells to DIN 43 595.

Plate size	Cell height (mm) (max.)	Cell width (mm) (max.)	Nominal capacity K_5 (Ah) with varying number of positive plates								
			2	3	4	5	6	7	8	9	10
PzS 55	365	198	110	165	220	275	330	385	440	—	—
PzS 70	425		140	210	280	350	420	490	560	—	—
PzS 80	505		160	240	320	400	480	560	640	—	800
PzS 100	595		200	300	400	500	600	720	800	900	1000
PzS 120	752		—	360	480	600	720	840	960	—	1200
length of cells (mm)			47	65	83	101	119	137	155	174	192

[a] Including terminal end with mounted intercell connectors.

Table 2.3 Survey on capacities of plates type PzS (normal) and PzS-H (high capacity).

Cell height (max) [mm]	Capacity C/PzS plate [Ah] series L (new) PzS…L	DIN (old) PzS	Capacity increase %
370	60	55	9
440	80	70	14
510	90	80	13
605	110	100	10
750	140	120	17

DIN 43 595 is preferred more and more as it has the following advantages:

- High operational safety through complete insulation.
- Improved cyclic durability through optimized masses and plate geometry.
- Great number of cycles through lowering of the mud fallout rate.
- Substantially higher maintenance intervals through electrolyte-tight cells.

Cells of these types undergo not only severe testing in practical applications, but also tests to the DIN 43 539 part 3, as well as the lEC tests of the same content and extent in laboratories for quality improvement, with endurance tests demanding over 1500 cycles in cyclic charging/discharging operation (see IEC 60 254-1).

Each standard needs an update following the technical development. So when the new international standard for dimensions of traction lead-acid cells IEC 60 254-2 was published and harmonized in the European Union to a European standard EN 60 254-1, DIN 43 595 was drawn back. In an additional technical information sheet, published by the German Battery Manufacturers Association, the (nominal) capacities in use were listed in relation to the cell dimensions. Table 2.3 shows the range of cell heights conforming to IEC (respective EN 60 254-2) together with the new series of higher capacities.

Compared with cells of the older design the “high-capacity cells” have an increased capacity between 9 to 17%. Table 2.4 shows the data for the new series of PzS cells.

Standards sheets also have existed apart from the above mentioned for battery trays for several years. In certain intervals standards sheets must be revised to consider new developments.

In the past, standardization of parts making up a battery such as cells, connectors, trays, parts of installation and terminals was ascribed a great advantage by the users’ side because of the great number of combinations possible to assemble a battery. Modification and repair of batteries was common then.

The main disadvantage of the single parts standards is that this leads to a huge amount of types and variants, as changed details can be accepted for new batteries, but by no means from the spare parts side.

Designers and manufacturers of industrial trucks and battery manufacturers have developed a standard of the 24-V and the 80-V standard batteries to take over

Table 2.4 Lead-acid traction cells with tubular plates, series L, dimensions conforming to IEC 60 254-2.

Designation code			Nominal capacity C_5[a] (Ah)	Code[b] tubular plate	Dimensions[d]		Weight including electrolyte (kg) (± 5%)	Lead content[c] (kg) (± 5%)
					a 0 −2	(h) (max.)		
2	PzS	120 L	120	PzS 60	47	370	8.4	6.2
3	PzS	180 L	180		65		11.8	8.8
4	PzS	240 L	240		83		15.5	11.5
5	PzS	300 L	300		101		19.0	14.1
6	PzS	360 L	360		119		22.5	16.8
7	PzS	420 L	420		137		26.1	19.4
8	PzS	480 L	480		155		29.8	22.2
2	PzS	160 L	160	PzS 80	47	440	9.8	7.3
3	PzS	240 L	240		65		14.0	10.4
4	PzS	320 L	320		83		18.1	13.5
5	PzS	400 L	400		101		22.6	16.8
6	PzS	480 L	480		119		26.6	19.8
7	PzS	560 L	560		137		31.1	23.1
8	PzS	640 L	640		155		35.2	26.3
2	PzS	180 L	180	PzS 90	47	510	12.0	9.0
3	PzS	270 L	270		65		16.9	12.6
4	PzS	360 L	360		83		21.6	16.1
5	PzS	450 L	450		101		26.3	19.5
6	PzS	540 L	540		119		31.1	23.1
7	PzS	630 L	630		137		36.1	26.9
8	PzS	720 L	720		155		40.8	30.3
10	PzS	900 L	900		192		50.3	37.4
2	PzS	220 L	220	PzS 110	47	605	14.3	10.6
3	PzS	330 L	330		65		20.3	15.1
4	PzS	440 L	440		83		26.0	19.4
5	PzS	550 L	550		101		31.8	23.6
6	PzS	660 L	660		119		37.9	28.2
7	PzS	770 L	770		137		43.8	32.6
8	PzS	880 L	880		155		49.8	37.0
9	PzS	990 L	990		174		55.7	41.5
10	PzS	1100 L	1100		192		61.5	45.7
3	PzS	420 L	420	PzS 140	65	750	25.4	18.9
4	PzS	560 L	560		83		32.9	24.5
5	PzS	700 L	700		101		39.9	29.7
6	PzS	840 L	840		119		47.2	35.2
7	PzS	980 L	980		137		54.8	40.8
8	PzS	1120 L	1120		155		62.3	46.3
10	PzS	1400 L	1400		192		76.7	57.1

[a] $C_5 = 5\,\text{h}$ rated capacity = nominal capacity (see IEC 60 254–1).

[b] Code of a plate with a capacity of, e.g. 60 Ah: PzS 60.

[c] Loss during production of 7% included.

[d] Width 198 mm −2.

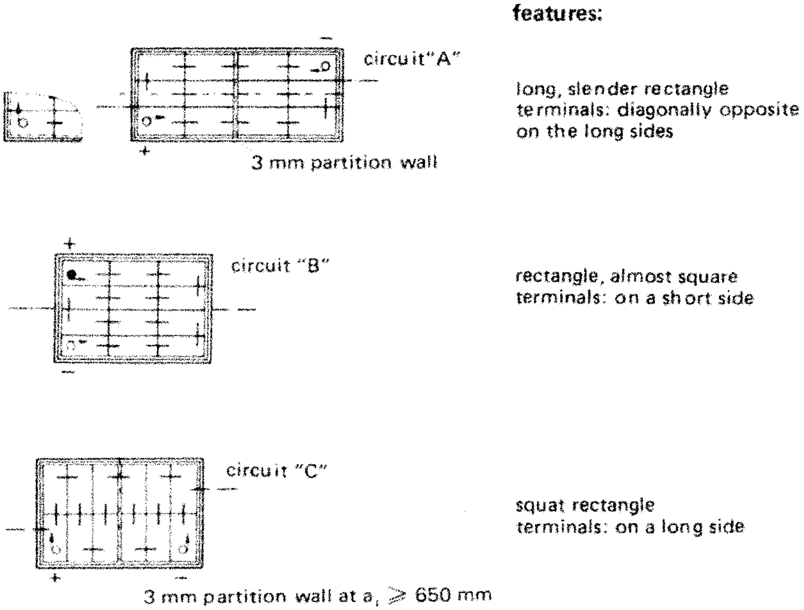

Figure 2.1 Circuits of 24-V traction batteries to DIN 43 535.

the older "component standards" (see Figures 2.1 and 2.2). The sheets in question are

- DIN 43 535 Lead-acid accumulators; traction batteries 24 V for industrial trucks.

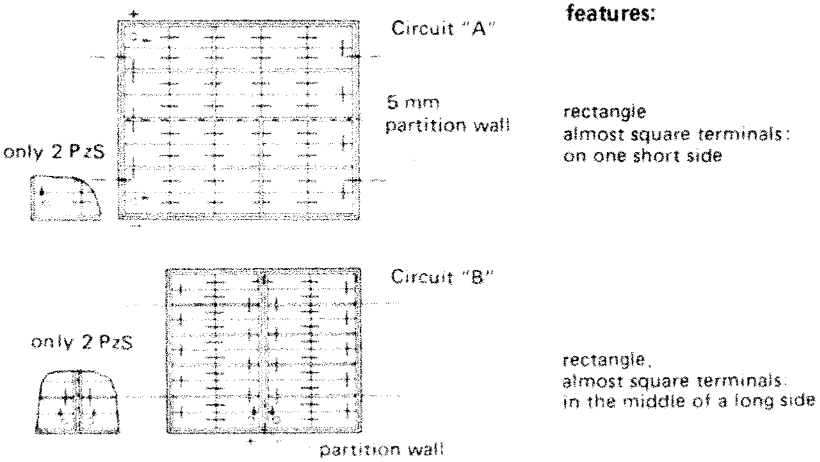

Figure 2.2 Circuits of 80-V traction batteries to DIN 43 536.

- DIN 43 536 Lead-acid accumulators; traction batteries 80 V for industrial trucks.

DIN 43 535 mentions three main circuits of type A, B, C:

- 19 batteries of the A circuit type.
- 15 batteries of the B circuit type.
- 12 batteries of the C circuit type.

that have been standardized, in all 46 batteries of 24 V.

DIN 43 536 mentions two main circuits of the types A and B:

- 18 batteries of type A.
- 6 batteries of type B.

that have been standardized, in all 24 battery types of 80 V.

In other countries 48-V and 72-V batteries are more popular and standardized. So it was necessary to complete the line of battery standards with DIN 43 531 for the 48-V traction batteries to conform to the two other above-mentioned standards for 24 and 80 V.

These standard batteries (see Figure 2.3) have the following in common:

- The battery trays are all of the same design.
- Length, width, and height are standardized.
- The design and location of the lifting eyes are standardized.
- The connecting terminals are described in a special informal sheet published by the German Battery Manufacturers Association.

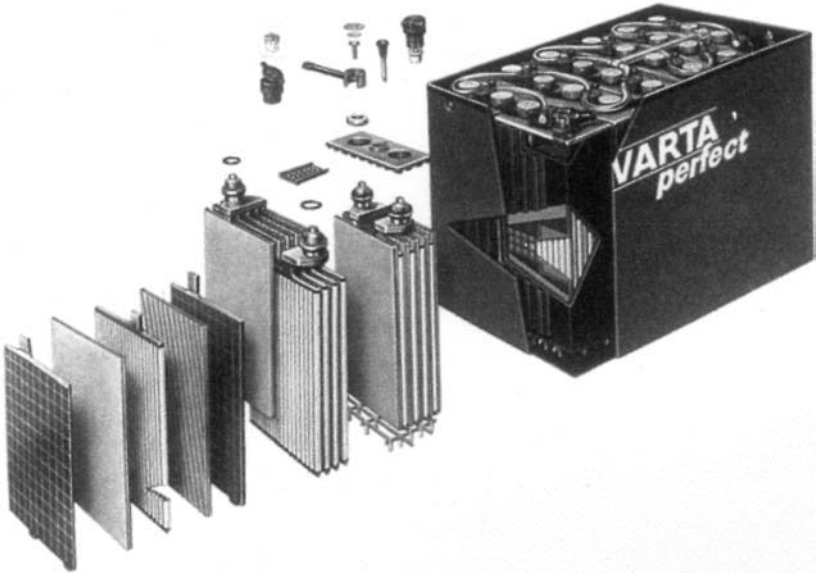

Figure 2.3 Design of a modern traction battery.

- Insulation of the tray (mostly a plastic coating) accords to VDE 0510-standards.
- Battery trays are always fitted with the greatest possible cell capacity.
- No ballast weights are employed.

Figure 2.3 shows the design of a modern 24-V traction battery with positive tubular plates to DIN 43 535.

With this step toward a reasonable standardization of batteries two substantially important aspects for future developments have come into close range:

- Following a certain transitional period a noticeable reduction of variants and types of cells and trays.
- Introduction of new technologies in battery design resulting in less maintenance.

Standard voltages for traction batteries for industrial trucks are fixed by the ISO 1044 standards as follows:

- Series I: 12, 24, 36, 48, 60, 72, and 96 V.
- Series II: 40 and 80 V.

In Germany only 24 V and 80 V are common values.

The above-mentioned traction batteries in grid plate design for smaller vehicles are treated by DIN 43 594. A revised standard will be edited for monobloc batteries in plastic containers (containers as in use for automotive batteries). The pasted plates are thicker; the batteries have a special separation between the plates (see Table 2.5).

A parallel new standard, DIN 43 598, is in preparation: Part 1 for small traction batteries with positive tubular plates in monoblocs corresponding to DIN 43 594. Part 2 for small traction cells in plastic trays. (See Tables 2.6 and 2.7.)

2.4 ENERGY/WEIGHT AND ENERGY/VOLUME RATIOS

The display of standardized values may create the impression of a power level being cemented or fixed. The applicant of lead-acid traction batteries today may not realize the improvements that have made concerning energy/weight and energy/volume ratios.

Forerunners of these more powerful batteries of the tubular plate type and also of the grid plate type have been tested in electric road vehicles. Naturally the classic lead-acid battery has a limit which lies far below the theoretical value of 161 Wh/kg. By showing the shares of weight of conductive material, excess mass, and excess electrolyte and inactive material, Figure 2.4 explains why the possibilities for improvement of the energy/weight ratio are so few.

The values for the energy/weight and the energy/volume ratios (like the above values) are related to a 5-hour discharge.

Figure 2.5 displays the specific drawable energy per kg dependent on the currents drawn in a much-simplified manner. At a load of the 5-hour discharge current, the PzS cells yield about 30 Wh/kg. Only about 50% of this value is available if the cell is drained with the 1-hour discharge current value. This amounts to only 10% of the theoretical value of 161 Wh/kg. This entitles the developer and the user to expect severe improvements, at least on the high-drain sector.

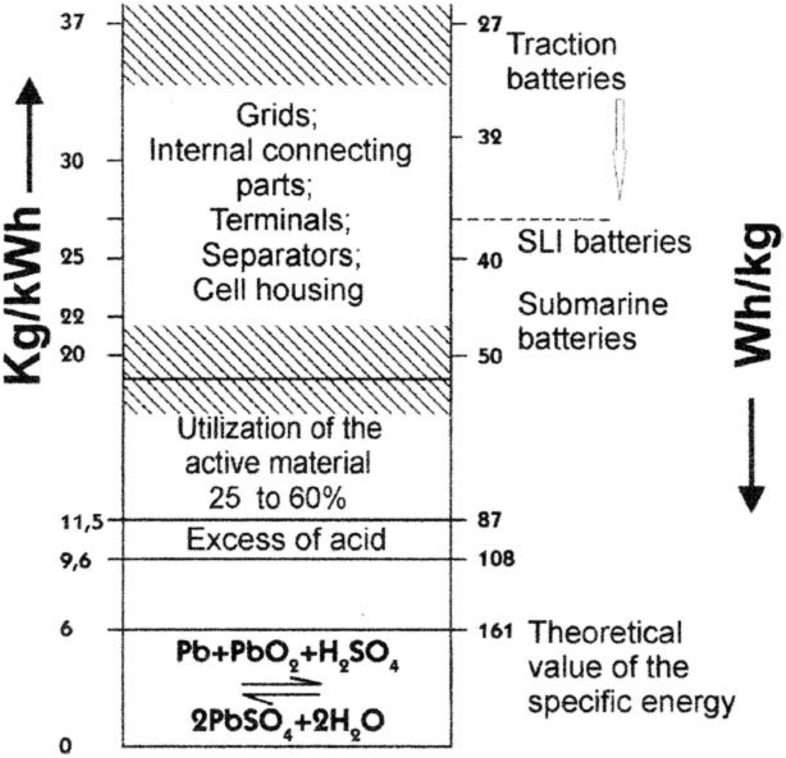

Figure 2.4 Theoretical and practical energy/weight ratio of lead-acid cells.

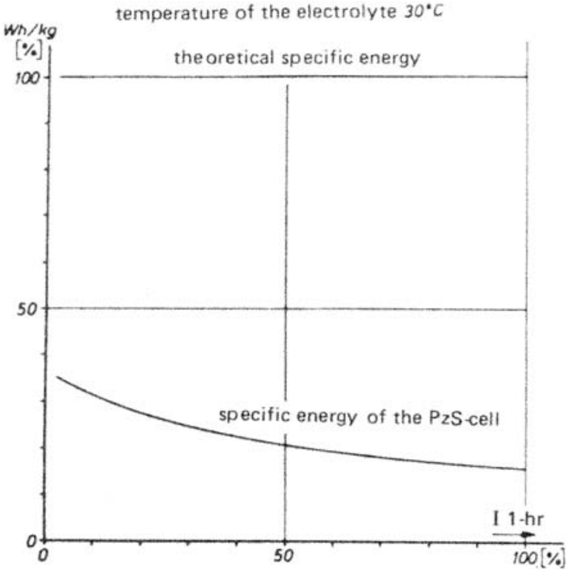

Figure 2.5 Comparison of specific energy yield of PzS cells.

Table 2.5 Lead-acid traction batteries, monobloc battery with pasted plates (DIN 43594).

Battery marking					Dimensions			
Short designation	Type no.	Voltage (V)	Nominal capacity[a] (Ah)	Nominal Monobloc type	a (max)	b (max)	h (max)	
6 V GiS 180	9 180.1	6	180	M 13	244	190	275	30
12 V GiS 40	9 540.1	12	40	H 4	211	175	190	14
12 V GiS 50	9 550.1	12	50	H 5	246	175	190	16
12 V GiS 60	9 560.1	12	60	H 6	306	175	190	20
12 V GiS 75	9 575.1	12	75	H 8	381	175	190	24
12 V GiS 105	9 605.1	12	105	M 20	513	189	223	40
12 V GiS 135	9 635.1	12	135	M 25	513	223	223	48
12 V GiS 180	9 680.1	12	180	M 33	518	291	242	64

[a] Nominal capacity after 10 discharges; electrolyte density 1.28 ± 0.01 kg/L; electrolyte temperature 25 °C.

Table 2.6 Lead-acid traction batteries, monobloc batteries with positive tubular plates (DIN 43 598 part 1).

Short designation	Nominal voltage (V)	Nominal capacity[a] (Ah)	Monobloc type	Dimensions			Total weight (kg ± 5%)
				a (max)	b (max)	h (max)	
6 V PzS 170	6	170	M 13	244	190	275	30
12 V PzS 75	12	75	M 20	513	189	223	34
12 V PzS 100	12	100	M 20	513	189	223	40
12 V PzS 130	12	130	M 25	513	223	223	48
12 V PzS 150	12	150	M 33	518	291	242	61
12 V PzS 170	12	170	M 33	518	291	242	64

[a] Nominal capacity after 10 discharges electrolyte density 1.28 ± 0.01 kg/L; electrolyte temperature 25 °C.

Table 2.7 Lead-acid traction batteries in plastic trays with single cells and positive tubular plates (DIN 43 598 part 2).

Short designation	Nominal capacity C_5[a] (Ah)	Circuit	Dimensions					Total weight filled (kg ± 5%)
			a_1 (max)	a_2 (max)	b_1 (max)	b_2 (max)	h (max)	
6 V PzS 104 H	104	A	248	253	168	168	235	22.7
6 V PzS 130 H	130	A	303	318	168	168	235	27.8
6 V PzS 172 H	172	A	245	251	194	194	280	34.2
12 V PzS 104 H	104	B	486	506	168	168	223	45.1
12 V PzS 130 H	130	B	486	506	205	205	223	55.3
12 V PzS 172 H	172	C	486	506	199	199	279	68.4

[a] Nominal capacity after 10 discharges; electrolyte density 1.28 ± 0.01 kg/L; electrolyte temperature 25 °C.

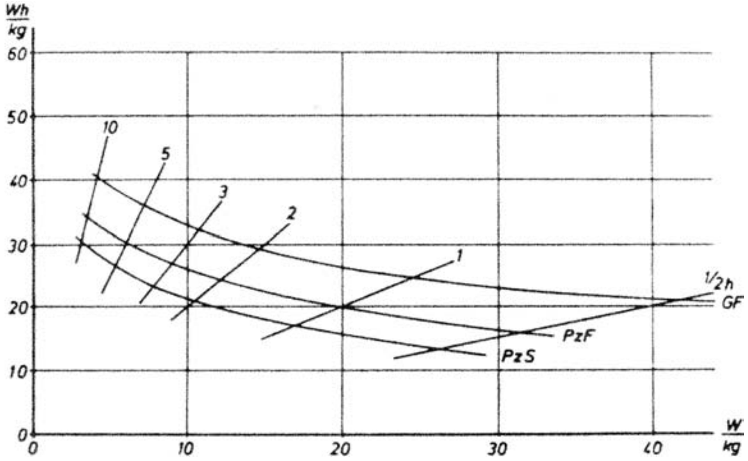

Figure 2.6 Useable fraction of the energy/weight ratio in Wh/kg of lead-acid PzS cells, PzF cells, and GF cells (GF = flat plate type).

Figure 2.6 shows the specific drawable energy of lead-acid traction batteries of different designs. The lower graph represents the capacity of the common PzS cells. Further development of this cell type for application in electric road vehicles of the PzF type yields accordingly higher values.

2.5 SERVICE LIFE AND ECONOMY

The service life of traction batteries, depending on the average load during operation, is located somewhere between 3 to 9 years. The average lifespan thus is 5.5 to 6 years, corresponding 1500 to 1600 discharges to 80% of the nominal capacity. It is understandable that no "standard" service life value can be given independent of the load profile. The following can influence lifetime and economy:

- Choice of a too small battery resulting in frequent or even permanent exhaustive discharges.
- Severe on-duty conditions and resulting permanent temperatures over 50 °C.
- Permanent overcharging because of faulty charging technique or maladjusted charging devices.
- Storage of uncharged batteries.

Especially the choice of too small battery capacity generally leads to bad results in service life. For further details see information sheet published by the German Battery Manufacturers Association.

2.6 CHARGING TECHNIQUES

Demands on charging techniques and monitoring systems include:

- Choice of a preserving charge method.
- Controlling of the charge process regarding the condition of the battery (electronic diary).
- Indication of the actual capacity.
- Current limitations.
- Deep discharge protection.
- Control of voltage and temperature of the battery and charging.

Charging devices should have a characteristic curve following DIN 41 773 and be equipped with a charge-control switch that limits the charging period, as shown in Figure 2.7 after gassing voltage of 2.4 V/cell has been reached.

The charging-control "Poehlertronic" switch actuates the additional charge considering the batteries age and temperature and compensates the mains' fluctuations optimally. This charging timer also prolongs the life span of a battery and facilitates maintenance as there is less water consumption, and overcharging is impossible even with older batteries (see Figure 2.8).

Apart from this, other principles for controlling the charging process of a battery are operational, such as the controlling of the charging process by measuring the gas adsorption rate with recombinators (HOC charging device from Hoppecke) and by monitoring the charging current (Belatron system from the Benning Corporation).

Several devices, ranging from a simple voltage controller to a sophisticated electronic apparatus minutely balancing the Ah household, can monitor state of charge. A type of safety switch has reached a high level of distribution as it automatically switches off the lifting fork when 20% of the nominal capacity is reached, and the driver is forced to charge the vehicles batteries.

For more details see Chapters 12 and 13 where charging methods and charger characteristics are described in detail.

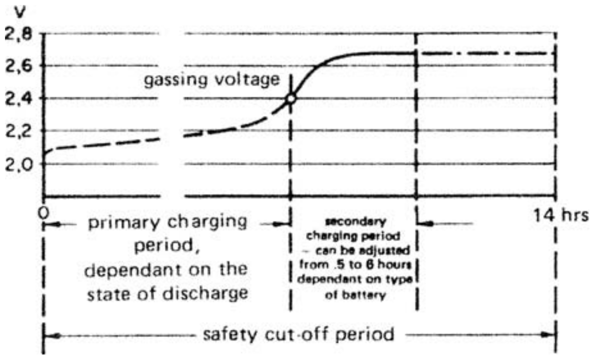

Figure 2.7 Switching timetable of a "Poehler" switch.

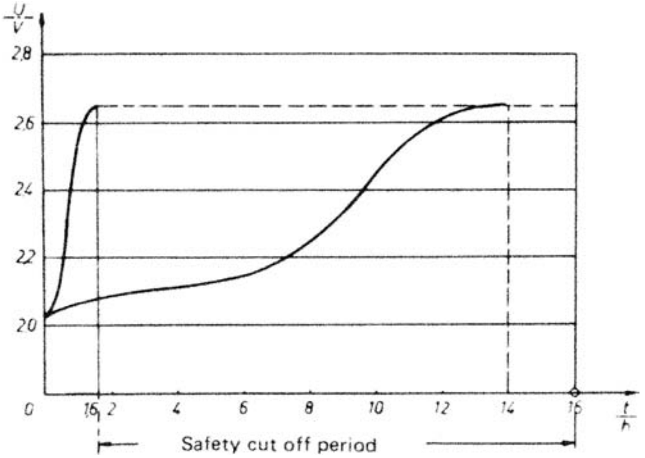

Figure 2.8 Switching periods of the charge-control "Poehlertronic" switch; duration of charge dependent on battery condition.

2.7 MAINTENANCE

Only very few details must be respected:

- Refill water at the end of charge.
- Keep the battery clean and dry.
- Recharge the battery immediately after discharge.
- Do not discharge a battery exhaustively (more than 80%).
- Do not overcharge the battery (charging factor maximum 1.2).
- Battery temperature must not exceed 55 °C.
- In case of malfunction, contact your local service office; they will gladly also check your charging devices and controllers.
- Use only safe and adequate lifting equipment.

2.8 SUMMARY AND OUTLOOK

The present lead-acid traction battery of the PzS type represents the highest standard of performance. Further development is possible, whereas the attainable limit for power density in the near future will in practice be around 35 to 40 Wh/kg.

Development on the forklift truck sector for higher transport performance naturally leads to greater stress on the battery. This could lead to shorter charging intervals of the vehicles. In connection with the limited space inside forklift trucks energy density of traction batteries will have to be improved. Most of the German battery manufacturers introduced a new generation of batteries averaging 15% more capacity than with the presently standardized types.

Total freedom of maintenance cannot be realized without peripheral devices because of the necessity of water replenishment. Even so, plastic housings totally electrolyte-tight, welded-on plastic lids, as well as totally sealed terminals make a new generation of batteries with high insulation resistances that are totally dry on the outside. Good insulation resistance is a demand that must be met, especially for modern impulse-guided vehicles, for resistance deficiency could cause malfunctions with these systems.

A higher grade of perfection can be attained through peripheral devices, such as a central water-refilling system or "puridrier" plugs, which make these batteries almost totally maintenance free. (See Figure 4.5 in Chapter 4.)

For a few years "enclosed" valve-regulated and maintenance-free traction batteries have been offered to the market. The electrolyte is immobilized, soaked in a fleece or as a gel (See Chapter 1). During the recharge, with limited voltage below 2.40 V/cell, the oxygen developed on the positive electrode is recombined on the surface of the negative electrode. Therefore gassing of this kind of battery is extremely low resulting in no need to refill water. Because the cells of such batteries are valve regulated, no water can be added, but gas can escape in the case of incorrect charging (overcharge with high voltage). At all times during recharge a small rate of hydrogen is developed, therefore battery containers must be vented. Future experience with this new generation of batteries will answer questions as to their duration and economy.

Figure 2.9 shows a 24-V traction battery in maintenance-free design (dimensions of DIN 43 535) and a special charger.

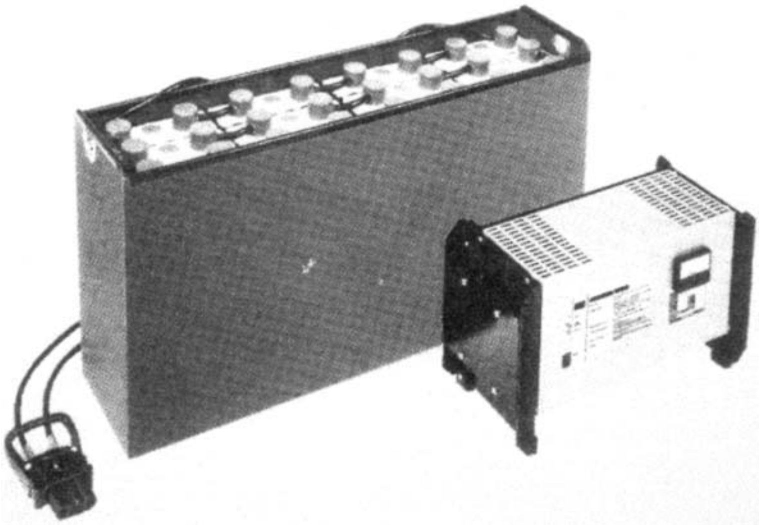

Figure 2.9 Traction battery 24 V (Dimensions DIN 43 535) in maintenance design, cells with positive tubular plates and charger.

A further possibility to increase the performance of lead-acid traction cells is electrolyte circulation, as proved in batteries for electric road vehicles and batteries for submarines. The principle is an airlift pump installed in each cell. The results are

- No electrolyte and temperature stratification.
- Extremely efficient charge acceptance and equalized load of the plates.
- Shortened charging time up to 30% and therefore less energy from the mains is needed.
- Shorter gassing period, less slugging of active mass of the positive plate, and less water consumption.
- Less temperature rise during the charge (up to 10 °C), therefore batteries applicable in so-called atmosphere with elevated temperature.
- Time of no use of the batteries is drastically reduced, an advantage for the application in plants working on two or three shifts.
- Booster charging enables heavy duty service.
- Maintenance intervals are longer which lowers costs.

Figure 2.10 shows a modern lead-acid traction cell designed by Varta with electrolyte circulation compared to a cell with electrolyte stratification. There are many electrochemical systems that will yield favorable accumulators (see Chapters 1 and 10), some of which have reached a very promising state of development. They will have to prove their versatility in practical application, especially with the aspect of economy in the future.

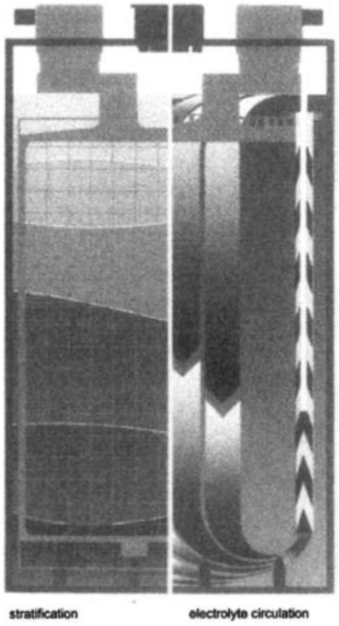

Figure 2.10 The principle of electrolyte circulation.

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3

Power Supply Concepts for Driverless Industrial Trucks

P. PREUSS

3.1 THE IMPORTANCE OF DRIVERLESS INDUSTRIAL TRUCKS

Although relatively unknown some years ago, driverless industrial trucks have come to occupy an important position within the framework of highly organized systems of driverless transport (DTS). The essential factors contributing to this fact are without doubt on the one hand the increased need for automation in industry, and on the other hand the high degree of flexibility afforded by these appliances. The overall view of these appliances (Figure 3.1) clearly shows that driverless industrial trucks (DIT) may as a whole be divided into three categories.

The majority of these installations will be found in the automotive industry, which requires a wide variety of applications specific to driverless trucks. In this context, considerable importance will be attached to the third generation of driverless transport systems used, for example, to create the link between individual pieces of manufacturing equipment or assembly workplaces. This task may be designated "product engineering transport" and represents the second transport assignment after "works transport" to be mastered successfully by driverless industrial trucks. A third transport assignment, "transport between factories", has so far been little investigated, but is becoming more and more the subject of discussion.

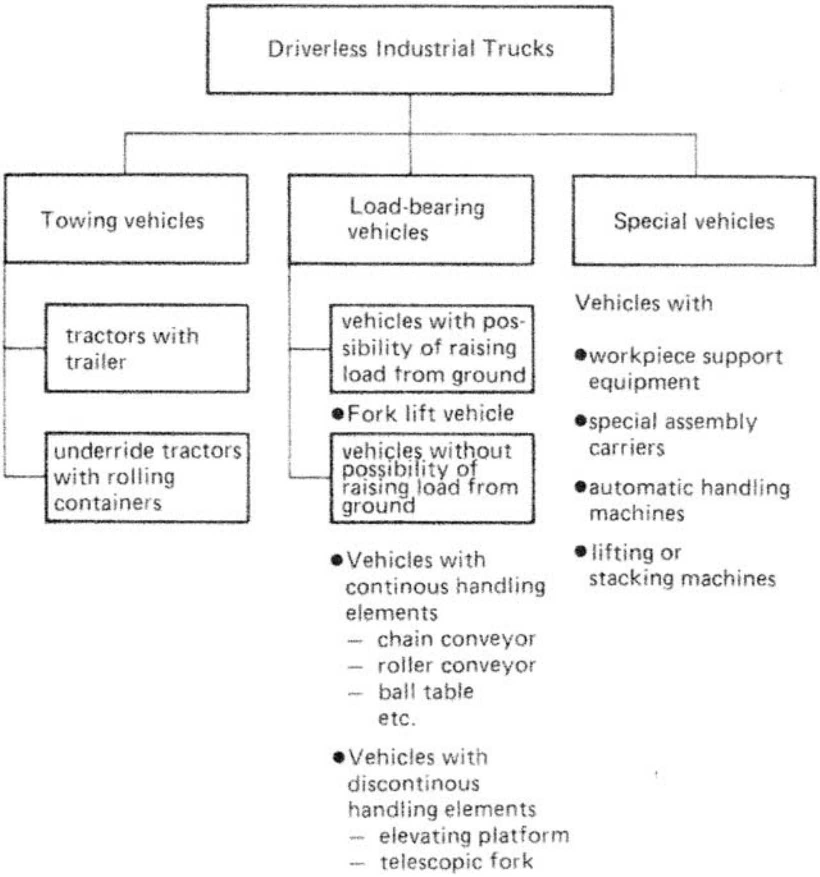


Figure 3.1 Structural family tree of driverless industrial trucks.

3.2 LOAD PLACED ON TRACTION BATTERIES BY DRIVERLESS INDUSTRIAL TRUCKS

Traction batteries are of central importance as suppliers of power. Together with the stationary charging set, or under certain circumstances the charging set located "on board", and the principles of charging of the system employed, drive batteries comprise the power supply. Experience has shown that the demands made on the battery differ from system to system. It is therefore not possible to refer to "the DIT battery", but widely differing systems of batteries are required to cover the range of applications lying between the two extremes (Figures 3.2a and b) of (a) capacitive operation and (b) cyclic operation.

A few explanations are given below on these two modes of operation.

- Capacitive operation signifies that the total, or practically total, useful battery capacity is consumed in the course of one discharge period, and then of necessity restored by being fully charged. Batteries in conventional

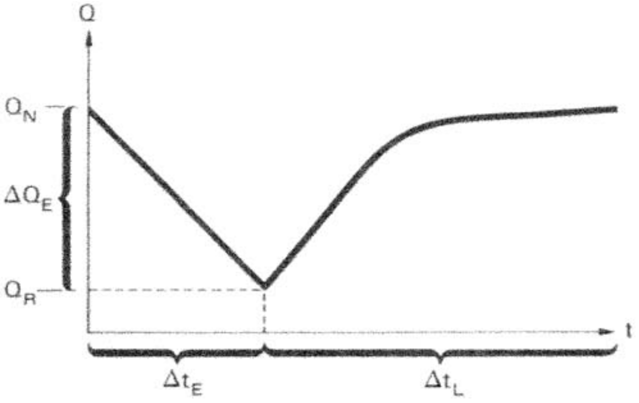


Figure 3.2a Capacitive operation.

industrial trucks have always been run in this way; the discharge time is here, for example, an 8-hour shift.

- Cyclic operation means that under certain circumstances only a very small portion of the battery's capacity is consumed during one discharge period (discharge cycle) and is immediately recharged (charge or boost charge cycle). Discharge and charge cycles can easily have the order of magnitude of only minutes or even seconds. Plants operating three shifts and weekend shifts are no rarity, so that full charging of batteries is not possible, at least not at acceptable intervals. The battery capacity will first fall under these application conditions, and then even out at a certain capacitance level after a calculable number of cycles, on account of the boost charge cycles. Such application conditions pose specific problems, to which further reference will be made below.

Purely cyclic operation is only run as an exception with conventional industrial trucks. Elements of this mode of operation can nevertheless be found in the form of

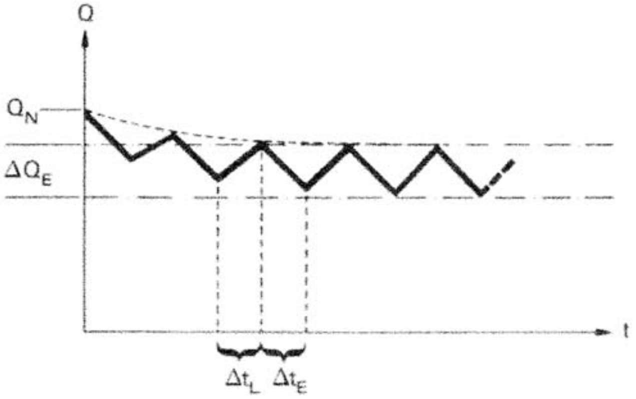


Figure 3.2b Cyclic operation.

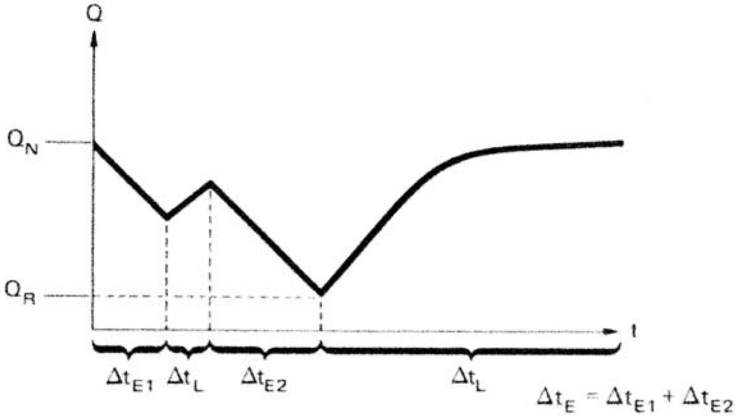


Figure 3.2c Capacitive operation with boost charge.

boost charges during rest periods, aimed at extending full capacity and thus increasing the period of use (Figure 3.2c). This combination of elements from capacitive and cyclic operation may be designated a mixed mode of operation.

Knowledge of the load placed on batteries in the course of the discharge phase will generally not suffice even in capacitive operation for the development of a reliable, functional power concept. The intervals between applications dictated by the sequence control system, which forms the basis for the plan of charging, have a decisive influence, particularly in the case of cyclic operation. Furthermore, attention must be paid to further basic application parameters. The more data known on the application of the batteries, the more reliable it is to specify the power concept.

3.3 TRACTION BATTERIES FOR DRIVERLESS INDUSTRIAL TRUCKS

In contrast to the sector of conventional trucks, practically all systems of batteries, which have proved successful in practice, are used in driverless industrial trucks. In addition to the lead-acid batteries (LAB) common in the sector of conventional industrial trucks nickel/cadmium batteries (NCB) have taken over quite a considerable slot in the market in the DIT sector, on account of their particular properties.

3.4 OPTIMIZATION OF TEMPERATURE

The plant operator expects from a concept of power supply that it will fulfill the following requirements:

1. It must guarantee readiness for use by the driverless industrial trucks at all times within the understanding of the system of sequence planning.
2. The point at which the battery requires renewing should be as late as possible, but should be recognized as early as possible.
3. It should be predominantly independent of any external supervision.

4. Operating costs should be at a minimum.

Requirements 1–3 naturally provide the prerequisite for 4.

3.4.1 Considerations on Battery Dimensioning

A concept of power supply can always be made on the basis of an efficient description of a battery's application. However, to fulfill the above-mentioned requirements, it is advisable to plan the battery dimensions based on principles which may be described as optimizing temperature factors. This method departs from the premise that any battery, which is not subject to impermissible heating under prescribed load, is bound to exhibit the necessary efficiency and service life, i.e. to have the desired operating reliability. The temperature of the electrolyte would ideally display a constant value, merely being dependent on the ambient temperature in the driverless industrial truck, which is itself only subject to minor fluctuations. The temperature of the electrolyte would in this way be directly related to normal ambient temperature. If this were to fall drastically in winter, additional measures would of course have to be taken to raise the temperature of the electrolyte.

3.4.2 Estimating Battery Load Rating

Heating of the battery system presented in Figures 3.3 and 3.4 with the same capacity and under equal load differs considerably during the charge and discharge phase due

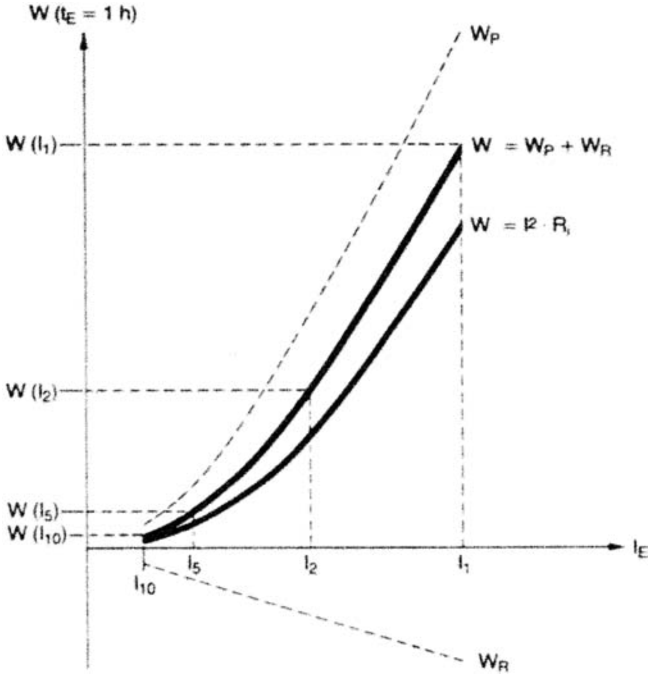
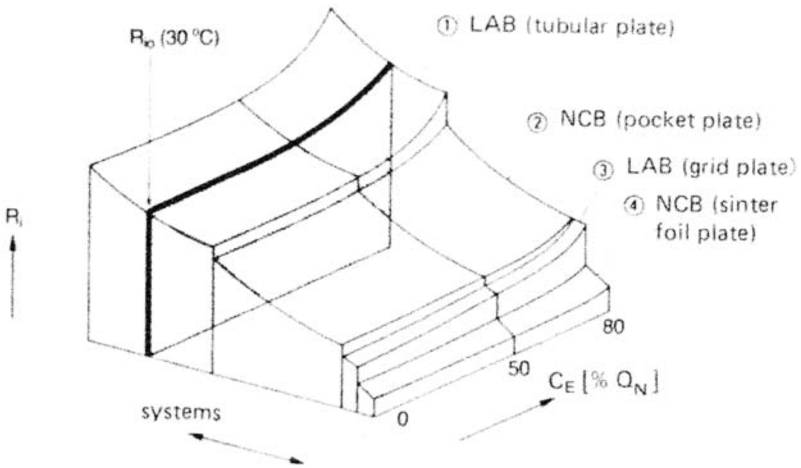


Figure 3.3 Depiction of thermal energy generated in 1 h in a tubular plate battery with different discharge currents.

a) $R_i = f$ (System, series, level of discharge)



b) R_i (TPB) = f (T_{el}, level of discharge)

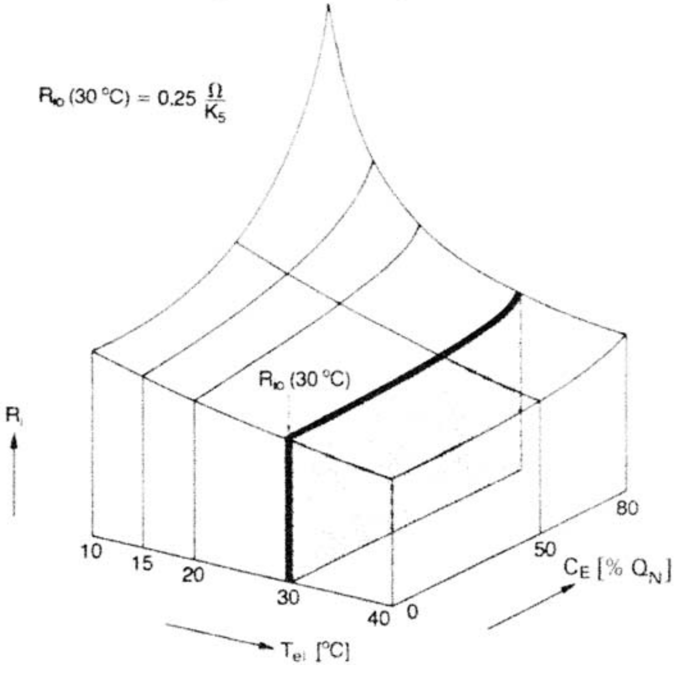


Figure 3.4 Internal resistance in the different battery systems, quality curves.

to the different systems employed (electrochemistry/design). This can be seen clearly by comparing the respective reaction and polarization heat component, which always exists. Determining the thermal differences by way of the electric heat generated at the internal battery resistance by the effective current value is only a rough form of estimation, and can also only be conducted during the discharge phase. Figure 3.3 shows the difference from the actual heat generated using a tubular plate battery as an example. Calculation by way of electric heat fails completely for the charge phase. Nevertheless, it is possible to estimate the load rating of a battery system with the aid of internal resistance. Figure 3.4 shows the curves for internal resistance in different battery systems at normal temperature, and the dependence on temperature of internal resistance in a tubular plate battery. Based on this estimation, and supported by results achieved in practice, Table 3.1 contains permissible load ratings for uninterrupted cyclic operation. Extreme plant conditions, which tend to be the exception in practice, always require an accurate calculation to be made of the rise and fall in temperature, particularly during charge phases.

3.5 THE CHOICE OF BATTERY

Apart from the specific load rating, there are a number of further parameters or relationships which require attention when developing a suitable concept of power supply. Although these are in fact self-evident, they will be repeated here for the purposes of completeness.

3.5.1 Maximum Permissible Capacity

The differing application requirements make necessary different levels of capacity between two charge cycles or phases, which need to be transformed into the nominal capacity, following the principles of temperature optimization, and including the specific system load ratings and any necessary temperature corrections. Examination of the capacity available in practice can thus, under certain circumstances, already lead to the choice of a particular system. Table 3.2 contains typical permissible

Table 3.1 Uninterrupted cyclic operation: maximal effective values for discharge/charge current.

		I_{Lmax}[a] in	
Battery system	I_{Emax}	ZL	VL
LAB with			
– tubular plates	I_5	I_5 / —	I_5
– grid plates	$1.5 \times I_5$	I_5 / —	I_5
NCB with			
– pocket plates	$1.5 \times I_5$	$1.5 \times I_5$ / —	—
– sintered plates	$5 \times I_5$	$10 \times I_5$ / $15 \times I_5$	—

ZL = Boost charge (minute/second range).
VL = Full charge (t_L (LAB) = 7–8 h).
[a] I_{Lmax} is not always possible, as in certain circumstances, and depending on the system, limitations to charging efficiency exist which evidence themselves in a shortened current flow time.

maximum levels of capacity. These show that there is no alternative to the tubular plate battery for medium to high capacitive loading.

3.5.2 Maximum Permissible Temperature in Battery Systems

A further selection criterion is provided by the different limit temperatures in the electrolyte, as is also depicted in Table 3.2. The use of a particular battery system becomes questionable when the ambient temperature approaches its maximum permissible temperature. Nickel/cadmium batteries have a significantly lower limit temperature than lead-acid batteries. The systems thus dictate that lead-acid batteries should exclusively be used when the ambient temperature exceeds 35 °C to 40 °C. In the case of extreme ambient temperatures, however, a renewal of batteries should also be planned for, in order not to jeopardize the long service life typical of the system, even when using tubular plate batteries.

3.5.3 Charging Requirements

The electrochemical processes occurring in the course of charging and discharging lead batteries with aqueous electrolytes lead, in time (particularly in high cells), to the well-known phenomenon of acid layer formation, unless measures are taken at regular intervals to counteract this development. These measures are necessary, as the formation of acid layers has a number of consequences, which lead to a reduction in capacity and service life of the battery. In practice, this means utilizing the convection arising in the course of full or equalizing charging by the controlled generation of hydrogen in the negative electrode, which can be relied on to equalize the specific gravity of the acid. In the case of cyclic operation, however, it is well known that the energy balance can be maintained by short boosting charges, which do not lead to any notable hydrogen evolution in aqueous electrolytes. This is also desirable in view of minimizing the amount of water used. Lead-acid batteries with aqueous electrolytes can therefore only be used if the opportunity exists, at least at acceptable intervals, of giving equalizing charges or of renewing the battery. If these conditions do not exist, a decision must be taken in favor of the nickel/cadmium battery, where the problem of electrolyte layer formation is known not to exist.

Table 3.2 Battery system limit capacity/limit temperatures.

Battery system	C_{limit} Ah (five hours)	Of which max. useful	T_{limit}°C
LAB with			
– tubular plates	1,400	80% C_{limit}	55
– grid plates	160	80% C_{limit}	55
NCB with			
– pocket plates	250	100% C_{limit}	45
– sintered plates	200	100% C_{limit}	40

3.6 DEVELOPMENT OF A CONCEPT OF POWER SUPPLY

The efficiency of any power supply concept depends greatly on the amount of relevant data available on its application. The more detailed the description of its application is, the more reliably the solution produced will be able to fulfill all requirements.

3.6.1 Nature and Scope of Application Data

Two examples of applications will show which data are required in order to develop an appropriate concept for power supply. Figure 3.5a shows the capacitive application of a high-lift truck over two shifts on 5 days (Monday to Friday). The necessary scope of data is small. It is sufficient to describe one shift, represented in a considerably simplified manner, by summarizing application times and rest periods. This shift represents the smallest, regularly repeated application period, referred to as cyclic element (CE). The description of application only indicates how often this CE is repeated per day (2 x), and how often this definition of the working day is repeated per week (5 x). The third shift is available each day for charging, the weekend is excluded for charging.

The example for cyclic operation (Figure 3.5b) appears somewhat more complicated, but is based on the interlinking of described data. As is shown, more complex sequences can also be recorded using minimum data. The depiction is again of the cyclic element (a sequence of discharge and charge cycles) which, repeated 10 times and completed by an additional charge phase, corresponds to one shift in the example. After being repeated twice, this is followed by a rest period, without the possibility of recharging. This description of the working day is then repeated regularly (7 x) for each day of the week.

These examples, which are admittedly shown in a simplified form, are intended to indicate which information is essential for producing the power supply concept:

- Different effective discharge current values.
- Actual flow times.
- Closed-circuit current required.

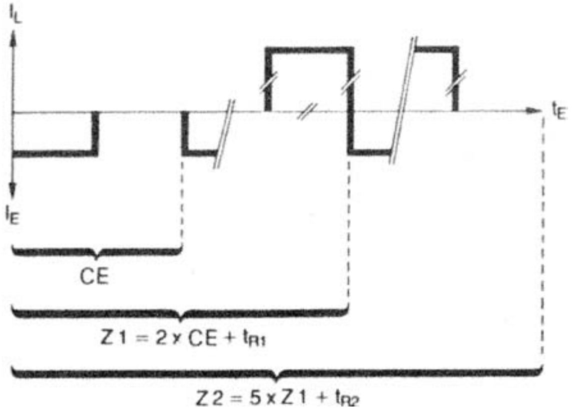


Figure 3.5a Capacitive application.

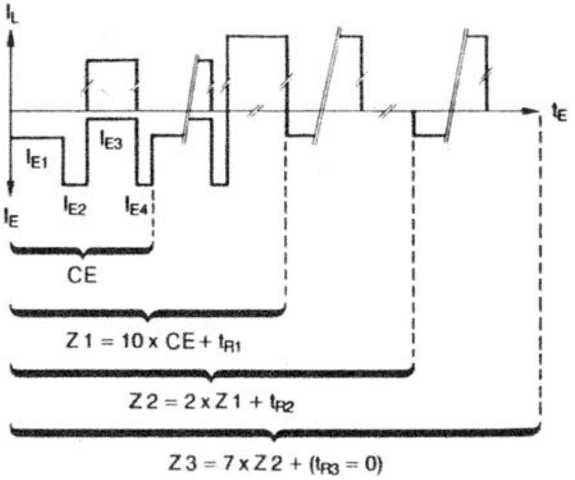


Figure 3.5b Cyclic operation.

- Rest periods, which can be used for charging (boost charge/full charge) and those which are pure rest periods without the possibility of charging.

These data must be further supplemented by the following application parameters:

- Ambiant temperature range.
- Minimum permissive discharge voltage.

Details on battery renewal, maximum weight, and volume would further complete the collection of application data, rendering it sufficient. There would now be no hindrance to determining the power supply concept, even if application conditions were to become more complicated (Figure 3.5c).

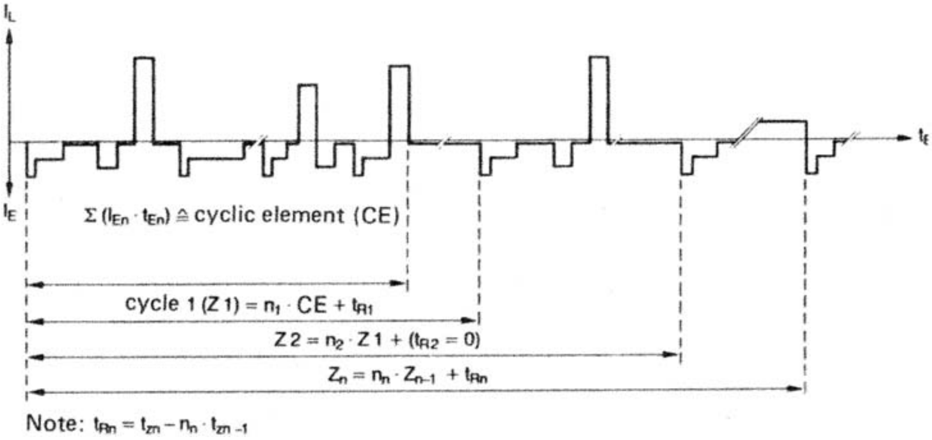


Figure 3.5c Cyclic operation: general example.

3.6.2 Processing and Transformation of Application Data

In view of the fact that an arbitrary number of different plans for use are feasible in installations with driverless industrial trucks (practice), it is not possible to postulate an easy system for determining the components in producing the power supply concepts. The reason for this lies in the at times widely differing properties (Figure 3.6) displayed by the various battery systems, which also have a great influence on charging technology. It is possible, however, to specify the steps, which actually need to be taken every time. These refer to the smallest, regularly repeated interval between applications, which at the same time contain the total feasible boost charge capacity, i.e. do not necessarily coincide with the cyclic element. The calculations are all based on simple mathematical relationships.

3.6.2.1. Determining the Capacity Required $Q\Delta_E$ in the Interval Between Applications Δ_{tE}

Capacity generally corresponds to the product of current time:

$$Q = \int_{to}^{to+T} i \, dt$$

With respect to an interval between applications with many current flow phases of different strengths, as will always be the case in problems of drive (acceleration phase, steady-state phase), this equation can be converted into

$$\Delta Q_E = \Delta Q_{E1} + \Delta Q_{E2} + \cdots + \Delta Q_{En}$$

By inserting individual currents and current flow times, this gives us

$$\Delta Q_E = i_{E1} \cdot \Delta t_{E1} + i_{E2} \cdot \Delta t_{E2} + \cdots + i_{En} \Delta t_{En}$$

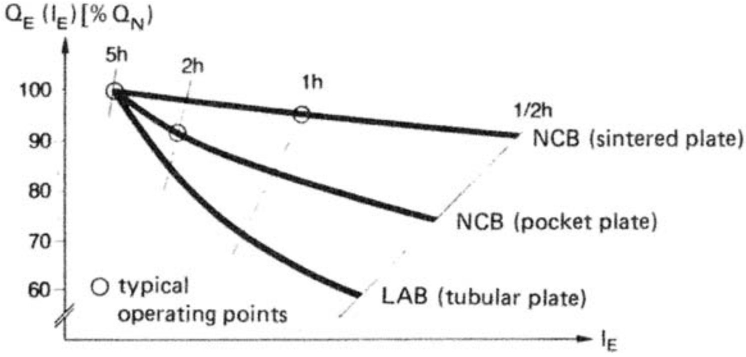


Figure 3.6 Differences in capacity for different battery systems with same hourly measurement, $T_{el} = T_N$.

which can be condensed into

$$\Delta Q_E = \sum_{n=1}^{k} \quad i_{En}\Delta t_{En}$$

3.6.2.2. Determining the Effective Discharge Current Value I_E in the Interval Between Applications Δ_{tE}

The effective value of the discharge current can be calculated by using the following formula:

$$I_E = \sqrt{1/Ti_{E2}dt}$$

Note: This actually comprises the root mean square value. As this is important for the heat generated in one pulse sequence, it is called the effective value. In the same way as we determined the capacity required, the formula my be quoted as follows:

$$I_E = \sqrt{1/\Delta t_E(i_{E1}^2\Delta t_{E1} + i_{E2}^2\Delta t_{E2} + \ldots + i_{En}^2\Delta t_{En})}$$

where

$$\Delta t_E = \sum_{n=1}^{k} \Delta t_{En}$$

3.6.2.3. Determining the Charging Set Nominal Current

Including a safety factor S, which mainly compensates for aging of the batteries and other imponderables which will always be present in a system concept, the charging current in steady-state condition can be determined by using the following formula:

$$I_L = S\frac{\Delta Q_E}{\Delta t_L}$$

where

$$\Delta t_L = \sum_{m=1} \Delta t_{Lm}$$

3.6.2.4. Determining Nominal Capacity

Experience has shown that this subject causes the most discussions. What needs to be considered in determining nominal capacity?

1. Load rating specific to the system. The different load rating of the various battery systems has been given in approximation in Table 3.1 for three-shift operation. The hypothetical capacity must first be determined with the aid of the permissible discharge current. This is subsequently checked using the permissible charge current. Not only the permissible effective values, but also the peak values must be observed.

2. Dependence on temperature. This must be considered if the temperature probably to be reached by the electrolyte is to lie clearly below the nominal temperature specific to the system. The capacity chosen should then be corrected on the basis of

$$Q_N = k\ QN$$

k corresponds to a correction factor including the temperature dependence of battery capacity as shown in Figure 3.7a.

3. The lower voltage limit. Voltage should not be allowed to fall below the minimum of U_{Bmin} at any time during the interval between applications discussed here. In addition, attention must be paid to the dependence of discharge voltage on discharge current, discharge level, and of course electrolyte temperature, as shown in Figures 3.7b and 3.10. It goes without saying that the hypothetical value must be

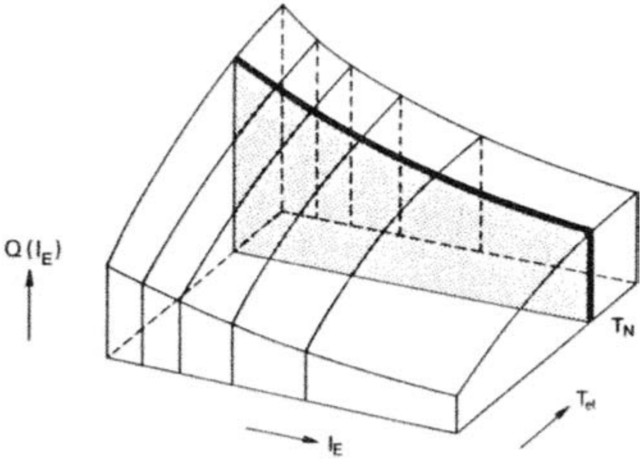


Figure 3.7a Temperature dependence of capacity: example of LAB with tubular plates.

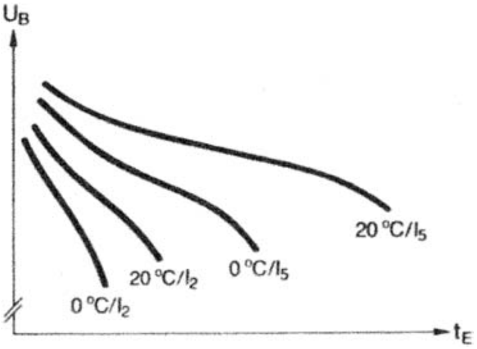


Figure 3.7b Temperature dependence of battery voltage: example of NCB with pocket plates at temperatures of 0 °C, 20 °C, and I_2, I_5.

greater than C_E calculated under 1. The typical values in cyclic operation lie between (a) $\Delta Q_E = 10\% Q_N$ depending on the battery system, length of cycle and element, and level of charging current and (b) $\Delta Q_E = 30\% C_N$. This will assure a high system reliability and service life.

Note: *Service life refers here to a time interval in absolute time units (e.g. years).*

3.6.3 Comparison of System

Assuming all battery systems to be possible, Figure 3.9 contains the result of a calculation on the basis of cyclic operation. Depending on the marginal conditions of their application, the example compares three possible systems. The tubular plate lead-acid battery exhibits by far the highest nominal capacity. The discharge range is then naturally lower (in relation to nominal capacity) than it is the case in the two nickel/cadmium batteries. All three variants in this hypothetical case are in the region of $U_B = 23.75\,V$. The tubular plate LA battery has 12 cells, the pocket plate nickel/cadmium battery 20 cells, and the sintered nickel/cadmium battery 19 cells (Figure 3.8). The application corresponds to a two-shift operation.

3.7 CURRENT STATE OF CHARGING TECHNOLOGY

The charging sets in current use (milkers) are almost exclusively based on the known IU curve, with elements of the characteristic curve specific to the installation attached. Uncontrolled processes of charging are becoming rarer, and are mostly only used in smaller installations with purely capacitive use of batteries. The charging sets are predominantly of stationary design. Plans for producing on-board charging sets have so far remained the exception.

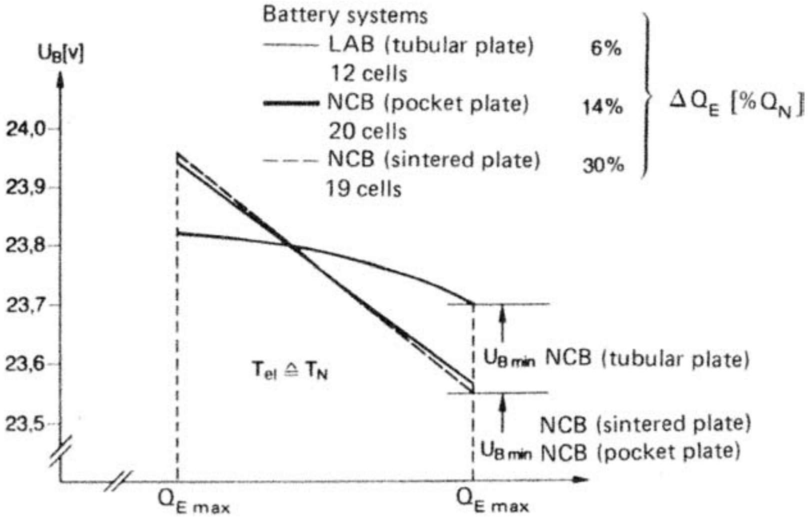


Figure 3.8 Voltage curves for different battery systems: example of cyclic operation/two-shift operation. (Depiction belongs to example for dimensioning.)

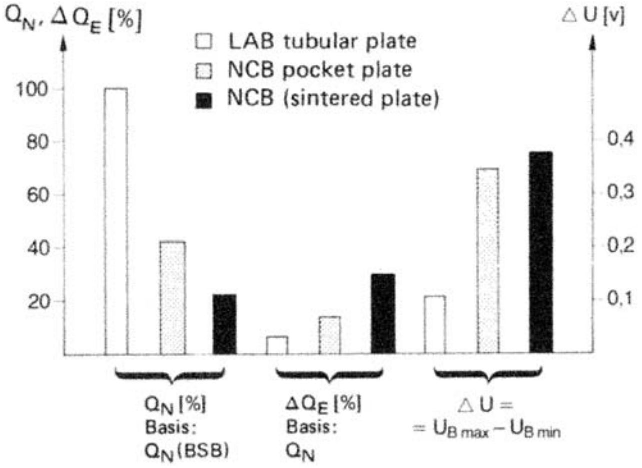


Figure 3.9 Comparison of system data for example of cyclic operation/shift application.

3.7.1 Methods of Control/Exchange of Information

Charging sets are generally actuated directly by the driverless industrial truck or by the sequence control system, i.e. they carry out instructions prompted by external control signals and at the same time supply information on the current state of charging (status signals).

The following functions have emerged as standard:

- Readiness on/off.
- Charging on/off.
- Include/exclude characteristic elements.

Execution of these functions can, for example, be initiated by jumps in potential ($OV \rightarrow U_S \rightarrow OV$).

Such digital status signals include

- Charging active.
- Current flow at high charging level OK.
- Characteristic curve identification.
- Collective fault warning (analysis of the type of fault is normally made by maintenance personnel) are supplied by the charging gear, e.g. indirectly by way of floating contacts.

3.7.2 Practical Example

Figure 3.10 depicts a basic method of charging which can in principle be used for all battery systems mentioned here and which permits both boost charges and full charges. The controller limit values I_{G1} = equipment nominal current, I_{G3} = recharrecharging current; U_{G1} and U_{G2} should first be set, depending on the specific battery system I_{G1} and U_{G1}, together with I_{G2}, should also be treated as being independent of the actual installation. In certain circumstances, U_{G1} must be

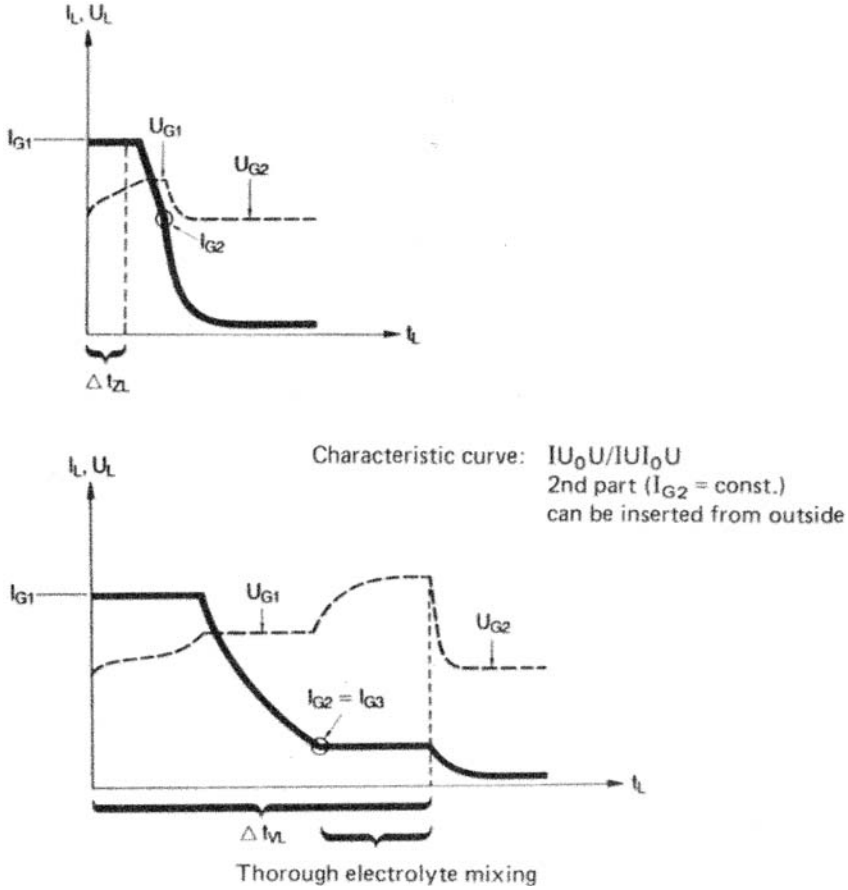


Figure 3.10 Basic charging process, suitable for boost/full charging of various battery systems.

corrected when starting up an installation, as the voltage losses during the high charging phase, especially at the contact points, are rarely known accurately. The level of I_{G1} is known to influence charging efficiency, and thus the balance of capacity in the first section of the charge curve ($I_{G1} = \text{const.}$). t_{ZLmax} should theoretically be at the end of the first section of the curve, as the charging energy supplied until this point would have been converted practically without loss into useful capacity. The curves in Figure 3.10 must naturally be seen as being dependent on temperature and aging, and the safety factor (S) introduced in the preceding section is thus justified.

3.8 SUMMARY AND OUTLOOK

The power storage unit on board a driverless industrial truck makes possible the required high level of mobility and even uninterrupted operation when combined with a concept of charging adapted to application. Highly efficient, well-proven battery systems with long service lives have been in existence for a long time. Thousands of driverless industrial trucks are currently running on such systems, thus proving the reliability of correctly dimensioned power supply concepts. There is no competitive relationship between the different battery systems, when it is considered that each system has its technical logical and economical field of application. It is thus only possible to assess a particular system in conjunction with the conditions under which it is employed. The tubular plate lead-acid battery occupies a leading position for good reasons, particularly as single cells of the smallest design have since become available on the market.

The intelligence of driverless industrial trucks will increase. Further development aims are on the one hand at traveling without a guide wire, and on the other hand at taking over the function of battery monitoring. Figure 3.11 depicts how a charge/discharge monitoring system might be integrated into a driverless industrial truck. The monitoring software would receive information on the battery at any time by way of a suitable sensor system, and would rely on fundamental battery-oriented knowledge stored in a memory for evaluating this information. Temperature and load dependence could be recalled by a set of formula and control folders specific to the system, thus saving space. The first steps have already been taken in this direction. With the aid of this higher intelligence (with an understanding of the battery), it would be possible for future driverless industrial trucks to handle power storage units even more economically and to provide even clearer proof of the reliability of this power concept.

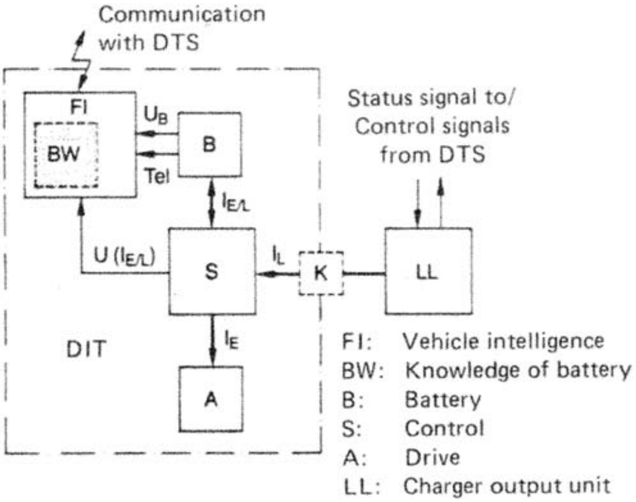


Figure 3.11 Battery monitoring by own DIT intelligence; depiction only takes into consideration information exchange between vehicle or DIT and power supply unit.

4

Batteries for Electric Road Vehicles

H. A. KIEHNE

4.1 INTRODUCTION

The so-called classic accumulator is not yet exhausted concerning development possibilities. The newest trends in research and development indicate that new production methods offer more cost-efficient methods for production of batteries than present production techniques, corresponding with presumptive large production numbers. Even though presently much work is being invested into conventional battery systems, hopes are focusing on new batteries of higher energy content, such as high temperature batteries, e.g. sodium/sulfur and lithium/sulfur batteries. It must be mentioned, however, that even though very good results can be expected, no "magic battery" will be invented by battery development teams or by teams in any other industry.

The traveling range of battery-powered vehicles will always be very limited compared to vehicles featuring combustion engines, if comparing the practically attainable energy contents of batteries (40 to 150 Wh/kg) to the gigantic 12,000 to 13,000 Wh/kg for gasoline, even though the efficiency of electric energy forms is about five times as high.

This chapter gives basic information on existing systems such as the lead-acid battery; other systems under development are described in Chapter 1 and Chapter 10.

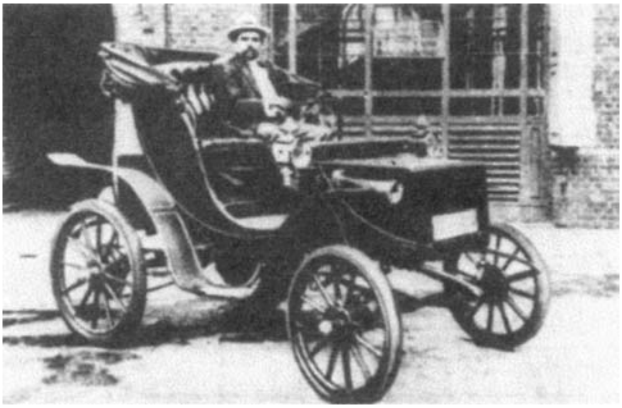


Figure 4.1 The first electric battery-powered car, the Runabout (1890).

The history of industrial production of batteries comprises almost a century; the electric car is of the same age. Adolf Mueller, founder of the AFA (Accumulatorenfabrik Aktiengesellschaft Varta), returned to Germany from a trip to the United States in 1893 with an electrically powered vehicle, the Runabout (see Figure 4.1). He drove this car for many years. Interest of the car manufacturers was very limited but was wakened at the turn of the century when reports of about 15,000 electric cars in operation in the United States reached the country. Very low energy cells and 20 Wh/kg for grid-plate cells were a great step forward. Electric taxis, buses, and trucks sprang up everywhere, and operated profitably. Unfortunately the combustion engine interrupted this development.

After World War II most of the electric vehicles disappeared, and electric industrial trucks, streetcars, and boats and submarines remained the only field of application for traction batteries, mostly lead-acid batteries. England has kept about 40,000 electrically powered trucks in service to this day, mostly for service in rural areas, for milk delivery and the like.

Development in the field of electric fuel cells came to attention in the second half of the 1960s and the 1970s when the oil price shock and later environmental conscience renewed worldwide interest for the electric powered car. First successes in battery development caused euphoria in some places, the electric vehicle becoming a visionary vehicle of the future with power supply by means of nuclear energy seeming limitless. Development problems? These problems could be solved by time and expenditure! So hopes were flying high. Disillusionment and disappointment followed on the one hand, but encouraging reports by the press on the other. What is our situation today?

At the 18th International Battery, Hybrid and Fuel Cell Electric Vehicle Symposium and Exhibition in October 2001 in Berlin, Germany, the world's largest event for electric vehicles, under the motto "Clean and efficient mobility for this millennium", development results and real hardware were presented, giving hope for solutions for the market not too far in the future (see *Proceedings EVS 18*).

Arguments for the electrically powered vehicle are still cogent if one accepts the following statements:

- The electric car could be a partial substitute for combustion engine cars at least as a supplement and can take over certain fields of operation.
- As its range is very limited, economic operation can only be maintained for short and medium ranges (100 to 150 km).
- Research and market introduction still needs to be improved.

The following advantages can be listed:

- Electrically powered vehicles are simple to operate and are almost maintenance free.
- Short-range operation poses no problems to the attainable range with the presently available systems.
- Electric power is clean and free of pollution emissions.
- Electric cars offer the same possibilities for exploitation as coal and nuclear power, but with substantially higher grades of efficiency than “artificial” fuels, such as methanol or hydrogen.

As already mentioned, environmental problems, both noise and emissions, and the responsible and expensive primary energy sources, especially crude oil, force us to develop and test alternatives. Most important, large-scale testing of these new technologies is necessary, and is being accomplished in several projects all over the world. Charging, energy distribution, and general operating conditions are only some of a multitude of problems that can presently be handled to a large extent.

4.2 ENERGY AND RAW MATERIALS

Alternative energy forms for future vehicles are synthetic hydrocarbons “artificial gasoline”, liquefied coal, methanol or ethanol, gasses such as hydrogen, and electricity. These so-called secondary energies must be reduced from primary forms of energy such as fossil coals, crude oil, gas, or nuclear power. Calculations of the GES (Gesellschaft for Elektrischen Strassenverkehr) and RWE (Rheinisch-Westfalische Elektrizitatswerke) made more than a decade ago showed that electricity for vehicle propulsion can be produced at about half the expenditure of primary fuels when reduced from different secondary forms of energy compared to powering by synthetic fuels, presumptive equal road performances, of course.

The fundamental question arises: will existing power plants cover such a change to electricity and the involved introduction of a great number of vehicles. This appears possible if, for instance, Germany, had 10% electric road vehicles. In 1980 about 369 billion kWh of electric energy were produced and, from statements from this industry, production of an additional 10 billion kWh presents no problem. 10 billion kWh would power 2 million road vehicles, each covering 10,000 km a year (a calculation easy to follow presuming that each kilometer covered consumes 0.5 kWh of mains electricity). With the generally rising demand of electricity, only 3% of the overall production would be available at any time for powering electric vehicles.

It will be pointed out in the following that for the foreseeable future only lead-acid accumulators will be available for powering vehicles. This of course raises the question whether there is enough lead available to cover such a demand. Newly

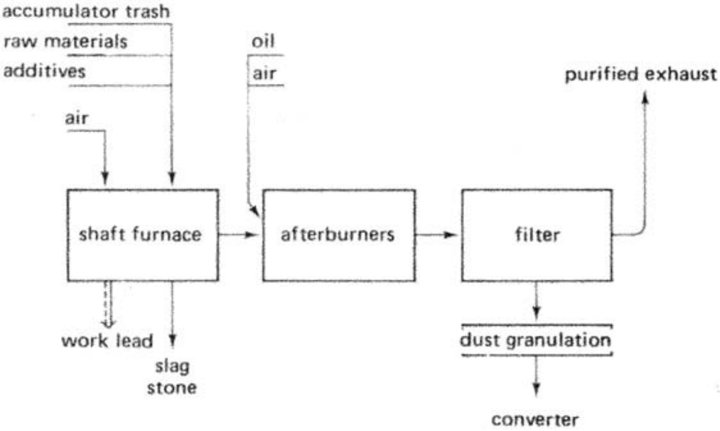


Figure 4.2 Diagram of a recycling procedure of lead batteries (Krautscheid).

developed batteries (see Chapter 10) have to demonstrate reliability in practical use and economy.

If one would start today to produce a stock of, let's say, 500,000 electric cars in Germany over the next 10 years, this would cause a momentous rise in production numbers of cars and batteries. In 10 years from now, an estimated annual production of about 100,000 batteries for new cars and about 30,000 batteries for replacements would be needed. Enough lead for about 30,000 batteries could be recycled by the same low-pollution techniques already practiced today (see Figure 4.2). A 120-V battery with an energy content of 19.2 kWh consumes about 370 kg of lead to the present state of art, resulting in additional 37,000 tons of lead in demand for one year. This is little more than 10% of the amount of lead consumed per annum in Germany. So in a foreseeable starting phase, no shortage of lead would occur, not even if demand were higher. If development of alternative energy accumulators, e.g. lithium/sulfur batteries, succeeds within the near future, the raw material question regarding lead will become obsolete.

Often the amount of primary energy needed for manufacturing a product has to be accounted for; this problem is not too grave since national energy resources, such as fossil coal or nuclear energy, can be exploited for production of electricity, thus lowering the import demand of crude oil to the country in question.

4.3 SOLUTION TO THE RANGE PROBLEM

As mentioned, the problem of a limitless range does not seem solvable with the "classic batteries" within a foreseeable period of time. Battery-powered vehicles thus are regarded as short-range vehicles. As to what is the optimal range, very different opinions are at hand due to the geography of the country in question: 40 to 80 km for European conditions and 150 miles (240 km) would be adequate for American conditions. Let's have a look at the general circumstances in Germany: The following values were found for passenger cars in West Germany in 1979 (these values can still be seen today as representative):

- Average length of one single drive: 12.1 km.
- Average total distance driven per day: 37.87 km.
- Average total distance covered per year: 13 400 km.

It can be derived that a very large number of cars are used for distances smaller than 40 km per day (very precise studies on the type of cars and the people who use them are available). Nonetheless, a great obstacle for the introduction of the electric car is the fear of having a breakdown en route. There is however a very simple way to prolong the range substantially: by recharging during driving breaks by a built-in charging device that enables the battery to be hooked up directly to the AC network current on a domestic wall outlet. Figure 4.3 demonstrates this option. Lines 1, 2, and 3 in the figure represent three different average cruising speeds in urban traffic in a distance/time diagram. The horizontal lines A and B represent the limits for a battery with sufficient capacity for a 40 and 80 km range. The time axis has a range of 14 hours, the time a vehicle should be available per day. The crossing points of the lines give the maximum possible cruising time at constant speed 1, 2, or 3. Generally only a fraction of this maximum cruising time is used and during breaks the cars can be intermediately charged at any power outlet. The diagram also features the values attainable when range prolongation through intermediate charging with 2 or 5 kWh is practiced: the intersections of lines L_1 and L_2 or $L_{1'}$ and $L_{2'}$ with the lines 1, 2, and 3.

The average speed of 30 km/h yields the greatest range:

- First case: a battery with about 10.8 kWh and 40 km range; intermediate charging with 2 kW prolongs the range by 125% to 90 km, with 5 kW by 260% to 144 km.
- Second case: a battery with about 21.6 kWh and 80 km range; intermediate charging with 2 kW prolongs range by 56% for 125 km, with 5 kW by 118% to 175 km.

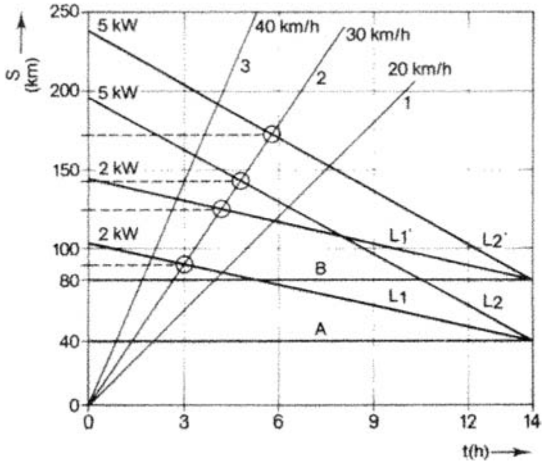


Figure 4.3 Prolongation of the range by built-in charging devices (from a publication of the GES).

This procedure is practicable and is open to optimization depending on how much of the actual stopping period is available for intermediate charging. The batteries' perfect function is not affected by this method. This indicates the following:

1. Service range can be substantially improved without high costs and without fitting a larger battery simply by intermediate charging.
2. Application of a larger battery without the employment of intermediate charging makes electromotive power more expensive (capital and interest rates).
3. Higher energy densities are primarily of interest for lowering battery weight and only secondarily for improving range.
4. Charging devices and mains adaptors can be incorporated in the vehicles and are state of the art.
5. This application can be used not only for lead-acid batteries, but also for any other secondary battery.

Now as it is evident that there are no arguments against the introduction of the electric car regarding the energy and raw material situation and with the range problem being almost solved, we will examine whether the requirements for the battery itself have been or can be solved.

4.4 BATTERY REQUIREMENTS: CONTRIBUTIONS TO SOLVING THE PROBLEM

The following goals exist for electric road vehicle batteries:

- Making batteries lighter by significantly higher energy and power densities, primarily weight-specific.
- Raising power content, weight-specific.
- As maintenance free as possible without sophisticated peripheral equipment.
- Service life should reach the life span of industrial trucks.
- 1200 cycles 80% C_5 lead-acid batteries.
- 2000 cycles 80% C_5 nickel/iron batteries.
- High efficiency/low charging factor: 1.01 to 1.05.
- No noticeable rise in price through energy consumption during use.
- Same or improved reliability compared to present products.

Furthermore:

- The ability to incorporate the energy-storing device into presently produced cars, raising the competitive situation (especially when only some basic models are produced): modularization.
- Mechanical stability without supporting devices. Solutions that dispense with battery trays (saving cost and weight) are especially advantageous.
- Tightness. Solutions that prevent leakage of electrolyte vapor and charging gasses are especially advantageous.
- Temperature resistance. The upper and lower temperature limits should be penetrable temporarily with no damage done to the battery.
- Long shelf-life and active life even after a long inactive period.
- Ability to withstand overcharging facilitating the charging procedure.

- Ability to withstand exhaustive discharge, preventing failure of the battery following severe strain and reducing exhaustive discharge protection requirements.
- Sustainable fast charging. In many cases recharging times of 10 to 16 hours are sufficient. The ability to sustain fast (0.5 to 1 hour) charging would solve the range problem and would also contribute substantially to making battery interchange superfluous.
- Reparability. Damaged or worn-out parts, such as cells and modules, must be replaced quickly to reduce breakdown periods.
- Easy activation. Expenditure of activation must be as low as possible at highest possible initial power output.
- State-of-charge indicator. This “marginal problem” has not been solved satisfactorily.
- Electrical and mechanical ruggedness regarding shock, vibrations, and crashes.
- Non polluting during operation, manufacturing, and recycling.

With knowledge of these requirements, developments have been carried through to improve the lead-acid, nickel/iron, and high-temperature lithium/sulfur systems to the above standards. Outstanding successes were made that can be regarded as milestones of battery development. The first lead battery systems as they were tested in MAN and Mercedes Benz buses, Volkswagon and Mercedes Benz vans, and other experimental vehicles should be mentioned here:

- Energy and power densities could be essentially improved.
- Parts optimization was carried through to reduce dead weight.
- Fully insulated batteries with 100% gas-tight terminal passes were developed (see Figure 4.4).

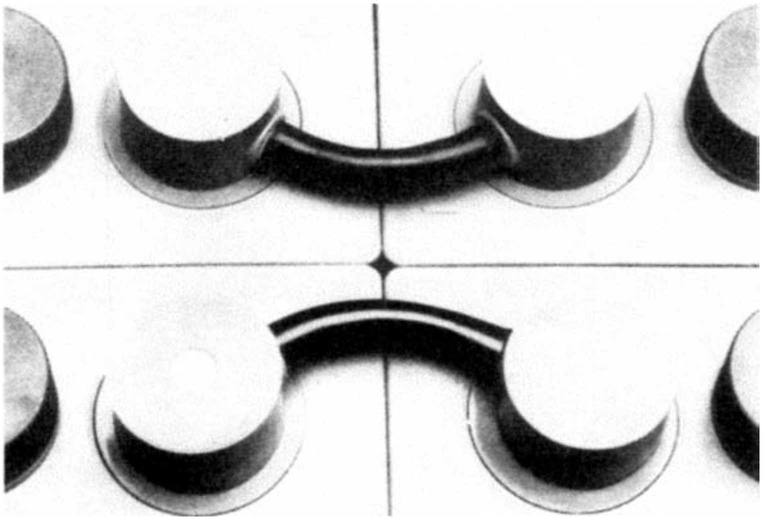


Figure 4.4 Fully insulated flexible connector technique.

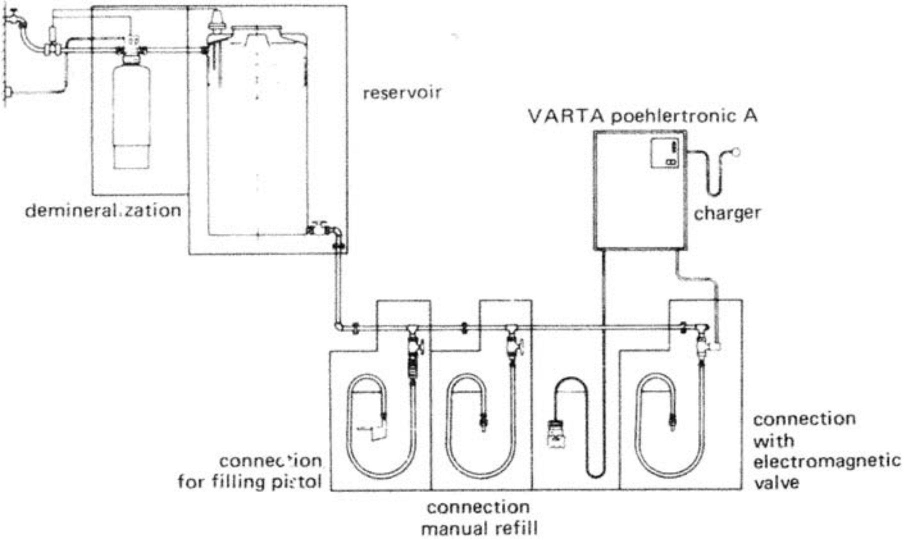


Figure 4.5 Peripheral devices: centralized water replenishing system (Varta aquamatic).

- Service life and reliability were improved coexistent with higher energy density values.
- Peripheral devices such as water replenishing systems, central gas adsorption, cooling systems, charging, and battery controlling equipment have been developed (see Figures 4.5 through 4.8) and have been successfully tested.
- Basic theoretical and experimental research work has yielded a lead-accumulator system.

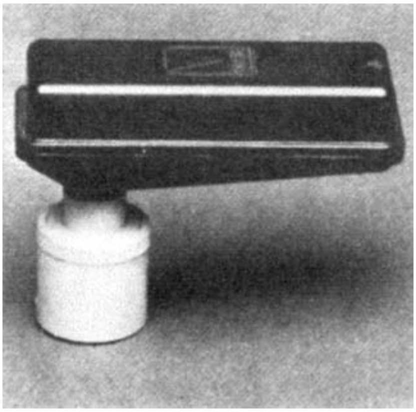


Figure 4.6 Peripheral devices: recombination plug.

Figure 4.7 Peripheral devices: water refill plug.

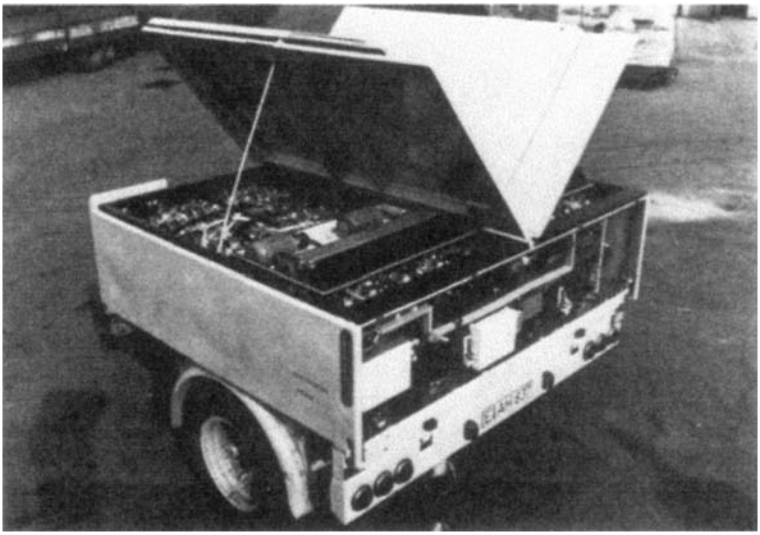


Figure 4.8 Peripheral devices: cooling system for the lead traction battery of an electric bus.

4.5 ALTERNATIVES TO LEAD-ACID SYSTEMS

The experiments that have been carried out with electric vehicles for several years now have shown that many requirements could be fulfilled to a large extent by focused research work. The cost factor regarding further developments shall be discussed later.

It is only natural that problems had to be solved in the course of the experiments; the combustion engine had to be refined over and over again as well before it reached the present high grade of perfection. More than 200 electric vans and over 20 electric buses have been in experimental operation in different cities of Germany. In Stuttgart and Wesel large-scale experiments involved over 20 hybrid buses and in Esslingen further research was made with “duo-buses”. Three systems have prevailed out of all these experiments with electrically powered vehicles:

- *The battery/electromotor drive*. Exclusively batteries maintain this. A charging station is frequented at certain intervals to recharge or change batteries or intermediate charging is made during stops.
- *Hybrid drives*. This drive also employs batteries, but with a certain change a diesel generator is frequently activated to recharge the batteries during operation. After the craft has departed from areas suffering from heavy pollution, the diesel generator is switched on.
- *Duo drives*. The vehicle runs mainly on battery power and frequent overhead power lines make recharging.

Spectacular advances in the applied battery systems cannot be expected, but surely another rise in energy density, perhaps by 10 to 20%, may be made regarding power density.

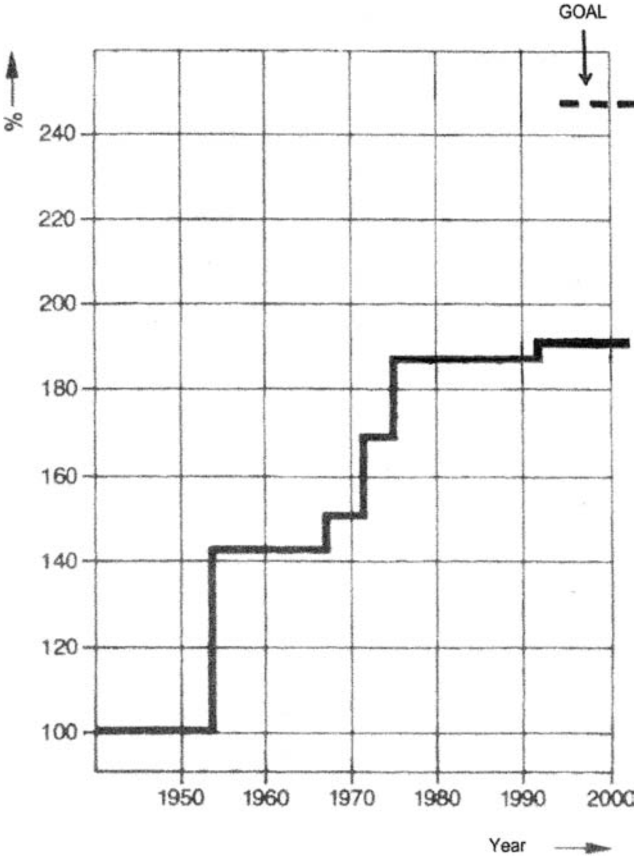


Figure 4.9 Development of energy density (percent Wh/kg) of lead-acid traction cells with future outlook.

Figure 4.9 shows the development of energy density of the lead-acid accumulator since 1945 in percent as well as the goal, which seems attainable presuming research work on improved mass utilization proves successful, e.g. by electrodes that are run through by the electrolyte, a principle presented by the supervisor of the AFA laboratories in Hagen, Carl Liebenow, in his famous experiment in 1895.

A decisive change, especially regarding price and economy can only be brought on by large-scale introduction. At present it is not possible to compare prices and costs of a new technology with those of a mass product. At best an estimation of those costs can be made caused by an actually comparable function and with the same operational parameters, also regarding further price rises for crude oil (see Section 4.6).

The presently available lead-acid batteries consist of cells and modules, with standard sizes for cells having been published in the DIN 43 537 standard. This type of cell is totally electrolyte-tight except for the refill and gas-emission openings for the vent plugs. The connectors are flexible and fully insulated (see Figure 4.10). All cells and modules can be fitted with central water-replenishing systems or with recombining systems (catalytic converters that recombine charging gases to water). The replenishing system is combined with a gas adsorption system. All of the gas produced inside the cells is ventilated to the outside air.

Certain types of cells, such as the HD types, can be fitted with a water-cooling system. This prevents the temperature from rising above a certain limit under heavy load and thereby allows higher loads and currents to be drawn.

Lead-acid cells and modules have attained the highest level of development, especially concerning reliability and attainable service life. The first generation of

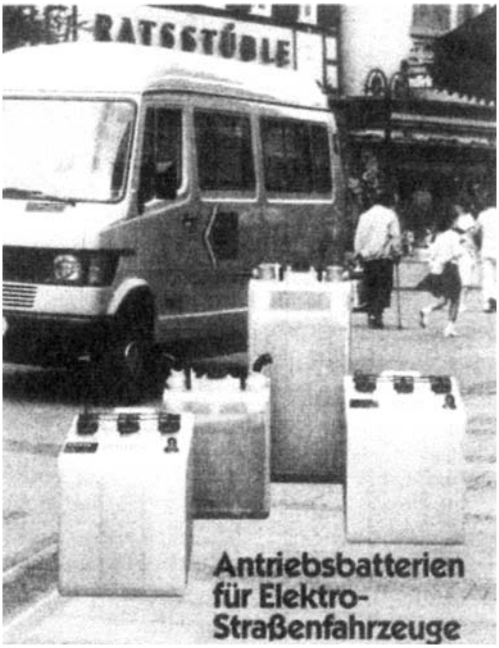
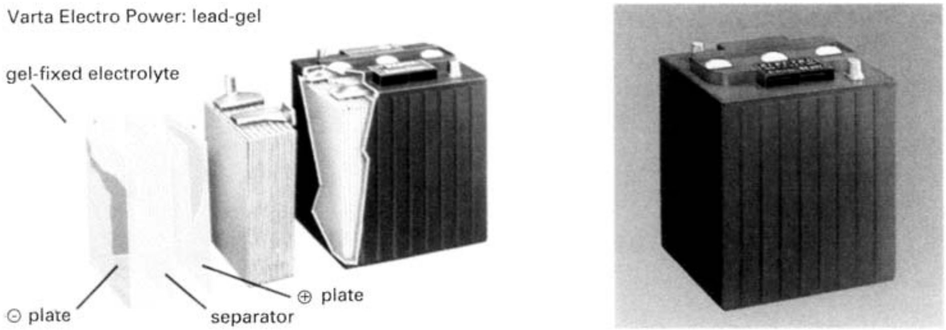
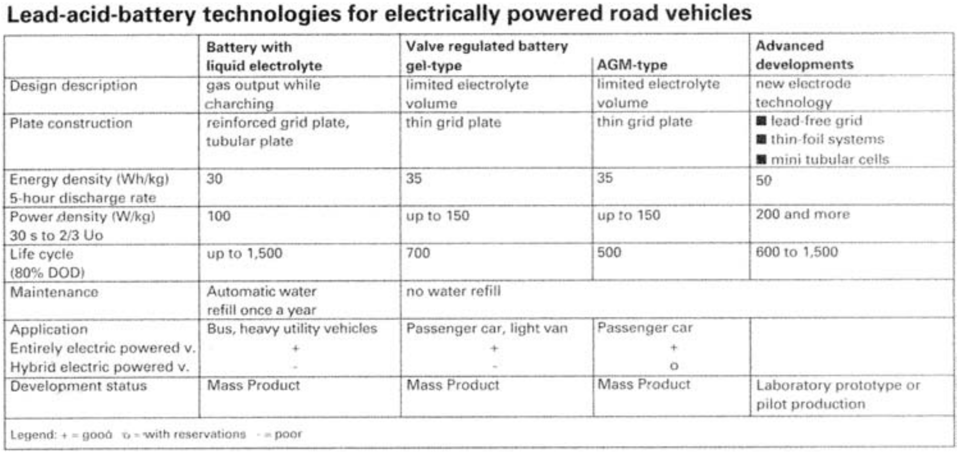


Figure 4.10 Present-state designs of vehicle traction batteries and battery modules.




Lead-acid-battery technologies for electrically powered road vehicles

	Battery with liquid electrolyte	Valve regulated battery gel-type	AGM-type	Advanced developments
Design description	gas output while charching	limited electrolyte volume	limited electrolyte volume	new electrode technology
Plate construction	reinforced grid plate, tubular plate	thin grid plate	thin grid plate	■ lead-free grid ■ thin-foil systems ■ mini tubular cells
Energy density (Wh/kg) 5-hour discharge rate	30	35	35	50
Power density (W/kg) 30 s to 2/3 Uo	100	up to 150	up to 150	200 and more
Life cycle (80% DOD)	up to 1,500	700	500	600 to 1,500
Maintenance	Automatic water refill once a year	no water refill		
Application	Bus, heavy utility vehicles	Passenger car, light van	Passenger car	
Entirely electric powered v.	+	+	+	
Hybrid electric powered v.	-	-	o	
Development status	Mass Product	Mass Product	Mass Product	Laboratory prototype or pilot production

Legend: + = good o = with reservations - = poor

Figure 4.11 Technology comparison of different types of lead-acid batteries.

batteries for electric vehicles will almost certainly be of the lead-acid battery family as they already fulfill most requirements at present and permit short-range traffic.

Figure 4.11 shows a three-cell monobloc valve-regulated lead-acid battery and a comparison of other lead-acid battery types with an outlook on possible future design.

4.6 BATTERY SYSTEMS OF THE NEAR FUTURE

To answer the question which system is the best alternative to combustion engine drives, it is necessary to look a bit closer at the problems of some experimental battery systems.

The first systems to be examined are the nickel/iron and the nickel/zinc systems. Values ranging from 60 to 80 kWh/kg seem realizable, without regard to life expectancy. The nickel/iron and nickel/zinc systems will always be more expensive than a comparable lead-acid battery for the following three reasons: the materials involved are more expensive, the production involves more expenditure, which is partly the case because a greater number of cells are required for the same voltage, and more cells are needed because each cell yields less voltage. So to be more economic these systems must have a longer service life than a lead accumulator. Even so, there are quite a few manufacturers researching the problems of development of the nickel/zinc battery.

In the field of nickel/iron batteries research has not terminated yet, so it is too early to speculate on the subject. Mainly life expectancy is examined by experiments with changing parameters.

The chlorine/zinc battery may also have potential in the near future. It has electrodes with pumped active material. 50 kWh prototypes have been built by Energy Development Associates, an American Gulf & Western Company.

In the mid-1990s several development teams (e.g. Varta) tried to improve the nickel/metal hydride system to make it applicable for electric road vehicles. Figure 4.12 shows a battery module with nickel/metal hydride cells; the given

Technical specifications
Nickel-metal-hydride-cells

Specific energy	50 to 80 Wh/kg
Energy density:	150 to 210 Wh/l
Maxim. power:	more than 300 W/kg
Charge time:	80% in 15 minutes
Life-cycle stability:	more than 2,000 cycles

Figure 4.12 Battery module with nickel/metal hydride cells and performance data.

Figure 4.13 Cross-section of battery with nickel/metal hydride monoblocs.

Figure 4.14 Neoplan Metroliner bus.

technical data show the improvement of performance. Figure 4.13 shows a cross-section of the complete battery with the modules shown in Figure 4.12. The battery was under test in a Neoplan Metroliner bus. Figure 4.14 shows the Neoplan Metroliner bus running in the city.

Parallel with the development activities on nickel/metal hydride batteries, the lithium-ion (also called 'lithium swing') system was developed and improved by Varta. Figure 4.15 shows a module with lithium-ion cells and the main technical performance data. The outer look conforms to the battery shown in Figure 4.14. The principle of lithium swing is shown in Figure 4.16. Not yet solved is the problem of cycle life, necessary for an economic use of the system. In portable batteries the system has been in successful use for years as an alternative to nickel/metal hydride batteries. (See Chapter 18.) A marketable system is not to be expected in the near future as some grave problems have not yet been solved, such as the control of the sophisticated peripheral devices; reliability; chlorine corrosion properties; low energy efficiency; shunt currents; the nonuniform dispersion of zinc making periodic total cleaning of the system necessary; and sealing of the cell to prevent chlorine from spilling to name a few.

4.7 HIGH-TEMPERATURE BATTERIES AND FUEL CELLS

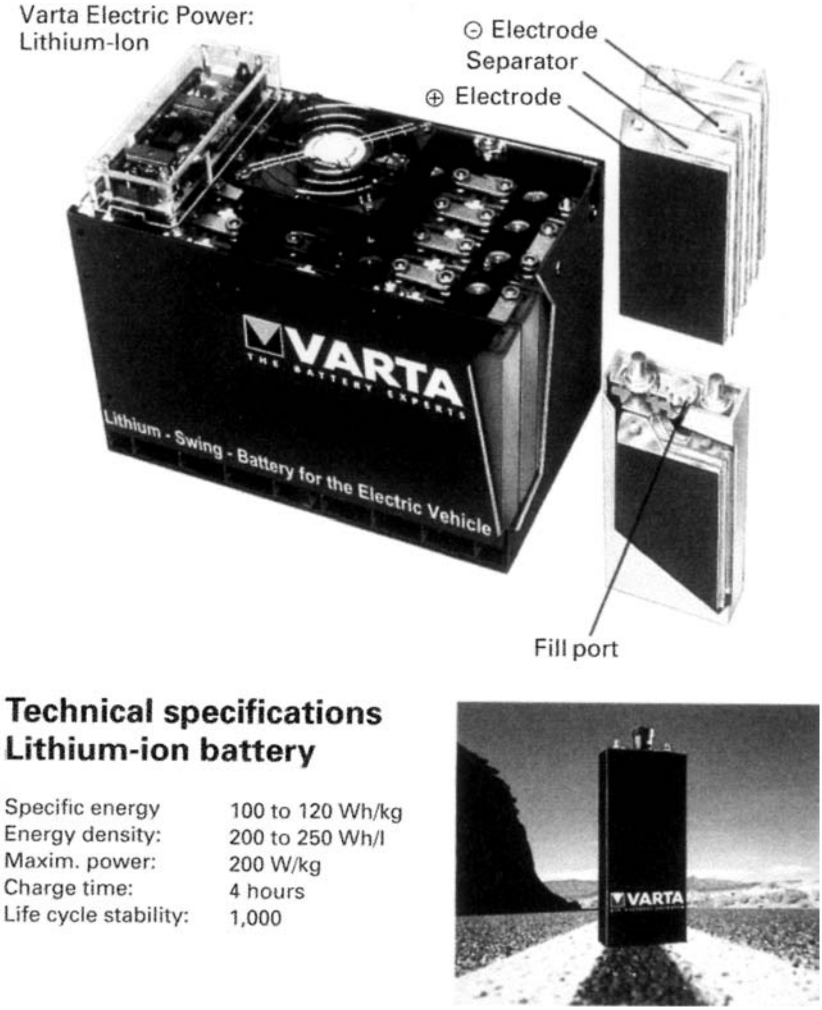
The most advanced system of this complex is the sodium/sulfur battery. Cost estimates on high-temperature batteries show that after the development phase has been completed and prototypes tested, these systems may operate well inside economical margins, assuming that mass production starts. In case these vehicles and their batteries are only produced in small numbers, the same problem will be at hand, as already discussed with the lead-acid battery. A deficiency of mass production makes vehicles and batteries artificially expensive.

Development of fuel cells also reached a considerable plateau with electrodes that reach service life spans of some 10,000 hours. The great interest for fuel cells remains high. Introduction to the market necessitates the creation of an infrastructure for providing the batteries with the gasses hydrogen and oxygen and their industrial production being state of the art. Much research is invested on making cheaper catalytic materials and electrodes for fuel cells that operate at moderate temperatures (20 to 90 °C) with alkaline electrolytes or at higher temperatures with acidic electrolytes. Yet chances for the future of these systems cannot be evaluated due to this situation. W. Fischer treats the subject of high-energy batteries in Chapter 10.

Figure 4.17, taken from a Varta publication, shows a comparison of the possible range performed by different battery systems by one charge. Presuming a positive result of the development efforts, the estimated values are given for the year 2005.

4.8 ECONOMIC VIABILITY

Economic viability for battery-powered vehicles today is far from realization. Economy can only be reached if electric vehicles, including all their parts and components, are produced in magnitude series. The step to magnitude series is only



Technical specifications Lithium-ion battery

Specific energy	100 to 120 Wh/kg
Energy density:	200 to 250 Wh/l
Maxim. power:	200 W/kg
Charge time:	4 hours
Life cycle stability:	1,000

Figure 4.15 Battery module with Varta lithium swing cells.

possible under the condition of general market acceptance for electric road vehicles or if the situation in the field of energy supply changes dramatically by shortage and cost rise of fuel.

Furthermore, three practical examples of application can be named for traction batteries with economic use compared to other propulsion systems:

- The ETA railway coaches with 440-V lead-acid batteries were in service for decades by the German Railways. (Today they are no longer in use because passenger cars are preferred for low distance traffic.)

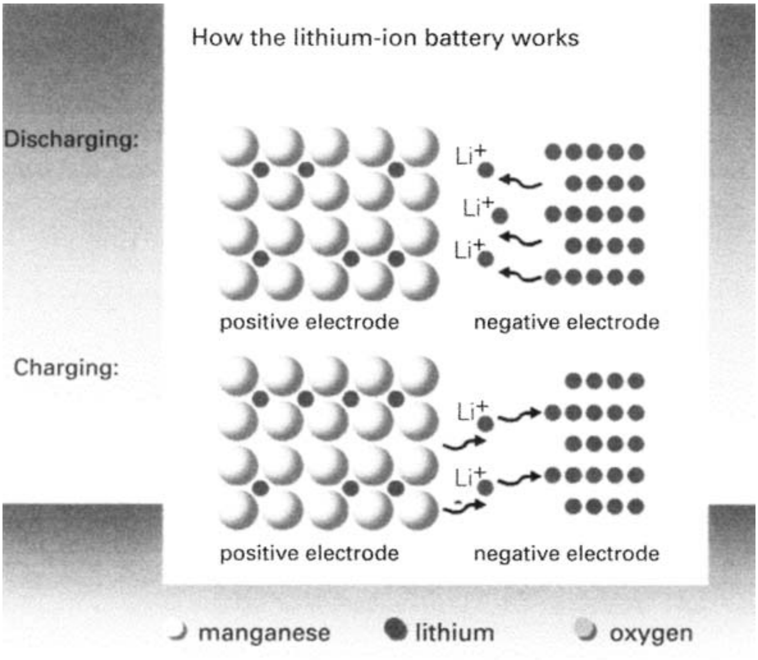


Figure 4.16 Principle of lithium swing.

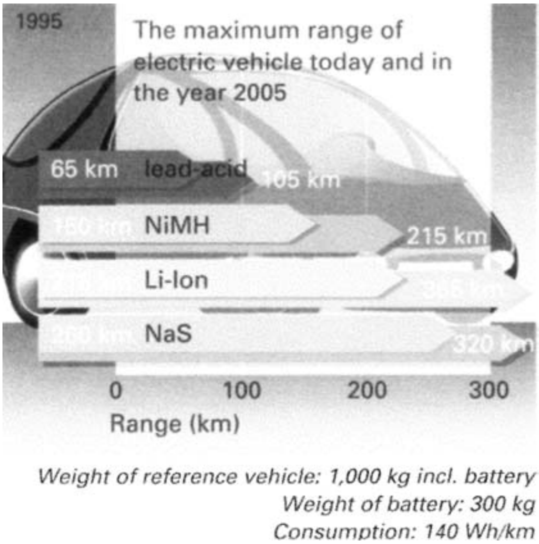


Figure 4.17 Possible ranges performed by different battery systems.

- Battery boats, e.g. for passenger sightseeing transportation on the Königsee.
- Battery-powered forklift trucks.

4.9 OUTLOOK

Despite considerable efforts of countless engaged engineers we are far from market acceptance for electric road vehicles. The technical state of the art is not sufficient. The expectations for possible development work on batteries surely had a level which was too high. Therefore we have to put an eye toward other special applications where battery-powered propulsion fulfills the demands. Progress in traction battery development showed advantages for other kinds of applications. One should not forget that our normal batteries have changed in the last decades in many details. New batteries will need many new parts to enable their employment or to improve their usefulness.

Everybody in Germany who took part in battery development can say, in our country top results could be presented in worldwide competition to realize advanced traction batteries. Expenses amounted to hundreds of millions of deutsch marks in the last 25 years just in West Germany, not to mention governmental fiscal support.

Finally here it will be stated, that all battery systems are “specialists”.

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5

Battery-Powered Traction—The User's Point of View

W. KÖNIG

5.1 INTRODUCTION

To transport people and material growing transportation systems are needed. More and more of the energy for these systems is drawn from secondary batteries. The reason for this trend is economic, but there is also an environmental need for a future chance for electric traction. The actual development of electrochemical storage systems with components like sodium–sulfur, sodium–nickel chloride, nickel–metal hydride, zinc–bromine, zinc–air, and others, mainly intended for electric road vehicles, make the classical lead-acid traction batteries look old-fashioned and outdated. Lead-acid, this more than 150-year-old system, is currently the reliable and economic power source for electric traction.

The main application of the lead-acid battery is vehicles for materials handling, such as forklift trucks, transporters, and so on, inside manufacturing plants and warehouses. Passenger transportation in areas where no pollution from exhaust gases can be tolerated is a further field of application for electric vehicles powered by batteries. Special machinery for lifting, cleaning, and other uses as well as electric boats, golf carts, and wheelchairs use and need the proven lead-acid traction battery.

In the following, battery design and operating conditions are described with a special view on economy and reliability. Optimal purchasing conditions are not always found from a central office with the responsibility for selection of products, but more information and exchange of experience are the bases for the preparation of sound decisions.

5.2 GENERAL REMARKS

Suppliers of traction batteries and electrical charge and control equipment today offer a large product scale, not easily comprehensible to a normal user. Users of only a few electric vehicles for materials handling or other battery-powered systems ask trustworthy suppliers for advice. But calling a second or third supplier results in varying offers and variants of application possibilities creating insecurity and difficulty in decisionmaking.

As a rule, for large users of traction batteries it is economic to handle things in a central office to collect information on available technologies and materials. Purchasing and acceptance, maintenance, and disposal responsibilities by internal specialists are effective. Smaller users can participate in the experience of these experts.

For investment of electric vehicles for materials handling it has to be regarded that in a normal use the costs of a traction battery during its useful life are between 50 and 75% of the costs of the vehicle (without the battery). Here is one example: the price for a forklift truck was 12,000 EUR; the service life was 8 years. In this time two to three traction batteries, each for a price of 3000 EUR had to be procured. This very simple comparison shows that it would have been more economical to purchase only two batteries instead of three. It has to be noticed that the extension of life of a battery depends on design and quality of the battery and the charging method and charging equipment.

Therefore it is indispensable for every user—from a middle- and a long-term view—to aspire to specialized knowledge for optimal system design. The user has to be informed on the market and the state-of-the-art technologies to form intelligent opinions.

Assistance to get the optimal operation of materials handling with all components is given by the recommendations of the VDI (Verband Deutscher Ingenieure), member of IEEE, the German Battery Manufacturers Association, and the relevant standards edited by DIN (Deutscher Industrie Normen) and EN (European Norm), the latter mentioned later in this chapter.

5.3 ADVANTAGES OF BATTERY-POWERED TRACTION

5.3.1 Impacts of Operation and Environmental Concerns

The alternative of battery-powered traction is the internal combustion (IC) engine. It has to be noticed that there are fields of operation where the former or the latter has to be preferred. Table 5.1 points out some differences. This relatively simple listing shows that the domain of battery-powered traction is indoor service, while economy can be expected up to 3–4 tons. The German regulation for hazardous goods (TRGS 554) claims in addition that the employment of battery-powered traction avoids emissions by IC engines (see Figure 5.1). The domain for Ic-powered traction is outdoor service and extremely high demands of performance. Newly reached positive results in cleaning the exhaust gases by filtering carbon particles and catalysts allow partial indoor service, but the competition of electric-powered vechicles with increased performance is high.

Table 5.1 Traction battery type for different kinds of service.

Kind of service	Kind of traction battery		
	Electric	Diesel	Liquid gas
Indoor service			
Food industry and food handling	+	–	o[a]
Basement operation	+	–[a]	–
Places with sufficient fresh air	+	o[a]	o[a]
Working areas	+	–	–
Places with no or little fresh air	+	–	–
Outdoor operation			
Cross-country-operation	–	+	+
Roadways in good condition	+	+	+
Working areas	+	o[a]	o[a]
Criteria for indoor and outdoor-operation			
High tonnage and high driving performance	–	+	+
Extreme temperatures	o	+	+
High rate of ascent	o	+	+
Explosive surrounding	+	–	–

+ = suitable; o = conditionally suitable; – = not suitable.
[a] Need for filtering the exhausted gases by particle filters and catalysts.

In principle the selection of the kind of traction has to be based on the kind of service and the environmental demands.

5.3.2 Physical Advantages of Battery-Powered Traction

Battery-powered traction means low noise generation, no pollution of gases, no vibration, simple mechanical propulsion components, simple electrical control and steering, usage of energy conforming to environmental demands, and last but not least lighter weight. This results in optimal conditions to fulfil environmental requirements and to make working areas healthier.

The relatively heavy weight of lead-acid batteries in relation to the useable performance has advantages for forklift trucks and other tractors (as counterweight or ballast), but is a great disadvantage for other traction systems such as electric road vehicles and mobile electric power supplies. Results in development with the aim to increase the specific energy and performance of battery systems and the minimization of their maintenance also have an impact on the employment of vehicles for materials handling.

5.3.3 Survey on Service Cost Calculation

Important factors to be regarded for the selection of the kind of traction battery to use are the fixed and running costs of the system. The guideline VDI 2695 "Ermittlung der Kosten für Flurförderzeuge" (Estimation of Costs for Vehicles for

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4.12 Limitation of operation

The local authorities can restrict the operation of diesel-powered vehicles in partly or totally closed rooms, if the same operation can be performed by traction systems free of pollution, e.g. electric traction. … Such restrictions can be ordered for the following cases:

- Driving in containers and partially closed trucks, railway wagons and ships.
- Driving in cold-storage houses and other storage houses.
- Supply of working places in factory buildings.
- Operation of drilling-equipment in mines.

4.7.1 Vehicles for materials' handling

Before purchasing of vehicles for materials' handling the user has to check whether the operation of diesel-powered vehicles can be partly or totally avoided in closed rooms. The operation of diesel-powered vehicles can be tolerated corresponding to the German legal regulation GefStoffV § 16.2-2, if:

- The transport task with electric powered vehicles needs less than one battery charge per shift, because
  a) A tonnage of less than 5 t is needed
  b) Seldom level differences of more than 1 m have to be overcome
  c) Average ranges less than 80 m per transport activity

- No extreme stress of the battery is expected, because
  a) No long breaks of operation occur (e.g. in seasonal operation)
  b) No extreme vibration occurs
  c) No extreme temperature exists (e.g. by operation in foundry)

Figure 5.1 Extract of survey on special regulations for the employment of internal combustion and battery-powered vehicles. Translation of German regulation TRGS 554.

Materials Handling), edited by VDI-Gesellschaft Materialfluss und Fördertechnik (VDI working group on materials handling and conveyance), is based on long-term practical experiences and enables—not only for forklift trucks—a relatively simple calculation for vehicles for materials handling. The guideline includes for a wide area of operation costs and calculation factors. The cost calculation concerns the following areas:

Time-dependent costs as to investment, write-offs, and interest, and *operational costs* as to energy consumption and maintenance, resulting in costs for 1 h of operation, in practice a useful and realistic estimate.

Table 5.2 shows an example of cost calculation based on the current VDI guideline. Not regarded is a calculating factor later on explained, the factor can be taken into account for different categories of service.

Category I—low duty

- Smooth and even surface of the roadway without essential ascent (up to 3%)
- Normal environmental conditions (e.g., temperature and humidity)
- Usage up to 50% (half the nominal load and half the time of service during one shift per working day)

Category II—normal (medium) duty

- Roadways with fastened surface, in addition to outdoor service on uneven roadways (ascents up to 6%)
- Increased pollution (dust, changing and higher temperatures)
- Usage up to 100% of the offered performance per 1-day shift

Category III—heavy duty

- Bad road conditions, cross-country operation (ascents > 6%)
- High pollution by dirt, temperature, aggressive atmosphere
- Usage mainly at 100% and two or three shifts

These categories of duty have direct impact on the economy of the relevant traction system. Generally the electric traction powered by batteries, e.g., for forklift trucks up to 3 tons, has the best economy for low and normal (medium) duty. Investment costs for electric vehicles are normally higher than those for IC-powered vehicles, but longer service life and lower operational costs compensate the higher rates for write-offs.

In practice an experienced user will not steadily calculate the costs, but will regard for the choice of the system company internal records and conditions of usage. Therefore, battery-powered and IC-powered systems will have their specific area of employment.

For the employment of special types of traction batteries the manufacturer can supply the client documents enabling practical cost calculations. As an example, see in Figure 5.2 a cost comparison for the Hagen battery types PzS and CSM-ECON. In any example all parameters have to be regarded resulting in such presentations.

5.4 DEMANDS ON BATTERIES

From the users' point of view, there are the following demands:

High electric performance by reasonable weight and volume
Long service life and minimal maintenance
Relatively low purchase costs
High reliability guaranteed by optimal finishing, not insensible to casual overload, deep discharge, or higher temperature
Type-spectrum of a manageable size

These demands cannot be realized at the same time. The physical properties of a lead-acid battery are limiting some combinations, e.g., long service life and service at high temperature.

Discussion of current technology regarding these parameters follows.

Table 5.2 Example of cost calculation based on current VDI Guideline 2695.

Investment	Factor	EUR	Service (years)	
Brand XXX, type YYY				
Basic equipment		5087.35	8	
Battery				
V =	24	1022.58	4	
Ah =	160			
Charger			16	
Special features			8	
Total investment		6109.93		
Operation duty category II	II			
Hours of service per year	600			
Fixed costs			EUR/Year	EUR/h
Write-offs			891.56	
Interest of 50% of the investment	11		672.09	
Calculated upkeep costs (fixed)	20%		127.06	
Safety check			102.26	
Calculated service costs			306.78	
Annual Fixed Costs			2099.75	
Fixed Costs per Operation Hour				3.50
Operation-dependent costs				
Battery traction				
Upkeep 0.8F (1.1+1.4)−2.4/2				
F = 0.12, category I				
F = 0.15, category II				
F = 0.17, category III	0.15		559.35	
Electr. energy per charge = (V)(Ah)(0.8)(1.8)/1000 (kWh)	6			
Electricity costs (EUR/kWh)	0.12			
Service hours per charge	3			
Energy costs per year			132.71	
Energy costs per service hour				0.22
IOC—traction				
Upkeep 0.8F (1.1+1.4)−2.4/2				
F = 0.15, category I				
F = 0.19, category II				
F = 0.22, category III			−51.13	
Specific fuel consumption (L/h)				
Costs for fuel (EUR/L)				
Sum per year			0.00	
Sum per service hour				0.00
Annual operation-dependent costs			640.93	
Sum of operation-dependent costs per service hour				1.07
Total annual costs			2740.68	
Total costs per service hour				4.57

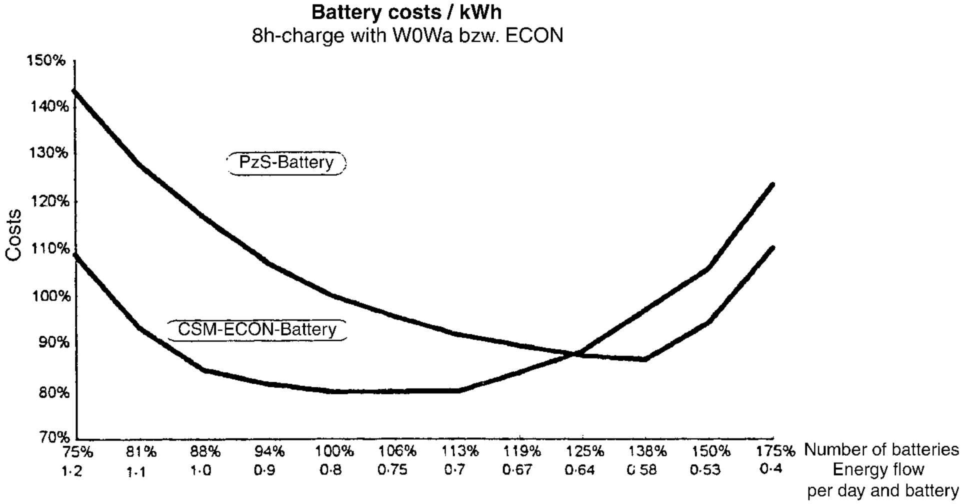


Figure 5.2 Comparison of costs for two different battery types.

5.4.1 Increase of Electrical Performance

The increase of electrical performance will be up to 20% by installing higher specific capacities by optimizing the grids and using the complete volume of a cell and increasing the electrolyte density. This requires more material (higher price), and the higher electrolyte density is restrictive to life expectancy.

5.4.2 Service Life

The service life of a lead-acid battery is influenced by several facts besides the quality of manufacturing, mainly by the kind of use. For example, deep discharges, higher temperatures, wrongly dimensioned chargers and charging methods, and high discharge currents reduce service life.

The temperature has the most important influence. A lead-acid battery can perform up to 10 years if the temperature is limited to 20 °C, while the same battery reaches the end of its life after only 1 year when operated at temperatures around 60 °C. Therefore all practicable measures should be performed to avoid higher temperatures if a long service life is wanted.

ZVEI has created a diagram (Figure 5.3) to determine the expected service life of a lead-acid traction battery with positive tubular plates; this diagram is a good basis for calculation, but it has to be noted that this diagram is only applicable for cells with a liquid electrolyte. For other cell types, e.g., the VRLA types, the diagram cannot be used.

5.4.3 Maintenance

Maintenance consists of two elements: servicing and upkeep, resulting in running (operating) expenses that get more and more expensive. Upkeep costs can sometimes be avoided, but servicing costs are calculable. To look for a maintenance-free design is important for the choice of a traction system.

5.4.4 Purchasing Costs

Purchasing costs of battery systems are regulated by competition. There are two procedures:

Purchasing the battery and the charger as a package from the supplier of the vehicle or truck

Buying and providing the battery and the charger by the user

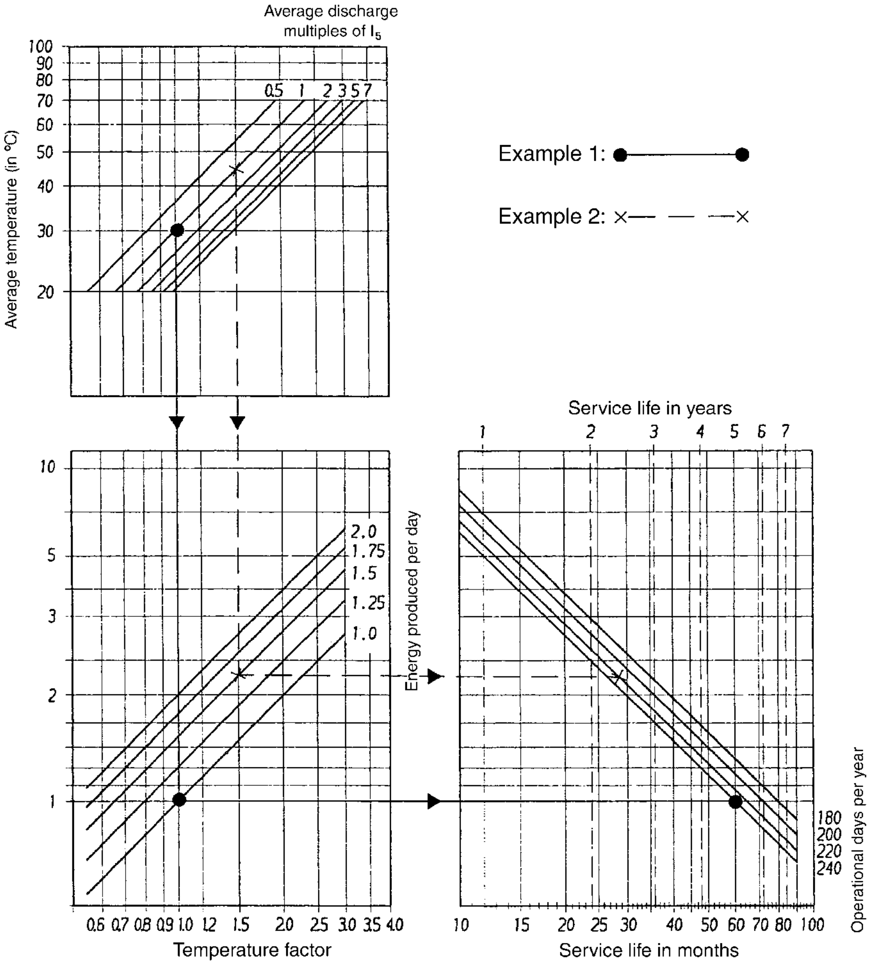


Figure 5.3 Diagram for calculation of the expected service life of a traction battery (type PzS with positive tubular plates).

Providing directly by the user makes more sense when better price conditions can be performed, depending on the quantity. Therefore central purchasing offices of big users have advantages. But also smaller users should check possible cost advantages of direct purchasing.

5.4.5 Safety of Operation

Safety of operation depends on the reliability of the components of a battery system. Falling outs of a battery system create quickly increasing costs for the user. Therefore a good mixture of demands on quality and price has to be found. The limits are between absolute quality not regarding the price level and the lowest price dominating, with risks of falling outs by low quality.

Looking at peripheral costs, as for installation, mounting, shipping, and fallout, today's recommendation must regard economy and ecology resulting in the choice of a product with high quality and a reasonable price.

To judge the operational safety a maximum of resistance against falling outs has to be noticed. Despite all planning in practice it cannot be avoided that from time to time a battery is deep discharged, overloaded, not sufficiently recharged, or operated at high temperature. Change of the kind of operation, failure of the mains, or other technical disturbances can be the cause. The higher the risks during operation, the higher should be the reserve in battery systems and vehicles. Today risks are often not calculated in order to keep the investment costs low. This can have a negative result as soon as a minimum of reserve is not at hand and when preventive servicing is not given. In general the outer limits are known by the suppliers and should be combined with the service schedules. Experiences of the user sometimes differ from the supplier's recommendations, but they have the higher priority.

5.4.6 Destinations of Types

Only standardized types should be chosen. The current states of the standards will be later demonstrated. In our region two standard types are established: DIN and BS, while in Germany the DIN types are dominating.

The selection of materials handling equipment should always include the right selection of the battery, especially when the user is the one who will order the batteries and the replacement batteries. Standardized batteries are cheaper and have shorter delivery times compared with specially designed batteries. This goes not only for the cells, but also for the trays. Here the vehicle suppliers often offer sophisticated solutions. To avoid extra costs for replacement the user should not accept such design.

It should also be mentioned that standardizing has disadvantages, because standards follow the state of the art of techniques with delay. Therefore a check is needed when purchasing new systems regarding how far a standard is necessary. Other disadvantages in application of the existing standards are that they are a compromise on a low level. But using the standards is always better than to accept the individual design of one supplier.

5.5 CONSTRUCTION AND SELECTION CRITERIA OF TRACTION BATTERIES

Notable manufacturers of traction batteries and chargers offer a wide scale of different constructions and designs making it difficult for the user to find an optimal solution. Cells with positive tubular plates (PzS) are most common in our region. Such cells perform between 1500 and 2000 cycles conforming to EN respective to DIN testing procedures. These cells are highly developed. So they are often chosen because of their high quality and long service life.

When only small traction performance is required, cells with flat plates (pasted plates) are used because of the lower price compared with the tubular cells. Cycles of 800 to 1000 can be performed. These types are on the market with a voltage of 24 V and capacities between 200 and 250 Ah.

In any case all advertising brochures of the suppliers should be read critically, and if arguments and figures are not plausible, the supplier should be asked for an explanation.

The following sections survey today's offering of systems and their classification to operational demands.

5.5.1 Standard Design of Cells Conforming to an Older Standard DIN 43 567

The lids of cells with positive tubular plates (PzS) are sealed with compound or the lids have a soft-rubber sealing; the terminals (poles) also have a soft-rubber sealing. That means this kind of cell is not electrolyte-tight. The cell connectors are from leaded copper bolted on the poles. Poles and connectors are insulated. These types of cells still have a relatively high content of antimony in the grids. The cells need maintenance such as cleaning and controlling of the cell connections. Therefore this standard has been withdrawn and is mentioned here only to give a complete survey. The use of this kind of design is no longer recommended.

5.5.2 Low-Maintenance Cells (Closed, but Not Sealed)

This "wet" design conforms to the older DIN 43 595 (dimensions conform to IEC 60254-2) and is the most popular type with tubular positive plates (PzS). The antimony content in the grids is very low; the cell covers and pole sealing are electrolyte-tight. The poles and cell connectors are insulated. The connectors' band end terminals can be delivered welded or bolted. This design is the today's European state-of-the-art of technology and basis for the following description of improved cell design.

Several manufacturers have developed special processes to produce cell connections to demonstrate product advantages against their competitors. Established manufacturers supply a good quality level, so the user finds no reason for a preference.

These low-maintenance cells are also available with high quality plug-in covers. This design only makes sense if the user has reason to open cells, e.g., for replacement of plate stacks or to remove mud from the cells to extend service life. This method is no longer of significant interest because of the high running costs and new better internal cell design (e.g., pocket separators) to avoid mud and short circuits. Last but not least environmental demands require high expense to ensure safe handling of sulfuric acid and its disposal, including the mud. So economical reasons together with improved cell design brought the end of this type for long-term usage.

The difference between welded and flexible bolted cell connectors cannot only be judged by looking at the manufacturing costs. The welded cell connector, made from lead, can only be removed by a drill process and be replaced by welding through educated personal (trained in hydrogen–oxygen welding). Easy removable bolted cell connectors ensure an optimal end terminal connection with no loss of material when cells have to be replaced. This design has economical advantages if the user performs maintenance and replacement in his own facilities. Figure 5.4 shows an end terminal design (Hagen patent).

5.5.3 Low-Maintenance in Improved Cell Design with Higher Capacities

Low-maintenance and enclosed cells with tubular positive plates (PZS) conforming to the older DIN 43 595 are also offered with improved capacities, up to 20% compared to the normal design. This could be performed by increasing the electrolyte density from 1.27 to 1.29–1.31 kg/L, enlarged plates and reduced space for mud collection, and a lower electrolyte level above the plates. These measures reduce service life, and therefore these cells should be used only if the higher capacity per volume is really needed, e.g., if a second battery per shift is no longer needed.

Very special among this kind of design are cells with the so-called CSM technique, delivered by the manufacturer Hagen. Instead of lead grids in the plates, leaded expanded copper sheets are used. This means a lower internal resistance,

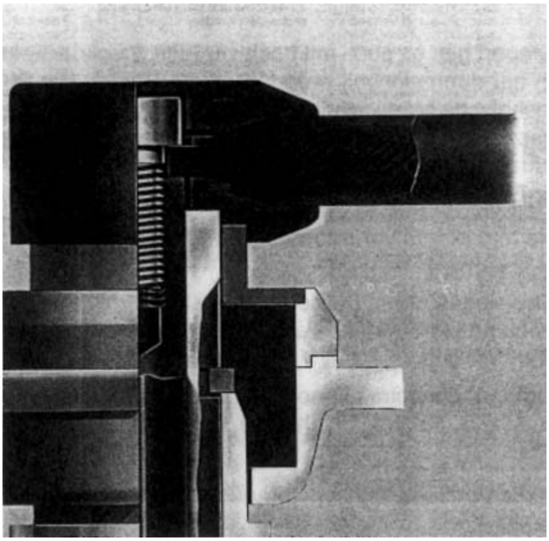


Figure 5.4 End terminal design, bolted and fully insulated (Hagen patent).

leading to a better voltage level, especially for higher voltage cells. For the use of this design the same argument pertains as mentioned before for cells with improved capacities.

5.5.4 Special Design for Heavy Duty

The demands for higher specific electrical performance, e.g., for operation in two or three shifts at elevated temperatures and the trend toward extremely reduced maintenance, were the reason to create batteries with battery water cooling and electrolyte circulation.

In cells with electrolyte circulation an air-pumping device is installed to mix the electrolyte of higher density in the bottom of the cell with electrolyte on top of the cell, where the electrolyte has a lower density. This means that the charging factor can be reduced from 1.2 to 1.03 with the effect that the charge time and the energy demand are reduced, while the water consumption is so low that water replenishment is only necessary after 200 to 250 cycles. The service life is as good as with normal vented cells. (See Figure 5.5.)

A further increase of performance for heavy duty operation with higher discharge currents can be performed by water cooling of the cells, leading to normal service life despite elevated environmental temperatures and heat generated by the higher discharge currents. The higher costs for this special design need technical consultation by the battery manufacturer to check if the application is economical.

5.5.5 Maintenance-Free Design—Valve Regulated Cells

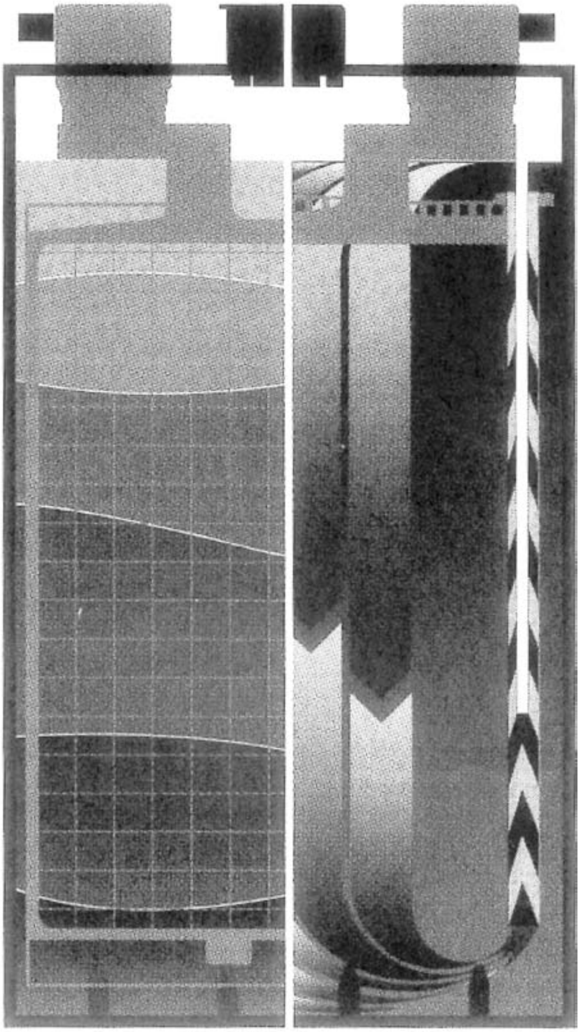
In cells in maintenance-free design the electrolyte is immobilized. The immobilization of the electrolyte reduces water losses when charged only with a limited voltage. Two designs are on the market: cells with a gelled electrolyte and cells where the electrolyte is fixed by a fleece between the plates. The cells are not totally sealed, because a vent is needed to regulate the internal air pressure of the cells. For more details see Chapter 1. The charging factor is lower as with normal cells: 1.05. Traction cells with gelled electrolyte have been introduced into the market by Sonnenschein in 1987 called dryfit. Other manufacturers followed and now there exists a standard and the design is well established for low and middle duty operation.

To get positive results with this design, the following rules should be regarded:

Operation only with low and middle discharge load and no extra stress by higher temperature; this means about 3.5 h of operation per day.
The depth of discharge should not be below 60 to 70% C_5.
The battery temperature should always be below 45 °C.
Charge methods and chargers conform to the battery manufacturer's specifications.

If these rules are regarded, the user will have good operational results.

Substantial for the economical success of this design is the maintenance-free operation. Water replenishment of wet cells to be managed by the driver of the vehicle is a critical procedure. Often the cells were overfilled resulting in spillage into


Electrolyte stratification

VARTA electrolyte circulation at the airlift principle

Figure 5.5 Cell with electrolyte circulation.

the trays with corrosion; or, if there was no replenishment in due time, the cells dried out and were damaged by heat.

For cells with immobilized electrolyte by fleece the same rules have to be regarded as for the gelled type. As an advantage it can be seen that in case of failure (water loss by overcharging), water can be added to continue with the service of the cells. Cells with fleece normally have pasted grid plates, while gelled types also with positive tubular plates operate with good results. Cells with fleece are offered mainly in smaller sizes as monoblocs.

5.6 CHARGING OF TRACTION BATTERIES

Besides the right selection of a battery to conform to the operational demands, the charging methods and chargers have a great influence on safety during service and service life. Optimal charging always means careful treatment but nevertheless effective for the battery and the operation.

The following demands on charging methods have to be regarded:

Limiting the temperature rise during charging
Switch-off when the battery is fully charged
Exact adaptation to the battery system to be charged
Enabling of booster charges and equalizing charges
Safe automatic switch-off to protect the battery in case of disturbances

5.6.1 Regulations and Manuals

Regulations concerning charging of batteries are numerous; only the important ones are mentioned here:

DIN/VDE 0510, Part 3	Accumulators and battery plants, traction batteries for electric vehicles
DIN 41 772	Rectifiers, shape and designation of charge characteristics
DIN 41 773, Part 1	Rectifiers, chargers with constant current/constant voltage characteristics
DIN 41 773, Part 3	Examples of characteristics
DIN 41 774	Rectifiers, chargers with taper characteristics
AGI	Working instructions: J 31: electrical facilities, buildings and rooms for battery service J 31, Part 2; charging stations, battery rooms

5.6.2 Chargers with Taper Characteristics

The most common chargers have taper characteristics, marked as W characteristics. (W for *Widerstand* in German, i.e., resistance). The internal resistance of the battery and the function of the transformer and rectifier control voltage and current during the charge process.

The simplest type is the **Wa characteristics** (a stands for switch-off). A charger of this type needs exact classification of the battery. To conform to the relevant standard the nominal current is $0.8 \times I_5$ (16 A/100 Ah) at 2.0 V/cell, decreasing when the battery voltage rises. When the gassing point of 2.4 V/cell is reached, the current has to be maximally $0.4 \times I_5$ (8 A/100 Ah) decreasing continuously to $0.2\ I_5$ (4 A/100 Ah). The charging time for an 80% discharged battery is about 11 h, limited by a timer. The simple design and the low price are reasons for the widespread use of these chargers.

A great disadvantage of this type of charger is the influence of the variation of the mains's voltage on the charge current and, corresponding to that, the variation of the charge time. Mainly overcharge can be observed together with elevated water consumption reducing the service life of the battery. Charging is normally performed at night after one-shift-per-day operation, a time when the mains has little load and an elevated voltage. (10% overvoltage of the mains means about a 50% elevated charge current.) Further on, batteries often are not discharged to 80%.

An improved characteristics is **WoWa** (o stands for switching from the first to the second taper characteristics). The first starts with a current 1.6 × I_5 (32 A/100 Ah). When the gassing point is reached (2.4 V/cell) by automatically switching with the second characteristic, the charge continues to conform to the above-mentioned Wa characteristic. By this method the charge time is reduced to 8 h, enabling shift operation. The same disadvantages as described before have to be regarded.

Chargers with W characteristics can be delivered with some improvements reducing the above-mentioned disadvantages. So a regulation of the main voltage stabilizes the charge current and the charge time. This kind of charger is cheaper than the chargers with voltage and current regulation.

When long service life and no maintenance is required, this type of charger should not be chosen.

5.6.3 Chargers with Regulated Characteristics

Chargers with regulated characteristics control current, voltage, and charging time corresponding to the data given by the battery. Originally this characteristic served as a means to get short charging times; now the reason for application is to get a smooth kind of charge. Therefore the range of application could be substantially extended. The price is not (or is only a little) higher than for modern taper chargers.

In the following section the functions of the regulated characteristics are briefly described. See also Chapter 12.

5.6.3.1 IU Characteristic—Charging with Constant Voltage

This characteristic limits the current I or the power P to the nominal values until the gassing voltage (max. 2.40 V/cell) is reached. Then the voltage is held constant with a little tolerance, so the charge current decreases.

This characteristic is applied in vehicles with IC engines (charged by generator) and as constant voltage charging for traction batteries. An advantage is the low gassing rate and the possibility for parallel charging of batteries having different capacities with the same nominal voltage. The application of relative high charge currents (1.5–2 × I_5) enables booster charging to 80% in a short time (3–4 h). The time to get a fully charged battery is very long (30–70 h), so for daily operation the amount of charge is not sufficient. Therefore every 5 days an equalizing charge has to be performed.

A disadvantage of the IU characteristic is that the individual battery cannot be controlled. Therefore it has to be regarded that only faultless batteries are charged by this method. This cannot be performed in practice, because failures of single cells can be overcharged and dry out by high temperatures.

5.6.3.2 IUIa Characteristic Enables the Optimal (Full) Charge

This characteristic has three steps, while variants work by the same basic principle. The U-step is held constant as long as the charge current drops to limited value, tolerable for the end period of charging. This current then is held constant while the voltage rises. The charge is switched off, controlled by a timer.

This characteristic offers a wide range of operation for all systems, charging the batteries very smoothly. A full charge can be performed in less than 8 h using a nominal current of 25 A/100 Ah. If there is no need for a very short charging time, the nominal current can be reduced to 10 A/100 Ah, corresponding to a charging time of 12–14 h. In any case the time available for the recharge always should be used to get the advantages of a lower purchasing price of the charger and the smooth charging.

The right correlation of the nominal current and the charge current for the third step has to be regarded. These values are independent of the charge time wanted and only dependent on the type of battery and its capacity. The controller is very flexible, able to be adjusted to the specifications of different battery types.

Figure 5.6 shows an example of the IUa characteristic; voltage and current have to be between specified tolerances.

The technical and operational demands on a modern charger are as follows.

All electrical functions include a faultless operation supplied by the mains as a TN/TT net with the allowed tolerances regarding disturbances or pulses (conforming with the specification VDE 0160). In addition the following properties can be specified: control of the electrolyte pumping system, the automatic replenishment system, and registration of all battery data during operation by computer management.

The design of the chargers is defined as a housing of steel sheet (protection class IP 21) with clear announcement of the corresponding class of battery (nominal voltage, nominal capacity and type of battery, nominal charge current). The front plate has to show the charge current, the charge voltage, and the following steps: "Charge," "Charge determined," and "Failure." Maximal length of cables to connect the charger with the mains and the battery with the charger is 3 m.

The factory code in the manual of the device shows the correlation of the charger to the battery. Later in the plant during operation, if necessary, an adjustment can be performed, but only by educated staff.

Modern electronic controllers offer additional information regarding different functions and failures regarding the given charge characteristics by the manufacturer.

From the author's point of view it is not the right way to have prescriptions for charge characteristics for all different battery trademarks and types. The better way is standardization.

5.6.3.3 Characteristics and Chargers for Special Charges

Float charge is a continuous charge with constant voltage—about 0.1 V higher than the open battery voltage (DIN 2.23 V/cell)—to compensate losses by self-discharge or in cases when a battery is out of order for longer time. Self-discharge is dependent on the type and the age of a battery. Maintenance-free cells are more insensible and can stay active up to around 1 year without any charge. Also low-maintenance batteries with liquid electrolyte may be stored without any charge up to 6 months. A precondition is always a fully charged battery. Aged batteries show self-discharge rates up to 1% per day.

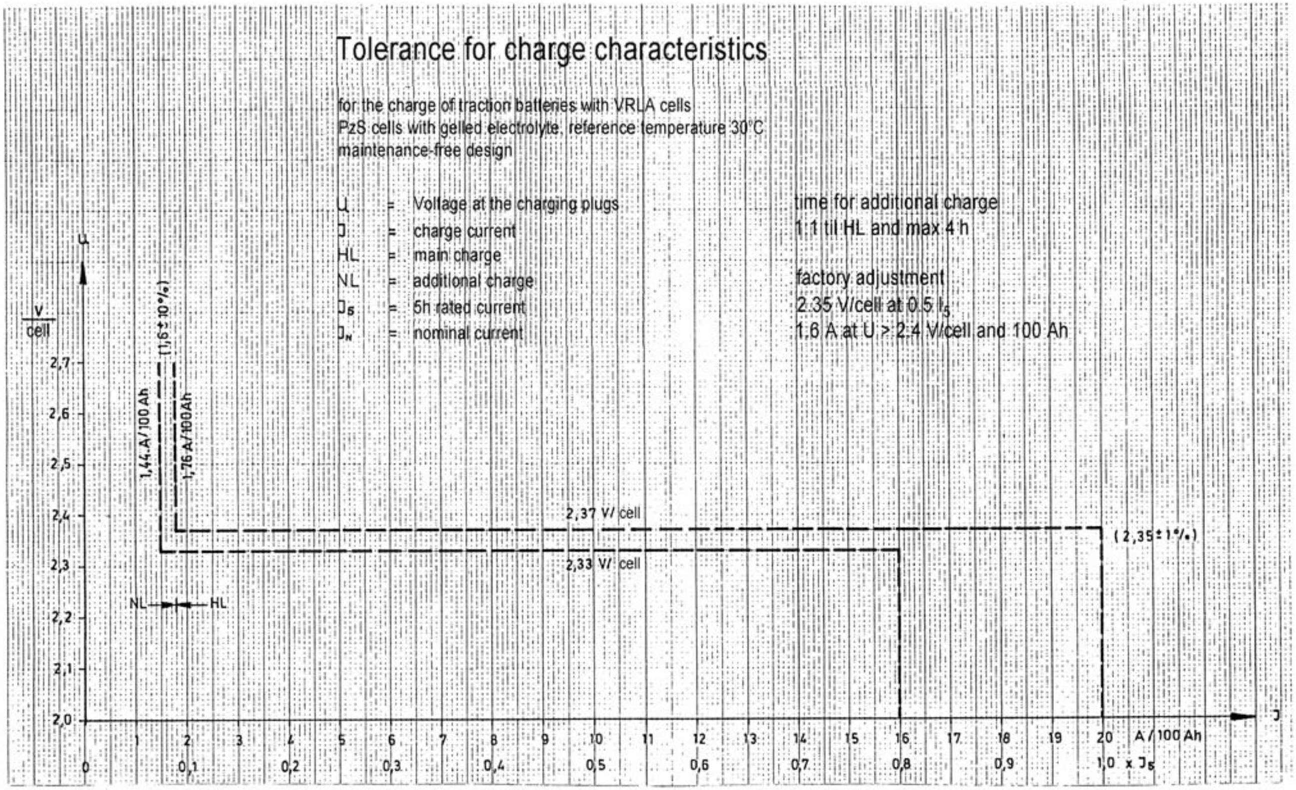


Figure 5.6 Diagram of the IUa characteristic.

To compensate self-discharge, constant voltage chargers (e.g., the IUIa type) may be used. The battery shall be connected to the charger in intervals of 6–8 weeks. The advantage of this method is that no special charger is needed.

Maintenance-free cells need careful float charge, best by an automatic charger to avoid extreme loss of water. This method is preferred if not all batteries are steadily in operation (rotation principle).

Equalizing charges are necessary to eliminate sulfate in the active material in cases when during operation phases of some days (e.g., 5 working days) no full charge can be performed by the constant voltage method. Further on the electrolyte stratification has to be equalized by charging in the gassing phase above 2.4 V/cell. Valve-regulated lead-acid (VRLA) cells show no electrolyte stratification, but the sensibility of these cells has shown that weekly equalizing charges are necessary because the normal charge is not a full charge.

Modern single chargers have characteristics performing automatically in long-time operation breaks to equalize charges, e.g., during the weekend. Educated staff can do it manually, e.g., with constant current 2 A/100 Ah for vented cells and 0.8 A/100 Ah for valve-regulated cells.

The measure for a successful equalizing charge is the electrolyte density, which only can be measured on vented cells. Valve-regulated cells need control of the open voltage after charge or a capacity test.

Booster charges are quick charges limited by the gassing voltage. Booster charges are a kind of "biberonage" to widen the range of a vehicle by an additional given capacity during pauses of operation. By this method in many cases the number of batteries can be reduced. It has to be considered that the service life of batteries often undergoing such booster charges is shortened, but the capacity in total taken out of the battery during operation is not shortened. Normally performing booster charges will reduce the battery costs.

Important for the realizing of booster charges with lead-acid batteries is a minimum time of 30 min; further beyond that the gassing point will not be passed over, and the maximum tolerable electrolyte temperature of 50 °C is observed. These parameters are difficult to plan and need experienced analysis at the scene.

The most critical charge is a charge to eliminate sulfurization. When deep discharge occurs often, re-maining of batteries in a discharged condition results in sulfurization of the active material. Often sulfurization cannot totally be eliminated by normal equalizing charges. Indications for sulfurization are losses of capacity and performance, rapid voltage, and temperature rise during charge.

With vented cells the sulfurization effect can be observed by measuring the electrolyte density when the nominal density cannot be reached. Vented cells need critical judgment of the open voltage or the result of a capacity test.

The measures to totally eliminate sulfurization are not economically possible. A controlled procedure—charging with a current between 0.1 and 0.15 A/100 Ah until a charge factor of 1.5 is reached—can be successful. This procedure needs days or weeks of time; therefore a decision on the scene is needed to do it or not. External service personnel for this task is very expensive; therefore sulfurization has to be avoided by regarding the manufacturer's instructions for charging and battery operation.

5.7 ORGANIZATION OF CHARGE OPERATION

Operational conditions of materials handling and the kind of buildings determine the course of battery charging. Only breaks during work periods can be used to recharge the batteries, either by a short booster charge or by a full charge with duration of 7 to 14 h. Normally the charging procedure is not watched over, so some measures to ensure operational safety and protection against accidents have to be regarded. DIN VDE 0510, Part 3, describes the safety regulations, in addition with DIN 0115, Parts 1 and 2, DIN VDE 0117, and DIN VDE 0122. In special cases, e.g., when explosion protection is required, additional regulations have to be regarded, prescribed in DIN VDE 0115, Parts 1 and 2, and DIN VDE 0170/0171. All the mentioned standards undergo harmonization by CEN and CENELEC resulting in European standards EN.

In the following section practical advice is given.

5.7.1 The Battery Room (Charging Room)

In battery rooms batteries and/or electric vehicles with batteries are temporarily placed to be charged. The chargers are placed in another nearby room, a "separate electric operation room." In the battery room the electrical plugs for the connection to the batteries are placed, protected by fuses. Control boards have signals for the steps of operation and for failures and breaks of the charging procedure. At any time by special switches the charge can be interrupted. This arrangement has the advantage that batteries and vehicles can be placed to provide ease of service. Installations of air ventilation can be centralized. All technical measures such as change of batteries, overhaul, and maintenance can be performed clearly. Educated personnel are necessary.

The chargers in the separate room are protected against aggressive gassing by the batteries, but longer cables and more equipment are needed for the remote serving of the plugs in the battery room. The voltage drop in the cables has to be calculated during planning. If extension of the charging time cannot be tolerated, special cabling for measurement only has to be installed; the installation of regulated transformers to compensate the voltage drop is more expensive.

The battery and vehicle manufacturers can provide special instruction sheets for the erection of battery rooms. (See recommendations J31, edited by Arbeitsgemeinschaft Industriebau e.V.–AGI.)

Rooms where batteries shall be charged are not under the rules for rooms with explosive atmosphere. The electrical installation and illumination equipment have to correspond to the standards for wet room installation. A minimum distance of 0.5 m between cells and electric spark–generating sources is strictly required.

Water outlets in the floor are very critical because acid separation from the water is required for the installation of a neutralization with no break control. These measures are very expensive and nowadays no longer practicable. Therefore no water outlets should be installed so sulfuric acid contaminated with lead cannot flow into the public sewer. To solve the problem of acid spillage the ground floor can be designed as a "tube" with a capacity to take the electrolyte of the biggest battery. Material to neutralize the electrolyte has to be in place. Proper disposal according to the legal regulations is necessary.

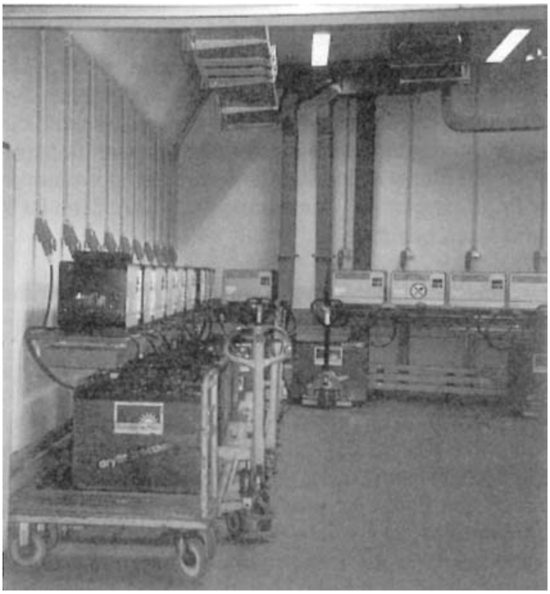


Figure 5.7 Charging station for batteries.

For air flow and ventilation see DIN VDE 0510, Part 3.

5.7.2 Battery Charging Station

A battery charging station is a room where batteries to be charged as well as chargers are placed together (Figure 5.7). Compared with the battery room the cables can be as short as possible for safe handling. Modern low-maintenance and valve-regulated types of lead-acid traction batteries—if sufficient airflow specified by DIN VDE 0510 is guaranteed—generate no corrosion of the chargers. This design is more economic as the one described in Section 7.7.1. The previous discussion of design and operation is similar.

5.7.3 Single Charge Point

To charge batteries in any working plants or storage rooms a single charging point can be installed. This is the most economic installation for the following reasons: There is no transport to the battery rooms or battery charging stations and no expense for the erection of battery rooms and charging stations. Booster charges are easily performed. This means dramatic cost reduction.

To realize such single charge points the following preconditions have to be regarded:

Sufficient room for the electric vehicle and the charger.
The single charge point has to be clearly marked as such; the place for the single charge point has to be free of other traffic and open for service.
A protection against other traffic in the neighborhood is recommended.

The charger has to be placed so it cannot be damaged.

Airflow and ventilation corresponding to DIN VDE 0510 has to be guaranteed.

No open fire, welding, or grinding in the neighborhood of the single charge point is allowed.

Batteries and chargers have to be protected against direct contact to dangerous voltage.

Modern types of low-maintenance and valve-regulated traction batteries fullfil the requirements so battery charging can be performed safely and under optimal economic conditions. In any case for overhaul, repairs, and maintenance there should be a workshop for internal or external educated personnel; the single charge point is not the right place for this.

5.7.4 Mobile Charge Stations

Mobile chargers are used to charge various batteries in different places. This application can be recommended only for special cases and the above-described rules are valid. The question of what shall be transported, the battery or the charger, has only one answer: preferably the battery. A special application is charging batteries in rail-bounded vehicles. Another special case is the electric vehicle with on-board charger. This design is very flexible in use, because a simple connection to the mains is sufficient. The user has to be advised that sufficient airflow is available when the battery is on charge. Preferably for small vehicles on-board chargers are in use.

But disadvantages of this design should also be mentioned. By installing the charger supplied by the mains in a vehicle the regulations of DIN VDE 100, Part 410 (DIN 57 100) have to be regarded; that means repair and overhaul can be done only by educated personnel. In addition the charger has to fullfil the specified requirements for vibration and shock resistance as for a nonspringy vehicle.

5.7.5 Protection Methods and Specifications

With all charging operations protection against accidents has to be regarded; the following main points are important:

Explosive gases generated by the batteries during charge are dissolved by normal or forced airflow. The battery charging area is a nonsmoking area!

Danger of short circuits from handling with current-conducting and noninsulated tools requires a total insulation of the battery intercell connectors and end terminals.

Danger of fire must not be underestimated. Defects and harms are rarities, but when they occur the costs are high. To avoid fire by high temperature, short circuits (due to defects on the cables, perhaps damaged by passing vehicles), etc., means prophylactic controlling and maintenance and keeping the batteries dry and in proper condition.

5.8 PERIPHERAL EQUIPMENT

Many different demands of users and variants of operation combined with different opinions about their realization forces suppliers to have high flexibility. This is demonstrated by the huge array of peripheral equipment offered for traction batteries. Not all of this equipment makes sense. In the following section some peripheral equipment is described and evaluated.

5.8.1 Venting Plugs

Venting plugs are a must for low-maintenance cells with liquid electrolyte. Simple plug-in vents with a 35 mm diameter have substituted bayonet caps. More solid is a hinged lid instead of one with a plastic film lid. Inserts to the plugs exist in many variants. Important is that the maximum and minimum electrolyte level can be watched easily. Electrolyte proof should be possible when the level is below the minimum. Good experience has been had with antispilling inserts to keep back the electrolyte in the cell during the gassing phase.

5.8.2 Electrolyte Level Indicator

Electrolyte level indicators are made from acryl rods fixed or bolted in the cell covers. They indicate the electrolyte level without the need of removing the vent plugs. The function can be explained by different brightness, depending on the deepness of the rod dipped in the electrolyte. The advantage is that watching the battery surface allows seeing the electrolyte level and the need for refill with water. Also there is an indication of the maximum electrolyte level to avoid overfill. The disadvantage is that annually this appliance has to be cleaned to remain at full functionality. This kind of appliance is until now seldom in use.

5.8.3 Regulating Vents

Vents in use on valve-regulated lead-acid cells with immobilized electrolyte instead of normal venting plugs have to be designed in a way such that the user cannot open or remove them.

5.8.4 Cell Connectors

Connectors between the cells have different designs depending on the manufacturer and are normally not interchangeable. If the user has its own repair facilities, this is a disadvantage in case single cells have to be replaced. Welded connectors can be replaced depending on the manufacturer’s design; bolted connectors need original spare parts.

5.8.5 Water Refill Equipment

For a long time automatic refilling devices for purified water have made maintenance easier; these are well known and reliable (Figure 5.9). There are two systems. The first is controlled by a vent plug with a mechanical working level indication, allowing

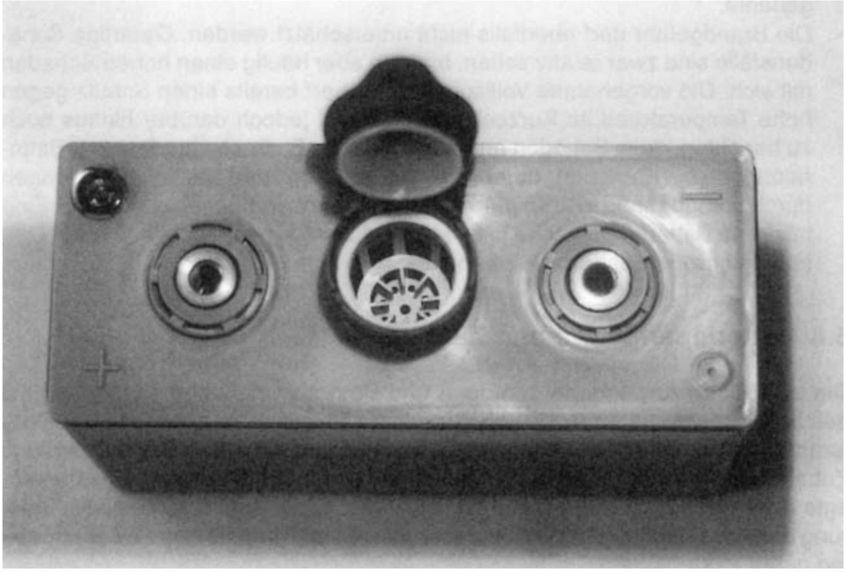


Figure 5.8 Cell with electrolyte level indicator, open vent plug with insert.

the check of the electrolyte density. There is a certain risk for overfilling, sensitivity to mechanical stress, and impurity of the water. The second one works with a so-called dipping pipe and is more precise allowing the check of the electrolyte level and density and is less sensitive to mechanical stress. In the case of mechanical defects both systems include the risk of overflowing the battery.

In any case refilling should start at the end of the charge. Water containers need a room free of frost. For large batteries with a high number of cells such water refill equipment is economical.

5.8.6 Recombination Plugs

Recombination plugs with a catalyst recombine the gases—hydrogen and oxygen—generated during charge to water flowing back into the cells. This method reduces the water loss to an extreme minimum, resulting in long maintenance intervals. In addition charging characteristics can also be influenced by the gassing rate, increasing the efficiency of the charge process. Important for the effective use of recombination plugs is the limitation of the surrounding temperature; otherwise the recombined water will not be condensed and escapes as vapor.

Recombination plugs have a fixed market share on stationary batteries as well as on mobile batteries. The mounting of the plugs has to be done very carefully, ensuring that cables do not move them from the right place disturbing their function by leakage. This point is the reason that recombination plugs have a limited field of application.

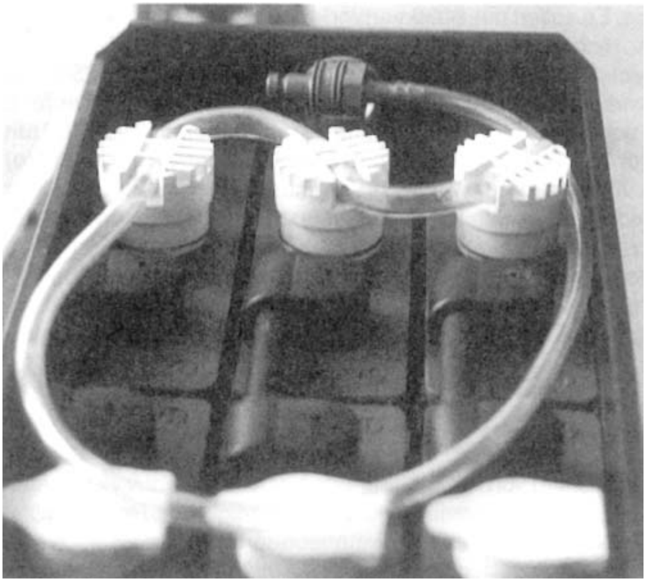


Figure 5.9 Watermaster refill plug.

5.8.7 Connections

Electrical plugs for traction batteries, chargers, electric vehicles, etc., exist in many variants. The European harmonized standard EN 1175-1 specifies required properties.

5.8.8 Capacity Indicators

Capacity indicators for traction batteries are on the market in many variants, of different reliability, and adapted to different battery types. This is understandable since the useful capacity of a lead-acid battery is dependent on several parameters, such as physical and chemical impacts, design and type of the battery, aging, temperature, and load. The user's demand in any case is to have a capacity indicator, comparable with a fuel indicator in a motorcar.

The very simple versions show only the battery voltage as a very rough indication of the capacity. Booster charges, aged batteries, and different battery types show a widespread scale of capacity values. The indication is not meant to avoid deep discharges.

Improvements in the development of electronics have allowed devices more accurate and easier for the user (Figure 5.10). These devices need only the battery voltage for indication, but show on a display the residual capacity, in percentage, of the nominal capacity and the remaining operation. The adjustment follows the individual characteristics of lead-acid batteries (low-maintenance or maintenance-free) or of nickel-cadmium batteries. Automatic switch-off breaks the operation of the lifting device of a forklift truck when there is danger for a deep discharge of the

Figure 5.10 Battery and time controller.

battery. The driver of a forklift truck can insert the right parameters in the capacity indicator in relation to a specific battery.

Another way to calculate the residual capacity of a traction battery is based on the evaluation of voltage and current. Both parameters have to be measured continuously, and the typical performance characteristics of a battery type have to be inserted in the calculation process. Often this type of capacity indication is part of the electronic control of a vehicle.

Normally the capacity indicator is a fixed part of a vehicle and is not considered by the buyer. The vehicle manufacturer makes the choice. Often during operation the indication is not watched because it seems not reliable enough. The vehicle is operated until a trouble occurs, e.g., the switch-off of the lifting device. This is to the debit of the safety of operation and the battery lifespan. Therefore the user should think about the expenses to get the right reliable capacity indicator.

5.8.9 Electronic Controllers

More and more costly control systems for batteries and charging equipment are of interest. Data collection and data transmission are used to identify a battery and to register the electric parameters under operation during discharge and charge. This enables the vehicle management of a plant a central controlling and steering of the electric vehicle fleet to identify the right time for service, maintenance, and replacement. Also this system has a great impact for leasing and rental systems.

Systems such as BICaT collect data via a microprocessor, a current measuring shunt, and a temperature sensor placed on a modified intercell connector and via a connection with the terminals of a traction battery. The transmission of all data is performed by a modern to a mobile data collector, e.g., a notebook.

Figure 5.11 shows the principle of the BICaT (**B**attery **I**nformation **C**ontroller **a**nd **T**ransmitter), a joint project of the following battery manufacturers: Hagen Batterie AG, Hoppecke Batterien, Sonnenschein GmbH, and Varta Batterie AG.

A system like this offers optimal organization, supervision, and steering of a battery fleet. It can be clearly understood that only successfully tested equipment has a chance on the market and this system is only for plants with major numbers of electric vehicles in use.

5.9 QUALITY ASSURANCE OF BATTERIES AND CHARGERS

To check qualified products the manufacturer has to install an efficient quality assurance system that guarantees the realization of all specified properties of a product. The best way for the manufacturer is to follow ISO 900. The purchaser can trust this system combined with a proven reputation of a product. If the purchaser defines the properties of the product, e.g., in technical terms of delivery, he has to also give detailed instructions for quality control. This goes for chargers as well as traction batteries, but it is easier for chargers than for batteries because capacity and life are the most important characteristics of a battery. These characteristics cannot be defined and measured easily. The main characteristics are defined in EN 60 241, Part 1, and the buyer of a battery can trust the supplier if he guarantees that he has tested the batteries corresponding to this standard with the following characteristics: (nominal) capacity or rated capacity, endurance in charge/discharge cycles, self-discharge, and water loss.

Regarding the expense of quality testing controlling quality characteristics, this can essentially be performed only in facilities of big users. Smaller users can profit from the testing of the big users; that means a product that is qualified by Deutsche Bahn AG, Deutsche Telekom, Bundeswehr, Mercedes Benz, or Volkswagen, just to mention some of the big users, is recommended for use also for smaller users.

Technische Lieferbedingungen (TL) are the technical purchasing conditions and *Technische Baurichtlinien* (TB) are the technical design rules that contain the modalities for quality assurance, both for qualification and for acceptance tests.

The tests for qualification are performed by the manufacturer and can be defined as a type test, e.g., that a battery shall have 100% of the nominal capacity

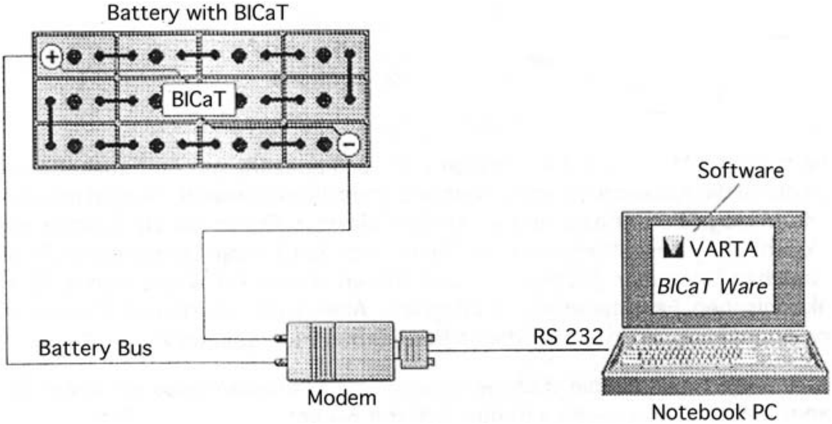


Figure 5.11 BICaT system. BICaT is mounted in the middle of the battery replacing an intercell connector.

after 10 discharge cycles with a DOD (depth of discharge) of 80%. New products require in addition a practical operation test of 12 months with a capacity test at the end of this period; the battery shall then have 100% of the nominal capacity.

Quality tests can be performed during acceptance tests and include optical control of the design and workmanship, dimensions, cabling, and accessories together with electrical tests. The electrical tests can be performed as sample tests.

Experience in practical use shows that not all manufacturers can guarantee the initially required performance data, but in all cases they can learn about and make improvements on their products to complete successfully.

Also the quality assurance of chargers make sense; worth mentioning is a type test and a sample test to check the main electrical and technical functions.

5.9.1 Capacity Tests

The capacity test of a traction battery is performed not only for quality assurance, but also to evaluate the endurance of the battery during operation. The capacity test is the only way to get a view of the electrical power of a battery. The test is described in EN 60 451, Part 1, as a discharge with a constant current I_5 (A), compensation of the temperature by 0.6% per degree if the electrolyte temperature differs from 30 °C. To execute a test qualified testing equipment and educated staff are needed.

Informative is the result if each cell of a battery is checked so that at the end of the test the capacity of all individual cells is known. This test can be performed annually and be limited on the second lifespan of the battery. This kind of surveillance will result in longer service life of the batteries in use. The test is only economic if enough samples can be chosen and the expenses for electronically controlled equipment (rectifier/alternator) are relatively low compared with the investment costs of the battery fleet. The normal user cannot run this kind of test.

5.10 MAINTENANCE AND UPKEEP

Besides the quality and the charge technique, maintenance and upkeep has an important impact on the service life of batteries. Regarding the investment costs for replacement batteries, upkeep reduces cost and prolongs battery service life. Upkeep includes all measures to preserve and to restore initial performance. In any case, inspection and maintenance are the first things to do.

Inspection and maintenance rules are set by the manufacturer and can differ from product to product, but the following daily inspection is always recommended:

- Inspection of the vehicle for safe operation (tires, steering, breakes, lights, and state of charge of the battery)
- In-time connection of the battery with the charger and control of the functions of the charger at the beginning of the charge
- Electrolyte level and refill with purified water
- Reporting of disturbances, especially those that can generate accidents, to the responsible office

To enable the operator or driver to take over the personal responsibility for the function of the vehicles and batteries, he has to be educated regularly and carefully.

Maintenance includes

- Cleaning (removal of dust and other substances)
- Preservation (measures to ensure endurance)
- Lubrication
- Refilling (e.g., water)
- Replacement of defective parts
- Adjustment (regulation in case of deviations),

Inspection includes

- Check of technical data compared with nominal values by measuring instruments
- Functional tests
- Optical check

Upkeeping includes

- Repair of parts
- Replacement of parts

When these tasks cannot be performed by the user but shall be the responsibility of the supplier, contracts on all details such as costs and scheduling should be arranged, keeping in mind competitive offers. Regarding the legal regulations to avoid accidents, the appointed times for inspection and maintenance remain the responsibility of the user.

If in the user's plant vehicles supplied by different manufacturers are operated, it can make sense to educate internal staff to perform maintenance and upkeep. Internal staff enables quick reaction on disturbances and shorter down times. Splitting routine work to performed internally and bigger upkeep tasks performed by external personnel also makes sense.

For upkeep by the user some advice is given in the following sections.

5.10.1 Traction Batteries

A critical check of the manufacturers' recommendations for maintenance is recommended because the operational conditions often require modifications. Normally for light duty operation the maintenance effort can be reduced. The type of battery and the peripheral accessories give important differences. Following is an example of the range of tasks for maintenance.

5.10.1.1 Daily Tasks of Operation/Charge

Charge the cell and keep the vent plugs of low-maintenance cells closed; remove cover mats; and limit electrolyte temperature to a maximum of 55 °C (random measurement by thermometer and density meter). Check the starting functions of the charger. After the end of charge control of the signal board of the charger, check the electrolyte level and remove moisture from the cell covers and connection of the battery to the vehicle.

5.10.1.2 Additional Weekly Tasks

Check the electrolyte level of all cells and refill with water if necessary. Remove moisture from the battery.

5.10.1.3 Additional Monthly Tasks

Check the electrolyte density of all cells; check the electrolyte temperature of a cell placed in the middle of the battery and make a written report. Control the fastening of the terminals.

5.10.1.4 Additional Tasks Every Three Months

Clean the battery; dry the wet surface of the battery; check the fastening of all intercell connectors; and grease if necessary.

5.10.1.5 Additional Tasks Every Half-Year

Check corrosion protection in the battery room. Clean the battery. Check the cables and plugs. Check the vent plugs. Check the open voltage of all cells and make a written report.

5.10.1.6 Additional Yearly Tasks

Clean the electrolyte level indicators. Check of the isolation of the battery (corresponding to DIN/VDE 0510) and make a written report. Perform capacity test (to be performed only in the second part of the lifespan of the battery) and make a written report.

5.10.1.7 Other Additional Tasks

Perform float charge for batteries stored out of operation (or every 2 months a normal charge for vented batteries, and an equalizing charge every 6 months for valve-regulated batteries).

Weekly perform an equalizing charge of batteries that are not normally fully recharged, e.g., batteries weekly charged by chargers with IU characteristics.

Perform equalizing charges of batteries showing sulfurization (if the nominal electrolyte density cannot be measured after a normal recharge).

Note: Maintenance work should be defined in technical instructions regarding the specific methods of operation for cleaning, all measurement procedures, capacity tests, and special charges.

5.10.2 Chargers

Maintenance of chargers is negligible. Optical control and a technical random check of the correctness of the charge characteristics are recommended.

For example, on a charger with IUIa characteristics and equalizing phase the following measurements should be performed:

- Voltage and current to the gassing point
- Voltage at half the nominal current

- Current in the third constant current period
- Equalizing current

If the charger is not operated in surroundings with extreme conditions, such as outdoor operation in wet or hot climate or in dusty atmosphere, a yearly inspection is sufficient. The tasks are as follows:

- Clean inside with airflow.
- Check the connection plugs.
- Check the fuses.
- Check all electrical functions and make a written report.
- Safety test corresponding to VDE 0100.

When battery-controlled systems are in use, there is no need to check the electrical functions because all data of the charger are registered by the system. It has to be noticed that upkeep inside the charger may be performed only by educated personnel (see VDE 0100). These recommendations are also valid for mobile and on-board chargers.

5.11 LEASING OF BATTERIES

Leasing and renting of batteries with full service provided is common nowadays. Complete batteries can be leased with full service avoiding any management problems for the user. These methods are economic for certain cases of operation.

After having read the previous sections, one may like the idea of leasing/renting with full service. There is no need for choosing the system and its components unaided, no need to organize maintenance; upkeep and disposal of spent material are taken care of. Such offers for leasing with full service, however, should be checked to see whether the technical service is qualified and financial conditions are appropriate.

In many cases, though, the user gains advantage by doing things internally when experienced staff is available and the distribution of this work with other work can be organized flexibly. Other users will see economies in external service.

5.12 DISPOSAL OF BATTERIES

The need for recycling of spent lead-acid batteries has been obvious for long time and did not need a political push. The recycling rate is near 100%, a result of contracts between user and supplier. The time when the user got reimbursement for lead batteries has passed because the recycling costs have increased partly due to the fact that the smelters have to fulfill many expensive measures against pollution. But this should be no reason for the user not to return the batteries and to avoid pollution despite the costs.

Recycling is not limited to the lead content of a battery. Plastic materials and metal parts can be recycled as well. Handling of sulfuric acid has to be done very carefully. Therefore normally the returned batteries will contain the electrolyte and the electrolyte is disposed of during the recycling process. Nowadays dismounting of plates and replacement of plates is no longer recommended because of environmental legislation demanding to keep wastewater clean. Neutralization and disposal of the electrolyte needs very expensive equipment.

5.13 FUTURE OUTLOOK

In the beginning of this chapter it was mentioned that the lead-acid battery, especially as a traction battery, will continue to maintain its premier position in the foreseeable future. Improvements are still possible. Besides improvements in performance and service life, we can expect the following coming improvements of traction batteries:

Maintenance requirements will be minimized.

There will be six instead of five even surfaces. All peripherical parts are hidden and protected against damage and dirt.

The electrical connections of the black box battery will be simplified, but technical internal tasks will be left to the experts.

Batteries with immobilized electrolyte having a cooling system and electrolyte circulation will be improved to a high degree of reliability and become more economical.

Battery controlling equipment will get a reliable finish, featuring easy data reading with a normal PC or notebook at an acceptable price.

European standards will be the basis for the improved design under fair conditions.

5.14 CONCLUSIONS

The lead-acid traction battery is the most important part for materials handling systems, but it needs optimal usage conditions, including product-specific training of its functions by qualified and educated personnel. This chapter gives the perspective of a large user of operating electric vehicles and trucks. Certainly, critical comments from other points of view are possible. There are as many opinions about operation, application, and maintenance as there are battery products. The common bases are the physical and chemical properties together with the electric behavior of a lead-acid battery, combined with the aim for economical and pollution-free operation.

REFERENCES

1. European Norm (EN) Standards (as listed in chapters 2 and 14).
2. Deutsche Institut für Normung (DIN) Standards (German Institute for Standardization) (as listed in chapters 2 and 14).

6

Safety Standards for Stationary Batteries and Battery Installations

H. WILLMES

6.1 INTRODUCTION

In Germany the generally acknowledged technical regulations are specified in the DIN standards (German Institute for Standards, Deutsches Institute für Normung). Specifically safety related standards must be observed providing for the protection of persons with reference to health and safety at work. In Germany safety related standards are classified as VDE regulations. The best known DIN VDE regulation for the "Erection of Electrotechnical Installations in Buildings" is DIN VDE 100, which has a "pilot function" and must be observed in general.

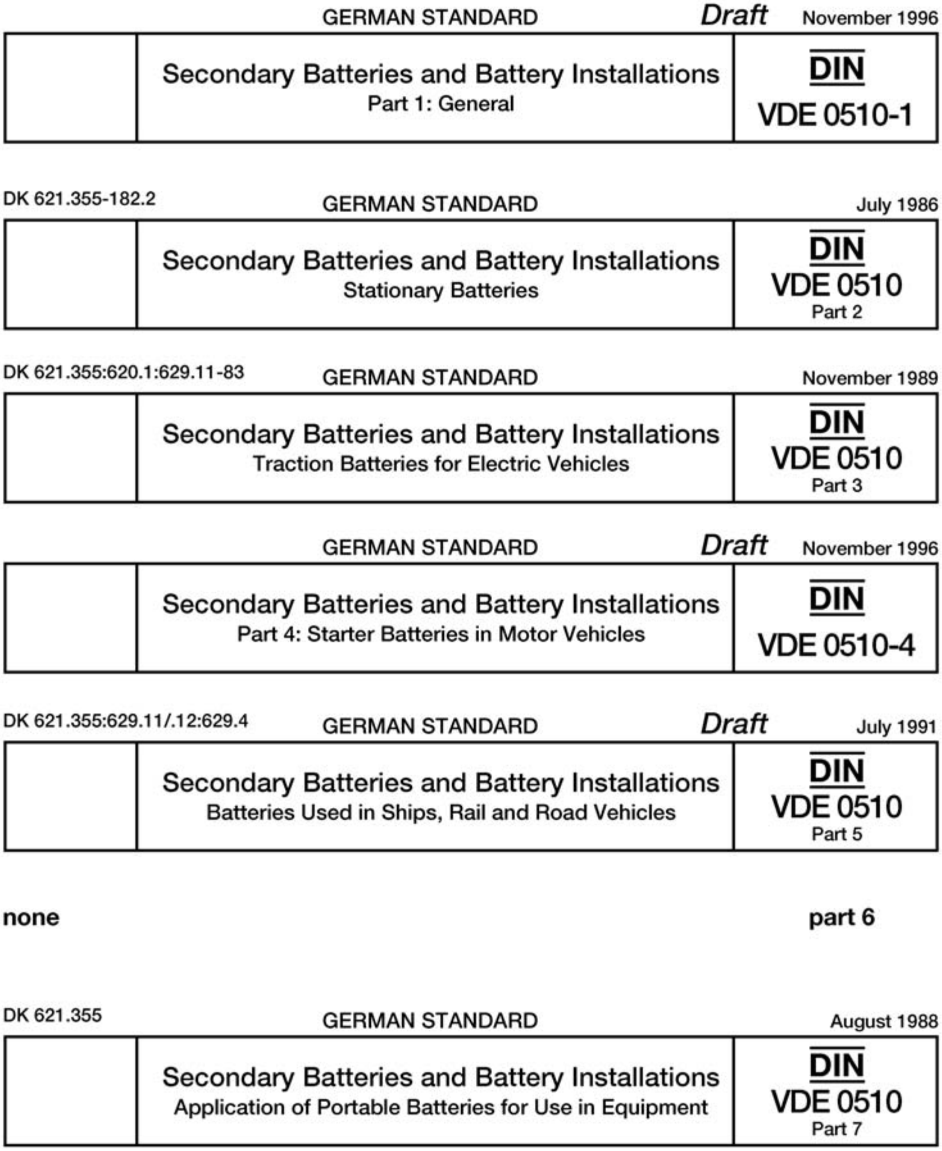
For batteries and battery installations DIN VDE 0510 applies (Figure 6.1). This VDE regulation includes the protective measures for avoidance of hazards and risks when installing and operating batteries. These practices are common in the following fields of application:

- Stationary battery installations.
- Traction batteries for electrical vehicles.
- Starter batteries in cars.
- On-board batteries in watercraft, rail, and road vehicles.
- Batteries for use in portable appliances.

6.2 SAFETY STANDARD DIN VDE 0510: "ACCUMULATORS AND BATTERY INSTALLATIONS"

In general the required measures specify how to avoid hazards and risks caused by

- Electricity.



GERMAN STANDARD *Draft* November 1996

Secondary Batteries and Battery Installations
Part 1: General

DIN
VDE 0510-1

DK 621.355-182.2 GERMAN STANDARD July 1986

Secondary Batteries and Battery Installations
Stationary Batteries

DIN
VDE 0510
Part 2

DK 621.355:620.1:629.11-83 GERMAN STANDARD November 1989

Secondary Batteries and Battery Installations
Traction Batteries for Electric Vehicles

DIN
VDE 0510
Part 3

GERMAN STANDARD *Draft* November 1996

Secondary Batteries and Battery Installations
Part 4: Starter Batteries in Motor Vehicles

DIN
VDE 0510-4

DK 621.355:629.11/.12:629.4 GERMAN STANDARD *Draft* July 1991

Secondary Batteries and Battery Installations
Batteries Used in Ships, Rail and Road Vehicles

DIN
VDE 0510
Part 5

none **part 6**

DK 621.355 GERMAN STANDARD August 1988

Secondary Batteries and Battery Installations
Application of Portable Batteries for Use in Equipment

DIN
VDE 0510
Part 7

Figure 6.1 List of published standards DIN VDE 0510.

- Electrolyte.
- Explosive gases.

resulting in

- Electrical protective measures, e.g. protection against direct and indirect contact.

Table 6.1 Survey of hazards and risks when operating batteries.

Hazard, risk	Potential of hazard
Electricity	High voltage and current, risk of short circuit
Electrolyte	Creeping currents (risk of fire), corrosion, caustic effects
Explosive gases	Hydrogen concentration >4% H_2 vol. in air is explosive, sources of ignition

- Protective measures against corrosive and caustic effects of the electrolyte, e.g. sulfuric acid (H_2SO_4) in lead-acid batteries and potassium hydroxide (KOH) in NiCd batteries.
- Requirements regarding ventilation of rooms, cabinets, and enclosures where batteries are located.

Table 6.1 summarizes which individual measures must be taken in relation to stationary lead-acid batteries.

6.3 DIN VDE 0510 PART 1 (DRAFT): “GENERAL”

Part 1, “General”, precedes the safety standards for the different areas of battery application, specifying basic, generally applicable requirements, for example,

- Nominal voltage of commonly used primary and secondary battery systems (Table 6.2).
- Preferred areas of application of different battery designs.
- Charge characteristics, limit values for charging currents, recharge time periods.
- Modes of operation (Figure 6.2).
- Electrical protective measures including cross-reference to pilot document DIN VDE 0100 Part 410.
- Reference values for currents and voltages for charging equipment relevant to the specific charging characteristics (Table 6.3).

Table 6.2 Nominal voltage of commercial secondary battery systems.

Designation	Electrodes +/−	Electrolyte	Nominal voltage	Gassing voltage
Lead-acid battery	Pb/PbO_2	H_2SO_4	2.00 V	~2.40 V
Nickel-cadmium battery	NiOOH/Cd	KOH NaOH (gas tight)	1.20 V	~1.55 V
Nickel-iron battery	NiOOH/Fe	KOH	1.20 V	~1.70 V
Silver-zinc battery	AgO/Zn	KOH	1.55 V	~2.05 V

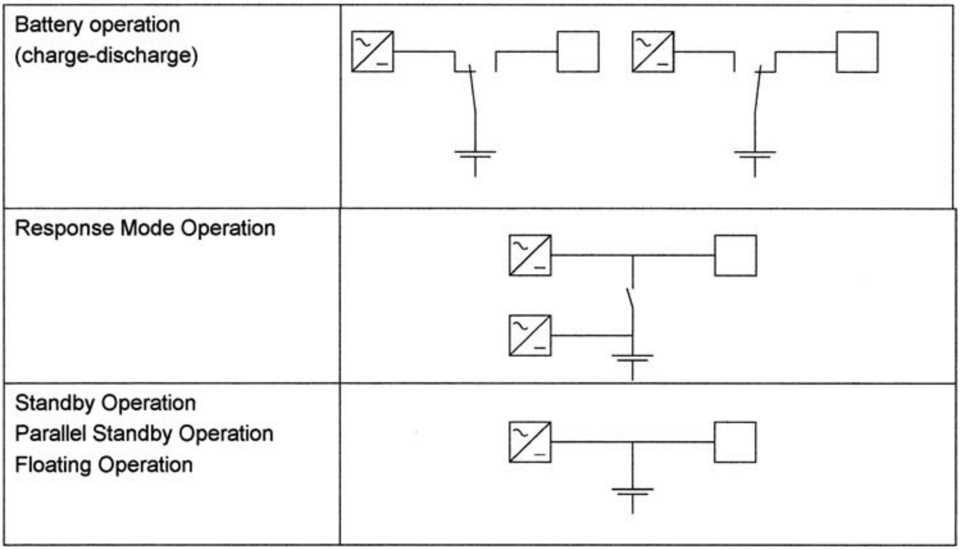


Figure 6.2 Modes of operation.

6.4 DIN VDE 0510 PART 2: “STATIONARY BATTERIES AND BATTERY INSTALLATIONS”

Some measures will be explained, e.g. in the case of stationary batteries providing an effective protection against hazards and risks during erection and operation of battery installations.

6.4.1 Hazards Caused by Electricity

Protective measures against direct and indirect contact (electric shock) are required depending on the battery nominal voltage and the chosen ground system of the electric network (Table 6.4). In the case of a system short circuit an effective protection can be achieved by incorporating a system with protective conductor and associated protective devices. In battery installations mainly an IT network or TN network is used.

Safe separation from the incoming mains supply by use of protection or isolation transformers is characteristic of a reliable DC power supply system and an effective protection measure (Figure 6.3).

A safe power source provides safety in case of failure of the transition of the AC voltage of the mains to the DC power side (Table 6.5).

Uninterruptible power supply (UPS) systems with galvanic connection to the incoming mains are an exception. In this case AC voltage against ground can be measured on the battery poles at the DC voltage side. (Recommendation: disconnect the entire UPS system for maintenance purposes.)

Electrostatic charge of the floor or of the clothing of personnel represents a specific risk when maintaining battery systems (Table 6.6). The energy of discharge sparks is sufficient to ignite battery charging gases (explosion!).

Table 6.3 Reference values for currents and voltages.
DIN VDE 0510 Part 1
Lead-acid batteries-Reference and limit values for currents and voltages applicable for charge equipment in dependance on the charger characteristic.
All currents are related to 100 Ah at nominal temperature.

		Ia characteristic current (A)		IU characteristic			IUIa characteristic			Wa characteristic			WoWa characteristic		
Lead-acid battery	Nominal capacity	With autom. disconnect when fully charged	Limit value for 72 h charge period	Initial charge current I (A) (reference value)[a]	Voltage limitation U (Vpc)[d]	Final charge current (A) (typical value)[a]	Initial charge current I (A) (reference value)[a]	Voltage limitation U (Vpc)[d]	Max. current, when fully charged I (A) (limit value)	At 2.0 Vpc	At 2.4 V/pc (limit value)	At 2.65 Vpc (limit value)	Initial charge current (A) at 2.0 Vpc (reference value)[a]	Switchover voltage U (Vpc) (0)	Current of taper characteristic (A) (limit value)
Traction battery GiS/PzS	C_5	5	2	20 to 30	2.4	2	20 to 30	2.33 to 2.4	5	16	8	4	20 to 30	2,4	8 at 2.4 Vpc 4 at 2.65 Vpc
Traction battery PzV[e]	C_5	–	–	10 to 20	2.23 to 2.4	0.1 to 1.5	10 to 20	2.3 to 2.4	1.5	–	–	–	–	–	–
Stationary battery OGi, OPzS, GroE	C_{10}	5	2	10 to 20	2.23 to 2.4	0.05 to 1.0	10 to 20	2.23 to 2.4	5	14	7	3.5	–	–	–
Stationary battery OGiV, OPzV[e]	C_{10}	–	–	10 to 20	2.23 to 2.4	0.1 to 1.5	10 to 20	2.23 to 2.4	1.5	–	–	–	–	–	–
Starter battery	C_{20}	10	2	50[b] 20[c]	2.4	2	–	–	–	24	12	6	–	–	–
Battery for portable equipment GiV[e]	C_{20}	–	–	20	2.27 to 2.4	0.1 to 1.5	–	–	–	–	–	–	–	–	–

[a] Current I is not limited when below gassing voltage. Specified values are valid for recharge periods of 8 to 14 hours, when IUIa, Wa, and WoWa characteristic is applied.
[b] For quick charge only.
[c] For traction purposes.
[d] After recharge is completed switch over to float charge or disconnect time-delayed (observe manufacturer's instructions!).
[e] Observe manufacturer's instructions.

Table 6.4 Hazardous voltages.

Voltage	Potential of hazard	Protection measure
<60 V	No risk	No specific protection measures required
>60 V <120 V	Hazardous	Protection against direct contact
>120 V	Lethal	Protection against direct contact and indirect contact

Table 6.5 Additional hazards caused by effects of the current.

Hazards	Measures
High currents (short circuit)	Limitation of short-circuit current by fuses or circuit breakers
	Short-circuit safe installation of leads
Corrosion	Keep insulation clean
	Prevent leakage current
Electrostatic charge	Prevent electrostatic charge of floors and cloths
Disturbed function caused by superimposed AC currents	During float charge: $l_{eff} \leqslant 5$ A per 100 Ah
	During charging: $I_{eff} \leqslant 20$ A per 100 Ah

Table 6.6 Prevention of electrostatic charge by certain conductivity.

Conductivity of surfaces/floors	
$R < 10^5\,\Omega$	Conductive
$10^5 < R < 10^8\,\Omega$	Not defined, surfaces conditionally conductive
$R > 10^8\,\Omega$	Insulating, electrostatic chargeable

6.4.2 Hazards Caused by the Electrolyte

Lead-acid batteries contain the electrolyte sulfuric acid (H_2SO_4). NiCd batteries contain mostly the electrolyte potassium hydroxide (KOH). Both electrolytes create burns and can cause injury to the skin. In the event of electrolyte entering the eyes burns of the cornea with permanent damage are possible (Table 6.7). For first aid wash with plenty of water and obtain medical attention.

Metal is corroded by sulfuric acid. Therefore metallic battery stands or cabinets must be protected by suitable paint or plastic coating. Potassium hydroxide is just as dangerous and attacks many organic materials. Use alkali-resistant paint.

Depending on the type and size of the installation use floor coverings resistive to the electrolyte or place in suitable trays. The warning sign WS2 according to DIN 40008 Part 3: “Warning for Hazards from Batteries” must be provided (Figure 6.4).

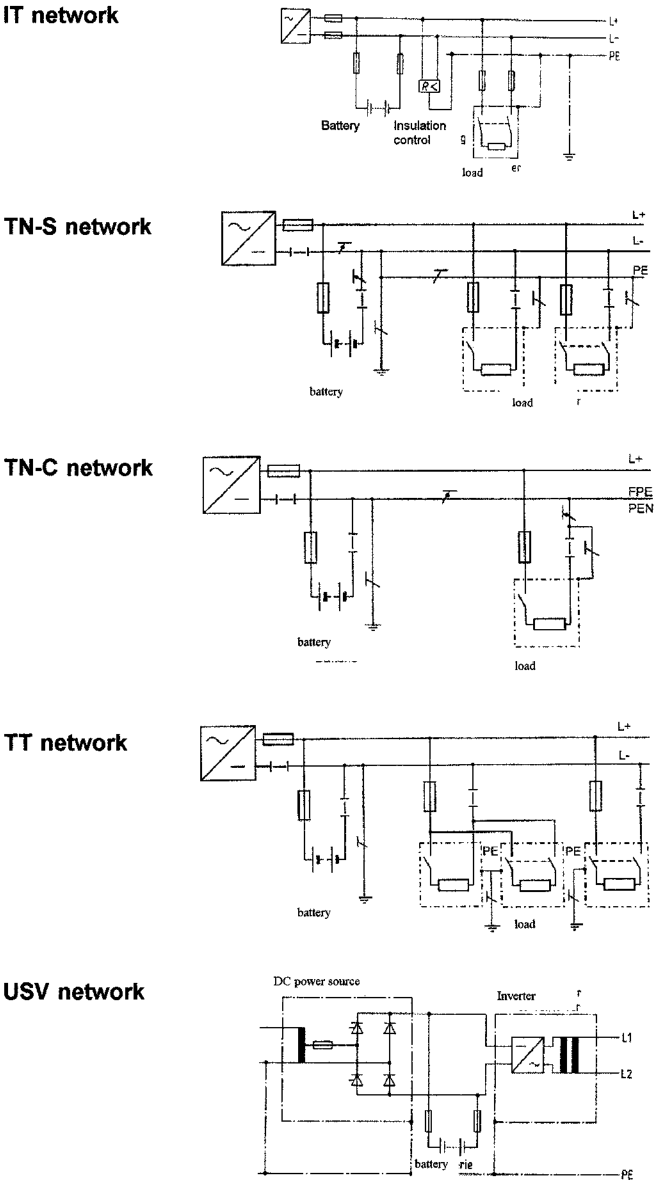


Figure 6.3 Network structures for DC power supply systems.

6.4.3 Explosive Charging Gases/Ventilation of Battery Rooms

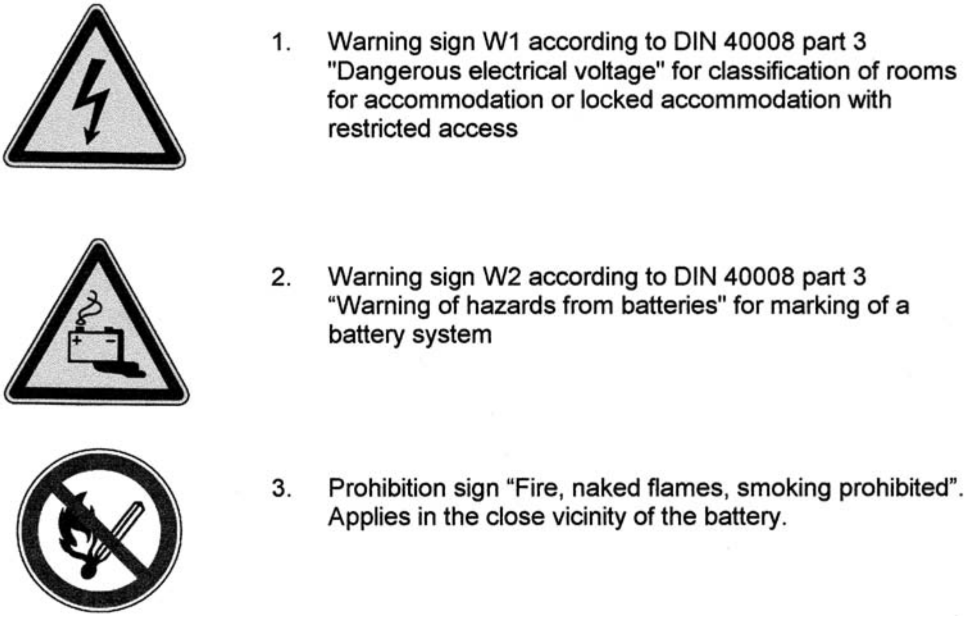
When charging batteries hydrogen gas (H_2) and oxygen gas (O_2) are formed as a result of electrolysis of the water. A content of 4% hydrogen in air is explosive. Basically the measures listed in Table 6.8 can be applied to prevent explosions. Dilution of hydrogen concentration is required by sufficient ventilation, because

Table 6.7 Effects from electrolyte.

Hazard	Measures
Burns of skin or eyes	Wear protective gloves and goggles. First aid measure: Wash with plenty of water. Medical attention required, especially in case of eye contact.
Corrosion of iron parts, concrete, a.s.o. due to spilled electrolyte	Electrolyte resistive floor or carpet. Electrolyte resistive paint. Limitation of spread of liquid electrolyte.
Sprayed electrolyte (aerosol)	Clean top of battery with water to prevent leakage currents. Use ceramic filter plugs.

generation of gases cannot be avoided when charging batteries. Spark-generating equipment in close vicinity of batteries is not permitted. (see Tables 6.9 and 6.10.)

The ventilation requirements for battery rooms, cabinets, and enclosures result from the required dilution of the hydrogen generated during charging and from the safety factors covering the battery aging and risk of failures (worst-case condition) (Figure 6.5). Ventilation is required for both ventilated and valve-regulated batteries. Also valve-regulated batteries release excessive charging gases through the valves.



1. Warning sign W1 according to DIN 40008 part 3 "Dangerous electrical voltage" for classification of rooms for accommodation or locked accommodation with restricted access
2. Warning sign W2 according to DIN 40008 part 3 “Warning of hazards from batteries" for marking of a battery system
3. Prohibition sign “Fire, naked flames, smoking prohibited”. Applies in the close vicinity of the battery.

Figure 6.4 Warning and prohibition signs.

Table 6.8 Measures to avoid explosion hazards.

Risk	Measure
Inflammable substances or mixtures of gases	Avoid these substances.
Sources of ignition	Dilute to noncritical concentration.
	Avoid sources of ignition.
	Sufficient distance.
	Protective encapsulation, "EX" protection.

Table 6.9 Sources of ignition for oxyhydrogen gas.

Naked flame
Flying sparks
Electrical, sparking equipment
Mechanical, sparking equipment
Electrostatic charge

Table 6.10 Measures to avoid explosions of oxyhydrogen gas.

Information for equipment in battery rooms
Sufficient natural or technical (forced) ventilation
No heaters with naked flames or glowing devices ($T < 300\,^\circ C$)
Separated battery enclosures with separate equipment
Antistatic clothes, shoes, and gloves (DIN 4843) surface resistance: $<10^8\,\Omega$
Cable hand lamp without switch (Protection class II)
Resp. battery hand lamp (Protection class IP54)
Warning and prohibition signs

Depending on the building conditions "natural" or "technical" (forced) ventilation can be applied for the technical design of the battery room ventilation. Aspects that must be considered are given in Tables 6.12 and 6.13.

At present, for stationary batteries, a safety distance of 0.5 m is specified according to DIN VDE 0510 Part 2. Inside this area ignition of charging gasses is possible. This applies for both vented and valve-regulated batteries.

The future European Standard EN 50272-2 (replacing DIN VDE 0510 Part 2) will have a new definition of the safety distance d (see Figures 6.6 and 6.7).

A frequent argument is that vented batteries require special battery rooms, but valve-regulated batteries do not. Valve-regulated batteries can be accommodated as one likes; but in this sense it is not correct. DIN VDE 0510 does not require separate battery rooms. This is a requirement of the owner/user who wants to have specific protection of the supply system, e.g. in case of fire or unauthorized access. This is to ensure system functionality even in cases of crisis (see DIN VDE 0108: "Safety Power Supply Systems for Public Premises", Regulations for Electrotechnical Installations in Buildings.)

Table 6.11 Reference values for current I (proposal for European standardization).

	Lead-acid battery vented type $Sb < 3\%$	Lead-acid battery valve-regulated type	NiCd battery vented type
Gas emission factor f_g	1	0.2	1
Safety factor for gas emission f_s (includes 10% faulty cells and aging)	5	5	5
Float charge voltage U_{float} V/cell	2.23	2.27	1.40
Typical float charge current I_{float} mA pro Ah	1	1	1
Current (float) I_{gas} mA pro Ah (refers only to the calculation of the airflow when float charging)	5	1	5
Boost charge voltage U_{boost} V/cell	2.40	2.40	1.55
Typical boost charge current I_{boost} mA pro Ah	4	8	10
Current (boost) I_{gas} mA pro Ah (refers only to the calculation of the airflow when boost charging)	20	8	50

Table 6.12 Technical design of "natural" ventilation of battery rooms.

Air inlet and outlet is required
Minimum free area of opening: $A \geq 28 \cdot Q$ (A in cm^2, Q in m^3/h)
(assumption: air velocity $A_{ir} = 0.1$ m/s)
Amplification of ventilation by use of a chimney (air ducts)
Ventilation into the outside ambient
(not to air condition systems or adjacent rooms)
Workplaces are considered to be sufficiently ventilated when the room volume exceeds $\geq 2.5 \cdot Q$

Table 6.13 Design of ventilation in battery rooms.

Forced ventilation with fan (exhauster)
Air exchange in accordance with air flow Q
Intake air must be clean
After-running of fan for 1 hour required when charging with plenty of gassing
Airflow = sum of Q when charging more than one battery in the room
Avoid ventilation short circuit by applying sufficient distance between air inlet and outlet

Ventilation air flow Q

$$Q = v \cdot q \cdot s \cdot n \cdot I \cdot \frac{C}{100\ \text{Ah}}$$

v = dilution factor = 96% air / 4% H_2 = 24

q = generated amount of hydrogen = $0.42 \cdot 10^{-3}$ m^3/Ah

s = safety factor = 5

n = no. of cells

I = current per 100 Ah

C = nominal capacity of battery

Combined factors:

$v \cdot q \cdot s = 0.05$

$$Q = 0.05 \cdot n \cdot I \cdot \frac{C}{100\ \text{Ah}} \qquad (Q \text{ in } m^3/\text{h},\ I \text{ in A})$$

Figure 6.5 Ventilation of battery rooms.

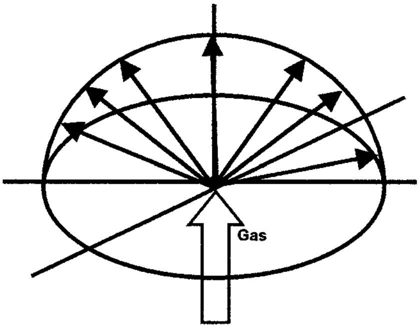
6.5 DIN VDE 0510 PART 3: "TRACTION BATTERIES FOR ELECTRIC VEHICLES"

Additional requirements for batteries in electric vehicles result from the legislation of the European Union, e.g. "Essential Safety Requirements of the Machinery Directive". This results in requirements like battery marking and declaration of precise battery weight (because of the counterweight of the battery in forklift trucks). Ventilation is also required during vehicle operation due to residual gases after charging.

For more details see chapter 4.

6.6 DIN VDE 0510 PART 5 (DRAFT): "BATTERIES ON BOARD CRAFTS OR VEHICLES"

Many national and international regulations must be observed in the case of ships or watercraft. An important deviation from the other parts of DIN VDE 0510 is the increased safety factor for the air ventilation (s = 10), because of the solid steel walls of the crafts or vehicles, e.g. of ships. The exchange of air may be hindered by air-tight bulk heads. This applies also for ventilation in passenger rooms, e.g. in trains or street cars having batteries below the passenger seats. Any risk of oxygen/hydrogen explosion must be avoided in these cases.



Volume of a hemisphere

$$V_h = \frac{2}{3}\,\pi\,d^3$$

Required air flow for the dilution to 4 % in air of generated hydrogen H_2

$$Q_{gas} = 0{,}05 \cdot (n) \cdot I_{gas} \cdot C \cdot 10^{-3} \left(m^3/h\right)$$

$$Q_{gas} = V_h / t$$

Required radius of hemisphere

$$d = 28{,}8 \cdot \left(\sqrt[3]{n}\right) \cdot \sqrt[3]{I_{gas}} \cdot \sqrt[3]{C} \;(\mathrm{mm})$$

Figure 6.6 Calculation of the safety distance d.

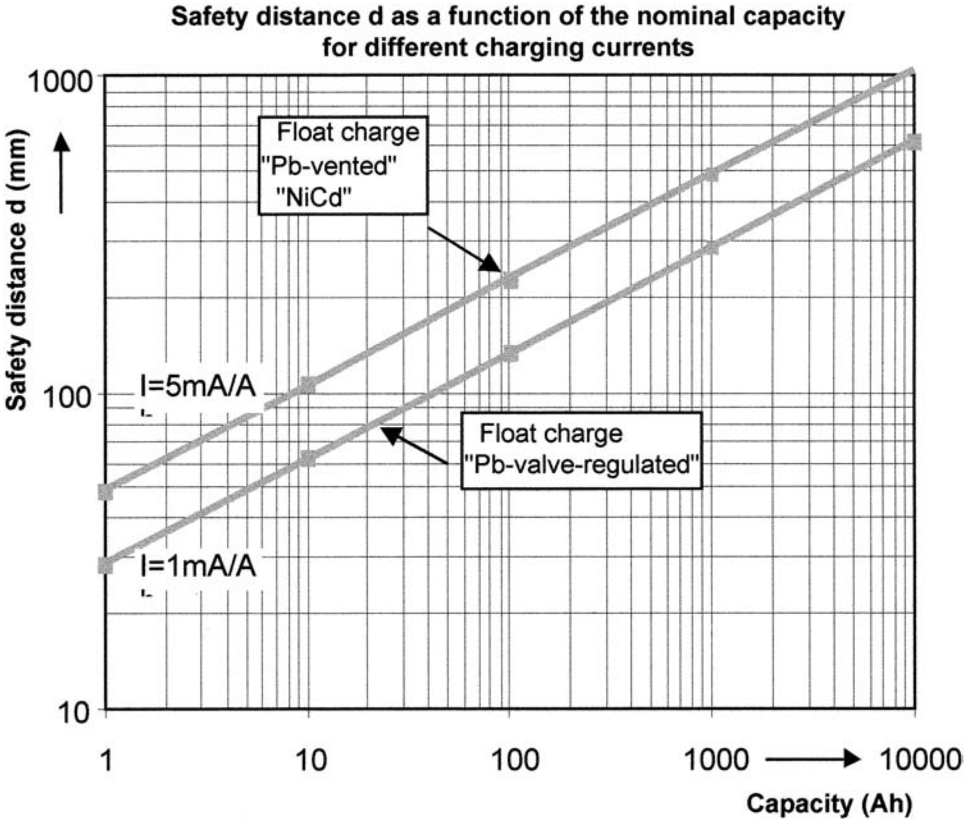


Figure 6.7 Safety distance d during float charge.

6.7 DIN VDE 0510 PART 6: "PORTABLE BATTERIES"

Small batteries are quite often an integral part of appliances, e.g. razors, mobile phones, computers, etc. Specific requirements must be observed, for example:

- Exchange with primary batteries.
- Marking of polarity, noninterchangeability.
- Ventilation of battery enclosures, which must not be hermetically sealed.
- Marking for protection of children, e.g. on button cells (swallowing hazard).

6.8 DIN VDE 0510 PART 4 (DRAFT): "SLI – STARTER BATTERIES"

These batteries are quite often used and charged outside cars. Repeated accidents are caused when jump-starting without expertise. The survey shown in Figure 6.8 gives information about the correct sequence for jump-starting.

1. Use the right "jump leads" for otto motors or diesel engines.
2. The capacity of the current supplying starter battery (e.g. 45 Ah) can be less than the capacity of the discharged battery.
3. Only batteries having identical nominal voltage (e.g. 12 V) should be interconnected by the "jump lead".
4. No contact shall exist or be made between the car bodies.
5. Keep away sources of ignition, like naked flames, cigars and cigarettes, sparks from starter batteries (risk of explosion).
6. Don't lean over starter batteries (risk of burns). The electrolyte of a discharged starter battery stays liquid even at low temperature.
7. The discharged starter battery should not be separated from the associated on-board electrical system.
8. Switch off the ignition of the car before connecting the "jump leads". Brakes must be pulled. Put gear stick into neutral, or park for automatics.
9. Attach the jump in such a way that they cannot be snagged by rotating parts of the motor.
10. Connect and disconnect the leads in the following order

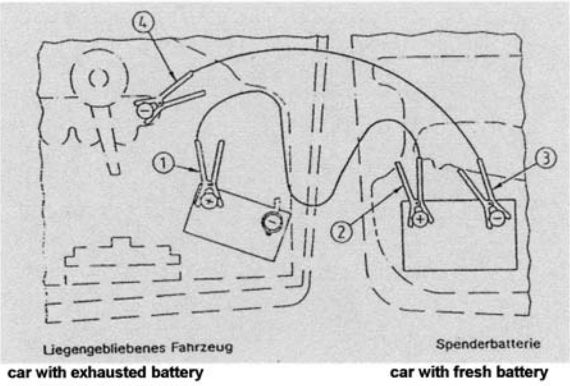


Figure 6.8 Information for the use of jump leads.

6.9 INTERNATIONAL STANDARDIZATION

The safety requirements shall be identical worldwide and must be standardized internationally. This is provided by the IEC (International Electrotechnical Commission). Within Europe national standards can form trade barriers, which must be harmonized. This work is done by CENELEC (European Committee for Electrotechnical Standardisation). Actually the safety standards for stationary batteries and battery installations are being drafted to become a European Norm. The norms for traction batteries and portable batteries will follow.

REFERENCES

1. CENELEC International Regulations, Parts 1–4.
2. DIN VDE 100 and DIN VDE 0510, German Institute for Standards.

7

Batteries for Stationary Power Supply

H. FRANKE

7.1 INTRODUCTION

Today the most important electrochemical storage systems for stationary applications are the lead-acid and the nickel/cadmium systems. Both of them have advantages and disadvantages which carefully have to be considered for best selection.

Batteries for telecom applications are specially designed for long service life and hours of discharging time. Batteries for UPS applications are designed for discharges with high current over short times (minutes). Special battery constructions are offered for the different requirements. In case of high safety demands, stationary batteries that ensure long service life are preferred.

Already today valve-regulated lead-acid batteries are in widespread use in many applications, and this trend will increase in the future since the reduction of maintenance is a significant advantage. This battery system requires high quality of all parameters that influence the performance and other characteristics. Valve-regulated lead-acid batteries that are installed in cabinets require sufficient air circulation to achieve equal temperature for all cells or monoblocs. Monitoring or control systems may be used.

For selection of the correct size of a stationary battery, manufacturers issue data curves and tables with the performance dates and installation rules to their customers. Most tables are calculated by special computer programs, and they include applications with varying current profiles during discharge.

Monitoring of stationary batteries is especially important to ensure a safe energy supply and the desired service life of the battery:

- For vented batteries there are many proven service methods.
- For valve-regulated batteries new methods of measurements and monitoring are necessary. Quite a number of automatic monitoring systems have been developed in the past; their reliability must be proved in the future.

7.2 STATIONARY BATTERIES

Stationary batteries have been applied for more than 100 years. During this time they have reached a technical design of very high reliability; they are the most reliable back-up power sources. Nevertheless, the application requirements for stationary batteries are quite different to a traction battery:

- A traction battery in general will be charged by a charger and then discharged, e.g. by a forklift. Thus the moment when it has to be ready for discharging is well known, e.g. the beginning of a shift, and the battery can be put into the required condition. Also the time for recharging can be adjusted. Thus the working cycle of the battery is determined.
- Stationary batteries, on the other hand, must do their work when the main power fails, and nobody can forecast when this will happen and how long the failure will last.

Many investigations have been made to find out how often and how long the main power network fails, but all of them are only statistics (see Figure 7.1). To accomplish such unexpected challenges stationary batteries need a high grade of reliability. Experience by important battery customers shows a failure rate below 0.25% per year. For example, when 8000 battery plants are installed by one customer, less then 20 of them will endure a failure during a year. Other investigations by a UPS manufacturer show mean time between failures (MTBF) of more than 100,000 hours, which means more than 11 years.

From the multitude of available storage systems – some of them only in a theoretical state – in stationary applications, mainly lead-acid and nickel/cadmium batteries are applied in a large scale. (Figure 7.2 shows examples of possible battery systems.) There is a wide field of application for stationary batteries. Figure 7.3 shows the most important applications for nickel/cadmium and lead-acid batteries. More than 90% of them employ the lead-acid systems.

The required discharge times are quite different: they can vary between some seconds in applications like diesel starting up to a month in solar plants. In some special cases there are further requirements, e.g. for UPS devices the connected power supply requires constant power. That means when the battery output voltage decreases, the discharge current automatically is increased. This has to be considered when selecting the battery.

In general, most applications can be divided in the following groups:

- Equipment for communication and information systems.
- Equipment for memory protection.
- Equipment to protect human lives.

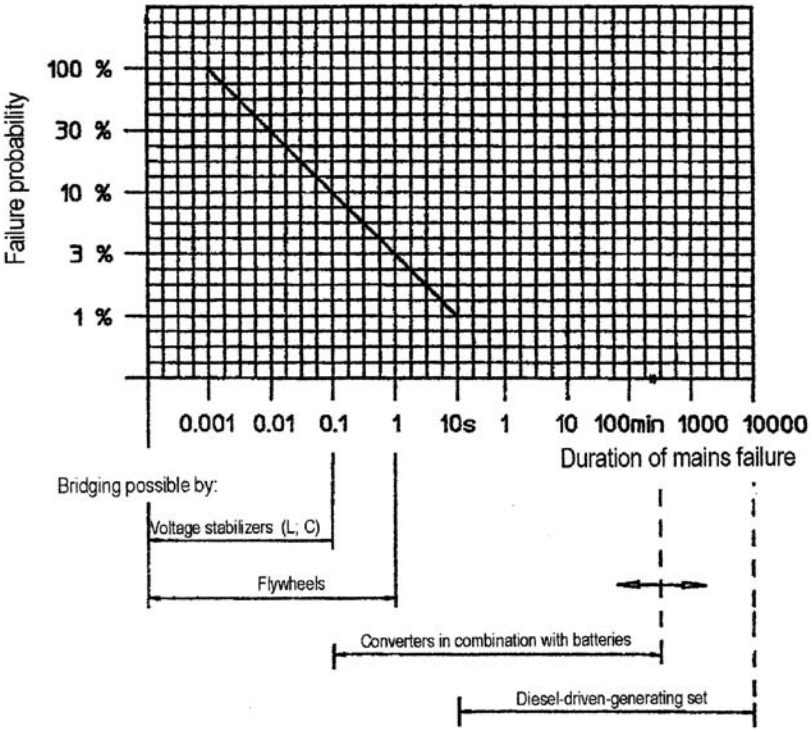


Figure 7.1 Power failure characteristic.

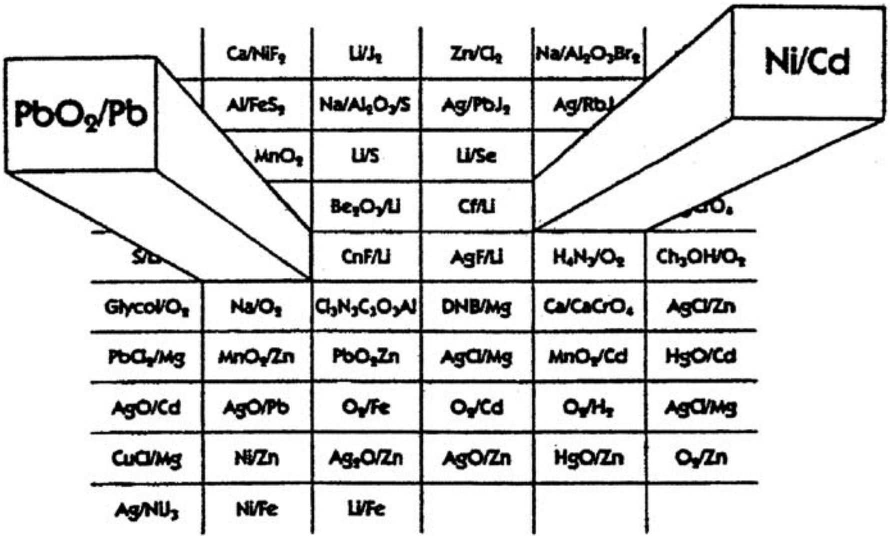


Figure 7.2 Examples of possible battery systems. Some of them are hypothetical, some important for today's portable applications like nickel/metal hydride or lithium-ion systems are not shown.

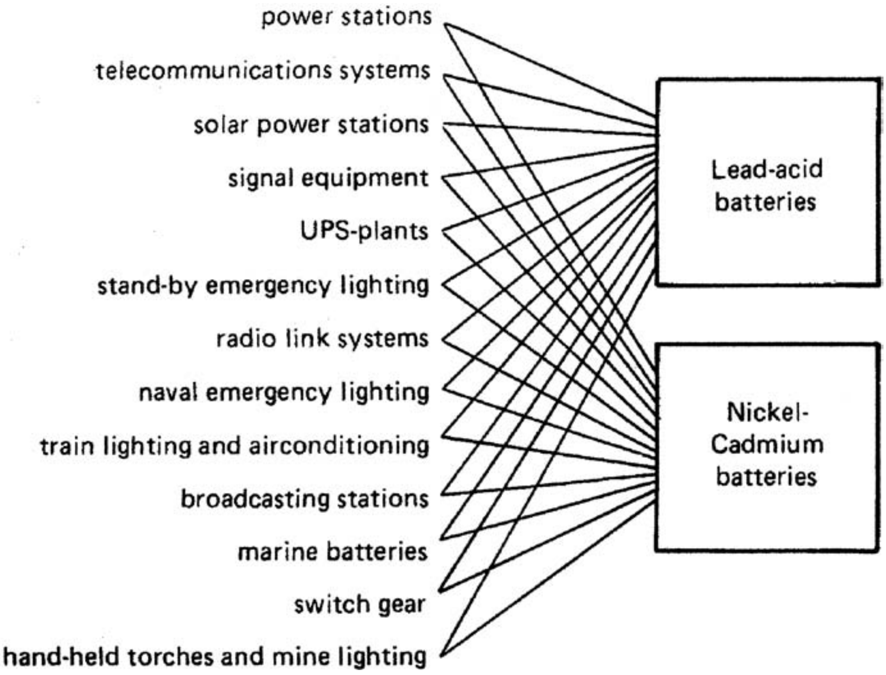


Figure 7.3 The most important applications for stationary lead-acid and nickel/cadmium batteries.

- Equipment for emergency power supply of technical facilities and processes.

Today stationary batteries are mostly connected in parallel with the DC power equipment and the consumers (see Figure 7.22). In case of emergency lighting also switching devices are usual. Batteries with additional cells that are switched in during discharge are more seldom seen, predominantly in older installations.

7.3 CELL AND PLATE DESIGN

Lead-acid and nickel/cadmium batteries differ in plate design, as shown in Figure 7.4. In lead-acid batteries the type of the *positive* plate designates the cell type. The *negative* plate always is a grid plate. In traditional nickel/cadmium cells and batteries the *positive* and the *negative* plates are of the same construction.

Figure 7.5 is a general survey of the different plate types and their combination in cells of both systems. In Figure 7.6 and Figure 7.7 the most usual plate construction for lead-acid batteries are shown, in Figure 7.8 today's construction of plates for nickel/cadmium cells.

Figures 7.9, 7.10, and 7.11 show examples for single cells and bloc batteries with lead and lead-dioxide electrodes; in figure 7.12 a nickel/cadmium cell with pocket plates is shown housed in a steel container.

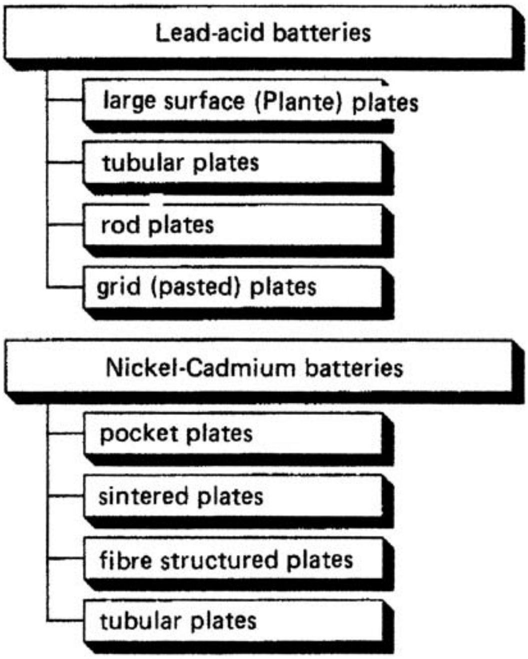


Figure 7.4 Different plate designs for lead-acid and nickel/cadmium batteries.

All cell constructions discussed above are of the *vented* type that have covers with openings that allow the escape of gas. Through this opening also water or electrolyte can be refilled. To reduce evaporation, usually the opening is closed by a vent cup.

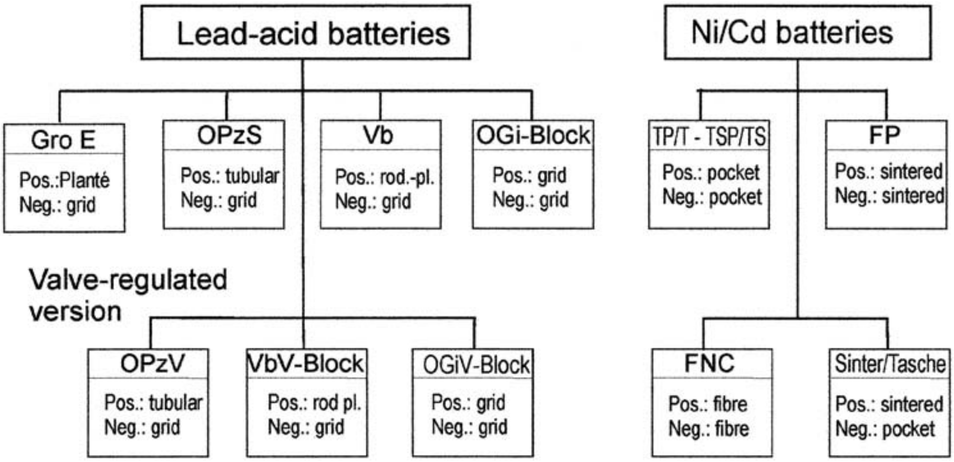


Figure 7.5 Cell types and plate combinations that are mostly used in stationary batteries. The top line in each box shows the termination according to DIN.

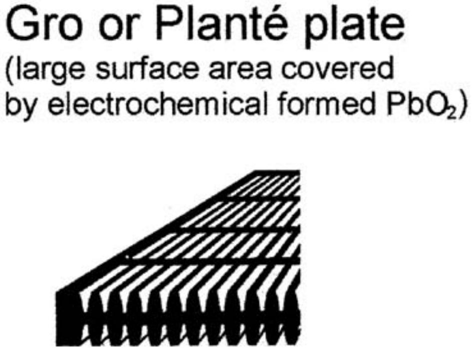


Figure 7.6 Planté and grid plate design.

Since the 1970s also maintenance-free valve-regulated lead-acid batteries have been in widespread use in the field of stationary applications. Sometimes they are called "*recombination cells*" or "*sealed lead-acid cells*". Their correct designation, however, is in accordance to DIN 40 729 *valve-regulated lead-acid batteries (VRLA batteries)*.

The various designations for the different cell constructions are formulated in the "International Electrotechnical Vocabulary, Chapter 486: Secondary cells and batteries". Valve-regulated cells are closed by a valve. It prevents the admission of air into the cell, but opens during normal operation when the internal pressure has increased to the opening value of the valve.

Stationary batteries are designed for special application, e.g. high current density or installation within electrical devices or in cabinets. Therefore each battery is more or less characterized by special construction elements.

Figure 7.13 compares the plate arrangement in different cell types:

- Left: a *vented* lead-acid bloc battery: Varta bloc (Vb).
- Right: a *valve-regulated* lead-acid bloc battery: Varta bloc V (VbV).

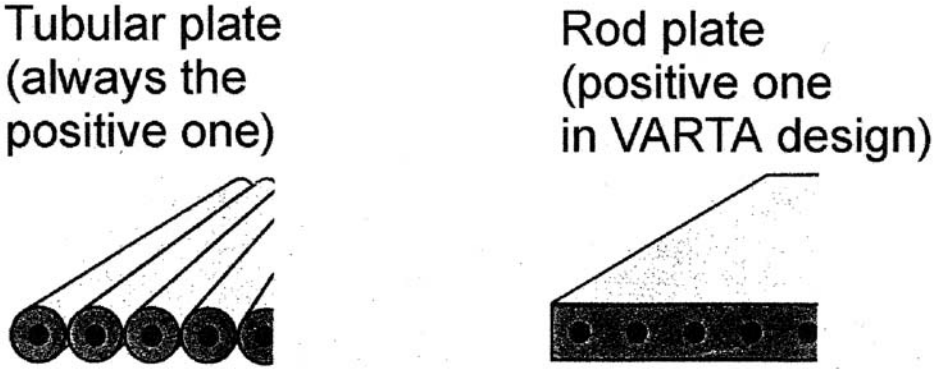


Figure 7.7 Tubular and rod plate design. The first one is used in OPzS cells, the latter one in Varta bloc and VbV batteries.

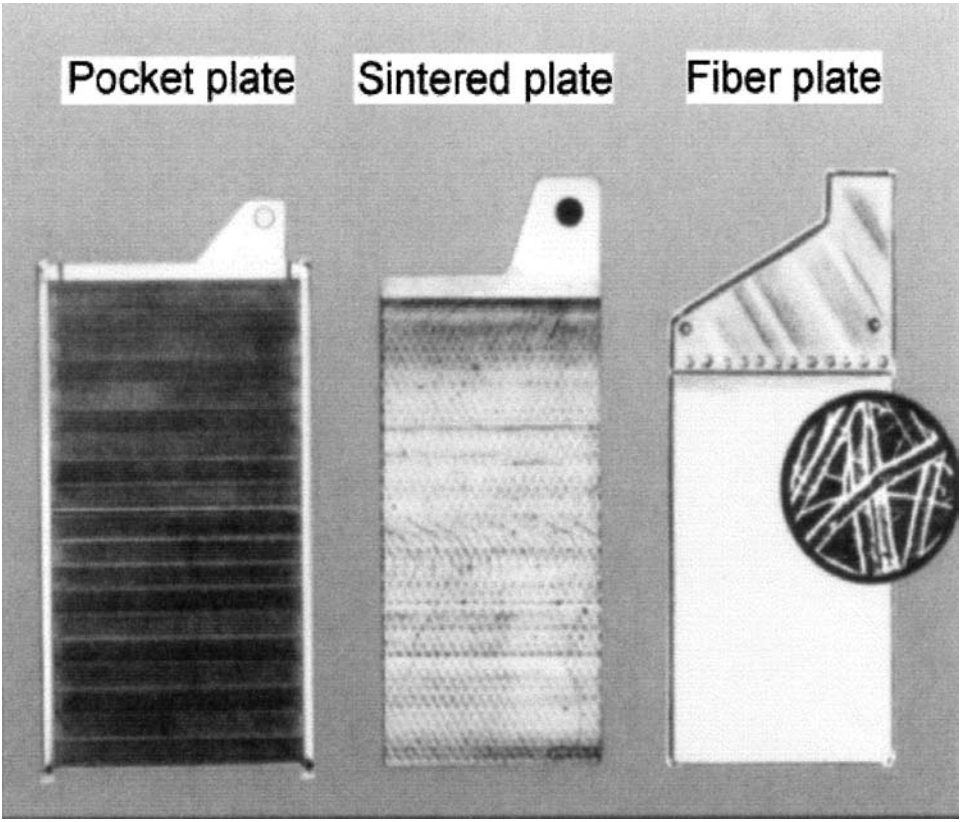


Figure 7.8 Various plate designs that are used in stationary nickel/cadmium batteries.

The Vb as well as the VbV batteries can be used in any stationary application. The UPS version is the result of optimizing work: plate thickness, internal connectors, new vents, and new dimensioning of the battery container – especially for application in UPS systems.

7.4 CHARACTERISTICS

A result of the different plate, cell, and battery designs and construction is the internal resistance of the battery. Figure 7.14 shows average values of the internal DC resistances for various cell designs, always referred to the nominal capacity of 100 Ah. Depending on various parameters, like electrode design and spacing, the observed internal resistor for *vented* cells is between 0.3 mOhm and 3.0 mOhm. A similar range applies for *valve-regulated* lead-acid cells and monoblocs, since their main construction elements are quite similar to those for the vented version. The internal resistance has a significant influence on the performance of the different designs, as is illustrated in Figure 7.15.

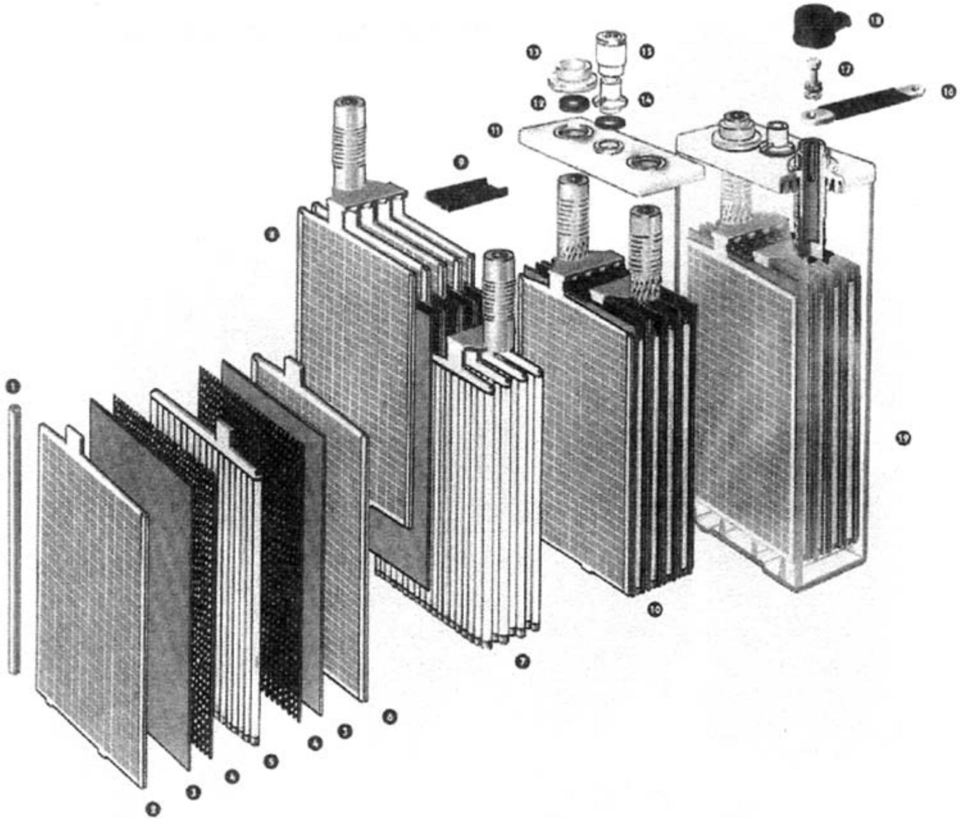


Figure 7.9 Exploded view of an OPzS cell (stationary battery with tubular plates). 1: Edge insulation (enlarged); 2: Negative end plate; 3: Microporous separator; 4: Perforated and corrugated PVC separator; 5: Positive tubular plate; 6: Negative plate; 7: Positive plate group with bus bar and Varta safety terminal; 8: Negative plate group with bus bar and Varta safety terminal; 9: Plastic cover plate; 10: Plate group; 11: Cell lid; 12: Pole sealing; 13: Washer; 14: Vent plug with washer; 15: Gas dehydrator; 16: Cell connector; 17: Connecting screw with locking device; 18: Pole cap; 19: Complete OPzS cell in transparent container.

For long discharge durations (in the range of 5 to 10 hours and correspondingly low current rates) no difference is observed, since all batteries reach their nominal capacity, but there is a large difference between the different types at high loads: the lower the internal resistance, the larger is the drawable amount of current.

For valve-regulated lead-acid batteries only one curve is shown in Fig. 7.15 that concerns a low resistance battery designed for high rates. However, dependent on their design also valve-regulated types would show a wide scattering, as indicated by the wide range of their internal resistance in Figure 7.14.

For many applications short discharge times are demanded. Then large differences are observed as indicated by the following comparison for a 10-minute discharge:

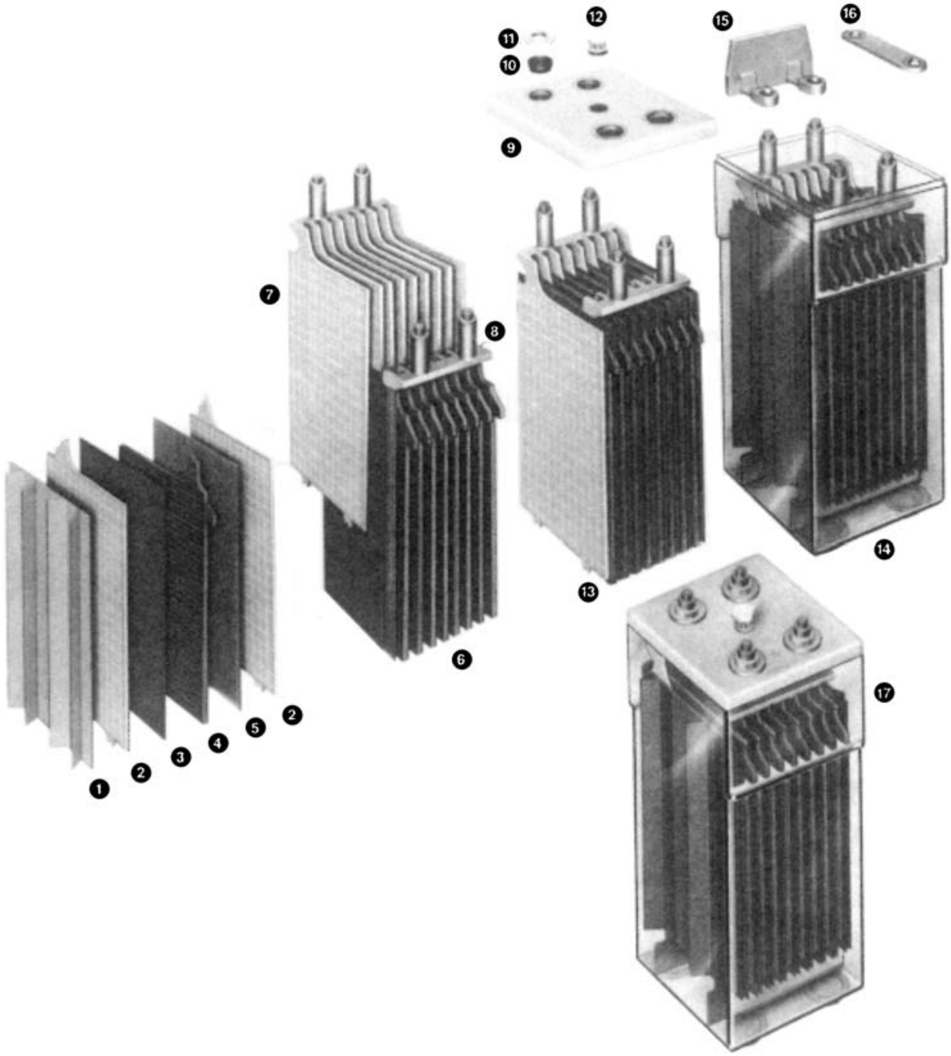


Figure 7.10 Exploded view of a Gro-E cell (with positive Planté plates). 1: End spacer; 2: Negative grid plate; 3: Microporous separator; 4: Positive Planté plate; 5: Corrugated plastic separator; 6: Positive plate group; 7: Negative plate group; 8: Bus bar and pole; 9: Lid with slot for glued joint; 10: Soft rubber seal; 11: Washer; 12: Vent plug with cap: 13: Plate group; 14: Complete Gro E cell in a transparent container.

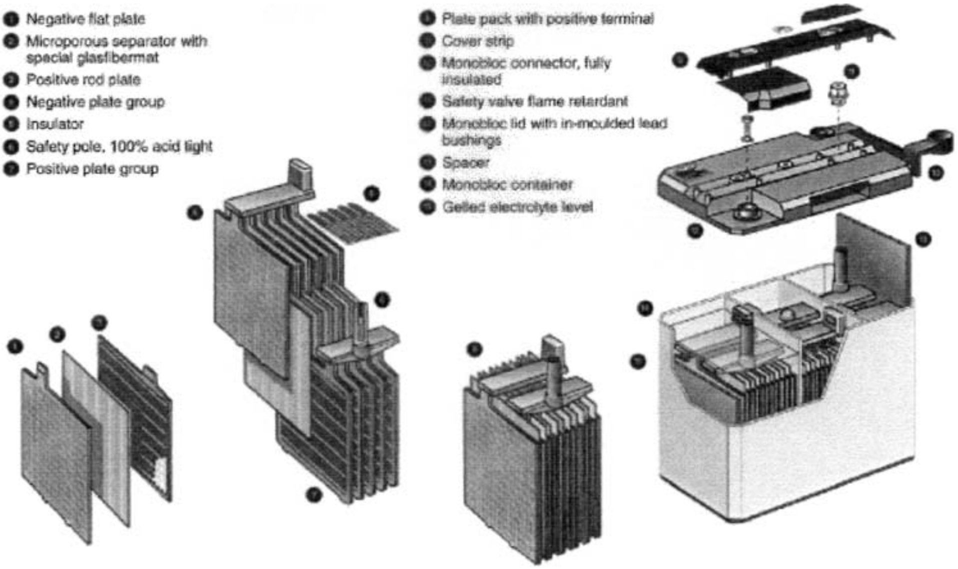


Figure 7.11 Exploded view of a Varta bloc battery (6-V monobloc).

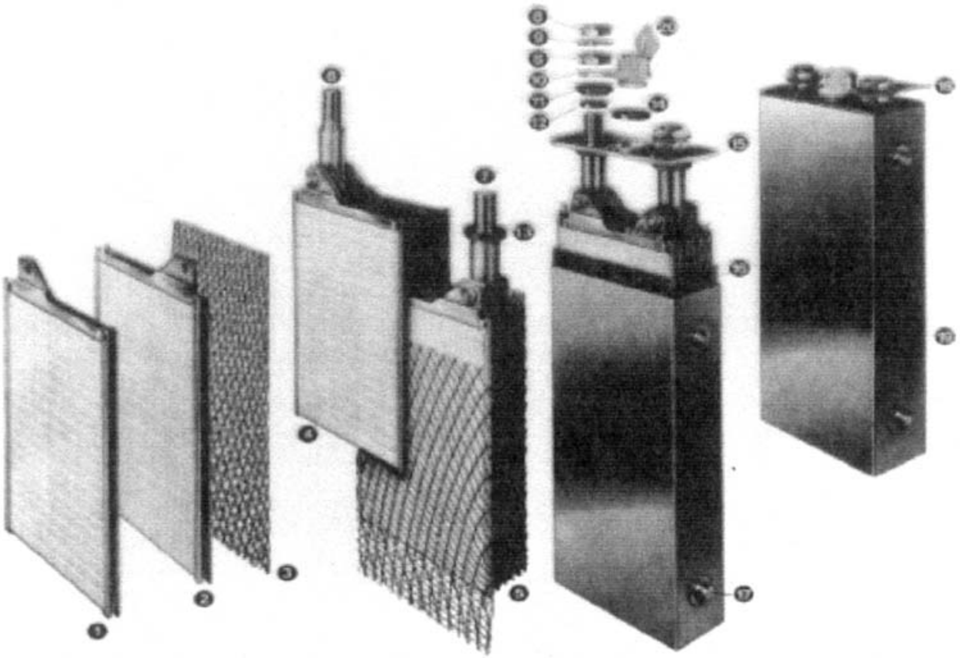


Figure 7.12 Exploded view of a nickel/cadmium cell with pocket plates. 1: Positive plate; 2: Negative plate; 3: Netlike PVC separator; 4: Positive plate group; 5: Negative plate group; 6: Positive post terminal; 7: Negative post terminal; 8: Washer; 9: Cell lid (welded); 10: Gas dehydrator plug; 11: Cell container; 12: Flat washer; 13: Pole nut; 14: Insulated cell connector; 15: Lock washer; 17: Connector nut; 18: Insulating cap.

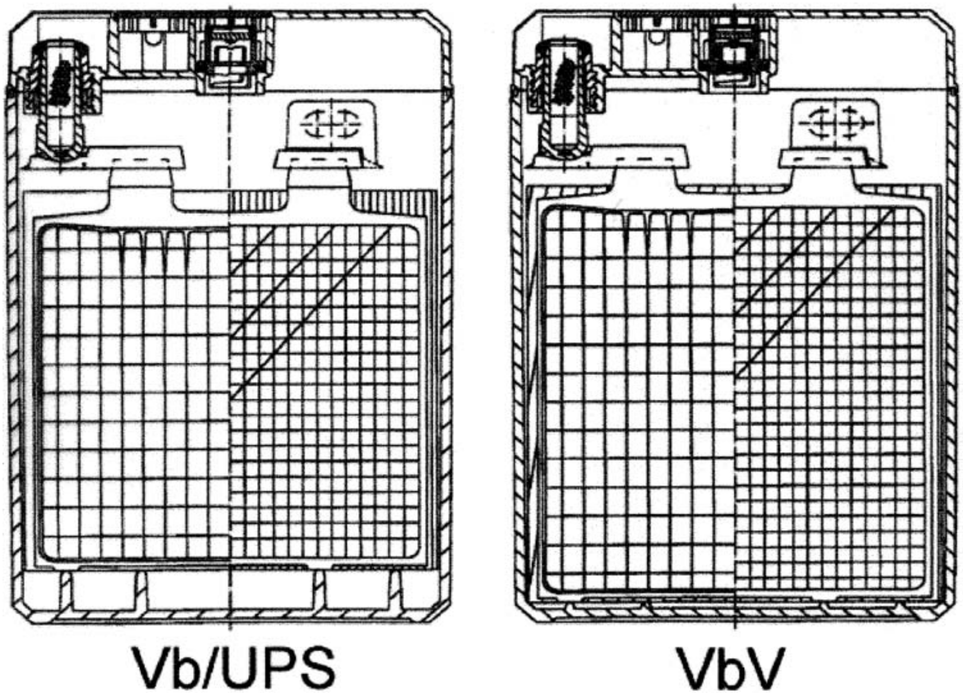


Figure 7.13 Plate group arrangement in a vented (Vb or UPS) and a valve-regulated lead-acid battery.

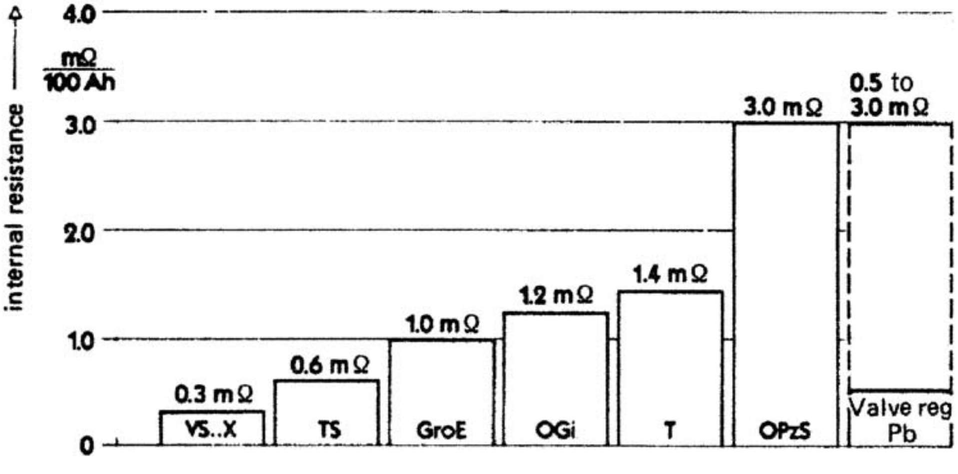


Figure 7.14 Specific values of the DC internal resistance for various cell types. To compare the different designs and construction, all dates and figures are related to 100 Ah nominal capacity.

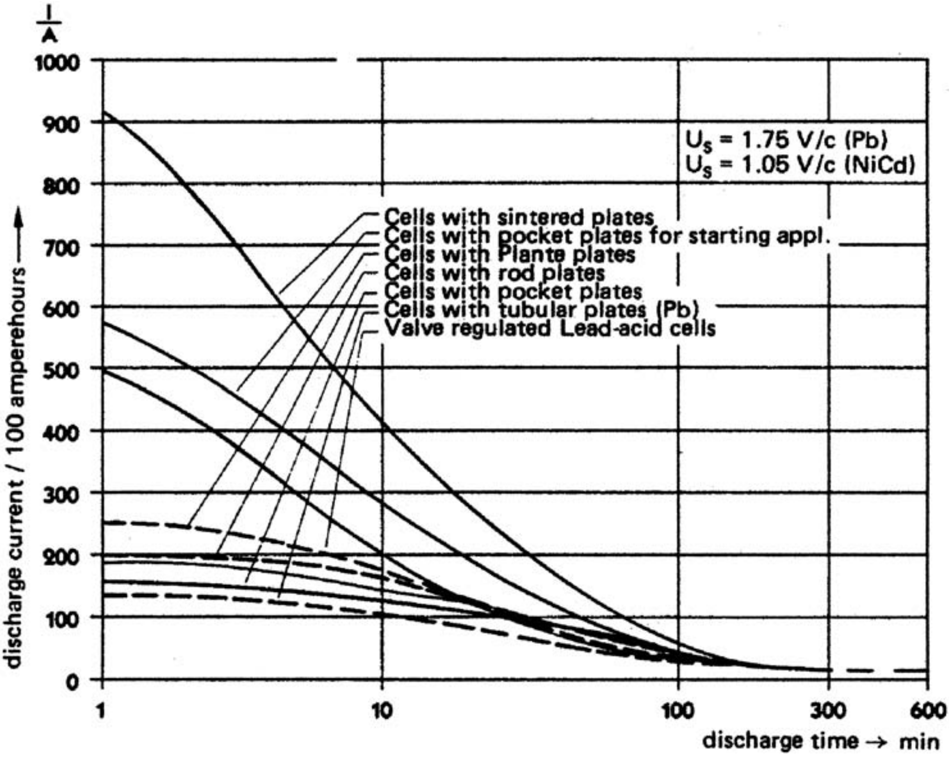


Figure 7.15 Discharging current per 100 Ah of nominal capacity versus discharge duration with an end-of-discharge voltage of 1.75 V/cell and 1.05 V/cell for lead-acid and nickel/cadmium batteries, respectively.

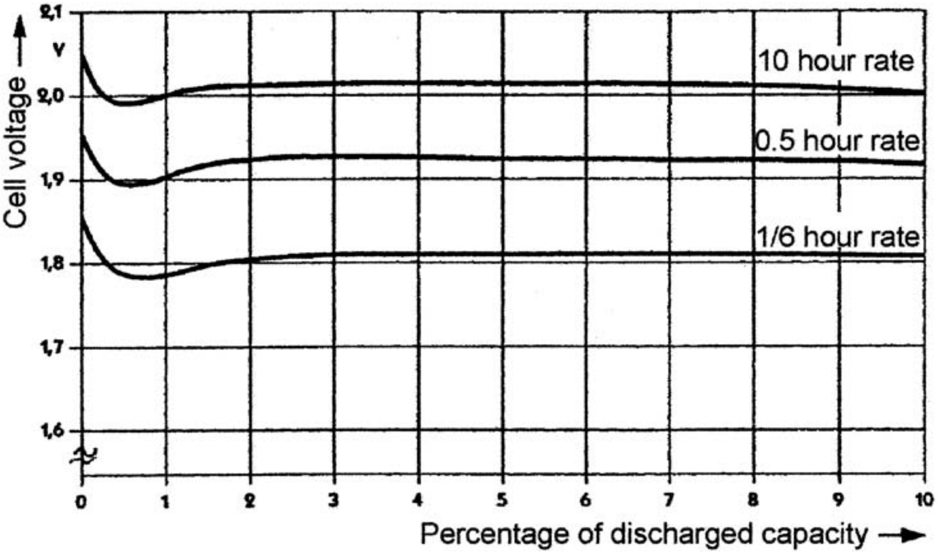


Figure 7.16 Coup de fouet at the beginning discharge of a fully charged lead-acid battery.

- 100 Ah OPzS cell = 100 A for 10 minutes
- 100 Ah Vb cell = 170 A for 10 minutes
- 100 Ah Ni/Cd sinter cell = 400 A for 10 minutes

Apart from the above mentioned – mostly design-dependent – characteristics, there are a number of further parameters that are to be observed and may cause advantages or disadvantages of the concerned battery system. The following examples are by no means complete but represent a selection of important properties that have to be recognized:

- Lead-acid batteries show a voltage drop – the *coup de fouet* – when discharged from the fully charged state, e.g. after a certain period of float charging. This voltage drop occurs within the first 1 to 2% of capacity drawn and is current dependent and must be respected, especially when high voltages are demanded and the voltage minimum determines the cut-off voltage (see Figure 7.16).
- Another important parameter is the dependence of the float current on float voltage and the temperature. Both parameters markedly influence the float current and thereby the water loss by electrolysis. Furthermore, both parameters also influence corrosion of the grid and all conducting elements that are connected to the positive plate.

Note: A quantity of 3 Ah that flows into the cell as an overcharging current decomposes approximately 1 cm^3 of water from the electrolyte!

Figure 7.17 shows the so-called Tafel – lines which more or less are valid for the float situation of lead-acid batteries. Such drawings allow quantified fundamental considerations concerning float charging:

- If the float voltage increases only up to 200 mV, the float current increases by a complete decade; with 50 mV voltage increase – that is approximately only 2.5% of the nominal float voltage – the float current will double! In valve-regulated batteries this increase is even higher, since the negative electrode is hardly polarized, and a voltage increase of only about 140 mV causes the current increase by one order of magnitude.
- Figure 7.17 also shows the great influence of the electrolyte temperature: Temperature rise by 10 °C approximately doubles the float current, and therewith also water consumption will be doubled.

As a consequence the accuracy of the float voltage has strictly to be observed, especially with devices that employ valve-regulated lead-acid batteries, since this type contains no surplus of electrolyte and water cannot be refilled. Therefore most of the battery manufacturers give directions (tables and curves) for float charging of their products.

But not only the float voltage, also the cell capacity depends on the electrolyte temperature, as shown in Figure 7.18.

The broken section in the curve for the lead-acid battery indicates that discharge may not be possible at such a low temperature since ice may be formed and dramatically increase the internal resistance. This is caused by acid consumption during discharge, which means that the acid density in a completely or deep discharged battery approaches the density of 1.00 kg/L. Therefore the operation of lead-acid batteries can be limited at very low temperatures.

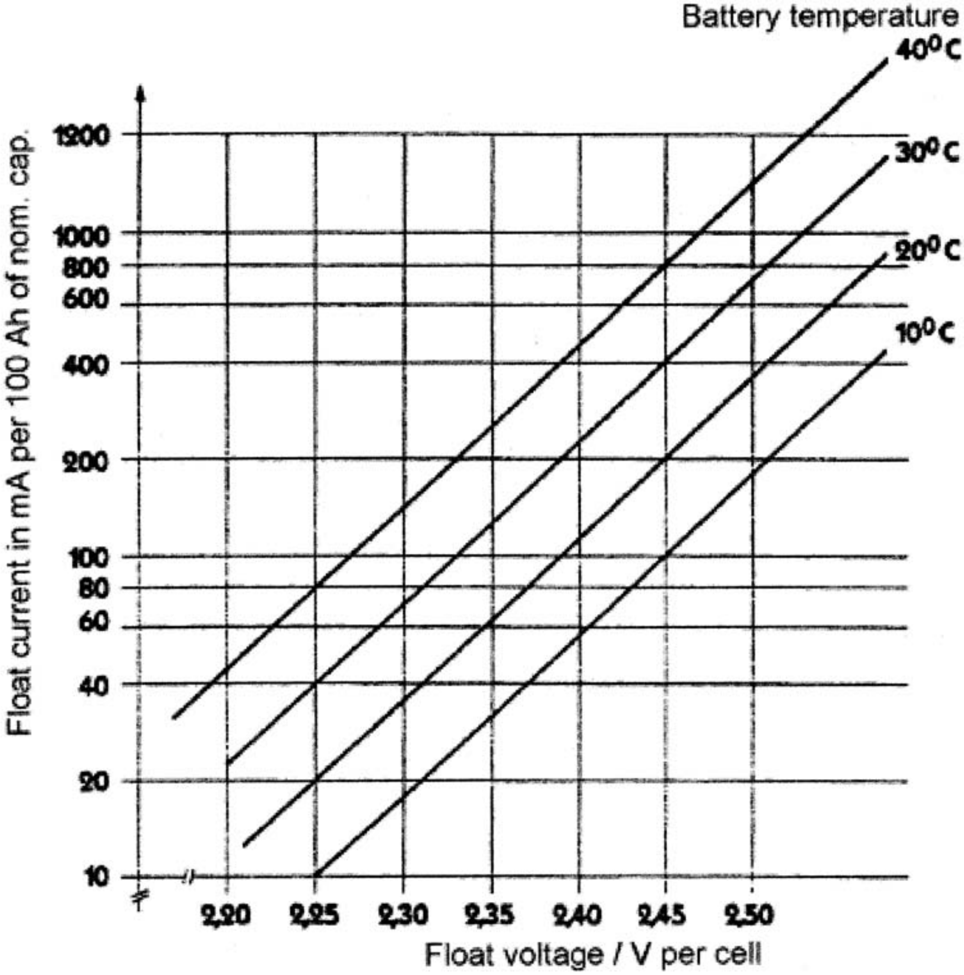


Figure 7.17 Float current versus float voltage of an aged OPzS battery at various temperatures referred to 100 Ah of nominal capacity.

In nickel/cadmium batteries the concentration of the electrolyte does not appreciably change and thus the problem of freezing does not exist. Usually freezing forms a sludge of frozen water in more concentrated acid, but at a very low acid concentration a solid ice can be formed that may destroy the container by its increased volume. Valve-regulated lead-acid batteries are advantageous, because of their immobilized electrolyte in a glass mat or as a gel which can never form a block of ice.

Many efforts have been made to keep the amount of the water consumption as low as possible. One way to reach this goal is to reduce the antimony content in the grid alloy, preferably in positive electrodes, or to eliminate antimony at all:

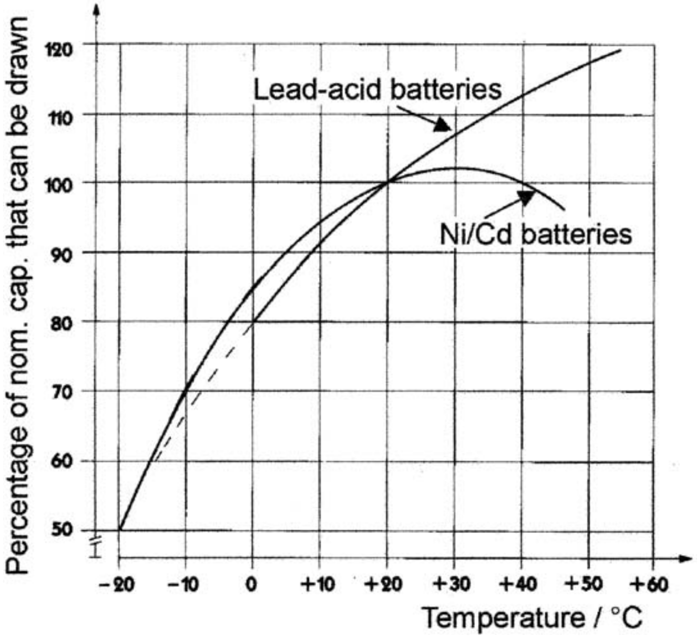


Figure 7.18 Actual discharge capacity of lead-acid and nickel/cadmium batteries at different temperatures (nominal capacity referred to 20 °C).

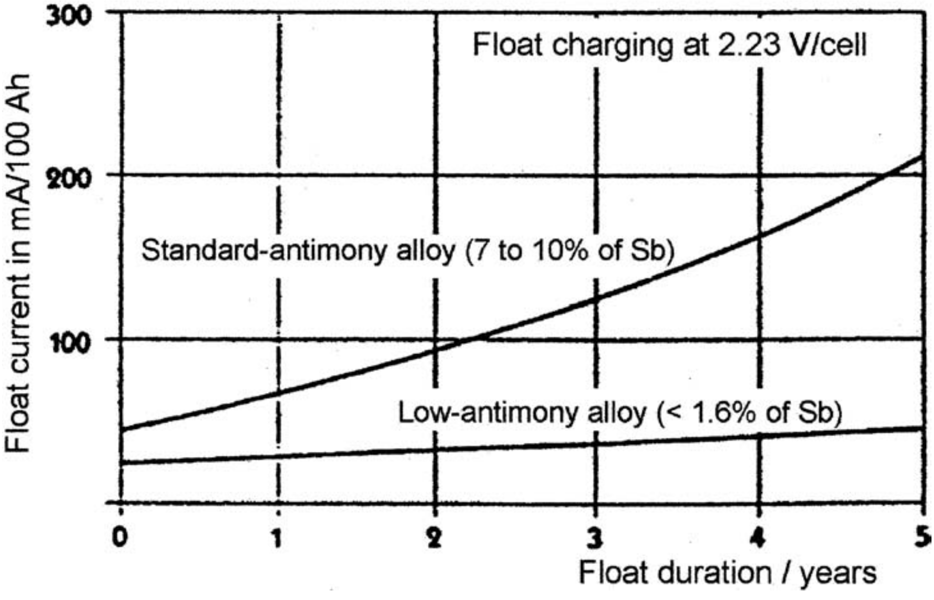


Figure 7.19 Alloy-dependent current increase during float charging.

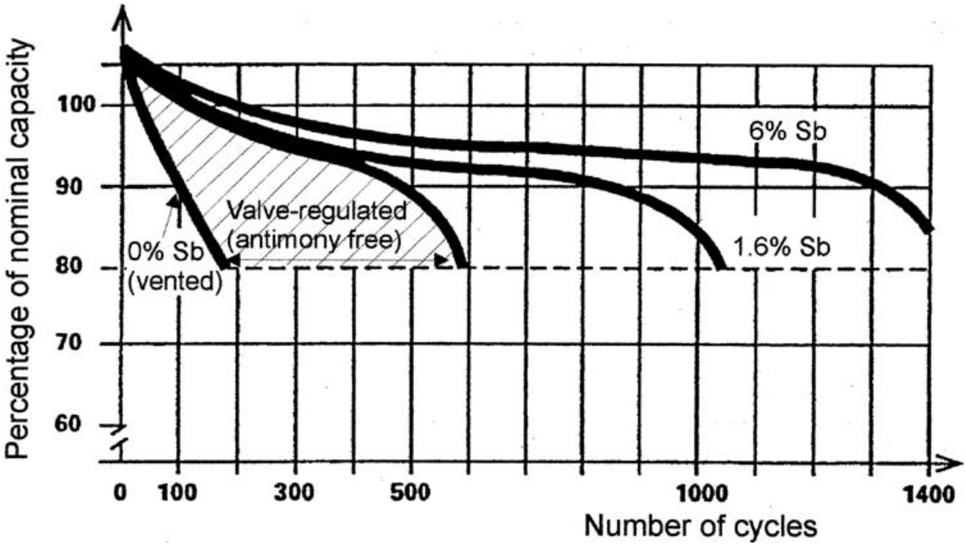


Figure 7.20 Influence of the alloy on cycle performance of vented and valve-regulated lead-acid batteries (rough approximation).

- The lead alloy used influences the float current (see Figure 7.19).
- The higher the antimony content in the grid of the *positive* electrodes, the higher is the float current – even for new batteries.
- The higher the antimony content in the grid of the *positive* electrodes, the higher is the increase of the float current during the float charging.

The best remedy would be to avoid the use of antimony. However, this would cause disadvantages for batteries that are used in "cycle applications". This almost never happens in applications where the battery mainly is used in standby operation, namely when the power supply is designed smaller than the load requires, e.g. for motors or switches. Then the back-up battery will repeatedly be discharged for short periods.

Figure 7.20 shows that normal lead-acid batteries with antimony-free alloys (e.g. Gro E cells have a cycle life of less than 200 cycles (DIN/IEC cycles)).

The immobilized electrolyte in valve-regulated lead-acid batteries favors cycle life. High quality stationary lead-acid batteries, e.g. the Varta bloc type (Vb), reach a cycle life up to 1400 cycles before the capacity falls below 80% of the nominal capacity. High quality *valve-regulated* lead-acid batteries, e.g. the type OPzV, reach more than 600 cycles.

Sometimes the *internal resistance* of a battery is required to calculate fuses in the DC power supply.

Figure 7.21 shows the internal AC resistance for lead-acid and Ni/Cd cells. It can be seen that up to more than 50% of discharge the resistance largely remains constant and then increases – more suddenly in the Ni/Cd battery.

Reliable emergency power supply requires an adequate combination of the electrical equipment and the back-up battery. Figure 7.22 shows various possibilities:

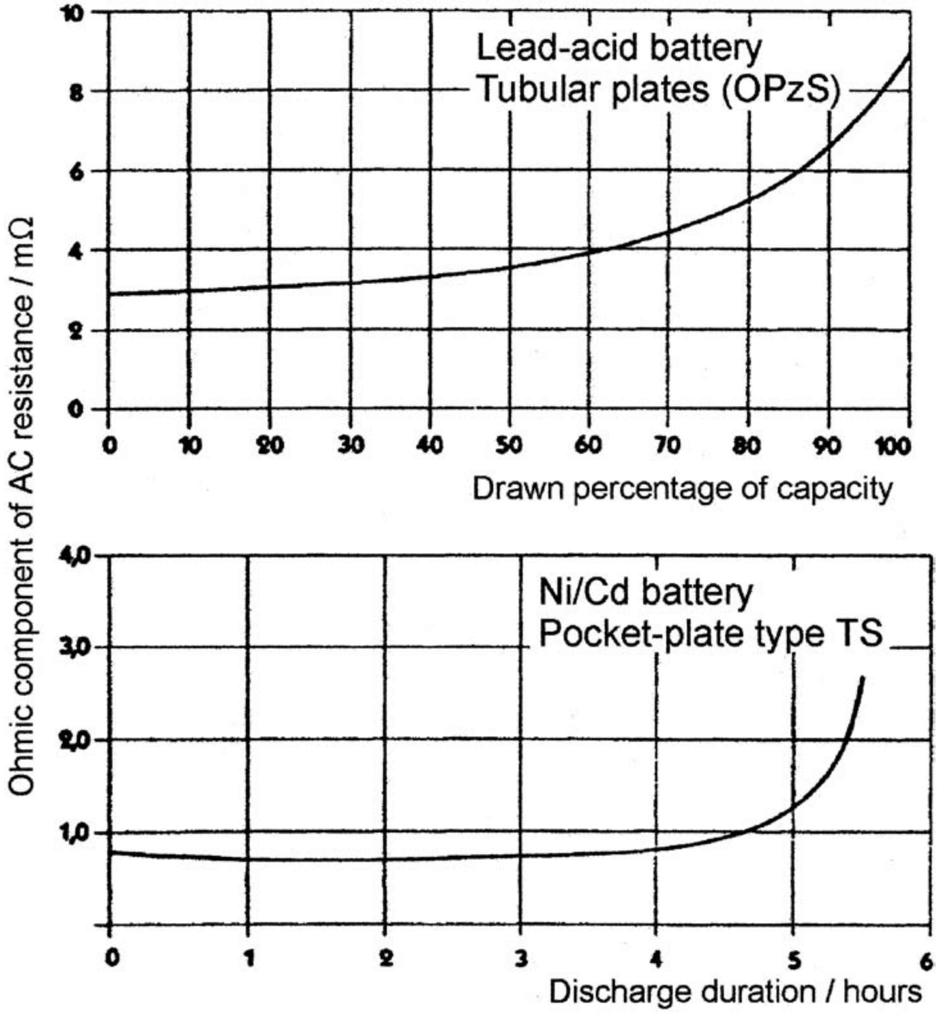


Figure 7.21 Internal resistance (ohmic component of 1000 Hz AC resistance) referred to 100 Ah of nominal capacity; 5 hour rate discharge.

- Most usual is the parallel connection, shown at the bottom in Figure 7.22. Under normal conditions the output of the power source is sufficient to supply the consumer and simultaneously keep the parallel connected battery in the fully charged state by slight overcharging ("*float charging*"). In the "*buffered mode*" the parallel connected battery has to serve power peaks of the load that cannot be balanced by the power supply. In practice, this situation sometimes occurs unnoticed.
- Today the switching mode is only seldom used, e.g. in emergency light devices. It is only possible in devices that can tolerate short voltage interruptions.

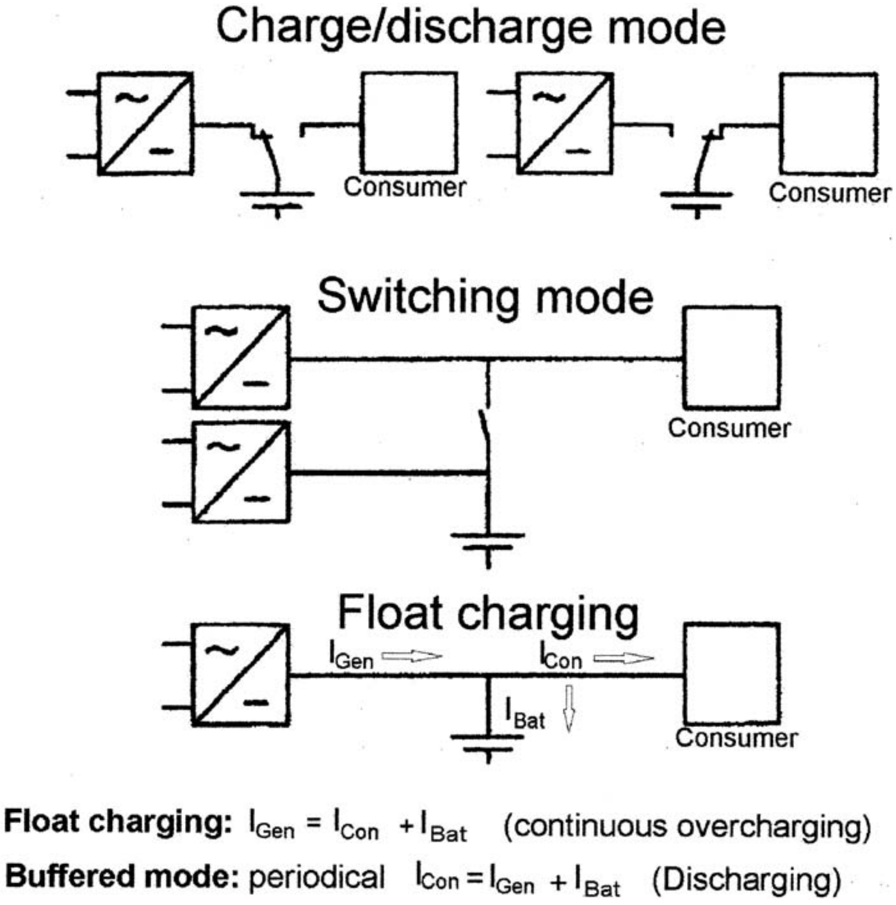


Figure 7.22 Possible methods to connect a stationary battery, the current supply, and the consumer.

- Today the use of main and additional cells to minimize the gap between charging and discharging voltage is observed only in older installations.

The rather simple charging technique for lead-acid batteries is advantageous compared to that of Ni/Cd batteries (see Figure 7.23):

- Lead-acid batteries in general are charged in parallel connection to the consumer, i.e. according to IU characteristics (at the low charging voltage of 2.23 V/cell). Also recharge can be achieved at this float voltage, but it may take more than 24 hours to reach the state of full charge.
- The charging technique for nickel/cadmium batteries demands far more expenditure. Charging is conducted according to the IU characteristics at a comparatively high voltage level for the time being. After the fully charged state has been reached, the charger switches over to a substantially lower

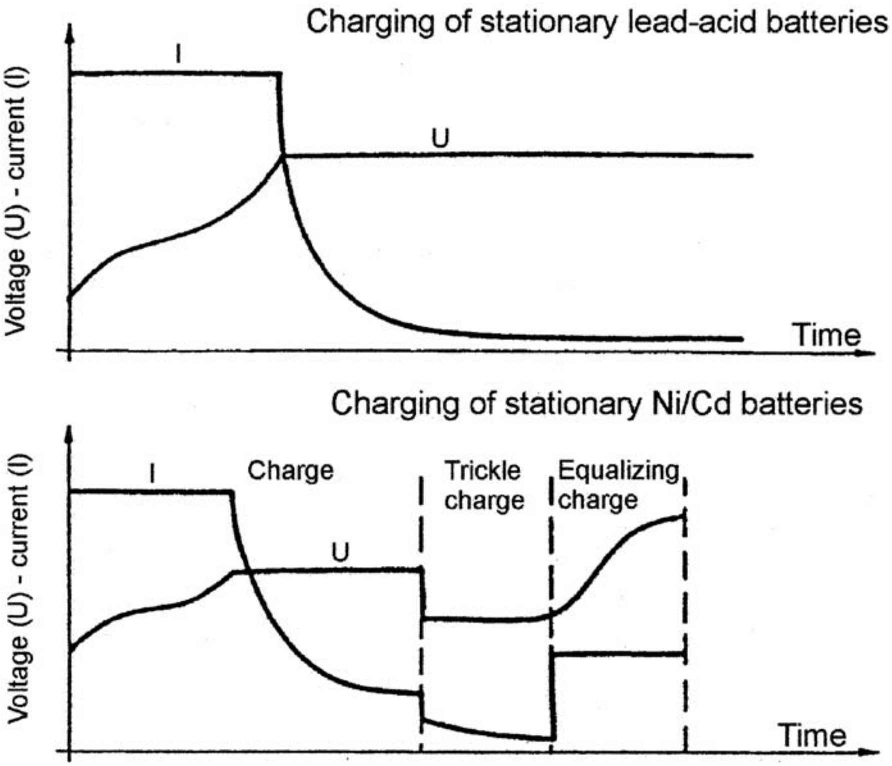


Figure 7.23 Charging schedules that are applied for stationary lead-acid and nickel/cadmium batteries.

voltage, which is applied for floating. Full capacity, however, is only preserved when periodically equalizing charges are applied at increased voltage (after about every 6 months). Otherwise, the battery has to be oversized by about 20% of nominal capacity.

- Nevertheless nickel/cadmium systems are economic under certain conditions, e.g. at very low temperatures.

The accuracy of the float voltage is very important. Figure 7.17 indicates the strong increase of the float current with cell voltage. For this reason all relevant standards give a tolerance of not more than +/ − 1% for the charger output voltage.

In strong connection to the accuracy of the voltage is the maximum value of charge current and also the ripple current. German and also European standards allow a *maximum ripple* of *5 A per 100 Ah of nominal capacity*. Future European standards will even stronger restrict the allowed ripple for valve-regulated lead-acid batteries.

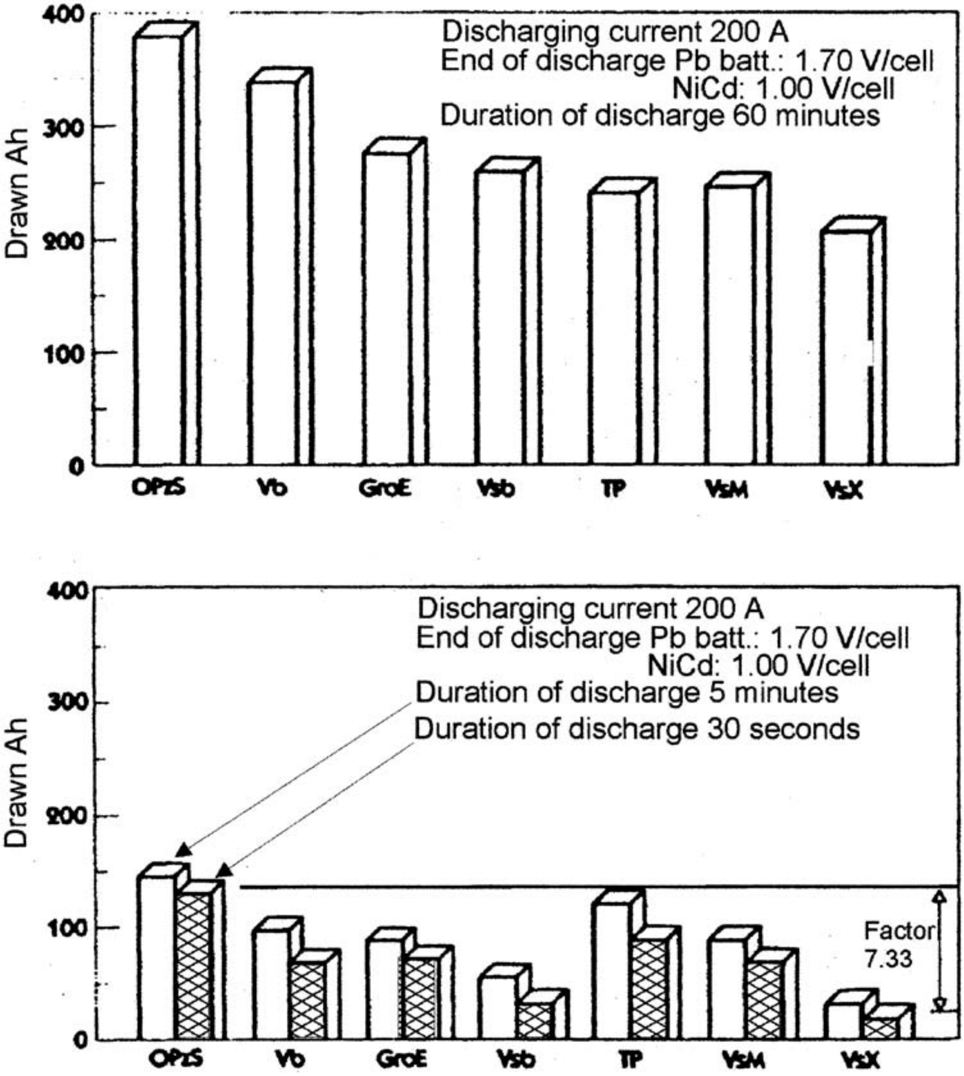
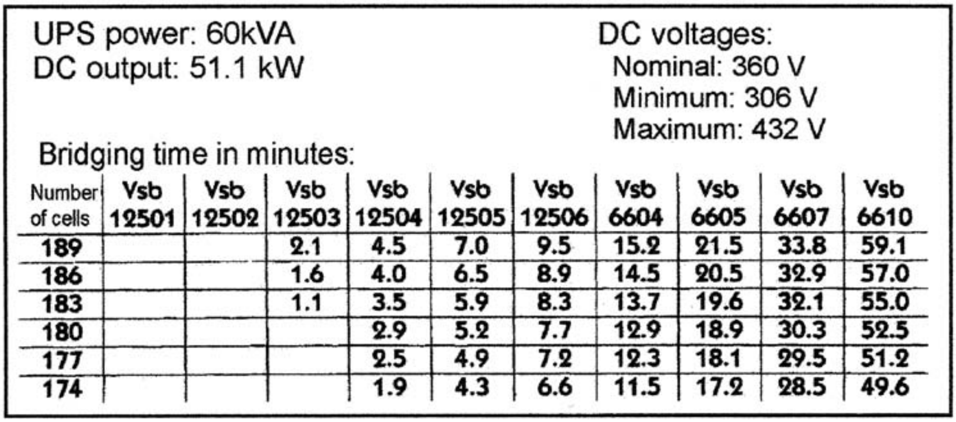


Figure 7.24 Comparison of the Ah that can be drawn from the various battery types under various discharge conditions.

7.5 SELECTION OF STATIONARY BATTERIES

Under consideration of these general facts it is already possible to make a selection of battery type, battery design, and battery size for a normal application. For the choice of batteries for simple constant current discharge, the manufacturers issue performance dates as curves or tables. Tables have the advantage that the relation between bridging time, required current, and minimum voltage can directly be seen and thus easy comparison is possible of the performance data of the various battery systems offered.



UPS power: 60kVA
DC output: 51.1 kW

DC voltages:
Nominal: 360 V
Minimum: 306 V
Maximum: 432 V

Bridging time in minutes:

Number of cells	Vsb 12501	Vsb 12502	Vsb 12503	Vsb 12504	Vsb 12505	Vsb 12506	Vsb 6604	Vsb 6605	Vsb 6607	Vsb 6610
189			2.1	4.5	7.0	9.5	15.2	21.5	33.8	59.1
186			1.6	4.0	6.5	8.9	14.5	20.5	32.9	57.0
183			1.1	3.5	5.9	8.3	13.7	19.6	32.1	55.0
180				2.9	5.2	7.7	12.9	18.9	30.3	52.5
177				2.5	4.9	7.2	12.3	18.1	29.5	51.2
174				1.9	4.3	6.6	11.5	17.2	28.5	49.6

Figure 7.25 Bridging times that would be reached by various numbers of cells of the concerned cell type under the given conditions of nominal, minimum, and maximum voltage. Such tables allow the selection of the battery that fits best the given conditions also in view of its price.

In Figure 7.24, a comparison is shown of the performance data for three different but typical applications:

- Required discharge duration 1 hour, discharge current 200 A (e.g. emergency light)
- Required discharge duration 5 minutes, discharge current 200 A (e.g. UPS application)
- Required discharge duration 5 seconds, discharge current 200 A (e.g. diesel starting)

With experience, based on the mentioned tables, battery sizing can also be calculated for more complex discharge schedules, e.g. for a two step discharging. But it is also possible (and recommended) to use the manufacturers' calculating computer programs.

In many applications, like a UPS, the stationary battery will be discharged with constant power. For this case battery and UPS manufacturers commonly issued curves and tables for the customer which consider the specific aspects of the concerned UPS equipment. Such documents allow the optimization of the battery by comparing alternatives of different cell size and cell numbers (as shown in Figure 7.25).

On request of the customer, stationary batteries can be installed on steel or wooden racks. More and more bloc batteries – especially valve-regulated lead-acid batteries – will be installed into battery cubicles. That minimizes the required footprint. But it is very important that there is sufficient air circulation inside the cubicles to equalize the temperature.

To avoid the formation of an explosive gas mixture within the cubicle, a certain quantity of airflow is required to attain sufficient ventilation. Relevant standards are to be found in the German Standard VDE 0510 Part 2.

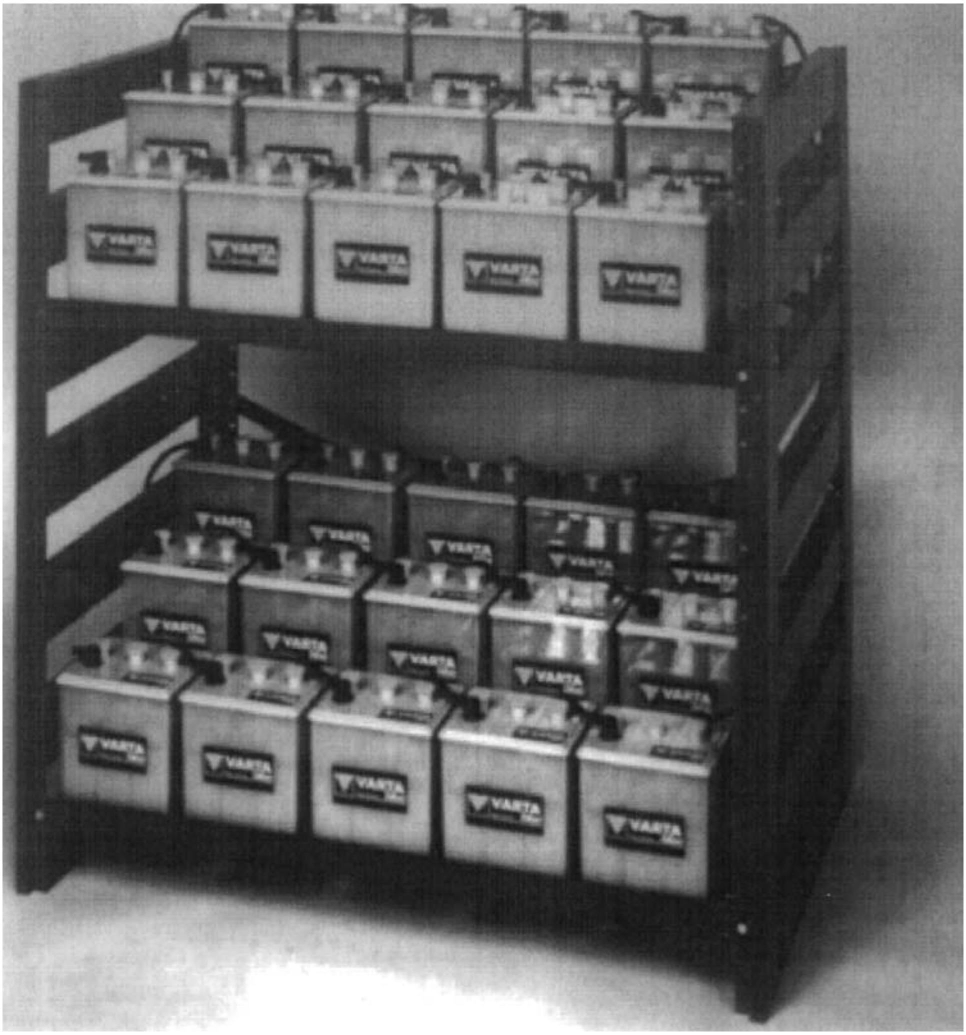


Figure 7.26 Steel rack in double-decker design for vented or valve-regulated batteries.

A special case of battery installation is a rack in double-decker design, according Figure 7.26.

Figure 7.27 shows a way to minimize the necessary floor space that is necessary with valve-regulated batteries. In the shown rack 64 bloc batteries are arranged in eight rows one above the other, installed in horizontal position. That makes service very simple because the terminals and connectors are in front of the rack and voltage readings can easily be taken.

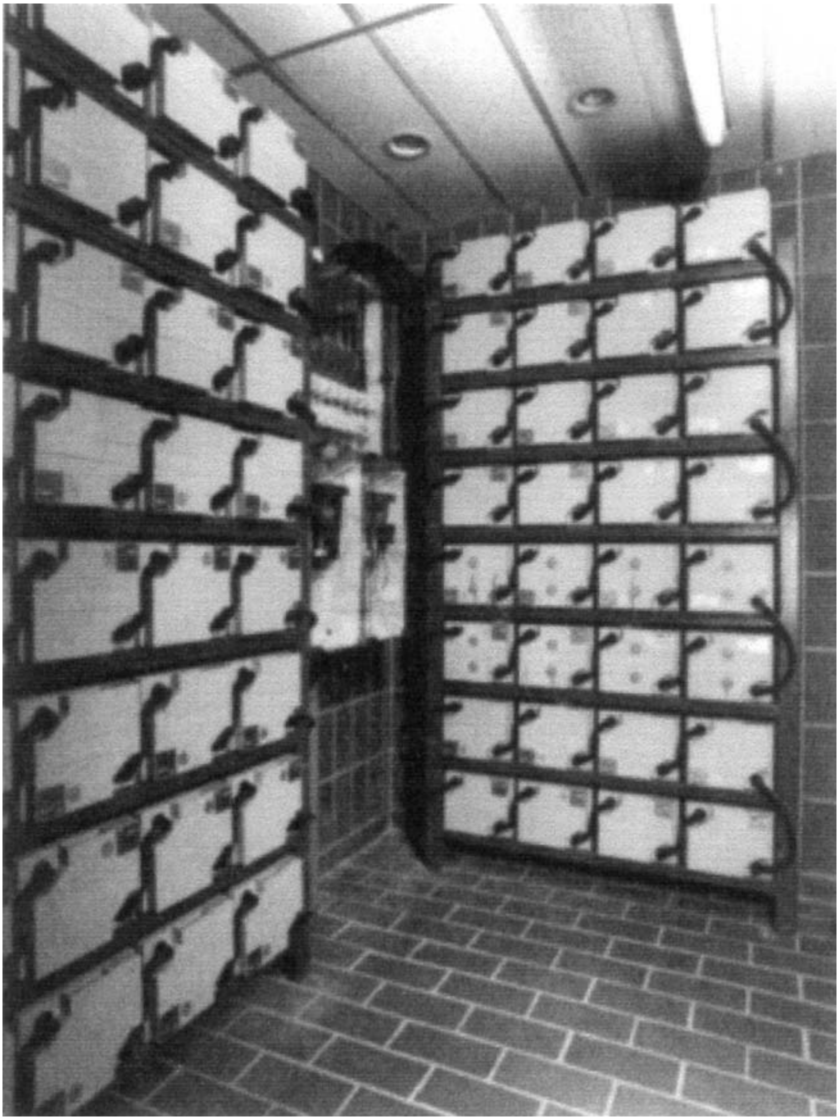


Figure 7.27 Valve-regulated monoblocs installed in horizontal position.

7.6 MAINTENANCE

A general problem with standby batteries is how to find out their state of charge and state of health, since in case of emergency the battery will fulfill its task only when it is sufficiently charged and when all cells are in proper state. As a consequence the battery must regularly be controlled, and with vented systems water loss has to be balanced by refilling.

The use of valve-regulated lead-acid batteries reduces maintenance expenditures markedly, since the refilling of water is no longer required. But the possibility

Figure 7.28 Manual service equipment that automatically registers the results and forms files that can be transferred into a PC for further processing.

to monitor such batteries is limited, since the acid density cannot be measured, and the amount of electrolyte left in each cell cannot be determined. Furthermore, in bloc batteries it is only possible to measure the bloc terminal voltage but not each cell voltage. With normal equipment it is a problem to attain reliable information about the state of charge and the general situation of the battery and its parts, except by testing its capacity. But this is not only expensive, it also means that during the period of discharge and subsequent recharge the battery is not available as emergency power supply. The only possibility to control the state of the battery is to monitor cell or monobloc voltages regularly and register any changes that might indicate problems within the concerned cells or monoblocs.

As a consequence, most battery manufacturers and also many electronics companies are developing monitoring systems and service equipment. The automatic

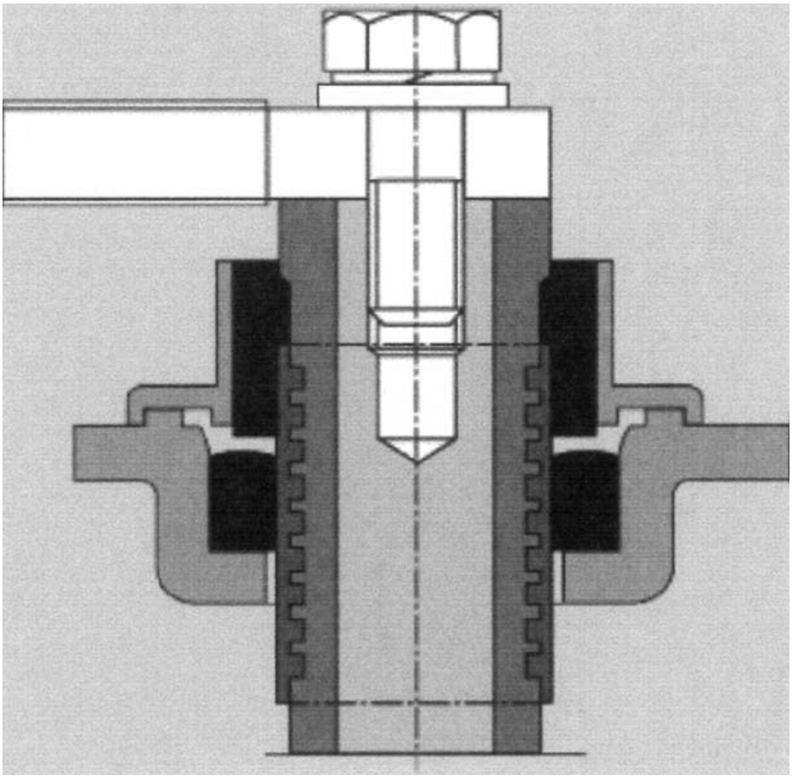


Figure 7.29 Durable electrolyte-tight safety pole.

surveillance of each cell in a battery is very expensive, especially in batteries with many cells. Usually the battery is divided into groups that are controlled and comparison of the group voltages often indicates problems in an early stage. Less expensive are manual methods like that shown in Figure 7.28.

Today in many cases the battery-monitoring equipment is integrated into the monitoring system of the complete equipment, e.g. the UPS. For remote monitoring many systems have special modem connectors.

7.7 POLE SEALING

A long service life of a lead-acid cell or bloc battery presupposes to have durable electrolyte and gas-tight pole sealing. Otherwise, in case of vented lead-acid batteries corrosion will take place at the connecting parts outside the cell. When valve-regulated lead-acid batteries have a pole leakage, oxygen from the surroundings can diffuse into the cells and will oxidize the *negative* plate and so influence the balance of the internal oxygen circle.

Thus, in valve-regulated lead-acid batteries electrolyte- and gas-tight pole bushings are a must, and vented batteries allow the use of copper inserts and screws for cell and battery connectors and thus install the battery as usual in electrotechnics.

Fully insulated connectors represent another safety aspect, especially when batteries are installed in racks.

A durable electrolyte and gas-tight pole bushing (the safety pole bolt) is shown in Figure 7.29. Its special design is

- Copper insert with inside thread.
- Fully insulated screw-on cell connector.
- Sealing rings around and injected plastic wrapper.
- Durable elastic sealing to the cell cover.
- Optical monitoring is possible.
- Plug connectors for external monitoring and test equipment.
- Connector for service equipment.

7.8 DELIVERY DESIGN

State of the art of the battery manufacturers is that vented cells and batteries are delivered in a dry charged condition. Such cells and batteries can be stored in their original wrapping for very long time. They will be activated when filled with acid and will deliver about 80% of the nominal capacity without any preceding charge. A 24-hour initial charge by the charging device at the plant (e.g. with 2.23 V per cell) is sufficient to attain a 100% charge. The issued battery manual gives corresponding information.

Today valve-regulated lead-acid cells and batteries are delivered to the customers in *filled and charged state, and* in most cases they have the filling date on it. That is the "birthday" of the battery, since with the filling of the acid all chemical and electrochemical reactions have started.

7.9 FUTURE ASPECTS

Battery development is ongoing. The lead-acid and nickel/cadmium systems will hold their dominant position in the field of stationary batteries. In the field of small portable power the *nickel/metal hydride system* has advantages because of its higher energy density compared to nickel/cadmium.

There are developments of nickel/metal hydride batteries with very high power density for application in hybrid road vehicles.

Valve-regulated lead-acid batteries already have displaced the vented types in many applications.

The technique for automatic battery monitoring will develop further. New technology and price decrease will open more applications.

Nevertheless, in very critical cases – e.g., nuclear power station – mostly vented lead-acid cells and batteries will also in future be used as standby, because of the better ability for controlling and monitoring, which are important safety aspects.

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8

The Operation of Batteries

U.-C. STAHL

8.1 INTRODUCTION

This chapter discusses aspects of the use of stationary batteries within the Deutsche Telekom AG. The names Deutsche Telekom or Telekom shall be used, although the responsibility for the area power supply for telecommunication networks was transferred to the Deutsche Telekom Immobilien und Service GmbH, (De Te Immobilien), a 100% subsidiary company of the Telekom, since January 1, 1996. At present, the DeTe Immobilien takes care of approximately 12,000 power supplies with a capacity overall of nearly 22 million Ah.

In the area of the Deutsche Telekom, most different battery systems are as shown in Figure 8.1. Primary batteries mainly are used in measuring instruments. Alkaline secondary batteries (accumulators) have a great importance in the area of communication technology, such as on mobile phones as well as on cordless phones. Still they are used as starter batteries for mobile network substitute installations (generator sets).

Lead-acid batteries are used, for example, as

- Traction batteries in industrial trucks.
- Starter batteries for cars, heavy trucks, and stationary network substitute installations.
- Stationary batteries in power supply installations for telecommunication networks.

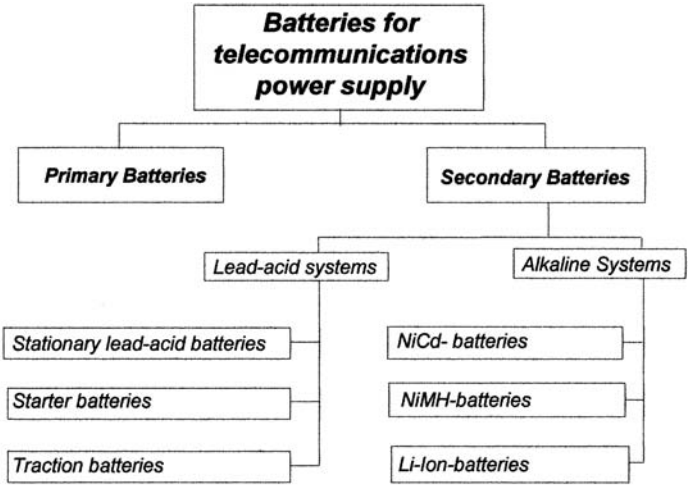

Figure 8.1 Overview of the batteries in use within Deutsche Telekom.

In Chapter 7 the series of the stationary batteries with Planté plates, tubular plates, and grid type plates as positive electrode are described in detail. In the following, stationary batteries are discussed.

8.2 THE DEVELOPMENT OF POWER SUPPLY FOR TELECOMMUNICATIONS

Batteries and telephones were developed in the first half of the 19th century. The power supply of the telephone consisted at the beginning of its development of primary batteries. Initially the batteries were placed in the telephone users' facilities and were called "Ortsbatterie" (stationary battery). In the course of further development, the batteries, now accumulators or secondary batteries, were installed in the central exchange office, in German im Amt, and therefore called "Amtsbatterie" (office battery). Until today the Amtsbatterie is retained from the subscriber.

In the early phase of the Ortsbatterie, the function of the telephone was dependent on the functionality of the battery at the subscriber's facility. The transition to the Amtsbatterie changed the situation in so far as an increasing number of connected subscribers were affected in case of battery failure. The battery became a central security element; continuous availability became necessary. Today, subscribers are responsible for the functionality of their equipment again when additional functions (cordless telephones, answering machines) are used which need a local power supply.

The direct current voltage which is necessary for the function of telephones was exclusively taken from a battery. When discharged by the consumer load by a switch the battery was disconnected from the consumer load. A second battery, in the meantime under charge, now was connected to the consumer load. The switch to the charger now connected the discharged battery. With this operating mode, which is called “change battery operation”, the batteries had to perform a high number of cycles.

With the onward development of the components as well as the control and steering technology, the possibility was created to provide consumers with a voltage derivative from the mains. That in parallel with the consumer-switched battery guarantees interruption-free parallel operation (see Figure 8.2).

The telecommunication equipment, that essentially consisted at this time of relays, spools, electromechanical selectors, and valve amplifiers, had a current demand dependent on conversation as characteristic. The current peaked on a “day curve” in which the ratio between minimum and maximum amounted to 1:10. For a long time the rectifiers were dimensioned so that the batteries were discharged if the top current was demanded, and at low consumer current were loaded again. This operating mode is called “boosting operation”. The batteries assume an undefined loading condition. Therefore only a part of the nominal capacity is disposable at a mains failure. With the operating mode of stand-by parallel operation, the rectifiers are dimensioned for the maximum current plus charging current, so that the battery stands constantly in stand-by and will be discharged only in case of a mains failure. The battery is here under float condition to equalize capacity losses by self-discharge. The battery is always fully charged. The rectifier installations of the Deutsche Telekom are so dimensioned that the batteries are discharged only in the case of mains failure. This requirement on the battery postpones/avoids a high number of cycles (change battery operation or boosting operation) to constant long-time behavior under float condition.

Another important characteristic of the electromagnetic exchange technology is a voltage with close tolerance required for the functionality. In order to fulfill this demand, different circuits were applied, which guaranteed that the consumers were not exposed to the full voltage range of the battery (especially the charge voltage). The battery however always stood at disposal. Possible circuit variants are pick-up technology (Figure 8.3) and counter-voltage technology (Figure 8.4).

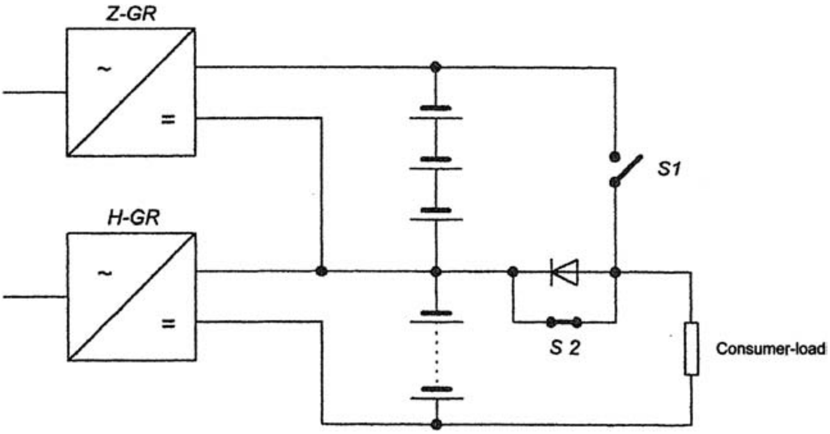

Figure 8.2 Power supply installation for parallel operation.

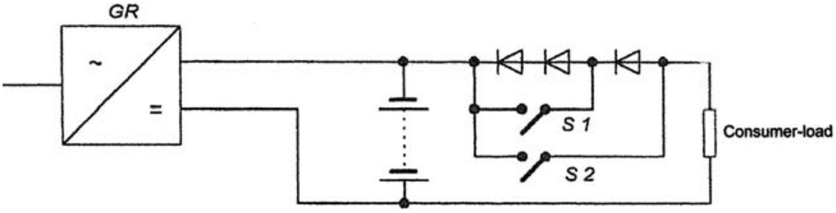

Figure 8.3 Power supply installation in the pick-up technology.

The principle of the circuit is based on the fact that at mains operation the consumers are switched parallel only with a part of the battery, with 27 cells with a 60-V power supply. The main rectifier is adjusted to an output voltage that corresponds to the float voltage of this part battery. The other cells get the charge voltage from the additional rectifier. In the case of mains failure consumers are switched with achievement of a corresponding voltage border to the total battery while S1 closes; meanwhile S2 opens. The decoupling diode makes possible the interruption-free switch.

With counter-voltage technology the entire battery gets the charge voltage of the rectifier. The necessary voltage reduction is reached over diodes switched in forward direction. With mains failure the diodes are bridged voltage dependent. In the end, the consumers are switched to the battery directly parallel. The performance moved by the diodes in heat causes poor efficiency.

The introduction of digital exchange technology brought numerous changes; among other things the output voltage of central power supply has a characteristic of a transfer voltage. Consumers are supplied by DC/DC converters, which have a large input voltage range. DC/DC converters are necessary because different voltages (5 V, 12 V, 27 V) are required for the function of the electronics of the exchange equipment. Consequently, rectifiers, batteries, and consumers could now be switched directly parallel, as shown in Figure 8.2.

The recharging after a mains failure is performed by a boost charge for a fixed time period or with float voltage. With the application of the boost charge, the taken energy is loaded more quickly into the battery again and is more quickly available again. In addition, these batteries show batter long-time behavior than batteries which were recharged under float conditions.

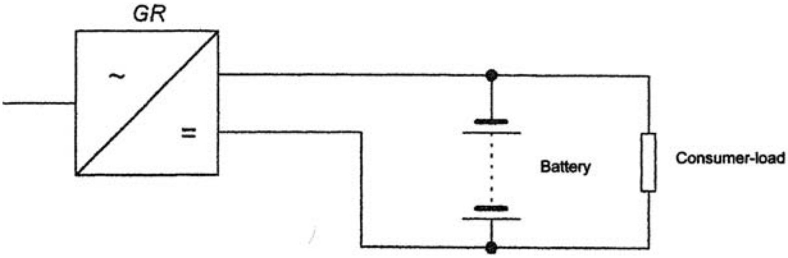

Figure 8.4 Power supply installation in counter-voltage technology.

With the decentralization of the exchange networks, separation of functional units into the surface, as well as the use of glass fiber, beside the batteries in the central office with high capacity, many batteries of inferior capacity had to be installed.

8.3 PRODUCT DEVELOPMENT AND PRODUCTS IN USE

The products which are used by telecommunications reflected the development of the industry in the area of stationary batteries. Big users like Telekom immediately tested many developments after the laboratory phase. The experience collected in practical use was evaluated, and knowledge about it went back in into the battery production. While in the early years of the central offices, batteries with Planté plates were used; these batteries were replaced by batteries with "narrow mounted" Planté plates. In the beginning of the 1970s the use of stationary batteries with positive tubular plates started. Stationary batteries with positive tubular plates of present production, especially in the capacity area up to 3000 Ah, clearly differ from those from the first production years. The container material hard rubber was replaced with SAN and pole sealing was modified many times to eliminate leakages and crevice corrosion. Still the connections between pole and covers must be shaped so that from plate growth resultant strengths cannot lead to rips in the covers or cover detachment of the container. An essential alteration was the lowering the amount of antimony of the plates. This was an advantage for the user because electrolyte loss was drastically lowered and the cycles for supplementing the electrolyte could be increased. In addition, an essential presupposition was created for the development of valve-regulated batteries.

Valve-regulated batteries have been use at Deutsche Telekom since the end of the 1980s. First these batteries were put into low scope purposes for testing. Their use was forced strongly with the extension of telecommunications in the "new countries" (area of the former GDR), so that today approximately 1700 locations (mainly cell capacities of 200 Ah up to 1500 Ah) with valve-regulated batteries are realized. Since these product series permit the use of batteries in applications in which the use of vented batteries is completely impossible, valve-regulated batteries of small capacity (bloc batteries up to 65 Ah) are used today in most facilities. Main focuses of use are converters for the transition from copper wires to glass fiber.

In the past the use of grid type batteries was restricted to operation tests. The collected experiences did not meet the expected results. Today, these products are more reliable in operation behavior; furthermore the use of grid type batteries is necessary in numerous applications on the basis of the low inside resistance and the good high current behavior.

To exchange equipment, peripheral facilities came with the introduction of digital exchange technology, for example, computer, printer, and other hardware components. This equipment needs mains without interrupt. To provide for these facilities in individual cases DC/DC converters or, usually, uninterruptible power supplies (UPS) are used. The UPS can be placed locally or centrally. The UPS are used mainly in order to bridge over short mains failure as well as for realizing a proper switch-off. Therefore the batteries in use must deliver a high current for a short time. Batteries with grid type plates fulfill this requirement optimally.

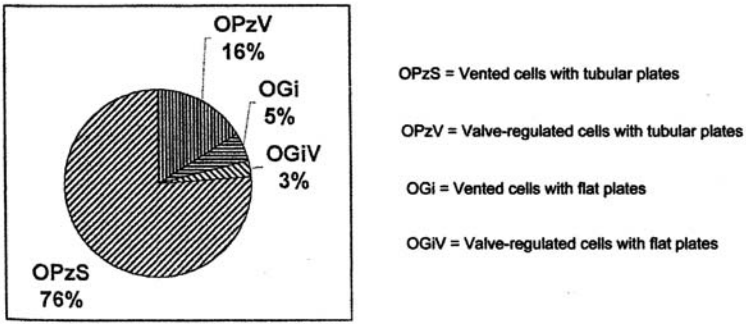

Figure 8.5 Shares of the series at the total stock.

Figure 8.5 gives an overview of the distribution of the series at the total stock. It is to be heeded that batteries with capacities up to 100 Ah are not considered.

8.4 CONCEPT OF ENERGY RESERVE

The basis of the conception and dimension of the power supply of a location is the "concept of energy reserve" of the Deutsche Telekom. It includes commitments to the general concept and the dimension of the components of the power supply on the basis of local conditions, including, in particular (a) importance of the telecommunication consumer, (b) power demands, and (c) attainability of the facility.

The importance of the telecommunication consumer depends on the consequences of a failure of the power supply for the connected subscribers. The importance is greater when more subscribers are affected by such failure, which determines whether the failure has an effect nationwide or only regionally. The demands of the consumer with the highest importance are decisive if different technical consumers are connected with a power supply.

The power demands of the consumer can be realized with a battery only for a certain time because of the limited energy reserve. The use of network substitute installations makes it possible to ensure a proper function even at long-lasting mains failure. For consumers nationwide, the energy reserve concept presupposes the use of network substitute installations on principle. With the introduction of digital exchange technology, a concentration of the components became possible on a small volume. The technology no longer used electromechanical components but pure electronics that could be concentrated in fractions of the previous volume. The limit of the concentration was the energy moved per volume and with it the loss performance attacking as waste heat. A completely new problem assumed shape, because the use of climate technology became necessary that had to be able to operate also in the case of mains failure. Either a network substitute installation is used or with smaller performances a battery supplies the DC/AC converter.

Attainability of the facility refers to the necessary time to reach the facility, even during bad weather conditions. The necessary time for the disturbance elimination must be considered as well. Normally, the battery capacity is planned for a discharge time of 4 hours. In facilities with network substitute installations, the battery is calculated for a discharge time of 2 hours.

Batteries with capacities over 250 Ah are divided for operation and security reasons into two groups of the same capacity. Both batteries are switched continually parallel. Further batteries of same capacity can be switched parallel if expansion of the battery capacity is necessary. Extensions are possible up to five battery groups. It is also possible to switch parallel batteries of different capacities (maximum capacity ratio 1:2). In practice, this is without meaning however.

Besides the energy reserve concept recommendations exist for special applications, for example facilities with mobile phone networks, with which a superposition of the ranges exists, so that the cancellation of a single location has hardly any effect on the total function of the mobile phone network.

8.5 OPERATION CONDITIONS

Batteries in central exchange offices had optimal environmental conditions in the past (Figure 8.6). In the normal case, the battery was mounted in a big cellar area with an annual average temperature of 18 °C. The windows were lined up northward, so that no warming appeared in the summer. Radiators prevented temperature deviations in winter.

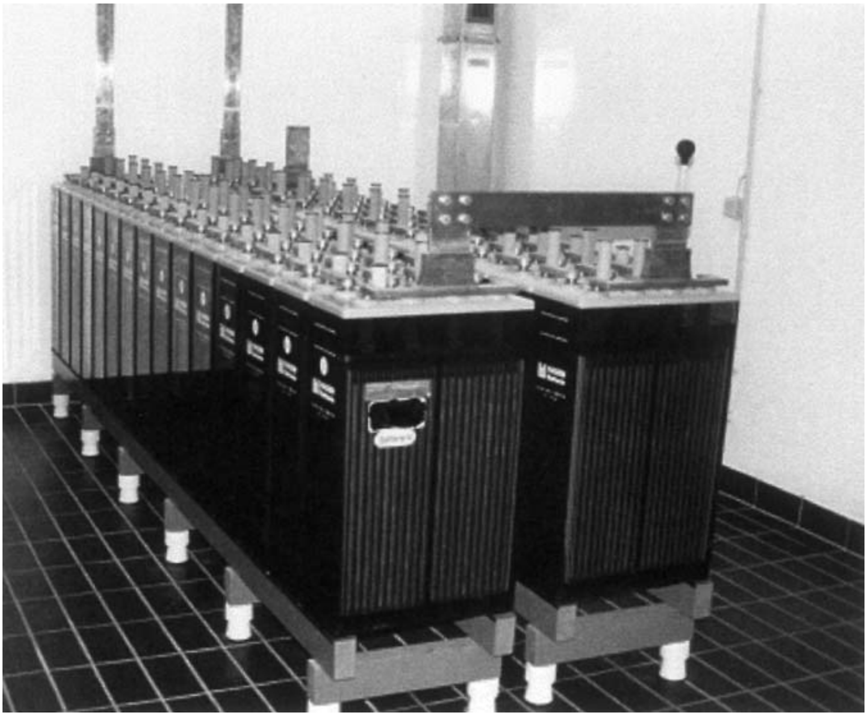

Figure 8.6 Classic battery area.

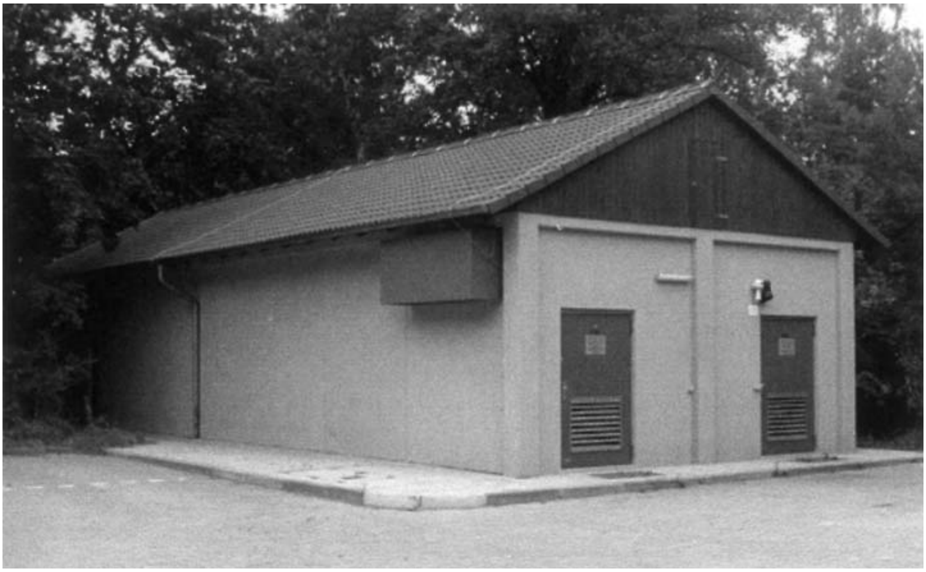

Figure 8.7 Multifunctional cubicle (MUK).

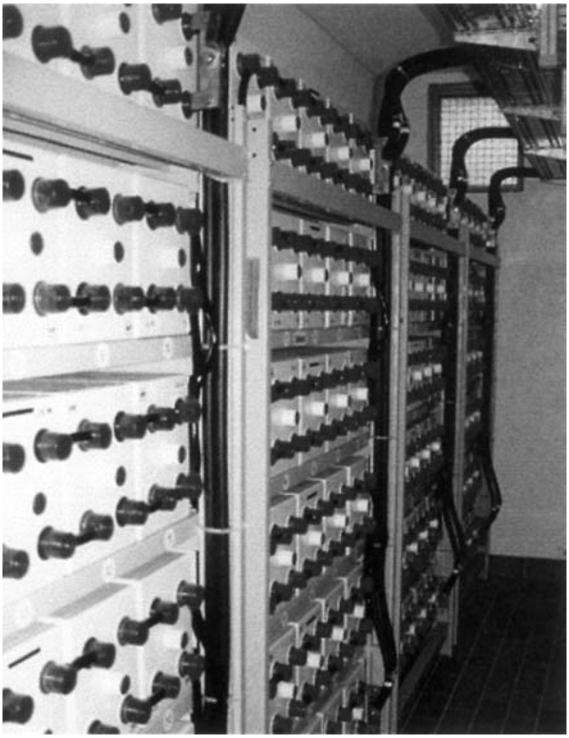

Figure 8.8 Battery area of the MUK.

With the introduction of digital exchange and glass fiber technology it became necessary to build up equipment outside the old central exchange offices. Of increasing scope, so-called character buildings, separately standing buildings with small bases, were developed and used. The environmental conditions for the batteries were no longer perfect since a certain temperature fluctuation appeared in these buildings and measures were met only against freezing.

With reunification, Deutsche Telekom got the big task to plan the extension of the telecommunication networks in the "new countries" within the shortest time possible and to manage an essential basis for further development. The high structural requirements had to be implemented in short time along with the technical ones so telecommunications equipment was first accommodated at main locations in containers and a large number in so-called multifunctional cubicles (MUK) (Figure 8.7)

They consist of assembled rings that are put on a strip foundation and are locked in front and behind (Figure 8.8). Exchange equipment and power supply, that is rectifiers and batteries with capacities up to 200 Ah, were put into one room together. The use of valve-regulated batteries (low gas emission, situation-independent mounting) became necessary. The accommodation of batteries of larger capacity takes place in a divided up area. To install batteries with a total capacity up to 4500 Ah in such a small area, again valve-regulated batteries were installed in horizontal position in steel racks. Because of the implementation of the building, the batteries are exposed to wide temperature fluctuations.

With the introduction of the glass fiber technology, local power supplies became necessary in large scope for the supply of intercession technical facilities and facilities for the transitions of fiberoptic to copper lines that lead to the participants and intensifiers to refresh the signals (light impulse) after a certain line length. In general, the necessary technology is installed into so-called Kabelverzweigerkästen (shortly KVz). The number of such facilities is approximately 18,000. Since these facilities must be able to function also at mains failure, a battery is applied in each case. Two variants exist for the accommodation of the battery. Either the battery is installed in the pedestal part of the KVz cabinets (Figure 8.9), or the batteries, which are used for the remote power supply of several of such facilities, are separately buried in a cable branch box (Figure 8.10). The battery becomes accessible when the cover of the cable branch caste (as can be seen in Figure 8.11 bottom right) is lifted up. The conditions to which batteries are exposed in the cable branch box comprise everything conceivable, including flooding with dirty water and mud and high temperatures. Nevertheless, the batteries work better than expected under these conditions.

8.6 BATTERY INSTALLATION

The installation conditions for batteries have changed over the years greatly. Today it is necessary to install the batteries to save space. This is possible by using metal battery racks and battery cabinets. It is to be heeded, however, that the specified ventilation and service ability of the batteries is ensured. A protection-leader connection must exist at the battery cabinets on principle. This demand is also put on battery racks for batteries with nominal tensions > 60 V DC. It is necessary that all construction elements be interconnected electrically leading together.

Figure 8.9 KVz cabinet with battery in the pedestal area.

All racks must be equipped with a particular coating, independent of the nominal voltage of the battery. For the admission of delivery at Deutsche Telekom, proof of the mechanical solidity, the chemical resistance against electrolyte, and the light insensibility of the coating through a production pattern examination have to be enforced at a neutral institute. In the end of the production process, each complete rack and all rack components are tested with a voltage of 4 kV; a protocol is prepared and is delivered with the rack.

Increasingly battery cabinets and battery fans find application in compact power supply installations. On installation, the fulfillment of the requirements of the ventilation is an essential admission criterion. Besides good accessibility of the batteries, a necessary electrolyte-resistive surface has great importance. On principle, for safety reasons acid-collecting tubes are also demanded under the installed valve-regulated batteries as for vented battery types.

8.7 PURCHASING AND QUALITY MANAGEMENT

The purchasing of batteries in use by Deutsche Telekom takes place over framework contracts. Through these it is guaranteed that only released batteries and released battery accessories are delivered to the Telekom. Further deliveries can be abandoned if there are problems with a certain product within a short time. The acceptance of the delivery to the Telekom is given if proof of the observance of "quality handicaps" is produced by a type pattern test and regular audits at the manufacturer. Tests of several years that are enforced in the central laboratory of the Telekom in Steinfurt are prerequisite for the transaction of the type pattern test. The quality handicaps are worked out in a form of technical delivery conditions for the individual series. It is important on this occasion that no particular products are

Figure 8.10 KVz cabinet with cable branch boxes.

described in the delivery conditions. The handicaps make it possible to select suitable products from all those offered.

On principle, the products that are used at the Telekom in the stationary area consist of DIN, German standard, and conformity products to make possible an interchangeability of the products of individual manufacturers. Increasingly, products that do not correspond to the handicaps of the DIN establish themselves at the market. This brings growing problems, because interchangeability is not always a given between the offered products, and the use of foreign products makes adaptations necessary.

In the past, each battery to be used at the Telekom was designed for production and the manufacture process was pursued. In the course of globalization of the markets, this expenditure is no longer justified. As well, the product itself stood in the center of the design planning with the enforced type pattern test. Today, very much time is spent on the examination of production conditions. On the basis of

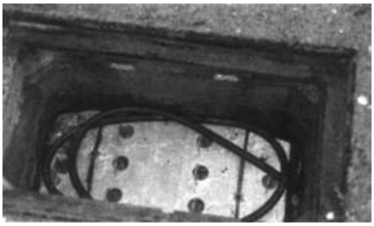

Figure 8.11 Battery in the cable branch box.

much experience, conclusions can already be determined on the quality of the manufacturers' products.

At the site of use, an acceptance test takes place, with which the quality of the product, the installation, the date fidelity, and so on are judged in presence of the supplier. As a further measure, an information system has been activated, through which problems with the products in the application are reported. The consistent evaluation of this information gives information about operation holding. With an accumulation of problems, it is possible to abandon the further procurement and stop the release of a product.

8.8 MAINTENANCE ACTIVITIES IN BATTERY PLANTS

The scope and timing of maintenance procedures are established for the activities at the batteries.

- Capacity tests in principle are enforced with constant current and the results are reported. They become enforced with the acceptance at the site, 6 weeks before the end of the guarantee period, and then in certain intervals. The capacity test during the acceptance procedure can be fall out, if the supplier includes the protocol of the capacity test performed at the end of the manufacturing process. Capacity tests outside the guarantee are enforced at batteries of the series with tubular and Planté plates after 9 years and at valve-regulated batteries after 4 years, calculated from the date of putting into operation. At batteries with grid type plates, a capacity test is planned after 6 years. The date of the next regular capacity test is fixed depending on the result of the previous capacity test.
- Inspections are enforced at batteries every 6 months and the results are documented. With the inspection visual check of the total condition of the battery is carried out (judgment of plates, container, connectors, rack, and so on). Investigation of the temperature of pattern cells is made. With vented batteries the electrolyte density is measured at different cells. Afterward the total voltage and the voltage of individual cells are measured for vented and valve-regulated batteries. Then follows the discharge of the battery with the consumer load. After approximately 10 minutes the total voltage and voltage of individual cells are measured again. If irregularities arise with the inspection, they are evaluated accordingly and countermeasures are started.
- The cleaning of all cells is prescribed every 12 months.

8.9 OPERATION EXPERIENCE

Altogether it can be said that the collected experience corresponds in a high degree with the theory. Figure 8.12 gives an overview of the total distribution of the disturbances covered on the series.

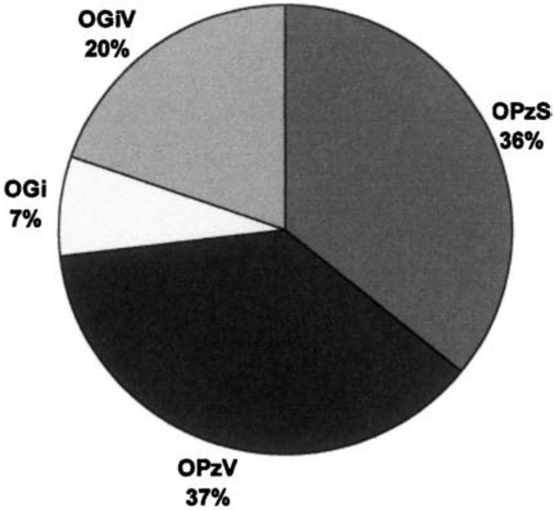

Figure 8.12 Distribution of the disturbance information absolute.

8.9.1 Vented Batteries

Vented batteries essentially show a stable behavior. With Planté plate batteries, whose use by Telekom is insignificant, 20 years of shelf-life is normal. Batteries with tubular plates are a largely uncritical product, with a typical shelf-life of 15–18 years. With these series often there is reason to select the ‘‘electrolyte consumption’’ that ascends with increasing age of the battery and not the actually capacity (must be $< 80\%\ C_N$). Recently there have sometimes been problems with growth on the plates. It has to be clearly distinguished from growth on the plates that is to some extent completely normal by aging and growth of the poles caused by crevice corrosion in the area of the pole bushing, a very critical defect.

There is not yet much experience available with grid type batteries of newest production. Products with high acid density have tended to have problems while being charged. Corresponding examinations should be enforced here.

8.9.2 Valve-Regulated Batteries

The introduction of valve-regulated batteries was accompanied by numerous problems. Many courses in the manufacturing process had to be changed and adapted for the particular case of the production of valve-regulated batteries.

Even bringing in these cells into a level rack is problematic. The containers are constructively identical with those of the vented batteries. If a cell is first put down on the front crossbar before the cell is pushed to the back, tensions appear in the container and damage occurs in the structure of the plastic. This leads inevitably to rips in the container if the valve is put in too tight, which causes it to open because the inside pressure is too high.

The attention to and adjustment of the correct product-specific charge voltage are of great importance with valve-regulated batteries. Furthermore, the temperature-dependent charge voltage with unstable temperature conditions is a basic requirement for the reliable function of the batteries. With valve-regulated batteries, environmental temperatures are to be ensured above 0 °C. Frost damage may appear if the batteries are unloaded at frost or are exposed to frost in the unloaded condition, for example at mains-disconnected equipment in which monitoring circuits lead to a deep discharged battery.

Contrary to the generally represented opinion that valve-regulated batteries dry up if loaded after a discharge with boost charge, it is to be noted that these batteries always reach a comparatively high shelf-life. Also the widespread opinion is wrong that in case of defect there is no electrolyte leakage in valve-regulated batteries. In some cases a little electrolyte leakage is possible, leading to the corresponding consequences for the surroundings. As well the thesis is often represented that valve-regulated batteries tend to fail spontaneously. This observation cannot be confirmed for the area of the Telekom.

The causes of premature failing are corrosion appearances, errors at the valve, or wrong charge voltages.

A very close and open cooperation with the manufacturers has helped to improve the production quality.

8.9.3 Accidents

Accidents appear again and again. Fortunately there have been no cases with personal injury for several years. The security concept developed with the Telekom has made an essential contribution. It consists of the consistent transposition of the demands of the prEN 50272 (draft of European standard) and the fact that for all vented batteries ceramic vent plugs are required. Recombination vent plugs were not in use because of the lack of return-ignition security up to now. A new generation should be reignition safe. Results of examination are not yet available.

Often problems arise when unfamiliar companies work in the operation areas of Telekom. Cooperation and communication with these companies have to be carried out carefully.

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9

Motor Vehicle Starter Batteries

G. SASSMANNHAUSEN and E. NANN

9.1 THE EUROPEAN MARKET

Lead-acid starter batteries are used in land, sea, and air vehicles. Batteries for vehicles are discussed in this chapter. The production of starter batteries approaches 60 million pieces. About 16 million pieces are used for motor vehicle production and about 38 million pieces keep the vehicles ready for operation as back-up batteries. A considerable number of imported and exported pieces play a part in this market. With these numbers Europe achieves about two-thirds of the U.S. production. The production in the Pacific area is in the range of the European market. Markets with growth expectations are within the area of the former eastern block countries, the countries of the Middle East, India, China, and South America.

The collection, processing, and reuse (recycling) of used motor vehicle starter batteries form an important business activity. The regulation of these activities in favor of environmental protection is done via the national versions of European directives, the used battery regulations, and trade restrictions for the distribution of used batteries in non-OECD countries (Basler list*).

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* The Basler list of hazardous wastes is part of the 1992 OECD regulations known as the "Basel Convention" banning the uncontrolled movement of hazardous wastes.

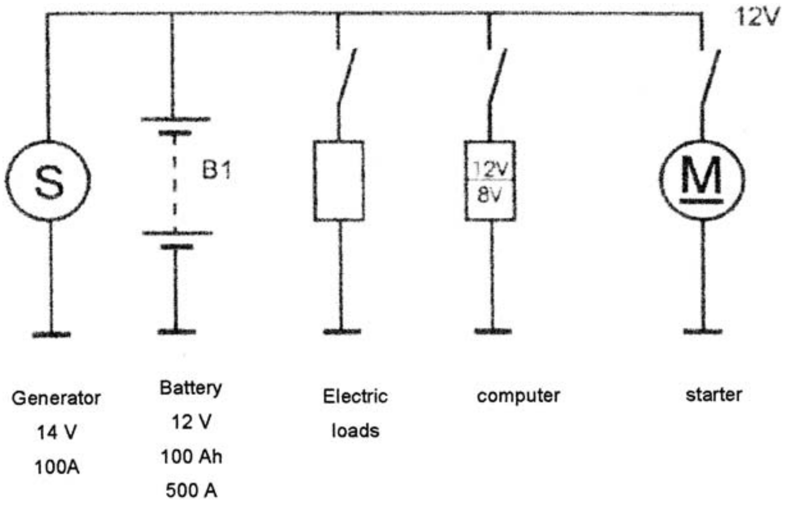


Figure 9.1 The board-net from a motor vehicle in schematic layout.

9.2 TASKS OF A MOTOR VEHICLE STARTER BATTERY

The functions result from the following description of the electrical system of a motor vehicle, the board-net (Figure 9.1). The activation of the system requires that the battery spends the energy for the starter engine and the computer electronics, including preheating or igniting. Security and important auxiliary systems are continuously supplied up to the total discharge of the battery.

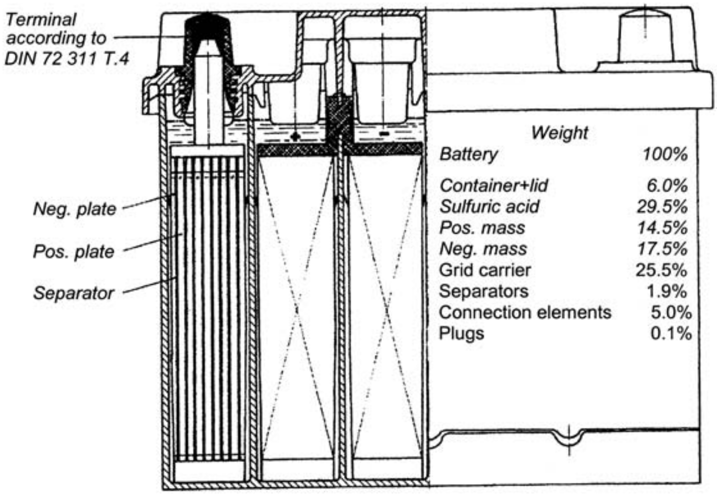
The current consumption of a starter battery varies for a very broad range of electric current demands of the board-net in the engine and generator off-state between 10 mA to 50 mA. In the engine idle state and during creep speed, for example, 20 A to 70 A from the battery are needed and the engine start requires, for example, 300 A for 0.3s to 3s. A 12-V 62-Ah battery results in the following specific charge of the electrode plate surface:

		Operating voltage
Board-net supply, 1	$20\,\mu\,A/cm^2$ (10^{-6} A)	12 V
Board-net supply, 2	$20\,mA/cm^2$ (10^{-3} A)	12 V
Engine ignition	$0.5\,A/cm^2$ (10^{-1} A)	9–11 V

As storage for electrical energy, the starter battery is also a consumer in the board-net. The state of charge depends on constructive features, physical/chemical laws, and a possible regulation in the rank order of the board-net consumers during limited energy production by the generator.

9.3 CONSTRUCTION OF A VEHICLE STARTER BATTERY

Figure 9.2 shows the basic structure of a motor vehicle starter battery, consisting of a container of high-impact-resistant polypropylene copolymer and positive and



Weight	
Battery	100%
Container+lid	6.0%
Sulfuric acid	29.5%
Pos. mass	14.5%
Neg. mass	17.5%
Grid carrier	25.5%
Separators	1.9%
Connection elements	5.0%
Plugs	0.1%

Figure 9.2 Construction of a vehicle starter battery.

negative plates in the cells connected in parallel. Separators electrically separate the plates of different polarity.

Figure 9.3 shows examples of basic grid structures which carry the active masses, with examples of size and the alloy composition. Metallurgists describe the characteristics of alloys made out of different metals by phases or temperature/concentration diagrams. Within these, the formed phases are located; metal components of different constitutions and physical condition are described depending upon the composition and temperature.

Examples of lead-antimony and lead-calcium alloys show the phase diagrams in Figures 9.4 and 9.5. In practice the influences are substantially more complex, because of additional alloy compounds beyond binary alloys.

At the lead grids, as a carrier framework of the lead-acid battery for the active masses, two requirements are placed:

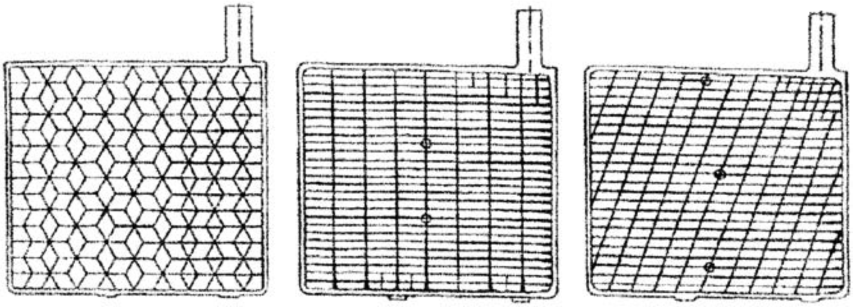


Figure 9.3 Different grid structures that contain the active masses.

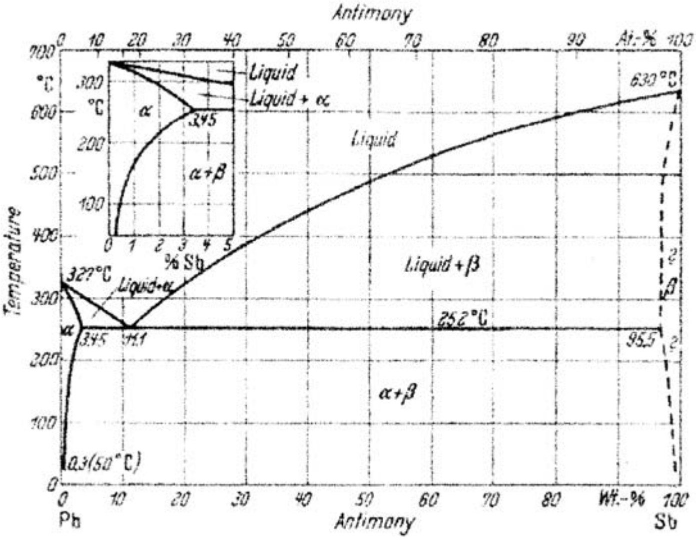


Figure 9.4 Phase diagram of a lead-antimony alloy.

- A mechanical stability depending on the manufacturing methods.
- A sufficient corrosion resistance of the grids for the positive electrode, under the influence of lead dioxide and sulfuric acid.

Optimization of alloy composition, casting parameters, and subsequent treatment provides the required characteristics.

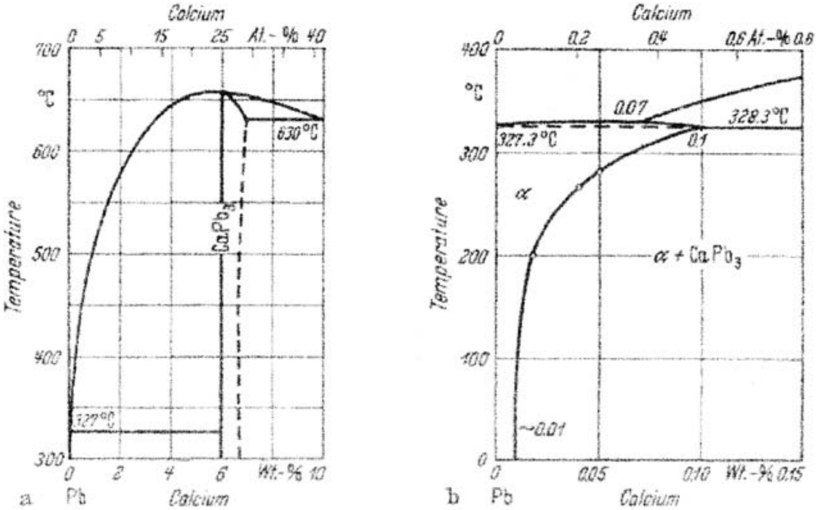


Figure 9.5 Phase diagram of two different lead-calcium alloys.

9.4 ACTIVE MASSES OF THE ELECTRODES

The paste-like lead oxide masses, which are applied on the grids, consist of lead dust (25% dispersed lead and 75% lead oxide (PbO)) produced out of the basic material soft lead. The production takes place in ball mills from the solid state or in reaction containers from the molten state.

The further processing of the lead dust must be coordinated with the process providing correct particle size distribution in order to obtain the desired electrochemical characteristics of the active masses.

Positive and negative paste compositions will be described in the following:

Positive paste:

PbO(pb)	+	H_2O	+	H_2SO_4	+	PbO H_2O	+	N PbO	$* PbSO_4$
lead dust		water		sulfuric acid		lead hydroxide		basic lead	sulfates

Negative Paste:

PbO(pb)	+	H_2O	+	H_2SO_4	+	C	+	Lignin	+	$BaSO_4$
lead dust		water		sulfuric acid		carbon black				barium sulfate

PbO H_2O	+	N PbO	* PbSO	+	$BaSO_4$	+	C	+	Lignin
lead hydroxide		basic lead	sulfates		barium sulfate		carbon black		

9.5 THE MANUFACTURING PROCESS

After applying the porous lead oxide masses on the carrier grids and a superficial drying, the plates are stapled and supplied to a curing process. Within this a control loop of plate moistness and temperature providing the crystal phase formation. The crystal size and plate microstructure are formed out of lead oxide and basic lead oxides. These then essentially determine the desired electrochemical battery characteristics by the resulting pore structure and pore surface. Afterward the plates can be formed, that is the lead oxide masses are electrochemically formed into the active porous positive lead oxide (PbO_2) and the negative lead (Pb) masses by applying direct current. This process is carried out for assembled batteries as well as for plates before the battery assembly process.

In the following the processes with masses and energy quantities are represented:

$2PbSO_4$	+	$2H_2O$	$\rightarrow$	Pb	+	PbO_2	+	$2H_2SO_4$
lead sulfate		water		lead		lead oxide		sulfuric acid (undiluted)
606 g		36 g		207 g		239 g		196 g

Theoretical conversion of a cell:

- Energy content: 53.6 Ah.
- Active mass in practice for a 12-V 54-Ah battery:

$$2400\ \text{g Pb};\ 2600\ \text{g}\ PbO_2;\ 300\ \text{g}\ H_2SO_4.$$

The battery assembly is to a large extent automated. For the electrical separation of positive and negative plates in the sulfuric acid electrolyte, a porous PL foil pocket separates the plates of the same polarity. For the assembly of the cell packages sequences of positive and negative plates are made depending on the desired electrochemical characteristics of the battery.

9.6 DIMENSIONS AND DETAILED SPECIFICATIONS

The following summary shows an overview of the resulting dimensions of the three major production series.

Total number of plates:

Positive plates	Negative plates
N	N + 1
N	N
N + 1	N

Battery dimensions:

Length (mm)	Width (mm)	Height (mm)	Application
212–381	175	175	Passenger car
212–381	175	90	Passenger car
327–518	175–291	210–242	Truck

Modern motor vehicle batteries are sealed with a lid which offers a central degassing system (Kamina). A more advanced technology solution is a central degassing outlet sealed by a porous plastic frit, preventing the ignition of the oxyhydrogen gas mixture from outside and at the same time the spilling of acid droplets, in combination with a parallel lid wall construction, the chamber lid (duplex).

9.7 MOUNTING POSITION IN THE MOTOR VEHICLE

The placement of the batteries in the motor vehicle presupposes the protection of electronic components from possible sulfuric acid emissions. The electrochemistry of the motor vehicle battery always leads to the formation of oxyhydrogen gas by water decomposition. Therefore, caution is required while handling operating batteries. Burning flames, arc, and sparks of electrostatic loadings ignite oxyhydrogen gas. The necessary ignition energy is extremely small.

The mechanical characteristics of motor vehicle batteries must be determined by the application field of the vehicles. The stress in motor vehicle applications during normal operation for acceleration is in the range of approximately 2 to 3 g. Therefore the tight fit of the plate packages in the cell of the battery container is sufficient.

Aside from road and off-road cars, agricultural vehicles require a much higher effort for the construction of plates and plate packages if a reduced service life cannot be accepted. For trucks, especially for vehicles for long-distance use on badly maintained roads or for construction and military vehicles, acceleration values up to 15 g can occur at 15 to 30 Hz. Here substantial construction measures must be taken for the plates and plate packages. With these measures the specific energy and efficiency weight of the batteries are reduced (Wh/kg or W/kg).

Motor vehicle batteries are fixed today by retaining strips on the bottom of the battery case or by handle spannings over the cover in the vehicle. Safety demands determine the retaining constructions. The battery must neither be destroyed nor torn from the mounting plate by sudden stopping.

9.8 ELECTRICAL PROPERTIES

The electrical characteristics of motor vehicle batteries are specified in general for the common 12-V nominal voltage in ampere-hours for the energy content and in amperes (A) for the power output as functions of the temperature and the state of charge (100%). The charge current acceptance often appears as an important characteristic as a function of temperature, state of charge, and charging voltage.

The dependence of the energy content of a battery on its discharge current must be emphasized. The usual specification in ampere-hours is related to 20 hours, for example:

$$\frac{100\,\mathrm{Ah}}{5\,\mathrm{h}} = 5\,\mathrm{A}$$

It results for a total energy withdraw over 5 h of

$$\frac{100\,\mathrm{Ah}}{5\,\mathrm{h}} \cdot 0.8 = 16\,\mathrm{A}$$

and not 20 A. The possible discharged energy content decreases to 80 Ah. In the same way the energy content is affected by decreasing temperature.

9.9 STANDARDIZATION OF BATTERY CHARACTERISTICS

General requirements and tests of lead starter batteries and the details of electrical and mechanical examinations which are to be carried out for motor vehicle starter batteries are described in DIN EN 60 095-1:1993. It eminated from the international standard IEC95-1:1988 and is valid in the EU and associated countries.

9.10 NEW DEVELOPMENT REQUIREMENTS

The demands for increased fuel savings make it necessary to improve the efficiency factor of the consumers, the alternators, and the intermediate storage of electrical energy in vehicles.

Increasing luxury features raise the energy demand on vehicle batteries compared to present batteries. It is required that surplus energy of the alternator can be stored by the batteries and lacking energy be drawn; in principle, this is not new. The standard criteria of a modern starter battery are consequently valid for all new board-net batteries. These are

- High energy content.
- High cold cranking power.
- Vibration-proof compared to present starter batteries.
- Deep discharge behavior.
- Low self-discharge.
- Maintenance-free over the whole service life.
- Operating temperature range between $-30\,^\circ\mathrm{C}$ and $+70\,^\circ\mathrm{C}$.
- Series availability.
- Costs comparable to today's batteries.

Since the load on batteries is increased in an optimized board-net and new loads are added, the batteries must be designed to meet these requirements. Start-and-stop systems already require manifold starting impulse power as compared to conventional vehicles.

9.11 VALVE-REGULATED LEAD-ACID BATTERIES

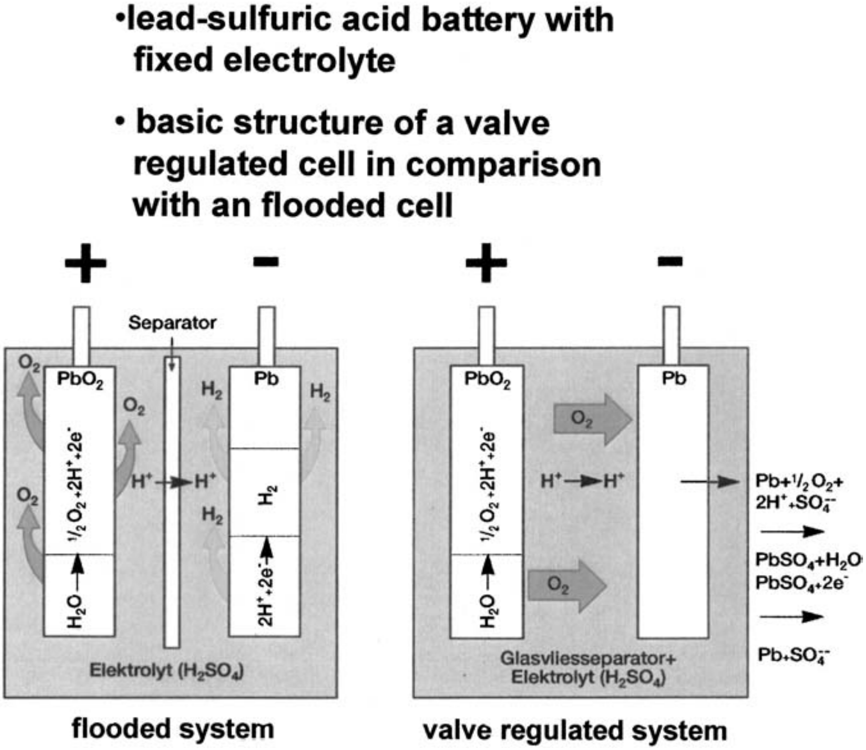
The increased loads in new cars show that the requirements mentioned cannot be fulfilled over a sufficient lifetime by present starter batteries in hybrid or PbCa technology. The requirement to be maintenance — free during the whole service life can only be fulfilled by a valve-regulated lead-acid (VRLA) battery. The high impulse power with the required potential shows that in the valve-regulated technology only the version with micro-glass-fiber separation (AGM) can be applied. This means a lead-acid battery where the electrolyte is fixed in a resistant glass fiber fleece by absorbing the sulfuric acid. A diagram comparing it to conventional systems is shown in Figure 9.6. While in the conventional system the gasses oxygen and hydrogen are generated at the end of charge, which escape from the cell and thus cause the water loss of a battery; the oxygen is internally recombined in the valve-regulated system. Hence a valve-regulated battery is maintenance-free over the full service life – and owing to the fixed electrolyte also independent of its position. A self-closing valve can reduce any overpressure.

Both the positive and negative grids in this new generation of board-net batteries consist of a PbCaSn alloy in order to obtain a high hydrogen overvoltage which is the basis for the recombination and for the extremely low water loss. In addition, the use of this alloy leads to low self-discharge and long shelf-life. The key element of this battery is the fleece separation, a micro-glass-fiber fleece, which fulfills the separator function and at the same time retains the electrolyte because of its high capillary activity.

By using the entire cell volume and a voltage-optimized cell design with optimized grid structure and centrally positioned lug, VRLA batteries can be produced which, compared to standard starter batteries, have a substantially higher cold cranking power in the same container. As a result the cold cranking power at $-18\,^\circ\mathrm{C}$ could be increased from 4.05 kW to 5.2 kW at point U_{30s} in comparison to the present starter battery in the size H8 container.

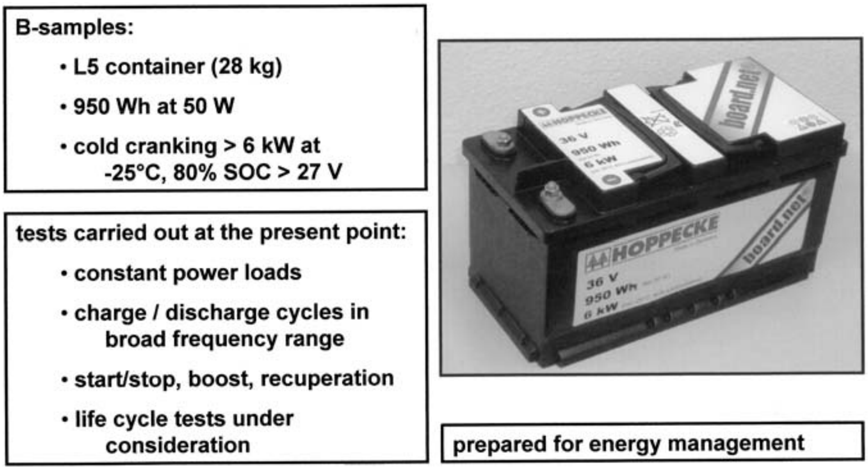
The advantages of the VRLA series are particularly obvious under cyclic load. Under comparative laboratory test conditions the cycle number achieved against today's sealed starter batteries could be increased by on factor of 3 (Figure 9.7) [4].

The properties and special features of the VRLA battery can be summed up as follows:



- lead-sulfuric acid battery with fixed electrolyte
- basic structure of a valve regulated cell in comparison with an flooded cell

Figure 9.6 Comparison of a flooded system and a valve-regulated lead-acid system in a lead/sulfuric acid battery with fixed electrolyte.



B-samples:

- L5 container (28 kg)
- 950 Wh at 50 W
- cold cranking > 6 kW at -25°C, 80% SOC > 27 V

tests carried out at the present point:

- constant power loads
- charge / discharge cycles in broad frequency range
- start/stop, boost, recuperation
- life cycle tests under consideration

prepared for energy management

Figure 9.7 Results of endurance tests of two 12-V 95-Ah batteries for passenger cars.

- Completely maintenance-free, no inspection expenditures.
- Battery is tilt- and spill-proof.
- Increased safety, no electrolyte escape.
- Low self-discharge, long shelf-life.
- Position-independent assembly easily carried out constructively through fixed electrolyte.
- Reduced explosion potential owing to O_2 recombination.
- Increased energy flow rate – prolonged life and/or savings of weight and volume compared to today's starter batteries.

9.12 TRENDS AND REQUIREMENTS FOR NEW BOARD-NET BATTERIES

Front window heating, electrical steering and braking systems, crank-shaft alternator, as well as electromagnetic valve control are being discussed in connection with the 42-V board-net. The new starter/alternator systems facilitate a feedback of braking energy into the board-net. On the other hand the starter can also be used as a boost function for accelerating the vehicle. The battery in such a board-net must be able to provide the necessary cold cranking capacity and the respective impulse capacity for the boost function, and on the other hand to take up the respective alternator energy. The requirements of the 42-V board-net are listed in Figure 9.8.

Boost functions, start-stop, recuperation, and other specific load profiles in a 42-V board-net have to be evaluated with regard to service life and durability, since current power, pulse duration, temperature, standing times, as well as charging voltage and charging durations have a considerable influence on the life span.

The required features of new board-net batteries listed in Figure 9.8 clearly indicate that the advanced battery generation must be specially distinguished by a higher energy throughput rate as compared to today's batteries.

The dual voltage board-net presents the possibility of an optimum adaptation of each battery according to the electrical demands. In this case the 36-V battery

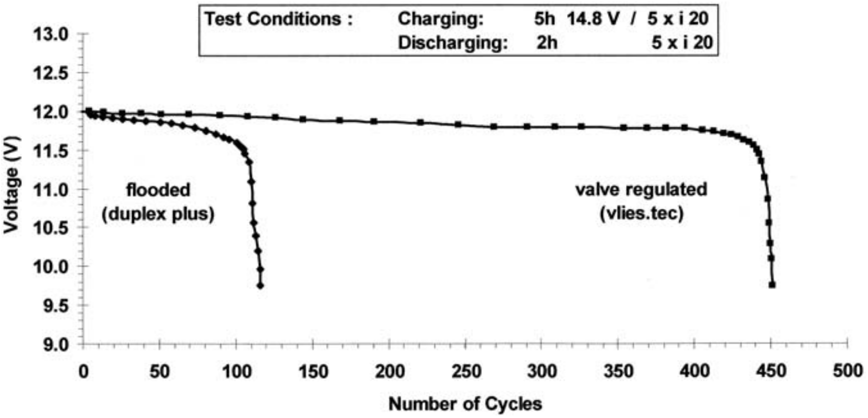


Figure 9.8 Requirements for advanced board-net battery systems.

could be optimized to a cyclically loaded power battery (P), and the 12-V battery to a cyclically loaded battery for standard and quiescent current consumers (LQ). A diagram of such a board-net is given in Figure 9.9.

In answer to requirements the design features of the 36-V battery are roughly the same as those of a present starter battery with central degassing and integrated flame retardant system. The conception provides a different connection technique to exclude any mix-up with the 12-V battery. The container accommodates 18 cells with direct cell connection through the wall as known from the 12-V techniques. Sketches of the battery are shown in Figure 9.10. The requirements of the battery regarding fastening, dimensions, degassing, and flame retardant features as included in the specification for 36-V batteries are fulfilled analogous to the 12-V VRLA batteries.

9.13 BATTERY SENSOR FOR DYNAMIC ENERGY MANAGEMENT

The knowledge of the state of charge and the state of health of the battery is necessary so that an energy management for future board-nets can release sufficient safeguard measures. The identification of the state of charge is also an absolute *must* for the feedback of braking energy into the battery since a nearly fully charged battery could not take up the current. Based on the parameters current, voltage, temperature, and time and using a battery-specific database, it is quite possible to determine the state of charge and the state of health – here meaning the loss of starting capacity – with sufficient precision. By using various characteristic equations of the battery it is also possible to answer essential questions of the battery in a vehicle, for instance: which requirements the battery can fulfill in the present condition.

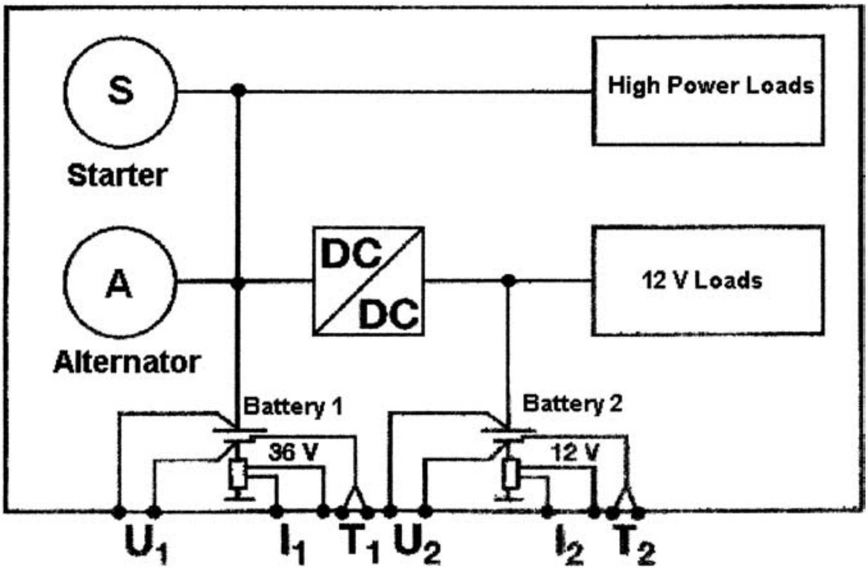


Figure 9.9 Block diagram for the future 42-V/14-V electrical system. Current, voltage, and temperature as a function of time determine the state of charge.

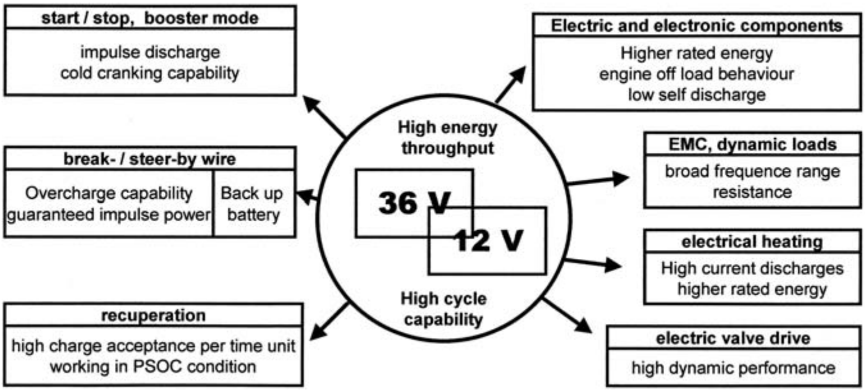


Figure 9.10 36-V valve-regulated lead-acid battery based on vlies.tec® 12-V technology.

Consequently, the knowledge of the state of charge (SOC) and state of health (SOH) permits specific and dynamic battery management. This could include consumption control, switching of quiescent and charging current, warning signs, as well as interference into alternator and motor control to increase the state of charge.

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10

High Energy Batteries

C.-H. DUSTMANN

10.1 INTRODUCTION

As I write this in the year 2002 electric vehicles (EVs) are practically irrelevant for road transport (Figure 10.1). In the year 2000 there were 109 electric cars registered in Germany out of 3,378,343 total (0.003%). Why do we talk about EVs at all?

Electricity is widely used in nearly all industrial and private areas because it can be converted easily into heat, light, and motion and runs all electric devices. Electricity is convenient, clean where it is used, and economical. To an increasing extent it is used with batteries in telephones, computers, tools, etc., independent from the direct connection to a power plant.

Electric motors with inverters using modern power electronics have the perfect characteristics for city vehicles. Due to the high torque from zero speed no clutch is necessary. Overload capability for acceleration makes an 18-kW electric motor more dynamic than a 42-kW gasoline engine (Figure 10.2). Electric vehicles are quiet, have no emissions and offer the option to use any renewable primary energy for mobility.

The only reason for which electric vehicles are used to the very limited extent they are now is the battery—the key component for the performance and autonomy of electric vehicles. In the following chapters those battery systems will be described that offer a specific energy of about 100 Wh/kg. This specific energy is necessary for the minimum range of 100 km in Europe or 100 miles in the United States under all normal driving conditions for a marketable electric vehicle. Figure 10.3 shows a substitution potential of 25% of cars in private households if the vehicle range is

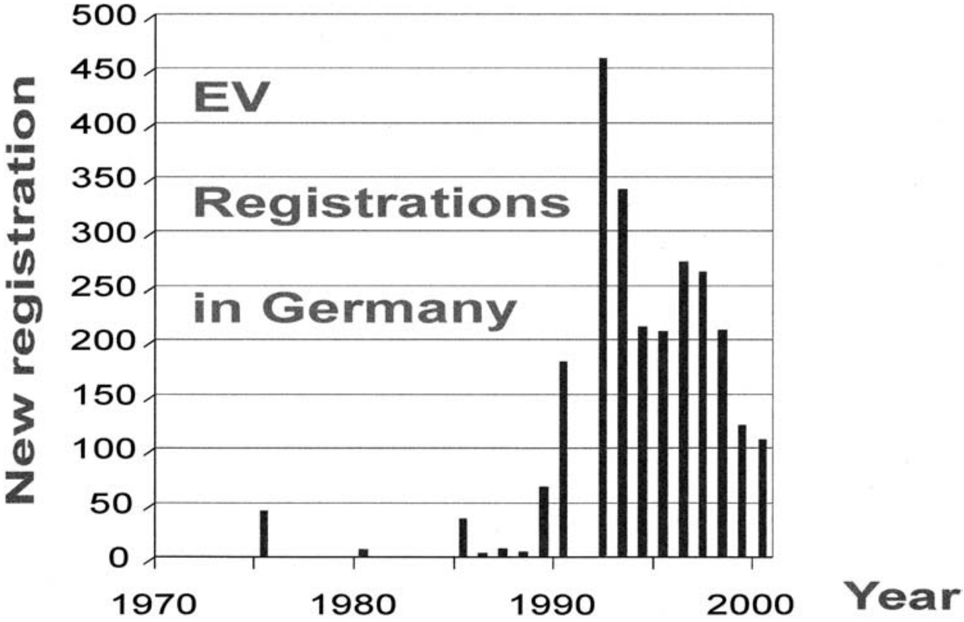


Figure 10.1 30 years EV registrations in Germany. (From Ref. 1.)

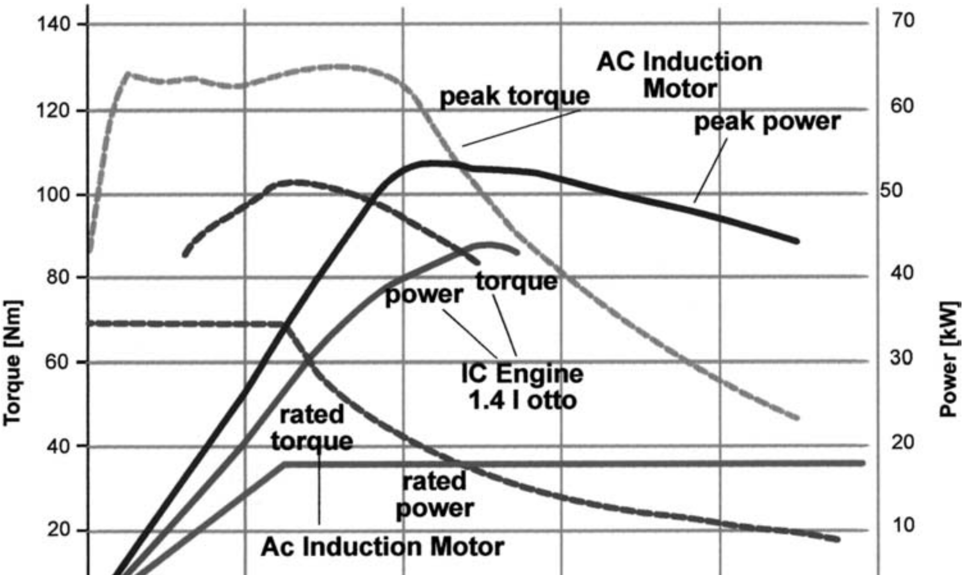


Figure 10.2 Torque and power characteristic of an electric motor with rated power of 18 kW and a 1.4 L gasoline engine. (From Ref. 2.)

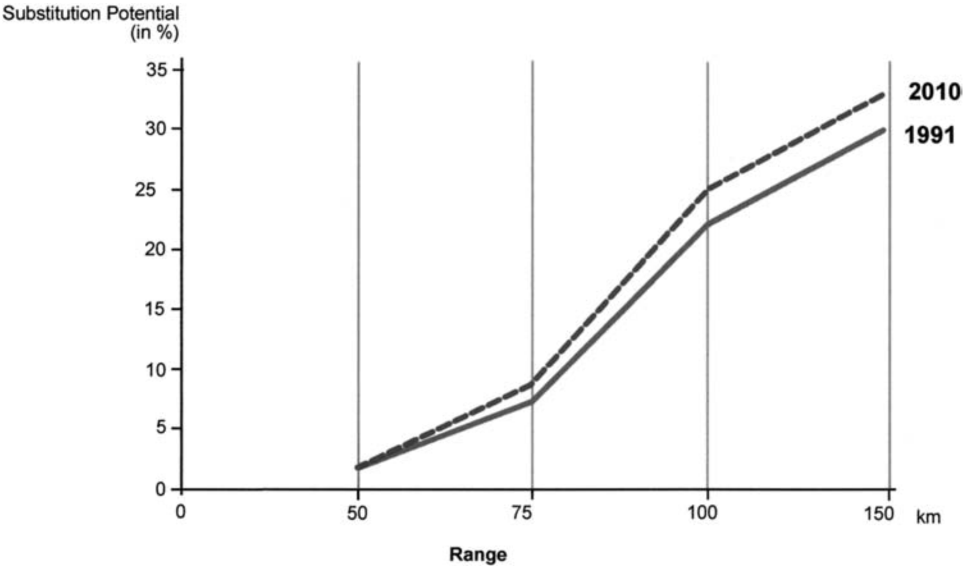


Figure 10.3 Substitution potential of electric vehicles dependent on the vehicle range without change of mobility behavior. (From Ref. 3.)

100 km without a change in the mobility behavior of the users. This is the result of an empirical mobility study [3].

As soon as such a battery is available in sufficient quantities and at a reasonable price, electric vehicles will be available at least for urban transportation. A cost comparison to conventional vehicles is presented in Section 10.7.2. Table 10.1 gives an overview of potential candidates from the present point of view.

10.2 ZEBRA BATTERY ($Na/NiCl_2$)

10.2.1 Technology

ZEBRA batteries use Ni power and plain salt for the electrode material; the electrolyte and separator is β''-Al_2O_3-ceramic, which is conductive for Na^+ ions but an insulator for electrons [4].

This sodium ion conductivity has a reasonable value of $\geqslant 0.2\ \Omega^{-1}\,cm^{-1}$ at 260 °C and is temperature dependent with a negative gradient [5]. For this reason the operational temperature of ZEBRA batteries has been chosen in the range of 270 to 350 °C.

Figure 10.4 illustrates the principle. During charge the salt (NaCl) is decomposed to sodium (Na) and chlorine (Cl). The sodium is ionized; one electron from the m3 shell is conducted by the charger to the higher potential of the anode (minus pole), where it recombines with the sodium ion (Na^+) which was conducted through the β''-Al_2O_3 electrolyte. The free chlorine reacts with nickel (Ni) in the vicinity to form nickel chlorine ($NiCl_2$) as a thin layer that covers the nickel grains.

Table 10.1 EV battery systems.

System	Pb/Pbo	NiMH	$Na/NiCl_2$	Na/S	Li-ion	LPB
Operating temperature (°C)	<45	<45	235–350	285–330	<50	60–80
Electrolyte	H_2SO_4	KOH	β''-ceramic	β''-ceramic	$LiPF_6$	Polyethylene oxide
Cell OCV (V)	2.0	1.2	2.58	2.1	4.0	4.0
Specific energy (Wh/kg)	25–35	40–60	100–120	110	80–120	100–120
Energy density (Wh/L)	50–90	120–160	160–200	135	200	200
Specific power (W/kg)	150	Up to 1000	150–180	<75	500–800	300–400
Comments	Largest use	[a]	EV battery	Stationary	[b]	

[a] Very high power cells for power assist HEV are available.
[b] Li-ion batteries can be optimized for high power or high energy.

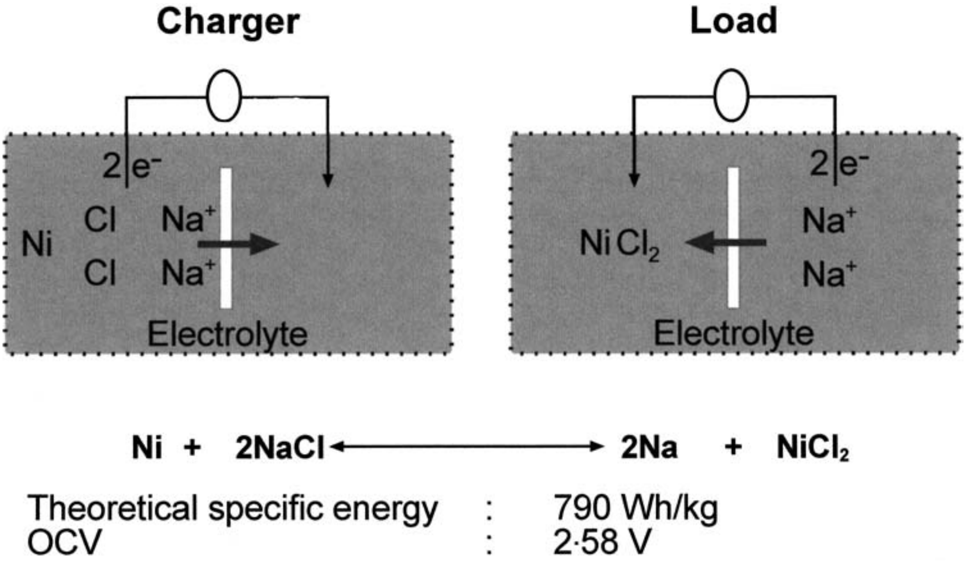


Figure 10.4 ZEBRA chemistry.

The reverse reaction during discharge is only possible by ionization of the sodium; the sodium ion is conducted back through the β''-Al_2O_3 electrolyte to the cathode, whereas the electron now delivers its energy that was previously taken from the charger to the load. In the cathode it recombines with the sodium to form salt and nickel again.

There is no side reaction and therefore the charge and discharge cycle has 100% charge efficiency; no charge is lost. This is due to the ceramic electrolyte.

The cathode has a porous structure of nickel and salt which is impregnated with $NaAlCl_4$, a 50/50 mixture of NaCl and $AlCl_3$. This salt liquefies at 154 °C, and in the liquid state it is conductive for sodium ions. It has the following functions, which are essential for ZEBRA battery technology:

1. Sodium ion conductivity inside the cathode. The ZEBRA cells are produced in the discharged state. The liquid salt $NaAlCl_4$ is vacuum impregnated into the porous nickel/salt mixture that forms the cathode. It conducts the sodium ions between the β''-Al_2O_3 ceramic surface and the reaction zone inside the cathode bulk during charge and discharge and makes all cathode material available for energy storage. It also provides a homogenous current distribution in the ceramic electrolyte.
2. Low resistive cell failure mode. Ceramic is a brittle material and may have a small crack or may break. In this case the liquid salt $NaAlCl_4$ gets into contact with the liquid sodium (the melting point of sodium is 90 °C) and reacts to salt and aluminum:

   $$NaAlCl_4 + 3Na \rightarrow 3NaCl + Al$$

   In case of small cracks in the β''-alumina the salt and aluminum closes the crack. In case of a large crack or break the aluminum formed by the above reaction shorts the current path between plus and minus so that the cell goes to low resistance. By this means long chains of 100 or 200 cells only lose the voltage of one cell (2.58 V) but can continue to be operated. The ZEBRA battery is cell-failure tolerant. It has been established that 5 to 10% of cells may fail before the battery can no longer be used.

This same reaction of the liquid salt and liquid sodium is relevant for the high safety standard of ZEBRA batteries: In case of mechanical damage of the ceramic separator due to a crash of the car the two liquids react in the same way, and the salt and aluminum passivates the $NiCl_2$ cathode. The energy released is reduced by about 1/3 compared to the normal discharge reaction of sodium with nickel chloride.

3. Overcharge reaction. The charge capacity of the ZEBRA cell is determined by the quantity of salt (NaCl) available in the cathode. In case a cell is fully charged and the charge voltage continues to be applied to the cell for whatever reasons, the liquid salt $NaAlCl_4$ supplies a sodium reserve following the reversible reaction

$$2NaAlCl_4 + Ni \leftrightarrow +2Na + 2AlCl_3 + NiCl_2$$

This overcharge reaction requires a higher voltage than the normal charge, as illustrated in Figure 10.5. This has three practical very welcome consequences:

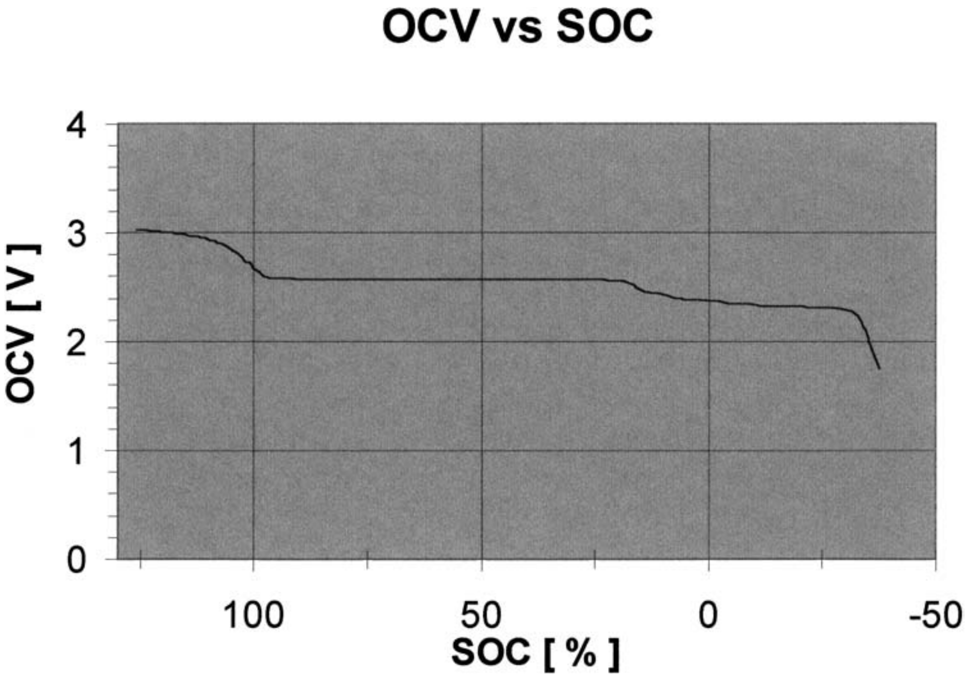


Figure 10.5 ZEBRA open circuit voltage (OCV) depending on the status of charge (SOC).

(a) Any further charge current is stopped automatically as soon as the increased open voltage equalizes the charger voltage.

(b) If cells are failed in parallel strings of cells in a battery, the remaining cells in the string with the failed cells can be overcharged in order to balance the voltage of the failed cells.

(c) For a vehicle fully charged in mountainous conditions there is an overcharge capacity of up to 5% for regenerative breaking so that the break behavior of the vehicle is fundamentally unchanged.

4. Overdischarge reaction. From the very first charge the cell has a surplus of sodium in the anode compartment so that for an overdischarge tolerance sodium is available to maintain current flow at a lower voltage, as indicated in Figure 10.5. This reaction is equal to the cell failure reaction but runs without a ceramic failure.

10.2.2 ZEBRA Cell Design and Production

ZEBRA cells are produced in the discharged state so that no metallic sodium can be handled. All the required sodium is inserted as salt. Figure 10.6 shows the cell design. The positive pole is connected to the current collector, which is a hair-needle shaped wire with an inside copper core for low resistivity and an outside nickel plating so that all material in contact with the cathode is consistent with the cell chemistry.

The cathode material in form of a granulated mixture of salt with nickel powder and traces of iron and aluminum is filled into the β-alumina tube (Figure 10.7). This tube is corrugated for resistance reduction by the increased surface and is surrounded and supported to the cell case by a 0.1-mm-thick steel sheet that forms a capillary gap surrounding the β-alumina tube. Due to capillary force the sodium is wicked to the top of the tube and wets it independently of the sodium level in the anode compartment.

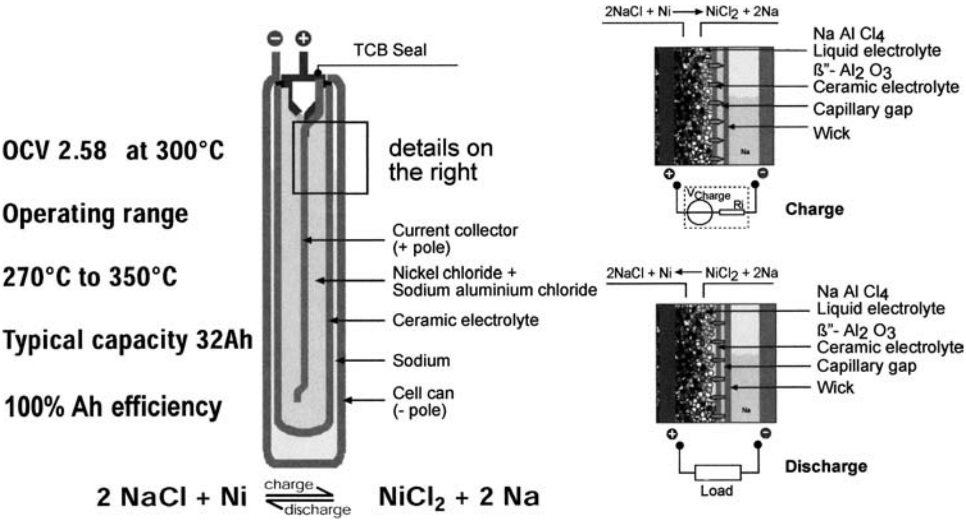


Figure 10.6 Typical ZEBRA cell design.

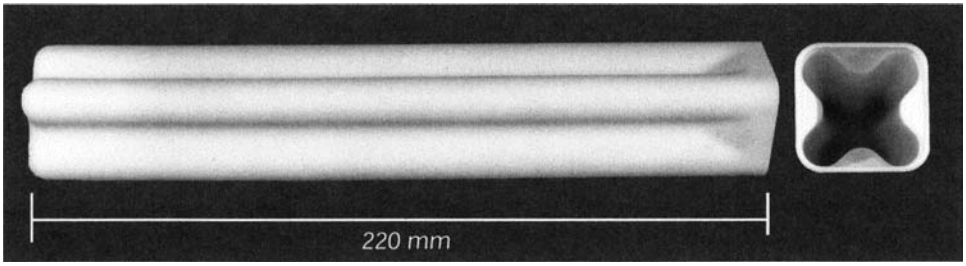


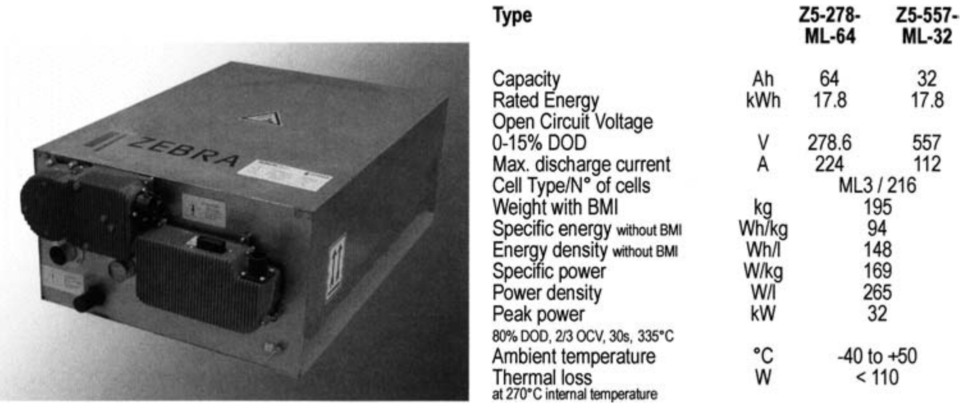
Figure 10.7 Beta-alumina tube.

The cell case is formed out of a rectangular tube continuously welded and formed from a nickel-coated steel strip and a laser-welded bottom cap. The cell case forms the negative pole.

The cell is hermetically sealed by laser-welded nickel rings that are thermocompression bounded (TCB) to an α-alumina collar which is glass brazed to the β-alumina tube.

10.2.3 ZEBRA Battery Design and Production

ZEBRA cells can be connected in parallel and in series. Different battery types have been made with one to five parallel strings, up to 220 cells in series, and 100 to 500 cells in one battery pack. The standard battery type Z5 (Figure 10.8) has 216 cells arranged in one (OCV = 557 V) or two (OCV = 278 V) strings. Between every second cell there is a cooling plate through which ambient air is circulated (Figure 10.9), providing a cooling power of 1.6 to 2 kW. For thermal insulation and mechanical support the cells are surrounded by a double-walled vacuum insulation typically 25 mm thick. Light plates made out of foamed siliconoxide take the atmospheric pressure load. This configuration has a heat conductivity of only 0.006 W/mK and is stable for up to 1000 °C.



Type		**Z5-278-ML-64**	**Z5-557-ML-32**
Capacity	Ah	64	32
Rated Energy	kWh	17.8	17.8
Open Circuit Voltage 0-15% DOD	V	278.6	557
Max. discharge current	A	224	112
Cell Type/N° of cells		ML3 / 216	
Weight with BMI	kg	195	
Specific energy without BMI	Wh/kg	94	
Energy density without BMI	Wh/l	148	
Specific power	W/kg	169	
Power density	W/l	265	
Peak power 80% DOD, 2/3 OCV, 30s, 335°C	kW	32	
Ambient temperature	°C	-40 to +50	
Thermal loss at 270°C internal temperature	W	< 110	

Figure 10.8 Standard ZEBRA battery type Z5C.

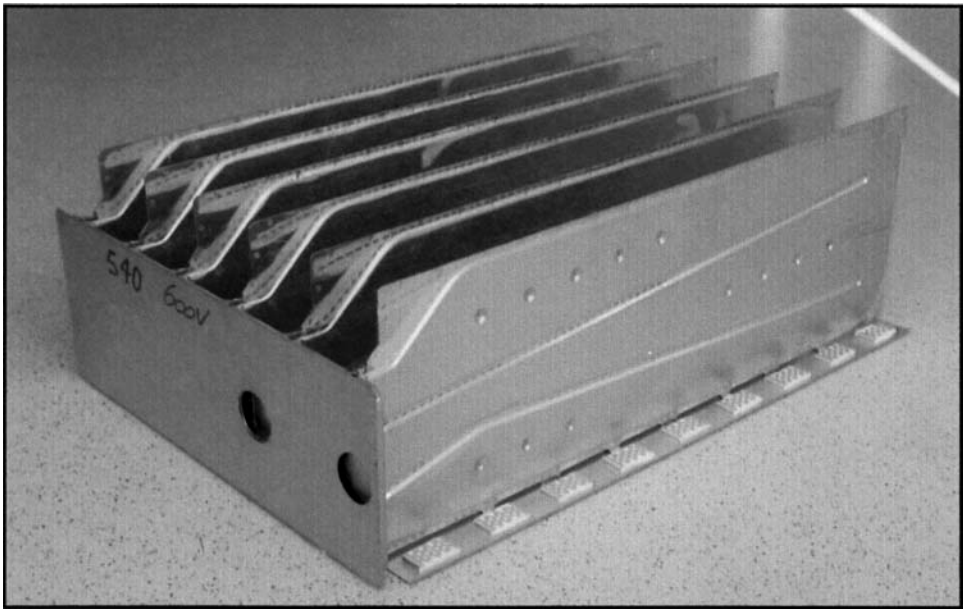
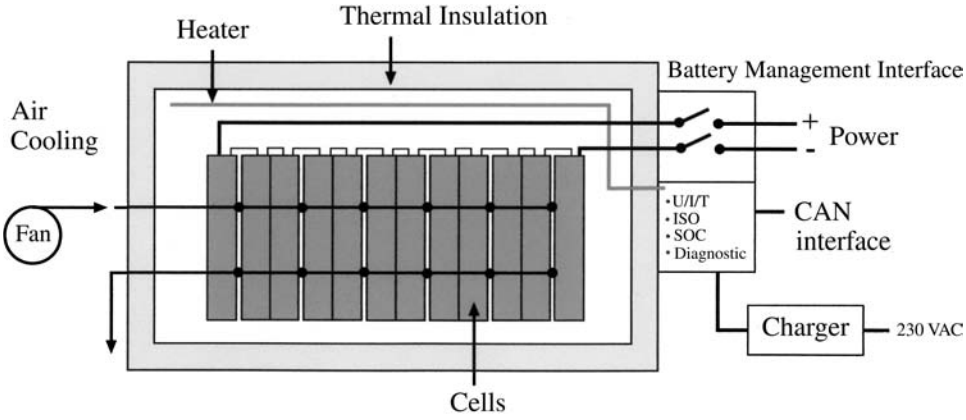


Figure 10.9 Z5C battery cooling plates.

10.2.4 Battery System Design

Figure 10.10 illustrates all components of the complete system ready for assembly. The ohmic heater and the fan for cooling are controlled by the battery management interface (BMI) for thermal management. Plus and minus poles are connected to a main circuit breaker that can disconnect from outside the battery. The circuit breaker is also controlled by the BMI.



Up to 16 battery units in parallel (285 kWh / 510 kW)

Figure 10.10 ZEBRA battery system.

The BMI measures and supervises voltage, current, status of charge, and insulation resistance of plus and minus to ground and also controls the charger by a dedicated PWM signal. A CAN-bus is used for the communication between the BMI, the vehicle, and the electric drive system. All battery data are available for monitoring and diagnostics with a notebook computer.

A multibattery server is designed for up to 16 battery packs to be connected in parallel in a multibattery system with 285 kWh/510 kW using Z5C batteries.

10.2.5 ZEBRA Battery Performance and Life Data

ZEBRA cells and batteries are charged in an IU characteristic with a 6-h rate for normal charge and a 1-h rate for fast charge. The voltage limitation is 2.67 V/C for normal charge and 2.85 V/C for fast charge. Fast charge is permitted up to 80% SOC. Regenerative breaking is limited to 3.1 V/C and 60 A/C so that high regenerative breaking rates are possible.

The peak power during discharge, defined as the power at 2/3 OCV, is independent of SOC so that the vehicle performance and dynamic is constant over the whole SOC range [6]. Obviously this is important for practical reasons. Typical battery parameters are summarized in Figure 10.8.

Battery life is specified as calendar life and cycle life. The calendar life of 11 years is demonstrated. The cycle life is measured by the accumulation of all discharged charge measured in Ah divided by the nameplate capacity in Ah, so that one nameplate cycle is equivalent to a 100% discharge cycle. This is a reasonable unit because of the 100% Ah efficiency of the system. Furthermore 100% of the nameplate capacity is available for use without influence on battery life. The expected cycle life is up to 2500 nameplate cycles.

10.2.6 Battery Safety

Battery safety is essential, especially for mobile applications keeping in mind that each battery should store as much energy as possible, but this energy must not be released in an uncontrolled way under any conditions. It is required that even in a major accident there is no additional danger originating from the battery. Many different tests are performed to ensure safety, e.g., crash tests of an operative battery against a pole at 50 km/h (Figure 10.11), overcharge tests, overdischarge tests, short circuit tests, vibration tests, external fire tests, and submersion tests of the battery in water have been specified and performed [7]. The ZEBRA battery passed all these tests because it employs a four-barrier safety concept [8,9]:

1. Barrier by the chemistry. In case of severe mechanical damage of the battery the brittle ceramic breaks, whereas the cell case made out of steel is deformed and most likely remains closed. In any case the liquid electrolyte reacts with the liquid sodium to form salt and aluminum equal to the overcharge reaction described above. These reaction products form a layer covering the $NiCl_2$ cathode and thus passivate it. This reaction reduces the thermal load by about 1/3 compared to the total electrochemically stored energy.

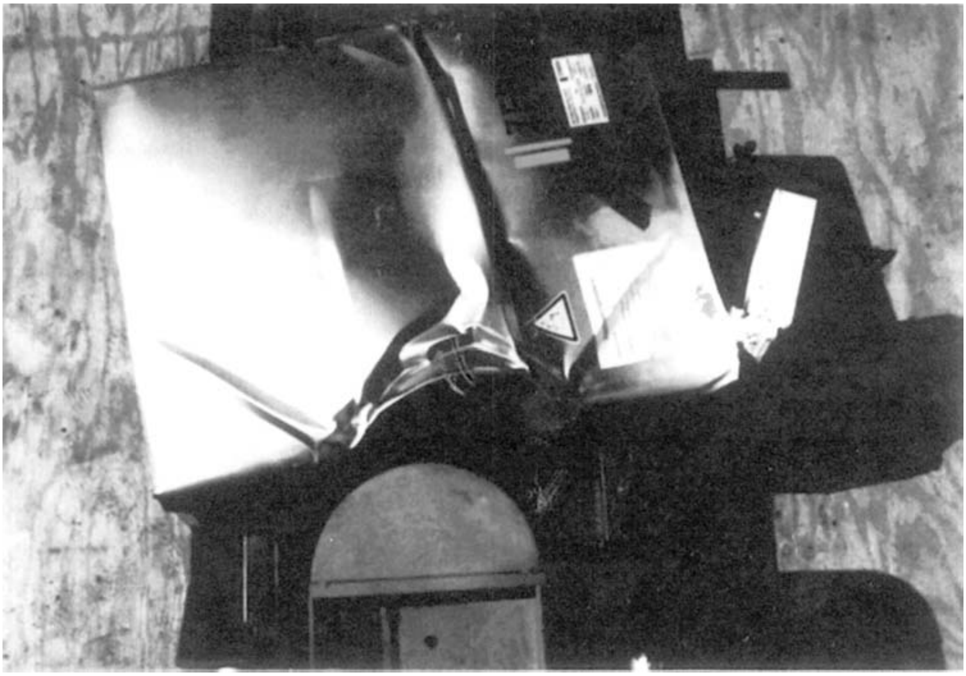


Figure 10.11 ZEBRA battery crashed against a pole at 50 km/h.

2. Barrier by the cell case. The cell case is made out of steel with glass-brazed thermocompression-bounded seal that remains closed for temperatures up to about 900 °C.
3. Barrier by the thermal enclosure. The thermal isolation material of the battery box is made out of foamed SiO_2 which is stable for above 1000 °C. In combination with vacuum like a thermus it has a heat conductivity of only 0.006 W/mK. This value is increased only by a factor of 3 without vacuum. Beyond its primary function of thermal enclosure it is a protective container for all fault or accident conditions.
4. Barrier by the battery controller. The battery controller supervises the battery and stops operation in any undesired situation.

10.2.7 Recycling

Nowadays any product that is introduced to the market has to be recycled at the end of its usage. ZEBRA batteries are dismantled. The box material is stainless steel and SiO_2, both of which are recycled by established processes. The cells contain Ni, Fe, salt, and ceramic. For recycling they are simply added to the steel melting process of the stainless steel production. Nickel and iron are contributed to the material production and the ceramic and salt is welcome to form the slag. The recycling is certificated and cost effective.

10.2.8 Applications

The ZEBRA battery system is designed for electric vehicles (Figure 10.12) which require a balance of power to energy of about 2, e.g., a 25 kWh battery has about 50 kW peak power. Other applications are electric vans, buses, and hybrid buses with ZEV range (Figures 10.13 and 10.14).

The present generation of ZEBRA batteries is not applicable for hybrid vehicles that have a small battery of about 3 kWh but high power up to 60 kW (a power to energy ratio of 15 to 20). Recently also prototypes for stationary applications have been constructed. These have great advantages in hot climates and for frequent cycling, where the lifespan of conventional batteries is reduced such that the two- to three-times higher price of ZEBRA batteries is overcompensated by its much longer life, resulting in lower life cycle cost and avoiding the exchange of batteries. For uninterrupted power source (UPS) applications the float voltage of 2.61 V/cell for ZEBRA batteries has been established.

10.3 NaS BATTERY

10.3.1 Technology

Sodium-sulfate batteries use metallic sodium and sulfur, both in the liquid state, for the electrode material and are assembled in the charged state. The electrolyte and separator is β''-Al_2O_3-ceramic as in the ZEBRA battery (Fig. 10.13). During discharge the sodium is conducted through the β-alumina to react with sulfur to form Na_2S_n with $3 < n < 5$. For charge the same reaction is reversed. The main components of the NaS cell are shown in Figure 10.14. The negative pole is connected to the sodium container in the center of the cell, which is made out of stainless steel. This container has a small hole at the bottom which is designed to limit the sodium flow in case of overheating or overvoltage. The container is

Figure 10.12 Electric vehicles.

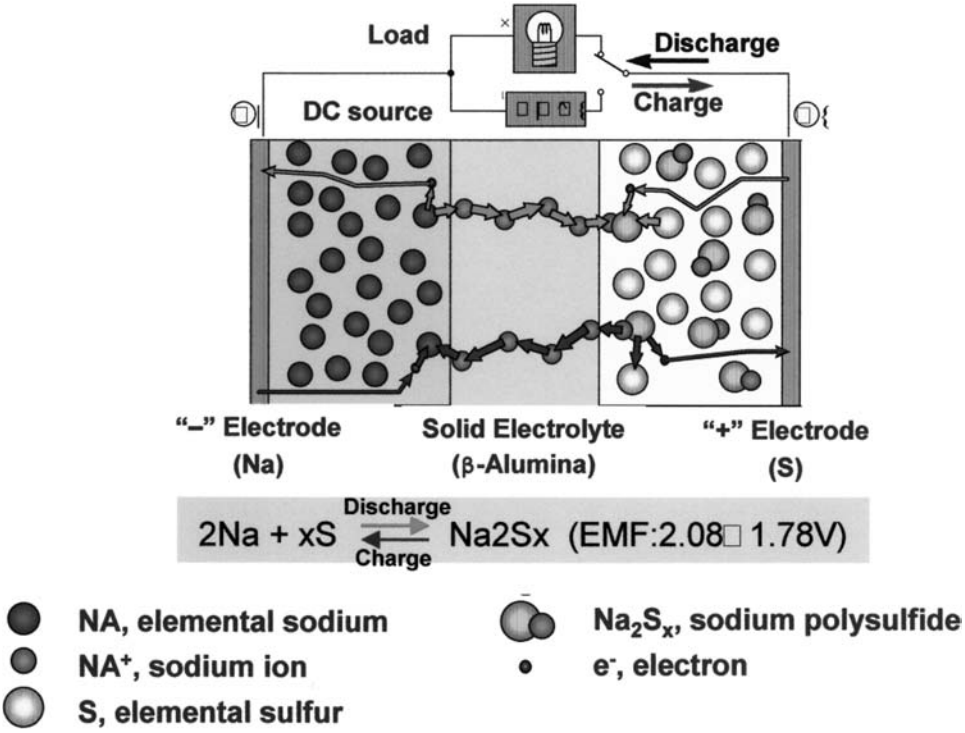


Figure 10.13 NaS battery chemistry.

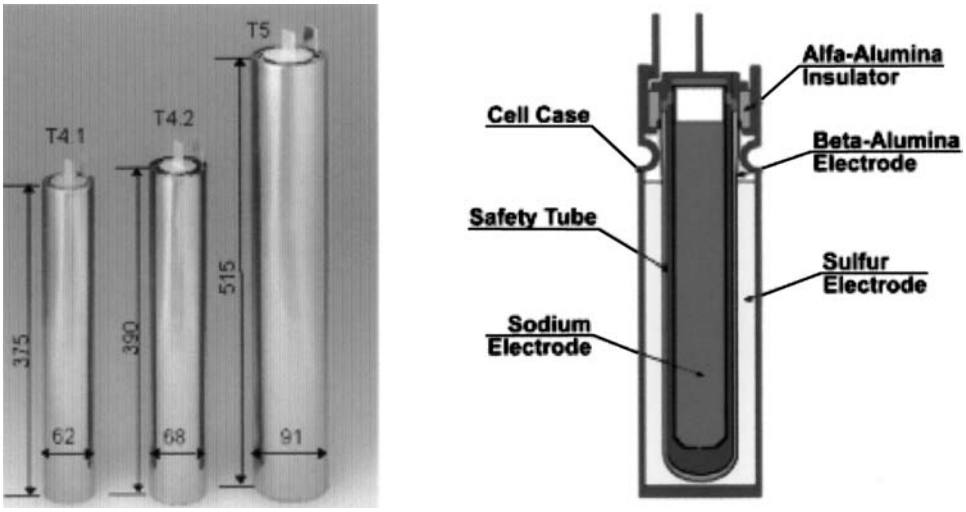


Figure 10.14 NaS cell components. (From Ref. 10.)

surrounded by a deep drawn safety insert in aluminum, which has a tight fit to the inner shape of the β-Al_2O_3 tube in order to form a capillary gap for the wetting of the ceramic electrolyte. The ceramic tube is hermetically sealed with a thermocompression-bound (TCB) seal to the negative and positive poles, which are formed by the cell case. The sulfur is contained in the space between the ceramic tube and the cell case. Sulfur and, in a partially discharged state, polysodium sulfur are both electrically nonconductive so that a carbon-felt is integrated for conductivity. The cell case is made out of aluminum and the inside coated with a conductive layer for corrosion protection.

The NaS cells now being produced by the Japanese company NGK Insulators have 632 Ah and 340 kWh/m^3. 320 of such cells have been connected in parallel and in series to form modules with 375 kWh and 3500 kg weight. These modules are connected together for load leveling and power quality plants with up to 6 MW/48 MWh. About 50 of such plants are in operation, the oldest since 1992.

Initially NaS batteries were developed for mobile and stationary applications. But during abuse testing and simulations of heavy accidents the sodium and sulfur reacted in an uncontrolled way and toxic gas was identified. For this reason NaS batteries are no longer considered for mobile applications, but only for stationary load leveling where damage due to accidents need not be considered (Figure 10.15).

10.4 LITHIUM-ION BATTERY

10.4.1 Technology

Lithium is a light and very reactive metal so that it is attractive for electrochemical energy storage if a stable electrolyte can be found. There are different Li salts used that are solved in nonaquatic solvents like methyl acetate or methyl formate. The positive electrode is $LiCoO_2$, which is mostly used today, but for car battery applications it is too expansive. $LiNiO_2$ and $LiMn_2O_4$ are under investigation and should lead to lower cost, but have less energy density.

The negative electrode is intercalated carbon that can store Li up to C_6 Li. The principle is shown in Figure 10.16.

Rechargeable Li-ion batteries were introduced to the market for consumer products like mobile phones and notebooks. For electric vehicles up to now only experimental cars have been demonstrated [12]. The main open tasks are related to safety under abusive conditions and cost. Li-ion batteries can be designed for high power or high energy (Table 10.1). It can be expected that they will be a candidate for 42-V car systems as soon as safety and cost levels are satisfactory.

10.5 LITHIUM–POLYMER BATTERY

Lithium–polymer batteries (LPBs) use intercalated carbon for the negative electrode, a polymer electrolyte, and metallic lithium that is deposited as a thin film as the negative electrode. This battery type is under development but not yet introduced to the market for electric vehicles.

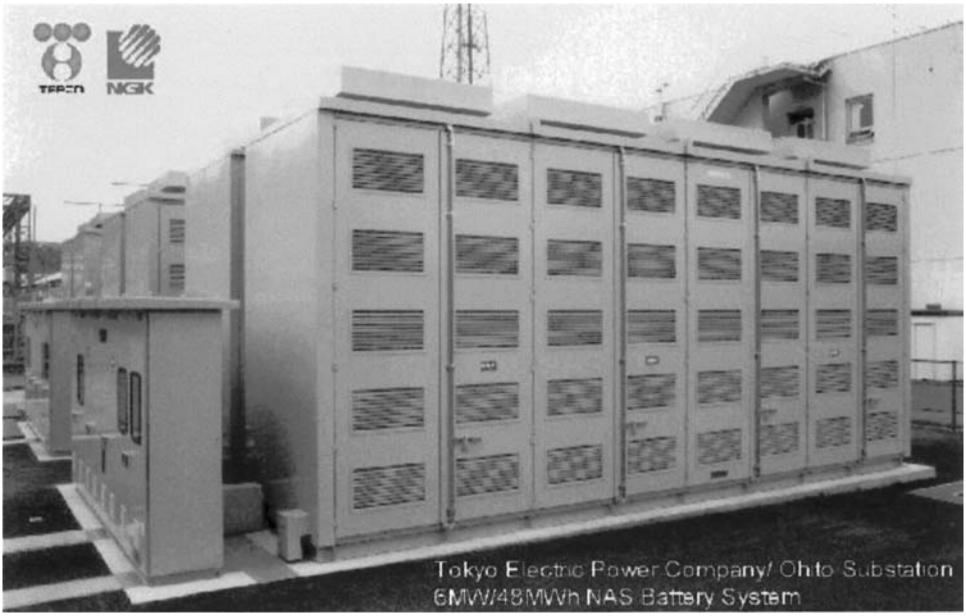


Figure 10.15 NaS battery load levelling plant built by NGK Insulators (Japan).

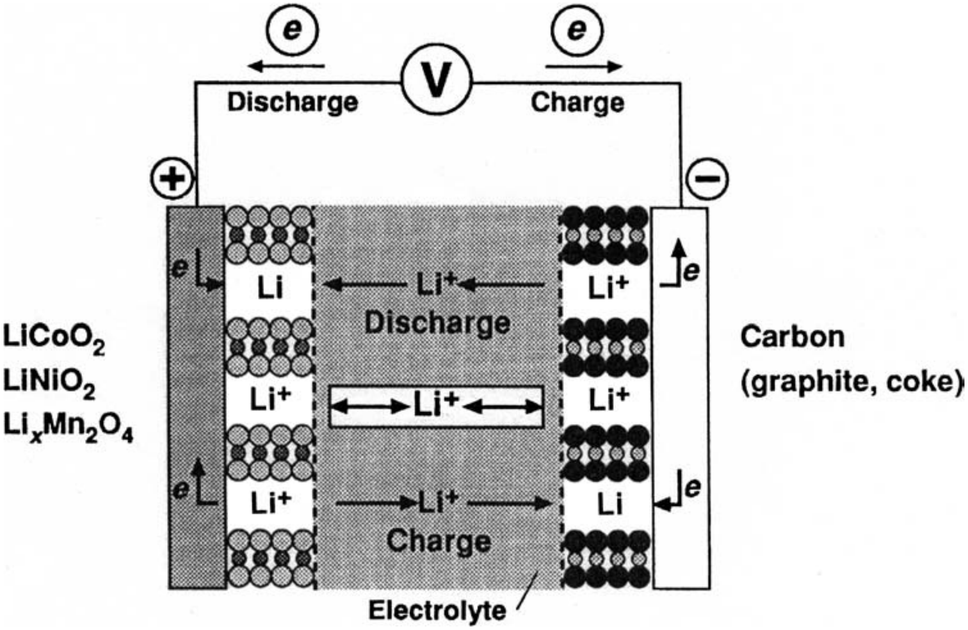


Figure 10.16 Schematic of a Li-ion battery. (From Ref. 8.)

10.6 OTHER BATTERY SYSTEMS

For completeness Zn-halogen and redox batteries should be mentioned. These types of batteries have the advantage of the ability to separate the electrolyte from the storage of an electrode material that is liquid and can be stored in tanks (Figure 10.17). By this means power and energy content are independent from one another. For mobile applications this battery type no longer has any relevance due to safety concerns. In case of accident the liquid could be spilled out and, e.g., bromine would be liberated. But for stationary applications the possibility to store large quantities of energy in tanks separate from the power-determining electrolyte justifies the leak detection effort. Therefore, redox battery systems are still under consideration for stationary electric energy storage.

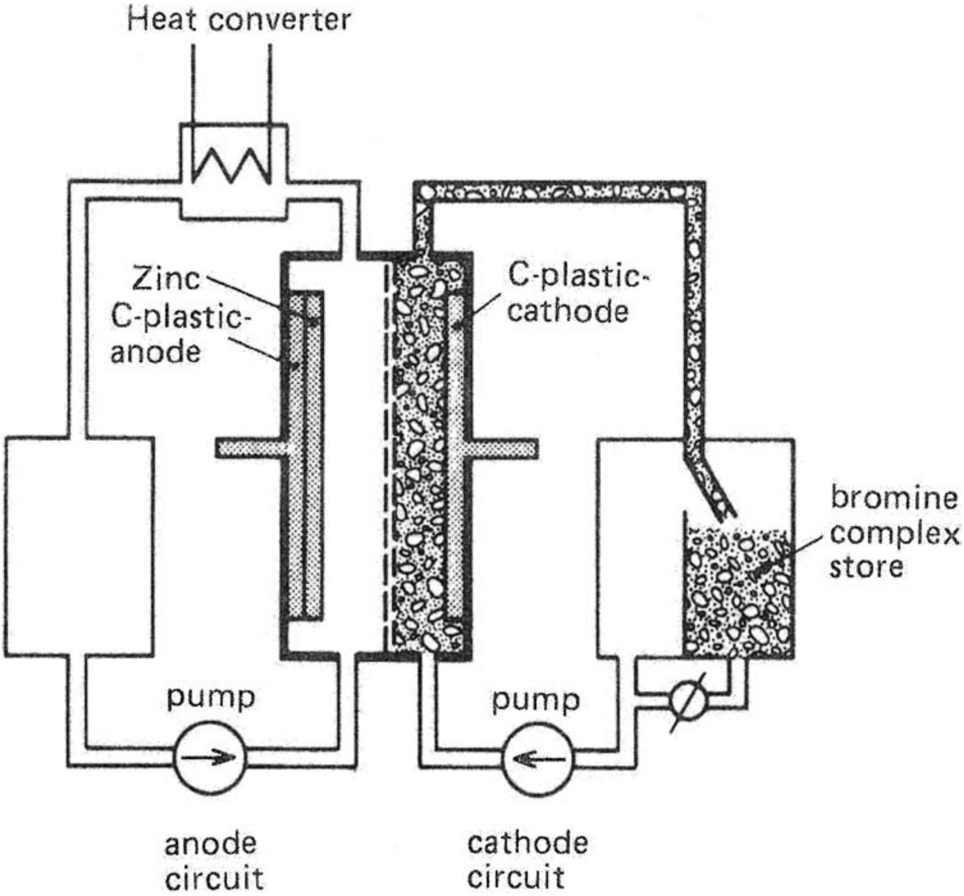


Figure 10.17 Principle of the Zn/halogen accumulator with two different electrolyte circuits.

10.7 BATTERY OVERVIEW

10.7.1 Minimum Requirements for EV Batteries

From mobility studies [13] it has been well established that the average distance driven in cars per day is 40–60 km and 40–60 miles in the United States, subdivided into 3.8 trips. At least during the introduction phase it cannot be assumed that public charging stations will be available and that the drivers are willing and able to plan their trips with such accuracy and detail that charging between trips during the day is acceptable. Therefore, the strategy for the introduction of electric vehicles can only be to charge at night and drive during the day. Therefore, the autonomy of EVs has to be 60 km (60 miles in the United States) plus a reserve of 30 to 40%. EV fleet tests [14] have shown that normal EV drivers use 60 to 70% of their capacity independent of the range because they feel comfortable only with a sufficient reserve. These above facts lead to the requirement of at least a 100-km range under any conditions, like severe weather. The other fundamental requirement is a top speed of 100 km/h because vehicles for urban traffic also use motorways where trucks are driving at 80 km/h and it must be possible to overtake them with a sufficient speed difference.

Figure 10.18 shows the range of a typical EV depending on its speed for three typical specific energy values of batteries. From this it is obvious that the battery of a marketable electric vehicle has to have about 100 Wh/kg as its minimum.

For the other requirements of safety, vibration resistance, climate, etc., the reader is referred to Chapter 4, Sec. 4.4.

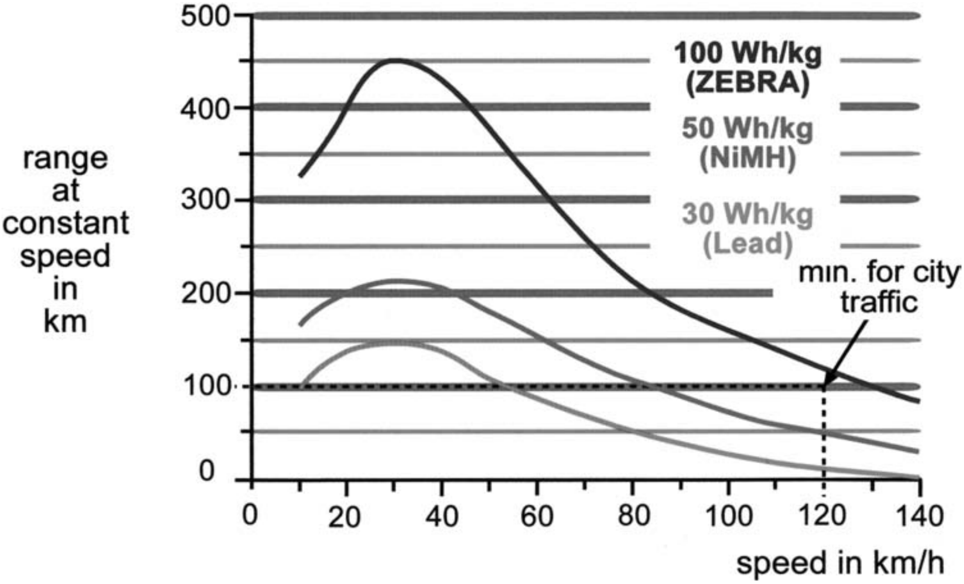


Figure 10.18 Range of electric vehicles depending on the speed and battery specific energy.

10.7.2 ZEV Life Cycle Costs Start to Be Competitive

A car for urban use drives typically 10,000 to 15,000 km per year for about 10 years so that the operating cost for 150,000 km should be considered. All investigations on vehicle cost indicate that the electric car cost without the battery is equal to or even a little less than a comparable thermal engine car, whereas for operation electricity is cheaper than fuel. Figure 10.19 shows that EVs reach breakeven cost at a fuel price of 1 EUR/L and a battery price of 300 Euro/kWh. For ZEBRA batteries the necessary battery life of 10 or more years and 1000 or more nameplate cycles have been demonstrated. It can be expected that the battery will last as long as the vehicle. Another option is battery rental, for which the monthly rental fee is paid out of the energy cost difference between electricity and fuel. For electric vehicles the maintenance costs (no oil replacement, nearly no break disk exchange due to electric regenerative breaking, no exhaust pipe replacement) irrespective of the energy costs and the assurance costs are less than for conventional cars.

These conditions are beginning to be realistic due to rise of crude oil price and the beginning of series production of at least the ZEBRA battery. Now electric vehicles are starting to become an option for urban traffic, about 100 years after their first period of success.

10.8 FUEL CELLS

Fuel cells have been known about for more than 150 years [15]. W. R. Grove operated the first fuel cell in his laboratory by 1842, 17 years before G. Planté built the first lead-acid accumulator. However, they never could compete with the thermomechanical process for electricity production. But they are being rediscovered nowadays because they offer the possibility to convert chemical energy to electricity

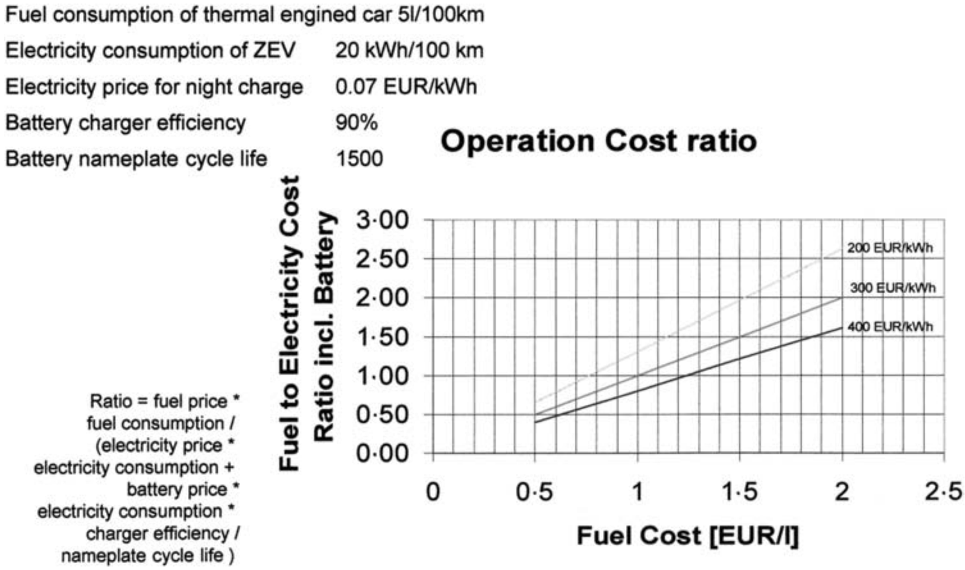


Figure 10.19 EV battery and electricity cost compared to fuel cost.

Table 2 Different fuel cell types.

Type	Electrolyte	Ionic conduction	Fuels	T (°C)
SOFC	ZrO_2 ceramic	O^{2-}	CH_4, CO, H_2	500–900
MCFC	$NaCO_3$ liquid	CO^{3-}	CO, H_2	650
AFC	KOH liquid	$(OH)^-$	Pure H_2	70
PAFC	H_2 PO_4 liquid	H^+	H_2	200
PEM	Polymer solid	H^+	Pure H_2	80

directly unconstrained by the Carnot efficiency. The different types of fuel cells are listed in Table 10.2.

The main effort of recent development work and investment is concentrated on the industrialization of PEM and SOFC type fuel cells. Both have advantages and disadvantages: PEM fuel cells are operated at a convenient low temperature of 80 °C, can be started from ambient temperature, and the technology is mature for first field tests. Its important disadvantage is that it operates only with pure H_2 as its fuel, which is not a generally available secondary energy with an existing infrastructure. The use of PEM fuel cells for electric vehicles requires the solution of another issue, the production, distribution and storage of hydrogen in large scale. SOFCs operate with any fuel because its ceramic electrolyte conducts oxygen ions that "burn" any fuel. The disadvantage is the high operating temperature of 500 to 900 °C. A small unit for about 5 kW is under development.

Actually there is a large interest in fuel cells and many updated publications are available [16,17]. For this reason a more detailed presentation of this subject is not attempted in this chapter.

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11

Solar Electric Power Supply with Batteries

H. K. KÖTHE[†]

11.1 INTRODUCTION

Solar electric plants shall be understood to be photovoltaic energy converters that are able to self-sufficiently satisfy a mean energy demand over a significant period of time, be it an appliance that is permanently hooked up or just for sporadic power supply of appliances. Such plants have in common that their input and output quantities fluctuate widely. They can therefore only be dimensioned on the basis of a mean value and are not able to satisfy this demand without the possibility to store energy.

The solar generator is to be dimensioned dependent on solar radiation and the demand to be encountered; the same goes for the battery. This difficult problem shall be treated first as it makes the problem definition for the energy storing device and the system on the whole clearer.

Afterward the construction of the system as whole and the most important components shall be discussed.

The demands for the energy storing devices and which system is best supplied with which battery shall be discussed with the help of some typical examples for design of such systems.

[†] Deceased.

11.2 DIMENSIONING A SOLAR ELECTRIC SYSTEM

11.2.1 Preconditions

The basic precondition is that the mean solar electric power supply must be at least equal to the mean power demand. Whenever demand and supply are exactly of the same size, the system is termed as being "critical", whereas systems that have a certain reserve that can be called upon anytime are termed "well dimensioned". Whenever this reserve is unnecessarily high, the reason for this can be only of economic nature (paradoxical, but most often the case) the system is termed "economically matched".

11.2.2 Calculation of the Mean Consumption

Figures 11.1, 11.2 and 11.3 explain how the mean demand is ascertained. The load demand currents throughout a day are shown for example by Figure 11.1 for a given system-dependent voltage level. Figure 11.2 shows an example for a statement made on the Ah consumption over a period of several days (Ah balance). Finally, Figure 11.3 manifests that over a longer period of time a curve of the mean consumption can be constructed which only varies slightly from the encountered consumption.

11.2.3 Calculation of the Mean Supply

A solar cell delivers a current proportional to its surface area and the intensity of radiation at 0.5 V. The effect the cell's temperature has on its performance can be neglected here. Figure 11.4 displays the typical flow of the current delivered by the solar cell on a summer day and a winter day. Figure 11.5 shows the corresponding daily Ah balances and the resulting Ah balance curves.

Solar cells that are exposed to natural sunlight over one year show balance curves similar to the one displayed in Figure 11.6, where the sums of the Ah supply are reproduced quite exactly every year even though seasonal fluctuations are encountered.

The curve of the Ah balance mean supply is represented by the tangent line in Figure 11.7 (curve 2) to the actual Ah balance curve (curve 1). The annual observation starts at point A_1 and ends at point B_1. In this period of time the 25 cm^2 silicon solar cell placed at Frankfurt/Main can at most satisfy a demand of 50 Ah per

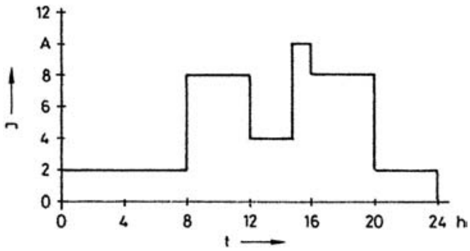

Figure 11.1 Typical profile for a day's current consumption.

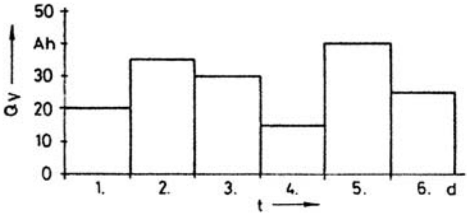

Figure 11.2 Typical Ah consumption for several days in succession.

month. If an appliance with a demand of ten times this value is to be operated, the surface area must measure ten times 25 cm^2.

11.2.4 Calculation of the Capacity

The precondition that the supply must be at least as large as the demand is fulfilled in the points A_1 and B_1 in Figure 11.7, but just after point A_1 this is not the case anymore. Only after point C_1 up to B_1 supply is again higher than demand. The precondition can however be fulfilled by application of a storage device. This storage device must be fully charged at point A_1 and must at least have a capacity of K_1 so it will be discharged in point C_1 and again recharged in point A_2.

11.2.5 Evaluation of the System

The system that is represented by curve 2 in Figure 11.7 having a tangent line as consumption curve to the supply curve and with a capacity of K_1 is termed "critical" as the battery will not be fully recharged if the annual supply falls short of the consumption. It is therefore more ingenious to let the supply curve rise as shown by curve 3 in Figure 11.7 so the batteries' capacity is only demanded in point A_2 and will again be fully recharged in point B_2.

This new design makes less use of the solar cells' surface area and leads to smaller storage capacities (K_2). If the corresponding system should have the same power rating as the critical one, the batteries' capacity and the surface area must be enlarged proportionally (factor: gradient of curve 2 divided by gradient of curve 3).

The advantage of this new system is the gain of the "reserve period TR", which is the period of time between point B_2 and point A_2, where the battery is employed

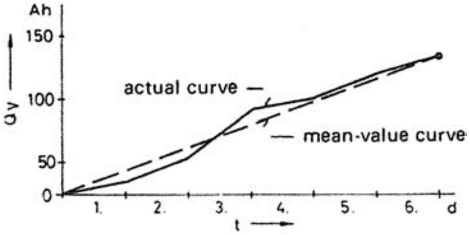

Figure 11.3 Derivation of the mean Ah consumption curve.

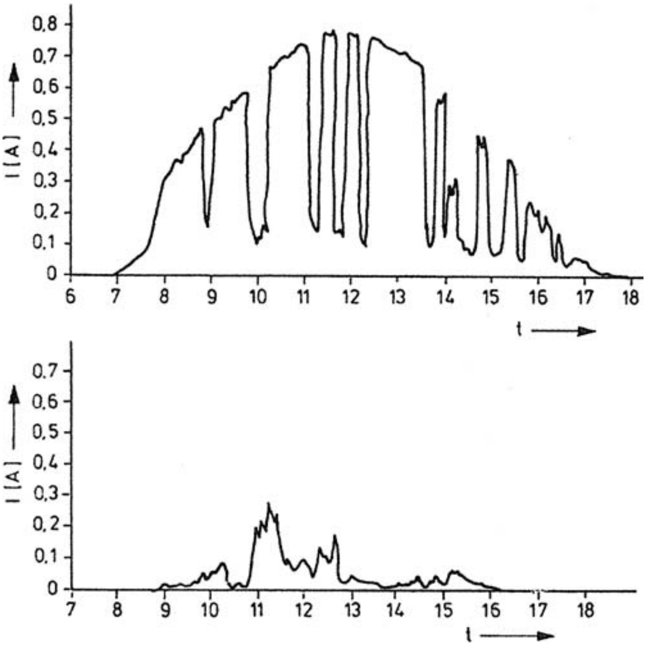

Figure 11.4 Typical profile of daily supply of current of a silicon solar cell of 25 cm^2, in summer (top) and in winter (bottom).

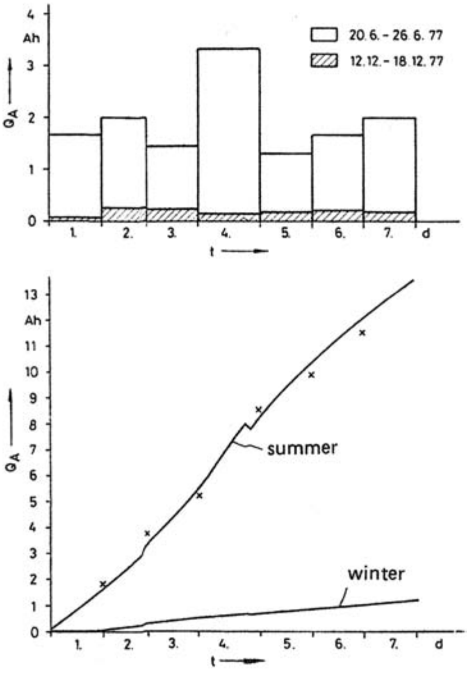

Figure 11.5 Supply of a silicon solar cell of 25 cm^2 surface area for successive days. Top: Ah balance. Bottom: Ah balance curve $Q_A(t)$.

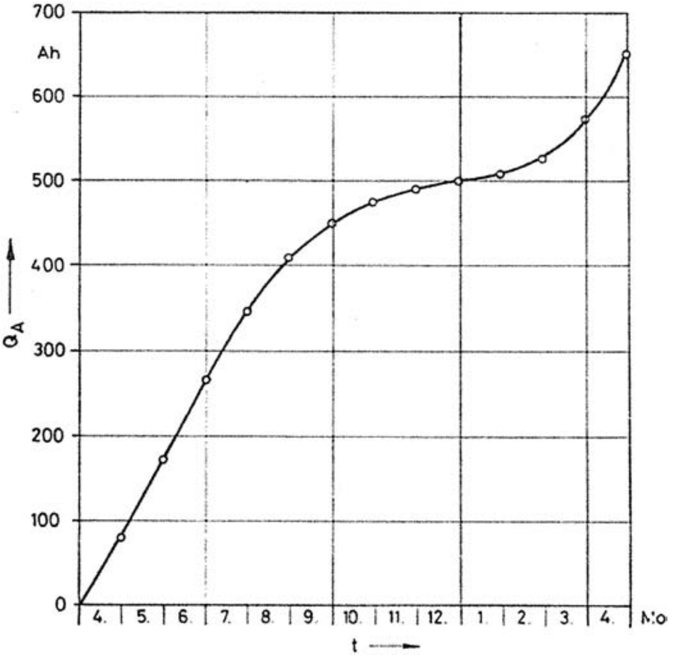

Figure 11.6 Ah balance curve $Q_A(t)$ of a 25 cm^2 silicon solar cell measured in Frankfurt/ Main 1976–1977.

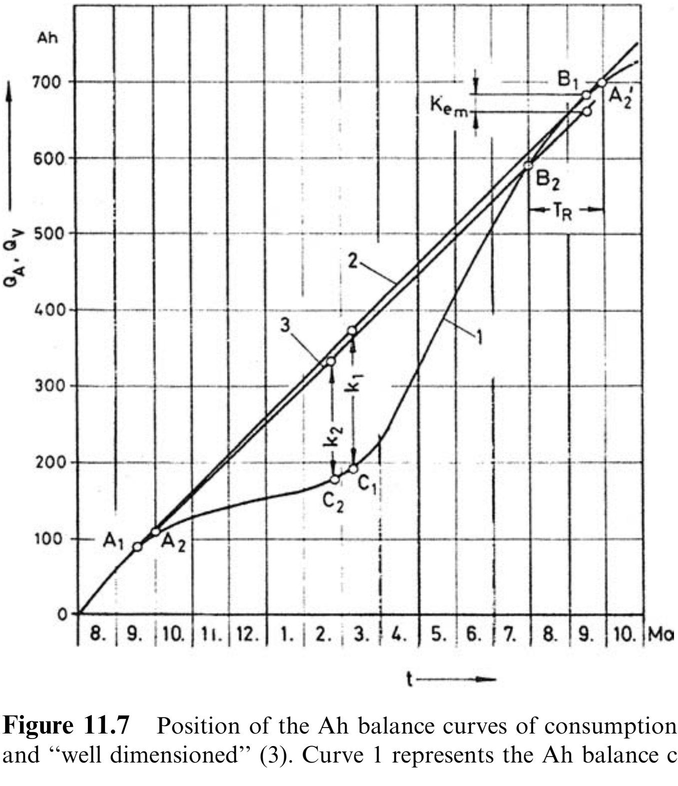

Figure 11.7 Position of the Ah balance curves of consumption at "critically matched" (2) and "well dimensioned" (3). Curve 1 represents the Ah balance curve of the supply.

once again. In this period of time an Ah reserve of up to the value Ke_m is at hand. Systems that have a “reserve period” of around 2 months can be termed “well matched”.

11.3 DESIGN OF SOLAR ELECTRIC SYSTEMS

11.3.1 The Power Source: The Solar Generator

This consists of a series connection of solar cells, mostly of the silicon type. Figure 11.8 shows a schematic cross-section and a wiring diagram of such a Si solar cell. Figure 11.9 manifests the typical characteristic diagram at different radiation intensities. If higher voltages are needed, an appropriate number of solar cells are series connected. In this way solar generator modules are formed. Commercial modules mostly consist of 32 to 36 series-connected solar cells and thereby have a voltage level that suffices to charge a 12-V accumulator.

If the ampere-hours supplied by one module are not sufficient, a corresponding number of modules in parallel connection will do the job. At present, mostly Si solar generators are employed and will probably be dominant for the next few years.

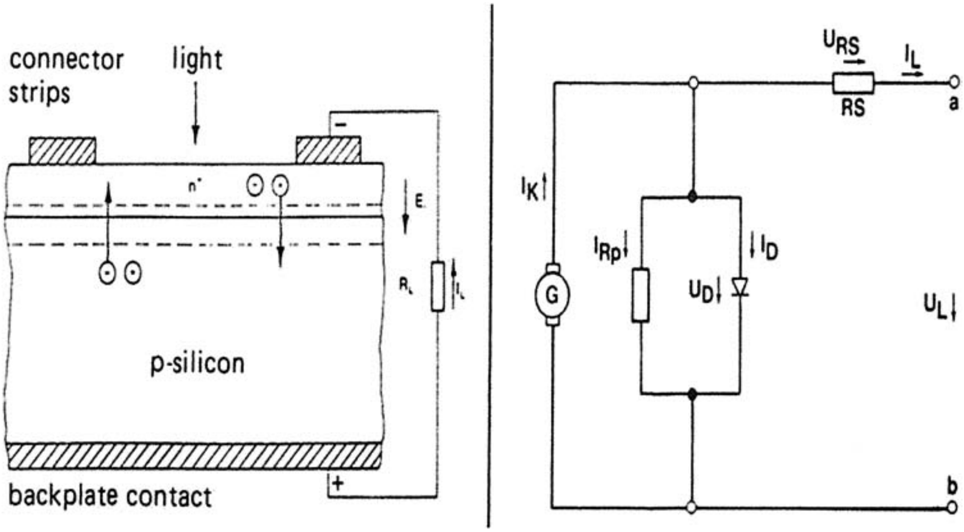

Figure 11.8 Schematic of a silicon solar cell. Left: cross-section. Right: wiring diagram.

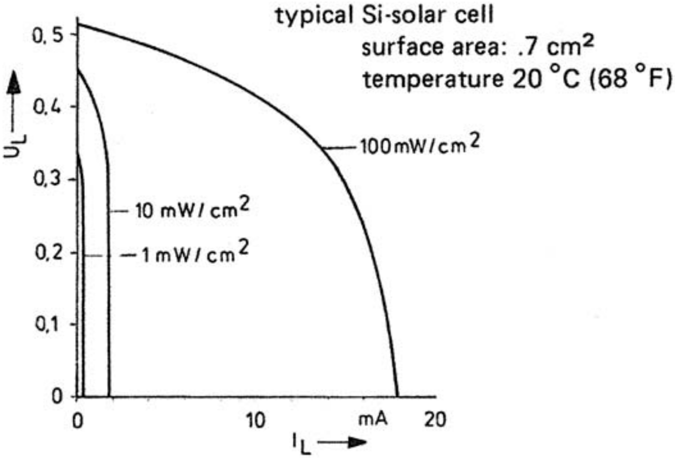

Figure 11.9 Characteristic curve of a silicon solar cell at different radiation intensities.

11.3.2 System Design

Figure 11.10 shows the principle design of a solar electric system. The solar generator is separated from the storage battery by built-in diode isolation (see Figure 11.8 on the right), which prevents discharge of the accumulator over the solar cell during low radiation periods. The consumer is usually directly connected to the battery, as only in very few cases does its input voltage range demand a processing plant.

11.3.3 The Isolating Diode

For this purpose mostly silicon power diodes are employed for various reasons. The diode should have a low conducting-state voltage as this voltage is actually subtracted from the total voltage of the solar electric generator. Schottky diodes are preferred.

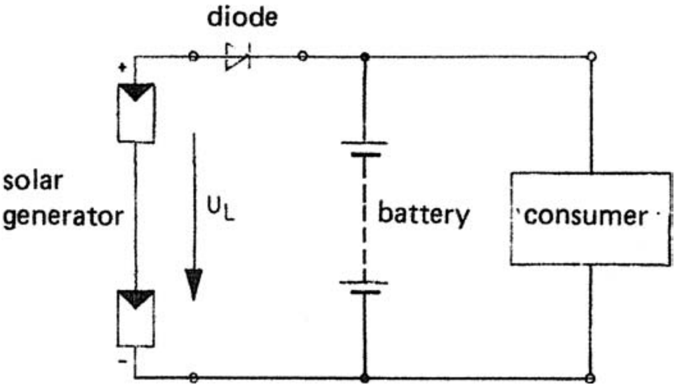

Figure 11.10 Principle design of a solar electric system.

11.3.4 The Battery

Batteries for this field of application are presently without exception electrochemical accumulators. As the demand situation differs with varying solar electric systems, it is advisable to analyze the demands closely before choosing a battery system. These subjects are explicitly treated in two separate chapters.

11.3.5 The Operating System

Solar electric power supply plants cannot be designed in such a simple manner as suggested by Figure 10.10, as the battery would have to be dimensioned large enough so it would never reach the fully charged state because overcharge operation would lead to shorter servicing intervals or for some battery types even to lasting damage. Therefore current limitations as shown in Figure 11.11 are indispensable and for larger plants the operating system will also have to take over other tasks such as prevention of exhaustive discharges.

11.4 ASPECTS FOR THE CHOICE OF THE BATTERY

11.4.1 Power Rating

Table 11.1 lists the power ratings of different solar electric power supply systems. This listing also shows the typical load ranges for the accumulators of Table 11.2.

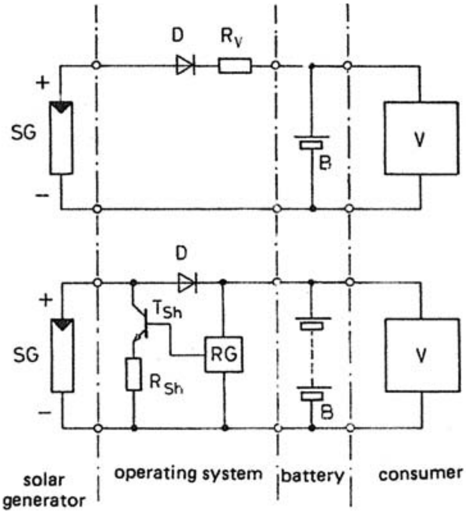

Figure 11.11 Examples for solar electric systems. Top: system with a gas-tight NiCd accumulator. Bottom: system with lead-acid accumulator, e.g. OPzS.

Table 11.1 Power ratings for solar electric power supply systems.

Power rating of the system	Typical consumer	Examples
µW	Appliances with integrated circuits and minimized energy consumption	Solar powered watches and calculators
mW	Appliances with low mean power consumption, e.g. due to occasional use	Portable radio equipment, automated ticket and lemonade machines, automatic fire and burgler alarms
W	Appliances and plants for communications and measuring purposes as well as low duty consumers	Sea markers and buoys, television convertors, radio relays, meteorologic and environmental measuring stations, power supply on boats and weekend homes, power supply for heat pumps
kW	Self-supporting networks for appliances and plants	Remote settlements, military applications

11.4.2 Feasible Battery Types

Whenever a system is dimensioned by the method introduced in Section 11.2, then the demanded capacity can be estimated and a feasible system for the accumulator can be found. The correlation between accumulator type and power rating according to Figure 11.12 is shown in Table 11.2.

Table 11.2 Typical operating conditions for accumulators of different power ratings of solar electric systems.

Power rating	Discharge depth (%)		Service intervals	Service life demand
	Daily	Yearly		
µW	1–5	1 × ca. 80	Maintenance-free	About 10 years for max. 100 full cycles (80% discharge)
mW	1–5	1 × ca. 80	Maintenance-free up to 1 year	About 10 years for max. 2000 full cycles (80% discharge)
	5–20	Several, about 80		
W	1–5	1 × ca. 80	1 to 3 years	About 10–20 years at about 20 full cycles;
	5–20	Several, about 80	Several times per year	About 5 years at about 200 full cycles
kW	25–50	Often up to 80	Several times a month	About 5 years at about 1500 full cycles

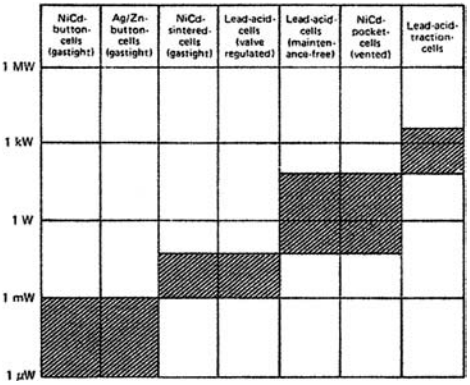

Figure 11.12 Correlation of the types of accumulators to the system-specific power ratings.

11.4.3 Application Technology

The final decision on the battery to be employed follows aspects of application technology. Aspects include the demanded electric power ratings, general operations data (on maintenance, lifespan, reliability), peripheral conditions (such as fitting conditions, mechanical stress, temperatures), and last but not least justifiable costs for investments (see Tables 11.3a–d).

11.5 DESIGNS OF OPERATING SYSTEMS

11.5.1 Systems with Current Limitation

These systems (see Figure 11.11, top) are preferably applied in connection with gas-tight NiCd accumulators. Systems that operate in the microwatts range are sufficiently protected by a simple ohmic resistor, whereas for higher power ratings a series connection of transistors is advised.

11.5.2 Systems with Voltage Limitation

These are employed especially for all types of lead-acid accumulators and open NiCd accumulators. Principal design is shown by Figure 11.11. The voltage is limited through keeping the resistor branch consisting of T_{SH} and R_{SH} variable and automatically controlled. As long as the battery has not reached its charging limit voltage, the transistor T_{SH} is nonconducting. Above this voltage the regulating device RG adjusts the transistor in such a way that the battery never reaches its end of charging marginal voltage.

11.5.3 Systems with Two-Step Regulators

Here the constant charging current is switched off at a certain upper limit voltage (e.g. 2.35 V/cell) and switched on again at a slightly lower value. The resulting mean

Table 11.3a Typical power values of Varta batteries for system power ratings in the microwatt range.

		Battery-specific data	
Power data	Desired values	NiCd gas-tight (DK, DKZ)	AgO/Zn gas-tight (VC 568)
Electrical data			
Capacity	Up to 1 Ah	0.01–1 Ah	0.17 Ah
Charging currents	0.1–1 I_{10}	0.3–3 I_{10}	0.01–0.3 I_{10}
Ah efficiency	Over 95%	Over 87%	About 90%
Charging method	I, W, IU, WU	I, W respective of voltage and temperature limits	IU 0.3 I_{10} up to 1.95 V/cell
Self-discharge	Below 10% per month	About 20% per month	About 2% per month
Operating data			
Full cycles	Over 100	300 to 400	About 100
Discharge	To 100%	Up to 100%	Up to 70%
Maintenance	None	None	None
Reliability	100%	99.9%	99.9%
Peripheral data			
Operating position	Any	Any	Any
Tightness	100% tight	Less than 100% tight	Less than 100% tight
Temperature	− 55 to + 65 °C	0 to + 45 °C	0 to + 45 °C
Vibration	MIL STD	MIL STD	MIL STD
Shock resistance	810 C	810 C	810 C

value of the pulsate charging current is very close to the ideal value if the upper and lower limit values are almost identical (e.g. 50 mV/2.35 V).

11.6 INFLUENCE OF GEOGRAPHIC POSITION

Figure 11.13 shows the Ah balance for different geographic positions in the northern hemisphere (7). These curves allow calculation of a compensating index composed of the ratio of capacity of the critical system to the Ah annual balance. This ratio is therefore a comparative value for the necessary storage capacity.

11.7 SUMMARY

Not only lower costs for solar generators, but also special "solar accumulators" with low costs per kWh are necessary for a wider distribution for photovoltaic systems. These solar accumulators will be distinguishable from present-day lead-acid accumulators because of a substantially lower power density.

Table 11.3b Typical power values of Varta batteries for system power ratings from 1 to 500 mW.

		Battery specific data	
Power data	Desired values	NiCd gas-tight (RS, SD)	Pb valve regulated (accumulator Pb)
Electrical data			
Capacity	Up to 50 Ah	Up to 15 Ah	Up to 10 Ah
Charging currents	0.1–2 I_{10}	0.5–10 I_{10}	Up to 4 I_{20}
Ah efficiency	Over 95%	Over 87%	Over 90%
Charging method	I, W, IU, WU	I, W respective of voltage and temperature limits	IU,U 4 I_{20} up to 2.3 V/cell total charging time 14 h unlimited for 2.25 V/cell
Self-discharge at 20 °C	Below 5% per month	About 35% per month	About 3% per month
Operating data			
Full cycles	Over 2000	Over 1000	About 200
Discharge	Up to 100%	Up to 100%	Up to 100%
Maintenance	None	None	None
Reliability	100%	99.9%	99.9%
Peripheral data			
Operating position	Upright	Upright	Upright
Tightness	Sealed 100%	Vented 100%	Vented
Temperature	− 55 to + 75 °C	− 20 to + 45 °C	− 30 to + 50 °C
Vibrations	MIL STD	MIL STD	Limits unknown
Shock resistance	810 C	810 C	Limits unknown

Table 11.3c Typical power values of Varta batteries for system power ratings from 0.5 to 500 W.

Power data	Desired values	Battery-specific data	
		Pb, valve-regulated (OPzS, Varta bloc)	NiCd sealed (TX, TP-series)
Electrical data			
Capacity	Up to 10000 Ah	12–12000 Ah	10–1250 Ah
Charging currents	0.01–2 I_{10}	0.01–2 I_{10}	0.5–3 I_{10}
Ah efficiency	About 100%	90–95%	About 80%
Charging method	I, W, IU, WU	IU 2 I_{10} up to 2.4 V/cell, total charging time: 20 h, at 2.33 V/cell unlimited	IU 2 I_{10} up to 1.65 V/cell, total charging time 12 h, at 1.40 V/cell unlimited
Self-discharge	Below 1% per month	2–3% per month 25% per year	24% per month 48% per year
Operating data			
Full cycles	Some 1000	>1000	>1500
Discharge	Up to 100%	Up to 80%	Up to 100%
Maintenance	None	Maintenance-free for 3 years	Maintenance-free for about 1.5–2 years
Reliability	100%	99.9%	99.9%
Peripheral data			
Operating position	Upright	Upright	Upright
Tightness	Sealed	Vented	Vented
Temperature	− 55 to + 75 °C	− 20 to + 55 °C	− 20 to + 45 °C
Vibrations Shock resistance	Inapplicable	Inapplicable	Inapplicable

Table 11.3d Typical power values of Varta batteries for system power ratings from 0.5 to 5 kW.

		Battery-specific data	
Power data	Desired values	NiCd, vented (series F)	Lead (traction) (PzS)
Electrical data			
Capacity	Up to 1000 Ah	30–300 Ah	50–1200 Ah
Charging currents	0.1–2 I_{10}	0.5–3 I_{10}	0.1–2 I_{10}
Ah efficiency	Over 95%	About 85%	About 80%
Charging method	I, U, IU, WU	IU 3 I_{10} up to 1,45 V/ cell, total charging time: 15 h	IU 2 I_{10} up to 2.4 V/ cell, total charging time: 10 h
Self-discharge	Below 1% per day	Max. 3% per day	Max. 1% per day
Operating data			
Full cycles	About 4000	About 3000	Over 1500
Discharge	Up to 100%	Up to 100%	Up to 80%
Maintenance	None	Once a year	Once a week
Reliability	100%	99.9%	99.9%
Peripheral data			
Operating position	Upright	Upright	Upright
Tightness	Sealed	Vented	Vented
Temperature	−55 to +75 °C	− 20 to + 45 °C	0 to + 55 °C
Vibrations	Inapplicable	Inapplicable	Inapplicable
Shock resistance			

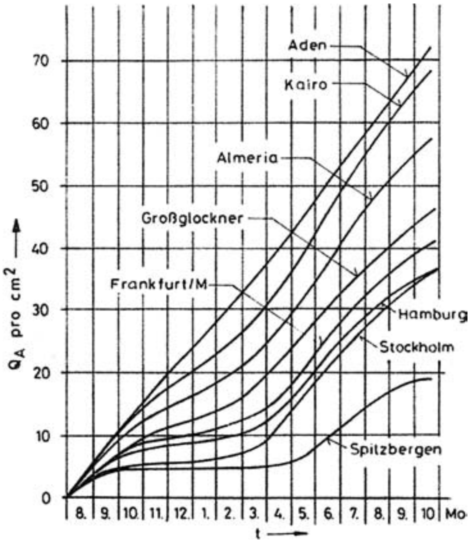

Figure 11.13 Ah balance curve for a horizontally installed 1 cm^2 silicon solar cell in different regions.

Every component of a solar electric system has to be treated by the described method for dimensioning these systems. Selection according to power ratings of these solar electric systems allows special demands oriented at the power demand to be put to the battery.

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12

Charging Methods and Techniques: General Requirements and Selection of Chargers

E. WEHRLE

12.1 THE BATTERY'S REQUIREMENTS FOR THE CHARGER

Charging of batteries must be conducted with direct current. Alternative current or rotary current have to be transformed. Mostly semiconductor rectifiers are employed for this task. Methods for battery charging vary with demand and the charging time is of great importance. The charging devices can be divided into those that charge above gassing voltage and those that do not. Chargers that exceed gassing voltage during charging are employed for charging one battery at a time, while the ones that do not exceed gassing voltage can be used for parallel charging of several batteries. The chargers that exceed gassing voltage attain short times for recharge, whereas with chargers that do not charge above gassing voltage very long charging times must be expected.

12.2 TECHNICAL DATA AND TERMS

Technical data on the charging process for lead-acid and NiCd accumulators are summed up in Table 12.1. The following illustrates the most common technical terms applied in connection with charging techniques (1).

Table 12.1 Technical data for charging of lead-acid accumulators.

	Traction batteries		Stationary batteries			
Line	GiS	PzS	Gro	GroE	OPzS	Automotive batteries
1 Rated capacity (C_n)	C_5	C_5	C_{10}	C_{10}	C_{10}	C_{20}
2 Charging coefficient	1.17	1.2	1.1	1.1	1.2	1.15
3 Energy efficiency after C_n has been drawn, standard values	0.70	0.68	0.75	0.75	0.68	0.75
4 Maximum permitted charging currents per 100 Ah nominal capacity (A)						
(a) current constant upon reaching gassing voltage (I characteristic)	5	8.5	5	5	10	
(b) decreasing current (W characteristic)						
allowed at 2.4 V/cell	8	12	12	7	12	
at 2.65 V/cell	4	6	6	3.5	6	
(c) nominal current of the charger for (b) at 2.0 V/cell (DIN 41774)	16	24	18	14	24	
5 Maximum for the final charging phase allowable for 2.5 days max., e.g. for IU characteristic (A)	2	3	3	2	2	
6 Float charge current (see line 10) (mA)	40–100					
7 Maximum initial current at 2.4 V/cell and 20°C (68°F) (U characteristic), tolerance ± 10% (A)	100	80	80	80	80	160

	Charging voltages (V/cell)						
8	Initial voltage at W characteristic and current as in 4(c)	Dependent on type and size between 2.1–2.15					
9	Charge end voltage at currents as in 4(c) and (b)	Dependent on type and size normally 2.6 to 2.7 V and for old and warm batteries 0.2 V/cell less					
10	Float charge current (see line 6)	2.20–2.25,					
11	Trickle charge voltage	2.25–2.35					
12	Constant voltage for IU charging	2.40	2.35 2.40	2.40	2.35 2.40	2.35	2.40
13	Secondary charging period (h)						
	at Wa characteristic	4.0	4.5				
	at WOWa characteristic dependent on the initial current	4.5–5	5–5.5				
	at IOIa characteristic dependent on the initial current	4.5–5	5–6				
	at IUIa characteristic and end of charge current as in 4(a)	3.5	4.0				

12.2.1 Battery Capacity, Discharge Current, and Charge Current

Electrical batteries are DC storage systems that can either store or produce electrical energy by chemical transformations. The process of storing energy is called 'charging', whereas the production of energy is called 'discharge'. The chemical transformations are proportional to the amount of current consumed, respectively produced, in Ah, corresponding to Faraday's laws. Therefore the size of a battery is given in Ah (amperes (A) × time (h)).

As the capacity is dependent on the discharge current and the duration of discharge, it is not a constant value. This can be derived by the designation given by the manufacturers. The nominal capacity is given for 5 hours discharge time (C_5) for vehicle batteries and NiCd batteries; whereas for stationary batteries (also common for gas-tight NiCd batteries) the 10-hour discharge capacity (C_{10}) is given; and for starter batteries, motorcycle batteries, and small lead-acid accumulators the capacity for a 20-hour discharge (C_{20}) is given. A C_5 of 100 Ah signifies that this battery produces 100 Ah during 5 hours of discharge and the 5-hour discharge current is $I_5 = 100/5 = 20$ A.

The corresponding discharge current (I_5, I_{10}) is also a measure for the charging current. If a charging current of $2 \times I_5$ is mentioned, this means that charging is conducted with twice the 5-hour discharge current. For a capacity of 100 Ah this amounts to $2 \times 100/5 = 10$ A.

12.2.2 Charge Coefficient

The ratio of amount of current needed for full recharge to the drawn current is called the charge coefficient. It amounts to 1.1–1.2 for lead-acid batteries depending on their design and between 1.2 and 1.4 for NiCd accumulators (see also Tables 12.2 and 12.3).

During every charging process a part of the applied amount of energy is lost, especially above the gassing voltage, through the process of chemical decomposition of water and hydrogen in the electrolyte. Therefore a greater amount of energy must be applied for charging than has been drawn prior to recharge. For example, given a battery with a nominal capacity of 125 Ah; 80% discharged (100 Ah); with a charging coefficient of 1.2; in order to attain fully charged state, $100\text{ Ah} \times 1.2 = 120$ Ah have to be provided.

12.2.3 Charging Time

The given charging times are idealized calculated values presuming that all battery- and rectifier-specific data are constant. Practically such conditions are not met as, for example, mains fluctuations influence uncontrolled chargers; aging of the battery and variant temperatures also have influence.

Variance of the electrolytes' temperature by 10°C (18°F) (reference temperature for traction batteries 30°C (86°F), for stationary batteries 20°C (68°F) and for starter batteries 27°C (80.6°F)) changes the charging time by 1 hour. If the temperature is lower than the corresponding reference temperature as above, then charging is prolonged, whereas higher temperature shorten charging time. As these disturbing variables cannot be controlled, they are not considered for calculations of

Table 12.2 Technical data for charging NiCd and NiFe accumulators.

		Nickel cadmium				Ni/Fe	
Line		R	T	TS	F	RE	TNE
1	Rated capacity (C_n)	C_5	C_5	C_5	C_5	C_5	C_5
2	Charging coefficient	1.4	1.4	1.4	1.2	1.4	1.4
3	Energy efficiency after C_n has been drawn, standard values	0.50–0.55	0.55–0.60	0.60	0.75	0.45–0.50	0.50–0.55
4	Maximum permitted charging currents per 100 Ah nominal capacity above gassing voltage (A)						
	a) constant current (I characteristic)	About 20–30 A limited by heating up current decrease			10	About 20–30 A limited by heating up current decrease	
	b) current decreasing[a]						
	allowable at 1.5 V/cell	40–50%			8		
	allowable at 1.6 V/cell				6	30–40%	
	c) nominal current of the charger as in b) at 1.2 V/cell				20		
5	Lowest possible charging current (A)	—	—	—	—	7	
6	Float charge current (see line 9) (mA)		20–60		100–300	—	—
	Charging voltages (V/cell)						
7	Initial voltage dependent of type, size, and current		1.3–1.4		1.3	1.4–1.6	
8	Charge end voltage dependent on type, size, and current		1.6–1.85		1.6	1.7–1.85	
9	Float charge voltage (see line 6)		1.38–1.40		1.36	—	—
10	Trickle charge voltage dependent on type		1.4–1.5		1.4	—	—
11	Buffer voltage at deactivation (vehicles						
11	and train lights)		1.6		1.5	—	—
12	Constant voltages for IU charging		1.6–1.7		1.5	1.7–1.75	
13	Secondary charging time (h)						
	for Wa characteristic, $I_N = I_5$	5.5	1.5	1.5	2.5		
	for WoWa characteristic	—	—	—	3.5		

[a] For R-, T-, and TS-type cells the W characteristic according to DIN 41775 with variable niveau. For F-type cells a W characteristic is employed, but adjusted by a ratio of 1.2:2.

Table 12.3 Allowed values for the charging current upon reaching gassing voltage for different types of cells.

Cell type (1)	Nominal capacity	Current (A) per 100 Ah nominal capacity for charging method			
		1 max.	2a max.	2b max.	3 max.
GiS, PzS	C_5	5	8	4	2
Gro (vehicle) *K*	C_5	10	14	7	3
Gro/GroE (stationary)	C_{10}	8,5	12	6	3
OPzS	C_{10}	5	7	3,5	2
Starter battery	C_{20}	10	12	6	2

Charging method 1: charging with constant current and deactivation upon reaching fully charged state (Ia characteristic).
Charging method 2: charging with decreasing current and deactivation upon reaching fully charged state.
2a: allowed current at 2.4 V/cell.
2b: allowed end-of-charge current at 2.65 V/cell.
Charging method 3: allowed end-of-charge current without deactivation for up to 3 days charging time.

the charging time. A variance of ± 0.5 hour of the charging time should therefore be expected.

12.2.4 Gassing Voltage

The voltage above which a battery shows significant gassing action is termed 'gassing voltage'. In reality the following values are encountered:

- 2.40 V/cell for lead-acid batteries.
- 1.65 V/cell for NiCd batteries, series T.
- 1.60 V/cell for NiCd batteries, series TS.
- 1.70 V/cell for NiCd batteries, series R.
- 1.50 V/cell for NiCd batteries, series F.

NiFe batteries show signs of gas emission immediately upon charge activation, but also in certain amounts during open circuit and discharge operation.

12.3 CHARACTERISTIC CURVES

The charging methods differ with respect to their current and voltage characteristics during charging and with the corresponding charging time. DIN 41 772 is the standardization for charging device characteristics.

A characteristic of a charging device is coordination of the DC voltage and the current valid for the given type of load.

The following progressions of characteristics have been determined by DIN 41 772 and fitted with the corresponding initial:

- Decreasing (taper) characteristic: W.
- Increasing characteristic: S.

- Limited characteristics: (I), (U).
- Constant characteristic: I, U.
- Assembled characteristics: e.g., IU, IUW, IO, la.

These abbreviations help describe the static behavior of the rectifier. Abbreviations for additional information are, e.g., 0, e, and a. Figures 12.1 and 12.2 show the most important modifications of charging characteristics.

Charging characteristics are generally influenced by external disturbances, such as variances of the mains voltage, its frequency, or the surrounding temperature. Special devices can largely diminish these influences. This is applied for constant and limited characteristics. The tolerances for constant characteristics must, if not stated otherwise, remain within the following marginal values:

- Mains voltage; ± 10%
- Mains frequency; ± 2%
- Ambient temperature; 0 to 40°C (32 to 104°F)
- Internal device temperature; 0 to 45°C (32 to 113°F)

The operating range for which the characteristics are valid can be found in the instruction manuals.

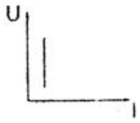
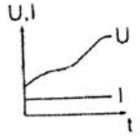
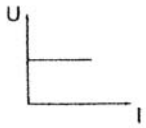
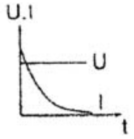
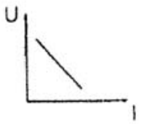
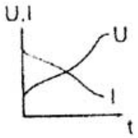
charging characteristic	abbreviation	temporal flow of the characteristic	application
	L		partial charging full charging overcharging deactivation by hand necessary
	U		Only permitted for limited periods of time temperature must be supervised
	W		only permitted for limited periods of time current has to be limited in such a way that the float-charge current can be harmless adsorbed by the battery

Figure 12.1 General charging characteristics.

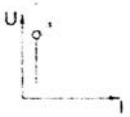
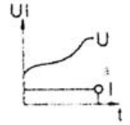
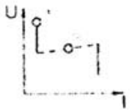
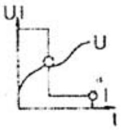
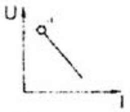
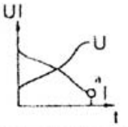
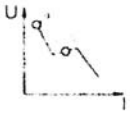
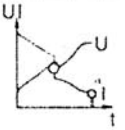
charging characteristic	abbreviation	temporal flow of the characteristic	application
	I_a		– for all large cells that would heat up beyond limits – for accelerated charging – for fast charging
	$I0I_a$		– partially charge up to a given deactivation-voltage, then – full charging conducted with reduced current
	W_a		– whenever the applications for an I_a-charger are to be fulfilled with low technical expenditure
	WOW_a		– whenever the applications for an $I0I_a$ type charger are to be fulfilled with low technical expenditure

Figure 12.2 Modification of the I and W characteristics.

12.3.1 Decreasing (Taper) Characteristics (W Type)

A characteristic is termed decreasing when the voltage decreases with increasing current (type W).

12.3.2 Increasing Characteristics (S Type)

A characteristic is termed increasing when the voltage increases with increasing current (type S).

12.3.3 Limited Characteristics

Characteristics which independent of external disturbances do not vary by more than ±10 from their nominal values are termed ‘limited characteristics’.

1. If the desired limited value is a voltage, then a limited voltage characteristic is at hand.
2. When the desired limited value is a current, then a limited current characteristic is at hand.

12.3.4 Constant Characteristics

Characteristics which independent of external disturbances do not vary by more than ±2% from their nominal values are termed 'constant characteristics'.

1. When the desired value is a voltage, then a constant voltage characteristic is at hand (type U).
2. When the desired value is a current, then a constant current characteristic is at hand (type I).

12.3.5 Assembled Characteristics

An assembled characteristic is at hand if different characteristics pass over into one another continuously or by a step (types WOWa, IU, SU).

12.4 EMPLOYMENT OF CHARGING METHODS

12.4.1 Installation and Operation of Batteries and Chargers

DIN 57 510/VDE 0510 (3) deals with operation and installation of batteries and chargers.

12.4.2 Demands of Vented Lead-Acid Accumulators

The most important feature of chargers for lead-acid accumulators is the current being limited when the gassing voltage (2.4 V/cell) is reached. When reaching this value, the charging current is partially employed for decomposition of the electrolytes' water, and heat is excessively produced. Therefore the charge current when the gassing voltage is reached has to be reduced to the values permitted by the battery manufacturer.

12.4.3 Demands of the Maintenance-Free Lead-Acid Battery

In order to prevent the formation of gas inside the battery, charging may not be conducted above the gassing voltage. The charging voltage is limited to 2.35 V/cell for cyclic operation.

12.4.4 Demands of Vented Nickel/Cadmium Batteries

Here the current must not be reduced above gassing voltage (exception: cells with sintered electrodes), but the allowed temperatures of 45°C (113°F) must be respected (for cells with pocket electrodes 35°C (95°F).

12.4.5 Charging Lead-Acid Batteries According to the W Characteristic

12.4.5.1 Application

1. Mainly for charging traction batteries. If 10 hours charging time is available, then charging is conducted according to the Wa characteristic; if only 7–9 hours are available, then the WOWa characteristic must be applied.
2. For charging small lead batteries with W characteristic with manual deactivation.
3. For charging centralized batteries of safety-lighting equipment in alternative charging operation to WOW characteristic.

12.4.5.2 Basic Demands

1. For protection of the battery the W characteristic must not allow the current limit values determined by the manufacturer to be exceeded at gassing voltage and at the end-of-charge voltage. The limit current values upon reaching gassing voltage are listed in DIN 57 510/VDE 0510, paragraph 12.2.3 (3), and in Table 12.3
2. The battery has to be disconnected manually (W) or automatically (Wa) upon reaching the fully charged state.

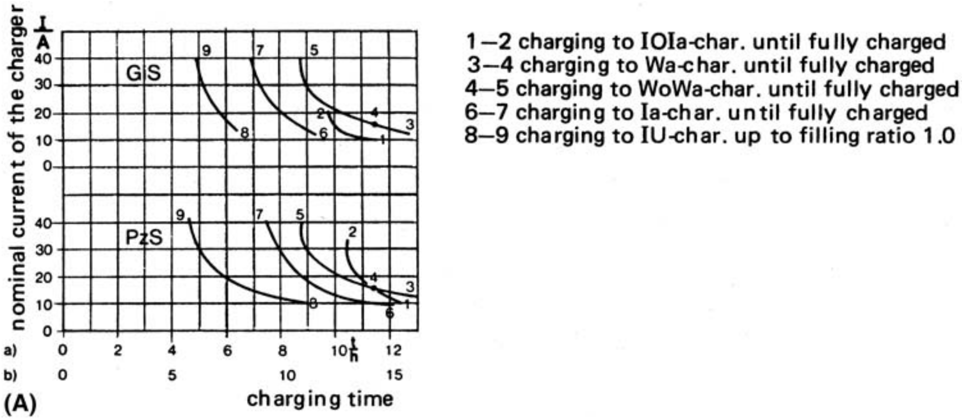


Figure 12.3 Charging time for lead-acid and NiCd batteries. (A) Rectifier nominal current for charging traction lead-acid cells GiS and PzS at 20°C (68°F) after discharge of (a) 80% and (b) 100% of C_5. (B) Rectifier nominal current for charging of stationary lead-acid cells OPzS, Gro, GroE at 20°C per 100 Ah K_5 after discharge of (a) 80% and (b) 100% of C_5 (operation conforming to DIN 40729). (C) Rectifier nominal current for charging R-, TN/TS-, and F-type cells at 20°C per 100 Ah C_5 after discharge of (a) 80% and (b) 100% of C_5 (operation conforming to DIN 40729).

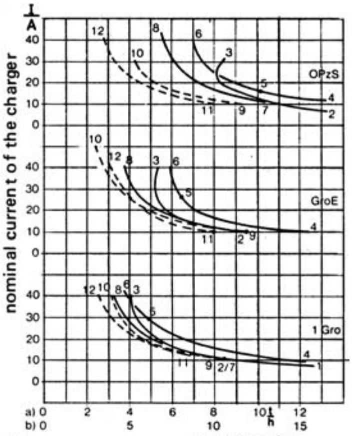
12.4.5.3 Characteristic

1. *Progression* (see Figures 12.1 and 12.2). Flow of the W characteristic is determined by three pairs of values:

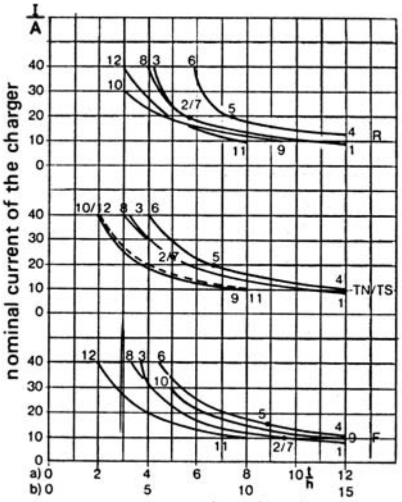
   Nominal current of the device at 2.0 V/cell.
   50% nominal current of the device at 2.4 V/cell.
   25% nominal current of the device at 2.65 V/cell.
   A tolerance of ± 0.05 V/cell is permitted.

2. *Nominal current of the device, charging current, and charging time* (Figure 12.3). Flow of the W characteristic allows a nominal current of

1–2 charging to Ia-char. until fully charged
2–3 charging to IOIa-char. until fully charged
4–5 charging to Wa*-char. until fully charged
5–6 charging to WoWa*-char. until fully charged
7–8 charging to IUIa-char. until fully charged
9–10 charging to Wa*-char. up to filling ratio .9
11–12 charging to IU-char. up to filling ratio 1.0
* characteristic according to DIN 41774



(B)



(C)

1–2 charging to Ia-char. until fully charged
2–3 charging to IOIa-char. until fully charged
4–5 charging to Wa*-char. until fully charged
5–6 charging to WoWa*-char. until fully charged
7–8 charging to IUIa-char. until fully charged no advantages to IOIa
9–10 charging to Wa*char. up to filling ratio 90%
11–12 charging to I, Ia-char. up to filling ratio 100%
* characteristic for R-, TN/TS-type cells acc. to DIN 41775 with adjustable niveau; characteristic for F-types acc. to DIN 41774 but adjusted by a ratio of 1.2:2 to 1.2 V nominal current at I_N

Figure 12.3 Continued.

the device (=charging current at 2.0 V/cell), which is twice as high as the allowed charging current at gassing voltage.

The initial charging current lies a bit lower than the device's nominal current as the battery voltage increases rapidly to 2.1 V/cell.

The nominal device current (I_L) related to 100 Ah is to be respected for the presently standardized lead-acid batteries (4). The device's nominal current I_{dn} leads to the following equation:

$$\text{Idn (A)} = I_L(A) \times \frac{\text{nominal capacity(Ah)}}{100(\text{Ah})}$$

If shorter charging times are demanded than the W characteristic allows for, then a higher device current can be adjusted, but must be limited to the battery-specific limit value for the charging current (see Table 12.3) above gassing voltage of 2.4 V/cell. This method corresponds to the WOWa characteristic (see Figure 12.2). Best efficiency (ratio of costs for the charger/charging time) is attained for a nominal device current of 32 Ah. The shortest charging time is attained with a nominal device current of 40 A per 100 Ah.

3. Influence of the mains voltage. Charging currents from chargers with a W characteristic are generally dependent on the mains voltage, which means the device's current yield is influenced by fluctuations of the mains voltage. A mains voltage increased by 5% increases the current by 25% at 2.0 V/cell, by 35% at 2.4 V/cell, and by 50% at 2.65 V/cell. Therefore the mains voltage must be closely observed upon reaching the gassing voltage of 2.4 V/cell. In order to prevent damage to the battery, the charging device must be adjusted to the augmented mains voltage (e.g. at night) by means of a step-down transformer.

12.4.5.4 Guidelines for Operation

1. The resistance of the cables between the charger and the battery may influence the gradient of the characteristic curve and therefore the charging current. The length of these cables must therefore be considered (generally the charging devices are adjusted to a certain cable length).
2. Charging of two or more batteries in parallel operation with a W-type charger is not allowable since the current limit is not guaranteed for each battery.
3. Charging in series operation is only allowable if the current value does not exceed the smallest battery's charge acceptance capability and the fully charged batteries are switched off in time.
4. Chargers with a W characteristic have only to be dimensioned thermally for 80% of the nominal device current (because of the course of the charging process). Therefore it is advisable to determine the nominal current by the following equation (see also Section 12.4.5.3):

$$\text{Idn} = I_L \times \frac{\text{nominal capacity(Ah)}}{100(\text{Ah})}$$

If a smaller nominal device current is chosen (for instance when there is enough time), this has to be respected for dimensioning the device.

12.4.6 Charging Lead-Acid Batteries Corresponding to the I Characteristic

12.4.6.1 Application

1. Mainly for charging starter batteries and batteries of the GroE type according to the la characteristic.
2. Especially suitable for initial charging (activation charging) following the la characteristic.
3. For charging batteries of the GiS and PzS type according to the IOIa characteristic.

12.4.6.2 Basic Demands

1. For protection of the battery, the I characteristic has to prevent the charging currents from rising above the manufacturer's specifications above gassing voltage. The limits for the charging currents are listed in Table 12.3.
2. The battery has to be manually (I) or automatically (la) disconnected from the charger upon reaching fully charged state.

12.4.6.3 Characteristic

1. *Progression* (see Figures 12.1 and 12.2). Charging is conducted with constant current throughout the charging period followed by the deactivation of the charger.
2. *Charging device nominal current, charging current, and charging time* (see Figure 12.3). Course of the I characteristic allows a charging device current (= charging current at 2.0 V/cell) of the same magnitude as the permitted charging current at gassing voltage (see Table 12.3). For the batteries of the GiS and the PzS type charging with a constant current (I, la) value results in excessively long charging times because the current values are very low, as Table 12.3 shows.

   In order to attain acceptable values in this regard, the initial current is increased until gassing voltage is reached, so an IOl characteristic is formed. For batteries of the GroE type and starter batteries, acceptable charging times are attained with the la characteristic.
3. *Mains voltage influence*. For simple controlled charging devices the constant current changes proportionally with the fluctuations of the mains voltage. This must be considered.

12.4.6.4 Guidelines for Operation

1. Parallel charging of batteries is not recommended as after gassing voltage has been exceeded, limitation of the current value must be guaranteed for every battery (see Table 12.3).

2. Series charging of starter batteries is common. Several batteries are series-connected dependent on the charging devices' voltage. Fully charged batteries are disconnected and reconnected when discharged.

12.4.7 Charging of Lead-Acid Accumulators According to the IUIa Characteristic

12.4.7.1 Application

1. Mainly for charging traction batteries when shortest possible charging time (below 8 h) is demanded.
2. For "heedful" charging.

12.4.7.2 Basic Demand

1. For protection of the battery the charging current has to be reduced in the second I period so it does not exceed the manufacturer's limits above gassing voltage.

   The limit values for the charging currents above gassing voltage are listed in Table 12.3. During the constant-voltage charging period (2.4 V/cell) an allowed tolerance of ± 1% may not be exceeded (5).
2. The battery must be disconnected manually (IUI) or automatically (IUIa) after the fully charged state has been attained.

12.4.7.3 Characteristic

1. *Progression*. Charging is initially conducted with constant current until gassing voltage is reached (first I part). Then the voltage is kept constant (U part), and the current decreases permanently as the battery's state of charge increases. As soon as the current has dropped to the allowed end-of-charge current (see Table 12.3), the final charging phase (second I part) is activated. Upon reaching the fully charged state, the battery has to be disconnected.
2. *Nominal device current, charging current, and charging time*. The charging current for the first I period does not have to be limited by the charging device. This is done, however, to protect the charging device and the equipment (charging cables, etc.). Charging with the IUIa characteristic permits charging times below 8 hours. Charging currents of twice or three times I_5 are not of interest as the gassing voltage is attained too fast and forces lowering of the charging current, and apart from that makes the chargers more expensive. The most economic solution is a nominal device current of 25 A per 100 Ah. The shortest charging time is attained with 40 A charging current per 100 Ah.
3. *Mains voltage influences*. The given tolerances of the characteristic curves (constant voltage ± 1%, constant current ± 2%) have to be guaranteed for mains fluctuations of ± 10% and frequency fluctuations of ± 2%. For devices that are not dimensioned to cope with these fluctuations, the manufacturer must specify the allowed ranges. If greater mains fluctua-

tions of private networks are to be expected, this must be mentioned when ordering the charging device.

12.4.7.4 Guidelines for Operation

Parallel charging of batteries is not recommended in the second I period for the charging-current limit must be guaranteed for all of the batteries charged (see Table 12.3). Devices with a possibility to switch over from IU to IUIa can be employed for parallel charging in the IU position.

12.4.8 Charging According to the IU characteristic

12.4.8.1 Application

1. Mainly for charging traction batteries, whereas IU-type charging is conducted in large battery stations for parallel charging of several batteries at a time.
2. For fast charging of batteries (in pauses, for increase of the operational time), whereas fully charged state is not attained.
3. For heedful charging of sulfated batteries. (The voltage does not exceed 2.4 V/cell; the initial current is low and only increases when the sulfatation has been reduced. Hereby the voltage even decreases for a transitory period of time. With an uncontrolled charging device the voltage would immediately rise above 2.4 V/cell, the initial current would be higher, the battery would start to gas strongly, and the temperature could rise to unallowed values.)

12.4.8.2 Basic Demand

For protection of the battery, the voltage of 2.4 V/cell must be kept constant within $\pm 1\%$ during the U phase (5).

12.4.8.3 Characteristic

1. *Progression.* Initial charging is conducted with constant current (I section) until gassing voltage is reached. Upon reaching the gassing voltage the charging device's voltage is kept constant (U section) and the charging current decreases. Fully charged state is only attained after a longer period of charging.
2. *Device's nominal current, charging current, and charging time.* The charging current during the I period would not have to be limited because of the battery, but only for protection of the charger and the equipment (charging cables, etc.). The battery is also indifferent to the tolerance of current limitation, but the smaller the tolerance, the better, as the charger's electric power is optimally employed and thus the charging time shortened (especially for simultaneous charging of several batteries). State of charge of 100%, respectively 80%, is attained by partial charge in very short periods of time. (Fully charged state corresponds to 120%, respectively 100%, with a charging coefficient of 1.2.)

3. *Mains voltage influences.* The given tolerances of the characteristic curves (constant voltage ±1%, constant current ±2%) have to be guaranteed for mains fluctuations of ±10% and frequency fluctuations of ±2%. For devices that are not dimensioned to cope with these fluctuations, the manufacturer must specify the allowed ranges. If greater mains fluctuations of private networks are to be expected, this must be mentioned when ordering the charging device.

12.4.8.4 Guidelines for Operation

1. Batteries may remain connected to chargers of the IU type for up to 3 days if the final value of the charging current does not exceed 10% of I_5. If the final charging-current value is higher, then charging must be interrupted upon reaching the maximum permissible electrolyte temperature of 35°C (131°F).
2. If the available daily charging time is not sufficient during the week, an equalizing charge has to be conducted once a week. If the batteries are fully charged during the day, then one equalizing charge every 4 weeks is sufficient. This equalizing charge can be conducted by a prolonged charging according to the IU characteristic during a weekend (guideline 1 must be respected!) or through charging with an increased voltage above gassing voltage (2.4 V/cell) if the charging devices are equipped with the corresponding device (such as an IU-IUW-IUI switch). The necessity for single charging during the W phase (for IUW) or the second I phase (for IUI) must be respected when parallel charging is conducted and the limit charging-current values listed in Table 12.3 are not exceeded.
3. When dimensioning the cables connecting the battery to the charger, a voltage drop of less than 2% should be realized for nominal current.
4. When charging according to the IU characteristic, the electrolyte gravity and temperature of every cell have to be checked once a week in order to notice shorts between plates in time.
5. If a battery of low capacity is charged with a charging device of strong nominal current, then the electrolytes' temperature has to be surveyed above 2.4 V/cell or the charging current has to be reduced.

12.4.9 Charging of Nickel/Cadmium Batteries

NiCd batteries are generally charged according to one of the following three charging methods: I (la)-, W (Wa)-, or IU-type charging.

Charging according to the IOIa, WOWa, and IUIa characteristics is of course possible but not common as these characteristics are not necessary for charging NiCd accumulators (except IOIa-type charging for cells with sintered electrodes).

12.4.9.1 Basic Demands

1. NiCd batteries (except sintered cells) do not demand limitation of the charging current. For protection of the battery, however, it must be guaranteed that the limits for the electrolyte temperature (45°C (113°F); for pocket-plate cells 35°C (95°F)) are not exceeded.

2. Batteries have to be disconnected upon reaching fully charged state.
3. Equalizing charging with a current value of 15 should be conducted for 15 hours every 2 to 3 months for NiCd batteries.

12.4.10 Charging of Nickel/Cadmium Batteries to the I Characteristics

12.4.10.1 Application

Suitable for all designs.

12.4.10.2 Characteristic

1. *Progression*. The charging-current value is kept constant throughout the charge and the battery must be disconnected manually (I) or automatically (la) upon reaching fully charged state.
2. *Device's nominal current, charging current, and charging time*. Currents of 0.5 to 1.5 times I_5 are applied. For NiCd cells with sintered electrodes, the charging current must be limited above gassing voltage (see Table 12.1). This causes long charging periods for cells with sintered electrodes. In order to attain shorter charging times, the initial charging current (up to the gassing voltage) is augmented, forming an IOI (IOIa) characteristic.

   For NiCd batteries of the R, T, and TS types, acceptable charging times are attained when applying a current of $1.5 \times I_5$.
3. *Mains voltage influences*. For regulated charging devices of simple design, the constant current changes proportionally to the mains fluctuations.

12.4.10.3 Guidelines for Operation

The charging current must be reduced for high electrolyte or ambient temperatures (greater than 45°C (113°F)).

12.4.11 Charging Nickel/Cadmium Batteries According to the W Characteristic

12.4.11.1 Application

For all types of constructions and designs this is the most common and heedful charging method (temperature and water consumption are kept especially low).

12.4.11.2 Characteristic

1. *Progression for series R, T, and TS NiCd cells*. As these series exhibit different initial voltage (1.25 to 1.5 V/cell), a range for the characteristic was fixed for which the characteristic of the charger must be adjustable (6). The adjustment in this range can be accomplished either by adjustment of the characteristics' niveau or gradient. As the gradient adjustment is of greater technical expenditure, the niveau adjustment method is more commonly applied. This kind of adjustability, however, is not demanded for the charging device when the charger is only applied for one type of

battery, which is generally practiced. Development has lead to the initial voltage generally being 1.4 V/cell as the voltage of lower-situated battery voltage levels rises quickly to this value when charged.

Two pairs of values therefore determine progression of the characteristic: (a) device's nominal current at 1.4 V/cell and (b) 40 to 50% of the devices' nominal current at 1.75 V/cell.

2. *Progression for series F NiCd cells.* For charging NiCd batteries with sintered electrodes a characteristic according to DIN 41 774 (W-type charging for lead-acid batteries) is employed with the following values:

   Device's nominal current (DNC) at 1.2 V/cell.
   About 40% of DNC at 1.5 V/cell.
   About 25% of DNC at 1.6 V/cell.

3. *Progression for Ni/Fe batteries.* Series RE and TNE also have different initial voltages (1.5 and 1.75 V/cell); therefore a range was determined in which the characteristic must be adjustable (6). Adjustability is also not demanded when the charger is only applied for one type of battery. The progression for an adjustable characteristic is determined by the following values: (a) DNC for 1.5 to 1m75 V/cell and (b) 40 to 50% of DNC for 1.65 to 1.9 V/cell.

   Ni/Fe batteries only attain fully charged state if the charging current does not drop below one-third of I_5 in the course of charge.
4. *Device nominal current, charging current, and charging time.* Adjustment of the DNC ($=$initial charging current) for type and size of the battery is determined by the time available for recharge. Standard value for the charging current is 0.5 to I_5 times I_5. The electrolytes' temperature is kept within acceptable limits for these charging currents.
5. *Mains voltage influences.* For charging devices with W characteristic the current value is generally influenced by mains fluctuation. Variance of 10% of the mains voltage results in 30 to 50% variance of the charging current. The battery is indifferent to these changes of current, but the charging device is not. Therefore in the case of mains fluctuations over longer periods of time, step-down transformers must stabilize the charger.

12.4.11.3 Guidelines for Operation

Parallel charging of batteries cannot be advised for W-type chargers as varying battery voltage levels result in unequal charging of the batteries and therefore in an uneven state of charge. For Ni/Fe batteries the lower current limit is not guaranteed during recharge.

12.4.12 Charging of NiCd Batteries According to the IU Characteristic

12.4.12.1 Application

This charging method is only employed in a very few cases for single-battery charging, but is mostly employed for parallel recharge of several batteries.

12.4.12.2 Characteristic

1. *Progression*. Charging is conducted with constant current (I section up to gassing voltage). After the gassing voltage has been reached, the device's voltage is kept constant (U part) and the current values decrease to lower values.

   Upon reaching the fully charged state the battery has to be disconnected. This constant voltage having a tolerance of ±2% (DIN 41 772) lies between 1.6 and 1.7 V/cell depending on the type of cell (2).
2. *Device's nominal current, charging current, and charging time*. The charging current (DNC for the first I section) is only limited by the electrolyte temperature. Charging currents of 1.5 to 2 times I_5 show good results for the charging time.
3. *Mains voltage influences*. The given tolerances of the characteristic curves (constant voltage ±2%, constant current ±2%) have to be guaranteed for mains fluctuations of ±10% and frequency fluctuations of ±2%.

12.4.12.3 Guidelines for Operation

1. When parallel charging is performed, only batteries with the same number of cells and of the same type are connected.
2. For high ambient and electrolyte temperatures (greater than 45°C (113°F)) the charging current must be reduced.

12.4.13 Charging Valve-Regulated Lead-Acid Batteries

12.4.13.1 Charging Methods

Two methods are commonly practiced: (a) charging according to the W characteristic and (b) charging according to the IU characteristic. The W method is not advisable as the charge current is dependent on mains fluctuations.

12.4.13.2 Charge Currents and Charging Time

Charging data are given in Table 12.4

Table 12.4 Comparison of charging data for W- and IU-type charging characteristics.

Characteristic	Charging current	Charging voltage[a]	Charging time	Filling ratio	Operation mode
W	Max. 2 × I_{20}	2.3 V/cell	ca. 14 h	90%	Cyclic operation
IU	2–10 × I_{20}	2.25–2.3 V/cell	14–4 h	90%	Float-charge operation (parallel operation)

[a] ambient temperature 20°C (68°F)

12.4.14 Charging Gas-Tight Nickel/Cadmium Batteries

12.4.14.1 Charging Methods

The two following methods are generally applied:

1. *Charging according to I (Ia, IOIa) characteristic.*
   IOIa characteristic;

   3 to 10 times I_{10} (series dependent) to end-of-charge voltage.
   Half of I_{10} to I_{10} to end of charge (full charging).
2. *Charging according to W (Wa, WOWa) characteristic.*
   W characteristic;

   $1.2 \times I_{10}$ initial charge current.
   $0.8\ I_{10}$ end-of-charge current.

Charging according to I and W characteristics without deactivation is only allowed for currents 0.1 to 0.3 times I_{10} (series dependent).

When charging with higher current values, deactivation of the charge process must be controlled as it is time-, voltage-, and temperature dependent.

Charging according to an IU characteristic is prohibited.

12.4.14.2 Application

The option for applying charging methods according to the I or W characteristics, respectively their modifications, can be derived from Figure 12.2.

12.4.14.3 Charging Currents and Charging Time

Charging data are given Table 12.5.

12.5 COMPARING CHARGING METHODS FOR LEAD BATTERIES

Table 12.6 compares some charging methods for lead batteries

Table 12.5 Charging data for gas-tight NiCd batteries.

Type of charge	Charging current	Charging period	Characteristic	Filling ratio
Standard charge	I_{10}	14 hrs	Ia	100%
Accelerated standard charge	$2 - 3 \times I_{10}$ (series-dependent)	7 – 4.5 hrs	Ia	100%
Fast charge	$3 - 10 \times I_{10}$ (series-dependent)	2.5 – 1 hrs	Ia	70–90%
Float charge	$0.1 - 0.3\ I_{10}$ (series dependent)	unlimited	I	

12.6 INSTALLATION COSTS OF CHARGING DEVICES

The costs for IU-type charging devices contain costs for one secondary charger for every three parallel charged batteries and for two secondary chargers for every three to eight batteries. The following comparison is on batteries 250 Ah, 80 V (= 40 cells). The battery-dependent charging currents of the charging devices are listed in Table 12.7.

Figure 12.4 shows a comparison between the initial costs for chargers of different characteristics.

12.7 GUIDELINES FOR THE SELECTION OF CHARGERS

This comparison of the charging method (Figure 12.3) and the initial costs (Section 12.6) allow for judgment of which devices are to be applied.

Device characteristics are to be chosen, when:

Wa: (a) The mains voltage fluctuations are less than ± 5%.
(b) A charging time of 10–12 hours is available.

WOWa: (a) The charging time is limited to 7–9 hours.
(b) The mains voltage fluctuations are less than ± 5%

IUIa: (a) Charging time is limited to 6–7 hours.
(b) The mains voltage fluctuations are significant.
(c) Heedful charging is desired.
(d) The high initial costs are acceptable.

IU: (a) Parallel charging of batteries is to be conducted.
(b) Short partial charging (e.g. at noon) is desired.
(c) The mains voltage fluctuations are significant.
(d) Additional secondary, respectively equalizing, charging is acceptable.

12.8 SPECIAL DEMANDS AND RECOMMENDATIONS FOR THE CHOICE OF CHARGER

12.8.1 Demands of Valve-Regulated Lead-Acid Batteries

To avoid gassing charge current, charge voltage and charging time are limited.

12.8.1.1 Charging Characteristic of Traction Batteries with VRLA Cells

The charge characteristic is specified by the battery manufacturer. Mostly this characteristic is a modification of the above-described IUI characteristics. The initial charge current is between 0.7 to 1 times I_5, the final charge current between 0.07 to 0.08 times I_5 (a following additional charge sometimes is performed in current pulses). The total charging time is between 11 and 14 hours. Standardized characteristics do not yet exist.

Charger manufacturers offer chargers allowing the charge of batteries designed by different manufacturers (the chargers are controlled by a microprocessor that recognizes the characteristics specified by the battery manufacturer).

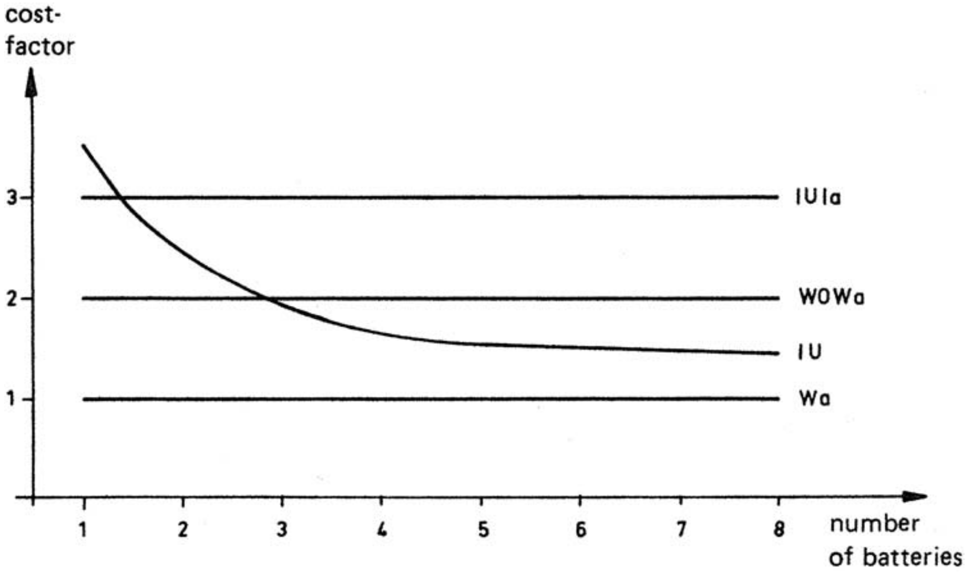


Figure 12.4 Initial costs for charging devices with different characteristics compared to the initial costs for a Wa-type charger (cost for Wa-type charger = 1).

12.8.2 Demands of Modified Traction Batteries

Note: *Traction batteries of the modified type are equipped with a device for electrolyte circulation).*

To increase the service life and to reduce maintenance to a minimum a heedful charge of the batteries is recommended. This can be performed by electrolyte circulation (reduced charging factor to 1.04 to 1.08, and reduced battery temperature means a double effect) or cooling with water or a cooling device (to reduce the battery temperature).

12.8.2.1 Charging of Modified Traction Batteries

The above-described charge characteristics Wa, WoWa, IU, and IUIa may be performed (depending on the battery manufacturer's advice for the modified form). The initial charge current is chosen depending on the charging time wanted.

The complete charging process needs in addition to the battery;

1. *Electrolyte circulation.* Charger with the specified characteristic and a correct charging factor (1.04 to 1.08), and a pumping device for the electrolyte circulation with a control set.
2. *Cooling with water.* Charger with the specified characteristic and a cooling device with connection to a fresh water supply.
3. *Cooling device.* Charger with the specified characteristic and cooling device.

Depending on the battery manufacturer these variants are offered as a complete system.

Table 12.6 Comparison of charging methods for lead batteries.

	Wa	WOWa	IUIa	IU
Progress of charge	Device nominal current $0.8 \times I_5$, current decreases with rising voltage	Device nominal current $1.6 \times I_5$, after gassing voltage of 2.4 V/cell is reached automatic changeover (0) to Wa characteristic	Device nominal current (1.5 to $2 \times I_5$) constant up to gassing voltage of 2.4 V/cell. Then automatic changeover to constant voltage until current has decreased to $0.2 \times I_5$, then automatic changeover to the Ia phase. Charging conducted with constant current until deactivated.	Device nominal current (1.5 to $2 \times I_5$) constant up to gassing voltage of 2.4 V/cell, then automatic changeover to constant current
Charging	10–12 h	7–9 h	6–7 h	2.5–3.5 h for 80% full charge with secondary charger 10–12 h
Advantages	Upon reaching fully charged state automatic deactivation (a); simple technology	Short charging periods; upon reaching fully charged state automatic deactivation (a); simple technology	Shortest charging period; especially heedful charging of the battery; mains voltage fluctuations (±10%) are without effect on the charging current	Partial charges up to 80% in very short periods of time; parallel charging of several batteries possible; less water loss through gassing; mains voltage fluctuations (±10%) are without effect on the charging current; no time-dependent deactivation

Table 12.6 Continued.

	Wa	WOWa	IUIa	IU
Disadvantages	Only single charging possible; charging current generally varies substantially with mains fluctuations	Only single charging possible; charging current varies substantially with mains fluctuations	Only single charging possible, but parallel charging also possible with additional devices	Very low gassing action during daily charge, therefore unfavorable mixture of the electrolyte. Equalizing charging necessary during the weekend; in some cases secondary charger is necessary; If one IU charger is employed for simultaneously charging several batteries a breakdown has more severe consequences than if several chargers were employed.

Table 12.7 Comparison of charging devices with different charging characteristics for a charging current for 40 cells with 250 Ah.

Wa characteristic	$0.8\ I_5 = 40\ \text{A}$
WOWa characteristic	$1.6 \times I_5 = 80\ \text{A}$
IU characteristic	$1.8 \times I_5 = 90\ \text{A}$
IUIa characteristic	$1.8 \times I_5 = 90\ \text{A}$

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13

Technical Aspects of Chargers and Current Transformers and Methods for Supervision

G. WILL

13.1 APPLICATION OF BATTERY CHARGERS

Battery chargers are employed for charging starter, traction, and stationary batteries as well as for supplying stand-by power. The demands for these devices are dependent on the operation conditions.

Charging starter and traction batteries is mainly conducted during recesses. Hereby the consumers are disconnected for charging batteries (Figure 13.1).

Charging for stationary batteries allows an ensured stand-by power supply for parallel and switch operation for DC consumers.

For switch operation (Figure 13.2) consumers are supplied by power through a rectifier or directly by three-phase supply. In the case of mains power failure, the most important consumers are supplied with energy by the battery until the mains power returns. A charger then charges the battery. If the charging process is terminated, a float-charge operation is activated so full capacity is available at any time.

For parallel operation the consumer and the battery are permanently operated in parallel and supplied by their common charger (Figure 13.3). In case of mains failure, the battery without interruption automatically supplies the consumer.

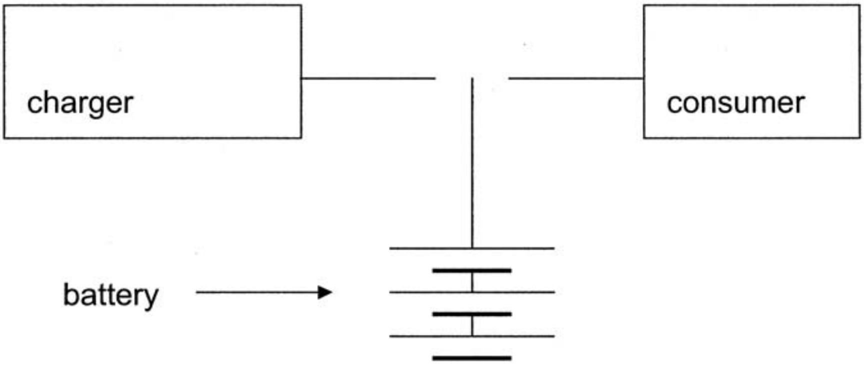


Figure 13.1 Charging operation for starter and traction batteries.

13.2 CHARACTERISTIC VOLTAGES OF LEAD-ACID AND NiCd BATTERIES

The characteristic voltage values for lead-acid and NiCd batteries are listed in Table 13.1.

13.3 CONSTRUCTION AND FUNCTION OF BATTERY CHARGERS

Battery chargers can generally be divided into two main groups: controlled and uncontrolled devices.

13.3.1 Controlled Battery Chargers

13.3.1.1 Thyristor Controlled Chargers

These consist of the following:

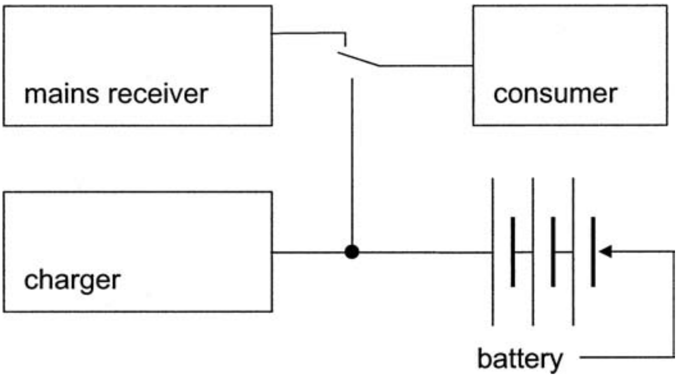


Figure 13.2 Switch operation for charging stationary batteries.

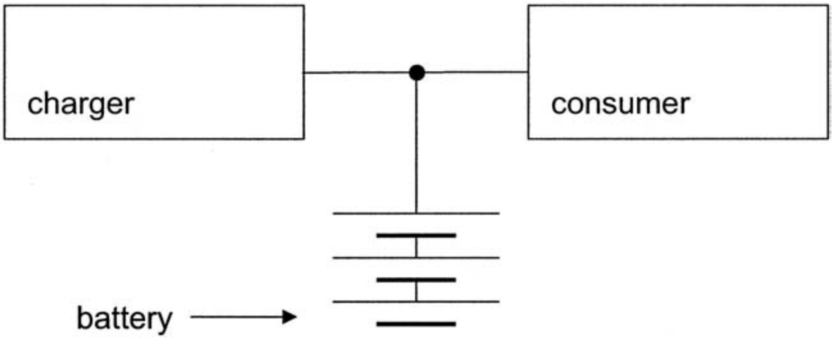


Figure 13.3 Parallel operation for charging stationary batteries.

- Transformer.
- Controllable rectifier.
- Control electronics.
- Smoothing filters.

They are applied for a wide current range and are, depending on the demanded power, one-phase or three-phase devices (Figure 13.4).

Transformer

The transformer (T1) adjusts the mains voltage to the desired DC voltage and simultaneously represents the galvanic separation between three-phase mains and DC output of the charger.

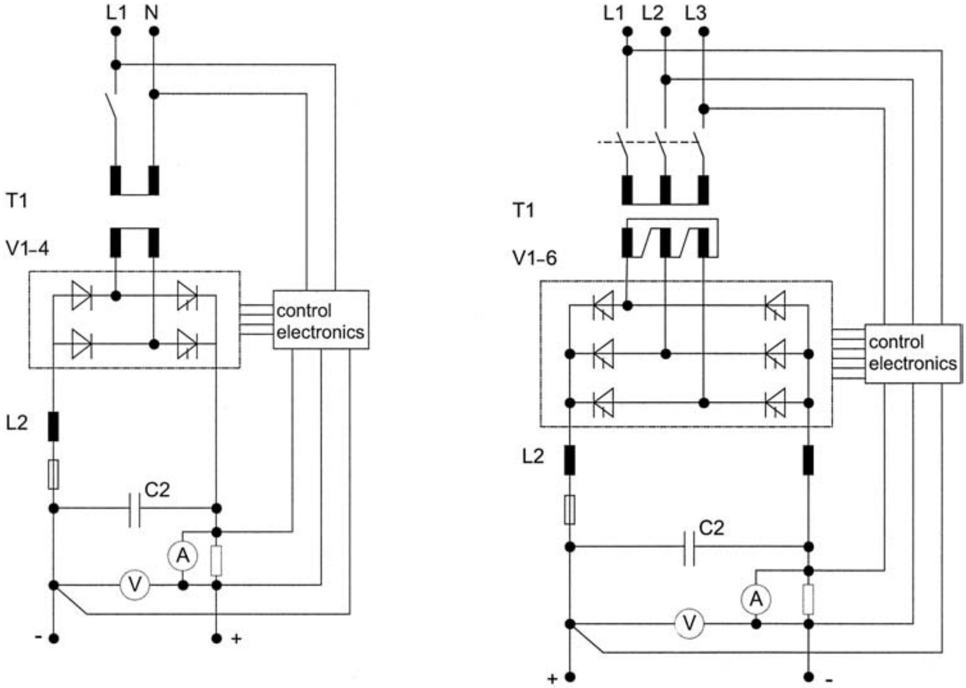
Rectifier

Line-commutating converters are employed as rectifiers. Three-phase types are preferably executed as fully controlled bridge circuit (V1-6), whereas for single-phase types the semicontrolled bridge circuit (V1-4) is employed.

Through application of controllable valves the rectifier acts as an actuator for the charging device's output voltage, which can be varied in a wide range. The valves employed are silicon semiconductors, such as power packs and thyristor modules (respectively thyristor diode modules).

Table 13.1 Characteristic voltage values for lead-acid and NiCd batteries.

	Pb battery	NiCd battery	Units
Nominal voltage	2.0	1.2	V/cell
Float-charge voltage	2.2–2.25	1.38–1.40	V/cell
Gassing voltage	2.4	1.6–1.7	V/cell
End-of-charge voltage	2.6–2.7	1.65–1.85	V/cell
Cutoff voltage	1.7–1.9	0.85–1.1	V/cell



single-phase type

three-phase type

Figure 13.4 Thyristor controlled chargers.

Control Electronics

A control unit topped by trigger equipment for static power converters triggers the thyristors, so the output voltage of the chargers is independent of the mains and load fluctuations. An automatic switchover unit and a corresponding set point to the controller allow these devices to yield constant voltage or constant DC current.

According to DIN 41 772 there are two standard characteristics for controlled battery chargers:

1. For the IU characteristics (Figure 13.5) the output voltage is kept between 2.23 and 2.40 V/cell and below the charger's nominal current.
2. For greater loads, the voltage control is substituted by current control. By lowering the output voltage the charger yields a constant current of the magnitude of the device's nominal current.

The IUIa characteristics (Figure 13.6) is composed of an IU characteristic with an attached charging phase. Upon reaching a certain lower current limit, charging is continued at slightly increased voltage with constant current (I-charging phase).

Upon terminating the charging process, the device is automatically switched off (a phase). Criteria for this switching can be a fixed charging period or voltage change du/dt.

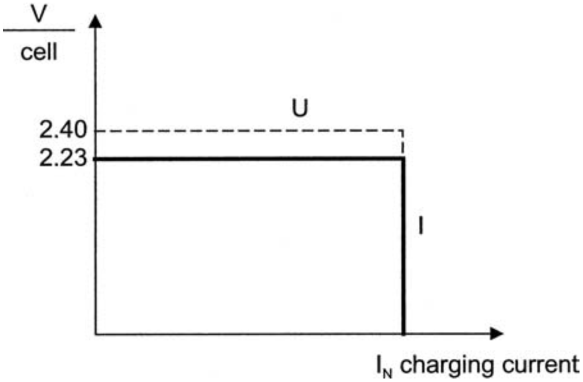


Figure 13.5 IU characteristics according to DIN 41 772.

Smoothing Filters
The rectifier superposes an alternating voltage on the DC voltage over the whole controlling range, which is greatest for an angle of 90 degrees. The alternating voltage has harmonics of the degree $v = pk$, ($k = 1,2,3, \ldots$; $p =$ pulse number). Therefore in three-phase types with fully controlled bridge circuits the 6th, 12th, and 18th harmonics, and in single-phase types the 2nd, 4th, and 6th harmonics are encountered (Figure 13.7).

The alternating voltage part is limited by a smoothing inductivity (L2) on the direct current side in order to prevent excessive stress for the battery and the connected consumer. For higher demands, such as in the case of application for power supply systems with small batteries or sensitive consumers, often additional smoothing capacities (C2) are necessary.

13.3.1.2 Transistor Controlled Chargers

Chargers with transistor series control are applicable for small loads as an economic alternative to thyristor controlled chargers (Figure 13.8). They consist of

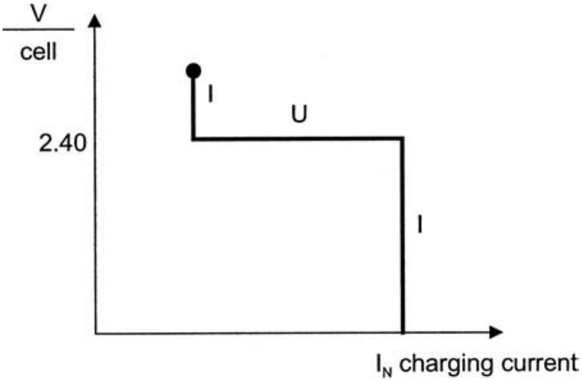


Figure 13.6 IUIa characteristics according to DIN 41 772.

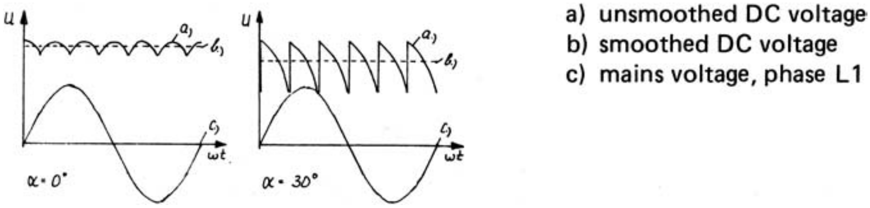


Figure 13.7 Voltage flow, three-phase bridge.

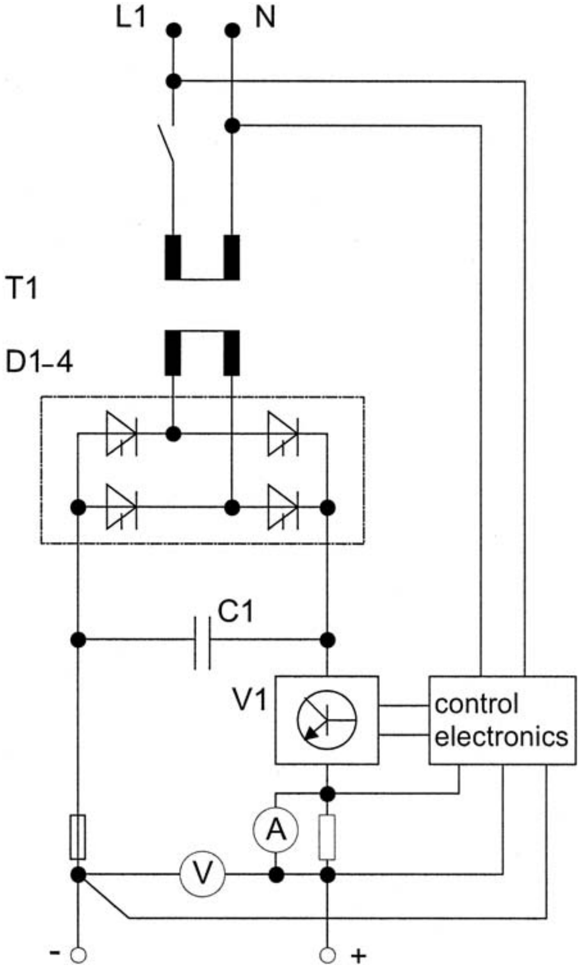


Figure 13.8 Transistor controlled charges.

- A transformer.
- An uncontrolled rectifier.
- A power transistor.
- Control electronics.
- The corresponding smoothing filters.

These devices' advantage is that their internal dynamic resistance is very low and therefore the voltage can be regulated very quickly. The losses in the series control are comparatively high and therefore the efficiency is low. Primary-chopped switching power supplies will more and more substitute these chargers (Figure 13.9). A more detailed description is therefore not made here.

13.3.1.3 Chargers with Primary-Chopped Switching Power Supplies

These chargers consist of

- Mains rectifier.
- Power stage.
- Ferrite transformer.
- Rectifier.
- Control electronics.
- Smoothing filters.

They are mainly employed for a power range of 24 V, 50 A. They are lighter than conventional devices and are more efficient. They can be of different design depending on power and demand. Figure 13.9 shows one example.

Mains Rectifier

The mains voltage is rectified by a diode bridge circuit (D1-4) and the capacity (C1) charged. This capacity is a smoother and an energy storage at the same time and delivers the input voltage for the mains supply circuit consisting of a power stage and a ferrite transformer.

Power Output Stage

The transistor (V1) is triggered by a frequency generator and "chops up" the rectified mains voltage with a frequency of, e.g., 20 kHz. It is at the same time a power output stage.

Transformer

The high-frequency AC voltage is separated galvanically from the mains and adjusted to the output voltage by a ferrite transformer (T1).

The high transformation frequency allows the transformer to be of very small design and therefore gains great advantages in weight and volume compared to devices with 50-Hz transformers.

Rectifier

Rectification and smoothing of the transformer output voltage is accomplished by a diode (D2) and a capacitor (C2), yielding a high-quality DC output voltage.

Control Electronics

Regulating mains and load fluctuations is attained by changing the pulse-duty factor triggering the transistor (V1). Transformers or optical couplers can accomplish

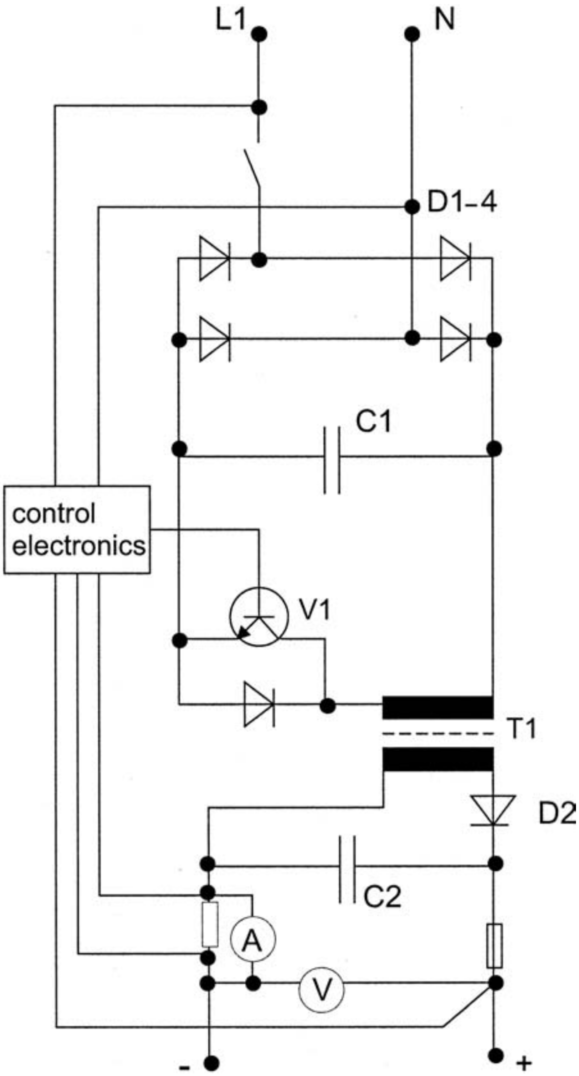


Figure 13.9 Chargers with primary-chopped switching power supplies.

transfer of the regulating signals. Regulation can be done according to an IU or IUIa characteristics.

13.3.2 Uncontrolled Chargers

These consist of a transformer and an uncontrolled rectifier. These devices are generally available in the same power ratings as controlled devices of the single-phase type or the three-phase type (Figure 13.10). Generally silicon diodes are employed as valves.

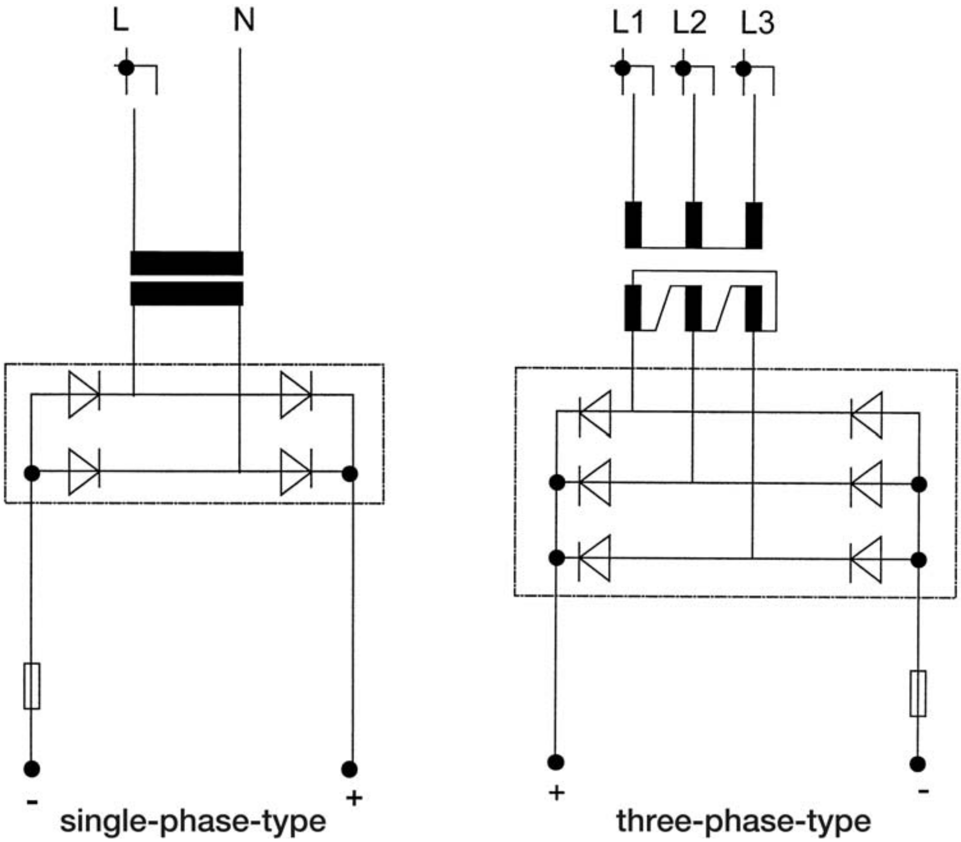


Figure 13.10 Uncontrolled chargers.

The output voltage of these devices is generally dependent on the mains voltage and the current of the load. The DC side output voltage therefore also changes when fluctuations of the mains voltage are encountered. The W characteristic is standardized according to a DIN standard (Figure 13.11) and passes the following three points for lead batteries:

- 2.0 V/cell at 1.0 N.
- 2.4 V/cell at 0.5 N.
- 2.64 V/cell at 0.25 N.

With the addition of an automatic switch-off step the W characteristic can be completed into a Wa characteristic.

13.4 CHARGERS FOR TRACTION BATTERIES AND STATIONARY BATTERIES IN SWITCH OPERATION

When charging a battery it is of great importance that the charge is carried out in a heedful manner and is terminated after a certain period of time. For the charging

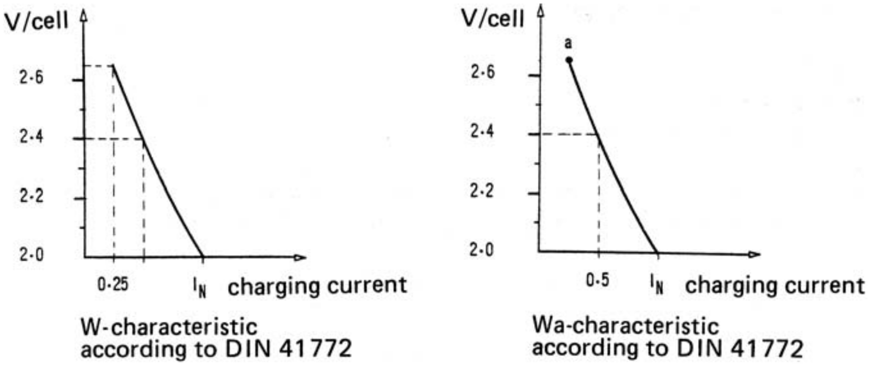


Figure 13.11 Characteristics of uncontrolled chargers.

process itself, controlled chargers with, for instance, an IUIa characteristic or uncontrolled chargers with Wa or a switchable WO-Wa characteristic can be employed.

One of the most important requirements for recharging traction batteries is very short charging periods.

For a PzS-type battery of 80% discharged state, the following recharging periods are required:

- IUIa: $>$ 7.5 h.
- WOWa: $>$ 8 h.
- Wa: $>$ 14 h.

The permitted charging currents are treated in VDE 0510 (see Table 13.2). The charging methods and techniques are explicitly treated in Chapter 12.

13.5 CHARGERS FOR STATIONARY BATTERIES IN PARALLEL OPERATION

For a guaranteed power supply the battery is in many applications permanently connected parallel to the consumer. To supply power to the consumer and battery, controlled chargers that fulfill the following criteria are mostly employed:

- The battery has to be charged.
- State-of-charge of the battery must be maintained.
- Voltage tolerances of the consumer must be obeyed.
- Dimensioning of the charger must correspond to the consumers current.
- A charging reserve must be available for recharging the battery after a mains failure.

As the voltage step between the gassing voltage and cut-off voltage of lead-acid and especially of NiCd batteries (Table 13.3) is significant, great care must be taken not to exceed the permitted voltage tolerance of the consumer. This is mostly ensured for lead-acid batteries in many applications through proper choice of the number of

Table 13.2 Permitted charging currents according to VDE 0510.

		Device current (A) per 100 Ah				
		Allowed acc. to VDE 0510 W-char.			Spec. VARTA IUI-char.	
Type of cell	Application	2.65 V	2.40 V	2.00 V	2.40 V	I = const.
Large surface cells						
Gro	Stationary	6	12	24	80	8.5
GroE	Stationary	6	12	24	80	5
Tubular plate cells						
OPzS	Stationary	3.5	7	14	80	5
PzS (PzF)	Traction	4	8	16	80	5
Grid-plate cells						
GiS	Traction	4	8	16	100	5
	Starter	6	12	24	160	10

cells, the battery's capacity, as well as limitation of the charging voltage to a float-charge voltage.

For application of NiCd batteries and charging lead-acid batteries above float-charge voltage the following measures are necessary:

- Employment of counter cells.
- Separation of the batteries' cells into stock and additional cells.
- Application of DC converters.

13.6 SURVEILLANCE AND ADDITIONAL DEVICES

Chargers are equipped on more-or-less expedient surveying equipment depending on their application. These have to register irregularities quickly, protect the battery and the attached consumers, and thereby ensure safe operation of the devices.

The following describes functions and actions of the most important surveying equipment (Figure 13.12).

Table 13.3 Voltages of lead-acid batteries.

	Lead-acid batteries		NiCd batteries	
Voltage	V/cell	Variances	V/cell	Variances
Gassing voltage	2.4	+ 20%	1.7	+ 42%
Float-charge voltage	2.23	− 11.5%	1.4	+ 16%
Nominal voltage	2.0	± 0%	1.2	± 0%
Cutoff voltage	1.75	− 12.5%	1.0	− 17%

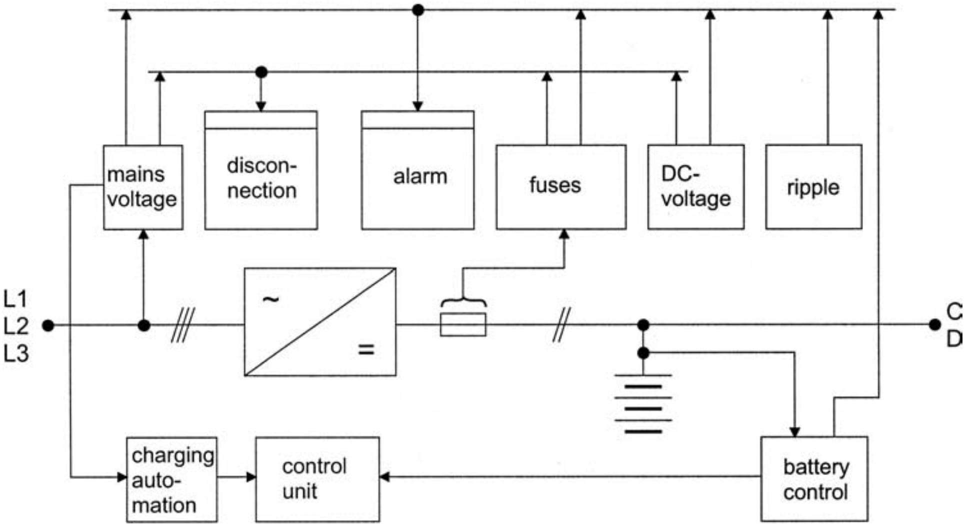


Figure 13.12 Surveying equipment and additional devices.

13.6.1 Mains Surveillance

Whenever the mains voltage lies outside of a certain tolerance or one phase fails, faultless function of the charger is no longer guaranteed.

Mains undervoltage or phase failure is followed by switch-off of the charging device and monitoring of the irregularity.

Mains overvoltage is also followed by switch-off of the charging device and monitoring of the irregularity.

If the voltage returns to normal values, the charging device is automatically reactivated.

13.6.2 DC Voltage Surveillance

An increase or decrease of the DC voltage outside of tolerance limits must be prevented for protection of the consumers attached and for satisfactory charging of the battery.

Overvoltage results from a fault at the charger. Undervoltage may be a result of mains failure or faulty functions of the charger. Overload of the charger can also be the reason, because the DC voltage decreases as the current limitation comes into effect.

During single charging operation DC overvoltage is followed by switch-off of the charging device and monitoring of the irregularity, and DC undervoltage is followed by (in the case of low DC voltage) monitoring of the irregularity.

When for redundancy purposes two or more chargers are attached to one power rail, the faulty device must be distinguishable in case of failure. In order to distinguish the faulty device the charger output current may be checked.

During parallel charging operation DC overvoltage is followed by switch-off of the faulty charger and monitoring of the irregularity; and DC undervoltage is followed by switch-off of the faulty charger and monitoring of the irregularity.

13.6.3 Surveillance of the DC Voltage Waviness

A fault in the converter or a failure of the smoothing filters may increase the AC voltage share at the DC side to a magnitude harmful to the consumer or the connected battery. It is therefore necessary to control the waviness of the DC voltage.

Upon notice the irregularity is monitored

13.6.4 Fuse Surveillance

Triggering a fuse may be the result of old age, overstress, or short circuit. This event is followed by switch-off of the charger and monitoring of the irregularity.

13.6.5 Automated Charging

Lead-acid cells and NiCd cells are often recharged after mains failure with an increased voltage value of 2.3–2.4 V/cell (for Pb) and 1.6 V/cell (for NiCd). Changeover to a higher voltage level is done manually or automatically. The automatic changeover is to float-charge operation after a given period of time.

13.6.6 State-of-Charge Surveillance

For fast and economical recharge, depending on the battery's state of charge, after mains failure and in order to utilize the battery's capacity optimally, continuous information on the state of charge and on the load is indispensable. Devices that register and process the different values of interest such as current, voltage, and temperature have been developed and tested.

13.7 HARMONIC OSCILLATIONS AND REACTIVE POWER

Converters take out a non-sine-shaped current from the three-phase supply. It is composed of a fundamental oscillation at mains frequency and several harmonic oscillations whose frequencies are integer value multiples of the mains frequency. These harmonic oscillations can be viewed by approximation as impressed current that are enforced on the three-phase supply. Harmonic voltages are encountered at mains impedances, which are superposed on the mains fundamental oscillation and therefore distort the mains voltage.

Whenever the harmonic currents exceed a certain value, generally resonances and therefore disturbances in the power supply system are encountered.

Through closely analyzing the converter currents and employing exact countermeasures it is possible to reduce the mains disturbances to a large extent. Therefore it is possible to operate large converters in the mains.

As battery chargers mostly have a low power consumption compared to the overall power consumption of the plant, they can be operated without difficulties. It is however indispensable to reduce these harmonic currents to a minimum for large stationary plants or on a large-scale employment of on-board chargers in electric vehicles.

A fully controlled three-phase bridge circuit and a primary-chopped switch mode power supply shall be viewed more closely in the following:

13.7.1 Three-Phase Bridge Circuit

The three-phase bridge circuit draws a square-wave current under ideal conditions from the mains (Figure 13.13). Harmonic oscillations of the ordinal $\nu = p(k \pm 1)$ are encountered (p = pulse number (p = 6); k = 1, 2, 3, ...). The amplitudes of the harmonic currents are inversely proportional to their ordinal number:

$$I(\nu) = \frac{1}{\nu} I_{(1)}$$

The most significant harmonics are the 5th, 7th, 11th, and 13th as the amplitudes of higher frequencies are very small.

Harmonic oscillations can be reduced by employing a higher number of pulses of the converter or application of filter circuits.

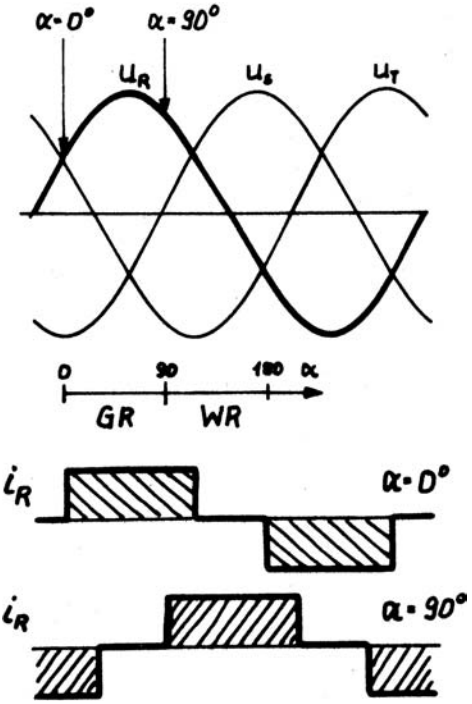


Figure 13.13 Mains current of a three-phase bridge circuit.

For a converter with a pulse number of 12, for instance, the 5th and 7th harmonic disappears. In many cases, however, the filtering circuits are the more economical solution (Figure 13.14). Filtering circuits are series resonance circuits with their frequencies adjusted exactly to those of the harmonic oscillation currents to be eliminated. Therefore they represent very low impedance for these harmonic oscillations and prevent their flowing into the power supply system.

Filtering circuits are mostly employed for the 5th, 7th, 11th, and 13th harmonic. In many cases, however, a filtering circuit for the 5th harmonic is sufficient.

A controlled bridge circuit most of all draws, apart from the distorted current, an induced reactive power from the mains, which, depending on the trigger delay angle, is greatest for 90 degrees (Figure 13.13). As filter circuits are always capacitors for fundamental oscillations, they automatically compensate part of the fundamental oscillation reactive power.

13.7.2 Primary-Chopped Switching Power Supply

Battery chargers with primary-chopped switching power supplies redress the mains voltage by means of an uncontrolled bridge circuit. The mains current only is conducted when the rectified mains voltage is at that time higher than the voltage at the capacitor C1 (Figure 13.9). Only peak currents with a large harmonic oscillation component where the 3rd harmonic is emphasized are drawn from the mains (Figure 13.15).

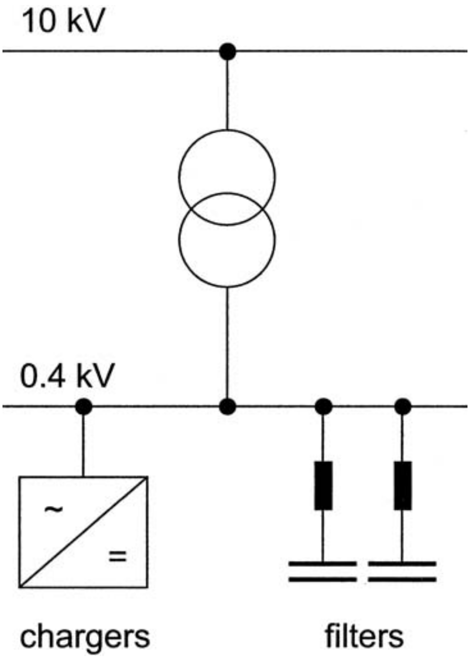


Figure 13.14 Compensation with filter circuits.

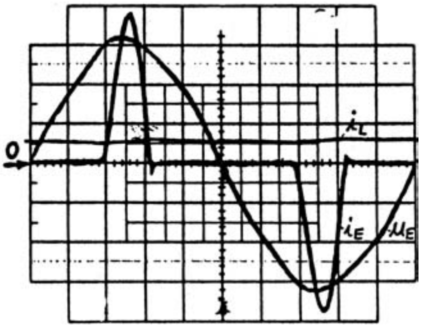


Figure 13.15 Mains current of primary-chopped switching power supplies.

An accumulation of devices of this kind will therefore always be problematic. It shall be mentioned at this point that for the application of chopped devices special measures for radio interference suppression must be taken.

This makes power supply circuits that draw harmonic currents from the mains indispensable, and therefore these devices are being developed and are undergoing testing. Their construction demands more technical expenditure than the devices employed at this time, making them more expensive. Their introduction to the market is largely dependent on the demands of the electric power supplying companies.

13.8 INVERTERS FOR ASCERTAINED POWER SUPPLY OF THREE-PHASE CONSUMERS

Power supply for three-phase consumers is presently mostly ascertained by systems consisting of rectifiers, batteries, and inverters. Controlled chargers with an IU characteristic are employed for rectifiers. They take over power supply for the inverters in normal operation and ascertain charging and float charging of the battery that takes over power supply in case of mains failure. The inverter changes the DC voltage to an AC voltage that is largely independent of fluctuations of the DC voltage or loads.

13.8.1 Inverters with Double-Phase Bridge Circuits

Self-commutating converters with regulative voltages are employed for inverters (Figure 13.16). During ignition of the valves V1 and V3 a positive voltage lies between the transformer terminals 1 and 2, whereas when the valves V2 and V4 are ignited, a negative voltage is encountered here. The “valves” each consist of a main thyristor and a clearing device with a reset thyristor; therefore an offset mode or a conducting mode can be controlled by the according enabling impulses.

Amplitude of the output voltage is controlled by means of pulse-width modulation. A harmonic or square-wave reference voltage with the same basic oscillation frequency as that of the output voltage and variable amplitude is sampled by a delta voltage of pulse frequency and constant amplitude (Figure 13.17).

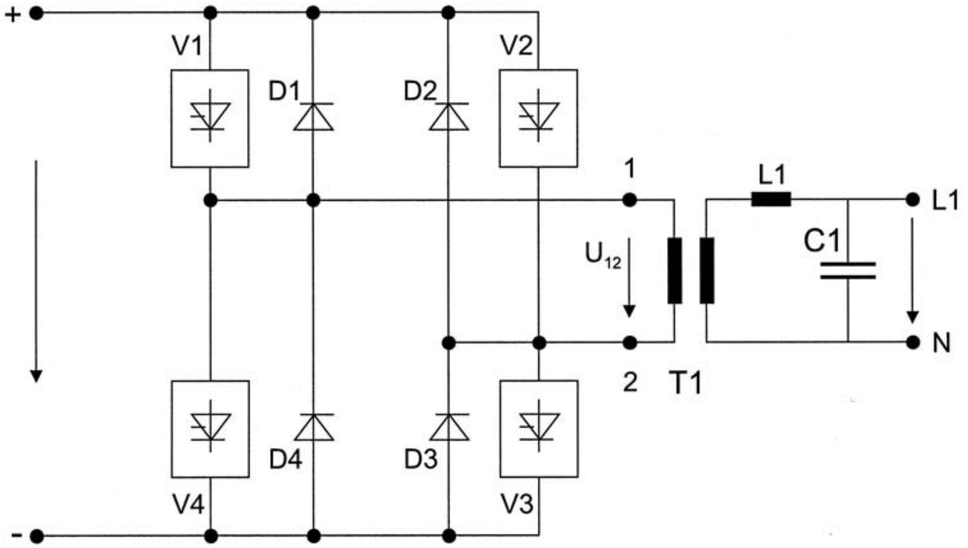


Figure 13.16 Inverter with double-phase bridge circuit.

The drive pulse for the thyristors is taken at the intersections, resulting in a pulsed output voltage. The load current can pass over the recovery diodes (D1-D4) during zero-voltage periods. In the case of the positive half-wave being blocked at valve V1, the current can flow over V3, D4, T1.

Transformer

The transformer T1 galvanically separates the battery and the consumer and can be additionally employed for voltage adaptation.

Output Filters L1, C1

A filter behind the transformer modifies the pulsed inverter output voltage into sine-shaped voltage. Less expensive low-pass filters (L1, C1) or band-pass filters can also be applied.

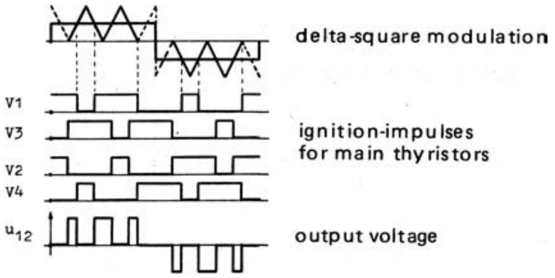


Figure 13.17 Voltage assembly by pulse-width modulation.

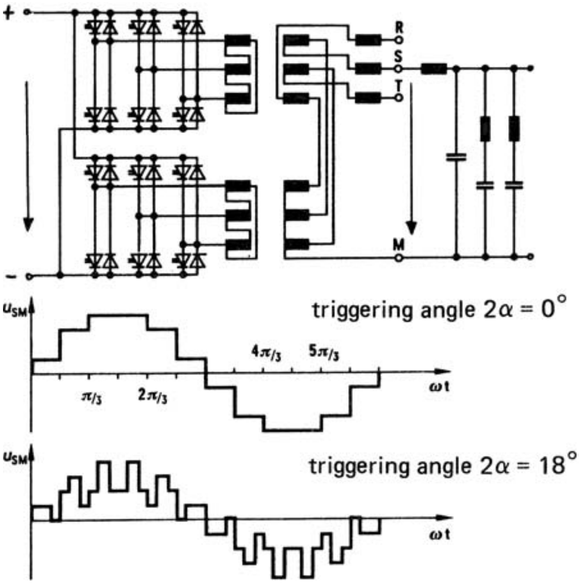


Figure 13.18 Twelve-pulse three-phase inverter. Circuit and flow of the unfiltered voltage.

13.8.2 Inverters with Three-Phase Bridge Circuits

Addition of a third strand to the single-phase inverter shown in Figure 13.16 yields a six-pulse three-phase inverter. Figure 13.18 shows an inverter that consists of two three-phase six-pulse partial inverters that yields a 12-pulse output voltage. The main advantage is that the filters can be made much smaller. More dynamic voltage regulation is attained.

Recent developments in the field of power electronics and forced employment of microelectronics as well as continuous development of systems and circuitry techniques will allow the construction of devices that will have lower drop-out rates at lower overall dimensions and power losses.

14

Standards and Regulations for Batteries and Battery Plants

H. A. KIEHNE

14.1 SIGNIFICANCE OF STANDARDS

Standards are appointments and may become enforceable by jurisdictional law and administrative regulations through signed contracts (for instance a sales contract) and can be understood to be “approved technology rules”.

The general features of standards are, in short:

- Standards are a service for technology.
- Standards are an economic and a technical form of cooperation (see also DIN 820 Part 1).
- Standards are planned unifications of material and immaterial objects to serve everybody.
- Standards may not lead to exceptional economic advantages for any party.
- Standards may not affect the progress of technology and innovations.
- Standards shall help to cut down trade barriers.

14.2 NATIONAL GERMAN STANDARDS AND REGULATIONS

The Deutsche Elektrotechnische Kommission (DKE) is in charge of designing standards and regulations for the electrotechnical sector for Germany. The three institutes for this job are the DIN (Deutsches Institut für Normung; German Institute for Standardization), the DKE (Deutsche Kommission für Elektrotechnik; German Electrotechnical Commission), and the VDE (Verein Deutscher Elektrotechniker; German member of IEEE). Results of their work are the Deutsche Normen, or German standards (DIN, DIN EN, and DIN IEC*), and the Bestimmungen, or regulations (VDE and DIN).

Federal and state laws are superior to these standards. For example:

- Explosion regulations (Ex V).
- Regulations on working environments (Arb. Staett. V).
- Building regulations (Elt Bau V).
- Regulations for assembly halls (V Staett V).
- Regulations for office buildings (Gh V).

For the European Community the EU directives and regulations are of the same importance and also gain law status through regulations.

Supporters and cosupporters of standards and regulations can also be corporate bodies, e.g. producer unions, associations, and institutes.

National carriers are also existent, for instance in Russia and France. France has a Ministry of Technology that issues these standards. In these countries standards are so-to-speak laws.

The following committees are in charge of standardization of batteries, that is secondary batteries (accumulators) and primary batteries (dry batteries) at the DKE:

K 371	Secondary rechargeable batteries (accumulators)
AK 371.0.2	Stationary lead accumulators
AK 371.0.3	Traction lead batteries
AK 371.0.4	Starter batteries
AK 371.0.5	Small valve-regulated lead-acid batteries
UK 371.1	Secondary alkaline batteries
UK 371.2	Regulations
K 372	Galvanic primary elements and batteries

Above this, further standardization work is accomplished by the following committees:

UK 351.4	Electric road vehicles
K 223	Emergency appliances and plants in buildings for public assemblies, etc.

14.2.1 How Standards Come into Being

Producers, branch associations (e.g. German Battery Manufacturers Association, member of ZVEI (Manufacturers Association of the Electronic and the Electrotechnical Industry)), and authorities can propose or request a standard at the DKE. In case the committee in charge accepts the proposal, a team is put in charge of forming the standards' layout (draft), which in turn must pass the committee. Then this layout is made public allowing for public opinion within a period of 4 months.

Any national drafted standard is automatically transformed to a European draft under the responsibility of Comité Européen de Normalisation Electrotechnique (CENELEC). The CENELEC members are asked to decide whether they want to create based upon the national proposal a European standard or let it pass as a national standard only in the country which made the proposal.

After reconciliation of the objections by the CENELEC committees and possible changes, the final vote and passing by the national committees follows. In case of approval all member states of the European Union have to take the layout of the final version to edit it as an EN Standard. In the case only a national standard has to be published the procedure is shown in Figure 14.1. Here only national objections have to be regarded by the German National Committee; after reconciliation of the objections and possible changes the final vote follows and the layout is then printed as German National Standard (DIN).

Other general rules that have to be considered due to the cooperation between CENELEC and IEC are not treated here, but can be referred to in special publications on the subject.

14.3 INTERNATIONAL STANDARDS

14.3.1 International Electrotechnical Commission

The IEC (International Electrotechnical Commission) features the following commissions in charge of standardization of batteries:

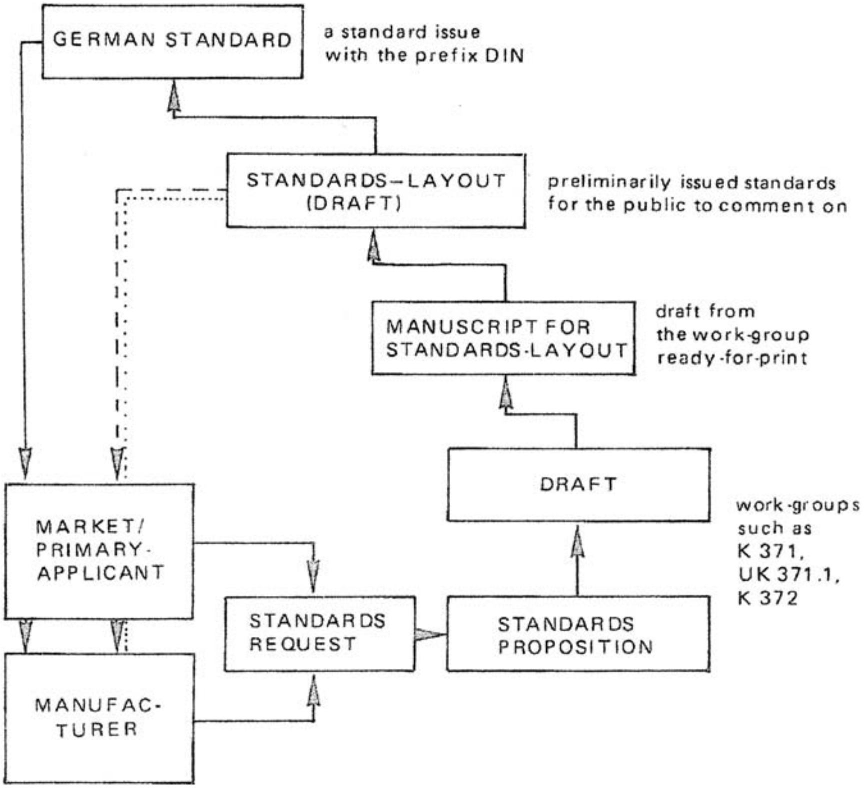


Figure 14.1 Schematic of the standardization process from the standard's request to the final standard. (From DIN 820.)

TC 21	Secondary rechargeable batteries (accumulators)
SC 21	A Secondary rechargeable alkaline batteries
TC 35	Dry batteries

Germany is a member of the IEC; the "reflecting committees" send their delegates to the IEC committees as German delegations represented by a speaker; this is usually the chairman of the corresponding German committee (called also "mirror-committee").

Consultations on standards' submissions are also made by working groups resulting in IEC standards. The first step toward a new standard is the distribution of draft documents to all member countries by the IEC's Central Office (CO) in Geneva.

The Central Office documents are subjected to a 2- or 6-month period of time for the members (national committees) to vote on. In case of a sufficient majority of votes, the CO document becomes an IEC standard, e.g. IEC Standard 60 254-1, Lead-Acid Traction Batteries (3). Sometimes the margins between the IEC and the ISO (International Standards Organization) are not clearly perceivable and may pose problems. All drafts of IEC standards run in parallel as CENELEC drafts under vote with aim to take over the IEC standard as EN Standard.

14.3.2 En Standards (CENELEC)

The CENELEC features "reflective committees" similar to the IEC, but these are activated only to a small extent to prevent work to be done twice, so there are only very few committees and working groups established.

Every IEC document (CO) or standard is followed by a questionnaire in CENELEC countries whether or not to start a standardization process on the same subject resulting in an EN standard. Depending on the result of the inquiry a halt of all national standardization activities follows in order to attain accordance with the international standards. The simplest way to do this is to make the IEC standard a national standard, partially or as a whole with the same significance. Details on the subject are referred to by special publications.

Obstacles for a fast integration into national standards are, for example:

- Established dimensions.
- Established safety-standards (Ex-directives VDE 0165, 0170, 0171).
- Different levels of technology.

Guideline for the work of all European National Standard Committees is to

Make proposals for international standards, not national standards and transfer international standards to national standards.

Figure 14.2 shows in a very rough manner the way to a standard, worldwide, on the European level, and on the national level. Cooperating partners of the standardization organizations are associations such as worldwide-operating BCI (Battery Council International, International Association of Battery Manufacturers). In Europe this function has EUROBAT (Federation of European Manufacturers of Batteries). A treaty allowing EUROBAT to propose directly to CENELEC standardization work links European battery manufacturers and CENELEC, avoiding the way via the national committees. In Germany the German

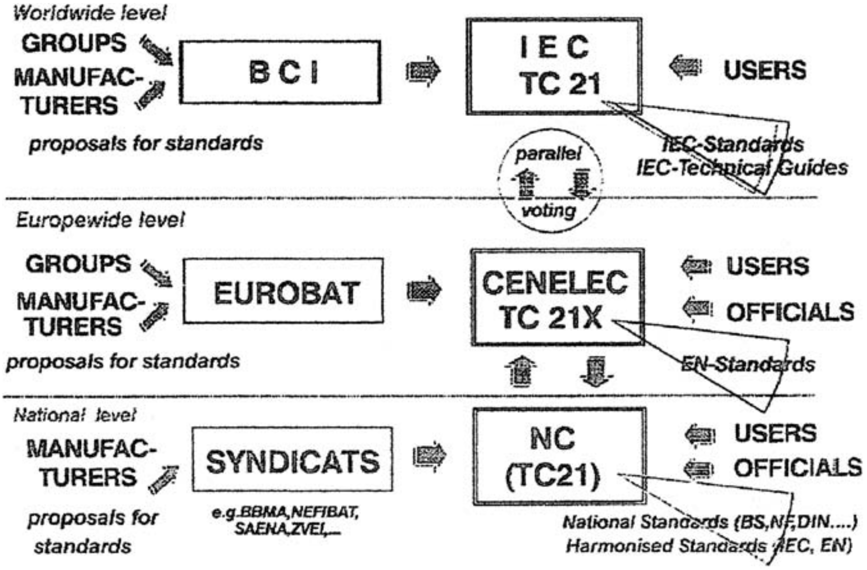


Figure 14.2 The way to standards: worldwide, Europewide, and nationwide.

Federation of Battery Manufacturers (member of ZVEI) cooperates with the DIN organization.

14.4 PRODUCT STANDARDS, TESTING STANDARDS, AND SAFETY STANDARDS

Standards can mainly be divided into these three main groups (6).

Product standards comprise main overall dimensions, weights, and electric data on production series or on single parts. Example: DIN 43 595, titled "Lead-acid accumulators; tubular plate-type cells for water- and land-bound vehicles, low maintenance type. Nominal capacities; main dimensions."

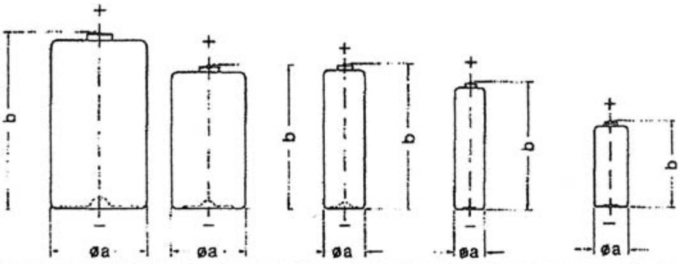
Testing standards include testing methods for type and acceptance tests. Example: DIN 43539, part 3 titled "Lead-acid accumulators; test methods, traction cells and batteries."

Combinations of dimensional and testing standards are also common.

Safety standards (or directives) comprise basic rules for the application of a product ranging from installation to employment. Example: DIN 57 510 (VDE 0510), titled "VDE Directives for Accumulators and Battery Plants."

14.5 STANDARDS FOR DRY BATTERIES (SELECTION)

- DIN IEC 86-1, Primary batteries. Part 1: General.
- DIN IEC 86-2, Primary batteries. Part 2: Standard sheets.



Designations	Mono	Baby	Mignon	Micro	Lady
dimensions height b mm Ø a mm	61.5 max. 34.2–2	50.0 max. 26.2–1.5	50.5 max. 14.5–1	44.5 max. 10.5–1	30.2 max. 12.0–1.3
IEC-designation acc. to IEC 86-2 primary cells	R 20	R 14	R 6	R 03	R 1
IEC-designation acc. to IEC 285-2 Ni/Cd, gastight	KR 35/62	KR 27/15	KR 15/51	KR 10/44	KR 12/30
designation acc. to ANSI	D	C	AA	AAA	N

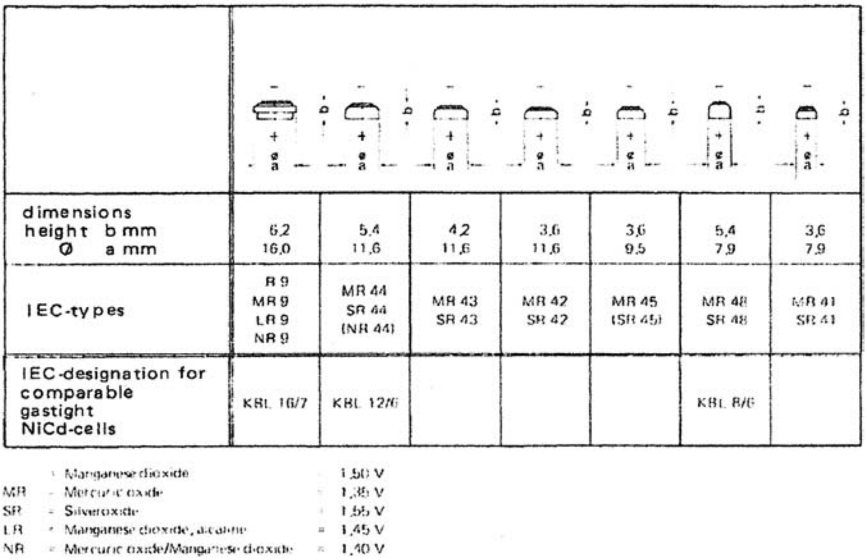
Figure 14.3 Survey on the most important standardized cylindrical (round) cells.

Dry batteries are employed in countless applications, for original equipment as well as for replacement. They are manufactured all over the world, making the need for standardization of dimensions, voltages, and connecting techniques understandable. Who has not heard of the classic sizes MONO, BABY, MIGNON, LADY, or A, AA, AAA, and AAAA? Figure 14.3 describes the most important standardized cylindrical cells. Figure 14.4 shows a survey on the most important standardized button-type cells.

14.6 STANDARDS FOR STARTER BATTERIES (SELECTION)

14.6.1 Existing German National Standards (Selection)

- DIN 72 310, Parts 1 and 2: Lead-acid accumulators; starter batteries. Series numbers, construction.
- DIN 72 311: Lead-acid accumulators; starter batteries (several parts).
- DIN 72 311, Part 1: Lead-acid accumulators; starter batteries for cranking lighting and ignition purposes, test methods.
- DIN 72 331, Parts 1 and 2: Lead-acid accumulators; starter batteries, battery poles for starter batteries.



dimensions height b mm Ø a mm	6,2 16,0	5,4 11,6	4,2 11,6	3,6 11,6	3,6 9,5	5,4 7,9	3,6 7,9
IEC-types	R 9 MR 9 LR 9 NR 9	MR 44 SR 44 (NR 44)	MR 43 SR 43	MR 42 SR 42	MR 45 (SR 45)	MR 48 SR 48	MR 41 SR 41
IEC-designation for comparable gastight NiCd-cells	KBL 16/7	KBL 12/6				KBL 8/6	

= Manganese dioxide = 1,50 V
MR = Mercuric oxide = 1,35 V
SR = Silveroxide = 1,55 V
LR = Manganese dioxide, alcaline = 1,45 V
NR = Mercuric oxide/Manganese dioxide = 1,40 V

Figure 14.4 Survey on the most important standardized button-type cells.

- DIN 72 332, Part 1: Lead-acid accumulators; starter batteries, battery terminals for starter batteries.
- DIN 72 333, Parts 1–4: Lead-acid accumulators; starter batteries, battery terminals for starter batteries, clamp fittings, terminal fittings with ground straps, ground connectors, light clamp fittings.
- DIN 43 539, Part 2: Lead-acid accumulators; test methods, starter batteries 12 V. Harmonized (see EN 60 095-1).

14.6.2 IEC and EN Standards (Selection)

- IEC 60 095-1, EN 60 095-1: Lead-acid starter batteries; general requirements and test methods.
- IEC 60 095-2, EN 60 095-2: Lead-acid starter batteries: Dimensions of batteries.
- IEC 60 095-3, EN 60 095-3: Lead-acid starter batteries: Dimensions and markings of terminals.

14.7 STANDARDS FOR TRACTION BATTERIES (SELECTION)

14.7.1 Existing German National Standards (Selection)

- DIN 43 531: Lead-acid accumulators; traction batteries, 48 V for industrial trucks: Dimensions, weights, electrical data.
- DIN 43 535: Lead-acid accumulators; traction batteries, 24 V for industrial trucks: Dimensions, weights, electrical data.

- DIN 43 536: Lead-acid accumulators; traction batteries, 80 V for industrial trucks: Dimensions, weights, electrical data.
- DIN 43 537: Lead-acid accumulators; traction batteries for road-bound electric vehicles, cells of low maintenance type: Nominal capacities, main dimensions.
- DIN 43 538: Lead-acid accumulators; traction batteries for road-bound electric vehicles; monobloc batteries of low maintenance type: Nominal capacities, main dimensions.
- DIN 43 539, Part 3: Lead-acid accumulators: Test methods, traction cells and batteries. Harmonized (see EN 60 254-1).
- DIN 43 595: Lead-acid accumulators; tubular-plate type cells for land- and water-bound vehicles, low maintenance type: Nominal capacities, main dimensions. Harmonized (see EN 60 254-2).

14.7.2 IEC and EN Standards (Selection)

- IEC 60 254-1, EN 60 254-1, Part 1: Lead-acid traction batteries: General requirements and methods of test.
- IEC 60 254-2, EN 60 254-2, Part 2: Lead-acid traction batteries: Dimensions of traction battery cells.

14.8 STANDARDS FOR STATIONARY LEAD-ACID BATTERIES (SELECTION)

14.8.1 Existing German National Standards (Selection)

- DIN 40 734: Lead-acid accumulators; stationary battery cells with positive grid-type plates: Capacities, main dimensions
- DIN 40 736, Parts 1 and 2: Lead-acid accumulators; stationary battery cells with positive tubular plates: Capacities, main dimensions, weights.
- DIN 40738: Lead-acid accumulators; stationary battery cells with Planté plates, high-performance construction: Capacities, main dimensions, weights.
- DIN 43 539, Part 4: Lead-acid accumulators; test methods, stationary battery cells and batteries. Harmonized (see EN 60 8961 and EN 60 896-2).

14.8.2 IEC and EN Standards (Selection)

- IEC 60 896-1, EN 60 896-1, Part 1: Stationary lead-acid batteries; vented types: General requirements and methods of test.
- IEC 60 896-2, EN 60 896-2, Part 2: Stationary lead-acid batteries, valve-regulated types (VRLA): General requirements and methods of test.

14.9 STANDARDS FOR PORTABLE MAINTENANCE-FREE, VALVE-REGULATED LEAD-ACID (VRLA) CELLS

14.9.1 Existing German National Standards (Selection)

All are harmonized.

14.9.2 IEC and EN Standards (Selection)

- IEC 60 056-1, EN 60 056-1, Part 1: Portable lead-acid cells and batteries: General requirements, functional characteristics, methods of test.
- IEC 60 056-2, EN 60 056-2, Part 2: Portable lead-acid cells and batteries: Dimensions, terminals, marking.
- IEC 60 056-3, EN 60 056-3, Part 3: Portable lead-acid cells and batteries: Safety recommendations for use in electric appliances.

14.10 STANDARDS FOR ALKALINE ACCUMULATORS (SELECTION)

14.10.1 Existing German National Standards (Selection)

All are harmonized.

14.10.2 IEC and EN Standards (Selection)

- IEC 60 285, EN 60 285: Alkaline secondary cells and batteries; sealed nickel/cadmium cylindrical rechargeable single cells.
- IEC 60 509, EN 60 609: Alkaline secondary cells and batteries; sealed nickel/cadmium button rechargeable single cells.
- IEC 60 622, EN 60 622: Alkaline secondary cells and batteries; Sealed nickel/cadmium prismatic rechargeable single cells.
- IEC 60 623, EN 60 623: Alkaline secondary cells and batteries; vented nickel/cadmium prismatic rechargeable cells.
- IEC 61 150, EN 61 150: Alkaline secondary cells and batteries; sealed nickel/cadmium rechargeable monobloc batteries in button cell design.
- IEC 61 438, EN 61 438: Possible safety and health hazards in the use of alkaline secondary cells and batteries: Guide to equipment manufacturers and users.

14.11 VDE REGULATIONS (SELECTION)

- VDE 0510: Regulation for accumulators and battery plants.
- VDE 0170: Regulation for mounting electric devices in medical facilities.
- VDE 0108: Regulation for mounting and operating emergency electric equipment in public assembly buildings.
- VDE 0122: Regulation for electric equipment of road-bound electric vehicles.

The German National Committee has proposed to transfer the revision of VDE 0510 in all parts into EN and IEC standards. This work is in progress with the relevant CENELEC working groups.

14.12 OTHER GERMAN STANDARDS AND GUIDELINES

- VG (military defense equipment).
- LN (aeronautical standards).
- BN (railway standards).
- VDI Guidelines

14.13 OTHER INTERNATIONAL STANDARDS AND COMMITTEES

- ANSI American National Standards Institute (formerly AESC, ASA, USASI)
- AQAP Allied Quality Assurance Publication (NATO demands and standards)
- ASTM American Society for Testing and Materials
- MIL Military Standards and Specifications
- MS Military Standards
- NEMA National Electric Manufacturers Association (United States)
- SAE Society of Automotive Engineers (United States)

14.14 SIGNIFICANCE OF STANDARDS AND REGULATIONS REGARDING MANUFACTURER LIABILITY

Manufacturer and product liability, both concerning the same issue, is not a new concept. The BGB (federal German law book) has commented the subject since 1915. Protection of the consumer has, similar to environmental protection, recently been more publicly discussed. The regulating law in this regard in Germany is paragraph 823 of the BGB, with a principle of indebtedness independent of liability (delict liability). According to this the fact that production techniques are state of the art is not sufficient. Observation of the DIN standards is not an excuse for the manufacturers, but is a first step toward lowering risks, as DIN standards have been included in many decrees.

The manufacturer is liable for:

- Development errors.
- Construction deficiencies.
- Manufacturing faults.

This implies the necessity for the manufacturer to survey the quality of its products and to check for compatibility of its product with other products.

Laws on the subject are not internationally uniform. In Germany manufacturing deficiencies are not generally followed by the manufacturer's liability, if the manufacturing company, apart from the faulty product, turns out products that correspond with standards and directions and the company disposes of a quality supervision system that operates flawlessly, so these manufacturing faults are taken as “uncontrollable drop-outs”.

(See EU Directive titled “Assimilation of the laws and directives of the member-states of the European Community on liability for faulty products”.)

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15

Batteries, an Overview and Outlook

H. A. KIEHNE, D. SPAHRBIER, D. SPRENGEL, and W. RAUDZSUS

15.1 TERMS, DEFINITIONS, AND CHARACTERIZING MARKS

Some terms, which will be repeated throughout this book, shall be defined more precisely:

- “Portable batteries” are understood to be all kinds of electrochemical energy-storing devices used in portable appliances regardless of whether they are rechargeable or not.
- Non-rechargeable batteries are called primary cells (batteries) or dry cells (batteries).
- Rechargeable batteries are called secondary batteries or accumulators.
- Also the terms “galvanic primary” and “galvanic secondary” cells are common.

According to the electromotive series of the elements there are innumerable pairs which will yield electrochemical energy accumulators. For instance, take a metal and a metallic oxide and immerse them in a liquid electrolyte. These are the main parts of a cell as Figure 15.1 demonstrates.

All batteries are chemical energy-storage devices and they are energy converters. A primary cell releases chemical energy while being discharged. Secondary cells have a reversible energy conversion characteristic:

$$\text{Chemical energy} \quad \overset{\text{Discharge}}{\underset{\text{Charge}}{\overset{\leftarrow}{\rightarrow}}} \quad \text{Electric energy}$$

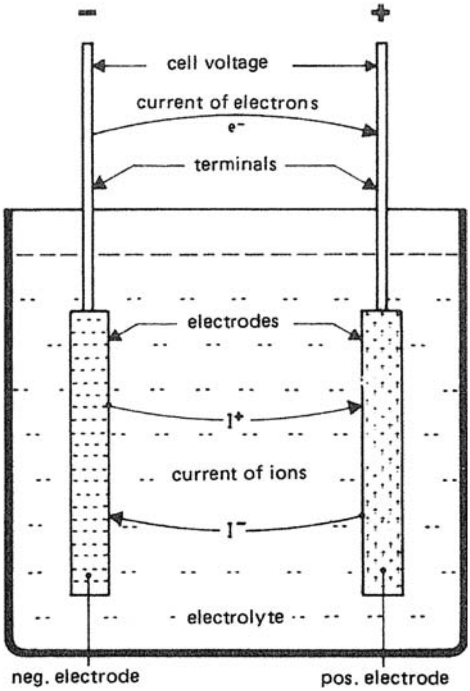


Figure 15.1 Scheme of an electrochemical cell.

Preconditions for the adoption of a storage system are its stable long-term durability, a reasonable voltage range, cheap raw materials, as well as controllable substances regarding production techniques, and also a regard for possible environmental damage.

The nominal voltage is a value that characterizes the system:

$$U_n = f\ (\text{system})$$

The off-load voltage is dependent on the system and temperature:

$$U_o = f\ (\text{system}, \delta)$$

and is calculable.

The discharge voltage is dependent on the current:

$$U_D = f\ (\text{system}, \delta, I_D)$$

For secondary cells the charging voltage is dependent on the current:

$$U_L = f\ (\text{system}, \delta, I_L)$$

The capacity of a battery is dependent on the system, the temperature, and the discharge voltage:

$$C = f\ (\text{system}, \delta, I_D, U_s)$$

Table 15.1 Survey of different primary systems, listed by nature of their electrolytes.

Electrolytes				
Liquid		Nonliquid		
Low acidic	Alcalic	Organic	Inorganic	Solid
MnO_2/Zn	MnO_2/Zn	MnO_2/Li	$SOCl_2$/Li	I_2/Li
(NH_4cl)	HgO/Zn	CF_x/Li	SO_2/Li	(P2VP)
	Ag_2O/Zn	CrO_x/Li		PbI_2/Li
MnO_2/Zn	AgO/Zn	CuS/Li		LiI(Al_2O_3)
($ZnCl_2$)	Luft/Zn	CuS/Li		PbS/Li
	Ni/Zn	FeS_2/Li		LiI(Al_2O_3)
Air/Zn	HgO/Cd			
(NH_4Cl)		Bi_2O_3/Li		
Air/Zn		CdO/Li		
($MgCl_2$, $MnCl_2$)				

Apart from the desired main chemical reactions, every electrochemical system is strained by secondary reactions (oxidation and corrosion), which cause a self-discharge; these are system- and temperature-specific.

The multitude of combinations of materials suitable for the electrode, especially metal oxides of higher energy densities and their combination with an abundance of different materials, cannot be treated here. For this reason Table 15.1 shows a survey of the most important substances presently used for anodes, cathodes, and electrolytes. Specialists for every profile of demand can be generated from combinations of this table, where the IEC and DIN standards define primarily the outer shape, so in international commerce interchangeability is guaranteed.

This applies to the same extent for secondary cells, which in small units are also used in many appliances. Table 15.2 shows a survey of the most important presently used main substances for the positive and negative electrodes and electrolytes.

There are several parameters relevant for describing the properties of batteries, such as:

- Capacity, energy content, on-load voltage range.
- Performance, energy density per volume and weight.
- Power density per volume and weight.

Table 15.2 Survey of secondary cells for portable batteries.

Positive electrode	Elelectrolyte	Negative electrode
PbO_2	$H_2SO_4 + H_2O$	Pb
NiOOH	$KOH + H_2O$	Cd
Ag_2O	$NaOH + H_2O$	Fe
HgO		Zn
O_2		C

- Internal resistance, storage life, self-discharge rate.
- Temperature resistibility, mechanic stability.
- Leak safeness, reliability, dimensional stability.
- Contact certainty, price-efficiency ratio.

For secondary batteries there are in addition the following relevant parameters: Wh efficiency factor Ah efficiency factor, rechargeability, and others. Especially important for the portable battery is its energy density per volume and weight.

Of all primary systems the Leclanché system has the lowest and the lithium, as well as the alkaline zinc/air system, the highest energy density. The rechargeable batteries are still inferior to the Leclanché system in this regard, but this is compensated by the possibility of some 100 to 1000 recharges apart from some other properties, such as the high current discharge ability.

Fresh primary cells and secondary batteries when charged have an open voltage close to the nominal voltage dependent on the electrochemical system. This voltage decreases during discharge via the average discharge voltage to the end voltage (see Table 15.3). Also the nominal voltage of the different electrochemical systems is different (see Table 15.3).

Significant for portable batteries is the representable energy density per volume in practice. Table 15.4 gives a survey on the ranges of energy densities per volume of primary and secondary systems, as they are at present available as single cells or batteries consisting of several cells. It is understandable that these values are much lower than the theoretical calculated ones, because the total amount of active material can not be converted into the discharge condition; while discharge increases the internal resistance of the active material results in a lower useful voltage.

Furthermore it has to be mentioned that the practically achievable energy density of course is lower than the theoretically calculated value because of nonactive parts needed for a technically usable system such as containers, seals, separators, and supporting frames. Also the active material of the electrode chemicals only is usable to the point of a suitable end-discharge voltage.

Table 15.3 Voltage behavior of battery systems.

Electrochemical system	Nominal voltage Volts	Average calculated discharge voltage Volts	Cutoff voltage advised Volts	Allowed Volts	Remarks
Leclanché (normal)	1.5	1.2	0.9	0.75	Primary cell
Alkaline-Manganese	1.5	1.2	0.9	0.75	Primary cell
Mercury-Zinc	1.35	1.2	0.9	0.9	Primary cell
Silveroxide-Zinc	1.55	1.4	0.9	0.9	Primary cell
Air-Zinc	1.4	1.15	0.9	0.9	Primary cell
Manganese dioxide-Lithium	3.0	2.4	1.8	1.5	Primary cell
Nickel-Cadmium (gas-tight)	1.2	1.2	1.0	0.75	Accumulator
Lead (maintenance-free)	2.0	1.9	1.7	1.6	Accumulator

Table 15.4 Ranges of the energy density per cm^3 of marketed electrochemical systems.

Electrochemical system	Nominal voltage V	Energy density mWh/ccm	Remarks
Carbon/Zinc Leclanche system	1.5	120–190	Primary cell as button, cylindric, or prismatic cell
Carbon/Zinc alkaline	1.5	200–300	Primary cell as button, cylindric, or prismatic cell
Zinc/Mercury oxide	1.35	400–520	Primary battery in button cell design
Zinc/Silver oxide valency: 1 or 2	1.55	350–650	Primary battery in button cell design
Air/Zinc with acidic electrolyte	1.45	200–300	Primary battery in cylindric design
Air/Zinc with alkaline electrolyte	1.4	650–800	Primary battery in button design
Lithium/Manganese dioxide	3.0	500–800	Primary battery button and cylindric cell
Nickel/Cadmium	1.2	40–80	Accumulator; button, cylindric, and prismatic designs
Lead/Lead dioxide	2.0	50–100	Accumulator; cylindric and prismatic designs

15.2 CONSTRUCTION, SIZES, AND MARKING

15.2.1 Construction

Primary and secondary batteries are produced in different designs; mainly the following can be distinguished:

- Round or cylindrical cells.
- Button-type cells.
- Prismatic cells and batteries.
- Foil-type cells.
- Special designs for civil and military use.

Very popular are five standard sizes of cylindrical cells as listed in Table 15.5. Inside the same outer shape very different constructions are hidden, e.g. as shown in Figure 15.2. Figure 15.3 shows the construction of a primary button cell. Figure 15.4 shows the construction of a zinc/air button cell. Figure 15.5 shows the construction of a lithium/manganese dioxide button cell; and Figure 15.6 the construction of cylindrical cells of the same system. Figure 15.7 shows the section of a lithium/chromium oxide cylindrical cell with molded electrodes. Figure 15.8 shows the

Table 15.5 Sizes and IEC designation of the most popular cylindrical cells.

Type	Code IEC	Code ANSI	Size Dia. × h (mm)
Mono	R 20	D	34.2 × 61.5
Baby	R 14	C	26.2 × 50
Mignon	R 6	AA	14.5 × 50.5
Lady	R 1	N	12 × 30
Micro	R 03	AAA	10.5 × 44.5

construction of a nickel/cadmium button cell with so-called “mass electrodes”. Figure 15.9 shows the construction of a cylindrical nickel/cadmium cell with rolled sintered electrodes.

One of the most popular prismatic batteries is the so-called “9-V transistor battery” with the IEC designation 6 F 22, available as Leclanché type and alkaline type as well as a rechargeable nickel/cadmium battery. Figure 15.10 shows a drawing and the dimensions.

Small portable maintenance-free valve-regulated lead-acid batteries (VRLA) with immobilized electrolyte are available as well in cylindrical as in prismatic design.

Figure 15.11 shows the section of such cell in maintenance-free design and Figure 15.12 a cylindrical cell (Gates).

15.2.2 The IEC Designation System for Primary Batteries Defined in IEC Standard 60 086 1

The designation system for primary batteries and cells gives the following information.

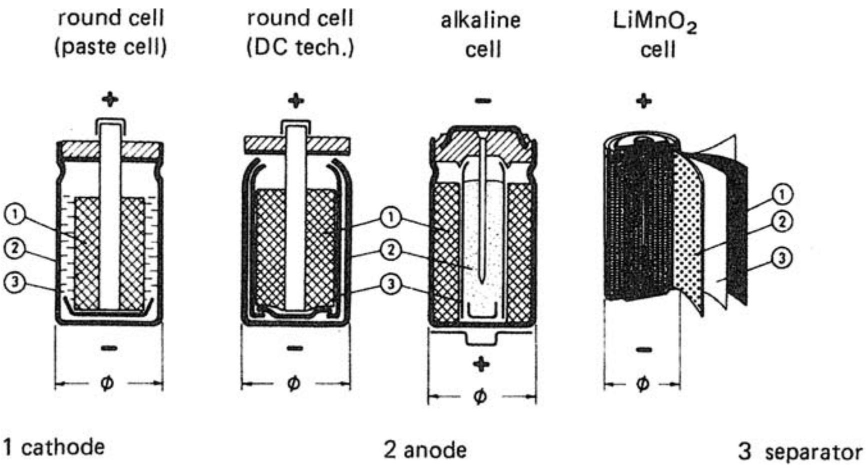


Figure 15.2 Comparison of different cell construction of cylindrical cells.

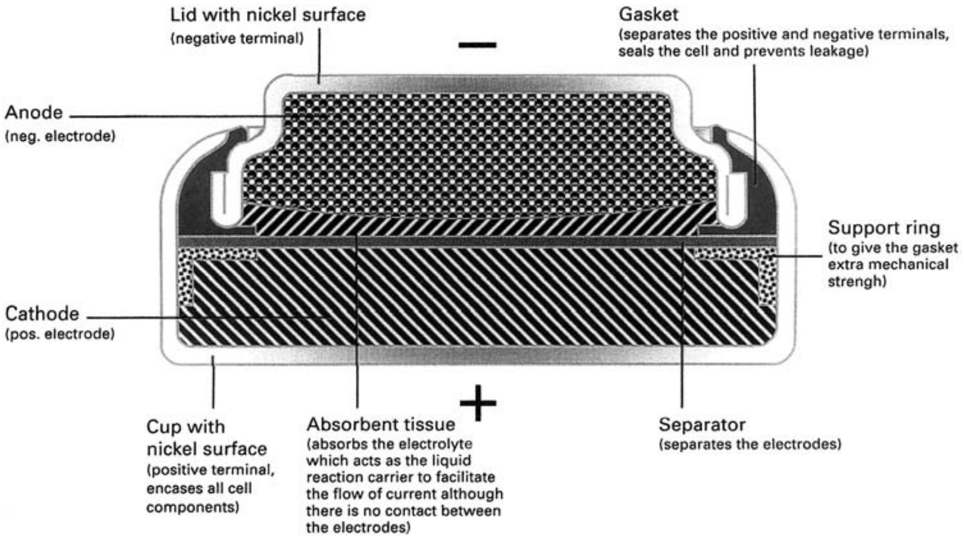


Figure 15.3 Section through a button cell.

15.2.2.1 *Construction*

The letters R, S, and F preceding a number mean:

- R = cylindrical cell or button cell.
- S = prismatic cell.
- F = flat cell.

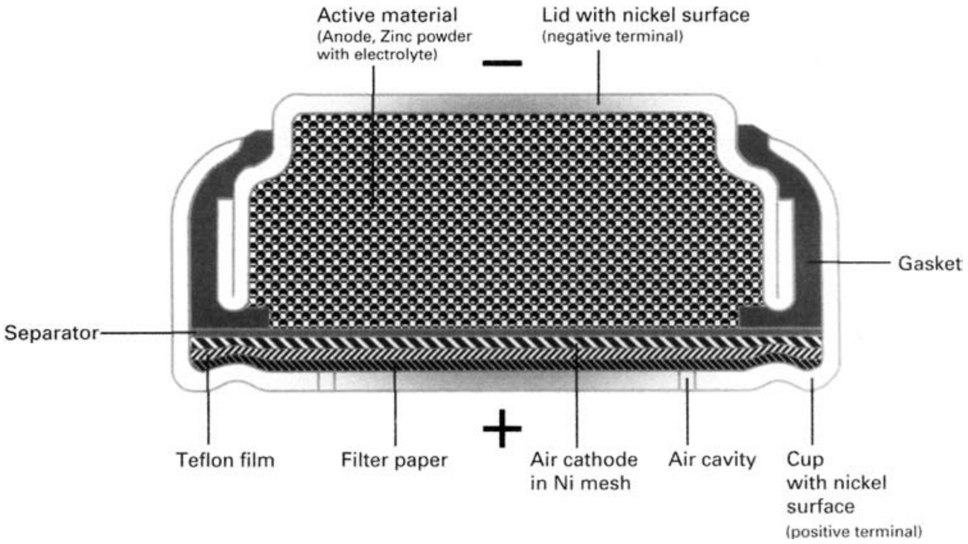


Figure 15.4 Section through a zinc/air button cell.

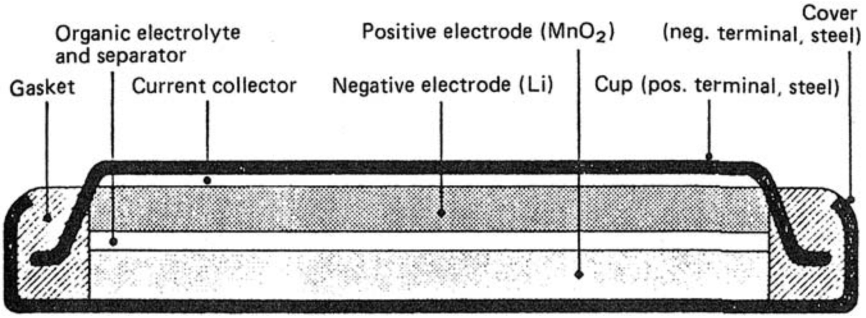


Figure 15.5 Section through a lithium/manganese dioxide button cell.

15.2.2.2 *Dimensions*

A designation number is distributed to cells and batteries laid down in data sheets of the IEC standard 60 086-2. This standard defines as well the dimensions and their tolerances. *Example: R 20 is the well-known mono cell, or D cell.*

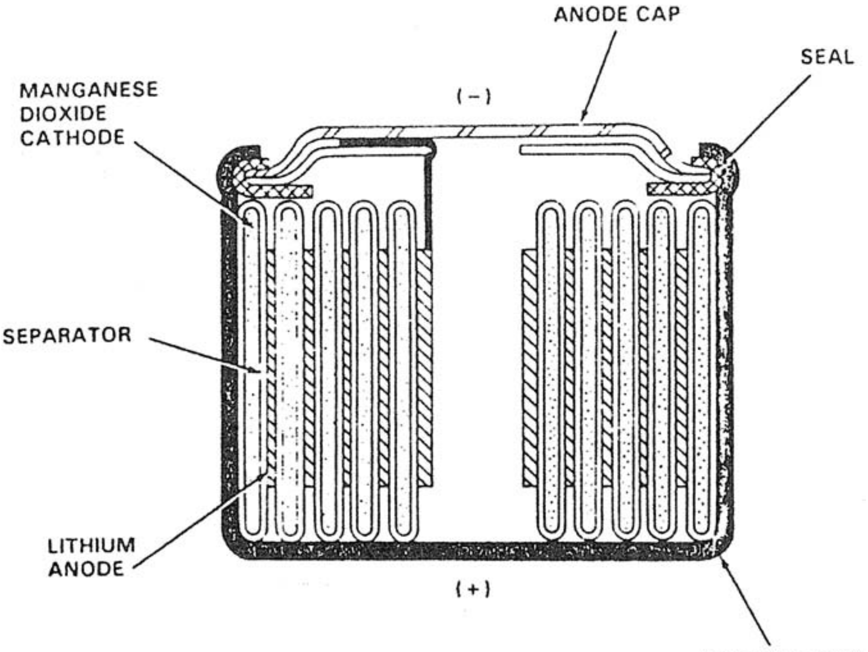


Figure 15.6 Section through a lithium/manganese dioxide cylindrical cell with rolled electrodes.

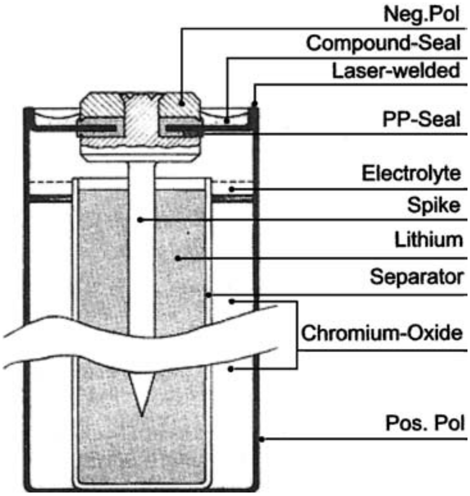


Figure 15.7 Section of a lithium/chromium oxide cylindrical cell.

15.2.2.3: Electrochemical System

A letter preceding the letters R, S, and F characterizes the electrochemical system (see Table 15.6). Normal Leclanché types do not have such an additional letter. *Examples: R 20 = mono cell (D cell) Leclanché; LR20 = mono cell (D cell) alkaline.*

Further letters are reserved to describe the following systems:

- BR: carbon monofluorid/lithium
- VL: vanadium pentoxide/lithium
- GR: copper oxide/lithium
- CL: carbon/lithium (rechargeable)
- H: nickel/metal hydride (rechargeable)

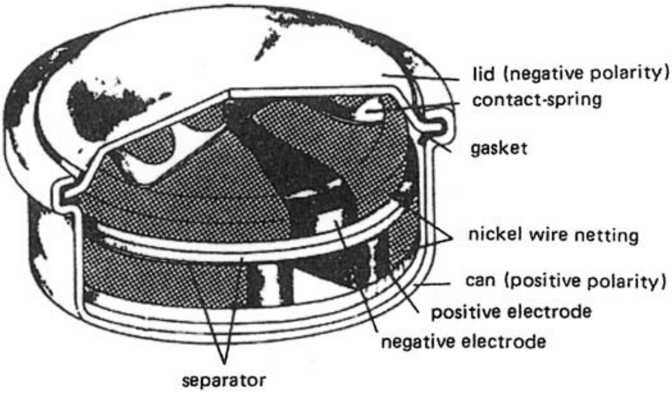


Figure 15.8 Section through a nickel/cadmium button cell with “mass electrodes”.

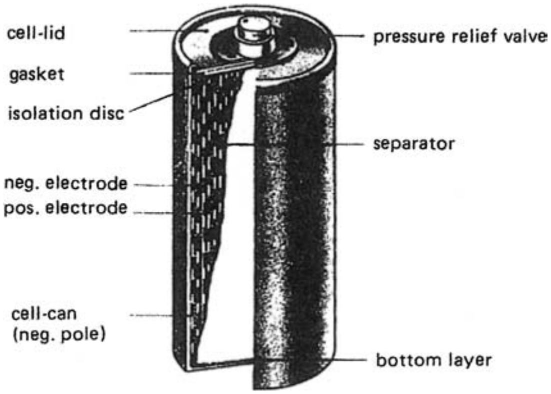


Figure 15.9 Section showing the construction of a cylindrical cell with positive and negative sintered electrodes.

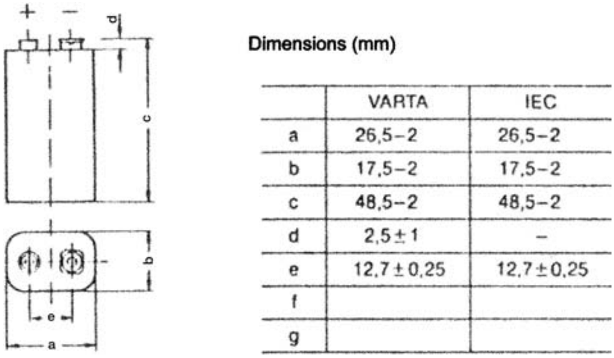
Note: The letter K always indicates a nickel/cadmium cell or a battery conforming to the specifications of IEC Standard 60 285, sealed nickel/cadmium cylindrical rechargeable single cell.

15.2.2.4 Number of Cells in Series

A number preceding the designation, e.g. 3, means, that three cells are connected in series. *Example: 3 R 20 = battery of three mono cells connected in series.*

15.2.2.5 Number of Cells in Parallel

A number connected to the designation at the end by a hyphen, e.g. -3, means that three cells are connected in parallel. *Example: R 20-3 = three mono cells connected in parallel.*



Dimensions (mm)

	VARTA	IEC
a	26,5−2	26,5−2
b	17,5−2	17,5−2
c	48,5−2	48,5−2
d	2,5 ± 1	–
e	12,7 ± 0,25	12,7 ± 0,25
f		
g		

Figure 15.10 Dimensions of the battery IEC 6 F22 (9-V transistor battery).

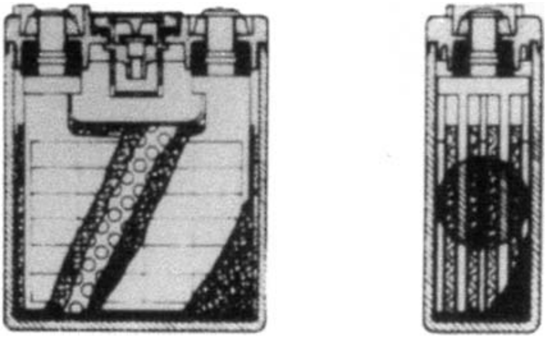


Figure 15.11 Principle design of a prismatic VRLA cell.

15.3 THE ALKALINE MANGANESE CELL

The birthyear of the alkaline manganese cell was 1945 but it was not until 1960 that it was successfully introduced to the market. The most common design is the round cell; here the user has many different designs to choose from, as in the field of Leclanché cells in Western Europe alone about 20 manufacturers of batteries in the sizes mono, baby, and mignon, and so on offer their products, not counting the hundreds of trademarks.

In all about 200 trademarks are registered. Apart from this, alkaline cells are offered in four different classes. The manufacturers attempt to make these classes differentiable by using certain labels, but a uniform designation has not been introduced. As has already been mentioned, choosing a product is a complex problem, with the consumer mainly making a decision on the brand and price.

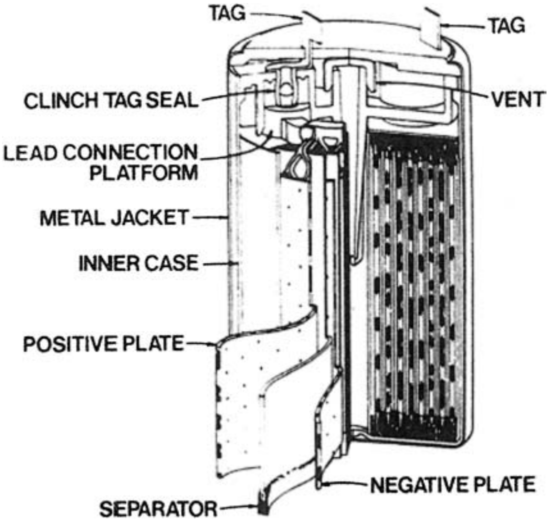


Figure 15.12 Principle of a cylindrical VRLA cell (Design of Gates, United States).

Table 15.6 IEC designation letters for electrochemical systems.

Letter	Positive electrode	Electrolyte	Negative electrode	Nominal voltage (V)
—	Manganese dioxide	Sal ammoniac, Zinc chloride	Zinc	1.5
A	Oxygen	Sal Ammoniac, Zinc chloride	Zinc	1.4
B	Carbon monofluoride	Organic electrolyte	Lithium	3
C	Manganese dioxide	Organic electrolyte	Lithium	3
L	Manganese dioxide	Alkaline electrolyte	Zinc	1.45
M	Mercury oxide	Alkaline electrolyte	Zinc	1.35
N	Mercury oxide + Manganese dioxide	Alkaline electrolyte	Zinc	1.4
P	Oxygen	Alkaline electrolyte	Zinc	1.4
S	Silver oxide Ag_2O	Alkaline electrolyte	Zinc	1.5
T	Silver oxide AgO	Alkaline electrolyte	Zinc	1.55

Concerning alkaline manganese cells the problem is far smaller, as only about ten manufacturers worldwide offer such batteries, all fitting in one class, mostly directly distributed by the manufacturers.

15.4 REGENERATION/RECHARGING

Regeneration of primary cells is generally not advisable. There is a danger of an augmented inner pressure which can lead to a leakage or explosion. Regeneration should especially not be taken into consideration with mercury oxide, alkaline manganese, and silver oxide batteries due to the mentioned risk of explosion.

Note: Several manufacturers have developed rechargeable alkaline manganese and silver oxide batteries and development is still going on but a broad presentation seems to be uneconomic at present; but these developments may gain importance in connection with solar cells for power supply of electric consumers with low power demand.

15.5 A NEW GENERATION OF BATTERIES: LITHIUM PRIMARY BATTERIES

Lithium cells and batteries have been subject of great interest by the consumer side. What kind of system is the right one, what are its advantages and disadvantages? These and other questions are often asked. The user's strong interest is understandable as the following advantages are presented:

- High energy density per volume weight.
- High voltage.
- Superior ability for a long storage time.
- Very low self-discharge rates.

- Good discharge, performance even at low temperatures.
- Also employable at high temperatures.
- Cheap.

What of the above is true? What are the disadvantages? How is the lithium system to be classified in relation to the other primary systems?

First of all it must be pointed out that every primary battery is a “specialist". A universal cell or system which is equally favorable for all applications is not existent. This is understandable regarding the variety of requirements that have to be met:

- High energy and power density.
- Stable discharge voltage.
- Wide temperature range for use and storage.
- Not harmful to the environment.
- Size and weight according to IEC or DIN standards.
- Easy manufacturability construction.
- Low material costs.
- Shock resistant, rugged design.
- Safety against leakage.
- Safety while in use and recharging.

Out of the multitude of possible choices the chemical periodic system of elements offers, the developer always had an eye on lithium and its feasibility as negative electrode. Lithium is the lightest of all metals in the periodic system of elements. In the last few decades a variety of publications and patents concerning different combinations of electrochemical elements with lithium in the negative electrode has been made. Prototypes of cells with liquid and solid electrolytes, with organic compounds and with dry electrolytes, and also models as fill-up elements or models that can be thermally activated, have been built. Many of these are listed products now with growing sales figures.

Some engineers have been keen on the idea of combining cells with water as electrolyte, but a general utilization of the principle has of course not been taken into consideration due to the brisance of the involved reactions.

The technicians have always been well aware of the problems not only in finding a suitable positive electrode, but also in dealing with this available and therefore not-too-precious element. Lithium reacts with humidity, especially with water, and has its melting point at 180°C. Apart from this, the fact that perchlorates and hydrides of lithium are poisonous and must be coped with.

The following rough classification of the electrochemical elements with lithium can be made:

1. Lithium cells with molten salts for electrolytes (e.g. lithium chloride).
2. Lithium cells with inorganic salts with an organic solution as electrolyte (e.g. $LiClO_4$ with the solution of propylene carbonate).
3. Lithium cells with inorganic, aprotic (=nonaqueous) liquids for electrolyte (e.g. sulfur oxide-dichloride $SOCl_2$).
4. Lithium cells with solid electrolyte (e.g. lithium iodide).

Advantages:

- High voltage rating 1.7–3.6 V.
- High energy density 500–800 mWh/ccm and 150–500 mWh/g.
- Wide temperature range – 55 to 75°C.
- High storage life up to 10 years.
- Very small self-discharge less than 1% p.a.

Disadvantages:

- Relatively high inner resistance (about 50–100 times higher than in so-called conventional systems).
- Relatively small power density.
- Danger of a short-circuit explosion (only wrapped cells).
- Relatively expensive production methods in dry atmosphere, relative humidity less than 1%.
- High requirement for seals.

For more about lithium cells and batteries see Chapter 4 of Volume II, Portable Batteries.

15.6 OUTLOOK

New user profiles have been generated through the known turbulent development on the electronics sector, as for instance an electronic watch with an analog display has a power consumption of only 0.3 microamps. This makes a theoretical lifespan of 5 or more years possible with the presently realizable energy density no matter whether lithium or conventional cells are used. Accommodation of the systems is necessary as the power consumption is of the size of parasite side-effects such as self-discharge, especially the longer lifespan sets high requirements for the seals to be met (possible but at greater expense: glass seals).

Design of watches has called for extremely thin batteries; the same goes for pocket calculators. After some efforts the manufacturers managed to meet this demand and have followed this trend. Independent from the developers' challenge, as shown by these examples, new profiles of demand can be listed and must be considered with new solutions. For this incitement, such as demands from the appliance industry, but also basic research and development, the need to make a system ready for marketing is necessary (e.g. solid electrolytes instead of liquid electrolytes).

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16

Feasibility Study for Appliances

H. A. KIEHNE and W. RAUDSZUS

16.1 BATTERY-OPERATED APPLIANCES

An immense variety of electric appliances is offered today. A significant number of these can optionally or exclusively be operated with batteries. The applications cover all fields, ranging from industrial to domestic and hobby applications. The advantages of battery-powered appliances are obvious: The user can operate a device independently of mains supply anywhere desired. A power cord is not necessary as the power source, the battery, is incorporated in the device.

While well-constructed devices are produced and sold in great numbers, others prove to be unsaleable and thus dead stock. The reason for this is often the use of a battery that is unsuitable for one of the following reasons:

- An inconvenient electrochemical system was chosen.
- The battery was not dimensioned correctly.
- Wrong presumptions regarding the battery's properties or the energy content were made.

A battery-powered device is said to be well designed when it resembles a mains-operated one in function as closely as possible.

While power consumption has only since the energy crisis become an important subject for mains-dependent appliances, it must be minutely treated and minimized when battery powering is demanded.

The goal is perfect function of the appliance with the lowest possible power consumption.

The engineer or designer of any appliance should exhaust all possibilities of lowering power consumption by raising the efficiency of a device with sophisticated electronics and modern materials before deciding which battery to use. A substantial amount of energy can be saved by these means.

Only when the design is ready and optimized, a load profile and power demand of the appliance can be issued. Now the task is installation of a small and cost effective but big enough battery. To take care of this task a great amount of experience is necessary.

Table 16.1 shows a selection of the most important applications. Primary button cells normally cover the load range from µA to mA. The mA range can be covered by primary and by secondary cells. For heavy loads in the A range mostly secondary batteries are chosen.

16.2 CALCULATIONS TO ESTIMATE CAPACITY

Battery-powered appliances with only very few exceptions are operated with direct current, so the experienced or calculated power consumption can be defined as

$$\mathrm{N} = \mathrm{U} \times \mathrm{I}(\mathrm{W})$$

with U = operating voltage of the appliance = discharge voltage of the battery = average discharge voltage, and I = current consumption of the appliance = discharge current of the battery.

Taking the efficiency (η) into consideration the nominal power output of the appliance amounts to

$$\mathrm{N} = \mathrm{U} \times \mathrm{I} \times \eta$$

The calculated power output is only to be regarded as an average value with a variance of ± 20%. Causes for this are

- The batteries do not have similar power characteristics (exception: very low loads).
- The battery's voltage drops continuously during discharge.
- The discharge current changes due to voltage dropping and the appliance's load profile changes.

It is important that the appliance's operation is satisfactory even when power yield is low with the battery becoming discharged.

As described in Chapter 15, new primary cells and fully charged accumulators have a nominal system-specific voltage value at the beginning of the discharge. (See Table 15.3). The voltage drops as time passes from the nominal voltage over the average voltage to the cut-off voltage, as Figure 16.1 shows.

The number of cells needed for an appliance can be calculated as follows:

$$\text{Number of cells} = \frac{\text{Nominal voltage of the appliance}}{\text{Nominal voltage of the chosen system}}$$

The nominal voltage of the appliance is identical with the battery's nominal voltage. During the battery's discharge the voltage drops permanently. Of course the

Table 16.1 Review of the most common important applications with load range data and voltage rating.

Application	Common nominal voltage V	Load range µA/mA/A	Discontinuous use yes/no
Cranking and starting	6.0 to 12.0	A	Yes
Wristwatches	1.2 to 2.4	µA, mA	No
Dictaphones	2.4 to 8.4	mA	No
TVs, radios, recorders	3.6 to 24.0	mA, A	Yes
Remote controls	4.8 to 12.0	mA	No
Filming equipment	4.8 to 12.0	mA	No
Film lighting	6.0 to 42.0	mA, A	No
Cameras	1.2 to 4.8	mA	No
Flashlights	2.4 to 12.0	mA, A	Yes
Walkie-talkies	4.8 to 12.0	mA	Yes
Garden appliances	3.6 to 7.2	mA, A	Yes
Handheld flashlights	2.4 to 6.0	mA, A	No
Hobby (airplanes, boats, cars)	1.2 to 12.0	mA, A	No
Hearing aids	1.2 to 2.4	µA, mA	No
Machine and device controls	2.4 to 24.0	mA	Yes
Medical equipment	1.2 to 12.0	mA	No
Measuring instruments	1.2 to 12.0	µA, mA	Yes
Models (airplanes, boats, cars)	1.2 to 12.0	mA, A	No
Motorcycle blink lights	2.4 to 6.0	A	Yes
Shaving sets	2.4 to 4.8	mA	No
Intercom systems	1.2 to 6.0	mA	No
Safety lights and illumination	2.4 to 12.0	mA	No
Miscellaneous toys	1.2 to 9.0	µA, mA	No
Pocket flashlights	1.2 to 4.8	mA	No
Pocket calculators	1.2 to 6.0	µA, mA	No
Clocks, signal and warning devices	2.4 to 24.0	mA, A	No
Continuous memory power supply	1.2 to 24.0	µA, mA, A	Yes
Tools (drills and cutters)	2.4 to 12.0	mA, A	Yes
Toothbrushes	1.2 to 2.4	mA	No
Bicycle lighting	2.4 to 6.0	mA	No

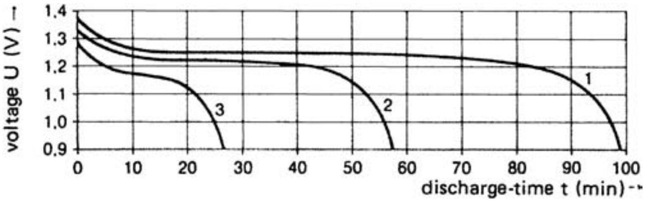

Figure 16.1 Voltage characteristics of a sealed cylindrical NiCd cell with sintered electrodes under different loads ($1 = 6 \times$ nominal current; $2 = 10 \times$ nominal current; $3 = 20 \times$ nominal current).

load is a major factor for this voltage drop (see Figure 16.1). The major influences are

- The specific behavior of the chosen electrochemical system and the battery's construction.
- The ratio of on-load current to battery capacity.
- Period of time of discharge, which is the condition of charge at the moment of evaluation.
- The ambient temperature when varying strongly from standard conditions.

The equation for nominal power output is to be fitted with the mean voltage instead of the nominal voltage, as the voltage is load dependent (see Figure 16.1).

The value for the mean discharge voltages given in Table 15.3 is similar to that experienced with domestic appliances and can therefore be employed for most calculations.

Table 15.3 also advises certain cut-off voltages. Battery-powered appliances should operate properly at least up to these cut-off voltages.

Table 15.3 also shows that certain electrochemical systems, given, the same size are interchangeable, e.g. a lithium cell can replace two carbon-zinc (dry) cells or two silver oxide cells; the same goes for three lead-acid cells compared to four alkaline manganese cells. In real life this is only possible to some extent, as certain specific properties of different electrochemical systems regarding their on-load characteristics, their energy content, and special constructive details resist this interchange. Two or three alternatives can always be found and should be evaluated.

While in pre-electronic times the nominal voltage of any electrical set was usually standardized to some low voltage value, nowadays any voltage above 1.2 V can be chosen, because electronic circuitry can equalize. Of course the nominal voltages of the different electrochemical systems must be respected. Therefore nominal voltage of a set is the product of the number of cells in series and the nominal voltage of the chosen battery system.

Sometimes faulty specifications are ignorantly made; this can easily be misunderstood: e.g. a nominal voltage of 4.8 V can sometimes be found on four alkaline primary cells. This value is incorrect as it was derived from the mean discharge voltage. The correct value is 6 V. Whenever the number and type of cells is clearly defined in the specification of an appliance, no doubts are possible.

Criteria for the nominal value and thus the number of cells are

- The demanded power output of the appliance.
- The demanded operational time for a set of batteries.
- The allowed size of the set, that is the available space for the batteries.

Sets with very low power consumption, that is in the μW and the lower mW range, are sufficiently powered by one or two cells. Miniature devices like wristwatches do not in any case incorporate enough room for several cells. Appliances of higher energy demand are more economic when operated on higher voltage. The most important fields of application are listed in Table 16.1 with their nominal voltages, as they are common in present-day appliances.

16.3 CAPACITY OF A BATTERY

The ability to do work is not specified in Wh as is common in the technical world. Specifications of this kind are only common in general presentations of electrochemical systems (see Figure 16.2). As the voltage characteristics of a cell are determined by the electrochemical system and the load is highly variable, batteries are classified by their ability to supply a certain amount of current in a certain period of time until the cut-off voltage is reached. This value is called "the capacity of a battery" and is given in mAh or Ah. The capacity of a battery is not a constant value.

Capacity and load capability of a battery are dependent on

- The electrochemical system.
- The construction.
- The volume of the battery.
- The type of load (see Section 16.4).

Generally,

- Higher discharge current results in a smaller rated capacity.
- The specified nominal capacity mostly defines the maximum capacity.

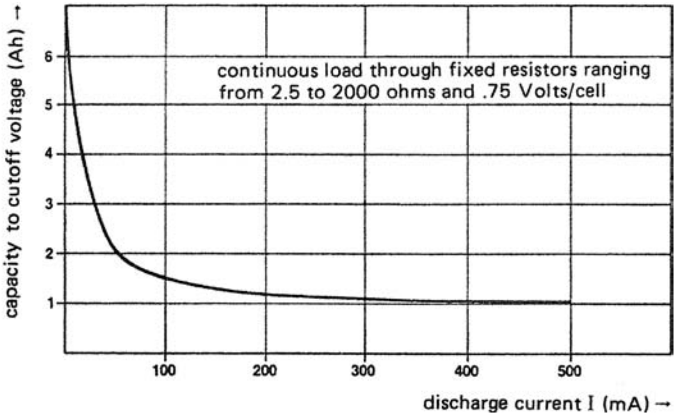

Figure 16.2 Capacity of a mono cell (Leclanché type) dependent on the load.

The possible variance of the rated capacities is shown in Figure 16.2. While with a load of about 30 mA, at least 4 Ah can be drawn resulting in a total time of operation of 133 hours until the cut-off voltage is reached, under a load of 200 mA only 1 Ah can be drawn. Apart from this the mean discharge voltage under high loads is very low. We are talking about a battery system that is only advisable for small loads.

To match the capacity of a battery with given number of cells and nominal voltage, the operating time for exclusive battery powering and the current consumption values must be derived. The operating time can amount to hours, days, or years, but must be expressed in hours as the capacity is specified in mAh or Ah.

The mean discharge current can be approximated by the nominal power output; this system is only satisfactory when the current load is steady. Under more-or-less discontinuous load practical tests with samples of the new design are necessary. Through these generated load profiles conclusions to the final battery design are made.

16.4 THE MOST IMPORTANT LOAD PROFILES OF ELECTRIC APPLIANCES

16.4.1 Continuous Current Load

This type of load is at hand when the load current is completely continuous or only shortly disrupted by impulsive changes up to 100% of the continuous value. Load current multiplied by the desired operating time results in the battery capacity; for current spikes the capacity estimate is raised by 2 to 10%.

If for instance an electronic memory bank with a continuous power consumption of 7 μA must be protected for at least 3 months, a battery with a capacity of 2200 hours × 7 μA is necessary. As the voltage is not allowed to drop below 1.2 V during operation, two primary button cells or two nickel/cadmium cells must be prescribed. A lithium cell would also do the job.

16.4.2 Intermittent Current Load

Whenever the load profile shows that the occurring current load changes can be five times the nominal value, the necessary battery capacity can accurately enough be approximated to be the mean load current value. The mean load current value in the given example, which accords to the loads occurring in some measuring equipment, is about 1.4 times I_N. With increasing duration of these peak loads the mean current load rises; this multiplied by the expected operating period results in the battery's capacity. With proceeding discharge it must be tested, however, whether the battery's voltage range is satisfactory (Figure 16.3). Even when peak loads are encountered the voltage must not drop below the specific cut-off voltage.

16.4.3 Severely Intermittent Load

Whenever current variations exceed five times the nominal value (for example 10 ×; see Figure 16.4), the magnitude of these peaks are a base for dimensioning the battery or otherwise the power loss of the battery would not be sufficiently taken into consideration. The load of the nominal current must additionally be considered.

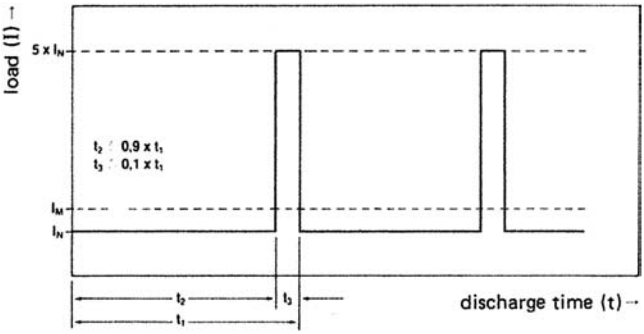

Figure 16.3 Simplified diagram of a load profile for an electric appliance with intermittent current load.

An intelligible example for this load characteristic is shown in Figure 16.4 for a wireless set, where in receiving operation the nominal current I_N is consumed, while in transmitting operation 10 times I_N is demanded for at least 10% of the operational time. A battery that reliably covers the operating-type "transmission" must be chosen; for the whole operating period it must remain above the lower voltage limit.

Example:

- *Wireless set nominal voltage: 12 V*
- *Device rated current: 10 mA (receiving)*
- *Maximum load: 300 mA (transmitting)*
- *Desired operating time: 10 h*
- *Receiving: 90%*
- *Transmitting: 10%*
- *Operating voltage 7.2 to 12 V:*
- *Necessary capacity:*$1 \times 300 = 300$ *mAh plus* $9 \times 10 = 90$ *mAh results in* 390 *mAh*

Thus a battery of 400 mAh is necessary for 1 hour's operation. The voltage may not drop below cut-off voltage after 1 hour's use with 400 mAh.

Eight primary cells of the alkaline type of eight NiCd accumulators fit these specifications.

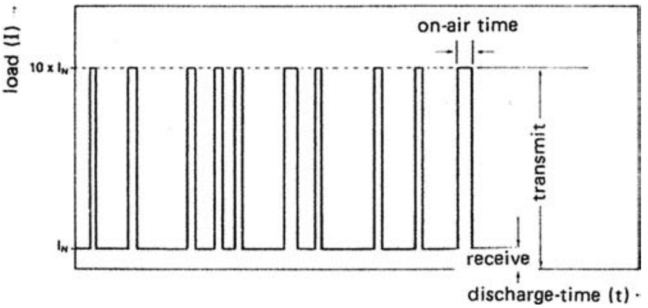

Figure 16.4 Simplified load profile of a wireless set; on-air time about 10% of the receiving time.

16.4.4 Short Peak Currents

Dimensioning a battery is much simpler when a relatively constant load (see Section 16.4.1) with short current peaks of up to 2 seconds, for instance to activate a signal, exist. The permanent current can in these cases derive the battery's size because short peaks do not influence the battery's capacity too much. It must be tested, however, whether the peaks cause a voltage drop below the cut-off value. Whenever this is the case, a larger battery than necessary on first sight or a battery of different design must be chosen.

16.5 INFLUENCE OF SELF-DISCHARGE AND TEMPERATURE

16.5.1 Self-Discharge

Every battery is during storage subject to self-discharges. The self-discharge rate of modern primary batteries is very low and negligible in most cases even when the appliance is not frequently used and deactivated in between. The storage life of common NiCd batteries is about 2 years. For batteries with a predestined operational time of 2 years an additional 2 to 10% of the capacity necessary for operation is sufficient to compensate self-discharge losses.

Lithium batteries have an essentially longer shelf-life. The self-discharge rate is lower than with electrochemical systems on a zinc basis and amounts to less than 1% per year. In case that long-term tests confirm these values, a permitted shelf-life of up to 10 years results.

Rechargeable accumulators, on the other hand, that are nickel/cadmium and lead-acid batteries have a higher self-discharge rate than primary cells. The reason for this is that secondary cells often are less stable electrochemical systems than primary cells, which is partly dependent on the design. When planning with a rechargeable battery the self-discharge rate must therefore be respected. This self-discharge is lowest with nickel/cadmium cells with mass electrodes, while cells with sintered electrodes may lose up to 1% of the nominal capacity per day (see Figure 16.5).

Self-discharge however must not be taken into consideration when the accumulator is discharged within a few days after loading. Whenever this is not the case, a lower capacity level must be coped with or the accumulator must be recharged directly before discharge. Accumulators have the great advantage, compared to primary cells, to be rechargeable several hundred times.

16.5.2 Influence of Temperature

General electrochemical systems work optimally between 15 and 25 °C. Typical characteristics change at higher temperatures, for instance discharge behavior improves while others such as rechargeability and self-discharge deteriorate. Limit for economic battery operation is about 65 °C. Naturally batteries can be operated above this temperature if over-proportional reduction of lifetime can be accepted.

Temperatures of less than 15 °C cause capacity to drop and at low temperatures under −10 °C primary cells on a zinc basis cannot be efficiently applied, except when a fraction of the nominal capacity is sufficient. Lithium batteries still show good load capability at −20 °C. The accumulator's capacity in

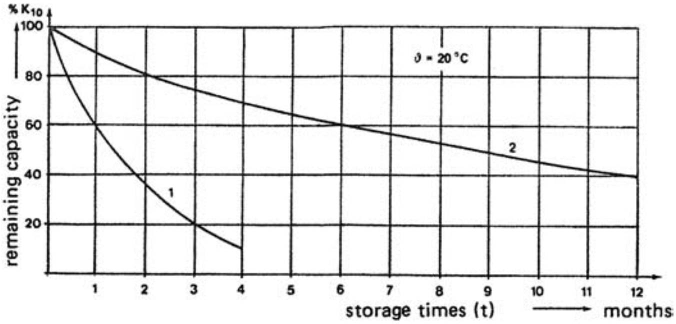

Figure 16.5 Self-discharge of NiCd accumulators with sintered electrodes (1) and mass electrodes (2).

general deteriorates but some designs like the NiCd series with sintered electrodes are still applicable to – 45 °C. Rechargeability is at these temperatures very poor except if the charging device is sophisticated enough to compensate this.

The following is a simplified summary of temperature limits for certain applications of portable batteries:

1. Primary cells on a zinc basis –10 °C to + 50 °C
   With alkaline electrolyte – 20 °C to + 50 °C
2. Lithium primary battery – 20 °C to + 60 °C
   Special designs – 40 °C to + 110 °C
3. Accumulators
   Lead-acid batteries, discharge – 20 °C to + 50 °C
   NiCd batteries, discharge – 45 °C to + 60 °C
   Charging action above 0 °C

Figure 16.6 shows the available capacity of two different NiCd cells dependent on the temperature.

16.6 DESIGN REQUIREMENT STUDY

- Estimate required power (experience).
- Determine nominal voltage.
- Ascertain load current through calculation and through testing.
- Prepare a load profile; ascertain I_N and I_{max}.
- Determine operating period per set of batteries (h).
- Calculate capacity: $C = I \times t$.
- Consider storage and temperature conditions.
- Choose an adequate electrochemical system, note load capability and profile.
- Determine number of cells.
- Undertake practical tests to make sure that under all circumstances the battery's voltage is always sufficient during the demanded operational period.

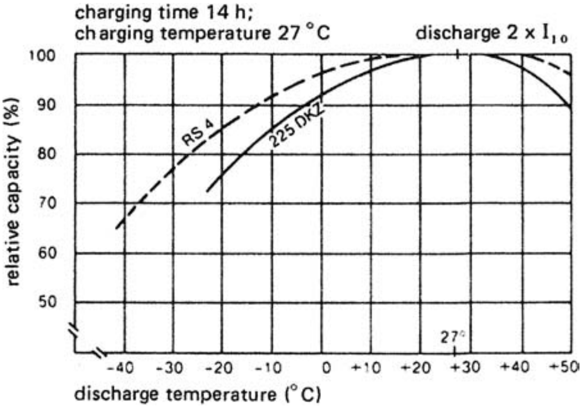

Figure 16.6 Available capacity of NiCd cells when discharged with twice the nominal current vs. temperature range (RS 4 = cell with sintered electrodes; 222 DKZ = cell with mass electrodes).

16.7 DESCRIPTION OF AVAILABLE PORTABLE BATTERIES

In the near future this already vast spectrum of available batteries will become even greater, with about five to ten variants of lithium batteries having been patented and some already available on the market. The different electrical systems are condensed in Table 15.4.

Data important to the designer for the most important designs follows in short, divided into primary cells and secondary cells (accumulators). For project work, these data are of course by no means sufficient, but the relevant industry will provide abundant descriptive literature.

16.7.1 Primary Cells

System: Zinc/Carbon (Leclanché)

- Nominal voltage: 1.5 V/cell
- Mean discharge voltage: 1.2 V/cell
- Cylindrical cells in international standardized sizes and two or three qualities
- Maximum capacity about 7.5 Ah
- Standardized and flat cell batteries for special applications up to 4.0 Ah available
- Temperature behavior: inefficient at low temperatures, about 20% capacity available at – 10 °C
- Storage life: 12 to 24 months

Examples of application: recorders, radios, dictaphones, filming equipment, toothbrushes, shaving sets, flashlights, watches, hobby devices, toys, etc.

System: Zinc/Carbon (Alkaline)

- Nominal voltage: 1.5 V/cell
- Mean discharge voltage: 1.2 V/cell
- Button cells from 40 mAh to 300 mAh
- Cylindrical cells (Alkaline manganese batteries) and flat cell batteries in internationally standardized sizes
- Maximum capacity: 10 Ah
- Temperature behavior: applicable to – 20 °C at 30% capacity
- Storage life: 24 months

Examples of application: recorders, radios, dictaphones, remote controls, pocket calculators, toothbrushes, walkie-talkies, flashlights, toys, etc.

System: Zinc/Mercury Oxide

- Nominal voltage: 1.35 V/cell
- Mean discharge voltage: 1.2 V/cell
- Button cells of 20 mAh to 1000 mAh
- Temperature behavior: applicable from – 10 °C to 60 °C
- Storage life: 24 months and more

Examples of application: hearing aids, cameras, etc.

See Table 16.2 for a summary of available electrochemical systems.

System: Zinc/Silver Oxide (Valence: 1)

- Nominal voltage: 1.55 V/cell
- Mean discharge voltage: 1.4 V/cell
- Button cells from 12 mAh to 180 mAh
- Temperature behavior: applicable from – 10 °C to 60 °C
- Storage life: 24 months and more

Examples of application: wristwatches, hearing aids, etc.

System: Zinc/Silver Oxide (Valence: 2)

- Nominal voltage: 1.5 V/cell
- Mean discharge voltage: 1.2 V/cell
- Button cells from 30 mAh to 90 mAh
- Temperature behavior: applicable from – 10 °C to 60 °C
- Storage life: 24 months and more

Examples of application: wristwatches, hearing aids, etc.

System: Zinc/Air (with Acidic Electrolyte)

- Nominal voltage: 1.45 V/cell
- Mean discharge voltage: 1.15 V/cell
- Cylindrical cells and batteries up to 70 Ah
- Temperature behavior: applicable from – 10 °C to 60 °C
- Storage life: 12 months and more

Table 16.2 Summary of available electrochemical systems with relevant data for the possible energy density per cm^3.

Electrochemical system	Nominal voltage V	Energy density mWh/ccm	Remarks
Carbon/Zinc Leclanche system	1.5	120–190	Primary cell as button, cylindric, or prismatic cell
Carbon/Zinc alkaline	1.5	200–300	Primary cell as button, cylindric, or prismatic cell
Zinc/Mercury oxide	1.35	400–520	Primary battery in button cell design
Zinc/Silver oxide valency: 1 or 2	1.55	350–650	Primary battery in button cell design
Air/Zinc with acidic electrolyte	1.45	200–300	Primary battery in cylindric design
Air/Zinc with alkaline electrolyte	1.4	650–800	Primary battery in button design
Lithium/Manganese dioxide	3.0	500–800	Primary battery button and cylindric cell
Nickel/Cadmium	1.2	40–80	Accumulator: button, cylindric, and prismatic designs
Lead/Lead dioxide	2.0	50–100	Accumulator; cylindric and prismatic designs

Examples of application: hearing aids, etc.

System: Zinc/Air (Alkaline)

- Nominal voltage 1.4 V/cell
- Mean discharge voltage: 1.2 V/cell
- Button cells up to 400 mAh
- Temperature behavior: applicable from – 10 °C to 60 °C
- Storage life: self-discharge less than 1% per year
- Activation only after contact with air

Examples of application: garden and farm appliances, electric fences, warning lights for roads under construction, etc.

Lithium Systems

- The most well known are lithium/manganese-dioxide, lithium/sulfur dioxide, lithium/copper oxide, and lithium/thionyl chloride
- Nominal voltages: from 1.5 to 3.8 V
- Button cells and cylindrical cells up to about 12 Ah
- Temperature behavior: partly also applicable with extreme temperatures
- Storage life: self-discharge less than 1% per year up to 10 years

Examples of application: calculators, film cameras, wristwatches, etc.

16.7.2 Secondary Cells, Accumulators

System: Nickel/Cadmium (with Mass Electrodes)

- Nominal voltage: 1.2 V/cell
- Button cells from 10 mAh to 1000 mAh
- Storage life: practically unlimited
- Temperature behavior: discharge – 20 °C to 45 °C (60 °C); charging: 0 °C to 45 °C

Examples of application: calculators, razors, flashlights, and memory back-ups

System: Nickel/Cadmium (with Sintered Electrodes) and Nickel/Metal Hydride

- Nominal voltage: 1.2 V/cell
- Cylindrical cells from 100 mAh to 7 Ah
- Prismatic cells from 2.4 Ah to 12 Ah
- Storage life: practically unlimited
- Temperature behavior: discharge – 45 °C to 65 °C (75 °C); charging: – 20 °C to 20 °C. Special designs rated for high voltage and high temperature application.

Examples of application: tools, flashlights, models, walkie-talkies, cranking and starting, etc.

System: Lead-Acid (VRLA)

- Nominal voltage: 2.0 V/cell
- Prismatic and cylindrical batteries in 2-, 4-, 6-, and 12-V units from 1 Ah to 63 Ah
- Storage life: recharge after 12 months
- Temperature behavior: – 30 °C to 50 °C

Examples of application: alarm systems, tape recorders, tools, portable lighting equipment, cranking and starting, etc.

System: Lithium-Ion

Examples of application: mobile phones, video cameras, laptops, etc.

16.8 NATIONAL AND INTERNATIONAL STANDARDIZATION

The most important portable batteries are nationally and internationally standardized. The engineer should under all circumstances take these standardized types into consideration (see Chapter 14).

Apart from the trading names the specifications of the IEC (International Electrotechnical Commission) are most commonly used, especially by European manufacturers. These IEC standards are superior to all other standards and specify the maximum overall sizes. The designer of an appliance should therefore make the battery compartment big enough to take batteries of these IEC standards, but also consider smaller batteries at the lower tolerance limit of the IEC standards, but also consider smaller batteries at the lower tolerance limit of the IEC standards and make

Table 16.3 Survey of the most important standardized cylindrical cells.

Trade specification	Lady	Micro	Mignon	Baby	Mono
Sizes:					
Height in mm (max.)	30,2	44,5	50,5	50,0	61,5
Diameter in mm	12,0 (– 1,3)	10,5 (– 1)	14,5 (– 1)	26,2 (– 1,5)	43,2 (– 2)
IEC spec. up to IEC 86-2	R/1	R 03	R 6	R 14	R 20
ANSI spec. (USA)	g N	AAA	AA	C	D
JIS spec. (Japan)	UM 5	UM 4	UM 3	UM 2	UM 1
DIN-IEC No.:	86-2	86-2	86-2	86-2	86-2

sure they are usable without contacting difficulties. This prevents bad surprises (see Tables 16.3, 16.4, and 16.5). The given heights in Table 16.3 are overall lengths including the contact buds.

The commonly used multi-cell dry batteries are also standardized; the "standard 4.2 V battery" and the "energy block 9 V" unfortunately are standardized only by IEC and DIN. The program of types of common dry cells, as far as standardized sizes are concerned, is still somewhat clear. Concerning button cells, development is at full pace; new cells with different sizes and technical specifications are introduced to follow development of appliances. Main reasons for this are extremely small cells and extremely long life.

The different electrochemical systems have been treated in Section 16.9.

16.9 THE INTERCHANGE-PROGRAM NiCd CELLS AND PRIMARY CELLS

For the most common dry cells identically sized rechargeable nickel/cadmium accumulators, which are rechargeable several hundred times, can be provided. The recharging process's costs are negligible and the use of these batteries is only economic in case of a considerable need of dry cells. The consumer can only be

Table 16.4 Standardized commercial primary cells with 4.2 and 9 V.

Commercial name	Standard 4.5 V battery	Energy block 9 V
Dimensions:		
Height in mm	67	48,5
Length in mm	62	26,5
Width in mm	22	17,5
IEC specification	3 R 12	6 F 22
DIN IEC No.	86-2	86-2

Table 16.5 Survey of the most common standardized button cells.

Dimension:							
height (mm)	6.2	5.4	4.2	3.6	3.6	5.4	3.6
diameter (mm)	6.0	11.6	11.6	11.6	9.5	7.9	7.9
IEC specification	MR 9	MR 44	MR 43	MR 42	MR 45	MR 48	MR 41
(examples)	LR 9	SR 44	SR 43	SR 42	SR 45	SR 48	SR 41
ANSI specifications	—	WM 15	WM 11	WM 10	—	WM 6	WM 5
(examples)	—	WS 15	WS 90	WS 12	—	WS 5	WS 4
JIS specifications	—	HS—C	—	HS—B	—	HS5	GS3
(examples)	—	G 13	G 12			G 5	
DIN specifications (examples)	R 9	SR 44	SR 43	MR 42	—	—	SR 41
DIN-IEC No.:	86-2	86-2	86-2	86-2	—	—	86-2

advised to employ NiCd accumulators when at least every two or three weeks a new set of dry cells would be necessary. Costs of the NiCd cells plus the charging device should not exceed that of one year's battery consumption.

An overall comparison of the energy content of dry cells and NiCd accumulators is not possible as these cells show very different characteristics. While small dry cells may have up to three times the energy content of sealed NiCd cells, the energy content of larger dry cells may only be two or three times greater. This comparison is positively influenced for the sealed NiCd cells when low temperature characteristics or heavy load situations are considered. To enable the user to get an estimated comparison Table 16.6 presents the IEC standards and the nominal capacity values of NiCd cells; statements regarding the energy content of dry cells of the same size are also made.

Table 16.6 Comparison of capacity ratings of dimensionally comparable NiCd accumulators and dry cells.

Size designations for dry cells	Dry cells		NiCd accumulators		
	IEC standards designation	Rated capacity mAh	IEC standard designation	Nominal capacity current	
				mAh	mA
Button cell	SR 48	70	KBL 8/6	10	1
Button cell	NR 07	210	KBL 12/6	20	2
Button cell	NR 9	360	KBL 16/7	60	6
Transitor battery	6F 22	500	—	100	10
Lady cell	LR 1	580	KR 12/30	150	15
Micro cell	LR 03	750	KR 10/44	180	18
Mignon cell	LR 6	1500	KR 15/51	500	50
Baby cell	LR 14	5000	KR 27/50	1800	180
Mono cell	LR 20	10000	KR 35/62	4000	400

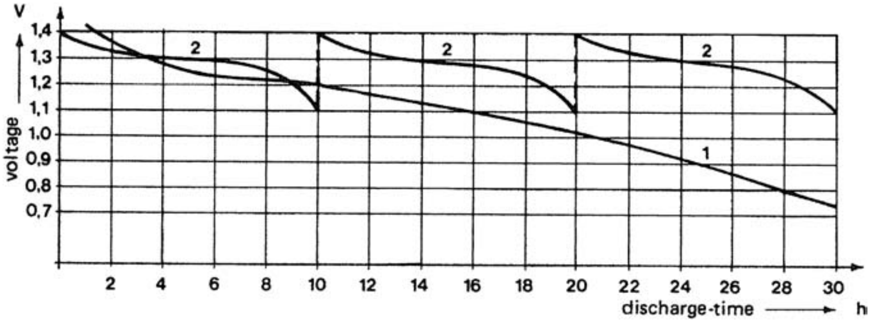

Figure 16.7 Comparison of the discharge curves of a dry cell battery and a NiCd accumulator. Curve 1 = discharge of a dry cell (mignon-sized alkaline). Curve 2 = discharge of a NiCd cell of the same size.

While nominal capacities are specified for NiCd accumulators, which correspond approximately with the drawable capacity, dry cells' nominal capacity is rated dependent on the profile of discharge. The largest dry cells with the greatest amounts of drawable current are taken into consideration.

Dry cells have a nominal voltage of 1.5 V, while NiCd accumulators only have a value of 1.2 V. This does not concern the interchangeability, as only mean discharge voltage is relevant.

The sealed cell has a more constant voltage than the primary cell under the same load, dropping from 1.3 V to a voltage of 1.0 V at the end of discharge, resulting in a mean discharge voltage of 1.24 V (see Figure 16.7), while dry cells show under maximum exploitation of the capacity a continuous voltage drop to 0.9 V or even 0.75 V, resulting in the mean discharge voltage possibly being even lower than with sealed cells.

Referring to Figure 16.7: Alkaline cells of the mignon (AA resp. R6) size, the most commonly used, have a drawable capacity of about 1200 mAh under a load of 20 mA. The NiCd cell of the same size has only about 200 mAh, which means it has to be recharged three times to yield the same capacity as the alkaline mignon cell. With a life expectancy of around 1000 discharges, the NiCd cell can substitute around 330 alkaline mignon cells. As the price ratio is about 1:10, a significant amount of money can be saved. Additionally, the time factor must of course be recognized in this calculation.

16.10 GUIDELINES FOR USE AND MAINTENANCE

Every owner's manual of any electric battery-powered appliance should contain guidelines for battery changes and the intervals at which to change them.

Naturally a legible short form of manual should be chosen, which must be tailored to fit the appliance. The battery case itself must also contain instructions for size, quality, and the right polarity of the batteries. The following should help to issue these important instructions.

16.10.1 Primary Batteries

Batteries are discharged when the appliance shows variation from normal functions, for instance, when

- Portable radio sets become noticeably fainter and when the sound is distorted when the volume is turned up.
- After short use the power indicators of reel or cassette recorders show "low" or they start wailing.

Other considerations include

- Used-up batteries are to be removed immediately. Deep discharged batteries tend to leak after a short period of time. Also all batteries should be substituted together as there is great danger of leakage of the discharged cells.
- It must always be made certain that the batteries are introduced into the appliance with the right polarity. When in series, operation of cells with one cell inversed may cause rupture. A leakage always follows and the appliance can be severely damaged.
- Batteries of different designs should not be operated together. As the batteries have capacities, some of the cells may get discharged very deeply and leak.
- Dry batteries are not rechargeable as accumulators are. Individuals that offer such charging devices under false pretenses are more than negligent because there is a great danger of explosion!
- The above does not concern the fact, given certain circumstances, that some regeneration of partly discharged cells is possible. These devices are designed in such a way that no damage can be done although no responsibility for this is taken from the manufacturer's side.
- Batteries are leak-proof if these guidelines are followed. In case of leakage as a result of faulty application, the battery chamber and the contacts are to be thoroughly cleaned, preferably with a soft absorbent tissue not to damage the appliance any further.
- Clean contacting surfaces and good contact must be ensured when a new set of batteries is inserted.
- Regard disposal instructions for spent batteries.

16.10.2 VRLA Batteries

- Operation in any position is tolerable.
- For stationary applications the vents shall be on the top or on the side.
- Never open the vents.
- Tolerable temperature for use: 30 to 50 °C.
- Store when not in use in clean and dry (0 to 35 °C) conditions. For charge intervals to compensate self-discharge, see manual.
- Recharge discharged batteries at the latest after one week.
- Charge only with limited voltage: 2.35 V/cell.
- Instructions of the battery manufacturer manual have to be regarded.
- Regard disposal instruction for spent batteries.

16.10.3 NiCd Batteries

When NiCd accumulators are used, the following simple rules must be followed:

- New cells must be charged directly before use with the nominal value I_{10} for 20 to 24 hours.
- After every normal discharge 14 hours of charge with the nominal charging current must be made. Prolonged charging now and then has no effect on the lifespan of a battery.
- When a battery has been completely discharged, for instance when switching off was forgotten, it must be charged with the nominal current I_{10} for 20 to 24 hours.
- Keep contacts of the set clean!
- Whenever the cells are not used for a longer period of time, they must be recharged as quoted above. After two to three recharging cycles, the batteries will have regained their full capacity.
- Regard disposal instructions for spent batteries.

16.10.4 Nickel/Metal Hydride Batteries

- Instructions of the battery manufacture's manual have to be regarded.
- Regard disposal instructions for spent batteries.

16.10.5 Lithium Batteries

- Instructions of the battery manufacturer's manual have to be regarded.
- Regard disposal instructions for spent batteries.

16.11 SUMMARY

The power consumption of an appliance determines the size of the battery, the period of operation, and the operating costs. Only those appliances that incorporate sufficiently dimensioned, safe, and easy-to-use power sources are highly efficient and thus have the best preconditions for being a success.

The process of choosing an electrochemical system as well as the design of the battery must be considered as important tasks and must be carefully accomplished, in which not only technical points of view, but also economic preconditions must be respected.

Because of the multitude of available battery types that can be fitted, which is neither surveyable by the user nor can be judged as to what concerns quality, the appliance's designer must give advice for the best battery system and name economic alternatives for this.

The problem for the designer therefore is as follows:

- The battery must be big enough yet at the same time as small possible; weight and size must be respected.
- Find the technically best solution but also take more economic alternatives into consideration.

- Standardized sizes must be provided as far as possible for good interchangeability for the user. Sets that are frequently used may be alternatively provided with rechargeable batteries.
- Shape must be considered for easy access to the battery case.
- Battery case should be separate from the rest of the appliance so in case of leakage no harm will be done.
- Rugged design and good fit of the contractors should be provided.
- For appliances with accumulators the charging device may be incorporated or the charging socket made easily accessible.
- Mark size and polarity and alternative powering clearly in the battery case.
- Provide legible instruction manuals.

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17

Maintenance-Free Lead Batteries with Immobilized Electrolyte

H. TUPHORN

17.1 INTRODUCTION

Since the maintenance-free sealed nickel/cadmium accumulator became of high importance in the market, in the middle of the 1950s (Figure 17.1), the German battery company Sonnenschein has invented the first maintenance-free portable lead-acid batteries in small sizes in modules of 2 to 12 V between 1 and about 30 Ah. These batteries have been absolutely maintenance free and because of their immobilized electrolyte they could be used in any position without leakage. Applications for these batteries were electronic flashlights, portable TVs, tape recorders, and electric lawn mowers. Also for emergency power supply and in alarm equipment these batteries in valve-regulated construction are used still today.

Important for the maintenance-free properties of these batteries was the possibility to use antimony-free grid alloys instead of the conventional lead-antimony alloys, which were used only at this time. Because antimony in the grid alloys provides a high cycle life for the battery, it was necessary to develop more sophisticated methods in battery manufacturing in order to achieve the required product properties.

Figure 17.1 Valve-regulated maintenance-free gel batteries from the 1950s.

17.2 FUNDAMENTALS

The basis for charging lead-acid batteries is the redox reaction of lead:

1. $PbSO_4 + 2H_2O = PbO_2 + H_2SO_4 + 2H^+ + 2e^-$
2. $PbSO_4 + 2H^+ + 2e^- = Pb + H_2SO_4$

Besides this main reaction, an additional reaction takes place at the electrodes during charging, which generates hydrogen and oxygen:

1a. $H_2O = 2H^+ 1/2\ O_2 + 2e^-$
2a. $2H^+ + 2e^- = H_2$

This water decomposition during charging, which requires the maintenance of topping up of water to the electrolyte, generally takes place in lead-acid batteries if charging is not stopped after full charge of the active masses, because no more lead ions for reactions (1) and (2) are available. This basically takes place during charging with constant current. But the reactions (1a) and (2a) take place generally during the main charging of the masses together with the power saving reactions (1) and (2), because hydrogen is thermodynamically more noble than lead. Because of the thermodynamical law, at the negative electrode basically the more noble element is reduced before the less noble one. The reason that charging of lead-acid batteries basically is possible is the so-called hydrogen overvoltage, which inhibits the reaction (2a), so that $PbSO_4$ can be reduced to Pb. So the amount of water decomposition during charging is generally influenced by the degree of hydrogen overvoltage.

In order to guarantee an almost maintenance-free operation of lead-acid batteries, which requires low decomposition rates of water, the usage of materials with high values of hydrogen overvoltage is needed. While lead basically fulfills that requirement, antimony, which is used more or less as an alloying component in conventional lead-acid batteries, decreases the overvoltage extremely.

In consequence the potential of the charging reaction of the negative plates is closer at the potential of hydrogen reduction, so that during charging considerable amounts of gas are evolved at the negative plate. The influence of antimony can be demonstrated by Figure 17.2, which indicates the charge characteristic of lead-acid cells containing grids with different alloys.

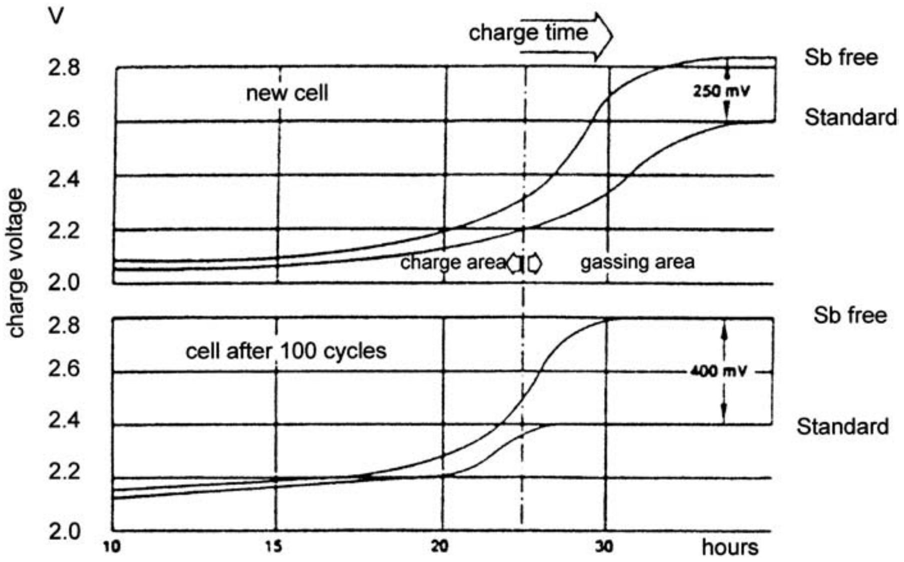

Figure 17.2 Antimony influence in the grid alloy on charge characteristic of vented lead-acid cells.

The upper part of Figure 17.2 indicates the situation on new flooded cells, and the increasing of the charge voltage at the end of charge of the active masses to the voltage of water decomposition is obvious. This voltage range between cells with 4.5% Sb and cells with antimony-free plates is about 250 mV. In the lower part of Figure 3.2 a higher decreasing of the water decomposition voltage is obvious. The reason is, because of anodic corrosion during charging, antimony from the positive plate is soluted and is electroplated at the surface of the negative plates. So the antimony amount at the surface of the negative plates increases extremely, and the battery reacts like a battery with plates of a higher amount of antimony. It is obvious that the voltage range between the new and the cycled batteries increases from 250 mV to 400 mV, and this finally can lead to the consequence that the battery never can be recharged, because the whole current generates hydrogen and oxygen (antimony poisoning).

Figure 17.3 indicates the influence of antimony on the gas extrication of lead-acid batteries during charging with constant voltage (Ford Test).

The self-discharge, too, is influenced by antimony, because this is a reaction of the negative mass with the sulfuric acid of the electrolyte under hydrogen evolution:

$$Pb + H_2SO_4 = PbSO_4 + H_2$$

If the evolution of hydrogen is inhibited because of an increased hydrogen overvoltage, then the speed of the self-discharge reaction is reduced significantly, as indicated in Figure 17.4

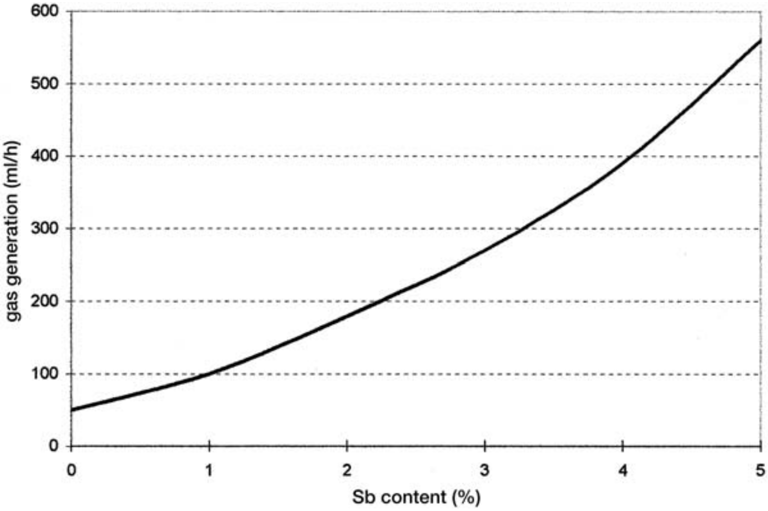

Figure 17.3 Antimony influence in the grid alloy on gas extrication in starter batteries during charging with U=4.2 V/cell.

17.2.1 OXYGEN RECOMBINATION

Besides the usage of clean materials and antimony-free lead alloys for the construction of batteries, the so-called oxygen recombination is the basis for the function of valve-regulated maintenance-free lead-acid batteries. Because of the thermodynamic locations of hydrogen and lead, a complete prevention of decomposition of small amounts of water generally is not possible. But the oxygen

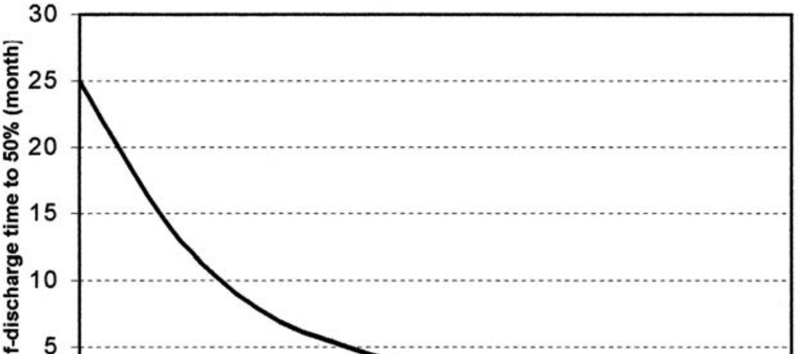

Figure 17.4 Antimony influence on self-discharge of lead-acid batteries.

recombination, which takes place in valve-regulated lead-acid batteries, prevents the extrication of small amounts of hydrogen-oxygen mixture during charging. The recombination is a cathodic reduction of oxygen gas, which still is formed by water decomposition during charging, with hydrogen ions at the negative electrodes to water. In this way a circulation of water-hydrogen-water happens. In order to achieve this, the oxygen which is formed at the positive plates must have the possibility to migrate to the surface of the negative plates, where it will be reduced. This process is demonstrated in Figure 17.5.

Basically required for the function of oxygen recombination are free channels between the positive and the negative plates to allow the oxygen to migrate from the positive plates, where it is formed to the negative plates, where it will be reduced. This is achieved by solidification of the electrolyte either by gelling (Dryfit technology) or by adsorption of the electrolyte in nonwoven glass fiber material, (AGM technology). The AGM method requires that the fiber separator is not fully saturated with electrolyte, so that the oxygen gas can find enough channels for migration to the cathode.

As soon as free oxygen reaches the surface of the cathode, it becomes depolarized, which means its voltage decreases, because the reduction of oxygen to water requires less energy than the reduction of hydrogen ions to hydrogen gas. Therefore at the negative plates oxygen is reduced:

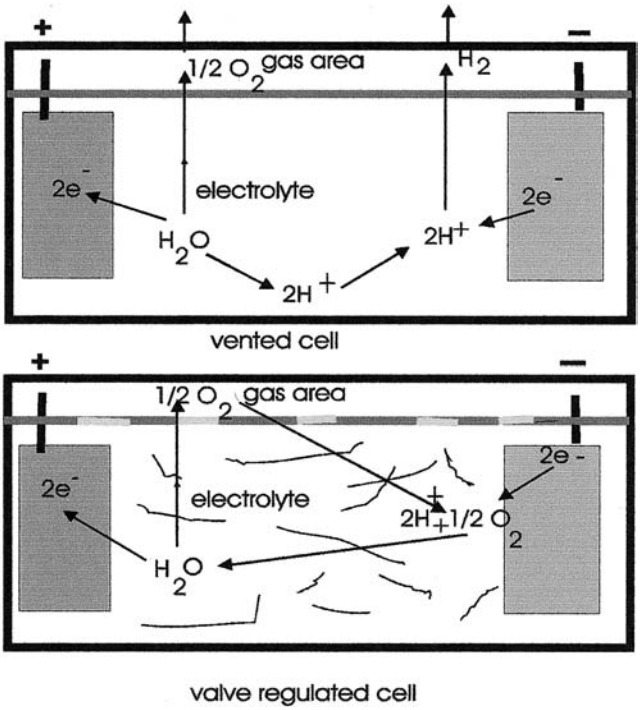

Figure 17.5 Oxygen recombination in lead-acid batteries.

$$1/2O_2 + 2H^+ + 2e^- = H_2O$$

instead hydrogen evolution:

$$2H^+ + 2e^- = H2.$$

17.3 CONSTRUCTION

As already pointed out, a significant feature of valve-regulated maintenance-free lead-acid batteries is the usage of lead-calcium instead of lead-antimony grid alloys. Because of the high requirements on the hydrogen overvoltage, high purity of all used materials, especially the electrolyte, is required, because small impurities may increase the self-discharging of the battery because of decreasing the hydrogen overvoltage.

In contrast to conventional lead-acid batteries, valve-regulated batteries do not require free space underneath the plates for mud collecting, because loosened mass particles are fixed between the plates and cannot fall to the bottom of the cell, forming short circuits. In valve-regulated batteries, this space can be used for increasing the plate length in order to increase the capacity.

In gel batteries high-porous plastic separators with very low resistance are used, while in AGM types nonwoven glass fiber mats are used to soak the liquid electrolyte. Simultaneously these glass mats have the function of separators.

An important feature of construction of valve-regulated batteries is the valve, which replaces the vent plug of conventional lead-acid batteries. The vent is necessary to allow the escape of small amounts of gas, which is generated in new batteries during charging. On the other side the vent has to be absolutely tight from outside to inside, in order to prevent the migration of oxygen from the air into the cells, where it would oxidize the negative mass because of the free channels:

$$Pb + 1/2\ O + H_2SO = PbSO_4 + H_2O$$

Therefore even marginal leakage would increase the self-discharge of that cell. Those cells in series of batteries would be deep discharged during the subsequent discharge operation of the battery with the consequence of premature depletion.

Valve-regulated batteries are constructed with flat plates. Also batteries with tubular plates for stationary and traction applications are produced in gel technology.

17.4 SYSTEMS AND PROPERTIES

17.4.1 Gel System

The electrolyte in gel batteries is gelled by addition of highly dispersed silica dioxide. In this way a thixotropic liquid is obtained, which solidifies after a short standing time after filling. Thus a gelled electrolyte with a high amount of fine capillaries is formed, which allows the oxygen to migrate from the anode to the cathode. Comparing the gas generation of a valve-regulated gel battery during overcharging for 90 hours with constant voltage of $U = 2.35$ V/cell with a conventional battery of

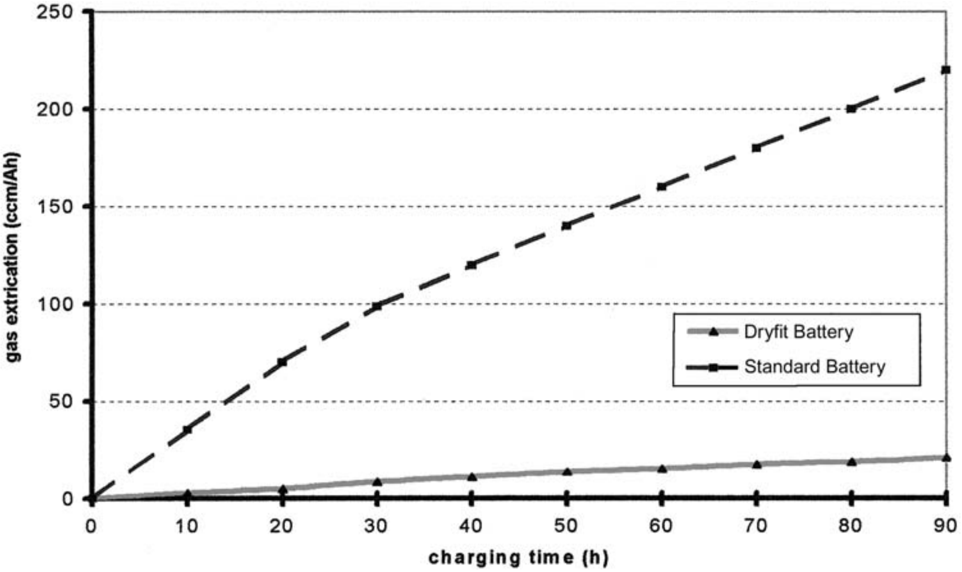

Figure 17.6 Comparison of gas extrication between gel batteries and conventional batteries during charging with U = 2.35 V/cell.

the same size indicates that the valve-regulated battery produces only 10% of gas compared with the conventional one (Figure 17.6).

This is valid for valve-regulated batteries in new condition. During longer operation the gas extrication decreases because of aging of the gel. Because of the initial decomposition of small amounts of water, new capillaries become formed, which increase the recombination rate by increasing the oxygen migration. Figure 17.7 illustrates an exponential decrease of the initial gassing during operation

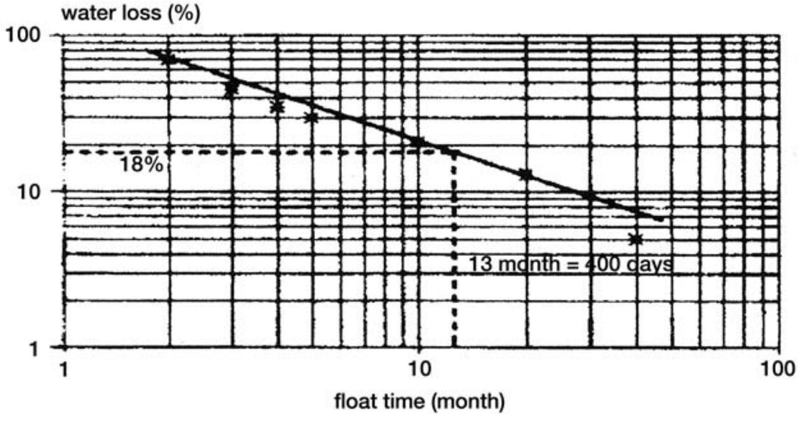

Figure 17.7 Decreasing of gas extrication of gel batteries during charging with U=2.3 V/cell.

time to a negligible rest. This process is the reason that valve-regulated gel batteries are never destroyed by drying out if they are operated under regular conditions.

Because of the solid structure of the electrolyte, gel batteries in new condition have a reduced capacity in comparison to flooded batteries. This is valid for similar constructions. Regarding the situation that gel batteries do not require free space underneath the plates, this capacity lack can be compensated partially by increasing the length of the plates. During cycling, gel batteries show a distinct capacity development, which increases over 100% of the nominal capacity in its maximum. During cycling with the 5-hour rate the maximum of the capacity is near 50 cycles, while at the end of life 80% of the nominal capacity is achieved with 250–300 cycles (Figure 17.8).

17.4.2 AGM System

Besides the gel system, during recent years the AGM system (adsorbed glass mat) was developed for the production of valve-regulated lead-acid batteries. This system is used by several battery companies. In this system the leakage of acid is prevented by adsorption of the liquid electrolyte in fiber separators.

In order to achieve the described oxygen recombination also in this system, during filling it has to be respected that an excess of electrolyte is avoided. In order to achieve free pores for the oxygen migration to the negative plates, the separator must not be saturated with liquid. With this technology, too, the initial capacity is significant below the capacity of vented batteries. Without additional measures, the initial capacity is 80–85%, like gel batteries. Figure 17.9 shows the influence of electrolyte saturation of AGM batteries on the recombination and capacity.

17.4.3 System Comparison

Comparing both valve-regulated battery systems, it is obvious that AGM batteries are full in oxygen recombination already in new condition if the electrolyte

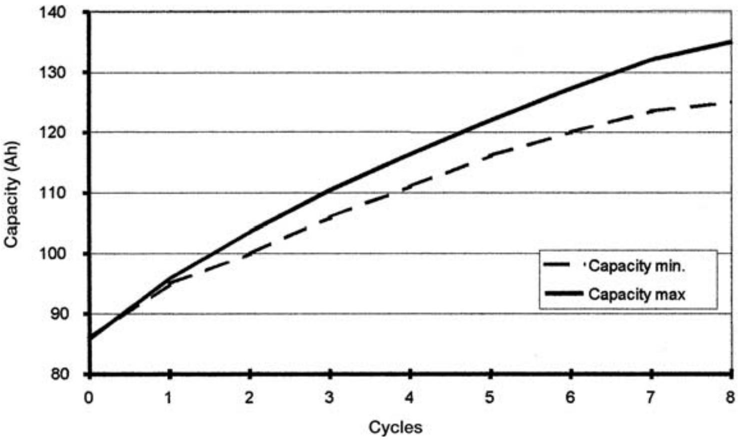

Figure 17.8 Capacity development of VR 110Ah gel batteries during cycling with I_5.

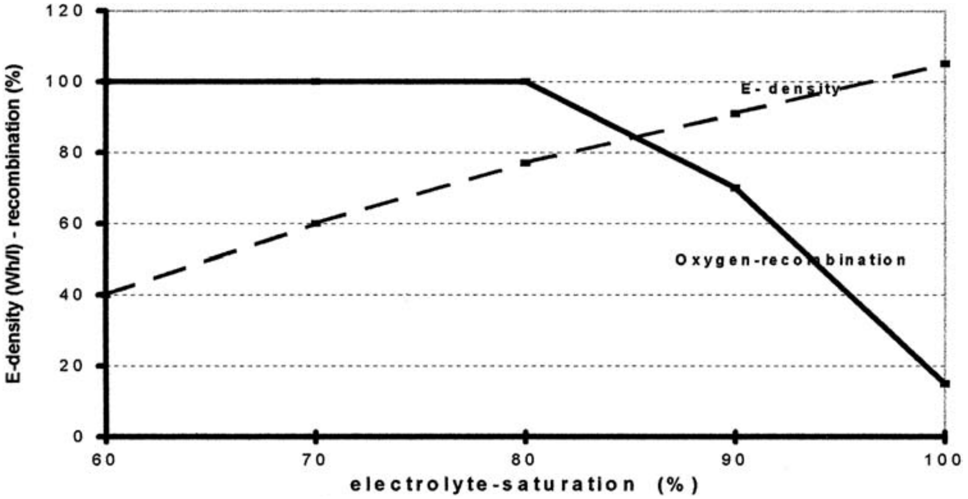

Figure 17.9 Influence of electrolyte saturation on energy density and oxygen recombination of AGM batteries.

saturation of the glass mat is significant below 100%. In contrast, gel batteries in new condition have still a very low gas extrication in the beginning of life. This water decomposition together with aging of the gel leads to the forming of more new capillaries, with the consequence of increasing oxygen recombination up to values which prevent any gassing. So in both systems drying out because of water decomposition will never be a reason of early end of life, as soon as the batteries are charged in correct condition. Because of the larger pores in AGM batteries, in comparison to the gel capillaries, the recombination rate of AGM batteries is about 20 times higher than that of gel batteries. The oxygen recombination is defined by the equation

$$R = 100 - \frac{V \times 100}{n \times i \times t \times 0.62} (\%)$$

where R = recombination rate (%), V = gas developed (L), i = average charging rate (A), t = charging time (h), n = number of cells. Because of the influence of the charge voltage on the charge current, the recombination rate R decreases with increasing charge current.

On principle the full function of the oxygen recombination, which is necessary for valve-regulated maintenance-free batteries, can be achieved with both technologies (Figure 17.10).

In one attribute both systems are substantially different, that is the charge condition. The reason is the big difference in the recombination rates of the two systems, caused by the different structures of the pores in the systems which are needed for the migration of the oxygen from the positive to the negative plates of the cells. While the glass fiber mat of AGM batteries has pore diameters of up to 100 microns, the capillaries of gel batteries are formed by shrinking of the gel because of aging. In this way capillaries are formed which are in maximum one-tenth of the

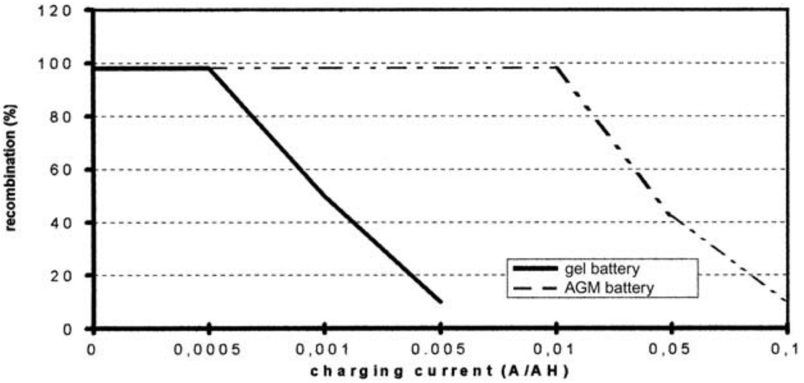

Figure 17.10 Oxygen recombination of valve-regulated battery systems. (From NTT.)

pores of the AGM material. This is the reason for the substantial difference of recombination of the two systems.

The recombination rate for gel batteries with 100% up to a charge current of 0.5 mA/Ah is fully sufficient for maintenance-free operation, because the EOC currents of gel batteries never exceed this value. In contrast, the consequence of a too high oxygen recombination depolarizes the negative plate extremely, so that the anodic potential increases are very high. Because this grade of polarization increases the oxygen development, the exothermic oxygen reduction to water, which takes place at the same time at the negative electrode, increases the temperature of AGM batteries more than gel batteries.

The current voltage curve (Figure 17.11) indicates the situation of the influence of the recombination rate on the charge current of valve-regulated lead-acid batteries. During charging with 2.3 V/cell the voltage divides up to 1.87 V at the positive plate and – 0.43 V at the negative plate. The corresponding charge current is 50mA/100Ah. For gel batteries the oxygen which reaches the negative electrode causes a depolarization from – 0.43 to – 0.40 V, which polarizes the positive plate to 1.89 V. The corresponding recombination current I_{gel} increases after that to 80 mA/ 100 Ah.

Because of the high oxygen concentration, at AGM batteries the negative plate is depolarized up to 0.34 V, which effects a polarization of the positive plate to 1.96 V. This causes an increasing of the recombination current I_{AGM} up to 800 mA/ 100Ah. The recombination current is effected by the redox reaction

$$H_2O \rightarrow 2H^+ + 1/2\ O_2 + 2e^- \rightarrow H_2O$$

which causes a strong heat development. This higher oxygen cycle in AGM batteries in contrast to gel batteries is responsible for the risk of thermal runaway if no removal of the reaction energy is possible. The thermal runaway, which causes a spontaneous end of life of batteries because of overheating, is often discussed in technical publications as a problem of valve-regulated lead-acid batteries. It is not observed in gel batteries, which is a consequence of the low recombination rate of this system.

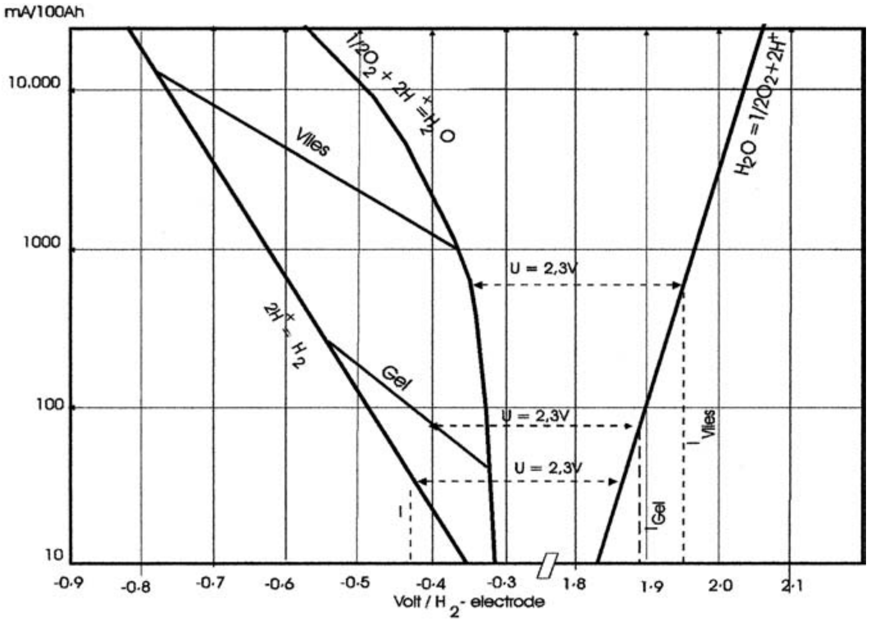

Figure 17.11 Influence of the oxygen recombination on the charge current of VRLA batteries of different systems.

A further distinction of both systems is the acid stratification. This often causes early end of life in flooded lead acid batteries. The acid stratification is caused by the dilution of the sulfuric acid electrolyte, which reacts with the active masses during discharging of the battery. During charging this sulfuric acid is formed in high concentration, which deposits to the bottom of the cell because of its higher concentration if no stirring of gas development occurs. So in flooded batteries which are charged maintenance free, which means without gas development, a stratification of the electrolyte takes place which forms low acid concentration in the upper regions and a high acid concentration in the bottom areas of the cells (Figure 17.12). This affects an acid limitation, which reduces the capacity of the cell spontaneously during cycling. But it is more dangerous; the high acid concentration at the bottom area of the cells causes corrosion of the positive grids in the low plate areas, which destroys the battery.

That those dangerous stratification effects never are observed in conventional batteries is a consequence of the water decomposition especially at the end of charge because of the charge method and the low hydrogen overvoltage of the lead-antimony grids. So during charging the formed oxygen and hydrogen gasses agitate the electrolyte, so that the different concentrations become mixed again. The maintenance-free starter batteries, as they are used in the automotive industry today, are vibrated during their operation in the car, so that here the electrolyte is agitated, too.

Figure 17.12 indicates this situation at 350 Ah for traction cells. In all cases the electrolyte had a gravity of 1.23 g/cm^3. It is obvious that in the flooded cell even after

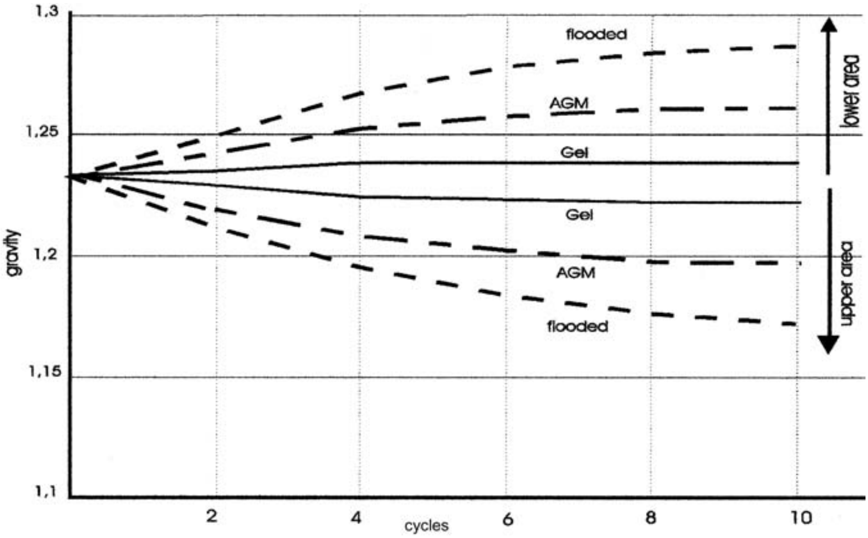

Figure 17.12 Acid stratification during cycling of maintenance free lead-acid batteries of different technologies.

10 cycles we find a difference of gravity between the upper and the lower parts of the cell between d = 1.16 and d = 1.29. Because of the lower mobility in AGM batteries here the stratification is almost halved but still relevant. Because of the immobilization of the electrolyte a vibration of the cell will not equalize the stratified electrolyte layers. By the structure of the gel electrolyte in gel batteries the sedimentation of the higher concentrated acid, which is formed during charging at the plate surface, is inhibited so extremely that the diffusion of the higher concentrated electrolyte prevents practically total stratification. Early failures because of acid stratification are never observed in gel batteries.

17.5 ELECTRICAL PROPERTIES

17.5.1 Methods of Charging

The charging voltage of lead-acid batteries depends on their open circuit voltage, which can be calculated according to the gravity of the electrolyte by the formula

$$\mathrm{OCV} = \mathrm{d} + 0.84(\mathrm{V})$$

In order not to exceed the voltage to the amount of the electrolyte decomposition, valve-regulated lead-acid batteries basically have to be charged with controlled voltage, which has to be above the OCV voltage but below the voltage for reduction of H^+ ions. At room temperature a charge voltage between 2.3 and 2.35 V/cell has to be used. Therefore for charging of valve-regulated lead-acid batteries IU chargers are to be used with a recommended current limitation of $I = 1$ to $2 \times I_5$.

During charging without current limitation the initial current increases up to 0.5 A/Ah. Then the increasing cell voltage decreases the current exponential to an EOC current of about 1 mA/Ah (Figure 17.13). By use of current-limited chargers the maximum current of the charger will remain as long as the current reaches the dotted line in Figure 17.13. After that it follows this current curve. For complete charging, a full discharged battery needs 15 hours to achieve 100% charge condition.

Because valve-regulated gel batteries are not damaged by partial charging, which is forbidden for conventional lead-acid batteries. Partial charge operations are allowed if after every five cycles the battery is fully charged again.

Figure 17.13 indicates that, for instance, a charging time of only 1 hour with U = 2.35 V/cell without current limitation brings the state of charge up to 50%. (This is valid for room temperature.) The temperature influence on the charge voltage is indicated in Figure 17.14. It has to be marked that the charge voltage for cycle operation has to be 50-100 mV/cell above the charge voltage for float application. The temperature influence on the charge voltage is due to the influence of the temperature on the charge reactions of the positive and negative masses as well as on the reaction of the water decomposition.

Charge units regulated by constant current or by constant resistance generally should not be used for charging of valve-regulated batteries unless highly experienced staff can control the whole charging operation with interruption of the current as soon as the end of charge voltage is achieved.

Besides the IU charging, an IUI charging is recommended for valve-regulated traction batteries which are switched together to high voltages. In this way the charge current has to be kept constant for 4 hours for equalization of the charge condition of the single cells, as soon as it has achieved a value of 20 mA/Ah.

An equalized charge condition on single cells before discharging a battery is important in order to avoid deep discharging or reverse charging.

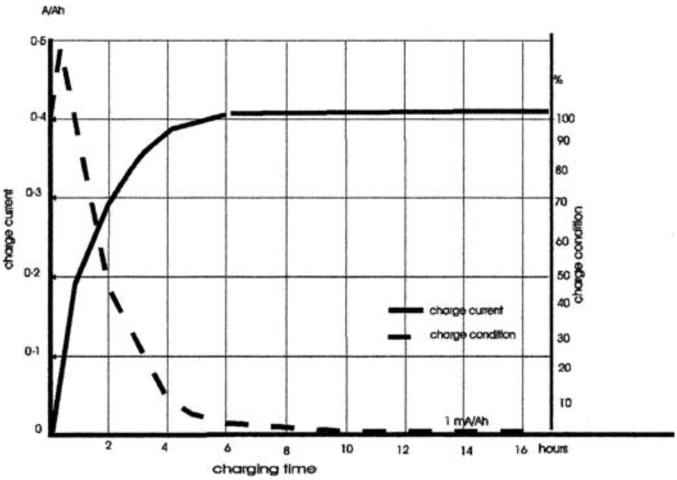

Figure 17.13 Charge characteristic of valve-regulated gel batteries with U=1.35 V/cell.

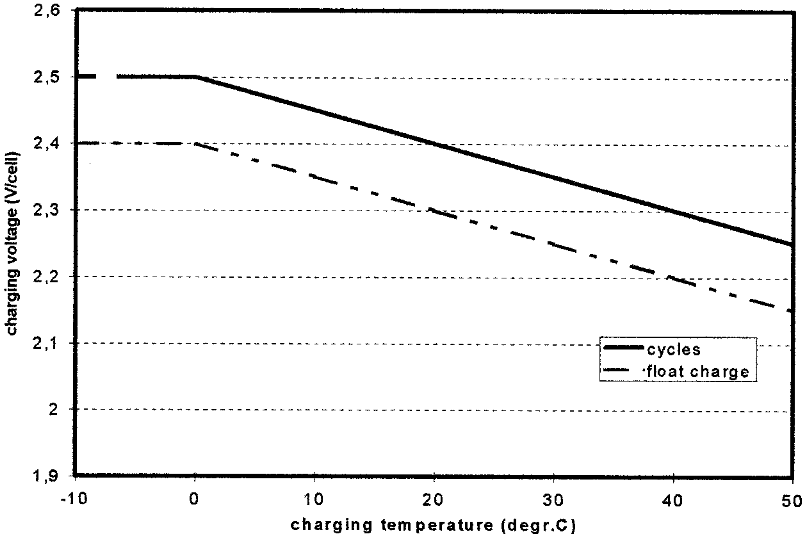

Figure 17.14 Temperature influence on charge voltage of valve-regulated gel batteries.

17.5.2 Discharge Conditions

The nominal capacity of valve-regulated batteries is defined between I_5 and I_{20} according to the application and the technology of the battery. For definition the rated capacity following discharge rates is valid at T = 20°C:

Cells with flat plates (nonmilitary types): I_{20}
Military batteries: I_5
Stationary batteries (tubular plates): I_{10}
Traction batteries (tubular plates): I_5

In a similar way as indicated by conventional battery systems, the capacity of valve-regulated batteries depends on the discharge current and on the temperature of the battery. With increasing of the discharge rate and decreasing of the temperature, the capacity decreases as indicated in Figure 17.15.

Although in valve-regulated batteries the electrolyte which takes part in the discharge reaction is immobilized and its diffusion is limited, valve-regulated batteries have a very good high rate performance at low temperatures, which is superior than conventional batteries. Figure 17.16 indicates on a 12-V 100-Ah battery, as used in military tanks, the discharge performance for discharging with $I = 25 \times I_5 = 500\,A$ at 0° and $-30°C$ and the performance of valve-regulated batteries is distinctly superior compared with flooded batteries. This can be explained because at high temperatures only a small part of the electrolyte takes place on the discharge reaction in combination with the oxygen recombination.

By the oxygen recombination the negative electrode becomes depolarized and so its voltage decreases to more positive values, with the result of increasing the voltage of the positive electrode, because the charge voltage is fixed (Figure 17.17). Because of the more positive voltage of the positive plate, this plate is shifted into a

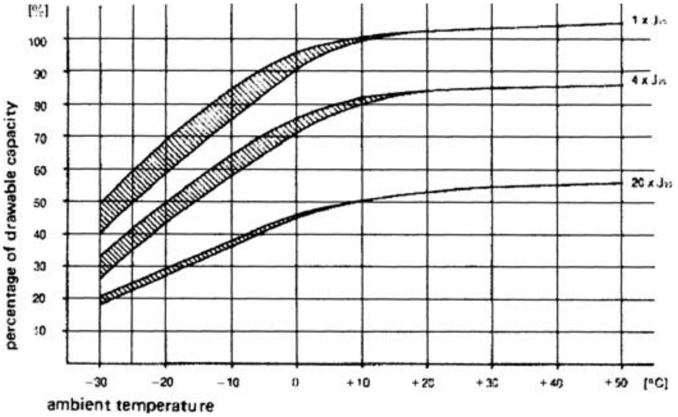

Figure 17.15 Influence of temperature and discharge rate on capacity of gel batteries.

higher state of charge. This superiority of valve-regulated batteries is clearer with decreasing temperature and decreasing discharge rate.

17.5.3 Life and Self-Discharge

During cycling operation between I_{10} and I_{20} at 20°C gel batteries with flat plates achieve a cycle life of about 250-300 cycles up to a residual capacity of 80% of the initial capacity. In order to achieve this life with antimony-free valve-regulated batteries an especially highly controlled production technology of the positive plates, which normally limit the cycle life of antimony-free batteries, is required.

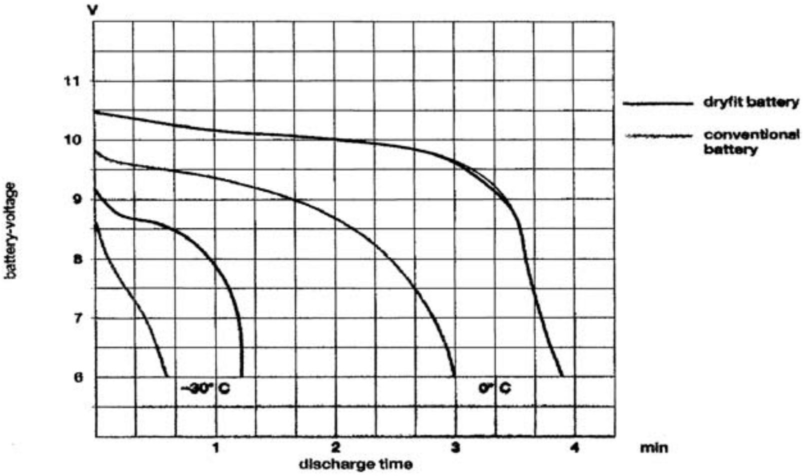

Figure 17.16 Discharge characteristic of different battery technologies at 0 and −30;°C with $I = 25 \times I_5$.

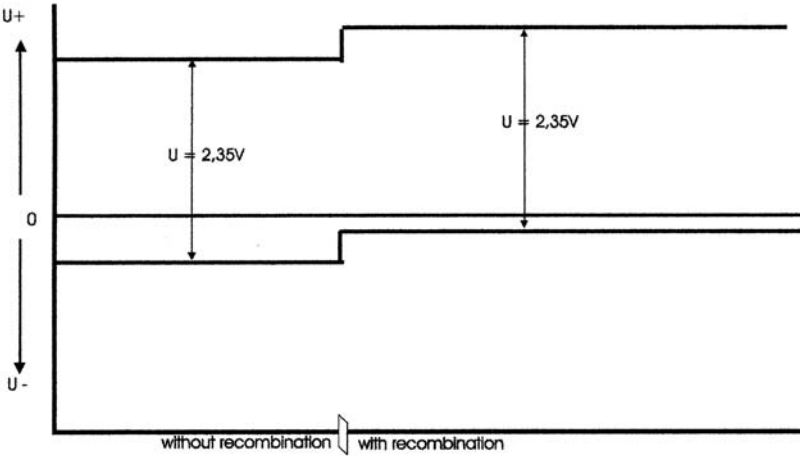

Figure 17.17 Influence of oxygen recombination on the single voltages of the electrodes of valve-regulated batteries.

Obviously the float life depends on the battery temperature, too. Figure 17.18 indicates the life results of an accelerated test. In the solid line the values achieved between 50° and 70°C are plotted. The charge voltages were adapted according the values in Figure 17.14. The results follow very well the Arrhenius equation since a temperature increasing of 10°C decreases the float life always to 50%. The extrapolation indicates an average float life at room temperature of 10-12 years, which is identical with practice.

According to the usage of antimony-free grid alloys, the self-discharge of valve-regulated batteries is extremely low. Figure 17.19 indicates values of a long-term test, and it is obvious that the self-discharge decreases with increasing time. Even after a

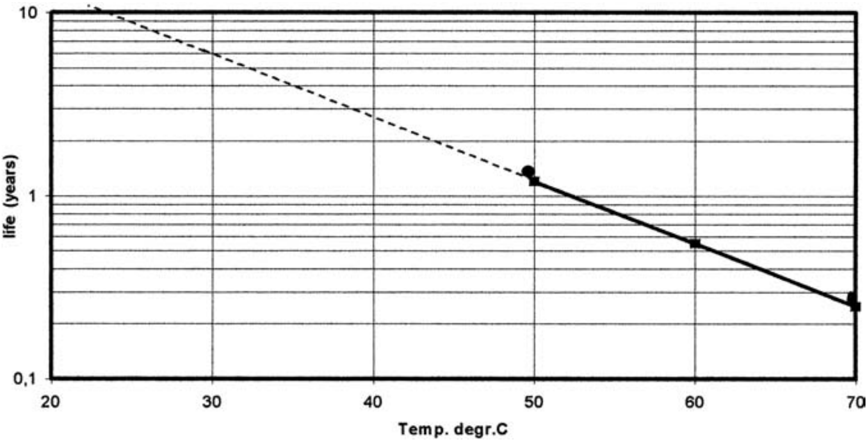

Figure 17.18 Influence of temperature on float life of valve-regulated gel batteries.

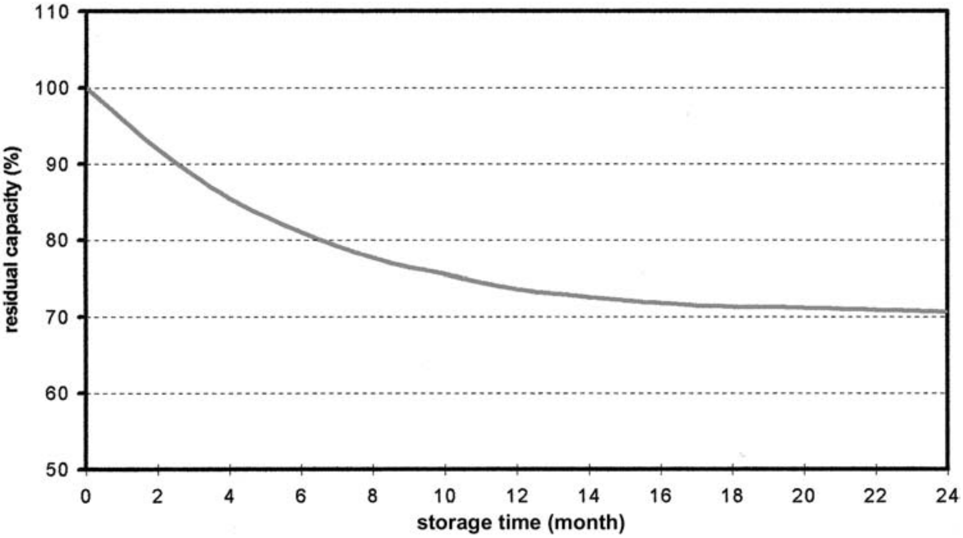

Figure 17.19 Self-discharge of 12-V 100-Ah gel batteries at room temperature.

storage time of 2 years, the residual capacity of gel batteries is still 70%, so that these batteries can be used without recharging even after 2 years storage.

17.5.4 Deep Discharge Ability

Conventional lead-acid batteries are sensitive against deep discharging and should never become fully discharged. After a complete discharging and the subsequent recharging of flooded batteries, often short circuits from lead dendrites growing from the negative to the positive plates are the result. The reason is that by reaction of the sulfuric acid with the active masses during discharging, the electrolyte dilutes up to neutrality. Because in neutral water the solubility of lead ions is 100 times higher than in sulfuric acid, lead ions are soluted in the electrolyte. During recharging of such a battery lead is precipitated in dendrite shape at the negative plates and grows through the separators to the positive plates.

In valve-regulated batteries the sulfuric electrolyte is reacting with the electrodes, too, so that here also the same dilution of the electrolyte takes place. But in contrast to flooded batteries, because of the solidified electrolyte, the lead ions are hindered from diffusion into the cell. Thus the concentration of lead ions near the plate surface increases extremely, so that because of the solution equilibrium a further solution of lead is prevented. Therefore the electrolyte cannot become saturated with lead ions and no precipitation of lead dendrites takes place.

This deep discharge ability was one of the reasons for introducing gel batteries in several military applications, because the early end of life of batteries because of deep discharging is a very frequent failure.

During recharging, deep discharged batteries have a different behavior than normal discharged batteries. Because of the very high resistance of the diluted electrolyte the initial current during recharging starts extremely low until enough acid is formed by charging. Then because of the higher conductibility of the electrolyte the charging current increases very steeply. The time for current increasing at charging of deep discharged valve-regulated batteries can last up to 1 or 2 hours.

17.6 BATTERY TYPES AND APPLICATIONS

Valve-regulated lead-acid batteries are used today in almost all applications which are applicable for conventional lead acid batteries. Since these batteries' generation was basically for portable batteries, this is still a market today, for instance in the medical area. Larger types, which were developed about 20 years ago, have a wide field in military applications. Since the 1980s modern tanks and military shelters have been equipped with the 123-V 100-Ah NATO type. Its advantage besides the high deep discharge ability is the maintenance-free behavior, especially due to the limited space conditions in modern tanks.

Figure 17.20 shows modern gel batteries in tubular plate construction as single cells for float application. Those batteries are used today in emergency equipment as well as for many uninterruptible power supply (UPS) applications.

Figure 17.20 Valve-regulated OPzS batteries: Dryfit A600 in gel technology.

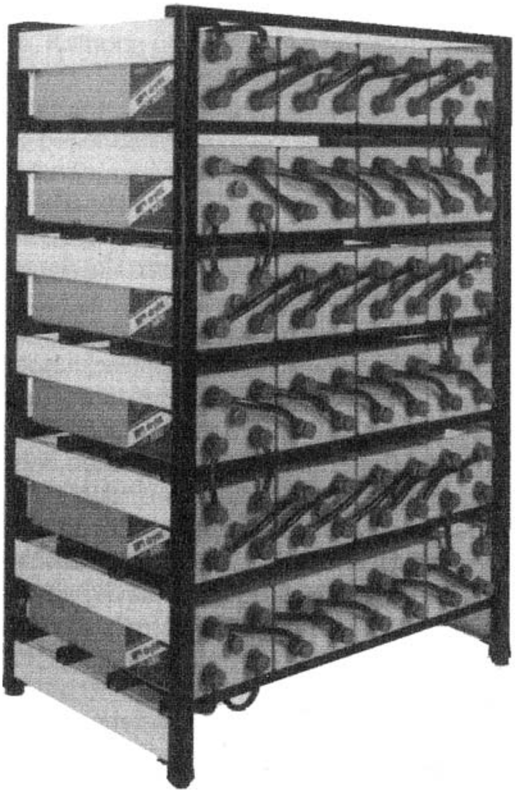

Figure 17.21 48-V battery for emergency power: Dryfit A600;–Horizontal.

Another advantage of valve-regulated batteries is the possibility for horizontal installation. Together with the low requirement for ventilation for valve-regulated batteries, this is a possibility for saving expensive space in the battery rooms (see Figure 17.21).

17.7 STANDARDS

Today the following international and European standards for valve-regulated lead-acid batteries are valid:

- IEC 61056-1: Portable lead-acid cells and batteries (valve-regulated types).
- EN 61056-1 Part 1: General requirements and methods of test.
- IEC 61056-2: Portable lead-acid cells and batteries (valve-regulated types).
- EN 61056-2 Part 2: Dimensions, terminals, and marking.
- IEC 61056-3: Portable lead-acid cells and batteries (valve-regulated types) and Part 3: Safety requirements.
- VG 96924: Portable lead-acid cells and batteries for military applications.

These standards describe the essential properties of valve-regulated batteries together with construction details and the test methods and technical demands for batteries of this technology.

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18

Lithium Batteries: The Latest Variant of Portable Electrical Energy

W. JACOBI

18.1 INTRODUCTION

During the last two decades of the 20th century the lithium battery technique played a more and more important part in the market,[1] at first for the more expensive special applications as, e.g. the military and air- and spacecraft technologies. Its technique is one of the more recent results of research and development in the fields of applied electrochemistry. New products like lithium batteries were accessible because of the progress in chemistry, physics, materials sciences, analytics, measurement and control technology, and finally production technology, leading to something new even if this was based on old ideas.[2]

An important stimulus for the new batteries was the need for small and lightweight energy sources for portable electronic devices, which have become smaller and smaller by the tremendous progress of miniaturization in our electronic age. So the scientifically and technically manageable product found its wide market. The miniaturization of consumer electronics and their mechanical parts has to be addressed first.

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[1] The extensive overviews of Refs. 1, 5, 6, and 9 are recommended to everybody who is interested in more electrochemical and technical details. In the past the battery industry regularly reported on lithium batteries in Boca Raton, Florida, too (10).

[2] The history of the lithium technology was described in more detail by Klaus Eberts in Ref. 11. Several of his figures have been adopted in this article.

Some desirable or necessary applications became accessible for the first time by lithium batteries: e.g. the cardiac pacemaker requires batteries with negligible self-discharge and extremely high reliability for service periods of 5 to 10 years. A control and display unit may be powered for all its service life of about 10 years by only one (primary) battery, which needs not to be changed before the whole unit is replaced at the end. Lithium batteries are able to power portable radio tranceivers under deep arctic temperature conditions for weeks and months. Modern handheld mobile phones and computers are usable for (many) hours with their lightweight and small rechargeable lithium accumulators.

In the following article we are first going to define what "lithium battery" means. The general advantages of its technology will then be presented. Related mainly to the non-rechargeable lithium batteries, the chemistry and physics of anode, cathodes, and electrolytes are described showing the details of the specific lithium technology. Selected examples of lithium primary batteries, which have been on the market for a long time, allow us to explain the details of the various technical ways of their realization.

Following the primary batteries we deal with (rechargeable) secondary lithium batteries, which within the last decade found their specific markets. Examples of them will be described. Finally we will see which special components within the battery system are needed, preferably when high rate versions are called for, which procure the desired reliability and safety, and how – according to the battery type – suitable ways are used for their disposal after the end of their life.

18.2 THE NAME "LITHIUM BATTERY"

The lithium battery family got its name from the metal of the anode (negative electrode), lithium, which is the most lightweight metal, the third element of the periodic system just behind hydrogen and helium. The Li/Li^+ electrode is positioned at the extreme negative end of the system of electrochemical elements. If combined with counter-electrodes of a far positive potential, the lithium electrode produces a very high open circuit voltage (OCV) and thus also a very high energy content in the respective galvanic cells. Lithium is used for anodes as pure metal, alloyed with other suitable metals, and as intercalation compounds. In practice, together with lithium, a multiplicity of cathodic (positive electrode) materials (see Table 18.1) can build an electrochemical energy store, whereas the requirements for primary and secondary applications are different only in part. Figure 18.1 shows the discharge curves of a selection of primary systems, which were then commercially available. Some of them reached an enduring market position; others were hardly more than prototypes or small series products.

The variety of electrolytes and electrolytic mixtures is comparable to that of the cathodes they are used for. The wide variety of applications may be recognized from the capacity range of industrialized products that reaches from a few mAh up to 10,000 Ah (Figure 18.2). The voltage of lithium cells is found between 1.5 and 4 V depending on the cathodic material used (Figure 18.1).

Production and handling of lithium batteries require special techniques on account of the specific features of the lithium metal and of some of the related cathodic substances. Here one has to deal primarily with the reactivity of lithium

Table 18.1 Classification of lithium primary batteries according to cathodes and electrolytes.

Classification	Electrolyte	Power	Capacity (Ah)	Temperature range (°C)	Shelf life (years)	Typical cathodes	Voltage (V)	Characteristics
Solved cathodes (fluid, gas)	Organic or inorganic	Medium to high W	0.5–20,000	−55–70 (150)	8–10	SO_2	3.0	High energy, high power, good deep temperature capability, long life
						$SOCl_2$	3.6	
						SO_2Cl_2	3.9	
Solid state cathodes	Organic	Low to medium, mW	0.01–10	−40–55 (200)	5–8	CrO_2	3.6	High energy, medium to low power, no internal overpressure
						V_2O_5	3.3–2.3	
						Ag_2CrO_4	3.1	
						MnO_2	3.0	
						$(CF)_X$	2.6	
						S	2.2	
						$Cu_4O(PO_4)_2$	2.2	
						CuS	1.7	
						FeS_2	1.6	
						FeS	1.5	
						CuO	1.5	
						$Bi_2Pb_2O_3$	1.5	
						Bi_2O_3	1.5	
Solid electrolyte	Solid	Very low μW	0.003–5	0–100	10–25	J_2	2.8	Very long life, very safe, very low power
						PbJ_2	1.8	
						PbS	1.8	

Source: Ref. 3.

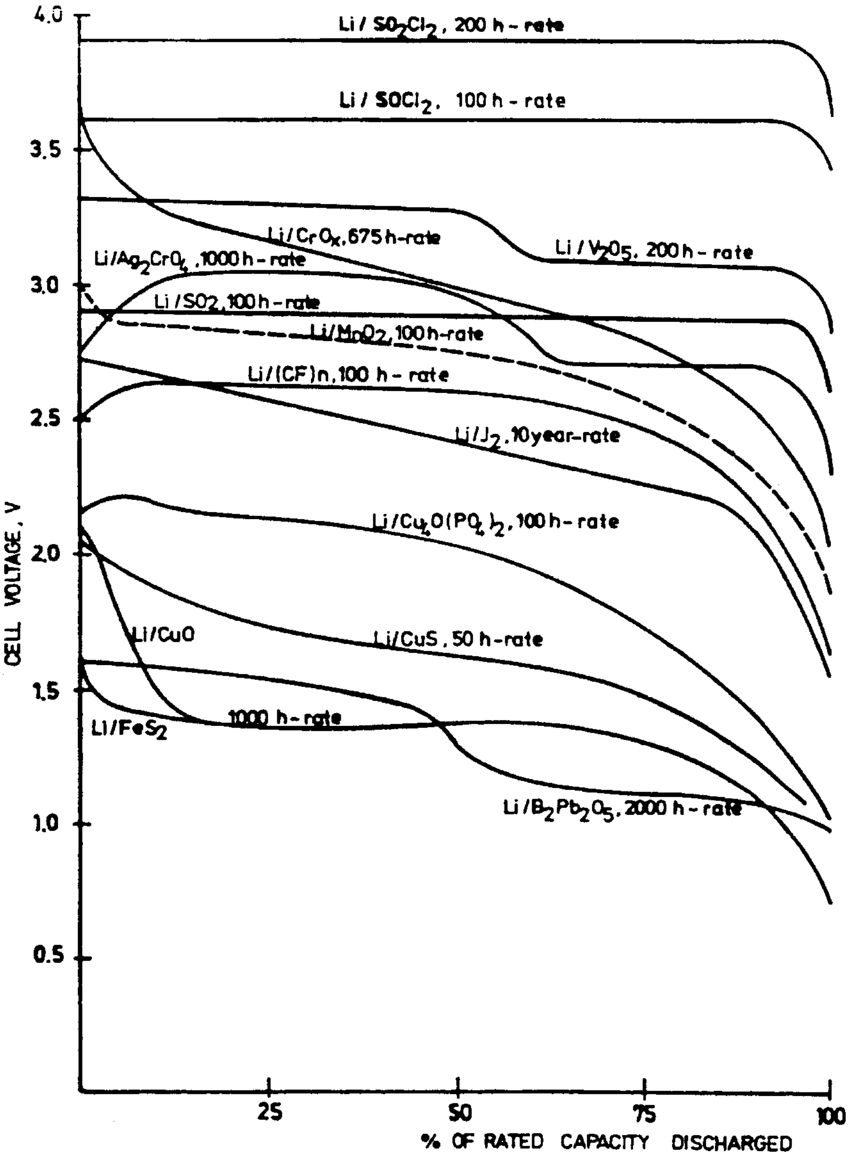

Figure 18.1 Discharge graphs of various lithium primary batteries. (From Ref. 3.)

with humidity and the main constituents of the atmosphere, i.e. nitrogen, carbon dioxide, and oxygen.

18.3 THE LITHIUM BATTERY'S SPECIAL ADVANTAGES

For defined applications lithium batteries show remarkable advantages if compared with traditional primary and secondary batteries.

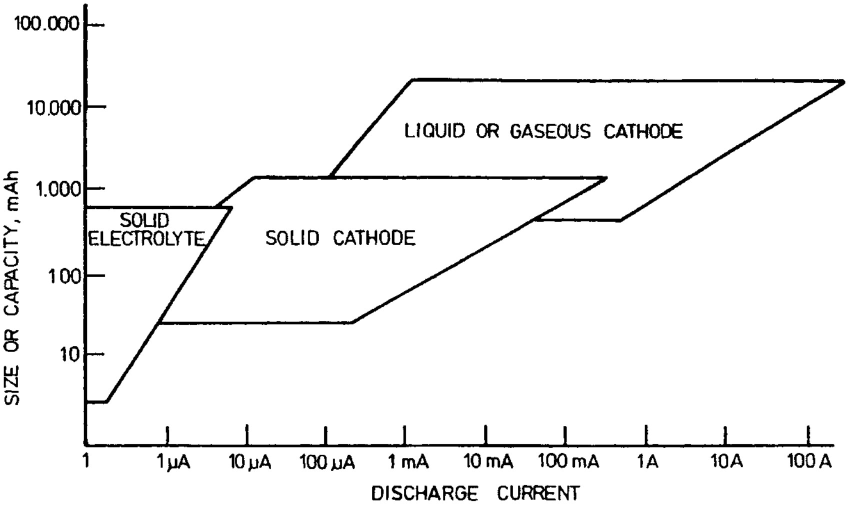

Figure 18.2 Typical regions of performance of lithium primary batteries by type of electrolyte and cathode (the upper right region has to be broadened up to 10,000,000 mAh at 10,000 A.) (From Ref. 3.)

18.3.1 High Cell Voltage

Most lithium battery systems show a cell voltage in the upper range of 1.5 to 4.0 V or even higher. This alone is an advantage with regard to the energy density and specific energy of those cells. So in many cases only one lithium cell suffices where otherwise two or three conventional Leclanché or alkaline cells are necessary.

18.3.2 Energy Content by Weight: Specific Energy

The mass related (gravimetric) energy content, the 'specific energy' (SE) of lithium batteries, is 100 to 500 Wh per kg depending on system and cell type. Preferably portable devices profit from a lithium power supply. For comparison: classic lead-acid batteries show a specific energy between 35 and 55 Wh/kg and NiCd batteries, a bit more powerful, from 50 to 70 Wh/kg. The said higher (lithium) values have, however, been only realized by primary systems until now.

18.3.3 Energy Content by Volume: Energy Density

The volumetric energy content, mostly understood as the 'energy density' (ED), goes from 300 to 1300 Wh/L. Lithium batteries therefore require less space than conventional battery systems. Leclanché cells, for example, deliver 165 and alkaline cells 330 Wh/L.

18.3.4 Loadability

One can choose between lithium primary batteries tailor-made as high rate batteries with a very low resistance for high loads or with a high resistance for low rate long-time applications. Until now secondary systems have been available only in the low capacity range for small and medium loads, i.e. with higher resistance.

18.3.5 Discharge Characteristic

Some lithium systems show an especially flat and stable curve (voltage against time) for the discharge of the whole capacity. This supports electronic devices which are designed for little tolerances of their feeding voltages.

18.3.6 Deep Temperature Capability

These batteries may be stored and operated within an extremely wide temperature range. For the first time especially the deep temperature range of -10 to -40 and even $-55\,^{\circ}\mathrm{C}$ can be supported by them without any additional means such as heaters or special insulation.

18.3.7 Shelf Life

Most of the lithium primary batteries may be stored for over 10 up to 20 years with negligible self-discharge, so that they still deliver most of their nominal capacity. They are continuously active, i.e. at all time ready for service. At normal temperature storage only 5 to 10% self-discharge after 10 years is typical.

18.3.8 Environmental Compatibility

If compared to metals used for common batteries such as lead or nickel and cadmium, lithium is not as poisonous as these to biological systems. Disposal of used lithium batteries is therefore a smaller problem.

18.4 CHEMISTRY AND PHYSICS OF LITHIUM PRIMARY BATTERIES

18.4.1 Properties of Anodic Metal Lithium

As can be seen by comparison with some other anodically used metals, lithium metal is the anodic material with the highest capacity and energy contents related to weight (Ah/kg and Wh/kg). It is number three in the periodic system of elements after hydrogen and helium. It is the most lightweight of the lightweight metals, the alkali metals. According to the rules of chemistry it behaves similarly as the other metals of the same column of the periodic system, sodium and potassium. In the electrochemical series of elements, which represents a measure of how 'easily' metals and other redox systems may offer or attract electrons, lithium occupies the extreme left, or negative, position. The electrical potential of the redox system Li/Li^+ related to the standard hydrogen electrode is −3.040 V.[3] That means that the lithium atom most readily gives up its outer valence electron. Combined with a suitable cathodic, i.e. electron-attracting, material it results in a high cell voltage. The complete cell reaction delivers an especially high amount of energy per formula turnover. So lithium batteries are ‘high energy’ batteries.

The silver-white lithium metal is soft and ductile, similar to lead and can be extruded or rolled into thin foils very easily. As long as it is not covered too much by passivation layers it may be welded simply by pressure in cold state and also onto copper as necessary, for example, for attachment of current collector tabs to the lithium electrode. Lithium readily reacts with water and air, similar to the other alkali metals, but not exactly as spontaneously and vigorously as its homologize sodium and potassium. Nonetheless the pure metal requires climate chambers of extremely dry air for handling.[4] In normal atmosphere on a fresh metallic surface of lithium a protective layer grows up from lithium hydroxide, lithium oxides, and lithium carbonate and – at normal humidity (water acts here in a catalytic manner) – mostly from the nitrogen compound Li_3N. These lithium compounds generate an extremely dense reaction layer, a so-called passivation layer, which is generally well known especially from aluminium and which in turn gives the essential condition for the technical applicability of aluminium. Without that passivation layer, a component made of aluminium would be destroyed very quickly under atmospheric conditions.[5] The lithium’s capability for passivation is advantageous for the said long shelf-life of lithium (primary) batteries. Also the concept of the fluid cathodes is possible only by passivation. Of course lithium as the pure soft metal is of no common mechanical use as aluminium.

So the very important advantage of the long shelf-life of lithium batteries depends on both its passivation ability not only in atmosphere, but also in suitable electrolytes. In spite of the passivation film the lithium electrode may be ‘activated’ quickly and easily: On an electrical load the layer breaks down very quickly within seconds or fractions thereof. High current densities may then be realized. On the other hand the passivation film in a cell without load hinders self-discharge by unwanted side reactions of the anodic metal with components (or even contaminants) of the electrolyte. This strongly hindered but not absolutely excluded self-discharge of cells not under load during shelf-life has to be understood as the further growth of the passivation layer, which proceeds as a solid-state reaction only extremely slowly. So shelf-lives of 10 to 20 years are possible under consumption of only 10 to 20% of the active metal. Depending on the special battery system, the

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[3] The potential of a single electrode is defined as the energy or work to be done for the transport of an elementary electrical charge (massless) from the virtual free space into the phase under consideration. This cannot be measured, as everybody knows. It normally is handled as the difference between the potentials of the electrode and a reference electrode, most often the standard hydrogen electrode (SHE).

[4] The standard condition is at a dew point (water) of −30 °C. This corresponds to water in air concentration of less than 2% of relative humidity at normal temperature.

[5] A passivation layer is a dense mechanically stable layer from compounds of the metal being protected and, e.g., oxygen, hydroxyl ions – from water – carbon dioxide CO, sulfuric acid H_2SO_4, and other components, preferably from the air. This passive layer – once grown – keeps off the said reactants from further direct access to the metal. Further reaction is possible only as ‘solid state reaction’, which proceeds by several powers of ten more slowly than the first or ‘direct’ reaction of the unprotected surface.

passivation layer consists of lithium chloride, lithium dithionite, lithium hydroxide, or also of lithium alcoholates, carbonate, and others, i.e. generally lithium and parts of the actual electrolyte mix.

Lithium is most often refined from the mineral spodumen.[6] Similarly to aluminium the refinement is done by electrolysis. It is consequently rather expensive but until now its availability has not been limited.

The energy density, measured as Wh/L, of the lithium electrode alone is not especially high. It is even slightly lower than the corresponding value of the classic battery material lead and remarkably lower than that of aluminum.[7] The reason is that even at extremely different atomic weights the atomic volumes of these three are relatively similar at about 10 to 20 cm^3/g atom, but during discharge lithium provides only one, lead two, and aluminium three electrons per metal atom. For comparison Table 18.2 gives a collection of the so-called equivalent volumes[8] of lithium and some other anodic metals which were used traditionally for batteries and accumulators. On the other hand the specific energy of lithium, measured as Wh/kg, is on top of the anodic materials considered. The energy content – both ED and SE – of a complete cell depends of course on the particular cathodic partner and type of housing and packing. So the theoretical data of the anode alone may not be overestimated.

18.4.2 Electrolytes for Lithium Batteries

18.4.2.1 Organic Solvents with Ionic Salts

The electrolyte of a battery[9], or rather of an electrochemical cell, is the mediator between the reactions in parts which proceed at the two electrodes and which deliver electrical energy out of the combined chemical process. Via the electrolyte the different levels of electrical charge at cathode and anode in a cell under load are levelled out. Its conductivity essentially contributes to the cell's energetic efficiency. For many lithium systems the electrolyte is made from an organic solvent and a salt solved in it (electrolyte salt) – usually a lithium salt. The following requirements rule the choice of the electrolyte for a lithium battery (see Table 18.3):

The dielectric constant (dc) of the solvent has to be as high as possible. The higher the dc, the better the electrolyte salt is solvated, i.e. solved and dissociated.

In order to have solvated ions of the electrolyte salt as mobile as possible and so to get a resistance for the current flow as low as possible, the viscosity of the electrolytic fluid has to be as low as possible.

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[6] Spodumen or triphane $\mathrm{LiAl(SiO_3)_2}$ belongs to the catena silicates or pyroxenes. It is found in pegmatites in the United States and also in Scotland and Austria.

[7] Aluminum as an anode for battery applications in the field of marine and standby power was only experimentally investigated recently.

[8] The equivalent mass of an ion is defined as the fraction of the atomic or molecular weight of this ion which carries one electrochemical equivalent, i.e. 96,450 Coulomb (Asec) of electrical charge. The equivalent volume is defined correspondingly.

[9] According to the official version the smallest unit of an electrochemical storage medium is a (galvanic) 'cell'. Several cells make a 'battery'. In this article 'battery' is often used colloquially when the term 'cell' would be more correct.

Table 18.2 Specific data to determine the equivalent volumes of some anodic metals for batteries.

Anodic metal Maximal oxidation state	Li Li^+	Pb Pb^{2+}	Al Al^{3+}	Zn Zn^{2+}	Na Na^+	Cd Cd^{2+}
Atomic weight (g)	6.939	207.19	26.98	65.37	22.99	112.40
Equivalent weight (g)	6.939	103.60	8.99	32.69	22.99	56.20
Specific gravity (g/ccm)	0.534	11.34	2.702	7.14	0.97	8.642
Equivalent volume (ccm/equiv.)	12.99	9.14	3.33	4.58	23.70	6.50

Generally the electrolyte of an electrochemical cell must not be electrolyzed, i.e. degraded by the potential difference, the voltage between the electrodes. Aqueous electrolytes with the degradation voltage of 1.23 V for the water molecule have to be excluded regularly from use in lithium cells with cell voltages between 2.5 and nearly 4.5 V. The scheme of Figure 18.3 explains this with the model of the molecular orbital (MO) and band theory[10]. The oxidation potential of the electrolyte has to be higher than the potential of the anode (or than the Fermi energy of the anodic metal) and the reduction potential has to be lower than the corresponding potential of the cathode (Fermi edge of the cathodic material). Where this requirement is not fulfilled, the thermodynamically demanded reaction between electrolyte and electrodes has to be blocked at least kinetically as realized in the lead-acid accumulator with its aqueous sulfuric acid electrolyte. The reactivity of the electrolyte's components against lithium (and the cathodic counterpart) has to be negligible to use the electrode quantitatively for its electrochemical purpose and not to get it consumed in a useless manner by self-discharge. A special case is the passivation of lithium in some systems under open circuit conditions (cell without load) and its electrochemical reactivity, i.e. discharge ability under load. This passivation is maintained by a very thin but very stable layer of reaction products between the lithium and one of the electrolyte's components. This layer then protects the bulk metal against further reaction. The passivation's barrier can be overcome only very slowly as is normal for a solid-state reaction. The electrochemical efficiency of the lithium anode for some lithium primary systems is within 60 to 90%. In any case water and alcohols, i.e. all protic solvents, have to be excluded from lithium cells, because they are not able to produce a sufficiently stable and really passivating layer.

The electrolyte should show a melting or solidification point as low as possible together with low viscosity even at low temperatures for high conductivity and high power. Typical limits for discharge of lithium batteries are between −40 and −55 °C.

Conductive salts for the electrolyte mixture are to be chosen with preferably low lattice energy. So solvation is easy and a high percentage of the solute might be dissociated in the solution. For most systems salts of lithium are chosen which are combined with big complex anions such as, e.g. lithium perchlorate $LiClO_4$, lithium tetrafluoroborate $LiBF_4$, lithium hexafluoroarsenate $LiAsF_6$, lithium hexafluoropho-

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[10] HOMO = highest occupied molecular (or atomic) orbital – here of oxygen, LUMO = lowest unoccupied molecular (or atomic) orbital – here of hydrogen. The difference between them is the decomposition voltage – here of water.

Table 18.3 Physical data of pure solvents used for lithium cells.

Name	Abbreviation	Boiling point (°C)	Melting point (°C)	Dielectric constant	Spec. gravity ($g\,cm^{-3}$)	Viscosity (cP)
Acetonitrile	AN	81.6	−45.7	35.95	0.777	0.34
γ-butyrolactone	BL	202	−43	39.1	1.13	1.75
1,2-dimethoxiethane	DME	83	−58	7.2	0.859	0.46
N,N-dimethyl formamide	DMF	153	−61	36.7	0.94	0.80
Dimethyl sulfoxide	DMSO	189	18,5	46.6	1.10	1.96
1,3-dixolane		78	−95		1.06	
Ethylenecarbonate	EC	248	36	89	1.32	1.90 (40 °C)
Methyl formiate	MF	31.5	−99	8.5	0.974 (20 °C)	0.35 (20.15 °C)
Nitromethane	NM	101	−29	36	1.13	0.63
Propylene carbonate	PC	241	−49	64	1.19	2.53
Phosphoroxichloride		105	1.2	13.7	1.645	1.06
Thionylchloride		78.8	−105	9.05 (22 °C))	1.63	0.60
Sulfurylchloride		69.4	−54.1	9.15 (22 °C)	1.65	0.67
Tetrahydrofurane	THF	66	−65	7.6	0.89	0.46

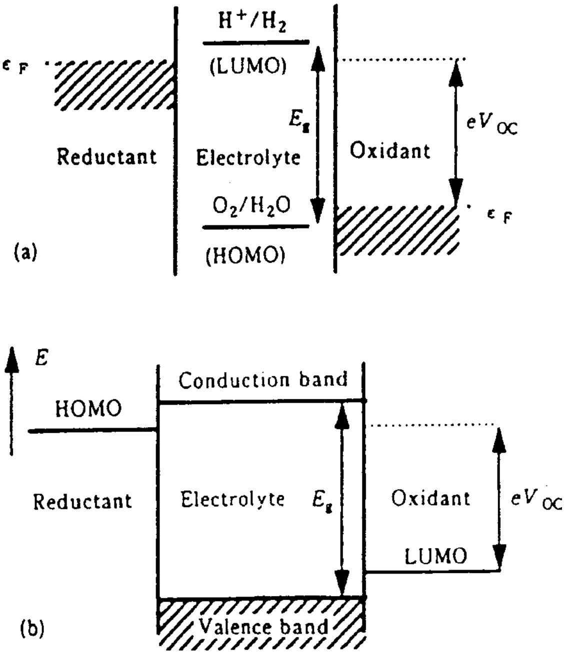

Figure 18.3 Position of the decomposition energies of electrolytes relative to the potentials of the anode (reductant is oxidized by discharge) and the cathode (oxidant is reduced by discharge) of a galvanic cell for (a) solid electrodes with fluid electrolyte and (b) fluid electrodes with solid electrolyte. (From Goodenough in Ref. 1.)

sphate $LiPF_6$, lithium tetrachloroaluminate $LiAlCl_4$. These anions seem to be big ones according to the simple formula. But in the solution these negatively charged ions are nonetheless relatively small because they are able to attract only a thin layer of "solvate ions". Consequently they show a high mobility and hence a good conductivity. The contrary is valid for the small central ion of lithium that is surrounded by an over-proportionally thick layer of solvate molecules, thus showing a reduced mobility and conductivity. In practice often electrolyte solutions with 1 mole electrolyte salt per liter are used.

But also under optimal conditions these electrolytes based on organic solvents yield a conductivity of about $10^{-2}\,\text{ohm}^{-1}\,\text{cm}^{-1}$, which is by more than one power of ten lower than in alkaline or acidic aqueous solutions.

18.4.2.2 Inorganic Electrolytes Acting as Cathodes

This class of electrolytes gives the technology of lithium primary batteries a special exotic attraction. The fluid electrolyte mixture acts as the media of transfer of electric charges between anode and cathode as described above. In addition it also contains the cathodic active substance, which is in direct contact to the anodic counterpart, the lithium metal, but nonetheless reacts separately in a distance from the anode at a cathodic support electrode by consumption of electrons from the outer circuit. This paradoxical behavior is possible because of the "cathode's" ability to create a passivation layer on the lithium surface, which protects the metal against further attack of the spontaneously (thermodynamically favored) reacting “cathode” and against quantitative self-discharge. On the other hand the passivation layer cracks if the cell is electrically loaded.

Also these inorganic electrolytes or their mixtures with organic solvents have to be polar, i.e. be constituted from molecular dipoles, and to show a high dielectric constant, again for a high ability to solve and dissociate the lithium electrolyte salt and the products of the discharge reaction.

The electrolytes acting as cathodes are mixed with a suitable electrolyte salt and with or without an organic co-solvent. The most important examples are thionylchloride with lithium chloride and sulfur dioxide with acetonitrile and lithium bromide. The organic co-solvent again ensures low viscosity and low melting points for good deep temperature operation.

With highly porous cathodic conductors battery systems with inorganic cathodic electrolytes may deliver especially high power. These systems, which have been proved for years, are operated under moderate ($SOCl_2$: about 0.5 to 5 bars) and high overpressure (SO_2: 4 to 32 bars) in the cells.

18.4.2.3 Solid Electrolytes

Solid electrolytes generally have a far lower conductivity than fluids because of the low ionic mobility, also in specially selected ionic crystals and other solids. The higher resistance in such a cell allows therefore only very low loads. But otherwise side reactions such as self-discharge – provided anode and cathode are also in the solid state – run only extremely slowly if at all. From this basic low reactivity such battery systems show especially high reliability also during shelf-lives and operational times of many years.

One example is the lithium iodide electrolyte in a typical cardiac pacemaker battery. Another one is the mixture of lithium halides with – for immobilization – magnesium oxide in some thermal batteries, and a further one a mixture of lithium iodide with aluminium oxide or silica for some memory back-up systems.

18.4.2.4 Electrolytes from Molten Salts

A difference between a molten substance and another fluid chemical of course simply depends on the standpoint: Here we deal with substances which at normal conditions – such as normal temperature – are in the solid state and are fluid only at elevated temperatures when the battery is to operate. So we get battery systems whose electrolyte in the solid state at normal temperature shows an extremely low conductivity so that all self-discharge and other undesired side reactions are in fact frozen in.

With ‘thermal batteries’ such electrolytes are used combined with a tailor-made rapidly acting pyrotechnic heating device. Typical temperatures of operation lie between 200 and 500 °C, depending on the system. A molten salt electrolyte is used, for example, in the lithium iron disulfide battery which is described below.

18.4.3 Cathodic Materials

Some substances commonly used for cathodes are shown in Table 18.4 explaining some important features.

18.4.3.1 Solid Cathodes: Intercalation Compounds and Others

Lithium intercalation compounds are preferably suitable for use as cathodes. The tiny lithium ion is easily inserted into and released from a certain number of inorganic solids at a potential that lies at positive values on the electrochemical series far away from the Li/Li^+ electrode. The lithium ion's small volume affects the host structure only slightly. The intercalation is merely not hindered so that this process is mostly reversible and hence suitable for rechargeable batteries.

18.4.3.2 Fluid Depolarizers

Table 18.4 also contains those substances, which are used in the fluid state at normal temperatures for cathodes. Their features were already described when we dealt with them as electrolytes. They are used with and without a co-solvent, they build up on the lithium metal's surface stable passivation layers which are cracked only under electrical load when during discharge lithium ions leave the surface. These "cathodes" are especially powerful if combined with highly porous cathodic conductors.

When a co-solvent is not needed – as in thionylchloride batteries – the system with the fluid depolarizer realizes an especially high energy density because this electrochemically non-active component of the co-solvent is avoided.

18.5 DESIGNS AND TECHNOLOGY OF PRIMARY LITHIUM BATTERIES

Lithium cells have to be hermetically sealed. Intrusion of atmospheric humidity is not allowed. On the other hand some of the cell components are not allowed to escape because of their aggressiveness and their high vapor pressure. This is obvious for sulfur dioxide for instance. The cell geometry is governed by mechanical requirements both from the standpoint of the manufacturing technique and the application. There are prismatic, cubic, and flat formats in different dimensions with cubic or circle shaped electrode stacks. There are preferably round cells, which contain the electrodes either in cylindrically wound or bobbin versions. In the case of the pressurized cell types, the round can is of course the most economic version of a pressure vessel.

The lithium anode is used in the pure metallic state as thin extruded or rolled foil with a thickness down to 25 μm or as a massive block, depending on the load to be applied. In special cases the lithium is applied also in alloys or, as in rechargeable batteries, in intercalation[11] compounds.

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[11] See also the description of the rechargeable lithium batteries in Section 18.7.

Table 18.4 Physical and electrochemical data of some cathodic materials for lithium batteries.

Cathodic material	Molecular weight	Valences involved	Specific gravity (g cm^{-3})	Electrochemical equivalent (Ah g^{-1})	Electrochemical equivalent (Ah cm^{-3})	Electrochemical equivalent (g Ah^{-1})	Calc. cell voltage (against Li) (V)
SO_2	64	1	1.37	0.419	—	2.39	3.1
$SOCl_2$	119	2	1.63	0.450	—	2.22	3.65
SO_2Cl_2	135	2	1.66	0.397	—	2.52	3.91
Bi_2O_3	466	6	8.5	0.35	2.97	2.86	2.0
$Bi_2Pb_2O_5$	912	10	9.0	0.29	2.64	3.41	2.0
$(CF)_n$	$(31)_n$	1	2.7	0.86	2.32	1.16	3.1
$CuCl_2$	134.5	2	3.1	0.40	1.22	2.50	3.1
CuF_2	101.6	2	2.9	0.53	1.52	1.87	3.54
CuO	79.6	2	6.4	0.67	4.26	1.49	2.24
CuS	95.6	2	4.6	0.56	2.57	1.79	2.15
FeS_2	119.9	4	4.9	0.89	4.35	1.12	1.8
MnO_2	86.9	1	5.0	0.31	1.54	3.22	3.5
MoO_3	143	1	4.5	0.19	0.84	5.26	2.9
Ag_2CrO_4	331.8	2	5.6	0.16	0.90	6.25	3.35
V_2O_5	181.9	1	3.6	0.15	0.53	6.66	3.4

Source: Ref. 8.

For separation many systems with fluid electrolytes use a micro-porous foil from polypropylene known as Celgard®. Alternatives are fluorinated hydrocarbons (e.g. Halar®) or glass fiber nonwovens.

Cathodes are made from a paste of the cathodic active material with binders and electronically conductive additives, which are rolled onto metallic foils or exmets from nickel or aluminium. These cathodes are used as flat electrodes or in spirally wound form. The bobbin form realizes the same design in principle, but the layers of the active materials are much thicker, which in turn reduces the typical load to be applied to these bobbin cells. For fluid depolarizers the cathodic conductor often carries a mixture of carbon black with Teflon® binder, which is impregnated with catalytically active substances.

Containers of lithium batteries are mostly made from stainless steel. Depending on the internal pressure of the system, the containers are round cells of IEC standard formats or of proprietary geometry or with prismatic rectangular geometry (also button cells and circle shaped bigger cells and special geometries as for cardiac pacemakers have been realized). These cells are mostly hermetically sealed by welding or – in case of negligible inner pressure – crimp-sealed with polymer gaskets.

For the electrical contacts in many cases the metallic container is one pole and a glass-to-metal seal (or ceramic-to-metal seal) the other. The container may also have to be potential free; then both contacts are made from the glass-to-metal seals.

For batteries under overpressure and/or for high power, a pressure vent is integrated into the cell case. Additionally melting fuses or back-setting fuses – so-called thermo switches – are used. All this protects the system against overheating and uncontrolled pressure rise in case of a short.

18.6 EXAMPLES OF LITHIUM PRIMARY BATTERY SYSTEMS

Figure 18.1 and Table 18.1 give an overview on the wide variety of lithium primary systems which have been at least temporarily introduced into the market. This variety gets remarkably wider if one takes into account also all those systems which were tested on the laboratory scale but not fully developed for practical applications. A small selection of lithium primary batteries which were successful in their special markets shall be described in detail here to show some design and building principles.

18.6.1 The System Lithium/Manganese Dioxide

For this cell type the pure metallic lithium electrode – mostly as a foil – is combined with a porous manganese dioxide electrode. Therefore the cathodic mass of a specially treated manganese dioxide MnO_2 together with a binder and some carbon black for improvement of the conductivity is pasted on a metallic carrier foil. The reaction scheme shows in a simplified manner that during discharge the positively charged lithium ions set free at the anode are built into the manganese dioxide's lattice, whereas the manganese formally changes its oxidation state from positive four to three:

$$\text{Anode:} \quad \text{Li} \longrightarrow \text{Li}^+ + \text{e}^-$$

$$\text{Cathode:} \quad \text{MnO}_2 + \text{e}^- \longrightarrow \text{MnO}_2^-$$

$$\text{Cell:} \quad \text{Li} + \text{MnO}_2 \longrightarrow \text{LiMnO}_2 \quad E^\circ = 3\,\text{V}$$

In most cases a mixture of propylene carbonate and dimethoxy methane with lithium perchlorate[12] or lithium trifluoromethane sulfonate[13] as electrolyte salt is applied. Mixtures of tetrahydrofurane, butyrolactone, and dioxolane are used also. As an example of a passivation layer on the lithium metal anode in a cell with a solid cathode and a fluid organic electrolytic solvent we see here the dense and stable layer of lithium carbonate as the reaction product of lithium with propylene carbonate.

The manganese dioxide – well known already from Leclanché and alkaline cells and also existing as spinel in nature – has to be dried thoroughly for application in lithium cells. At the elevated temperatures used for the drying operation two modifications of the spinel structure can be generated: up to 250 °C the γ-phase is preferred, between 250 and 350 °C both the γ- and β-phase coexist, and beyond 350 °C the β-phase alone is stable. The geometry of both structures may be recognized in Figures 18.4 and 18.5. The intercalation of the small Li^+ ion is supported by the wider channel structure of the γ-phase. So a γ-rich substance is preferred.

Lithium/manganese dioxide cells are manufactured as button cells, round cells of the spirally wound and bobbin type, and according to the customer's requirements combined to power modules fitting individually into diverse appliances. They are delivered in steel cases in welded and crimp-seal versions. High rate types are equipped with back-setting thermo fuses and burst vents. Figure 18.6 shows a cut through of a button cell (Varta) and Figure 18.7 of a round cell (Eveready).

The batteries are applied to watches, calculators, memories, sensors, hearings aids, cameras, radios, razors, torches, and radio tranceivers and in safety and rescue equipment. Combined with lithium iodide cells (see Section 18.6.5) they also serve in the medical field for defibrillation in case of heart irregularities. Typical discharge curves for a 190-mAh button cell (Union Carbide) are shown in Figure 18.8. Figure 18.9 presents discharge curves of equivalent cells and batteries of the Leclanché (zinc/carbon), alkaline, and lithium/manganese dioxide types. Versions A and B require two cells to deliver an overall voltage of about 3 V comparable with that of one single lithium cell. Here the advantage of the higher specific energy of lithium cells is obvious besides the relatively stable voltage level during the major part of the discharge. The cells are leakproof even when crimp-sealed. The shelf-life is given as the self-discharge rate: It is about 1% per year for the crimped and 0.5% per year for the welded version. Cells and batteries may be used from −40 to +80 °C.

The lithium/manganese technology is based on the research work of Sanyo in 1975. In addition to this company and the other ones cited above we have to mention, as suppliers, all well-known Japanese companies and Rayovac, Varta, Berec, Friwo, Litronic, and Renata.

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[12] Typical data are conductivity $> 10^{-2}\ \Omega^{-1}\,\text{cm}^{-1}$ and viscosity < 3 cP.

[13] LiCF_3SO_3.

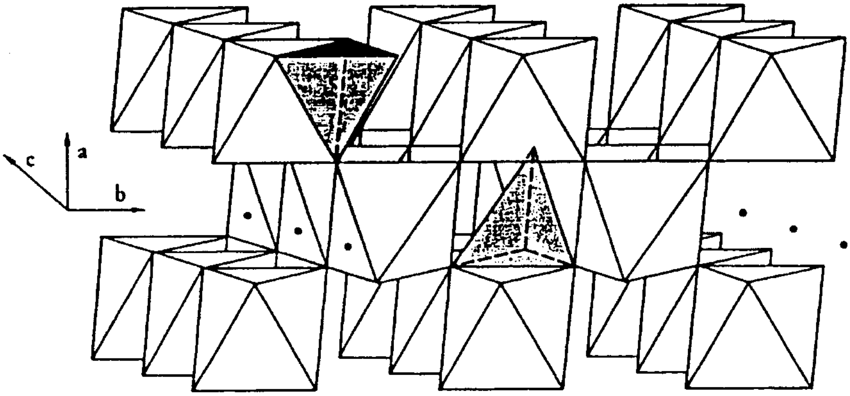

Figure 18.4 Manganese dioxide β-phase (high temperature) with single channels for incorporation of lithium. (From Ref. 2.)

18.6.2 The System Lithium/Carbon Monofluoride

The design principle of lithium/carbon monofluoride cells is comparable to that of the $LiMnO_2$ cells. The cathode however uses as its active material the said carbon monofluoride. The reaction scheme

$$\text{Anode:} \quad xLi \longrightarrow xLi^+ + xe^-$$

$$\text{Cathode:} \quad CF_x + xe^- \longrightarrow xLiF + C$$

$$\text{Cell:} \quad xLi + CF_x \longrightarrow xLiF + C(0.9 \leqslant \times \leqslant 1.2); \quad E^\circ = 3.2\,V$$

shows that during discharge the lithium ion from the anode formally reacts with the fluoride of CF_x to produce LiF and carbon. Electrons for charge equalization are provided by the outer part of the circuit for the CF system. The reaction product carbon is finally divided in the cathode. So the cathode's electronic conductivity is improved during discharge.

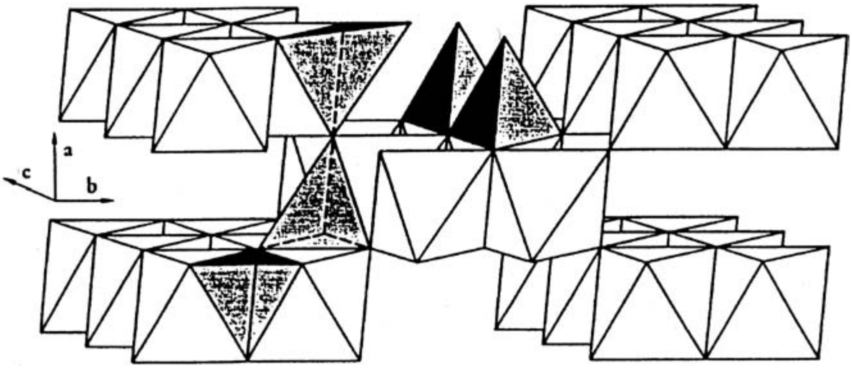

Figure 18.5 Manganese dioxide γ-phase (deep temperature) with double channels for incorporation of lithium. (From Ref. 2.)

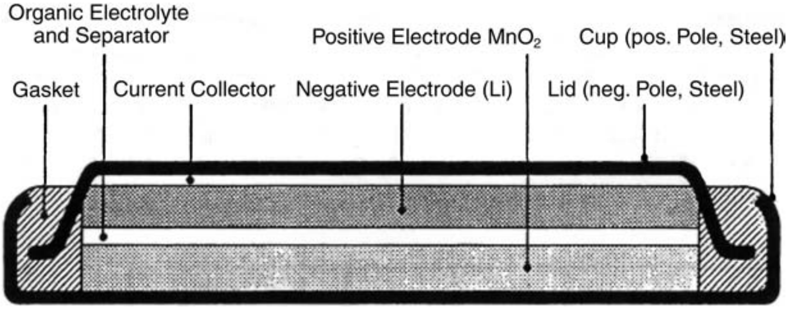

Figure 18.6 Cross-section of a lithium/manganese dioxide cell (Varta).

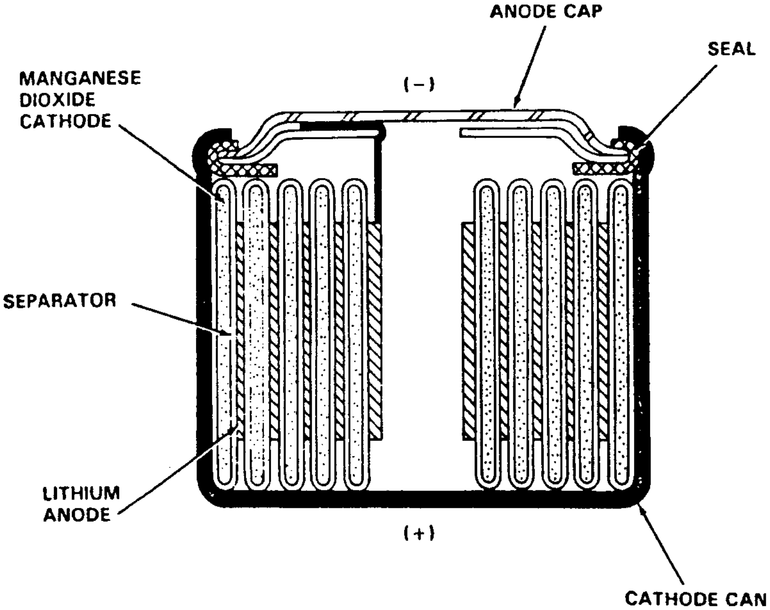

Figure 18.7 Cross-section of a lithium/manganese dioxide round cell (Eveready).

Most often a 1:1 mixture of propylene carbonate and dimethoxiethane with the conducting salt lithium tetrafluoroborate is used for the electrolyte. An alternative is lithium hexafluoroarsenate in γ-butyrolactone.

The cathodic material carbon monofluoride CF_x is made from graphite, coke, or active coal by fluorination at 200 to 800 °C as black $CF_{0.5}$ or white $CF_{1.0.}$[14] Thereby to each second or each single carbon atom one F atom is bound according to a ratio of C:F from 1:0.5 to 1:1. These substances behave similarly to PTFE. So CF_x is also used as a thermo-resistant lubricant and coating. The first cell with this

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[14] The literature refers to CF_x as compositions with $0.13 < x < 2.0$. Matsushita uses CF_x with $0.9 < x < 1.2$.

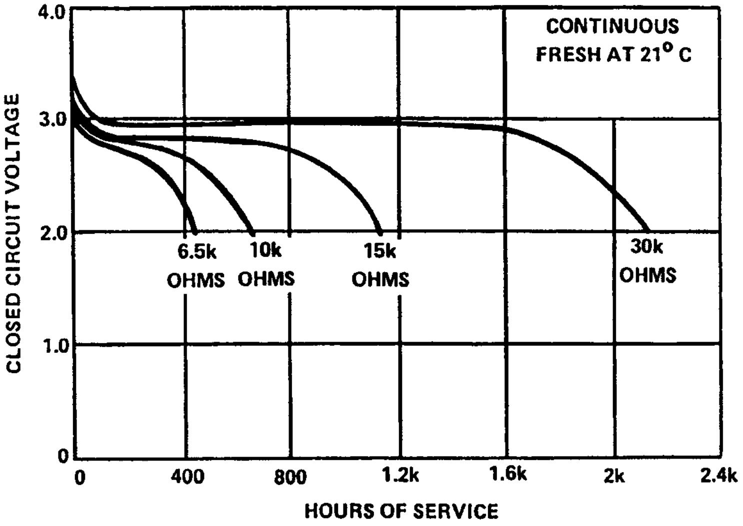

Figure 18.8 Discharge graph of a 190-mAh lithium/manganese dioxide button cell under various loads (Union Carbide).

cathodic material was developed in the early seventies by Matsushita. The capacity of a cell is proportional to the degree of fluorination. As carbon monofluoride, contrary to graphite, is a very bad electronic conductor, carbon black with some PTFE binder is added to the active CF_x mass for an enhanced conductivity. The structure of CF_x as compared to the graphitic structure is shown in Figure 18.10.

Lithium carbon monofluoride cells are manufactured as button cells, also as ultra-thin discs, as round cells, or as small "pins". Such pins (e.g. with a diameter of 2.2 mm, a length of 115 mm) are used for fishing line floats. The round cells are mostly designed as bobbin cells for low rate applications.

Indeed carbon monofluoride cells preferentially are suitable for low rate discharge as in memory back-up and other memory applications. Compared to the

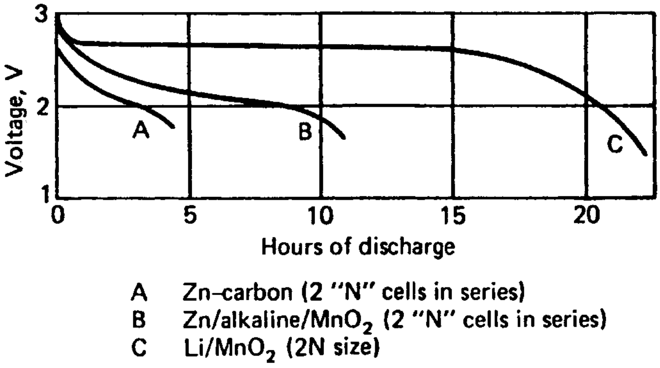

Figure 18.9 Discharge graph of old and new primary batteries: A = Leclanché, B = alkaline, C = lithium/manganese dioxide. (From Ref. 3.)

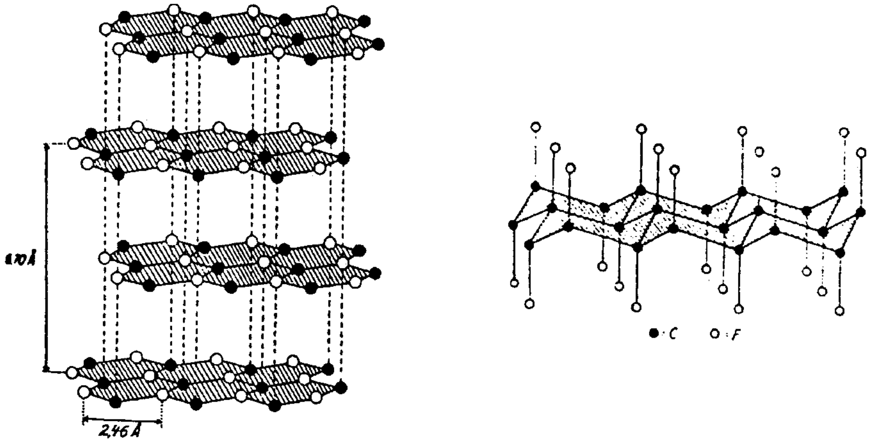

Figure 18.10 Comparison of the structures of (hexagonal) graphite and carbon monofluoride. (From Ref. 4.)

MnO_2 technology the CF_x technique is favored by a clearly higher specific capacity and energy. For CF_x a specific capacity of 2.380 Ah/L and a specific energy of 350 Wh/L are reported, whereas for MnO_2: 1.550 Ah/L and 200 Wh/L. This might be understood from the pairing of lithium and fluorine as the most extreme partners in electrochemical series. That system can also be designed especially compact. It may normally be applied from −40 to +85 °C, but cells are also known with special equipment for use at up to 150 °C. The reliability and environmental acceptability are excellent. The discharge characteristic is flat and 'hard'. So this system is a considerable competitor for the MnO_2 technique, apart from lower loadability.

A collection of typical discharge curves of a CF_x cell (C size, Matsushita) can be recognized from Figure 18.11. Figure 18.12 demonstrates how little discharge time or capacity depends on the operational temperature. The closed circuit voltages (CCV) as function of temperature, however, vary widely between 2.9 V (60 °C) and 1.8 V (−40 °C). Lithium CF_x cells are produced by Matsushita (Panasonic) and under their license by Eveready, Eagle Picher, Rayovac, Wilson Greatbatch, Duracell, and others.

18.6.3 The System Lithium/Thionylchloride

The battery system lithium/thionylchloride is the most important system with a fluid depolarizer, i.e. with a fluid cathodic substance, which offers an outstanding practical energy density and specific energy at especially high loadability.

Within the cell reaction

$$\text{Anode:}\quad 4Li \longrightarrow 4Li^+ + 4e^-$$

$$\text{Cathode:}\quad 2SOCl_2 + 4e^- \longrightarrow S + SO_2 + 4Cl^-$$

$$\text{Cell:}\quad 4Li + SOCl_2 \longrightarrow S + SO_2 + 4LiCl, \quad E^\circ = 3.2\,V$$

as reaction products in addition to lithium chloride also sulfur and sulfur dioxide are found. The sulfur is mostly related to the aspects of safe handling of these high energy and high rate systems (see below). The thionylchloride in this case is both electrolyte and cathodic material combined with lithium tetrachloroaluminate salt with concentrations between 1.0 and 1.8 molar for improved ionic conductivity. The thionylchloride itself is an acridly smelling colorless liquid, which heavily attacks the breathing system. It boils at 76 °C. It is applied in an anhydrous and pure state as for gas chromatography. The system is based on the already described paradox of the direct contact between anode and "cathode" because of the passivation layer between them. The growth of the passivation layer depends both on temperature and concentration of the electrolyte salt. It is supposed that on a very thin and homogeneous primary layer of lithium oxide or lithium carbonate the bulk reaction product of the contact with the electrolyte, lithium chloride, grows in a more porous structure as a secondary layer. Figure 18.13 shows the measured and expected capacity conservation during shelf-life of up to 10 years at 23 and 72 °C, respectively. One may see the very low effect of self-discharge, which is caused by the solid-state reaction of the passivation layer's growth. It is provided here that during the whole shelf-life there is indeed no interruption of the passivation layer by short periods of discharge.

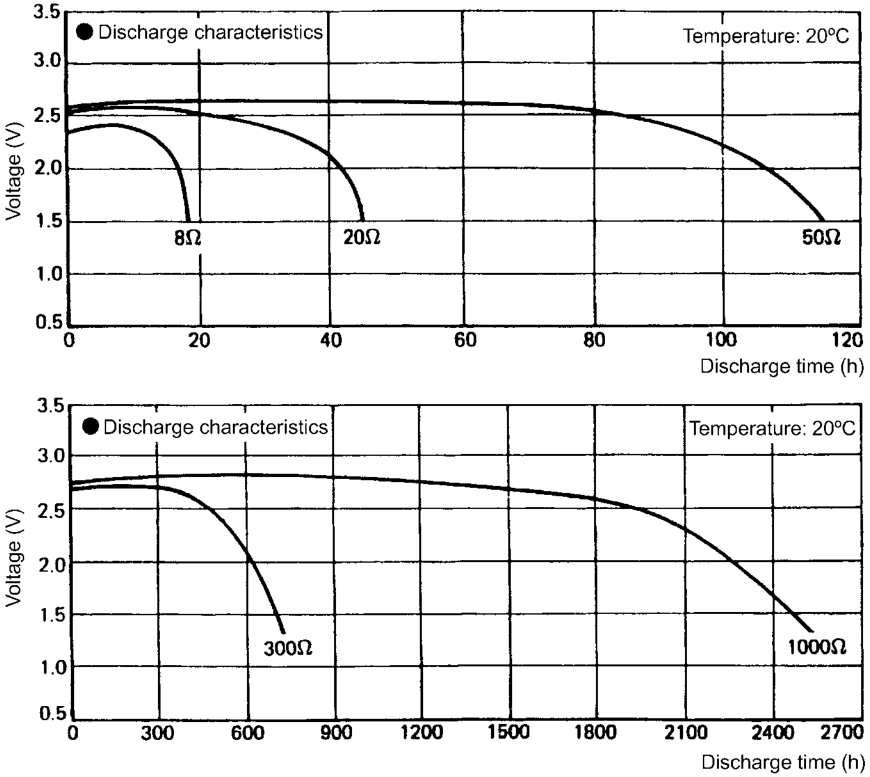

Figure 18.11 Discharge graphs of lithium/carbon monofluoride cells (C size) depending on the load (Matsushita).

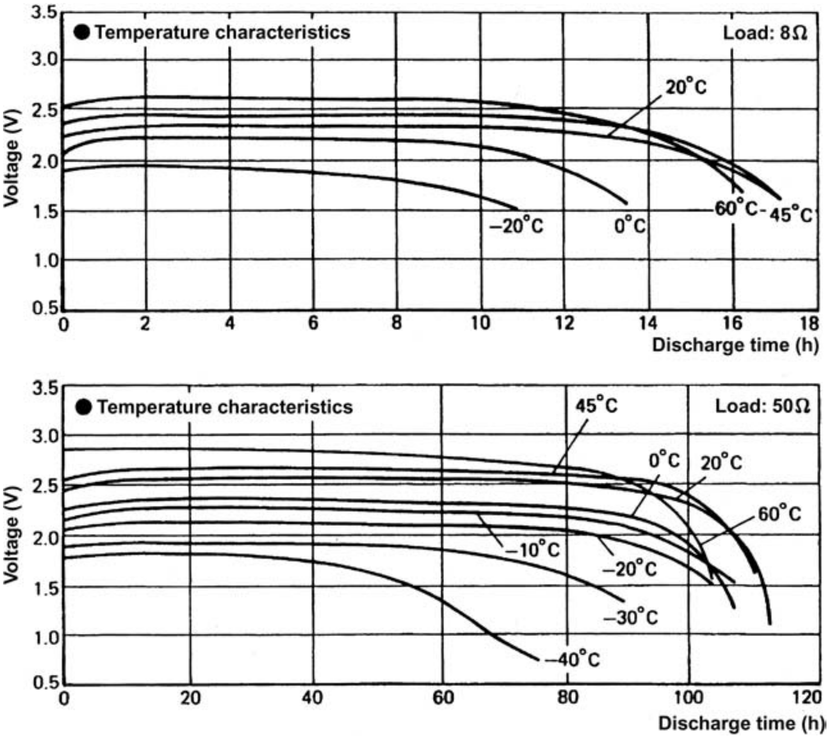

Figure 18.12 Discharge graphs of lithium/carbon monofluoride cells (C Size) depending on the temperature (and load) (Matsushita).

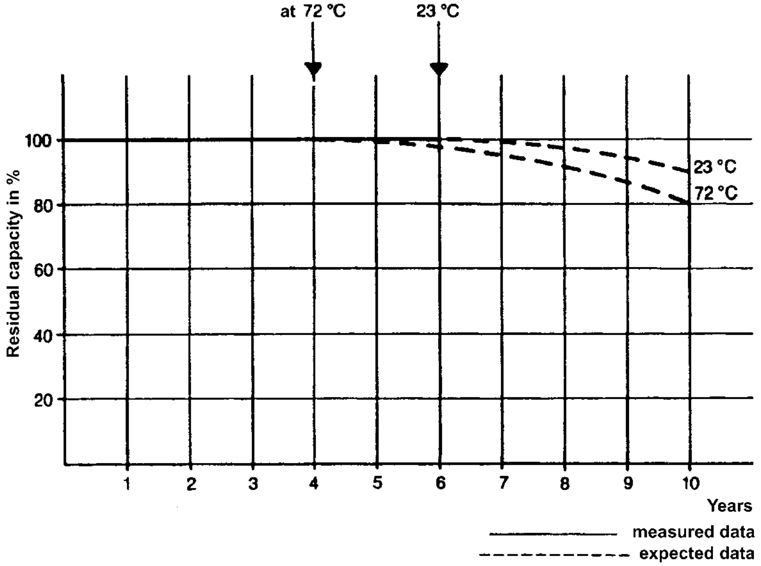

Figure 18.13 Retention of capacity of lithium/thionylchloride cells during storage at normal temperature and 72 °C (Sonnenschein).

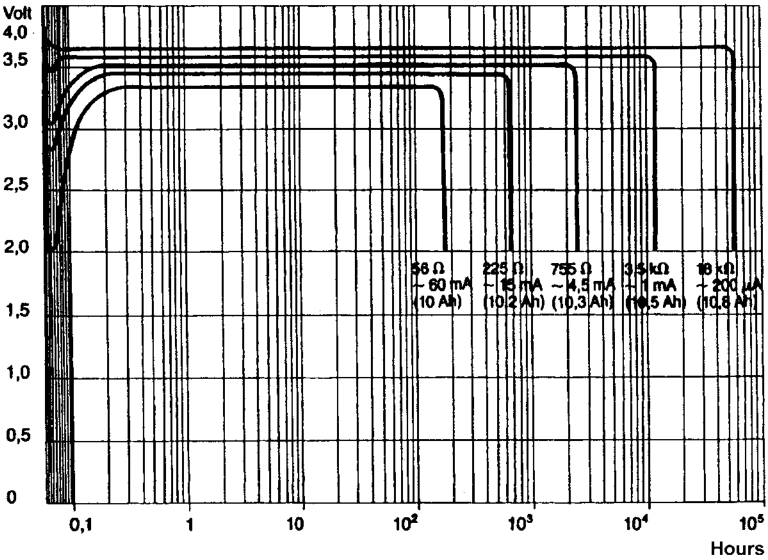

Figure 18.14 Discharge graphs at various loads of lithium/thionylchloride cells (10.5 Ah, bobbin type) after 1 year storage at normal temperature (Sonnenschein).

The useful stability of the passivation layer with respect to shelf-life and low self-discharge on the other hand causes a shorter or longer breakdown of the cell voltage at the beginning of a high rate discharge – the 'voltage delay'. This holds especially after longer shelf-lives. In Figure 18.14 from the discharge curves of a 10.5-Ah bobbin type cell (Sonnenschein) after one year's storage at 25 °C, the voltage delay can be seen preferably at higher rates. The passivation layer can be influenced by addition of lithium oxide Li_2O or sulfur dioxide SO_2 for shorter and shallower voltage delays, but only at the expense of shelf-life. Figure 18.15 shows the positive influence of an additive not described by the manufacturer – it may be PVC from other hints in literature – on the voltage delay that is here to be attributed clearly to the anode.

The cathodic current collector is made from carbon black – sometimes also from carbon fibers – with PTFE and a catalyst[15] on a substrate of nickel foil. Here the pore volume and geometry govern loadability and capacity of the system. Figure 18.16 shows some discharge curves of a cell of the spirally wound form (Saft) which can be compared to those of Figure 18.14. The former may obviously be loaded higher than the latter. The spirally wound electrodes are especially thin and provide a large surface both macroscopically and microscopically.

For the separation glassy nonwovens are used. They are not expensive and yield a low resistivity. For high rate cells which are also loaded mechanically a porous foil of Tefzel® is used, too, but on account of the higher resistance the deep temperature capacity is reduced.

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[15] For example, the cobalt compound cobalt tetramethoxyphenylene porphyrine.

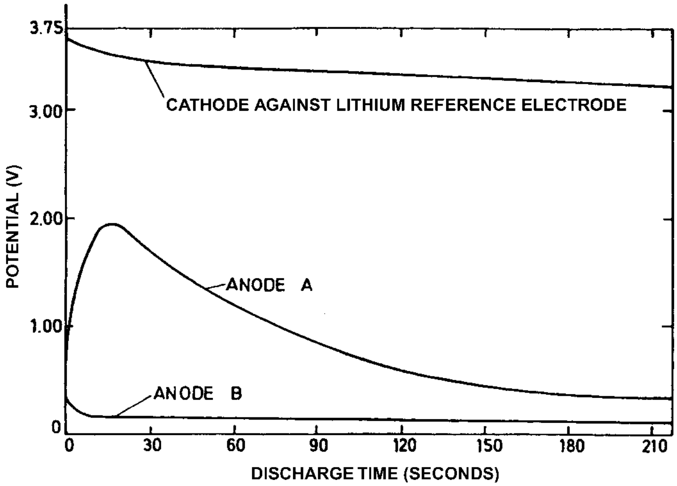

Figure 18.15 Suppression of the voltage delay at the beginning of the discharge of a lithium/thionylchloride cell: effect of an additive (GTE).

The OCV of 3.66 V per cell enables CCV values of 2.8 to 3.6 V, depending on design and load. With various design versions these cells may be operated between −55 °C and more than +150 °C.

Until now thionylchloride cells have been produced – within wide boundaries of sizes and with capacities ranging from a few mAh up to 20,000 Ah – in the form of round cells of the bobbin, spirally wound, and flat electrode types. Flat electrodes are also used for prismatic geometries. These prismatic cells and also bigger round cells

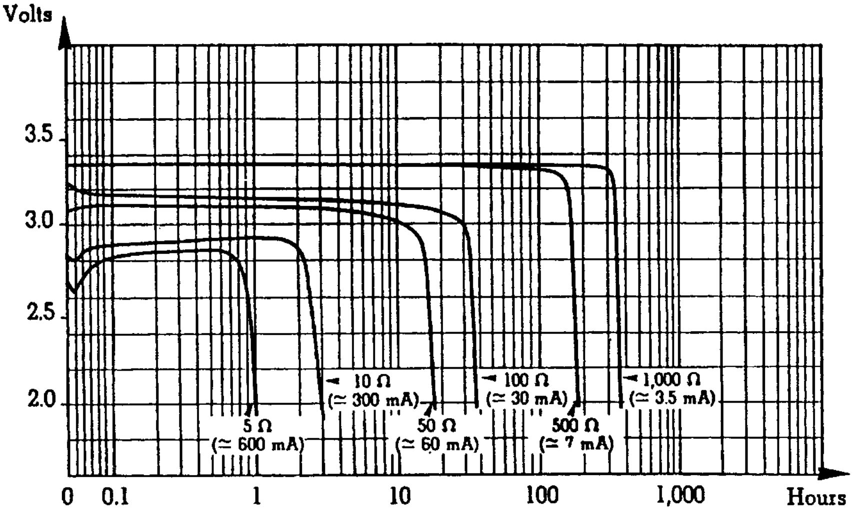

Figure 18.16 Discharge graphs of 1-Ah lithium/thionylchloride cells (spirally wound) (Saft).

with relatively thin walls are possible because of the "reduced" overpressure in these cells under operational conditions – at least if compared to the sulfur dioxide system (see next section). Nonetheless cells bigger than 1 Ah and all high rate versions are to be equipped with a burst vent as part of the cell case with the aim of opening only in a controlled manner when overheated.

For military applications also 'activateable' batteries were developed whose electrolyte during shelf-life is separated from the electrode stack and pushed into the cell within seconds only just before use of the battery.[16] Of course the shelf-life of such batteries is still longer than that of "active" batteries of the thionylchloride type with their capacity loss of 10% during 10 years of storage. But for military purposes the reliability of the improved system and the avoidance of the initial voltage delay make the activateable technology more attractive than the reduction of self-discharge.

On account of the especially high energy density, the necessarily hard cell cases and the poisonous components, the handling and the use of Li-$SOCls_2$ cells ought to be carried out only according to the following safety instructions:

- Do not recharge!
- Protect parallel strings with diodes!
- Do not short!
- Do not assemble with reversed polarity!
- Do not open, puncture, or crush!
- Do not throw into fire!
- Assemble batteries only after contacting the cell supplier!
- Use cells and batteries only in containers that are not blocking the escape of gases!

Li-$SOCl_2$ cells are applied to memory back-ups, to radio transceivers, and to emergency or safety power supplies. Figure 18.17 shows the discharge curve of a special military emergency power supply of 200-Ah capacity with a 350-hour low rate discharge and short high rate pulses. Even under high rate load the voltage level remains constant until shortly before the end of discharge.

In the former Minuteman missile silos, thionylchloride batteries of 10,000-Ah cells were used as the redundant and grid- (mains)-independent power supply. From Figure 18.18 one may see the especially flat and constant curve of the voltage-time graph of this type of battery during a low rate discharge lasting longer.

Thionychloride cells are manufactured in Germany by Sonnenschein Lithium and FRIWO, worldwide by Eagle Picher, Saft, Honeywell, Power Conversion, Philips USFA, and others.

18.6.4 The System Lithium/Sulfur Dioxide

This system operates with sulfur dioxide SO_2; this is also a fluid depolarizer from which the thionychloride is deduced chemically. Design and mechanisms of both

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[16] The cell of PCI – 5.1 g of weight delivering 280 mAh of capacity – contains the electrolyte within a glass ampoule, which is broken under operation so that the electrolyte is able to fill the space between the electrodes.

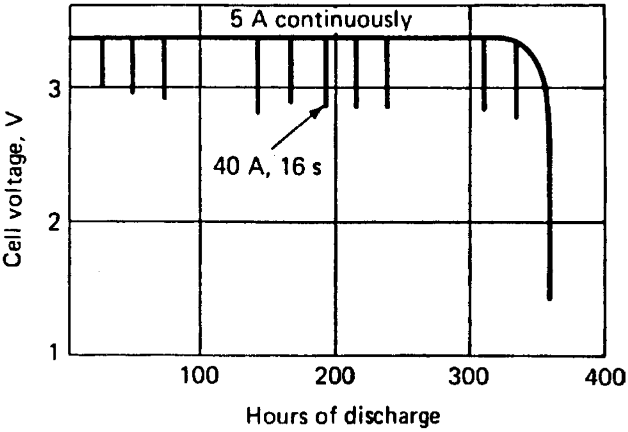

Figure 18.17 Discharge graph of a 200-Ah lithium/thionylchloride cell under mixed continuous and pulse load: 5 A continuously, several pulses of 40 A and 16 sec (GTE).

systems are identical to a large extent. In the 1970s based on research activities at American Cyanamid during the 1960s the SO_2 system was the first lithium high-energy product being manufactured in series.[17] The following reaction equations show lithium dithionite $Li_2S_2O_4$ as the (main) discharge product, which is a colorless substance, also being the main component of the passivation layer on lithium in this cell type:

$$\text{Anode:}\quad 2Li \longrightarrow 2Li^+ + 2e^-$$

$$\text{Cathode:}\quad 2SO_2 + 2e^- \longrightarrow S_2O_4^{2-}$$

$$\text{Cell:}\quad 2Li + 2SO_2 \longrightarrow Li_2S_2O_4 \quad E^\circ = 2.95\,V$$

Under normal conditions sulfur dioxide SO_2 is a colorless acridly smelling gas that is a strong poison when breathed similar to thionylchloride $SOCI_2$. It condenses at $-10\,°C$ and solidifies at $-73.5\,°C$. To be put into the Li-SO_2 cells it has to be liquefied and kept in the cells under its own vapor pressure of 3 to 4 bars at normal temperature.

The twofold function of SO_2 as electrolyte and cathode is possible because of the passivation layer built up on the lithium surface as in the $SOCl_2$ cells. Although being its own solvent SO_2 is combined with a co-solvent of acetonitrile (AN) or propylene carbonate (PC) and with lithium bromide as electrolyte salt which has to be pure to a high degree and water free (HO_2 content $\leqslant$ 100 ppm). The salt is solved (solvated) mostly by the SO_2, whereas the acetonitrile – building a compound-like complex with the SO_2 – serves for low viscosity and consequently for good conductivity also at low temperatures.[18] But nonetheless the vapor pressure of SO_2 mixed with acetonitrile is lowered only slightly.

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[17] The technical realization was achieved by the companies Duracell, Honeywell, and PCl. With know-how from PCl the German FRIWO installed a production since 1978.

[18] A typical SO_2-AN-LiBr electrolyte shows a conductivity of $5 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ at 20 °C and of $2.2 \times 10^{-2}\,\Omega^{-1}\,cm^{-1}$ at −50 °C.

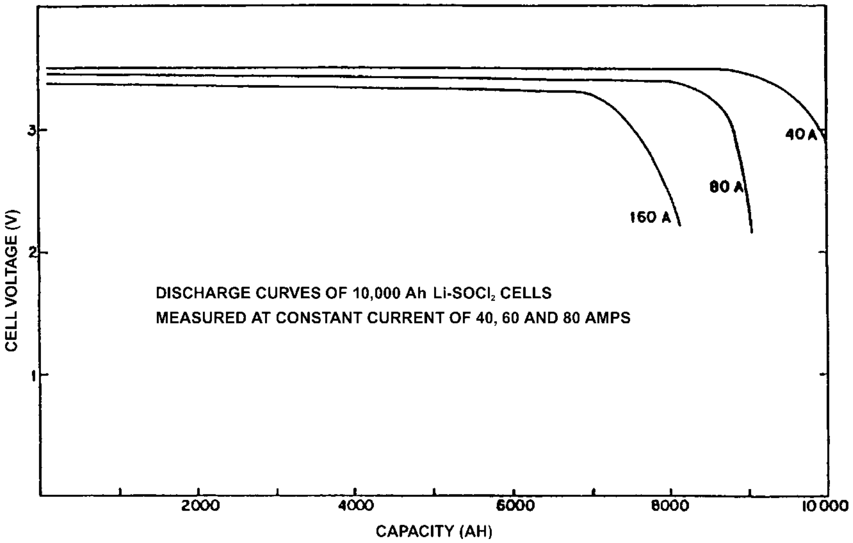

Figure 18.18 Discharge graph of the 10,000-Ah Minuteman lithium/thionylchloride cells under various loads (GTE).

Concerning the cell design it was found that Li and SO_2 have to be used as close to the 1:1 ratio as possible. Under an excess of lithium – which, however, is useful for high rate pulses[19] – the danger prevails that at the end of discharge, i.e. complete consumption of SO_2, the remaining Li metal depassivates and then reacts vigorously with the co-solvent AN producing lithium cyanide and methane. Once the cell after warming up opens under the overpressure, the escaping methane may catch fire spontaneously. Therefore the balanced design is required for multicell batteries where one or the other cell may be deeply discharged – even into reversal, which means a recharge of the single cell under reversed polarity – because of the unavoidable, production-based fluctuations of the capacities of the single cells.

The passivation layer of lithium dithionide breaks down easily also at the first load after a longer period of storage. The cell shows only a very short voltage delay which is less deep than with the "early" $SOCl_2$ product. This can be recognized from the characteristic discharge curves of Figure 18.19 together with the especially stable and constant discharge voltage. Compared to the $SOCl_2$ system, however, the self-discharge effect also at lower temperatures is a little faster with SO_2 cells, the reason being the faster growth of the passivation layer (see Figure 18.20, Duracell). To get extreme long shelf-lives one should avoid checking the OCV from time to time because the disturbed passivation layer would then have to recover again repeatedly, which would mean an acceleration of the self-discharge rate.

At least for high rate discharges the cathodic current collector may also limit the capacity of the system. It is made of a highly porous mixture of carbon black, Teflon®, and a catalyst pasted on an aluminum-expanded metal. It is plausible that

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[19] Special cells are applied for radio buoys, which operate indeed with some excess lithium, but this is a safety risk that can be borne in the buoys' environment.

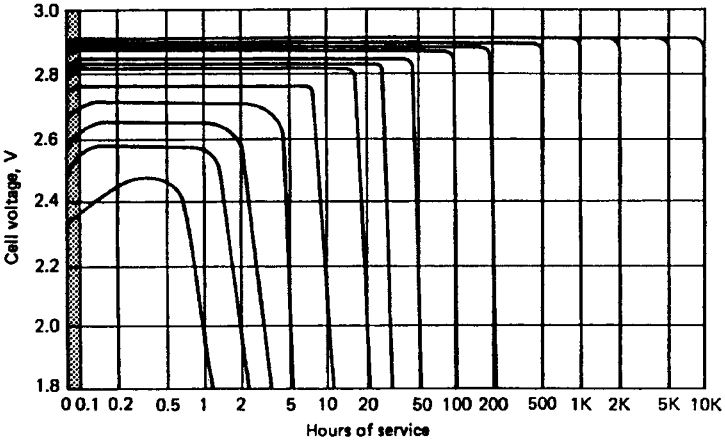

Figure 18.19 Discharge graphs of lithium/sulfur dioxide cells of the spirally wound technique under various loads (Duracell).

the use of the pore volume of the current collector by the deposition of the reaction product lithium dithionite depends mostly on the current density during discharge. In the geometric model of those pores, formed like bottles, preferably the bottlenecks are covered with the reaction product under high rate conditions. Already after a partial discharge the depth of the pore's bottle is no more available for the reaction and the reaction product's disposal on account of the blocked bottleneck. In this way the (high rate) discharge has ended prematurely. Deep temperatures enhance this effect. Both influences are documented in Figure 18.21.

At higher temperatures the internal pressure of SO_2 cells is also high, up to 30 bar and more. So the geometry of these cells is restricted to round tubes, which may be easily and economically used as pressure vessels. They are manufactured in standard or customized sizes from stainless steel – exclusively hermetically welded

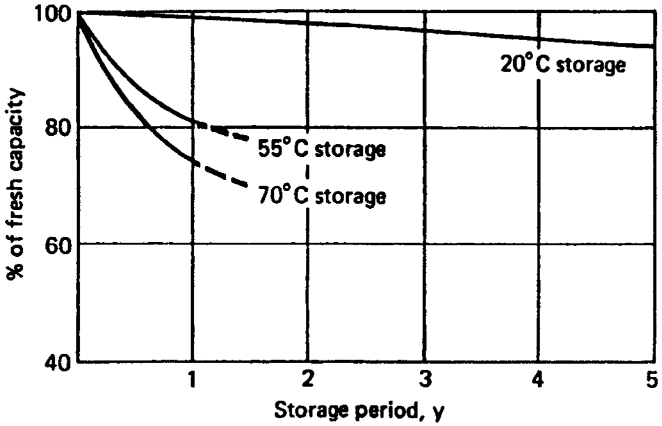

Figure 18.20 Retention of capacity of lithium/sulfur dioxide cells during storage at various temperatures (Duracell).

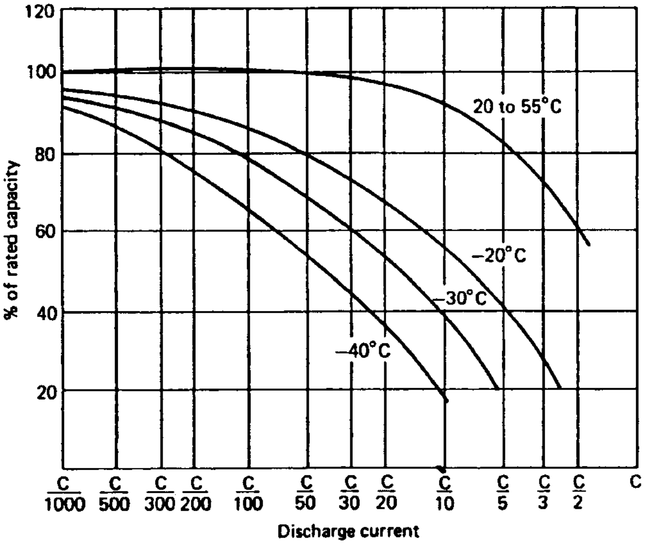

Figure 18.21 Dischargeable capacity of lithium/sulfur dioxide cells depending on their discharge temperature (Duracell).

with glass-to-metal seals from special glasses[20], which have to be resistant against electrochemical corrosion under these conditions. The electrodes for high rates are of the spirally wound type. Because of the high SO_2 gas pressure, a safety vent is an absolute must. During discharge, however, the internal pressure is gradually reduced as shown in Figure 18.22 at various temperatures. Nonetheless the safety layout of course has to suffice also for fresh cells with their high-energy content and high internal pressure.

The OCV of the system is about 2.95 V. SO_2 cells may be heavily loaded: A standard D cell with 7 to 8 Ah nominal capacity may be discharged by 2 A continuous current and 30 A pulses. Its specific energy of about 275 Wh/kg is lower than that of the competing $SOCI_2$ cells. The shelf-life is very good with a self-discharge rate of about 10% after 10 years (see Figure 18.20).

The SO_2 cells are applied as single cells or battery packs to radio tranceivers, to emergency equipment with long shelf-lives, to memory back-ups, to film and video cameras, and others. The most important customer is the military, which is especially concerned in long shelf-life, high energy density, and applicability for all climatic zones.

The SO_2 cells are often equipped with back-setting thermo switches as protection against overload and to avoid an action of the safety (bursting) vent. Battery packs often have a built-in resistor, which may be switched on for safe discharge of capacity rests before final disposal (see Figure 18.23).

The SO_2 cells are manufactured in Germany by FRIWO, worldwide by Honeywell, PCI, and Duracell.

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[20] Under the influence of an electric field also glasses, depending on their composition, may relatively easily corrode.

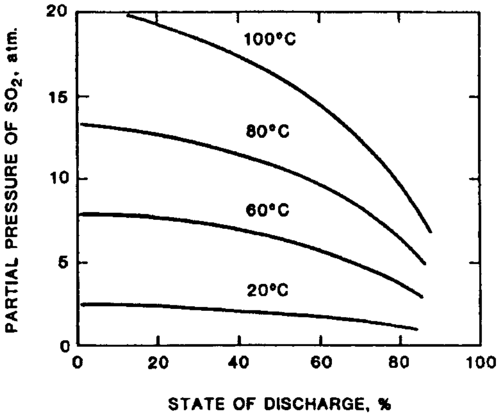

Figure 18.22 Pressure drop in lithium/sulfur dioxide cells during discharge at various temperatures (from P. Bro).

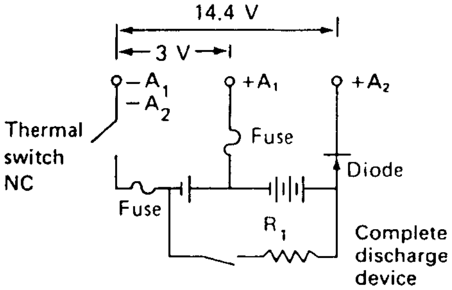

Figure 18.23 Electric circuit of the lithium/sulfur dioxide battery pack BA-5598 equipped with various safety components. (From Reddy in Ref. 5.)

18.6.5 The System Lithium/Iodine

The first lithium/iodine cardiac pacemaker battery was implanted in 1972. This type of battery proved to be very successful in this field[21] and for other applications, too. The special features of this solid state battery are explained with its technique, which is limited with its extremely high energy density and reliability, especially for low rate applications. This technique is based firstly on the electrode couple of lithium and iodine with its high energy content[22] – the OCV of the lithium/iodine cell is 2.80 V – and secondly on the favorable fact that the product of the cell reaction, the lithium iodide (LiJ), forms very tight and continuous layers between the active material of the electrodes, which are acceptable ionic conductors with negligible electronic

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[21] Until 1990 about 2 million batteries were used for cardiac pacemakers exclusively of the LiJ type.

[22] Iodine belongs to the chemical elements of the 7th column of the periodic system, to the halogens. By reaction between the halogens and the alkaline metals, e.g. lithium, especially high energy is released.

conductivity. The cell reaction follows the reaction scheme

$$\text{Anode:}\quad 2\text{Li} \longrightarrow 2\text{Li}^+ + 2\text{e}^-$$

$$\text{Cathode:}\quad \text{P2VP}\cdot \text{nJ}_2 + 2\text{e}^- \longrightarrow \text{P2VP}\cdot(\text{n}-1)\text{J}_2 + 2\text{J}^-$$

$$\text{Cell:}\quad 2\text{Li} + \text{P2VP}\cdot\text{nJ}_2 \longrightarrow \text{P2VP}\cdot(\text{n}-1)\text{J}_2 + 2\text{LiJ}\quad E^\circ = 2.79\text{V}$$

In this way the reaction product lithium iodide represents the electrolyte as well as the separator for this cell simultaneously. It is being created already as a thin reaction layer between the electrode materials once the active materials of anode and cathode are brought into contact during the manufacturing process without any additional separator. This solid electrolyte layer grows during discharge more and more with the consequence of an enhanced resistivity of the cell. The early pacemaker batteries therefore showed a markedly declined discharge characteristic. Figure 18.24 shows this for a pacemaker battery (Medtronic), whose second half of capacity could be discharged only with continuously lowered CCV because of the exponentially rising resistance.

The cathodic material is a mixture of iodine with poly-2-vinylpyridine (abbreviated as P2PV).[23] The P2PV acts as a stabilizer for the iodine and as conducting agent. The high vapor pressure of pure iodine is thereby reduced remarkably. The cathodic mixture was poured into the early pacemaker batteries as a fluid. During discharge there was a volume contraction on account of the generation of the separating electrolyte salt LiJ. It was accompanied by the solidification of the electrolyte-cathode system. Then the components were solidified but not tightly packed within the cathode. So the inner resistance of the cell was comparable to that shown in Figure 18.24. The further development introduced thoroughly compressed cathodic pellets, which reduced the rise of the inner resistance during discharge noticeably. Figure 18.25 shows some discharge curves of a lithium iodine button cell manufactured that way (Catalyst Research). But even with this improvement these cells fit only best for low rate long-time applications with μA currents for a couple of years. The CCV of cells being used for medical purposes is around 2.7 V. Pacemaker batteries are used starting at 2.8 to 2.7 V and are replaced at the latest at 2.3 to 2.0 V. For the pacemaker application a flatter curve is appreciated at the end of discharge to keep a safety reserve before the battery's final exchange.

The iodine cathode is the capacity-limiting partner of this system. It is especially reliable and safe (this means 'good tempered') and gives no problems when mishandled. The operational temperature is between −55 °C and +125 °C.

The system's theoretical energy density is 1930 Wh/L. Practically it amounts to 1000 to 1300 Wh/I. The practical specific energy is about 300 Wh/kg.

Lithium iodine batteries are available mostly in the pacemaker shape, i.e. in that flat nearly semicircle geometry of, e.g. 5 × 30 × 40 mm, with 1 to 3 Ah capacity at a weight of 10 to 30 g. For industrial applications flat rectangular formats are made with contact pins that make them mountable onto electronic boards. Button cells are also realizable. All cells have glass-to-metal seals for both polarities or for the negative one only. A button cell's cross-section is shown in Figure 18.26

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[23] Iodine and P2VP are mixed at a ratio of 20:1 to 30:1. They react to form a complex compound.

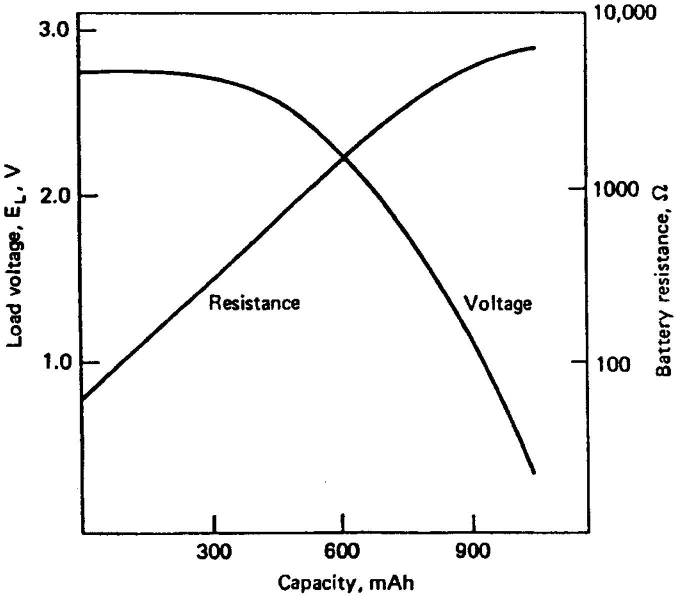

Figure 18.24 Discharge graph of voltage and inner resistance of an early lithium/iodine pacemaker battery, discharged with the relatively high current of 100 mA (Medtronic).

(Catalyst Research). It is applied to typical low rate systems as memories, sensors, and monitoring devices, but preferably as cited above in pacemakers. So they were used more recently combined with lithium/manganese dioxide cells (earlier also with vanadium oxide cells) in so-called pacemaker defibrillators, too.[24] Although other lithium systems were also used for pacemakers, the lithium iodine technique had the major market share.

The efforts for quality control of the production of pacemaker batteries and others for medical applications, which may remain implanted for 5 to 10 years or longer, are very intensive. They amount to a multiplicity of the value of the material used.[25] That explains the high prices (several hundreds of DM). The design of a typical pacemaker battery is shown in Figure 18.27.

Manufacturers of lithium iodine batteries are Catalyst Research, who developed the technique originally, Wilson Greatbatch, and Medtronic (in Germany Litronic).

18.6.6 The System Lithium-Aluminum/Iron Disulfide

The so-called 'thermal batteries' belong to the family of 'activateable' batteries, which are put into activity by a defined physical process if they are to become dischargeable. For thermal batteries this process means their being heated up by several hundred degrees centigrade. At normal temperatures the active components

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[24] Defibrillation serves to counteract ventricular fibrillation, i.e. to re-establish the correct heartbeat.

[25] Pacemaker batteries, e.g., are checked 100% during several weeks at 37 °C (body temperature) for their function and are only then released for service.

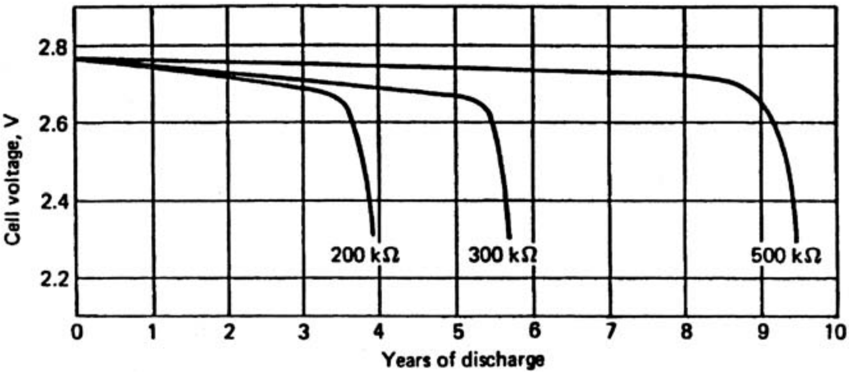

Figure 18.25 Discharge graphs of a lithium/iodine button cell at long time discharge (Catalyst Research).

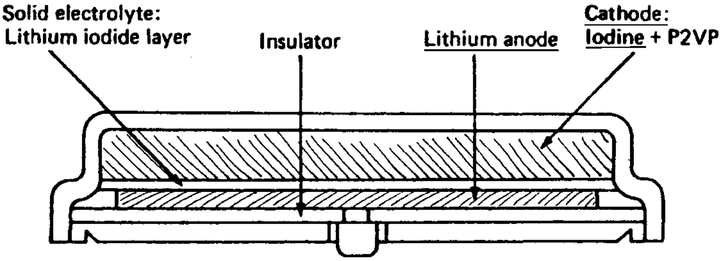

Figure 18.26 Cross-section of a lithium/iodine button cell (Catalyst Research).

of these batteries are in the solid state. So virtually no reaction takes place between them. But at the operating temperature of between 400 and 500 °C the salt mixture acting as the electrolyte is molten and the electrode materials – still being solid – are sufficiently reactive to let them react with the required speed.

For a long time thermal batteries were available for discharge times of several minutes. The relatively new thermal battery system lithium-aluminum/iron disulfide makes the thermal technology also applicable for discharges lasting several hours with acceptable voltage time curves. For this system the energy conversion is based on the discharge of the lithium anode against the cathode of iron disulfide to produce iron sulfide – pyrite – and lithium sulfide according to the reaction scheme

Anode: $2\text{Li} \longrightarrow 2\text{Li}^+ + 2\text{e}^-$

Cathode: $\text{FeS}_2 + 2\text{e}^- \longrightarrow \text{FeS} + \text{S}^{2-}$

Cell: $2\text{Li} + \text{FeS}_2 \longrightarrow \text{FeS} + \text{Li}_2\text{S} \quad E^\circ = 3.65\,\text{V}$[26]

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[26] This unusually high OCV is related to traces of heavy metals like Ni, Co, and Cr in the FeS_2. On load the voltage falls below 2 V.

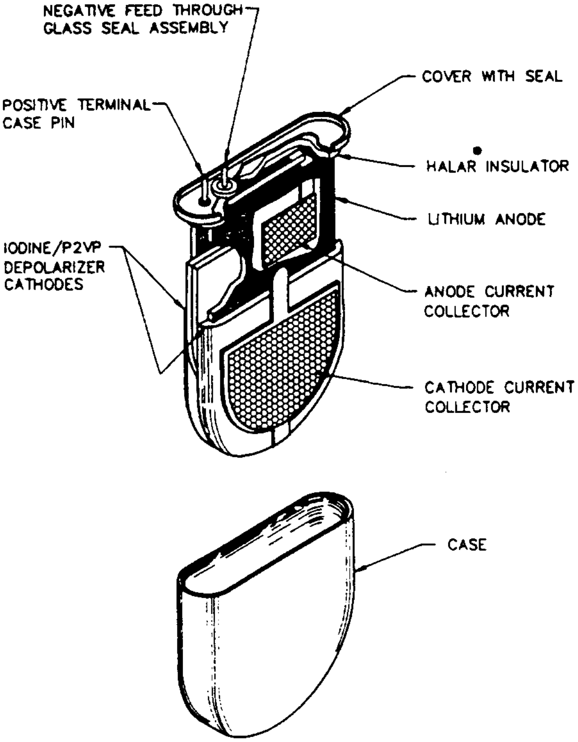

Figure 18.27 Pacemaker battery with pressed cathode and double anode. (From Jolson et al. in Ref. 5.)

The effective CCV for this discharge process is only 1.5 to 1.8 V depending on the design of the system.[27] The ternary system lithium-iron-sulfur is far more complex than can be recognized from the reaction scheme. In Figure 18.28 one can see the two iron-sulfur phases FeS and FeS_2 and additionally also the phase FeS_{1-x} together with several areas of coexistence of the species being involved. The iron sulfide can be discharged indeed beyond the stage of FeS: The discharge of the first species FeS_2 is done with a relatively constant CCV. After complete consumption of the FeS_2, the discharge voltage declines by discharge of FeS step by step over several reduction states of iron down to pure metallic iron as the final cathodic reaction product. Usually only the first discharge step of the system is used. FeS_2 shows sufficient electronic conductivity. So conductors as additives to the cathode are not necessary. FeS_2 decomposes above 550 °C into FeS and S. Therefore the operating temperature should not exceed this temperature level. The cathodic discs (see below) are compressed from powder mixtures of FeS_2 and LiCl-KCl eutectic – for improvement of reactivity and loadability – together with some SiO_2 (silica).

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[27] This cell voltage is not so favorable if compared to that of other lithium systems. But we have to take into account those other characteristics explained below which are desirable for the special applications of these thermal batteries.

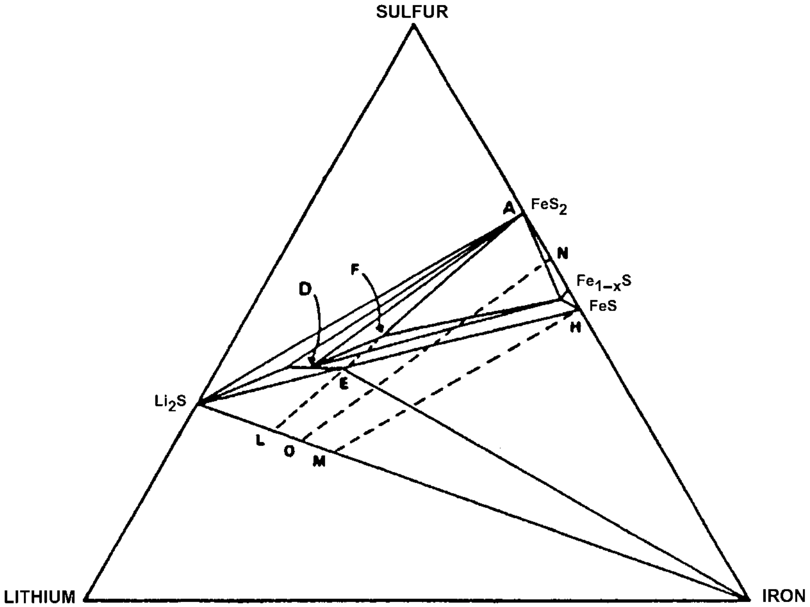

Figure 18.28 The lithium/sulfur-iron phase diagram.

The anode is made from the LiAl β-alloy (see Figure 18.29), which contains both components nearly at a ratio of 1 to 1. Its melting point is about 690 °C. These anodes are compression moulded from the pure alloy powder. The potential of this lithium electrode remains constant during the discharge, provided one does not leave the coexistence region of 8 to 47% lithium content between the β-phase and the Al α-phase, which is poor in lithium. Li-Fe and Li-Si mixtures are also used as anodes with a sufficiently stable potential during discharge.

It applies for both electrodes of the lithium/iron disulfide cell that the active materials can be used up during discharge only to a small extent.

Suitable electrolytes for the lithium thermal batteries may be chosen from the low melting eutectics[28] of the lithium halides. Their melting points are from 300 to 350 °C. For improved stability they are mixed with magnesia and compressed to flat discs for assembly into the cell stacks. The eutectic point of the LiCl-KCl electrolyte is at 352 °C and that of a LiCl-LiBr-KBr electrolyte is at 310 °C.

For most military applications the thermal batteries are to be heated up and activated as quickly as possible. This is done by heat-generating tablets made from 'Thermit'-like[29] mixtures of iron powder Fe and potassium perchlorate $KClO_4$. This

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[28] Mixtures of at least two components with a defined mix ratio, which are completely immiscible in the solid state and completely miscible in the liquid state, are called 'eutectic'. The eutectic mix ratio is defined by the minimum melting point of all possible mixtures (combinations) of the components. It means in practice that at temperatures exceeding the eutectic one at least a part of the mixture is liquid. In the solid state the eutectic is a mixture of finely divided tiny crystals of – in most cases – two different compositions.

[29] The Thermit or aluminothermic process for constructing railways by welding the rails in place: A powder mixture of FeO and Al is ignited by BaO_2. The heat of reaction is sufficient to let the iron as the reaction product liquefy and flow into the welding gap.

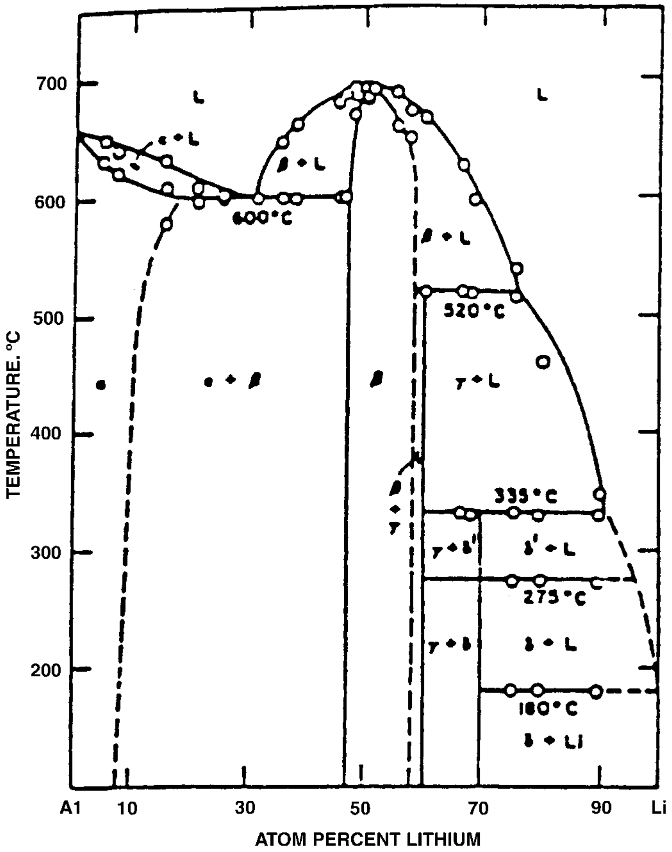

Figure 18.29 The lithium-aluminum phase diagram.

mixture is ignited via firing strips made from paper being pyrotechnically impregnated. The paper consists of zirconium Zr and barium chromate (VI) $BaCrO_4$ combined with a suitable fiber material. The firing strips themselves are ignited by electrically fired ignite pills. The burning front of the firing strips proceeds with a speed of about 250 mm/sec. So depending on the battery size they get heated up within 100 msec to 2 sec.

Typically thermal batteries are constructed as stacks or 'piles', according to Figures 18.30 and 18.31. Usually multiples of circle-shaped cell units of anode, electrolyte separator, cathode, and heating tablet are stacked one on top of the other according to the required operating overall voltage. The total unit is placed into a pressure-proof stainless steel container that thermally insulated as well as possible. These batteries are produced in controlled rooms with dry air, as normally used for the production of lithium batteries. All battery components have to be extremely dry.

Lithium thermal batteries are produced mostly for military applications to support control and trigger functions within weapon systems such as aircraft, missiles, and high-caliber gun ammunition. They are offered for power requirements

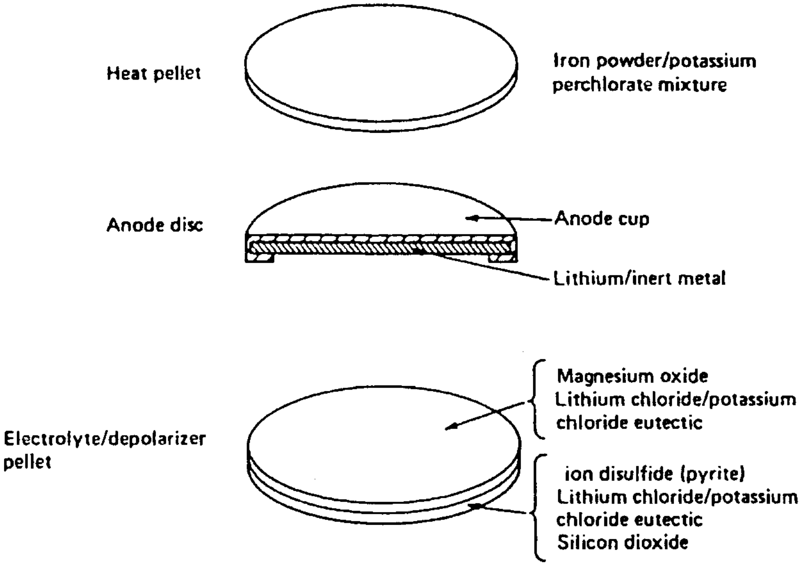

Figure 18.30 The pile structure of a single lithium/aluminum/iron disulfide thermal cell. (From Ref. 3.)

ranging from 1 W for 10 ms to several kW for up to two hours. Figure 18.32 shows the relation between volume, power, and available discharge time for typical lithium thermal batteries. In spite of the built-in insulation, it is the rapid cooling down that limits the operational time. If the temperature falls below the working temperature

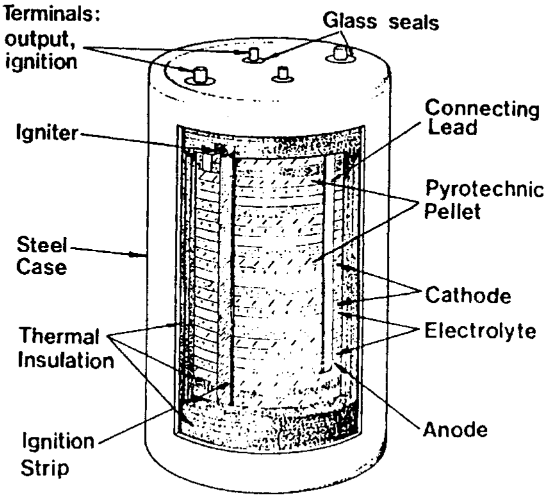

Figure 18.31 Inner structure of a multi-cell thermal battery. (From Ref. 5.)

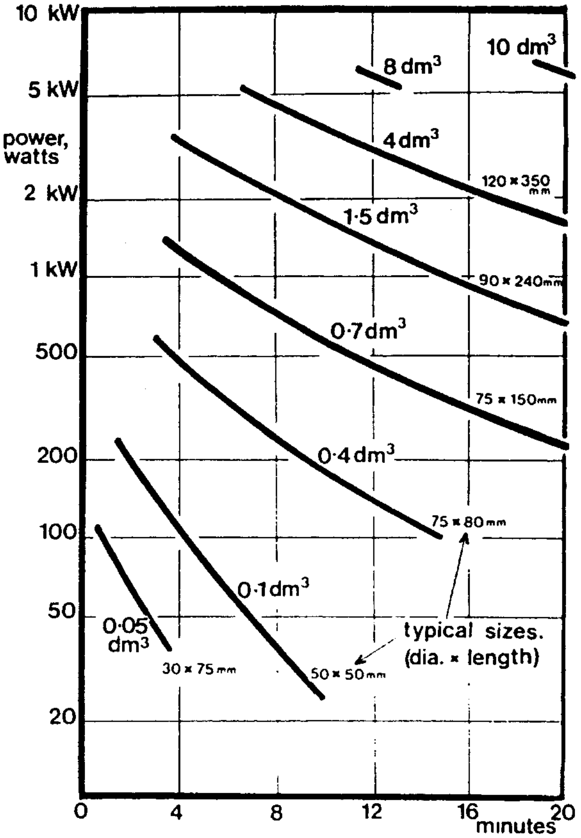

Figure 18.32 Relation between volume, power, and operation time of various Li-FeS_2 thermal battery sizes. (From Attewell in Ref. 5.)

of 400 °C and eventually below the eutectic point of the electrolyte, the battery becomes – even if not fully discharged – highly resistive.

Older versions of thermal batteries use calcium or magnesium anodes with cathodes from alkaline metal chromates, tungstates, ferrates, or vanadates. Figure 18.33 presents discharge curves of three different thermal battery systems of comparable construction size but varying voltage levels and discharge times. Discharge over longer periods of time than shown is impossible with all three systems because of the thermal losses and – with the Ca/Mg systems – because of several side reactions.

From environmental temperatures between −40 and +70 °C thermal batteries may be activated and used indiscriminately. Their extremely good storability in the "frozen" state at normal temperatures makes them especially suitable for military applications in weapons and equipment whose system shelf-life in total is often shorter than that of the integrated batteries. Because of their compactness thermal batteries are particularly resistant against shock, vibration, acceleration, and spin.

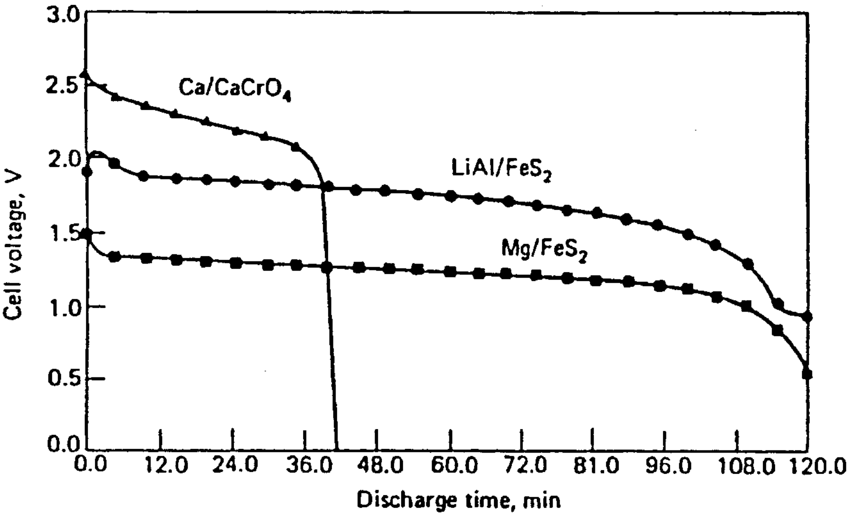

Figure 18.33 Discharge graphs of old (Ca-Ca-chromate, Mg-FeS_2) and new thermal batteries (Li-Al-FeS_2). (From Ref. 3.)

At least temporarily a lithium/aluminum/iron disulfide battery was also under development as a rechargeable high temperature system for use in electric submarine vehicles.[30]

The roots of the thermal battery technology go back to German research and development efforts at the end of World War II. Today thermal batteries are manufactured by MSA, Eagle Picher, PCI, Leclanché, and SAFT.

18.7 SECONDARY LITHIUM BATTERIES

Soon after the introduction of the first primary lithium batteries into the market in the 1980s, it was attempted to develop also rechargeable lithium cells. These first approaches were based on pure metallic lithium anodes. It was simply an attempt to make existing primary systems rechargeable. The first secondary battery on the market was a Canadian product (Moli Industries) – a lithium/molybdenum disulfide system. This and other concepts were not successful, however. The reason was mainly the impossibility to deposit the lithium anode during recharge in such a compact and stable way that the lithium advantages of the primary systems – low self-discharge and few side reactions – could be maintained. This goal was not achieved at that time.[31] The first secondary lithium batteries had some safety problems because of the uncontrolled deposition of the lithium metal yielding large microscopic surfaces of high reactivity.

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[30] Lithium/iron disulfide batteries were also made as active primary systems for normal operating temperatures with a metallic lithium anode and one of the well-known conducting salt-solvent mixtures as their electrolyte. The product, as button or cylindrical cell, with its CCV of about 1.5 V was thought to become a cheaper competitor to the AgO-Zn cell. But they were not successful in the market.

[31] The only exception was a rechargeable Li-MnO_2 battery of Tadiran for very special applications.

A tricky approach was more successful, which has already been explained together with the thermal system Li(Al)/iron disulfide:[32] A stable inert matrix which does not react with other cell components was offered to the anodic lithium to be built into it repeatedly during recharge in an unchanged manner. In such a way and with precise charging and voltage control safe rechargeable lithium batteries could be introduced also for the consumer market. The best known and most widely spread system today (2002) is that of the lithium-ion battery as described below, which operates with a lithium-carbon intercalation compound as an anode.

18.7.1 The Special Aspects of a Secondary Lithium Battery Technology

Whoever has knowledge about batteries from application of lead-acid or nickel/cadmium batteries must consider several specifics of the rechargeable lithium batteries to understand their technology. These specifics are a consequence of the simple fact that during discharge the reactive agent of the anode – the lithium – not only changes its oxidation state, but also migrates quantitatively to the cathode. So the structure of the anode is totally decomposed during discharge and built up again during recharge. This central problem been solved by the development and realization of the secondary lithium cell.

- In lithium cells the current between the electrodes, i.e. through the electrolyte and the separators, is fully maintained by migration of positively charged lithium ions, independent from the primary or secondary mode of operation. The lithium metal is solved during discharge losing one electron per lithium atom and thus yielding a lithium cation, which migrates through the electrolyte and is finally incorporated in the cathode under charge equilibration by intake of an electron, which in turn is part of the current flow through the outer circuit.[33] In contrast to this the cadmium metal in the NiCd accumulator's anode and also the lead metal in the lead-acid accumulator's anode does not leave the electrode during discharge. The metal atoms here also change their oxidation state but stay at their place by taking in hydroxide and sulfate ions for charge equilibration. In both systems the charge transfer, the current, is maintained by ions from the aqueous electrolyte: the hydroxide ion in the NiCd and the sulfate and the hydrogen ion in the lead-acid batteries. The lithium electrode by contrast is an electrode whose metal atoms are dissolved ('solvation electrode', the potential of the electrode is controlled by the dissolved cations) or an electrode of the 'first type', whereas the traditional secondary batteries operate with anodes of the second type (cadmium) or pseudo second type (lead-acid) (the potential of which is controlled by the corresponding anion in the electrolyte). Here the electrodes undergo the same states from cycle to cycle and virtually maintain their constant

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[32] The lithium has also to be stabilized for the operation of the Li(Al)/iron disulfide thermal battery at over 300 °C. Otherwise because of its low melting point of only 180 °C, the lithium would vigorously react already during the short pyrotechnic heat-up period.

[33] The mechanism is in more detail explained below.

macroscopic geometry. So they are also geometrically cyclable. But if the pure metallic lithium anode, after its discharge normally as a compact foil, should be recharged, it would not yield a smooth and compact foil again but a mossy structure of dendrites, i.e. microscopically thin crystal fibers, which have a far larger surface than at the beginning. So the lithium electrode does not work reversibly in the sense of the required macroscopic structure, even if it is reversible thermodynamically because of the relatively low negative potential of deposition.

- For cyclic operation a large microscopic surface is not desirable indeed because during each cycle active lithium is lost and efficiency and cyclability of the system are severely affected. That is why the dendritically deposited lithium metal reacts at the surface also with the normally used aprotic solvents of the electrolyte to form the required compact reaction layer, which slows down the further attack to such a degree that the electrode can be regarded as stable (passive) at least temporarily. This passivation, however, irreversibly consumes active material, and this happens again and again during each new cycle. This of course makes the rechargeability the poorer, the higher its amount counts per cycle. The lithium consumed by passivation during recharge can't really be regenerated. The passivation reaction occasionally also strangles whole dendritic crystallites. Consequently their metallic remainders – not yet consumed by the reaction with the electrolyte's components – cannot be used any longer electrochemically because they have lost their metallic electronically conducting contact to the bulky mass of the electrode. A far quicker decay of capacity during cycling is the consequence.
- The capacity losses on account of the lithium's side reactions are increasing with the depth of discharge (DOD) per cycle. There are secondary lithium systems that reach many cycles only under very shallow discharge conditions. But there are also applications where secondary cells with such characteristics prove useful.
- Dendritic[34] metal deposition during recharge might also generate a metallic short through the pores of the separator between anode and cathode. This might end disastrously for the cell because of the afore-emphasized high reactivity of the lithium.
- For these reasons, as explained, the rate of self-discharge in secondary lithium cells might be higher than in the primary cells described earlier.
- Just as for primary systems the electrolyte mixture for secondary cells should be chosen with respect to stability against the high voltage of the cell. The electrolyte does not withstand cell voltages of more than about 4.0 to 4.8 V. Of course this also holds for the even more-or-less higher charging voltages: It must not lead to any decomposition reaction.

Today rechargeable lithium batteries – up from a few 100 mAh capacity – based on the reasons given have an anode from a lithium alloy or, more often, a nonmetallic

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[34] A dendrite is a tiny needle-like crystal with ramifications like a tree. It develops when a crystal during deposition preferably grows in the direction of only one crystallographic plane and branches out here and there.

but very good electronically conducting carbon matrix of various crystallinity. The potential level of both types of electrodes differs only little from that of the pure metallic lithium anode. The electrode reactions are sufficiently reversible needing only low overvoltages. Consequently the values of the discharge and charge voltages of most of these cells are comparable.

In all cases a matrix is also used for the cathode, where the small lithium is inserted and released easily. The prototype of these matrices is the manganese dioxide, already well known from the primary technology.[35] With the proper choice of crystal structure the lithium ions are inserted or intercalated and released easily here. From this ability the name ‘intercalation compounds’ has been chosen for this type of crystalline material.

Electrolytes are mixtures of suitably selected organic solvents – as already well known from the primary cells – which should be good solvation (solving) agents, should show low viscosity and should be combined with effective conducting salts (see Section 18.4.2).

A number of different lithium secondary systems serve for very low energy demands of electronic modules as memories and clocks. The batteries for these fields of application are manufactured as button cells. These cells are described first. Then for medium and high energy requirements lithium-ion batteries are explained. Today they are widely applied for portable electronic devices such as cellular phones and notebooks, which need much more energy than the aforementioned components for as many hours as possible (practically today up to 4 hours in notebooks). On the developmental stage it has been attempted to apply the lithium-ion technology also for much bigger accumulators, e.g. for so-called hybrid vehicles with a combined combustion and electric propulsion system.[36]

18.7.2 Rechargeable Lithium Batteries for Low Energy Applications (Button Cells)

Rechargeable lithium button cells are available at the market sized from 621 up to 3036[37] with typical weights of 0.3 to 6 g and with capacities of 0.010 to about 100 mAh. These very small accumulators are produced for applications with very shallow cycles, where a deeper discharge is possible from time to time but only as an exception. These button cells are for the support of memories and timers.

It is no surprise that the Japanese, who are the market leaders for electronic products for mass consumer articles, dominate the market for these very small accumulators. Manufacturers of these accumulators are Matsushita, Sanyo, Seiko,

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[35] Complex compounds of lithium and heavy metal oxides as nickel oxide and cobalt oxide are working more effectively than the lithium/manganese oxide spinel which incorporates lithium ions into its tube-like voids whereas the former with their layered structure take up and release lithium ions more easily.

[36] Since 1997 the Japanese car manufacturer Toyota has offered the Prius as a hybrid-driven car produced in series. Today however it is still equipped with a nickel/metal hydride battery.

[37] Their type number describes the geometric dimensions of rechargeable lithium batteries systematically: It contains for the button and cylindrical types the diameter in mm and the height in 0.1 mm. The cell size 18650, e.g., has a diameter of 18 mm and a height of 65 mm. Cubic constructions are designated with the smallest dimension (height) in mm, with the next larger one (width) in mm, and with the largest one (length) in mm. The cell size 102248, e.g., is 10.5 mm high (flat), 22.5 mm wide, and 48 mm long.

and Toshiba. Some systems which are available on the market are described in the next section and a compilation is in Ref. 3.

18.7.2.1 The System Lithium-Aluminum/Manganese Dioxide

This product can be obtained in several button cell sizes. In the charged state the anode is a lithium-aluminum alloy with manganese and chromium additions. The manganese dioxide cathode is a crystalline mixture of lithium manganate (layered structure) and manganese dioxide (channel structure). This type of battery is able to deliver more than 500 shallow cycles – where "shallow" means a depth of discharge of about 10%. The electrolyte of this cell is a mixture of EC and BC[38] combined with one of the already cited conducting salts. The storability of these small accumulators is rather good: self-discharge being less than 5% per year. After deep discharge such a cell may also be stored for longer periods (see Figure 18.34 for a 14 month shelf-life in the deep discharge condition).

18.7.2.2 The System Lithium-Aluminum/Vanadium Oxide

This product of Matsushita operates similarly to the manganese dioxide cell described with a lithium-aluminum alloy anode, but with a cathode made from vanadium pentoxide. The discharge voltage's average value is about 3 V with a flat discharge characteristic as long as the cell is discharged slowly, i.e. with the 100-hour rate or even more slowly. This cell type is insensitive to overcharging. The energy density is between 100 and 140 Wh/L. The field of application is in memories.

18.7.2.3 The System Lithium Alloy/Polyaniline

This system, again with an alloy anode, is marketed by Seiko, the watch manufacturers. On the cathodic side the lithium ions are charged and discharged by the polymer polyaniline.[39] The discharge characteristic is strongly declining between 2 and 3 V. It depends on the concentration of lithium in the cathodic polyaniline. Small accumulators of this kind may be used for more than 1000 cycles with 20 to 30% DOD and low discharge currents of I_{500} or lower. The energy density is very low: it is 11 Wh/L. An important advantage of this accumulator is that it is free of heavy metals in the active parts and offers no environmental problems of disposal.

18.7.2.4 The System Lithium Alloy/Activated Carbon

Matsushita offers this rechargeable lithium battery system, which operates anodically with a host alloy for lithium containing bismuth, lead, tin, and cadmium. These components form low melting alloys with melting points – depending on the ratios of composition – between 60 and 120 °C. The Matsushita product uses the long- and well-known "wood" metal composed of bismuth, lead, tin, and cadmium at a ratio of 4:2:1:1 and melting at 70 °C. Accordingly the obviously low lattice energy of this alloy allows for easy implementation and release of lithium atoms/

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[38] EC = ethylene carbonate; BC = butylene carbonate.

[39] Polyaniline is known as 'conducting polymer'.

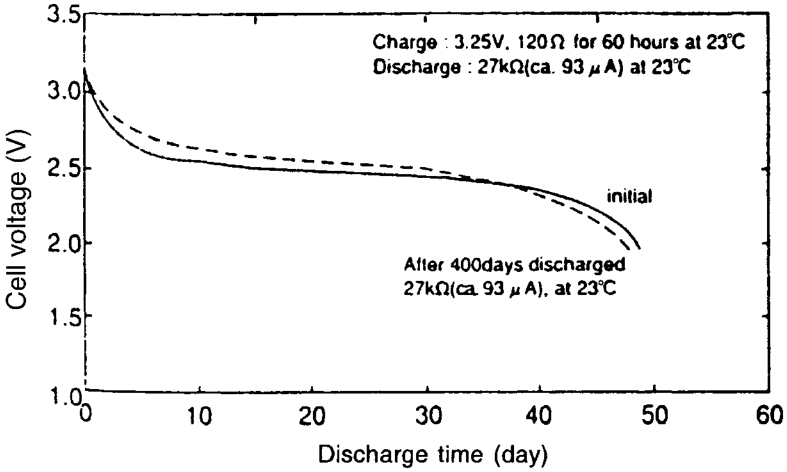

Figure 18.34 Storability of rechargeable lithium/manganese dioxide button cells (Sanyo ML2430) in the discharged condition (From Nishio/Furukawa in Ref. 6.)

ions. The especially low melting point however limits thermally the range of application and the size of those accumulators. The cathode consists of activated carbon with an inner microscopic surface of about 1000 m^2/g. Presumably the lithium ions are stored at those inner surfaces of the microporous structure of the carbon particles and not inserted into the graphitic layers[40] of the structure of these particles. The discharge characteristic drops comparatively quickly between 3 and 2 V. The energy density is only 4 Wh/L.

18.7.2.5 The System Lithium LGH/Vanadium Oxide

This system, offered by Toshiba, works with the so-called lithium LGH[41] electrode, a graphitic intercalation electrode. The cathode is a mixture of vanadium pentoxide and phosphor pentoxide. The discharge characteristic of this cell declines progressively from 3 to 1.5 V. The energy density of the system is about 96 Wh/L.

18.7.2.6 The System Niobium Oxide/Vanadium Oxide

This cell type, marketed by Matsushita, operates with heavy metal oxide intercalation compounds on both the anodic (niobium oxide) and cathodic (vanadium oxide) side. The system is especially capable of rapid recharge. Deep discharge is tolerated well. With shallow discharges one may expect more than 700 cycles. The button cell size 1616 shows an energy density of 37 Wh/L.

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[40] Various carbon materials are described more in detail in Section 18.7.3.1.

[41] LGH = linear graphite hybrid is a special graphitic carbon preparation.

18.7.2.7 The System Titanium Oxide/Manganese Dioxide

This product is also marketed by Matsushita and contains anodically a lithium titanate of the spinel type and of the composition $Li_{1,33}Ti_{1,66}O_4$ that at 800 °C forms a mixture of titanium oxide (anatase) and lithium hydroxide. The cathode is the manganese dioxide of "combined" structure as described in Section 18.7.2.1. For cycle life 400 cycles are reported. A typical average discharge voltage is 1.5 V. Compared to this, the only slightly higher charging voltage demonstrates the high reversibility of the electrode reactions. The energy density is 45 Wh/L. These batteries are applied to watches, memories, and small solar systems. The cells are offered with capacities between 1.2 and 3.0 mAh.

The rechargeable lithium button cells described so far are manufactured in sizes of 1 to 100 mAh of capacity being suitable for appliances which are shut off the grid during breaks and whose operation periods connected to the grid should suffice for recharge of the small accumulators, or for small devices which are equipped with solar cells for recharge during the periodically changing sunshine.

18.7.3 Lithium-Ion Batteries

In order to power appliances and applications of higher energy demand by rechargeable lithium batteries, the technology described so far had to be developed further on towards higher energy contents accompanied by improved specific energy and energy density values, i.e. towards more reactive mass in limited space – and towards better cyclability with 1000 cycles and more at 100% DOD (nominal). These requirements were to be fulfilled of course without any restriction to safety of operation.

Batteries of this quality have been available on the market since the beginning of the 1990s under the name 'lithium-ion batteries'. A pioneer in developing and marketing of this product was Sony, which was able to realize batteries of about 1 Ah capacity in those days.

The lithium-ion technique operates with 'host lattices' for both anode and cathode, between which lithium (ions) are exchanged during discharge and charge. The anode of carbon in the graphitic or coke form contains the lithium in the charged state and delivers it to the cathode made from cobalt oxide CoO_2 during discharge where it is able to build in a maximum amount of lithium corresponding to the formula $LiCoO_2$. The lithium ions migrate during cycling forth and back between the two host lattices of C_x and CoO_2. The following reaction scheme shows this in a simplified manner:

Anode: $LiC_6 \longrightarrow C_6 + Li^+ + e^-$

Cathode: $CoO_2 + Li^+ + e^- \longrightarrow LiCoO_2$

Cell: $LiC_6 + CoO_2 \longrightarrow C_6 + LiCoO_2 \quad E^\circ = 3.9\,V$

For recharge the arrows have to be reversed. This back and forth of the lithium ions is named 'rocking chair' or 'swing' principle. The varieties and specialties of the electrodes and other cell components are investigated as follows.

18.7.3.1 Modifications of Carbon as Host Lattices for the Lithium Anode

Carbon is a candidate for anodic host lattices because of its ability to form small particles of graphitic-layered structures and to build stable, highly porous agglomerates from those particles, which easily incorporate lithium and show good electronic conductivity. The redox potential for the lithium incorporation is near to the potential of the electrochemical solution and deposition of the pure metallic lithium. Consequently, with secondary lithium-ion cells one can expect high cell voltages and energy densities or specific energies, respectively.

Pure carbon is found in nature as graphite and diamond – the two extremely different ideal modifications of this element. Graphite is soft, lubricious, and electronically conductive, whereas diamond is extremely hard, non-fissionable, and electrically insulating. Pure graphite is built from parallel staggered carbon layers (see Figure 18.10), whose carbon atoms are positioned at the corners of symmetrical hexagons, which represent a two-dimensional network like honeycombs. So each carbon atom is bound to the three nearest neighbors in its layer by equivalent forces/chemical bonds. It is formally a 1.5-fold bond between each pair of carbon atoms, a σ-plus a π-bond in part. This results in the significant honeycomb structure.[42] The honeycomb layers can be staggered according to the scheme ABAB... (hexagonal graphite) or the scheme ABCABC... (rhombohedral graphite). The lattice energies, however, and the respective activation energies are so small that one structure may be transformed into the other very easily and in practice both structures are found in a graphite sample. The van der Waals forces[43] – no chemical bonds – between the carbon planes are comparatively weak so that the layers can be shifted easily against each other. Therefore graphite is a useful and well-known dry lubricant and the normal distance between the layers of 3.35 Angstrom may be widened by incorporation of foreign atoms, ions, and molecular components. This behavior is the basis to enable the use of natural graphite and many synthetic graphite and carbon modifications for intercalation of lithium and so as intercalation electrodes.

During the intercalation of lithium cations between the graphitic carbon layers, the accumulation of positive charge is compensated in part by the intake of electrons into the conducting band of the π-bonding system. In most cases the lithium ion electron household is not fully balanced so that a remarkable enhancement of the electronic conductivity follows by quasi-free electrons.[44] The capacity for intake of lithium ions is limited. It was found that lithium ions could be incorporated into

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[42] The chemical bond within the graphite layers is a combination of covalent single bonds – so-called σ-bonds and a delocalized π-bond system, which is found also in the benzene ring molecules. The π-system is distributed over the complete even honeycomb structure of each graphite layer and is responsible for its electronic conductivity because the electrons are free to “move” within the whole layer. Between adjacent graphite layers act no σ- or π-bonds but only weak van der Waals forces (see below), which let the layers glide easily one against the other. Compared with this the diamond crystal has to be understood as one huge three-dimensional molecule where the carbon atoms are connected to each other by four single σ-bonds per carbon atom being oriented into a tetrahedron’s edge. The diamond “molecule” (crystal) has no “free” electrons. That is why it is an insulator.

[43] The van der Waals forces by means of so-called dipole interactions make the cohesion between molecules and molecule clusters in fluids and solids which are not linked by chemical bonds in the true sense (ionic or covalent ones).

[44] These carbon intercalation compounds are also called ‘synthetic metals’.

regular undisturbed graphite structures under normal conditions up to the formula LiC_6 at the most[45] (Figure 18.35). Lithium can also be built as clusters into heavily disturbed carbon preparations (see below).

As already described the distances between the carbon layers have to be enhanced only slightly for that lithium incorporation as can be shown by x-ray analysis of lithium containing graphite and pure graphite. So only little activation energy is needed for that in-out migration of lithium, and consequently the closed circuit voltage (CCV) under load, when lithium leaves the anodic host, is only a little lower than the OCV and only a small overvoltage is needed for recharge – when lithium is inserted again.

During that incorporation of lithium the structure of the graphite crystallite is not only stretched into the direction of the c-axis, i.e. perpendicular to the honeycomb planes. The single layers are also slightly shifted within their planes against each other so that the ABAB order or the ABCABC order becomes an AAAA sequence. In the c-axis direction chains of C_6-Li-C_6-Li-C_6-Li-C_6 are generated that way. The 'bond' between the lithium ion and the nearest C_6 rings compensates for the loss of fit of the closest package of the carbon atoms in pure graphite. Graphitic carbons with a highly disturbed lattice, i.e. with chemical bonds also between the C planes, are not able to allow a total or perfect rearrangement of the carbon planes and hence not able to take lithium up to the maximum of the formula LiC_6.

A graphite crystal gives access to the lithium incorporation only from the edges of the layered structure – as long as there is no disorder within the planes. The geometry of the edges is either of the 'arm chair' or of the 'zigzag' type (Figure 18.36). Here the carbon atoms themselves are also reactive to a certain extent leading to reactions with the electrolytic solvents (see below)[46]. For the "charging" of lithium into the layered structure Figure 18.37 shows a stepwise response of its potential where each potential level or plateau corresponds to equilibrium between two 'load' levels. These load levels[47] thermodynamically represent different "phases" of the lithium carbon intercalation compound. From the more-or-less declined charge and discharge/time characteristic ($U = f(t/C)$) of a lithium-ion battery with graphite anode you can recognize this passing through those different charge and potential levels.

As can be seen in Figure 18.38 during the charging process, both charging and discharging proceed nearly at the same highly negative redox potential as the solvation and deposition of the pure lithium metal (see above), i.e. the energy contents of the pure lithium metal and the lithium intercalated into graphite differ only little. Consequently lithium ion cells deliver high CCV values similarly to lithium primary cells, which are based mostly on a pure metal anode. The usefully high CCV – with respect to the cell's energy density – requires a very precise charging technique which assures that metallic lithium deposition does not happen

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[45] Under high pressure (60 kbar) and high temperature (300 °C) conditions LiC_2 can be also prepared, but degrades then at normal conditions slowly again into LiC_6 and lithium.

[46] See also Section 18,7.3.3 about electrolytes.

[47] The load levels or phases of the lithium intercalation compound are called 'step I' to 'step IV' depending on the number of carbon layers between adjacent interlayers loaded with lithium.

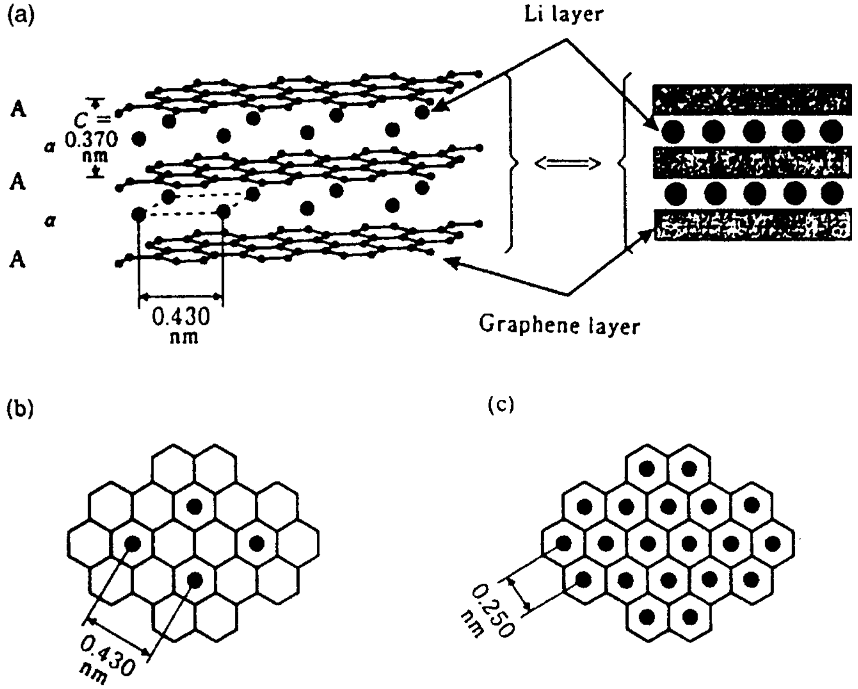

Figure 18.35 Incorporation scheme of lithium in graphite: (a) sequence of layers of LiC_6; (b) distribution of lithium within an interlayer in case of LiC_6; (c) distribution of lithium within an interlayer in case of LiC_2. (From Winter and Besenhard in Ref. 1.)

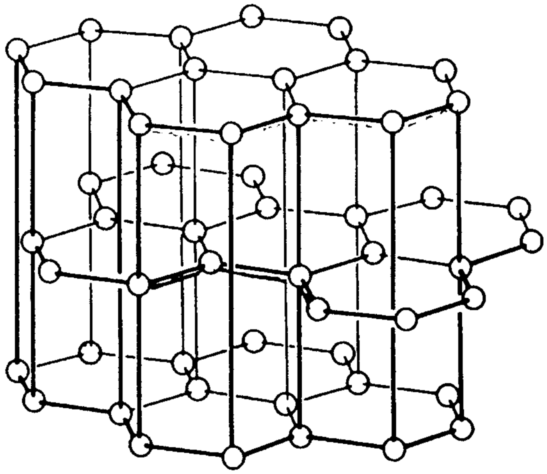

Figure 18.36 Geometry of the edges of hexagonal graphite, 'zig-zag' above and 'armchair' in the middle. In case of incorporation of lithium the ABAB sequence of layers is abandoned in favor of the AAA sequence. (From Ref. 7.)

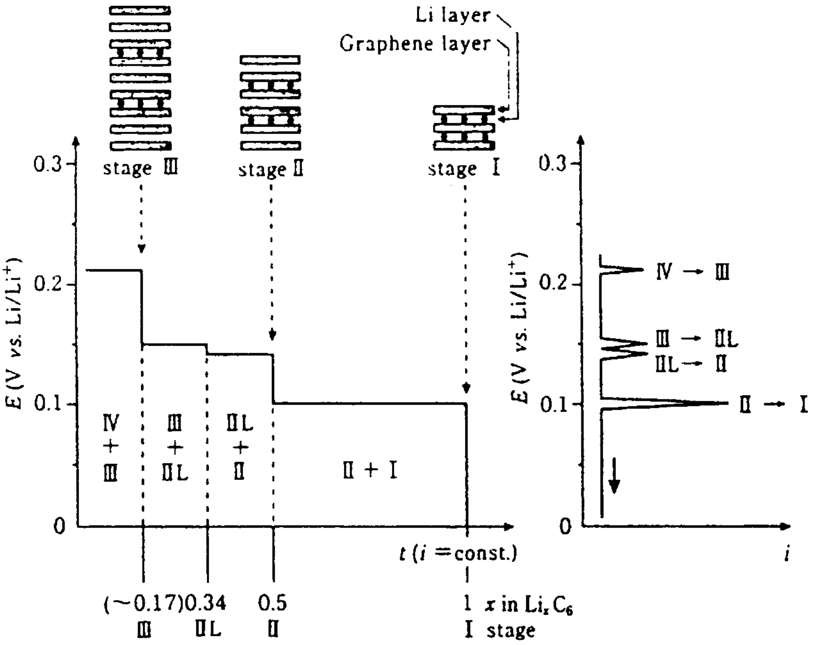

Figure 18.37 Stepwise electrochemical intercalation of lithium in graphite: shown on the left by E = f(x), i = const., in Li_xC_6; on the right by i = f(E), dE/dt = const. (From Winter and Besenhard in Ref. 1.)

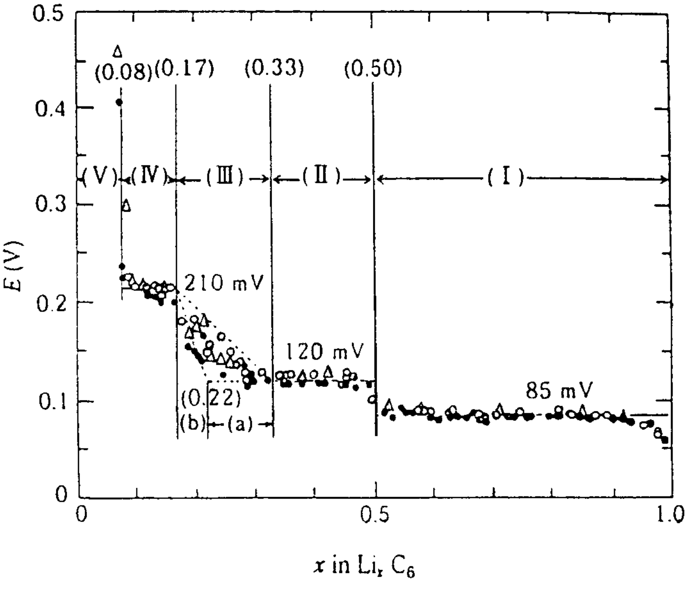

Figure 18.38 Reversible potential (against Li metal) of various Li-graphite intercalation compounds depending on their composition. (From Ohzuku from Besenhard in Ref. 1.)

simultaneously with its intercalation. The redox potentials of both processes are close together, with only 0.1 V difference between metal and full graphite electrode.

For the graphitic carbons as addressed above their 'crystallinity', i.e. their similarity to ideal graphite, is an important criterion for quality, which is described by the average thickness L of the graphite layers being staggered (more-or-less regularly) one upon the other. The degree of disturbance of the layered structure is measured as the deviation of that average distance between the carbon layers in real substances from the "ideal" value of $d = 3.35$ A in undisturbed graphite. For natural graphite one measures $L > 1.000$ A and $d = 3.354$ A, and in artificial graphite produced at elevated temperatures it is $L < 1.000$ A and $d = 3.36$ A. Both substances are really close to the ideal value of $d = 3.35$ A. The degree of disturbance is far higher in various pitch cokes with smaller crystalline areas and wider plane distances: $L = 10–20$ A and $d = 3.38$-3.80 A.

Graphite is a modification of carbon, which is found naturally in a high grade of purity. Far more carbon is found in nature as coal, which is not as pure as graphite. Both are degradation and metamorphic products of floral substances, which were secluded from the air and under high pressure underground for long periods of history (about 350 million years since the Carboniferous period). Coal contains pure carbon but also other elements, constituents of organic substance such as sulfur, oxygen, and hydrogen. The structure of the coal is similar to the graphitic one in tiny areas. The layered structure of coal is highly disturbed, partly already within the graphitic planes themselves because of the incorporation of those three foreign atoms whose bonding geometry is different to the symmetrical bonding of carbon in graphite. So small areas around the foreign atoms deviate from the honeycomb pattern. Practically most of the volatile foreign components of the coal can be withdrawn by high temperature treatment. Nearly pure carbon remains: coke, which is still far different from the said graphite. There are still only tiny areas of the ideal honeycomb and layer structure, which in turn are oriented irregularly to each other and interconnected chemically by 'bridging' atoms. The result is a three-dimensional structure which gives the coke its hardness and stability, which differs a lot from the soft and lubricant behavior of graphite based on the easy gliding of carbon planes against each other. Non-graphitic carbons can also be made from coal tar or pitch, the by-product of the coke "distillation", or from pitch-like high boiling fractions of petroleum or from organic polymers by heating up to 1500 °C or higher under nitrogen atmosphere (pyrolysis). The materials thus prepared from all the various basic substances differ greatly from the highly crystalline graphite because of the said disturbances of the carbon lattice, which limit the carbon planes' sizes and widen the distances of the layers. The hotter, however, and the longer the transformation is carried through, the more graphite-like the product can become. This is valid especially with fluid base materials such as oil pitch, the high boiling fraction of petroleum and coal tar. The various carbon products (cokes) made by such dry distillation are also designated as 'hard' or 'soft' carbons depending on their similarity or dissimilarity to graphite and their mechanical behavior. Especially hard non-graphitic carbons are generated by heating phenolic resins or polymers of furfuryl alcohols up to the respective temperatures (1000 to 2000 °C).

Depending on the solvent used within a lithium battery, graphitic anodes under cyclic operation tend more and more to get their layered structure distorted. This happens when solvate[48] molecules from the electrolytic mix are inserted also into the carbon layers. It is the bigger volume of the solvated ions that destroys the connection between the carbon layers and hence its crystal lattice.[49] Because of its more-or-less poor cyclability, the graphitic carbon is mixed with hard non-graphitic ones. These varieties of coke (made at relatively high temperatures of about 1000 °C) stabilize the graphitic parts of this mixture against distortion. Even if it is accompanied with the loss of specific capacity, this is balanced by the gain in cycles. On the other hand the electrolytic solvent is chosen for the lowest possible degree of incorporation so that the degradation of the layered structure is minimized.

Hard carbons, which are produced mostly at higher temperatures beyond 1000 °C, partly show a remarkable higher specific capacity than the optimal natural graphite at the beginning of their cycle life. This behavior is explained by the "card house" structure of these substances, which can be understood as irregularly connected agglomerates of single carbon sheets or thin multilayer plates of graphitic carbon. These structures have very few regular graphitic interlayer sites for lithium insertion but present many tiny cavities of Ångstrom dimensions. The experts believe that lithium caught as clusters in these cavities and covering both sides of the carbon sheets may explain the high specific lithium capacity of these hard carbons. The potential however of this lithium charge and discharge is less favorable than for graphite and the high specific capacity of the first charges may be lost by cycling.

For battery applications the secondary structure of the carbons is relevant also. The preparations mostly used have a particle sizes of about 10 µm. Electrodes made from these particles together with carbon black[50] and binders[51] are highly porous with an extremely big microscopic inner surface. Hence, even at low microscopic current densities the lithium anodes of the intercalation type can be loaded nearly as high as the very reactive but relatively small macroscopic surfaces of the compact pure metallic anodes of primary batteries.

Lithium ions may enter the intercalation structure only from the surrounding sides and edges of the carbon layers. For some products, to enhance the ratio of "accessible" graphitic edges and sides of the carbon particles' total surface, synthetic microscopically small graphite balls[52] are used which may be understood as turned (machined) from the layered graphitic structure. Micro-short carbon fibres are also successfully applied as anode hosts.

The most important parameter of a lithium ion accumulator, its specific energy, of course depends on how much – reversibly dischargeable – lithium is stored in the carbon host lattice. The ideal maximum charge of the sum formula LiC_6 corresponds to the specific capacity of $372\,mAh\,g^{-1}$. In practice natural graphite shows 330 to $350\,mAh\,g^{-1}$, artificial graphite a bit less.

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[48] Solvate = dissolved, i.e. lithium ions surrounded by molecules of the solvent.

[49] See more details in Section 18.7.3.3 about electrolyte solutions.

[50] To increase the electronic conductivity.

[51] For example, Teflon® particles.

[52] MCMB = mesocarbon microbeads.

18.7.3.2 Transition Metal[53] Oxides as Host Lattices for the Lithium Battery Cathode

In lithium-ion batteries substances should be used as cathode material which can intercalate and discharge lithium ions at a highly positive potential[54] – compared to the intercalation into the carbon anode – and with only low kinetic hindrance, i.e. at low over-voltage or nearly reversible. The first requirement is fulfilled especially by transition metal oxides[55] and halides and also, to a lesser extent, by sulfides. The second requirement of low kinetic hindrance for insertion and release of lithium ions is meant as a requirement of high mobility of lithium ions and electrons within the cathodic lattice and of unhindered mass transfer across phase boundaries as far as phase transitions happen in the host lattice during in- and excorporation of lithium. As the transition metal halides are poorer electronic conductors than oxides, only the latter are used in practice.

The said components and structures are preferable because of the easy redox transition of valence electrons in the $3d^n$ bands of transition metals, which is necessary to compensate for the simultaneous intake or release of lithium ions (Figure 18.39): the metal atoms of these compounds easily change their valence whereas the geometry of their crystal structure is changed only slightly by the lithium in- and excorporation. The function of the $Ni(OH)_2/NiOOH$ electrode during cycling is similarly based on the in and out of hydrogen atoms and acts also as intercalation compound.

Oxides of manganese, nickel, and cobalt have lattice structures, which fit to the requirements of intercalation of lithium. In practice $LiCoO_2$, $LiNiO_2$, and LiO_2O_4 have been proved as useful cathodic materials for lithium-ion batteries. The formulas above correspond more or less to the cathodes in the discharged condition of the cell when most of the lithium ions have migrated from the carbon anode to the oxide intercalation cathode. $LiCoO_2$ and $LiNiO_2$ have a layered structure being similar to that of sodium ferrate (III) $NaFeO_2$ (Figure 18.40), with a cubic closest package of its oxide layers. During discharge of the cell the Li^+ ions are inserted between those $(MeO_2)_x$ layers ($Me = Co, Ni$). The first commercial lithium-ion batteries were equipped with $LiCoO_2$ cathodes. One reason might have been that this substance can easily be made from a mixture of $LiCO_3$ and $CoCO_3$ by heating up to 850 to 950 °C for 20 hrs. This product made so easily can be improved only marginally by further treatment – curing at 850 °C in pure oxygen atmosphere. The critical parameter here is the specific – dischargeable – capacity, which for $LiCoO_3$ cathodes amounts to 150 to 160 $mAh\,g^{-1}$. The cobalt oxide delivers a good and relatively flat discharge characteristic of 4.0 to 3.9 V against the Li/Li^+ anode at limited rates.

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[53] Chemistry calls the elements of groups 3 through 11 'transition metals'. They have an incomplete d shell or can generate cations with an incomplete d shell.

[54] The electrochemical potentials of the partners of the cell reaction describe the energy contents of the various species – ions and electrons – in the corresponding phases. The chemical and electrical components of these potentials can be separated and result then – after rearrangement in a suitable way – in the Nernst equation, which relates the measurable cell voltage to the reaction's free enthalpy.

[55] Also transition metal sulfides as, e.g., TiO_2 are able to intercalate and were intensively investigated correspondingly. The specific redox potential however is much lower than for the oxides.

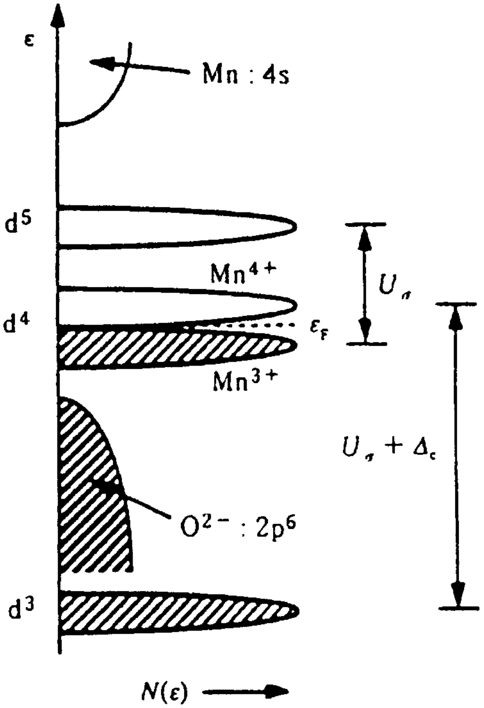

Figure 18.39 Electronic energy levels within the Mn_2O_4 spinel sublattice as given in $LiMn_2O_4$. (From Goodenough in Ref. 1.)

Because of the relatively high cost of the cobalt this technique is not an especially satisfying lasting solution. Corresponding investigations on $LiNiO_2$ cathodes led to promising results. The more economic nickel compound, which by the analog heating resulted in the best capacities, is accessible from a mixture of LiOH and $Ni(OH)_2$, the product giving a specific capacity of only 70 mAh g^{-1} in raw condition. An additional equalization at slightly lower temperatures of 750 °C show practically the same specific capacity as with the cobalt compound – only the voltage declines a little faster during the second half of discharge. As an explanation for this it was found that at higher temperatures the oxide lattice in part of the nickel oxide is disturbed heavily so that far fewer lattice positions are available for lithium incorporation. It is also shown that the similar treatment at 750 °C, but in a pure oxygen atmosphere, improves the compound's quality further, up to reported 190 mAh g^{-1}. Mixed oxides of cobalt and nickel were also investigated with acceptable results. Consequently one may expect that nickel or mixed oxide electrodes will be available for use in the future.

Mn_2O_4 is also less expensive than cobalt and nickel and is easily available as raw material; the manganese dioxide is also environmentally more tolerable than Ni or Co. Therefore, and also because manganese materials have a long tradition as active substances in batteries (more recently also in lithium primary batteries), its applicability for lithium-ion batteries is under investigation.

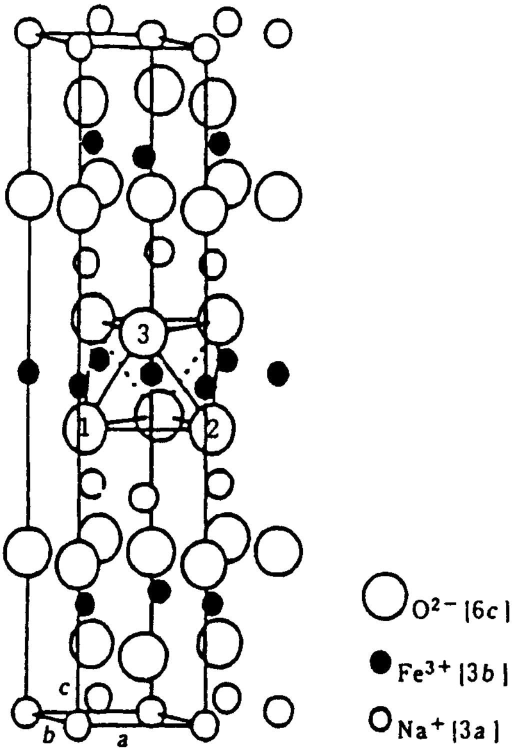

Figure 18.40 Layered structure of α-sodium ferrate (III) as analogy of lithium cobaltite and lithium nickelite. (From Goodenough, Ref. 1.)

Mn_2O_4, $LiMn_2O_4$, and $Li_2Mn_2O_4$ have a structure of the spinel type with cubic symmetry. The $Li_2Mn_2O_4$ structure tends to change easily into the atacamite structure. The spinel structure resembles a three-dimensional system of tube-like voids made from the lattice of manganese and oxygen atoms. Here lithium is not only easily built into but also transported from one void to the other. So far with respect to the ionic conductivity the manganese structure exceeds the layered structures of the cobalt and nickel oxides. The cathodic discharge reaction (and, by reversal, charge reaction) roughly resembles the following equations:

$$Mn_2O^4 + Li \longrightarrow LiMn_2O_4$$

or better

$$Li_xMn_2O_4 + (1 - x)Li \longrightarrow LiMn_2O_4$$

and

$$LiMn_2O_4 + Li \longrightarrow Li_2Mn_2O_4$$

The first step of the lithium incorporation takes place at a cell voltage, against the lithium anode, of about 4 V, the second at about 3 V. Especially the second step suffers from very poor cyclability. So until now it has not been used for practical operation of a rechargeable battery. But also the energetically favored 4 V step shows slow capacity decay during cycling: It amounts to about 40% up to the 100th cycle. For both cases this decay is explained by an irreversible spinel-to-atacamite transformation. Lithium manganese spinels are very promising. Here up to a sixth of the lattice's Mn position is replaced by Cr or better Co. The improved cathodic material delivers up to 400–500 cycles without remarkable loss of capacity (<10%). The endowment obviously hinders the said irreversible phase transition.

18.7.3.3 Electrolytes for Lithium-Ion Batteries

The quality criteria for lithium primary batteries, as far as organic solvents are used, also hold for the secondary cells.[56]

For the application in a high-energy cell with a CCV of 3 to 4 V or higher a sufficient chemical and electrochemical stability of the electrolytic solvents is usually required which ensures that there is no degradation during operation.

The mixture of electrolytic salt and solvents must have a high dielectric constant and a low viscosity and, in most cases combined with it, a low freezing point.

From the cyclic application of a lithium-ion battery additional aspects must be considered for the right choice of the optimal electrolyte. This applies especially to the reactivity of the electrolyte's solvent with the carbon of the anodic host lattice.

The list of suitable solvents which were preferably used for primary cells contains a number of alkyl carbonates, of which the cyclic esters, propylene carbonate (PC), and ethylene carbonate (EC) excel by their high dielectric constant. This ensures the good solvation of the used electrolytic salts. Both, however, are highly viscous because of their polarity, EC higher than PC. To compensate for it, low viscous representatives of straight alkyl carbonates, e.g. the esters dimethyl carbonate (DMC) or diethyl carbonate (DEC), are added as well. These components are stable also at the negative potential of the anode, which does not hold as well for the ethers dimethoxyethane (DME) and tetrahydrofurane (THF). Today lithium-ion batteries with electrolyte mixtures of PC + DEC and EC + DMC are found in the market. As in primary systems lithium salts with voluminous anions are used as electrolyte salts: $LiClO_4$, $LiBF_4$, $LiAsF_6$, $LiPF_6$, and $LiAlCl_4$ (see Section 18.4.2). Lately even more spacious anions have been investigated for their applicability as electrolyte components, e.g. lithium perfluoromethylsulfonimide $Li(CF_3SO_2)_2N$ and the corresponding lithium perfluoromethylsulfomethanide $Li(C_2F_5SO_2)_{2N}$ and lithium perfluoromethylsulfomethanide $Li(CF_3SO_2)_3C$.

The examples of the mixtures of PC/DME and PC/THF with $LiClO_4$ in Figure 18.41 explicitly show that the 1:1 mixtures exhibit an optimum of the conductivity as a matter of fact. The optimal combination of dc and viscosity enhances the molar conductivity by nearly one order of magnitude compared to the data of the components alone. With each special mixture, however, you also have to take into account the kind of solvation of the electrolyte salt, showing total dissociation or perhaps generation of larger ion pairs, which might control the effective conductivity. It is the so-called donor or acceptor ability of the solvents which is responsible for an effective dissociation, depending on how the solvent molecule offers or accepts negative charge to or from the solved ion.

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[56] See also Section 18.4.2 for electrolytes for primary lithium cells.

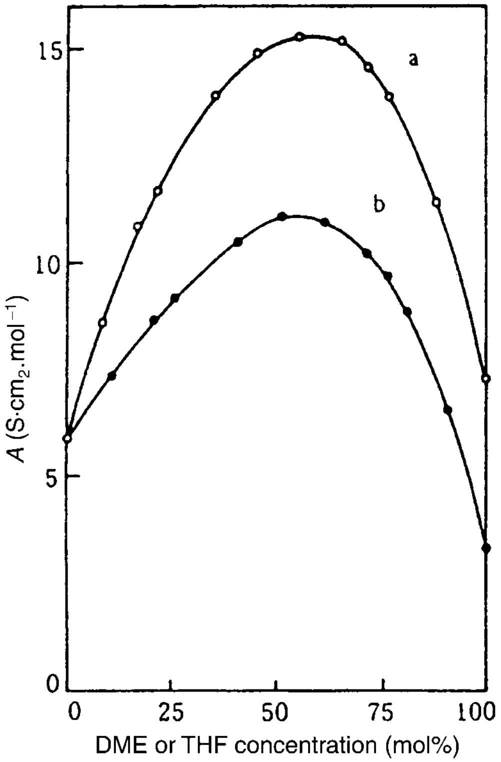

Figure 18.41 Molar conductivity of 1 molar lithium perchlorate solutions, in mixtures of (a) PC + DME and (b) PC + THF (From Matsuda in Ref. 1.)

Besides the optimization of the conductivity, the proper choice of suitable electrolytes depends on for how many cycles it remains stable against the anode. The way any reaction takes place (if at all) with the carbon of the anode determines the cyclability of the system in a crucial sense. The soft carbons, e.g. which were favored first for their good capacities, tend to decompose PC during the charging process: finally a film of lithium carbonate Li_2CO_3 deposits on the carbon surface. The cyclability of the anode now depends on its stability and permeability, differing with various carbon qualities and co-solvents. So for the use of graphitic carbons a mixture of $LiAsF_6$ in EC/DEC composed at a ratio of 3:1 has proved best.

The so-called 'exfoliation' is also based on interactions between carbon and solvent thus destroying the cohesion of the carbon layers during the discharge-charge cycles. Stepwise whole solvent molecules or fragments of it are inserted together with lithium ions by the charging step. These voluminous components are not "discharged" again as done with the lithium ions during the next discharging step and the graphitic interlayer distances do not return to the original values. The anode swells in this way to a macroscopically measurable extent. This problem may be overcome by using, at least in part, the less ideally structured but far more stable hard carbons for the intercalation anode or by application of solvents which can't be inserted as easily.

18.7.4 The System Lithium (Carbon)/Lithium (Cobalt Oxide)

Since 1986 Sony had developed a rechargeable lithium battery, which in 1991 was introduced into the fast growing market of portable telephones, camcorders, CD players, and laptop computers. Based on a lithium carbon intercalation anode and a lithium cobaltite intercalation cathode it was the first product on the market which offered the lithium technology's advantages of light weight and high energy density in a rechargeable and safe version. From 1992 on a modified version with improved cyclability and a protective feature against overcharging has been provided for mobile phones and laptops. Stepwise the capacity was remarkably further enhanced in 1995 and 1997.

The early product was based on soft coke carbon with mostly graphitic structure as the anode. As explained before the lithium is inserted here as ions into the graphite interlayer gaps up to a maximum concentration corresponding to the formula LiC_6 and to a specific capacity of the carbon of 372 $mAh.g^{-1}$ The discharge characteristic of the complete cell was relatively hard with a high OCV even at the end of discharge. But it was recognized that the capacity soon declined during cycling. Computer tomograms of spirally wound cells showed that the anodes were visibly swollen already after about 100 cycles. This was interpreted as destruction of the graphitic structure by 'exfoliation'.

Now instead of soft carbons hard ones were introduced as anodes. The hard carbons have a more stable irregular structure consisting of very small and thin platelets of carbon which are interconnected. Within this network the lithium ions are no longer bound as the C_6-Li-C_6-Li-C_6-Li-C_6 chains perpendicular to the graphite planes already described, but are agglomerated on both sides of the C platelets and inside the cage-like submicroscopic voids of the irregular structure. Thus the specific capacity of the carbon can be enhanced to about 500 $mAh.g^{-1}$. Only beyond this value do NMR spectra show traces of lithium deposited as metallic clusters. With the help of Li NMR it can be shown that the lithium in both the graphite and the hard carbon is bound ionically at least below that mentioned threshold. Besides the higher specific capacity, compared to the soft carbons, the hard carbons are more stable and therefore have a longer cycle life. A disadvantage is the voltage time curve, which declines here earlier at the end of discharge. But this behavior may also be seen as an advantage because in that way it allows us to recognize the state of (residual) charge. The anodic mass is mixed with polyvinylidene fluoride (PVDF) as a binder and some solvent and pasted on both sides of a 10-μm collector foil.

Meanwhile specialists praise the even better features of the matrix of natural graphite for the anode. Now it seems to be possible to suppress the undesired interaction between graphite and solvent. So by Sony and Sanyo today 1.35 Ah and more than 1.000 cycles are claimed for the cell size 18650, whereas the former values were 0.9 (0.95) Ah and 500 cycles.

The Sony battery uses the intercalation compound $LiCoO_2$ for the cathode. The preparation of the lithium cobaltite (by dry heating of a one-to-one mixture of cobalt oxide or carbonate with lithium carbonate in an air stream up to 950 °C) was modified twice. First to get larger particles of cobaltite, polyvinyl alcohol (PVA) is added to the powder mix of the two components during the mixing and granulating process before the heat treatment. The PVA is an organic compound being sometimes used as a glue by battery makers. It burns and evaporates without residues in the heat. Instead of 1- to 5-µm granules made without glue the additive yields granules with 15- to 20-µm diameters. Electrodes made from this material react more inertly under short conditions and hence the cells are less prone to overheating. The second improvement concerns a safety feature built into the cathodic substance. We know that overcharging may deposit metallic lithium at the anode, which is dangerous because of its high reactivity. As a protective measure a slight excess of Li_2CO_3 is added to the cathode mix which is decomposed by overcharging at voltages of over 4.80 V and thus creates overpressure in the hermetically sealed cell by its gaseous reaction products. A suitably designed membrane bulges consequently and interrupts the contact between the cathode and the battery's positive pole. The cathodic material is mixed, in analogy to the anodic side, with PVDF and solvent, and pasted on both sides of an aluminum conducting foil.

The cathode manufacturing process as described here shows that the electrodes are prepared and assembled to complete cells in the discharged state. This is a basic requirement because of the sensitiveness and reactivity of the lithium-charged anode, which is charged best for the first time in situ, in the cell.

For the improved cell with hard carbon anode a 1-molar solution of $LiPF_6$ in a 1:1 mixture of PC/DEC was applied. The PC, which reacts by decomposition on graphite, is practically stable with hard carbon. With its relatively low viscosity (compared to EC) it enables good deep temperature discharge ability.

Twofold stretched polyethylene (PE) is used as separator. Stretching which lets the ionic current pass through the polymeric network generates the pores. The pore structure is stable, however, only at normal operating temperatures. With the temperature being enhanced beyond a defined threshold value, the separator "remembers" its state before the stretching and shrinks again, closing the pores. The separator becomes highly resistive and the discharge reaction is interrupted. Neither of the components can react in an uncontrolled way (any longer).

The lithium-ion cell is manufactured as a cylindrical round cell from a pair of electrode strips being spirally wound together with two separator foils. The electrode coil may also be flattened and put into a prismatic housing. The Sony (and Sanyo) round cells have steel containers and these are, e.g. with the sizes 18650 or 18500, negatively polarized. The lid is positive and is insulated electrically and sealed against the can by a plastic gasket. The lid contains (sandwich-like) the outer contact, a thermo switch foil (Polyswitch®) and that disconnecting membrane that might be activated by overpressure. The Polyswitch® is made of a polymer foil, which is conductive at normal temperature but becomes non-conductive at a defined threshold temperature, here at about 100 °C. In contrast to the separator's shutdown and the switch-off of the membrane the Polyswitch® is reset again by simply cooling down, i.e. the Polyswitch® foil becomes conductive again when the temperature drops.

The specific energy (Wh/kg) of this system and its energy density (Wh/L) are remarkably higher[57] than the traditional NiCd or nickel/metal hydride systems as we might expect and as it can be seen in Figure 18.42. Therefore portable devices driven

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[57] For the cited Sony cell 18650 (new design) the energy density is 295 Wh/L and the specific energy 120 Wh/kg.

Chemistry	ED (Wh/l)	SE (Wh/kg)
NiCd	120-150	40-50
NiMH	250-300	70-80
LiIon	280-320	110-130

Figure 18.42 Comparison of the energy contents of the competing battery systems nickel/cadmium, nickel/metal hydride, and lithium-ion (Energizer). (From Braun in Ref. 10.)

by it may operate far longer. The data of the nickel/metal hydride system were also improved recently.

Typical discharge curves of a lithium-ion battery of another producer are shown in Figures 18.43 and 18.44 for various loads, from a 15-minute to a 5-hour discharge of the nominal capacity, and at normal and reduced or enhanced temperatures from −20 to +60 °C. A good discharge ability at high rates and at low temperatures is recognized here, too. The charging curve in Figure 18.45 demonstrates how a lithium-ion battery is fully recharged within 3 hours and up to 95% within 1.5 hours. The charger, however, has to be a little sophisticated: The charging current and voltage are to be limited according to the shown I-U scheme. The side reactions which might occur otherwise (deposition of metallic lithium and decomposition of the electrolyte solvent) would jeopardize the safety and the cycle life of the battery.

But with controlled chargers, lithium-ion batteries are well cyclable. Figure 18.46 shows how the usable capacity of an AA cell of Tadiran develops during 1000 cycles. More than 80% of the initial capacity is still available thereafter.

Batteries being assembled from a larger number of single cells as, for example, necessary for laptops (Figure 18.47) are equipped with an even more complicated

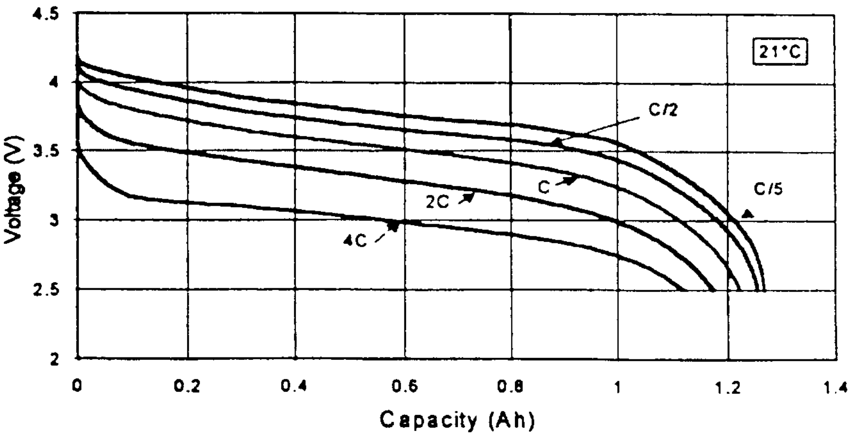

Figure 18.43 Discharge graphs of a lithium-ion cell 18650 at various loads (PolyStor), (From Juzkow in Ref. 10.)

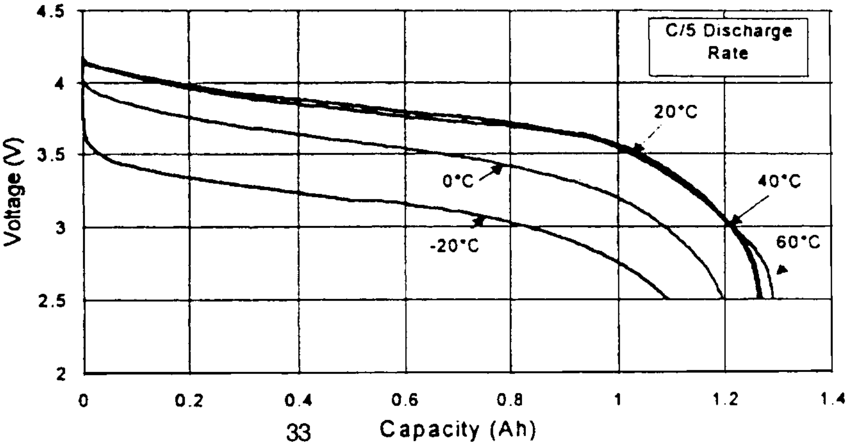

Figure 18.44 Discharge graphs of a lithium-ion cell 18650 at 5 hours discharge and various temperatures (PolyStor). (From Juzkow in Ref. 10.)

electronic device for control and safety. It protects the battery against too high currents during charge and discharge, against deep discharge, and it assists recharge after deep discharge on account of extended storage. Figure 18.48 contains a corresponding wiring scheme. A back-setting thermo switch (Polyswitch, PTC), a fuse, a safety vent, and a thermocouple (NTC) are the elements of the safety equipment in addition to safety components of each single cell.

The example of Sony in Figure 18.49 shows how a typical cylindrical cell is designed. Flat cubic cell formats are also supplied, e.g. the cell type UF 101248 of Sanyo with 750 mAh and dimensions of 10.5 mm × 22.5 mm × 48 mm.

Lithium-ion batteries were very carefully checked during development for their safety and reliability (see also Section 4.8). According to national and international

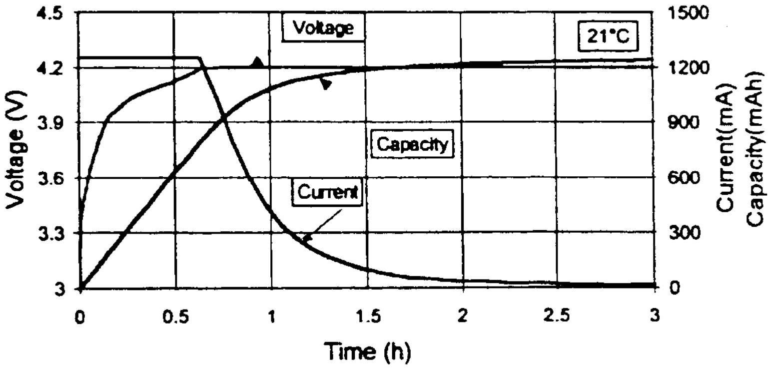

Figure 18.45 Charge characteristics of a lithium-ion cell 18650 (PolyStor). (From Juzkow in Ref. 10.)

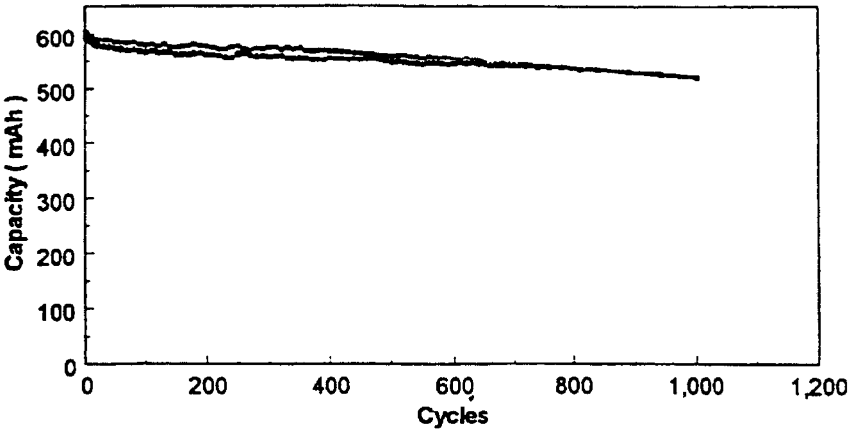

Figure 18.46 Dischargeable capacity during the cycle life of a lithium-ion battery (Tadiran). (From Luski et al. in Ref. 10.)

regulations the prototypes are investigated before official acknowledgment and release for the following impacts and environmental conditions:

- Continuous charging.
- Overcharging.
- (Forced) deep discharge.
- High rate discharge.
- External short.
- Shock and vibration.
- Changing pressure.
- Open fire.
- Heat.

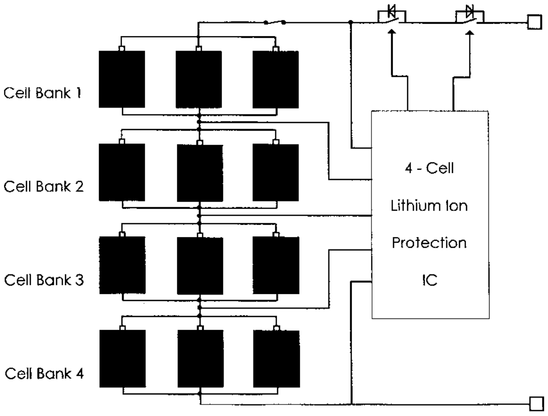

Figure 18.47 Circuit diagram in principle of a multi-cell lithium-ion battery with four groups in series of three cells in parallel each (Energizer) (From Braun in Ref. 10.)

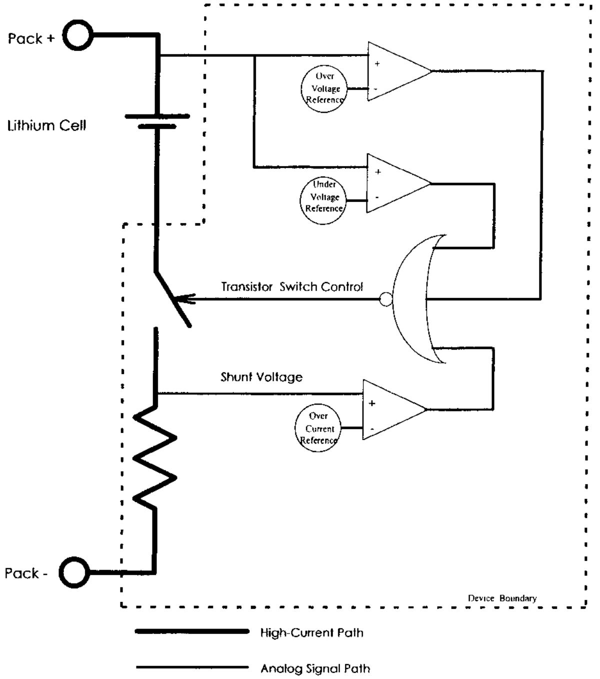

Figure 18.48 Circuit diagram of the surveillance and control electronics of a multi-cell lithium-ion battery (Energizer) (From Braun in Ref. 10.)

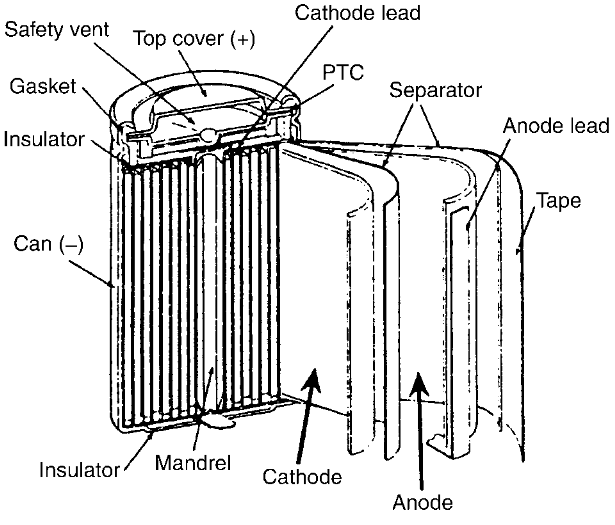

Figure 18.49 Design of the Sony lithium-ion cell. (From Nishi in Ref. 1.)

- Thermal shock.
- Mechanical damage, crushing.
- Puncture.

Sony, Sanyo, Panasonic, Eveready (Energizer), Tadiran, Yardney, and others nowadays produce lithium-ion batteries.

18.7.5 Other Rechargeable Lithium Batteries

The technology of rechargeable lithium batteries is being developed continuously. Goals are larger batteries, e.g. for the hybrid propulsion system of vehicles,[58] environmentally more compatible components, especially for the cathode, lower priced materials, longer cycle lives, more inert electrodes, etc. So-called solid-state batteries with polymeric electrolyte are also to be mentioned here. They are lithium-ion cells with an inert polymer matrix or a gel, which contains the electrolytic solvent-conductive salt mix.[59] Herewith, the use of the normal heavy steel containers, which cannot be manufactured with heavily reduced wall thickness anyway, can be abandoned; and a plastic laminated aluminum foil can be applied instead. In this way lightweight and very thin cells of a card format can be made.

The field of research and development is wide. The urge of competition is high and the preliminary results are promising.

18.7.6 Potential Safety Impacts

One substantial problem of the lithium technology is the fact of the lithium metal's melting point at 180°C. The liquid metal is highly reactive in contrast to the solid state. So within a cell it tends to react with the cathode material and the components of the electrolyte just when its melting point is reached. This reaction delivers a high amount of thermal energy. So in many cases the melting of lithium leads to the damage of the cell case.

The potential of rapid reaction is generally higher with primary cells of high loadability than with low rate types or secondary cells with alloy or intercalation anode. Primary reaction products can also initiate additional undesired reactions if they possess suitable reactivity. The sulfur which is released during the discharge of thionyl chloride cells belongs to this category.

Another risk is a rapid increase of the internal pressure following fast rise of temperature if there are low boiling components or reaction products in the cell (e.g. S_x, SO_2, $SOCl_2$).

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[58] Since 1997 Toyota has been selling their hybrid passenger car Prius with growing success. Until now this car uses a nickel/metal hydride battery for buffering its energy.

[59] The principle is well known from sealed lead-acid batteries, which contain their electrolyte immobilized, by glass mats or silica gel. For lithium rechargeable batteries it is called SPE (solid polymer electrolyte) or gel technology.

18.7.7 Safety Measures

Lithium batteries ought to be intrinsically safe by layout and design: Here we mean, for example, the balanced cathode-anode design, the stabilization of the lithium metal by an alloying partner metal, or another solid state substratum, which all enhance the critical temperature significantly. They also comprise the thermally soft or weak separators, which close their pores at a defined (high) temperature and stop any further discharge reaction, and finally an electrode surface as small as possible which limits the discharge rate but also hinders the thermal runaway if the cell is shortened. The electrolyte solvents have to be chosen to minimize undesired reactions.

Special design features serve to gradually realize safety. If safety mechanisms operate early enough, a worse result can be avoided. These safety mechanisms are, e.g., bursting vents which open the hermetically sealed system instantaneously and thus release (as in the case of the sulfur dioxide system) a pressurized component that will not be able to react any longer. Secondary risks, e.g. release of sulfur dioxide in closed rooms, have to be taken into consideration, too.

All mechanisms which operate at a defined threshold temperature can be reckoned as built-in safety means. These are fuses for "single" applications or thermo switches which recover by cooling down again. Features like these are effective only with problems caused by the outer circuitry the cell or battery is embedded into.

The new secondary systems are mainly safety controlled by electronic charge and discharge control devices to avoid any damage by faulty operation. Here we mean the limitation of charge and discharge voltages, thermo control devices and switches, and membranes to avoid overpressure.

Eventually safe operation and handling of lithium batteries may be also based on observation of operation instructions; therefore at least the high power versions of lithium batteries have to be kept away from consumers, and the use of these batteries is only meant for experts who can abide by the necessary safety instructions.

As international safety standard IEC 60086-4, Primary Batteries, Part 4: Safety Standard for Lithium Batteries, is valid for lithium primary batteries and IEC 61960-1 and 61960-2, Secondary Lithium Cells and Batteries for Portable Applications, Part 1: Secondary Lithium Cells and Part 2: Secondary Lithium Batteries, apply to the secondary techniques. Here the details of test and approval procedures can be found.

18.8 DISPOSAL OF LITHIUM BATTERIES

Besides the risks for health and equipment, the question of environmental compatibility of the disposal of lithium batteries after use and of scrap of the production has to be answered. The entire chemical, thermal, electric, and toxic aspects of the lithium battery technology have to be considered. The lithium metal is far less harmful than the heavy metal mercury. On the other hand thermal decomposition of a lithium high rate battery might be locally much more disastrous than a bursting alkali manganese or lead-acid battery.

After the approaches in the German Federal Republic to a "free agreement" between manufacturers and traders of conventional batteries to minimize the problems of the poisonous metals mercury and cadmium, we consequently have to talk about lithium batteries, too. This will become difficult, because the large variety of different lithium battery systems hinders a quick and simple analysis of the battery scrap and an assessment of the related risks. This might be difficult to carry out at least for local environmental authorities.

The present situation is made easier by the comparably low turnover of lithium batteries. Partly batteries are disposed of as harmless in normal sanitary landfills (like primary lithium/manganese dioxide cells), partly more active systems are brought to special landfills (like lithium/sulfur dioxide together with neutralizing amounts of limestone), and partly batteries are burned in special ovens in combination with oil (like lithium/thionylchloride batteries).

Various domestic and external companies[60] offer the disposal and the recycling of lithium battery scrap. Most procedures comprise shredding, washing, recuperation of the cell case metals, and concentration and burning of those components that can't be reused. It is a basic requirement of all recycling methods that the user and consumer fully support all activities of collection and sorting of the batteries in question.

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[60] For $LiMnO_2$: RVD process of Accurec, Mülheim, Germany; for lithium-ion batteries: S.N.A.M. in St. Quentin Fallavier, France. Also for all types of batteries: Batrec AG of Dietikon, Switzerland, Recymet S.A. of Nyon, Switzerland, Toxco of Trail, B.C., Canada.

19

The Disposal of Portable Batteries

J. L. FRICKE and N. KNUDSEN

19.1 PORTABLE BATTERY SYSTEMS AND THEIR RELEVANCE TO THE ENVIRONMENT

Batteries are generally galvanic cells which convert chemical energy into electrical energy. As mobile sources of energy, we can no longer imagine life in the modern world without them. Every year in Germany, approximately 1 billion portable batteries are sold, an equivalent of around 30,000 tons (Table 19.1). We can state that 85% of the battery market comprises non-rechargeable primary batteries and 15% rechargeable secondary batteries.

Since production and use of portable batteries have become of little ecological relevance, the main focus has now turned to the spent product, the waste. Avoidance, recycling, and then disposal is the order prescribed by the German Waste Management and Recycling Act (law to promote life cycle management and to ensure environmentally friendly waste disposal (KrW-/AbfG) dated 27 September 1994). In principle, the battery industry is in agreement with these goals. It is even setting an example to others in many fields. In so doing, the main focus is on avoiding hazardous substances in terms of disposal and establishing recycling procedures.

19.1.1 Main Systems and Their Implementation

In the following overview, you will find a selection of current electrochemical systems and their typical areas of application (Table 19.2). These varied areas of application

Table 19.1 Batteries brought into circulation by GRS users in 1999 and 2000.

		1999 in tons (app.)	2000 in tons (app.)
Primary			
Round cells	ZnC	9,206	9,118
	AlMn	12,156	15,083
	Zinc-Air	30	32
	Lithium	264	351
Round cells R9	HgO	6.6	7.0
	AgO	54	51
	AlMn	31	34
	Zinc-Air	45	44
	Lithium	92	90
Subtotal		21,885	24,810
Secondary			
Round cells	Lithium-Ion	333	426
	NiMH	672	1,689
	AlMn	6.6	19
	Pb	290	482
	NiCd	1,840	1,840
Round cells R9	Lithium-Ion	0.5	4.7
	NiMH	4.5	9.9
	NiCd	1.5	3.9
Subtotal		3,138	4,475
Total		**25,023**	**29,284**

Source: GRS Batterien.

Table 19.2 Areas of application.

System	Area of application (example)
Primary batteries	
AlMn	Tape recorders, flashlights
ZnC	Kitchen clocks, travel alarm clocks
Lithium	Cameras
Round cell batteries R9	Toys, watches, hearing aids
Secondary batteries	
NiCd	Drill/drivers, electric toothbrushes
NiMH/Li-ion	Mobile phones, laptop computers
Lead	Starter and drive batteries
Round cell batteries R9	Calculators, computers

Source: GRS Batterien.

Table 19.3 The best-selling battery sizes.

International designation	Conventional designation	AlMn	ZnC	Voltage (Volts)
AA	Mignon	LR 6	R 6	1.5
AAA	Micro	LR 03	R 03	1.5
C	Baby	LR 14	R 14	1.5
D	Mono	LR 20	R 20	1.5
9V	E-block	6 LR 61	6 F 22	6 × 1.5 = 9
4.5V	Normal/flat	3 LR 12	3 R 12	3 × 1.5 = 4.5

Source: Duracell GmbH.

necessitated the manufacture of numerous sizes (Table 19.3). The R9 round cells also come in a variety of sizes.

Depending on the electrochemical system, some portable batteries contain hazardous substances such as mercury, cadmium, and lead. Table 19.4 shows an overview of the main substances contained in portable batteries in percentages by weight. (The material composition varies significantly depending on the battery size, type, and composition. All figures are mean averages.)

Mobile applications of the future require both power and energy capacity and low weight, a combination which can no longer be provided by conventional battery types and systems. It is conceivable that in the future polymer electrolyte fuel cells (PEMs) may even be used in the field of portable applications. Prototypes of laptops and mobile phones which run on PEMs instead of conventional batteries have already been developed.

19.1.2 Significance of Heavy Metals for Disposal

Without going into detail regarding the toxicity and ecotoxicity of the heavy metals contained in batteries, it is clear that large quantities of mercury, cadmium, or lead must not be disposed of in domestic waste disposal facilities (normal tips) as contamination of the surrounding areas cannot definitively be prevented.

The basic principles of the European and, in particular, the German battery industry therefore call for the avoidance of environmentally harmful substances in battery systems or, where this is unavoidable, the separation and recycling of these batteries. Avoidance is not always possible.

Lead and cadmium are used as active substances in lead batteries with up to 65% lead by weight and nickel/cadmium batteries with up to 15% cadmium by weight. Mercury is used as a passive component in R9 round cells with up to 2% by weight.

19.1.2.1 Mercury

In December 1998 (Directive 98/101/EU of 22.12.1998), as part of an amendment to the existing 1991 battery directive (91/157/EEC), the European Commission banned the marketing of batteries and accumulators with a mercury content of more than 5 ppm (parts per million) effective from January 1, 2000. The ban includes batteries

Table 19.4 Main substances contained in batteries.

	Metals									Electrolytes					Non-metals
System	Pb	Ni	Cd	Zn	Mn	Ag	Hg	Li	Fe	H_2SO_4	KOH	NH_4Cl, $ZnCl_2$	Organ. Electr.	H_2O	Plastics, paper, carbon, soot
Pb/PbO_2	65									8				17	10
NiCd (steel c.)		20	15						45		5			10	5
Zn/MnO_2															
acid				20	25				20			5		10	20
alkaline				20	30				20		5			10	15
Zn/AgO_2				10		30	1	40		3			6	10	
Zn/HgO				10			30		40		3			6	11
Zn/O_2				30			2		45		4			8	12
Li/MnO_2					30			2	50				10		10

Source: Batteries Association in the ZVEI.

and accumulators built into devices. Only round cell batteries and batteries constructed from round cell batteries with a mercury content of not more than 2 percent by weight are excluded from this ban. This directive still awaits implementation as national law.

The addition of mercury has been completely and successfully eliminated from non-rechargeable portable batteries (primary batteries). The major battery suppliers in Europe (they cover approximately 95% of the market) have been offering them mercury-free since 1994. The financial expenditure for the development and the operating costs for mercury-free production were and still are considerable.

The waste stream, however, will also continue to contain a certain amount of mercury for some time after the mercury ban. This has consequences for the recycling process (see Figure 19.1).

As another major contribution to the reduction of hazardous substances, the European battery manufacturers had already decided in mid-1999 to cease sales of mercury oxide round cell batteries, which are mainly used in hearing aids. As an alternative, zinc/air batteries with a low mercury content (far less than 1 percent of weight in Hg) are used. Advances made in hearing aids and battery technology now make it possible to use these batteries even in hearing aids for the extremely hard of hearing. Zinc/air batteries have been on offer for ordinary hearing aids for more than a decade now.

As part of the aforementioned implementation of the EU Directive, the marketing of mercury oxide batteries should also be banned effective from January 1, 2000. This directive still awaits implementation in national law.

Batteries containing mercury are labelled as in Figure 19.2.

19.1.2.2 Cadmium

Batteries containing nickel/cadmium are rechargeable (secondary) batteries. They are alkaline accumulators in which the positive mass consists primarily of nickel

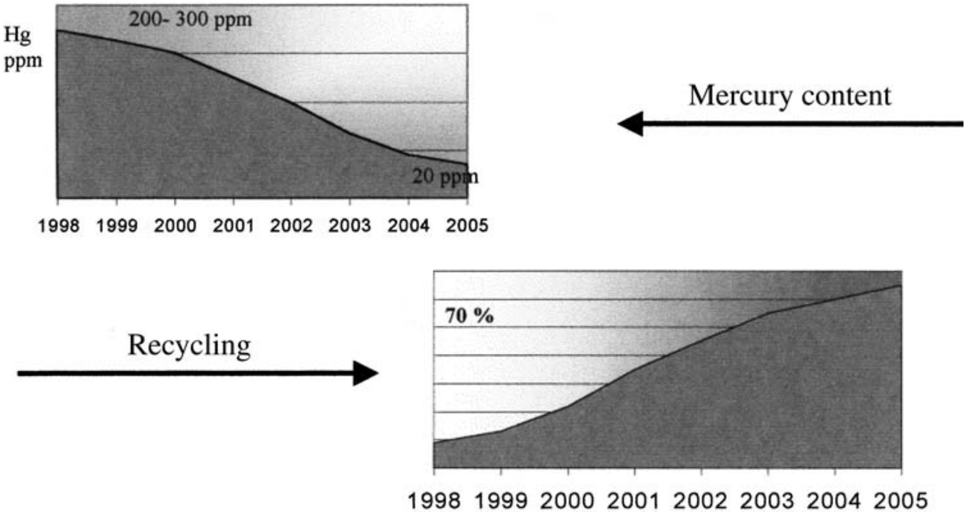


Figure 19.1 Mercury content-recycling interdependence. Source: GRS.

Figure 19.2 Labelling of batteries containing mercury. Source: BattV.

hydroxide and the negative mass mainly of cadmium. The German Battery Decree includes nickel/cadmium accumulators in the category of batteries containing harmful substances. In certain areas of application, they are increasingly being replaced with cadmium-free nickel/metal hydride batteries. Recently, lithium-ion batteries have been offered on the market, particularly for laptop computers and mobile phones. These, too, contain no mercury, cadmium, nor lead.

Batteries containing cadmium are labelled as in Figure 19.3.

19.1.2.3 Lead

A lead battery is an accumulator in which the electrodes consist primarily of lead, while a diluted sulfuric acid is used as an electrolyte. The lead is used in the form of bivalent and quadrivalent compounds ($PbSO_4$ and PbO_2) and as a porous lead sponge for active masses, as well as in the form of lead-antimony or lead-calcium alloys for grids in lead batteries. The level of use of lead batteries in the portable appliance market is low. The main areas of application are starter and drive batteries as well as for uninterrupted power supply to stationary systems.

Batteries containing lead are labelled as in Figure 19.4.

A variety of battery systems will still be required in the future, as there will be no such thing as a "universal battery" that is equally suitable for all applications.

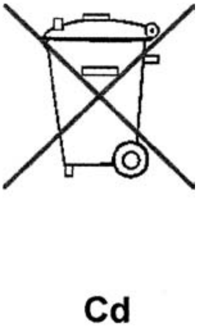


Figure 19.3 Labelling of batteries containing cadmium. Source: BattV.

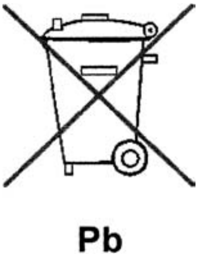


Figure 19.4 Labelling of batteries containing lead. Source: BattV.

19.1.3 Basic Prerequisites for Recycling

19.1.3.1 Collection

Batteries must first be collected before they can be recycled. Portable batteries are normally collected as a mixture, as end users cannot perform the meticulous presorting required for recycling. Thus a comprehensive nationwide system for the collection of batteries has been developed and is in place today.

End users can either return their used portable batteries to their retailers or to the collection points set up by the communities. Commercial end users are likewise provided with collection and transport containers free of charge for the collection of their used batteries. (GRS collection containers [see Figure 19.5].)

19.1.3.2 Sorting

Battery sorting facilities work according to different procedures. Two of them are presented in brief in the following.

Sorting by Means of Electrodynamic Sensors

The EPBA/Sortbat and Eurobatri facilities work with electrodynamic sensors. This process has already been implemented in routine operation for sorting portable battery mixtures (see Figures 19.6 and 19.7).

The batteries are mechanically and magnetically sorted into different fractions according to their composition, i.e. after hand sorting, during which incorrectly sorted batteries and larger batteries are removed, they are sorted by size, and the R9 cells are sieved out. The round cells are run across a magnetic separator. The non-

Figure 19.5 Pictures of the GRS collection containers. Source: GRS Batterien.

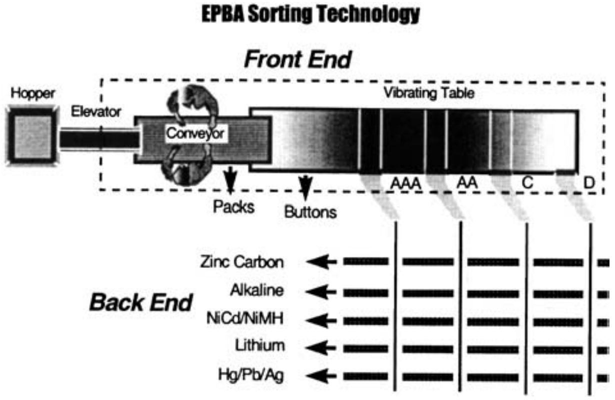


Figure 19.6 Battery sorting facility. Source: EPBA.

magnetic batteries (paper jacket, primarily ZnC, make up approximately 15% of the round cells) are not sorted any further automatically. The magnetic batteries are identified by an electrodynamic sensor based on their "magnetic fingerprints".

To put it simply, the sensor consists mainly of a spool through which current flows, generating a magnetic field. Depending on which electrochemical system is passing the sensor at any given moment, the magnetic field changes. Based on this change, the respective battery system is identified. This process sorts the batteries at a speed of six batteries per second.

LSI has developed a new electrodynamic sensor which also facilitates the separation of NiCd and NiMH batteries.

Sorting by Means of X-Ray Sensors

In this process, after hand and size sorting, the batteries are separated from a stock silo via different conveyor belts and fed to the x-ray sensor. The radioscopy unit consists of an x-ray tube and a sensor installed in a radiation protection cabin. The electrochemical battery type is identified in real time. The batteries fall off the conveyor belt and are pushed out of their trajectory by compressed air blasts from

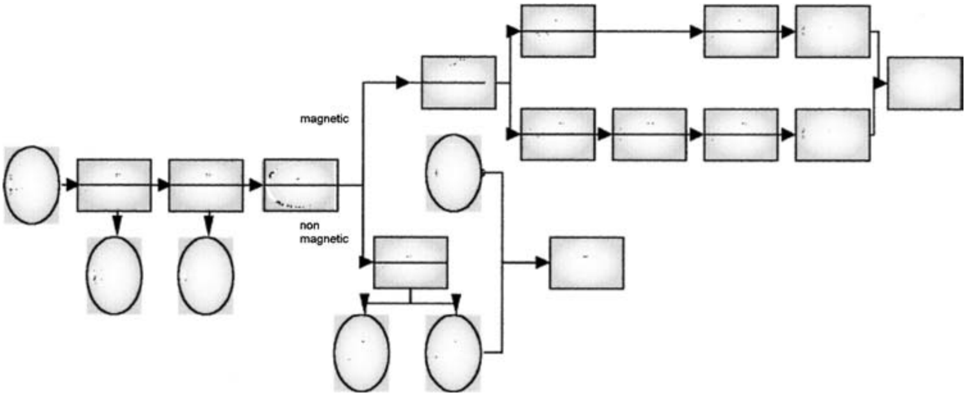


Figure 19.7 Processing principle of the battery sorting facility. Source: GMA, Schortens.

the side or from above. In this fashion several fractions can be reliably separated. Sorting speeds of up to 10 batteries per second are achieved with battery intervals of approximately 7 mm. The analysis ensues by computer, which likewise identifies the battery types based on the gray levels of the x-ray image. A prototype of this system has been in operation since early 2000.

The UV Detector

For the further recycling of the AIMn and ZnC systems it is important to separate the batteries containing mercury from the mercury-free batteries after separation into the various electrochemical systems.

Since the mid-1990s, these batteries have been produced only in mercury-free form by the European manufacturers, but older batteries or imported batteries containing mercury still make their way into the waste disposal system. In order to separate these in the sorting facilities from the mercury-free batteries, for which recycling procedures already exist, the European battery manufacturers have coded their own AIMn brands and some of the ZnC batteries with a UV-sensitive varnish, so that in future batteries containing mercury can be separated by means of sensors from mercury-free batteries.

19.2 RECYCLING PROCEDURES AND LEVEL OF RECYCLING

Batteries contain a range of recyclable metals and can thus be used as sources of raw materials. Below you will find a selection of the major recycling procedures for portable batteries from the various electrochemical systems. There are sufficient facilities to deal with round and button cell batteries containing lead, nickel/cadmium, nickel/metal hydride, and mercury. For the newer nickel/metal hydride and lithium systems, however, recycling is still in the early stages. For all the other aforementioned systems, such procedures have been in place for some time now.

19.2.1 Lead Batteries

Lead can rightly be termed the classic recycling material. The first facilities for the recovery of lead from used lead batteries were developed about 100 years ago. In the beginning this was due exclusively to economic considerations, as lead has always been a valuable raw material. With the dramatic growth of automobile traffic, ecological aspects became increasingly important over the past few decades. What has remained the same? The trick of using lead without consuming it.

There are basically two processes for recovering lead from used accumulators. Either the battery waste is prepared before metallurgical processing and separated according to composition (lead, plastic, acid, etc.), or the batteries are processed whole. In the shaft furnace process, the second method is used. The batteries are emptied of liquid acid and remain otherwise whole. Without further preparation they are put into the shaft furnace, where they undergo metallurgical processing in a mixture with aggregates such as coke, limestone, and iron. These aggregates enhance the combustion and conversion processes in the shaft furnace and help to recover the lead stepwise and to purify it of contaminants. The result is raw or pig lead (see Figure 19.8).

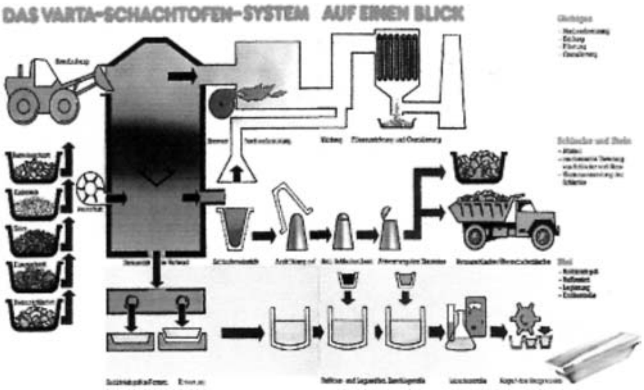


Figure 19.8 Functional diagram of the VARTA facility. Source: VARTA.

19.2.2 Nickel/Cadmium Batteries

For the recycling of used Ni/Cd batteries, again only thermal procedures have hitherto gained any significance. Generally, the cadmium is precipitated in a vacuum or an inert atmosphere and the remaining steel-nickel compound is worked into iron-nickel for steel production. Due to the comparatively small quantities of nickel/cadmium batteries used (8000 tons/year), the capacities offered by the existing facilities in Germany, France, and Sweden are sufficient for the recycling of all batteries in Western Europe (see Figure 19.9).

19.2.3 Batteries Containing Mercury (R9 Cells)

In Germany, there are currently several processing facilities for batteries containing mercury. Some of them work according to the ALD procedure. This procedure is used chiefly for the removal of mercury from mercury-containing components in natural gas production and chlorine-alkali electrolysis. It can also be used for the removal of volatile components from various materials and compounds. With the ALD procedure, the mercury-containing waste products undergo vacuo-thermal treatment. This is done in special, hermetically sealed facilities in batches. With temperatures between 350°C and 650°C, the mercury vaporizes and then condenses at lower temperatures (see Figure 19.10).

19.2.4 Nickel/Metal Hydride Batteries

Just after the market launch of nickel/metal hydride batteries, the German company NIREC began work on the recycling of these batteries in order to put the nickel back into the cycle of materials. The system places procedural emphasis on the separation, reclamation, and use of the high-quality nickel content and the potential risk of hydrogen. Due to the possibility of hydrogen being released as the NiMH batteries are broken down, the processing must be done in a vacuum environment. Thus, using a vacuum system, the batteries are passed through a cutting chamber which opens up the casing and releases the stored hydrogen. This is constantly drawn off by

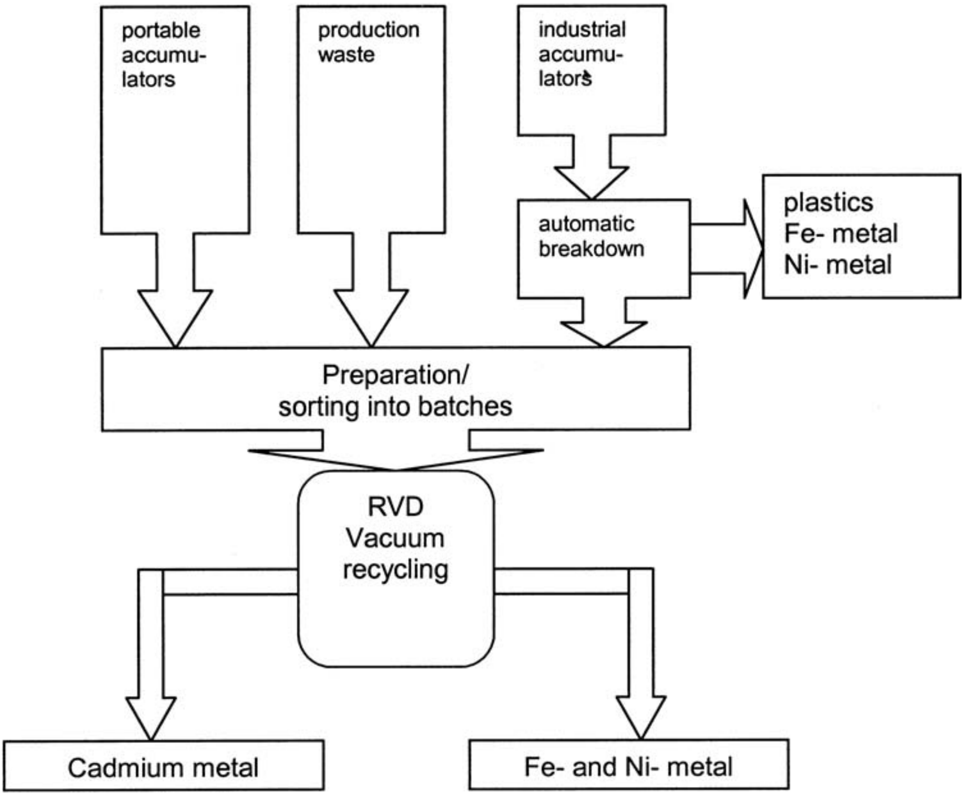


Figure 19.9 Recycling process of Accurec. Source: Accurec.

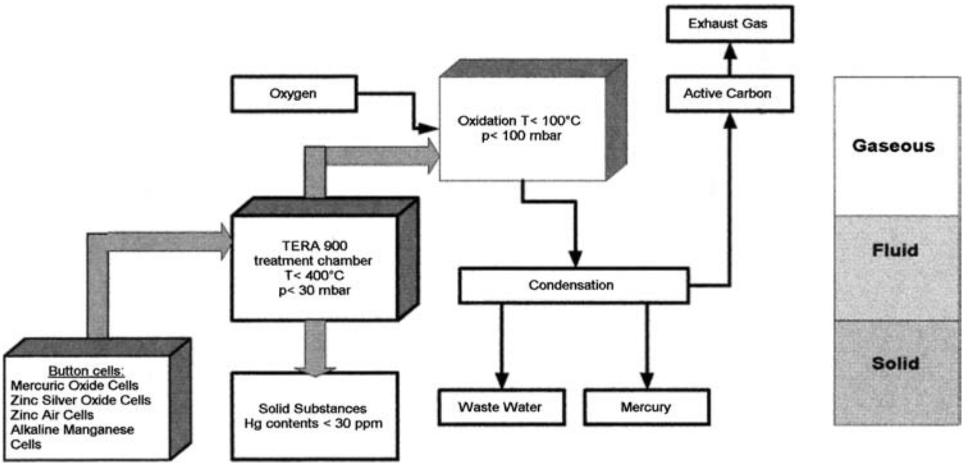


Figure 19.10 Recycling of R9 batteries containing mercury. Source: EPBA.

the difference in pressure. The batteries then go into a collecting tank. After expiry of a stabilization period monitored by sensors and then aeration to render it inert, the material can then be taken out. After separation of the plastic content, a usable product is obtained with a high nickel content, which can then be reused as a significant alloy component in stainless steel production (see Figure 19.11).

19.2.5 Lithium Batteries

Recycling procedures have also been developed fairly recently for the newer lithium primary and secondary systems. They are currently in the pilot phase but the early stages look promising. Thus, for example, the Mülheim-based company Accurec has developed the RVD (recycling through vacuum distillation) procedure for lithium manganese oxide (Li-MnO^2) batteries (see Figure 19.12).

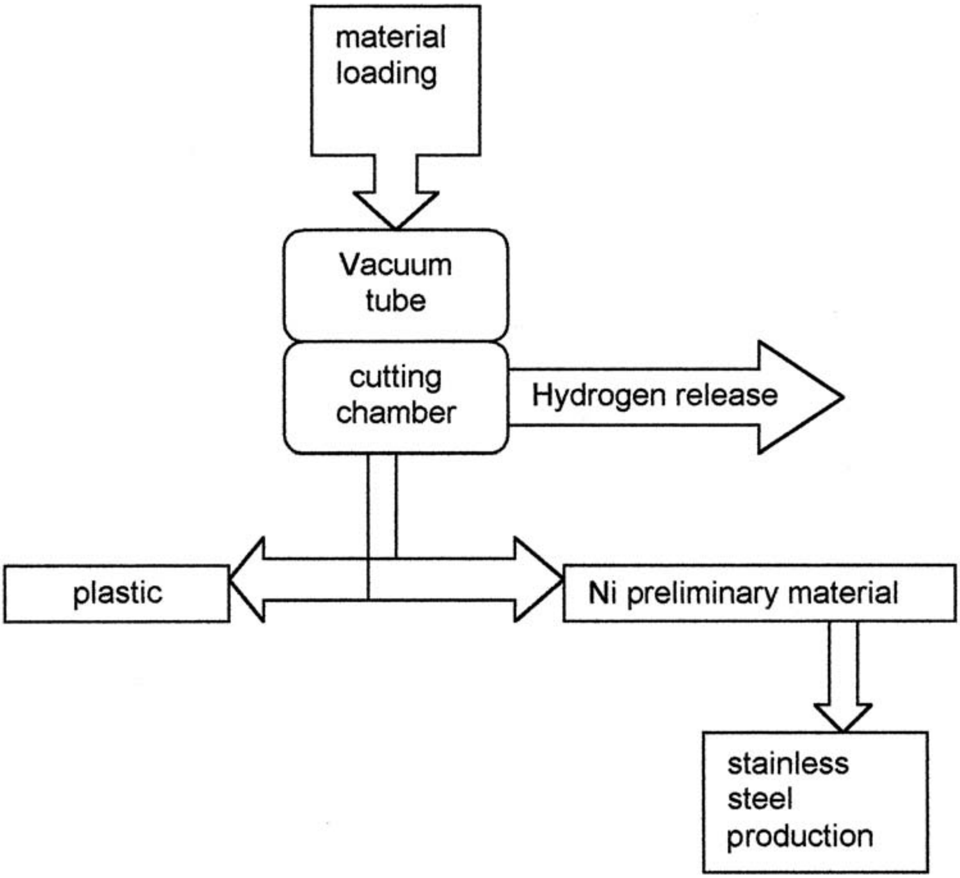
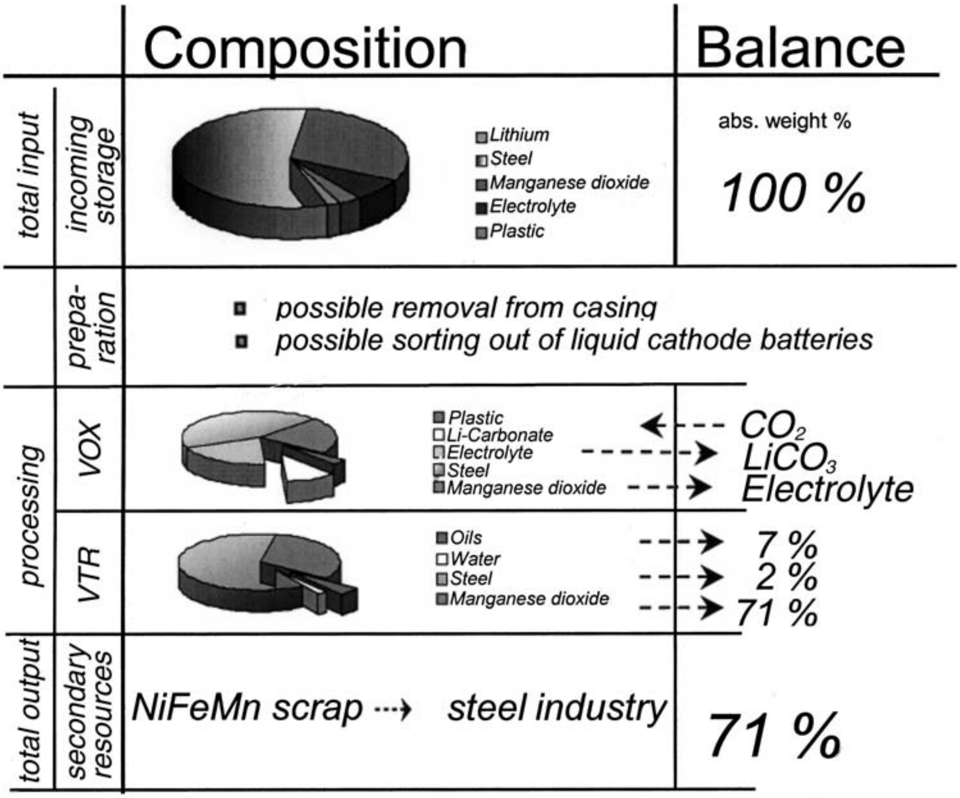


Figure 19.11 Process diagram for the NiMH battery recycling facility. Source: NIREC.



*Rest: CO_2 from graphite, water from the electrolyte

Figure 19.12 Recycling balance for lithium batteries. Source: ACCUREC.

S.N.A.M. in St. Quentin Fallavier (France) also offers a reprocessing procedure for lithium secondary systems, which is currently in the pilot stage. Here, after deactivation the metals are separated and returned to the production cycle (Figure 19.13).

19.2.6 Zinc-Carbon and Alkali-Manganese Batteries

Previously, zinc-carbon and alkali-manganese batteries still contained mercury. There were no recycling facilities and removal of the small quantities of mercury using the existing recycling technologies was extremely costly. This resulted in two major developments for the recycling of these batteries:

1. Development of technologies for the avoidance of mercury in these primary batteries.
2. Development and promotion of battery-specific recycling processes to extract mercury and other metals.

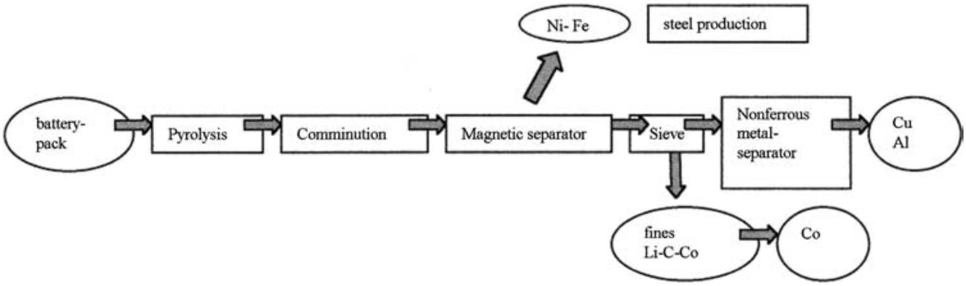


Figure 19.13 Lithium-ion processing. Source: S.N.A.M.

In the early 1980s, the battery industry agreed to reduce the mercury content from the then 1% by weight to ultimately reach 0% by weight in AlMn and ZnC batteries. For some years now, European manufacturers have been producing these batteries without mercury. As soon as the battery waste flow is nearly free of mercury, and batteries containing mercury can be separated from mercury-free batteries in sorting facilities, recycling makes economic and ecological sense (see Figure 19.14).

Below is a description of several recycling procedures for alkali-manganese, zinc-carbon and zinc/air batteries.

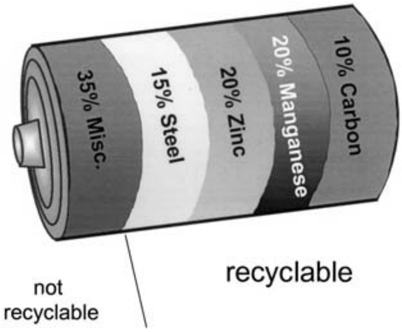


Figure 19.14 Average composition of a primary battery. Source: EPBA.

19.2.6.1 Rotary Furnace

The rolling process is a metallurgical process carried out in an inclined furnace which rotates around its own axis, known as the rotary furnace or drum furnace. The zinc-containing waste is loaded into the rotary furnace together with aggregates (sands) and reducing agents (coke). These flow through the rotary furnace, which is tilted 2.5°, in a reverse flow to the hot process gases. The loaded material is thereby gradually heated to the operating temperature. Within the material bulk, the zinc, lead, and iron compounds are reduced at temperatures of up to 1300 °C. Zinc and lead evaporate due to their low vapor pressure. Fresh air is supplied in a counterflow to the fixed bed flowing through the rotary furnace. Under these oxidizing conditions, zinc oxide and lead oxide are formed again. These oxides leave the furnace with the process gases. The waste gas first flows through the dust chamber, where a part of the entrained dust as well as the material backflow caused by a material jam in the furnace build up. This material is fed directly back into the furnace. The waste gas is then cooled. In these downstream coolers and filters, the metal oxides are emitted as high-quality rolled oxide. The process gas, which has been purified of the rolled oxide, is then sucked through an adsorption filter to remove gaseous pollutants. The material in the furnace, now largely free of zinc and lead, together with the coke ash, forms the so-called rolled slag, which undergoes a partial reoxidation of the iron near the furnace discharge area due to the prevailing oxidizing conditions there. At the furnace discharge, this slag falls through a slag chute into a water jet and is conveyed to a water basin in granulated form. The rolled slag is used in, among other things, road construction. The rolled oxide is forwarded to primary zinc foundries (smelting furnaces or electrolyses) and thus returned to the zinc metal cycle.

19.2.6.2 The Imperial Smelting Process

Alkali-manganese and zinc-carbon batteries (up to a maximum of 100 ppm Hg) are melted together with other preliminary materials. The zinc is reclaimed during the gaseous phase and thus permanently separated from most of the accompanying elements (Figure 19.15).

19.2.6.3 Electric Arc Furnace/Steel

Electric arc furnaces use a variety of processes to manufacture either steel or ferromanganese. In both cases the zinc is reclaimed as zinc dust and then converted to pure zinc in the rotary furnace. Any slag that develops is used in road construction. Electric furnaces are heated with electricity, either by means of an electric arc formed between two carbon electrodes or in an induction furnace by means of resistance heating. Because contamination by fuel and firing gases cannot occur, the soft electric steel is distinguished by its high degree of purity (see Figure 19.16).

Nedstahl in Amsterdam now processes ZnC batteries in this way for the Common Battery Recycling and Collection System run by battery manufacturers in The Netherlands (STIBAT).

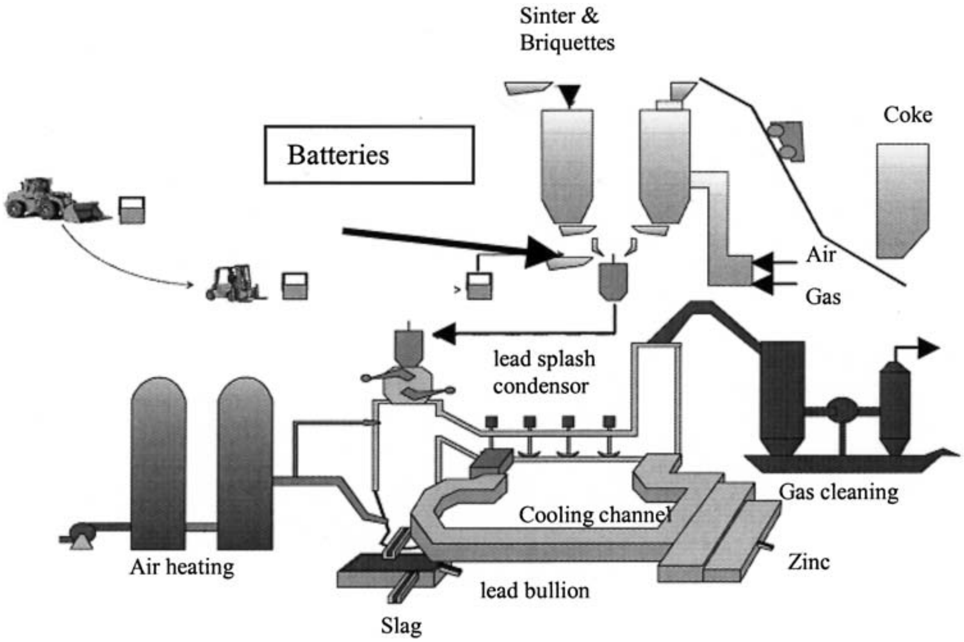
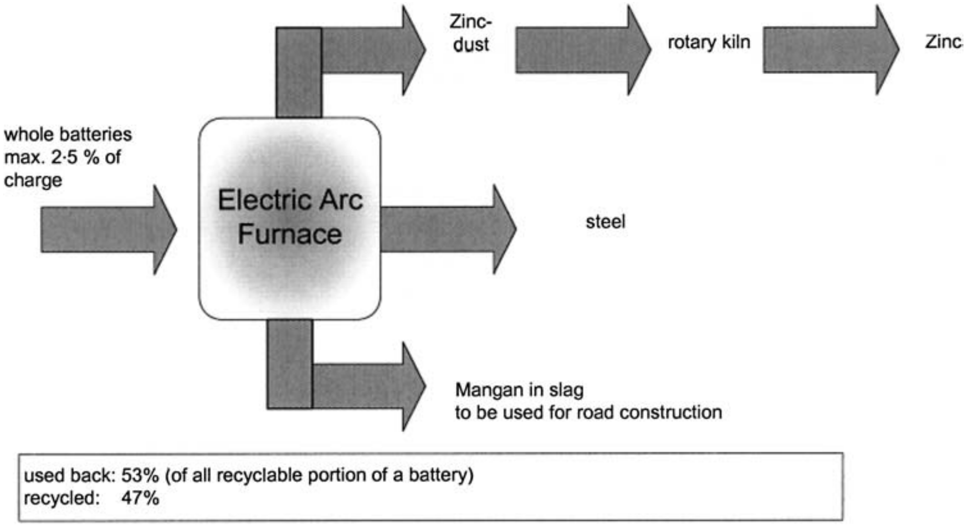


Figure 19.15 System diagram. Source: MHD M.I.M.



used back: 53% (of all recyclable portion of a battery)
recycled: 47%

Figure 19.16 Steel production in an electric arc furnace. Source: EPBA.

19.2.6.4 Electric Arc Furnace/Ferromanganese

Valdi in Feurs (France) also offers this procedure for alkali-manganese and zinc-carbon batteries containing mercury (Figure 19.17).

19.2.6.5 Converter Steel Furnace/Ferromanganese

Instead of the electric arc furnace, ZnC and AIMn mercury-free batteries can also be processed in conventional converter steel furnaces. Tests have already been carried out at the Duisburg copper foundry. Work is still in progress for the commercial use of this process.

In the blast furnace, under the influence of the coke, the iron oxide is reduced to raw iron and the material is separated into recyclable products. Zinc is vaporized in the blast furnace and reclaimed in the gas purification process in the form of zinc concentrate, which is forwarded to zinc foundries. The raw iron is run off from the blast furnace in elementary form and the slag recycled.

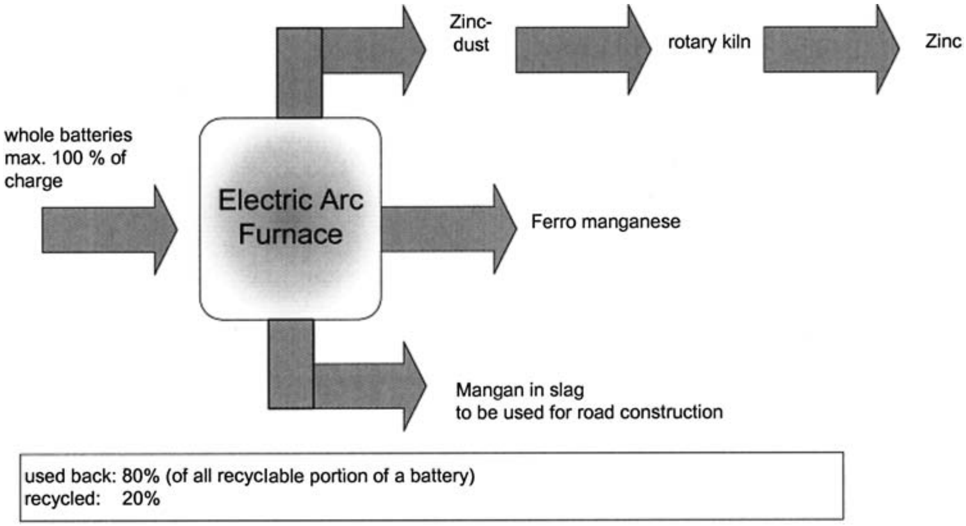
19.2.6.6 Oxy Reducer

Citron, in Le Havre, France, offers this process, which emphasizes the recycling of alkali-manganese and zinc-carbon batteries containing mercury (Figure 19.18). The quality of the sorting is allegedly not so important in this process.

During the oxy reducer process,

- The waste is heated.
- Metals (e.g. Zn, Cd, Pb, etc.) are vaporized and oxidized.
- The mercury is condensed in metallic form.
- Organic components are completely burned off.
- The metal oxides are reduced.

Table 19.5 provides an overview of the procedures described above.



used back: 80% (of all recyclable portion of a battery)
recycled: 20%

Figure 19.17 Ferromanganese production in electric arc furnaces. Source: EPBA.

Table 19.5 Overview of recycling processes.

Process	Rotary furnace	Imperial smelting furnace/ISF	Electric arc furnace/ EAF/steel	Electric arc furnace/ EAF/ferromanganese	Converter steel furnace/ ferromanganese	Oxy reducer
System (examples)	BUS, Freiberg	MHD, M.I.M., Duisburg,	Nedstahl, Ablasserdam (Netherlands)	Valdi, Feurs (France)	DK, Duisburg	Citron, Le Havre (France)
Battery input	10–20%	2–3%	2–3%	100%	2–3%	100%
Product	Zinc oxide, slag (alk.)	Zing, slag	Zinc dust, slag, steel	Zinc dust, slag, manganese steel	Zinc dust, lead, slag, raw iron	Zinc oxide, nickel-cobalt alloy, iron manganese oxide, mercury

Source: GRS Batterien.

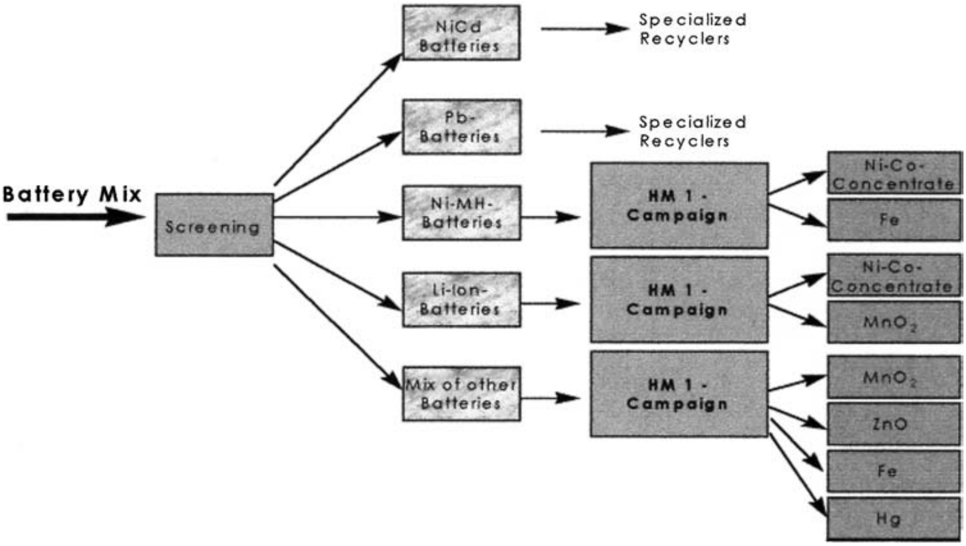


Figure 19.18 Citron Process for the Recycling of Batteries. Source: Citron.

19.3 THE GERMAN BATTERY DECREE

The German Battery Decree (decree concerning the collection and disposal of used batteries and accumulators (BattV) of March 27, 1998) came into force in two phases: the first phase concerned labeling provisions and a ban on marketing and has been in place since April 1, 1998. This is a direct implementation of the EU Directive. The second phase concerned the obligations of the manufacturers, importers, distributors, municipalities, and end consumers and had to be implemented by these parties after October 1, 1998: Manufacturers and importers are obliged to provide distributors and municipalities with suitable collecting tanks and must take away the collected portable batteries free of charge.

Manufacturers/importers can join a common collection system or carry out the collection individually. Individual collection by single manufacturers and via third parties commissioned to do so is permitted in accordance with §4(3) in combination with §16 of the German Battery Decree. This makes sense primarily for batteries used for special purposes, in which batteries of one brand or type (e.g. construction site batteries, lithium batteries for heat meters, etc.) occur in isolated instances.

The distributors and municipalities have a duty to collect the batteries free of charge and regardless of the brand or system.

Wherever batteries are sold, these must be taken back free of charge. However, the public waste disposal services (districts and independent municipal entities) will take back batteries free of charge from private end users and small businesses within the framework of the mobile and stationary collection of hazardous substances.

It is not just a question of the manufacturers' duty to *collect*, however; it is also the end consumers' duty to *return* the batteries. Regardless of their electrochemical system and hazardous substance content, used batteries may no longer be disposed of in domestic waste. The end user is the first in the collection chain: he must return used batteries to the distributors or the municipalities.

19.4 THE MANUFACTURERS' COMMON COLLECTION SYSTEM

The new German Battery Decree obliged manufacturers and importers to take charge of the sorting, recycling, and disposal of used portable batteries. Under §4(2), the German Battery Decree provides for a common collection system among manufacturers. As a result of this, Duracell, Panasonic, Philips, Energizer, Saft, Sanyo, Sony, Varta, and the German Electrical and Electronic Manufacturers' Association established a foundation: the Common Battery Collection and Recycling System (GRS Batterien) as a non-profit organization. The Senate of the City of Hamburg approved the foundation in May 1998.

The service provided by GRS is equally available to all manufacturers and importers. The users of GRS pay a contribution towards waste disposal costs for the batteries marketed by them in Germany, according to weight and system. The foundation provides distributors and municipalities as well as commercial users with appropriate collection and transportation containers free of charge and organizes sorting and disposal in accordance with the German Battery Decree.

In the meantime, more than 400 manufacturers and importers of portable batteries have joined GRS. These users put approximately 30,000 tons of portable batteries into circulation in 2000.

There are now approximately 130,000 retail outlets equipped with an initial 240,000 collection boxes and 400,000 transportation containers in a closely meshed network covering Germany nationwide. Numerous commercial users and nearly all public waste disposal services likewise use the GRS collection system and have been equipped with roughly 65,000 plastic containers for collection and pick-up.

Since 1998 the quantity collected has risen continuously. In 2000 9266 Mg were collected, an increase of approximately 11% over 1999 (8336 Mg). In 2000, an average of 112 g per head of the population was collected (see Figure 19.19).

Due to the increased circulation of UV-coded batteries, their sorting via UV detectors, and the general reduction of the mercury content in the battery waste stream thanks to the prohibition against bringing ZnC and AIMn batteries containing mercury into circulation, the proportion of recycled batteries will rise successively to over 70% in the year 2005 (see Figure 19.20).

End users have been made aware of the free battery disposal through numerous public relations measures. Battery return has never before been so easy for end consumers.

After the batteries have been collected, GRS Batterien organizes the sorting of the batteries into the various electrochemical fractions and the subsequent disposal. Between 6000 and 7000 orders per month reflect the resounding acceptance of the system (see Figure 19.21).

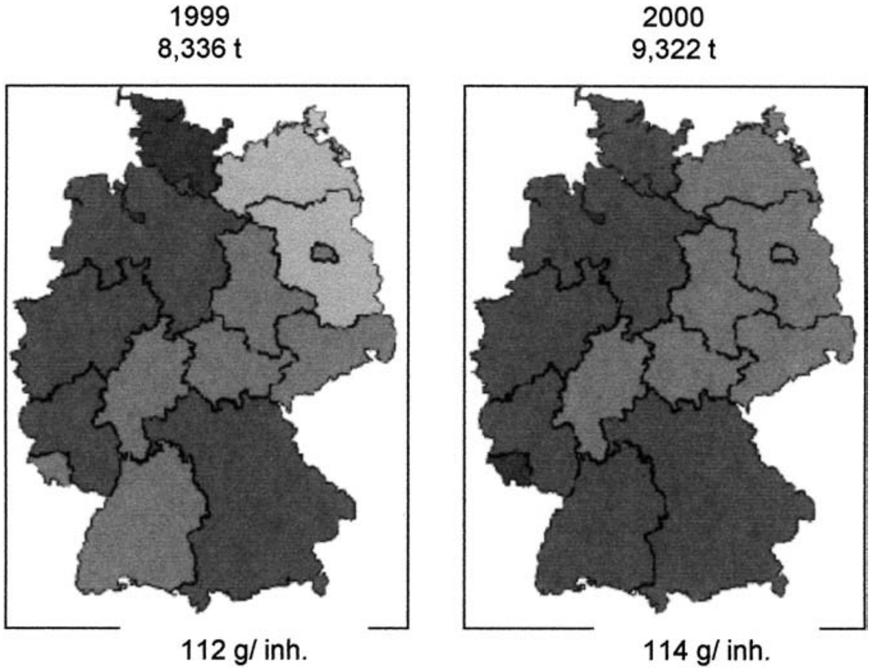


Figure 19.19 Collection by land. Source: GRS Batterien.

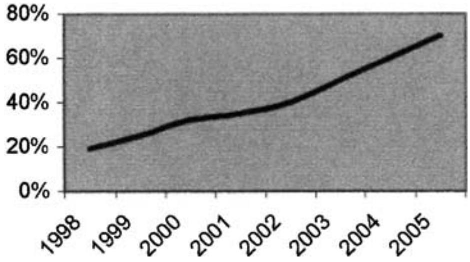


Figure 19.20 Increase of share of recycling.

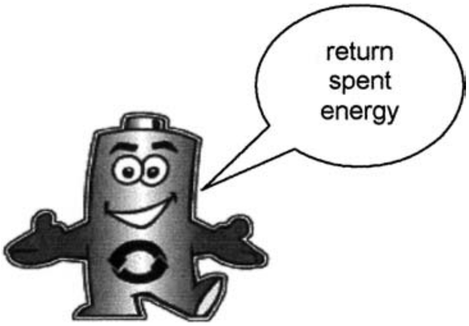


Figure 19.21 Batt-Man. Source: GRS.

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20

History

H. A. KIEHNE

20.1 EARLY BEGINNINGS

In Chapter 4 of the first English edition of the book *Portable Batteries* by K. Eberts you can read:

> Our present knowledge of battery techniques traces back to times of four and a half thousand years ago. We can be sure that the copper vessels that were found from this time could only have been plated with gold by electrochemical means.
>
> In 1936 there was an archeological sensation. Near to the present Baghdad in a Parther settlement that had flourished about from 250 B.C. to 225 A.D. an electrical element was found. A copper tube was placed in a clay vessel filled with an organic acid into which an iron rod insulated by asphalt was inserted. The element produced 5 volts and surely was not a battery of our understanding, but must be accepted as a base for this technology. It might have served galvanic purposes. [See Figure 20.1.] For about 2000 years until 1799 the knowledge of these ancient cultures was obviously forgotten, as Volta based his research on more recent knowledge, on Galvanis' frog leg experiment. With his work the scientific side of our branch was introduced.

20.2 PRIMARY AND SECONDARY CELLS

The inventor of the first usable primary battery is with full right George Leclanché, whose 1868 invention used amalgamated zinc as negative electrode and a mixture of manganese dioxide and coal as positive electrode with a current collector of coal and as electrolyte a solution of ammonium chloride.

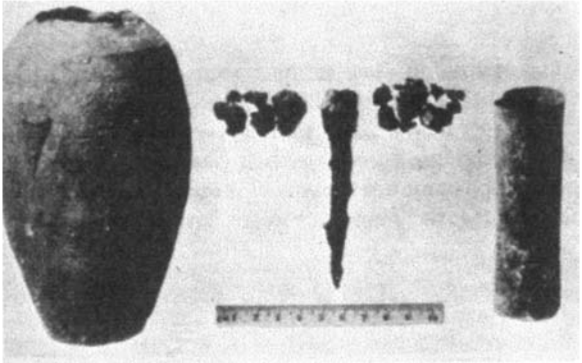

Figure 20.1 Prehistoric finds of the galvanic element from Khujut Rabuah close to Baghdad.

After Alessandro Volta (1800) presented the so-called Volta cell, practicable applications were wanted. First example of use of the Volta cell was the electrical telegraph invented by Sömmering in 1810. Here the voltage of the Volta cell was served for the transmission of letters of the alphabet through a four-line cable from one place to another. The hydrogen development observed on the positive electrode limited extremely the application. So scientists tried to eliminate the polarization originated by hydrogen with chemicals, e.g. with oxidizing agents.

One of the most popular cells in the beginning of the 19th century was the so-called *Grove* element with nitric acid as electrolyte. Bunsen improved the *Grove* element by introducing a carbon rod instead of a platinum rod (1841).

Many other elements and results of research could be named here, but many theories about the use of primary cells from that early time have been lost. Gassing elements, filled with fluid electrolytes with electrodes to be replaced after use offered no possibility for a wide application. By this we come back to the Leclanché cell, the first element that was made technically applicable. The first Leclanché cells were filled with a fluid electrolyte, so these cells could not be moved by transportation or used in just any position. Not before the end of the 19th century the Leclanché system was so far improved by using a zinc cup instead of a glass cup, i.e. the negative electrode was used as cell container.

The rise of production started with 20,000 Leclanché cells in 1868 to some million in 1918 to nowadays some thousand millions. In the course of time many steps of improvement could be watched. It was a long way from the soldered zinc cup to a dragged zinc cup, or from ground coal to graphite and later to soot, or from a clay cylinder to paper. Of extreme importance was the so-called immobilization of the electrolyte using a paste of ammonium chloride, zinc oxide, and gypsum, mixed with starch and flour. These so-called "pasted cells" dominated for decades the market for primary cells, especially for flashlights. Who later invented or improved the Leclanché system is difficult to describe and would need many pages; its development can be read in publications and patents or books on the history of electrochemistry. In many publications Gassner is called the inventor of the first "dry cell". In his patent specification, published in 1887 (Deutsches Reichspatent 45,250), he described a paste consisting of a solution of ammonium chloride mixed with zinc oxide and gypsum. This created the first dry cell, or pasted cell.

Until some years ago in dry cells amalgamated zinc was used, an effect already in 1870 described by Sturgon was the elimination of the passivation. Today the same effect can be reached without using mercury, but by the choice of extremely pure materials. That manganese dioxide is not purely manganese dioxide has been known for a long time. Since the beginning of the last century in many research centers of the world intensive work was done to understand the chemical attributes of the different qualities of manganese dioxide. The aim was to produce cells with higher electrical performance and with a lower self-discharge rate. A great success in 1940 was the start of producing manganese dioxide by electrolysis.

Further remarkable steps in the development of the Leclanché cells was the introduction of the so called "paper-lined" construction in 1950, followed in 1962 by the so-called "segment cell" for high loads. The steel sheet-protected cell was invented in 1940 (still today known as the "leak-proof" type), but was not introduced into the market before 1957. In the 1960s Huber in the German Pertrix manufacturing lines introduced the zinc-chloride technique. This was a great step toward extreme high-leakage-proof manganese dioxide cells.

Until now the Leclanché cell has had a great share of the market, efficiently completed by the "alkaline manganese dioxide cell" introduced in 1945. The alkaline cells could be established on the market not earlier than 1960. The difference between both principles of construction are shown in Figure 20.2. The secret of the high performance of the alkaline cell is the fine zinc powder (which was originally amalgamated) as active material. The large surface area of the powder allows higher

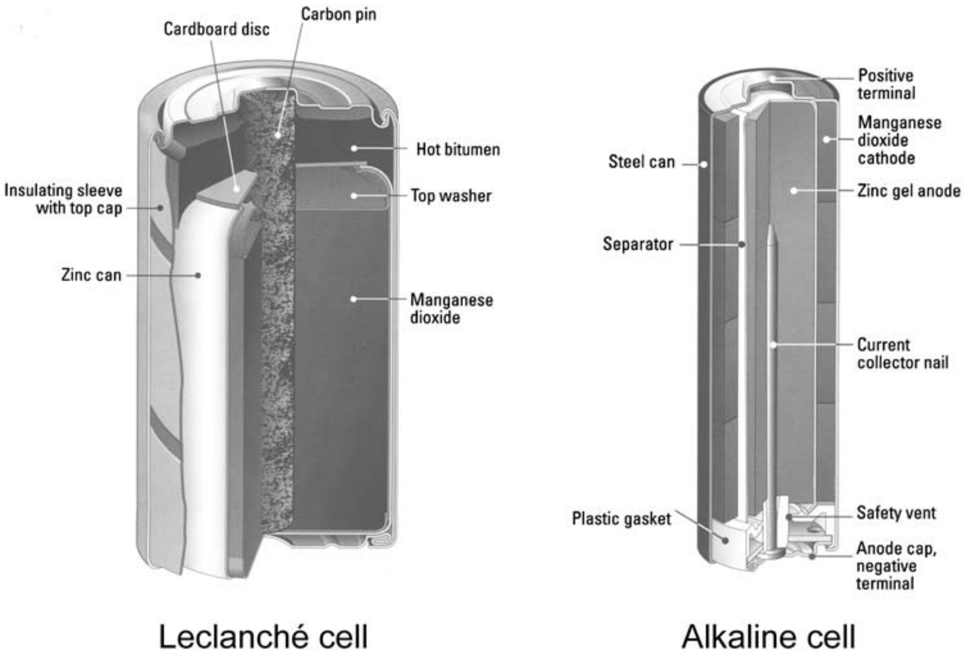

Figure 20.2 Construction of the Leclanché cell and the alkaline cell.

current densities, an absolute necessity for the newer portable and cordless electric devices with high current demand, e.g. recorders, cameras, etc.

From year to year improvements were made, either in the sealing and compound technology, in the use of better plastic materials, or by better exploitation of the active materials. Last but not least it has to be mentioned that today alkaline cells are free of mercury, a result of effective but expensive research and development. A pollution problem has been solved (see Chapter 19, Sec. 19.1.2.7).

Besides the family of manganese dioxide cells with zinc as negative electrode during the last decades manifold other battery systems have been developed and produced for the market. More capacity and higher load ability were the motivation for research. Here can be named the mercury zinc cell, produced in millions of button cells each year for hearing aids, calculators, watches, cameras, etc. Never was it possible to create one "universal cell" doing the job for all kinds of applications. Always it has to be noticed that primary cells are specialists, exactly designed for a special application. So in 1980 the smallest button cell of the world was made by Varta with a diameter of 6.8 mm and a thickness of 0.7 mm for wristwatches.

Very early in the beginning of the 19th century the polarization effect of air on the positive electrode was known. So Grove described a first, so-called "gas battery" by giving the fundamentals for today's well-known zinc-air cells in button cell design, e.g. for hearing aids and many other applications. Bigger sizes are in use for the illumination of roadwork or for electric fences around cattle pastures. The high energy output of zinc-air cells is given by the principle of the "reaction electrode" using oxygen from the air coming into the cell through small holes in the cell surface, while oxidizing substances as active material are not needed, giving space for more zinc in the counter-electrode.

Research and development teams tested in the last century nearly all theoretically possible combinations of electrodes and electrolytes. The scientists were highly interested on lithium as a light metal for use as the negative electrode. From the beginning of their research the scientists knew about the difficulties in processing the non-precious lithium, despite of its high availability; lithium reacts with humid air, especially with water very intensively. The melting point is low, 180 °C.

For laymen the area of lithium cells is difficult to overlook. Consider that since 1960 more than 100 systems have been patented, but only few could establish a market share. Advantages of the lithium cells are the high voltage (1.7 to 3.6 V) and the very high energy density, a multitude of the so-called "classic" systems described above. Lithium cells furthermore can be used in a wider temperature range and the self-discharge rate p.a. is, at less than 1%, extremely low. (For more about lithium systems, see Chapter 16, Sec. 16.2.2.12, and Chapter 18.)

Since the beginning of primary cells it was tried again and again to make secondary cells from primary cells. By definition secondary cells are such cells which firstly have to be charged before electrical energy can be discharged. This is contrary to primary cells, which can be discharged immediately when they have left the production lines. Thanks to the research efforts on alkaline cells by Kordesch, who was responsible for remarkable progress; nevertheless the alkaline cells are no genuine secondary cells, because after a few discharge/charge cycles (10 to 20) a maximum 50% of the original capacity is available. Therefore the cost/performance ratio is poor for the user. (Some consumer associations defined them as expensive nonsense.) The risk that some users think that now all primary cells are rechargeable may not be ignored; therefore safety standards do not allow the charge of primary cells as such, except where the manufacturer declares its cells as secondary cells.

But the problem can be solved, as has been shown by the development groups of rechargeable lithium-ion batteries. Nickel/metal hydride cells (having 50% more capacity and no cadmium content) had just started to penetrate the market to the debit of nickel/cadmium cells, and are being pushed away now by rechargeable lithium-ion batteries. Main applications are cellular phones, mobile phones, and video cameras. It cannot yet be foreseen whether nickel/cadmium will disappear from the market, because they cannot be substituted for in the use in tools. Never in the past has a new battery system eliminated an established system totally.

Development on primary cells shows no standstill, because new applications with new demands require adoption of the existing "battery specialist".

Rechargeable elements trace back to Johann Wilhelm Ritter, while the invention of the lead-acid battery is attached to such famous names as Gaston Planté, Camille Faure, Henry Tudor, and Volkmar. The industrial production began over 100 years ago and it demonstrates the difficulty implemented in electrochemical elements that even today sometimes the behavior of a battery can't be foreseen or explained totally. On the field of maintenance-free lead-acid batteries Otto Jache made a break-through in 1957 after extensive preparatory work by many others.

Rechargeable secondary alkaline cells are connected with two famous names: Thomas A. Edison and Valdemar Jungner. While Edison was the inventor of the nickeliron battery, Jungner tried to improve the secondary alkaline battery by using cadmium for the negative electrode. The different constructions are described in detail in Chapter 1, Sec. 1.8.2, and Chapter 7, Sec. 7.3.

In the field of well-established rechargeable systems, lead-acid and nickel/cadmium for traction and stationary use, much progress was made. Higher performance, longer service life, less maintenance, and lower cost may be listed here. Let us wait and see what in the future can be realized; the only limit is Faraday's law.

20.3 FUEL CELLS AND HIGH TEMPERATURE CELLS

New Developments and state-of-the-art technologies are described in detail in Chapter 10, secs. 10.2, 10.3, 10.4, and 10.6.

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