

Electrochemical Energy Storage

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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).

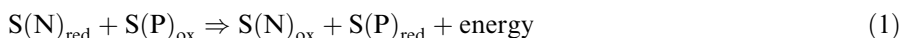
Thus at the negative electrode oxidation of $S(N)_{\text{red}}$ occurs according to



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



Both together form the cell reaction



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 ($S(N)_{\text{red}} + S(P)_{\text{ox}}$) and its final state ($S(N)_{\text{ox}} + S(P)_{\text{red}}$) 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



for a primary battery (Leclanché battery), where zinc (Zn) and manganese dioxide (MnO₂) are the compounds of higher energy content and



as the (simplified) cell reaction of the rechargeable nickel/cadmium battery. In this case cadmium (Cd) and nickel hydroxide (Ni(OOH)), which contains Ni³⁺ 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).

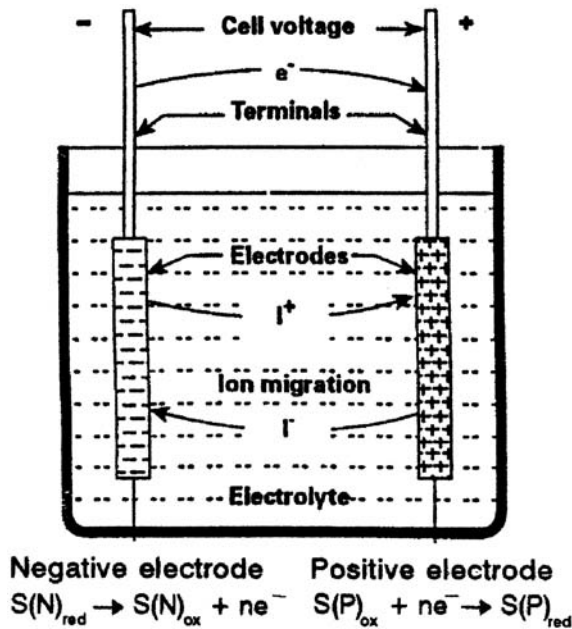


Figure 1.1 The electrochemical cell and the split up of the cell reaction. S(N)_{red} and S(P)_{ox} are the components of the negative and the positive electrode respectively. They are oxidized into S(N)_{ox} at the negative and reduced into S(P)_{red} at the positive electrode, when the battery is discharged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

$$\Delta G = \Delta H - T \cdot \Delta S \quad \text{or} \quad \Delta H - \Delta G = T \cdot \Delta S \quad (4)$$

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 $U^0(V)$ is given by

$$U^0 = - \frac{\Delta G}{n \cdot F} \quad (5)$$

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 ($1 \cdot F = 26.802\text{Ah/equiv.}$; $2 \cdot F = 53.604\text{Ah/equiv.}$); $n \cdot F \cdot U^0$ 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

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

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 Electrode material		4	5	6	7 U^{oa} Volt	8 Specific energy Wh/kg		9
	Battery system	Positive	Negative	Electrolyte	Cell reaction			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 ₂ O	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 ₂ SO ₄	Pb + PbO ₂ + 2 · H ₂ SO ₄ ⇔ 2 · PbSO ₄ + 2 · H ₂ O	2 ^b	161	20–50
8	Nickel/cadmium	NiOOH	Cd	KOH	Cd + 2NiOOH + 2 · H ₂ O ⇔ 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 ⇔ 2Ni(OH) ₂	1.3 ^e	≈ 300 ^g	50–80
10	Lithium-ion	Li _(1-x) MnO ₂	Li _x C	Organ.	Li _x C ₆ + Li _(1-x) Mn ₂ O ₄ ⇔ C ₆ + Li _x Mn ₂ O ₄	3.6	> 450	≈ 100
Special battery systems								
11	Sodium/sulfur ^h	S	Na	Solid	2Na + 3S ⇔ Na ₂ S ₃	2.1	795	90–120
12	Sodium/nickel chloride ^h	NiCl ₂	Na	Solid	2Na + NiCl ₂ ⇔ 2NaCl + Ni	2.6	719	90–100
13	Zinc/bromine	Br ₂	Zn	ZnBr ₂	Zn + Br ₂ ⇔ 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 (SOCl₂) 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); $\Delta G^{\circ,s}$: 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’:

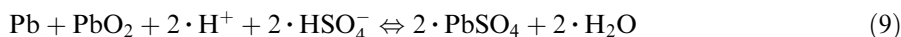
$$U^{\circ} = U^{\circ,s} - \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{\prod (a_i)_{\text{react}}^{j_i}}{\prod (a_i)_{\text{prod}}^{j_i}} \quad (7)$$

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

$$U^{\circ} = U^{\circ,s} - \frac{0.0592}{n} \cdot \log \frac{\prod (a_i)_{\text{react}}^{j_i}}{\prod (a_i)_{\text{prod}}^{j_i}} \quad \text{V} \quad (8)$$

under consideration that $\ln(..) = 2.303 \log(..)$; $R = 8.3145 \text{ J}/(\text{K} \cdot \text{mole})$; $F = 8.3145 \text{ Ws}/(\text{K} \cdot \text{mole})$, $F = 96485 \text{ As}/\text{equiv.}$; 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 $2 \cdot \text{H}^+$ and SO_4^{2-} . In consideration of the actual state of dissociation, the cell reaction can be written



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:

$$U^{\circ,s} = 1.931 \text{ V} \quad (10)$$

which applies for a_{H^+} , $a_{\text{HSO}_4^-}$, and $a_{\text{H}_2\text{O}} = 1 \text{ mole/L}$ and is approached by an acid of the density $1.066 \text{ g}/\text{cm}^3$ 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° 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:

$$U^{\circ} = 1.931 + 0.0592 \cdot \log \frac{a_{\text{H}^+} \cdot a_{\text{HSO}_4^-}}{a_{\text{H}_2\text{O}}} \text{ V} \quad (11)$$

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:

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

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.*

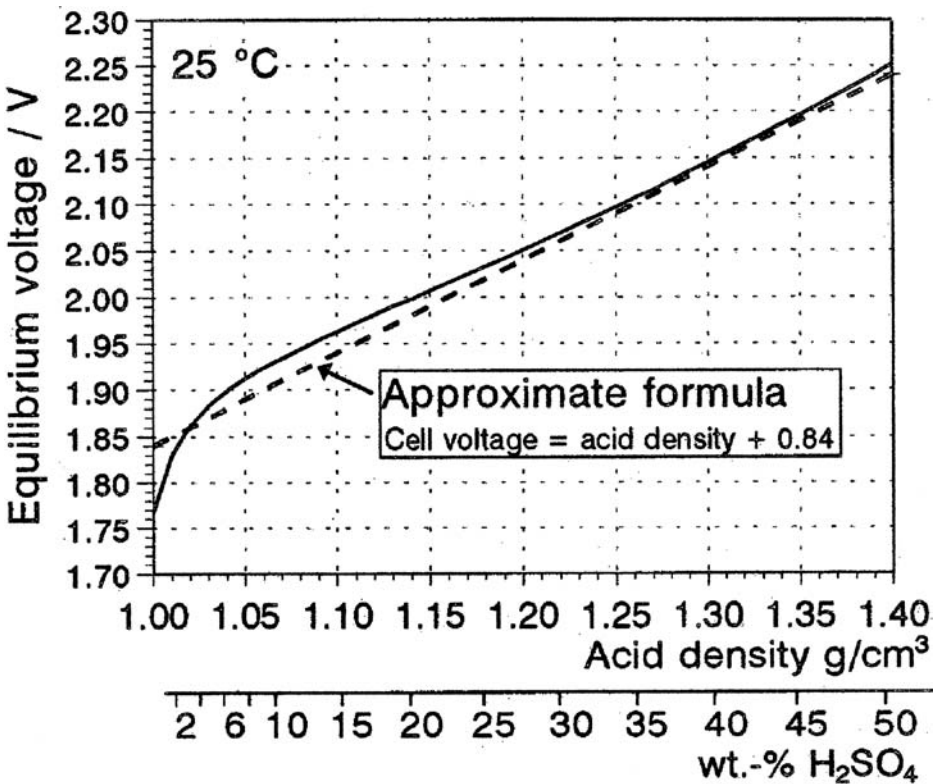


Figure 1.2 Equilibrium cell voltage of the lead-acid battery referred to, acid density, and acid concentration in wt% H₂SO₄.

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

$$\frac{dU^0}{dT} = -\frac{\Delta S}{n \cdot F} \quad (13)$$

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 ($U^0 \cdot n \cdot F$) 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 ($\text{Hg}/\text{Hg}_2\text{SO}_4$) 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’ $T \cdot \Delta S_{\text{irr}}$). 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^0 . The difference $U - U^0$, 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.

$$\text{polarization} = \text{overvoltage} + \text{ohmic voltage drops} \quad (14)$$

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 ($\text{Cd}(\text{OH})_2$) and

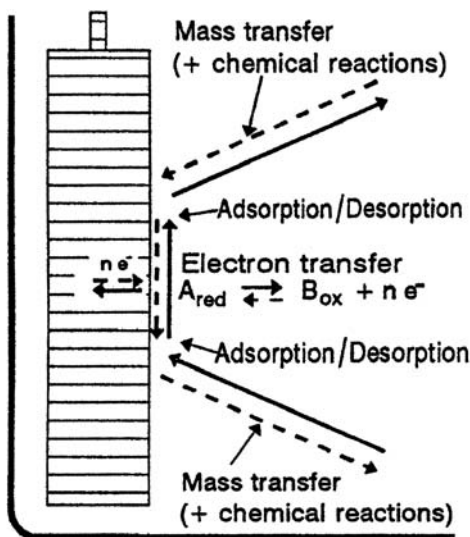


Figure 1.3 Course of an electrochemical reaction. Charge transfer often can only occur with adsorbed species, then adsorption/desorption steps are included. Furthermore, chemical reactions may precede or follow the electron transfer step.

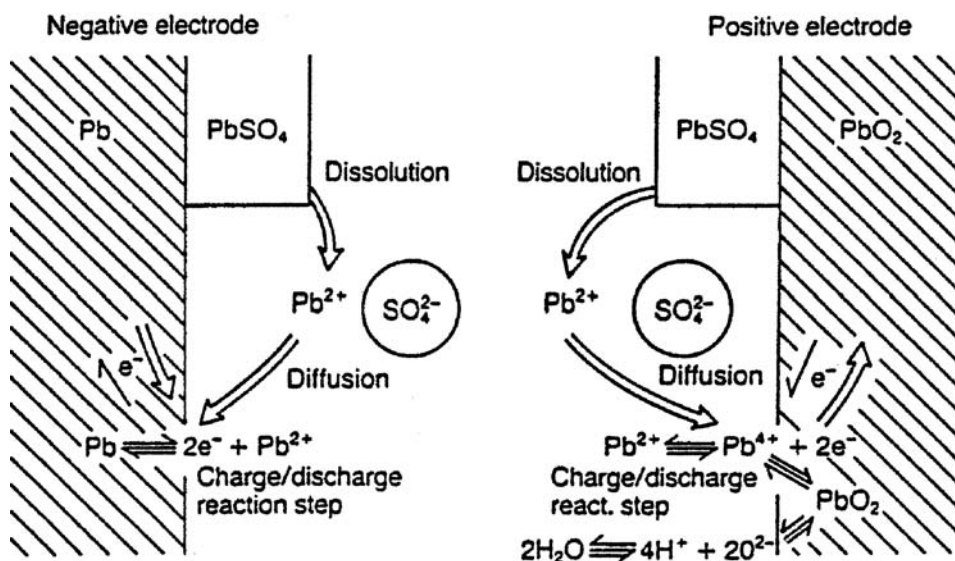


Figure 1.4 Reaction steps in the lead-acid battery. Double-lined arrows mark the charging reaction.

lead sulfate (PbSO₄) causes precipitation of the formed new compound, as illustrated for the lead-acid system in Fig. 1.4.

During discharge, lead ions (Pb²⁺) are dissolved at the negative electrode. A corresponding number of electrons is removed from the electrode as negative charge. The solubility of the Pb²⁺ ions is, however, limited to about 10⁻⁶ mole/dm³ in the presence of HSO₄⁻ or SO₄²⁻ ions (sulfuric acid, cf. Eq. (10)). As a consequence, the dissolved Pb²⁺ ions form lead sulfate (PbSO₄) 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 (Pb²⁺) are formed by the reduction of tetravalent lead ions (Pb⁴⁺) acquiring two electrons. The Pb²⁺ ions also dissolve and immediately form lead sulfate (PbSO₄). In addition, water is formed at the positive electrode during discharging, because oxygen ions (O²⁻) are also released from the lead dioxide (PbO₂) that combine with the protons (H⁺) of the dilute sulfuric acid to H₂O 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 (PbO₂) are formed from lead sulfate (PbSO₄).

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 Pb²⁺ 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

	Initial state	After discharge	After recharge
Soluble product of reaction		 Electrode material to a large extent dissolved	 Precipitation causes shape changing
Product of reaction is (nearly) unsoluble		 Product of reaction widely covers surface	 Precipitation of the initial component causes little changes in structure

Figure 1.5 Effect of the solubility of the reaction products on electrode structure when the discharging/recharging 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

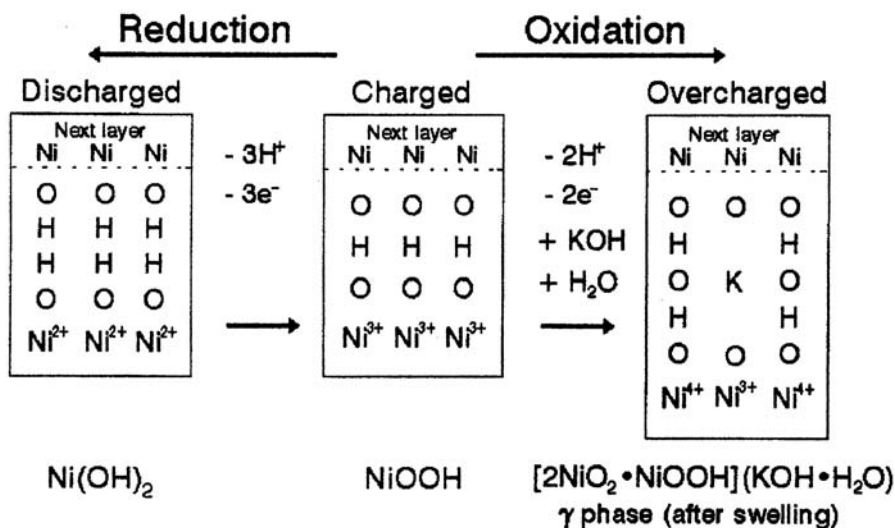


Figure 1.6 Simplified charge and discharge mechanism of the nickel-hydroxide electrode with simultaneous release and absorption of protons (H^+ ions) and incorporation of a small amount of potassium ions (K^+).

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.

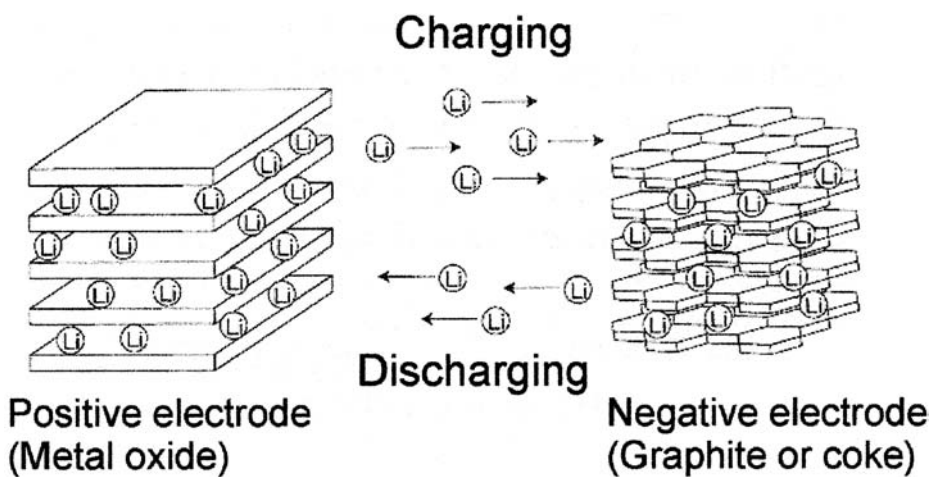


Figure 1.7 Charging/discharging of lithium-ion batteries. In the charged state, the carbon electrode is filled with lithium. During discharge, lithium ions are intercalated into the oxide (from Ref. 7).

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 $\text{Li}_x\text{Mn}_2\text{O}_4$). 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 ($\text{Me}^{4+} + x \cdot e^- \Rightarrow \text{Me}^{(4-x)+}$). The (simplified) cell reaction is



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

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

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

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

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

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

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

where addend 1 describes the anodic reaction (e.g. $\text{Pb} \Rightarrow \text{Pb}^{2+} + 2 \cdot e^-$); 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^0) 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 $\eta = U - U^0$. This leads to the usual form of Eq. (18):

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

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.

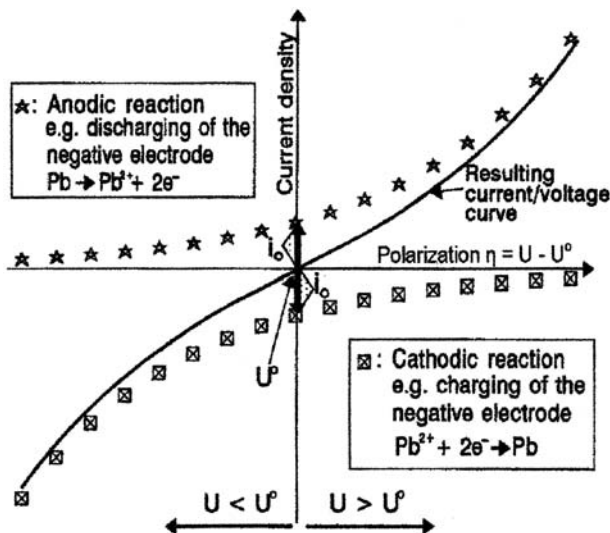


Figure 1.8 The current/voltage curve. The horizontal axis (abscissa) represents polarization $\eta = U - U^\circ$, the vertical axis (ordinate) current density i , which is synonymous to the reaction rate. i_0 is the exchange current density that characterizes the dynamic equilibrium. According to Eq. (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

$$\eta_+ = U_+ - U_+^\circ \quad \text{or} \quad \eta_- = U_- - U_-^\circ \quad (20)$$

with η_+ and η_- : polarization of positive and negative electrodes respectively; U_+ and U_- : actual potential; U_+° and U_-° : equilibrium potential of positive and negative electrodes, respectively.

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

$$U = U^\circ + \eta_+ - \eta_- \quad (21)$$

with U° : 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 ($\eta_- \leq 0$) while for a charged positive electrode a positive polarization is required ($\eta_+ \geq 0$).

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

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

This equation can be rearranged into

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

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)):

$$\eta = a + b \cdot \log(|i|) \quad (24)$$

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

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

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

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

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

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

with N_j : 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

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

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

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

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

$$t_+ + t_- = 1 \quad (30)$$

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

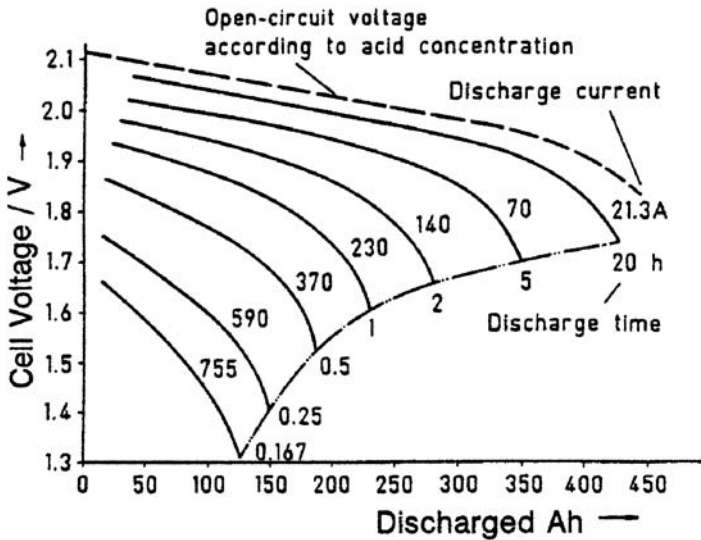


Figure 1.9 Discharge curves relative to the drawn amount of Ah. The dashed curve shows the equilibrium voltage according to the Nernst equation. It reflects the dilution of the acid with progressing discharge (cf. Fig. 1.2).

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 or 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

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

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 $n \cdot F$:

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

with n : number of exchanged electrons; F : Faraday constant ($= 96485 \text{ As/equivalent}$); 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

$$U_{\text{cal}} = U^{\circ} - \frac{Q_{\text{rev}}}{n \cdot F} \quad \text{V} \quad (33)$$

as ‘caloric 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

$$U_{\text{cal}} = - \frac{\Delta H}{n \cdot F} \quad (34)$$

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

$$dQ_{\text{Joule}}/dt = \Delta U \cdot i \quad (35)$$

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°). Then the Joule effect reads according to Eq. (35):

$$dQ_{\text{Joule}}/dt = (U - U^{\circ}) \cdot i \quad /W \quad (36)$$

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

$$Q_{\text{Joule}} = \int_0^t \{(U - U^{\circ}) \cdot i\} dt \quad /Wh \quad (37)$$

Note: $U - U^{\circ}$ means polarization. It includes the voltage drop caused by 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. $U - U^{\circ}$ 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

$$Q_{\text{total}} = Q_{\text{Joule}} + Q_{\text{rev}} \quad / \text{Wh} \quad (38)$$

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

$$\frac{dQ_{\text{total}}}{dt} = \frac{dQ_{\text{Joule}}}{dt} + \frac{dQ_{\text{rev}}}{dt} \quad / \text{W} \quad (39)$$

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 $(U - U^0) \cdot i$ and gives

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

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

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

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, $Q_{\text{gen}} = -Q_{\text{total}}$ 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	$\text{Pb} + \text{PbO}_2 + 2 \cdot \text{H}_2\text{SO}_4 \Rightarrow 2 \cdot \text{PbSO}_4 + 2 \cdot \text{H}_2\text{O}$	$\text{NiOOH} + \text{Cd} \Rightarrow \text{Ni}(\text{OH})_2 + \text{Cd}(\text{OH})_2$	$\text{H}_2\text{O} \Rightarrow \text{H}_2 + 1/2\text{O}_2$	
3	ΔH_s	Eq. (4) − 359.4 kJ	$\approx -282 \text{ kJ}$	285.8 kJ	
4	ΔG_s	Eq. (4) − 372.6 kJ	$\approx -255 \text{ kJ}$	237.2 kJ	
5	$T\Delta S_s = Q_{\text{rev}}$	Eqs. (4), (31) 13.2 kJ	$\approx -27 \text{ kJ}$	48.6 kJ	
6	$U^{o,s}$	Eq. (5) 1.931 V	$\approx 1.3 \text{ V}$	1.227 V	
7	$Q_{\text{rev}}/\Delta G_s$	− 3.5%	$\approx 11\%$	20.5%	
8	U_{cal}	Eqs. (33), (34) $U_o - 0.068 \text{ V}$	$\approx 1.44 \text{ V}$	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).

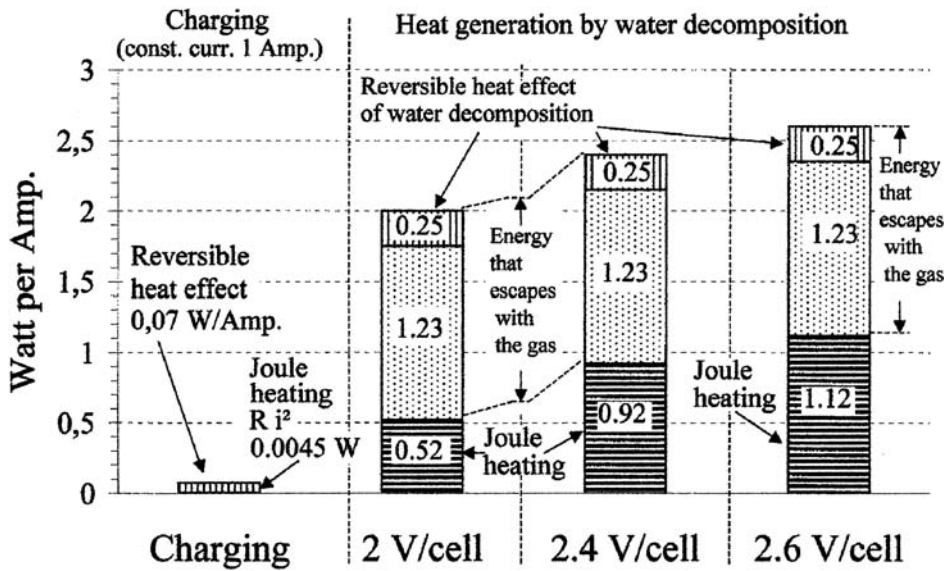


Figure 1.10 Heat generation in a vented lead-acid battery by the charging reaction and by water decomposition, relative to a current of 1 A. Assumed internal resistance 4.5 mΩ per 100 Ah of nominal capacity as in Fig. 1.11.

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 $U_{\text{cal}} \cdot i = 1.48 \text{ Wh/A}$.

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 $(U - 1.48) \cdot i \text{ (Wh)}$ 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 ($I_5 = 20 \text{ A/100 Ah}$). The broken line represents the calorific voltage U_{cal} , the full line the actual discharge voltage U .

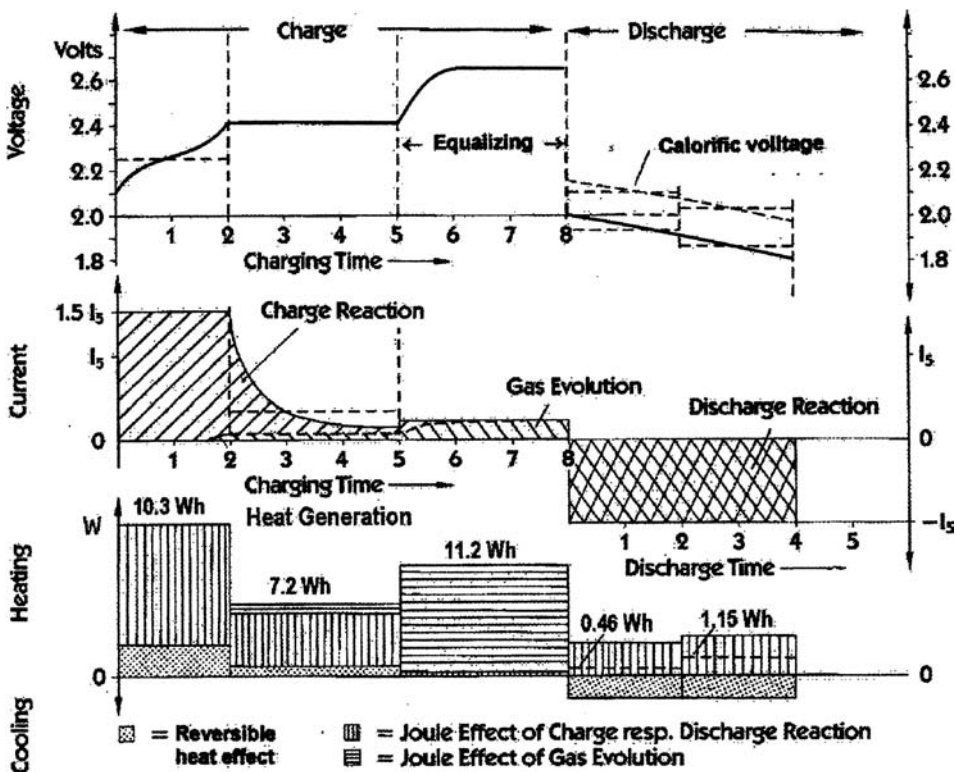


Figure 1.11 Charging/discharging cycle of a vented traction battery.

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. (40 Ah $\approx$ 85 Wh is

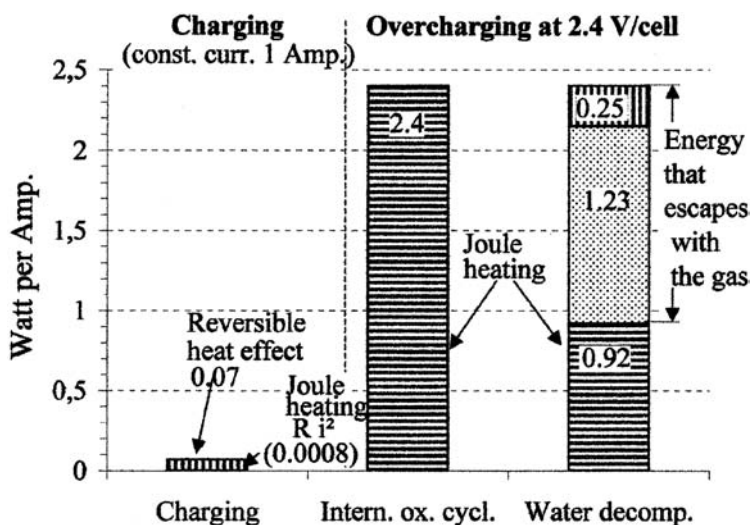


Figure 1.12 Heat generation in valve-regulated lead-acid batteries by charging and overcharging, referred to a current of 1 A.

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 $3 \text{ Wh} = 11 \text{ kJ}$.)

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 $40 \text{ A}/100 \text{ Ah}$ ($2 \times I_5$; 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 $5 \text{ A}/100 \text{ Ah}$ 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

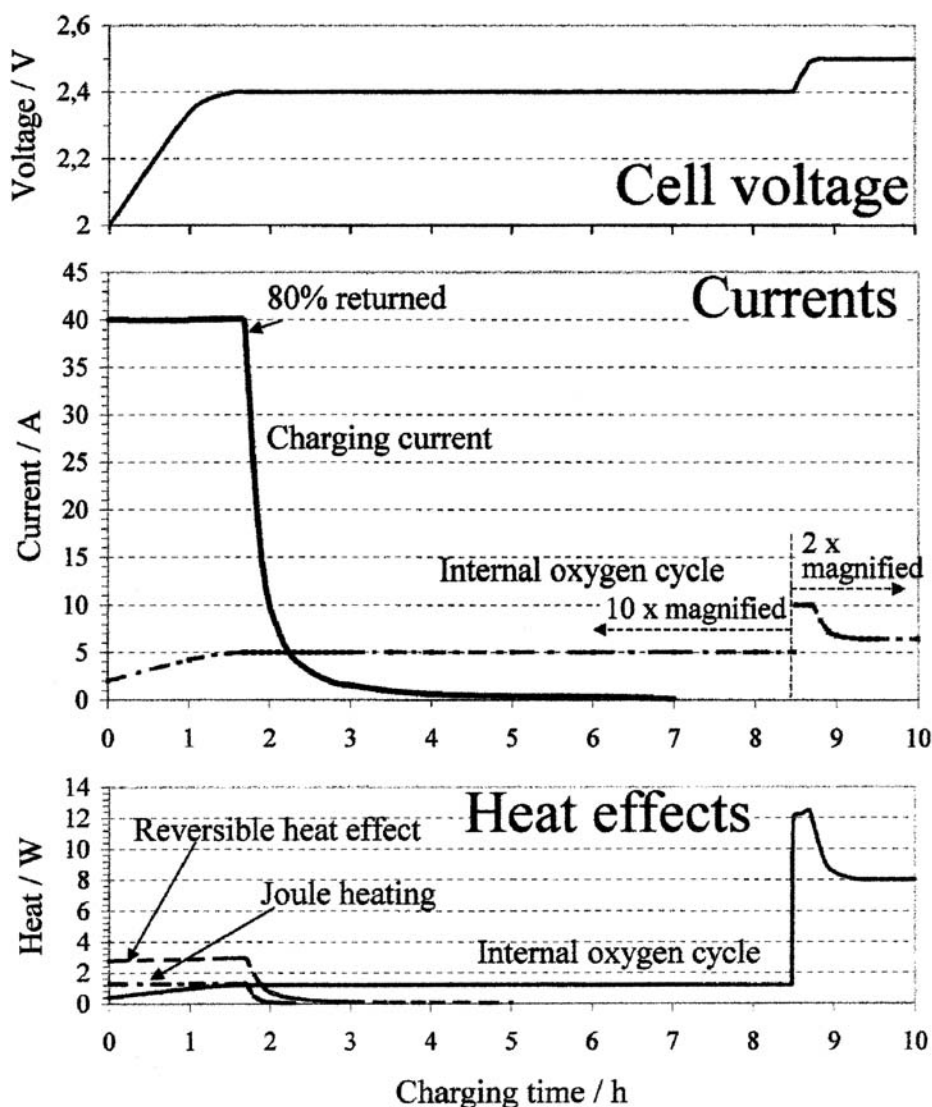


Figure 1.13 Charging of a VRLA battery at 2.4 V/cell, calculated curves, constant temperature, and 100% of recombination efficiency assumed. Internal resistance 0.8 m Ω (single cell). 1.5 hours equalizing at 2.5 V/cell at a current limit of 5 A. Heating of the battery during charging is not considered. 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 m Ω /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 $U^0 = 1.3 \text{ V}$ (Table 1.1) and the calorific voltage $U_{\text{cal}} = 1.44 \text{ V}$ (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 capacity). During the first 2 hours, the

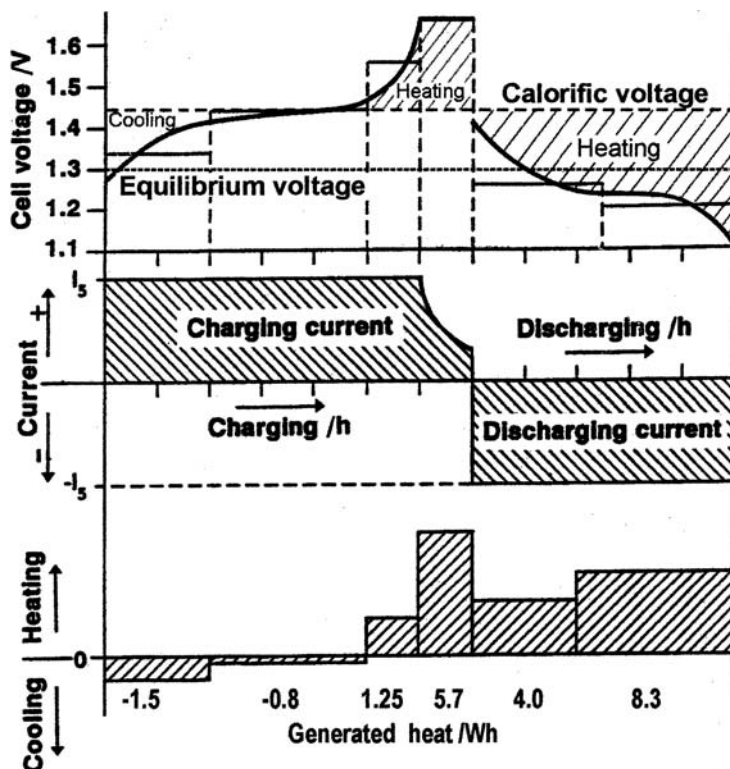


Figure 1.14 Heat generation during charge and discharge of a vented nickel/cadmium battery. Charging with constant current I_5 (5 hour rate) until 1.65 V/cell is reached. Discharge also with I_5 .

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 $U - U_{\text{cal}}$ determines the effect of heating or cooling. (Calculation based on $U^0 = 1.3 \text{ V}$; $U_{\text{cal}} = 1.44 \text{ V}$.) 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 $264.7 \text{ kJ} = 73.53 \text{ Wh}$ of heat are generated, referred to a nominal capacity of 100 Ah. These figures are much larger than the $31.2 \text{ Wh}/100 \text{ Ah}$ 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.

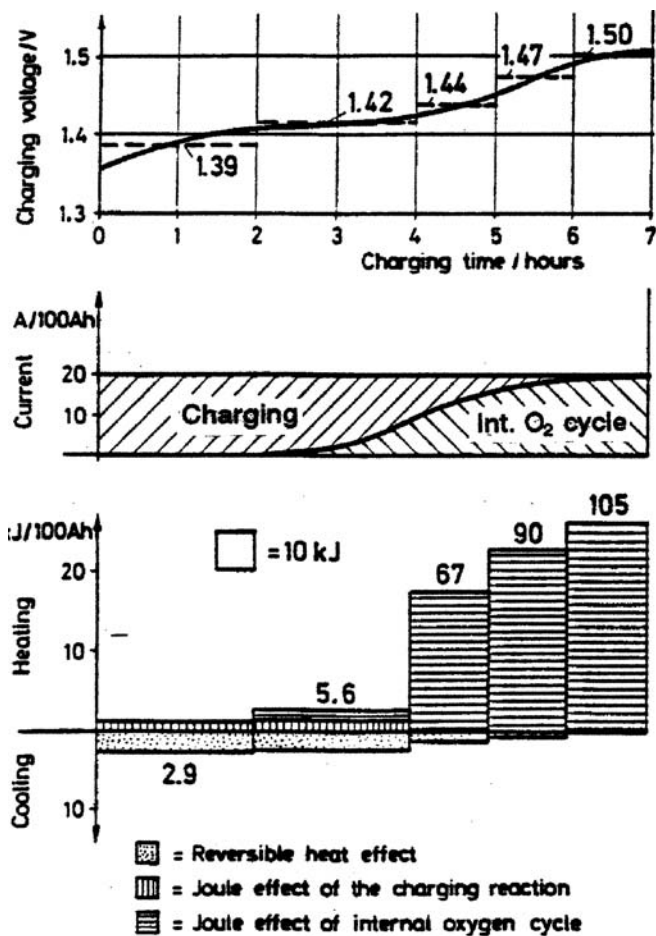


Figure 1.15 Charging of a sealed nickel/cadmium battery with constant current 0.2 C(A). During 7 hours 140% of the nominal capacity are recharged, which corresponds with a charge factor 1.4. For comparison, all values are converted to 100 Ah of nominal capacity. Actually, batteries of this type and for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

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

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} ($\text{in J} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) defined by

$$\sum [m(i) \cdot C_p(i)] = C_{\text{Batt}}. \quad (43)$$

with $m(i)$: component i in kg; (i) : the components in the battery; $C_p(i)$: 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 $1.25 \text{ J kg}^{-1} \text{K}^{-1}$ 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 $dQ_{\text{gen}}/dt = dQ_{\text{diss}}/dt$.

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.

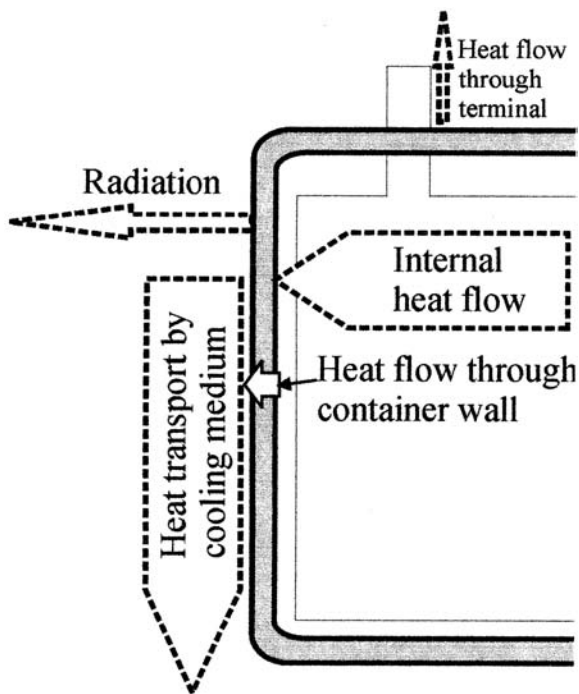


Figure 1.16 The various ways of heat escape from the battery.

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 ($5.67 \cdot 10^{-8} \text{ W} \cdot \text{m}^{-2} \cdot \text{K}^{-4}$); 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

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

which means that a battery emits by radiation about 5-6 W/m² 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/m² 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

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

with f: surface area in m²; λ: specific heat conductance (J · s⁻¹ · m⁻¹ · 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 · m⁻¹ · K⁻¹. Thus heat conduction through the container wall can be approximated

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

which means for a wall thickness of 4 mm

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

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

Material	Heat conductance W · m ⁻¹ · 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 · 10 ⁻⁵
Air	1.5 · 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

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

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
		$\text{W} \cdot \text{m}^{-2} \cdot \text{K}^{-1}$	
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 ($\text{S(P)}_{\text{ox}} + n \cdot \text{e}^- \Rightarrow \text{S(P)}_{\text{red}}$), 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 ($\text{S(N)}_{\text{red}} \Rightarrow \text{S(N)}_{\text{ox}} + n \cdot \text{e}^-$) 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 ($\text{Pb} \Rightarrow \text{Pb}^{2+} + 2 \cdot \text{e}^-$), but the cathode during charging. The opposite applies to the positive electrode: $\text{Pb}^{4+} + 2 \cdot \text{e}^- \Rightarrow \text{Pb}^{2+}$ 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 hydride, 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 modern 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

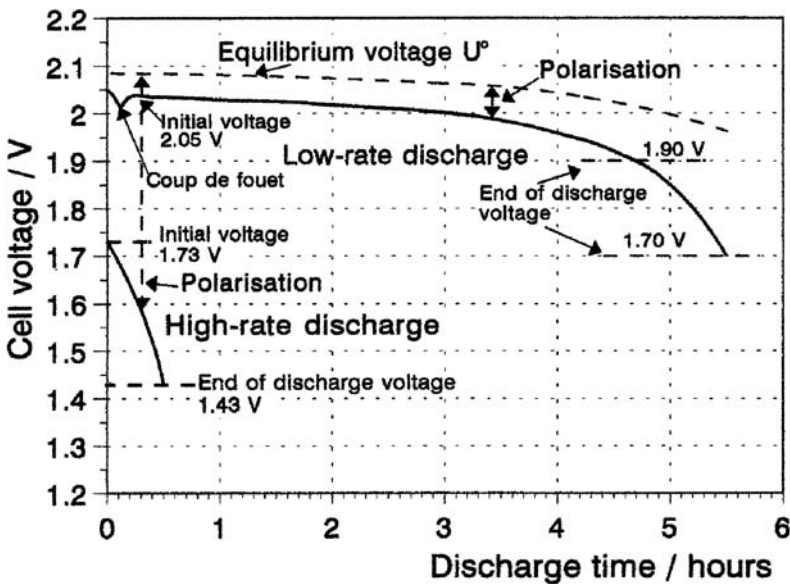


Figure 1.17 Typical low-rate discharge and high-rate discharge curves of a lead-acid battery and the main discharge parameters. The broken curve denotes the equilibrium or open circuit voltage.

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

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

A more general definition would be

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

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° remains approximately constant. The difference between the actual discharge curves and U° 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

$$i = m \cdot C_r \quad (53)$$

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

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

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 $R(\Omega)$ = constant as resistive load, the following relation applies

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

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/cm³. 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/cm³ (zinc/carbon) up to 1.2 Wh/cm³ (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

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

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

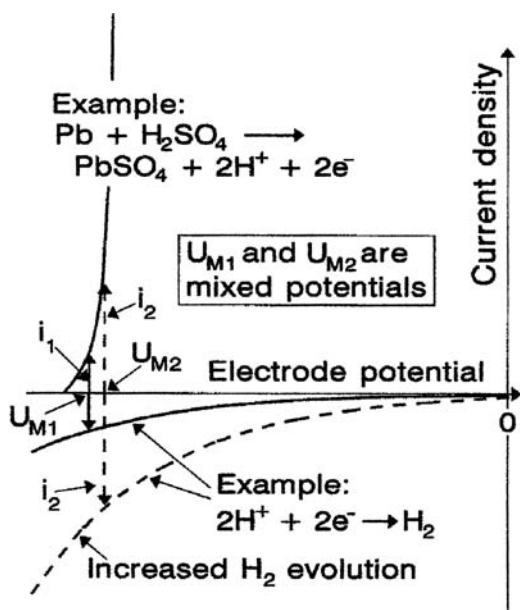


Figure 1.18 Mixed potential between discharge of the lead electrode and hydrogen evolution with the result of self-discharge. The dashed curve represents reduced hydrogen overvoltage. U_M : mixed potential. i_1 , i_2 : rate of self-discharge

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



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



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	6270 Wh/kg	3588 Wh/kg	4690 Wh/kg
	3.06 V	6.07 V	5.62 V	5.45 V
Cl ₂	1000 Wh/kg	2520 Wh/kg	1830 Wh/kg	1732 Wh/kg
	1.36 V	3.99 V	3.99 V	3.08 V
Br ₂	354 Wh/kg	1116 Wh/kg	941 Wh/kg	755 Wh/kg
	1.07 V	3.62 V	3.61 V	2.59 V

(Br₂) in Table 1.7 and their combinations with lithium (Li), sodium (Na), and magnesium (Mg). The halogens F₂, Cl₂, and Br₂ 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/LiI/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.

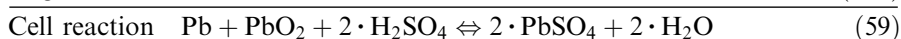
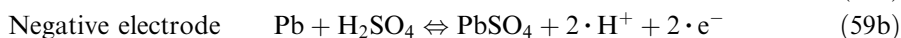
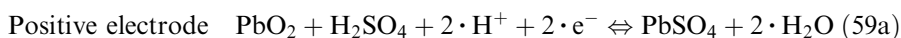
1.8 FUNDAMENTAL ASPECTS OF EXISTING BATTERY SYSTEMS

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

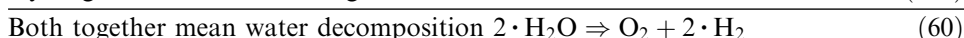
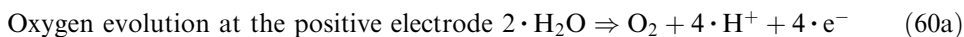
The lead-acid battery (Line 7 in Table 1.1) has repeatedly been mentioned. It is the oldest secondary system, widely used, and well known. It is characterized by the fact that lead is used in both electrodes as the active material. In the negative electrode, lead (Pb) is oxidized by discharging into 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:

Charging $\Leftrightarrow$ Discharging



The nominal equilibrium voltage amounts to $U^0 = 2.0 \text{ V}$ as the difference between the equilibrium values of the electrode reactions $U_{\text{PbO}_2/\text{PbSO}_4}^0 = 1.7 \text{ V}$ and $U_{\text{Pb}/\text{PbSO}_4}^0 = -0.3 \text{ V}$ (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.



The equilibrium voltage of this reaction is $U^0 = 1.23 \text{ V}$ (the difference $U_{\text{H}_2\text{O}/\text{O}_2}^0 = 1.23 \text{ V} - U_{\text{H}^+/\text{H}_2}^0 = 0 \text{ V}$) 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



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 $\text{Pb} \Rightarrow \text{PbSO}_4$. At the potential of the positive electrode, lead is further oxidized to lead dioxide (PbO_2) that forms a protecting layer according to



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).

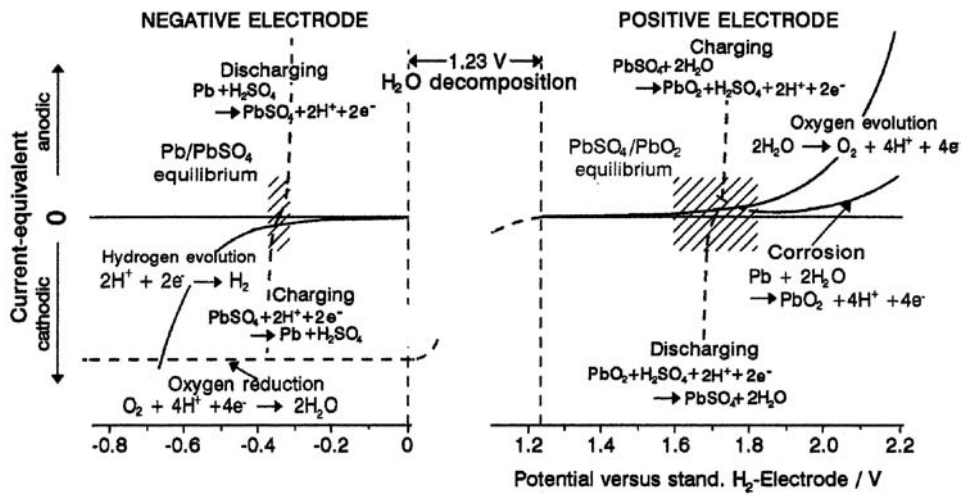


Figure 1.19 Reactions that occur in lead-acid batteries plotted vs. electrode potential. The rates of these reactions are indicated by current potential curves.

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 $\text{PbSO}_4/\text{PbO}_2$ 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.

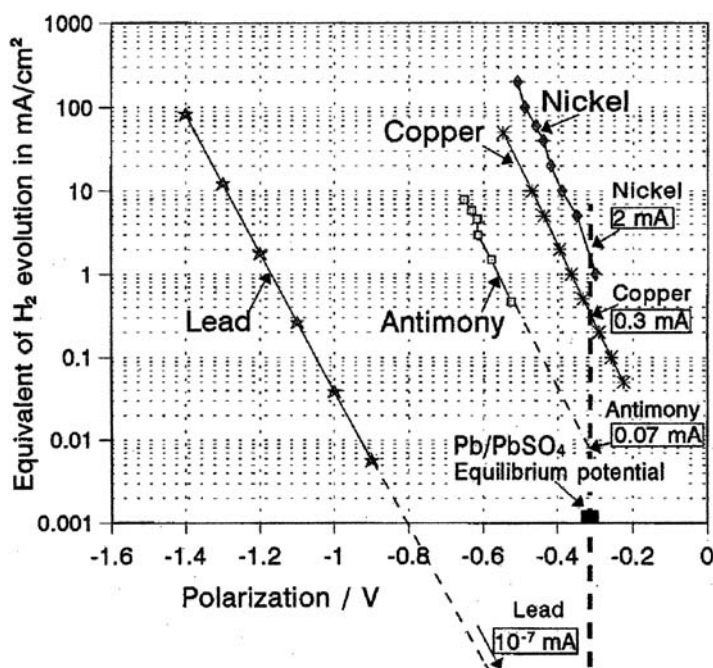


Figure 1.20 Hydrogen evolution in sulfuric acid at various metal surfaces in a semilogarithmic plot versus electrode potential (polarization). The origin of the horizontal scale is the equilibrium potential of the hydrogen electrode. The enframed figures represent the gassing rates at the open circuit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

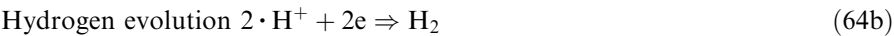
The rate of oxygen reduction (according to Eq. (61)) is largely determined by the rate of oxygen transport and therefore does not depend on the potential of the negative electrode. It is characterized as a ‘limiting current’ (cf. Eq. (29)) by the horizontal curve in Fig. 1.19. In conventional batteries 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),



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



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/cm², 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/PbSO₄ 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/cm²)). At nickel, copper, and antimony, hydrogen is evolved at the rate of 2, 0.3, and 0.07 mA/cm², 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 m² per 100 Ah of nominal capacity. Multiplied by this surface area, the 10⁻⁷ mA/cm² 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



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



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.

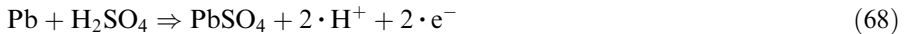
This great difference between the transport rates explains why oxygen reduction is hardly noticed at a charged negative plate that is submerged into water or acid, while a moist charged plate heavily reacts with oxygen according to $\text{Pb} + 1/2\text{O}_2 \Rightarrow \text{PbO}$ when exposed to the 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	$D_{\text{air}} = 0.18 \cdot \text{cm}^2 \cdot \text{s}^{-1}$
Diffusion coefficient of oxygen in 20% H_2SO_4	$D_{\text{liq}} = 2 \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$
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



which equals the discharge reaction of the negative electrode, and its equilibrium potential is $U_{\text{Pb}/\text{PbSO}_4}^0 = -0.3 \text{ V}$, 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

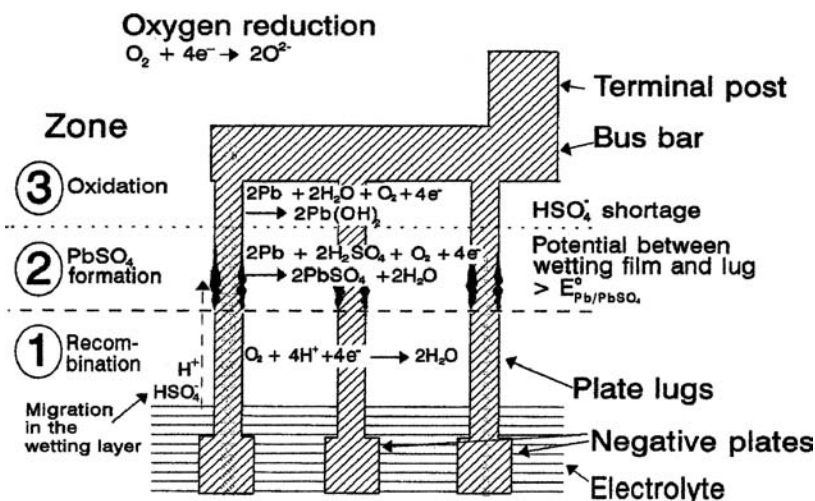


Figure 1.21 Corrosion at negative plate lugs that occasionally is observed. Current flow along the wetting layer of the nonimmersed parts causes a potential shift within that layer. Thus, ‘cathodic corrosion protection’ may no longer exist above a certain distance from the electrolyte level. The situation 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).

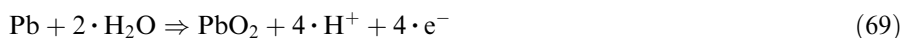
conductivity of the wetting layer and increases the voltage drop along the layer. Furthermore, corrosion roughens the surface and that again increases current and voltage drop. Thus the progressing corrosion accelerates the process.

- **Zone 3** in Fig. 1.21 is characterized by lack of HSO₄⁻ 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 (Pb⁴⁺) is the stable state that forms lead dioxide (PbO₂). Thus grid corrosion in the positive electrode means the conversion of lead (Pb) into lead dioxide (PbO₂) according to



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



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 $\text{PbO}_2/\text{PbO}_x$ 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.

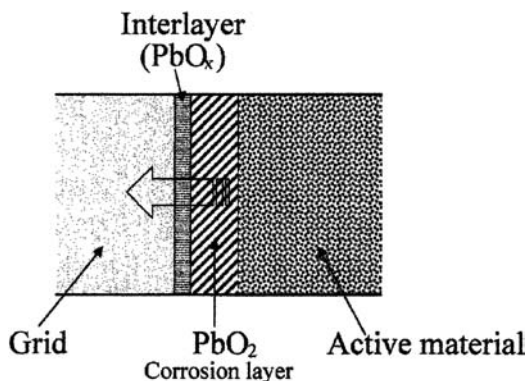


Figure 1.22 Structure of the corrosion layer at the surface of the positive grid.

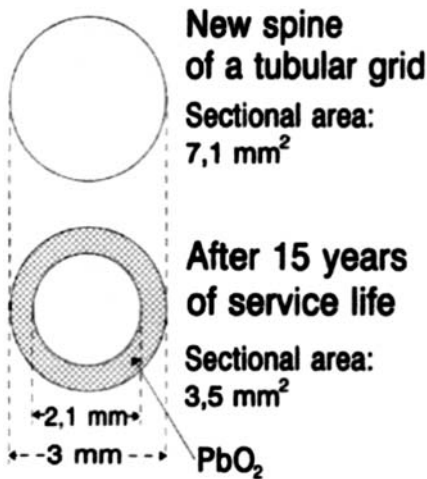


Figure 1.23 Conversion of grid material into lead dioxide by corrosion at a corrosion rate of 0.03 mm/year which corresponds to experience with 1.6% antimony grid alloys. Spine of a positive tubular plate. New plate: 3 mm diameter means 7.1 mm² cross-section (πr^2 with $r = 1.5$ mm). Aged plate: reduction of r by $0.03 \times 15 = 0.45$ mm means $\pi r^2 = 3.5$ mm².

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 cm² in a tubular electrode and about 4000 cm² 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.

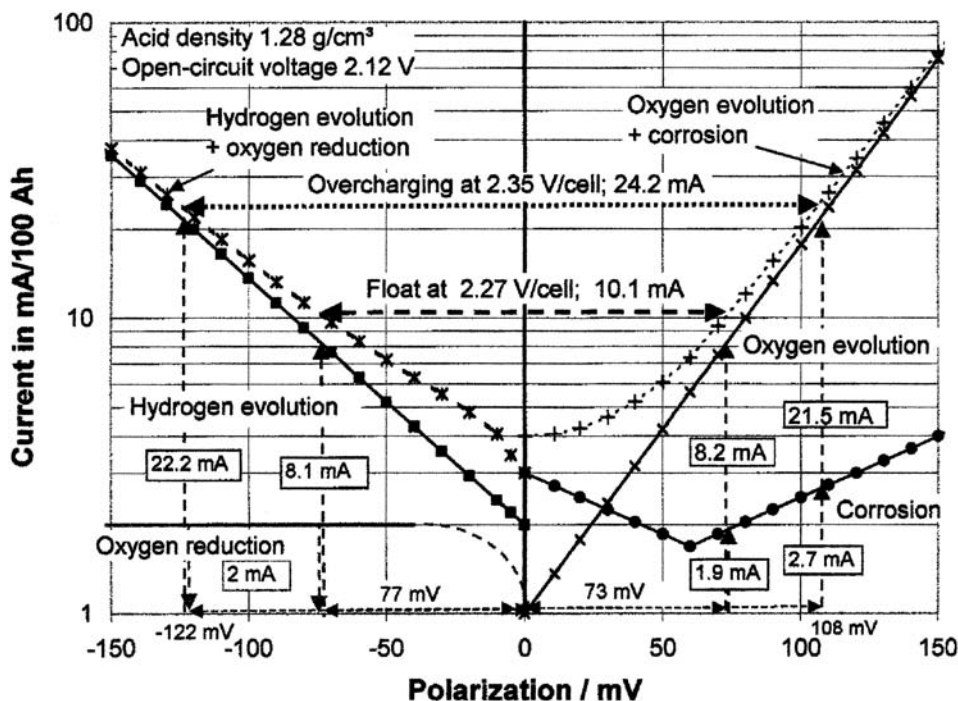


Figure 1.24 Overcharging and float charging of a flooded battery. Current voltage curves as current equivalents in a semilogarithmic scale versus polarization, referred to the open circuit potential of the negative and positive electrodes. Values based on generalized data. Actually they depend on the 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

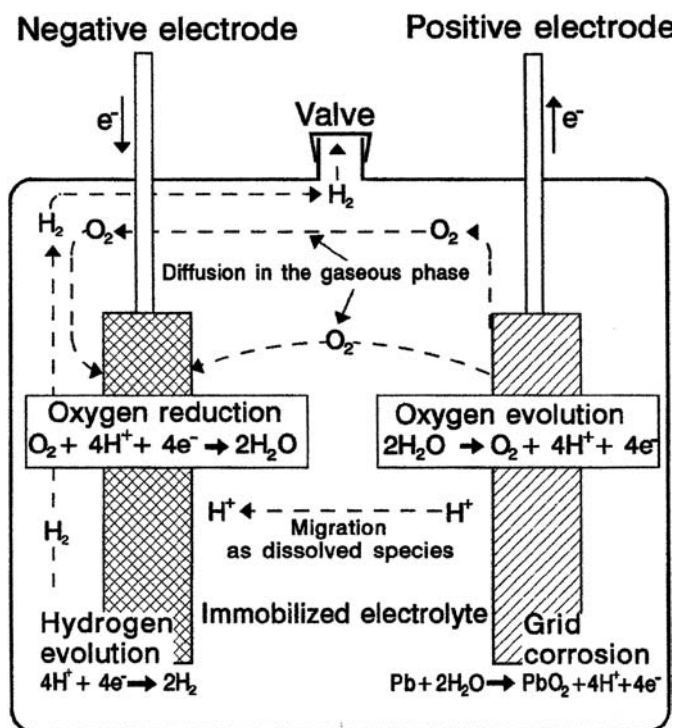


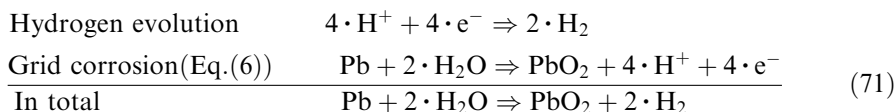
Figure 1.25 Internal oxygen cycle in a valve-regulated lead-acid battery (VRLA battery).

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



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 $1\text{ }\mu\text{m}$ and 'fine' types with a diameter of about $0.5\text{ }\mu\text{m}$, 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

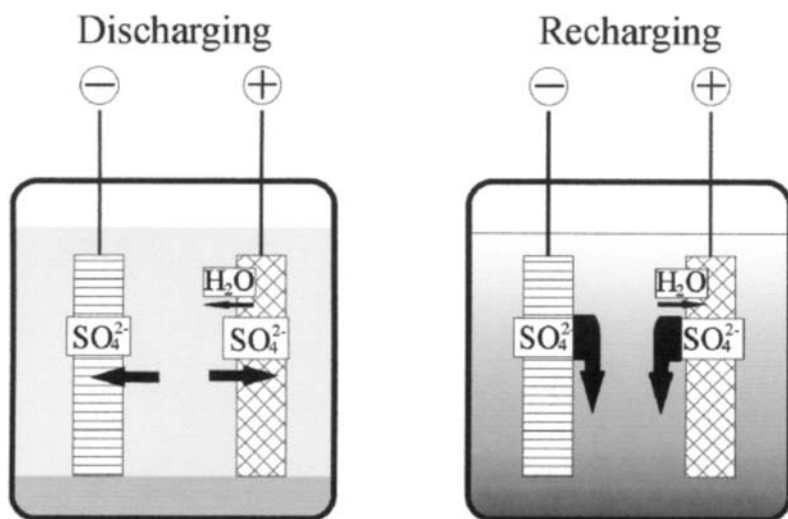


Figure 1.26 The emergence of acid stratification in lead-acid batteries with liquid electrolyte.

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

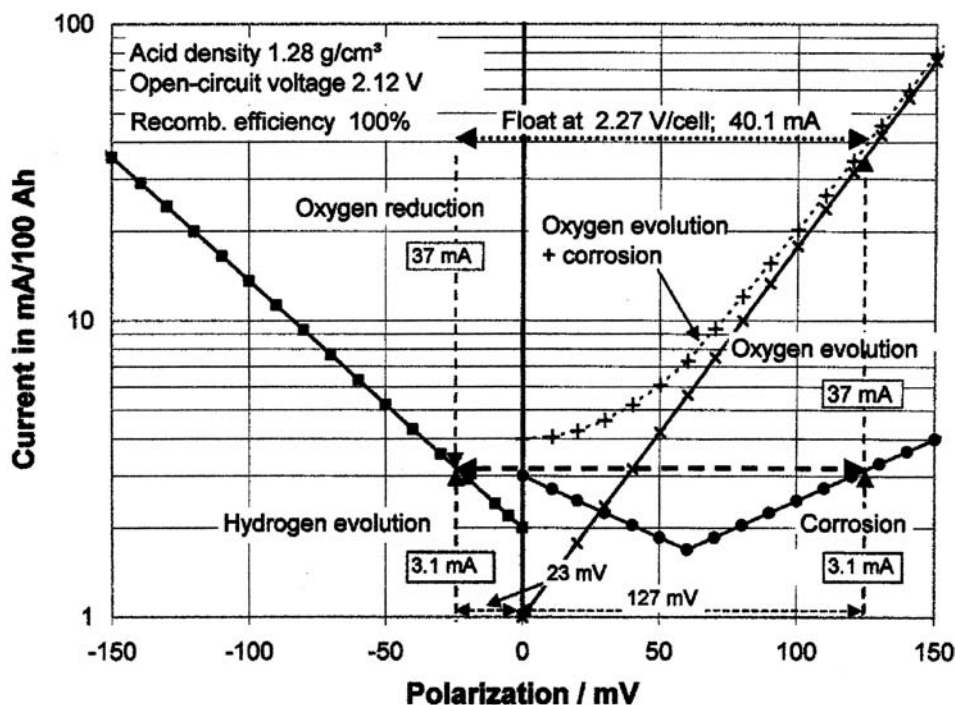


Figure 1.27 The float-charging situation of a VRLA battery. Current voltage curves as in Fig. 1.23, but at 100% of recombination efficiency of the internal oxygen cycle.

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 mV and -23 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).

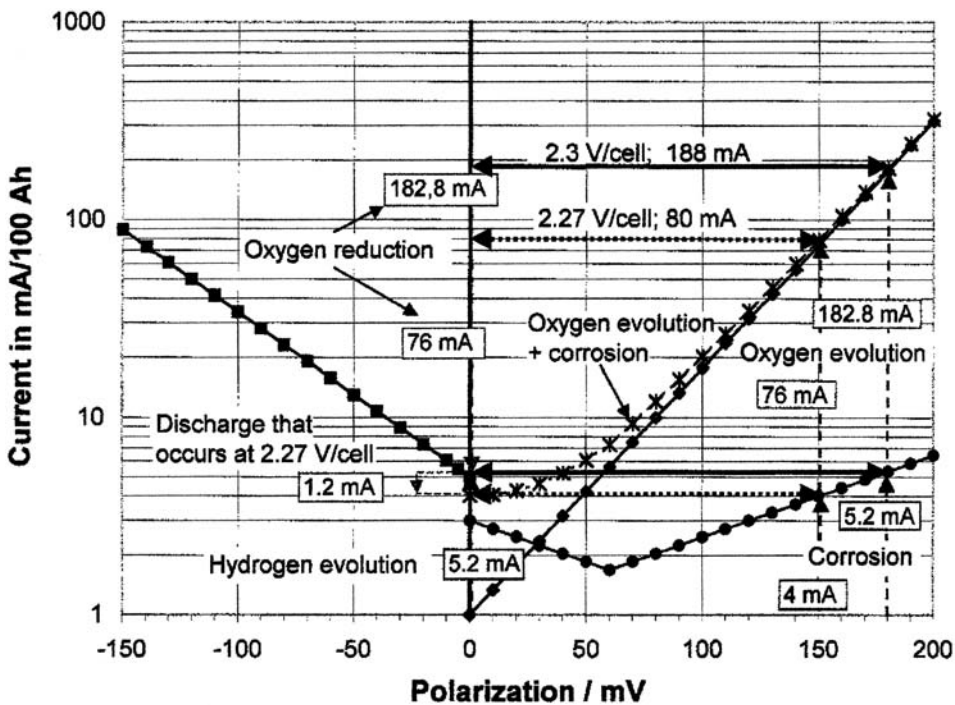


Figure 1.28 Overcharging of a VRLA battery. Characteristics as in Fig. 1.27, except an increased hydrogen evolution by the factor 2.5. 100% of recombination efficiency. (Zero point of polarization: $E_0 = 2.12$ V i.e. acid density 1.28 g/cm^3).

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 $2 \cdot \text{H}_2\text{O} + \text{Pb} \Rightarrow 2 \cdot \text{H}_2 + \text{PbO}_2$ (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 fugacity 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 $5.2 \text{ mA} - 1.2 \text{ mA} = 4 \text{ mA}$ 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

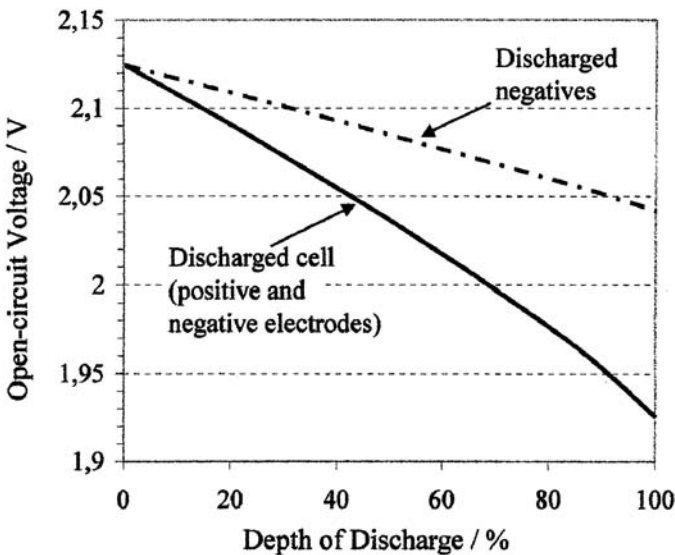


Figure 1.29 Open circuit voltage vs. depth of discharge (DOD), caused by acid dilution (cf. Fig. 1.2). The continuous line indicates the relation when both electrodes are discharged according to Eq. (59). The broken line represents the relation when only the negative electrode is discharged (Eq. (59b)).

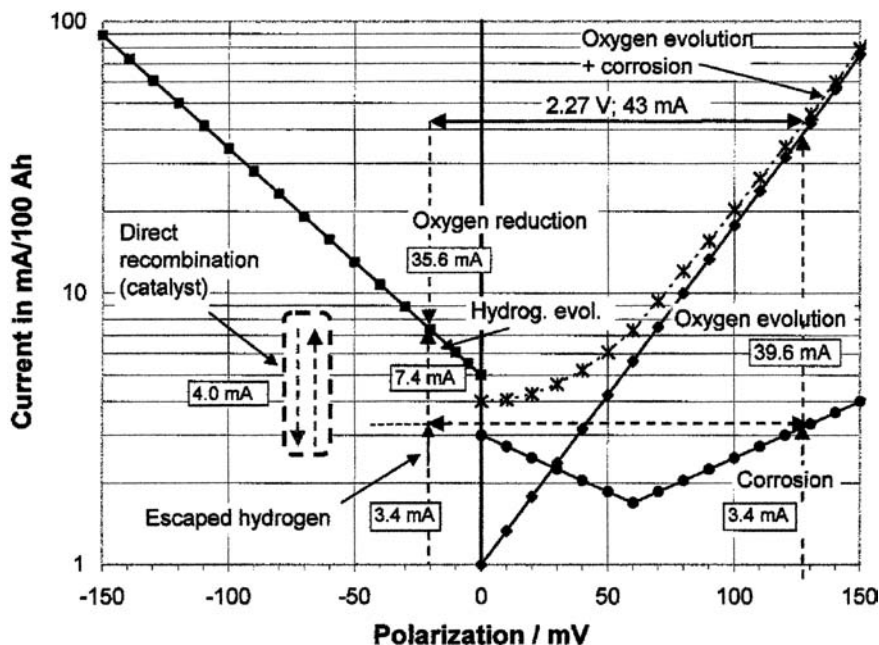


Figure 1.30 Effect of a catalyst. Characteristic data as in Fig. 1.28. Efficiency of the catalyst is 4.0 mA or 10% of the internal oxygen cycle. The efficiency of the internal oxygen cycle is thereby reduced to 90%.

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.

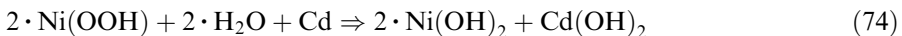
The positive electrode, the nickel-hydroxide electrode, already has been mentioned and its reaction mechanism sketched in [Fig. 1.6](#). When it is discharged, Ni^{3+} ions are reduced to Ni^{2+} according to the (simplified) equation



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



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



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 $2 \cdot \text{NiOOH}$ as the charged state more precisely should be written



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

$$\Delta G = \approx -256 \text{ kJ} \quad (76)$$

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

$$U^0 \approx 1.32 \text{ V} \quad \text{in practice } U^0 \approx 1.3 \text{ V} \quad (77)$$

The sign ' $\approx$ ' 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

$$\frac{dU^{\circ}}{dT} \approx -0.45 \text{ mV/K} \quad (78)$$

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

$$Q_{\text{rev}} = T \cdot \Delta S \approx -26 \text{ kJ} \quad (79)$$

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.)

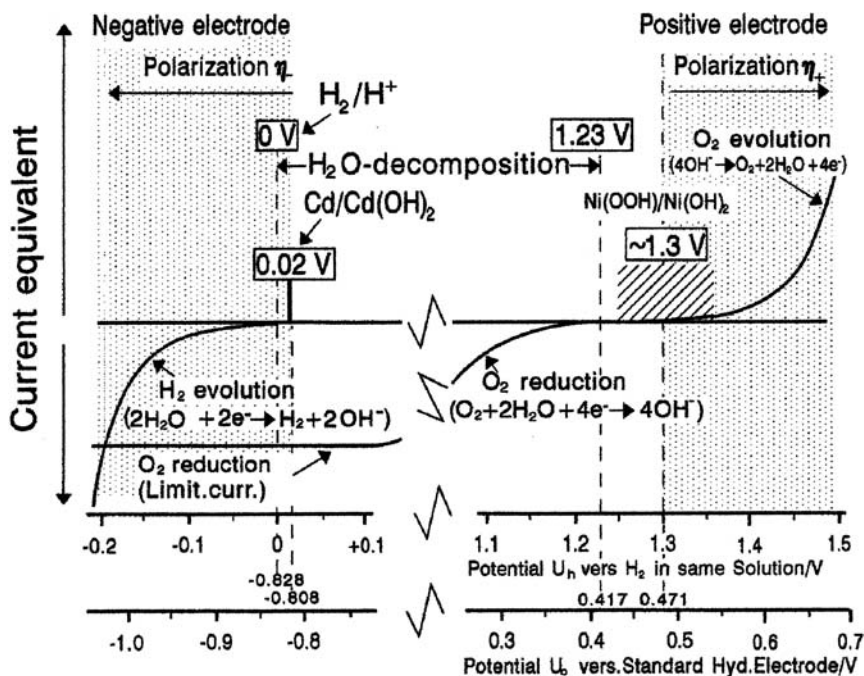


Figure 1.31 Equilibrium potentials of the negative and positive electrodes in a nickel/cadmium battery, and current/voltage curves for O₂ and H₂ evolution and O₂ reduction.

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/cm³ 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

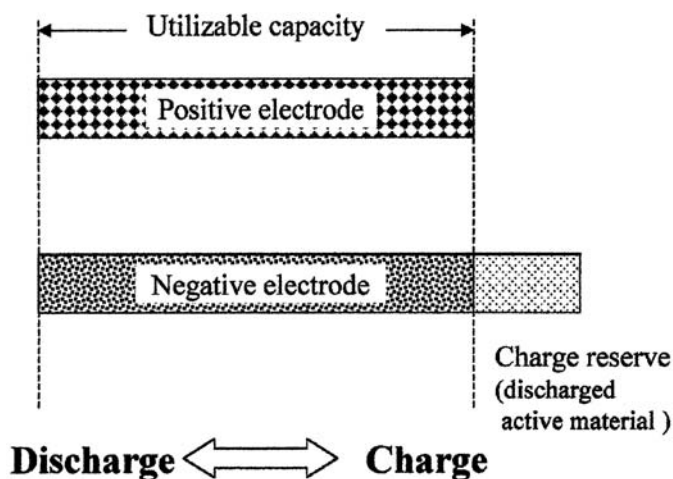


Figure 1.32 Cell balance of a sealed nickel/cadmium battery.

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 $\text{Cd}(\text{OH})_2$) 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 $7 \cdot 10^6 \text{Pa}$ (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.

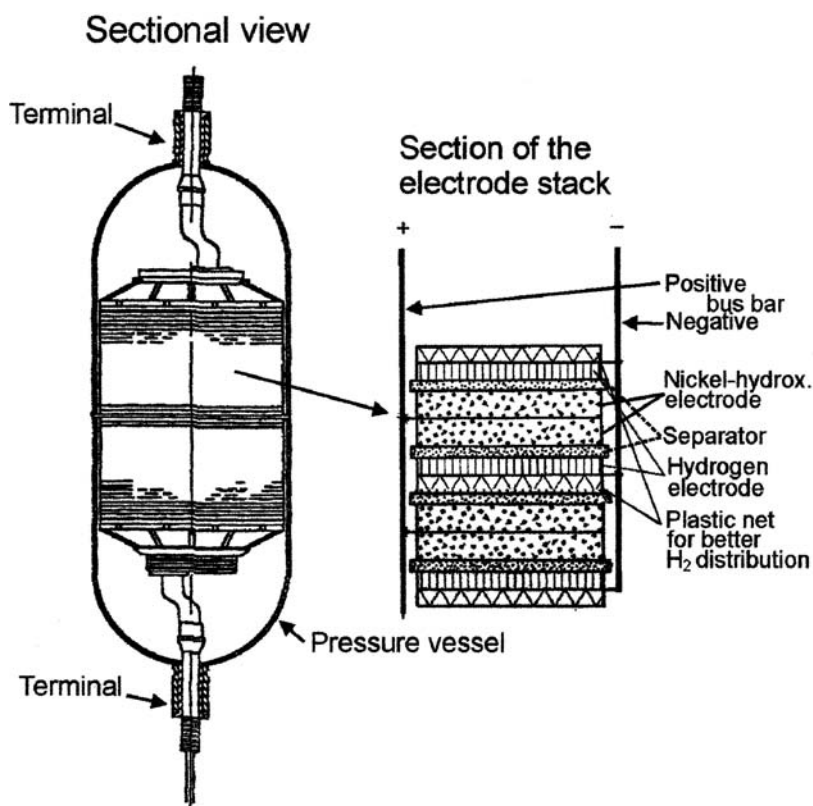


Figure 1.33 Sectional view of a nickel/hydrogen cell and details of the electrode stack.

1.8.3.1 Thermodynamic Situation

The discharge reaction of the negative electrode is



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)



During discharge, NiOOH is reduced to Ni(OH)₂ and hydrogen is consumed. During charge, this equation is reversed, and the released hydrogen (H₂) stored as a gas in each cell.

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

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

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

$$U^\circ = 1.34 \text{ V}$$

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:

$$U^\circ \approx 1.3 \text{ V} \quad (83)$$

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

$$U^\circ / dT \approx -0.6 \text{ mV/K} \quad (84)$$

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

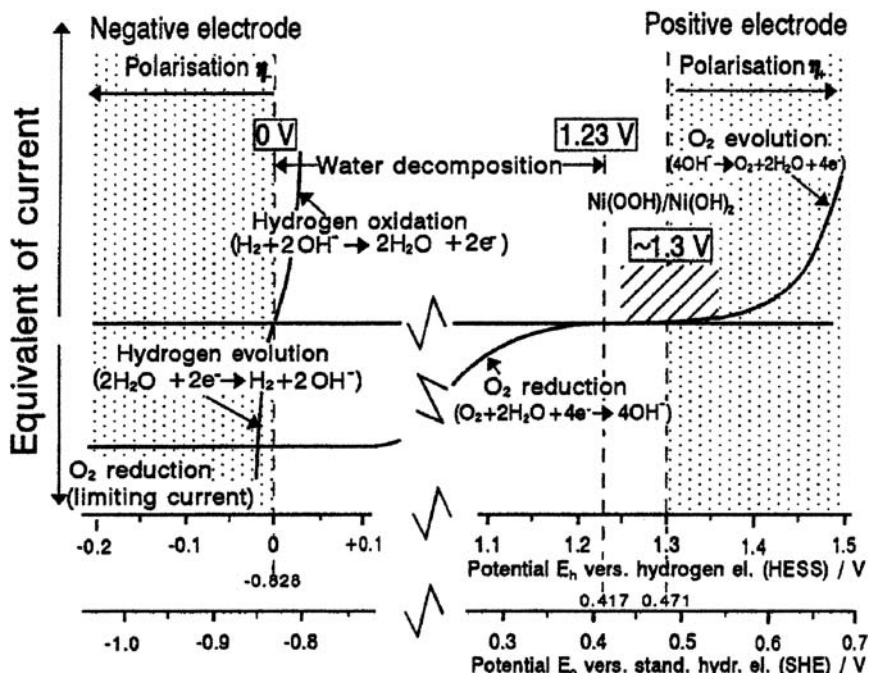


Figure 1.34 Equilibrium potentials and current/voltage curves in a nickel/hydrogen or a nickel/metal hydride battery. Current/voltage curves for O_2 evolution and reduction and for H_2 evolution and oxidation. For the x-axis, the electrode potential, two scales are employed as in Fig. 1.31.

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



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 $30^\circ C$ (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/dm³, 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 ($\approx 100\text{V}$). 24 of such batteries will power the International Space Station (ISS). Cell capacity 85 Ah; stored energy $\approx 8\text{ kWh}$ 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).

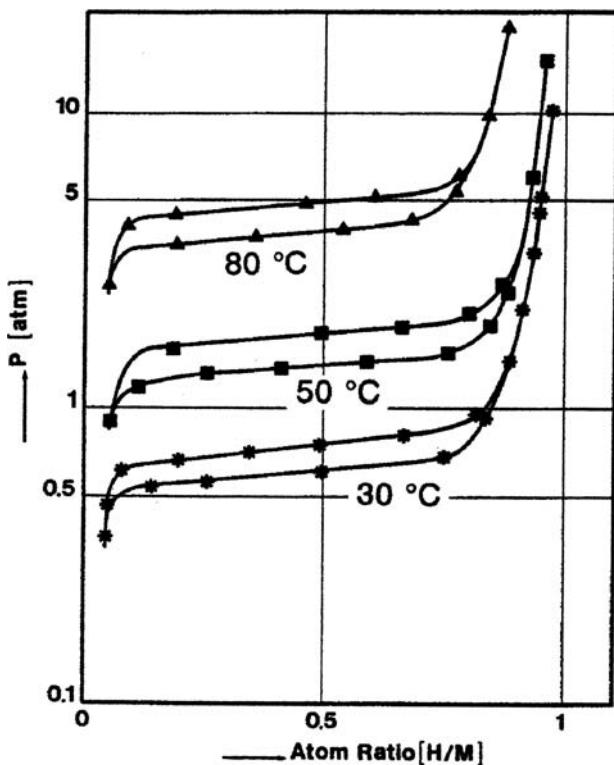


Figure 1.36 Pressure composition isotherms (PCI curves) of an AB₅ alloy with nickel partly substituted by aluminum (LaNi_{4.7}Al_{0.3}) vs. hydrogen content (from Ref. 72).

1.8.4.3 Hydrogen-Absorbing Alloys

An important prerequisite for nickel/metal hydride batteries was the development of alloys that absorb and desorb 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 cm³ palladium is able to store up to 0.24 g of H₂, which corresponds to 2800 cm³ of gaseous H₂ 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 rare earths, 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
4	A_2B (Ti_2Ni)	A: Mg, Ti B: Ni		in cars and as electrodes (68)

^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.

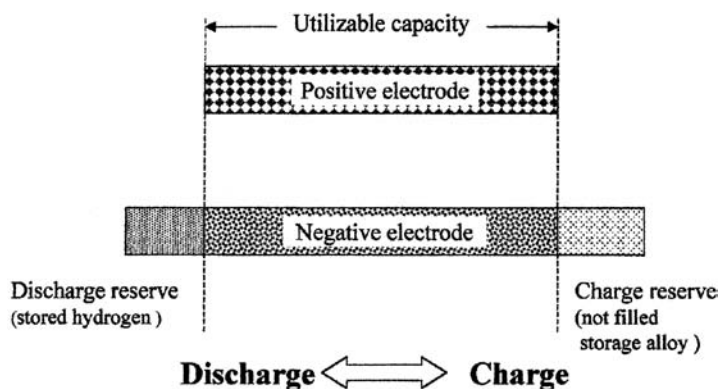


Figure 1.37 Balance of electrode capacities (cell balance) in a nickel/metal hydride battery by means of charge reserve and discharge reserve.

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



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



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.

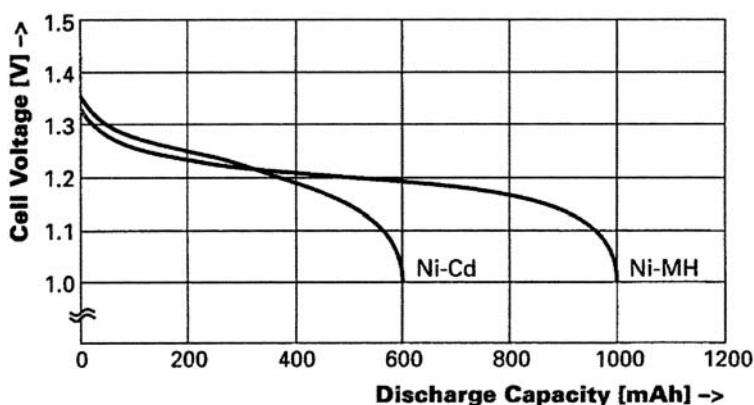


Figure 1.38 Comparison of discharge voltage and capacity between nickel/cadmium and nickel/metal hydride batteries of the same size. Cylindrical cells, AA type, discharging current 0.2 CA (≈ 5 hours) (from Ref. 74).

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 ($\text{O}_2 + 4 \cdot \text{e}^- \Rightarrow 2 \cdot \text{O}^{2-}$). 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.

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

^a Assuming that chlorine is stored as $[\text{Cl}_2 \cdot 7\text{H}_2\text{O}]$.

^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 ≈ 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



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 ($\text{Cl}_2 \cdot x\text{H}_2\text{O}$; $6 \leq x \leq 8$). 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)

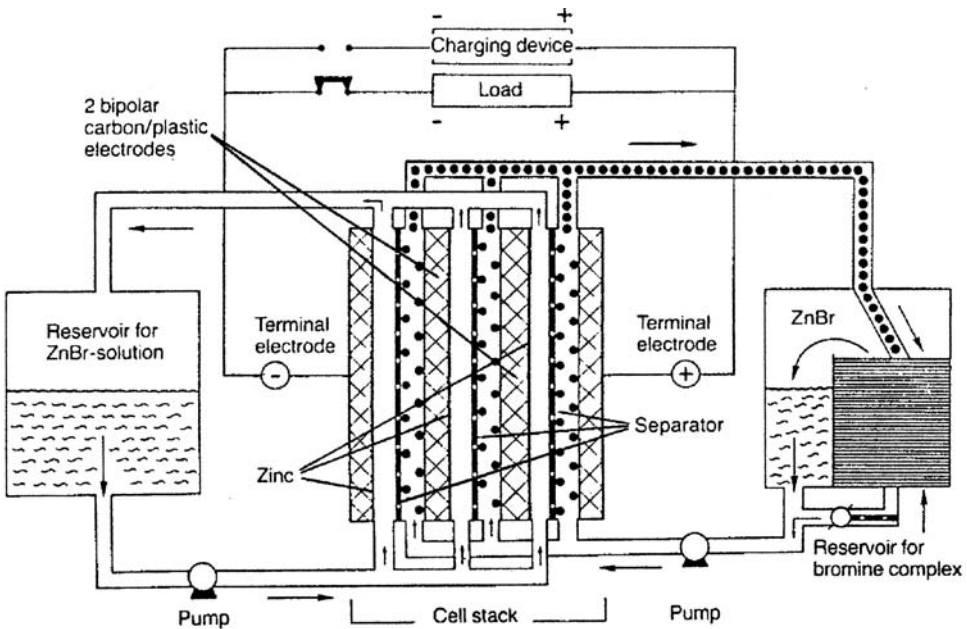
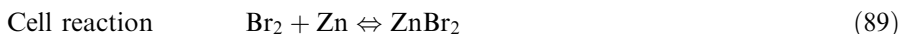
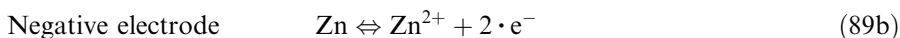
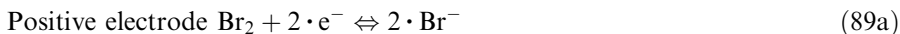


Figure 1.39 Zinc bromine battery (from Ref. 77).

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

Charging $\Leftrightarrow$ Discharging



During charging, Zinc (Zn) is precipitated as a solid metal, that is dissolved as zinc bromide (ZnBr₂) during discharge. At the positive electrode, the charged material is bromine (Br₂) 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 NH₄Cl).

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 (ZnBr₂) concentration is correspondingly increased.

At the positive electrode, bromine (Br₂) 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 Br₂ 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 (Br₂) is released.

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

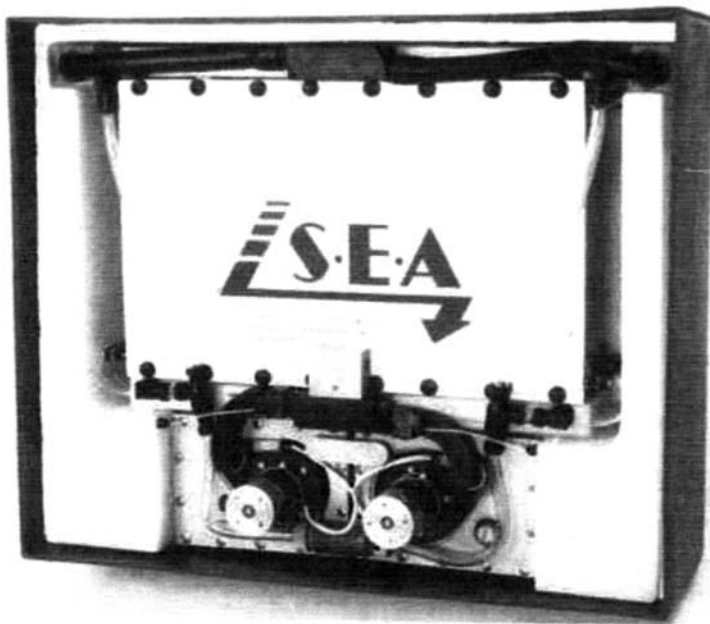


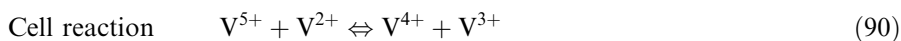
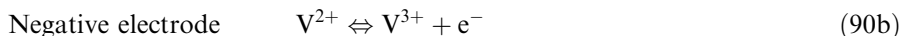
Figure 1.40 Prototype of a Zn/Br battery, 48 V, 5 kW. The cell stack is arranged in the center seen in the upper part. The pumps are to be seen below the cell stack. The storage tanks enframe both on the left- and on the right-hand side (from Ref. 79).

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:

Charging $\Leftrightarrow$ Discharging



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/dm³), shown in [Table 1.11](#). They are caused by the

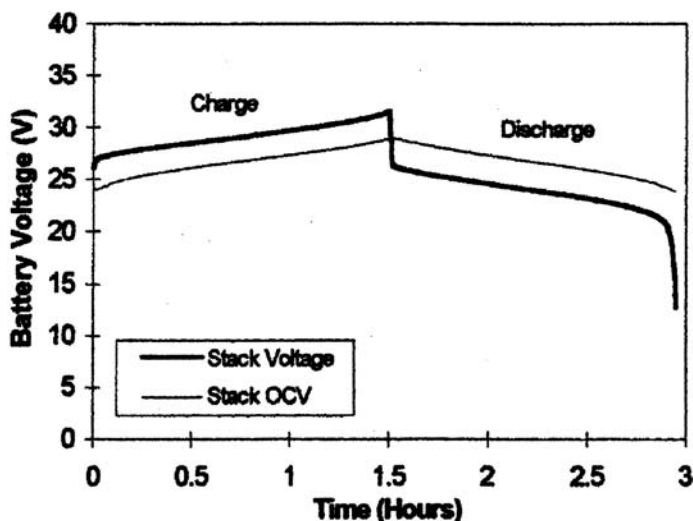


Figure 1.41 Charge/discharge curves of a vanadium redox battery. The cell stack consisted of 17 cells. Constant current of 100 Ah for charging and discharging (from Ref. 80).

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.

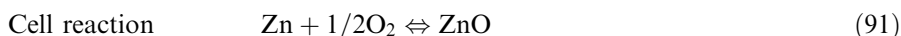
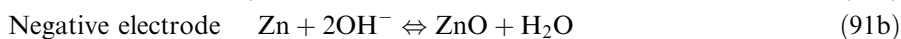
Shunt currents, as mentioned with the zinc/bromine system are also in this system unavoidable. To keep these parasitic currents low, the connecting tubes must be small, but this simultaneously limits the high rate performance.

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

Charging $\Leftrightarrow$ Discharging



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 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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