Part I
Fundamentals and General Aspects of Electrochemical Energy Storage

Handbook of Battery Materials, Second Edition. Edited by Claus Daniel and Jürgen O. Besenhard.

1

Thermodynamics and Mechanistics

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1.1

Electrochemical Power Sources

Electrochemical power sources convert chemical energy into electrical energy (see Figure 1.1). At least two reaction partners undergo a chemical process during this operation. The energy of this reaction is available as electric current at a defined voltage and time [1].

Electrochemical power sources differ from others such as thermal power plants in the fact that the energy conversion occurs without any intermediate steps; for example, in the case of thermal power plants, fuel is first converted into thermal energy (in furnaces or combustion chambers), then into mechanical energy, and finally into electric power by means of generators. In the case of electrochemical power sources, this multistep process is replaced by one step only. As a consequence, electrochemical systems show some advantages such as high energy efficiency.

The existing types of electrochemical storage systems vary according to the nature of the chemical reaction, structural features, and design. This reflects the large number of possible applications.

The simplest system consists of one electrochemical cell – the so-called galvanic element [1]. This supplies a comparatively low cell voltage of 0.5–5 V. To obtain a higher voltage the cell can be connected in series with others, and for a higher capacity it is necessary to link them in parallel. In both cases the resulting ensemble is called a *battery*.

Depending on the principle of operation, cells are classified as follows:

1) *Primary cells* are nonrechargeable cells in which the electrochemical reaction is irreversible. They contain only a fixed amount of the reacting compounds and can be discharged only once. The reacting compounds are consumed by discharging, and the cell cannot be used again. A well-known example of a primary cell is the Daniell element (Figure 1.2), consisting of zinc and copper as the electrode materials.

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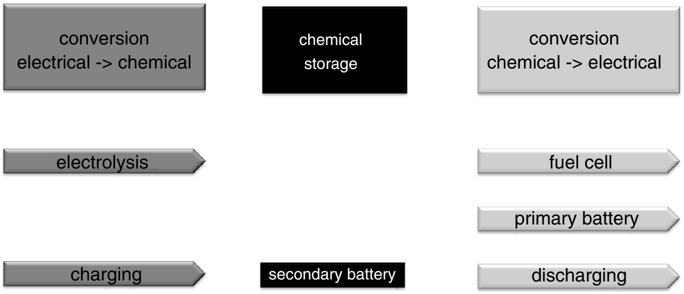


Figure 1.1 Chemical and electrical energy conversion and possibilities of storage.

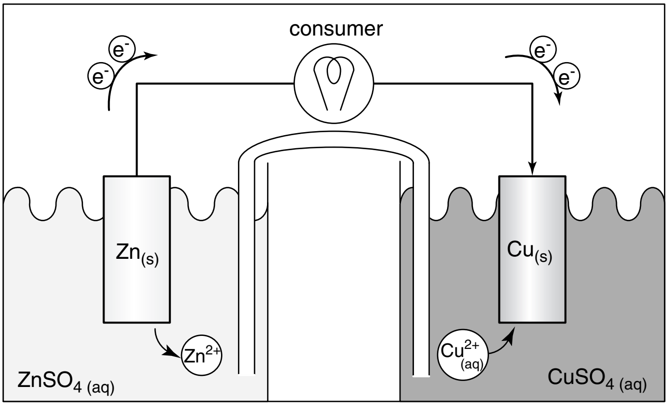


Figure 1.2 Daniell element.

2) *Secondary cells* are rechargeable several times [1]. Only reversible electrochemical reactions offer such a possibility. After the cell is discharged, an externally applied electrical energy forces a reversal of the electrochemical process; as a consequence the reactants are restored to their original form, and the stored electrochemical energy can be used once again by a consumer. The process can be reversed hundreds or even thousands of times, so that the lifetime of the cell can be extended. This is a fundamental advantage, especially as the cost of a secondary cell is normally much higher than that of a primary cell. Furthermore, the resulting environmental friendliness should be taken into account.
3) *Fuel cells* [2]: In contrast to the cells so far considered, fuel cells operate in a continuous process. The reactants – often hydrogen and oxygen – are fed continuously to the cell from outside. Fuel cells are not reversible systems.

Typical fields of application for electrochemical energy storage systems are in portable systems such as cellular phones, notebooks, cordless power tools,

Table 1.1 Comparison of cell parameters of different cells [4].

Cell reaction	Standard potential	Terminal voltage	Capacity (Ah kg^{-1})	Specific energy (Wh kg^{-1})
$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$	$\varepsilon_{00}(Zn/Zn^{2+}) = -0.76\ V$ $\varepsilon_{00}(Cu/Cu^{2+}) = 0.34\ V$	$\Delta\varepsilon_{00} = 1.10\ V$	238.2	262
$Cd + 2NiOOH + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$	$\varepsilon_{00}(Cd/Cd^{2+}) = -0.81\ V$ $\varepsilon_{00}(Ni^{2+}/Ni^{3+}) = 0.49\ V$	$\Delta\varepsilon_{00} = 1.30\ V$	161.5	210
$Li + MnO_2 \rightarrow LiMnO_2$	$\varepsilon_{00}(Li/Li^{+}) = -3.04\ V$ $\varepsilon_{00}(Mn^{3+}/Mn^{4+}) = 0.16\ V$	$\Delta\varepsilon_{00} = 3.20\ V$	285.4	856.3

Table 1.2 Comparison of the Efficiencies.

System	Coulometric efficiency	Energy efficiency
Lead–acid accumulator	0 .80	0.65–0.70
Nickel–cadmium accumulator	0.65–0.70	0.55–0.65
Nickel–metal hydride accumulator	0.65–0.70	0.55–0.65

Table 1.3 Comparison of Primary and Secondary Battery Systems.

System	Specific energy (theoretical) (Wh kg^{-1})	Specific energy (practical) (Wh kg^{-1})	Energy density (practical) (Wh L^{-1})
Alkaline (zinc)–manganese cell	336	50–80	120–150
Zinc–carbon	358	60–90	140–200
Lead–acid	170	35	90
Nickel–cadmium	209	50	90
Nickel–metal hydride	380	60	80
Lithium-ion–metal oxide	500–550	150	220

SLI (**s**tarter-**l**ight-**i**gnition) batteries for cars, and electrically powered vehicles. There are also a growing number of stationary applications such as devices for emergency current and energy storage systems for renewable energy sources (wind, solar). Especially for portable applications the batteries should have a low weight and volume, a large storage capacity, and a high specific energy density. Most of the applications mentioned could be covered by primary batteries, but economical and ecological considerations lead to the use of secondary systems.

Apart from the improvement and scaling up of known systems such as the lead–acid battery, the nickel–cadmium, and the nickel–metal hydride batteries, new types of cells have been developed, such as the lithium-ion system. The latter seems to be the most promising system, as will be apparent from the following sections [3].

To judge which battery systems are likely to be suitable for a given potential application, a good understanding of the principles of functioning and of the various materials utilized is necessary (see Table 1.1).

The development of high-performance primary and secondary batteries for different applications has proved to be an extremely challenging task because of the need to simultaneously meet multiple battery performance requirements such as high energy (watt-hours per unit battery mass or volume), high power (watts per unit battery mass or volume), long life (5–10 years and some hundreds of charge-discharge cycles), low cost (measured per unit battery capacity), resistance to abuse and operating temperature extremes, near-perfect safety, and minimal environmental impact (see Table 1.2 and Table 1.3). Despite years of intensive worldwide R&D, no battery can meet all of these goals.

The following sections therefore present a short introduction to this topic and to the basic mechanisms of batteries [4]. Finally, a first overview of the important criteria used in comparing different systems is given.

1.2
Electrochemical Fundamentals

1.2.1
Electrochemical Cell

The characteristic feature of an electrochemical cell is that the electronic current, which is the movement of electrons in the external circuit, is generated by the electrochemical processes at the electrodes. In contrast to the electric current in the external system, the transportation of the charge between the positive and the negative electrode within the electrolyte is performed by ions. Generally the current in the electrolyte consists of the movement of negative and positive ions.

A simplified picture of the electrode processes is shown in Figure 1.3. Starting with an open circuit, metal A is dipped in the solution, whereupon it partly dissolves. Electrons remain at the electrode until a characteristic electron density is built up. For metal B, which is more noble than A (see Section 1.2.2), the same process takes place, but the amount of dissolution and therefore the resulting electron density is lower.

If these two electrodes are connected by an electrical conductor, an electron flow starts from the negative electrode with the higher electron density to the positive electrode. The system electrode/electrolyte tries to keep the electron density constant. As a consequence additional metal A dissolves at the negative electrode forming A^+ in solution and electrons e^-, which are located at the surface

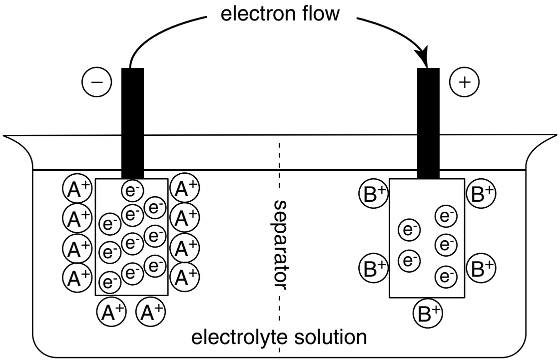


Figure 1.3 Electrochemical cell with negative and positive electrodes.

of metal A.

$$A \rightarrow A^+ + e^-$$

At the positive electrode the electronic current results in an increasing electron density. The system electrode B/electrolyte compensates this process by the consumption of electrons for the deposition of B^+-ions:

$$B^+ + e^- \rightarrow B$$

The electronic current stops if one of the following conditions is fulfilled:

- the base metal A is completely dissolved
- all B^+-ions are precipitated.

As a consequence, it is necessary to add a soluble salt to the positive electrode compartment to maintain the current for a longer period. This salt consists of B^+-ions and corresponding negative ions. The two electrode compartments are divided by an appropriate separator to avoid the migration and the deposition of B^+-ions at the negative electrode A. Since this separator blocks the exchange of positive ions, only the negative ions are responsible for the charge transport in the cell. This means that for each electron flowing in the outer circuit from the negative to the positive electrode, a negative ion in the electrolyte diffuses to the negative electrode compartment.

Generally, the limiting factor for the electronic current flow is the transport of these ions. Therefore the electrolyte solution should have a low resistance.

An electrolyte is characterized by its *specific resistance* $\rho(\Omega\,\text{cm})$, which is defined as the resistance of the solution between two electrodes each with an area of 1 cm^2 and at a distance apart of 1 cm. The reciprocal of this value is known as the specific conductivity κ ($\Omega^{-1}\,\text{cm}^{-1}$) [5]. For comparison, the values for different materials are given in Figure 1.4.

The conductivity of different electrolyte solutions varies widely. The selection of a suitable, highly conductive electrolyte solution for an electrochemical cell

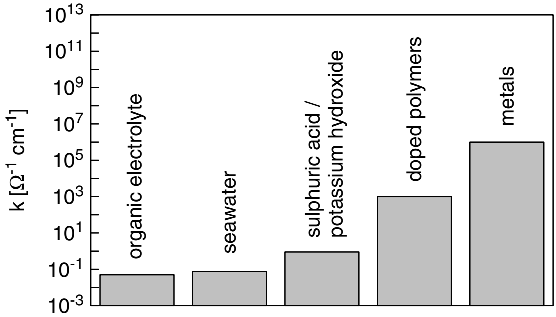


Figure 1.4 Comparison of the specific conductivity of different materials.

depends on its compatibility with the other components, particularly the positive and negative electrodes.

From the chemical viewpoint, a galvanic cell is a current source in which a local separation of oxidation and reduction process exists. In the following, this is explained using the example of the Daniell element.

Here the galvanic cell contains copper as the positive electrode, zinc as the negative electrode, and the sulfates of these metals as the electrolyte.

A salt bridge serves as an ion-conducting connection between the two half cells. On closing the external circuit, the oxidation reaction starts with the dissolution of the zinc electrode and the formation of zinc ions in half cell I. In half cell II copper ions are reduced and metallic copper is deposited. The sulfate ions remain unchanged in the solution. The overall cell reaction consists of an electron transfer between zinc and copper ions:

$$\begin{aligned} \mathrm{Zn} &\rightarrow \mathrm{Zn}^{2+} + 2\mathrm{e}^- \quad \text{oxidation/half cell I} \\ \mathrm{Cu}^{2+} + 2\mathrm{e}^- &\rightarrow \mathrm{Cu} \quad \text{reduction/half cell II} \\ \mathrm{Zn} + \mathrm{Cu}^{2+} &\rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu} \quad \text{overall cell reaction} \end{aligned}$$

A typical feature of a redox reaction is an exchange of electrons between at least two reaction partners. It is characterized by the fact that oxidation and reduction always occur at the same time. For the Daniell element, the copper ions are the oxidizing agent and the zinc ions the reducing agent. Both together form the corresponding redox pair:

$$\begin{aligned} \mathrm{Red}_1 + \mathrm{Ox}_2 &\rightarrow \mathrm{Ox}_1 + \mathrm{Red}_2 \\ \mathrm{CuSO}_4 + \mathrm{Zn} &\rightarrow \mathrm{ZnSO}_4 + \mathrm{Cu} \end{aligned}$$

The electrode at which the oxidation dominates during discharge is named the anode (negative pole), and the other, where the reduction dominates, is the cathode (positive pole). This nomenclature is valid only for the discharging reaction; for the charging reaction the names are reversed.

1.2.2
Electrochemical Series of Metals

The question arises, which metal is dissolved and which one is deposited when they are combined in an electrochemical cell. The electrochemical series indicates how easily a metal is oxidized or its ions are reduced, that is, converted into positive charged ions or metal atoms respectively. To compare different metals we use the standard potential, which is described below.

In Galvanic cells it is only possible to determine the potential difference as a voltage between two half cells, but not the absolute potential of the single electrode. For the measurement of the potential difference it has to be ensured that an electrochemical equilibrium exists at the phase boundaries (electrode/electrolyte). At least it is required that there is no flux of current in the external and internal circuit.

To compare the potentials of half cells a reference had to be defined. For this reason it was decided arbitrarily that the potential of the hydrogen electrode in a 1 M acidic solution should be equal to 0 V at a temperature of 25 °C and a pressure of 101.3 kPa. These conditions are called *standard conditions* [6].

The reaction of hydrogen in acidic solution is a half-cell reaction and can therefore be handled like the system metal/metal salt solution.

$$H_2 + 2\,H_2O \;\rightarrow\; 2\,H_3O^+ + 2\,e^-$$

An experimental setup for the hydrogen half cell is illustrated in Figure 1.5.

The potentials of the metals in their 1 M salt solution are all related to the standard or normal hydrogen electrode (NHE). To measure the potential of such a system, the hydrogen half cell is combined with another half cell to form a Galvanic cell. The measured voltage is called the *normal potential* or *standard electrode potential* ε_{00} of the metal. If the metals are arranged in the order of their normal potentials, the resulting order is named the electrochemical series of the metals (Figure 1.6). Depending on their position in this potential series, they are called *base* ($\varepsilon_{00} < 0$) or *noble* ($\varepsilon_{00} > 0$) metals.

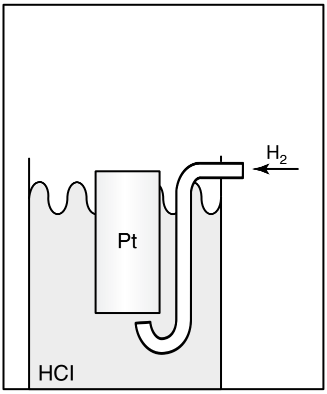


Figure 1.5 Hydrogen electrode with hydrogen-saturated platinum electrode in hydrochloric acid.

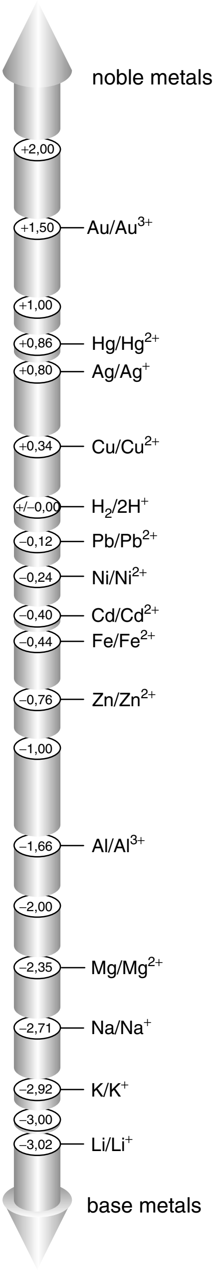
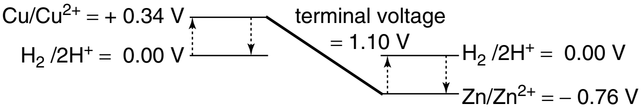


Figure 1.6 Electrochemical series of metals and the standard potential in volt (measured against NHE).

$$Zn \rightarrow Zn^{2+} + 2\ e^-, \text{normal potential } \varepsilon_{00} = -0.76\ V_{NHE}$$
$$Cu \rightarrow Cu^{2+} + 2\ e^-, \text{normal potential } \varepsilon_{00} = +0.34\ V_{NHE}$$

For the Daniell element in Figure 1.2 the following potential difference is obtained:

$$\Delta\varepsilon_{00} = \varepsilon_{00,\,Cu/Cu^{2+}} - \varepsilon_{00,\,Zn/Zn^{2+}} \tag{1.1}$$



Under equilibrium conditions the potential difference $\Delta\varepsilon_0$ corresponds to the terminal voltage of the cell.

If there are no standard conditions or if it should not be possible to measure the standard potential, the value can be determined by thermodynamic calculations (see Section 1.4.1).

For the arrangement of a galvanic cell for use as a power source the half cells are chosen such that their potentials $\varepsilon_{I,II}$ are as far apart as possible. Therefore, it is obvious why alkaline metals, especially lithium or sodium, are interesting as new materials for the negative electrode. As they have a strong negative standard potential and a comparatively low density, a high specific energy can be realized by combination with a positive electrode.

The following examples, the Daniell element, nickel-cadmium cells, and lithium-manganese dioxide cells, show the influences of the electrode materials on different cell parameters.

1.2.3
Discharging

During the discharge process, electrons are released at the anode from the electrochemically active material, which is oxidized. At the same time, cathodic substances are reduced by receiving electrons. The transport of the electrons occurs through an external circuit (the consumer).

Looking at first at the anode, there is a relationship between the electronic current I and the mass m of the substance which donates electrons, and this is known as the *first Faraday law* [7]:

$$m = \frac{M}{z \cdot F} \cdot I \cdot t \tag{1.2}$$

m = active mass
M = molar mass
z = number of electrons exchanged
F = Faraday constant: 96 485 C mol^{-1} = 26.8 Ah mol^{-1}.
t = time

The Faraday constant is the product of the elementary charge e (1.602×10^{-19}C) and the Avogadro constant N_A (6.023×10^{23} mol^{-1}).

$$F = \frac{I \cdot t}{n} = \frac{Q}{n} = N_A \cdot e \tag{1.3}$$

Q = quantity of electricity, electric charge
n = number of moles of electrons exchanged.

For the Daniell-element the electron-donating reaction is the oxidation of zinc. In the following the active mass m which is necessary to deliver a capacity of 1 Ah, is calculated.

$Zn \rightarrow Zn^{2+} + 2\,e^-$

$M = 65.4$ g mol^{-1}, $z = 2$, $F = 26.8$ Ah mol^{-1}, $Q = 1$ Ah

$$m = \frac{M}{z \cdot F} \cdot Q$$
$$m = 1.22 \text{ g}$$

Of course, Faraday's first law applies to cathodic processes. Therefore, the deposition of 1 Ah copper ions results in an increase in the electrode mass of $m = 1.18$ g.

In addition, Faraday recognized that for different electrode reactions and the same amount of charge the proportion of the reacting masses is equal to the proportion of the equivalent masses

$$\frac{m_A}{m_B} = \frac{M_A \cdot |z_B|}{M_B \cdot |z_A|} \tag{1.4}$$

Equation 1.4 expresses the fact that 1 mol electrons discharges

- 1 mol monovalent ions,
- 1/2 mol bivalent ions, or
- $1/z$ mol z-valent ions.

1.2.4
Charging

The charging process can only be applied to secondary cells, because, in contrast to primary cells, the electrochemical reactions are reversible. If primary cells are charged, this may lead to electrochemical side reactions, for example, the decomposition of the electrolyte solution with dangerous follow-up reactions leading to explosions [8].

While charging, ions are generally reduced at the negative electrode and an oxidation process takes place at the positive electrode. The voltage source must be at least equivalent to the difference $\Delta\varepsilon_{00}$ between the equilibrium potentials of the two half cells. Generally the charge voltage is higher.

1.3
Thermodynamics

1.3.1
Electrode Processes at Equilibrium

Corresponding to chemical reactions, it is possible to treat electrochemical reactions in equilibrium with the help of thermodynamics.

As well as determining the potential at standard conditions by means of measurement, it is possible to calculate this value from thermodynamic data [9]. In addition, one can determine the influence of changing pressure, temperature, concentration, and so on.

During the determination of standard electrode potentials an electrochemical equilibrium must always exist at the phase boundaries, for example, electrode/electrolyte. From a macroscopic viewpoint, no external current flows and no reaction takes place. From a microscopic viewpoint or on a molecular scale, however, a continuous exchange of charges occurs at the phase boundaries. Figure 1.7 demonstrates this fact at the anode of the Daniell element.

The exchange of charge carriers in the molecular sphere at the phase boundary zinc/electrolyte solution corresponds to an anodic and an equal cathodic current. These compensate each other in the case of equilibrium.

Three kinds of equilibrium potentials are distinguishable:

1) A *metal ion potential* exists if a metal and its ions are present in balanced phases, for example, zinc and zinc ions at the anode of the Daniell element.
2) A *redox potential* exists if both phases exchange electrons and the electron exchange is in equilibrium; for example, the normal hydrogen half cell with an electron transfer between hydrogen and protons at the platinum electrode.
3) If two different ions are present, only one of which can cross the phase boundary, which may exist at a semi-permeable membrane, one gets a so-called

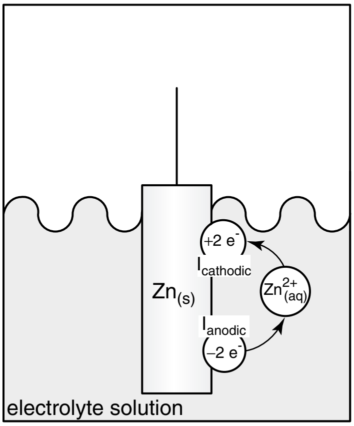


Figure 1.7 Phase boundary metal (zinc)/electrolyte solution (zinc sulfate) in equilibrium.

membrane potential. Well-known examples are the sodium/potassium ion pumps in human cells.

1.3.2
Reaction Free Energy ΔG and Equilibrium Cell Voltage $\Delta\varepsilon_{00}$

Instead of measuring the equilibrium cell voltage $\Delta\varepsilon_{00}$ at standard conditions directly, this can be calculated from the reaction free energy ΔG for one formula conversion. In this context one of the fundamental equations is the GIBBS–HELMHOLTZ relation [7].

$$\Delta G = \Delta H - T \cdot \Delta S \tag{1.5}$$

For the electrochemical cell reaction, the reaction free energy ΔG is the utilizable electric energy. The reaction enthalpy ΔH is the theoretical available energy, which is increased or reduced by $T \cdot \Delta S$. The product of the temperature and the entropy describes the reversible amount of heat consumed or released during the reaction. With tabular values for the enthalpy and the entropy it is possible to obtain ΔG.

Using the reaction free energy, ΔG, the cell voltage $\Delta\varepsilon_0$ can be calculated. First, the number n of exchanged moles of electrons during an electrode reaction must be determined from the cell reaction. For the Daniell element (see example below), 2 mol of electrons are released or received, respectively.

$$1\ \text{mol Zn} \rightarrow 1\ \text{mol Zn}^{2+} + 2\ \text{mol e}^-$$
$$1\ \text{mol Cu} \rightarrow 1\ \text{mol Cu}^{2+} + 2\ \text{mol e}^-$$

With the definition of the Faraday constant (Equation 1.3), the amount of charge of the cell reaction for one formula conversion is given by the following equation:

$$Q = I \cdot t = n \cdot F \tag{1.6}$$

With this quantity of charge, the electrical energy is

$$\Delta\varepsilon_{00} \cdot Q = \Delta\varepsilon_{00} \cdot n \cdot F \tag{1.7}$$

The thermodynamic treatment requires that during one formula conversion the cell reaction is reversible. This means that all partial processes in a cell must remain in equilibrium. The current is kept infinitely small, so that the cell voltage ε and the equilibrium cell voltage $\Delta\varepsilon_{00}$ are equal. Furthermore, inside the cell no concentration gradient should exist in the electrolyte; that is, the zinc and copper ion concentrations must be constant in the whole Daniell element. Under these conditions, the utilizable electric energy, $\Delta\varepsilon_{00} \times z \times F$ per mol, corresponds to the reaction free energy ΔG of the Galvanic cell, which is therefore given by

$$\Delta G = -z \cdot F \cdot \Delta\varepsilon_{00} \tag{1.8}$$

For the Daniell element under standard conditions $T = 298\ \mathrm{K}$

$$\mathrm{Zn} + \mathrm{CuSO_4} \longrightarrow \mathrm{ZnSO_4} + \mathrm{Cu}$$

Reaction enthalpy	$\Delta H = -210.1\ \mathrm{kJ\ mol^{-1}}$
Entropy	$\Delta S = -7.2\ \mathrm{J\ K^{-1}\ mol^{-1}}$
Reaction free energy	$\Delta G = \Delta H - T \cdot \Delta S$ $\Delta G = -208\ \mathrm{kJ\ mol^{-1}}$
Faraday constant	$F = 96\,485\ \mathrm{C\ mol^{-1}}$
Number of exchanged electrons	$z = 2$
Cell voltage	$\Delta\varepsilon_{00} = -\frac{\Delta G}{z \cdot F}\left[\frac{\mathrm{kJ\ mol^{-1}}}{\mathrm{C\ mol^{-1}}}\right]$ $\Delta\varepsilon_{00} = 1.1\ \mathrm{V}$

1.3.3
Concentration Dependence of the Equilibrium Cell Voltage

It is established from the chemical thermodynamics that the sum of the chemical potentials μ_i of the substances ν_i involved in the gross reaction is equal to the reaction free energy.

$$\Delta G = \sum \nu_i \cdot \mu_i \tag{1.9}$$

Here ν_i are the stoichiometric factors of the compounds used in the equation for the cell reaction, having a plus sign for the substances formed and a negative sign for the consumed compounds.

As a result of the combination of Equations 1.8 and 1.9, the free reaction enthalpy ΔG and the equilibrium cell voltage $\Delta\varepsilon_{00}$ under standard conditions are related to the sum of the chemical potentials μ_i of the involved substances.

$$-\frac{\Delta G}{z \cdot F} = \Delta\varepsilon_{00} = \frac{1}{z \cdot F}\sum \nu_i \cdot \mu_i \tag{1.10}$$

Earlier it was shown that the equilibrium cell voltage $\Delta\varepsilon_{00}$ is equal to the difference of the equilibrium potentials of its half cells, for example, for the Daniell element:

$$\Delta\varepsilon_{00} = \varepsilon_{00,\,\mathrm{Cu/Cu^{2+}}} - \varepsilon^{2+}_{00,\,\mathrm{Zn/Zn}} \tag{1.11}$$

The chemical potential of one half cell depends on the concentrations c_i of the compounds, which react at the electrode:

$$\mu_i = \mu_{i,0} + R \cdot T \cdot \ln c_i \tag{1.12}$$

R = universal gas constant: $8.3\ \mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$.

As a consequence, the equilibrium potential of the single half cell also depends on the concentrations of the compounds. The NERNST equation (Equation 1.13), which is one of the most important electrochemical relations, expresses this [10]. It results if Equation 1.12 is inserted into Equation 1.10 with regard to one half cell:

$$\Delta\varepsilon_0 = \Delta\varepsilon_{00} + \frac{R \cdot T}{z \cdot F} \cdot \sum \nu_i \cdot \ln c_i \tag{1.13}$$

For a metal-ion electrode the NERNST equation is

$$\Delta\varepsilon_0 = \Delta\varepsilon_{00} + \frac{R \cdot T}{z \cdot F} \cdot \ln \frac{c_{\mathrm{Me}^{z+}}}{c_{\mathrm{Me}}} \tag{1.14}$$

and this is used in the following example for the calculation of the concentration dependence of the zinc electrode.

For one half cell of the Daniell element at a temperature of $T = 298$ K

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2\,\mathrm{e}^-$$

with the concentration	$c_{\mathrm{Zn}^{2+}} = 0.1\ \mathrm{mol\ L^{-1}}$
universal gas constant	$R = 8.3\ \mathrm{J \cdot mol^{-1} \cdot K^{-1}}$
Faraday constant	$F = 96\,485\ \mathrm{C \cdot mol^{-1}}$
number of exchanged electrons	$z = 2$
standard potential vs NHE,	$\Delta\varepsilon_{00}(\mathrm{Zn/Zn^{2+}}) = -0.76\ \mathrm{V}$

$$\Delta\varepsilon_0 = \Delta\varepsilon_{00} + \tfrac{R \cdot T}{z \cdot F} \cdot \ln \tfrac{c_{\mathrm{Zn}^{2+}}}{c_{\mathrm{Zn}}}$$

$$\Delta\varepsilon_0 = -0.79\ \mathrm{V}$$

The variation of the concentration from 1 mol $\mathrm{L^{-1}}$ (standard condition) to 0.1 mol $\mathrm{L^{-1}}$ is related to a change in the potential of −0.03 V.

If the concentrations of the copper and zinc ions within a Daniell element are known, the following cell voltage $\Delta\varepsilon_0$ results:

$$\Delta\varepsilon_{00} = \varepsilon_{0,\,\mathrm{Cu/Cu^{2+}}} - \varepsilon_{0,\,\mathrm{Zn/Zn^{2+}}} \tag{1.15}$$

1.3.4
Temperature Dependence of the Equilibrium Cell Voltage

The temperature dependence of the equilibrium cell voltage forms the basis to determine the thermodynamic variables ΔG, ΔH, and ΔS. The values of the equilibrium cell voltage $\Delta\varepsilon_{00}$ and the temperature coefficient $\mathrm{d}\Delta\varepsilon_{00}/\mathrm{d}T$, which are necessary for the calculation, can be measured exactly in experiments.

The temperature dependence of the cell voltage $\Delta\varepsilon_0$ results from Equation 1.10 by partial differentiation at a constant cell pressure.

$$\left(\frac{\partial\ \Delta\varepsilon_0}{\partial T}\right)_p = -\frac{1}{z \cdot F} \cdot \left(\frac{\partial \Delta G}{\partial T}\right)_p \tag{1.16}$$

For the temperature coefficient of the reaction free energy follows, because of thermodynamic relations [7], by partial differentiation of Equation 1.5:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_p = -\Delta S \tag{1.17}$$

$$\left(\frac{\partial\ \Delta \varepsilon_0}{\partial T}\right)_p = -\frac{1}{z \cdot F} \cdot (-\Delta S)_p \tag{1.18}$$

The *reversible reaction heat of the cell* is defined as the reaction entropy multiplied by the temperature (Equation 1.5). For an electrochemical cell this is also called the *PELTIER effect* and can be described by the difference between the reaction enthalpy ΔH and the reaction free energy ΔG. If the difference between the reaction free energy ΔG and the reaction enthalpy ΔH is less than zero, the cell becomes warmer. On the other hand, for a difference greater than zero, it cools down. The reversible heat of formation W of the electrochemical cell is therefore:

$$\begin{aligned} W &= \Delta G - \Delta H \\ W &= -T \cdot \Delta S \end{aligned} \tag{1.19}$$

For the Daniell element at standard conditions, $T = 298\,\text{K}$

$\text{Zn} + \text{CuSO}_4 \longrightarrow \text{ZnSO}_4 + \text{Cu}$

reaction enthalpy $\Delta H = -210.1\ \text{kJ mol}^{-1}$
reaction free energy $\Delta G = -208\ \text{kJ mol}^{-1}$
Heat $W = \Delta G - \Delta H$
$W = 2.1\ \text{kJ mol}^{-1}$

The reversible amount of heat of $2.1\,\text{kJ}\cdot\text{mol}^{-1}$ is consumed by charging and released by discharging.

The relationship between free reaction enthalpy, temperature, cell voltage, and reversible heat in a Galvanic cell is reflected by the GIBBS–HELMHOLTZ equation (Equation 1.20).

$$\Delta H = \Delta G - T \cdot \left(\frac{\partial\ \Delta G}{\partial T}\right)_p \tag{1.20}$$

Insertion of Equation 1.8 for ΔG results in

$$\Delta H = z \cdot F \cdot \left[\Delta \varepsilon_{00} + T \cdot \left(\frac{\partial\ \Delta \varepsilon_0}{\partial T}\right)_p\right] \tag{1.21}$$

Earlier it was deduced that for ΔS and ΔG:

$$\Delta S = z \cdot F \cdot \left(\frac{\partial\ \Delta \varepsilon_0}{\partial\ T}\right)_p \tag{1.22}$$

$$\Delta G = -z \cdot F \cdot \Delta \varepsilon_0 \tag{1.23}$$

From experiments it is possible to obtain the temperature coefficient for the Daniell element, $\Delta\varepsilon_0/T = -3.6 \times 10^{-5}\ \mathrm{V\,K^{-1}}$:

temperature	$T = 298\ \mathrm{K}$
equilibrium cell voltage	$\Delta\varepsilon_{00} = 1.1\ \mathrm{V}$
Faraday constant	$F = 96\,485\ \mathrm{C\,mol^{-1}}$
number of exchanged electrons	$z = 2$
reaction enthalpy	$\Delta H = z \cdot F \cdot \left[\Delta\varepsilon_{00} + T \cdot \left(\frac{\partial\ \Delta\varepsilon_0}{\partial T}\right)_p\right]$ $\Delta H = 212.2\ \mathrm{kJ\,mol^{-1}}$
reaction entropy	$\Delta S = z \cdot F \cdot \left(\frac{\partial\ \Delta\varepsilon_0}{\partial\ T}\right)_p$ $\Delta S = -2.1\ \mathrm{kJ\,K^{-1}}$
free reaction enthalpy	$\Delta G = -z \cdot F \cdot \Delta\varepsilon_0$ $\Delta G = -208\ \mathrm{kJ\,mol^{-1}}$

The calculation of the free reaction enthalpy is possible with Equation 1.8, and the determination of the reaction entropy ΔS follows from Equation 1.22.

1.3.5
Pressure Dependence of the Equilibrium Cell Voltage

It is obvious that the cell voltage is nearly independent of the pressure if the reaction takes place between solid and liquid phases where the change in volume is negligibly low. On the other hand, in reactions involving the evolution or disappearance of gases, this effect has to be considered [11].

The pressure dependence of the reaction free energy is equal to the volume change associated with one formula conversion.

$$\left(\frac{\partial \Delta G}{\partial p}\right)_T = \Delta V \tag{1.24}$$

With $\Delta \mathrm{G} = -n \times F \times \Delta\varepsilon_0$ and $\Delta V = -RT/p$ we have

$$\left(\frac{\partial\ \Delta\varepsilon_0}{\partial p}\right)_T = -\frac{R \cdot T}{n \cdot F} \cdot \frac{1}{p} \tag{1.25}$$

By integration, the equilibrium cell voltage as a function of the partial pressure of the solved gas (with the integration constant K equivalent to $\Delta\varepsilon_{00}$ [10]) is obtained:

$$\Delta\varepsilon_0 = K - \frac{R \cdot T}{n \cdot F} \ln p \tag{1.26}$$

The following example of a hydrogen/oxygen fuel cell illustrates this relationship.

For a hydrogen/oxygen fuel cell at standard conditions, $T = 298\,\text{K}$ and $p = 101.3\,\text{kPa}$, where

cell reaction is	$2\,H_2 + O_2 \rightarrow 2H_2O$
standard potential (oxygen)	$\varepsilon_{00} = +1.23\text{ V}$
standard potential (hydrogen)	$\varepsilon_{00} = 0\text{ V}$
standard cell voltage	$\Delta\varepsilon_{00} = +1.23\text{ V vs NHE}$
For the anode	$\varepsilon_0 = \varepsilon_{00} + \frac{R\cdot T}{n\cdot F}\ln p_{O_2} = 1.23 + 0.03\text{ V}$
	$\varepsilon_0 = 1.26\text{ V}$
For the cathode	$\varepsilon_0 = \varepsilon_{00} - \frac{R\cdot T}{n\cdot F}\ln p_{H_2}^2 = 0 - 0.06\text{ V}$
	$\varepsilon_0 = -0.06\text{ V}$
	$\Delta\varepsilon_0 = 1.26\text{ V} - (-0.06\text{ V}) = 1.32\text{ V}$

an increase in the pressure to 1013 kPa results in an increase in the standard cell voltage of 0.09 V.

1.3.6
Overpotential of Half Cells and Internal Resistance

The potential of the electrode surface is determined using the Nernst equation introduced in Section 1.3.3. In equilibrium, the currents in anodic and cathodic direction are equal. If they are related to an electrode area, they are called *exchange current densities* j_0.

$$j_a = |j_c| = j_0 \tag{1.27}$$

$j_{a,c}$ represents anodic, cathodic current density (A cm^{-2}).

If a current flows, for example, while discharging a battery, a shift in the potential of the single half cell is measured. This deviation is called *overpotential*, η [12]. Thus, the real potential $\Delta\varepsilon_{\text{real}}$ has to be calculated using the following equation:

$$\Delta\varepsilon_{\text{real}} = \Delta\varepsilon_0 - \sum|\eta| \tag{1.28}$$

It is obvious that for a half cell the sum of the overpotentials should be as low as possible. Depending on their origin, a distinction has to be made between:

- *Charge transfer overpotential*: The charge transfer overpotential is caused by the fact that the speed of the charge transfer through the phase-boundary electrode/electrolyte is limited. It generally depends on the kind of substances that are reacting, the conditions in the electrolyte, and the characteristic of the electrode (for example, what kind of metal). The formulae which deal with this form of overpotential are called the *Butler–Volmer equation* and the Tafel equation [10].

- *Diffusion overpotential*: When high current densities j at electrodes (at the boundary to the electrolyte) exist, depletion of the reacting substances is possible, resulting in a concentration polarization. In this case the reaction kinetics is determined only by diffusion processes through this zone, the so-called Nernst layer. Without dealing with its derivation in detail, the following formula is obtained for the occurring diffusion overpotential (j_{limit} being the maximum current density):

$$\eta_{\text{diff}} = \left| \frac{RT}{zF} \cdot \ln\left(1 - \frac{j}{j_{\text{limit}}}\right) \right| \tag{1.29}$$

  As expected, the value of η_{diff} increases with increasing current densities.
- *Reaction overpotential*: Both the overpotentials mentioned above are normally of greater importance than the reaction overpotential. But sometimes it may happen that other phenomena which occur in the electrolyte or during electrode processes such as adsorption and desorption are the rate-limiting factors.
- *Crystallization overpotential*: This can occur as a result of the inhibited intercalation of metal ions into their lattice. This process is of fundamental importance when secondary batteries are charged, especially during the metal deposition at the negative side.

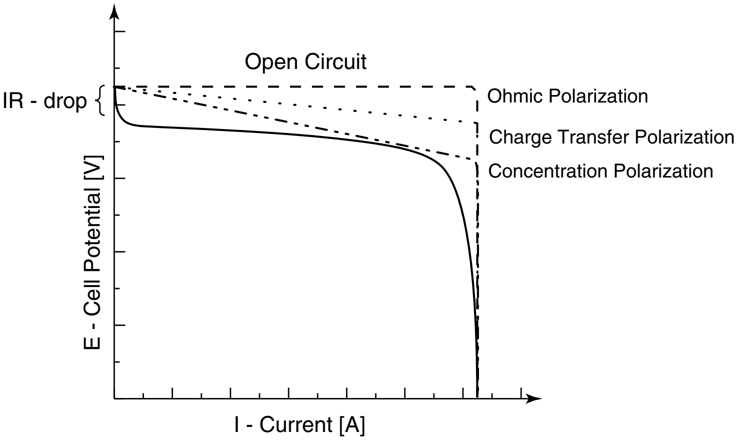


Figure 1.8 Cell polarization as a function of operating current.

Corresponding to the change in the potential of the single electrodes, which is related to their different overpotentials, a shift in the overall cell voltage is observed (see Figure 1.8). Moreover, an increasing cell temperature can be noticed. Besides joulic heat, caused by voltage losses due to the internal resistance R_{i} (electrolyte, contact to the electrodes, etc.) of the cell, thermal losses W_{K} (related to overpotentials) are the reason for this phenomenon.

$$W_{\text{J}} = I^2 \cdot R_{\text{i}} \cdot t \tag{1.30}$$

$$W_{\text{K}} = I \cdot \sum \eta_{\text{i}} \cdot t \tag{1.31}$$

1.4
Criteria for the Judgment of Batteries

The need to operate electrically powered tools or devices independently of stationary power sources has led to the development of a variety of different battery systems, the preference for any particular system depending on the field of application. In the case of a occasional use, for example, for electric torches in the household or for long-term applications with low current consumption such as watches or pacemaker, primary cells (zinc–carbon, alkaline manganese, or lithium–iodide cells) are chosen. For many other applications such as notebooks, MP3-players, cellular phones, or starter batteries in cars only rechargeable battery systems, for example, lithium-ion batteries or lead–acid batteries, can be considered from the point of view of cost and the environment.

The wide variety of applications has led to an immense number of configurations and sizes, for example, small round cells for hearing aids or large prismatic cells like lead–acid batteries for use in trucks. Here the great variety of demands has the consequence that nowadays no battery system is able to cope with all of them. The choice of the ‘right’ battery system for a single application is therefore often a compromise.

The external set-up of different battery systems is generally simple and in principle differs only a little from one system to another. A mechanically stable cell case carries the positive and negative electrodes, which are kept apart by means of a membrane and are connected to electrically conducting terminals. Conduction of the ions between the electrodes takes place in a fluid or gel-like electrolyte [13].

To assess the different battery systems, their most important features need to be compared.

1.4.1
Terminal Voltage

During charging and discharging of the cell the terminal voltage U between the poles is measured. Also, it should be possible to calculate the theoretical thermodynamic terminal voltage from the thermodynamic data of the cell reaction. This value often differs slightly from the voltage measured between the poles of the cell because of an inhibited equilibrium state or side reactions.

1.4.2
Current–Voltage Diagram

An important experimentally available feature is the current–voltage characteristic. This gives the terminal voltage provided by the electrochemical cell as a function of the discharge current (see Figure 1.9). The product of current and the accompanying terminal voltage is the electric power delivered by the battery system at any time.

$$P = I \cdot U_{\text{terminal voltage}} \tag{1.32}$$

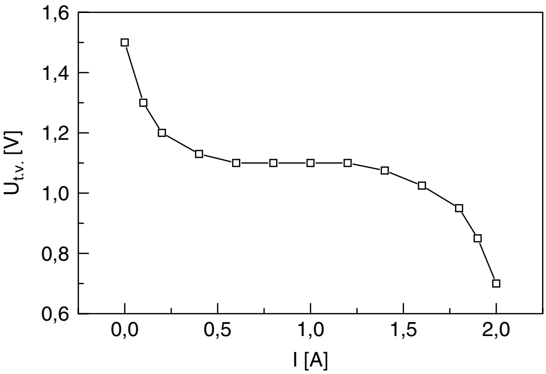


Figure 1.9 Current-voltage characteristic of a Leclanché element.

The power as a function of the battery weight is known as the power density P_s of the element in watts/kilogram. Figure 1.9 shows the current-voltage characteristic of a Leclanché element.

1.4.3
Discharge Characteristic

The discharge curve is another important feature of battery systems. Here, the terminal voltage is plotted against the discharge capacity. For an ideal battery the terminal voltage drops to zero in a single step when the whole of the stored energy is consumed.

The discharge rate C is defined by the discharge current and the nominal capacity of the secondary cell. It is equal to the reciprocal value of the discharging time:

$$\mathrm{C} = \frac{\text{discharge current}}{\text{nominal capacity}} \tag{1.33}$$

The nominal capacity of every system is defined by a specific value of C; for example, for th nickel–cadmium system, it is $\frac{1}{20}$C. By discharging at a higher current, the final capacity obtainable becomes lower because the IR losses and the polarization effects increase (see Figure 1.10).

The mode of the discharge (for example, at constant current, constant load, or constant power) can also have a significant effect on the performance of the battery. It is advisable that the mode of discharge used in a test or evaluation setup should be the same as the one used in the application.

1.4.4
Characteristic Line of Charge

During charging, the secondary cell receives the same amount of electric energy as that previously released, and this is stored in the form of chemical energy (see Figure 1.11 for nickel–cadmium system). Terminal voltage, charging time, number

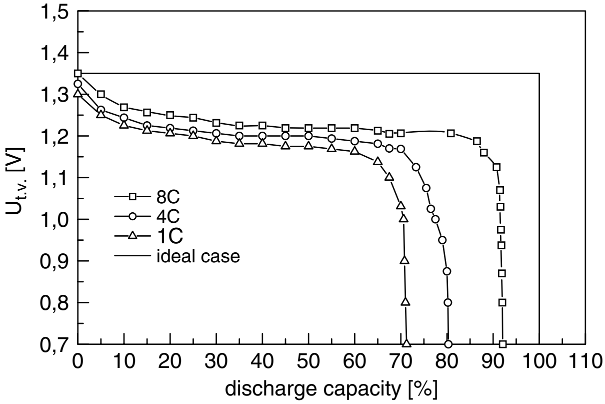


Figure 1.10 Ideal discharge characteristic of a nickel–cadmium system.

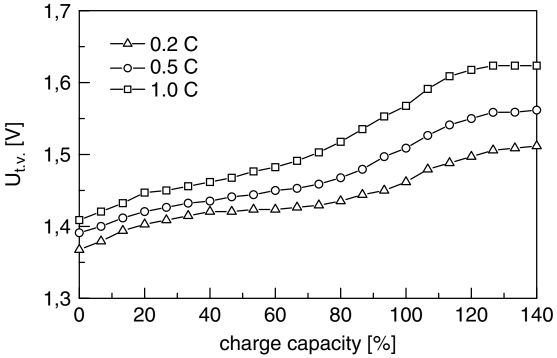


Figure 1.11 Dependence of the cell voltage on the charge capacity for three different currents in the nickel–cadmium system: $Cd + 2\ NiOOH + 2\ H_2O \rightarrow Cd(OH)_2 + 2\ Ni(OH)_2$.

of cycles, and other parameters are influenced by the charging procedure in a single battery system.

1.4.5
Overcharge Reactions

Nearly all electric consumers demand a high voltage, which is realized by connecting cells in series. Since the single cells have different capacities, it is impossible to maintain the optimal charge voltage in the weakest cell at the end of the charge process, while to charge, current passes through all the serially connected cells. As a consequence, the cell voltage increases, and, as well as the main charging reaction, chemical or electrochemical side reactions are possible. A well-known problem is the decomposition of the electrolyte solution (for example, water to hydrogen at the negative electrode or to oxygen at the positive electrode). In some battery systems these evolved gases react back with formation of educts. For example, in the nickel–cadmium cell oxygen is formed at the positive electrode and reacts back at the negative electrode, warming up the cell [8].

To avoid this problem, computer-controlled charging systems in modern battery stacks regulate the voltage for each individual cell.

1.4.6
Coulometric Efficiency and Energy Efficiency

The *efficiency during an energy conversion* is defined as the ratio of the energy converted to the energy consumed. This parameter is only decisive for secondary systems. The charge (Q_{charge}) necessary to load a secondary cell, is always higher than the charge ($Q_{\text{discharge}}$) released during discharge. This is caused by an incomplete conversion of the charging current into utilizable reaction products. Useless side reactions with heat production may occur. Here, numerous parameters are important such as the current density, the temperature, the thickness, the porosity of the separator, and the age of the cell.

There are two possible ways to describe the efficiency of batteries – the coulometric efficiency and the energy efficiency.

- *Coulometric efficiency*:

$$q_{\text{Ah}} = \frac{Q_{\text{discharge}}}{Q_{\text{charge}}} \tag{1.34}$$

  The reciprocal value $f = \frac{1}{q_{\text{Ah}}}$ of the coulometric efficiency is called the *charging factor*. The coulometric efficiency for electrochemical energy conversion is about 70–90% for nickel–cadmium and nearly 100% for lithium-ion batteries [14].

- *Energy efficiency*:

$$q_{\text{Wh}} = q_{\text{Ah}} \cdot \frac{\overline{U}_{\text{discharge}}}{\overline{U}_{\text{charge}}} \tag{1.35}$$

  Here, $\overline{U}_{\text{discharge}}$ and $\overline{U}_{\text{charge}}$ are the average terminal voltages during charge and discharge. The discharge voltage is normally lower than the charge voltage because of the internal resistance and overpotentials. For this reason the coulometric efficiency is always higher than the energy efficiency. It is influenced by the same terms as the charge efficiency but in addition by the discharge current and the charging procedure.

1.4.7
Cycle Life and Shelf Life

Another important parameter to describe a secondary electrochemical cell is the achievable number of cycles or the lifetime. For economic and ecological reasons, systems with a high cycle life are preferred. The number of cycles illustrates how often a secondary battery can be charged and discharged repeatedly before a lower limit (defined as a failure) of the capacity is reached. This value is often set at 80% of the nominal capacity. To compare different battery systems, the depth of discharge has to be quoted as well as the number of cycles.

Additionally, batteries deteriorate as a result of chemical side reactions that proceed during charging and discharging, but also during storage. Cell design, temperature, the electrochemical system, and the charge state affect the shelf life and the charge retention of the battery.

1.4.8
Specific Energy and Energy Density

With respect to the specific energy (the electric energy per unit mass) of today's battery systems, there is a major difference between the performance of aqueous systems and that of nonaqueous systems [15]. Apart from batteries for some special applications, there are

- Aqueous batteries with about 140 $\mathrm{Wh\,kg^{-1}}$ for primary and about 80 $\mathrm{Wh\,kg^{-1}}$ for secondary systems
- Nonaqueous batteries with about 400 $\mathrm{Wh\,kg^{-1}}$ for primary and about 180 $\mathrm{Wh\,kg^{-1}}$ for secondary systems
- For comparison: the utilizable electric or mechanic energy of a gasoline engine is 3000 Wh per 1 kg gasoline.

The zinc–carbon and alkaline manganese cells are primary battery systems, while lead, nickel–cadmium, and nickel–metal hydride batteries are secondary batteries with aqueous electrolyte solutions. The aqueous battery systems generally show only a limited performance at low temperatures. Because of the decomposition of the water, the voltage of a single cell is limited. For this reason lithium-ion batteries are of great interest when using organic or polymer electrolytes, allowing cell potentials of up to 4.5 V to be achieved.

1.4.9
Safety

Batteries are sources of energy and deliver their energy in a safe way when they are properly used. Therefore it is of crucial importance to choose the right electrochemical system in combination with the correct charge, discharge, and storage conditions to assure optimum, reliable, and safe operation.

There are instances when a battery may vent, rupture, or even explode if it is abused. To avoid this, a cell and/or a battery should include protective devices to avoid

- application of too high charge or discharge rates
- improper charge or discharge voltage or voltage reversal

- short-circuiting
- charging primary batteries
- charging or discharging at too high or too low temperatures.

To ensure that the right operating conditions are used every time, a type of electronic control, the so-called battery management system, can be used. This is especially important for the lithium-ion battery, where a too low end of discharge voltage, a too high end of charge voltage, or a too high charge or discharge rate not only can affect the lifetime and the cycle life but also can amount to abuse of the equipment resulting in possible rupture or explosion of the cell.

1.4.10
Costs per Stored Watt Hour

The cost per watt hour delivered from a primary battery is the ratio between the price of the battery and its capacity. For a secondary battery the cost of the battery installation has to be taken into consideration as well as the ratio of the charging cost to the delivered energy.

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