1

GENERAL ASPECTS

1.1 DEFINITION

Batteries are a variety of *galvanic cells*, that is, devices containing two (identical or different) electron-conducting *electrodes*, which contact an ion-conducting *electrolyte*. Batteries are destined to convert the energy of a chemical reaction between solid electrode components into electrical energy providing an electric current (when the circuit is closed) between two not-identical electrodes having different values of the *electrode potential* (positive and negative terminals). A battery comprises one or several single galvanic cells. In each such cell a comparatively low voltage is generated, typically 0.5–4 V for different classes of cells. Where higher voltages are required, the necessary number of cells is connected in series to form a galvanic battery. Colloquially, the term "battery" is often used to denote single galvanic cells acting as electrochemical power sources as well as groups of single cells. This is retained in this book. Some battery types retain the term "cell" even for groups of single cells (e.g., fuel cell, not fuel battery). The term "cell" is also used when it is necessary to compare different aspects of single-cell and multicell batteries.

1.2 CURRENT-PRODUCING CHEMICAL REACTION

Reactions in batteries are chemical reactions between an oxidizer and a reducer. In reactions of this type, the reducer being oxidized releases electrons while the oxidizer

Electrochemical Power Sources: Batteries, Fuel Cells, and Supercapacitors, First Edition.
Vladimir S. Bagotsky, Alexander M. Skundin, and Yurij M. Volfkovich

being reduced accepts electrons. An example of such a redox reaction is the reaction between silver oxide (the oxidizer) and metallic zinc (the reducer):

$$Ag_2O + Zn \rightarrow 2Ag + ZnO \tag{1.1}$$

in which electrons are transferred from zinc atoms of metallic zinc to silver ions in the crystal lattice of silver oxide. When reaction (1.1) is allowed to proceed in a jar in which silver oxide is thoroughly mixed with fine zinc powder, no electrical energy is produced in spite of all the electron transfers at grain boundaries. This is because these transfers occur randomly in space and the reaction energy is liberated as heat that can raise the temperature of the reaction mixture to dangerous levels. The same reaction does occur in batteries, but in an ordered manner in two partial reactions separated in space and accompanied by electric current flow (Fig. 1.1).

In the simple case a battery (cell) consists of two *electrodes* made of different materials immersed in an electrolyte. The electrodes are conducting metal plates or grids covered by reactants (*active mass*); the oxidizer is present on one electrode, the reducer on the other. In silver–zinc cells the electrodes are metal grids, one covered with silver oxide and the other with zinc. An aqueous solution of KOH serves as electrolyte. Schematically, this system can be written as

$$Zn\ |KOHaq|\ Ag_2O \tag{1.2}$$

When these electrodes are placed into the common electrolyte enabling electrolytic contact between them, an open circuit voltage (OCV) ϵ develops between them (here $\epsilon = 1.6$ V), zinc being the negative electrode. When they are additionally connected by an electronically conducting external circuit, the OCV causes electrons

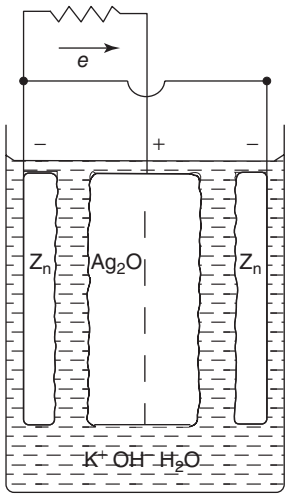

Figure 1.1. Schematic of a silver–zinc battery.

to flow through it from the negative to the positive electrode. This is equivalent to an electric current I in the opposite direction. This current is the result of reactions occurring at the surfaces of the electrodes immersed into the electrolyte: zinc being oxidized at the negative electrode (anode)*

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \tag{1.3}$$

and silver oxide being reduced at the positive electrode (cathode)

$$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^- \tag{1.4}$$

These electrode reactions sustain a continuous flow of electrons in the external circuit. The OH^- ions produced by reaction (1.4) in the vicinity of the positive electrode are transported through the electrolyte toward the negative electrode to replace OH^- ions consumed in reaction (1.3). Thus, the electric circuit as a whole is closed. Apart from the OCV, the current depends on the cell's internal resistance and the ohmic resistance present in the external circuit. Current flow will stop as soon as at least one of the reactants is consumed.

In contrast to what occurred in the jar, in the batteries, the overall chemical reaction occurs in the form of two spatially separated partial electrochemical reactions. Electric current is generated because the random transfer of electrons is replaced by a spatially ordered overall process (*current-producing reaction*).

1.3 CLASSIFICATION

By their principles of functioning, batteries can be classified as follows:

1. **Primary (single-discharge) batteries**. A primary battery contains a finite quantity of the reactants participating in the reaction; once this quantity is consumed (on completion of discharge), a primary battery cannot be used again ("throw-away batteries").
2. **Storage (multiple-cycle) batteries** (also called secondary or rechargeable batteries). On the completion of discharge, a storage battery can be recharged by forcing an electric current through it in the opposite direction; this will regenerate the original reactants from the reaction (or discharge) products. Therefore, electric energy supplied by an external power source (such as the grid) is stored

*This definition of the negative electrode as anode (at which an oxidation reaction take place) and the positive electrode as cathode (with a reduction reaction) is valid only for the discharge process of batteries. For the charging process of storage batteries (as well as for electrolyzers) when the current flow and the electrode reactions are in the direction opposite to that during discharge, the opposite definition is encountered, that is, the negative electrode works as cathode and the positive electrode as anode. For this reason in the case of storage batteries preferably only the terms of positive or negative electrode instead of anode or cathode should be used.

in the battery in the form of chemical energy. During the discharge phase this energy is delivered to a consumer independent of the grid. During the charging phase the electrode reactions and the overall current-producing reaction occur in the direction opposite to that during discharge. Thus, these reactions must be chemically reversible (the notion of chemical reversibility must not be confused with that of thermodynamic reversibility). Good rechargeable batteries will sustain a large number of such charge–discharge cycles (hundreds or even thousands). The classification into primary and storage batteries is not rigorous because under certain conditions some primary battery may be recharged and storage batteries after a single use are sometimes discarded.

The silver–zinc battery is a storage battery: after discharge, it can be recharged by forcing through it an electric current in the reverse direction. In this process the two electrode reactions (1.3) and (1.4) as well as the overall reaction (1.2) go from right to left.

3. **Fuel cells.** In the fuel-cell mode of operation, reactants are continuously fed into the cell (or battery) while reaction products are continuously removed. Hence, fuel cells (the more appropriate term of fuel battery is not commonly used) can deliver current continuously for a considerable length of time, which largely depends on external reactant storage.

Batteries are also classified according to their chemistry (their system), that is, the chemical nature of reactants. The above-mentioned battery with silver oxide as an oxidant at the positive electrode and metallic zinc as negative electrode is called "silver–zinc battery."

Sometimes other methods of classification are also used, for example, on the basis of the application (stationary or mobile batteries), shape (cylindrical, prismatic, disk-shape batteries), size (miniature, small-sized, medium-sized, or large-sized batteries), electrolyte type (alkaline, acidic, or neutral electrolyte, with liquid or solid (solidified), or molten salt electrolyte), voltage (low voltage or high voltage batteries), electric power generation (low power or high power batteries), and so on.

1.4 THERMODYNAMIC ASPECTS

Each electrode j of a battery brought into contact with the electrolyte develops a certain *electrode potential* E_j. The concept of "potential" is an experimental, undefined parameter, that is, it has a real physical meaning and reflects a real physical phenomenon, but cannot be determined from experimental data (even from thought experiments). Only potential differences between the given electrode and another electrode (reference electrode) are measurable. (Similarly, the height of a certain geographic point is defined and can be measured only when referred to the height of another point, e.g., sea level). Values of electrode potentials are commonly referred to as the potential of the standard hydrogen electrode (SHE). Potentials of different electrodes can be either negative (i.e., more negative than the potential of the SHE) or positive. The OCV of a battery U is the potential difference between the positive

electrode and the negative electrode:

$$U = E_+ - E_- \tag{1.5}$$

According to this definition, the OCV is always positive (provided the potentials of both electrodes are referred to the same reference electrode).

Thermodynamically, electrode reactions can be either reversible or irreversible. In case of a reversible reaction, the electrode potential is called reversible (thermodynamic electrode potential). The corresponding OCV is traditionally called "electromotive force" (EMF) and is denoted as ϵ.

The EMF of a battery with reversible electrodes can be defined by the thermodynamic relation

$$\epsilon = \frac{\Delta G}{nF} \tag{1.6}$$

where ΔG is the difference of the Gibbs energy G during the current-producing reaction—the difference of the Gibbs energies of all reactants and all reaction products—n is the number of electrons taking part in one elementary act of the electrode reaction, $F = 96485$ C/mol is the Faraday constant. The reversible potential of an electrode contacting an electrolyte, all ions of which have a thermodynamic activity $a_j = 1$ mol/l, is called standard electrode potential and is denoted by ${E_j}^0$.

Values of standard electrode potentials for some reactions are shown in Table 1.1. Values for other reactions as well as of the Gibbs energy G for different reaction components can be found in special reference books.

TABLE 1.1. Standard Electrode Potentials (25 °C)

Reaction	E^0, V (SHE)	Reaction	E^0, V (SHE)
$Li^+ + e^- \rightleftarrows Li$	−3.045	$HgO + H_2O + 2e^- \rightleftarrows Hg + 2OH^-$	0.098
$K^+ + e^- \rightleftarrows K$	−2.935	$Sn^{4+} + 2e^- \rightleftarrows Sn^{2+}$	0.154
$Ca^{2+} + 2e^- \rightleftarrows Ca$	−2.866	$Cu^{2+} + e^- \rightleftarrows Cu^+$	0.153
$Na^+ + e^- \rightleftarrows Na$	−2.714	$AgCl + e^- \rightleftarrows Ag + Cl^-$	0.2224
$Mg^{2+} + 2e^- \rightleftarrows Mg$	−2.363	$Hg_2Cl_2 + 2e^- \rightleftarrows 2Hg + 2Cl^-$	0.2676
$Al^{3+} + 3e^- \rightleftarrows Al$	−1.662	$Cu^{2+} + 2e^- \rightleftarrows Cu$	0.337
$Ti^{2+} + e^- \rightleftarrows 2e^- \rightleftarrows Ti$	−1.628	$Fe(CN)_6{}^{3-} + e^- \rightleftarrows e(CN)_6{}^{4-}$	0.36
$Zn(OH)_2 + 2e^- \rightleftarrows Zn + 2OH^-$	−1.245	$Cu^+ + e^- \rightleftarrows Cu$	0.521
$Mn^{2+} + 2e^- \rightleftarrows Mn$	−1.180	$I_2 + 2e^- \rightleftarrows 2I^-$	0.536
$2H_2O + 2e^- \rightleftarrows H_2 + 2OH^-$	−0.822	$O_2 + 2H^+ + 2e^- \rightleftarrows H_2O_2$	0.682
$Zn^{2+} + 2e^- \rightleftarrows Zn$	−0.764	$Fe^{3+} + e^- \rightleftarrows Fe^{2+}$	0.771
$S + 2e^- \rightleftarrows S^{2-}$	−0.48	$Br_2 + 2e^- \rightleftarrows 2Br^-$	1.065
$Fe^{2+} + 2e^- \rightleftarrows Fe$	−0.441	$O_2 + 4H^+ + 4e^- \rightleftarrows 2H_2O$	1.229
$Cd^{2+} + 2e^- \rightleftarrows Cd$	−0.403	$Cl_2 + 2e^- \rightleftarrows 2Cl^-$	1.358
$Ni^{2+} + 2e^- \rightleftarrows Ni$	−0.250	$PbO_2 + 4H^+ + e^- \rightleftarrows Pb^{2+} + 2H_2O$	1.455
$Sn^{2+} + 2e^- \rightleftarrows Sn$	−0.136	$Ce^{4+} + e^- \rightleftarrows Ce^{3+}$	1.61
$2H^+ + 2e^- \rightleftarrows H_2$	0.0000	$F_2 + 2e^- \rightleftarrows 2F^-$	1.87

1.5 HISTORICAL DEVELOPMENT

In 1791 the Italian physiologist Luigi Galvani (1737–1798) demonstrated in remarkable experiments that muscle contraction similar to that produced by the discharge of a Leyden jar, will occur when two different metals touch the exposed nerve of a frog. This phenomenon was in part correctly interpreted in 1792 by the Italian physicist Alessandro Volta (1745–1827), who showed that this galvanic effect originates from the contacts established between these metals and between them and the muscle tissue. In March 1800, Volta reported a device designed on the basis of this same phenomenon, which could produce "inexhaustible electric charge." Now known as the *Volta pile*, this was the first example of an electrochemical device: an electrochemical power source (*a battery*). No special oxidizer was used in the Volta pile and this role was played by water molecules that were reduced at the silver cathode to gaseous hydrogen. As a result of such a weak oxidizer, the OCV of a single cell in this pile was only about 0.4 V. If high voltages and high discharge current were needed, very large batteries had to be built. One pile manufactured in 1803 comprised 2100 individual cells.

The Volta pile (certainly not inexhaustible!) was of extraordinary significance for the developments both in the science of electricity and of electrochemistry, because a new phenomenon, a continuous flow of charges (an electric current), hitherto not known, could for the first time be realized. Soon various properties and effects of the electric current were discovered, including many electrochemical processes. In May 1801, William Nicholson and Sir Anthony Carlisle in London electrolyzed water-producing hydrogen and oxygen. The Volta pile was also of significance for the development of many new fields of science of technology in the nineteenth century.

In order to circumvent the limited possibilities of the original Volta pile, the following period saw the development of other battery systems in which special oxidizers were introduced. In 1836, J. F. Daniell (1796–1845) developed a cell with an oxidizer in the form of copper ions in a copper sulfate solution. Cells with the use of nitric acid as oxidizer were developed in 1838 by W. R. Grove (1811–1896) and in 1841 by R. Bunsen (1811–1899). Cells containing sodium bichromate dissolved in sulfuric acid were developed in 1843 by Ch. Poggendorff (1824–1876) and in 1856 by Grenet.

A considerable improvement of electrical batteries was achieved after the replacement of liquid oxidizers (mainly in aqueous solutions) by solid oxidizers, in the form of different metal oxides. In 1865, the French engineer G.L. Leclanché (1839–1882) made a battery containing manganese dioxide as an oxidizer (positive electrode) and zinc as a reducer (negative electrode) and an aqueous solution of ammonium chloride as an electrolyte. In the following, the liquid electrolyte in this battery was replaced by an electrolyte solidified by different gelling agents. These "dry" Leclanché batteries proved to be very simple with regard to manufacture and reliable in usage. As early as 1868, more than twenty thousands of such cells were being manufactured. A further advance in battery technology was the development of rechargeable batteries.

In 1859, the French scientist Gaston Planté (1834–1889) made the first prototype of a lead acid rechargeable battery. An alkaline nickel–cadmium rechargeable battery was developed in 1899 by the Swedish engineer W. Jungner (1869–1924) and an alkaline nickel–iron battery was developed two years later by the well-known American inventor Thomas A. Edison (1847–1931). Up to the seventh decade of the nineteenth century, electrochemical batteries remained the only sources of electrical current and power.

After the appearance of the Volta pile and other improved versions of batteries, extended experiments with the new phenomenon of a continuous electrical current became possible and soon different properties of this current could be established: in 1820 Ampère's law of interaction between electrical currents; in 1827 Ohm's law of proportionality between voltage and current; in 1831 Joule's law of the thermal effect of electrical current; in 1831 Faraday's law of electromagnetic induction, and many others. These achievements led to the development of the *theory of electrodynamics* and practice of electrical engineering and, as a result, to the appearance of a revolutionary new power source: the electromagnetic generator invented in 1866 by Werner von Siemens (1816–1872), which soon surpassed their predecessors both in electrical and economic parameters.

After the development of the electromagnetic generator, a large-scale production of electric power became possible ("grid electricity"). Nevertheless, despite the worldwide expansion of electric grids, batteries retained their significance as autonomous power sources up to now. According to a 2001 Report (cited from the online encyclopedia Wikipedia), the worldwide battery industry generates US$ 48 billion in sales every year, with 6% annual growth. One of the reasons for the widespread acceptance of batteries is the tremendous large range of power that can be delivered. Wrist watches are powered by miniature batteries with a power of about 10^{-5} W. Huge storage batteries with power up to 10^{9} W are used in submarines. The mass of a single power unit can vary from 0.1 g to a hundred tons. It is striking that both miniature and huge batteries operate with the same high efficiency. No other type of electric power source could be said to be as flexible or as versatile.

1.6 NOMENCLATURE

As yet a complete worldwide nomenclature for batteries fully specifying all their characteristics including shape and size (which determine battery interchangeability) is not established. Different countries and different battery manufacturers use different systems for designating and labeling batteries (see in the online encyclopedia Wikipedia the entry "List of battery sizes"). Two battery types widely used for household purposes have well-established designations that facilitate interchangeability: (i) cylindrical "dry" batteries—AA, A, B, C, and so on, with dimensions (height + diameter in millimeters), for example, for AA (44 + 10), for A (50 + 13.5), and for D (49 + 24), and (ii) disc cells—for example, A2325, where A is the battery chemistry type, 23 is the diameter in millimeters, and 25 is the height in 0.1 mm (i.e., 2.5 mm).

REVIEWS AND MONOGRAPHS

Bagotsky VS, Skundin AM. *Chemical Power Sources*. London: Academic Press; 1980.

Daniel C, Besenhard JO, editors. *Handbook of Battery Materials*. 2nd ed. Chichester, Weinheim: Wiley-VCH; 2011.

Heise GW, Cahoon NC, editors. *Primary Batteries*. Vol. 1. New York: Wiley; 1971.

Liebhafsky HA, Cairns EJ. *Fuel Cells and Batteries*. New York: Wiley; 1968.

Linden D, Reddy TB, editors. *Handbook of Batteries*. McGraw-Hill; 2002.

Vincent CA, Scrosati B. *Modern Batteries. An Introductory to Electrochemical Power Sources*. London: L. Edward Arnold Ltd.; 1997.