1

Introduction to Electrochemical Cells

R. Vasant Kumar[1] and Thapanee Sarakonsri[2]

[1] *University of Cambridge, Department of Materials Science and Metallurgy, 27 Charles Babbage Road, Cambridge CB3 0FS, UK*
[2] *Chiang Mai University, Department of Chemistry, Faculty of Science, Chiang Mai 50200, Thailand*

COPYRIGHTED MATERIAL

1.1 What are Batteries?

The purpose of this chapter is to provide basic knowledge on batteries, which will allow for their general understanding. Therefore, after defining their components and structure, an overview of the quantities that characterize these storage devices will be given. Scientifically, batteries are referred to as electrochemical or galvanic cells, due to the fact that they store electrical energy in the form of chemical energy and because the electrochemical reactions that take place are also termed galvanic. Galvanic reactions are thermodynamically favorable (the free-energy difference, ΔG, is negative) and occur spontaneously when two materials of different positive standard reduction potentials are connected by an electronic load (meaning that a voltage is derived). The material with the lower positive standard reduction potential undergoes oxidation providing electrons by the external circuit to the material with the higher positive standard reduction potential, which in turn undergoes a reduction reaction. These half-reactions occur concurrently and allow for the conversion of chemical energy to electrical energy by means of electron transfer through an external circuit. It follows that the material with the lower positive standard reduction potential is called the negative electrode or anode on discharge (since it provides electrons), while the material with the higher positive standard reduction is called the positive electrode or cathode on discharge (since it accepts electrons). It follows that the discharge process occurs in the electrochemical cells upon operation of the devices they power.

In addition to the electrodes, the two other constituents that are required for such reactions to take place are the electrolyte phase/solution and the separator. The electrolyte is an ion-conducting material, which can be in the form of an aqueous, molten salt, or solid solution, while the separator is a membrane that physically prevents direct contact between the two electrodes and allows ions but not electrons to pass through; it, therefore, ensures electronic insulation for charge neutralization in both the anode and cathode once the reaction is completed and

Rechargeable Ion Batteries: Materials, Design, and Applications of Li-Ion Cells and Beyond, First Edition. Edited by Katerina E. Aifantis, R. Vasant Kumar, and Pu Hu.
© 2023 WILEY-VCH GmbH. Published 2023 by WILEY-VCH GmbH.

prevents internal short-circuiting of electrons. Internal short-circuiting implies the movement of electrons from the anode to cathode through the electrolyte, which dissipates the chemical energy without providing electrical potential in the external circuit. When the electrolyte is solid, it simultaneously functions as a membrane (separator) and an ionic conductor. Two final parts required to complete a commercial galvanic cell are the terminals. They are necessary when applying the batteries to electrical appliances with specific holder designs to prevent a short circuit from the reverse installation of the battery, and they are shaped to match the receptacle facilities provided in the appliances. For example, in cylindrical batteries, the negative terminal is either designed to be flat, or to protrude out of the battery end, while the positive terminal extends as a pip at the opposite end. A simple galvanic cell is illustrated in Figure 1.1a, while Figure 1.1b shows terminal designs for cylindrical batteries.

To meet the voltage or current used in specific appliances, cylindrical galvanic cells are connected in series or parallel. Figure 1.2a,brepresents parallel and series connections; parallel connections allow for the current to be doubled, while series connections allow for the voltage to be doubled.

In addition to cylindrical battery cells, as those shown in Figures 1.1 and 1.2, flat battery configurations are also quite common. The biggest impetus for these configurations came from the rapid growth of portable radios since the flat cells use the space of the battery box more efficiently than cylindrical ones. The electrodes are made in the form of flat plates, which are suspended in the electrolyte and are held immobilized in a microporous separator (Figure 1.3a). The separator

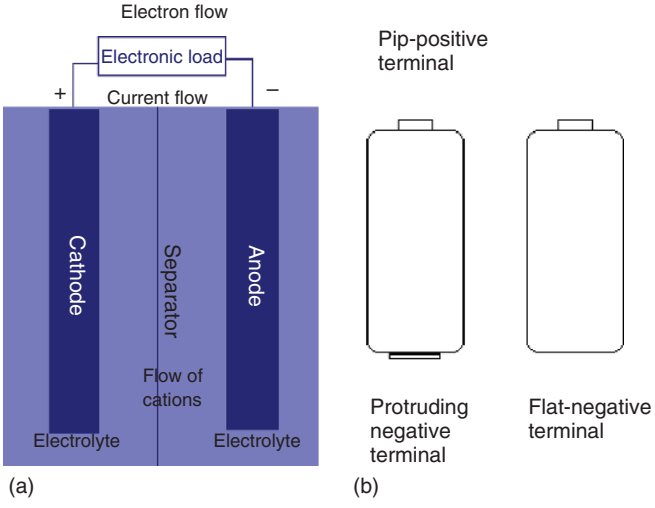

Figure 1.1 (a) The schematic diagram of a simple galvanic cell. (b) Terminal designs for cylindrical batteries.

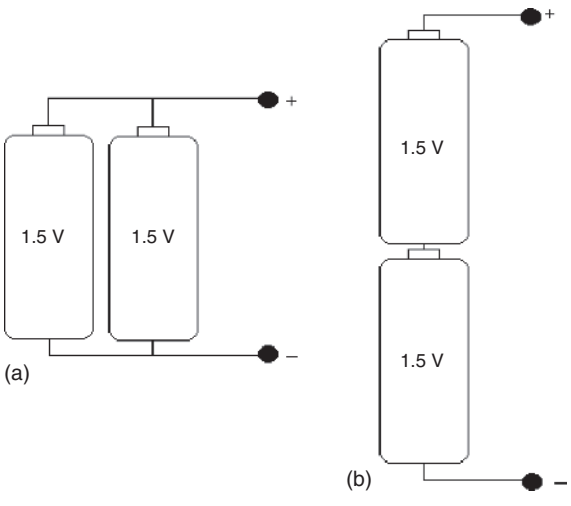

Figure 1.2 (a) An illustration of batteries connected in parallel to obtain double current. (b) An illustration of batteries connected in series to obtain 3 V.

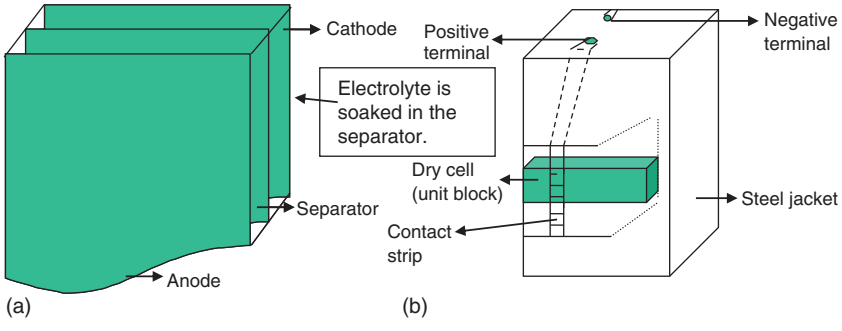

Figure 1.3 (a) Single-flat-cell configuration; (b) composite-flat-cell configuration.

also helps in isolating the electrodes, preventing any short-circuiting whereby ions can directly move internally between the anode and cathode. Short-circuiting will result in capacity loss, parasitic reactions, and heat generation. This can also lead to catastrophic situations causing fires, explosions, leakage of materials, and accidents. The configuration of Figure 1.3a can be scaled up to very large sizes, for high currents and large storage capacities, by placing each cell inside a plastic envelope and stacking them inside a steel jacket. Connector strips are used to collect and connect the positive and the negative electrodes to a common positive and negative terminal; a sketch of such cell compaction is shown in Figure 1.3b.

Both cylindrical and flat cells come in various sizes so that they can fit a wide range of portable appliances and devices. Table 1.1 summarizes the various battery sizes that are available commercially.

Table 1.1 Dimensions of commercially available battery sizes [1].

Battery size	Diameter (mm)	Height (mm)
N	12	30.2
AAA	10.5	44.5
AA	14.5	50.5
C	26.2	50
D	34.2	61.5
F	32.0	91.0
Length (mm)	**Width (mm)**	**Thickness (mm)**
Flat cells		
24	13.5	6.0
43	43	6.4
Rectangular cells		
48.5	26.5	17.5

Source: Republished with permission of Linden and Reddy [1], Copyright Clearance Center, Inc.

1.2 Quantities Characterizing Batteries

Upon operation of galvanic cells, implying that the device is in power mode, it is said that the galvanic cell is discharged and electrons flow, through an external circuit, from the anode to the cathode. As a result, the cathode attains a negative charge, while the anode becomes positively charged. Consequently, cations are attracted from the anode to the cathode (and vice versa for the anions) and diffuse through the electrolyte. Typical electrochemical redox reactions that may take place upon operation of batteries are shown in Table 1.2, whereas the quantities that characterize batteries are defined in Table 1.3.

To better understand the differences between various battery chemistries, some of the quantities in Table 1.3 are further elaborated on below.

1.2.1 Voltage

The theoretical standard cell voltage, E^0(cell), can be determined using the electrochemical series and is given by the difference between the standard electrode potential at the cathode, E^0(cathode), and the standard electrode potential at the anode, E^0(anode) [2] as

$$E^0(\text{cathode}) - E^0(\text{anode}) = E^0(\text{cell}) \tag{1.1}$$

The standard electrode potential, E^0, for an electrode reaction, written (by convention) as a reduction reaction (i.e. involving consumption of electrons), is the potential

Table 1.2 Standard electrode potentials in aqueous electrolyte at 298 K (written as reduction reactions by convention).

Reaction	E^0 (V)
$Li^+ + e^- \rightarrow Li$	−3.10
$Na^+ + e^- \rightarrow Na$	−2.71
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.36
$^1/_2H_2 + e^- \rightarrow H^-$	−2.25
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$MnO_2 + 2H_2O + 4e^- \rightarrow Mn + 4OH^-$	−0.98
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	−0.82
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$Ni(OH)_2 + 2e^- \rightarrow Ni + 2OH^-$	−0.72
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.26
$MnO_2 + 2H_2O + 4e^- \rightarrow Mn(OH)_2 + 2OH^-$	−0.05
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.16
$Ag_2O + H_2O + 2e^- \rightarrow 2Ag + 2OH^-$	+0.34
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
$2NiOOH + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$	+0.48
$NiO_2 + 2H_2O + 2e^- \rightarrow Ni(OH)_2 + 2OH^-$	+0.49
$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	+0.62
$2AgO + H_2O + 2e^- \rightarrow Ag_2O + 2OH^-$	+0.64
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77
$Hg^{2+} + e^- \rightarrow Hg^+$	+0.80
$Ag^+ + e^- \rightarrow Ag$	+0.80
$2Hg^{2+} + 2e^- \rightarrow Hg^+$	+0.91
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
$ZnO + H_2O + 2e^- \rightarrow Zn + 2OH^-$	+1.26
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	+1.47
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	+1.70
$F_2 + 2e^- \rightarrow 2F^-$	+2.87

Table 1.3 Battery characteristics.

Battery characteristics	Definition	Unit
Open-circuit voltage	Maximum voltage in the charged state at zero current	Volt (V)
Current	Low currents are characterized by activation losses, while the maximum current is normally determined by mass-transfer limitations	Ampere (A)
Energy density	The energy that can be derived per unit volume of the weight of the cell	Watt-hours per liter ($Wh\ m^{-3}$)
Specific energy density	The energy that can be derived per unit weight of the cell (or sometimes per unit weight of the active electrode material)	Watt-hours per kilogram ($Wh\ kg^{-1}$)
Power density	The power that can be derived per unit weight of the cell	Watt per kilogram ($W\ kg^{-1}$**)**
Capacity	The theoretical capacity of a battery is the quantity of electricity involved in the electrochemical reaction	Ampere-hours per gram ($Ah\ g^{-1}$).
Shelf life	The time a battery can be stored inactive before its capacity falls to 80%	Years
Service life	The time a battery can be used at various loads and temperatures	Hours (usually normalized for ampere per kilogram ($A\ kg^{-1}$) and ampere per liter ($A\ l^{-1}$))
Cycle life	The number of discharge/charge cycles it can undergo before its capacity falls to 80%	Cycles

Source: Reproduced with permission from Weal et al. [2]/University of Cambridge.

generated by that reaction under the condition that the reactants and the products are in their standard state in relation to a reference electrode. (A reactant or product is defined to be in its standard state when the component in a condensed phase is at unit activity and any component in the gas phase is at a partial pressure of 1 atm.) In aqueous systems, the standard hydrogen potential is taken as the universal reference electrode, whose potential is defined as zero. In practical terms, the standard hydrogen electrode can be constructed as follows: (i) a high surface area of platinum is deposited on a platinum foil or plate, which is then dipped into an acid solution of unit activity of H^+ ions, corresponding to 1 M acid solution, then (ii) pure hydrogen at one atmosphere is passed over this electrode. A list containing selected standard electrode potentials at 298 K in an aqueous solution is given in Table 1.2 and these refer to equilibrium potentials at zero net current values at each of the electrodes. The batteries that make use of these materials as electrodes will be described in Chapter 2. It should be noted that the standard electrode potential for a reduction reaction in an aqueous solution is relative to the hydrogen electrode, which is taken as zero. Thus, potentials that are defined for half-cells are represented as reduction

reactions. In a battery, two half-cells are present such that reduction takes place on one electrode and oxidation on the other.

To obtain a true estimate of the actual open-circuit cell voltage, E_{eq} in the fully charged state for operation of the battery; the theoretical cell voltage is modified by the Nernst equation, which takes into account the nonstandard state of the reacting component as

$$E_{eq} = E^0 - RT \ln Q \tag{1.2}$$

where T is the operating temperature in kelvin (k), $Q = a_{products}/a_{reactants}$ is the chemical quotient for the overall cell reaction, and R is the gas constant ($8.314\,J\,k^{-1}\ mol^{-1}$). Q is represented in the same way as the equilibrium constant K, except that the activities (a) and partial pressures (p) in Eq. (1.2) reflect the actual nonstandard values prevailing in the system. For example, for the electrode reaction

$$M^{2+} + 2e^- = M \tag{1.3}$$

the actual Nernstian electrode potential (E), also referred to as open-circuit voltage (OCV) under equilibrium (for net zero current) is

$$E = E^o - \frac{RT}{2F} \ln \left(\frac{a_M}{a_{M^{2+}}} \right) \tag{1.4}$$

Notation E_e (rather than E) is also often used to denote that the actual equilibrium potential of the electrode is determined by the Nernst equation and the standard electrode potential E^0 refers to a very specific situation of reaction species being held in their "standard states," The Nernstian potential in Eq. (1.4) will change with time due to any self-discharge by which the activity (or concentration) of the electroactive component in the cell is modified. Thus, the nominal voltage is determined by the cell chemistry at any given point of time. M and M^{2+} refer to the effective concentrations of the two components in the phase within which they are present. (For the hydrogen reaction, as an example where a gas phase is involved, the activity of metal is replaced by the partial pressure term, pH_2.)

The operating voltage produced is further modified as a result of discharge reactions actually taking place and will always be lower than the thermodynamically calculated theoretical voltage (also referred to as equilibrium potential) by the Nernst equation (OCV) due to polarization losses (these arise from overpotentials for overcoming activation barrier and/or diffusional limitations) and the resistance losses (IR drop) of the battery as the voltage is dependent on the current, I, drawn by an external load and the cell resistance, R, in the path of the current. Specifically, polarization losses arise to overcome any activation energy for the electrode reaction and/or concentration gradients near the electrode(s). The factors determining the overpotentials are dependent upon electrode kinetics from rates of electrodic reactions and diffusional rates of one or more active components, and, thus, vary with temperature, state of charge, and with the age of the cell. It is important to note that the actual voltage appearing at the terminal needs to be sufficient for the intended application.

1.2.2 Electrode Kinetics (Polarization and Cell Impedance)

Before continuing to the other quantities indicated in Table 1.3, the electrode kinetics, which was previously shown to affect the voltage, must be described. Thermodynamics expressed in terms of the electrode potentials can tell us the theoretical and open-circuit cell voltage, as well as how feasible it is for a cell reaction to occur. However, it is necessary to consider kinetics to obtain a better understanding of what the actual cell voltage maybe, since the charge transfer, the rates of the reactions at the electrodes and diffusional barriers are usually the limiting factors. In continuing, therefore, the main kinetic issues that affect battery performance are summarized.

1.2.2.1 Electrical Double Layer

When a metal electrode is in an electrolyte, the charge on the metal will attract ions of opposite charge in the electrolyte, and the dipoles in the solvent will align. This forms a layer of charge in both the metal and the electrolyte, called the *electrical double layer*, as shown in Figure 1.4. The electrochemical reactions take place in this layer, and all atoms or ions that are reduced or oxidized must pass through this layer. Thus, the ability of ions to pass through this layer controls the kinetics, and is, therefore, the limiting factor in controlling the electrode reaction. The energy barrier toward the electrode reaction, described as the activation energy of the electrochemical reaction, lies across this double layer.

1.2.2.2 Rate of Reaction

The rates of the chemical reactions are governed by the Arrhenius relationship, such that the rate of reaction, k, is

$$k \propto \exp(-Q^*/RT) \tag{1.5}$$

where Q^* is the activation energy for the reaction, T is the temperature in Kelvin, and R is the universal gas constant.

In this case, the rate of the reaction can be measured by the current produced, since current is the amount of charge produced per unit amount of time, and therefore proportional to the number of electrons produced per unit amount of time that is proportional to the rate of the reaction.

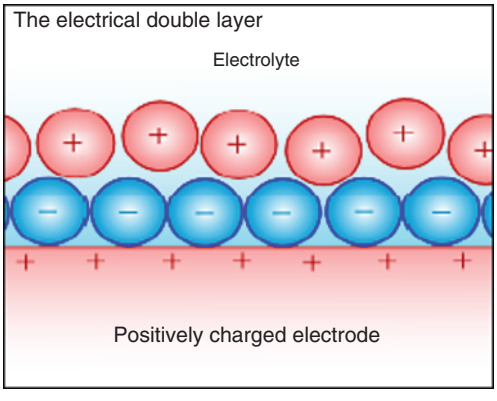

Figure 1.4 Illustration of double layer. Source: Reproduced with permission from Weal et al. [2]/ University of Cambridge.

1.2.2.3 Electrodes Away from Equilibrium

When an electrode is not at the equilibrium potential, an *overpotential* exists, given by

$$\eta = E - E_e \tag{1.6}$$

where η is the overpotential, E is the actual potential, and E_e is the equilibrium potential, calculated using the Nernst equation. Overpotential is used synonymously with polarization potential and described as arising from "polarization process" at a given electrode.

1.2.2.4 The Tafel Equation

The Tafel equation provides a relationship between the current and the overpotential during the oxidation or reduction reaction of an electrode. Consider a general reaction for the oxidation of a metal anode:

$$M \rightarrow M^{z+} + ze^- \tag{1.7}$$

where z is the number of cations/electrons. The rate of this reaction, k_a, is governed by the Arrhenius relationship:

$$k_a = A\ \exp(-Q/RT) \tag{1.8}$$

where A is a frequency factor, which takes into account the rate of collision between the electroactive species and the electrode surface. From Faraday's law, one can express the rate in terms of the exchange current density at the anode, $i_{0,a}$:

$$i_{0,a} = zFk_a = zFK\ \exp(-Q/RT) \tag{1.9}$$

where $F = 96\,540\ \text{C mol}^{-1}$ is Faraday's constant. If an overpotential η_a ($\eta_a = E_a - E_e$; where E_e is the Nernst potential for the oxidation half-cell) is now applied in the anodic direction, the activation energy of the reaction becomes

$$Q = \alpha zF\eta_a \tag{1.10}$$

where α is the "symmetry factor" of the electrical double layer, nominally taken as 0.5, assuming symmetrical behavior in both directions.

Therefore the anodic current density, i_a, is

$$i_a = zFK\ \exp(-[Q - \alpha zF\eta_a]/RT) = zFK\ \exp(-Q/RT)\ \exp(\alpha zF\eta_a/RT) \tag{1.11}$$

which by Eq. (1.9) reduces to

$$i_a = i_{0,a}\ \exp(\alpha zF\eta_a/RT) \tag{1.12}$$

The subscript a here refers to process at the anode. Equation (1.12) is known as the *Tafel equation*. By taking natural logs and rearranging them, Eq. (1.12) can be written as

$$\eta_a = (RT/\alpha zF)\ \ln(i_a/i_{0,a}) \tag{1.13}$$

By setting $RT/(\alpha zF) = b_a$ and $\ln i_0 = -a_a/b_a$, Eq. (1.13) can be rewritten as

$$\eta_a = a_a + b_a\ \ln i_a \tag{1.14}$$

Or in terms of the anode potential, E_a,

$$\ln(i_a) = \ln(i_{0,a}) + (E_a - E_e)\,\alpha z F/RT \tag{1.15}$$

Solving Eq. (1.15) for E_a, gives

$$\eta_a = b_a \log(i_a/i_{0,a}) \tag{1.16}$$

where b_a is the anodic Tafel slope. Similarly, we can consider the reduction of metal ions at a cathode:

$$M^{z+} + ze^- \rightarrow M \tag{1.17}$$

The activation energy will be decreased by $(1-\alpha)zF\eta_c$ (subscripts c indicate cathode), giving the cathodic current density as

$$i_c = i_{0,c} \exp([1-\alpha]zF\eta_c/RT) \tag{1.18}$$

and

$$\eta_c = \left(RT/([1-\alpha]zF) \ln(i_c/i_{0,c})\right) \tag{1.19}$$

Therefore, the cathode overpotential is $\eta_c = E_c - E_e$, where E_e is the Nernst potential, and E_c is expressed as

$$E_c = b_c \log(i_c/i_{0,c}) \tag{1.20}$$

where b_c is the cathodic Tafel slope. A typical representation of a Tafel plot – a plot of log i vs. E – is shown in Figure 1.5. Thus, for an applied potential, the current density, i, can be found from the Tafel plot in an electrolytic cell when the battery is being charged or discharged.

1.2.2.5 Example: Plotting a Tafel Curve for a Copper Electrode

Let us consider an electrode made of copper immersed in a half-cell containing copper ions at a 1 M concentration, referring to an aqueous solution. The half-cell reaction for copper is

$$Cu^{2+} + 2e^- \rightarrow Cu \qquad E^0 = +0.34\,V \tag{1.21}$$

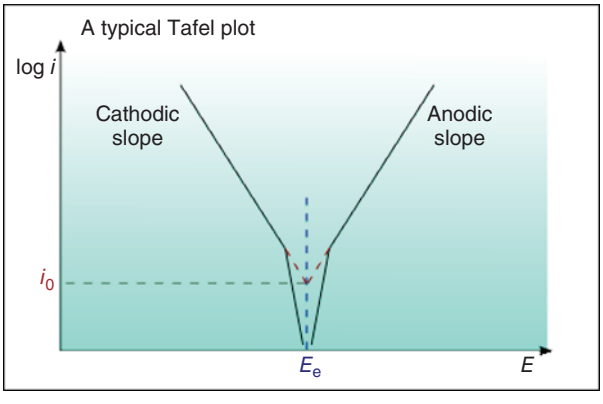

Figure 1.5 A typical Tafel plot. Source: Reproduced with permission from Weal et al. [2]/ University of Cambridge.

The exchange current density at 1 M concentration of copper ions, for the above reaction, is $i_0 = 1\,\mathrm{A\,m^{-2}}$, reflecting the current density at zero overpotential (thus at E_e, in this example $E_e = E^0$, as both Cu and $Cu^{2+}(aq)$ are in their standard states), that is, at zero net reaction (and thus at zero net current). Therefore, the magnitude of the exchange current density is a reflection of the reversibility of a given electrode reaction and signifies the rate at which equilibrium is established on being disturbed away from a given equilibrium condition.

For the Tafel equation

$$\eta = a + b\ \log(i) = a + b\ \log(i/i_0) \tag{1.22}$$

the general expression for the Tafel slope is

$$b = (\pm)\ 2.303RT/\alpha zF \tag{1.23}$$

Taking $T = 300\,\mathrm{K}$, and allowing for copper $\alpha = 0.5$ and $z = 2$, the Tafel slopes are calculated as $b_a = 0.059\,\mathrm{V\,decade^{-1}}$ of current and $b_c = -0.059\ \mathrm{V\ decade^{-1}}$ (of log current). Furthermore, for the anodic curve

$$\eta_a = E_a - E_e;\ \ E_a = E_e + \eta_a \tag{1.24}$$

and for the cathodic curve

$$\eta_c = E_e - E_c;\ \ E_c = E_e - \eta_c \tag{1.25}$$

The corresponding Tafel plot for copper is shown in the diagram in Figure 1.6. For example, during discharge, if the redox reaction is in the direction opposite of Eq. (1.21), where Cu is oxidized to copper ions in the solution, the electrode potential will be less than 0.34 V along the polarization line. The greater the operating current density, the lower the electrode potential. This in-effect contributes to the reduction in the cell potential during discharge as a result of overpotential losses, signifying the energy barrier for the electron-transfer reaction. On the other hand, during charging, the electrode potential increases with the applied current, thus increasing the potential required for charging the cell back to its original state (by electrochemical reduction in this example). For a faster charging rate, a higher

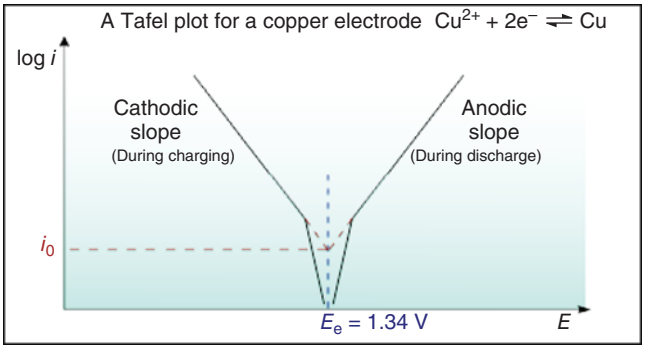

Figure 1.6 Tafel plot for a copper electrode. Source: Reproduced with permission from Weal et al. [2]/University of Cambridge.

current density is desirable, but this can arise only at the expense of a higher applied voltage (higher energy) to overcome the increasing overpotentials. (Note that E^0 is modified by the Nernst equation to obtain a value for E_e, for species in nonstandard states.)

1.2.2.6 Other Limiting Factors

At very high currents, a limiting current may be reached as a result of the concentration overpotential, η_c, restricting mass-transfer rates to the diffusion rate of the electroactive species. A limiting current arises, which can be derived from Fick's first law of diffusion, under the condition that the electrode surface is depleted of the ion, and the recovery of the ion concentration is limited by ion transport through the electrolyte diffusion boundary layer.

The limiting current is diffusion limited, and can be determined by Fick's law of diffusion as

$$i_L = zFDC/\delta \tag{1.26}$$

where i_L is the limiting current density over a boundary layer, D is the diffusion coefficient of metal cations in the electrolyte, C is the concentration of metal cations in the bulk electrolyte, and δ is the thickness of the boundary layer. Typical values for Cu^{2+}, for example, would be $D = 2\times10^{-9}$ m^2 s^{-1}, $C = 0.05\times10^4$ kg m^{-3}, and $\delta = 6\times10^{-4}$ m; these values give a limiting current density of $i_L = 3.2\times10^2$ A m^{-2}.

The concentration overpotential, thus, represents the difference between the cell potential at the electrolyte concentration and the cell potential at the surface concentration because of depletion (or accumulation) at high-current densities, given by

$$\eta_c(\text{conc}) = 2.303RT/zF \ln(i/i_L) \tag{1.27}$$

A Tafel curve showing this diffusion limiting of the current is depicted in Figure 1.7.

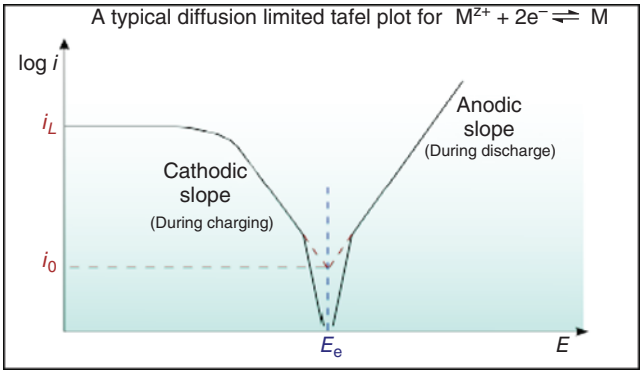

Figure 1.7 Diffusion limited current for the cathodic reaction. Source: Reproduced with permission from Weal et al. [2]/University of Cambridge.

1.2.2.7 Tafel Curves for a Battery

In a battery, there are two sets of Tafel curves present, one for each electrode material. During discharge, one material will act as the anode (termed as the negative [−] electrode being at the lower potential) and the other as the cathode (termed as the positive [+] electrode being at the higher potential). During charging, the roles will be reversed such that at the negative [−] electrode, cathodic reactions take place and at the positive [+] electrode, anodic reactions occur by an externally applied potential difference to recover species back to the state before discharge. The actual potential difference between the two electrodes for a given current density can be found in the Tafel curve. The total cell potential is the difference between the anodic potential, E_a, and the cathodic potential, E_c.

In a galvanic cell, the actual potential, $V'_{\text{cell, discharge}}$, is less than the Nernst potential

$$V'_{\text{cell,discharge}} = E_c - E_c - |\eta_c| + E_\alpha - |\eta_a| \tag{1.28}$$

E_a, η_c, E_c, and η_a are defined in Section 1.2.2.3. Upon discharge, the cell potential may be further decreased by the ohmic drop due to the internal resistance of the cell, r. Thus, the actual cell potential is given by

$$V_{\text{cell,discharge}} = V'_{\text{cell,discharge}} - iAr \tag{1.29}$$

where A is the geometric area relevant to the internal resistance and i is the cell current density.

Similarly, on charging, the applied potential is greater than the Nernstian potential and can be calculated by the equation

$$V'_{\text{cell,charge}} = E_c + |\eta_c| + E_\alpha + |\eta_a| \tag{1.30}$$

The cell-charging potential may now be increased by the ohmic drop, and the final actual cell-charging potential is given by

$$V_{\text{cell,charge}} = V'_{\text{charge,harge}} + iAr \tag{1.31}$$

In summary, it can be stated that to maximize the power density (P with units $\mathrm{W\,m^{-2}}$), which is the product of the cell potential and the current density, it is important to achieve the most optimum value of the cell potential at the lowest overpotential and internal resistance. Usually at low-current densities, overpotential losses arise from an activation energy barrier related to electron-transfer reactions, while at a high-current density, the transport of ions becomes rate-limiting, giving rise to a current limit. Ohmic losses (iAR) arising from the current (current density $i \times$ surface area A), flowing through a resistor R, arise with increasing current and can be further increased due to additional ohmic resistance by the formation of insulating phases during the progress of charging or discharging and also from any non-redox parasitical chemical reactions. Power is the product of voltage and current; therefore, decreasing the current density by increasing the true surface area can also, in principle, result in a high-power density. However, unwanted side reactions may also be enhanced.

1.2.3 Capacity

The bar graph of Figure 1.8 shows the difference between the theoretical and actual capacities in mAh g^{-1} for various battery systems.

The theoretical molar capacity of a battery is the quantity of electricity involved in the electrochemical reaction. It is denoted as Q_{charge} and is given by

$$Q_{\text{charge}} = xnF \tag{1.32}$$

where x is the number of moles of a chosen electroactive component that take place in the reaction, and n is the number of electrons transferred per mole of reaction. The mass of the electroactive component can be calculated as

$$M = x\,M_r \tag{1.33}$$

where M denotes the mass of the electroactive component in the cell and M_r the molecular mass of the same component. The capacity is conventionally expressed as Ah kg^{-1} (numerically equal to mAh g^{-1}) thus given in terms of mass, often called specific capacity, C_{specific}, and it is expressed as

$$C_{\text{specific}} = nF/M_r \tag{1.34}$$

If the specific capacity is multiplied by the mass of the electroactive component in the cell, one will obtain the rated capacity of a given cell. It is important to note that the mass may refer to the final battery mass including packaging or it may be reported with respect to the mass of the electroactive components alone. It is quite straightforward to recalculate the capacity in terms of the mass of the cell by dividing the rated capacity by the total mass of the cell.

In practice, the full battery capacity can never be realized, as there is a significant mass contribution from nonreactive components, such as binders, conducting

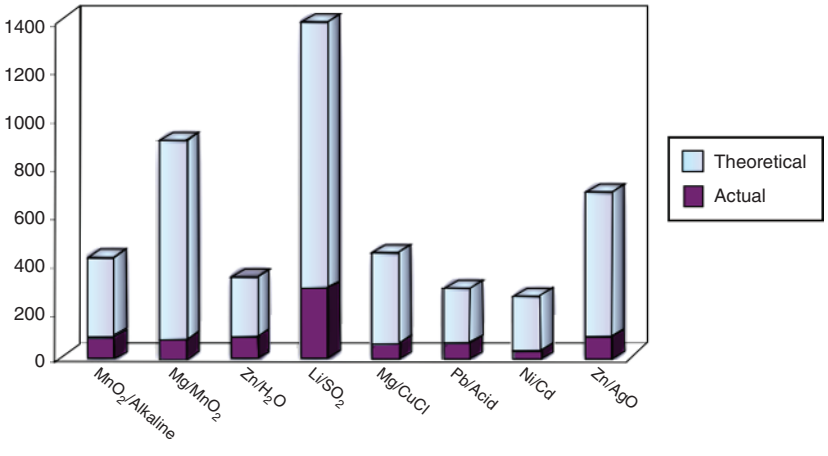

Figure 1.8 Theoretical and actual voltages of various battery systems. Source: Reproduced with permission from Weal et al. [2]/University of Cambridge.

particles, separators, electrolytes, current collectors, substrates, and packaging. Additionally, the chemical reactions cannot be carried out to completion; either due to unavailability of the reactive components and inaccessibility of the active materials or due to poor reactivity at the electrode/electrolyte interface. The capacity is strongly dependent upon the load and can decrease rapidly at high-drain rates as defined by the magnitude of current drawn, due to increased overpotential losses and ohmic losses that can exacerbate the problems with completion of the reaction. At higher drain rates denoting high-operating currents, a battery will be discharged faster.

1.2.4 Shelf Life

A cell may be subject to self-discharge in addition to discharge during operation. Self-discharge is caused by parasitic reactions, such as corrosion, which occur even when the cell is not in use. Thus, the chemical energy may slowly decrease with time. Further energy loss may occur as a result of discharge where insulating products may be formed or the electrolyte may be consumed. Therefore, shelf life (or storage from manufacturing to use in electronic devices) is limited by factors relating to both non-use and normal usage.

1.2.5 Discharge Curve/Cycle Life

The discharge curve is a plot of the voltage against the percentage of the capacity discharged. A flat discharge curve is desirable as this means that the voltage remains constant as the battery is used up. Some discharge curves are illustrated in Figure 1.9, where the potential is plotted against time as the battery is discharged through a fixed load. In the ideal mode, the cell potential remains steady with time until the capacity is fully exhausted at the same steady rate and then it falls off to a low level. Some of the primary lithium cells display this type of nearly ideal flat discharge characteristics. In most other real batteries, the voltage may slope down gently with time as in primary alkaline cells or do so in two or more stages during discharge as in Leclanché cells (see Table 1.4).

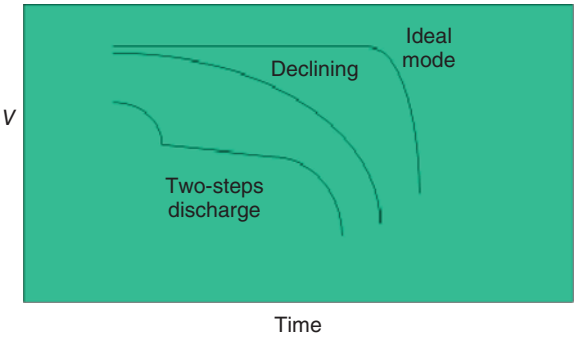

Figure 1.9 Change of voltage with time behavior in different cells. Source: Reproduced with permission from Weal et al. [2]/ University of Cambridge.

Table 1.4 History of electrochemical cell development tabulated with years and inventors.

Type	Year	Inventor	Battery
Primary batteries	1800	Alessandro Volta	Voltaic pile
	1836	John Frederic Daniel	Daniel cell
	1844	William Robert Grove	Grove cell
	1860	Callaud	Gravity cell
	1866	Georges-Lionel Leclanché	Leclanché wet cell
	1888	Carl Gassner	Zinc–carbon dry cell
	1955	Lewis Urry	Alkaline battery
	1970	No information	Zinc-air battery
	1975	Sanyo Electric Co	Lithium–manganese cell
	2004	Panasonic Corporation	Oxyride battery
Secondary batteries	1859	Raymond Gaston Planté	Planté lead–acid cell
	1881	Camille Alphonse Faure	Improved lead–acid cell
	1899	Waldemar Jungner	Nickel–cadmium cell
	1899	Waldemar Jungner	Nickel–iron cell
	1946	Union Carbide Company	Alkaline manganese secondary cell
	1970	Exxon laboratory	Lithium–titanium disulfide
	1980	Moli Energy	Lithium–molybdenum disulfide
	1990	Samsung	Nickel–metal hydride
	1991	Sony	Lithium-ion
	1999	Sony	Lithium polymer

1.2.6 Energy Density

The energy density is the energy that can be derived per unit volume of the cell and is often quoted as $\mathrm{Wh\,l^{-1}}$, (watt-hour per liter). This value is dependent upon the density of the components and the design by which the various materials are interfaced together. In many applications, availability of space for placing a battery must be minimized and thus, the energy density should be as high as possible without greatly increasing the weight of the battery to attain a given energy level. The battery flat cell, described in Figure 1.2, is an example of efficient design that increases energy density.

1.2.7 Specific Energy Density

The specific energy density, $\mathrm{Wh\,kg^{-1}}$(watt-hour per kilogram), is the energy that can be derived per unit mass of the cell (or sometimes per unit mass of the active electrode material). It is the product of the specific capacity and the operating voltage in one full discharge cycle. Both the current and the voltage may vary within a

discharge cycle and, therefore, the specific energy derived is calculated by integrating the product of the current and the voltage over time

$$\text{Specific Energy} = \int V \cdot I \, dt \tag{1.35}$$

The discharge time is related to the maximum and minimum voltage thresholds and is dependent upon the state of availability of the active materials and/or the avoidance of an irreversible state for a rechargeable battery. The maximum voltage threshold may be related to an irreversible drop of voltage in the first cycle, after which that part of the cycle is not available. The minimum threshold voltage may be determined by a lower limit below which the voltage is deemed to be too low for practical use or set the limit for some irreversible losses, such that the system can only inadequately provide energy and power.

An active component may be less available due to side reactions, such as (i) zinc reacting with the electrolyte in alkaline or silver-oxide–zinc batteries, (ii) dendrite formation in rechargeable batteries, and (iii) formation of passivation layers on the active components. Since batteries are used mainly as energy-storage devices, the amount of energy (Wh) per unit mass (kg) is the most important property quoted for a battery. It must be noted that the quoted values only apply to the typical rates at which a particular type of battery is discharged. The specific- energy-density values vary typically between 40 and 300 Wh kg^{-1} for primary batteries (single-use as these are not designed for recharging) and nominally 30 and 260 Wh kg^{-1} for secondary (rechargeable) batteries, used commercially.

1.2.8 Power Density (Wh g^{-1})

The power density is the power that can be derived per unit mass of the cell. At higher drains, signifying higher currents relating to high-power densities, the specific energy tends to fall off rapidly, hence, decreasing the capacity. This trade-off between power and energy density is best expressed in a Ragone plot, an idealized version of which is given in Figure 1.10. It is obvious that a certain battery has a range of values for specific energy and power, rather than a battery having a specific

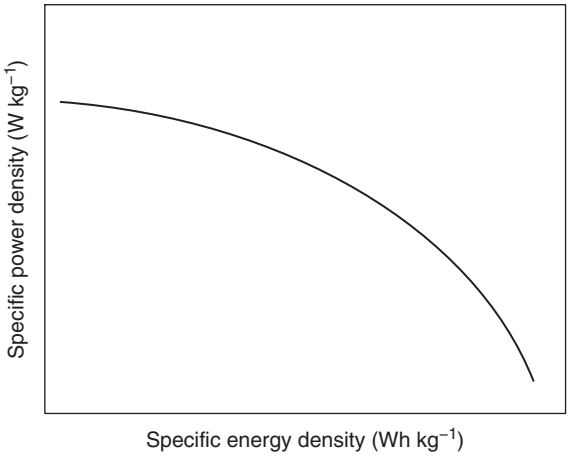

Figure 1.10 Ideal Ragone plot.

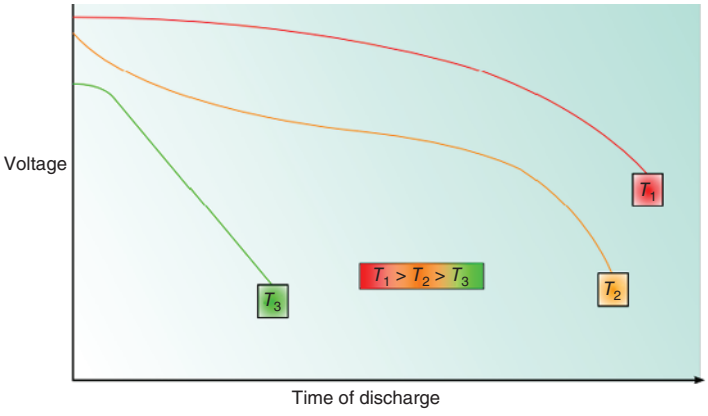

Figure 1.11 Effects of temperature on battery capacity. Source: Reproduced with permission from Weal et al. [2]/University of Cambridge.

value of energy and power. To derive the maximum amount of energy, the current or the power drain must be at the lowest practical level. For given cell chemistry, increasing the surface area of the electrodes can increase the cell's current at a given current density and, thus, deliver more power. The most efficient way to deliver a high-power density is to increase the effective surface area of an electrode while keeping the nominal geometric area constant. It is important to consider any increase in parasitic reactions that may be enhanced due to the increase in the effective surface area. For example, in systems where corrosion is a concern, simply increasing the surface area may enhance the corrosion reactions while depleting the active material. Under these circumstances, the cell capacity will decrease along with the shelf life.

1.2.9 Service Life/Temperature Dependence

The rate of the reaction in the cell is temperature dependent according to kinetics theories. The internal resistance also varies with temperature; low temperatures give a higher internal resistance. At very low temperatures, the liquid electrolyte may freeze giving a lower voltage as ion movement is impeded. At very high temperatures, the chemicals may decompose, or there may be enough energy available to activate unwanted and reversible reactions, reducing the capacity. The rate of decrease of voltage with increasing discharge will also be higher at lower temperatures, as will the capacity; this is illustrated in Figure 1.11.

1.3 Primary and Secondary Batteries

It should be mentioned that there are two main classifications of batteries: primary and secondary batteries. In primary batteries, the chemical energy stored in the cell is such that it can be used only once to generate electricity; that is, once the cell is

fully discharged it cannot be of further use. In secondary batteries, the reverse redox reaction (also referred to as electrolysis or simply as charging) can occur when the current is applied at a potential higher than the cell potential (E_{cell}) and the battery can be used reversibly numerous times. During charging, electrons flow to the negative [−] electrode through the external circuit for facilitating a cathodic reaction (electrochemical reduction) typically with cations (e.g. Cu^{2+} ions) from the positive [+] electrode diffusing through the electrolyte. The external current is maintained by an anodic reaction (electrochemical oxidation) at the [+] electrode generating electrons flowing through the external circuit. The power supply maintains the voltage difference between the [+] and the [−] electrodes to sustain the charge movement.

In Table 1.4, a timeline depicts the historic development of batteries. Presently, the most advanced technology of primary batteries is the Oxyride battery, developed by Panasonic Corporation but not yet widely used. For the secondary batteries, the lithium-polymer battery is the most commercially advanced, mostly used as a power backup in laptop computers and slim and lightweight mobile phones. The most common secondary battery used commonly in communication devices, such as cellular phones, is the lithium-ion battery.

Batteries are also sometimes classified in terms of the mode in which they are used:

- **Portable batteries:** These cover a wide range of batteries from those used in toys to those used in mobile phones and laptops.
- **Transport batteries:** The largest application of these is in the starting, lighting, and ignition (SLI) for cars or in electrical vehicles (e.g. in e-scooters and hybrid electrical vehicles).
- **Stationary batteries:** Include applications for standby power, backup in computers, telecommunications, emergency lighting, and load-leveling with renewable energy, such as solar cells during darkness and windmills during very calm weather.
- **Electrical Vehicle (EV) Batteries:** Anticipated to grow rapidly starting from this decade in competition with IC-engine-based vehicles and ultimately fully replacing the IC-engine vehicles.
- **Energy-Storage Systems (ESS):** Growth in this area will parallel the growth in renewable energy sources applications as in solar farms and wind turbines. The EV and the ESS batteries will dominate battery applications for decades assuming development proceeds as planned.

Thus, batteries are correctly perceived as a critical enabling technology and future improvements are continuously sought. Various battery chemistries will be examined in detail in the following chapters.

1.4 Conclusions

Now that a general overview of batteries has been given, starting from their main components and configuration, to how they function and are disposed of, specific battery systems will be examined. The first two chapters that follow, present a

historic timeline describing the development of batteries from the first cells of the 1800s to the commercial cells of the twentieth-first century. It will be seen that Li batteries are the most promising high-energy-storage devices and therefore the majority of the following chapters focus on the next-generation Li cathodes, anodes, and electrolytes that will significantly increase their lifetime and applications.

References

1 Linden, D. and Reddy, T.B. (2002). *Handbook of Batteries*, 3e. New York: McGraw-Hill.
2 Weal, E., Tan, J.C., and Kumar, R.V. (2005). *University of Cambridge DoITPoMS Teaching and Learning Packages*. Cambridge: University of Cambridge http://www.doitpoms.ac.uk/tlplib/batteries/index.php.