1
Introduction to Electrochemical Cells

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1.1
What are Batteries?

The purpose of this chapter is to provide the 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 an oxidation reaction 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 the 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).

In addition to the electrodes, the two other constituents that are required for such reactions to take place are the electrolyte solution and the separator. The electrolyte is an ion conducting material, which can be in the form of an aqueous, molten, or solid solution, while the separator is a membrane that physically prevents a direct contact between the two electrodes and allows ions but not electrons to pass through; it therefore ensures electrical insulation for charge neutralization in both the anode and cathode once the reaction is completed. 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
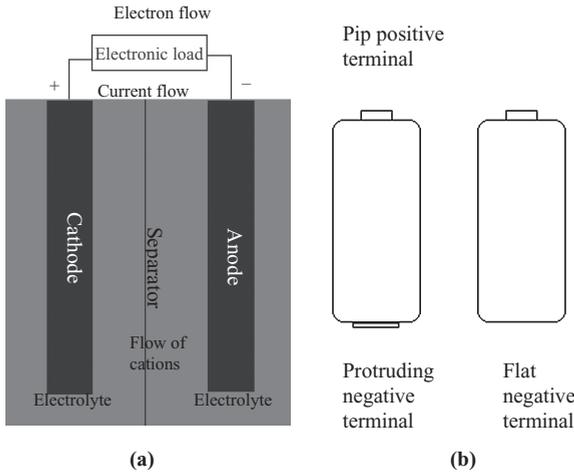
Figure 1.1 (a) The schematic diagram of a simple galvanic cell. (b) Terminal designs for cylindrical batteries.
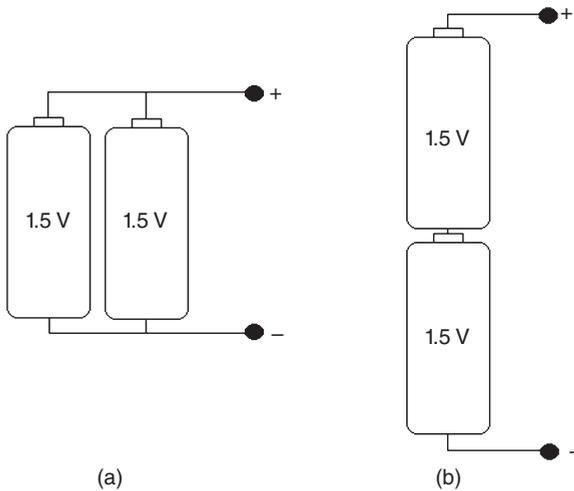
Figure 1.2 (a) An illustration of batteries connected in parallel to obtain double current. (b) An illustration of batteries connected in series to obtain 3 V.

designs in order to prevent short-circuit by battery reverse installation, and they are shaped so as to match the receptacle facilities provided in the appliances. For example, in cylindrical batteries, the negative terminal is either designed so as 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.

In order to meet the voltage or current used in specific appliances, cylindrical galvanic cells are connected in series or parallel. Figures 1.2a, and b represent
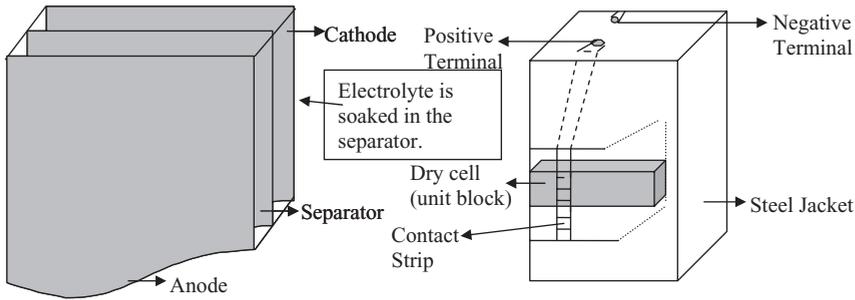
Figure 1.3 (a) Single-flat cell configuration; (b) composite flat cell configuration.

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 cells. 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 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 a 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.

1.2
Quantities Characterizing Batteries

Upon operation of galvanic cells, meaning that the device is on power mode, it is said that the galvanic cell is discharged and electrons flow, through an external circuit, from the anode to the cathode, which as a result attains a negative, and consequently cations are attracted from the anode to the cathode to which they diffuse through the electrolyte. The electrochemical reactions that take place upon operation of different batteries are shown in Table 1.2, whereas the quantities that characterize batteries are defined in Table 1.3.

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

Flat cells

Length (mm)	Width (mm)	Thickness (mm)
24	13.5	6.0
43	43	6.4
Rectangular cells		
48.5	26.5	17.5

In order to better understand the differences between various materials chemistries, some of the quantities in Table 1.3 are further elaborated in the following pages.

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 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 atmosphere.) 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 by passing pure hydrogen at one atmosphere over an electrode of platinized platinum, where a high surface area of platinum is deposited on a platinum foil or plate, which is dipped into an acid solution of unit activity of H^+ ions, corresponding to 1 M acid solution. A list containing selected standard electrode potentials at 298 K in an aqueous

Table 1.2 Standard electrode potentials in an 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
$\frac{1}{2}H_2 + e^- \rightarrow H^-$	−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
$Hg^{2+} + 2e^- \rightarrow Hg$	+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

solution is given in Table 1.2. The batteries that make use of these materials as electrodes will be described in the next chapter. It should be noted that the standard electrode potential for a reaction defined arbitrarily as zero.

In order to obtain a true estimate of the actual open circuit cell voltage 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

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

Table 1.3 Battery characteristics [2].

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/dm^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)
Power density	The power that can be derived per unit weight of the cell	Watt per kilogram (W/kg)
Capacity	The theoretical capacity of a battery is the quantity of electricity involved in the electrochemical reaction	Ampere-hours per gram (Ah/g).
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) and ampere per liter (A/lt^3))
Cycle life	The number of discharge/charge cycles it can undergo before its capacity falls to 80%	Cycles

where $Q = a_{\text{products}}/a_{\text{products}}$ is the chemical quotient for the overall cell reaction and R is the gas constant ($R = 8.31$ J/(kmol)). Q is represented in the same way as the equilibrium constant K, except that the activities and partial pressures in Eq. (1.2) reflect the actual nonstandard values prevailing in the system. For example, for the electrode reaction

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

the actual Nernstian electrode potential is

$$E = E^0 - RT \ln a_M / a_{M\,2+} \tag{1.4}$$

The Nernstian potential in Eq. (1.4) will change with time due to the 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.

The operating voltage produced is further modified as a result of discharge reactions actually taking place and will always be lower than the theoretical voltage due to polarization (http://www.msm.cam.ac.uk/Teaching/mat1b/courseB/BH.pdf) 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. Polarization rises in order to overcome any activation energy for the electrode reaction and/or concentration gradients near the electrode. These factors are dependent upon electrode kinetics and, thus, vary with temperature, state of charge, and with the age of the cell. Of course 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 as was previously shown affect the voltage, will be elaborated on. 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 in order to obtain a better understanding of what the actual cell voltage may be, since the charge transfer and the rates of the reactions at the electrodes 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
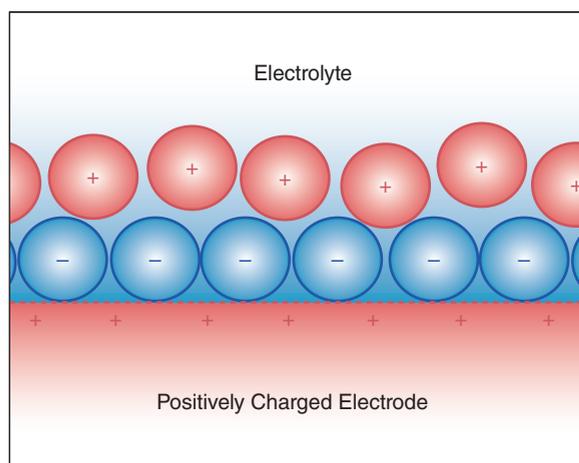
Figure 1.4   Illustration of double layer [2].

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 k 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 of time, and therefore proportional to the number of electrons produced per unit of time, that is, proportional to the rate of the reaction.

1.2.2.3 Electrodes Away from Equilibrium
When an electrode is not at equilibrium an *overpotential* exists, given by

$$\eta = E - E_0 \tag{1.6}$$

where η is the overpotential, E is the actual potential, and E_0 is the equilibrium potential.

Overpotential is used synonymously with polarization.

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:

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

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 $F = 96540\,C/mol$ is Faraday's constant. If an overpotential 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 0.5.

Therefore the anodic current density, i_a, is

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

which by Eq. (1.9) reduces to

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

Equation (1.12) is known as the *Tafel equation*. By taking natural logs and rearranging, Eq. (1.12) can be written as

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

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

$$\eta_a = a_a + b_a \ln i_a \quad (1.14)$$

Or in terms of the anode potential, E_a,

$$\ln(i_a) = \ln(i_{0,a}) + (E_a - E_0)\alpha zF/RT \quad (1.15)$$

Solving Eq. (1.15) for E_a, gives

$$E = b_a \log(i_a/i_{0,a}) + a_a \quad (1.16)$$

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

$$M^{z+} + ze^- \rightarrow M \quad (1.17)$$

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

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

and

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

Therefore, the cathode potential, E_c, is expressed as

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

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. The half-cell reaction for copper is

$$Cu^{2+} + 2e^- \rightarrow Cu \quad E^0 = +0.34 \text{ V} \quad (1.21)$$

The exchange current density for the above reaction is $i_0 = 1 \, A \, m^{-2}$, reflecting the current density at zero overpotential, that is, at zero net reaction. Thus, the
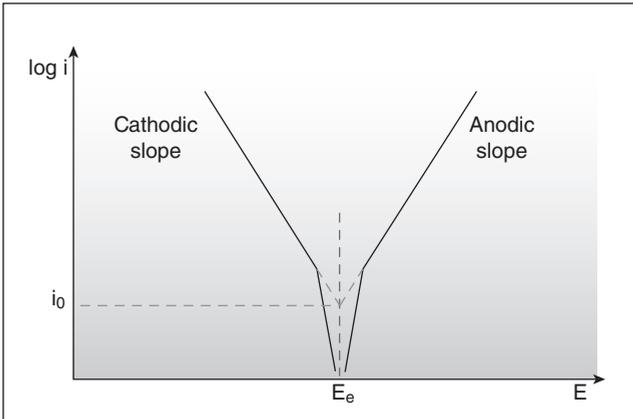
Figure 1.5 A typical Tafel plot [2], where i_0 is the exchange current density and E_e the equilibrium potential.

magnitude of the exchange current density is a reflection of the reversibility of a given electrode reaction.

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 of current and $b_c = -0.059\,\mathrm{V}/$decade of current. Furthermore, for the anodic curve

$$\eta_a = E_a - E_0;\ E_a = E_0 + \eta_a \tag{1.24}$$

and for the cathodic curve

$$\eta_c = E_c - E_0;\ E_c = E_0 + \eta_c \tag{1.25}$$

The corresponding Tafel plot for copper is shown in the diagram of 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 into the solution, the electrode potential will be less than $0.34\,\mathrm{V}$ 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 current density is desirable, but this can arise only at the expense of a higher applied voltage (higher energy) in order to overcome the increasing overpotentials.
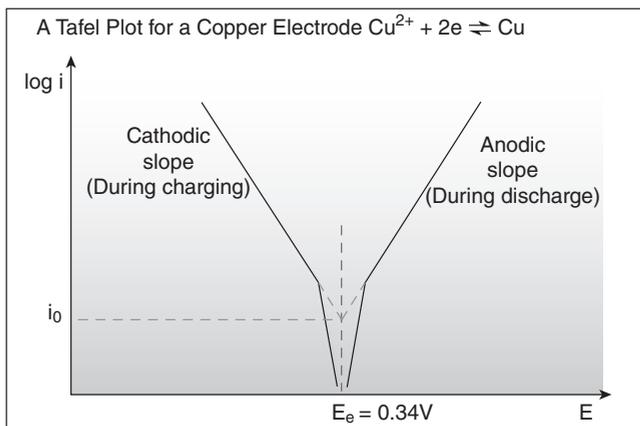
Figure 1.6 Tafel plot for a copper electrode [2].

1.2.2.6 Other Limiting Factors

At very high currents a limiting current may be reached as a result of concentration overpotential, $\eta_{(conc)}$, 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.

As the limiting current is diffusion limited, it 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 $D = 2 \times 10^{-9}\,m^2s^{-1}$, $C = 0.05 \times 10^4\,kg\,m^{-3}$, $\delta = 6 \times 10^{-4}\,m$; these values give $i_L = 3.2 \times 10^2\,A\,m^{-2}$.

The concentration of the 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 shown in Figure 1.7.

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 and the other as the cathode. During charging the roles will be reversed. The actual potential difference
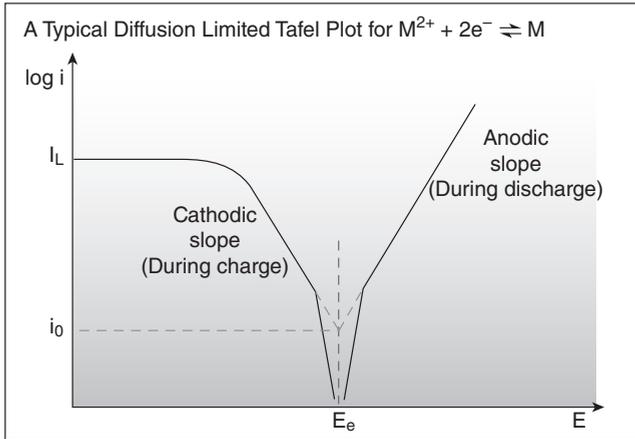
Figure 1.7 Diffusion limited current for the cathodic reaction [2].

between the two electrodes for a given current density can be found from 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, $V'_{cell,discharge}$, is less than the Nernst potential

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

Upon discharge the cell potential may be further deceased by the ohmic drop due to the internal resistance of the cell, r. Thus, the actual cell potential is given by

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

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

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

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

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

In summary, it can be stated that in order to maximize power density, it is important to achieve the most optimum value of cell potential at the lowest overpotentials and internal resistance. Usually at low current densities, overpotential losses arise from an activation energy barrier related to electron transfer reactions, while at a higher current density, the transport of ions becomes rate limiting giving rise to a current limit. Ohmic losses increase with increasing current, and can be further enhanced by the increased formation of insulating phases during the progress of
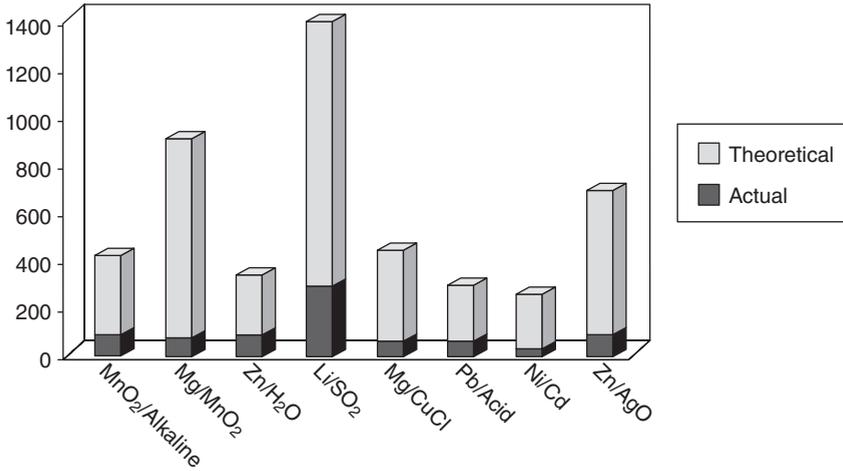
Figure 1.8 Theoretical and actual voltages of various battery systems [2].

charging. Power is a product of voltage and current; therefore, decreasing the current density by increasing the true surface area can also in principle result in a higher 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

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

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

$$M = xM_r \tag{1.33}$$

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 $Ah\,kg^{-1}$ thus given in terms of mass, often called specific capacity, $C_{specific}$

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

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 with the total mass of the cell.

In practice, the full battery capacity could never be realized, as there is a significant mass contribution from nonreactive components such as binders & conducting particles, separators & electrolytes and current collectors and substrates, as well as packaging. Additionally, the chemical reactions cannot be carried out to completion; either due to unavailability of reactive components, inaccessibility of active materials or 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 which 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, that occur even when the cell is not in use. Thus, the chemical energy may slowly decrease with time. Further energy loss may arise as a result of discharge during which insulating products may form or the electrolyte may be consumed. Therefore, shelf-life is limited by factors related to both nonuse 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
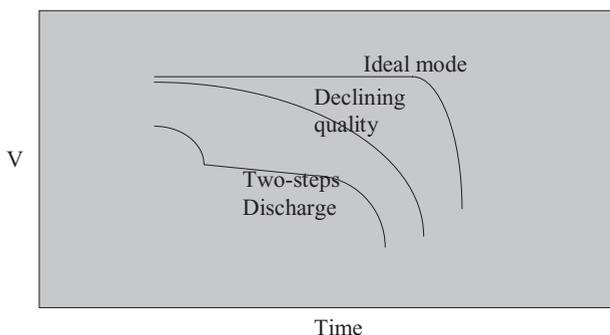
Figure 1.9 Change of voltage with time behavior in different cells [2].

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 Lechlance cells.

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 Wh/lt, where lt stands for 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 designing that increases the energy density.

1.2.7
Specific Energy Density

The specific energy density, Wh/kg, 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, E, derived is calculated by integrating the product of the current and the voltage over time

$$E = \int V \cdot I \, \mathrm{d}t \tag{1.35}$$

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 sets 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, (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 for the typical rates at which a particular type of battery is discharged. The specific
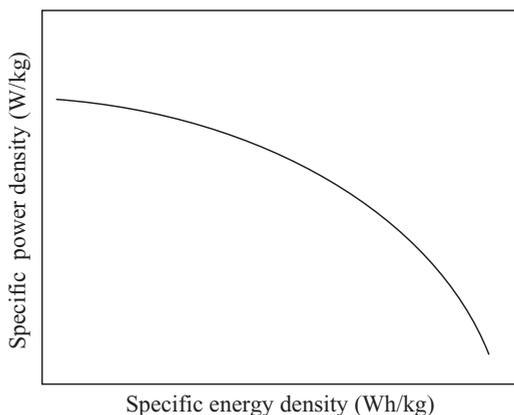
Figure 1.10 Ideal Ragone plot.

energy density values vary between 45 and 300 Wh/kg for primary batteries and 30 and 240 Wh/kg for secondary (rechargeable) batteries.

1.2.8
Power Density

The power density is the power that can be derived per unit mass of the cell (W/kg). At higher drains, signifying higher currents relating to higher 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 value of energy and power. In order to derive the maximum amount of energy, the current or the power drain must be at the lowest practical level. For a 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 higher power density is to increase the effective surface area of an electrode while keeping the nominal 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
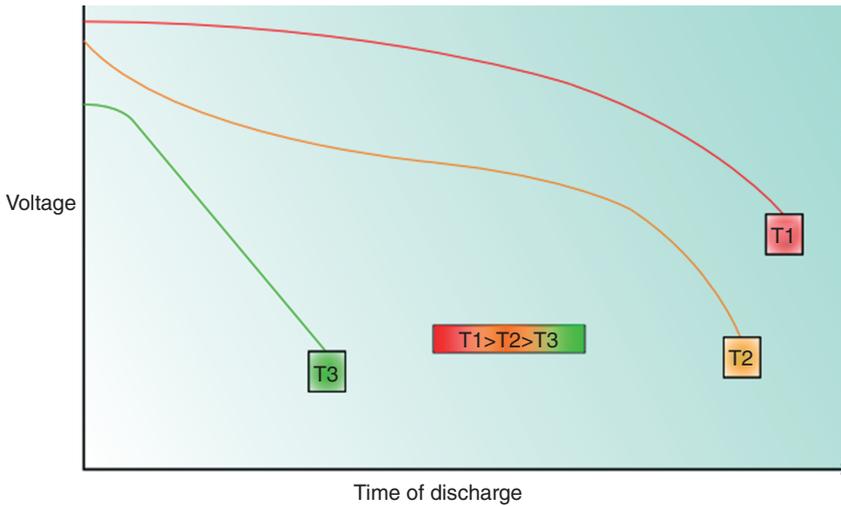
Figure 1.11   Effects of temperature on battery capacity [2].

give a higher internal resistance. At very low temperatures the 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, 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 types 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 and 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 many times. During charging, electrons flow to the anode through the external circuit and cations from the cathode diffuse through the electrolyte to the anode.

In Table 1.4, a timeline depicts the historic development of batteries separated into two blocks of primary and secondary battery histories. 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 advanced, mostly used as a power backup in

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	Waldmar Jungner	Nickel–cadmium cell
	1899	Waldmar 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

laptop computers and slim and light weight mobile phones. The most common secondary battery used 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 stand-by power, backup in computers, telecommunications, emergency lighting, and for load-leveling with renewable energy, such as solar cells, during darkness, and wind during very calm weather.

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

1.4
Battery Market

It is estimated that the total market for all batteries in the year 2007 was worth $80 billion, with an annual growth of over 8%, and rapid growth in demand coming from China, India, Europe, South America, and Russia. Forecast for 2010 is shown in Table 1.5. It can be seen that the secondary batteries are expected to dominate over the primary batteries reversing the historical situation until recently. More than 50% of the primary market is from the alkaline cells, while more than half of the secondary market is dominated by lead-acid batteries.

In the secondary battery market, several new cells have been introduced just within the last two decades, for example, the Ni–MH cell (1990), Li-ion cell

Table 1.5 Global battery market forecast for 2010.

Type of battery	Global demand in US$, 98 billion
Primary	Primary total: 42%
Carbon–zinc	8%
Alkaline	22%
Others	12%
Secondary	Secondary total: 54%
Lead acid	28%
Ni–Cd/Ni–MH and others	12%
Li	14%
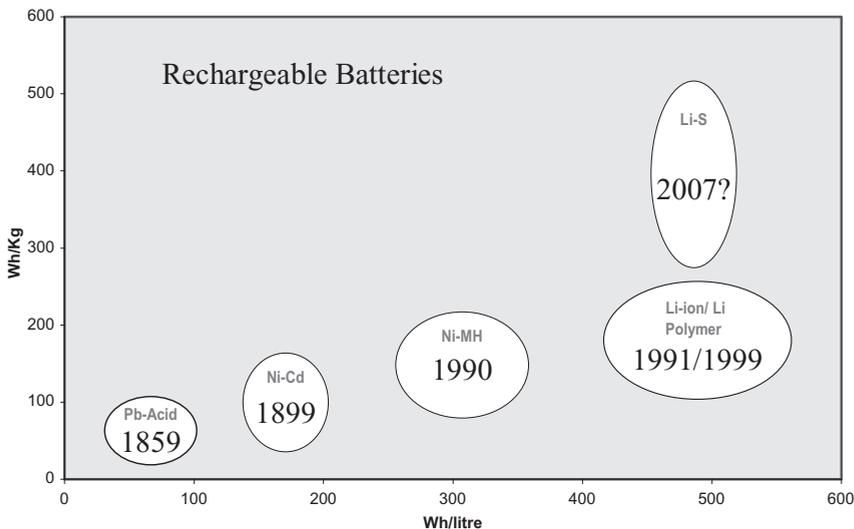
Figure 1.12 Comparison of energy density for various rechargeable battery chemistries.

(1991), rechargeable alkaline cells (1992), Li polymer (1999), and also the concept of mechanically rechargeable Zn-air batteries (2001). The new batteries, especially those based on the Li chemistries have not only met some of the existing demand, but can be said to have revolutionized the battery market by accelerating demand for laptops, mobile phones, and cordless hand held tool products.

An inspection of Figure 1.12 clearly reveals that with time, the specific energy (Wh/kg) and the energy density (Wh/lt) have continued to grow as batteries advance. It is this combination of high values of Wh/kg and Wh/lt that have been the key factors heralding this rapid growth. The number of batteries produced each year is staggering. The relatively newcomers, Li-ion batteries, alone are produced in quantities exceeding 1.2 billion cells per year.

1.5
Recycling and Safety Issues

The batteries consumed in households amount to approximately 4 billion cells per year. Batteries are important for everyday life but they can be a source of health problems and contamination. Besides the caution of using each type of battery the right battery for the appropriate function, the proper disposal is also a critical issue that needs to be urgently considered.

The alkaline cells do not have any toxic constituents, and although their disposal will incur energy and landfill penalty, they do not contaminate the environment with toxic pollutants. Some households have recharged primary alkaline cells despite warnings and against the advice of the manufacturers. Recharging is to some extent possible, provided the cells have not been discharged beyond 50% of their total capacity. With each recharge, the capacity of the cells begins to fade, further extenuated by the degree of depth of discharge. Furthermore, there is danger of explosion in recharging primary alkaline cells due to the release of hydrogen gas.

Rechargeable versions of alkaline batteries are made safe, but do suffer from low current capacity arising from the high internal cell resistance. In 1992, these types of cells were specifically developed as a low-cost power source for consumer goods.

It is important to note that choosing to purchase rechargeable batteries will decrease numerous global battery wastes. It is a fact that 600 primary batteries can be replaced by only two AA nickel cadmium secondary batteries. By new technology, rechargeable batteries come out as USB rechargeable batteries (see Figure 1.13), which is convenient and does not require a charger. However, due to the hazardous nature of heavy metals contained in a battery, some batteries have been reformulated. Alkaline batteries are manufactured as a mercury-free battery since 1992. The mercuric oxide button cell was finally replaced by mercury-free batteries, such as silver oxide or zinc air batteries. However, the nickel cadmium battery has not been totally replaced by other nonhazardous batteries yet. Moreover, some

Figure 1.13   USB rechargeable batteries (www.reghardware.co.uk).

appliances have the nickel cadmium battery built-in, which is difficult for battery recycling.

The annual number of batteries discarded run in billions worldwide; safe disposal and recycling are crucial in this important energy storage chain. Many countries are forced by legislations to have battery recycling plants such as in the USA, the UK, Germany, France, Turkey, Italy, and Poland. In the USA, the battery manufactures (Panasonic, Duracell, and Eveready Energizer) have formed a "Rechargeable Battery Recycling Corporations (RBRC) Battery Recycling Program" to take back dead batteries, especially button and Ni–Cd batteries. In the state of California all types of batteries are recycled. Used batteries can be disposed at any drop off site or at any participating retailers. Batteries are classified by the US federal government into nonhazardous and hazardous wastes. Used alkaline, carbon zinc, lithium-ion, nickel metal hydride, and rechargeable alkali manganese batteries are considered as nonhazardous waste and can be thrown away in the trash. Used Ni–Cd, lead-acid, silver oxide, and button cells containing mercuric oxide, silver oxide, lithium, alkaline, and zinc-air are classified as hazardous wastes and need to be recycled. Nonhazardous batteries must also be recycled, however, since throwing these batteries together with other wastes is dangerous as some of them may not be completely dead and may generate charge and spark which can lead to a fire and an explosion. They also should not be burned or incinerated which can result in an explosion and contamination of the environment.

In the near future, not recycling batteries will not be an available option. The lead-acid batteries have led the way in recycling, achieving over 95% recycling rates in many parts of the world such as in North America, Western Europe, and Japan. Emerging markets are also witnessing improving trends in recycling lead-acid batteries. Lead is relatively easy to recycle and recover as metallic lead. Currently, lead-acid batteries are recycled mainly using a high-temperature, pyrometallurgical process. A 10 000 ton per annum plant would be deemed small, with some plants processing 100 000 tons or even 200 000 tons of secondary lead per year.

In particular, the lead-acid battery recycling process stages are as follows:

- **Collection:** At repair workshops, garages, decontamination centers, clean points. The batteries and other lead-containing scrap are consolidated at intermediate agents or scrap dealers.

- **Transportation to appropriate plants.**

- **Materials preparation and sorting.**

- **Transportation to appropriate plants.**

- **Breakage:** Lead-acid batteries are composed of a variety of materials (Table 1.6), so they must be taken apart. Scrap batteries are broken apart in a hammer mill. The plastic casing (typically made of polypropylene, ebonite, and/or PVC) is shredded and recycled at extrusion plants. The sulfuric acid is also recovered and used in processes such as the manufacture of gypsum. Meanwhile, paste comprising lead sulfate ($PbSO_4$), and the lead metallic grids are extracted. In conventional lead recycling, the grids are normally added to the smelter; however, this is not always necessary, and instead they can be melted and refined at lower temperatures. Table 1.7 shows the typical composition of the lead-acid paste.

- **Neutralization:** Sodium hydroxide is added to the discharged battery paste to neutralize residual sulfuric acid and desulfurise, which avoids sulfur dioxide (SO_2) emissions during smelting. Aqueous sodium sulfate, possibly containing

Table 1.6 Typical composition of lead-acid battery [3].

Component	Wt.%
Lead–antimony alloy components (i.e., grids, poles, etc.)	25–30
Electrode paste	35–45
Sulfuric acid	10–15
Polypropylene	4–8
Other plastics (e.g., PVC, PE, etc.)	2–7
Ebonite	1–3
Other (e.g., glass, etc.)	<0.5

Table 1.7 Typical composition of lead-acid battery paste.

Material	Wt.%
Lead sufate	55–65
Lead dioxide	15–40
Lead monoxide	5–25
Metallic lead	1–5
Carbon black, plastics, fibers, other sulfates	1–4

some residual dissolved lead(II) together with colloidal particles, is then discharged. Depending on the country, the consent concentrations for this discharge to sewers range from a few ppm down to zero; the upper limits are likely to be decreased in the future.

- **Smelting or electrowinning:** The dry neutralized paste is usually smelted, along with the metallic grids, with a reducing agent in a high temperature Isasmelt or reverbatory or rotary furnace to produce lead. Coal or coke is the source of energy. The smelting takes place either in stand-alone reactors, or more often with lead concentrates derived from lead sulfide ores. Any lead or antimony slag is reheated with refining dross in a rotary furnace producing lead–antimony (Pb/Sb) alloy and waste slag. Instead of smelting, some large-scale operations dissolve the lead sludge/filter cake in powerful acids such as HCl, H_2SiF_6 or HBF_4 and recover lead by electrowinning.

- **Refining and blending:** A finished alloy is produced by adding the Pb/Sb alloy to the almost-pure lead metal in a refining and blending process.

- **Transport:** Assuming recycling and manufacture plants are separate entities, the lead then must be transported from the former to the latter.

- **New battery manufacture:** Recovered lead is reoxidized to PbO granules. Sulfuric acid (H_2SO_4) is added to the granules to form a paste applied to lead grids to manufacture new battery electrodes. After battery assembly, electrical energy is used to convert PbO to Pb in the anode and PbO_2 in the cathode. An overview of the lead-acid battery recycling process is given in Figure 1.14.

Over 90% of the lead from batteries can be extracted and reused, so with such high recovery rates, the secondary lead production is now a huge business. According to official estimates, more than 40% of the world's refined lead is now derived from secondary battery production. Table 1.8 presents some recycling input ratios (RIR) around the world. RIR quantify the contribution that recovered lead makes to the overall production of refined metal.

Lead-acid batteries are, in fact, one of the most efficiently recycled products in the world – albeit with varying environmental standards. In developed nations a variety of organized schemes are in operation. For example, Sweden, Germany, and Italy operate levy systems related to the lead market: when the lead price is so low that battery recovery is not economic, a levy is imposed on new batteries to finance recycling of used batteries. Italy and Ireland also have a national collection and recycling schemes. In the United States, many states require retailers to accept used car batteries when customers purchase new batteries. Several American states even require a cash deposit on new battery purchases, which is refunded to the consumer once the used battery is returned to the retailer. Elsewhere, battery collection is normally market driven. In the UK, for example, where organized systems do not exist, car repair shops and scrap metal dealers collect used batteries.

These RIR figures are based on official data collected from governments around the world. As such they are likely to underestimate true lead recovery rates because

Figure 1.14 Overview of the current lead-acid battery recycling process flow (Adapted from: Brandon *et al.* 2003; Exide/GNB Technologies Poster ["*Recycling for a Better Environment*"]).

Table 1.8 Apparent recycling input ratios (RIR) for lead in 2006.

Region	RIR
Europe	62.7%
Americas	74.2%
Asia	15.7%
World	41.6%

in many countries, especially in the developing world, the informal nature of lead recycling makes obtaining reliable data on secondary lead usage impossible. This is particularly true for Asian countries: lead is so highly priced there that it is likely that almost 100% of the metal from batteries is reused. Since formal data may not be fully available, the details are thus anecdotal.

The recycling record in other types of batteries has still a long way to go to catch up with what is achieved for the lead-acid batteries. All spent batteries represent a valuable resource of metals and materials, such as Ni, Cd, Ag, Co, polymers, carbon, and oxides. New legislations are being steadily introduced to encourage recycling of batteries. For example, in 2006 Directives on batteries and accumulators were adopted in the European Union. The Directive has set new national targets for nations within the EU for collection of consumer batteries. For example, according to this Directive, the UK is required to collect 25% by weight of batteries sold by 2012 and the target is set to increase to 46% by 2016. New infrastructures have to be made available that allow consumer batteries to be safely collected, sorted, and recycled.

Some countries are leading the way for recycling consumer batteries, such as Belgium which has already achieved a collection rate that is over 65%. Disposal of some batteries such as Ni–Cd can cause major environmental problems. Cd is toxic and can seep into the water supply. Ni is also semitoxic. Primary Li batteries are fire hazards, especially if they are not fully discharged. Most secondary Li batteries contain the toxic element Co. Both primary and the secondary Li batteries contain toxic and flammable electrolytes. It must be stated, however, that, in general, recovery of metals from batteries is energy intensive. Therefore is pressing need for further research for developing environmentally friendlier recycling technologies that do not give rise to an unsustainable energy penalty.

Having given a general overview of batteries, starting from their main components, and configuration, to how they function and are disposed of, specific battery systems can now be examined. The first two chapters that follow present a historic timeline describing the development of batteries from the first galvanic cells of the 1800s to the commercial cells of the 21st century. It will be seen that Li batteries are the most promising high energy storage devices and therefore Chapters 4–8 focus on the next-generation Li cathodes, anodes, and electrolytes that will significantly increase their lifetime and range of applications.

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