Chapter 9
Introduction to Electrochemical Energy Storage

9.1 Introduction

Among the various methods that can be used for the storage of energy that are discussed in this text, electrochemical methods, involving what are generally called *batteries*, deserve the most attention. They can be used for a very wide range of applications, from assisting the very large scale electrical grid down to tiny portable devices used for many purposes. Battery-powered computers, phones, music players, etc. are everywhere, and one of the currently hot topics involves the use of batteries in the propulsion of vehicles, hybrid autos, plug-in hybrids, and fully electric types.

Many students are put off from discussions of electrochemical systems because of unfamiliarity with electrochemistry. It will be shown here that one can understand the major phenomena and issues in electrochemical systems without considering their truly electrochemical features in detail. As an example, it will be shown that the driving forces of electrochemical cells are related to the driving forces between the electrically neutral components in the electrodes. Electrochemical considerations only come into play in certain features of their mechanisms.

Electrochemical energy storage involves the conversion, or *transduction*, of chemical energy into electrical energy, and vice versa. In order to understand how this works, it is first necessary to consider the *driving forces* that cause electrochemical transduction in electrochemical cells as well as the major types of *reaction mechanisms* that can occur.

This is followed by a brief description of the *important practical parameters* that are used to describe the behavior of electrochemical cells, and how the basic properties of such electrochemical systems can be modeled by the use of *simple equivalent electrical circuits*.

Also included in this chapter is a brief discussion of the principles that determine the major properties of electrochemical cells, their voltages, and their capacities.

R.A. Huggins, *Energy Storage*, DOI 10.1007/978-3-319-21239-5_9

9.2 Simple Chemical and Electrochemical Reactions

Consider a simple *chemical reaction* between two metallic materials A and B, which react to form an electronically conducting product AB. As discussed in Chap. 4, this can be represented simply by the relation

$$A + B = AB \tag{9.1}$$

The driving force for this reaction is the difference in the values of the *standard Gibbs free energy* of the products, only AB in this case, and the standard Gibbs free energies of the reactants, A and B.

If A and B are simple elements, this is called a *formation reaction*, and since the standard Gibbs free energy of formation of elements is zero, the value of the Gibbs free energy change that results per mol of the reaction is simply the *Gibbs free energy of formation* per mol of AB, that is:

$$\Delta G_{\mathrm{r}}^{\mathrm{o}} = \Delta G_{\mathrm{f}}^{\mathrm{o}}(\mathrm{AB}) \tag{9.2}$$

Values of this parameter for many materials can be found in a number of sources, e.g. [1].

While the morphology of such a reaction can take a number of forms, consider a simple one-dimension case in which the reactants are placed in direct contact and the product phase AB forms between them. The time sequence of the *evolution of the microstructure* during such a reaction is shown schematically in Fig. 9.1. Later times are at the bottom.

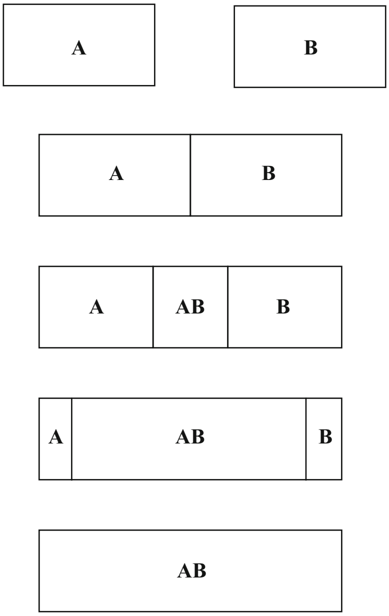

Fig. 9.1 Simple schematic model of the chemical reaction of A and B to form AB, indicating how the microstructure of the system varies with time

It is obvious that in order for the reaction product phase AB to grow, atoms of either A or B must move (*diffuse*) through it to reach its other side to come into contact with the other reactant. If, for example, A moves through the AB phase to the B side, additional AB will form at the AB/B interface. Since some B is consumed, the AB/B interface will move to the right. Also, since the amount of A on the A side has decreased, the A/AB interface will likewise move to the left. The AB will grow in width in the middle. One should note that the same thing will happen in the case that the species B, rather than the species A, moves through the AB phase in this process. There are experimental ways in which one can determine the identity of the moving species in this type of reaction, but it is not necessary to be concerned with them here.

Now suppose that this process occurs by an *electrochemical mechanism*. The time dependence of the microstructure in this case is shown schematically in Fig. 9.2. As in the chemical reaction case, the product AB must form as the result of a reaction between the reactants A and B. But there is an additional phase present in the system, an electrolyte.

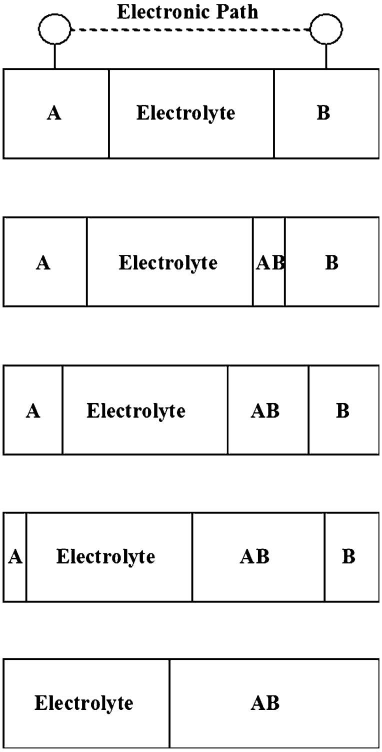

Fig. 9.2 Simple schematic model of the time evolution of the microstructure during the electrochemical reaction of A and B to form AB, a mixed conductor. In this case it is assumed that A^+ ions are the predominant ionic species in the electrolyte. To simplify the figure, the external electronic path is shown only at the start of the reaction

The *function of the electrolyte* is to *act as a filter* that allows the passage of ionic, but not electronic species. This means that the electrolyte contains ions of either A or B, or both, and is an *electronic insulator*.

But the reaction between A and B involves *electrically neutral atoms*, not just ions. This means that in order for the reaction to proceed there must be a path whereby electrons can also move through the system. This is typically an external electrical circuit that connects A and B. In the case that it is A that is transported in the system, and that the electrolyte contains A^+ ions, negatively charged electrons, e^-, must pass through the external circuit in equal numbers, or at an equal rate, to match the charge flux due to the passage of A^+ ions through the electrolyte to the other side.

During an electrochemical discharge reaction of the type illustrated in Fig. 9.2, the reaction at the interface between the phase A and the electrolyte can be written as

$$A = A^+ + e^- \tag{9.3}$$

with the A^+ ions moving into the electrolyte phase and the electrons entering the external circuit through a *current collector*. At the same time there will be a corresponding reaction on the other side of the electrolyte

$$A^+ + e^- = A \tag{9.4}$$

with ions arriving at the interface from the electrolyte and electrons coming to the interface from the external circuit through the electronic current collector. The result is to deposit A atoms onto the adjacent solid phase AB. The result is that the A/electrolyte interface and the electrolyte/AB interface both move incrementally to the left in Fig. 9.2. There must be *interdiffusion* of A and B atoms within the phase AB so that its surface does not have only A atoms. In addition, this phase must be an electronic conductor.

The fact that the overall reaction is between neutral species, and that this requires the concurrent motion of either A or B ions through the electrolyte, and electrons through external circuit, has several important consequences. One is that if flow in either the electronic path or the ionic path is impeded, the whole reaction must stop. For example, if the external electrical circuit is opened so that no electrons can flow through it, no ions can flow through the electrolyte, and the reaction halts. Likewise, if the flow of ions in the electrolyte is impeded—for example, by the presence of some material with a very high resistance for the moving ionic species, or a loss of contact between the electrolyte and the two materials on its sides—there will be no electronic current in the external circuit.

When the electronic circuit is open, and there is no current flowing, there must be a force balance operating upon the electrically charged ions in the electrolyte. A *chemical driving force* upon the mobile ionic species within the electrolyte in one direction is simply balanced by *an electrostatic driving force* in the opposite direction.

The *chemical driving force* across the cell is due to the difference in the chemical potentials of its two electrodes. It can be expressed as the *standard Gibbs free energy change per mol of reaction*, $\Delta G_r{}^\circ$. This is determined by the difference in the *standard Gibbs free energies of formation* of the products and the reactants in the *virtual chemical reaction* that would occur if the *electrically neutral* materials in the two electrodes were to react chemically. It makes no difference that the reaction actually happens by the transport of ions and electrons across the electrochemical system from one electrode to the other.

The electrostatic energy per mol of an electrically charged species is $-zFE$, where E is the voltage between the electrodes, and z is the *charge number* of the mobile ionic species involved in the virtual reaction. The charge number is the number of elementary charges that they transport. F is the *Faraday constant* (96,500 C per equivalent). An *equivalent* is *Avogadro's number* (1 mol) of electronic charges.

The balance between the chemical and electrical forces upon the ions under open circuit conditions can thus be simply expressed as a chemical energy–electrostatic energy balance

$$\Delta G_r^o = -zFE \tag{9.5}$$

Here the value of ΔG_r^o is in Joules per mol of reaction, as 1 J is the product of 1 C and 1 V.

Thus this is an interesting situation in which a chemical reaction between neutral species in the electrodes determines the forces upon charged particles in the electrolyte in the interior of an electrochemical system.

If it is assumed that the electrodes on the two sides of the electrolyte are good electronic conductors, there is an externally measurable voltage E between the points where the external electronic circuit contacts the two electrodes. As the result of this voltage, electrical work can be done by the passage of electrons in an external electric circuit if ionic current travels through the electrolyte inside the cell.

Thus this simple electrochemical cell can act as a *transducer* between chemical and electrical quantities; forces, fluxes, and energy. In the ideal case, the chemical energy reduction due to the chemical reaction that takes place between A and B to form mixed-conducting AB is just compensated by the electrical energy transferred to the external electronic circuit.

The flow of both internal ionic species and external electrons can be reversed if a voltage is imposed in the electronic path in the opposite direction that is larger than the voltage that is the result of the driving force of the chemical reaction. Since this causes current to flow in the reverse direction, electrical energy will be consumed and the chemical energy inside the system will increase. This is what occurs when an electrochemical system is recharged.

From these considerations it is obvious that it is not important whether the ionic species are related to element A or to element B. However, the answer to this question will influence the configuration of the cell. The example illustrated schematically in Fig. 9.2 deals with the case in which there are predominantly A^+ ions in the electrolyte. The chemical reaction proceeds by the transport of A^+ ions across the electrolyte and electrons in the external circuit from the left (A) side of the cell to the right-hand side. This involves two electrochemical reactions. On the left side, A atoms are converted to A^+ ions and electrons at the A/electrolyte interface. The electrons travel back through the metallic A and go out into the external electronic circuit. The reverse electrochemical reaction takes place on the other side of the cell. A^+ ions from the electrolyte combine with electrons that have come through the external circuit to form neutral A at the electrolyte/AB interface.

As before, the physical locations of the interfaces, the A/electrolyte interface, the electrolyte/AB interface and the AB/B interface, will move with time as the amounts of the various species in the different phases vary with the extent of the reaction.

It must be recognized that the reaction product AB will not form unless there is a mechanism that allows the newly-arrived A to react with B atoms to form AB. Thus the transport of either A or B atoms within the AB product phase is necessary in this case, as it was in the chemical reaction case illustrated in Fig. 9.1 above. If this did not happen, pure A would be deposited at the right hand electrolyte interface. The chemical composition on both sides of the electrolyte would then be the same, and there would be no driving force to cause further transport of ionic species through the electrolyte, and thus no external voltage.

If B^+ ions, rather than A^+ ions, are present in the electrolyte, so that B species can flow from right to left, the direction of electron flow, and thus the voltage polarity, in the external circuit will be opposite from that discussed above, and the reaction product will form on the left side, rather than on the right side.

It is also possible, of course, that the ions in the electrolyte are negatively charged. In that case, the direction of electron flow in the external circuit will be in the opposite direction.

In any case, it is important to realize that the basic driving force in an electrochemical cell is a *chemical reaction of neutral species* to form an *electrically neutral product*. This is why one can use standard chemical thermodynamic data to understand the equilibrium (no current, or open circuit) potentials and voltages in electrochemical cells.

For any given chemical reaction, the open circuit voltage is independent of the identity of the species in the electrolyte and the details of the reactions that take place at the electrode/electrolyte interfaces.

The situation becomes different if one considers the kinetic behavior of electrochemical cells, for then one has to be concerned with phenomena at all of the interfaces, as well as in the electrodes, the electrolyte, and the external circuit. Such matters will be discussed in some detail later.

9.3 Major Types of Reaction Mechanisms in Electrochemical Cells

As discussed above, the operation of electrochemical cells involves the transport of neutral chemical species into and out of the electrodes, their ionic parts move through the electrolyte, and the charge-balancing electrons move through the external electrical circuit. In many, but not all, cases, this results in changes in the chemical constitution of electrodes, i.e., the amounts and chemical compositions of the phases present.

The result is that the microstructure of one or more of the electrode materials gets significantly changed, or *reconstituted*. There are a number of important chemical, and thus possible electrochemical, reactions in which some phases grow and others disappear.

Reactions in which there is a change in the identity or amounts of the phases present are designated as *reconstitution reactions*.

Phase diagrams are useful *thinking tools* to help understand these types of phenomena. As discussed in Chap. 4, they are graphical representations that indicate the phases and their compositions that are present in a materials system under equilibrium conditions, and were often called *constitution diagrams* in the past. In Chap. 4 the discussion was focused upon phenomena that occur as the result of changes in the temperature. Electrochemical systems, on the other hand, generally operate at a constant temperature, i.e., isothermally. This involves consideration of what occurs as the composition moves horizontally, rather than vertically, across phase diagrams.

Two major types of reconstitution reactions that are relevant to electrochemical systems will be briefly mentioned here, *formation reactions* and *displacement reactions*. This will be followed by an introduction to *insertion reactions*, which play a major role in the operation of electrodes in a number of important modern battery systems.

9.3.1 Formation Reactions

The simple example that was discussed earlier in this chapter, represented by the equation

$$A + B = AB \tag{9.6}$$

is a *formation reaction*, in which a new phase AB is formed in one of the electrodes from its atomic constituents. This can result from the transport of one of the elements, e.g., A, passing across an electrochemical cell through the electrolyte from one electrode to react with the other component in the other electrode. Since

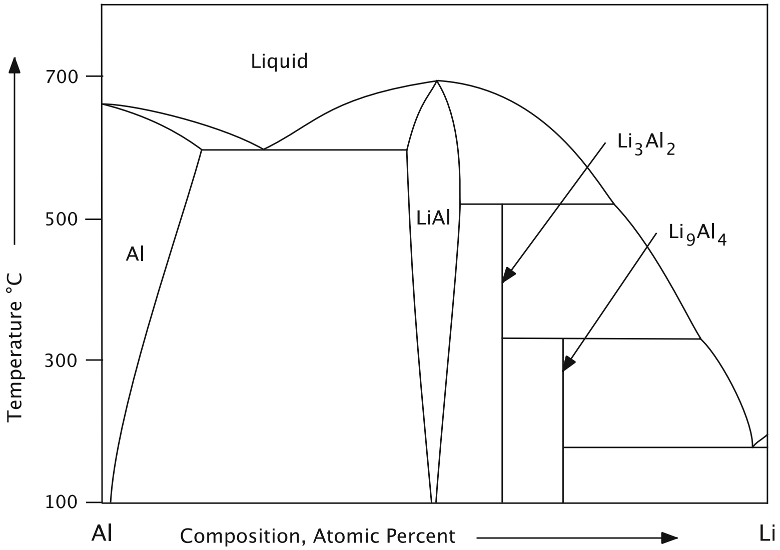

Fig. 9.3 Equilibrium phase diagram of the aluminum–lithium system

this modifies the microstructure, it is an example of one type of *reconstitution* reaction.

There are many examples of this type of formation reaction. There can also be subsequent additional formation reactions whereby other phases can be formed by further reaction of an original product.

As an example, consider the reaction of lithium with aluminum. Lithium-aluminum alloys were explored for use as electrodes in high temperature lithium batteries some time ago [2, 3], and their critical thermodynamic and kinetic properties were studied by the use of molten salt electrolyte electrochemical cells [4–6].

The reactions in this alloy system can be understood by use of the *lithium–aluminum system* phase diagram, as shown in Fig. 9.3.

Assume that the negative electrode is lithium and the positive electrode is initially pure aluminum. Upon the imposition of current by making lithium positively, and aluminum negatively charged, lithium ions pass across the cell and react with the aluminum in the positive electrode, changing its chemical composition. If this were to happen at 100 °C, the lowest temperature in Fig. 9.3, and it could be assumed that equilibrium conditions can readily be attained, it can be seen that a solid solution is initially formed, in which a small amount of lithium dissolves into the aluminum.

As more lithium is passed across the cell the solubility limit of lithium in aluminum is reached, and the composition moves into a region of the phase diagram in which both the lithium-saturated aluminum phase Al_{sat} and a new phase “LiAl” are present in the positive electrode. The quotation marks are used here, for the composition of the phase is not exactly 1:1 Li/Al. Thus in this part of the phase diagram the formation reaction

$$\mathrm{Li} + \mathrm{Al}_{\mathrm{sat}} = \text{“LiAl”} \tag{9.7}$$

takes place. As more lithium passes across the electrochemical cell, the overall composition traverses the two-phase $\mathrm{Al}_{\mathrm{sat}}$ + “LiAl” region, more “LiAl” is formed, and the amount of $\mathrm{Al}_{\mathrm{sat}}$ decreases. By the time the overall composition reaches the low-Li boundary of the “LiAl” region, there is no more of the $\mathrm{Al}_{\mathrm{sat}}$ present.

The addition of more lithium causes the overall composition to go across the range of the “LiAl” phase. Thereafter, there is another two-phase formation reaction

$$\mathrm{Li} + \text{“LiAl”} = \mathrm{Li_3Al_2} \tag{9.8}$$

that is later followed by the reaction

$$\mathrm{Li} + \mathrm{Li_3Al_2} = \mathrm{Li_9Al_4} \tag{9.9}$$

as more lithium reacts with the structure that results from reaction (9.8).

The electrical potential varies with the chemical composition of electrodes in the Li-Al alloy system, as well as others that exhibit either ranges of solid solution or multi-phase reactions. This will be discussed in substantial detail in later chapters.

It is also not necessary that both reactants in formation reactions are solids or liquids, of course. For example, the phase LiCl can result from the reaction of lithium with chlorine gas, and ZnO can form as the result of the reaction of zinc with oxygen in the air. $\mathrm{Zn/O_2}$ cells, in which ZnO is formed, are commonly used as the power source in hearing aids.

9.3.2 Displacement Reactions

As discussed in Chap. 4, another type of *reconstitution reaction* involves a *displacement* process, which can be simply represented as

$$\mathrm{A} + \mathrm{BX} = \mathrm{AX} + \mathrm{B} \tag{9.10}$$

in which species A displaces species B in the simple binary phase BX, to form AX instead. A new phase consisting of elemental B will be formed in addition. There will be a driving force causing this reaction to tend to occur if phase AX has a greater stability, i.e., has a more negative value of $\Delta G_f{}^\circ$, than the phase BX. An example of this type that was discussed in Chap. 4 was

$$Li + Cu_2O = Li_2O + Cu \tag{9.11}$$

in which the reaction of lithium with Cu_2O results in the formation of two new phases, Li_2O and elemental copper.

A change in the chemical state in the electrode results in a change in its electrical potential, of course. The relation between the chemical driving forces for such reactions, and the related electrical potentials, will be discussed for this case in later chapters.

9.3.3 Insertion Reactions

Again, as mentioned in Chap. 4, a quite different type of reaction mechanism can also occur in materials in chemical and electrochemical systems. This involves the *insertion* of guest species into normally unoccupied interstitial sites in the crystal structure of an existing stable host material. Although the chemical composition of the host phase initially present can be changed substantially, this type of reaction does not result in a change in the identity, the basic crystal structure, or amounts of the phases in the microstructure. However, in most cases the addition of interstitial species into previously unoccupied locations in the structure causes a change in volume. This involves mechanical stresses, and mechanical energy. The mechanical energy related to the insertion and extraction of interstitial species plays a significant role in the hysteresis, and thus energy loss, observed in a number of reversible battery electrode reactions.

In the particular case of the insertion of species into materials with layer-type crystal structures, insertion reactions are sometimes called *intercalation reactions*. Such reactions, in which the composition of an existing phase is changed by the incorporation of guest species, can also be thought of as a solution of the guest into the host material. Therefore, such processes are also sometimes called *solid solution reactions*.

Generally, the incorporation of such guest species occurs *topotactically*. This means that the guest species tend to be present at specific (low energy) locations inside the crystal structure of the host species, rather than being randomly distributed.

A simple reaction of this type might be the reaction of an amount x of species A with a phase BX to produce the product A_xBX. This can be written as

$$xA + BX = A_xBX \tag{9.12}$$

for such a case. The solid solution phase can have a range of composition, i.e., a range of values of x. As an example, the incorporation of lithium into TiS_2 produces a product in which the value of x can extend from 0 to 1. This was an important early example of this type of insertion reaction [7], and it can be simply represented as

$$x\mathrm{Li} + \mathrm{TiS}_2 = \mathrm{Li}_x\mathrm{TiS}_2 \tag{9.13}$$

It is also possible to have a *displacement reaction* occur by the replacement of one interstitial species by another inside a stable host material. In this case, only one additional phase is formed, the material that is displaced. The term *extrusion* is sometimes used to describe this process.

In some cases, the new element or phase that is formed by such an *interstitial displacement process* is *crystalline*, whereas in other cases, it can be *amorphous*.

9.4 Important Practical Parameters

When considering the use of electrochemical energy storage systems in various applications, it is important to be aware of the properties that might be relevant, for they are not always the same in every case.

The energy and power available per unit weight, called the *specific energy* and *specific power*, are of great importance in some applications, such as vehicle propulsion.

On the other hand, the amount of energy that can be stored per unit volume, called the *energy density*, can be more important in some other areas of application. This is often the case when such devices are being considered as power sources in portable electronic devices, such as cellular telephones, portable computers, and video camcorders.

The power per unit volume, called the *power density*, can also be especially important for some uses, such as cordless power tools, whereas in others the *cycle life*—the number of times that a device can be effectively recharged before its performance, e.g., its capacity, or perhaps its output kinetics, is degraded too far—is critical. In addition, cost is always of concern, and sometimes can be of overriding importance, even at the expense of reduced performance.

Methods will be described later that allow the determination of the maximum theoretical values of some of these parameters, based upon the properties of the materials in the electrodes alone. However, practical systems never achieve these maximum theoretical values, but instead, often provide much lower performance. One obvious reason is that a practical battery has a number of passive components that are not involved in the basic chemical reaction that acts as the energy storage mechanism. These include the electrolyte, a separator that mechanically prevents the electrodes from coming into contact, the current connectors that transport electrical current to and from the interior of the cell, and the container. In addition, the effective utilization of the active components in the chemical reaction is often less than optimal. Electrode reactant materials can become electronically disconnected, or shielded from the electrolyte. When that happens they cannot participate in the electrochemical reaction, and have to be considered passive. They add to the weight and volume, but do not contribute to the transduction between electrical and chemical energy.

Table 9.1 Approximate values of the practical specific energy and energy density of some common battery systems

System	Specific energy (Wh/kg)	Energy density (Wh/l)
Pb/PbO_2	40	90
Cd/Ni	60	130
Hydride/Ni	80	215
Li-Ion	135	320

A rule of thumb that was used for a number of the conventional aqueous electrolyte battery systems was that a practical cell could only produce about 1/5 to 1/4 of its maximum theoretical specific energy. Optimization of a number of factors has made it now possible to exceed such values in a number of cases. In addition, the maximum theoretical values of some of the newer electrochemical systems are considerably higher than those that were available earlier.

Some rough values of the practical *energy density* (Wh/l) and *specific energy* (Wh/kg) of several of the common rechargeable battery systems are listed in Table 9.1. These particular values should not be taken as definitive, for they depend upon a number of operating factors and vary with the designs of different manufacturers. Nevertheless, they indicate the wide range of these parameters available commercially from different technologies.

In addition to their energy capacity, another important parameter relating to the practical use of batteries is the amount of power that they can supply. This is often expressed as specific power, the amount of power per unit weight, and it is very dependent upon the details of the design of the cell, as well as the characteristics of the reactive components. Therefore, values vary over a wide range.

The characteristics of batteries are often graphically illustrated by the use of *Ragone plots*, in which the specific power is plotted versus the specific energy. This type of presentation was named after David V. Ragone, who was the chairman of a governmental committee that wrote a report on the relative properties of different battery systems many years ago. Such a plot, including very approximate data on three current battery systems, is shown in Fig. 9.4.

9.4.1 The Operating Voltage and the Concept of Energy Quality

In addition to the amount of energy stored, another important parameter of a battery system is the voltage at which it operates, both during discharge, when it supplies electrical energy and power, but also when it is being recharged.

As discussed earlier in this chapter, the open circuit, or equilibrium, cell voltage is primarily determined by the thermodynamics of the chemical reaction between the components in the electrodes, for this reaction determines the driving force for the transport of ions through the electrolyte, and electrons through the external

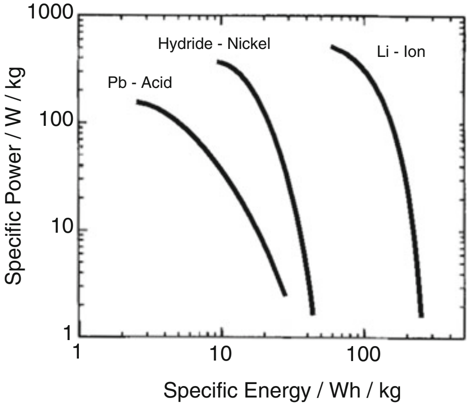

Fig. 9.4 Ragone plot showing approximate practical values of specific power and specific energy of three common battery systems

circuit. During actual use, however, the operating voltage will vary from these theoretical values, depending upon various kinetic factors. These will be discussed extensively later in this text.

In discussing electrochemical energy storage it is useful to consider another parameter, its *quality*, and how it matches the expected applications. The concept of *energy quality* is analogous to the concept of *heat quality* that is well known in engineering thermodynamics.

It is widely recognized that high temperature heat is often more useful (e.g., has higher quality) than low temperature heat in many applications. Similarly, the usefulness of electrical energy is often related to the voltage at which it is available. High voltage energy is often more useful (has higher quality) than low voltage energy. For example, in simple resistive applications the electrical power P is related to the practical (not just theoretical) voltage E and the resistance R by

$$P = E^2/R \tag{9.14}$$

Thus the utility of an electrochemical cell in powering a light source or driving an electric motor is particularly voltage-sensitive. Because of the square relation, high voltage stored energy has a much higher quality for such applications than low voltage stored energy.

Rough energy quality rankings can be tentatively assigned to electrochemical cells on the basis of their output voltages as follows:

3.0–5.5 V	High quality energy
1.5–3.0 V	Medium quality energy
0–1.5 V	Low quality energy

There are a number of applications in which a high voltage is required. One example is the electrical system used to propel either hybrid- or all-electric vehicles. Auto manufacturers typically wish to operate such systems at over 200 V. For this type of high voltage application it is desirable that individual cells produce the highest possible voltage, for the greater the voltage of each individual cell, the fewer cells are necessary. There is also the movement toward the use of 36 or 42 V systems, instead of the current 12 V batteries, for the starter, lighting and ignition systems in normal internal combustion engine automobiles, as mentioned earlier.

Despite the implications of this matter of energy quality, it is important that the voltage characteristics of electrochemical energy storage systems *match the requirements of the intended application*. It is not always best to have the highest possible cell voltage, for it can be wasteful if it is too high in some applications.

A further matter that can become especially important in some applications is safety, and this can be a potential problem with some high potential electrode materials. As a result, development efforts aimed at large batteries for vehicle traction applications have been investigating materials that sacrifice some cell voltage to obtain greater safety.

9.4.2 The Charge Capacity

The *energy contained* in an electrochemical system is the integral of the voltage multiplied by the *charge capacity*, i.e., the amount of charge available. That is,

$$\text{Energy} = \int E dq \tag{9.15}$$

where E is the output voltage, which can vary with the state of charge as well as kinetic parameters, and q is the amount of electronic charge that can be supplied to the external circuit.

Thus it is important to know the maximum capacity, the amount of charge that can theoretically be stored in a battery. As in the case of the voltage, the maximum amount of charge available under ideal conditions is also a thermodynamic quantity, but it is of a different type. Whereas voltage is an *intensive quantity*, independent of the amount of material present, charge capacity is an *extensive quantity*. The amount of charge that can be stored in an electrode depends upon the amount of material in it. Therefore, capacity is always stated in terms of a measure such as the number of Coulombs per mol of material, per gram of electrode weight, or per ml of electrode volume.

The *state of charge* is the current value of the fraction of the maximum capacity that is still available to be supplied.

9.4.3 The Maximum Theoretical Specific Energy (MTSE)

Consider a simple insertion or formation reaction that can be represented as

$$xA + R = A_xR \tag{9.16}$$

where x is the number of moles of A that reacts per mol of R. It is also the number of elementary charges per mol of R. If E is the average voltage of this reaction, the theoretical energy involved in this reaction follows directly from Eq. (9.15). If the energy is expressed in Joules, it is the product of the voltage in volts and the charge capacity, in Coulombs, involved in the reaction.

If W_t is the sum of the molecular weights of the reactants engaged in the reaction, the maximum theoretical specific energy (MTSE), the energy per unit weight, is simply

$$\text{MTSE} = (xE/W_t)F \tag{9.17}$$

MTSE is in J/g, or kJ/kg, when x is in equivalents per mol, E is in volts, and W_t is in g/mol. F is the Faraday constant, 96,500 C per equivalent.

Since 1 W is 1 J per second, 1 Wh is 3.6 kJ, and the value of the MTSE can be expressed in Wh/kg as

$$\text{MTSE} = 26{,}805(xE/W_t) \tag{9.18}$$

9.4.4 Variation of the Voltage as Batteries Are Discharged and Recharged

Looking into the literature, it is seen that the voltage of most—but not all—electrochemical cells varies as their chemical energy is deleted. That is, as they are discharged. Likewise, it changes in the reverse direction when they are recharged. That may not be a surprise. However, not only the voltage ranges but also the characteristics of these state of charge-dependent changes vary widely between different electrochemical systems. It is important to understand what causes these variations.

A characteristic way to present this information is in terms of *discharge curves* and *charge curves*, in which the cell voltage is plotted as a function of the state of charge. These relationships can vary greatly, depending upon the rate at which the energy is extracted from, or added to, the cell.

It is useful to consider the maximum values, the relation between the cell voltage, and the state of charge under equilibrium or near-equilibrium conditions. In this case, a very useful experimental technique, known as *Coulometric titration*, can provide a lot of information. This will be described in a later section.

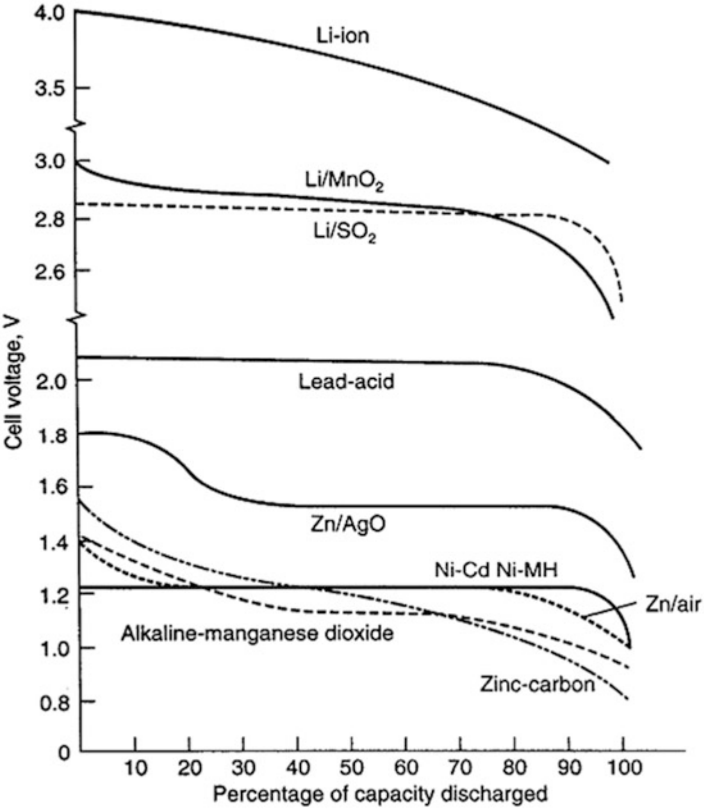

Fig. 9.5 Examples of battery discharge curves, showing the variation of the voltage shown as a function of the fraction of their available capacity

Some examples of discharge curves under low current, or near-equilibrium, conditions are shown in Fig. 9.5. These are presented here to show the cell voltage as a function of the state of charge parameter. However, different battery systems have different capacities. Thus one has to be careful to not compare the energies stored in different systems in this manner.

The reason for presenting the near-equilibrium properties of these different cells in this way is to show that there are significant differences in the *types* of their behavior, as indicated by the shapes of their curves. It can be seen that some of these discharge curves are essentially flat. Some have more than one flat region, and others have a slanted and stretched S-shape, sometimes with an appreciable slope, and sometimes not. These variants can be simplified into three basic types of discharge curve shapes, as depicted in Fig. 9.6. The reasons behind their general characteristics will be discussed later.

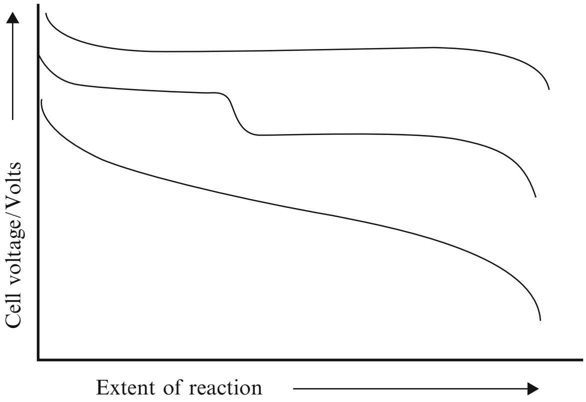

Fig. 9.6 Schematic representation of different types of discharge curves

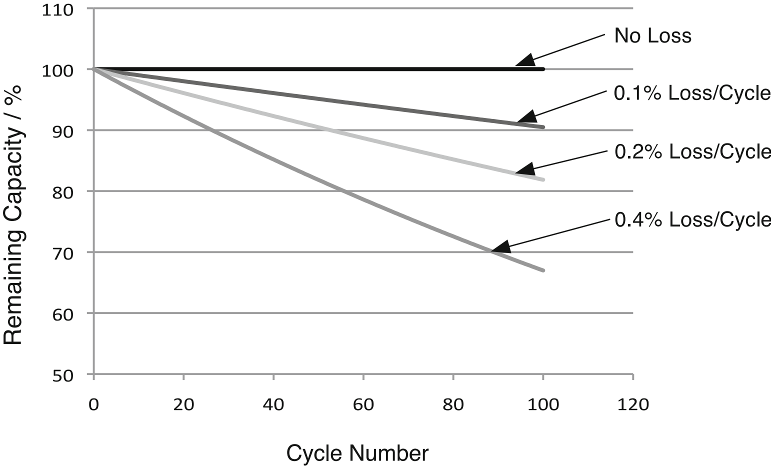

Fig. 9.7 Influence of Coulombic efficiency upon available capacity during cycling

9.4.5 Cycling Behavior

In many applications a battery is expected to maintain its major properties over many discharge–charge cycles. This can be a serious practical challenge and is often given a lot of attention during the development and optimization of batteries. Figure 9.7 shows how the initial capacity is reduced during cycling, assuming three different values of the *Coulombic efficiency*—the fraction of the prior charge capacity that is available during the following discharge. This depends upon a number of factors, especially the current density and the depth of discharge in each cycle.

It is seen that even a minor amount of inefficiency per cycle can have important consequences. For example, 0.1 % loss per cycle causes the available capacity to drop to only 90 % of the original value after 100 cycles. The situation is worse if the Coulombic efficiency is lower.

Applications that involve many cycles of operation require that cells are designed and constructed such that the capacity loss per cycle is extremely low. This typically means that compromises must be made in other properties. *Supercapacitors* are expected to be used over a very large number of cycles, and they typically have much lower values of specific energy than electrochemical cells which are used for applications in which the amount of energy stored is paramount.

9.4.6 Self-Discharge

Another property that can be of importance in practical cells is called *self-discharge*. Evidence for this is a decrease in the available capacity with time, even without energy being taken from the cell by the passage of current through the external circuit. This is a serious practical problem in some systems, and is negligible in others.

The main point to understand at this juncture is that the capacity is a property of the electrodes. Its value at any time is determined by the remaining available extent of the chemical reaction between the neutral species in the electrodes. Any self-discharge mechanism that reduces the remaining capacity must involve a reduction in either the transport of neutral species, or the concurrent transport of neutral combinations of charged species, through the cell. If such a process involves the transport of charged species, it is *electrochemical self-discharge*.

There are also several ways in which individual neutral species can move from one electrode to the other across a cell. These include transport through an adjacent vapor phase, through cracks in a solid electrolyte, or as a dissolved gas in a liquid electrolyte. Since the transport of charged species is not involved in these processes. They produce *chemical self-discharge*.

It is also possible that impurities can react with constituents in the electrodes or the electrolyte so as to reduce the available capacity with time.

9.5 General Equivalent Circuit of an Electrochemical Cell

It is often useful to devise electrical circuits whose electrical characteristics are analogous to the behavior of important phenomena in physical systems. By examination of the influence of changes in the parameters in such *equivalent circuits*, they can be used as *thinking tools* to obtain useful insight into the significance of particular phenomena to the observable properties of complex physical systems. By use of this approach, the techniques of circuit analysis that have been developed for

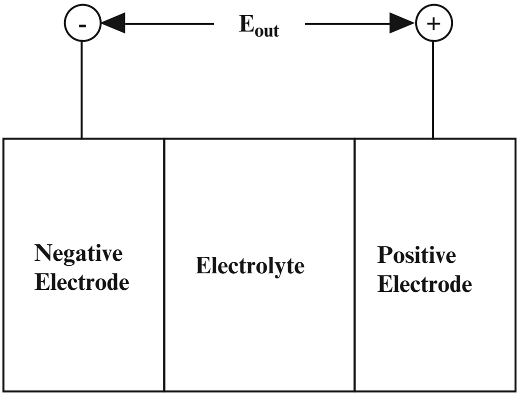

Fig. 9.8 Simplified physical model of electrochemical cell

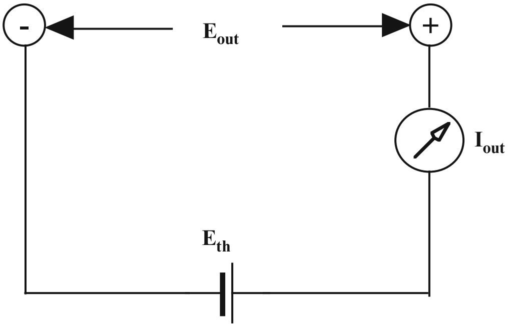

Fig. 9.9 Simple equivalent circuit model of an ideal electrochemical cell

use in various branches of electrical engineering can be very helpful in the analysis of interdependent physical phenomena.

This procedure has proven to be very useful in some areas of electrochemistry, and will be utilized later in this text for a number of purposes. At this point, however, it will only be considered for the case of an ideal electrochemical cell. It will show what happens if the electrolyte is not a perfect filter, and also allows the flow of some electronic current in addition to the expected ionic current through the electrolyte. An electrochemical cell can be simply modeled as shown in Fig. 9.8, and the basic equivalent circuit as shown in Fig. 9.9.

The value of the electrical equivalent of the theoretical chemical driving force is E_{th}, which is given by

$$E_{\mathrm{th}} = -\Delta G_{\mathrm{r}}^{\circ}/zF \tag{9.19}$$

as the result of the balance between the chemical and electrical forces acting upon the ionic species in the electrolyte, as mentioned earlier. If there are no impedances or other loss mechanisms, the externally measurable cell voltage E_{out} is simply equal to E_{th}.

9.5.1 Influence of Impedances to the Transport of Ionic and Atomic Species Within the Cell

In practical electrochemical cells E_{out} is not always equal to E_{th}. There can be several possible reasons for this disparity. There will always be some impedance to the transport of the electroactive ions and the related atomic species across the cell. One source is the resistance of the electrolyte to ionic transport. There may also be significant impeding effects at one or both of the two electrolyte/electrode interfaces. Furthermore, there can be a further impedance to the progress of the cell reaction in some cases related to the time-dependent solid state diffusion of the atomic species into, or out of, the electrode microstructure.

Note that *impedances* are used in this discussion instead of resistances, because they can be time-dependent if time-dependent changes in structure or composition are occurring in the system. The impedance is the instantaneous ratio of the applied force (e.g., voltage) E_{appl} and the response (e.g., current) across any circuit element. As an example, if a voltage E_{appl} is imposed across a material that conducts electronic current I_{e}, the electronic impedance Z_{e} is given by

$$Z_{\mathrm{e}} = E_{\mathrm{appl}}/I_{\mathrm{e}} \tag{9.20}$$

The inverse of the impedance is the *admittance*, which is the ratio current/voltage. Under steady-state (time-independent) DC conditions, the impedance and resistance of a circuit element are equivalent.

If current is flowing through the cell, there will be a voltage drop related to each of the impedances to the flow of ionic current within the cell. Thus if the sum of these internal impedances is Z_{i} the output voltage can be written as

$$E_{\mathrm{out}} = E_{\mathrm{th}} - I_{\mathrm{out}}Z_{\mathrm{i}} \tag{9.21}$$

This relationship can be modeled by the simple circuit in Fig. 9.10.

9.5.2 Influence of Electronic Leakage Through the Electrolyte

The output voltage E_{out} can also be different from the theoretical electrical equivalent of the thermodynamic driving force of the reaction between the neutral species in the electrodes E_{th} even if there is no external current I_{out} flowing. This

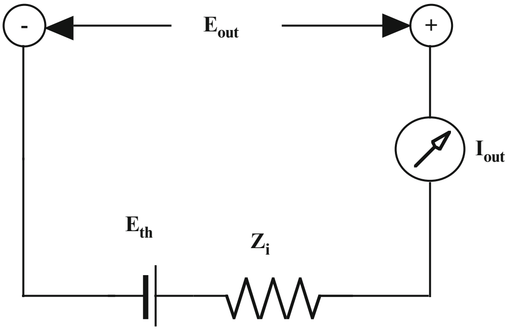

Fig. 9.10 Simple equivalent circuit for a battery or fuel cell indicating the effect of the internal ionic impedance Z_i upon the output voltage

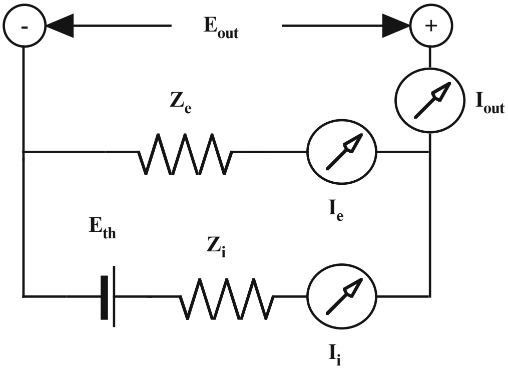

Fig. 9.11 Modified circuit including electronic leakage through the electrolyte

can be the result of electronic leakage through the electrolyte that acts to short-circuit the cell. This effect can be added to the previous equivalent circuit to give the circuit shown in Fig. 9.11.

It is evident that, even with no external current, there is an internal current related to the transport of the electronic species through the electrolyte I_e. Since the current must be the same everywhere in the lower loop, there must be a current through the electrolyte I_i with the same magnitude as the electronic current. There must be *charge flux balance* so that there is no net charge buildup at the electrodes.

The current through the internal ionic impedance Z_i generates a voltage drop, reducing the output voltage E_{out} by the product I_i Z_i, which is equal to I_eZ_e.

$$E_{out} = E_{th} - I_iZ_i \tag{9.22}$$

In addition, the fact that both ionic and electronic species flow through the cell means that this is a mechanism of *self-discharge*. This results in a decrease of the available charge capacity of the cell.

9.5.3 Transference Numbers of Individual Species in an Electrochemical Cell

If more than one species can carry charge in an electrolyte, it is often of interest to know something about the relative conductivities or impedances of different species. The parameter that is used to describe the contributions of individual species to the transport of charge when an electrical potential difference (voltage) is applied across an electrolyte is the transference number. This is defined as the fraction of the total current that passes through the system that is carried by a particular species.

In the simple case that electrons and one type of ion can move through the electrochemical cell, we can define the transference number of ions as t_i, and electrons as t_e, where

$$t_i = I_i/(I_i + I_e) \tag{9.23}$$

and

$$t_e = i_e/(I_i + I_e) \tag{9.24}$$

and I_i and I_e are their respective partial currents upon the application of an external voltage E_{appl} across the system. It can readily be seen that the sum of the transference numbers of all mobile charge-carrying species is unity. In this case:

$$t_i + t_e = 1 \tag{9.25}$$

Instead of expressing transference numbers in terms of currents, they can also be written in terms of impedances. For the case of these two species, the transport of charge by the motion of the ions under the influence of an applied voltage E_{appl},

$$t_i = \left(E_{appl}/Z_i\right)/\left[\left(E_{appl}/Z_i\right) + \left(E_{appl}/Z_e\right)\right] = Z_e/(Z_i + Z_e) \tag{9.26}$$

and likewise for electrons:

$$t_e = Z_i/(Z_i + Z_e) \tag{9.27}$$

Whereas these parameters are often thought of as properties of the electrolyte, in actual experiments they can also be influenced by what happens at the interfaces between the electrolyte and the electrodes, and thus are properties of the whole electrode-electrolyte system. They are only properties of the electrolyte alone if there is no impedance to the transfer of either ions or electrons across the electrolyte/electrode interface or atomic and electronic species within the electrodes.

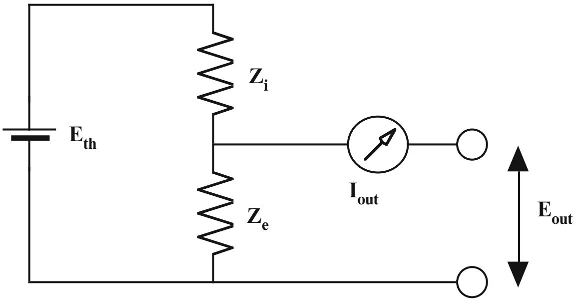

Fig. 9.12 Different representation of general equivalent circuit

9.5.4 Relation Between the Output Voltage and the Values of the Ionic and Electronic Transference Numbers

Making the simplifying assumption that the internal impedance is primarily due to the behavior of the ions, the general equivalent circuit of Fig. 9.10 can be rearranged to look like that in Fig. 9.12.

When drawn this way, it can be readily seen that the series combination of Z_i and Z_e acts as a simple voltage divider.

If no current passes out of the system, i.e., under open circuit conditions, the output voltage is equal to the product of E_{th} and the ratio $Z_e/(Z_i + Z_e)$.

$$E_{out} = E_{th} Z_e / (Z_i + Z_e) \tag{9.28}$$

Introducing Eq. (9.26), the output voltage can then be expressed as

$$E_{out} = E_{th} t_i \tag{9.29}$$

or

$$E_{out} = E_{th}(1 - t_e) \tag{9.30}$$

These are well-known relations that can be derived in other ways, as will be shown later. It is clear that the output voltage is optimized when t_i is as close to unity as possible.

9.5.5 Joule Heating Due to Self-Discharge in Electrochemical Cells

Electrochemical self-discharge causes heat generation, often called *Joule heating,* due to the transport of charged species through the cell. The *thermal power* P_{th} caused by the passage of a current through a simple resistance R is given by

$$P_{\mathrm{th}} = I^2 R \tag{9.31}$$

But as shown earlier, if self-discharge results from the leakage of electrons through the electrolyte there must be both electronic and ionic current, and they must have equal values. Thus the thermal power due to this type of self-discharge is:

$$P_{\mathrm{th}} = I_{\mathrm{i}}^2 Z_{\mathrm{i}} + I_{\mathrm{e}}^2 Z_{\mathrm{e}} = I_{\mathrm{e}}^2 (Z_{\mathrm{i}} + Z_{\mathrm{e}}) \tag{9.32}$$

Measurements of the rate of heat generation by Joule heating under open circuit conditions can be used to evaluate the rate of self-discharge in practical cells.

9.5.6 What If Current Is Drawn from the Cell?

If current is drawn from the cell into an external circuit, the normal mode of operation when chemical energy is converted into electrical energy, it flows through the ionic impedance, Z_{i}. This results in an additional voltage drop of $I_{\mathrm{out}}\,Z_{\mathrm{i}}$, further reducing the output voltage. If there were no electrochemical self-discharge, this can be written as

$$E_{\mathrm{out}} = E_{\mathrm{th}} t_{\mathrm{i}} - I_{\mathrm{out}} Z_{\mathrm{i}} \tag{9.33}$$

The value of the ionic impedance of the system, Z_{i}, may increase with the value of the output current as the result of current-dependent impedances at the electrolyte/electrode interfaces. The difference between E_{th} and E_{out} is often called *polarization* in the electrochemical literature.

The result of the presence of current-dependent interfacial impedances to the passage of ionic species that increase Z_{i} is that the *effective transference number* of the ions t_{i} is reduced, since $t_{\mathrm{i}} = Z_{\mathrm{e}}/(Z_{\mathrm{i}} + Z_{\mathrm{e}})$. This causes an additional reduction in the output voltage.

But in addition to a *reduced output voltage*, there will also be additional *heat generation*. The total amount of Joule heating is the sum of that due to the passage of current into the external circuit I_{ext} and that due to electrochemical self-discharge.

$$P_{\mathrm{th}} = I_{\mathrm{ext}}^2 Z_{\mathrm{i}} + I_{\mathrm{e}}^2 (Z_{\mathrm{i}} + Z_{\mathrm{e}}) \tag{9.34}$$

In most cases, the first term is considerably larger than the second term.

Measured discharge curves vary with the current density as conditions deviate farther and farther from equilibrium. This is shown schematically in Fig. 9.13.

A parameter that is often used to indicate the rate at which a battery is discharged is the so-called *C*-Rate. The discharge rate of a battery is expressed as *C*/*R*, where *R* is the number of hours required to completely discharge its nominal capacity.

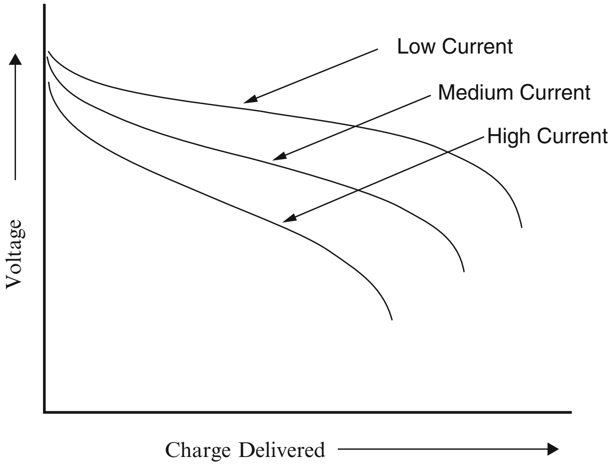

Fig. 9.13 Schematic drawing showing the influence of the current density upon the discharge curve

As an example, if a cell has a nominal capacity of 5 Ah, discharge at the rate of $C/10$ means that it would be fully discharged in 10 h. Thus the current is 0.5 A. And if the discharge rate is $C/5$ the discharge current is 1 A.

Although the C-Rate is often specified when either complete cells or individual electrodes are evaluated experimentally, and the current can be specified, this parameter is often not time-independent during real applications. If the electrical load is primarily resistive, for example, the current will decrease as the output voltage falls. This means that the C-Rate drops as the battery is discharged. Nevertheless, it is often important to consider the C-Rate when comparing the behavior of different materials, electrodes, and complete cells.

It is obvious that not only the average voltage but also the charge delivered can vary appreciably with changes in the C-Rate. But in addition, the amount of energy that can be supplied, which will be seen in later chapters to be related to the area under the discharge curve, is strongly C-Rate dependent.

A further point that should be kept in mind is that not all of the stored energy may be useful. If the load is resistive, the output power is proportional to the square of the voltage according to Eq. (9.14), so that the energy that is available at lower voltages may not be of much benefit.

This behavior can be understood in terms of the equivalent circuit of the battery. The internal ionic impedance Z_i, the sum of the impedances in the electrolyte and at the two electrode/electrolyte interfaces, is a function of the local current density in the cell. This impedance typically also varies with the state of charge. The mechanisms responsible for this behavior will be discussed later in the text.

References

1. Barin I (1995) Thermochemical Data of Pure Substances, 3rd edn. VCH, Weinheim, Published Online 24 Apr 2008. ISBN 9783527619825
2. Yao NP, Heredy LA, Saunders RC (1971) J Electrochem Soc 118:1039
3. Gay EC et al (1976) J Electrochem Soc 123:1591
4. Wen CJ, Boukamp BA, Weppner W, Huggins RA (1979) J Electrochem Soc 126:2258
5. Wen CJ, Weppner W, Boukamp BA, Huggins RA (1980) Met Trans 11B:131
6. Wen CJ, Ho C, Boukamp BA, Raistrick ID, Weppner W, Huggins RA (1981) Int Metals Rev 5:253
7. Whittingham MS (1976) Science 192:1126