Chapter 10
Principles Determining the Voltages and Capacities of Electrochemical Cells

10.1 Introduction

In the prior chapter it was shown that the fundamental driving force across an electrochemical cell is the virtual chemical reaction that would occur if the materials in the two electrodes were to react with each other. If the electrolyte is a perfect filter that allows the passage of ionic species, but not electrons, the cell voltage when no current is passing through the system is determined by the difference in the electrically neutral chemical compositions of the electrodes. The identity and properties of the electrolyte and the phenomena that occur at the electrode/electrolyte interfaces play no role. Likewise, it is the properties of the electrodes that determine the capacity of an electrochemical cell.

These general principles will be extended further in this chapter. Emphasis will be placed upon the equilibrium, or near-equilibrium state. This will address the ideal properties of such systems, which provide the upper limits of various important parameters.

Real systems under load deviate from this behavior. As will be shown later, this is primarily because of kinetic factors. Such factors vary from one system to the next, and are highly dependent upon both the details of the materials present, the cell construction, and the experimental conditions. As a result, it is difficult to obtain reproducible and quantitative experimental results. Such matters will appear later in this text. First, the factors that determine the equilibrium, or near-equilibrium, behavior will be discussed.

10.2 Thermodynamic Properties of Individual Species

It was shown in Chap. 9 that the overall driving force across a simple electrochemical cell is determined by the change in Gibbs free energy, ΔG_r° of the virtual chemical reaction that would occur if the materials in the electrodes were to react

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with one another. If there is no current flowing, this chemical driving force is just balanced by an electrical driving force in the opposite direction.

Individual species within the electrolyte in the cell will now be considered. Under open circuit conditions (and no electronic leakage) there is no net current flow. Thus there must be a *force balance* acting on all mobile species.

The thermodynamic properties of a material can be related to those of its constituents by using the concept of the *chemical potential* of an individual species. The chemical potential of species i in a phase j is defined as

$$\mu_{\mathrm{i}} = \partial G_{\mathrm{j}} / \partial n_{\mathrm{i}} \tag{10.1}$$

where G_{j} is the molar Gibbs free energy of phase j, and n_{i} is the mol fraction of the i species in phase j. In integral form this is

$$\Delta\mu_{\mathrm{i}} = \Delta G_{\mathrm{j}} \tag{10.2}$$

Since the free energy of the phase changes with the amount of species i, it is easy to see that the chemical potential has the same dimension as the free energy. Thus gradients in the chemical potential of species i produce chemical forces causing i to tend to move in the direction of lower μ_{i}. It was shown in Chap. 1 that when there is no net flux in the electrolyte, this chemical force must be balanced by an electrostatic force due to the voltage between the electrodes. The energy balance in the electrolyte, and thus in the cell, can be written in terms of the single species i:

$$\Delta\mu_{\mathrm{i}} = -z_{\mathrm{i}} F E \tag{10.3}$$

where z_{i} is the number of elementary charges carried by particles (ions) of species i.

The chemical potential of a given species is related to another thermodynamic quantity, its *activity*, a_{i}. The defining relation is

$$\mu_{\mathrm{i}} = \mu_{\mathrm{i}}^{\mathrm{o}} + RT \ln a_{\mathrm{i}} \tag{10.4}$$

where $\mu_{\mathrm{i}}^{\mathrm{o}}$ is a constant, the value of the chemical potential of species i in its standard state. R is the gas constant (8.315 J/mol degree), and T is the absolute temperature.

The activity of a species can be thought of as its *effective concentration.* If the activity of species i, a_{i}, is equal to unity, it behaves chemically as though it is pure i. If a_{i} is 0.5, it behaves chemically as though it is composed of half species i, and half something else that is chemically inert. In the case of a property such as vapor pressure, a material i with an activity of 0.5 will have a vapor pressure half of that of pure i.

Consider an electrochemical cell in which the activity of species i is different in the two electrodes, $a_{\mathrm{i}}(-)$ in the negative electrode, and $a_{\mathrm{i}}(+)$ in the positive electrode. The difference between the chemical potential on the positive side and that on the negative side can be written as

$$\mu_{\mathrm{i}}(+) - \mu_{\mathrm{i}}(-) = RT[\ln a_{\mathrm{i}}(+) - \ln a_{\mathrm{i}}(-)] = RT \ln[a_{\mathrm{i}}(+)/a_{\mathrm{i}}(-)] \tag{10.5}$$

If this chemical potential difference is balanced by the electrostatic energy from Eq. (10.2):

$$E = -(RT/z_\mathrm{i}F)\ln[a_\mathrm{i}(+)/a_\mathrm{i}(-)] \qquad (10.6)$$

This relation, which is often called the *Nernst equation*, is very useful, for it relates the measurable cell voltage to the chemical difference across an electrochemical cell. That is, it transduces between the chemical and electrical driving forces. If the activity of species i in one of the electrodes is a standard reference value, the *Nernst equation* provides the relative electrical potential of the other electrode.

10.3 A Simple Example: The Lithium/Iodine Cell

As an initial example, the thermodynamic basis for the voltage of a lithium/iodine cell will be considered. Primary (non-rechargeable) cells based upon this chemical system were invented by Schneider and Moser in 1972 [1, 2], and they are currently widely used to supply the energy in cardiac pacemakers.

The typical configuration of this electrochemical cell employs metallic lithium as the negative electrode and a composite of iodine with about 10 wt% of poly-2-vinylpyridine (P2VP) on the positive side. The composite of iodine and P2VP is a charge transfer complex, with the P2VP acting as an electron donor, and the iodine as an acceptor. The result is that the combination has a high electronic conductivity and the chemical properties are essentially the same as those of pure iodine. Reaction between the Li and the (iodine, P2VP) composite produces a layer of solid LiI. This material acts as a solid electrolyte in which Li^+ ions move from the interface with the negative electrode to the interface with the positive electrode, where they react with iodine to form more LiI. The transport mechanism involves a flux of lithium ion vacancies in the opposite direction. Although LiI has relatively low ionic conductivity, it has negligible electronic transport, meeting the requirements of an electrolyte.

This system can be represented simply as

$$(-)\mathrm{Li}/\mathrm{electrolyte}/\mathrm{I_2}(+) \qquad (10.7)$$

The *virtual reaction* that determines the voltage is thus

$$\mathrm{Li} + 1/2\mathrm{I_2} = \mathrm{LiI} \qquad (10.8)$$

More and more LiI forms between the lithium electrode and the iodine electrode as the reaction progresses. The time evolution of the microstructure during discharge is shown schematically in Fig. 10.1.

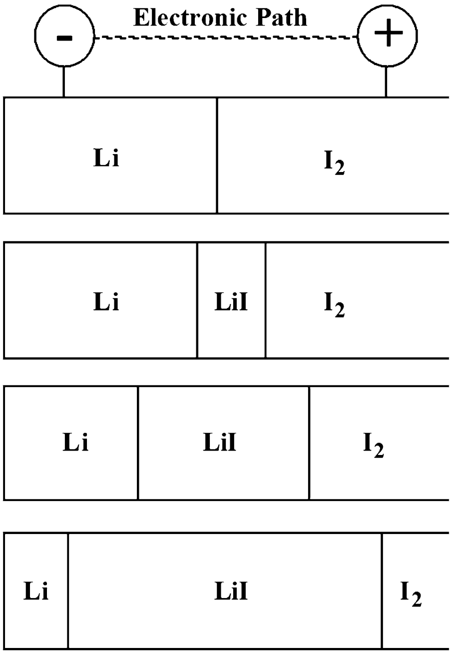

Fig. 10.1 Schematic representation of the microstructure of a Li/I_2 cell at several stages of discharge

The voltage across this cell under open circuit conditions can be readily calculated from the balance between the chemical and electrical driving forces, as shown in Chap. 9:

$$E = -\Delta G_r / z_i F \tag{10.9}$$

where

$$\Delta G_r = \Delta G_f(\mathrm{LiI}) \tag{10.10}$$

and z_i is +1, for the electroactive species are the Li^+ ions.

According to the data in Barin [3], the Gibbs free energy of formation of LiI is −269.67 kJ/mol at 25 °C. Since the value of the Faraday constant is 96,500 C per equivalent (mol of electronic charge), the open-circuit voltage can be calculated to be 2.795 V at 25 °C.

Data on the properties of commercial Li/I_2 cells are shown in Fig. 10.2 [4]. It is seen that during most of the life of this battery the voltage corresponds closely to that which was calculated above. It is also seen in this figure that the resistance across the cell increases with the extent of reaction, due to the increasing thickness of the solid electrolyte product that grows as the cell is discharged. Such cells are

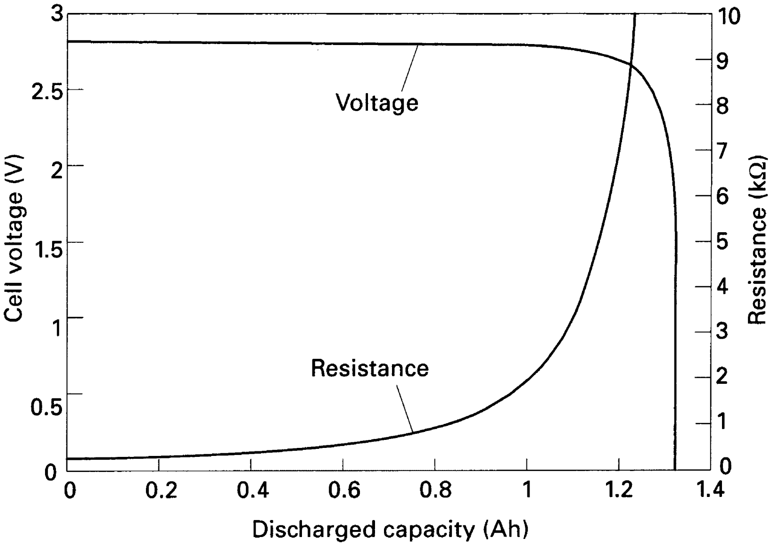

Fig. 10.2 Output voltage and internal resistance of a typical Li/I_2 battery of the type used in cardiac pacemakers. After [4]

typically designed to be *positive-electrode limited*. This means that the positive electrode capacity is somewhat less than the negative electrode capacity, and therefore is the part of the cell that determines the overall capacity.

10.3.1 Calculation of the Maximum Theoretical Specific Energy

The value of the maximum theoretical specific energy of a Li/I_2 cell can now be calculated from this information and the weights of the reactants. It was shown in Chap. 9 that the MTSE, in Wh/kg, is given by

$$\text{MTSE} = 26{,}805(xE/W_\text{t}) \tag{10.11}$$

The reactant weight W_t is the weight of a mol of Li (6.94 g) plus half a mol of I_2 (126.9 g), or 133.84 g. The value of x is 1, and E was calculated to be 2.795 V. Thus the value of the MTSE is 559.77 Wh/kg.

This is a large number, about 15 times the value that is typical of the common Pb-acid cells that are so widely used as SLI batteries in automobiles, as well as for a number of other purposes. The lack of rechargeability as well as the cost of the ingredients and the low discharge rate unfortunately limit the range of application of Li/I_2 cells, however.

10.3.2 The Temperature Dependence of the Cell Voltage

As it has been seen, the quantity that determines the voltage is the Gibbs free energy change associated with the virtual cell reaction between the chemical species in the electrodes. That quantity is, however, temperature dependent. This can be seen by dividing the Gibbs free energy into its enthalpy and entropy components:

$$\Delta G_{\mathrm{r}} = \Delta H_{\mathrm{r}} - T\Delta S_{\mathrm{r}} \tag{10.12}$$

so that

$$\mathrm{d}(\Delta G_{\mathrm{r}})/\mathrm{d}T = -\Delta S_{\mathrm{r}} \tag{10.13}$$

and

$$\mathrm{d}E/\mathrm{d}T = \Delta S_{\mathrm{r}}/z_{\mathrm{i}}F \tag{10.14}$$

The value of ΔS for the formation of LiI is given by

$$\Delta S_{\mathrm{r}}(\mathrm{LiI}) = S(\mathrm{LiI}) - S(\mathrm{Li}) - 1/2S(\mathrm{I_2}) \tag{10.15}$$

Entropy data for these materials, as well as a number of others, are given in Table 10.1. Note that these entropy values are in J/mol deg, whereas Gibbs free energy values are typically in kJ/mol. From these data, the value of ΔS_{r} for the formation of LiI is −1.38 J/K mol. Thus, from Eq. (10.13), the cell voltage varies only -1.43×10^{-5} V/K. This is very small. As will be seen later, the temperature dependence of the voltage related to many other electrochemical reactions, and thus

Table 10.1 Entropy data for some species at 25 and 225 °C [3]

Species	S (25 °C) (J/K mol)
Li	29.08
Zn	41.63
H_2	130.68
O_2	205.15
Cl_2	304.32
I_2	116.14
LiF	35.66
LiCl	59.30
LiBr	74.06
LiI	85.77
H_2O (liquid)	69.95
ZnO	43.64
H_2	145.74
O_2	220.69
H_2O (gas)	206.66

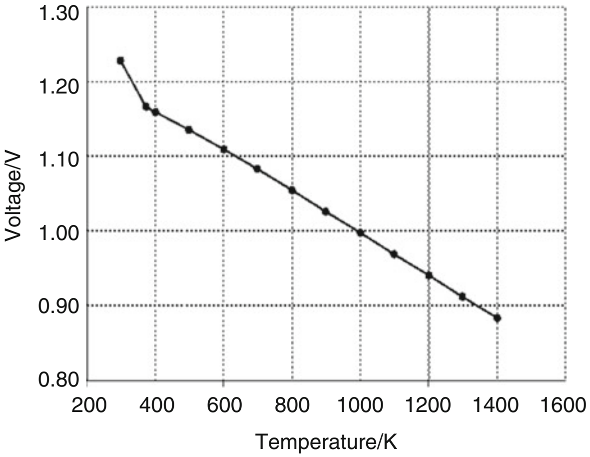

Fig. 10.3 Theoretical open-circuit voltage of a H_2/O_2 fuel cell as a function of the absolute temperature

of other batteries, is often much greater. An example is the small Zn/O_2 battery that is commonly used in hearing aids, where it is -5.2×10^{-4} V/K.

The data in Table 10.1 show that the entropy values of simple solids are considerably lower than those of liquids, which, it turn, are lower than gases. This is reflected, of course, in the temperature dependence of electrochemical cells.

An interesting example is the H_2/O_2 fuel cell. In that case the voltage varies -1.7×10^{-3} V/K near room temperature where water, the product of the reaction, is a liquid. But at 225 °C, where the product of the cell reaction is a gas, steam, the variation is only -0.5×10^{-3} V/K. The resultant variation of the cell voltage with temperature from about room temperature to the operating temperature of high temperature oxide-electrolyte fuel cells is shown in Fig. 10.3. Operation at a high temperature results in a significantly lower voltage. The theoretical open-circuit voltage is 1.23 V at 25 °C, but only 0.91 V at 1025 °C.

10.4 The Shape of Discharge Curves and the Gibbs Phase Rule

It was shown earlier that the voltage of batteries often varies with the state of charge, and it was pointed out that their discharge curves typically have one of three general shapes. Some are relatively flat, others have more than one relatively flat portion, and others have a slanted or stretched-S shape, sometimes with a relatively large slope. The data in Fig. 10.2 show that the Li/I_2 cell falls in the first category.

To understand how the voltage across an electrochemical cell varies with the state of charge, and why it is essentially flat in the case of the Li/I_2 cell, it is useful to consider the application of the *Gibbs phase rule* to such systems.

The *Gibbs phase rule* is often written as

$$F = C - P + 2 \tag{10.16}$$

in which C is the *number of components* (e.g., elements) present, and P is the *number of phases present* in this materials system in a given experiment. The quantity F may be more difficult to understand. It is the *number of degrees of freedom*; that means the number of *intensive thermodynamic parameters* that must be specified in order to *define the system* and *all of its associated properties*. One of these properties is, of course, the electric potential.

To understand the application of the phase rule to this situation, it must be determined what thermodynamic parameters should be considered. They must be intensive variables, which means that their values are independent of the amount of material present. For this purpose, the most useful thermodynamic parameters are the temperature, the overall pressure, and either the chemical potential or the chemical composition of each of the phases present.

How does this apply to the Li/I_2 cell? Starting with the negative electrode; there is only one phase present, Li, so P is 1. It is a single element, with only one type of atom. Thus the number of components C is also equal to 1. Thus F must be equal to 2.

What is the meaning of $F = 2$? It means that if the values of two intensive thermodynamic parameters, such as the temperature and the overall pressure, are specified, there are no degrees of freedom left over. Thus the *residual value of* F is zero. This means that all of the intensive properties of the negative electrode system are fully defined, e.g., have fixed values.

Thus in the case of the lithium negative electrode the chemical potentials of all species (i.e. the pure lithium), as well as the electrical potential, have fixed values, *regardless of the amount* of lithium present. The amount of lithium in the negative electrode decreases as the cell becomes discharged and the product LiI is formed. That is, the amount of lithium varies with the state of charge of the Li/I_2 battery. But since $F = 2$, and thus the residual value of F, if the temperature and total pressure are held constant, is zero, none of the intensive properties change. This means that the electrical potential of the lithium electrode is independent of the state of charge of the cell. This is shown schematically in Fig. 10.4.

On the other hand, if some iodine *could* dissolve into the lithium, forming a solid solution, *which it does not*, the number of components in the negative electrode would be two. In a solid solution there is only one phase present. Thus $C = 2$, $P = 1$ and $F = 3$.

In this hypothetical case the system would not be fully defined after fixing the temperature and the overall pressure. There would be a residual value of F, i.e., 1. Thus the electrical potential of the lithium-iodine alloy would not be fixed, but would vary, depending upon some other parameter, such as the amount of iodine in the Li-I solid solution. This is shown schematically in Fig. 10.5.

Although it is *not true* in the lithium/iodine cell it is quite common in other electrochemical cells for the electrical potential of electrodes to vary with the

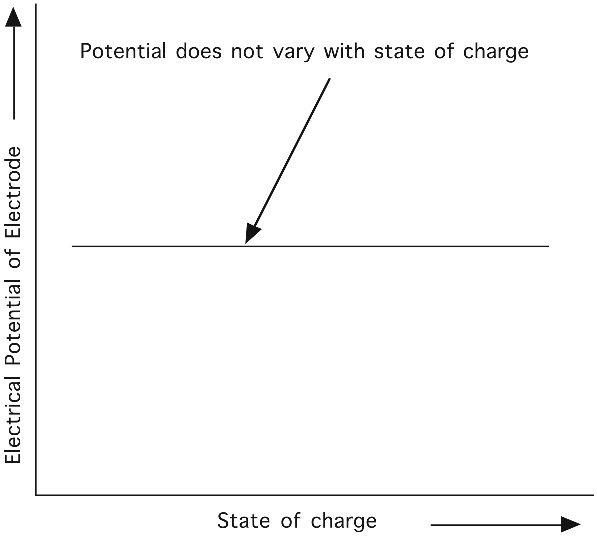

Fig. 10.4 The potential of a pure lithium electrode does not vary with the state of charge of the Li/I_2 cell

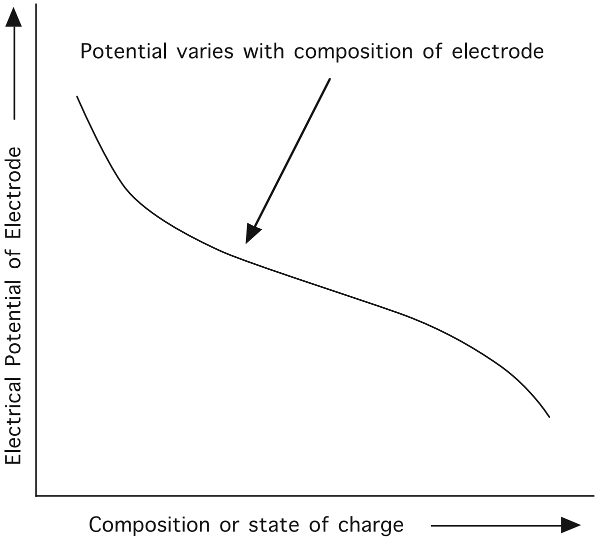

Fig. 10.5 Schematic representation of the variation of the electrical potential of an electrode as a function of its composition for the case in which the residual value of F is not 0

composition, and thus with the state of charge. A number of examples will be discussed in subsequent chapters.

Now consider the positive electrode. There is only one active component (element) present, iodine. There is also only one electrochemically active phase, iodine. Thus both C and P have values of 1. The number of degrees of freedom is thus again 2. Therefore, the values of all intensive variables and associated properties, such as the electrical potential, of the iodine electrode will be determined if the values of the two independent thermodynamic parameters, the temperature and the total pressure, are fixed.

This means that the potential of the I_2 electrode does not vary with its state of charge. Since both the negative and positive electrode potentials are independent of the state of charge, the voltage across the cell must also be independent of the state of charge of the Li/I_2 battery. This was illustrated in Fig. 10.2.

The earlier discussion showed that the chemical potential of an element depends upon its activity, and for the case of the iodine electrode

$$\mu(\mathrm{I}_2) = \mu^{\mathrm{o}}(\mathrm{I}_2) \tag{10.17}$$

where $\mu^\circ(\mathrm{I}_2)$ is the chemical potential of iodine in its standard state, i.e., pure iodine at a pressure of one atmosphere at the temperature in question. When the activity is unity, i.e., for pure I_2,

$$\mu(I_2) = \mu^{\mathrm{o}}(\mathrm{I}_2) \tag{10.18}$$

Now consider the voltage of the Li/I_2 cell. This is determined by the Gibbs free energy of formation of the LiI phase, as given in Eqs. (10.8) and (10.9). But it is also related to the difference in the chemical potential of iodine at the two electrode/electrolyte interfaces according to the relation

$$E = -\Delta\mu(\mathrm{I}_2)/z_{\mathrm{i}}F \tag{10.19}$$

where the value of z_{i} is -2. Therefore the activity of iodine at the positive side of the electrolyte is unity, but it is very small at the interface on the negative electrode side. Likewise, the cell voltage is related to the difference in the chemical potential of lithium at the two electrode/electrolyte interfaces:

$$E = -\Delta\mu(\mathrm{Li})/z_{\mathrm{i}}F \tag{10.20}$$

in which the value of z_{i} is +1. In this case the activity of lithium is unity at the negative interface, and very small at the positive interface, where the electrolyte is in contact with I_2.

Whereas this discussion has focused on the potential of a single electrode, the shape of the equilibrium discharge curve (voltage versus state of charge) of an electrochemical cell is the result of the change of the potentials of both electrodes as the overall reaction takes place. If the potential of one of the electrodes does not vary, the variation of the cell voltage is obviously the result of the change of the potential of the other electrode as its overall composition changes.

There are a number of materials that are used as electrodes in electrochemical cells in which more than one reaction can occur in sequence as the overall discharge process takes place. In some cases, these reactions are of the same type, whereas in others they are not.

As one example, a *series of multiphase reactions* in which the number of residual degrees of freedom is zero can result in a discharge curve with several constant voltage plateaus. This is illustrated schematically in Fig. 10.6.

It is also possible for an electrode to undergo sequential reactions that are not of the same type. An example of this is the reaction of lithium with a spinel phase in the Li-Ti-O system. Experimental data are shown in Fig. 10.7 [5].

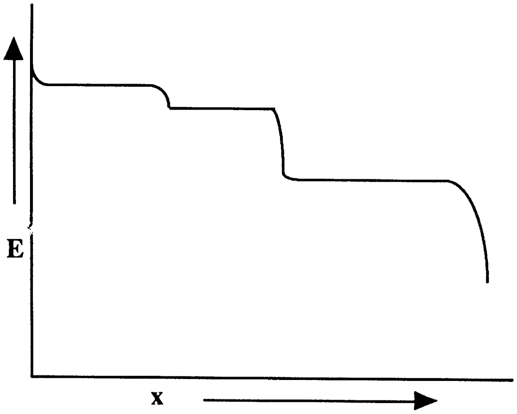

Fig. 10.6 Schematic equilibrium discharge curve of an electrode that undergoes a series of multiphase reactions in which the residual value of *F* is 0

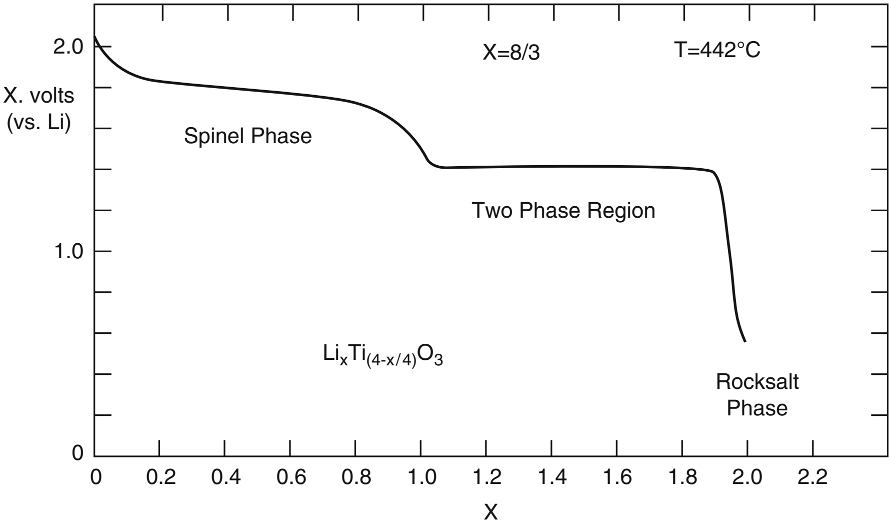

Fig. 10.7 Equilibrium discharge curve of a material in the Li-Ti-O system that initially had a composition with a spinel type of crystal structure

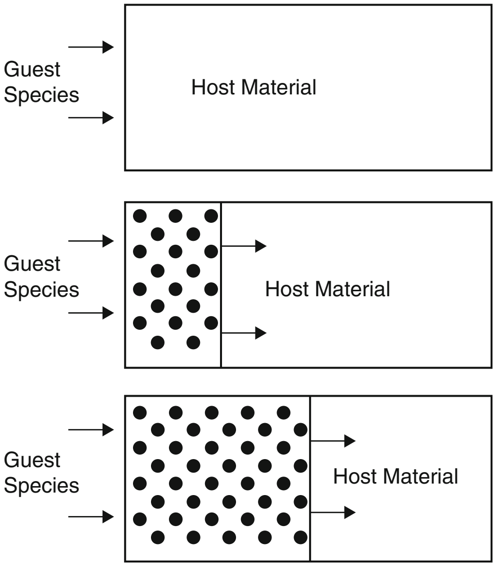

Fig. 10.8 Schematic representation of a one-dimensional moving interface reaction

In this case approximately one Li per mol could be inserted into the host spinel phase as a *solid solution reaction*. Thus the potential varied continuously as a function of composition.

The introduction of additional lithium causes the nucleation, and subsequent growth, of a second phase that has the rocksalt structure and a composition of approximately two Li per mol of the original host. Thus a *reconstitution reaction* takes place when more than one lithium was added. During a reconstitution reaction there are two regions within the material with different Li contents. As the reaction proceeds the compositions of the two phases do not change, but the relative amount of the phase with the higher Li content increases, and that of the initial solid solution phase is reduced. This occurs by the *movement of the interface* between them. This type of a *moving interface reconstitution reaction* can be schematically represented as shown in Fig. 10.8.

Another example, in which several reactions occur as the overall composition is changed is the Li-Mn-O system. In this case there is a series of three different reactions. This is seen from the shape of the equilibrium discharge curve in Fig. 10.9 [6]. There is a two-phase plateau, followed by a single-phase solid solution region, and then by another two-phase plateau.

This interpretation was reinforced by the results of X-ray diffraction experiments, which are shown in Fig. 10.10 [6]. It is seen that the lattice parameters remain constant within two-phase regions, and vary with the composition within the single-phase solid solution region.

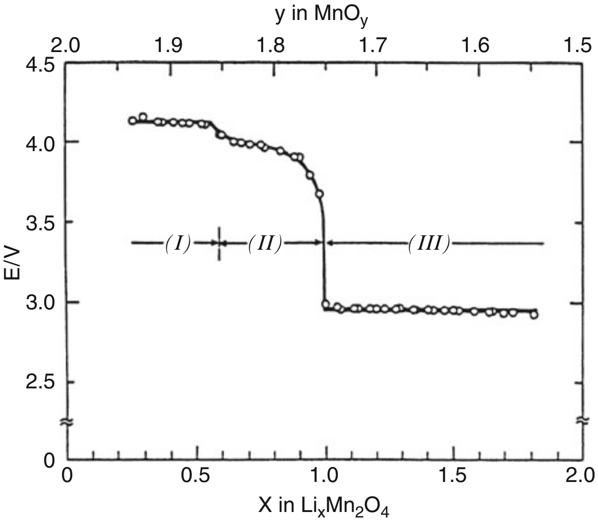

Fig. 10.9 Equilibrium discharge curve for $Li_xMn_2O_4$. After [6]

10.5 The Coulometric Titration Technique

The simple examples that have been discussed so far in this chapter assume that the requisite thermodynamic data are already known. Thus one can calculate the open-circuit voltage of an electrochemical cell from the value of the Gibbs free energy of the appropriate virtual reaction, and the ideal capacity can be determined from the *reaction's stoichiometry*.

It is also possible to do the opposite, using electrochemical measurements to obtain thermodynamic information. A useful tool for this purpose is the *coulometric titration technique*, which was first introduced by Wagner [7] to study the phase $Ag_{2+x}S$, which exists over a relatively narrow range of composition x. Its composition, or stoichiometry (the relative amounts of silver and sulfur) depends upon the value of the activity of silver within it. One can use a simple electrochemical cell to both change the stoichiometry and evaluate the activity of one of the species, e.g., silver in this case.

This method was further developed and applied by Weppner and Huggins [8] to the investigation of poly-phase alloy systems. It was demonstrated that the phase diagram can be determined, as well as the thermodynamic properties of the individual phases within it, by the use of this technique.

Consider the use of the following simple electrochemical cell to investigate the properties of the *vario-stoichiometric* (the stoichiometry can have a range of values) *phase* A_yB. This can be represented schematically as

$$A/\text{Electrolyte that transports } A^+ \text{ ions}/A_yB$$

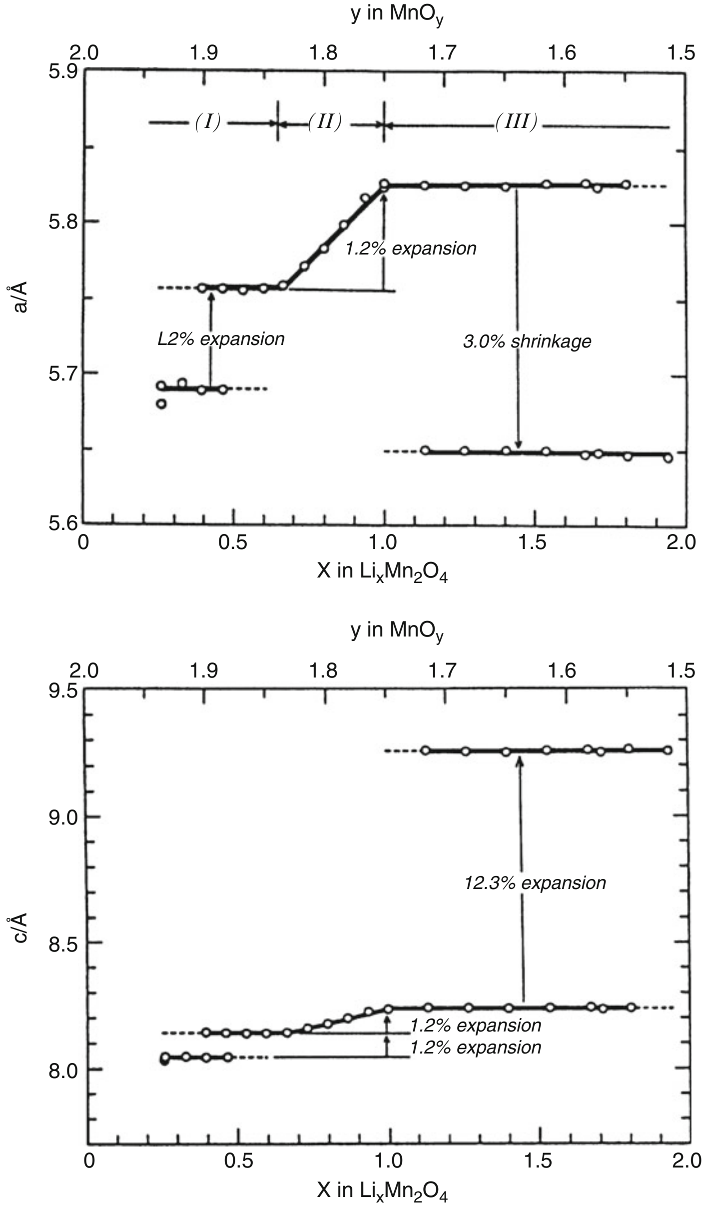

Fig. 10.10 Changes in unit cell dimensions as a function of composition in $Li_xMn_2O_4$ [6]

In this case, the element A acts as both a source and sink for the electroactive species A and a thermodynamic reference for component A. For simplicity, it can be assumed that this electrode is pure A, and thus has an activity of unity. It can also be assumed that both A and A_yB are good electronic conductors, that the ionic transference number in the electrolyte is unity, and that the system is under isobaric and isothermal conditions.

Under these conditions, the open-circuit voltage E is a direct measure of the chemical potential and the activity of A in the phase $\mathrm{A}_y\mathrm{B}$ according to Eq. (10.5) that appeared earlier. As the electrode of pure A has an activity of unity, this relation can be written as

$$E = -\Delta\mu_{\mathrm{A}}/(z_{\mathrm{A}},F) = -(RT/z_{\mathrm{A}},F)\ln a(\mathrm{A}) \tag{10.21}$$

where $z_{\mathrm{A}+}$ is the charge number of the A^+ ions in the electrolyte, which is 1.

If a positive current is passed through the cell by the use of an electronic source, A^+ ions will be transported through the electrolyte from the left electrode to the right electrode. An equal current of electrons will go through the outer circuit because of the *requirement for charge flux balance*. The result is that the value of y in the $\mathrm{A}_y\mathrm{B}$ phase will be increased.

For the case that a steady value of current I is applied for a fixed time t, the amount of charge Q that is passed across the cell is simply

$$Q = It \tag{10.22}$$

The number of mols of species A that are transported during this current pulse is

$$\Delta m(\mathrm{A}) = Q/z_{\mathrm{A}},F \tag{10.23}$$

so that the change in the value of y, the mol fraction of species A, is

$$\Delta y = \Delta m(\mathrm{A})/m(\mathrm{B}) = Q/(z_{\mathrm{A}},Fm(\mathrm{B})) \tag{10.24}$$

where $m(\mathrm{B})$ is the number of moles of B present in the electrode.

This method can be used to make *very minute* changes in the composition of the electrode material. One can see how sensitive this procedure is by putting some numbers into this relation.

Suppose that the electrode has a weight of 5 g, and the component B has a molecular weight of 100 g/mol. The value of $m(\mathrm{B})$ is thus 0.05 mol. Now suppose that a current of 0.1 mA is run through the cell for 10 s. The value of Q is then 0.001 C. With $z_{\mathrm{A}+} = 1$ equivalent per mol and $F = 96{,}500$ C per equivalent, then Δy is only about 2×10^{-7}.

This is very small. Thus it is possible to investigate the compositional dependence of the properties of phases with very narrow compositional ranges. It is very difficult to get such a high degree of compositional resolution by other techniques.

By waiting for a sufficiently long time to allow the composition to become homogeneous throughout the electrode material, as evidenced by reaching a steady-state value of open-circuit voltage, information can be obtained about the equilibrium chemical potential and activity of the mobile electroactive species as a function of composition. This technique has been used to investigate a wide variety of materials of potential interest in battery systems, and numerous examples will be discussed in later chapters.

The success of this method depends upon a number of assumptions. One is that the electrolyte is essentially only an ionic conductor, i.e., the ionic transference number is very close to unity. Another is that there can be no appreciable loss of either component from the electrode material A_yB by evaporation, dissolution, or interaction with the electrical lead materials, the so-called *current collectors*. Furthermore, the rate of *compositional equilibration via chemical diffusion* in the electrode material must be sufficiently fast. This means that it may be necessary to use thin samples as electrodes in order to reduce the time necessary for concentration homogenization.

It should also be recognized that this coulometric titration technique gives information about the influence of compositional changes, but not the absolute composition. That must be determined by some other method.

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