Chapter 14
Insertion Reaction Electrodes

14.1 Introduction

The topic of *insertion reaction electrodes* did not even appear in discussions of batteries and related phenomena just a few years ago, but is a major feature of some of the most important modern battery systems today. Instead of reactions occurring on the surface of solid electrodes, as in traditional electrochemical systems, what happens *inside* the electrodes is now recognized to be of critical importance.

A few years after the surprise discovery that ions can move surprisingly fast inside certain solids, enabling their use as solid electrolytes, it was recognized that some ions can move rapidly into and out of some other (electrically conducting) materials. The first use of insertion reaction materials was for non-blocking electrodes to assist the investigation of the ionic conductivity of the (then) newly discovered ambient temperature solid electrolyte, sodium beta alumina [1–3]. Their very important use as charge-storing electrodes began to appear shortly thereafter.

This phenomenon is a key feature of the electrodes in many of the most important battery systems today, such as the lithium-ion cells. Specific examples will be discussed in later chapters.

Many examples are now known in which a mobile guest species can be *inserted into*, or *removed (extracted) from*, a *stable host crystal structure*. This phenomenon is an example of both *soft chemistry* and *selective equilibrium*, in which the mobile species can readily come to equilibrium, but this may not be true of the host, or of the overall composition. The mobile species can be atoms, ions or molecules, and their concentration is typically determined by equilibrium with the thermodynamic conditions imposed on the surface of the solid phase.

In the simplest cases, there is little, if any, change in the structure of the host. There may be modest changes in the volume, related to changes in bond distances, and possibly directions, but the general character of the host is preserved. In many

R.A. Huggins, *Energy Storage*, DOI 10.1007/978-3-319-21239-5_14

cases the *insertion* of guest species is reversible, and they can also be *extracted*, or *deleted*, returning the host material to its prior structure.

The terms "*intercalation*" and "*de-intercalation*" are often used for reactions involving the insertion and extraction of guest species for the specific case of host materials that have *layer-type crystal structures*. On the other hand, "*insertion*" and "*extraction*" are more general terms. Reactions of this type are most likely to occur when the host has an open-framework or a layered type of crystal structure, so that there is space available for the presence of additional small ionic species. Since such reactions involve a change in the chemical composition of the host material, they can also be called *solid solution reactions*.

Insertion reactions are generally *topotactic*, with the guest species moving into, and residing in, specific sites within the host lattice structure. These sites can often be thought of as *interstitial sites* in the host crystal lattice that are otherwise empty. The occurrence of a *topotactic* reaction implies some three-dimensional correspondence between the crystal structures of the parent and the product. On the other hand, the term *epitaxy* relates to a correspondence that is only two-dimensional, such as on a surface.

It has been known for a long time that large quantities of hydrogen can be inserted into, and extracted from, palladium and some of its alloys. Palladium-silver alloys are commonly used as hydrogen-pass filters, i.e., filters that let only hydrogen pass through. Several types of materials with layer structures, including graphite and some clays, are also often used to remove contaminants from water by absorbing them between the layers in their crystal structures.

The most common examples of interest in connection with electrochemical phenomena involve the insertion or extraction of relatively small guest cationic species, such as H^+, Li^+, and Na^+. However, it will be shown later that there are also some materials in which anionic species can be inserted into a host structure.

It should be remembered that electrostatic energy considerations dictate that only neutral species, or neutral combinations of species, can be added to, or deleted from, solids. Thus the addition of cations requires the concurrent addition of electrons, and the extraction of cations is accompanied by either the insertion of holes or the deletion of electrons. Thus this phenomenon almost always involves materials that have at least some modicum of electronic conductivity.

The term "*soft chemistry*," or *chimie douce* in French, as much of the early work took place in France [4, 5], is sometimes used to describe reactions or chemical changes that involve only the relatively mobile components of the crystal structure, leaving the balance of the structure relatively unchanged.

Such reactions are often highly reversible, but in some cases, the insertion or extraction of mobile atomic or ionic species causes irreversible changes in the structure of the host material, and the reversal of this process does not return the host to its prior structure. In extreme cases, the structure may be so distorted that it becomes *amorphous*. These matters will be discussed below.

Insertion reactions are much more prevalent at lower temperatures than at high temperatures. The mobility of the component species in the host structure generally increases rapidly with temperature. This allows much more significant changes in the overall structure to occur, leading to *reconstitution reactions*, with substantial structural changes, rather than only the motion of the more mobile species, at elevated temperatures. Reconstitution reactions typically can be thought of as involving bond breakage, atomic reorganization, and the formation of new bonds.

14.2 Examples of the Insertion of Guest Species into Layer Structures

A number of materials have crystal structures that can be characterized as being composed of rather stiff *covalently bonded slabs* containing several layers of atoms. These slabs are held together by relatively strong, e.g., covalent, bonds. But adjacent slabs are bound to each other by relatively weak *van der Waals* forces. The space between the tightly-bound slabs is called the *gallery space*, and additional species can reside there. Depending upon the identity, size and charge of any inserted species present, the inter-slab dimensions can be varied.

Materials with the CdI_2 structure represent a simple example. They have a basic stoichiometry MX_2, and can be viewed as consisting of close-packed layers of negatively charged X ions held together by strong covalent bonding to positive M cations. In this case, the cations are octahedrally coordinated by six X neighbors, and the stacking of the X layers is hexagonal, with alternate layers directly above and below each other. This is generally described as ABABAB stacking.

This structure can be depicted as shown schematically in Fig. 14.1. Examples of materials with this type of crystal structure are CdI_2, $Mg(OH)_2$, $Fe(OH)_2$, $Ni(OH)_2$,

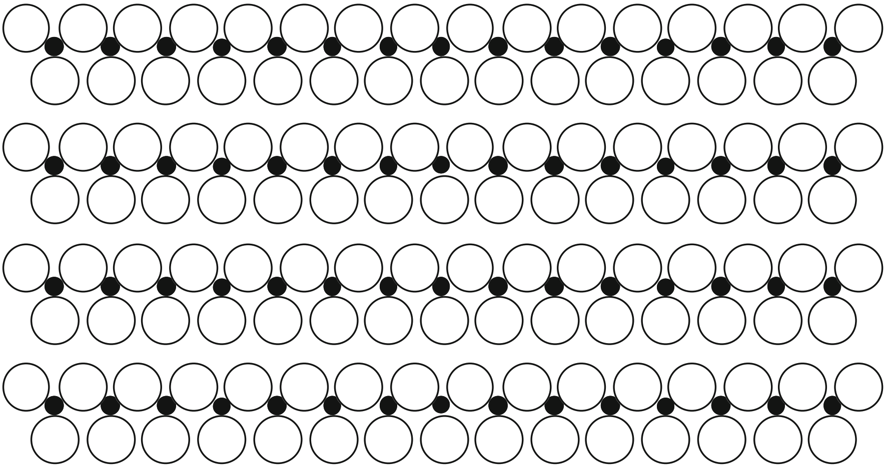

Fig. 14.1 Simple schematic model of a layer-type crystal structure with hexagonal ABABAB stacking. The *empty areas* between the covalently bonded slabs are called galleries

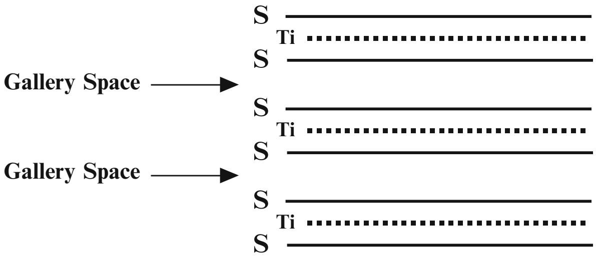

Fig. 14.2 Another type of model of a layer-type crystal structure. The example is TiS_2

and TiS_2. Another, simpler, way to depict these structures is illustrated in Fig. 14.2 for the case of TiS_2.

14.3 Floating and Pillared Layer Structures

In many cases, the mobile species move into and through sites in the previously empty gallery space between slabs of host material that are held together only by relatively weak van der Waals forces. The slabs can then be described as floating, and the presence of guest species often results in a significant increase in the inter-slab spacing.

However, in other cases the slabs are already rigidly connected by *pillars*, which partially fill the galleries through which the mobile species move. The pillar species are typically immobile, and thus are different from the mobile guest species. Because of the presence of the static pillars, the mobile species move through a two-dimensional network of interconnected tunnels, instead of through a sheet of available sites.

The presence of pillars acts to determine the spacing between the slabs of the host material, and thus the dimensions of the space through which mobile guest species can move. Examples of this kind will be discussed later. A simple schematic model of a pillared layer structure is shown in Fig. 14.3.

14.4 More on Terminology Related to the Insertion of Species into Solids

Sheets	Single layers of atoms or ions. In the case of graphite, individual sheets are called *graphene* layers.
Stacks	Parallel sheets of chemically identical species.
Slabs or Blocks	Multilayer structures tightly bound together, but separated from other structural features.

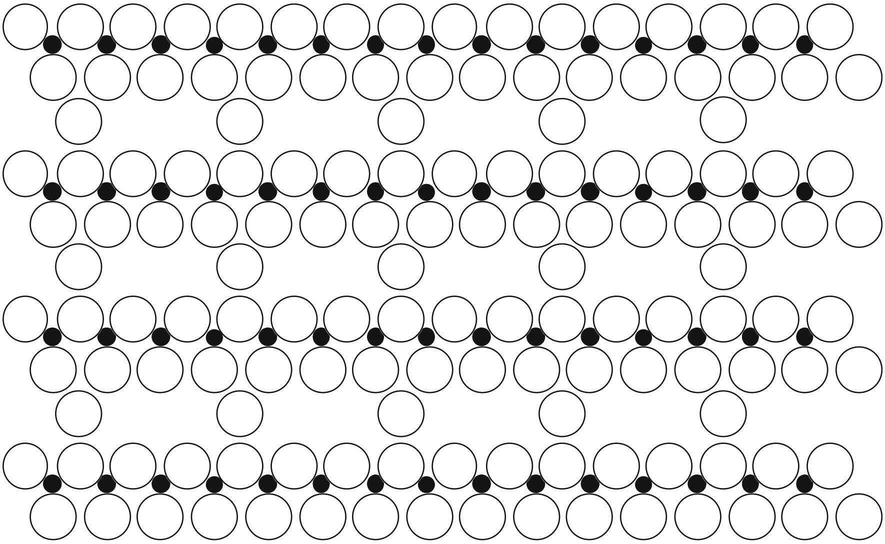

Fig. 14.3 Schematic model of pillared layer structure

	Example: covalently bonded MX_2 slabs such those shown above in the CdI_2 structure.
Galleries	The spaces between slabs in which the bonding is relatively weak, and in which guest species typically reside.
Pillars	Immobile species within the galleries that serve to support the adjacent slabs and to hold them together.
Tunnels	Connected interstitial space within the host structure in which the guest species can move and reside. Tunnels can be empty, partly occupied, or fully occupied by guest species.
Cavities	Empty space larger than the size of a single atom vacancy.
Windows	Locations within the host structure through which the guest species have to move in order to go from one site to another. Windows are typically defined by structural units of the host structure.

14.5 Types of Inserted Guest Species Configurations

There are several types of insertion reactions. In one case the mobile guest species randomly occupy sites within all of the galleries, gradually filling them all up as the guest population increases. When this is the case the variation of the electric potential with composition indicates a single-phase solid solution reaction, and there can be transient composition gradients within the gallery space.

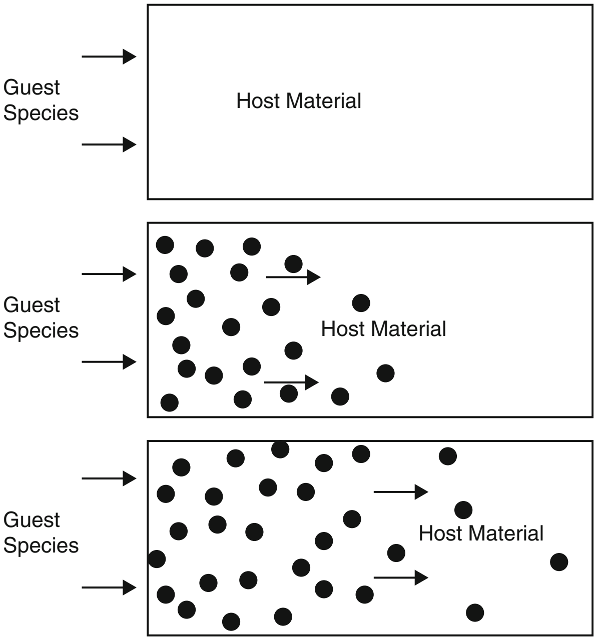

Fig. 14.4 Random diffusion of guest species into gallery space

If, however, the presence of the guest species causes a modification of the host structure, the insertion process can occur by the motion of an interface that separates the region into which the guest species have moved from the area in which there are no, or fewer, guest species. Thermodynamically, this has the characteristics of a polyphase reconstitution reaction, and occurs at a constant potential.

Alternatively, there can be two or more types of sites in the gallery space, with different energies, and the guest species can occupy an ordered array of sites, rather than all of them. When this is the case, changes in the overall concentration of mobile species requires the translation of the interface separating the occupied regions from those that are not occupied, again characteristic of a constant-potential reconstitution reaction. These moving interfaces can remain planar, or they can develop geometrical roughness. Several possibilities are illustrated schematically in Figs. 14.4, 14.5, and 14.6.

14.6 Sequential Insertion Reactions

If there are several different types of sites with different energies, insertion generally occurs on one type of site first, followed by the occupation of the other type of site. Figure 14.7 shows the potential as a function of composition during the

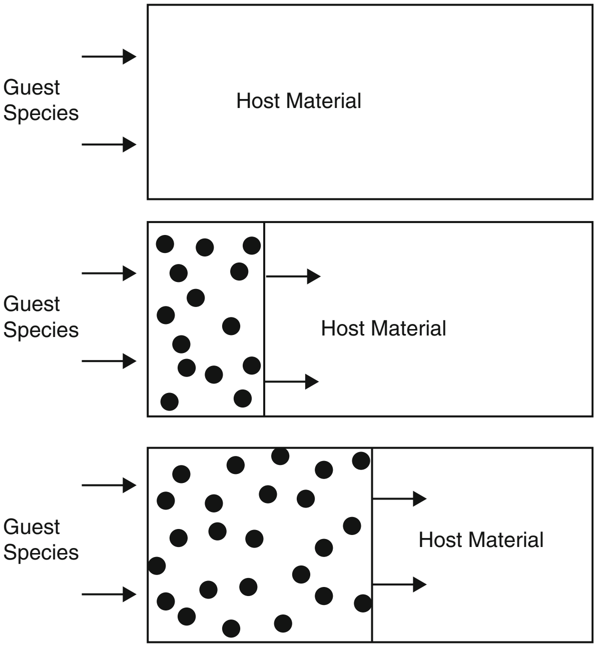

Fig. 14.5 Motion of two-phase interface when the guest species is not ordered upon possible sites

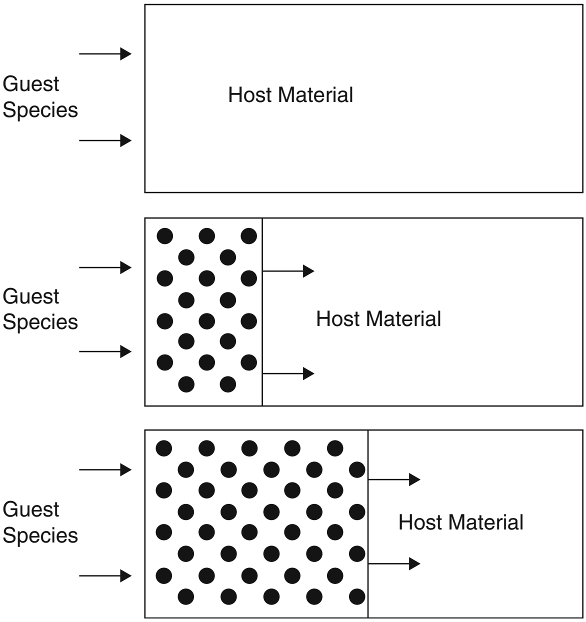

Fig. 14.6 Motion of two-phase interface when the guest species is ordered upon possible sites in the gallery space

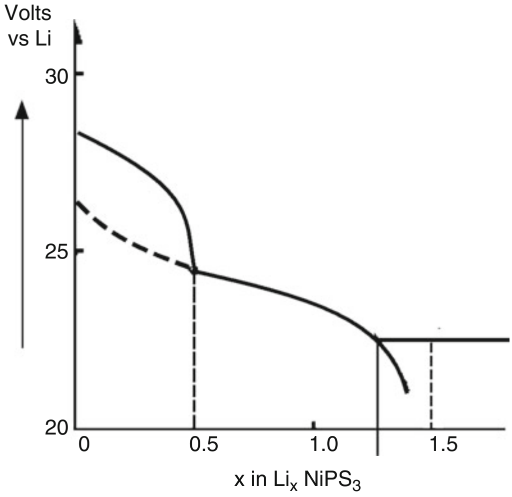

Fig. 14.7 Coulometric titration curve related to the insertion of lithium into $NiPS_3$. There is random filling of the first two types of sites. A reconstitution reaction occurs above about 1.25 Li [6]

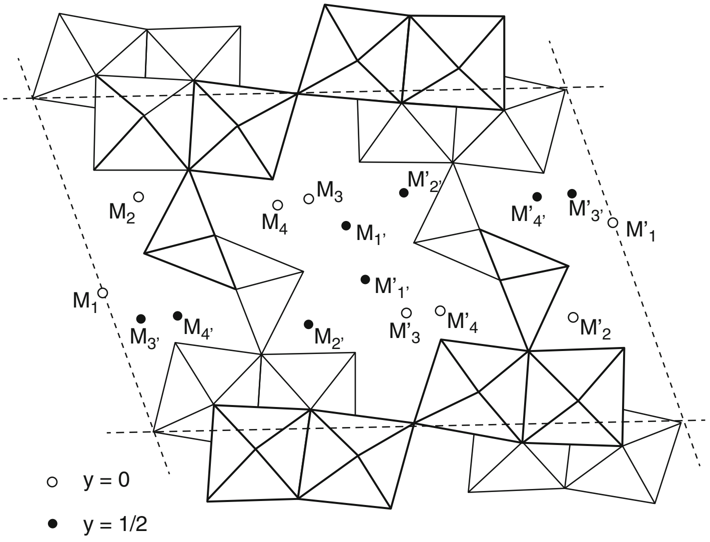

Fig. 14.8 (010) projection of the $K_xV_2O_5$ structure, showing the different types of sites for the guest species. After [6]

insertion of lithium into $NiPS_3$, in which there are two types of sites available. They are occupied in sequence, with random occupation in both cases.

Another example in which there are also different types of sites available for the insertion of Li ions involves the host $K_xV_2O_5$ structure. The host crystal structure illustrating the several different types of sites for guest ions is shown schematically in Fig. 14.8 [6].

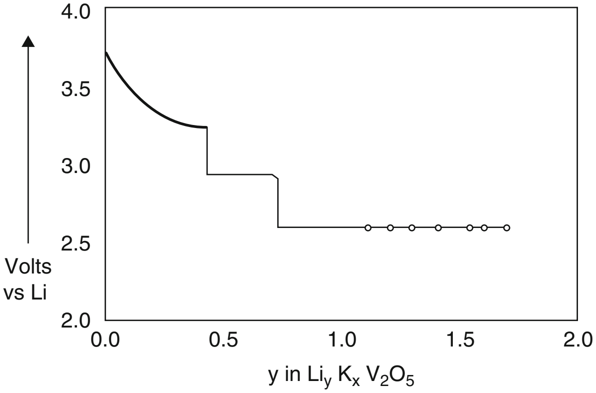

Fig. 14.9 Coulometric titration curve for the insertion of Li into $K_{0.27}V_2O_5$. After [6]

The experimentally measured coulometric titration curve for the insertion of Li ions into a member of this group of materials is shown in Fig. 14.9 [7]. It shows that the reaction involves three sequential steps. Up to about 0.4 Li can be incorporated into the first set of sites randomly. This is followed by the insertion of another 0.4 Li into another set of sites in an ordered arrangement. This means that there are two different lithium arrangements, with a moving interface between them. Thus there are two phases present, so this corresponds to a reconstitution reaction. This is then followed by another reconstitution reaction, the insertion of about one additional Li into another ordered structure.

A different type of ordered reaction involves selective occupation of particular galleries, and not others, in a material with a layered crystal structure. This phenomenon is described as “staging.” If alternate galleries are occupied and intervening ones are not, the material is described as having a “second-stage” structure. If every third gallery is occupied, the structure is “third-stage,” and so forth. A simple model depicting staging is shown in Fig. 14.10.

14.7 Co-insertion of Solvent Species

In some cases it is found that species from the electrolyte can also move into the gallery space. This tends to be the case when the electrolyte solvent molecules are relatively small, so that they can enter without causing a major disruption of the host structure. This is found to occur in some organic solvent systems, and also some aqueous electrolyte systems where the electroactive ion is surrounded by a water hydration sheath. This is a matter of major concern in the case of negative electrodes in lithium systems, and will be discussed at much greater length in a later chapter.

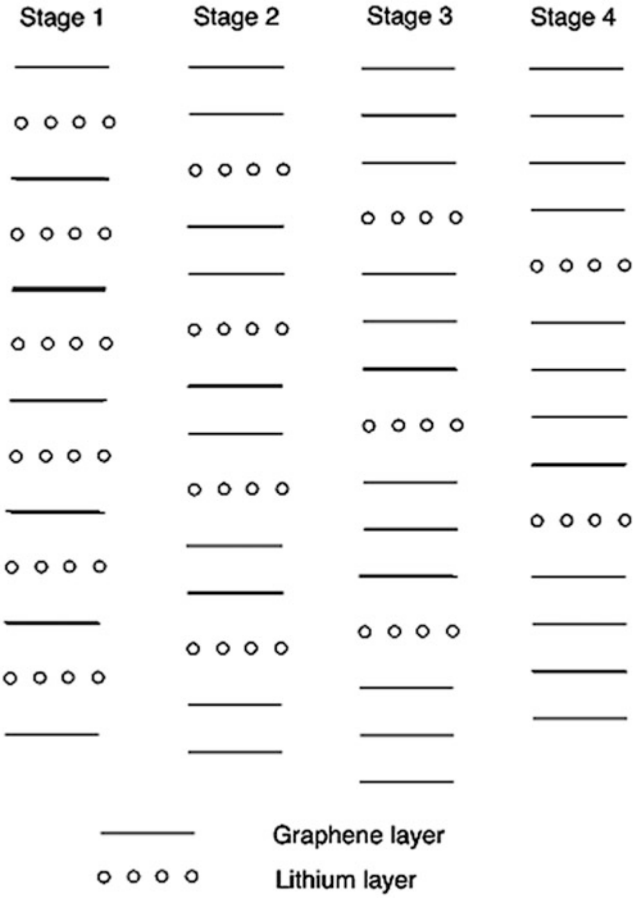

Fig. 14.10 Simple model depicting staging when potassium is inserted in the galleries of graphite

14.8 Insertion into Materials with Parallel Linear Tunnels

The existence of staging indicates that, at least in some materials, the presence of inserted species in one part of the structure is “seen” in other parts of the structure. An interesting example of this involves the presence of mobile guest species in the material Hollandite that has a crystal structure with parallel linear tunnels, rather than slabs.

A drawing of this structure is shown in Fig. 14.11. At low temperatures the interstitial ions within the tunnels are in an ordered arrangement upon the available sites. In addition, there is coordination between the arrangement in one tunnel with that of other nearby tunnels. Thus there is three-dimensional ordering of the guest species.

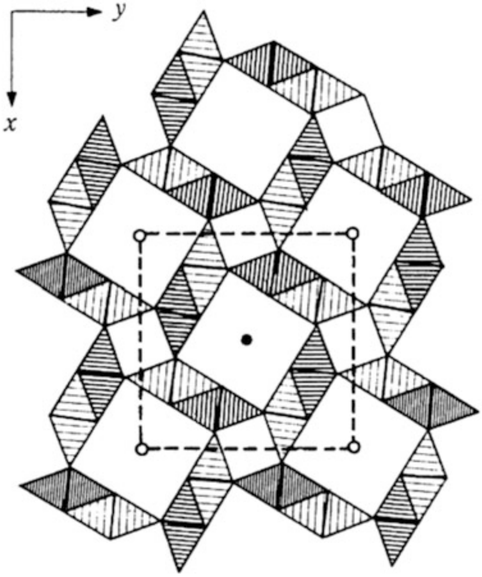

Fig. 14.11 Hollandite structure. Viewed along the c-axis

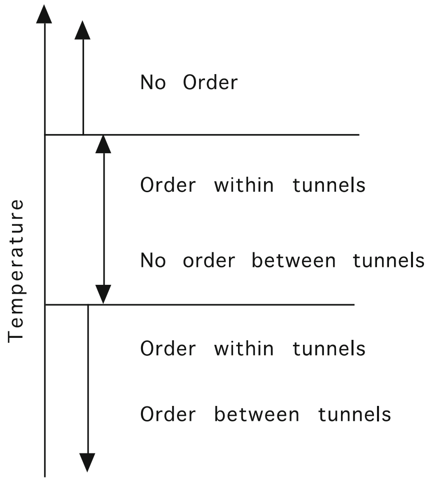

Fig. 14.12 Influence of temperature upon various types of order in a structure with parallel tunnels

As the temperature is raised somewhat, increased thermal energy causes the ordered interaction between the mobile ion distributions in nearby tunnels to relax, although the ordering within tunnels is maintained.

At even higher temperatures the in-tunnel ordering breaks down, so that the species are distributed randomly inside the tunnels, as well. The influence of temperature is illustrated schematically in Fig. 14.12.

14.9 Changes in the Host Structure Induced by Guest Insertion or Extraction

It was mentioned earlier that the insertion or extraction of mobile guest species can cause changes in the host structure. There are several types of such structural changes that can occur. They will be briefly discussed in the next sections.

14.9.1 Conversion of the Host Structure from Crystalline to Amorphous

There are a number of examples in which an initially crystalline material becomes amorphous as the result of the insertion of guest species, and the corresponding mechanical strains in the lattice. This often occurs gradually as the insertion/extraction reaction is repeated, e.g., upon electrochemical cycling. One example of this, the $Li_xV_6O_{13}$ binary system, is shown in Figs. 14.13 and 14.14 [8]. In this case, the shape of the potential curve during the first insertion of lithium into crystalline V_6O_{13} shows that a sequence of reconstitution reactions take place that give rise to a series of different phases, and a discharge curve with well-defined features.

After a number of cycles, however, the discharge curve changes, with a simple monotonous decrease in potential, indicative of a single-phase insertion reaction. X-ray diffraction experiments confirmed that the structure of the material had become amorphous.

Another example of changes resulting from an insertion reaction is shown in Fig. 14.15. In this case, lithium was inserted into a material that was initially

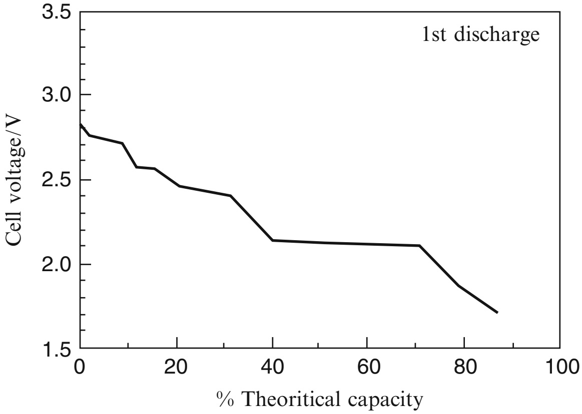

Fig. 14.13 Discharge curve observed during the initial insertion of lithium into a material that was initially V_6O_{13}. After [8]

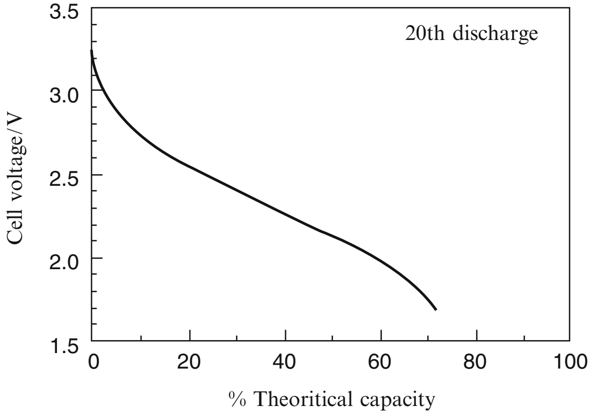

Fig. 14.14 Discharge curve observed during the 20th insertion of lithium into a material that was initially V_6O_{13}. After [8]

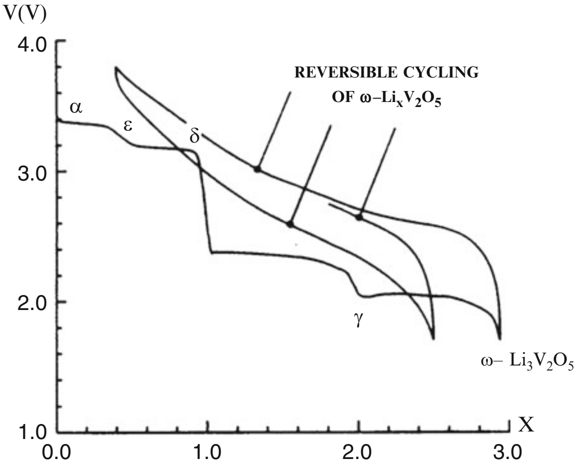

Fig. 14.15 The variation of the potential as lithium is added to V_2O_5. When the composition reached $Li_3V_2O_5$ an amorphous phase was formed. After [9]

V_2O_5 [9]. The result is similar to the V_6O_{13} case, with clear evidence of the formation of a series of different phases as lithium was added. It was found that the insertion reaction was reversible, forming the ε and δ structures, if only up to about 1 Li was inserted into α-V_2O_5. The addition of more lithium resulted in the formation of different structural modifications, called the γ and ω structures, which have nominal compositions of $Li_2V_2O_5$ and $Li_3V_2O_5$, respectively. These two reactions are not reversible, however.

When lithium was extracted from the ω phase, its charge–discharge curve became very different, exhibiting the characteristics of a single phase with a wide range of solid solution. The amount of lithium that could be extracted from this phase was quite large, down to a composition of about $Li_{0.4}V_2O_5$. Upon the reinsertion of lithium, the discharge curve maintained the same general form, indicating that a reversible amorphous structure had been formed during the first insertion process.

14.9.2 Dependence of the Product upon the Potential

It has been found that displacement reactions can occur in a number of materials containing silicon when they are reacted with lithium to a low potential (high lithium activity). An irreversible reaction occurs that results in the formation of fine particles of amorphous silicon in an inert matrix of a residual phase that is related to the precursor material [10, 11]. Upon cycling, the amorphous Li-Si structure shows both good capacity and high reversibility.

However, it has also been shown [12] that if further lithium is inserted, going to a potential below 50 mV, a crystalline Li-Si phase forms instead of the amorphous one.

Because of the light weight of silicon, the large amount of lithium that can react with it, and the attractive potential range, silicon or its alloys may play an important role as a negative electrode reactant in lithium batteries in the future.

14.9.3 Changes upon the Initial Extraction of the Mobile Species

Similar phenomena can also occur during the initial extraction of a mobile species that is already present in a solid. This is shown in Fig. 14.16 for the case of a material with an initial composition of about $Li_{0.6}V_2O_4$ [13]. It can be seen that the

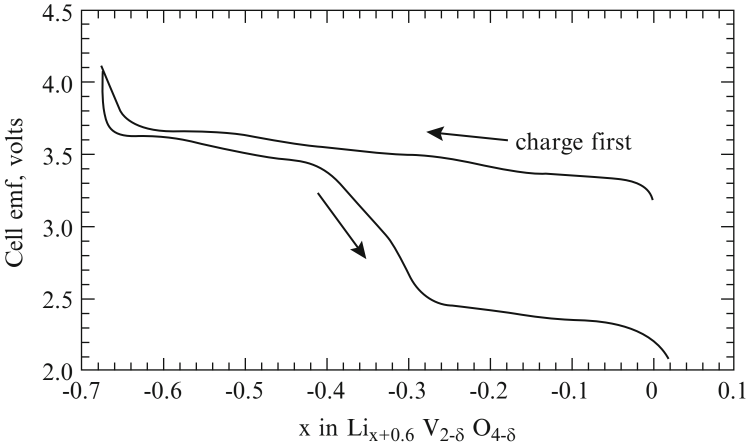

Fig. 14.16 Initial charging and discharge curves of a material with a composition of $Li_{0.6}V_2O_4$. After [13]

reaction starts between 3.0 and 3.5 V vs. pure Li, as is generally found for materials that have come into equilibrium with air. The reason for this will be discussed later.

The initial lithium could be essentially completely deleted from the structure, causing the potential to rise to over 4 V vs. pure lithium. When lithium was subsequently reinserted, the discharge curve had a quite different shape, indicating the presence of a reconstitution reaction resulting in the formation of an intermediate phase.

14.10 The Variation of the Potential with Composition in Insertion Reaction Electrodes

14.10.1 Introduction

The externally measured electrical potential of an electrode is determined by the electrochemical potential of the electrons within it, η_{e^-}. This is often called the *Fermi level*, E_F. Since potentials do not have absolute values, they are always measured as differences. The voltage of an electrochemical cell is the electrically measured difference between the Fermi levels of the two electrodes:

$$\Delta E = \Delta \eta_{e^-} \tag{14.1}$$

As has been demonstrated many times in this text already, the measured potential of an electrode often varies with its composition, e.g., as guests species are added to, or deleted from, a host material. The relevant compositional parameter is the chemical potential of the electrically neutral electroactive species. If this species exists as a cation M^+ within the electrode, the important parameter is the chemical potential of neutral M, μ_M. This is related to the electrochemical potentials of the ions and the electrons by

$$\mu_M = \eta_{M^+} + \eta_{e^-} \tag{14.2}$$

Under open circuit conditions there is no flux of ions through the cell. Since the driving force for the ionic flux through the electrolyte is the gradient in the electrochemical potential of the ions, for open circuit

$$\frac{d\eta_{M^+}}{dx} = \Delta \eta_{M^+} = 0 \tag{14.3}$$

Therefore, the measured voltage across the cell is simply related to the difference in the chemical potential of the neutral electroactive species in the two electrodes by

$$\Delta E = \Delta \eta_{e^-} = \frac{-1}{z_{M^+} q} \Delta \mu_M \tag{14.4}$$

The common convention is to express both the difference in the electrical potential (the voltage) and the difference in chemical potential as the values in the right-hand (positive) electrode less those in the left-hand electrode.

A general approach that is often used is to understand the potentials of electrons is based upon the *electron energy band model*. The critical features are the variation of the density of available states with the energy of the electrons, and the filling of those states up to a maximum value that is determined by the chemical composition. The energy at this maximum value is the *Fermi level*.

In the case of metals the variation of the potential of the available states is a continuous function of the composition, and the *free electron theory* can be used to express this relationship.

In nonmetals, semiconductors and insulators, the density of states is not a continuous function of the chemical composition. Instead, there are potential ranges in which there are no available states that can be occupied by electrons. In the case of the simple semiconductors such as silicon or gallium arsenide, one speaks of a *valence band*, in which the states are generally fully occupied, an *energy gap* within which there are no available states, and a *conduction band* with normally empty states. The concentrations of electrons in these energy bands varies with the temperature due to *thermal excitation*, and can also be modified by the presence of aliovalent species, generally called *dopants*. *Optical excitation* has an effect similar to that of *thermal excitation*.

In a number of materials, particularly those in which the electronic conductivity is relatively low, it is convenient to think of the relation between the occupation of energy states and a change in the formal valence, or charge, upon particular species within the host structure. For example, the addition of an extra electron could result in a change of the formal charge of $W^{6+}$to W^{5+}, Ti^{4+} to Ti^{3+}, Mn^{4+} to Mn^{3+}, or Fe^{3+} to Fe^{2+} in a transition metal oxide. Such phenomena are called *redox* reactions.

These different cases will be discussed below, and it will be seen that there is a clear relationship between them.

14.10.2 The Variation of the Electrical Potential with Composition in Simple Metallic Solid Solutions

There are a number of metals in which insertion of mobile guest species can occur. As mentioned already, this can be described as a solid solution of the guest species in the host crystal structure. The important quantity controlling the potential is the variation of the chemical potential of the neutral guest species as a function of its concentration. This can be formally divided into the influence of the change in the electron concentration in the host material, and the effect due to a change in the concentration of the ionic guest species, M^+.

In the case of a random solid solution in a material with a high electronic conductivity the two major contributions are the contribution from the composition dependence of the Fermi level of the degenerate electron gas that is characteristic of such mixed conductors, and that due to the composition dependence of the enthalpy and configurational entropy of the guest ions in the host crystal lattice [14].

14.10.3 Configurational Entropy of the Guest Ions

If the guest ions are highly mobile and can readily move through the host crystal structure we may assume that all of the identical crystallographic sites are equally accessible. There will be a contribution to the total free energy due to the *configurational entropy* S_c which is related to the random distribution of the guest atoms over the available sites. This can be expressed as

$$S_c = -k\left(\ln\frac{x}{x_0 - x}\right) \tag{14.5}$$

where x is the concentration of guest ions and x_o is the concentration of identical available sites. k is Boltzmann's constant. The configurational entropy contribution to the potential is the product of the absolute temperature and the entropy. This is plotted in Fig. 14.17.

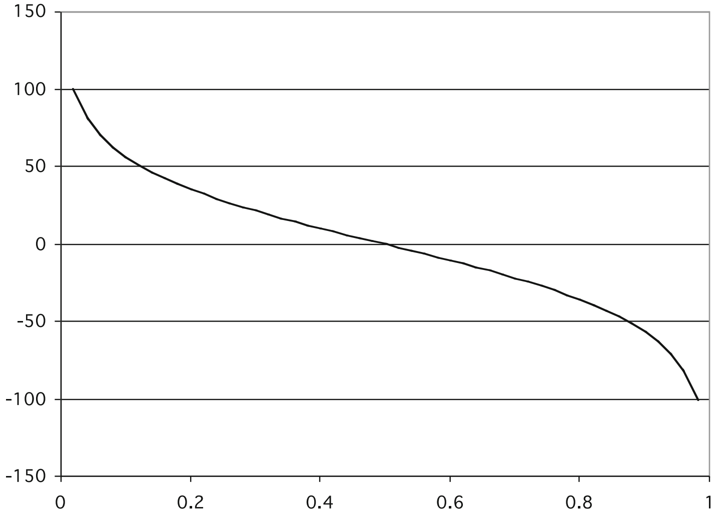

Fig. 14.17 Contribution to the potential due to the configurational entropy of a random distribution of guest ions upon the available identical positions in a host crystal structure. The values on the abscissa are the fractional site occupation, and those on the ordinate are mV [14]

This model assumes that there is no appreciable interaction between nearby guest species, and that there is only one type of site available for them to occupy.

14.10.4 The Concentration Dependence of the Chemical Potential of the Electrons in a Metallic Solid Solution

In a simple metal the electron concentration is typically sufficiently high that at normal temperatures the electrochemical potential of the electrons can be approximately by the energy of the Fermi level E_F.

In the free electron model this can be expressed as

$$E_F = \frac{h^2}{8m\pi^2}\left(\frac{3\pi^2 N_A}{V_m}\right)^{2/3} N^{2/3} \tag{14.6}$$

where m is the electron mass, N_A is Avogadro's number, V_m is the molar volume, and E_F is calculated from the bottom of the conduction band.

Thus the electronic contribution to the total chemical potential is proportional to the 2/3 power of the guest species concentration if the simple free electron model is valid. More generally, however, the electron mass is replaced by an effective mass m^*. This takes into account other effects, such as the influence of the crystal structure upon the conduction band.

Then the chemical potential of the electrons is directly related to the Fermi level, E_F, which can be written as

$$E_F = (\text{Constant})\left(\frac{x^{2/3}}{m^*}\right) \tag{14.7}$$

where x is the guest ion concentration and m^* is the effective mass of the electrons.

14.10.5 Sum of the Effect of These Two Components upon the Electrical Potential of a Metallic Solid Solution

Thus the composition dependence of the electrode potential in a metallic solid solution can be written as the sum of the influence of composition upon the configurational entropy of the guest ions, and the composition dependence of the Fermi level of the electrons. This can be simply expressed as

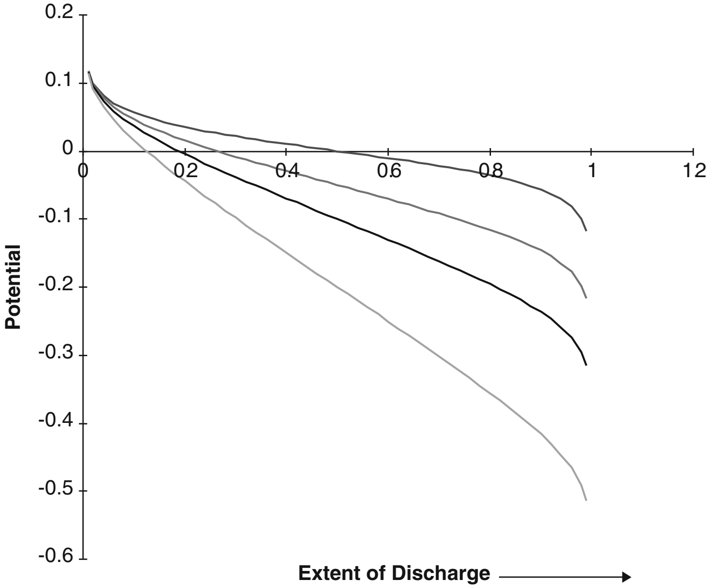

Fig. 14.18 Calculated influence of the value of the electronic effective mass upon the composition dependence of the potential in an insertion reaction in a simple metal [14]

$$E = (\text{Constant})\left(\frac{x^{2/3}}{m^*}\right) - \left(\frac{\text{RT}}{\text{zF}}\right)\ln\left(\frac{\text{x}}{\text{1-x}}\right) \qquad (14.8)$$

This relationship is illustrated in Fig. 14.18 for several values of the electron effective mass. It also shows the influence of the value of the electron effective mass upon the general slope of the curve. From Eq. (14.8) it can be seen that smaller effective masses make the first term larger, and this results in the potential being more composition dependent.

An example showing experimental data [14] that illustrate the general features of this model is shown in Fig. 14.19. The host material in this case was an oxide, a "tungsten bronze." In this family of oxides the electronic conductivity is very high, and the electron energy spectrum approximates that of a free electron metal.

It should be remembered that although the band diagrams commonly used in discussing semiconductors are plotted with greater energy values higher, the scale of the electrical potential is in the opposite direction. This is because the energy of a charged species is the product of its charge and the electrical potential, and the charge on electrons is negative.

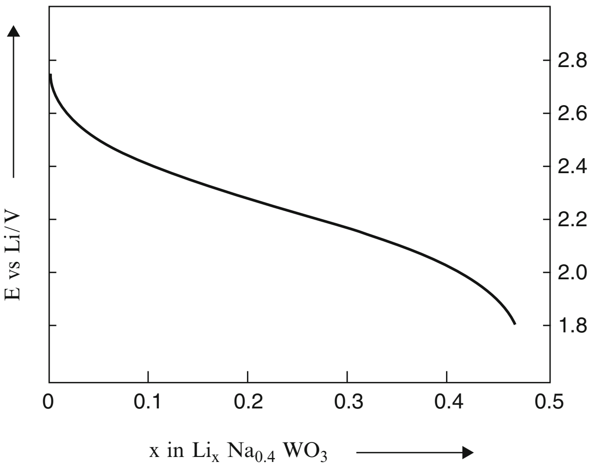

Fig. 14.19 Variation of the electrical potential as a function of lithium concentration in $Li_xNa_{0.4}WO_3$. After [14]

14.10.6 The Composition Dependence of the Potential in the Case of Insertion Reactions That Involve a Two-Phase Reconstitution Reaction

The earlier discussion of the influence of the Gibbs Phase Rule upon the compositional variation of the potentials in electrodes pointed out that when there are two phases present in a two-component system, the potential will have a fixed, or constant, value, independent of the composition. This will also be the case for materials that act as pseudo-binaries, regardless of how many different species are actually present. A number of insertion reaction materials are of this type, with one relatively mobile species inside a relatively stable host structure. If, in the time span of interest, the host structure does not undergo any changes it can be considered to be a single component thermodynamically. This is the case in a number of materials in which the host structure is a transition metal oxide.

One example in which the potential is composition-independent involves the insertion and extraction of lithium in materials with the nominal composition $Li_4Ti_5O_{12}$, which has a defect spinel crystal structure [15].

The normal composition of spinel structure materials can be described as AB_2O_4, where the A cation species resides on tetrahedral sites, and the B cation species on octahedral sites within a close-packed face-centered cubic oxygen lattice. This composition can also be written as $A_3B_6O_{12}$.

If this material were to have the $Li_4Ti_5O_{12}$ stoichiometry, an extra lithium ion must be present, and a titanium ion is missing.

This can be accomplished replacing a missing titanium ion with an extra lithium ion on an octahedral B site in the structure. The other three lithium ions would

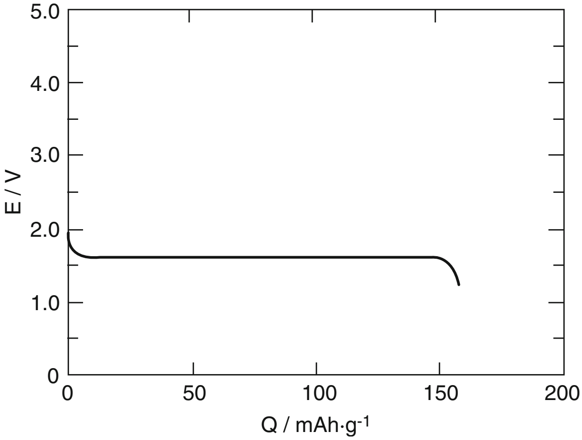

Fig. 14.20 Charge and discharge curve of $Li_4Ti_5O_{12}$ cell. After [15]

remain on their normal tetrahedral A sites. Thus the composition can be written as $Li_3[LiTi_5]O_{12}$, or alternatively, $Li[Li_{1/3}Ti_{5/3}]O_4$.

It has been found that an additional lithium ion can react with this material, and this can be written as

$$Li + Li\left[Li_{1/3}Ti_{5/3}\right]O_4 = Li_2\left[Li_{1/3}Ti_{5/3}\right]O_4 \tag{14.9}$$

X-ray diffraction data have indicated that all the lithium ions now occupy octahedral sites, instead of tetrahedral sites. Since there are only as many octahedral sites available as oxide ions in this structure, they must now be all filled. This is likely why the capacity of this electrode material is limited to this composition.

Experiments were performed on samples of these materials that were prepared in air, and were white in color. As with all essentially all materials prepared in air, their potential was initially near 3 V versus lithium. In electrochemical experiments, when lithium was added by transfer from the negative electrode, lithium in carbon, the potential went rapidly down to 1.55 V, and remained there until the reaction was complete. Thus this insertion reaction has the characteristics of a moving-interface reconstitution reaction.

Upon deletion of the inserted lithium the potential retraced the discharge curve closely, with very little hysteresis. This is illustrated in Fig. 14.20 [15]. Because of the small volume change, negligible hysteresis and rapid kinetics this material acts as a very attractive electrode in lithium cells. The one disadvantage is that its potential is, unfortunately, about half way between the negative and positive electrode potentials in most lithium batteries.

As will be discussed later, hysteresis, which leads to a difference in the composition-dependence of the potential when charging and discharging, is often related to mechanical strain energy, i.e., dislocation generation and motion, as a

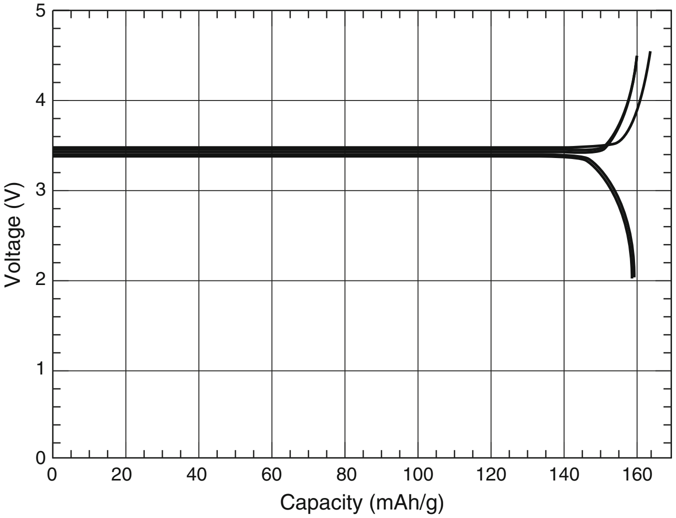

Fig. 14.21 Charge and discharge curves for the reaction of lithium with $FePO_4$. After [16]

consequence of volume changes that occur due to the insertion and extraction of guest ions.

Another example of an insertion-driven reconstitution reaction is the reaction of lithium with $FePO_4$, which also happens readily at ambient temperature. This also has a very flat reaction potential, as shown in Fig. 14.21 [16]. In this case the material is prepared (in air) as $LiFePO_4$, and the initial reaction within the cell involves charging, i.e., deleting lithium from its crystal structure. This lithium goes across the electrochemical cell and into the carbon material in the negative electrode. The reaction that occurs at the operating potential during the initial charge can be simply written as

$$LiFePO_4 = Li + FePO_4 \tag{14.10}$$

Upon discharge of the cell, the reaction goes, of course, in the opposite direction.

This material is now one of the most important positive electrode reactants in lithium batteries, and will be discussed further in a later chapter.

14.11 Final Comments

This chapter is intended to be only a general introduction to the scope of insertion reactions in electrode materials. This is a very important topic, and will be addressed further in the discussions of specific materials in later chapters.

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