Chapter 15
Electrode Reactions That Deviate from Complete Equilibrium

15.1 Introduction

The example that was discussed earlier, the reaction of lithium with iodine to form LiI, dealt with elements and thermodynamically stable phases. By knowing a simple parameter, the Gibbs free energy of formation of the reaction product, the cell voltage under equilibrium and near-equilibrium conditions can be calculated for this reaction. If the cell operates under a fixed pressure of iodine at the positive electrode and at a stable temperature, the Gibbs phase rule indicates that the number of the residual degrees of freedom F in both the negative and positive electrodes is zero. Thus the voltage is independent of the extent of the cell reaction in both cases.

This is a case in which the reaction involves species that are *absolutely stable*. The description of a phase as absolutely stable means that it is in the thermodynamic state, e.g., crystal structure, with the lowest possible value of the Gibbs free energy for its chemical composition.

15.2 Stable and Metastable Equilibrium

On the other hand, there could be several versions of a phase with different structures that might be stable in the sense that they have lower values of the Gibbs free energy than would be the case with minor changes. Such a situation, in which a phase is stable against small perturbations, is described by the term *metastable*. On the other hand, it may be less stable than the *absolutely stable* modification. This can be illustrated schematically by the use of a simple mechanical model, as is illustrated in Fig. 15.1.

This situation can also be described in terms of the changes in the potential energy of a simple block. If the block sits on its end, it is in a metastable state, and if it is tipped a small amount, its potential energy will be increased, but it will tend to

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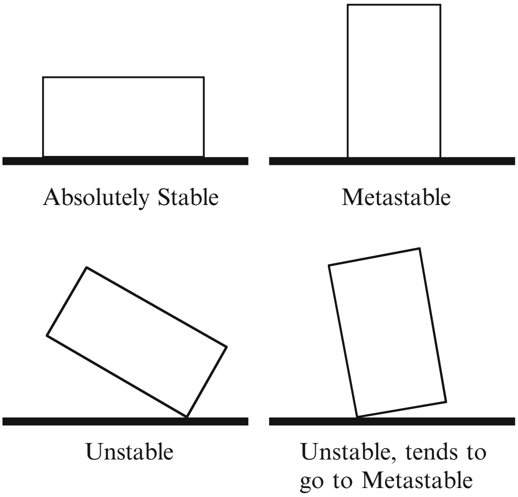

Fig. 15.1 Simple mechanical model illustrating metastable and absolutely stable states

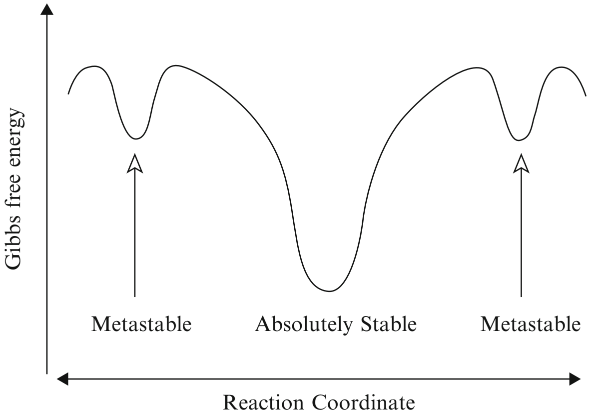

Fig. 15.2 Reaction coordinate representation of a system with metastable and absolutely stable states

revert back to its initial metastable condition. But a larger perturbation will get it over this potential energy hump so that it will tip over and land in the flat position, the absolutely stable state.

This situation can also be illustrated by the use of a reaction coordinate diagram of the type often used in discussions of chemical reaction kinetics, as shown in Fig. 15.2.

This discussion does not only apply to single phases, for it is possible to have a situation in which a material has a microstructure that consists of a metastable single phase, whereas the absolutely stable situation involves the presence of two, or perhaps more, phases. In order for the system to go from the metastable single-phase situation to the more stable *polyphase* structure it is necessary to *nucleate* the additional phase or phases as well as to change the composition of the initial metastable phase. This may be kinetically very difficult.

In the case of the Li/I system, where there is only one realistic structure for the reactant and product phases, only the absolutely stable situation has to be considered.

However, in other materials systems the situation is often different at lower temperatures from that at high temperatures, where absolutely stable phases are generally present. As will be discussed later, metastable phases and metastable crystal structures often play significant roles at ambient temperatures.

15.3 Selective Equilibrium

There is also the possibility that a material may attain equilibrium in some respects, but not in others. Some of the most interesting and important ambient temperature materials fall into this category.

A number of the reactants in ambient temperature battery systems have crystal structures that can be described as a composite consisting of a highly mobile ionic species within a relatively stable host structure.

Such structures are sometimes described as having two different *sub-lattices*, one of which has a high degree of mobility, and the other is highly stable, for its structural components are rigidly bound. The guest species with high mobilities are typically rather small and move about through interstitial tunnels in the surrounding rigid host structure. The species in the mobile sub-lattice can readily come to equilibrium with the thermodynamic forces upon them, whereas the more tightly bound parts of the host structure cannot.

The term *selective equilibrium* can be used for this situation. Under these conditions, the stable part of the crystal structure can be treated as a single component when considering the applicability of the Gibbs phase rule. An example that will be discussed later is the phase Li_xTiS_2. The structure of this material can be thought of as consisting of rigid planar slabs of covalently bonded TiS_2, with mobile lithium ions in the space between them. The lithium species readily attain equilibrium with the external environment at ambient temperatures, whereas the TiS_2 part of the structure is relatively inert so that it can be considered to be a single component. Thus at a fixed temperature and total pressure the number of residual degrees of freedom is 1. This means that the value of one additional thermodynamic parameter will determine all of the intensive variables. As an example, a change in the electrical potential causes a change in the equilibrium amount of lithium in the structure, the value of x in Li_xTiS_2, but has no influence upon the TiS_2 slabs.

15.4 Formation of Amorphous vs. Crystalline Structures

An amorphous structure can result when a phase is formed under conditions in which complete equilibrium and the expected crystalline structure cannot be attained. Although they may have some localized ordered arrangements, amorphous structures do not have regular long-range arrangements of their constituent atoms or ions. Amorphous structures are always less stable than the crystalline structure with the same composition. Thus they have less negative values of the Gibbs free energy of formation than their crystalline cousins.

If the phase LiM can be electrochemically synthesized by the reaction of lithium with species M, a type of reconstitution reaction, there will be a corresponding constant voltage two-phase plateau in the titration curve related to that reaction. The magnitude of the plateau voltage is determined by the Gibbs free energy of the product phase, as described earlier. Because of its less negative Gibbs free energy of formation, the potential of the plateau related to the formation of an amorphous LiM phase must always be lower than that of the corresponding crystalline version of LiM. This is illustrated schematically in Fig. 15.3.

This has interesting consequences for the case in which two intermediate phases can be formed. As an example, assume that lithium can react with material M to form two phases in sequence, LiM and $\mathrm{Li_2M}$. The reaction for the formation of the first phase, LiM is

$$\mathrm{Li} + \mathrm{M} = \mathrm{LiM} \tag{15.1}$$

and if the phase LiM has a very narrow range of composition, the equilibrium titration curve, a plot of potential E versus composition, will look like that shown in Fig. 14.3.

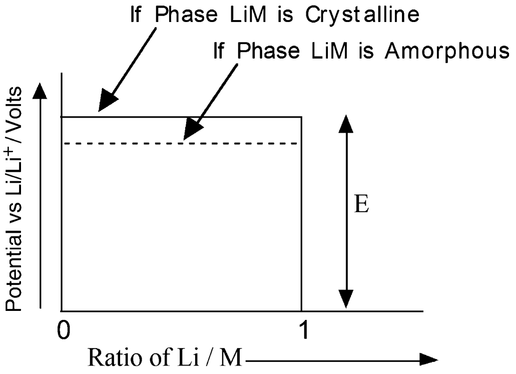

Fig. 15.3 Schematic drawing of the voltage of galvanic cell as a function of overall composition for a simple formation reaction Li + M = LiM for two cases, one in which the LiM product is crystalline, and the other in which it is amorphous

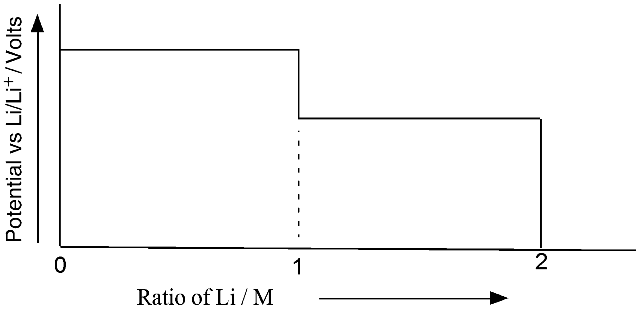

Fig. 15.4 Schematic titration curve for a sequence of two reactions of Li with M, first forming LiM, and then forming Li_2M

The plateau voltage is given by

$$E = -\Delta G_f^{\circ}(\mathrm{LiM})/F \tag{15.2}$$

If additional lithium can react with LiM to form the phase Li_2M there will be an additional voltage plateau, whose potential is determined by the reaction

$$\mathrm{Li} + \mathrm{LiM} = \mathrm{Li_2M} \tag{15.3}$$

This is shown schematically in Fig. 15.4.

The voltage of the second plateau is lower than that of the first, and is given by

$$E = -\left[\Delta G_f^{\circ}(\mathrm{Li_2M}) - \Delta G_f^{\circ}(\mathrm{LiM})\right]/F \tag{15.4}$$

But what if the first phase, LiM, is amorphous, rather than crystalline? As mentioned above, this means that Gibbs free energy of formation of that phase is smaller and the voltage of the first plateau is reduced.

The total Gibbs free energy of the two reactions is determined, however, by the Gibbs free energy of formation of the final phase, Li_2M. This is not changed by the formation of the intermediate phase LiM. The total area under the curve is thus a constant. The interesting result is that if the voltage of the first plateau is reduced, the voltage of the second one must be correspondingly increased. This can be depicted as in Fig. 15.5.

Thus the lower stability of the intermediate phase reduces the magnitude of the step in the titration curve. Therefore the overall behavior approaches what it would be if the intermediate phase did not form at all, and there would only be one reaction, the direct formation of phase Li_2M.

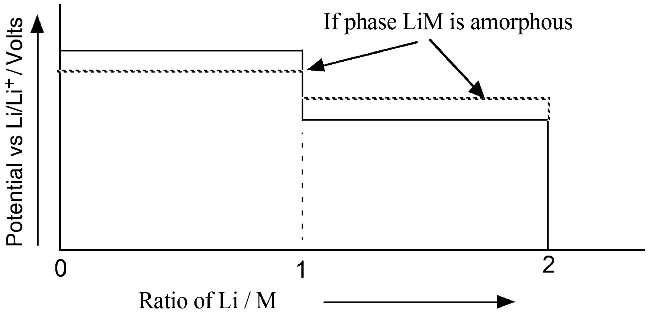

Fig. 15.5 Change in the schematic titration curve if the first product, LiM, is amorphous. The voltage of the second plateau must be higher to compensate for the reduced voltage of the first plateau

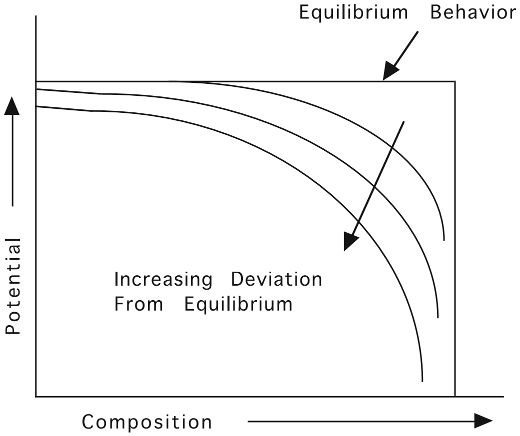

Fig. 15.6 Schematic representation of the influence of kinetic limitations upon both the potential and capacity of an electrode reaction

15.5 Deviations from Equilibrium for Kinetic Reasons

The observed potentials and capacities of electrodes are often displaced from those that would be expected from equilibrium thermodynamic considerations because of kinetic limitations. There may not be sufficient time to attain the compositional and/or structural changes that should, in principle, occur. This is more likely to occur at lower temperatures, and under higher current conditions.

The influence of increasing deviations from equilibrium conditions upon the behavior of a simple reconstitution reaction is shown schematically in Fig. 15.6. It is seen that both the potential and the apparent capacity can deviate significantly from equilibrium values.

The kinetics of electrode reactions, and methods that can be used to evaluate them, will be discussed in subsequent chapters.