

6. Insertion reaction electrodes (Huggins, ch. 6)

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- Mobile guest species can be inserted into, or removed (extracted) from, a stable host crystal structure
- In many cases the *insertion* of guest species is reversible
- 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 → “insertion” and “extraction” are more general terms → 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. The occurrence of a topotactic reaction implies some 3-D correspondence between the crystal structures of the parent and the product.
cf. the term epitaxy relates to 2-D, such as on a surface

-hydrogen can be inserted into, and extracted from, palladium and some of its alloys. Palladium–silver alloys are commonly used as hydrogen-pass filters

-graphite and some clays, used to remove contaminants from water by absorbing them into their crystal structures

-most common guest cationic species: H^+ , Li^+ , and Na^+

-electrostatic energy considerations dictate that only neutral species, or neutral combinations of species, can be added to, or deleted from, solids → 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 → this phenomenon almost always involves materials that have at least some modicum of electronic conductivity

-In some cases, however, the insertion or extraction of mobile atomic or ionic species causes irreversible changes in the structure of the host material. In extreme cases, the structure may be so distorted that it becomes *amorphous*

1. Examples of the Insertion of Guest Species into Layer Structures

-*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 interslab dimensions can be varied.

e.g. CdI_2 structure → stoichiometry MX_2 , 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 (Fig. 6.1)

CdI_2 , $\text{Mg}(\text{OH})_2$, $\text{Fe}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, and TiS_2

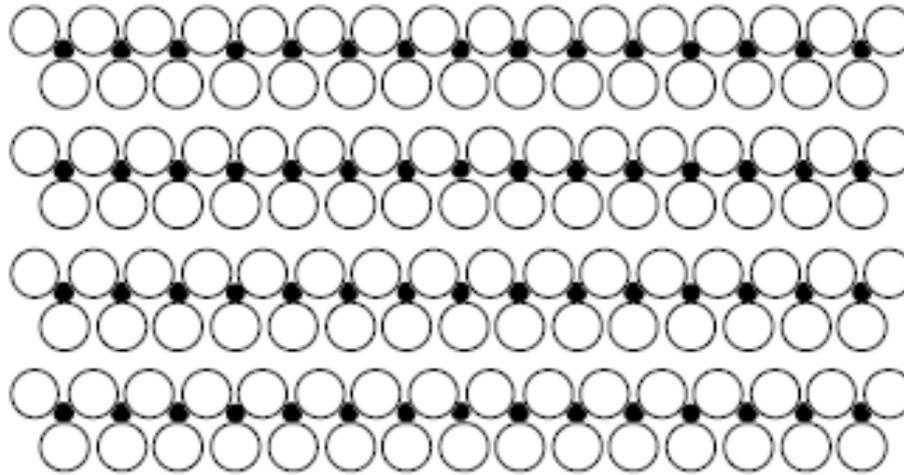


Fig. 6.1 Simple schematic model of a layer-type crystal structure with hexagonal ABABAB stacking. The empty areas between the covalently bonded slabs are called galleries

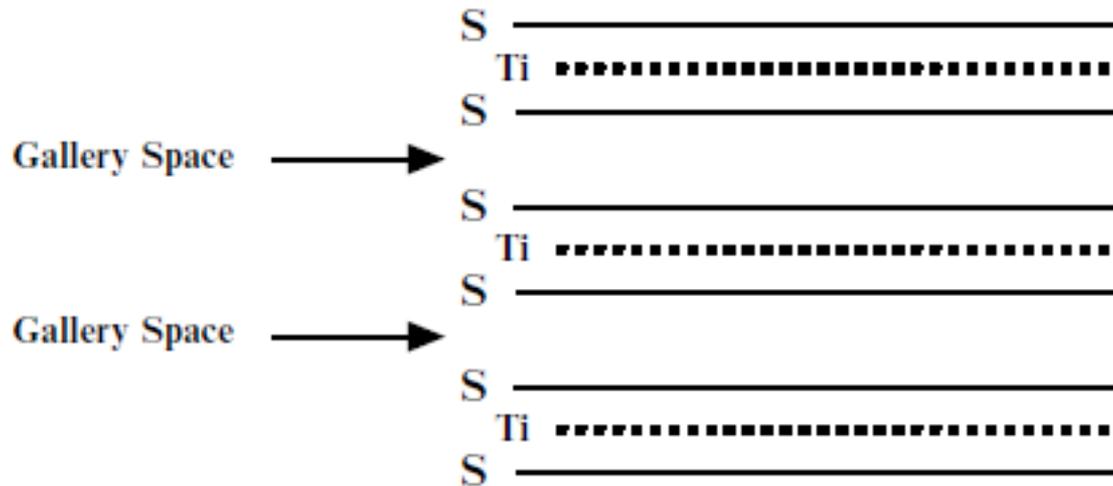


Fig. 6.2 Another type of model of a layer-type crystal structure. The example is TiS_2

2. Floating and Pillared Layer Structures

-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. → floating → guest results in a significant change in the interslab spacing

-in other cases the slabs are already rigidly connected by *pillars*, which partially fill the galleries through which the mobile species move → the mobile species move through a 2-D network of interconnected tunnels, instead of through a sheet of available sites

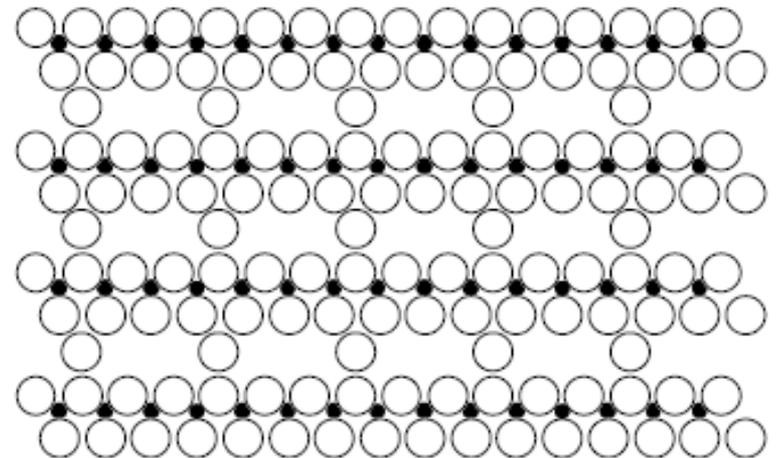


Fig. 6.3 Schematic model of pillared layer structure

3. 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. e.g. covalently bonded MX_2 slabs such CdI_2
- 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

4. Types of Inserted Guest Species Configurations

-several types of insertion reactions. In one case the mobile guest species randomly occupy sites, gradually filling them all up as the guest population increases → the variation of the electric potential with composition indicates a single-phase solid solution reaction

-if 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.

-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

require 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. 6.4–6.6.

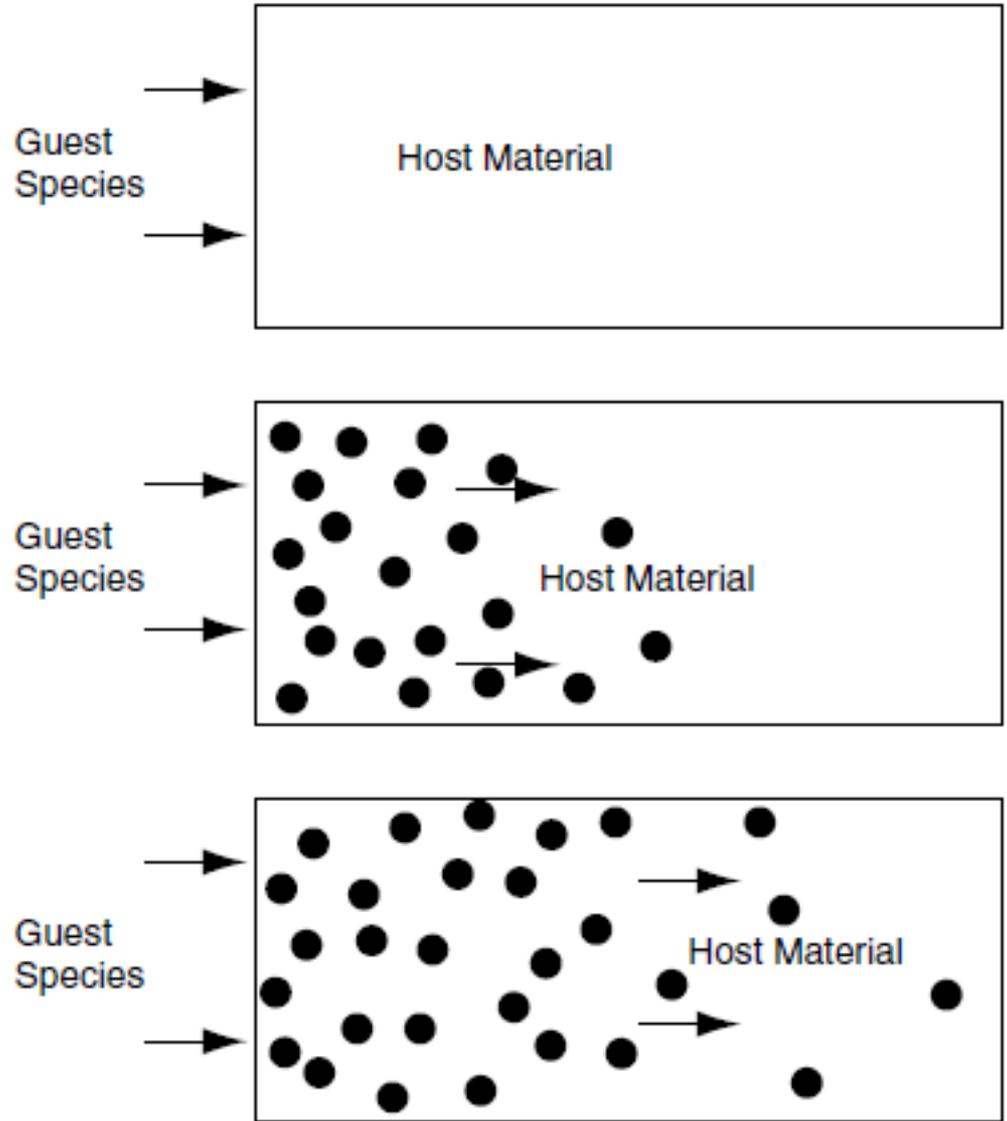


Fig. 6.4 Random diffusion of guest species into gallery space

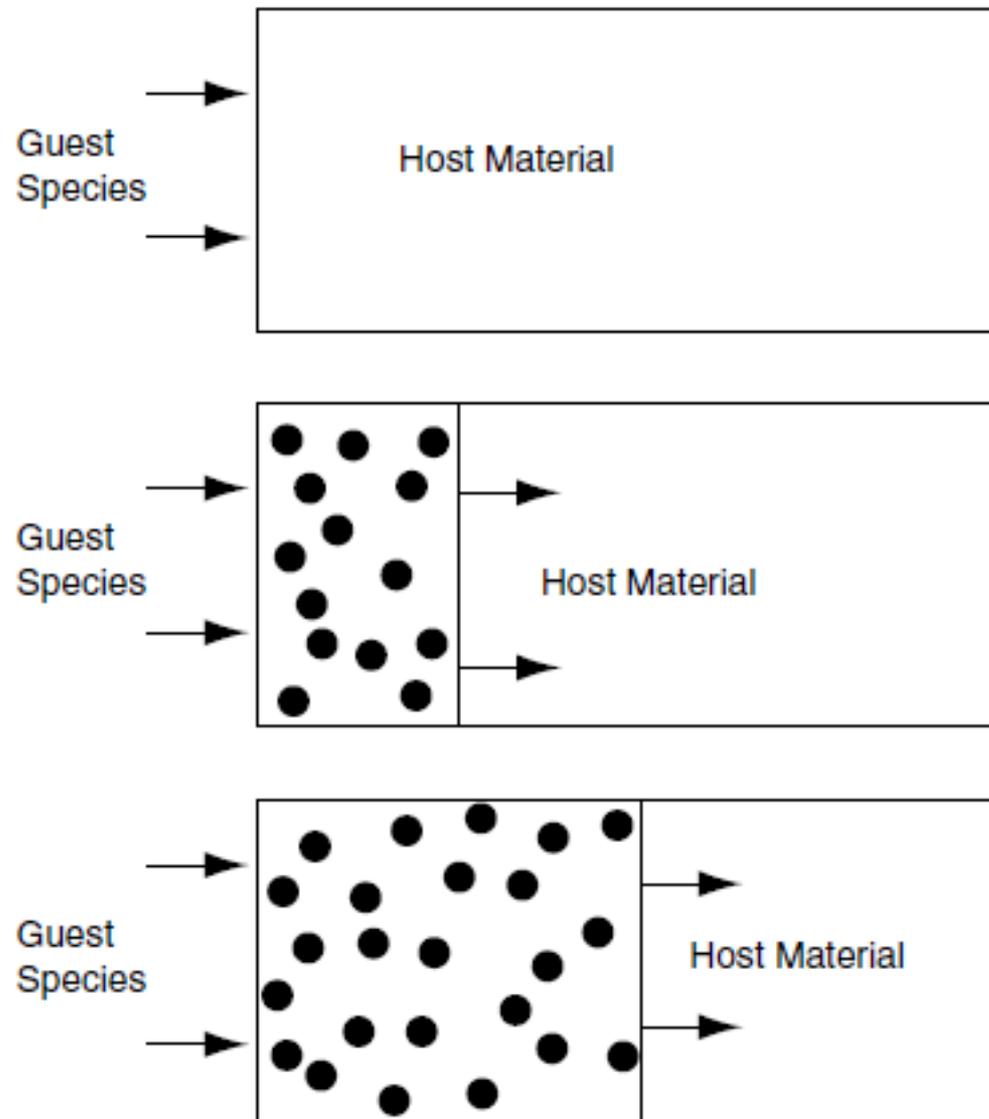


Fig. 6.5 Motion of two-phase interface when guest species is not ordered upon possible sites

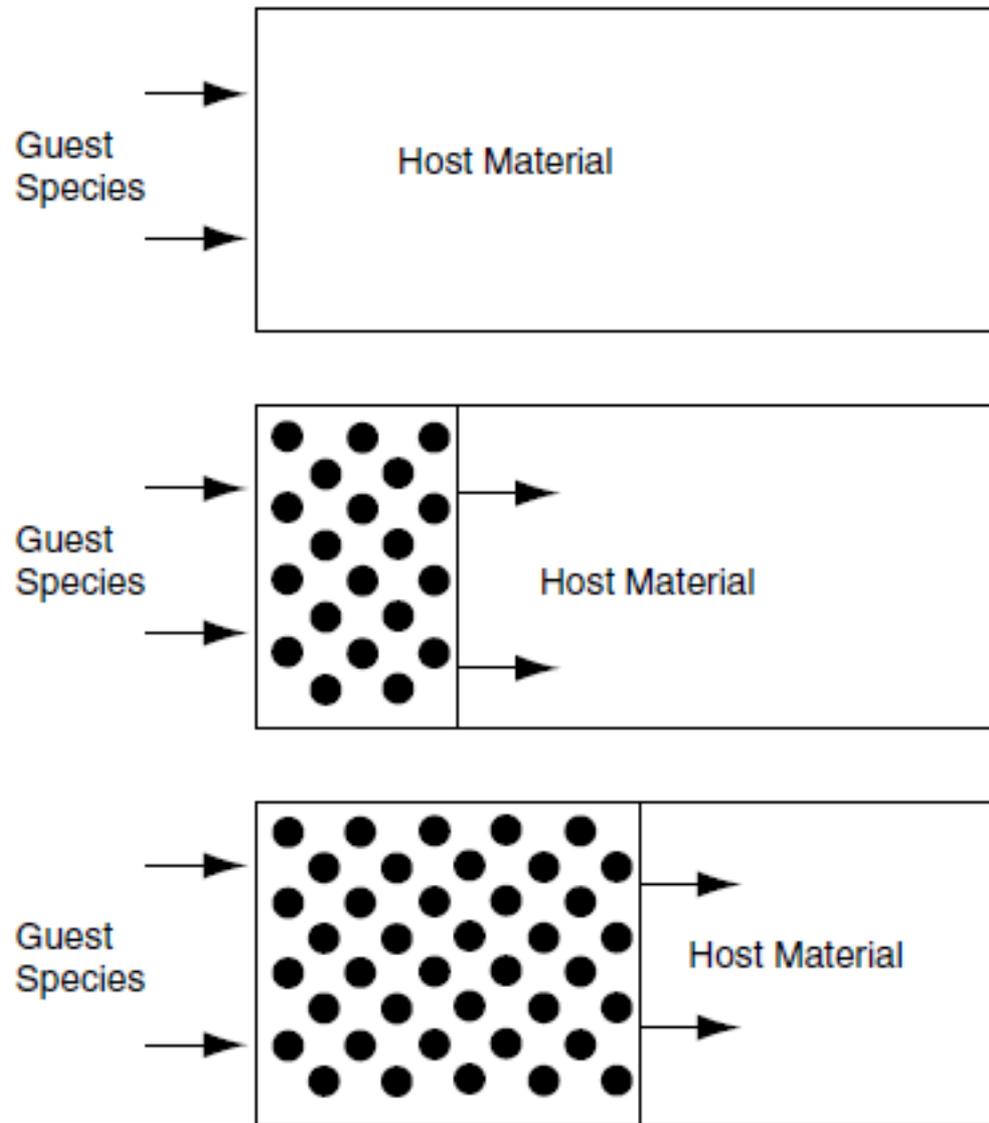


Fig. 6.6 Motion of two-phase interface when guest species is ordered upon possible sites in the gallery space

5. 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 6.7: insertion of lithium into NiPS_3 \rightarrow two types of sites available (random occupation in both cases) \rightarrow 1.4 Li

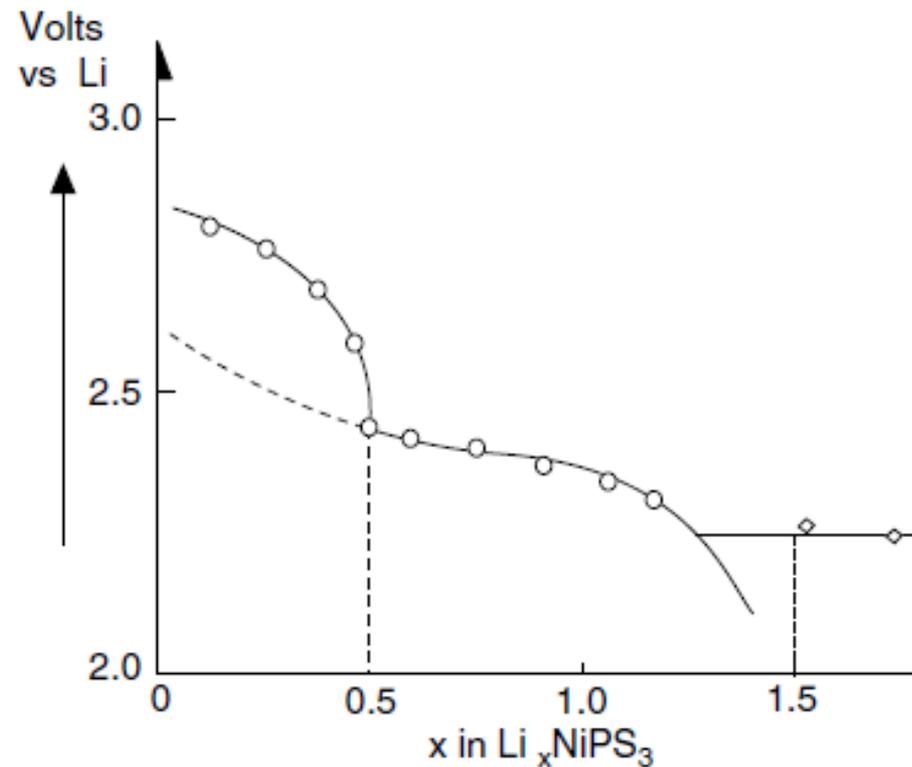


Fig. 6.7 Coulometric titration curve related to the insertion of lithium into NiPS_3 . There is random filling of the first two types of sites. A reconstitution reaction occurs above about 1.4 Li

Another example: different types of sites available for the insertion of Li ions involves the host $K_xV_2O_5$ structure \rightarrow different types of sites for guest ions

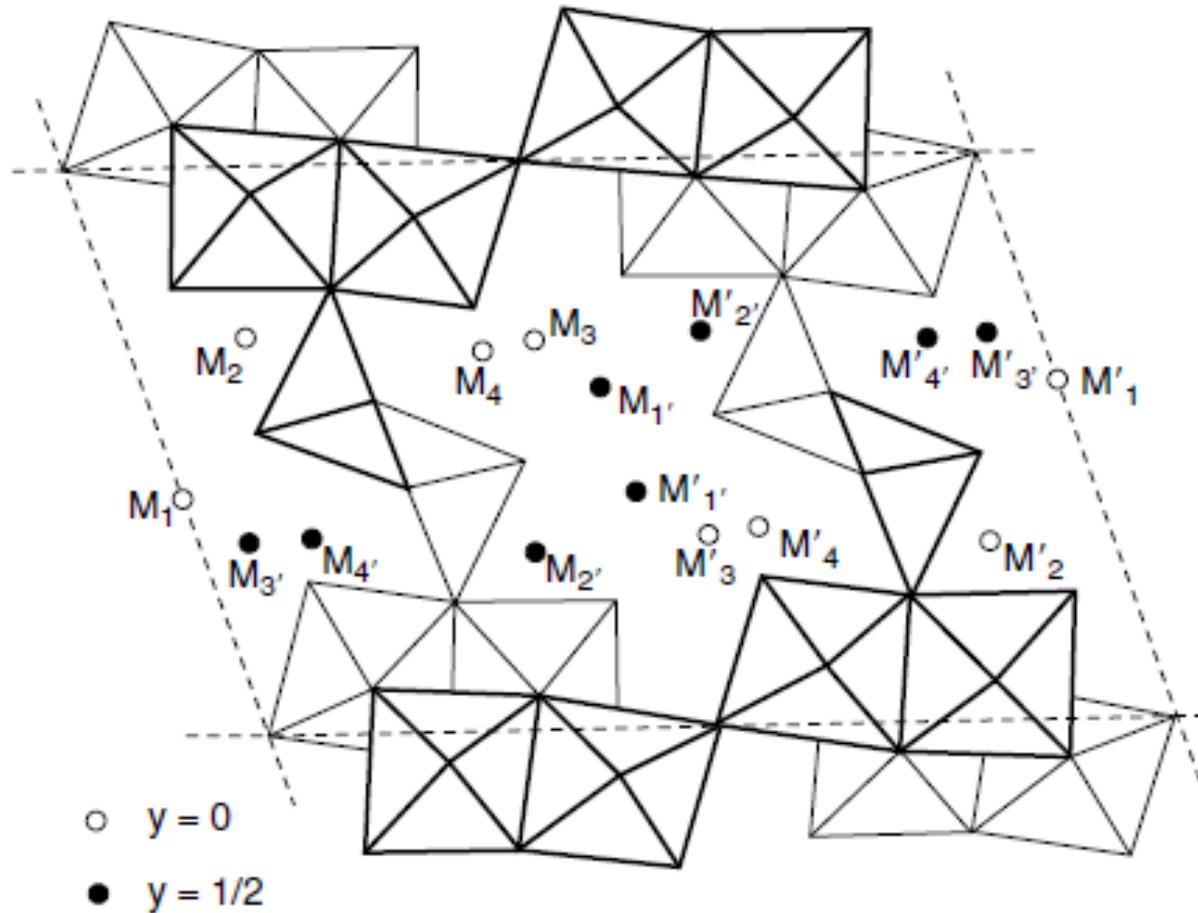


Fig. 6.8 (010) projection of the $K_xV_2O_5$ structure, showing the different types of sites for the guest species

Coulometric titration curve for the insertion of Li ions into a member of this group of materials → the reaction involves three sequential steps.

- (i) Up to about 0.4 Li can be incorporated into the first set of sites randomly.
- (ii) This is followed by the insertion of another 0.4 Li into another set of sites in an ordered arrangement → there are two different lithium arrangements, with a moving interface between them → two phases present, so this corresponds to a reconstitution reaction
- (iii) This is then followed by another reconstitution reaction, the insertion of about one additional Li into another ordered structure.

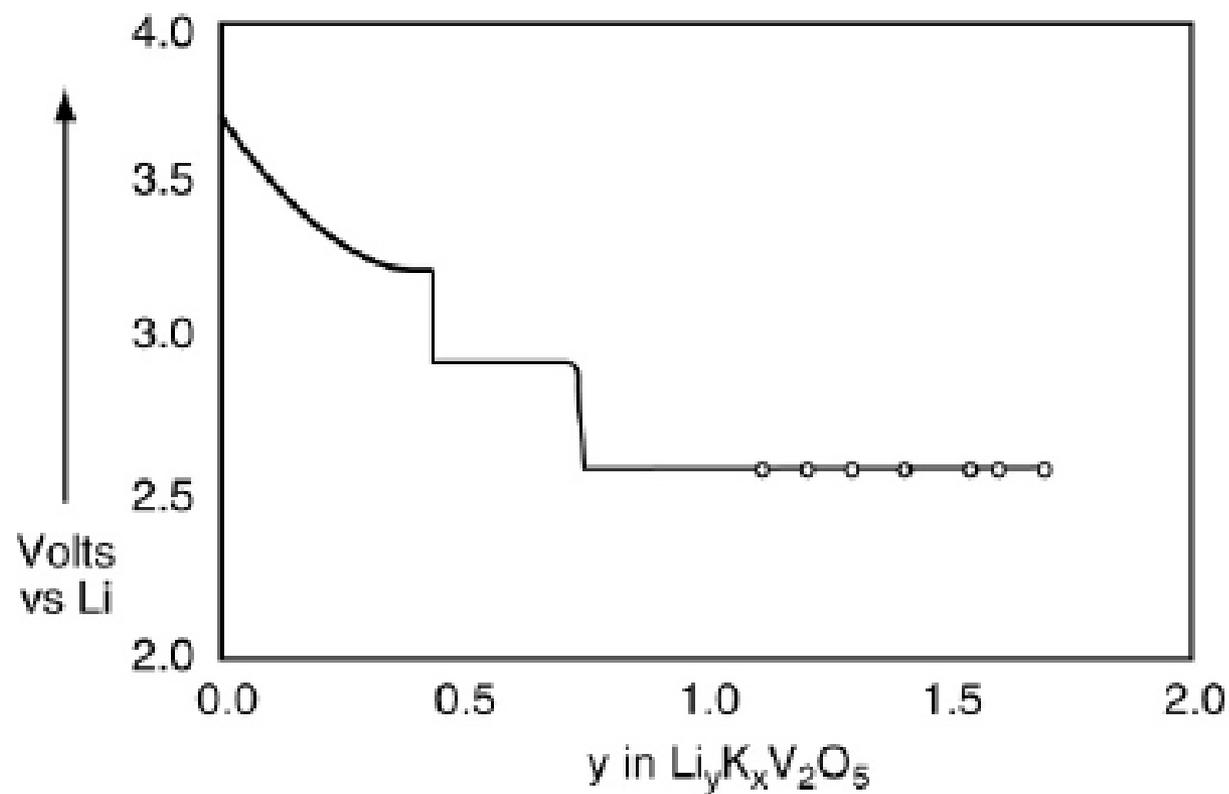


Fig. 6.9 Coulometric titration curve for the insertion of Li into $\text{K}_{0.27}\text{V}_2\text{O}_5$

6. Coinsertion 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 major disruption of the host structure.

7. Insertion into Materials with Parallel Linear Tunnels

-mobile guest species in the material Hollandite, that has a crystal structure with parallel linear tunnels, rather than slabs. 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 3-D ordering of the guest species.

Fig. 6.11

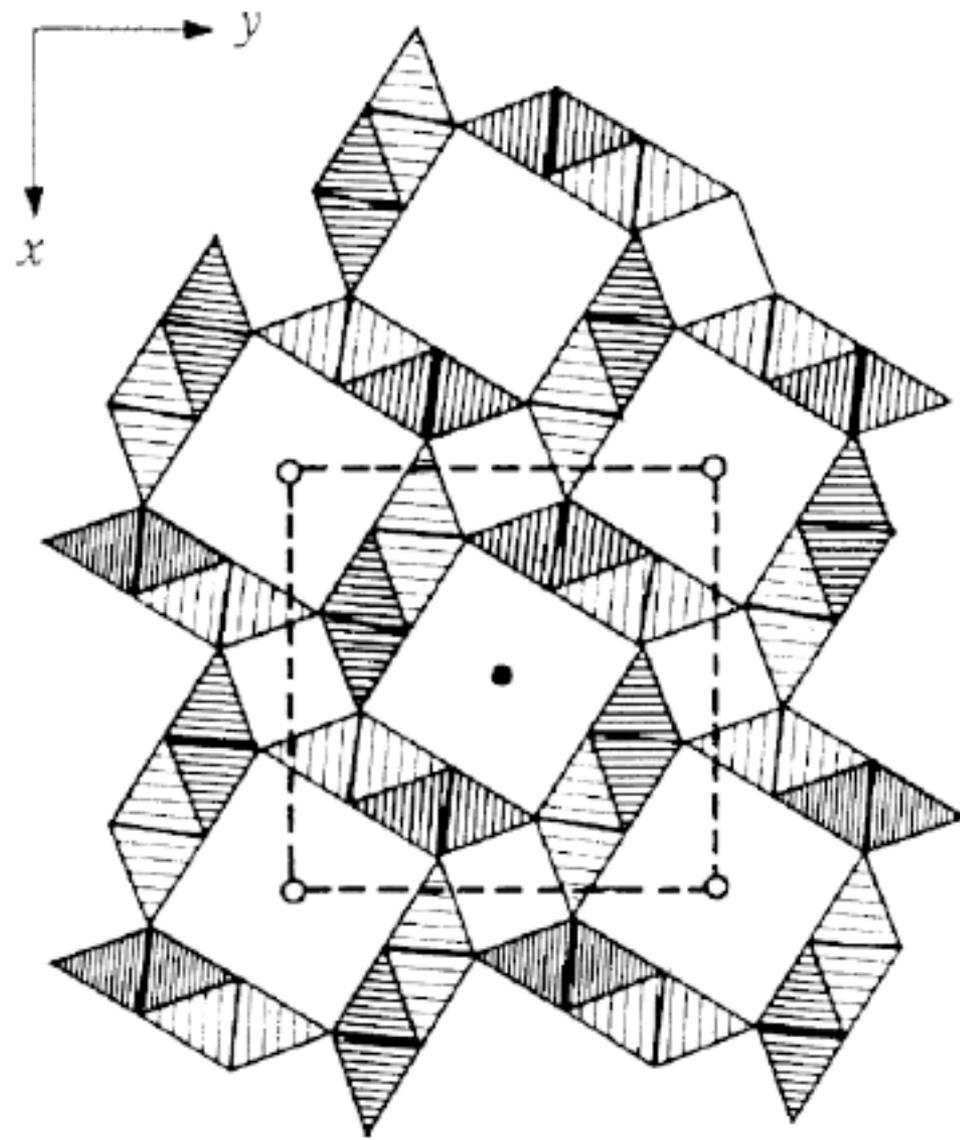


Fig. 6.11 Hollandite structure. Viewed along the c -axis

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.

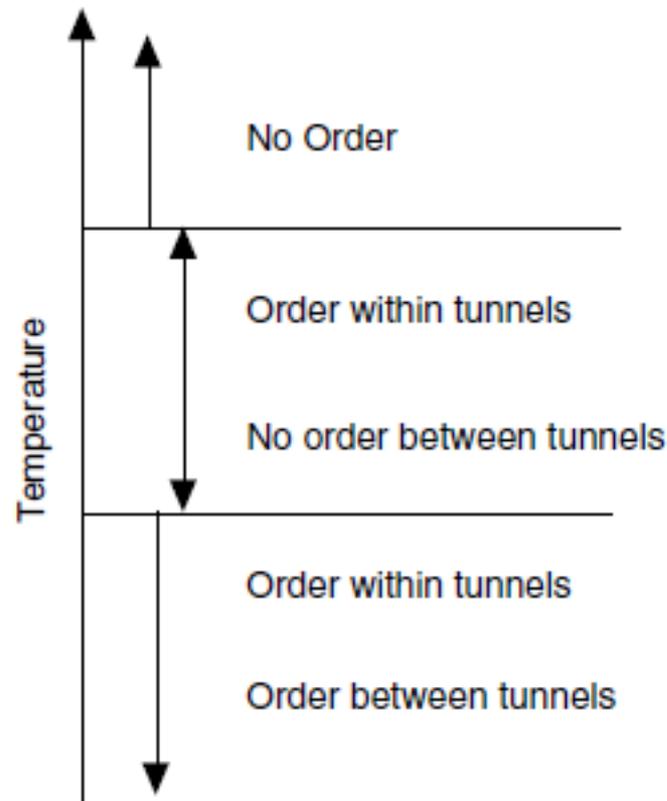


Fig. 6.12 Influence of temperature upon various types of order in structure with parallel tunnels

8. Changes in the Host Structure Induced by Guest Insertion or Extraction

(1) Conversion of host structure from crystalline to amorphous
-examples in which an initially crystalline material becomes amorphous as a 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

$\text{Li}_x\text{V}_6\text{O}_{13}$ binary system

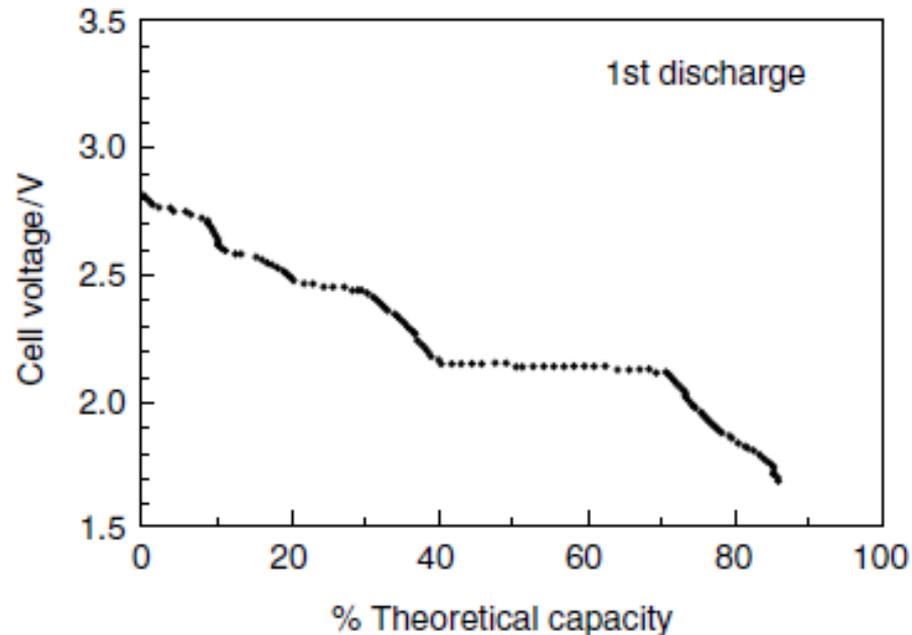


Fig. 6.13 Discharge curve observed during the initial insertion of lithium into a material that was initially V_6O_{13}

Fig. 6.13. 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

Fig. 6.14. After a number of cycles \rightarrow a single-phase insertion reaction. X-ray diffraction experiments confirmed amorphous

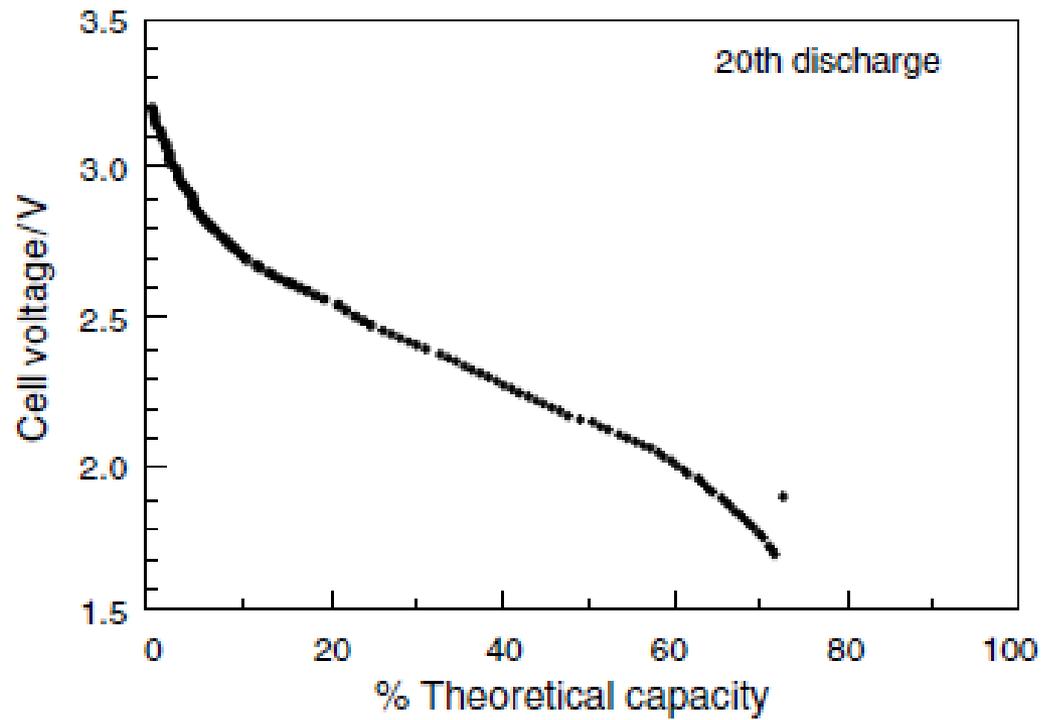


Fig. 6.14 Discharge curve observed during the 20th insertion of lithium into a material that was initially V_6O_{13}

Fig.6.15. lithium inserted into initially V_2O_5

Formation of a series of different phases as lithium added

→ forming the ϵ and δ structures, if only up to about 1 Li was inserted into αV_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.

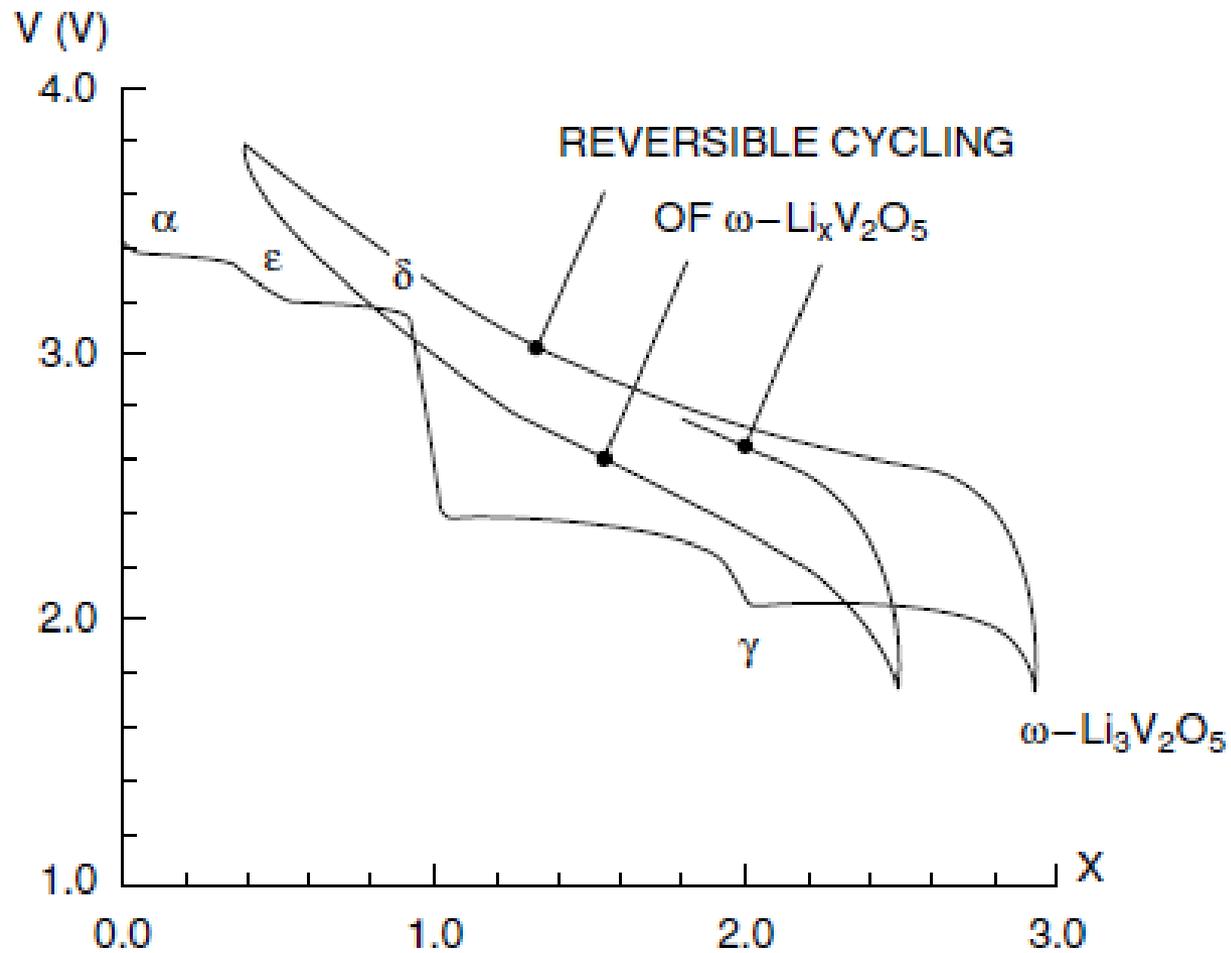


Fig. 6.15 The variation of the potential as lithium is added to V_2O_5 . When the composition reached $Li_3V_2O_5$ an amorphous phase was formed

(2) Dependence of the Product upon the Potential

-Si or other materials: reacted with lithium to a low potential (high lithium activity) → irreversible reaction occurs that results in the formation of fine particles of amorphous silicon in an inert matrix. Upon cycling, the amorphous Li–Si structure shows both good capacity and reversibility. However, if further lithium is inserted, going to a potential below 50mV, 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, it appears as though silicon or its alloys may play an important role as a negative electrode reactant in lithium batteries in the future.

(3) Changes upon the Initial Extraction of the Mobile Species

-initial extraction of a mobile species that is already present in a solid → initial composition of about $\text{Li}_{0.6}\text{V}_2\text{O}_4$ → the potential starts between 3.0 and 3.5V vs. pure Li

The initial lithium could be essentially completely deleted from the structure, causing the potential to rise to over 4V. 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.

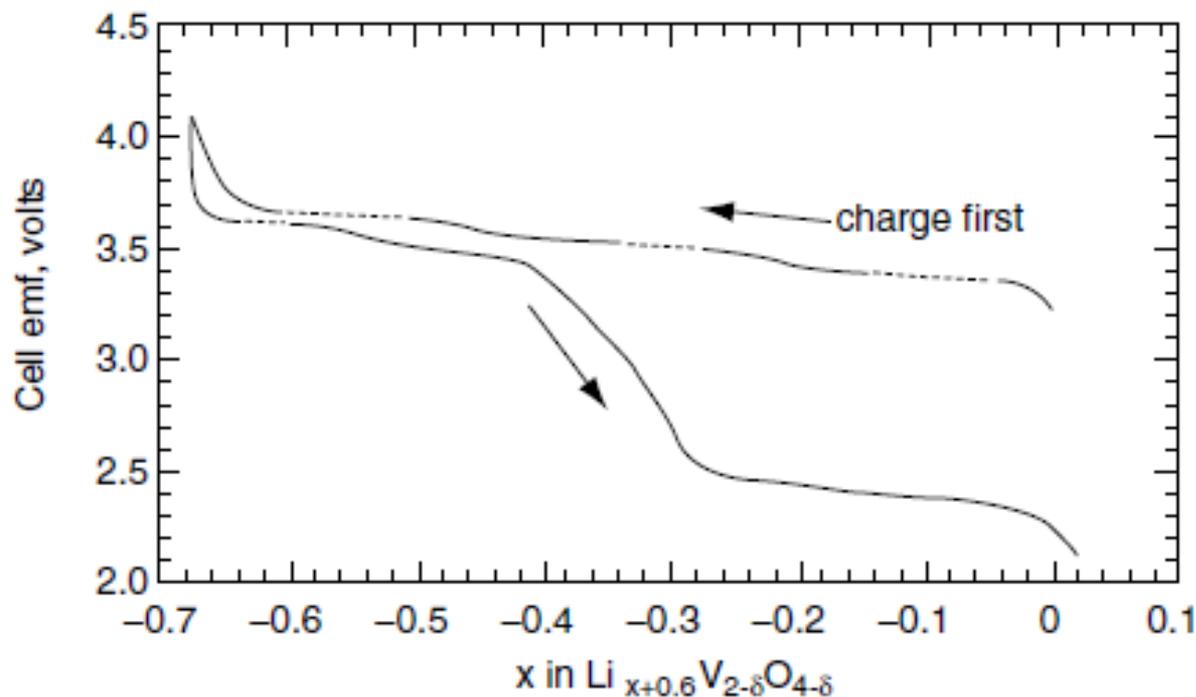


Fig. 6.16 Initial charging and discharge curves of a material with a composition about $\text{Li}_{0.6}\text{V}_2\text{O}_4$

9. The Variation of the Potential with Composition in Insertion Reaction Electrodes

(1) Introduction

The externally measured electrical potential of an electrode is determined by the electrochemical potential of the electrons within it, η_{e^-} , called Fermi level, $E_F \rightarrow$ not absolute value, always measured as differences \rightarrow voltage of electrochemical cell is the electrically measured difference between the Fermi levels of the two electrodes

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

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 M^+ within the electrode, the chemical potential

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

Under open circuit conditions there is no flux of ions through the cell

$$d\eta_{M^+}/dx = \Delta\eta_{M^+} = 0$$

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

$$\Delta E = \Delta\eta_{e^-} = (-1/z_{M^+}q)\Delta\mu_M$$

-to understand the potentials of electrons is based upon the electron energy band model

Metal: free-electron theory

Semiconductor: CB, VB, energy gap, dopants....

(2) The Variation of the Electrical Potential with Composition in Simple Metallic Solid Solutions

insertion of mobile guest species → a solid solution of the guest species in the host crystal structure → potential is the variation of the chemical potential of the neutral guest species as a function of its concentration → two components, electron concentration in the host material and concentration of the ionic guest species, M^+

(3) Configurational Entropy of the Guest Ions

-guest → host

-There will be a contribution to the total free energy due to the configurational entropy S_c related to the random distribution of the guest atoms over the available sites.

$$S_c = -k \ln[x/(x_0 - x)]$$

where x is the concentration of guest ions and x_0 is the concentration of identical available sites. k is Boltzmann's constant

This configurational entropy contribution to the potential is the product of the absolute temperature and the entropy.

Assumption: (i) no interaction between nearby guest species,
(ii) only one type of site available for occupation

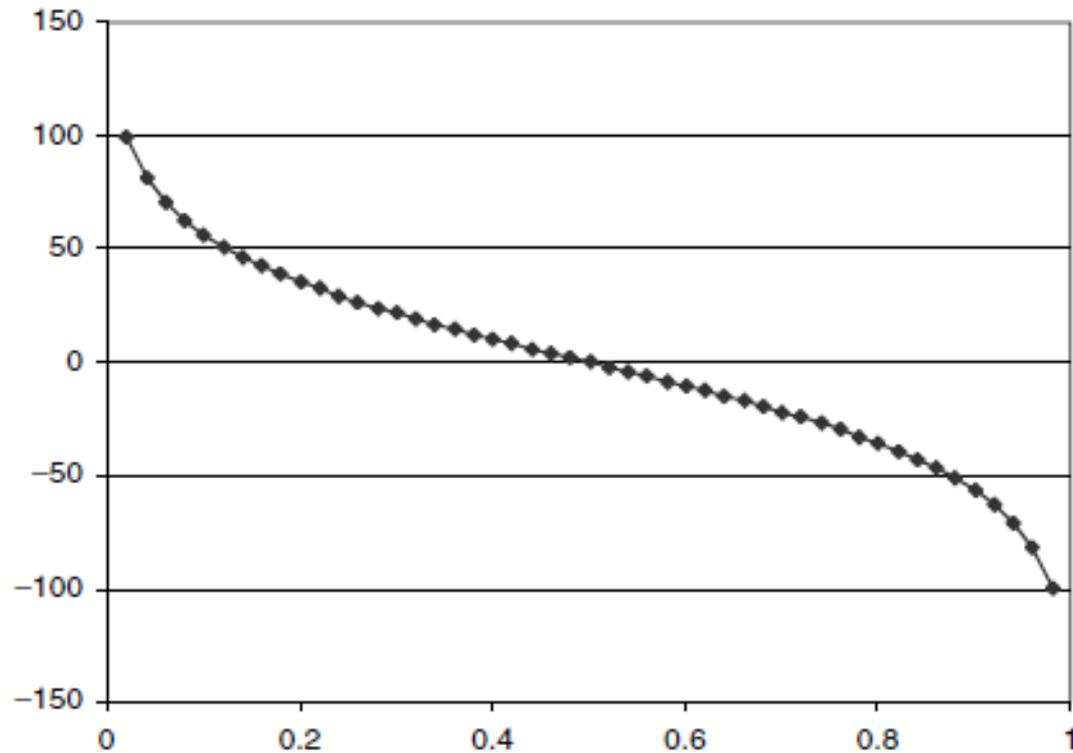


Fig. 6.17 Contribution to the potential due to the configurational entropy of a random distribution of the guest ions upon the available identical positions in a host crystal structure. The values on the abscissa are the fractional site occupation, and those on the ordinate are mV

(4) The Concentration Dependence of the Chemical Potential of the Electrons in a Metallic Solid Solution
electrochemical potential of the electrons can be approximated by the energy of the Fermi level E_F .

In the free-electron model

$$E_F =$$

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

→ the electronic contribution to the total chemical potential is proportional to the two-third the power of the guest species concentration. More generally the electron mass is replaced by an effective mass m^*

→

(5) Sum of the Effect of These Two Components upon the electrical potential of a metallic solid solution → composition dependence of the electrode potential in a metallic solid solution

smaller effective masses make the first term larger, and thus results in the potential being more composition – dependent

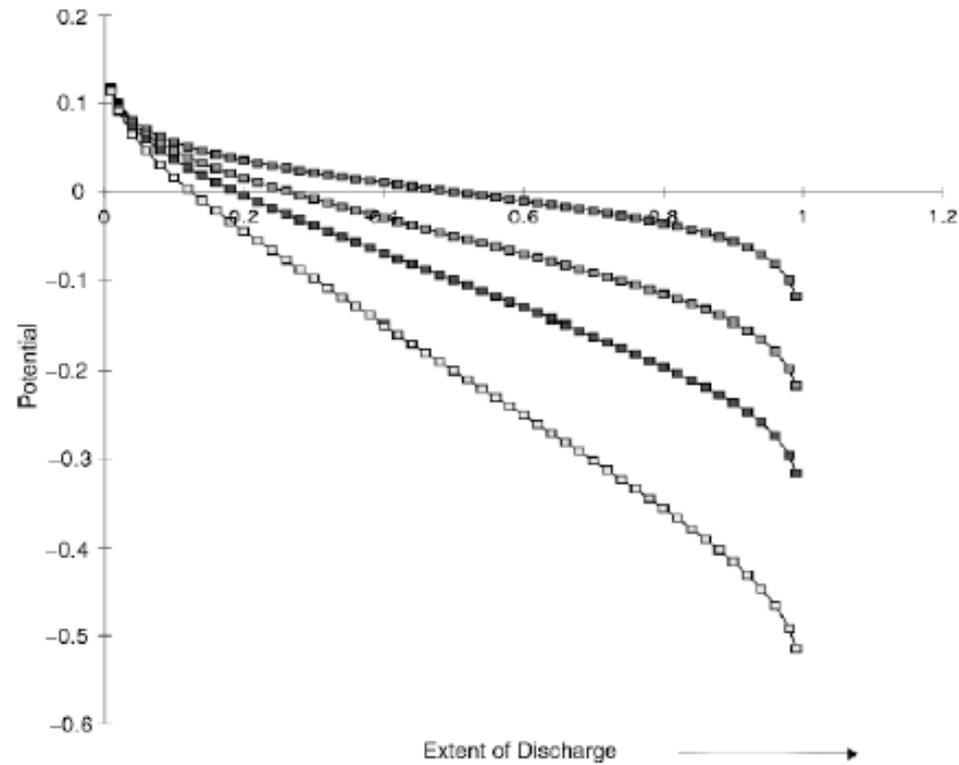


Fig. 6.18 Calculated influence of the value of the electronic effective mass upon the composition dependence of the potential in an insertion reaction in a simple metal

“tungsten bronze.” In this family of oxides the electron energy spectrum approximates that of a free-electron metal.

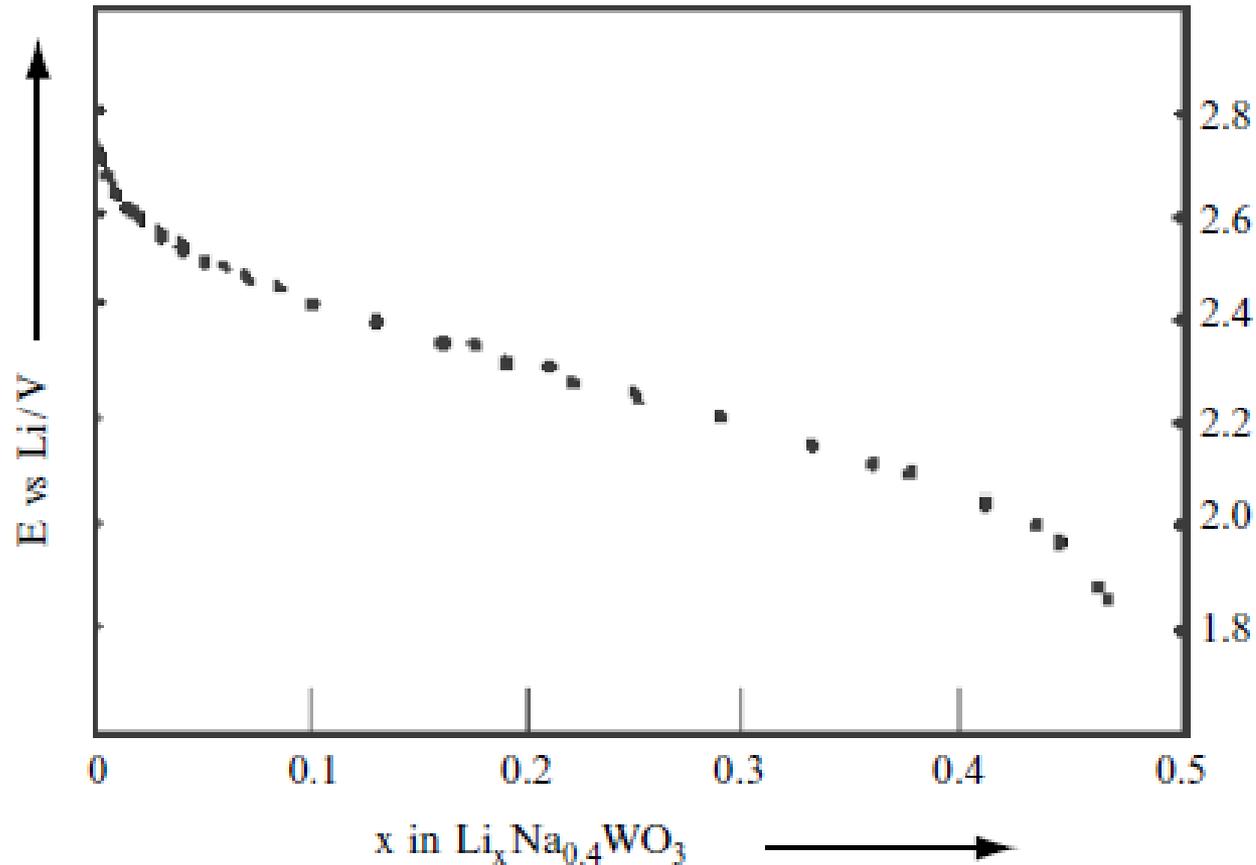


Fig. 6.19 Variation of the potential as a function of lithium concentration in $\text{Li}_x\text{Na}_{0.4}\text{WO}_3$

(6) The Composition: Dependence of the Potential in the Case of Insertion Reactions that Involve a Two-Phase Reconstitution Reaction

e.g. potential is composition-independent:

insertion and extraction of lithium in materials with the composition $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (spinel structure). spinel structure: AB_2O_4 , where the A species resides on tetrahedral sites and the B species on octahedral sites within the close-packed face centered cubic oxygen lattice. If one assumes this general stoichiometry, one of the four lithium ions would share the octahedral sites with the titanium ions, and the other ones would reside on tetrahedral sites. Thus the composition can be written as $\text{Li}_3[\text{LiTi}_5]\text{O}_{12}$, or alternatively, $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$.

additional lithium ion can react with this material,



→ a moving-interface reconstitution reaction.

Fig. 6.20. Because of the small volume change, negligible hysteresis, and rapid kinetics. The one disadvantage is that its potential is unfortunately about half way between the negative and positive electrode potentials in most lithium batteries.

-hysteresis (when charging and discharging): related to mechanical strain energy, i.e., dislocation generation and motion, as a consequence of volume changes that occur due to the insertion and extraction of the guest

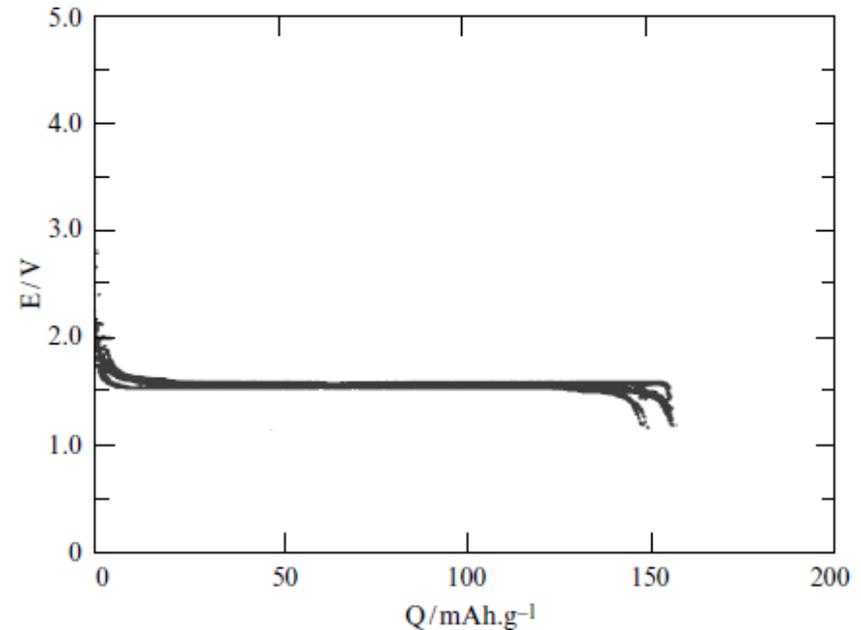


Fig. 6.20 Charge and discharge curves for two different $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cells

lithium with FePO_4

Material is prepared (in air) as LiFePO_4 , and the initial reaction within the cell involves charging, i.e., deleting lithium from it.

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

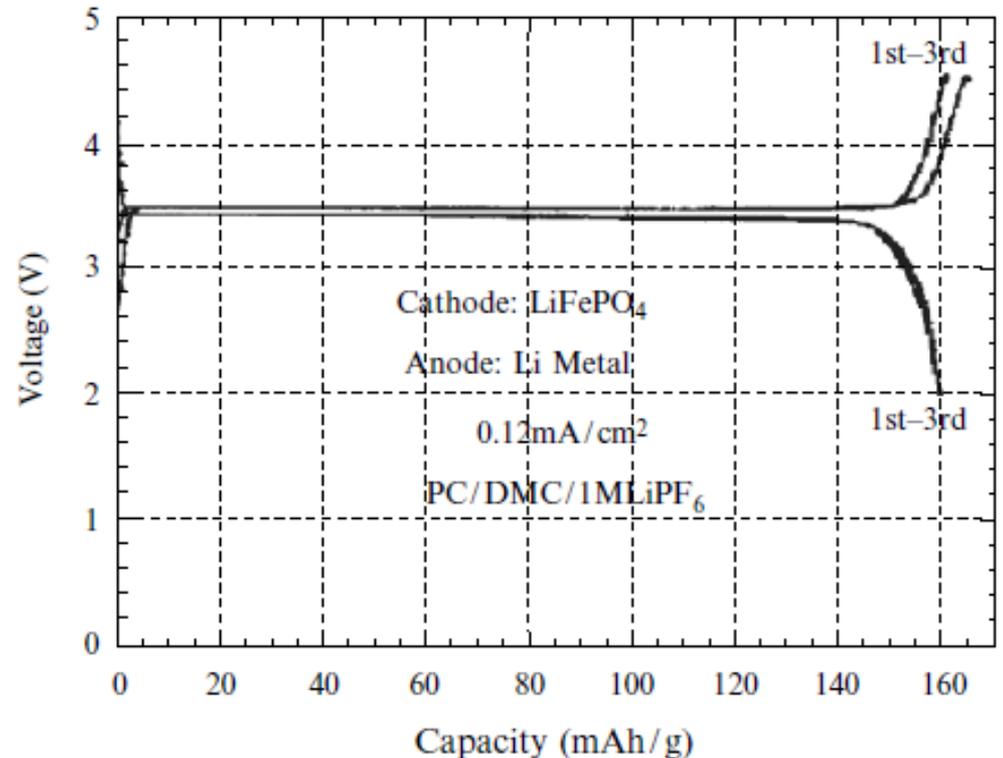
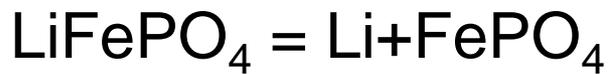


Fig. 6.21 Charge and discharge curves for the reaction of lithium with FePO_4