

MECHANISTIC STUDIES OF REVERSIBLE LAYER-TYPE ELECTRODES

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Summary

In layered type intercalation electrodes ions are stored reversibly during the functioning of secondary batteries. The behaviour of the system depends on geometrical and electronic factors. The geometrical factors are concerned with the localization of the ions in the host structure; they deal with average structure determinations and local ordering problems. The diffusion properties of the intercalated ions depend on the site geometry, the population of the van der Waals gap, the ionicity of the bonds in the host, the stoichiometry of the host, and the mechanical properties of its slabs. Electrons have to be accommodated by the host. The band structure of the host plays an important role in respect of the ability to intercalate, the phase limit, and the stability of the products. Metal-insulator transition may be induced. Other possible factors such as Jahn-Teller effects have also to be considered.

Introduction

When an intercalation compound is formed, ions or molecules are accepted by a host lattice. The process is reversible: it is possible to return to the initial state through appropriate electrical, chemical, or thermal actions. Furthermore, in the case of ionic intercalation compounds, the intercalation ions are mobile and electrons have been donated to the host which may induce, or increase, an electronic conductivity. These particular properties explain why intercalation compounds have been proposed as electrodes, essentially cathodes, in new, advanced secondary batteries. The key words are ionic conductivity, electronic conductivity, and reversibility.

Solids with low dimensionality provide us with some of the best host structures to practice intercalation chemistry. These solids can be regarded as being built of structural units such as slabs or fibers in which there are strong ionic-covalent or metallic bonds, whereas the slabs or fibers are separated by rather large distances (generally of the order of the van der Waals radii), in agreement with weak interlayers or interchain bondings. The process of intercalation results in the pulling apart of these groups.

In such systems the problems concern (i) the ions: there are static problems dealing with the average structure of the intercalation compound or local ordering, and dynamic diffusion problems; (ii) the electrons: where do the electrons lost by the intercalated species go? These problems will be considered successively in connection with the use of the corresponding materials for batteries.

Transition metal dichalcogenides (TMDC) and related materials will form the basis of the discussion. They present a remarkable unity as far as the van der Waals gap is concerned. However, in respect either of the electron configuration or the geometry of the slabs (octahedral arrangement as in TiS_2 or prismatic arrays as in NbS_2), they offer a large variety of possibilities. A study of the mechanism is possible by considering these various factors in turn.

A^+ ions in host structures

The great number of phases obtained with various TMDC host structures and alkali metals can be classified according to the coordination of the A^+ ions between the slabs and their presence in all (stage I compounds) or some (multistage phases) of the van der Waals gaps.

The surroundings of the alkali metal can be either octahedral or trigonal prismatic (Fig. 1). It depends on three factors: the size of the alkali metal, the amount of intercalation, and the nature of the slabs of the host structure [1]. An octahedron represents a better charge equilibrium and therefore it can accommodate higher charges on the anions than can a trigonal prism. Thus, the general ionization scheme xA^+ , MX_2^{x-} explains why, for a given

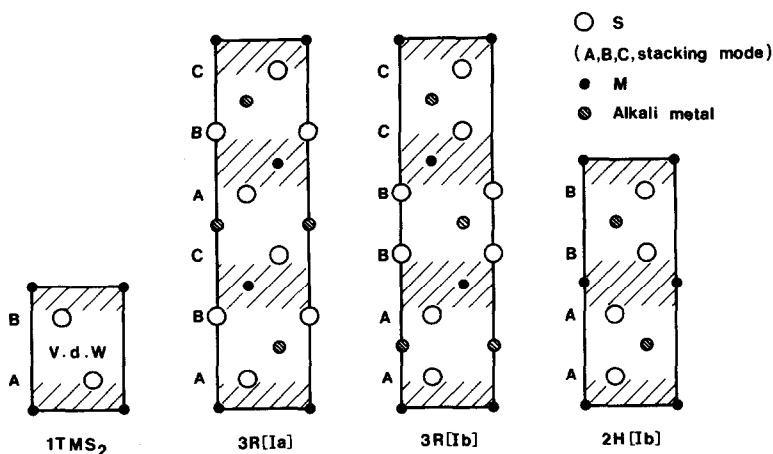


Fig. 1. Structural types of first stage intercalates in a CdI_2 -like host structure 3R [Ia] and 3R [Ib] (3 slabs rhombohedral structure of first stage compound with, respectively, octahedral or TP sites for A^+ ions); 2H [Ib] (2 slabs hexagonal structure of a first stage compound with TP sites for A^+ ions).

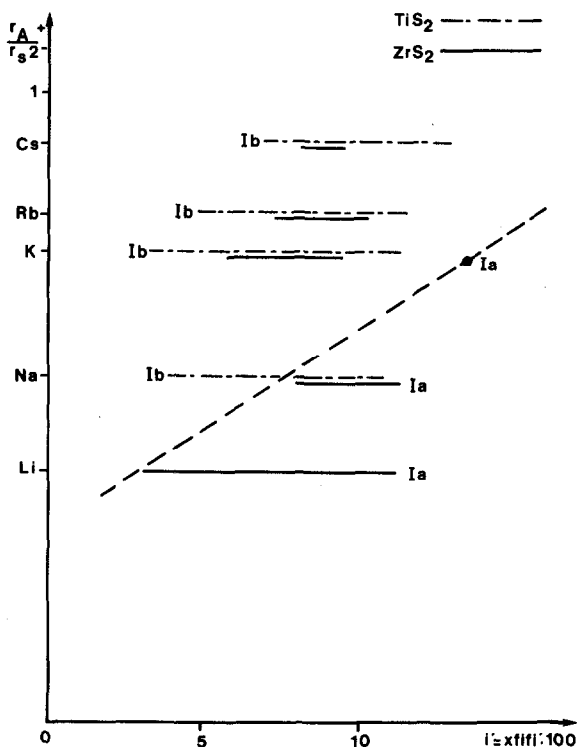


Fig. 2. Ionicity-structure diagram for intercalates in CdI_2 -like host structures.

alkali metal, the octahedral forms may appear for the higher values of x whereas the trigonal prismatic forms are obtained for the lower values of x . With a larger alkali metal the chalcogen layers are more distant and the trigonal prismatic structure is favoured. The last factor involves the covalency of the host structure: ZrS_2 , more ionic, favours the formation of octahedral species as compared with TiS_2 (for example, KZrS_2 is octahedral but KTiS_2 is trigonal prismatic). In accordance with the above, a general diagram involving the ionicity-structure relationship in intercalation compounds can be proposed [2]. By plotting the r_A/r_S^2 -ratio, which expresses the size effect, versus a function related to stoichiometries and to the fractional ionicities of the M-S and A-S bonds, it is possible to draw an unambiguous limit between octahedral and trigonal prismatic domains (Fig. 2). Such a diagram is very useful in the search for new cathode materials: it shows where a wide range of compositions may be found in a given system. Lithium appears to be a very favorable case with often large homogeneous domains in octahedral sites ($0 < x \leq 1$ in Li_xTiS_2). In addition, ionicity-structure diagrams draw attention to the critical values at which a border line appears between two types of sites, which is very important in respect of diffusion properties. In fact, lithium in TiS_2 is very probably in this situation: it will be able to use the tetrahedral sites (twice as numerous as the octahedral sites) for its dis-

placements. It is possible that it occupies them more or less partially *vs.* temperature [3].

Recent work on LiZrS_2 has shown that a phase transition takes place at 300°C with the lithium ions in tetrahedral coordination [4]. We move from a 3R octahedral structure at room temperature to a spinel structure. This transition does not need much energy because the anion stacking is not modified. LiZrS_2 remains of the NiAs type, which is in agreement with the more covalent character of the host. By contrast, in the case of $\text{Li}_x\text{Y}_x\text{Zr}_{1-x}\text{S}_2$ phases, an NaCl structure is reached for the higher value of x ($x = 1$), following a spinel and a 3R octahedral model, which is again in agreement with ionicity considerations.

In low dimensional systems a given structural transition linked to a simple shifting of the slabs must not receive too much importance. In fact, it may not be a drawback as far as cathodic use is concerned. This is the case of the so-called pseudo-monophased systems. After a few cycles the e.m.f. plateau in a discharge curve, meaning a two phased region, may disappear. This is due to a disorganization of the stacking in the host structure. The slabs must shift during the intercalation process and behave more and more independently of each other. Finally, we come to some one dimensional amorphous situations (along the direction perpendicular to the slabs) with no visible plateau in the discharge curve. This allows use of some initially biphased systems in batteries. A drawback is the difficulty in ascertaining phase limits through electrochemistry except when considering the first discharge curve. An example is provided by the Na-TiS₂ system.

An aspect of intercalation chemistry which is magnified by structural studies is the parameter expansion in the direction perpendicular to the slabs of the host. For a given structural type and the same amount of intercalation, it is proportional to the radius of the A^+ intercalated ion. This expansion may be a severe drawback to the use of a given material as a cathode. Trigonal prismatic phases with a higher Δc value are less favorable than octahedral compounds, in spite of better diffusion conditions.

After intercalation the host structure may relax. Δc will change with time, which is equivalent to annealing at room temperature. When heated the samples rapidly reach an equilibrium. The Li-ZrS₂ system at room temperature shows a continuity in the 3R octahedral phase for $0.30 < x \leq 1$. Heating the samples at 300°C leads to this spinel form which corresponds to the same ABC anionic stacking, but the corresponding c value in an hexagonal indexation would be much lower (Fig. 3). Similar structural contraction probably exists in various systems. It has been observed without any structural change in Li-ZrSe₂ [5]. It may be the case for Li-TiS₂ phases and would provide an explanation for the differences observed in ^7Li NMR spectra in the case of samples prepared at various temperatures.

In addition to the geometrical effect associated with the size of the A^+ ion, the Δc expansion depends also on an electronic term. In respect of this electronic factor, one may consider an increasing repulsion between slabs which are now negatively charged, but also an attraction between these slabs

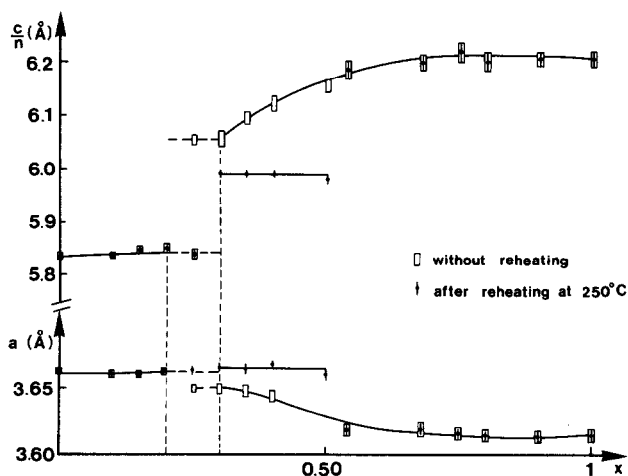


Fig. 3. a and c parameters vs. x in $\text{Li}_x\text{-ZrS}_2$ system.

and the A^+ positive layers. The balance is certainly in favour of the latter term as shown by the fact that true layer oxides do not exist due to the strong coulombic repulsion between O^{2-} layers, but A_xMO_2 derivatives exist which are isostructural with A_xMS_2 intercalates [6]. The A^+ ions located in the van der Waals gap stabilize the two-dimensional arrangement.

The electronic transfer to the host provides an essential contribution to the Δc expansion. In the case of Li-TiS_2 it was recently shown that the lattice expansion on intercalation is associated with this charge donation to the host rather than to propping of the layers by a large Li^+ ion [7]. Let us consider similar van der Waals gaps between sulfur layers in disulfides, and a similar population of these van der Waals gaps, which means the same electronic transfer to the host. Δc appears to be directly proportional to the initial size of the van der Waals gap represented here by the sulfur-sulfur distance on each side (Fig. 4). One can extrapolate a critical value of $\approx 3.20 \text{ \AA}$ for which no Δc would be observed. This is the case for NiPS_3 , and, indeed, there is no Δc in NiPS_3 . This simple diagram shows that there is at least an initial geometrical effect in TiS_2 .

The electronic effect is more apparent when increasing the population in a given intercalate. If we consider TP compounds with a large Δc , when x increases, Δc decreases, which is again in favour of a predominant effect of the attraction between A^+ layers and negative slabs. In the case of octahedral phases which are compact, this effect is not so clear.

The A^+ ions repel each other as a first type of ion-ion interaction, and this should lead, at least at sufficiently low temperatures, to an ordering between A^+ ions and vacancies in the van der Waals gap. Such an ordering is well known in the case of graphite intercalates. Ordered structures have also been observed by X ray diffusion techniques in the case of a single crystal of TiS_2 electrochemically intercalated with sodium [8]. An ordered occupancy

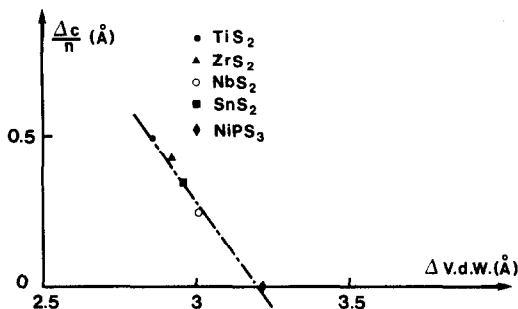


Fig. 4. Δc expansion in Li host intercalates as a function of the initial size of the van der Waals gap.

of the van der Waals sites has an effect on the discharge curves of the batteries. This is well illustrated by the Li-NiPS₃ system. NiPS₃ presents a structure which is of the TiS₂ type with two thirds of the octahedral voids of the slabs occupied by Ni²⁺ ions and one third with (P-P) pairs. This is expressed by the formulation [SNi_{2/3}(P₂)_{1/3}S].

In the van der Waals gap, octahedral voids are divided into two kinds depending on the neighbour type (2d and 4h sites in the Wyckoff notation). A break at Li_{0.5}NiPS₃ corresponds exactly to the filling of the 2d sites [9].

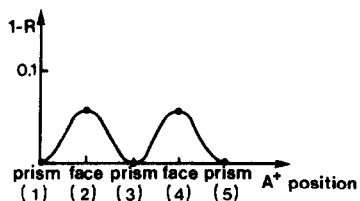
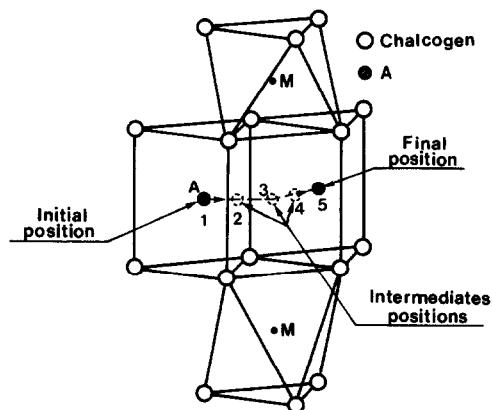
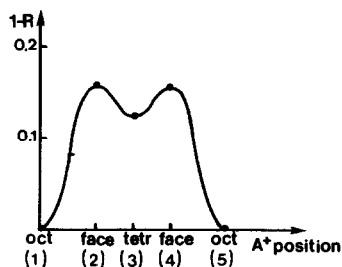
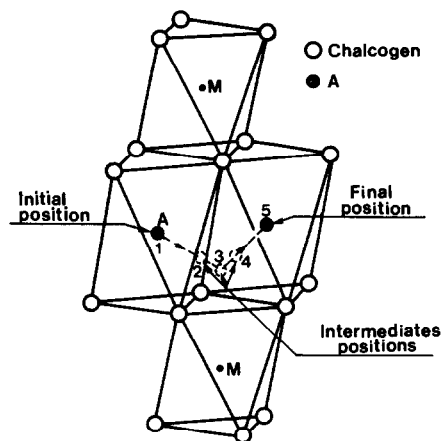
The problem of the mobility of the A⁺ intercalated ions governs the reversibility of the batteries. It depends on factors which are the same as those described for superionic conductors. In addition, there are specific effects in relation to the non-stoichiometry of the host and the mechanical properties of the slabs. The immediate factors which obviously play a role are:

(i) The ratio between the number of intercalated ions and the available vacancies. This is more apparent in the case of systems involving a larger cation such as Na⁺ than in the case of Li⁺ intercalates.

(ii) The nature of the bonds in the host structure. The dependence on the activation energy is expected since the ionicity of the structure determines the potential barrier for the alkali ions. The activation energies are much lower in TMDC than in the structurally related oxides.

(iii) The site geometry. The activation energy is weaker in trigonal prismatic sites than in octahedral sites. This is related to larger sites with more distant anionic layers and to the existence of large windows between adjacent TP sites [10]. In the case of an octahedral site occupancy the alkali metal ion has to use adjacent tetrahedral sites during its displacement (Fig. 5).

These effects have been discussed previously in various papers [11, 6, 12]. The role of the non-stoichiometry of the host is also well known. When non-stoichiometric, TMDC usually presents excess metal cations in the van der Waals gap, corresponding to the formulation M_{1+x}X₂. These extra metal atoms will impede the diffusion. They link the slabs and we lose the advantage of having a 2D structure.



(a)

(b)

Fig. 5. Diffusion pathways in TP and octahedral structures (after ref. 10): (a) pathways, (b) steric variations of the activation energy.

A very interesting point arising from the 2D character is provided by the mechanical properties of the slabs, which are not usually considered. This is qualitatively obvious if we compare $\text{Ta}_2\text{S}_2\text{C}$ with a thick, five layer slab and TaS_2 . Both structures exhibit similar van der Waals gaps. During the topochemical intercalation reactions, however, the reduction or oxidation speeds in the $\text{Ta}_2\text{S}_2\text{C}/\text{Ta}_2\text{S}_2\text{C}^{x-}$ system are far lower than those observed in the $\text{TaS}_2/\text{TaS}_2^{x-}$ system. This has been associated with the elastic slab distor-