

## Intercalation chemistry and chemical bonding

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### Abstract

In contrast to amphoteric graphite, the layer-type oxides or chalcogenides generally play the role of acceptors in chemical or electrochemical intercalation reactions. Due to the more ionic character of the M–O bonds, the structural evolution of the oxides may usually be explained on hand of electrostatic considerations, or in terms of cation oxido-reduction. For the more covalent chalcogenides, the occupancy of higher energy levels in the band structure by the transferred electrons constitute mostly a prevailing factor, giving rise to structural changes but also to modifications of the physical properties. The ionic character of the M–O bonds accounts for the strong tendency of the oxides to undergo 2D → 3D transformations as a result of intercalation processes.

Such features are determining for the choice of the electrode materials for lithium-ion batteries as far as users require high electrode capacity, stability, and cyclability. © 2000 Elsevier Science S.A. All rights reserved.

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Graphite, due to its monolayer structure and to the existence of delocalized  $\pi$ -electrons, has a certain number of specific properties: ability to play the role of either an electron acceptor or of a donor, formation of a large variety of multistage intercalation compounds respecting the cluster rule of Daumas and Herold [1] with strong repulsions between the C-layers (see for instance, Ref. [2]).

The sandwich-type oxides and chalcogenides differ clearly from the graphite intercalation compounds: as a rule, the sheets have an acceptor character, i.e. are Lewis acids. Chemical or electrochemical intercalation mostly leads to stage 1-insertion despite higher negative charge of the host-structure.

In fact, the ionicity difference between the M–O bonds within the oxide sheets and the more covalent bonds in homologous 2D-chalcogenides give rise to behaviors which allow distinction from the structural point of view, as well as by the resulting physical properties. It is particularly true when the intercalated species is either lithium or a 1B-cation such as  $\text{Cu}^+$  or  $\text{Ag}^+$ .

It has been shown that in the sheet compounds, for instance by NMR Knight shift determinations, as a result of an ionization process, such atoms occupy the Van der Waals gap of the network as cations with only a small

local presence of external s-electrons [3]. As a consequence, we have to simultaneously consider in the intercalation compounds, the influence of both  $A^+$  cations and liberated s-electrons which now occupy upper levels in the energy diagram of the sheets using the rigid band model.

In the lattice, the  $A^+$  cations actually play a double role: they consume mechanical strain energy in pushing away the sheets from each other, conversely they stabilize the materials, thanks to Coulomb attraction with the neighboring negatively charged sheets.

The stronger influence of the first factor explains that in the chalcogenides  $\text{Li}^+$  or  $\text{Na}^+$  intercalation leads to growing  $c$ -parameter, especially at beginning of the process. As a rule, the  $\Delta c$  enhancement increases for homologous compounds with rising size of the intercalation cation and decreasing value of the initial Van der Waals gap [4].

On the contrary, Coulomb attraction of the inserted cations has a strong influence in oxides, as the effective anionic charge is higher than in more covalent sulfides or selenides. This feature accounts for the fact that most  $A_x\text{MO}_2$  compounds only exist when  $x > 0.5$  and explains that the  $c$ -parameter decreases at rising  $x$  (Fig. 1).  $\text{MoO}_3$  constitutes an exception due to the strong covalency of the Mo–O bonds [16]. Delmas et al. [5,17] have shown that the structural changes observed during the electrochemical intercalation–deintercalation reactions can be explained in a rather simple way: no structural modification occurs within the oxide sheets (the temperature is too low to

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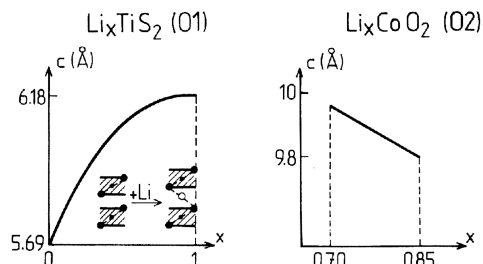


Fig. 1. Influence of the intercalation process on the  $c$ -parameter of  $\text{Li}_x\text{TiS}_2$  and of  $\text{Li}_x\text{CoO}_2$  layer-type compounds. Mechanical expansion due to lithium intercalation and increasing Coulomb attraction are in competition.

allow the internal M–O bonds to break), but the sheets may glide with respect to each other. This gliding process results from the modification of the electrostatic interactions between oxygen layers facing each other in the intersheet gap (Fig. 2). Two phase-families related by simple sheet gliding and respecting each ABC circular permutations of the oxygen packing are shown to result either from an intercalation reaction or from a low temperature cation exchange process [5–7].

Such electrostatic phenomena clearly account for the fact that in  $\text{A}_x\text{MO}_2$  or  $\text{A}_x\text{MS}_2$  series, increasing  $x$  values favor the passage of a trigonal prismatic surrounding of  $\text{A}^+$  to a more stable octahedral one, leading to a strong weakening of the  $\text{A}^+$  ion conductivity [18]. Let us mention here, as a significant example, the investigations of Fouassier et al. [8] on the  $\text{Na}_x\text{CoO}_2$  series (Fig. 2). In a similar way, Trichet et al. have shown that in  $\text{KTiS}_2$  potassium has a TP surrounding due to the strong covalency of the competing Ti–S bonds in opposition to the O environment in  $\text{KZrS}_2$  where weakening of the bonds within the sheets increases the negative charge of sulfur [9]. Similar considerations explain the TP coordination of the large  $\text{A}^+$  cations (Rb, Cs) and the O coordination of lithium in homologous series [10,17]. The tetrahedral surrounding may occur only for  $\text{Li}^+$  and  $\text{Cu}^+$  cations, implying a strong covalent bonding. In the delafossite-type phases, the  $\text{Cu}^+$  or  $\text{Ag}^+$  ions are situated along the edges of facing trigonal oxygen prisms, as  $sd$  hybridization leads to linear coordination (e.g. in  $\text{CuAlO}_2$ ). This particular structure is even observed for  $\text{Pd}^+$  or  $\text{Pt}^+$  in  $\text{PdCoO}_2$  as a result of  $d_{z^2}$  hybridization [24].

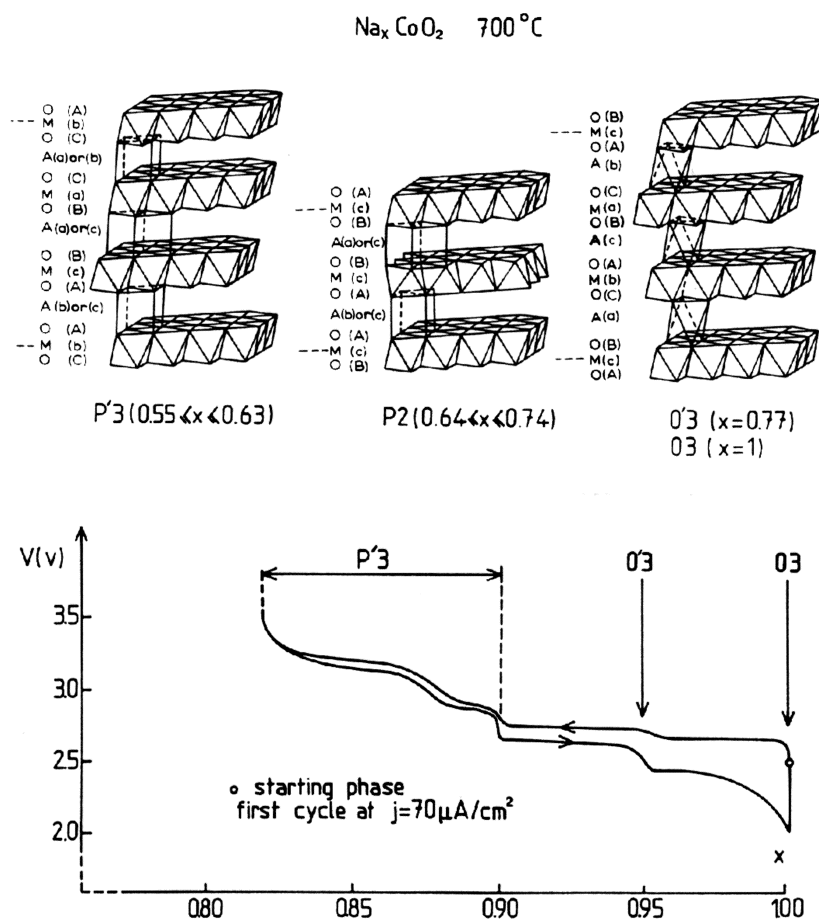


Fig. 2. (a) The structures of the P3, P2, and O3 phases obtained at rising  $x$  by synthesis in sealed gold tubes at  $700^\circ\text{C}$  in the  $\text{Na}_x\text{CoO}_2$  system. (b) Electrochemical intercalation or deintercalation leads only to P3 or O3 starting with each one of the two phases as a result of the stability of the sheet structures which only allows a  $\text{CoO}_2$  gliding mechanism.

The influence of the outer electrons injected into the host lattice differs with the materials concerned. When they occupy *discrete levels*, the upper intercalation limit depends not only on the available sites (as in the MOCl layer compounds with  $M = V, Cr, Fe$ ) but also on the lowest oxidation state which is stable in the conditions of the reaction [11]. The intermediate compounds are characterized by a classical hopping mechanism. As an example, Nadiri [13] has shown that only two lithium atoms can be intercalated into the cage structure of  $Fe_2(SO_4)_3$  or  $LiTi_2(PO_4)_3$  despite the availability of four empty sites. The presence of alkali cations should give rise to unit cell shrinking, whereas the reduced oxidation state of Ti or Fe favors dilatation. As a consequence, careful examination of the precise variation of the cell parameters can bring evidence of the type of site occupied by the alkali cations in the host matrix (G. Le Flem).

In the Chevrel phases built up by  $Mo_6$  octahedra enclosed in chalcogen cubes, only a part of the six available sites are occupied, as the  $Mo_6$  clusters provide 20 electrons for a maximum population of 24 in the 12 discrete molecular levels. As a result of the saturation of the available energy levels, the intercalation is thus limited to two divalent or four monovalent cations [15].

Rouxel [4] and Liang [12] have shown that for the chalcogenides, electronic occupation of the *conduction band* actually accounts as well for the reactivity of the  $MX_2$  compounds as for the structure obtained and the corresponding physical properties, in particular, electrical conduction. The existence of a large  $T_{2g}$ -type conduction band explains, for instance, the easy intercalation up to  $x = 1$  of lithium in  $TiS_2$ , the obtained  $Li_xTiS_2$  compounds having a metallic behavior. Easy intercalation of lithium in the P-variety of  $TaS_2$  (with a trigonal prismatic coordination of tantalum) appears to result from the progressive filling of a low energy  $d_{z^2}$ -band, which compensates for a stronger repulsion between sulfur layers belonging to the same sheet. As expected, the material is metallic except when  $x \approx 1$  leads to full band occupancy.

Another significant example is the intercalation of lithium into  $MoS_2$ , which has the structure of  $TaS_2$ -P but an already saturated  $d_{z^2}$ -band: intercalation of lithium becomes difficult with rising  $x$  in comparison with  $TaS_2$  due to occupancy by the additional electrons of high energy levels in the antibonding  $T_{2g}$ -band. As a result of the Li intercalation, semiconducting  $MoS_2$  becomes metallic (Fig. 3). However, the capacity of  $MoS_2$  as an electrode would be limited by the instability of the high energy transferred electrons.

An obvious consequence of the bond strength difference for the intercalation processes in oxides and chalcogenides is the 3D-character of the obtained oxides, which contrasts with the tendency of the intercalants to order in the Van der Waals gap of the sulfides (as a consequence of strong cation–cation repulsion). This feature is clearly illustrated by the easiness lithium intercalated in layer oxides with

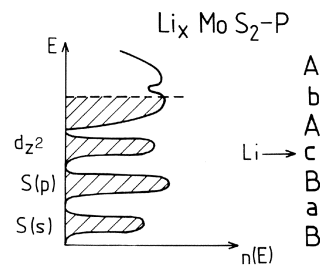


Fig. 3. Band structure of  $Li_x MoS_2$  in a rigid band model explaining the instability of Li-rich  $Li_x MoS_2$  due to progressive filling of high energy  $T_{2g}$  electronic levels.

defect NaCl-type structure lead to spinel lattices in making advantage of the occurrence of a similar c.f.c. oxygen packing [19,20a,20b]. The stabilization of  $Li^+$  in tetrahedral sites is illustrated by lithiation of rutile-type  $\beta$ - $MnO_2$ , which does not lead to a NiAs-type phase with the same h.c. oxygen packing but after sheet gliding to a spinel phase of formulation close to  $LiMn_2O_4$  [23].

A detrimental aspect of this tendency to 2D  $\rightarrow$  3D transformation is the easy migration of the transition elements into the Van der Waals gap of the layer type oxides. Such a phenomenon is observed during  $Li_x NiO_2$  deintercalation: the  $c$ -parameter shrinks due to some nickel transfer into the lithium layers. This shortening makes more difficult the  $Li^+$  reintercalation later and the subsequent utilization as cathode in a secondary battery [21,22]. A similar migration occurs in sulfides only for very high over-voltages [24].

The success of Li-ion batteries lies much on their high voltage and low weight. However, other main features such as intercalation range or cyclability depend even more on the choice of the materials used, especially at the positive electrode. As a consequence, battery behavior results largely from the bond strength and modifications within those materials. Once more, industrial development can be enhanced by appropriate fundamental thinking [25,26].

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