



Lithium intercalation into transition metal oxides: A route to generate new ordered rock salt type structure

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ABSTRACT

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Lithium intercalation in oxides is a topic of capital importance for the development of lithium batteries materials. We review herein the lithium insertion process involved in different structures 3D, 2D and 1D. In most of the cases, starting from an anionic cubic close packed array, the topotactic process of alkaline ion insertion, associated with a biphasic process in the potential-composition electrochemical curve, generates an ordered rock salt type structure for the fully reduced phase. Such a behavior allowed us to imagine other fully lithiated compositions that could show really good electrochemical behavior toward the lithium insertion/deinsertion.

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1. Introduction

Electrochemical intercalation of alkaline ion and especially lithium ion in transition metal oxides has attracted considerable attention these last decades due to the potential of the involved

reactions for the realization of Li-ions batteries [1]. Intercalation reaction requires the insertion of guest species (ion or molecule) into a solid host without structural modification of the host. In an actual intercalation reaction, the bonding within the host may be slightly perturbed. But in some compounds, larger structural modifications may occur, which still involve topotactic reactions. Intercalation reactions are generally possible in a host structure comprising 3D framework structures containing interconnected channels and tunnels, 2D layered or 1D ribbons type framework.

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The reversibility of the intercalation process will depend how drastic are the structural modifications.

Lithium intercalation into the host structure can be carried out either chemically or electrochemically. Chemical lithium intercalation involves mainly the reaction of the host lattice with *n*-butyllithium in aprotic solvents like hexane. In electrochemical method, lithium can be intercalated or deintercalated into/from the host structure by reduction or oxidation in non aqueous electrolyte and using lithium metal as counter electrode. Electrochemical method has the advantage of the lithium control.

Also, the host structure should contain reducible species. Thus, transition metal oxides are good hosts for the intercalation reactions because of their possibility of various oxidation states. The search on new materials for energy storage can be driven by these few crystallographic and thermodynamics considerations.

Thus, a great deal of work has been carried out in this field on various families of oxides – nickel, cobalt, iron, manganese, vanadium, titanium, niobium, tungsten, and molybdenum -, whose redox potential values are in adequation with the batteries applications. In most of these studies, the parent structure selected for the electrochemical intercalation is either bidimensionnal or three-dimensional with cages or tunnels allowing a reversible intercalation of lithium without any drastic modification of the structure [2].

Beside the well known compounds that are now going to be optimized for such applications, there remains a vast field for the discovery of new materials, which has not been investigated so far. The discovery of these oxides requires to take into consideration mainly three criteria: the values of the redox potential of the involved transition metal element, the open character of the crystallographic structure of the oxide, and the particle size of the material. In addition, typical electrode material compounds are transition metal oxides that have close packed oxygen arrays which provide a framework structure and specific site for topotactic insertion and removal of lithium ions.

Bearing in mind these considerations, investigations about new frameworks and their possible intercalation and exchange reactions with lithium have been the topics of several studies. Therefore, in order to generate new frameworks, new structures never described before, a strategy has to be developed, indeed two routes could be chosen. The first route is obvious and is a direct synthesis. This approach will not be developed here and concerns mostly polyanionic frameworks prepared by low-temperature synthesis like condensation, hydrothermal, etc...[3].

Another route we can take to discover new framework, new materials for the lithium intercalation, consists in revisiting ionic oxides based on transition metal that show a layered or tunnel type structure. Thus through ionic exchange, lithium insertion, one could end up with a new framework [4].

We will show here that a great number of reactions, that are at the origin of Li ion accumulators, start from a transition metal oxide, using the chemical or electrochemical reduction and end up in the rock salt type structure.

Because of the relevance of this work, it is worth nothing that the capacity *Q* delivered from an electrode material depends on its molecular weight *M* and on the number of lithium reversible Δx inserted into the structure ($Q(\text{mAh/g}) = \Delta x \times 26.8/M$). Thus, the best candidate for this application should have a large number of lithium and a cation over anion ratio close to one. Such a requirement is satisfied for rock salt structure $\text{Li}_{1-x}\text{M}_x\text{O}$ where the amount *x* of transition element *M* should be minimum. This well known structure displays octahedral coordination for both cations and anions and the small cations are occupying octahedral site between the cubic close packed anions

layers. Mather et al. [5] reviewed the cation ordered rock salt type structure in oxides. They describe several superstructures based on Pauling rule of electroneutrality. The sum of electrovalency of the nearest neighbor cations should equal the charge of the anion. For ternary rock salt oxides systems: $\text{A}_a\text{B}_b\text{O}_{a+b}$ with $\text{A} = \text{Li}$, they show that there exist only few frameworks for which the electroneutrality is preserved: ABO_2 , A_2BO_3 and A_5BO_6 . For other frameworks, the Pauling electroneutrality second rule is not satisfied; that is to say the charge is not neutralized locally, either due to the presence of a Jahn–Teller cation or due to the charge of the cation that induces a covalent character between the metal–oxygen bonds. In this case, the structures are more complex even if they could be described as an ordering of cations in a close packed oxygen array.

General consideration could be pointed out in the ionic structure; the anionic network is the most bulky (O^{2-} radius = 1.40 Å) and consequently tends to generate close packed network. Then, the cation will fill the empty space. The geometrical requirement for lithium ($r = 0.76$ Å [6]) accommodation appears only to be the existence of a coordination polyhedron with four to six near oxygen neighbors at distances of approximately 2 Å, a common occurrence in transition metal oxides. This ability of Li to have equilibrium coordination polyhedra of different geometry is probably one key factor in its accommodation into a wide variety of insertion hosts.

Thus, we will see that typical electrode material compounds are transition metal oxides that have close packed oxygen arrays (large light color spheres on Fig. 1), which is the first condition required in order to generate a rock salt type structure. Furthermore, the transition metal element and lithium are occupying octahedra sites (small dark color spheres on Fig. 1).

We wish to show hereby the great flexibility and potential of transition metal oxides and also the large tolerance of nature that allows complex ordered rock salt type structures containing lithium to be synthesized from various 3D, 2D and 1D transition metal oxide frameworks. We will see that such an approach allows us to anticipate the discovery of new structures and more importantly new electrode materials for the energy storage.

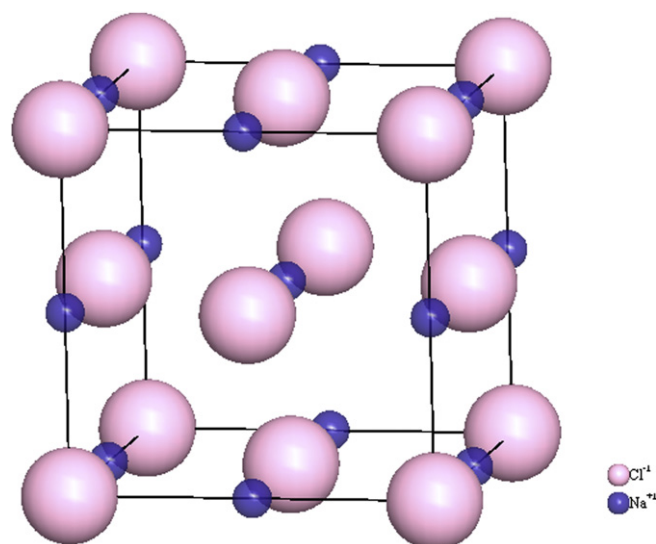


Fig. 1. Structure view of NaCl. The anions and cations are shown as large light color spheres and small dark spheres, respectively.

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