

MECHANISMS OF THE REVERSIBLE ELECTROCHEMICAL INSERTION OF LITHIUM OCCURRING WITH NCIM_s (NANO-CRYSTALLITE INSERTION-MATERIALS)

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A new family of insertion-compound electrodes, so called NCIM_s (Nano-Crystallite-Insertion-Materials) has been proposed: the major requirement is that the electrode materials have to be polycrystalline with a crystallite and particle size as small as possible (the accepted definition being that many crystallites make a particle). Indeed, by minimizing the size of the crystallites, the formation of defects is favored, particularly at the crystallite surface, acting as reversible (de)grafting sites of Li⁺. Also, the cation-anion bonding is weakened not only in the grain boundary region but also within the crystallite close to its surface: then the electrochemical insertion of Li⁺ takes place through easy bonding rearrangements.

1. INTRODUCTION

In the last 20 years much attention has been focussed on A_xMO₂-type intercalation compounds (A = Li, Na and M = Co, Ni, Mn . . .), which are used as positive electrodes in reversible alkali electrochemical cells (see for example refs. 1).

However, a very long-term cyclability (i.e., over 10³ cycles) might be hardly achievable, particularly for corresponding electrodes having a large grain size, probably because the Li⁺ (de)intercalation process slightly perturbs the host lattice.¹

Some of us have patented, a few years ago, a new strategy and related experiments that have enabled us to put forward a rather new family of insertion-

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TABLE I. SOME NANOCRYSTALLITE INSERTION MATERIALS

Sample	Class	Average grain size (Å)	Insertion rate x (measured in LiClO_4 (p.c.), $1.5 \text{ V} < V(\text{Li}) < 3.5 \text{ V}$)
$\text{Li}_x\text{SrTiO}_3$	D	80	$0 \leq x \leq 0.3$
Li_xCrO_2	I	30	$0 \leq x \leq 1$
$\text{Li}_x\text{Mn}_2\text{O}_3$	I	50	$0 \leq x \leq 2$
$\text{Li}_x\text{Fe}_2\text{O}_3$	D	150	$0 \leq x \leq 0.5$
Li_xNiO_2	I	60	$1 \leq x \leq 2$
Li_xCuO_2	I	50	$1 \leq x \leq 2$
Li_xWO_3	D	40	$0 \leq x \leq 2$

compound electrodes able to sustain long-term Li^+ electrochemical cyclability [2]. The major requirement is that the electrode materials are polycrystalline with a crystallite and particle sizes as small as possible. Therefore, we later called the polycrystalline electrode materials NCIM_S (for nano-crystallite-insertion material) [3, 4].

Table 1 gives important examples related to mixed-valency metal oxides [2, 5]. For clarity, the examples listed in Table 1 have been divided into two classes, I and D, according to whether the resistivity tends to increase (class I) or to decrease (class D) upon the electrochemical Li^+ insertion process.

Rather similar considerations were reported by Barloux *et al.* and concern the spinel LiMn_2O_4 [6]. Also apparently related to that, Kumagai *et al.* [7] have reported that the positive electrode $\text{MnO}_2 \cdot y\text{V}_2\text{O}_5$, was formed by incorporation of V_2O_5 into MnO_2 matrices and the crystallinity of the oxide decreased with increase in V_2O_5 content incorporated: they have shown that the amount of Li^+ ions that can be reversibly electrochemically (de)inserted increased with increasing y value, *i.e.*, with decrease in the crystallinity; it reached about 1 Li^+ per mole of transition metal with $y = 0.6$ [7].

In this paper, the framework of the model accounting for the reversible electrochemical Li^+ insertion occurring in the NCIM_S , is presented.

We also show, for the first time, that the model accounts for the evolution of the open circuit voltage of the electrodes, versus the fraction, x , of the alkali.

2. MECHANISMS OF THE REVERSIBLE ELECTROCHEMICAL INSERTION OF LITHIUM OCCURRING WITH NCIM_S

First of all, by minimizing the size of the crystallites we tend to:

- (i) favor the formation of defect bonds, particularly at the crystallite surface (of its vicinity), such as anions adjacent to cation vacancies: *these defects may act as reversible (de)grafting sites for Li^+ .*
- (ii) weaken the cation-anion bonding not only on the grain boundary region but also within the grain close to its surface: *then the electrochemical insertion of Li^+ may be expected to occur through easier bonding rearrangements [3].*

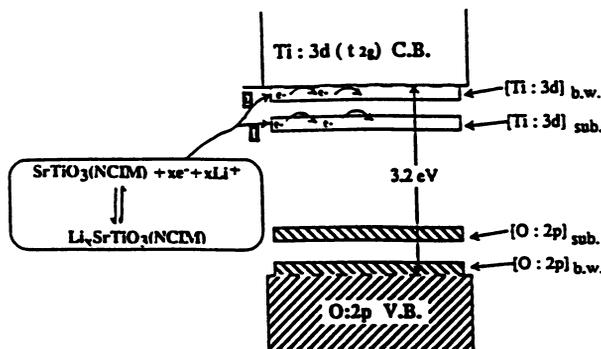


FIGURE 1

This is depicted below for $\text{SrTiO}_3\text{-NCIM}$, taken as a non-limiting but illustrative example.

First of all, fig. 1 illustrates the electron conduction via $[\text{Ti}: 3d]_{\text{sub}}$ or $[\text{Ti}: 3d]_{\text{b.w.}}$ energy states:

- $[\text{Ti}: 3d]_{\text{sub}}$ represents deep subband-gap energy states arising from cation defects adjacent to an anion vacancy. They are lowered below the Π^* conduction band of $\text{Ti}^{4+}: 3d^0(t_{2g})$ parentage. Conversely, anion defects adjacent to cation vacancies occur. They introduce acceptor states $[\text{O}: 2p]_{\text{sub}}$ arising from the $\text{O}^{2-}: 2p^6$ valence band. According to the model, the latter defects act as reversible (de)grafting sites for Li^+ , (see (i)).
- the $[\text{Ti}: 3d]_{\text{b.w.}}$ and $[\text{O}: 2p]_{\text{b.w.}}$ energy states originate from Ti — O bond weakening. This bond weakening induces Li^+ (de)insertion as mentioned above (see (ii)).

We will see, now, that the model accounts for the differences observed between the open-circuit voltage (OCV) versus x (the fraction of the alkali) curves related to polycrystalline electrodes having different sizes of crystallites. For sake of simplicity, such a behavior is illustrated only for two n -type electrodes Si_xSnO_2 and Li_xWO_3 (fig. 2a, b).

The concentration of the “sub” and b.w.” states increases as the crystallite size is reduced. This obviously causes, *only for the lower x values*, a pushing of the Fermi-energy (E_F) (i.e., higher electron affinity) and therefore, of OCV towards cathodic values. Indeed, for the lower x values, the OCV are higher for the electrodes having the smallest crystallite size (fig. 2a and 2b for $x \lesssim 0.15$).

For higher x values ($x \gg 0.15$), and when the inside-crystallite structure is well adapted for the reversible intercalation of lithium as occurs for Li_xWO_3 , an inversion of the OCV is observed (fig. 2b): indeed, for $x \gg 0.15$, all the subband gap energy states $[\text{W}^{6+}: 5d^0]_{\text{sub}}$ and $[\text{W}^{6+}: 5d^0]_{\text{b.w.}}$ (the “twin states” of $[\text{Ti}^{4+}: 3d^0]_{\text{sub}}$ and b.w. reported in fig. 1) are filled with electrons. Therefore, the lithium intercalation within the nanocrystallites can now take place; it is accompanied with a “delocalization” of the injected electrons in the conduction band. On the other hand, it is well established that the band-energy width increases as the

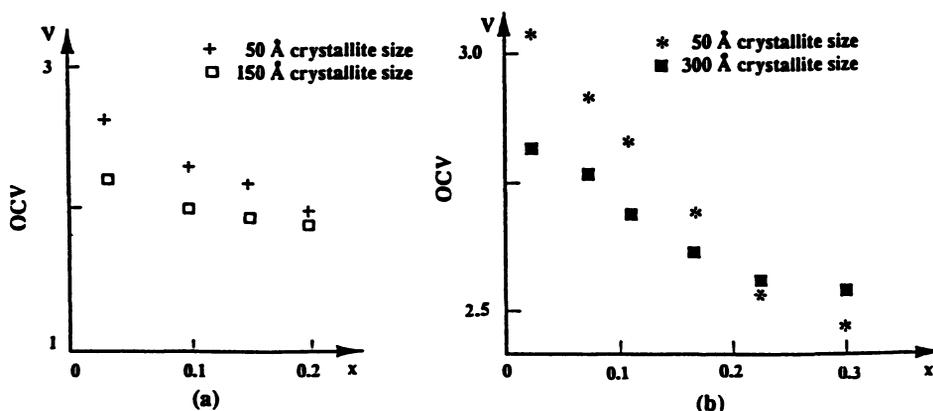


FIGURE 2

crystallite size decreases [8]. Therefore, the WO_3 electrodes having the smallest crystallite size have their conduction-band edge shifted towards anodic values: this causes a decrease of E_F , and therefore, of OCV, towards anodic values (as illustrated on fig. 2b for $x \gg 0.15$).

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