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MECHANISMS OF THE REVERSIBLE ELECTROCHEMICAL INSERTION OF LITHIUM OCCURRING WITH NCIMs (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 bonds 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.

I. INTRODUCTION

In the last 20 years, much attention has been focused on A_xMO_2—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 10^3 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.

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-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 particule sizes as small as possible. Therefore, we later called the polycrystalline electrode materials NCIM$_s$ (for nano-crystallite-insertion material)[3,4].

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TABLE I
Some nanocrystallite insertion materials (NCIMs)

Sample	Class	Average grain size (Å)	Insertion rate x (measured in $LiClO_4$ (p.c.), $1.5V \leq V(Li) \leq 3.5V$)
Li_xSrTiO_3	D	80	$0 \leq x \leq 0.3$
Li_xCrO_2	I	30	$0 \leq x \leq 1$
$Li_xMn_2O_3$	I	50	$0 \leq x \leq 2$
$Li_xFe_2O_3$	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	$0 \leq x \leq 2$

Table I gives important examples related to mixed-valency metal oxides[2,5]. For clarity, the examples listed in Table I 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 $MnO_2 \cdot yV_2O_5$ 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)insered increased with increasing y value, i.e., with decrease in the crystallinity; it reached about 1 Li^+ per mole of the oxide 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, vs the fraction, x, of the alkali.

II. MECHANISMS OF THE REVERSIBLE ELECTROCHEMICAL INSERTION OF LITHIUM OCCURING 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 anion adjacent to cation vacancies: ***these defects 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^+ occurs through easy bonding rearrangements[3].***

That is depicted below for $SrTiO_3$-NCIM, ***taken as a non-limiting but illustrative example.*** First of all, Fig. 1 illustrates the electron conduction via $[Ti:3d]_{sub}$ or $[Ti:3d]_{bw}$ energy states.

- $[Ti:3d]_{sub}$ represents deep subband-gap energy states arising from cation defects adjacent to an anion vacancy. They are lowered below the π^* conduction

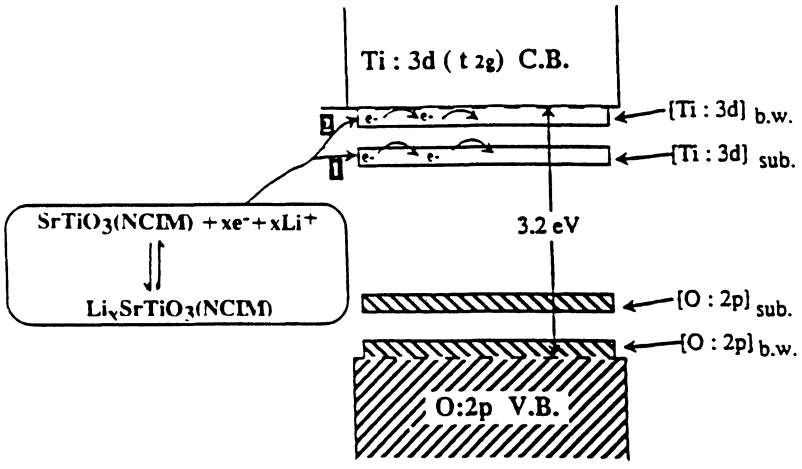

FIGURE 1 Simplified band energy scheme of $SrTiO_3$-NCIM.

band of $Ti^{4+}:3d^0(t_{2g})$ parentage. Conversely, anion defects adjacent to cation vacancies occur. They introduce acceptor states $[O:2p]_{sub}$ arising from the $O^{2-}:2p^6$ valence band. According to the model, the latter defects act as reversible (de)grafting sites for Li^+, (see (i)).

- the $[Ti:3d]_{bw}$ and $[O:2p]_{bw}$ 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) vs 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 Li_xSnO_2 and Li_xWO_3 (Fig. 2a, b).

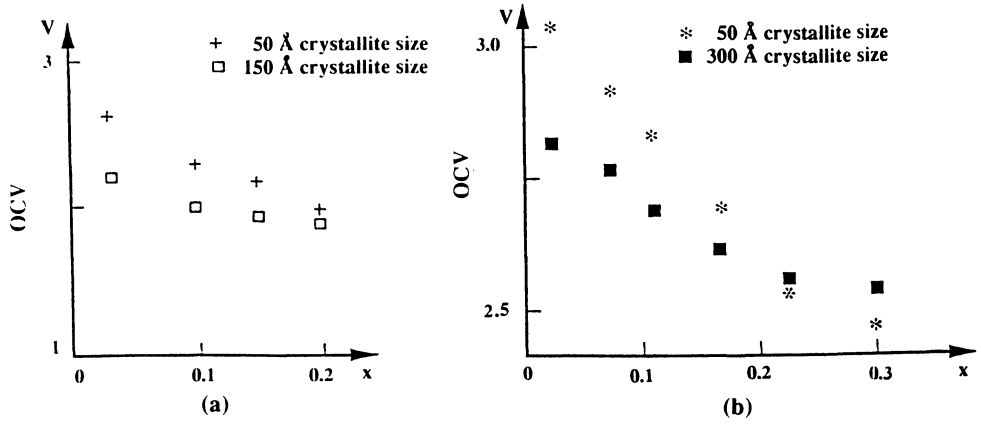

FIGURE 2 Equilibrium OCVs vs x for some Li/$LiCF_3SO_3$/NCIMs (a:Li_xSnO_2; b:Li_xWO_3).

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) and thereby 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 ($x >> 0.15$) and when the inside-crystallite structure is well adapted for the reversible intercalation of lithium as it occurs for Li_xWO_3, an inversion of the OCV is observed (Fig. 2b): indeed for $x >> 0.15$ all the subband gap energy states $[W^{6+}:5d^0]_{sub}$ and $[W^{6+}5d^0]_{bw}$ (the "twin states" of $[Ti^{4+}:3d^0]_{sub}$ 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 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 thereby of OCV, towards "anodic" values (as it is illustrated on Fig. 2b for $x >> 0.15$).

III. THE NCIM HAVE BEEN INVESTIGATED IN DIFFERENT FORMS: EITHER POWDERED ELECTRODES (A) OR COMPOSITE ELECTRODES (B) OR THIN FILM ELECTRODES (C).

1. Powdered Electrodes or Composite Electrodes

They can be efficiently used as positive electrodes for rechargeable lithium batteries of high energy density. Figure 3 shows the charge-discharge curves for powdered and composite electrodes.

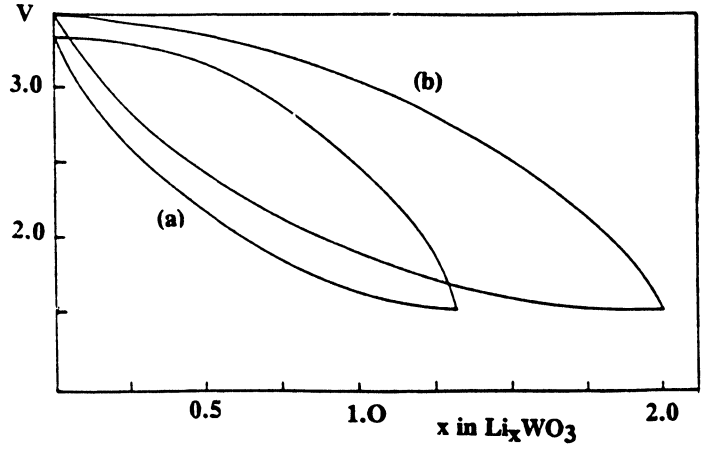

FIGURE 3 Charge-discharge curves of: (a) $Li/LiClO_4$-p.c./WO_3-NCIM (50Å size), (b) $Li/LiClO_4$-p.c./"soft" composite electrode consisting of WO_3-NCIM (50Å size) dispersed in conductive polymer.

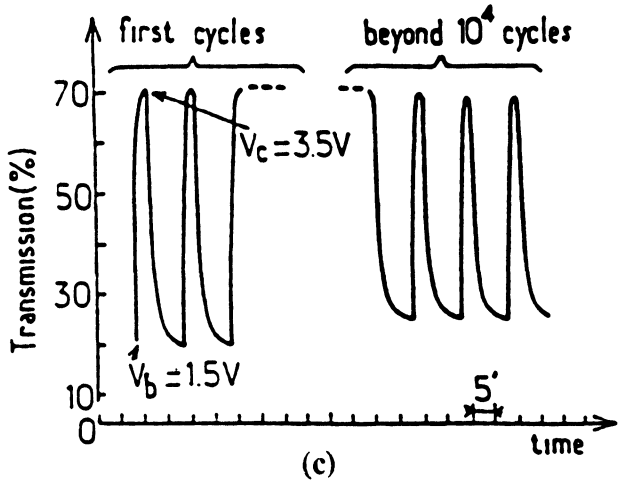

FIGURE 4 Transmission (λ = 550 nm) vs time for repeated coloring and bleaching cycles with the NCIM (50 Å) counter electrodes $Li_{2-x}NiO_2$ (c). The Li^+ insertion rate, x, varies within 0 and 1. The coloring and bleaching potentials Vc and Vb are measured vs Li in $LiClO_4$ p.c. electrolyte.

2. *Thin Film Electrodes*

They can be efficiently used either as positive electrodes for thin-film rechargeable batteries of high energy density or as counter electrodes for electrochromic windows. Transmission vs time for repeated coloring and bleaching cycles is shown in Figure 4.

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