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 NCIMs (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 $A_xM_2O_7$-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.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-
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 NCIMs (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⁺/Li insertion process.

Rather similar considerations were reported by Barloux et al. and concern the spinel LiMn₂O₄ [6]. Also apparently related to that, Kumagai et al. [7] have reported that the positive electrode MnO₂·yV₂O₅, was formed by incorporation of V₂O₅ into MnO₂ matrices and the crystallinity of the oxide decreased with increase in V₂O₅ 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 NCIMs, is presented.

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

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

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].

### TABLE I. SOME NANOCRYSTALLITE INSERTION MATERIALS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Class</th>
<th>Average grain size (Å)</th>
<th>Insertion rate x (measured in LiClO₄ (p.c.), 1.5 V &lt; V(Li) &lt; 3.5 V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiₓSrTiO₃</td>
<td>D</td>
<td>80</td>
<td>0 ≤ x ≤ 0.3</td>
</tr>
<tr>
<td>LiₓCrO₂</td>
<td>I</td>
<td>30</td>
<td>0 ≤ x ≤ 1</td>
</tr>
<tr>
<td>LiₓMn₂O₃</td>
<td>I</td>
<td>50</td>
<td>0 ≤ x ≤ 2</td>
</tr>
<tr>
<td>LiₓFe₂O₃</td>
<td>D</td>
<td>150</td>
<td>0 ≤ x ≤ 0.5</td>
</tr>
<tr>
<td>LiₓNiO₂</td>
<td>I</td>
<td>60</td>
<td>1 ≤ x ≤ 2</td>
</tr>
<tr>
<td>LiₓCuO₂</td>
<td>I</td>
<td>50</td>
<td>1 ≤ x ≤ 2</td>
</tr>
<tr>
<td>LiₓWO₃</td>
<td>D</td>
<td>40</td>
<td>0 ≤ x ≤ 2</td>
</tr>
</tbody>
</table>
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 $\Pi^*$ conduction 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) 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 $\text{Si}_x\text{SnO}_2$ and $\text{Li}_x\text{WO}_3$ (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 $x \leq 0.15$).

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 $\text{Li}_x\text{WO}_3$, an inversion of the OCV is observed (fig. 2b): indeed, for $x \gg 0.15$, 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 WO₃ 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 \( x \gg 0.15 \)).

REFERENCES
