

## REVERSIBLE LITHIUM INTERCALATION IN NANO-SIZED $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>

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In the early 80's, numerous studies focussed on the electrochemical reduction of 3d-metal oxides (M = Mn, Co, Fe, V) in lithium cells. When starting from oxides with low metal oxidation state (Cu<sub>2</sub>O, NiO, MnO, FeO, CoO), metallic nanograins/clusters are formed as soon as the reduction process starts. In contrast, when starting from higher cationic oxidation states (Co<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>, Mn<sub>3</sub>O<sub>4</sub>, Fe<sub>2</sub>O<sub>3</sub>), intermediate reduced phases are expected in the early stage of the reduction process. This was well documented by *Thackeray et al.* who clearly showed that rock salt-type lithiated metal oxides are formed through lithium insertion and concomitant cationic jump. Upon further reduction, these phases decompose into metallic clusters and lithia [1-3].

In a recent study, we observed that either CoO or Li<sub>x</sub>Co<sub>3</sub>O<sub>4</sub> would form upon reduction of spinel Co<sub>3</sub>O<sub>4</sub> depending on the applied current density (i.e. discharge rate / surface area ratio)[4]. In the present study, we focus in a similar way on the particles size effect on the reduction of iron oxides.

In the case of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (hematite) it was reported that a small amount of inserted lithium (referred to as  $x_c$ ) initiated a transition of the close-packed anion array from hexagonal to cubic stacking [1]. We found that this critical concentration actually corresponds to the intercalation of lithium in the corundum structure (voltage feature at ca. 1.6 V vs. Li<sup>+</sup>/Li, **fig. 1**), and that this  $x_c$  value is mainly governed by the size of the reactive particles. In this work, we compare the reactivity of two samples of hematite labelled as follows: M-Fe<sub>2</sub>O<sub>3</sub> made of large particles (~0.5  $\mu$ m), and n-Fe<sub>2</sub>O<sub>3</sub> made of nano-sized particles (200 Å). While around 0.05 Li per formula unit can be inserted in M-Fe<sub>2</sub>O<sub>3</sub>, up to 1 Li can be inserted in n-Fe<sub>2</sub>O<sub>3</sub> without phase transition (**fig. 1**). Unsuccessful attempts to increase  $x_c$  values by applying lower currents suggest that the particles size is the main parameter herein involved. Through OCV and *in situ* XRD experiments, we clearly established the biphasic nature of the reduction reaction for M-Fe<sub>2</sub>O<sub>3</sub> (**fig. 2**) and the monophasic process along lithium insertion in n-Fe<sub>2</sub>O<sub>3</sub>, leading to  $\sim\alpha$ -Li<sub>1</sub>Fe<sub>2</sub>O<sub>3</sub> (**fig. 3**). The reduction products were also characterized by EXAFS/XANES and Mössbauer effect spectroscopy. The better structural reversibility of the monophasic process with respect to the biphasic one was confirmed by electrochemical cycling tests conducted on hematite samples with various particles sizes.

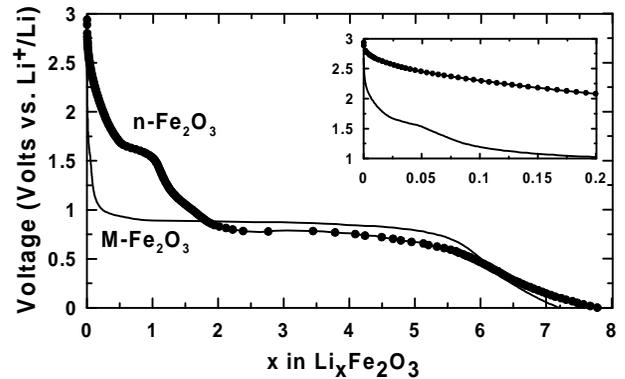
Through this work, we wish to stress that a careful control of the texture of electrochemically active oxide particles represents an alternative and a promising route in view of reversible and benign intercalation reactions in materials so far totally disregarded for such applications.

[1] M.M.Thackeray, W.I.F.David and J.B.Goodenough, *Mat. Res. Bull.* **17**, 785-793 (1982)

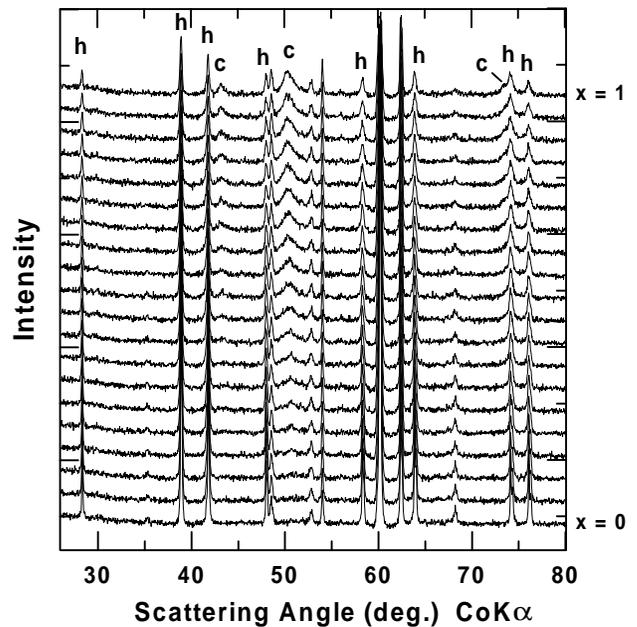
[2] M.M.Thackeray, S.D.Backer and K.T.Adendorff, *Solid State Ionics* **17**, 175-181 (1985)

[3] M.M.Thackeray, W.I.F.David, P.G.Bruce and J.B.Goodenough, *Mat. Res. Bull.* **18**, 461-472 (1983)

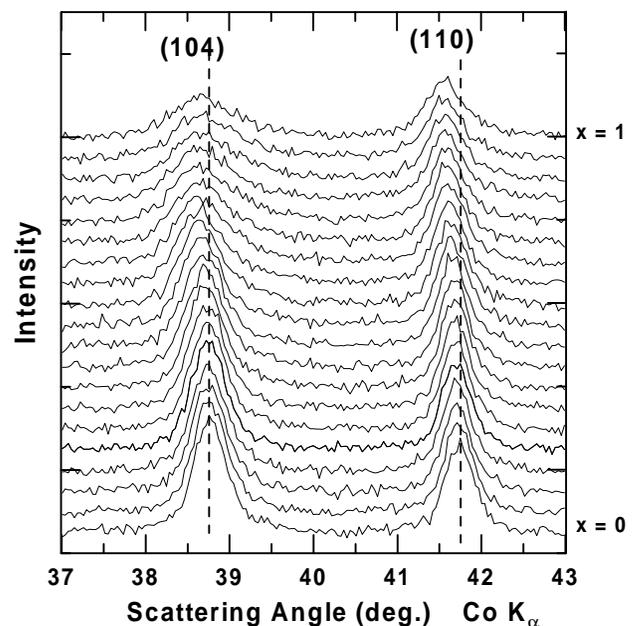
[4] D.Larcher, G.Sudant, J.B.Leriche, Y.Chabre and J.M.Tarascon, *J. Electrochem. Soc.*, in press.



**Fig. 1:** Composition vs. voltage curve for nano-sized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (n-Fe<sub>2</sub>O<sub>3</sub>) and micron-sized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> (M-Fe<sub>2</sub>O<sub>3</sub>). Rate: 1 Li in 5 hours.



**Fig. 2:** *In-situ* XRD evolution upon reduction of micron-sized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> vs. Li ( $0 < x < 1$  per Fe<sub>2</sub>O<sub>3</sub>), c=rock-salt phase, h= $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>. Rate = 1 Li in 5 hours.



**Fig. 3:** Bragg peak shift of nano-sized  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> upon reduction in Li cell ( $0 < x < 1$  per formula unit) at a constant rate of 1 Li in 5 hours.