

## On the Lithiation-Delithiation Process of Carbon-coated $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> Nanoparticles obtained from Ferrocene

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Since several years metal oxides ( $M_xO_y$ ,  $M = Cu, Fe, Co, Ni, \text{etc.}$ ) are considered as attracting active materials for the realization of advanced electrochemical storage devices<sup>1</sup>.  $M_xO_y$  belong to the so-called conversion materials, and during electrochemical cycling a reduction of  $M_xO_y$  to metal ( $M$ ) and lithium oxide ( $Li_2O$ ) takes place, followed by an oxidation of  $M$  to  $M_xO_y$ .

Among the various  $M_xO_y$  considered so far, hematite iron oxide ( $Fe_2O_3$ ) appears one of the most promising. As a matter of fact,  $Fe_2O_3$  displays high theoretical capacity ( $1007 \text{ mAh g}^{-1}$ ), is cheap, safe and environmentally friendly. Because of these advantageous features, in the past decade the use of  $Fe_2O_3$  as active material in lithium-ion batteries (LIBs) and supercapacitors (SCs) has been widely investigated<sup>2-6</sup>. So far, however, the introduction of  $Fe_2O_3$  in real devices has been hindered by its poor reversibility. In order to overcome this limitation several strategies have been proposed, and the use of carbon-coated nanoparticles is presently considered as the most promising<sup>1-2</sup>.

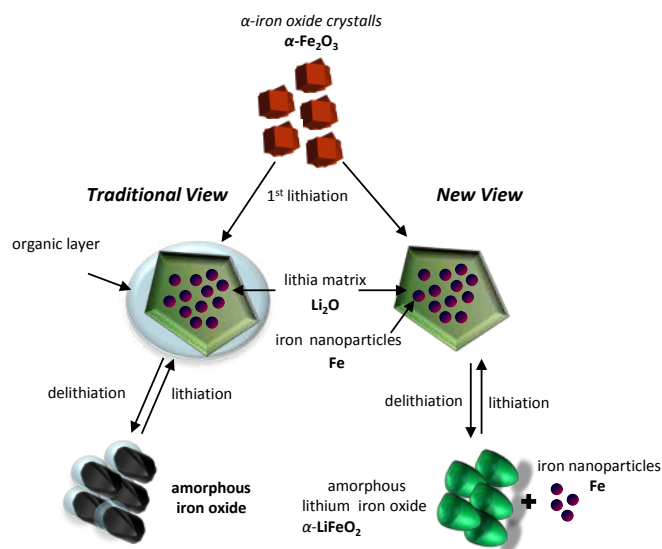
Ferrocene can be used as a precursor for the synthesis of carbon-coated  $\alpha$ - $Fe_2O_3$  nanoparticles (cIOs). The pyrolysis of ferrocene leads to the formation of a compound that can be fully converted into cIOs via a simple oxidation in air. This simple, fast and cheap synthetic route enables the realization of cIOs with particle size in the range of 50-150 nm and tunable carbon-coating. When used in combination with conventional electrolytes cIO-based electrodes display high specific capacity (over  $800 \text{ mAh g}^{-1}$  at  $0.13 \text{ A g}^{-1}$ ), excellent cycling retention (higher than 99 % after 50 cycles) and remarkable rate performance (over  $400 \text{ mAh g}^{-1}$  at  $5 \text{ A g}^{-1}$ )<sup>2</sup>.

Due to the promising rate performance these electrodes can be considered as interesting material, not only for LIBs, but also for the realization of high energy lithium-ion capacitors (LICs). We performed some preliminary tests and could show that the use of cIO enables the realization of a LIC with an operative voltage of 3.4 V, and promising values of energy and power.

It is interesting to note that even if many studies have been dedicated to  $Fe_2O_3$ , the (reversible) lithiation-delithiation mechanism of this material is still not completely understood. Larcher et al. showed that the lithiation process leads to the formation of very fine iron clusters ( $10\text{-}15 \text{ \AA}$ ) dispersed in a lithium oxide matrix<sup>4</sup>. Both iron and lithium oxide are in turn embedded in a gel-like organic layer, which is formed upon decomposition of the electrolyte<sup>4-5</sup>. Concerning the delithiation process,

the information available in literature is not that detailed. It is accepted that a conversion of  $Fe$  to  $Fe_2O_3$  (or other iron oxide phases) takes place, but it is not completely clear which phases might be formed during this oxidation process. More accurate information about the delithiation process would be very beneficial for the understanding of the charge-discharge mechanism of  $Fe_2O_3$  (and in general of  $M_xO_y$ ). This information could be in turn of importance for the improvement of the poor reversibility of this material.

Herein we report a study of the lithiation-delithiation mechanism of carbon-coated  $Fe_2O_3$  nanoparticles obtained from ferrocene<sup>2</sup>. Due to the high purity and high homogeneity of these nanoparticles they are a suitable material for the investigation of the lithiation-delithiation mechanism. The lithiation-delithiation process of these nanoparticles was investigated by means of electrochemical techniques, X-ray diffraction (XRD), <sup>57</sup>Fe Mössbauer spectroscopy and EXAFS (Extended X-ray absorption fine structure). The results of this investigation indicated that at the end of the delithiation process the lithium iron oxide  $\alpha$ - $LiFeO_2$  is formed. The formation of this compound may be the explanation for the irreversible capacity loss in the first cycle, which is usually assigned to the formation of an organic gel-like layer. Based on these results a new charge-discharge mechanism of hematite in LIBs is proposed and discussed.



**Figure 1.** Comparison between the “traditional” and “new” lithiation-delithiation mechanism of carbon-coated  $Fe_2O_3$  based electrode.

### References

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