

INORGANIC NANOCRYSTALLINE AND HYBRID NANOCRYSTALLINE PARTICLES AND THEIR CONTRIBUTION TO ELECTRODE MATERIALS FOR LITHIUM BATTERIES.

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Traditional electrode materials based on well-crystallized host compounds, such as layered $\text{LiCo}_{1-x}\text{Ni}_x\text{O}_2$, have been considered, for a long time, as the best choice for rechargeable lithium batteries because their crystal regularity insures an easy diffusion of Li^+ ions in the ionic-covalent lattice according to ‘Solid-State Ionics’. However, along with the ‘nanoscience’ progress, it was recently found that nanoparticles electrochemical behavior is much different from that of well-crystallized microparticles. Indeed, high density of surface defects occurs in nanocrystalline materials, which can be advantageously used to enhance their electrochemical activity¹. Related to that, various examples (SnO_2 , WO_3 , LiMn_2O_4 , $\text{Li}_{0.5}\text{Ni}_{0.5}\text{O}$, $\text{Li}_{0.5}\text{Cr}_{0.5}\text{O}_{1.25}$, V_2O_5 , TiO_2) showed that the crystallite size control was a key-point for the specific capacity and the cycling efficiency of the electrodes. Such an enhanced electrochemical activity of these nanocrystalline cathode materials, (compared to their microcrystalline homologues) occurs *only* when the first significant electrochemical step is an insertion of Li^+ ions (Li battery discharge). This insertion begins with the electrochemical grafting of Li^+ ions, promoted by structural defects at/near the nanocrystallite surface (Fig.1). Indeed, surface defects induce many sub-band-gap states between the conduction band and valence band, so that the insertion (process 1, Fig.1) fills these localized sub-band-gap states; consequently a smoother discharge curve takes place for nanocrystalline samples in comparison with well-crystalline homologue and good reversibility is achieved. This model, which highlights the surface effects, provides a useful insight to develop effective electrodes since it can foresee the use of nanocrystalline rather than microcrystalline electrodes. We illustrate this aspect choosing the $\gamma\text{-Fe}_2\text{O}_3$, and nanohybrid inorganic-organic materials derivatives ($\gamma\text{-Fe}_2\text{O}_3/\text{PPy}$) study (Fig.2). As opposed to microcrystalline one, nanocrystalline pristine maghemite exhibits a rather large but partially reversible capacity (Fig.2a). The introduction of polypyrrole (PPy), which, on its own shows a progressive capacity decrease (Fig.2b), illustrates the influence of surface modification induced by physisorption of PPy on nanograins (Fig.2c). The synergy in the nanohybrid sample is very efficient compared to the precursors.

In order to get a better understanding on the electrochemical processes involved at the grain surface, we performed an electrochemical impedance spectroscopy (EIS) investigation. Fig.3 illustrates the typical diagrams obtained at different potentials (various Li^+ insertion rates). The curves shape of exhibits different capacitive loops characteristic of the existence of different interfaces²; this is particularly obvious for the highest insertion rates. The diagrams drastic changes with the potential electrode show that EIS is a powerful technique

to investigate surface modification. The study of impedance measurements is still in progress.

1. N. Treuil *et al.*, *J. Phys. Chem. B*, **103**, 2100 (1999).

2. H. Li *et al.*, *J. Power Sources*, **81-82**, 340 (1999).

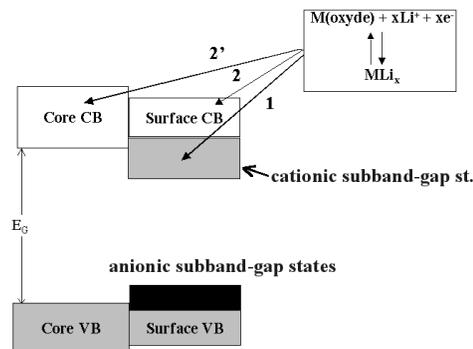


Fig. 1. Schematic band model for the electrochemical grafting process.

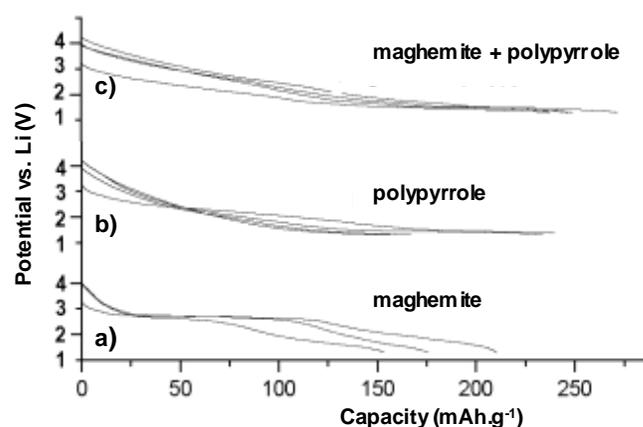


Fig. 2. Variation of the voltage vs. Li (first four discharge curves) for the: a) nanocrystalline maghemite b) PPy conducting polymer and c) nanohybrid material PPy/maghemite (current density: 8 mA/g, potential range: 1.3 - 4.3 V).

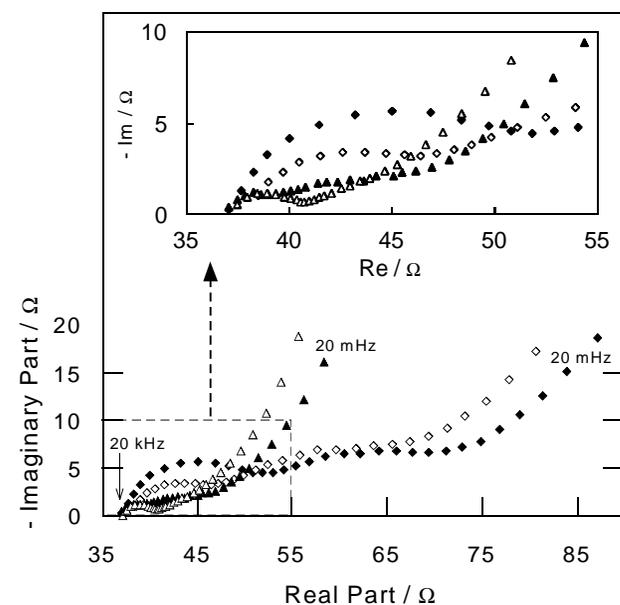


Fig.3. Electrochemical impedances for various discharge states of a lithium battery in the Nyquist plane. Nanocrystalline $\gamma\text{-Fe}_2\text{O}_3$ was used as working electrode. (\blacklozenge) $E = 1.7 \text{ V vs Li}$, (\diamond) $E = 1.9 \text{ V vs Li}$, (\blacktriangle) $E = 2.2 \text{ V vs Li}$, (\triangle) $E = 3.5 \text{ V vs Li}$.