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$ZnFe_2O_4$ and ZnO/Fe_2O_3 nanoparticles as anode materials for lithium-ion batteries: understanding of the lithium storage mechanism

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Lithium-ion batteries have been widely used in portable electronic devices for years. With the depletion of fossil fuels and the growing environmental concerns, lithium-ion batteries received considerable attention to contribute to the development of electric vehicles and storage devices for renewable energies. However, existing lithium-ion batteries cannot reach sufficient energy density to address the needs for such applications. One of the issues limiting the energy density is the low specific capacity of the graphite anode (372 mAh/g).

Mixed-transition metal oxides (also called ternary oxides) with a spinel structure (AB_2O_4 with A and B transition metals) appear as a promising solution to replace graphite with a higher theoretical capacity (between 750 and 1000 mAh/g depending on the oxide)[1]. Among various oxides, $ZnFe_2O_4$ is an interesting substitute for graphite, as an abundant, cheap, non-toxic and environmentally friendly material with a high theoretical capacity of 1000 mAh/g. This capacity corresponds to 9 Li^+ ions stored per formula unit as shown in the widely accepted storage mechanism described below[2].

<u>1st lithiation:</u>
$ZnFe_2O_4 + 9\,Li^+ + 9e^- \rightarrow ZnLi + 2Fe + 4Li_2O$

<u>Following cycles:</u>
$ZnLi \leftrightarrow Zn + Li^+ + e^-$
$Zn + 2Fe + 4Li_2O \leftrightarrow ZnO + Fe_2O_3 + 8Li^+ + 8e^-$

In fact, after the first cycle, $ZnFe_2O_4$ is not recovered but replaced by separated phases of ZnO and Fe_2O_3. To understand the lithium storage mechanism, comparative studies between $ZnFe_2O_4$ nanoparticles and a mixture of ZnO and Fe_2O_3 nanoparticles were conducted.

$ZnFe_2O_4$, ZnO and Fe_2O_3 nanoparticles presented in this work were synthesized by laser pyrolysis (fig.1). In this process, an aerosol containing droplets of the precursors produced by a nebulizer is flown into the reactor using a carrier gas. In the reactor, a 10.6 µm-CO_2 laser beam decomposes the precursors to obtain nanopowders which are then collected on a filter. The key advantage of laser pyrolysis is the ability to obtain nanomaterials in large amounts with a high purity while controlling the grain size with the appropriate parameters.

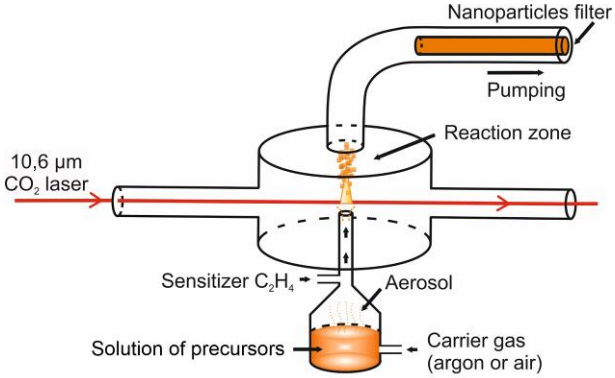

Figure 1. Laser pyrolysis experimental setup

Aqueous solutions of $ZnCl_2$ and $FeCl_3.6H_2O$ dissolved in DI water were used for the synthesis of $ZnFe_2O_4$ nanoparticles while ZnO and Fe_2O_3 nanoparticles were synthesized separately using $ZnCl_2$ and $Fe(Acac)_3$. Ethylene was chosen as absorbent for the CO_2 laser to allow the decomposition of the precursors and either argon or air was used as the carrier gas.

Two types of electrodes were then prepared using $ZnFe_2O_4$ or a mixture of ZnO and Fe_2O_3 (50% at. for each) as active material (70% wt. of the electrode). CMC (carboxymethylcellulose) was used as binder (12% wt.) and VGCF (9% wt.) and carbon black (9% wt.) as additives.

Galvanostatic cycling tests were performed at C/10 (1000 mA/g) and 1C (100 mA/g) from 0.01V to 3.0V in order to compare the electrochemical performance of both materials vs lithium metal. Besides, post-mortem SEM images of the electrodes were taken to observe the electrodes morphology after cycling.

To better understand the lithium storage mechanism, cyclic voltammetry from 0.01V to 3.0V with a scan rate of 0.1 mV/s was also conducted (fig. 2).

For the ZnO/Fe_2O_3 mixture, two main cathodic peaks at 0.38V and 0.72V are observed for the first cycle, which should correspond to the reduction of ZnO[3] and Fe_2O_3[4] respectively. For $ZnFe_2O_4$, only one intense reduction peak is observed for the first cycle, located between the two peaks of ZnO and Fe_2O_3, at 0.55V. For the subsequent cycles, one reduction peak is maintained for both materials, at 0.92V for $ZnFe_2O_4$ and at 0.82V for ZnO/Fe_2O_3.

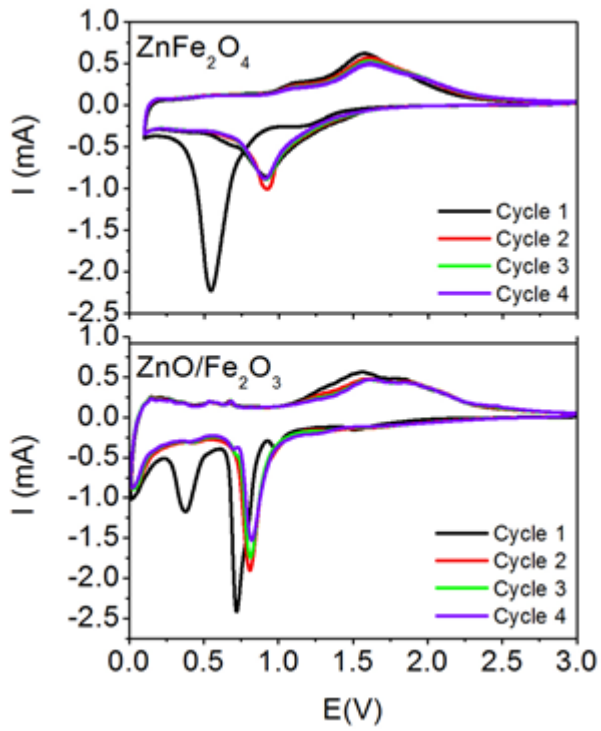

Figure 2. Cyclic voltammetry for $ZnFe_2O_4$ and ZnO/Fe_2O_3

Operando XRD, Mössbauer ^{57}Fe and XAS investigations of these materials are currently conducted to gain deeper insight in the lithiation/delithiation processes of $ZnFe_2O_4$ and of the ZnO/Fe_2O_3 mixture.

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