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ZnFe₂O₄ and ZnO/Fe₂O₃ nanoparticles as anode materials for lithium-ion batteries: understanding of the lithium storage mechanism

Samantha Bourrioux¹ – Yann Leconte¹ – Moulay Tahar Sougrati² – Lorenzo Stievano² – Laure Monconduit² – Zhichuan J. Xu³ – Madhavi Srinivasan³ – Alain Pasturel⁴

¹CEA, IRAMIS, NIMBE, CNRS UMR 3685, F- 91191, GIF-SUR-YVETTE, FRANCE

²Institut Charles Gerhardt- UMR5253 Université de Montpellier Place Eugène Bataillon, 34095 Montpellier, FRANCE

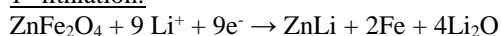
³School of Materials Science and Engineering, Nanyang Technological University, SINGAPORE

⁴SIMAP, UMR CNRS 5266, Grenoble INP, BP 75, 38402 SAINT-MARTIN D'HERES, FRANCE

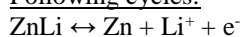
Lithium-ion batteries have been widely used in portable electronic devices for years. With the depletion of fossil fuels and the growing environmental concerns, lithium-ion batteries received considerable attention to contribute to the development of electric vehicles and storage devices for renewable 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 (AB₂O₄ 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, ZnFe₂O₄ 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 below².

1st lithiation:



Following cycles:



In fact, after the first cycle, ZnFe₂O₄ is not recovered but replaced by separated phases of ZnO and Fe₂O₃. To understand the lithium storage mechanism, comparative studies between ZnFe₂O₄ nanoparticles and a mixture of ZnO and Fe₂O₃ nanoparticles were conducted.

ZnFe₂O₄, ZnO and Fe₂O₃ 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-CO₂ 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.

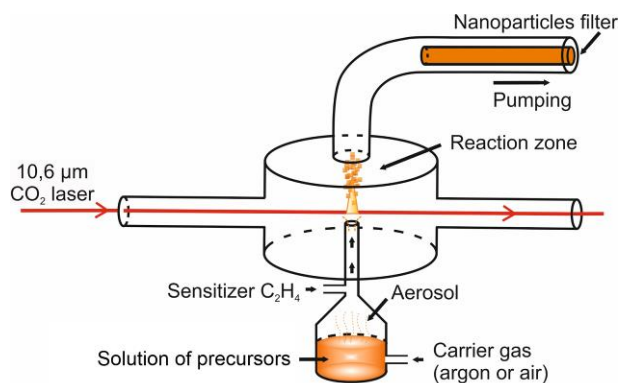


Figure 1. Laser pyrolysis experimental setup

Aqueous solutions of ZnCl₂ and FeCl₃·6H₂O dissolved in DI water were used for the synthesis of ZnFe₂O₄ nanoparticles while ZnO and Fe₂O₃ nanoparticles were synthesized separately using ZnCl₂ and Fe(Acac)₃. Ethylene was chosen as absorbent for the CO₂ 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 ZnFe₂O₄ or a mixture of ZnO and Fe₂O₃ (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 (100 mA/g) and 1C (1000 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/Fe₂O₃ mixture, two main cathodic peaks at 0.38V and 0.72V are observed for the first cycle, which should correspond to the reduction of ZnO³ and Fe₂O₃⁴ respectively. For ZnFe₂O₄, only one intense reduction peak is observed for the first cycle, located between the two peaks of ZnO and Fe₂O₃, at 0.55V. For the subsequent cycles, one reduction peak is maintained for both materials, at 0.92V for ZnFe₂O₄ and at 0.82V for ZnO/Fe₂O₃.

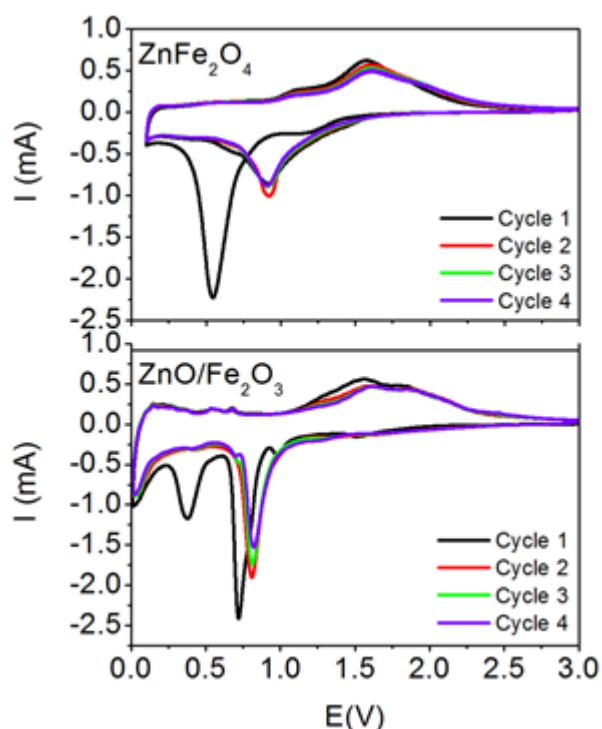


Figure 2. Cyclic voltammetry for ZnFe₂O₄ and ZnO/Fe₂O₃

Operando XRD, Mössbauer ⁵⁷Fe and XAS investigations of these materials are currently conducted to gain deeper insight in the lithiation/delithiation processes of ZnFe₂O₄ and of the ZnO/Fe₂O₃ mixture.

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