

Understanding the Li insertion / extraction mechanism at microscopic level is important to design next generation batteries

UNDERSTANDING LI INSERTION MECHANISM FOR NEXT GENERATION BATTERIES

Lithium iron phosphate (LiFePO_4) is a good candidate for positive electrodes in lithium-ion batteries to be installed in new electric vehicles. Its cost is low, it has an excellent life cycle and it is safe. To obtain the best performances in terms of electrical conductivity it is synthesized in nanocomposite with grain size between 50 and 300nm.

The discharge-charge mechanism implies a delithiation of LiFePO_4 into FePO_4 and a successive insertion of Li into the iron phosphate. The mechanism of Li insertion / extraction at the microscopic level wasn't confirmed and at least four different models have been proposed.

The difference between the various models lies in the relative position, shape and dimension of the two phases, LiFePO_4 , FePO_4 during the process. Two of these models imply core shell structures (bulk or radial), another one a spinoidal decomposition at the nanoscale level of two Li and Fe rich end members (spinodal model), and the last one where the nanoparticles are either fully lithiated or fully delithiated (Domino-cascade model).

A phase mapping technique able to identify the lithiated and delithiated phase at the nanoscale can obviously solve the dilemma. Unfortunately the problem is complicated by the very similar unit cell parameters of LiFePO_4 and FePO_4 which differ from each other by less than 5%. ASTAR system can solve the problem by collecting the NanoBeam Electron Diffraction (NBED) patterns in precession mode.

Precession diffraction, on the one hand reduces the dynamical effects so that the patterns are closer to a kinematical simulation of the templates and on the other, it enables the collection of a higher number of reflections from high order Laue zones reducing the ambiguity in indexing the patterns. In this way ASTAR system has been able to detect that the nanocrystalline grains of the nanoparticles are either fully lithiated or fully delithiated giving strong support to the domino-cascade model (fig. 2). The results have been confirmed also using HRTEM imaging and EFTEM / EELS analysis.

The challenge:

Identify Li doped particles between two different phases having <5 % difference in cell parameters and particle size <50 nm

Solution:

ASTAR technique coupled with precession electron diffraction

Environmental friendly energy sources



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Crystal Structure

LiFePO_4 : Orthorhombic
 $a=10.33 \text{ \AA}$, $b=6.01 \text{ \AA}$, $c=4.69 \text{ \AA}$
 FePO_4 : Orthorhombic
 $a=9.81 \text{ \AA}$, $b=5.79 \text{ \AA}$, $c=4.78 \text{ \AA}$

Experimental Data

TEM type: Jeol 2010 FEF
Spot size: 2.7 nm
Step: 5 nm
Scanned area 1 x 1 μm

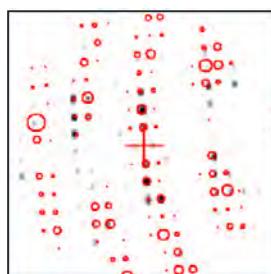


figure 1

Experimental precessed patterns and its indexation with the LiFePO_4 (red) and FePO_4 (green) templates with the corresponding agreement factors.

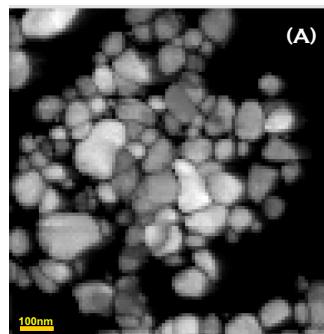
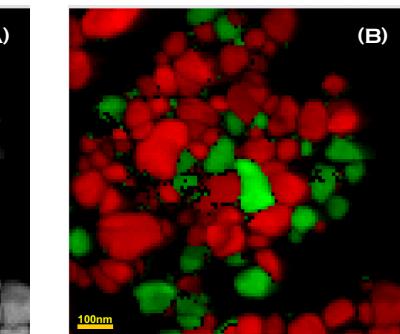


figure 2



LiFePO₄ FePO₄

Reconstructed bright field image (a), phase determination map (b). Crystal grains of the nanocomposite mixture of LiFePO_4 (red), FePO_4 (green) during different phases of the charge-discharge cycle. There is no mixing of the two phases inside the same crystal grain.

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