Understanding Li Insertion Mechanism for Next Generation Batteries

Lithium iron phosphate (LiFePO₄) 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 300 nm.

The discharge-charge mechanism implies a delithiation of LiFePO₄ into FePO₄ 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, LiFePO₄, FePO₄ 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 (spinoidal 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 LiFePO₄ and FePO₄ 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.

**Figure 1**
Experimental precessed patterns and its indexation with the LiFePO₄, (red) and FePO₄, (green) templates with the corresponding agreement factors.

**Figure 2**
Reconstructed bright field image (a), phase determination map (b), Crystal grains of the nanocomposite mixture of LiFePO₄, (red), FePO₄, (green) during different phases of the charge-discharge cycle. There is no mixing of the two phases inside the same crystals.

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