Phase mapping of nanopowders for Li-ion batteries

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Lithium iron phosphate (LiFePO₄) is a promising material for positive electrodes of lithium-ion batteries of the new generation of electric vehicle. It combines low cost, excellent cycle life and safety. Despite its scientific importance, the mechanism during cycling of insertion of Li in FePO₄ powder or extraction from LiFePO₄ is not yet fully understood. The controversy among scientists concerns the exact insertion/extraction mechanism at the microscopic/nanoscopic scale: core shell, radial core shell, domino cascade or spinodal decomposition models. These four models proposed a two phase-mechanism which could not be distinguished by conventional XRD due to the lack of spatial resolution.

Electron microscopy analysis offers a unique tool to differentiate and give a spatial distribution of these two phases. Nevertheless appropriate techniques have to be used to provide 2D mapping in a reasonable time. In order to differentiate these phases either the crystallography or the chemistry could be analysed. This paper introduces correlated analysis on cycled electrodes obtained by a recent TEM technique based on precession electron diffraction (PED) coupled with chemical mapping by Energy Filtered TEM (EFTEM). Both techniques provide a tool to map the two phases but are complementary. PED is obtained with the ASTAR system commercialised by the NanoMEGAS Company [1], which combined PED and template matching. LiFePO₄ and FePO₄ have the same crystallography structure but their lattice parameters differ by of few percent. Diffraction patterns are collected using PED which are closed to kinematics conditions and template analysis does an image correlation allowing to differentiate the two phases. The chemical approach uses electron energy loss spectroscopy (EELS) which shows differences in chemical bonding visible either in the Valence EELS (VEELS) region [2] or on the O-K (512eV) or FeL23 (708 eV) edges [3]. In this work, the large pre peak present in the VEELS area (4-7 eV) only for the non lithiated phases has been used as major features to characterised the phases. For this purpose, series of EFTEM images in the Low Loss region were recorded to reconstructed local spectrum and get rapid and easy mapping.

The two techniques were first validated on three types of powder: powders containing either FePO₄ or LiFePO₄ single phase particules or powders of partially electrochemically delithiated FePO₄ particules [4]. Then, measurements were done on real electrodes cycled with an “industrial” process. Figure 1 shows the PED analysis on the three known powders. It demonstrates the power of the technique that can differentiate the two kinds of phase and provide phase maps. Figure 2 shows VEELS investigation: EFTEM imaging with a slit center on the pre-peak can also differentiate the two phases. This analysis done on the partially electrochemically delithiated FePO₄ particles i.e. on an partly charged particules, confirmed the domino cascade mechanism [5] at the nanoscale level. Indeed, it was shown that 95% of the particles are either fully lithiated or fully delithiated.

The real electrodes were extracted from the device by ultramicrotomy. Slices of 80 nm thick were performed and analysed by both techniques. Figure 3 shows an example of the phase mapping on the same area obtained by PED and EFTEM. To get a better contrast the EFTEM image was normalised using the Plasmon peak. Analysis done on many ultramicrotomy lamellae coming from
different electrodes with different cycling process show clearly that delithiation preferentially happens on small particles and that delithiation tend to occur on linked regions.

The complementary of the two techniques, PED and EFTEM, will be discussed.

References

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Figure 1. exemple of phase identification obtained by PED for (a) LiFePO₄ (b) FePO₄ and (c) partially charged with 56% of FePO₄.

Figure 2. (a) 3 particles of the partially lithiated powder agglomerated at the edge of a C film. V EELS measured on the (b) FePO₄ and (c) LiFePO₄ phases. The pre-peak around 4-7eV is clearly visible for the FePO₄. (d) Chemical map obtained by EFTEM at energy 5eV on (a) area.

Figure 3. Same area investigated by both (a) PED and (b) EFTEM (c) and (d) show characteristic PED patterns on FePO₄ and LFP nanoparticles, (e) and (f) Valence EELS measured on the same LiFePO₄ and FePO₄ particles respectively. The two populations are clearly differentiated on large area and very good similarity is obtained.