

EELS Analysis Of Lithiation/Delithiation Reactions In LiFePO₄

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LiFePO₄ has emerged as an important cathode material for Li-ion batteries because of its stability and high rate capabilities. It is now well established that lithiation-delithiation occurs via a two-phase reaction. At high charge/discharge rates, the process of nucleation and growth of a two-phase reaction is too slow and a non-equilibrium single phase reaction has been proposed followed by relaxation into LiFePO₄ and FePO₄ end product phases [1]. In this study, we studied reaction mechanisms and determined the spatial distribution of lithiated/delithiated phases by STEM/EELS spectrum imaging.

LiFePO₄ particles from partially charged or discharge electrodes were observed with a cold cathode field emission Hitachi HD2700C STEM and Gatan Enfina EELS spectrometer. The energy resolution of the combined STEM/EELS system was 0.5 eV. The energy was calibrated with respect to the main O-K peak at 539 eV. Typical EELS spectrum for LiFePO₄ and FePO₄ are shown in Fig.1a and 1b respectively. A characteristic feature of delithiated FePO₄ phase is the presence of an oxygen pre-peak marked by an arrow in Fig.1b. The existence of this O prepeak has been attributed to a transition from O 1s to 2p hybridized state with Fe 3d [2]. In addition the change in Fe valence state from LiFe²⁺PO₄ to Fe³⁺PO₄ is accompanied with a shift to higher energy of Fe-L₃ peak position of about 1.5 eV. In this study we have quantified the existence of these two lithiated and delithiated phases from the shift in Fe-L₃ peak energy, Fe L₃/L₂ peak intensity ratio and from quantification of normalized pre-O peak intensity. Measurements made from about 50 particles reveal two clusters of data with average Fe-L₃ peak energy of 708.2 eV and 709.8 eV with O pre-peak intensity ratio of 0.037 and 0.16 respectively. These two data clusters correspond to the lithiated LiFePO₄ and delithiated FePO₄ phases. The spectrum images of the lithiated LiFePO₄ and delithiated FePO₄ expressed as the normalized O pre-peak intensity are shown in Fig.2a and 2b respectively revealing uniform lithiation throughout the particles, i.e. the particles are either fully lithiated or fully delithiated in accordance with the non-equilibrium solid solution transformation path followed by relaxation. An ADF-STEM image taken from an area with many particles and the corresponding phase distribution map are shown in Fig.3a and 3b respectively, revealing a non-uniform distribution of phases with agglomeration of fully lithiated and delithiated regions that include many particles.

References

- [1] F. Omenya et al. *Adv. Energy Mater.* 4 (2014) 1401204 (9pp)
- [2] M.K. Kinyanjui et al. *J. Phys. Condens. Matter*, 22 (2010) 275501 (8pp)
- [3] Supported by NECCES a DOE-BES-EFRC funded center under Grant DE-SC0001294.

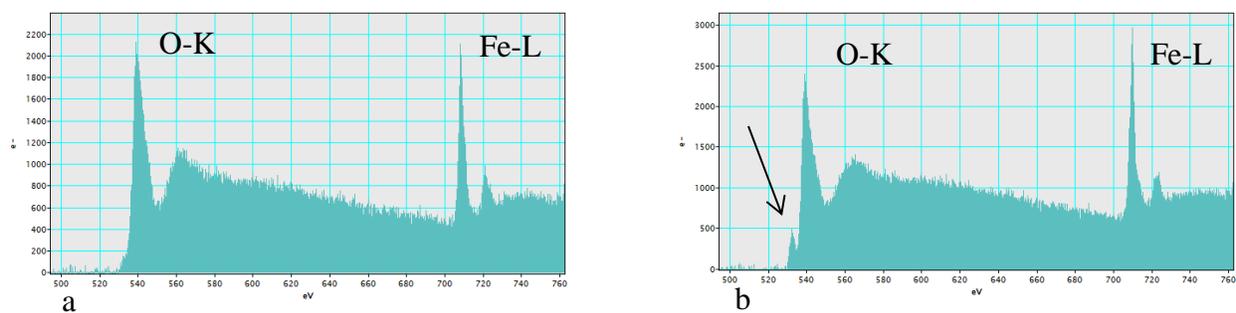


Fig. 1. EELS spectra of (a) fully lithiated LiFePO_4 and (b) fully delithiated FePO_4 showing characteristic O-K prepeak marked by an arrow.

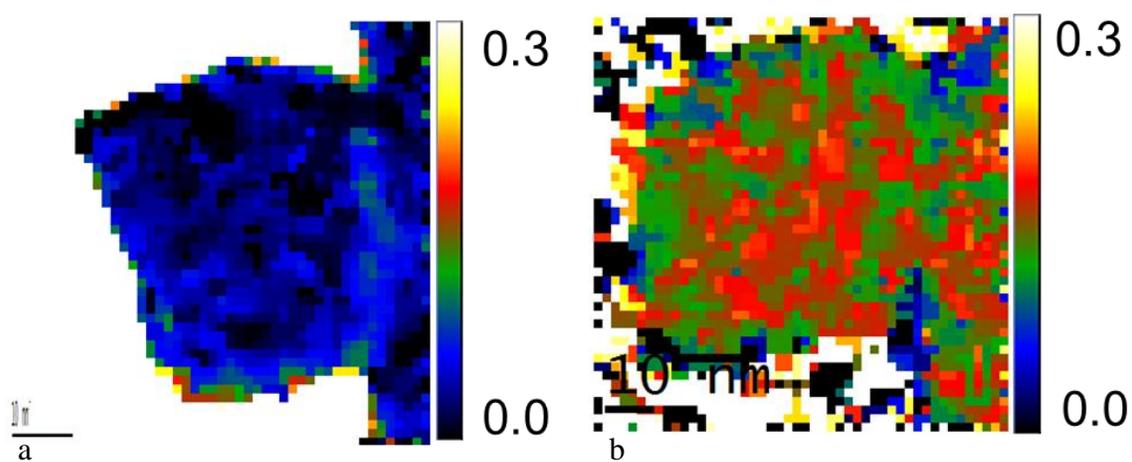


Fig.2. Normalized oxygen pre peak intensity map for (a) LiFePO_4 and (b) FePO_4

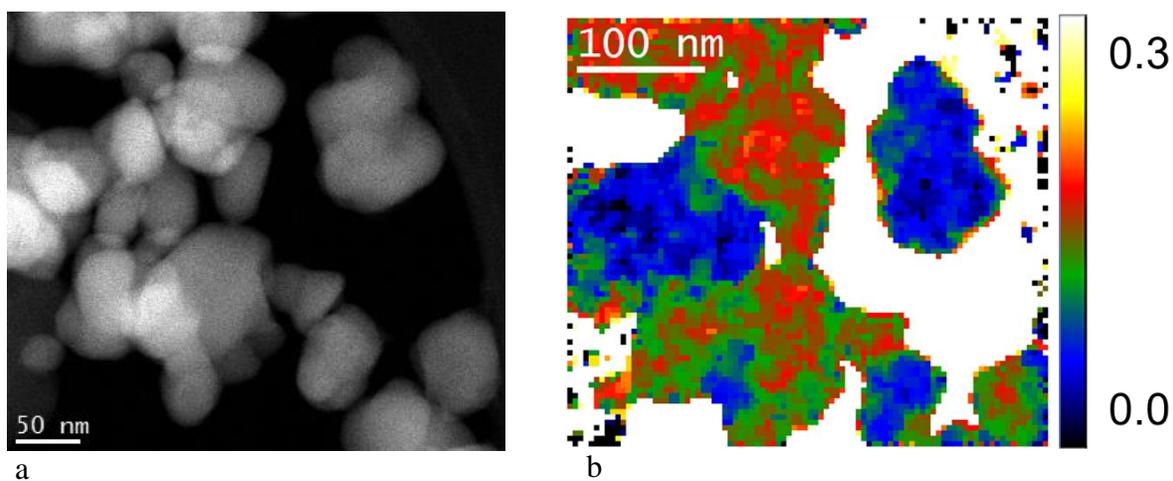


Fig.3. (a) ADF-STEM image of 50% delithiated LiFePO_4 and (b) corresponding normalized oxygen pre peak intensity map.