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EELS Analysis Of Lithiation/Delithiation Reactions In $LiFePO_4$

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$LiFePO_4$ has emerged as an important cathode material for Li-ion batteries because of it 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 $LiFePO_4$ and $FePO_4$ 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.

$LiFePO_4$ 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 0.5eV. The energy was calibrated with respect to the main O-K peak at 539 eV. Typical EELS spectrum for $LiFePO_4$ and $FePO_4$ are shown in Fig.1a and 1b respectively. A characteristic feature of delithiated $FePO_4$ 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 $LiFe^{2+}PO_4$ to $Fe^{3+}PO_4$ is accompanied with a shift to higher energy of Fe-L_3 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-L_3 peak energy, Fe L_3/L_2 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-L_3 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 $LiFePO_4$ and delithiated $FePO_4$ phases. The spectrum images of the lithiated $LiFePO_4$ and delithiated $FePO_4$ 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

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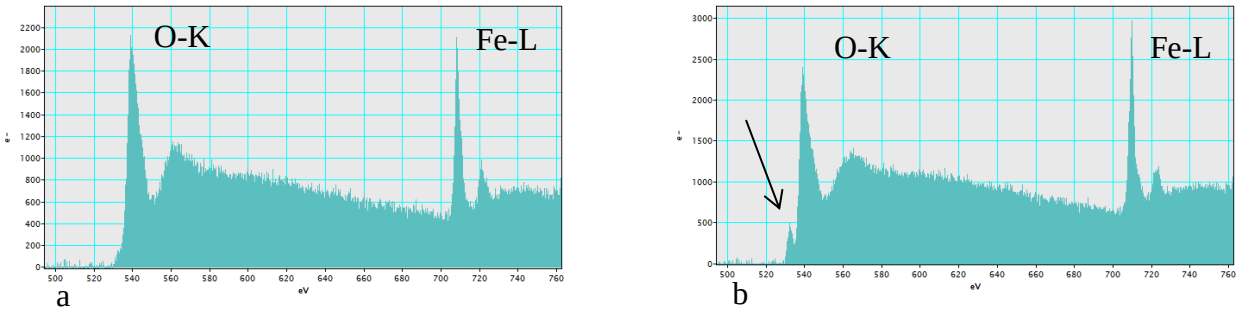

Fig. 1. EELS spectra of (a) fully lithiated LiFePO4 and (b) fully delithiated $FePO_4$ showing characteristic O-K prepeak marked by an arrow.

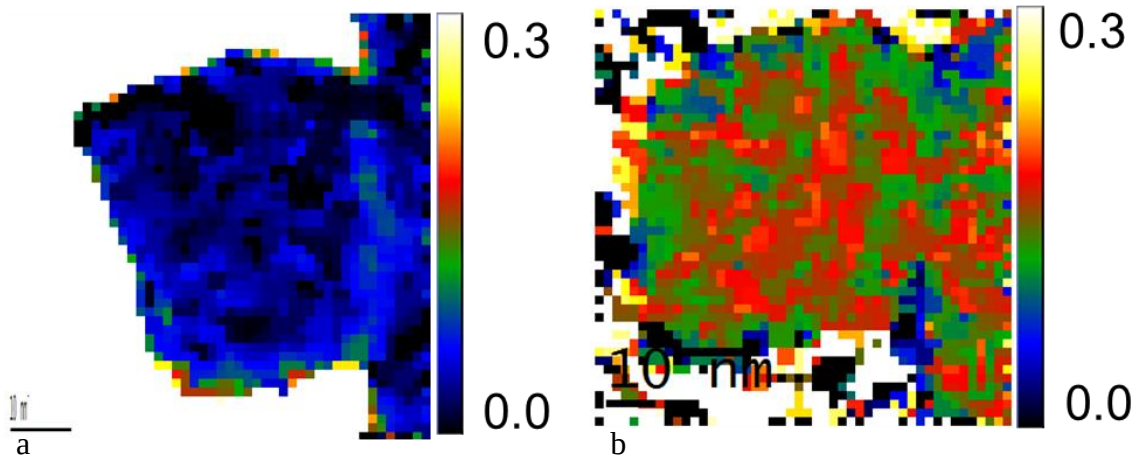

Fig.2. Normalized oxygen pre peak intensity map for (a) $LiFePO_4$ and (b) $FePO_4$

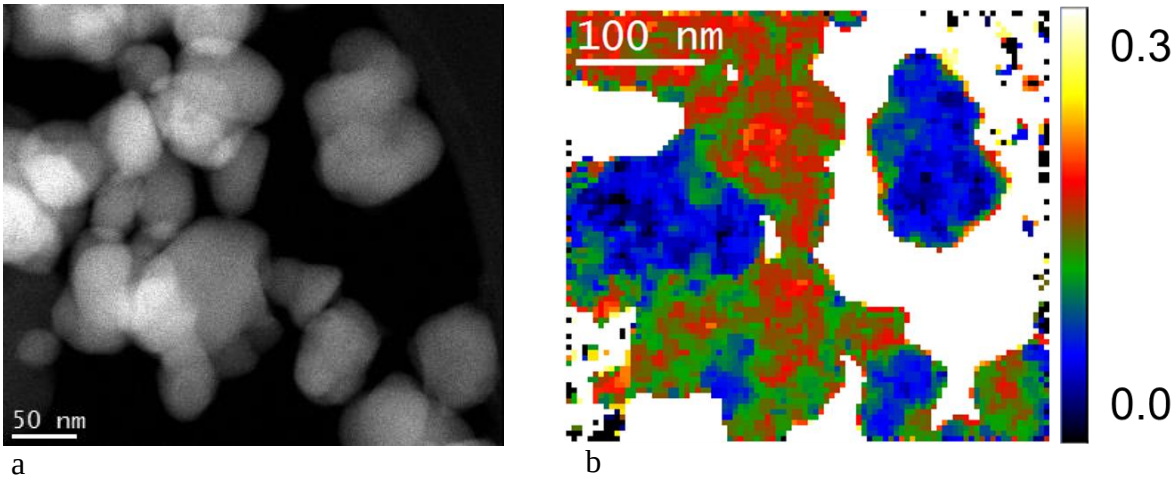

Fig.3. (a) ADF-STEM image of 50% delithiated $LiFePO_4$ and (b) corresponding normalized oxygen pre peak intensity map.

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