Microstructural change of $Li_{1-x}FePO_4$ associated with lithium intercalation studied by scanning transmission electron microscopy and spectroscopy

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$LiFePO_4$ is used as a practical active material for positive electrodes of lithium-ion secondary batteries. It shows several advantages such as low cost, excellent cycle life and safety compared to other candidate materials. Its lithium insertion/extraction proceeds via a two phase mechanism: $LiFePO_4 \Leftrightarrow FePO_4 + Li^+ + e^-$. Several models for the charge-discharge mechanism of this material have been proposed, though the Domino-cascade model [1] is now recognized as the most plausible to explain the observed experimental results. However, the path-dependence, the characteristic polarization behavior depending on the preceding charge/discharge history [2] cannot be explained by this model. In this study we re-examine the microstructure of electrochemically half charged $Li_{0.5}FePO_4$ electrodes using scanning transmission electron microscopy (STEM) and electron energy loss spectroscopy (EELS) to clarify the standing problem above.

The electrodes were fabricated by coating aluminum foils with a mixture of $LiFePO_4$ particles, carbon black and polyvinylidene difluoride binder. Lithium content of $Li_{1-x}FePO_4$ electrode was controlled electrochemically using a two-electrode cell. Thin specimens for STEM were prepared by focused ion beam. STEM-EELS spectrum imaging (SI) applied using a Jeol JEM ARM200F equipped with a GIF Quantum EELS, operated at 200 kV. O-K and Fe-$L_{2,3}$ spectra were simultaneously measured to distinguish between $LiFePO_4$ (LFP) and $FePO_4$ (FP) phase.

As shown in Figure 1 as typical examples, $Li_{0.5}FePO_4$ particles prepared by lithium extraction exhibited structure of LFP outside/FP inside. On the other hand, in Figure 2 particles set by lithium insertion show FP outside/LFP inside, contrary to the Domino-cascade model. Figure 3 shows extracted component spectra corresponding to LFP and FP, applying a multivariate curve resolution technique [3]. To clarify the phase transition mechanism, the core-shell structure of each particle was examined. Figure 4 shows the size dependence of the core/total volume ratio. From these experimental results, we assume that the reaction occurs on the surface of particles and LFP/FP interface proceeds from surface inward, and the rate of phase transition is proportional to the surface area of each particle. The theoretical prediction based on the model in plotted with the broken line in Figure 4. Assuming the shell layer to act as resistance for ion diffusion, the path-dependence can be roughly explained by the present model.

References
[1] C. Delmas, *et al.*, *Nature Materials* 7, 665 (2008).
[2] V. Srinivasan, *Electrochem. Solid-State Lett.*, 9, A110 (2006).
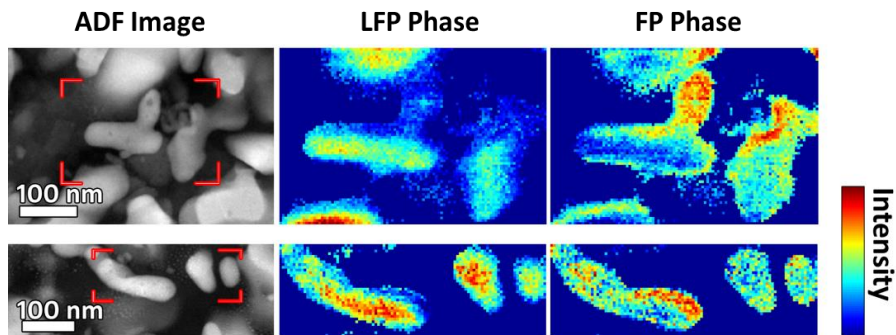[3] S. Muto, *et al.*, *Mater. Trans.* 50, 964 (2009).

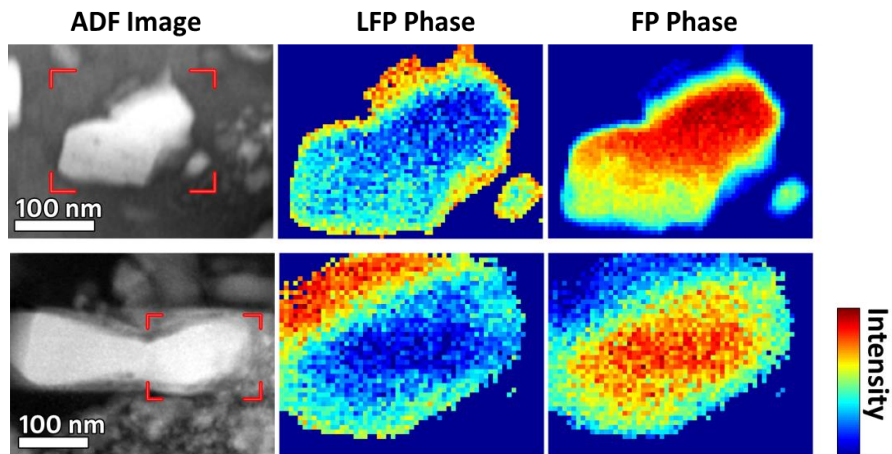Fig. 1: ADF images and spatial phase distributions of $Li_{0.5}FePO_4$ particles prepared by Li extraction

Fig. 2: ADF images and spatial phase distributions of $Li_{0.5}FePO_4$ particles prepared by Li insertion
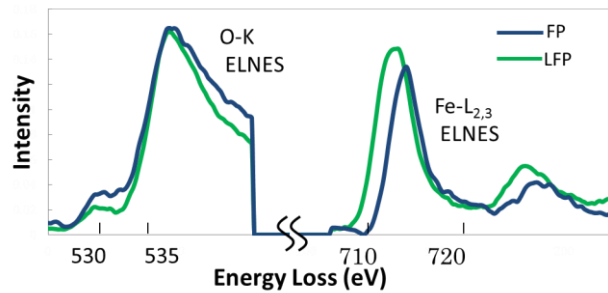

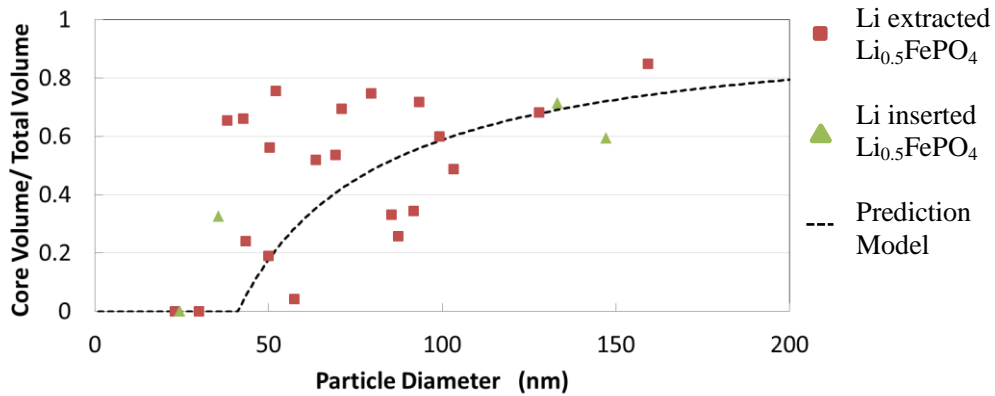Fig. 3: Extracted component spectra corresponding to LFP and FP

Fig. 4: The size dependence of the core/total volume ratio of
experimental results and the prediction model