

## ***In Situ* Electron Microscopy and Spectroscopy of Battery Materials**

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*In situ* transmission electron microscopy (TEM) studies have enormous potential for battery science. Of key importance is the lithiation mechanism of battery materials, such as LiFePO<sub>4</sub>, where the intercalation of Li<sup>+</sup> is a limiting factor in their performance [1]. To observe these electrochemical processes on the nanometer scale, we use a liquid cell TEM holder incorporating electrodes, one of which is on the viewing membrane. Valence electron energy-loss spectroscopy (EELS) is a technique to observe delithiation in the liquid cell, where options for *in situ* chemical identification are limited. We demonstrate *in situ* cycling of a LiFePO<sub>4</sub> battery and observe the lithiation and delithiation of particles of LiFePO<sub>4</sub> using energy-filtered TEM (EFTEM).

Valence EELS provides a method for chemical identification in liquid, where traditional options are limited: the X-ray detector is shadowed by the liquid cell holder, and core-loss EELS is degraded by multiple scattering events in thick layers. Valence EELS, however, is feasible in layers as thick as ~6 inelastic mean free paths because there is little lower-energy plural scattering. Another advantage to valence EELS is that many liquids have large optical gaps, while chemically active particles tend to exhibit strong excitations at lower energies. Thus low-energy particle excitations can be observed with a low background from the liquid [2].

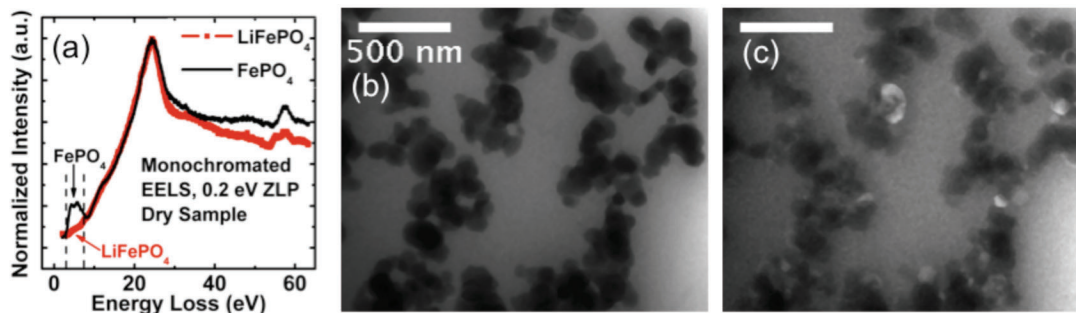
We study the Li-ion battery material LiFePO<sub>4</sub> in 0.5 M Li<sub>2</sub>SO<sub>4</sub> aqueous solution by valence EFTEM in a monochromated FEI Tecnai F20, which enables rapid (~1s) spectroscopic mapping. When LiFePO<sub>4</sub> is delithiated to FePO<sub>4</sub>, a strong 5 eV energy transition appears in EELS that is not present in the lithiated state [3], (Fig. 1(a)). Thus we can observe the FePO<sub>4</sub> using the 5 eV signal in EFTEM, as highlighted in Fig. 1(a). At 0 eV, in Fig. 1(b), the predominantly elastic signal is dominated by the liquid. However, in the optical gap of the liquid in Fig. 1(c), the 5 eV image shows the delithiated particles exhibiting strong transitions.

*In situ* valence EFTEM can correlate the state of lithiation with the voltage cycling data, performed in an activated carbon (AC)/Li<sub>2</sub>SO<sub>4</sub>/LiFePO<sub>4</sub> aqueous Li-ion *in situ* battery. We reference the voltage to the AC anode, so between 0 and 1 V (de)intercalation of Li<sup>+</sup> should occur. During cycling, the 5 eV spectroscopic images are acquired. In (Fig. 2a) we show the average of six denoised 5 eV images at low potential (a1, a3, a5) and high potential (a2, a4, a6). We observe more bright spots of FePO<sub>4</sub> at high potentials, corresponding to delithiation. Fig. 2b shows the current profile at ±10 nA, corresponding to ~10C. Fig. 2c shows the voltage profile.

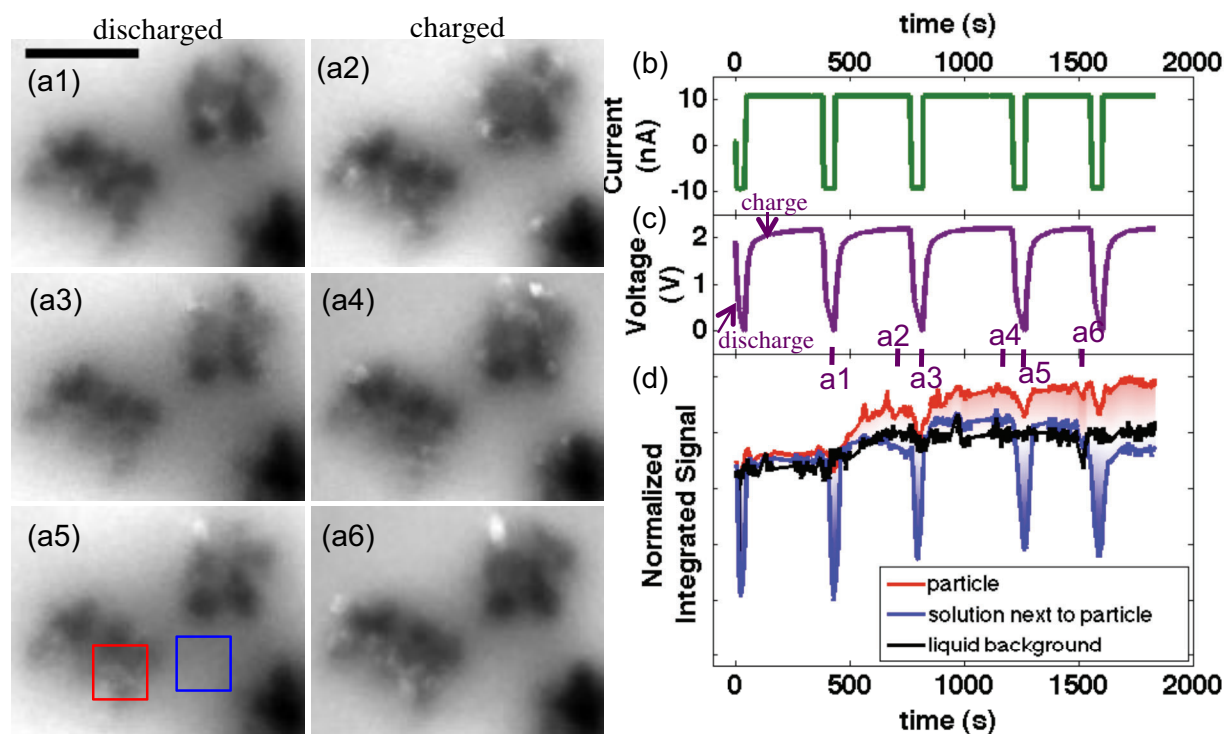
To understand the 5 eV intensity changes during voltage cycling, integrated signal over three regions as shown in Fig. 2(d). The intensity of the solution distant from the particles is relatively constant, while the intensity of the solution next to the particles (location shown by blue box in (a5)) drops during discharge. This may reflect the conversion of solution Li<sub>2</sub>SO<sub>4</sub> to bisulfate as Li<sup>+</sup> is removed from solution. Additionally, the intensity from the particles (location shown by the red box in (a5)) rises during charge, indicating an increase in FePO<sub>4</sub>, and drops during discharge. The changes in contrast are correlated with the cycling and are reversible, while radiation damage effects are expected to be irreversible. Since we see individual particles lithiating one at a time, this *in situ* spectroscopic analysis suggests lithiation in LiFePO<sub>4</sub> follows the domino cascade model. [5]

## References

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**Figure 1.** (a) Monochromated EELS of  $\text{LiFePO}_4$  and  $\text{FePO}_4$  shows a 5 eV peak for  $\text{FePO}_4$  that is not present in  $\text{LiFePO}_4$ . EFTEM of the particles in aqueous solution with a 5 eV energy slit around: (b) 0 eV where the liquid dominates the signal and (c) 5 eV in the optical gap of the liquid highlighting the  $\text{FePO}_4$  transitions, selecting the peak between the arrows in (a).



**Figure 2.** *In situ* EFTEM cycling of the battery cathode material  $\text{LiFePO}_4$ . In (a) the 5 eV images of charging and discharging are shown with a 400 nm scale bar, corresponding to times marked in (c). Bright regions are delithiated  $\text{FePO}_4$  and dark regions are  $\text{LiFePO}_4$ . There are more bright regions of  $\text{FePO}_4$  at the end of charge cycles and less during the discharges. (b-c) show the current-voltage profile. (d) shows the integrated intensity over various regions, tracking with the voltage profile, from the regions shown by the boxes in (a5).