Time-Resolved Chemical Mapping of Phase Transformations in Li-ion Battery Electrodes

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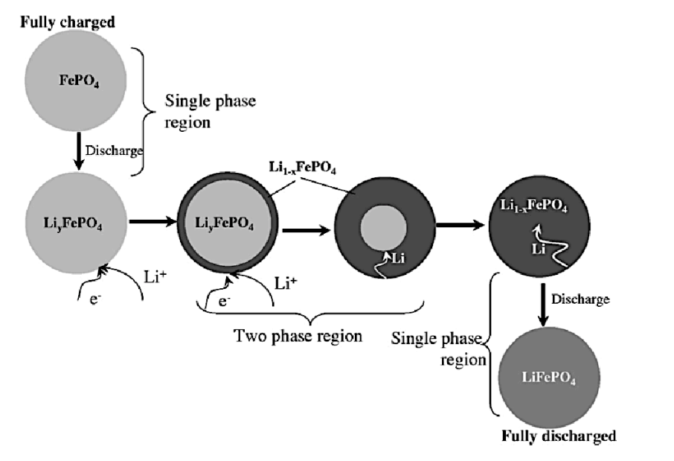
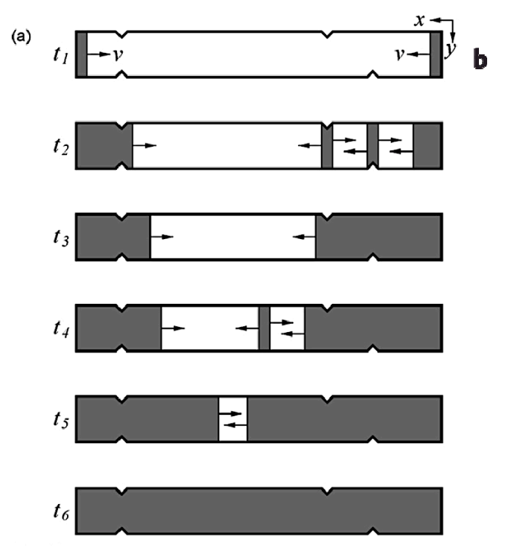
Problem

Understanding the Li intercalation pathway in Li-ion battery electrode materials is of crucial technological importance. The mechanisms governing the dynamics of Li transport directly determine the current density, charge/discharge rate and efficiency of the cathode. An intimate understanding of these mechanisms gives us the opportunity to enhance them by engineering optimized microstructures.

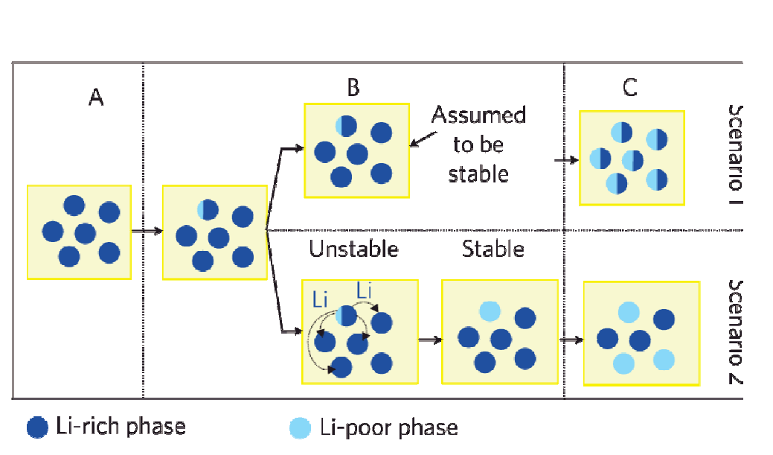
$\mathrm{Li_xFePO_4}$ ($0 \leq x \leq 1$) is one of the most promising positive battery electrode materials. It undergoes a first-order phase transformation at well known compositions when Li is added or removed. There have been many proposed mechanisms for this phase transformation in the literature (shown below).



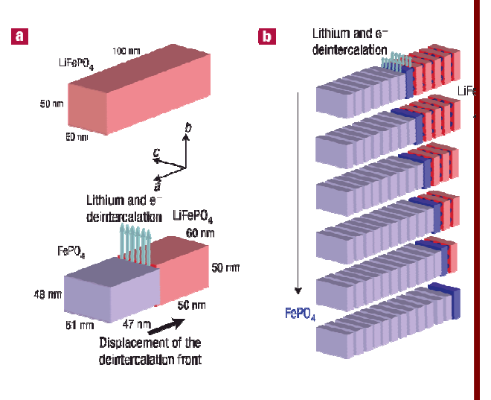
Shrinking Core Model[1,2]



Phase Transformation Waves[3]



The Mosaic Model[4,5,6]



Domino-Cascade Model[7]

[1] A.K. Padhi, et al., J Electrochem Soc 144 (1997)
[2] V. Srinivasan, et al., J Electrochem Soc 151 (2004)
[3] G.K. Singh, et al., Electrochim Acta 53 (2008)
[4] A.S. Andersson, et al., J Power Sources 97-8 (2001)
[5] W. Dreyer, et al., Nat Mater 9 (2010)
[6] R. Malik, et al., Nat Mater 10 (2011) 587
[7] C. Delmas, et al., Nat Mater 7 (2008)

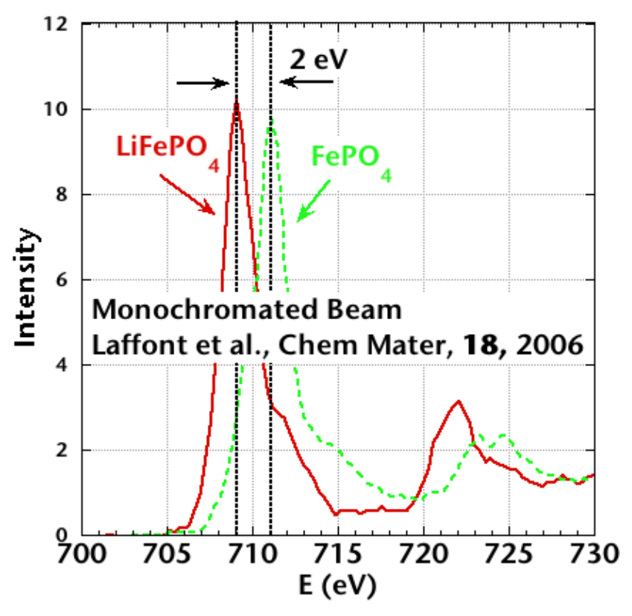
Answering how the phase transformation occurs requires measuring the Li content across the entire cross-section of the electrode particle by particle. There are two major challenges is making such a measurement:

1. How to section an electrode so that its particles are not rearranged and it is thin enough for electron microscopy?
2. How to perform high spatial resolution electron spectroscopy and prevent electron beam damage from changing the sample during the observation?

Approach

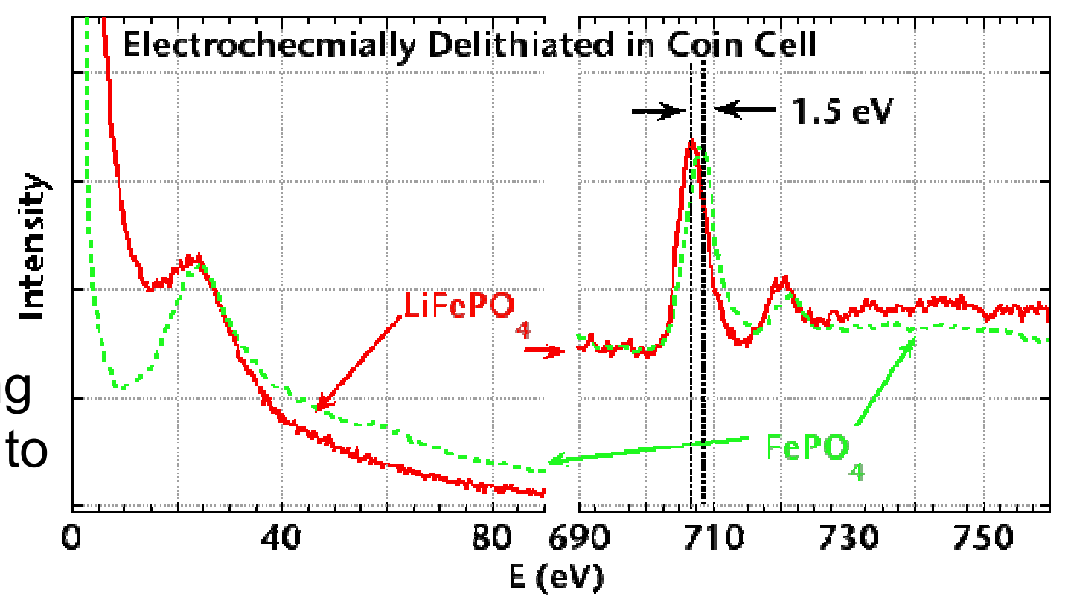
We developed two new capabilities in response to the questions above.

1. An ultramicrotome technique for making thin electrode cross sections that span the entire electrode.
2. A quantitative TEM-based spectroscopy approach to measure the Fe oxidation state in $\mathrm{Fe^{3+}PO_4}$ and and $\mathrm{LiFe^{2+}PO_4}$ without electron beam damage.

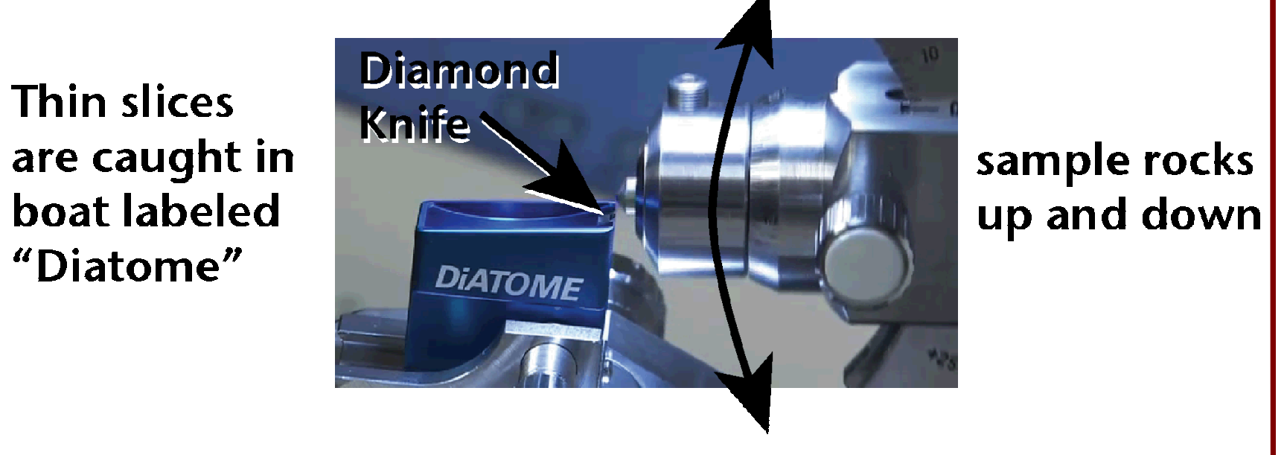


(Left): EELS spectrum of $\mathrm{LiFePO_4}$ and $\mathrm{FePO_4}$ showing shift of Fe L23 edge when Fe changes oxidation state.

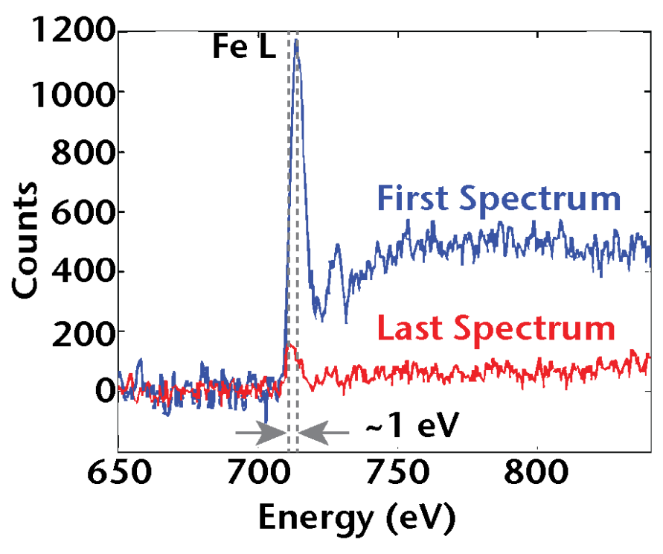
(Right): EELS spectrum showing monochromator is not required to observe the Fe L23 shift.

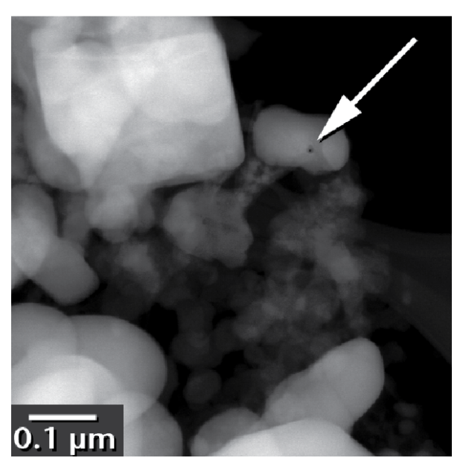


Sample Preparation:
We thin sections of electrodes from disassembled operational batteries using the ultramicrotome. This keeps the electrode microstructure intact, does not cause artifacts or damage, and produces a sample appropriately thin for TEM and EELS.

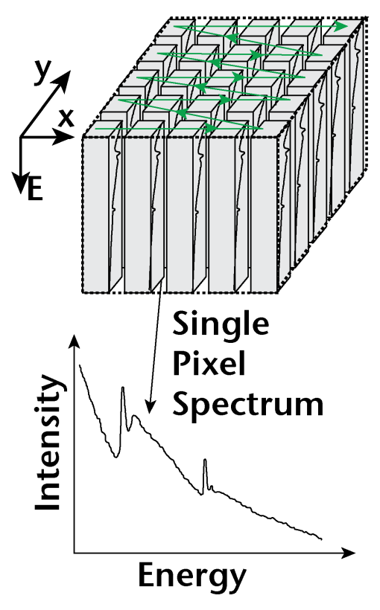


Data Collection:
The electron beam can change the sample. We show on the right that in $\mathrm{FePO_4}$, the electron beam removes material (arrow) and changes the oxidation state of the Fe after 50 sec of exposure. Therefore we will use a technique that uses a parallel electron beam (energy-filtered TEM) rather than a focused one to slow the damage process.

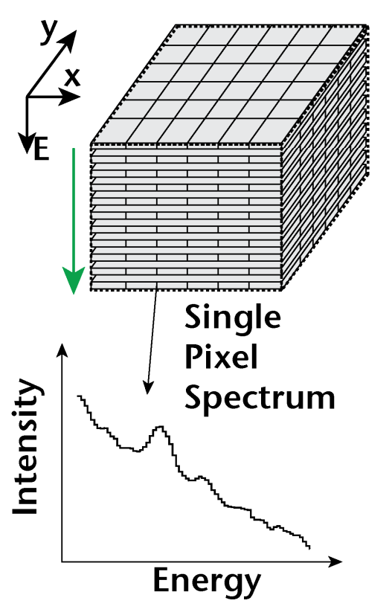




STEM-EELS:
Parallel energy, serial spatial data collection. Beam damage occurs.



EFTEM-SI:
Serial energy, parallel spatial data collection. Beam damage does not occur. Correct for spatial drift & non-isochromaticity

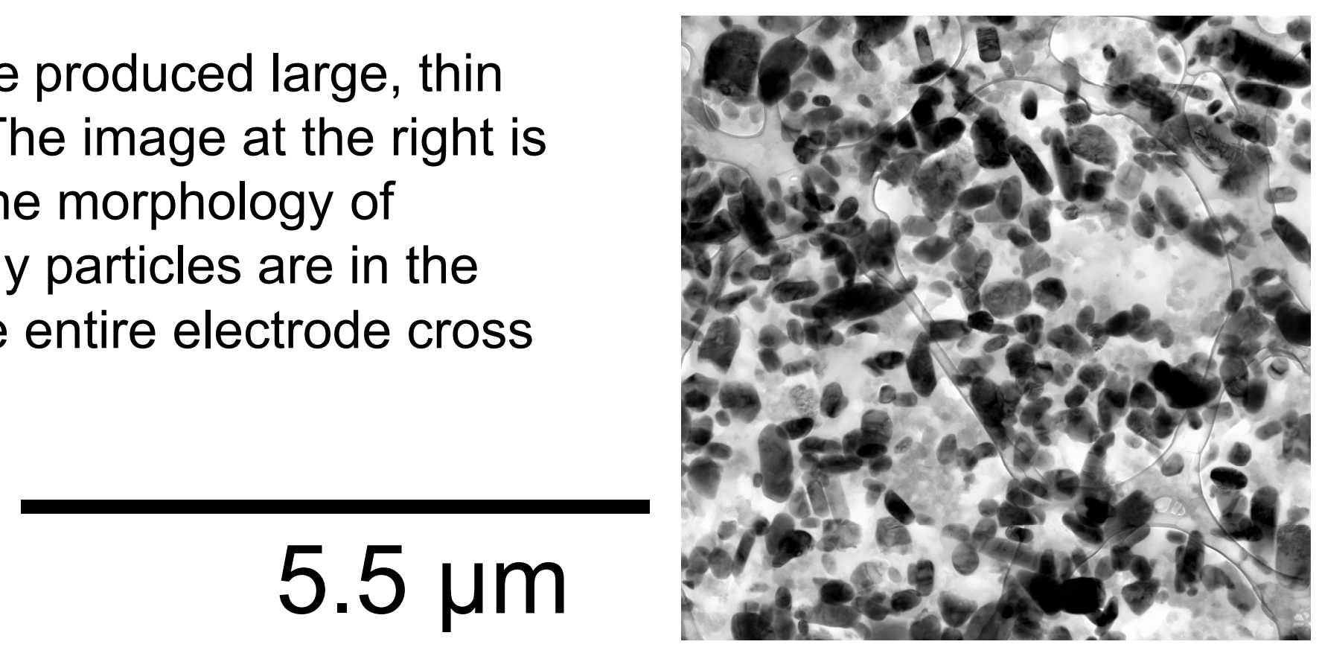


Data Processing:
The small shifts in energy of the Fe L23 edge are detected with the use of Multivariate Statistical Analysis (MSA) software developed at Sandia[8-11].

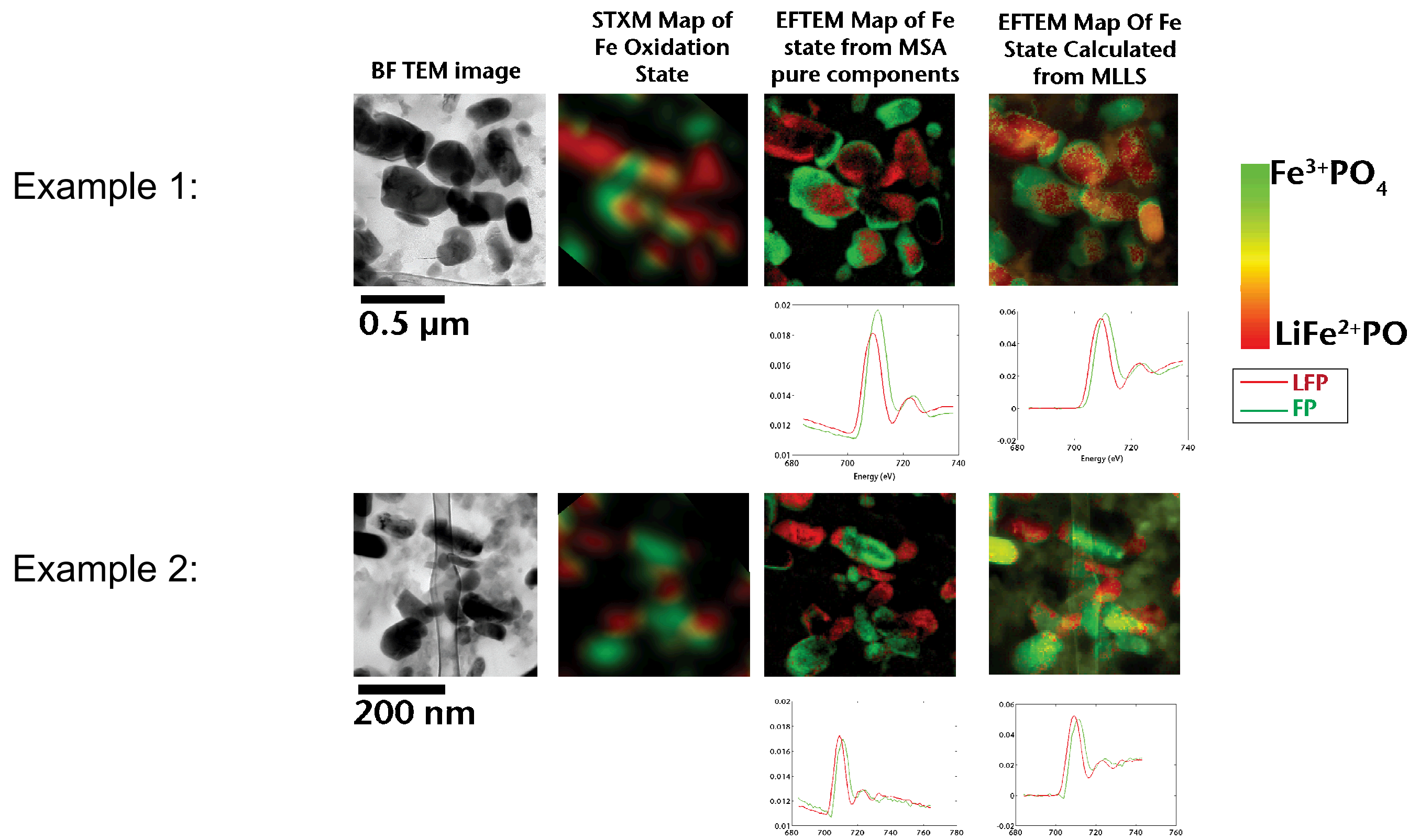
[8] M.R. Keenan, Surface and Interface Analysis 41 (2009)
[9] M.R. Keenan, et al., Surface and Interface Analysis 36 (2004)
[10] P.G. Kotula, et al., Microscopy and Microanalysis 12 (2006)
[11] P.G. Kotula, et al., Microscopy and Microanalysis 9 (2003)

Results

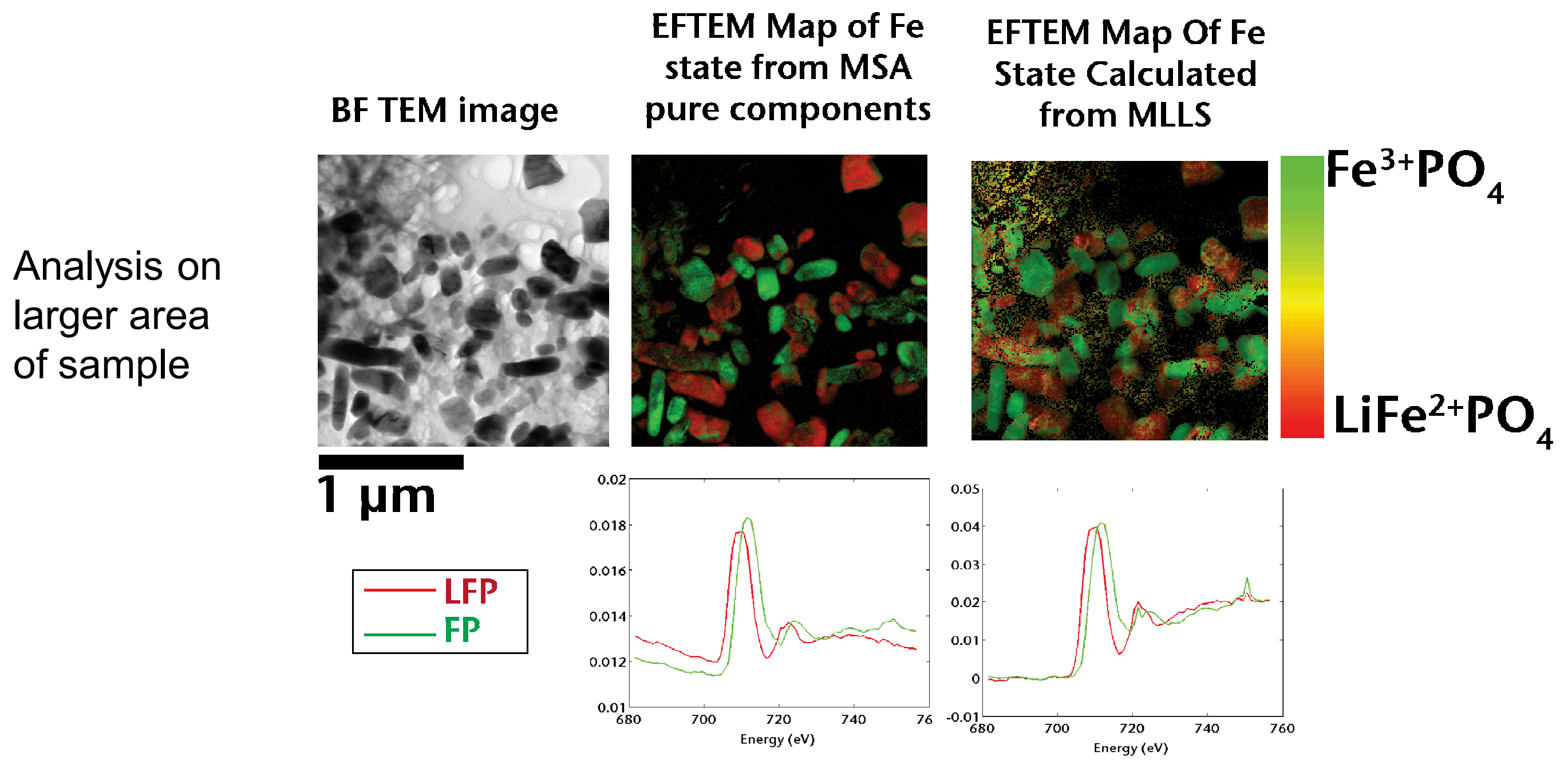
Sample preparation using the ultramicrotome produced large, thin electrode areas for spectroscopic analysis. The image at the right is an example of ultramicrotomed electrode. The morphology of individual particles is readily visible and many particles are in the field of view. The thin area extends along the entire electrode cross section (too large to show here).



We compared our EFTEM-SI based measurements to data collected from a synchrotron-based scanning transmission x-ray microscope (STXM). The two measurements agreed well, which validated our EFTEM-based approach. In the figures below we show that the MSA output finds two pure spectral components with a ~1.5 eV shift in the position of the Fe L23 edge. These components correspond to the pure $\mathrm{LiFe^{2+}PO^4}$ and $\mathrm{Fe^{3+}PO_4}$ phases. We also show references used for a multiple least squares (MLLS) fitting of the data. This creates composite maps that are yellow when the two phases mix and give a direct comparison to the STXM data.



When a large number of particles are investigated we find that only 2% of them are a mixture of the $\mathrm{LiFePO_4}$ and $\mathrm{FePO_4}$ phases. The mixed (yellow) areas in the map are more commonly caused by the overlap of multiple particles in the viewing direction or non-linear thickness effects. Our data confirms the proposed mosaic model for the transformation route.



Significance

- We developed a technique for cross-sectioning battery electrodes using the ultramicrotome that does not introduce artifacts (e.g. the FIB damages the sample).
- We developed a quantitative TEM-based spectroscopy technique for measuring Fe oxidation state with none of the beam damage artifacts introduced by other TEM techniques.
- The charge/discharge reaction depends entirely on the nucleation rate of the phase transformation. After nucleation, the rate at which an individual particle transforms is irrelevant.
- Our experiments led us to develop a simple model for nucleation-limited charge/discharge transformation kinetics. The results show us that measurements of nucleation rate with time would allow us to determine the overpotential (b) at different states of charge. Ultimately this information could be used to optimize the performance of a battery.

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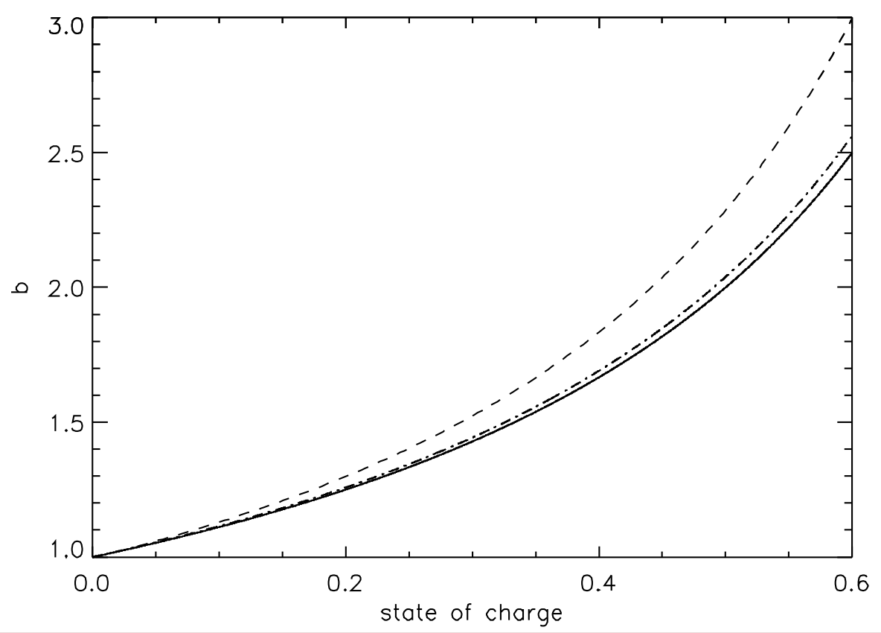
References:
Chueh et al., "Intercalation Pathway in Many-Particle $\mathrm{LiFePO_4}$ Electrode Revealed by Nanoscale State-of-Charge Mapping." *Nano Letters,* 2012 submitted.
Sugar et al., "Fe Oxidation State Mapping in $\mathrm{LiFePO_4}$ Battery Electrodes using EFTEM Spectrum Imaging," In progress, 2012.



Solid line: Constant nucleation rate

Dashed line: Nucleation rate is proportional to surface area. Larger particles transform first.

Dot-Dashed line: Small particles transform twice as often as large ones.

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