

## Nanoscale Fe State-of-Charge Mapping in $\text{LiFePO}_4$ : A Comparison of EFTEM and STXM Spectrum Imaging.

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Modern electrodes of Li-ion batteries have composite microstructures. The active material is in the form of particles 10–1000 nm in diameter. The mechanism of the intercalation reaction in  $\text{LiFePO}_4$  particles, an active electrode material, is an open subject of debate. In principle, one way to determine the mechanism would be to perform forensic analysis on electrochemically cycled particles and map the distribution of Li. This, however, is difficult because Li is a light element and conventional x-ray microanalysis will not work. Furthermore, the K-shell absorption edge for Li overlaps with the M edge of many transition metals used in conventional electrode materials, which complicates the ability to map Li using EELS. Several developments in electron microscopy-based techniques have enabled mapping the spatial distribution of Li. These include STEM-EELS, electron diffraction, low-loss EELS, annular bright-field imaging, etc. [1-4]. Here, we will show a parallel-beam based technique that utilizes energy-filtered TEM to map the Fe state of charge and exhibits reduced beam damage artifacts compared to STEM.

We will compare a number of different sample preparation techniques and show that ultramicrotomy results in uniformly thin samples that span the entire width of the electrode and enable particle-by-particle analysis. EFTEM data can be processed using multivariate statistical analysis routines and multiple-least squares fitting to map the Fe state of charge in electrochemically cycled particles. Furthermore, we will compare our results to Scanning Transmission X-ray Microscopy (STXM) data acquired at the Advanced Light Source and show that they are consistent. After analyzing over 400 particles, a simple phenomenological model is developed that is consistent with the data. In this model, the phase transformation of  $\text{LiFePO}_4$  to  $\text{FePO}_4$  during electrochemical cycling of  $\text{LiFePO}_4$  electrodes is nucleation limited. Therefore, improvements in charge/discharge rate require an increase in the nucleation rate of the electrochemically driven phase transformation.

[1] P. Moreau, *Appl Phys Lett* **94** (2009)

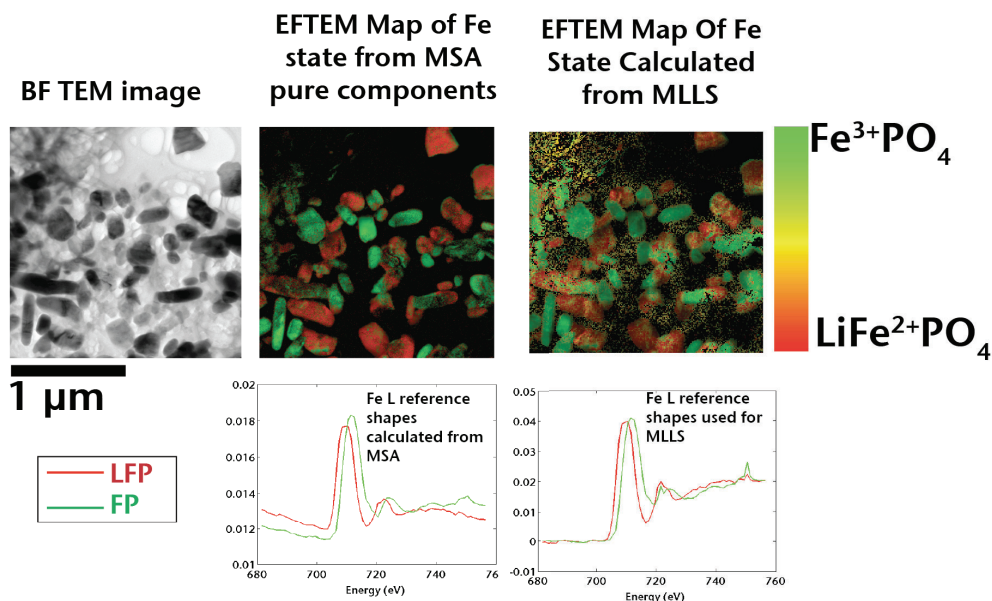
[2] L. Laffont, et al., *Chem Mater* **18** (2006)

[3] L. Gu, et al., *J Am Chem Soc* **133** (2011)

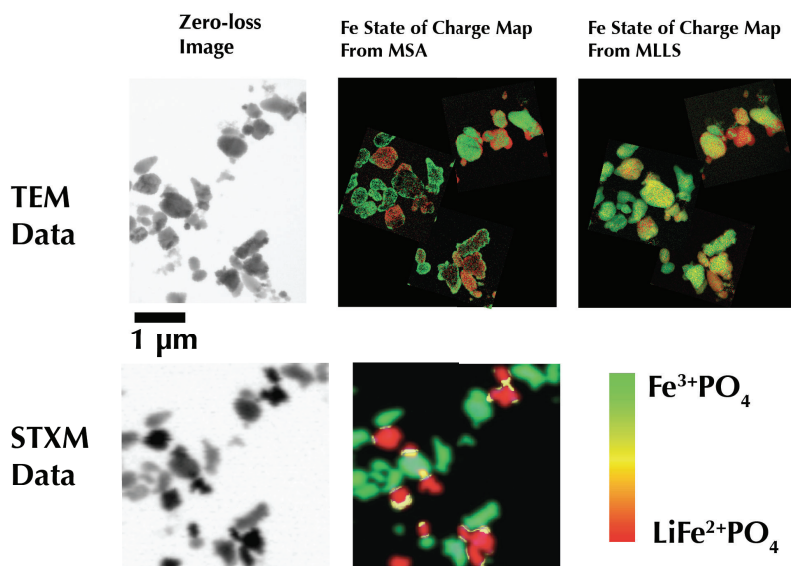
[4] G. Brunetti, et al., *Chem Mater* **23** (2011)

[5] Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

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**Figure 1.** Fe state of charge map in an ultramicrotomed section calculated from EFTEM spectrum image data. The particles imaged were electrochemically charged to a 50% state-of-charge. The particles have the same microstructural arrangement as in the functional battery. The map shows that the particles are generally either completely charged ( $\text{FePO}_4$ ) or completely discharged ( $\text{LiFePO}_4$ ), and rarely exhibit a mixed Fe valence within one particle. The state of charge maps are calculated and shown both using multiple statistical analysis (MSA) techniques and multiple least squares fitting (MLLS).



**Figure 2.** A comparison of Fe state of charge maps calculated from EFTEM spectrum image data and STXM. This data is for electrochemically cycled  $\text{LiFePO}_4$  particles suspended on a  $\text{Si}_3\text{N}_4$  window. The techniques two are in generally good agreement as shown by the relative similar distribution of red (2+) and green (3+) Fe valence. The center of the particles shows ambiguous mixed valence due to non-linear thickness effects in the EELS spectra. This ambiguity is reduced when samples are produced using ultramicrotomy as in Figure 1.