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MICROSCOPY & MICROANALYSIS 2011
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Imaging Li Using EFTEM Spectrum Imaging and Multivariate Statistical Analysis

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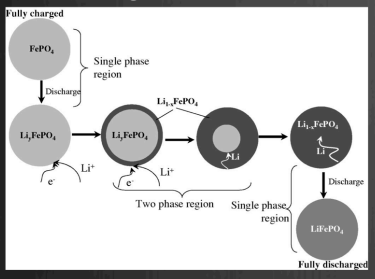
  - F. El Gabaly Marquez, A. McDaniel, K. McCarty: Sandia National Labs, Livermore, CA
  - T. Tyliszczak: Advanced Light Source, LBNL, Berkeley, CA
- EFTEM Spatial Drift Correction Script
  - B. Schaffer: SuperSTEM, Daresbury UK
  - B. Schaffer, W. Grogger, & G. Kothleitner, Ultramicroscopy, **102**, 2004
- Protochips In Situ TEM holder and E-chips
  - Ben Jacobs, Steven Mick, John Damiano, Steve Shannon: Protochips, Inc., Raleigh, NC

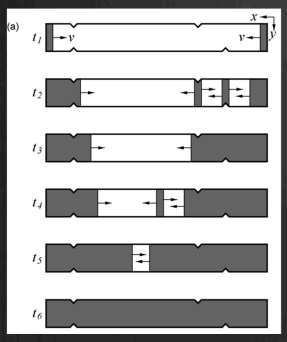
What is the Phase Transformation Mechanism?

Shrinking Core/Core-Shell



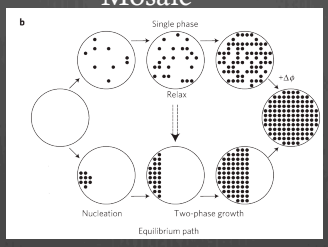
Srinivasan et al., JECS, **151**, 2004
Padhi et al., JECS, **144**, 1997

Phase-transformation Waves

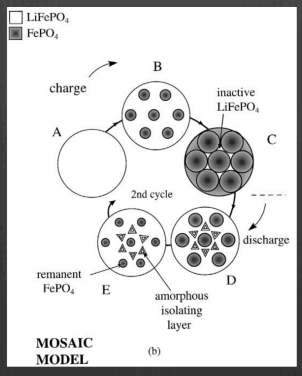


Singh et al., Electr Acta, **5,3** 2008

Mosaic

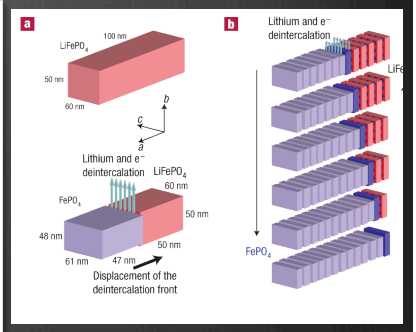


Malik et al., Nat Mat, **10**, 2011



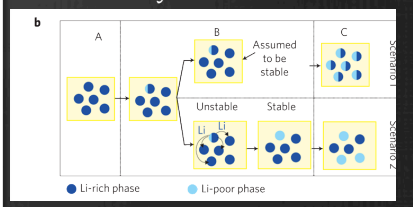
Andersson et al., J Pow Sources, **97-98**, 2001

Domino-Cascade



Delmas et al., Nat Mat, **7**, 2008

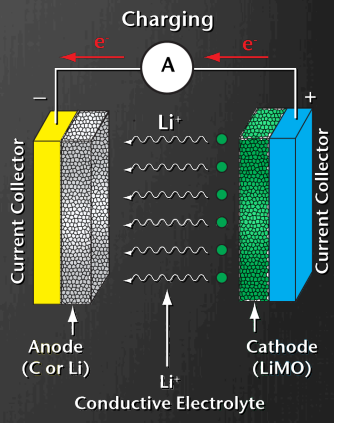
Many-Particle

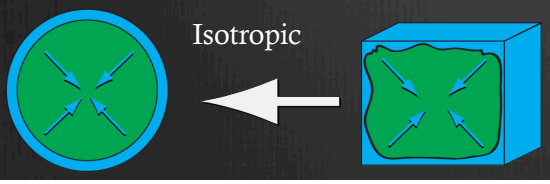


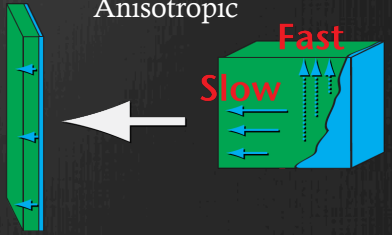
Dreyer et al., Nat Mat, **9**, 2010

Phase Transformations are Critical to Battery Performance

- Li-ion battery performance depends critically on
  - Electron transport properties
  - Ionic transport properties
  - Phase transformation kinetics
    - $xLi+BX \rightarrow Li_xBX$
    - Power Density
    - Charge/Discharge rates
    - Failure mechanisms (e.g. mismatch at interface)
- Understanding mechanism of phase transformation guides optimized microstructural engineering

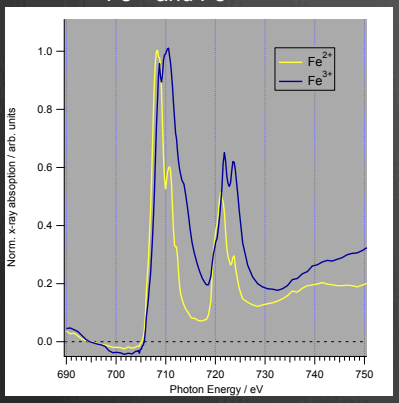




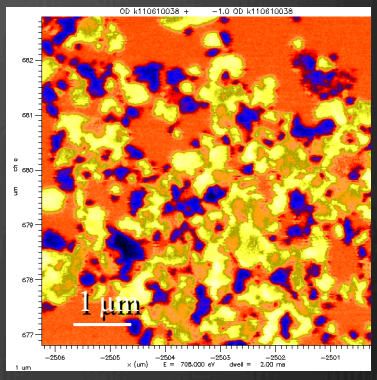


What is the Phase Transformation Mechanism?

X-ray absorption near-edge spectra distinguish Fe^{2+} and Fe^{3+}



$LiFePO_4$ nanoparticles from a 10%-charged commercial battery cathode

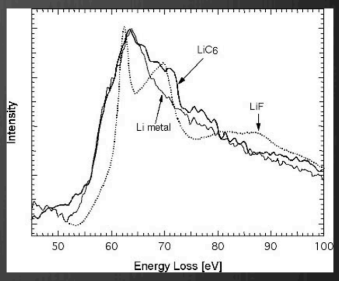


Chueh, Lai et al., 2011

Need higher spatial resolution: TEM

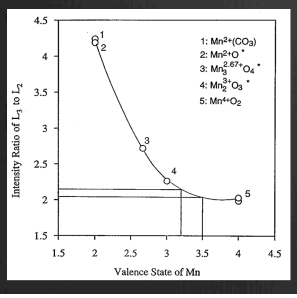
Direct Observation of Li Front During Transformation

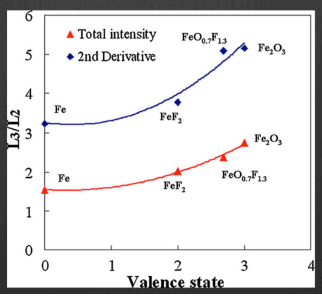
- Low-loss region of EELS spectrum
  - Li K-edge at 55 eV
  - Plasmon peak overlap
  - M-edge overlap Mn (49 eV) and Fe (54 eV)

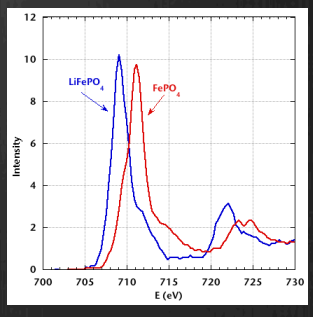


Okamoto et al., 2005

- Core-loss region
  - ELNES can be used to measure valence of transition metals
    - Mn: Wang et al., APL, **70**, 1997
    - Fe: Cosandey et al., Micron, 2011; Laffont et al., Chem Mater, **18,** 2006







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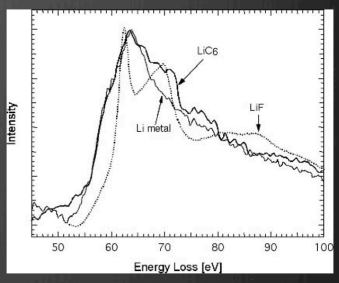
  - Li distribution is inferred
    - $Li^{+}Fe^{2+}PO_4^{3-} \rightarrow Li^{+} + e^{-} + Fe^{3+}PO_4^{3-}$
    - $Li^{+}Mn_2^{3.5+}O_4^{2-} \rightarrow Li^{+} + e^{-} + 2Mn^{4+}O_2^{2-}$



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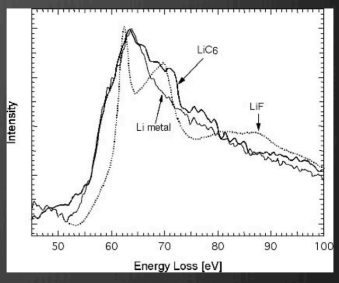
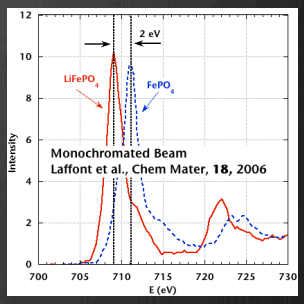
  - Combine both regions and look for correlations using multivariate statistical analysis (MSA) routines



Okamoto et al., 2005

Reference Spectra for Pure States

- $LiFePO_4$ purchased from MTI Xtal
  - Chemically delithiated/oxidized by soaking in NO_2BF_4 for 3 days in glove box



- Electrochemically charged $LiFePO_4/FePO_4$

Electrochemical cycling performed by W. Lai MSU

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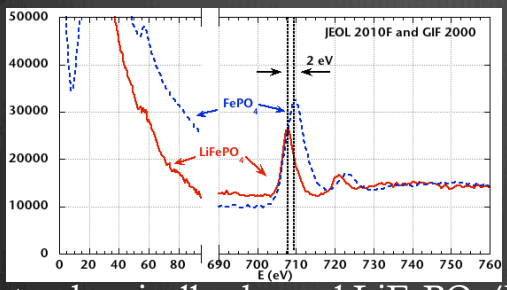

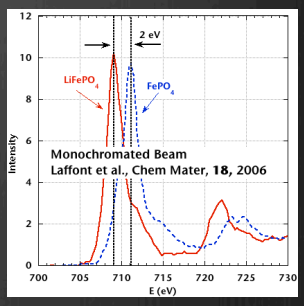

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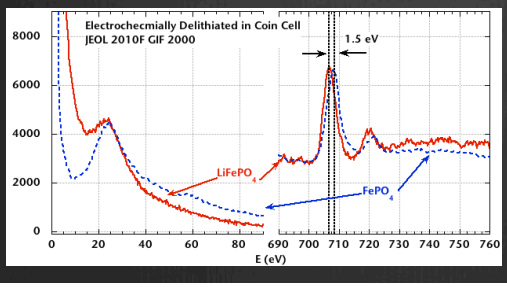
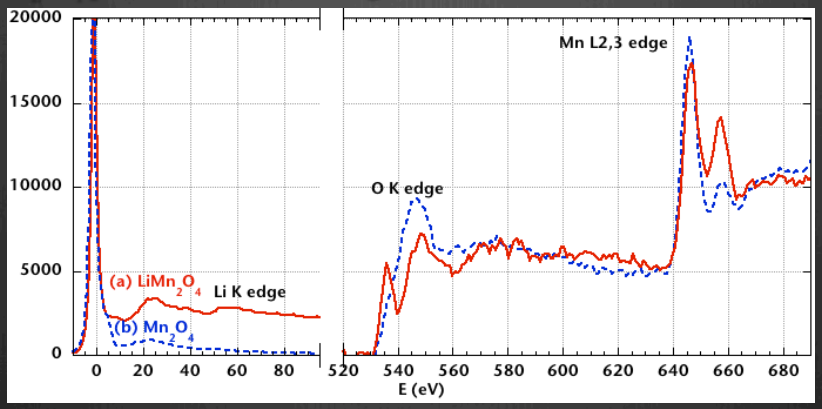


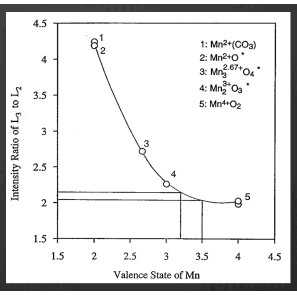
Electrochemical cycling performed by W. Lai MSU

Reference Spectra for Pure States

- $LiMn_2O_4$ purchased from Sigma Aldrich and soaked in NO_2BF_4



- Double-Step BG subtraction Pearson et al., PRB, **47** 1993
  - $LiMn_2O_4$: L3/L2=2.15 ($Mn^{3.5+}$)
  - Mn2O4: L3/L2=5.69 (Mn^{4+})?
- Oxidized L3/L2 ratio is larger but it should be smaller

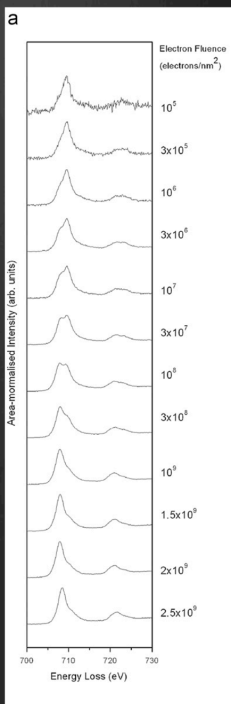


Wang et al., APL, **70**, 1997

Electron Beam-Induced Reduction

- Beam-induced reduction of Fe^{3+} has been observed in $FePO_4 \cdot 2H_2O$
  - Pan et al., Ultramicroscopy, **110**, 2010
- STEM-EELS spectrum image
  - 1 s/pixel
  - 50 pixels
  - 30 µm condenser aperture
  - 1 nm spot size

Increasing electron fluence (e/nm²)



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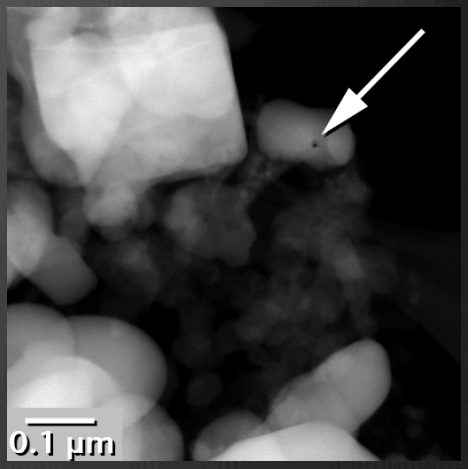
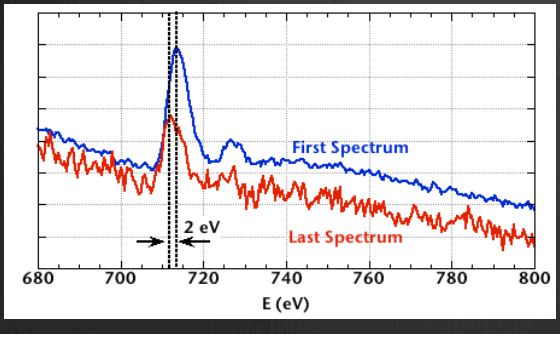
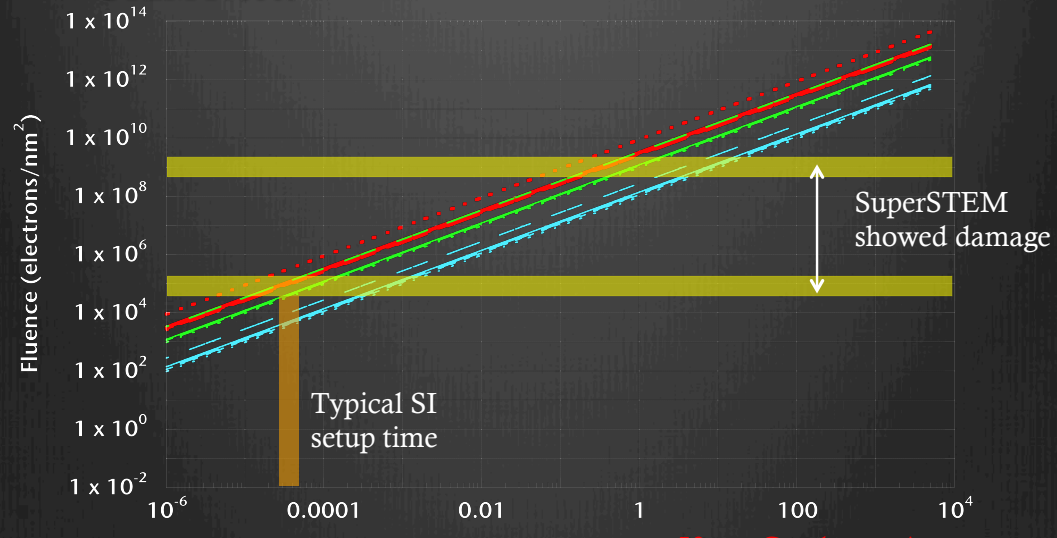




Electron Beam-Induced Reduction

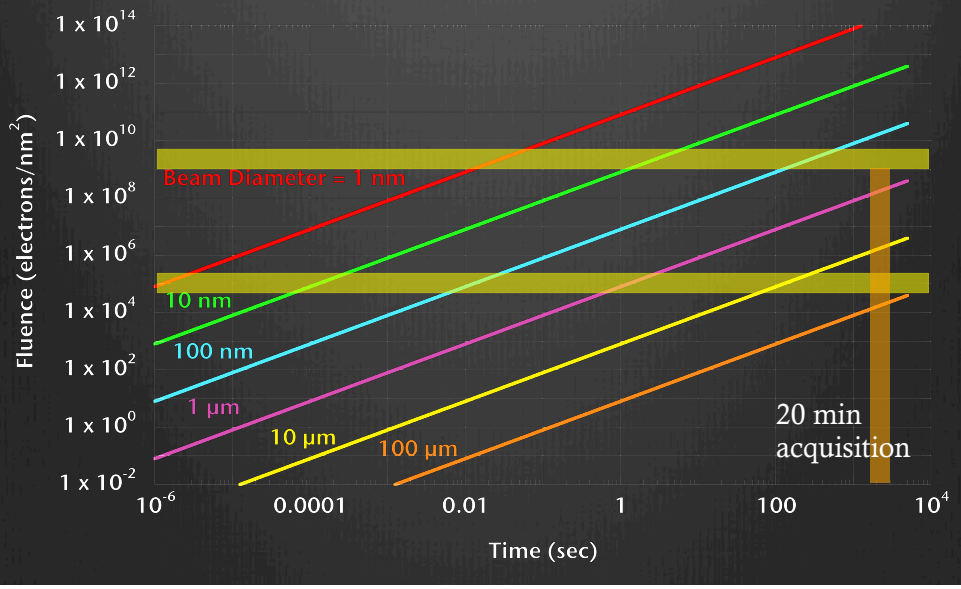
- Measured beam current with Gatan 646 holder Faraday cup
  - STEM Probes



1.6 nm, 1.3 nm, 1.0 nm, 0.7 nm, 0.5 nm, 0.2 nm probes

Electron Beam-Induced Reduction

- Measured beam current with Gatan 646 holder Faraday cup
  - STEM Probes
  - CTEM/EFTEM



Is EFTEM Sensitive Enough?

- Scraped powder from a coin cell electrode charged to 90%
  - 90% $FePO_4$
  - 10% $LiFePO_4$

730 eV image
5 eV slit

- EFTEM SI
  - 5 eV slit; [680:780]
  - SDSD drift corrected
    - B. Schaeffer et al., Ultramicroscopy, 102, 2004
  - AXSIA eigenanalysis and MCR-ALS
    - P. Kotula et al., Micros & Microa, **9**, 2003
    - P. Kotula et al., Micros & Microa, **12** 2006
  - Varimax rotated spatial simplicity
    - M. Keenan, Surf and Int Anal, **41**, 2009
  - No weighting (artifacts)
    - Electron/photon relationship
    - Dark current drift
    - Non-linear thickness (>0.5 t/ λ) effects

Wed 2-2:15 A06B P. Kotula Multivariate Statistical Analysis Strategies of EELS Spectral Images

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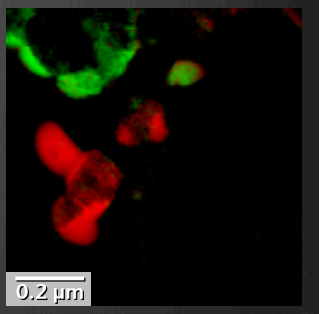
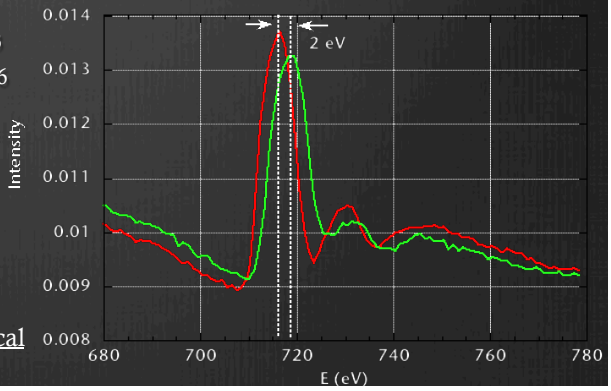
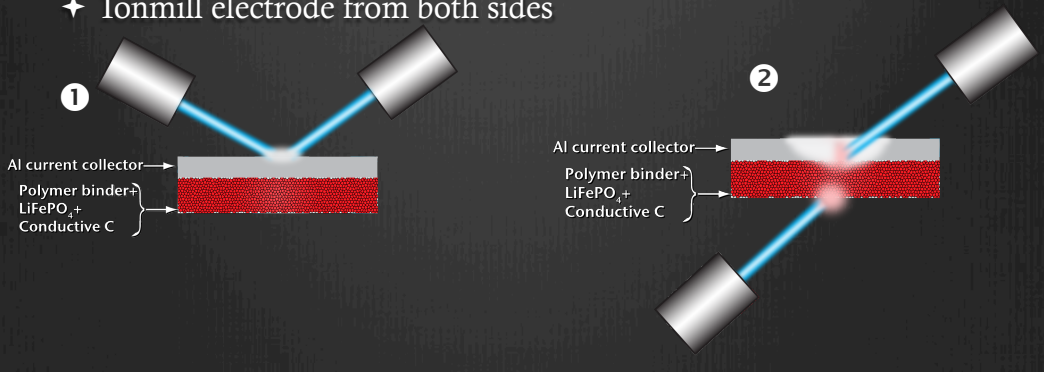




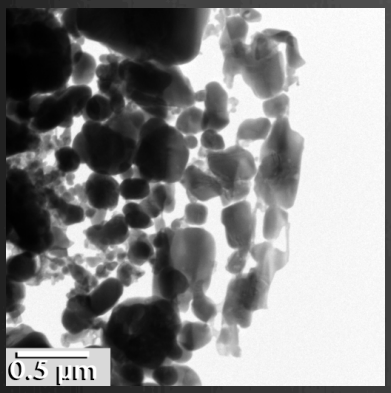
Wed 2-2:15 A06B P. Kotula Multivariate Statistical Analysis Strategies of EELS Spectral Images

Microstructural Fidelity?

- Scraping material off changes the arrangement and microstructure of particle
- Want to freeze the microstructure and view it as is
- Conventional TEM sample prep
  - Punch 3-mm disc
  - Ionmill Al current collector away from one side
  - Ionmill electrode from both sides

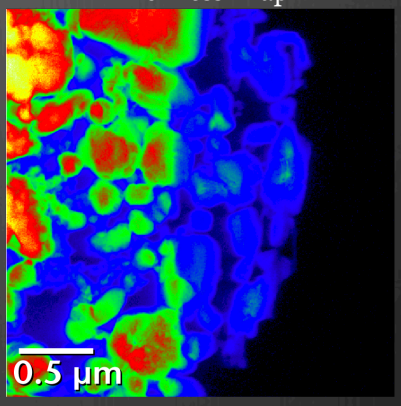


0% Charged: Thickness

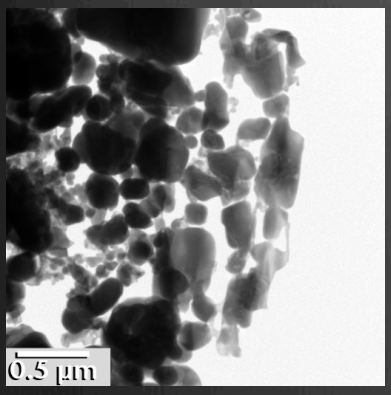


Zero-Loss Image
5 eV slit

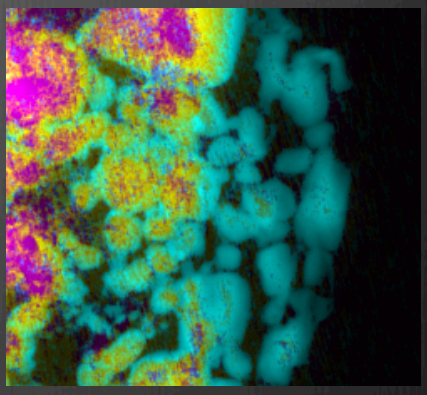
Thickness Map



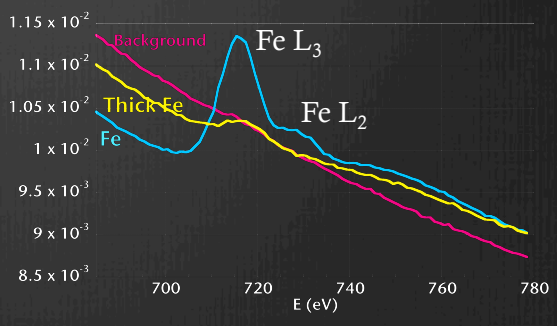
0% Charged: Core Loss



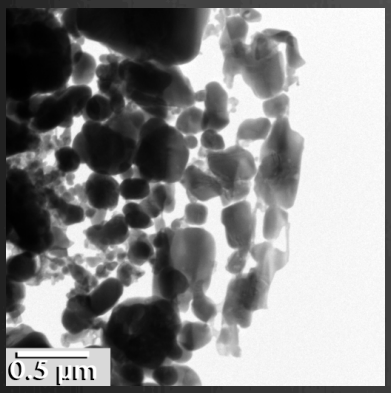
Zero-Loss Image
5 eV slit



5 eV slit
1 eV step
5 s integration time
Total time: 13 min (slit overhead)
MCR Spatial Simplicity Calculations
No Weighting
3 Components

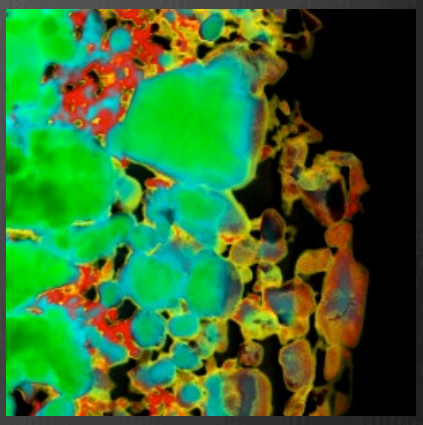


0% Charged: Low Loss

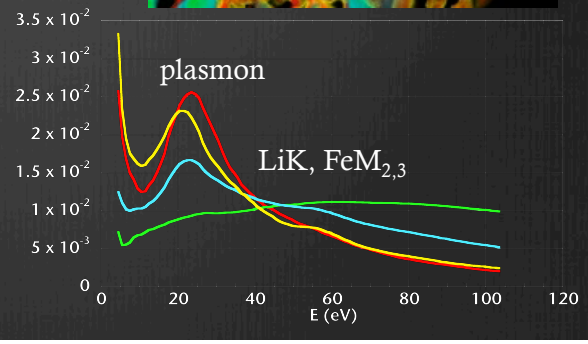


Zero-Loss Image
5 eV slit

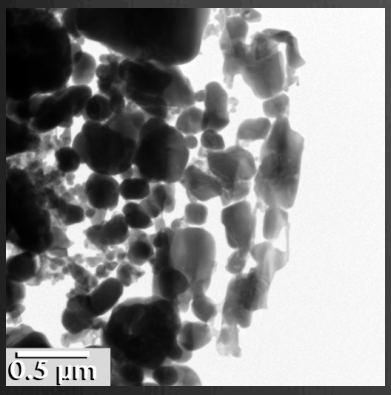
C
Thin Fe
Thick Fe
Thin Fe+C



5 eV slit
1 eV step
0.5 s integration time
Total time: 5 min (slit overhead)
MCR Spatial Simplicity Calculations
No Weighting
11 Components: diffraction artifacts and vacuum not shown

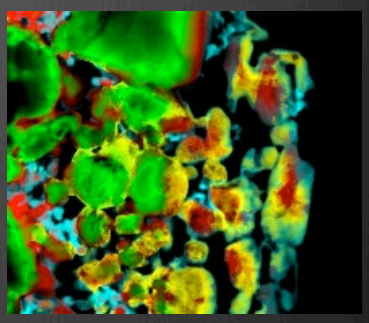


0% Charged: Core+Low Loss

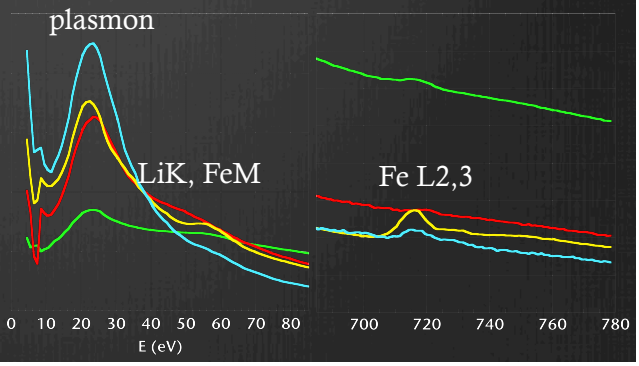


Zero-Loss Image
5 eV slit

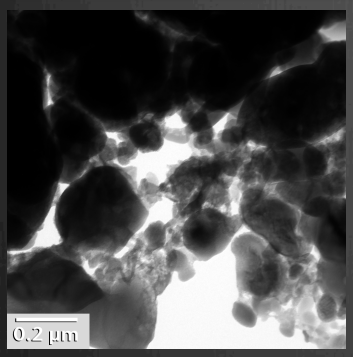
C (redeposit)
Thin Fe
Thick Fe
C



- DM Volume Manipulation tool
- SDSD Drift corrected composite stack
- MCR Spatial Simplicity Calculations
- No Weighting
- 15 Components: diffraction artifacts, vacuum, single particle components not shown

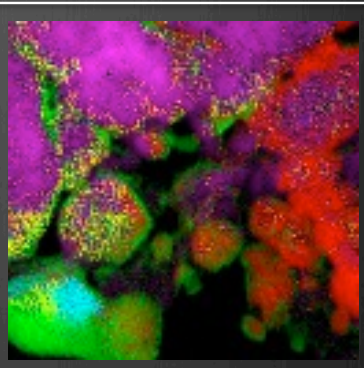


50% Charged: Core Loss

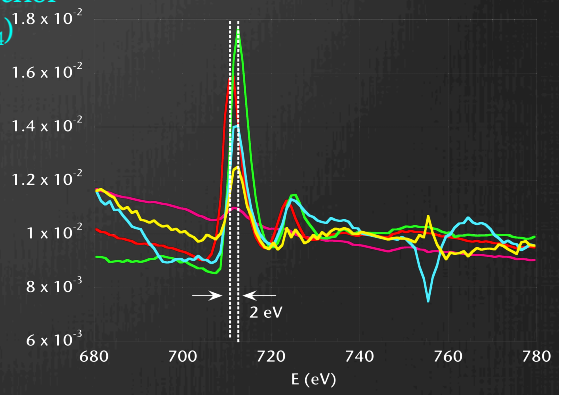


Zero-loss image
2.5 eV slit

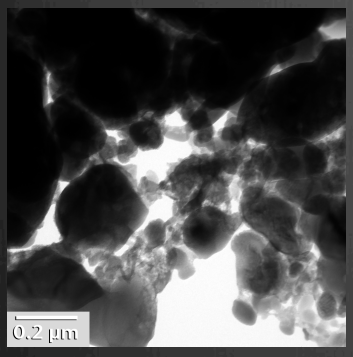
$LiFePO_4$
$FePO_4$
Thick material (90% $LiFePO_4$)
Mixture on Surface (70% $LiFePO_4$)
Mixture in Interior (48% $LiFePO_4$)



2.5 eV slit
1 eV step
12 s Integration time
Total: 20 min
MCR Spatial Simplicity
Not weighted

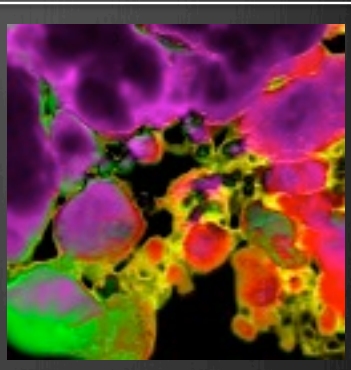


50% Charged: Low Loss

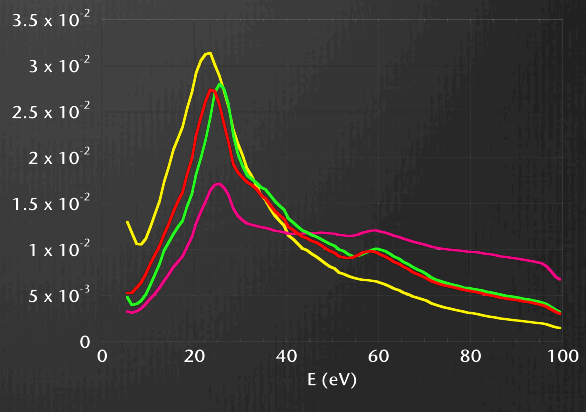


Zero-loss image
2.5 eV slit

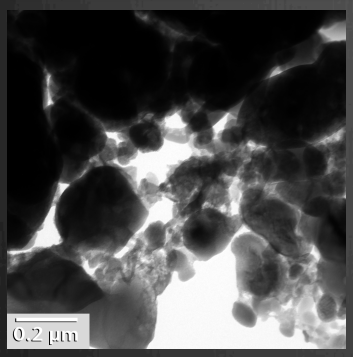
$LiFePO_4$
$FePO_4$
Thick material
Mixture on Surface
Mixture in Interior



2.5 eV slit
1 eV step
0.1 s Integration time
Total: 4 min
MCR Spatial Simplicity
Not weighted

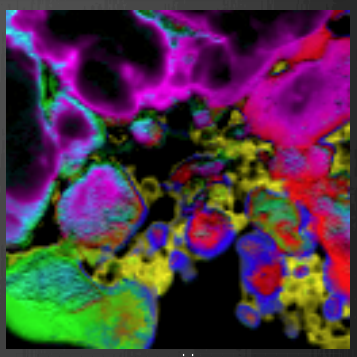


50% Charged: Core+Low

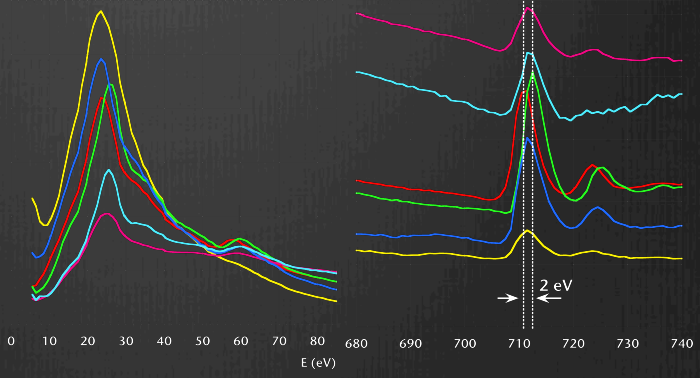


Zero-loss image
2.5 eV slit

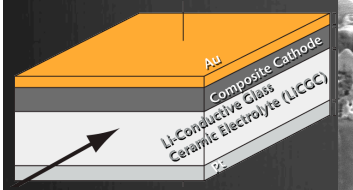
$LiFePO_4$
$FePO_4$
Thick material
(84% $LiFePO_4$)
Mostly C
73% $LiFePO_4$
43% $LiFePO_4$

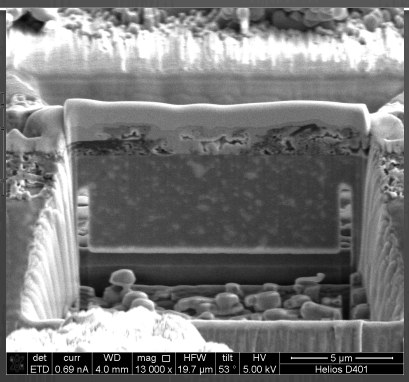


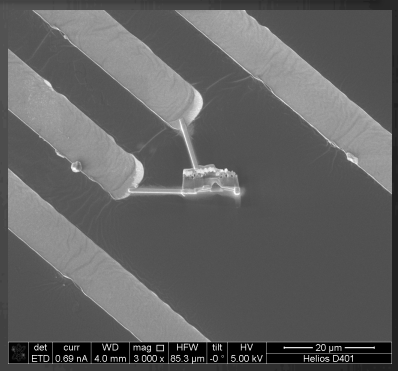
Combined with Volume tool
Drift Corrected with SDSD
MLSQ fits to quantify
amount of lithiation

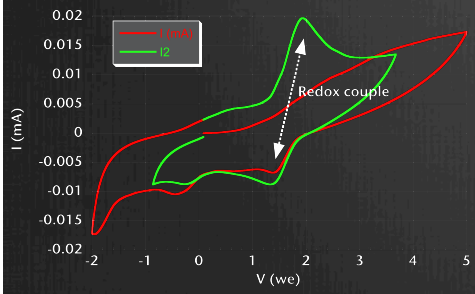


Future Work: Solid-State In Situ Battery



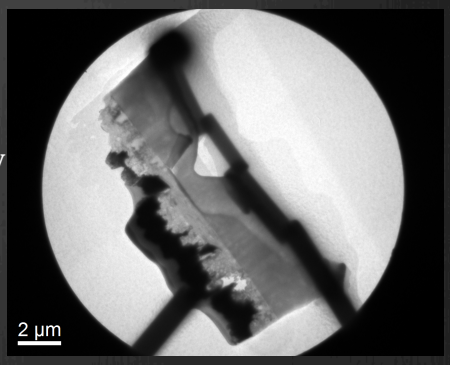






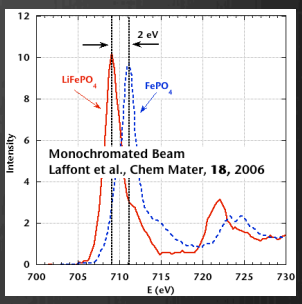
Aduro Platform

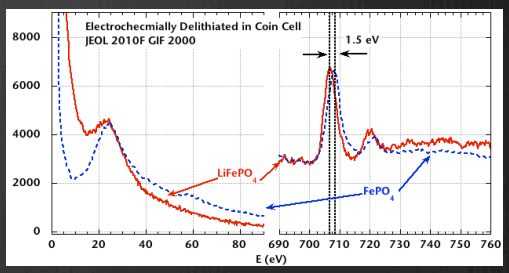
E-chip supplied by
Protochips, Inc.,
Raleigh, NC



Summary

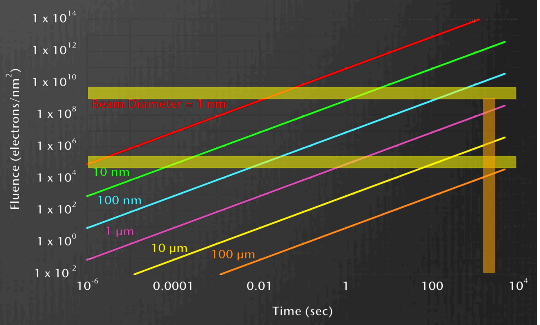
- The Fe ELNES shape allows us to determine whether a phase is $LiFePO_4$ or $FePO_4$





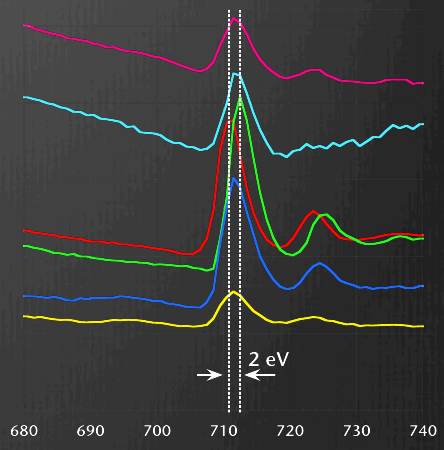
Summary

- The Fe ELNES shape allows us to determine whether a phase is $LiFePO_4$ or $FePO_4$
- Electron beam induced reduction can occur during STEM EELS, but can be avoided in EFTEM.



Summary

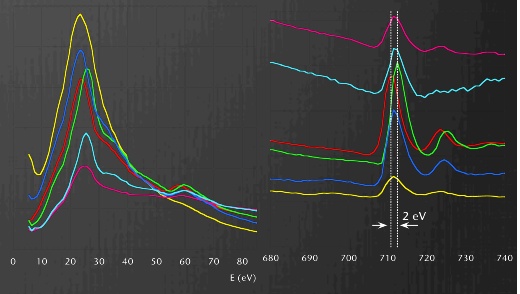
- The Fe ELNES shape allows us to determine whether a phase is $LiFePO_4$ or $FePO_4$
- Electron beam induced reduction can occur during STEM EELS, but can be avoided in EFTEM
- MSA calculations can help differentiate $LiFePO_4$ from $FePO_4$ in EFTEM data



Summary

- The Fe ELNES shape allows us to determine whether a phase is $LiFePO_4$ or $FePO_4$
- Electron beam induced reduction can occur during STEM EELS, but can be avoided in EFTEM
- MSA calculations can help differentiate $LiFePO_4$ from $FePO_4$ in EFTEM data

- Volume manipulation + SDSD allows us to combine low loss and core loss data stacks for MSA analysis



Conclusions

- MSA + EFTEM shows promise as a technique for measurement of the interphase interface in transition metal battery electrode materials
- Much of the MSA calculation is dominated by thickness effects, and it is not clear that much is gained from the low loss region
  - Carbon becomes a component
  - Deconvolution has been unsuccessful
- Future work with FIBed samples could be more promising