Phase Behavior and Solid State Chemistry of Olivines

BATT Task 1.2

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This presentation does not contain any proprietary or confidential information.

Purpose of Work

- Synthesize and evaluate alternative cathode and anode materials with improved energy density, safety, and cycle life.
- Support cell development and diagnostics tasks through chemical and structural characterization of cell components.
- Investigate mechanisms that may contribute to impedance rise in composite electrodes or that may lead to improved electrode designs.

Responses to Reviewers' Comments

2006 BATT Merit Review

"Work to optimize both power performance and tap density of materials."

- Our mechanistic and phase transformation studies have focused on highly crystalline active material particles of uniform size and shape. These characteristics are essential for high density electrodes.

"Increase effort on solid solution alloy anodes."

- A post-doc was hired in December 2007 to work on this task.

"Investigate how the electrochemical properties are related to particle morphologies."

- We have studied the electrochemical properties of both stoichiometric and solid solution olivine crystals of different sizes and shapes.

Barriers

- PHEV: Available energy, cycle life.
- EV: Low energy, poor cycle life.

High density electrodes cannot be made using nano-sized cathode materials.
A high energy density anode is also desirable.

Approach

- Identify candidate electrode compositions by systematic analysis of phase diagrams and literature reports.
- Synthesize materials with novel compositions or unique morphologies to facilitate evaluation.
- Employ *in situ* and *ex* situ diffraction methods, microscopies, spectroscopies, and electroanalytical techniques to determine relevant characteristics of the materials and evaluate their applicability to EV and PHEV batteries.

Performance Measures

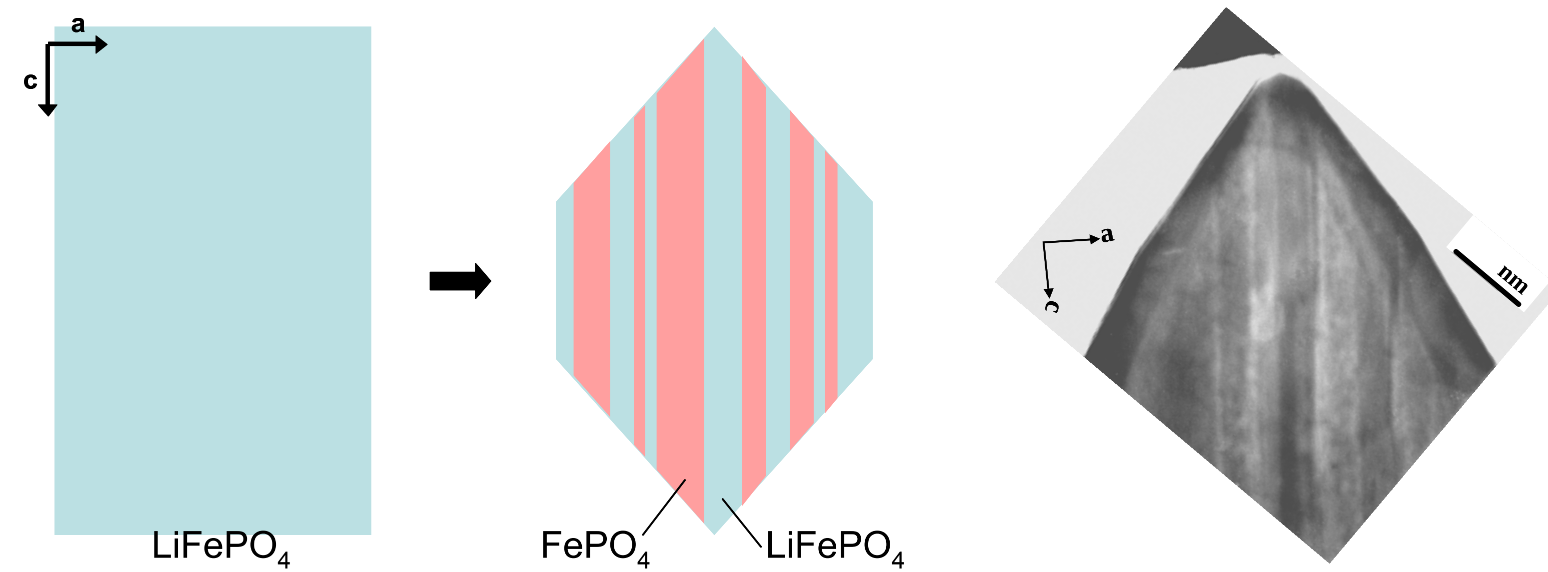
- Gravimetric and volumetric capacities for anode (600 Ah/kg) and cathode (150 Ah/kg) active materials.
- Power: better than 90 % retention at 10 C rate.
- Absence of side reactions or physical degradation that would be detrimental to cycle life.

Technical Accomplishments

- Prepared and characterized Li-Mg foils and cermets with high capacities and no irreversible first cycle losses.
- Extended cermet technique to Li-Si and Li-Mg-Si systems.
- Determined effects of particle size and morphology on $LiFePO_4$ utilization and internal stress.
- Investigated the role of solid solutions in electrochemical charging and discharging of Li_xFePO_4 crystals.
- Identified $MnPO_4$ decrepitation as contributing factor in poor performance of $LiMnPO_4$ cathodes.

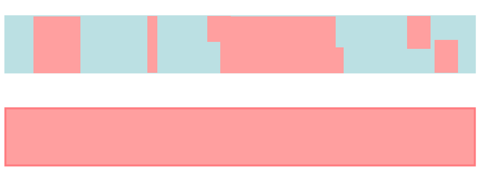
Technical Accomplishments

Olivines: Importance of b-axis dimension

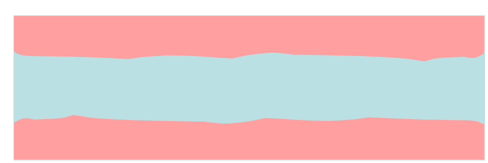


transition zones penetrate in ***bc*** plane

transition zones progress in ***a*** direction



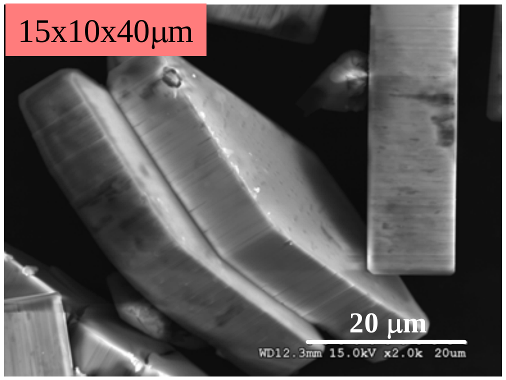
thin crystal fully delithiated



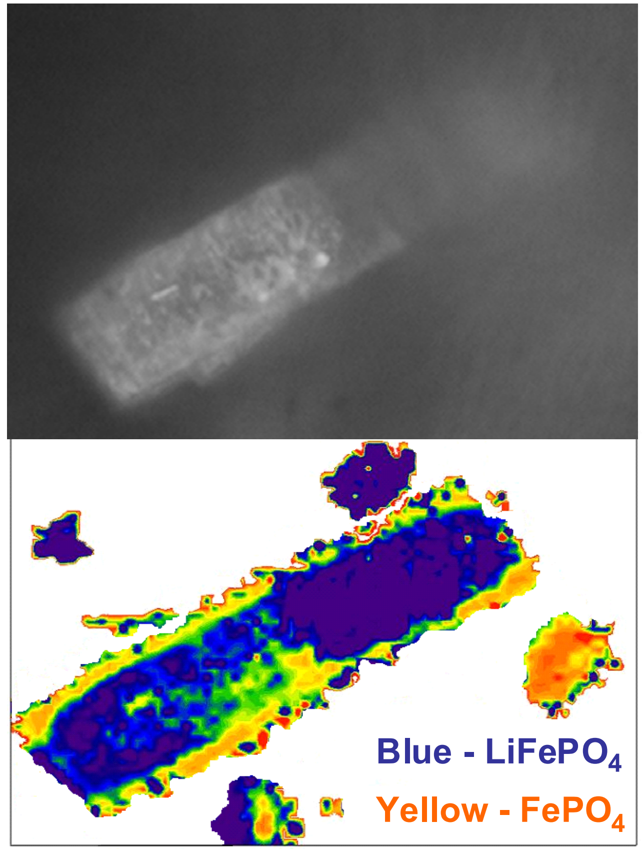
thick crystal partially delithiated

Technical Accomplishments

Olivines: Importance of b-axis dimension



Reagent	% $FePO_4$
0.01M Br_2	18
0.1M Br_2	20
0.1M Br_2, then 0.1M NO_2BF_4	20
0.1M NO_2BF_4	30



Raman Map by R. Kostecki, LBNL

Penetration Depth ~ 1µm

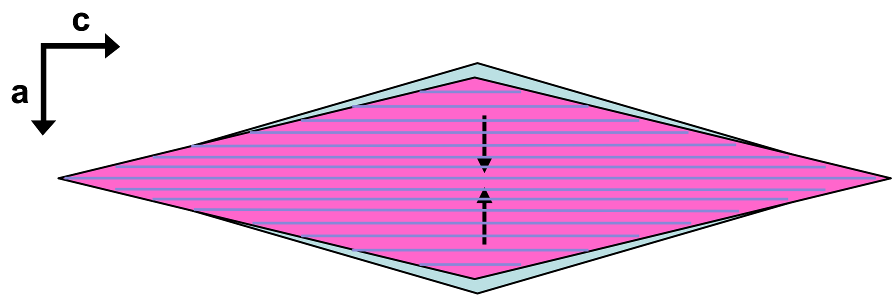
Once the ac surface is converted to $FePO_4$, the underlying $LiFePO_4$ is inaccessible.

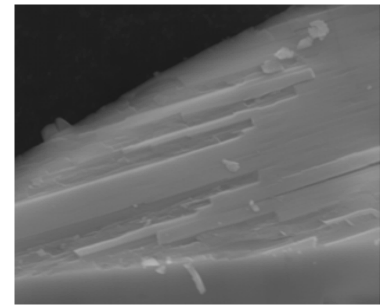
Technical Accomplishments

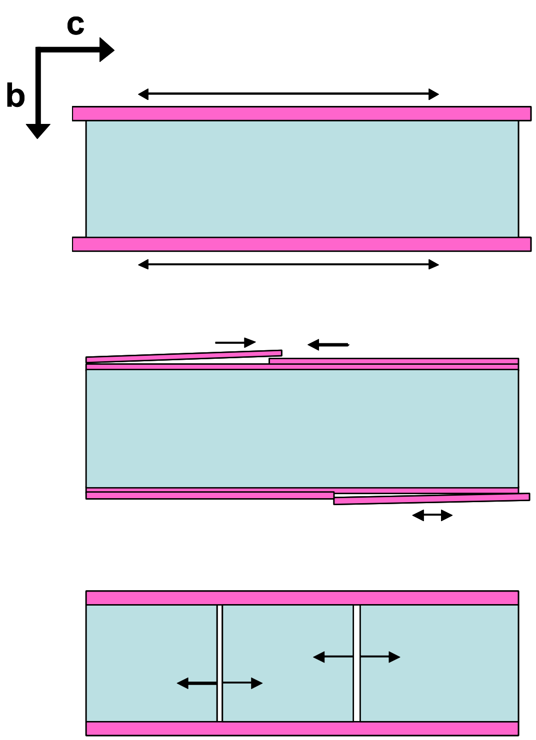
Internal stresses at phase boundaries

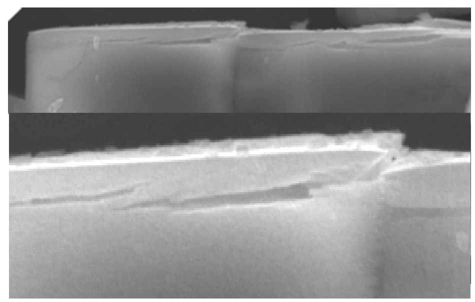
$LiFePO_4 \rightarrow FePO_4$

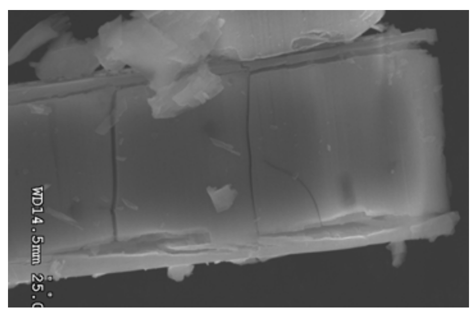
Δ ***a***	**- 5%**
Δ ***b***	**- 3.6%**
Δ ***c***	**+ 2%**

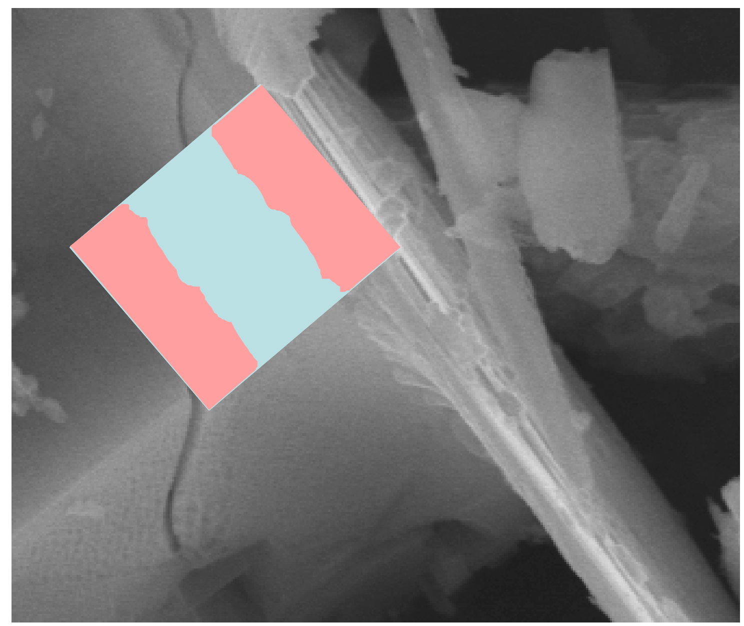






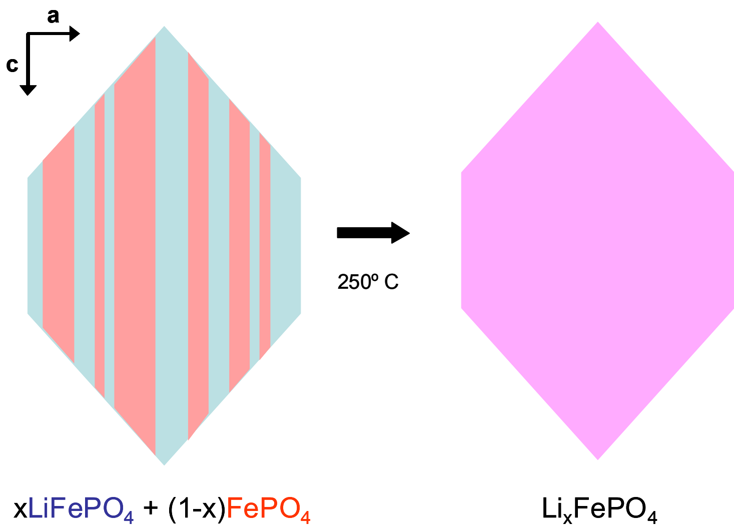


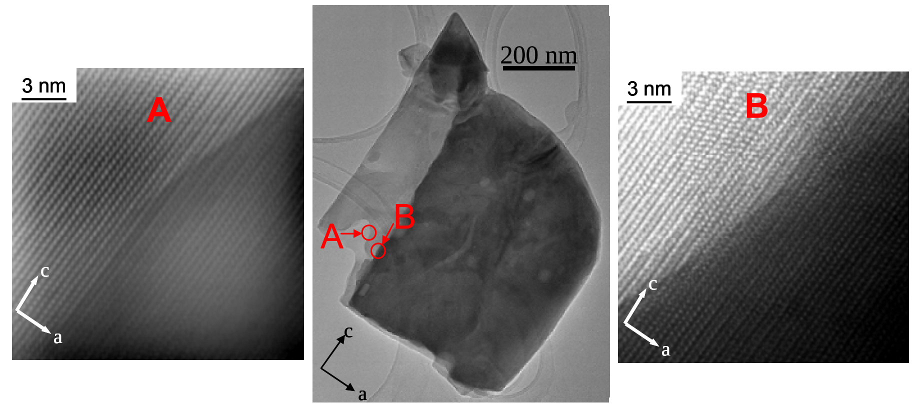


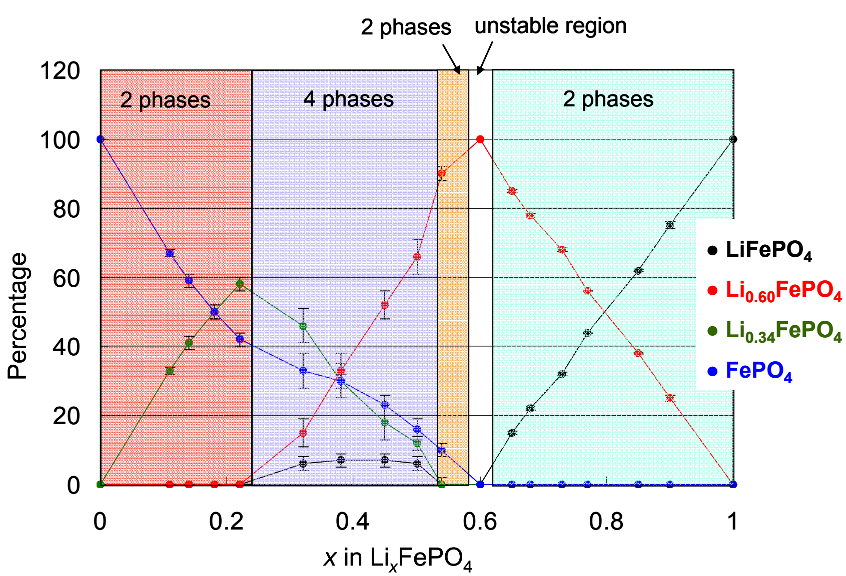


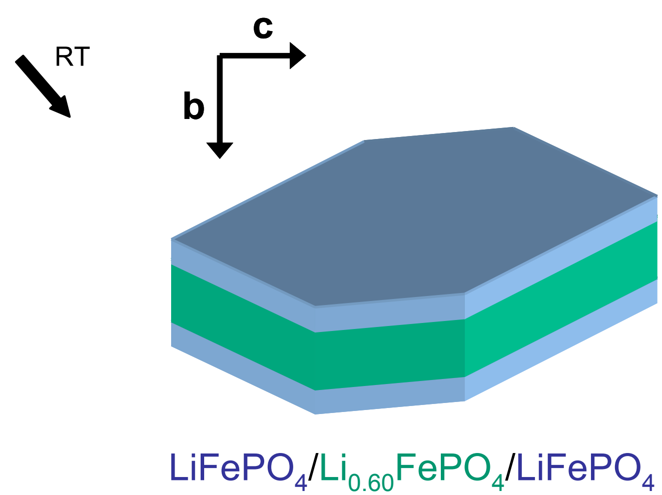
Technical Accomplishments

Solid solutions and intermediate phases



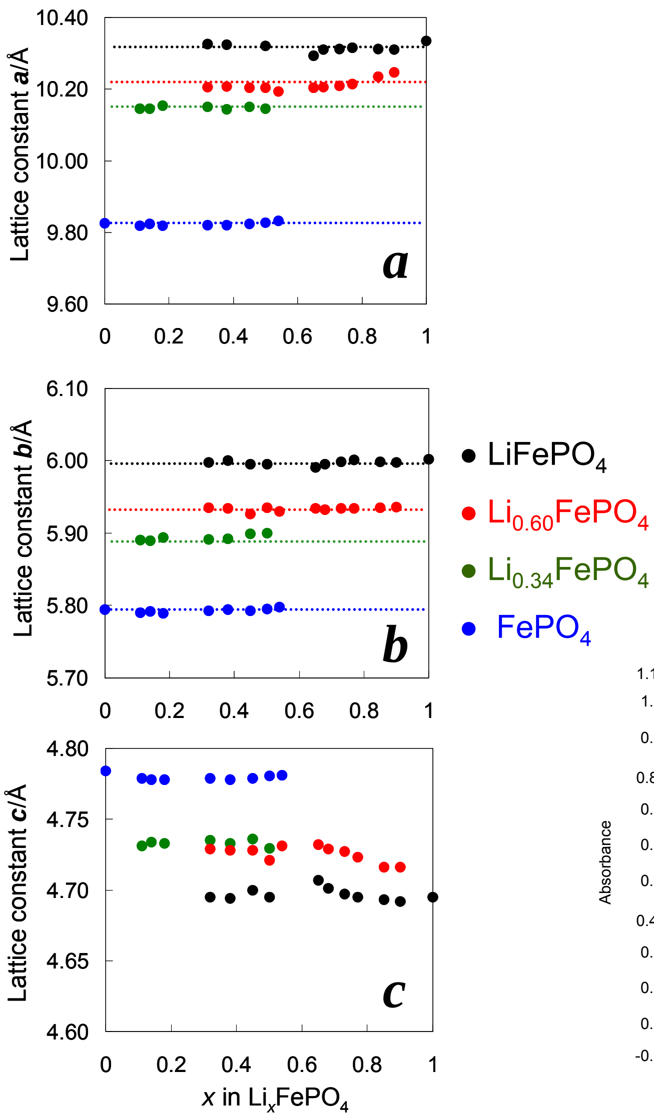


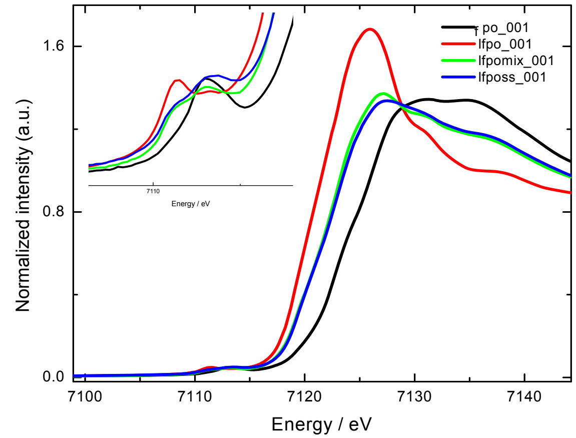




Technical Accomplishments

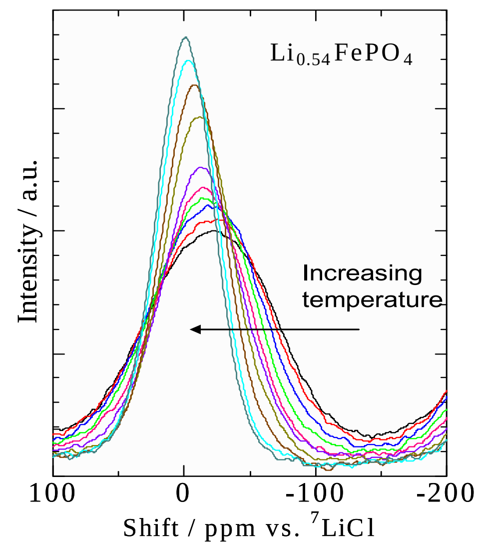
Solid solutions and intermediate phases

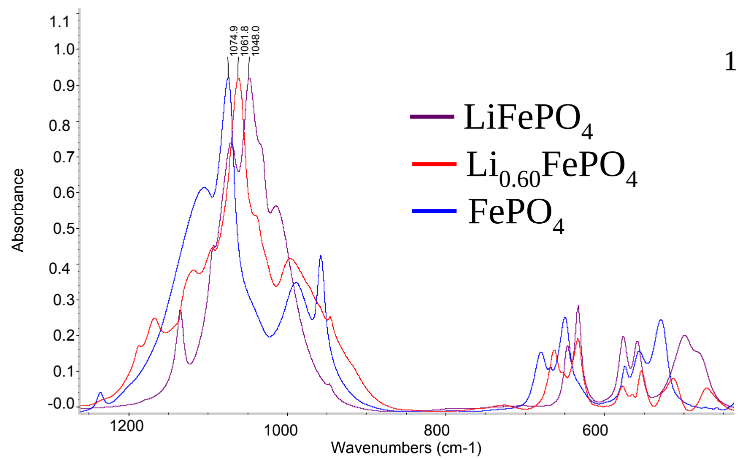




XANES (Yang)

NMR (Grey)





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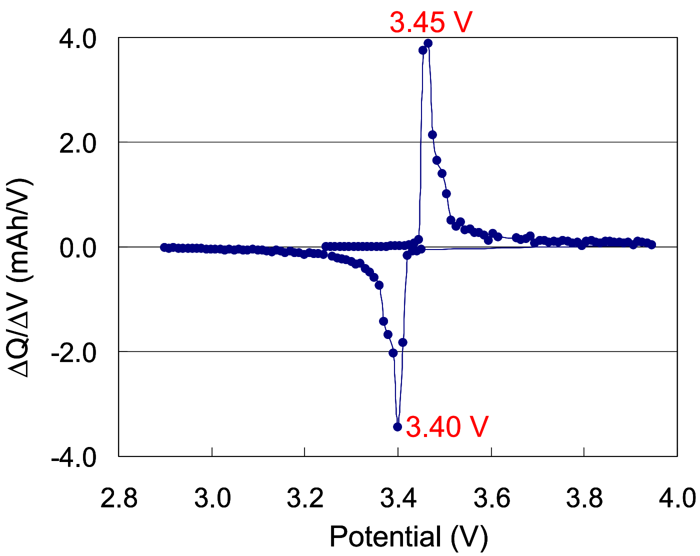
Technical Accomplishments

Electrochemistry of intermediate phases

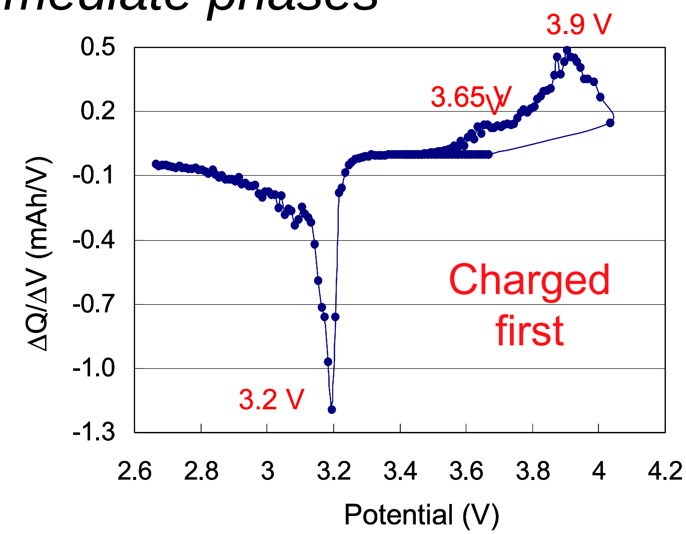
Potentiostatic Intermittent Titration (PITT)

Of Microcrystal Electrodes

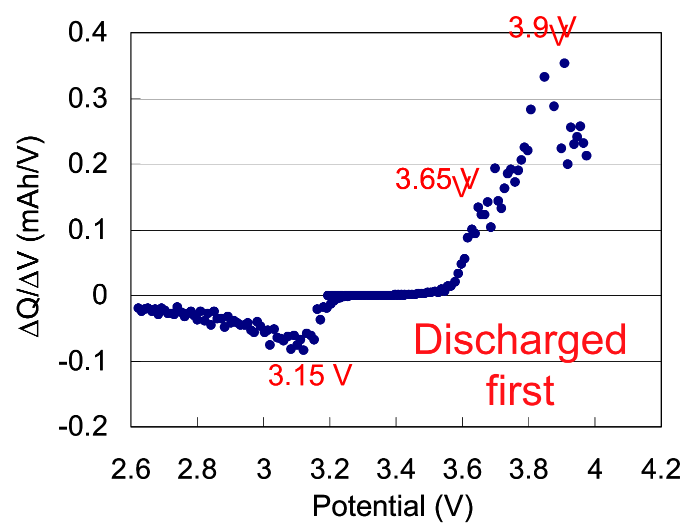


$LiFePO_4$

Sharp peaks, no hysteresis, no evidence of non-stoichiometry

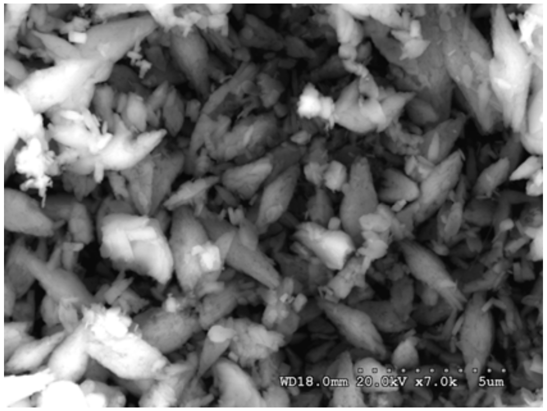


$Li_{0.68}FePO_4$

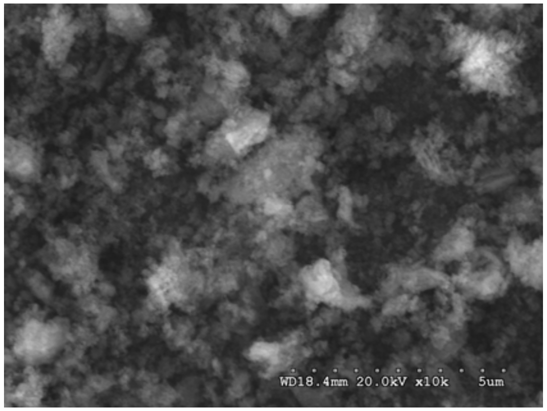


Technical Accomplishments

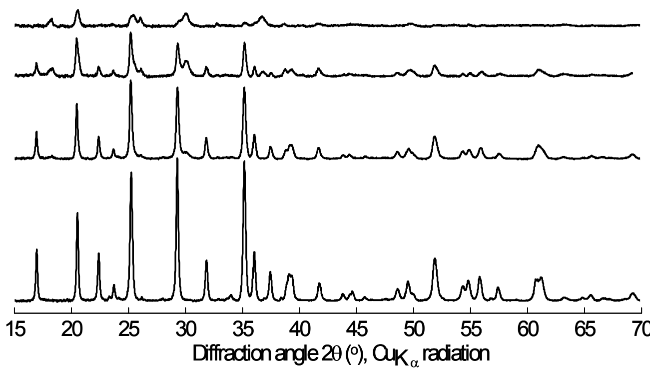
$LiMnPO_4$ degradation mechanism



Hydrothermal $LiMnPO_4$

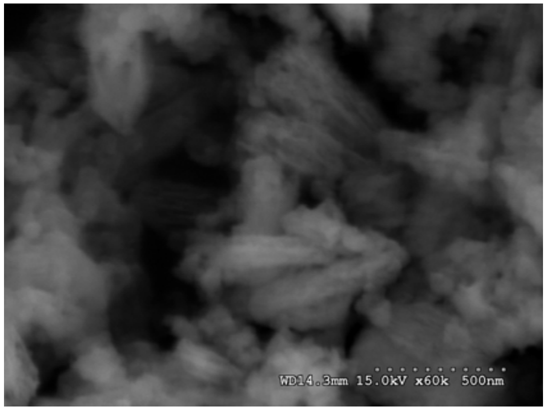


70% delithiated

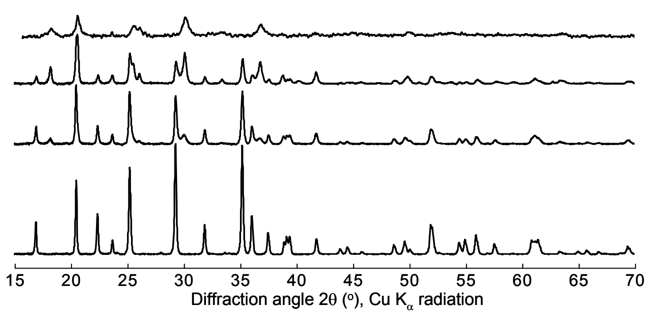


Physical decrepitation of $MnPO_4$

$LiMn_{0.8}Mg_{0.2}PO_4$



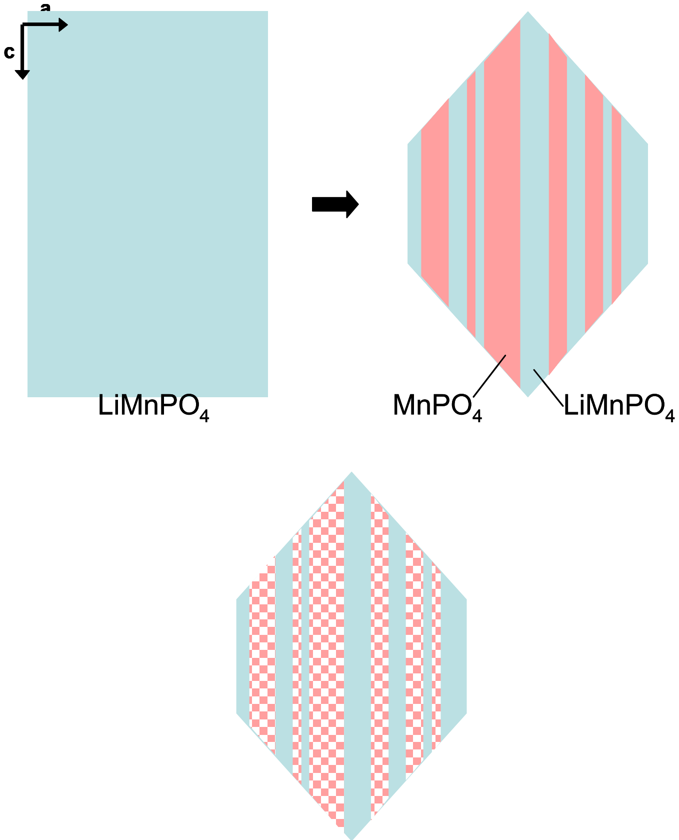
100% delithiated



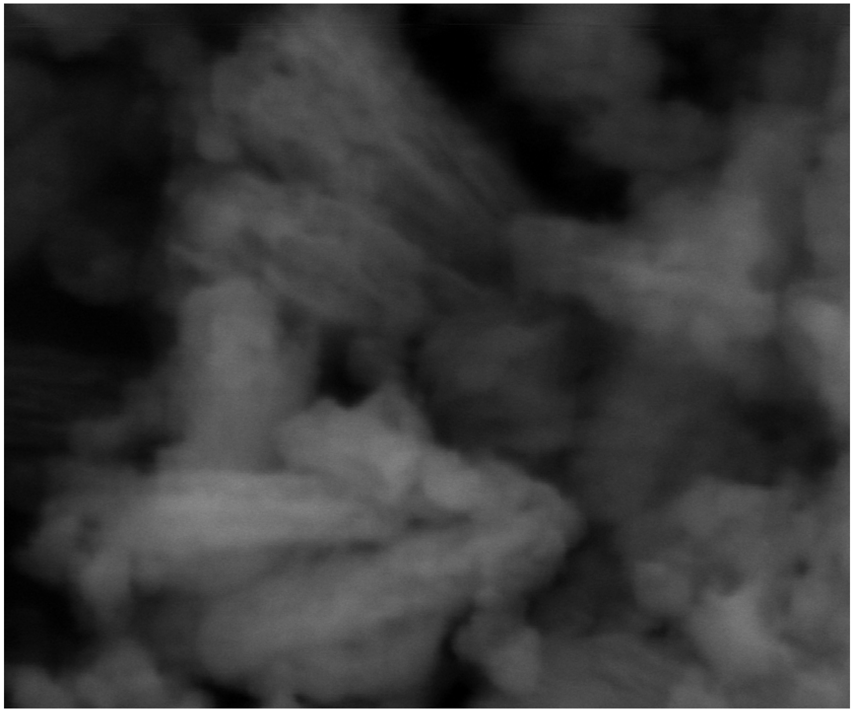
Better retention of crystallinity in $Li_{0.1}Mn_{0.9}Mg_{0.1}PO_4$

Technical Accomplishments

$LiMnPO_4$ degradation mechanism



Decrepitation of $MnPO_4$



TEM (not shown) indicates that the grooves are oriented along the *c*-axis and that in partially-delithiated crystals, the lithiated phase makes up most of the volume

Future Work

- Prepare and characterize porous Li-Mg and Li-Si electrodes using the cermet approach.
- Determine Li diffusion coefficients, current limitations, and cycling stability.
- Obtain more detailed information about $LiMnPO_4$ degradation and investigate potential mitigation measures.
- Determined effects of particle size and morphology on $LiMnPO_4$ utilization and internal stress.

Summary

- Electric and hybrid electric vehicles point the way to reduced oil consumption. Batteries are the most important components.

- Safety, energy density, and cycle life are paramount issues. Our work addresses all three.

- We have shown the importance of controlling cathode particle sizes and shapes. These are especially critical in high energy density batteries.

- We continue to study the detailed solid state chemistry of candidate cathodes and anodes for high energy density cells.

Collaborations

Robert Kostecki (LBNL) - Raman Spectroscopy, XRD

Clare Grey (SUNY Stonybrook) - NMR Spectroscopy

Xiao-Qing Yang (BNL) - X-ray Spectroscopy, XRD

Heike Gabrisch (U. New Orleans) - TEM

Jinghua Guo (ALS) - X-ray Spectroscopy

Saiful Islam (U. Bath) - Theory

Marca Doeff (LBNL) – Electrode Fabrication

Publications and Patents

"Electron Microscopy Study of the $LiFePO_4$ to $FePO_4$ Phase Transition," G. Chen, X. Song, and T. J. Richardson, *Electrochemical and Solid State Letters*, **9**, A295 (2006).

"Metastable Solid Solution Phases in the $LiFePO_4/FePO_4$ System," G. Chen, X. Song, and T. J. Richardson, *Journal of the Electrochemical Society*, **154**, A627 (2007).

"Solid Solution Lithium Alloy Cermet Anodes," G. Chen and T. J. Richardson, *Journal of Power Sources*, **174**, 810 (2007).

"Lithium Insertion Chemistry of Some Iron Vanadates," S. Patoux and T. J. Richardson, *Electrochemistry Communications*, **9**, 485 (2007).

"Microwave Plasma Chemical Vapor Deposition of Nano-Structured Sn/C Composite Thin-Film Anodes for Li-ion Batteries," M. Marcinek, L. J. Hardwick, T. J. Richardson, X. Song, R. M. Kostecki, *Journal of Power Sources*, **173**, 965 (2007).

USPTO Patent application **60**/944,932, "Metal alloy cermets and method for making same." June 19, 2007.