U.S. DEPARTMENT OF ENERGY

LBNL

Cell Analysis – High-Energy Density Cathodes and Anodes

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Project ID: ES053

OVERVIEW

Timeline

- PI Joined BATT 2001
- Cathodes Task Started 2001
- Anodes Task Started 2006

Budget

- FY09 $475K
- FY10 $530K

Barriers Addressed

- Available Energy
- Cycle life
- Abuse tolerance

Partners

- Collaborations: Grey (Stony Brook) Kostecki, Srinivasan, Doeff, Cabana (BATT-LBNL), Radmilovic (NCEM), Kunz, Rotenberg (ALS), Misra (SSRL, APS)
- Interactions: Zaghib (HQ)
- Project lead: John Newman

OBJECTIVES

- Synthesize and evaluate new electrode materials with improved energy density.
- Investigate the relationships of structure, morphology and performance of cathode and anode materials.
- Explore kinetic barriers and utilize the knowledge gained to design and develop electrodes with improved energy density, rate performance and stability.

MILESTONES

June 2009	Report rate and cycling performance of Li alloy and/or intermetallic electrodes with capacity exceeding 500 mAh/g.
July 2009	Report on mechanisms governing $LiMnPO_4$ performance and measures to improve utilization and rate.
September 2009	Report experimental results on new cathode materials.
March 2010	Report capacities and charge-discharge potentials for new cathode materials.
July 2010	Report on reduction of anode irreversible capacities.

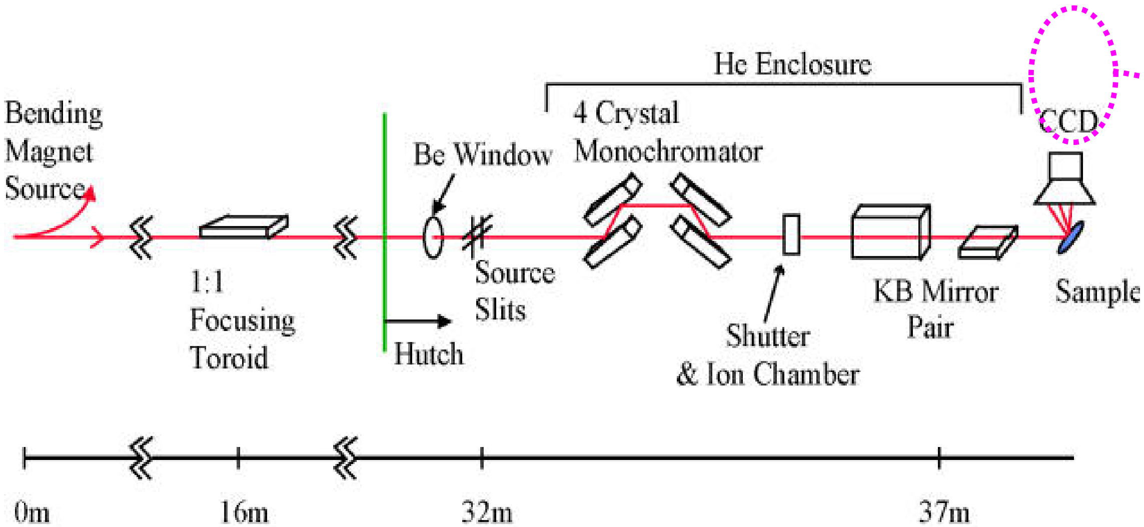
APPROACH

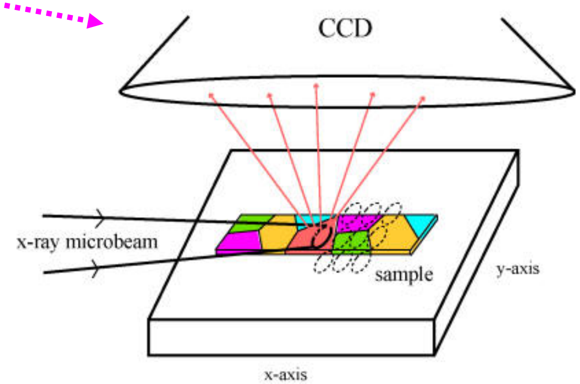
- Identify candidate cathode compositions by systematic analysis of phase diagrams and literature reports.
- Synthesize novel materials and/or unique structures and employ XRD, electron microscopy, vibrational spectroscopies, and electroanalytical techniques to determine their applicability to BATT goals.
- Develop and test strategies to reduce capacity losses in conventional and alternative anodes.
- Explore kinetic barriers, and utilize the knowledge gained to design and develop electrodes with improved energy density, rate performance and stability.

TECHNICAL ACCOMPLISHMENTS

Visualization of Charge Distribution in an Electrode by Synchrotron Microdiffraction

with Martin Kunz, Kai Chen and Nobumichi Tamura, Advanced Light Source, LBNL

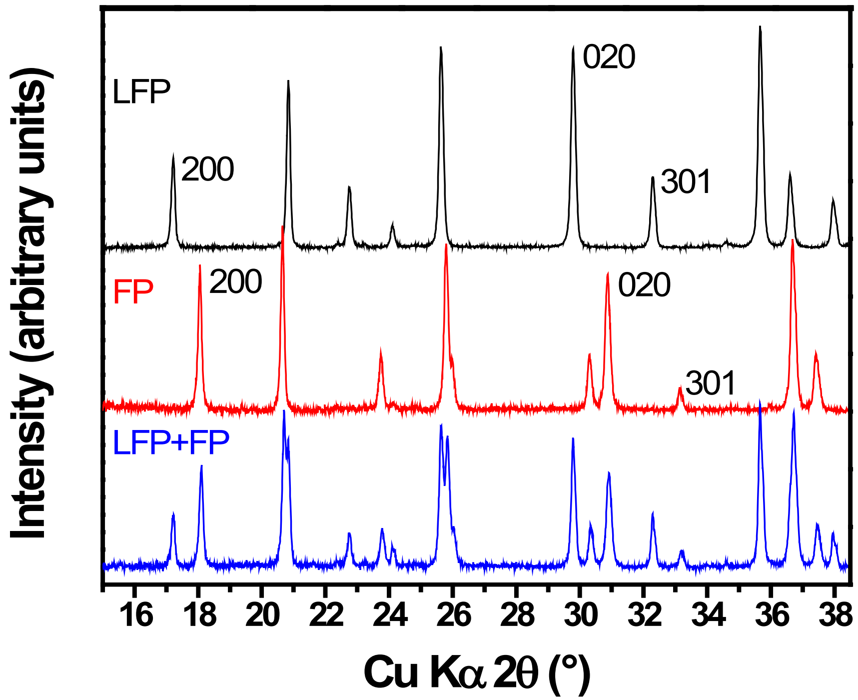




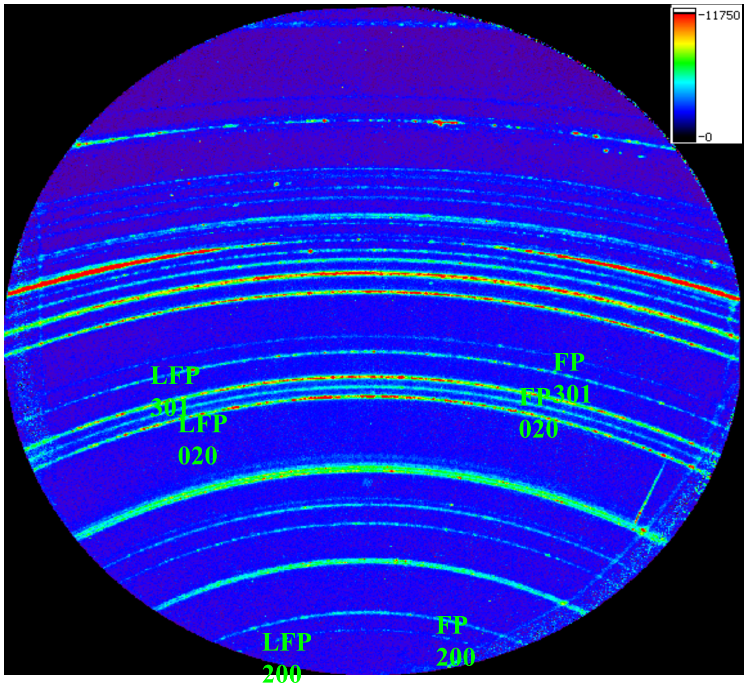
- Beam size can be as small as 1 μm x 1 μm

TECHNICAL ACCOMPLISHMENTS

Visualization of Charge Distribution



XRD patterns of $LiFePO_4$, $FePO_4$ and a 1:1 mixture



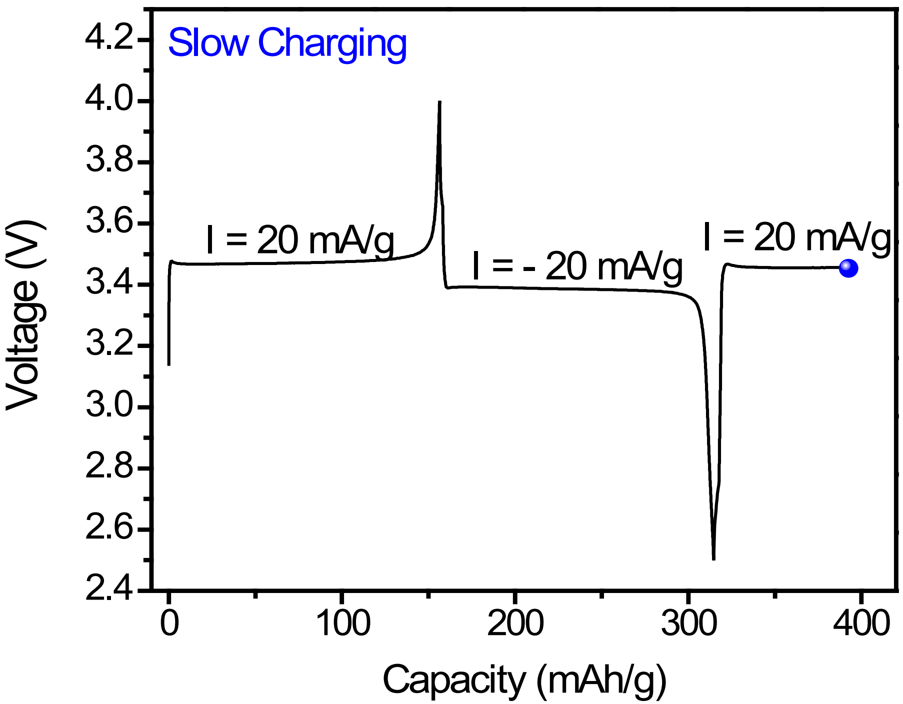
Stereographic XRD patterns collected by CCD at 6 keV

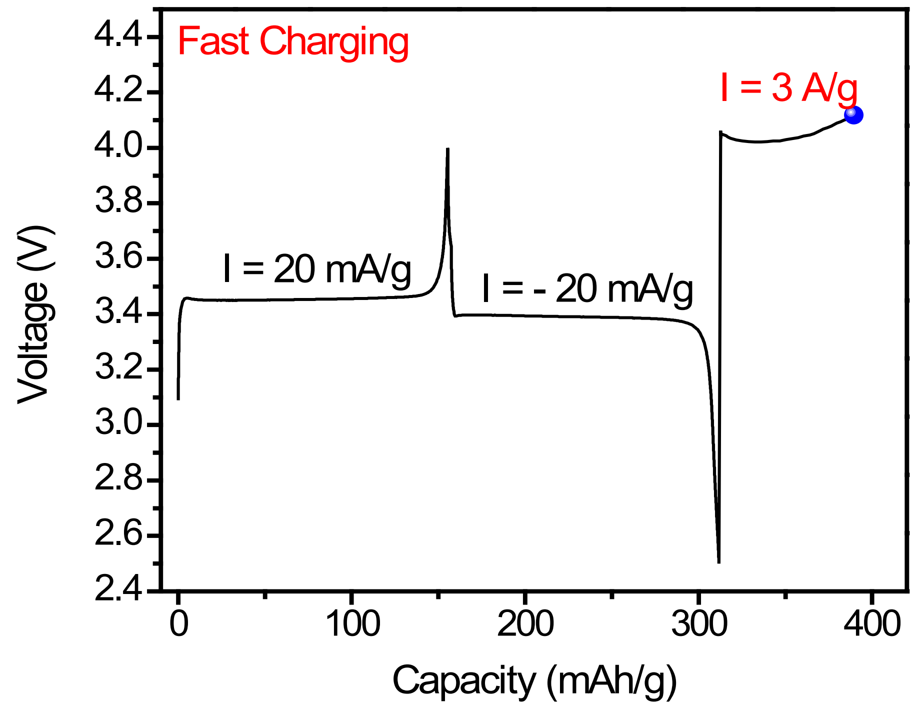
020 peaks were used to determine the phase distribution, which is "frozen" due to the two-phase nature of the $LiFePO_4$ system

TECHNICAL ACCOMPLISHMENTS

Visualization of Charge Distribution

12.5 mm diameter Swagelok cell electrodes

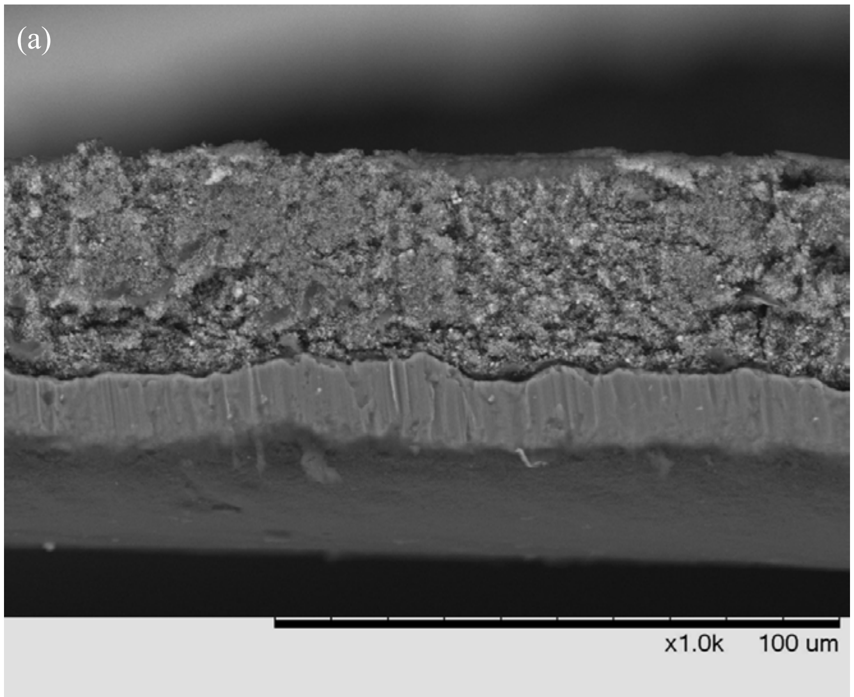


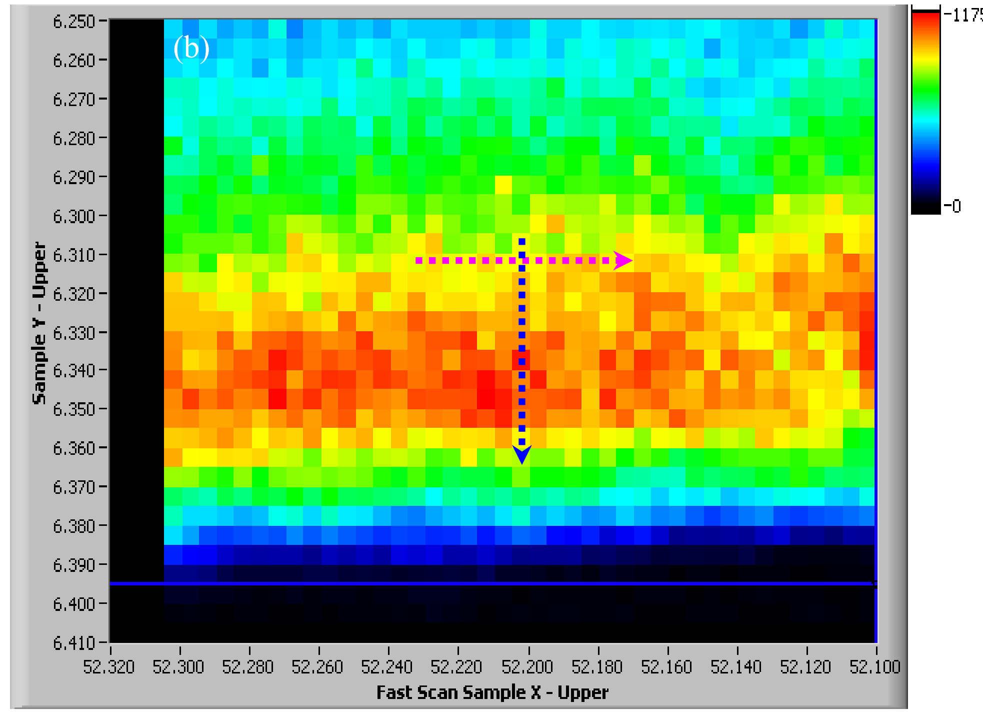


Both cells charged to 50% of first discharge capacity

TECHNICAL ACCOMPLISHMENTS

Visualization of Charge Distribution





Electrode cross-section is ~ 50 µm

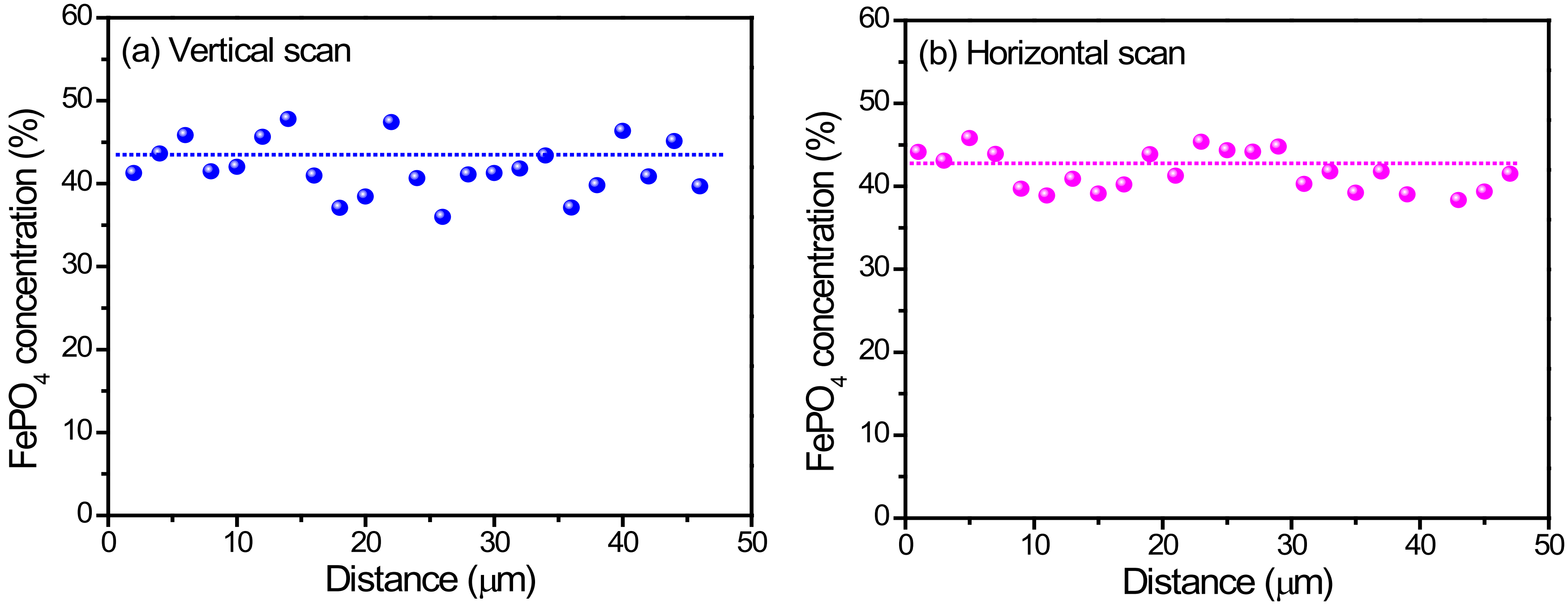
Fe fluorescence locates the active layer

XRD data collected from cross section at 2 µm intervals

TECHNICAL ACCOMPLISHMENTS

Visualization of Charge Distribution

20 mA/g charge

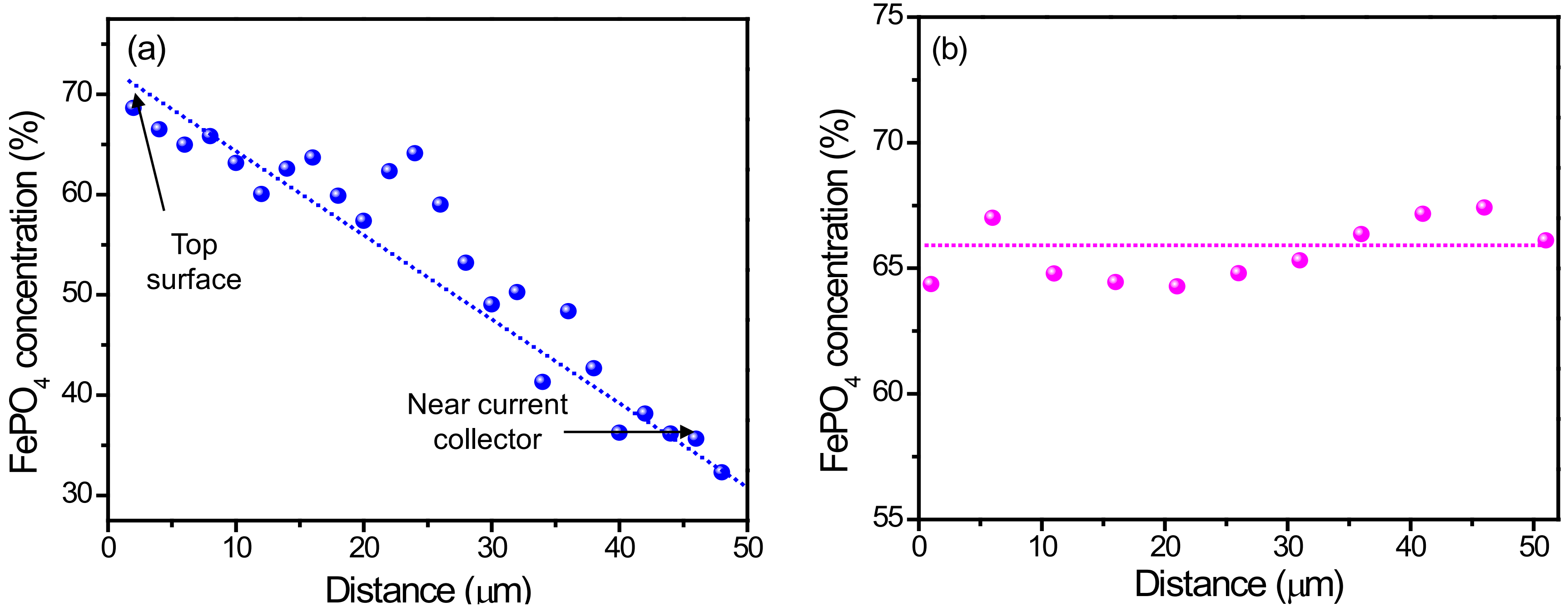


Phase distribution in electrode cross-section after slow charging is quite uniform

TECHNICAL ACCOMPLISHMENTS

Visualization of Charge Distribution

3000 mA/g charge

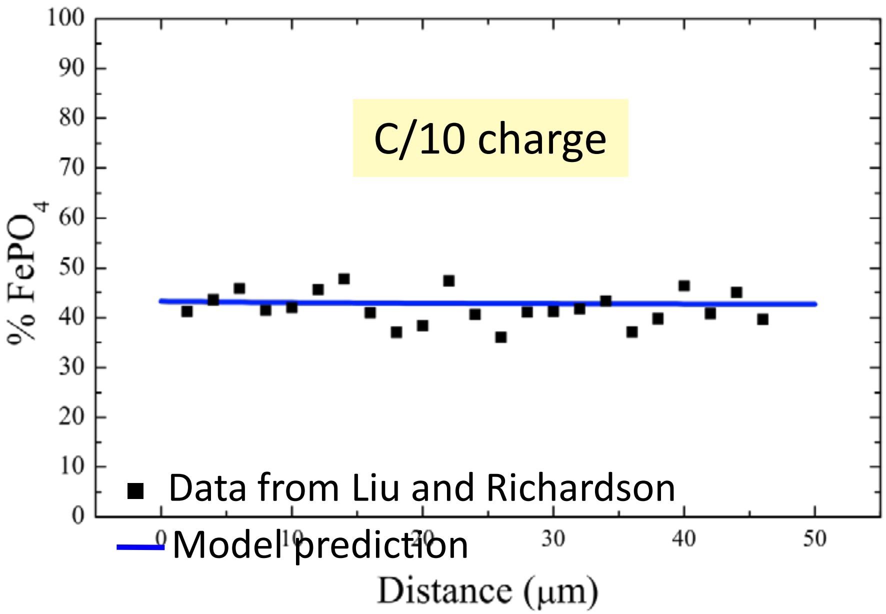


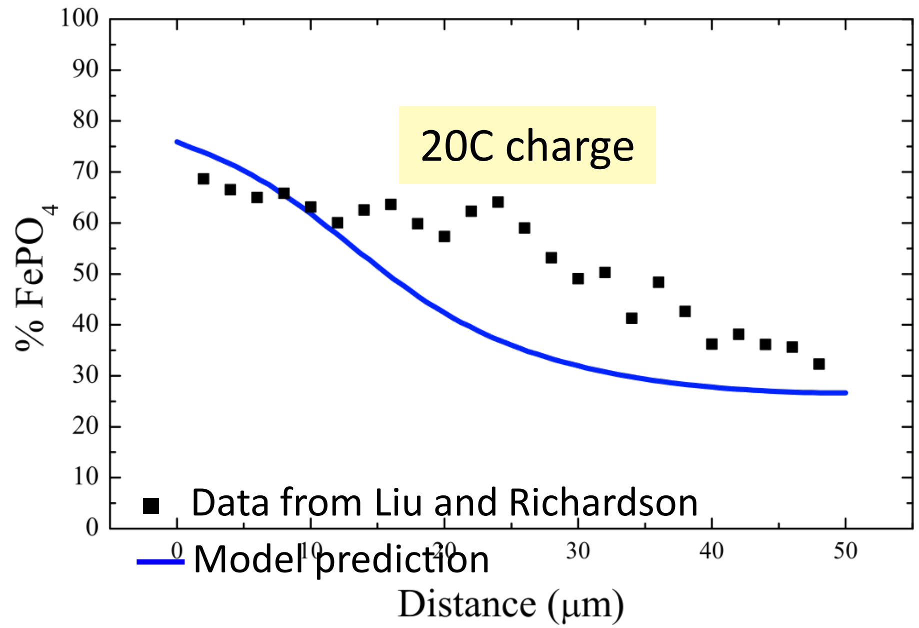
Phase distribution in electrode cross-section after fast charging is uniform in-plane but varies dramatically from top to bottom

TECHNICAL ACCOMPLISHMENTS

Liquid Phase Transport Model (V. Srinivasan, LBNL)

Porous electrode model including electrolyte transport properties, thickness, porosity, and tortuosity used to predict the charge distribution



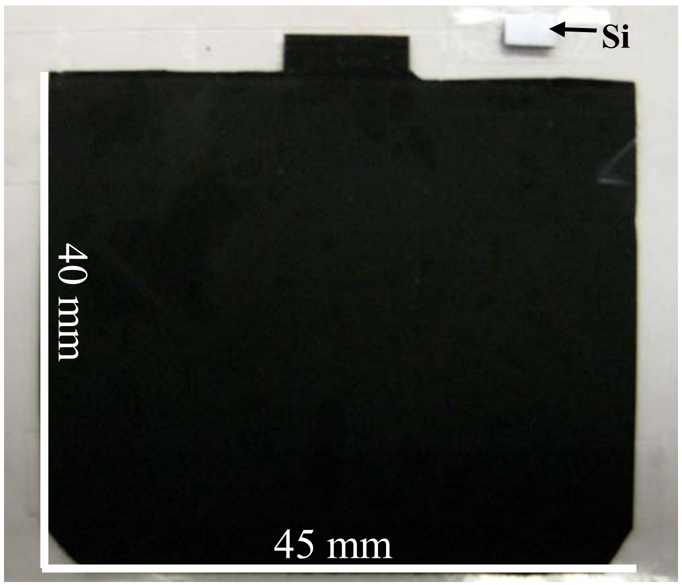


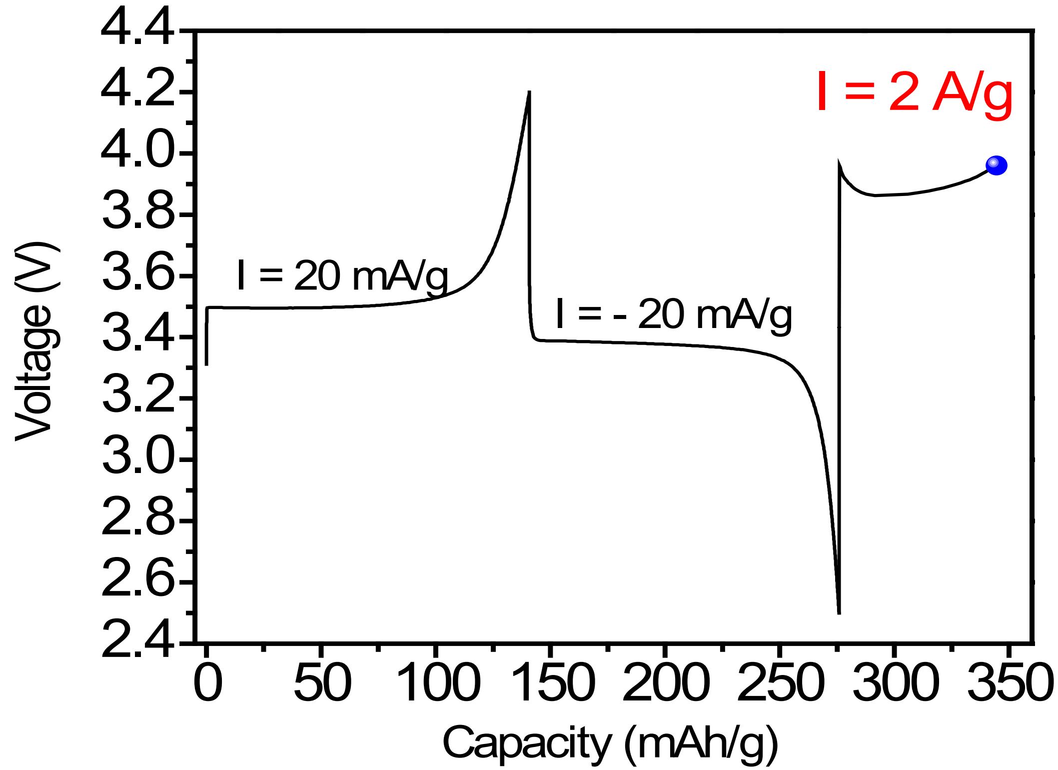
- Model predicts data well
  - Slight overprediction of the impact of electrolyte transport at higher rates
- Data provides a means of tuning the model, especially for lower porosities- Future work

TECHNICAL ACCOMPLISHMENTS

Visualization of Charge Distribution

4 cm x 4.5 cm pouch cell electrode

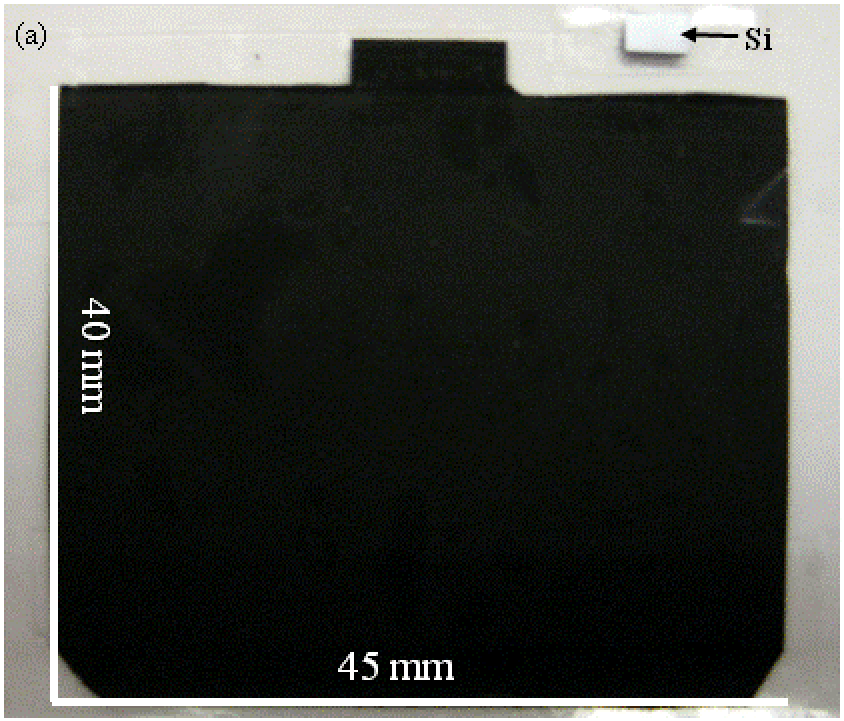


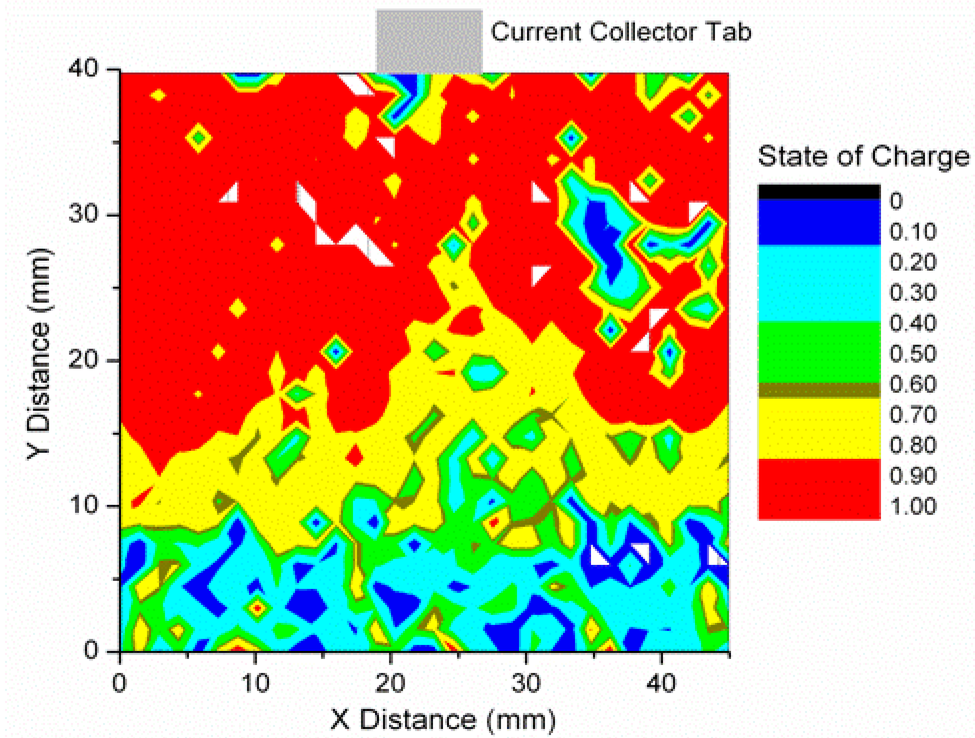


Large polarization when charged at high current density

TECHNICAL ACCOMPLISHMENTS

Visualization of Charge Distribution





Phase distribution in plane of electrode at 50 % SOC is highly non-uniform, controlled by electronic conductivity

Islands of poorly connected active material are evident

SUMMARY – CELL ANALYSIS

Charge Distribution by Microdiffraction

- The charge distribution in lithium battery electrodes has been visualized for the first time using synchrotron microdiffraction
- For swagelok-type cells, the non-uniform distribution of the delithiated phase ($FePO_4$) in the cross-section of an electrode charged with high current density is due to electrolyte polarization in the pores of the electrode
- Calculations by V. Srinivasan agree well with the observed distribution
- For a rectangular electrode in a pouch cell configuration, the non-uniform charge distribution is due to electronic resistance in the Al substrate and porous composite

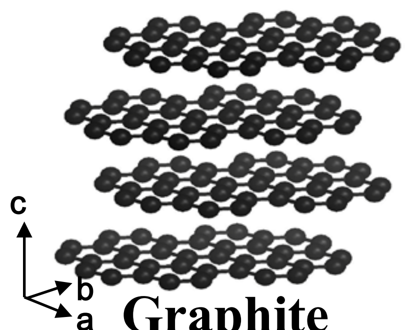
APPROACH - ANODES

Carbon anodes

- Merits
  - Good cyclability
  - Relatively low cost

- Demerits
  - Limited capacity
    : Graphite (LiC_6: 372 mAh/g)
  - Slow rate capability
  - Poor initial coulombic efficiency
    ➔ SEI layer formation

- Species
  - Graphite (MCMB, Natural graphite), Soft carbon, and etc.



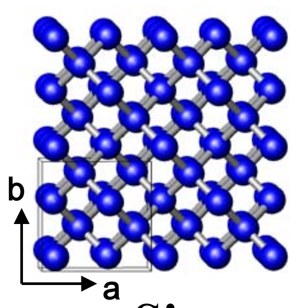
Graphite

Alloying anodes

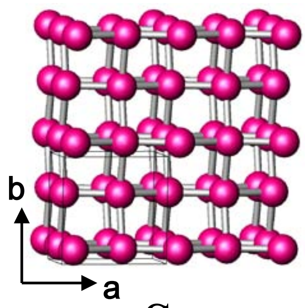
- Merits
  - High capacity
    : $Li_{4.4}Si$ (4100 mAh/g) & $Li_{4.4}Sn$ (990 mAh/g)
  - Good rate capability
  - Less safety problems

- Demerits
  - Poor cyclability
    ➔ Volume expansion
  - Poor initial coulombic efficiency
    ➔ SEI layer formation

- Species
  - Sn, Si, and etc.



Si



Sn

APPROACH - ANODES

Lithium nitride is a convenient and inexpensive source of lithium for reduction of irreversible capacity losses in:

Solid solution alloys:

$$2Li_3N + 3Mg \rightarrow 6Li + Mg_3N_2$$

$$2Li_3N + (3+x)Mg \rightarrow Li_6Mg_x + Mg_3N_2$$

Intermetallics:

$$Li_3N + Al \rightarrow 3Li + AlN$$

$$4Li_3N + 4Al \rightarrow 3LiAl + AlN$$

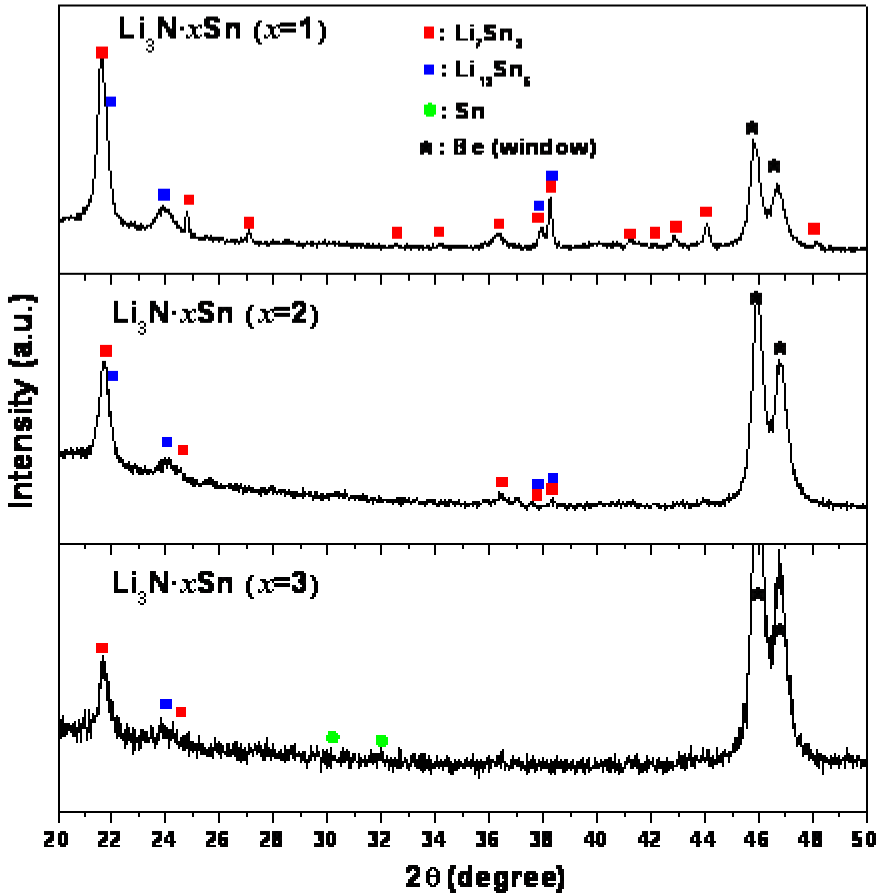
$$Li_3N + x Si(Sn) \rightarrow 3LiSi(Sn)_{0.33x} + \tfrac{1}{2}N_2$$

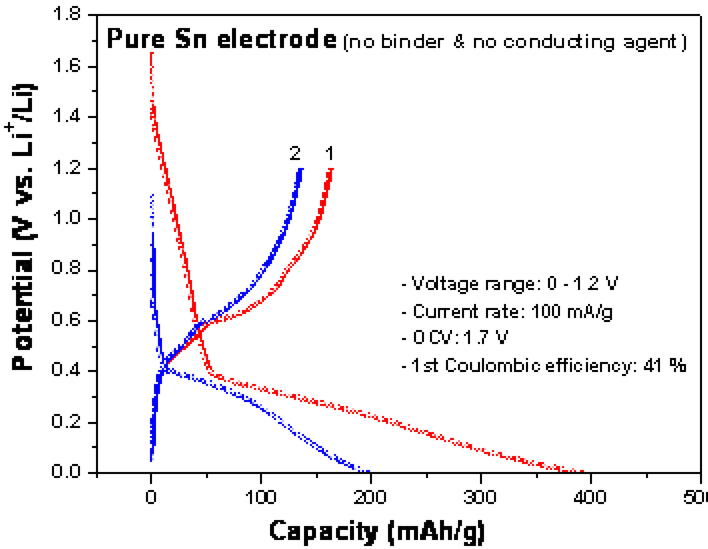
Carbon anodes:

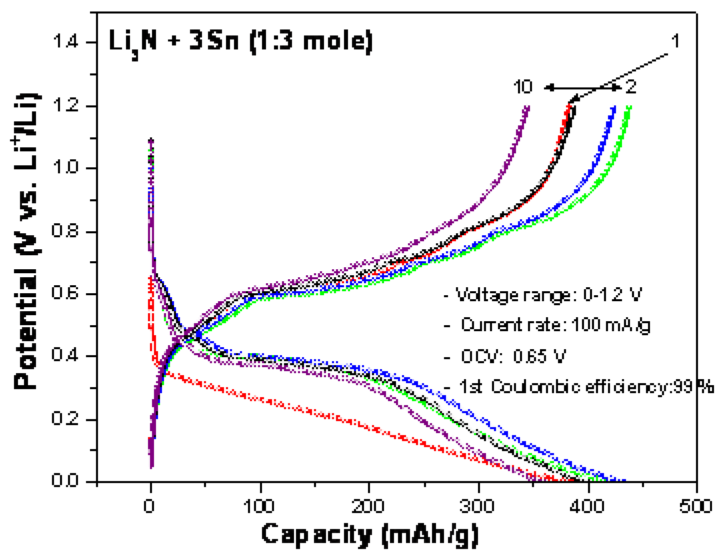
$$Li_3N + Al + 18C \rightarrow 3LiC_6 + AlN$$

TECHNICAL ACCOMPLISHMENTS

Prelithiated Sn synthesized from Li_3N & Sn





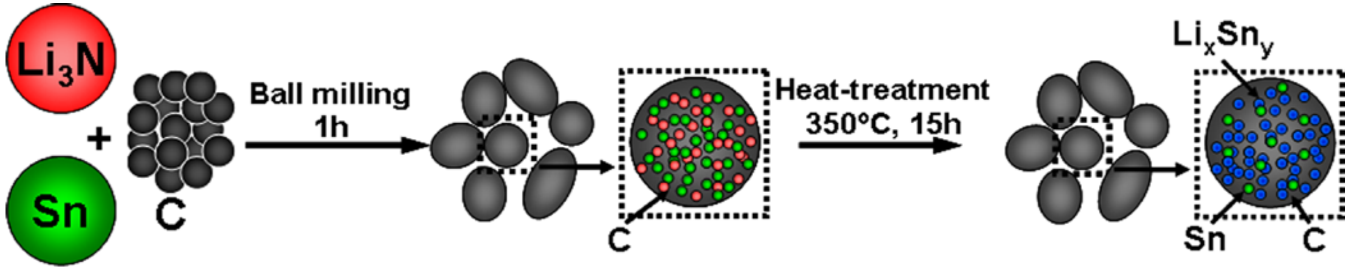


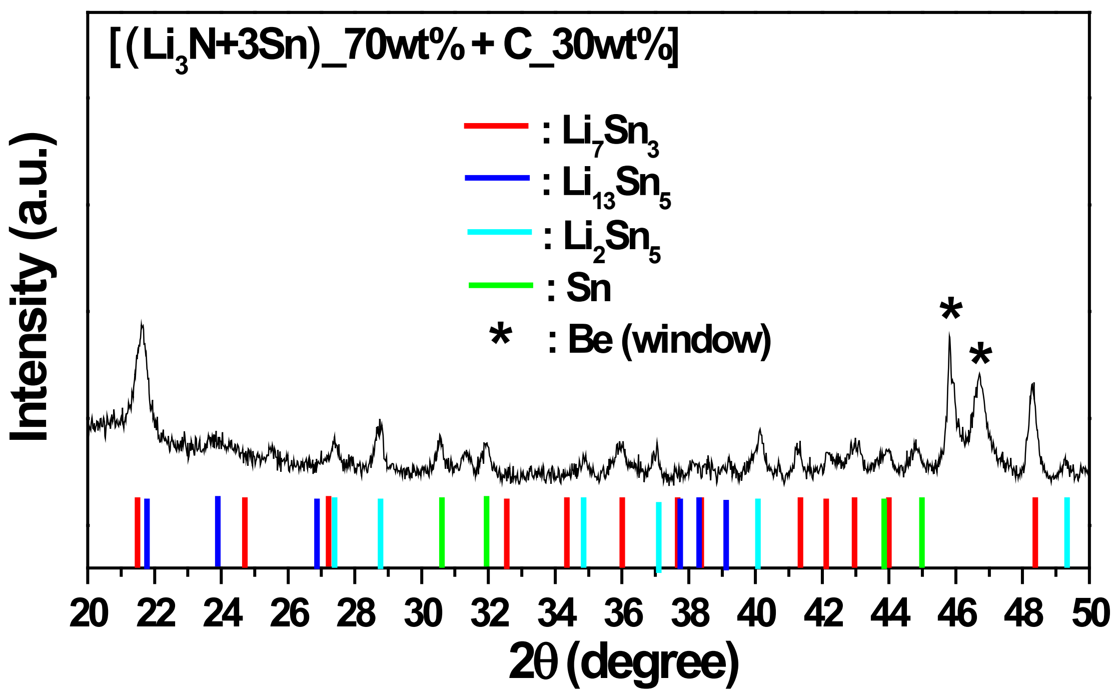
$Li_3N + xSn$ ($x=1,2,3$) ➔

Li-Sn (Li_7Sn_3 & $Li_{13}Sn_5$) + N_2↑

TECHNICAL ACCOMPLISHMENTS

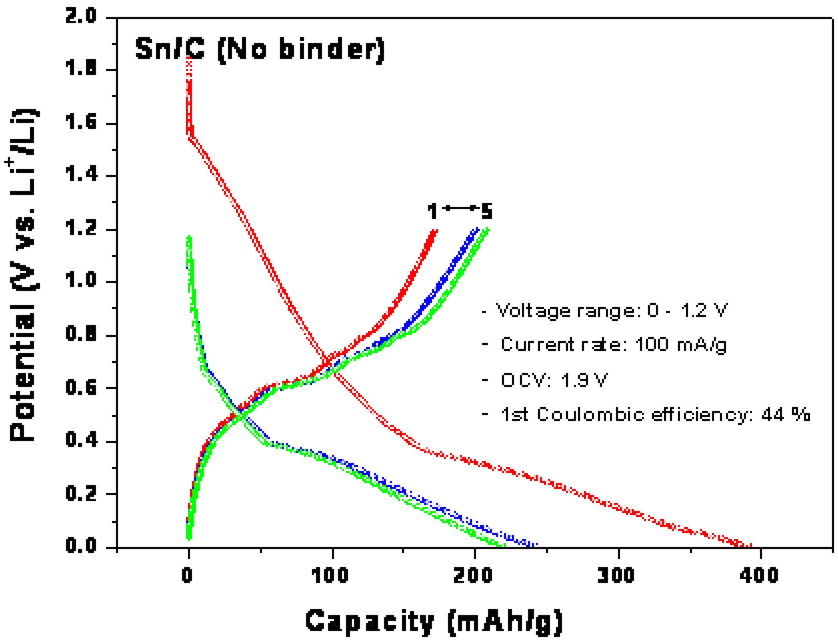
Prelithiated Sn/C composites

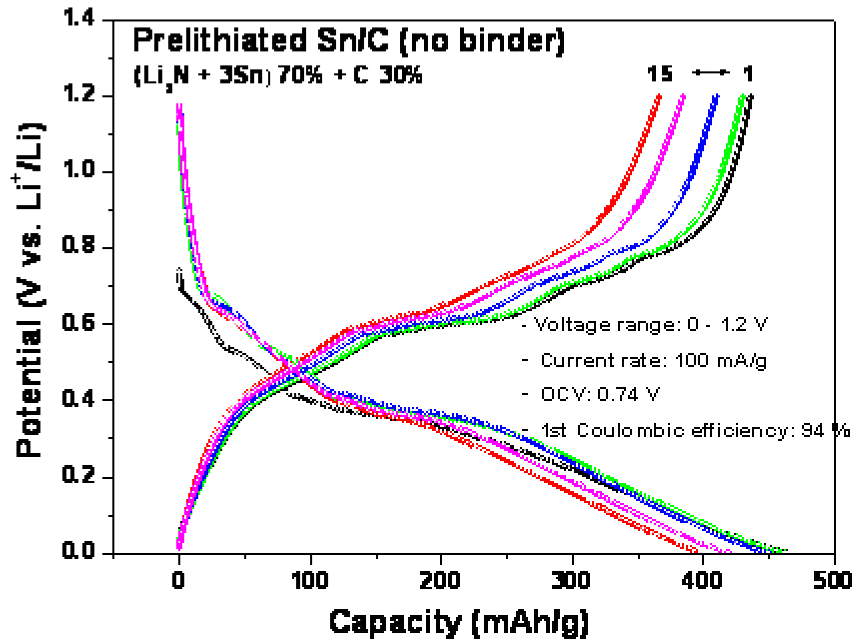




TECHNICAL ACCOMPLISHMENTS

Prelithiated Sn/C composites

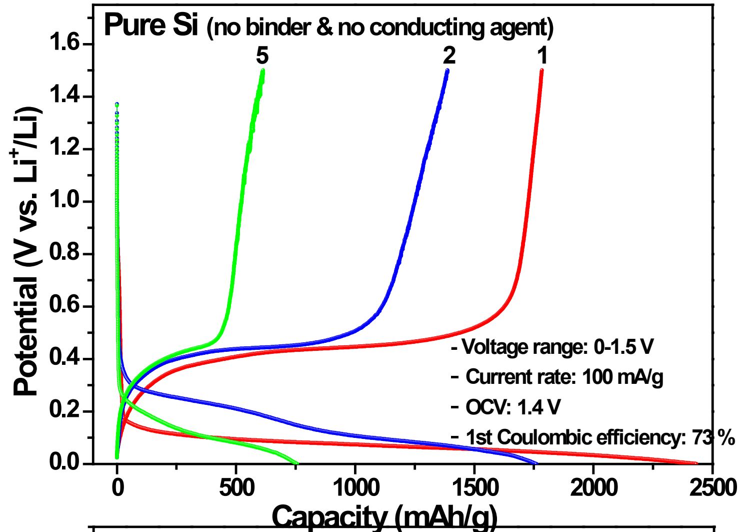


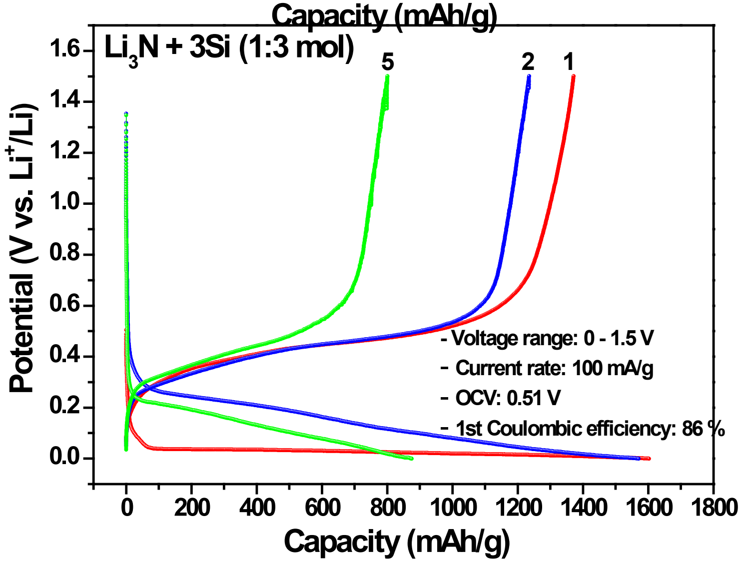


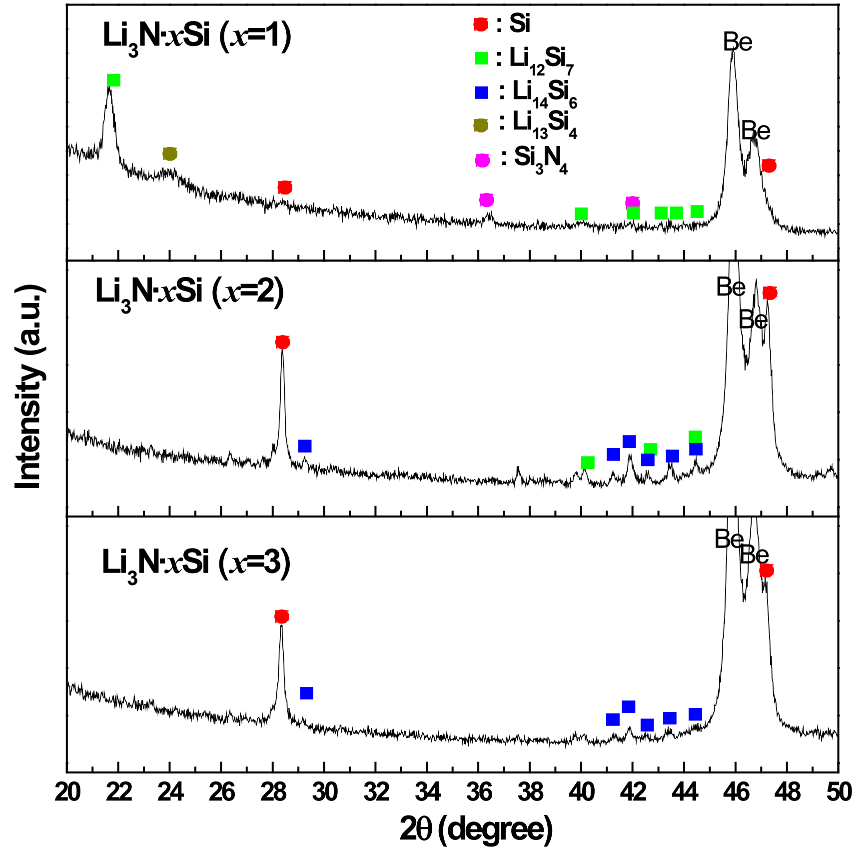
- Carbon inhibits coarsening of tin particles, improves matrix conductivity
- Prelithiation can be carried out after mixing
- Excellent first cycle efficiency, good capacity retention
- Addition of binder is expected to improve performance further

TECHNICAL ACCOMPLISHMENTS

Prelithiated Si synthesized from Li_3N & Si





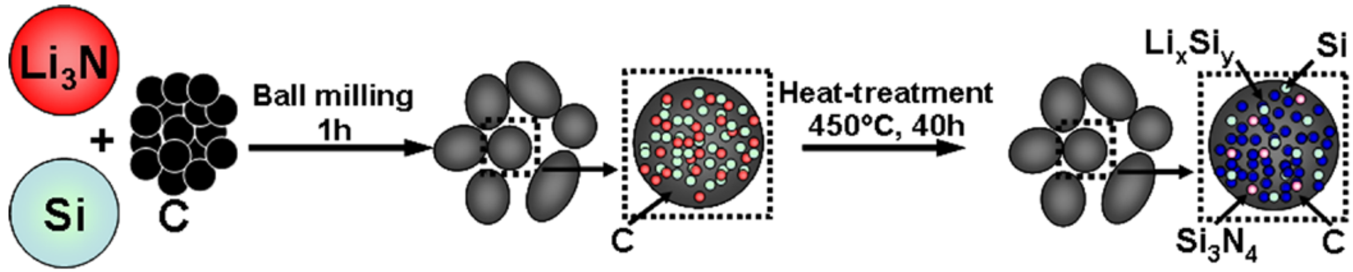


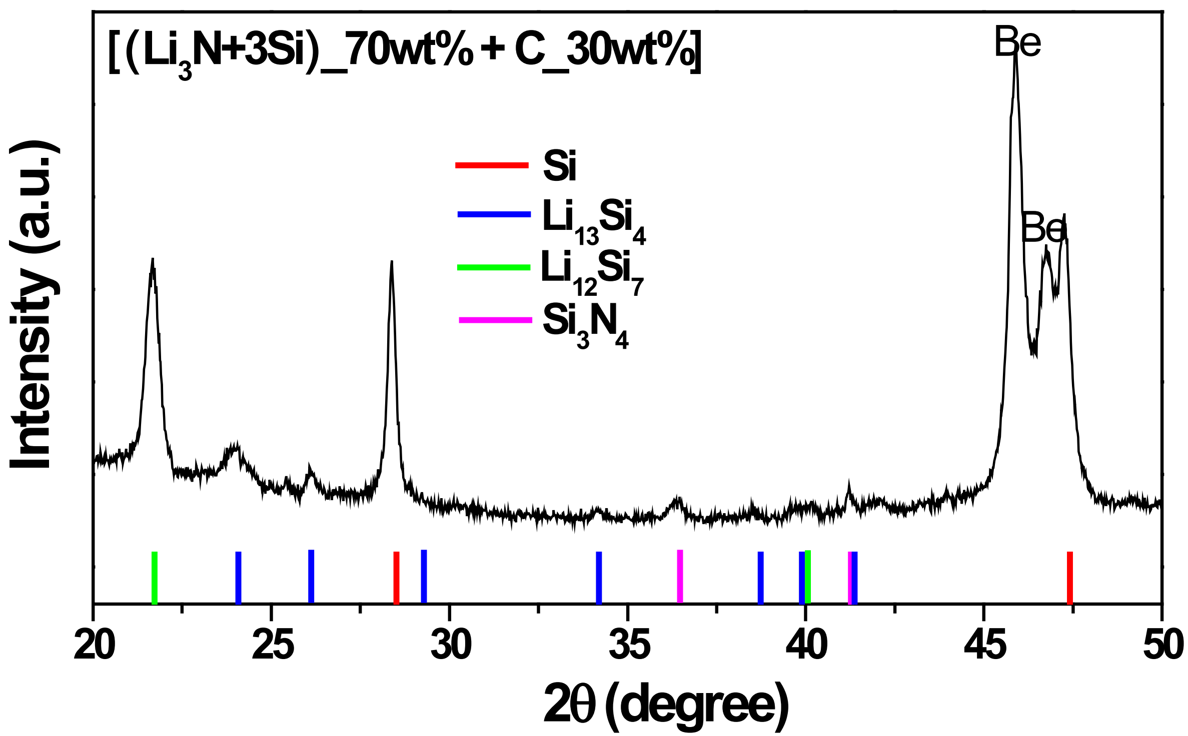
$Li_3N + x$Si (x=1,2,3) →

Si + Li_ySi_z ($Li_{12}Si_7$, $Li_{14}Si_6$, $Li_{13}Si_4$) + Si_3N_4

TECHNICAL ACCOMPLISHMENTS

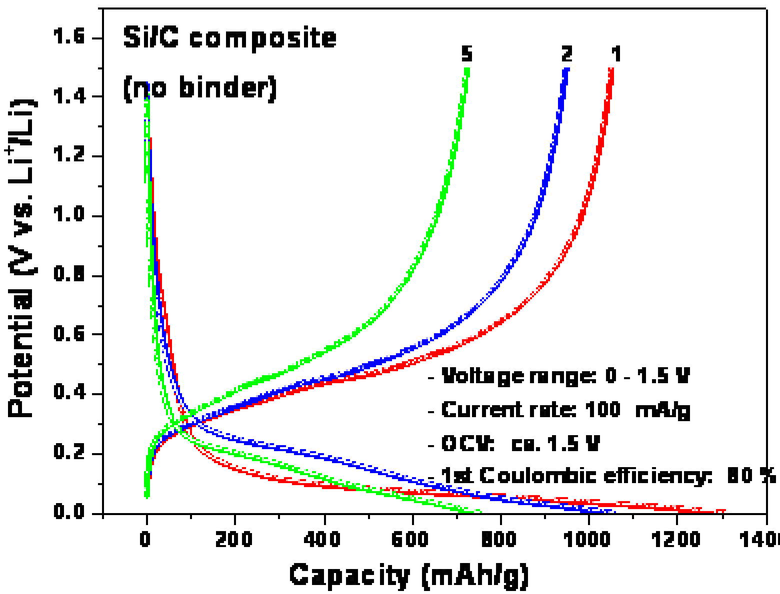
Prelithiated Si/C composites

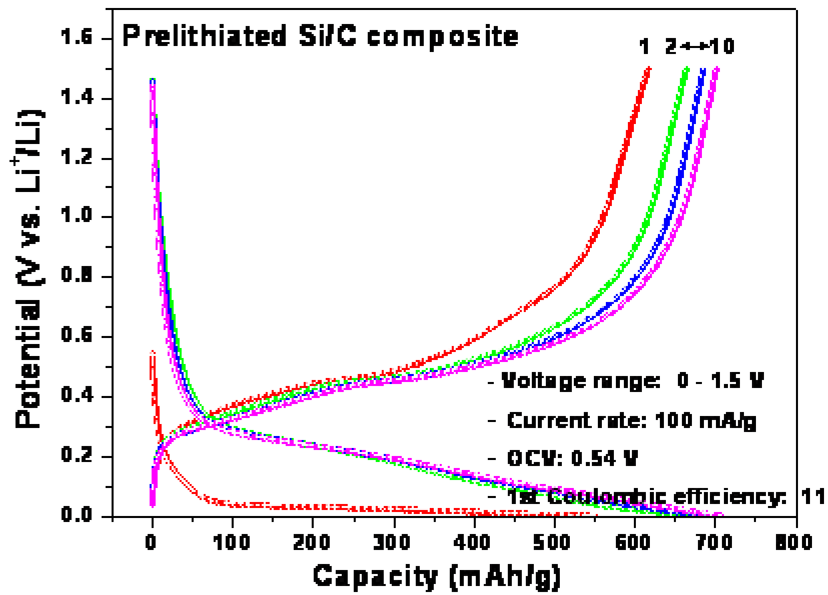




TECHNICAL ACCOMPLISHMENTS

Prelithiated Si/C composites





- While mixing with carbon enhances the performance somewhat, prelithiation improves cycling stability
- First cycle efficiency > 100%, good capacity retention
- Addition of binder is expected to improve performance further

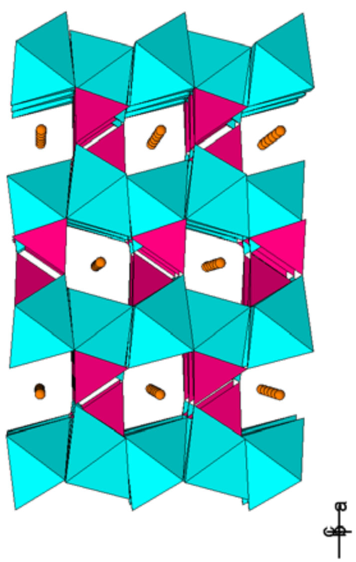
SUMMARY - ANODES

Prelithiated Anodes

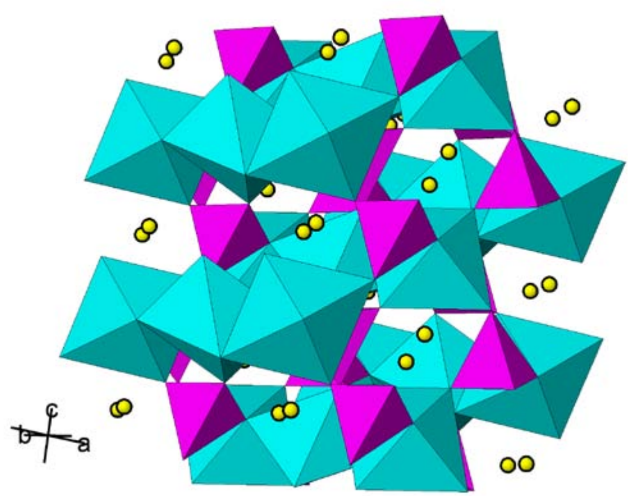
- Reactions of lithium nitride with Sn and Si are simple, safe, effective
- Carbon can be added before reaction, products are free-flowing powders
- Prelithiated Sn & Si electrodes have low open circuit voltages
- Stable SEI formation with little or no irreversible capacity losses
- Small volume changes enhance cycle life

APPROACH - CATHODES

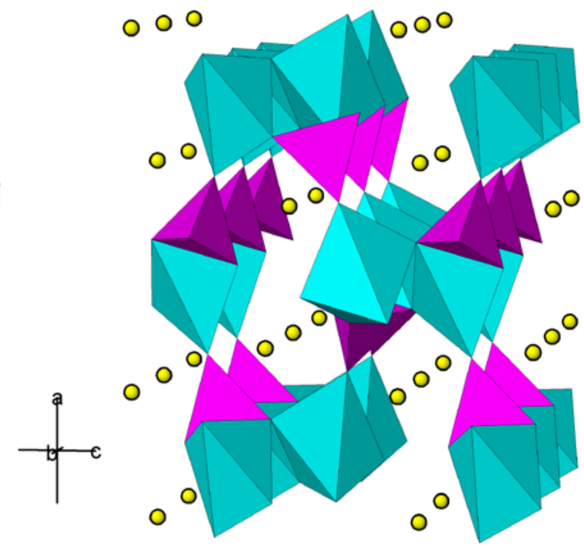
- Explore alternative (non-olivine) phosphates of Co, Cu
- Prepare Na^+, K^+, NH_4^+ phosphates
- Convert to Li^+ phosphates by ion exchange
- Utilize Cu(II)/Cu(III) couple?



Olivine $LiCoPO_4$



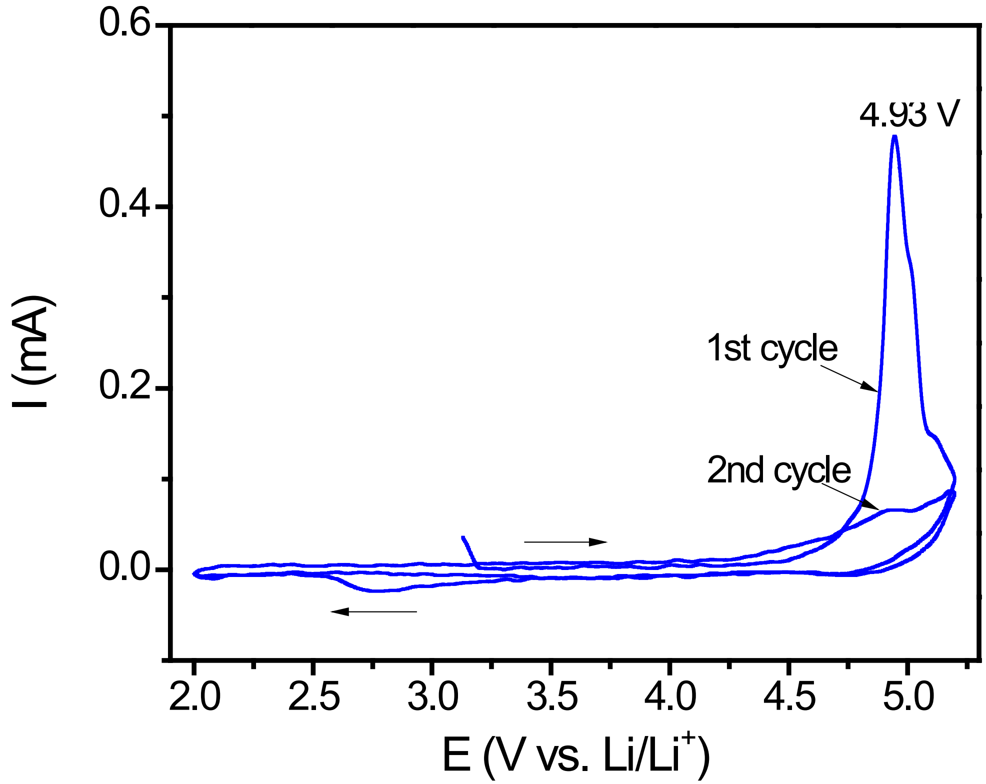
α-$NaCoPO_4$



$NaCuPO_4$

TECHNICAL ACCOMPLISHMENTS

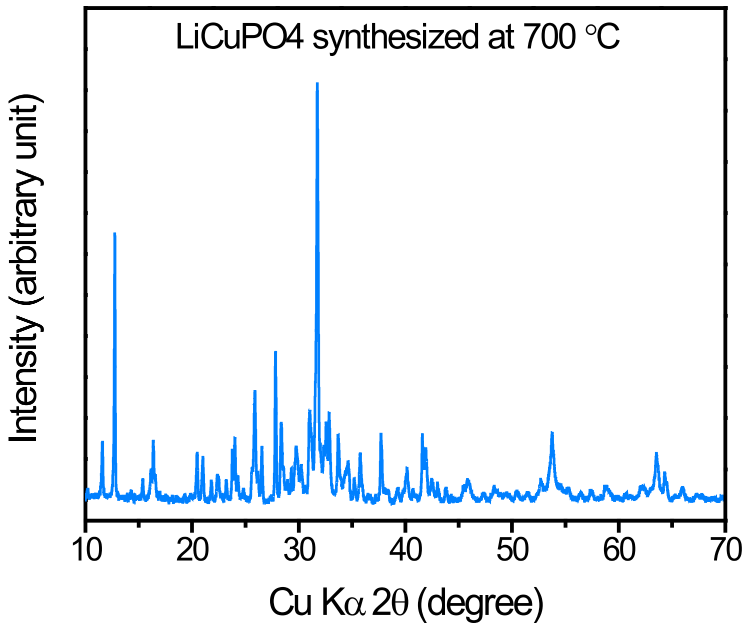
$Li_xNa_{1-x}CoPO_4$ from α-$NaCoPO_4$

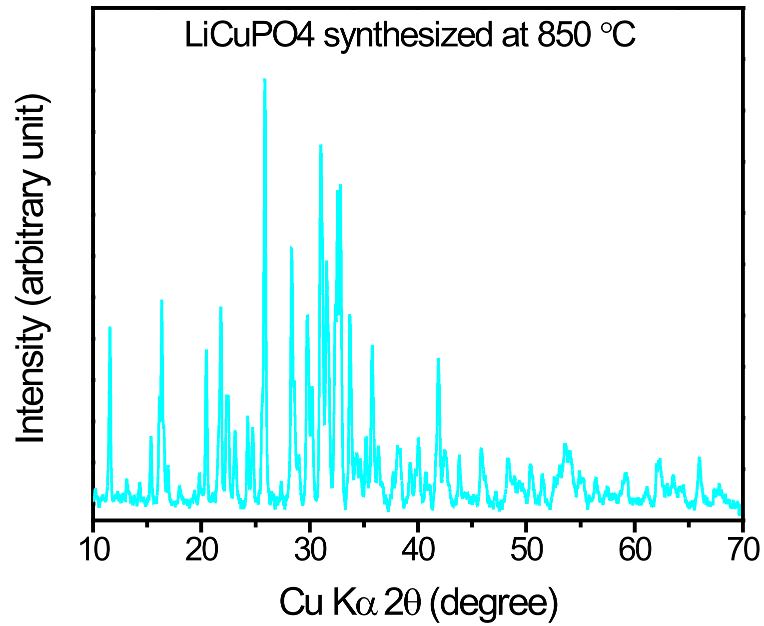


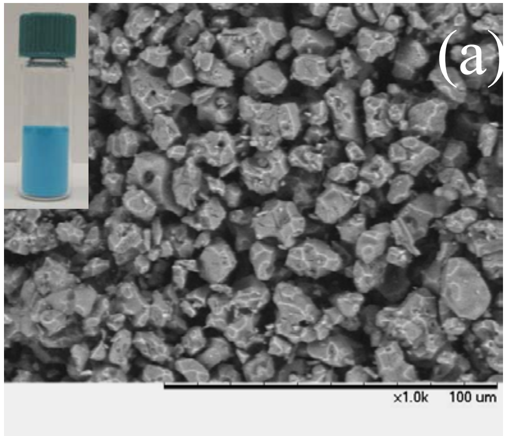
- Ion exchange at 160 °C in hexanol, small lattice shrinkage
- ~ 0.3 Li was extracted at 5 V during the first charge
- Only 0.08 Li was inserted during discharge
- No significant high voltage capacity on subsequent cycles

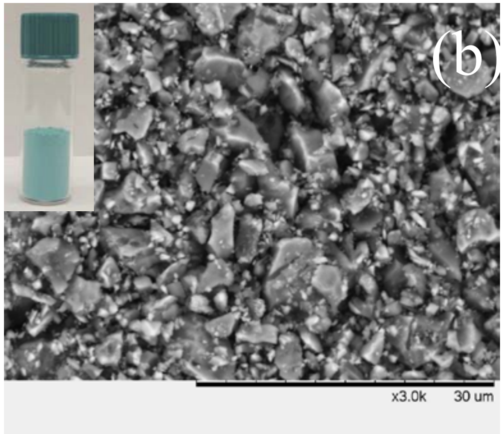
TECHNICAL ACCOMPLISHMENTS

"$LiCuPO_4$"



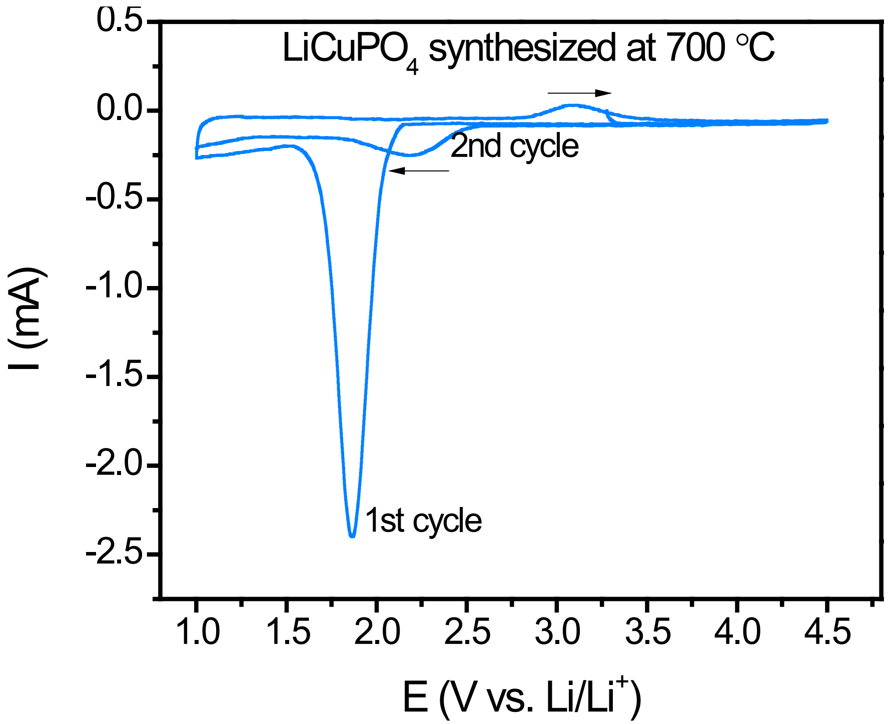


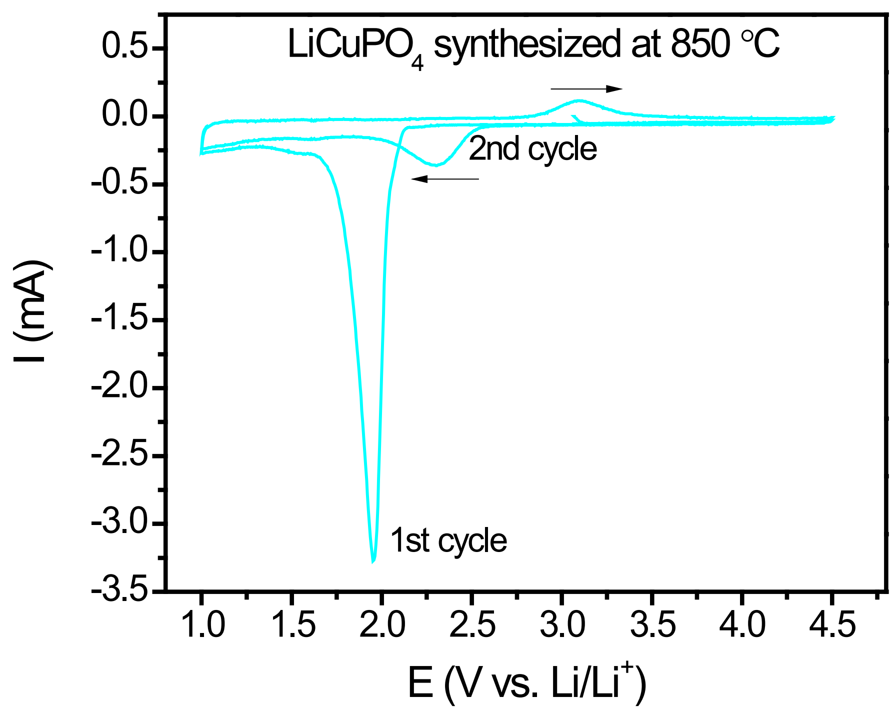




TECHNICAL ACCOMPLISHMENTS

Electrochemical behavior of "$LiCuPO_4$"





- Ex-situ XRD indicates that $LiCuPO_4$ decomposes during the first discharge
- The redox couple in second cycle appears to be $Li_{1.5}CuO_2$ and $Li_{1.5-x}CuO_2$

SUMMARY - CATHODES

Non-olivine Phosphates

- $NaCuPO_4$, $KCuPO_4$, NH_4CuPO_4 decomposed during ion exchange
- Direct electrochemical extraction of Na^+ did not occur below 5.5 V
- Attempts to prepare $LiCuPO_4$ by solid state synthesis resulted in a different phase from that reported by Amine (US Patent 6,319,632)
- The new phase had no charge capacity below 5 V
- The new phase decomposed to $Li_{1+x}CuO_2$ and Li_3PO_4 on lithiation

COLLABORATIONS

- Grey, Cabana (Stony Brook): NMR studies of solid solutions in iron and manganese phosphates
- Kostecki (LBNL): Raman and FTIR characterization of materials and electrodes
- Srinivasan (LBNL): visualization and modeling of current and charge distribution in composite electrodes
- Chen, Doeff, Cabana (LBNL) and Misra, Toney (SSRL): *in situ* X-ray diffraction and absorption
- Radmilovic, Lee et al. (NCEM): High resolution TEM of anode and cathode materials
- Kunz, Tamura, Rotenberg (ALS): XAS and XPS of anode materials

Each of these collaborations has already or soon will lead to a major publication.

FUTURE WORK

CELL ANALYSIS

- Extend charge distribution study to electrodes with a range of different compositions, thicknesses, and porosity.
- Extend study to electrodes salvaged from commercial cells.

ANODES

- Identify binders and solvents that are compatible with partially prelithiated anode materials.
- Establish optimum prelithiation levels for tin, silicon, graphite.

CATHODES

- Continue to search for alternative cathode materials with high energy density, low cost, and safety.
- Increase electrode loading of conventional materials through improved microstructures and intrinsic conductivity.

PROJECT SUMMARY

CELL ANALYSIS

- A new technique was developed to visualize charge distribution in composite electrodes.
- The observed distributions in plane and in cross section are consistent with expectations from modeling.

ANODES

- Partial prelithiation of anodes leads to reduced capacity losses, more efficient cycling.
- Excellent results for tin and silicon anodes.

CATHODES

- Continued to search for non-olivine phosphate cathode materials with high energy density, low cost, and safety.
- In common with all other groups, the challenge remains.