

Olivines and Substituted Layered Materials

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Project ID es052

Overview

Timeline

- ▶ Start-ongoing
- ▶ Ends Sept. 30, 2011 (up for renewal)

Budget

- 100% DOE
- 545k FY10
- 545k FY11
- Currently supports one postdoc and one graduate student

Barriers

- ▶ Barriers addressed
 - ▶ Cost
 - ▶ Power and Energy Density
 - ▶ Cycle Life

Partners/Collaborations

- BATT-LBNL: J. Cabana-Jimenez, T. Richardson, G. Chen, V. Battaglia
- Other Institutions: A. Mehta (SSRL), E. Cairns (U.C. Berkeley), A. Deb (U. Michigan)

Objectives

- ▶ Develop lower cost cathode materials with improved performance and low toxicity, consistent with the goals of FreedomCar/USABC.
- ▶ Depending on cell design and choice of material, cathodes can be up to 50% of the materials cost in a battery
 - Lower cost of $\text{Li}[\text{Ni}_x\text{Co}_y\text{Mn}_z]\text{O}_2$ electrodes by full or partial replacement of Co with other metals-understand effects of substitution on structure and performance.
 - Al substitution to improve cycling and thermal behavior
 - Ti substitution to increase capacity
 - Develop low-cost methods for synthesizing high performance electrode materials
 - Spray Pyrolysis
 - Aqueous processing-environmentally friendly
 - Easily scaled, can be made continuous
 - Can control particle size, morphology, coatings
 - Minimizes heating times and processing steps (e.g., grinding), lowering processing costs

Milestones

► FY '10 Milestones

- Synthesize and electrochemically characterize $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1-y}\text{Al}_y\text{Mn}_{0.45}]\text{O}_2$ series. (Jun.'10) Achieved
- Develop spray pyrolysis method for synthesis of cathode materials, including polyanionic compounds. (Sep.'10) Achieved

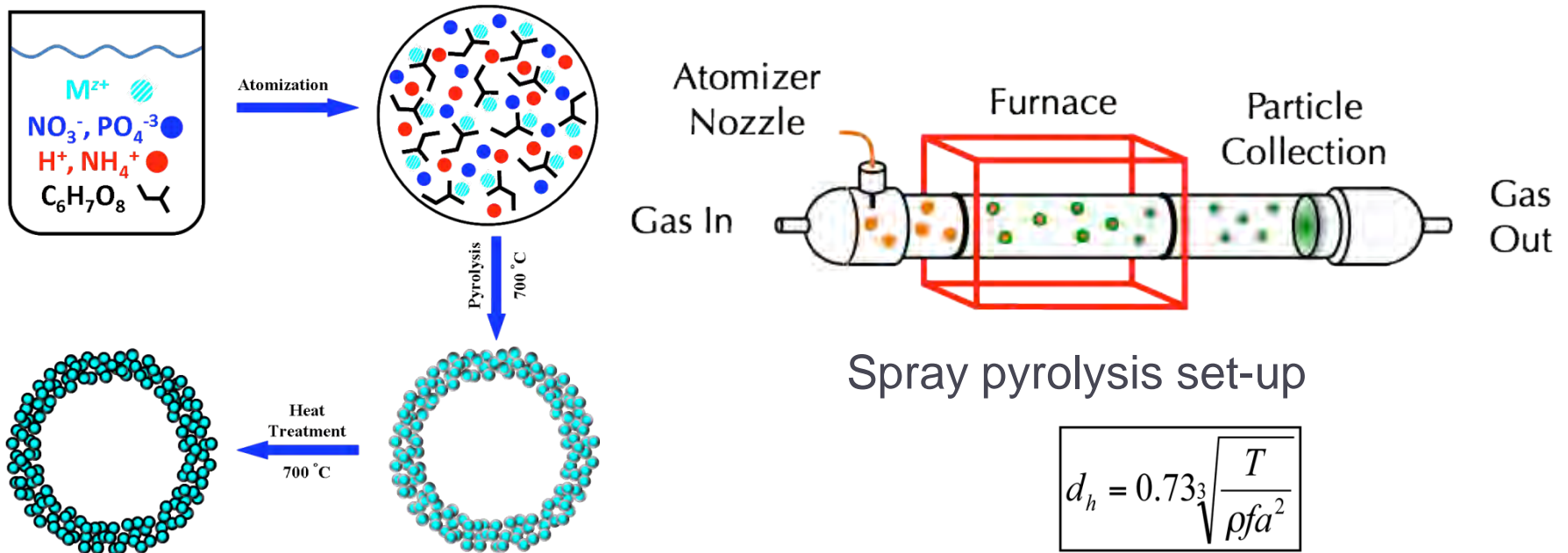
► FY '11 Milestones

- Complete structural and electrochemical characterization of $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1-y}\text{Al}_y\text{Mn}_{0.45}]\text{O}_2$ system using synchrotron techniques. (Jun. 11) on track
- Finish survey of Ti-substituted NMCs and select most promising materials for further study. (Jun. '11) on track
- Decrease particle size of polyanionic compound/C composites prepared by spray pyrolysis. Investigate synthesis of new materials by this method and others for comparison. (Sep. '11) on track (Caveat: we may not need to decrease particle size, depending on material of interest)

Approach / Strategy

- ▶ Cathode materials are synthesized and characterized electrochemically. Relevant physical properties are measured in conjunction with the diagnostics teams. Emphasis is placed on reducing cost two ways: 1) decreasing the content of expensive components such as Co and 2) developing low-cost, environmentally friendly synthesis methods.
 - $\text{Li}[\text{Ni}_x\text{Co}_{1-2x-y}\text{M}_y\text{Mn}_x]\text{O}_2$; $\text{M}=\text{Al}, \text{Ti}$
 - In FY10, this was extended to low Co compositions ($x=0.45$)
 - Investigate origins of the beneficial effects of Al and Ti substitution
 - Investigate structural and electrochemical effects of substitution
 - Spray Pyrolysis
 - Uses aqueous solutions of precursors (environmentally friendly)
 - Can co-synthesize carbon coatings by incorporating soluble carbon sources
 - Very pure products
 - Spherical particles are easy to process into electrodes
 - Can control carbon contents, particle sizes and morphologies, porosities, etc.
 - Does not require exotic or expensive equipment

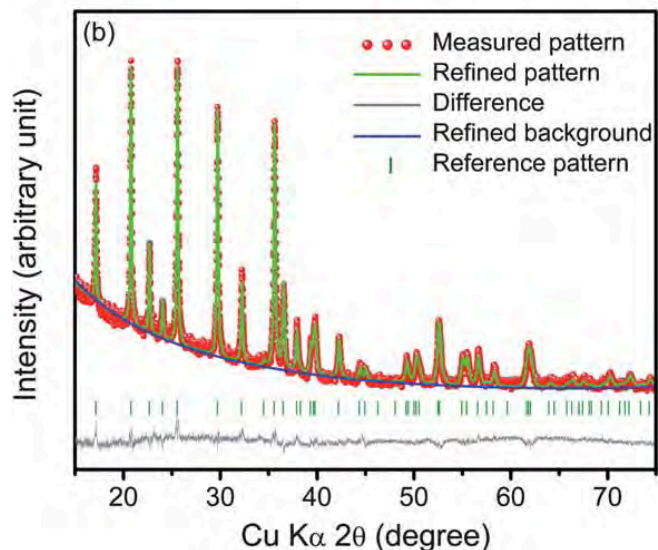
Spray Pyrolysis of Olivines



Precursors: citric acid, $\text{NH}_4\text{H}_2\text{PO}_4$, lithium nitrate, iron nitrate or cobalt acetate dissolved in water

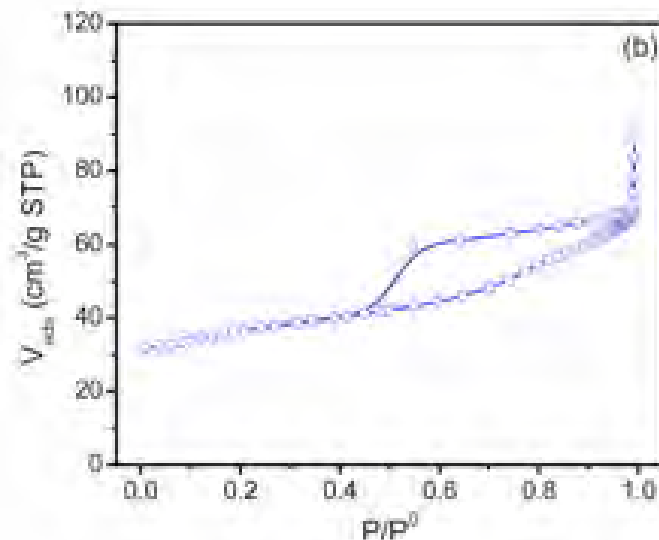
Particle diameter is determined by atomizer frequency, geometry of furnace tube, and precursor concentrations

Structure and Characterization-LiFePO₄/C



Phase-pure LFP

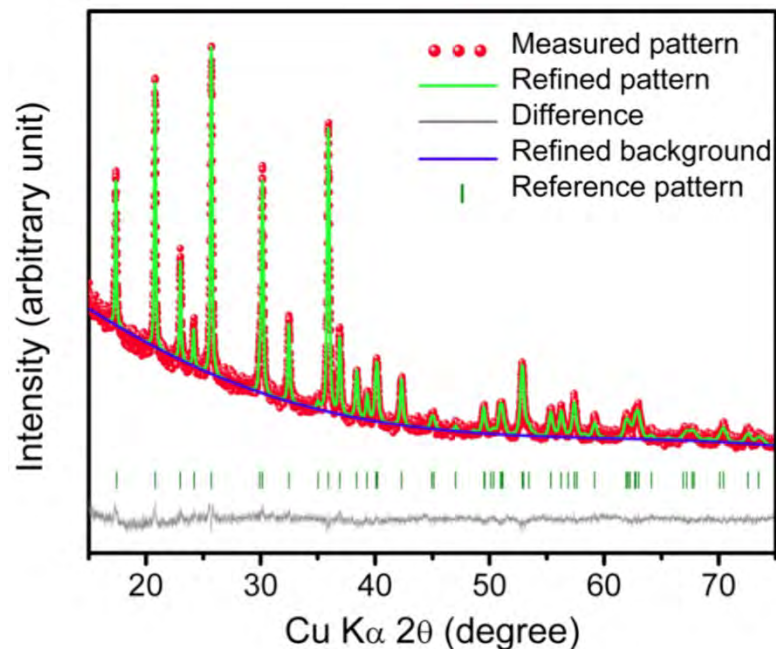
Primary particle size ~70nm
7.2% C content



BET N₂ adsorption-desorption isotherms

102 M²/g; pore size 75 nm
Behavior consistent with nanoporosity

Structure and Characterization-LiCoPO₄/C

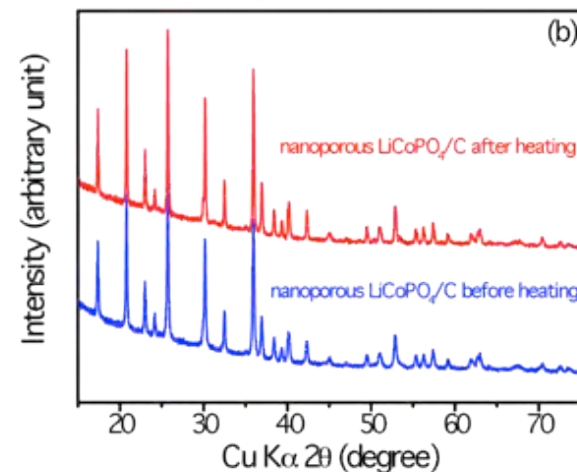
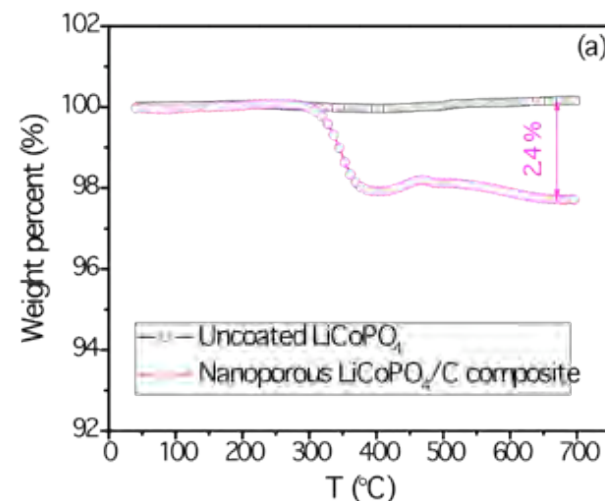


Phase-pure LCP

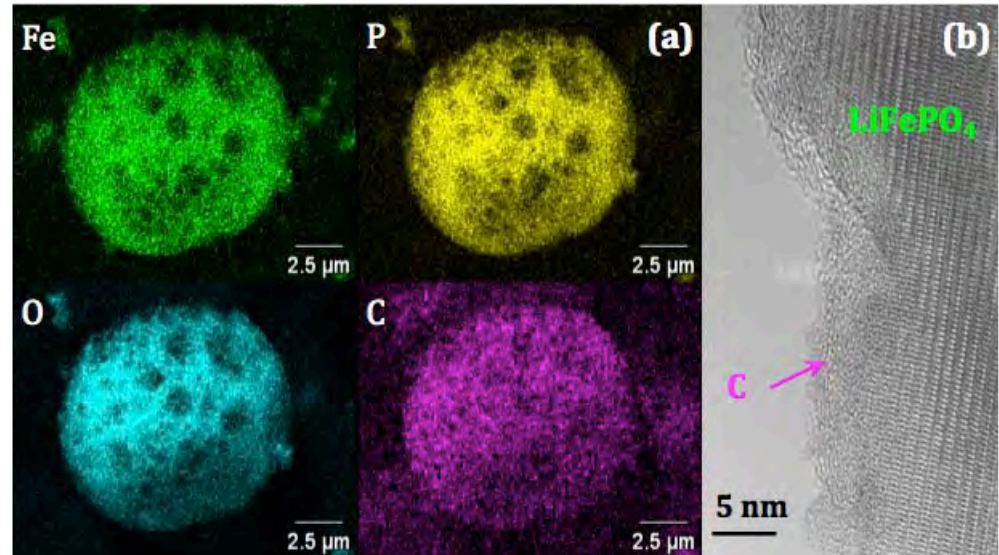
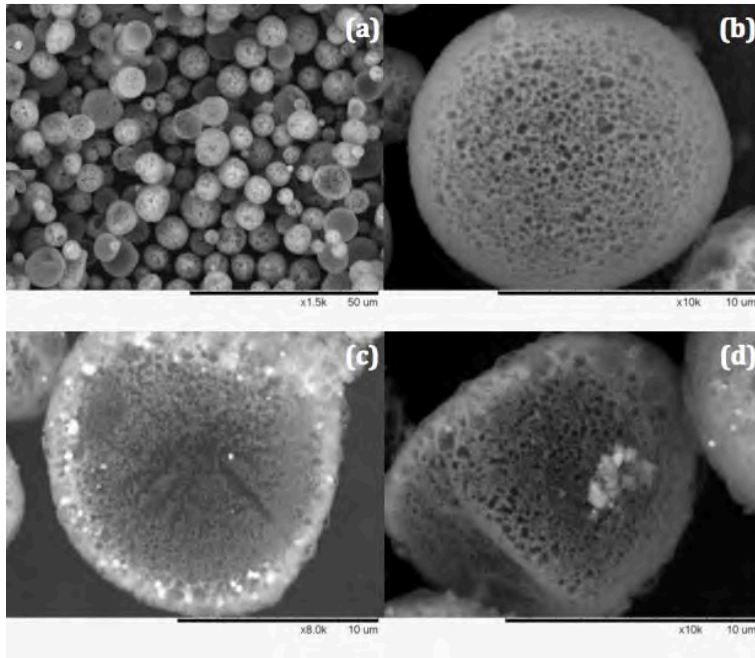
Primary particle size ~70 nm

2.4% C

76 M²/g, 68 nm pore size

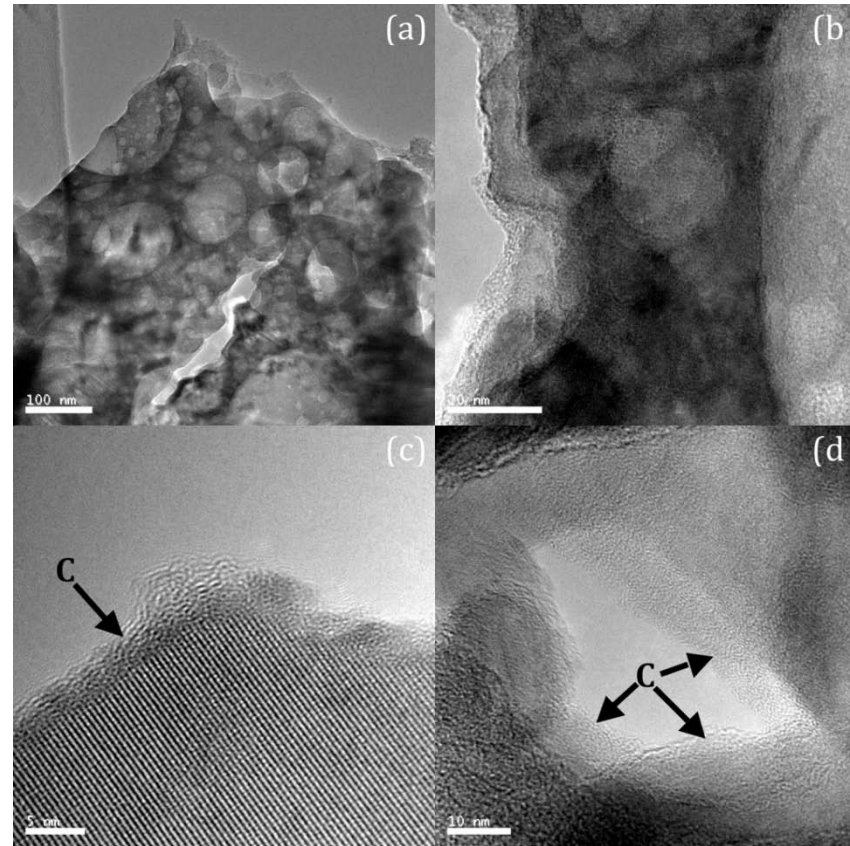
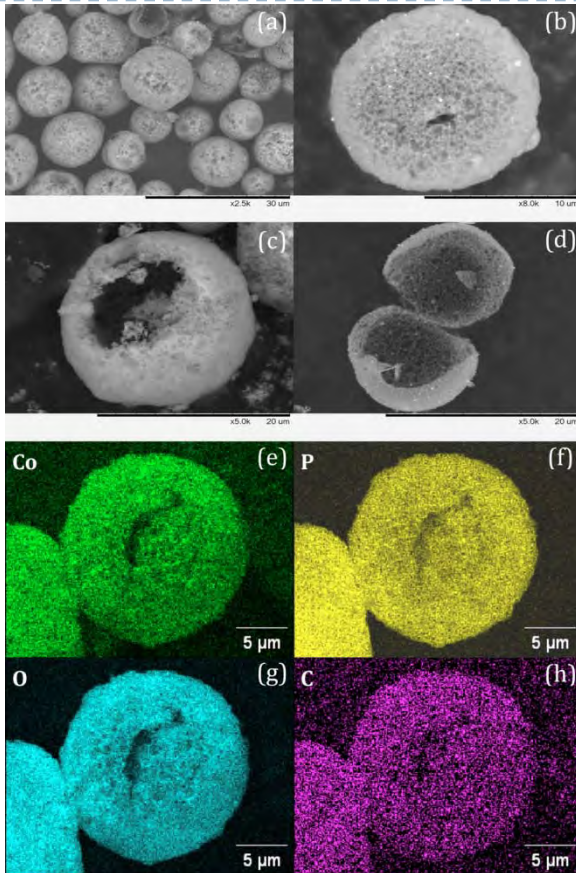


Particle Morphologies-LiFePO₄/C



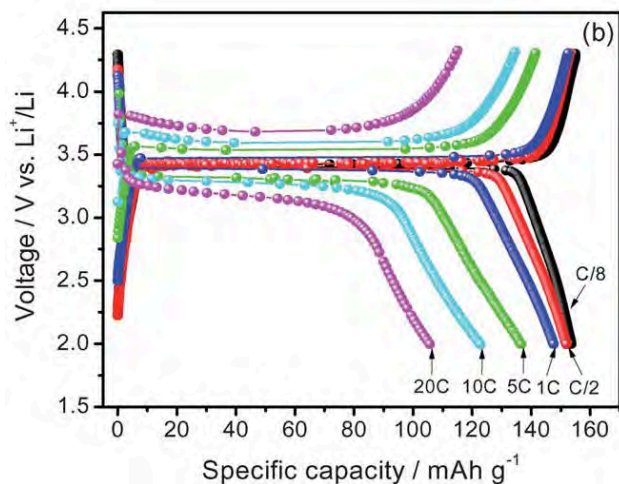
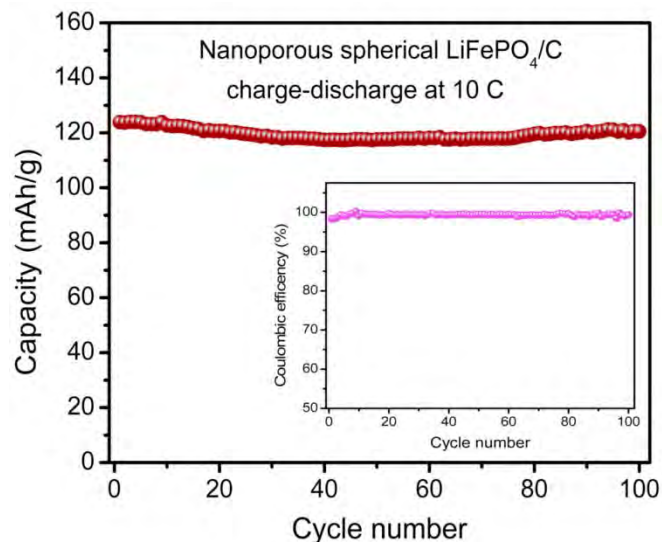
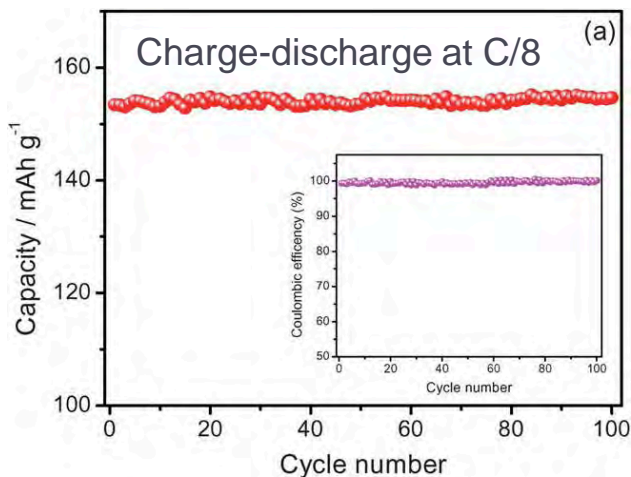
~10 μm nanoporous spheres with uniform composition and distribution of carbon. TEM image shows amorphous carbon coating on an interior surface of a broken sphere.

Particle Morphologies LiCoPO₄/C



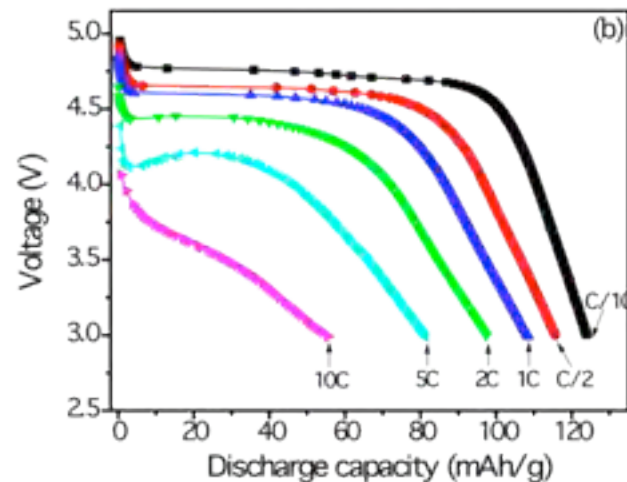
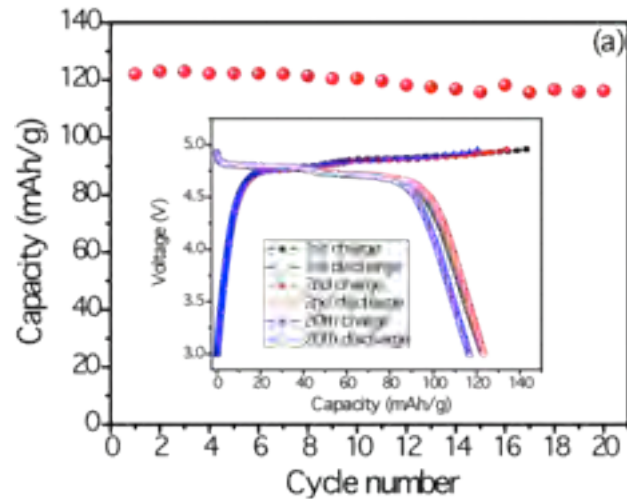
~10 μm nanoporous spheres, some hollow, with excellent homogeneity. TEM images show thin amorphous carbon layers on surfaces and in pores.

Electrochemical Performance of LiFePO_4/C



Excellent rate capability
120 mAh/g cycled at 10C rate
High coulombic efficiencies
Excellent cycling

Electrochemical Performance of LiCoPO_4/C



Typical two-plateau voltage profile

1wt. % LiBOB used to decrease coulombic inefficiencies

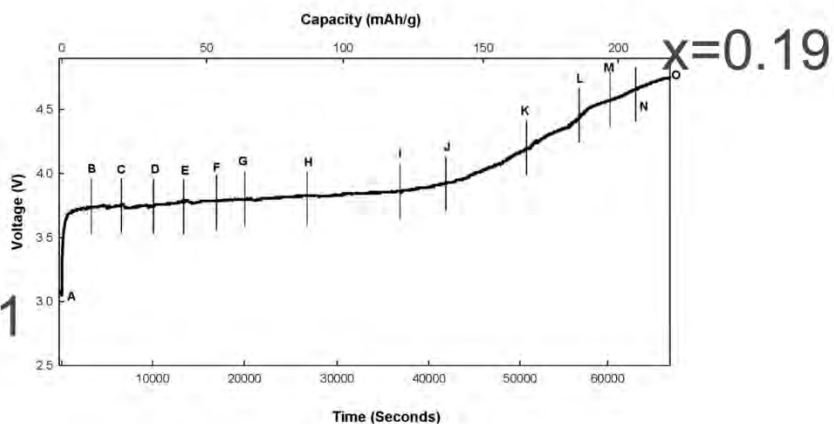
97% efficient after 1st cycle

Stable cycling of 123 mAh/g at C/10

82 mAh/g at 5C

Excellent rate capability due to nanostructuring

XAS Studies of $\text{Li}_x[\text{Ni}_{0.4}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mn}_{0.4}]\text{O}_2$



C/25 charge and discharge

In situ XAS measurements at points A-O

White-line energy shift vs. x (top right)

$1 \leq x \leq 0.55$, $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$

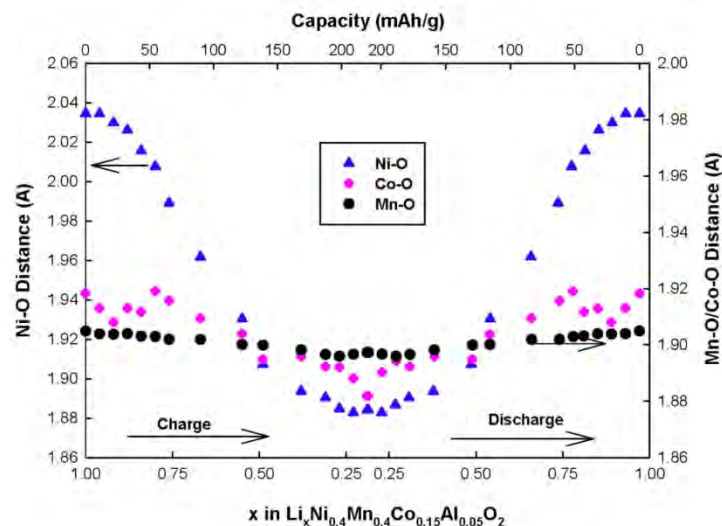
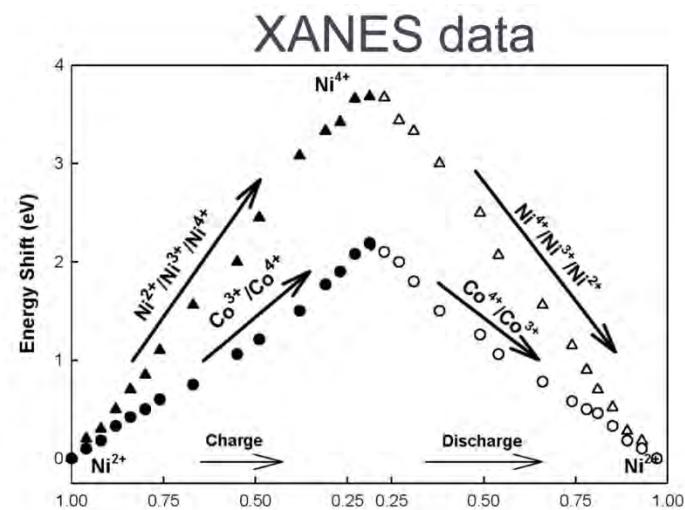
$0.55 \leq x \leq 0.23$, $\text{Ni}^{3+} \rightarrow \text{Ni}^{4+}$

Co participates throughout!

M-O bond distances (bottom right)

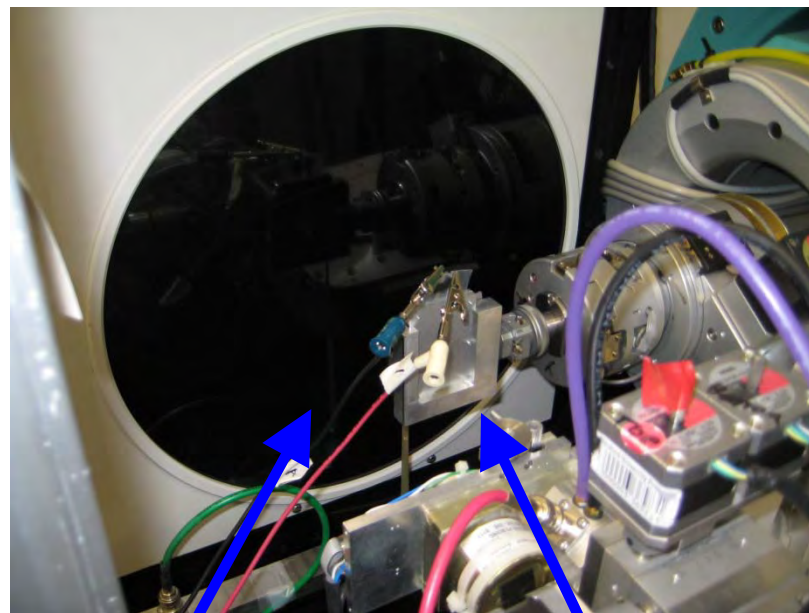
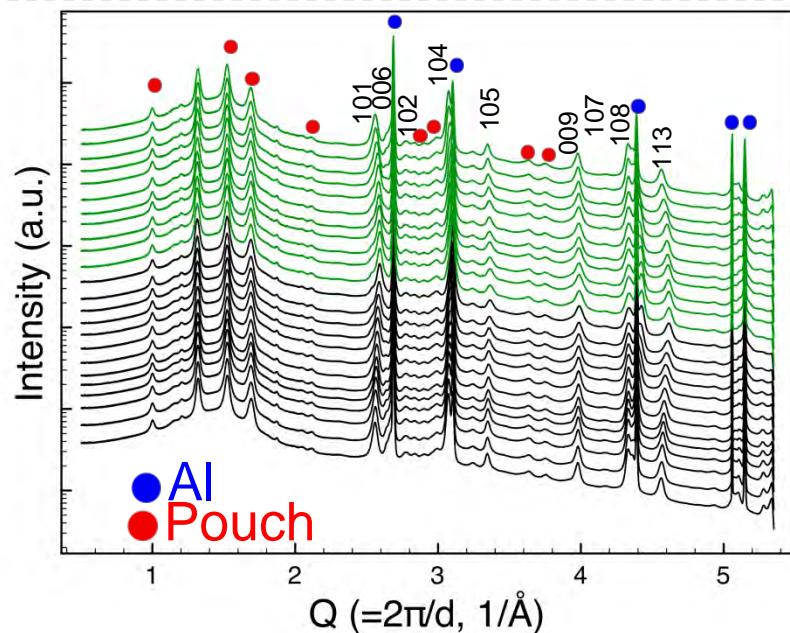
Biggest changes for Ni-O

Very good reversibility



EXAFS data

In situ Synchrotron XRD Studies



Detector

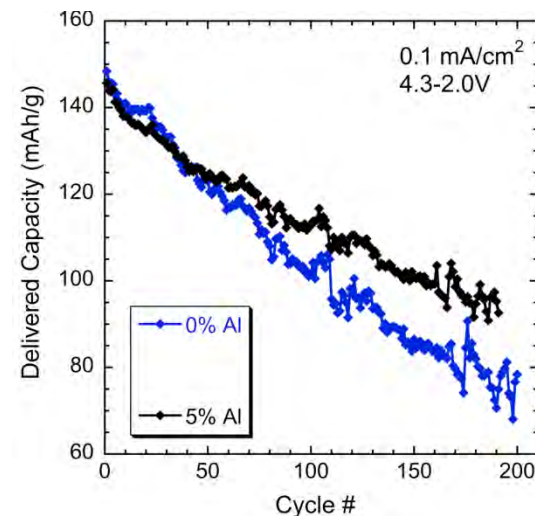
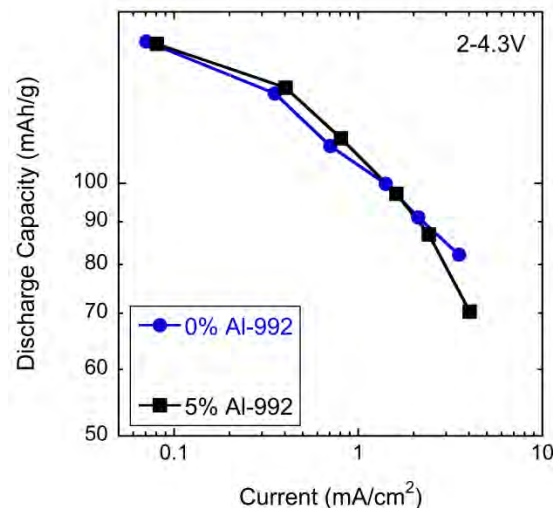
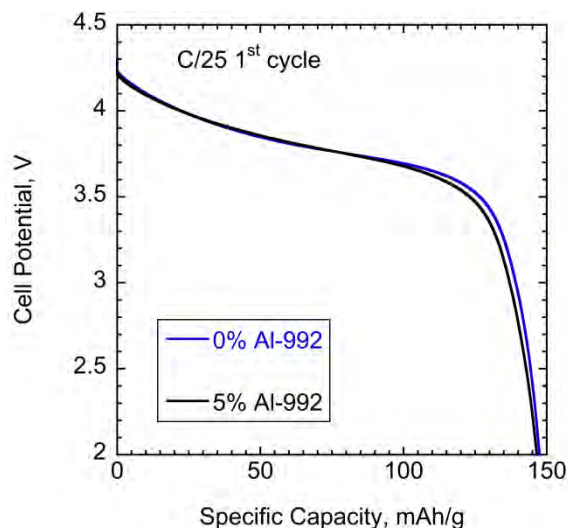
Pouch Cell

C/25 Charge Discharge



SSRL BL 11-3

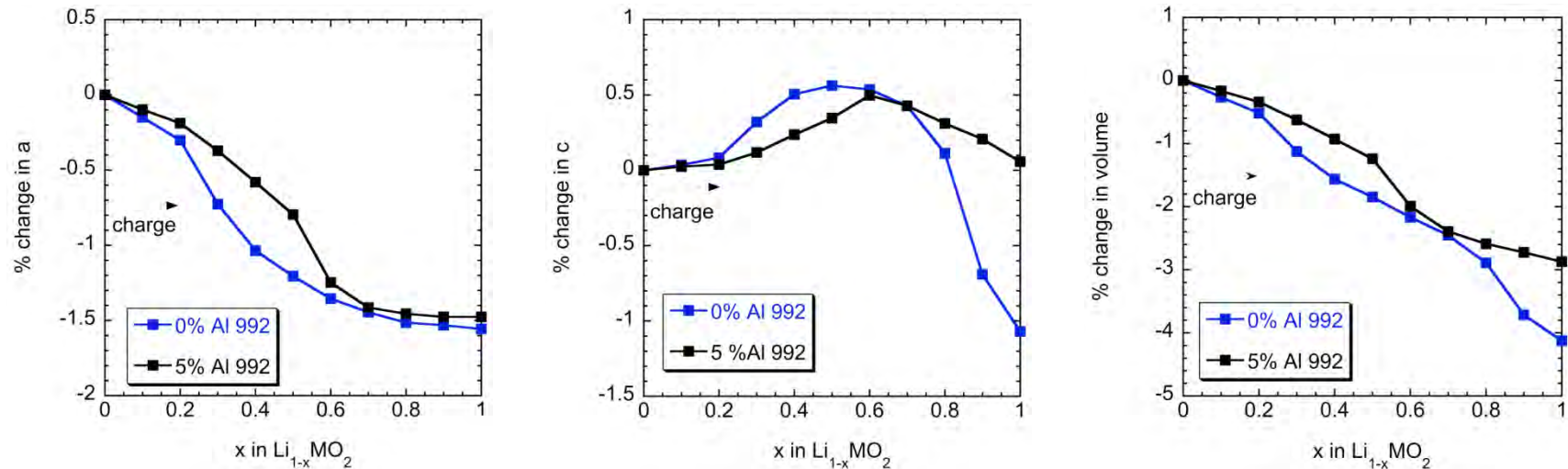
Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}O₂]-effect of Al substitution



Replacement of ½ the cobalt does not affect practical capacity or rate capability. Extended cycling shows better capacity retention of the Al-substituted variant (Li[Ni_{0.45}Co_{0.05}Al_{0.05}Mn_{0.45}]O₂).

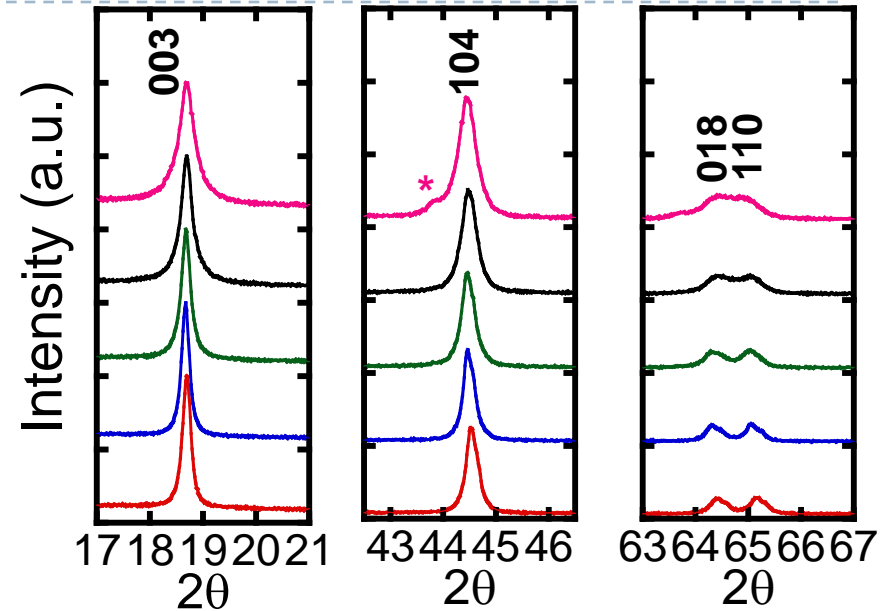
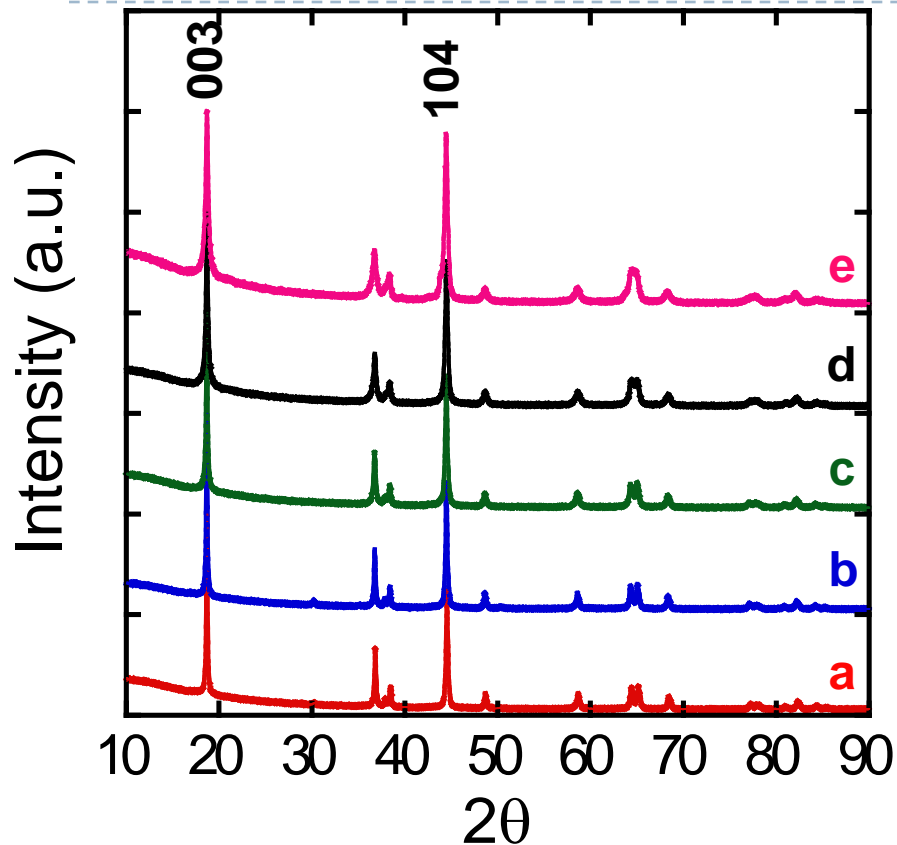
Why does Li[Ni_{0.45}Co_{0.05}Al_{0.05}Mn_{0.45}]O₂ cycle better than Li[Ni_{0.45}Co_{0.1}Mn_{0.45}]O₂?

Lattice Parameter Changes During Charge/Discharge



A smaller change in the c -parameter during charge is observed for $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.05}\text{Al}_{0.05}\text{Mn}_{0.45}]\text{O}_2$ than for $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1}\text{Mn}_{0.45}]\text{O}_2$, which may explain the improved cycling performance

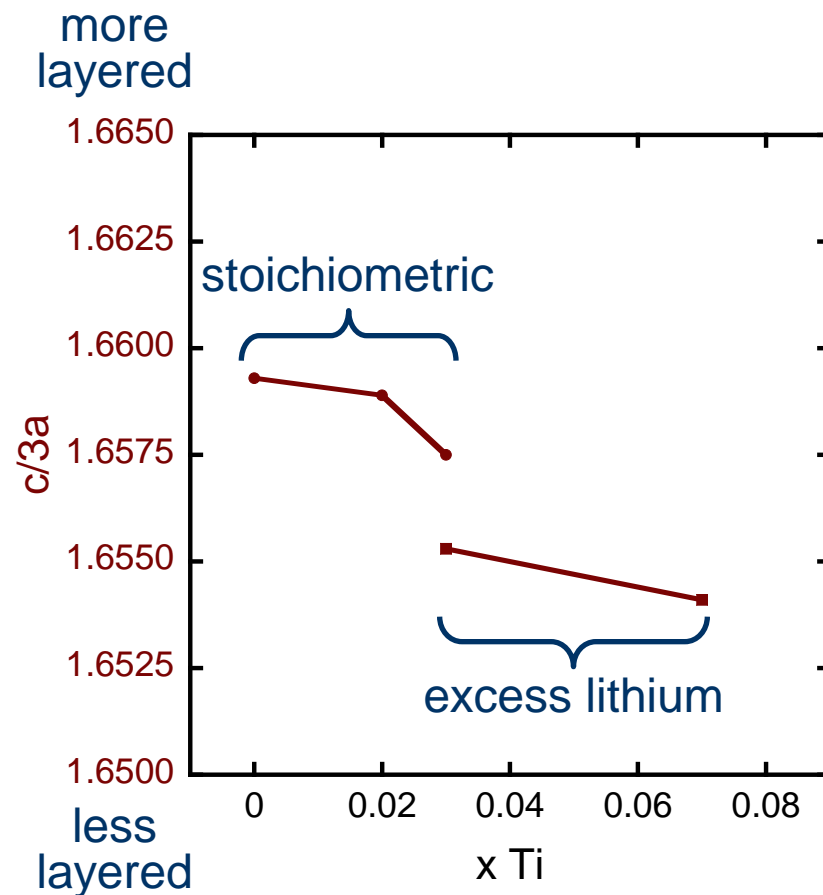
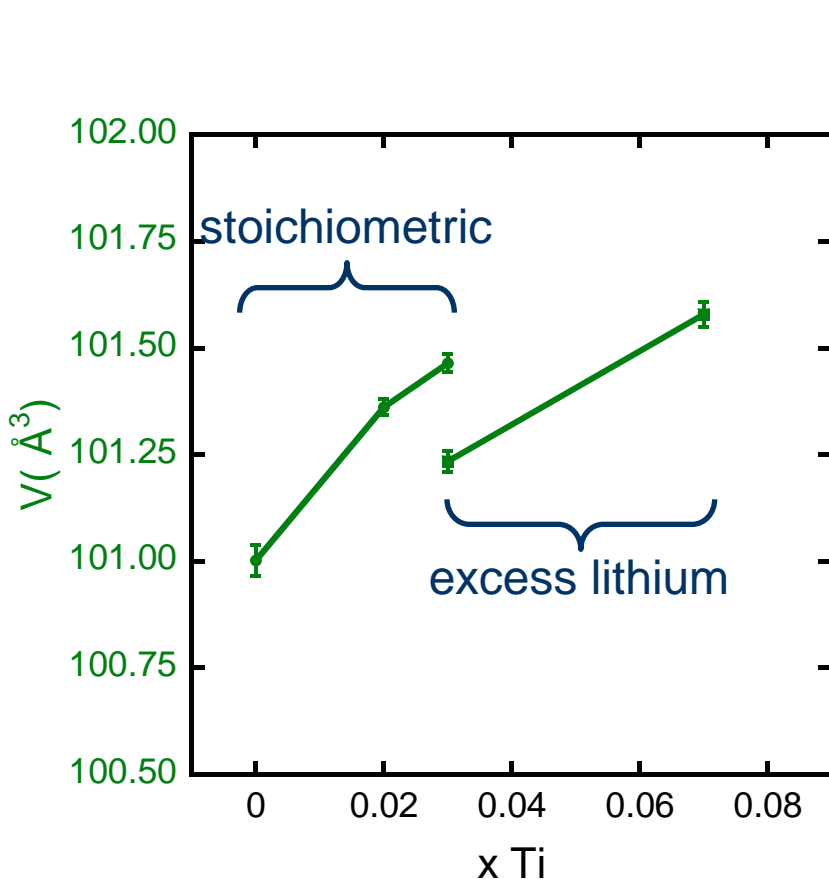
Ti Substitution in the 333 System



- Limited Ti-substitution solubility
- $\text{Li}[\text{Ni}_{0.33}\text{Co}_{0.33-y}\text{Ti}_y\text{Mn}_{0.33}]\text{O}_2$ or
- $\text{Li}_{1+x}[\text{Ni}_{0.33}\text{Co}_{0.33-y}\text{Ti}_y\text{Mn}_{0.33}]_{1-x}\text{O}_2$

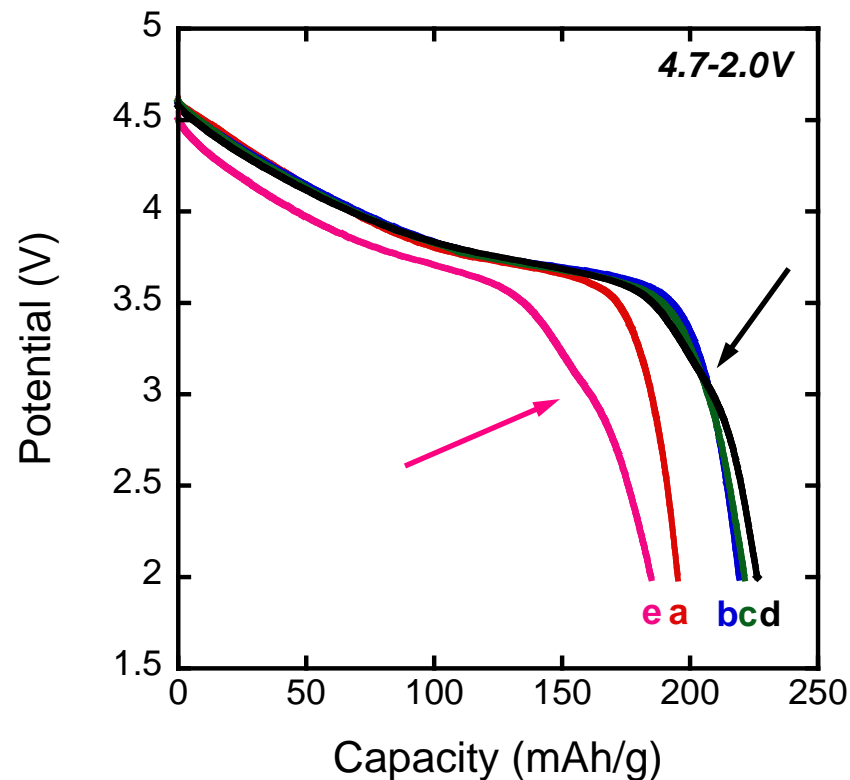
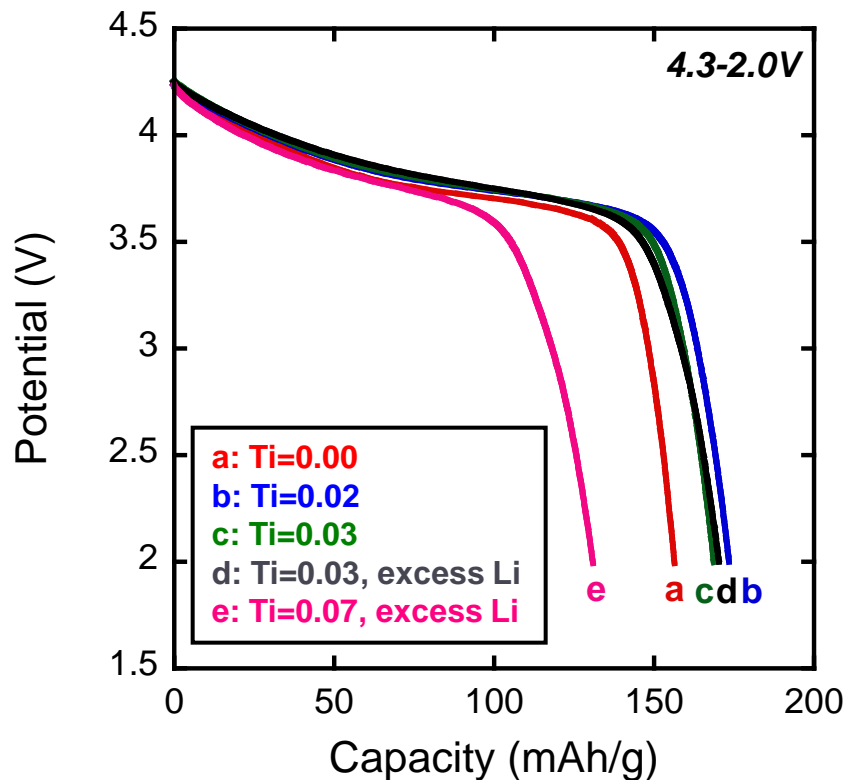
a: Ti=0.00
b: Ti=0.02
c: Ti=0.03
d: Ti=0.03, excess Li
e: Ti=0.07, excess Li

Rietveld Refinement



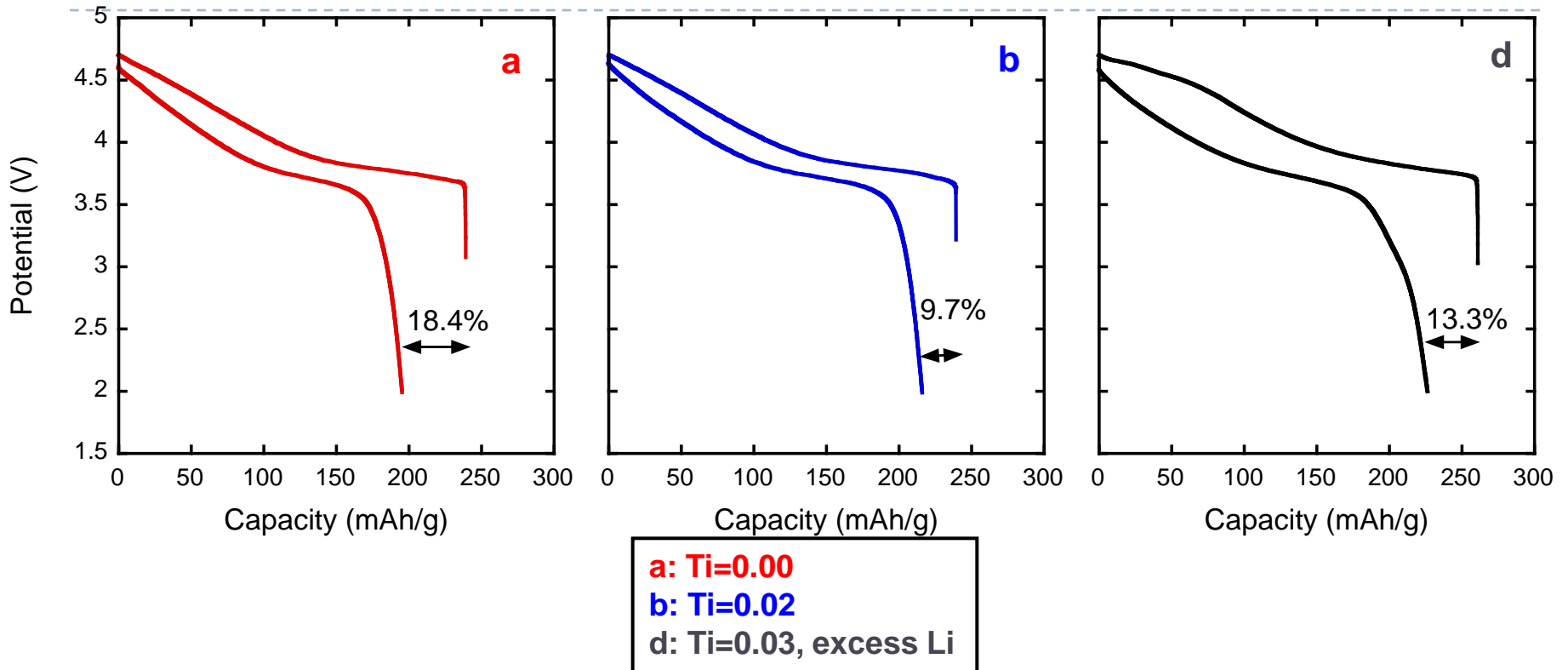
Increase in cell volume is consistent with substitution of larger Ti^{4+} for smaller Co^{3+}

Discharge Profiles



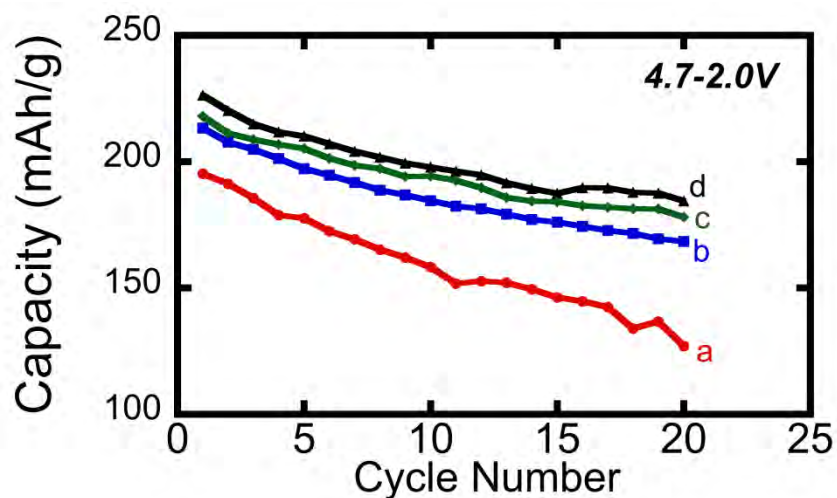
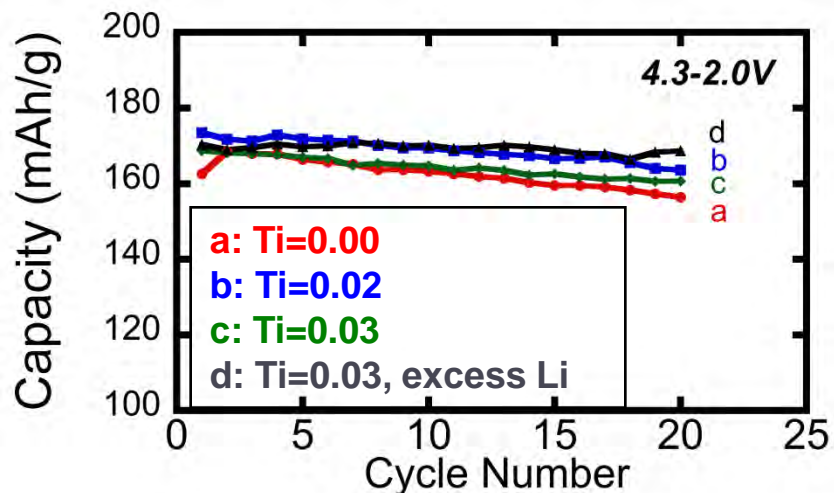
Ti-substitution improves capacity (with exception of impure sample)
Li-excess materials behave differently-evidence of formation of redox active Mn after charge to high potentials.

First Cycle Coulombic Inefficiencies



First cycle coulombic inefficiencies are characteristics of NMCs and are seen even with very conservative charge limits (kinetic limitations)
Ti substitution decreases inefficiencies, increasing discharge capacities
Li-excess material shows intermediate behavior (due to irreversible formation reaction)

Preliminary Cycling Data



- Better cycling for Ti-substituted variants
- All electrodes show accelerated fading when cycled to 4.7V
- Fade rate is lower for Ti-substituted materials cycled to 4.7V
- 15% higher capacity for Ti-substituted variants cycled to 4.7V
- Aliovalent Ti substitution in Li-stoichiometric materials allows increased capacity without requiring a formation cycle

Collaboration and Coordination with Other Institutions

- ▶ Spray pyrolysis work with T. Richardson (LBNL, BATT)
- ▶ XAS measurements on $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mn}_{0.4}]\text{O}_2$ with A. Deb (U. of Michigan), E. Cairns (UCB) and J. E. Penner-Hahn at the Advanced Photon Source (Argonne National Lab)
- ▶ Synchrotron XRD and XAS work on $\text{Li}[\text{Ni}_{0.45}\text{Co}_{0.1-y}\text{Al}_y\text{Mn}_{0.45}]\text{O}_2$ with J. Cabana (LBNL, BATT), and A. Mehta (SSRL) at the Stanford Synchrotron Radiation Lightsource
- ▶ Testing of $\text{Li}[\text{Ni}_{0.4}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mn}_{0.4}]\text{O}_2$ in full cells with V. Battaglia (LBNL, BATT)-ongoing

Proposed Future Work

▶ Spray pyrolysis

- ▶ For the rest of FY'11 and FY'12: transition to **high energy** systems
 - ▶ We have successfully synthesized the high voltage material $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMS)
 - ▶ We can reduce calcination times substantially, lowering the tendency to form Mn^{3+} , which adversely affects cycling performance
 - ▶ Examine carbon composites of high capacity polyanionic compounds (e.g., Li_2MSiO_4 ; $\text{M}=\text{Mn}+\text{Fe}$)
 - ▶ Reduction of secondary particle size may not be necessary (milestone 3) but each system needs to be optimized individually (primary particle size, porosity, carbon content, etc.)

▶ Layered oxides

- ▶ Experiments to understand mechanism of aliovalent substitution of Ti and reduction of coulombic inefficiencies, higher capacities
 - ▶ Magnetic measurements, XAS, conductivity measurements
 - ▶ Relevant to milestone 2
- ▶ Experiments to understand origins of improved cycling stability for Al substituted compounds (*ex situ* XRD on cycled electrodes implies structural changes)
 - ▶ Consider high resolution XRD at Advanced Photon Source
 - ▶ relevant to milestone 1
- ▶ Improve cycling to 4.7V to take advantage of higher capacity. Consider coatings on particles, electrolyte additives, combined substitutions (Al, Ti) to take advantage of better stability and higher capacities.

Summary

- ▶ This year, we successfully synthesized high-performance olivines as proof of principle for our spray pyrolysis technique. We will apply our knowledge to other high energy, low cost systems (LNMS, Li_2MSiO_4).
- ▶ Using synchrotron techniques, we have shown that structural changes in Al-substituted layered oxides are very reversible, and that the lattice changes are smaller than for the baseline materials. This can explain the improved cycling behavior we observed.
- ▶ We have been able to increase the practical capacities of layered metal oxides up to 15% via aliovalent Ti-substitution, without necessarily involving a formation step. Initial results suggest improved cycling stability to high voltages. Using electrolyte additives and coating particles may improve results further.