Olivines and Substituted Layered Materials

ES 052

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Overview

Timeline

ongoing

Barriers

- Cost
- Power/Energy Density
- Cycle Life

Budget

FY 2009: 525k
FY 2010: 550k

Supports 1 postdoc and 1 student

Partners/Collaborations

BATT-LBNL:J. Cabana-Jimenez, T. Richardson G. Chen, V. Battaglia, K. Persson, R. Kostecki
BATT-other institutions: S. Whittingham, C. Grey
Apurva Mehta, SSRL
Elton Cairns, UC Berkeley
Anirrudha Deb, U. of Michigan

Development of lower cost cathode materials with improved performance and low toxicity, consistent with the goals of FreedomCar/USABC.

Recent and ongoing work:

- Lower cost of $Li[Ni_xCo_yMn_z]O_2$ electrodes by full or partial replacement of Co with other metals-understand effects of substitution on structure and performance.
- Use $LiMnPO_4$ as a model compound for development of spray pyrolysis technique, based on our improved understanding of this material developed in FY08-09.
- Investigate new materials synthesized by pyrolysis.

Relevance

Objectives

Cathode materials are synthesized and characterized electrochemically. Relevant physical properties are measured in conjunction with the diagnostics teams. Emphasis is placed on reducing cost and improving electrochemical properties.

- $Li[Ni_xCo_{1-2x-y}M_yMn_x]O_2$; M=Al, Ti
  - In FY10, extend 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
- $LiMnPO_4$ and variants (started in FY08)
  - Synthesis via combustion synthesis and characterization of nanostructured $LiMnPO_4$/C composites completed in FY09
  - Use as a model system for spray pyrolysis set-up
  - Extend spray pyrolysis to other polyanionic materials (silicates, borates)

Approach

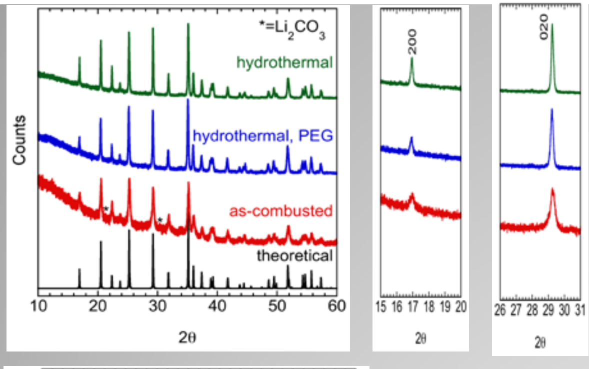
(a) Synthesize and electrochemically characterize $Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$ series. (Jun.'10) on schedule

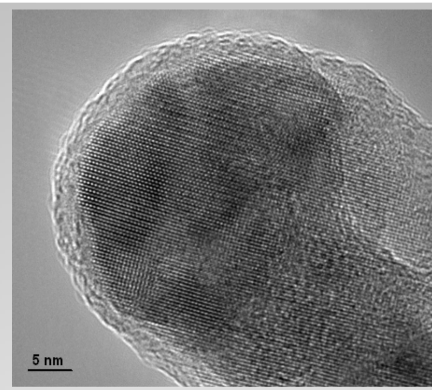
(b) Develop spray pyrolysis method for synthesis of cathode materials, including polyanionic compounds. (Sep.'10) on schedule

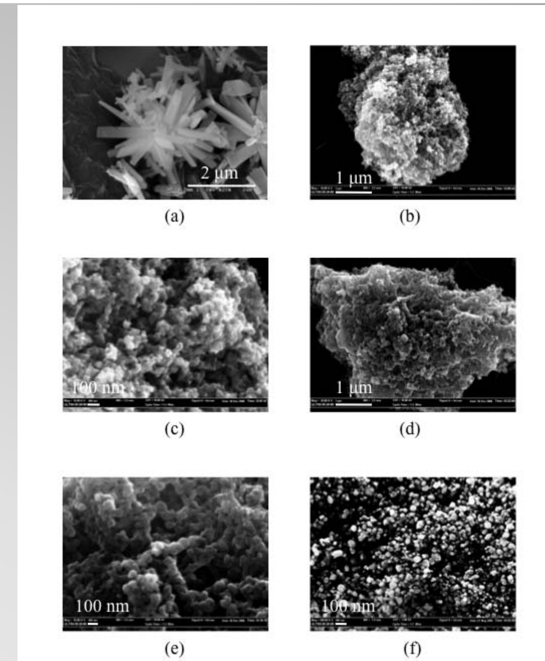
Milestones (FY10)

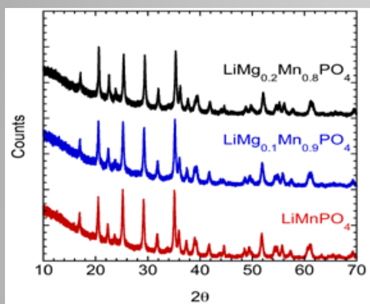
Technical Accomplishments/Progress

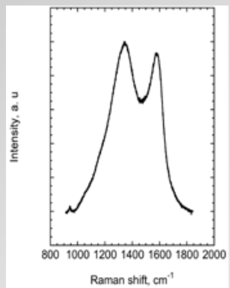
$LiMg_yMn_{1-y}PO_4/C$ nanocomposites-synthesis



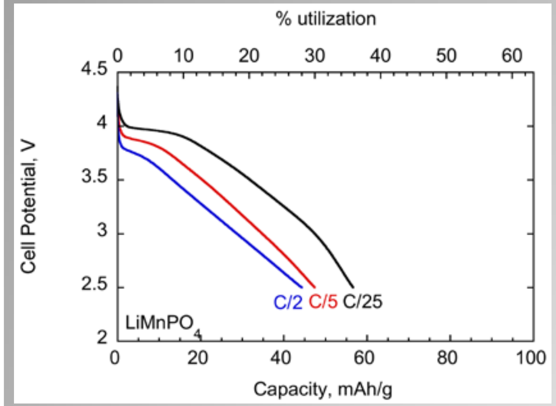


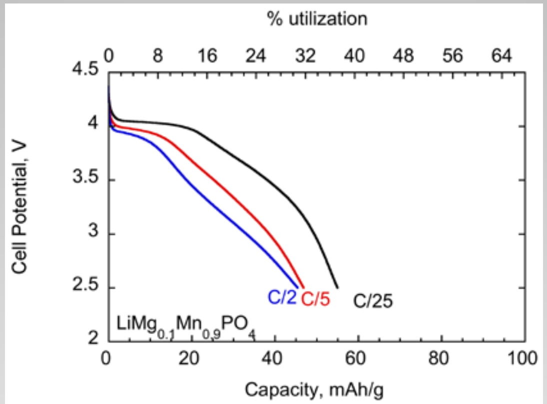


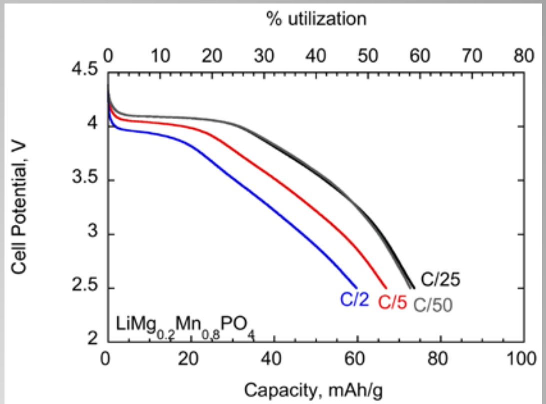


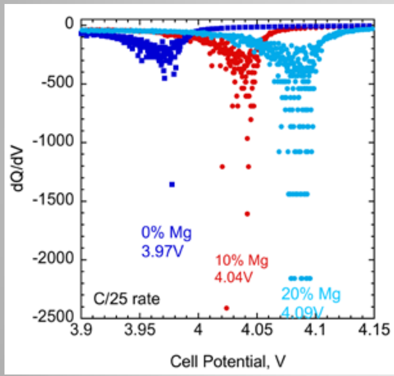


XRD patterns of combusted samples and hydrothermal samples (left, top).Mg-substituted materials can be prepared by combustion (left, bottom). SEM images show large plate-like particles for hydrothermally prepared materials (right, image a) and varying degrees of agglomeration for the small carbon-coated primary particles (right, images b-f, and TEM image, middle) produced by combustion. Raman shows that the carbon is disordered (left, bottom). Carbon content of combusted samples is a complex function of synthesis conditions and varied from 6-21 wt. %.





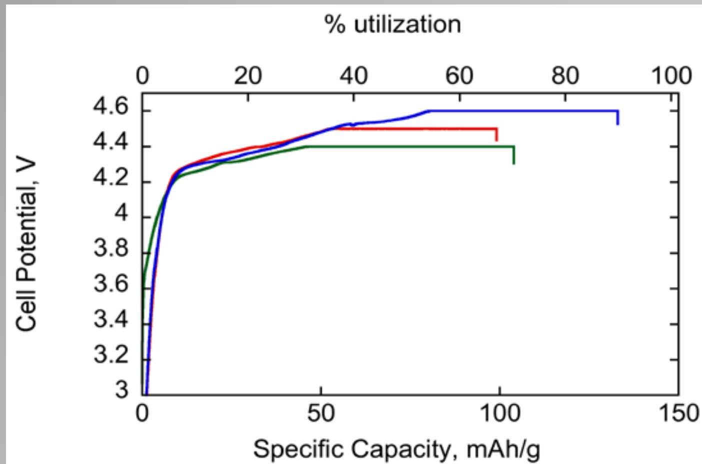


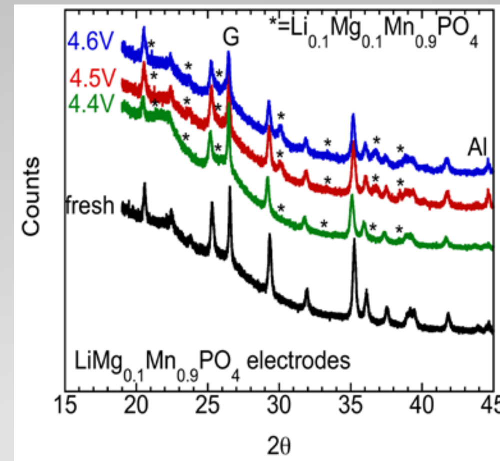


After CCCV charging to 4.4V, Li/$LiMnPO_4$ cells show lower than expected utilization upon discharge. Increasing the carbon content does not help, but Mg-substitution improves results. An increase in the discharge potential (left) as Mg content is increased suggests improved kinetics. Higher current densities, surprisingly, have only a modest negative impact on utilization. This suggests that some of the $LiMg_xMn_{1-x}PO_4$ particles have very good electrochemical characteristics, but some are less accessible due, most likely, to agglomeration.

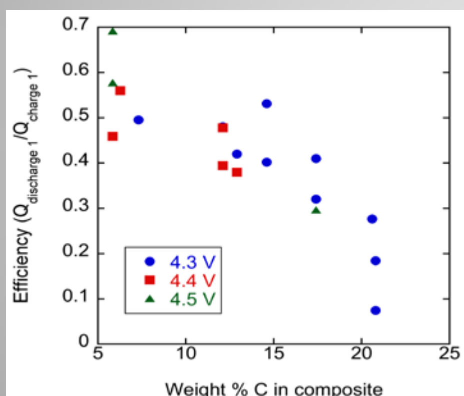
Technical Accomplishments/Progress

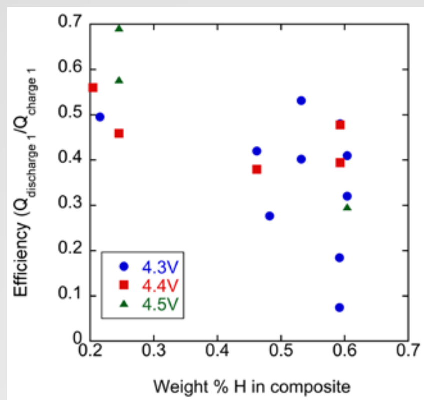
$LiMg_xMn_{1-x}PO_4$/C nanocomposites- electrochemical characteristics





Coulometry suggests high degrees of delithiation on first charge (top, left), but XRD of charged electrodes (top, middle) show that $LiMg_{0.1}Mn_{0.9}PO_4$ is still the major phase, regardless of voltage limit. This indicates that there is a competing parasitic side reaction during charge.

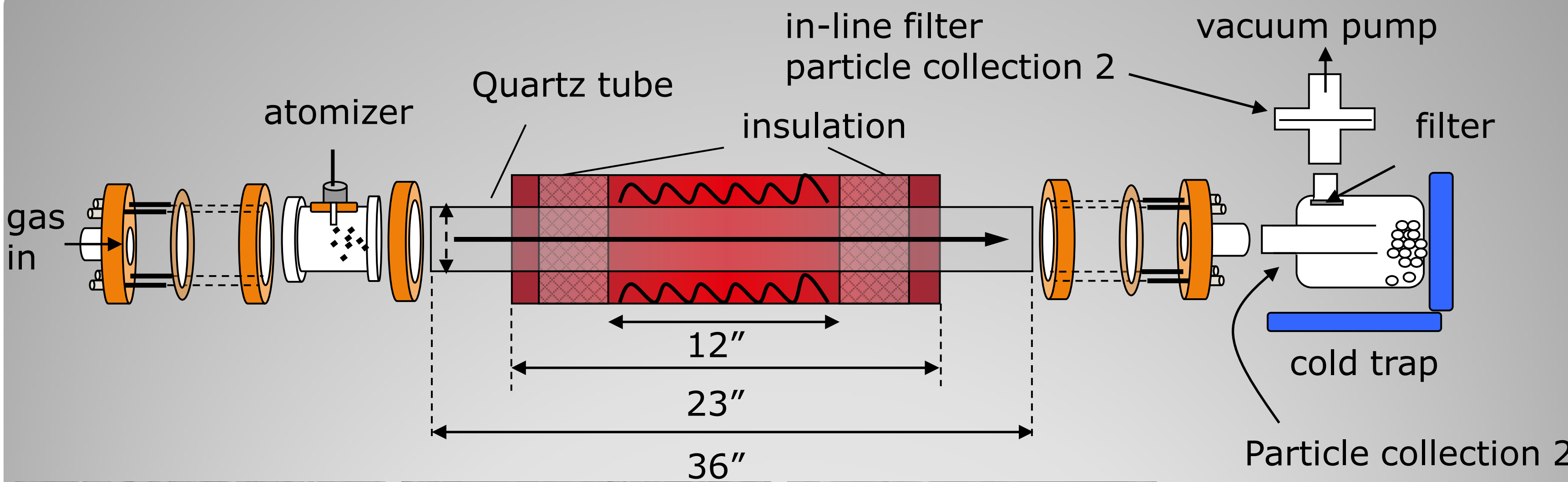


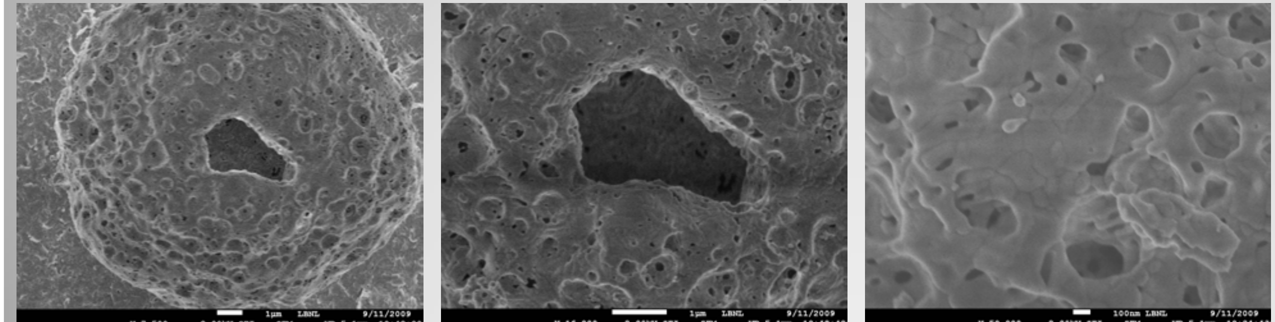


Coulombic inefficiencies are very high on the first cycle (but not on subsequent cycles). The inefficiencies scale with the carbon contents in the composites, but not with the voltage limit (bottom, left). This indicates that the side reaction is not oxidation of electrolyte The inefficiencies show only a weak correspondence with hydrogen content. Although the side reaction involves carbon, it is not necessarily simply a reaction with remaining functional groups.

Technical Accomplishments/Progress

$LiMg_xMn_{1-x}PO_4$/C nanocomposites- electrochemical characteristics





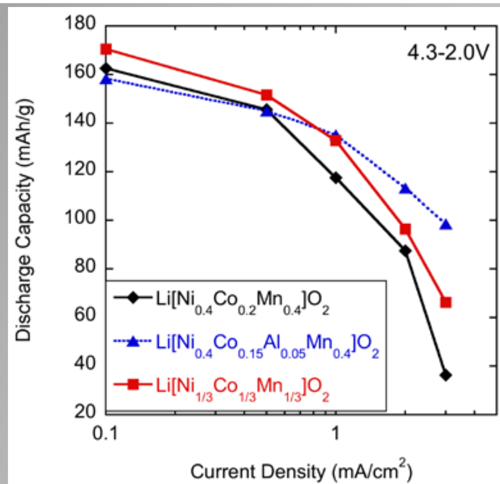
Large, hollow porous spherical particles of $LiMnPO_4$ are currently being produced. LMP is being used as a model compound for us to optimize conditions.

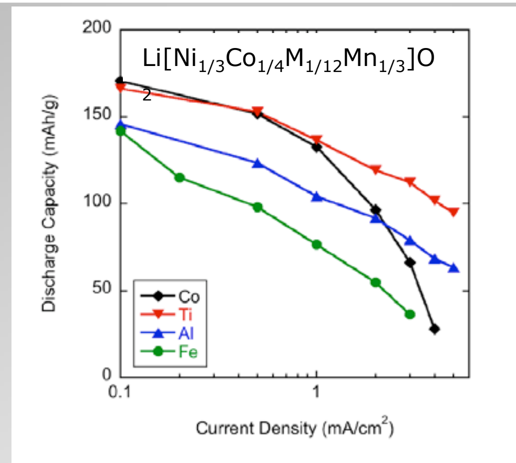
Technical Accomplishments/Progress

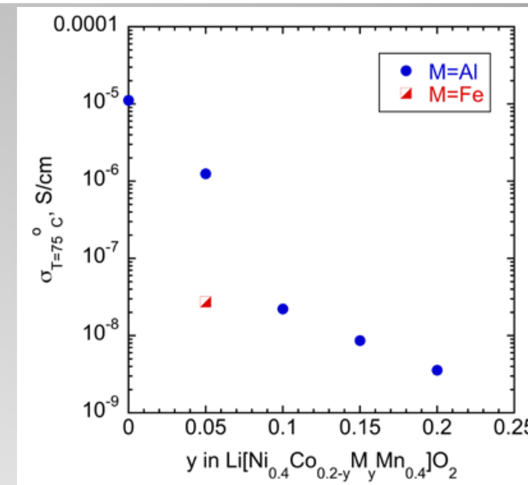
Spray pyrolysis

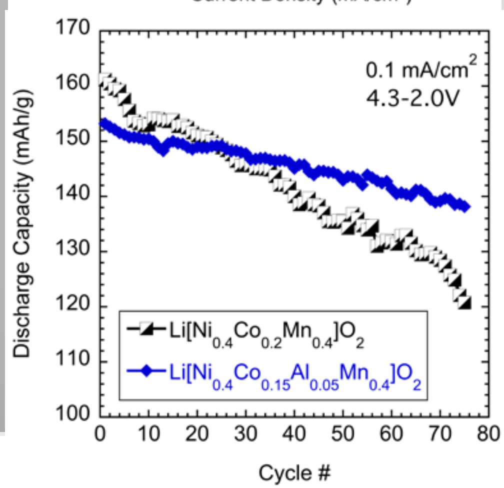
Technical Accomplishments/Progress

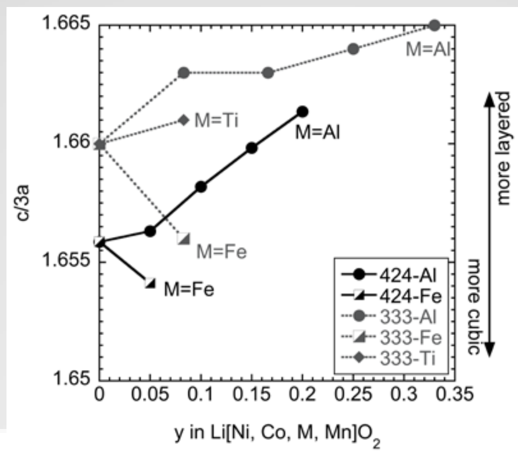
Substituted Layered NMCs-Background



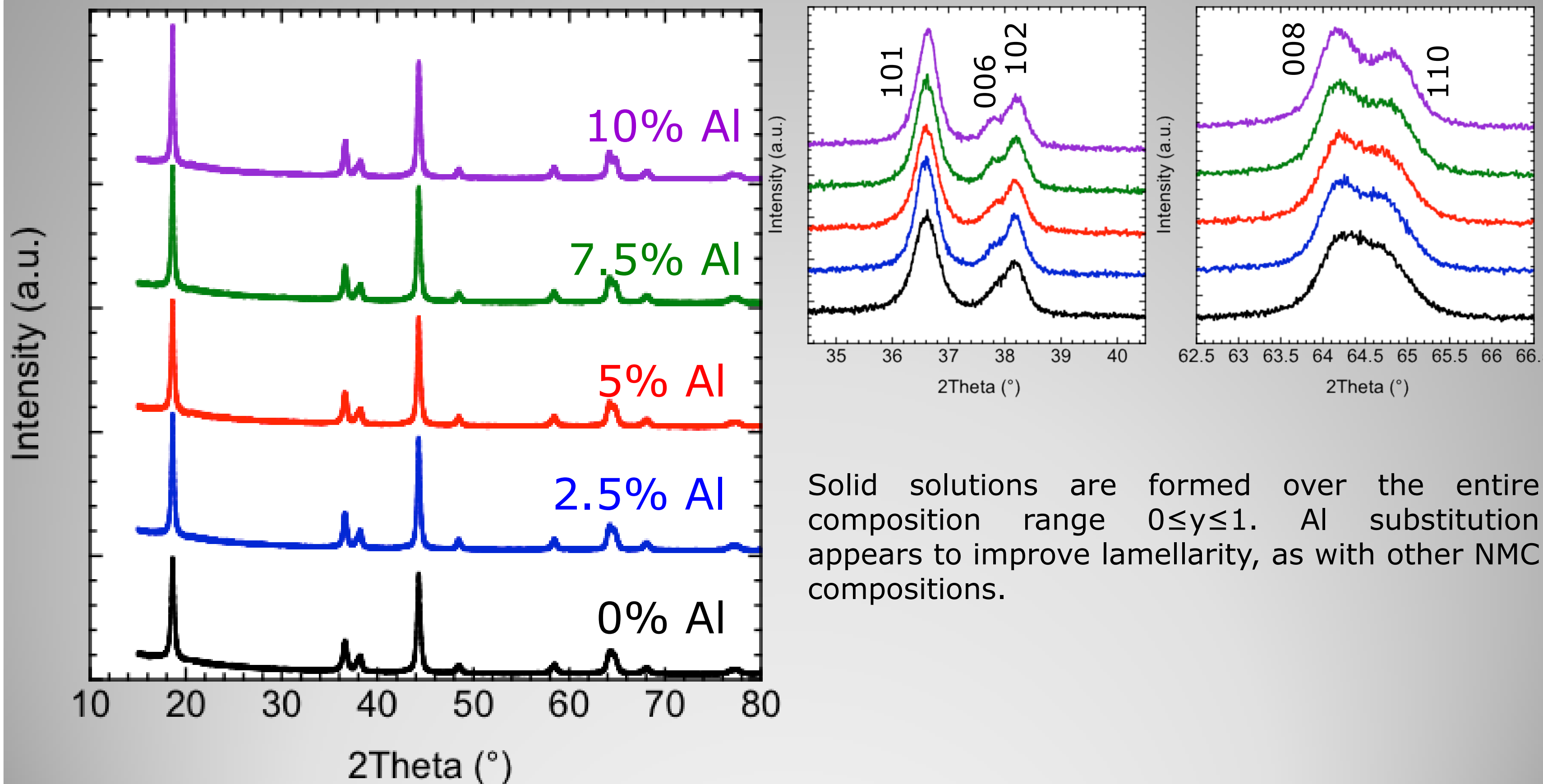








Our previous work indicates that low levels of Al or Ti substitution have beneficial effects on electrochemical performance, while Fe is deleterious. Both Al and Fe lower electronic conductivity (top right). Al and Ti improve the lamellarity (bottom, middle) while Fe decreases it. This structure effect may explain the rate effects.



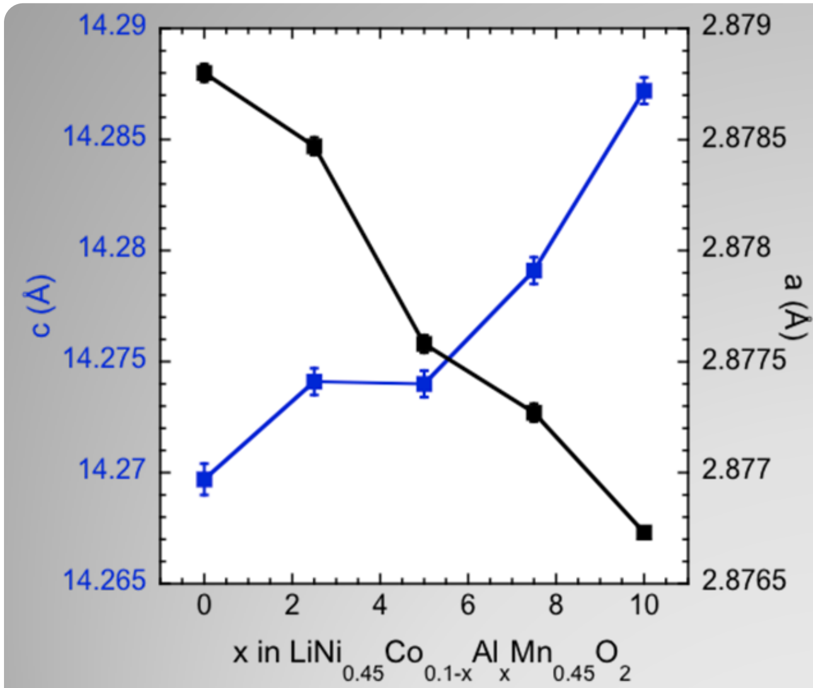
Solid solutions are formed over the entire composition range 0≤y≤1. Al substitution appears to improve lamellarity, as with other NMC compositions.

Technical Accomplishments/Progress

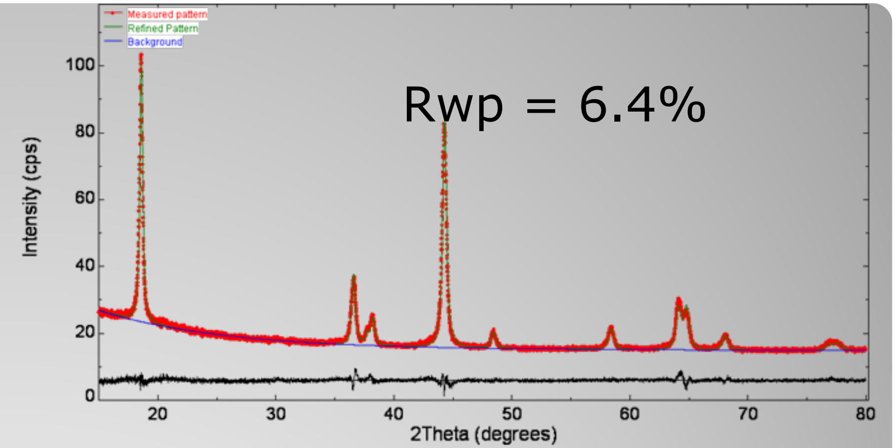
$Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$

Technical Accomplishments/Progress

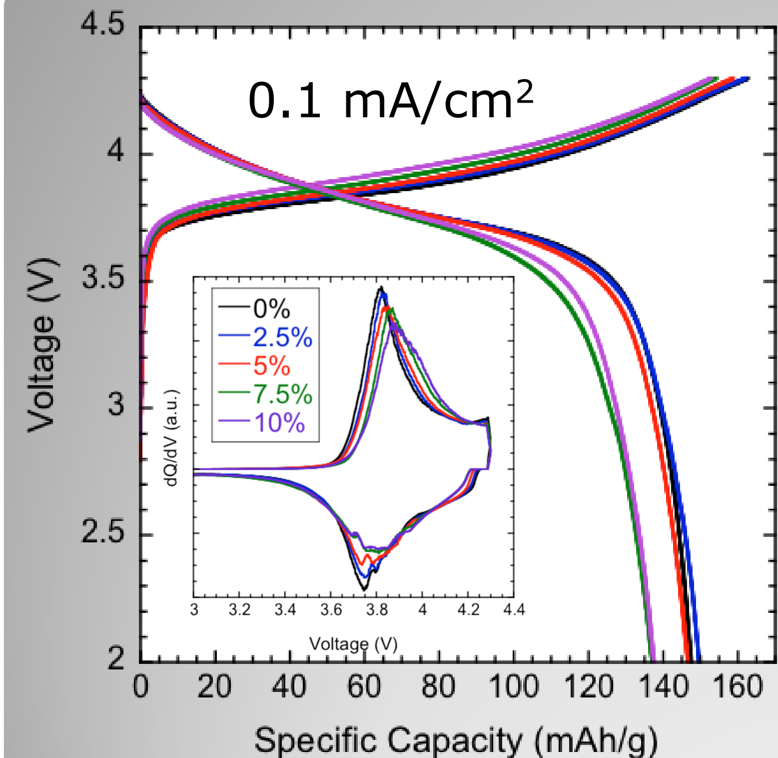
$Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$-structure

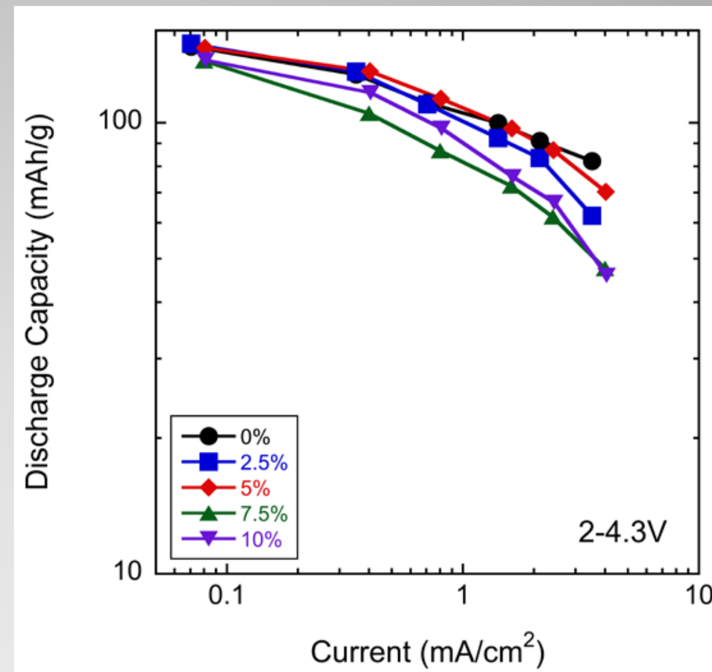


Good fit with 10% Li/Ni ion mixing
c increases 0.12%
a increases 0.07%



Al substitution	c/3a
0%	1.652
2.5%	1.653
5%	1.653
7.5%	1.654
10%	1.655

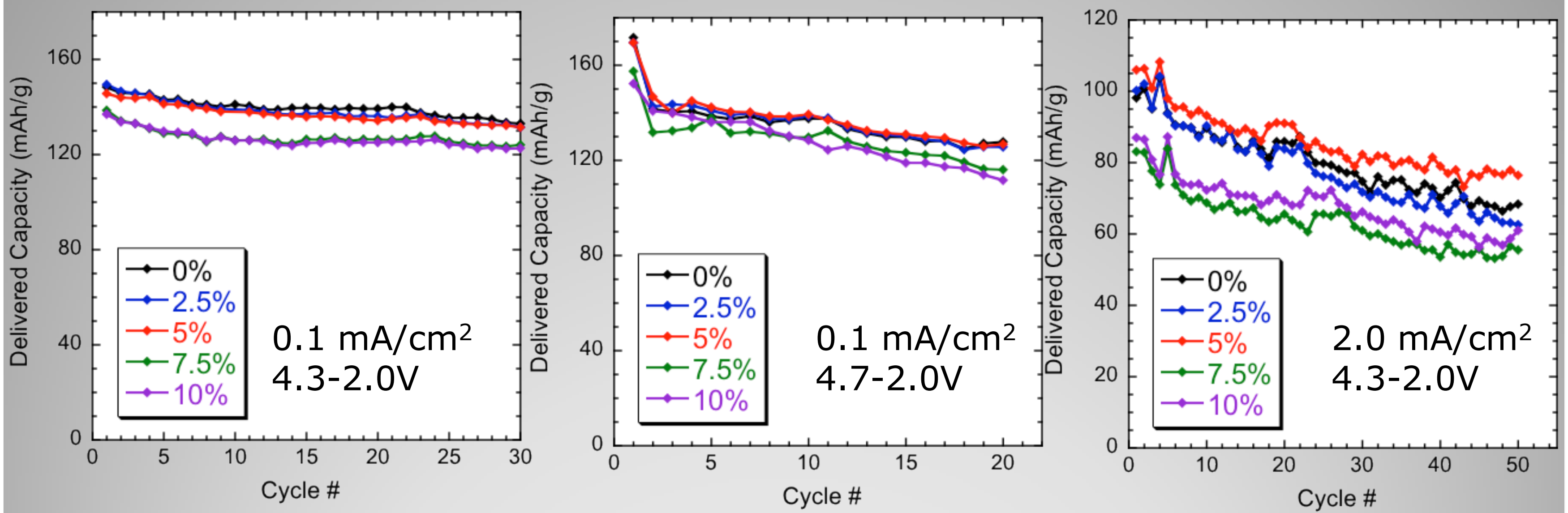




Low levels of Al substitution do not affect capacity or rate capability. This allows further reduction of Co content without adversely affecting performance.

Technical Accomplishments/Progress

$Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$-electrochemical characteristics



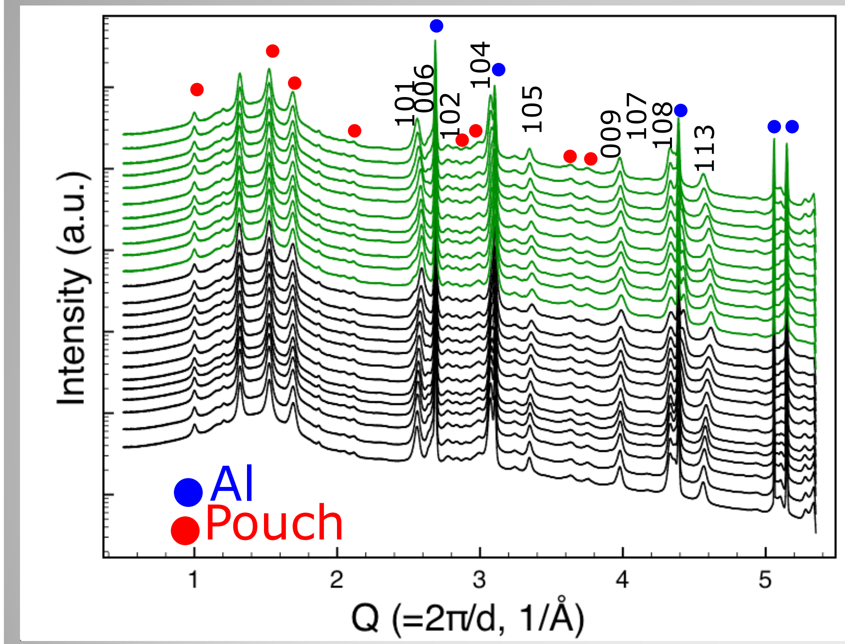
0-5% Al shows similar behavior at low rates (left and middle). Increasing the voltage limit results in higher delivered capacity, but faster fade rates for all samples (middle). 5% Al sample outperforms others at higher discharge rates (right).

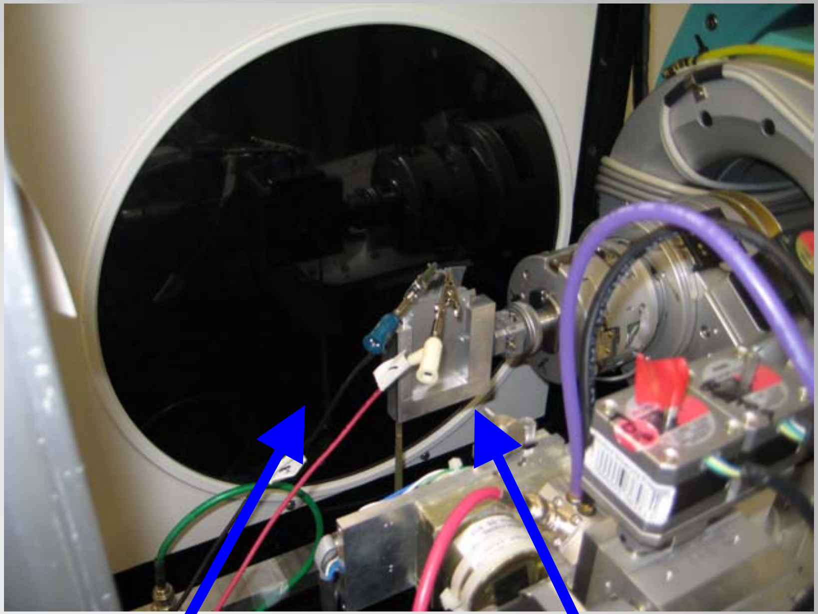
Technical Accomplishments/Progress

$Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$-electrochemical characteristics

C/25 **Charge** **Discharge**

SSRL BL 11-3



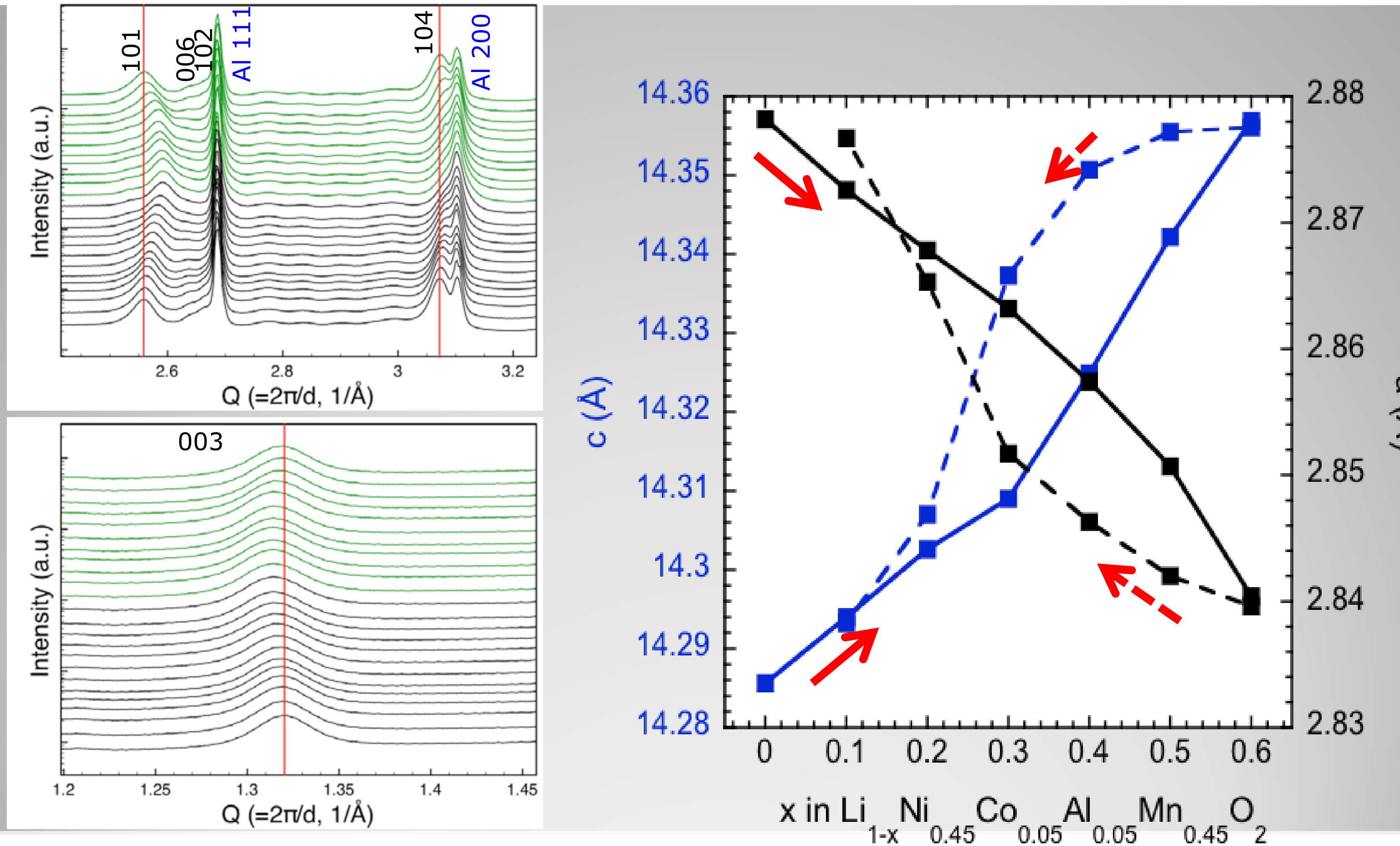


Detector

Pouch Cell

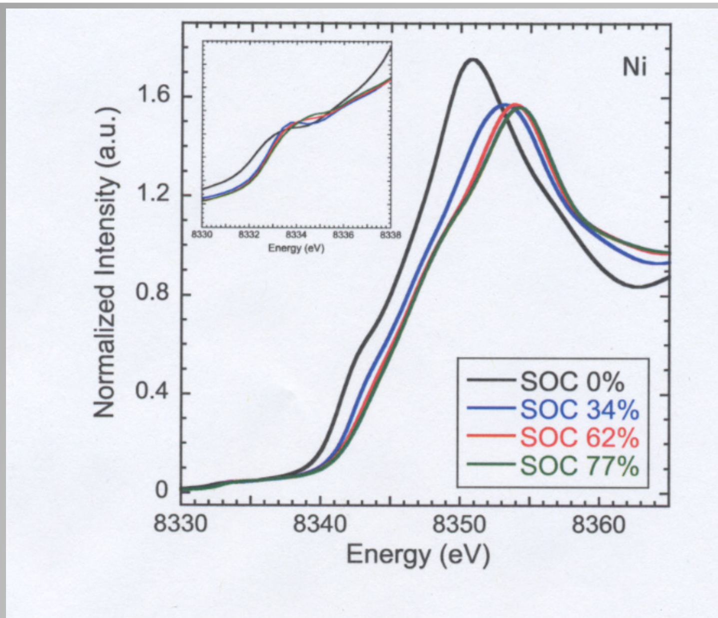
In situ XRD

$Li[Ni_{0.45}Co_{0.05}Al_{0.05}Mn_{0.45}]O_2$

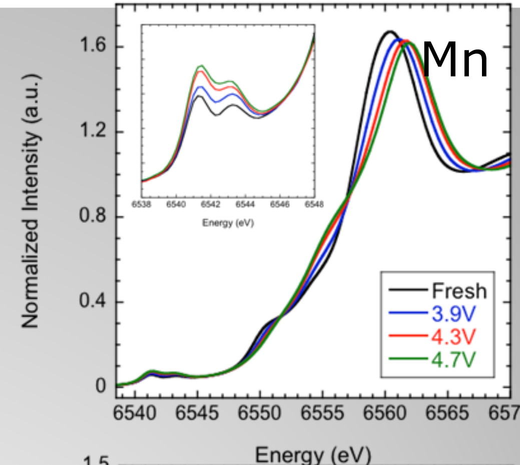


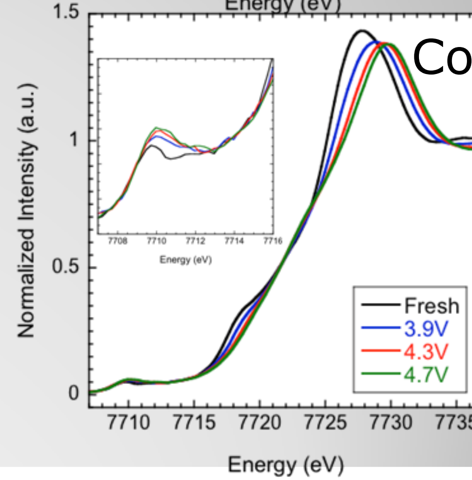
In situ XRD

$Li[Ni_{0.45}Co_{0.05}Al_{0.05}Mn_{0.45}]O_2$



Transition metal K-edges (SSRL BL 4-3)
Ni shows oxidation change
No significant change in Mn, Co edges



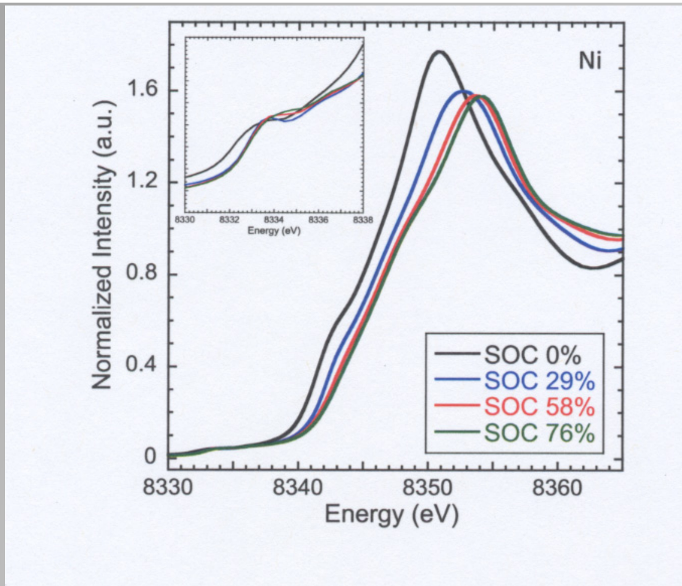


XANES

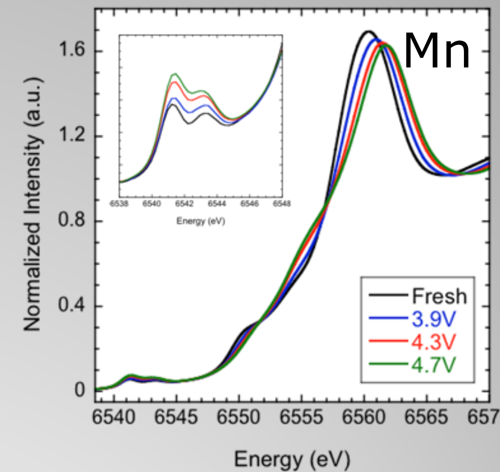
$Li[Ni_{0.45}Co_{0.1}Mn_{0.45}]O_2$

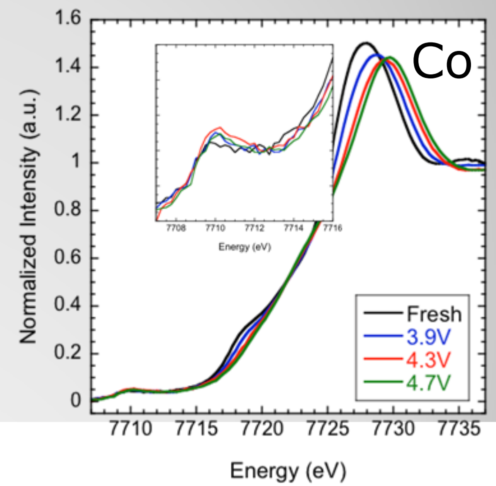
XANES

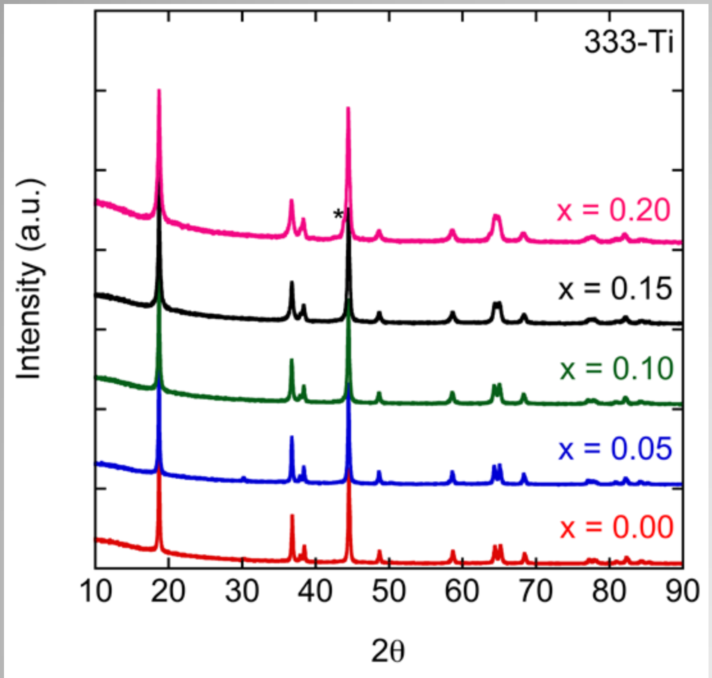
$Li[Ni_{0.45}Co_{0.05}Al_{0.05}Mn_{0.45}]O_2$

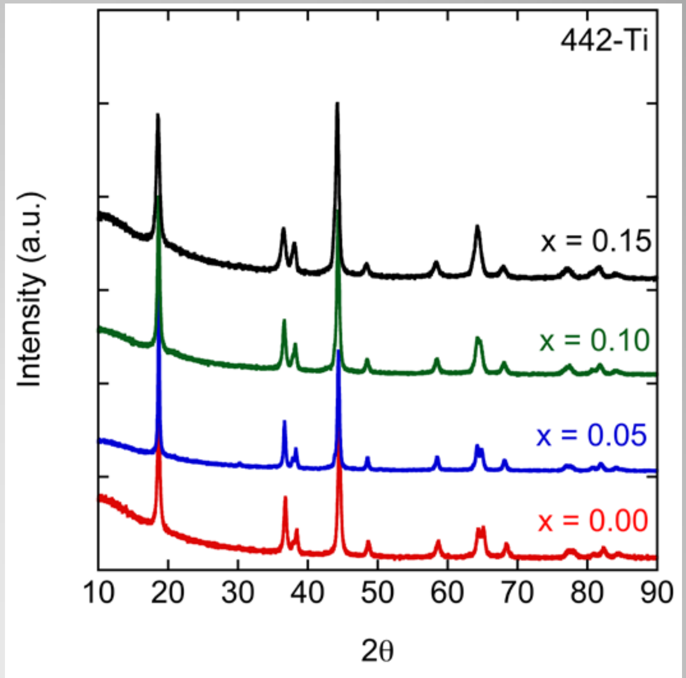


Transition metal K-edges (SSRL BL 4-3)
Ni shows oxidation change
No significant change in Mn, Co edges
Al substitution does not change redox









Somewhat limited solubility range for Ti substitution

Ti substitution in NMCs

$Li[Ni_{1/3}Co_{1/3-y}Ti_yMn_{1/3}]O_2$ and $Li[Ni_{0.4}Co_{0.2-y}Ti_yMn_{0.4}]O_2$

- Jordi Cabana-Jimenez, LBNL (XAS and in situ XRD at SSRL)
- Apurva Mehta, SSRL (XAS and in situ XRD at SSRL)
- Tom Richardson, LBNL (XAS and in situ XRD at SSRL)
- Guoying Chen, LBNL (XAS and in situ XRD at SSRL)
- Elton Cairns, UC Berkeley (EXAFS and associated techniques)
- Anirrudha Deb, U. of Michigan (EXAFS and associated techniques)
- Vince Battaglia, LBNL (scale-up and cell testing)
- Stan Whittingham, SUNY Binghamton (magnetic measurements)
- Clare Grey, SUNY Stonybrook/Cambridge (NMR measurements)
- Kristin Persson, LBNL, materials modeling
- Robert Kostecki, LBNL, Raman microprobe spectroscopy

Collaborations

- Modify spray pyrolysis set-up to decrease particle size
  - Minimize via surface tension (solvent)
  - Density (concentration)
  - Frequency (atomizer)
  - Narrower, longer tube
  - Solution concentration

$$d_h = 0.73\sqrt[3]{\frac{T}{\rho f a^2}}$$

- Use $LiMnPO_4$/C as a test case, then move on to other polyanionic compounds
- Continue working on substitution of layered NMCs
  - Structure, redox state, as a function of state-of-charge and cycling history using in situ XRD and XAS at SSRL
    - Does Ni move into Li layer?
    - How does the Li slab spacing change with state-of-charge?
    - Is it different for Al-substituted materials compared to baseline materials?
  - Do a comprehensive study of Ti substitution, which may be beneficial for performance

Future Work

- Combustion synthesis of $LiMg_yMn_{1-y}PO_4/C$ nanocomposites was carried out
  - Mg substitution improves performance
  - Lower than expected capacities due to agglomeration
  - Rate does not affect delivered capacity greatly, suggesting a portion of the material has good electrochemical properties
  - Transition to spray pyrolysis to control particle size, agglomeration and homogeneity, which should improve results
- Substitution of layered NMCs was extended to $Li[Ni_{0.45}Co_{0.1-y}Al_yMn_{0.45}]O_2$ series
  - Beneficial effects of low (~5%) Al substitution are observed, as with $Li[Ni_{1/3}Co_{1/3-y}Al_yMn_{1/3}]O_2$ and $Li[Ni_{0.4}Co_{0.2-y}Al_yMn_{0.4}]O_2$ series studied in previous years
  - In situ synchrotron XRD and XAS studies have been initiated to further understand structural effects thought to be the origin of the improvement
  - Synthesis of Ti-substituted NMCs was started

Summary