Development of High-Capacity Cathode Materials with Integrated Structures

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Vehicle Technologies Program

Overview

Timeline

- Start date: FY12
- End date: On-going
- Percent complete:

  - 50% (This project carries over from FY2012, but was integrated into the 'voltage fade' program)

Budget

- Total project funding

  - 100% DOE
- Funding in FY12: $300K
- Funding in FY13: $300K

Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

Partners

- Lead PI: Michael Thackeray
- Collaborators:
  - CSE, Argonne: Brandon Long, Jason Croy, Donghan Kim, Kevin Gallagher, Zonghai Chen (materials design, synthesis and electrochemical characterization)
  - APS, Argonne: Peter Chupas, Karena Chapman, Matthew Suchomel (HR-XRD and PDF analyses)
  - ABR 'Voltage Fade' Team
  - BASF, Toda Kogyo, LG Chem, Envia Systems

Objectives

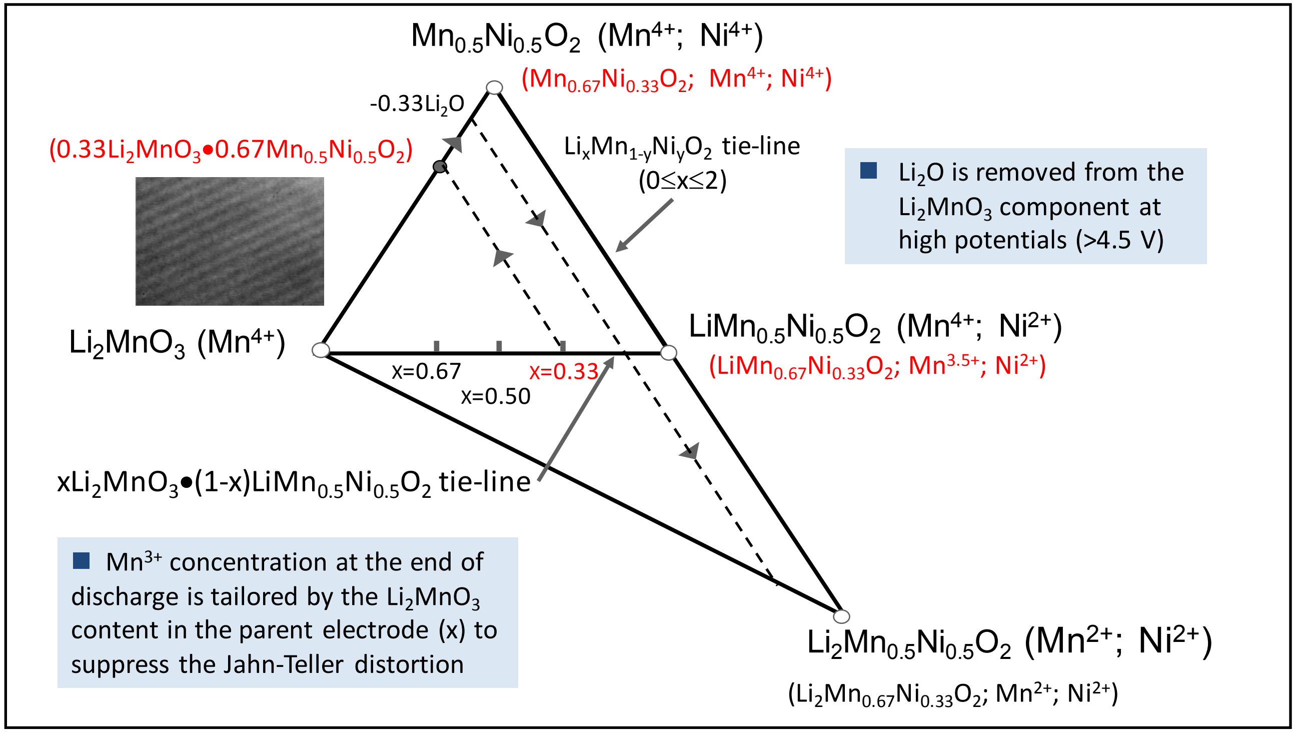
- Develop low cost, high-capacity cathode materials with good structural, electrochemical and thermal stability for PHEVs
  - Design and synthesize Li- and Mn-rich oxides with integrated structures, notably 'layered-spinel' materials, to *counter the voltage fade phenomenon* observed in 'layered-layered' electrode materials
  - Identify and overcome performance degradation issues
  - Exchange information and collaborate closely with others in ABR's 'voltage fade' team
  - Supply promising high-capacity cathode materials for PHEV cell build

Milestones FY12

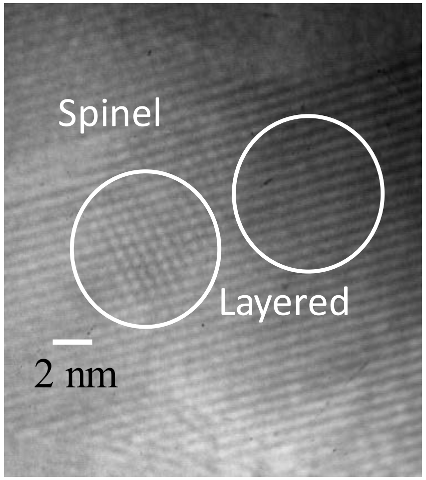
- Explore/optimize the electrode composition using phase diagrams as guide – *on-going*
- Evaluate electrochemical properties of ‘layered-spinel’ electrode materials in lithium half cells and a full Li-ion cell configuration with various anode materials – *on-going*
- Investigate both bulk and surface effects – *on-going*
- Initiate detailed structural analyses of composite electrode structures at the Advanced Photon Source (APS) by X-ray diffraction (XRD), X-ray absorption (XAS) and pair-distribution-function (PDF) analyses – *on-going*

Background: Integrated Cathode Structures

'Layered-Layered' Li_2MnO_3-$LiMO_2$-MO_2 (M=Mn, Ni) Phase Diagram



'Layered-Spinel'
0.7Li_2MnO_3•0.3$Li_4Mn_5O_{12}$



- Compatibility of ccp planes in layered Li_2MnO_3 (C2/m, 001) with those in layered $LiMO_2$ (R-3m, 003) and spinel LiM_2O_4 (Fd3m, 111) allows structural integration of the two components
- Strategy: Use the 'layered-layered' component to provide high capacity and the spinel component to act as a stabilizer to counter voltage fade

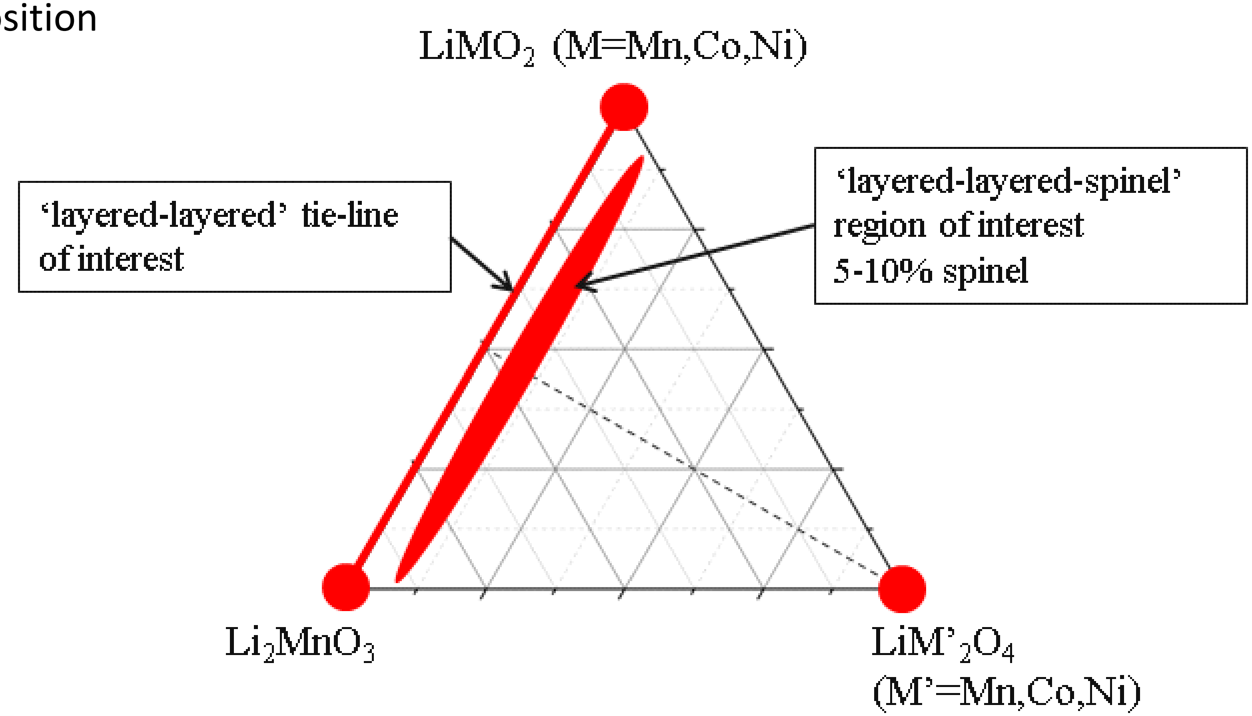
Strategy / Approach

Part I

- Embed stabilizing spinel component in 'layered-layered' electrode utilizing phase diagram

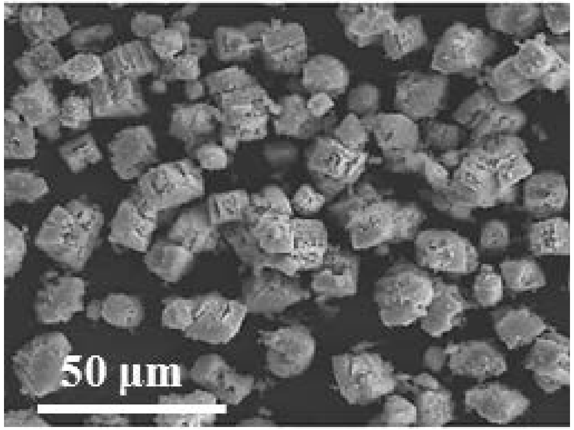
Part II

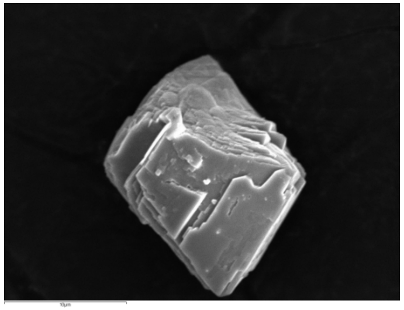
- Structurally and electrochemically characterize 'layered-layered' and spinel end-members of phase diagram to gain understanding of 'layered-layered-spinel' structure and degradation
- Utilize end-member structural knowledge to optimize composite composition
  - Spinel stability
  - Li_2MnO_3 activation and Li reserve
  - Layered capacity



Methods

- Electrode materials made from solid state reaction of mixed metal oxalates (formed via co-precipitation) and Li_2CO_3 precursors
- Materials heated to 550°C for 12 hours in air at 2°C/min
- Final heating typically 850°C for 12 hours in air
- Electrochemistry performed in half-cell configuration
- SEM micrographs of typical final product shown below





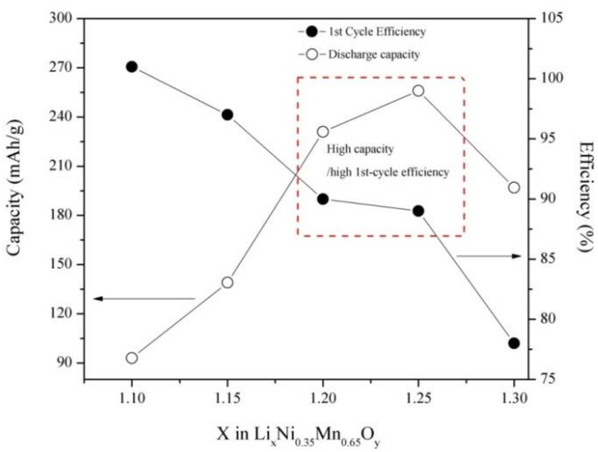
Cleaved crystallites, believed to be result of H_2O/CO_2 loss from oxalate precursor, contribute to porosity of secondary particles

$Li_xMn_{0.65}Ni_{0.35}O_y$ System

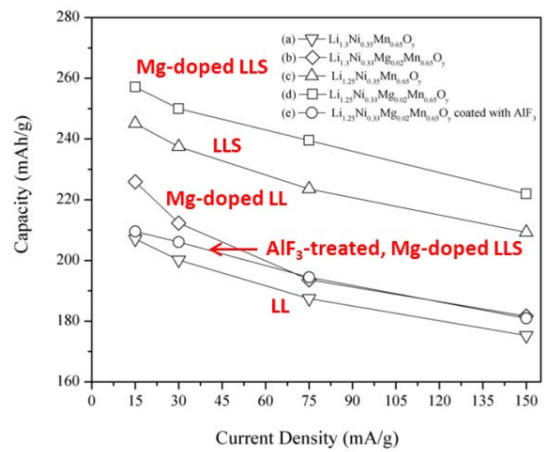
RECAP: Strategy: Embed spinel component in Mn/Ni system

- The $Li_xMn_{0.65}Ni_{0.35}O_y$ system has end-members of $0.3Li_2MnO_3\bullet0.7LiMn_{0.5}Ni_{0.5}O_2$ (x=1.3; y=2.3), and $LiMn_{1.3}Ni_{0.7}O_4$ (x=0.5; y=2)
- Lowering the Li : transition metal ratio in $xLi_2MnO_3\bullet(1-x)LiMO_2$ embeds a spinel component in the structure

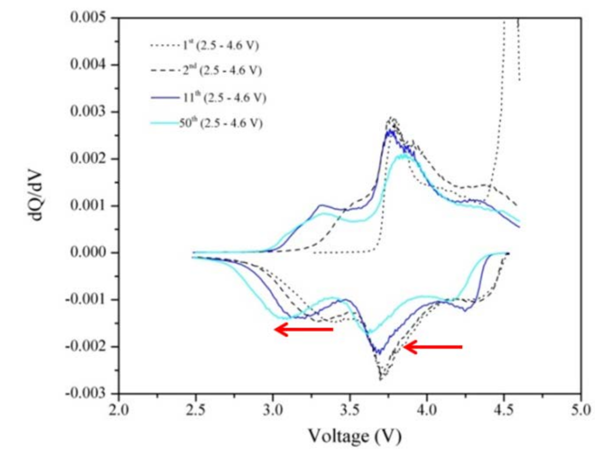
1st Cycle Efficiency



Doping / Rate Capability



Electrochemical Performance

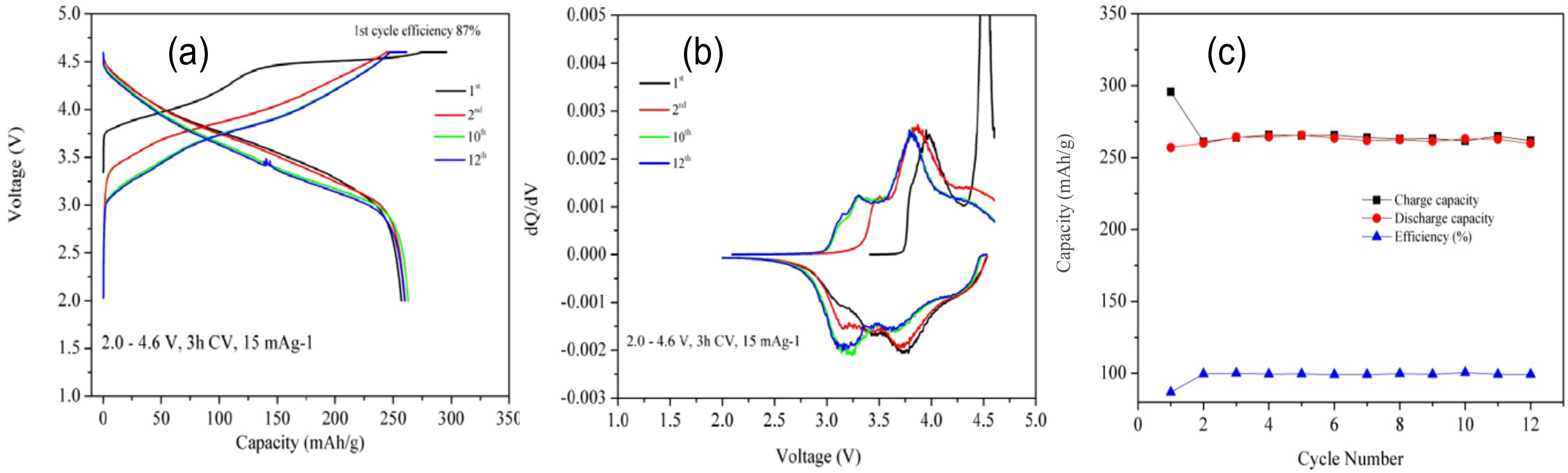


- 5-10% spinel provides best performance
- 1st cycle efficiency of 99% achieved for x=1.25 when cycled at 4.6-2.0 V
- ‘Layered-layered-spinel’ electrodes exhibit higher capacities than ‘layered-layered’ electrodes
- Voltage fade phenomenon still present

Co Containing Mn-rich ‘layered-layered-spinel’

Strategy: Add Co to ‘layered-layered-spinel’ (5% spinel)

- Addition of Co content to ‘layered’ component of Mn-Ni rich composite
- $Li_{1.4}Ni_{0.22}Co_{0.12}Mn_{0.66}O_{2.42}$ alternatively
  $0.95[0.44Li_2MnO_3 \bullet 0.56LiNi_{0.39}Co_{0.22}Mn_{0.39}O_2] \bullet 0.05Li_{0.5}Mn_{0.75}Ni_{0.25}O_2$
- Co assumed to be in ‘layered-layered’ component although variations in cation distribution likely

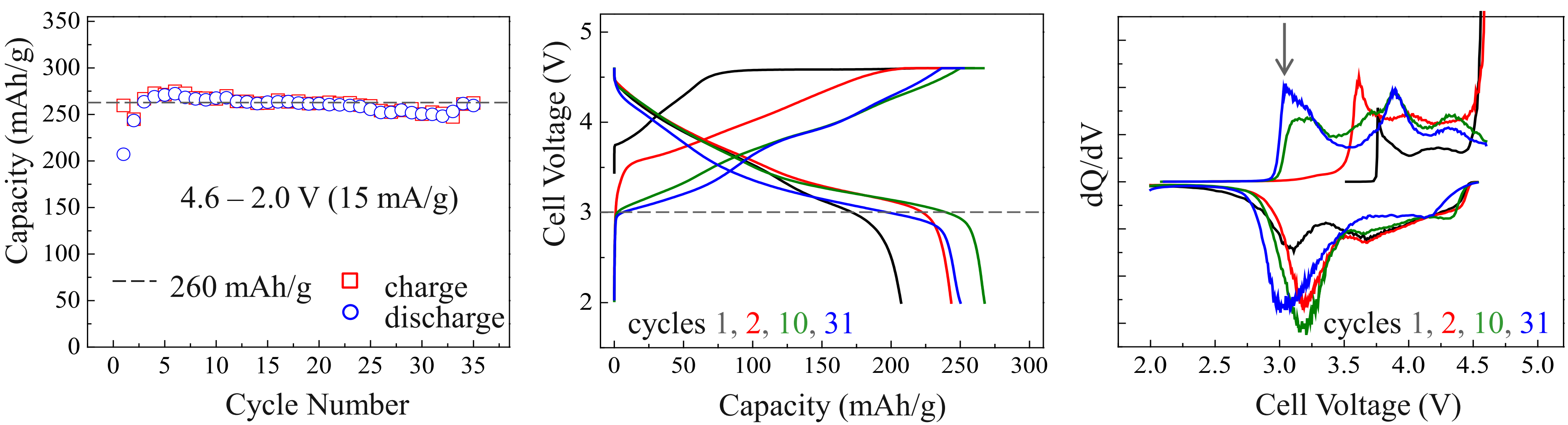


- High capacity and cycling stability achieved
- Spinel-like regions formed during cycling improve stability, but lowers voltage

Baseline Mn-rich ‘layered-layered’ Member

Part II Strategy: Evaluate performance of Mn-rich ‘layered-layered’ member

- The effect of Li_2MnO_3 content in $xLi_2MnO_3 \bullet (1-x)LiMn_{0.5}Ni_{0.5}O_2$
- Comparison of x = 0.7, 0.8, and 0.95 with various annealing temperatures
- x = 0.7 (850°C) showed best performance (data below)

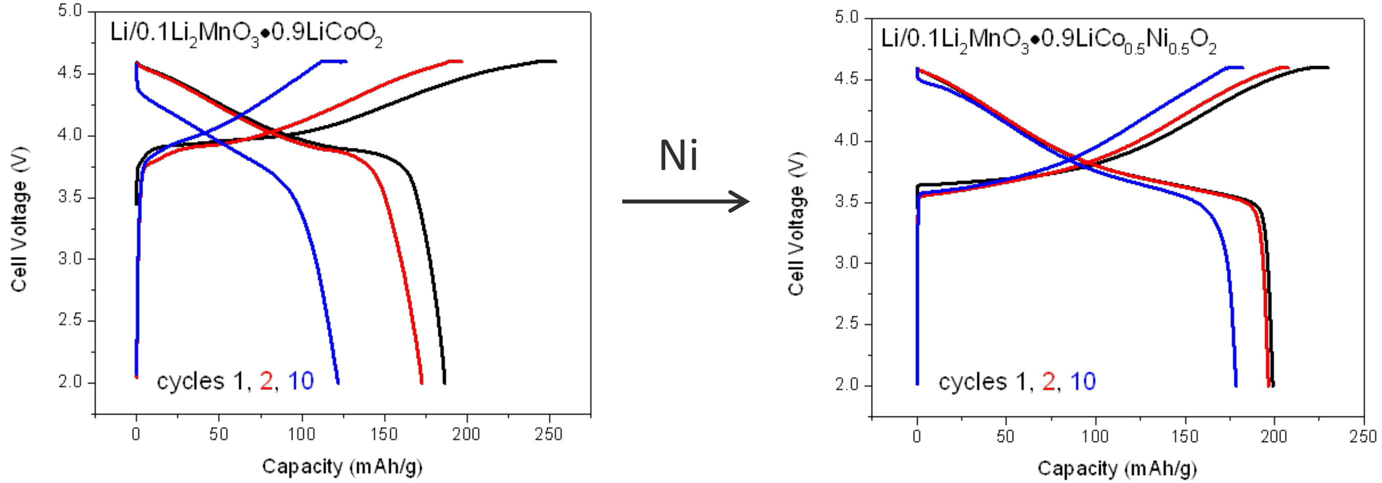


- Li_2MnO_3 component activated during first 2 cycles before reaching steady capacity of ≈260 $mAhg^{-1}$
- Voltage profile shows the cell delivered ≈240 $mAhg^{-1}$ above 3.0 V for ≈10 cycles

Increasing Ni Content in $0.1Li_2MnO_3 \bullet 0.9LiCo_yNi_{1-y}O_2$

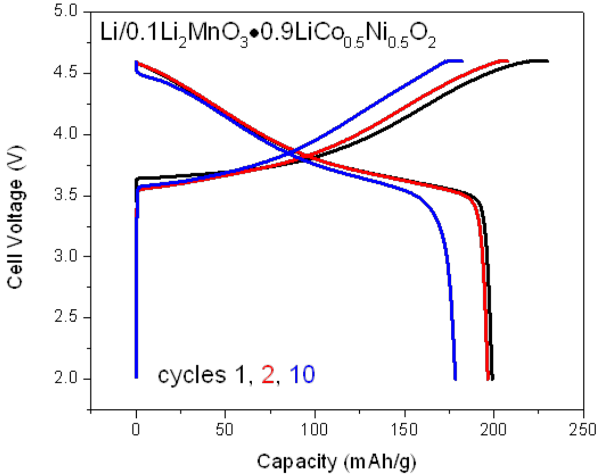
Strategy: Incorporate stabilizing component to Co/Ni-rich electrodes

- Evaluating the addition of a stabilizing Li_2MnO_3 component, which can act as a reserve for Li, and Ni substitution to conventional $LiCoO_2$ cathode materials for improved performance

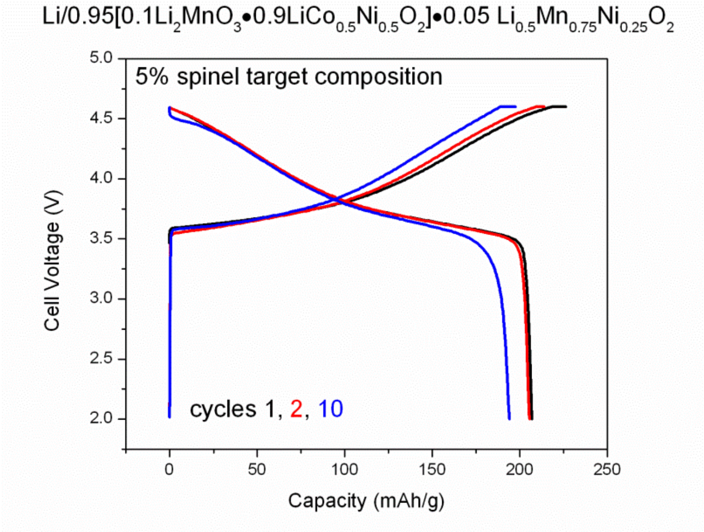


- Increasing Ni content in $0.1Li_2MnO_3 \bullet 0.9LiCo_yNi_{1-y}O_2$ system improves 1st cycle efficiency from 74% (y=1) to 87% (y=0.5)
- Cycling stability improved at cycle 10 from 120 $mAhg^{-1}$ (y=1) to 178 $mAhg^{-1}$ (y=0.5)
- 190 $mAhg^{-1}$ of capacity delivered above 3.5 V during first cycles

Embedding a Spinel Component in $0.1Li_2MnO_3 \bullet 0.9LiCo_{0.5}Ni_{0.5}O_2$



Embed
5% spinel
→

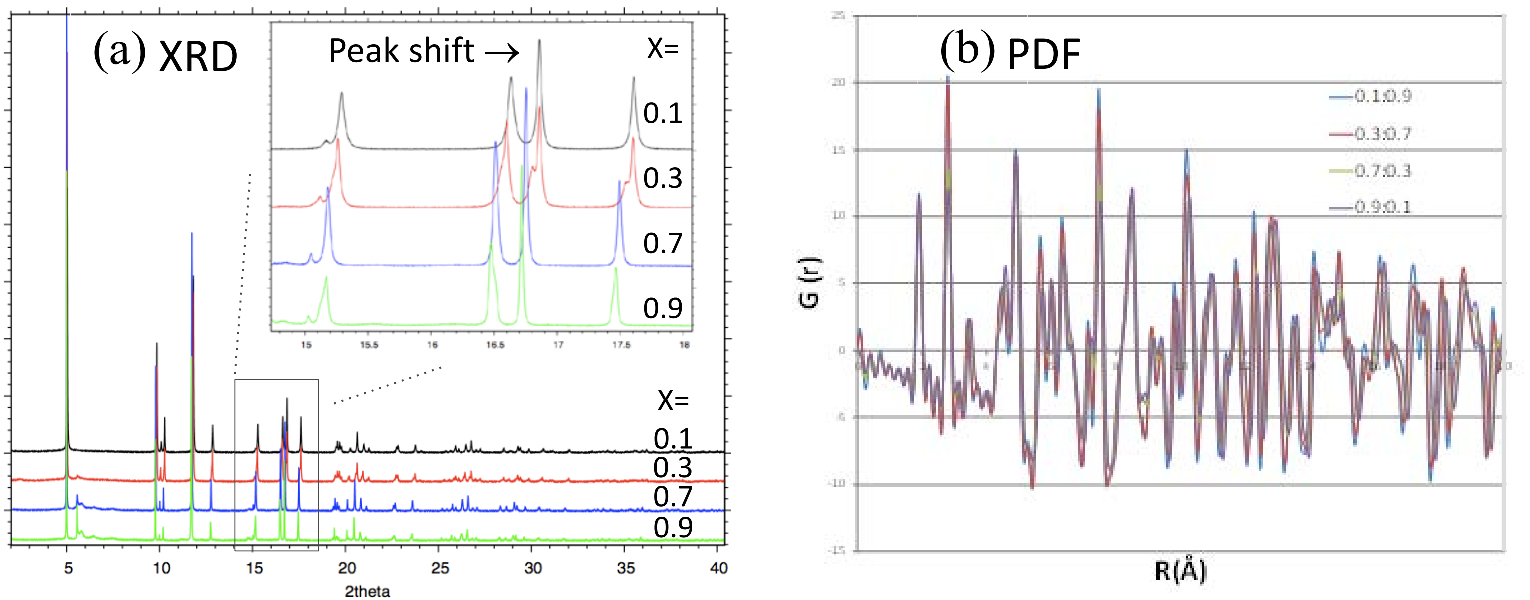


- 5% spinel phase improves:
  - First cycle efficiency (86% to 91%)
  - Cycling stability improved at cycle 10 from 178 $mAhg^{-1}$ to 188 $mAhg^{-1}$
- Can cycling be improved by smaller voltage window?
- What is spinel structure in Co/Ni-rich electrodes?
  What is behavior of Mn, Co, and Ni in spinel?
  - Utilize X-ray characterization to understand structure
  - Study spinel components individually

X-ray Structural Analyses of $xLi_2MnO_3 \bullet (1-x)LiCoO_2$

- High-resolution X-ray diffraction (XRD) and pair-distribution function measurements (PDF) have been initiated at the Advanced Photon Source (APS)

Recap:



- XRD data suggests complex structure behavior as a function of x; "solid solution" of Li_2MnO_3 and $LiCoO_2$ domains in a common ccp oxygen array
- PDF data show short range environment of Mn, Co remains constant as a function of x (to R ≈ 15Å) (M-M correlations: CN = 3 for Mn in Li_2MnO_3 layers; CN = 6 for Co in $LiCoO_2$ layers)
- How do end-members behave? What is composition/atomic arrangement?

X-ray Structural Characterization

Strategy: Stabilize 'layered-layered' Mn/Ni system with atoms that have strong layered character ➔ Co

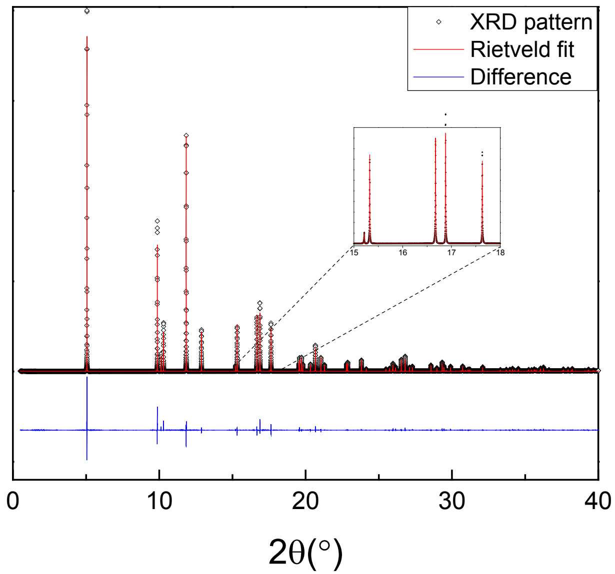
$xLi_2MnO_3 \bullet (1-x)LiMn_{0.5}Ni_{0.5}O_2$
Strong, dependent Mn-Ni

? ⟷

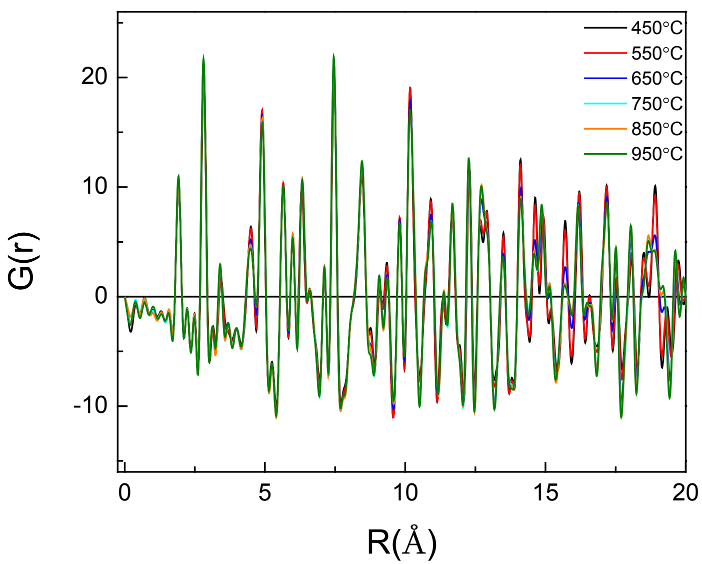
$xLi_2MnO_3 \bullet (1-x)LiCoO_2$
No/weak Mn-Co interaction

- What happens to domains and individual components of a "domain structure", i.e. $xLi_2MnO_3 \bullet (1-x)LiCoO_2$, with the addition of Ni?
- Utilize high-resolution synchrotron XRD and PDF for structural characterization of end-members

$LiCoO_2$ 850°C



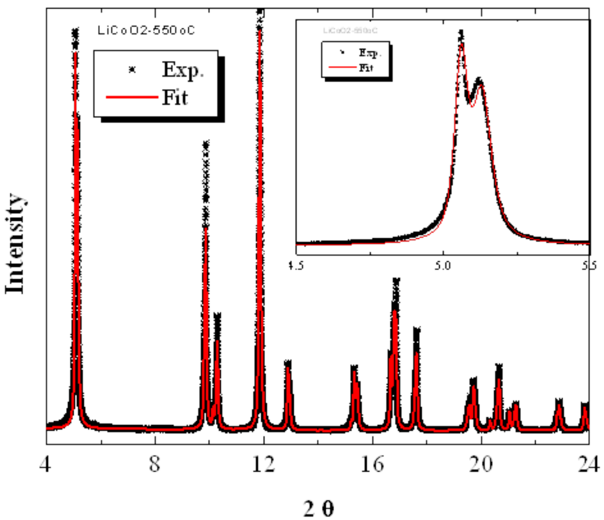
$LiCoO_2$



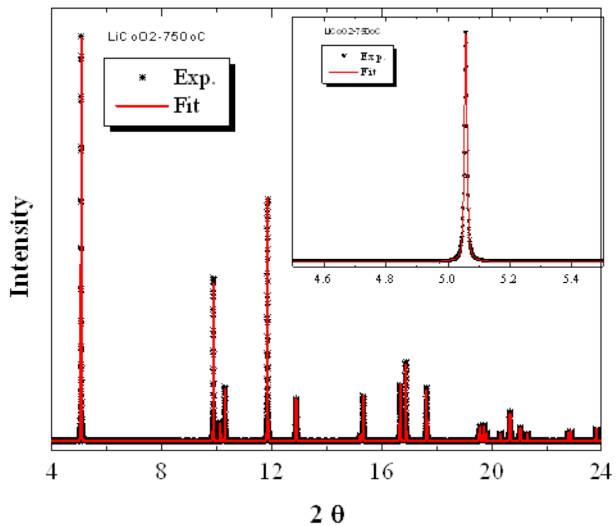
Baseline XRD of Li_2MnO_3 and $LiCoO_2$ End-members

Strategy: Study end-members of 'layered-layered' system as baseline to composite structure

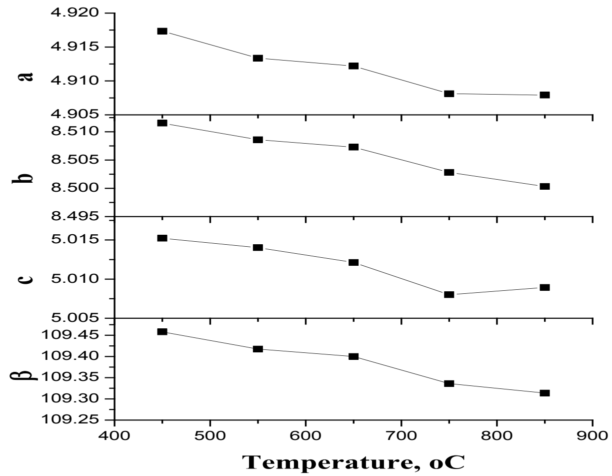
XRD fit of $LiCoO_2$ at 550°C



XRD fit of $LiCoO_2$ at 750°C



X-ray PDF fit of Li_2MnO_3



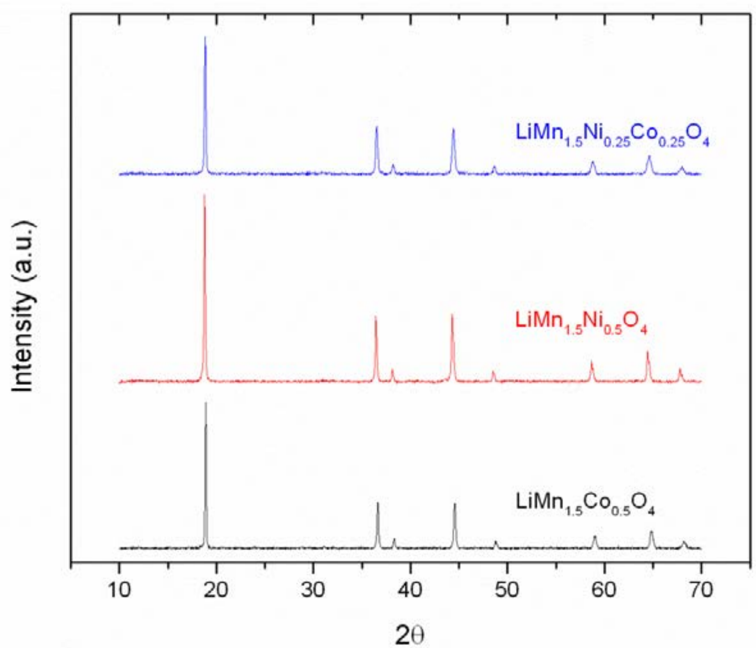
- $LiCoO_2$ data shows spinel phase decreasing with increasing synthesis temperature
- Li_2MnO_3 data shows decreasing lattice parameters with increasing synthesis temperatures
- Knowledge gained from structural analysis will be directed towards composite 'layered-layered' material

Spinel End-members

Strategy: Investigate spinel end-members for structural and electrochemical insight into composite electrodes

- Evaluation of spinel materials for optimal starting composition and insight into Mn,Ni, and Co mixed composites coupled with X-ray structural analysis
- Structures synthesized and electrochemical testing in progress

XRD of materials heated at 750°C for 12 hours



Electrochemical testing in progress

Future work

- Composition optimization
  - Continue to screen 'layered-layered-spinel' electrodes and 'layered-layered' & 'spinel' end-members to determine optimized composition and the spinel content to circumvent voltage fade;
  - Select two most promising compositions/chemistries for exhaustive electrochemical evaluation and characterization of their chemical, physical and thermal properties;
  - Evaluate electrodes in a full lithium-ion cell configuration.
- Collaboration
  - Collaborate with other ABR participants, academic and industrial partners to understand and combat voltage fade phenomena and the cause thereof.

    For example, continue to explore detailed structure-electrochemical relationships of relatively simple 'layered-layered' & end-member baseline materials (e.g., $xLi_2MnO_3 \bullet (1-x)LiCoO_2$) and 'layered-layered-spinel' derivatives by XRD, XAS and PDF analyses with collaborators at the Advanced Photon Source.

Summary

- 'Layered-layered' composite electrode structures, stabilized by a spinel component, hold promise for countering voltage fade
- 'Layered-layered-spinel' electrodes counter the first-cycle irreversible capacity loss of 'layered-layered' electrodes
- Determination of optimal high Li_2MnO_3 content to enhance capacity and stability of 'layered-layered' composite
- Increasing Ni content in high Co content electrodes provides stability

- Many questions are still to be answered: Further work is required 1) to obtain a detailed understanding of the reasons for voltage fade phenomena, 2) identify optimized 'layered-layered-spinel' compositions to best counter these effects (a basis for collaborative studies with academia and industry)

Acknowledgment

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