Studies on Oxide Cathode Crystals

Guoying Chen

Lawrence Berkeley National Lab

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Project ID: ES069

Overview

Timeline

- Start date: October, 2009
- End date: September, 2012
- Percent complete: 60%

Barriers Addressed

- Energy density
- Cycle life
- Safety

Budget

- Total project funding
  - FY2010 $300K
  - FY2011 $300K

  Supports 1 postdoc and 70% of the PI

Partners

- Collaborations: Grey (Stony Brook/Cambridge), Richardson, Kostecki, Doeff, Cabana (LBNL), Gabrisch (UNO), NCEM, ALS, SSRL
- Project lead: Venkat Srinivasan

Objectives

- Investigate phase transition mechanisms, explore kinetic barriers, and evaluate stability of high-energy cathode materials.
- Establish direct correlations between crystal structure, composition, morphology, performance, and stability.
- Provide guidelines to design and develop electrode materials with improved energy density, rate capability, and safety, especially with regard to thermal stability.

Milestones

March 2011	Report the synthesis of layered oxide crystals with various compositions.
June 2011	Report the phase transformation and thermal behavior of $LiMMnPO_4$ (M = Mg, Fe, Co and Ni).
August 2011	Report structure and property evaluation of the layered oxide crystals.
September 2011	Report the synthesis of $LiNi_{0.5-x}Mn_{1.5+x}O_4$ crystals.

Approach

- Prepare well-formed crystals of cathode materials with various crystal structures, chemical compositions, sizes, and morphologies.

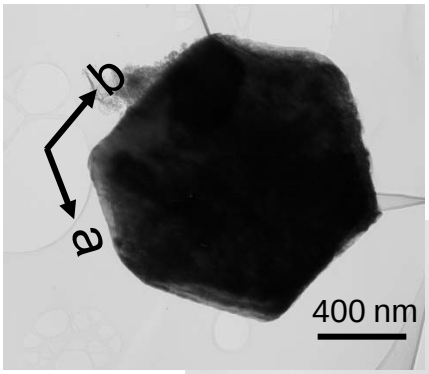
- Characterize physical properties and investigate solid state chemistry of the crystals using chemical and electroanalytical methods**,** synchrotron based spectroscopies and spectromicroscopies, X-ray and neutron diffractions**,** vibrational spectroscopies, scanning calorimetry, and electron microscopic techniques.

- Optimize synthesis and processing conditions, improve performance and safety of the cathode materials based on the structural and mechanistic understandings.

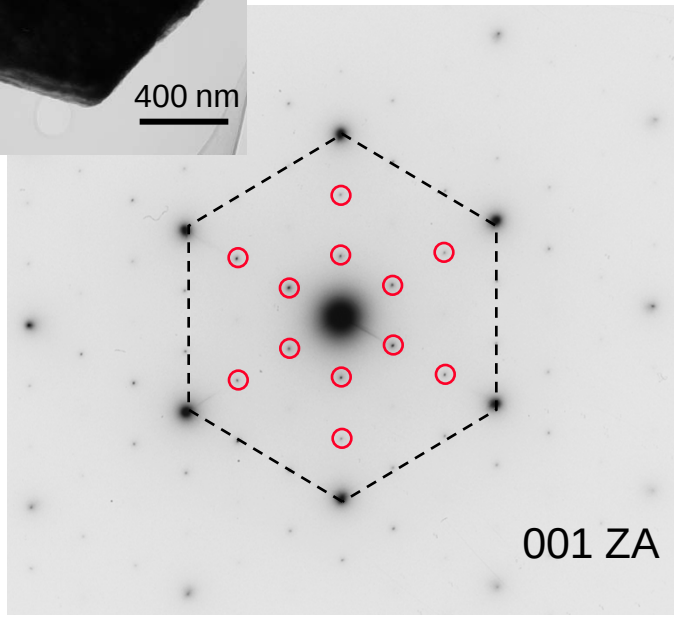
Layered $Li_{1+x}M_{1-x}O_2$

- Understand the relationship between structural ordering, kinetic behavior, and stability of the oxide.
- The use of single crystals allows us to:
  - Eliminate sample non-uniformity for unambiguous results.
  - Utilize unique techniques in microscopy and spectroscopy to probe intrinsic properties.
- Technical accomplishments/progress made in the following topics:
  - Effect of excess Li on structure and performance.
  - Effect of chemical composition and synthesis conditions on cation ordering and transition metal layer stacking.
  - Effect of crystal size and morphology.
  - Effect of excess Li and Mn on structure and performance.
  - The activation mechanism of Li_2MnO_3 in the high-energy $xLi_2MnO_3 \cdot (1-x)LiMO_2$ composites.

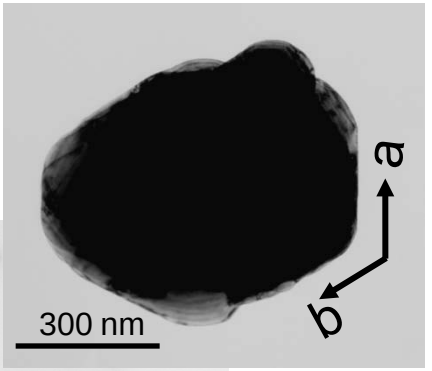
Effect of Excess Li

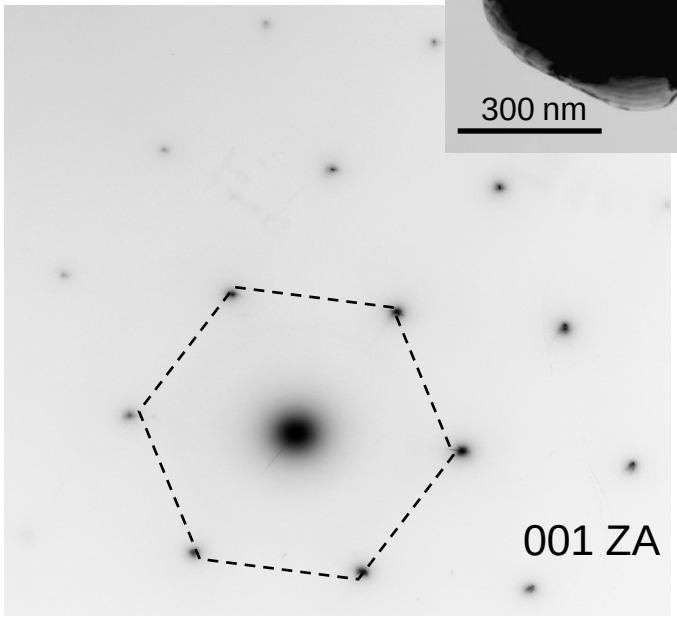


“Li-excess” (x=0.14)



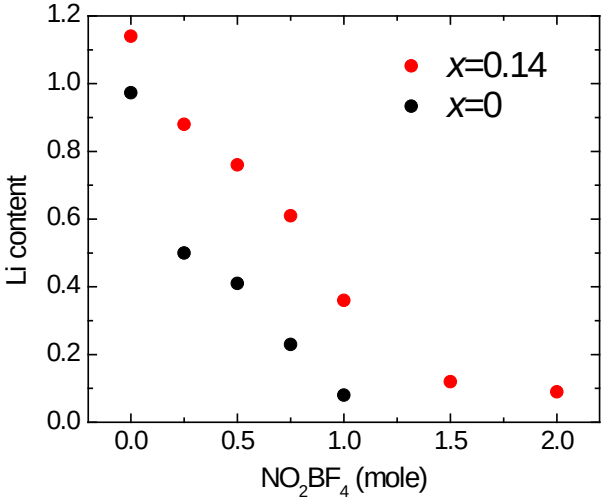
“Li-stoichiometric” (x=0)





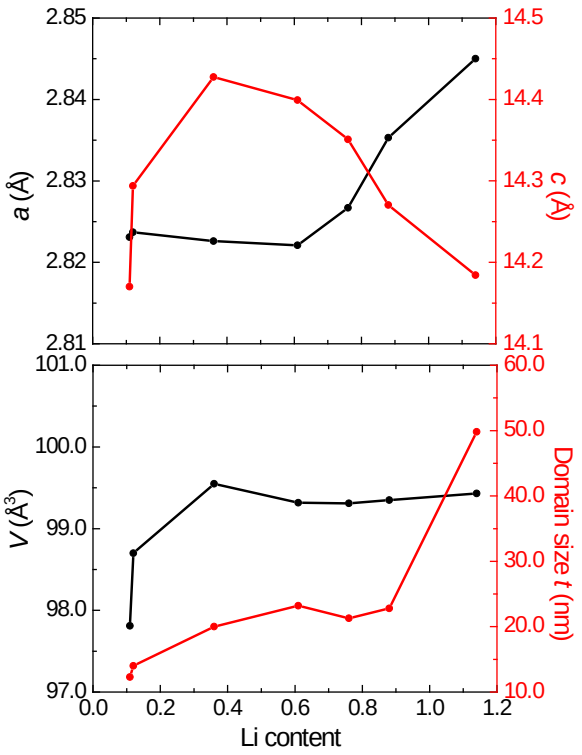
- $Li_{1+x}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{1-x}O_2$ (NMC333) single crystals were prepared in eutectic LiCl-$LiNO_3$ for x=0.14 and KCl molten salt for x=0.
- $\sqrt{3}a_{hex} \times \sqrt{3}a_{hex}$ superlattice reflections present in x=0.14 but not in x=0.

Volume Change on Delithiation



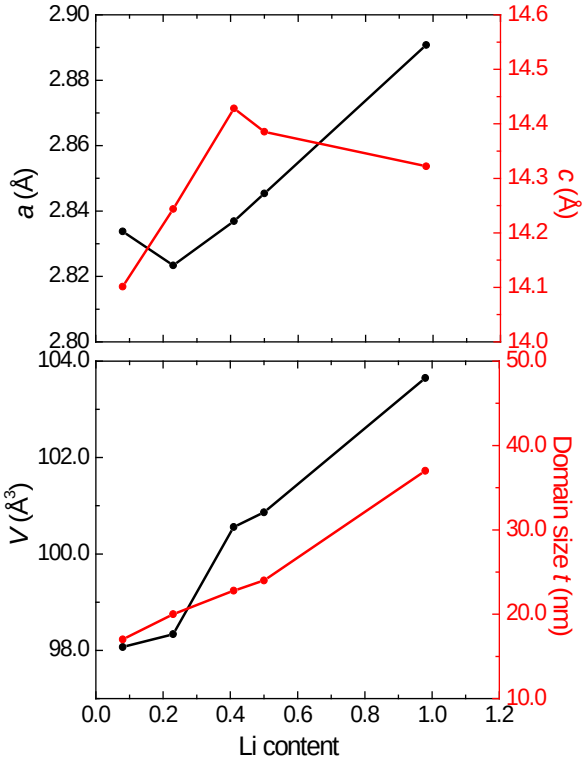
- Crystals chemically delithiated by NO_2BF_4.

***x*=0.14**



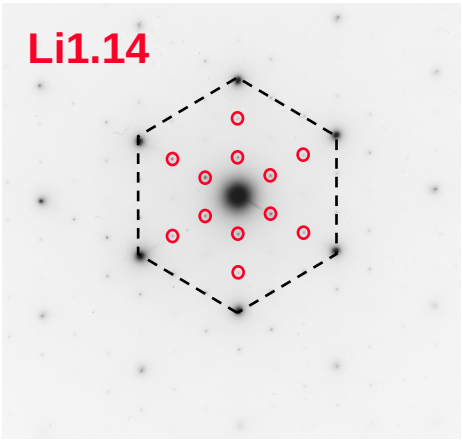
- Cell volume constant up to Li0.36. Reduced by 1.6% at Li0.09.
- Phase transition from O3 to P3 evident when Li ≤ 0.12, after extraction of 1.02 mol Li.

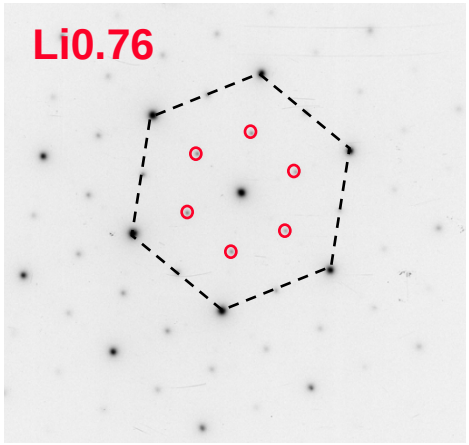
***x*=0**

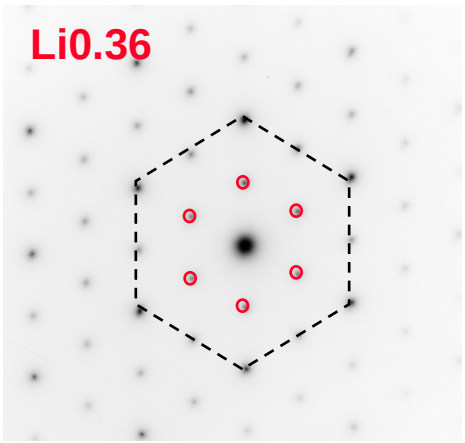


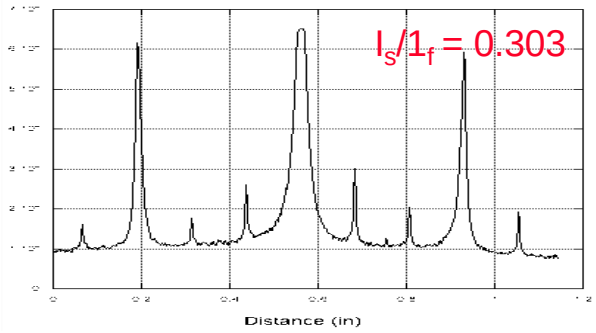
- Continuous decrease in cell volume. Total reduction of 5.4% at Li0.08.
- O3 to P3 phase transition significant at Li = 0.23, after extraction of 0.77 mol Li.

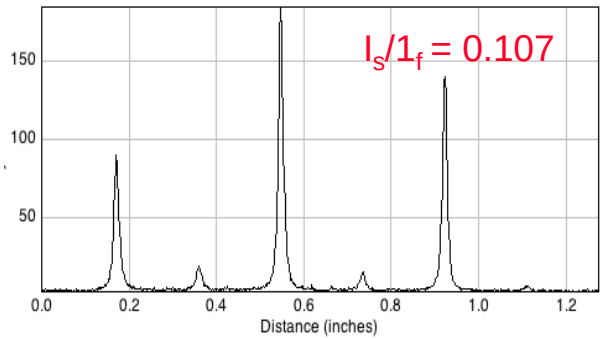
Structural Change on Delithiation

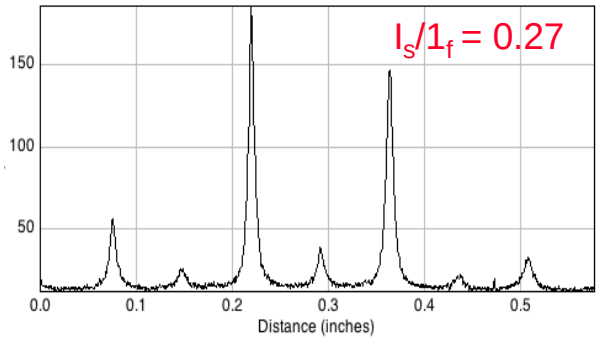






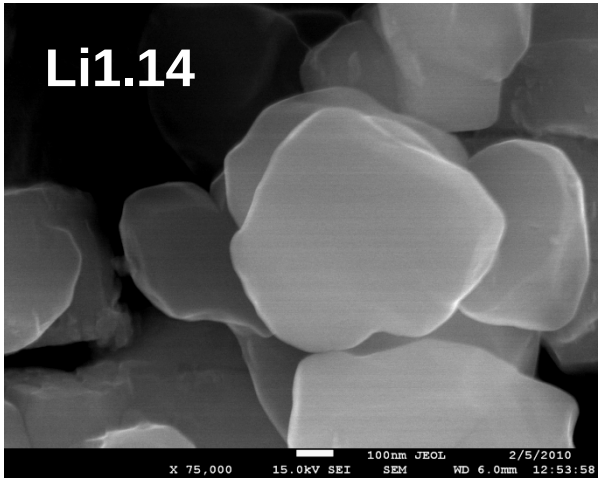


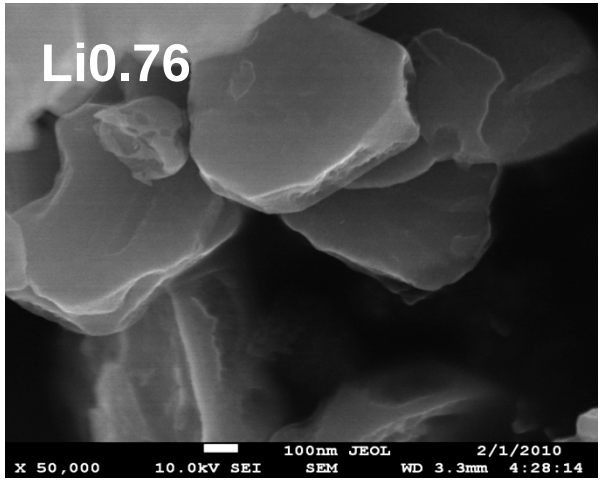


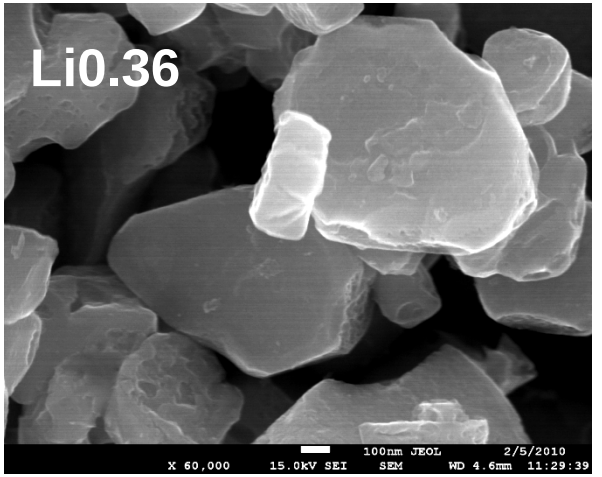


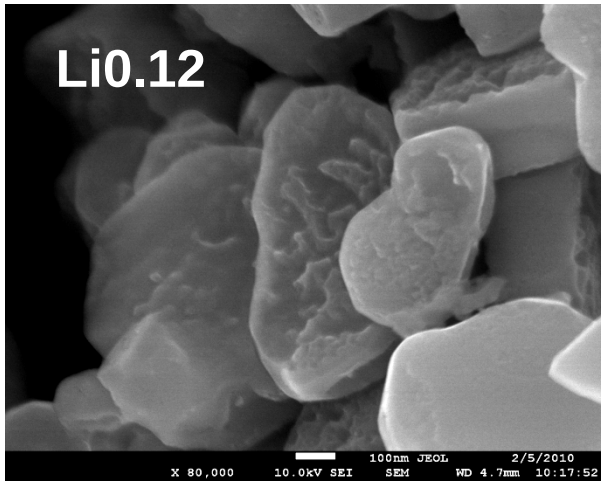
- Disappearance of $\sqrt{3}a_{hex} \times \sqrt{3}a_{hex}$ and appearance of new superlattice reflections suggest change of in-plane cation ordering upon delithiation of Li-excess oxide (x=0.14).
- Intensity of superlattice reflections increases with further Li removal.
- No ordering change on Li-stoichiometric sample (x=0).

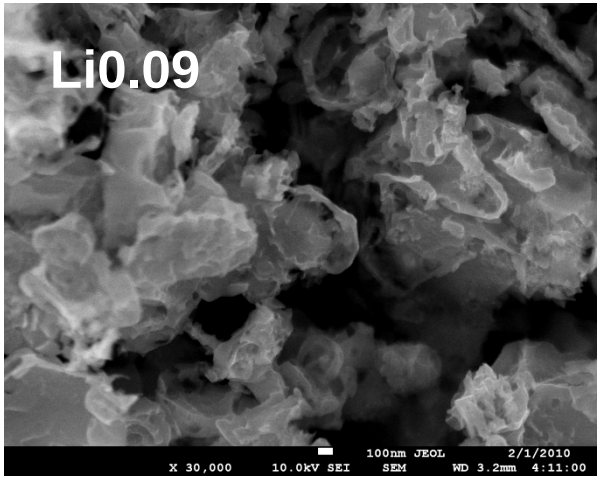
Morphology Change on Delithiation





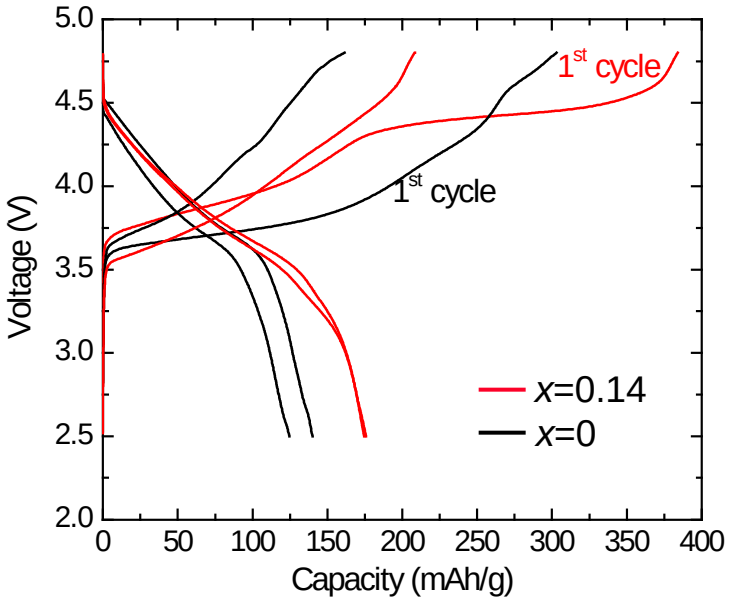


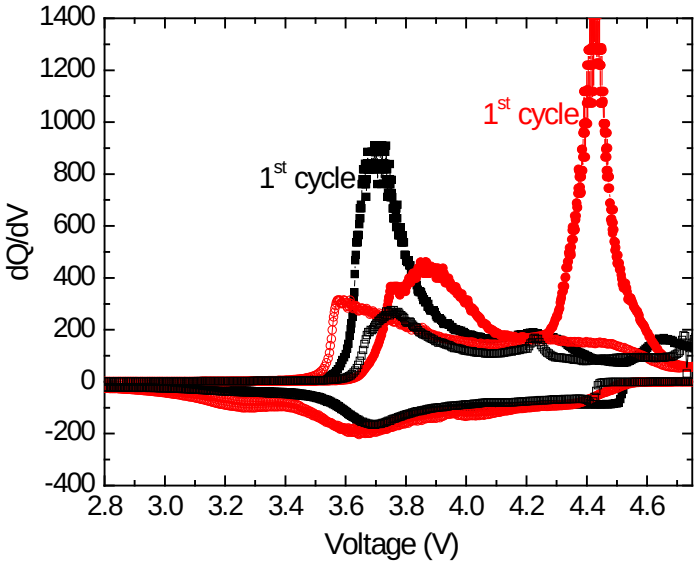


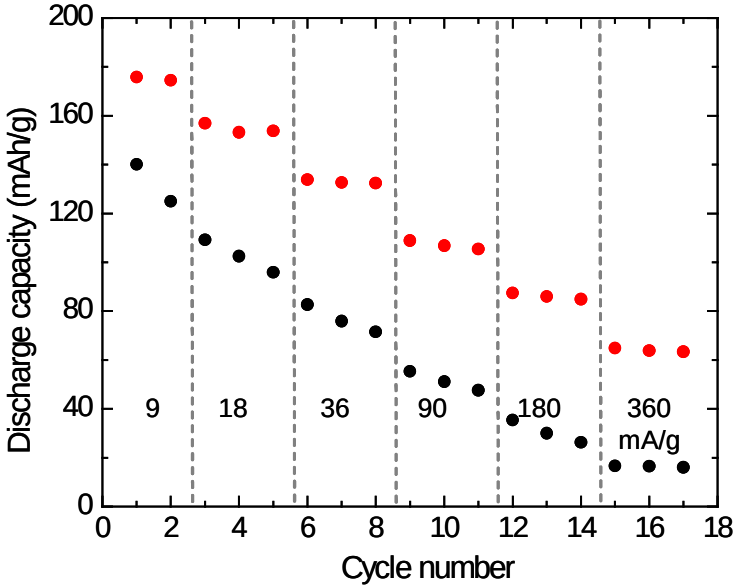


- Morphological damage significant on x=0.14 but not on x=0.
- Oxygen evolution has a larger effect on crystal physical stability than volume change or phase transition.

Capacity and Rate Capability

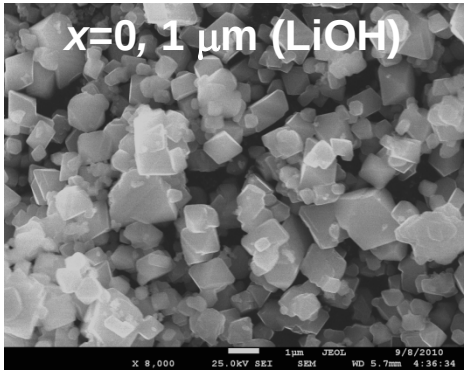


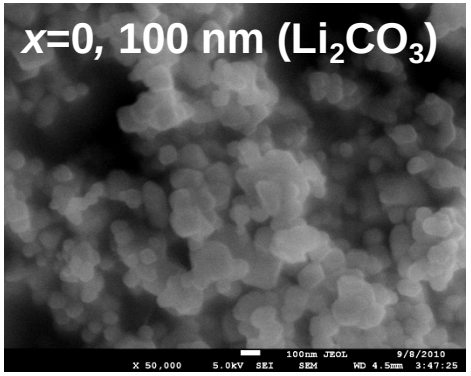


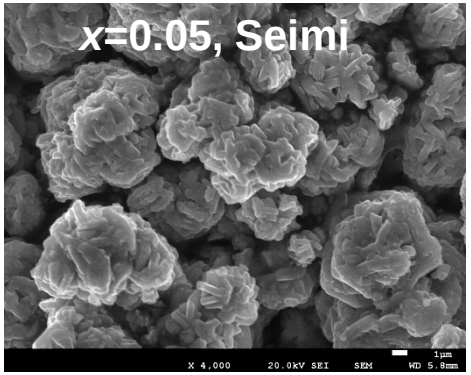


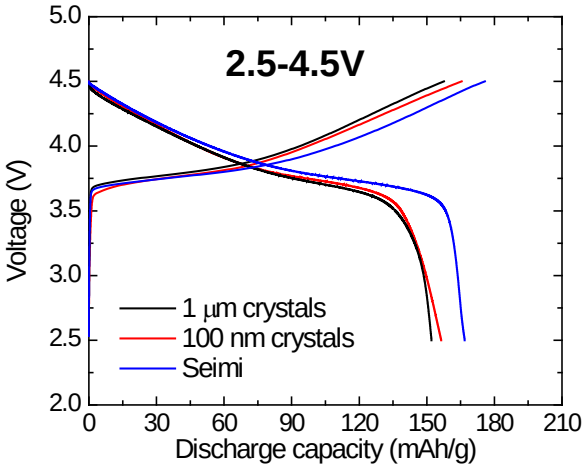
- Presence of charging plateau at 4.5 V in the overlithiated sample.
- Lowered polarization after charging through the plateau.
- Higher discharge capacity and improved rate capability in the overlithiated oxide.
- Larger influence from phase stability than morphological stability.

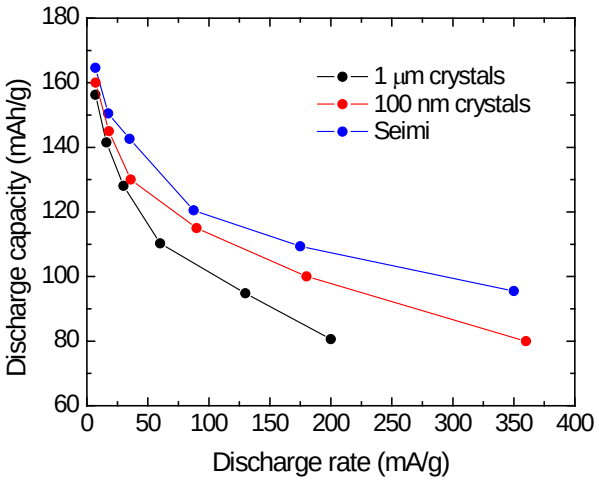
Effect of Crystal Size

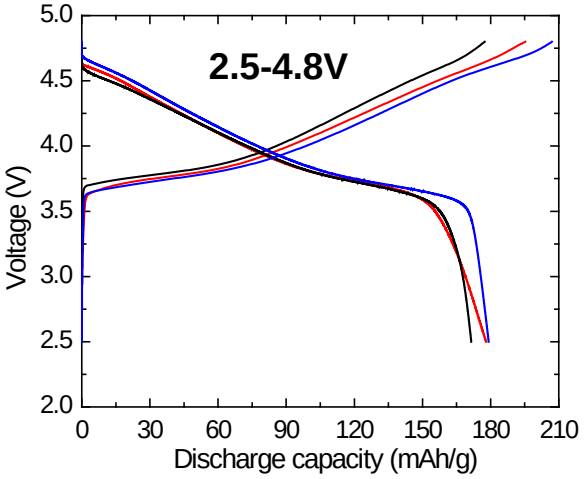


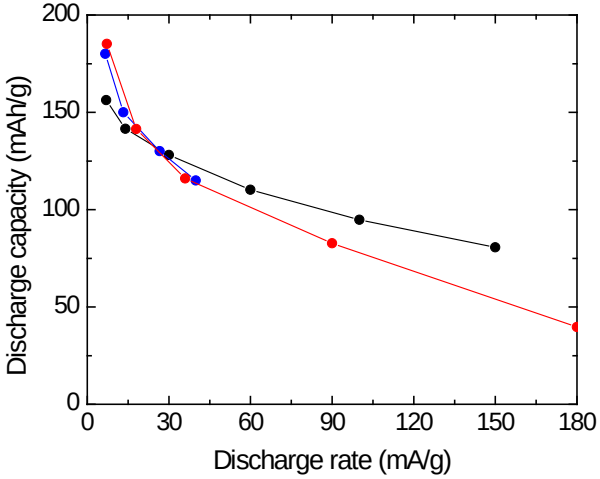






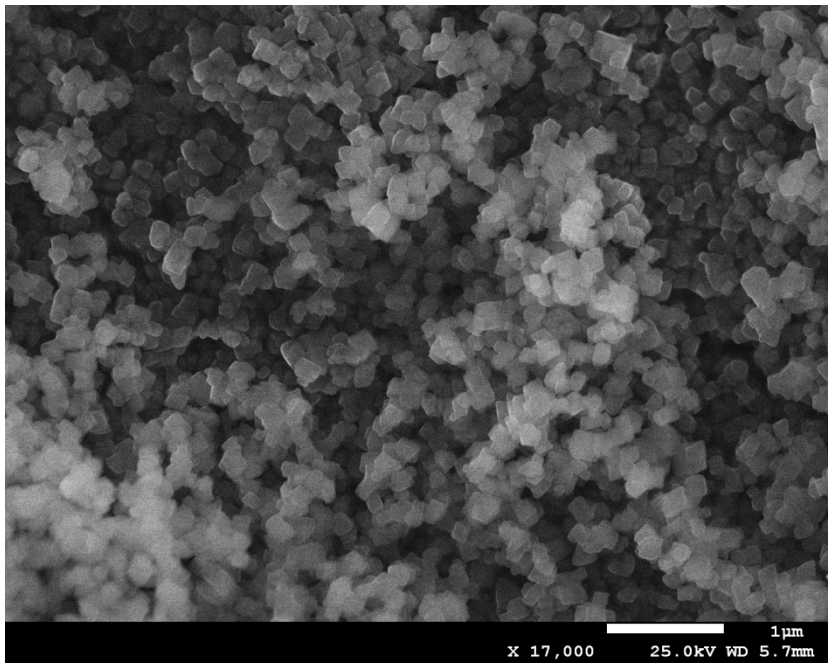


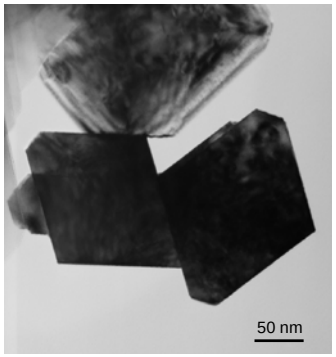


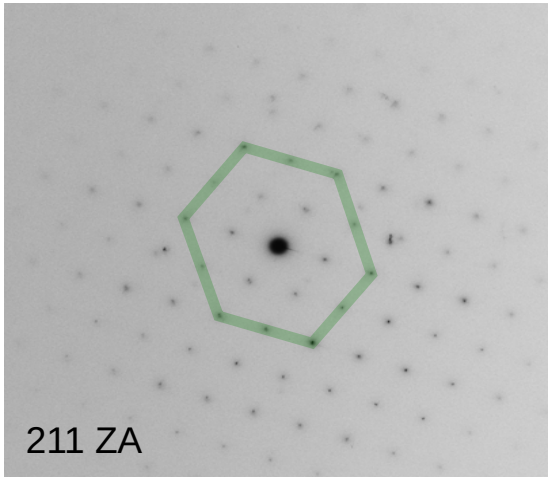


- Small crystals showed higher rate capability at 4.5 V cutoff, but larger crystals performed better at higher cutoff voltages.
- Side reactions at high voltage is likely the cause of the difference.

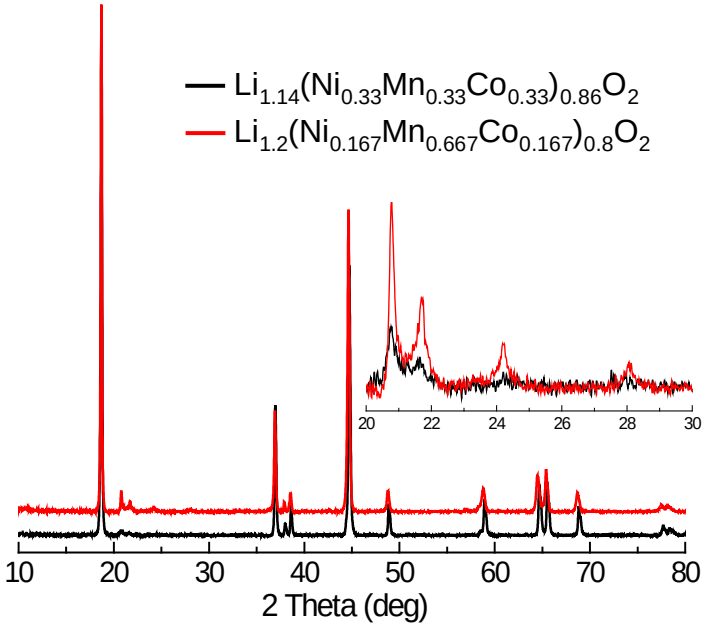
Effect of Excess Li and Mn



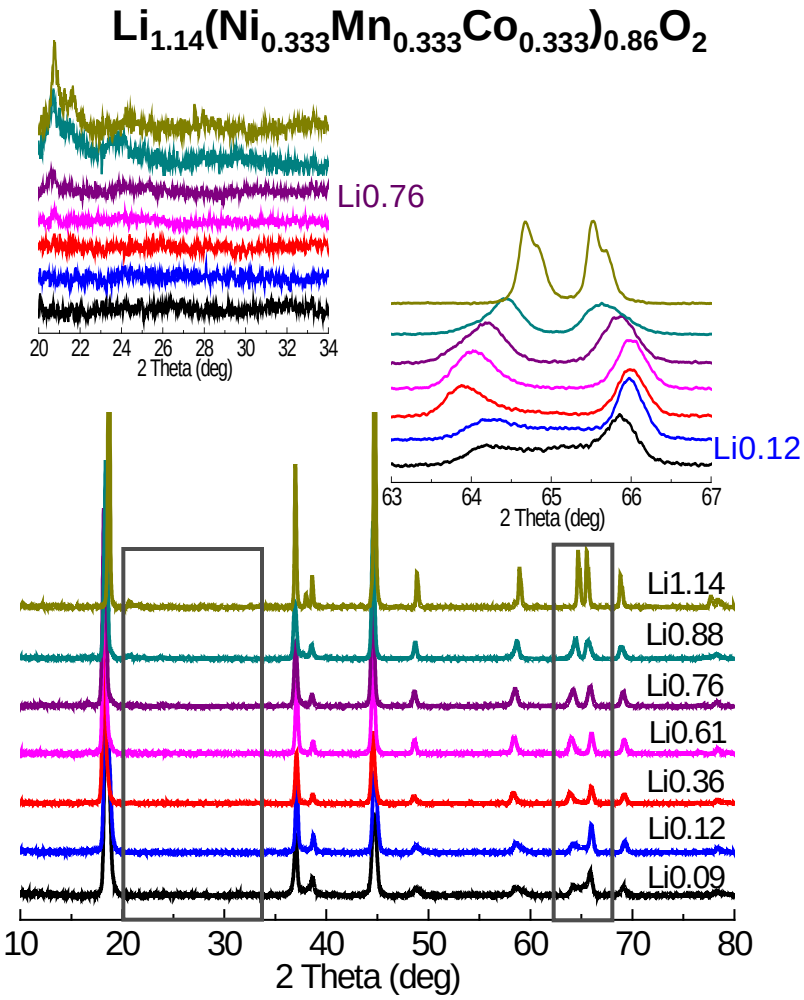


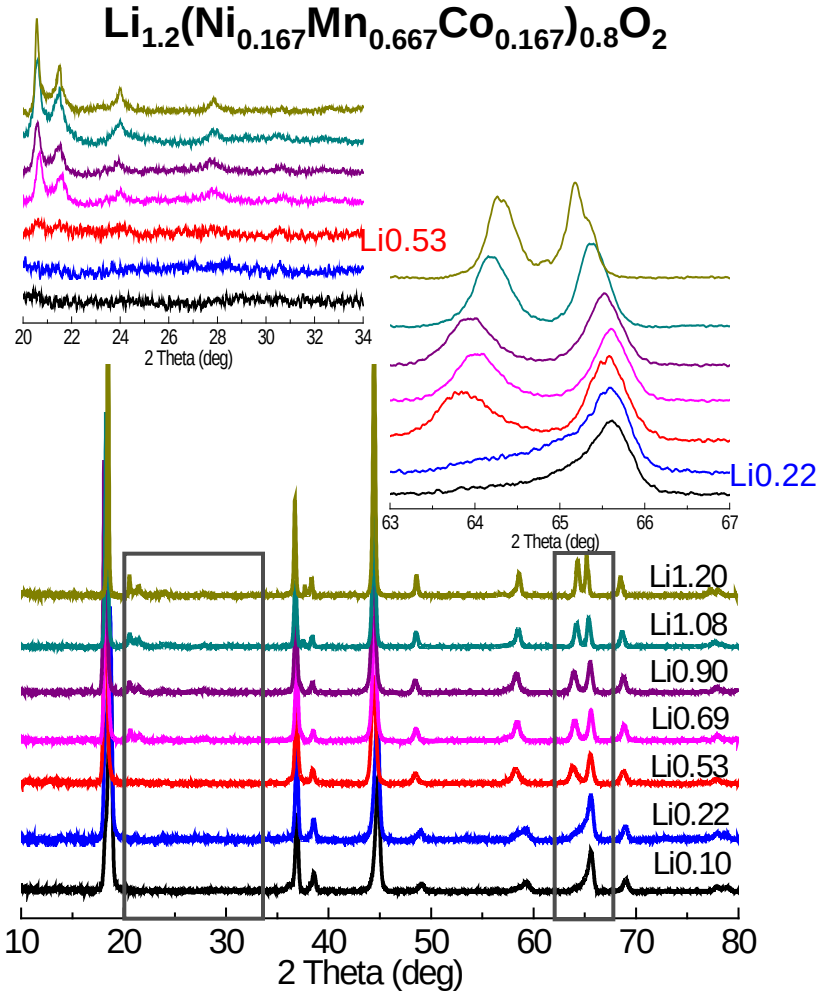


- $Li_{1.2}(Ni_{0.167}Mn_{0.667}Co_{0.167})_{0.8}O_2$ (or $0.5Li_2MnO_3 \cdot 0.5LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$) single crystals with 200 nm average size were prepared in KCl flux.
- Sharper and stronger superlattice peaks suggest enhanced structural ordering.



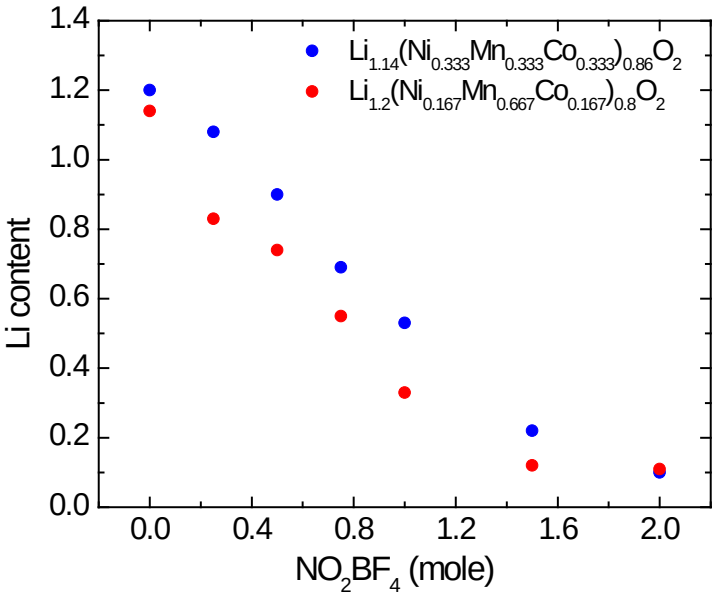
Delithiation – Phase Stability

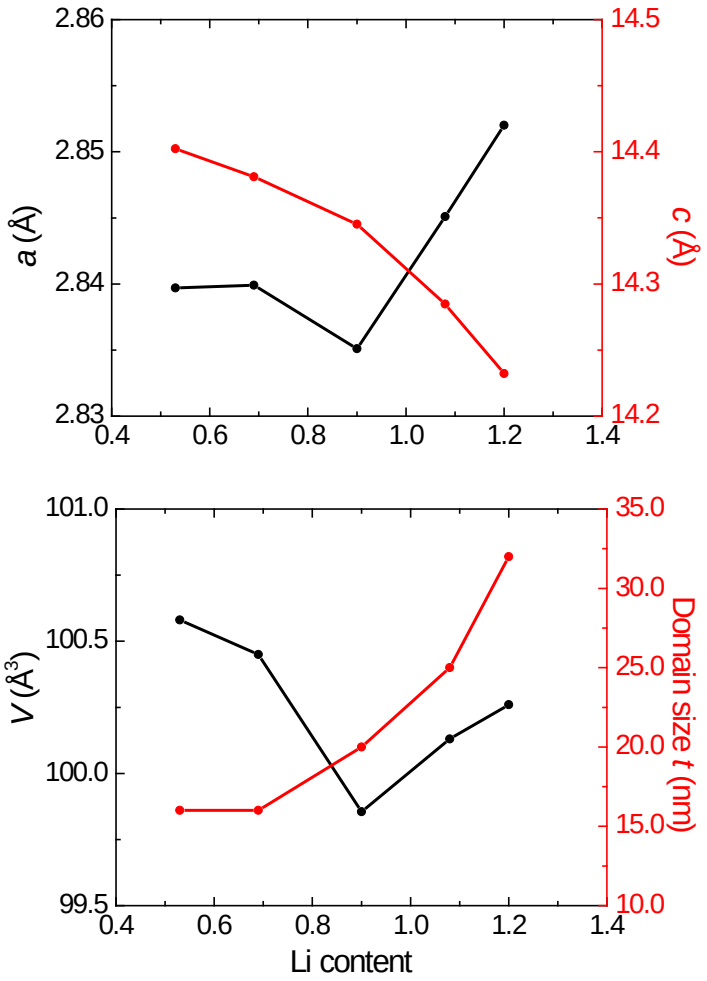




- Disappearance of superlattice peaks at Li0.53.
- Lowered O3 phase stability with excess Mn – mostly P3 phase at Li0.22.

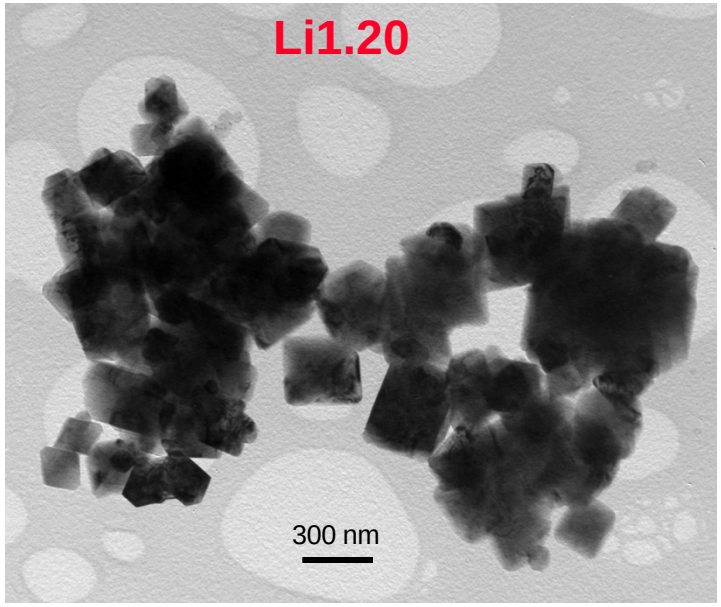
Delithiation – Cell Dimensions

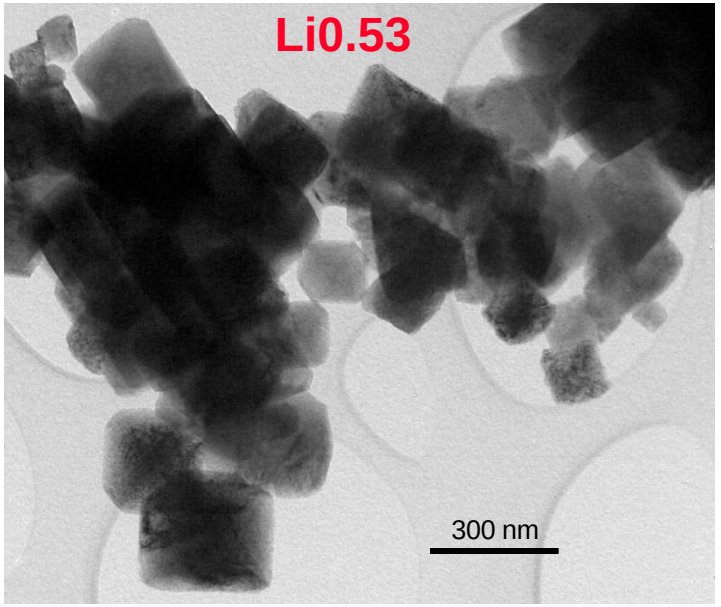




- Delithiation kinetics similar to Li-excess NMC333.
- Continuous expansion in the *c* direction in the O3 phase. Cell volume contracts and then expands. Total volume change less than 0.5%.

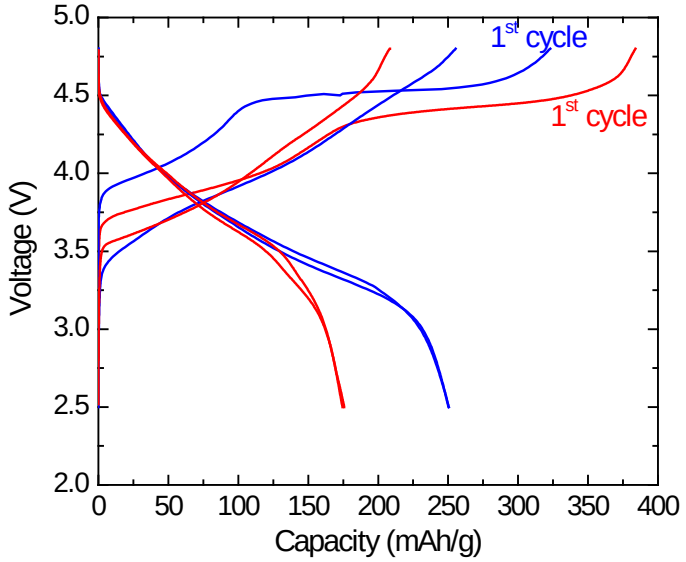
Delithiation – Morphology

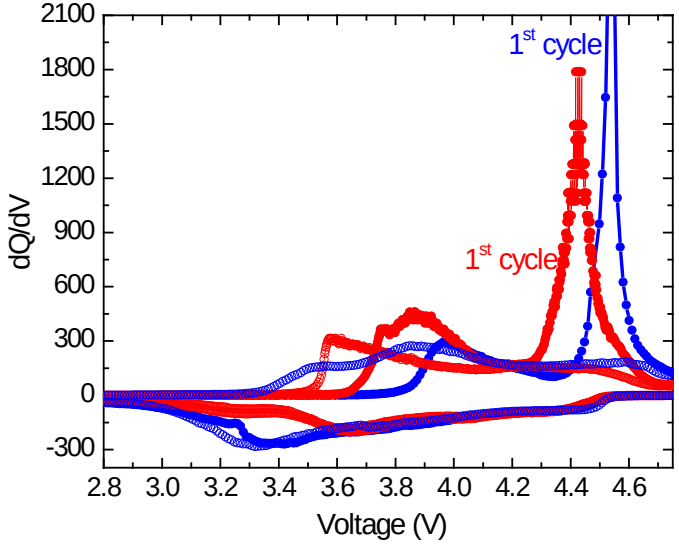


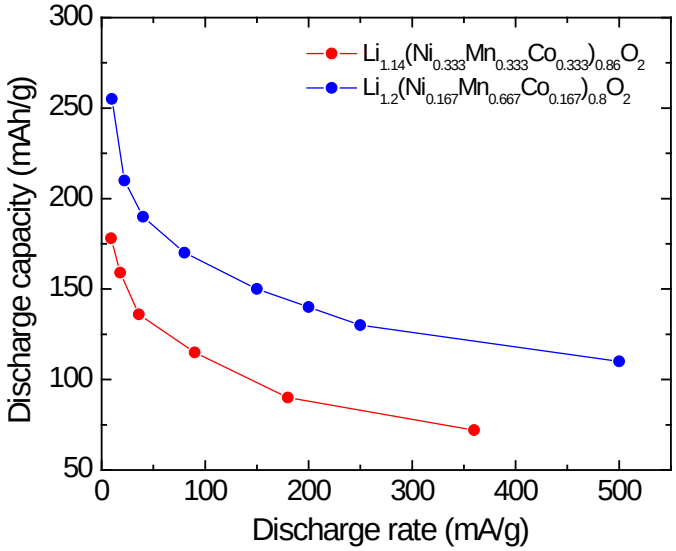


- Preliminary evaluation showed no obvious morphological change after delithiation.
- Improved physical stability towards oxygen evolution in smaller crystals.

Electrochemical Performance



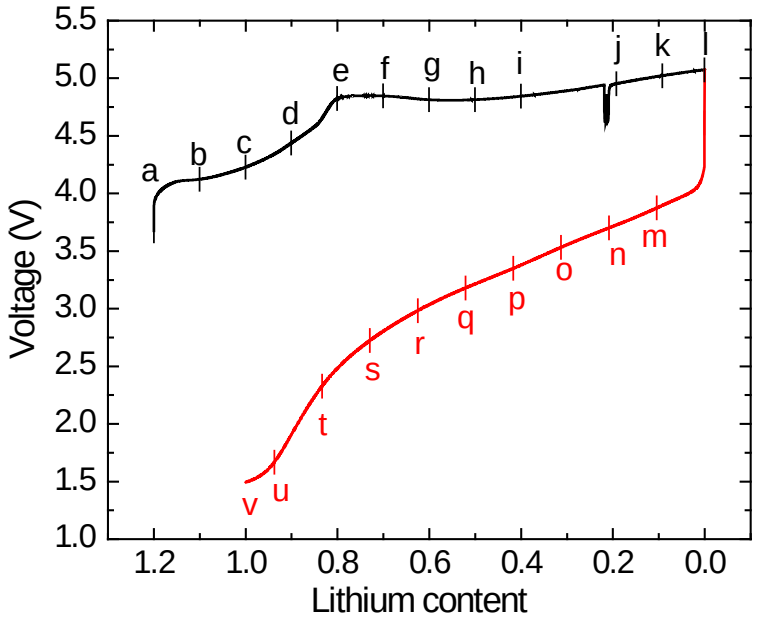


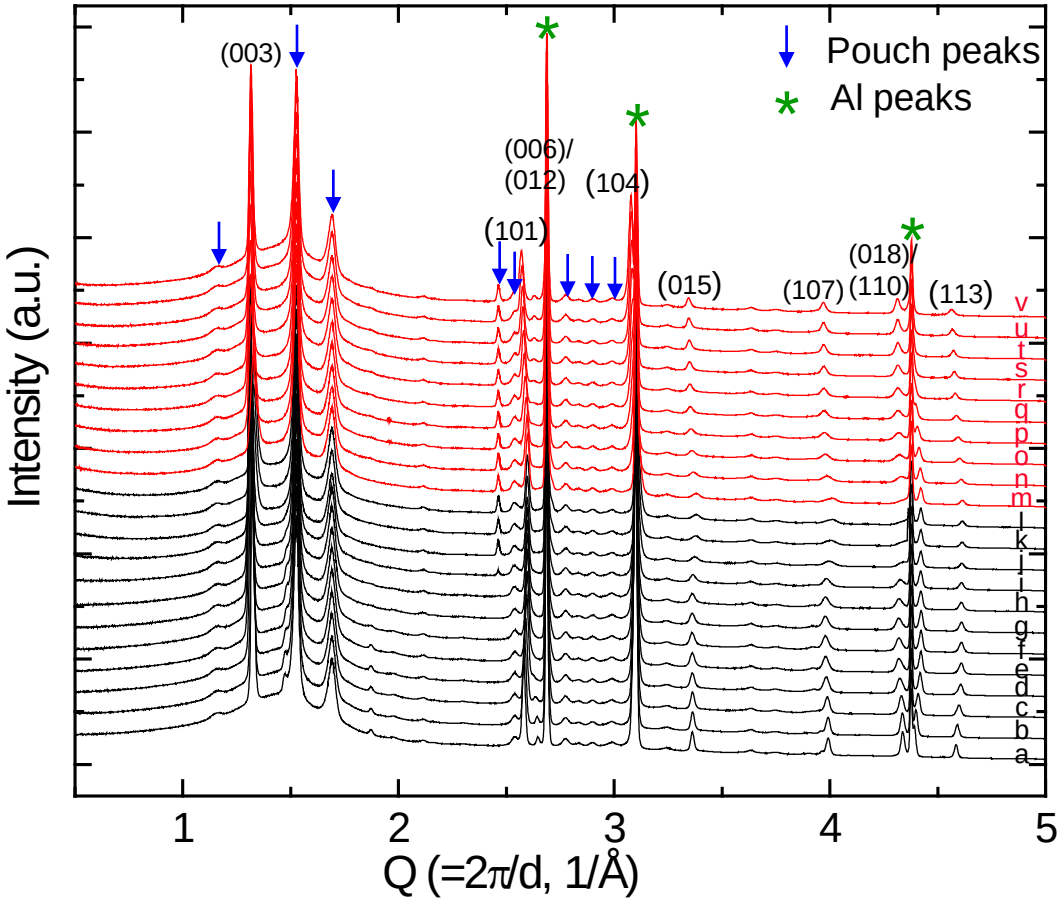


- $0.5Li_2MnO_3 \cdot 0.5LiMn_{0.333}Ni_{0.333}Co_{0.333}O_2$ compared to $0.33Li_2MnO_3 \cdot 0.67LiNi_{0.5}Co_{0.5}O_2$ (Li-excess NMC333).
- About 200 mV increase in Li_2MnO_3 activation voltage.
- Two charging peaks observed after first cycle activation. Discharge voltage shifted lower with increasing Li_2MnO_3 content.
- Improved rate capability.

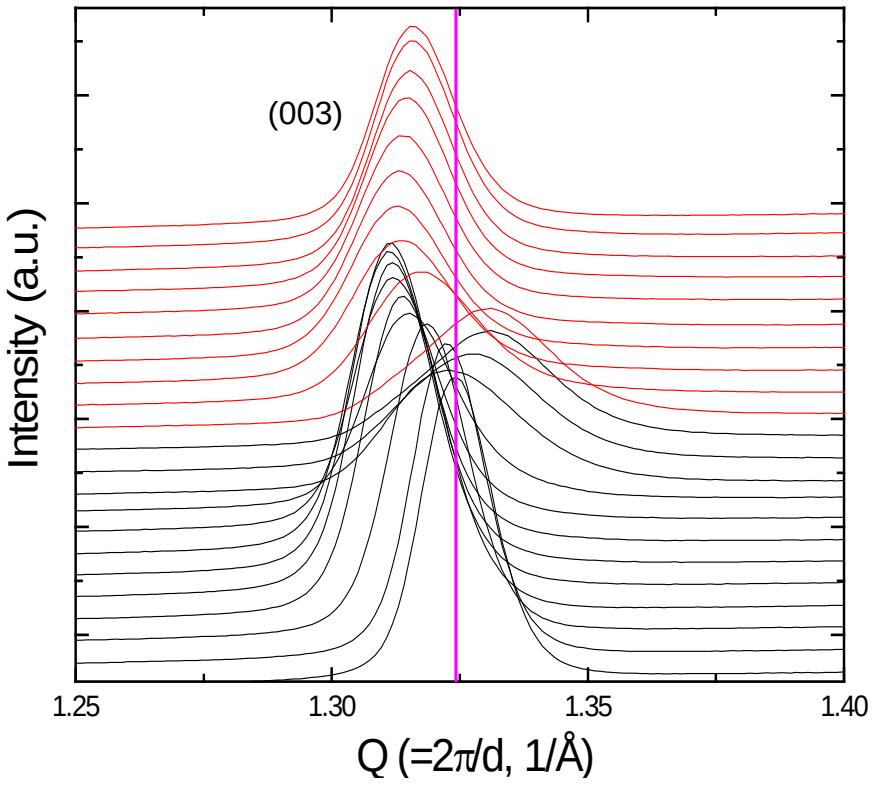
Synchrotron *in situ* XRD

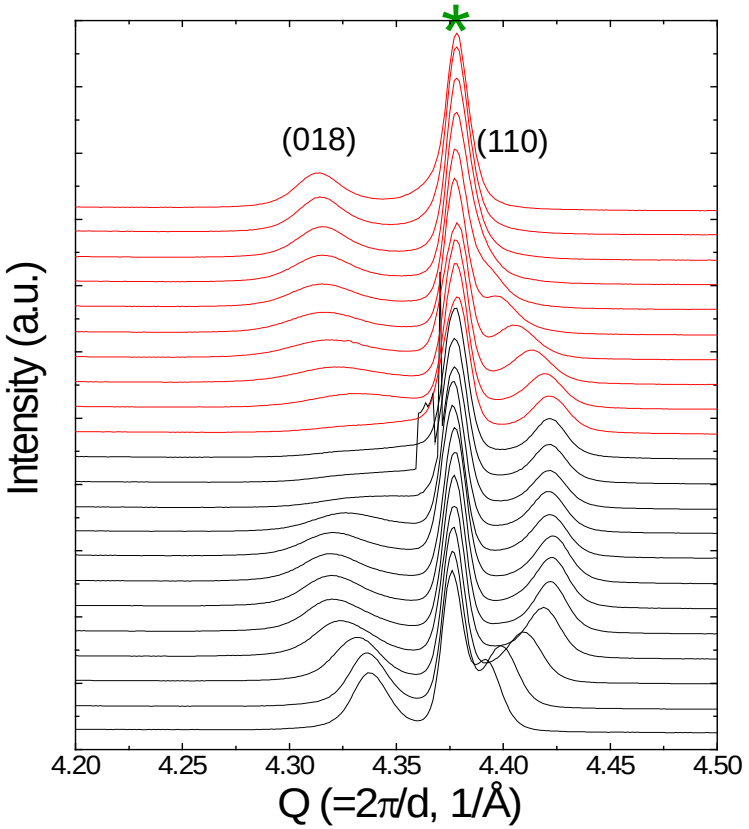
SSRL BL 11-3
C/20 Charge and Discharge





Synchrotron *in situ* XRD





- Phase transition from O3 to P3 upon deep Li extraction.
- Change in cell dimensions consistent with the results from chemical delithiation.

$LiMn_{1.5}Ni_{0.5}O_4$ Spinel

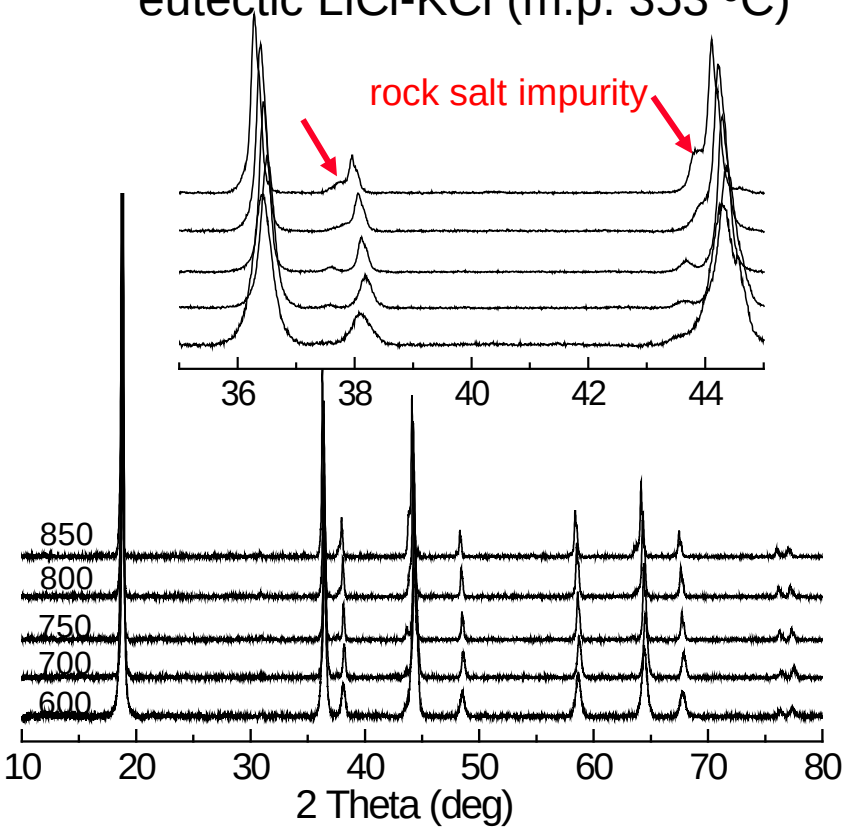
- Work with BATT Ni/Mn Spinel Focus Groups to understand side reactions and transport phenomena of the cathode under high voltage operation.

- Work on single crystals to establish relationships between crystal structures (ordered vs. disordered), size and morphology, Mn^{3+} content, energy density, rate capability (transport properties), and stability (side reactions) of the cathode.

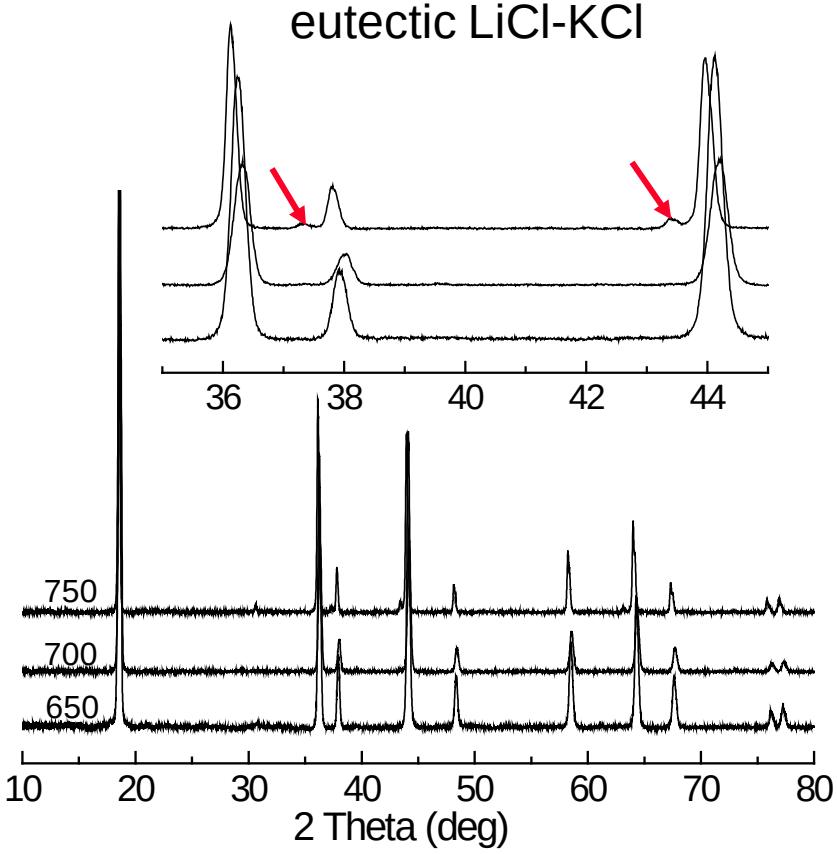
- Technical accomplishments/progress made in the following area:
  - Phase pure $LiNi_{0.5}Mn_{1.5}O_4$ single crystals with various sizes and morphologies prepared.
  - Characterization of the crystals and preliminary evaluation of Li extraction/insertion processes performed.

Crystal Synthesis – Temperature

LiOH, MnO_2 and $Ni(OH)_2$, eutectic LiCl-KCl (m.p. 353 ^oC)



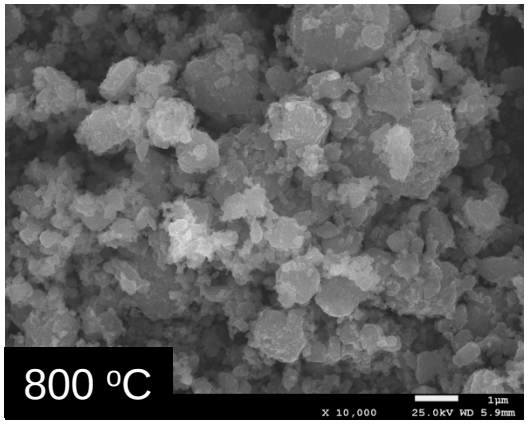
$Mn(NO_3)_2$ and $Ni(NO_3)_2$, eutectic LiCl-KCl

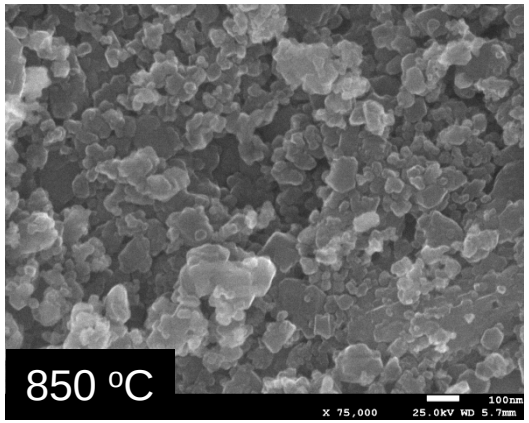


- Phase pure spinel forms around 550 ^oC.
- Rock salt impurity appears above 600 ^oC with the hydroxide and 700 ^oC with the nitrate precursors.
- Lattice expands with temperature, suggesting increased Mn content at higher temperatures.

Crystal Synthesis – Temperature

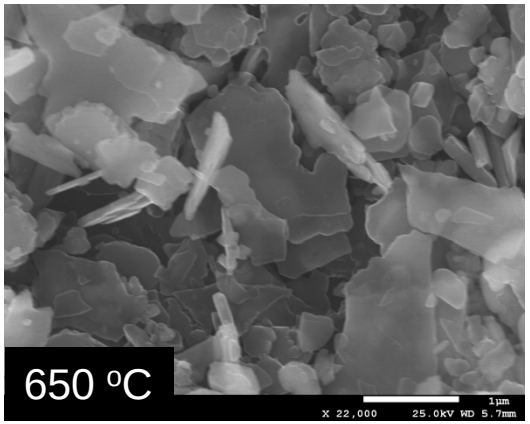
LiOH, MnO_2 and $Ni(OH)_2$
KCl (m.p. 771 ^oC)

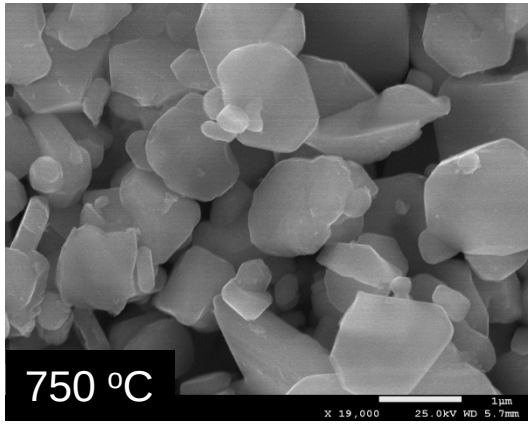




- Formation of small spherical crystals with oxide precursors.
- Improved crystallinity at higher temperatures.

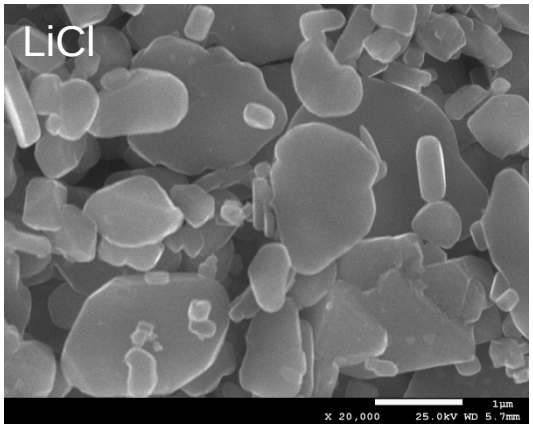
$Mn(NO_3)_2$ and $Ni(NO_3)_2$
LiCl (m.p. 610 ^oC)

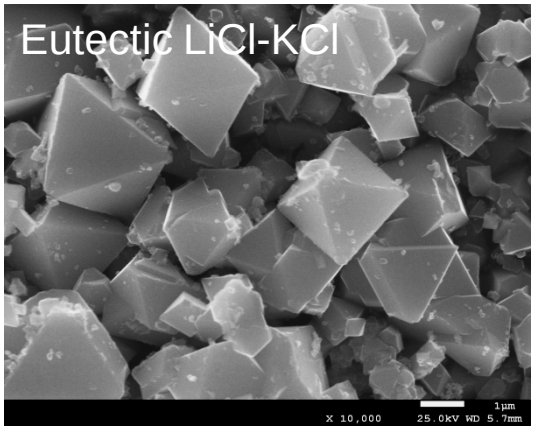


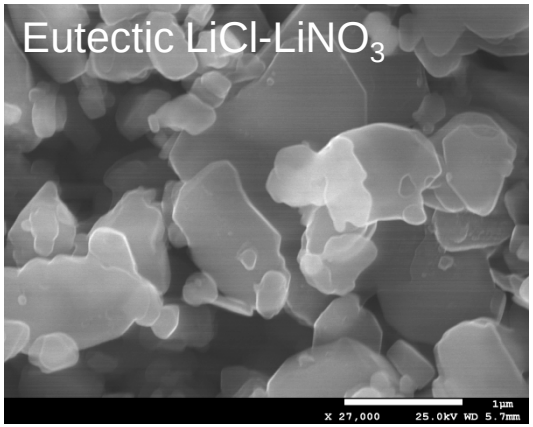


- Formation of plate-shaped, micron-sized crystals with nitrate precursors.
- Increased plate thickness at higher temperatures.

Crystal Synthesis – Molten Salt

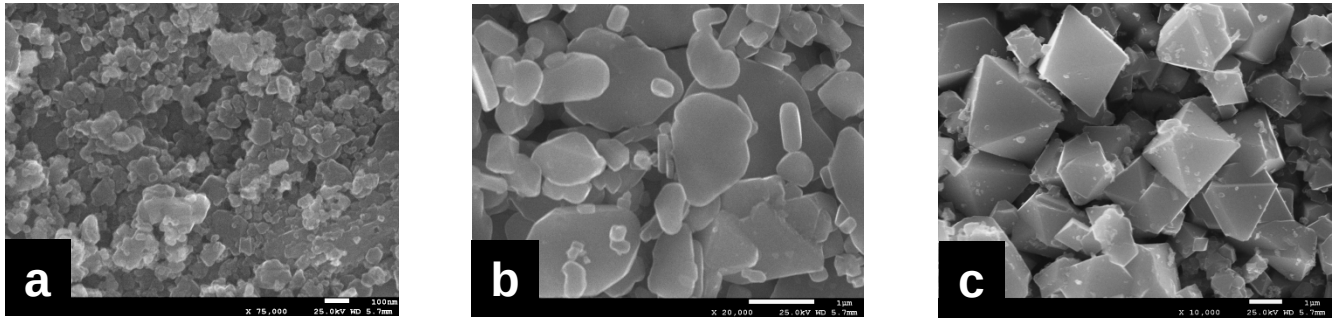


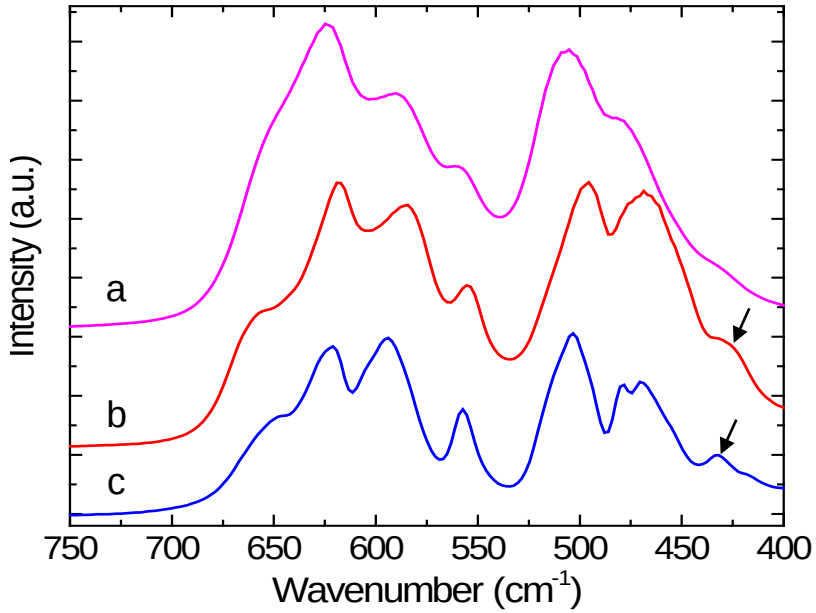




- Plate-shaped spinel crystals formed in LiCl and octahedron-shaped formed in LiCl-KCl flux.
- Only layered-phase crystals formed when LiCl-$LiNO_3$ flux was used.

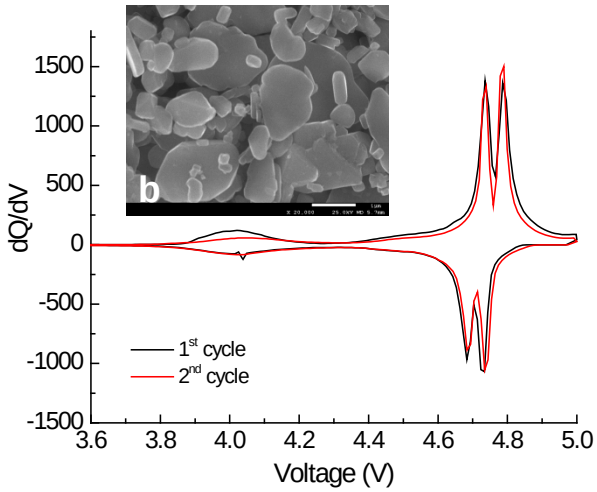
Morphology Effect – FTIR

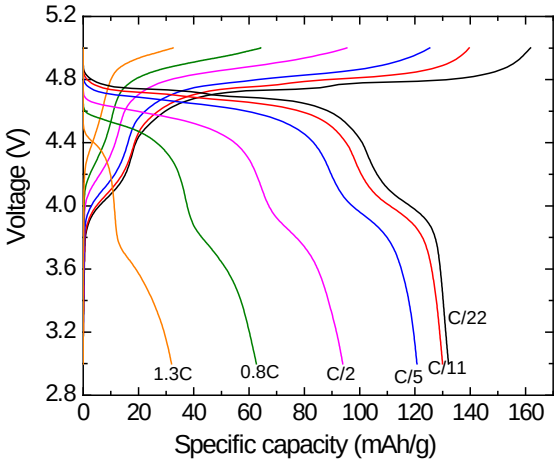


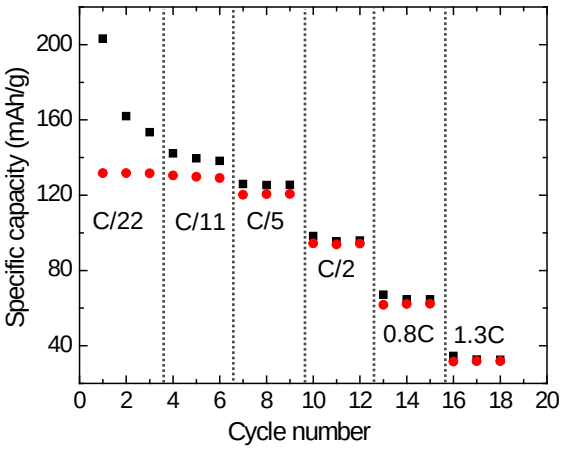


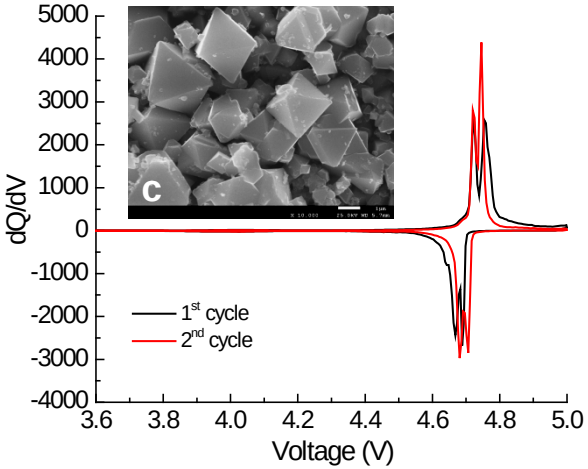
- Peak around 430 cm^{-1} is characteristic of the ordered phase.
- Crystal size has larger impact on structural ordering than the morphology.

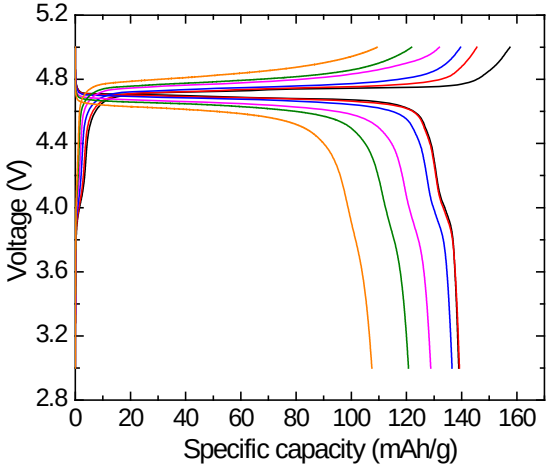
Morphology Effect – Performance

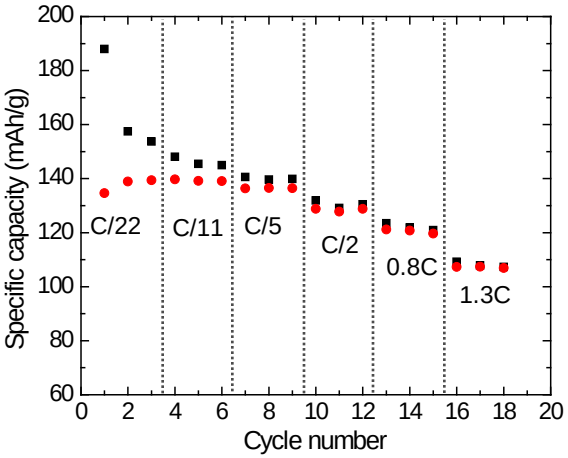












- Good rate capability from the octahedron-shaped, large crystals.

Collaborations

- Tom Richardson (LBNL) – Material synthesis and characterization
- Clare Grey (SUNY Stonybrook/Cambridge) and Jordi Cabana (LBNL) – NMR measurements
- Heike Gabrisch (U. New Orleans) – TEM studies on iron and manganese phosphates
- Robert Kostechi (LBNL) – Raman and FTIR characterization
- Austen Angell (ASU) and John Kerr (LBNL) – TGA and DSC studies
- Jordi Cabana, Marca Doeff, Tom Richardson (LBNL) and Joy Hayter, Apurva Mehta (SSRL): TXM, *in situ* XRD and XAS of cathode crystals
- Vince Battaglia and Marca Doeff (LBNL) – Cell fabrication and testing

Future Work

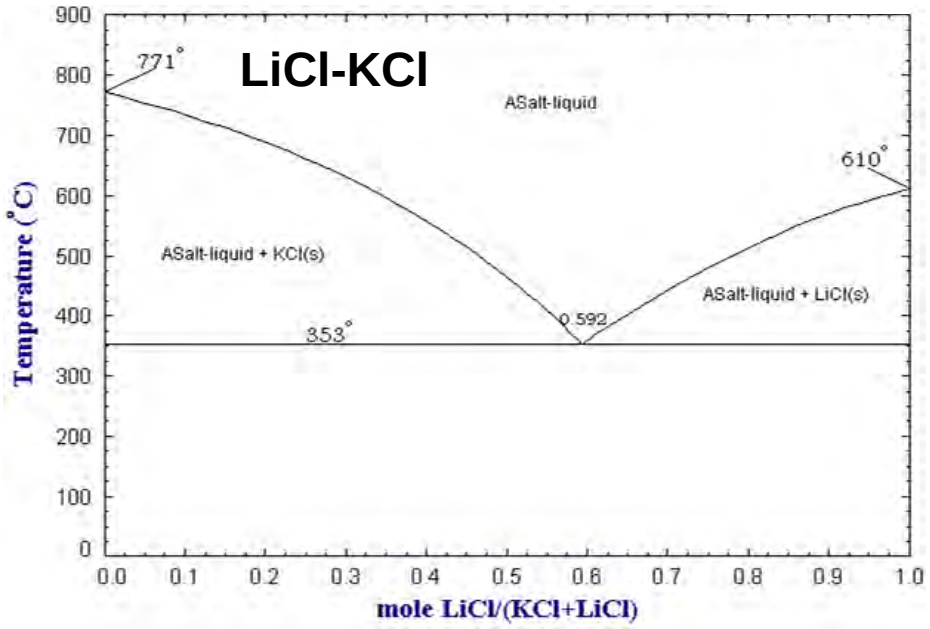
- **Layered $Li_{1+x}M_{1-x}O_2$:**
  - Prepare Li and Mn excess oxide crystals with other composition, size and morphology.
  - Further correlate the physical attributes and performance (including rate capability, cycle life, stabilities) of the oxides.
  - Evaluate structural change on the delithiated and relithiated crystals. Investigate oxygen evolution mechanism and its impact on performance.
- **Ni/Mn spinel:**
  - Continue to prepare $LiNi_{0.5-x}Mn_{1.5+x}O_4$ ($x \leq 0.1$) crystals with various size and morphology, Mn^{3+} content and crystal structure (ordered vs. disordered).
  - Investigate the relationship between size, morphology, kinetic properties and stability.
  - Evaluate the impact of Mn^{3+} content on structure, conductivity, practical energy density, rate capability and stability.
  - Investigate phase transition mechanism.

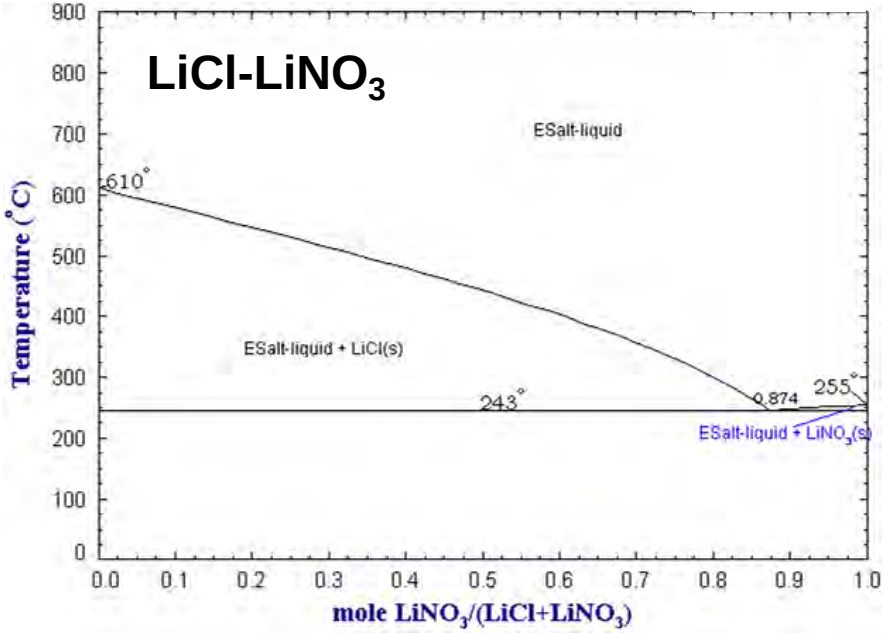
Summary

- Excess Li in $Li_{1+x}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{1-x}O_2$ promotes the formation of $\sqrt{3}a_{hex} \times \sqrt{3}a_{hex}$ super cells, decreases unit cell volume change upon Li extraction and insertion, increases phase stability, extractable Li in the structure and energy density of the oxide.
- Small NMC333 crystals showed higher rate capability at 4.5 V cutoff, but larger crystals performed better at higher cutoff voltages.
- Increasing Mn content in the overlithiated NMC333 improves rate capability but decreases stability of the initial O3 phase.
- Oxygen evolution during Li_2MnO_3 activation induces significant morphological damage on micron-sized crystals but not on 200 nm crystals.
- Phase stability has larger effects on rate capability and cycle life than morphological changes of the oxide crystals.
- Phase-pure spinel crystals form around 550 ^oC in the molten salts. Both synthesis temperature and flux choice play important roles in the physical characteristics of the crystals.
- Good rate capability achieved on large, micron sized spinel crystals.

Technical Back-Up Slides

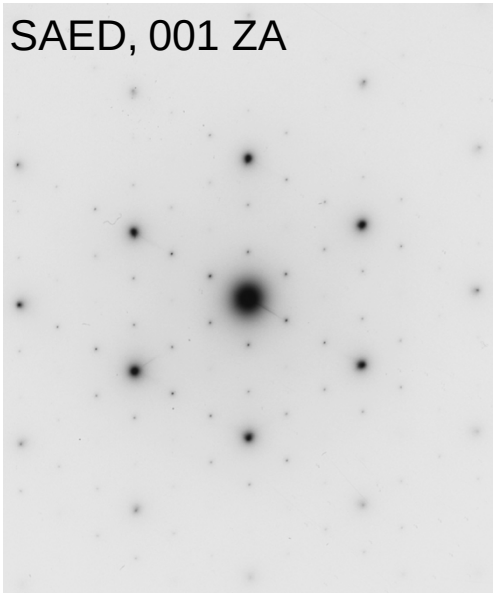
Molten-Salt Phase Diagrams

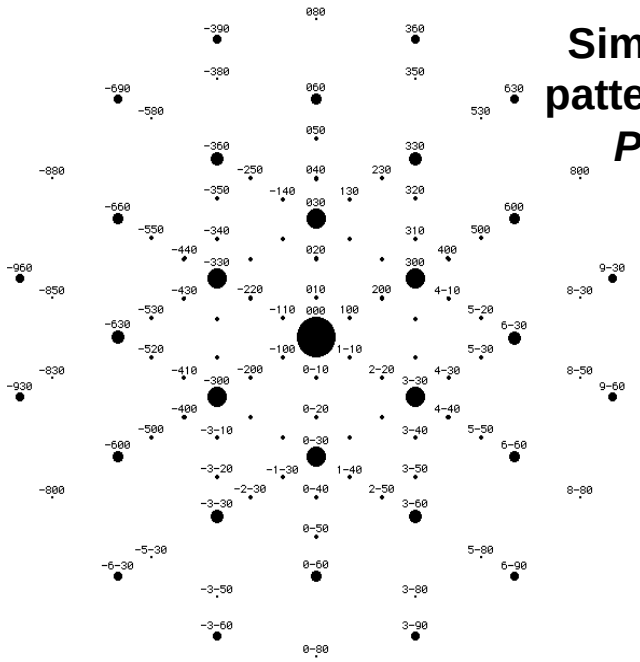




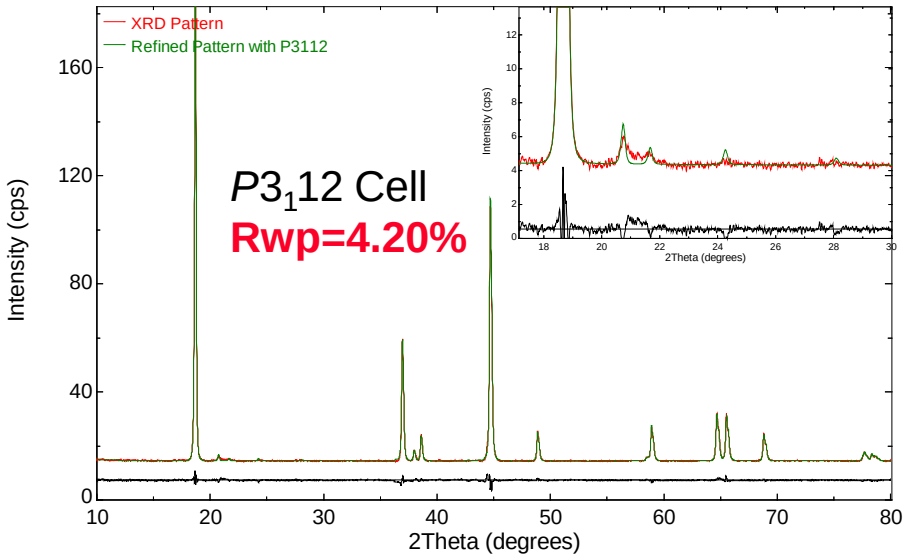
Ref: *FACT Salt Phase Diagrams*

Ordering in Li-Excess NMC333



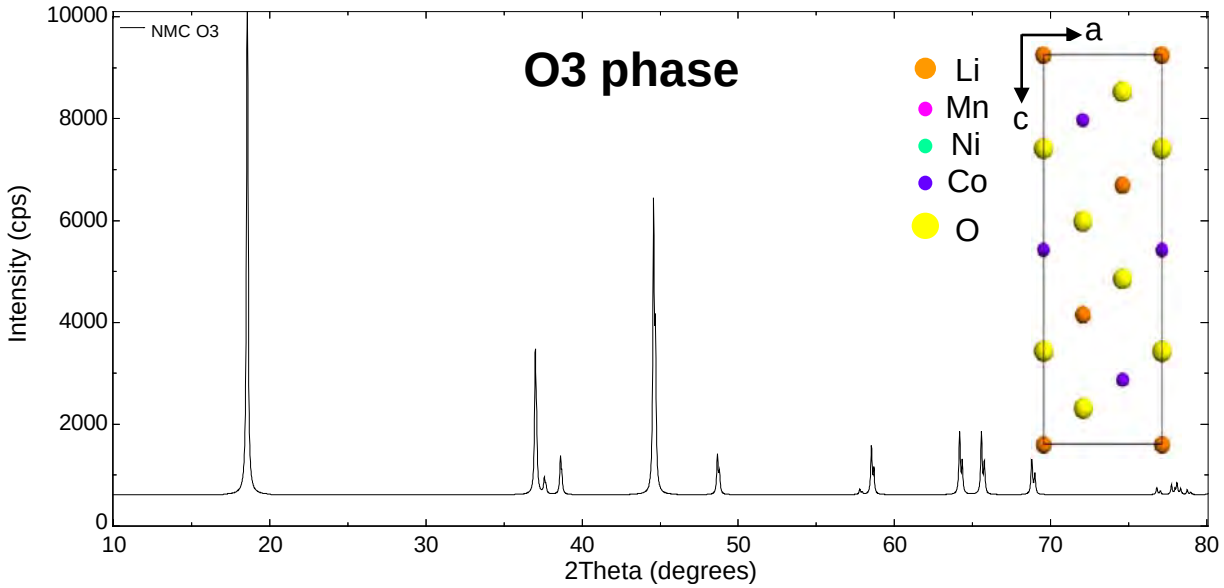


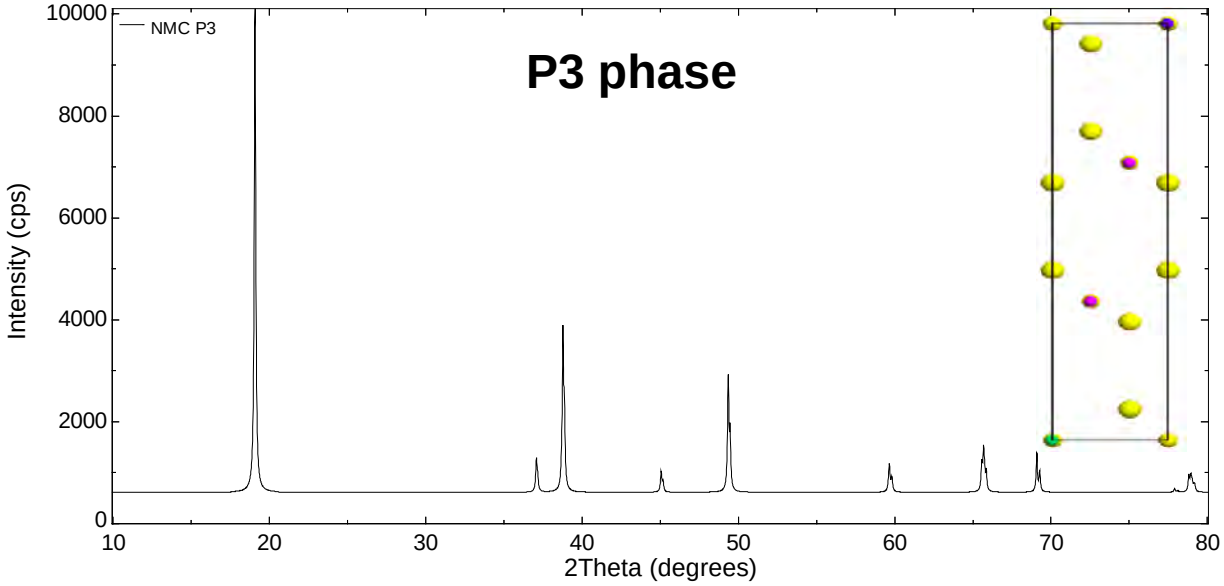
Simulated pattern from $P3_112$



- Well-defined superlattice peaks in Li-excess NMC333 suggest long-range ordering in the transition metal layers.
- Presence of $\sqrt{3}a_{hex} \times \sqrt{3}a_{hex}$ superstructure converts *R*-3*m* to $P3_112$ space group.

Phases Transition in $Li_{1+x}M_{1-x}O_2$

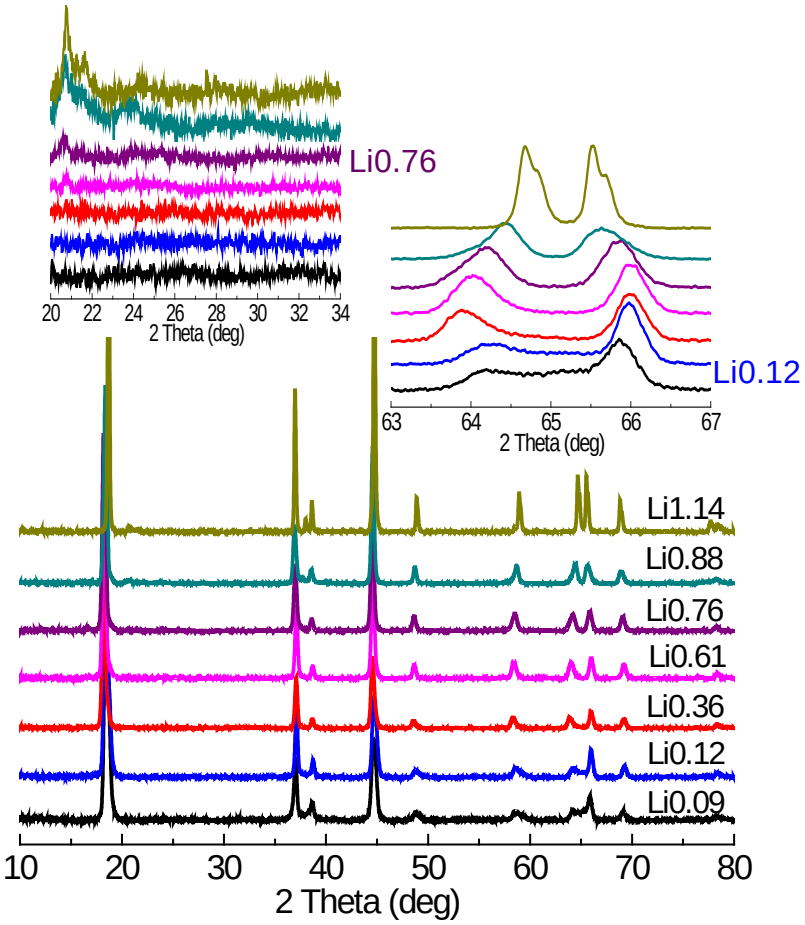




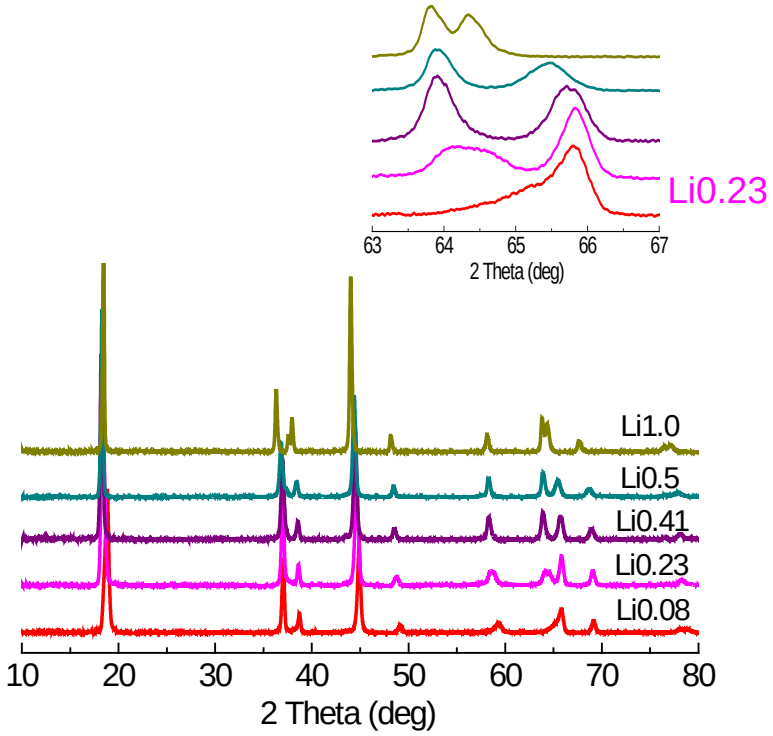
- Both O3 and P3 phases have three MO_2 sheets per unit cell. The difference lies in the oxygen stacking sequence.
- The transformation between O3 and P3 results from the sliding of MO_2 sheets during Li extraction/insertion. The process can have a significant impact on performance.

Delithiation of NMC333 – XRD

$Li_{1.14}(Ni_{0.333}Mn_{0.333}Co_{0.333})_{0.86}O_2$



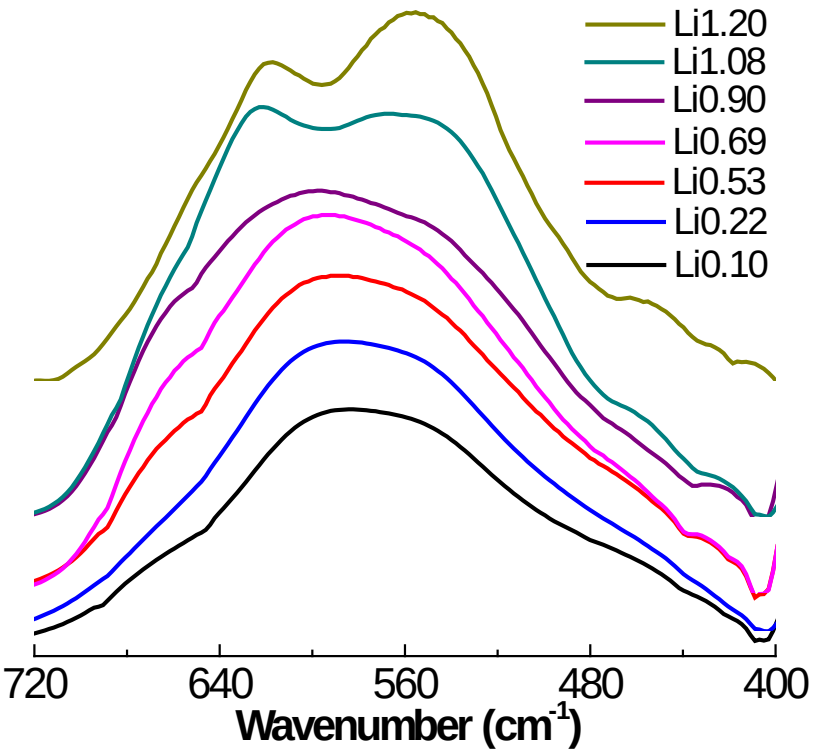
$LiNi_{0.333}Mn_{0.333}Co_{0.333}O_2$



- Delayed phase transition in the overlithiated NMC333.

Delithiation – FTIR

$Li_{1.2}(Ni_{0.167}Mn_{0.667}Co_{0.167})_{0.8}O_2$



$Li_{1.14}(Ni_{0.333}Mn_{0.333}Co_{0.333})_{0.86}O_2$