Design and Synthesis of Advanced High-Energy Cathode Materials

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Project ID: ES225

LAWRENCE BERKELEY NATIONAL LABORATORY

Overview

Timeline

- Start date: October, 2012

- End date: September, 2016

- Percent complete: 40%

Budget

- Total project funding
  - FY2013 $500K
  - FY2014 $500K

Barriers Addressed

- Energy density

- Cycle life

- Safety

Partners

- Collaborations: Kostecki, Doeff, Ross (LBNL), Grey (Cambridge), Chiang (MIT), Lucht (URI), NCEM, ALS, SSRL

- Project lead: Venkat Srinivasan

Objectives – Relevance

- Obtain fundamental understandings on phase transition mechanisms, kinetic barriers, and instabilities in high-energy cathode materials.

- Control cathode-electrolyte interfacial chemistry at high operating voltages and minimize solid-state transport limitations through particle engineering.

- Develop next-generation electrode materials based on rational design as opposed to the conventional empirical approaches.

Milestones

December 2013	Synthesize at least five new cathode crystal samples with at least two new morphologies (Completed)
March 2014	Characterize the interface between the high-voltage cathode and the electrolyte. Identify the role of particle surface planes in interfacial reactivity (Completed)
June 2014	Complete the studies on structural evolution during initial Li extraction/insertion and extended cycling. Illustrate the impact of structural changes and phase transformation on rate capability and stability (On schedule)
September 2014	Go/No-Go: Continue low-temperature based solvothermal synthesis. Criteria: If the crystal samples show similar quality and performance to those made at high temperatures (On schedule)

Cathode materials are complex

LiMn$_{1.5}$Ni$_{0.5}$O$_4$ Performance and Stability

Morphology (primary and secondary particle shape, porosity, grain boundary)

Size (primary and secondary)

Ionic and e$^-$ Conductivities

Phase Transition Mechanism

Ni/Mn Ordering

Mn^{3+} Content

Impurities (rock-salt)

Oxygen non-stoichiometry

Ni/Mn ratio
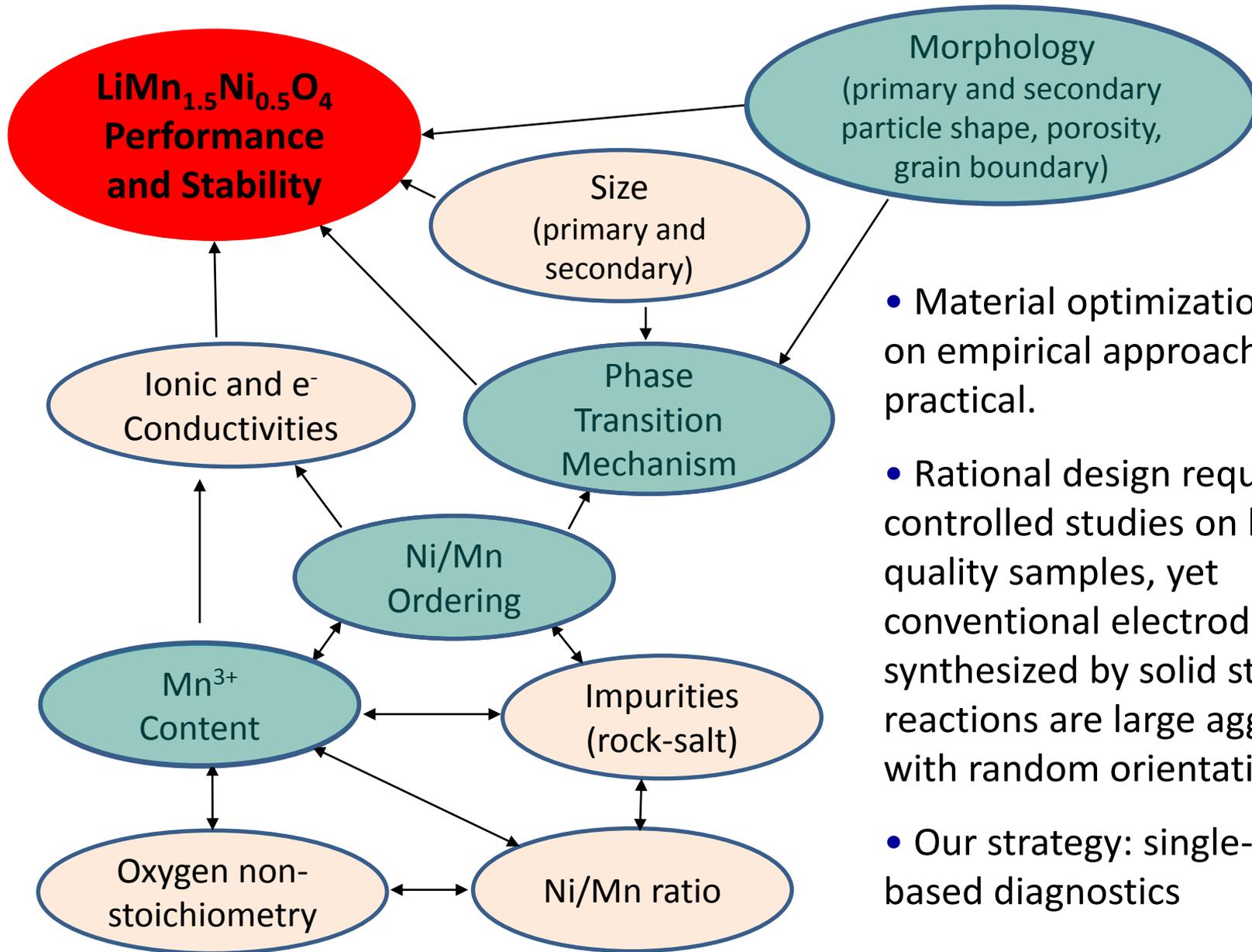
• Material optimization based on empirical approaches not practical.

• Rational design requires well-controlled studies on high-quality samples, yet conventional electrode materials synthesized by solid state reactions are large agglomerates with random orientations.

• Our strategy: single-crystal based diagnostics

Approach

- Use single-crystal model systems to investigate solid state chemistry, kinetic barriers and instabilities in high-energy cathode materials.

- Perform advanced *ex situ* and *in situ* studies to characterize crystal-plan specific transport properties and interfacial chemistry. Establish direct correlations between crystal structure, composition, morphology, performance, and stability.

- Design and synthesize optimized electrode materials based on the structural and mechanistic understandings.

Technical accomplishments: overview

- Synthesis techniques developed to prepare a variety of cathode crystal samples.

- Using single-crystal studies on high-voltage $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO) and layered-layered oxides as examples, we demonstrated the importance of rational design and engineering of active particles in electrode performance and stability. Impacts are shown in several issues:
  - Self-discharge during storage
  - Side reactions with electrolyte during cycling
  - Transport properties
  - Phase transformation behavior
  - First-cycle activation kinetics

- For the first time, room-temperature $Li_xMn_{1.5}Ni_{0.5}O_4$ (Li_xMNO) solid solution phases were synthesized and isolated through thermal treatment and their properties characterized. This enables more detailed investigation on kinetic implication of solid-solution *vs*. two-phase reaction pathways.

- Established several diagnostic techniques for the particle-level investigation of cathode materials.

Cathode single crystals with a variety of sizes and shapes synthesized

$$Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$$
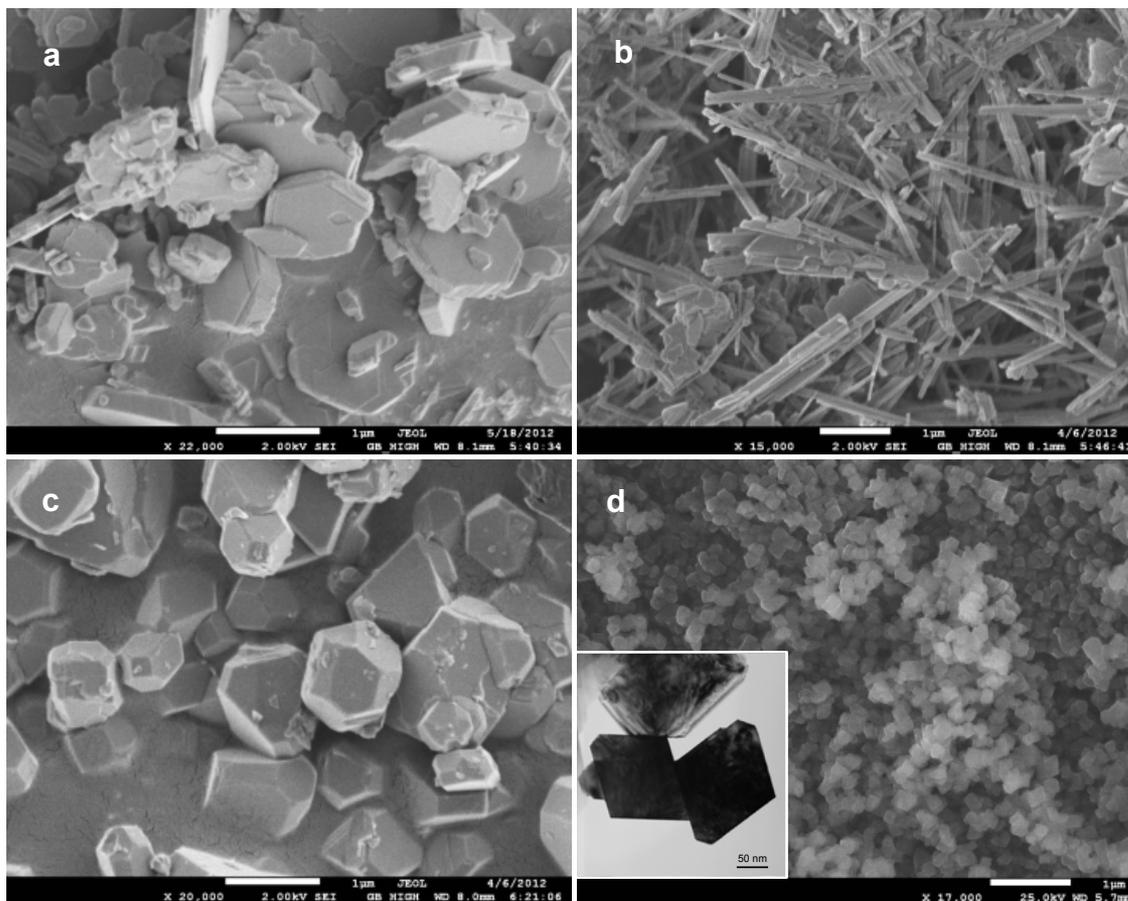
- Various layered-oxide crystal samples synthesized by changing the reaction precursors and/or fluxes.

# Cathode single crystals with a variety of sizes and shapes synthesized
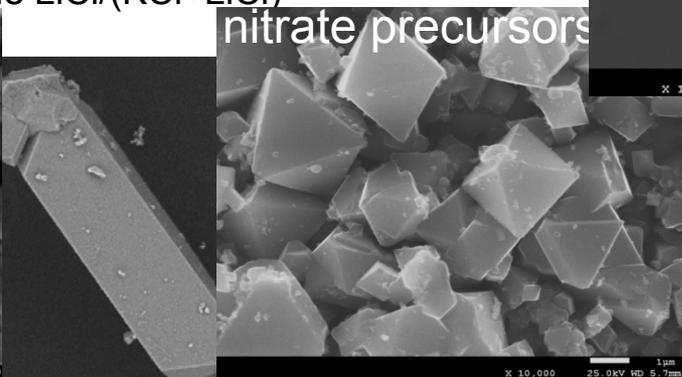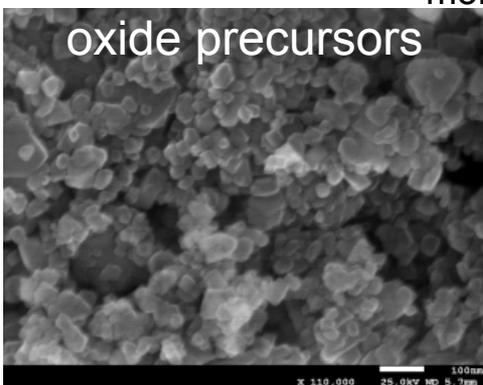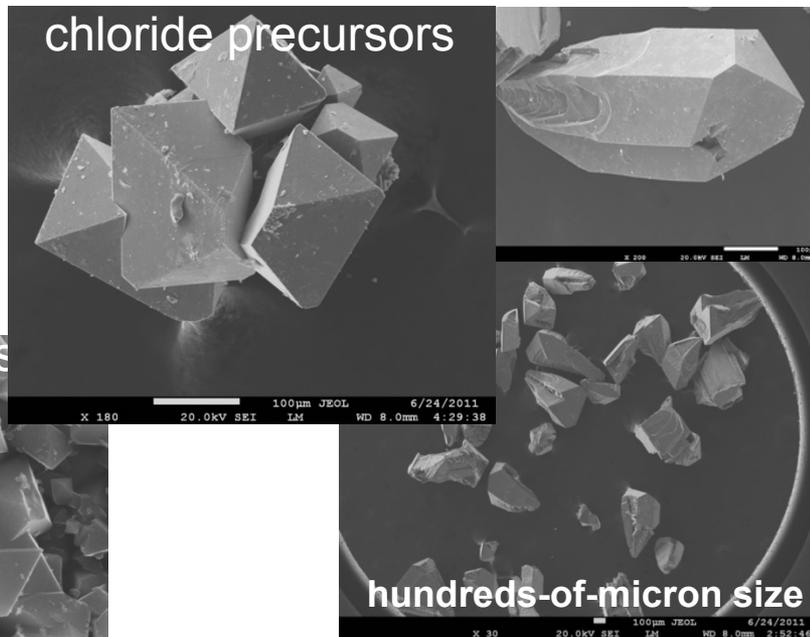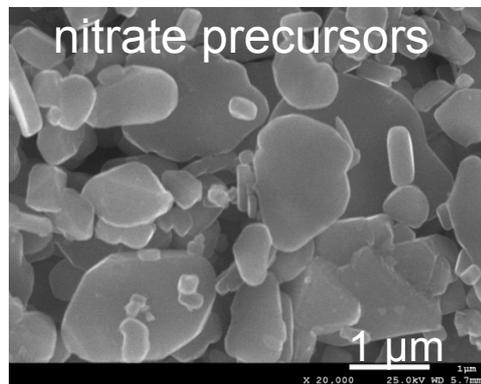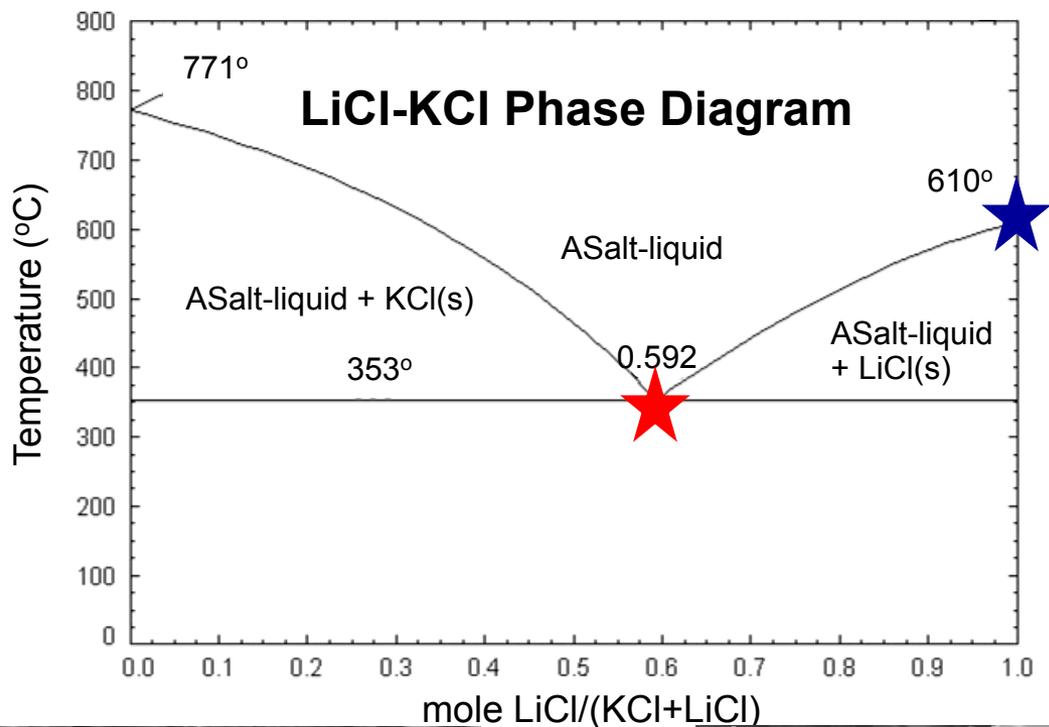
LiCl-KCl Phase Diagram

771°

ASalt-liquid

ASalt-liquid + KCl(s)

610°

353°   0.592

ASalt-liquid + LiCl(s)

mole LiCl/(KCl+LiCl)

$LiMn_{1.5}Ni_{0.5}O_4$ (LMNO)

nitrate precursors

1 µm

chloride precursors

oxide precursors

nitrate precursors

tens-of-micron size

hundreds-of-micron size

Cathode single crystals with a variety of sizes and shapes synthesized

$LiMn_{1.5}Ni_{0.5}O_4$ (LMNO)
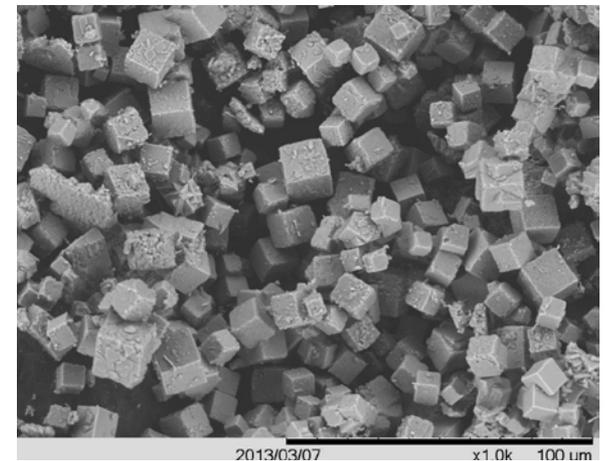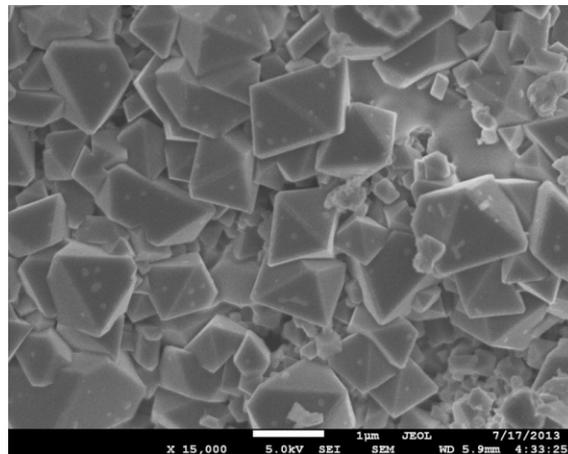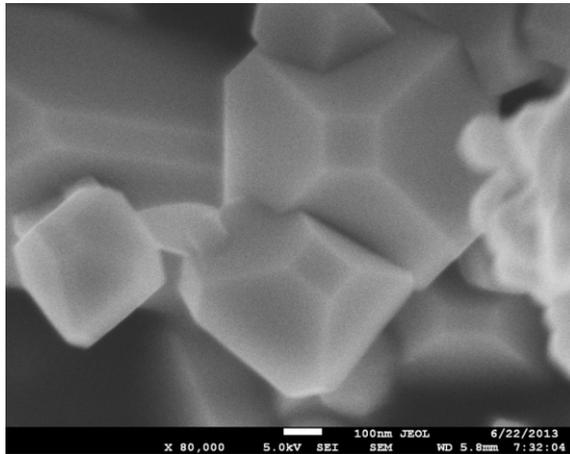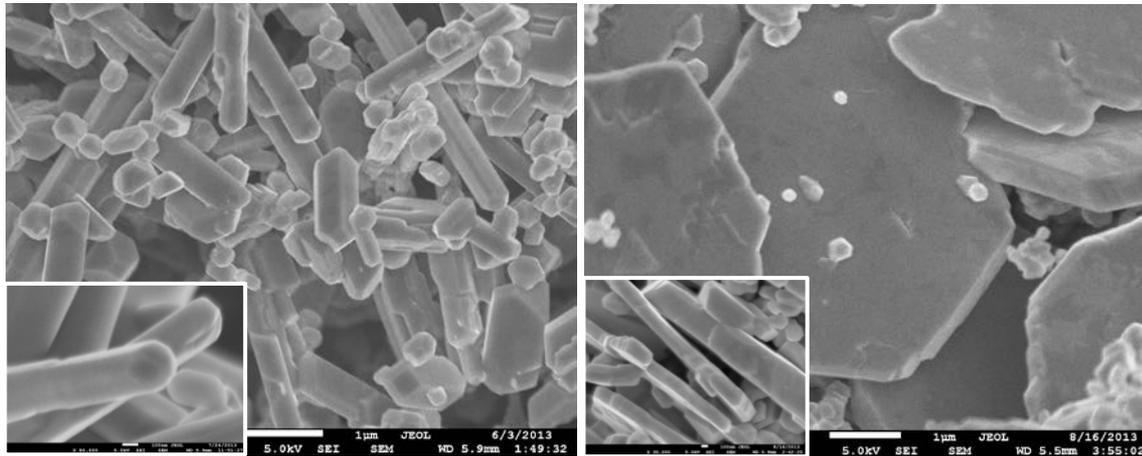
- Solvothermal synthesis produced unique morphologies inaccessible at high temperature.

LMNO crystals with (111) and (112) facets

(112)

ZA:112

1-11   111

1-1-1   11-1

ZA:112
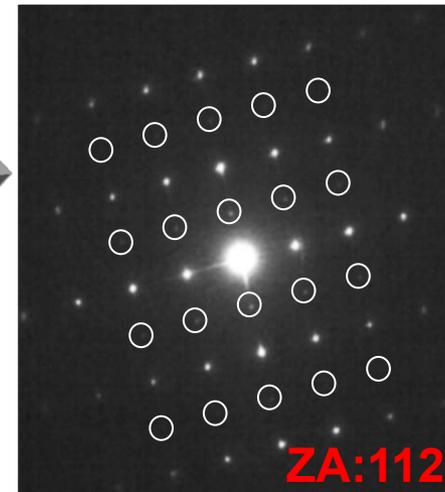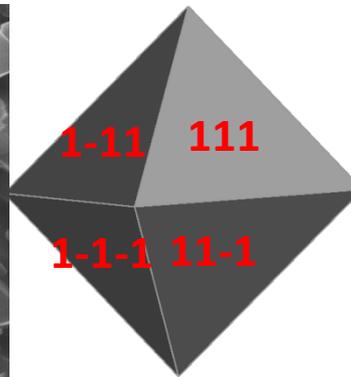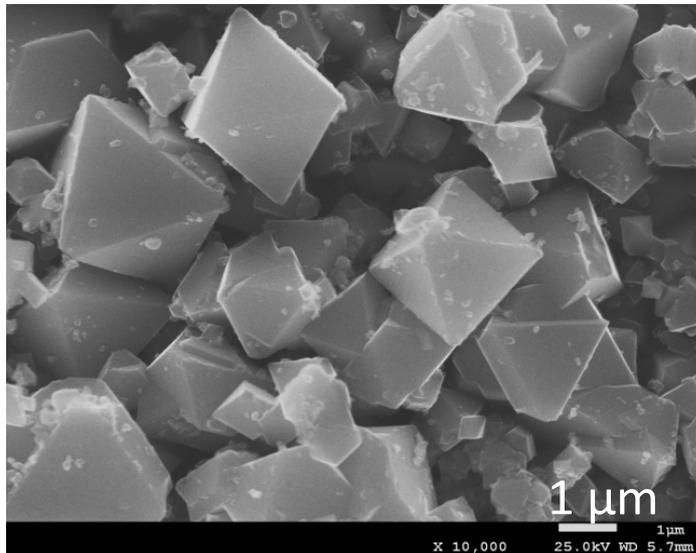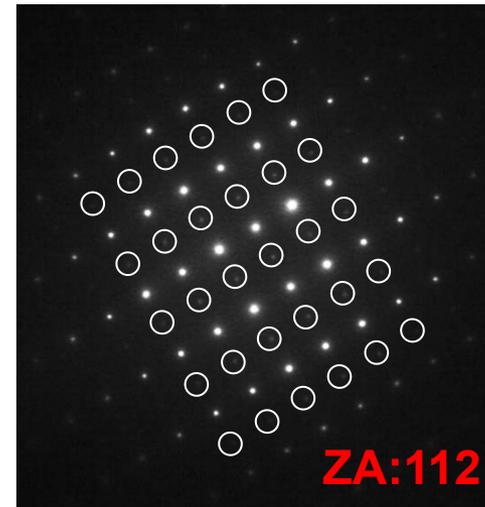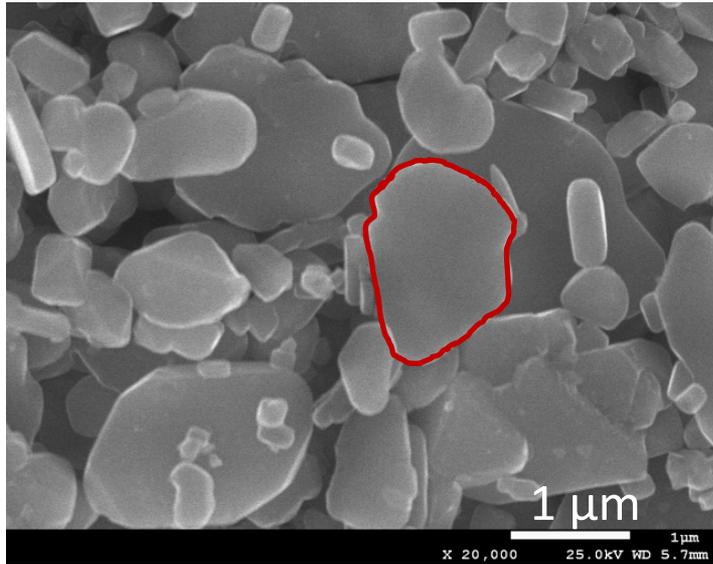
(111) *vs.* (112) crystal planes

(111) plane

(112) plane

MnO$_6$

NiO$_6$

Li
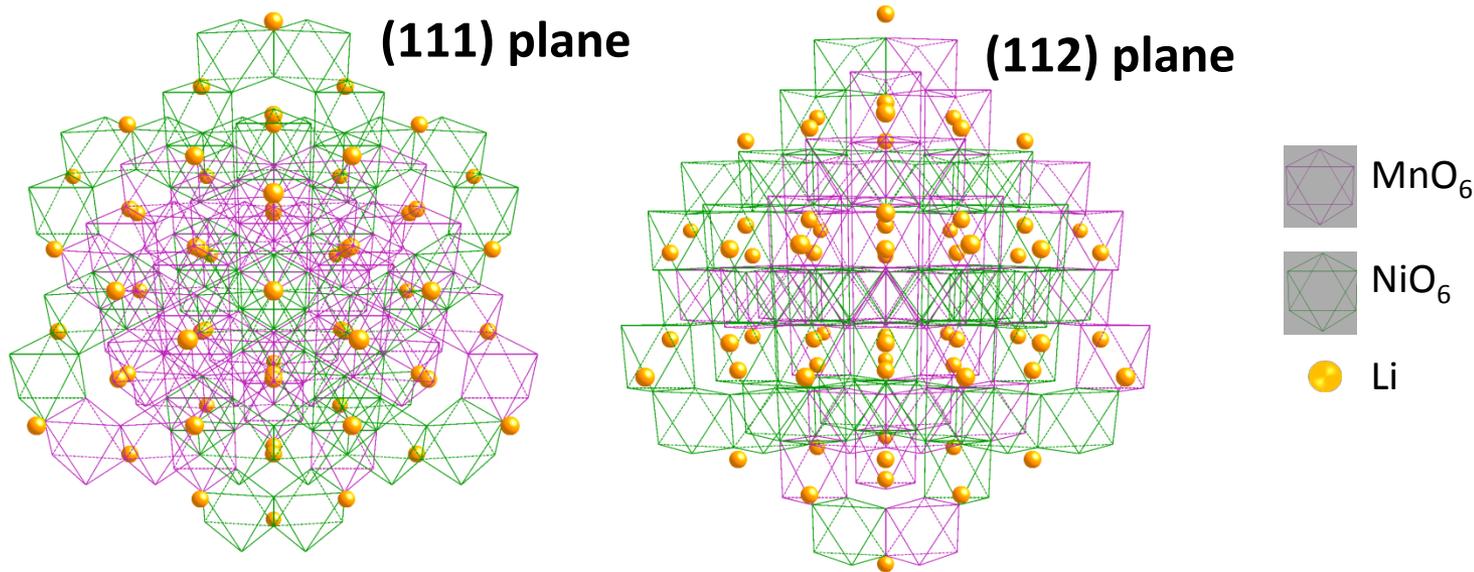
Calculated Surface Energies (J/m²)

LiMn$_2$O$_4$ Surfaces	J/m² (GGA)	J/m² (GGA + U)
(100) (010) (001)	0.97	0.62
(111)	0.52	0.36
(110) (101) (011)	0.83	0.57

$$E_{cleav} = (E_{slab} - E_{bulk})/2S$$

(100)
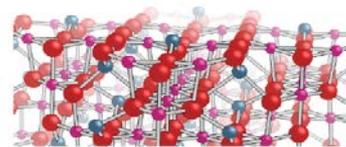
Under-coordinated Mn and Li

(111)
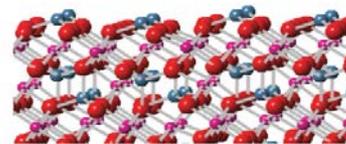
Under-coordinated Li

K. Persson et al

• First-principle calculation predicts (111) has the lowest energy in LiMn$_2$O$_4$ spinel. Surface energies in LMNO to be determined.

Self-discharge severe in delithiated LMNO

Week   1   2   3   4   5

Week   1   2   3   4   5
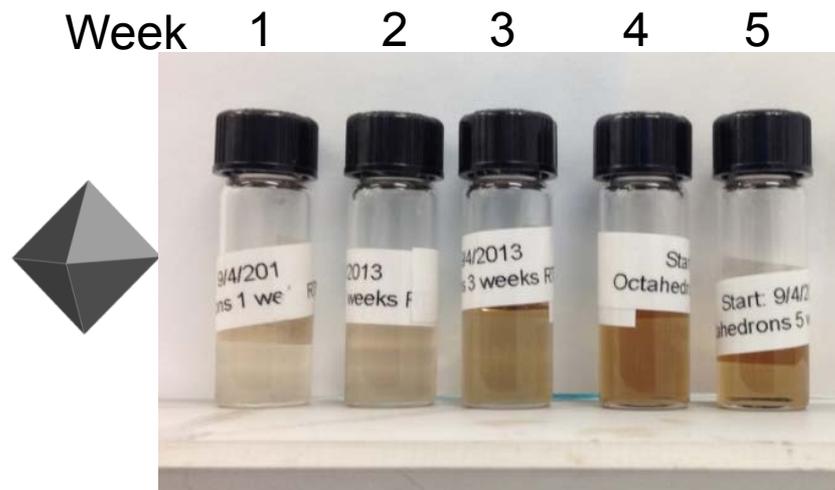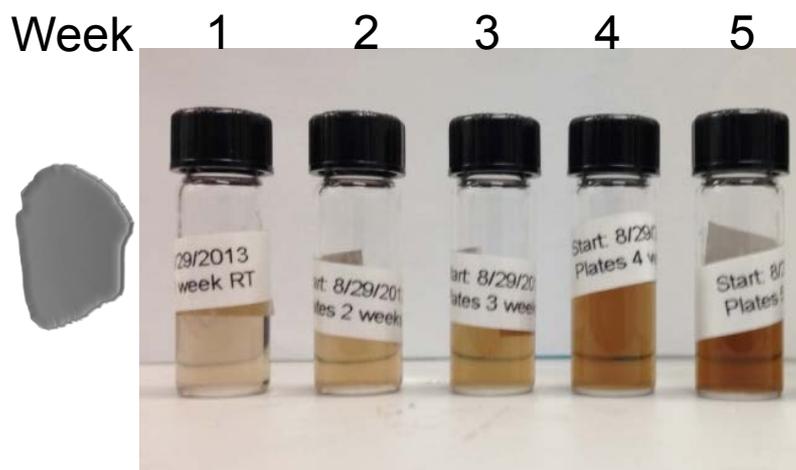

- Aging of fully delithiated LMNO plates and octahedrons in 1M $LiPF_6$ in EC:DEC electrolyte for 5 weeks.

- Electrolyte color developed as a result of side reactions.

- Process is influenced by state of charge and storage temperature. Morphology also matters.

Reduced self-discharge on (111) facets

Phase I: $Li_{1.0}MNO$ **Phase II**: $Li_{0.5}MNO$ **Phase III**: MNO
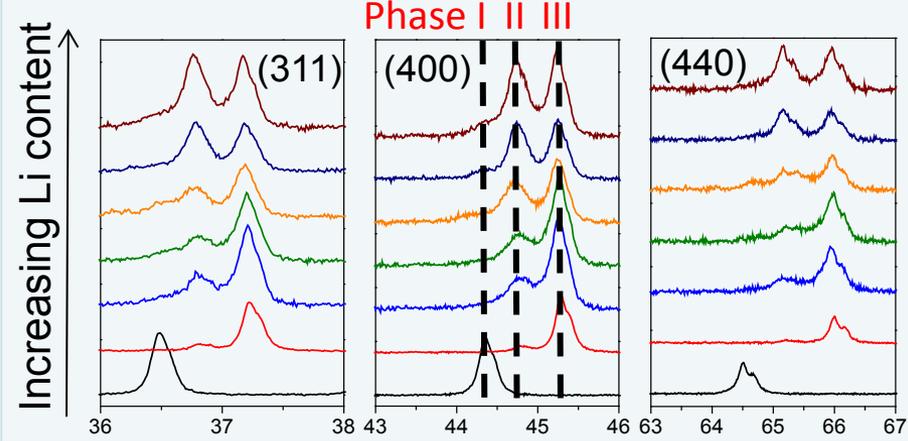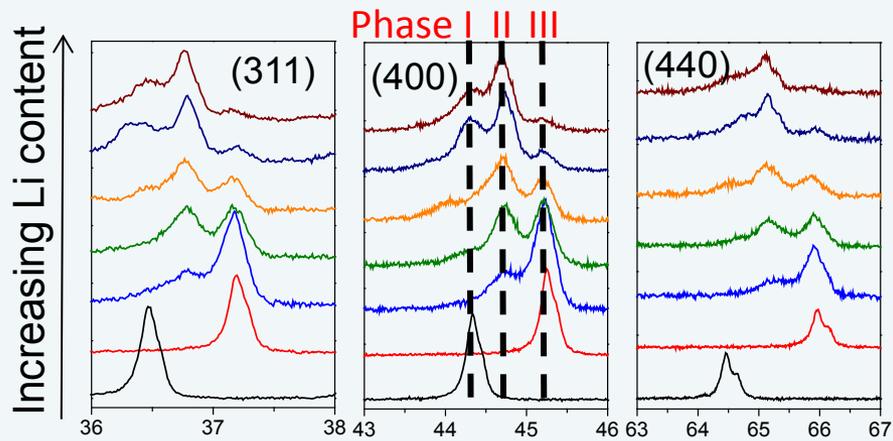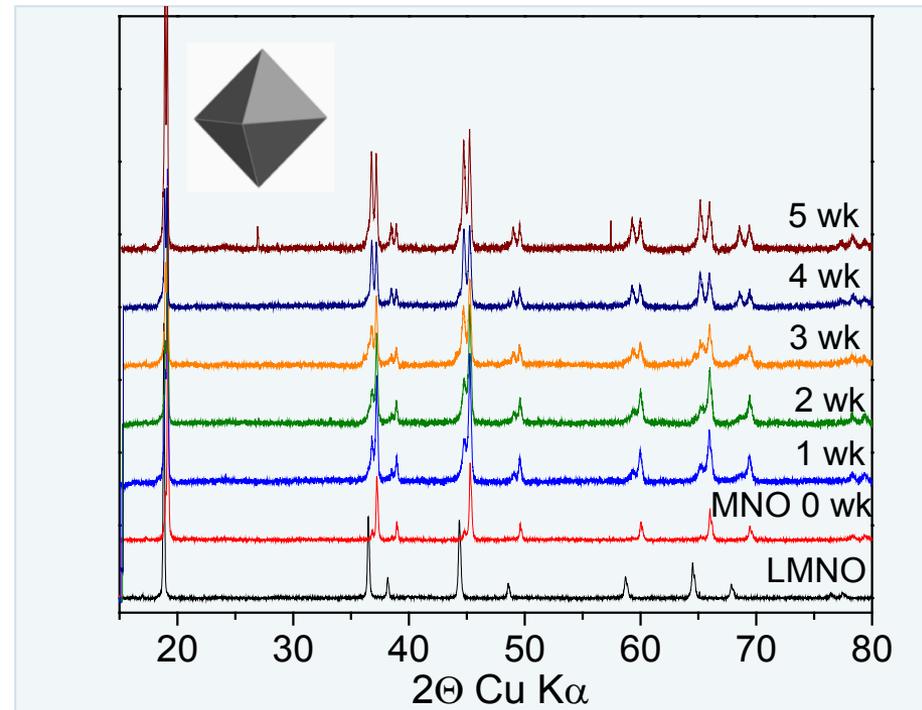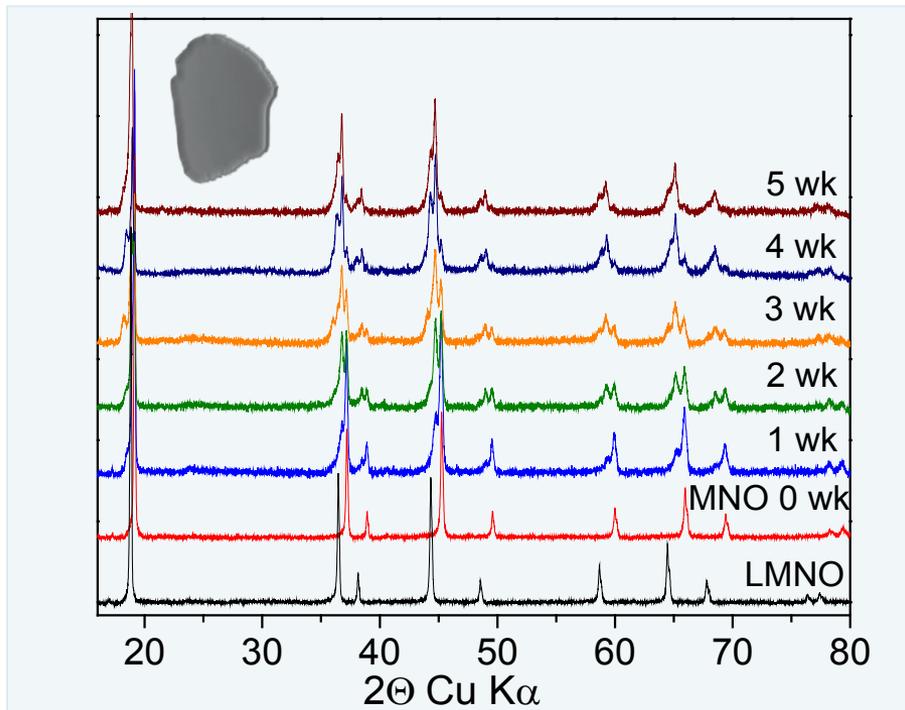
Reduced self-discharge on (111) facets
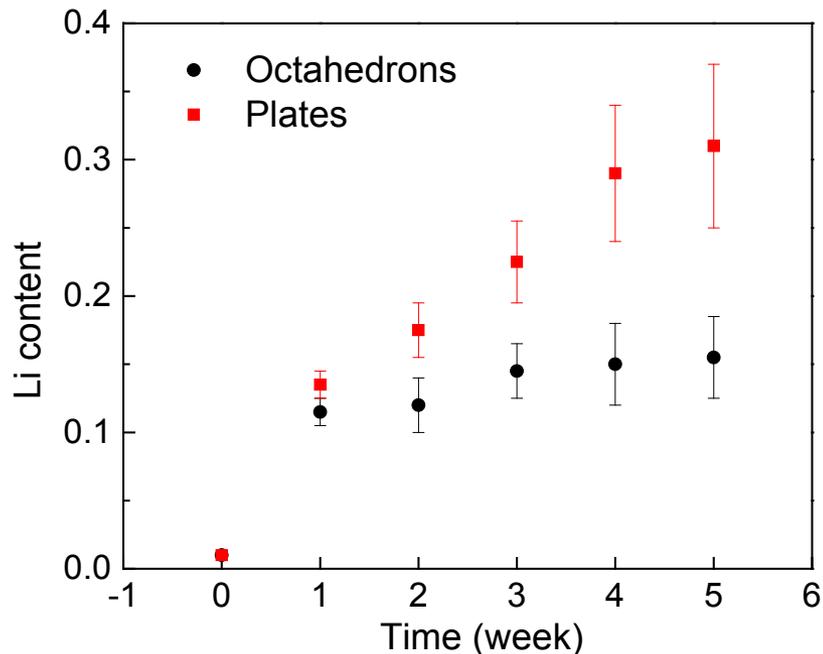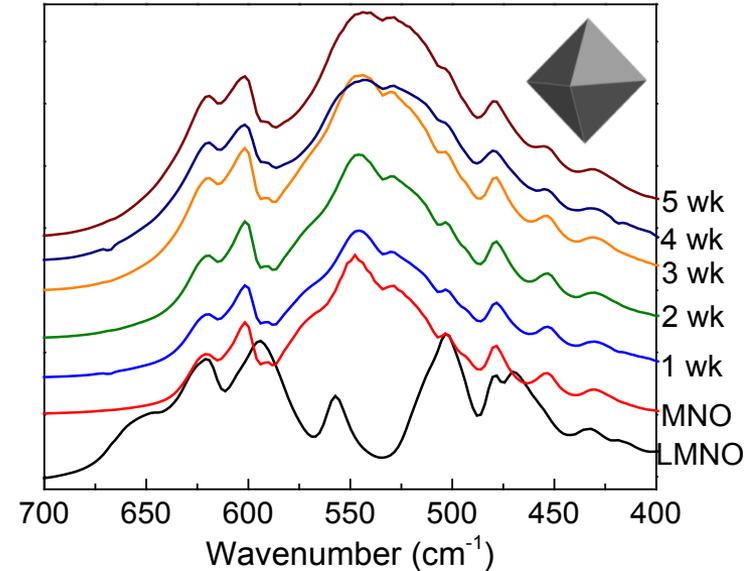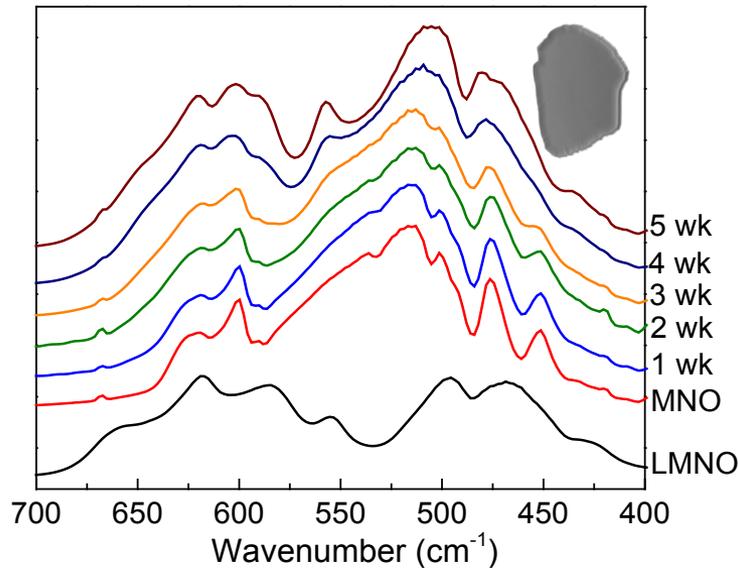
- Estimated lithium content after 5 weeks RT aging: 0.2-0.3 (plates) and 0.1-0.2 (octahedrons).

- Particle morphology design can minimize relithiation.

- Relithiation may be used as a kinetic index for side reactions between cathode and electrolyte.

Reduced side reactions on (111) facets
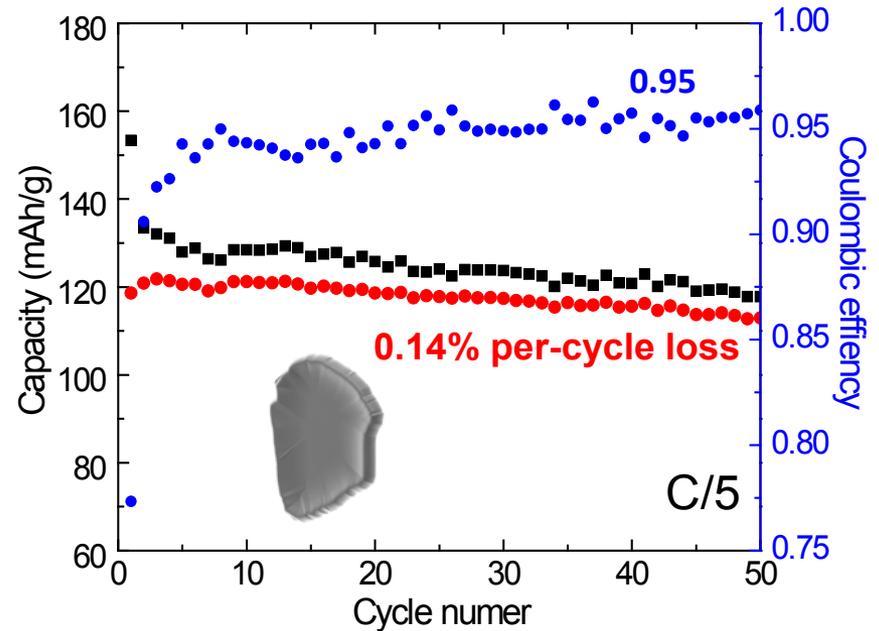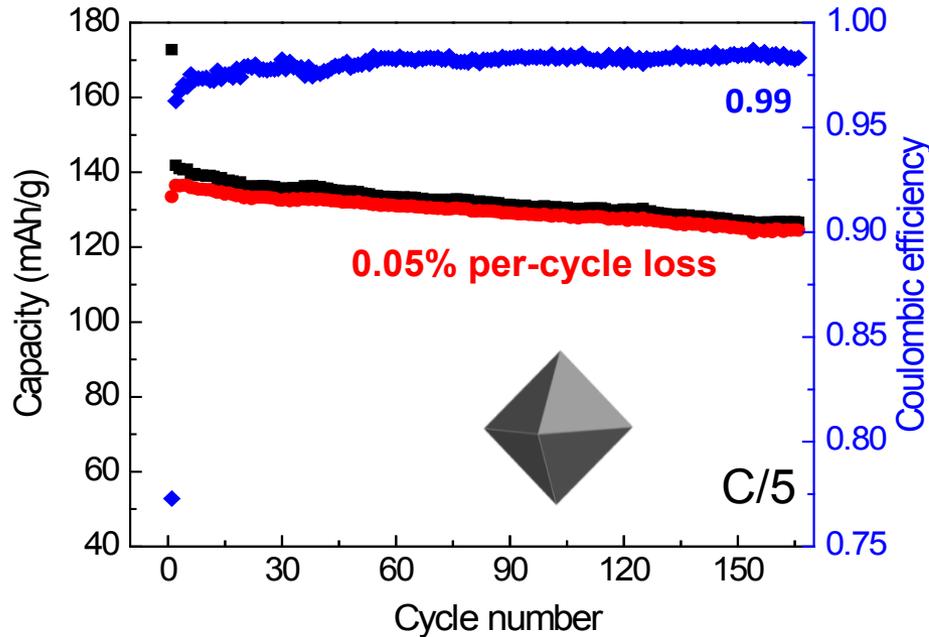
- Better cycling efficiency and lower per-cycle capacity loss in octahedrons.
- Enhanced side reactivity on plate (112) surface facets.

Reduced side reactions on (111) facets
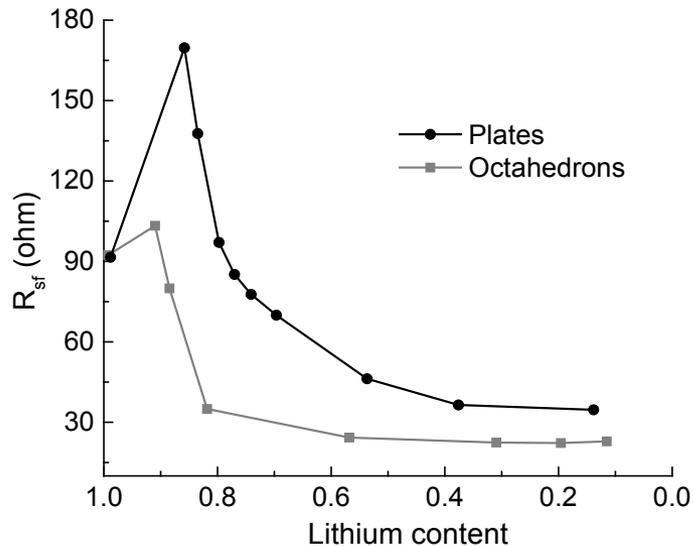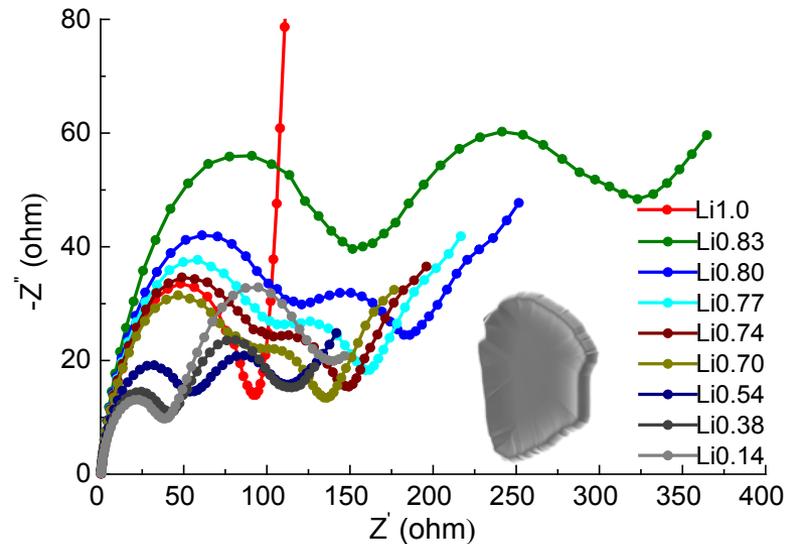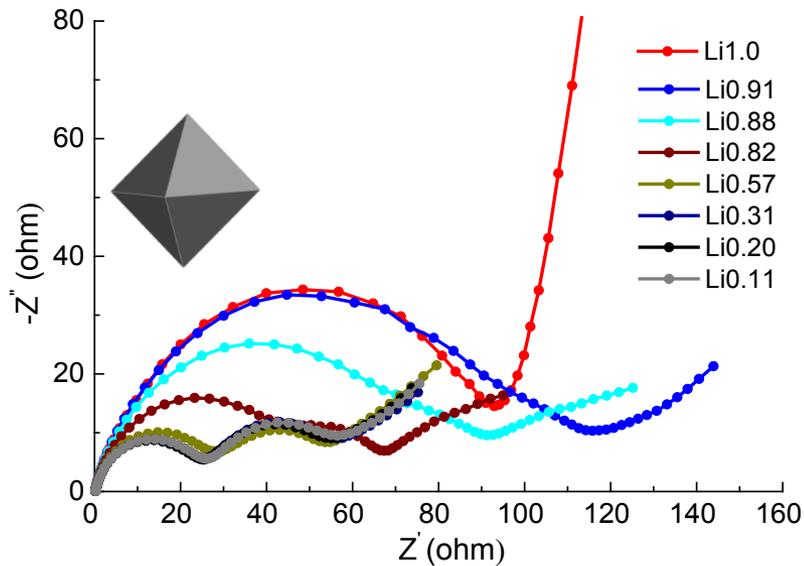
- Larger increase in surface resistance on plate with (112) surface facets, consistent with higher impedance in the electrode.

- Is this a result of different species and/or thickness of the surface deposit from side reactions?

Side reactions and cathode surface layer

ALS tender XPS at 9.3.1 &
soft XPS at 9.3.2

*Collaboration with P. Ross and E. Crumlin*

$LiMn_{1.5}Ni_{0.5}O_4$ XPS Spectra collected at $hv = 4$ keV:
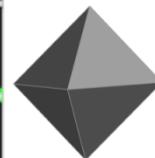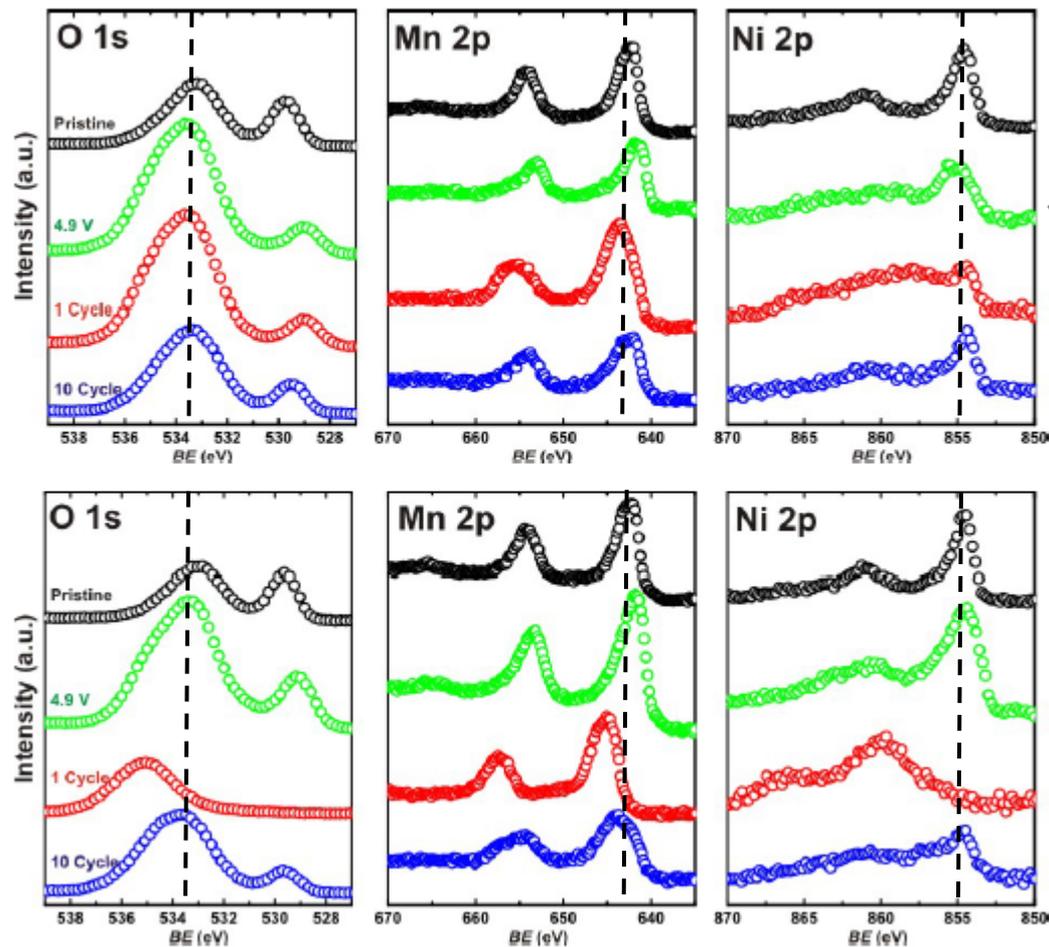
- Data collected on carbon and binder free electrodes under UHV (~10^{-7} torr)
- Side reaction products are surface-facet dependent.

Side reactions and cathode surface layer

Probing depth: ~ 10-15 nm   ~ 1-3 nm

• Depth profiling shows variation in surface species along the layer thickness.

• Dynamic nature of the surface deposits – chemical species evolve with cycling.

• The effect of surface facet more dominant deeper into the surface layer.
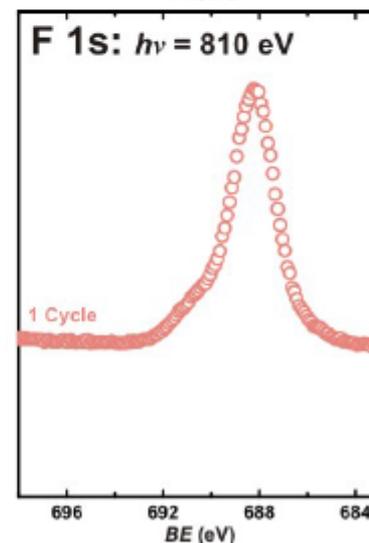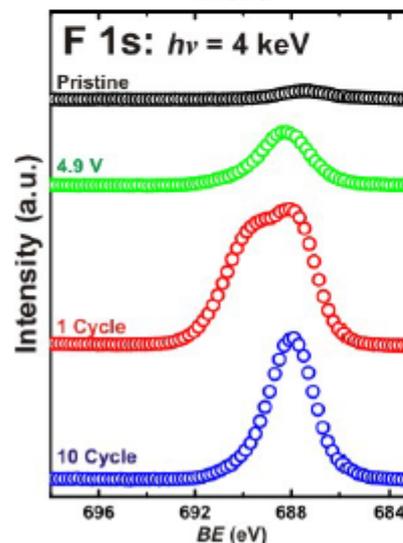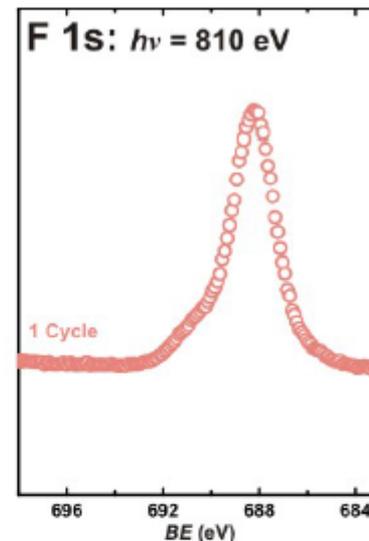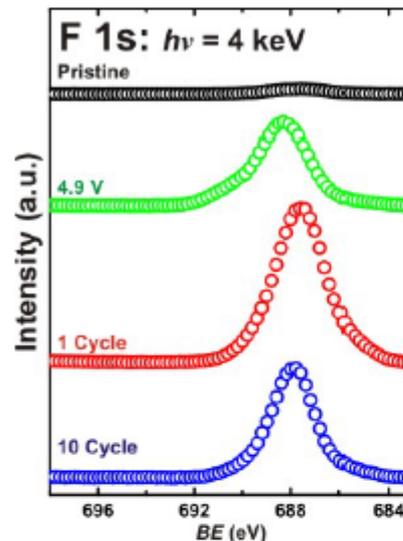
# Enhanced rate capability on (111) facets
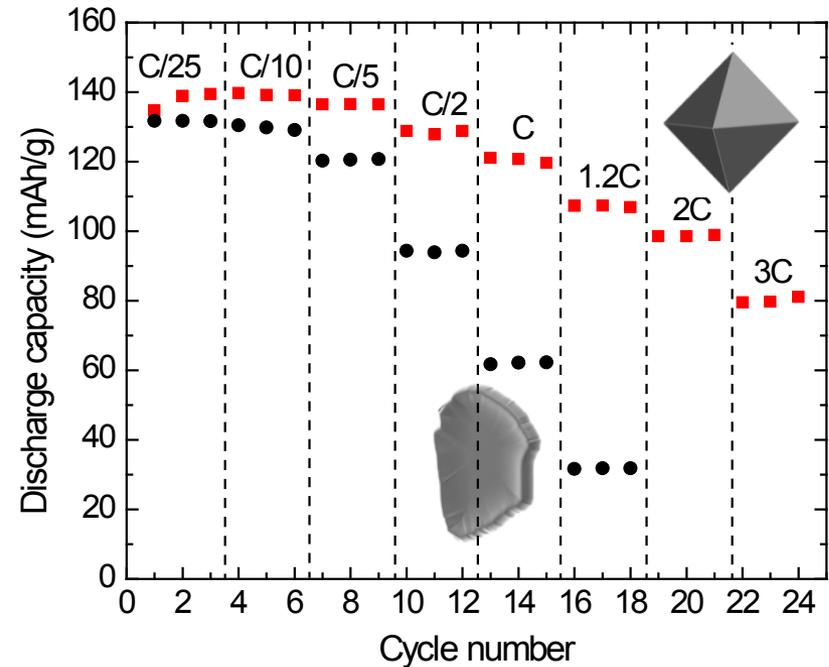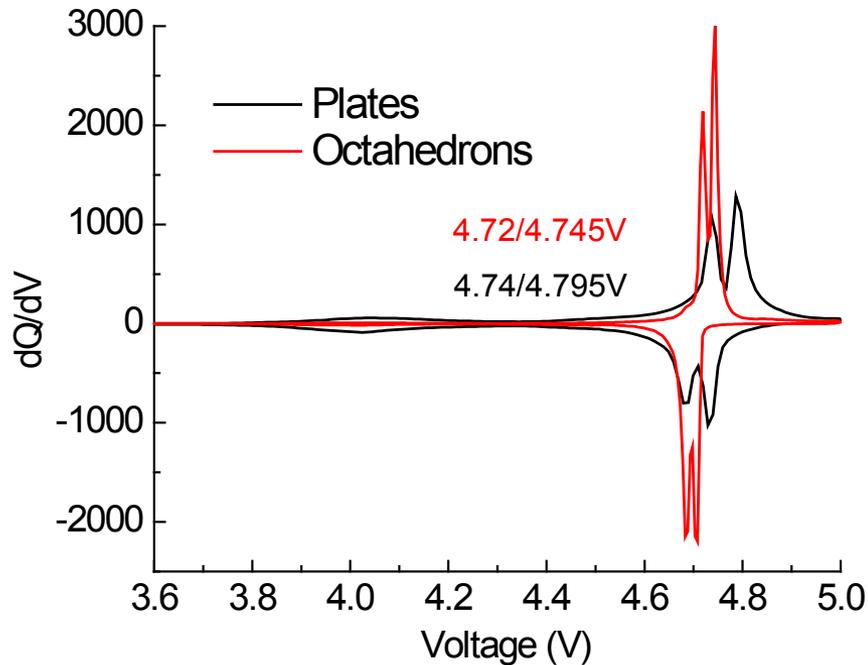
- Charging peak voltage upshift suggests increased resistance for Li extraction from the plates.

- Higher rate capability in octahedrons suggests better Li transport properties on (111).

- Does phase transition mechanism play a role?

Phase transformation in plates

SSRL BL 11-3, *In situ* C/20 Charge and Discharge
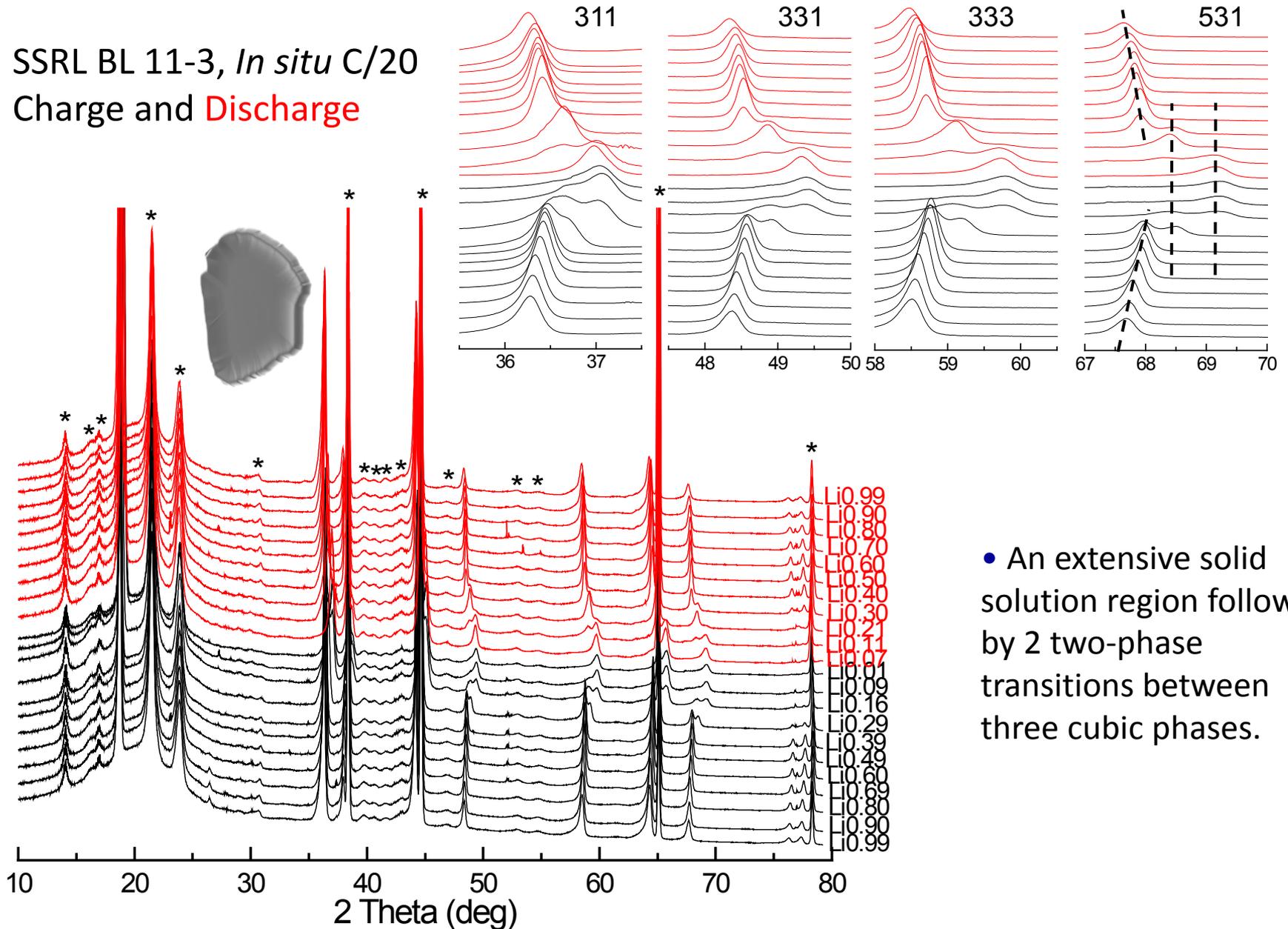
- An extensive solid solution region followed by 2 two-phase transitions between three cubic phases.

Phase transformation in octahedrons

• A much smaller solid solution region followed by 2 two-phase transitions between three cubic phases. Estimated volume changes: 2.5 and 3%.

Solid-solution *vs.* two-phase transition mechanisms

• Conventional wisdom says the access to solid-solution reaction pathways increases rate capability and cyclability.

• Solid-solution Li intercalation as a function of cation order/disorder suggested by theory (Persson et al), which predicts full-range solid solution transformation in perfectly disordered spinel. Perfectly ordered or disordered LMNO, however, practically impossible to make.

• Questions: can we obtain RT Li_xMNO solid-solution phases with a wide *x* range? What are their physical and electrochemical properties? What is the kinetic implication of solid solution *vs.* two-phase transitions in LMNO?

• Single crystal samples are excellent platform to gather detailed knowledge on Li_xMNO solid solution phases.

Persson et al, Chem. Mater. 2013, 25, 2885–2889
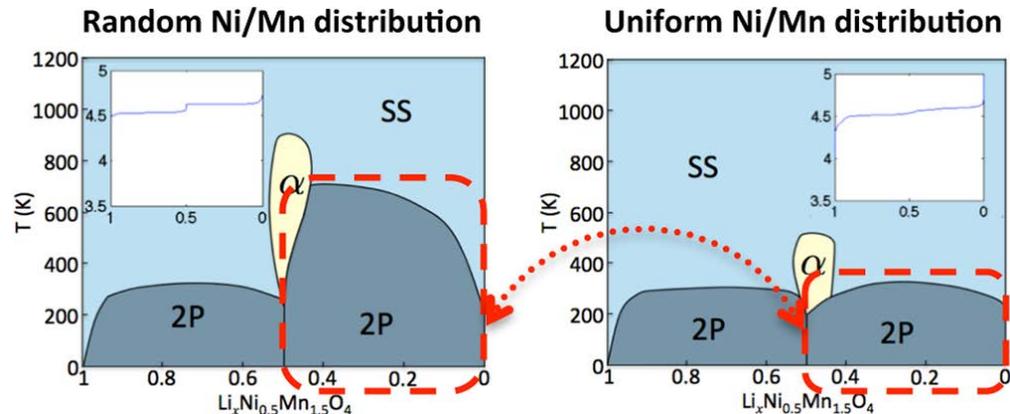
Chemically delithiated LMNO crystals prepared
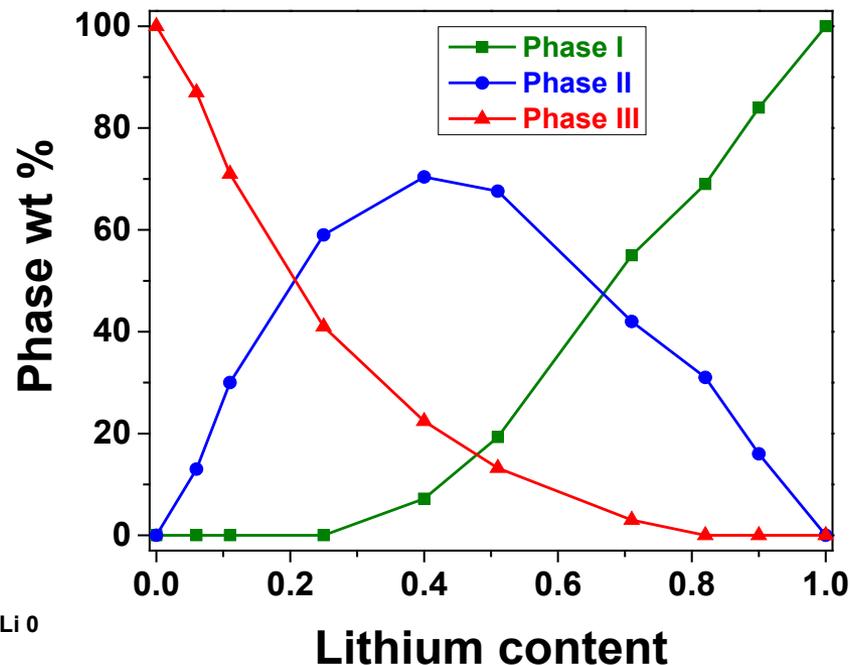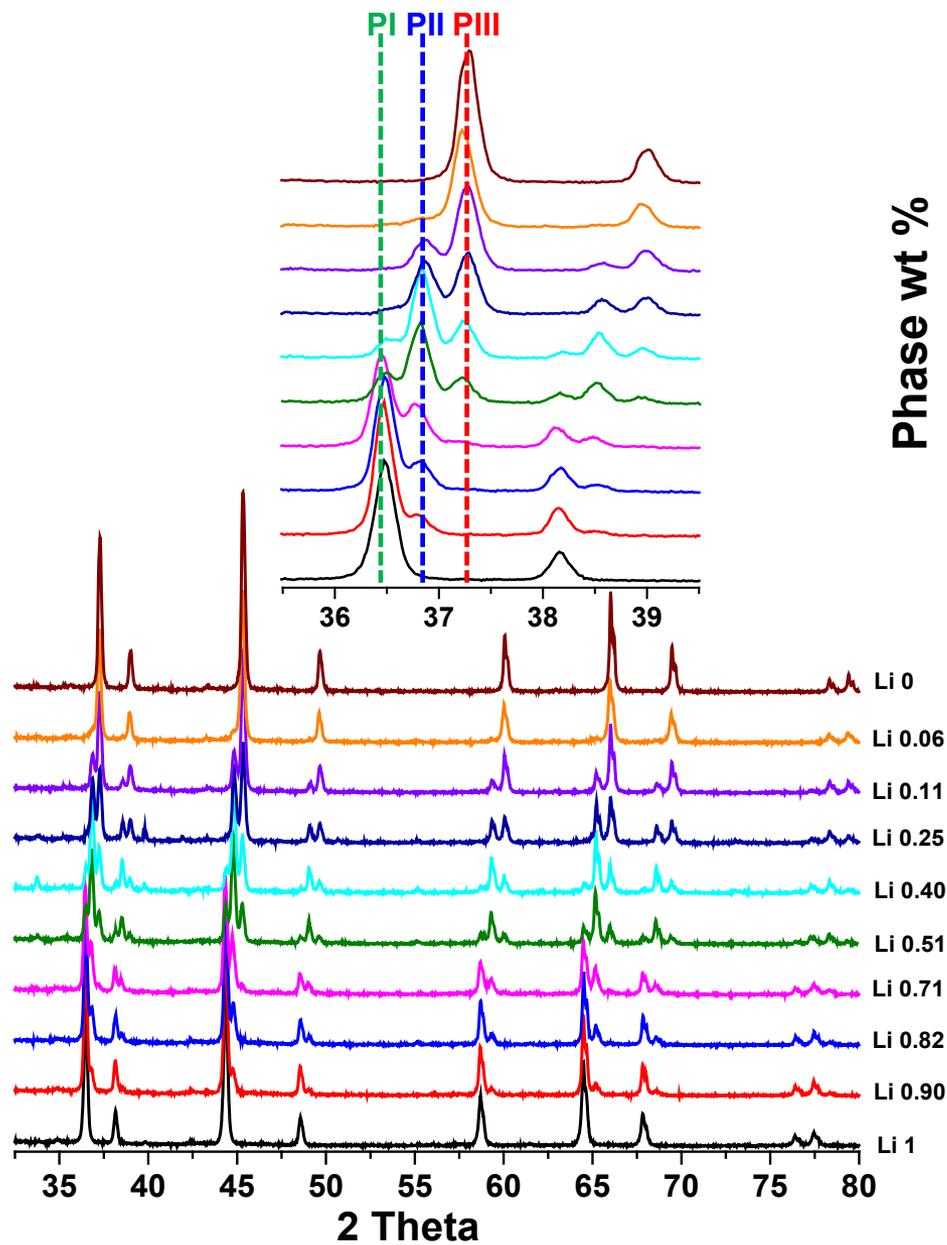
• As-prepared Li$_x$Mn$_{1.5}$Ni$_{0.5}$O$_4$ (Li$_x$MNO) samples are varying mixtures among 3 cubic phases.

Thermal-driven Li$_x$MNO solid solution formation
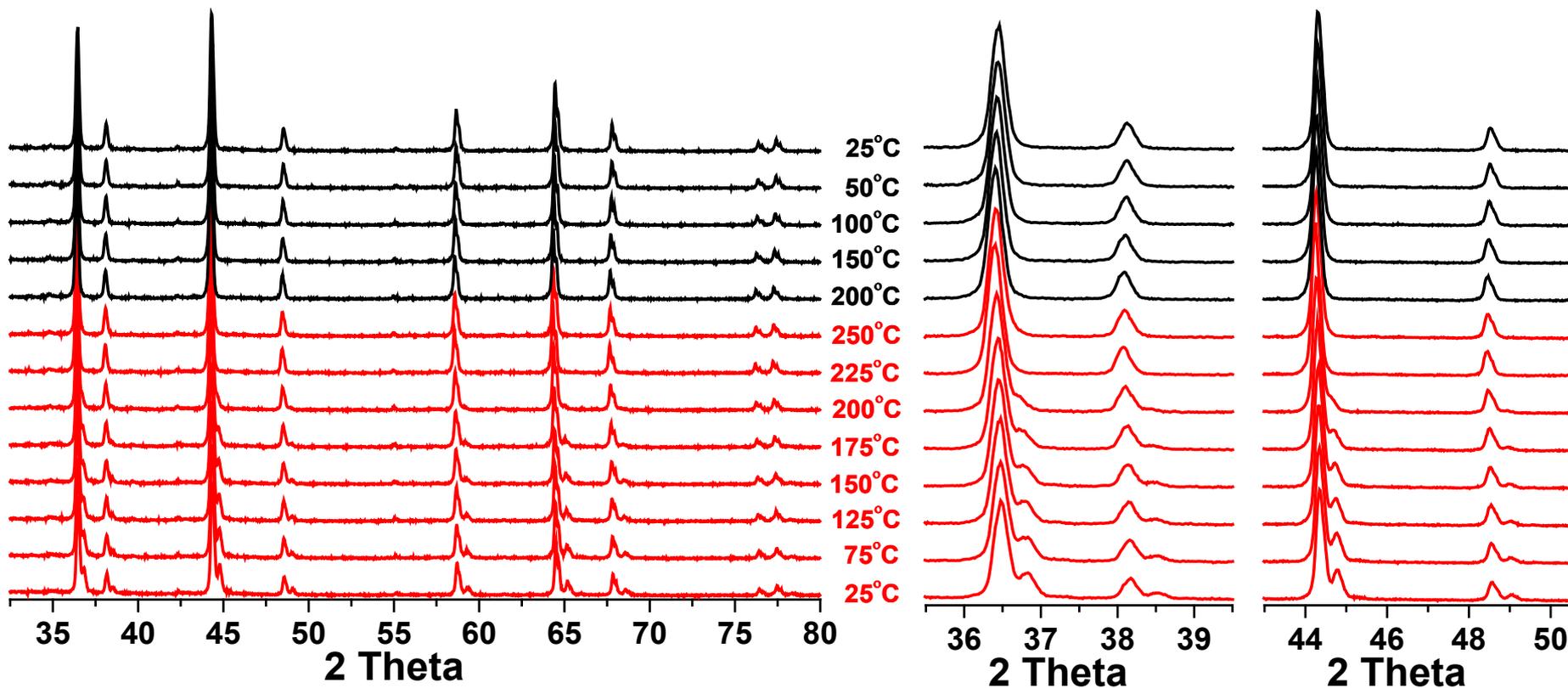
- In situ XRD collected during thermal treatment of Li$_{0.82}$MNO.

- At elevated temperatures, the cubic phases can merge into a single solid-solution phase.

# Thermal-driven Li$_x$MNO solid solution formation

• At elevated temperature, phase-pure solid solutions form in samples with high Li content (above Li0.51) but impurities form at low Li content.
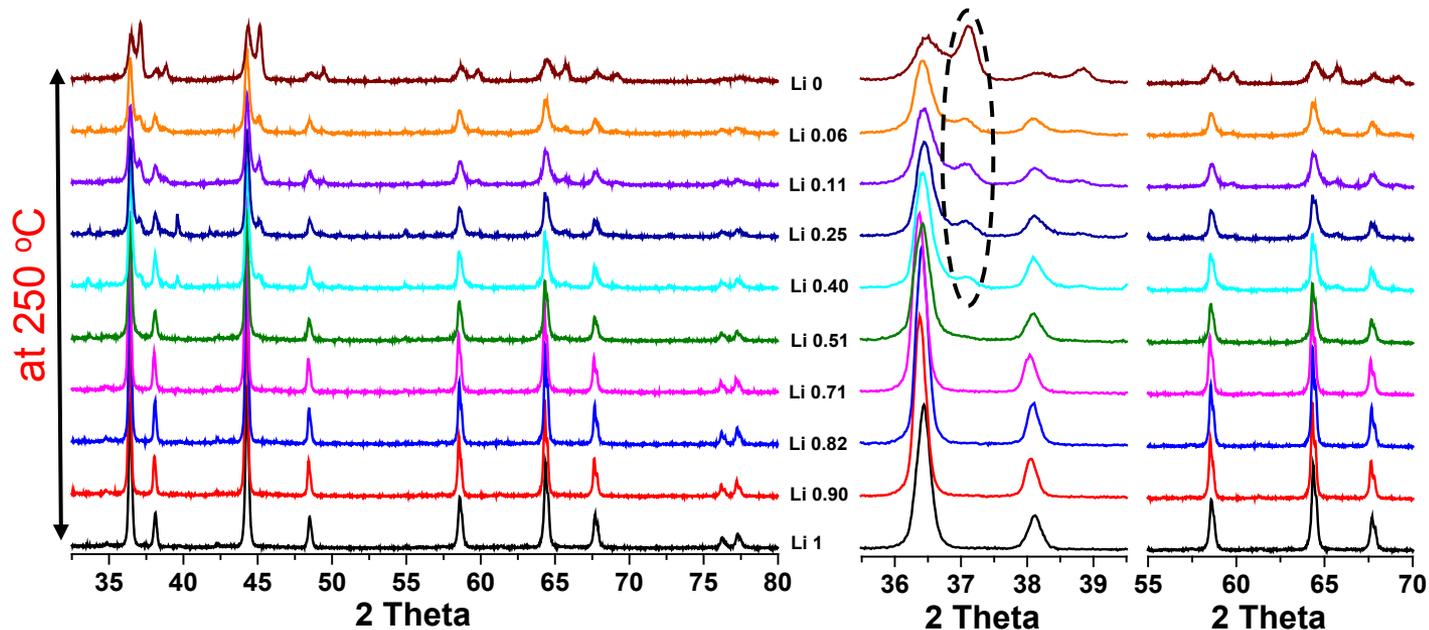
• Formed solid solutions remain phase pure after cooling to RT.
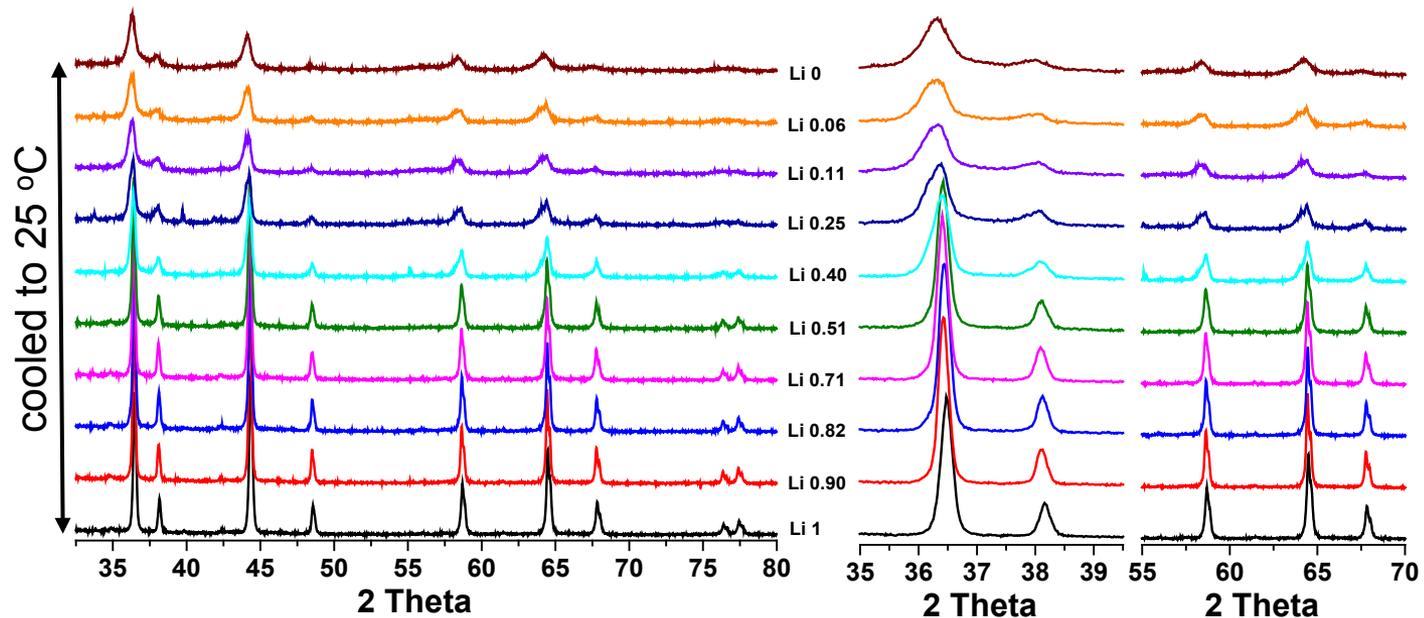
Thermal-driven Li$_x$MNO solid solution formation
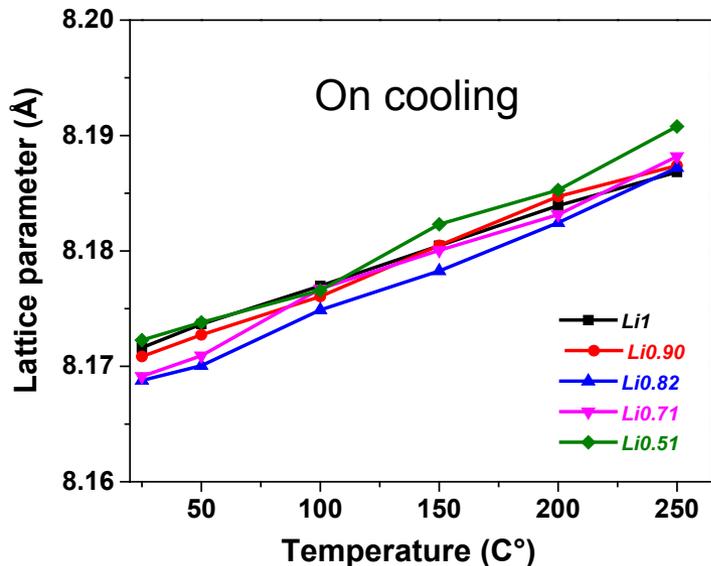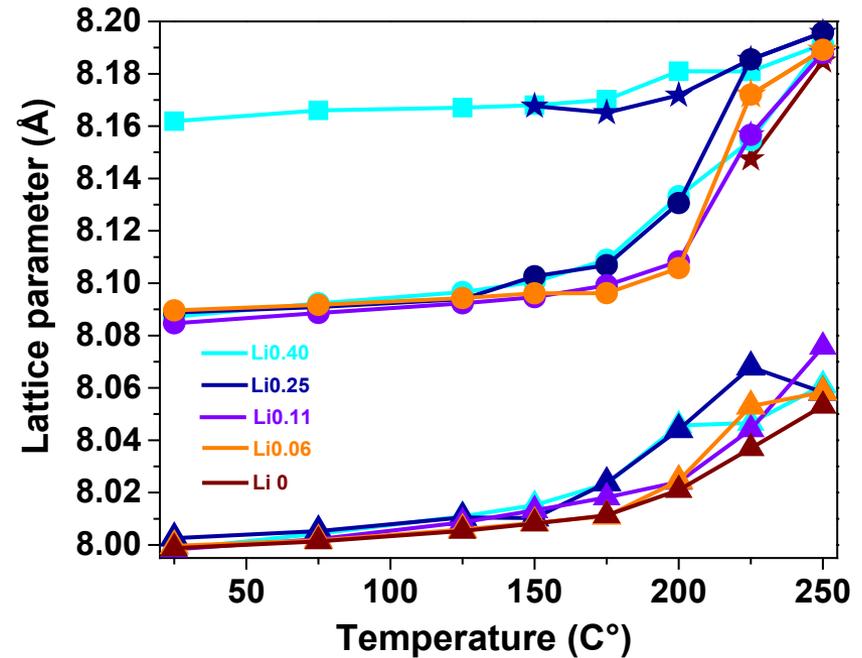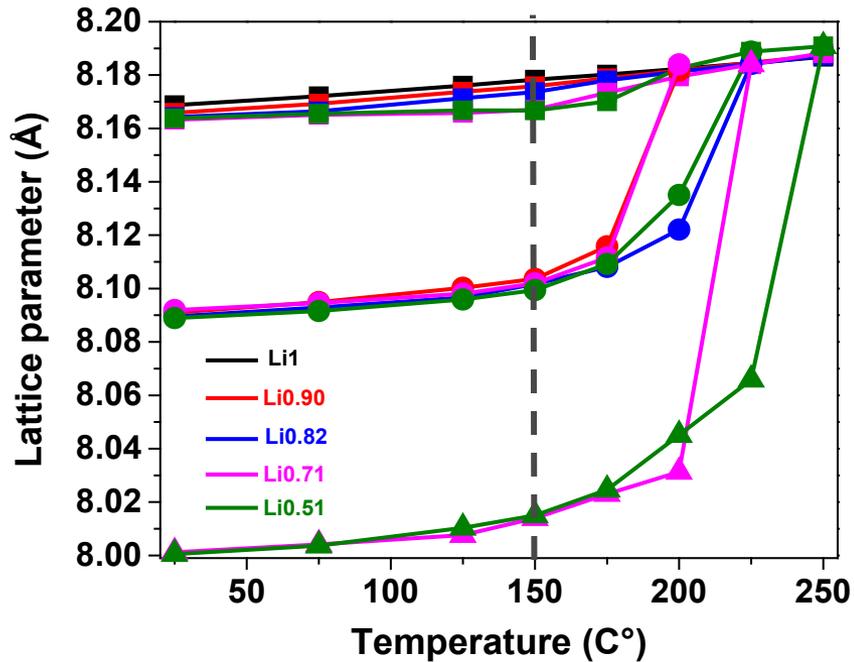
- Formation of solid solutions initiated around 150 °C and completed around 250-265°C.

- Cooling of solid solution phases follow thermal expansion behavior with no phase separation.

- Thermal behavior is Li content dependent.

Characterization of Li*x*MNO – Raman

Collaboration with R. Kostecki
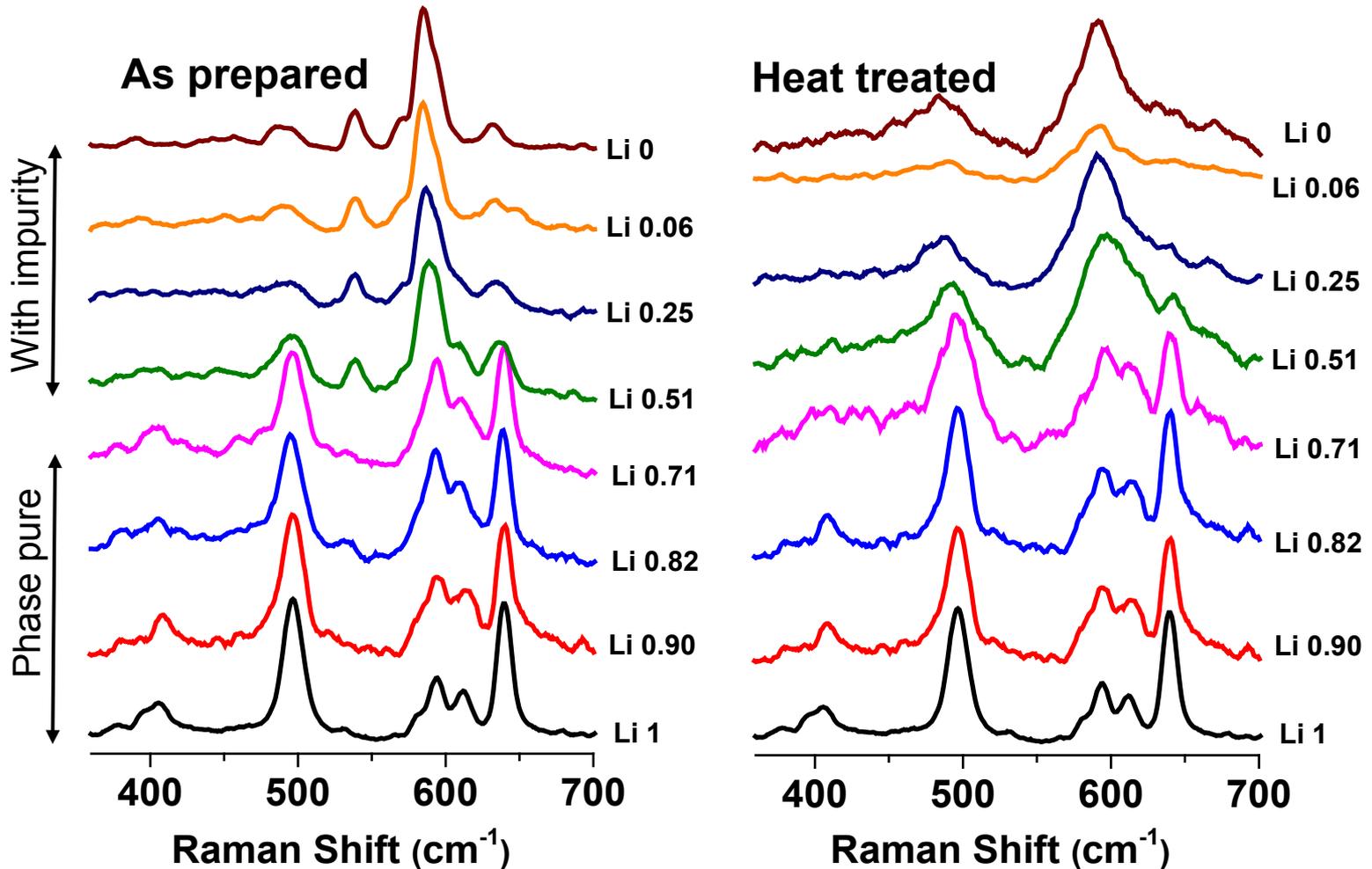
- Raman features of solid solutions resemble that of pristine LMNO.
- Rapid structural changes occur at Li content between 0.71 and 0.51.

Characterization of Li$_x$MNO – FTIR

As prepared

Heat treated

Li0
Li0.06
Li0.25
Li0.51
Li0.71
Li0.82
Li0.90
Li1

Wave number (cm^{-1})
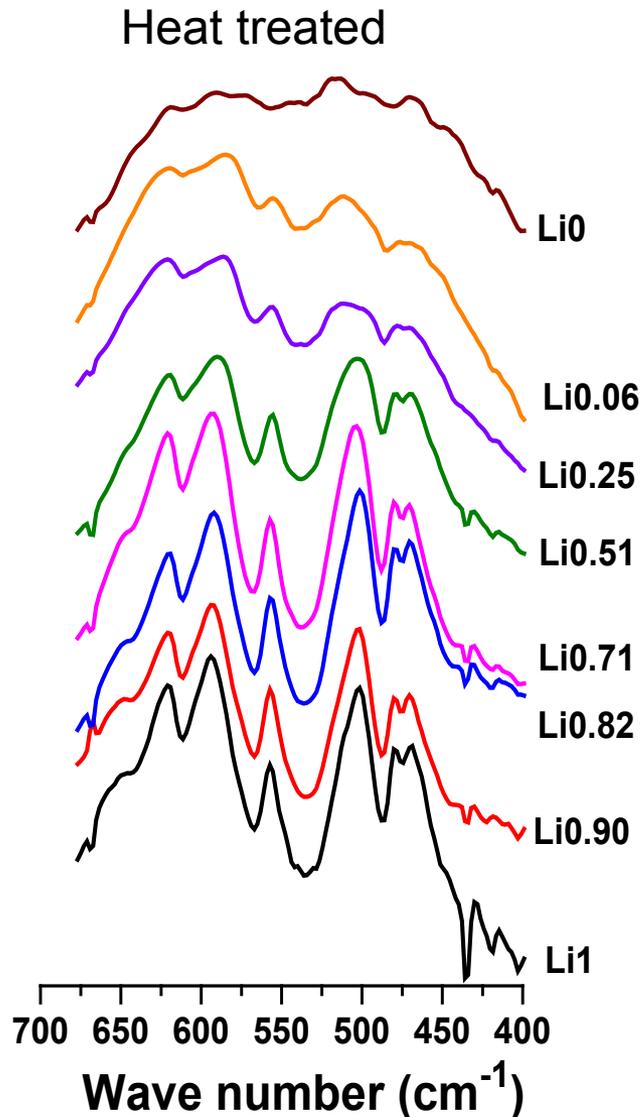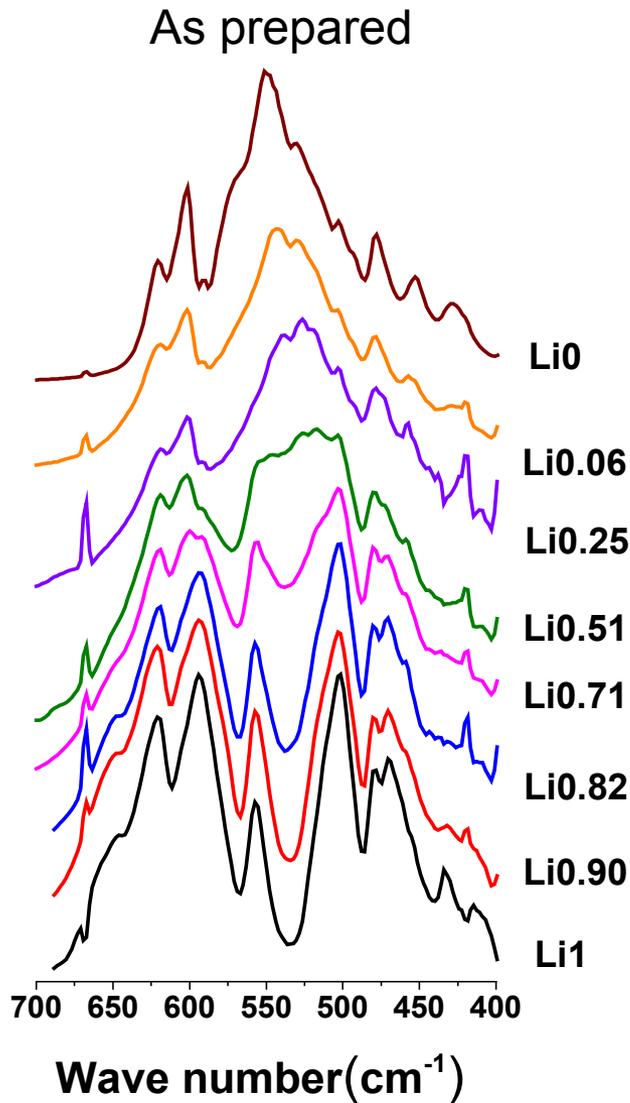
- Major structural changes concur with the large increase in phase III (MNO) content between Li0.71 and Li0.51.

- Cubic phase I and II merge into solid solution on heating, but phase III decomposes which leads to the presence of impurity in samples with low Li content.

Characterization of Li$_x$MNO – XAS


As prepared

Legend: 1, 0.90, 0.82, 0.71, 0.51, 0.25, 0.06, 0

Normalized intensity (a.u) vs Energy (eV)

Heat treated

Legend: 1, 0.90, 0.82, 0.71, 0.51, 0.25, 0.06, 0

Normalized intensity (a.u) vs Energy (eV)

Energy (eV) vs Lithium content — As-prepared, Heat treated
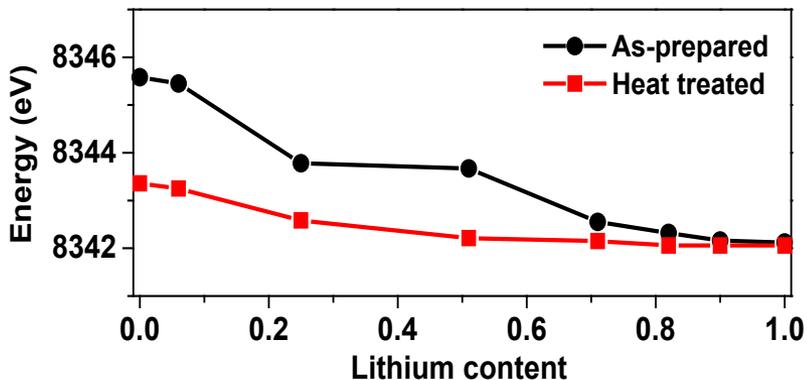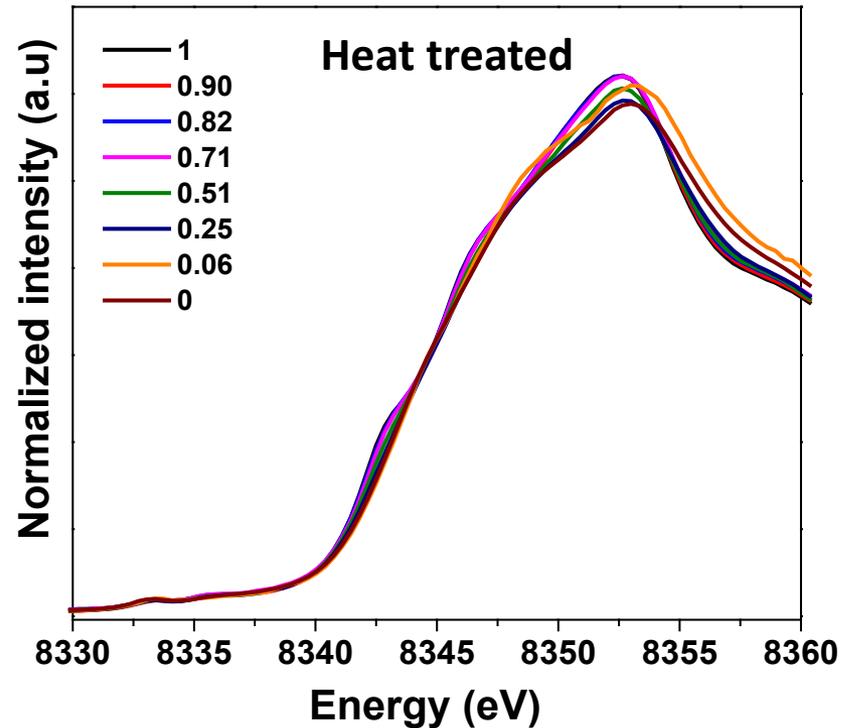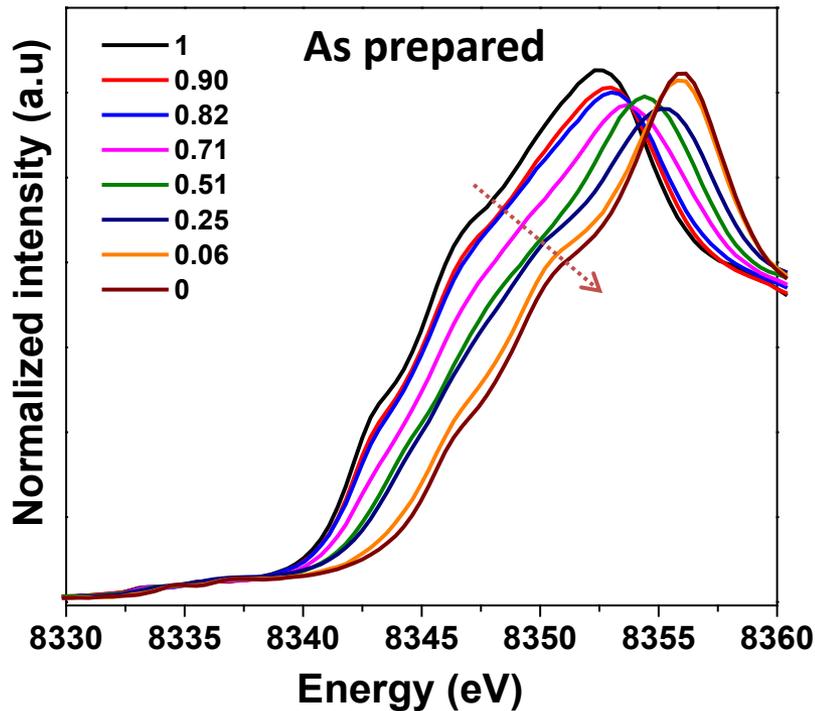
• XANES spectra show lower Ni oxidation state in heat-treated samples with low Li content (x≤0.51), suggesting that the formation of the impurity is related to Ni reduction.

Characterization of Li$_x$MNO – XAS

As prepared
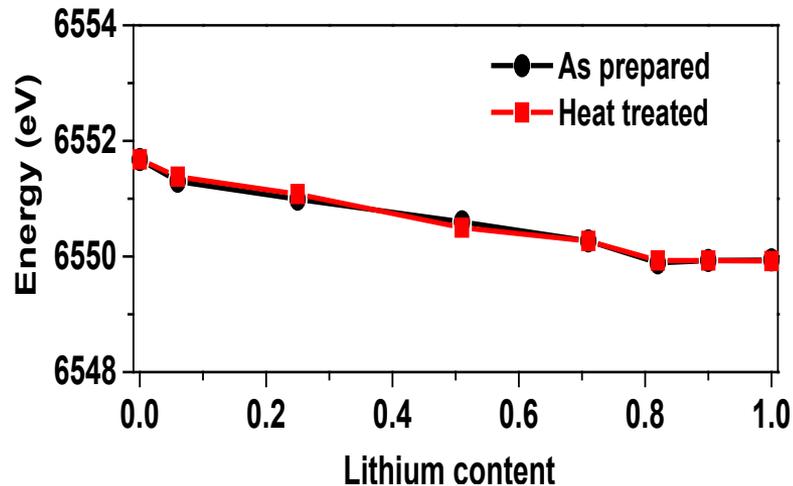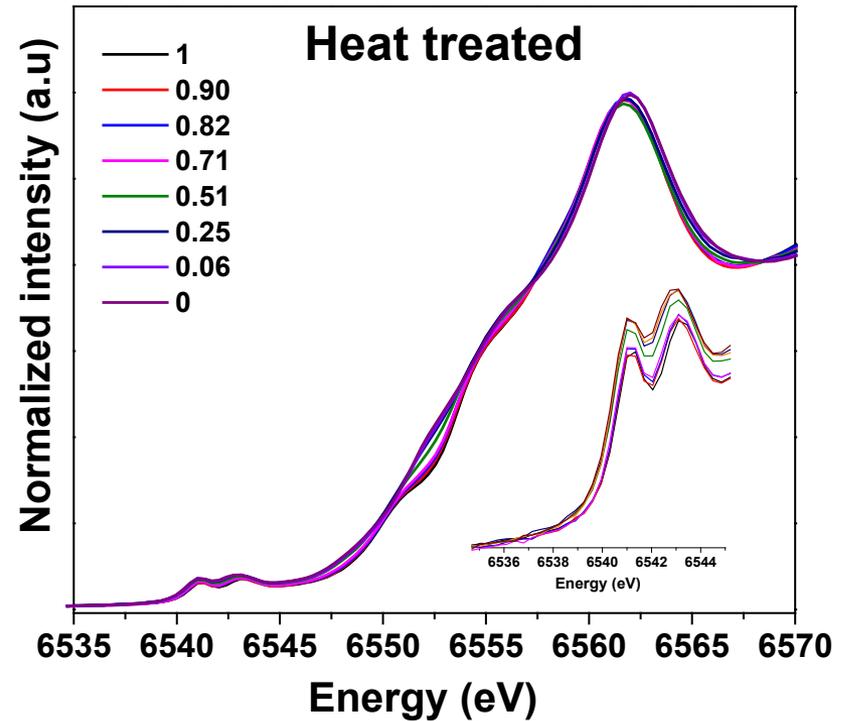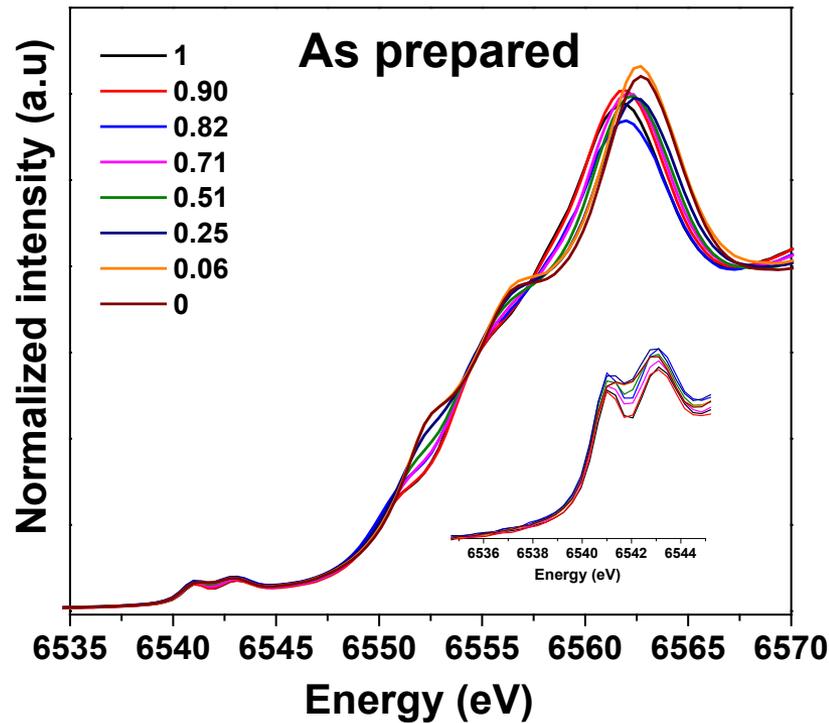
Heat treated

• No significant changes in Mn oxidation state. Mn remains at 4+.

Characterization of Li$_x$MNO – XAS
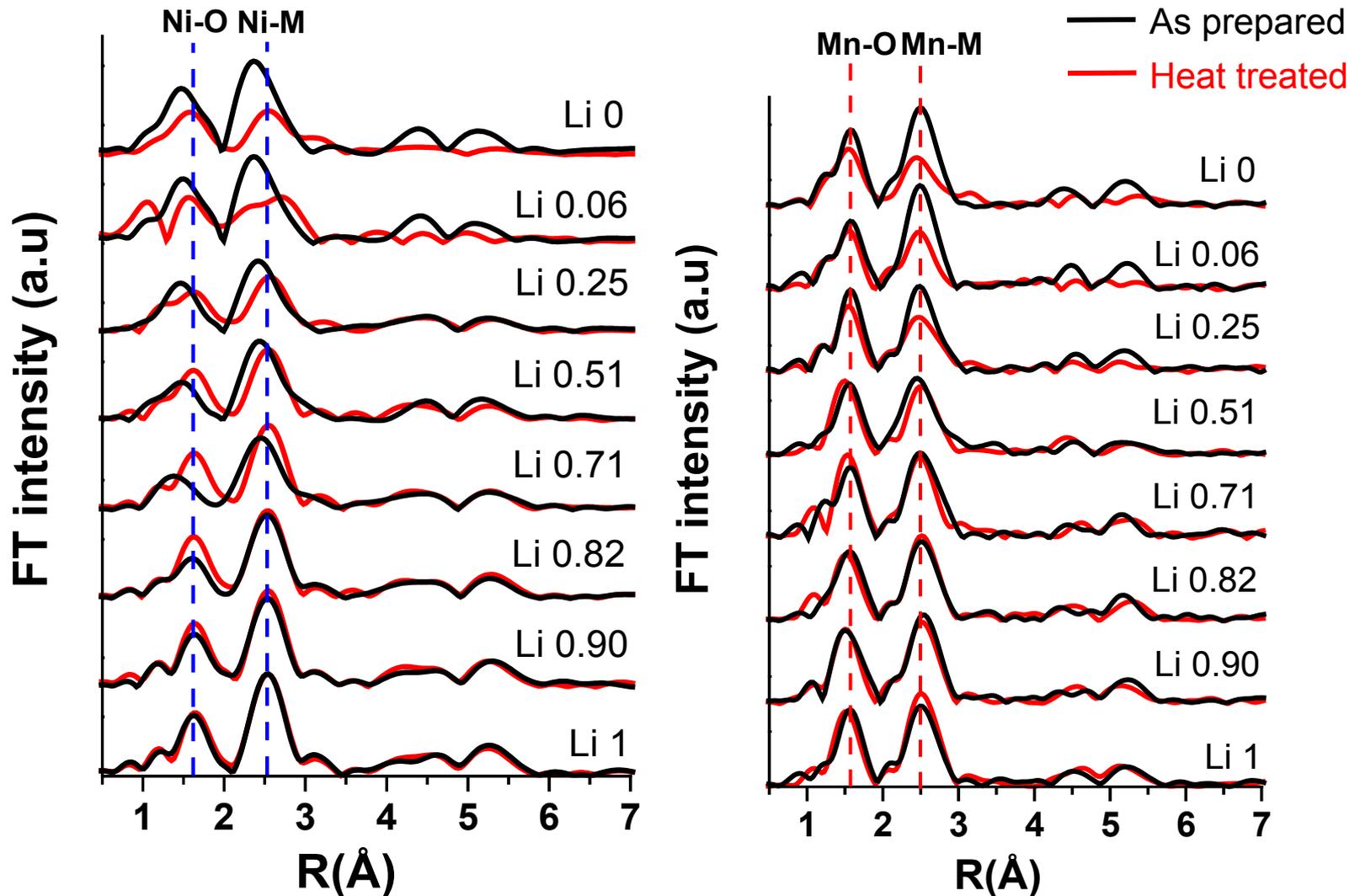
• On EXAFS spectra, expansion of Ni-O and Ni-M bonds was observed in heat-treated samples with high SOCs (x≤0.51), consistent with Ni reduction.

Layered oxide composites – activation kinetics

$Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$
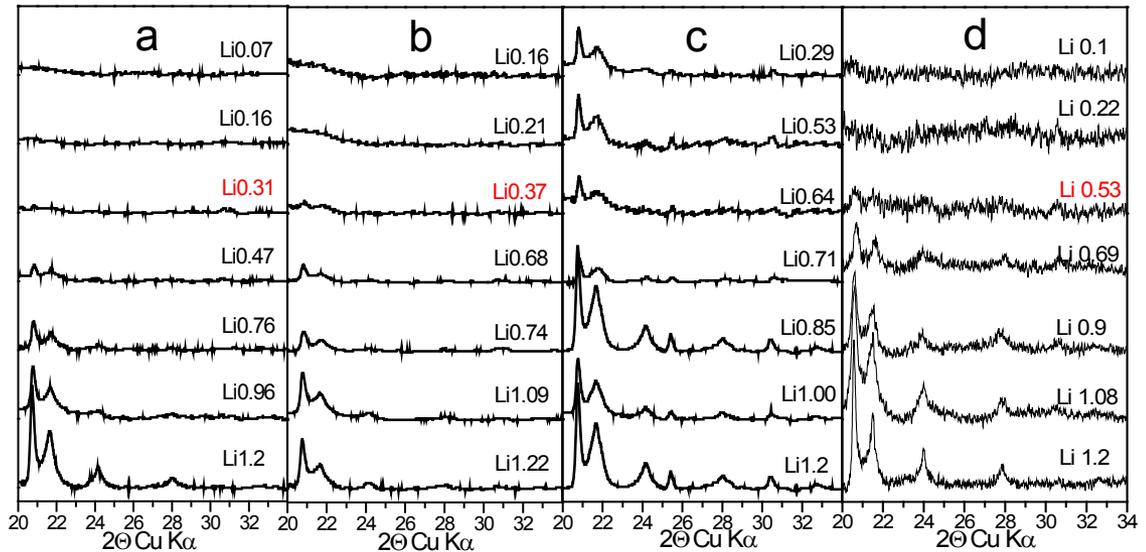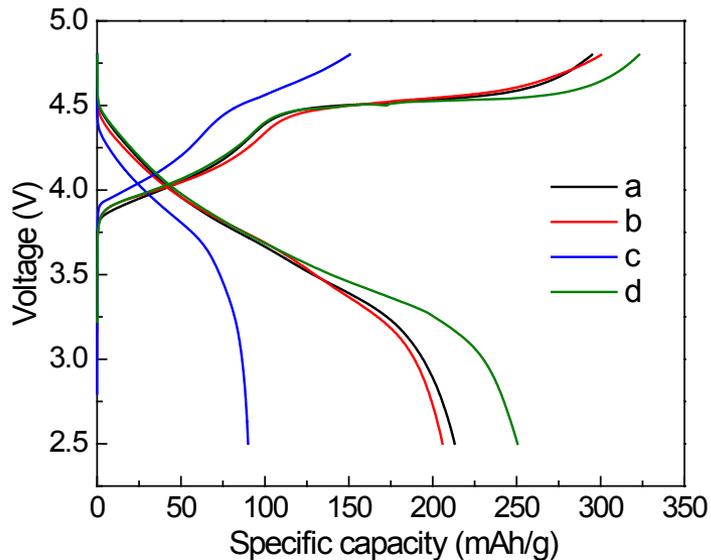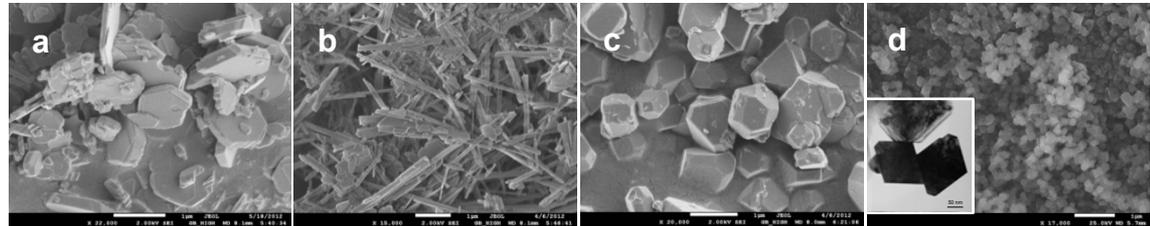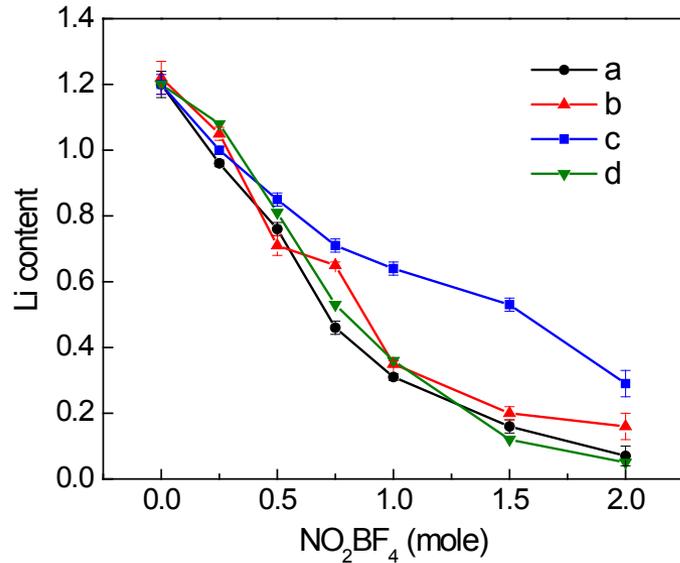
- Size and morphology have major impact on structural evolution and first-cycle activation kinetics.
- Worst kinetics on polyhedron morphology but size reduction can help.

Cycling induces TM reduction

Soft X-ray absorption spectroscopy
(SSRL beamline 10-1)
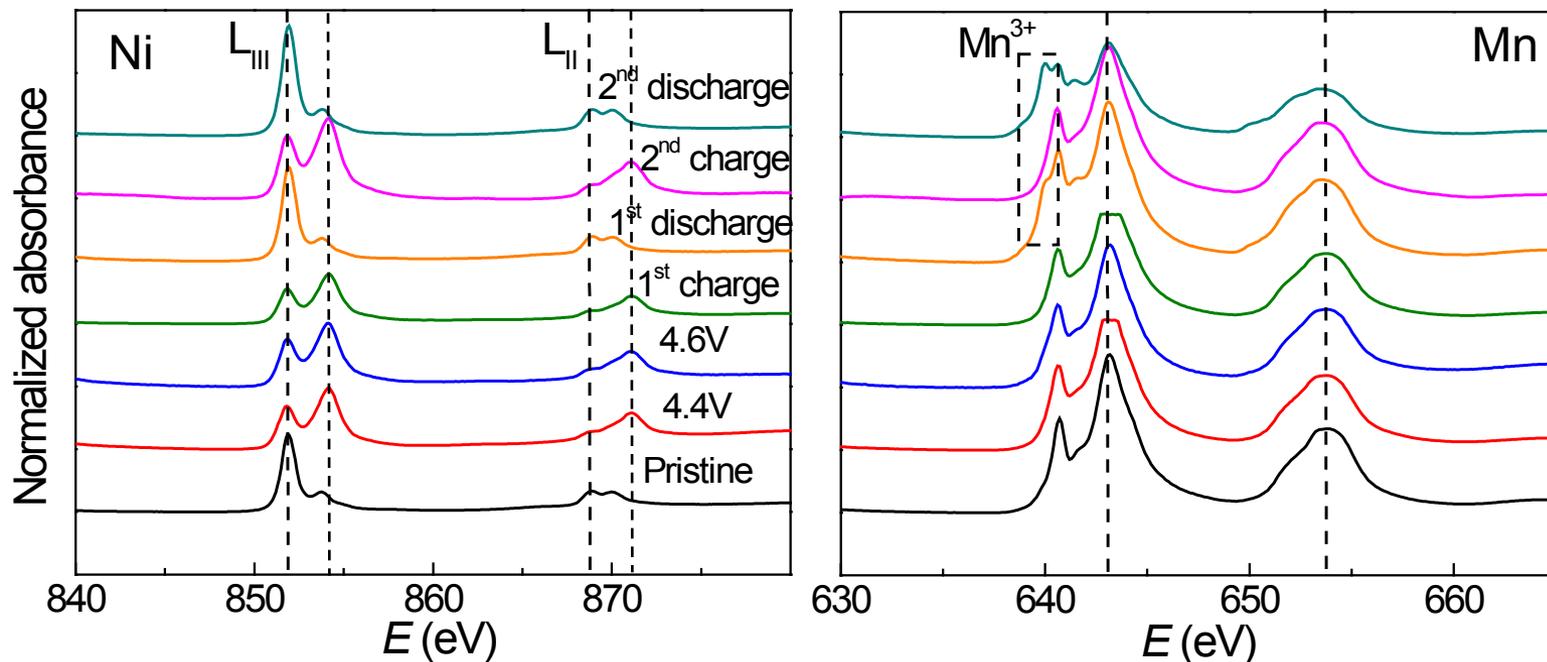
- Bulk reduction of TM oxidation state observed upon continuous cycling of binder and carbon free electrodes.

- What's the cause? Where does it initiate? Can we visualized this change at particle-level to gain mechanistic understandings?

Particle-level mapping of TM oxidation state

Collaboration with T. Tyliszczak
STXM, BL 11.0.2 (ALS)
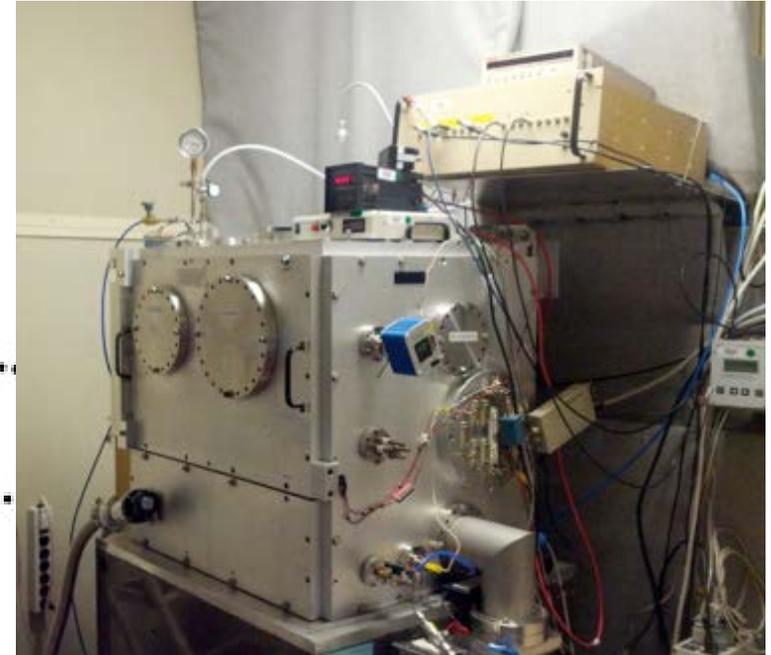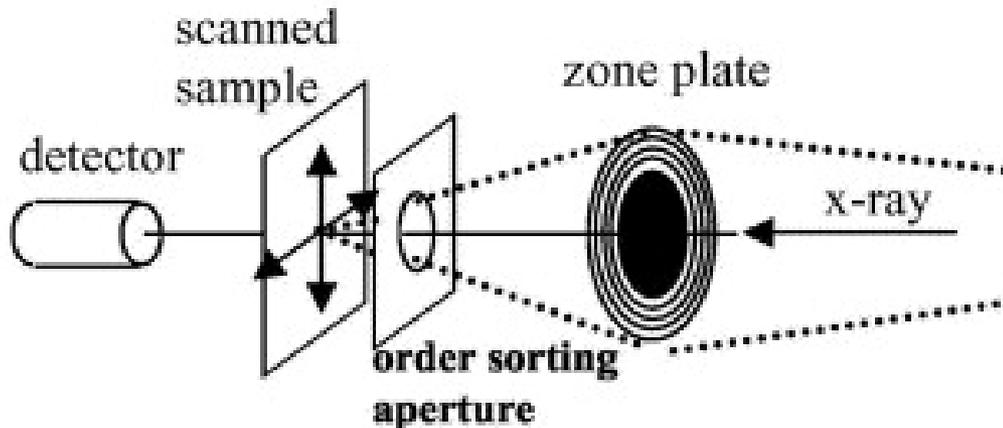
• Transmission mode imaging on bulk of the particle but at a spatial resolution of 25 nm (single pixel).

• Energy range of 200 -1900 eV, suitable for many TM detection.

Mapping of TM oxidation state – pristine oxide
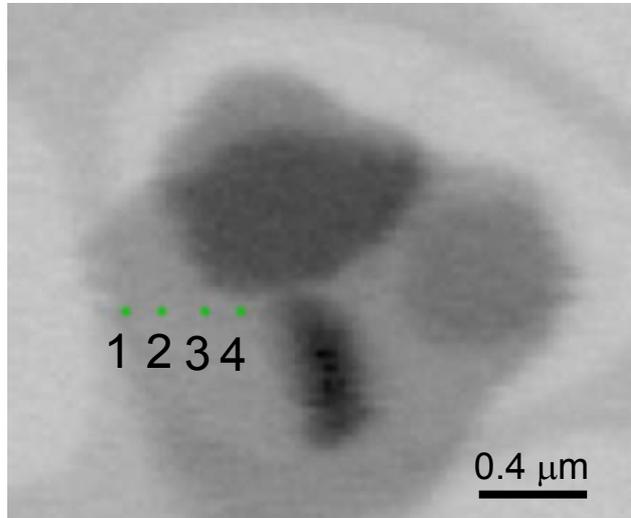
- Single pixel spectra collected on $Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$ crystals.
- Mn and Ni are 4+ and 2+, respectively, consistent with the measurement on the bulk sample.
- No variation in oxidation state from the center to the edge of the crystal.
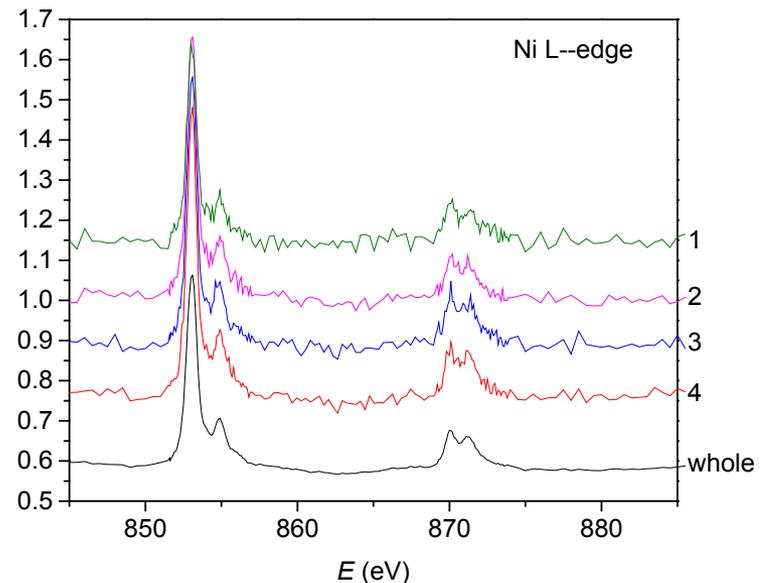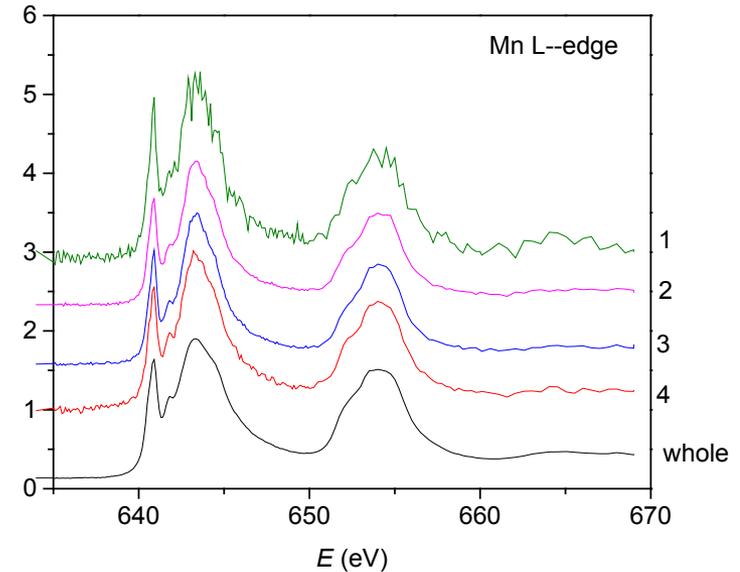
Mapping of TM oxidation state – charged oxide
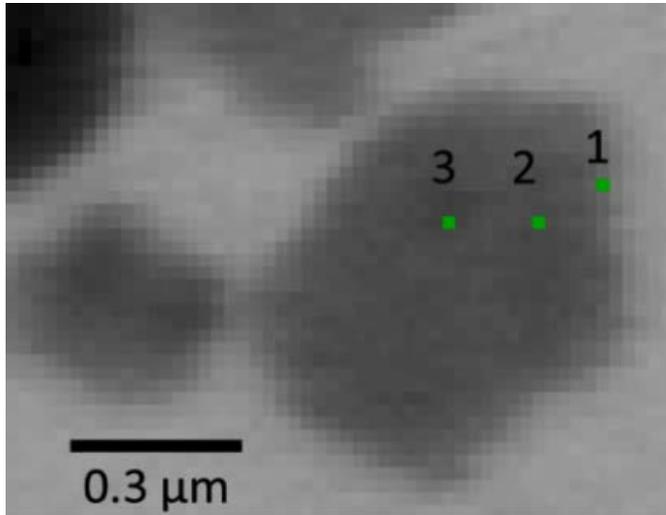
- TM less oxidized at the edge.

- Surface structural reconstruction resulting from side reactions with the electrolyte? Phase transition related to O_2 release at the interface?

- Further studies on extensively cycled samples planned.
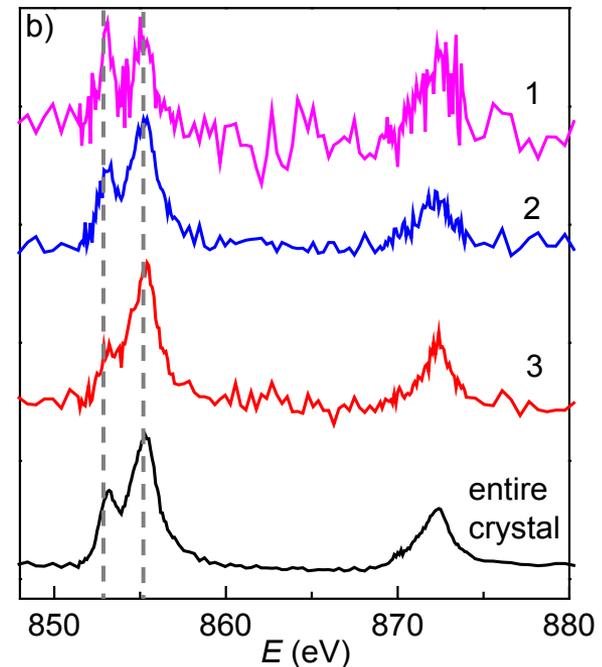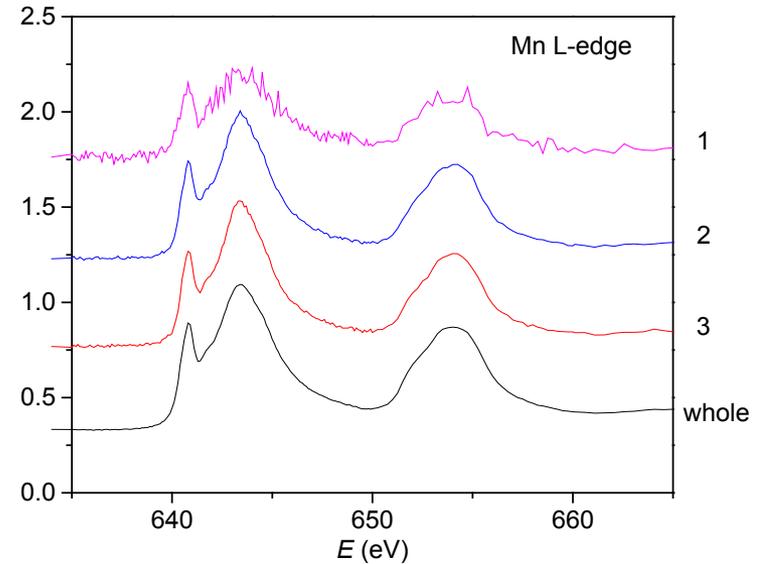
Collaborations

- Robert Kostecki (LBNL) – Raman and FTIR characterization of electrode materials

- Vassilia Zorba (LBNL) – laser induced breakdown spectroscopy

- Kristin Persson (LBNL) – modeling

- Clare Grey (Cambridge) – NMR studies

- Marca Doeff and Phil Ross (LBNL), Zhi Liu, Ethan Crumlin and Tolek Tyliszczak (ALS) – synchrotron *in situ* and *ex situ* XRD, XAS, XPS and STXM

- Yet-Ming Chiang (MIT) – conductivity measurement and acoustic emission studies

- Brett Lucht (URI) – electrolyte interactions

Future Work

- Complete the construction of L_xMNO phase diagram. Establish solid-solution *vs*. 2-phase behavior as functions of Li content and temperature.

- Perform electrochemistry to evaluate cycling and kinetic properties of L_xMNO solid solution phases. Investigate kinetic implication of solid-solution *vs*. 2-phase reaction pathways in LMNO.

- Further evaluate the impact of surface properties, including surface modifications, on side reaction kinetics and products as well as capacity fade in high-voltage cathode materials. Explore other aspects of particle engineering to improve cathode performance and stability.

- Perform single-particle diagnostic studies to understand cycling and aging induced structural changes and their impact on voltage fade, rate limit and DC resistance increase in layered oxides.

Summary

- Well-formed single crystals of high-voltage cathode materials with a variety of sizes and morphologies were synthesized.

- Single-crystal based studies enabled following understandings:

  o Self-discharge severe on charged LMNO but the process can be manipulated by particle morphology engineering.

  o Particle size and surface facet play critical roles in cathode performance and stability, including transport properties, side reactivity with the electrolyte, phase transformation, layered oxide activation kinetics.

- RT L$_x$MNO solid solution phases were synthesized and characterized. Electrochemical studies planned.

- Diagnostic techniques developed for the single-crystal investigation relevant to cathode performance and stability.