Design and Synthesis of Advanced High-Energy Cathode Materials

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Project ID: ES225

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Overview

Timeline

- Start date: October, 2012
- End date: September, 2016
- Percent complete: 70%

Barriers Addressed

- Energy density
- Cycle life
- Safety

Budget

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

Partners

- Collaborations: LBNL, UCB, Cambridge, ORNL, PNNL, NCEM, ALS, SSRL
- Project lead: Venkat Srinivasan

Objectives – Relevance

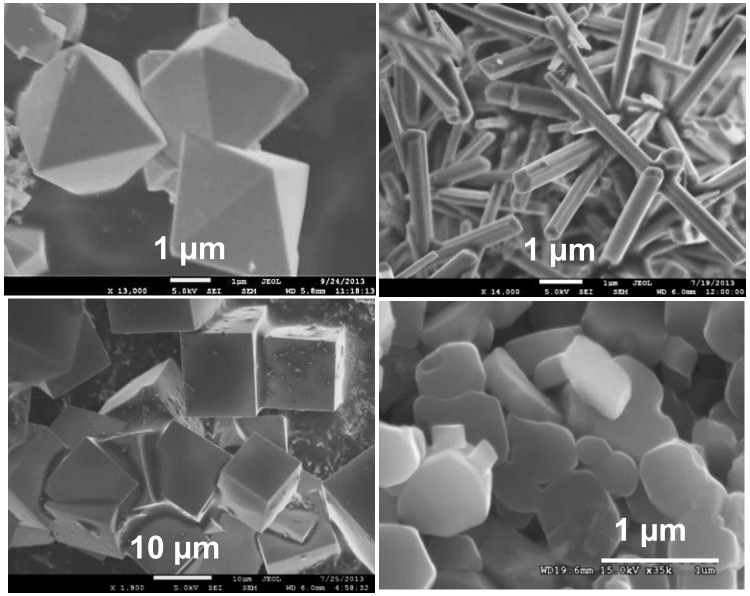
- Obtain fundamental understandings on phase transition mechanisms, kinetic barriers, and instabilities in high-energy cathode materials.
- Control cathode-electrolyte interfacial chemistry at high operating voltages and minimize solid-state transport limitations through particle engineering.
- Develop next-generation electrode materials based on rational design as opposed to the conventional empirical approaches.

Milestones

December 2014	Characterize Ni/Mn spinel solid solutions and determine the impact of phase transformation and phase boundary on rate capability (Completed)
March 2015	Complete the investigation on crystal-plane specific reactivity between Li-rich layered oxides and the electrolyte. Determine morphology effect in side reactions (Completed)
June 2015	Develop new techniques to characterize reactions and processes at the cathode-electrolyte interface. Evaluate the effect of surface compositions and modifications on side reactions and interface stability (On schedule)
September 2015	Go/No-Go: Continue the approach of using synthesis conditions to vary surface composition if significant structural and performance differences are observed (On schedule)

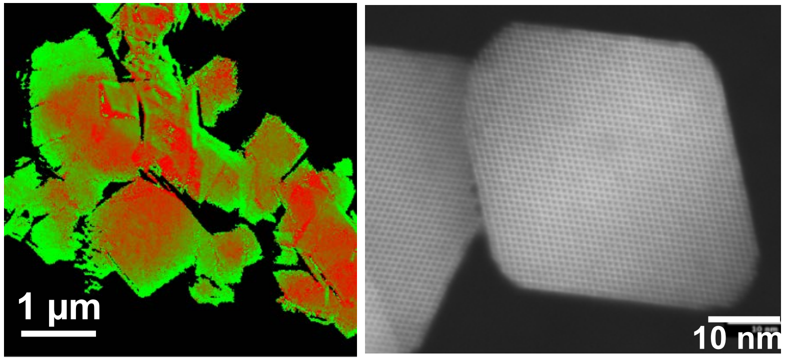
Approach

1) Remove the complexity in high-energy cathode materials – synthesize crystal model systems with defined attributes for the investigation of solid state chemistry, kinetic barriers and instabilities.

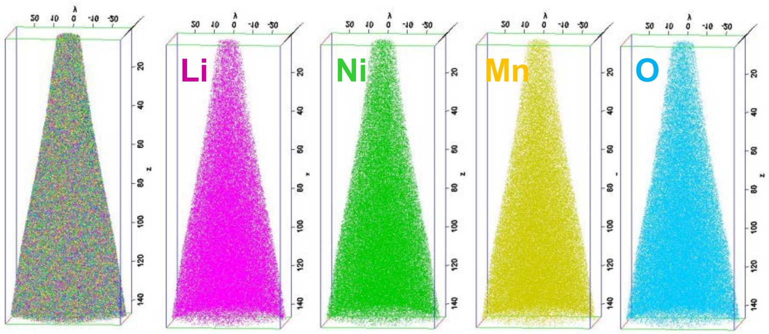


2) Perform advanced diagnostics for insights – *ex situ* and *in situ* studies to characterize crystal-plan specific transport properties and interfacial chemistry. Establish direct correlations between physical properties, performance, and stability.

Phase distribution (TXM/SSRL) and atomic imaging (HRTEM/NCEM)



3D compositional mapping (APT/PNNL)



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

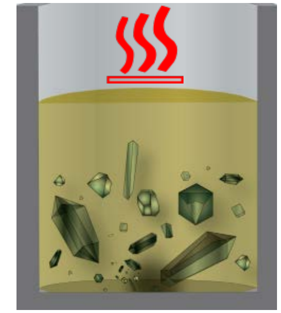
Technical accomplishments: overview

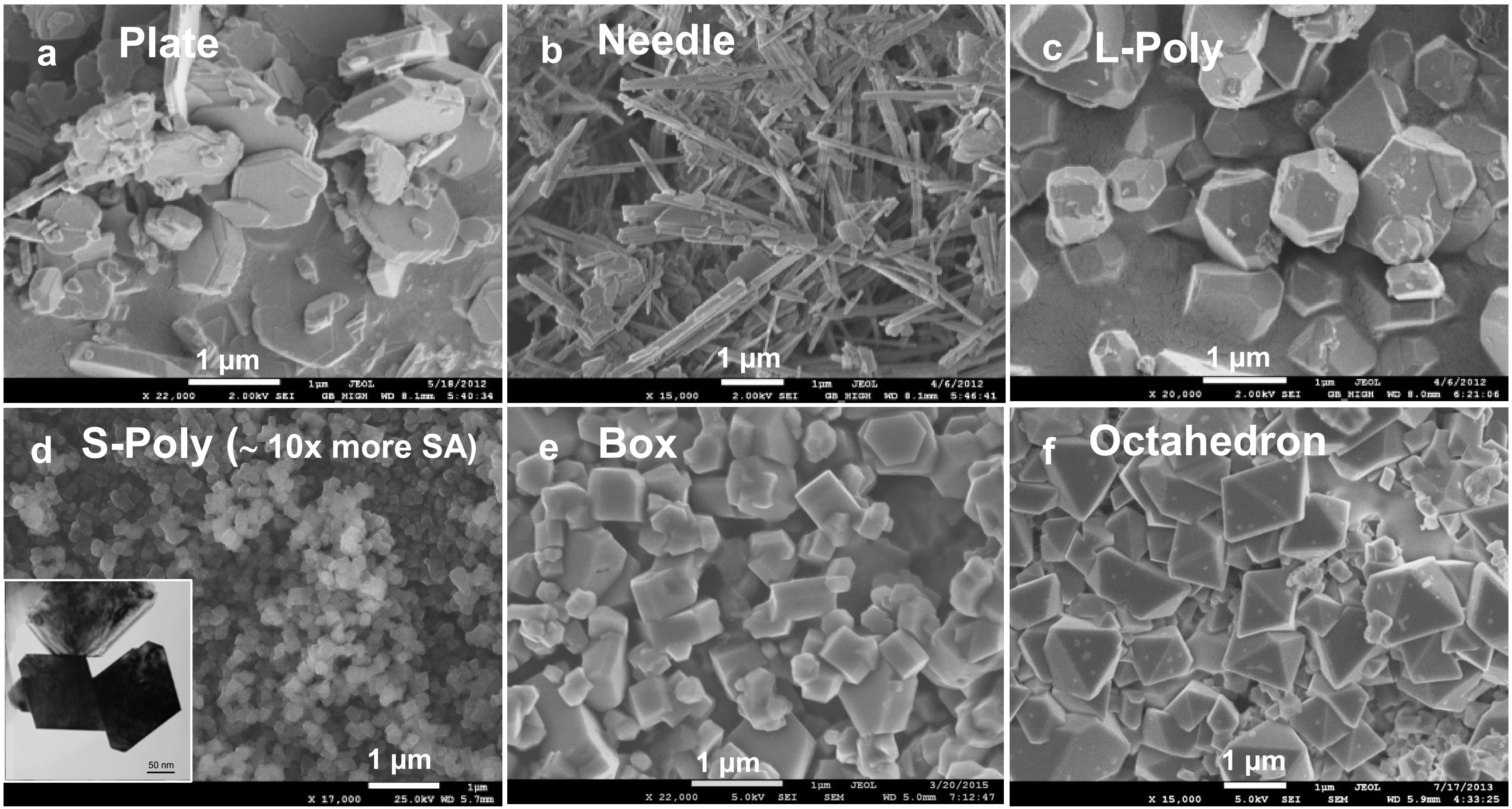
1) Determined structural make up of the entire Li and Mn rich NMC (LMR-NMC) crystal
2) Revealed the contribution of key surface properties to the material challenges facing LMR-NMC, including:
   - First cycle irreversibility and rate capability (kinetics)
   - TM reduction and dissolution during cycling
   - Capacity retention and side reactions with the electrolyte
   - DC resistance increase
   - Voltage fade
3) Investigated the kinetic implication of solid-solution *vs*. biphasic reaction pathways in intercalation cathode materials
   - Synthesized and characterized room-temperature $Li_xMn_{1.5}Ni_{0.5}O_4$ solid solution phases for the first time
   - Evaluated the role of phase boundaries and phase transformation in the kinetics of materials with first-order transition
4) Diagnostic techniques developed for the use of single-particle based investigation relevant to cathode performance and stability.

This presentation mainly focuses on 1) and 2).

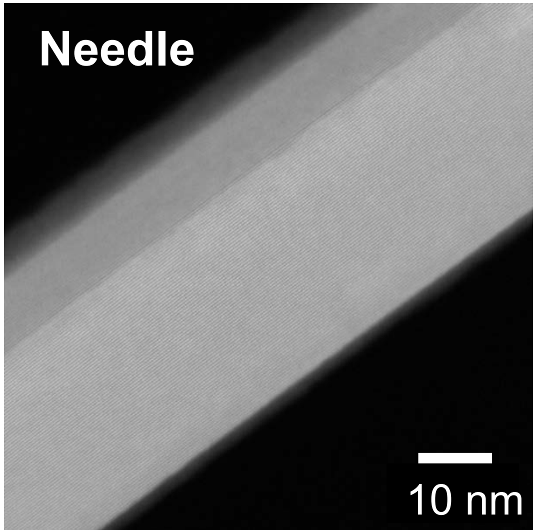
Synthesis of LMR-NMC crystal samples

- Molten-salt method: high-temperature solution based synthesis promotes crystal nucleation and growth in the flux.
- Morphology of LMR-NMC ($Li_{1.2}Ni_{0.13}Mn_{0.54}Co_{0.13}O_2$) crystals varied by adjusting reaction precursors, flux, heating temperature and time.

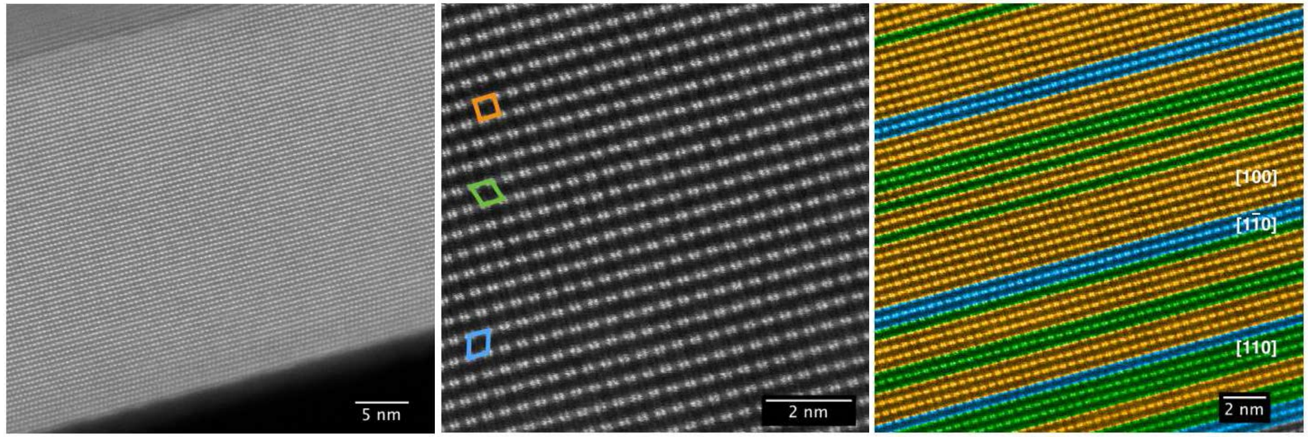


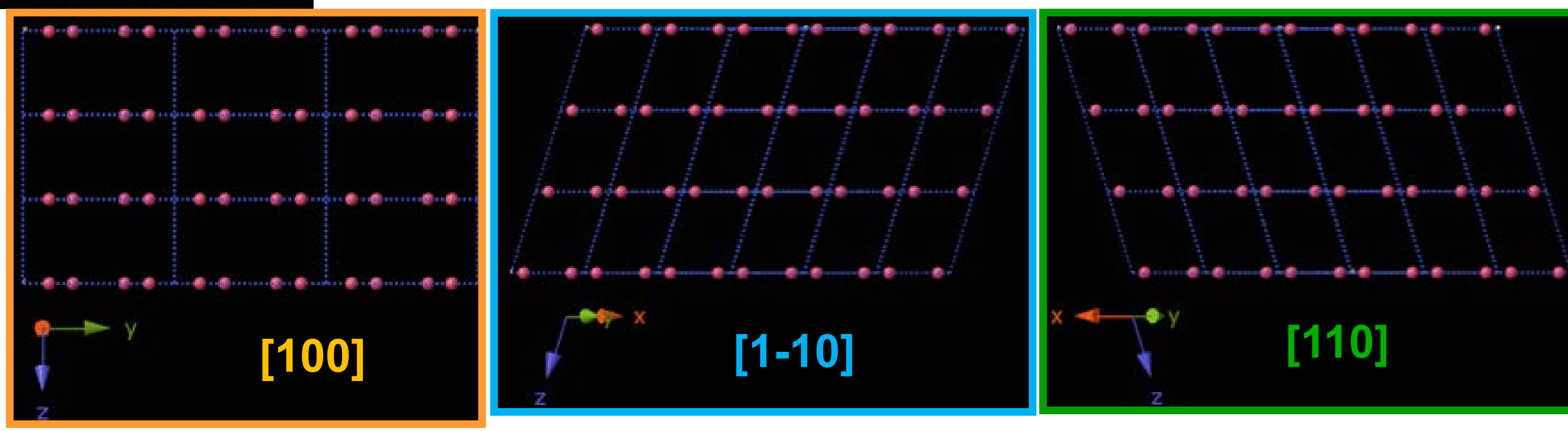


Our crystals are monoclinic single phase



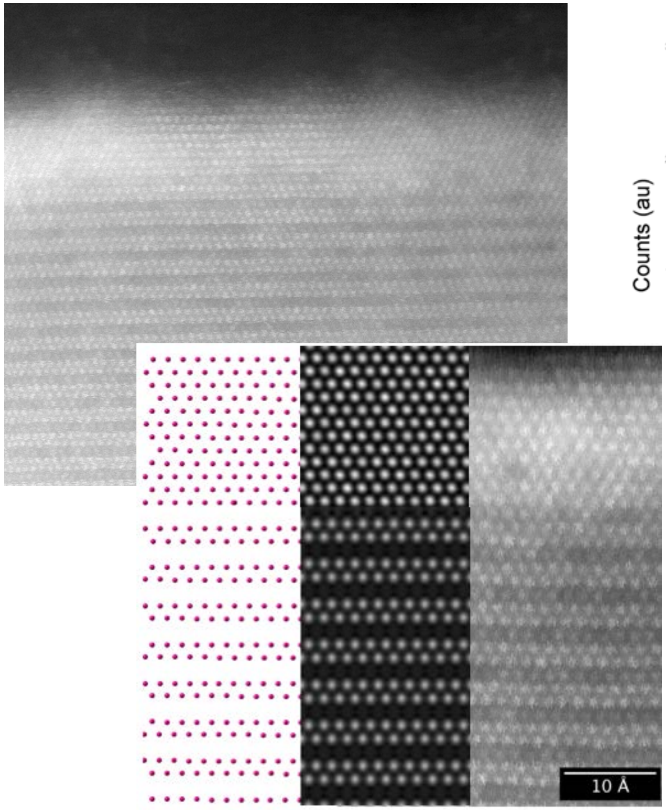
HAADF STEM imaging (Alpesh Shukla, LBNL)



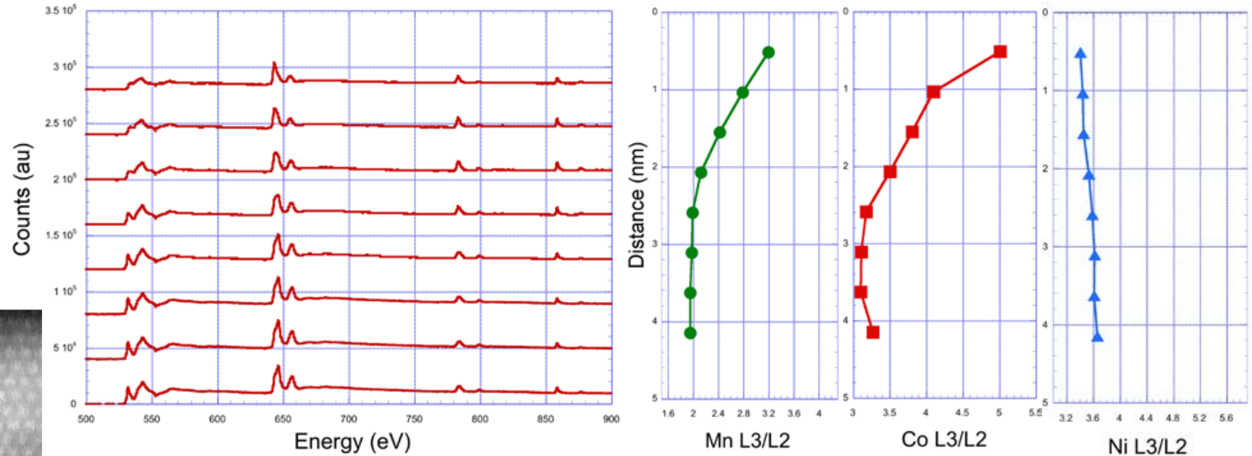


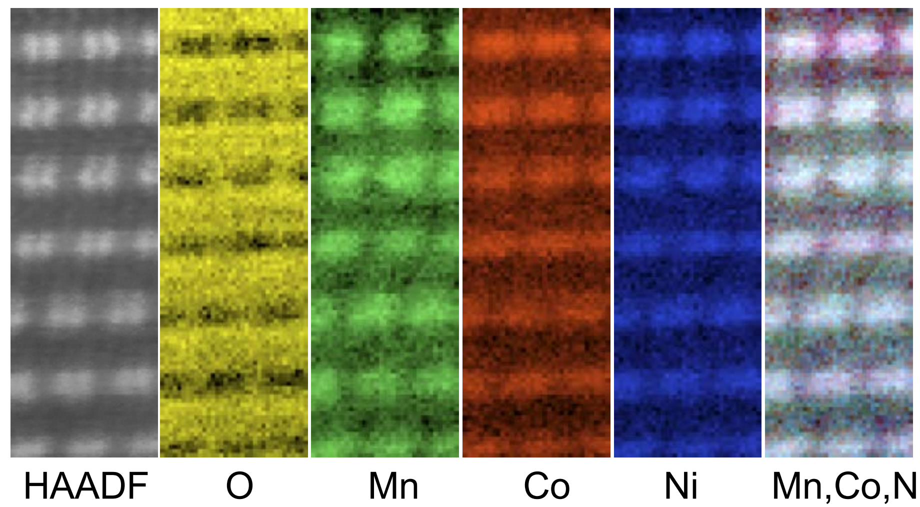
- Domains of three monoclinic variants in random distribution in the entire crystal.
- Not a composite with R-3m and C2/m nano-domains.
- Crystal structure independent of morphology.

Pristine oxide has reduced TM on surface



Atomic resolution EELS mapping (Alpesh Shukla, LBNL)



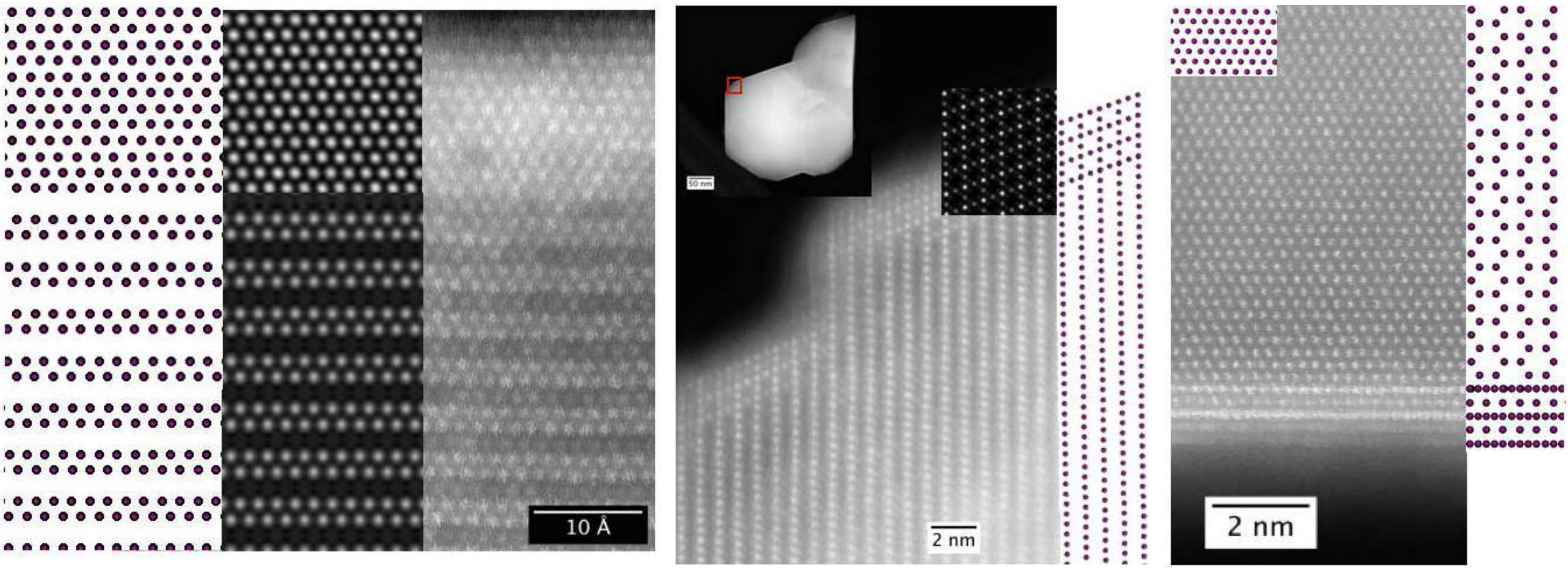


- Bulk Mn, Co and Ni at 4+, 3+ and 2+, respectively.
- Mn and Co reduced but Ni remains at 2+ on the surface layer (about 2 nm thick).

Reduced surface TM in spinel structure

Multiple zone axes HAADF STEM imaging (Alpesh Shukla, LBNL)

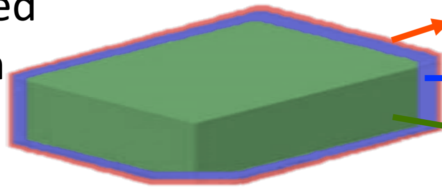
$[111]_s$ and $[103]_M$ $[110]_s$ and $[010]_M$ $[121]_s$ and $[001]_M$

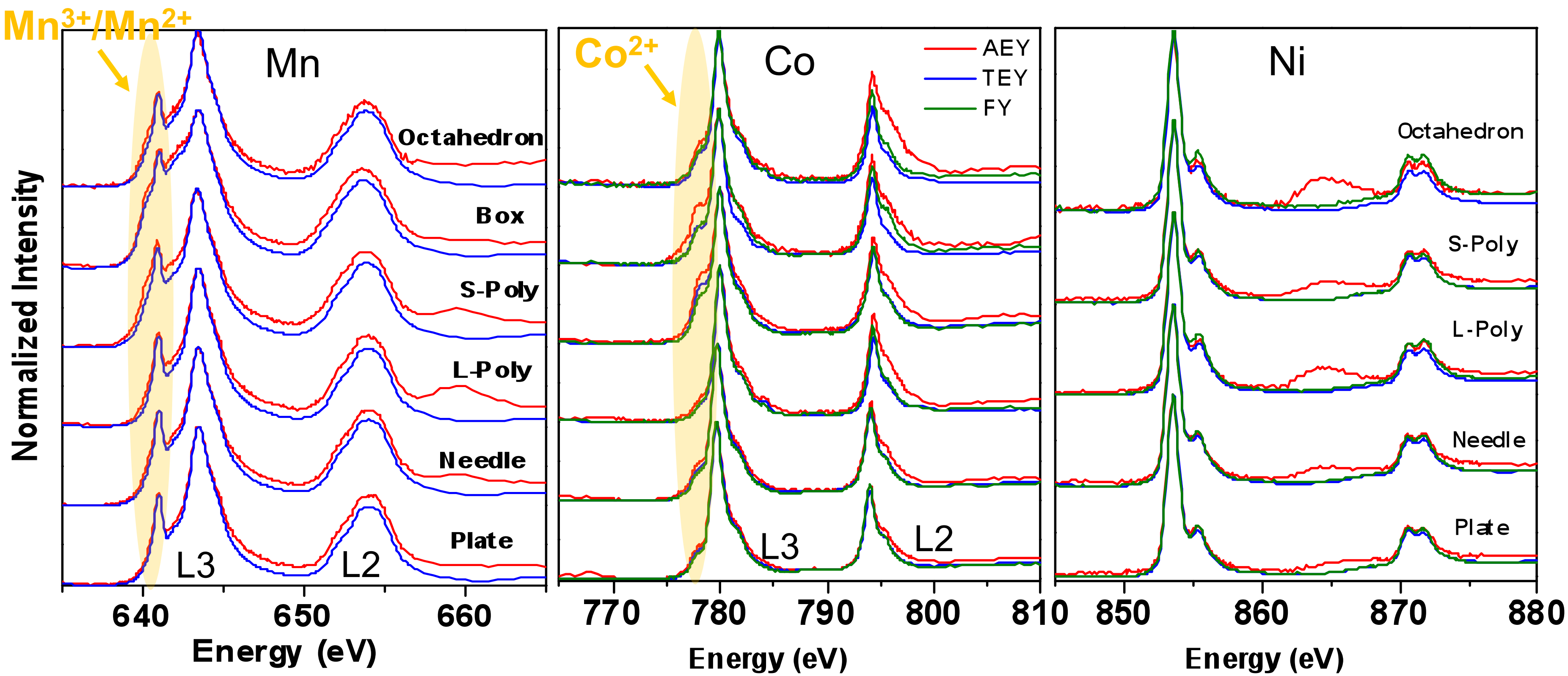


- STEM imaging in multiple zone axes is essential for determine the structures.
- Bulk has monoclinic structure while surface has spinel structure with reduced TM.
- Spinel formation on pristine surface is directional/morphology dependent – minimal spinel formation in the TM layer stacking direction.

Pristine surface TM reduction morphology dependent

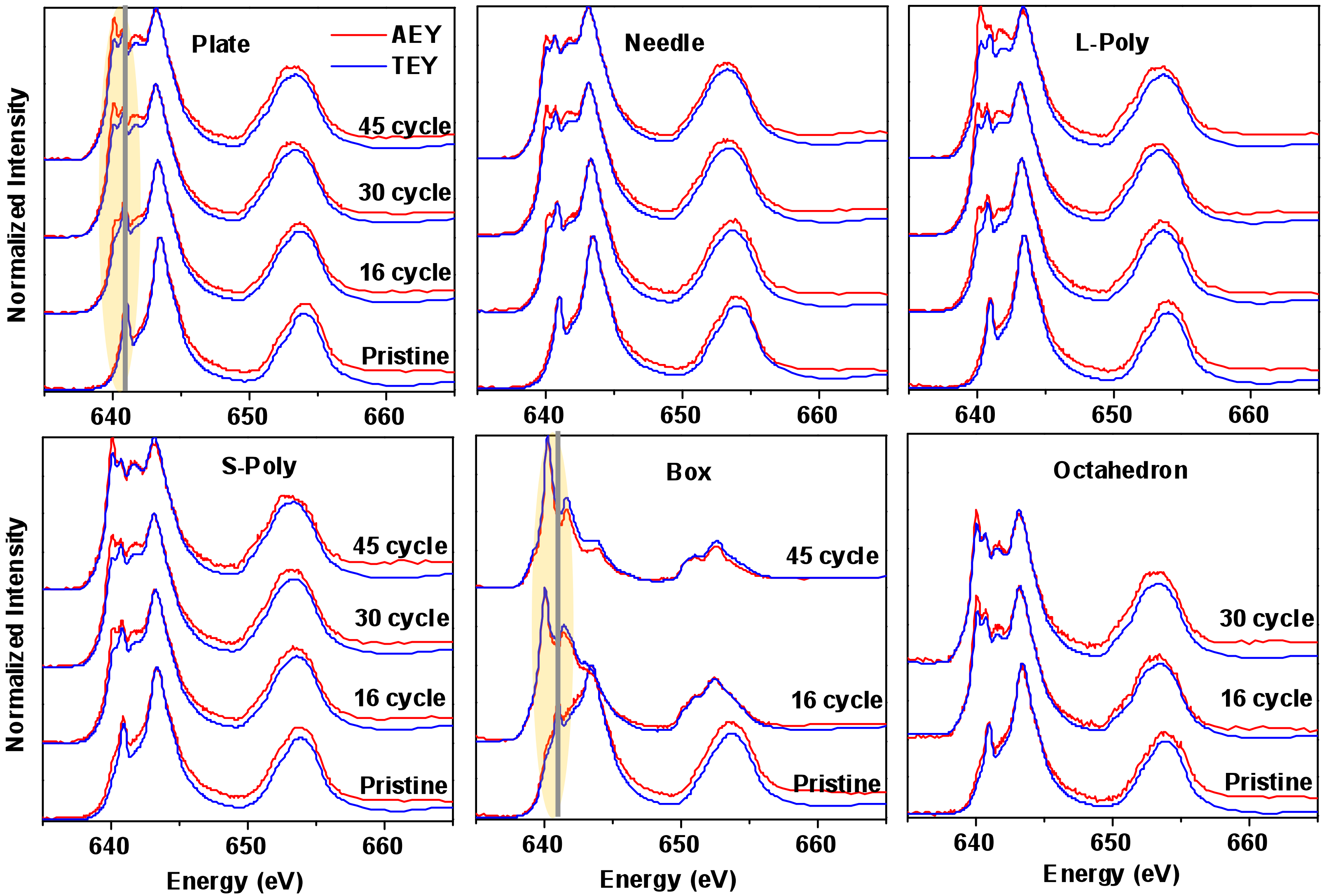
Soft XAS *L* edge spectra collected on composite electrodes with carbon and binder *(SSRL beamline 10-1)*





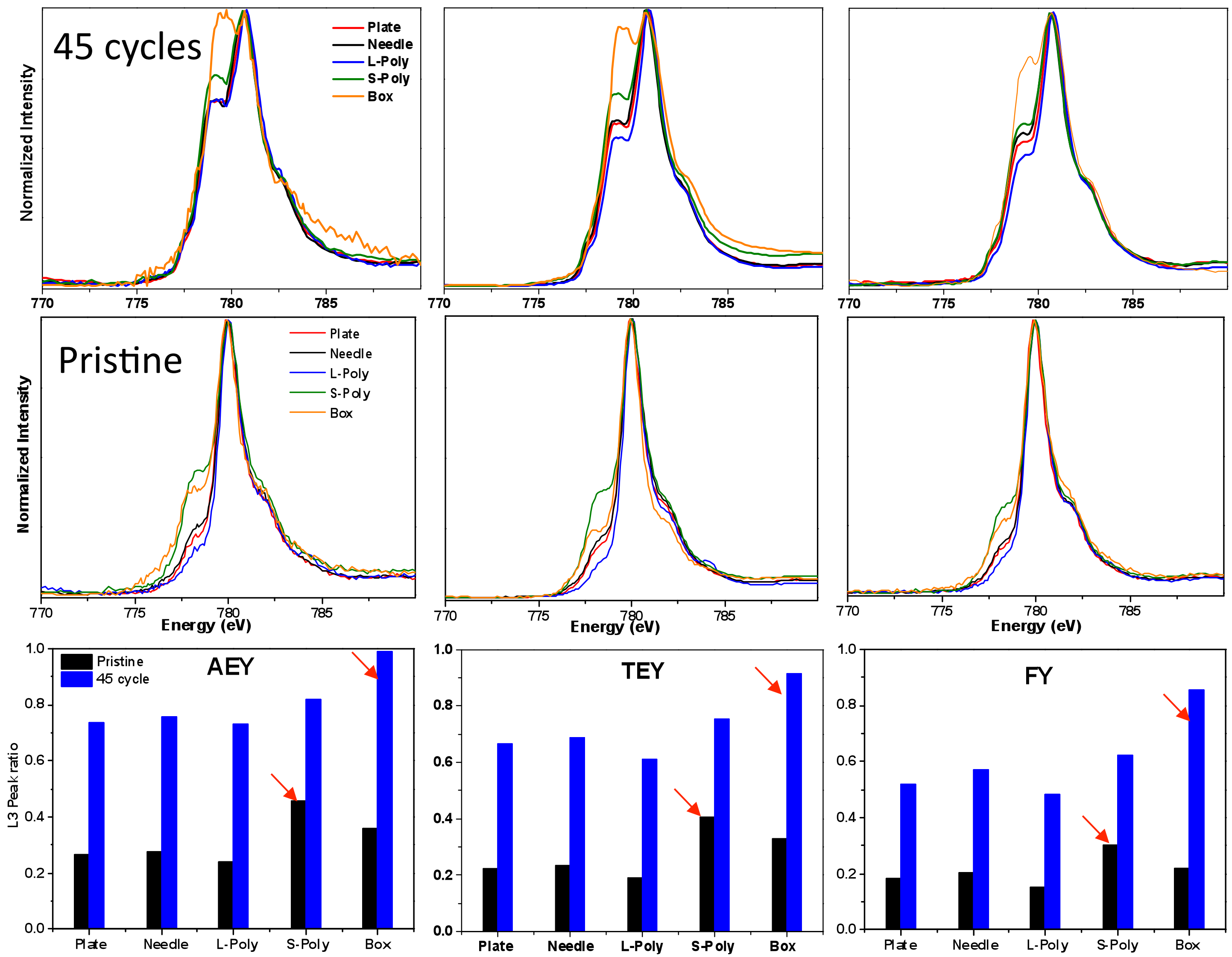
- Depth-resolved XAS confirms reduced Mn and Co on the top surface (a few nm) while Ni remains at 2+ in entire particle.
- Effects of surface facet and surface area – TM reduction least on Plate and L-Poly samples with predominantly TM layer surface while most on S-Poly and Box samples.

Surface TM reduction increases with cycling



- Mn XAS spectra show lower valent Mn content increases with cycling (2.5-4.6 V).
- Cycling-induced surface Mn reduction occurs on all samples but most extensive on the Box sample.

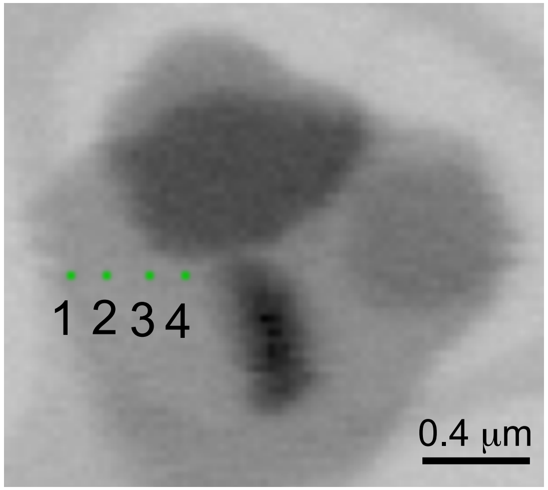
Cycling-induced TM reduction surface dependent

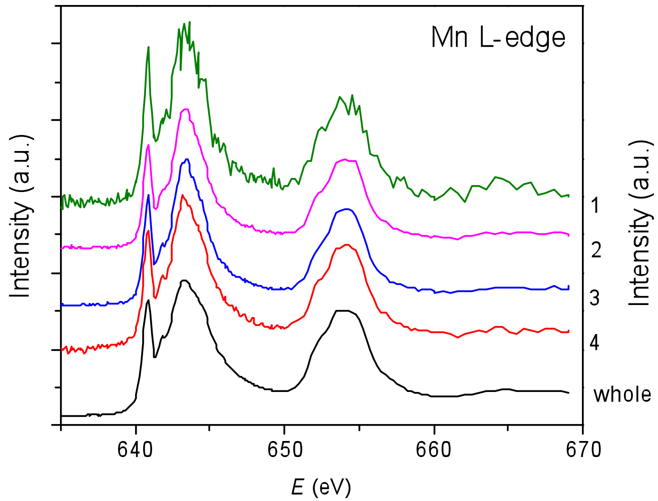


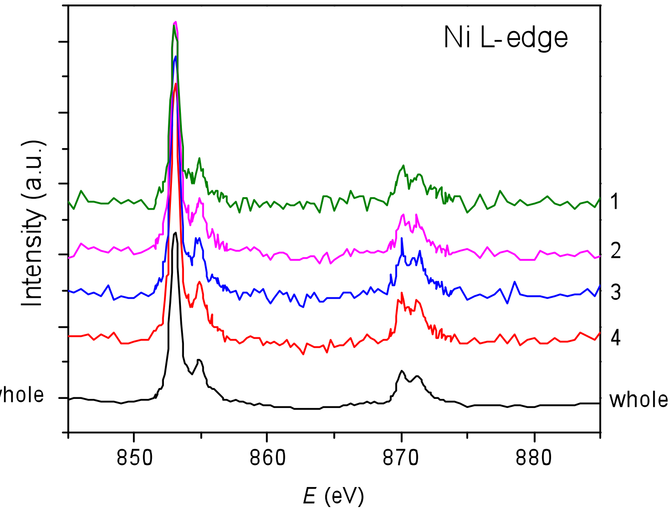
- Cycling-induced TM reduction progresses from the surface to the bulk.
- Effects of morphology and initial spinel content – most TM reduction during cycling occurred on Box while least on L-Poly sample.

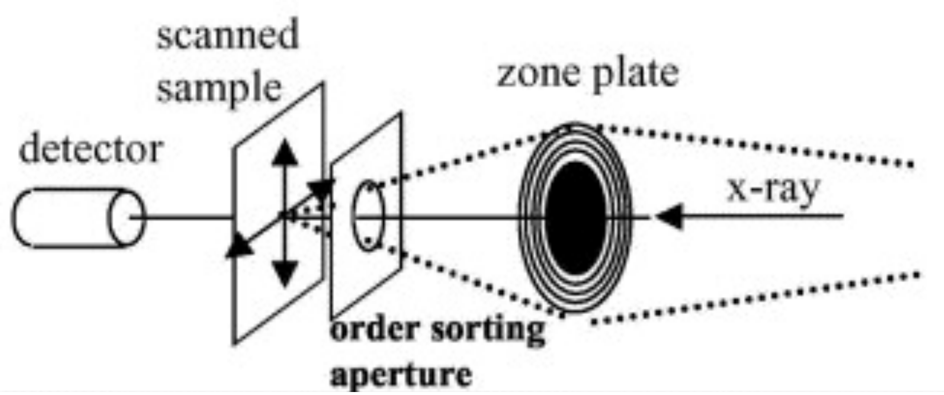
Chemical distribution of TM at particle level – pristine

STXM, BL 11.0.2 (with T. Tyliszczak, ALS)



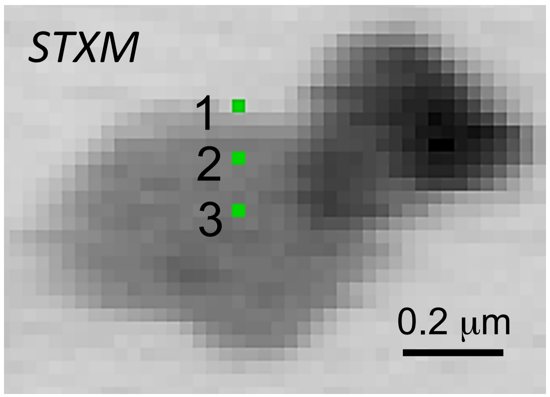


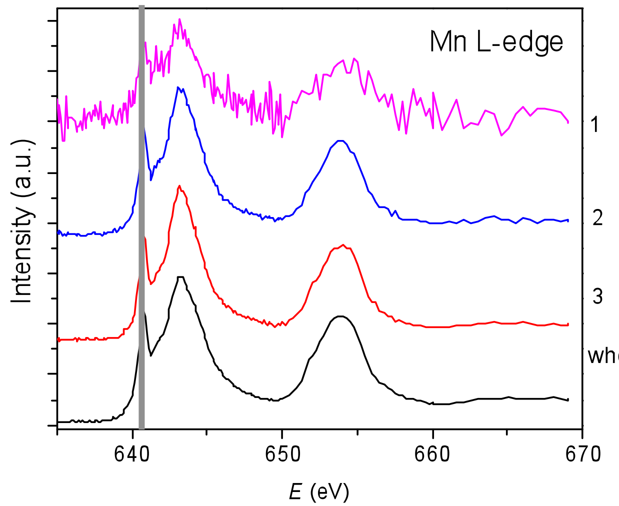


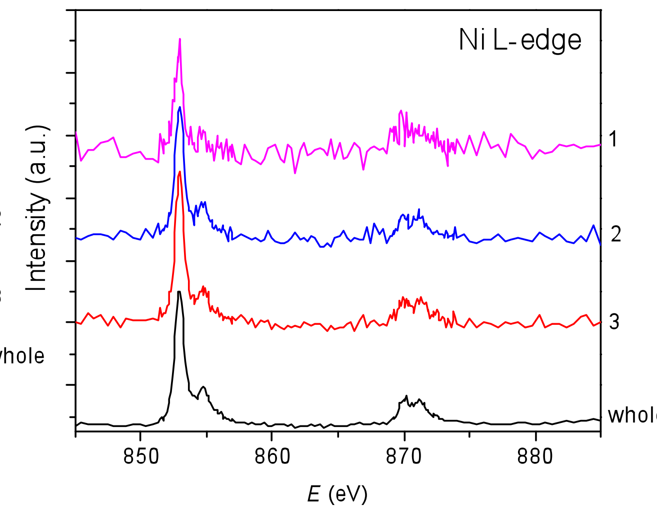


- Transmission mode imaging on LMR-NMC crystals at a spatial resolution of about 20 nm (single pixel).
- Mn and Ni are 4+ and 2+, consistent with the measurement on the bulk sample.
- No variation in oxidation state from the center to the edge of the plate crystal, consistent with minimum TM reduction on the pristine plates.

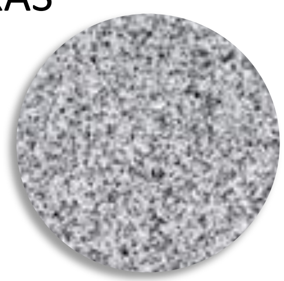
Chemical distribution of TM at particle level – cycled

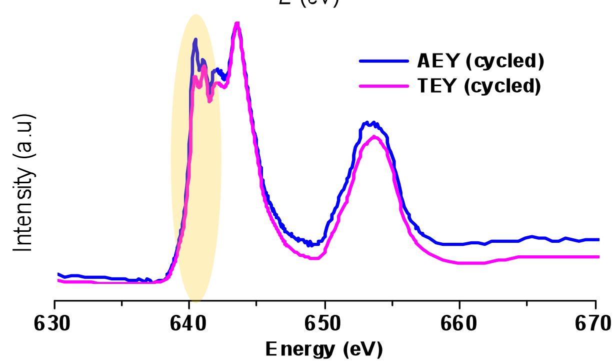






Soft XAS



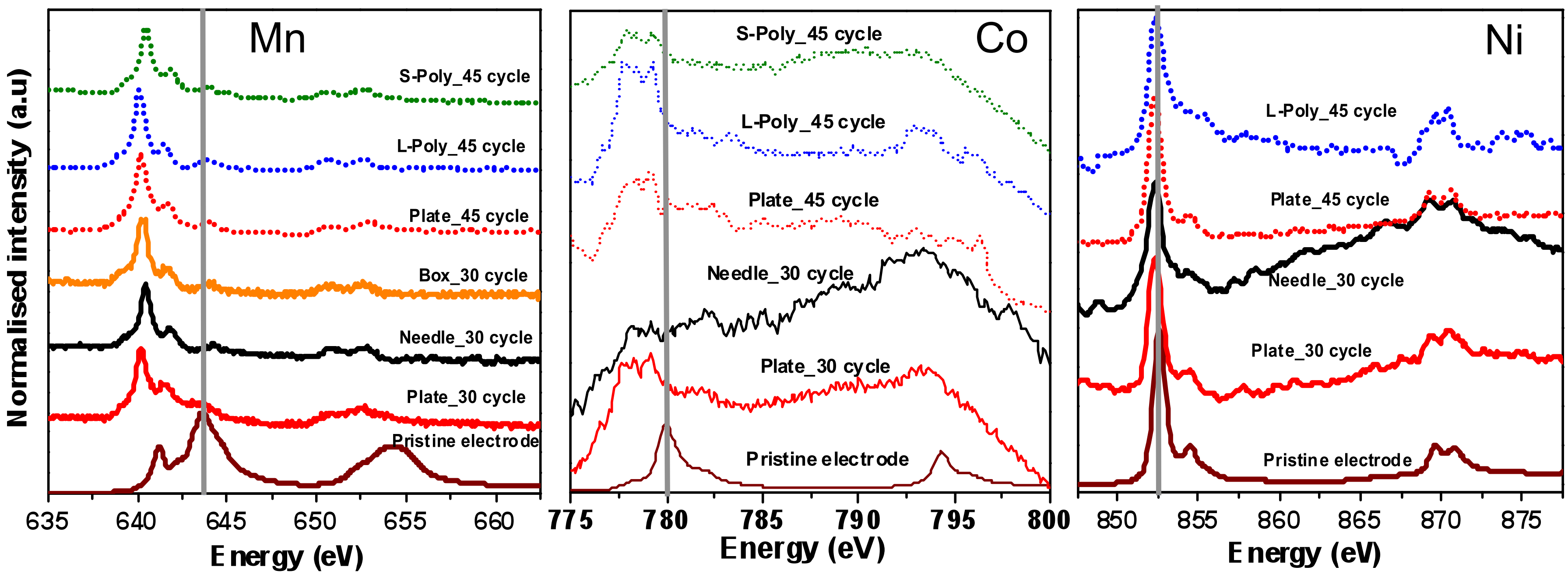


- Some Mn and Co reduction on particle surface but significantly less than the large amount detected by XAS on the electrodes.
- Are the reduced Mn and Co observed on cycled electrodes structural to the crystal or surface deposits resulting from the TM dissolution/migration/precipitation process?

Cycling-induced TM dissolution/migration/precipitation

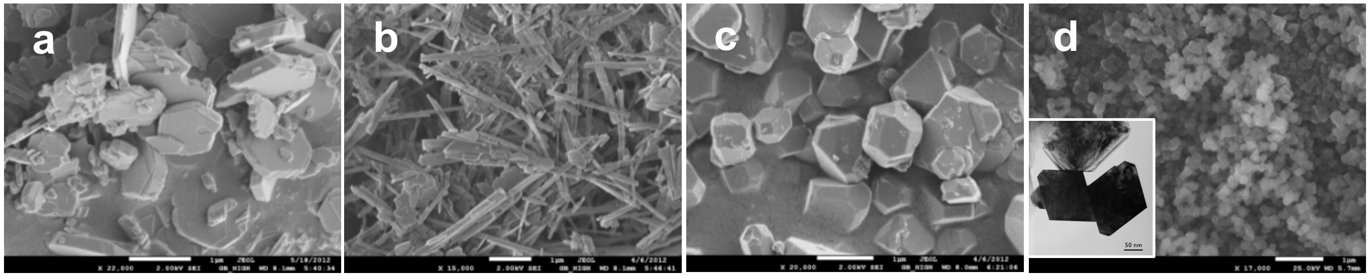
Separators recovered from the cycled half cells:

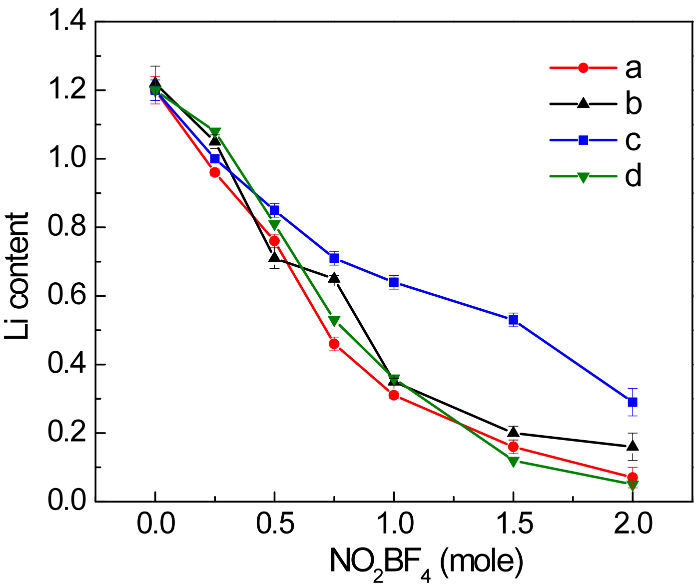
- The side facing lithium covered with black deposits which increase with cycling.
- Soft XAS (*L* edge, TEY mode) shows presence of Mn, Co and Ni on the separator, all at 2+ oxidation state.

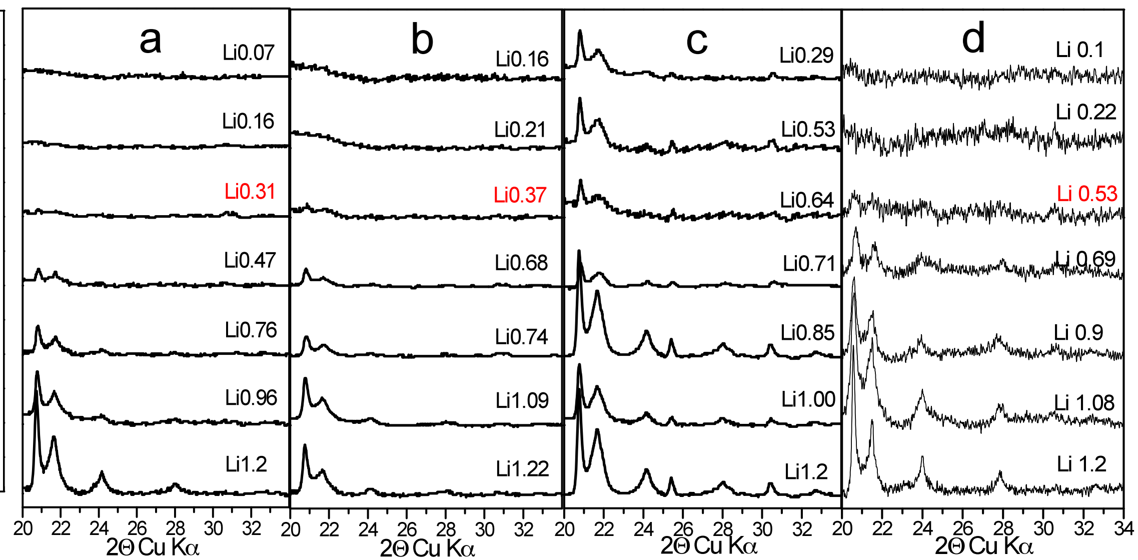


- Surface properties of pristine oxide, both morphology and initial spinel content, affect TM dissolution.

Surface properties impact first-cycle activation kinetics

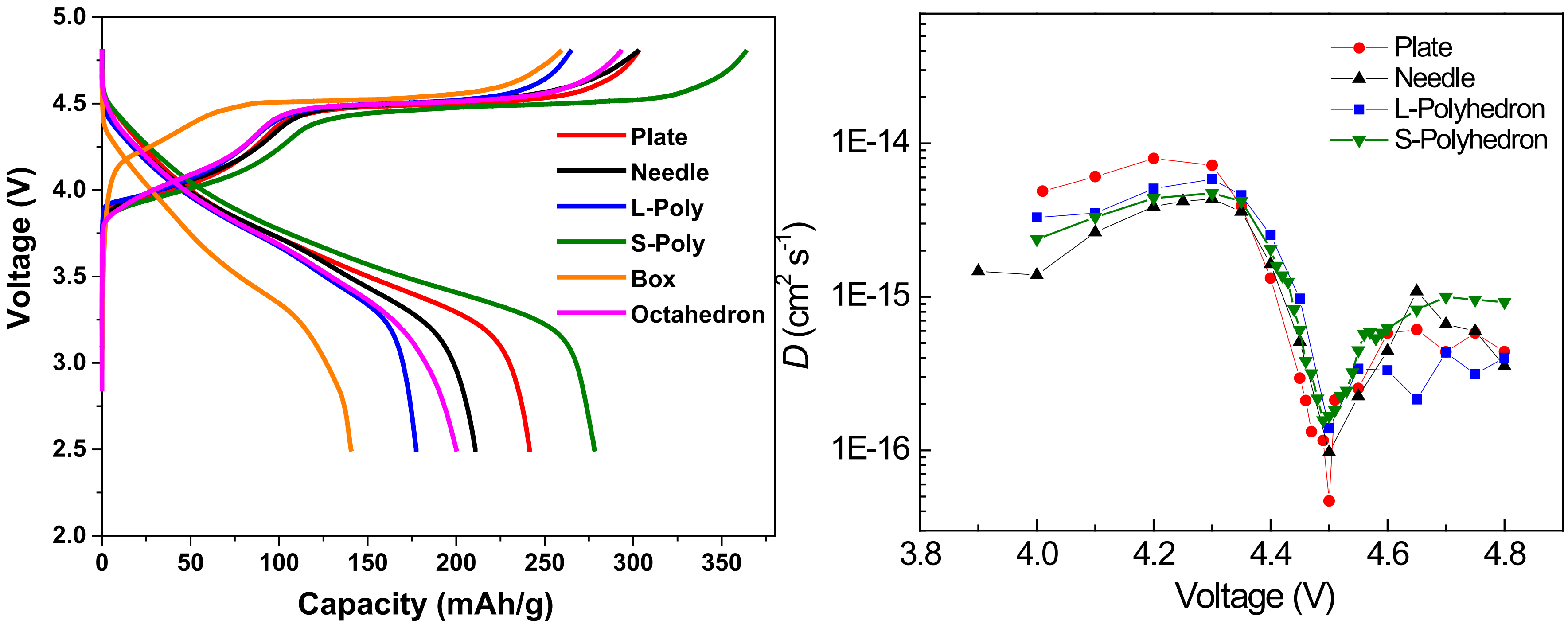






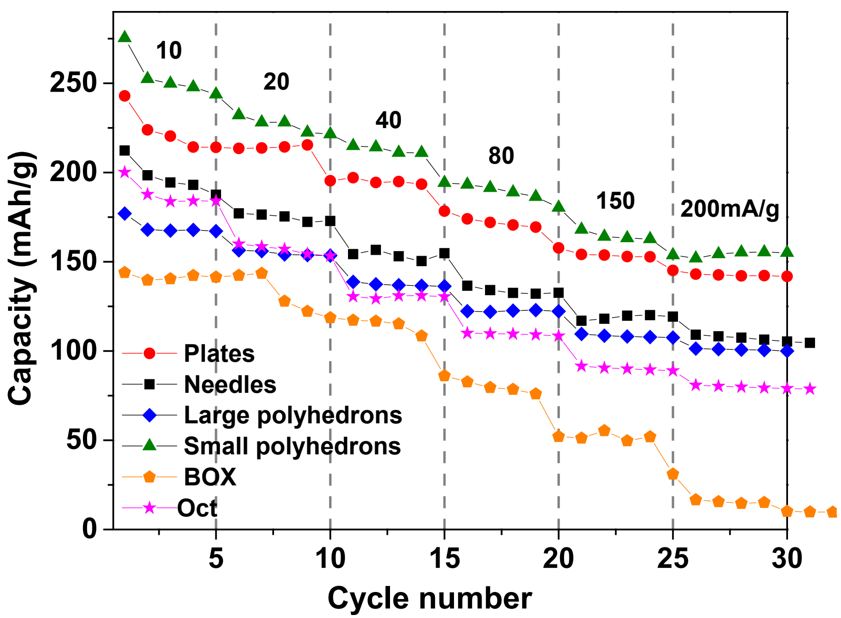
- Both size and surface facet have major impact on structural evolution and first-cycle activation kinetics during chemical delithiation with NO_2BF_4/CH_3CN.
- Size critical for kinetics – best performance on S-Poly sample with the smallest particles.

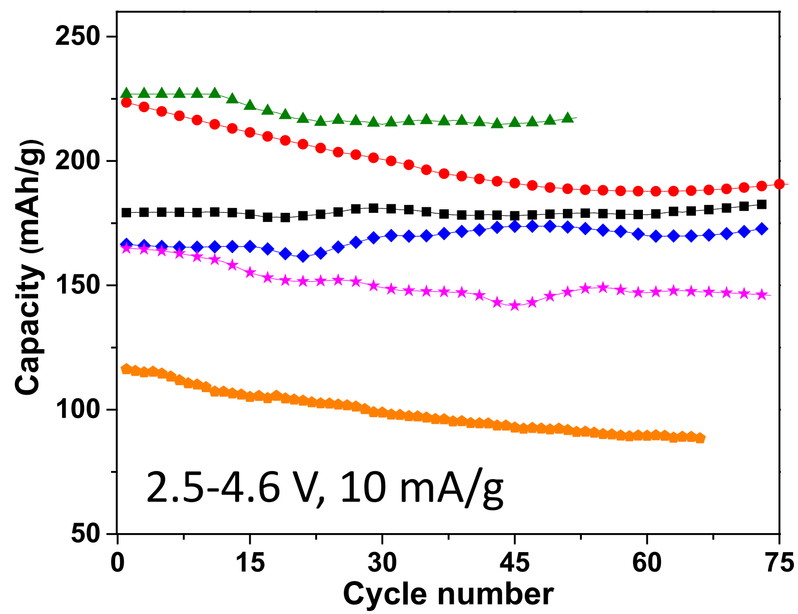
Surface properties impact first-cycle activation kinetics

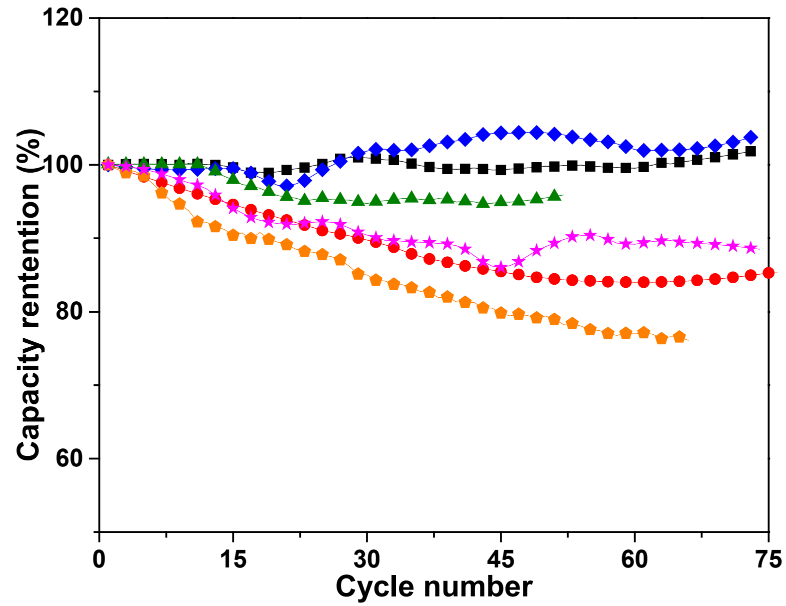


- Effect of particle size – best activation kinetics observed on S-Poly sample.
- Effect of surface facet – among large crystals, Plate easiest while Box most difficult to activate upon electrochemical charging.
- Diffusion coefficient nearly two orders magnitude smaller at the activation plateau.

Surface impact rate capability and capacity retention

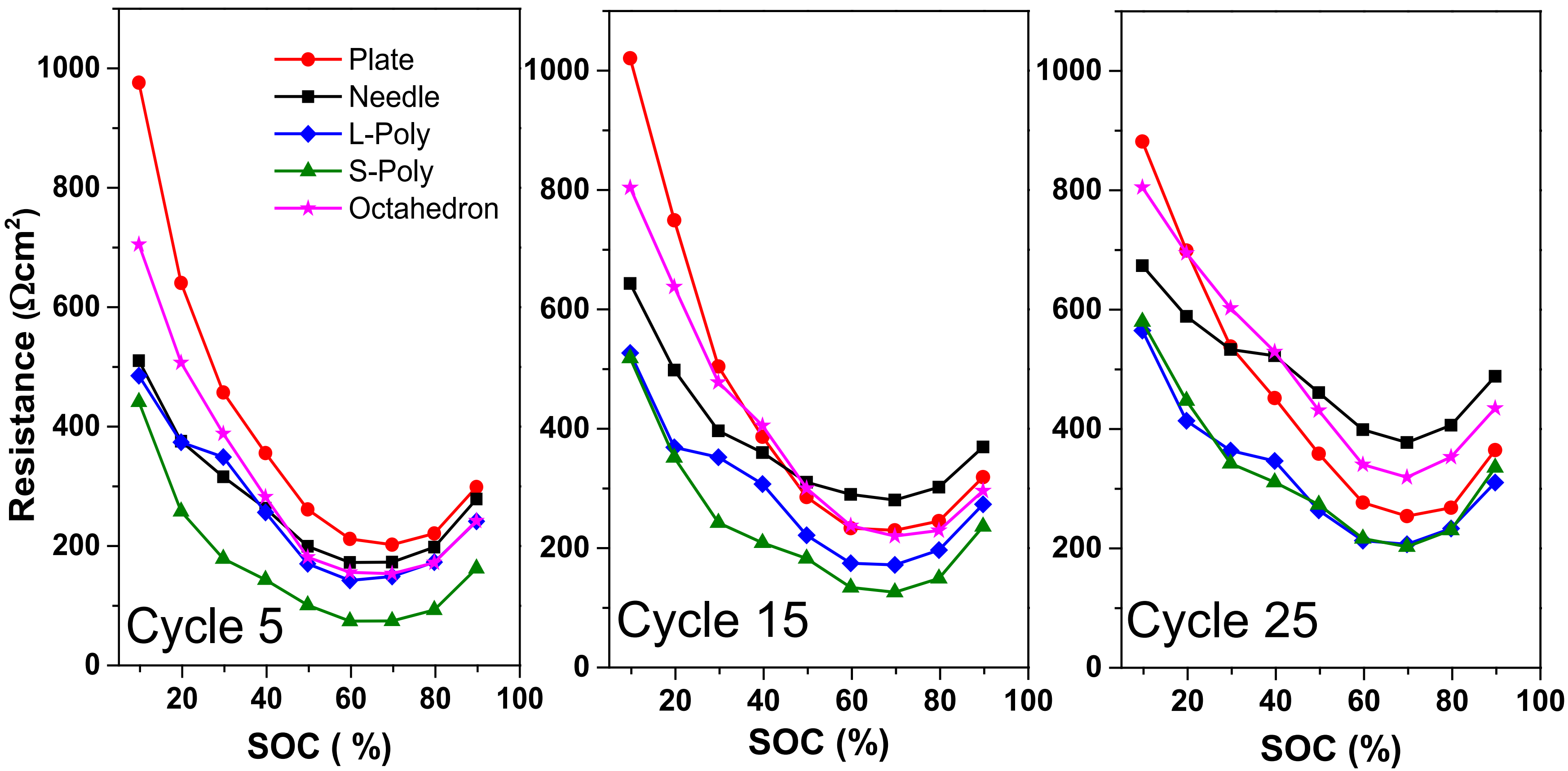






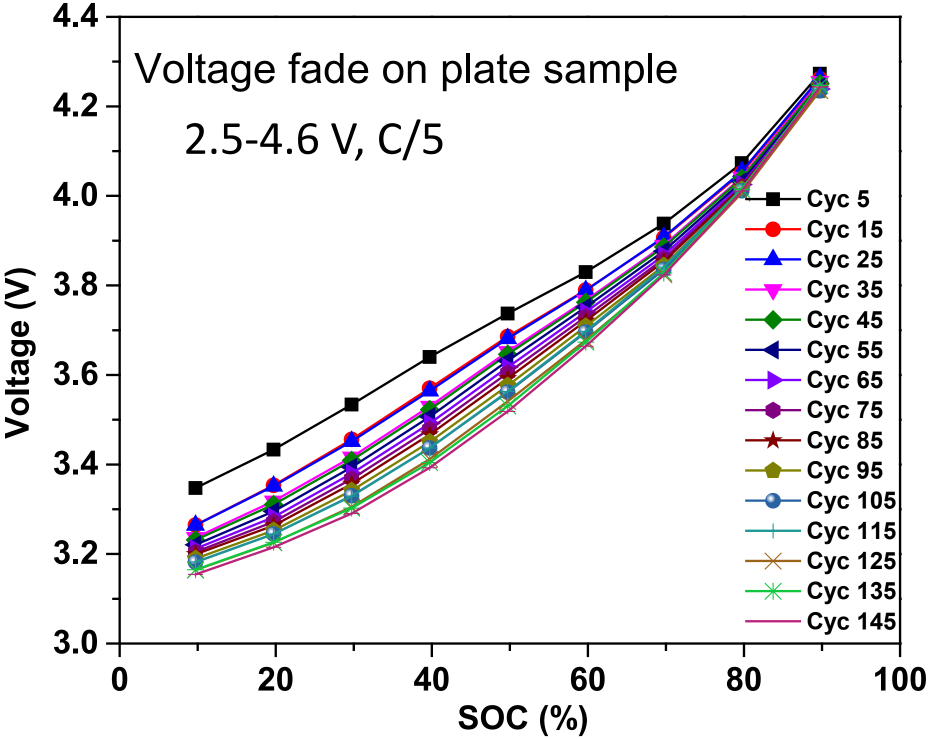
- Effect of particle size – best rate capability and most capacity from the S-Poly sample.
- Effect of surface facet – Plate best while Box worst among large-sized samples.
- Worst capacity retention on Box sample with the most TM reduction during cycling.

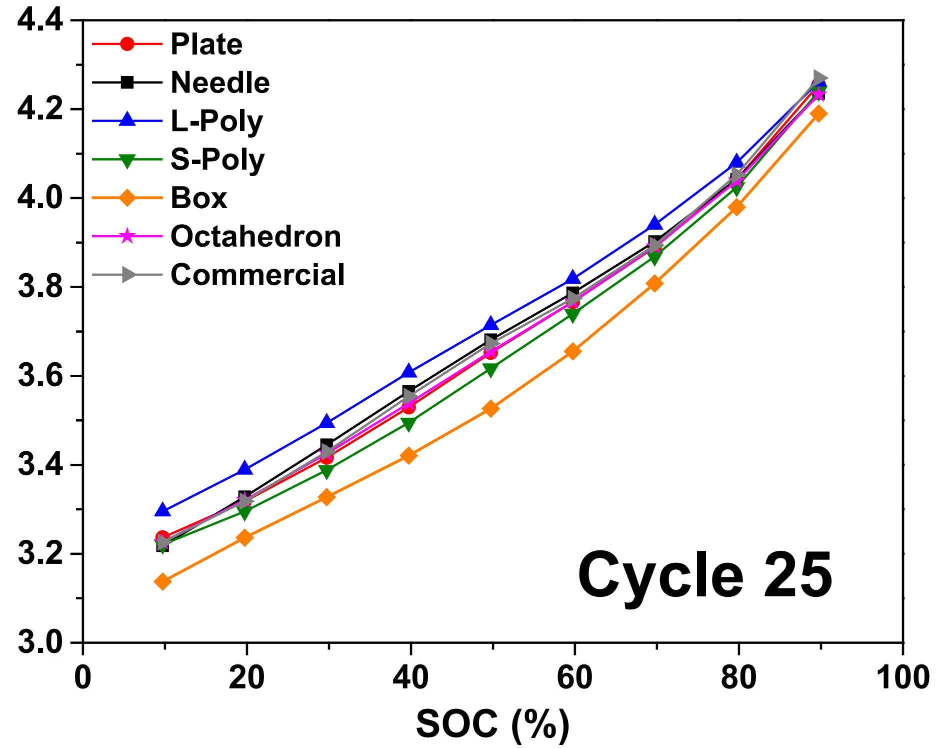
Surface impact on DC resistance rise



- DC resistance rise at low SOC (<50%) reduces usable energy of the material.
- DC resistance rise occurs on all our samples.
- Effect of particle size – much improved on S-Poly sample with smaller particles.

Surface impact on voltage fade

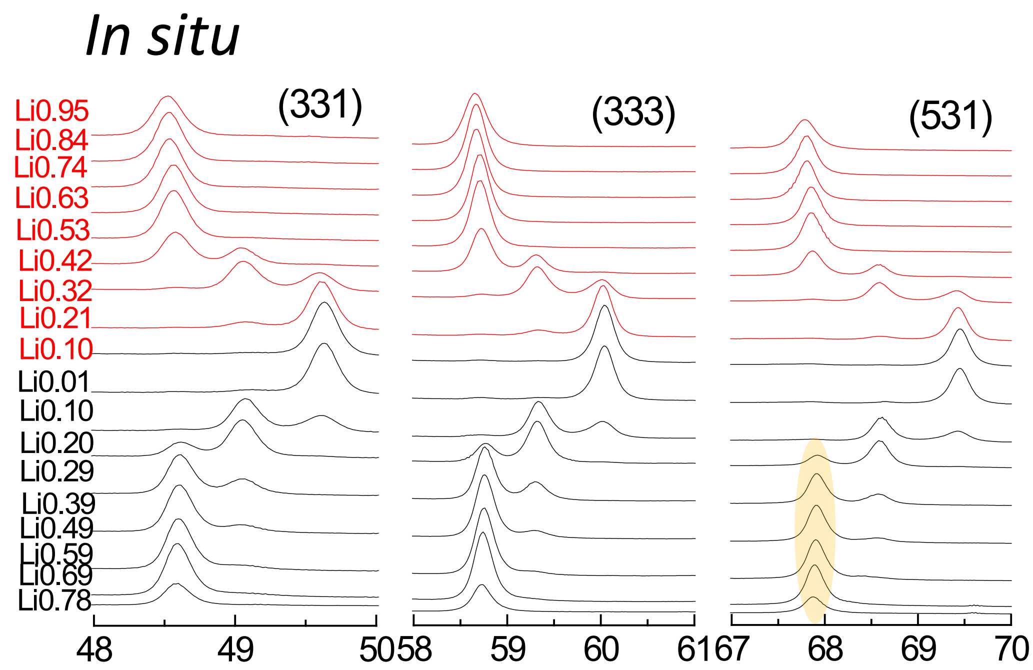


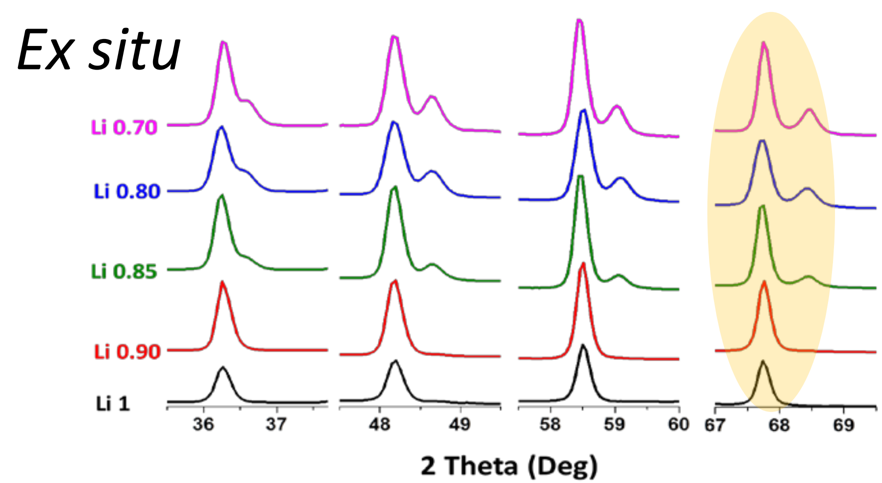


- Voltage fade occurs on all our samples.
- Voltage fade is associated with TM reduction during the cycling – Box sample has the most voltage fade while L-Poly has the least.

Phase boundaries and kinetic behavior in materials with first-order phase transition

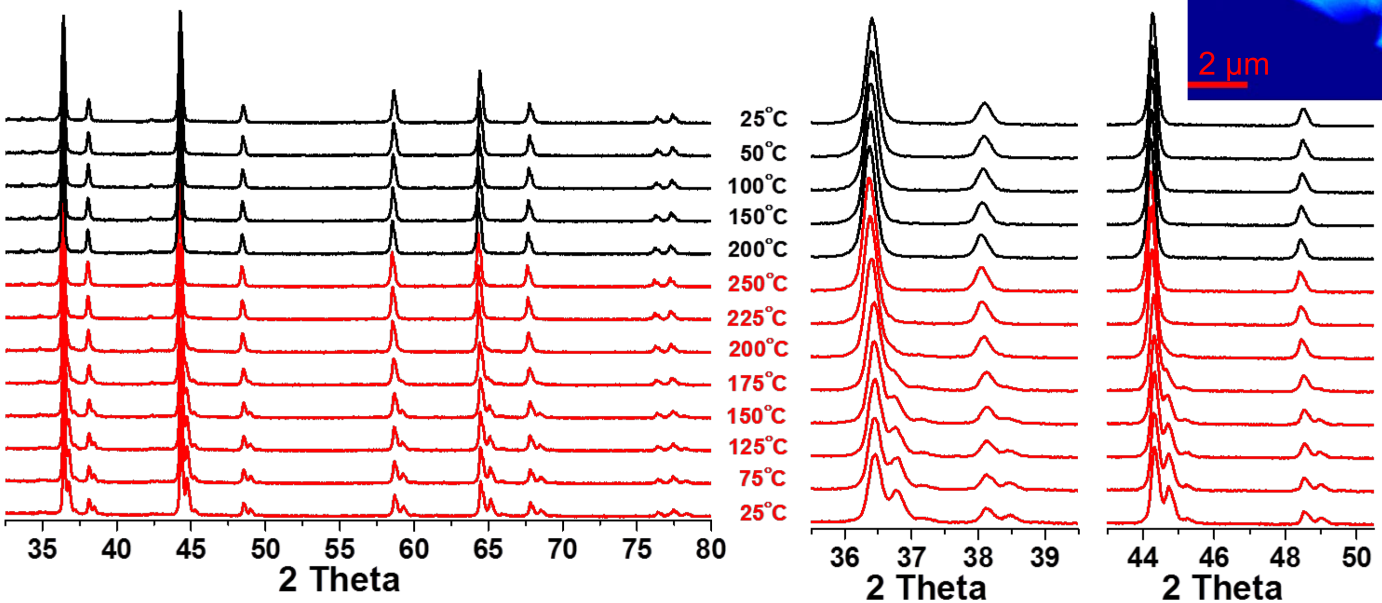
- Conventional wisdom says the access to solid-solution reaction pathways increases rate capability and cyclability.
- Is there correlation between kinetics and the extent of solid solution transformation in two-phase systems? Kinetics as a function of solid solution transformation?
- But solid solutions are metastable and difficult to isolate for their physical and kinetic properties evaluation.

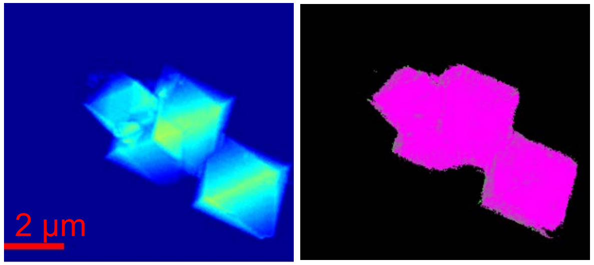




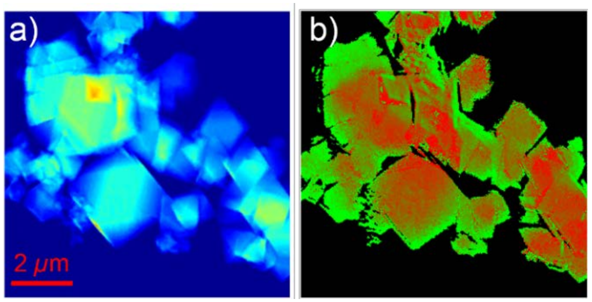
Synthesis/isolation and characterization of solid solutions

TXM, BL 6.0.3 (SSRL) with Jordi Cabana (UIC)





- The cubic phases merge into a single solid-solution phase at elevated temperatures which remains phase pure upon cooling to RT.
- Thermal behavior is Li content dependent.
- Particle level distribution of phases monitored.
- Physical properties of solid solution similar to the pristine.



Collaborations

- Drs. Marca Doeff and Phil Ross (LBNL), Drs. Ethan Crumlin and Tolek Tyliszczak (ALS), Drs. Apurva Mehta and Yijin Liu (SSRL) – synchrotron *in situ* and *ex situ* XRD, XAS, XPS, STXM and TXM studies
- Dr. Robert Kostecki (LBNL) – Raman and FTIR characterization of electrode materials
- Prof. Clare Grey (Cambridge) – NMR studies
- Prof. Bryan McCloskey (UC Berkeley) – gassing under high-voltage operation of cathodes
- Prof. Jordi Cabana (UIC) – synchrotron TXM studies
- Prof. Shirley Meng (UCSD) – synchrotron coherent X-ray diffractive imaging (APS)
- Dr. Ashfia Huq (ORNL) – neutron diffraction
- Dr. Chongmin Wang (PNNL) – TEM
- Dr. Arun Devaraj (PNNL) – atom probe tomography
- Dr. Jagit Nanda (ORNL) – new cathode material synthesis and characterization

Future Work

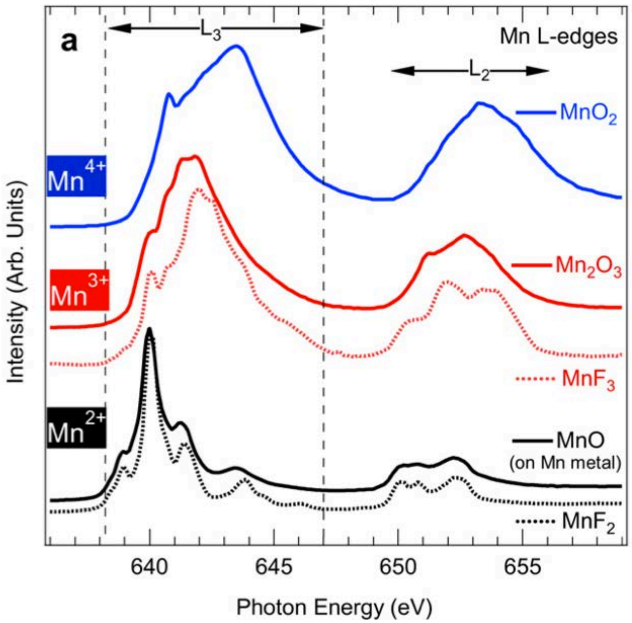
- Further investigate the impact of synthesis, particle morphology, native and artificial surface modification on the rate performance, cycling and thermal stabilities of Li-TM-oxides.
- Determine Li concentration and cycling dependent transition-metal movement in (through structural rearrangement process) and out of (through TM dissolution process) the oxide particles and examine the mechanisms.
- Investigate interfacial chemistry between high voltage cathode and electrolyte. Determining the dynamic structural and chemical changes at the interface.
- Identify key surface properties and features hindering stable cycling of Li-TM-oxides at high voltages.
- Explore other aspects of particle engineering to improve cathode performance and stability.

Summary

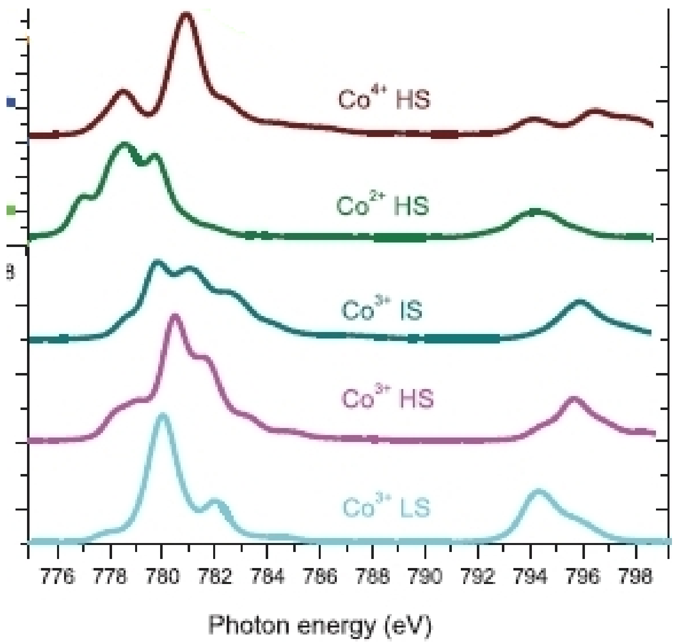
- Thin layer of defective spinel with reduced TM exists on the surface of pristine LMR-NMC. The amount of spinel formation is largely controlled by particle morphology (surface facet and surface area).
- Both morphology and surface spinel on pristine impact kinetics and stability, particularly:
  - Structural stability – pristine surface TM reduction and spinel formation, cycling-induced TM reduction, DC resistance changes and voltage fade
  - Kinetics – chemical delithiation, first cycle activation and rate capability
  - Reactivity – capacity retention, coulombic efficiency and TM dissolution
- TM reduction increases with cycling which progresses from the surface to bulk.
- Not all reduced TM is structural. TM dissolution/precipitation largely contributes to the reduced TM on cycled electrodes detected by surface sensitive XAS.
- RT L_xMNO solid solution phases were synthesized and characterized. The roles of phase boundaries and phase transformation in the kinetics of materials with first-order transition investigated.

Technical Back-Up Slides

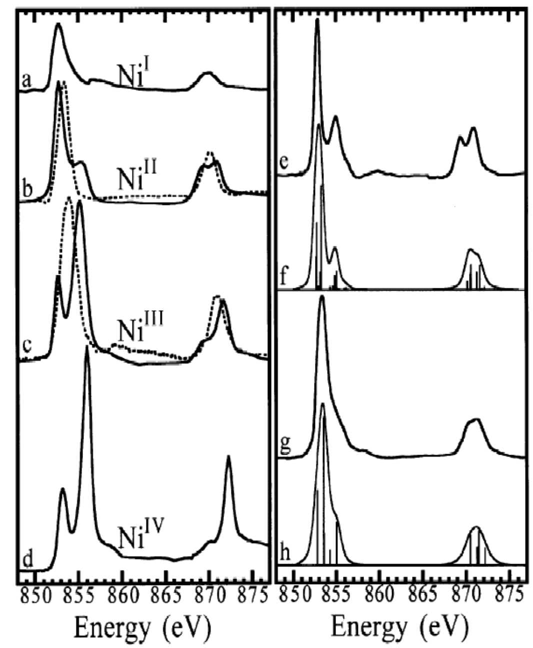
Standard soft XAS spectra for transition metals



Journal of Electron Spectroscopy and Related Phenomena 190, 64–74 (2013)

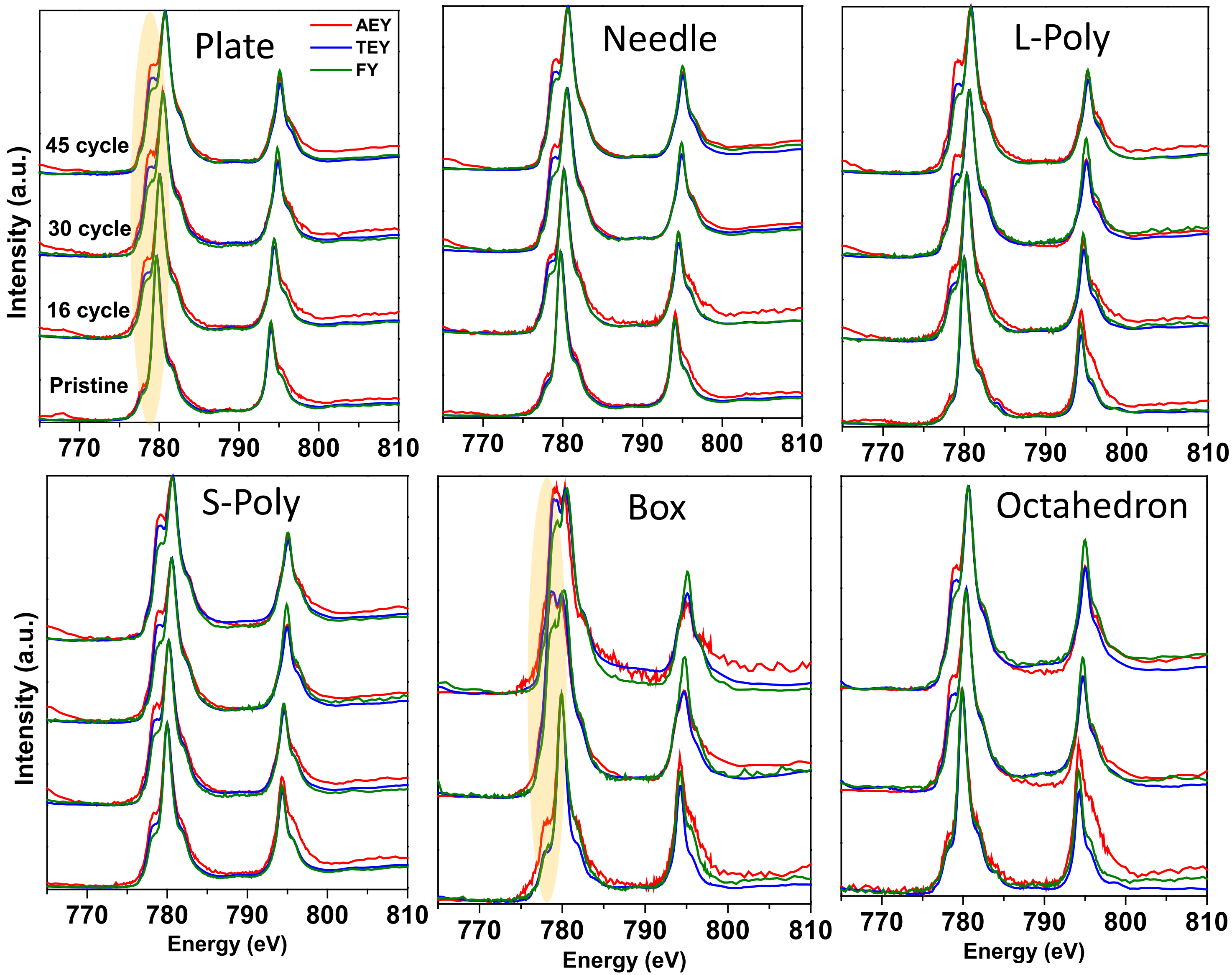


Physical Review B 84, 014436 (2011)



Journal of Electron Spectroscopy and Related Phenomena 114–116, 855–863 (2001)

Surface Co reduction increases with cycling

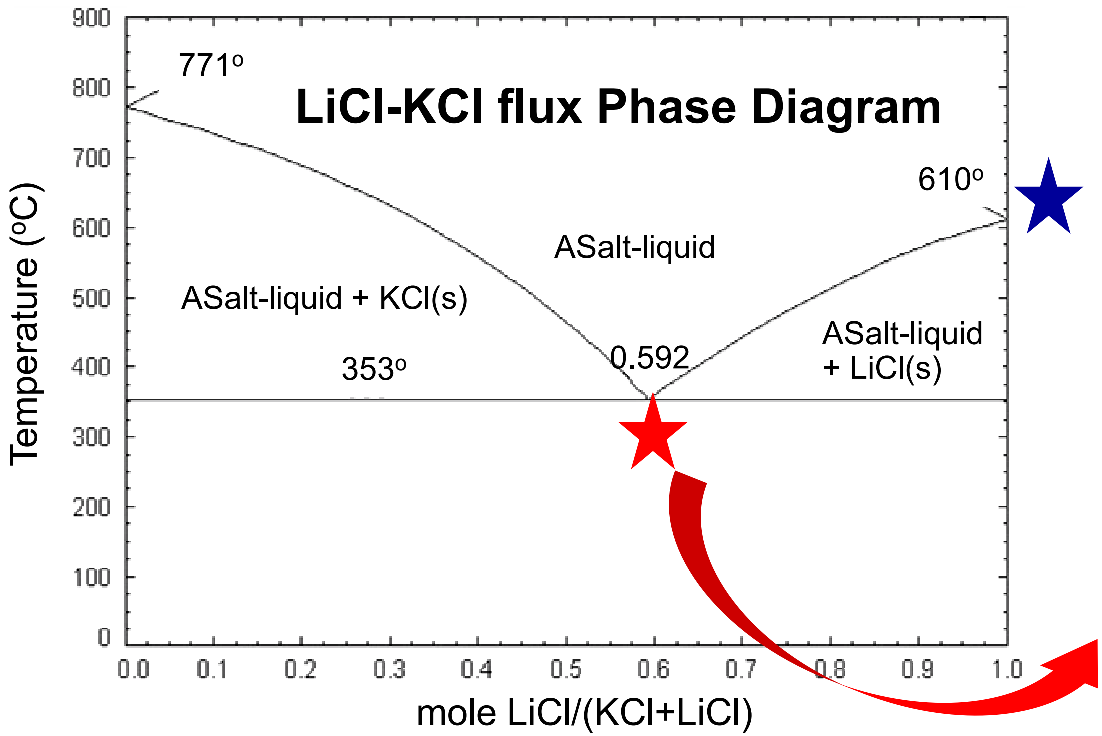


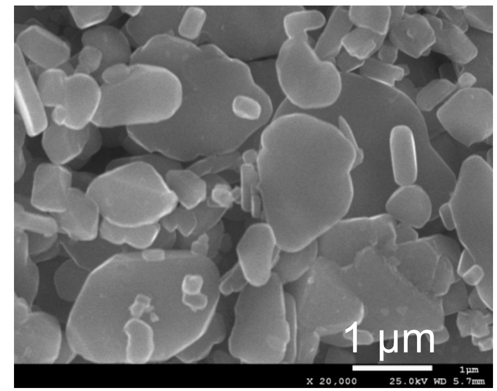
- Co *L*-edge XAS spectra show the formation of Co^{2+} increases with cycling.

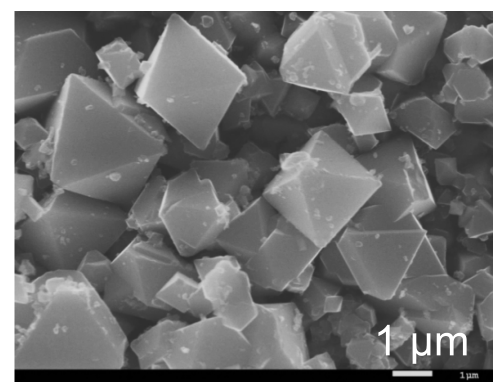
Property-controlled crystal synthesis

- We utilize high-temperature and low-temperature solution based synthesis techniques, including solvothermal and molten-salt synthesis, to prepare high-quality crystal samples.

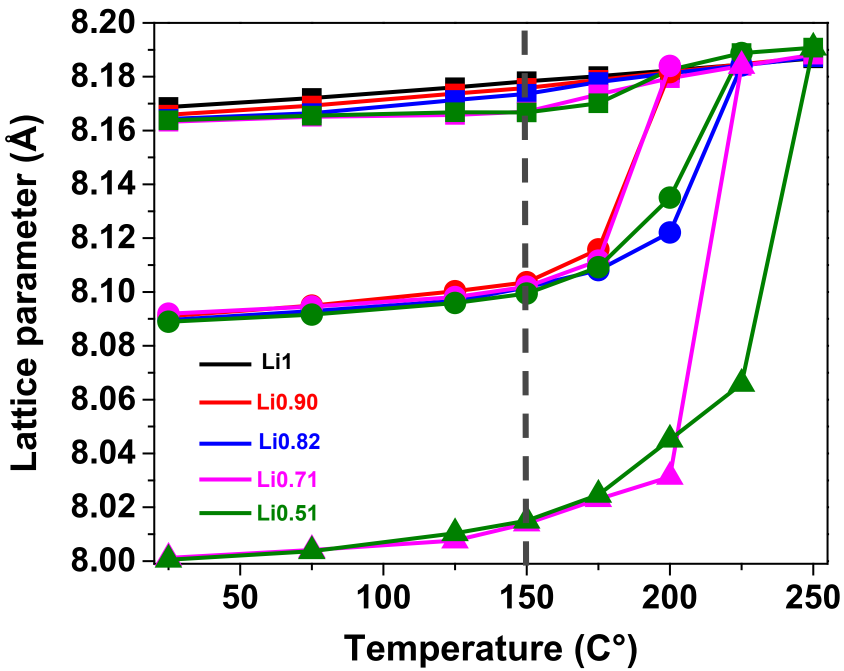
Effect of flux on $LiMn_{1.5}Ni_{0.5}O_4$ *morphology*

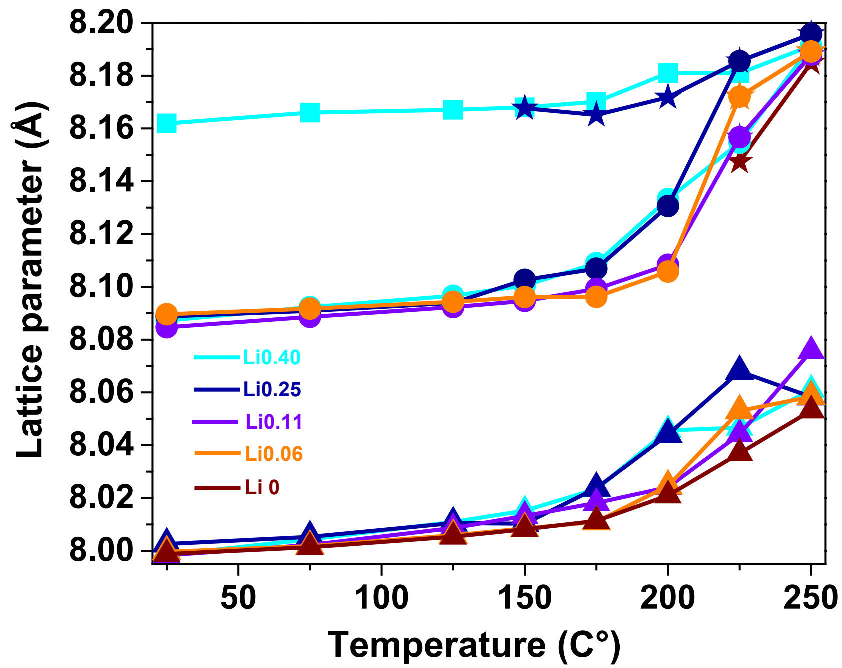


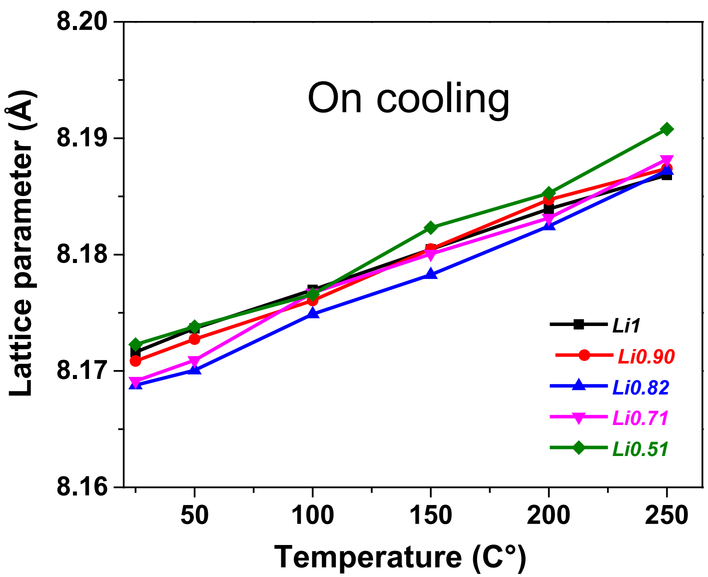




Thermal-driven Li_xMNO solid solution formation







- Formation of $Li_xMn_{1.5}Ni_{0.5}O_4$ (Li_xMNO) solid solutions initiated around 150 ^oC and completed around 250-265^oC.
- Cooling of solid solution phases follow thermal expansion behavior with no phase separation.
- Thermal behavior is Li content dependent.

Li_xMNO phase diagram on heating