

# Design and Synthesis of Advanced High-Energy Cathode Materials

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Lawrence Berkeley National Laboratory

June 9, 2016

Project ID: ES225

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# Overview

## Timeline

- Start date: October, 2012
- End date: September, 2016
- Percent complete: 90%

## Budget

- Total project funding
  - FY2014        \$500K
  - FY2015        \$500K

## Barriers Addressed

- Energy density
- Cycle life
- Safety

## Partners

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

# Relevance/Objectives

- 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.

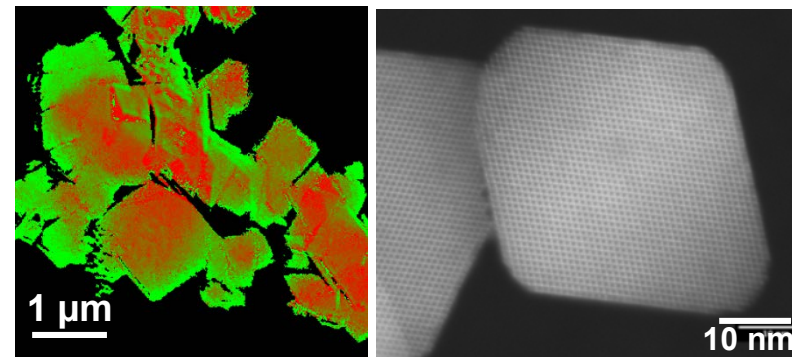
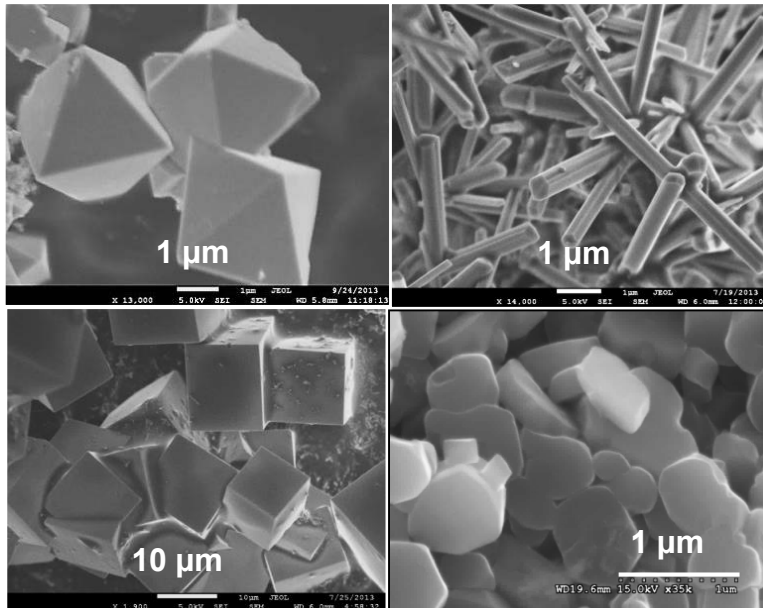
# Milestones

Date	Milestones and Go/No-Go Decision	Status
December 2015	<u>Milestone</u> Establish synthesis-structure-electrochemical property relationship in high-voltage Li-TM-oxides.	Completed
March 2016	<u>Go/No-Go Decision</u> Downselect alternative high-energy cathode materials for further investigation, if the material delivers > 200mAh/g capacity in the voltage window of 2-4.5 V.	Completed
June 2016	<u>Milestone</u> Determine Li concentration and cycling dependent transition-metal movement in and out of oxide particles. Examine the mechanism.	On schedule
September 2016	<u>Milestone</u> Identify key surface properties and features hindering stable high-voltage cycling of Li-TM-oxides.	On schedule

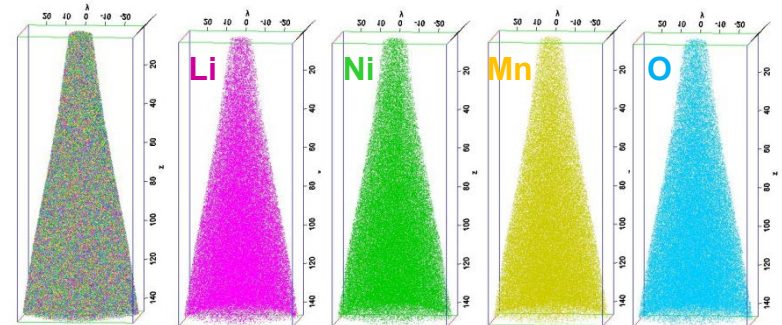
# Approach/Strategy

- 1) Remove the complexity in active particles – synthesize crystal model systems with defined properties for well-controlled studies of solid state chemistry, kinetic barriers and instabilities in high-energy cathode materials.
- 2) Perform advanced *ex situ* and *in situ* diagnostic studies at both particle and electrode levels for insights. Establish direct correlations between physical properties, performance, and stability.

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

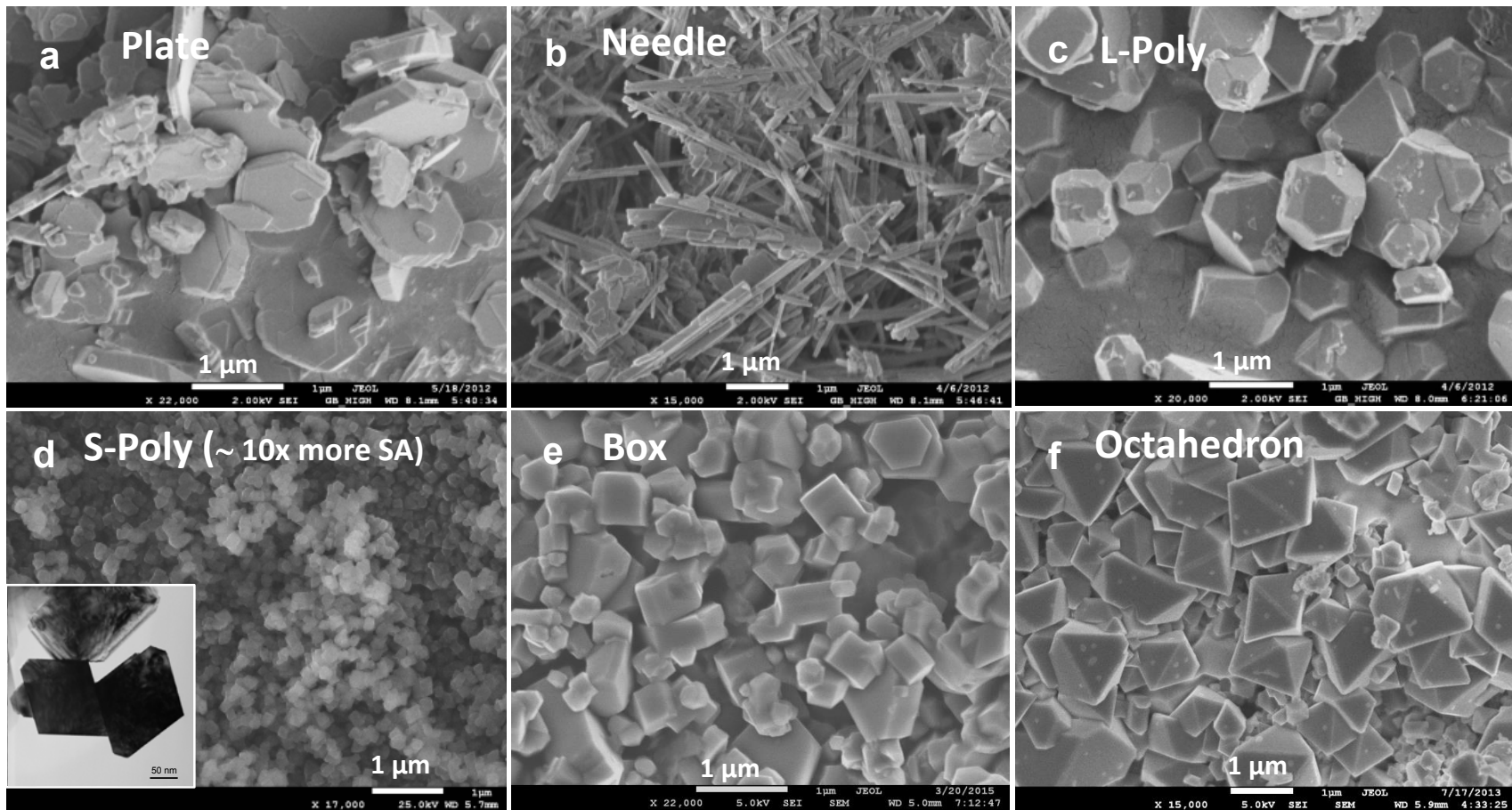


3D compositional mapping (APT/PNNL)



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

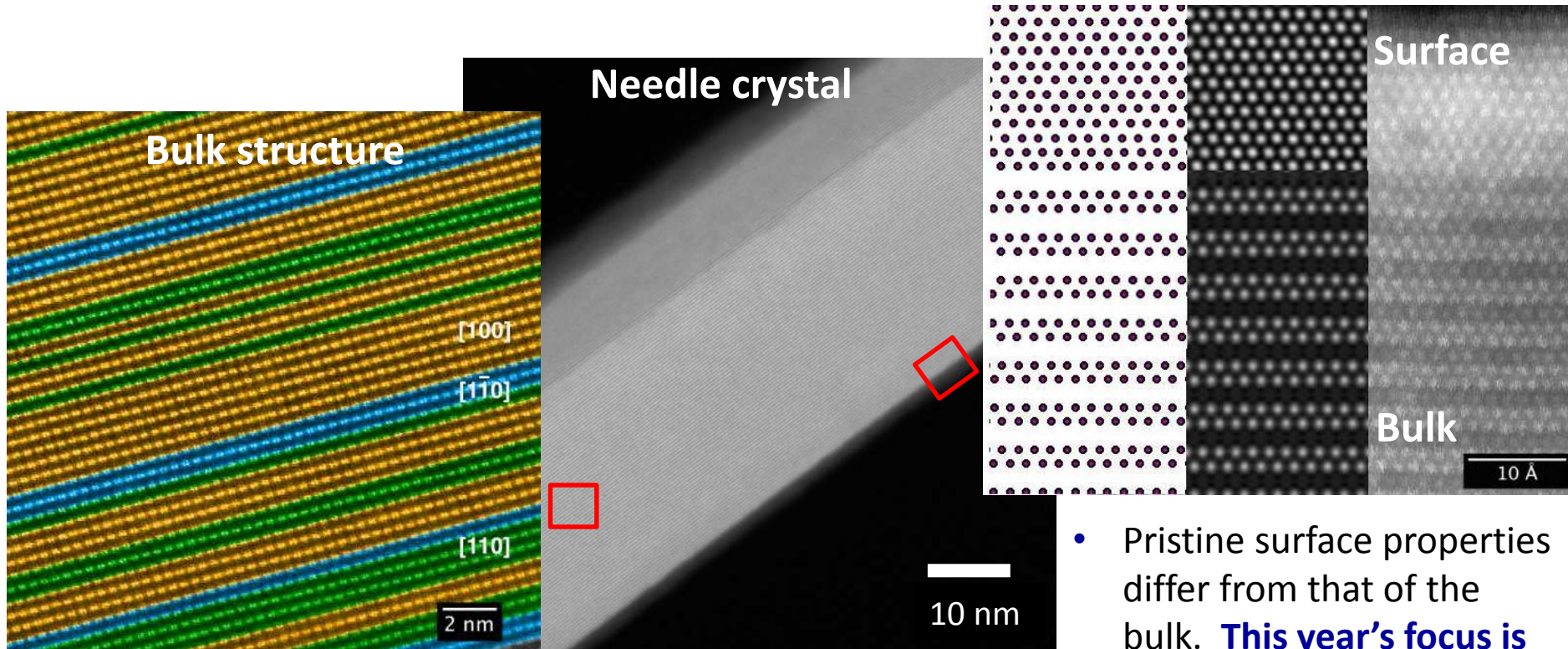
# Previous achievements



- Li- and Mn-rich layered oxide crystals ( $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Mn}_{0.54}\text{Co}_{0.13}\text{O}_2$ , LMR-NMC141) with varied surface terminations and surface areas synthesized.



# Previous achievements



- Bulk – a single phase with domains of three monoclinic variants in random distribution. Critical new insights on the design and synthesis of advanced LMR-NMC cathode materials.

- Comprehensive studies on entire particles made possible by using our well-formed crystal samples.

- Pristine surface properties differ from that of the bulk. **This year's focus is therefore to define these surface/bulk heterogeneities and determine their role in cathode performance and stability.**

# Recent technical accomplishments: overview

I. Revealed facet-dependent surface properties on pristine LMR-NMC particles.

- Elemental – selective Co and/or Ni enrichment on certain facets
- Chemical – selective TM reduction on certain facets
- Structural – selective defective spinel formation on certain facets

***Implication – in order to interpret cycling-induced changes using conventional, randomly orientated secondary particles, pristine samples need to be carefully characterized.***

II. Established the relationship between pristine surface chemical composition and facet reactivity; correlated the reactivity to cathode structural, cycling and thermal stabilities.

***Implication – particle engineering important! Improved stabilities on oxide particles with maximum expression of surface facets resistant to TM reduction.***

III. Investigated coating approach for surface engineering of particles with given facets.

- Coating modifies surface properties without changing particle surface termination or surface area.
- Coating leads to selective chemical modification on surface.
- Coating effect is facet-dependent.

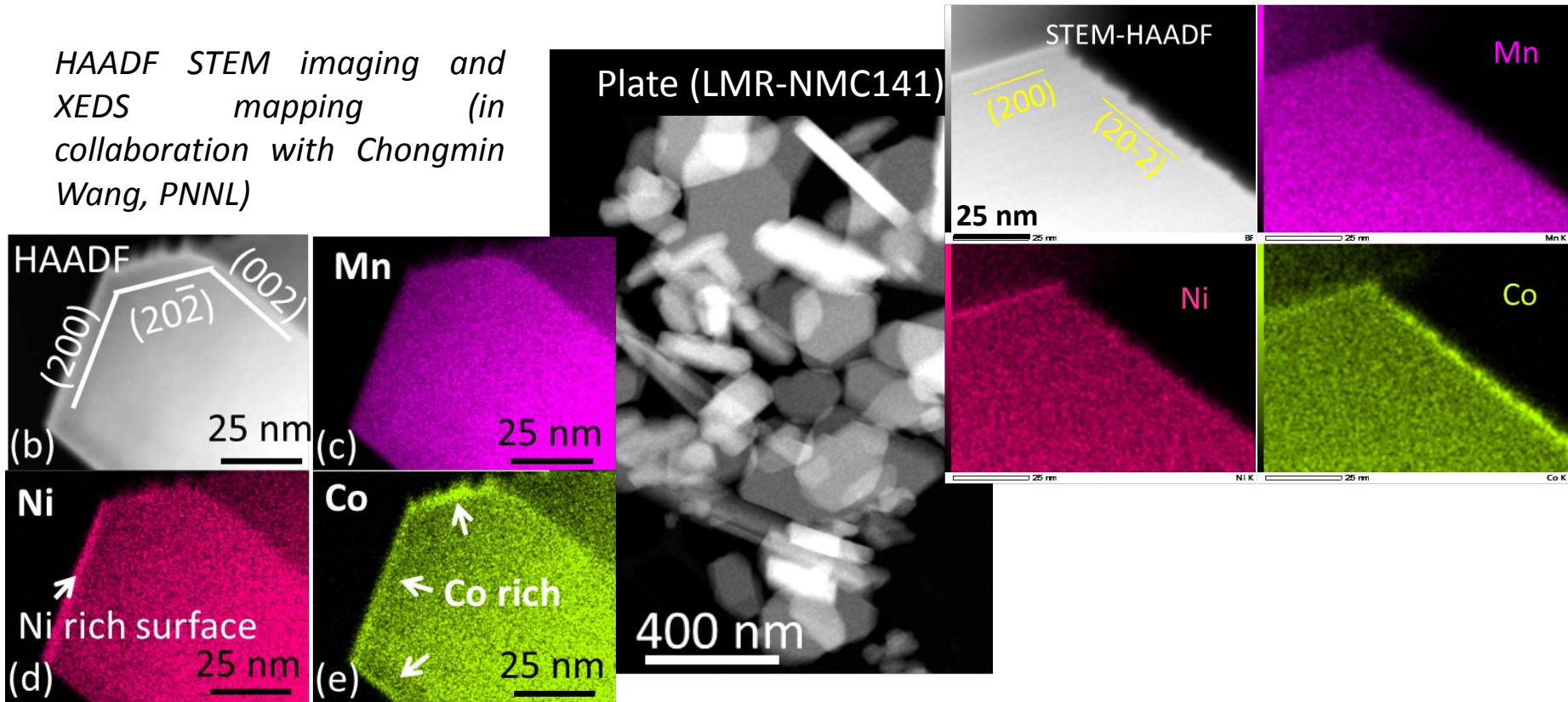
***Implication – coating investigation needs to take account of particle morphology and other surface attributes.***

IV. Visualized phase distribution and revealed the phase transformation mechanism in a first-order intercalation cathode (LMNO).



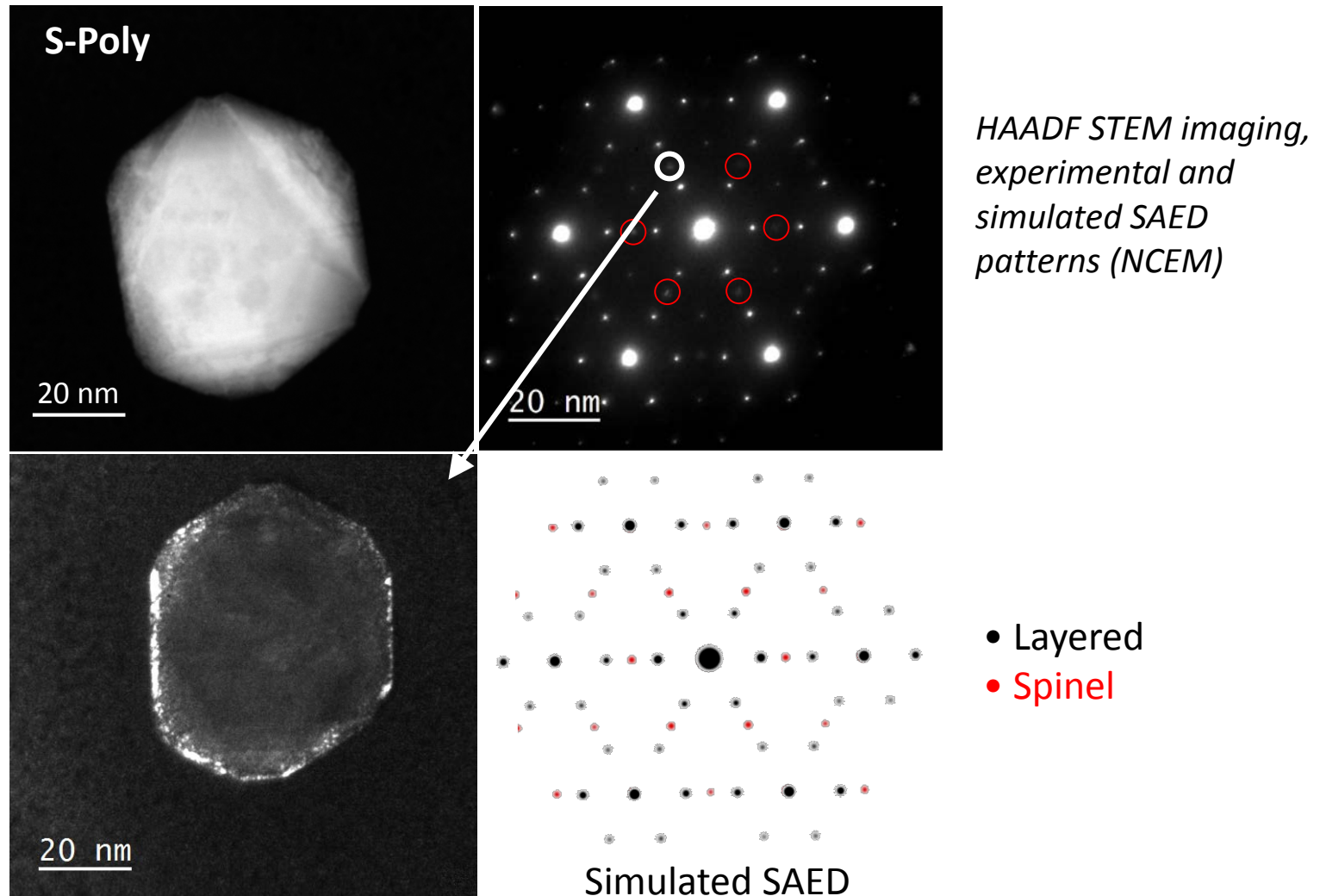
# Accomplishment I – pristine surface elemental composition depends on termination

HAADF STEM imaging and XEDS mapping (in collaboration with Chongmin Wang, PNNL)



- Selective Ni enrichment on (200) and Co enrichment on (20-2) planes.
- Roles of surface Ni and Co enrichment in structural stability and cathode performance currently under investigation.

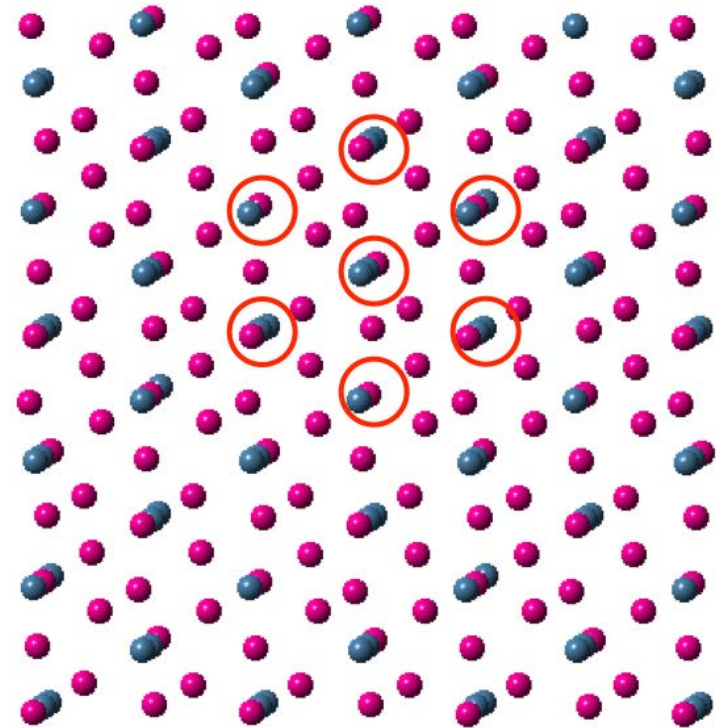
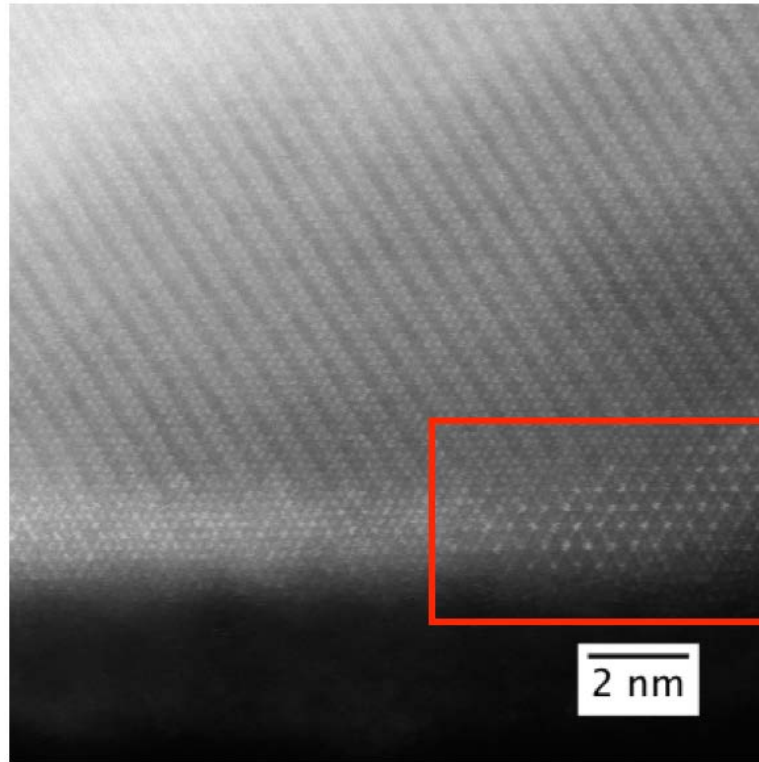
# Accomplishment I – pristine surface crystal structure depends on termination



- Selective surface facets are covered with a spinel layer.

# Accomplishment I – pristine surface layer has a defective structure

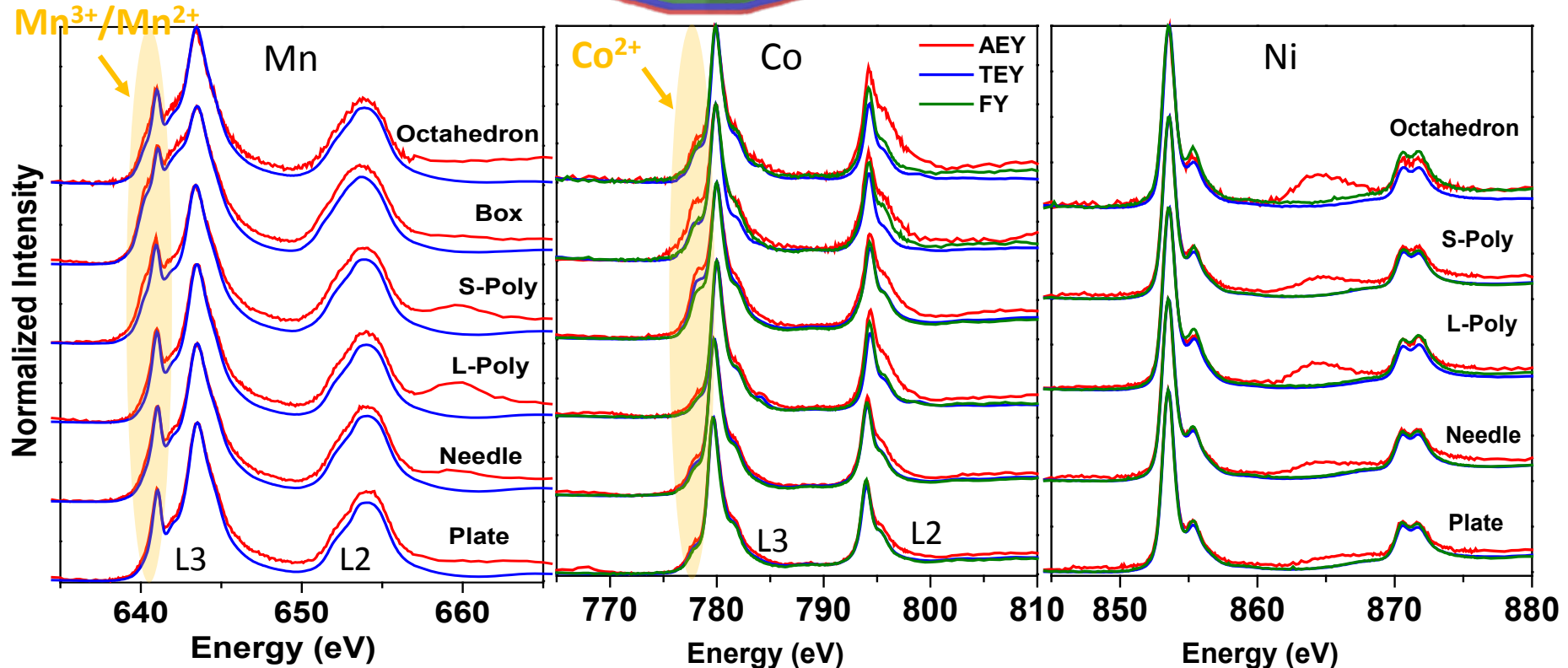
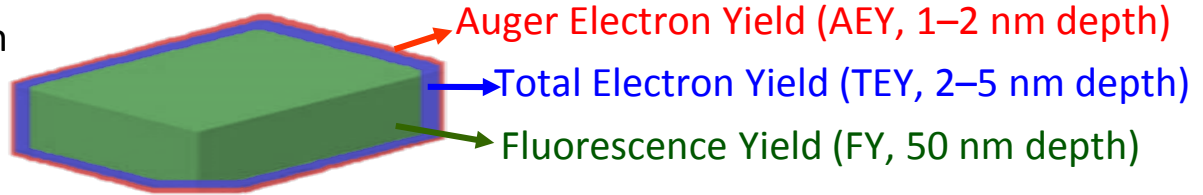
*HAADF STEM imaging and atomic simulation (Alpesh, LBNL)*



- Surface spinel has antisite defects, with columns of mixed Li and TM atoms (TM in the Li sites).
- EELS analysis shows reduced Mn and Co in the surface layer – changes in chemical composition.

# Accomplishment I – surface chemical composition depends on termination

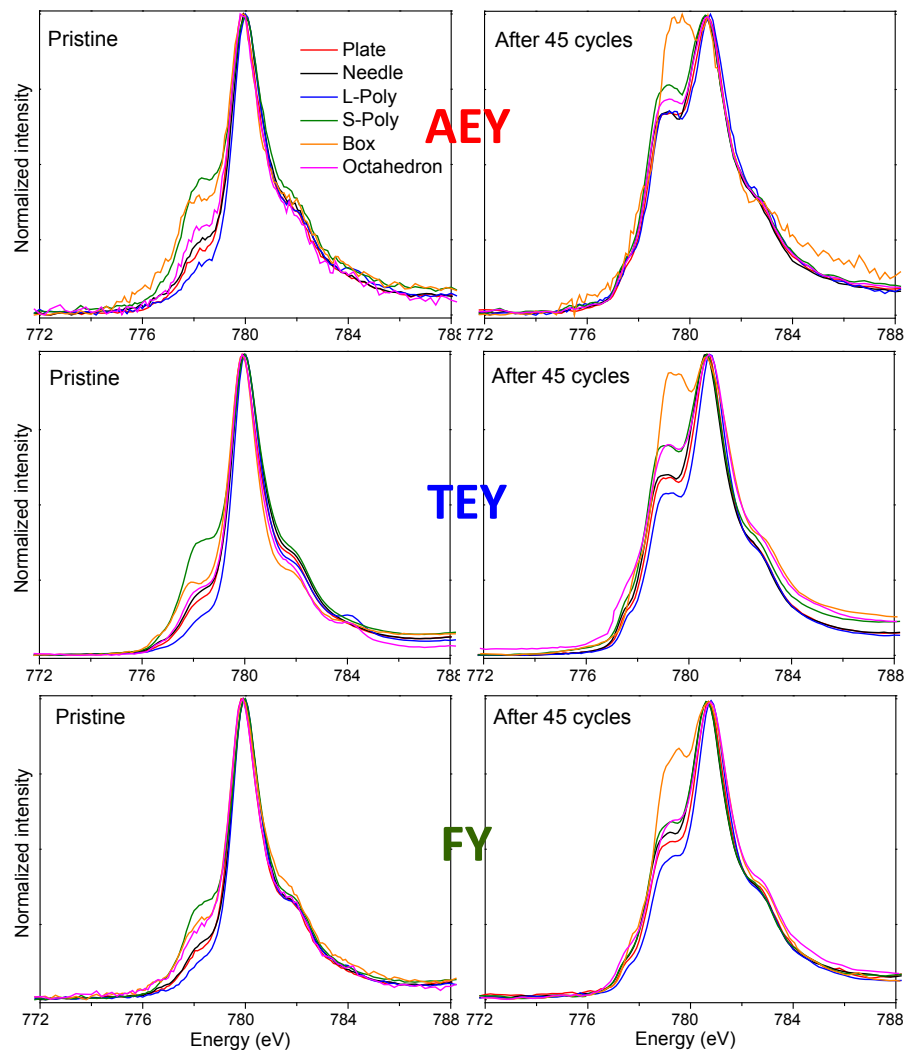
Soft XAS L edge spectra collected on composite electrodes with carbon and binder (SSRL beamline 10-1)



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

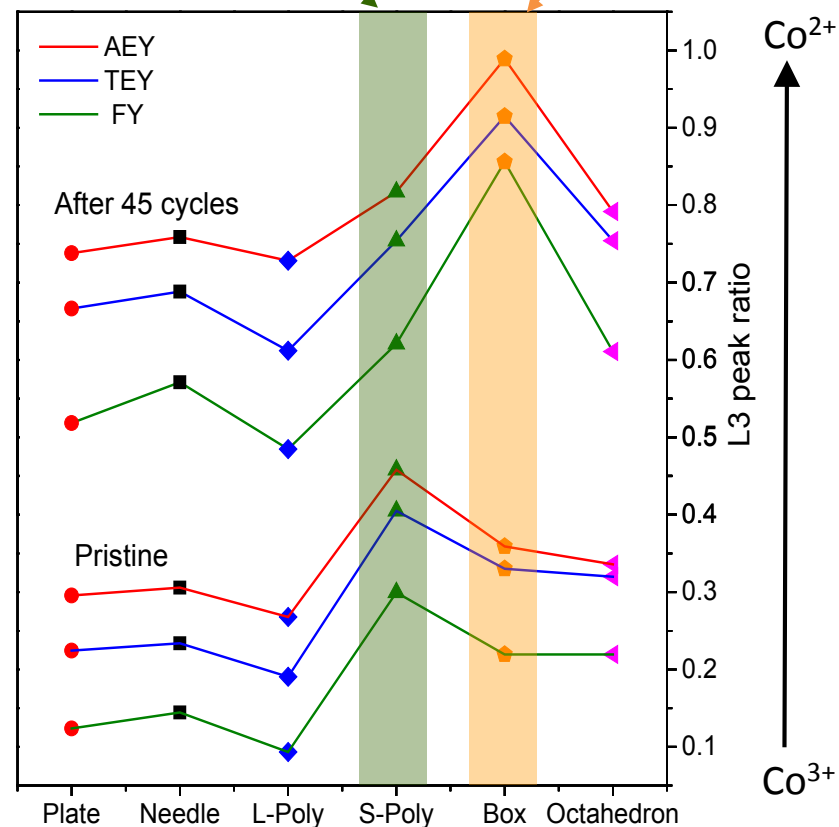


# Accomplishment II – pristine surface chemical composition indicator of facet reactivity



- Pristine surface with reduced TM does not passivate but further promotes TM reduction into the bulk upon cycling.

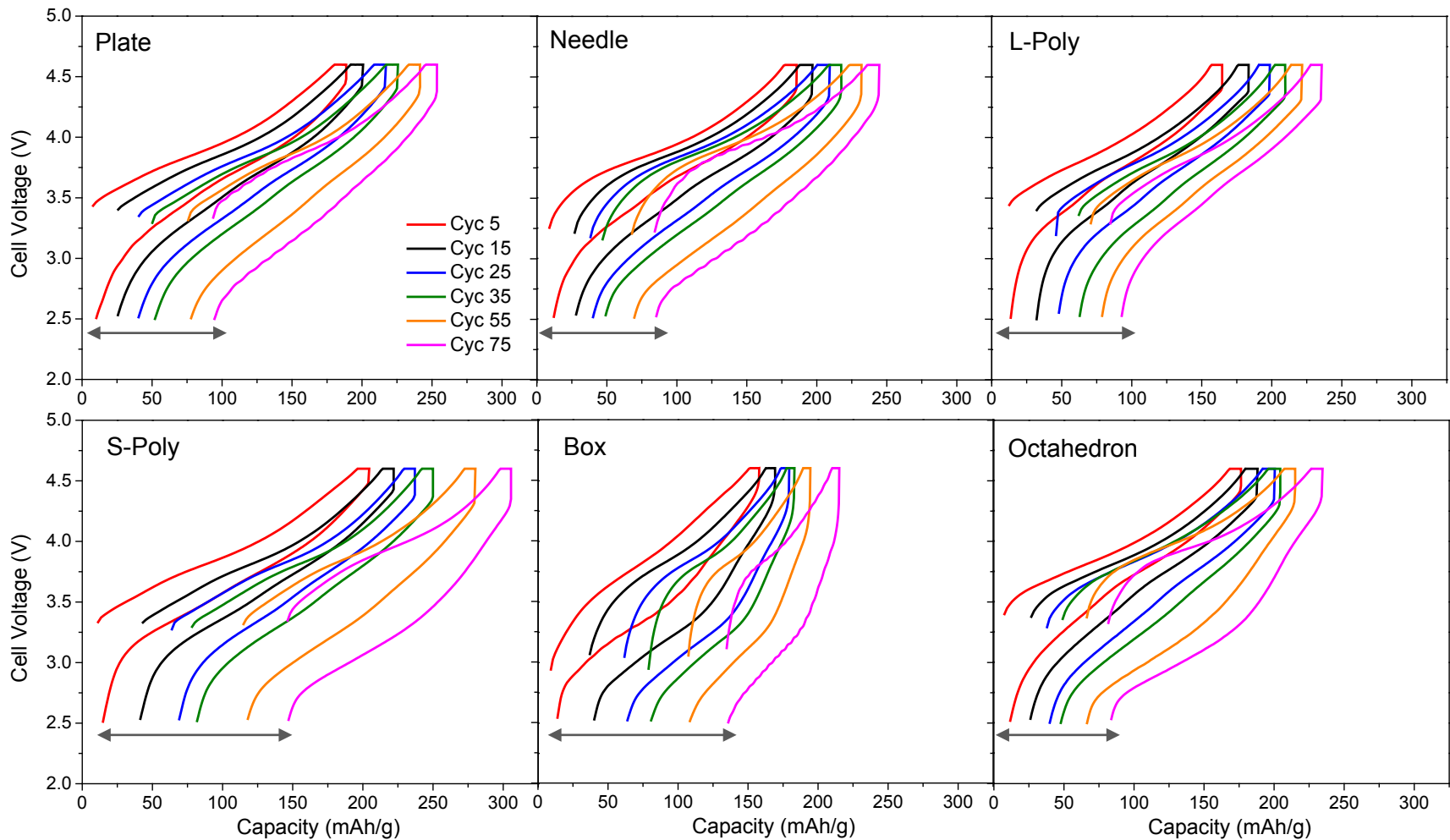
more surface area      more reactive facets



- Higher reduced TM content (normalized to area) on pristine suggests more reactive facets with stronger tendency in further TM reduction during cycling – a surface structural stability indicator.
- Facet effect more dominant than surface area.

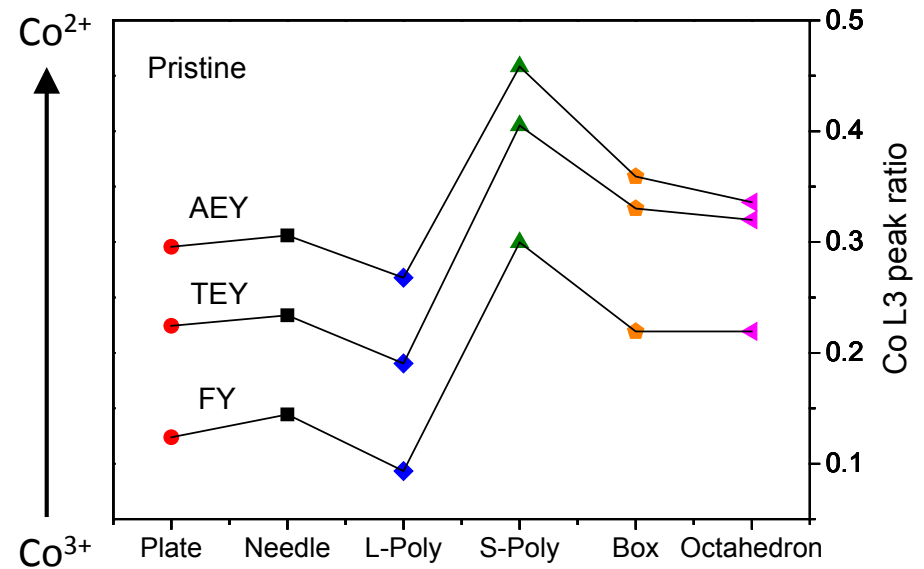
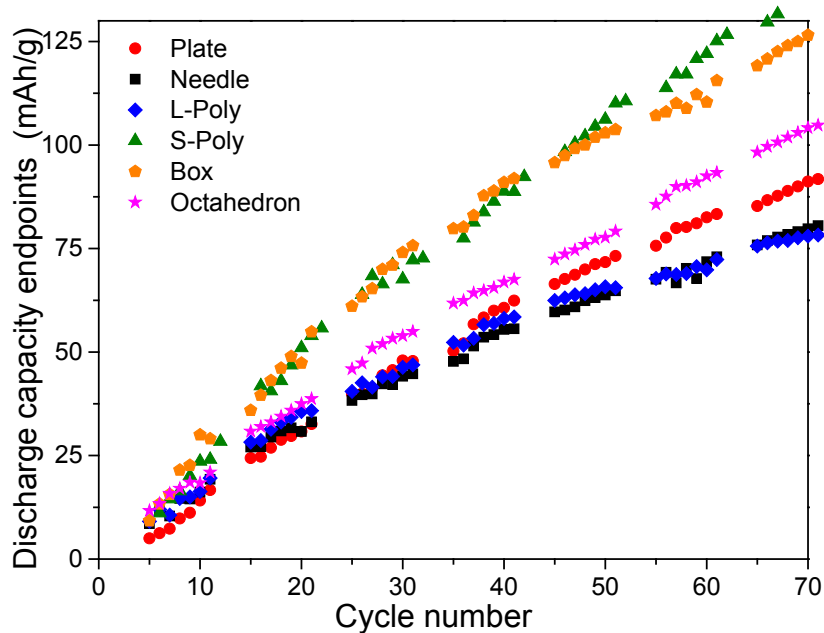


# Accomplishment II – facet reactivity and side reactions



- Effect of both surface termination and surface area – parasitic reactions most on S-Poly and box samples, shown by the highest marching rates.

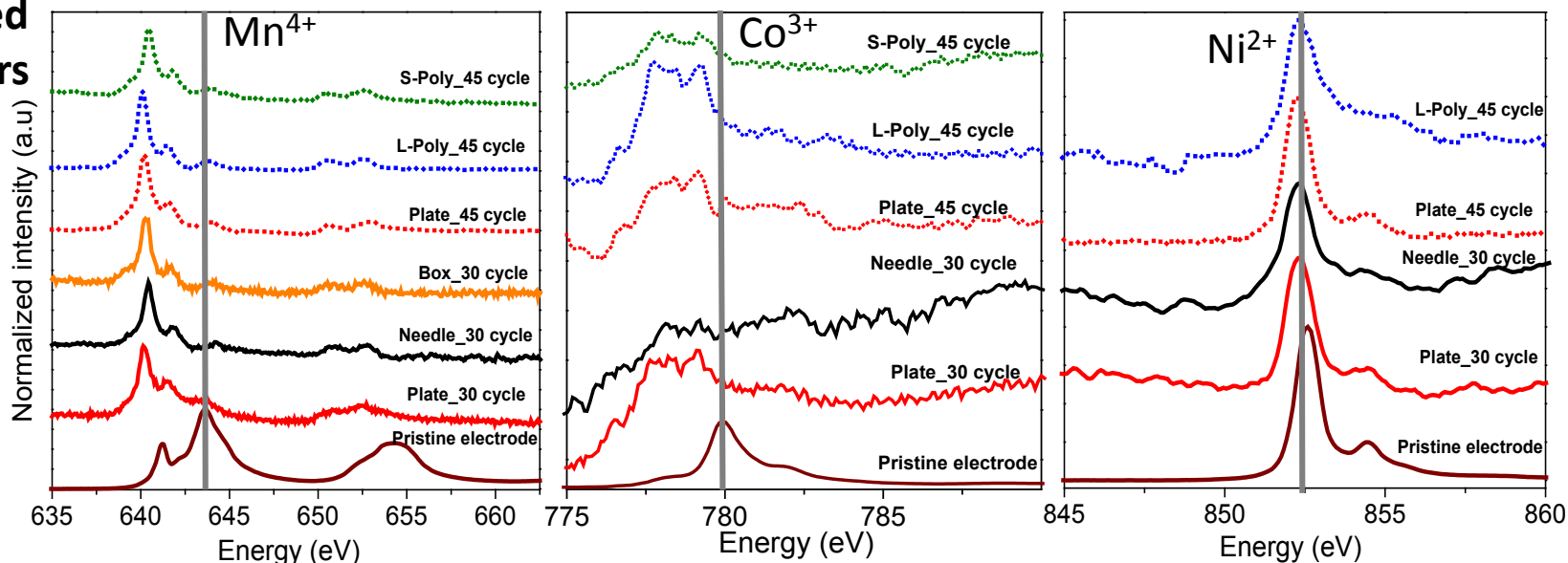
# Accomplishment II – facet reactivity and side reactions



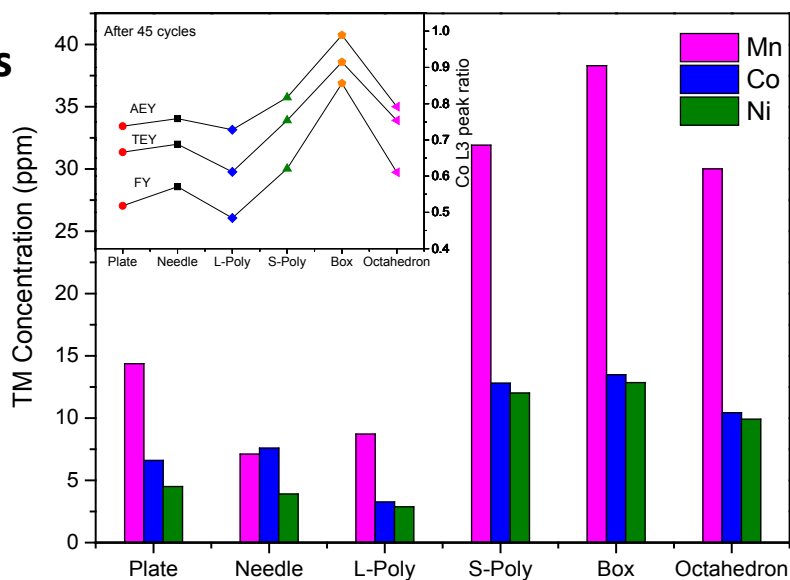
- The extent of parasitic reactions correlates with the trend of reduced TM content on pristine – a side reactivity indicator.

# Accomplishment II – facet reactivity and TM dissolution

## Recovered separators

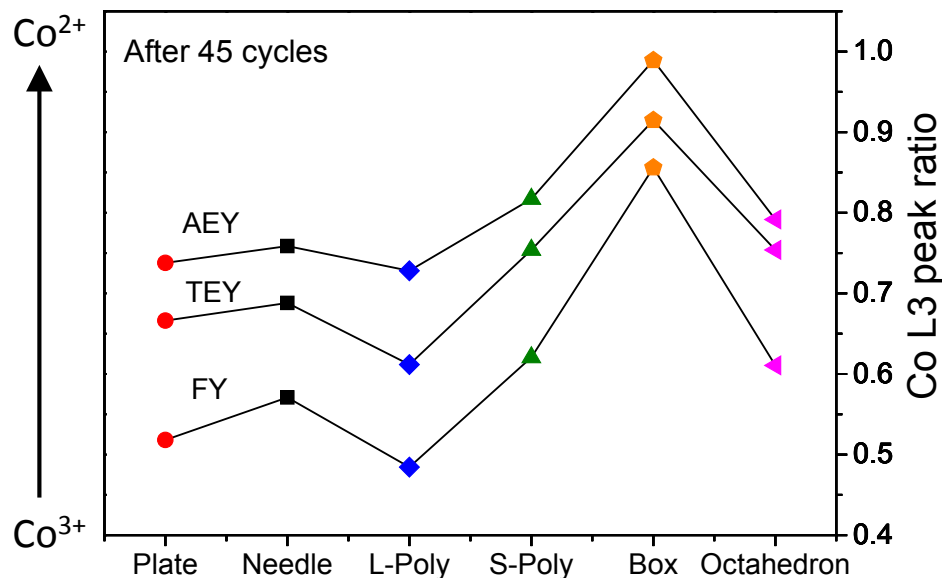
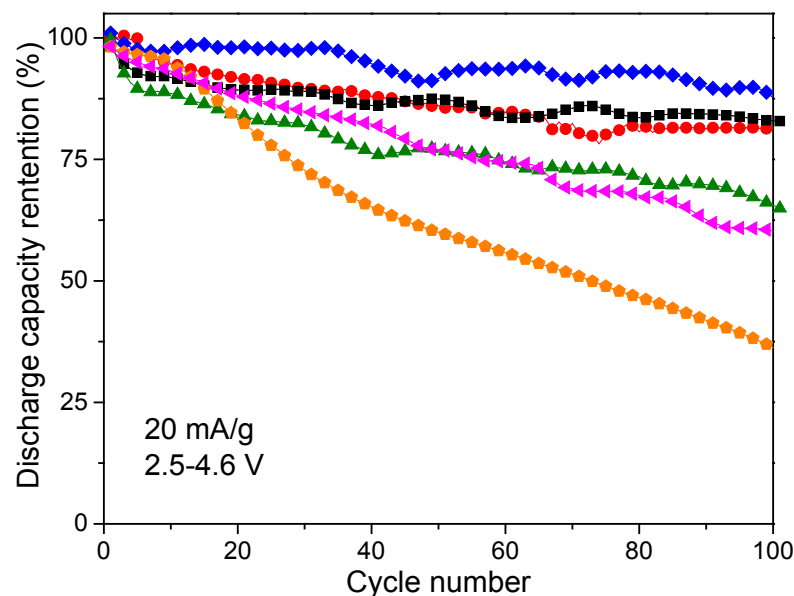


## Recovered electrolytes (45 cycles)



- Soft XAS (*L* edge, TEY mode) detects M<sup>2+</sup> (M=Mn, Co and Ni) on recovered separators. M<sup>2+</sup> content increases with cycling but morphology dependent.
- Extent of TM dissolution in electrolyte correlates with facet reactivities.

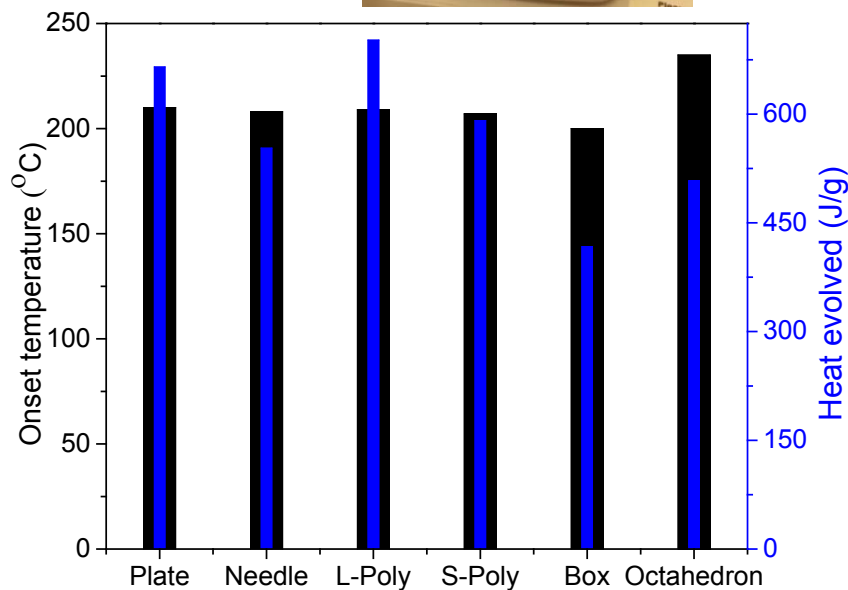
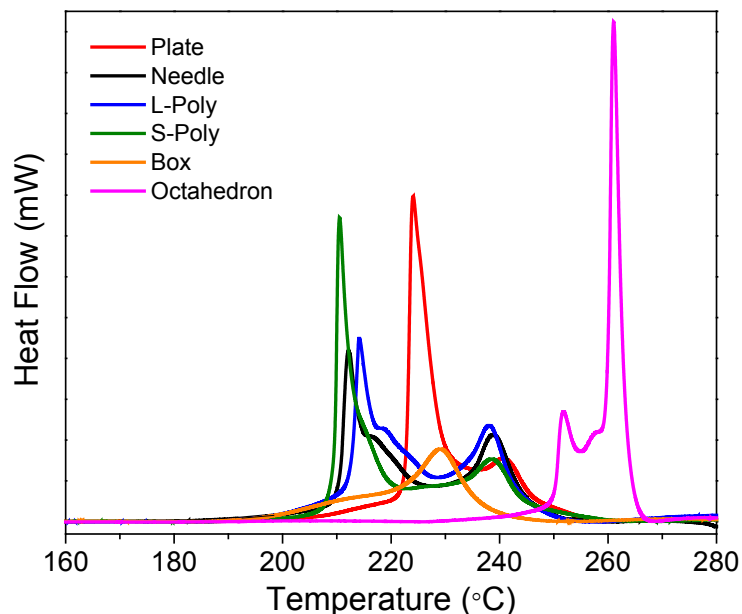
# Accomplishment II – facet reactivity and cycling stability



- Capacity retention correlates with the extent of cycling-induced TM reduction.

# Accomplishment II – facet reactivity and thermal stability

High-Pressure DSC Capsules



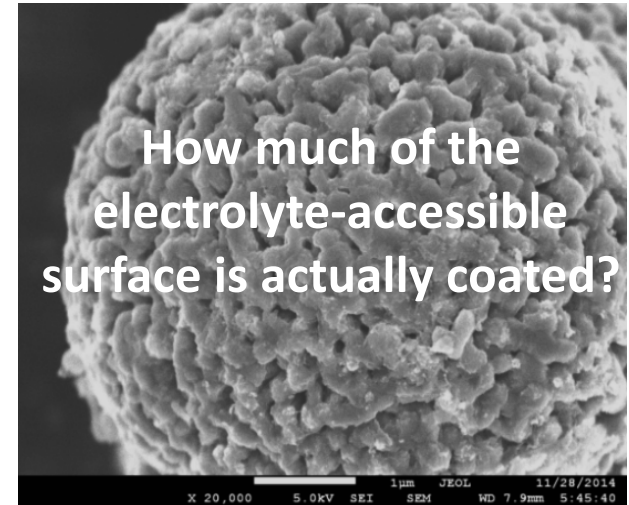
- Samples were fully delithiated by chemical method. Evolved heat measured in the presence of a liquid electrolyte.
- Surface with more reduced TMs improves safety – least heat from Box and most from Plate and L-Poly samples.



# Accomplishment III – coating to modify surface reactivity of given facets

- **Why study coatings?**

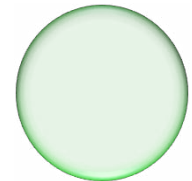
- Coating widely used to influence cathode/electrolyte interfacial chemistry by creating a physical barrier and/or changing particle surface properties.
- Coating studies are often poorly controlled and poorly understood, largely due to the use of particles with complex microstructure.
- Coating on particles with specific surface facets can create model cathode/electrolyte interfaces for investigating the interfacial chemistry.



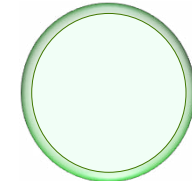
- **Understanding coating**

- How does coating modify surface properties of given facets and material's behavior?
- What is the effect of coating material choice? Differences between native surface modification vs. an add-on coating layer?
- Are coating effects facet-dependent? Material dependent?

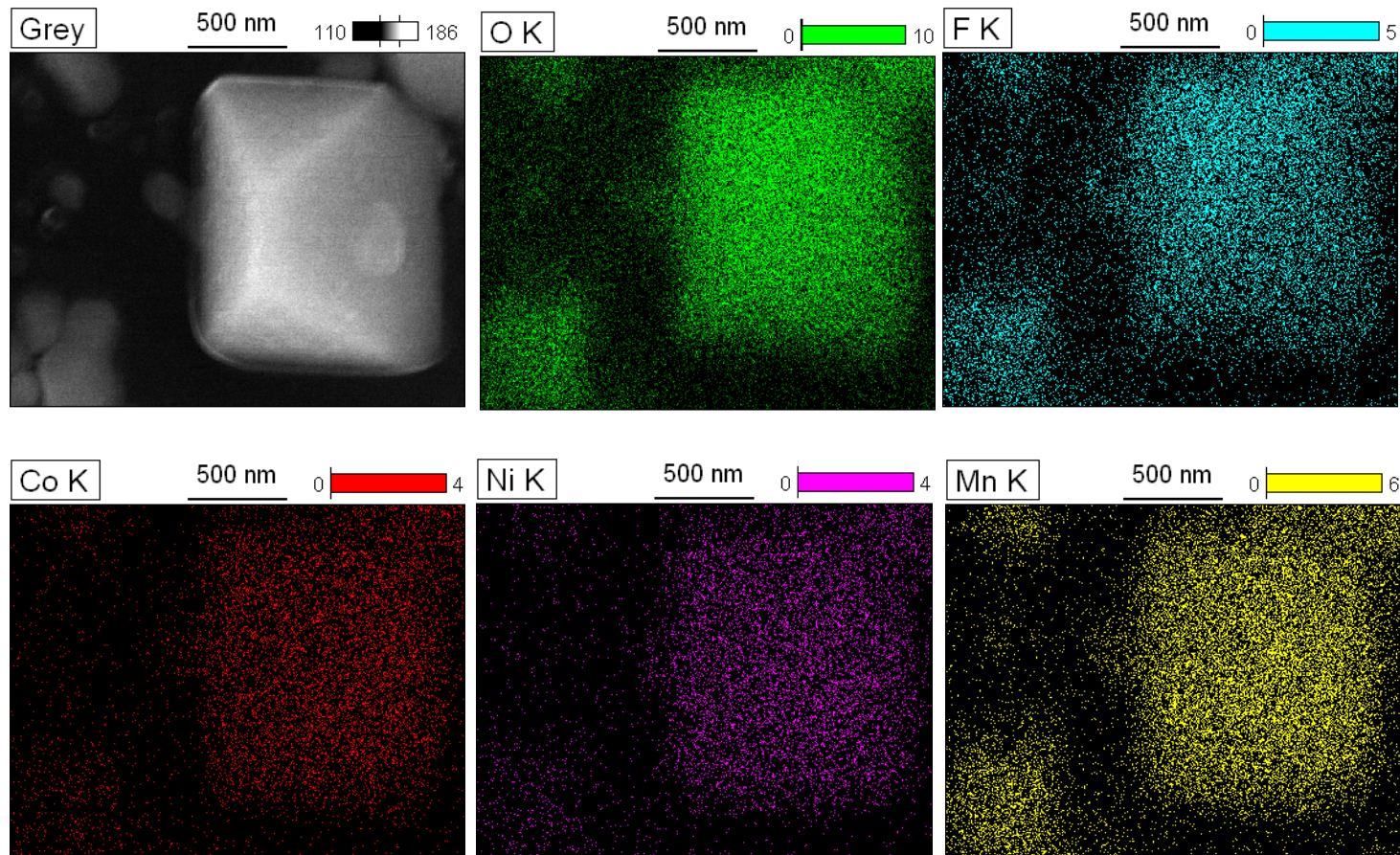
Native coating



Add-on coating

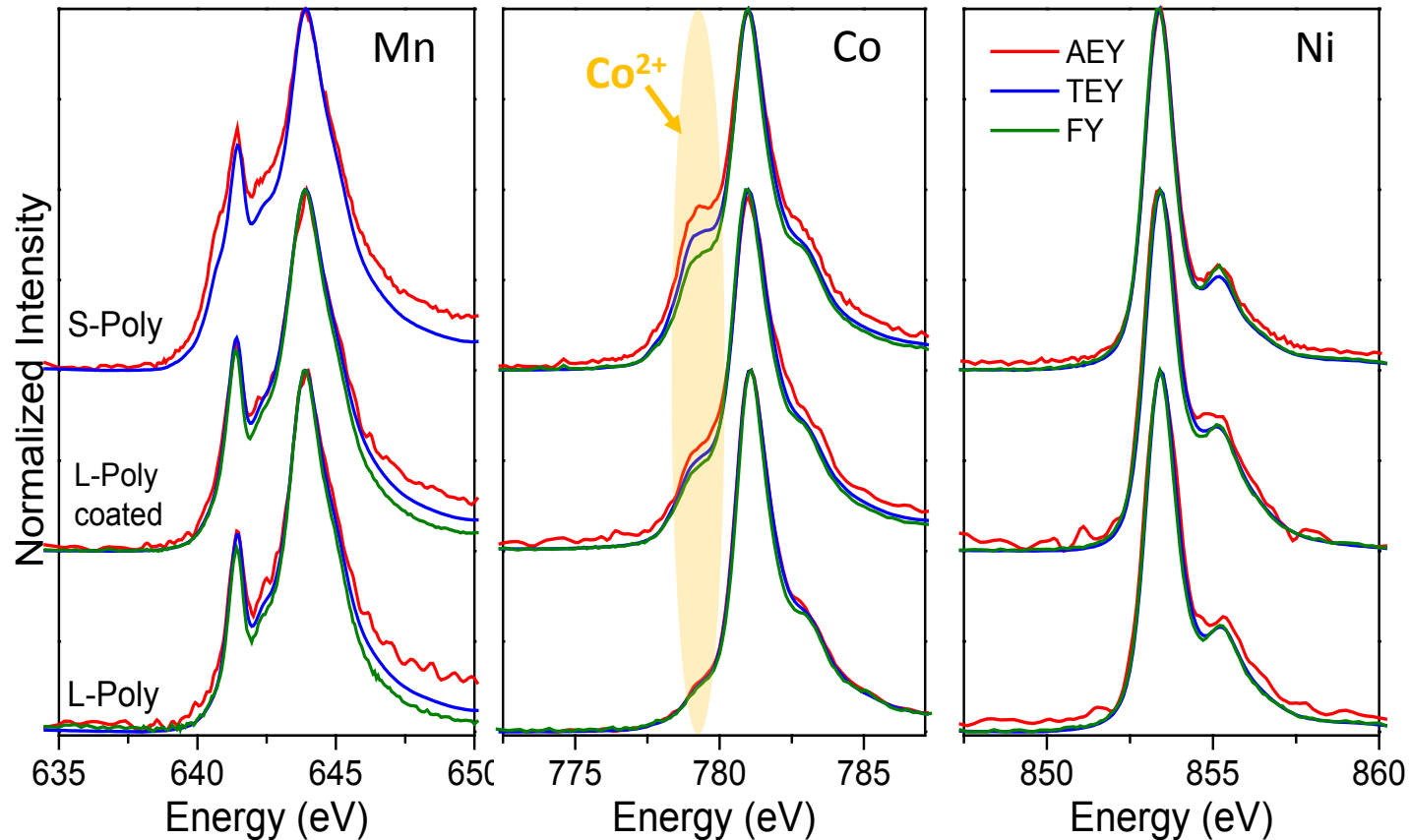


# Accomplishment III – surface coating with fluorinated agents (an example)



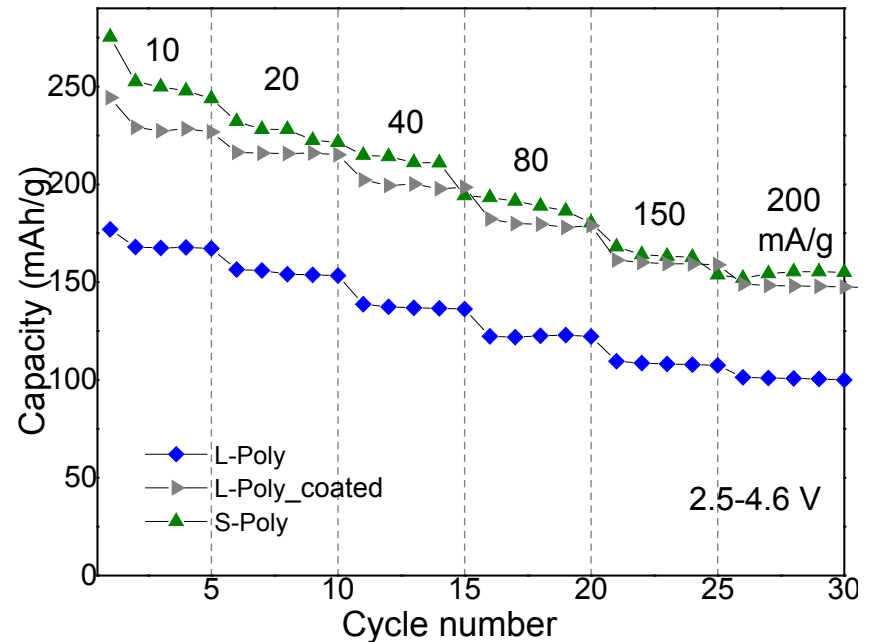
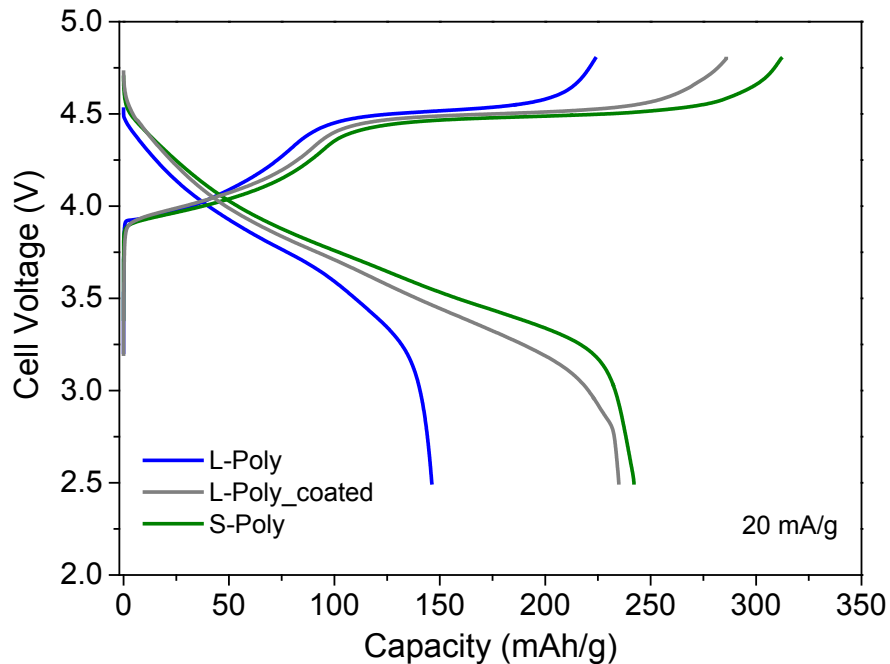
- $\text{NH}_4\text{F}$  (5 wt.%) mixed with L-Poly LMR-NMC141 crystals and heated in air at  $300^\circ$  for 6 h.
- Decomposition of  $\text{NH}_4\text{F}$  to  $\text{NH}_3$  and HF allows modification of the crystal native surface without introducing an add-on coating layer.

# Accomplishment III – coating leads to selective surface chemical modification



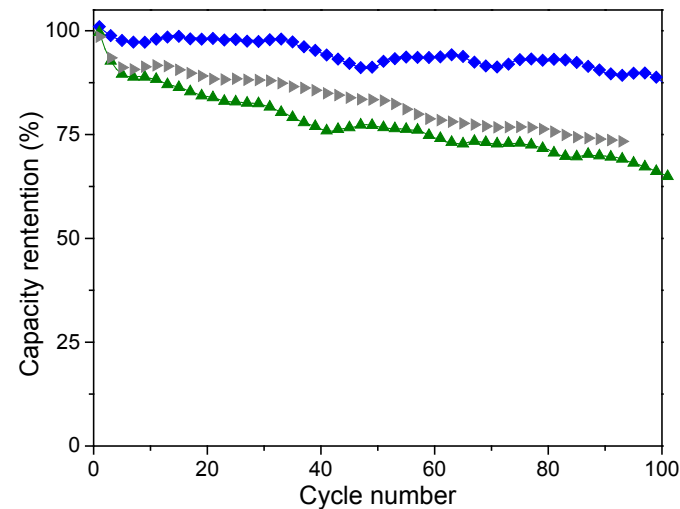
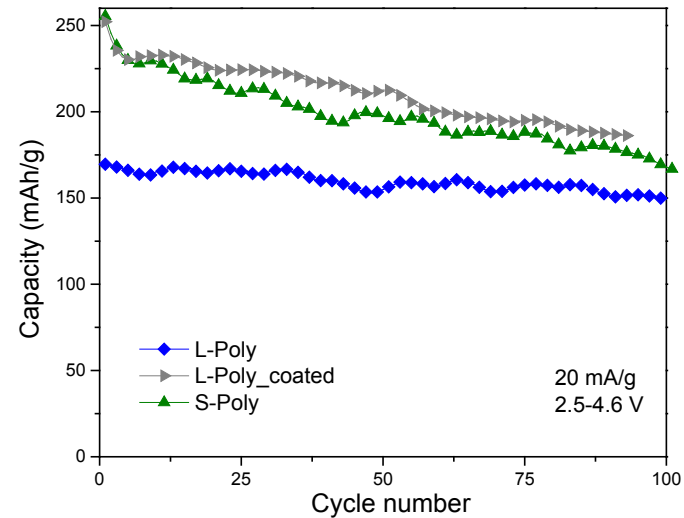
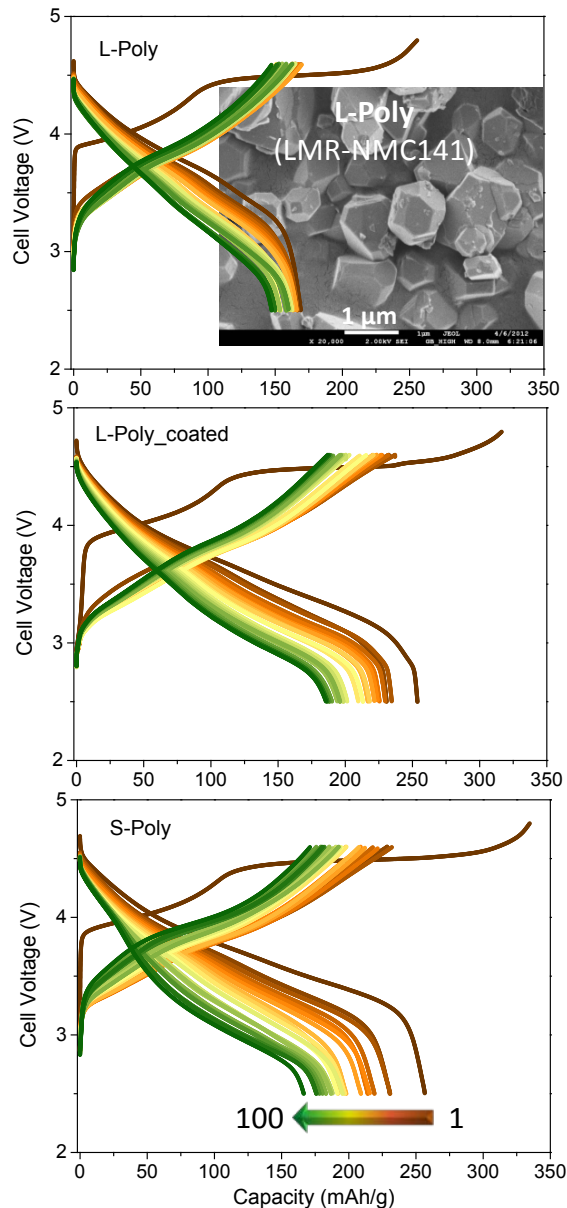
- Coating has no effect on Mn and Ni but enhances Co reduction in the pristine – decoupled chemical modification of TMs.
- STEM/EELS studies on structural and elemental modifications in progress (collaborative effort with PNNL).

# Accomplishment III – coating improves utilization and kinetics



- Particles with less accessible surface can be modified by coating to achieve better activation, utilization and rate capability.

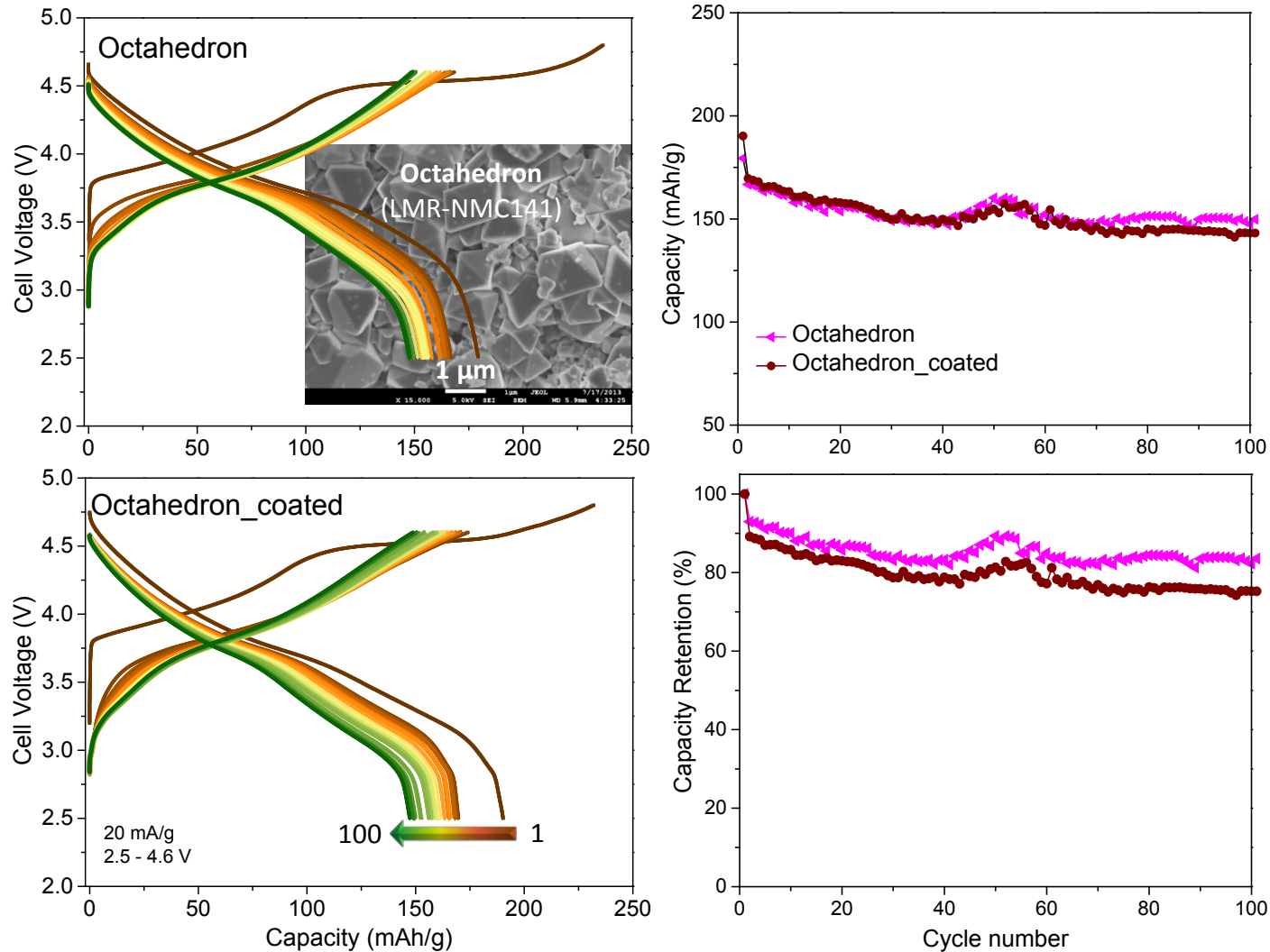
# Accomplishment III – coating lowers capacity retention



- Trade-offs between utilization (capacity) and capacity retention.



# Accomplishment III – coating effect morphology dependent

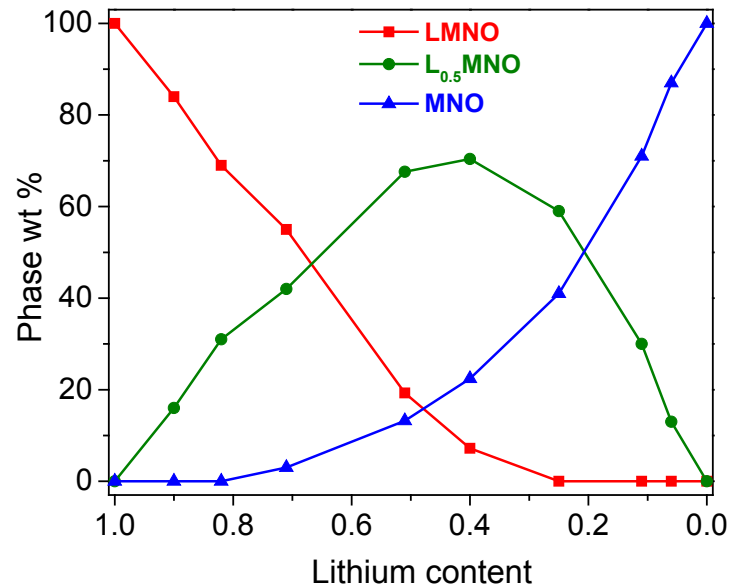
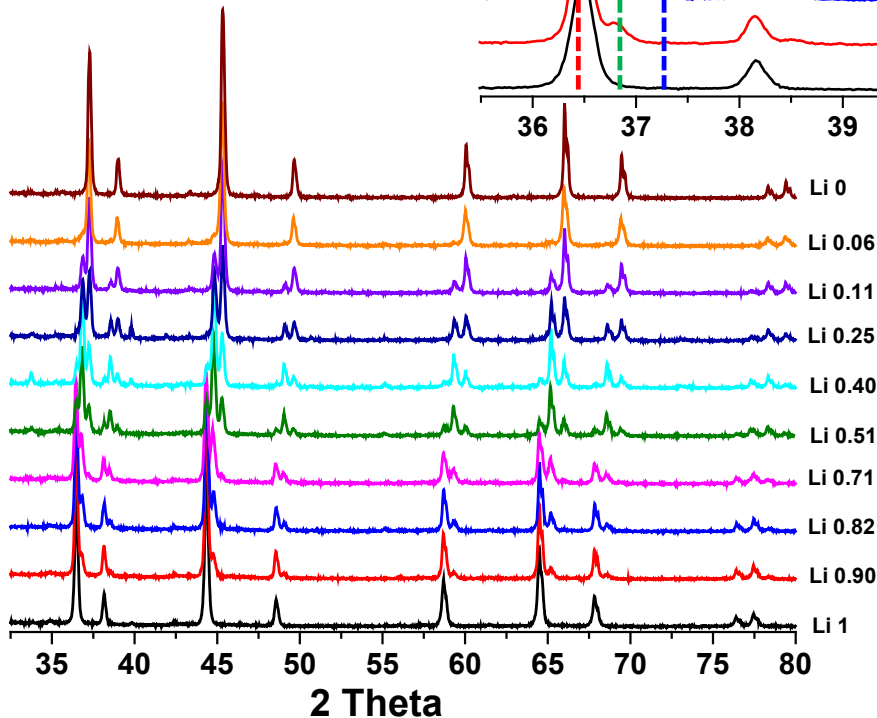
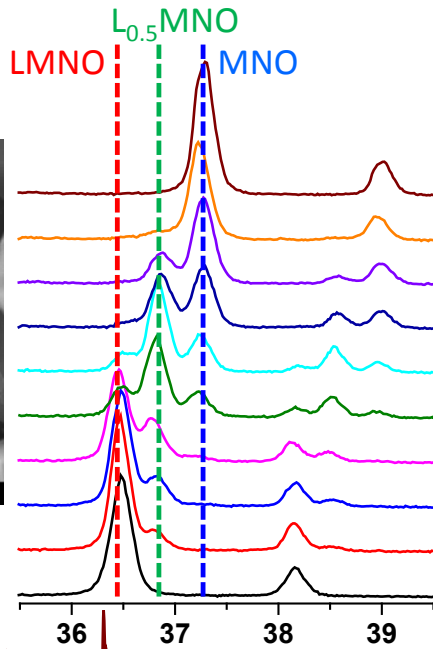
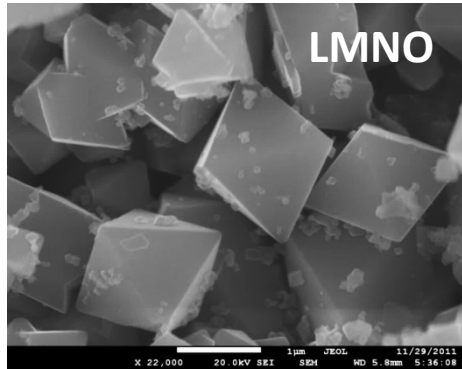


- Coating effect not obvious on octahedron sample – facet dependent behavior of coating.

# Accomplishment IV – phase transition mechanism and kinetic barriers in first-order intercalation cathodes

- **Why study phase transformation?**
  - Two-phase reactions with large lattice misfit between the phases are common among electrode materials. Well-known examples are  $\text{LiFePO}_4$  (LFP) and  $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  (LMNO).
  - Both LFP and LMNO show good rate capability despite two-phase reactions associated with large lattice volume changes (ca. 7% and 6%). High rate in LFP only possible at small size where the existence of metastable phases and solid-solutions mitigates the lattice strain and enables fast rate. LMNO has fast rate even at micron size regime.
  - Conventional wisdom says first-order phase transition reduces rate capability and cyclability but the relationships between kinetics, strain and phase boundary movement are currently unknown.
  - High spatial- and chemical-resolution visualization of phase boundary propagation at the particle level provides us with fundamental understanding of the phase transformation mechanism and associated mechanical damage/fracture. This will guide the design of particle morphology and other properties to achieve improved electrode performance.

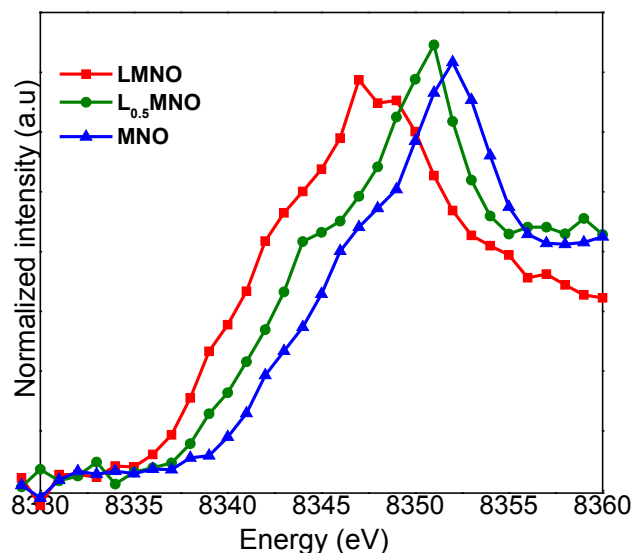
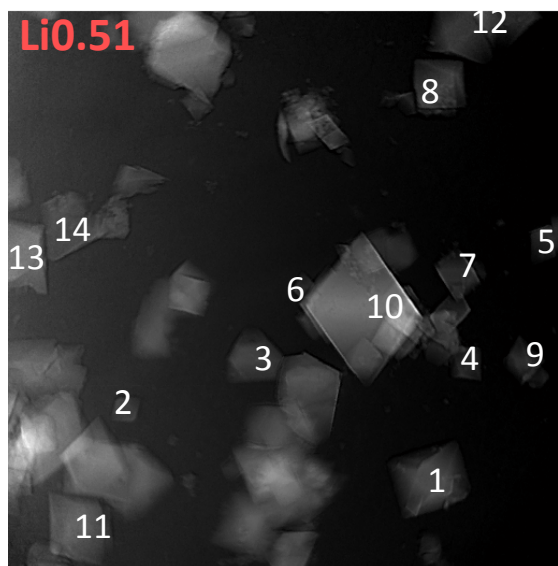
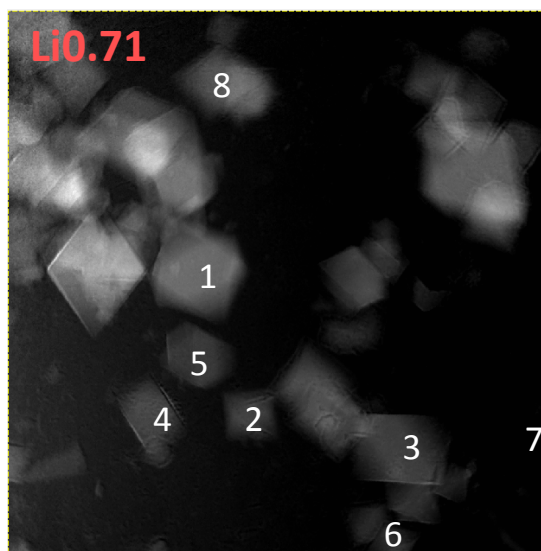
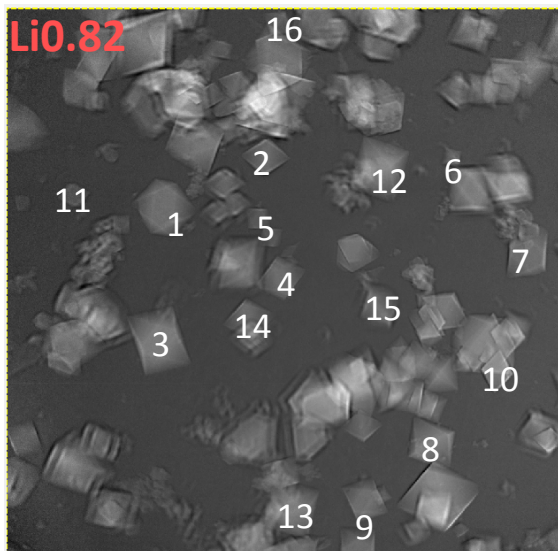
# Accomplishment IV – chemically delithiated $\text{Li}_x\text{MNO}$



- Two 2-phase transitions among three cubic phases of LMNO,  $\text{L}_{0.5}\text{MNO}$  and MNO.
- As-prepared  $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$  ( $\text{Li}_x\text{MNO}$ ) samples are varying mixtures of the three phases.
- Volume changes were 2.5% (LMNO and  $\text{L}_{0.5}\text{MNO}$ ), 3% ( $\text{L}_{0.5}\text{MNO}$  and MNO) and 5.5% (LMNO and MNO).

# Accomplishment IV – standard XANES spectra

25  $\mu\text{m}$



Field of view of Full-field Transmission X-ray Microscopy combined with X-ray Absorption Near Edge Structure imaging (FF-TXM-XANES)

*Collaboration with Dr. Yijin Liu (SSRL, BL 6-2c)*

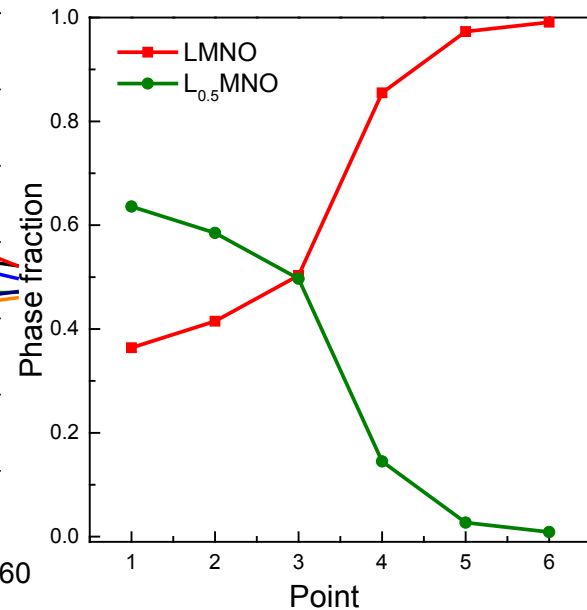
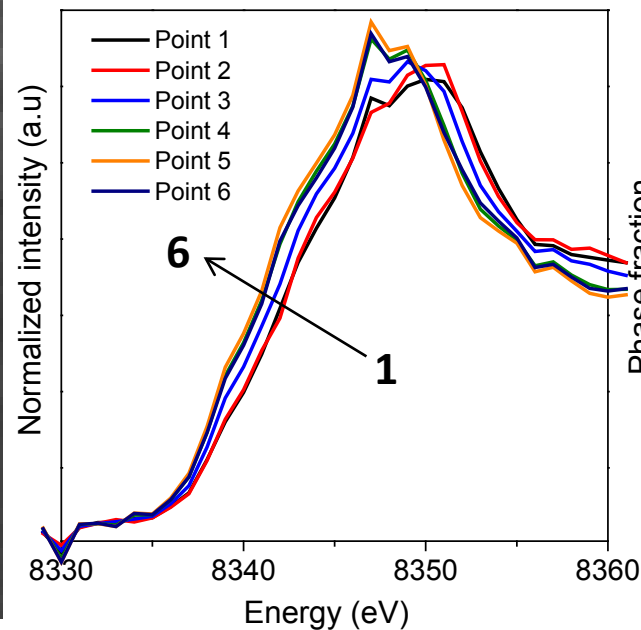
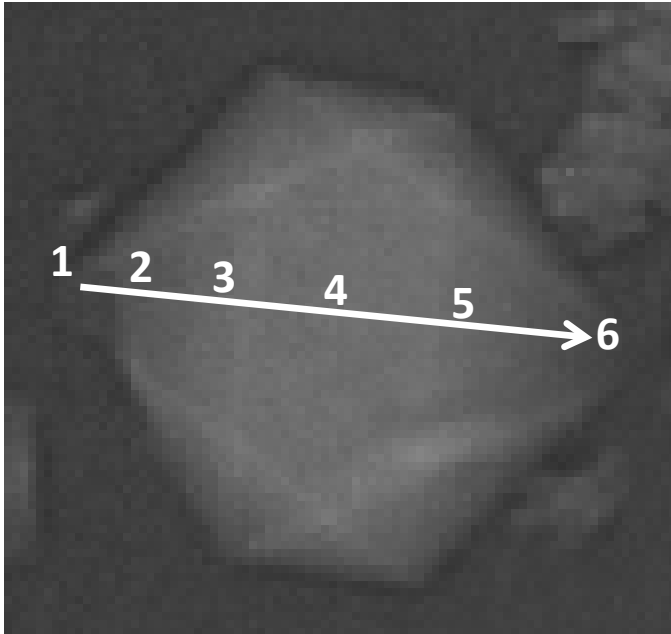
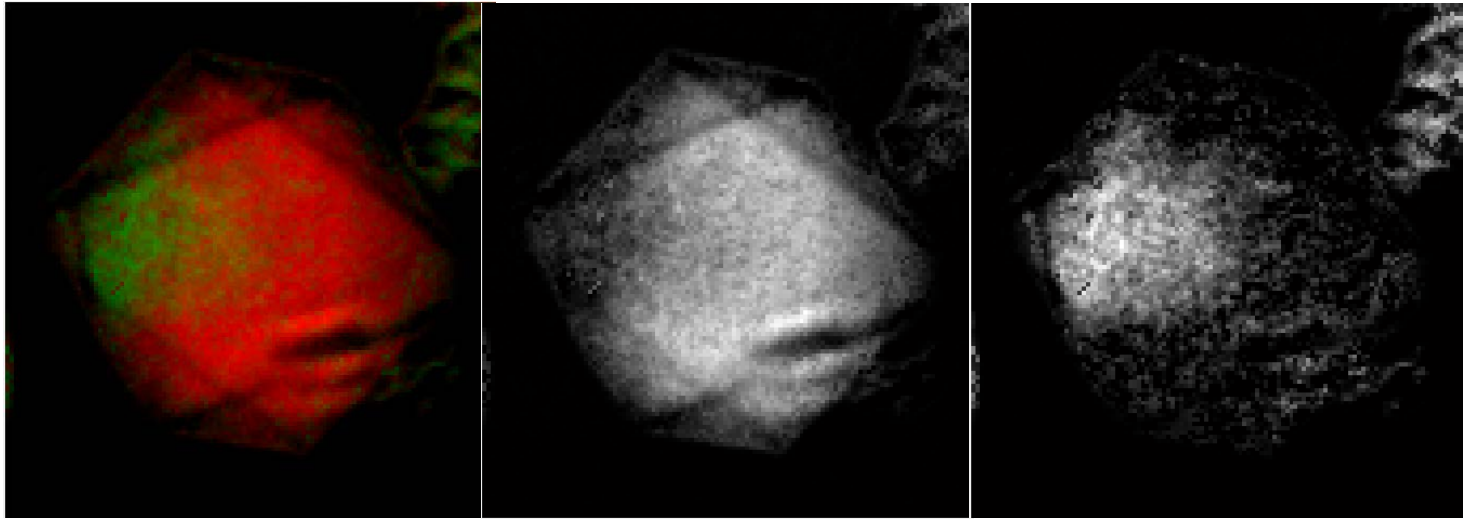
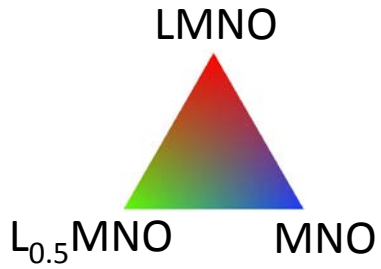
- Standard XANES spectra for LMNO and MNO end members were collected.
- Pure  $\text{L}_{0.5}\text{MNO}$  XANES spectrum was extrapolated for the first time, using linear combination fitting of  $\text{L}_{0.40}\text{MNO}$  data with LMNO and MNO spectra.

# Accomplishment IV – $\text{Li}_{0.82}\text{MnO}$ 2D FF-TXM-XANES

Chemical phase map

LMNO

$\text{L}_{0.5}\text{MnO}$





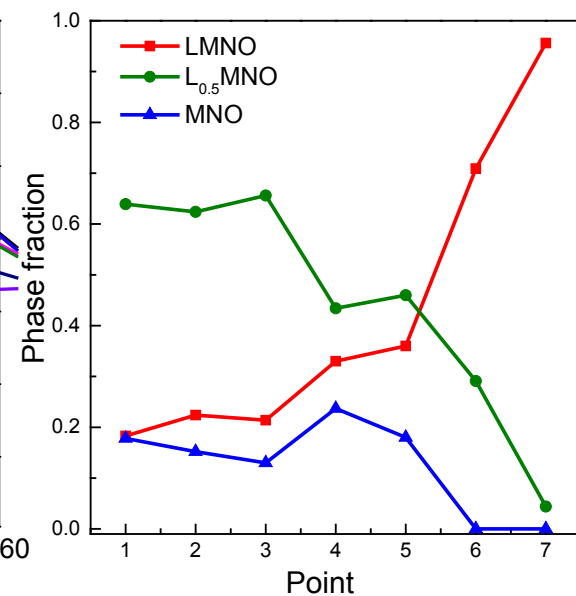
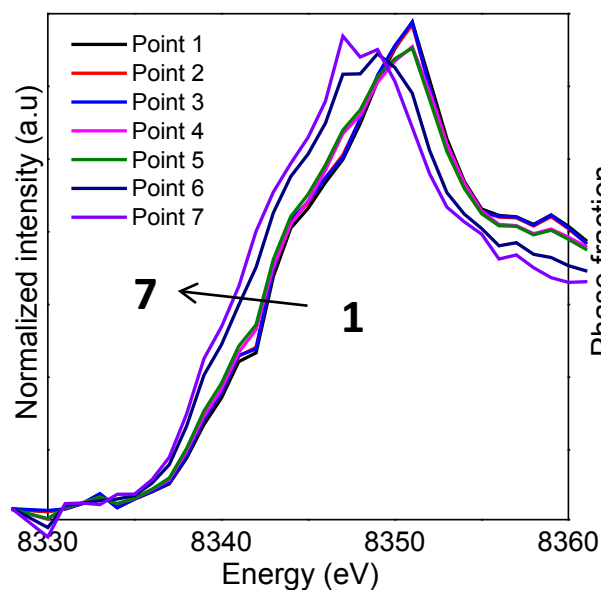
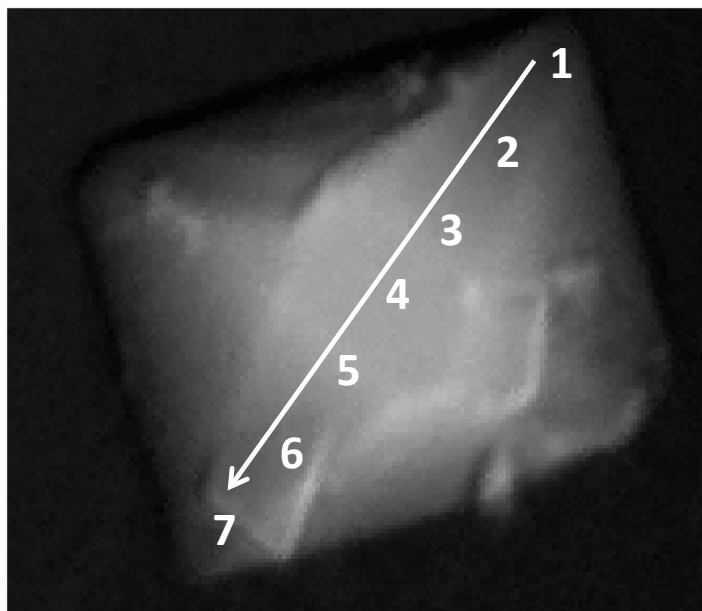
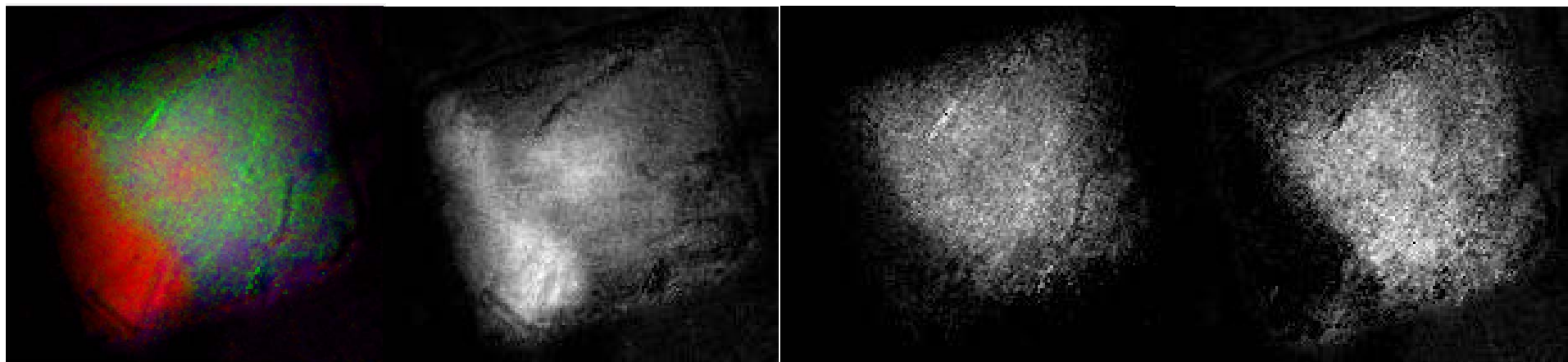
# Accomplishment IV – $\text{Li}_{0.51}\text{MNO}$ 2D FF-TXM-XANES

Chemical phase map

LMNO

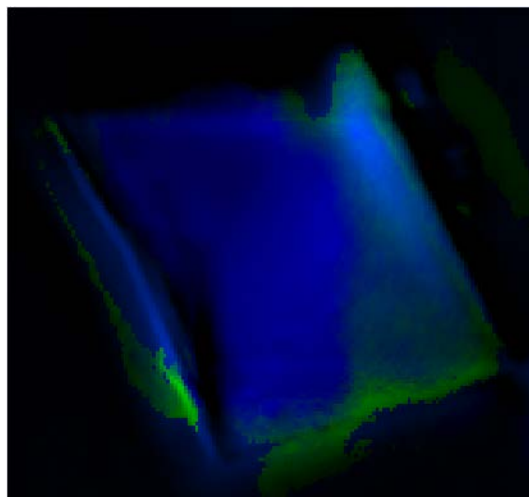
$\text{L}_{0.5}\text{MNO}$

MNO

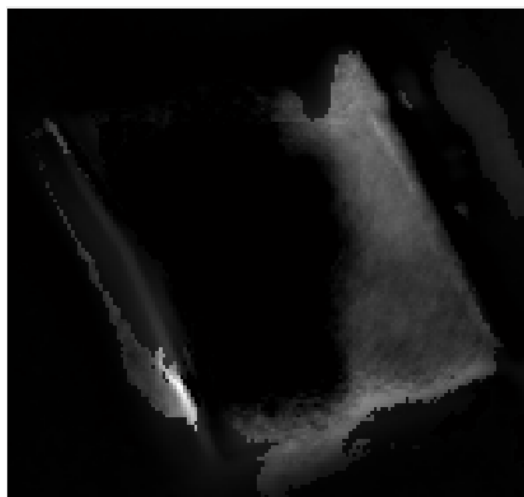


# Accomplishment IV – $\text{Li}_{0.25}\text{MnO}$ 2D FF-TXM-XANES

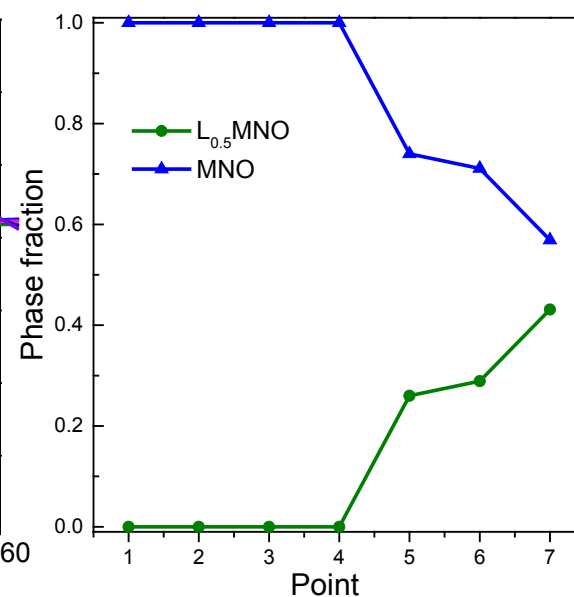
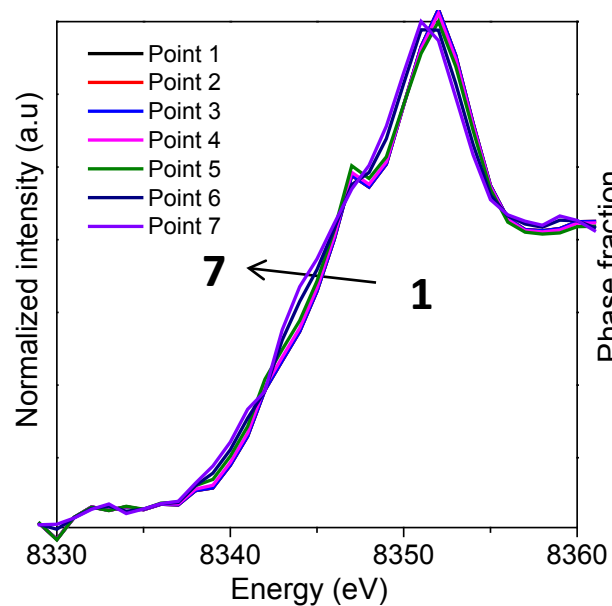
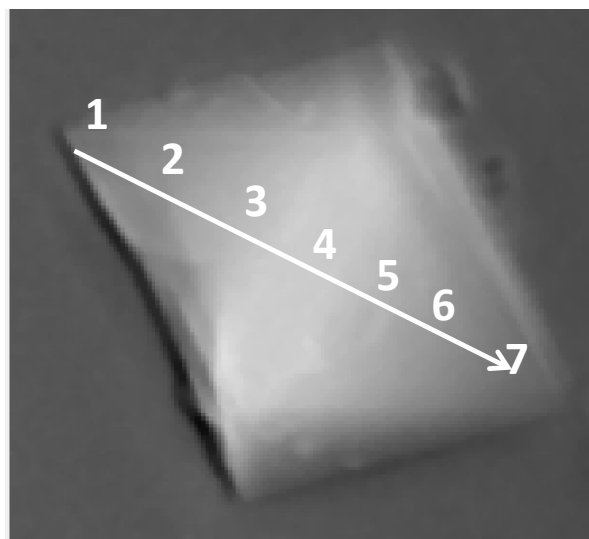
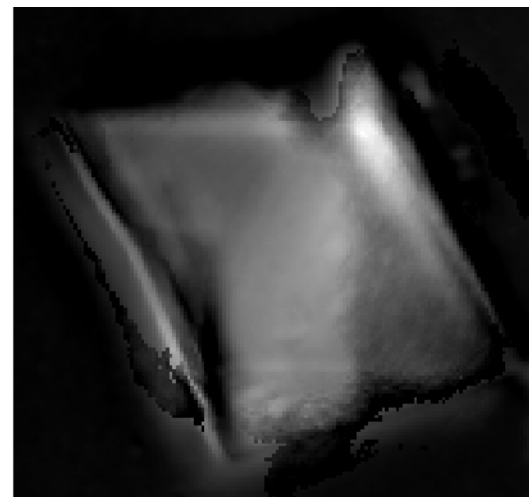
Chemical phase map



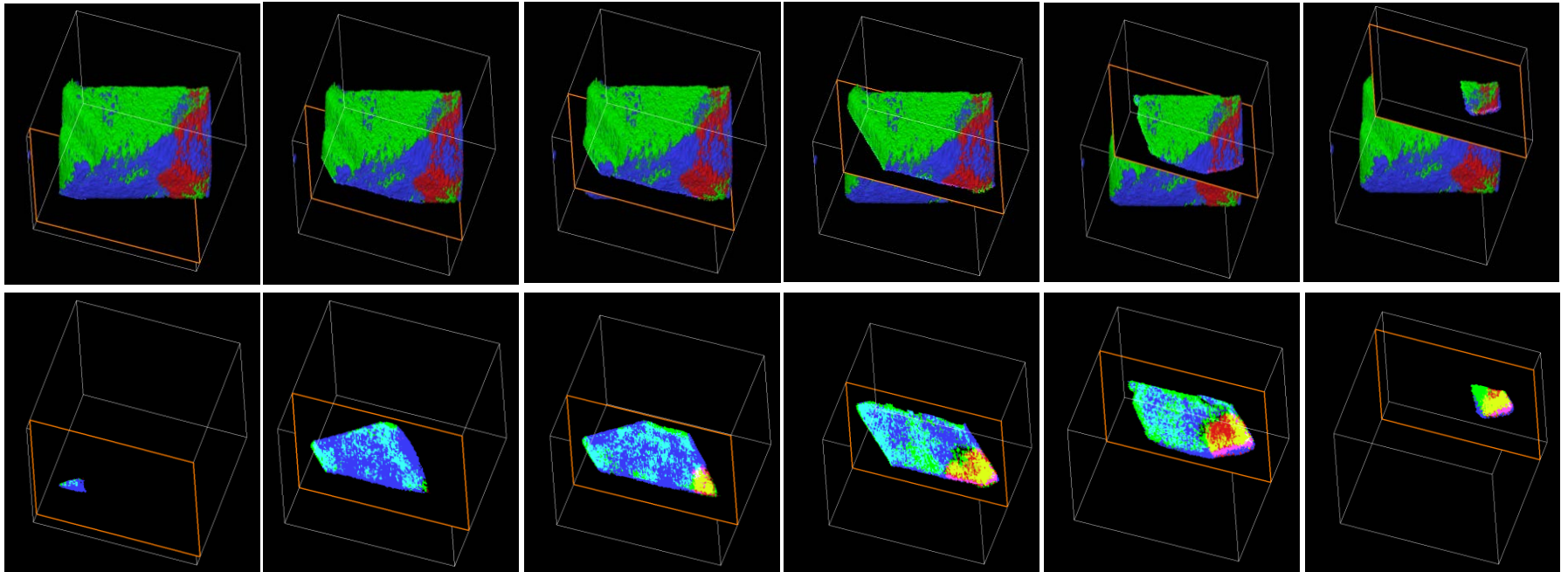
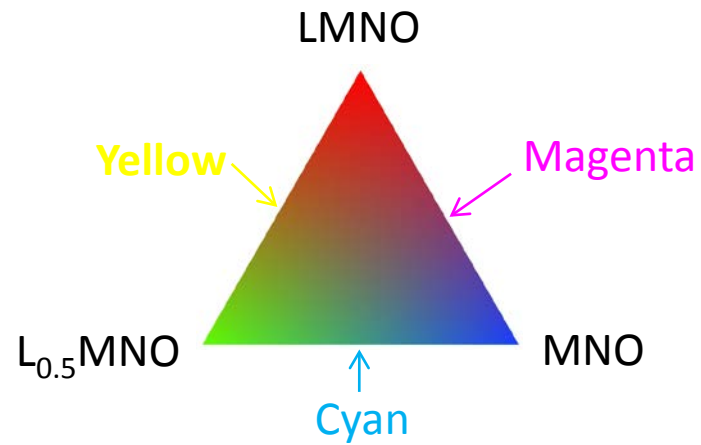
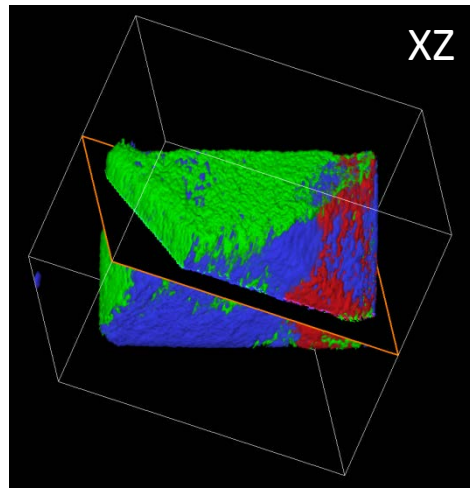
$\text{L}_{0.5}\text{MNO}$



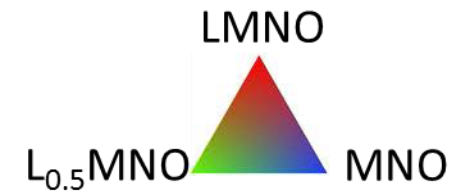
MNO



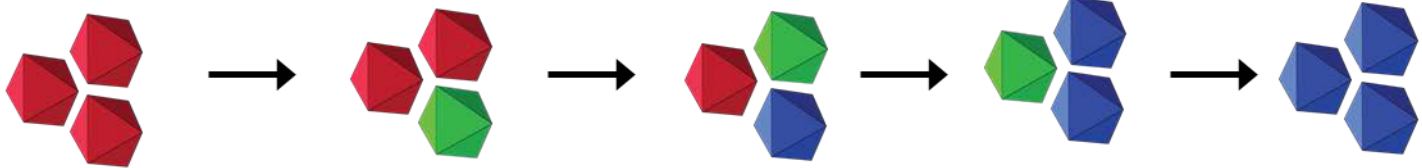
# Accomplishment IV – $\text{Li}_{0.51}\text{MNO}$ 3D FF-TXM-XANES



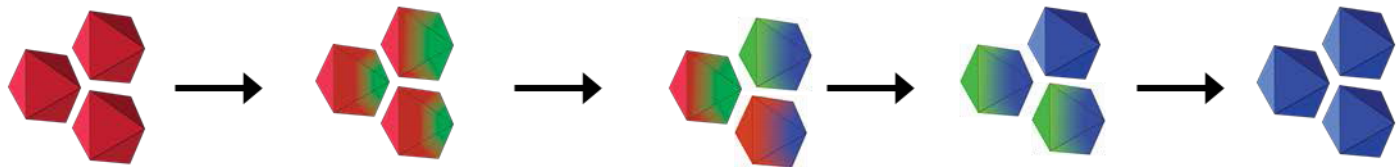
# Delithiation mechanism of LMNO



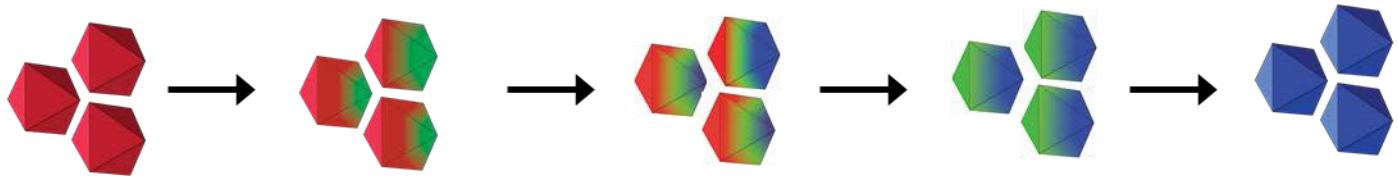
Particle-by-particle mechanism



2-phase mechanism



3-phase mechanism **(only this one supported by experiments)**



- The observation of all three phases on a single particle supports the 3-phase mechanism.

# Responses to Previous Year Reviewers' Comments

DOE Merit Review, June 2015

A total of three reviewers evaluated the project. In general, the reviewers' comments were very positive and they noted that "the approach was solid and strong", "the work has been superbly carried out and the results are really insightful" and "there is outstanding collaboration". Only reviewer 3 submitted specific comments and suggestions which are addressed below:

**Recommendation/Comment:** The project team needed to provide statistics on the performance data in order to rank S-poly, L-poly and plate results and to identify one morphology with overall good performance.

**Response/Action:** The performance data of each sample were statistically evaluated based on at least five coin cell testing. We thank the reviewer for pointing out the omission of this information.

**Recommendation/Comment:** Some explanations are needed on how the surface spinel group affected the voltage fade which was thought to be induced by bulk structural change. The impact of electrode fabrication, for example, grinding, mixing, etc., on the morphology of the crystals, should be quantified since the morphology might not be maintained after the electrode fabrication and after the first activation charge when O<sub>2</sub> gas was evolved at high cut-off voltage.

**Response/Action:** We thank the reviewer for the suggestions. Extensive studies are needed in order to assess the contribution of surface processes in performance issues such as voltage fade and this part of research is ongoing. Our electrodes were made by simple mixing of crystals, carbon and binder without the use of mechanical grinding. SEM studies confirmed that morphology remained intact during the fabrication process. First-cycle activation induced morphology damage is likely but not unique to our crystals. Our crystal samples, however, are ideal for investigating cycling-related morphology changes and we plan to look into this in our future studies.

**Recommendation/Comment:** The project team needed to propose more specific surface modification techniques to improve the cathode stability by leveraging insights gained on the surface defect spinel.

**Response/Action:** We have initiated the surface modification effort this year. Studies on coating and its effect on surface chemistry were performed and the preliminary results are included in this year's review.

# Collaborations

- Drs. Marca Doeff (LBNL), Apurva Mehta and Yijin Liu (SSRL) – synchrotron *in situ* and *ex situ* XRD, XAS and FF-TXM-XANES studies
- Drs. Ethan Crumlin, Jinghua Guo and Tolek Tyliczszak (ALS) – synchrotron XPS, XAS and STXM studies
- Dr. Phil Ross (LBNL) and Prof. Simon Mon (Gwangju Institute of Science and Technology, Korea and SPring-8, Japan) – Hard X-ray Photoelectron Spectroscopy
- Prof. Clare Grey (Cambridge) – NMR studies
- Dr. Ashfia Huq (ORNL) – neutron diffraction
- Dr. Chongmin Wang (PNNL) – STEM/EELS
- Dr. Arun Devaraj (PNNL) – atom probe tomography
- Dr. Jagit Nanda (ORNL) – new cathode material synthesis and characterization





# Remaining Challenges and Barriers

- Surface properties of the pristine layered oxides were shown to be different from that of the bulk. The next phase of study need to address the following:
  - What is the effect of synthesis conditions on the surface properties of the oxides?
  - What is the effect of cathode chemistry on pristine surface properties?
  - What is the contribution of surface processes in LMR-NMC performance issues such as voltage fade and impedance rise at low SOC?
  - Pristine surface properties are facet dependent – comparative studies of pristine and cycled samples always need to take consideration of crystalline orientation which may be challenging.
- Cathode/electrolyte interfacial chemistry is very complex and needs comprehensive understanding. It is important to know what reactivity is due to cathode instability and what reactivity is due to electrolyte instability at high voltages.
- Cathode particles needs to be optimized/engineered to bring out the best of the material itself can offer.
- Coating effect likely depend on coating materials and coating techniques.

# Proposed Future Work

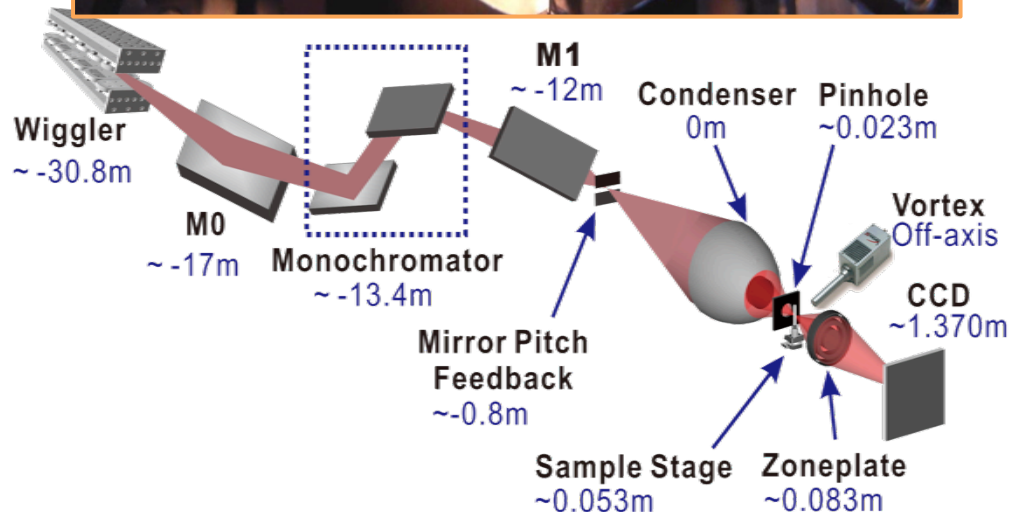
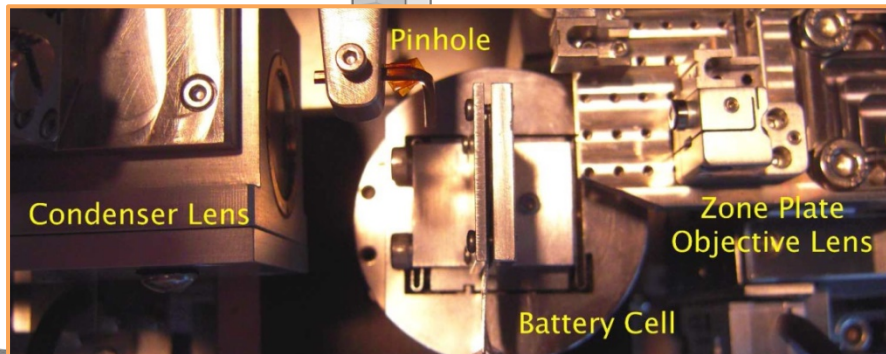
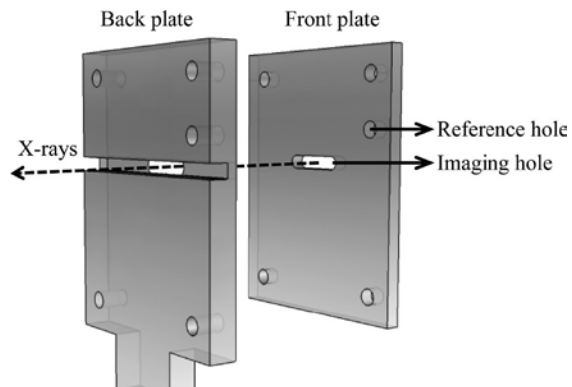
- Further investigate the impact of surface properties and bulk structure on the performance and stability of LMR-NMCs. Identify key properties and features hindering stable cycling of LMR-NMC cathodes.
- Perform studies to understand synthesis-bulk/surface properties-performance relationships in oxide cathode materials.
- Obtain comprehensive understanding on the cathode/electrolyte interfacial reactions and processes, particularly the roles of cathode chemistry (LCO, NMCs, LMR-NMCs etc.), surface properties and electrolyte stability.
- Determine the contribution of surface-related processes in the overall failure mechanisms of LIB cathodes.
- Understand coating effect on facet-specific surfaces and cathode/electrolyte interfacial reactivity.
- Explore other aspects of particle engineering and surface modification to improve cathode performance and stability at high operating voltages.

# Summary

- Surface properties of LMR-NMCs differ from that of the ideal bulk. Crystal structure, elemental and chemical compositions of the surface are facet dependent.
- Materials by design important – oxide structural and cycling stabilities improve with maximum expression of surface facets stable against TM reduction.
  - Surface termination determines material's tendency in TM reduction, both during synthesis and cycling.
  - Extent of surface TM reduction on pristine material is an indicator for surface reactivities.
  - TM reduction increases with cycling and progresses from the surface to bulk.
- Decomposable  $\text{NH}_4\text{F}$  coating improves first-cycle activation and overall kinetics but decreases capacity retention.
- Coating effect facet dependent. It is important that coating investigation takes account of particle morphology and other surface properties.
- Chemical phase mapping shows the coexistence of Li-rich and Li-poor regions on a single  $\text{Li}_x\text{MNO}$  particle, suggesting concurrent phase transformation instead of the particle-by-particle process.

# **Technical Back-Up Slides**

# Synchrotron FF-TXM-XANES technique

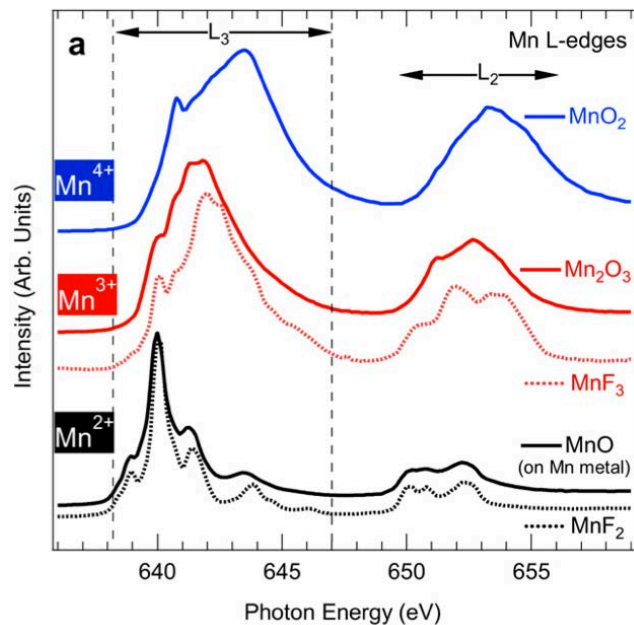


Full-field Transmission X-ray  
Microscopy X-ray Absorption Near  
Edge Spectroscopy (FF-TXM-  
XANES)

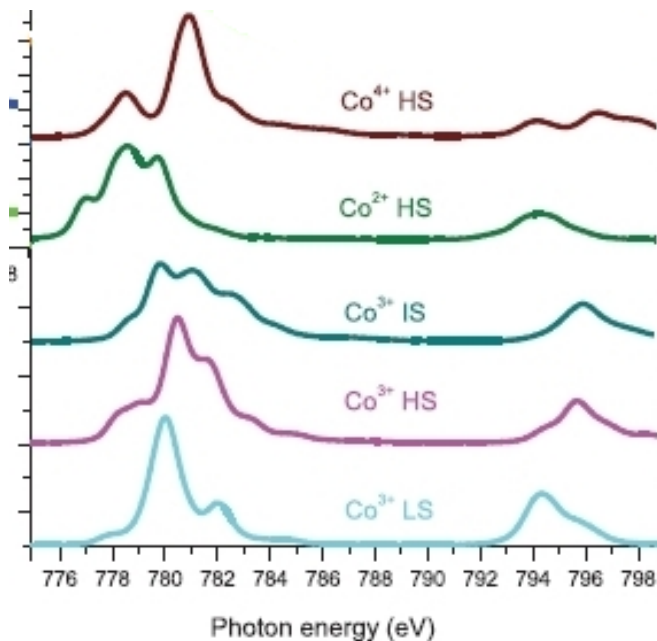
*Collaboration with Dr. Yijin Liu  
(SSRL, BL 6-2c)*

Spatial resolution: 30 nm  
Field of view (FOV): 30+  $\mu\text{m}$   
Energy range: ~4 - 13 keV  
2D and 3D Tomography  
imaging  
Energy scanning for XANES  
imaging  
Fluorescence microprobe (micron-  
scale)  
Typical exposure time:  $\frac{1}{2}$  second

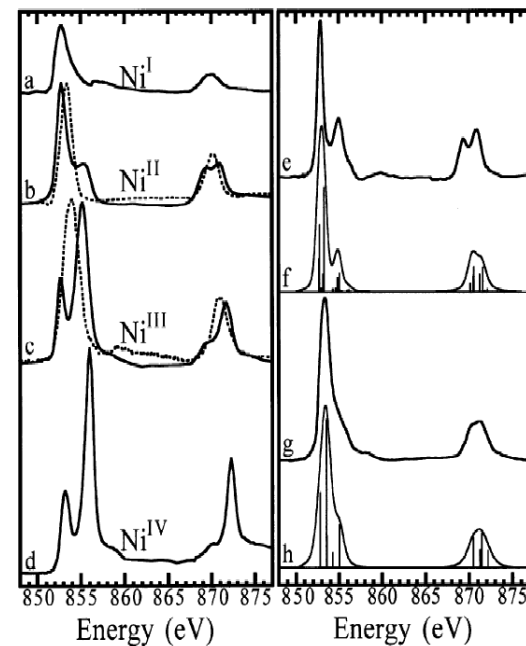
# Standard soft XAS spectra for transition metals



*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)