User Facilities for Energy Storage Materials Research

Project ID: ES235

Principal Investigator: Michael Thackeray

Co-PI: Jason R. Croy

Chemical Sciences and Engineering Division

Argonne National Laboratory

Annual Merit Review

DOE Vehicle Technologies Program

Arlington, VA

8-12 June, 2015

Overview

Timeline

- Start: October 1, 2012
- End: Sept. 30, 2015
- Percent complete: 75%

Budget

- Total project funding
  - 100%
- FY15 - $300K

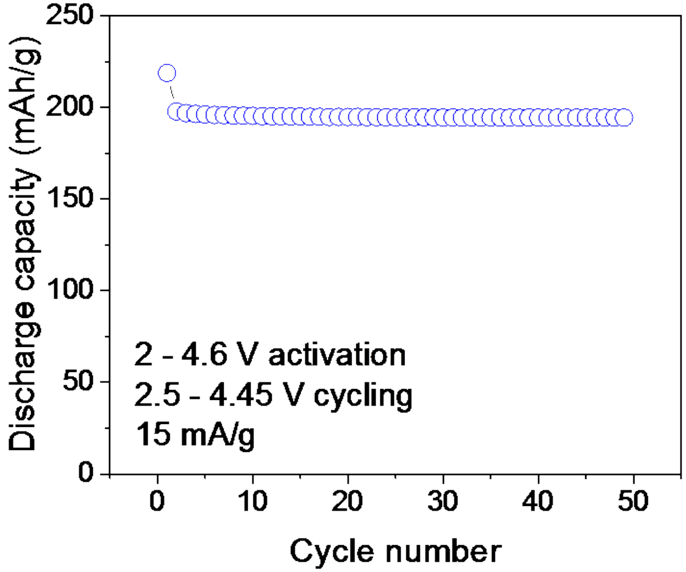
Barriers

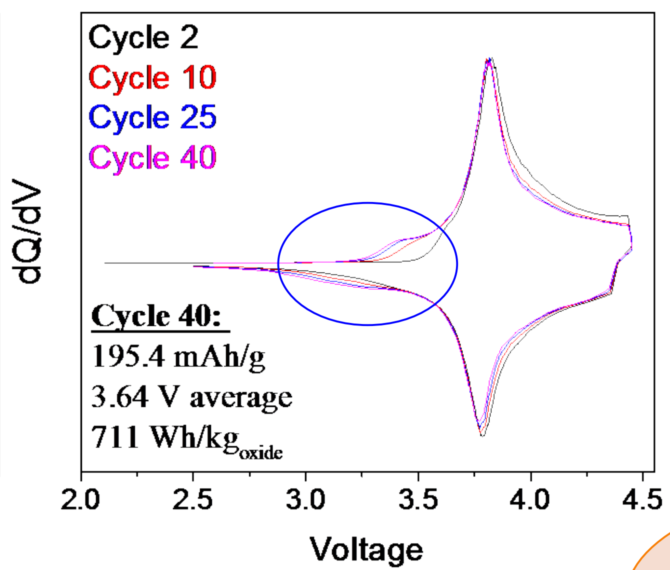
- Develop a better understanding of multi-scale structure-property relationships that allow for rational design of more robust cathode structures

Partners

- Lead PI: Michael Thackeray, Co-PI: Jason R. Croy
- Collaborators:
  - CSE, Argonne: Brandon Long, Joong Sun Park, Eungje Lee, Roy Benedek, Jeff Elam
  - APS: Mali Balasubramanian (XAS)
  - EMC/CNM: Dean Miller, Jianguo Wen (TEM)
  - ES: Greg Krumdick, Young-Ho Shin
  - Rutherford Appleton (ISIS, UK): Bill David and Thomas Wood (ND)
  - NUANCE, Northwestern University: Vinayak Dravid (TEM)

Relevance (See M. Thackeray, ES049)

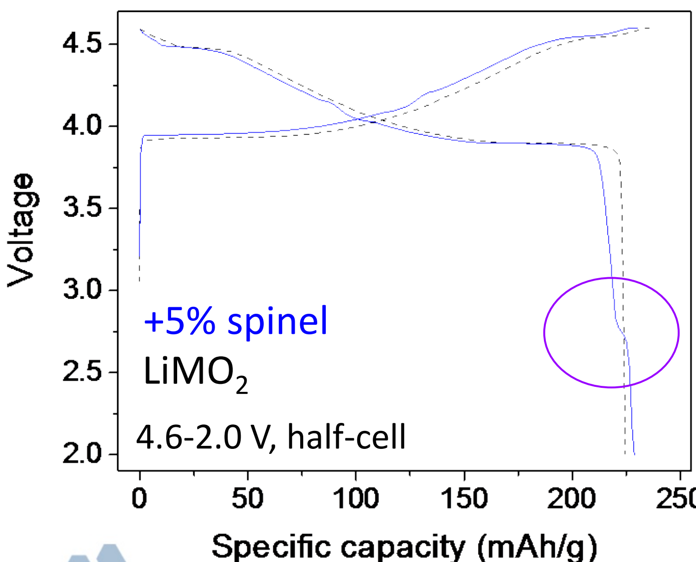


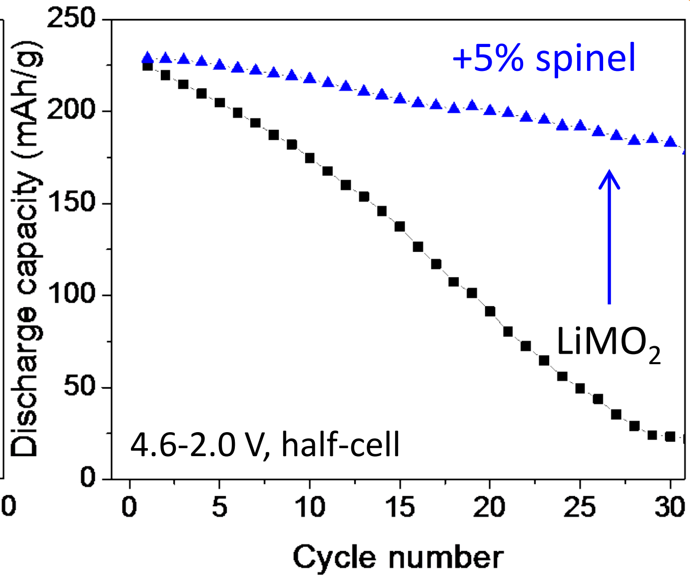


Layered-Layered-Spinel

- High capacity
- Mn-rich
- Good stability

Can we further improve capacity and stability?



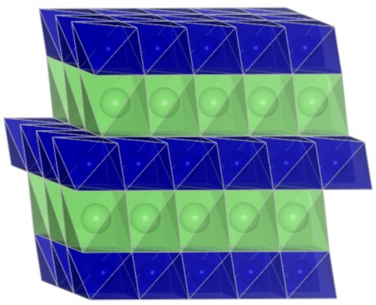


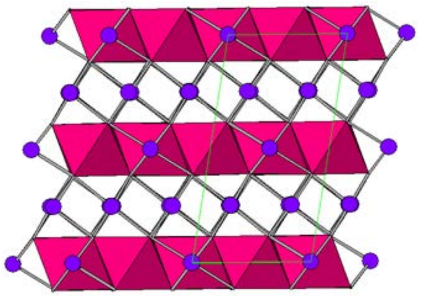
Layered-Spinel

- Improved stability
- High capacity

Relevance

Unique design opportunities rely on complex structure-property relationships





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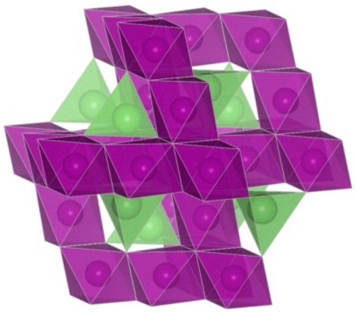

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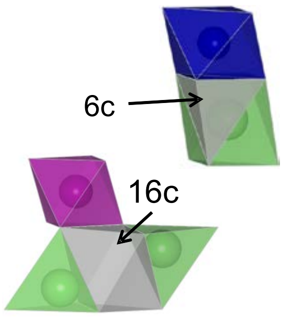
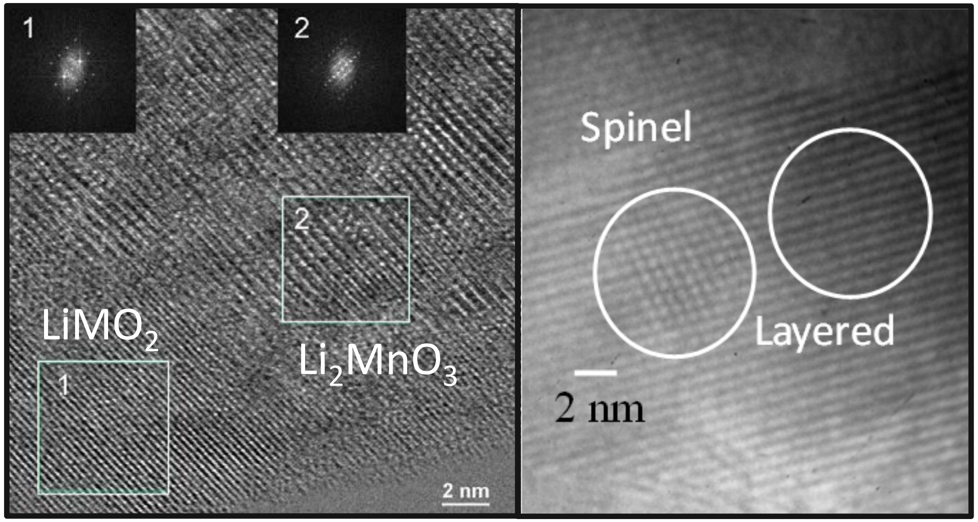


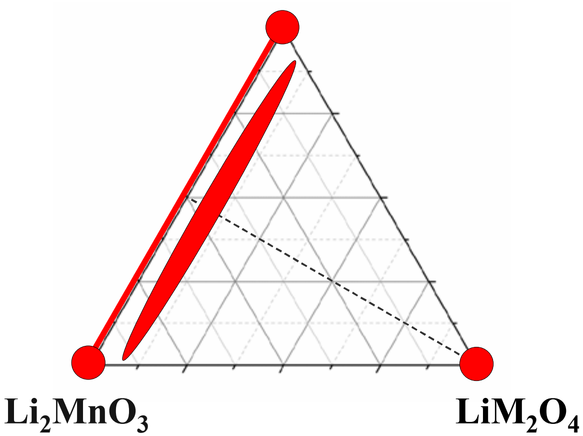
Stable performance
Low capacity

Low cost, high capacity
Not stable

High power
Low capacity

Unique pathways
& TM migration





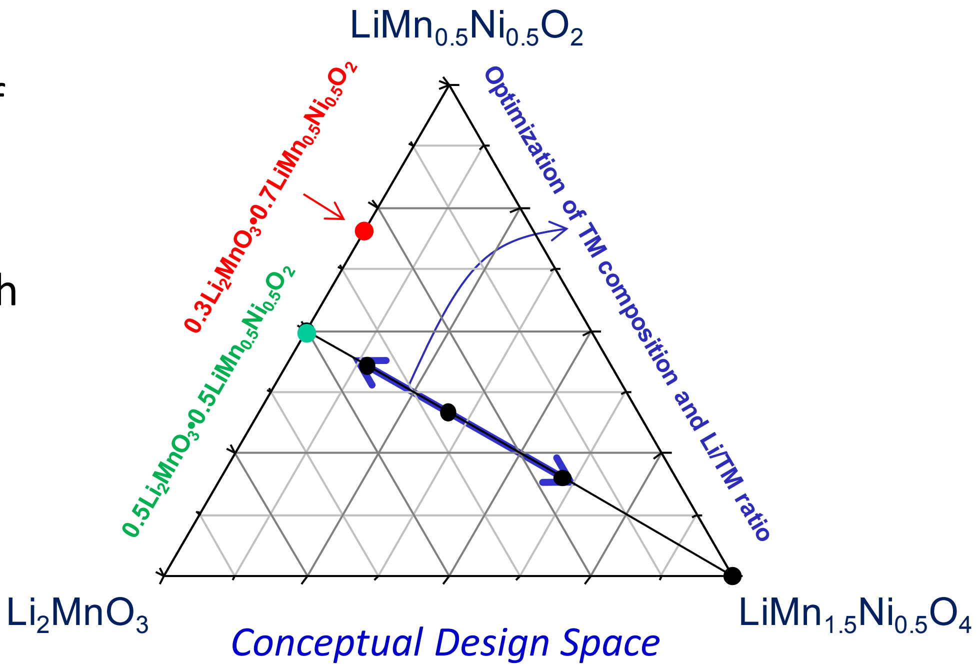
Conceptual Design Space

Approach "Baseline" pristine materials

- Composites of interest are intergrowths of prototypical cathode structures

- Structural *and* elemental composition each have an impact on performance

- Control and characterization of elemental compositions of the different, integrated motifs is challenging



- A systematic study of end-member and integrated composite structures is in progress to create "structural baselines"

- Baseline/model structures will be utilized for studies on cycled and working electrodes

End-goal: Structure-property relationships that lead to more robust cathode structures

Approach Powerful techniques → insights → materials design

Advanced Photon Source: Brightest source of X-rays in the Western Hemisphere

- X-ray absorption spectroscopy (XANES, EXAFS) – Element specific local/chemical info
- High resolution X-ray diffraction and PDF (HR-XRD) – short to long-range structures

Electron Microscopy Center: Electron beam microscopy and spectroscopy

- Chromatic-aberration corrected TEM – one of only 3 such instruments world-wide
- STEM/HAADF/EELS/EFI…sample prep (FIB-SEM)

ANL/LBNL: High performance computing for STEM

- Fusion – 320 node computing cluster within ANL's Computing Resource Center
- NERC – The National Energy Research Scientific Computing Center at LBNL

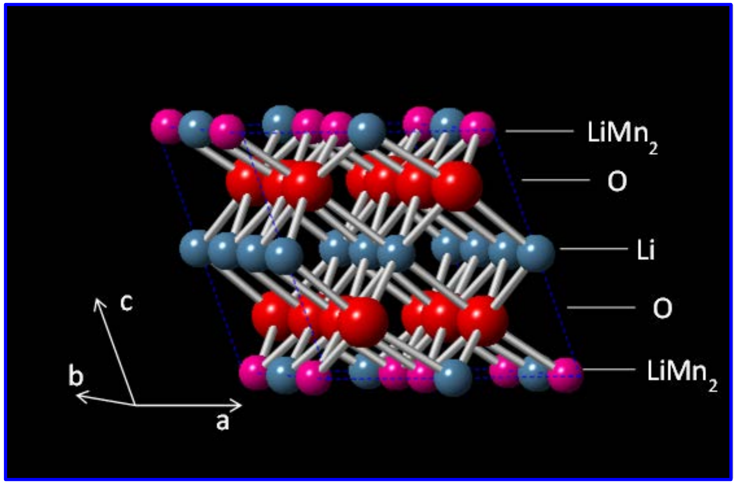
ISIS pulsed neutron source: Rutherford Appleton Laboratory, UK

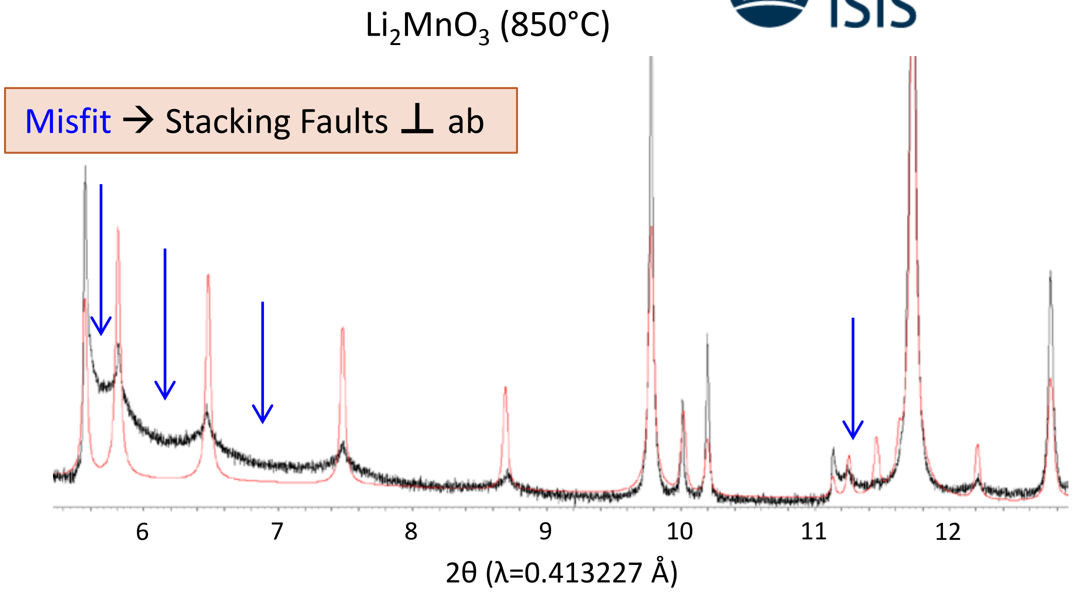
- Polaris – high intensity source, fast acquisition times, small sample volumes, in-situ
- Established international collaboration with leading experts (Prof. Bill David)

Other capabilities:

- ANL: Post-test Facility, MERF, NMR, Raman…Northwestern: NUANCE (Prof. V. Dravid)

Progress Li_2MnO_3 end-member





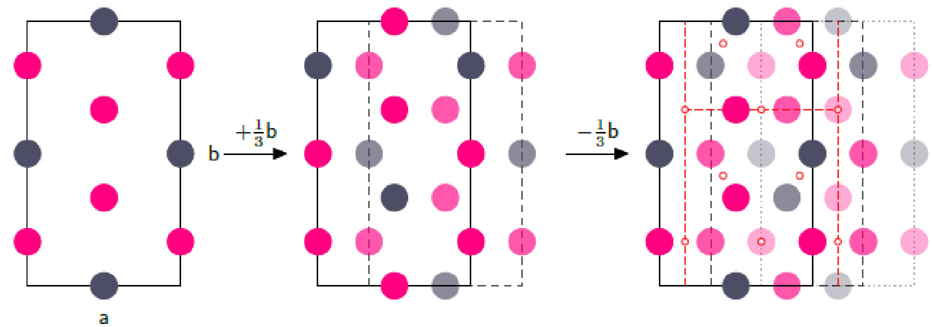
- Standard Rietveld analysis of Li_2MnO_3 end-member does not capture stacking faults
- So-called superstructure peaks complicate analysis of integrated materials
- Stacking faults further complicate analysis and a fitting model is being explored

Understanding stacking faults in Li_2MnO_3 will lead to better models for composite structures

Progress Li_2MnO_3 end-member

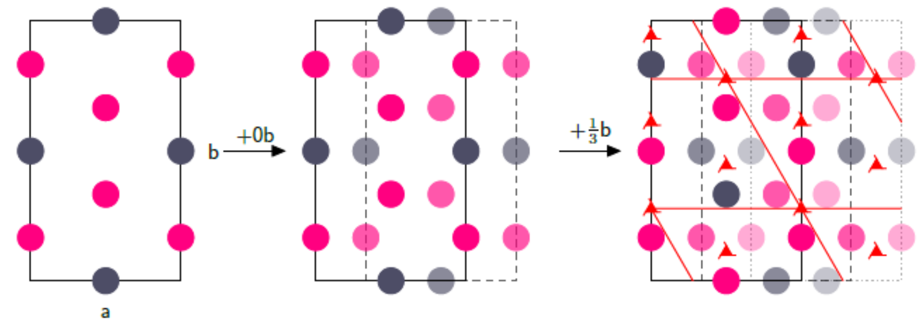
Simplest model considers layer-to-layer shifts of +⅓b, 0b, - ⅓b

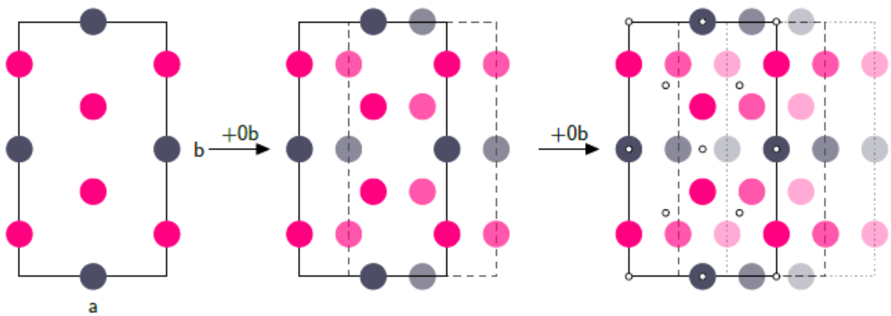
C2/c



Four possible, three-layer fault combinations give new unit cells

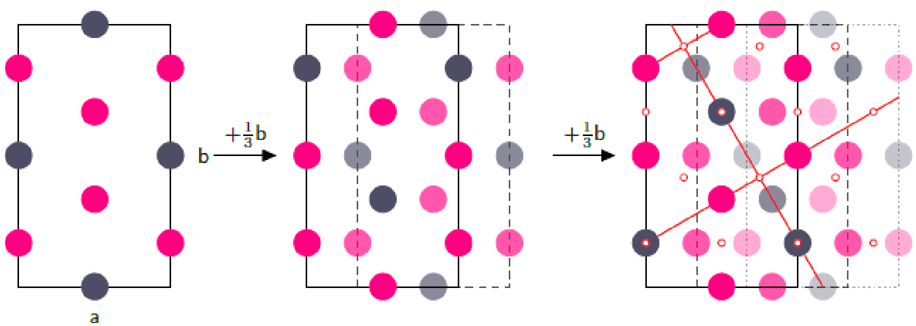
$P3_112$





C2/m

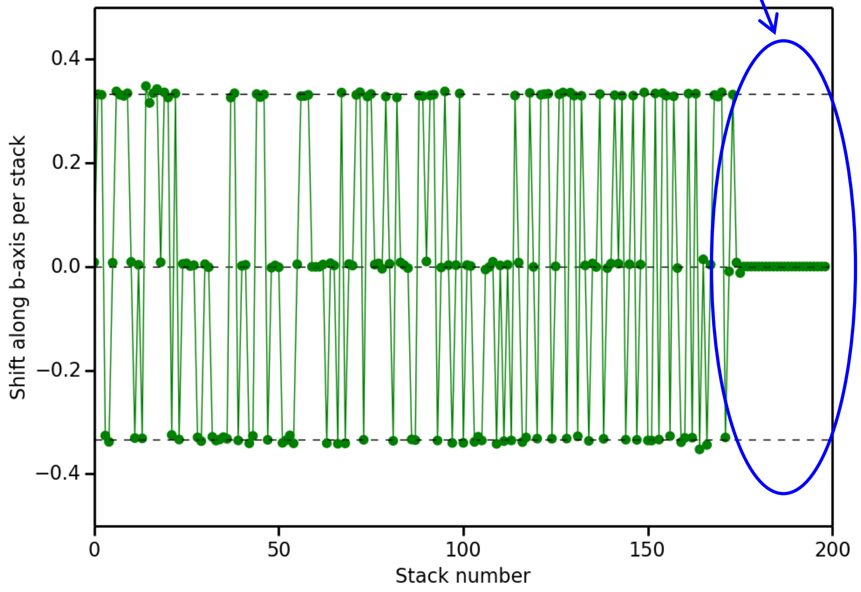
Fourth possibility returns ***C2/m*** with the ab plane reoriented by 120° w.r.t. original



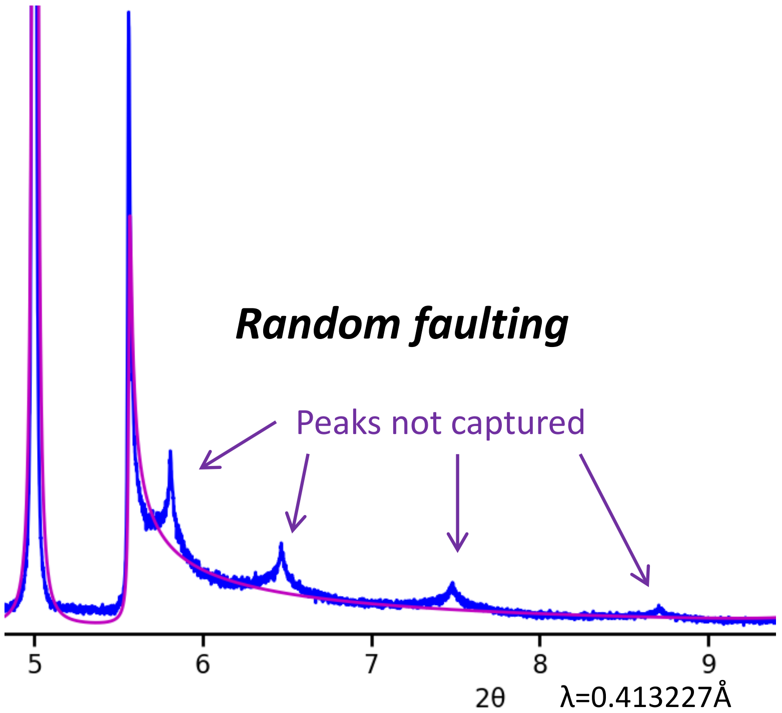
C2/m (120°)

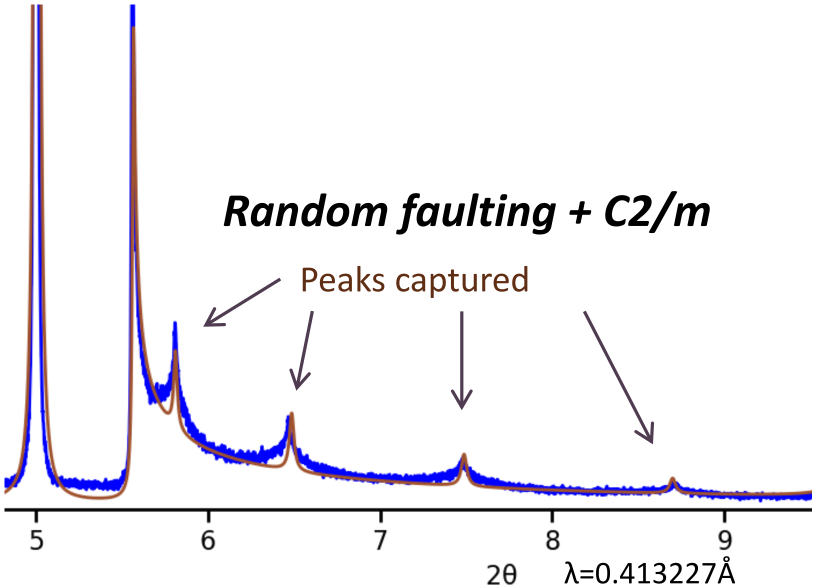
Progress Li_2MnO_3 end-member

- DIFFaX analysis shows that a randomly faulted ***C2/m*** structure fits diffuse background
- In order to capture ***C2/m*** peaks between 5-9, 2θ ~25% of the layers were given pure stacking along c axis

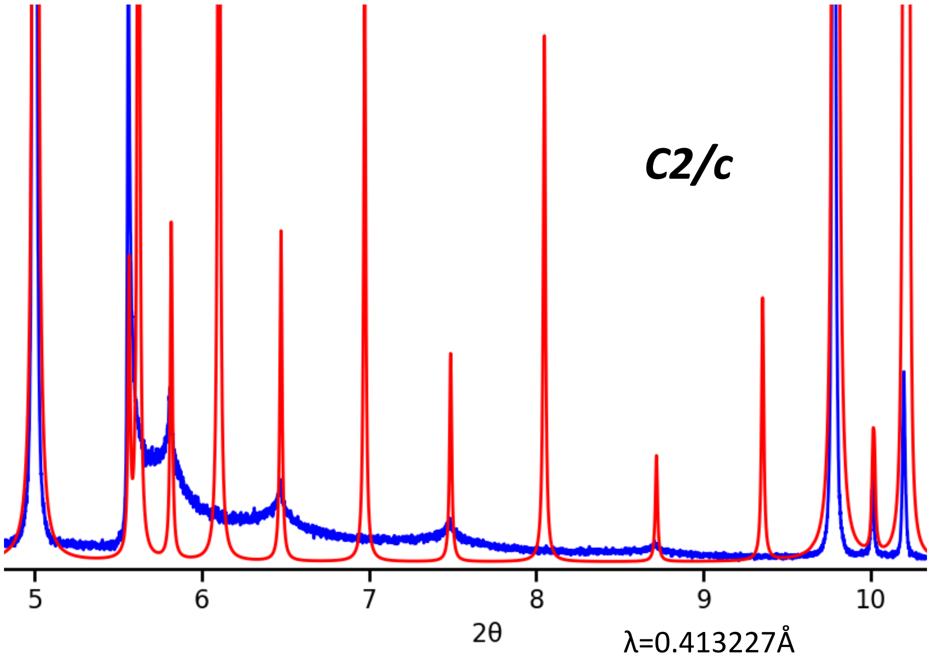


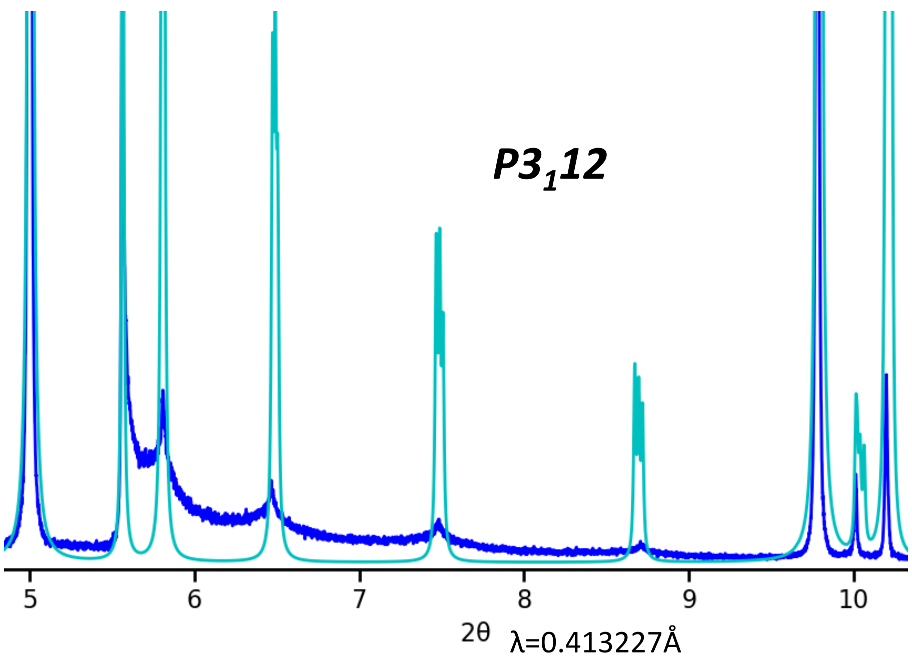
Model can give an indication of domain size





Progress Li_2MnO_3 end-member



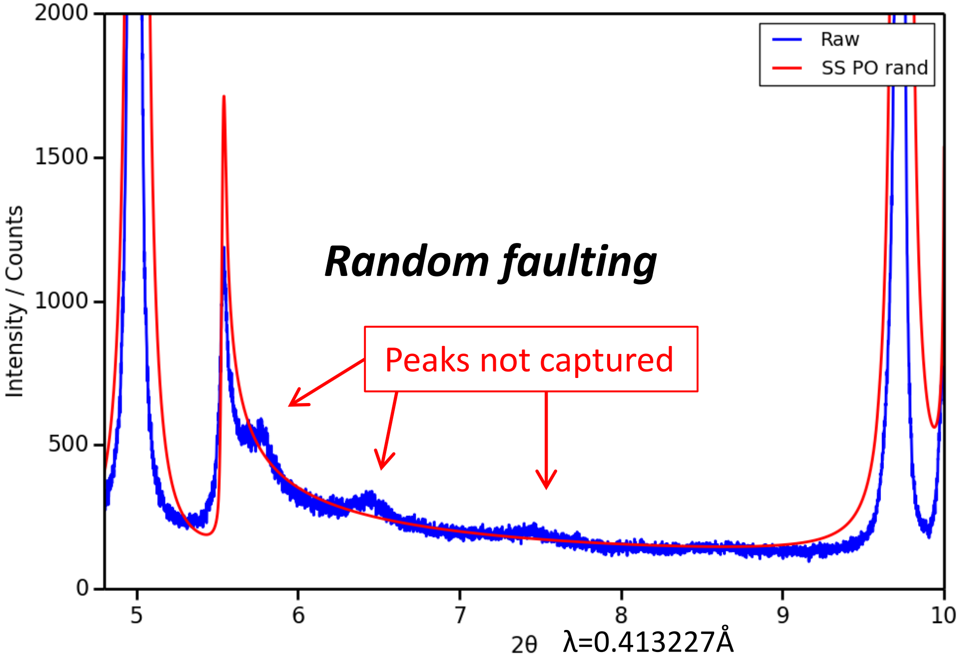


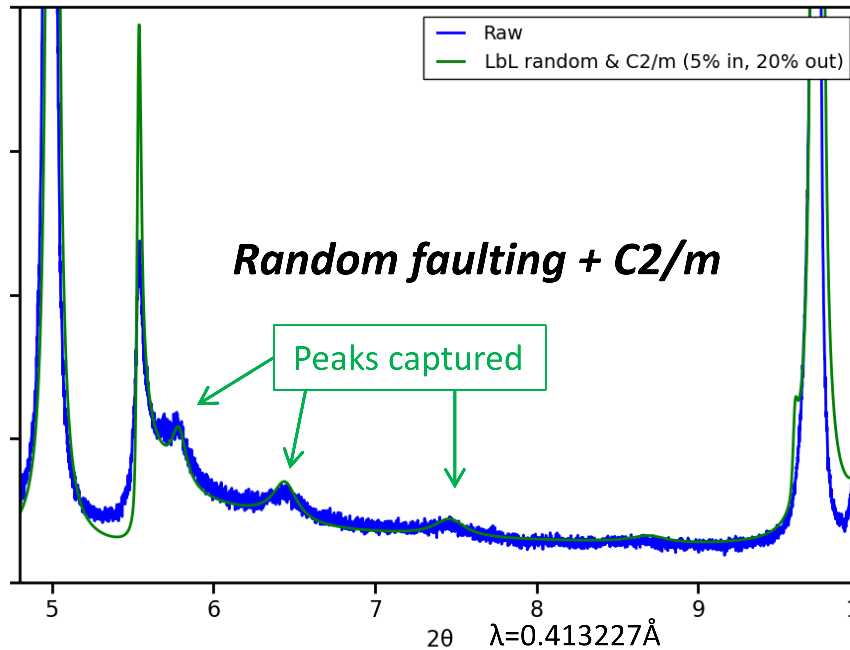
- ***C2/c*** and ***$P3_112$*** models give extra peaks that do not appear in the data

- ***C2/c*** and ***$P3_112$*** stacking do not exist over extended length scales

- Temperature dependence of faults in Li_2MnO_3 is currently being modeled

Progress $0.5Li_2MnO_3 \cdot 0.5LiMn_{0.5}Ni_{0.5}O_2$

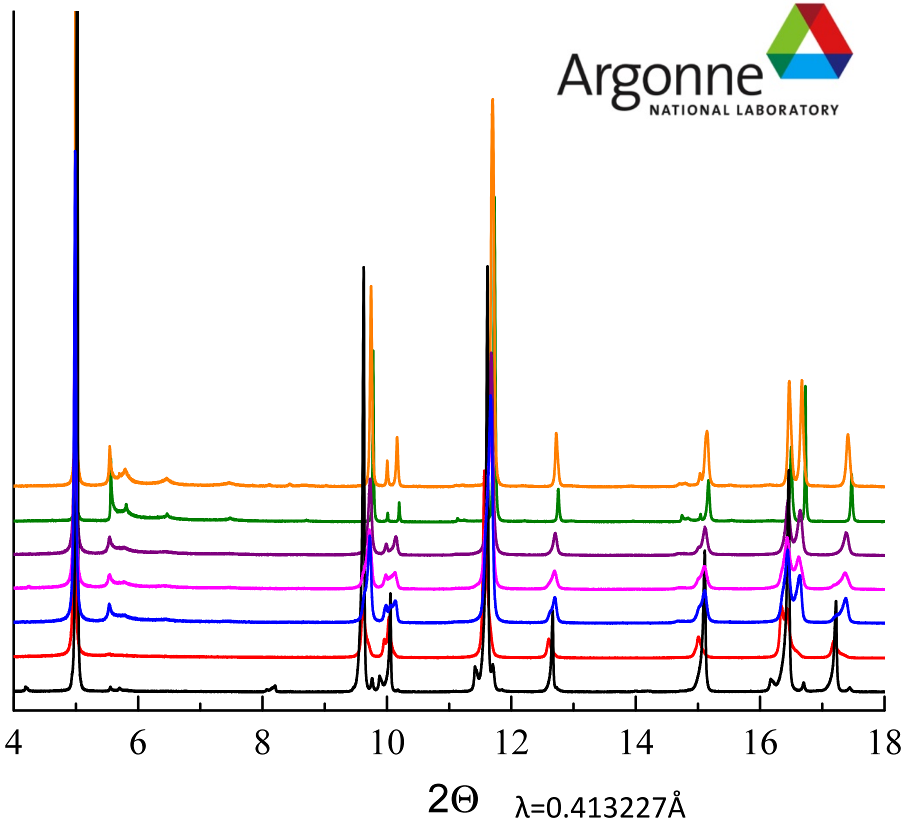


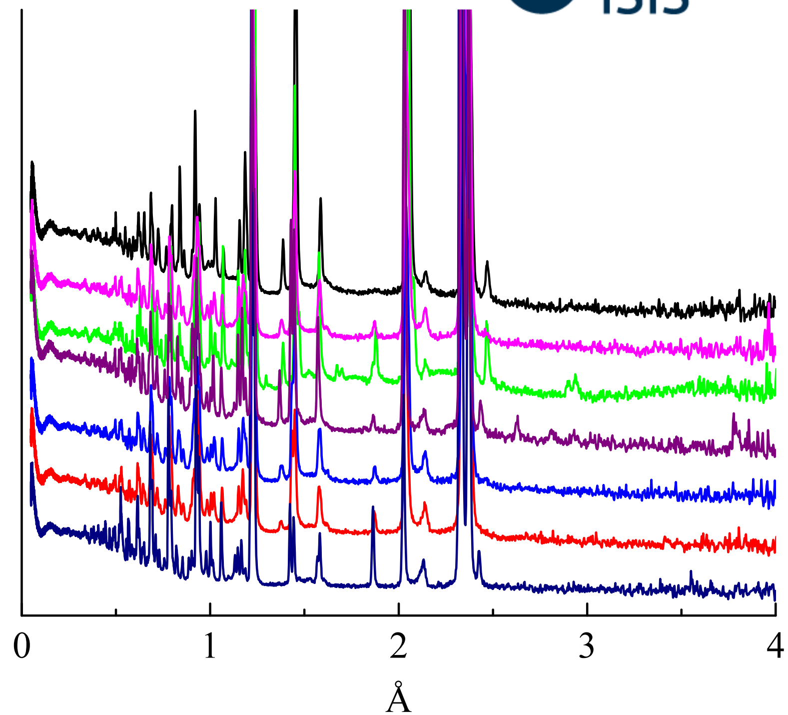


- As in Li_2MnO_3, composite structure requires some amount of coherent , ***C2/m*** stacking in order to capture peaks between 5-9, 2θ

- Different compositions and synthesis conditions are also under study

Progress Composite and end-member HR-XRD/neutron data

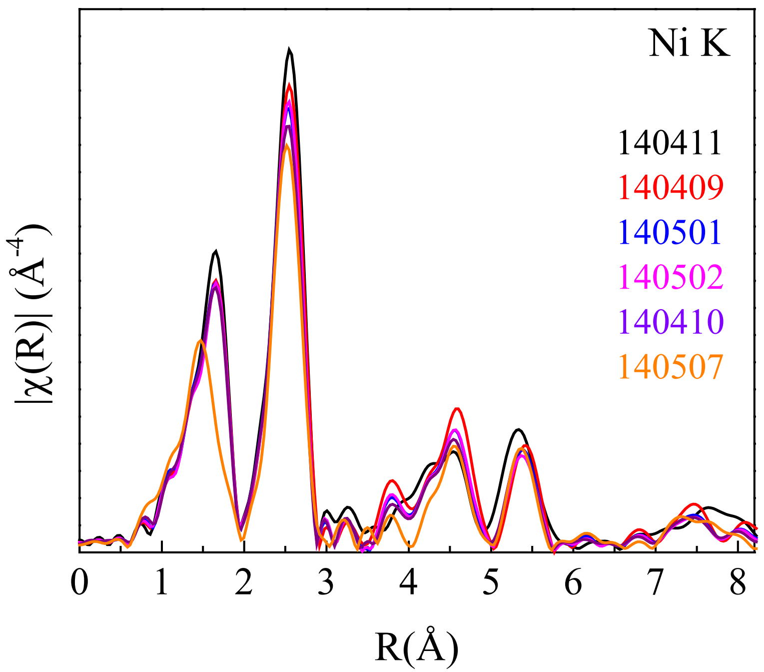


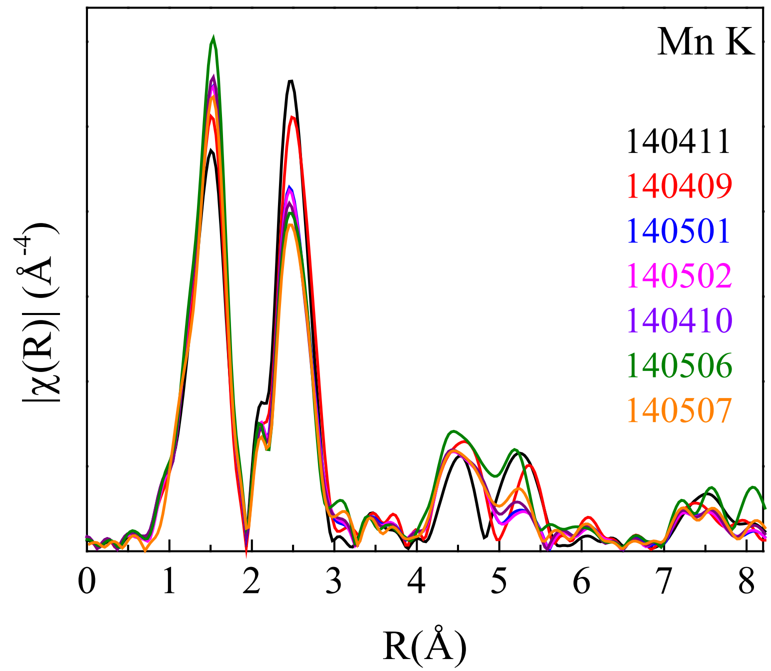


$x[yLi_2MnO_3 \bullet (1\text{-}y)LiMO_2] \bullet (1-x)[LiM_2O_4]$ (M=Mn, Ni, Co) $0 \leq x \geq 1$, $0 \leq y \geq 1$

- High resolution, synchrotron X-ray and neutron diffraction data have also been acquired for end-member and composite compounds of interest
- Analysis and modeling are ongoing

Progress Composite and end-member XAS





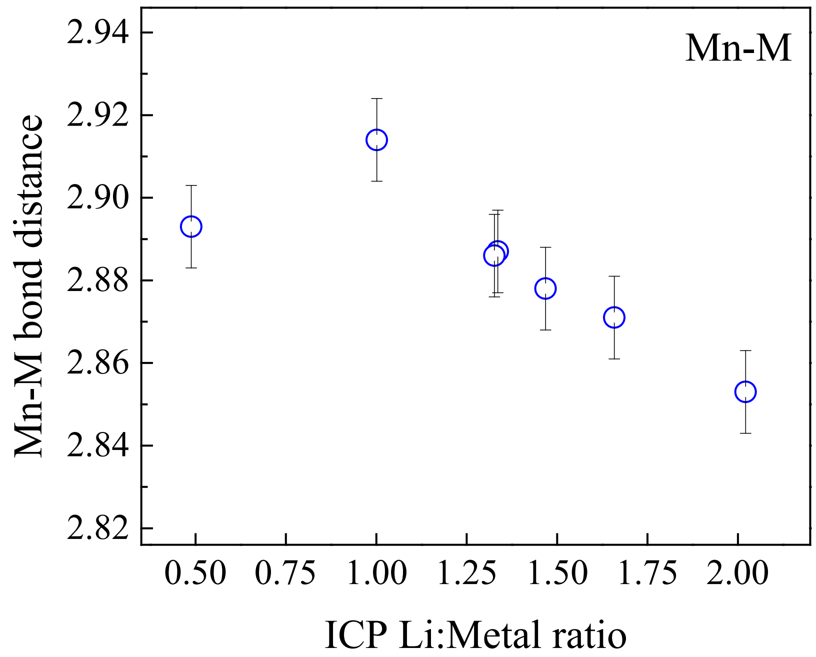
- Complementary XAS data have been *collected* and *analyzed* on composite and end-member compounds of interest (Advanced Photon Source, Argonne)
- Complementary neutron data have been *collected* at Rutherford Appleton Lab (ISIS, UK) on same set of compounds

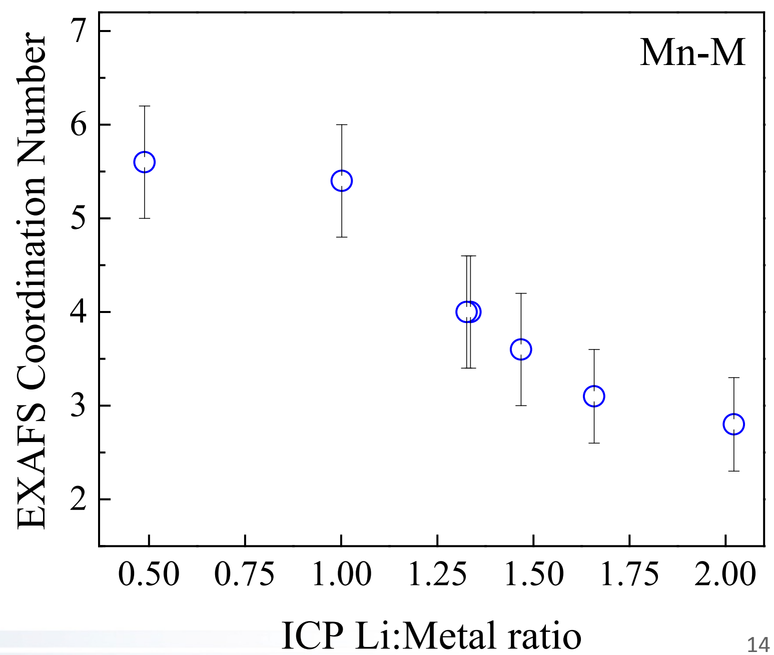
Progress Composite and end-member XAS

Sample ID	Layered notation	Li:M (ICP)
140411	$Li_{0.5}Mn_{0.75}Ni_{0.25}O_2$	0.49
140409	$LiMn_{0.5}Ni_{0.5}O_2$	1.00
140502	$Li_{1.15}Mn_{0.58}Ni_{0.27}O_2$	1.33
140501	$Li_{1.16}Mn_{0.58}Ni_{0.26}O_2$	1.34
140410	$Li_{1.2}Mn_{0.6}Ni_{0.2}O_2$	1.47
140507	$Li_2Mn_{0.65}Ni_{0.35}O_3$	1.66
140506	Li_2MnO_3	2.02

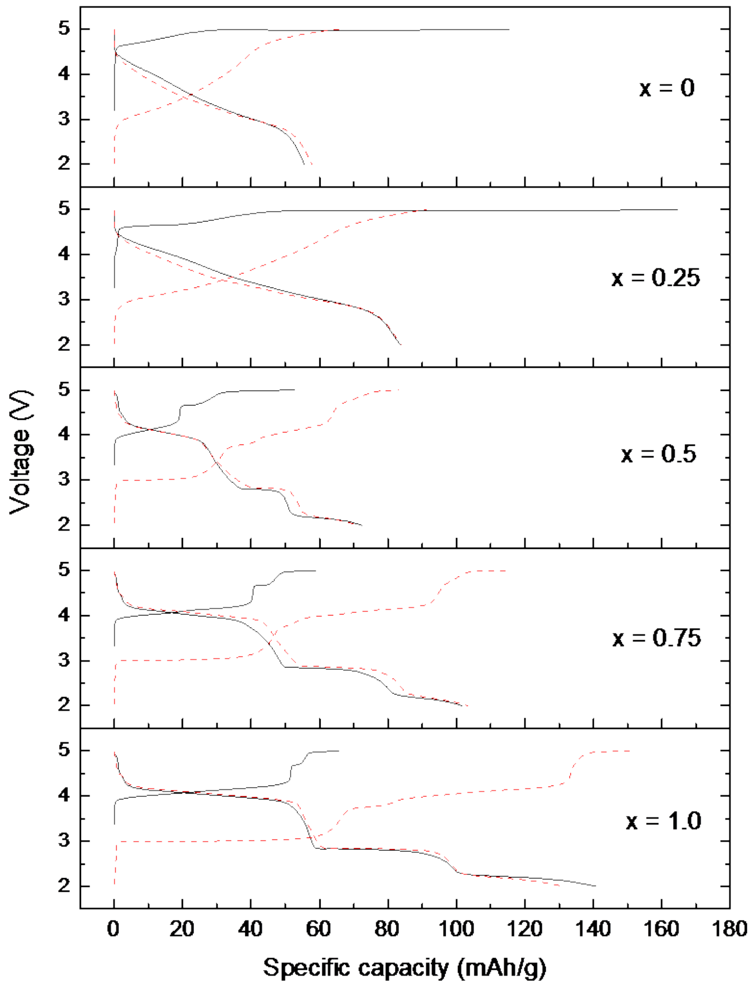
- ICP and XAS analysis give Metal-M/O coordination and bond distances as a function of Li:TM ratios

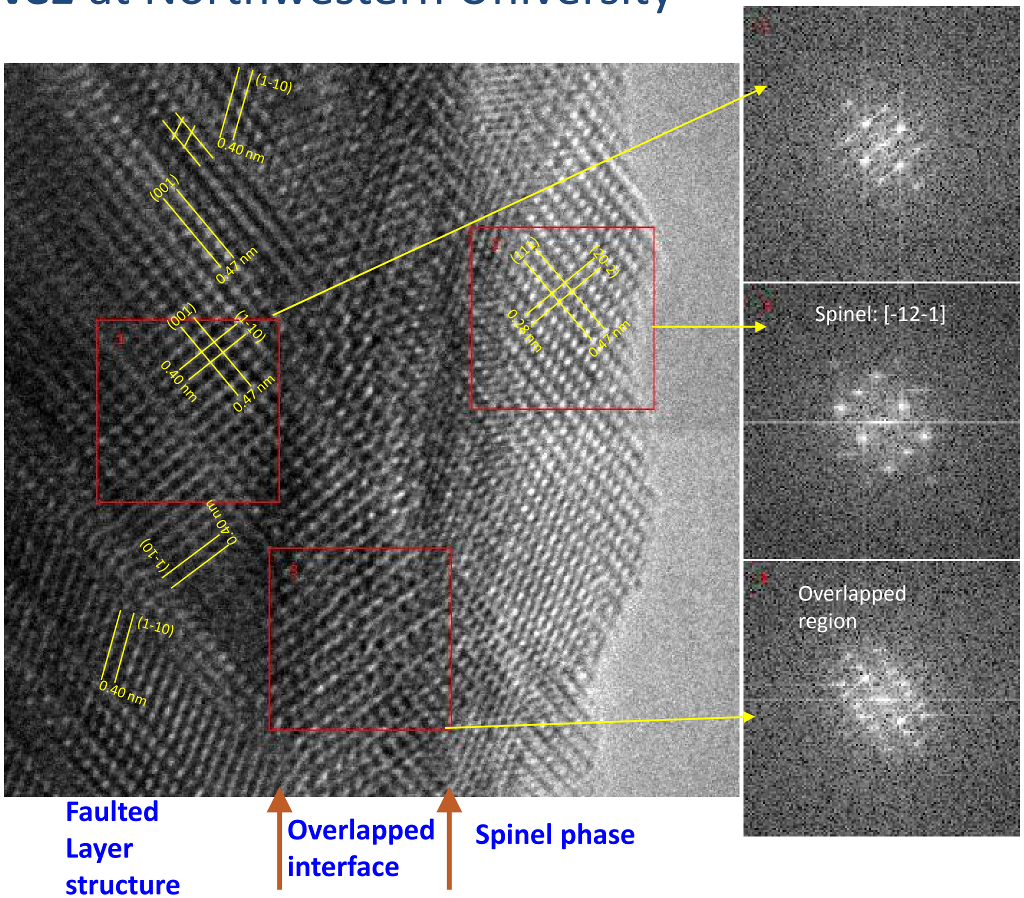
- Local information from XAS can be coupled with PDF and XRD for a more complete description of composite structures





Progress: Microscopy from ***NUANCE*** at Northwestern University

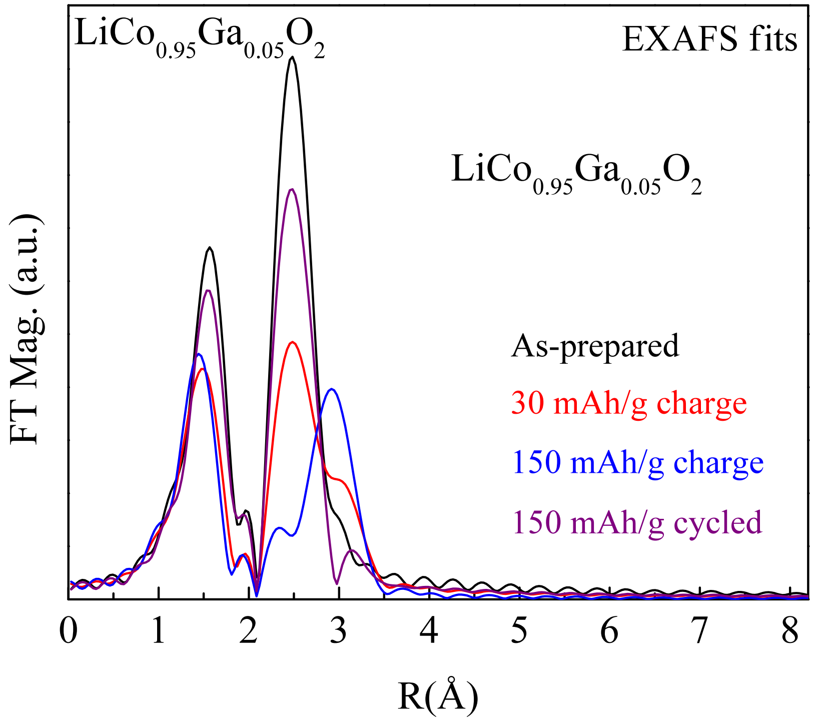


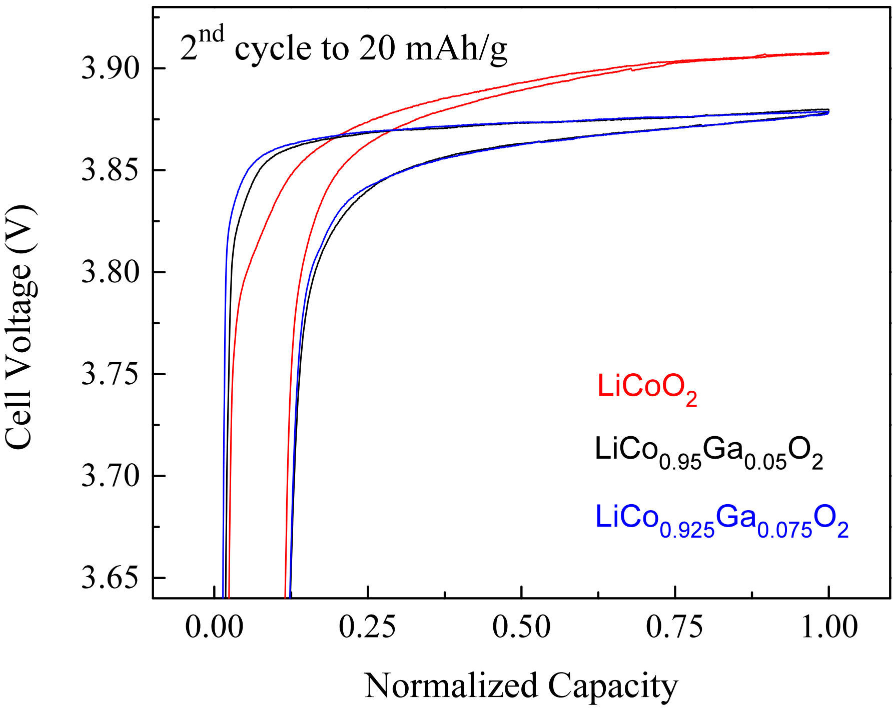


- Synthesis, electrochemistry, and microscopy combined to understand performance

- Intergrowth of two phases in $Li_{2-x}MnO_y$ (x=1) is observed determined by HRTEM

Progress: Active vs. non-active cation migration





- Ga migrates to tetrahedral sites immediately on charge, 60% at ~10% delithiation (30 mAh/g)
- Ga is not redox active but clearly alters electrochemical profiles during migration
- Variation in Metal-oxygen bonding may play a role?
- Others systems (active and non-active) currently under study by theory and experiment

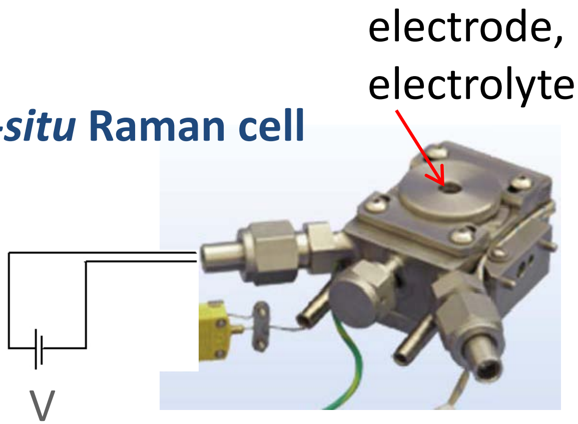
Progress: In-situ UV-vis tunable resonance Raman spectroscopy

***in-situ* resonance Raman spectroscopy**:

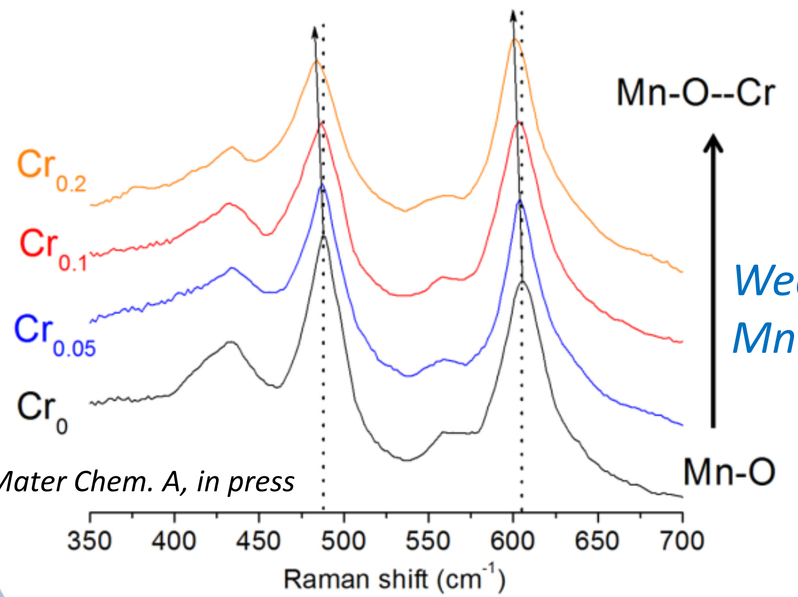
- High detection sensitivity
- Vibrational-electronic information

Battery research:

- Structural variation at the molecular level, Crystalline structure, Local disorder
- Change in bond length and angle
- *In-situ* study of electrode and electrolyte



LMR-NMC with Cr doping



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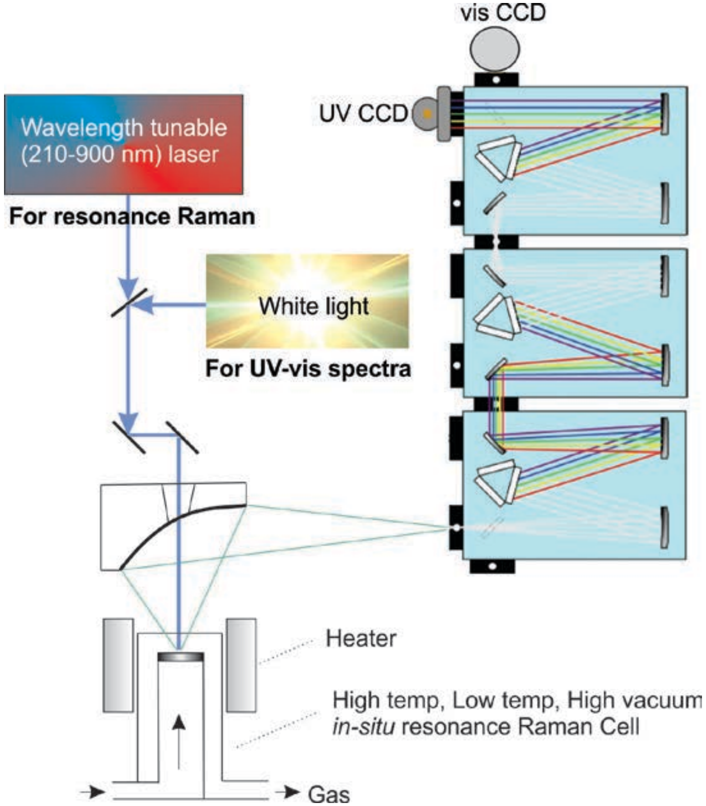
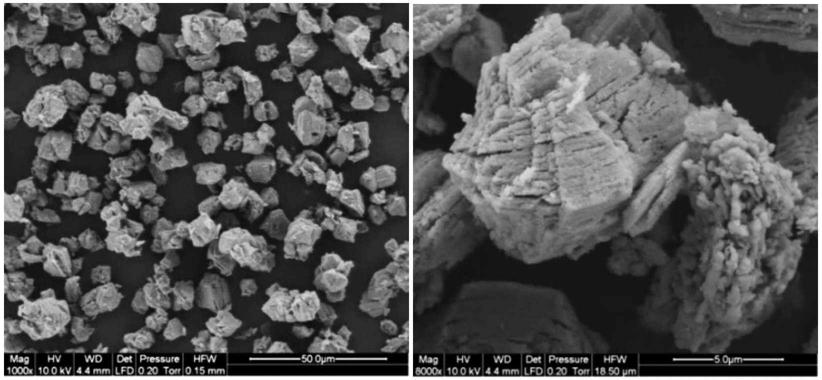
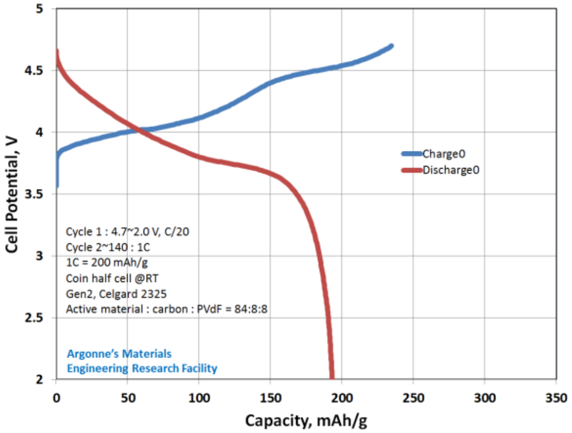


Progress: Collaboration with Argonne's MERF **(See M. Thackeray, ES049)**

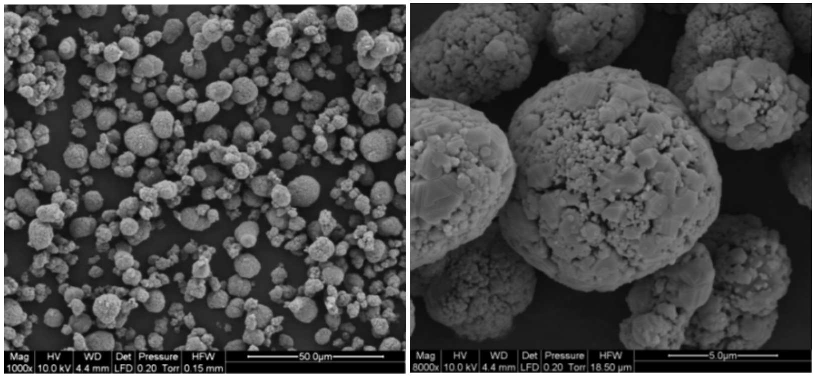
Target composition: 0.85 [0.25 Li_2MnO_3•0.75 $LiMn_{0.375}Ni_{0.375}Co_{0.25}O_2$]• 0.15 $Li_{0.5}M'O_2$

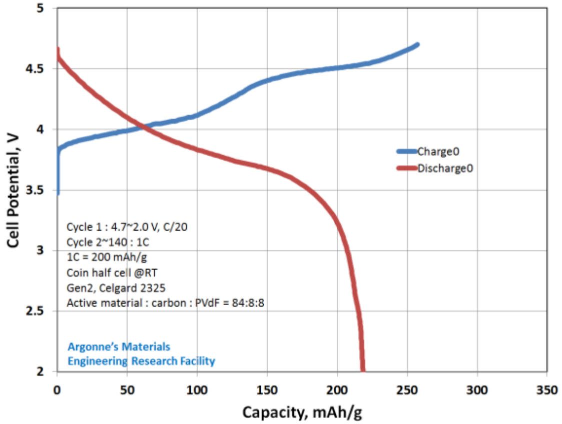
Bench-scale material 1st disch. capacity = 193 mAh/g





Pre-pilot (scale-up) material 1st disch. capacity = 218 mAh/g



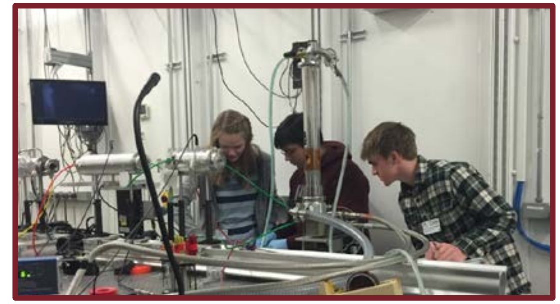


- Promising composite materials have been scaled up for further testing and analysis

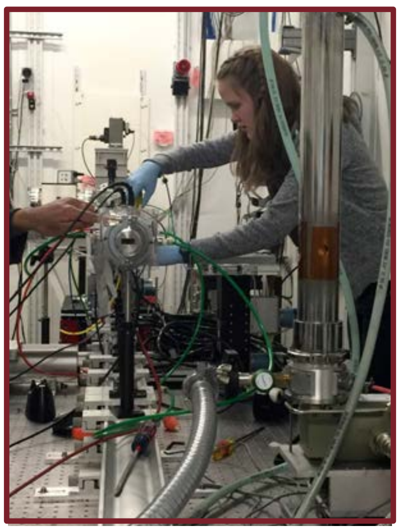
- Argonne's MERF facility is engineering improved materials based on bench-scale designs

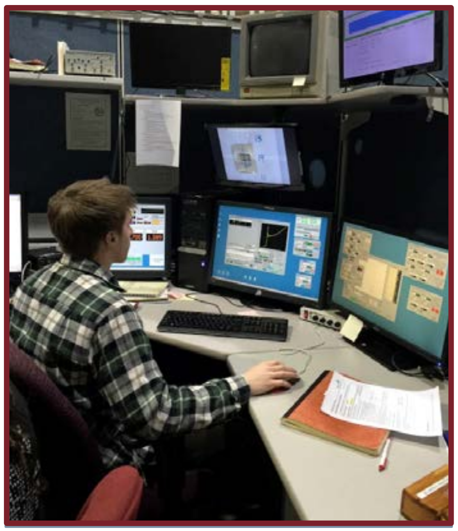
Progress: Outreach and Education

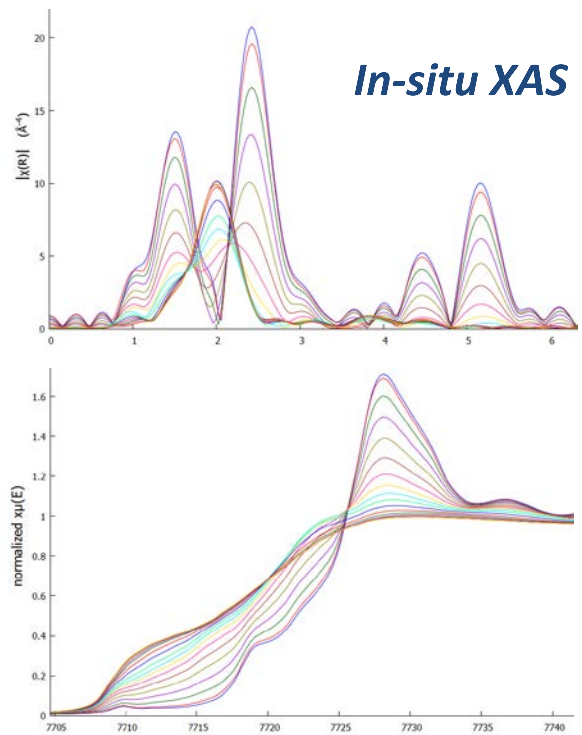
Exemplary Student Research Project



- Using the Advanced Photon Source, local high school students and teachers work with Argonne scientists to:
  - Prepare a proposal
  - Design an experiment
  - Set up the experiment, gather and analyze data
  - ***Present results at the annual User Meeting***







- Students designed an experiment to look at various TM species under certain electrochemical conditions – *results to be presented at the 2015 User Meeting*

Future work planned

- Continue to provide comprehensive analytical and characterization support for materials synthesis and design initiatives, with a prime focus on layered-layered-spinel electrode systems

- Complete stacking fault modeling on end-member and composite electrode structures

- Use theory and modeling to support experimental observations of transition metal migration in lithium-metal-oxide electrodes, and find ways to suppress or eliminate the migration

- Design improved high capacity cathode materials through knowledge gained from characterization/diagnostic studies

Summary

- Integrated, composite structures show promise for near-term advancements with respect to lithium-ion cathodes – *design space is large and complex*

- Expert personnel and Advanced characterization techniques have been brought together for the purpose of a better understanding of design considerations

- End-member and composite compositions within this complex space are being thoroughly studied in concert by:

  - High Resolution Synchrotron X-ray Diffraction
  - Neutron Diffraction
  - X-ray Absorption Spectroscopy
  - Electron Microscopy
  - UV-vis Tunable Resonance Raman
  - Theory and Modeling

- This "baseline" knowledge of pristine structures will be used to understand the structure-property relationships of complex, integrated electrode materials

Acknowledgments

Support for this work from the BMR Program, Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Tien Duong, David Howell