# Processing and Characterization of High Capacity Composite Electrode Structures

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*Chemical Sciences and Engineering Division*
*Argonne National Laboratory*

*Annual Merit Review*
*DOE Vehicle Technologies Program*
*Washington, DC*
*6-10 June, 2016*

**ES235**

# Overview

## Timeline

- Start date: FY16
- End date: FY18
- Percent complete:
  - 15%

## Budget

- Total project funding
  - 100% DOE
- Funding in FY16:  $300K

## Barriers

- Low energy density
- Cost
- Abuse tolerance limitations

## Partners

- Lead PI: Michael Thackeray, Co-PI: Jason R. Croy
- Collaborators:
  - CSE, Argonne: Bryan Yonemoto, Joong Sun Park, Eungje Lee, Roy Benedek
  - APS: Mali Balasubramanian (XAS)
  - ES: Greg Krumdick, Young-Ho Shin (Processing)
  - ORNL: Debasish Mohanty (ND)
  - PNNL: Chongmin Wang (TEM)
  - Northwestern University:  Vinayak Dravid (TEM), Chris Wolverton (Theory)
  - Industry:  Argonne licensees and collaborators

# Objectives

- Explore the fundamental, atomic-scale processes that are most relevant to the challenges of next-generation, energy-storage technologies, in particular, high capacity structurally-integrated electrode materials.

- Capitalize on a broad range of facilities to advance the field through cutting-edge science, collaborations, and multi-disciplinary efforts to characterize and model structurally-integrated electrode systems, notably those with both layered and spinel character.

# Milestones (FY16)

- Characterize bulk and surface properties of structurally-integrated electrode materials using DOE's User Facilities at Argonne (APS, EMC and ALCF) and facilities elsewhere, e.g., neutron spallation sources at SNS (Oak Ridge) and the NUANCE characterization center (Northwestern University). (Sept-16).

- Use complementary theoretical approaches to further the understanding of the structural and electrochemical properties of layered-spinel electrodes and protective surface layers (Sept-16).

- Analysis, interpretation, and dissemination of collected data for publication and presentation. (Sept-16).

# **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

***EMC/PNNL/NUANCE***: 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

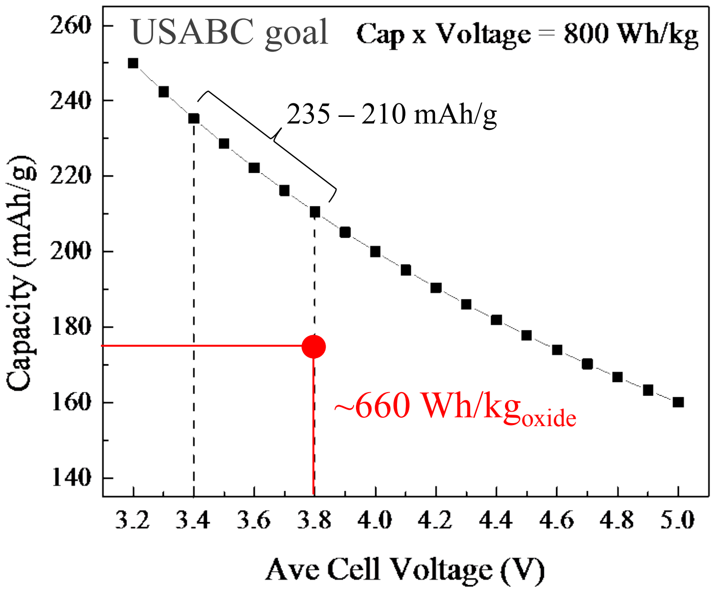
***ISIS pulsed neutron source***: Rutherford Appleton Laboratory, UK

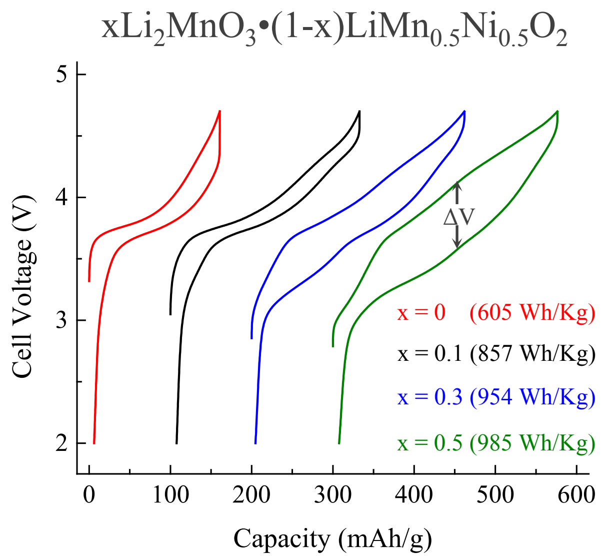
- Polaris – high intensity source, fast acquisition times, small sample volumes, in-situ
- Established international collaboration with leading experts (Prof. Bill David)

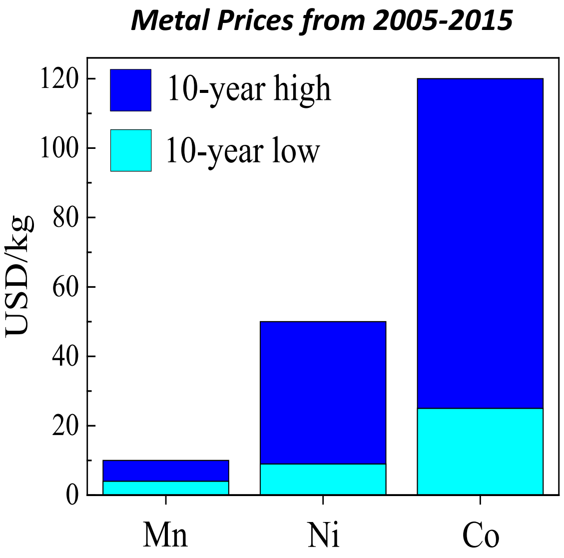
***Other capabilities***:

- ANL: Post-test Facility, MERF, NMR, Raman, theory (NU)…

# Relevance: High-Capacity, Low Cost Materials



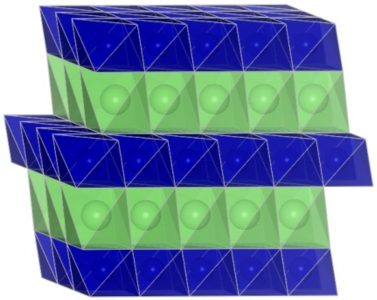




- Current lithium-ion cathodes deliver a cell energy that is limited to less than 700 Wh/kg$_{oxide}$ (●)
- Lithium- and ***manganese-rich*** cathodes can deliver considerably higher energies

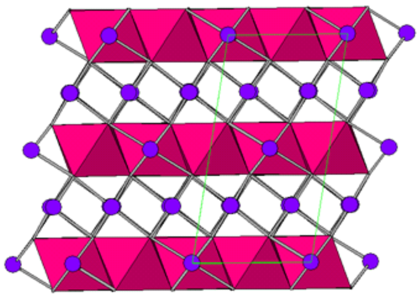
Complex atomic-scale processes govern performance and stability: Insights and understanding are critical to successful development

# Strategy

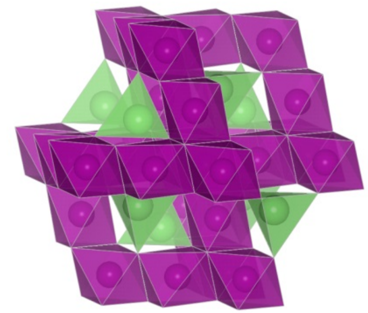
Embed spinel-type domains to stabilize layered-layered structures at high capacities



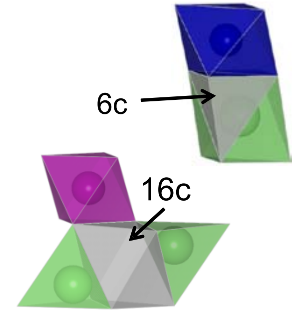
Stable performance
Low capacity



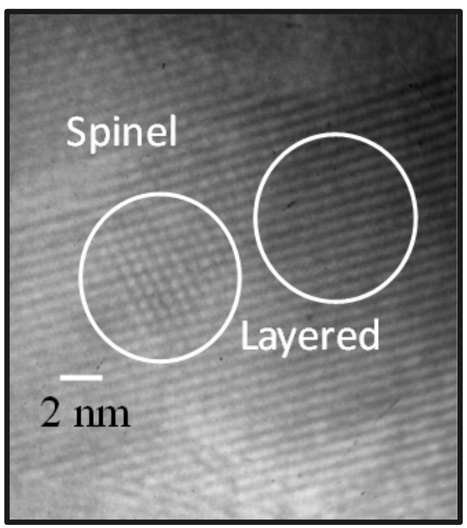
Low cost, high capacity
Not stable

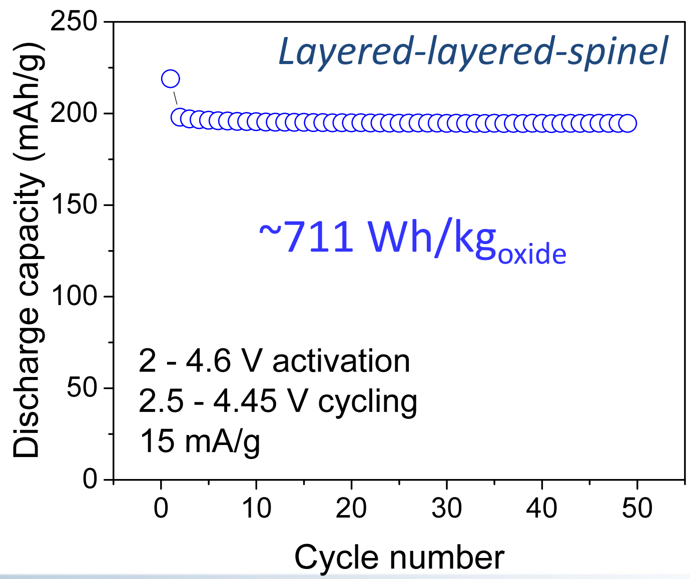


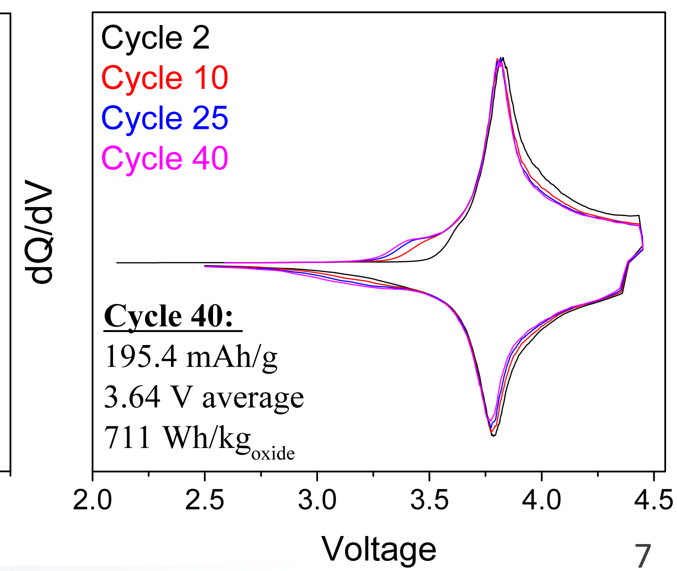
High power
Low capacity



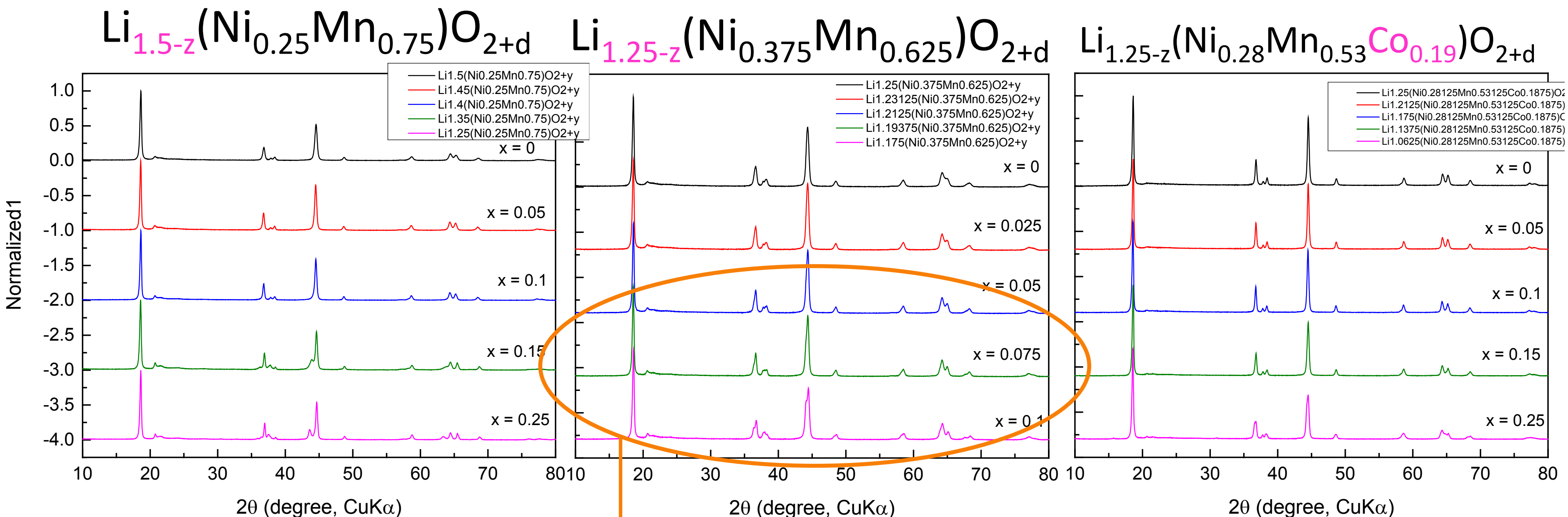

Unique pathways
& TM migration

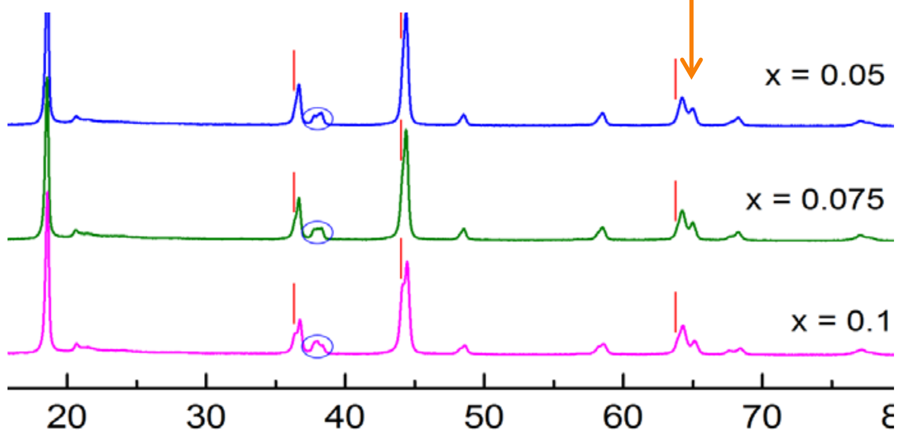


# Progress: Compositional Effects of “Spinel” Incorporation



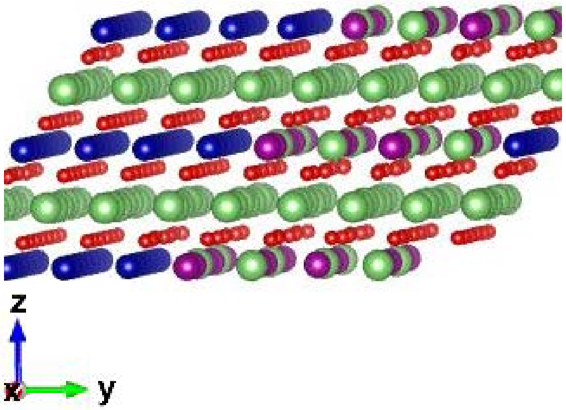




- New phase begins to appear between 0.05≤x≥0.1 (x=targeted spinel %)
- Different for different compositions
- Spinel & LiNiO-type phases can be hard to distinguish especially @ low %

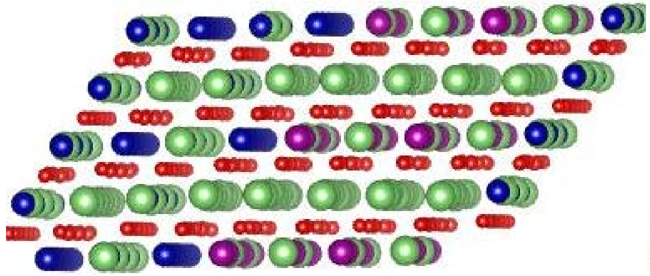
Spinel-type defects can be introduced into complex compositions – ND, TEM, X-ray studies are ongoing to correlate local domain structure with E-chemical performance

# Progress: Characterization of Spinel Components (see ES049)

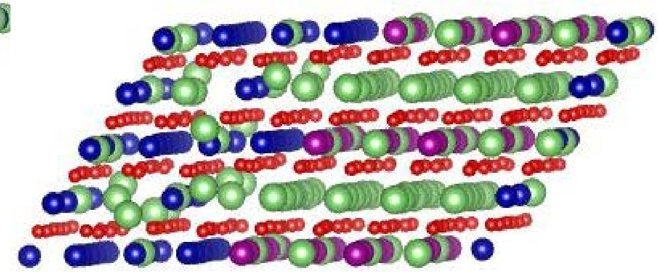
$LiCoO_2 \bullet Li_2MnO_3$




$Li_2Co_2O_4 \bullet Li_2MnO_3$



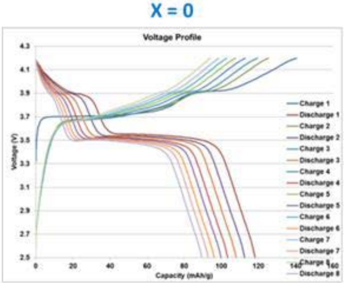
$Li_{2-x}Co_2O_4 \bullet Li_2MnO_3$



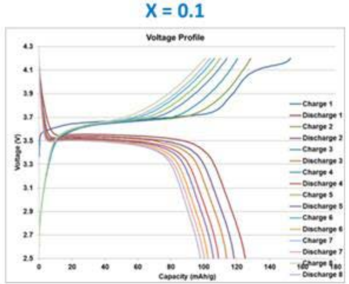
**Co: blue; Mn: purple; Li: green**

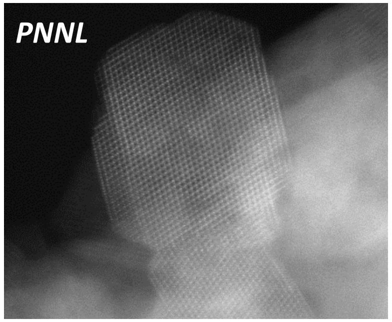
- Co-based spinels are being studied for possible integration into LLS materials (E. Lee)
- Simulations on the stability of model, composite systems are being explored (R. Benedek)
- Collaboration with Northwestern/PNNL – stability/synthesis of single spinel compounds $LiMnNi_xCo_{1-x}O_4$ – experiment and theory (S. Kim, E. Lee, C. Wolverton, C. Wang)

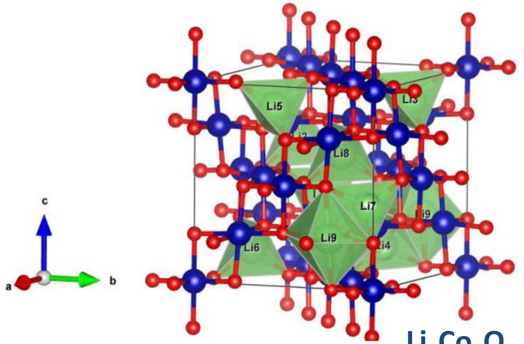
X = 0




X = 0.1



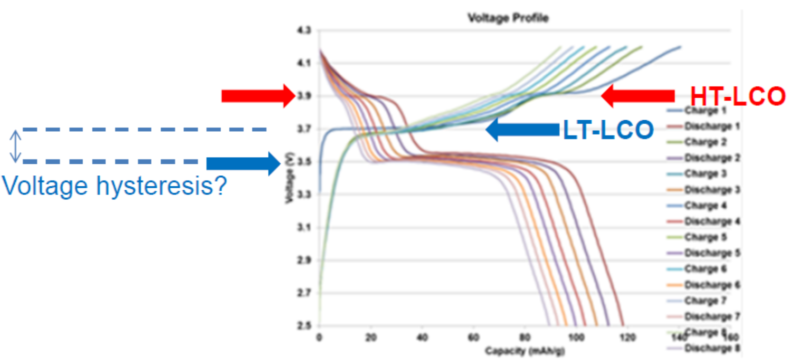

$Li_2Co_2O_4$

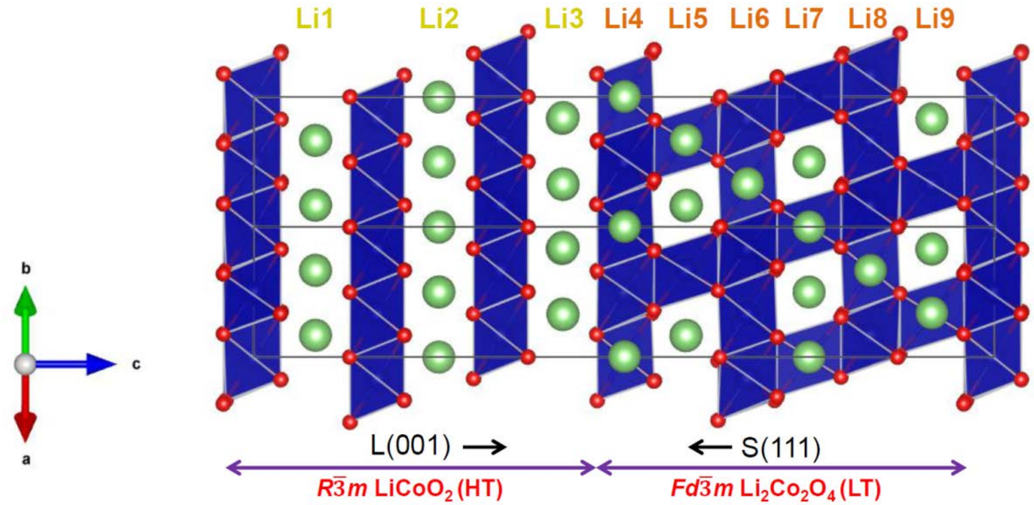
# Progress: Characterization of Spinel Components (see ES049)

**Table II.** Calculated *vs.* experimental voltages of LT-LCO and HT-LCO

| Voltage [V *vs.* Li/Li$^+$] | LT-LCO | HT-LCO |
|---|---|---|
| GGA + *U* | 3.31 | 3.58 |
| Charge (*experiment*) | ~3.7 | ~3.9 |
| Discharge (*experiment*) | ~3.5 | ~3.9 |

*** 0.2 ~ 0.3 V difference between theory and experiment*



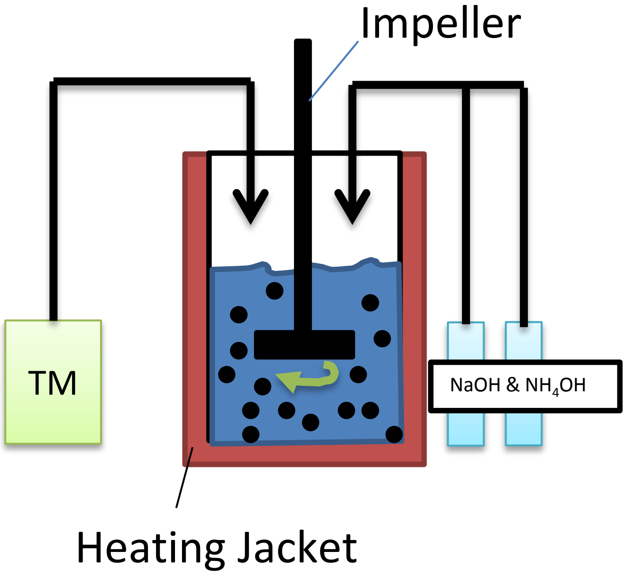

| Location | Li1 ~ Li3 | Li4 ~ Li9 |
|---|---|---|
| Voltage [V]** | 3.94 | 3.87 |

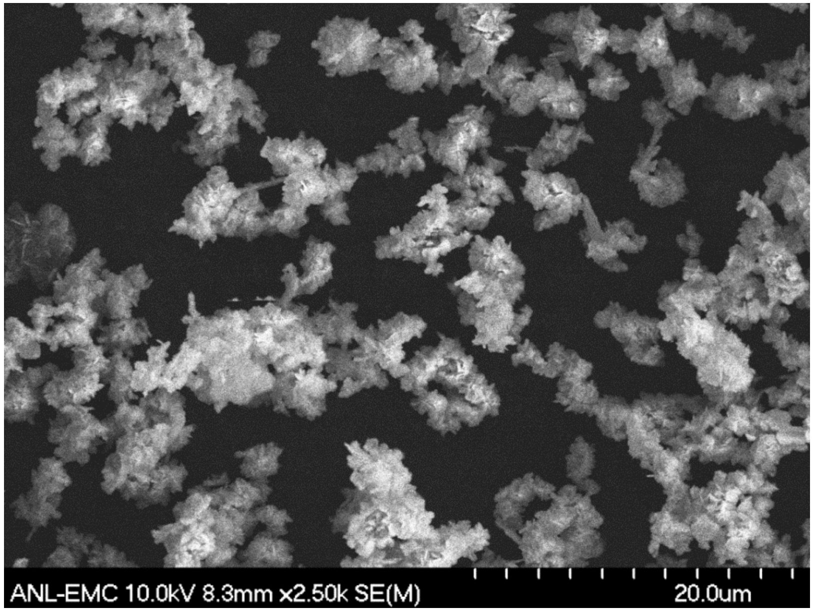
** 12 Li atoms were removed from HT- and LT-$Li_{24}Co_{24}O_{48}$ supercells, respectively.

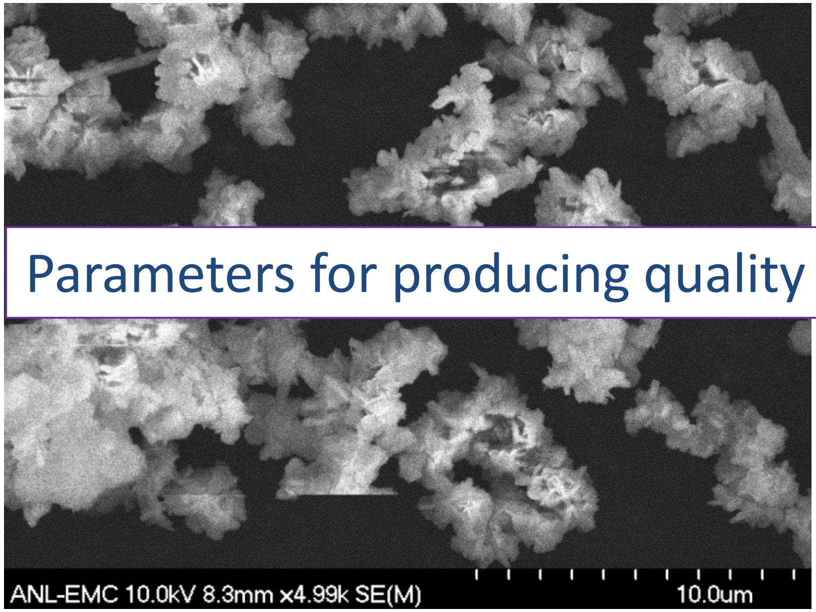
- Voltage profiles of Co-based, layered-spinel cathodes show distinct features
- Theory explains voltage profiles as an integration of LT-LCO and HT-LCO

Theory is being used to understand the E-chem of complex layered-spinel structures

# Progress: Processing Studies of High-Capacity LLS Materials



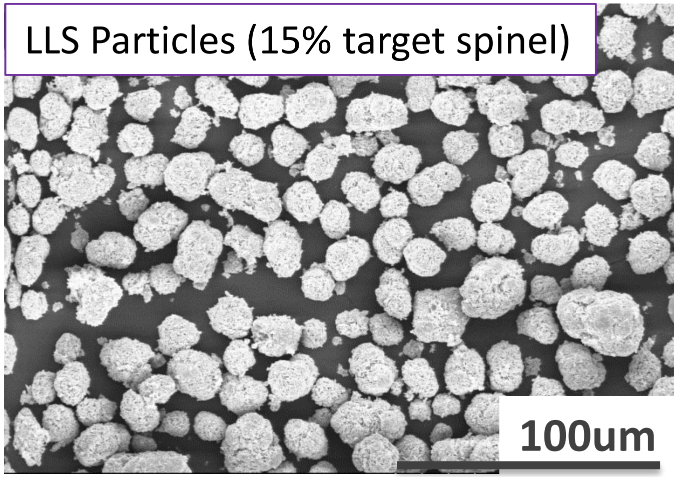



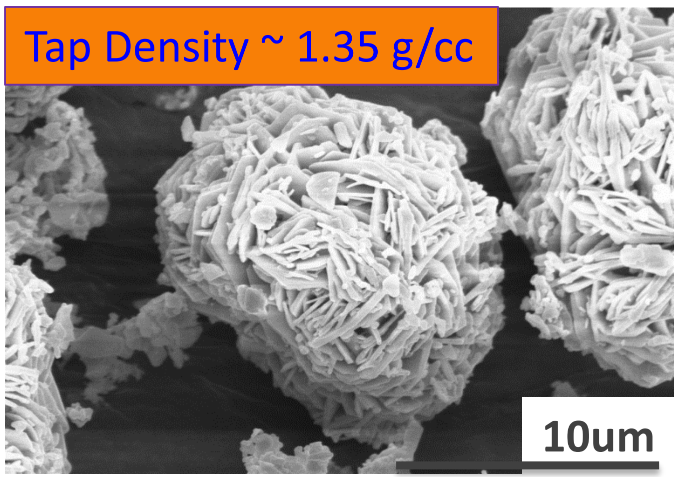



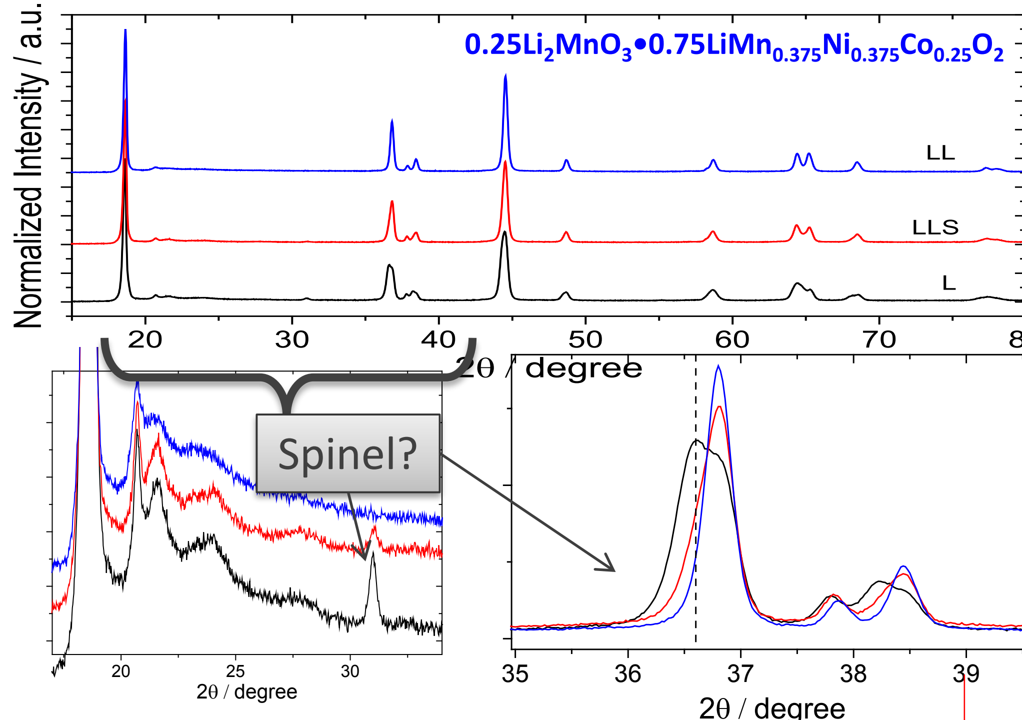


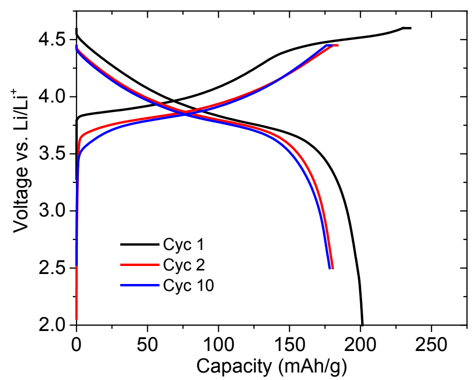
Parameters for producing quality LLS compositions are unexplored

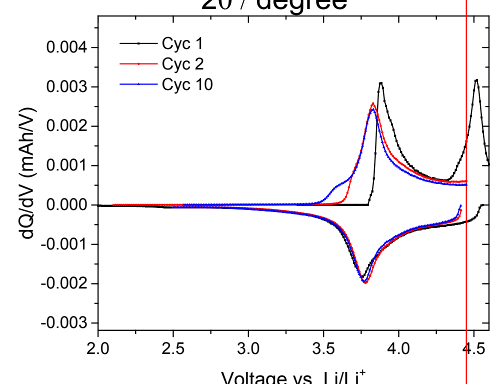
# Progress: Processing Studies of High-Capacity LLS Materials



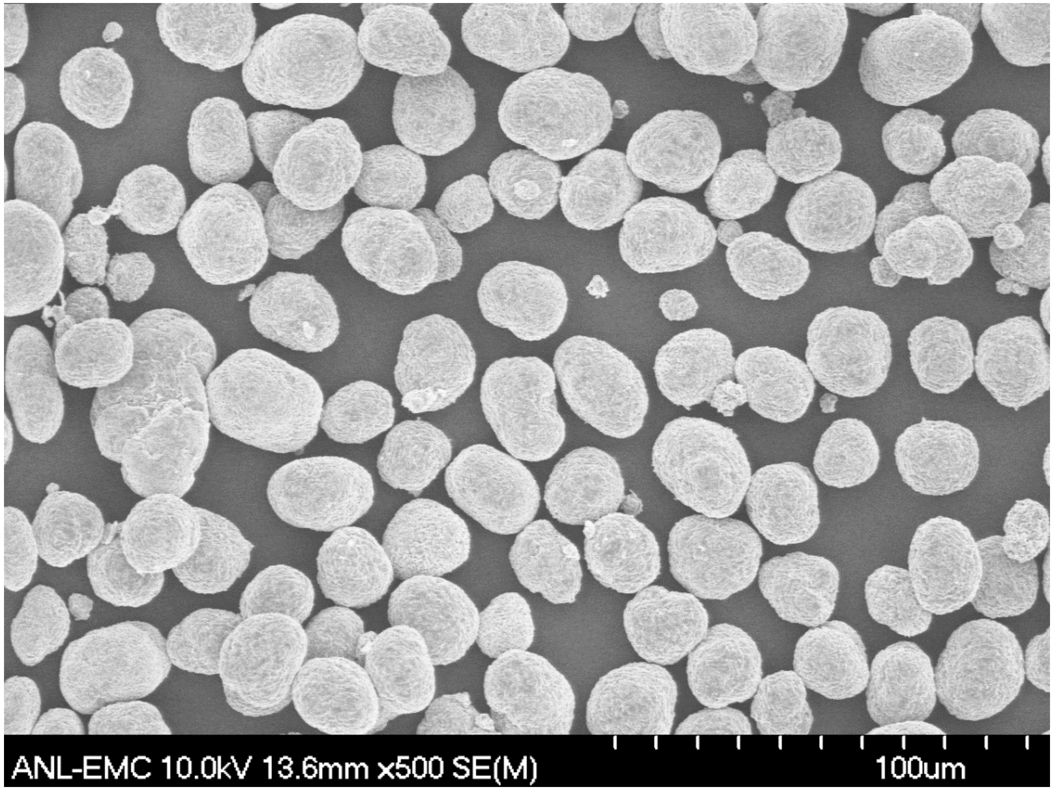



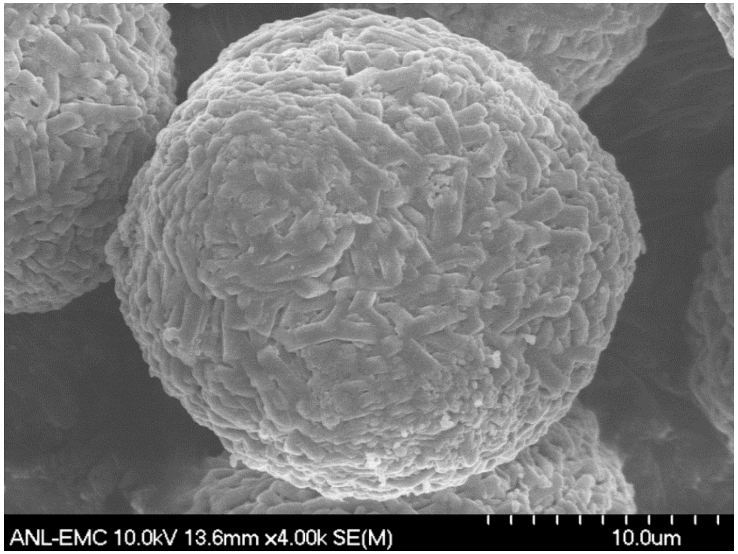



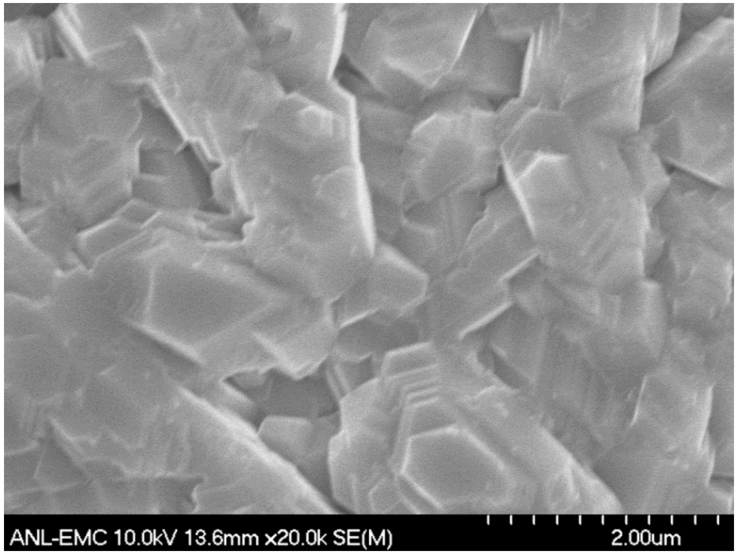




Progress quickly made in improving reactor conditions to produce LLS particles

# Progress: Processing Studies of High-Capacity LLS Materials



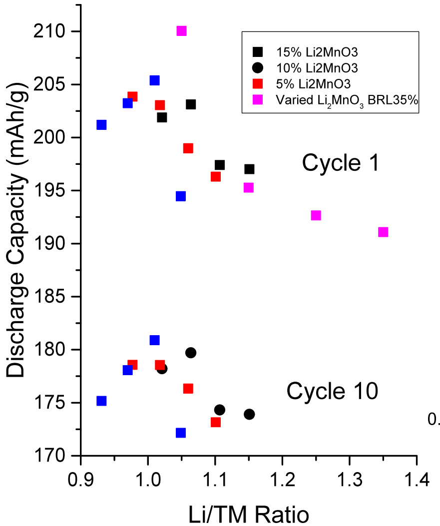



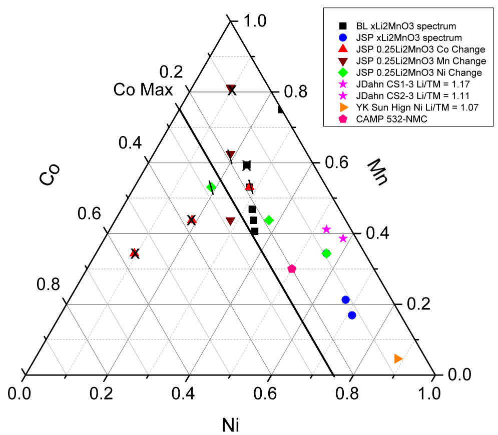

LLS cathode particles from a ~0.5 kg batch

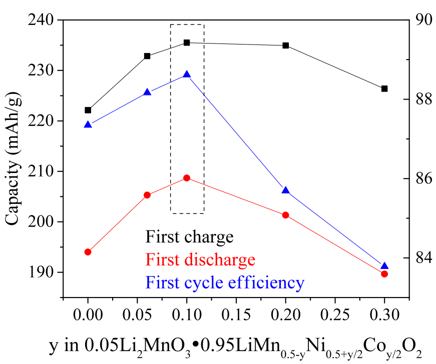
Tap Density ~2.25 g/cc

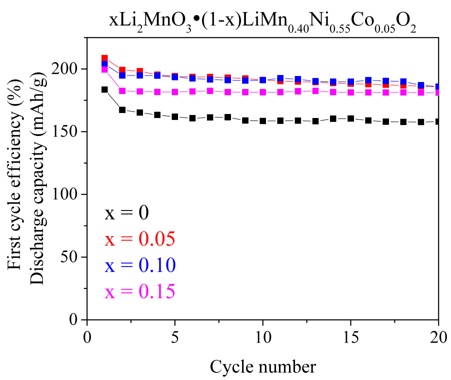
Further progress in producing high tap-density, LLS particles (0.5kg batches)

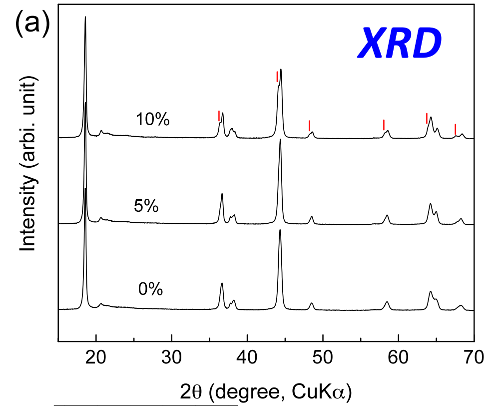
## Compositional Studies ⟷ Characterization Studies

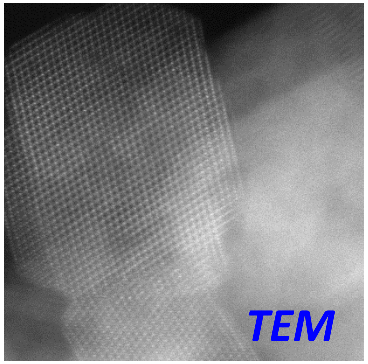


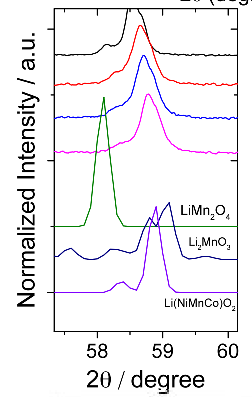



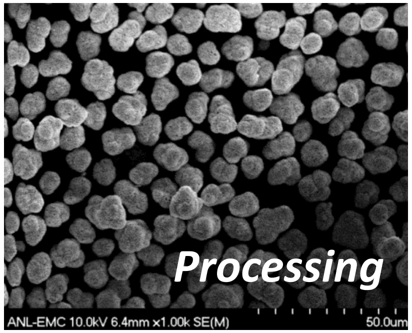



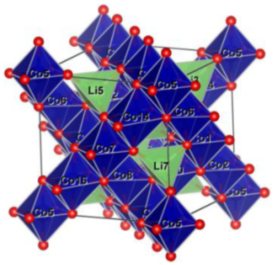



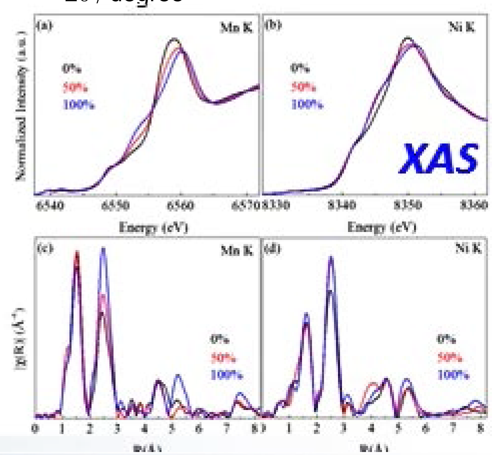



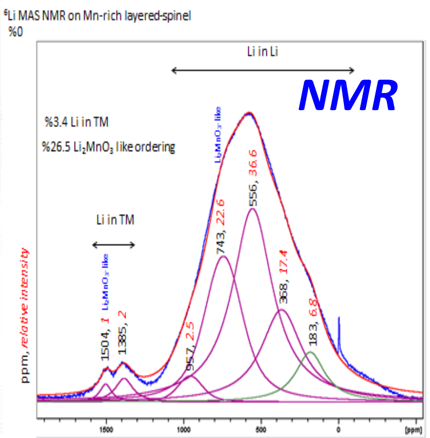



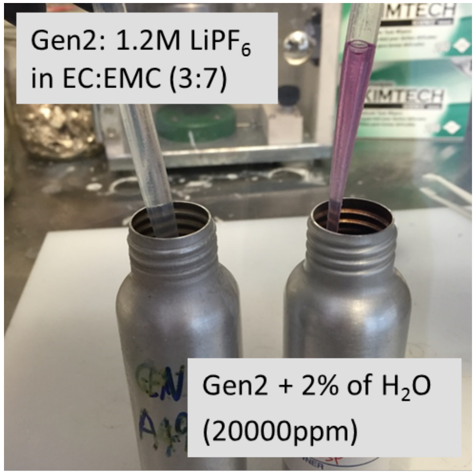



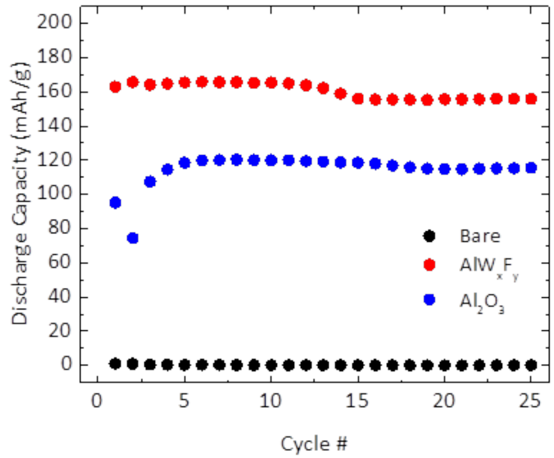




Major, ongoing effort between synthesis, electrochemical testing, and advanced characterization to understand, design, and produce high-energy LLS cathodes (see ES049)

# Progress: Surface or Near Surface Fabrication/Characterization

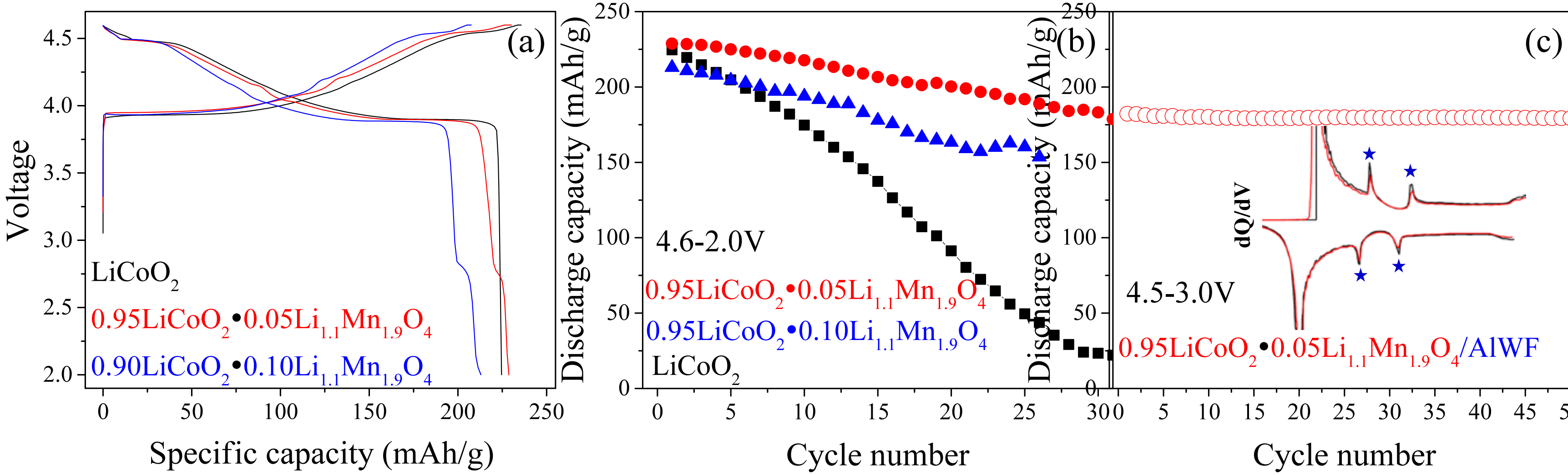
- Fluoride-based ALD Coatings on $LiCoO_2$ (baseline material)




- Cells were cycled (~25 cycles, 4.4-2.5V) with 20,000 ppm of water in the electrolyte
- AlWF-coated sample provided a capacity similar to that in standard (dry) electrolytes
- $Al_2O_3$-coated sample provided a significantly lower capacity
- Uncoated sample did not cycle!

- Surface-modified Spinel Structures

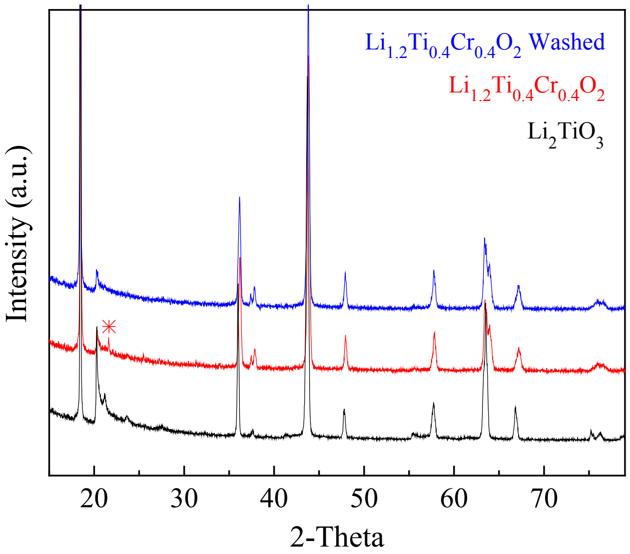



- Incorporation of a spinel component at the surface of oxide particles may provide stability against oxygen loss and TM migration

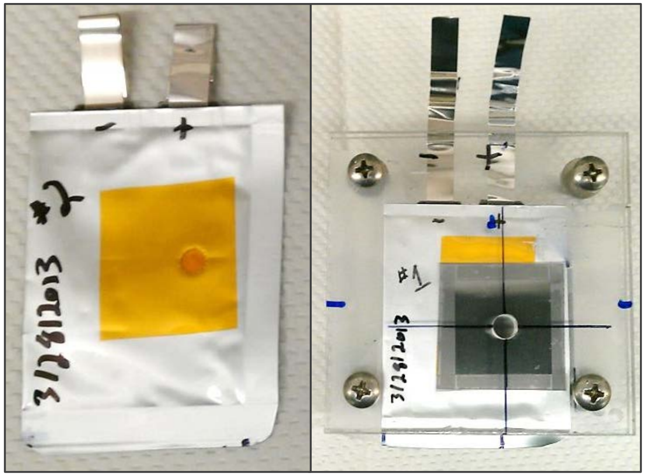
# Progress: Characterization of Model Systems

- Stabilization of Li-excess materials is necessary –> inactive $Li_2M'O_3$ (M'=Mn, Ti, Zr,)
- Integrated materials show unique behavior – e.g., $Li_2MnO_3$, $LiCrO_2$
- Combination of $Li_2TiO_3$ and $LiCrO_2$ ($Li_{1.2}Ti_{0.4}Cr_{0.4}O_2$) gives high capacity!

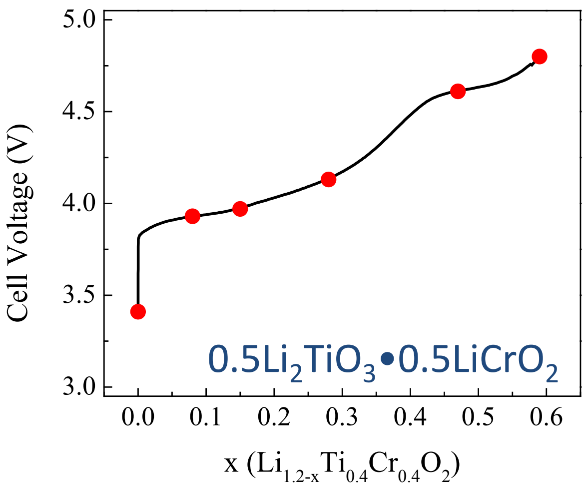
***XRD of synthesized powders***



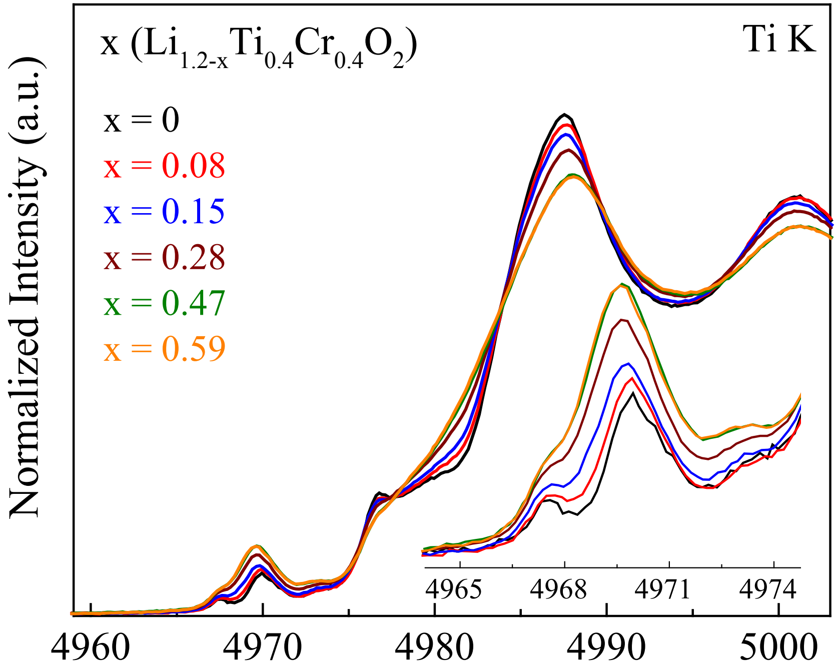

***Pouch-cells for beamline***

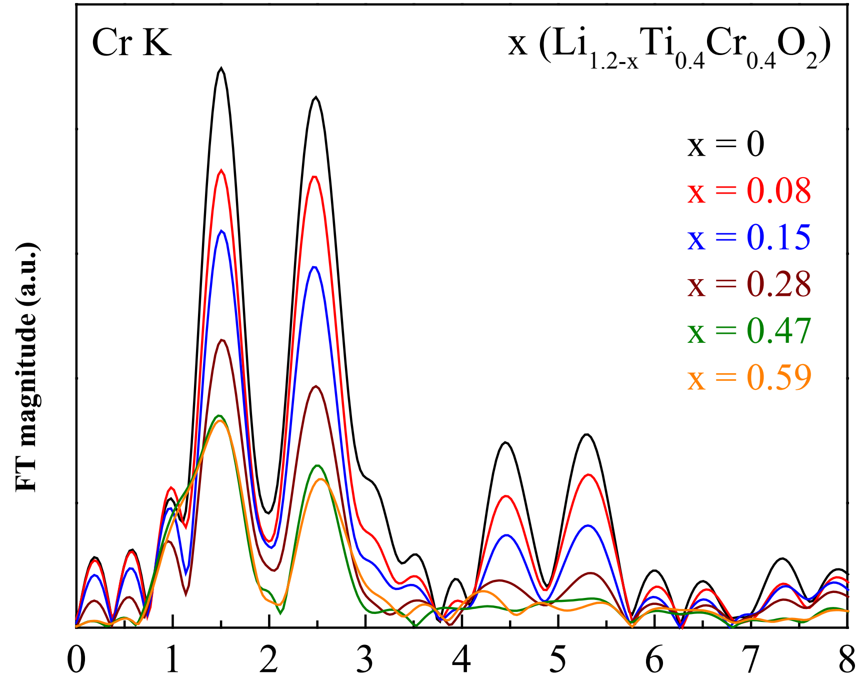


***First-cycle in situ charge***



# Progress: Characterization of Model Systems




- Ti pre-edge also shows an increase in intensity as well as a shift to lower energy
- EXAFS correlations show severe damping of all peaks and a 10% change in Ti-O CN -->different than $Li_2MnO_3$ counterpart
- XANES data of model, Ti compounds show increased intensities in pre-edge and shifts to lower energy as Ti-O coordination goes from 6 (octahedral) to 4 (tetrahedral)

Data reveals the migration of $Ti^{4+}$ from octahedral to tetrahedral sites – stability of "inactive" $Li_2TiO_3$ environment is dependent on stability of adjacent domains

# Future Work - FY2016/FY2017

- 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 analysis of recently acquired neutron and X-ray data on: $Li_{1.5-z}(Ni_{0.25}Mn_{0.75})O_{2+d,}$ $Li_{1.25-z}(Ni_{0.375}Mn_{0.625})O_{2+d,}$ $Li_{1.25-z}(Ni_{0.28}Mn_{0.53}Co_{0.19})O_{2+d}$ LLS cathodes to evaluate spinel incorporation as a function of composition

- Continue theory and modeling efforts in support of experiment to understand and design Co-stabilized, LLS electrodes

- Continue the study of reactor synthesis in order to provide high-quality, LLS compositions at large scale to Argonne's CAMP facility and interested industrial partners for large-scale testing in full-cell, pouch-cells

# 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 developed, 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
  - Processing and Scale-up

# Acknowledgments

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