

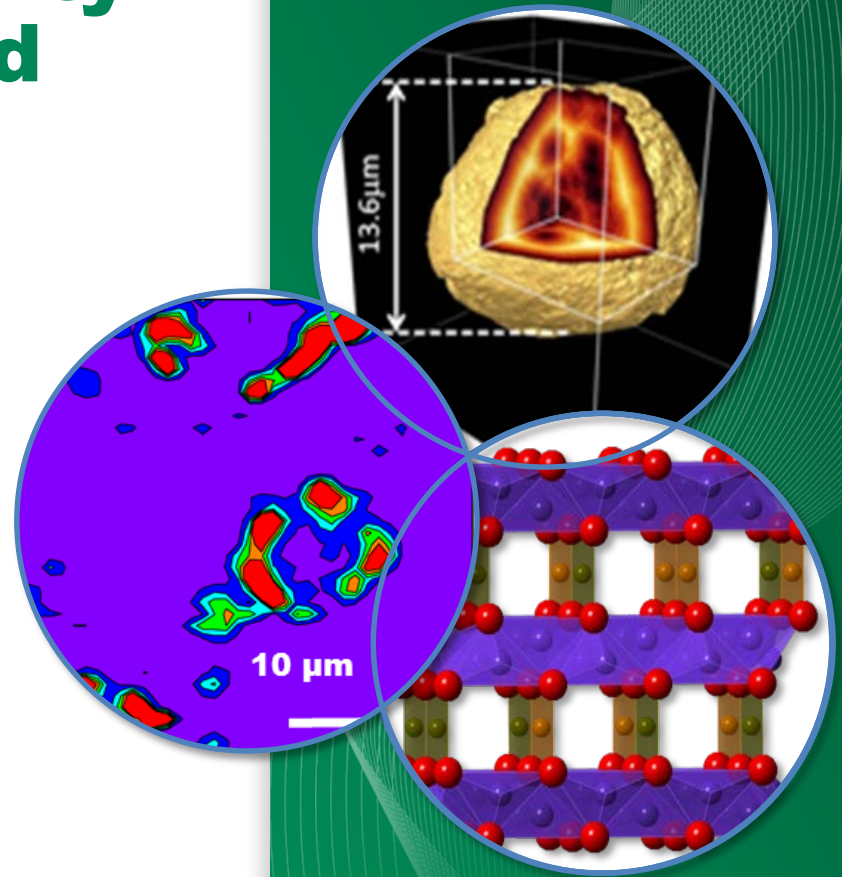
Studies on High Capacity Cathodes for Advanced Lithium-Ion Systems

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Oak Ridge National Laboratory

June 10, 2015

Project ID # ES106



This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

- Project start date: October 1, 2011
- Project end date: Sept 30th 2015
- Percent complete: 75%

Budget

- Total project funding
DOE: \$1,600,000
- Funding received in FY14: \$400K
- Funding for FY15: \$400K

Barriers

Performance: High energy density for PEV applications with cell level targets $\geq$ 400 Wh/kg and 600 Wh/L

Life: More than 5000 deep discharges (SOC range) over the entire life

Safety: Thermally stable and abuse tolerant

Partners

- *Lawrence Berkeley Laboratory*
In-situ X-ray absorption spectroscopy & interfacial studies
- *Brookhaven National Laboratory*
Synchrotron X-ray diffraction and microscopy
- *SSRL, SLAC, Stanford CA*
XANES and X-ray imaging
- *CAMP Facility, Argonne National Laboratory*

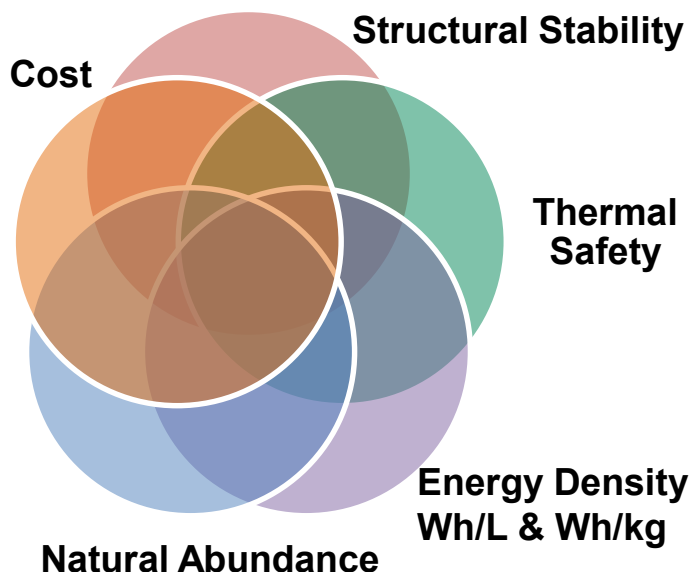
Industrial Advisor

Andy Drews, Ford Research and Advanced Engineering

Relevance and Project Objectives

Develop high energy density lithium-ion cathodes for EV and PHEV applications that meet or exceed DOE USDRIVE/USABC cell level targets (400 Wh/kg and 600 Wh/L)

Desired Attributes



Current high voltage cathodes and major issues

Lithium manganese-rich NMC	• Voltage fade • Mn dissolution • Electrolyte decomposition
High V Mn-Ni Spinel	• Order-disorder transition • Mn dissolution • Electrolyte decomposition
Others LiCoPO_4	• Structural stability • Electrolyte decomposition • Cost

There is a critical need to develop alternative high capacity cathodes

Milestones 2014 -15

Due Date	Description	Status
06/30/2014 (Q3)	Determine interfacial charge transfer and area specific impedance at various SOC for LMR-NMC cathodes	Complete
09/30/2014 (Q4)	Local morphology and chemical structure analysis of pristine and cycled LMR-NMC and other high capacity cathodes	Complete
12/31/2014 (Q1)	Investigation of the surface reactivity, disorder, and interfacial kinetics of LMR-NMC composite cathodes to mitigate voltage fade and transition metal dissolution.	Complete
03/31/2015 (Q2)	Undertake temperature dependent EIS measurements to separate the charge transfer and passive film resistance for LMR-NMC full cells as a function of SOC and cycle life (using baseline graphite anode).	Complete (Go/No go)
06/30/2015 (Q3)	Undertake <i>in-situ</i> and <i>ex-situ</i> X-ray synchrotron and spectroscopic studies to correlate changes in local structure, surface chemistry, and morphology of cycled high energy density electrodes and compare the changes with pristine or uncycled electrodes	In progress
09/30/2015 (Q4)	Stabilize the structure and electrochemical performance of high capacity $\text{Li}_2\text{Cu}_x\text{Ni}_{1-x}\text{O}_2$ cathodes to achieve capacity ~ 250 mAh/g at C/3 rate	In progress

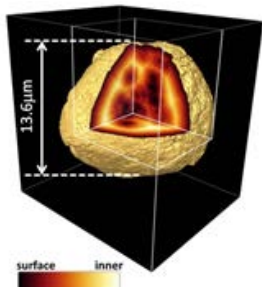
Approach

Part-I

Address and mitigate factors contributing to voltage fade in high capacity cathodes

- Investigate the role of Li_2MnO_3 as a dominant factor causing voltage fade or suppression in high voltage LMR-NMC
- Correlate structure and interfaces with electrochemical performance

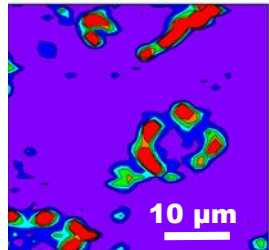
X-ray Imaging and Spectroscopy (XANES)



- 3D elemental mapping and tomography of pristine and cycled cathode particles
- Measure transition metal (TM) oxidation state, migration, and segregation which lead to voltage fade

Micro-Raman mapping of high voltage cathodes

- Monitor changes in crystal chemistry as a function of charge and electrochemical cycling
- Evaluate electrode homogeneity



Synchrotron X-ray absorption (XAS)

3-Electrode EIS as function of SOC and temperature



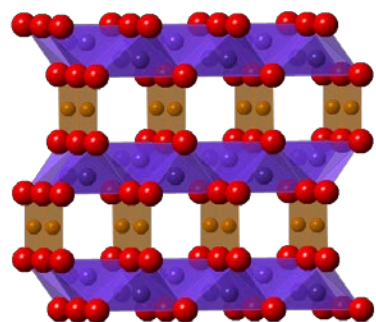
Approach

Part-II

Develop alternative 2-lithium cathode compositions that are high capacity but not necessarily high voltage (Milestone Q4)

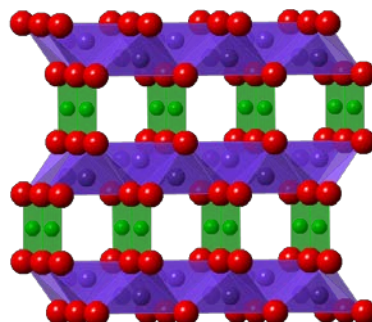
Criteria

- (i) Reversible capacity > 250 mAh/g at C/3
- (ii) Structurally stable under > 1 lithium transfer per TM
- (iii) Include relatively low cost transition metals: Cu, Ni, Fe
- (iv) Cathode compositions guided by modeling* (DFT and phase diagram)



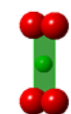
245 mAh/g (1 Li)

489 mAh/g (2 Li)

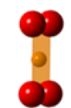


255 mAh/g (1 Li)

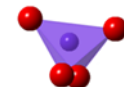
510 mAh/g (2 Li)



NiO₄
square plane



CuO₄
square plane



LiO₄
tetrahedra

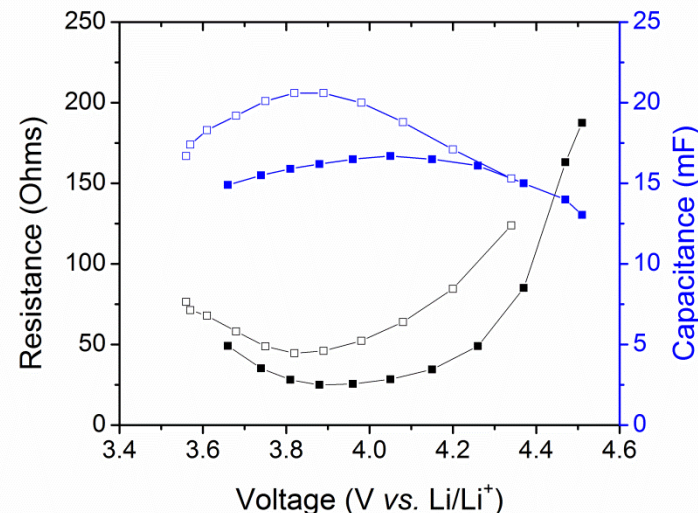
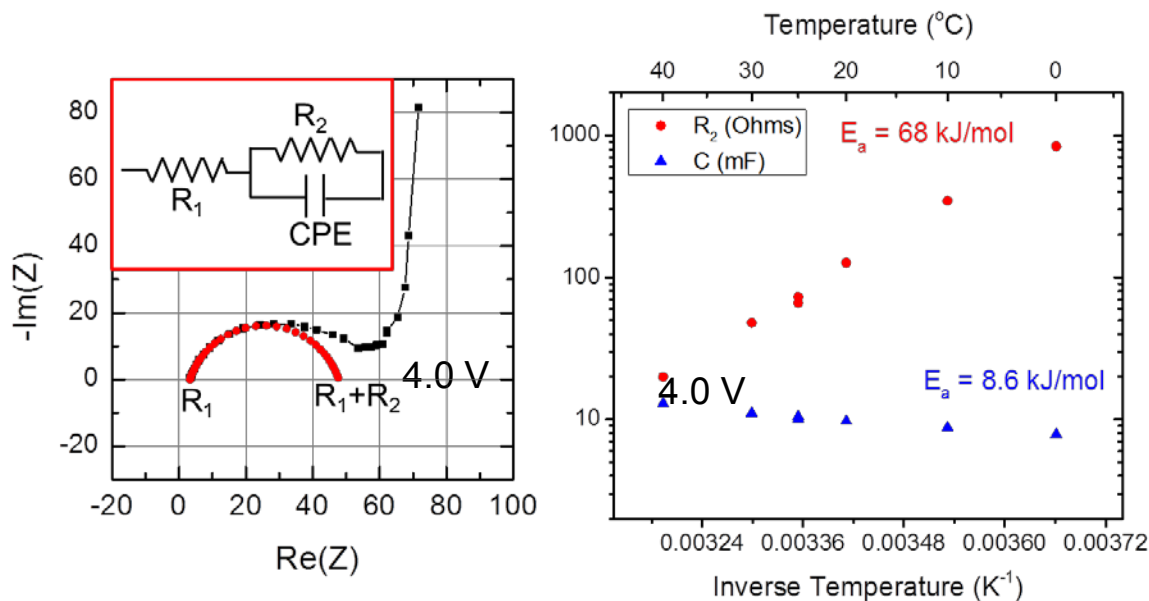
→ Synthesize and test new high capacity materials with upper voltage cutoff < 4.4 V
Initial Targets: Li₂Mⁱ_xMⁱⁱ_{1-x}O₂ and related system (Mⁱ and Mⁱⁱ = Cu, Ni, Fe)

*Ceder, G., et al., *Chem. Mater.* **2004**, 16 (13), 2685-2690; Godshall, N. A., *Solid*

State Ionics **1986**, 18-9, 788-793.

Technical Accomplishment

EIS results show that the charge transfer resistance and double layer capacitance of the LMR-NMC high-V cathode are strongly voltage dependent with large hysteresis between charge and discharge.

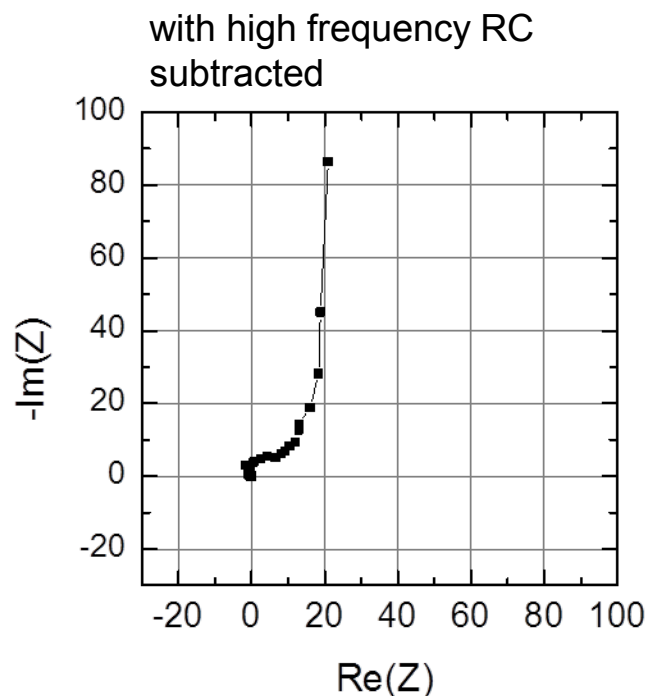
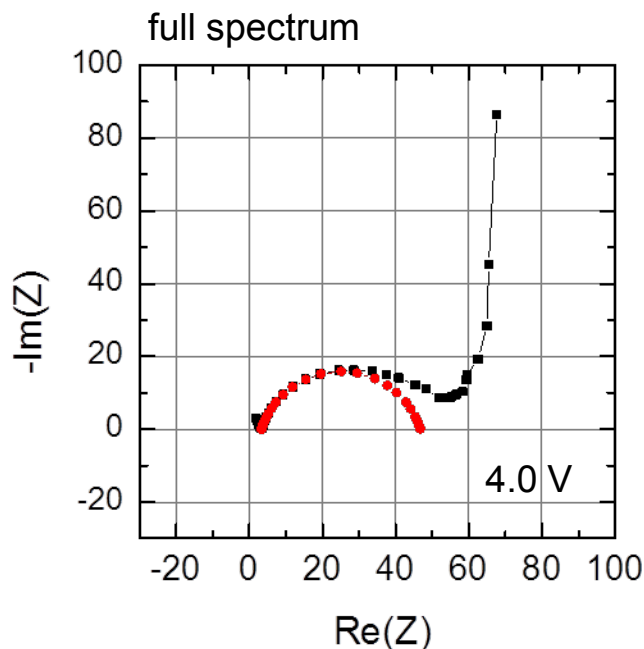


- All measurements done in a 3 electrode EL-Cell with lithium as reference (LMR-NMC cathode & graphite anode)
- Charge transfer resistance at the cathode has an activation energy of 68 kJ/mol consistent with lithium desolvation

Bryant Polzin and Andrew Jansen, Camp Facility Argonne National Lab: High-V cathode and graphite electrodes

Technical Accomplishment

Finite diffusion impedance is easily separated from charge transfer resistance and double layer capacitance



In principle, the concentration of mobile lithium and lithium diffusion coefficient can be extracted from the finite diffusion impedance

Challenges:

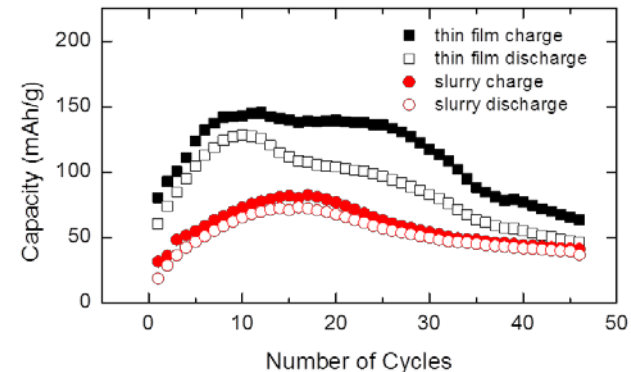
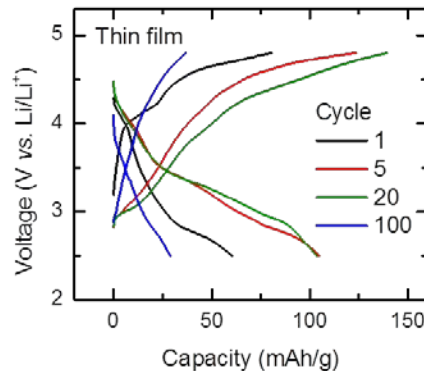
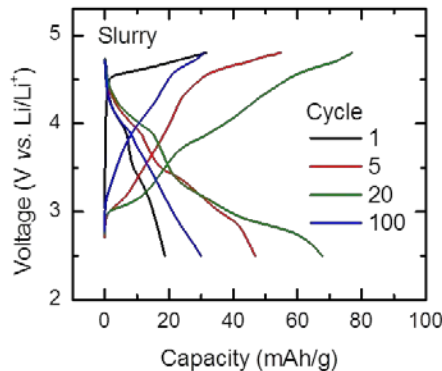
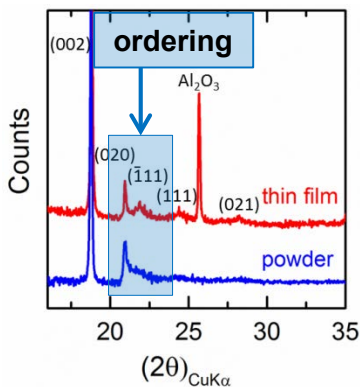
- Spectra must be acquired down to very low frequencies (200 μHz)
- Impedance spectra slowly change even while resting at OCP. Steady-state was not reached after 8 days, likely due to slow phase transformations or other chemical reactions, complicating quantitative analysis (Go/No Go)

Technical Accomplishment

Studied the electrochemical activity of Li_2MnO_3 which constitutes a major component of high-voltage LMR-NMC

- Understand the role of Li_2MnO_3 in voltage fade
- Investigate thin film vs. slurry electrode performance

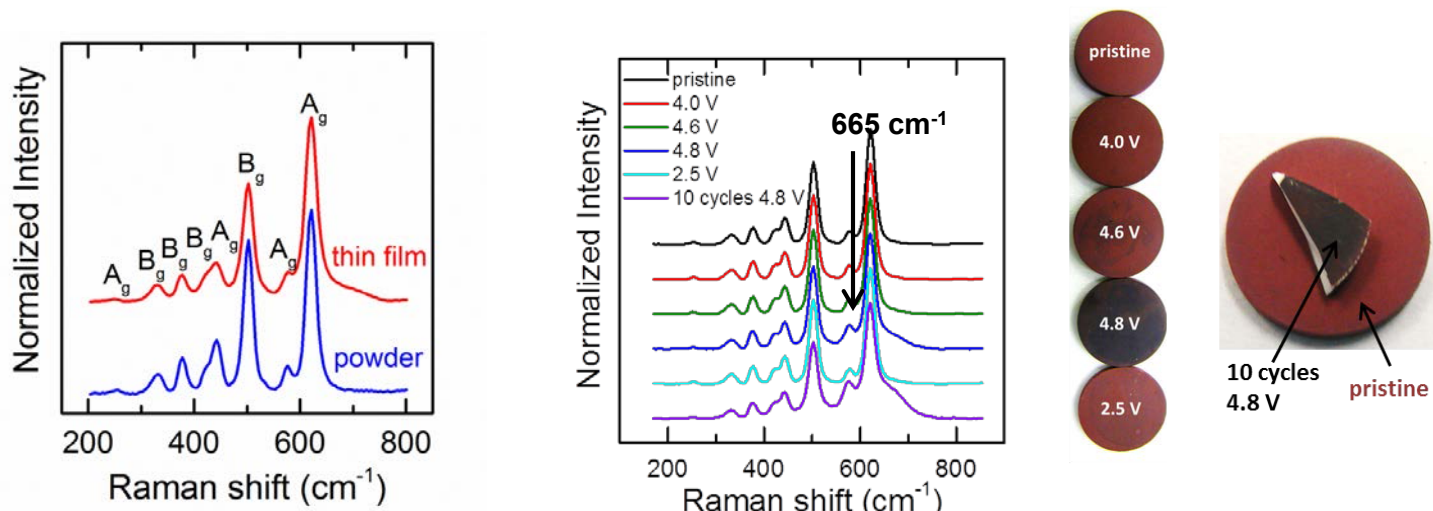
XRD



- XRD confirms formation of desired phase and ordering of lithium in the transition metal layer
- Thin films show higher ordering than powder
- Thin films and slurries exhibit similar cycling behavior
- Only 1/4th or less of the total theoretical capacity can be extracted from either
 - Poor electronic conductivity
 - Particles are micron size, films are 1 micron thick

Technical Accomplishment

Raman spectra of delithiated, cycled Li_2MnO_3 electrodes identify new phases which could be forming in LMR-NMC but are more difficult to observe in a composite cathode

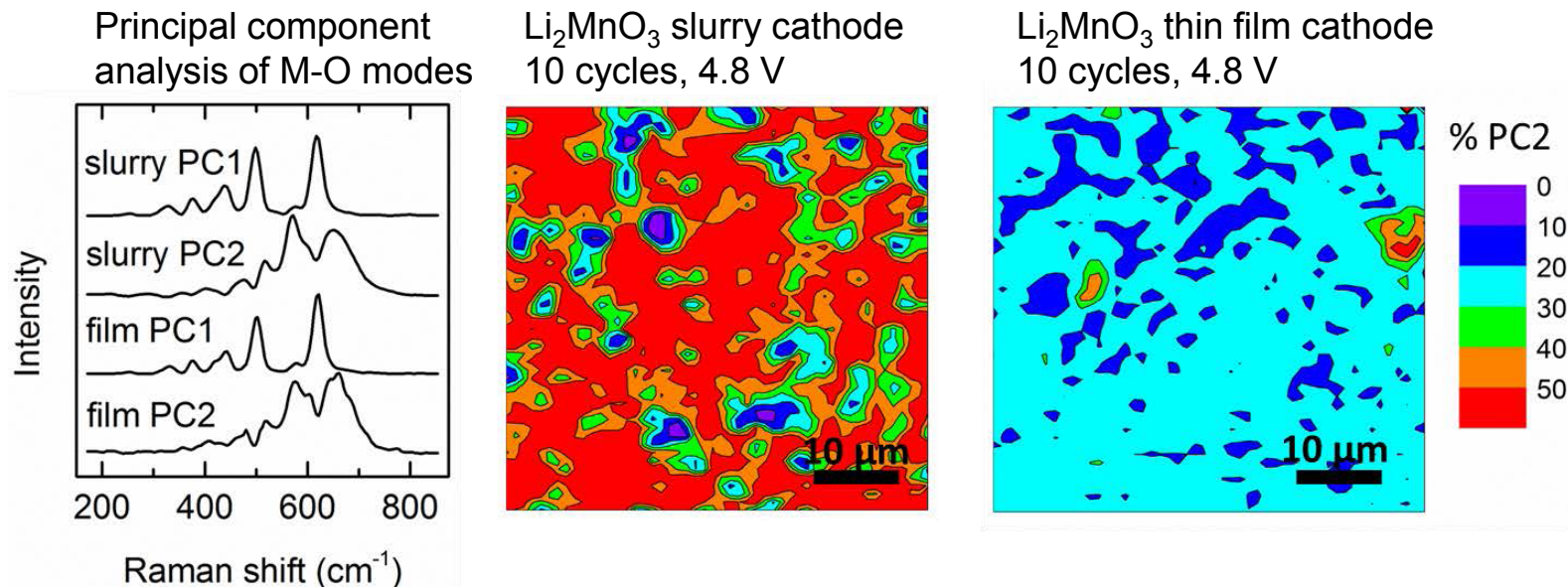


- Raman active vibrational modes were assigned for the first time using DFT calculations
- For Li_2MnO_3 : $\Gamma = 7A_g + 8A_u + 8B_g + 13B_u$
- $7A_g$ and $8B_g$ modes are Raman active and $7A_u$ and $11B_u$ modes are infrared active as predicted from group theory
- At high voltages ($V > 4.6 \text{ V}$) new features appear at 665 cm^{-1} for both slurry and thin film electrodes corresponding to MnO_2 , Li-birnessite, and/or $\text{Li}_{0.52}\text{MnO}_{2.1}$ spinel
- Some increase in electronic conductivity as we delithiate Li_2MnO_3

with G. Veith, H. Dixit, and V. Cooper

Technical Accomplishment

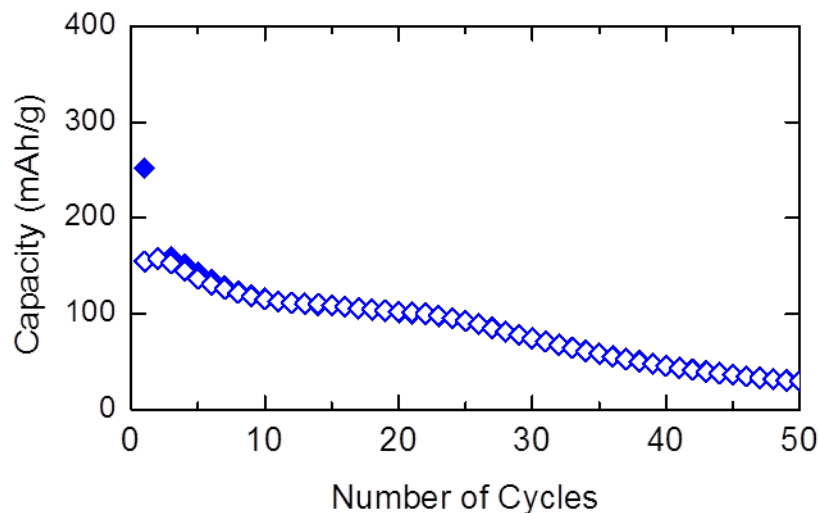
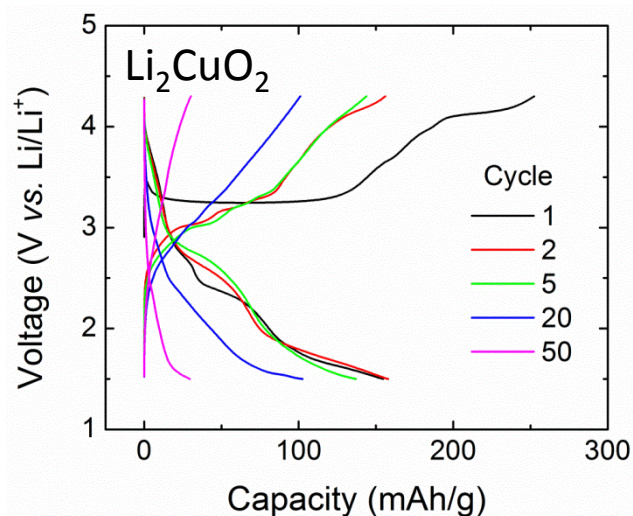
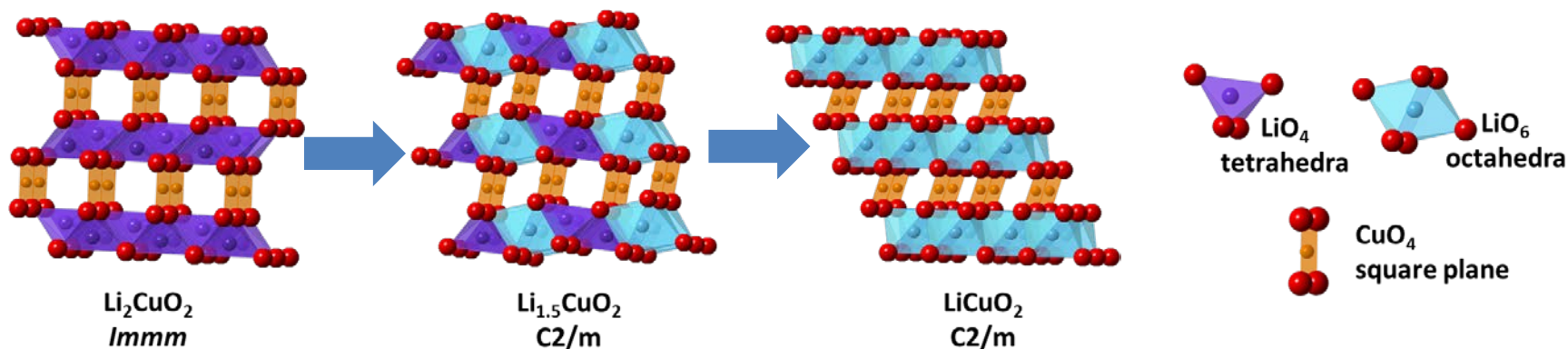
Principal component analysis (PCA) of the cycled, delithiated Li_2MnO_3 reveals the degree of spatial variation and distribution of the MnO_2 phase



- Raman mapping reveals significant heterogeneity in the oxide structure in both thin film and slurry Li_2MnO_3 electrodes. In contrast, earlier work on LMR-NMC electrodes showed the structure was highly uniform across large areas of the electrode
- Principal component analysis supports the formation of MnO_2 -type phases with lithium removal and cycling. Birnessite and spinel structures are good matches for PC2
- DFT calculations support the formation of new phases (not only lithium vacancies)

Technical Accomplishment-Part-II

Two lithium copper oxides: Li_2CuO_2

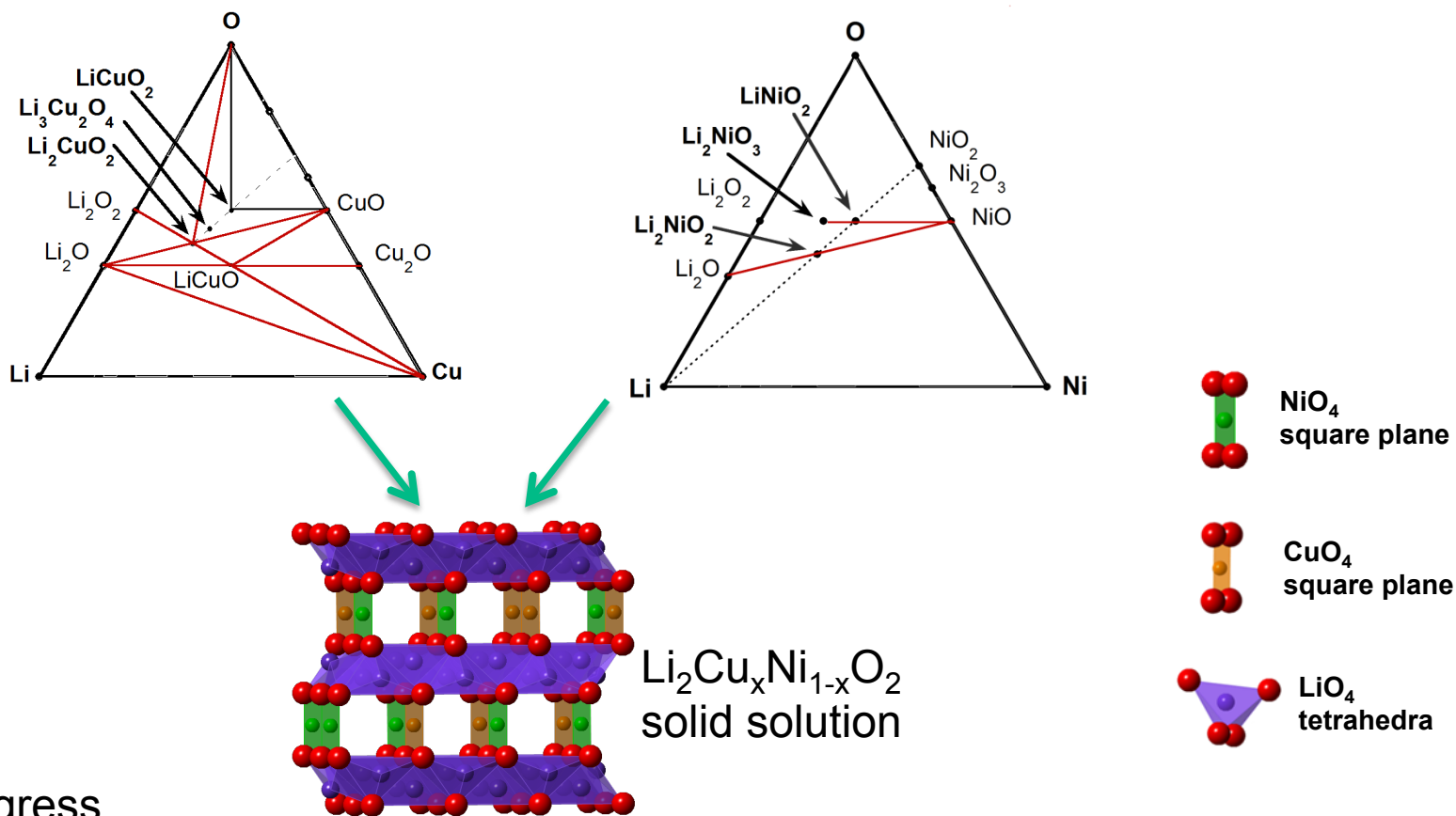


Unpublished
results, ORNL

Li_2CuO_2 cycles poorly due to large structural changes and gas evolution

Technical Accomplishment

To overcome issues with pure copper phases we propose nickel-stabilized high-capacity $\text{Li}_2\text{Cu}_x\text{Ni}_{1-x}\text{O}_2$ cathodes



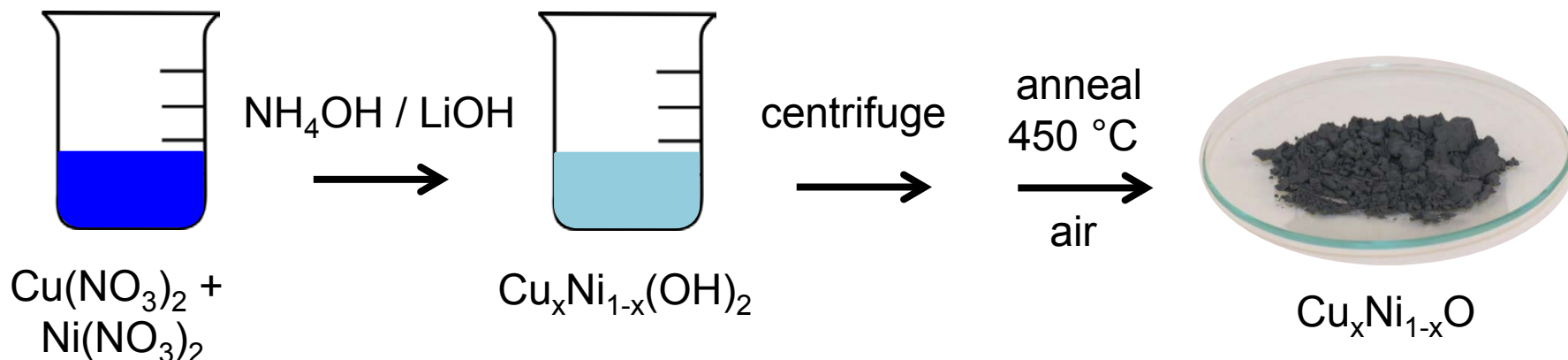
Work in progress

- Stabilize the structure to harness high capacity by Ni substitution
- Take advantage of the high redox voltage of Ni
 - Replace oxygen with other polyanionic groups
 - Limit the cycling voltage window to avoid Cu^+

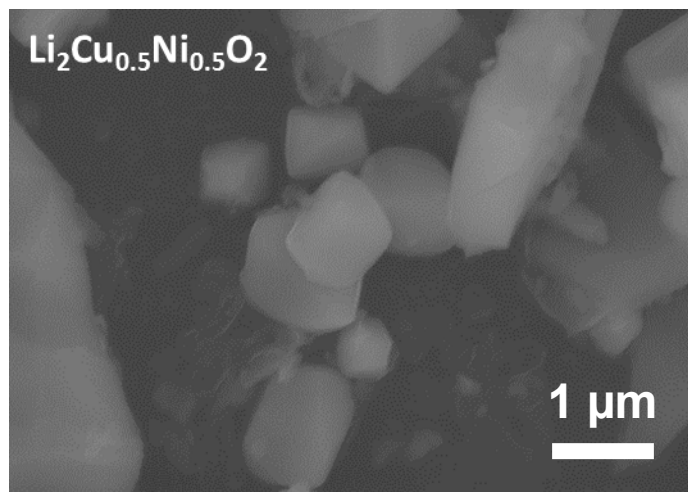
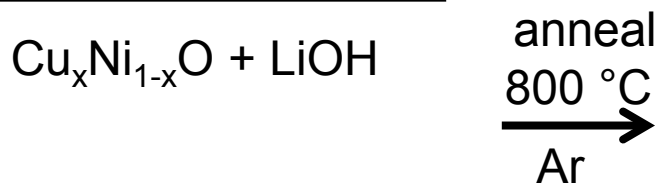
Technical Accomplishment

Synthesized a new high capacity 4 V Li-ion cathode material, $\text{Li}_2\text{Cu}_x\text{Ni}_{1-x}\text{O}_2$, with $x=0.5$ with initial capacities exceeding 200 mAh/g

1. Co-precipitation of nitrate salts



2. Solid state reaction



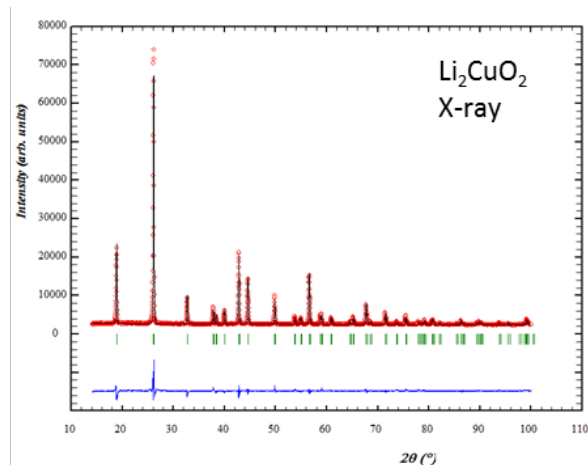
- Simple solid state synthesis method
- Scalable to large quantities
- Low-cost precursors

Developed new synthesis that reduces NiO impurity phase

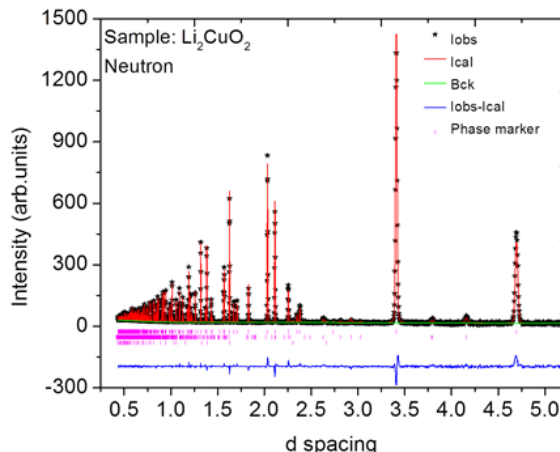
Technical Accomplishment

X-ray and neutron diffraction and XAS confirm the phase and purity of Li_2CuO_2 and $\text{Li}_2(\text{Cu,Ni})\text{O}_2$ compositions

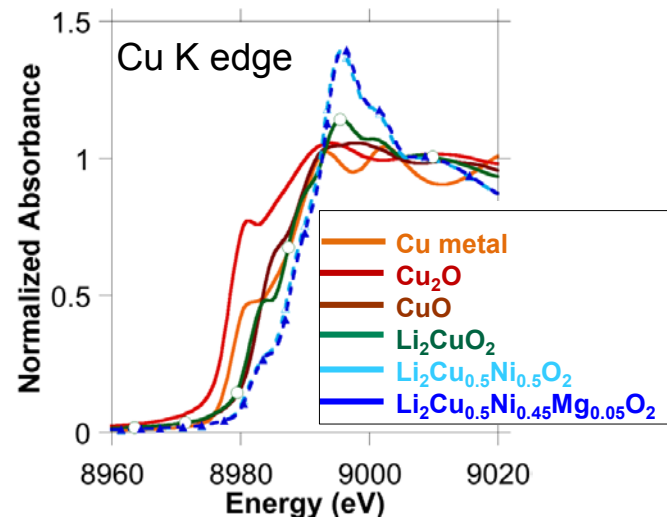
XRD



Neutron diffraction



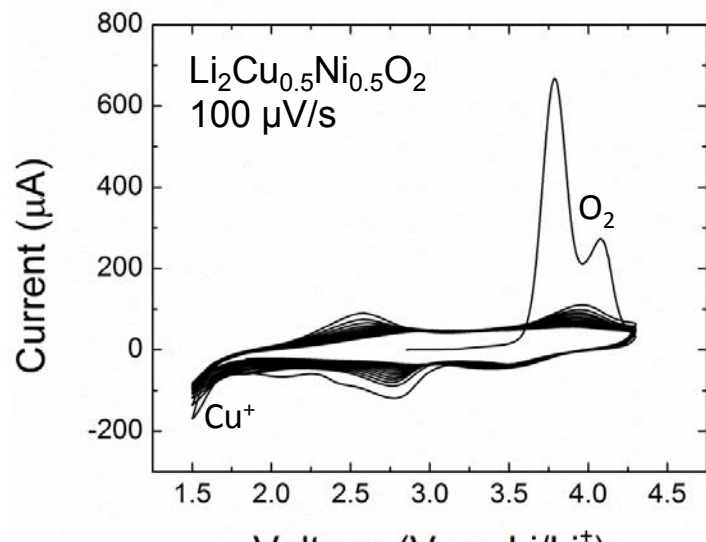
XANES



- X-ray and neutron diffraction confirm formation of Li_2CuO_2 and $\text{Li}_2(\text{Cu,Ni})\text{O}_2$
- Refinement indicates Li_2CO_3 , $\text{Li}_x\text{Ni}_{1-x}\text{O}_2$, and Li_2O are primary impurities (87% pure phase)
- XANES confirms transition metal oxidation states: Cu^{2+} and Ni^{2+}
- New syntheses underway to further reduce impurities

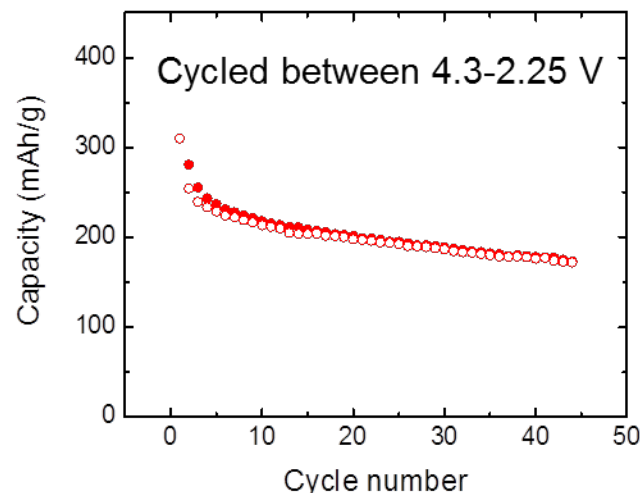
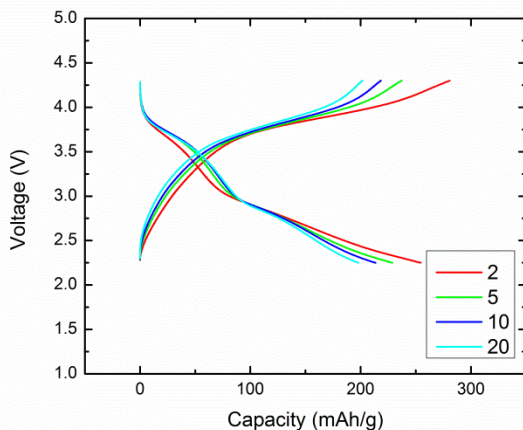
Technical Accomplishment

Electrochemical stability of high capacity $\text{Li}_2\text{Cu}_x\text{Ni}_{1-x}\text{O}_2$ cathodes can be improved by limiting Cu^+ formation and avoiding gas generation



Progress

- Electrochemical stability can be improved by avoiding Cu^+ formation
- Higher voltage cycling results in O_2 generation
- Higher capacity and better retention can be attained through improved electrode formulation such as new binders

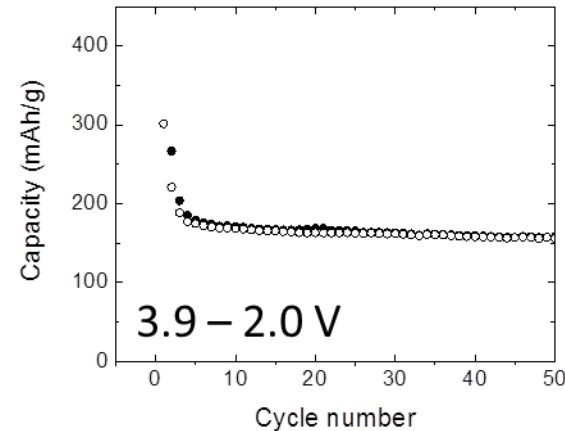
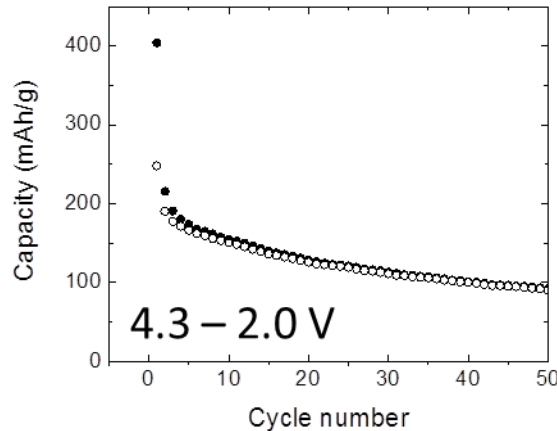
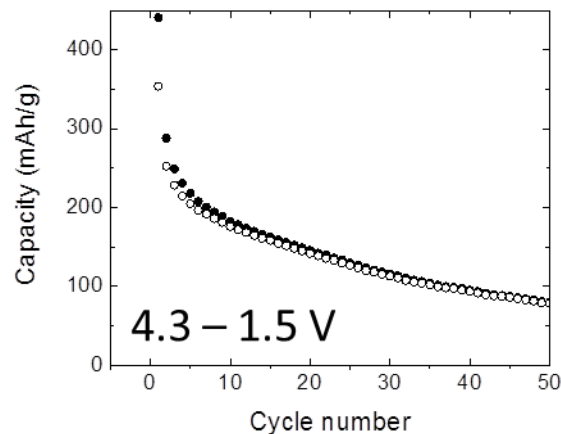
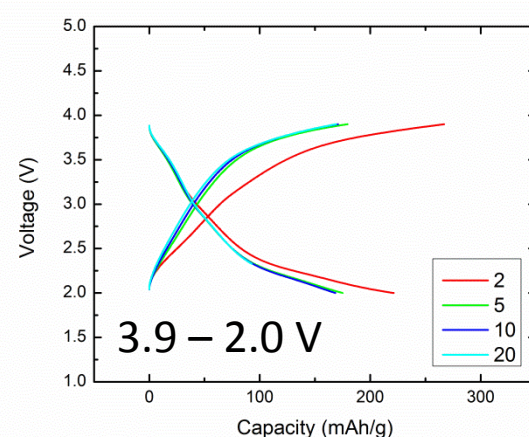
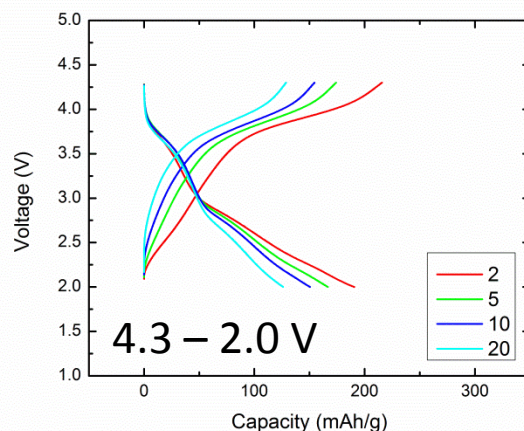
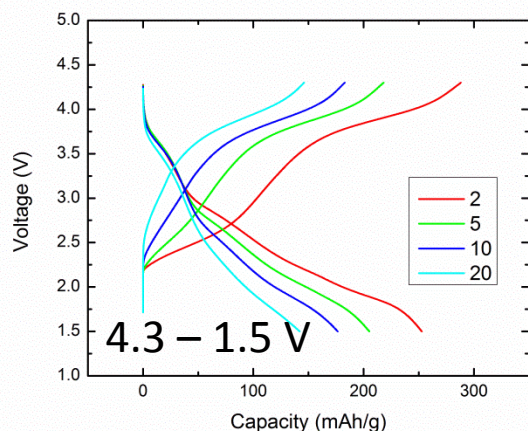


Preliminary electrochemical cycling results are impressive $\sim 200\text{-}250 \text{ mAh/g} > 25 \text{ cycles}$

Technical Accomplishment

Electrochemical stability and capacity retention can be improved by limiting the voltage window.

1. Avoid Cu^+ formation
2. Gas generation at higher charging voltage



Summary Slide

- EIS results show that the charge transfer resistance and double layer capacitance of the LMR-NMC high-V cathode are strongly voltage dependent with large hysteresis between charge and discharge.
- The capacity degradation in Li_2MnO_3 thin film and slurry cathodes provides vital clues towards the degradation and voltage fade in LMR-NMC cathodes. Under delithiation Raman clearly shows a new feature at 665 cm^{-1} corresponding to MnO_2 , Li-birnessite, and/or $\text{Li}_{0.52}\text{MnO}_{2.1}$ spinel.
- Raman mapping reveals significant heterogeneity in the oxide structure in both thin film and slurry Li_2MnO_3 electrodes. In contrast, earlier work on LMR-NMC electrodes showed the structure was highly uniform across large areas of the electrode.
- A new, high-capacity, 4 V Li-ion cathode material, $\text{Li}_2\text{Cu}_x\text{Ni}_{1-x}\text{O}_2$, with $x=0.5$ shows initial capacities exceeding 200 mAh/g
- Electrochemical stability of high capacity $\text{Li}_2\text{Cu}_x\text{Ni}_{1-x}\text{O}_2$ cathodes can be improved by limiting Cu^+ formation and avoiding gas generation

Response to Reviewers Comments

AMR-June 2014 and USDRIVE review at ORNL September-2014

Reviewer 1 &3 [AMR]: In the opinion of multiple reviewers, the projects is trying to tackle too many issues ranging from interfacial stabilization to developing new cathode compositions. They propose a stand-alone project related to new cathode development.

Response: We have completed the interfacial studies related to high V cathodes and electrolyte additives in FY14. We are focusing on development of high capacity multivalent cathodes in FY15 and beyond.

Reviewer 4 [AMR] observed that “the result of electrolyte additives was not surprising, and the new cathode material $\text{Li}_2\text{Cu}_{0.5}\text{Ni}_{0.5}\text{O}_2$ showed poor cyclability and a poor voltage profile.”

Response: We have improved the stability and cyclability of Cu-Ni composition. Results are in this year’s AMR slides.

Reviewer-USDRIVE: “Consider splitting off the third approach (Li_2CuO_2 and related development) into a stand-alone project”

Response: We have revised our tasks and dropped the high-V LMR-NMC cathode task.

Ongoing Partnership and Collaboration



In situ XAS Study of High Capacity Cathodes
Dr. Guoying Chen



In-operando X-ray Synchrotron Studies and Microscopy
Dr. Feng Wang



CAMP Facility: Dr. Bryant Polzin and Andrew Zansen



Synchrotron X-ray microscopy and 3D microstructure
Drs. Yijin Liu and Johanna Nelson



Industrial Advisor
Cell and Electrode Targets and Performance
Dr. Andy Drews, Ford Advanced Engineering and Research

Remaining Challenges and Barriers

- Develop and improve the synthesis methods to make phase pure $\text{Li}_2\text{Cu}_{0.5}\text{Ni}_{0.5}\text{O}_2$ with smaller particle size
- Identify a commercial binder that does not react with Cu-Ni phase. PVDF binder has issues
- Improve capacity retention and cycle life to ~ 250 mAh/g & 100 cycles
- Find a substituent that will make the TM-O bonds more stable against gas release at higher voltage. Possible candidates: Al, Mg, or Ga
- Investigate the role of Ni substitution and stoichiometry in stabilizing the structure using diagnostic methods and correlate with electrochemical performance

Proposed Future work

FY 15-16

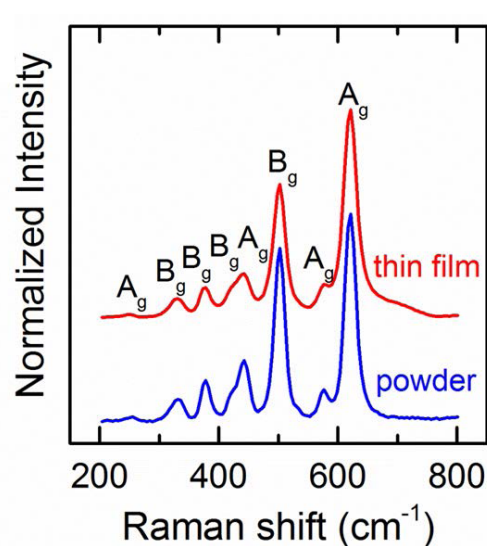
- Continue synthesis efforts of high-capacity 2-lithium Cu-Ni oxides to improve electrochemical performance and capacity retention
 - (i) Reduce the particle size to improve kinetics
 - (ii) Eliminate impurity phases and vary composition
 - (iii) Improve the stability of Cu-O and Ni-O during delithiation by cation substitution
- Fabricate sputtered thin films of $\text{Li}_2\text{Ni}_x\text{Cu}_{1-x}\text{O}_2$ and study the structure and electrochemical reactivity
- Investigate the rate capability of $\text{Li}_2\text{Ni}_x\text{Cu}_{1-x}\text{O}_2$ for $x = 0.4, 0.5$, and 0.6
- Study the lithiation-delithiation mechanism and determine the stability of redox active Cu and Ni using *in situ* synchrotron XAS and diffraction

Beyond

- Synthesize new, highly lithiated copper/nickel cathode materials that incorporate polyanionic groups
- Incorporate Fe into compositions for improved capacity retention, oxidative stability, and cost

Technical backup slides

Theoretical calculation of Raman bands using DFT



$$\Gamma = 7A_g + 8A_u + 8B_g + 13B_u$$

$7A_g$ and $8B_g$ modes are Raman active and $7A_u$ and $11B_u$ (optical) modes are infrared active as predicted from group theory

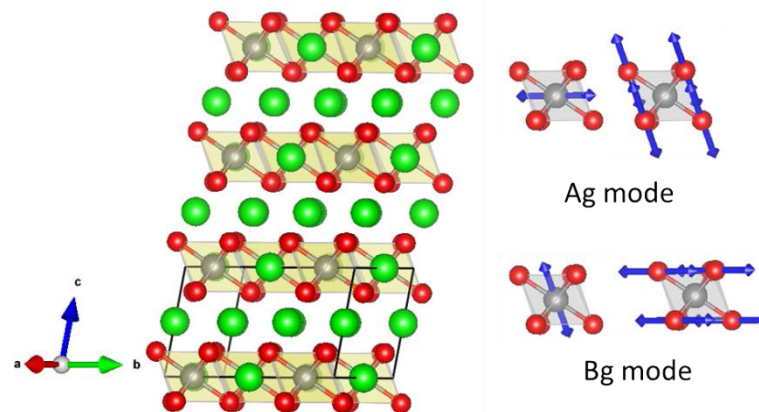


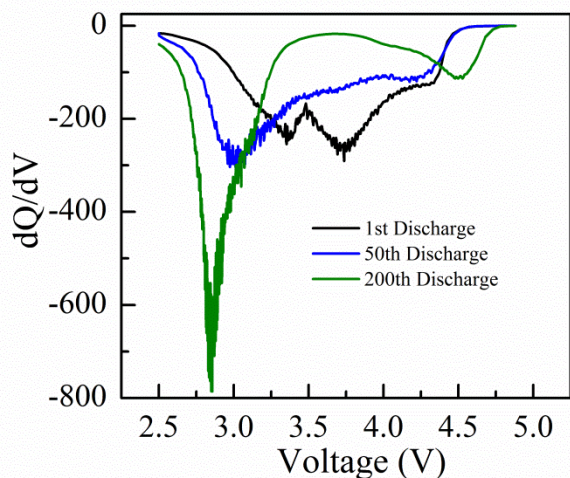
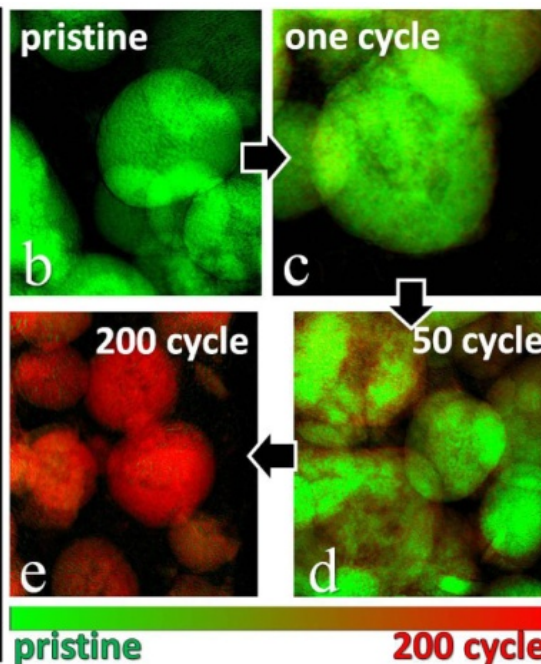
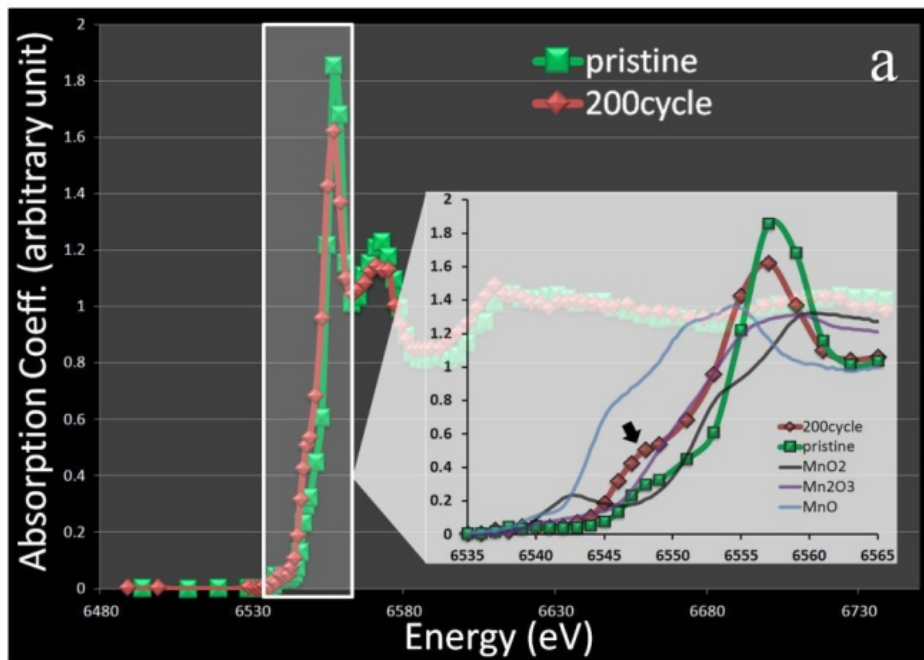
Figure 2: Crystal structure of Li_2MnO_3 (Li:green, Mn:gray and Oxygen:red in color) and schematic illustration of Raman active modes which arise due to the parallel or perpendicular motion of cations or anions, with respect to the b -axis.

cm^{-1}								
Experimentally observed	621	574	502	442	422	377	330	252
Calculated phonon freq.	621	577	498	448	426	377	338	260

H. Dixit & V. Cooper

Technical Accomplishment-FY14

TXM-XANES reveals change in Mn oxidation state and strong correlation with voltage fade [$\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}\text{O}_2$]

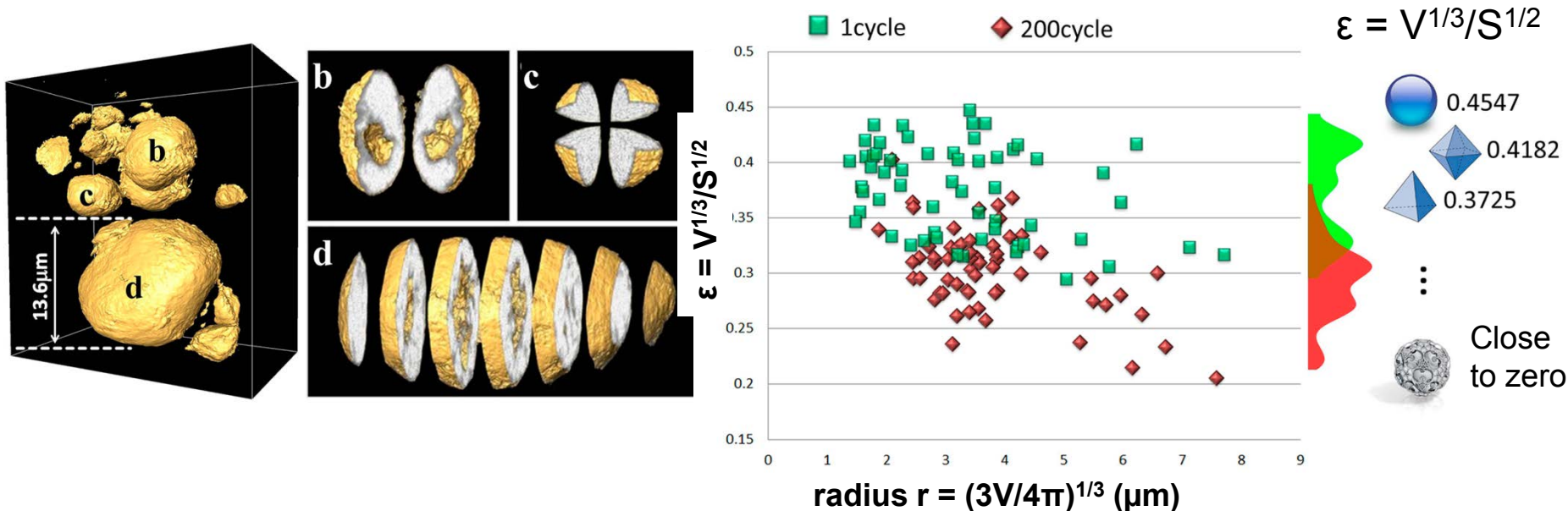


- Average Mn oxidation state changes from **more oxidized** to **more reduced** with cycling
- Shift in Mn K edge correlates well with voltage fade as shown by the dQ/dV results (left)
- Reaction begins at the surface and moves into bulk

From AMR Presentation 2014

Technical Accomplishment FY-14

TXM-XANES monitors changes in LMR-NMC cathode particle morphology under high voltage electrochemical cycling $[\text{Li}_{1.2}\text{Mn}_{0.525}\text{Ni}_{0.175}\text{Co}_{0.1}\text{O}_2]$



Analysis performed on >120 cathode particles

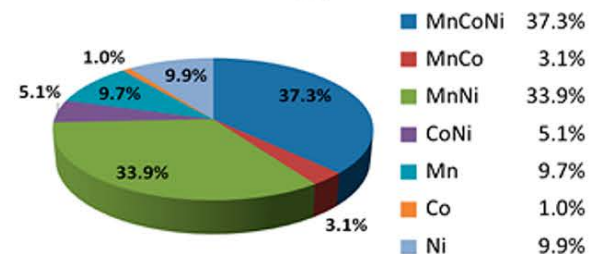
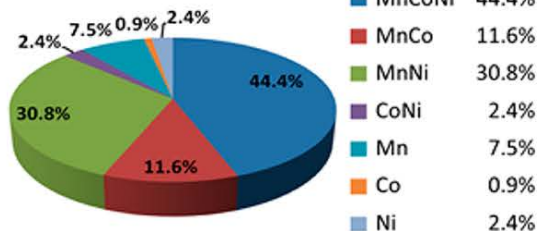
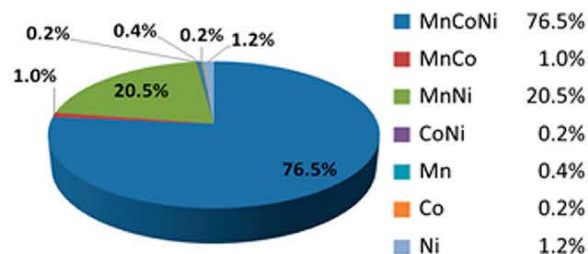
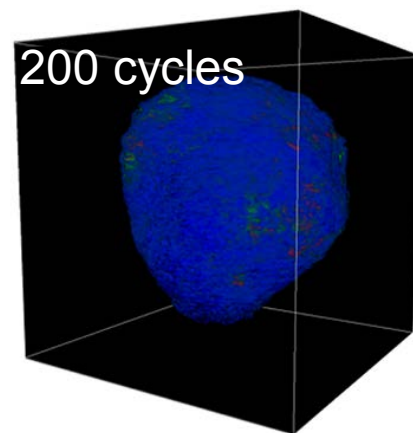
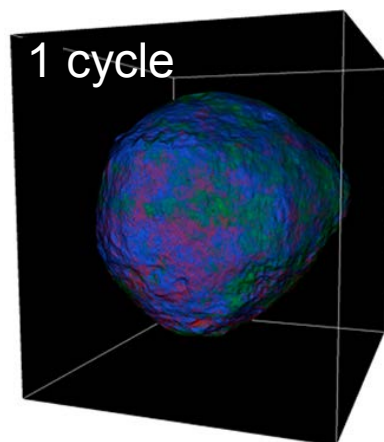
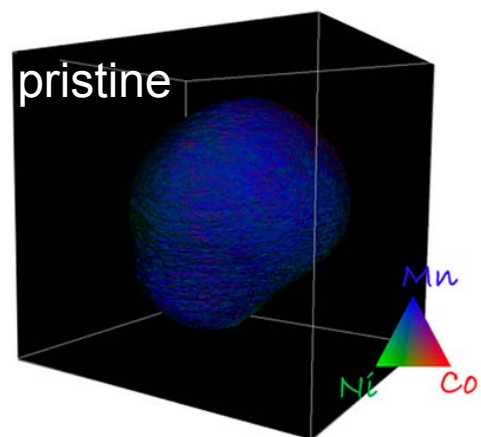
Significant internal stress under high voltage cycling

Particles change their morphology exposing more surface area

- increased surface reactivity with electrolyte
- surface coatings alone may not be sufficient to stabilize the structure

Technical Accomplishment-FY15

TXM-XANES maps 3D elemental compositions to monitor TM migration



Cathode particles cycled even once (4.9 - 2.5 V) show a redistribution of TM phases with 8% Mn pure phase

Further TM segregation with cycling to 10% pure Mn and 10% pure Ni phase

Relative increase in Mn-rich phase at surface

Phase segregation may impact lithium diffusion and TM dissolution