Studies on High Capacity Cathodes for Advanced Lithium-Ion

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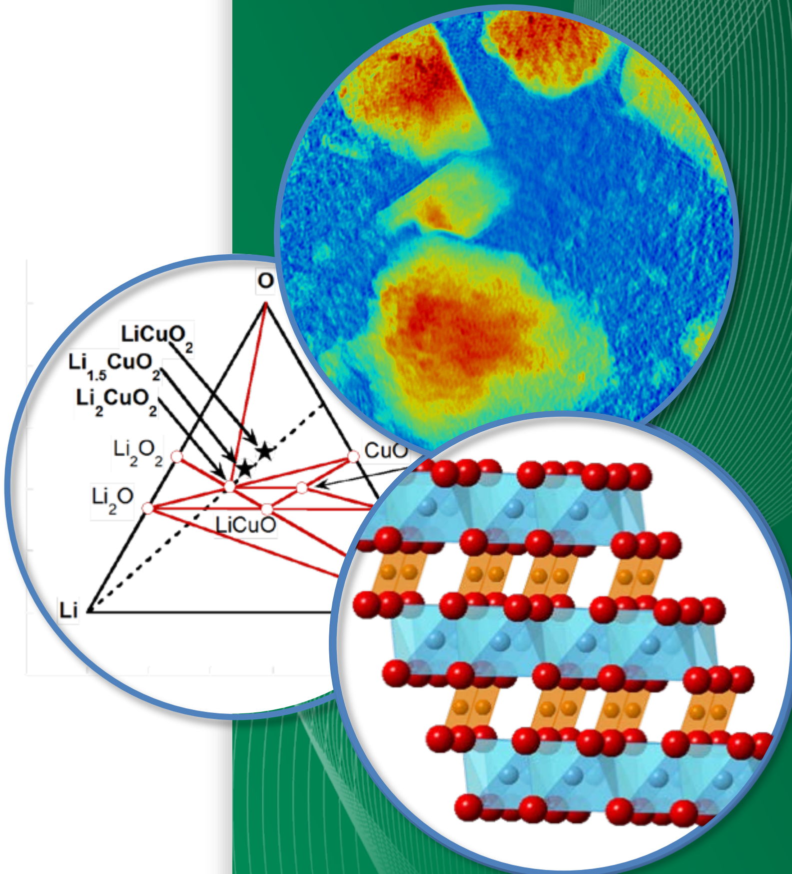
Oak Ridge National Laboratory

June 2016



Project ID # ES106

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Overview

Timeline
- Project start date: October 1, 2015
- Project end date: Sept 30^{th} 2018
- Percent complete: 30%

Barriers
Performance: High energy density for PEV applications with cell level targets ≥ 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

Budget

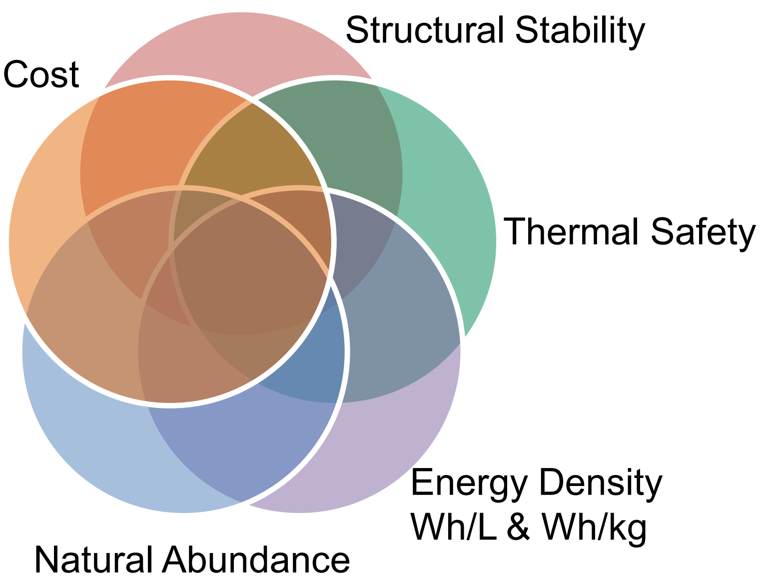
- Funding received in FY15: $400K
- Funding received in FY 16: $400K

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*

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 700 Wh/L)

Desired Attributes



Current high voltage cathodes and limitations

Lithium Manganese-rich NMC
- Voltage fade / phase changes
- Mn dissolution
- Electrolyte decomposition

High V Mn-Ni Spinel
- Order-disorder transition
- Mn dissolution
- Electrolyte decomposition

Polyanionic: Phosphates, Sulfates, Silicates, Fluorophosphates
- Structural degradation
- Electrolyte decomposition
- Lower capacity

There is a critical need to develop alternative high capacity cathodes to meet high energy density at cell level.

Milestones 2015-16

Due Date	Description	Status
06/30/2015 (Q3)	Determine interfacial charge transfer and area specific impedance at various SOC for LMR-NMC cathodes	Complete
09/30/2015 (Q4)	Local morphology and chemical structure analysis of pristine and cycled LMR-NMC and other high capacity cathodes	Complete
12/31/2015 (Q1)	Synthesize three compositions of $Li_2Cu_xNi_{1-x}O_2$ cathodes with x between 0.4-0.6 and improve their anionic stability by fluorination. Subtask-1.1: Fluorination of Li_2CuO_2	Complete
03/31/2016 (Q2)	Subtask-1.2: Fluorination of $Li_2Cu_xNi_{1-x}O_2$ with x ~ 0.4-0.6	In progress
06/30/2016 (Q3)	Identify the roles of Ni and F towards obtaining reversible redox capacity at higher voltage and stabilize Ni-rich compositions. Subtask-2.1 XANES, microscopy, and XPS studies	70% complete
09/30/2016 (Q4)	Identify the roles of Ni and F towards obtaining reversible redox capacity at higher voltage and stabilize Ni-rich compositions. Subtask 2.2 Gas evolution and electrochemistry	In progress

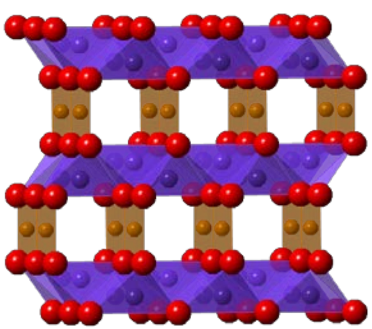
Approach-I

Synthesize and stabilize solid solutions of high capacity 2-lithium cathode compositions belonging to $Li_2M^{i}_{x}M^{ii}_{1-x}O_2$ & $Li_2M^{i}_{x}M^{ii}_{1-x}O_3$ (where M^{i} and M^{ii} = Cu, Ni, Fe, Mn).

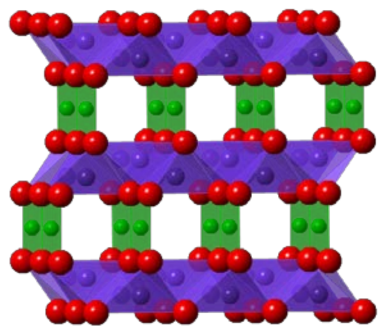
Criteria

(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)

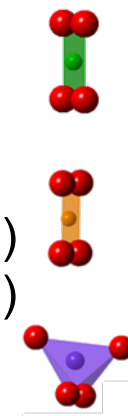
An example of ongoing work



Li_2CuO_2
245 mAh/g (1 Li)
489 mAh/g (2 Li)



Li_2NiO_2
255 mAh/g (1 Li)
510 mAh/g (2 Li)

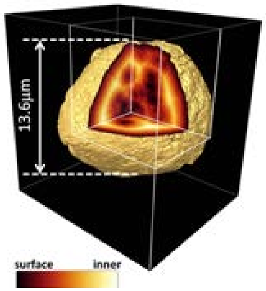


→ Synthesize and test high capacity nickel-stabilized $Li_2Cu_xNi_{1-x}O_2$ and evaluate the role of Ni in stabilizing the copper oxide phase. Improve the electrochemical performance and achieve higher redox voltage by methods such as fluorination.

*Ceder, G., *et al., Chem. Mater.* **2004,** *16* (13), 2685-2690; Godshall, N. A., *Solid State Ionics* **1986,** *18-9*, 788-793.

Approach-II

- Increase the redox voltage of cathodes by stabilizing transition metals in higher oxidation state.
- Improve the oxidative stability and capacity loss of high voltage cathodes by anionic substitution, coatings, and post-processing.
- Correlate structure and interfaces with electrochemical performance.

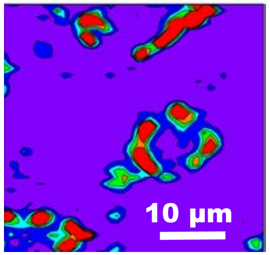


X-ray Imaging and Spectroscopy (XANES)

- 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

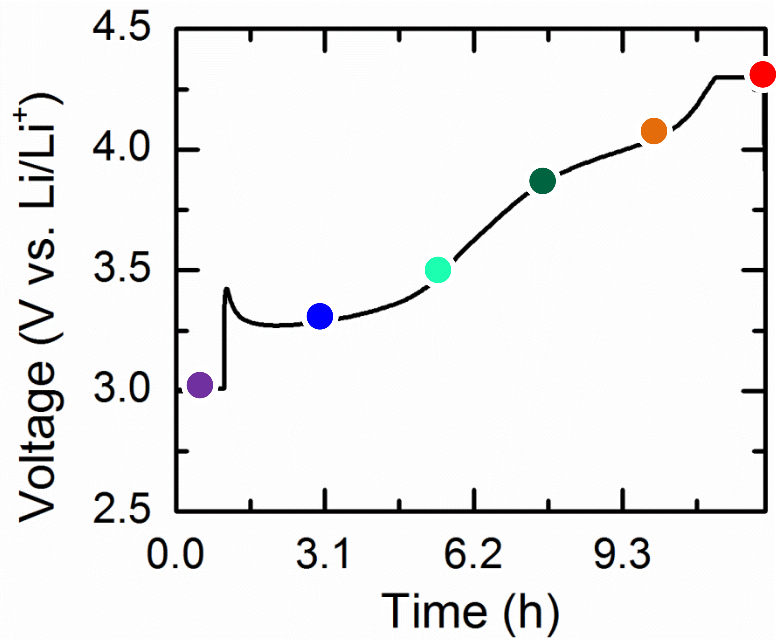
- Monitor changes in crystal chemistry as a function of charge and electrochemical cycling
- Evaluate electrode homogeneity

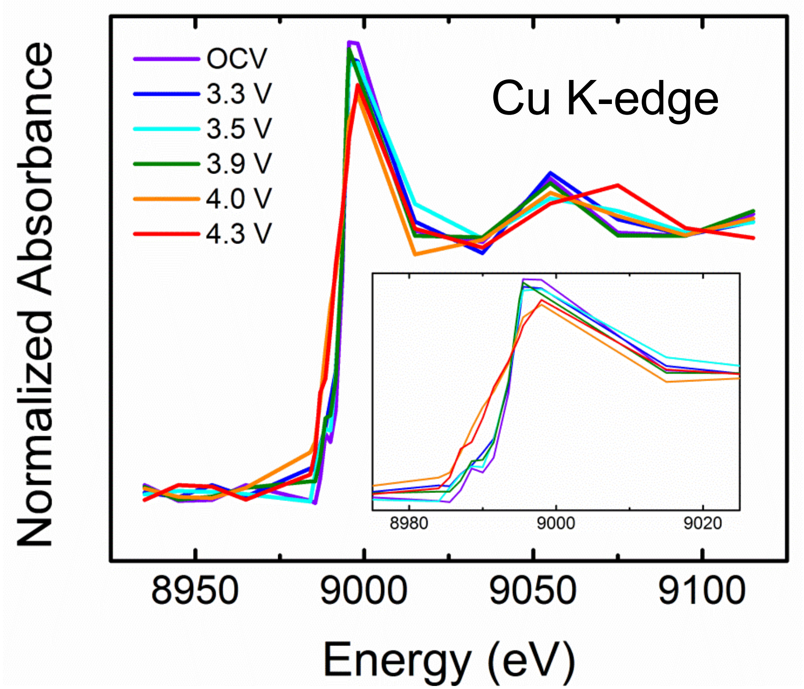


3-Electrode EIS as function of SOC and temperature

Technical Accomplishment:

In situ XANES explains chemical and structural transformations in $Li_2Cu_{0.5}Ni_{0.5}O_2$ during cycling

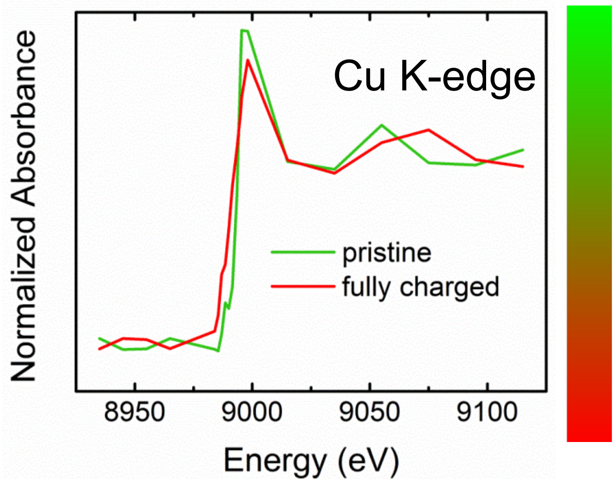




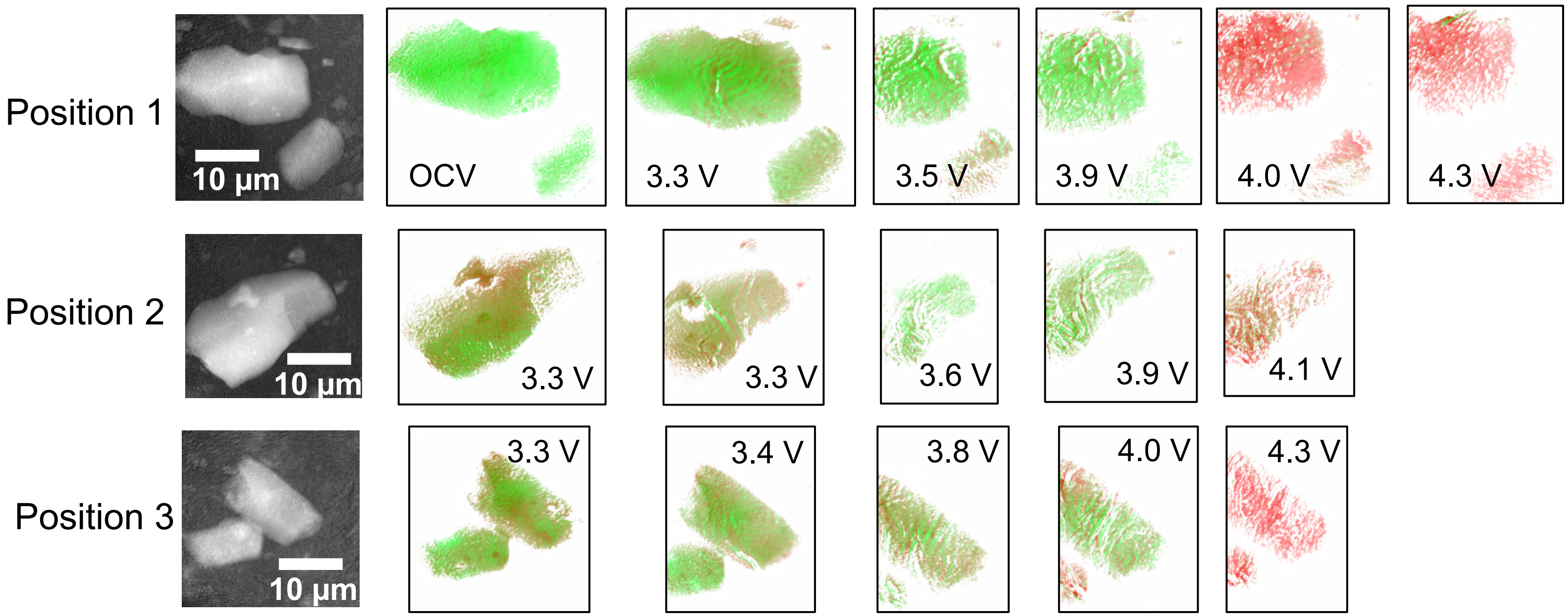
- Cu K-edge shows significant shifts only > 3.9 V
- Direction of shift is inconsistent with Cu oxidation
- Change in Cu XANES likely reflects structural transformations at high voltage

J. Nelson Wecker, SSRL-SLAC

Technical Accomplishment:
In situ XANES microscopy maps out structural transformations

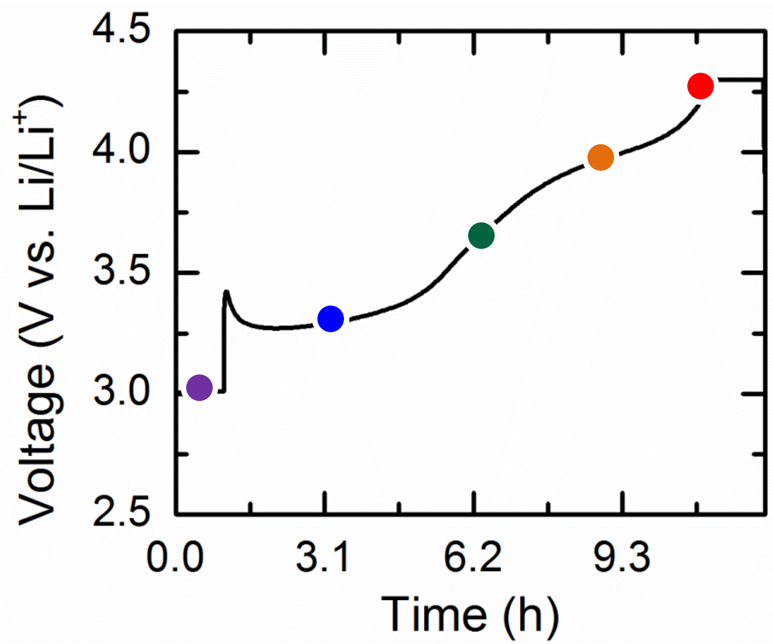


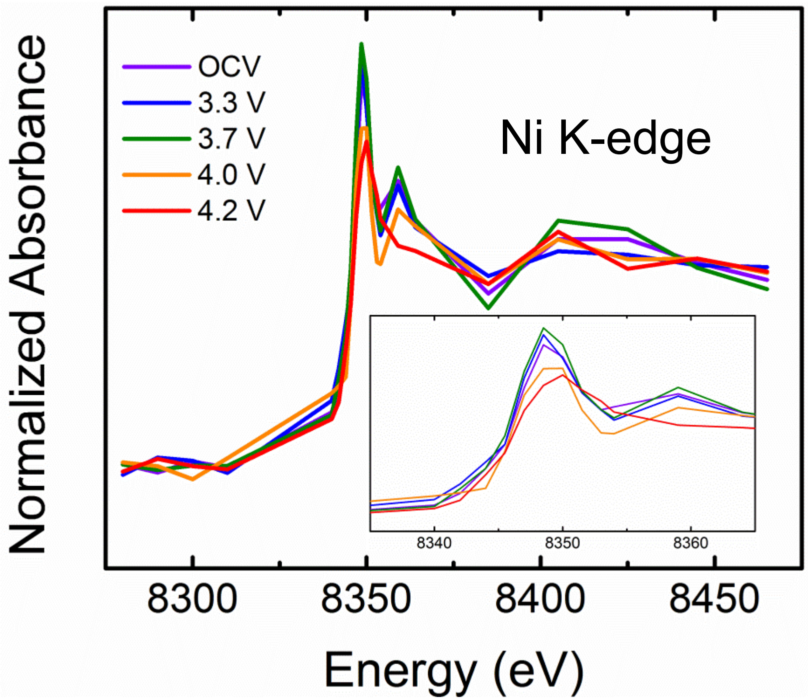
- XANES maps were generated by linear combination fitting
- Some structural transformation may occur at the particle surface prior to bulk structural change
- Structural change is complete > 4.0 V



R. Ruther *et al*. unpublished 2016

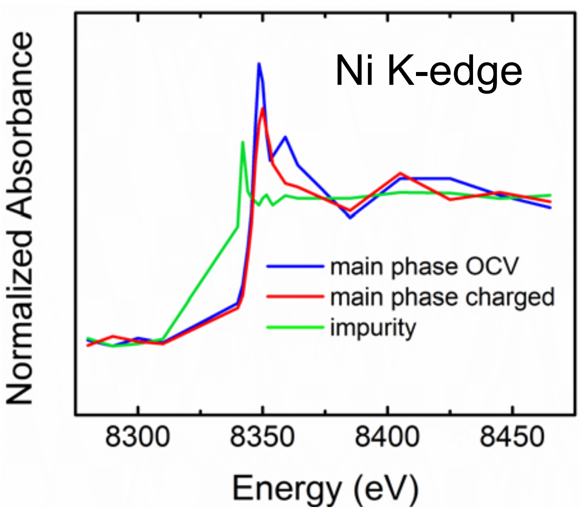
Technical Accomplishment:
XANES at Ni K-edge tracks chemical changes *in situ*

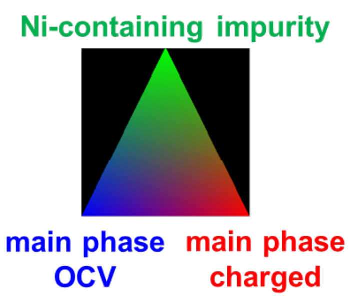


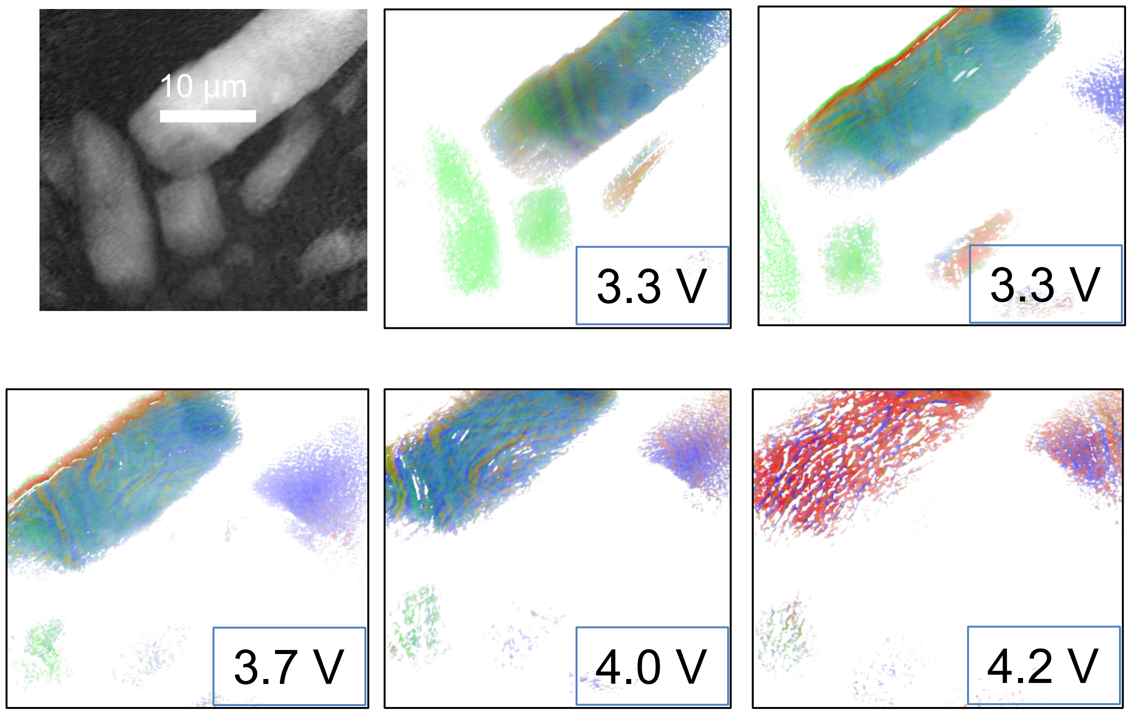


- Spectral analysis is complicated by Ni-containing impurities and phase transformation at high voltage
- Overall shift to higher binding energy confirms our previous work showing Ni oxidation during charge [R. Ruther *et al*. Chem Mater. 227, 6746-6754, 2015]

Technical Accomplishment:
In situ XANES microscopy reveals phase changes and impurity



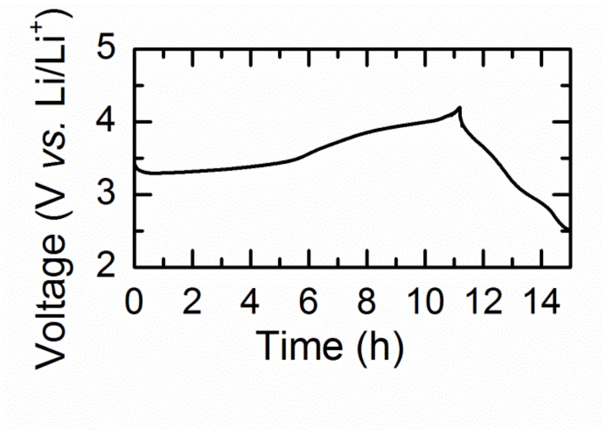


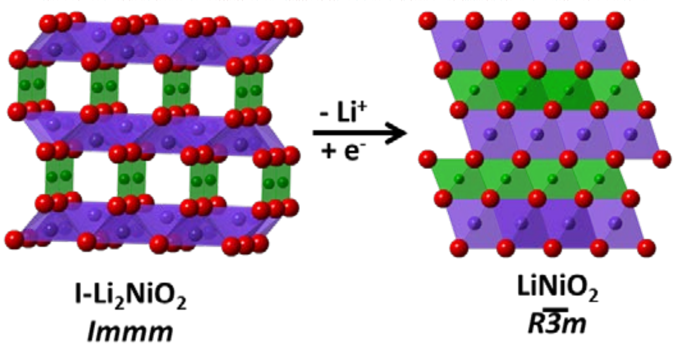


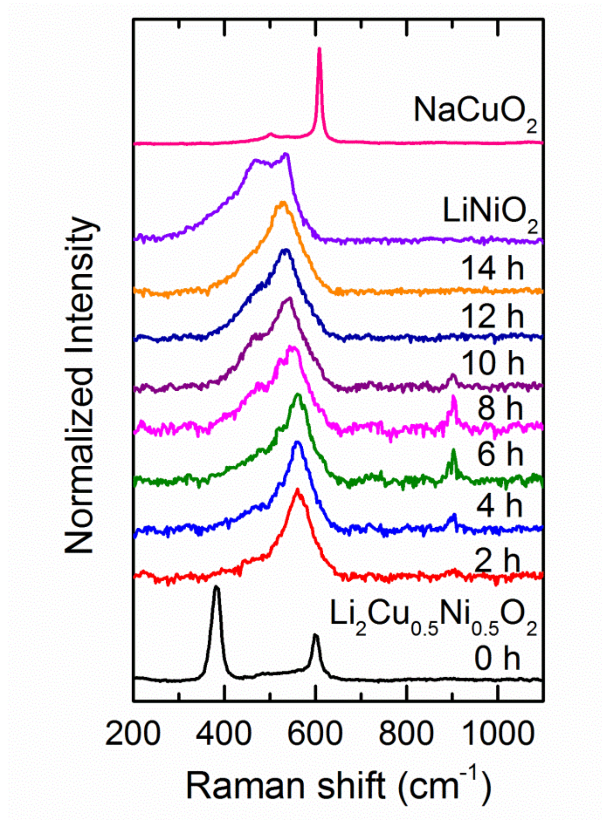
- XRD shows $Li_{1-x}Ni_xO$ as the only Ni-containing impurity.
- However, $Li_{1-x}Ni_xO$ is not expected to be electrochemically active and impurity phase is indistinguishable from main phase after charge.

R. Ruther *et al*. unpublished 2016

Technical Accomplishment:
In-situ Raman confirms close-packed lattice forms when charged



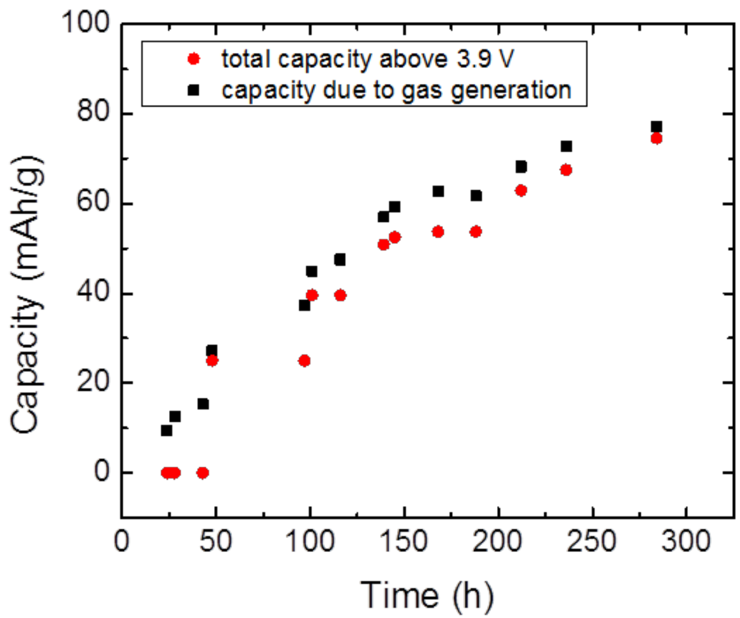


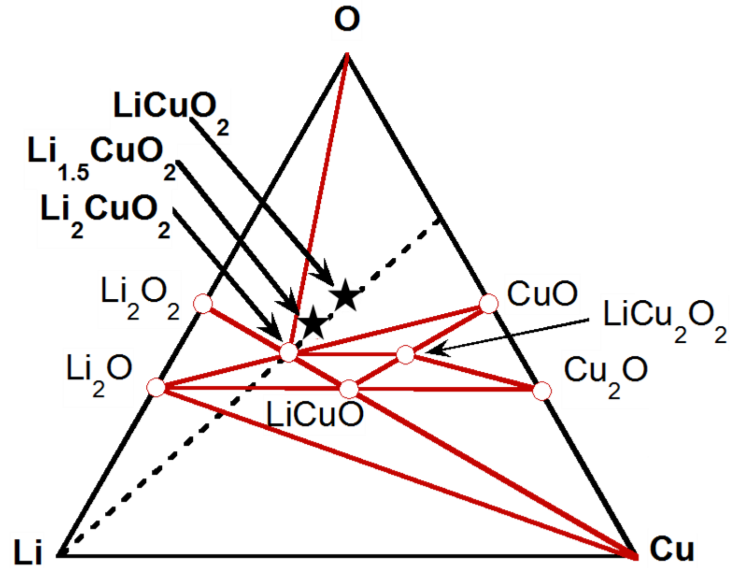


- *In situ* Raman spectra were compared to standards of $LiNiO_2$ (close-packed) and $NaCuO_2$ (monoclinic).
- Raman spectroscopy confirms that the structure of $Li_2Cu_{0.5}Ni_{0.5}O_2$ transforms from orthorhombic to close-packed layered during charge, similar to previous studies of Li_2NiO_2.

R. Ruther *et al.* Chem. Mater. 227, 6746-6754, 2015

Technical Accomplishment:
Quantitative gas evolution measurements show capacity of $Li_2Cu_{0.5}Ni_{0.5}O_2$ above 3.9 V is due to oxygen evolution

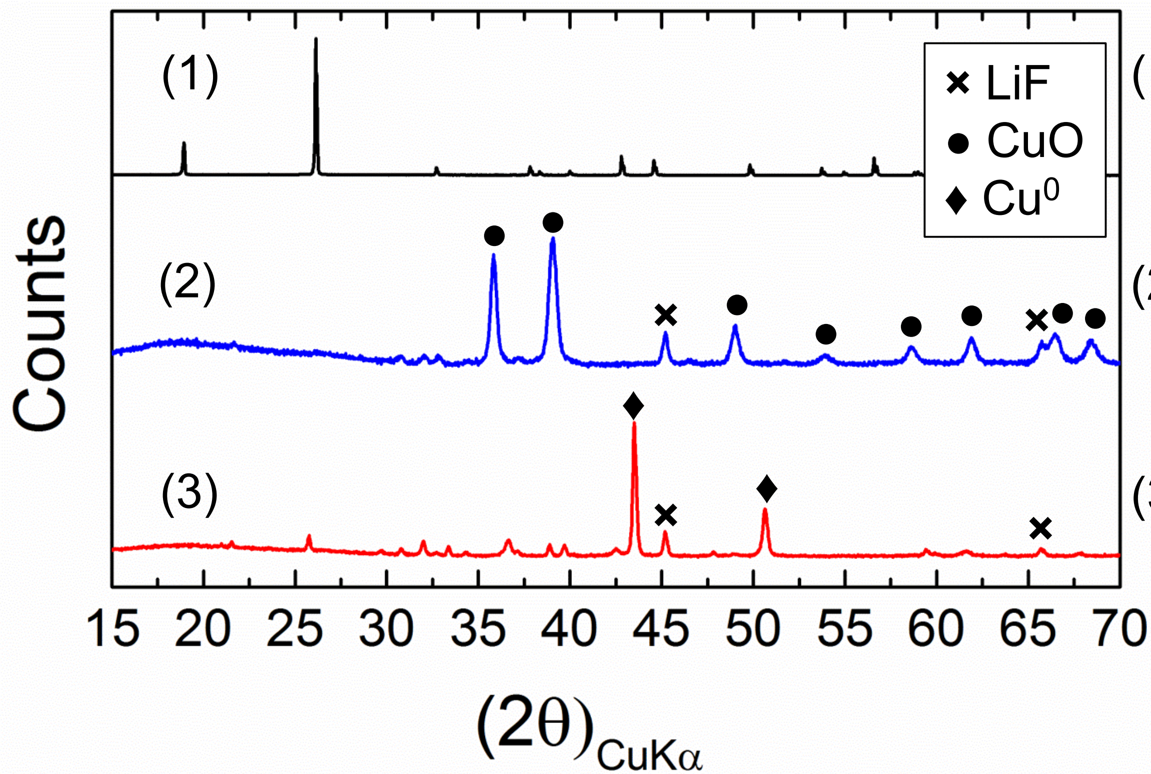




- Gas evolution in pouch cells was quantified using Archimedes' principle
- Using the ideal gas law, the moles of gas generated were calculated from the change in pouch cell buoyancy.
- All capacity extracted above 3.9 V can be attributed to gas evolution, assuming 4 e^- per mole of gas.
- O_2 and CO_2 were main gasses detected by mass spectrometry.

G. Veith and F. Delnick

Technical Accomplishment:
Fluorination of Li_2CuO_2 using F-containing polymers is a “no go”

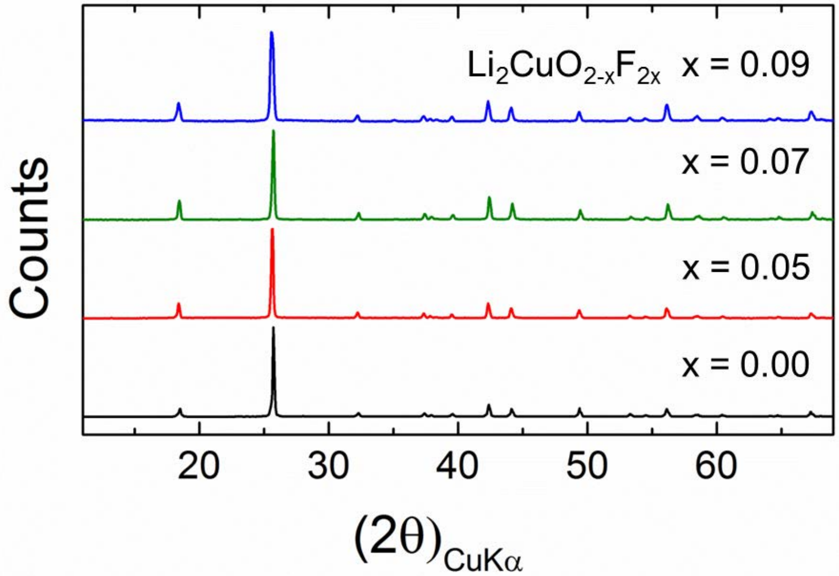


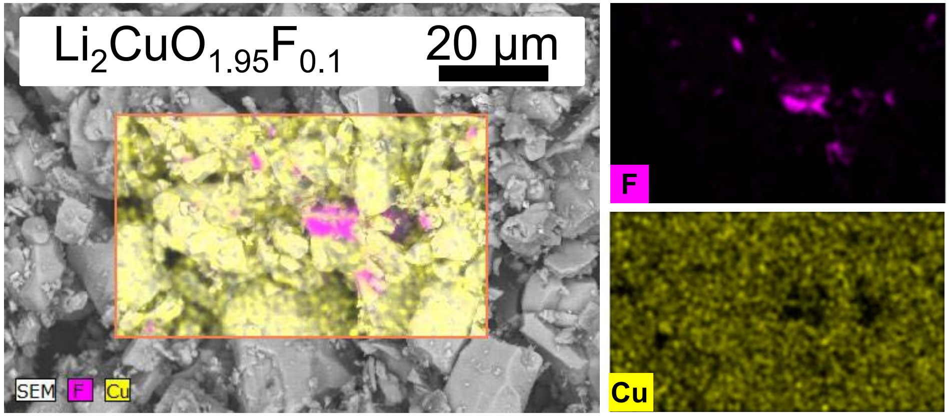
- Fluorination of Li_2CuO_2 should suppress oxygen evolution at high voltage.
- Borrowing from work with copper-based superconductors, teflon and PVDF polymers were selected as fluorinating agents for safety and ease of use.
- Reactions carried out in O_2 at 375 – 400 °C resulted primarily in decomposition of Li_2CuO_2 to LiF and other Cu-containing phases.

Technical Accomplishment

Li_2CuO_2 is fluorinated using LiF, but the product is not homogeneous

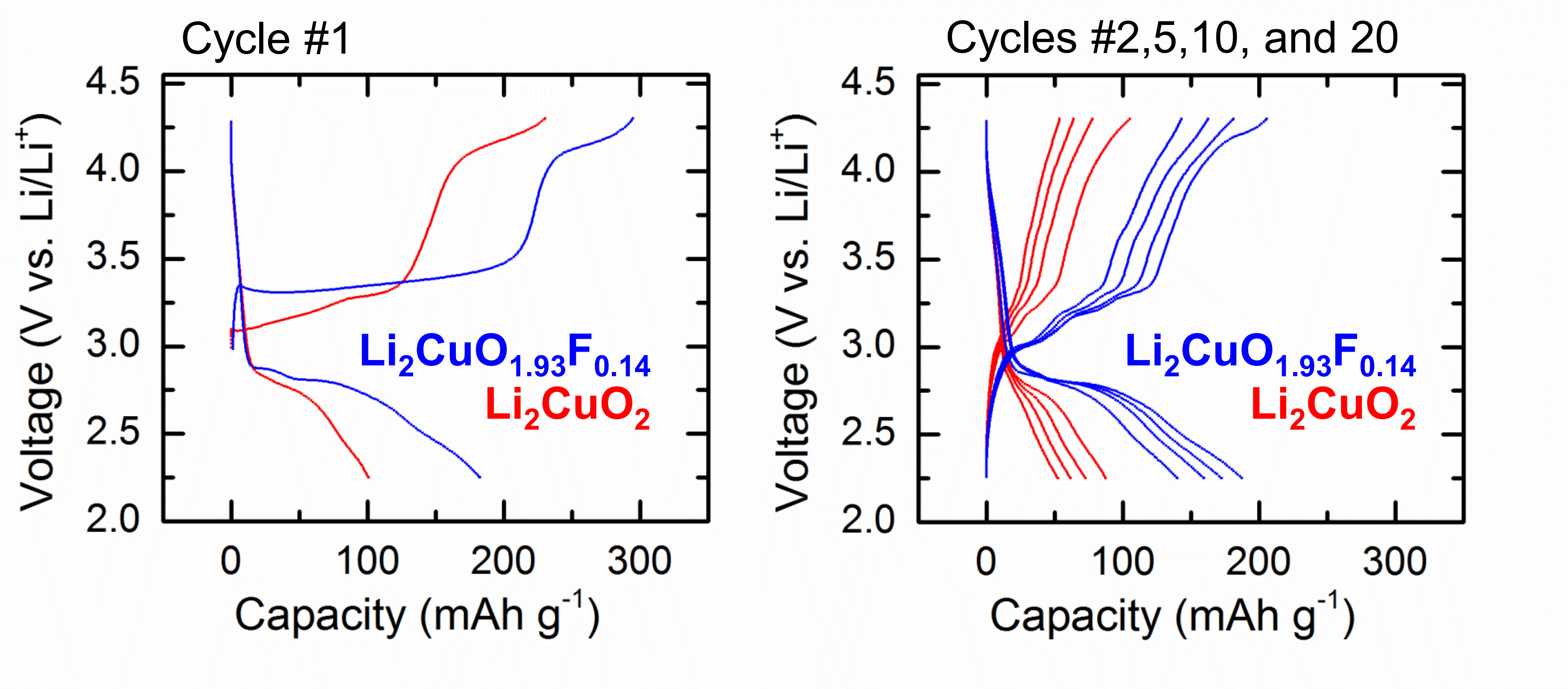
$$(2-2x)LiOH + 2xLiF + CuO \xrightarrow{800\ °C,\ air} Li_2CuO_{2-x}F_{2x} + (1-x)H_2O$$





- Fluorination was carried out by substituting LiF for LiOH during synthesis
- XRD indicates formation of a single phase, but is not very sensitive to LiF
- EDS shows F is not uniformly doped and some LiF remains as a separate phase

Technical Accomplishment:
Doping with LiF improves electrochemical performance of Li_2CuO_2

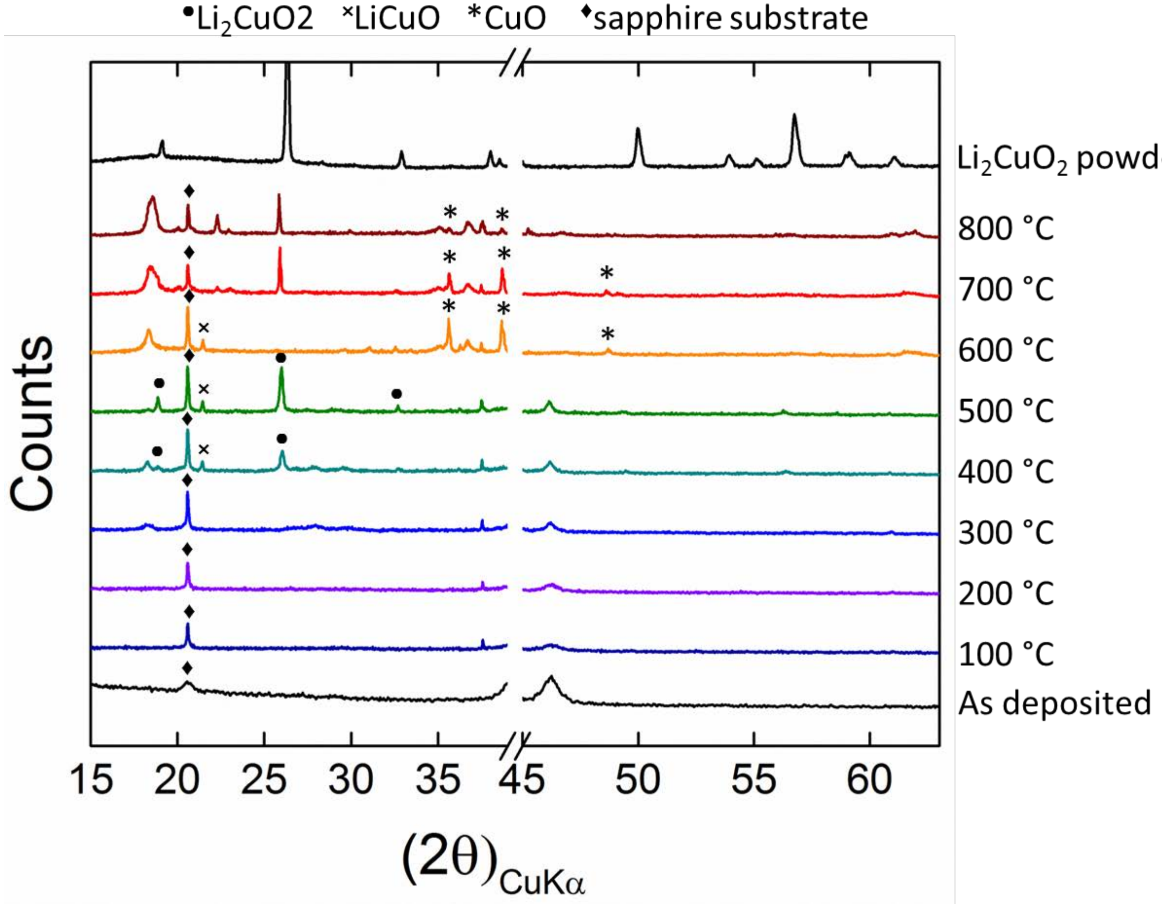


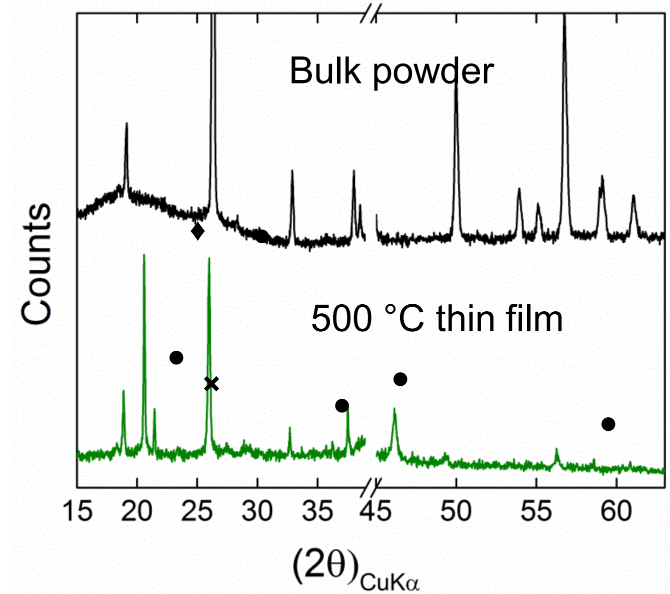
- Fluorination increases initial capacity and reduces first-cycle irreversible loss.
- Fluorination does not reduce the overall capacity fade and sensitive to synthesis and processing parameters.
- Fluorination of Ni-stabilized compositions is underway to increase the voltage profile.

Unpublished 2016

Technical Accomplishment:

Li_2CuO_2 thin films (~ 1 µm thick) are successfully deposited





- Thin films of Li_2CuO_2 were deposited by RF sputtering from a Li_2CuO_2 target.
- *In situ* XRD shows that the desired phase forms around 500 °C in dry air.
- Thin film Li_2CuO_2 will serve as a model system to evaluate cathode properties such as lithium-ion diffusivity and electrode-electrolyte interfaces.

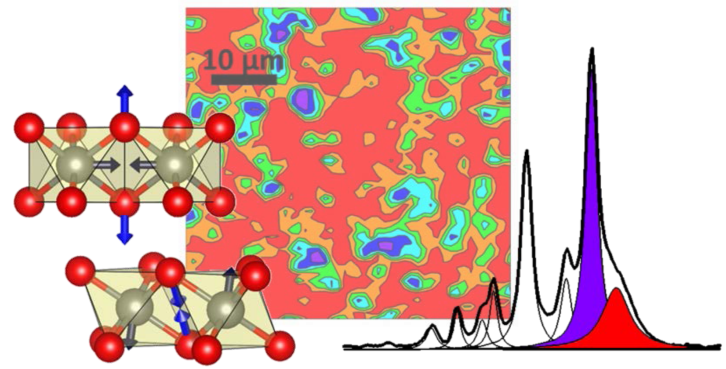
A. Kercher

Summary

Technical Approach:

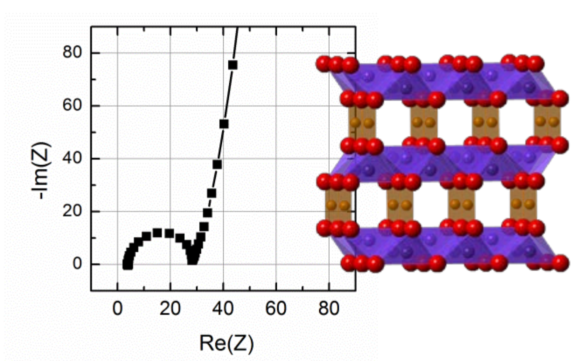
Design and synthesis of high voltage, high capacity cathodes guided by *state-of-the-art* characterization and modeling

- Synthetic approaches include anionic substitution and advanced coatings to stabilize the interface and bulk structure.
- Diagnostic tools include a suite of microscopic and sprectroscopic techniques.



Accomplishments:

- Identified chemical and structural changes that occur in $Li_2Cu_{0.5}Ni_{0.5}O_2$ under in situ conditions and mapped out phase transformations using TXM-XANES.
- Unraveled mechanisms of electrochemical activity and degradation of $Li_2Cu_xNi_{1-x}O_2$ cathodes using a combination of X-ray and neutron diffraction, *in situ* Raman spectroscopy, electrochemistry, and gas evolution experiments.
- Developed fluorination routes to stabilize Li_2CuO_2 cathodes to minimize oxygen loss and capacity degradation at higher voltages.



Ongoing work:

- Partial fluorination of high capacity $Li_2Cu_xNi_{1-x}O_2$ cathodes to improve stability at high voltage and prevent oxygen loss.
- Synthesis of Ni-rich compositions of $Li_2Cu_xNi_{1-x}O_2$.
- Fabrication and testing of thin film $Li_2Cu_xNi_{1-x}O_2$ cathodes to extract fundamental physical properties (ionic and electronic transport, interfacial reactions).

Response to Reviewers Comments

Reviewers 1&3: Both reviewers noted that the work on $Li_2Cu_xNi_{1-x}O_2$ cathodes is encouraging, but the structure needs to be stabilized. PI should narrow the scope of work and explore this system exhaustively.

Response: In the current year, we focused on $Li_2Cu_xNi_{1-x}O_2$ and improved the electrochemical performance and oxidative stability of this system. We also performed more detailed X-ray synchrotron studies to investigate the chemical and structural transformations that occur in this material and limit reversibility.

Reviewer 2 noted the need to eliminate impurities, improve the stability by cationic substitution, and reduce the particle size to improve the rate performance.

Response: New synthesis and precursors are used to address the above issues. With respect to stability, we have pursued anionic substitution to limit oxygen participation in the redox process.

Reviewer 3 saw no clear strategy to mitigate oxygen evolution and wondered if cation substitution will help. He/she also commented that the voltage profile is still not attractive.

Response: This year we tried fluorination of $Li_2Cu_xNi_{1-x}O_2$ with 5-7% F atoms substituting oxygen. This should suppress oxygen evolution and prevent capacity loss at higher voltage. We succeeded in fluorinating Li_2CuO_2. Gas evolution studies and work with Ni-containing samples are in progress.

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

Electron Microscopy
Dr. Chong Ming Wang

Synchrotron X-ray microscopy and 3D microstructure
Dr. Johanna Nelson Weker

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

Remaining Challenges and Barriers

- Improve the synthesis methods to make phase pure $Li_2Cu_xNi_{1-x}O_2$ with smaller particle sizes including carbon coating to improve capacity retention
- Synthesize and stabilize Ni-rich $Li_2Cu_xNi_{1-x}O_2$ compositions to increase the voltage profile
- Investigate the role of fluorine in improving the capacity retention and provide further evidence that fluorine is substituting for oxygen
- Investigate the role of Ni substitution in stabilizing the structure and correlate with electrochemical performance

Proposed Future Work

FY 16-17

- 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 rate performance
  (ii) Eliminate impurity phases and vary composition
  (iii) Continue fluorination of nickel-rich $Li_2Ni_xCu_{1-x}O_2$ to increase the redox voltage
- Fabricate thin films of $Li_2Ni_xCu_{1-x}O_2$ by RF sputtering and study the structure and electrochemical reactivity at the interface
- Investigate the rate capability of $Li_2Ni_xCu_{1-x}O_2$ for x = 0.4, 0.5, and 0.6
- Study the lithiation-delithiation mechanism and determine the reversibility of Cu and Ni redox activity using *in situ* synchrotron XAS and diffraction

Beyond

- Synthesize other copper/nickel cathode compositions using polyanionic groups that stabilize transition metals in higher oxidation states
- Study model cathode compounds to monitor lattice oxygen loss at higher redox potentials and understand the mechanism of oxygen loss