Discovery of High-Energy Lithium-Ion Battery Materials

Wei Tong

Lawrence Berkeley National Laboratory

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Project ID: bat307

Overview

Timeline

- October 1st , 2016
- September 30th, 2018
- Percent complete: 83%

Barriers

- Energy density
- Cycle life
- Safety

Budget

- Total project funding
    - FY2016 $450,000
    - FY2017 $450,000
    - FY2018 $450,000

Partners

- Collaborations
    - SSRL, ALS, APS
    - UCB
- Project Lead: Marca Doeff

Relevance and Project Objectives

- Develop a cathode that can cycle > 200 mAh/g while exhibiting minimal capacity and voltage fade
  - Target at Li-rich compositions in Li-Ni-O chemical space that utilizes Ni^{2+}/Ni^{4+} redox to potentially overcome capacity limitation per transition metal
  - Integrate a second transition metal on the first and second row to improve structural stability and/or contribute electrochemically active redox

- Gain in-depth understanding on the correlation between composition and electrochemistry in Li-rich layered oxides
  - Understand the contribution of cationic and anionic redox in electrochemistry
  - Investigate the potential impact of transition metal on oxygen reactivity

Milestones

- Complete the electrochemical characterization to determine the activation of lattice oxygen in Li-rich Ni-based metal oxides by varying testing conditions and optimizing electrode kinetics. (12/31/2017) **Complete**

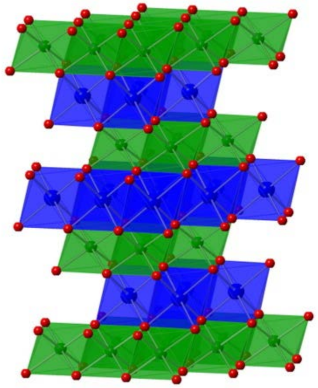
- Investigate the structural evolution upon Li (de)insertion in Li-rich Ni-based metal oxides. (3/31/2018) **Complete**

- Synthesize alternative Li-rich Ni-based oxide cathodes with varied metal contents and characterize the crystal structures. *Go/No-go decision:* The alternative compound delivers a capacity > 200 mAh/g. (6/30/2018) **On track**

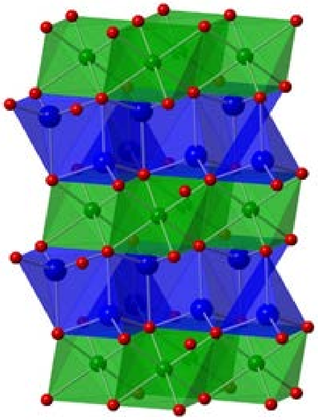
- Investigate crystal structure evolution in selected Li-rich Ni-based layered oxide at various charge-discharge states. (9/30/2018) **On track**

Approach/Strategy

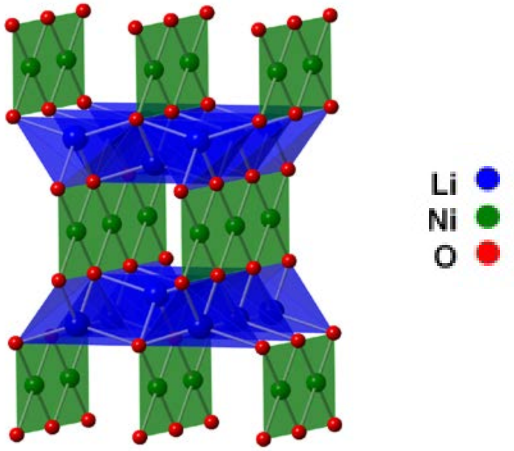
- **Known Material Chemistry in Li-Ni-O Space**
  - $LiNiO_2$: $R\bar{3}m$ space group, Ni^{3+}/Ni^{4+} redox, > 270 mAh/g
  - Li_2NiO_2: $P\bar{3}m1$ and $Immm$ space group, Ni^{2+}/Ni^{4+} redox, 513 mAh/g
- **General Material Design**
  - Electrochemical redox: Ni^{2+}/Ni^{4+}
  - Structural stabilizing TM: multivalent metals enabling Ni redox and improving structural stability



$LiNiO_2$ ($R\bar{3}m$)



Li_2NiO_2 ($P\bar{3}m1$)



Li_2NiO_2 ($Immm$)

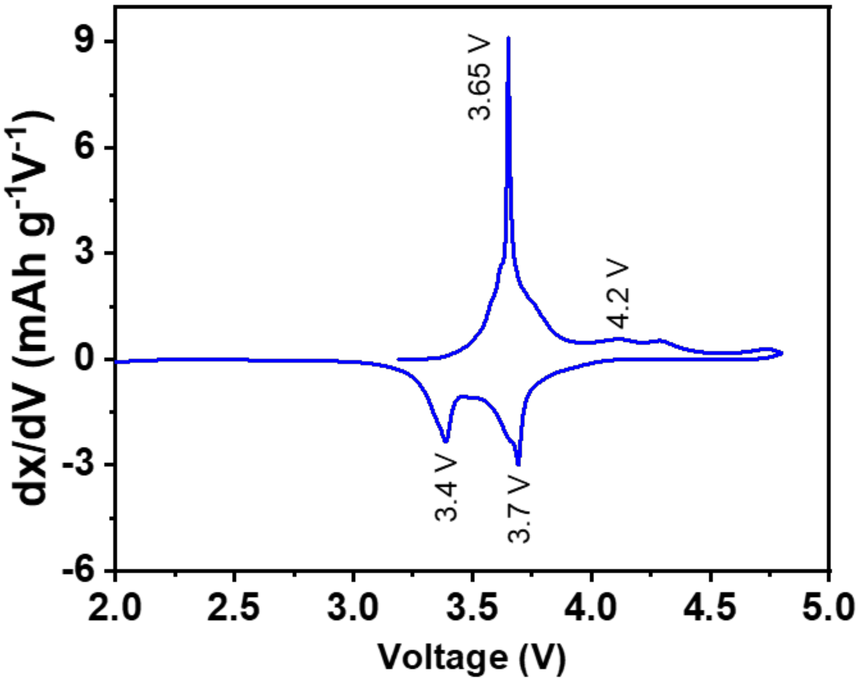
Approach/Strategy

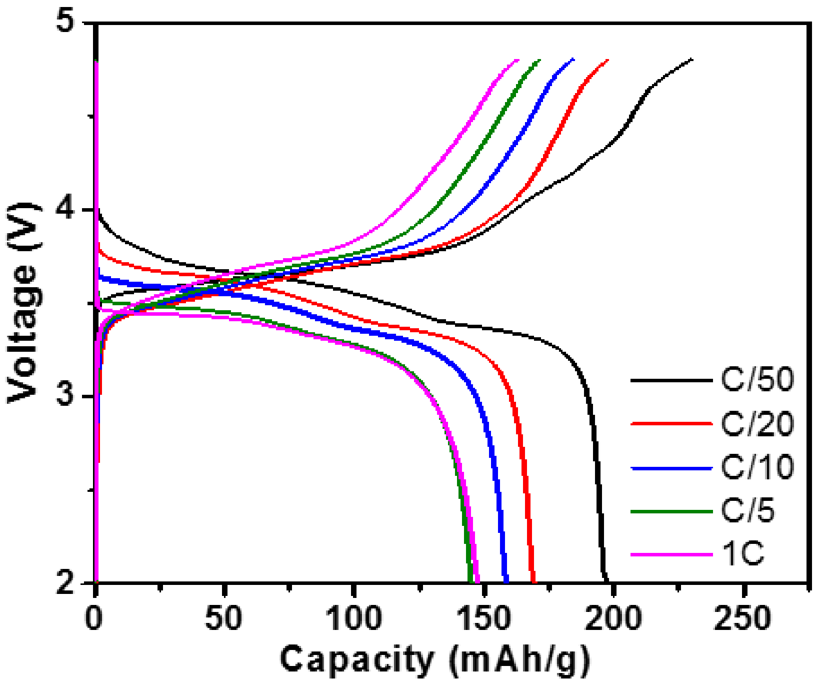
- Inherit the wisdom of high capacity Li-rich oxide cathodes, design compositions that contain Li excess and utilize Ni^{2+} to Ni^{4+} redox along with a second transition metal to achieve high capacity and good structural integrity

- Investigate the impact of anionic oxygen activity on voltage fade in Li-rich metal oxides by combining differential electrochemical mass spectrometry (DEMS), advanced synchrotron spectroscopy and electrochemical characterization

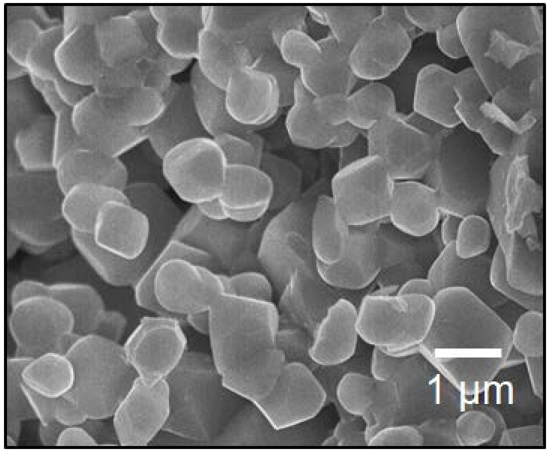
- Design materials to elucidate the potential impact of transition metal on oxygen activity during electrochemistry

Anionic Oxygen Activity in LNRO

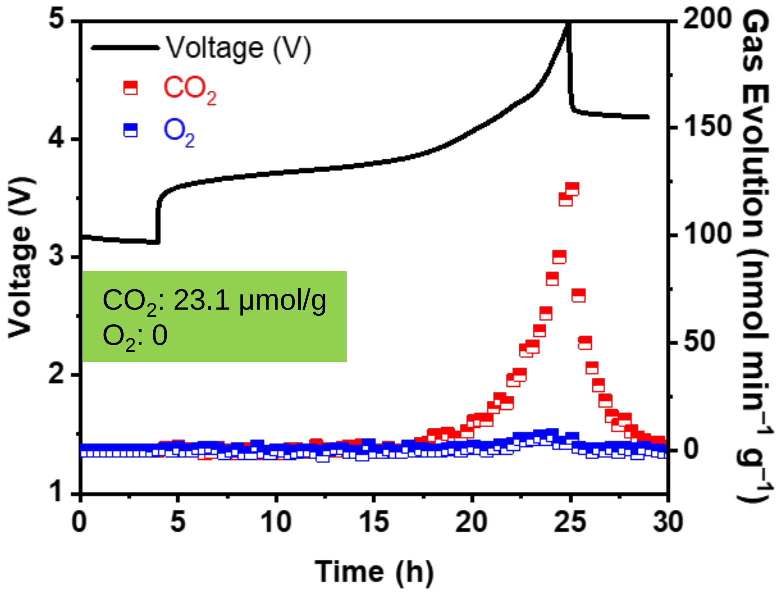




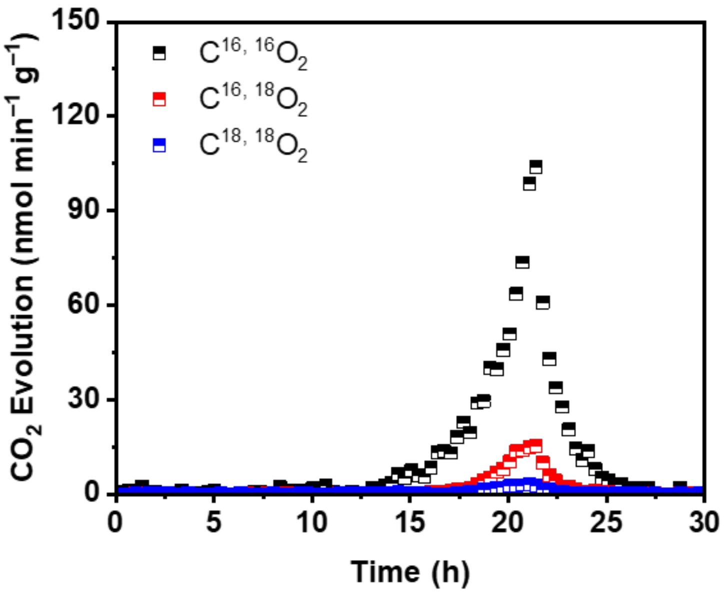
- Absence of high V plateau on initial charge and limited rate capability previously observed for $Li_{1.2}Ni_{0.2}Ru_{0.6}O_2$ (LNRO)
- Need to explore the impact of kinetics (e.g., low Li^+ diffusivity and/or electrical conductivity) on oxygen redox

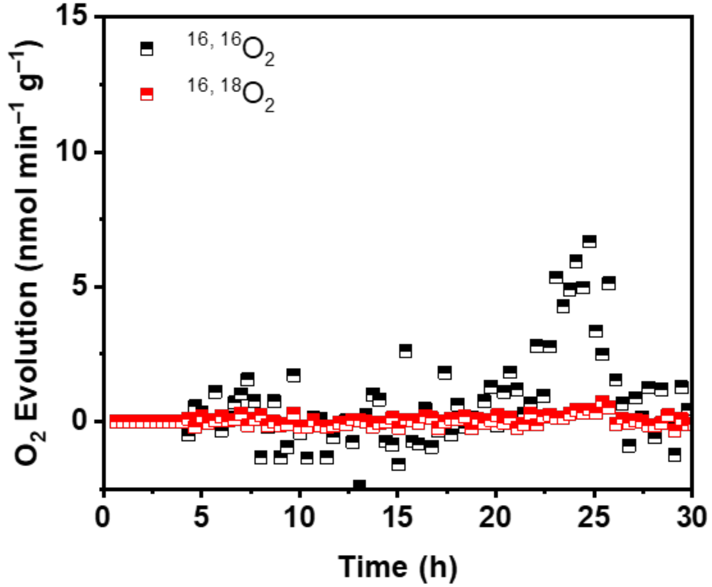


Gas Evolution for ^{18}O-LNRO



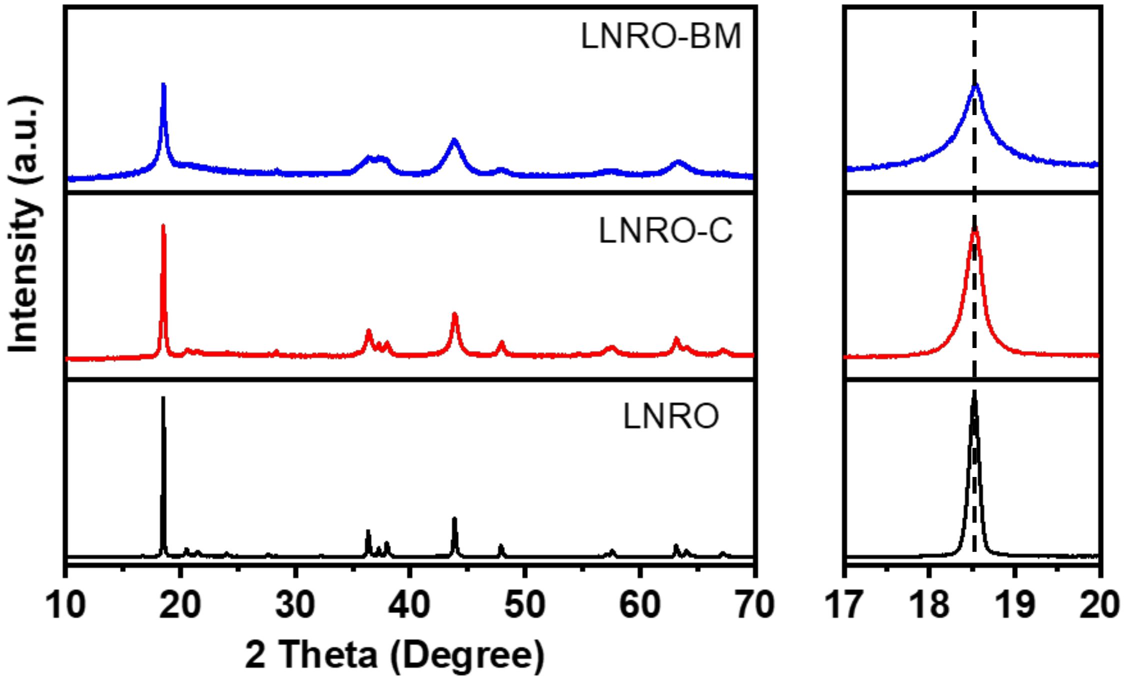
In collaboration with Bryan McCloskey at UCB

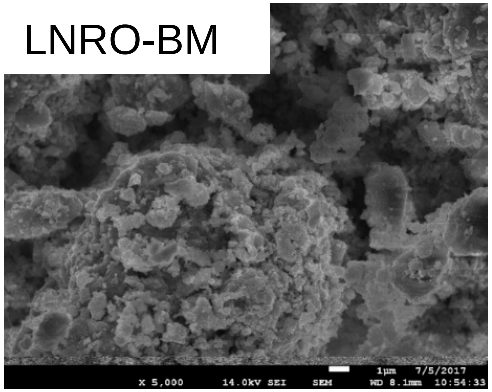


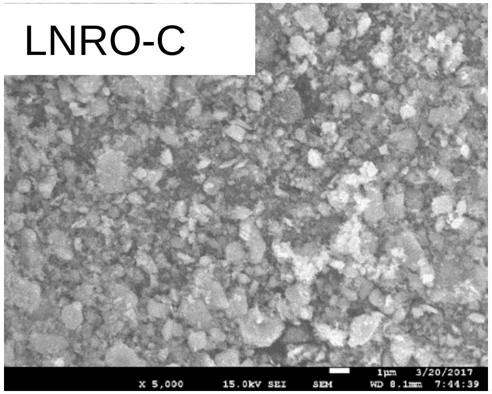


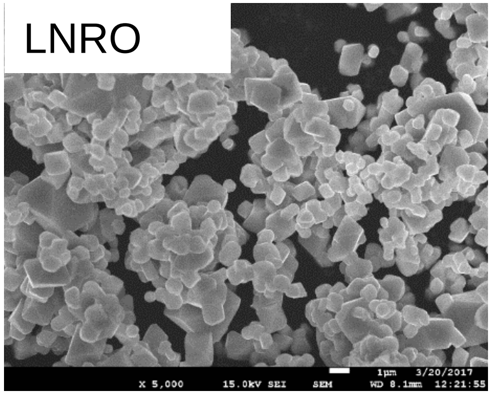
- Large increase in CO_2 evolution at 5 V, with $C^{16,16}O_2$, $C^{16,\,18}O_2$, $C^{18,\,18}O_2$ of 85.7%, 11.7% and 2.6%
- Almost no O_2 evolution detected, and minimal contribution from ^{18}O in LNRO
- No extra capacity confirms absence of anionic oxygen redox in LNRO even at 5 V cutoff

Impact of LNRO Particle Size & Morphology



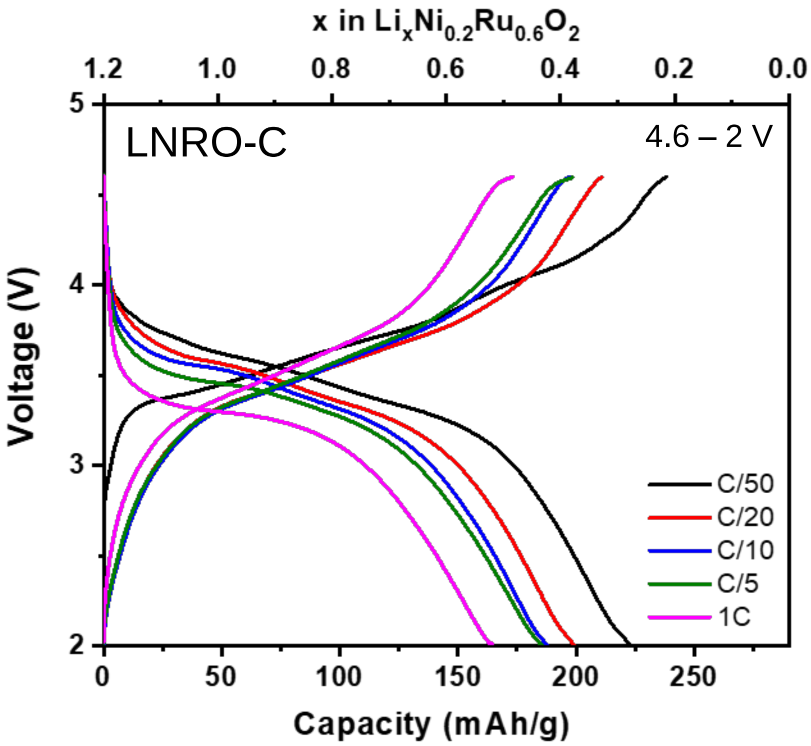


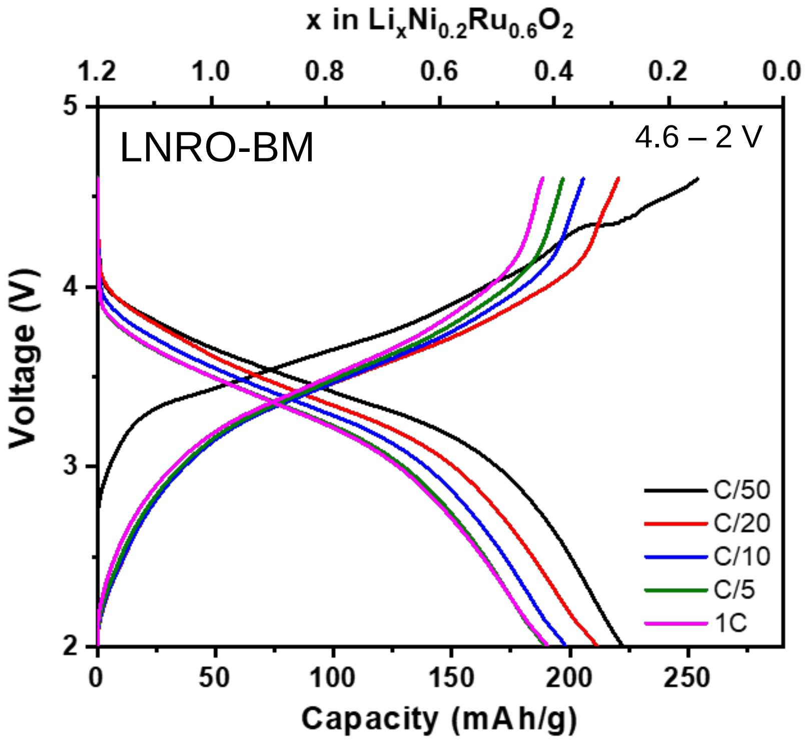




- Ionic and electrical conductivity explored by reducing LNRO particles *via* ball milling method (LNRO-BM) and use of conductive carbon matrix (LNRO-C)
- Particle size & morphology largely modified, but bulk crystal structure mostly reserved

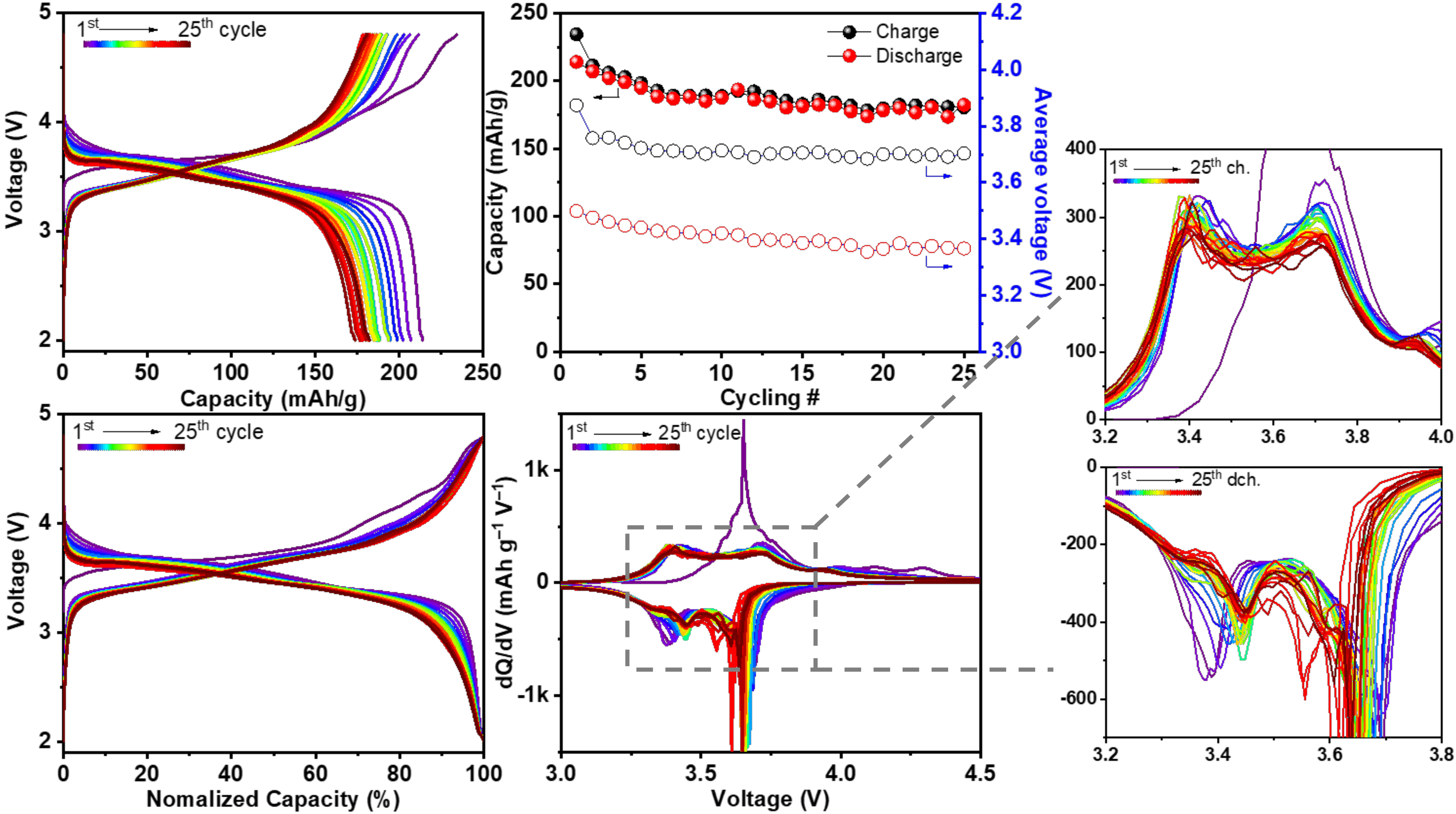
Electrochemistry of Modified LNRO





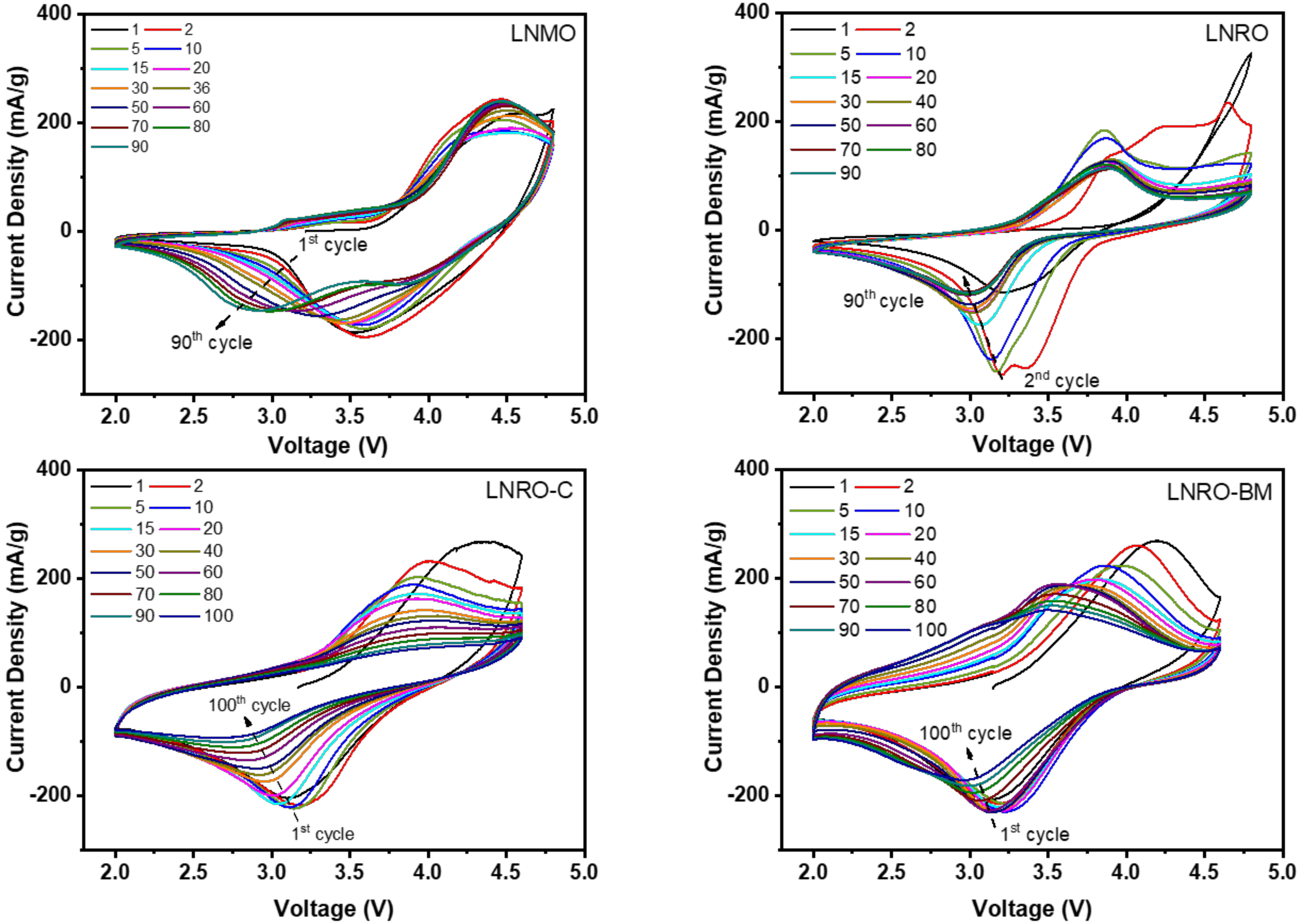
- Higher Li^+ conductivity anticipated for LNRO-BM due to particle size reduction, and electrical conductivity for LNRO-C
- Modification results in a higher capacity, but still accountable for Ni/Ru redox
- Better rate capability of LNRO-BM suggests a dominating factor of ionic conductivity in LNRO compound

Cycling Performance of LNRO



- Different voltage retention behavior observed for LNRO
- Absence of oxygen redox in LNRO useful to study role of oxygen redox in voltage fade (currently revisited) from a different perspective

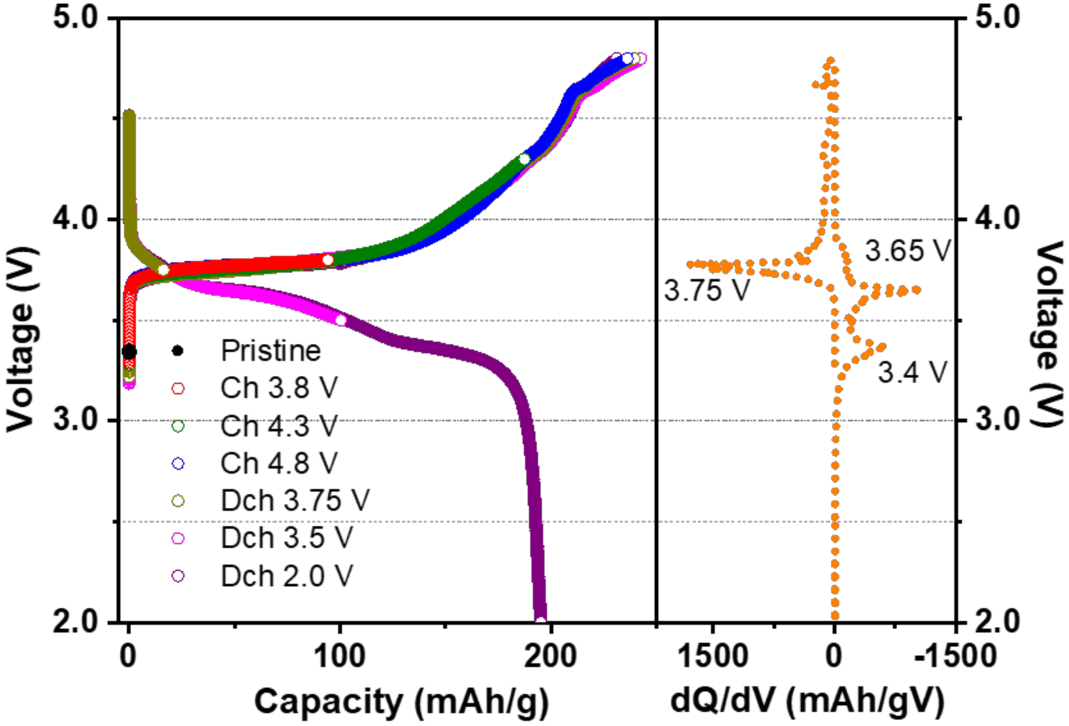
Voltage Retention of LNRO



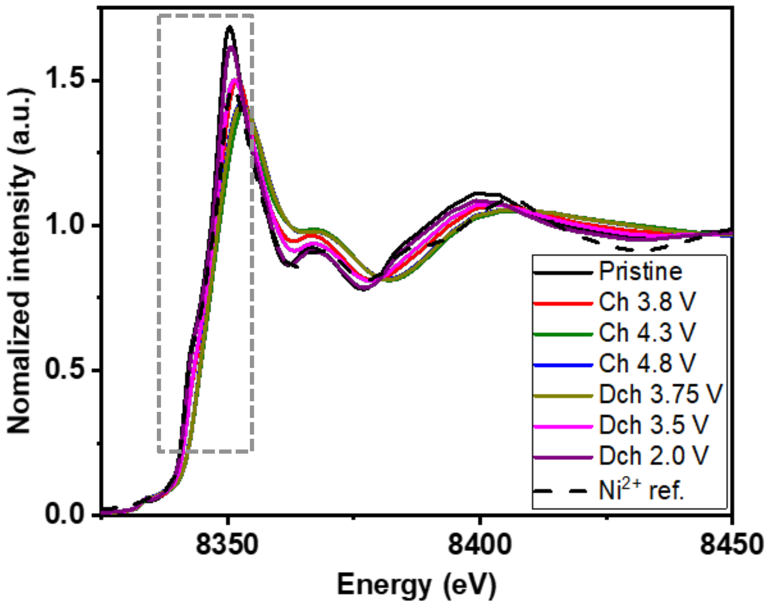
4.8 – 2.0 V
0.5 mV/s

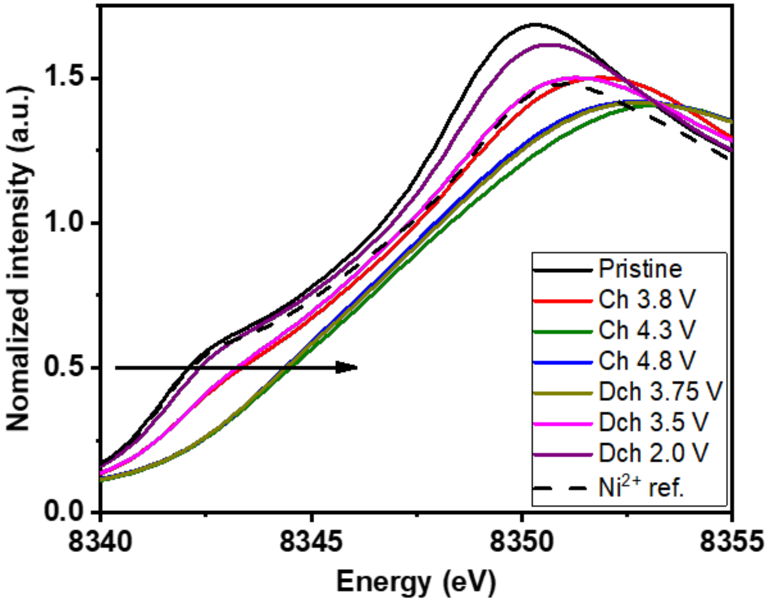
- Voltage fade more visible in modified LNRO, but at a much lower degree compared to $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$ (LNMO)

Ni Redox during Initial Cycle



Hard XAS collected at SSRL

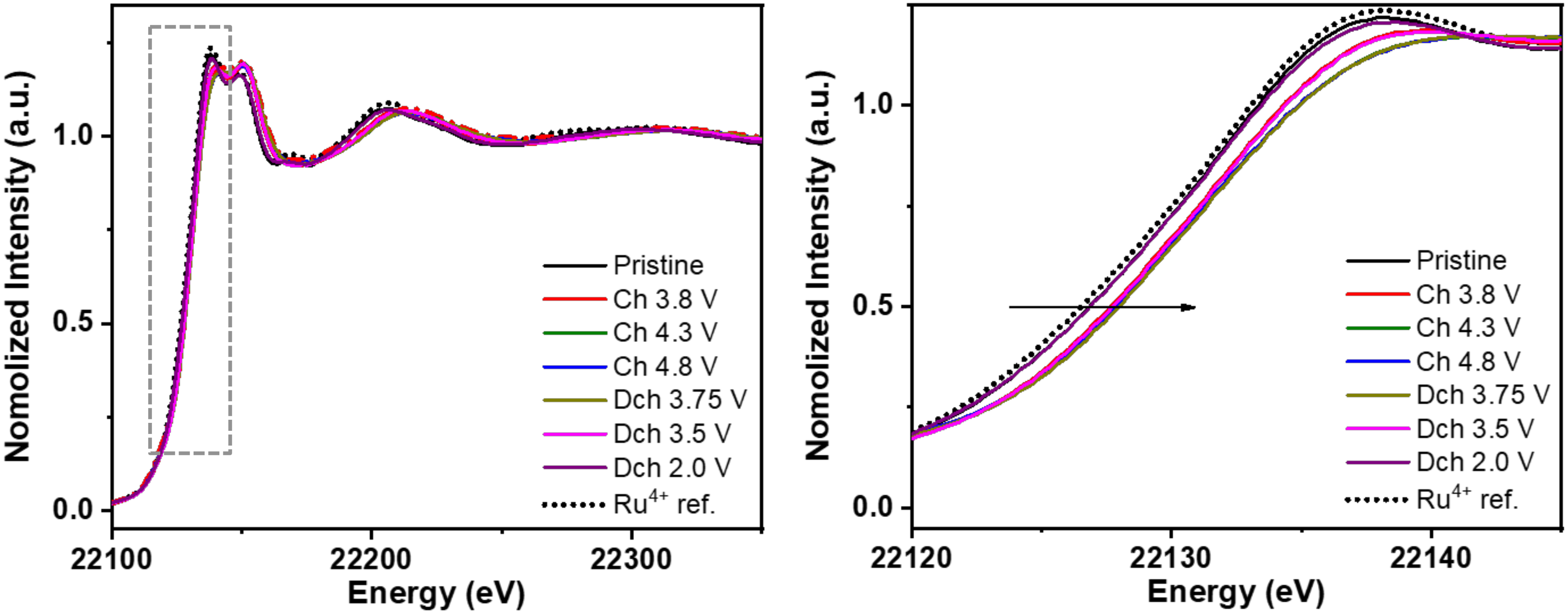




- Ni is 2+ in pristine LNRO
- Ni oxidation occurs across anodic peak at 3.75 V and completes at 4.3 V, reduction continues across both cathodic peaks at 3.6, 3.4 V

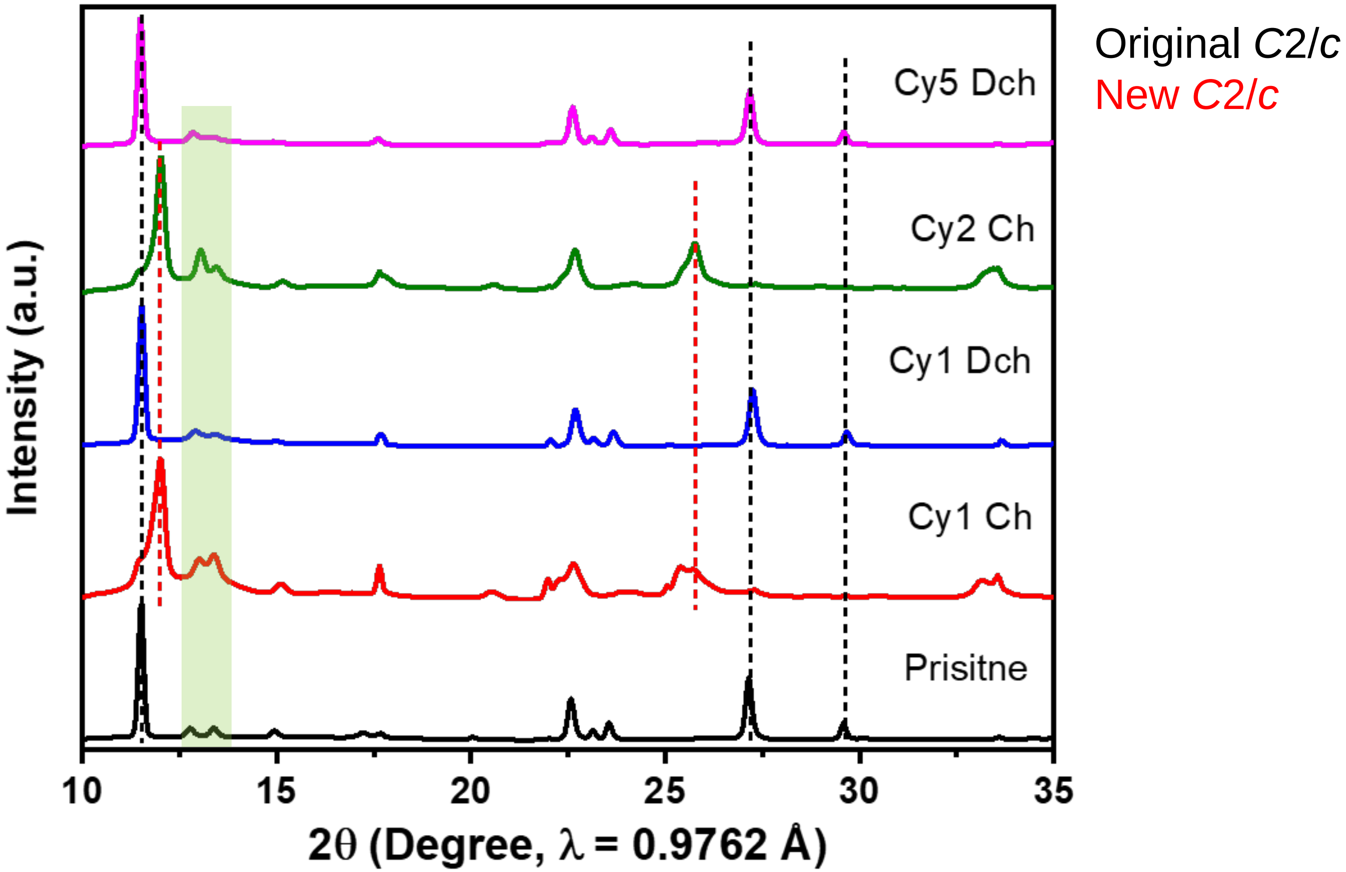
Ru Redox during Initial Cycle

Hard XAS collected at SSRL



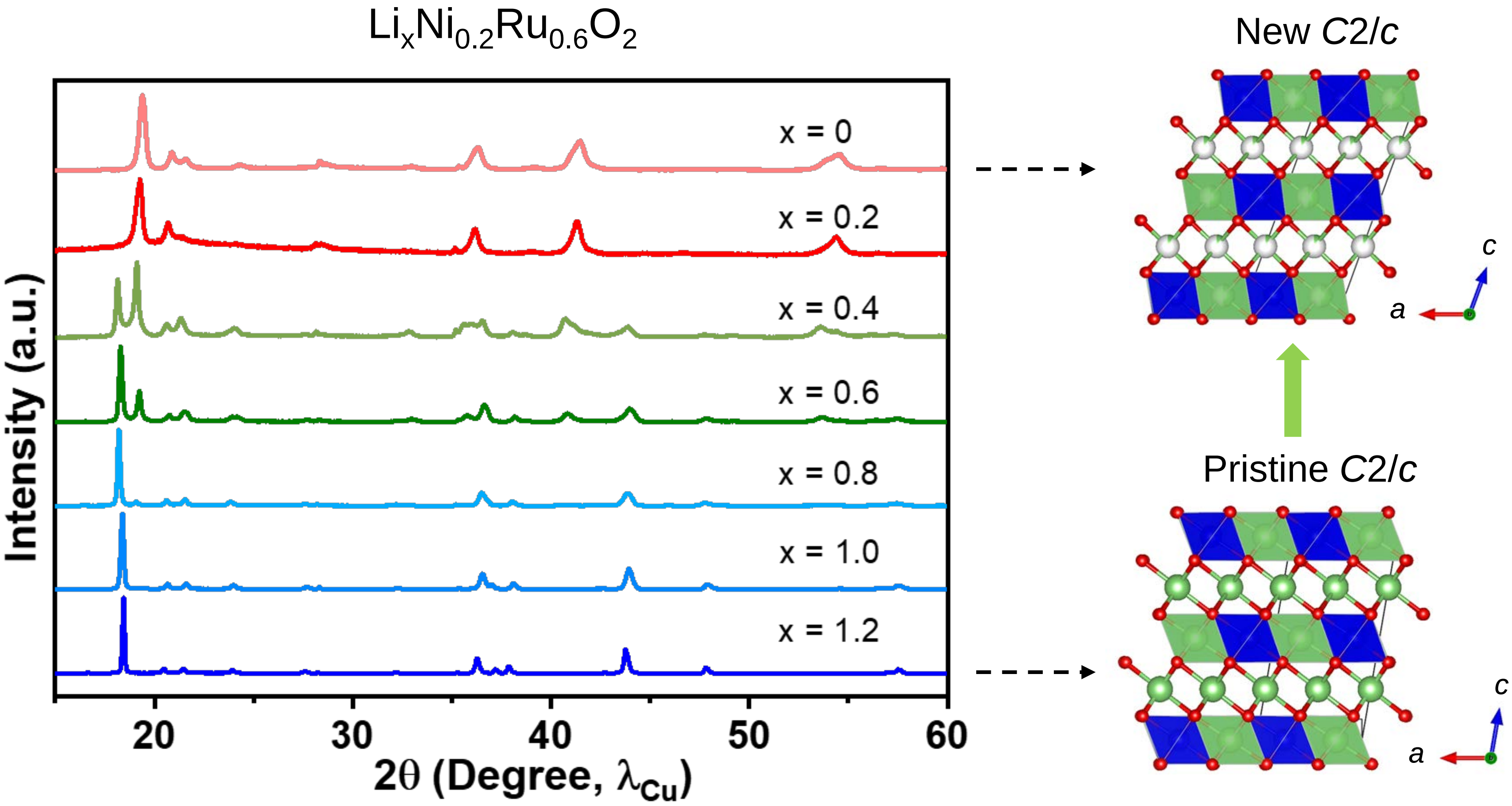
- Ru is 4+ at pristine state
- Ru oxidation/reduction follows similar trend to Ni, but substantial charge compensation occurs at low V region (cathodic peak of 3.4 V)

Structural Evolution of LNRO during Cycling



- Super lattice peaks around 13º (green highlight) reserved upon cycling
- Structure is a key factor in electrochemistry (i.e., V fade) of Li-rich layered oxides beyond oxygen redox

Structural Evolution of LNRO Upon Delithiation

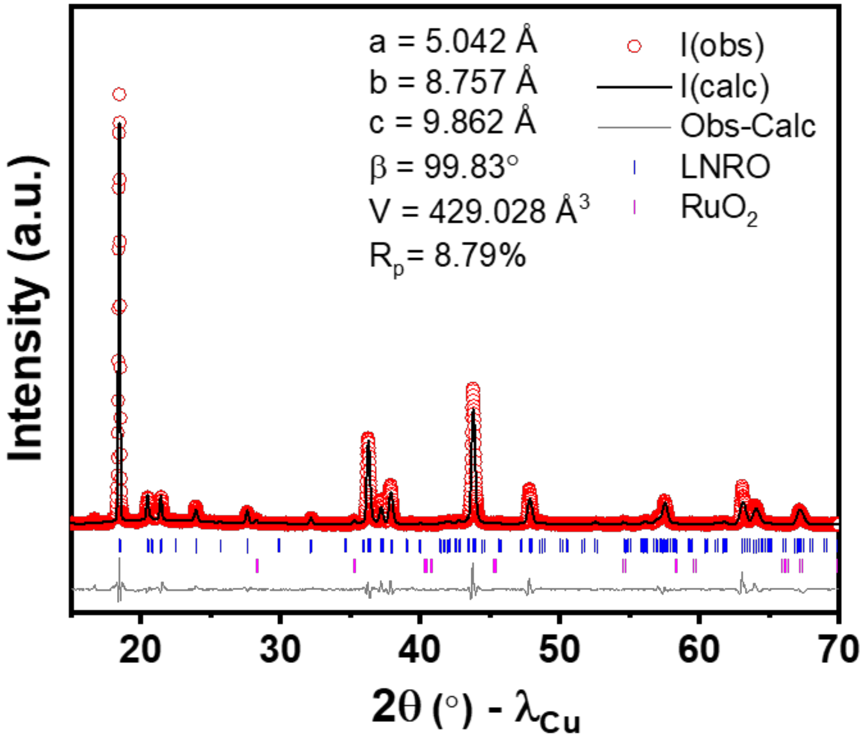


Note: Li content (x) is theoretical #

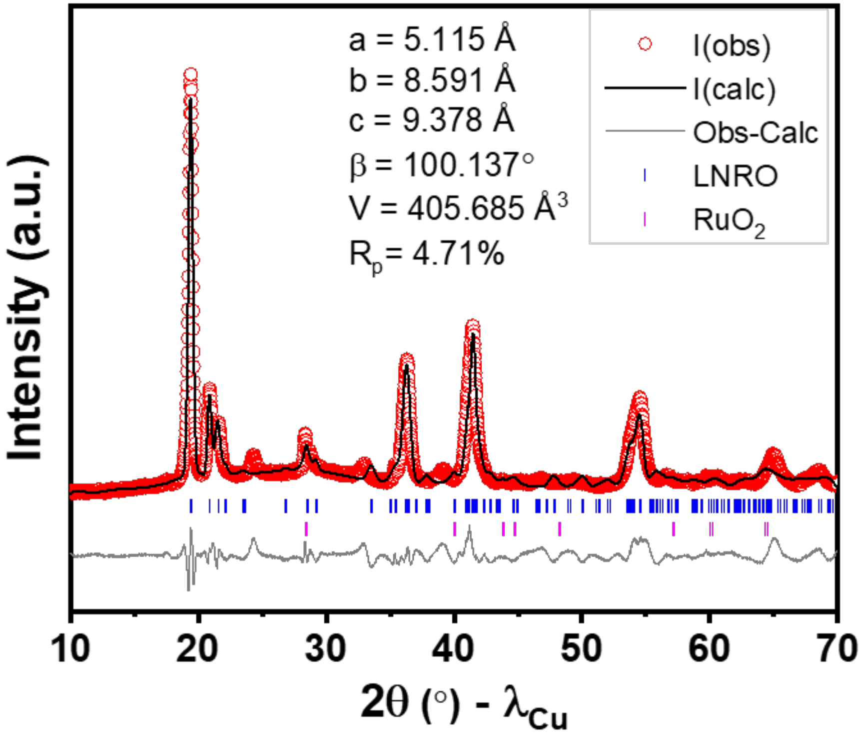
- Delithiated samples prepared by chemical oxidation method
- Different from Li-rich LNMO, a new monoclinic *C2/c* phase formed at ~ 0.6 Li

Structure Characterization of LNRO Upon Delithiation

Pristine LNRO

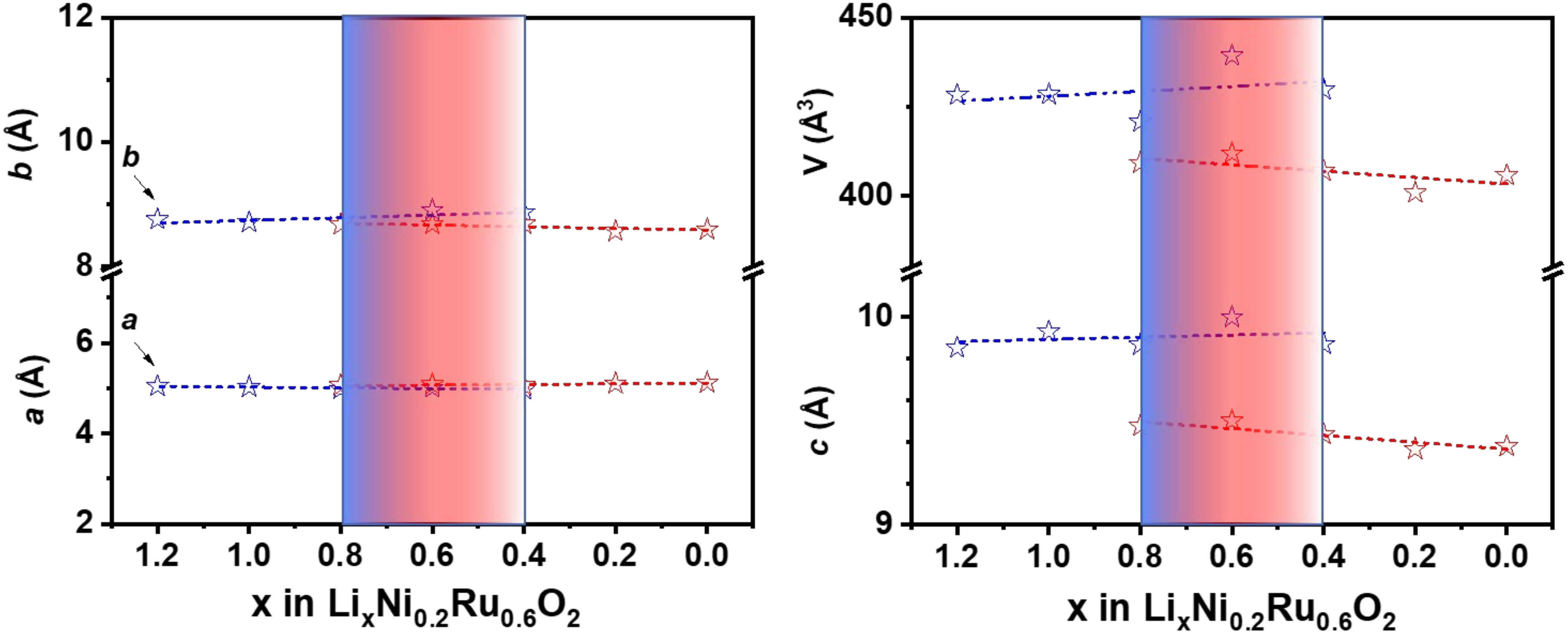


Delithiated LNRO



- Rietveld refinement of pristine and delithiated LNRO XRD patterns, based on monoclinic *C*2/*c*, gives a good fit but different lattice parameters (ΔV = 5.4%)

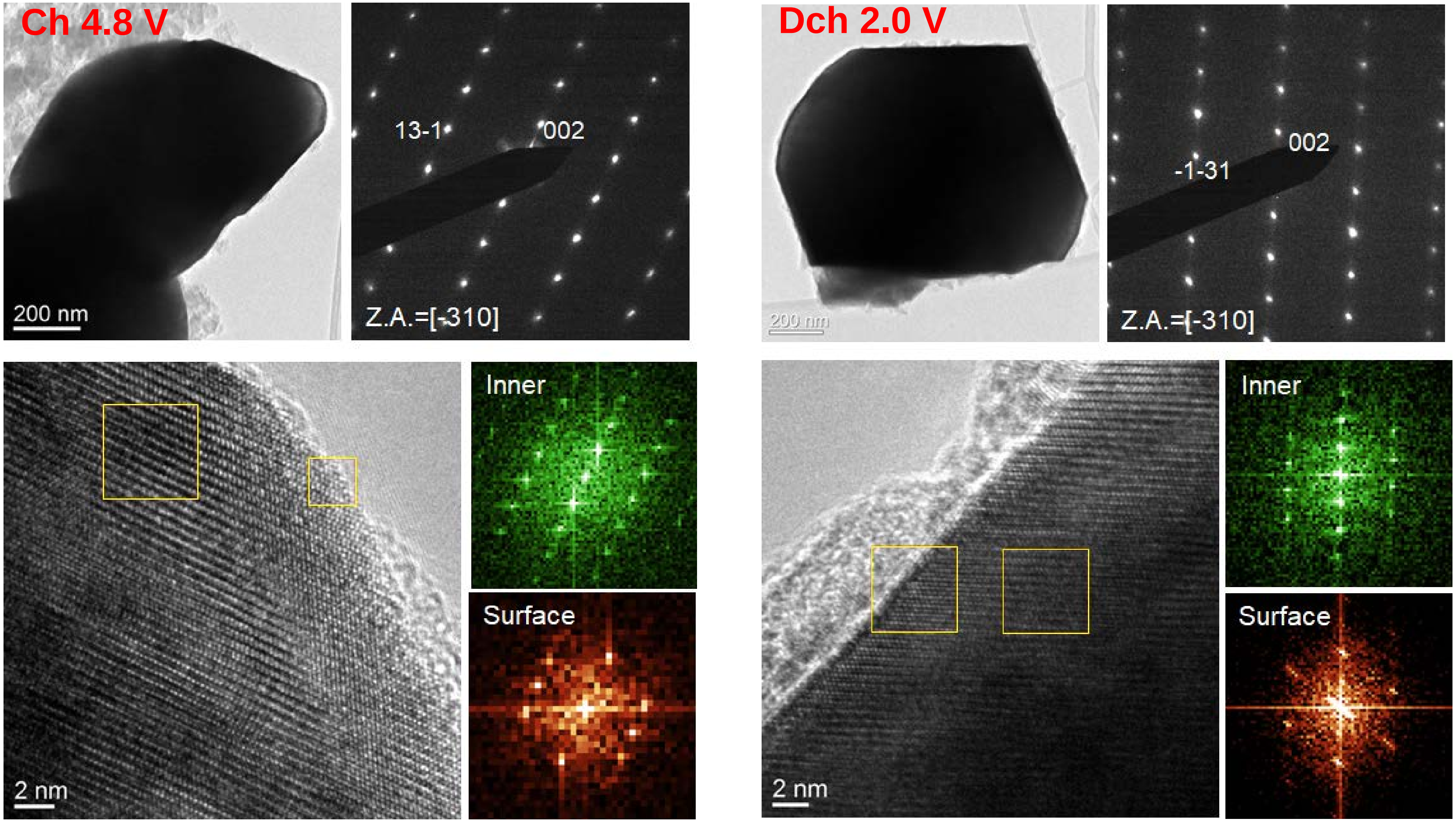
Structure Characterization of LNRO Upon Li Extraction



- XRD reveals original *C*2/*c* at 1.2 ≤ x ≤ 0.8, a new *C*2/*c* phase at x < 0.4 with two phases in between
- Subtle change in lattice parameter *a*, *b*, but *c* lattice shrinks for new *C*2/*c* phase

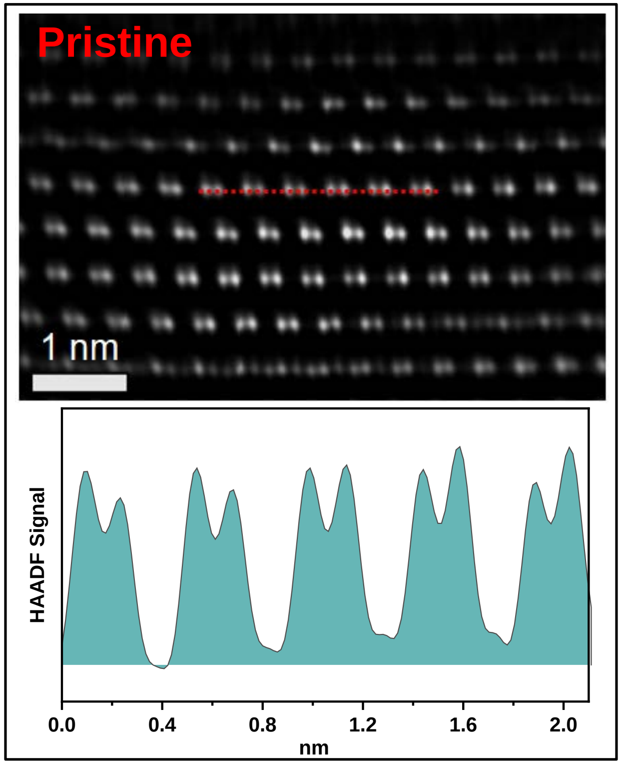
Structural Evolution Probed by HR-TEM

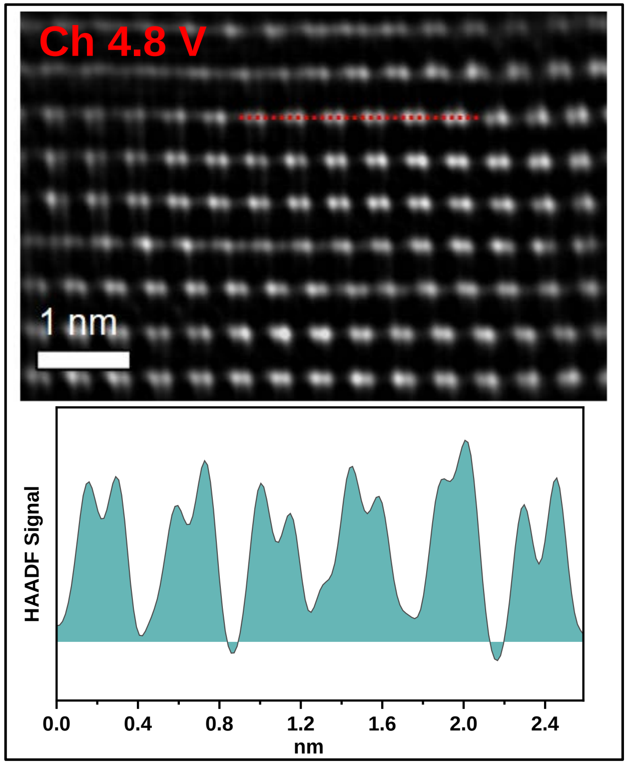
In collaboration with Dong Su at BNL

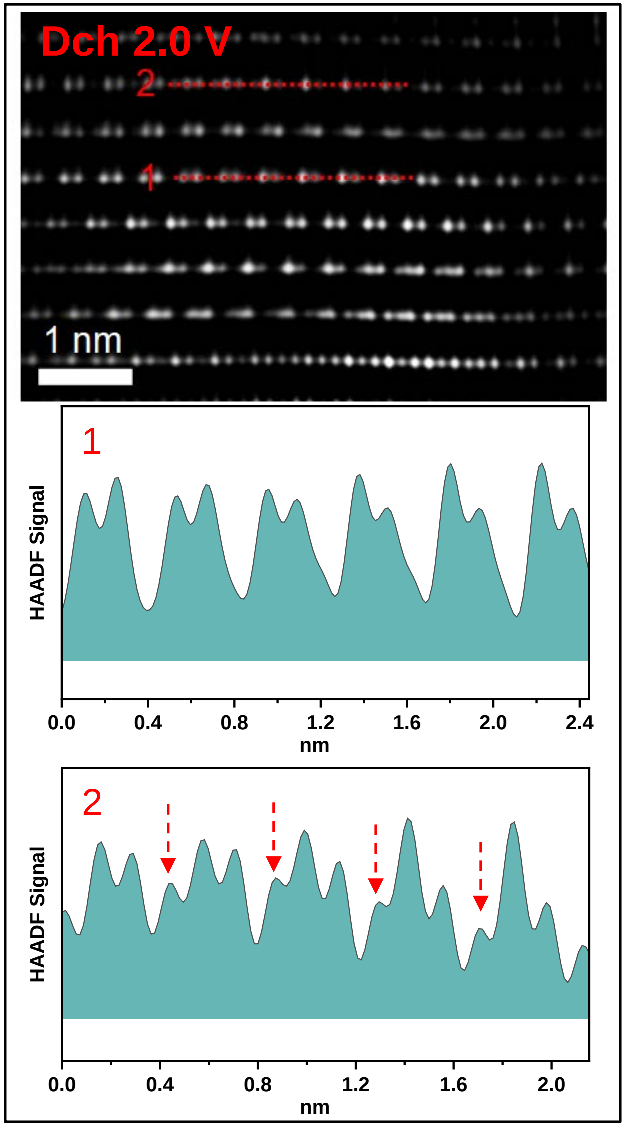


- LNRO layered structure remained after initial charge and discharge
- New monoclinic *C*2/*c* phase after charge and *c* lattice parameter confirmed by HR-TEM & STEM (9.91, 9.34 and 9.81 Å at pristine, charged and discharged state, respectively)

Structural Evolution Probed by HAADF-STEM





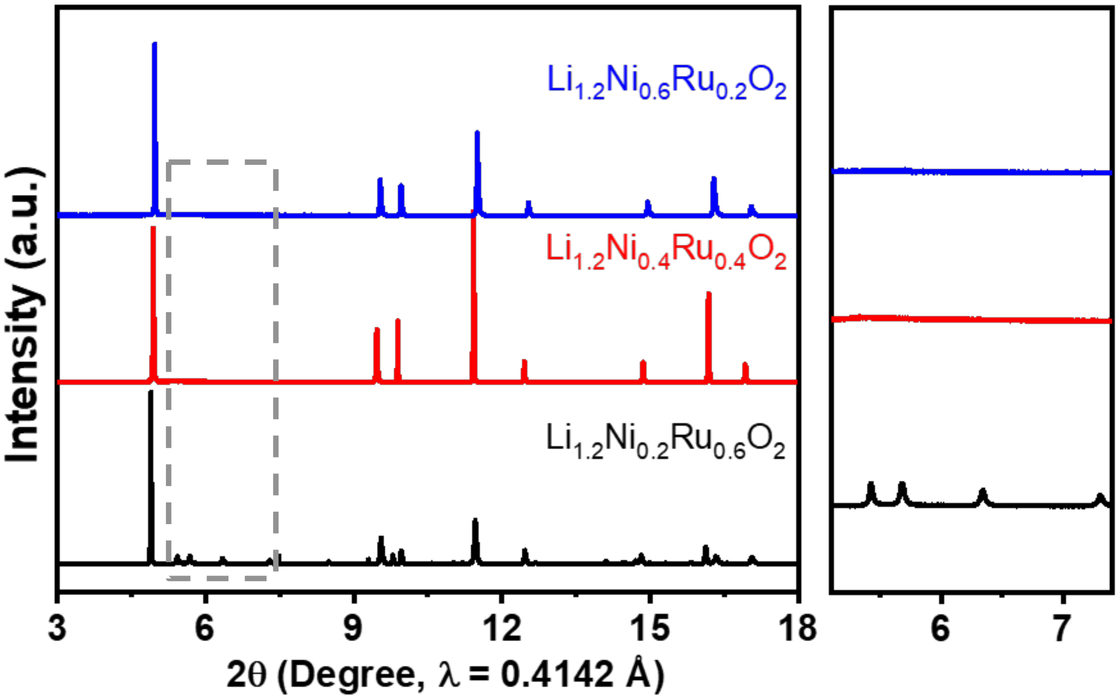


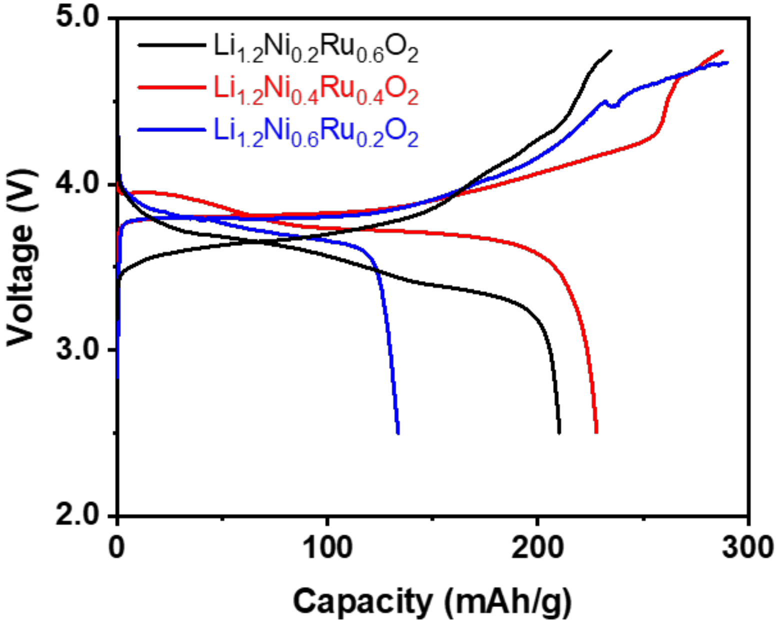
- Layered structure and Li/TM ordering in TM layer well remained after charge
- Local Li/TM ordering tends to decrease after discharge, such local TM environment change likely correlates with V decay

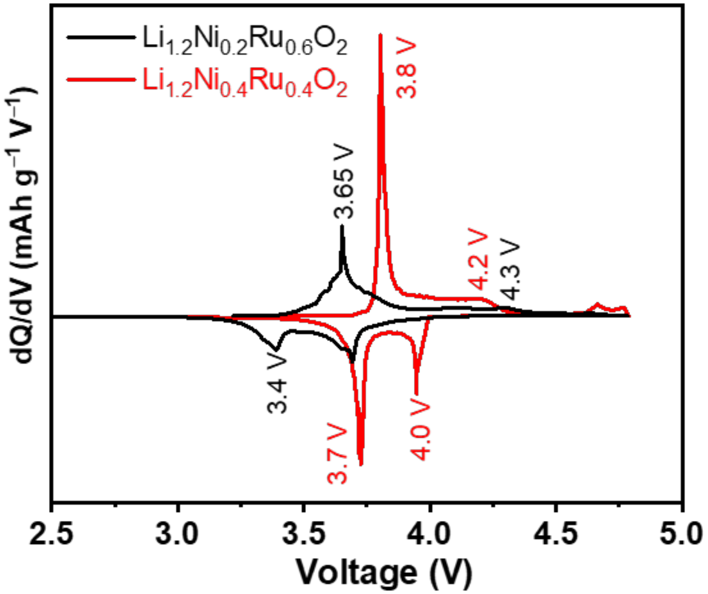
In collaboration with Dong Su at BNL

Crystal Structure Varies with Ni/Ru Ratio

Synchrotron XRD collected at APS



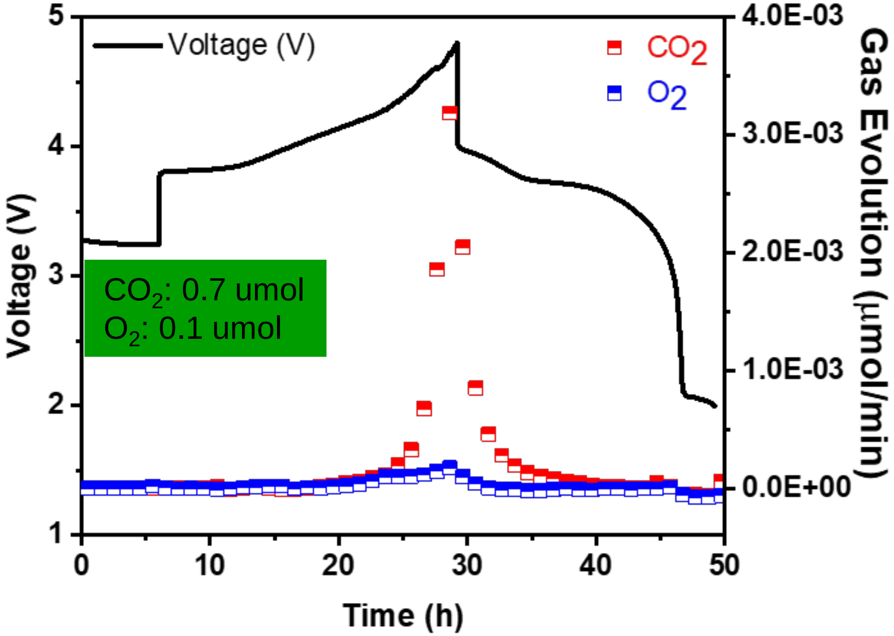




- LNRO compositions synthesized to examine the correlation between anionic oxygen redox and TM redox combination
- Crystal structure and electrochemistry clearly varies with TM ratio, resembling that of layered oxide

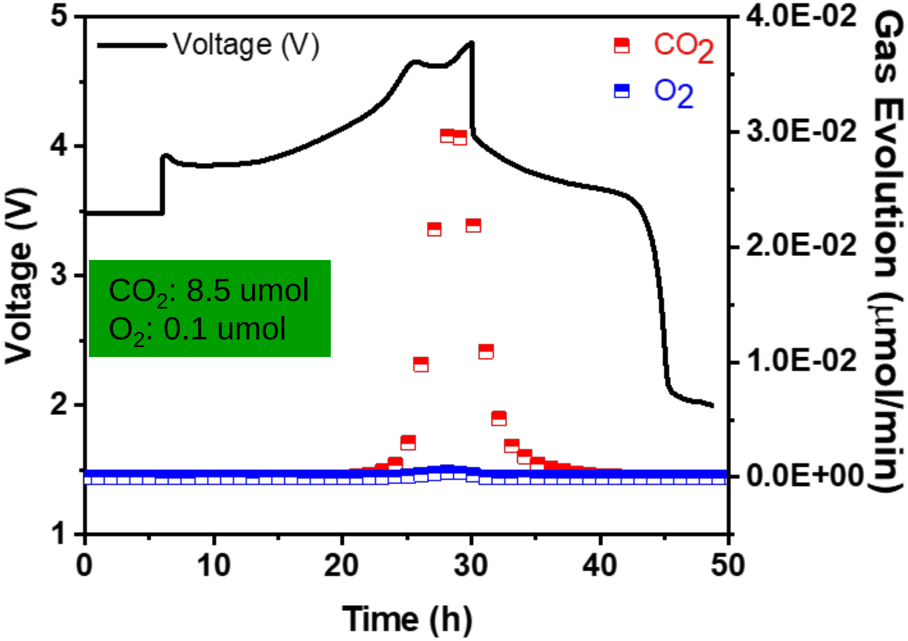
Gas Evolution of Varied Ni/Ru Ratio

$Li_{1.2}Ni_{0.4}Ru_{0.4}O_2$



CO_2: 0.7 umol
O_2: 0.1 umol

$Li_{1.2}Ni_{0.6}Ru_{0.2}O_2$



CO_2: 8.5 umol
O_2: 0.1 umol

In collaboration with Bryan McCloskey at UCB

- CO_2 evolution increases with Ni content, however, it remains low compared to Li-rich LNMO
- Minimal O_2 detected in LNRO of varied Ni/Ru ratio, regardless of crystal structure, reversible O redox may differ

Responses to Previous Year Reviewers' Comments

- *Comment #1*: All reviewers commented the significance and relevance in understanding oxygen activity and its involvement in Li-rich layered oxides, but one reviewer questioned the purpose of Ru use
  - ✓ *We appreciate the positive comment. Li-rich systems are promising to warrant high capacity. Understanding origin of its high capacity beyond TM redox is of critical importance. Oxygen redox appears intuitive because Mn4+ can not be further oxidized. But direct probe of oxygen is challenging. Mn-, and Ru-based compounds enable studies on oxygen redox, impact of TM and its possible correlation with voltage fade from a material perspective*
- *Comment #2:* Early charging at < 4.5 V should be due to Mn(III) to Mn(IV) because of CO_2/O_2 evolution
  - ✓ *No O_2 detected before a plateau at 4.55 V. Isotopic labeling and in-situ gas analysis reveals CO_2 evolution originates from carbonate residual. Therefore, Mn3+ to Mn4+ does not contribute capacity at < 4.5 V*
- *Comment #3:* Reviewers suggested to focus on a fundamental and thorough study that give a complete understanding of the material system
  - ✓ *It is a valuable advice, we focus on fundamental understanding of oxygen activity in compounds based on Ni/Ru to explicit the key factor in oxygen involvement in Li-rich metal oxides*

Collaborations

- Drs. Marca Doeff, Guoying Chen (LBNL), Drs. Wanli Yang, Matthew Marcus (ALS), Drs. Dennis Lordnund, Apurva Mehta (SSRL) – synchrotron *in-situ* and *ex-situ* XRD, XAS
- Prof. Bryan McCloskey (UC Berkeley) – gas evolution measurement
- Dr. Vince Battaglia – *in-situ* cell fabrication
- Dr. Dong Su (BNL) – HR-TEM, STEM
- Dr. Ashfia Hua (ORNL) – neutron diffraction
- Dr. Robert Kostecki (LBNL) – Raman spectroscopy
- Prof. Gerbrand Ceder, Kristin Persson (UC Berkeley) – material modelling
- Prof. Shirley Meng (UCSD) and Dr. Jagjit Nanda (ORNL) – layered oxide cathode development & characterization

Remain Challenges

- Distinctive anionic oxygen redox activity of layered oxides with different TMs has been revealed. However, fundamental understanding of the key factor(s) to activate anionic oxygen redox and promote its reversibility/suppress irreversibility in Li-rich systems is not fully understood, therefore, selection of favorable TMs is challenging

- Role of anionic oxygen redox in voltage fade of Li-rich layered oxide is being revisited. Utilization of reversible oxygen redox without voltage fade is the key to practically implement high energy Li-ion cathode

Proposed Future Work

- Further investigate the impact of TM combination on anionic oxygen redox in Li-rich layered oxides to understand the key factors in oxygen redox involvement
  - $LN_{1-y}R_yO$ of varied Ni/Ru ratio, thus different Ni/Ru redox contribution in electrochemistry, enables studies on oxygen redox and its correlation with TM redox

- Determine the crystal structure of $LN_{1-y}R_yO$ of varied Ni/Ru ratio, particularly, best performing $Li_{1.2}Ni_{0.4}Ru_{0.4}O_2$

- Identify the chemical state of Ni/Ru in pristine $LN_{1-y}R_yO$ and electronic evolution of TM and O during electrochemistry

- Investigate the voltage retention behavior, identify the role of crystal structure and oxygen redox in voltage fade

Any proposed future work is subject to change based on funding levels

Summary

- Kinetic factors potentially influencing oxygen activity in LNRO investigated to verify absence of oxygen redox, suggesting competition of TM redox with O redox
- Voltage fade phenomenon observed in LNRO, but at a much lower degree, suggesting other factor(s) beyond oxygen redox accounts for voltage fade in Li-rich layered oxides, but oxygen redox accelerates V fade
- Structural evolution mechanism in LNRO during cycling studied to explore the correlation between crystal structure and voltage fade
- Layered monoclinic structure remained after initial charge, but Li/TM ordering in TM layer decreases, likely contributes to voltage fade during cycling
- LNRO compounds of varied Ni/Ru ratio synthesized to further investigate impact of TM combination on oxygen redox, as well as role of crystal structure and oxygen redox, if any, in voltage fade