Project ID: bat319

Advanced Microscopy and Spectroscopy for Probing and Optimizing Electrode-Electrolyte Interphases in High-Energy Lithium Batteries

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Overview

Timeline

- October 1st, 2016
  (delayed start Feb. 2017)
- September 30th, 2019
  (NCE to Jan. 2020)
- Percent complete: 70%

Barriers

- Barriers addressed
  - Anion redox and oxygen evolution
  - Poor voltage stability
  - Interface chemical changes and structure instability

Budget

- Total project funding
  - US$ 1,200,000 (10% non-federal matching)
- Funding received in FY18
  - US$ 360,000
- Funding for FY19
  - US$ 327,600 (matching non-federal US$ 36,400)

Partners

- Interactions/ collaborations
  - Oak Ridge National Lab
  - Lawrence Berkeley National Lab
  - Argonne National Lab
  - Ningbo Institute of Materials Technology and Engineering China
  - Battery500 Consortium

Relevance and Project Objectives

Overall Objectives:

- ❑ The proposed research aims to develop advanced microscopy and spectroscopy tools to probe, understand, and optimize the anion activities that govern the performance limitations in high energy Li-excess transition metal oxides cathode materials.
- ❑ The above mentioned characterization tools will be extended to diagnose various anode types, such as Li metal anode.

Objectives in this Period:

- ❑ Propose strategies to optimize the anion activities in Li-excess NMC cathode materials.
- ❑ Characterizing single particle behavior of modified Li-excess NMC materials.

Project Impact:

- ❑ The insights and knowledge provided by the characterization tools will have the critical importance of enabling a major breakthrough in commercial applications for high voltage and high energy density cathode material for lithium ion batteries used for vehicle applications.

Milestones

- BCDI and STEM/EELS characterization of modified Li-excess NMC single particle(June-18). - **Complete**
- Propose strategies to optimize the anion activities in Li-excess NMC cathode materials (Sept.-18). **- Complete**
- Influence of metal-ion electrolyte additive on electrochemically deposited Li metal (Dec.-18). **– Complete**
- Benchmarking electrochemical performance with the optimized Li-excess materials (Mar.-19). **- Complete**
- Conducting XPS and DEMS characterization of anion evolution on modified Li-excess NMC (June-19). **– On track**
- Carrying out STEM/ EELS characterization on modified Li-excess NMC single particle using optimized electrolyte (June-19). **– On track**

Approach

- This project combines STEM/EELS, operando BCDI, and Ab initio computation as diagnostic tools for probing anion redox and oxygen evolutions in Li-excess NMC materials.

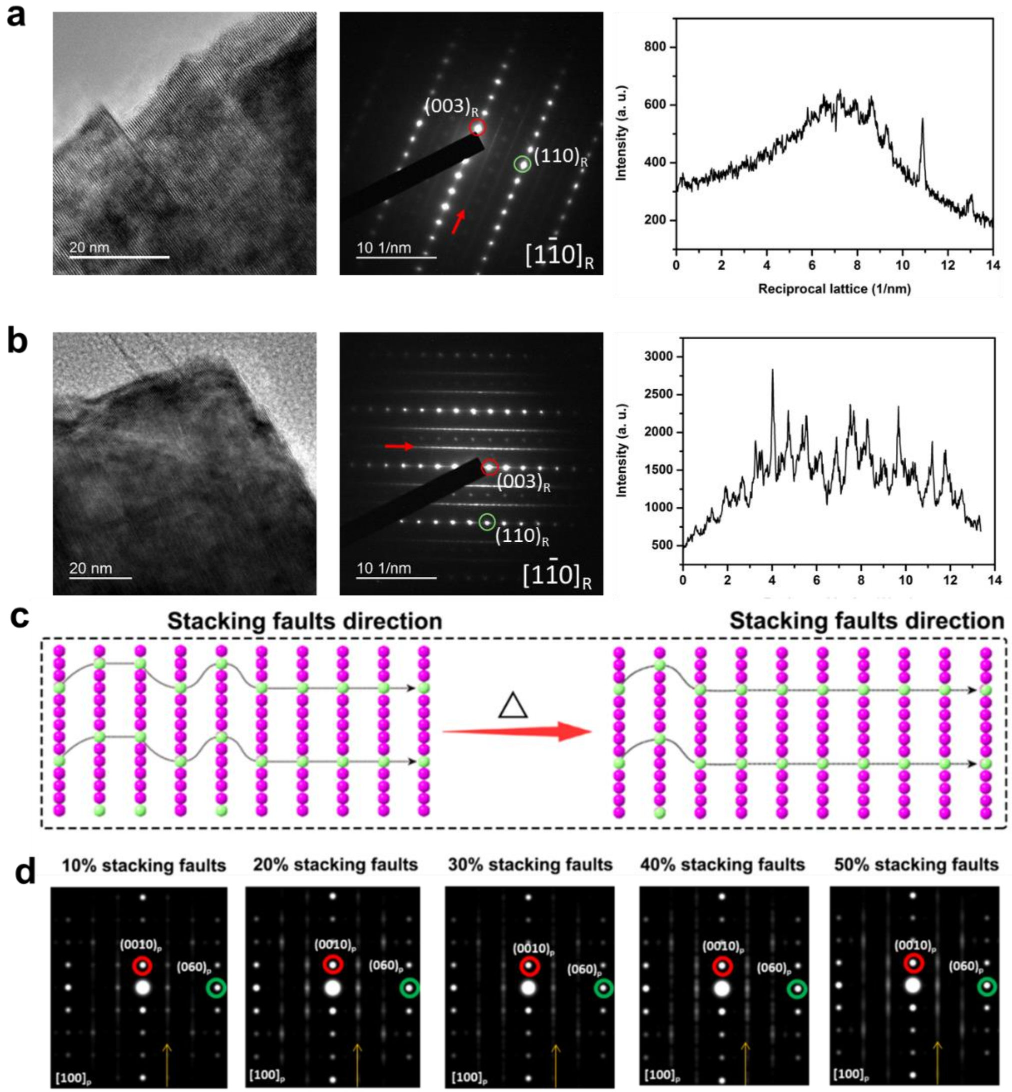
- Neutron enables the characterization of bulk material properties to enhance and further optimize high energy electrode materials.

- The approach allows for pinning down the atomistic/molecular mechanism of anion oxidation and determining the speciation compositions and surface characteristics for enabling high rate and long life in the proposed materials.

- In this period, our approach successfully identified the role of defects and strain in the voltage decay issue in Li-excess NMC cathode materials.

Accomplishment to Date FY 19

HRTEM/ED characterization on structural recovery of single particle for LRLO after electrochemical cycling

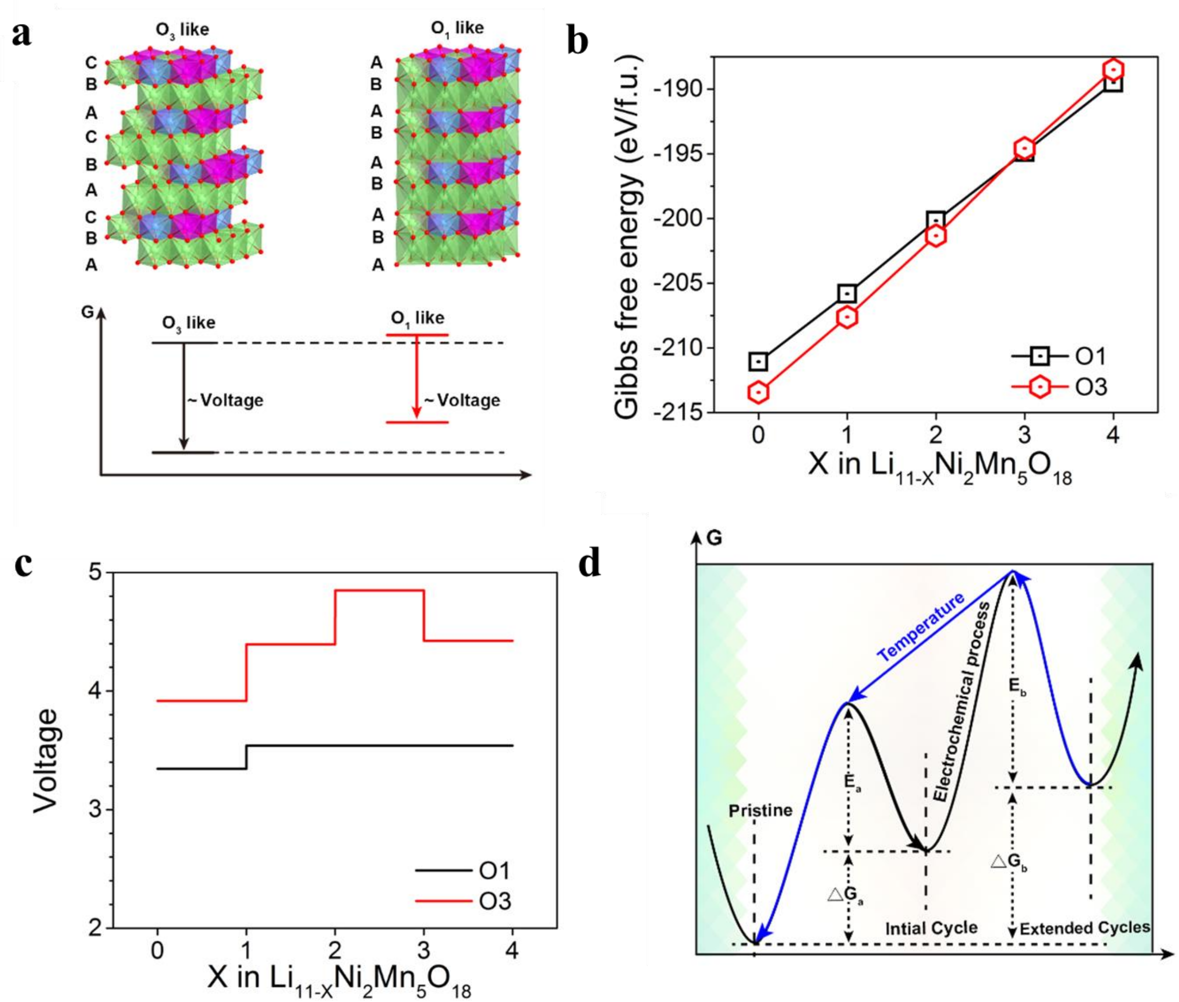


- The diffraction spots along the streaks in ED pattern becomes more obvious compared with the cycled bulk structure.
- The ED analysis implies the stacking faults generated in the bulk structure during the electrochemical cycling can be partially eliminated by the heat treatment.
- The structure ordering along the layers stacking direction is partially restored.

M. Zhang, B. Qiu, Y.S. Meng et al., 2019, in submission

Accomplishment to Date FY 19

The impact of defects generation on the structure metastability and voltage decay for LRLO



- ❑ The nucleation of line defects dramatically modifies the local lithium environment by perturbing the sequence of oxygen layers.
- ❑ This results in a smaller average voltage for the structure with more defects.
- ❑ The highly cycled LRLO material is trapped in a metastable state with an energetically unfavourable local lithium environment, which is mainly responsible for the issue of voltage decay.

M. Zhang, B. Qiu, Y.S. Meng et al., 2019, in submission

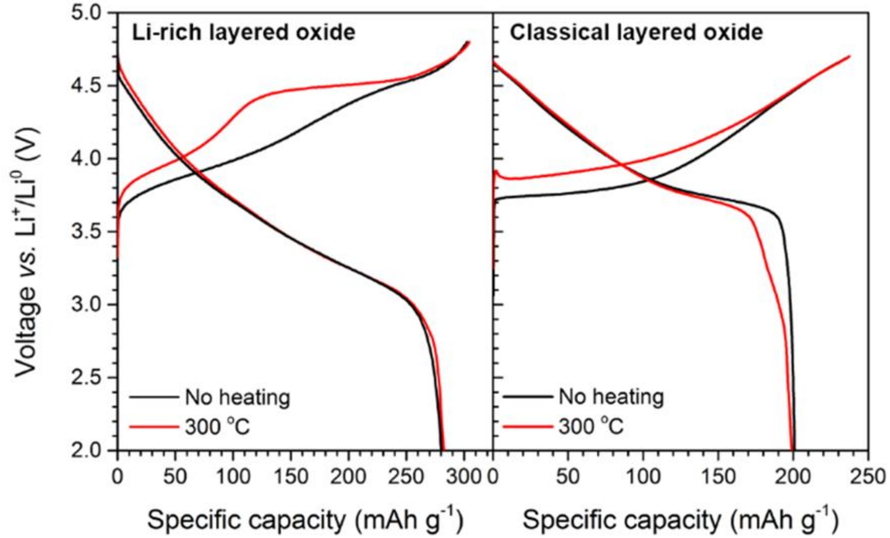
Accomplishment to Date FY 19

Voltage recovery enabled through the unique anionic redox in LRLO materials

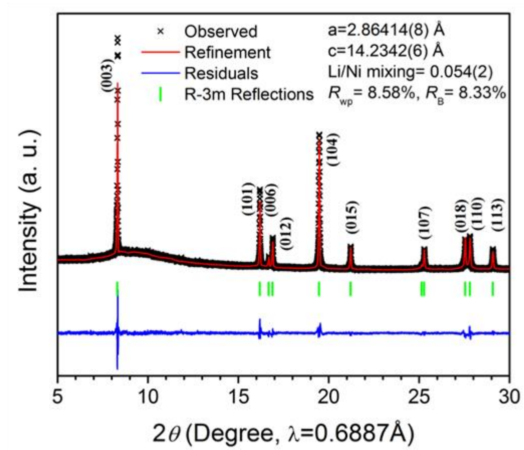
- The metastable cycled state is the unique feature of LR-NCM nanoparticles, which enables thermal energy plays an effective role in structure and voltage recovery.

- While for the cycled cathode material without anionic redox, thermal energy can only introduce cation disordering.

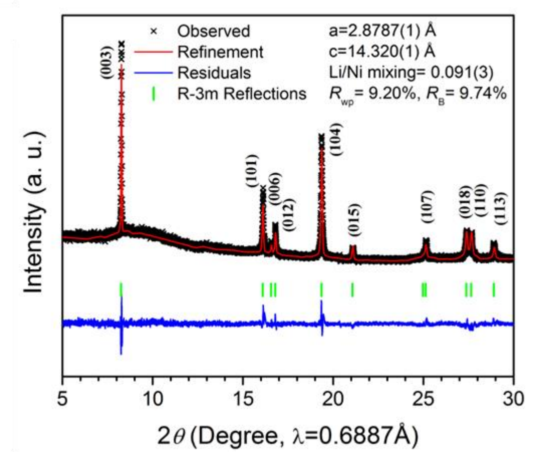
- As a result, lower energy efficiency with larger overpotential is observed for the classical layered oxide $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ annealed at 300 °C.



Classical layered oxide without heating



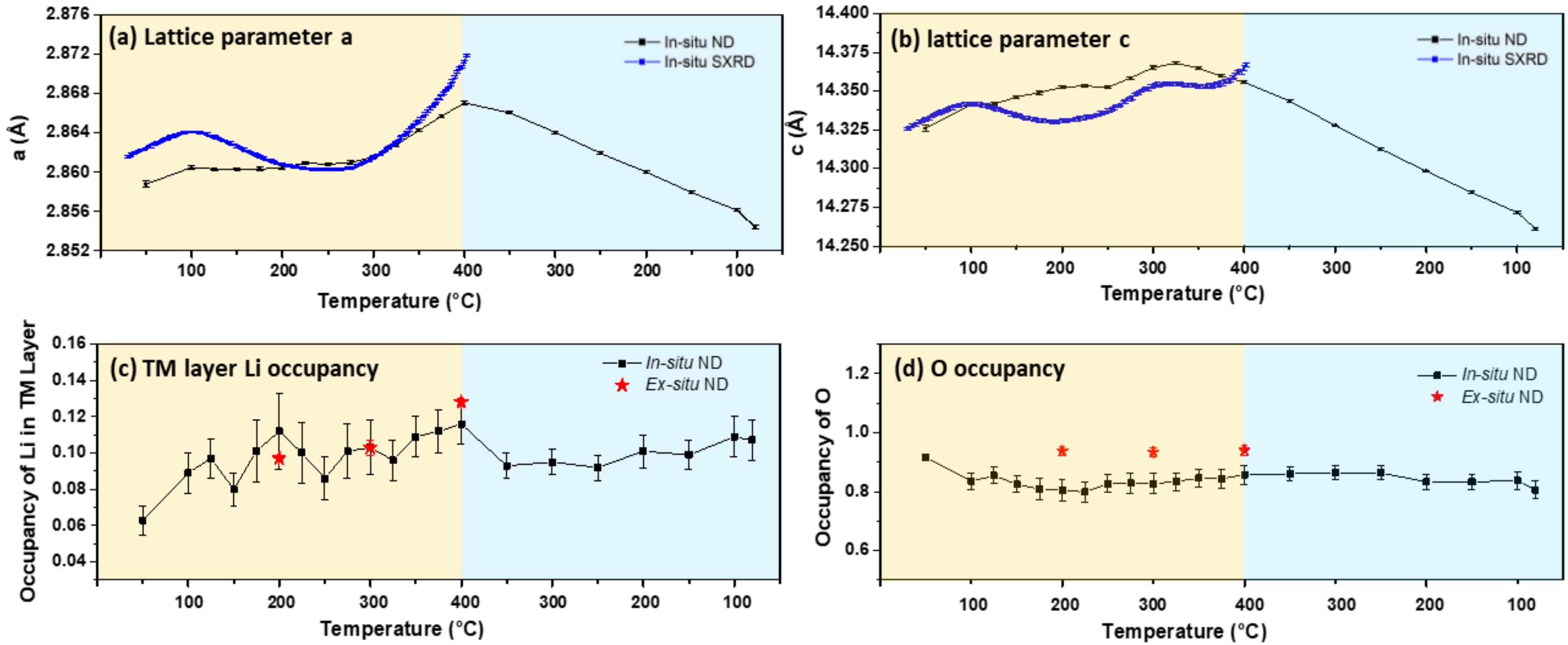
Classical layered oxide heated at 300 °C



M. Zhang, B. Qiu, Y.S. Meng et al., 2019, in submission

Accomplishment to Date FY 19

In-situ neutron diffraction study of the performance improvement in LRLO under heat treatment



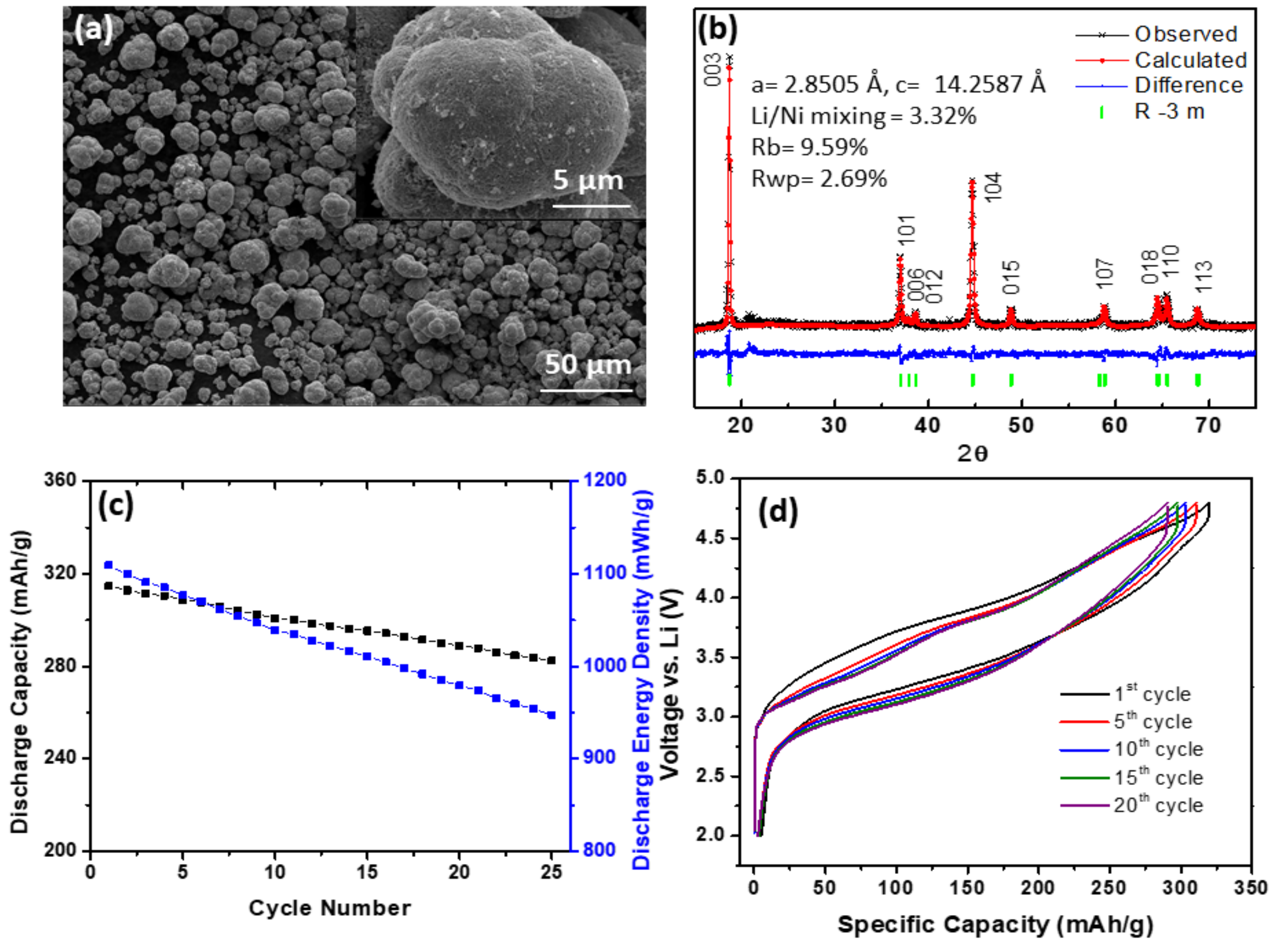
- The flat region or decrease in both lattice parameter a and c from 100 to 250 °C indicates a phase transformation in the structure.
- The occupancy of Li in transition metal (TM) layer experiences an increase over heating and a small decrease over cooling, which indicates that Li goes back to the TM layer under heat treatment.

Y. Li, M. Zhang, Y.S. Meng et al., 2019, in preparation

Accomplishment to Date FY 19

Benchmark modified LRLO cathodes performance

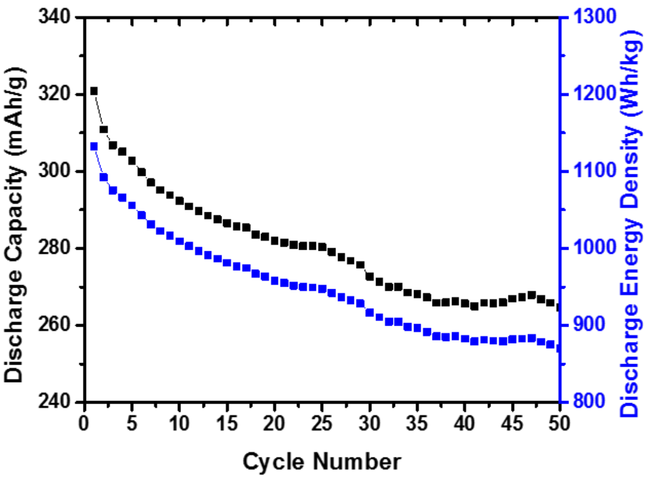
- ❑ A gas-solid interface reaction (GSIR) was introduced to achieve delicate control of oxygen activity in LRLO.
- ❑ After activation, it delivers a discharge capacity of 314 mAh/g and an energy density of 1109 mWh/g at the 1st cycle (0.1 C).
- ❑ The GSIR modified LRLO has been chosen as the benchmark cathode for its high specific capacity and coulombic efficiency.

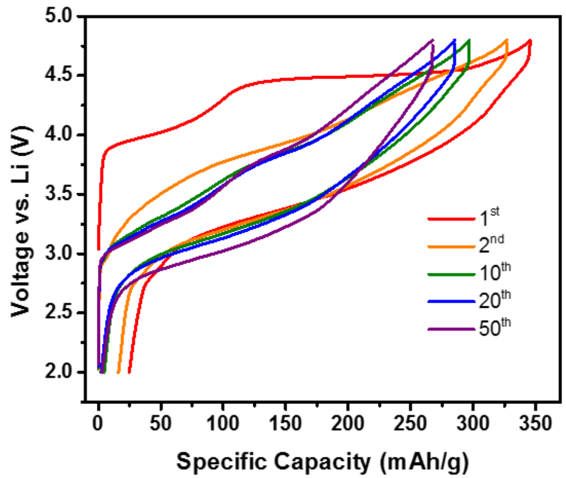


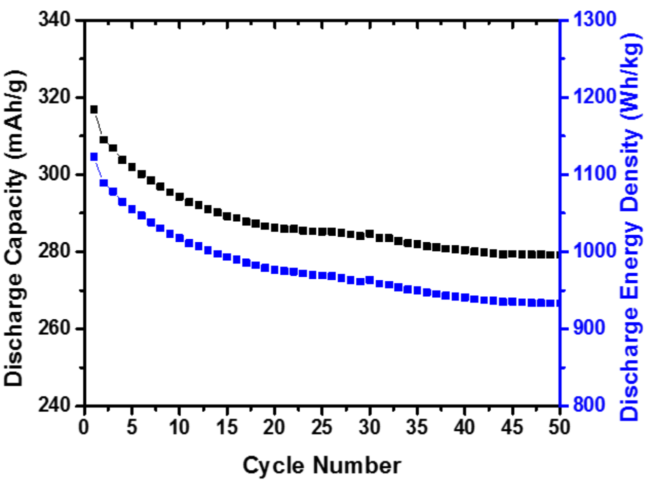
Accomplishment to Date FY 19

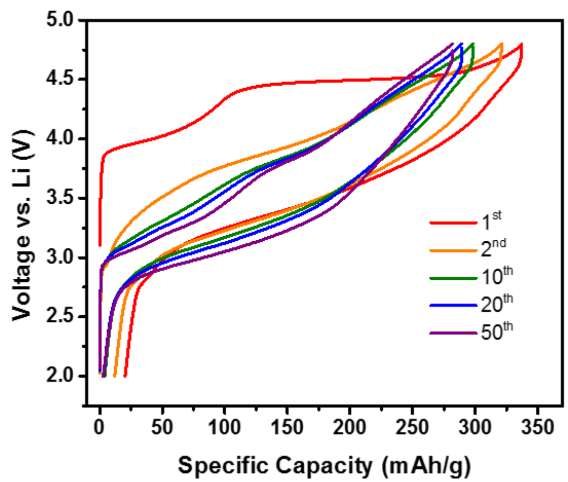
Benchmarking new electrolyte performance on modified LRLO cathodes

1M LiPF6 in EC/DMC = 3/7 (V%)







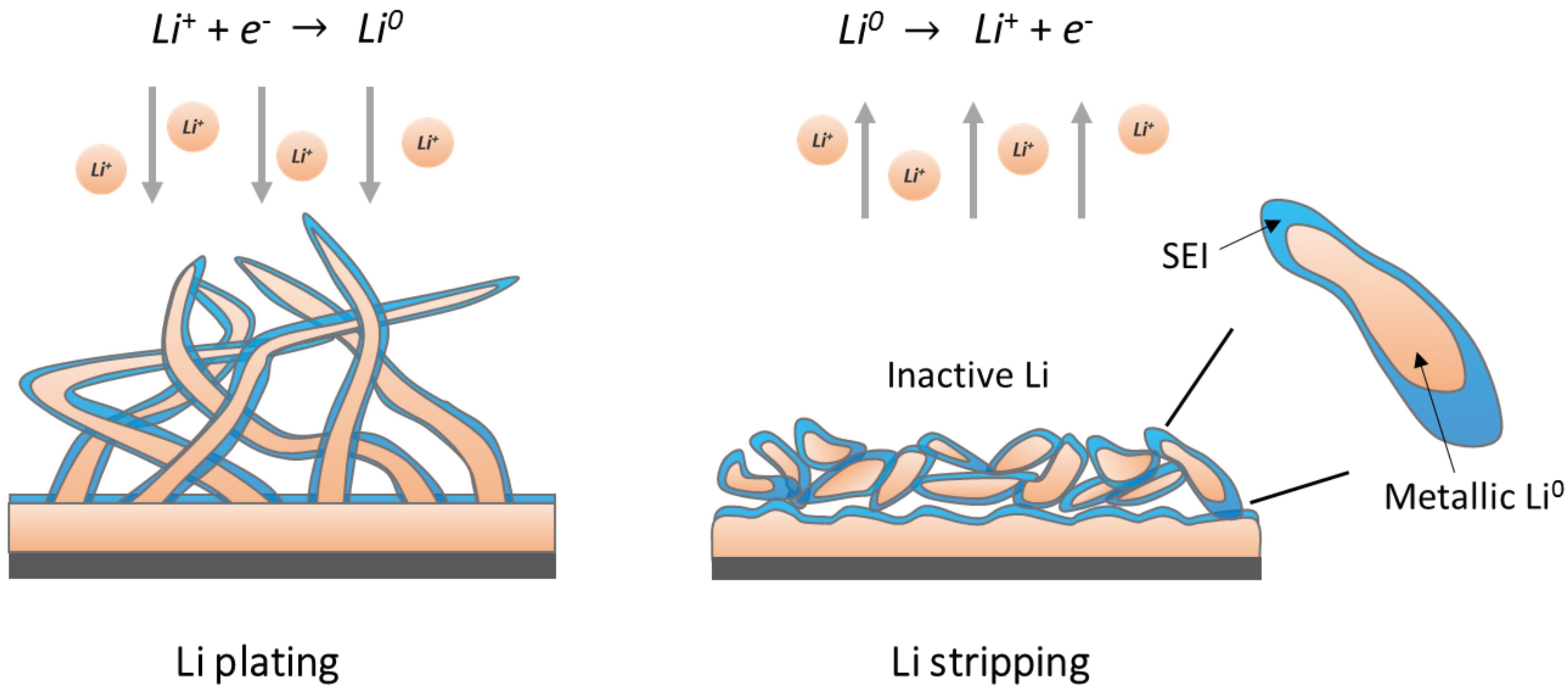


0.98M LiPF6 +0.02M LiBOB in EC/DMC = 3/7 (V%)

- LiBOB additives in the conventional carbonate based electrolyte can effectively improve the cycling performance (0.1 C) of modified LRLO cathodes.
- This novel electrolyte could create a more stable cathode electrolyte interface (CEI) in the system, which will be investigated in detail through XPS and STEM/EELS.

Accomplishment to Date FY 19

Electrochemical reactions of Li plating/stripping, dendrite formation and inactive Li formation

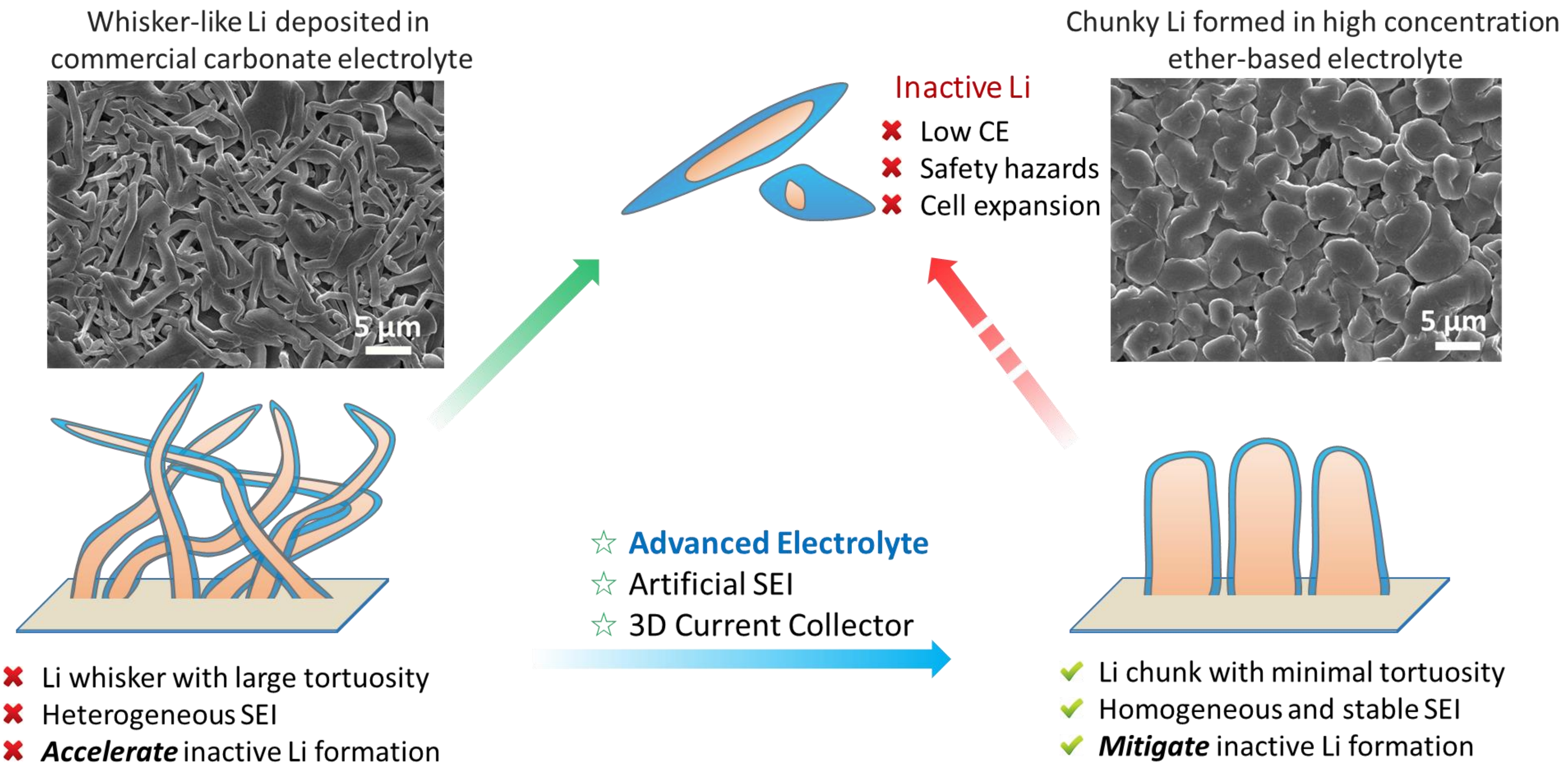


- ❑ In a Li metal battery, during the plating, Li^+ deposits on the fresh Li. In commercial carbonate-based electrolytes, Li deposits exhibit whisker-like morphology.
- ❑ If the dissolution occurs firstly on the roots of the Li whiskers, the top parts will disconnect from the electronic conductive network and thus become electrochemically inactive, forming inactive Li.

C. Fang, X. Wang, Y.S. Meng, Trends in Chemistry, 2019, in print

Accomplishment to Date FY 19

The cause and solution for the Li metal problems



- ❑ The continuous formation of inactive Li is the direct cause of low CE, safety hazards and cell expansion in Li metal batteries.
- ❑ To reduce inactive Li formation, advanced electrolyte engineering will be primary method, with the assistance of artificial SEI and 3D current collector.

C. Fang, X. Wang, Y.S. Meng, Trends in Chemistry, 2019, in print

Responses to Previous Year Reviewers' Comments

General Comments:

- To the reviewer, the plans for the Li-rich layered oxide (LRLO) materials as well as the Li anode seem well defined and make use of state-of-the-art characterization methods. It is not clear how the DFT methods can be used to study heat treatment in these materials.
- The reviewer noted that the diagnostic results provide certain insights on the degradation mechanism of a Li-rich cathode. However, the reviewer was very doubtful about the heat-treatment scheme for resolving the fading problem of this category of cathode.
- The proposed future research appeared to the reviewer to be on track with the overall objectives of the proposed research. However, the reviewer was very conservative regarding the method of heat treatment and high-pressure treatment for resolving the fading problem.
- The proposed future work is well planned, according to the reviewer who suggested that the team study the atomistic-/molecular-level interactions between the electrolyte and the electrode during/after cycling at high voltages.

Responses to Previous Year Reviewers’ Comments

Response:

- In this period, DFT calculations were applied to understand the influence of defect generation on the structural metastability and voltage decay.
- Based on our DFT results, both lithium vacancies in the TM layer and stacking sequence faults raise the system energy, creating metastable state of the cycled LRLO material. Through defect elimination, heat treatment serves as a driving force to enable the system to cross over the energy barrier, relaxing to the most stable state.
- We acknowledge that the heat treatment strategy is not that practical for direct industrial applications. However, the direct comparison between cation and anion redox based cathode material on the effect of thermal energy manifests our findings are not trivial. The insights about uniqueness and complexity of anionic redox reveal that the voltage fade in LRLO can be reversible and call for new paradigms for improved design of oxygen-redox active materials.
- We thank all the reviewers for their comments. XPS combined with STEM/EELS investigation is ongoing for CEI study during cycling at high voltages.

Collaboration and Coordination with Other Institutions

Dr. Ashfia Huq (ND)
Dr. Miaofang Chi (STEM/EELS)

OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

Dr. Ich Tran (XPS)
Irvine Materials Research Institute

IMRI

Dr. Ross Harder
(Operando BCDI)

Argonne NATIONAL LABORATORY

Dr. Bao Qiu and Dr. Zhaoping Liu
(Heat treatment of LRLO)

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Remaining Challenges and Future Research

Remaining Challenges:

- Further improvement is needed to evade the decrease in energy density and the increase of hysteresis over cycling of LRLO cathode materials.
- Atomistic-level Interactions between the electrolyte and the electrode after cycling at high voltages need to be characterized of modified Li-excess layered materials with novel electrolytes.

Future Research:

- XPS and DEMS Characterization of anion evolution on modified Li-excess NMC cathode materials.
- STEM/ EELS Characterization on modified Li-excess NMC single particle using optimized electrolyte.
- EELS and XPS Characterization of SEI on electrochemically deposited Li metal.

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

Summary

- We proposed mitigation strategies to modify the Li excess NMC cathodes. One of the most effective methods is the mild heat treatment.
- We have found through a combination of computation and experiments that defect generation and dynamics play a key role in the voltage fading issue. We quantitatively identified the correlation between strain/dislocation and voltage fade.
- Novel electrolyte with LiBOB additives has been introduced to improve the cycling performance (0.1 C) of modified LRLO cathodes.
- We successfully extended our characterization tools to study the chemical composition and structure of electrochemically deposited Li metal at nanoscale.