Characterization Studies on Li-Metal Anode and High-Ni Cathode Materials

Peter Khalifah, Enyuan Hu, and Xiao-Qing Yang
Brookhaven National Laboratory (BNL)

2021 DOE Vehicle Technologies Office
Annual Merit Review

Washington, DC, June 25, 2021

BAT367

Overview

Timeline

- Project start date: 10/01/2016
- Project end date: 9/30/2021
- Percent complete: 90 percent

Barriers addressed

- Develop Li-ion batteries using Li metal anodes with a cell-level energy density of 500 Wh/kg
- Achieve lifetime of 1,000 cycles with the technology
- Mitigate safety issues associated with Li metal

Budget

Total project funding: DOE share $50M

Funding received in FY 2020: $10M

Funding for FY 2021: $10M

Collaborators

- Army Research Laboratory (ARL)
- Argonne National Laboratory (ANL)
- Binghamton University
- Idaho National Laboratory (INL)
- Pacific Northwestern National Laboratory (PNNL)
- Stanford Linear Accelerator Center (SLAC)
- University of California San Diego (UCSD)
- University of Maryland – College Park
- University of Texas - Austin

Relevance and Project Objectives

- Accelerate development of 500 Wh/kg batteries with Li metal anodes
- Develop and deploy characterization techniques to:
  1. Select and optimize high energy density cathode materials
  2. **<u>Diagnose failure mechanisms with spatial and temporal resolution</u>**
  3. Parameterize & validate whole-cell models, leading to improved cell designs
- Emphasis on synchrotron (diffraction and spectroscopy) methods
  - Done both locally at BNL and externally at other DOE facilities

Milestones

Month/Year	Milestones
Dec/2020	Complete the studies of electrolyte salt concentration effects on the Li solvation and good SEI formation on Li metal anode using x-ray and neutron PDF ➥ *Completed.*
Mar/2021	Complete the studies of electrolyte additive functionality on Li and S deposition on Li metal anode using x-ray fluoresce (XRF) imaging technology in Li-SPAN system ➥ *Completed.*
Jun/2021	Complete resonant inelastic x-ray scattering (RIXS), tomography and spectro-imaging studies of NMC811 at both the electrode-level and the particle-level. ➥ *On schedule.*
Sep/2021	Develop new synchrotron-based characterization techniques (xPDF, XRF mapping, XRD and XAS) to diagnose failure mechanisms of Li-metal and Li-S cells with spatial and temporal resolution ➥ *On schedule.*

Approach – methods

- Studies using **multi-modal** and **multi-dimensional** techniques

- **Multi-modal:**
  - Integrate physical (X-ray) and (electro)chemical probes (echem, reactivity)

- **Multi-dimensional:**
  - 2D lateral mapping coin / pouch cell studies done *ex situ* or *in operando*

Approach – goals

- **Probe capacity loss mechanisms w/ spatial & temporal resolution**
  - Coin cell failure mechanisms diagnosed through *ex situ* lateral mapping studies
  - Pouch cell SOC inhomogeneity investigated through *operando* mapping studies
  - Robust proof of LiH in SEI (differentiated from LiF) by time-resolved XRD

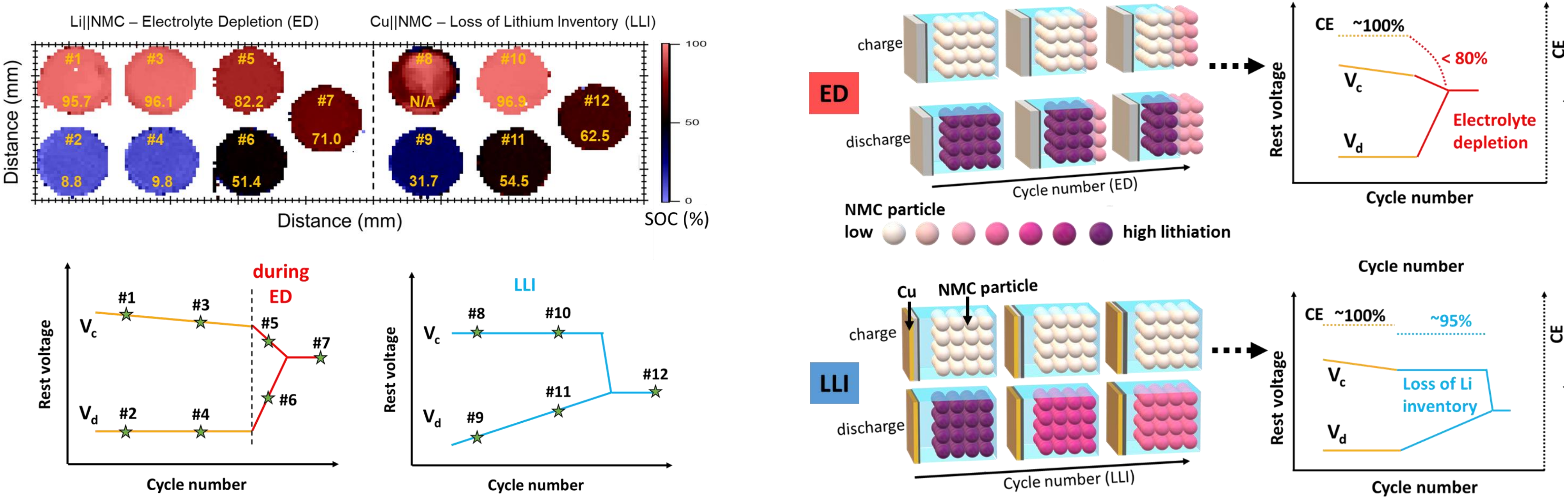
Technical accomplishments – highlights

- XRD validation of echem signatures for 3 key failure mechanisms in Li metal cells

- Quantified relationship between local NMC loading and local cycling rate
- Probed dependence of edge inhomogeneity on cell SOC and cycling rate

- Discriminated between LiH and LiF in SEI despite near-identical XRD patterns

1. XRD signatures of key Li/NMC failure mechanisms

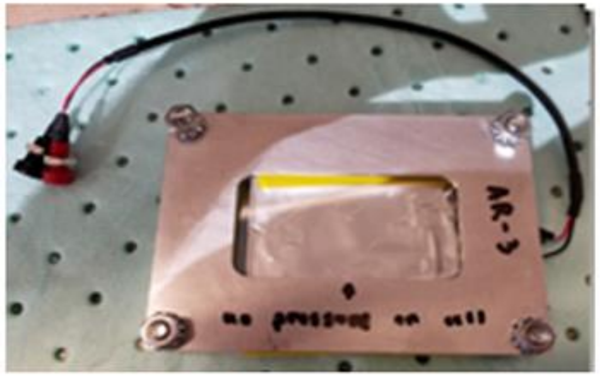


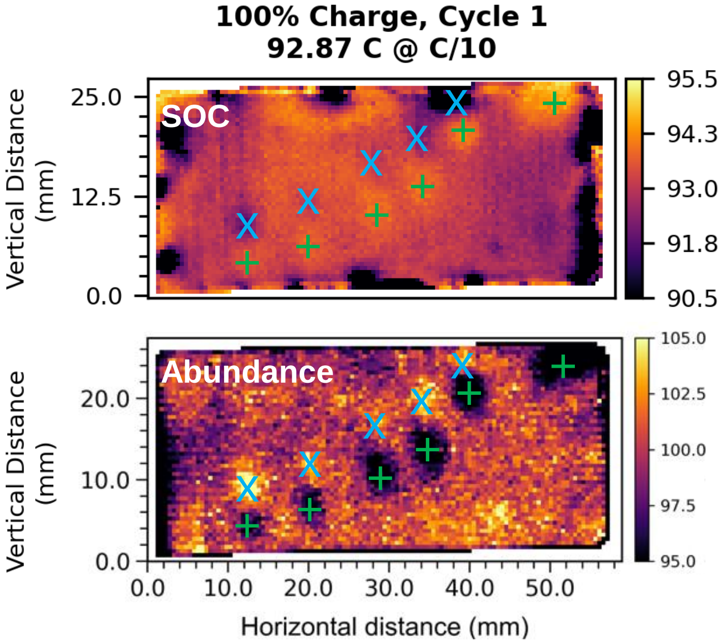
- Studied coin cells designed to have 3 different failure mechanisms
  - Electrolyte depletion (ED), loss of lithium inventory (LLI), and increased cell impedance (ICI)
- Used synchrotron XRD to identify/validate echem signatures of each mechanism
  - Enables fast identification of failure mechanism without use of synchrotron

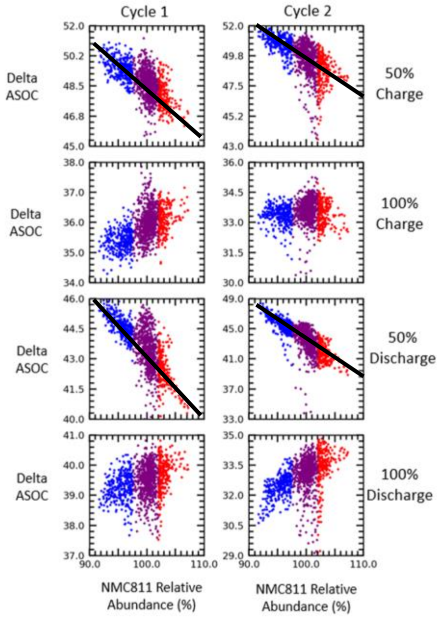
Team: P. Khalifah (BNL), Y.S. Meng (UCSD), B. Li and E. Dufek (INL)

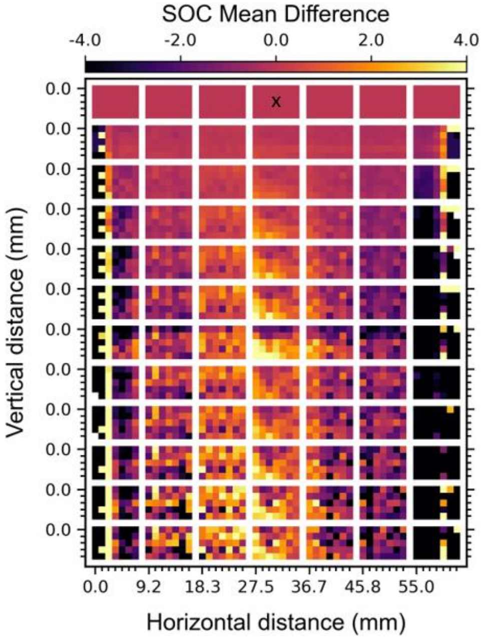
N. Gao, A. Abboud, G. Mattei, Z. Li, A. Corrao, C. Fang, Boryann Liaw, Y.S. Meng, P. Khalifah, E. Dufek, B. Li, "Fast Diagnosis of Failure Mechanisms and Lifetime Prediction of Li Metal Batteries", *Small Methods* (2020), 10.1002/smtd.202000807.

2. *Operando* mapping of Li/NMC811 pouch cell





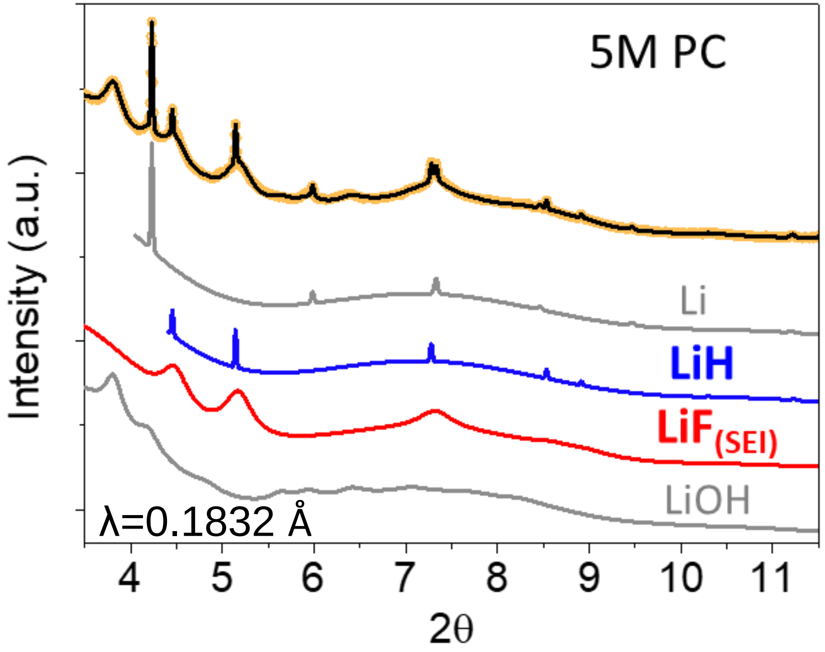


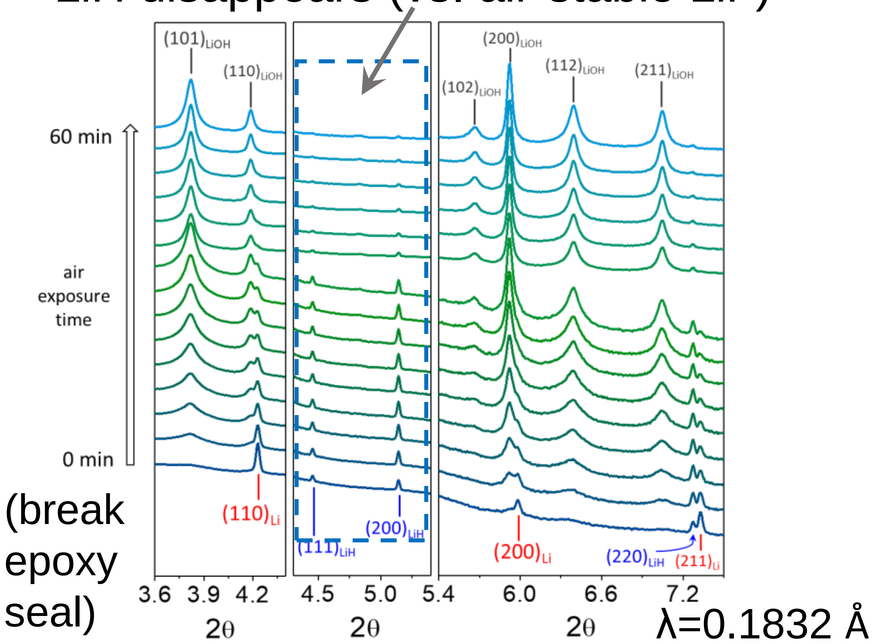


- High energy lateral mapping (HELM) studies of cycling NMC811/Li cell
  - Mapped with excellent spatial resolution (0.5 x 0.5 mm) and time resolution (fine slicing)
- Two origins of inhomogeneity in SOC distribution are observed
  - Influence of relative NMC loading on cycling performance was quantified
  - Dependence of edge inhomogeneity on cell SOC and cycling rate was observed

Team: P. Khalifah (BNL), J. Xiao (PNNL), B. Liaw and E. Dufek (INL)

3. Robust validation of LiH as key SEI component





- Presence of LiH as an SEI component has been debated for decades
  - Existence of LiH proved by combination of physical (XRD) and chemical (air exposure) tests
- LiH is both more crystalline and more conductive than LiF (and other SEI components)
  - LiH is seen in SEI for many electrolytes that contact Li metal (*e.g.*, PC, DMC, DME)

Team: E. Hu, X.-Q. Yang, and S. Ghose (BNL), J. Liu and J. Xiao (PNNL), K. Xu (ARL), C. Wang (U. Md.)

Z. Shadike, H.-K. Lee, O. Borodin, X. Cao, X. Fan, X. Wang, R. Lin, S.-M. Bak, S. Ghose, K. Xu, C. Wang, J. Liu, J. Xiao, X.-Q. Yang & E. Hu, “Identification of LiH and nanocrystalline LiF in the solid–electrolyte interphase of lithium metal anodes”, *Nature Nanotechnology* (2020), 10.1038/s41565-020-00845-5.

BATTERY 500 CONSORTIUM

BROOKHAVEN NATIONAL LABORATORY

Response to last year's reviewer comments

- Comment: The reviewer saw no reference to working on Li-metal batteries although it is one of the main project objectives.
- Response: The work this year includes *operando* studies on Li-metal batteries that build on last years proof-of-principle *ex situ* studies on extracted cathodes.
- Comment: These are outstanding technological and modeling developments. The reviewer wanted to know if the effect of large pores or regions of especially low porosity can be correlated with failure caused by local over-potentials.
- Response: We have recently quantified the correlations between the local NMC loading and the local performance. However, we do not have a good way of measuring the local pore size / porosity.
- Comment: It was unclear to the reviewer how the *ex situ* and *in situ* measurement results are being used by collaborators to improve the performance and durability of NMCs and sulfur electrodes. For example, how do collaborators use the "hot spots" (Slide 10) and cracking (Slide 12) observations to improve the electrode and the NMC particles?
- Response: "Hot spot" failure was due to electrolyte depletion. Improved electrolytes are actively being developed and tested. Similarly, more single crystalline particles are predicted to mitigate NMC cracking.

Collaborations with other institutions

- ANL (Shin)
  - High-Ni NMC materials with concentration gradients
- Binghamton University (M.S. Whittingham)
  - High-Ni NMC materials and analysis
- INL (E. Dufek, B. Li, B. Liaw)
  - Electrochemical evaluation of cells; well-characterized samples for *ex situ* and *operando* studies
- PNNL (J. Zhang, J. Xiao, D. Lu)
  - High-Ni NMC samples and analysis, NMC cathode films and pouch cells, Li-S electrodes and cells
- SLAC (Y. Liu)
  - TXM studies on high-Ni NMC
- UT-Austin (A. Manithram)
  - High-Ni NMC materials and analysis
- U. Maryland – College Park (C. Wang)
  - High sulfur loading S cathode material synthesized by carbonizing oxygen-rich PTCDA and nitrogen-rich PAN with sulfur (SPAN)
- Army Research Lab (K. Xu)
  - Solvent-dependent SEI formation
- UCSD (P. Liu, Y.S. Meng)
  - High-Ni NMC materials and analysis, thick films for depth profiling analysis, first-cycle capacity loss studies

Remaining challenges and barriers

- N/A

Proposed future research

- Relate Li-S intermediate XRD peaks to specific polysulfide phases
- Operando lateral mapping of Li-S cells

- Synchrotron x-ray photoelectron spectroscopy (XPS) and x-ray absorption spectroscopy (XAS) studies of cathode electrolyte interphase (CEI)
- Synchrotron x-ray fluorescence (XRF) imaging to study the transition metal dissolution at high-voltage charging

Summary

- Deployed advanced characterization methods to meet B500 needs
  - Focused on SEI formation and failure mechanisms

- Able to follow reactivity- and cycling-induced changes
  - Both time-resolved and spatially resolved XRD studies
  - Deeper understanding when correlated with (electro)chemical reactivity

- Insights enabled by high flux & precision of synchrotron XRD methods
  - Overcame weak scattering & broad peaks of SEI phases (LiH, LiF, *etc.*)
  - Operando pouch cell mapping studies required rapid XRD data collection
  - Precise (~0.1%) quantification of both abundance and SOC for NMC cathodes

Technical back-up slides

None