# Advanced In Situ Diagnostic Techniques for Battery Materials

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BAT287

# Overview

## Timeline

- ▣ Start: 10/01/2022
- ▣ Finish: 09/30/2023

## Barriers addressed

- To reduce the production cost of a PHEV battery
- Na-ion and Na-metal batteries with long calendar and cycle life
- Na-ion and Na-metal batteries with superior abuse tolerance

## Budget

- ▣ Funding received in FY22

  DOE: $425k
- ▣ Funding received in FY23

  DOE: $425k

### Collaborators

- Pacific Northwest National Laboratory (PNNL)
- SLAC National Accelerator Laboratory (SLAC)
- University of Maryland at College Park
- University of California at San Diego (UCSD)
- Harvard University
- Virginia Tech

# Relevance and Project Objectives

***✓ Diagnostics studies aimed to address and improve the performance of next-generation battery materials.***

- **To study morphology and structural/chemical state changes of electrode materials in advanced LIBs and next-generation batteries (beyond Li-ion such as Li-metal, Li-S, and Na-ion).**
- **To reveal the performance degradation mechanisms in newly developed electrode materials in advanced LIB batteries, Li/S and Na-ion batteries, such as Ni-rich $Li(NiCoMn)O_2$, Li-rich $Li_{1+x}(NiMnCo)O_2$ and composite cathodes materials, as well as sulfur-based cathode materials, especially polymeric S-cathode materials such as S-PAN for Li-S batteries. Multi-modal synchrotron-based X-ray spectroscopy/scattering/imaging techniques are used to better understand these advanced materials**

***✓ Diagnostics study aimed to improve the calendar and cycle life of advanced batteries.***

- **To develop and apply in situ diagnostic techniques with surface and bulk sensitivity to improve the calendar and cycle life of batteries through investigating the mechanism of capacity, voltage, and power fading of LIB cathode materials such as Ni-rich $Li(NiCoMn)O_2$, Li-rich $Li_{1+x}(NiCoMn)O_2$, and sulfur cathode materials.**
- **To study material degradation and electrode/electrolyte interphase growth.**
- **To develop novel techniques to reveal the morphology and chemical changes of advanced Li-ion cathode materials throughout multi-cycling to provide information to improve cycle life of advanced LIB systems Na-ion and Li-S batteries, including development of novel in situ spectroscopic (XAS) techniques combined with X-ray imaging (TXM) techniques.**

***✓ Diagnostics study of electrode materials with lower cost potential.***

# Milestones

| Month/Year | Milestones |
|---|---|
| Dec/2022 | Complete PDF studies of the amorphous components in solid-electrolyte-interphase (SEI) for Cu‖Li, NMC‖Li, and NMC‖Cu cells using low concentration 1M lithium bis(fluorosulfonyl) imide (LiFSI) in 1,2 dimethoxyethane (DME) electrolyte. ↪ *Completed.* |
| Mar/2023 | Complete studies of sulfur mapping on lithium metal anode (in NMC‖Li cell using LiFSI-based electrolyte) to understand spatial distribution of interphase species in SEI. ↪ *Completed.* |
| Jun/2023 | Complete the study of the beam damage phenomenon in in-situ transmission x-ray microscopy (TXM) experiment of NMC‖Li coin cells and its implications on data analysis. ↪ *On schedule.* |
| Sep/2023 | Complete the study of mitigating beam damage for in-situ TXM experiment of NMC‖Li cells by manipulating the cell configurations ↪ *On schedule.* |

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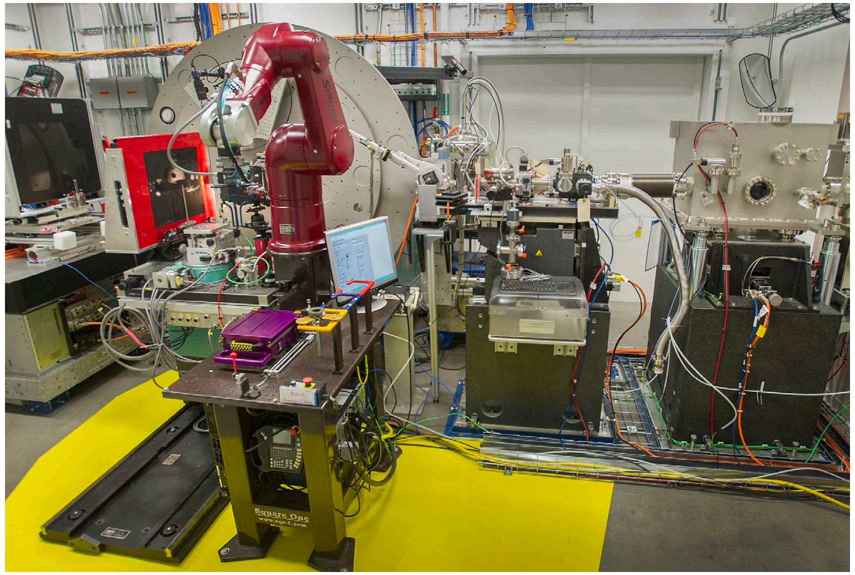
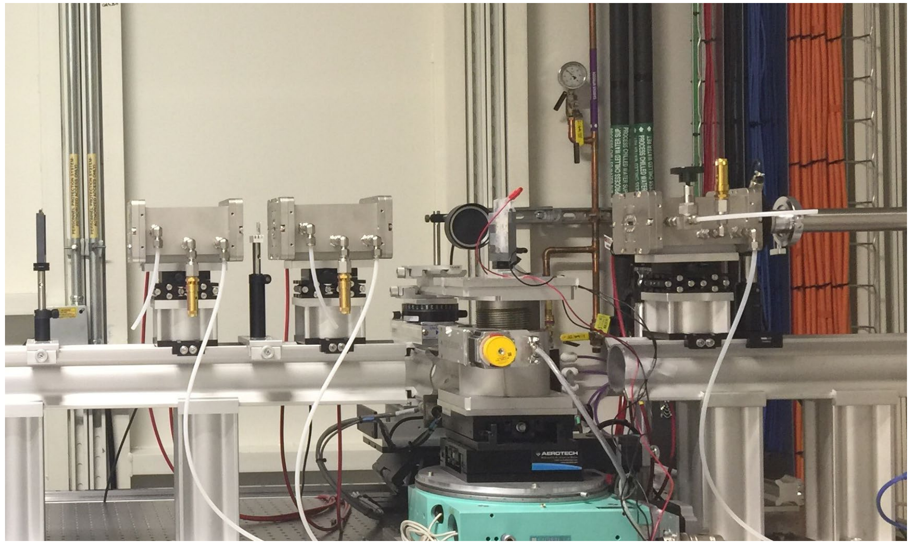
# Approaches

- Developing and applying synchrotron-based x-ray diffraction (XRD) and pair distribution function (PDF) techniques to study the structural and chemical changes of cathode materials, as well as the solid electrolyte interphase (SEI) and cathode electrolyte interphase (CEI) of advanced batteries (Li-ion, Li-metal, Na-ion, and Li-S) during charge-discharge cycling.
- Developing and applying synchrotron-based *in situ* X-ray absorption spectroscopy (XAS) and X-ray photoelectron spectroscopy (XPS) techniques to study both the cationic (transition metal elements) and anionic (oxygen) redox contributions of new cathode materials for advanced batteries (Li-ion, Li-metal, Na-ion, and Li-S)
- Developing and applying synchrotron based soft x-ray absorption spectroscopy (sXAS) to study the redox contribution of oxygen of cathode materials for advanced batteries.
- Developing and applying combined multi-modal synchrotron-based X-ray spectroscopy/scattering/imaging techniques to study the advanced materials for these battery systems.
- Extended collaboration with other US and international academic institutions and US industrial partners.

# Approaches

## In situ x-ray scattering and absorption beamlines of NSLSII at BNL





The photo of X-ray Powder Diffraction (XPD) beamline capable to do in situ/ex situ x-ray diffraction (XRD) and pair distribution function (PDF) studies of advanced battery materials at NSLSII.

The photo of Quick X-ray Absorption and Scattering, or QAS beamline capable to do in situ/ex situ x-ray absorption (XAS) studies of advanced battery materials at NSLSII.

# Approaches: Synchrotron X-ray techniques for advanced battery studies

## 23-ID-2 and 7-ID-1 @NSLS-II

### Soft X-ray absorption spectroscopy (sXAS)

- Extremely surface sensitive
- Different modes with different probing depth
  - Auger electron yield (AEY): ~ 1nm
  - Total electron yield (TEY): ~10nm
  - Partial electron yield (PEY): ~5nm
  - Total fluorescence yield (TFY): ~ 500nm

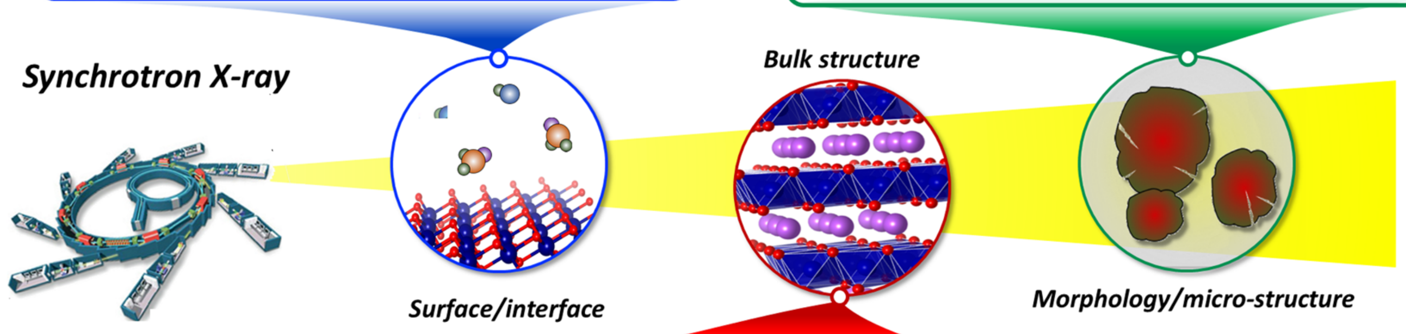
- Requires UHV condition : limit in situ capability for liquid electrolyte

## 18-ID and 3-ID @NSLS-II

### Scanning/Transmission X-ray microscopy (STXM/TXM)

- Morphology and micro-structure evaluation in micro/meso/macro scale
  : Micro-crack, particle fracture, tortuosity

- Chemical information (elemental/chemical mapping)
  : concentration gradient, oxidation state in single/multiple particle level (chemical inhomogeneity)




### X-ray diffraction (XRD)

- Average crystal structure (long-range order)
  - Lattice parameter
  - Phase
  - Strain
  - Atomic position
  - Site occupancy
  - Texture
  - Stacking faults

## 28-ID-2@NSLS-II

### Pair distribution function (PDF)

- Total scattering (Bragg+diffuse scattering)
- Local structure information
  : Inter-atomic distance, coordination numbers

- Cover middle range structure between XRD and EXAFS

## 28-ID-1@NSLS-II

### Hard X-ray absorption spectroscopy (XAS: XANES and EXAFS)

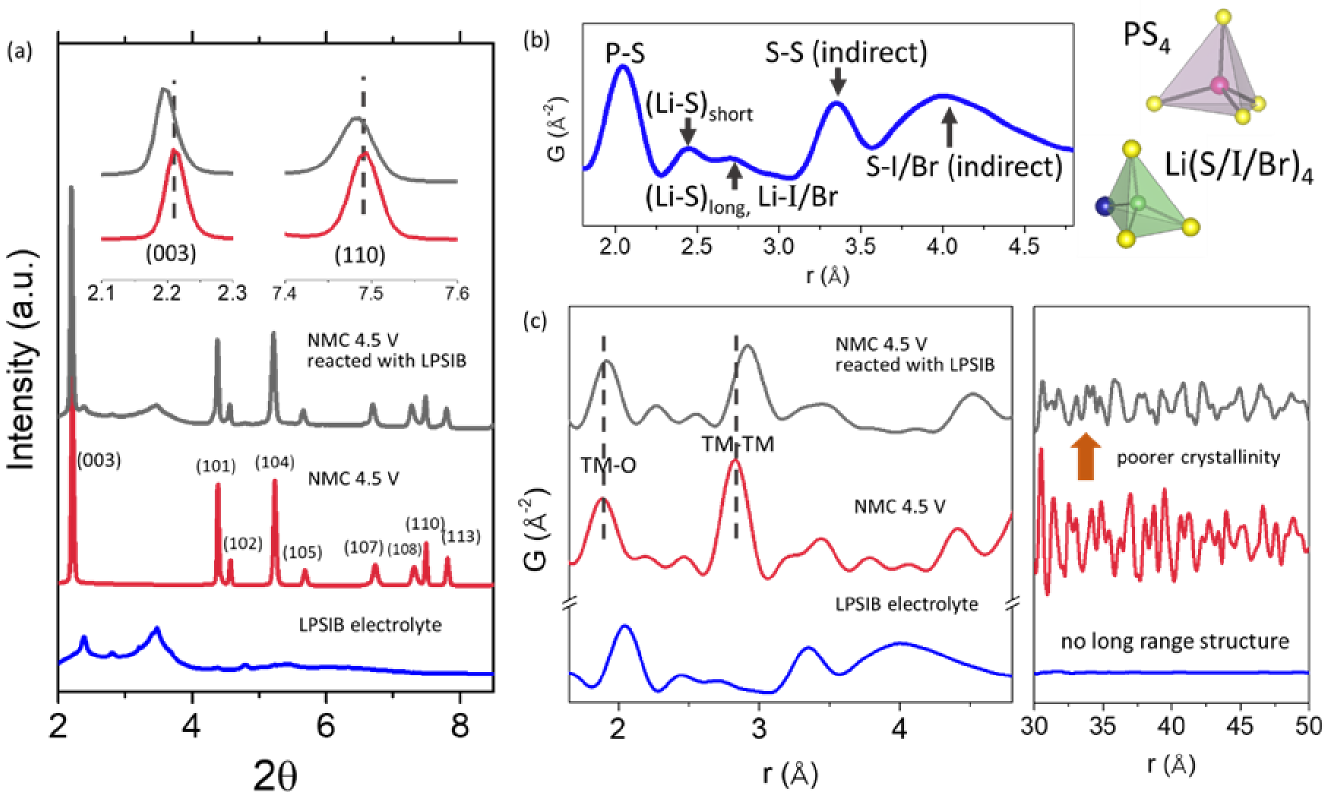
- Valence state changes during electrochemical reaction
  : revealing charge compensation mechanism in elemental specific way
- Coordination environment
  (e.g., octahedral, tetrahedral etc.)
- Local structural changes
  : bond length, degree of disorder

## 8-ID and 7-BM@NSLS-II

# Technical Accomplishments (Collaboration with PNNL)

## XRD, and PDF studies of $Li_7P_2S_8I_{0.5}Br_{0.5}$ (LPSIB) to understand its stability at high voltage charging when used as solid electrolyte for NMC811 cathode

Both lattice parameter "a" and "c" of NMC811 expanded after mixing with LPSI showing the reduction of transition metals possibly caused by the S element in LPSIB

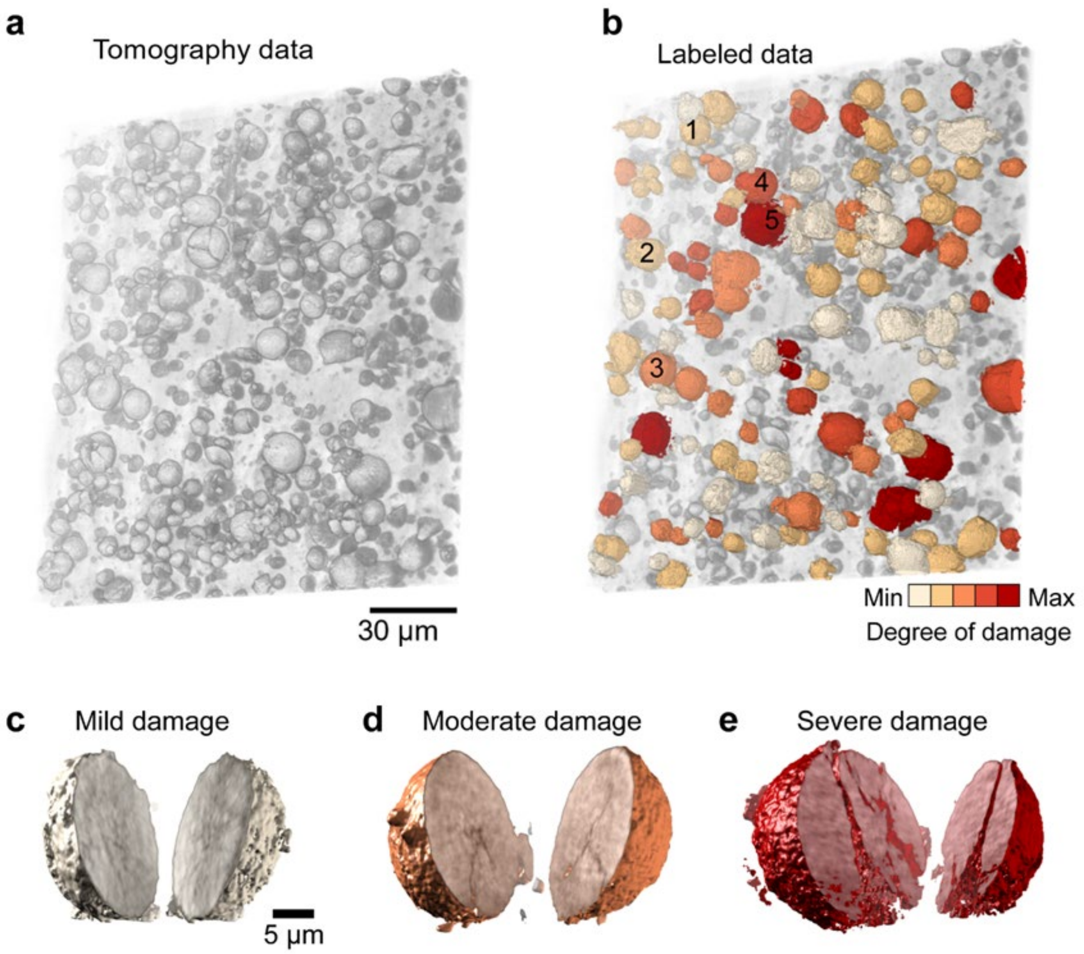



➢ (a) Synchrotron XRD of #1: LPSIB (blue); #2: NMC811 charged to 4.5 V (red); #3: sample #2 mixed with LPSIB (black). (b) the short-range PDF data of LPSIB electrolyte with $SP_4$ and $Li(S/I/Br)_4$ tetrahedra in the structure shown. (c) the short- and long-range PDF data of the samples #1, #2, and #3.

# Technical Accomplishments (Collaboration with SLAC)

## Electrode level computed tomography (CT) of NMC811cathode after 100 cycles (2.8-4.4V)

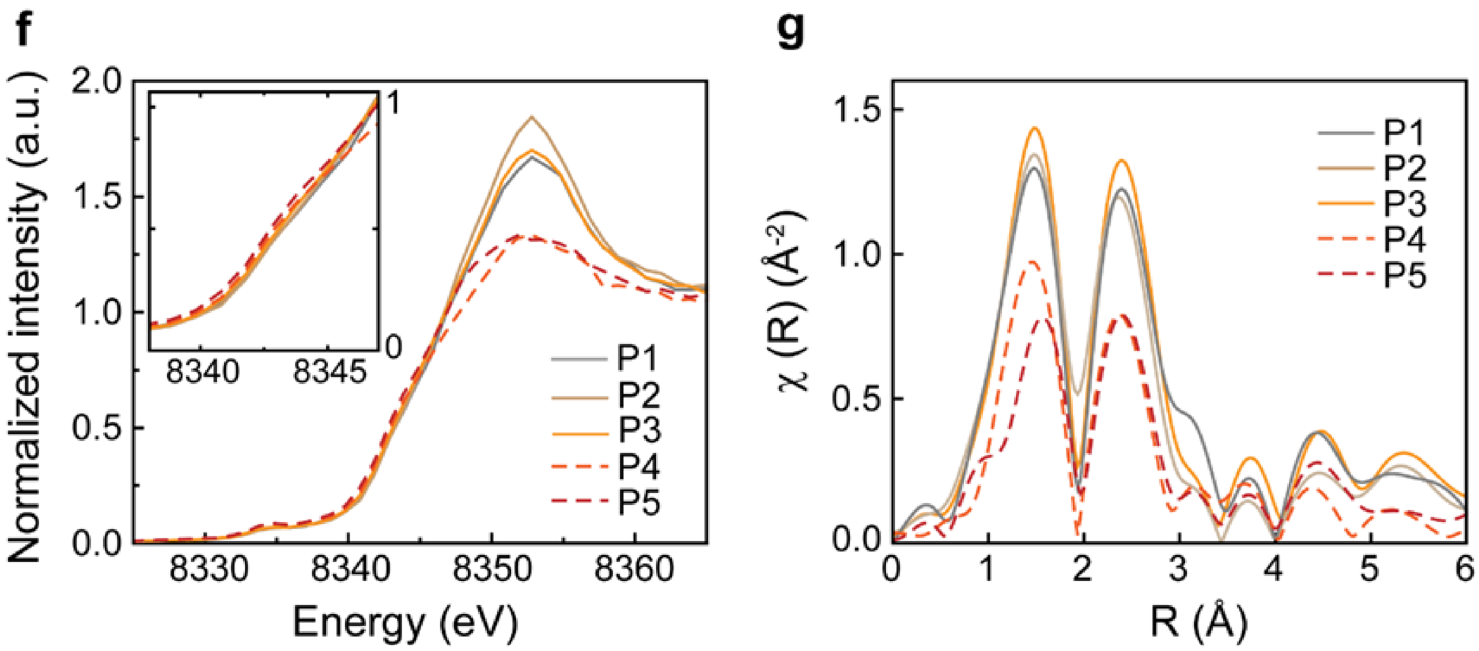
These results show that the oxygen loss at high voltage charging plays an important role in the crack formation and capacity degradation of NMC811 particles, suggesting that tuning the oxygen activity and suppressing the oxygen loss can potentially help reducing the cracking in NMC811 particles




- (a) computed tomography scan image of cycled NMC811 electrode; (b) particles labelled based on their degrees of morphological damage; (c) to (e) detailed CT images of representative particles having various degrees of damage.

# Technical Accomplishments (Collaboration with SLAC)

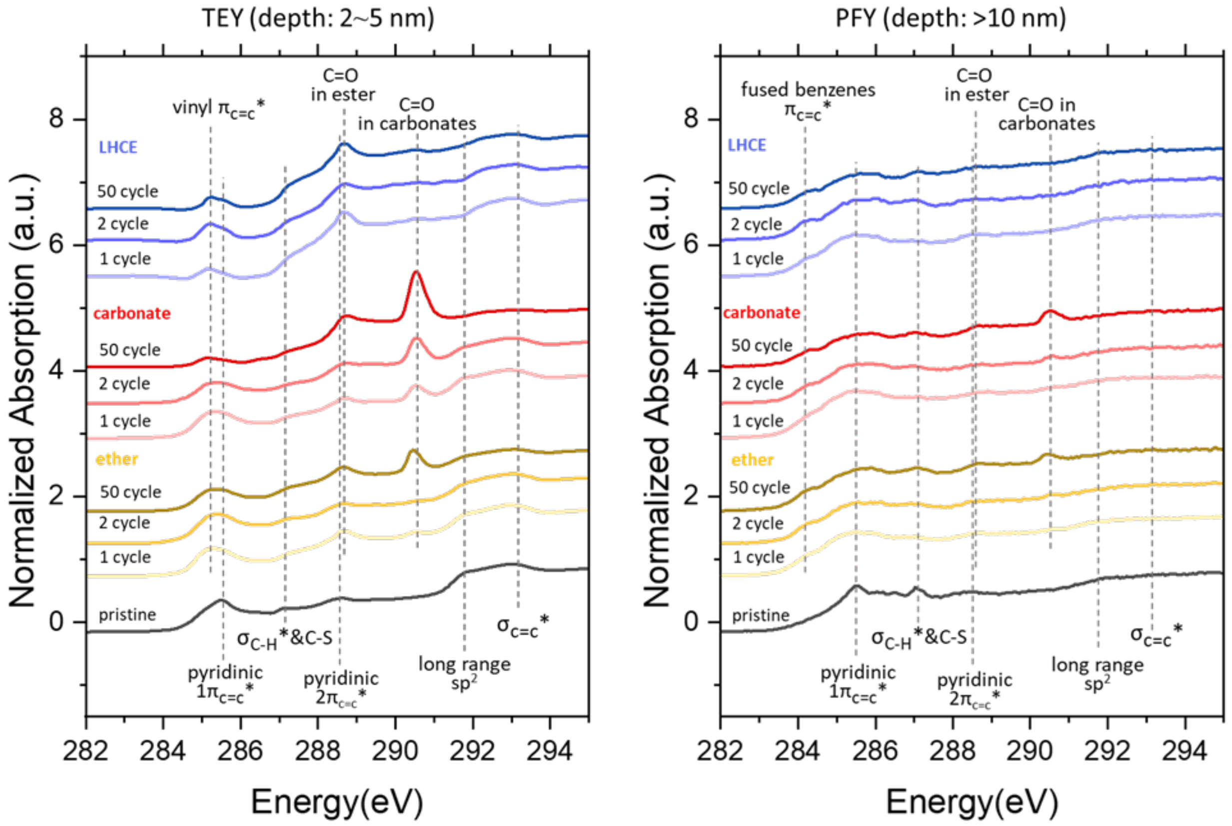
## XANES and EXAFS spectra at Ni K-edge of NMC811cathode particles labeled in (b) of previous slide




- (f) XANES data of selected particles labeled in (b) of previous slide;
- (g) ft-EXAFS data of selected particles labeled in (b) of previous slide.

# Technical Accomplishments (Collaboration with UCSD)

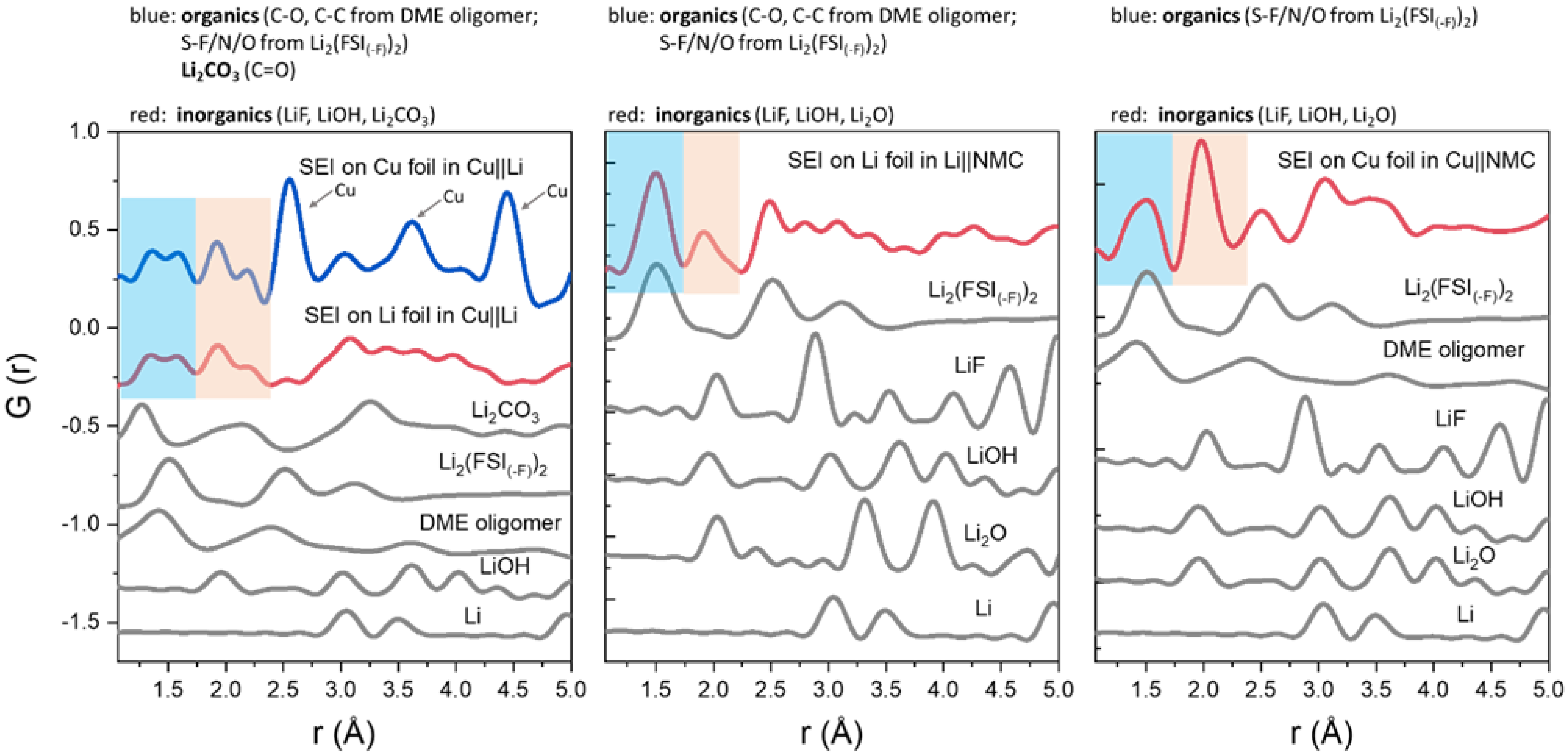
## (sXAS) studies of polymeric sulfur (sulfurized polyacrylonitrile, or SPAN) cathode to understand electrolytes influence the cathode-electrolyte-interphase (CEI).




- ➢ Soft x-ray carbon K-edge ex situ XAS studies of SPAN electrodes cycled in various electrolytes: localized high concentration electrolyte (LHCE, top group), carbonate (2nd group), and ether (3rd group)
- ➢ in TEY (left panel) and PFY (right panel).

# Technical Accomplishments

## PDF studies of the amorphous components in (SEI) for Cu||Li, NMC||Li, and NMC||Cu cells using low concentration 1M lithium bis(fluorosulfonyl) imide (LiFSI) in 1,2 dimethoxyethane (DME) electrolyte




These results demonstrate that PDF is capable of probing both crystalline and amorphous phases in SEI, revealing the relative content of organics from solvent decomposition, inorganics from anion decomposition in SEI

PDF studies of the amorphous components in (SEI) for Cu||Li, NMC||Li, and NMC||Cu cells using low concentration 1M lithium bis(fluorosulfonyl) imide (LiFSI) in 1,2 dimethoxyethane (DME) electrolyte. Left panel: measured PDF data of SEIs on Cu foil and on Li foil in Cu||Li cells. Middle panel: PDF data of SEI on Li foil in Li||NMC cells. Right panel, PDF data of SEI on Cu foil in Cu||NMC cells. Calculated PDF patterns of possible SEI components are also shown for data analysis.

# Technical Accomplishments

- Through collaboration with PNNL, XRD and PDF studies of $Li_7P_2S_8I_{0.5}Br_{0.5}$ (LPSIB) to understand its stability at high voltage charging when used as solid electrolyte for NMC811 cathode. It was found that the crystallinity of LPSIP is quite low, both lattice parameter “a” and “c” of NMC811 expanded after mixing with LPSI showing the reduction of transition metals possibly caused by the S element in LPSIB
- Through collaboration with SLAC, many-particle TXM studies on NMC811 cathode to understand its chemical and morphological heterogeneities at the electrode level were carried out. It was found that the oxygen loss at high voltage charging plays an important role in the crack formation and capacity degradation of NMC811 particles. This suggests that tuning the oxygen activity and suppressing the oxygen loss can potentially help reducing the cracking in NMC811 particles. The results are being analyzed for publication.
- PDF studies of the amorphous components in solid-electrolyte-interphase (SEI) for Cu||Li, NMC||Li, and NMC||Cu cells using low concentration 1M lithium bis(fluorosulfonyl) imide (LiFSI) in 1,2 dimethoxyethane (DME) electrolyte were carried out, demonstrating that PDF is capable of probing both crystalline and amorphous phases in SEI, revealing the relative content of organics from solvent decomposition, inorganics from anion decomposition in SEI. The results are being analyzed for publication.

# Response to last year's reviewer comments

## N/A This project was not reviewed in FY2022

# Collaborations with other institutions and companies

- Pacific Northwest National Lab. (PNNL)
- SLAC National Accelerator Laboratory (SLAC)
- University of California at San Diego (UCSD)
- University of Maryland at College Park
- Harvard University
- Virginia Tech

# Proposed Future Work for *FY 2021* and *FY2022*

▣ **FY2023 Q3 Milestone:**

**Complete the study of the beam damage phenomenon in in-situ transmission x-ray microscopy (TXM) experiment of NMC||Li coin cells and its implications on data analysis.**

▣ **FY2023 Q4 Milestone:**

**Complete the study of mitigating beam damage for in-situ TXM experiment of NMC||Li cells by manipulating the cell configurations.**

**More FY2023 work proposed:**

- ▣ **Using synchrotron-based pair distribution function (PDF) techniques to study the polysulfides in Li-S batteries.**
- ▣ **Using synchrotron-based X-ray fluorescence mapping (XRF) technique to study the dissolving, deposition, and distribution of polysulfides in Li-S batteries .**
- ▣ **The collaborative research with US academic research institutions and industrial partners will be further expanded and strengthened.**

# Summary

- **Relevance**
  - ✓ *To increase the energy density, searching for new cathode materials for advanced Li-ion, Na-ion and Li-S batteries.*
  - ✓ *Diagnostics study aimed to improve the calendar and cycle life of these advanced batteries.*
  - ✓ *Diagnostics study of new electrode materials with lower cost potential of these advanced batteries.*
- **Approaches**
  - *Synchrotron-based In situ and ex situ x-ray diffraction (sXRD)*
  - *Synchrotron based x-ray pair distribution function (xPDF)*
  - *Synchrotron-based In situ and ex situ x-ray absorption spectroscopy (XAS) and soft x-ray absorption spectroscopy (sXAS)*
  - *Synchrotron-based transmission x-ray microscopy (TXM) and combined multi model spectroscopy and imaging techniques.*
- **Technical Accomplishments**
  - *XRD and PDF studies of $Li_7P_2S_8I_{0.5}Br_{0.5}$ (LPSIB) to understand its stability at high voltage charging when used as solid electrolyte for NMC811 cathode.*
  - *Many-particle TXM studies on NMC811 cathode to understand its chemical and morphological heterogeneities at the electrode level.*
  - *PDF studies of the amorphous components in solid-electrolyte-interphase (SEI) for Cu||Li, NMC||Li, and NMC||Cu cells using low concentration 1M lithium bis(fluorosulfonyl) imide (LiFSI) in 1,2 dimethoxyethane (DME) electrolyte.*
- **Proposed Future work**
  - *Studies on the beam damage phenomenon in in-situ transmission x-ray microscopy (TXM) experiment of NMC||Li coin cells and its implications on data analysis*
  - *Studies on the mitigating beam damage for in-situ TXM experiment of NMC||Li cells by manipulating the cell configurations. .*