

# Molecular-Level Understanding of Cathode/Electrolyte Interface

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**bat409**

# Overview

## Timeline

Project start date: 01/01/2019

Project end date: 09/31/2021

Percent complete: 55%

## Budget

Total project funding

DOE share (FY2019-21): \$1350K

Funding for FY2019

SLAC (\$285K)

U.S. Army Res. Lab.(\$125K)

LBL (\$40K)

Funding for FY2020

SLAC (\$285K)

U.S. Army Res. Lab.(\$125K)

LBL (\$40K)

## Barriers and Technical Targets

### -Performance

High-energy next-generation Li-ion battery electrochemistries require the utilization of high-voltage cathode materials ( $> 4.5$  V). Their full potential has to date been hampered by the limited knowledge of the underlying chemistry and physics of the buried cathode/electrolyte interface

### -Lifetime

Stabilization of high-voltage cathode/electrolyte interface remains critical to improve the cycling performance of next-generation Li-ion battery. This remains unresolved due to lack of mechanistic understanding of the degradation mechanisms and development of the stabilization strategy

## Partners

Project lead: SLAC

Collaboration: US Army Res. Lab./LBL

# Relevance

## Impact

Understanding of the degradation mechanism and development of stabilization strategy for cathode/electrolyte interface (CEI) is critical to the utilization of high-voltage transition metal oxide (TMO) cathodes and the improvement of the energy density in Li-ion batteries (LIBs)

## Overall Objectives

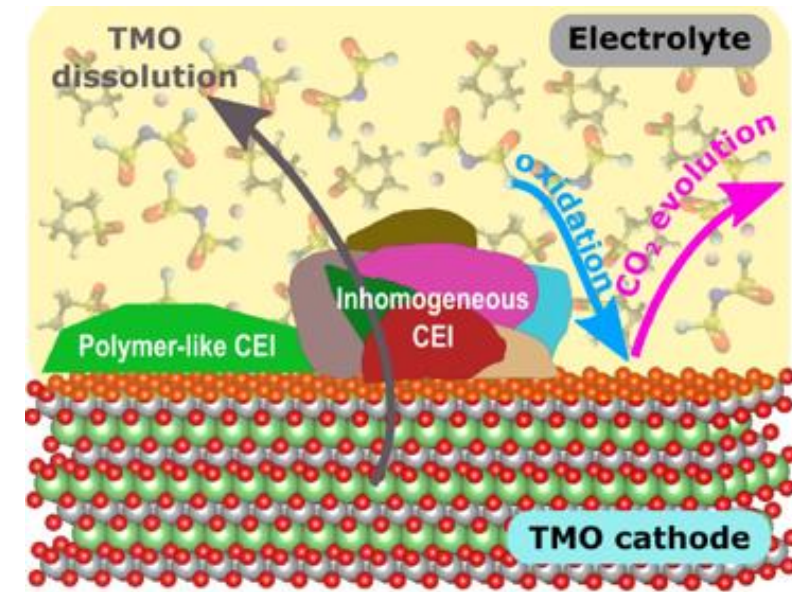
- Understanding underlying chemistry and physics that between cathode and electrolyte high-voltage LIBs
- Developing strategies that enable the stabilization of CEI under strongly oxidizing conditions

## Objective this period

- ✓ Initial surface X-ray scattering experiments of electrolyte-model oxide interface
- ✓ Initial X-ray measurements of experiments of CEI growth on epitaxial TMO thin film cathode

## Impact & Relevance to VT Office

Offer foundational knowledge of the interfacial transitions and stabilization of cathode that can be translated to the rational design of improved LIBs chemistries and electrolytes



Formation processes of CEI

# Milestones

## FY 2020

01/01/2020-10/01/2020

Initial surface X-ray scattering experiments of electrolyte-model oxide interface

01/01/2020

**Complete**

Initial X-ray measurements of experiments of CEI growth on epitaxial TMO thin film cathode

04/01/2020

**Complete**

Complete combined X-ray and MD analysis of electrolyte-model oxide interface

07/01/2019

**On track**

Complete X-ray spectroscopy experiments of CEI growth on epitaxial TMO thin film cathodes

10/01/2019

**On track**

**Go/no-go:**

Successful comparison of X-ray and MD analysis of electrolyte-model oxide interface

## FY 2021

10/01/2020-09/31/2021

Compare and co-verify *in-situ*, *ex-situ* X-ray experiments of CEI growth with DFT predictions of CEI forming reactions

01/01/2020

Identify missing measurements and simulations and perform final measurements and simulations of CEI growth

04/01/2020

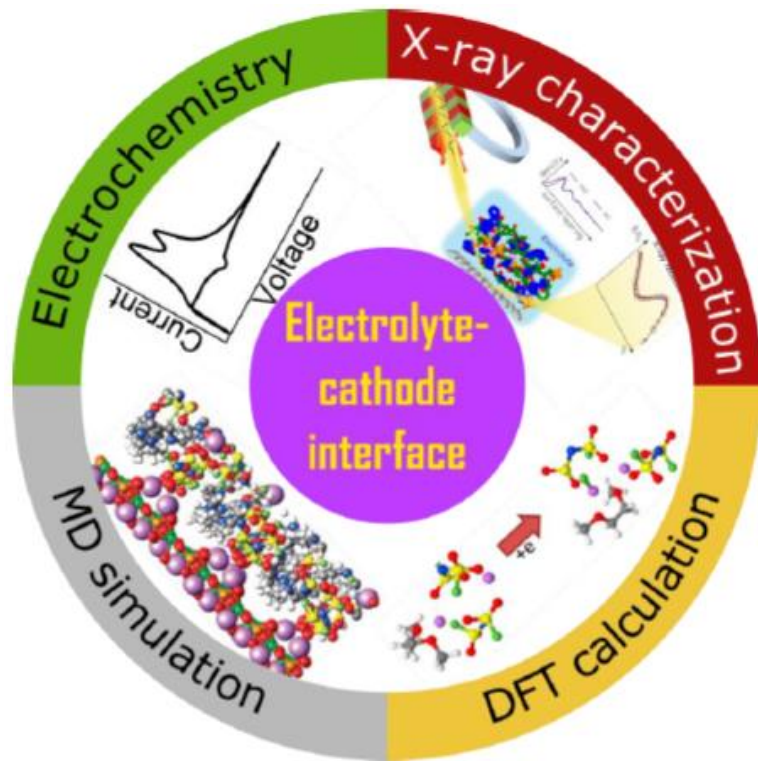
Complete analysis of experiment and modeling of CEI growth

07/01/2020

Concluding the project, prepare a series of publications providing a comprehensive descriptions of underlying chemistry and physics of the cathode interface

10/01/2020

# Approach/Strategy



Combining molecular-scale molecular dynamics (MD) simulation and density functional theory (DFT) calculation with advanced X-ray surface scattering, X-ray spectroscopy, and electrochemical characterizations using model, thin-film TMO electrodes and high-purity electrolytes

## **Electrolyte**

From baseline carbonate-based electrolytes to fluorinated electrolytes

## **TMO cathode**

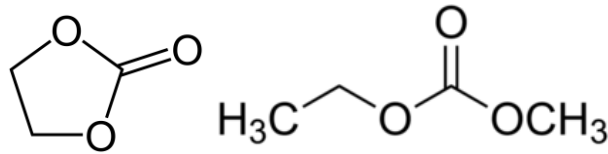
From particles to model thin-films (grown by pulsed laser deposition, PLD) with controlled surface structure

## **Interphase**

From chemical reactions (soaking in electrolytes at open-circuit voltage conditions) to electrochemical reactions

# Technical Accomplishments and Progress

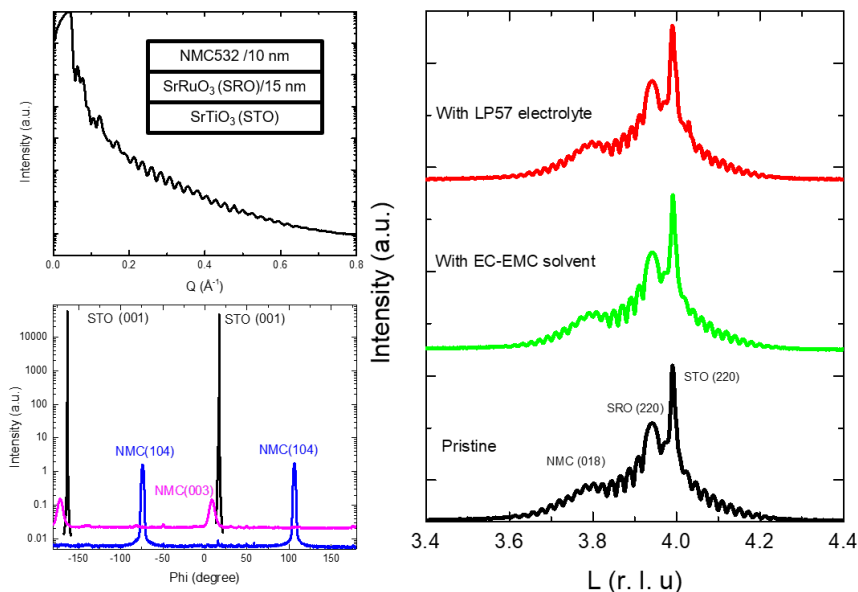
Experimental studies: X-ray surface scattering of chemical evolution of NMC thin-films in carbonate-based solvents and electrolytes



Ethylene carbonate (EC); Ethyl methyl carbonate (EMC)

LP57 electrolyte: 1 M LiPF<sub>6</sub> in EC: EMC (3:7 wt.%)

**Structural evolution of PLD-derived NMC532 films with/without carbonate-based solvents and electrolytes (soaking for 2h)**



X-ray reflectivity of PLD-derived NMC-SRO-STO films (left top); Off-specular phi-scans of STO {001} (black), NMC {104} (blue), and NMC {003} (pink) (left bottom); Specular X-ray diffraction of NMC films after soaking in LP57 electrolyte and EC-EMC solvent for 2 hours (right)

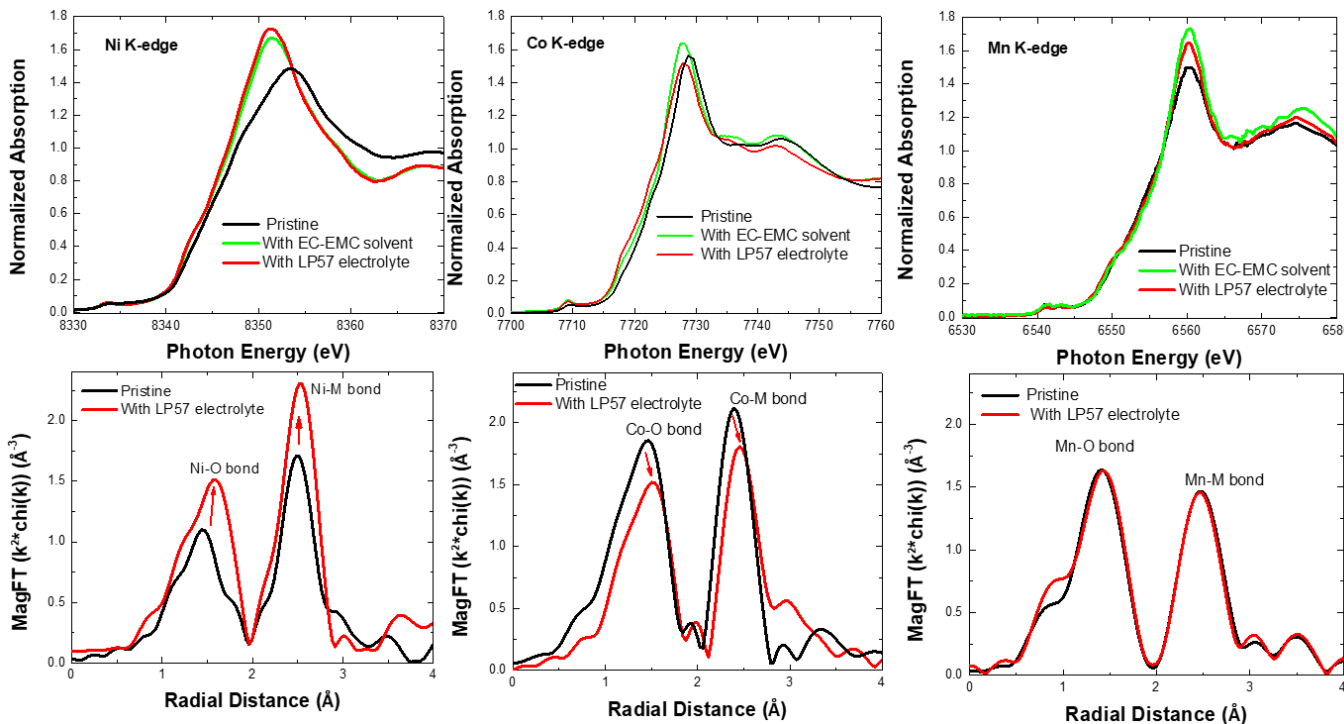
- **Successful controlled PLD growth of NMC films on SRO-STO**
- **As indicated by the similar peak positions and profiles of NMC {018} peak for films in X-ray diffraction (right bottom), the out-of-plane structure of epitaxial NMC thin films remains largely unchanged after soaking in carbonates-based solvent and electrolytes**



# Technical Accomplishments and Progress

Experimental studies: Solvent-induced metal-dependent chemical reduction of NMC532 probed by total-reflection X-ray spectroscopy

## Chemical evolution of NMC532 film surfaces with/without carbonate-based solvents and electrolytes



(Top row) Grazing incidence X-ray absorption near edge structure (XANES) spectra of pristine and soaked films at Ni, Co, and Mn K-edges, respectively.

(Bottom row) Local structure results derived from extended X-ray absorption fine structure (EXAFS) spectra of pristine and soaked films

**Surface-sensitive total reflection X-ray spectroscopic elucidated:**  
**Reduction degree in NMC: transition metal-dependent degradation**  
Ni (reduced by 1.2 e) > Co (reduced by 0.4 e) > Mn (small changes)

**Chemical reaction: solvent vs. electrolyte (with  $\text{LiPF}_6$ )**

EC/EMC solvents appears to be the major contributor to reduction;  
Salt effect appears less significant



**Evidences of Proton trapping in Layered Cathodes:**

➤ **Charge compensation:**

Increased local coordination while reduced oxidation states in Ni sites

➤ **Positively charged small protons:**

**Significant chemical reduction from spectroscopy while unchanged structure from X-ray surface scattering**

# Technical Accomplishments and Progress

## Previous theoretically predictions

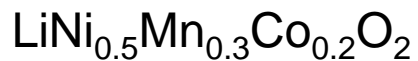
- Solvent dehydrogenation on NMC surface leads to degradation of carbonate-based electrolytes
- Protons tend to be trapped in layered cathode materials

Reference:

*Energy Environ. Sci.* 2020,13, 183-199; *Nano Energy* 2019, 55, 216–222;  
*Chem. Mater.* 2008, 20, 17, 5485-5490; *Chem. Mater.* 2006, 18, 5, 1169-1173.

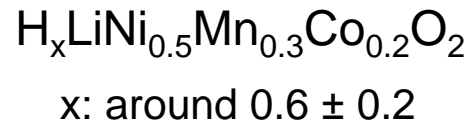
## Hypothesis on interfacial cathode-electrolyte interactions

EC + EMC



Interfacial  
degradation  
→

EC\* + EMC\*



## The combined X-ray and theoretical studies:

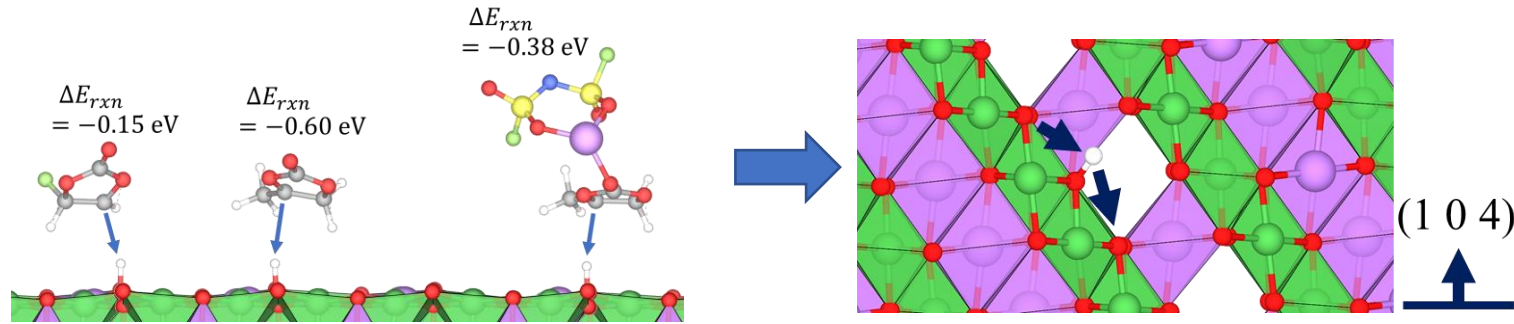
- ✓ revealed the underlying oxide-electrolyte interfacial protonation reactions
- ✓ directly elucidated the cathode degradation from solvent protonation
- ✓ offered fundamental insights into the structural reactivity before cycling, which rationalizes stabilization strategies of high-voltage cathodes in LIBs

Deprotonation of solvent donates proton to NMC lattice, yielding radicals. Protons are mobile in NMC, and hence reduce Ni and Co sites.



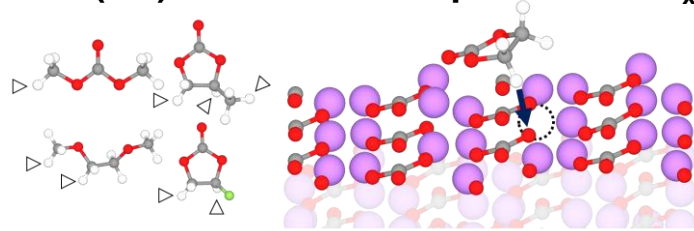
# Technical Accomplishments and Progress

## Theoretical modeling of solvent deprotonation and proton transfer in layered cathode and CEI ( $\text{Li}_2\text{CO}_3$ )

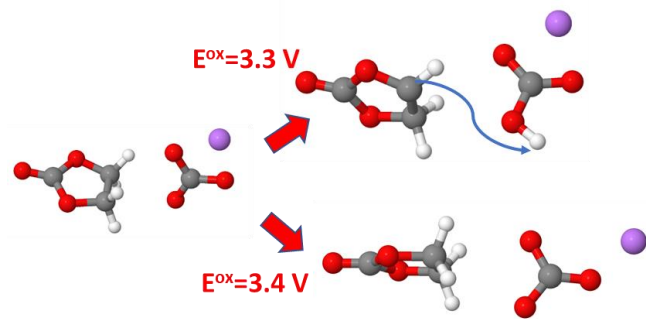


Solvent (EC) and salt decomposition at  $\text{Li}_x\text{NiO}_2$

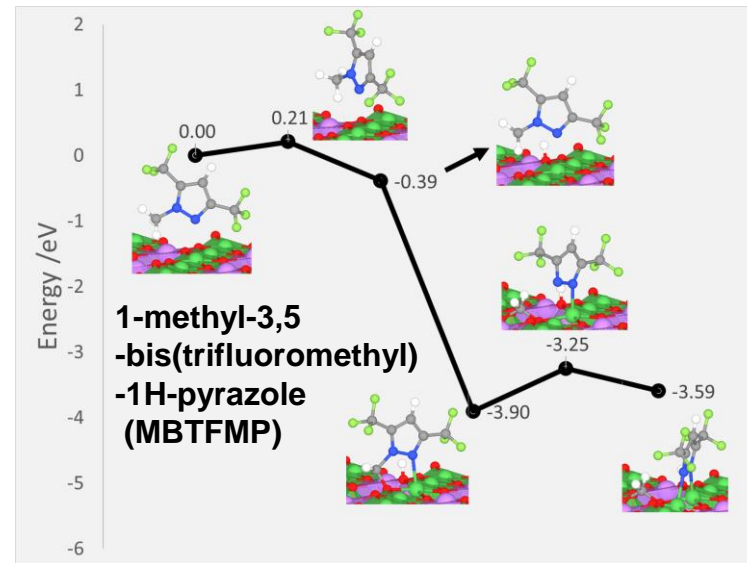
H transport in the layered cathode



CEI ( $\text{Li}_2\text{CO}_3$ ) delithiation and reactivity



$\text{LiCO}_3$  - solvent (EC) oxidation, H-transfer



The reactivity of MBTFMP additive at  $\text{Li}_x\text{NiO}_2$

## Importance:

Molecular-level insights into solvent degradation pathways at cathode surface

Theoretical calculations elucidated

- ✓ As compared with salt, solvents tend to be more unstable due to the deprotonation reaction at layered cathode surface
- ✓ Possible proton transport pathways in layered cathode
- ✓  $\text{Li}_2\text{CO}_3$  would accelerate solvent oxidation process through delithiation, leading to facilitated proton transfer from solvent
- ✓ Rationalization of stability enhancement *via* advanced additives

# Response to Previous Year Reviewers' Comments

The reviewer remarked that as the project just started, collaboration between the partners is not clear

*The research is well coordinated by frequent team meetings and intensive discussions. This collaboration can be seen in how the modeling informs the experiments in terms of the electrolyte degradation processes (slides 8 & 9) at OCV. The proposed mechanism resulted from discussion among the project participants.*

The reviewer said that as the project has very recently started, there is limited progress to report. Some NMC532 films have been produced and analyzed electrochemically, showing very different behavior based on processing conditions. The reviewer pointed out that while PLD is controllable, it is difficult to know which surfaces are relevant to real systems. Preliminary modeling work shows some success with EC electrolytes (not yet sulfolane), but the same challenge holds here for creating an appropriate surface

*While it is difficult to determine active surfaces in realistic batteries, thin films have been developed as model system to reduce the complexity in particle surfaces. This allows us to controllably explore the effect of defects levels, stress states, and different surface orientations on the reactivity and stability of cathode. The obtained insights will be compared with that of more realistic thin films. A similar approach holds for the theoretical modeling which will be related to the experiments on PLD polycrystalline and films. By investigating several surface orientations we expect to obtain insight that is generalizable to actual cathode particles.*

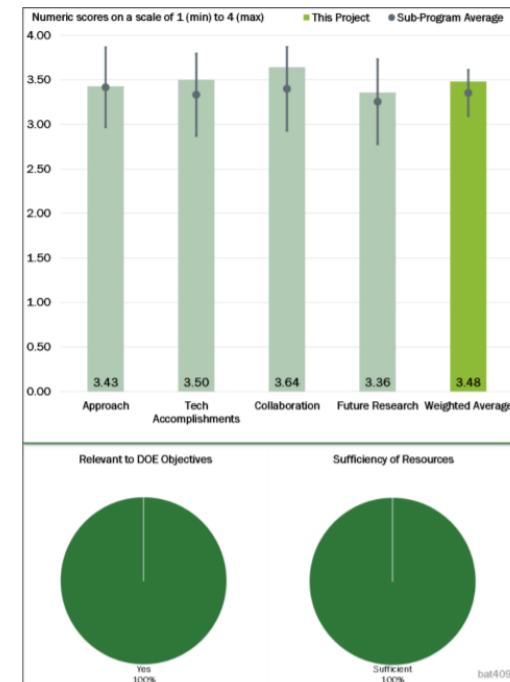


Figure 2-80 – Presentation Number: bat409 Presentation Title: Molecular-Level Understanding of Cathode/Electrolyte Interfaces Principal Investigator: Mike Toney (SLAC National Accelerator Laboratory)

# Partners/Collaborators



- *Providing the purified electrolytes*
- *Performing DFT calculation and MD simulation of CEI*



*Providing epitaxial oxide thin film cathode  
by PLD growth and polymer-assisted deposition*



*Providing the Time-of-Flight Secondary Ion Mass  
Spectrometry (TOF-SIMS) studies of cathodes*

# Remaining Challenges and Barriers

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- A primary challenge for cathode-electrolyte interaction is that the buried interfaces hinder direct experimental access

*Our strategies:*

*Operando surface-sensitive X-ray studies to probe the buried interfaces*

- In parallel, the reaction complexity and the heterogeneous nature in TMO cathode surfaces create challenges for probing (electro)-chemical processes regarding the evolution and stabilization of CEI

*Our strategies:*

*Model TMO cathode surfaces with controlled surfaces and defects would be combined with high-purity electrolyte and theoretical modeling to understand the underlying degradation mechanism and interfacial reactions*

# Proposed Future Research in FY2020 And FY2021

- Quantitative confirmation of protonation and Li contents in the soaked cathode films by time-of-flight secondary ion mass spectrometry (TOF-SIMS)
- Elucidate the influence of cathode protonation on the structural degradation in LIBs
- Explore the molecular mechanisms of fluorinated solvents on the stabilization of cathode surface
- *Operando* X-ray surface scattering and spectroscopy monitoring the evolution of cathode surface and CEI on epitaxial thin films and the electrochemical double layer (EDL) at cathode side
- Further computational modeling of solvent decomposition on cathode materials and model carbonate and fluorinated interphase

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

# Summary

## ➤ Accomplishments

- ✓ The combined scattering and spectroscopy studies elucidated the significant chemical transforms on the chemical and electronic properties of Ni and Co sites in cathode films when subject to carbonate-based solvents and electrolytes at open circuit conditions
- ✓ The protonation reaction between cathode surface and carbonate-based solvents accounts for the metal-dependent chemical degradation in cathodes
- ✓ DFT calculations revealed the dehydrogenation of carbonate solvents on the cathode surface

## ➤ Technical highlights

- ✓ Elucidating the interfacial evolution of cathode surface by the combined surface-sensitive X-ray studies, high-purity electrolytes, and controlled PLD growth of model thin-film NMC cathodes, and theoretical modeling

## ➤ Impact toward VTO Objectives

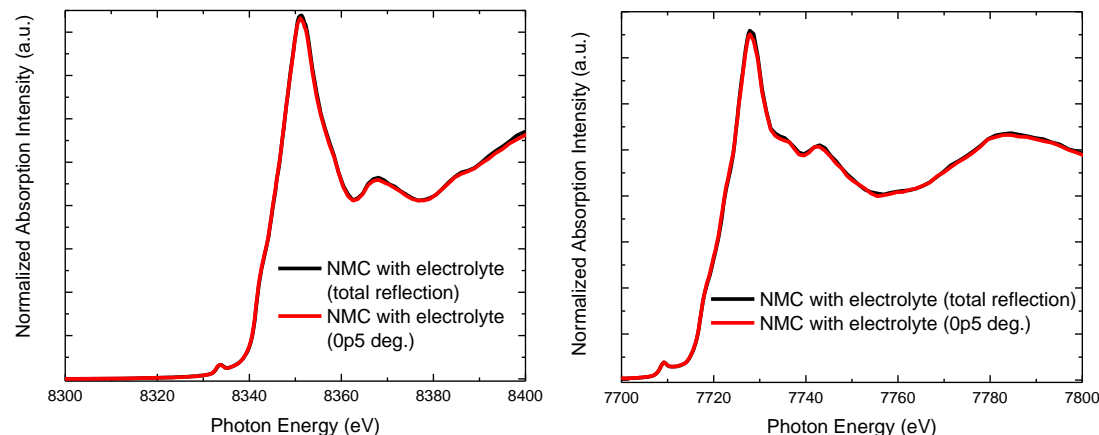
This project will offer foundational knowledge of the interfacial transitions and stabilization of cathode that can be translated to the rational design of improved NG-LIBs chemistries and electrolytes



# **Technical Backup Slides**

# Technical Backup Slides

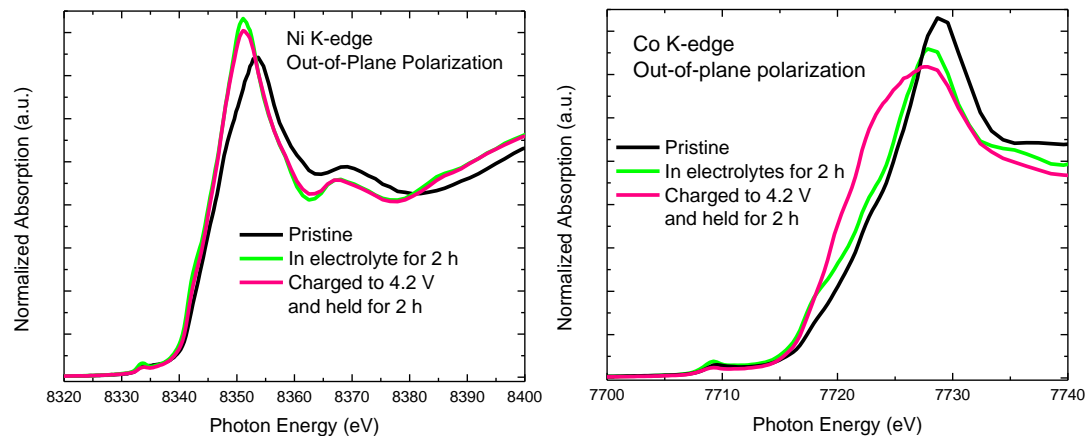
## The comparison of the chemical transformation of soaked NMC532 films in surface and bulk



X-ray absorption near edge structure (XANES) spectra of soaked films at total-reflection geometry (top surface) and an incidence angle of 0.5 degree (the whole film) at Ni and Co K-edges, respectively

- The protonation of the cathode is not limited to the surface, while goes deep into the whole 10 nm films

## The comparison of the stability of pristine and charged NMC532 films in LP57 electrolytes



XANES spectra of pristine, soaked films and charged NMC532 films at total-reflection geometry) at Ni and Co K-edges, respectively

- The de-lithiated cathode surfaces are more reactive and easier to be subject to hydrogenation