Molecular-Level Understanding of Cathode/Electrolyte Interface

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Overview

Timeline

Project start data: 01/01/2019
Project end data: 10/01/2021
Percent complete: 17%

Budget

Total project funding
DOE share (FY2019): $450K

Funding for FY2019:
SLAC ($285K)
U.S. Army Res. Lab.($125K)
LBNL ($40K)

Barriers

Barriers addressed:

-Performance

High-energy next-generation Li-ion battery electrochemistries require the utilization of high capacity and high-voltage cathode materials (> 4.5 V). Their full potential has to date been hampered by the paucity of understanding the underlying chemistry and physics of the cathode interfaces

-Lifetime

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

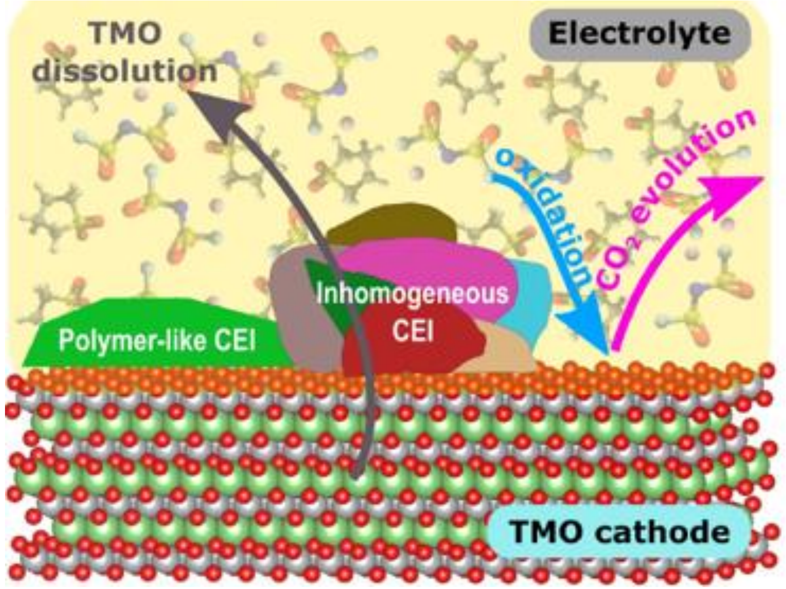
Partners

Project lead:	SLAC
Collaboration:	US Army Res. Lab./LBNL

Relevance

Impact

Research into 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)



Formation processes of CEI

Overall Objectives

Understanding underlying chemistry and physics that control CEI formation in next-generation high-voltage LIBs

Developing strategies that enable the stabilization of CEI under strongly oxidizing conditions

Objective this period

Purify baseline electrolyte

Perform first molecular dynamics (MD) modeling of electrolyte-model oxide interface

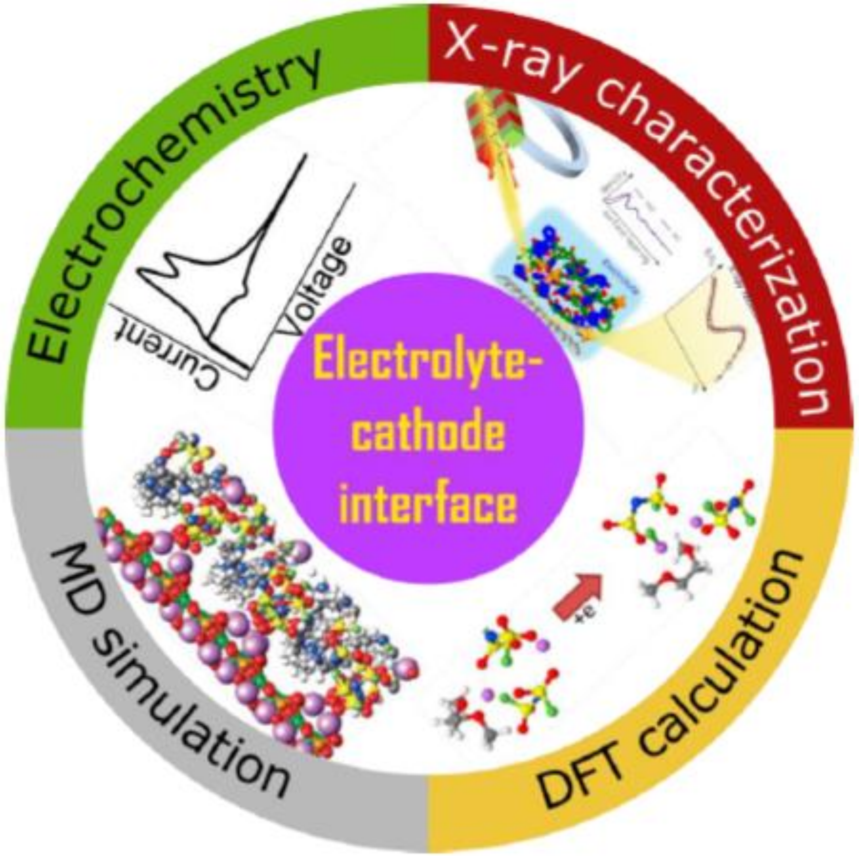
Impact & Relevance to VT Office

Guide the knowledge-driven design of optimized electrolytes and cathode surfaces to accelerate the development and deployment of next-generation LIBs

Milestones

FY 2019 01/01/2019-10/01/2019	FY 2020 10/01/2019-10/01/2020
Purify baseline electrolyte 01/01/2019 ***Complete***	Initial surface X-ray scattering experiments of electrolyte-model oxide interface 01/01/2020
Perform first MD simulation of electrolyte-model oxide interface 04/01/2019 ***Complete***	Initial X-ray measurements of experiments of CEI growth on epitaxial TMO thin film cathode 04/01/2020
Initial successful growth of epitaxial oxide thin film cathode 07/01/2019 ***On track***	Complete combined X-ray and MD analysis of electrolyte-model oxide interface. 07/01/2020
Electrochemistry of epitaxial thin-films in cone cell 10/01/2019 ***On track***	Complete X-ray spectroscopy experiments of CEI growth on epitaxial TMO thin film cathodes 10/01/2020
Go/no-go Success in growing epitaxial oxide thin-film cathode and successful cyclic voltammetry measurements	**Go/no-go** Successful comparison of X-ray and MD analysis of electrolyte-model oxide interface

Approach/Strategy



Electrolyte

From baseline carbonate-based electrolytes
to high-voltage electrolytes

TMO cathode

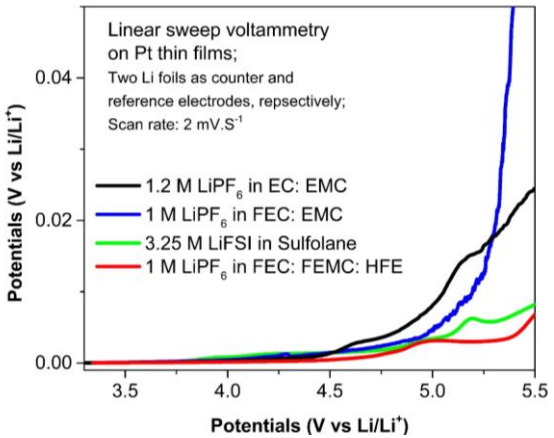
From particles
to model thin-films (grown by pulsed laser deposition, PLD) with controlled surface structure

Combining molecular-scale 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

Technical Accomplishments and Progress

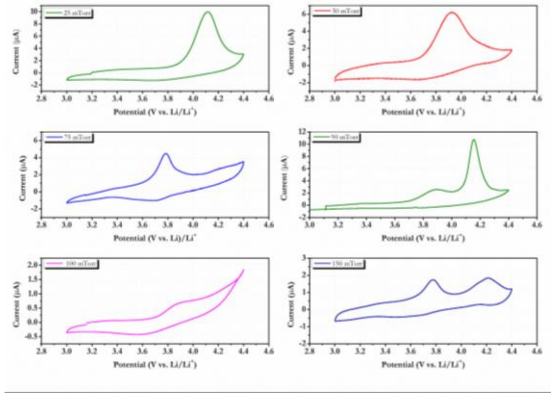
Experimental studies:

Electrochemical studies of the purified highly-fluorinated and sulfolane-based electrolytes and PLD-derived $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) thin films



Electrochemical stability windows of different electrolytes

EC (Ethylene carbonate); EMC (ethyl methyl carbonate);
FEC (Fluoroethylene carbonate);
FEMC (methyl (2,2,2-trifluoroethyl) carbonate); HFE (2,2,2-Trifluoroethyl 1,1,2,2-tetrafluoroethyl ether); LiFSI (lithium bis(fluorosulfonyl)imide)

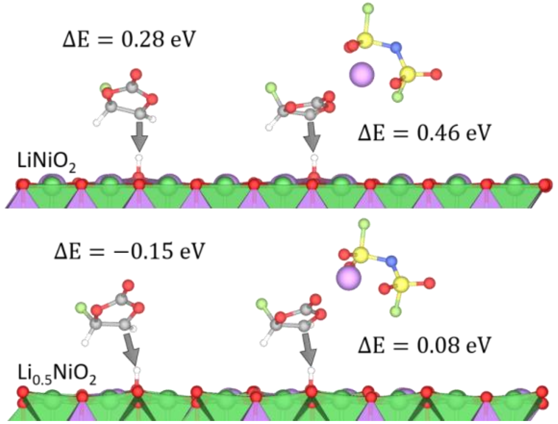


Influence of oxygen pressure during PLD growth on the electrochemical properties of NMC532 thin films

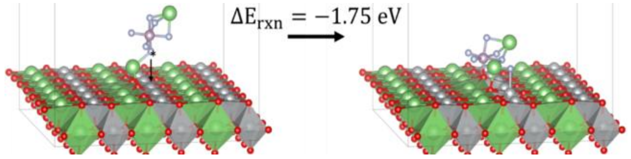
Experimental condition:
Scan rate: 0.1 mV. S^{-1};
Electrolyte:
1 M $LiPF_6$ in EC: DEC (diethylene carbonate)

Computational studies:

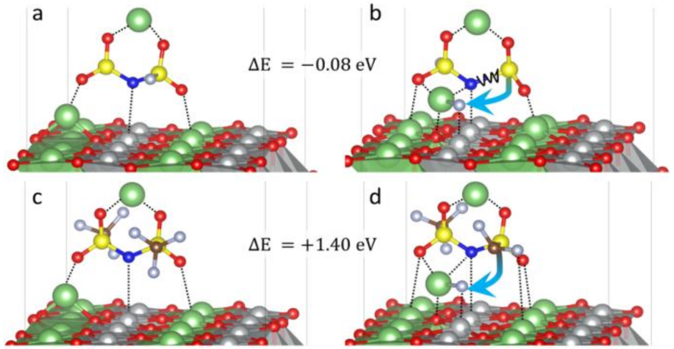
DFT calculations revealed the decomposition behaviors of different solvents and salts on the cathode surface



Influence of LiFSI on the EC solvent oxidation on Li_xNiO_2 cathode surface
Colors: Li (light pink), S (yellow), O (red), N (blue), F (light green), H (white), C (black), Ni (green).
Arrows indicate deprotonation reaction



$LiPF_6$ Salt decomposition on $LiNiO_2$
Colors: Li (green), O (red), Ni (dark grey), F (light grey), P (light grey)



Reaction mechanism of Li_2FSI and Li_2TFSI on $LiNiO_2$ (104) surface

Colors: Li (green), S (yellow), O (red), N (blue), Ni (dark grey), F (light grey), C (brown)

Partners/Collaborators

DEVCOM
ARMY RESEARCH
LABORATORY

Providing the purified electrolytes

Performing DFT calculation and MD simulation of CEI

BERKELEY LAB

Providing epitaxial oxide thin film cathode
by PLD growth

Remaining Challenges and Barriers

- A primary challenge for CEI is that the buried interfaces hinder direct experimental access

- In parallel, the heterogeneous nature of CEI and uneven surface in TMO cathodes create challenges for probing (electro)-chemical processes regarding the evolution and stabilization of CEI

Proposed Future Research

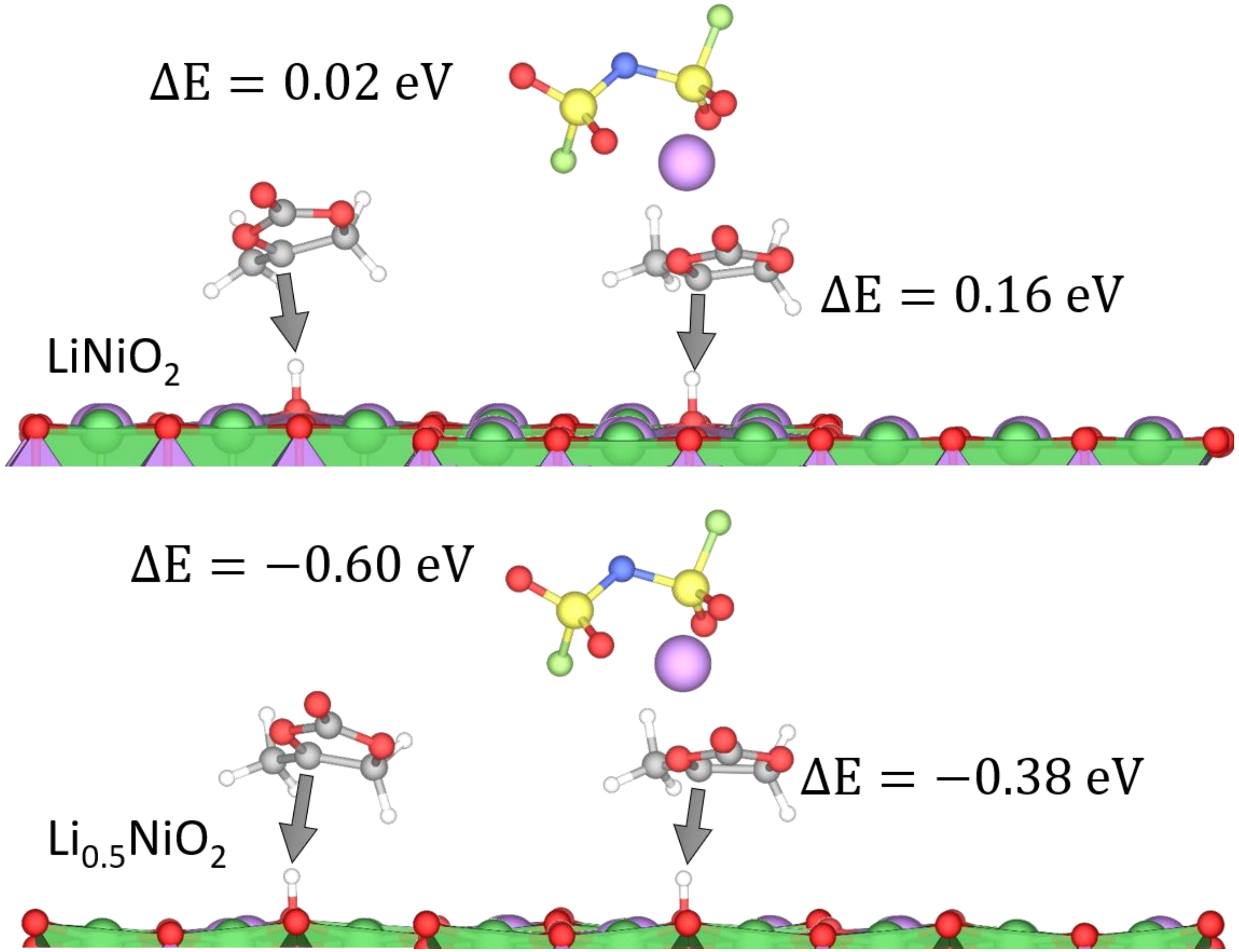
- Optimize the PLD growth of the epitaxial thin-film model cathode ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$)
- Electrochemical study of thin-film cathode with different electrolytes
- *In-operando* and *real-time* X-ray surface scattering and spectroscopy studies of CEI evolution on epitaxial thin films
- Further computational studies of CEI formation

Summary

- As compared with baseline carbonates-based electrolyte, there are extended electrochemical stability windows in highly-fluorinated and sulfolane-based electrolytes
- DFT calculations revealed the decomposition of solvent and salt on the cathode surface
- There are different electrochemical behaviors of thin-film cathodes derived from different PLD growth conditions
- Next step will focus on optimizing the PLD growth of model cathode thin-films and conducting the operando X-ray characterizations of cathode-electrolyte interfaces

Technical Backup Slides

DFT calculation of deprotonation reaction



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Reviewer-Only Slides

Publications

Peer-reviewed Journals

- *Energy & Environmental Science 2019, 12, 780-794*
- *Current Opinion in Electrochemistry 2019, 13, 86-93*
- *Small 2019, 15, 1804670-18046680*

Critical Assumptions and Issues

- *How to track the structural and chemical evolution of buried interface between cathode and electrolyte ?*

  We will carry out in-situ X-ray surface scattering, and ex-situ x-ray spectroscopy, as well as other spectrometry measurements at the TMO epitaxial thin film cathode-electrolyte interface utilizing our in-situ three-electrode electrochemical cell

- *Relevance of model system studies with the real Li-ion batteries*

  The use of these model systems allows careful control of interfacial interaction and the ability to obtain detailed insight into the interface chemistry and physics and to be directly compared with the modeling predictions
  Experiments will be related to electrochemical studies and compared to standard structural and chemical characterization of conventional powder samples

- *Comparison of experimental results with MD analysis of CEI*

  Interfacial structures will be compared with experimental data for validation and used to expand interpretation of the surface X-ray scattering-derived density profiles
  Experimental information on the CEI composition and thickness will inform MD simulations of CEI