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Advancing Solid-Solid Interfaces in Li-ion Batteries

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Argonne National Laboratory

06/12/2019

Project Manager: Tien Duong (DOE/EERE)

Project ID # BAT310

Overview

Timeline

- Start: 2016
- Finish: 2019
- 85%

Budget

- Total project funding
  - DOE share: 1300 K
- FY 16: $ 100 K
- FY 17: $ 400 K
- FY 18: $ 400 K
- FY 19: $ 400 K

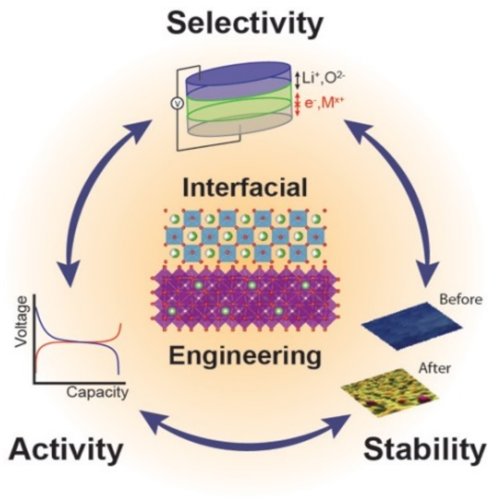
Barriers

- Barriers addressed
  - Stability
  - Ion transport
  - Efficiency

Partners

- Interactions/ collaborations
  - Jeff Sakamoto (UM)
  - John Mitchell (ANL)
  - Mercouri Kanatzidis (NU)

Solid-solid Interfaces in Li-ion Batteries



General Objective

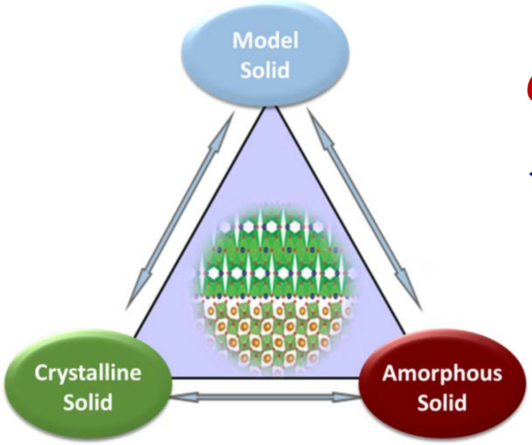
Develop and use state of the art experimental and computational techniques to *establish functional links between activity (cyclability), stability, selectivity and conductivity of electrochemical interfaces and bulk materials in Li-ion battery systems.*

Strategy

Science-based approach -fast transfer of fundamental knowledge from model to real world systems.

Systems:

- ✓ All solid-solid battery (*solid electrodes and solid electrolytes*)



Solid-solid systems

General Challenge:

- ✓ *To develop a mechanically/chemically stable and Li ion conductive (≥2 x 10^{-4} S/cm at 298K) nonflammable solid electrolyte capable of protecting a metal Li anode, and that can operate at cathode potentials > 5V.*

Relevance

Milestones

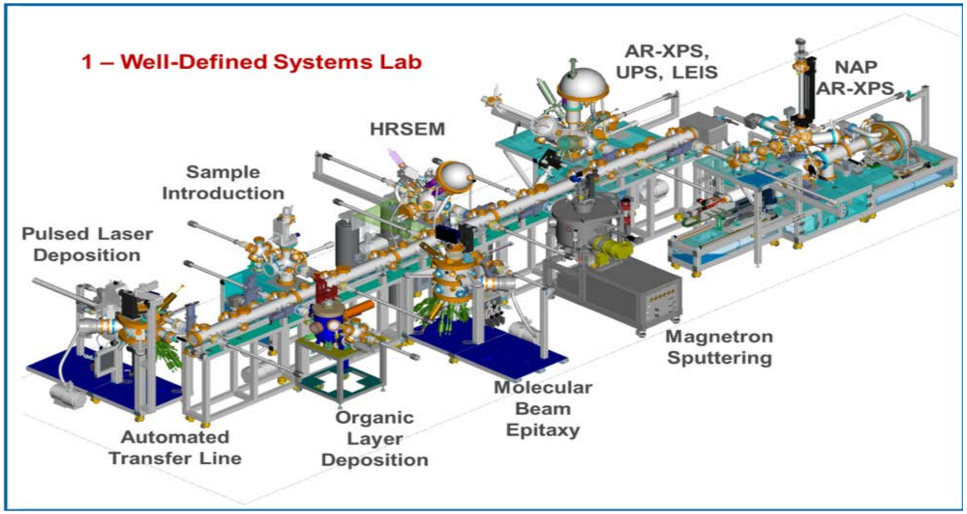
Month/Year	Milestones
Dec/18	**Understand the impact of different dopants in LLZO (Nb vs. Ta vs. Al) on reactivity by surface and bulk sensitive techniques and spectroscopic methods.** ***Completed.***
March/19	**Determine of the impact of solid electrolyte crystallinity (single crystal vs. polycrystalline vs. amorphous) on electrolyte reactivity by surface- and bulk-sensitive techniques and spectroscopic methods.** ***Completed.***
June/19	**Distinguish chemical vs. electrochemical reactivity at the interface and bulk of model solid-state electrochemical systems with Li metal anodes and $LiCoO_2$ cathodes by electrochemical testing and characterization.** ***In progress.***
Sep/19	**Determine dopant-dependent impact on chemical reactivity of different interfaces of solid state electrolytes with lithium metal by computational characterization.** ***On schedule.***

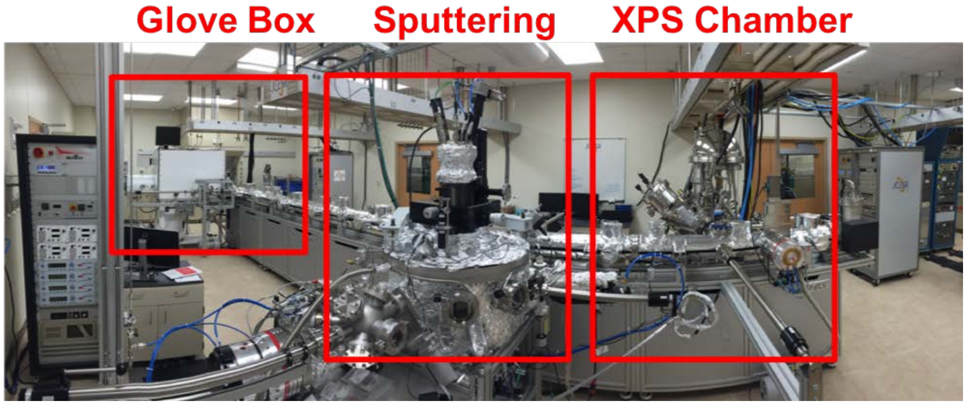
"Surface Science" Approach

Synthesis methods

Combination of physical and chemical methods

- ✓ Sputtering
- ✓ Pulse Laser Deposition
- ✓ High throughput modeling
- ✓ Solid Solution
- ✓ Chemical Vapor Deposition
- ✓ Electrochemical





Characterization methods

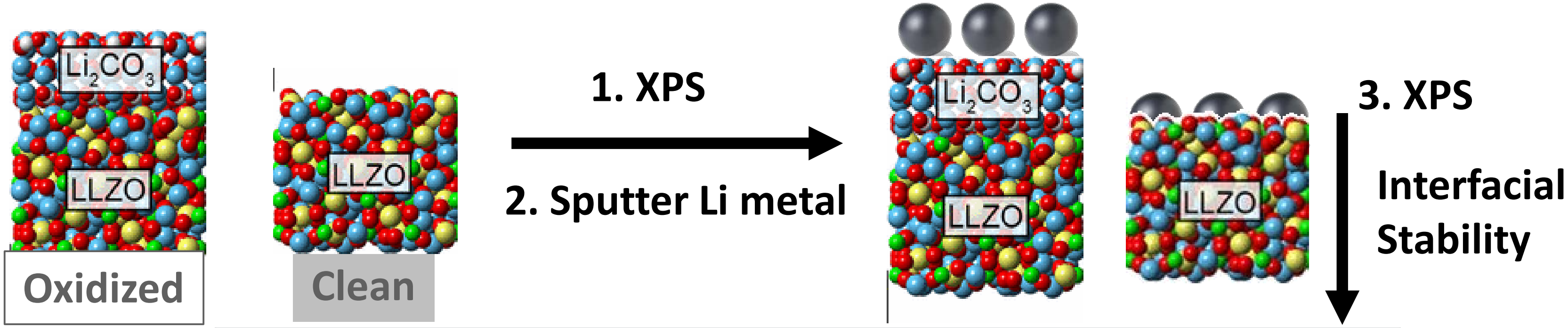
Various ex situ and in situ experimental tools and first principles modeling

- ✓ Low Energy Electron Diffraction
- ✓ X-Ray/Ultraviolet Photoel. Spect.
- ✓ Impedance
- ✓ DFT and molecular dynamics
- ✓ Fourier Transform Infrared Spectroscopy
- ✓ Differential Electroch.Mass Spectrometry
- ✓ Scanning Probe Microscopies
- ✓ Soft X-Ray Spectroscopy

XAS,XRD, HAXPES

Coin cell assembly

Li /doped LLZO Interface Stability: Summary of Previous Work



Oxidized

Clean

1. XPS

2. Sputter Li metal

3. XPS

Interfacial Stability

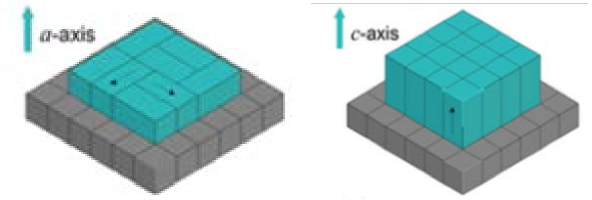
Samples	La	Zr	Doping element
0.5Nb-LLZO Li6.5La3Zr1.5Nb0.5O12	-	-	-
	-	7.5% Zr^{2+}	15.9% Nb^{4+} 9.0% Nb^{3+} 13.2% Nb^{2+} 10.8% Nb^{1+}
0.5Ta-doped Li6.5La3Zr1.5Ta0.5O12	-	-	-
	-	2.4% Zr^{2+}	-
0.25Al-doped Li6.25La3Zr2Al0.25O12	-	-	unknown
	-	9.3% Zr^{2+} 2.8% Zr^{0}	unknown

- Developed new synthesis and characterization tools for controlled deposition of lithium on solid electrolytes
- XPS indicates dopant-dependent interface reactivity

From Interface to Bulk: Stability and Charge Transport

Interface Orientation/Anode ➡ S_{Li}-S_{EL}-S_{CE} ⬅ **Interface Orientation/Cathode**

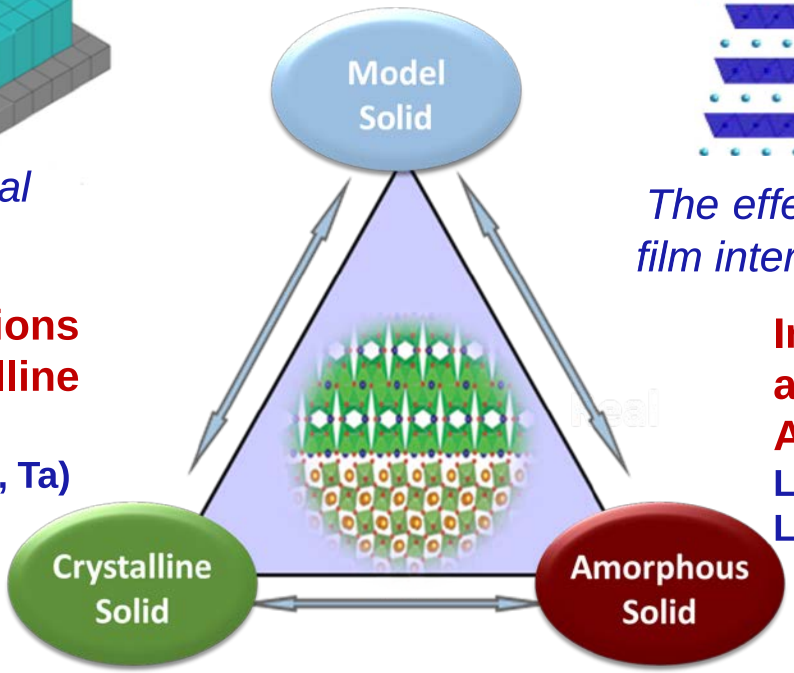
$Li/Li_{3x}La_{2/3-x}TiO_3$ (LLTO)



Atomistic View of Chemical Transformations

$Li/LiCoO_2$

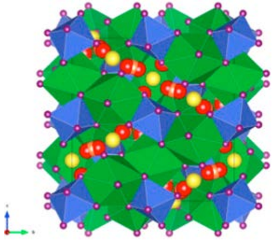
The effect of crystal orientation in thin film interfaces from experiment/theory



Interface/Bulk Reactions and Transport in Crystalline Oxides

$Li/Li_{6.5}La_3Zr_{1.5}M_{0.5}O_{12}$ (M=Nb, Ta)

$Li/Li_{6.25}Al_{0.25}La_3Zr_2O_{12}$

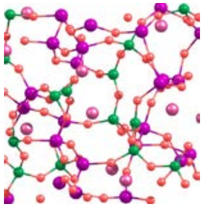


Dopants stabilize cubic phase
The role of dopants in interfacial/bulk reactivity

Interface/Bulk Reactions and Transport in Amorphous Oxides

$Li/Li_{3x}La_{2/3-x}TiO_3$ (LLTO)

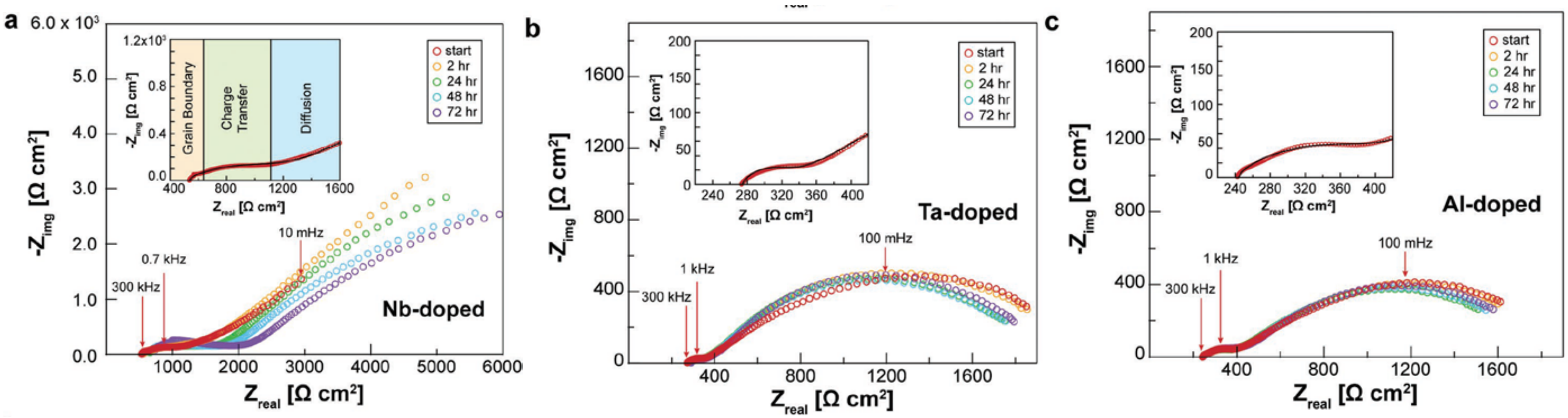
$Li/Li_7La_3Zr_2O_{12}$ (LLZO)



Impact of structure on interfacial/bulk properties

Objective: To develop an atomistic model for minimizing Li-dendrite formation and interfacial/bulk corrosion in real systems

Li/doped LLZO Interface Stability Correlated with Impedance

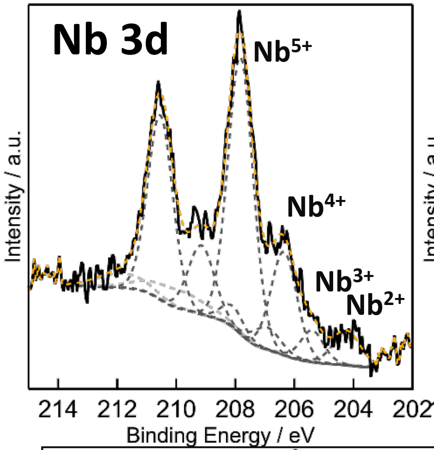


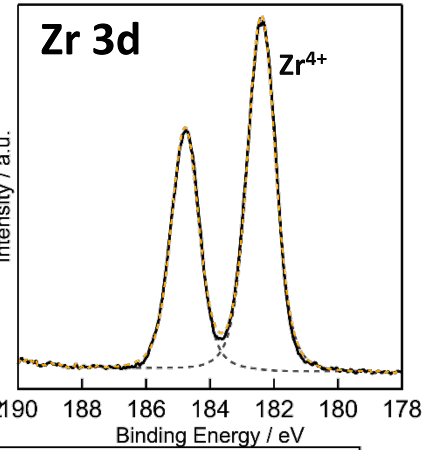
- Initial charge transfer resistance values for Al- and Ta-doped LLZO are comparable (≈100 and ≈50 Ω cm^2, respectively) and for Nb-doped LLZO is ≈800 Ω cm^2.
- These resistance values are quite low as a result of the highly conformal Li–LLZO interface that is generated *from vacuum deposition* of Li metal.
- Impedance of Nb-LLZO increases with time --> Li continues to react with Nb-LLZO electrolyte
- Impedance of Ta-LLZO unchanged
- Al-doped LLZO exhibits very low interfacial impedance which suggests significant interfacial reactivity may lead to spontaneous stabilization of the interface.

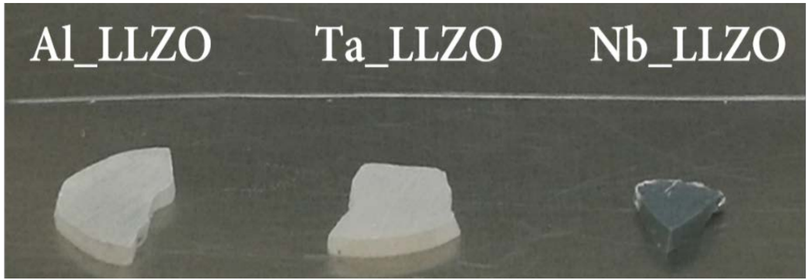
Li/Nb-doped LLZO interface is the least stable, while higher stability correlates with low impedance for vacuum deposited Li /Ta- and Al-doped LLZO interfaces

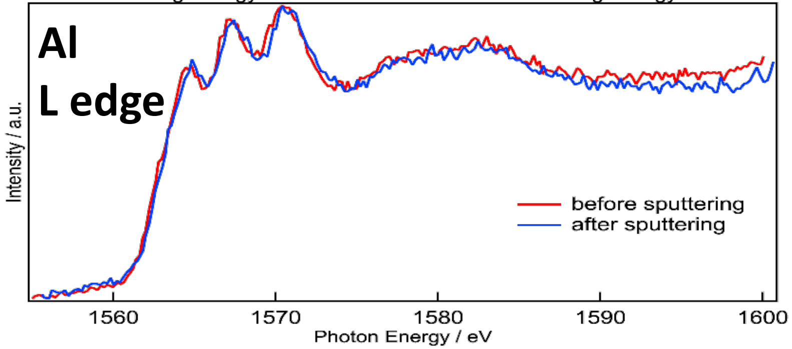
Adv. Energy Mater. 2019, 9, 1803440

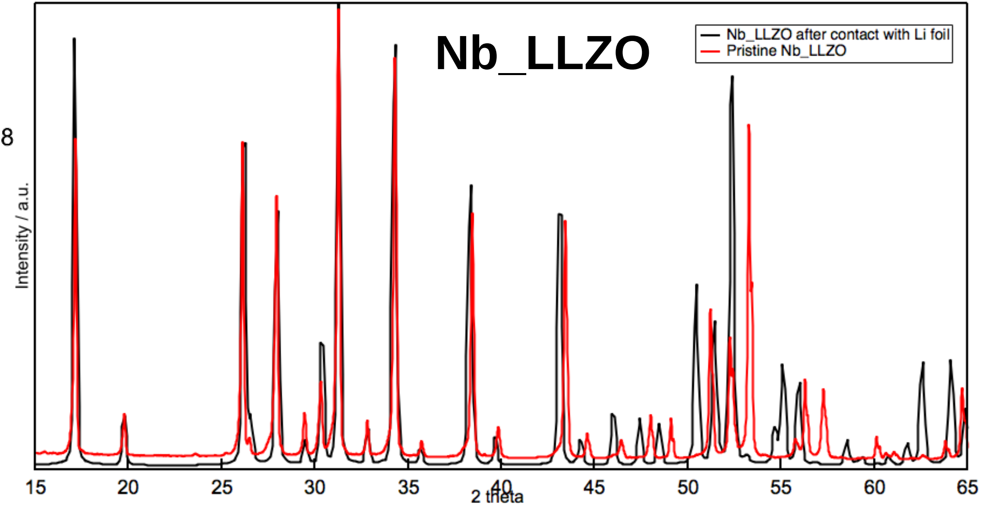
Li/doped LLZO Stability: Bulk changes in Nb-LLZO











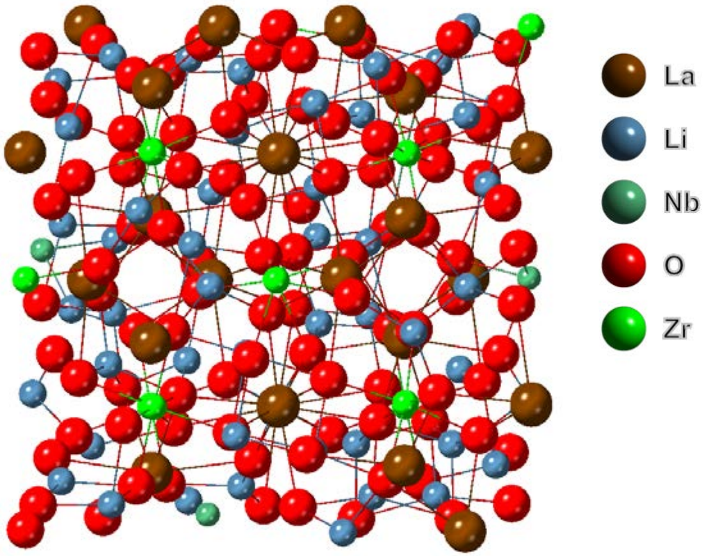
- Bulk Nb^{5+} reduction is confirmed by XPS after removing ~0.2mm from surface by polishing
- Other elements (La, Ta, Al) did not change

- No second phases
- Lattice expanded
- Bulk change in Nb/Ta/Al LLZO will be measured with HAXPES

Nb reduction at Li metal/cleaned Nb-LLZO is not surface limited

Computational studies of Li/doped LLZO interface

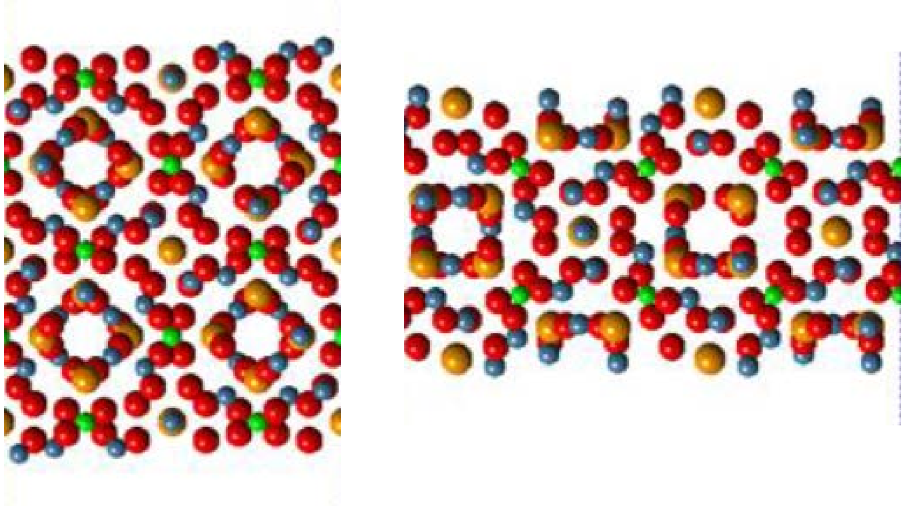
Bulk Li $_{7-x}$La$_3$Zr$_{2-x}$M$_x$O$_{12}$: M=Nb, Ta; x=0.5



Cubic: (high conductivity), Li sites:
24d – tetrahedral
48g –octahedral
96h -octahedral

- Occupation of tetrahedral/octahedral sites 0.542/0.448
- Short range correlations as in experiment

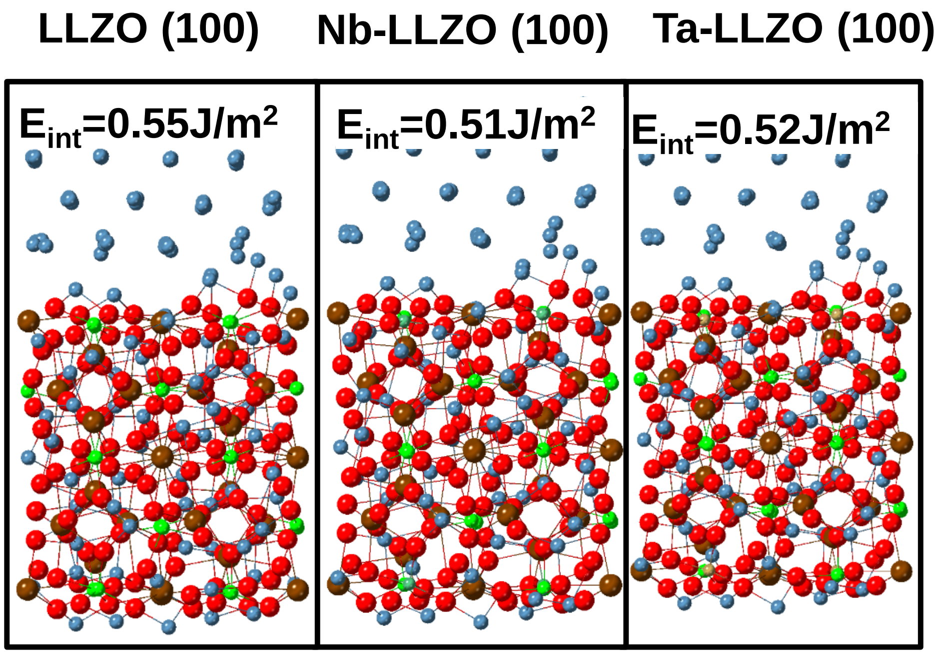
LLZO (100) and LLZO (110) surfaces

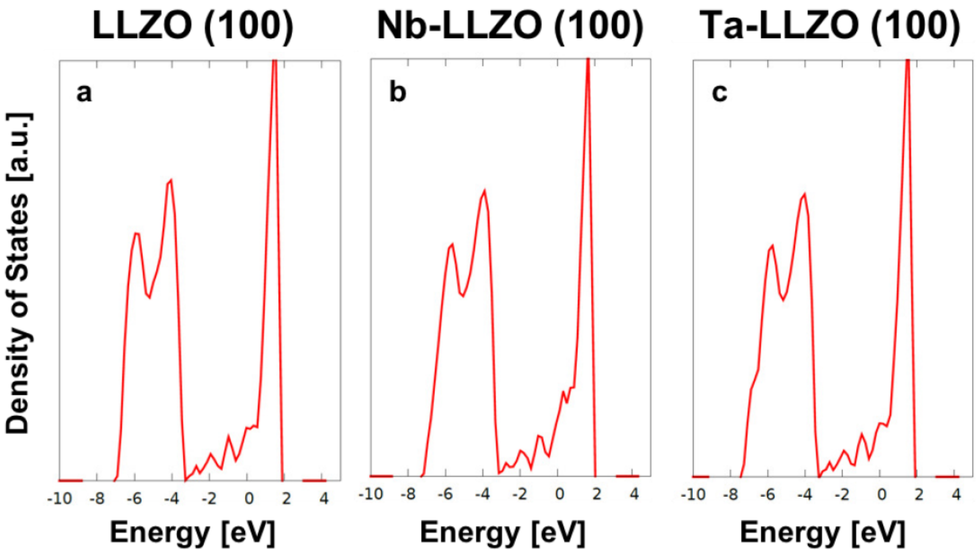


LLZO Li-terminated (100) and (110) surfaces are the most stable - Thomson et al., ACS Energy Letters, 2017, 2, 462

Our bulk and surface structures as well as DOS are consistent with previous studies

Li/doped LLZO interface: binding energies and DOS



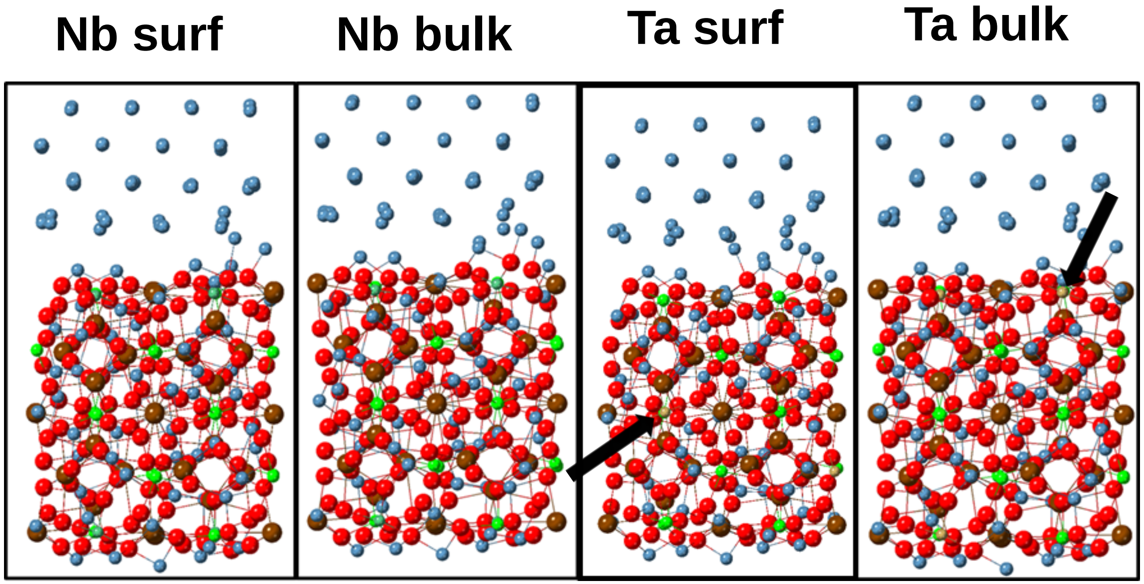


- Li/LLZO (100) interface energy is similar for undoped, Nb-doped and Ta-doped LLZO

- Density of states (DOS) shows only slight differences for Nb-doped Li/LLZO as compared to Ta-doped and undoped cubic LLZO

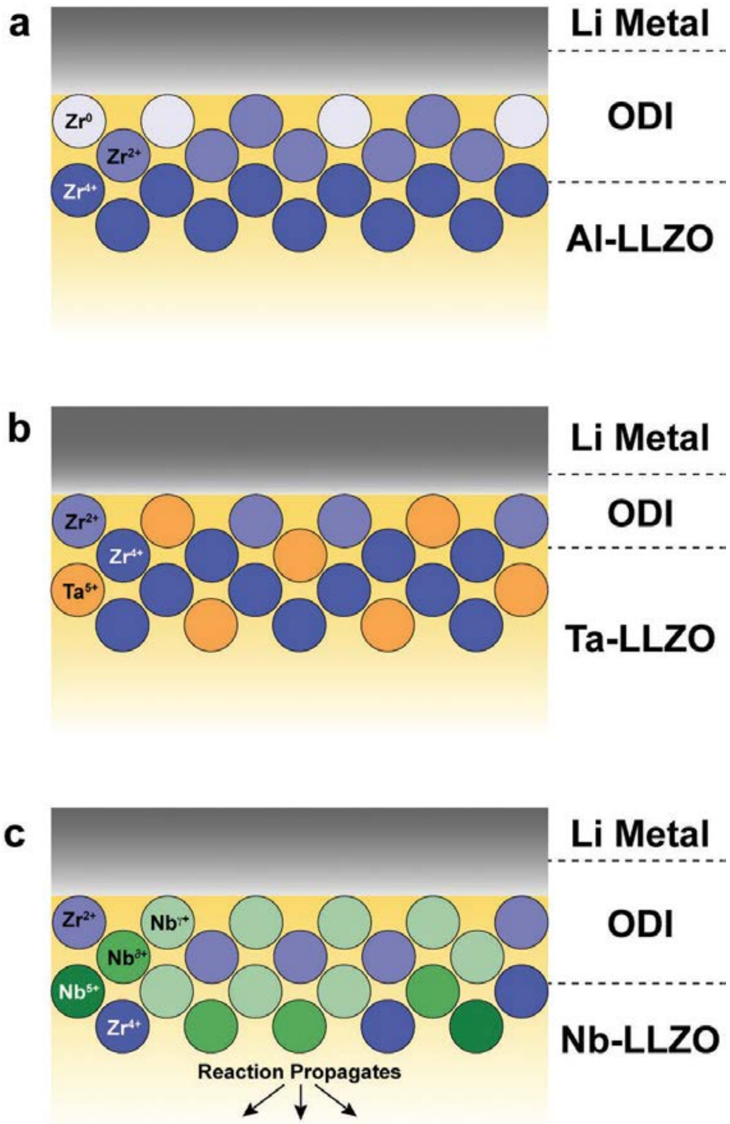
- DOS: No obvious reason for difference in chemical reactivity for different dopants

Li/doped LLZO interface: dopant distribution



- Multiple configurations with Nb or Ta substituted near the surface or in the bulk of (100) LLZO with and without Li.
- Ta-doped LLZO with Ta near the surface or in the bulk has small difference in substitution energy: on average, <0.01eV/dopant without Li and <0.01 eV/atom difference for surface vs bulk substitution with Li.
- Nb-doped LLZO with Nb near the surface or in the bulk has large difference in substitution energy: on average, 0.23 eV/dopant without Li and 0.19 eV/dopant preference for surface vs bulk substitution with Li.
- **Provides thermodynamic driving force for structure changes in case of Nb**

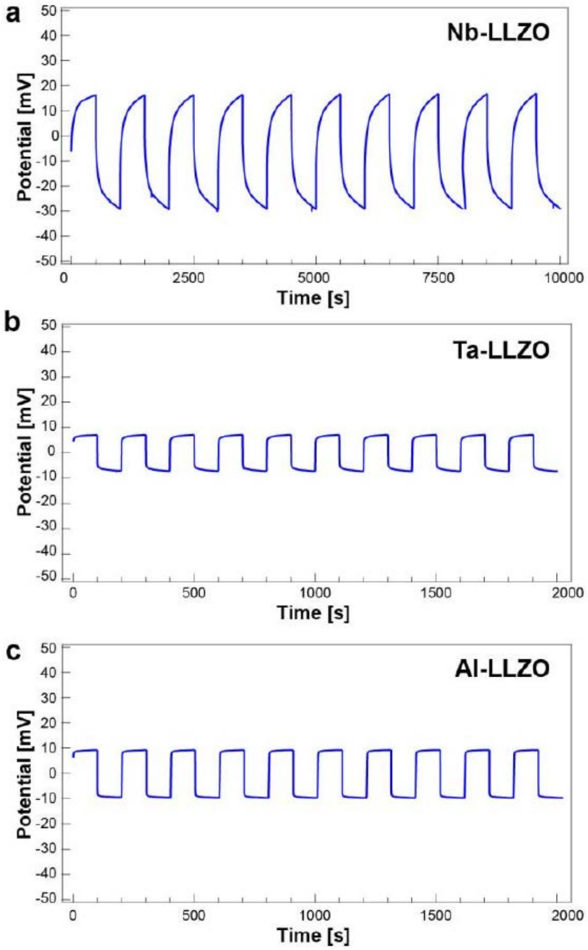
Li/doped LLZO Interface Stability: Oxygen Deficient Interface



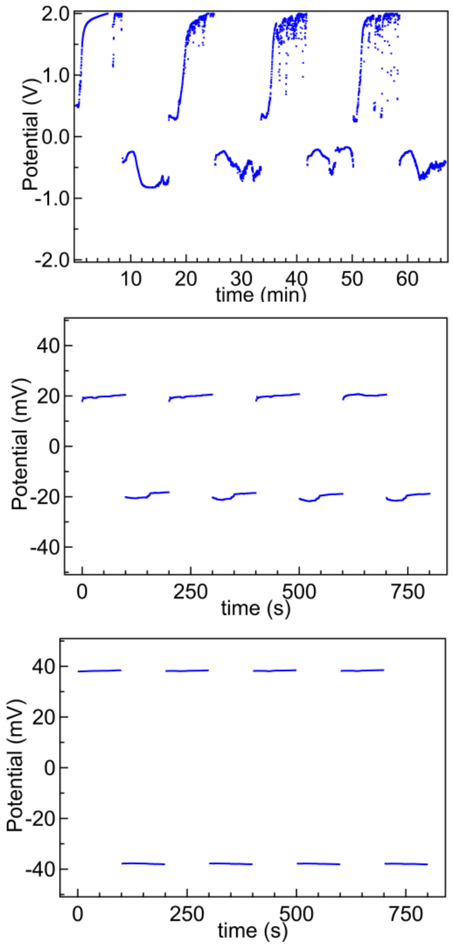
- We suggested that LLZO in contact with Li metal results in the *Oxygen Deficient Interphase* (ODI).
- The dopant type impacts the chemical makeup of the Zr sublattice and the resulting structure/ thickness of the ODI.
- Reduction of Zr^{4+} is observed for all doped LLZO samples, consistent with the formation ODI layer. The extent of ODI formation increases as Ta < Nb < Al.
- Despite the significant Zr reduction observed on Al-doped surfaces, impedance spectroscopy indicates that the more extensive ODI layer formation on Al-doped LLZO serves to stabilize reactivity of this material with Li and maintains a low interfacial impedance.

Li/doped LLZO Stability: Electrochemical Reactivity

Low current density cycling: 8 µAcm^{-2}



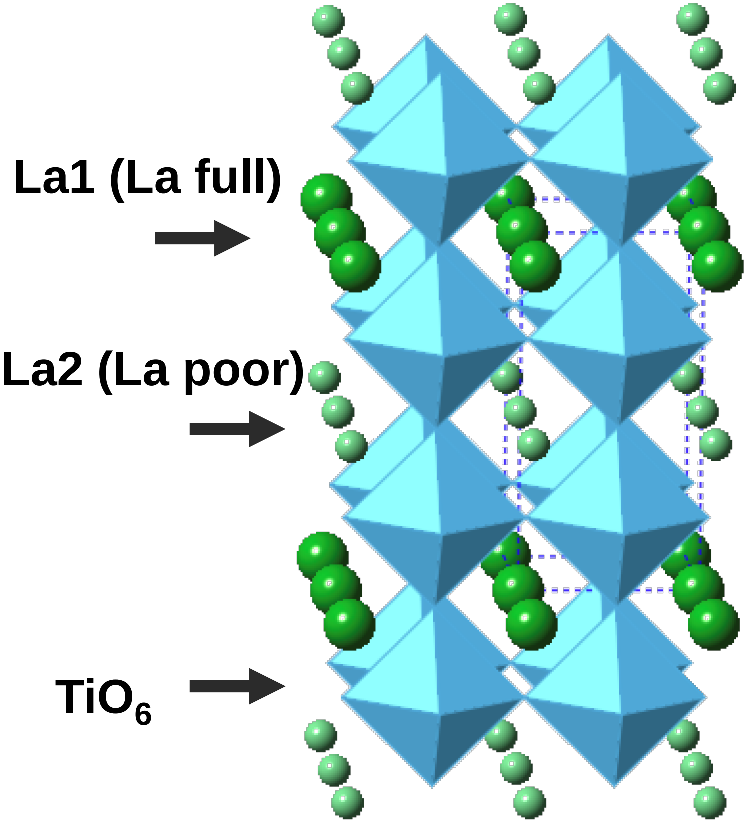
High current density cycling: 2 mAcm^{-2}

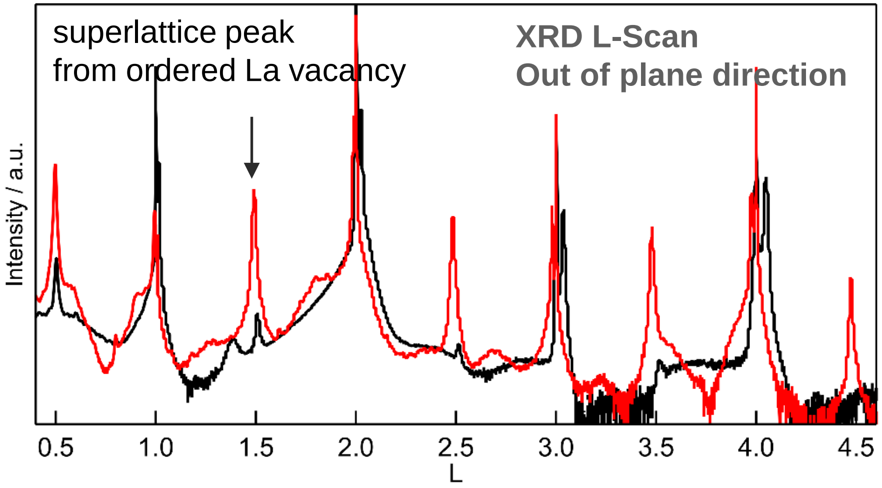


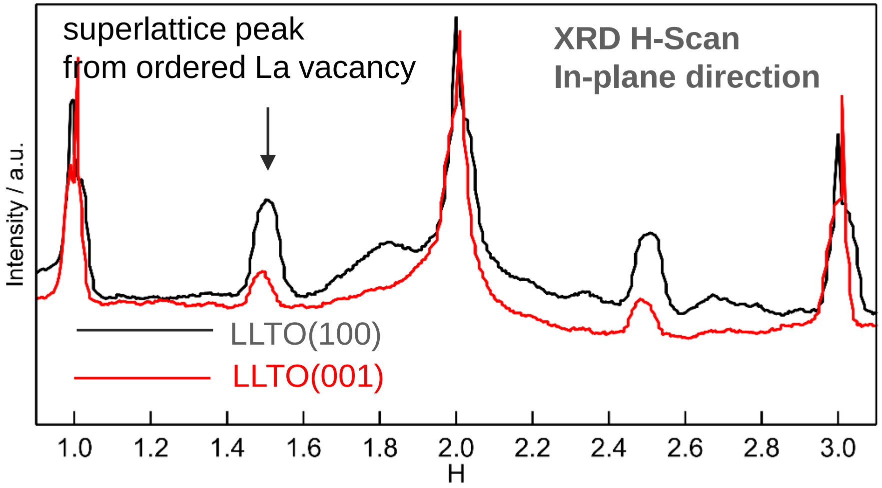
- Galvanostatic cycling of Li/doped LLZO/Li at 8 µAcm^{-2} (left) and 2 mAcm^{-2} (right) shows similar Ohmic behavior for Al- and Ta- doped samples.
- Higher polarization and significantly longer cycle times needed to reach quasi-steady-state conditions for Nb-doped material.

Li/ LLTO Interface Stability: Impact of Orientation

- Li film (~10s nm) on oriented single crystal LLTO film

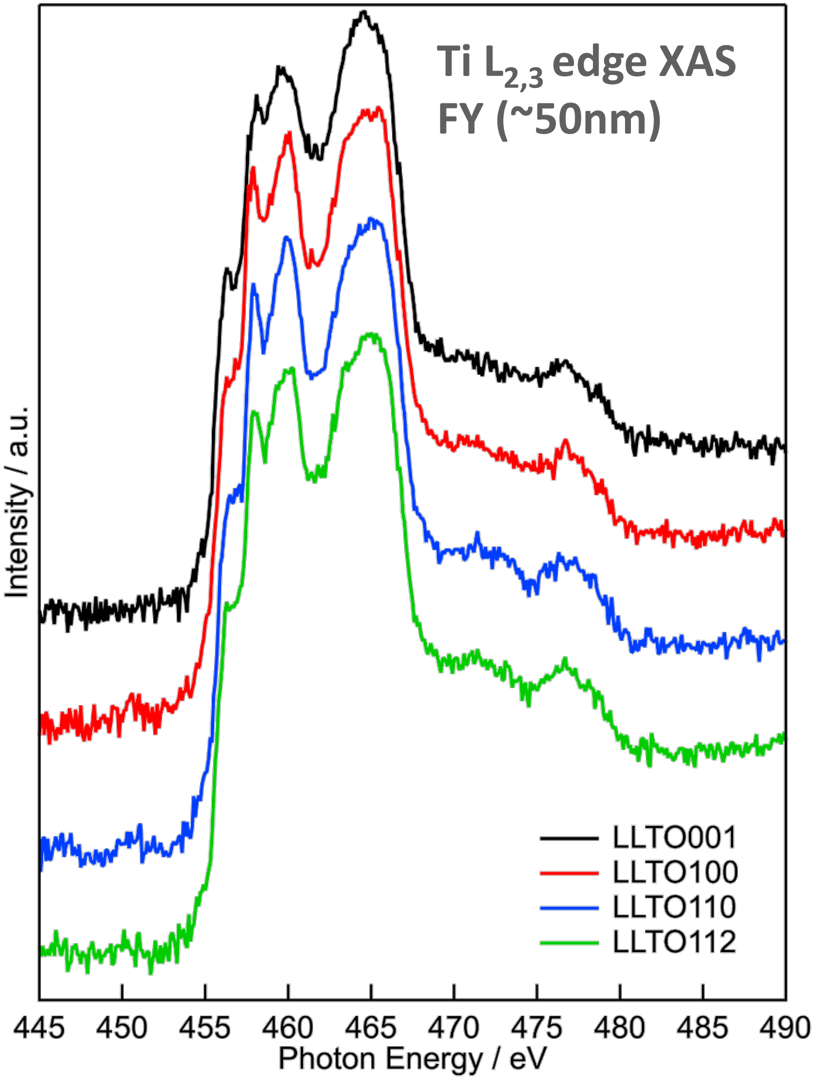






- La ordering persists in LLTO film structure grown in two orientations.
- The ordering in the film suggests faster Li diffusion in (001) oriented LLTO correlating with more Ti reduction, as shown by our XPS results.

Li/ LLTO Bulk Stability: Long-term Reactivity



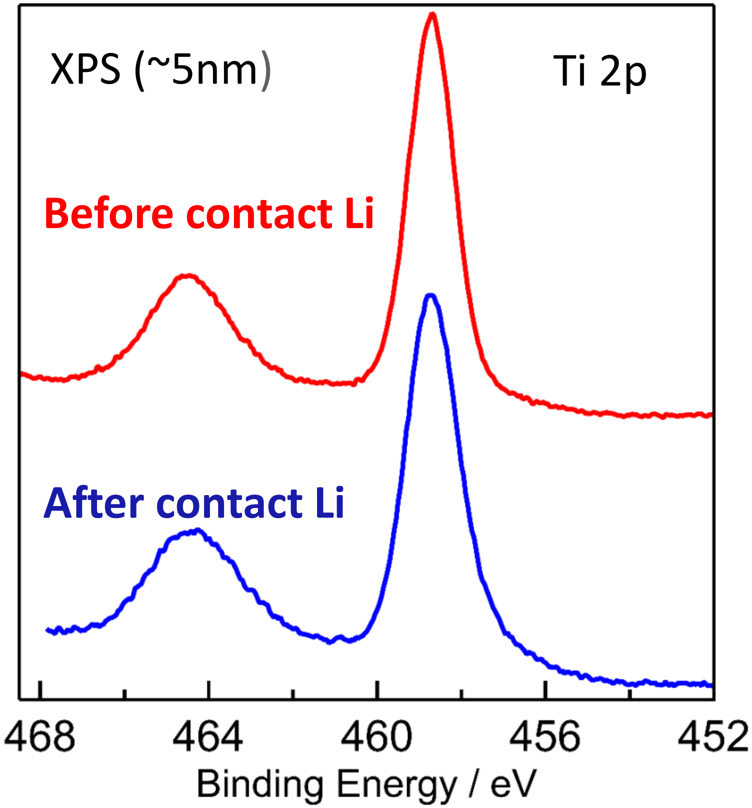
- XAS spectra were collected for four different epitaxial LLTO film orientations with 100-200 nm thickness in contact with Li.
- When LLTO thin films were in contact with Li foil for 3 days, similarity of XAS spectra for different orientations suggests similar amount of Ti reduction (Ti^{3+}/Ti^{4+}) for all orientations.
- Lattice expansion occurred for all four orientations.

While LLTO interface reactivity is dependent on orientation (previous XPS results), long term bulk behavior with abundant Li is orientation-independent.

Li/ Amorphous LLTO Interface and Bulk Stability

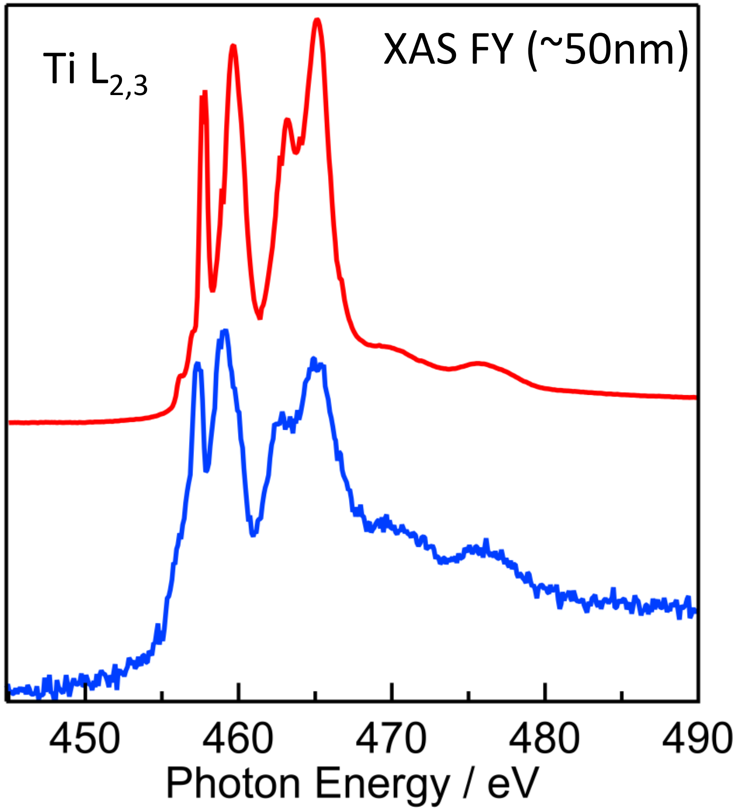
Interface

Sputtered metallic Li film



Bulk

In contact with Li foil for 3 days



Amorphous LLTO film found to be stable in contact with Li:

- After sputtering ~20nm of metallic Li, no Ti reduction observed with XPS.
- After LLTO disk being in contact with Li foil for 3 days, no Ti reduction in XAS.

Response to last year reviewer’s comments

Comment: The reviewer expressed concern with the overall method and somewhat with the technical gap between using “lithium/SSE/lithium” as a platform in modeling and using battery cells. According to the reviewer, there are some reports of Li dendrites growing through LLZO grain boundaries; meanwhile, some companies demonstrated good cycling solid-state cells without observing negative impacts of Li dendrite growth. This is a good indication that battery cell configurations, such as cathode/SSE/Li, could be a more realistic modeling platform than Li/SSE/Li.

Response: We are making a transition to battery cell configurations. Our preliminary results on the LLZO/cathode interface indicate extensive chemical reactions, and we would like to understand each of the electrode/electrolyte interfaces. The mechanism of the dendrite growth is not yet well understood, and our approach can help to address electrochemical reactions involved.

Comment: The reviewer remarked that the team has demonstrated several technical accomplishments and progress in the overall project. The project is in good shape in terms of milestones. The team has not reported much in terms of mechanics of solid electrolytes, which are important for developing mechanically robust solid electrolytes.

Response: Our synchrotron based techniques provide strain values which will help to investigate the mechanical properties of SSE. We also collaborate with Jeff Sakamoto, who is an expert on mechanical properties of SSE.

Response to last year reviewer’s comments

Comment: The reviewer recommended collaborating with someone doing DFT calculations as this might help to explain the chemistry a little better.

Response: Two of the investigators, co-PI Larry Curtiss and Peter Zapol are doing first-principles modeling. Density functional theory calculations for Li interface with doped LLZO are published together with the experimental results and also reported here.

Collaborations with other Institutions and Companies

- Jeff Sakamoto (UM)
  - ✓Anode/Electrolyte interfaces, Li/LLZO
- Mercouri Kanatzidis (Argonne MSD)
  - ✓Synthesis and Characterization of Amorphous Materials
- John Mitchell (Argonne MSD)
  - ✓Synthesis and Characterization of Complex Oxide Materials

Remaining Barriers and Challenges

- Measurements of Li metal anode behavior in a realistic cell. Controlling interface properties on the cathode side to make a transition to battery cell configurations.
- Mechanistic understanding of differences between amorphous and crystalline electrolyte behavior and their impact on electrochemical cycling.

Proposed Future Work

FY2019 Li-Solid Electrolyte systems:

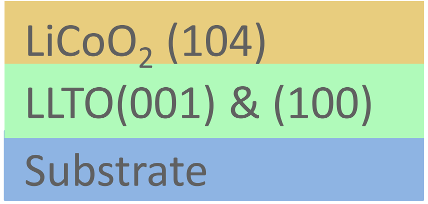
- Perform electrochemical testing to distinguish chemical vs. electrochemical reactivity at the interface and bulk of doped LLZO with Li metal anodes and work towards making full cells.
- Perform DFT calculations to understand reactivity of different interfaces of solid state electrolytes with lithium metal.

FY2020 Toward full cells with Li metal anode:

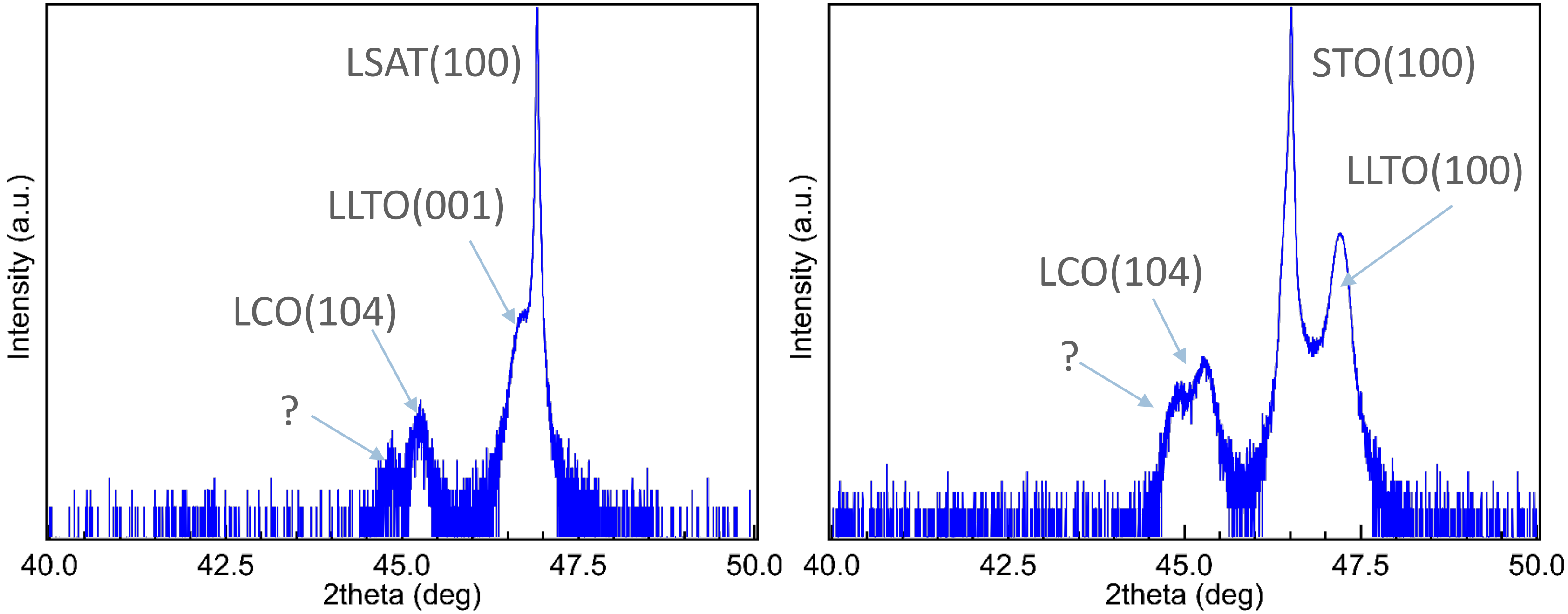
- Understanding origins of interfacial resistance at solid electrolyte/cathode
- The role of amorphous/crystalline structure on reactivity/transport at the interfaces
- Stability of interfaces in Li/SSE/cathode using experiment and theory

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

In Progress: $LiCoO_2$/LLTO Interface Stability (preliminary work)


$LiCoO_2$ (104)
LLTO(001) & (100)
Substrate

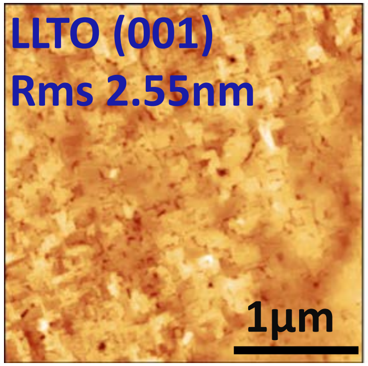
$LiCoO_2$/LLTO interface (new phase at the interface)



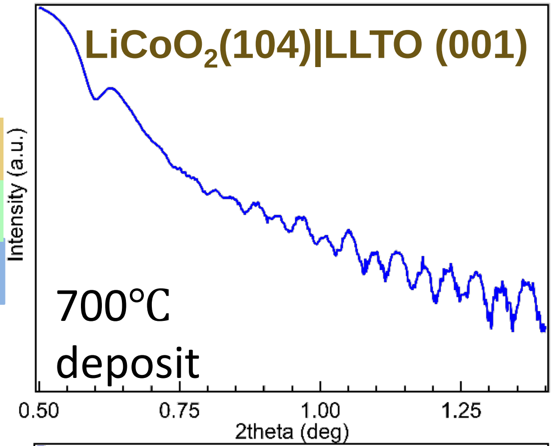
- To improve contact between solid electrolyte and cathode material, $LiCoO_2$ cathode is deposit/sputter onto LLTO at high temperature (>600 ℃)
- Due to high mobility of Co (in cathode) and La (in electrolyte) across cathode/electrolyte interface, reactions happen resulting in formation of a new phase with different lattice parameters.

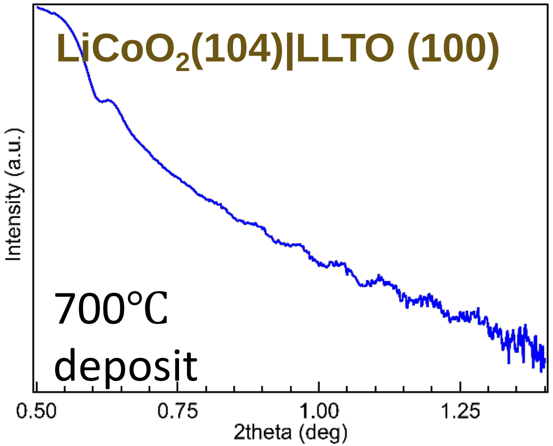
In Progress: $LiCoO_2$/LLTO Interface Stability (preliminary work)

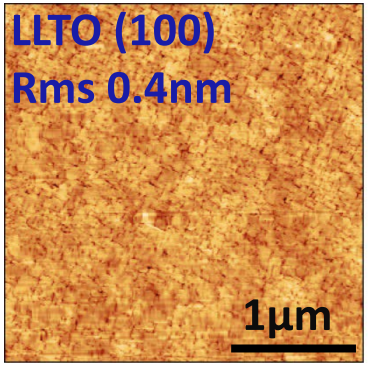
$LiCoO_2$/LLTO interface roughening (reflectivity)



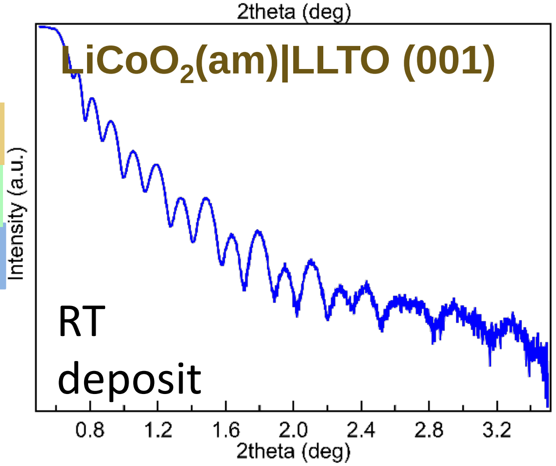
$LiCoO_2$(104)
LLTO(001)(100)
Substrate

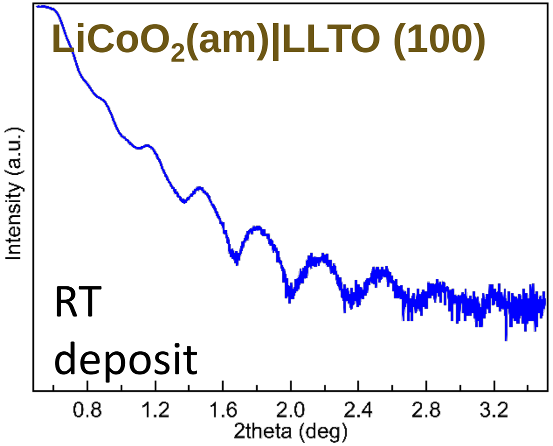






$LiCoO_2$(am)
LLTO(001)(100)
Substrate





- Interfacial roughening occurred when $LiCoO_2$ deposited onto LLTO at both 700℃ and room temperature
- Roughness of pristine LLTO(100) film is lower than LLTO(001) from AFM, but interface roughens more after deposition of $LiCoO_2$

Summary

- ✓ Based on impedance measurements and HAXPES for all dopants, Li/Nb-doped LLZO interface is the least stable, while higher stability correlates with low impedance for vacuum deposited Li /Ta- and Al-doped LLZO interfaces.
- ✓ DFT calculations indicate that there is a thermodynamic preference for Nb to be at the interface, but not for Ta in doped LLZO.
- ✓ We suggest that LLZO in contact with Li metal results in the Oxygen Deficient Interphase.
- ✓ Galvanostatic cycling of Li/doped LLZO/Li at 2 mAcm^{-2} shows stable behavior for Al- and Ta- doped samples, but high polarization for Nb-doped.
- ✓ While LLTO interface reactivity is dependent on orientation (previous XPS results), long term bulk behavior with abundant Li is orientation-independent.
- ✓ Amorphous LLTO film found to be more stable in contact with Li than crystalline.