

Low Impedance Cathode/Electrolyte Interfaces for High Energy Density Solid-State Batteries

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2021 DOE Vehicle Technologies Office Annual Merit Review
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Overview

Timeline

- Project Start: 10/01/2019
- Project End: 02/28/2023
- Percent Complete: 40%

Budget

- Total Project Funding: \$1,250,000
 - DOE Share: \$1,000,000
 - Cost Share: \$250,000
- FY 2021 Funding received: \$0

Barriers

- **Cost** - Beyond Li-ion (BLI) cells are one way to reduce costs, however, cell chemistries that potentially provide higher energy density have life and performance issues.
- **Performance** - For solid-state BLI the primary performance limitation is high solid-electrode/solid-electrolyte interfacial impedance.
- **Life** - BLI cells containing Li-metal anodes suffer major cycle and calendar life issues with mechanistic understanding still in its infancy.

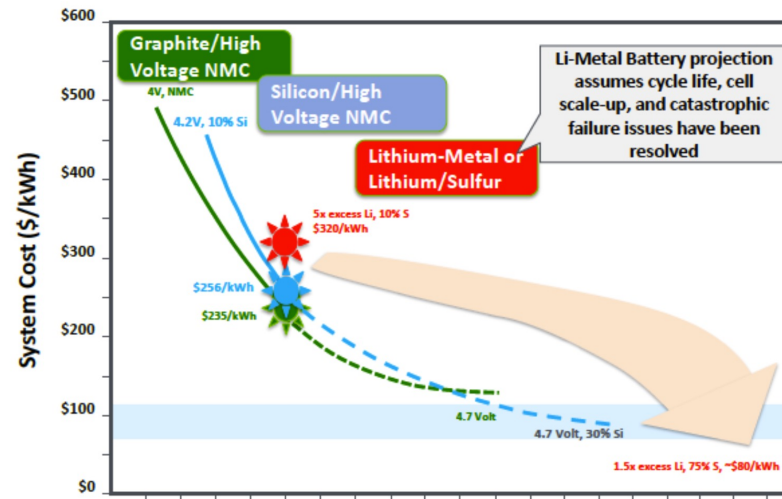
Partners

- Extensive collaboration with numerous universities and national labs through US (DOE) - German (BMBF) cooperation on solid-state battery interfaces 

Relevance

Objectives

- Identify and demonstrate interfacial layers to achieve low-impedance and stable NMC/LLZ interfaces;
- Develop novel processing techniques to fabricate NMC/LLZ composite cathodes with low interfacial resistance;
- Enable high-performance ASSBs with an energy density of 450 Wh/kg and 1400 Wh/L and negligible degradation for 500 cycles.



Developing strategies to reduce NMC/solid electrolyte interfacial resistance to enable high energy density and cycling stability Li-metal solid-state batteries.

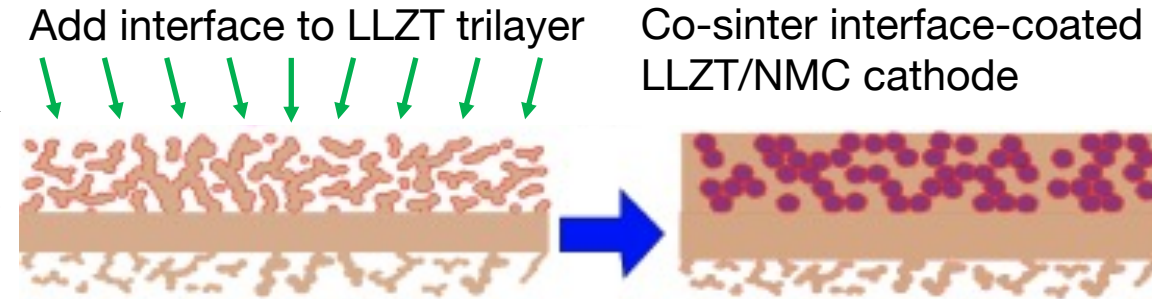
Impact

- Fundamental study and understanding of solid electrolyte-cathode interfaces regarding stability, decomposition, and resistances under a wide variety of synthesis, processing and operating conditions;
- The safe garnet-type solid electrolyte with the unique porous structure and surface coating to enable Li dendrite free cycling under current densities up to 10 mA/cm²;
- A unique and transformative LLZ framework to enable high-energy-density, safe Li-metal batteries approaching ~ 400 Wh/kg.

Approach and Milestones

Approach. Build on demonstrated expertise with garnet-solid-state battery cells to accomplish the following:

1. Engineer interfaces to overcome high NMC/LLZ interfacial impedance and interfacial degradation;
2. Develop processing and fabrication techniques to achieve high loading NMC/LLZ composite cathodes with low resistance and high cyclability;
3. Integrate the NMC/LLZ cathodes into all-solid-state Li-metal/LLZ cells to achieve high energy density batteries.



Milestones

FY20Q2: Computationally determine the interfacial stability between LLZ solid electrolytes and NMC cathode. **(Completed)**

FY20Q3: Determine thermochemical stability between LLZ and NMC. **(Completed)**

FY20Q4: Computationally determine the mechanism of interfacial stabilization between LLZ and NMC through coating layers. **(Completed)**

FY20Q4: *Go/No-Go* - Computationally determine appropriate compositions to stabilize the LLZ-NMC interface. **(Completed)**

FY21Q1: Experimentally determine thermochemical stability between interface-coated LLZ and infiltrated NMC. **(In-Progress*)**

FY21Q2: High-throughput computations of coating materials to determine compositions to stabilize the LLZ-NMC interface. **(Completed)**

FY21Q4: *Go/No-Go* - Demonstrate 10X reduction in interfacial impedance between coated and uncoated LLZ/NMC interfaces. Design capable of meeting performance requirements. **(In-Progress)**

FY22Q1: Determine thermochemical stability between LLZ and interface-coated NMC.

FY22Q2: Compare experimental results with computational results and refine model including understanding side reactions and process optimization. Demonstrate 10X reduction in interfacial impedance by co-sintering.

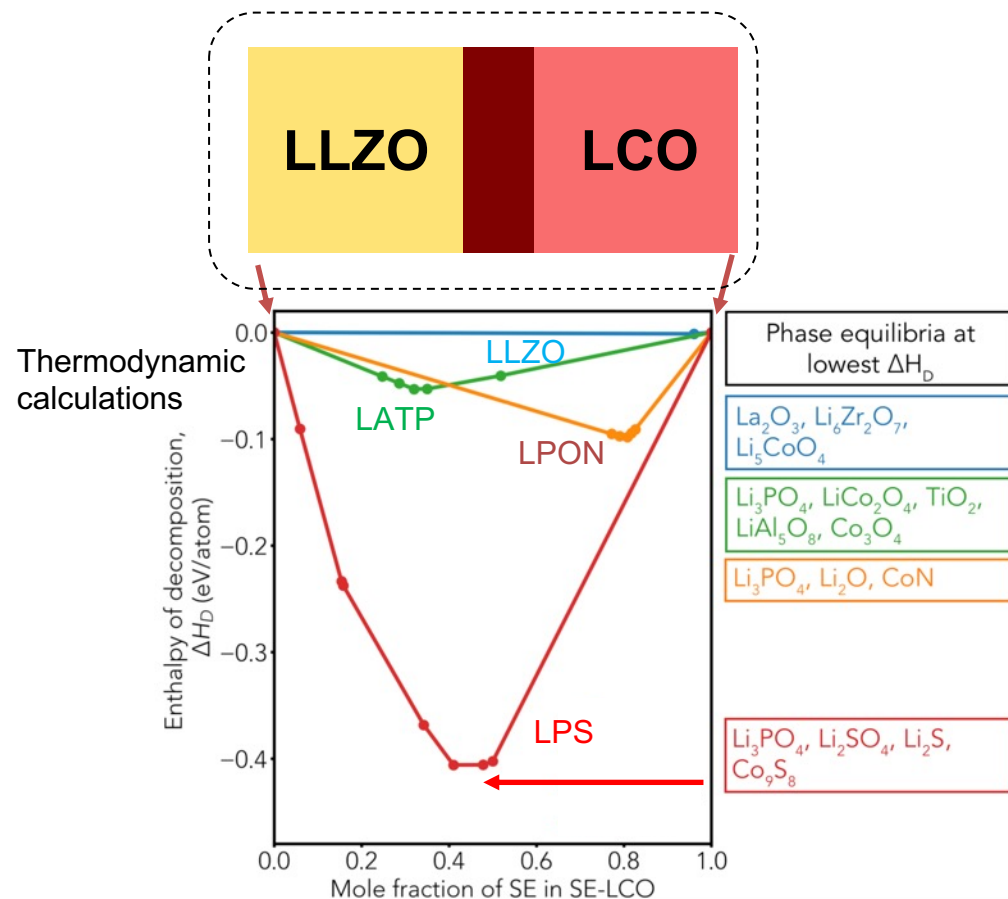
FY22Q3: Fabricate trilayer cell with composite NMC-LLZ cathode layer and measure impedance, cell capacity, and cycle life.

FY22Q4: *Go/No-Go* - Demonstrate >350 Wh/kg energy density Li-metal/LLZ/LLZ-NMC cell with 80% capacity retention, 1000 cycles at C/3.



Thermodynamic Computation Scheme for Studying Interface Stability between Solid Electrolyte and Cathode

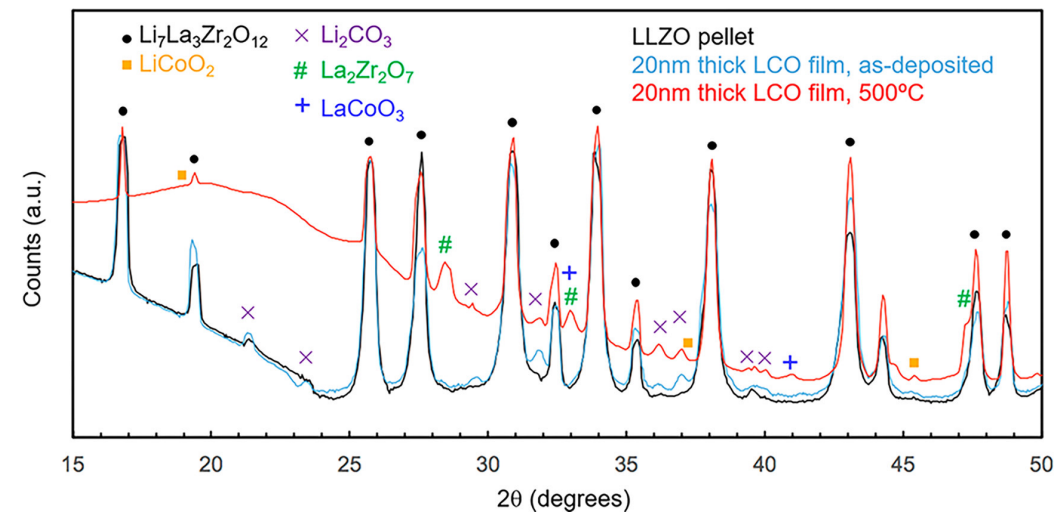
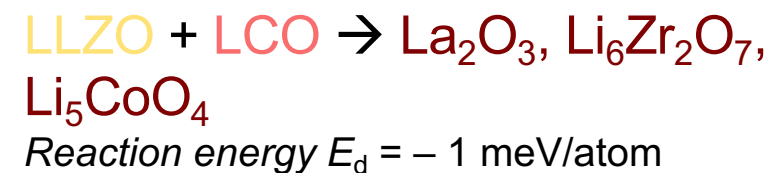
- For each mixing ratio of solid electrolyte (e.g. LLZO) and cathode (e.g. LiCoO₂), evaluate the thermodynamic phase equilibrium (i.e. most favorable reaction products), and Identify the reaction energies.



Zhu, He, Mo, *J. Mater. Chem. A*, 2016,4, 3253-3266

Nolen, Zhu, He, Bai, Mo, *Joule* 2018, 2, 2016-2046

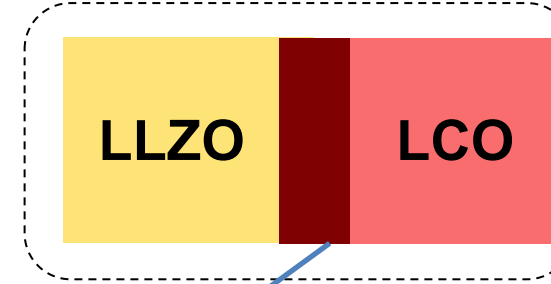
Phase equilibria



Vardar et al., *Chem. Mater.* **2018**, 30, (18), 6259-6276

Interface Stability between LLZO Solid Electrolyte and Cathode

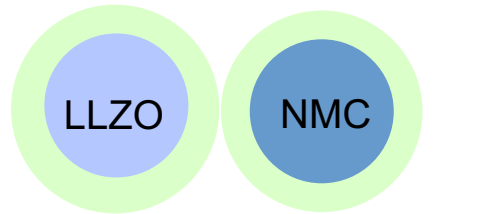
- Identified interface stability between LLZO and cathode (e.g. LiCoO₂ and NMC).
- Different NMC compositions studied.
- Delithiated cathodes have poorer interface stability.
- Higher Mn content leads to relatively lower interfacial stability.



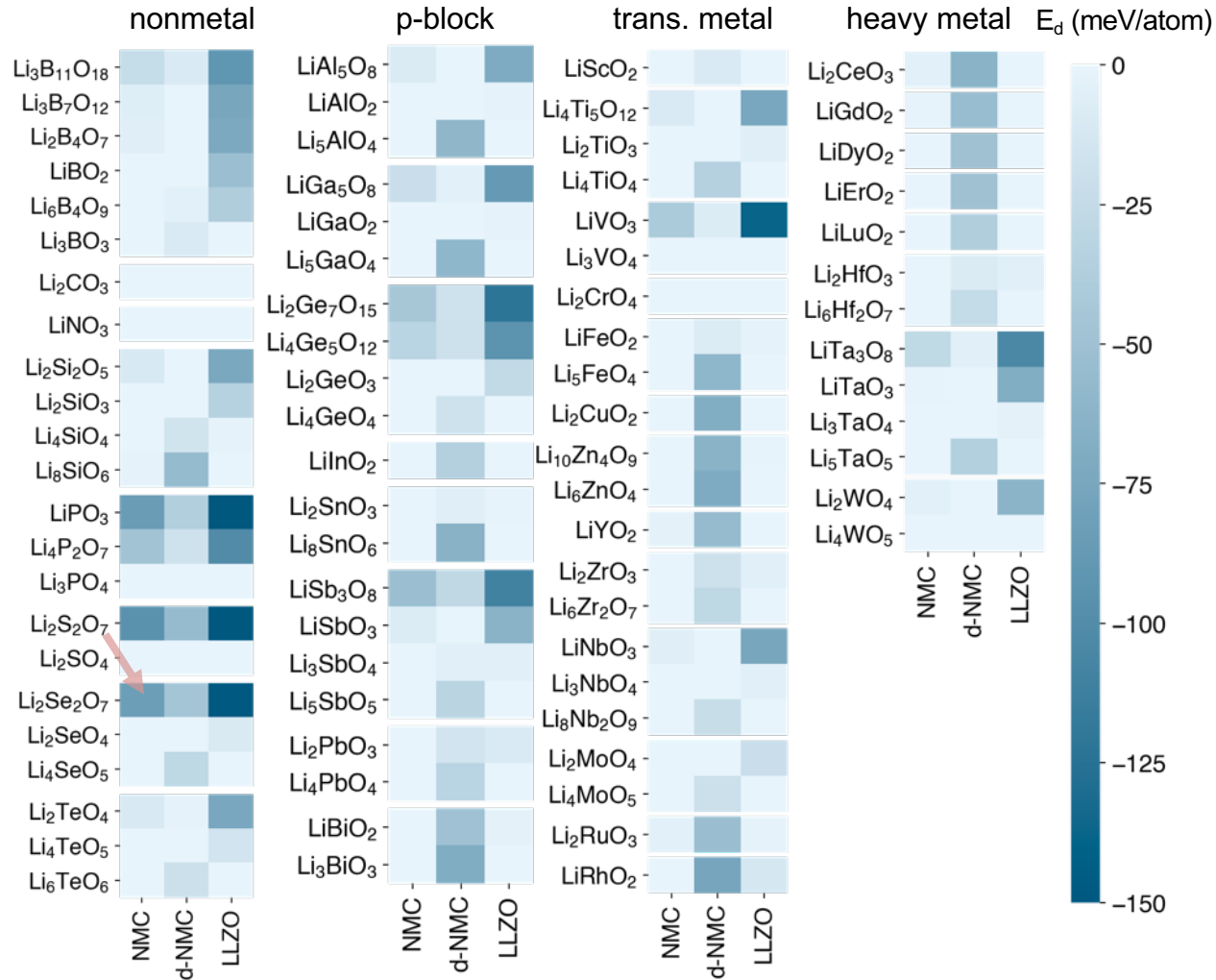
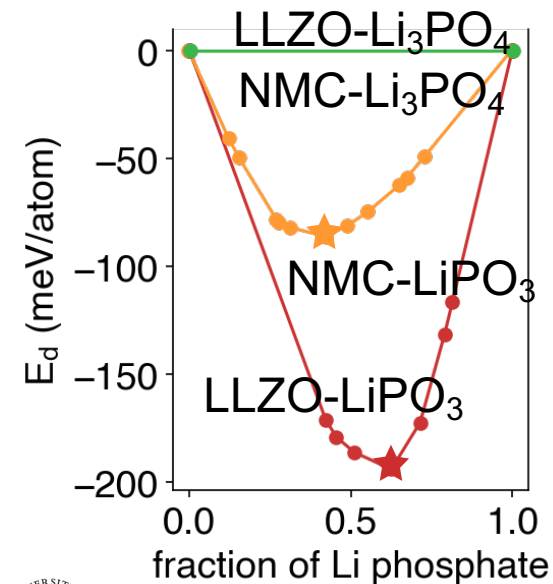
C _{cathode}	x _{LLZO}	E _d with LLZO (meV/atom)	Phase equilibria at x _{LLZO}
LiCoO ₂	0.96	-1.3	Li ₅ CoO ₄ , La ₂ O ₃ , Li ₆ Zr ₂ O ₇
Li(CoO ₂) ₂	0.47	-39	La ₂ O ₃ , O ₂ , Li ₇ Co ₅ O ₁₂ , La ₂ Zr ₂ O ₇
LiNiO ₂	--	0	--
Li(NiO ₂) ₂	0.46	-41	NiO, Li ₂ NiO ₃ , LaNiO ₃ , La ₂ Zr ₂ O ₇
LiMnO ₂	--	0	--
LiMn ₂ O ₄	0.46	-61	Li ₂ MnO ₃ , LaMnO ₃ , La ₂ Zr ₂ O ₇ , LiMnO ₂
MnO ₂	0.70	-127	La ₂ O ₃ , La ₂ Zr ₂ O ₇ , Li ₂ MnO ₃
NMC 111	0.15	-12	La ₂ O ₃ , Li ₂ MnO ₃ , Li ₄ CoNi ₃ O ₈ , NiO, La ₂ Zr ₂ O ₇ , Li ₇ Co ₅ O ₁₂
d-NMC 111	0.53	-50	O ₂ , Li ₂ MnO ₃ , Li ₇ Co ₅ O ₁₂ , Li ₂ NiO ₃ , La ₂ Zr ₂ O ₇ , La ₂ O ₃
NMC 532	0.76	-0.8	Li ₆ Zr ₂ O ₇ , La ₂ O ₃ , Li ₂ MnO ₃ , Li ₄ CoNi ₃ O ₈ , Li ₅ CoO ₄ , NiO
d-NMC 532	0.46	-46	La ₂ Zr ₂ O ₇ , Li ₇ Co ₅ O ₁₂ , Li ₂ NiO ₃ , Li ₂ MnO ₃ , Li ₄ CoNi ₃ O ₈ , La ₂ MnNiO ₆
NMC 811	0.71	-0.5	Li ₆ Zr ₂ O ₇ , Li ₂ NiO ₃ , Li ₂ MnO ₃ , La ₂ O ₃ , NiO, Li ₅ CoO ₄
d-NMC 811	0.46	-43	Li ₂ NiO ₃ , Li ₄ CoNi ₃ O ₈ , Li ₂ MnO ₃ , Li ₁₀ CoNi ₉ O ₂₀ , La ₂ MnNiO ₆ , La ₂ Zr ₂ O ₇

High-throughput Computation to Identify Stable Coating Materials with LLZO and NMC

- For a given compound, identify the interface stability with both lithiated and delithiated cathode (discharged and charged). Identify those materials with good cathode stability during the cycling range.



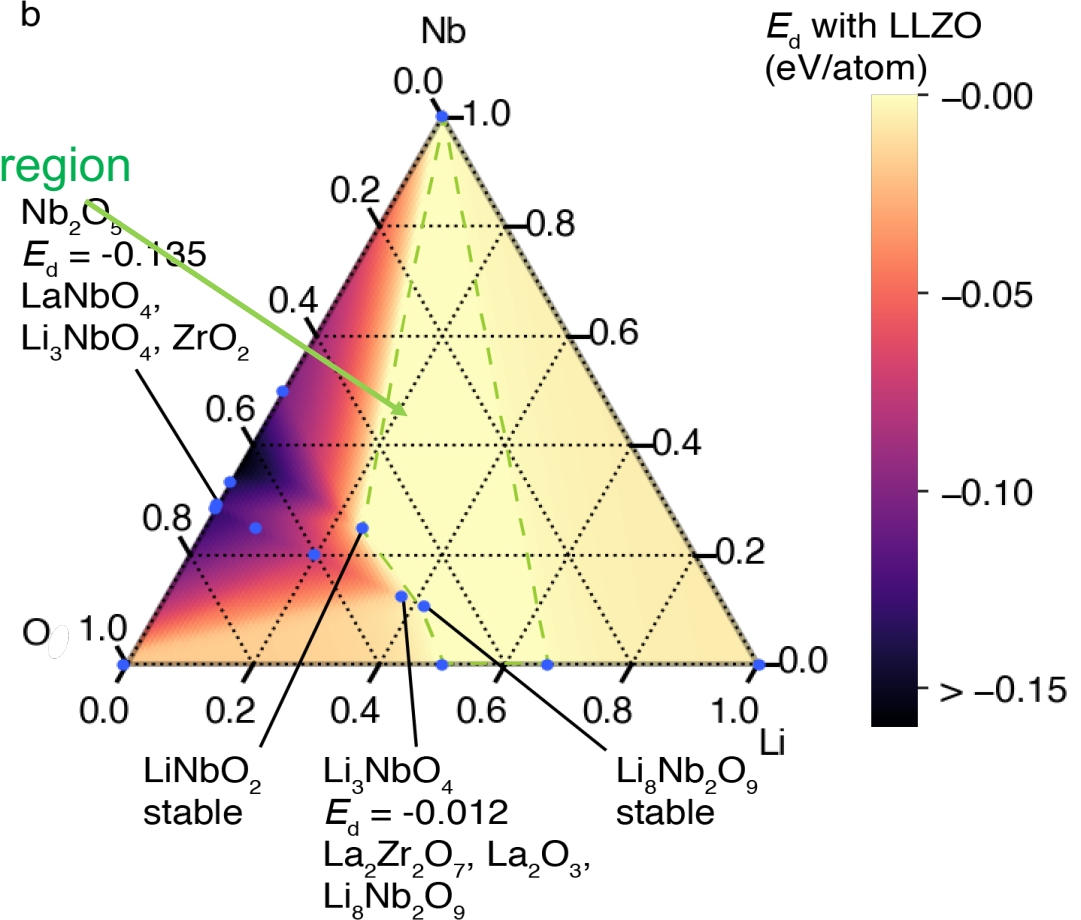
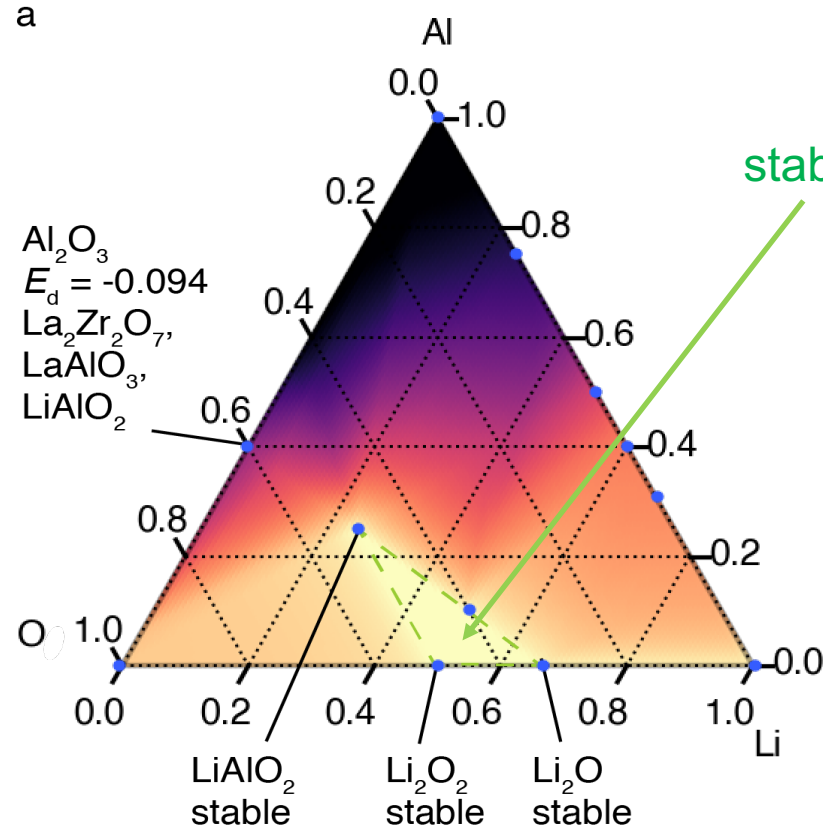
Li_3PO_4 coating stable
with LLZO and NMC



- Studied wide range of lithium ternary compounds for stability with NMC cathode and LLZO.
- Materials stability varies with cation and Li concentrations: LLZO stable with high-Li versus delithiated-NMC stable with low-Li
- Computation effectively narrows materials selection for further experiments

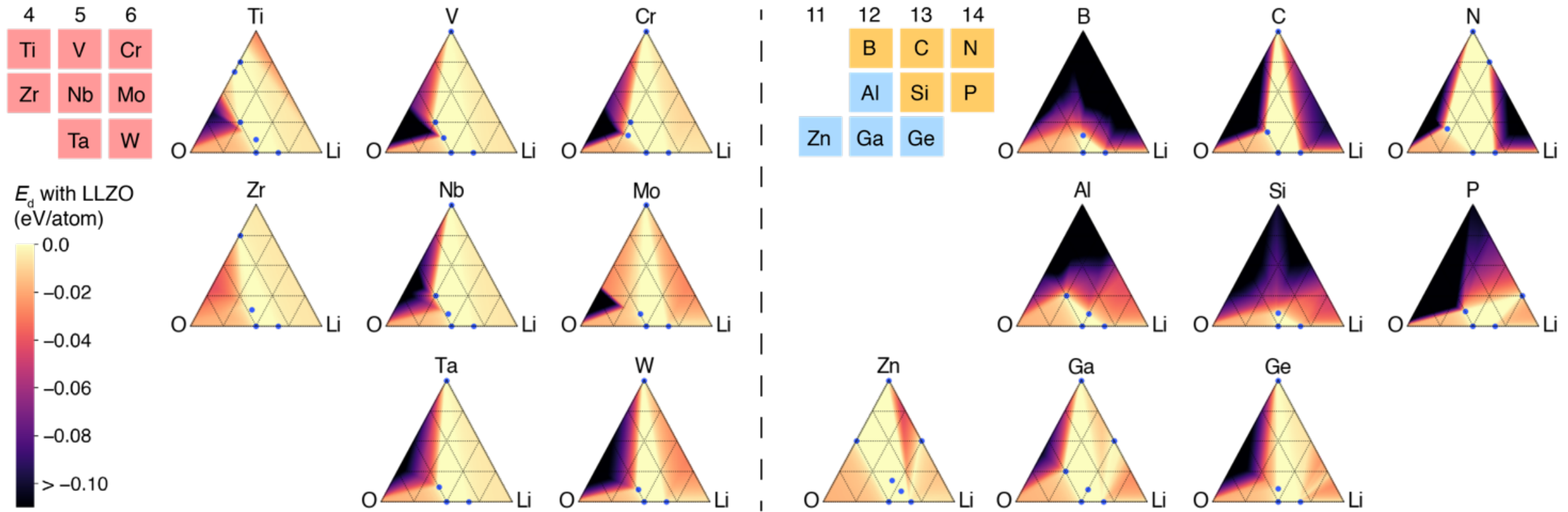
Stability of ALD oxides coating of different compositions with LLZO

- ALD coatings have a range of composition and coating compositions may change during battery cycling.
- We studied the stability of oxide coatings over the entire composition range with LLZO
- Different cations (e.g. Al vs Nb) exhibit different stability range.
- Understand the mechanisms of why Nb or Nb oxides coatings are good.



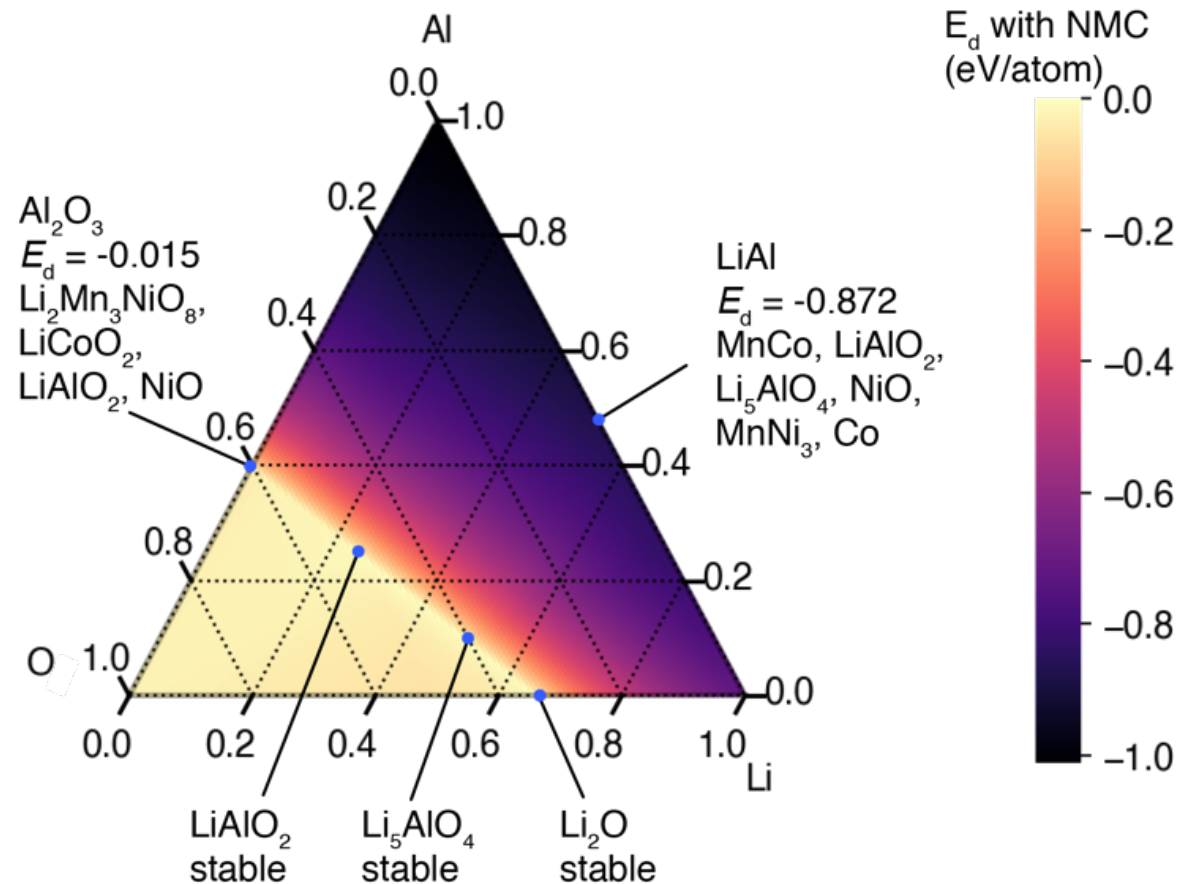
Identify Stable Coatings with LLZO over a wide range of compositions

- High-throughput computation for LLZO stability with wide range of oxide coating compositions.
- Identify the elements and compositions with the widest stability range as promising coating candidates, guiding next stage experiments.



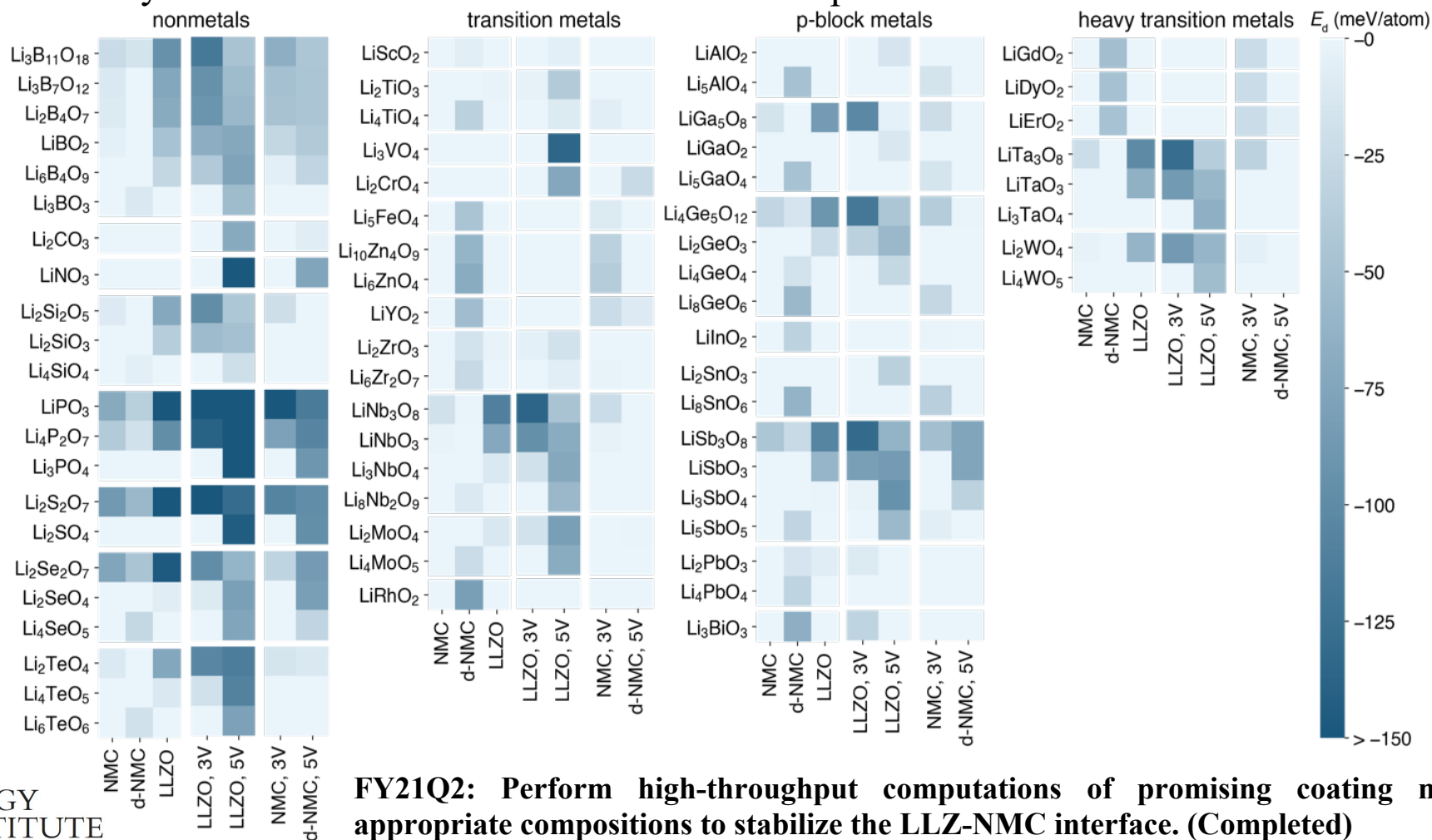
Stability of ALD oxides coating of different compositions with NMC

- ALD coating may have a range of compositions, and coating compositions may change during battery cycling.
- We studied the stability of coating over the entire composition range with NMC and under voltages. Similar stability range are found for cathodes.



High-throughput Computation Identify Stable Materials with LLZO and NMC under Voltage

- Studied a wide range of lithium ternary compounds for stability with NMC cathode and LLZO.
- Materials stability varies great with cation and Li concentrations: LLZO stable with high-Li versus delithiated-NMC stable with low-Li
- Computation effectively narrows materials selection for further experiments



FY21Q2: Perform high-throughput computations of promising coating materials to determine appropriate compositions to stabilize the LLZ-NMC interface. (Completed)

High-throughput Computation Identification of Stable Materials with LLZO

- High-throughput computation for LLZO stability with wide range of oxide coating compositions/cation-elements.
- Identify the compositions with the best stability as promising coating candidate, guiding next stage experiments.

Summary

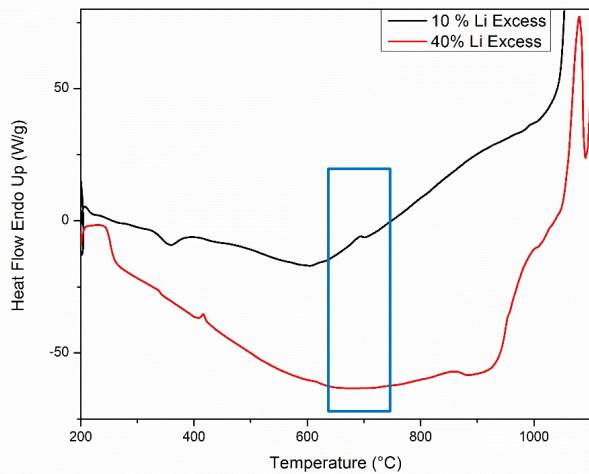
M in Li-M-O	M stable with LLZO?	Li-M-O with E_d with LLZO and NMC > -0.05 eV/atom	Li-M-O with E_d with LLZO and NMC > -0.05 eV/atom at 3 V and 5 V
B	No	LiBO_2 , Li_3BO_3 , $\text{Li}_6\text{B}_4\text{O}_9$	--
C	Yes	Li_2CO_3	--
N	Yes	LiNO_3	--
Al	No	LiAlO_2 , Li_5AlO_4	LiAlO_2 , Li_5AlO_4
Si	No	Li_2SiO_3 , Li_4SiO_4	Li_4SiO_4 , $\text{Li}_{21}\text{Si}_5$, $\text{Li}_{13}\text{Si}_4$
P	No	Li_3PO_4	--
Ti	No	Li_4TiO_4 , Li_2TiO_3	Li_4TiO_4 , Li_2TiO_3
V	Yes	Li_3VO_4	--
Cr	Yes	Li_3CrO_4 , LiCrO_2 , Li_2CrO_4	--
Zn	Yes	$\text{Li}_{10}\text{Zn}_4\text{O}_9$, Li_6ZnO_4 , ZnO	ZnO
Nb	Yes	$\text{Li}_8\text{Nb}_2\text{O}_9$, Li_3NbO_4	--
Mo	Yes	Li_2MoO_4 , Li_4MoO_5	--
Sn	Yes	Li_2SnO_3 , Li_8SnO_6	Li_2SnO_3 , Li_7Sn_2 , $\text{Li}_{17}\text{Sn}_4$, Li_5Sn_2 , Li_7Sn_3 , Li_3Sn
Ta	Yes	Li_5TaO_5 , La_3TaO_4	Li_5TaO_5

FY20Q4: Go/No-Go Computationally determine appropriate compositions to stabilize the LLZ-NMC interface. (Completed)

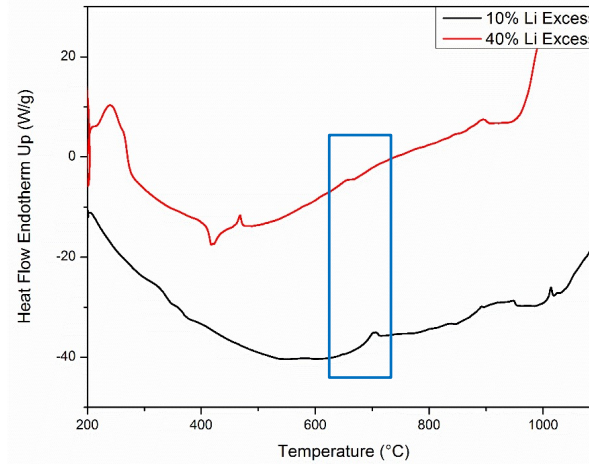


Li Content Effect on LLZO Stability against Different Cathodes

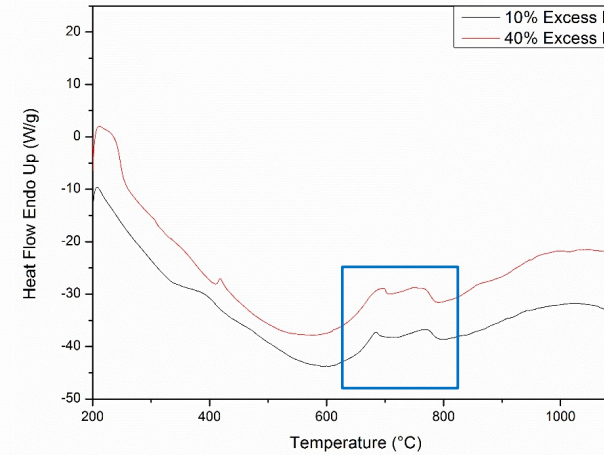
LCO



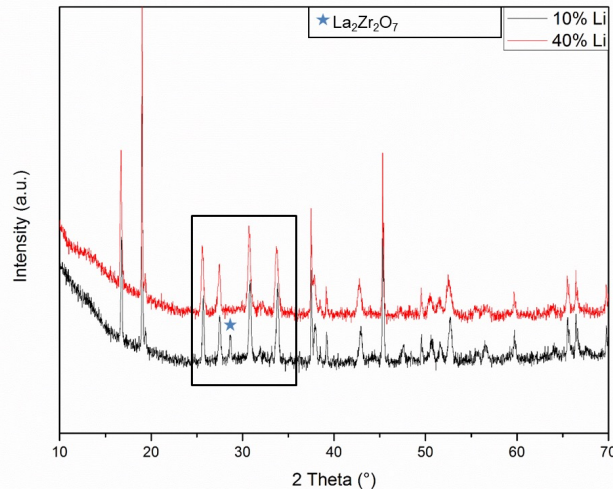
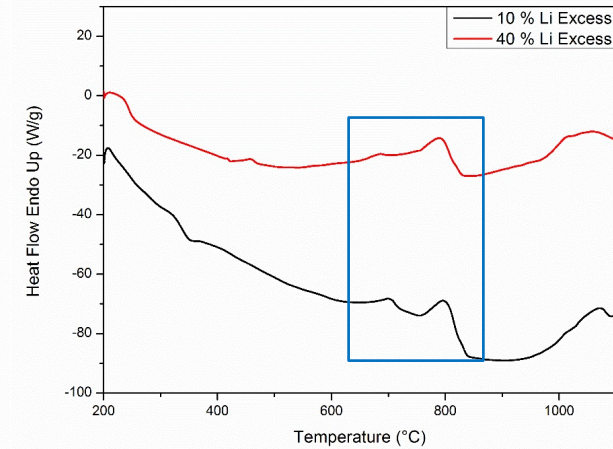
NMC111



LNMO



LMO

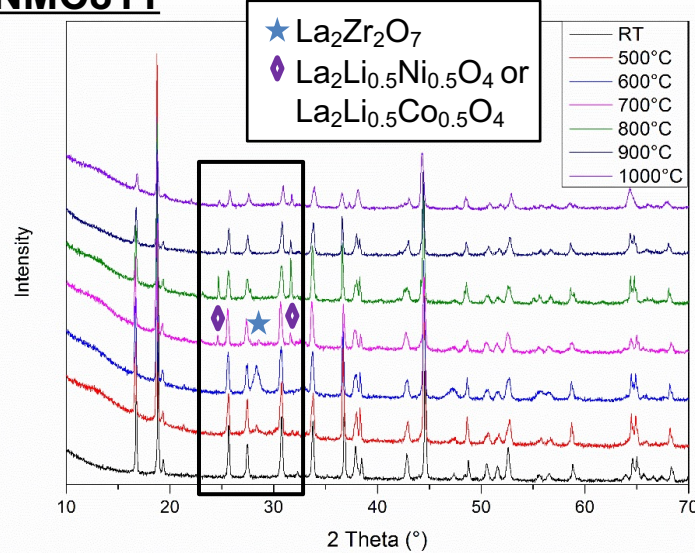


- DSC on 10% and 40% Li excess (control by adding LiOH)
- 40% excess Li shows the decrease in the endotherm peak at 700°C in all tested cathodes/LLZO.
- Endotherm peak at 400~500°C: probably LiOH melting (MP= 462°C)
- Endotherm is not significantly reduced with 40% excess Li at 700°C and 800°C
- No presence of $\text{La}_2\text{Zr}_2\text{O}_7$ phase after co-sintering with 40% excess Li

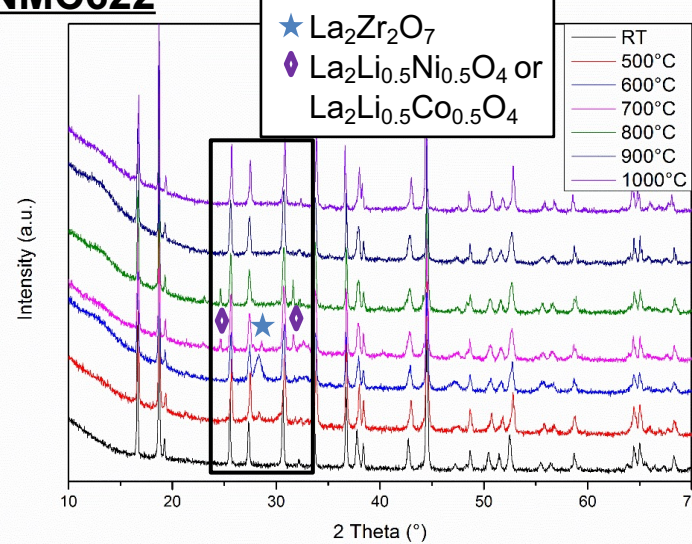
Consistent with computational results excess Li minimizes the cathode/LLZO reaction up to 700°C

Thermal Stability of LLZO with Different NMC Compositions

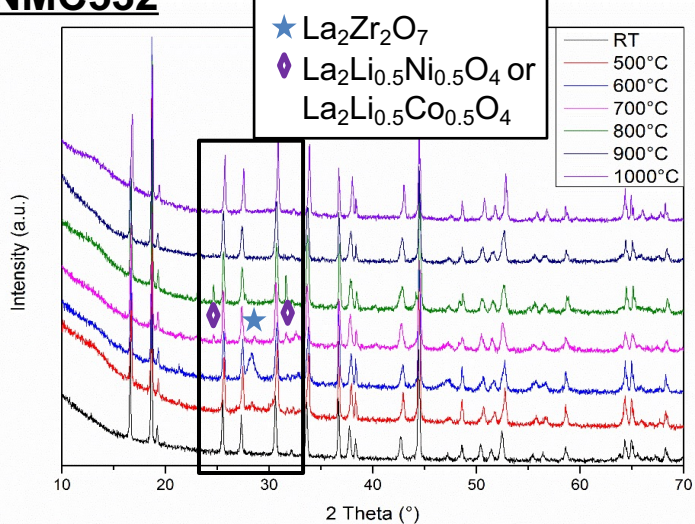
NMC811



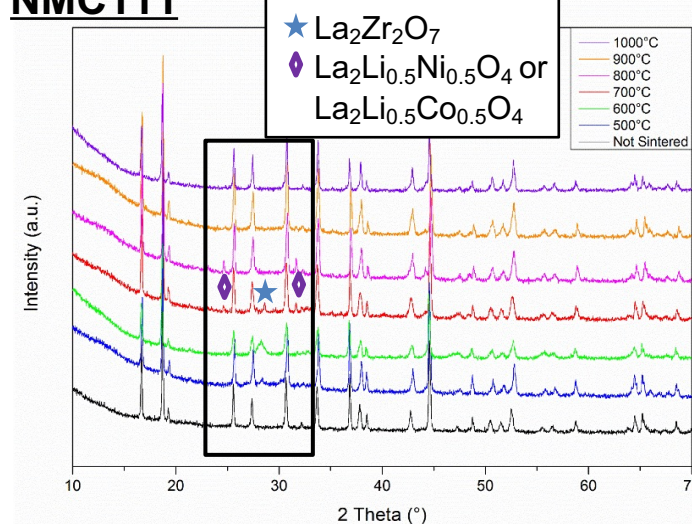
NMC622



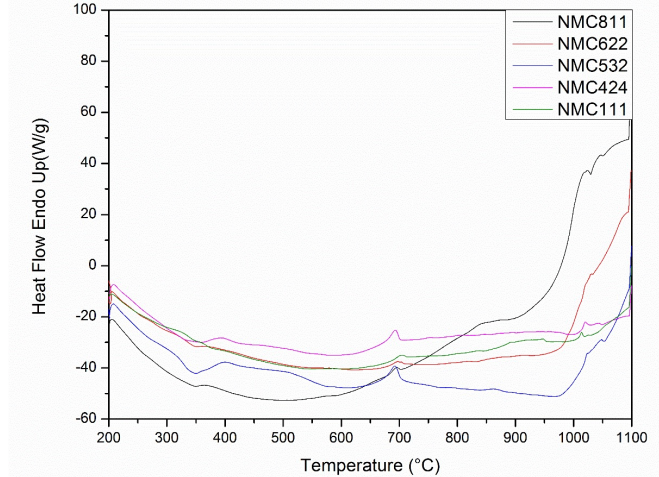
NMC532



NMC111



DSC on different NMC compositions with 10% excess Li



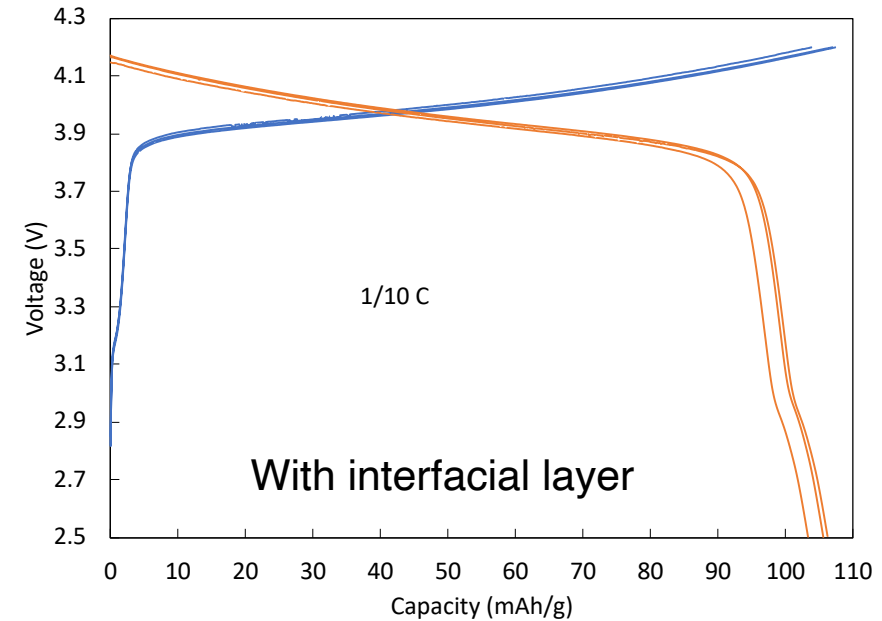
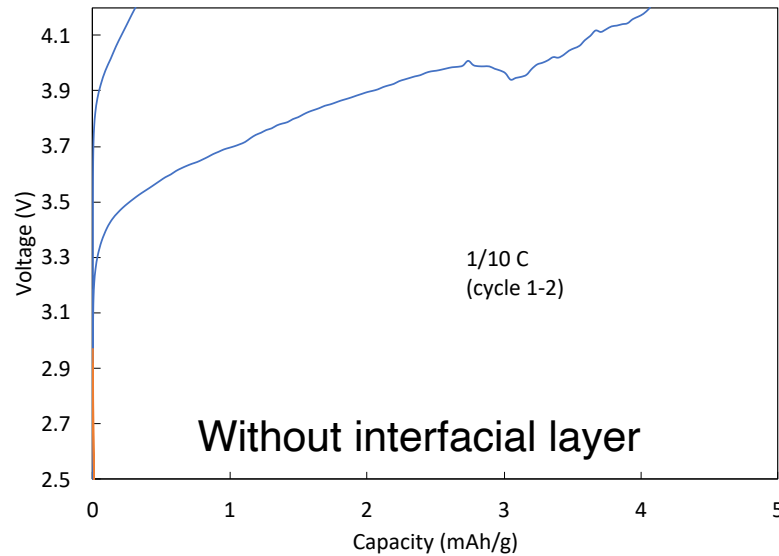
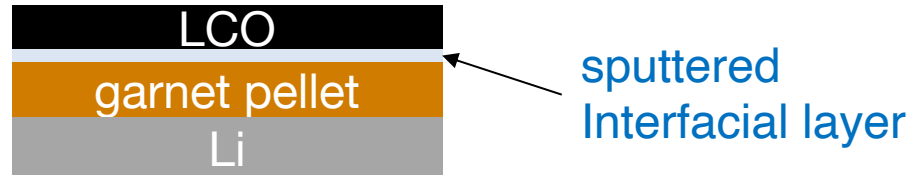
- Similar impurity formation for all NMCs
- Slight reaction starting at 500-600°C
- NMC and LLZTO retain crystallinity up to 1000°C
- NMC811 forms the most amount of impurities and furthermore loses crystallinity >900°C
- NMCs show an endotherm at 700°C -LaCoO/LaCo_{1-x}Ni_xO formation*
- Stability >1000°C decreases with increasing Ni content

Consistent with computational results for NMCs, the increase in Ni content increases NMC/LLZO reactivity.

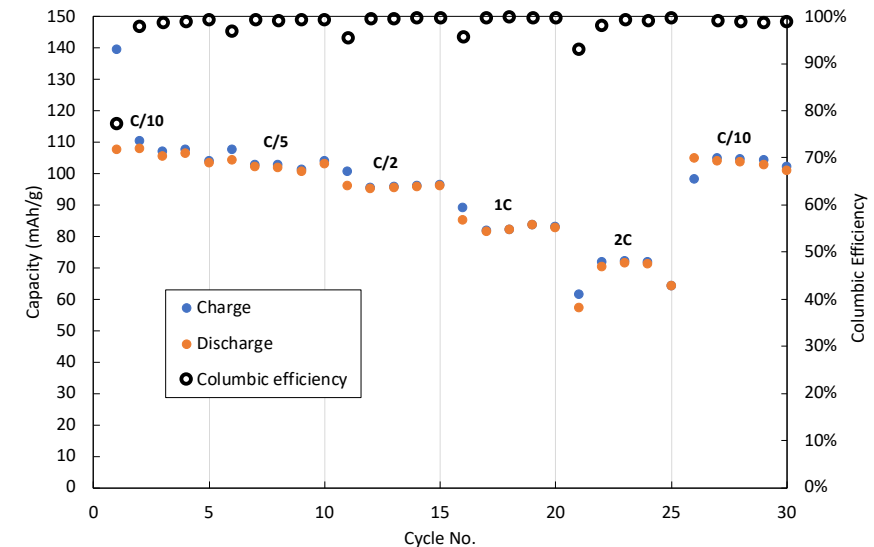
FY20Q3: Determine thermochemical stability between LLZ and NMC. (Completed)

*Finsterbusch M; et al. *ACS Applied Materials & Interfaces* 2018, 10 (26), 22329–22339

Interface Modified Solid-State Li/Garnet/LCO



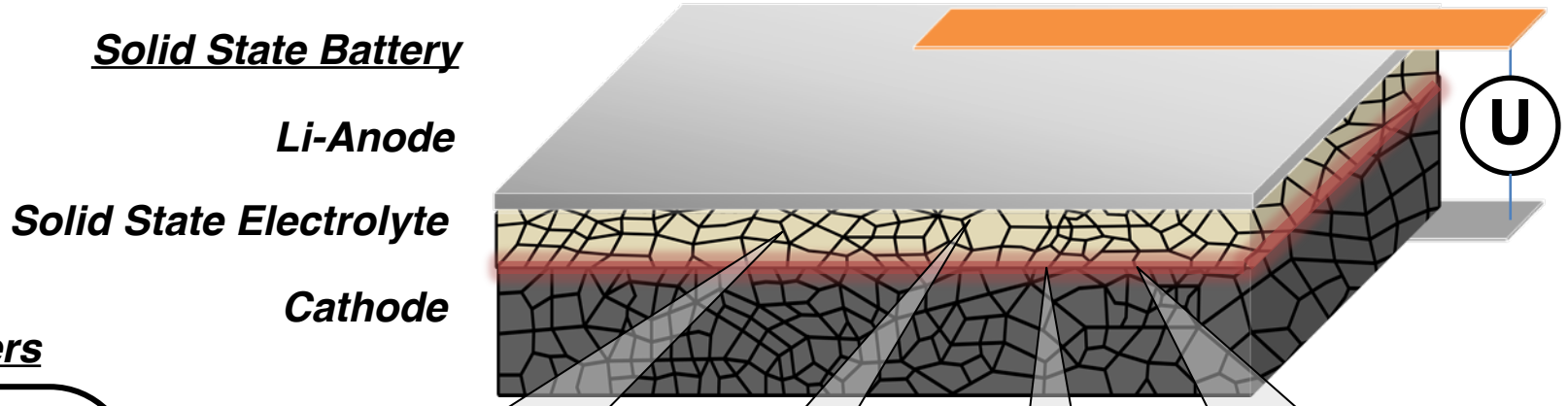
- Samples annealed @800°C and tested @RT
- Without interfacial layer the cell can be barely cycled
- With interfacial layer the cell can be stably cycled even at 2C





US – German Cooperation on Solid State Battery Interfaces

CatSE – Project Partners and Objectives



U.S. - Partners

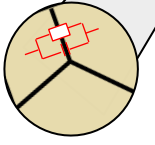
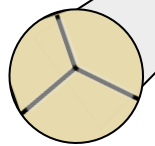








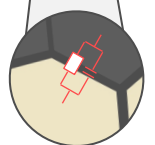
MARYLAND ENERGY INNOVATION INSTITUTE



Formation of Secondary Phases

Grain Boundary Resistance

Internal Ceramic Interface



Charge Transfer at the Materials Interface

Materials Reaction at the Interface

Cathode Electrolyte Interface

German - Partners





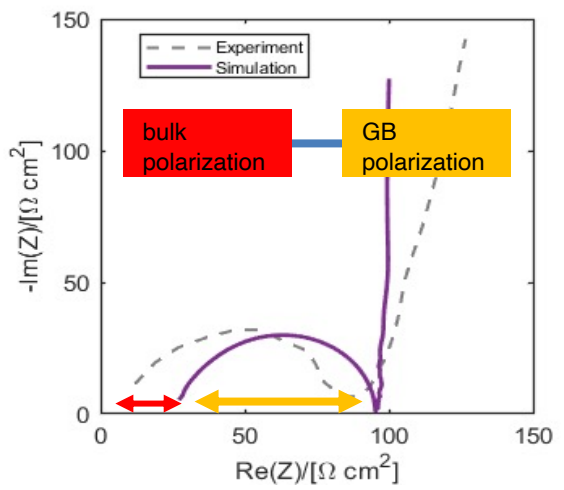
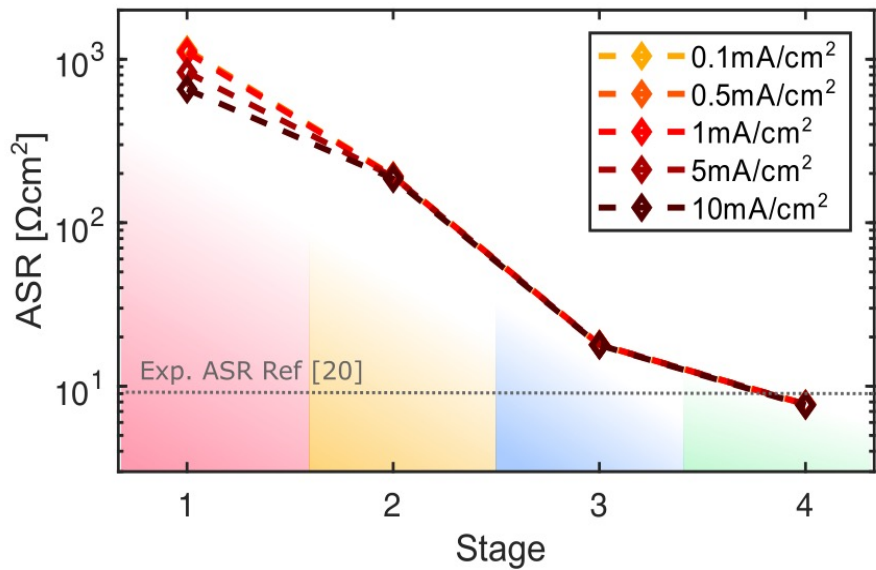
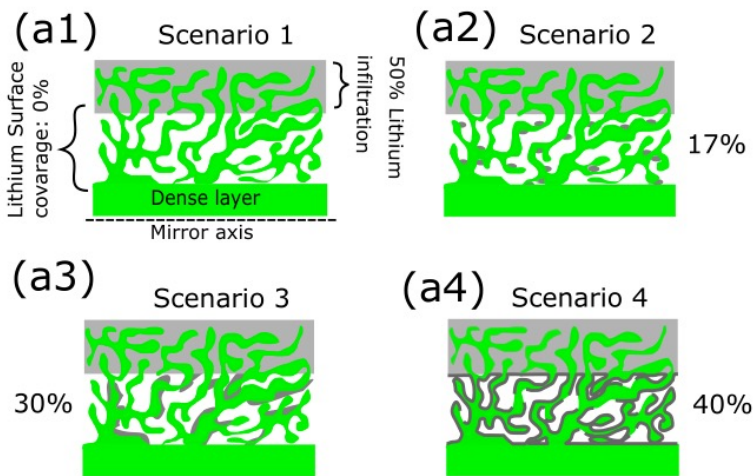
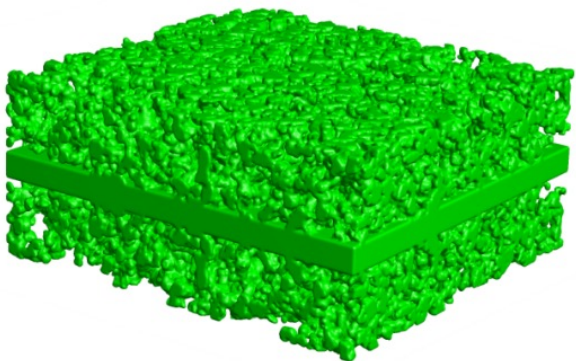




US – German Cooperation on Solid State Battery Interfaces

Effect of Structure on Electrode Performance

- Trilayer: 100 μm | 20 μm | 100 μm
- Quantitative FIB/SEM 3D reconstruction and EIS data
- Impact of surface-wetting/interface-impedance
- Model includes grain boundary contributions



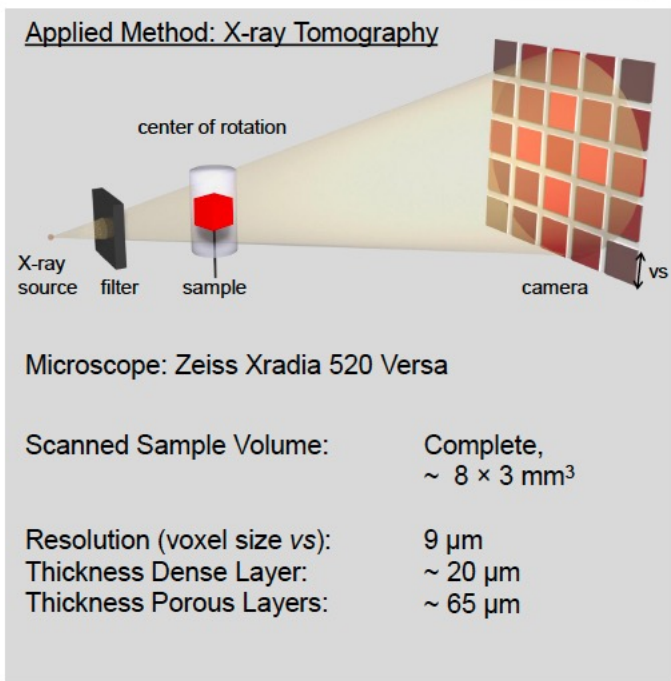
- Simulation of Trilayer ASR for varying current densities up to 10 mA/cm²
- Initial cycles show highest ASR
→ ASR reduces and stabilizes during cycling
- Lithium coverage of the pore space reduces the ASR by two orders of magnitude
- Percolating lithium film is necessary to enable low ASR of the Trilayer

Model indicates gradient porosity structure will perform better

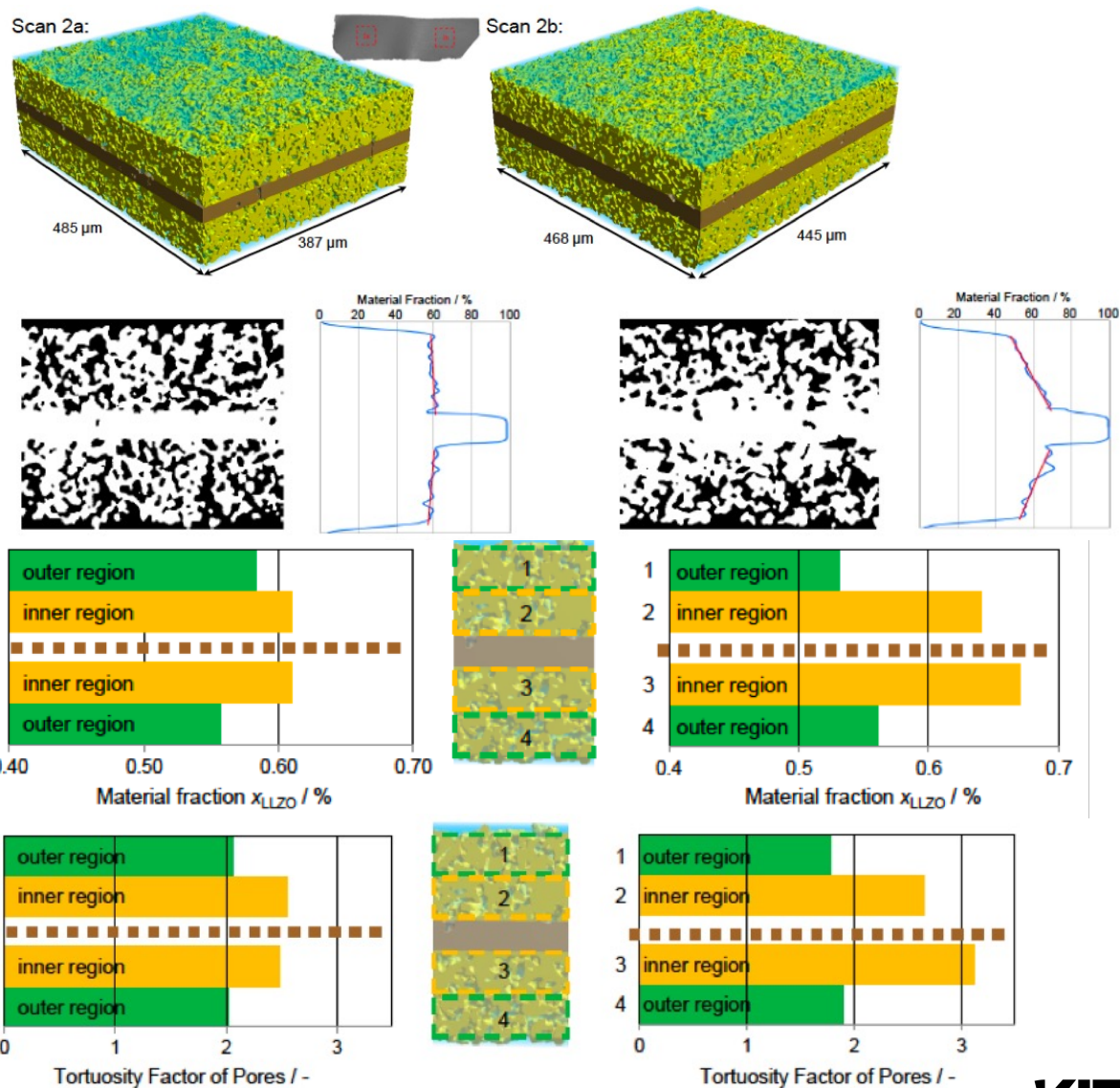


US – German Cooperation on Solid State Battery Interfaces

Effect of Structure on Electrode Performance



Fabricated gradient porosity structure and characterized by X-ray tomography



Response to Previous Year Comments

- Not reviewed last year

Remaining Challenges and Barriers

- Experimentally determine thermochemical stability between interface-coated LLZ and infiltrated NMC. Uniformly infiltrating NMC particles into porous garnet layer is challenging, especially when the porous layer is thick.
- Demonstrate 10X reduction in interfacial impedance between coated and uncoated LLZ/NMC interfaces.
- Determine thermochemical stability between LLZ and interface-coated NMC.
- Compare experimental results with computational results and refine model including understanding side reactions and process optimization.
- Demonstrate 10X reduction in interfacial impedance by co-sintering.
- Fabricate trilayer cell with composite NMC-LLZ cathode layer and measure impedance, cell capacity, and cycle life.
- Demonstrate >350 Wh/kg energy density Li-metal/LLZ/LLZ-NMC cell with 80% capacity retention, 1000 cycles at C/3.

Proposed Future Research

FY21

- Experimentally determine thermochemical stability between interface-coated LLZ and infiltrated NMC.
- Demonstrate 10X reduction in interfacial impedance between coated and uncoated LLZ/NMC interfaces. Design capable of meeting performance requirements.

FY22

- Determine thermochemical stability between LLZ and interface-coated NMC.
- Compare experimental results with computational results and refine model including understanding side reactions and process optimization.
- Demonstrate 10X reduction in interfacial impedance between coated LLZ/NMC and uncoated LLZ/NMC interfaces obtained by co-sintering.
- Fabricate trilayer cell with composite NMC-LLZ cathode layer with $> 25 \text{ mg/cm}^2$ NMC and measure impedance, cell capacity, and cycle life.
- Demonstrate $> 350 \text{ Wh/kg}$ energy density Li-metal/LLZ/LLZ-NMC cell with 80% capacity retention after 1000 cycles at C/3.

Summary

- Computationally determined the interfacial stability between LLZ solid electrolytes and NMC cathode.
- Experimentally determined thermochemical stability between LLZ and NMC.
- Computationally determined the mechanism of interfacial stabilization between LLZ and NMC through coating layers.
- Computationally determined appropriate compositions to stabilize the LLZ-NMC interface.
- Performed high-throughput computations of promising coating materials to determine appropriate compositions to stabilize the LLZ-NMC interface.
- Demonstrated interfacial layer can stabilize LLZ-LCO interface to enable fast Li-ion transfer.
- Quantified microstructure in collaboration with German colleagues

Publications and Presentations

- “Effect of the 3D Structure and Grain Boundaries on Lithium Transport in Garnet Solid Electrolytes,” A. Neumann, T. R. Hamann, T. Danner, S. Hein, K. Becker-Steinberger, E. D. Wachsman, and A. Latz, *Applied Energy Materials*, (2021) <https://doi.org/10.1021/acsaem.1c00362>
- “Solid-State Chemistries Stable with High-Energy Cathodes for Lithium-Ion Batteries,” Adelaide M. Nolan, Yunsheng Liu, Yifei Mo*, *ACS Energy Letters*, **4**, 2444-2451 (2019)
- “Solid-State Chemistries Stable with High-Energy Cathodes for Lithium-Ion Batteries”, A. Nolan, Y. Liu, Y. Mo, ECS PRIME (10/2020) (Invited)
- “Data-Driven Discovery of New Materials for Solid-State Batteries”, Y. Mo, ECS PRIME (10/2020)
- “Interlayer for Solid Cathode-Electrolyte Interface,” Yaoyu Ren & Eric D. Wachsman, Invention Disclosure
- “Computation-Guided Discovery of Coating Materials to Stabilize the Interface Between Lithium Garnet Solid Electrolyte and High-Energy Cathodes,” Adelaide M. Nolan, Eric D. Wachsman & Yifei Mo, (submitted)