Multi-scale Modeling of Solid State Electrolytes for Next Generation Lithium Batteries

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DOE merit review

June 21-25, 2021

Project ID# bat424

Overview

Timeline

- Start: 2020
- Finish: 2022
- Completed: 50 %

Barriers

- Barriers addressed
  - Low Conductivity
  - High interfacial impedance
  - Dendrite growth

Budget

- Total project funding
  - DOE share: $ 1.295 M
  - Contractor 0
- FY 20: $395 K
- FY 21: $ 450 K
- FY 22: $ 450 K

Partners

- Interactions/ collaborations
  - Pallab Brai, ANL
  - Z. Chen, ANL
  - B. Narayanan, U of Louisville

Project Objectives and Relevance

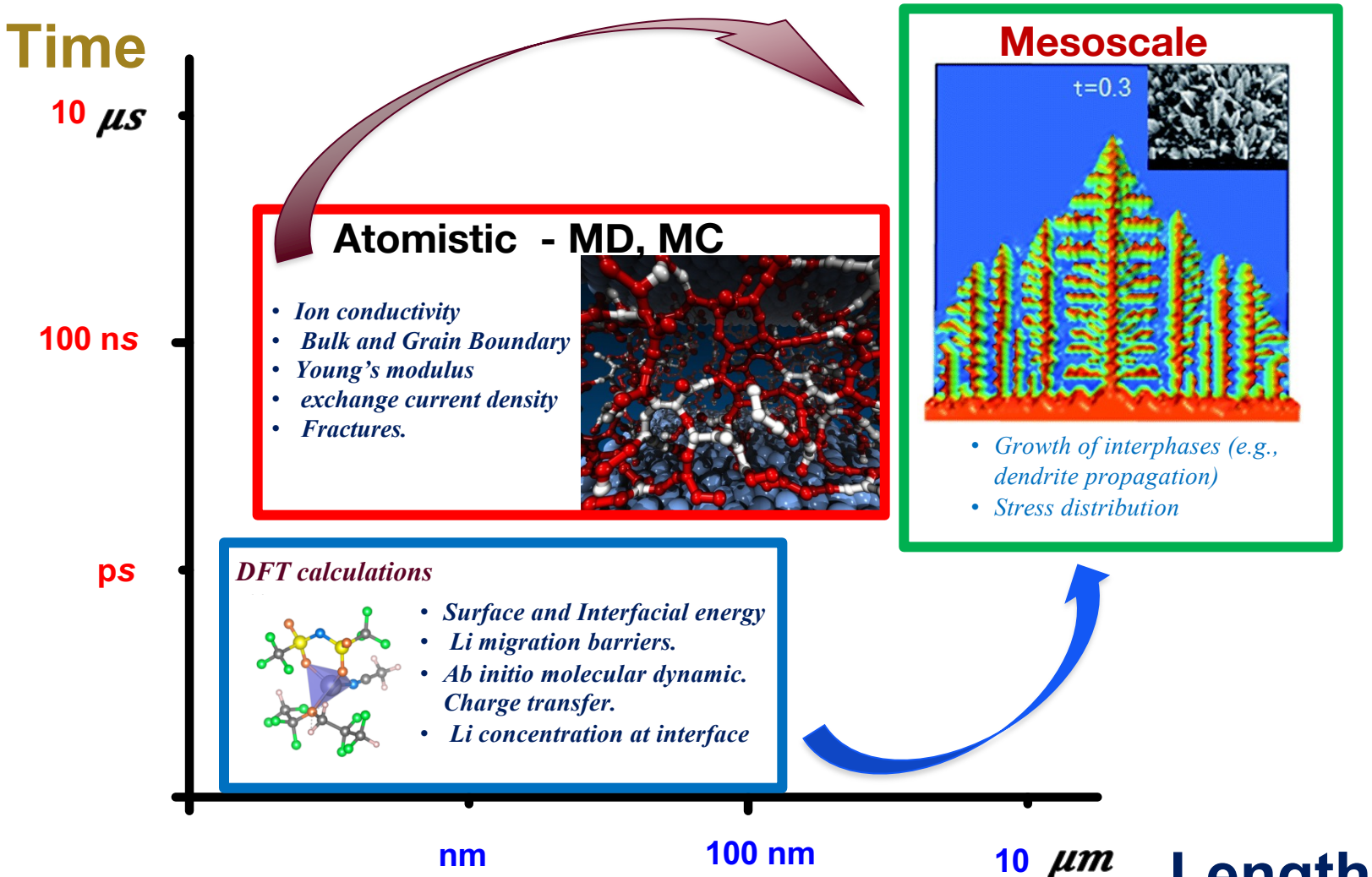
- In order to improve the safety of present day lithium ion batteries, replacement of liquid electrolytes with their solid state counterparts is a necessity.
- Multi-scale modelling efforts have been adopted to obtain an *in-depth* understanding of the interaction between the electrode and the solid electrolyte aimed at developing highly efficient solid state electrolytes batteries.
- Properties estimated from DFT calculations are fed into the mesoscale models, that analyze overall stability of solid electrolytes against cathodes and anodes.
- Solid state electrolytes with lithium metal anode and cathode have the potential to substantially increase the energy density of present day lithium ion batteries.

FY21 Milestones

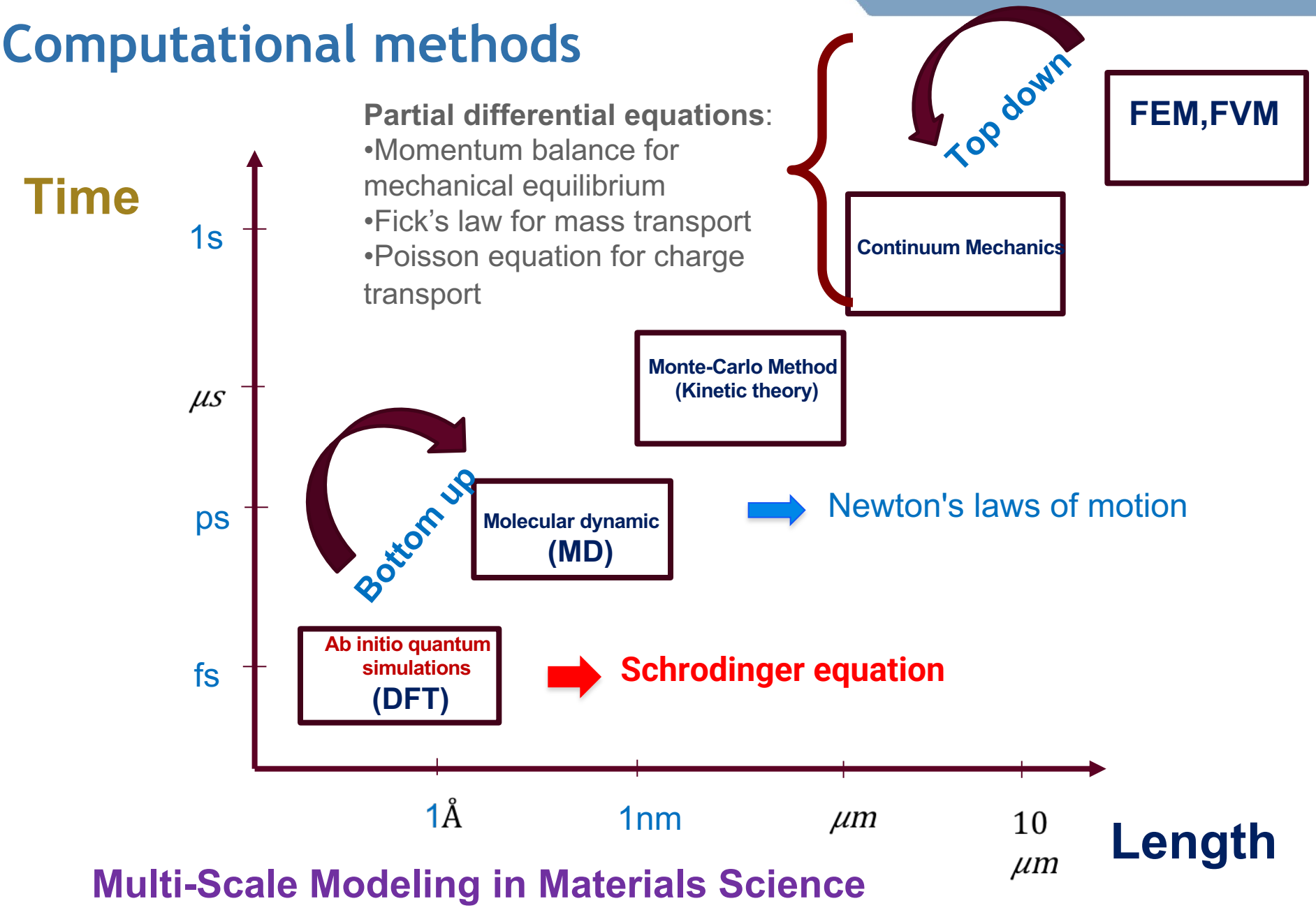
Month/ Year	Milestones
Dec/20	Determine stable surface of the Li_6PS_5Cl SSE and the NMC-811/Li_6PS_5Cl interface. (Q1, FY 2021; **Completed**)
Mar/21	Conduct AIMD study of electrochemical interface between NMC-811/Li_6PS_5Cl. (Q2, FY 2021; **Completed**)
Jun/21	Investigate Li-ion transport of the NMC-811/Li_6PS_5Cl interface, and calculate exchange current density. (Q3, FY 2021; **Initiated**)
Sep/21	Incorporate information obtained from the atomistic calculations into the mesoscale model, and predict the impact on performance. (Q4, FY 2021; **Initiated**)

Strategy: A multiscale approach has been adopted, where transport and elastic properties of lithium and solid state electrolytes have been computed at the nanoscale using DFT calculations, and then the properties have been transferred to the continuum scale model where the mesoscale electrode electrolyte behavior has been analyzed.

Multi-Scale Modeling methods



Computational methods

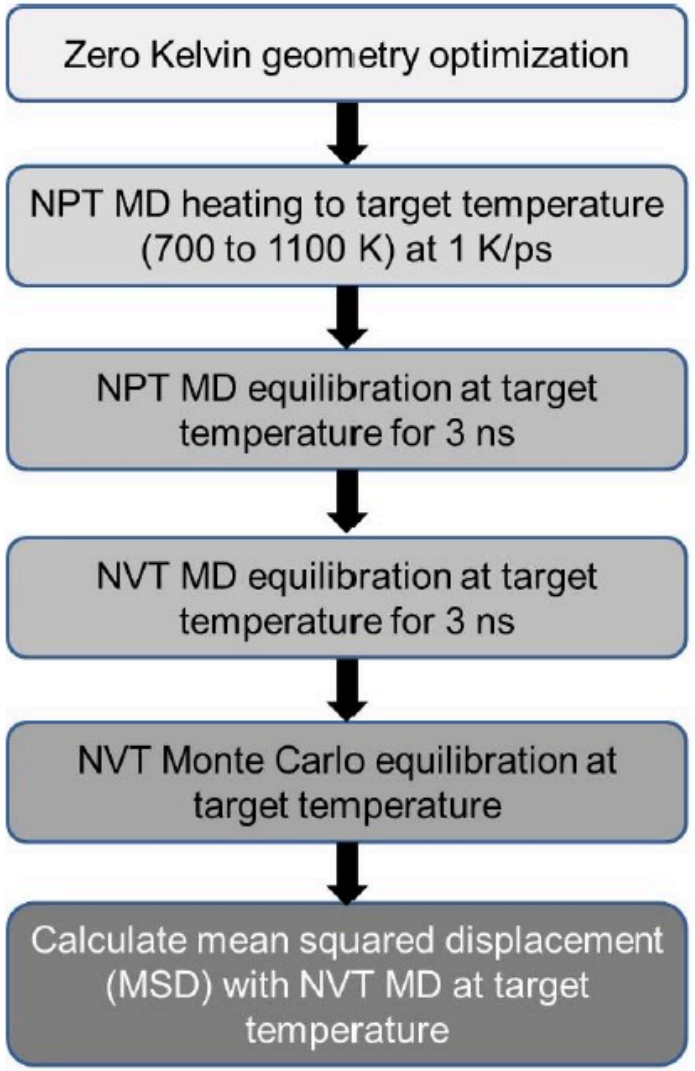


Multi-Scale Modeling in Materials Science

Summary of the computational procedures of the MD simulations

- Temperature-based materials simulations.
- Molecular dynamic and Monte-Carlo at operation T.
- LAMMPS code

- Elastic and transport properties estimated from the DFT and MD calculations have been imput into the mesoscale simulations, where continuum equations were solved using these parameters to estimate the interfacial stability between solid state electrolyte and anodes and/or cathodes. System size ~ 1.9 M atoms
- For mesoscale analysis, all the partial differential equations were solved using a set of codes developed at ANL using MATLAB solver libraries.



Technical Accomplishments

I. Prediction of transport properties in LLZO

- Using DFT, MC and MD simulations, lithium ion conductivity in the bulk and grain-boundary of LLZO has been predicted from previous year .
- Exchange current density between the LBCO/NMC and LBCO/LLZO have been computed.

II. Prediction of mechanical properties of NMC/LBCO/LLZO interface

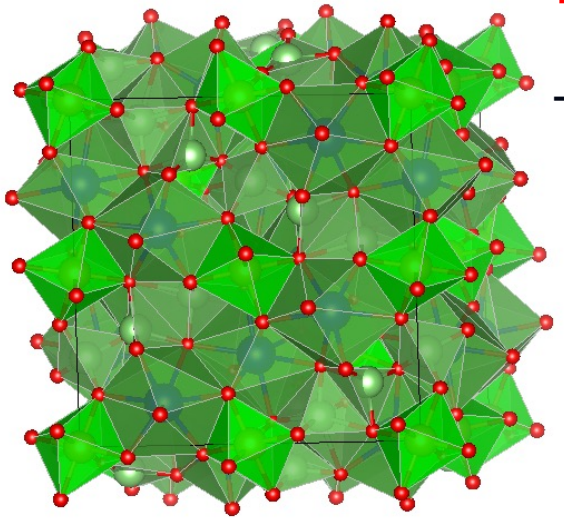
- Young's modulus in the bulk and grain-boundary of LLZO has been predicted by MD simulations in previous quarter.
- Fracture energy of NMC/LBCO/LLZO interface has been calculated.

III. Incorporation with mesoscale models

- The elastic modulus of LLZO bulk and GB, fracture energy of NMC/LBCO/LLZO interface, conductivity of Li within bulk and GB of LLZO, and exchange current density between Li/LLZO and NMC/LBCO/LLZO, computed at the atomistic level, have been incorporated into the mesoscale model.
- Extent of interfacial delamination is predicted using the mesoscale computation.
- How the LBCO interphase layer can minimize the interfacial detachment is investigated.

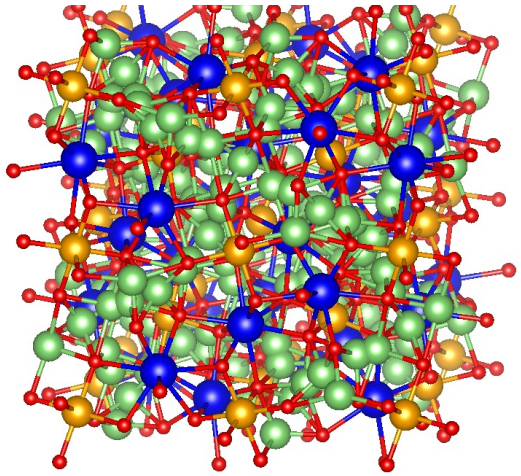
Electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO)

Depending on synthesis temperatures



Tetragonal phase :
C ~ 10^{-6} S/cm

- **Wide working potential, good compatibility with cathode and anode.**
- **Formation of lithium dendrite along grain boundary, difficult to manufacture, potential stress across the electrode/electrolyte interface**
- **Anode: mostly Li, although it can be graphite and Si**
- **Cathode: LiFePO4, LiMn2O4, LiCoO2, NMC**

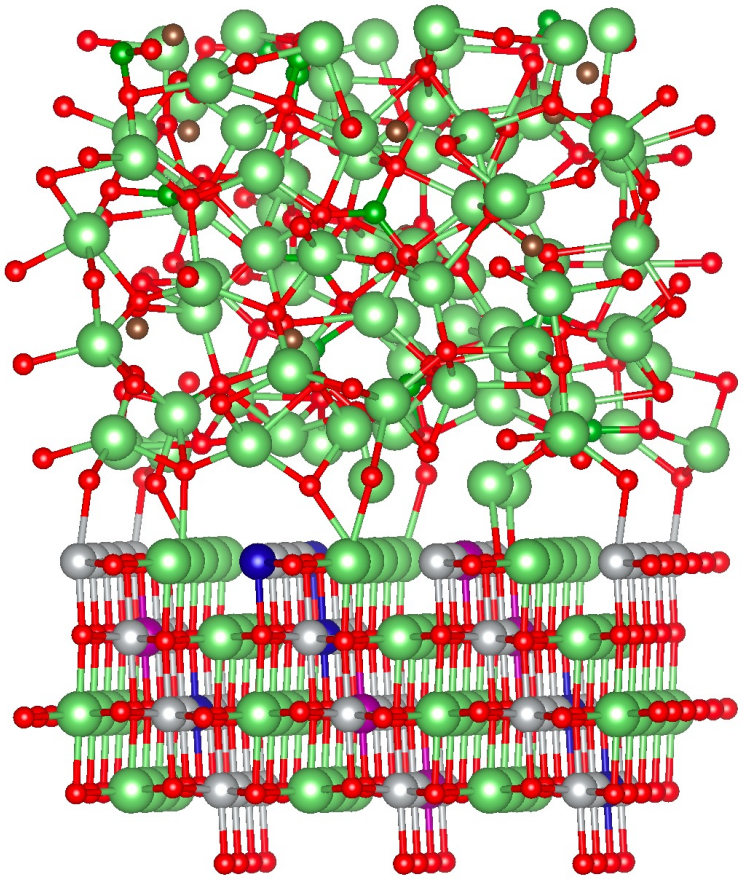


Cubic phase :
C ~ 10^{-3} S/cm. T ~ 25 ^{0}C

K. Kerman et. al. Journal of The Electrochemical Society, 164 (7) A1731-A1744 (2017)
T. Thompson et. al. ACS Energy Lett., 2017, 2 (2), pp 462–468

DFT Analysis: NMC/LBCO/LLZO interfacial calculations

- Plane Wave Projector Augmented-Wave (PAW) Density Functional Theory (DFT) methods
- VASP code Spin polarized calculations and DFT+U Calculations.
- Generalized Gradient Approximation. Exchange correlation is described by Perdew-Burke-Ernzerhof (PBE) functional.
- Two interfaces modeled through stoichiometric slabs
- Each supercell contains 400 atoms

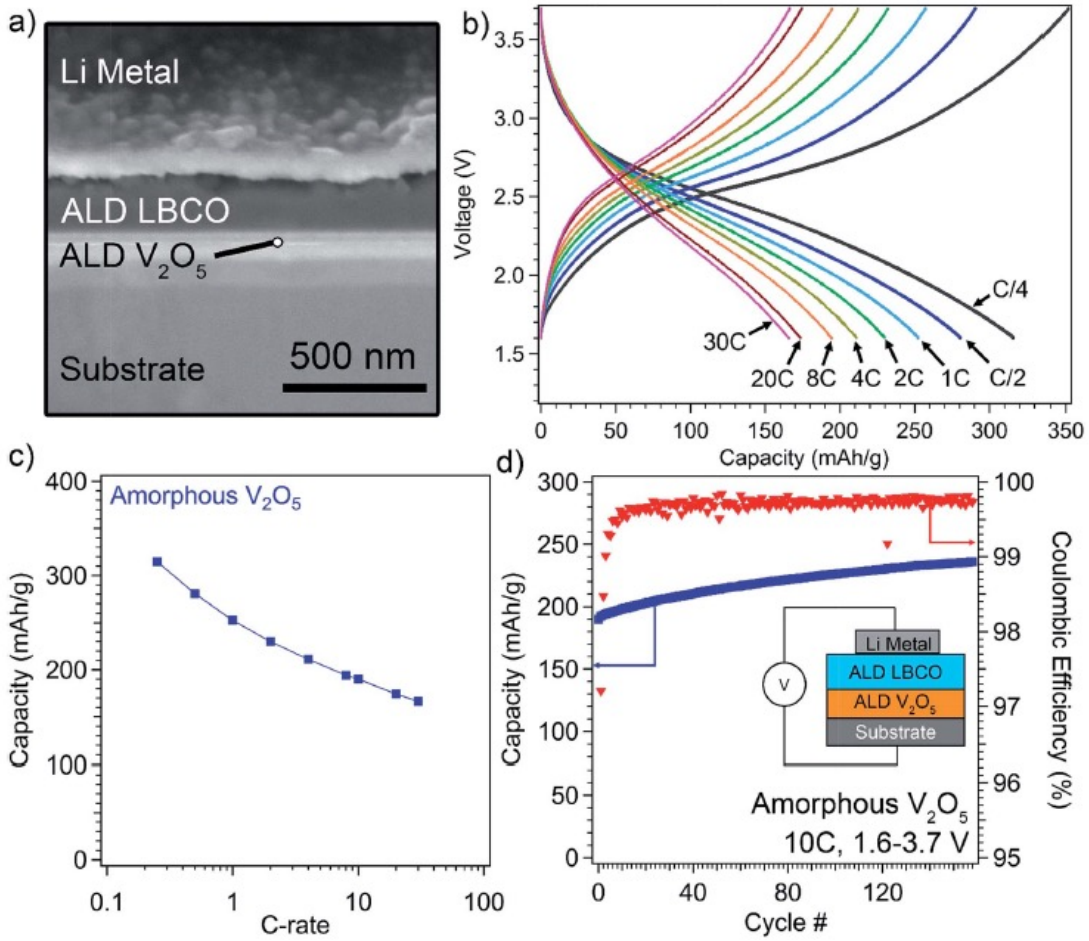


Representation of the interface studied using first principles calculations. The Interface of LLZO with the $(10\bar{1}4)$ surface of NMC811

Motivation of LBCO

LBCO (Lithium Borate + Lithium Carbonate) layer exhibits the high conductivity

These films exhibit ionic conductivities up to 2.2×10^{-6} S cm^{-1}

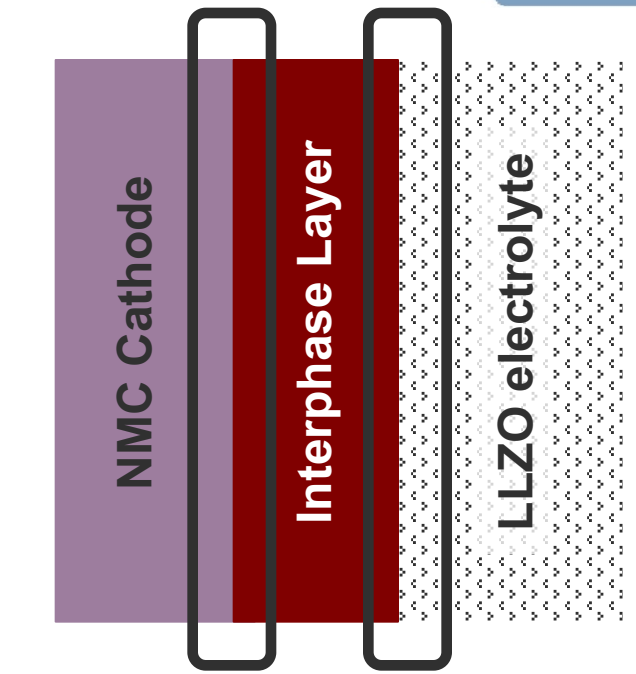


(a) SEM image of FIB cross-section of full cell stack used in electrochemical measurements. (b) Charge and discharge curves at different rates for full cells, with schematic inset of cell architecture. (c) Discharge capacity at varying rates corresponding for crystalline and amorphous ALD V2O5 cathode films (d) plot of discharge capacity and coulombic efficiency for cell cycled at 10C.

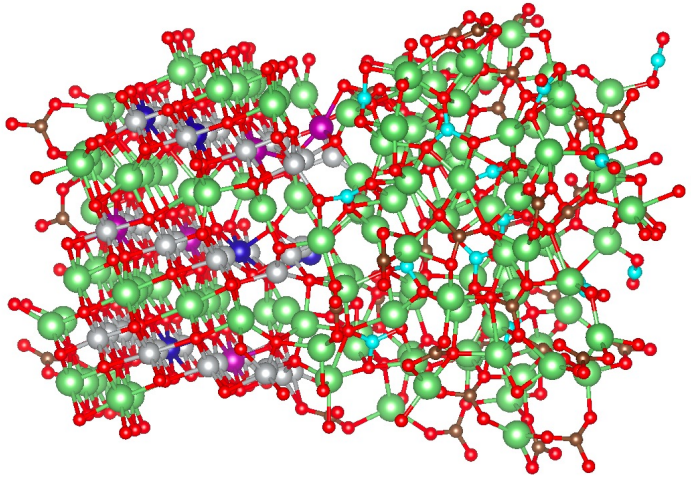
J . Mater. Chem. A. 6, 19425-19437, (2018)

Two interface system

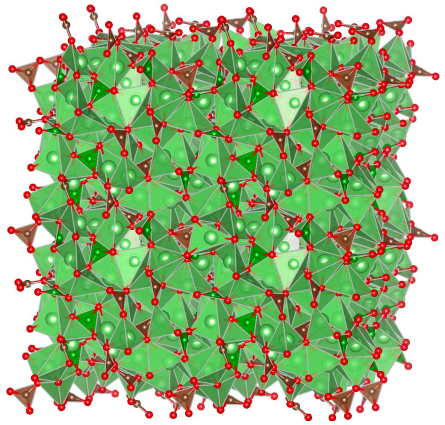
When a cathode is coated, the cathode/SSE interface is replaced by two new interfaces:
the cathode/ coating interface and
the coating/SSE interface



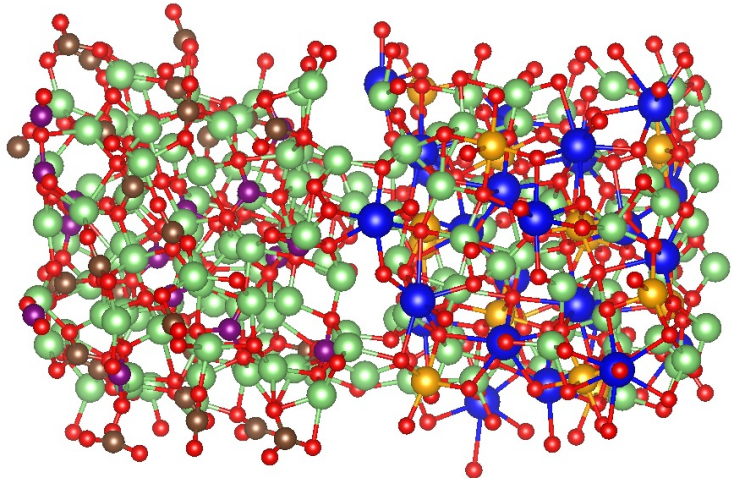
LBCO (Li_3BO_3-Li_2CO_3)



NMC-LBCO interface

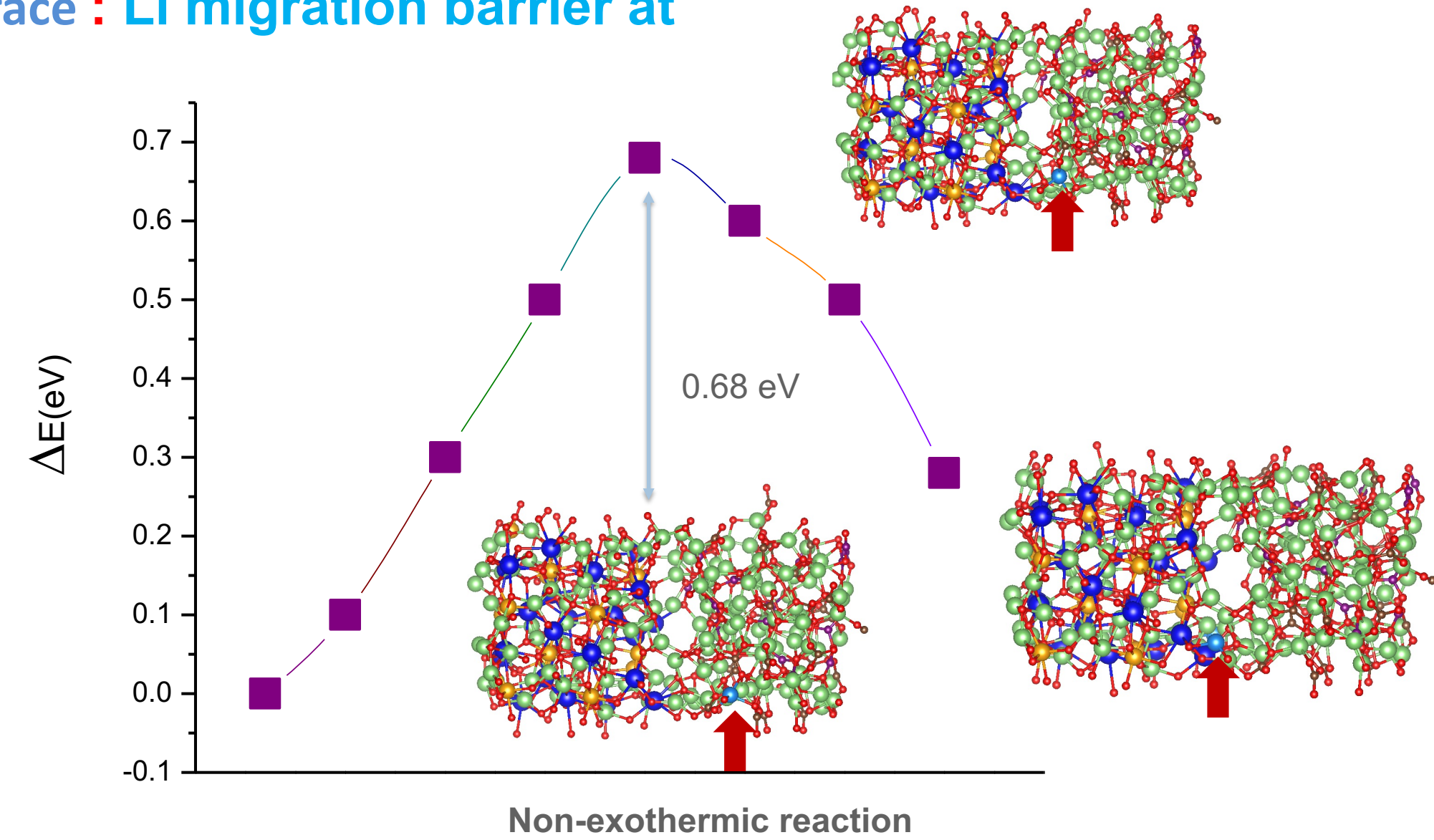


Interphase Layer LBCO



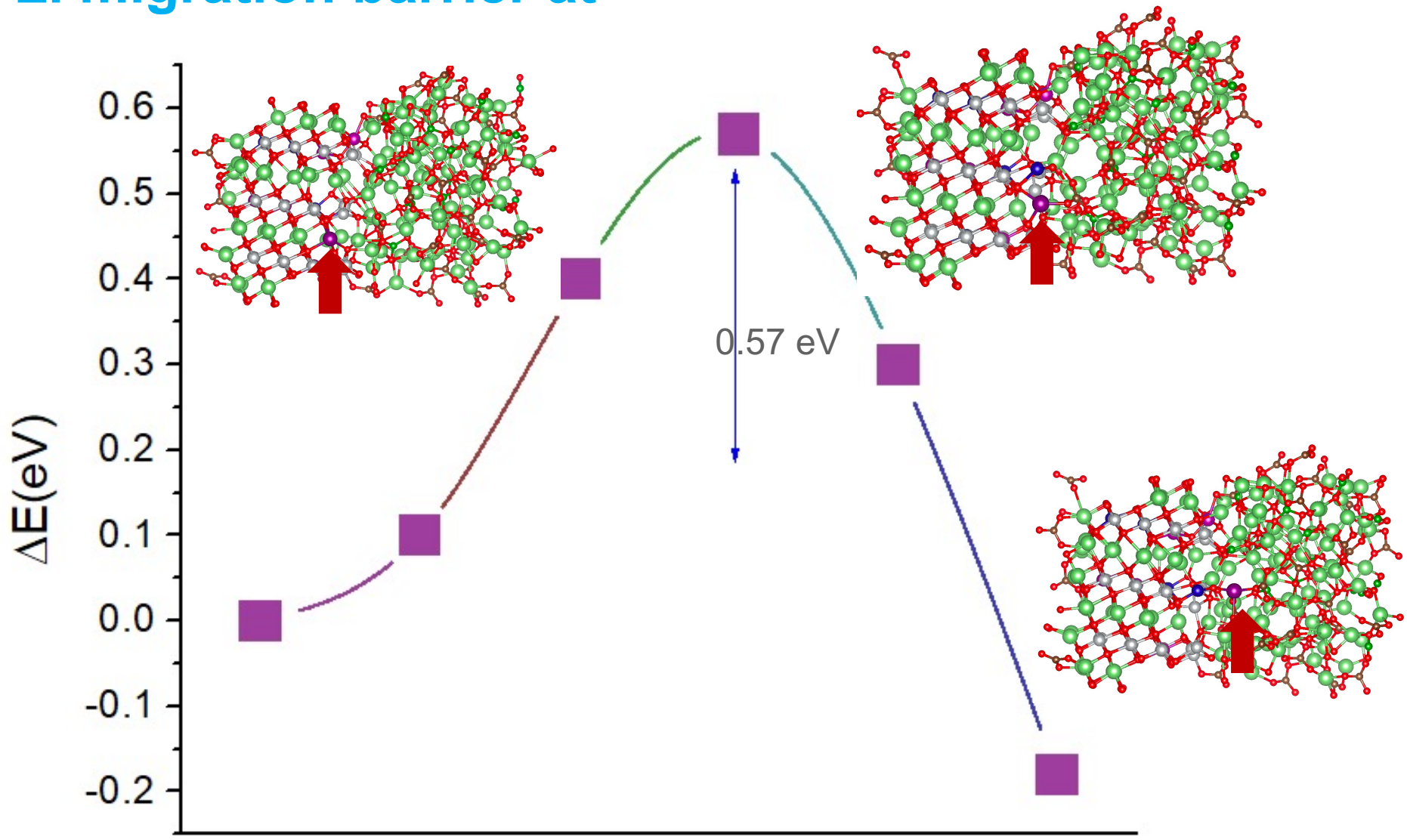
LLZO-LBCO interface

LLZO-LBCO interface : Li migration barrier at interface



Li migration at the LLZO-LBCO interface
Migration barrier : 0.68 eV

NMC-LBCO interface : Li migration barrier at interface

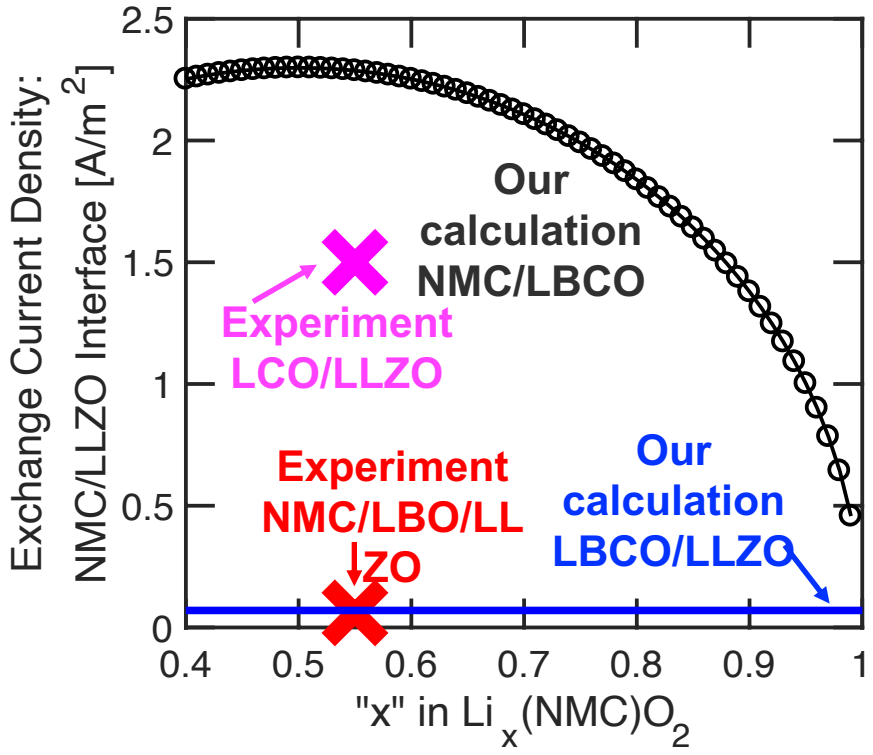


Li migration at the NMC-LBCO interface
Migration barrier : 0.57 eV

Exothermic reaction

Prediction of exchange current densities from atomistic simulations

Material interface	Energy barrier (eV)	Reaction rate constant (m/s)	Exchange current density (A/m²)	Experimental results (A/m²)
NMC/LLZO	0.6	7.5×10^3	4.0	N/A
NMC/LBCO	0.57	1.33×10^3	2.32	N/A
LBCO/LLZO	0.68	1.45×10^3	0.07	

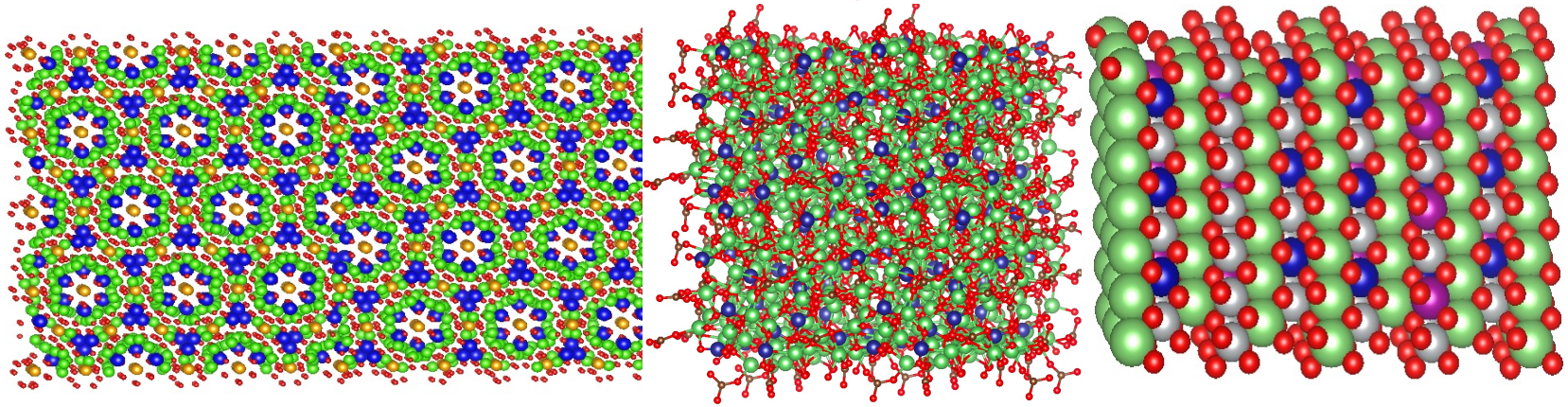


The sluggish transport across NMC/LBO/LLZO layer can be attributed to the larger energy barrier across LBCO/LLZO interface.

Impact of the LBCO Layer on the delamination

NMC/LLZO interface has the delamination: 75%

Interphase Layer LBCO



Fracture energy 3.8 J/m^2
Barrier 0.67eV

Approximate delamination: 40%

Fracture energy 6.5 J/m^2
Barrier 0.57 eV

Approximate delamination: 20%

LBCO interphase layers to minimize cathode/LLZO delamination

Interphase layer: LBCO (Lithium Borate + Lithium Carbonate)

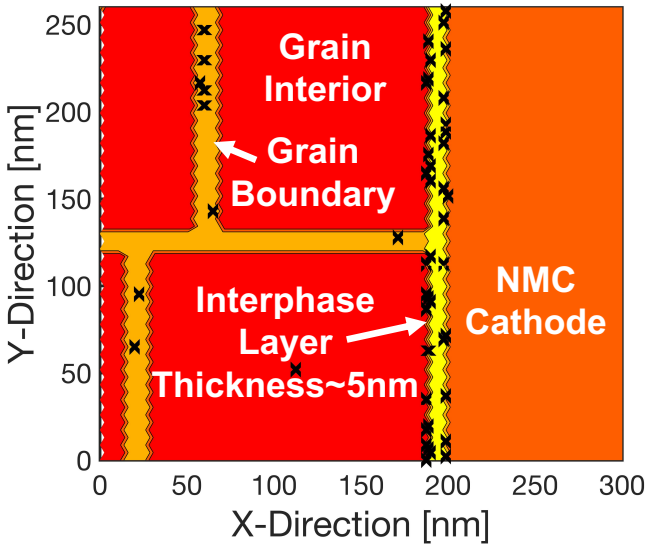
$$\kappa_{LBCO} = 10^{-2}\kappa_{LLZO}$$

$$YM_{LBCO} = 0.5 \cdot YM_{LLZO}$$

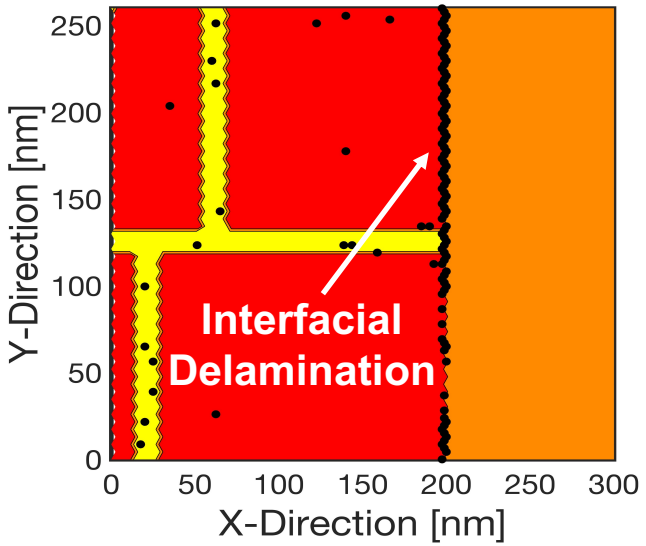
CC-CV Charge and CC Discharge

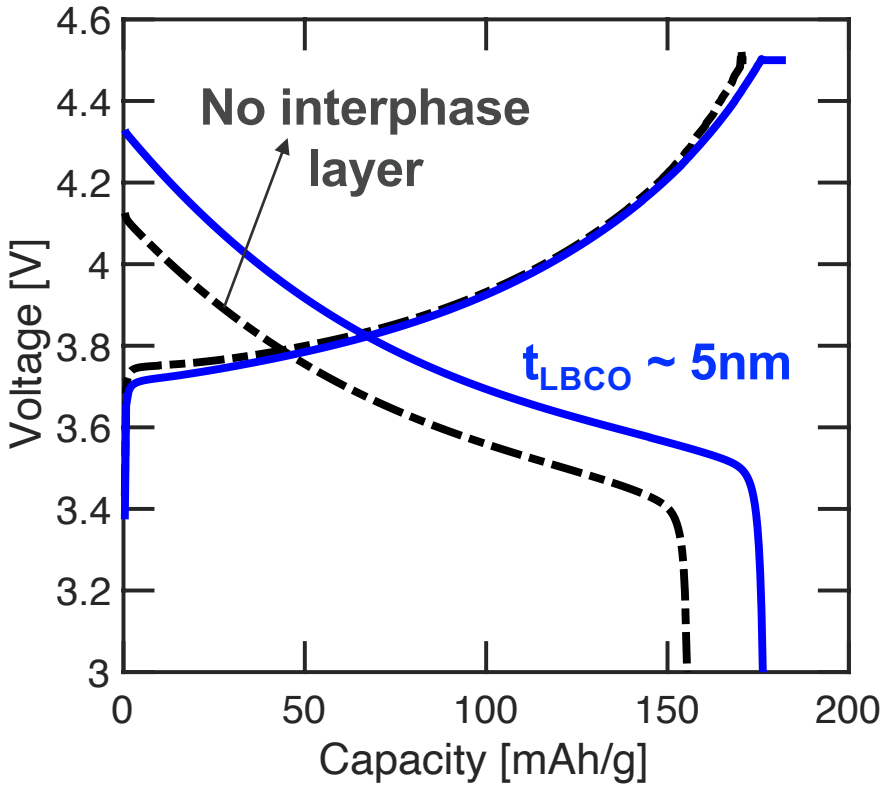
I_{app} = 1A/m²

Voltage window: 3.0V – 4.5V



After Discharge t_{LBCO} =0



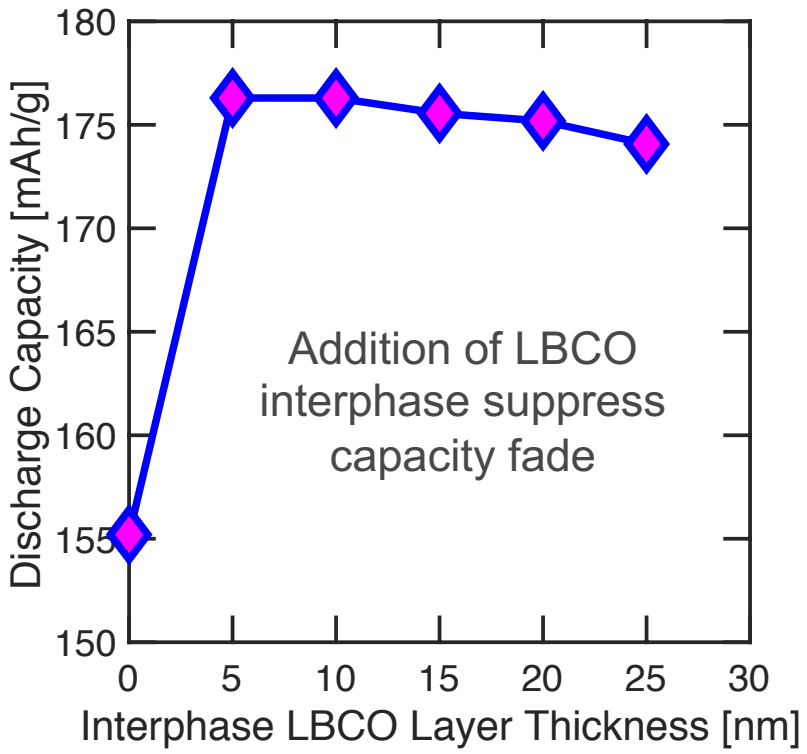


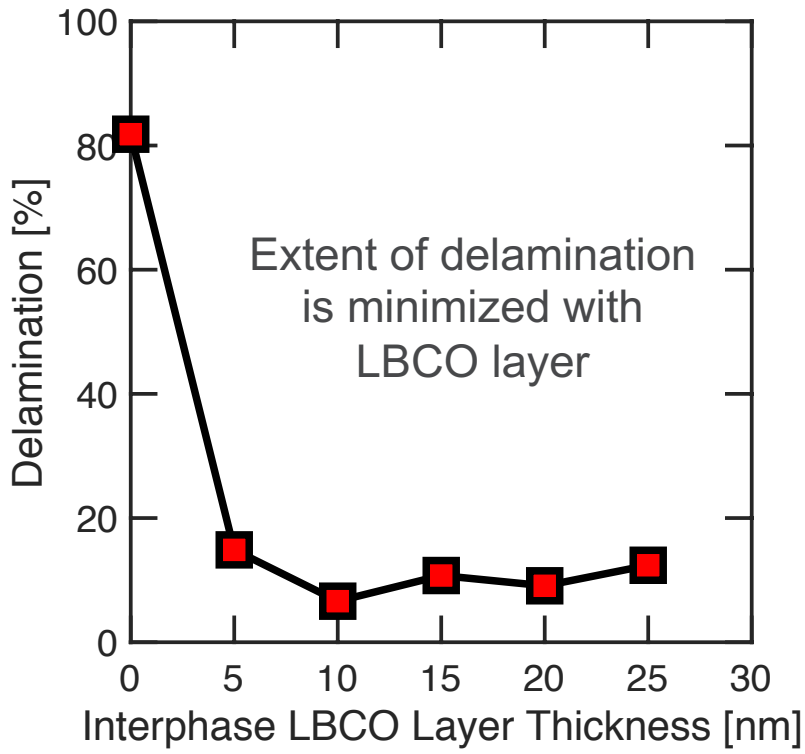
LBCO interphase layers help to mitigate interfacial delamination and subsequent capacity fade.

Impact of LBCO Layer Thickness on Capacity and Extent of Delamination

LBCO interphase layer thickness varied between 5 nm and 25 nm.

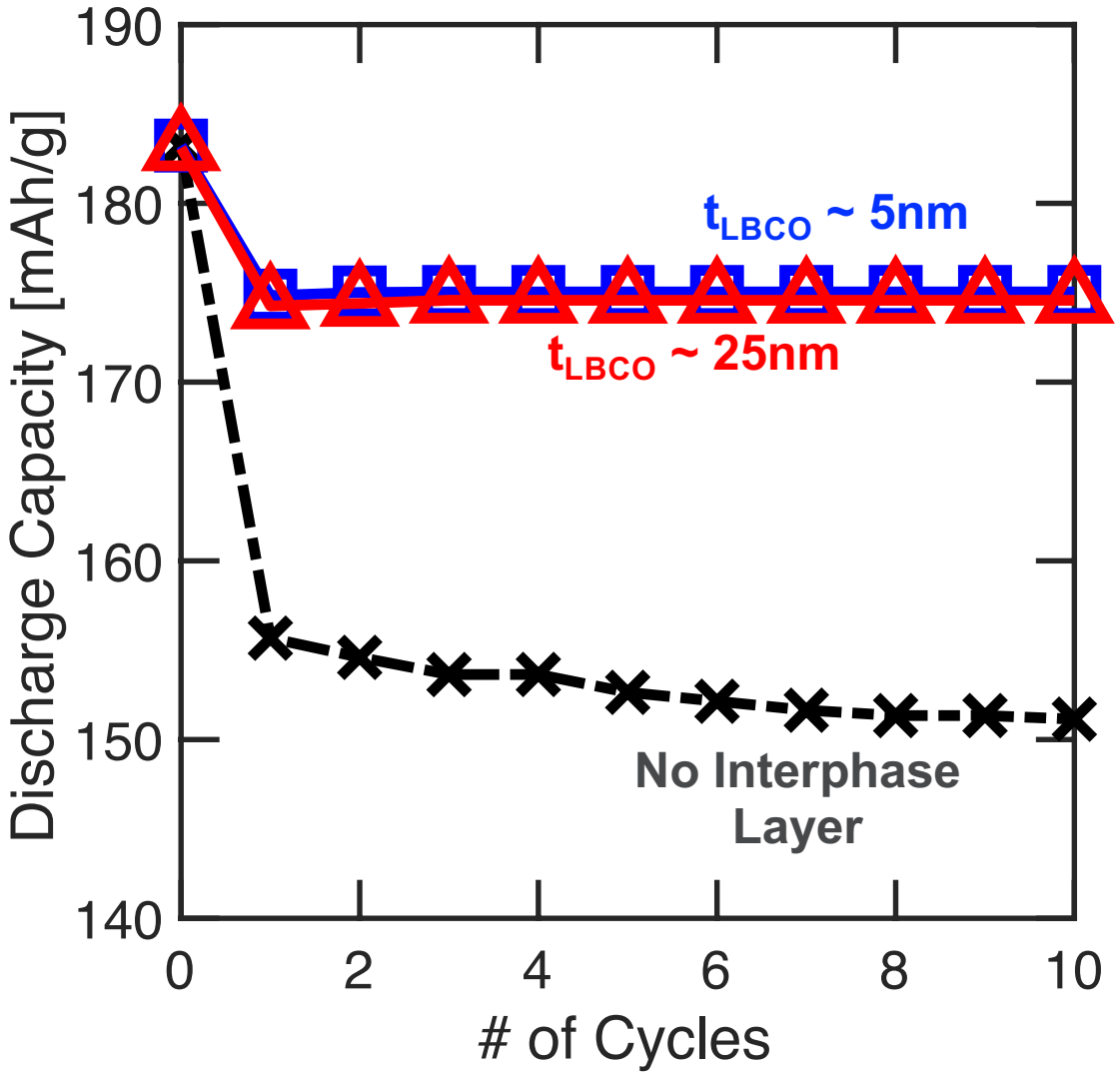
$I_{app} = 1A/m^2$





Ohmic potential drop causes extra first cycle capacity fade for thicker LBCO.LBCO interphase layers help to mitigate interfacial delamination

Influence of Multiple Cycles on the Delamination Induced Capacity Fade



$$\kappa_{LBCO} = 10^{-2}\kappa_{LLZO}$$

$$YM_{LBCO} = 0.5 \cdot YM_{LLZO}$$

CC-CV Charge and CC Discharge

I_{app} = 1A/m^2

Voltage window: 3.2V – 4.5V

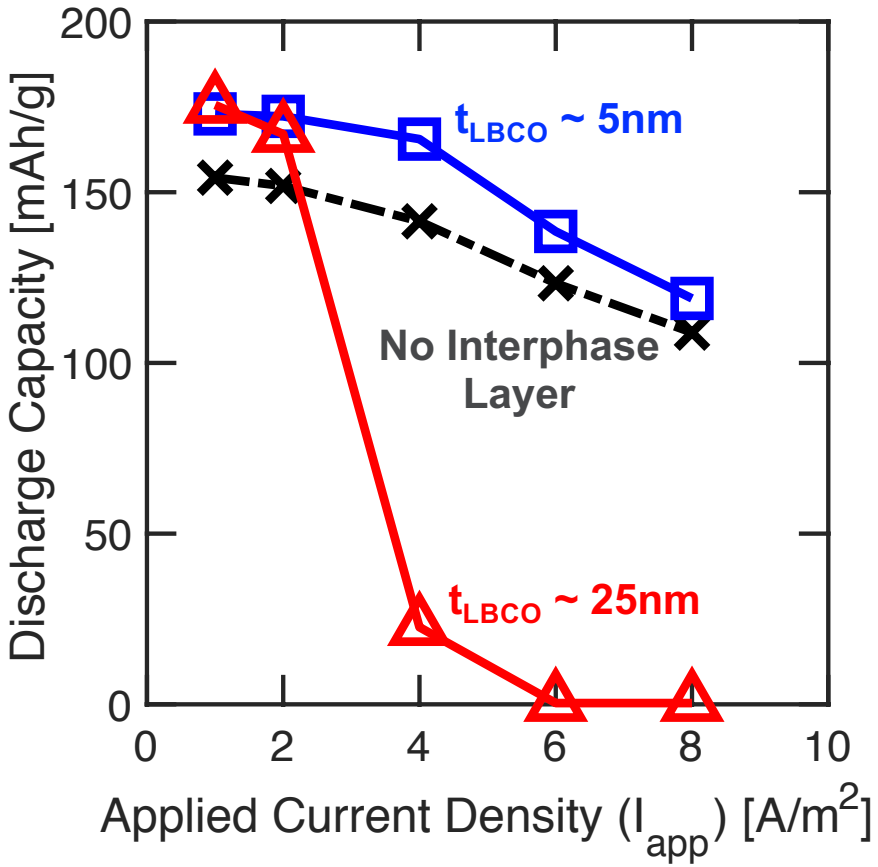
Capacity fade observed in two steps:

1. Large capacity fade in the first cycle
2. Slow capacity fade later

LBCO interphase layer can mitigate the initial capacity fade as well as the slow capacity decay for longer cycles.

Influence of LBCO Layer in Capacity Retention at Higher Current Densities

First cycle discharge capacity



Conductivity $\kappa_{LBCO} = 10^{-2}\kappa_{LLZO}$

Voltage window: 3.2V – 4.5V

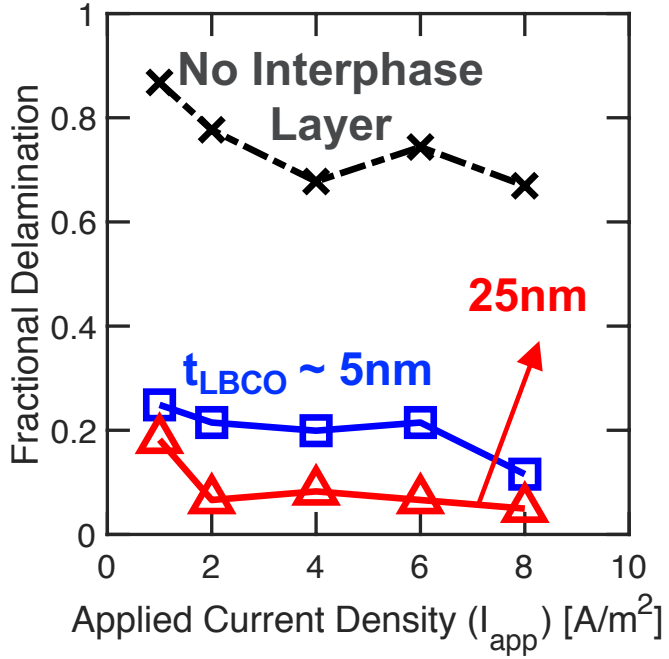
CC-CV Charge and CC Discharge

Two possibility behind lower capacity at higher currents:

1. **Enhanced delamination induced fade**
2. **Higher ohmic drop from small conductivity of LBCO**

Lower conductivity of LBCO is a challenge.

Better interphase layers with higher conductivity needs to be designed.



Response to last year reviewer's comments

No comments from last year.

Proposed Future Work

- Estimation of lithium transport barrier at the Li_6PS_5Cl SSE and the NMC-811/Li_6PS_5Cl interface :
  - Effective exchange current density will be estimated at NMC/ and Li_6PS_5Cl SSE interface
  - Interfacial formation/Binding energy between the NMC cathode with Li_6PS_5Cl SSE will be calculated
- Estimation of the extent of interfacial delamination between NMC and Li_6PS_5Cl solid electrolytes.
- Application of interphase layers in minimizing the delamination between NMC cathodes and soft sulfide-based electrolytes.
- Interdiffusion of transition metal ions between cathode and solid-electrolyte and formation of a passivating interphase layer, which is more prominent for sulfide based solid-electrolytes.

Proposed Future Work (cont.)

- Incorporate the parameters estimated from atomistic calculations into the continuum level mesoscale model
  - Predict the effect of grain boundary resistance on the overall voltage-capacity performance
  - Estimate the impact the delamination and inter-granular fracture on the overall impedance behavior.

- Investigate the impact of interfacial layer on the possibility of minimizing the interfacial delamination between the cathode and solid-electrolytes.

Collaborations with other institutions and companies

- V. Srinivasan, P. Barai, ANL
  - Development of continuum based mesoscale models for running simulations using the parameters obtained from atomistic analysis.
- Z. Chen, ANL
  - Experimental characterization of electrode-electrolyte interface
- B. Narayanan, U of Louisville
  - Discussions regarding the atomistic analysis conducted at ANL to estimate elastic and transport properties of LLZO.

Summary

- Atomistic level calculations were used to obtain parameters, DFT, ab initio MD, atomistic MD and MC needed for accurate mesoscale modeling of LLZO grain-interior, grain-boundary, and LLZO/LBCO/NMC cathode interfaces .

- Interfacial and mechanical degradation mechanisms were investigated at the atomistic level to develop a strategy for minimizing impact on performance.

- Incorporation of LBCO interphase layers between NMC and LLZO can help to minimize the extent of delamination and subsequent capacity fade.

- Lower ionic conductivity of LBCO is a challenge in obtaining good performance at higher current densities. Design of better interphase layers with higher ionic conductivities is necessary for successful application in solid-state lithium-ion batteries.