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

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DOE merit review

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Project ID# bat424

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

- Start: 2018
- Finish: 2023
- Completed: 40 %

Barriers

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

Budget

- Total project funding
  - DOE share: $ 995 K
  - Contractor 0
- FY 18: $ 300 K
- FY 19: $ 300 K
- FY 20: $395 K

Partners

- Interactions/ collaborations
  - V. Srinivasan, ANL
  - Z. Chen, ANL
  - B. Narayanan, U of Louisville

Project Objectives and Relevance

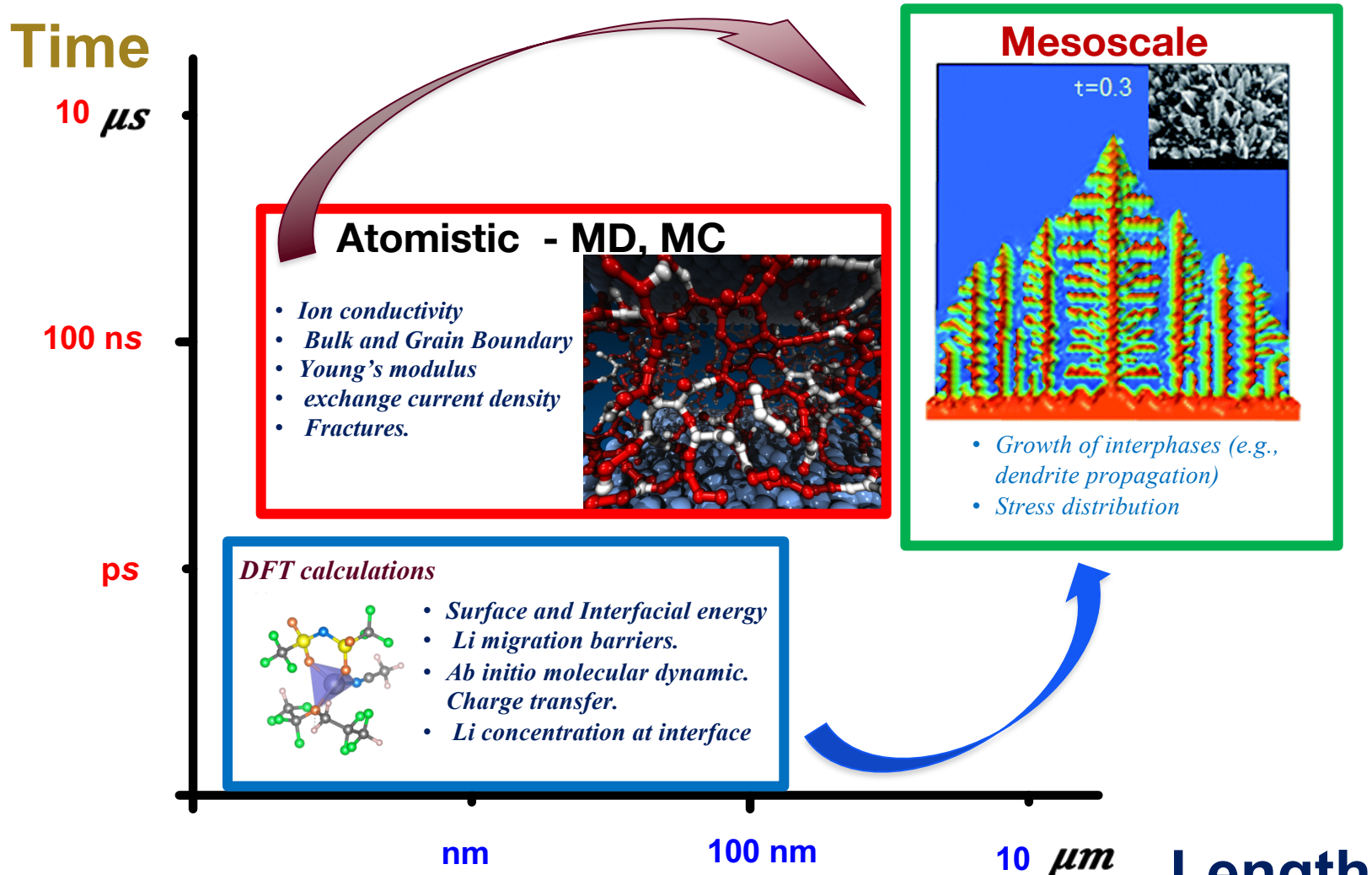
- In order to improve the safety of present day lithium ion batteries, replacement of liquid electrolytes with their solid state counterparts is a necessity.
- Multi-scale modelling efforts have been adopted to obtain an *in-depth* understanding of the interaction between the electrode and the solid electrolyte aimed at developing highly efficient solid state electrolytes batteries.
- Properties estimated from DFT calculations feed 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.

FY20 Milestones

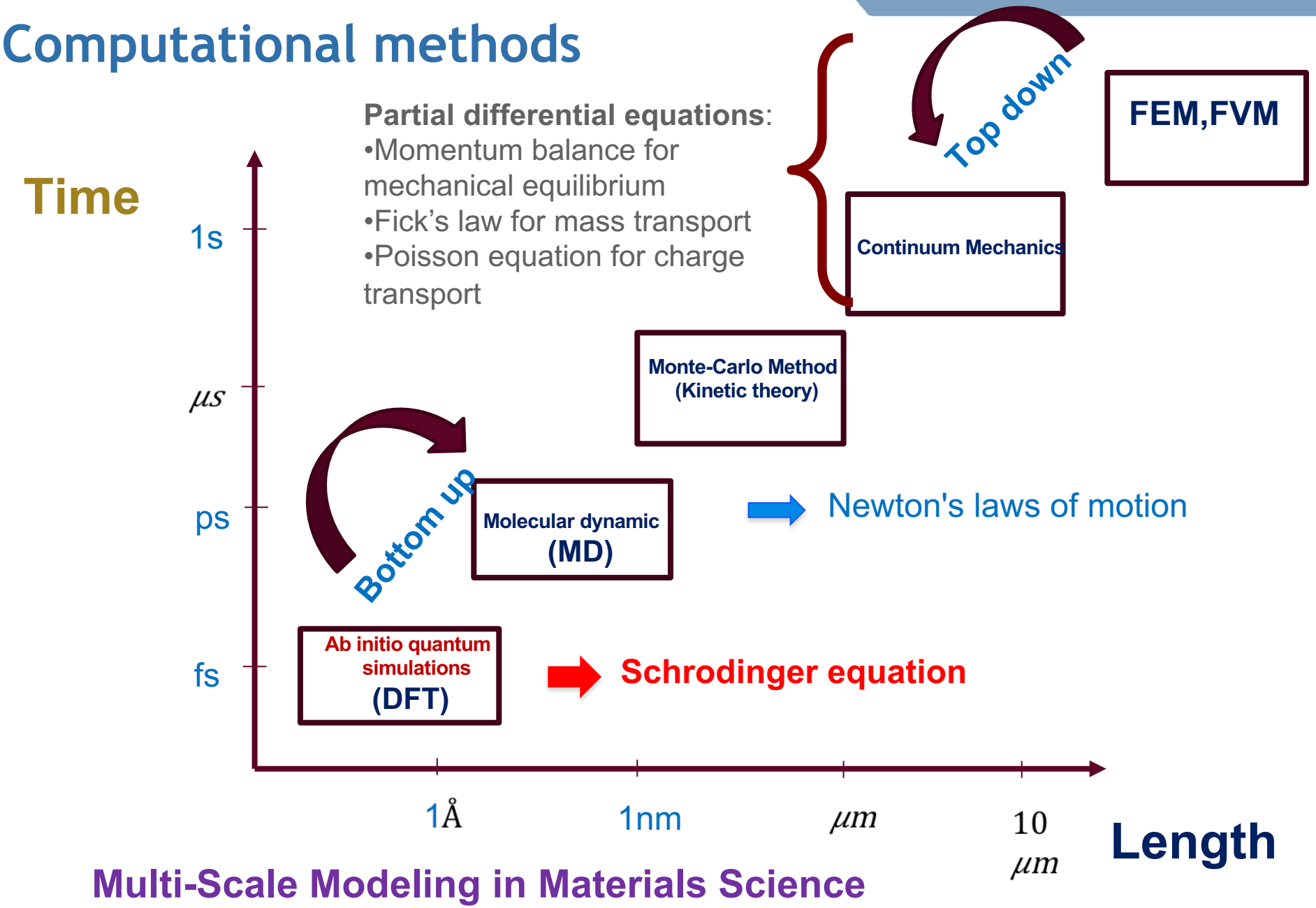
Month/ Year	Milestones
Dec/19	Determine the most stable interface between LLZO solid electrolyte and LBCO coating material. Calculate Li migration barriers at interface from LLZO to LBCO material. Q1 (**Completed**)
Mar/20	Determine the most stable interface between NMC cathode and LBCO coating material and Calculate Li transport barrier from NMC to LBCO material. Q2 (**Completed**)
Jun/20	Calculated fracture/interfacial energy. Estimate exchange current density associated with charge transfer from LBCO coating to LLZO and NMC. Q3 (**Initiated**)
Sep/20	Incorporate the information obtained from the atomistic calculations into the mesoscale model and predict the impact of coating on performance NMC/LBCO/LLZO performance. Q4 (**Initiated**)

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

Multi-Scale Modeling methods



Computational methods

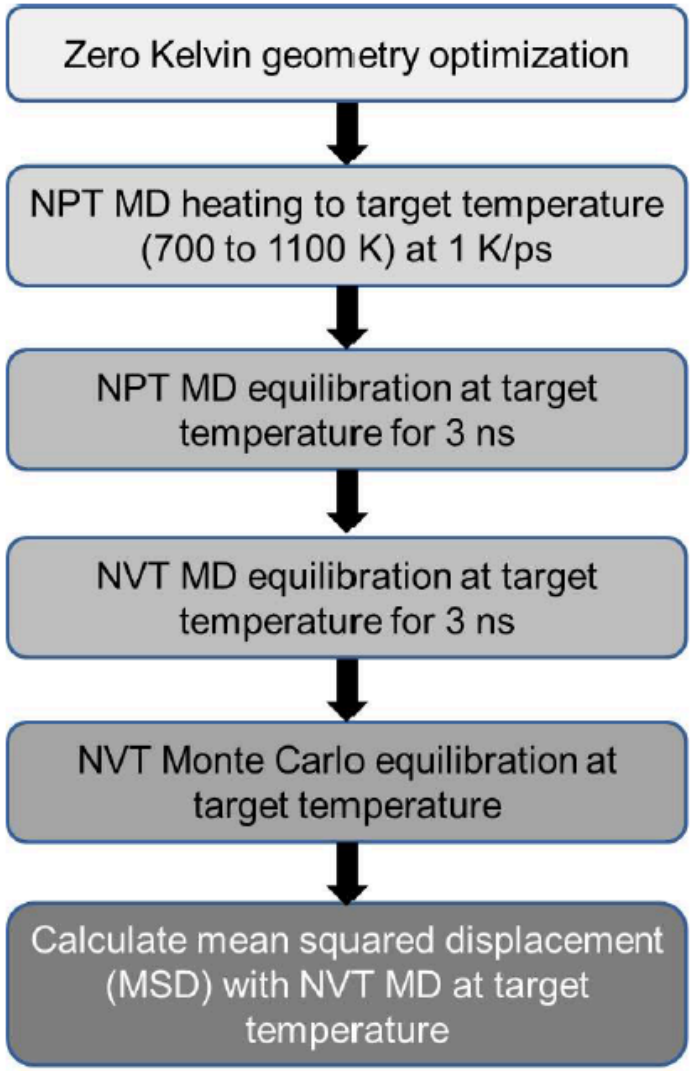


Multi-Scale Modeling in Materials Science

Summary of the computational procedures

- 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 imported 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 ~ 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. Estimation of transport properties in LLZO

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

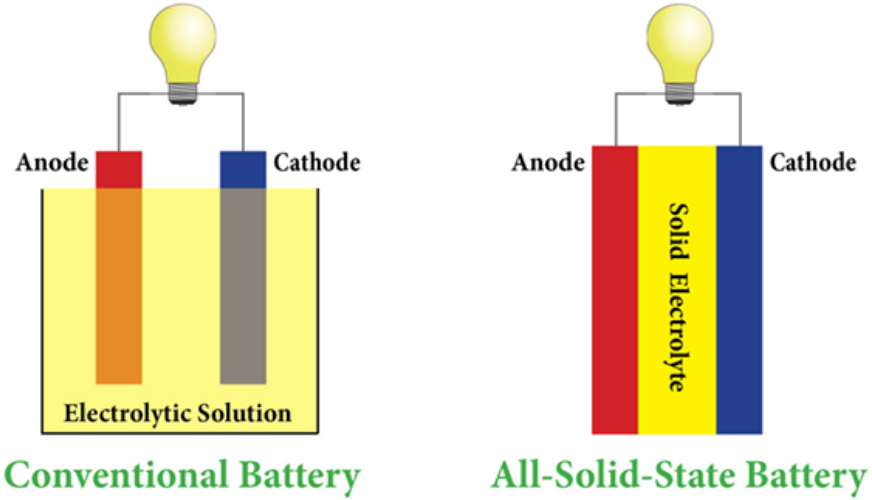
II. Estimation of mechanical properties of NMC/LLZO interface

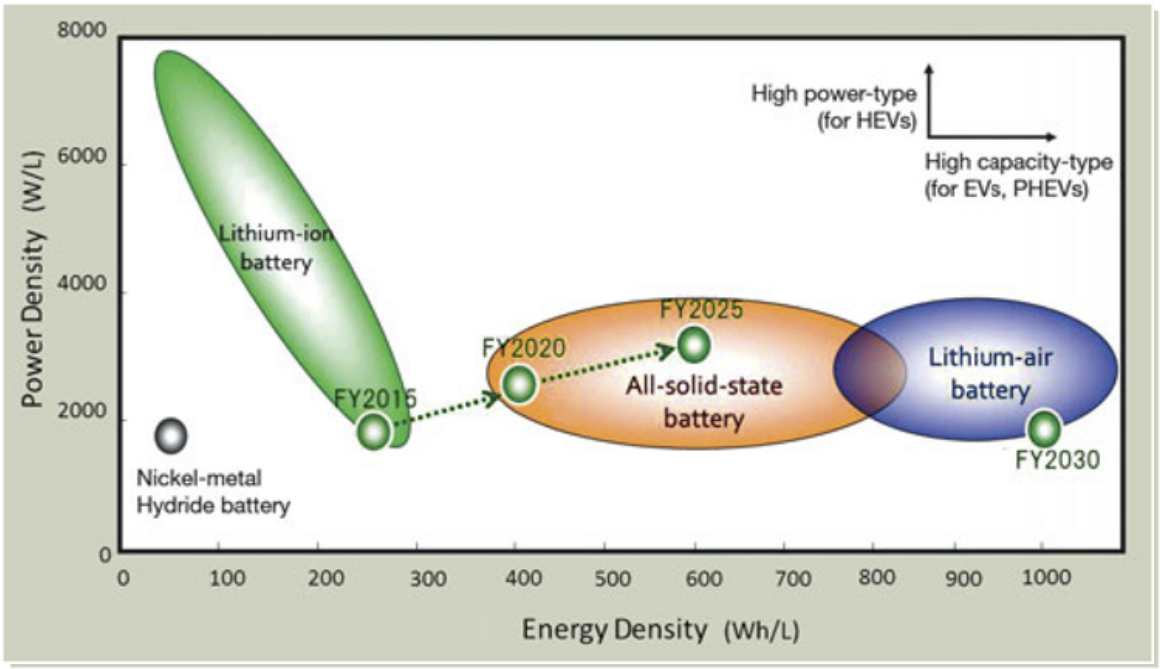
- Young's modulus in the bulk and grain-boundary of LLZO has been predicted by MD simulations in previous quarter.
- Fracture energy of NMC/LLZO interface has also been estimated.

III. Incorporation with mesoscale models

- The elastic modulus of LLZO bulk and GB, fracture energy of NMC/LLZO interface, conductivity of Li within bulk and GB of LLZO, and exchange current density between Li/LLZO and NMC/LLZO, estimated at the atomistic level, have been incorporated into the mesoscale model, where volume expansion/contraction of NMC cathode induced delamination at the NMC/LLZO interface have been studied.

Why solid state batteries?





Potentially:

- Better safety
  - No liquid
  - No flammable solvents
- Easier battery management
  - Bipolar design
  - Small number of cells
- Higher volumetric energy density.

From Toyota

Objectives of solid state electrolyte multi-scale modeling

Overall objectives :

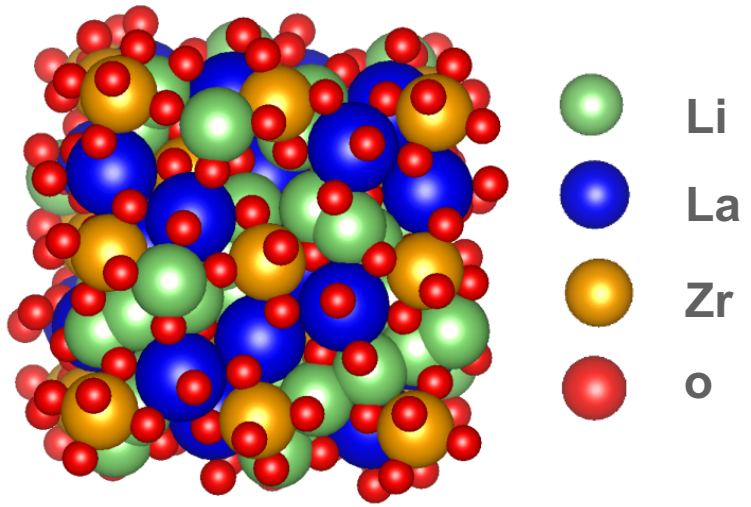
- Develop atomistically-informed microscale models capable of successfully capturing the multi-scale multi-physics phenomena that occurs during Li-metal deposition processes.
- Devise strategies to minimize the impact of degradation mechanisms and enhance the performance and lifetime of next-generation Li-ion batteries.

Atomistic level objectives

- Use atomistic level calculations to obtain parameters needed for accurate mesoscale modeling of grain-interior, grain-boundary, and electrode-electrolyte interfaces
- Investigate degradation mechanisms at the atomistic level to contribute to strategy for minimizing impact on performance

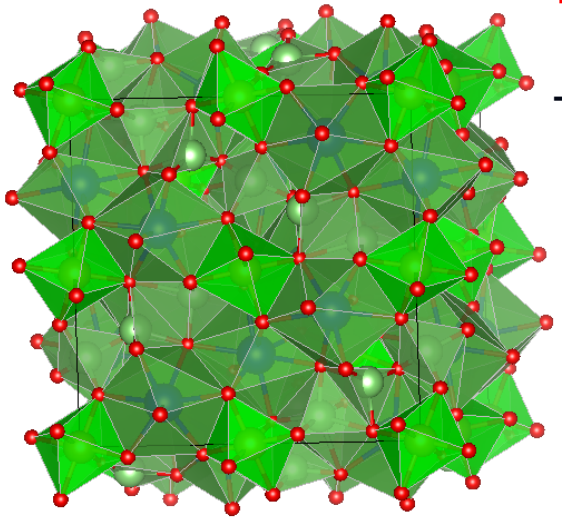
Initial focus:

Electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO)



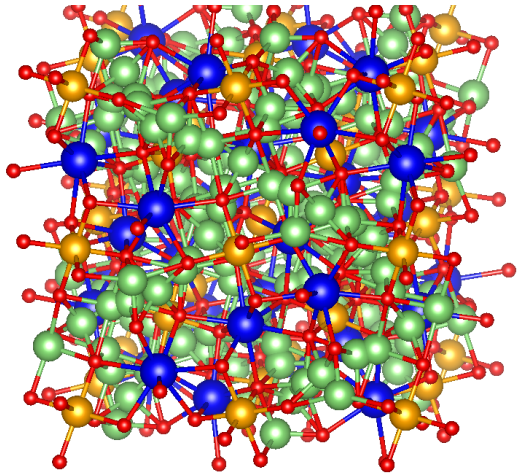
Electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO)

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**

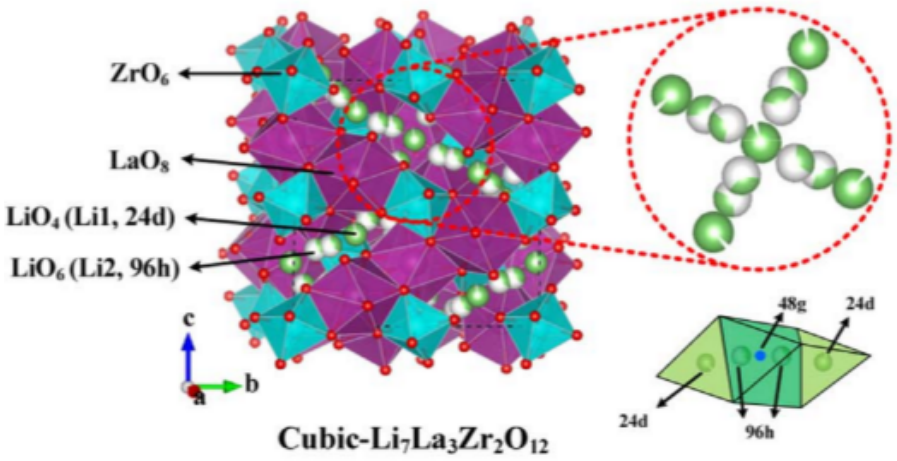


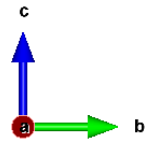
Cubic phase :
C ~ 10^{-3} S/cm. T ~ 25 ^{0}C

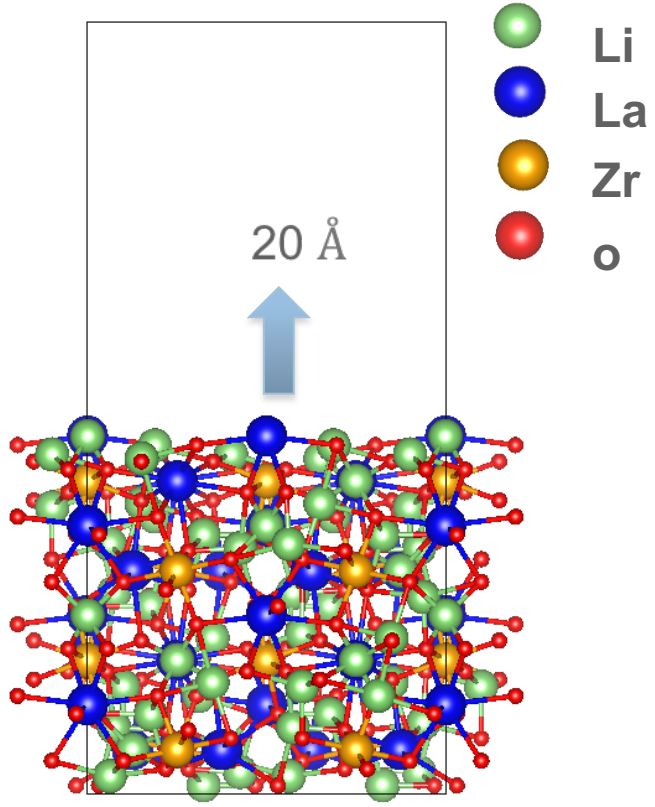
K. Kerman et. al. Journal of The Electrochemical Society, 164 (7) A1731-A1744 (2017)
T. Thompson et. al. ACS Energy Lett., 2017, 2 (2), pp 462–468

DFT Analysis: LLZO Surface calculations

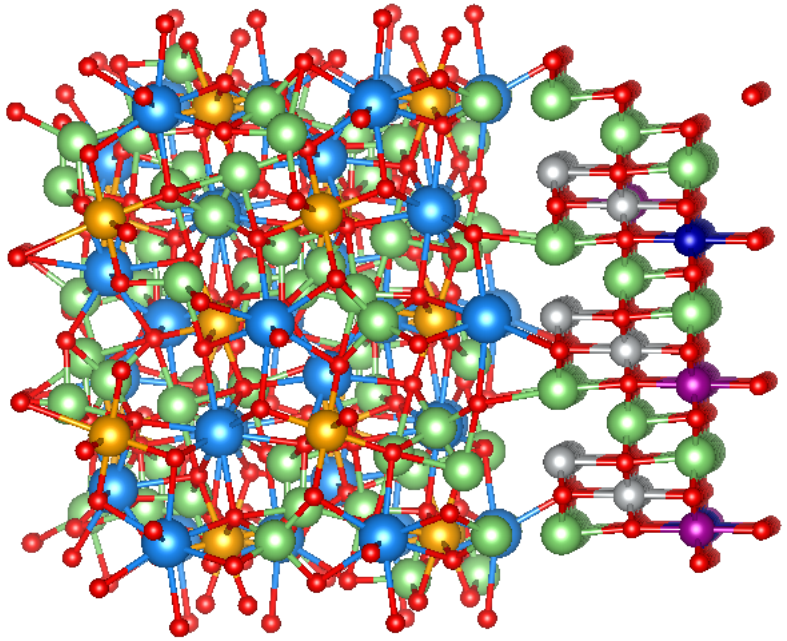
- Plane Wave Projector Augmented-Wave (PAW) Density Functional Theory (DFT) methods
- VASP code Spin polarized calculations.
- Generalized Gradient Approximation. Exchange correlation is described by Perdew-Burke-Ernzerhof (PBE) functional.
- 7 surfaces, modeled through stoichiometric slabs with 4 different terminations (28 calculations).
- Supercell : 192 atoms





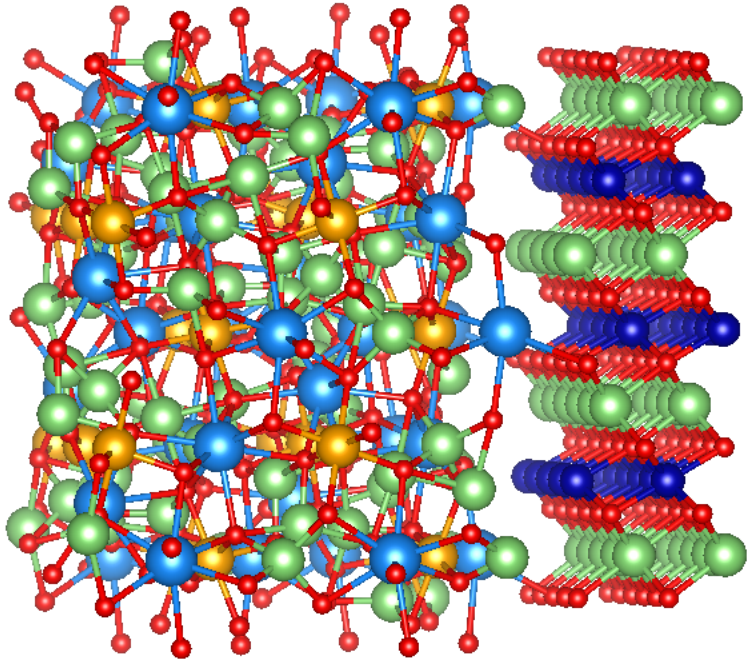


The Interface Between LLZO and NMC cathode



LLZO (100) Li termination/NMC(10-14)

~ 11 % mismatch



LLZO (100) Li termination/NMC(10-10)

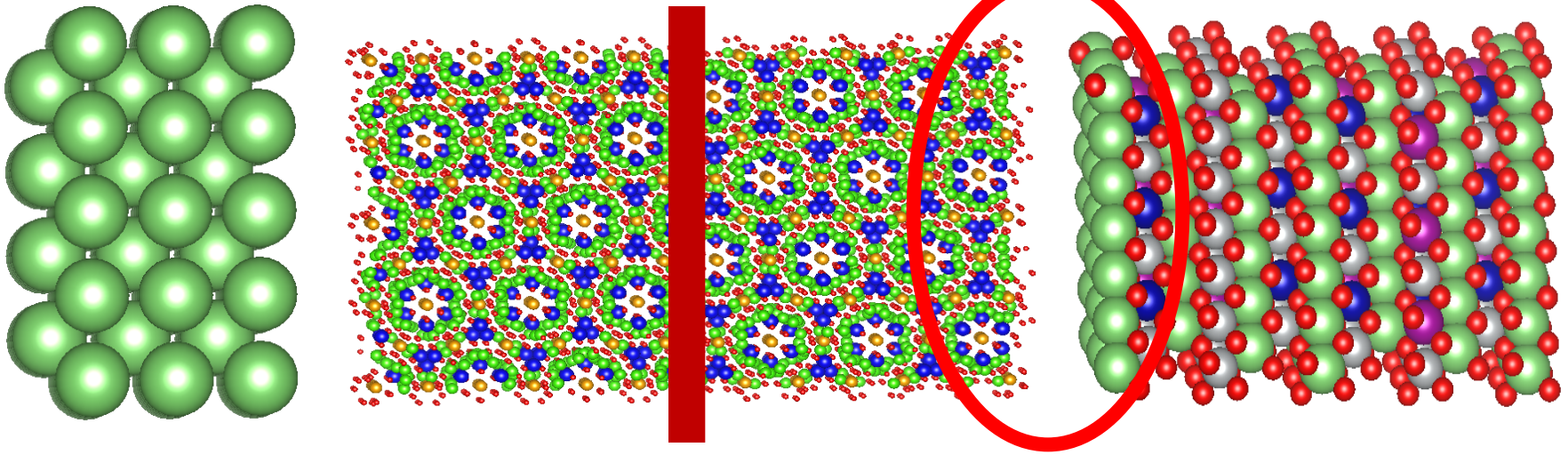
~ 5.8 % mismatch

Li/ solid-electrolyte interface /Cathode

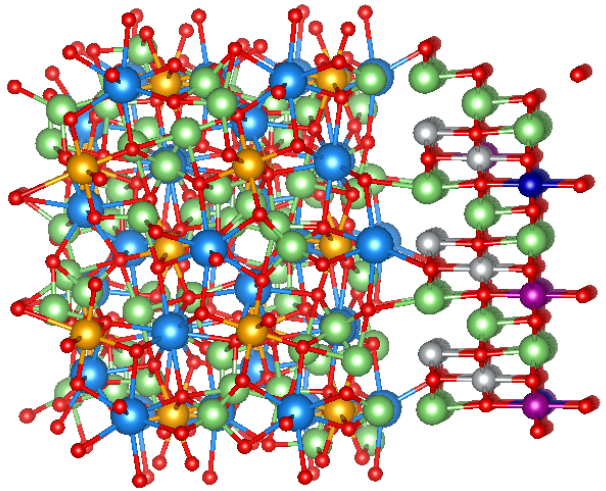
Li anode

LLZO

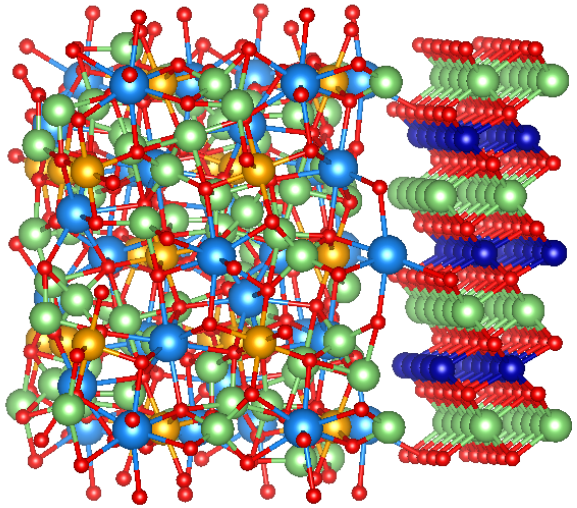
NMC622 cathode



Two different NMC622 surfaces are being analyzed Using DFT+U with spin polarized calculations



LLZO (100) Li termination/NMC(10-14) ~ 11 % mismatch



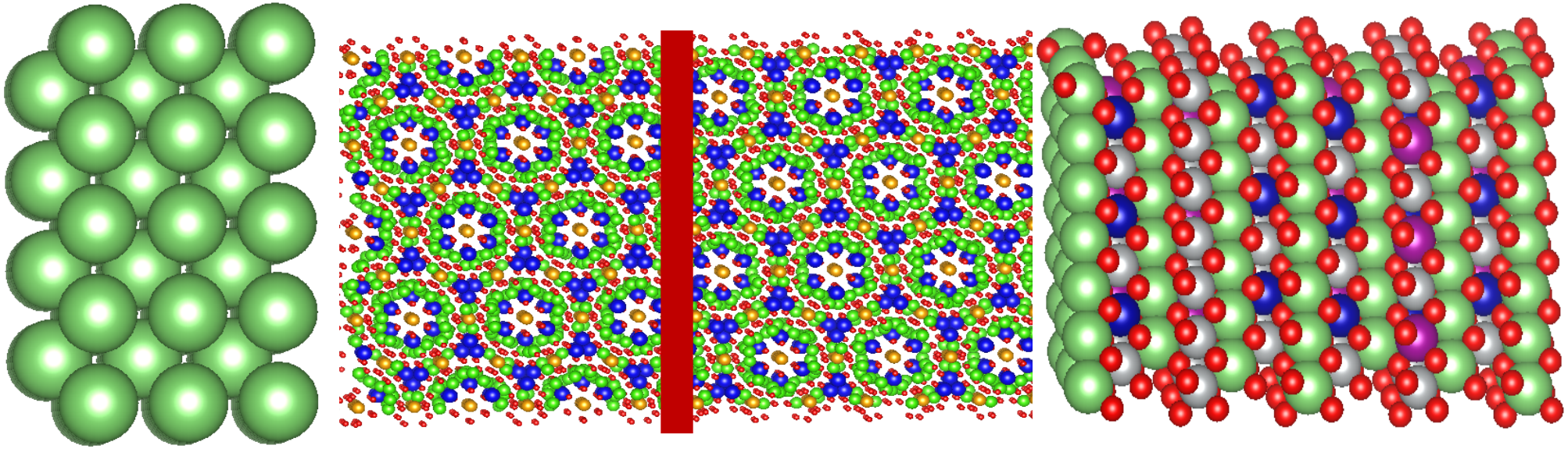
LLZO (100) Li termination/NMC(10-10) ~ 5.8 % mismatch

Li-LLZO-NMC interfaces

Li anode

LLZO

NMC cathode



Li (100) /LLZO (100) with Li termination

spin polarized DFT

LLZO (100) with Li termination \ NMC(10-14) \ NMC(10-10)

- Exchange current density is defined as:

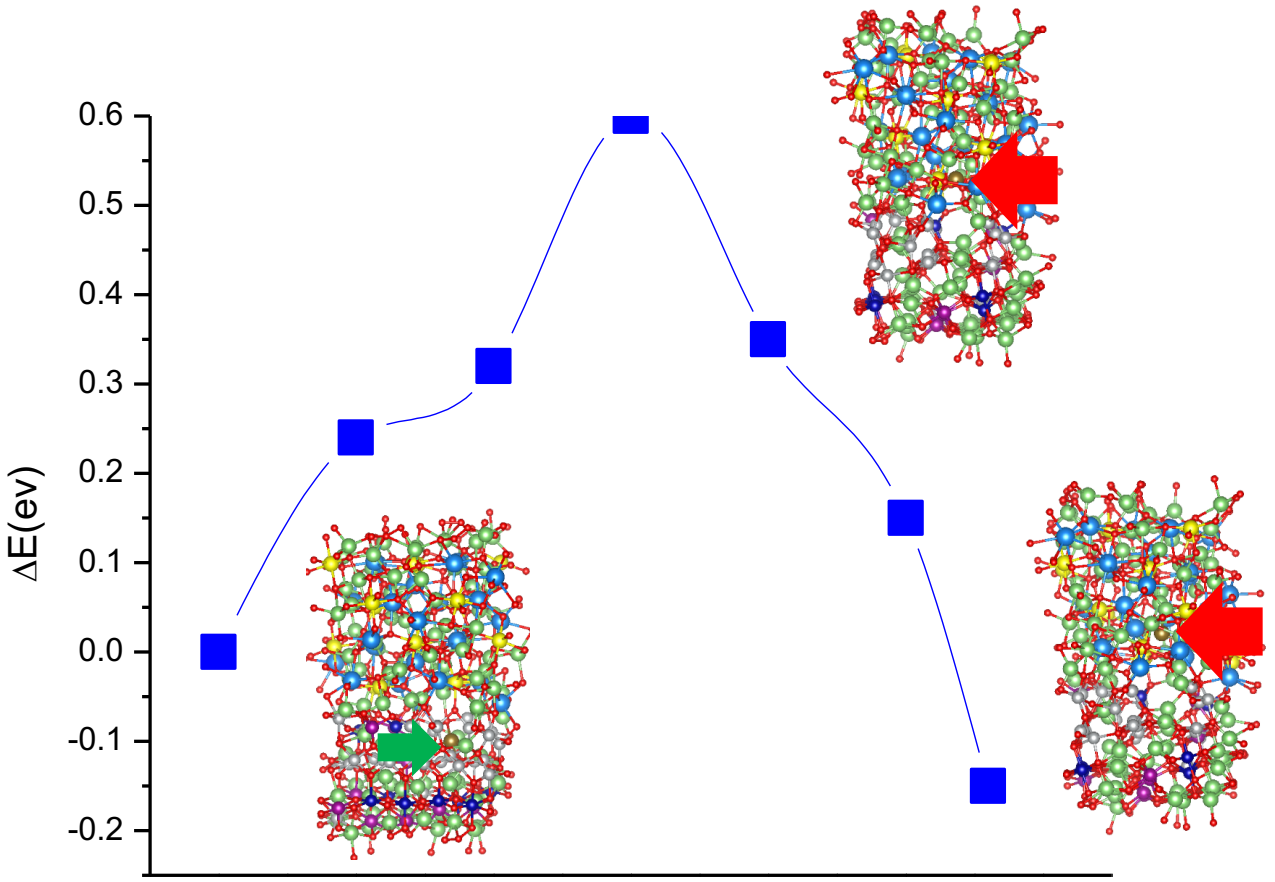
$$i_0 = Fk_{ref} \cdot \left(c_{Li^+}\right)^{0.5} \cdot \left(c_s\right)^{0.5} \cdot \left(c_{s,\max} - c_s\right)^{0.5}$$

- Reaction rate constant can be written as:

$$k_{ref} = k_0 \exp\left(-\Delta G/\left(k_B T\right)\right)$$

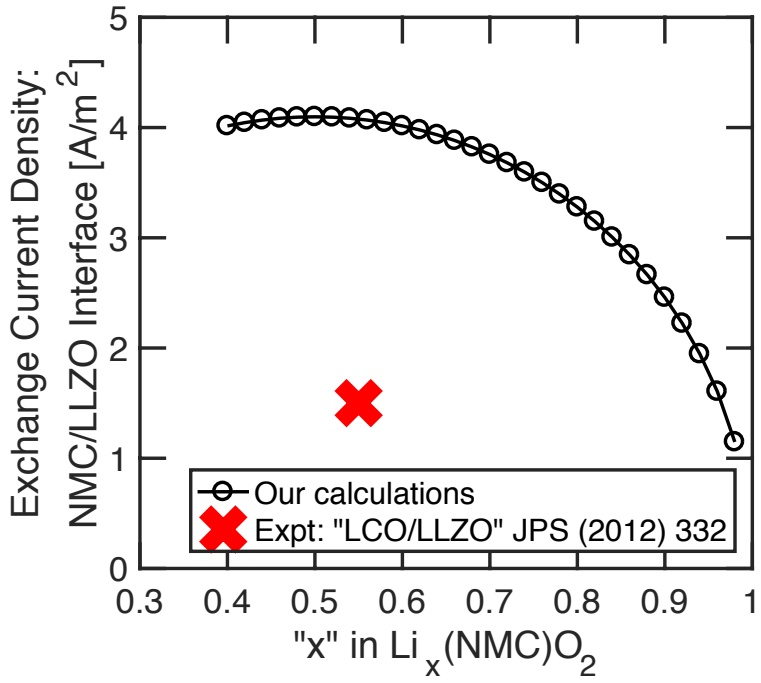
Activation energy barrier between LLZO and NMC 622

DFT+U with spin polarized calculations:
Li moves from NMC to LLZO
Energy Barrier is **0.6 eV**



Exchange current density as predicted from the atomistic calculations

- Exchange current density is defined as: $$i_0 = Fk_{ref} \cdot \left(c_{Li^+}\right)^{0.5} \cdot \left(c_s\right)^{0.5} \cdot \left(c_{s,\max} - c_s\right)^{0.5}$$
- Reaction rate constant can be written as: $$k_{ref} = k_0 \cdot \exp\left(-\Delta G / \left(k_B T\right)\right)$$



Our theoretical predicted exchange current density is within the same order of magnitude as that observed in experiments.

Estimation of Interfacial formation energy or fracture energy

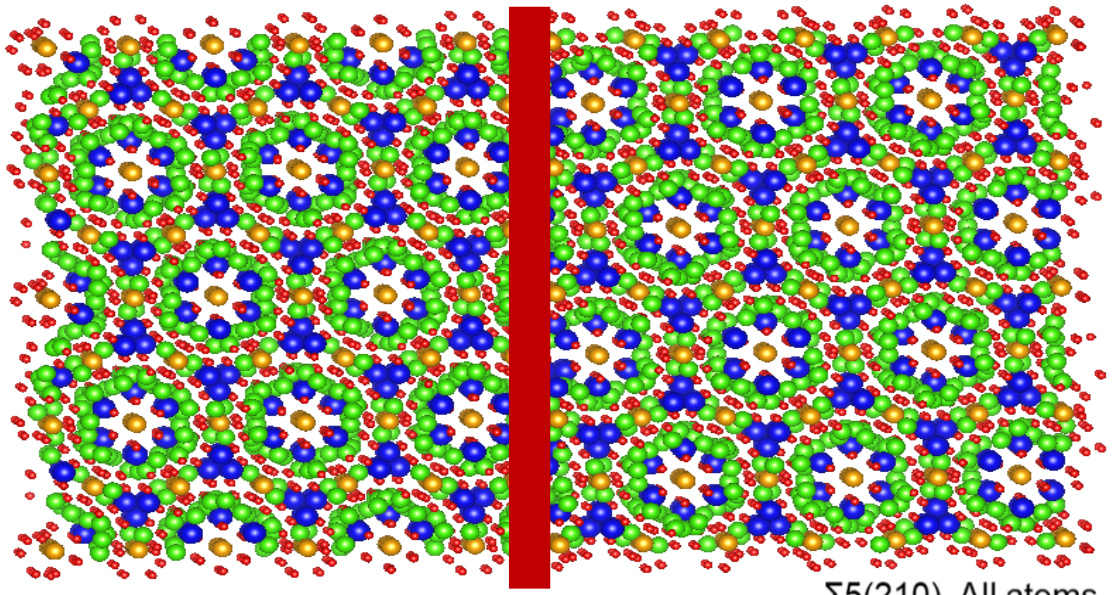
Interfacial formation energies obtained from ab initio calculations

(DFT+U with spin polarized calculations).

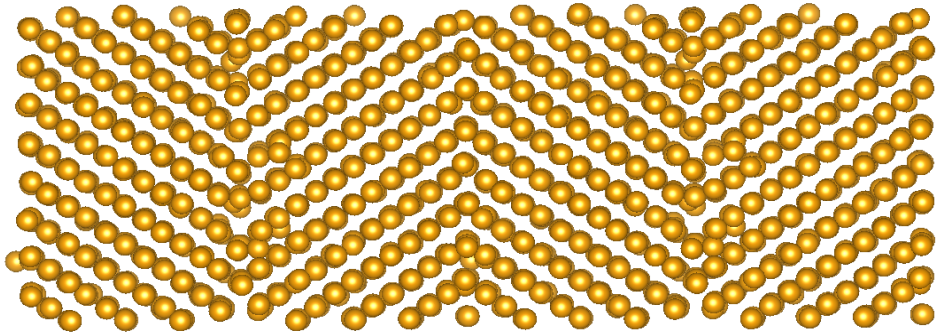
$$E_f = (E_{AB} - N_A.E_A - N_BE_B - Est\ ) / 2S$$

	(10-10) NMC/LLZO	(10-14) NMC/LLZO
GGA (SP)	1.27 J/m2	1.81 J/m2
GGA+U (SP)	1.23 J/m2	1.75 J/m2

MD Analysis: LLZO grain boundaries



Σ5(210), All atoms



Only Zr atoms

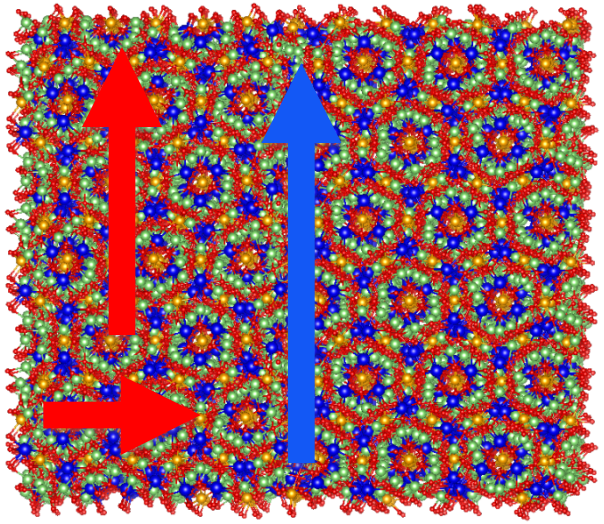
Properties input for continuum modeling studies:

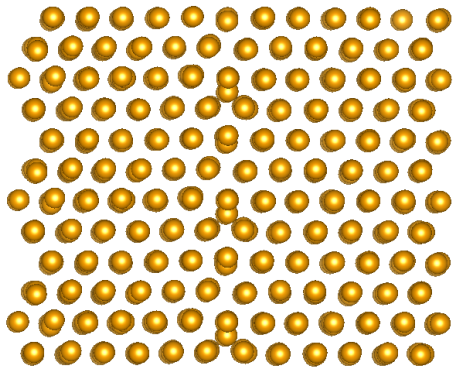
- barriers for lithium migration at the interface.
- Li ion concentration at GB
- *exchange current density*
- ionic conductivity
- Young's modulus
- Fractures

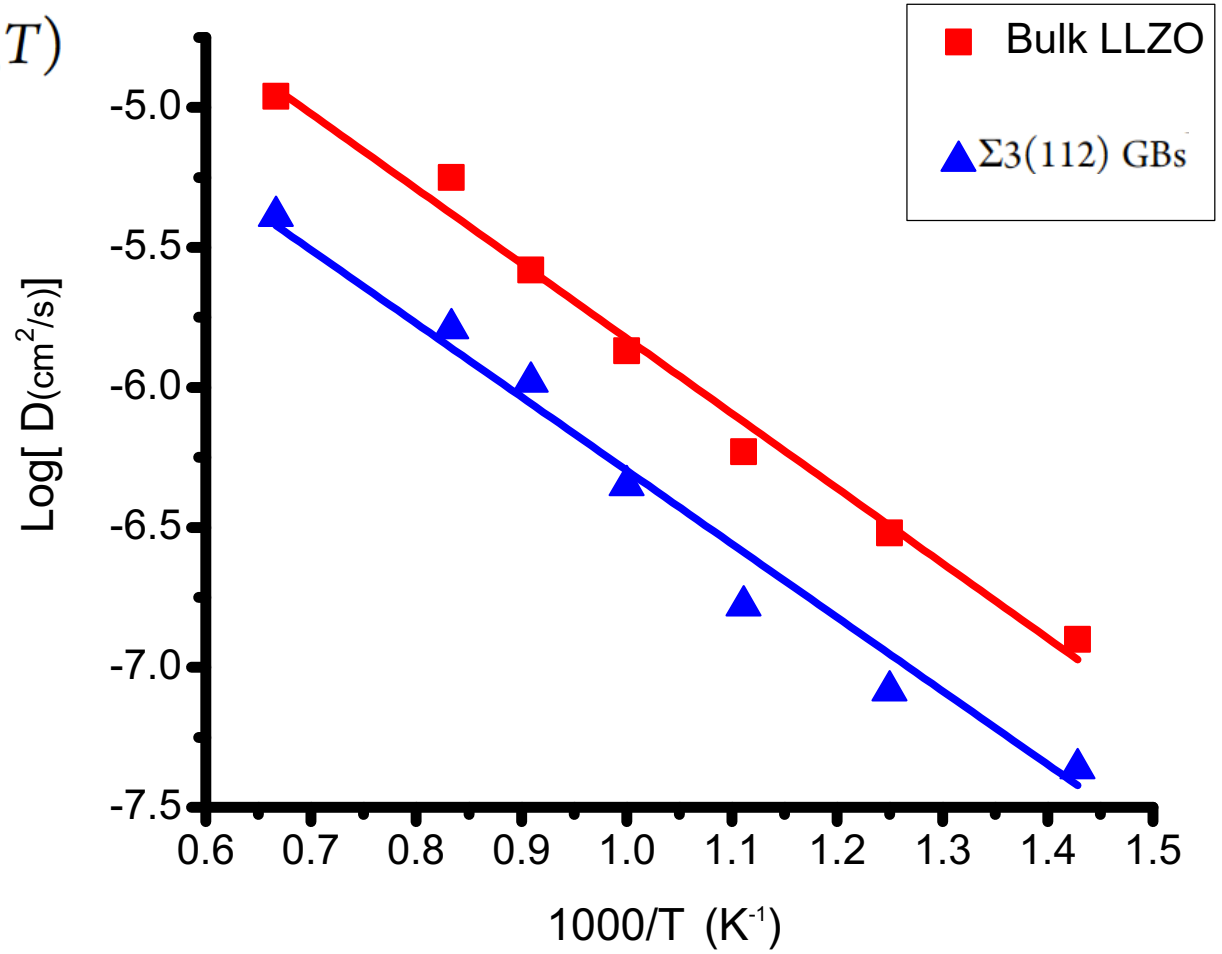
Calculated Li-ion diffusivity *D* for GB and Bulk

Σ3(112) GBs

$$D(T) = D_0 \exp(-E_a/k_B T)$$



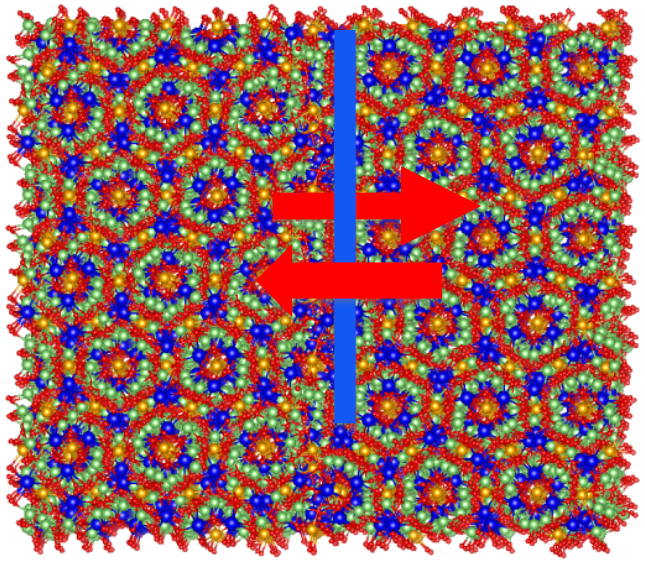




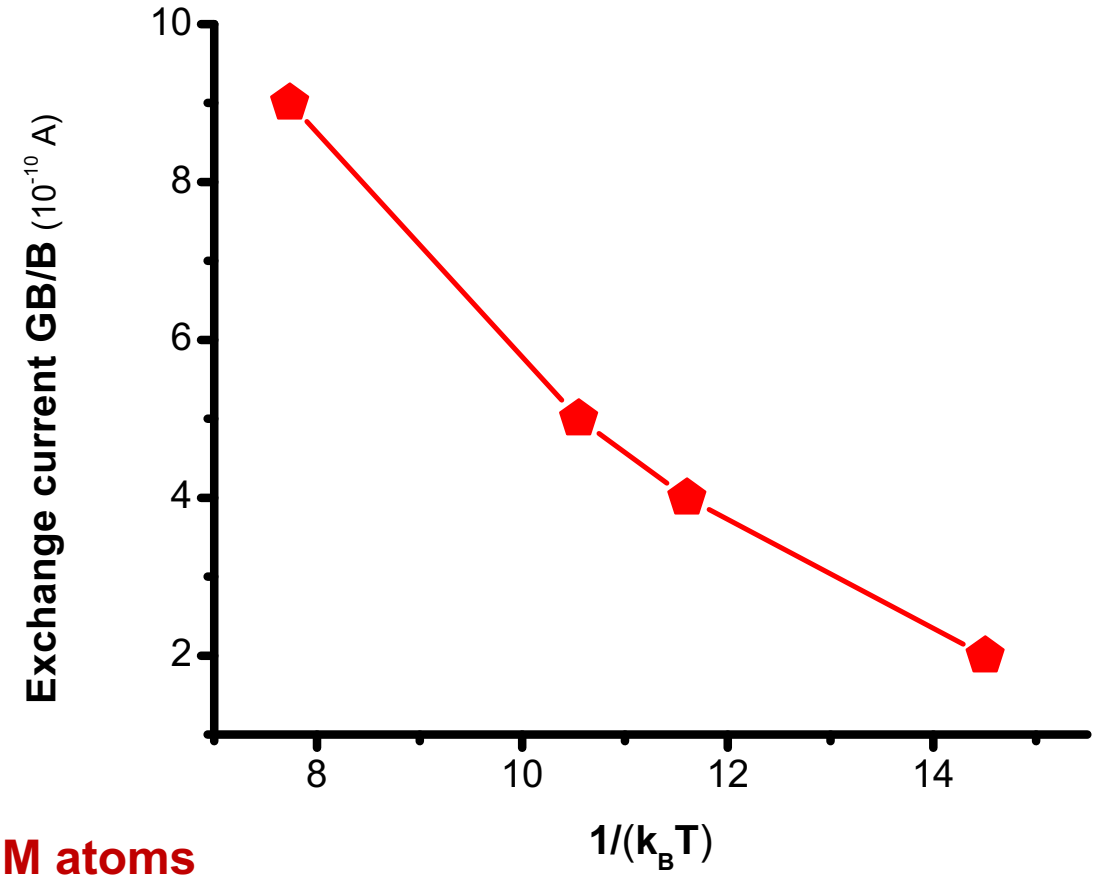
- **Ionic conductivity for solid state electrolytes (LLZO)** :

$$\kappa = \frac{F^2}{RT} \cdot D_+ c_+$$

Exchange current between GB and B

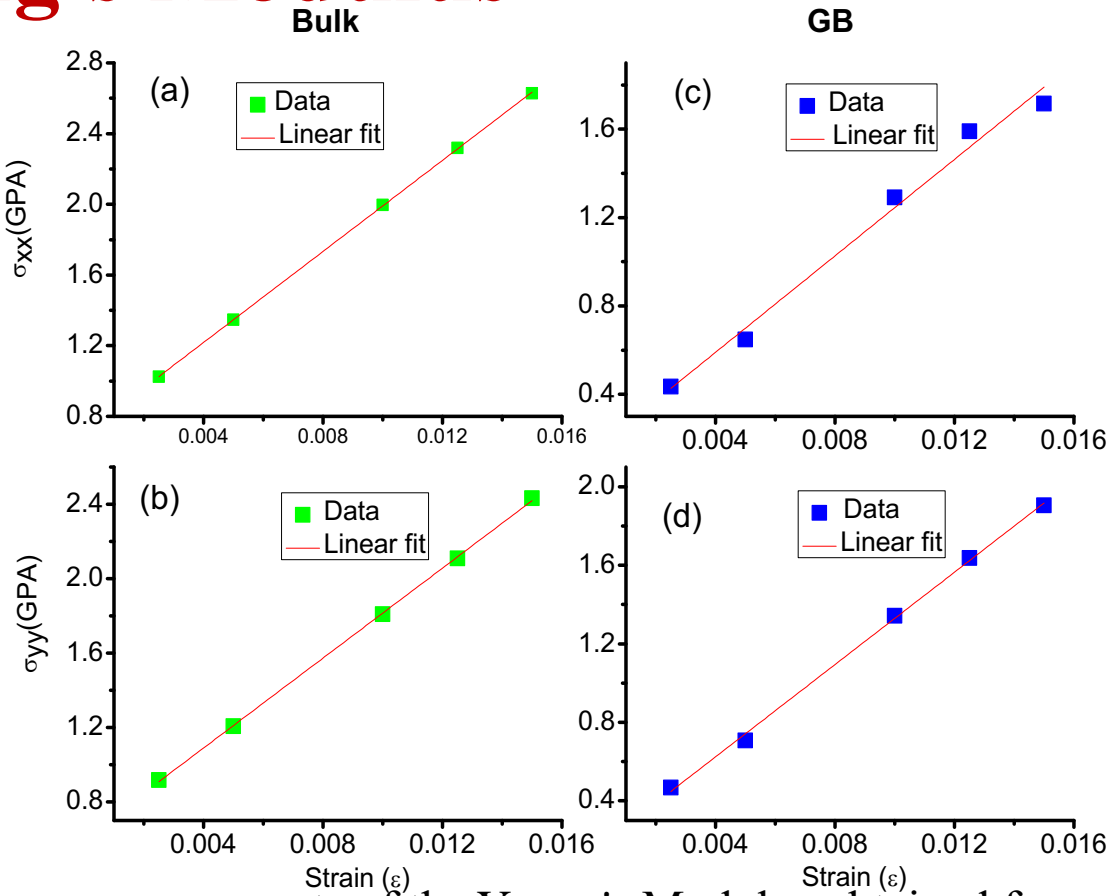


$$I = \Delta Q/\Delta t = (n_+ - n_-)/\Delta t$$



Each *T* we consider : ~ 1.9 M atoms

Young's Modulus

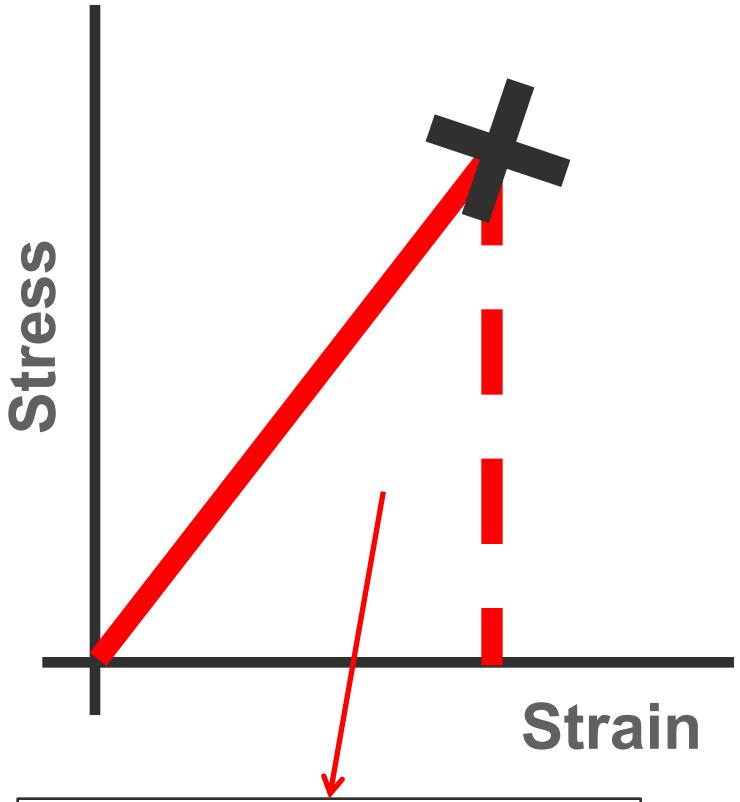


The x, y components of the Young's Modulus obtained from our model. (a) and (b) are for the bulk region while (c) and (d) are for GB regions of the $\Sigma_3(112)$ grain boundary.

A linear fit gave an average value of Young's Modulus E= 143 GPa for bulk LLZO and E =121 GPa for the $\Sigma_3(112)$ grain boundary. **(exp. data 149 GPa),**

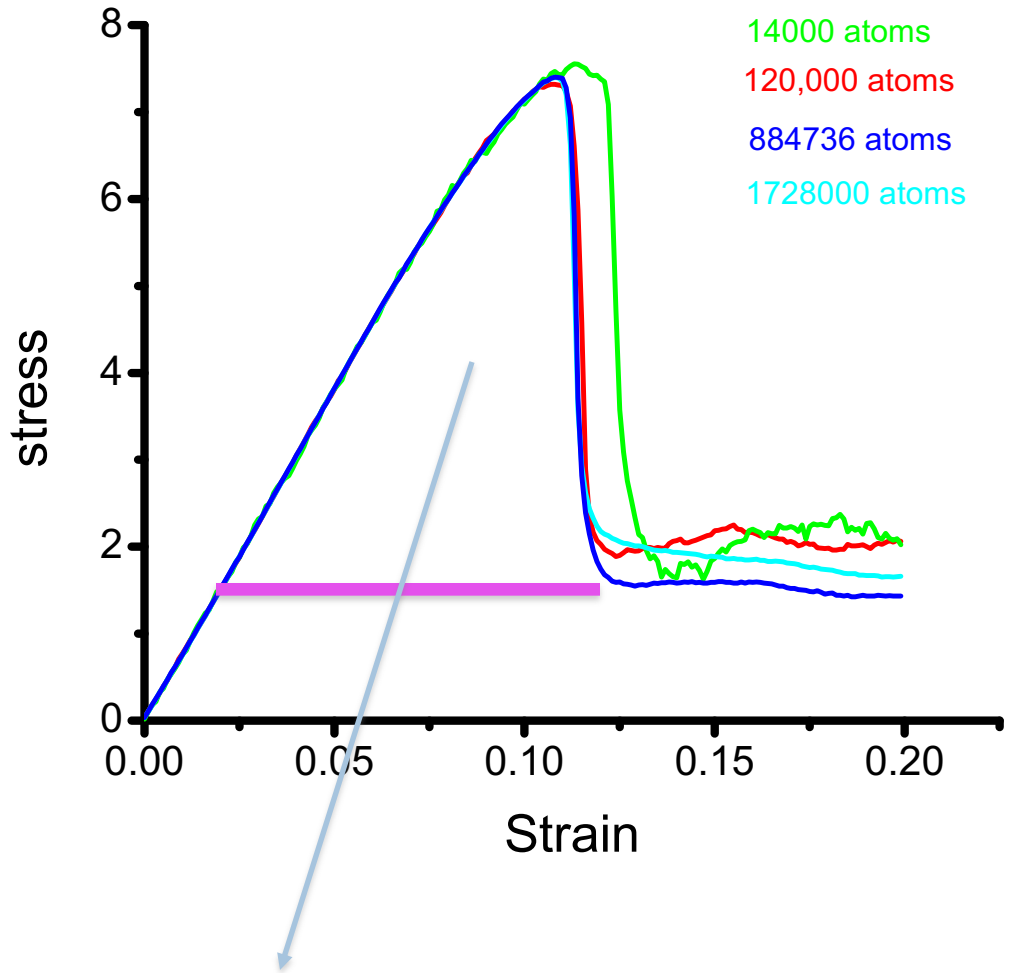
J Mater Sci (2012) 47:7978–7985

Fracture threshold energy



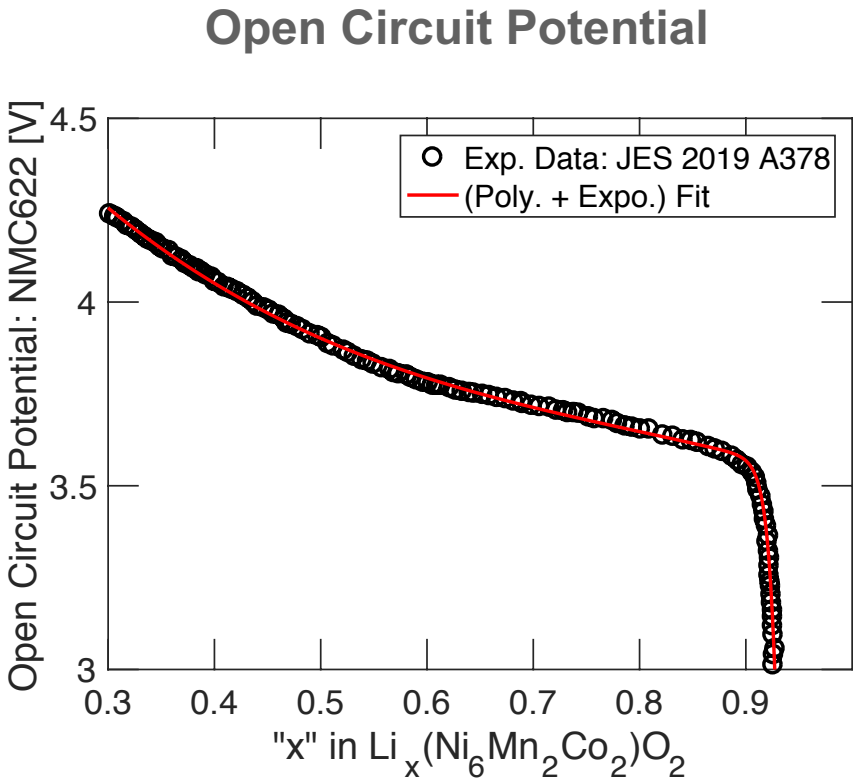
Area under the curve ➔
Fracture threshold energy
Unit: [J/m^2]

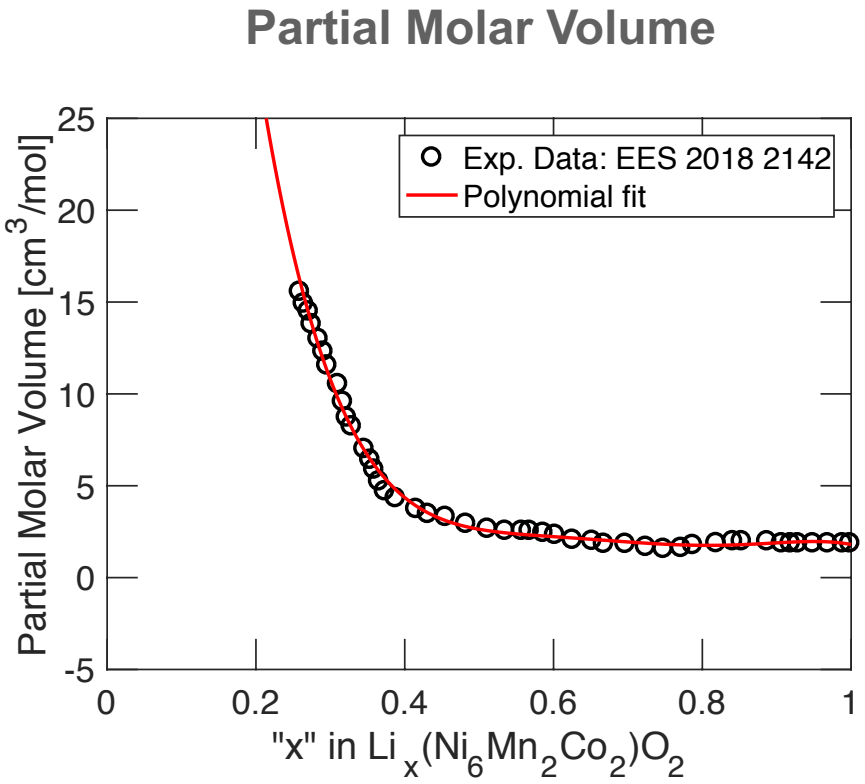
Our simulations for $\Sigma 3(112)$ GBs



5.3 J/m^2

Open circuit potential and partial molar volume for nmc622 cathodes

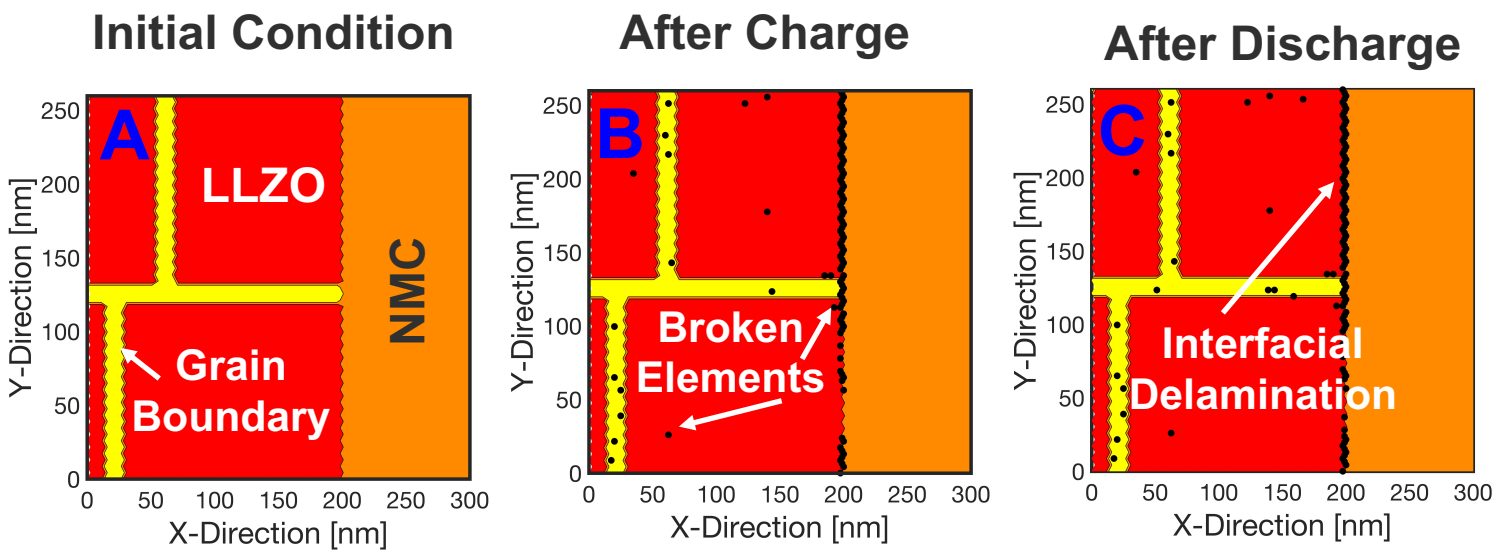




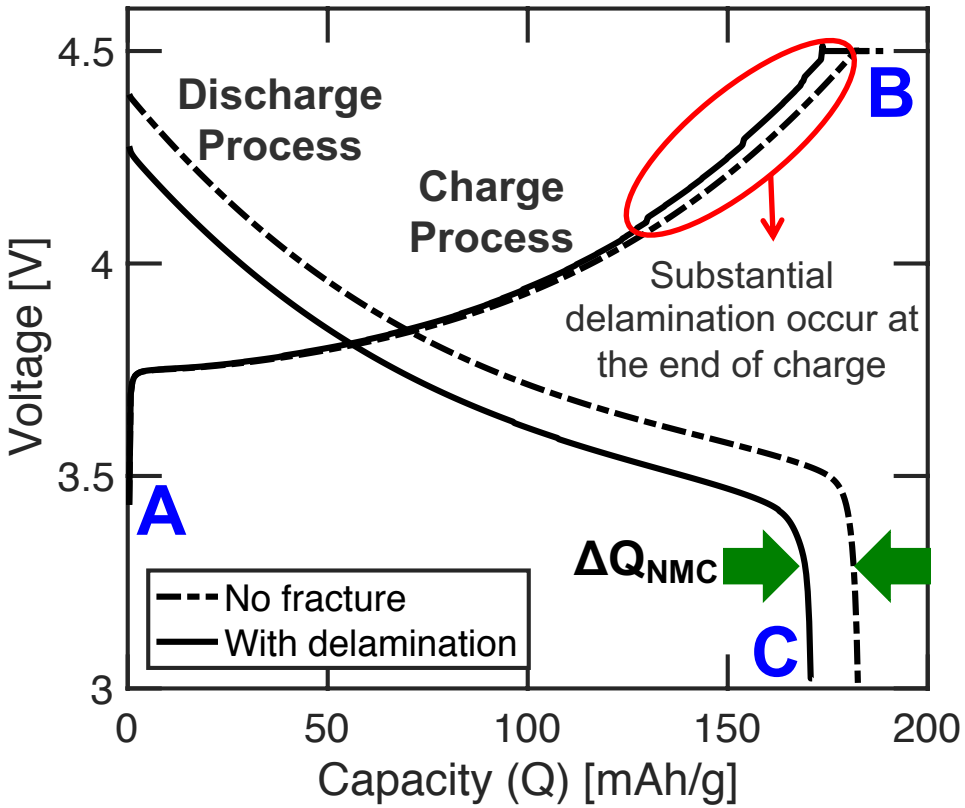
The fitted equations are used in the mesoscale computational analysis.

Delamination at LLZO/NMC622 interface during operation and capacity fade

LLZO/NMC interface:
LLZO grain size, d ~ 150 nm



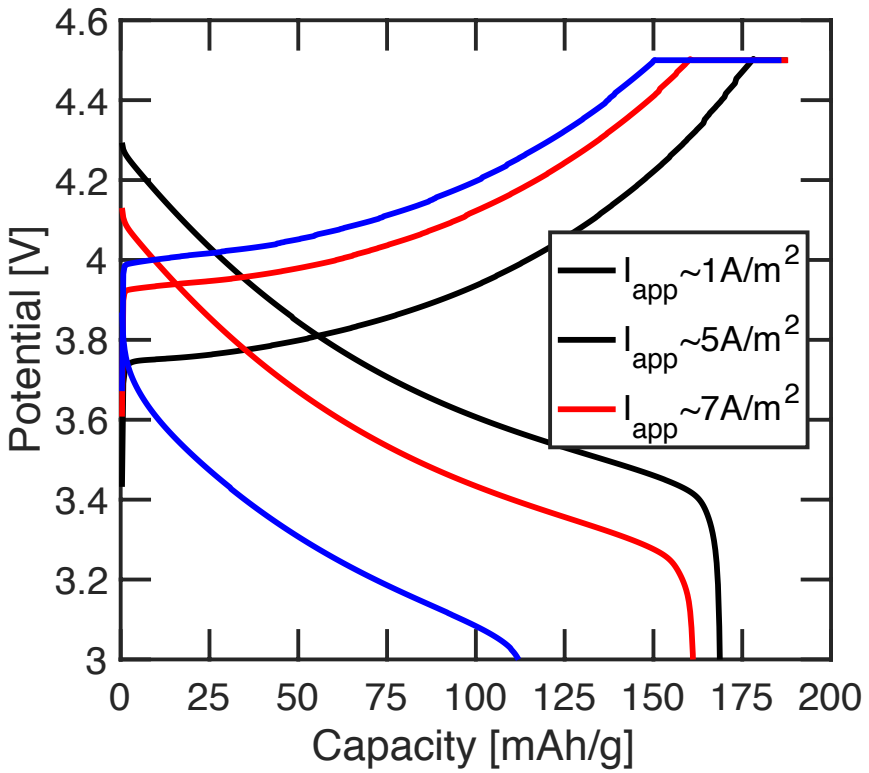
Capacity fade observed during charge and discharge process



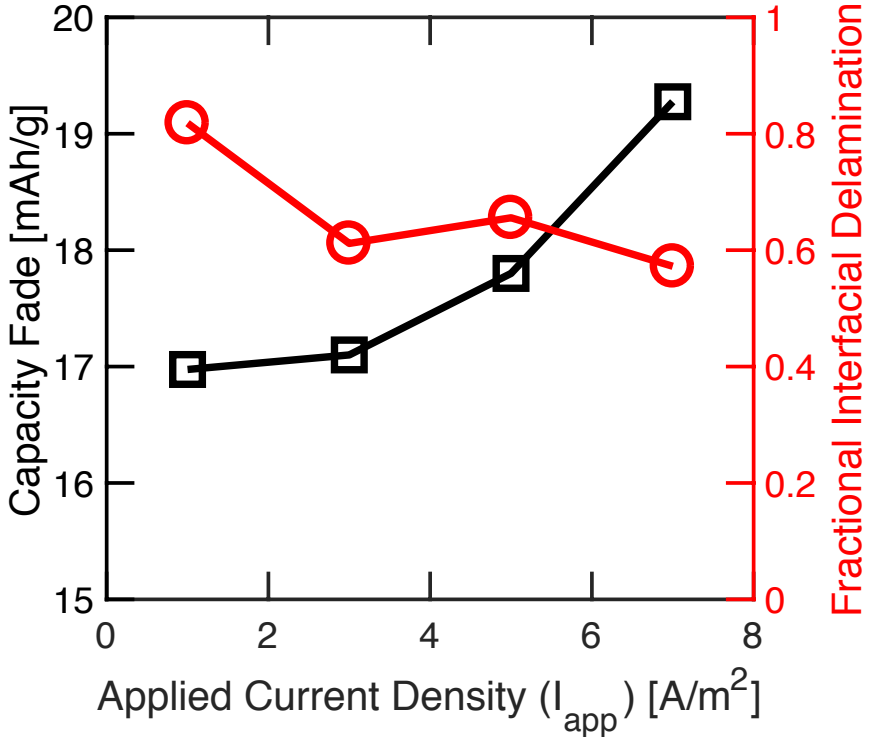
Delamination in NMC mostly occurs at the time of charge process.

Variation in capacity fade during operation at different current density

Charge discharge curves obtained by cycling NMC/LLZO cells between 4.5 V – 3.0 V at different current densities.

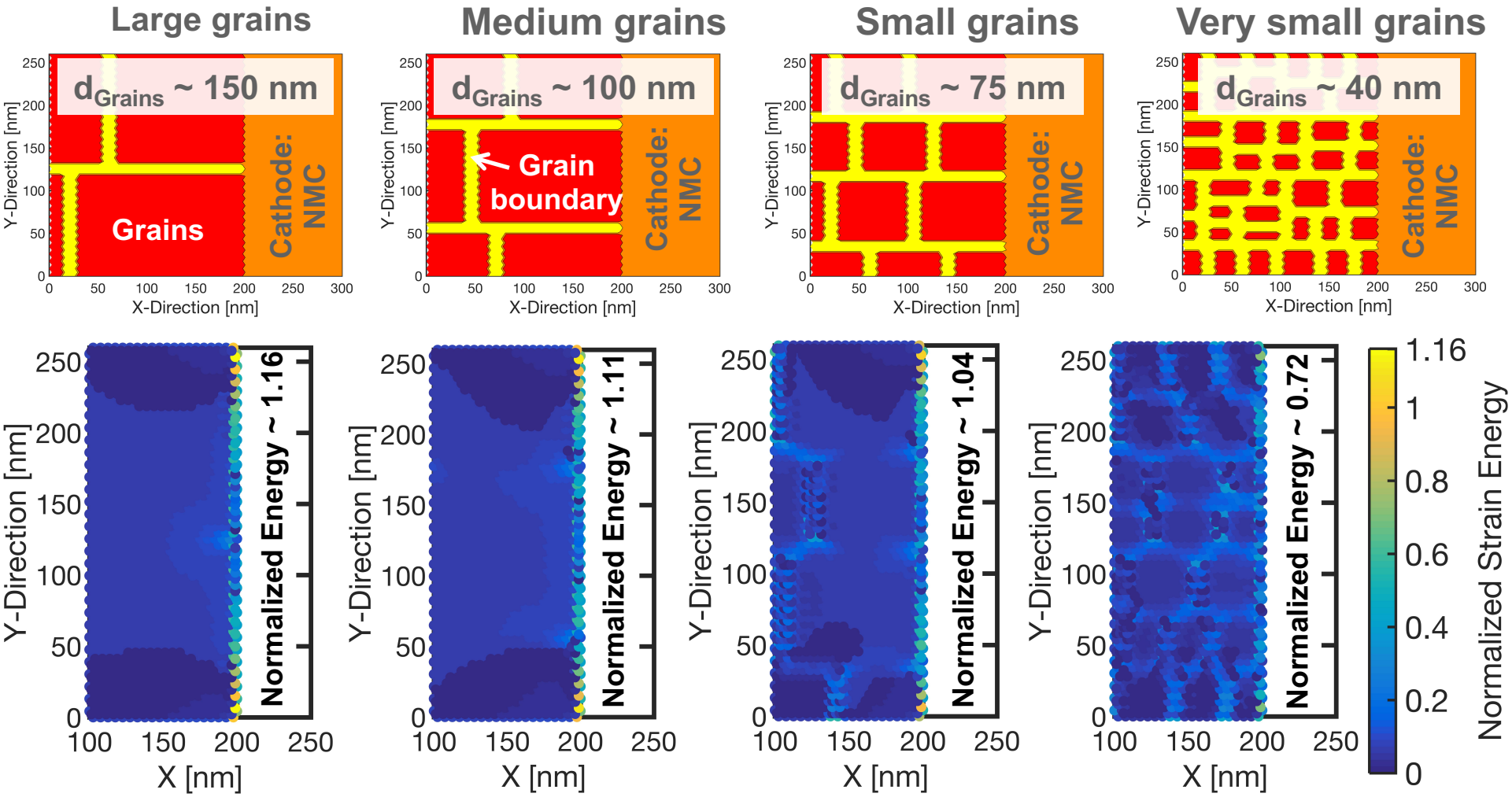


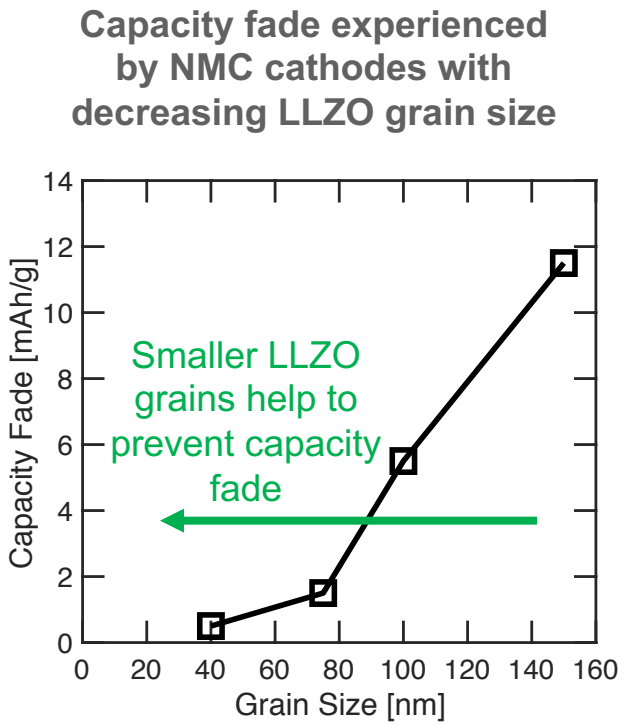
Extent of delamination and subsequent capacity fade during operation at various current densities.



Capacity fade increases with increasing current density because of the rise in interfacial resistance associated with delamination.

How to minimize interfacial delamination at the NMC/LLZO interface





Decreasing LLZO grain size leads to development of smaller strain energy density at the interface, which helps to minimize the interfacial delamination, and subsequent capacity fade.

Response to last year reviewer's comments

No comments from last year.

Proposed Future Work

- Estimation of lithium transport barrier at the NMC/ and LLZO/LBCO amorphous interface:
  - Impact of vacancy within NMC and LLZO structure will be studied
  - Effective exchange current density will be estimated at NMC/ and LLZO/LBCO interface
  - Interfacial formation/Binding energy between the LLZO/ and NMC cathode with LBCO will be calculated
- Selection of materials sandwich between cathode/LLZO interphase

Criterion for determining the most appropriate interphase material:

1. Electrochemical stability
2. Should be chemically stable against both cathode and LLZO solid electrolyte.
3. Sufficiently high Li ion conductivity
4. Zero electronic conductivity is not a necessity
5. **Low charge transfer resistance**
6. **Low elastic modulus of the interphase material**
7. **Large fracture energy (or formation energy) of:**
   a) **NMC – interphase material**
   b) **Interphase material – LLZO**

Basic requirements

More specific criterion

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/NMC cathode interfaces .

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

- LLZO electrolytes with small grain sizes can help to minimize the interfacial delamination between the cathode and solid-electrolytes.
  - Small grained LLZO electrolytes can also help to minimize the dendrite growth process.

- It is possible to minimize the interfacial delamination in NMC cathodes by decreasing the potential window of operation from 3.0V – 4.5V to 3.0V – 4.1V.
  - Such a decrease in upper cutoff voltage helps to avoid SOC values where substantial increase in the partial molar volume of NMC is observed.