Understanding and Strategies for Controlled Interfacial Phenomena in Lithium-Ion Batteries and Beyond

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Texas A&M University

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Project ID #: bat329

Overview

Timeline

- Start date: October 1, 2016
- End date: September 30, 2019
- Percent complete: 40%

Budget

- Total funding: $1,333,335
  - DOE share: $1,200,000
  - Contractor share: $133,335
- Funding received
  - FY17: $398,390
  - FY18: $401,766

Barriers

- Barriers/targets addressed
  - Loss of available capacity
  - Materials degradation during cycling
  - Lifetime of the cell

Partners

- Interactions/ collaborations
  - J. Seminario (TAMU Co-PI)
  - P. Mukherjee (Purdue U. Co-PI)
  - Horowitz, Somorjai, UC Berkeley
  - R. Shahbazian Yassar (U. Illinois)
  - M. Vijayakumar (PNNL)
- Project lead: TAMU

Relevance/Objectives

- **Objective:** Evaluate and characterize *interfacial phenomena* in lithiated Si and Li metal anodes and develop strategies leading to *controlled reactivity* at electrode/electrolyte interfaces using advanced modeling techniques based on first-principles.
- **FY 2018 goals**: Identify modes of Li deposition as a function of surface structure and deposition rates; characterize SEI formation near deposits; dendrite formation and growth.
- **Addressing targets and barriers**:
  - Anode architectures with better storage capacities; understand and model life-limiting mechanisms incorporating microscopic features.
- **Impact:**
  - Implementation of *stable* Si alloys and Li metal anodes depends on *structural evolution* during battery operation. Understanding SEI reactions, cracking, and dendrite formation will allow rational electrolyte and electrode architecture design.

Relevance/Milestones (18-19)

- Q3/Y1: Evaluate and quantify the relative influence of mechanical and chemical degradation interplay in Si active particles. (June 17) **Completed**
- Q4/Y1: Characterize SEI growth as a function of SEI composition. Compare the SEI rate growth with experimental trends in the literature and from collaborators (Go-No Go); if there is any disagreement revise respective modeling approach. (Sept.17) **Completed**
- Q1/Y2: Complete analysis of effects of Li-substrate interactions on Li deposition. (Dec.17) **Completed**
- Q2/Y2: Complete study of SEI reactions over Li deposits. (March 18) **In progress**
- Q3/Y2: Complete analysis of operating conditions on dendrite growth. (June18)
- Q4/Y2: Complete evaluation of co-deposition effects. Establish comparisons with experimental trends (Go-No Go) (Sept. 18)
- Q1/Y3: Characterize Li deposition in presence of other ions (Dec. 18)
- Q2/Y3: Characterize macroscopic effects during cycling with Si and Li metal anodes. (March19)

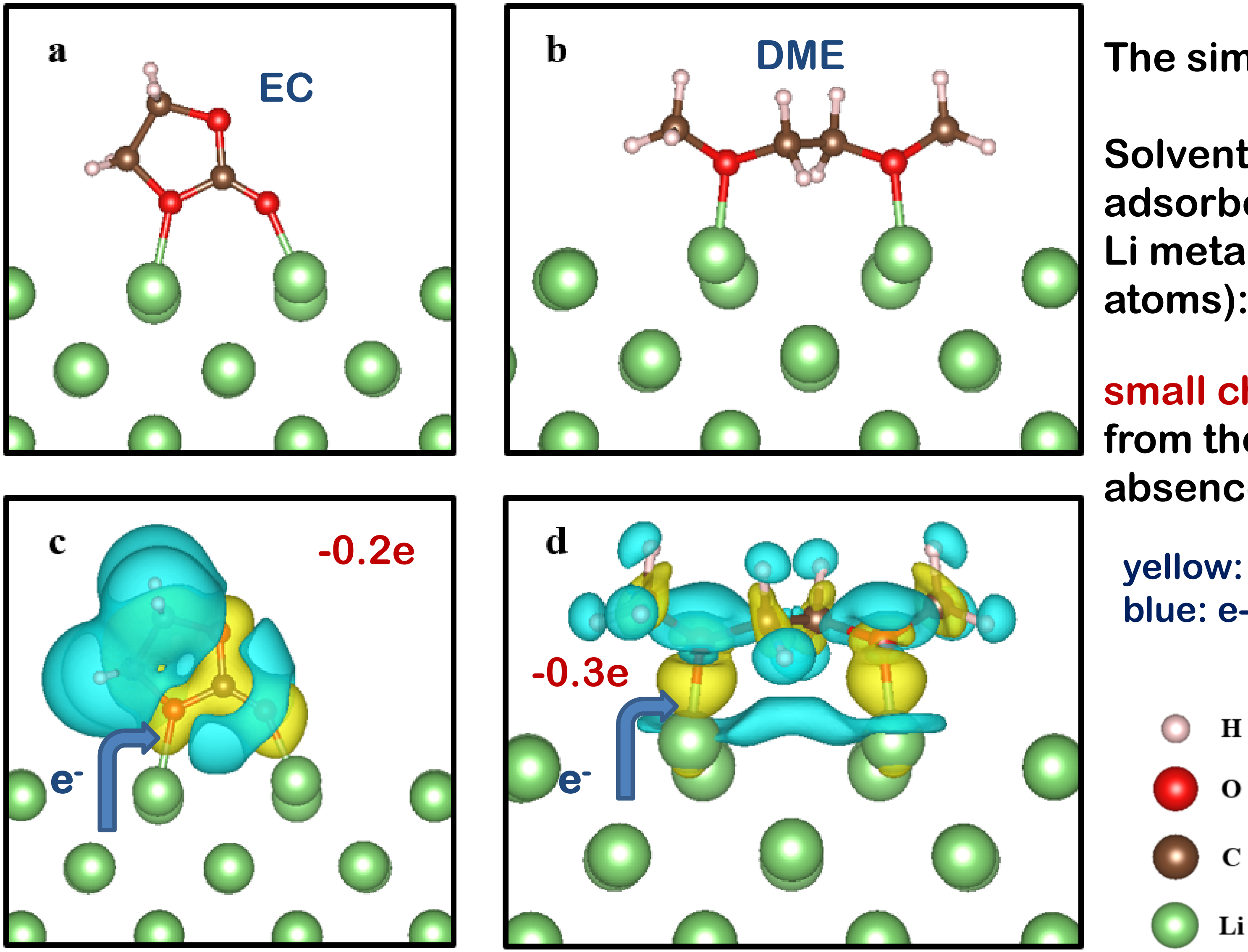
Approach/Strategy

- **Overall technical Approach**:
  - Interfacial problems (SEI growth, Si particle cracking due to volume expansion, Li dendrites formation) addressed with *synergistic multiscale modeling* (ab initio, classical molecular dynamics, and mesoscopic level models).
  - All findings rigorously compared with experimental evidence. In many cases, first-principles approach allows prediction and interpretation of new and experimentally observed phenomena.
  - Addresses technical barriers/targets: Rate of SEI growth as a function of electrolyte composition characterizes *SEI evolution*. Cracking of Si nanoparticles, identification of SEI reforming, and dendrites formation elucidate *anode capacity loss* and *cell lifetime*.
  - Collaboration within TAMU and Purdue U. and with experimental groups (UC Berkeley, PNNL, and UI Chicago).
- **Progress towards FY18 and FY19 milestones and Go/No Go decisions**: SEI components and growth elucidated. Chemical origin of dendrites identified. Dendrite growth analyzed at nano and mesoscopic levels. Coating-based dendrite mitigation strategies explained.

Technical Accomplishments: Barriers Addressed

- **Loss of available capacity**
  - Origins of uneven ***Li plating*** elucidated; ***SEI growth*** characterized.
- **Materials evolution during cycling**
  - Study reveals ***dendrite nucleation and growth*** as Li deposits on various SEI-covered substrates.
- **Lifetime of the cell**
  - Mitigation strategies to ***prevent dendrite formation*** for extended cell lifetime.

Technical Accomplishments: Understanding Li plating



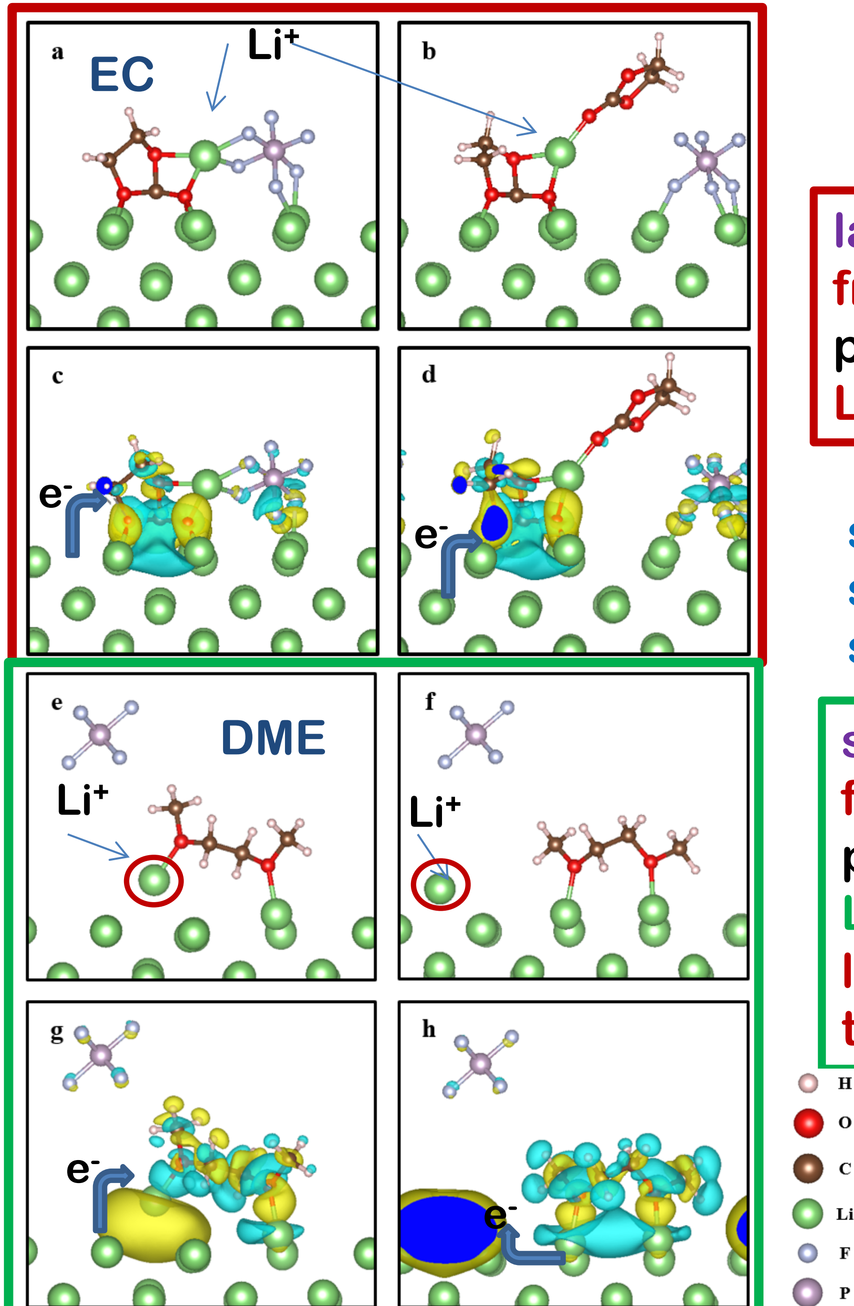
The simplest case:

Solvent molecules adsorbed over Li metal surface (green atoms):

small charge transfer from the surface in absence of a Li salt

yellow: e- accumulation
blue: e- depletion

Technical Accomplishments: Understanding Li plating



Solvent + salt Li+ PF_6^-)
on Li-metal surface

large charge transfer
from the surface to EC (-1.84 e) in presence of a Li ion; EC is reduced;
Li+ is not reduced (+0.87 e)

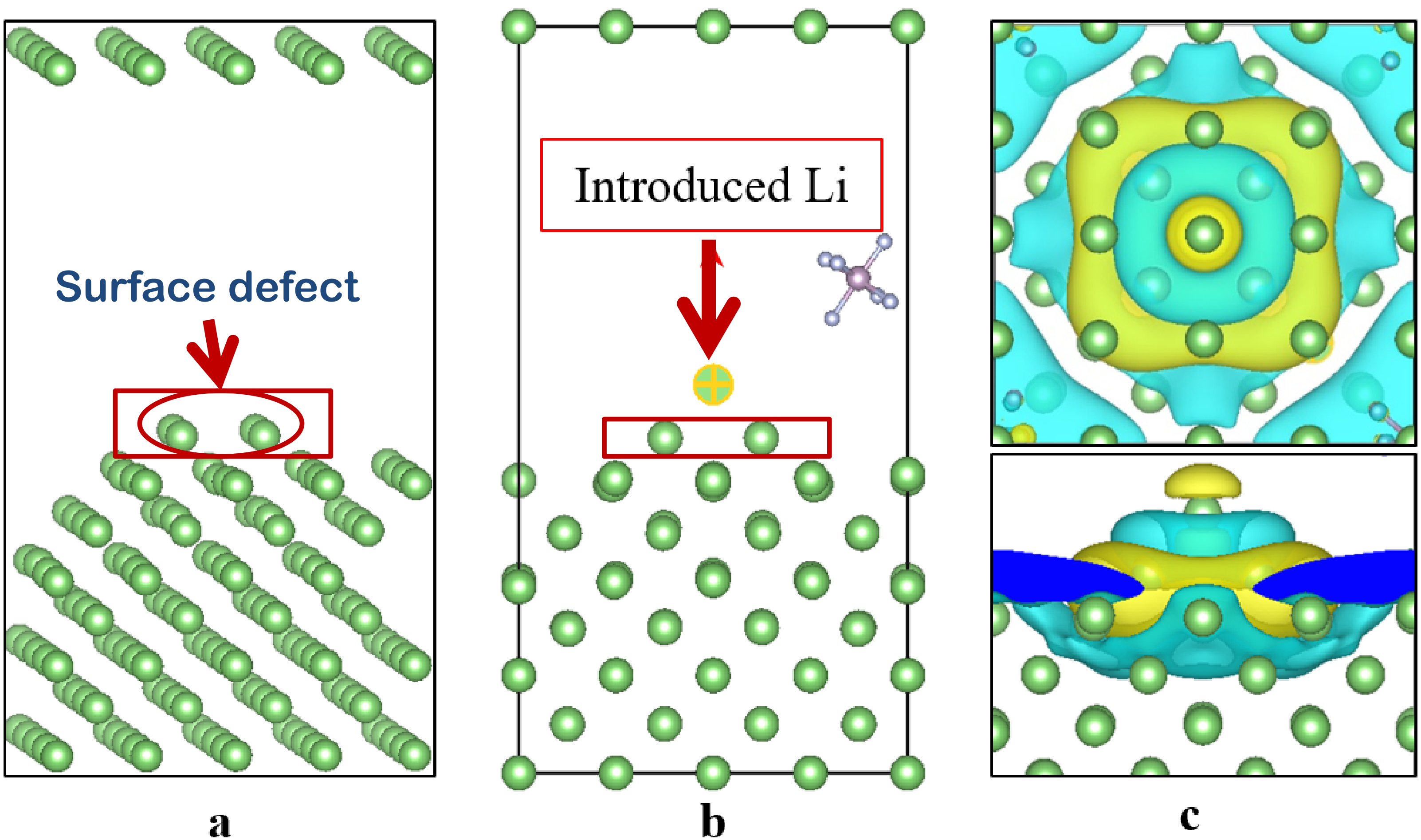
solvent electron affinities and solvation properties decide whether the solvent or the Li ion are reduced

small charge transfer
from the surface to DME (-0.15 e) in presence of a Li ion; DME is not reduced;
Li+ is reduced;
large electron accumulation on the surface

yellow: e- accumulation
blue: e- depletion

Technical Accomplishments: Understanding Li plating

Li^+ reduced over the defect



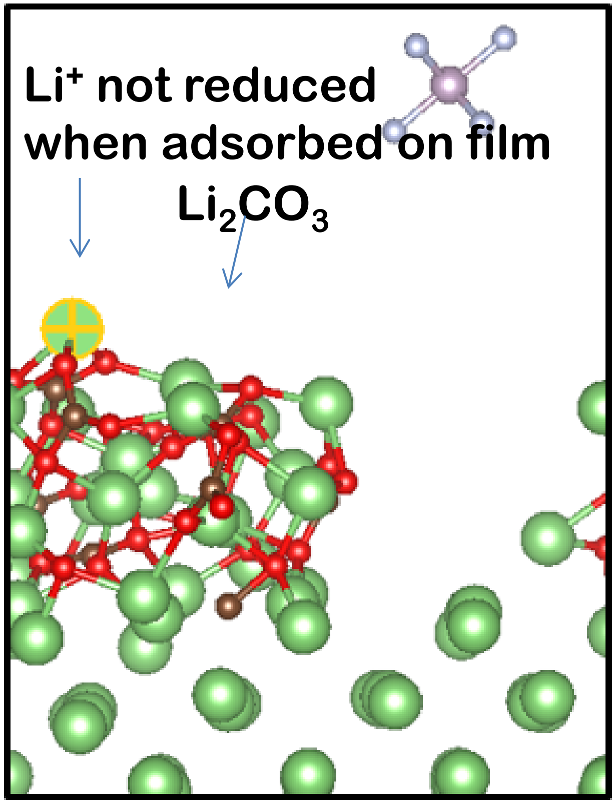
yellow:
e^- accumulation
light blue:
e^- depletion

dark blue region:
cross-section of
charge density

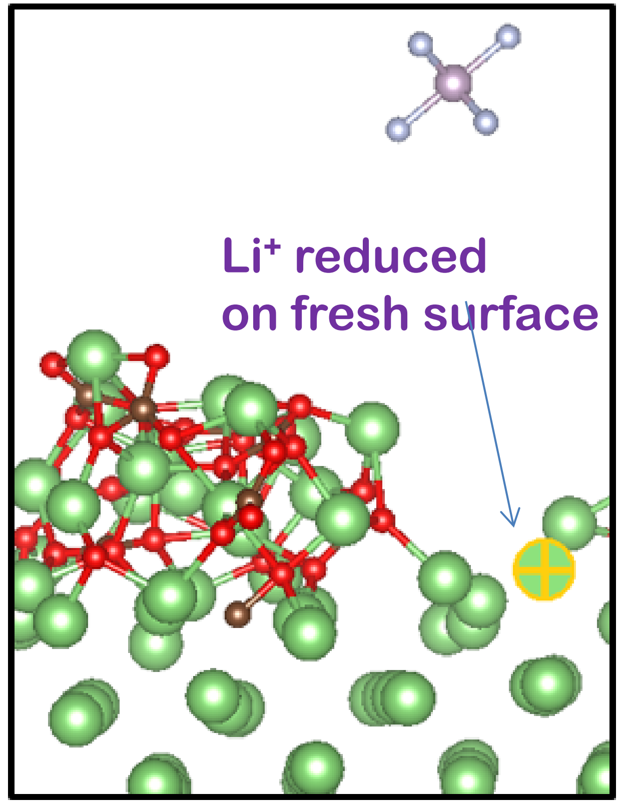
Li^+ is reduced; large electron accumulation region near reduced Li:
It may attract and reduce further Li cations (needle growth) and electrolyte (SEI)

Technical Accomplishments: Understanding Li plating

Li_2CO_3 partially covered surface

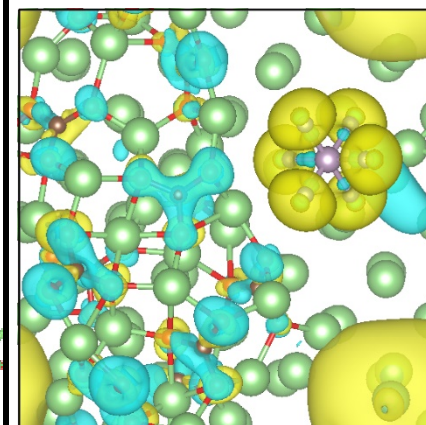


a



b

top view showing
e accumulation (yellow)



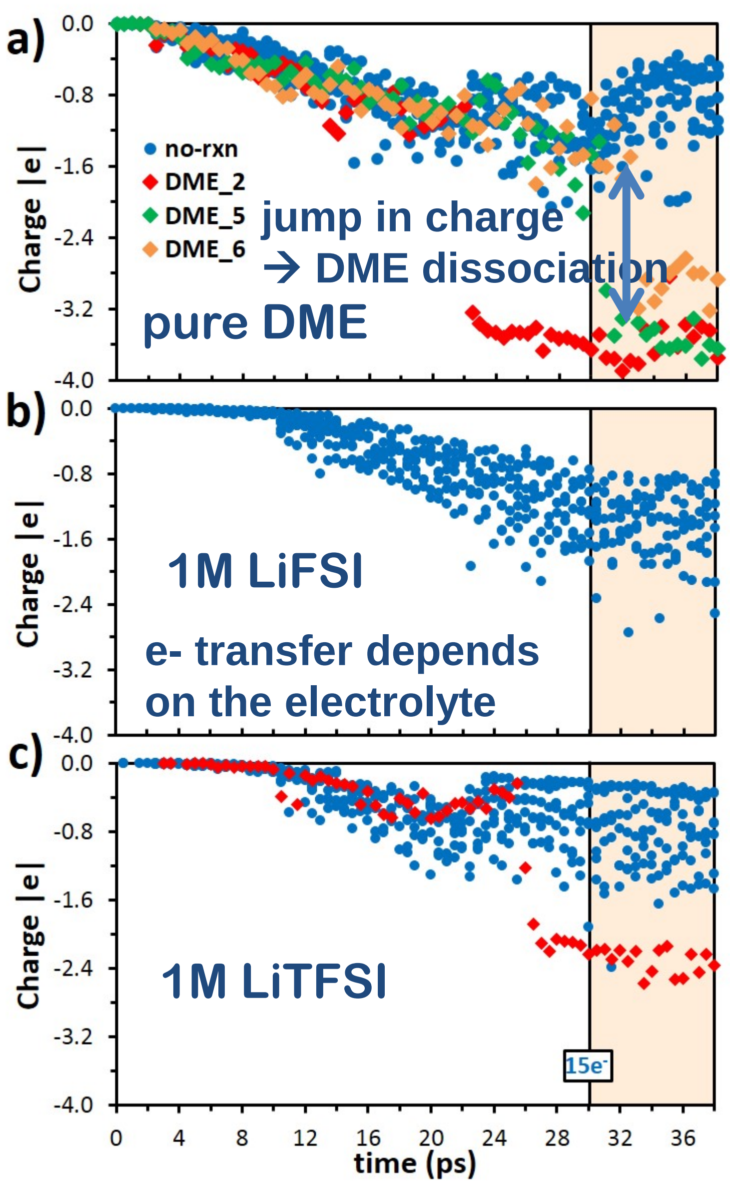
X. Qin, M. Zhao, and P. Balbuena, submitted

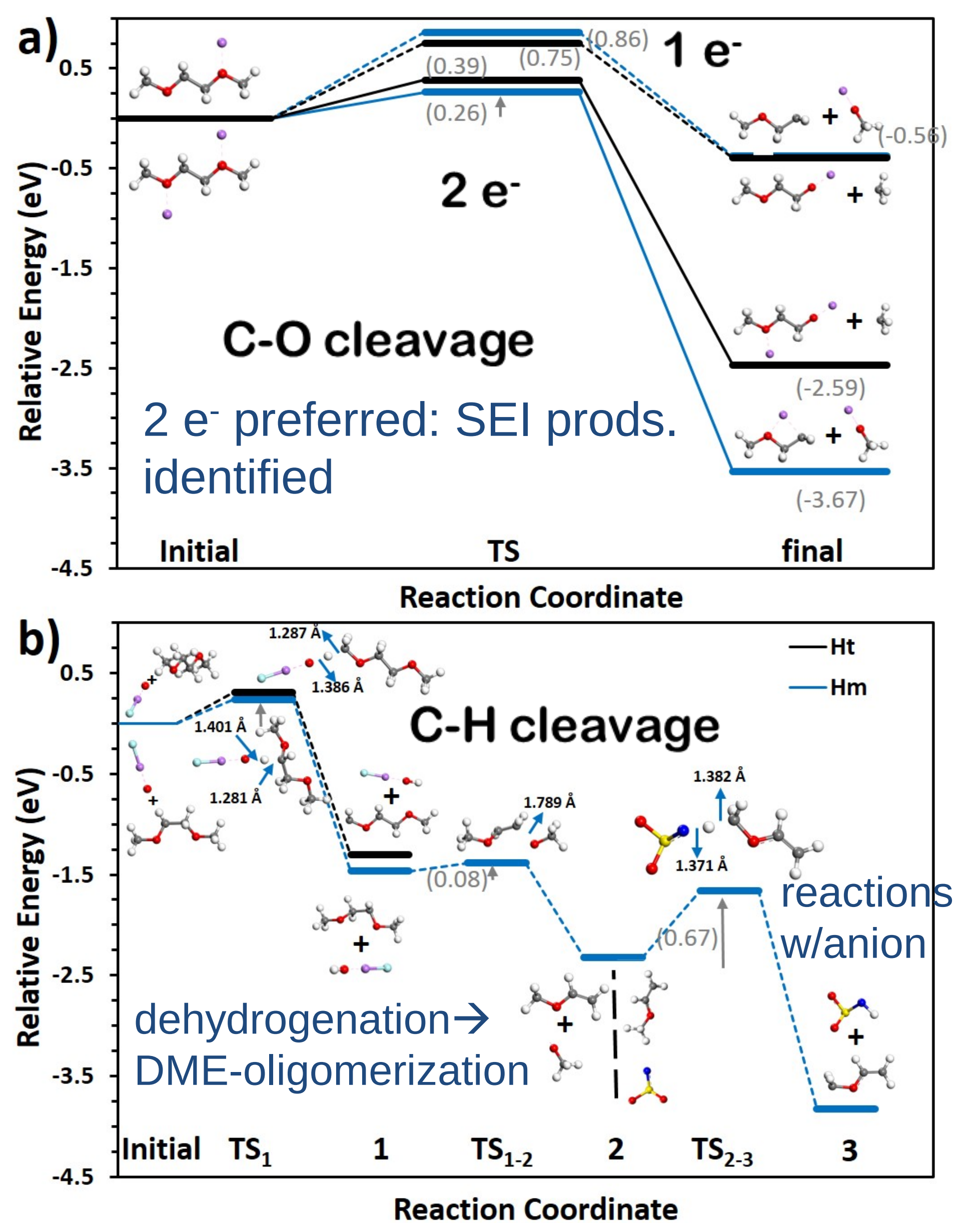
Conclusions: Li deposition generates an uneven distribution of charges near the reduction site; such large e^- accumulation can attract more Li cations → favoring further plating on localized regions instead of smooth deposition

Technical Accomplishments: SEI reaction mechanisms

Camacho-Forero and Balbuena, PCCP, 2017

Slow DME decomposition kinetics needs e^- rich environments

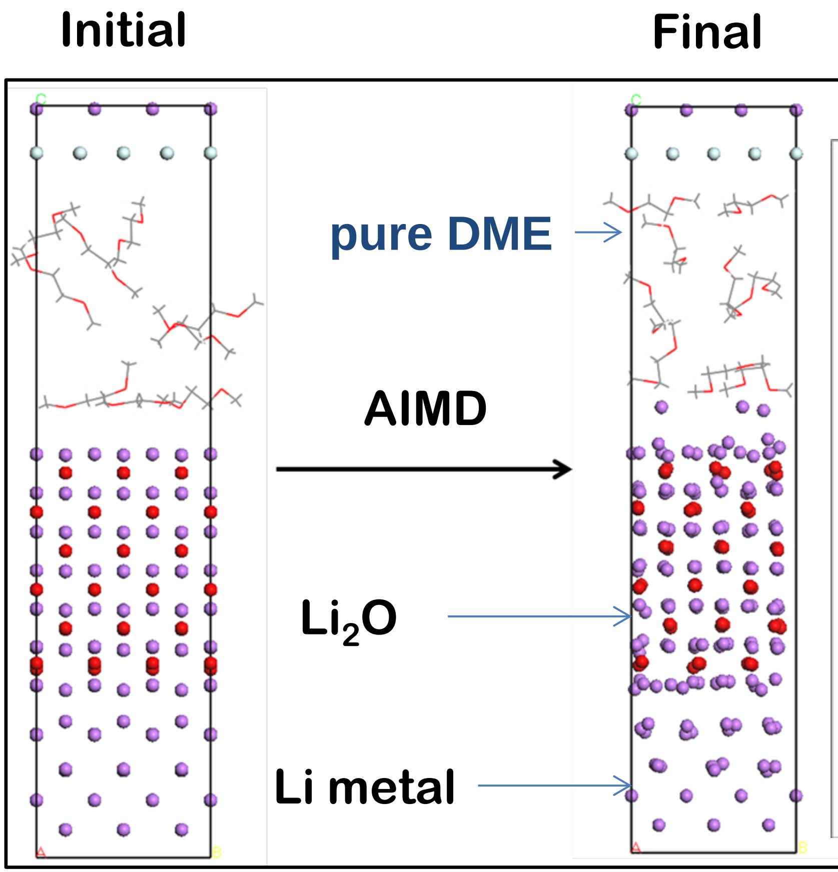


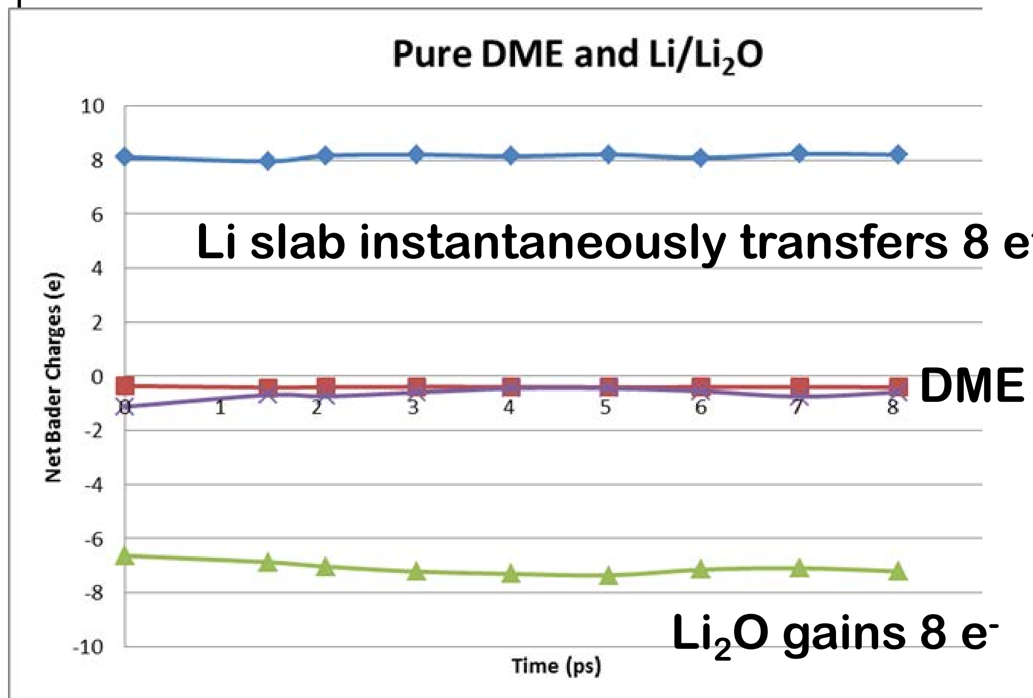


Technical Accomplishments:
Effect of SEI on Li metal reactivity

DME on Li_2O/Li metal

Significant charge transfer from Li metal slab to Li_2O coating;
negligible charge transfer to DME



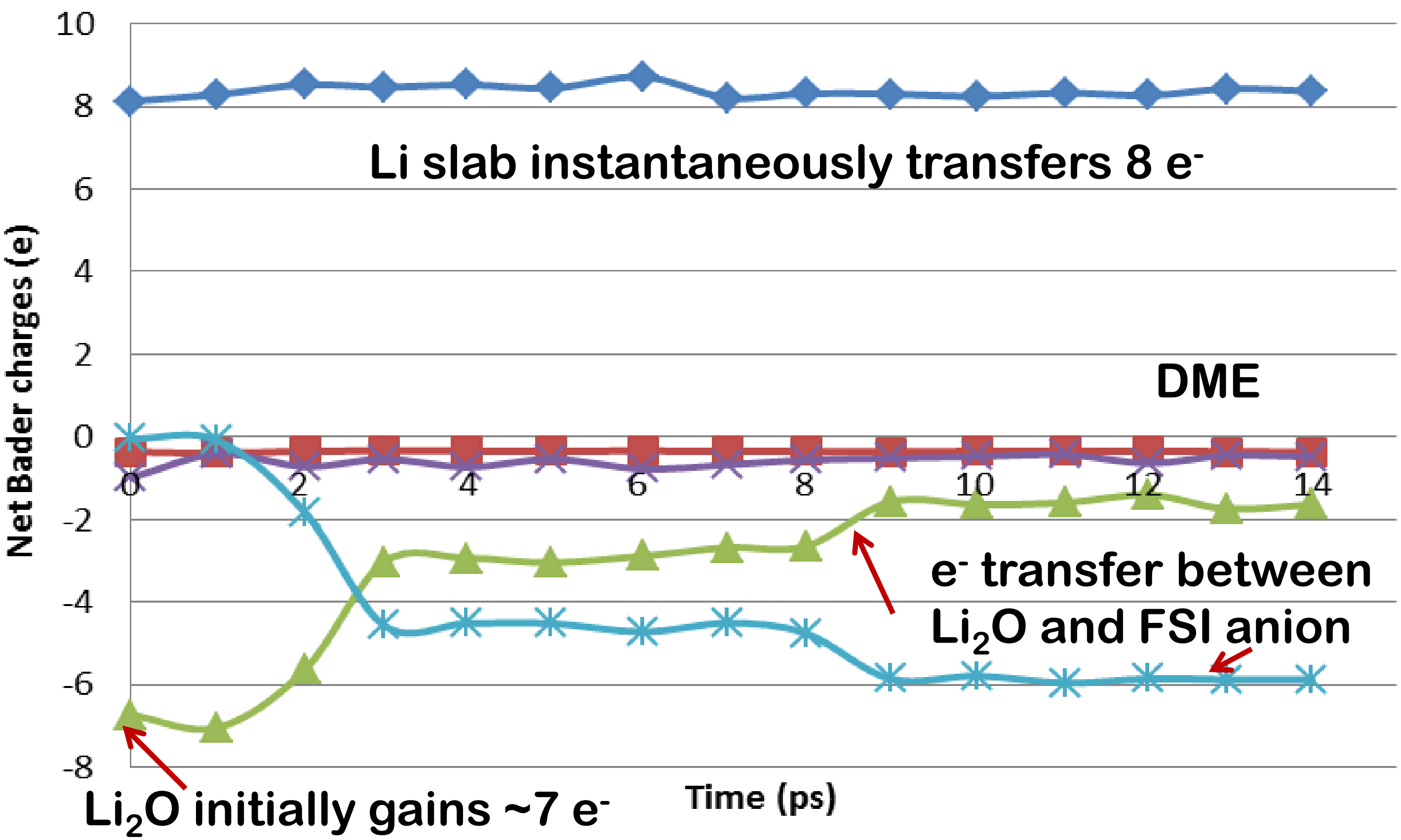


Little to-no interfacial arrangements that could lead to time-dependent charge transfer; Li_2O can receive/hold electrons

Collaboration with M. Vijayakumar, PNNL (experiments in progress)

Technical Accomplishments:
Effect of SEI on Li metal reactivity

1M LiFSI in DME on Li_2O/Li metal

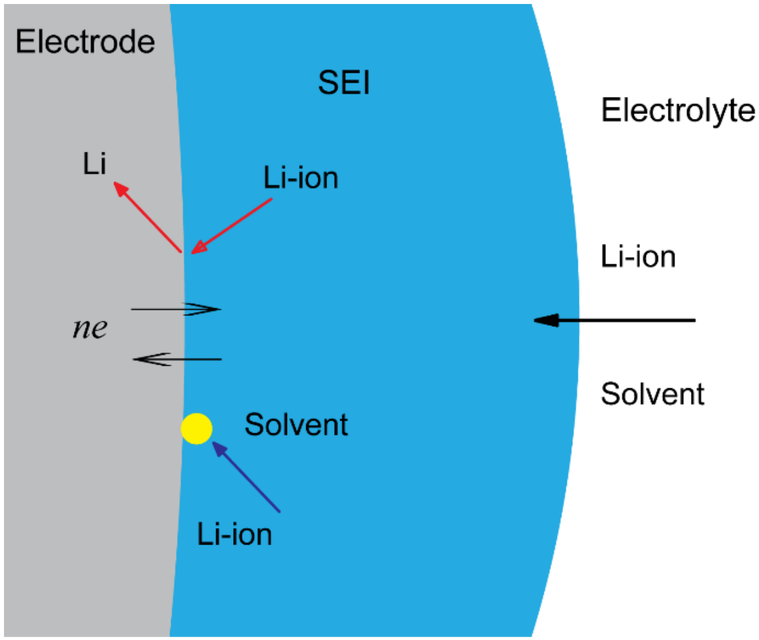


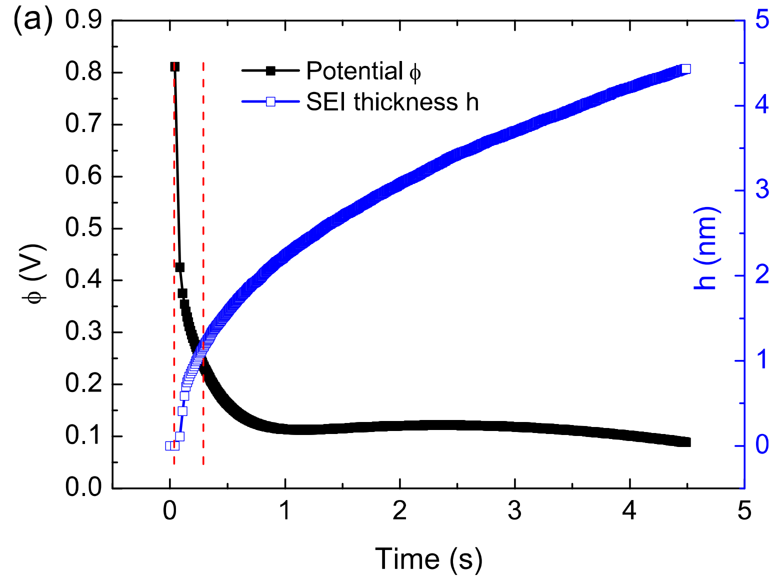
Note changes in charges of Li_2O (green) and corresponding changes in charge of FSI^- (light blue)

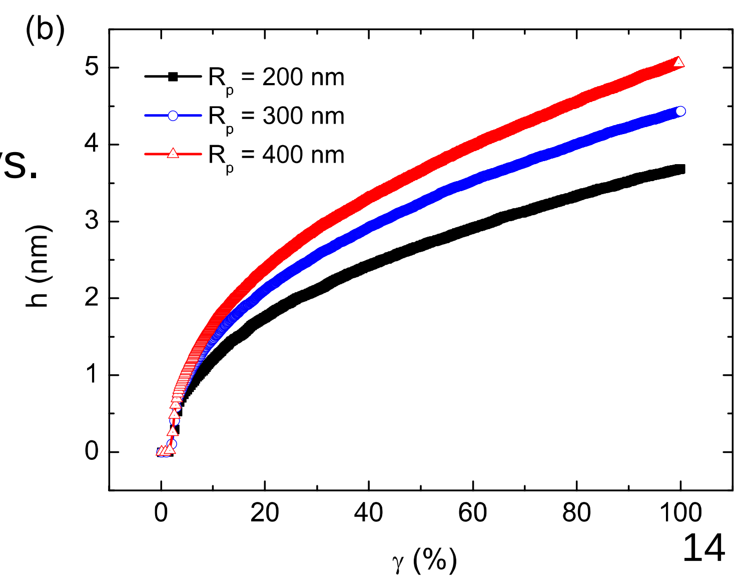
FSI$^-$ anion breaks down extensively over the coated surface; even though Li metal is not exposed

Technical Accomplishments:
Mesoscopic model of homogeneous SEI growth

interfacial redox reactions







Kinetic Monte Carlo Model

(a) Potential ϕ and SEI growth on anode surface vs. time at 1st charge. Particle radius R_p = 300 nm, E_{a1} = 0.48 eV (Li^+ diffusion barrier in SEI), and E_{a2} = 0.7 eV (solvent diffusion barrier in SEI).

(b) SEI growth profiles for single particles with various radii. SEI grows when the anode potential reduces to 0.8 V, consistent with experiments.

The larger the particle, the thicker SEI becomes.

Technical Accomplishments:
Mesoscopic model of heterogeneous SEI growth

SEI has A&B components: **purple (A)**; white (B). In (a) and (b) SEI morphologies shown for varying volume ratios of B.

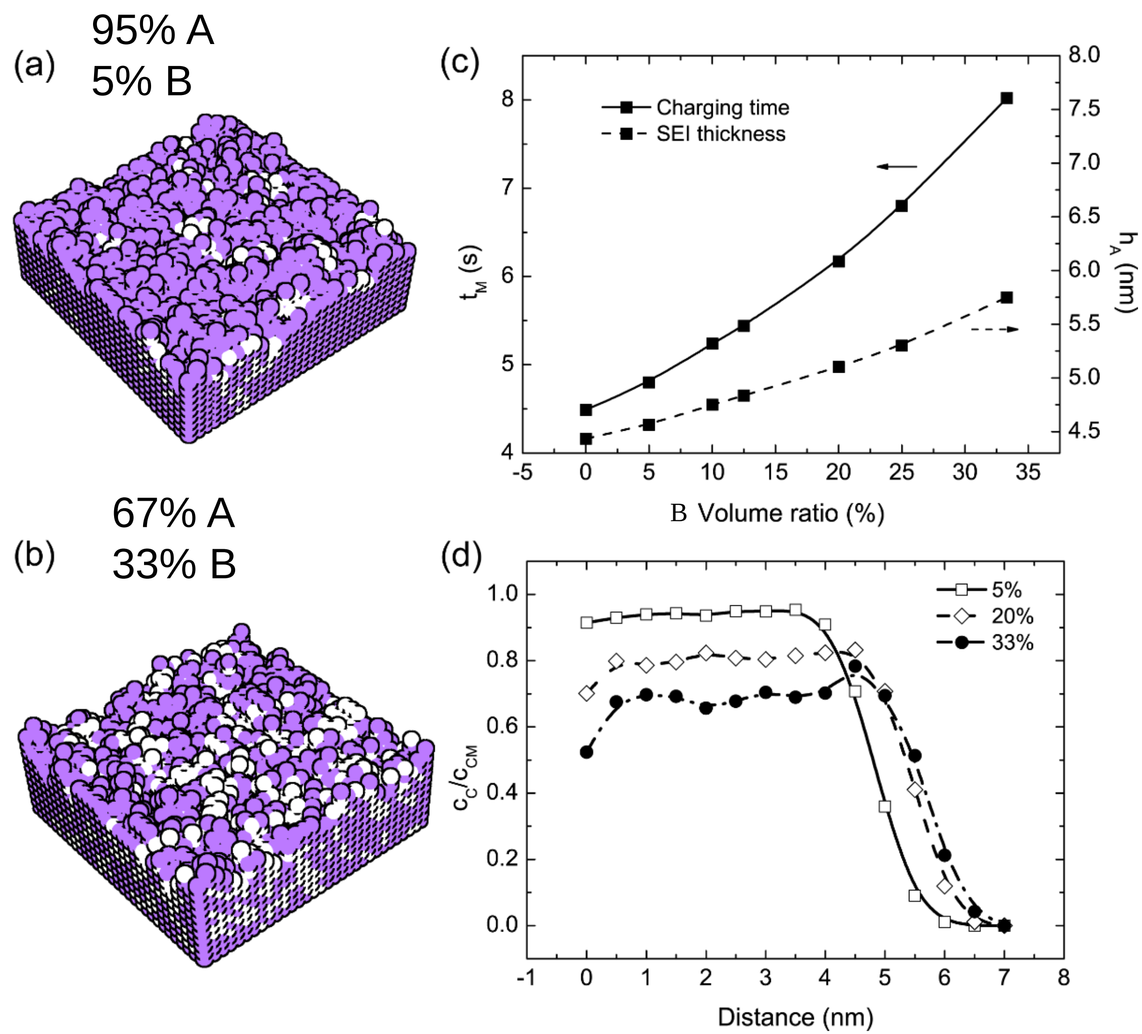
(c) Total charging time and SEI thickness with varying volume ratios of B for the 1st charge.

(d) Li content profiles for various volume ratios of B

Li diffusion barrier in:
A (purple): 0.48 eV
B (white): 0.67 eV

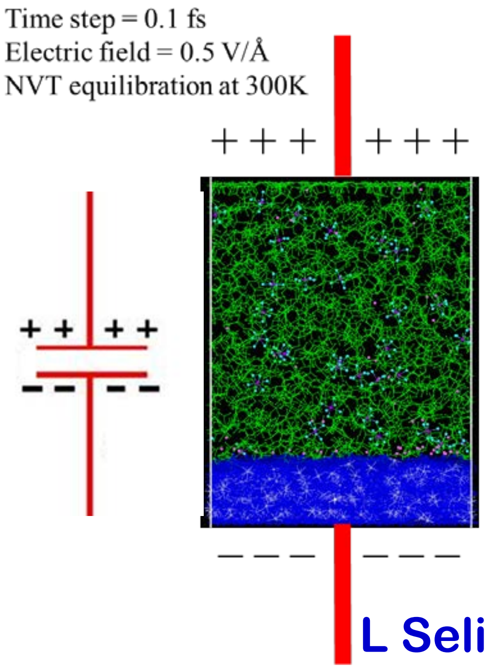
Charging time and SEI thickness increase with increasing 'B' volume ratio.

Li content fluctuates through the SEI layer.

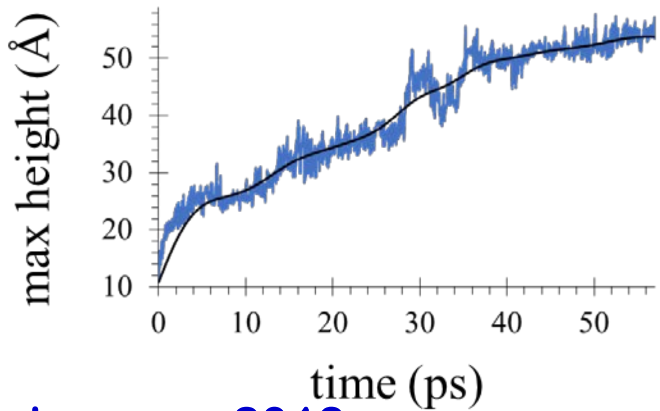


F. Hao, Z. Liu, P. B. Balbuena, and P. P. Mukherjee, JPCC, 2017

Technical Accomplishments: Li-dendrite nucleation



Classical Molecular Dynamics simulation cell; an electric field is applied to drive migration of Li ions to the anode surface where they are reduced.

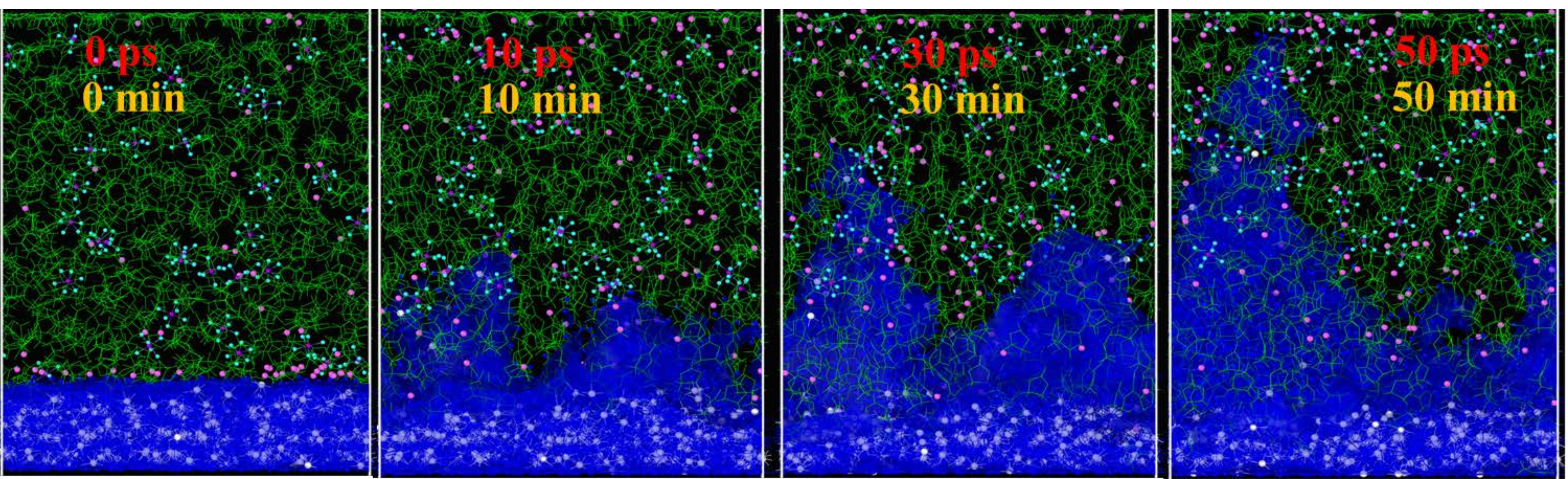


electrolyte solution:
1 M LiPF6 in EC

Li metal anode

L Selis and JM Seminario, RSC Advances, 2018

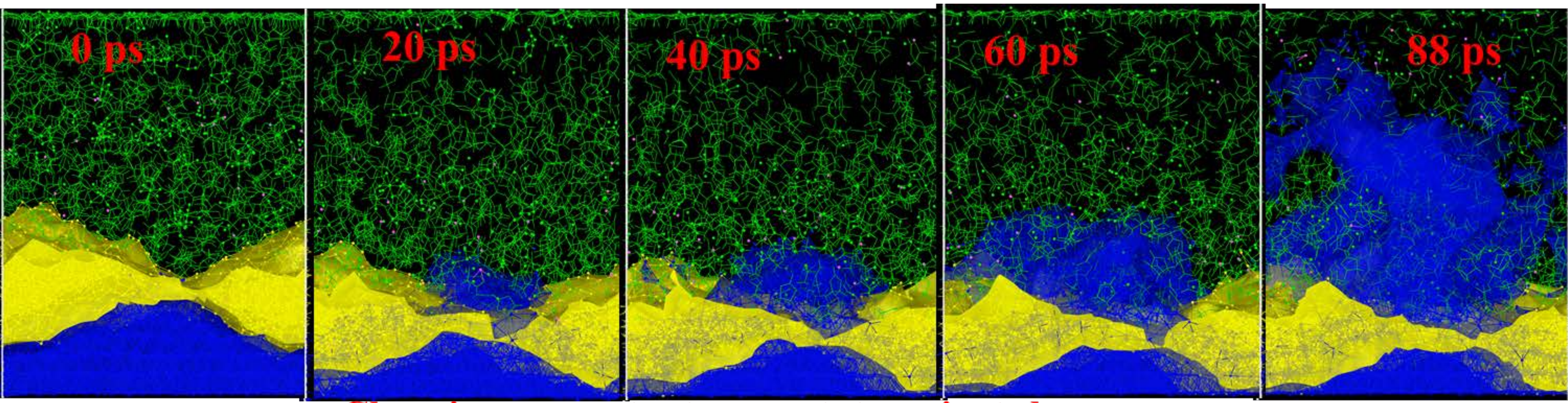
Time shown in ps is simulation time; time in min estimated for a charge at 1C



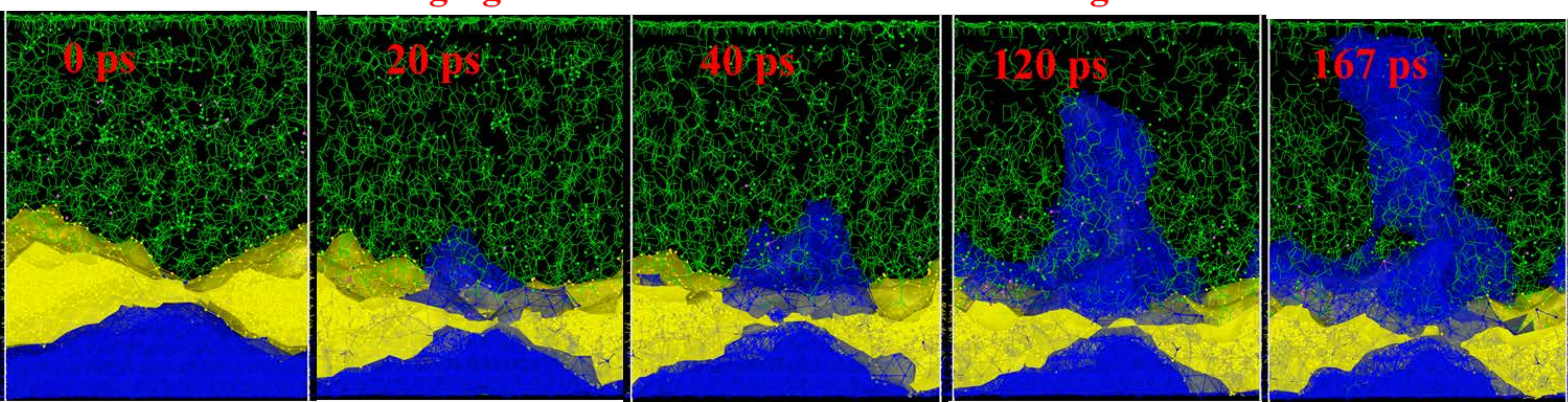
Technical Accomplishments:
Evolution of dendrite growth within cracked SEI

MD simulation setting (side views): SEI (LiF, yellow).
Electrolyte (green) access the SEI hole in direct contact with anode surface (blue) leading to Li^+ (purple) deposition and dendrite formation.

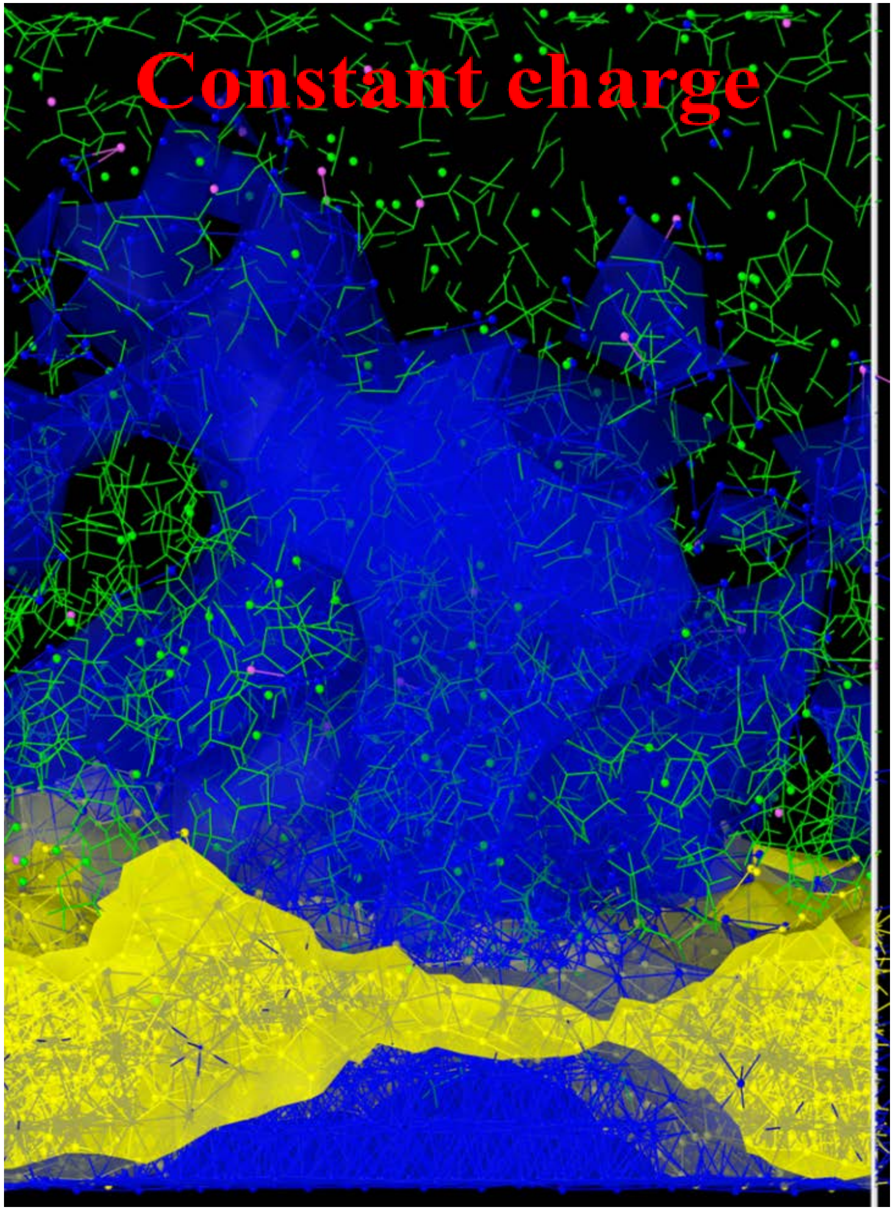
Charging at constant charge: net charge = zero

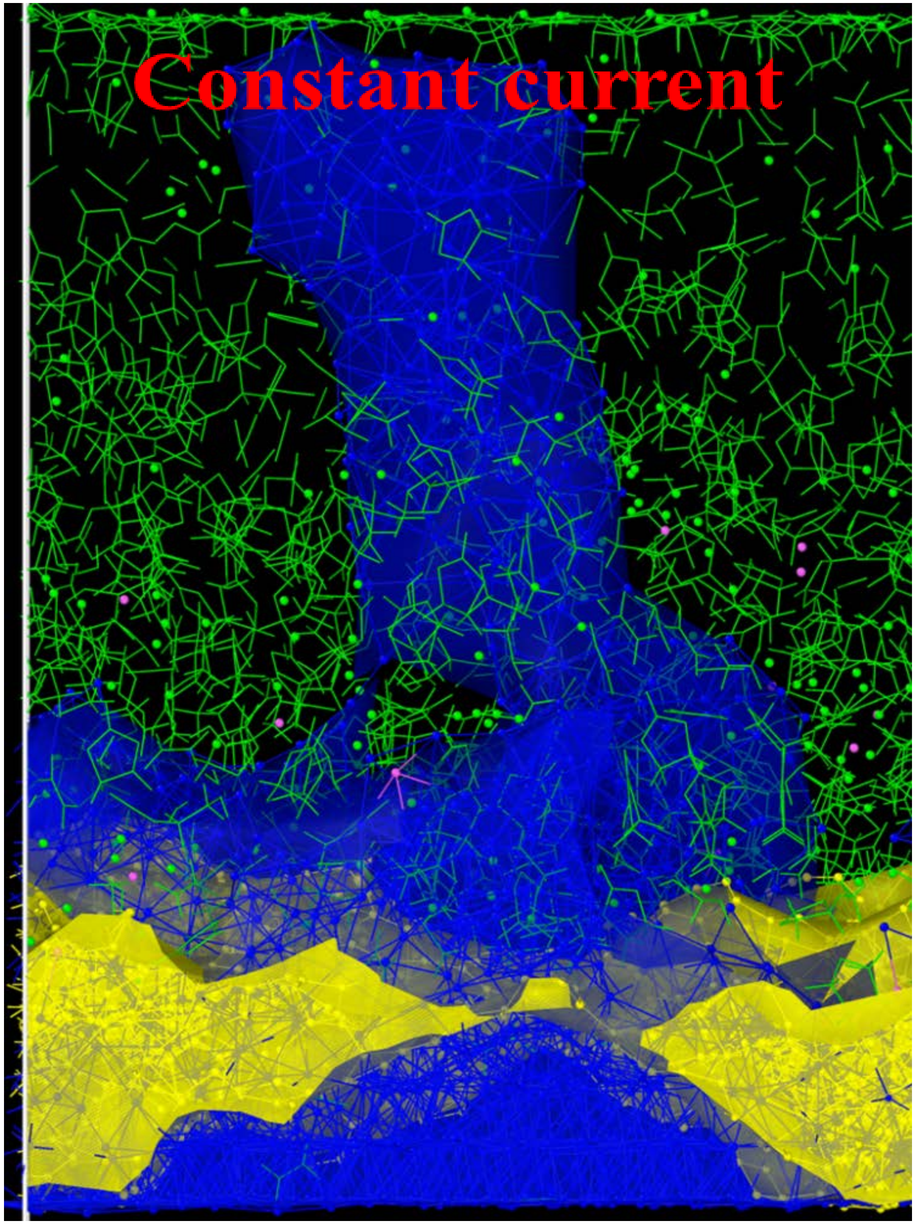


Charging at constant current: transient charge

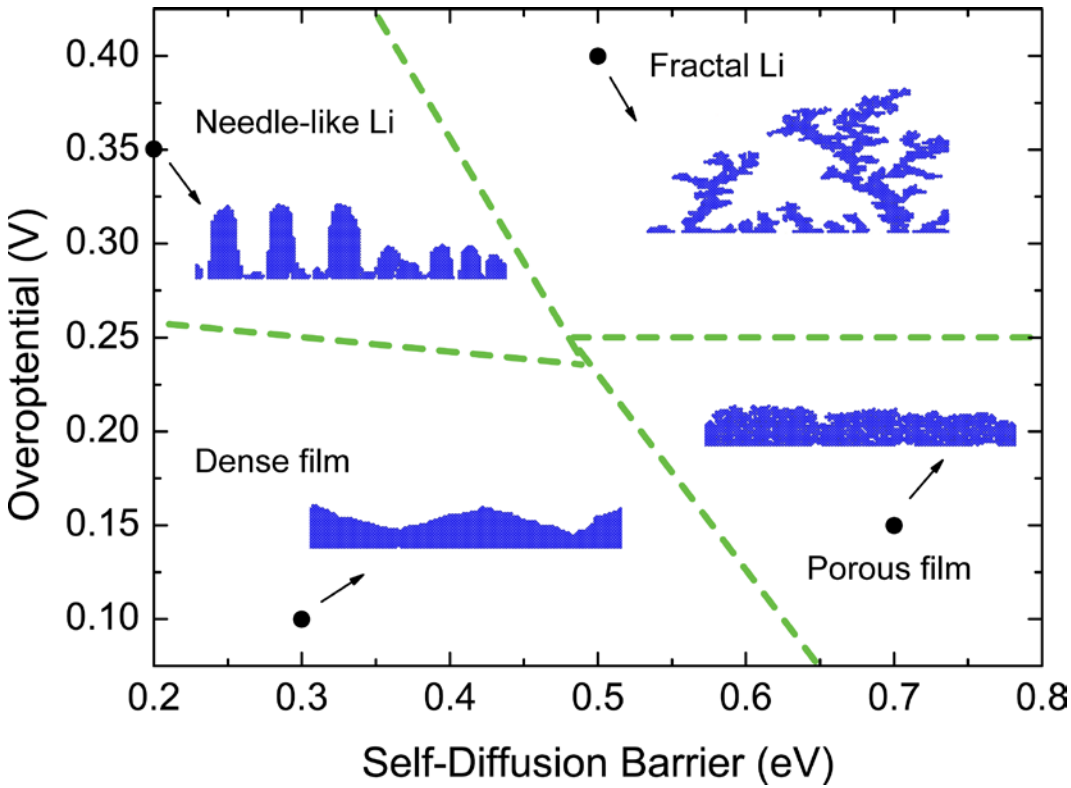


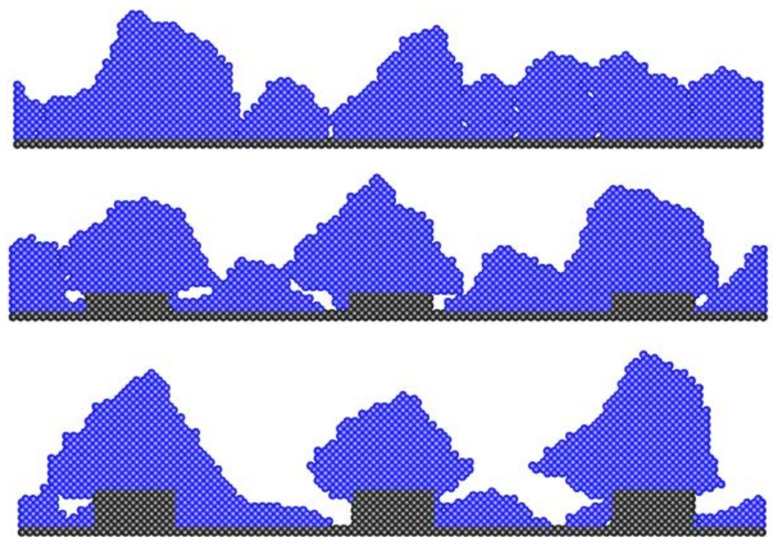
Technical Accomplishments: Dendrite growth through SEI crack





Technical Accomplishments:
Mesoscopic model of dendrite growth





Substrate roughness features favor formation of dendritic deposits on the substrate.

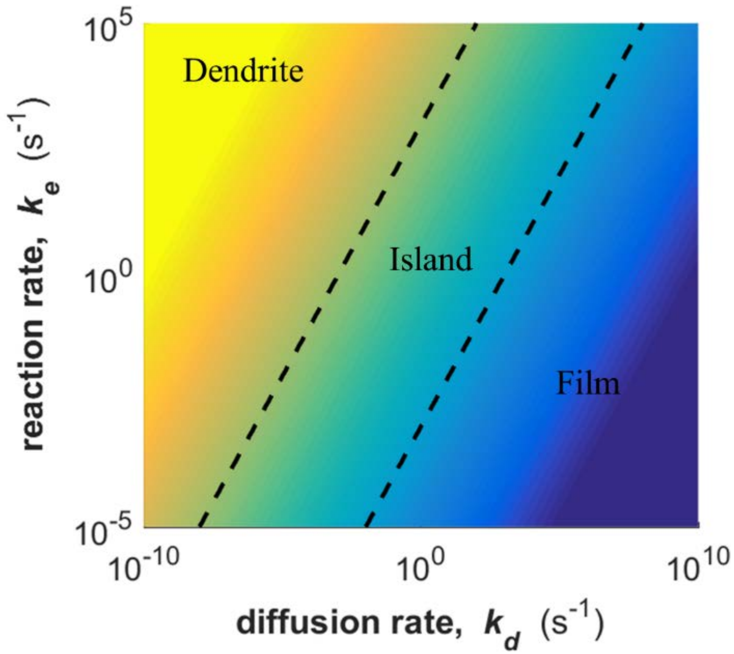
Structural inhomogeneities lead to spikes in reaction current densities near the protrusions, and preferential deposition near these features.

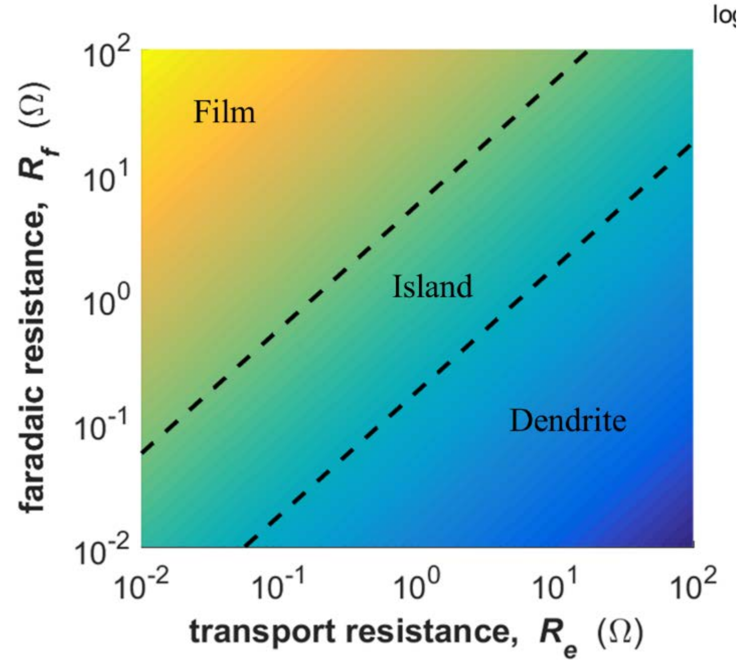
Factors affecting morphology:

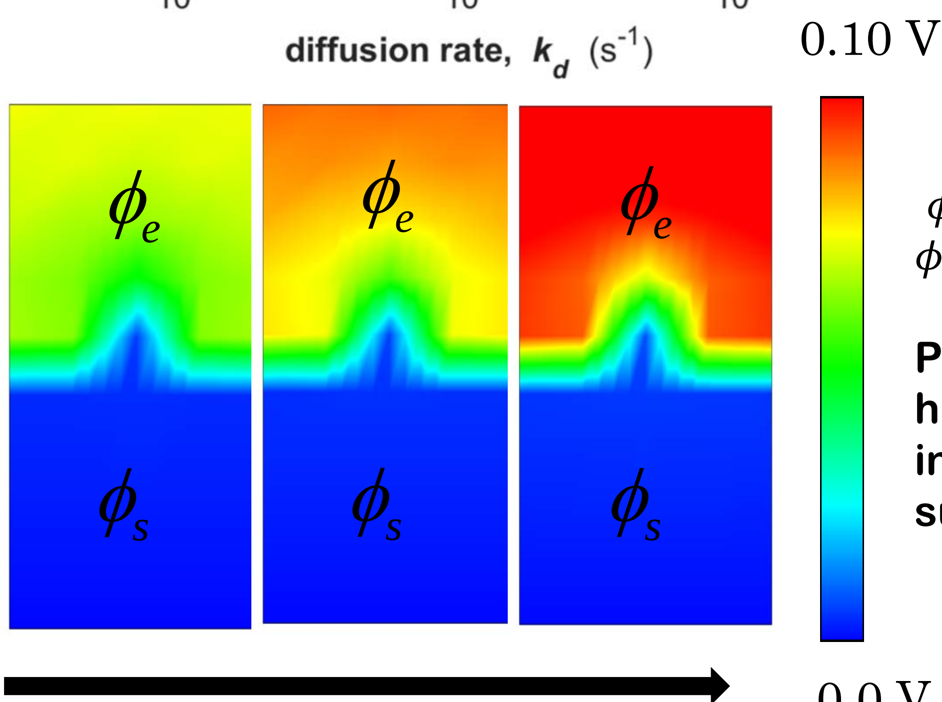
- **Overpotential: Surface inhomogeneity, applied current**
- **Li self-diffusion: Crystal orientation, Electrolyte, Surface defect**

D. Tewari, Z. Liu, P. B. Balbuena, and P. P. Mukherjee, submitted

Technical Accomplishments: Li-deposition regimes







Increasing current density

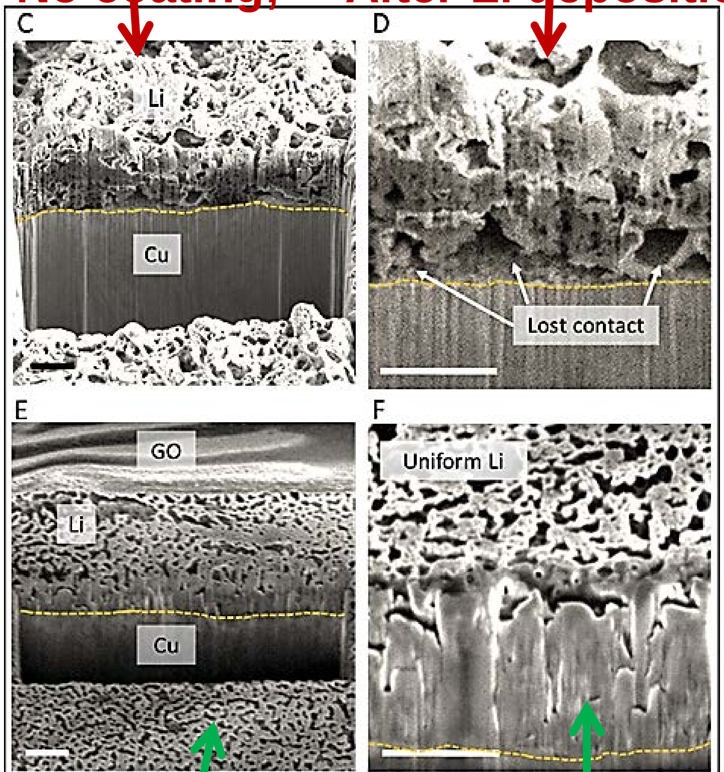
ϕ_s: solid phase potential,
ϕ_e: electrolyte phase potential

Presence of surface features leads to relatively higher current density at the peaks → increased propensity for Li deposits at the surface.

Technical Accomplishments: Dendrite mitigation strategies

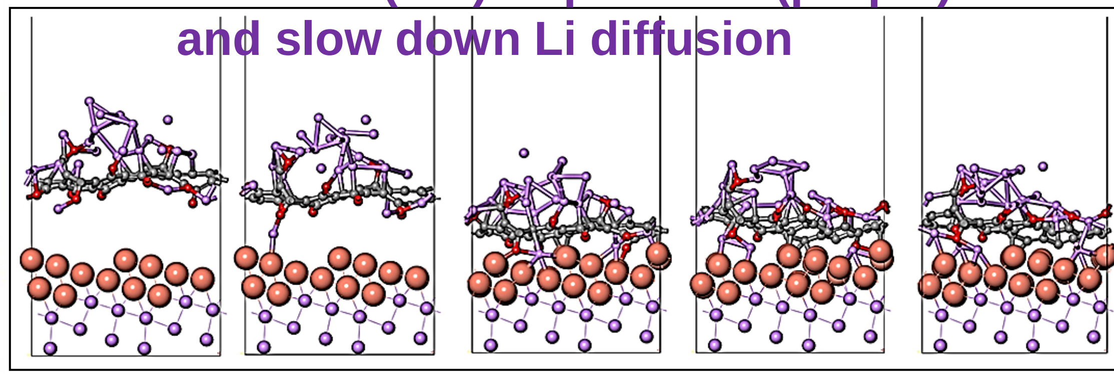
Cu surface coated with a 2-D graphene oxide layer
Experimental: microscopy; in operando optical & electrochemical measurements
Computational: DFT + AIMD: modes of Li diffusion + deposition

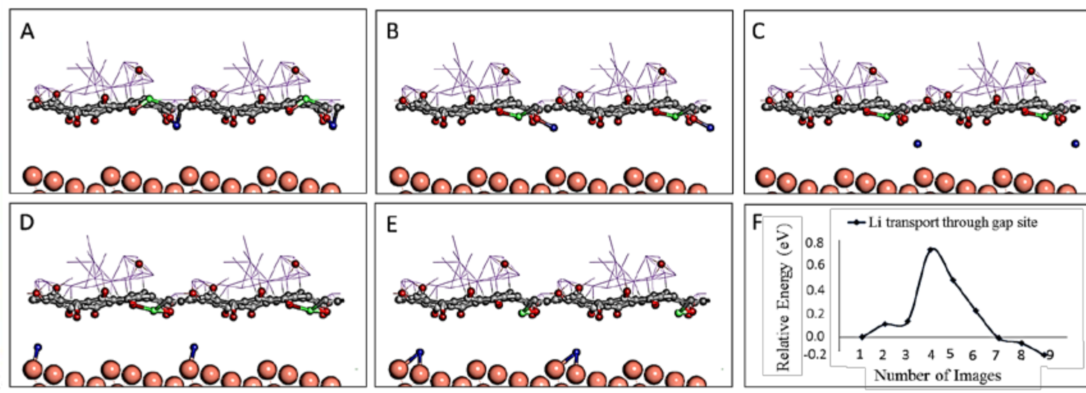
No coating; After Li deposition



w/GO coating; After Li deposition

O atoms (red) trap Li ions (purple) and slow down Li diffusion





Reduced diffusion rates are critical for smooth deposition at high currents

T. Foroozan, F. A. Soto et al, Adv. Funct. Mater., 1705917, (2018)

Work in collaboration with Prof. Shahbazian-Yassar, University of Illinois at Chicago

Responses to Previous Years Reviewers' Comments

Project was not reviewed last year

Collaboration and Coordination with Other Institutions

- Texas A&M University (prime) and Purdue U. (sub-awardee): Prof. Jorge Seminario (Co-PI, TAMU), classical MD simulations, and Prof. Partha Mukherjee (Co-PI, Purdue), mesoscopic modeling, have contributed large part of the reported work.

- UC Berkeley: Sum frequency generation vibrational spectroscopy (Y. Horowitz, Hui-Ling Han, Gabor Somorjai, UCB) is used together with ab initio molecular dynamics simulations (TAMU) to characterize SEI formation at the surface of amorphous Si anodes.

- PNNL: Experimental (M. Vijayakumar) and theoretical characterization of electrolyte reduction over Li metal surfaces (TAMU) covered by selected SEI components

- University of Illinois at Chicago: Graphene oxide coating materials examined as protection of Cu current collectors where Li is plated. The surface changes and reactions are characterized by surface science techniques (Prof. Shahbazian-Yassar, UIC), and DFT and AIMD simulations (TAMU)

Remaining Challenges and Barriers

- We have made significant progress determining a) the chemical origin of dendrite formation, b) the subsequent stages of dendrite growth; and c) dendrite mitigation strategies have been analyzed and demonstrated. We plan to develop ***possible strategies toward controlling the excessive accumulation of electrons that accompanies Li deposition even at very low currents***.
- We developed further understanding of ***SEI formation and growth and passivation role***. Additional challenges due to dynamic ***nucleation of these complex layers, SEI cracking, and restructuring*** will be addressed in the future.
- Additional work needs to address the ***effects of salt concentration, substrate roughness, and substrate chemistry on Li plating***.

Proposed Future Work

- **Rest of FY18**:
  - characterize Li^+ electrodeposition in presence of other ions (Na^+, K^+)
  - effects of operating conditions (temperature, C-rate on dendrite formation)
- **FY19:**
  - macroscopic effects during cycling of Si and Li anodes
  - identify electrolyte or electrode additives that may help mitigating the just-discovered chemical effects in Li metal anodes
  - identify electrolyte additives or other strategies for Si anodes
  - develop alternative charging strategies for Li metal anodes

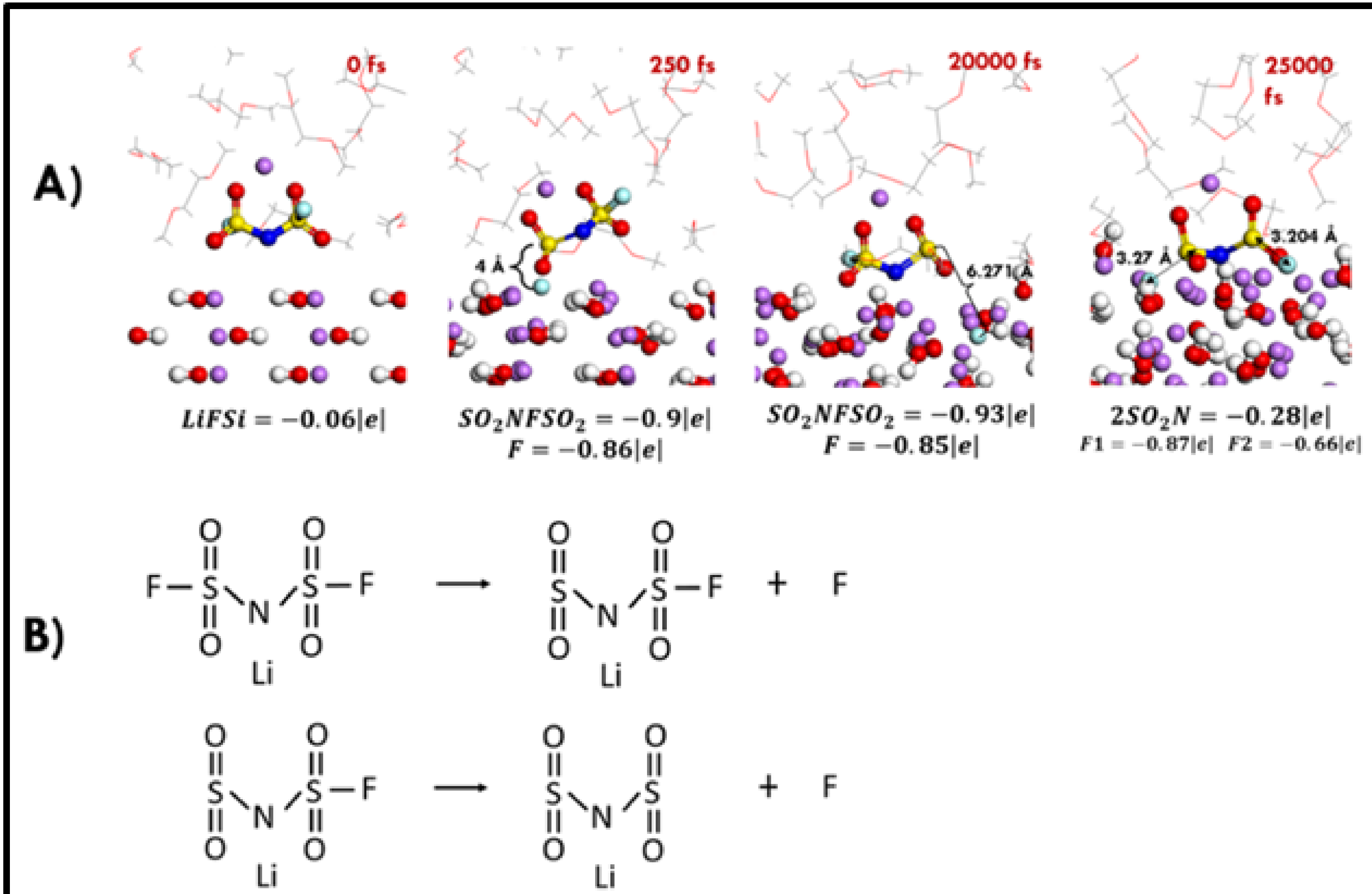
Any proposed future work is subject to change based on funding levels

Summary Slide

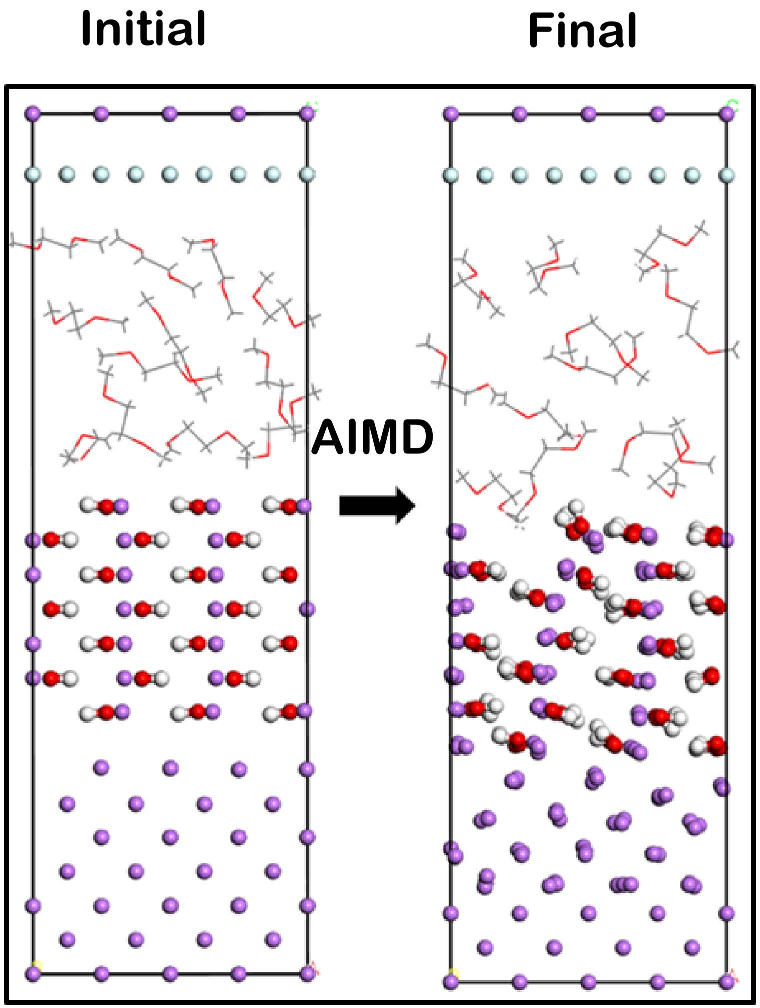
- **Relevance:** **Elucidation of SEI formation and cracking on Si alloys and SEI and dendrite formation on Li metal is crucial for *controlling irreversible capacity loss* and *improving lifetimes*.**
- **Approach:** **Characterization of issues that impede extended lifetimes in Si and Li metal anodes via *multiscale modeling*: from electronic structure and dynamics, through atomistic classical molecular dynamics, and mesoscopic modeling.**
- **Technical Accomplishments:** **identification of chemical origin of dendrite formation; elucidating of passivation role of SEI layer on Li metal; initial studies of SEI growth; multiscale characterization of dendrite growth; test and analysis of coatings for mitigation of dendrite growth on Li metal.**
- **Collaborations:** **Synergistic multiscale modeling approach (TAMU/Purdue); SEI formation in amorphous Si surfaces (with UCB); effect of current collector coatings on dendrite formation (with UIC); passivation role of SEI (with PNNL).**
- **Future Work:** **Develop strategies for control of deposition effects on Li metal and for enhancing practical utilization of Si anodes.**

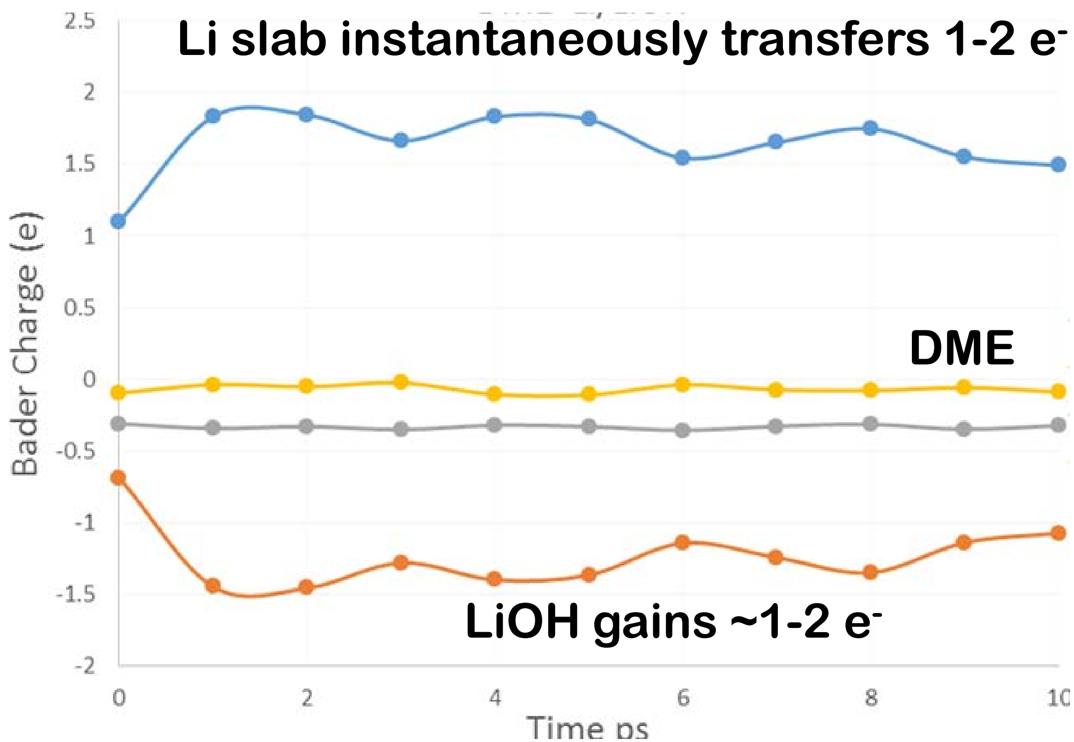
Technical Back-Up Slides

Anion decomposition on Li_2O



Other passivation layer: LiOH on Li metal

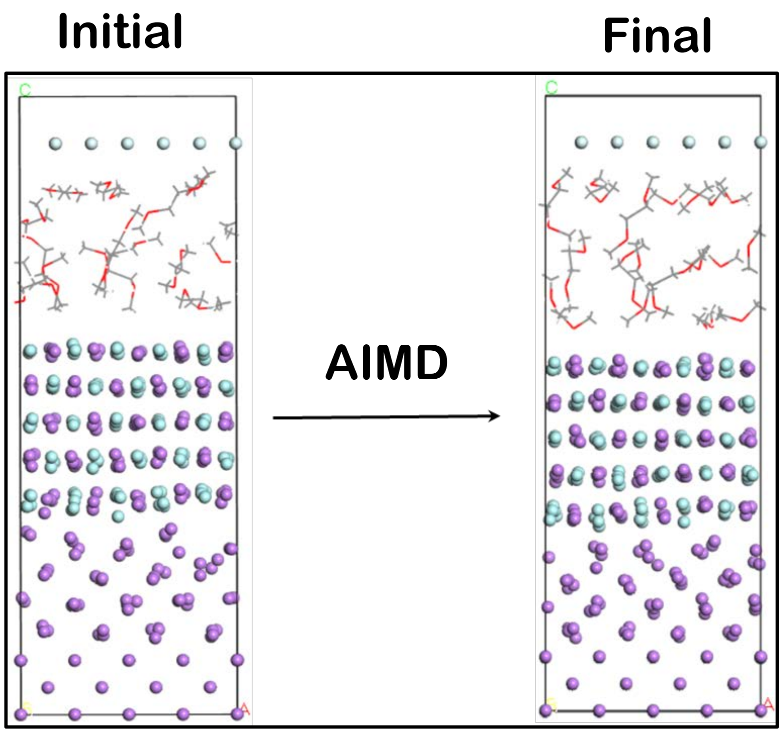


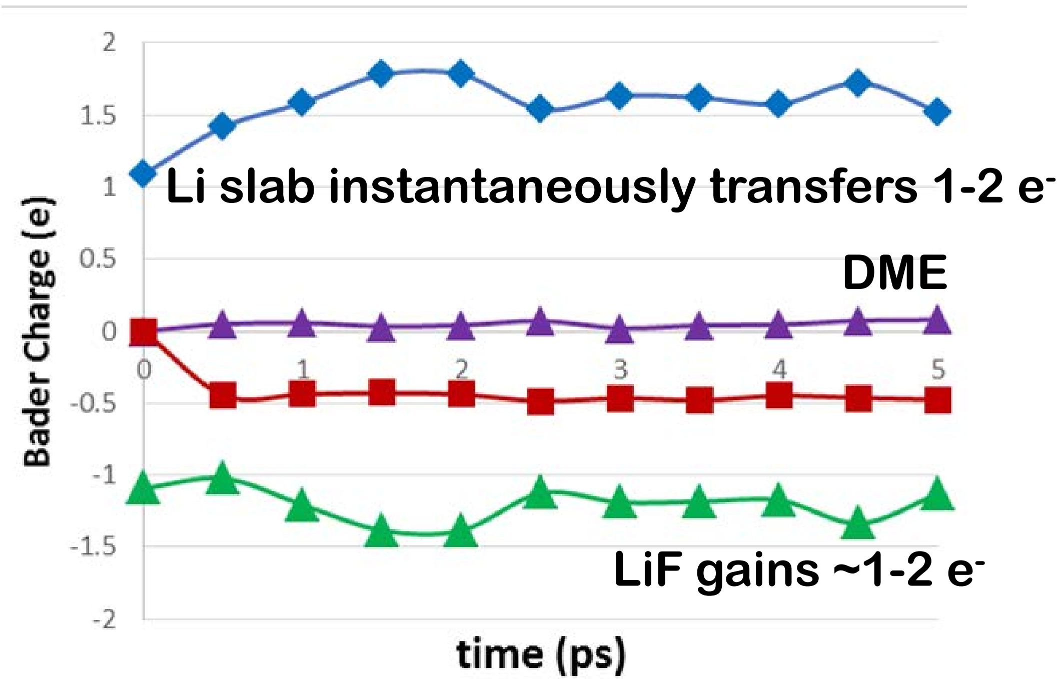


LiOH undergoes extensive rearrangement that could be the reason for the delayed charge transfer

LiFSI is less extensively reduced than on Li_2O

Other passivation layer: LiF on Li metal





Some interfacial rearrangement that could be the reason for the delayed charge transfer

LiFSI is reduced similarly to reduction on LiOH/Li

Monitoring properties from classical MD simulations shown in slide 17 and 18