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

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June 1-4, 2020

Project ID #: bat329

Overview

Timeline

- Start date: October 1, 2016
- End date: September 30, 2020
- Percent complete: 90%

Budget

- Total funding: $1,333,335
  - DOE share: $1,200,000
  - Contractor share: $133,335
- Funding received
  - FY19: $399,844
  - FY20: $0.0

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)
  - V. Murugesan (PNNL)

- Project lead: TAMU

Relevance

Impact:

The *stability of* Li metal anodes depends on their *structural evolution* during battery operation that is strongly affected by the nature and chemistry of the electrolyte. Understanding SEI reactions and nucleation, with simultaneous Li deposition and nucleation is necessary to design proper electrolyte solutions, able to stabilize Li metal anodes. Achieving such goal will have large impacts on clean energy technologies.

Objective:

Evaluate and characterize *interfacial phenomena* in Li-metal anodes and develop strategies leading to *controlled reactivity* at electrode/electrolyte interfaces using advanced modeling techniques based on first-principles. It addresses the understanding of life-limiting mechanisms taking into account microscopic phenomena.

Milestones

Time	**Description (*status*)**
June 2019	Complete study of improved electrolytes for Li anodes. (*Completed*)
September 2019	Complete evaluation of alternative charging strategies for Li anodes. (*Completed*)
December 2019	Complete thermal and chemical/electrochemical analysis of dendrite growth (*Completed*)
March 2020	Complete analysis regarding SEI formation and electrodeposition processes (*Completed*)
June 2020	Complete studies on cationic additive effect on electrodeposition (*In progress*).
September 2020	Complete mesoscale investigation on external field effects on electrodeposition

Approach

Methods:

Interfacial problems (Li deposition and nucleation, SEI formation) addressed with *synergistic multiscale modeling* (ab initio, classical molecular dynamics, and mesoscopic level theories).

All findings rigorously compared with experimental evidence (collaborations with PNNL).

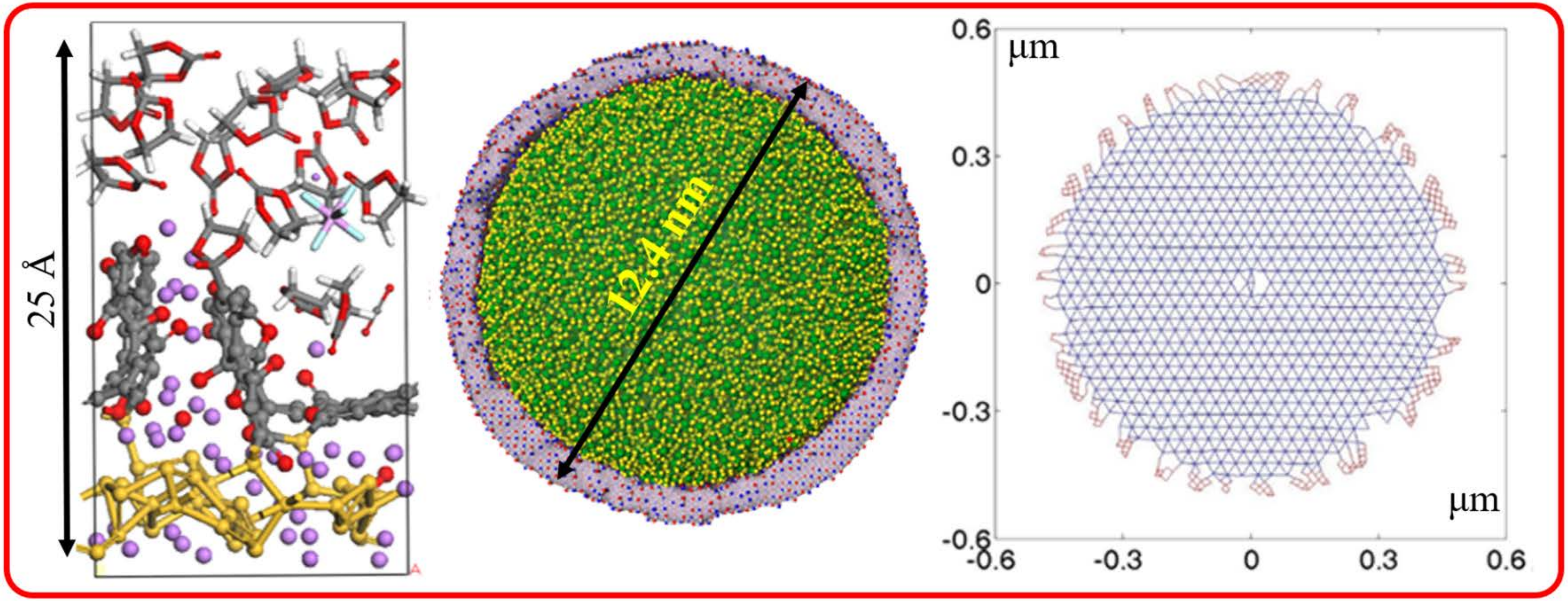
First-principles approach allows prediction and interpretation of observed and new phenomena.

Addresses technical barriers/targets: SEI nucleation near Li deposits as a function of electrolyte composition and applied potential characterizes *SEI evolution*. SEI reforming and dendrites formation elucidate *anode capacity loss and cell lifetime*.

Progress towards FY20 milestones: Dendrite nucleation and growth analyzed at nano and mesoscopic levels. Thermal and chemical effects on nucleation investigated. Alternative charge strategies suggested.

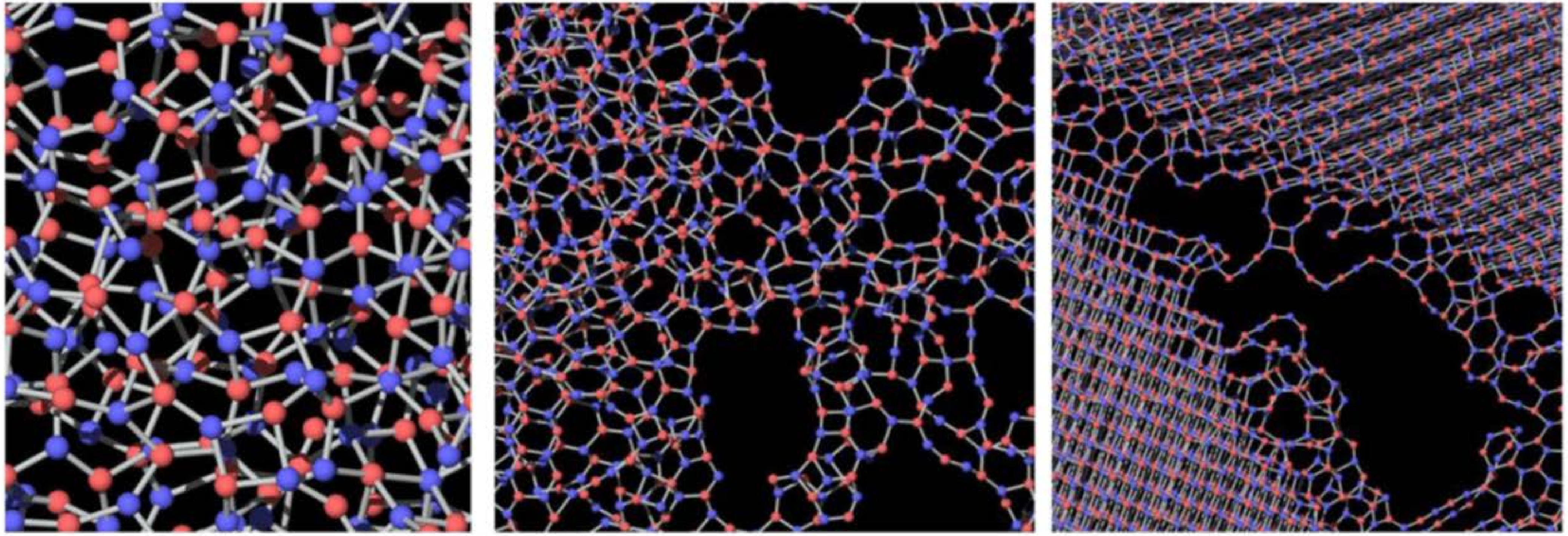
Technical Accomplishment: Coupling of Modeling Scales

from 10^{-10} to 10^{-8} to 10^{-6} m



The team published a review paper on the degradation of Si anodes, J Power Sources, 419, 208-218 (2019).

Technical accomplishment: Understanding degradation of SEI layers



(a) (b) (c)

Types of deformation due to volume expansion during the lithiation of Si anode:
(a) Only amorphization, (b) amorphization + fracture (c) only fracture

Galvez Aranda et al., J Power Sources, 419, 208-218, (2019)

Technical Accomplishments: Development of a simple model to describe Li nucleation

The electronic structure of Li_x nanoclusters (x =2-20) were used to investigate nucleation and growth of lithium dendrites from an *ab-initio* perspective

Kamphaus, Hight, Dermott, Balbuena, PhysChemChemPhys 2020

We showed that kinetic processes have more control over non-uniform growth than thermodynamics processes. Based on this, we developed a Matlab code to describe Li nucleation of up to 2,000 atoms

Thermodynamic calculations of reduction of Li ions on Li_x nanoclusters indicated that there is no directionality in the growth

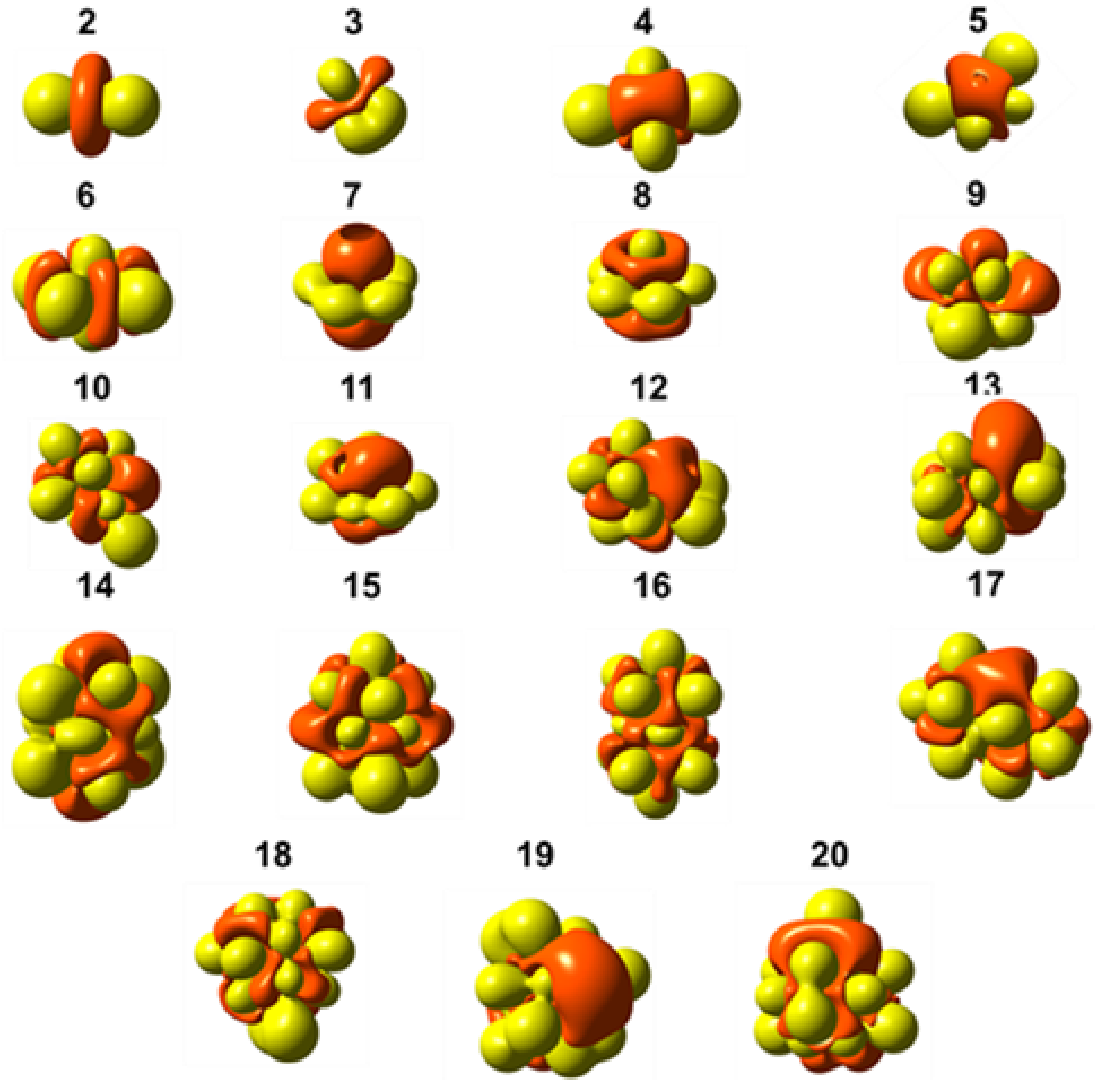
Technical Accomplishments: Development of a simple model to describe Li nucleation

The important forces guiding the Li^+ ion in the range between bulk solvent and reduction distance will be electrostatic interactions which will come from two places: the electrostatic potential (ESP) and electric field from the electrode

We calculated the ESPs for the nanoclusters: that is the locations where the cluster may attract or repel a charged positive ion. Orange are attractive (negative) regions for the Li cation; yellow are repulsive (positive) regions

The ESP is attractive to the Li^+ ions at interstitial locations

Kamphaus, Hight, Dermott, Balbuena, PhysChemChemPhys 2020

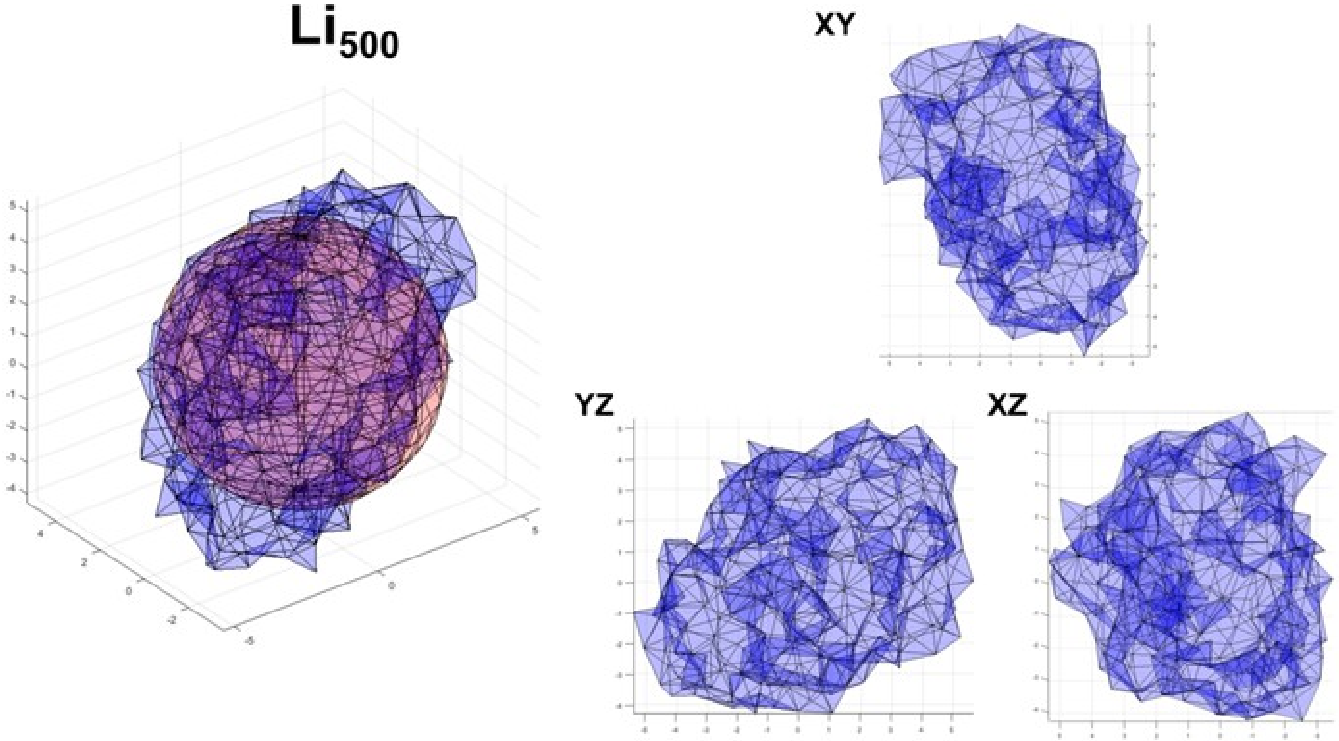


Isosurface value of .008 au

Technical Accomplishments: Development of a simple model to describe Li nucleation

Using this information about the shape and magnitude of the Li cluster’s ESP with and without an external electric field, we executed new Li^+ ion addition and reduction calculations. Instead of placing the Li ions in unique locations anywhere on the cluster, Li ions were only placed at unique sites that had negative ESP.

Based on this, we built an **evolution nucleation model** that is computationally inexpensive and allows for the growth of large Li clusters (up to 5,000 atoms)



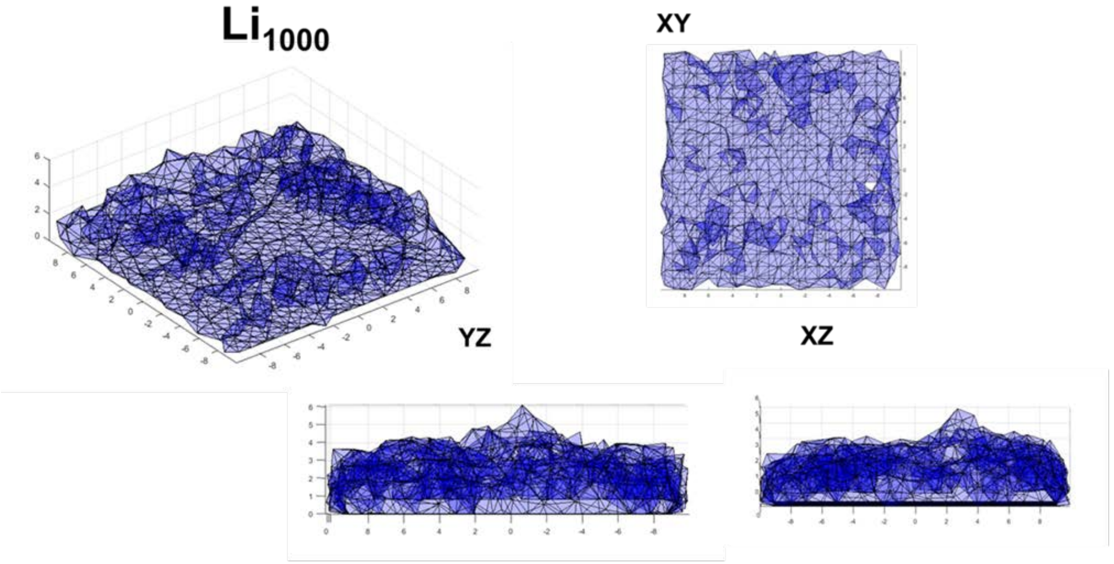
Most acentric Li_{500} cluster after 1000 Li deposition events. Blue is surface of cluster, orange is a unit sphere to provide perspective

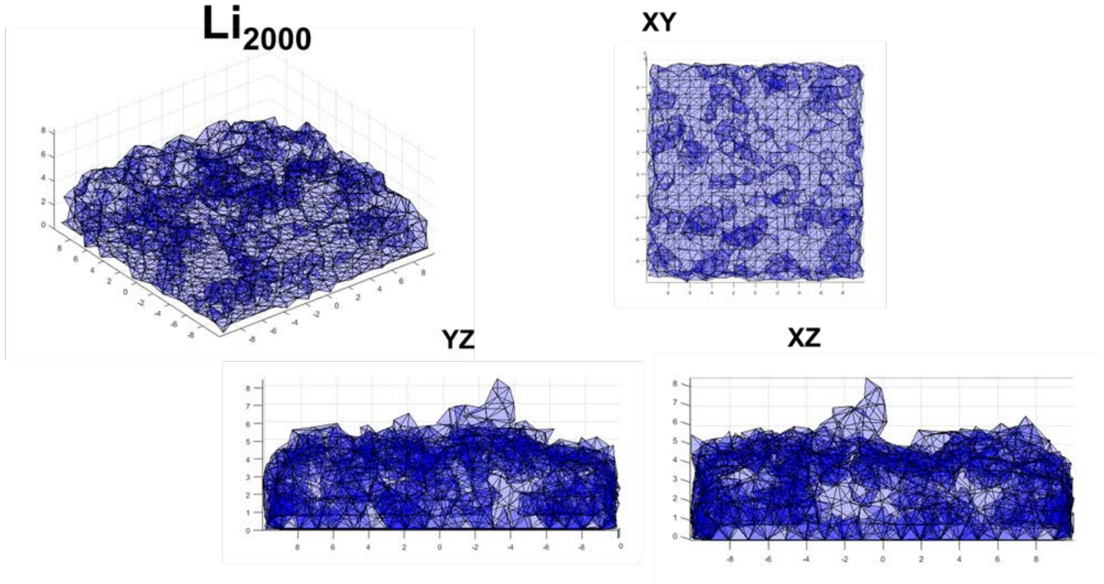
Kamphaus, Hight, Dermott, Balbuena, PhysChemChemPhys 2020

Technical accomplishments: Growth on a surface

Top structure: Li_{1000} model electrode with the observed largest dendritic growth case (lateral, top, and side views).

Bottom structure: Li_{2000} electrode with the observed largest dendritic growth case (lateral, top, and side views).

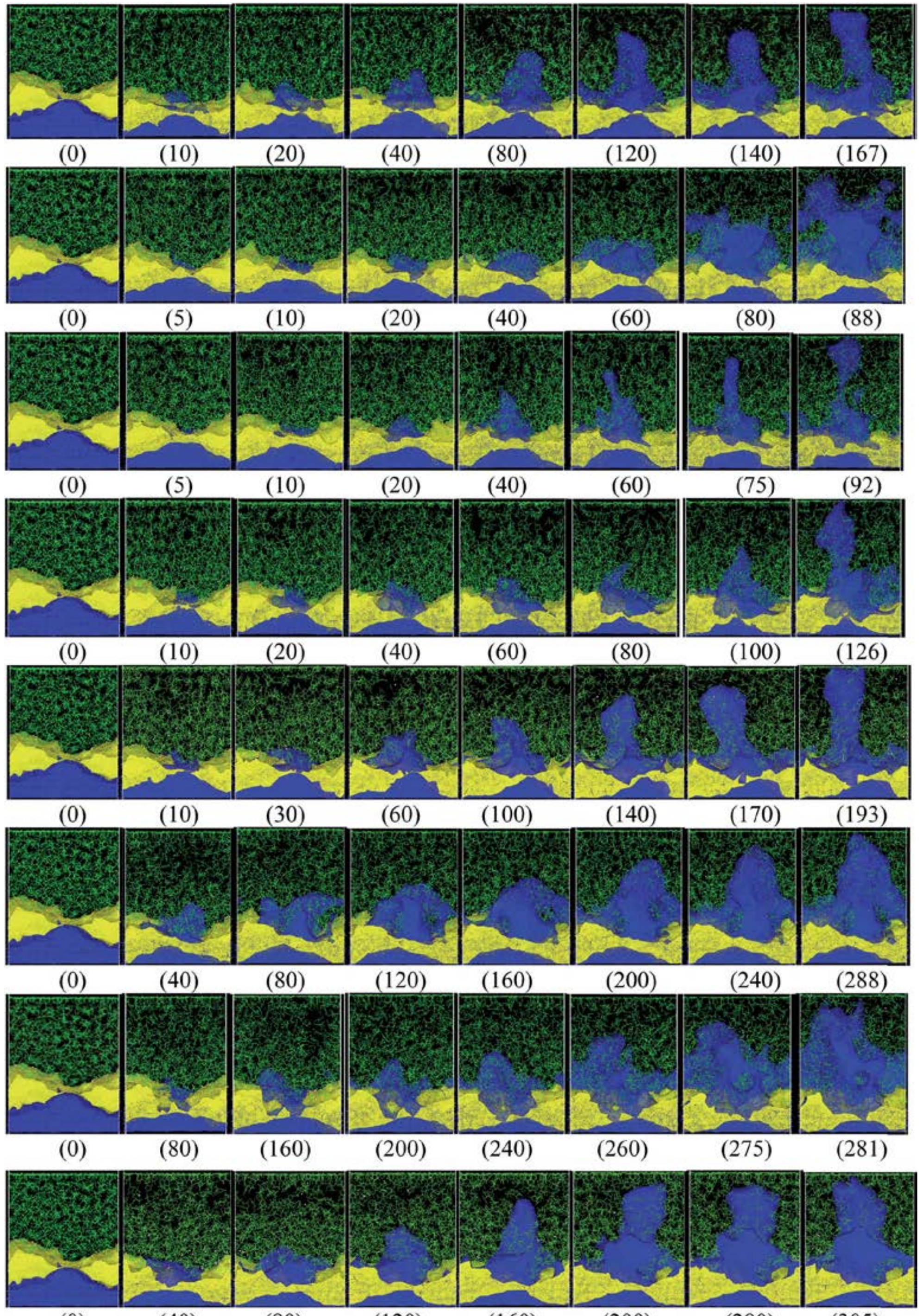




These simulations demonstrate that with very few rules based on the ESP from first principles simulations, dendritic structures have been observed in the electrode surface.
This gives important insights into the fundamentals of lithium dendrite nucleation and growth and mitigation strategies to counteract dendrites.
Based on this model, solutions to changing how dendrites grow should focus on manipulating the electrostatic potential whether by insulating or ensuring homogeneity.

Kamphaus, Hight, Dermott, Balbuena,
PhysChemChemPhys 2020

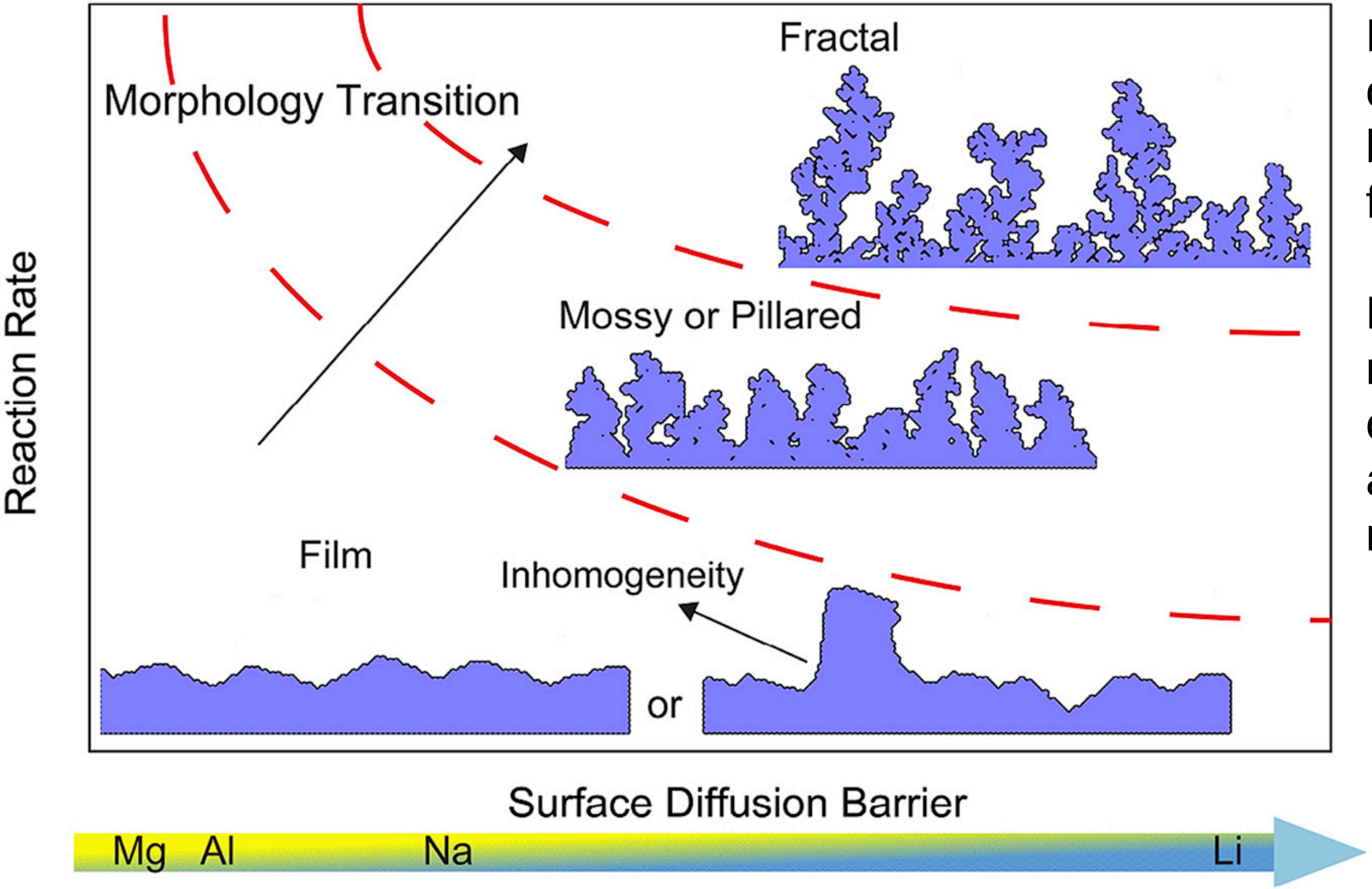
Technical Accomplishments: Dendrite growth through a cracked SEI layer



Dendrite growth from MD simulations for 8 cases of lithiation respectively (shown from top to bottom rows.
The label (inside parentheses) indicates the time in ps when the snapshot is taken.
Color code: Li-metal (blue), Li+ (pink, very hard to see them), EC and PF6 (green), LiF (yellow).

LA Selis & JM Seminario, RSC Adv., 2019, 9, 27835

Technical Accomplishment: Understanding Li Electrodeposition

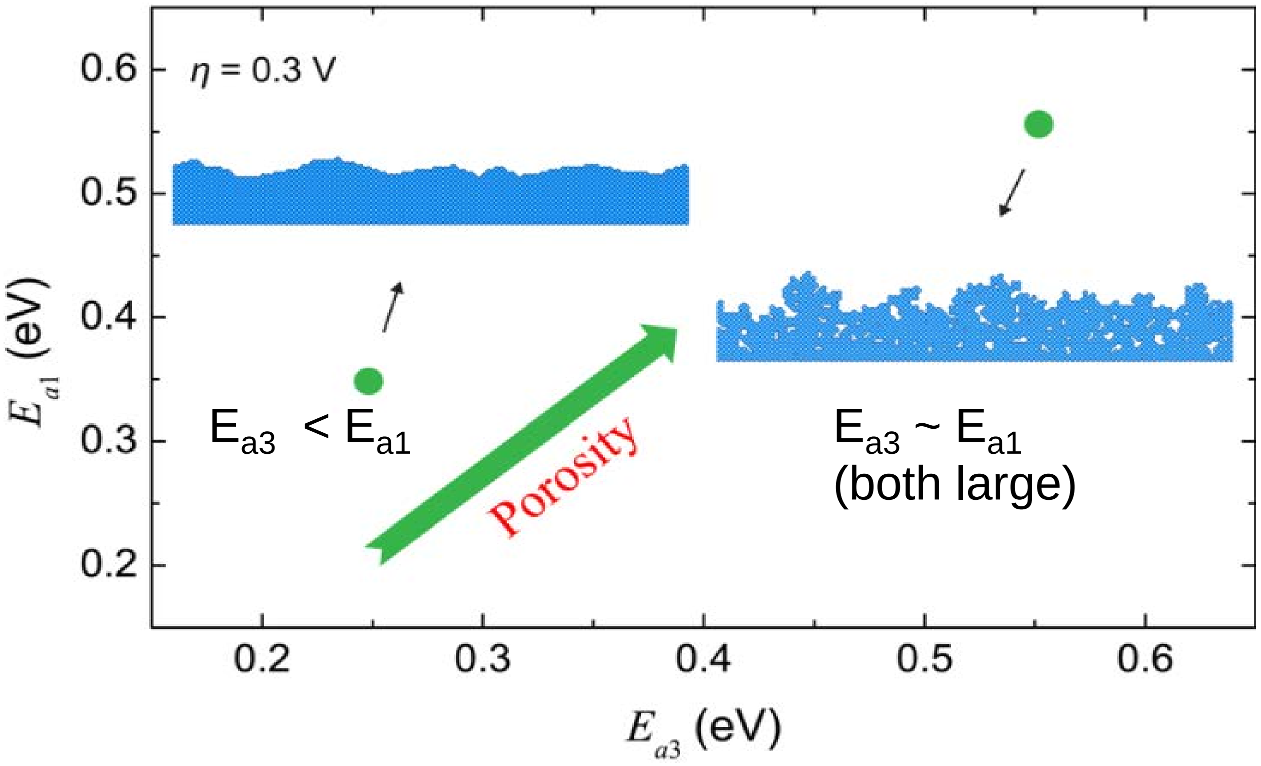


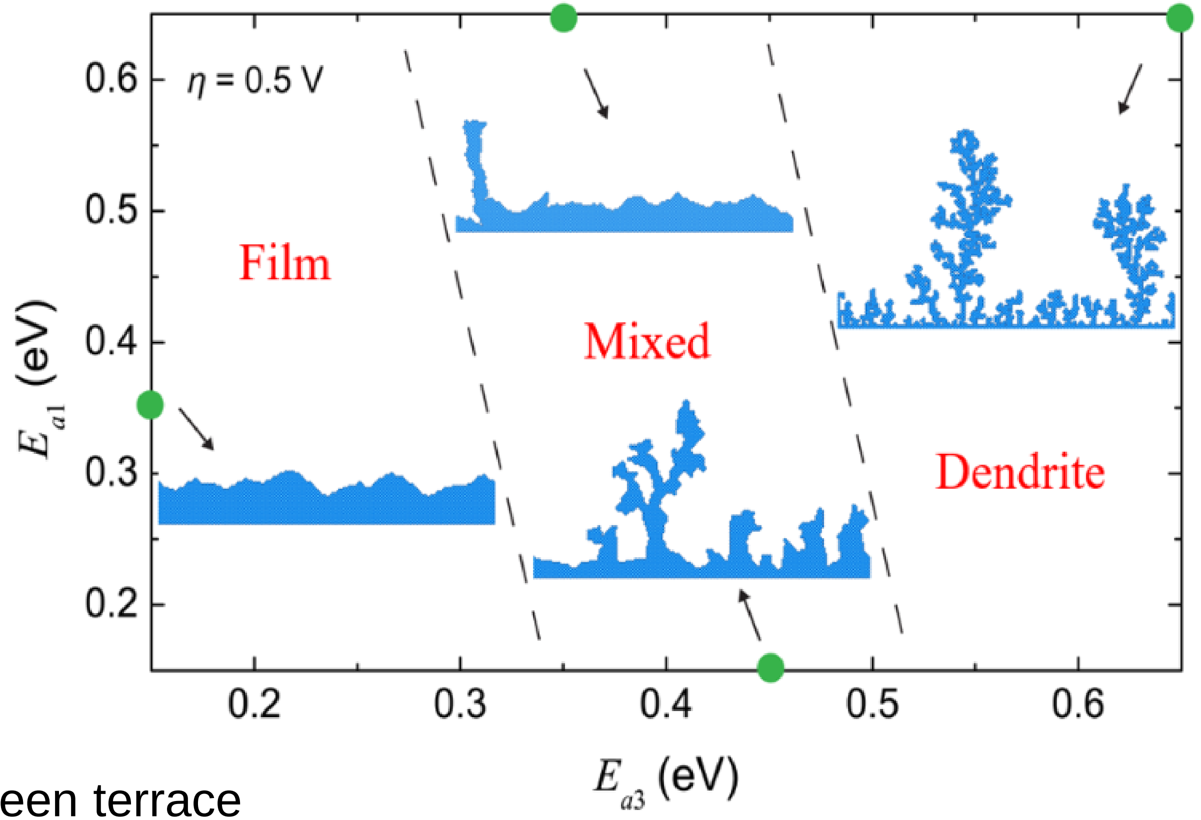
Mesoscopic model reveals the effects of electrochemical deposition rate and barrier for ionic surface diffusion for various metals.

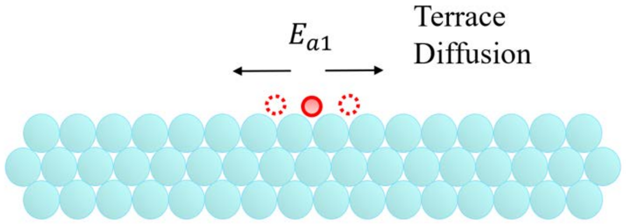
Li high surface diffusion barriers make them the easiest to form all sorts of inhomogeneities, becoming worst as at higher electrochemical deposition rates.

Hao, Verma and Mukherjee, *Energy Storage Materials*, **20,** 1 (2019)

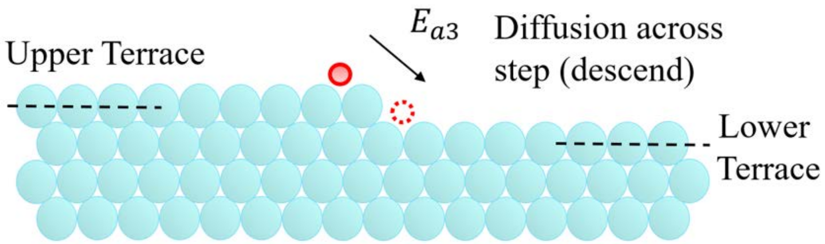
Technical Accomplishment:
Effects of Surface Diffusion on Electrodeposition Morphology





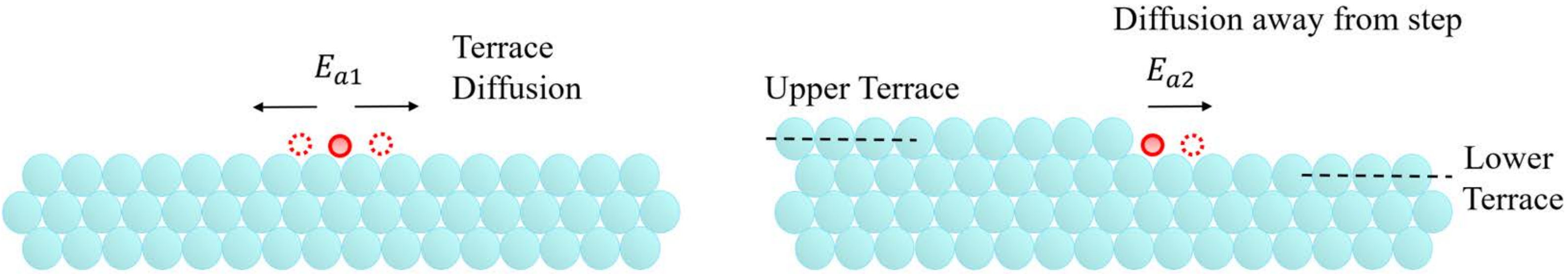


Competition between terrace and lower terrace diffusion induces growth morphologies



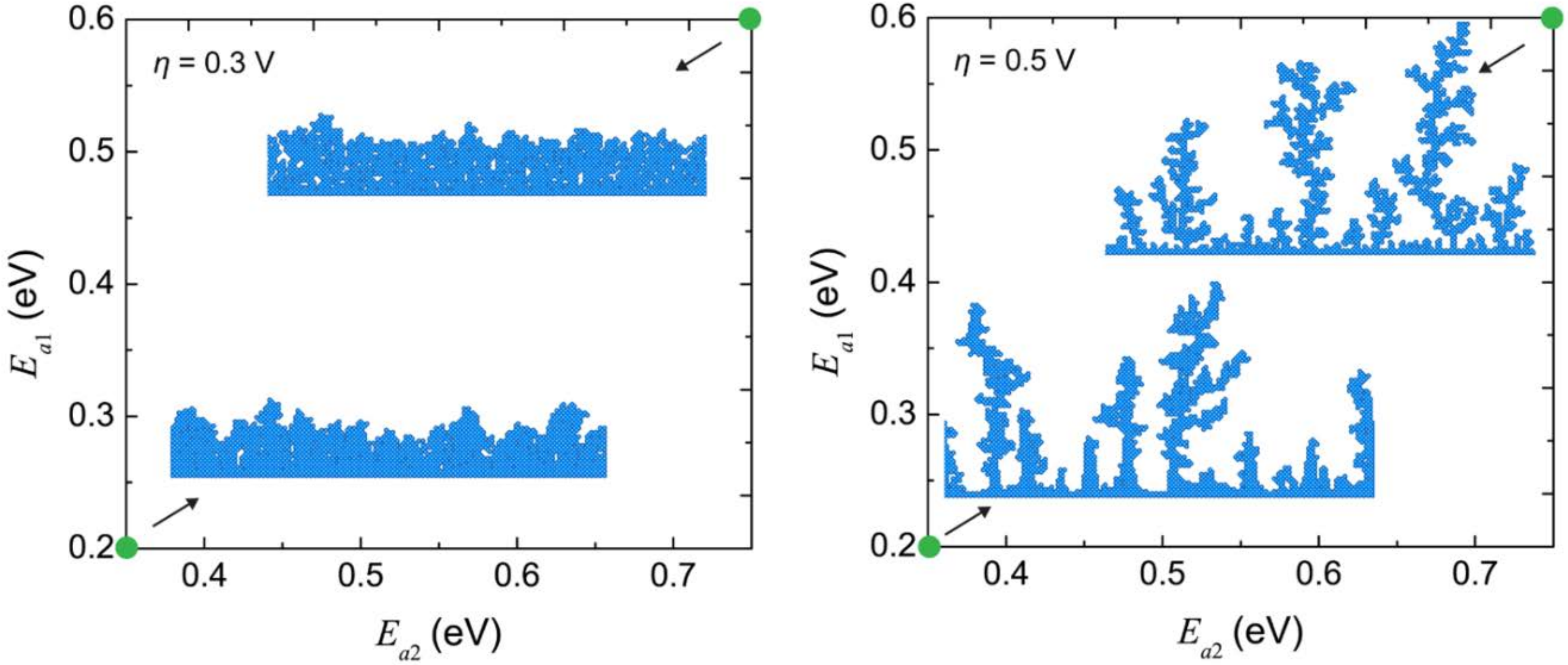
Vishnugopi, Hao, Verma and Mukherjee (2020) under review

Technical Accomplishment:
Effects of Surface Diffusion on Electrodeposition Morphology

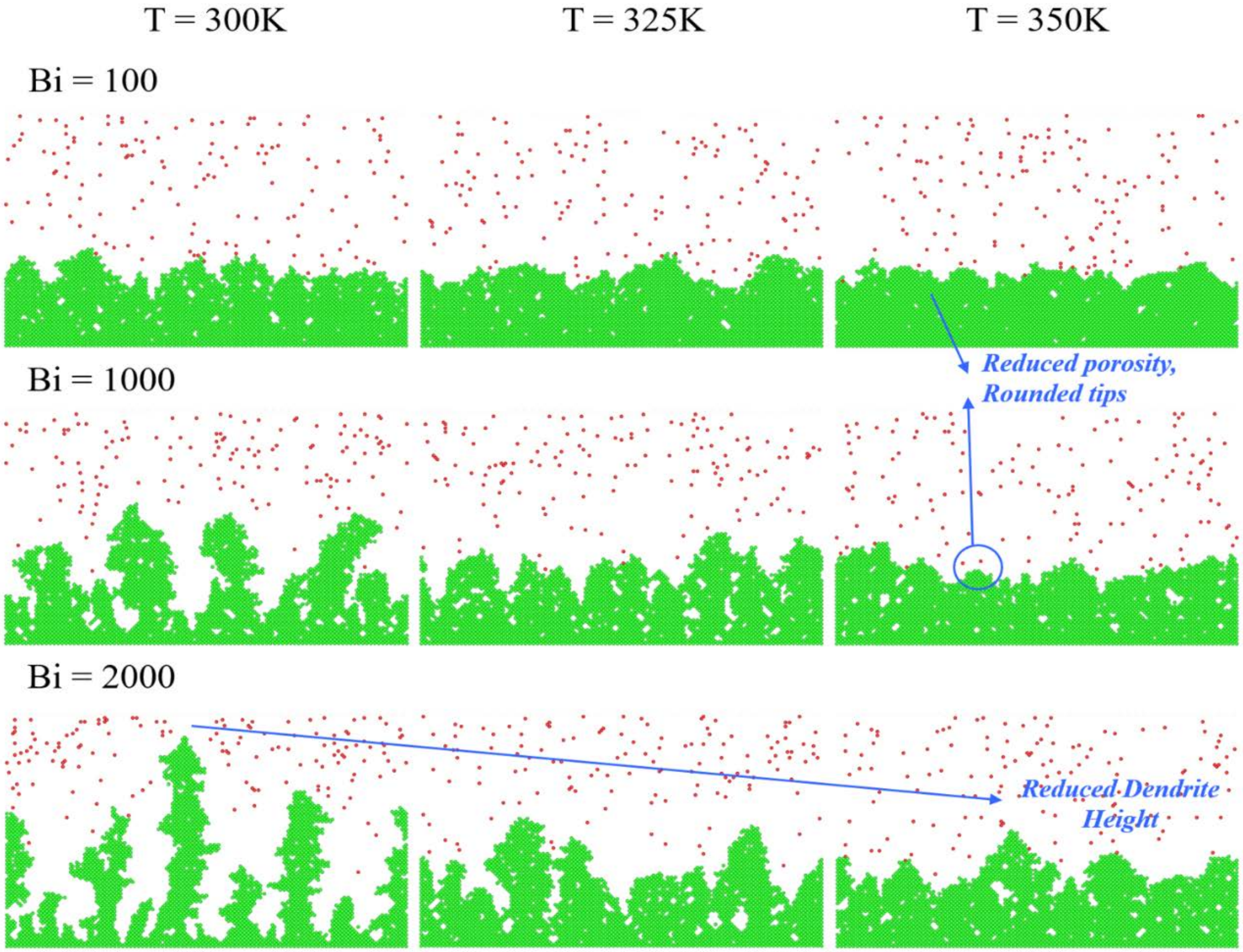


Competition between terrace diffusion and diffusion across a step

*Vishnugopi, Hao, Verma and Mukherjee (2020) under review



Technical Accomplishments: Alternative charge strategies based on thermal effects



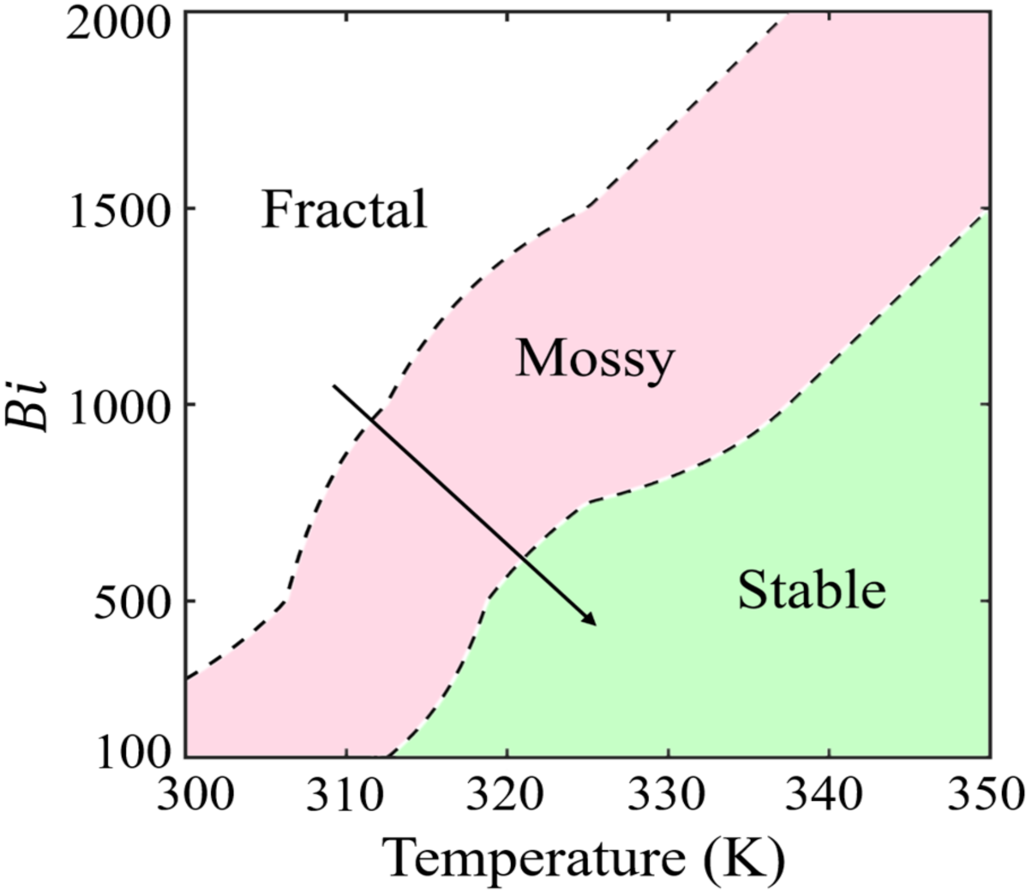
The Biot number (Bi) is a dimensionless number that is proportional to the ratio of the rate of electrochemical reaction over the rate of ion diffusion in the electrolyte.

Electrodeposition morphologies of Li are obtained with varying *Bi* for a uniform thermal field

An increase in temperature results in reduced porosity, formation of rounded tips and lowered dendrite height.

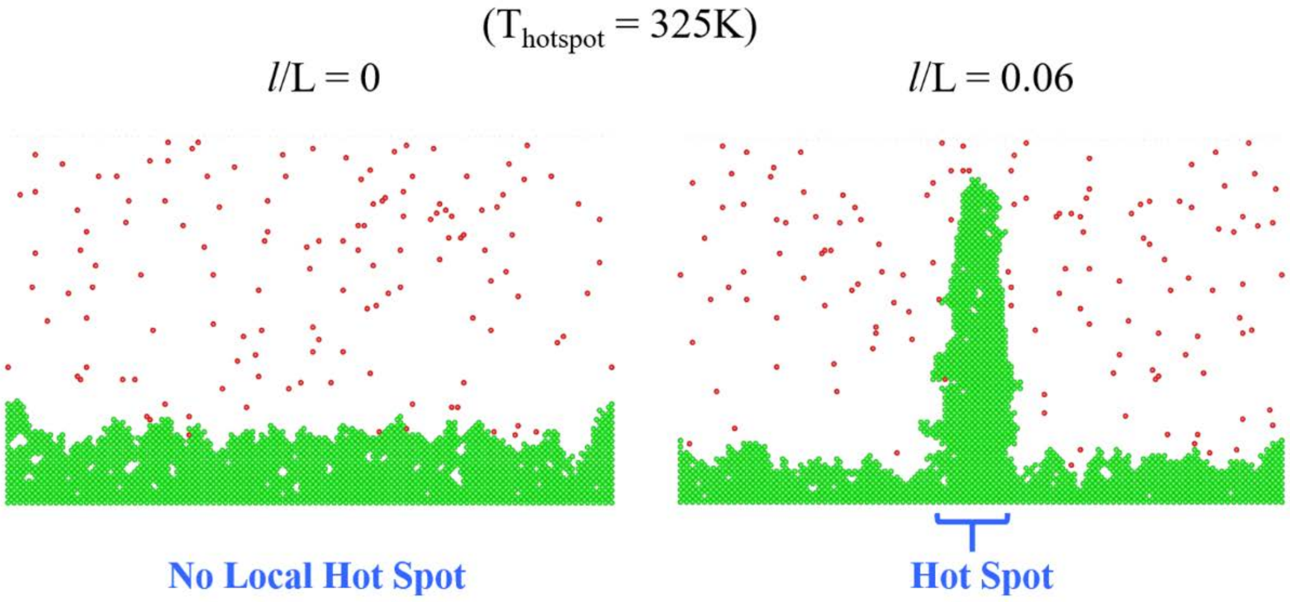
Vishnugopi, Hao, Verma and Mukherjee (2020) under review

Technical Accomplishments: Effect of Temperature on Li Dendrites



Phase map of Li morphologies
in terms of *Bi* and temperature

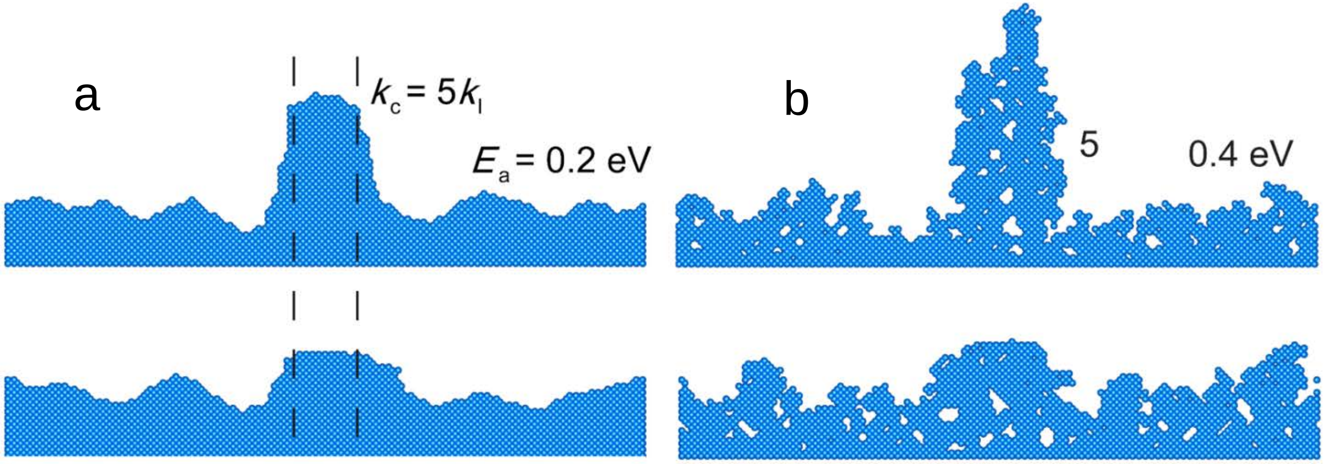
Effect of a local thermal hot spot



High temperatures favor homogeneous growth
at least for low Bi numbers (i.e. low electrochemical
reaction rates or high ion diffusion in the electrolyte)

Vishnugopi, Hao, Verma and Mukherjee (2020) under review

Technical accomplishments: Cationic Shield Mediated Electrodeposition Stability



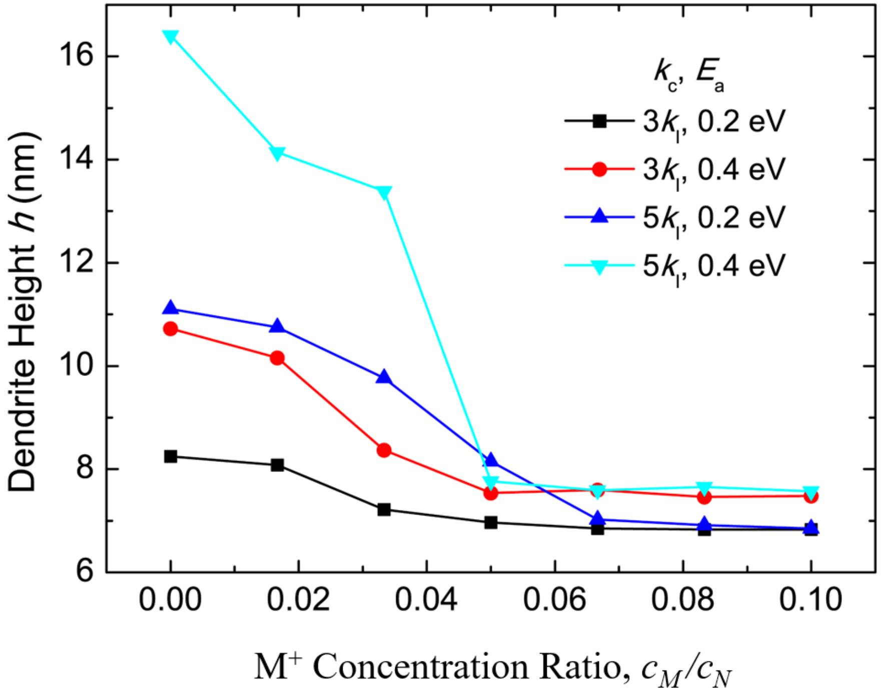
Hao, Verma and Mukherjee, *J. Mater. Chem. A*, **7**, 18442 (2019)

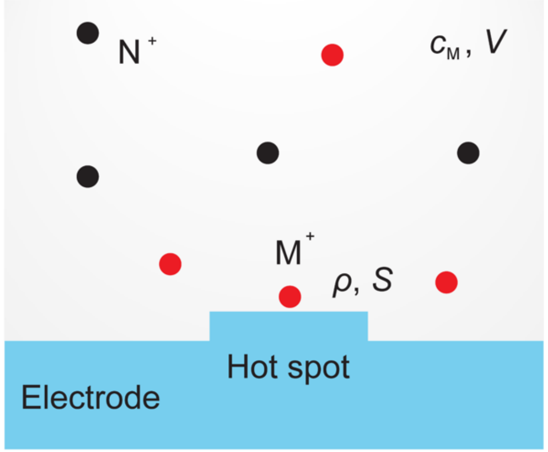
Dendrite height as a function of additive/metal ion concentration

A critical concentration ratio appears ~ 0.05

Suppression of inhomogeneity induced dendrites

Upper/lower morphology obtained without/with the Cationic Shield effect under two diffusion barriers (E_a) and reaction rate (k_c) shown at left and right





adding specific cations to the electrolyte solution

Responses to Previous Year Reviewers' Comments

- Q1. Reviewer 3 thought our project was experimental and criticized that no experimental results were presented; however our project is based on multiscale modeling. Also, this Reviewer asked about the Si anodes work, but that was presented during the first year report. Reviewer 4 said that our results "do not lend to experimental confirmation"; however most of the SEI products detected in our simulations were found through spectroscopy and other experimental tools (sometimes after we reported them).
- Q2. Reviewer 2 and 3 did not see the connection to experiments; however that was illustrated in the report by the XPS measurements from PNNL. It was collaborative work and it was published in ACS Appl. Mat and Int., 2019.
- Overall, the main question is related to "validation of the theory". The results of our analyses not always can be "validated" by experiments because there are no experiments that cover such scale of times and lengths. New "in situ" and "in operando" experiments can eventually provide further microscopic insights that will certainly be compared with our results. In the same way, theory and simulations are additional tools, that provide new microscopic insights.

Collaborations and Coordinations with Other Institutions

- In previous years we collaborated with V. Murugesan from PNNL who carried out XPS experiments. The analysis was complemented with results from our AIMD simulations.

- The progress shown this year reflects collaboration between the prime (TAMU) and participant (Purdue) institutions.

Remaining challenges and barriers

- This project generated numerous new insights into the problems existent at electrolyte/anode interfaces. In previous years we focused on liquid electrolyte solutions structure and dynamics and their decomposition on Si anodes, crack formation on SEI, and dendrites growth on both lithiated Si and Li anodes. These insights have been communicated through numerous publications.
- As we advance in our understanding we also realize the remaining challenges. In our experience multiscale modeling approaches are great tools to elucidate complex phenomena and complement experimental tools.

Proposed Future Research

- This is the last year of this project.

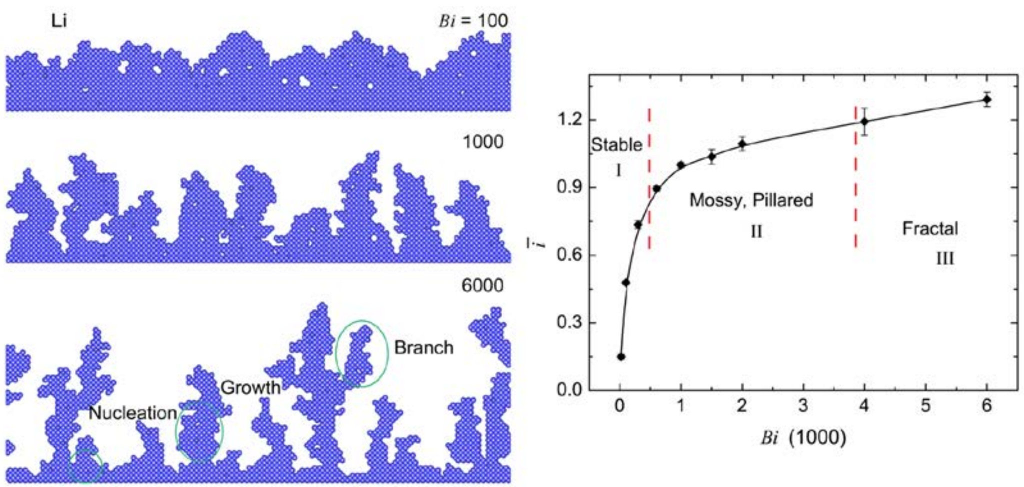
Any proposed future work is subject to change based on funding levels

Summary Slide

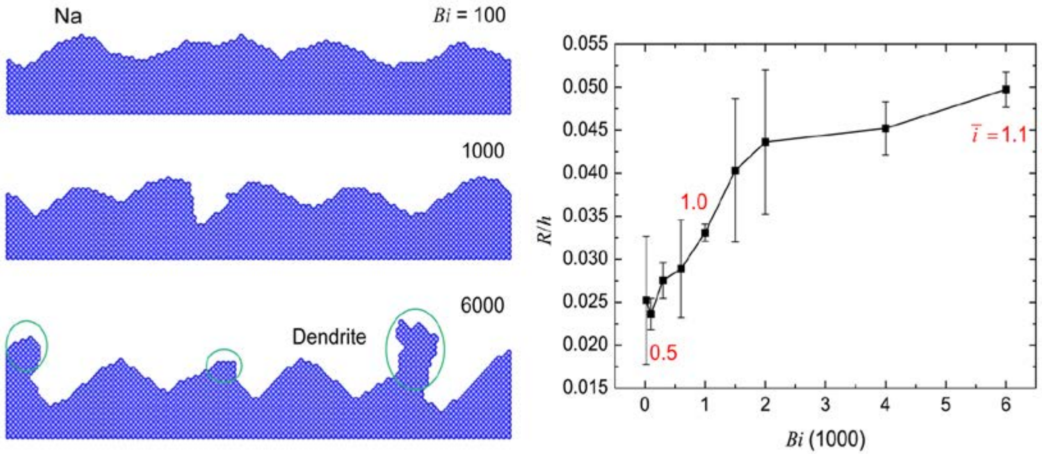
- New insights were obtained from microscopic and mesoscopic models for dendrite growth and possible mitigation strategies
    - ➢We demonstrated that the electrostatic potential of the nucleating Li phase dictates the nucleation mode. We suggested a promising strategy based on the modulation and tuning of such electrostatic potential based on the changes induced by specific electrolytes, SEI and/or artificial coating.
    - ➢We demonstrated that alternative charging strategies could be based on the addition of cations or other additives and/or temperature modulation during charge.

Technical backup slides (maximum 5)

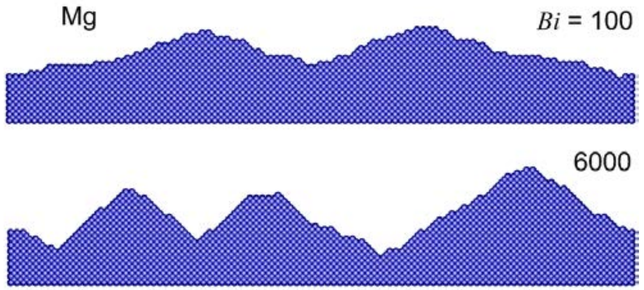
Biot number is a dimensionless number representing the ratio between the reaction rate and the ion transport rate



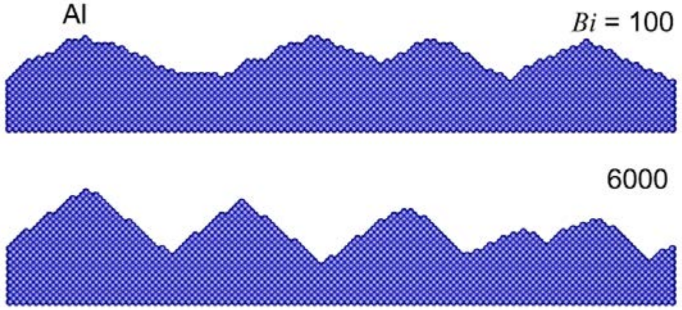
Li electrodeposition morphologies with varying Biot numbers
Three regimes identified: stable, mossy (or pillared), and fractal



Na electrodeposition morphologies with varying *Bi*
Surface roughness of the metal electrode with increasing *Bi*



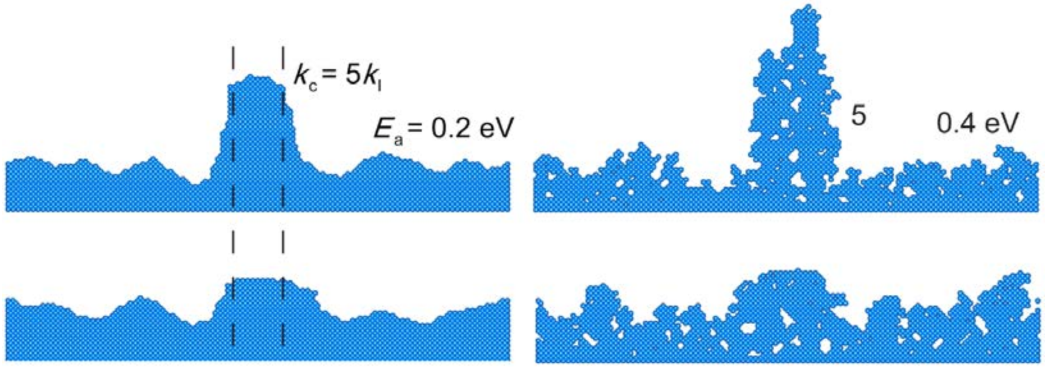
Mg electrodeposition morphologies with varying Bi
Formation of peaks and valleys on the electrode



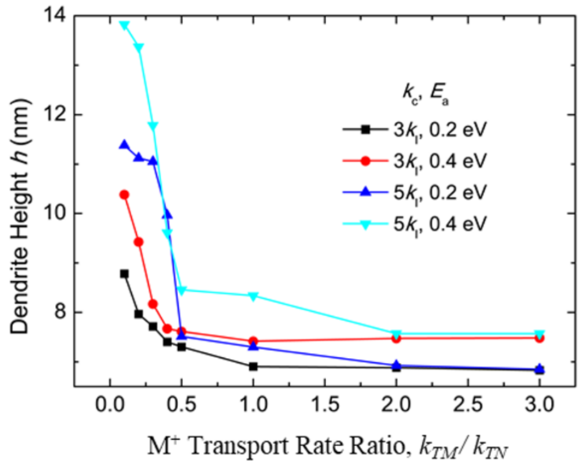
Al electrodeposition morphologies under different Bi

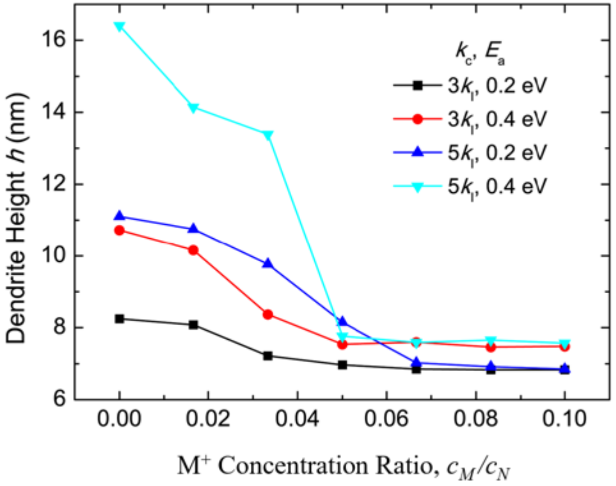
*Hao, Verma and Mukherjee, *Energy Storage Materials*, **20,** 1 (2019)

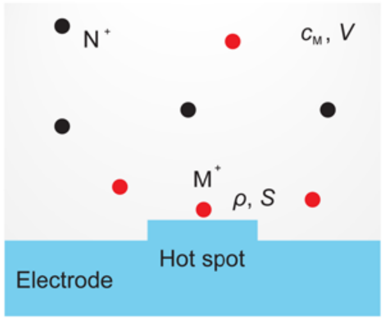
Cationic Shield Mediated Electrodeposition Stability



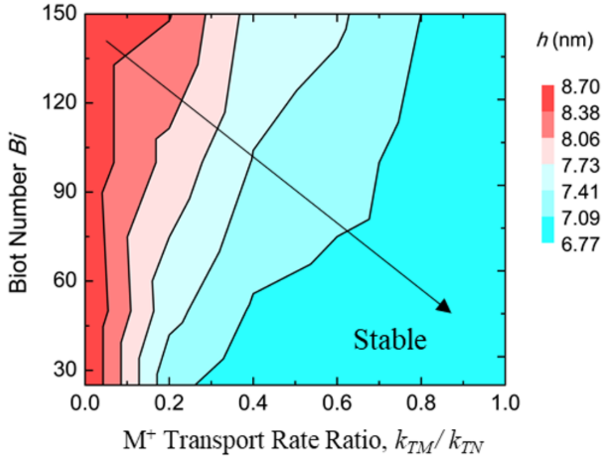
- Suppression of inhomogeneity induced dendrites
- The upper/lower morphology is obtained without/with the Cationic Shield effect







- Dendrite height as a function of additive/metal ion concentration
- A critical concentration ratio appears around 0.05



- The additive transport rate dependence of dendrite suppression.

*Hao, Verma and Mukherjee, *J. Mater. Chem. A*, **7**, 18442 (2019)