Development of Solid-State Electrolyte for Safe and Ultra-High Capacity Batteries for NASA's Future Missions

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LaSPACE Fall 2021 Council Meeting

Annual Meeting of the NASA Space Grant and ASA EPSCoR Programs in Louisiana on October 29, 2021

Outline

1. **What are the capabilities at UL Lafayette and who we are**
   Institute for Materials Research and Innovation

2. **What are the current research projects at IMRI at UL Lafayette?**
   Energy; manufacturing; space; and environmental biology

3. **NASA EPSCoR project overview**
   Scope of work; team members, partnership, and milestones

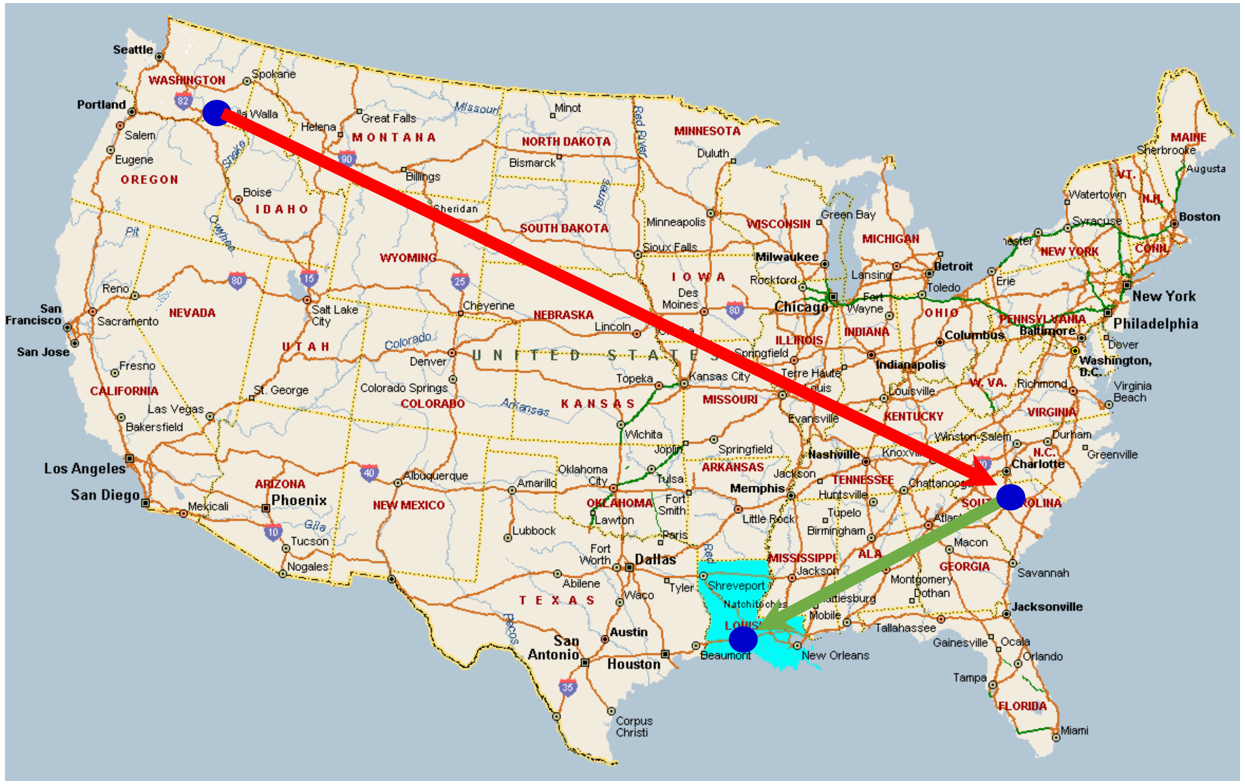
4. **Current results**
   The origin towards a stable battery

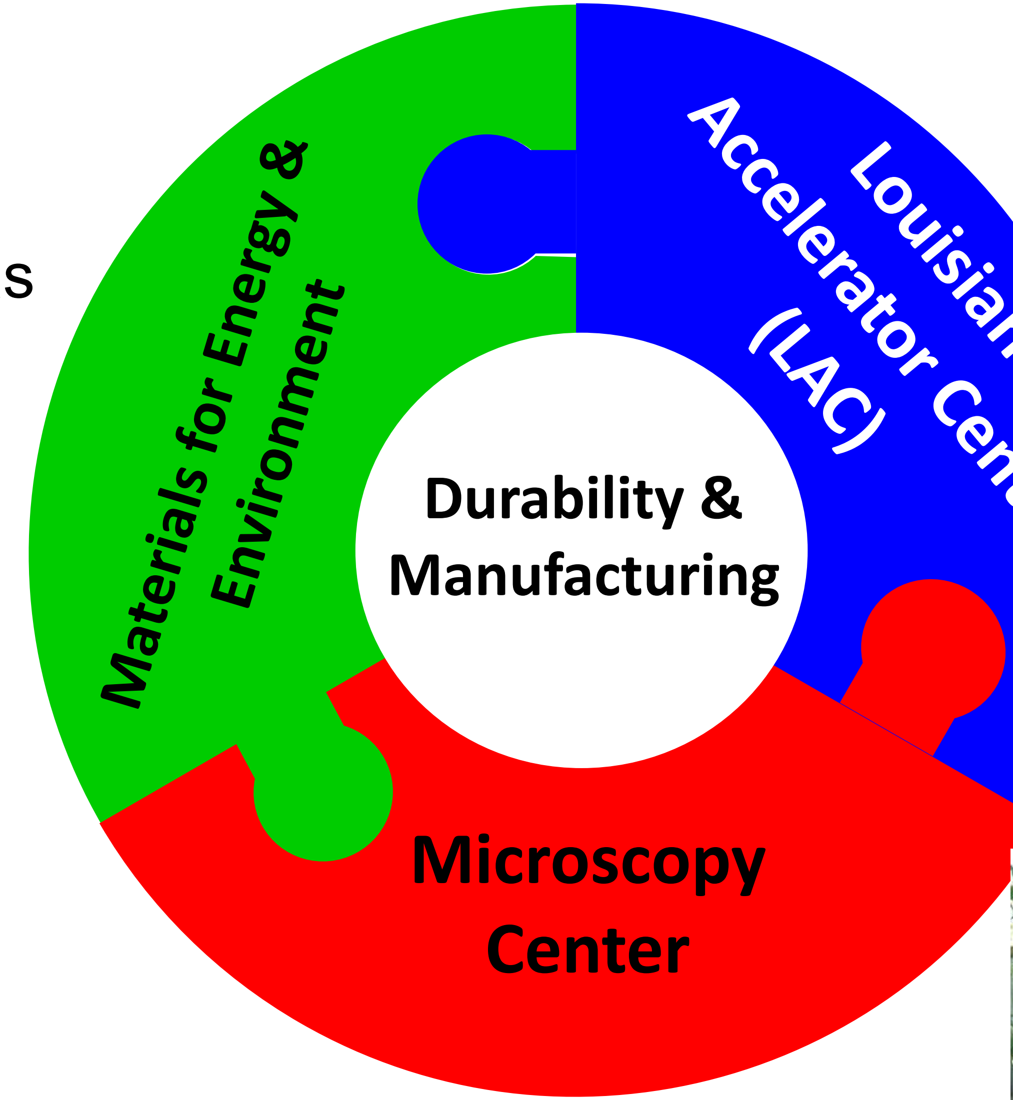
5. **Conclusions and summaries**

http://lgefund.net/investments/

Institute for Materials Research and Innovation (IMRI) at UL Lafayette

- 10% of US oil reserves in Louisiana
- #2 oil-producing state in United States
- Natural Gas: larger deposits than oil
- 25% of the nation's supply of natural gas

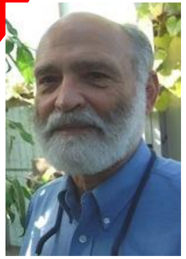



Materials for Energy & Environment

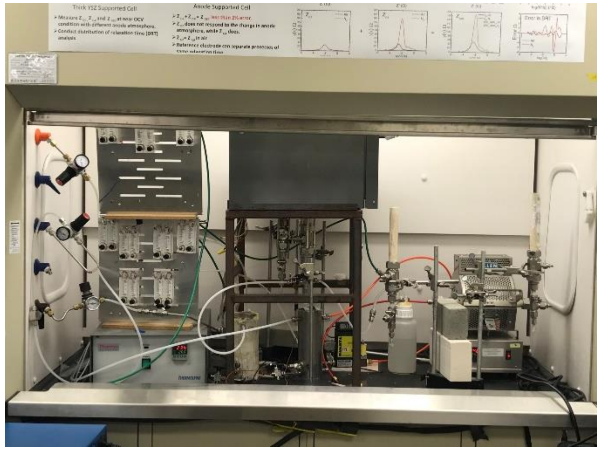
Louisiana Accelerator Center (LAC)

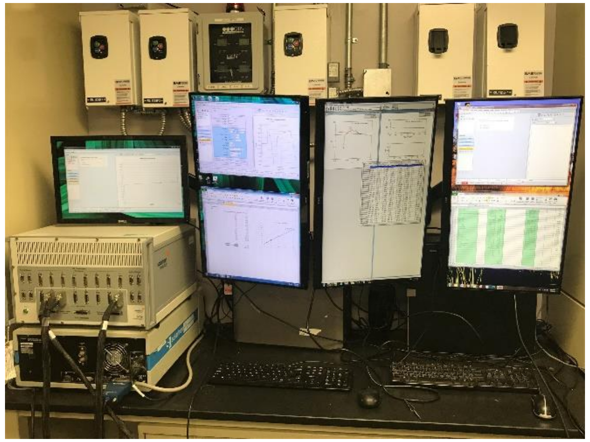
Durability & Manufacturing

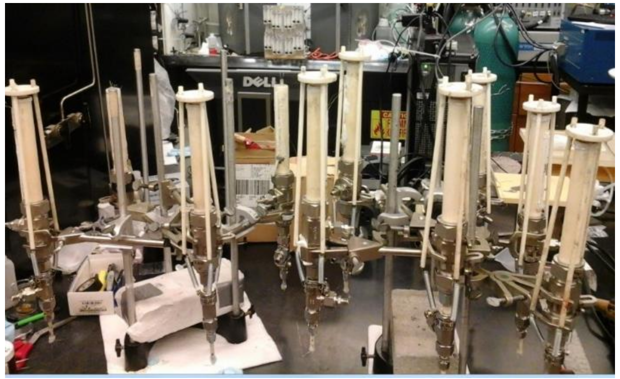
Microscopy Center

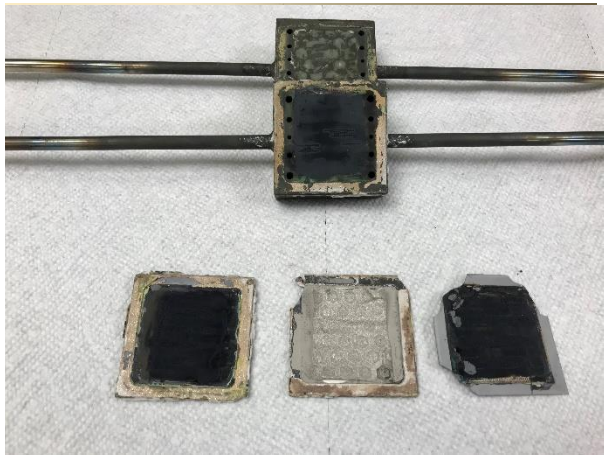


Battery and Fuel Cell Testing Lab

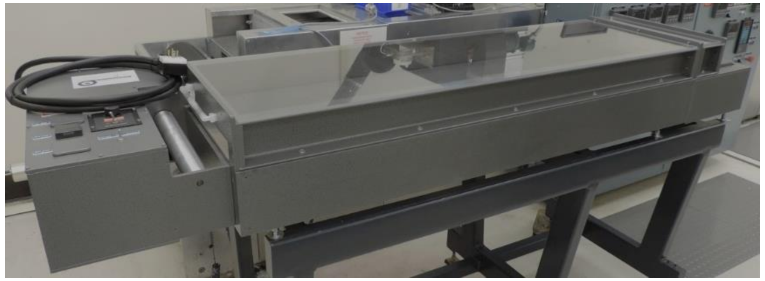








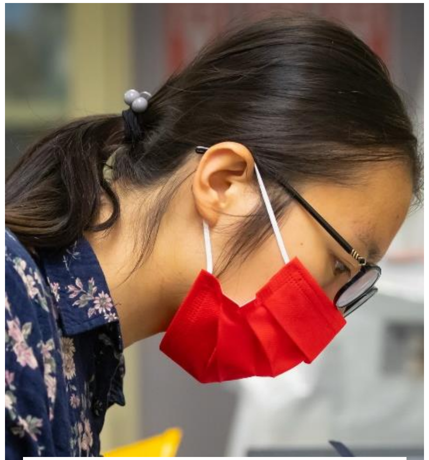
Cell Fabrication Lab (SOCs and Batteries)

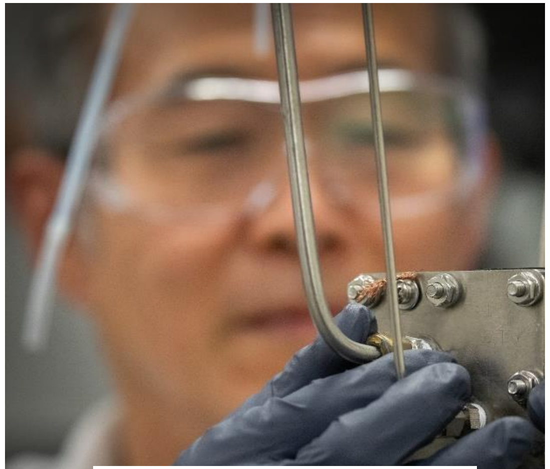


Two tape casters, plastic extruder, custom-built hydraulic pump (415 MPa); isostatic laminator; two hot press machines; laser cutter (Speedy 360); two glove boxes; three Lindberg/Blue M furnaces (1500^{o}C).

Team Members – Solid Oxide Cells (SOCs)


Yudong Wang
Graduate Student


Dr. Yanhua Sun
Postdoc


Dr. Gordon Xia
Research Professor


Josh Wilson
Graduate Student


Dr. Yanhua Sun
Research Asst. Prof.


Alex Tucker
Under/graduate Student


Christabel Tettah
Graduate Student


Tam Tran
Graduate Student


Austin Schilling
Undergrad Student


April Bourlet
Undergrad Student

Eleanor Stelz-Sullivan
Undergrad Student

Noah Richard
Undergrad Student

Jacob C Hoffpauir
Undergrad Student

Team Members – IMRI Staff

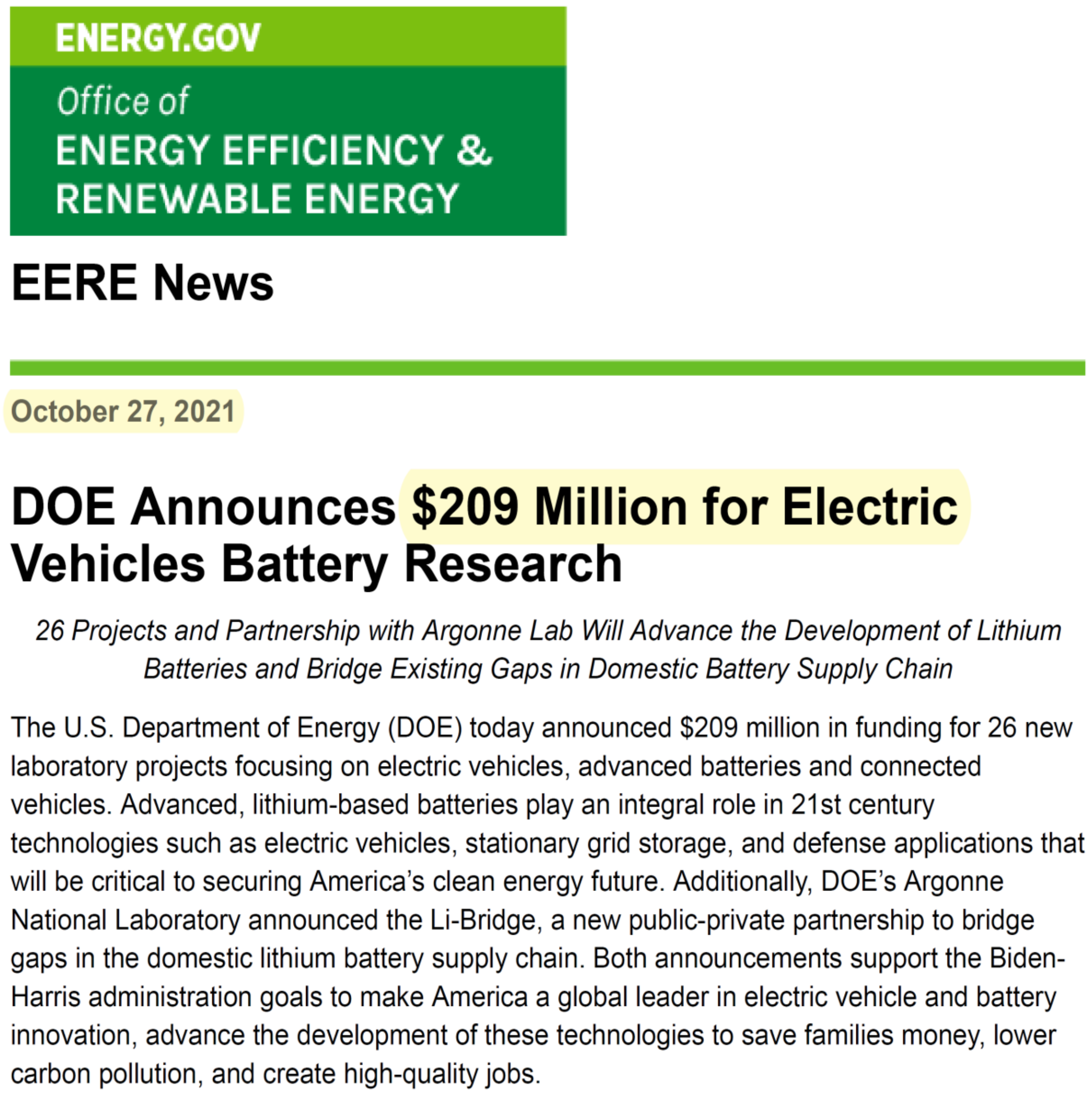
Barbara Marchetti
Research Assistant Professor
Computational and spectroscopic chemistry

Jonathan Raush
Assistant Professor
Alloys and manufacturing

Xingwen Yu
Research Associate Professor
Solid state chemistry, batteries, and PEMFC

Sushant Sahu
Instructor in Chemistry
Carbon chemistry and catalysis

Rapid Growth in All Solid-State Batteries



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RENEWABLE ENERGY

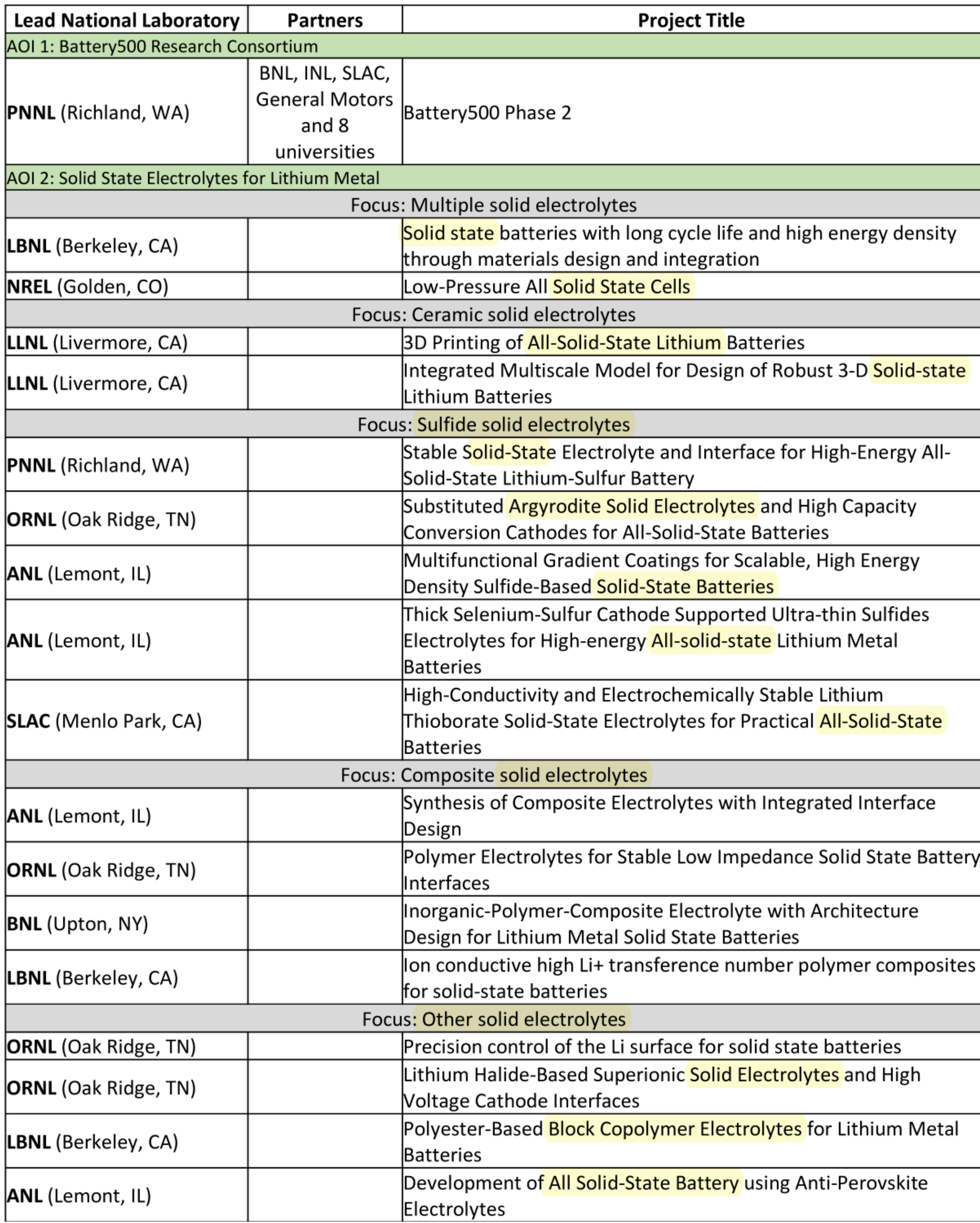
EERE News

October 27, 2021

DOE Announces $209 Million for Electric Vehicles Battery Research

26 Projects and Partnership with Argonne Lab Will Advance the Development of Lithium Batteries and Bridge Existing Gaps in Domestic Battery Supply Chain

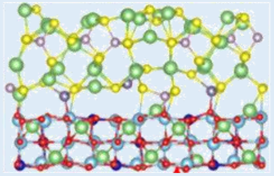
The U.S. Department of Energy (DOE) today announced $209 million in funding for 26 new laboratory projects focusing on electric vehicles, advanced batteries and connected vehicles. Advanced, lithium-based batteries play an integral role in 21st century technologies such as electric vehicles, stationary grid storage, and defense applications that will be critical to securing America's clean energy future. Additionally, DOE's Argonne National Laboratory announced the Li-Bridge, a new public-private partnership to bridge gaps in the domestic lithium battery supply chain. Both announcements support the Biden-Harris administration goals to make America a global leader in electric vehicle and battery innovation, advance the development of these technologies to save families money, lower carbon pollution, and create high-quality jobs.



Lead National Laboratory	Partners	Project Title
AOI 1: Battery500 Research Consortium		
PNNL (Richland, WA)	BNL, INL, SLAC, General Motors and 8 universities	Battery500 Phase 2
AOI 2: Solid State Electrolytes for Lithium Metal		
Focus: Multiple solid electrolytes		
LBNL (Berkeley, CA)		Solid state batteries with long cycle life and high energy density through materials design and integration
NREL (Golden, CO)		Low-Pressure All Solid State Cells
Focus: Ceramic solid electrolytes		
LLNL (Livermore, CA)		3D Printing of All-Solid-State Lithium Batteries
LLNL (Livermore, CA)		Integrated Multiscale Model for Design of Robust 3-D Solid-state Lithium Batteries
Focus: Sulfide solid electrolytes		
PNNL (Richland, WA)		Stable Solid-State Electrolyte and Interface for High-Energy All-Solid-State Lithium-Sulfur Battery
ORNL (Oak Ridge, TN)		Substituted Argyrodite Solid Electrolytes and High Capacity Conversion Cathodes for All-Solid-State Batteries
ANL (Lemont, IL)		Multifunctional Gradient Coatings for Scalable, High Energy Density Sulfide-Based Solid-State Batteries
ANL (Lemont, IL)		Thick Selenium-Sulfur Cathode Supported Ultra-thin Sulfides Electrolytes for High-energy All-solid-state Lithium Metal Batteries
SLAC (Menlo Park, CA)		High-Conductivity and Electrochemically Stable Lithium Thioborate Solid-State Electrolytes for Practical All-Solid-State Batteries
Focus: Composite solid electrolytes		
ANL (Lemont, IL)		Synthesis of Composite Electrolytes with Integrated Interface Design
ORNL (Oak Ridge, TN)		Polymer Electrolytes for Stable Low Impedance Solid State Battery Interfaces
BNL (Upton, NY)		Inorganic-Polymer-Composite Electrolyte with Architecture Design for Lithium Metal Solid State Batteries
LBNL (Berkeley, CA)		Ion conductive high Li+ transference number polymer composites for solid-state batteries
Focus: Other solid electrolytes		
ORNL (Oak Ridge, TN)		Precision control of the Li surface for solid state batteries
ORNL (Oak Ridge, TN)		Lithium Halide-Based Superionic Solid Electrolytes and High Voltage Cathode Interfaces
LBNL (Berkeley, CA)		Polyester-Based Block Copolymer Electrolytes for Lithium Metal Batteries
ANL (Lemont, IL)		Development of All Solid-State Battery using Anti-Perovskite Electrolytes

Research Roadmap for the Project

Task 1: Theory

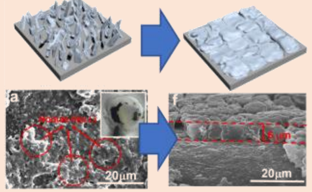


- Computation of dendrite growth rates
- Solid-state mechanic model in composite electrolytes
- Atomistic modeling of dendrite-induced failure in solid-state batteries

Experimental feedbacks to theory (electrical and mechanical properties)

Theoretical guidelines for materials design

Task 2: Component Materials

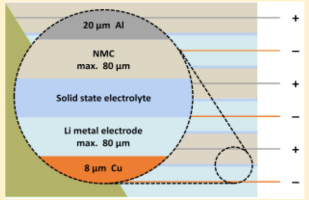


- Inorganic/polymer composite electrolyte
- Uniform plating in a pouch cell
- NMR analysis of electrodes and electrolytes

Feedbacks from battery test and post analysis (cyclability, rate-capacity and electrochemical properties)

Materials and interfaces with desirable properties for assembling battery cells

Task 3: Battery Cells



- All-solid-state batteries with a composite electrolyte, novel NMC and Li-metal electrodes
- Battery testing under radiation and at low T
- Protected Li-electrode in an all-solid-state battery

Collaborative Projects, Publications, and Proposals

Team Members and Task Leaders

Greg Guzik
Professor of Physics
Principal Investigator

Science-I
Manage
science
activities

Dr. Zhou, ULL
Endowed Prof
Task 3 Lead

Dr. Arges, LSU
Asst Prof
Institution-PI
Task 2 Lead

Dr. Khonsari, LSU
Endowed Prof
Task 1 Lead

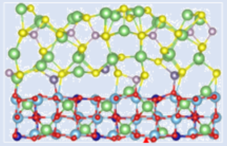
Dr. Fei, ULL
Asst Prof
Institution-PI
Task 3 Co-Lead

Dr. Chen, LaTech
Asst Prof
Institution-PI
Task 1 Co-Lead

Dr. Harris, ULL
Asst Prof
Task 2 Co-Lead

Partners and Their Roles in Each Task

Task 1: Theory

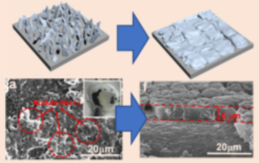


- Computation of dendrite formation and dendrite growth rates
- Solid-state mechanic model in composite electrolytes
- Atomistic modeling of dendrite-induced failure in solid-state batteries

Experimental feedbacks to theory, including electrical properties, microscopic images, dendrite growth rates, and stability.

Theoretical guidelines for the design of materials and interfaces

Task 2: Component Materials

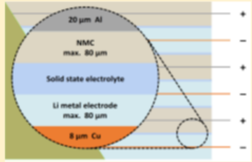


- Inorganic/polymer composite electrolyte
- Uniform plating in a pouch cell
- NMR analysis of electrodes and electrolytes

Feedbacks from battery test and post analysis (cyclability, to identify the key challenges in materials science and engineering to achieve stable and high-performance solid-state batteries.

Materials and interfaces with desirable properties for the assembly of coin cells and pouch cells

Task 3: Battery Cells



- All-solid-state lithium-ion batteries with a composite electrolyte, novel NMC architecture and Li-metal electrodes
- Battery testing under radiation and at low temperatures
- Protected Li-metal electrode in an all-solid-state batteries

Collaborative Projects, Publications, and Proposals

Host visiting faculty, postdoc and students to perform research

Mentor junior faculty & students to support energy workforce development

Test and evaluate prototype materials and batteries

Provide advice on the scientific efforts

On the thermodynamic origin for the formation of Li-dendrites

Yudong Wang
Anil Virkar
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Lithium battery can catch fire in many applications; but what's the real reason?

Laptops

E-cigarettes

Hoverboards

Cell Phones

EVs

Battery Factory

Photo Source:
https://www.rochesterfirst.com/weather/weather-blog/winter-wonders-how-icicles-get-their-unique-shape/
https://www.eeweb.com/lithium-battery-performance-degradation/
https://blog.rentacomputer.com/2018/07/02/dont-fly-with-your-laptops/
https://www.reviewed.com/laptops/features/its-time-to-stop-freaking-out-over-every-battery-that-catches-fire
https://www.thedrive.com/news/28420/parked-teslas-keep-catching-on-fire-randomly-and-theres-no-recall-in-sight
https://www.cnet.com/news/tesla-battery-fire-renewable-energy-plant-australia/

What is the thermodynamic driving force for dendrite formation?

$H_2O(l) \leftrightarrow H_2O(s)$

$\Delta G = N(\mu_{H_2O(s)} - \mu_{H_2O(l)})$

T > 0°C

$$\mu_{H_2O(s)} - \mu_{H_2O(l)} > 0$$

Ice or snow melts into water

T < 0°C

$$\mu_{H_2O(s)} - \mu_{H_2O(l)} < 0$$

Water freezes into icicle.

$Li(?) \leftrightarrow Li(s)$

$\Delta G = N(\mu_{Li(s)} - \mu_{Li(?)})$

$\mu_{Li(s)} - \mu_{Li(?)} < 0$

Dendrite forms

Q:

What is the form of Li in the solution?

How to calculate $\mu_{Li(?)}$

Gibbs free energy $\Delta G = G_f - G_i$

$p, T = Const.$

- $\Delta G < 0$: process is spontaneous
- $\Delta G > 0$: reverse process is spontaneous
- $\Delta G = 0$: equilibrium

μ_j is the chemical potential of j

- Function of T
- Function of partial pressure in the gas/gas mixture. Ideal gas:

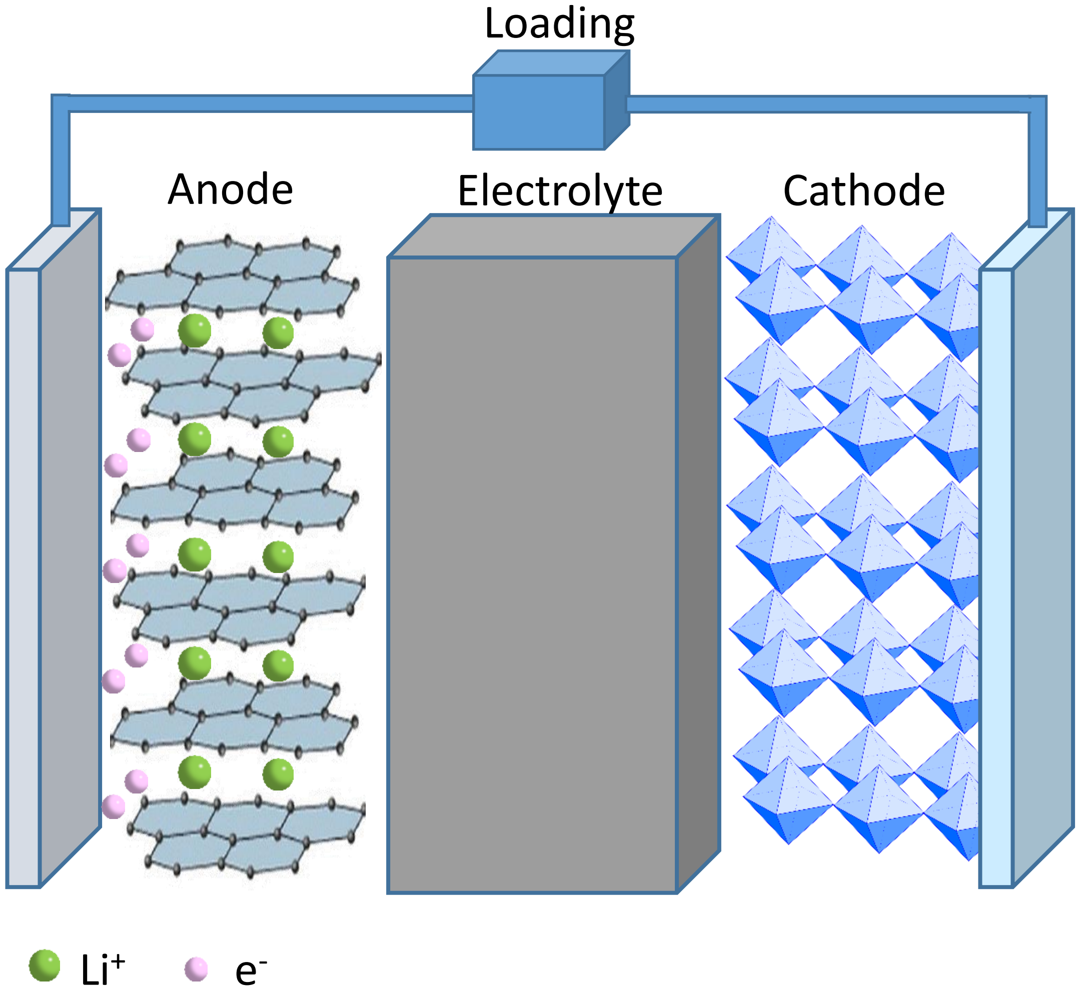
$$\mu_j = \mu_j^0 + RTln(\frac{p_j}{p^0})$$

- Function of its concentration, c_j, in the ideal solution

$$\mu_j = \mu_j^0 + RTln(\frac{c_j}{c^0})$$

Wang, Virkar, and Zhou, J. Electrochem. Soc., 168, 100503, 2021

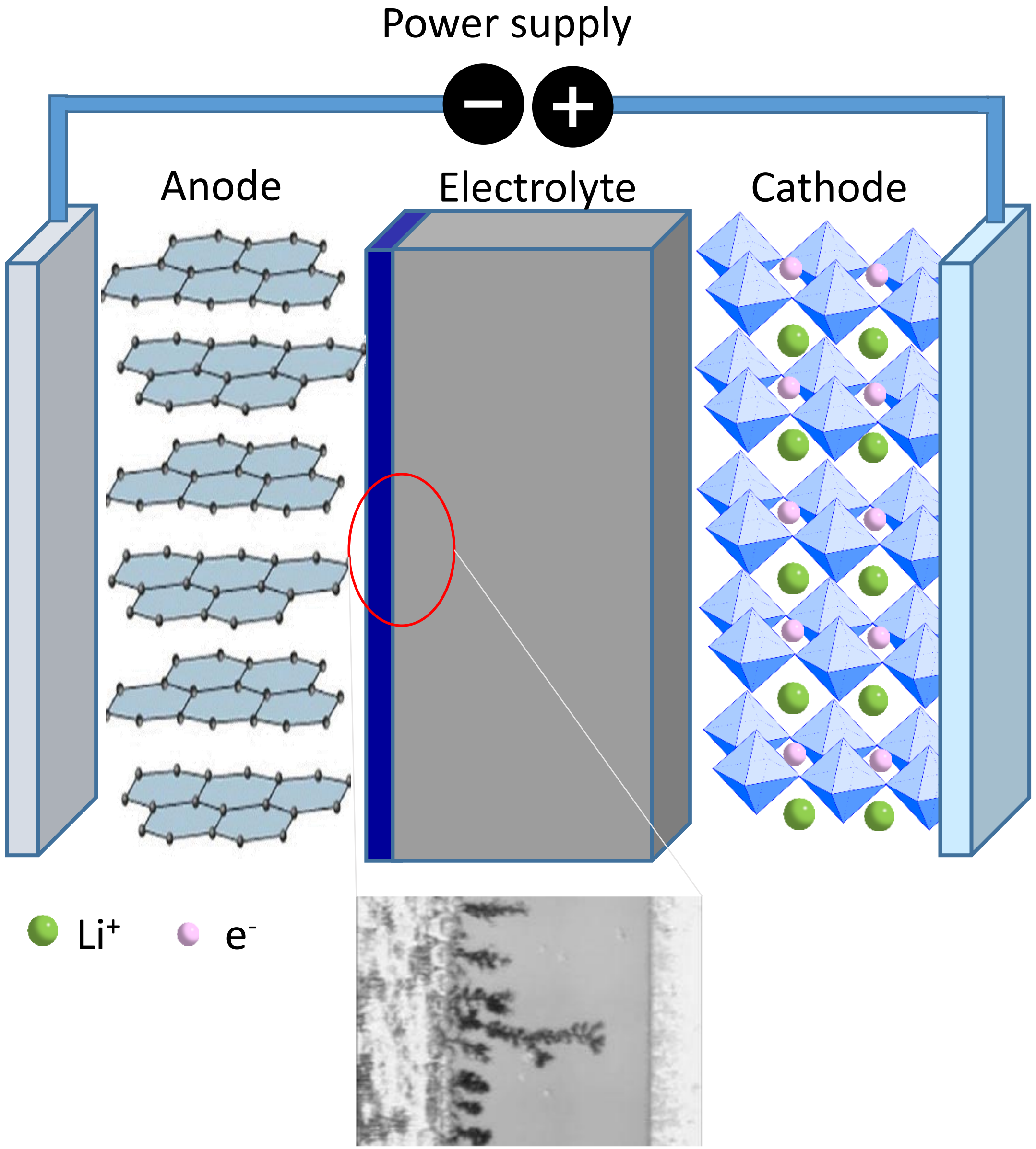
How does a Li-Battery work?



Discharging: $\mu_{Li}^{anode} > \mu_{Li}^{cathode}$

Lithium ion (through the electrolyte) and electrons (mainly via external circuit) moves from anode to cathode

How does a Li-Battery work?



Discharging: $\mu_{Li}^{anode} > \mu_{Li}^{cathode}$

Lithium ions (through the electrolyte) and electrons (mainly via external circuit) moves from anode to cathode

Charging: External power supply driven

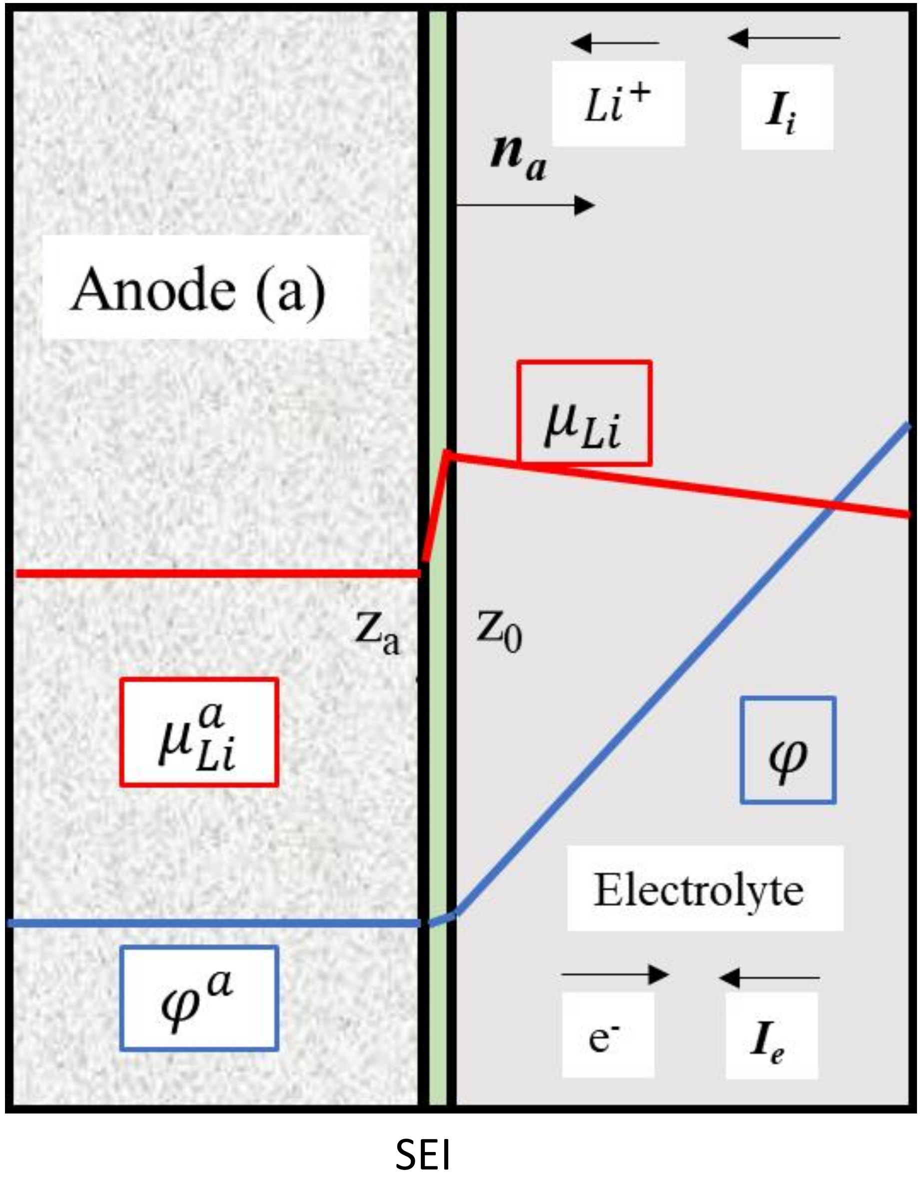
Lithium ions (through the electrolyte) and electrons (mainly via external circuit) moves from cathode to anode

Solid electrolyte interphase (SEI):
A layer between anode and electrolyte formed by reaction between lithium and electrolyte.
Lower ionic conductivity than electrolyte.

Part of lithium ions don’t go further inside and form metal deposit near the SEI. Dendrite initiates.

Wang, Virkar, and Zhou, J. Electrochem. Soc., 168, 100503, 2021

How to use thermodynamics to understand the dendrite formation?



$$\mathrm{Li}(\vec{r}) \rightleftharpoons \mathrm{Li}^{+}(\vec{r}) + e^{-}(\vec{r})$$

- Local chemical equilibrium assumption
  $\mu_{Li}(\vec{r}) = \mu_{Li^+}(\vec{r}) + m\mu_{e^-}(\vec{r})$
- Two independent charge carriers: Li^+ and e^-
- Corresponding current density:
  $\boldsymbol{I_i} = -\frac{\sigma_i}{F}\boldsymbol{\nabla}\boxed{\tilde{\mu}_{Li^+}}$ and $\boldsymbol{I_e} = -\frac{\sigma_e}{F}\boldsymbol{\nabla}\boxed{\tilde{\mu}_{e^-}}$
- Governing equations at steady state:

Charge balance: $\boldsymbol{\nabla}\cdot(\boldsymbol{I_i} + \boldsymbol{I_e}) = 0$

Lithium balance: $\boldsymbol{\nabla}\cdot\left(\frac{\boldsymbol{I_i}}{\boldsymbol{F}}\right) = 0$

Electrochemical potential:

$\tilde{\mu}_{M^{m+}} = \mu_{M^{m+}} + \mathrm{mF}\Phi$

Abstract, cannot be measured directly, etc..

- Electrical potential is defined:

$$\varphi = -\frac{\tilde{\mu}_{e^-}}{F}$$

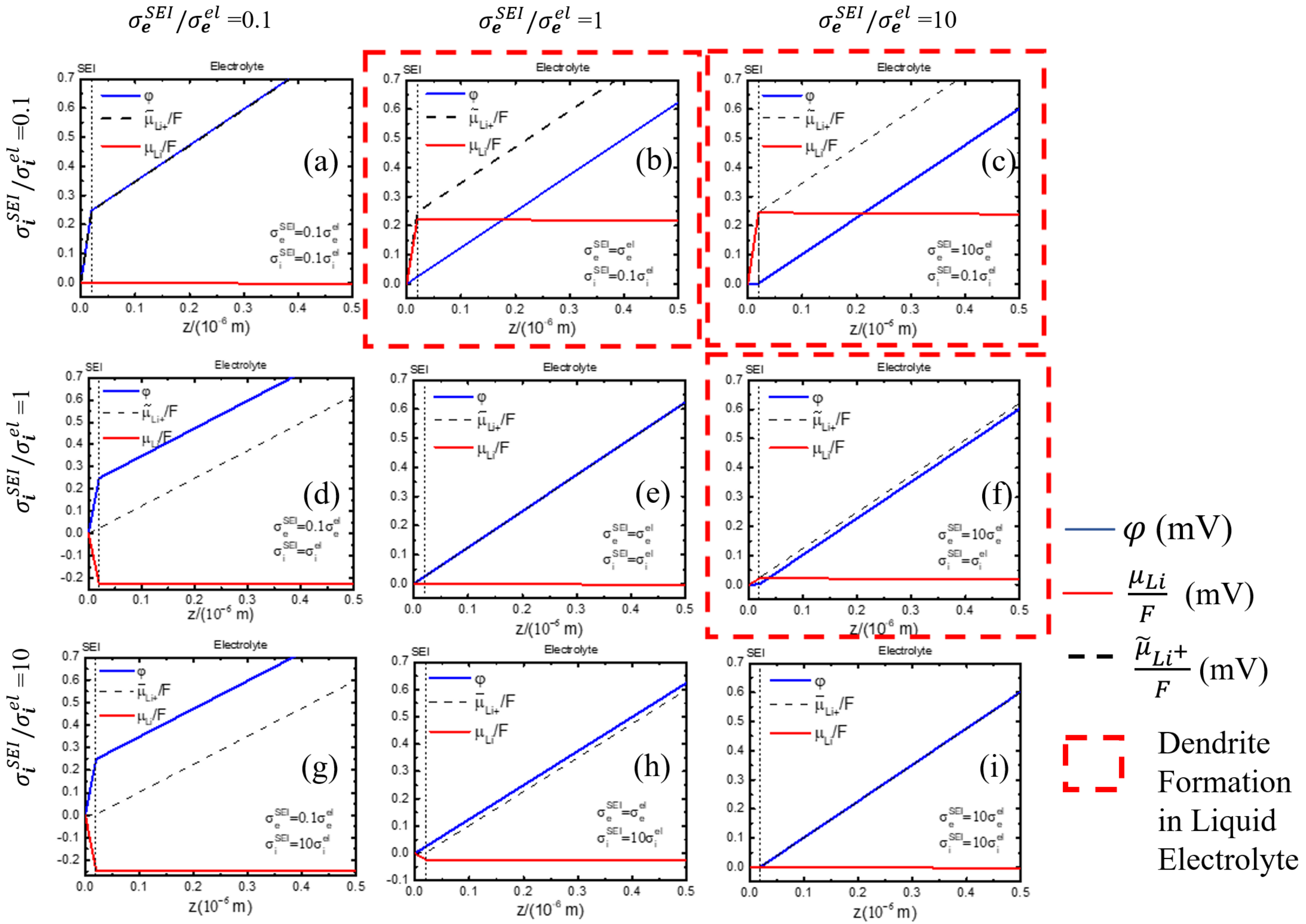
- Cell voltage $= \varphi^c - \varphi^a$ keeps constant in the simulation

  $\tilde{\mu}_{Li^+}, \tilde{\mu}_{e^-}$ are converted into μ_{Li}, φ.

Wang, Virkar, and Zhou, J. Electrochem. Soc., 168, 100503, 2021

Dendrite is not always formed!

What are the conditions for the dendrite formation?



$Li(el) \rightleftharpoons Li(s)$

$\Delta G = \mu_{Li}^S - \mu_{Li}^{el} + W$

W is the additional work need to form a lithium metal phase in the electrolyte (or SEI layer), e.g. surficial tension, normal stress..

$W \approx 0$ in the liquid electrolyte

$\mu_{Li}^S = 0$ by definition

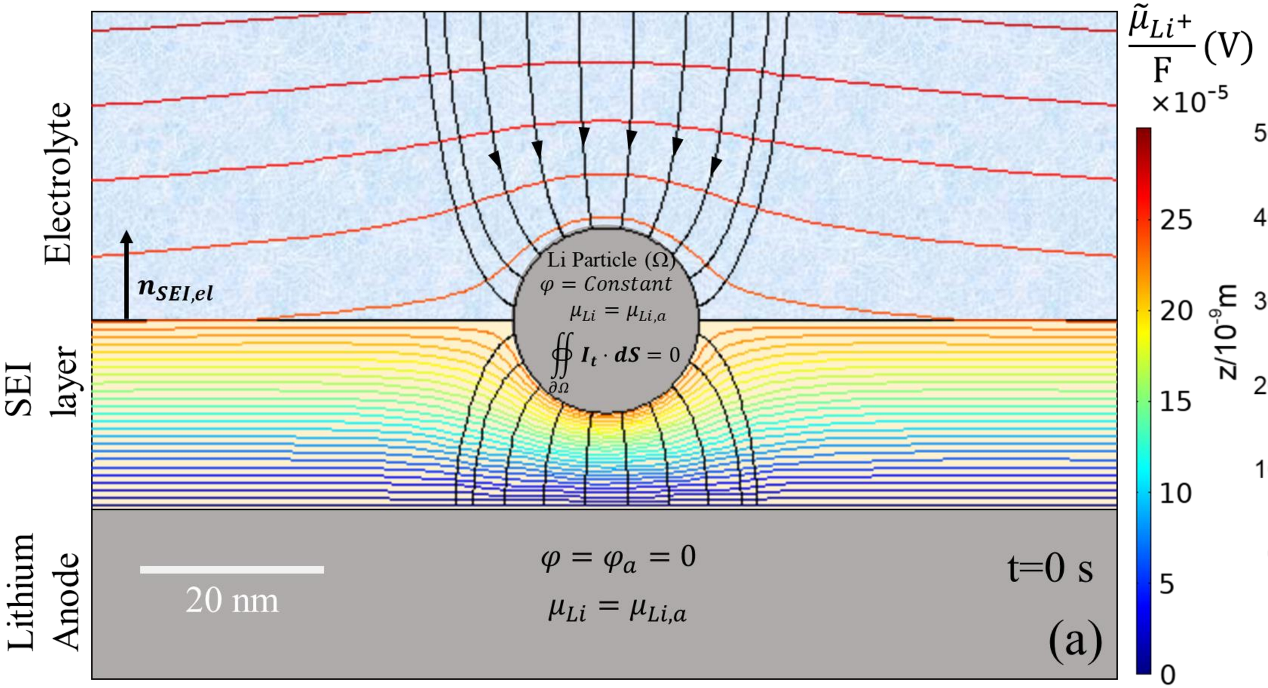
$\Delta G < 0$ only if $\mu_{Li}^{el} > 0$

The formation of lithium metal is thermodynamically preferred

To suppress the lithium deposition in near the SEI

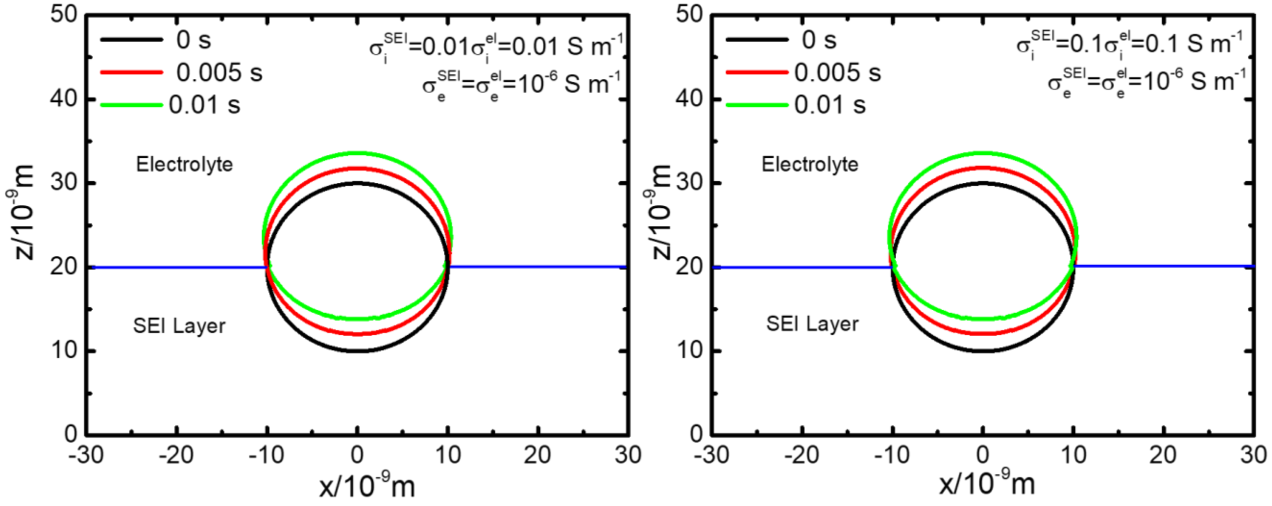
- High SEI ionic conductivity
- Low SEI electronic conductivity

Conditions when dendrite is formed

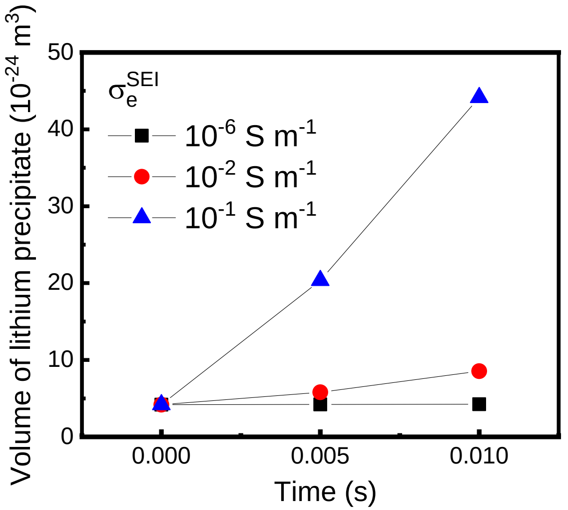


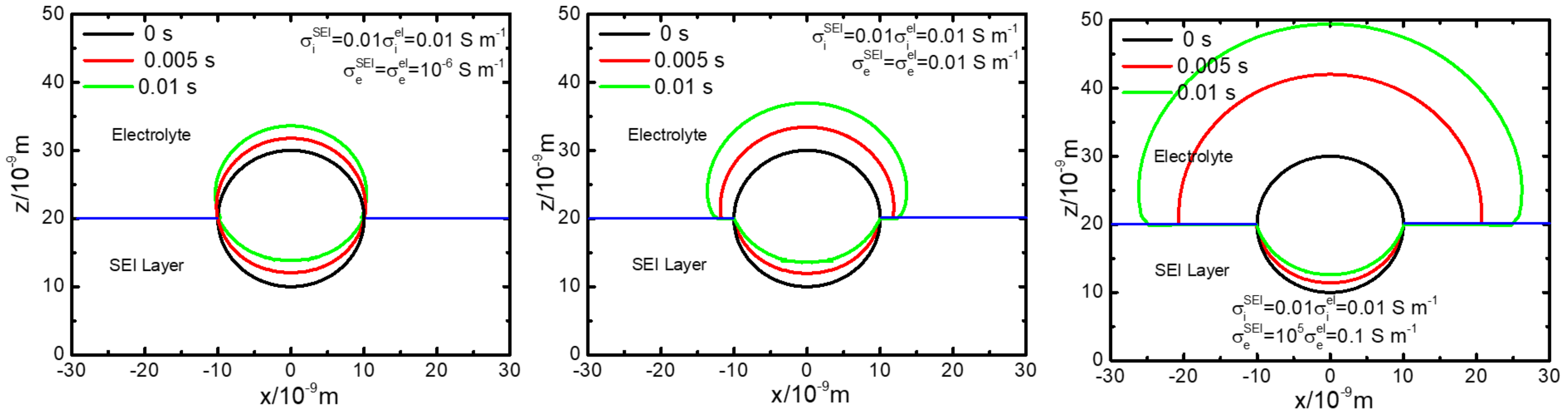
(1) Increase σ_i^{SEI} by 10 times

Almost no impact

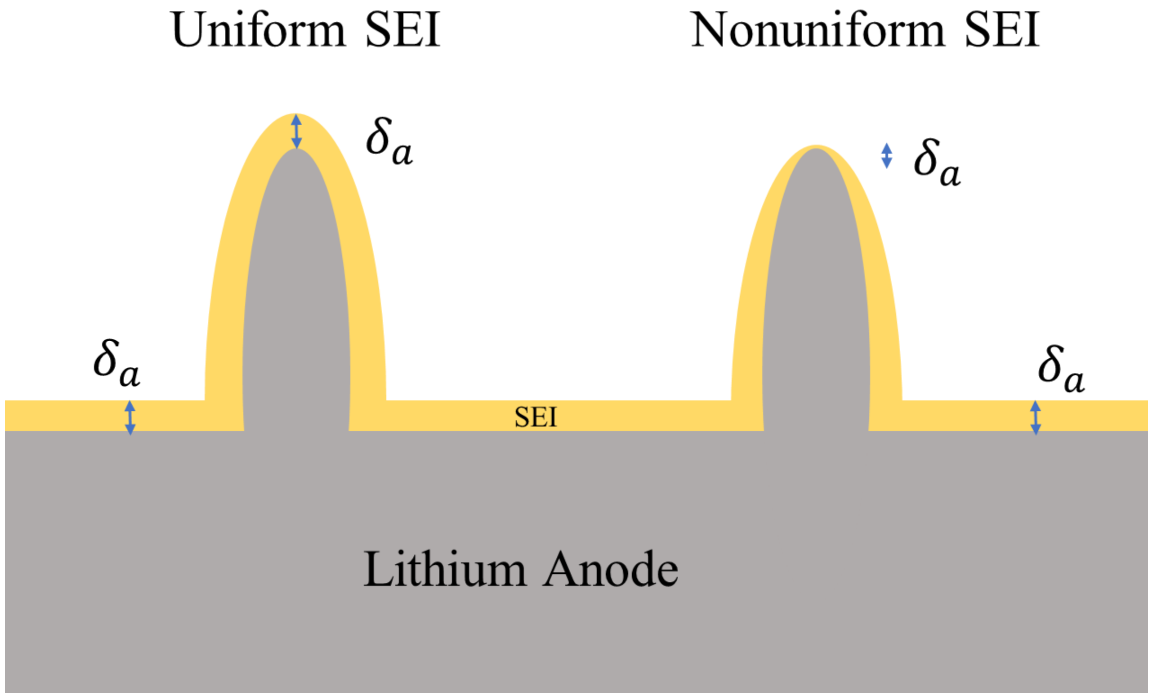


(2) Increase σ_e^{SEI} from 10^{-6} to 0.01 and 0.1 S/m





Growth of Dendrite, with nonuniform SEI



- The thickness of SEI may not be uniform – the kinetics of SEI formation is slower than lithium deposition.
- The tip of the lithium deposit has a thinner SEI layer thickness than other regions
- The difference in σ_{i} bents the flux curve
- Growing rate is proportional to the lithium flux perpendicular to electrode surface

$$q = -\frac{V_{Li}}{F}\boldsymbol{I_i} \cdot \boldsymbol{n_p}$$

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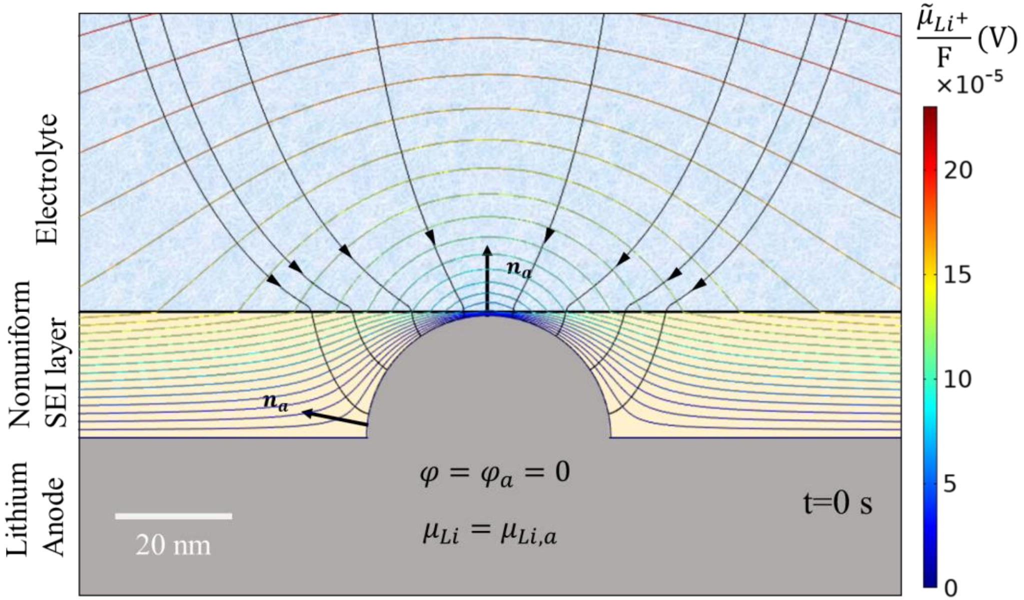
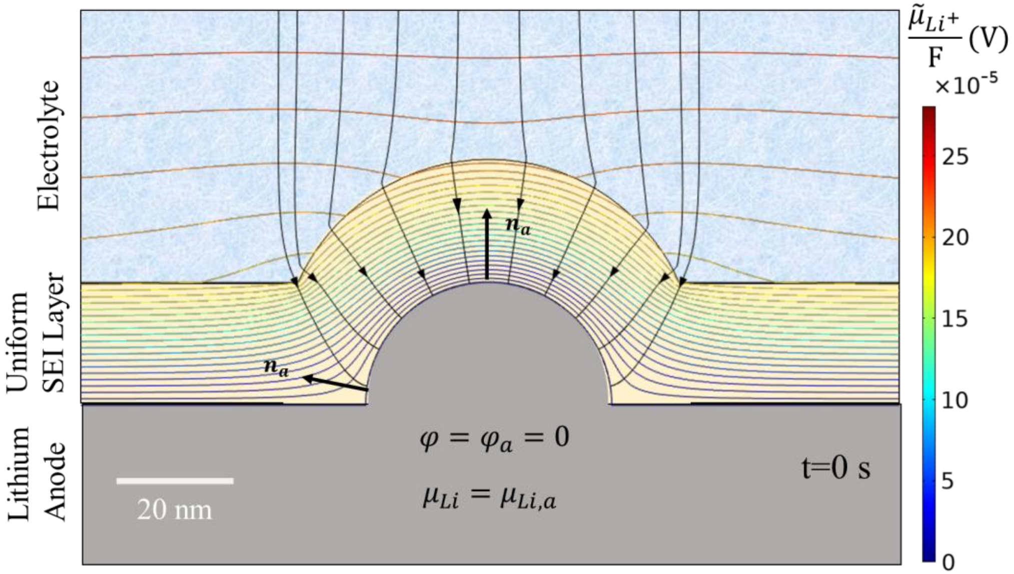
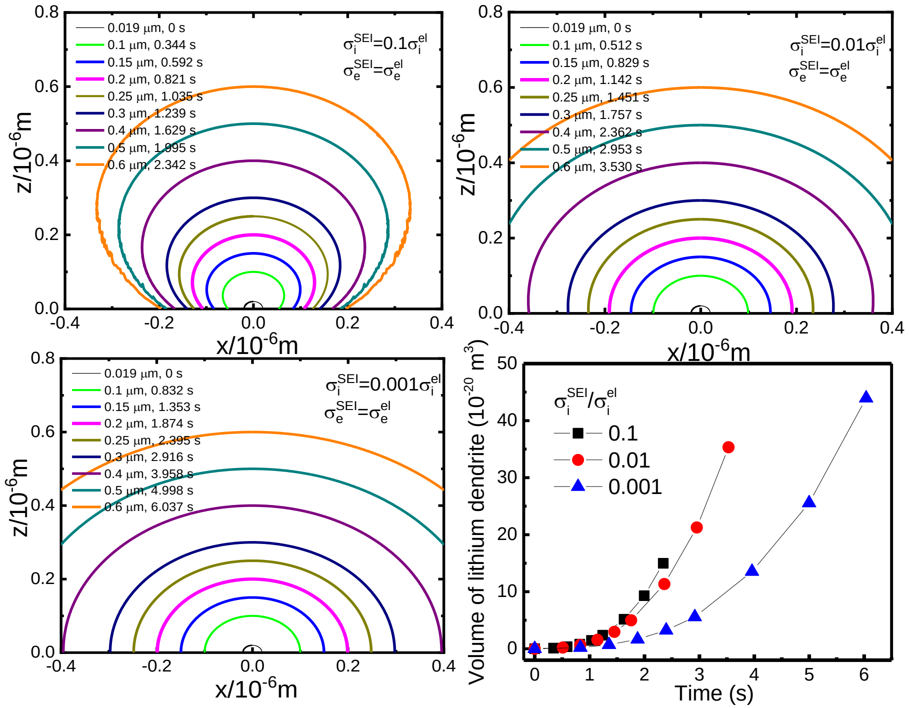




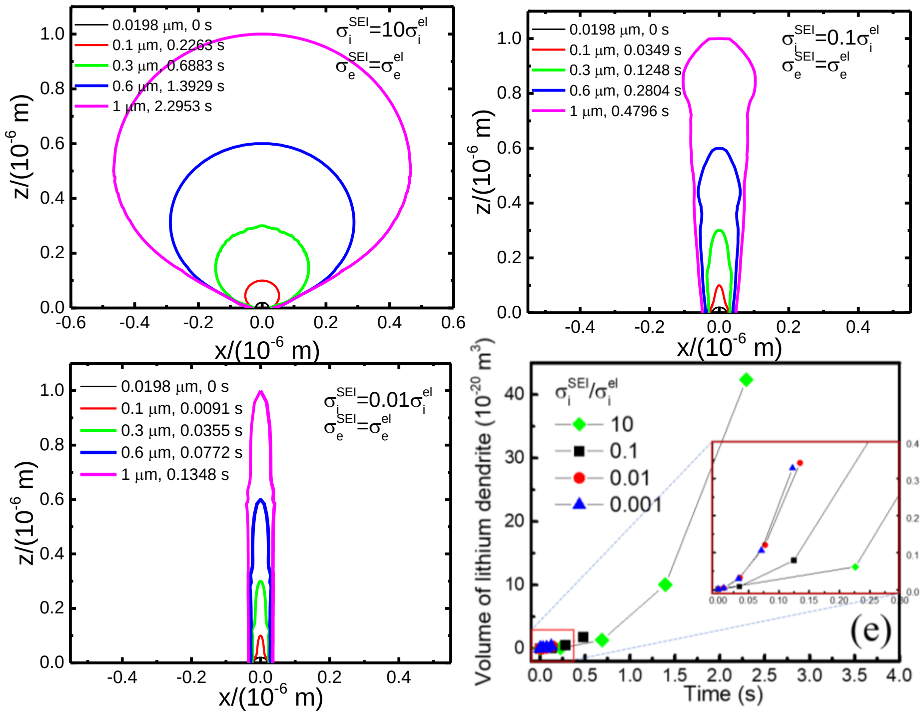
Growth of Dendrite, conductivity effect

Uniform SEI layer

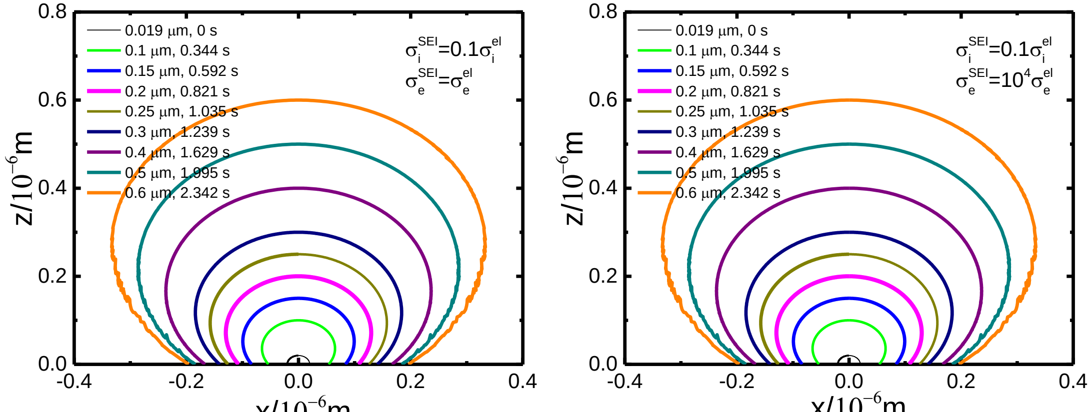


- Keeps spherical shape
- Growing rate is faster with larger σ_i^{SEI}

Nonuniform SEI layer



- The metallic lithium is sharper with SEI of lower ionic conductivity, thickness effect is more significant.



- σ_e^{SEI} does not affect the deposition on the lithium electrode

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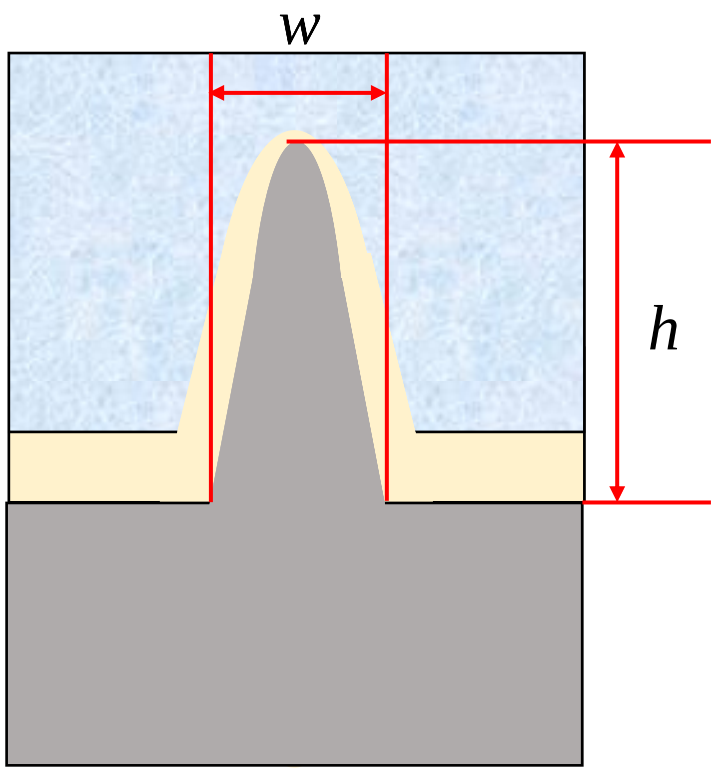
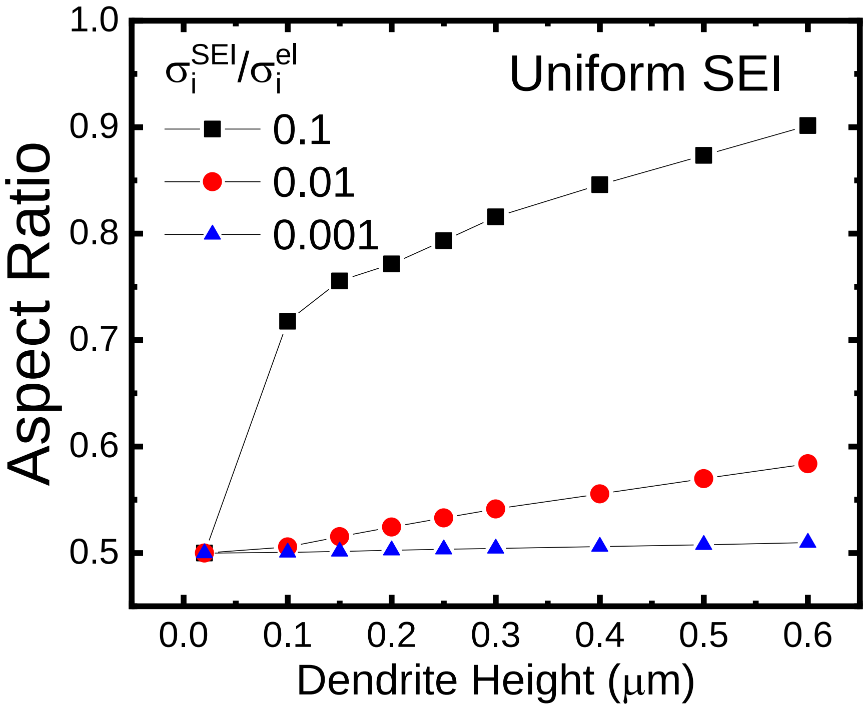
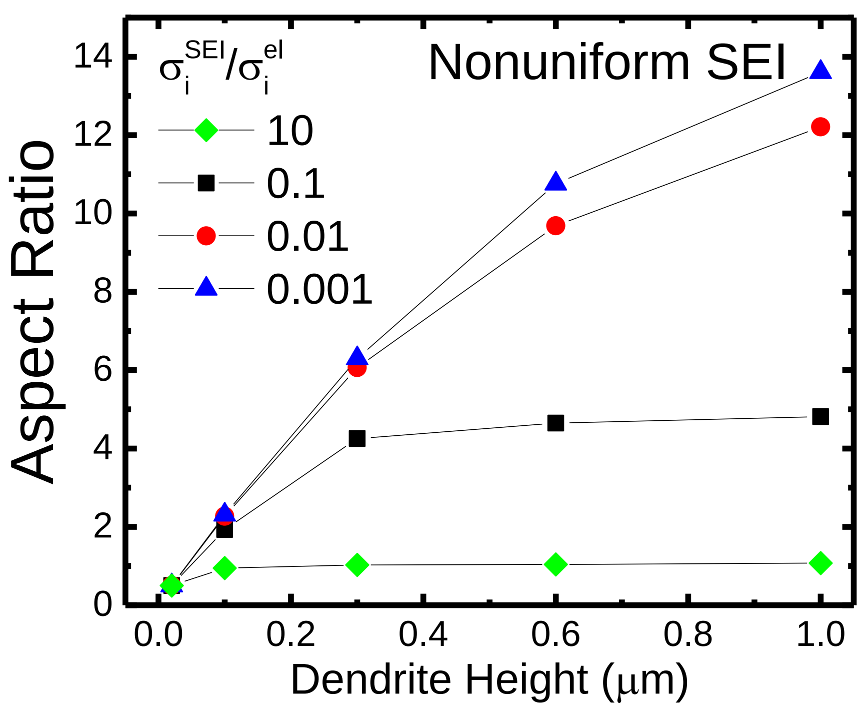
Aspect Ratio, Sharpness of the Dendrite



- $Aspect\ Ratio = \frac{h}{w}$
- Half sphere $\frac{h}{w} = 0.5$
- Sphere $\frac{h}{w} = 1$



- $Aspect\ Ratio$ <1
- $Aspect\ Ratio$ grows slowly
- Stay a spherical shape



- $Aspect\ Ratio$ can reach 12
- $Aspect\ Ratio$ increases fast at initial stage, the one with higher σ_i^{SEI} is smaller.
- Sharper cylindrical shape is formed - dendrite

Wang, Virkar, and Zhou, J. Electrochem. Soc., 168, 100503, 2021

Summaries

1. By applying local thermodynamic and chemical equilibrium and considering the electronic current, two measurable parameters, μ_{Li} and φ, are used to study the deposition kinetics of neutral species at quasi-steady state.

2. The high σ_i^{SEI} reduces the μ_{Li} in the SEI layer and suppresses lithium precipitate formation. In addition, a higher σ_i^{SEI} allows more homogeneous ion flux on the lithium metal surface and prevents lithium dendrite formation. The high σ_i^{SEI} also leads to faster electrode kinetics, reduced charging time, and less energy loss during cycling. As a result, durability and high performance could be achieved simultaneously through a proper choice of electrolyte/electrode materials that lead to SEI layer with low electronic conductivity and a high ionic conductivity rather than a tradeoff with the optimized properties of the SEI layer

3. The stretching of SEI layer during lithium electrodeposition could lead to nonuniform thickness or even cracks, which induces a nonuniform I_i on the lithium electrode surface, which leads to a high aspect ratio over 10 and sharper dendrite geometry. Enhancing mechanical strength and the SEI formation kinetics can improve the stability of the lithium metal electrode.

4. Though the electronic current does not affect the ionic flux on the metal electrode surface, a highly electrically insulating SEI layer suppresses the formation and growth of lithium precipitate in the SEI layer during charging. Further reducing electronic conduction in the SEI layer would be a more efficient approach than developing an artificial SEI layer with higher ionic conductivity to achieve better durability.

On the thermodynamic origin for the formation of Li-dendrites

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