Lithium Metal Anodes: Host and Ageing Corrosion Study

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BATTERY 500 CONSORTIUM

Project ID: bat361

Overview

Timeline

- Start: Oct 1, 2016
- End: Sep 30, 2021
- Percent complete: 90%

Budget

- Total project funding
  $50,000k from DOE
- Funding for FY19
  $10,000k
- Funding for FY20
  $10,000k

Barriers

Barriers addressed

Increasing the energy density of advanced lithium (Li) batteries beyond what can be achieved in today's Li-ion batteries is a grand scientific and technological challenge.

Partners

- Project lead: PNNL
- Battery500 Core Team: Binghamton Univ., BNL, INL, Stanford Univ./SLAC, UC San Diego, Univ. of Texas Austin, Univ. of Washington
- 10 seedling projects

Project Objective and Relevance

- Develop lithium-metal based full batteries with 500 Wh/kg specific energy to power electric vehicle and decrease the high cost of batteries.

- Design and fabricate Li metal anodes with high capacity, high coulombic efficiency and long cycle life.

- Screen electrolyte and additives for stable anodes and cathodes.

Milestones

FY20
Q1, Quantifying inactive Li using B500 electrolytes and protocols (completed)
Q2, Develop new 3D anode structures and test such using coin cell standard protocols to achieve 300-350 Wh/kg (cell-level) for 200 cycles (completed)
Q3, Develop new polymer protective layers for Li anode, test and report such using coin cell standard protocols (completed)
Q4, Select 3D Li architectures and polymer protective layers for pouch cells (single layer and multilayers) (completed)

FY21
Q1 Compare new Li anode architecture with 50 micron Li anode using protocols for 350 Wh/kg cells (completed)
Q2, Measure solid or semisolid (oxides, polymer or composites) electrolyte performance using protocols for 350 Wh/kg cells (SLAC) (completed)
Q3, Characterizing Li metal-solid electrolyte interface with cryoEM (in progress)
Q4, Develop a new polymer as interfacial layer or solid electrolyte (in progress)

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Approach

Cell design, fabrication and validation

1) Establish cell parameters and requirements for coin cells and pouch cells
2) Integrate nanostructured materials in full cells

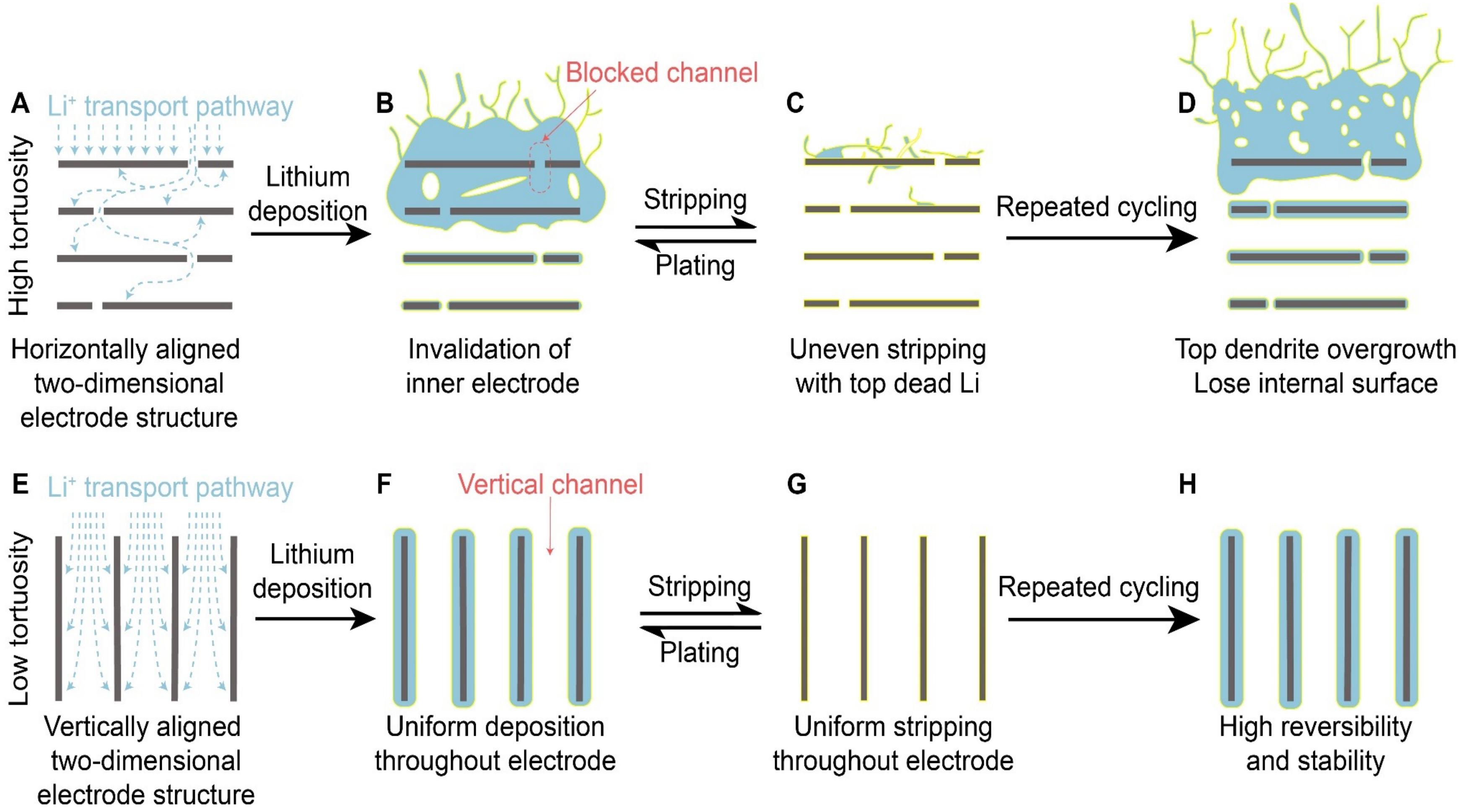
3D Li metal host anode and interfacial modification

1) Design and synthesize Li metal with 3D host composite to overcome volume expansion and contraction problems.
2) Design surface modification techniques to generate stable interphase by gas phase reaction and advanced polymer coatings
3) Screen electrolytes which can generate stable interface.

Structure and property characterization

1) Transmission electron microscopy
2) Cryogenic electron microscopy
3) In operando X-ray diffraction and transmission X-ray microscopy

Tortuosity of rGO host for Li metal



Hao Chen, Yi Cui *Joule* (2020), DOI: 10.1016/j.joule.2020.03.008

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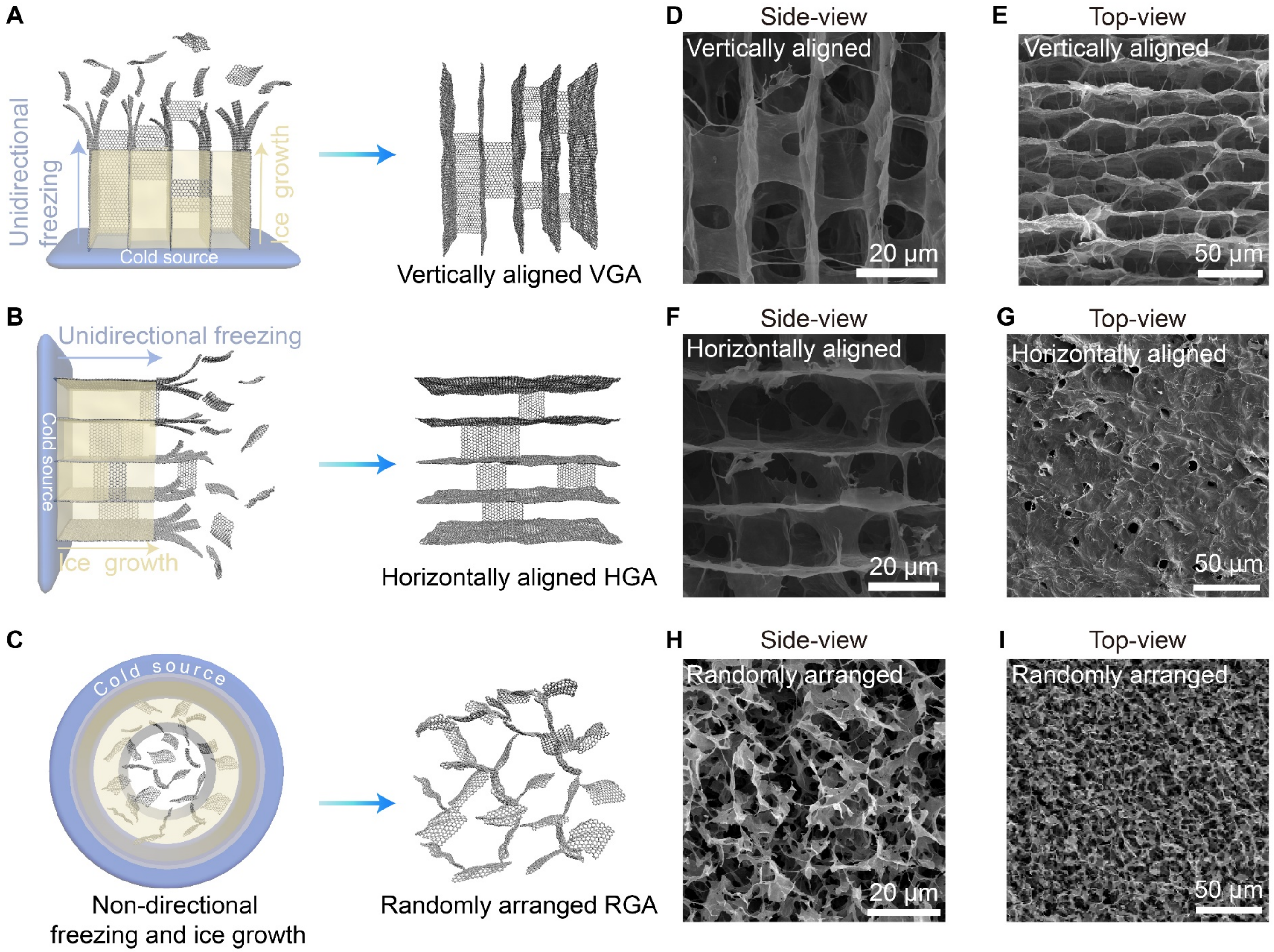

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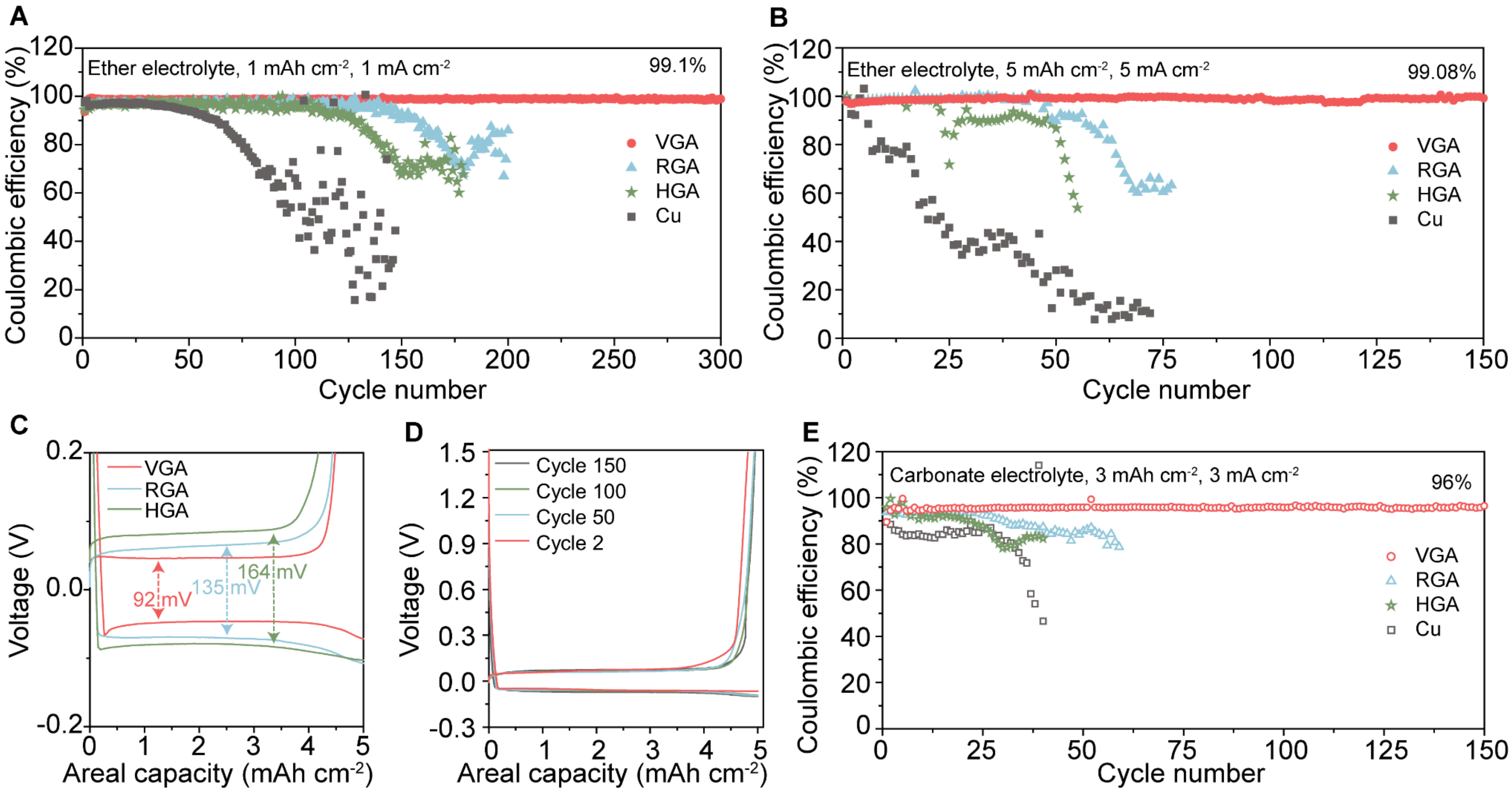
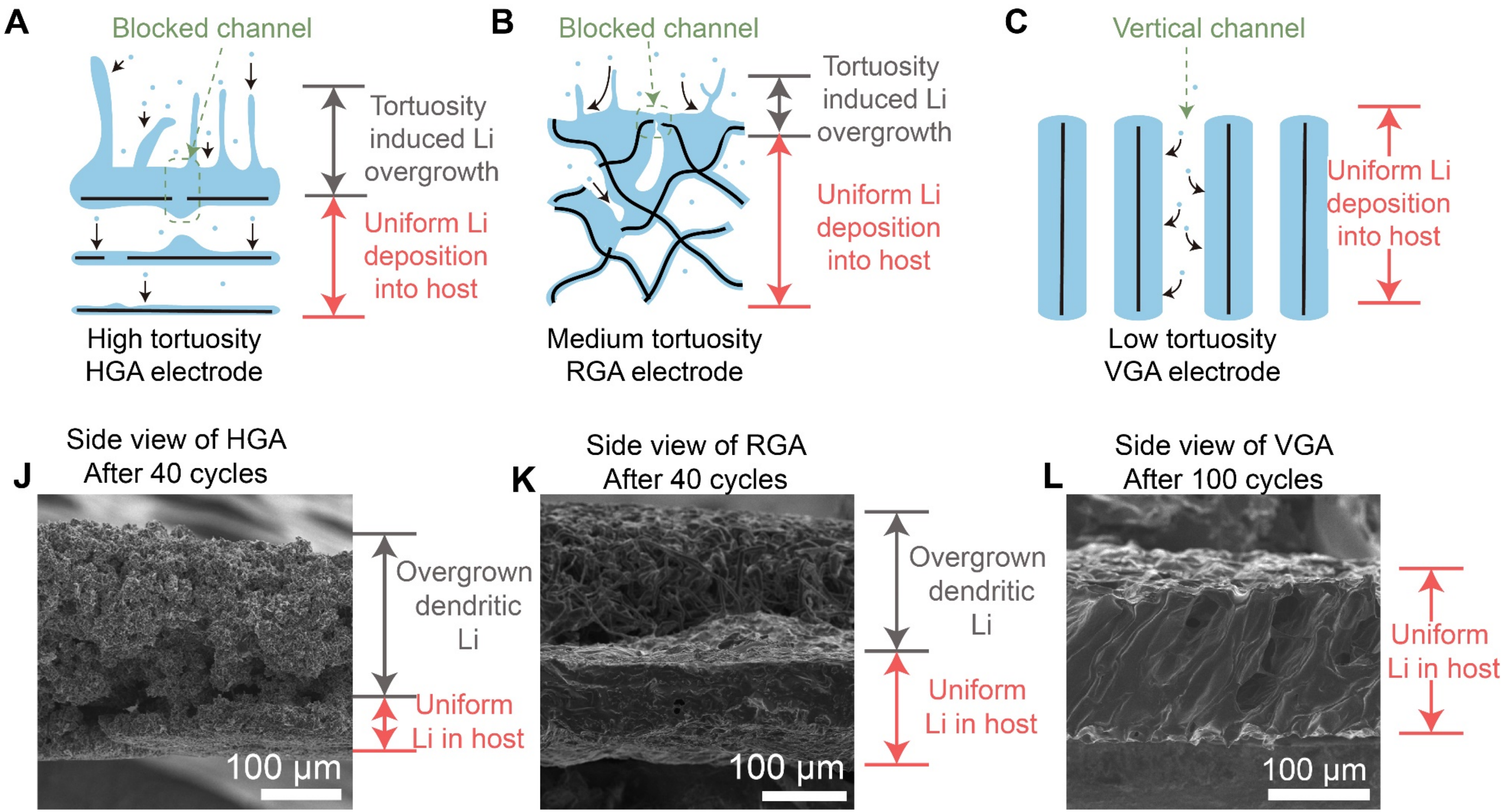


Hao Chen, Yi Cui *Joule* (2020), DOI: 10.1016/j.joule.2020.03.008

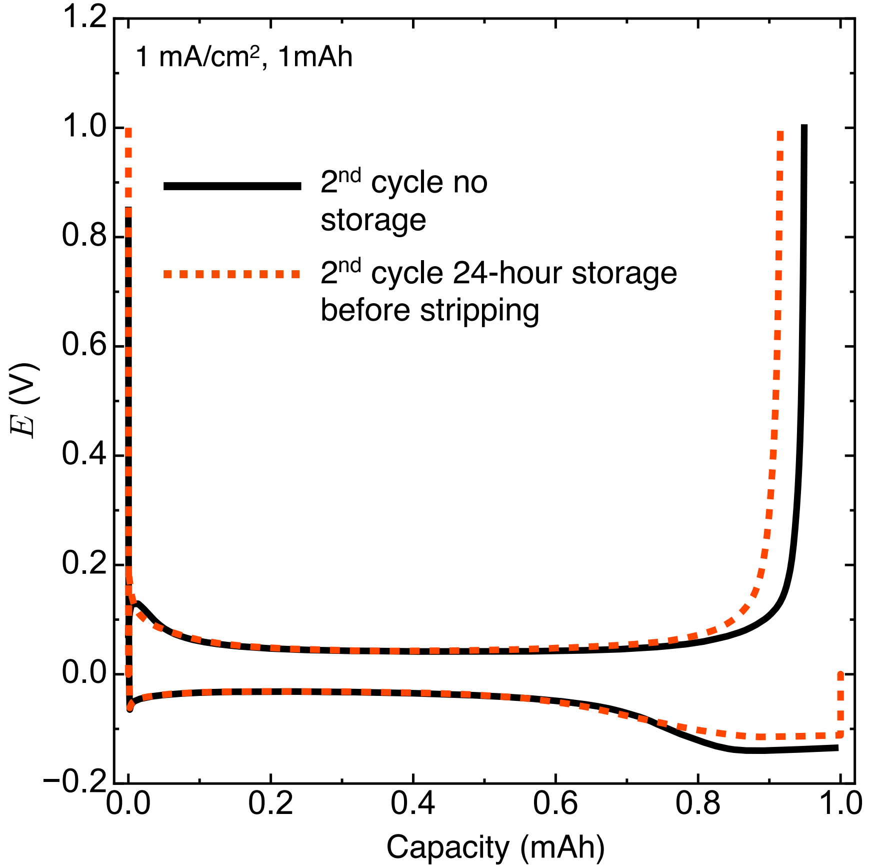
Tortuosity: 4.46 (horizontal), 1.76 (random), 1.25 (vertical)



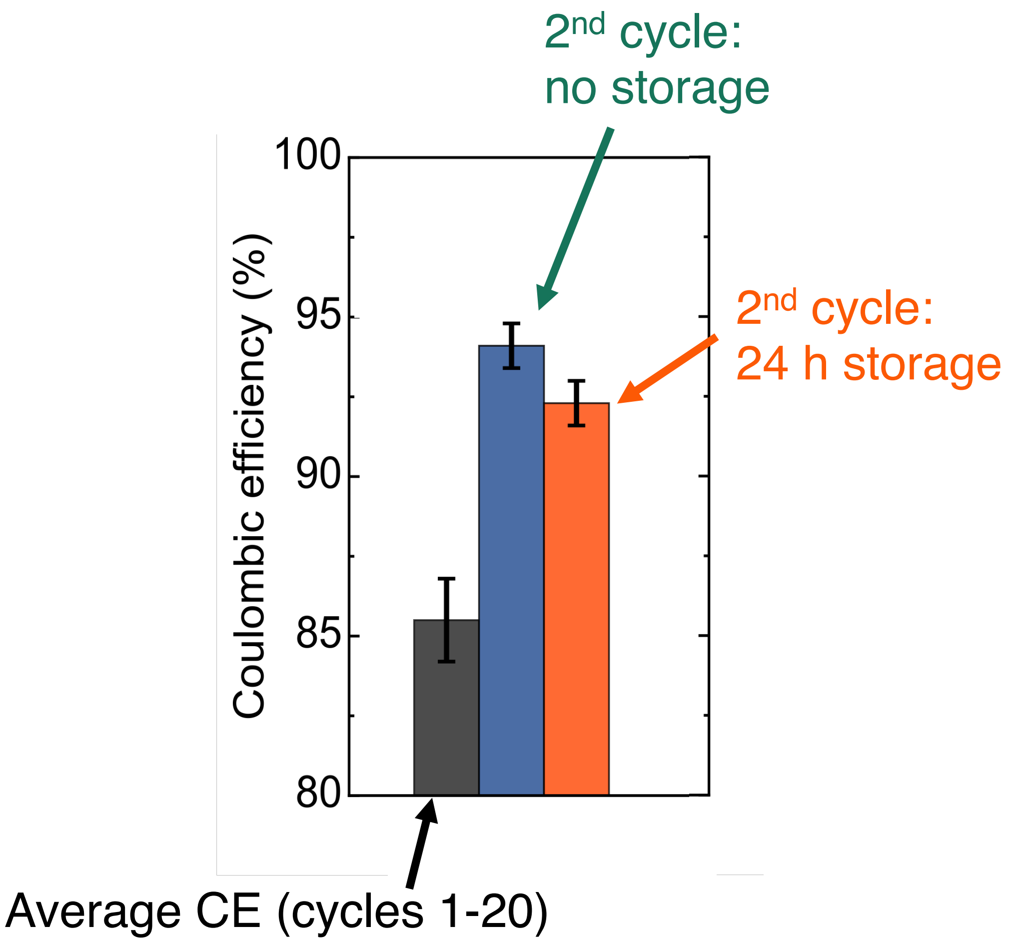
Hao Chen, Yi Cui Joule (2020), DOI: 10.1016/j.matt.2020.04.011

Effect of Aging on Li metal Rechargeability

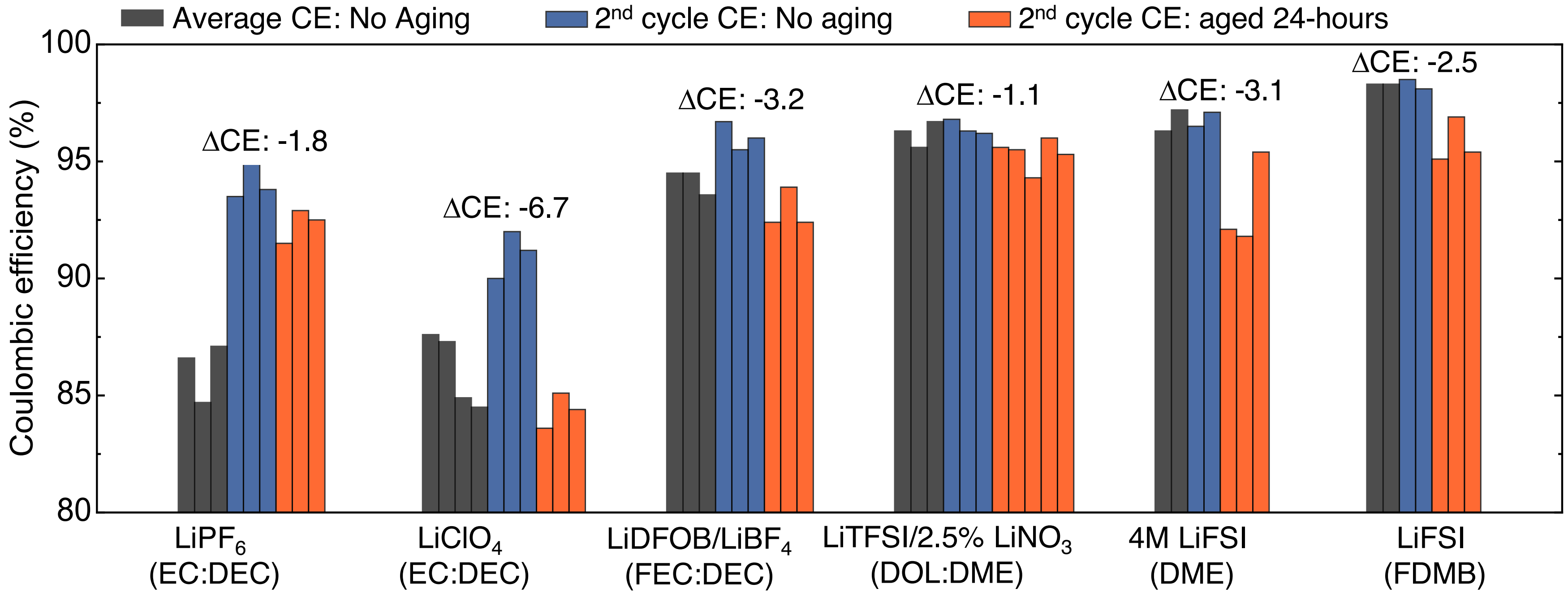
Commercial carbonate electrolyte $LiPF_6$ (EC:DEC)
Preformed SEI by holding at 0V versus Li metal for 24hrs



- Storage for 24 hours causes a ΔCE = -1.8%



Effect of Electrolyte Chemistry



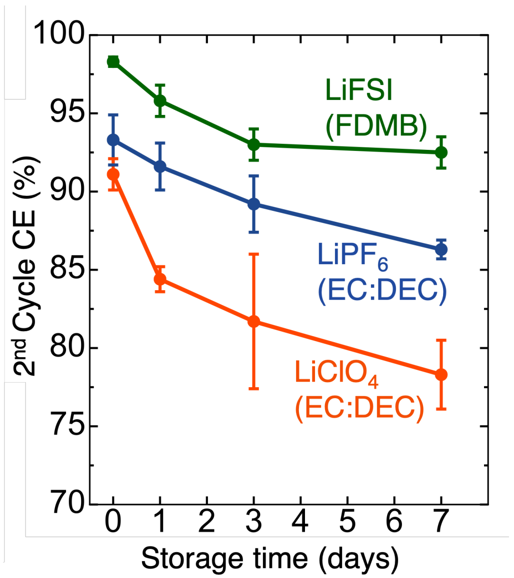
<u>Low performance</u>
- Commercial Carbonates

<u>High performance</u>
- Dual salt
- Additives
- High concentrations
- Ether and Fluorinated solvents

- Typically, ~2-3% of capacity is lost during 24 hours of storage
- Both high and low performance electrolytes show losses

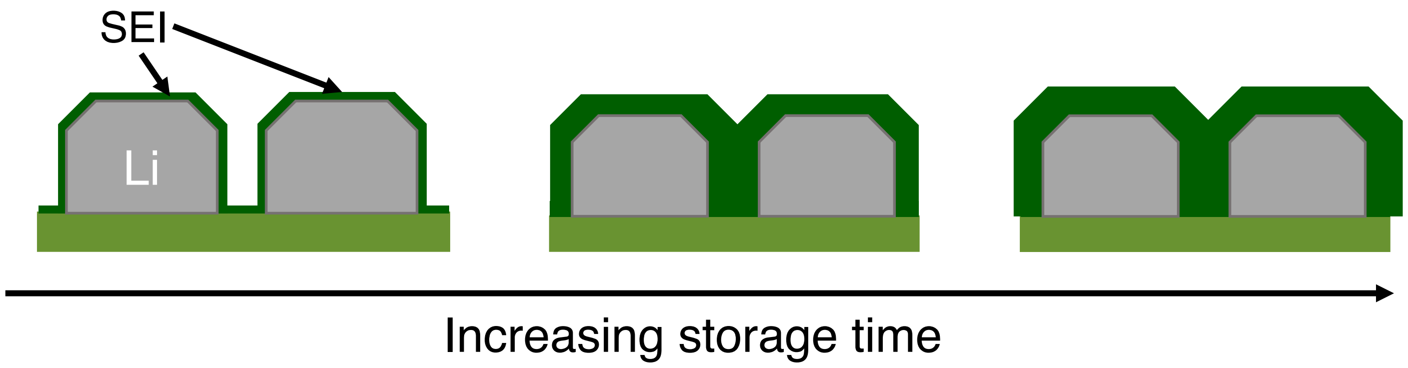
Can we identify the cause of these capacity losses?

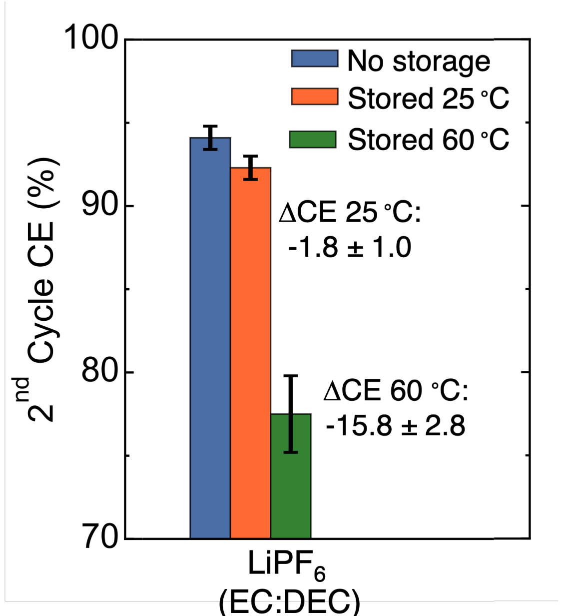
Unique storage conditions suggest SEI causes DCE



Storage time

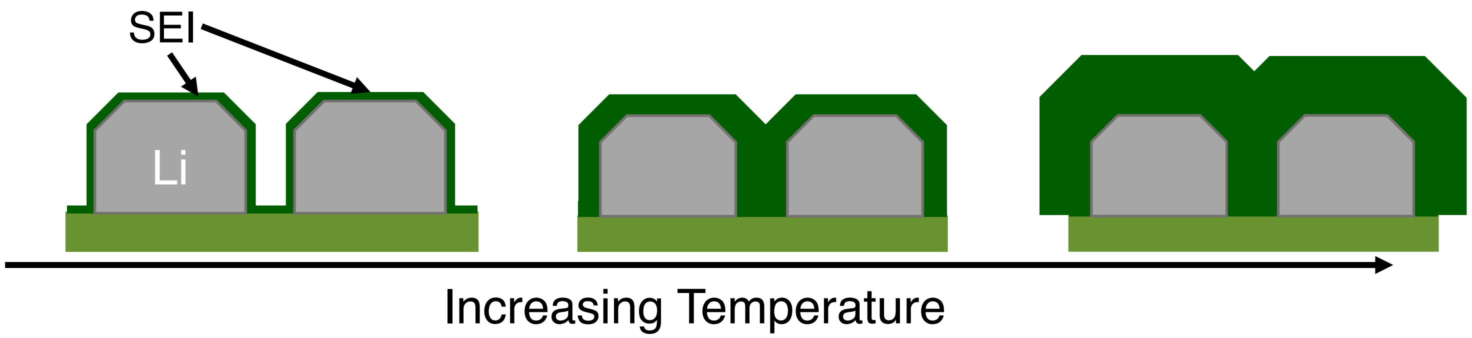
- Capacity loss smoothly increases with time – consistent with SEI growth





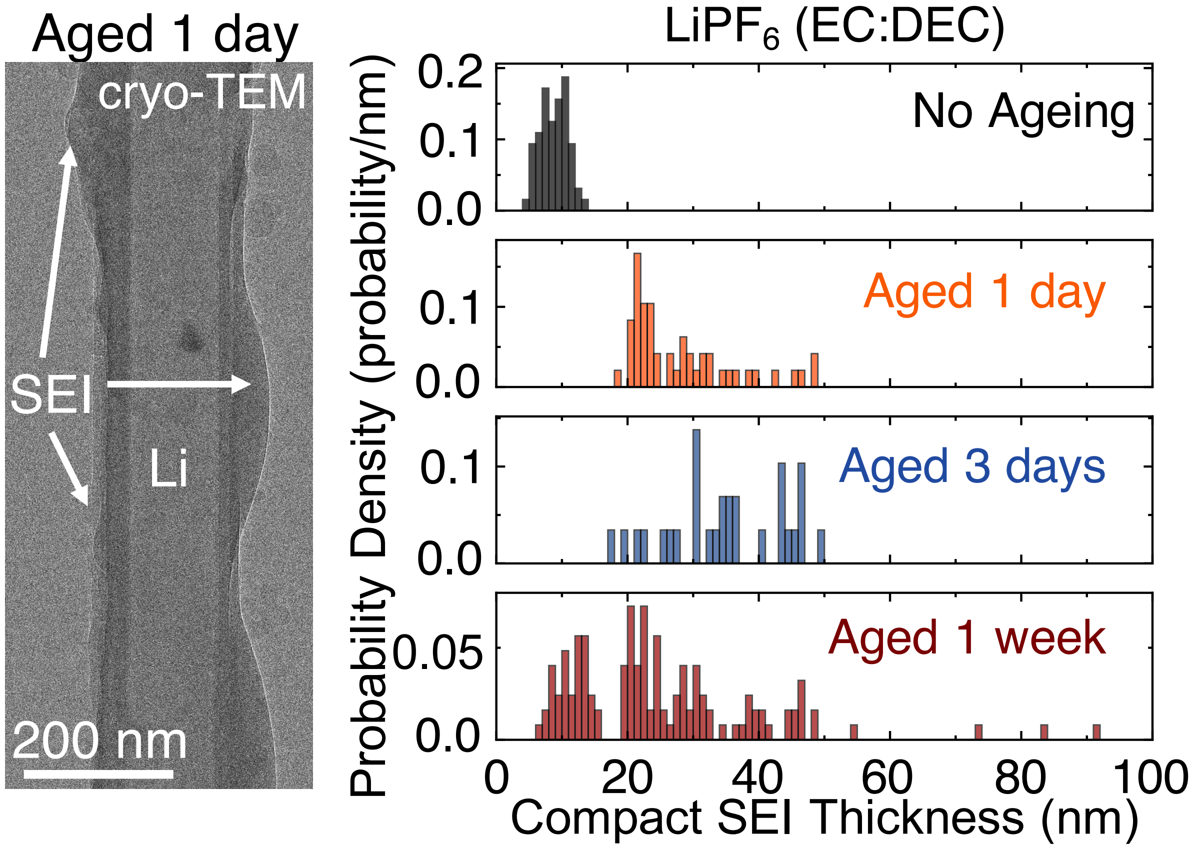
Temperature

- Capacity loss increases sharply with temperature

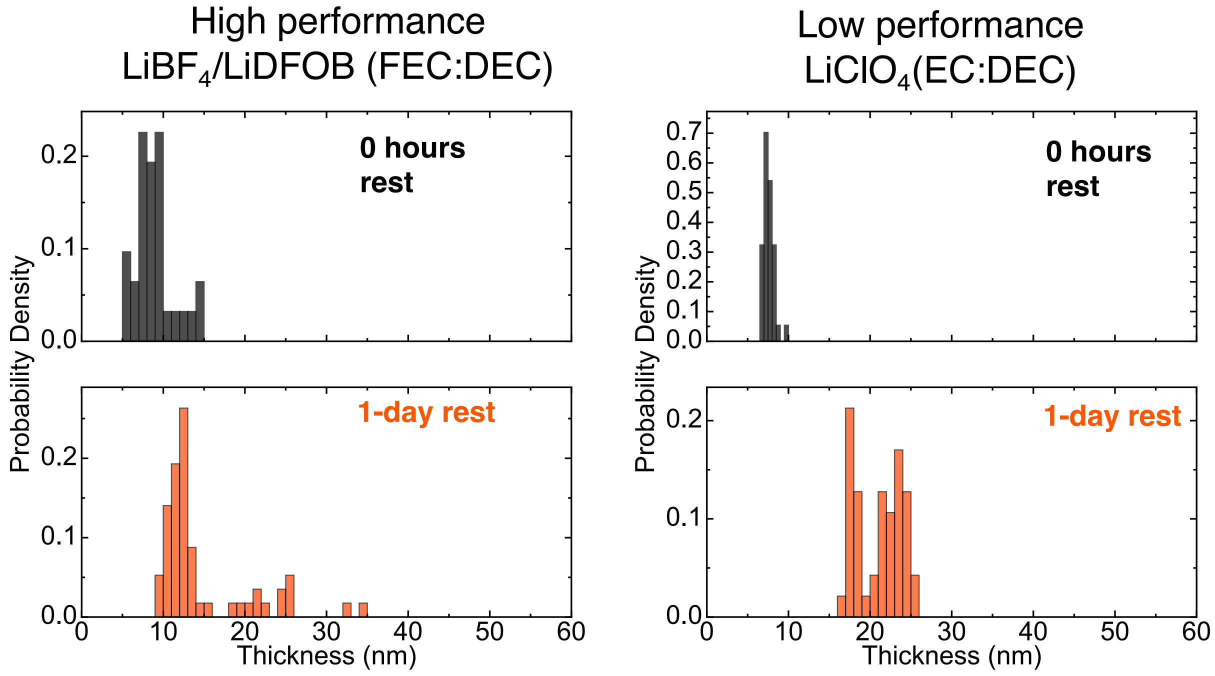


Heterogeneous growth of the SEI

- Thickness and heterogeneity of the compact SEI increases with longer storage times

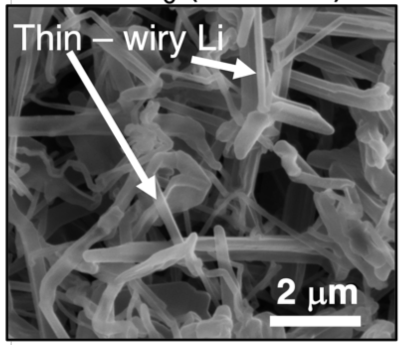


- Both low and high-performance electrolytes have similar SEI growth



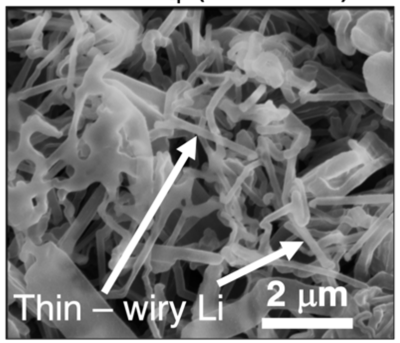
Rate of SEI Growth and Surface Area of Li

$LiPF_6$ (EC:DEC)



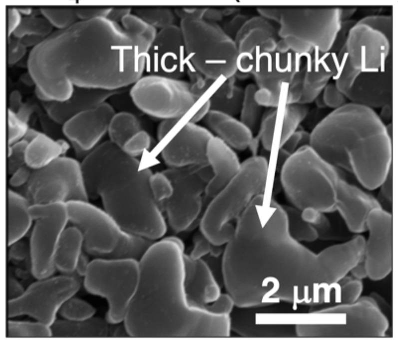
Slow SEI growth
High SA

$LiClO_4$ (EC:DEC)



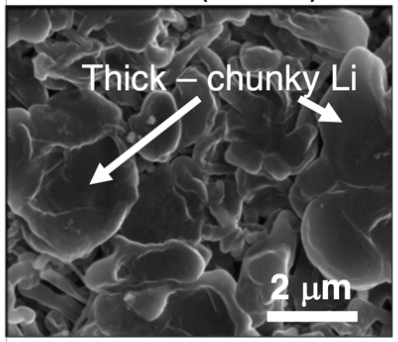
Fast SEI growth
High SA

$LiBF_4$/LiDFOB (FEC:DEC)



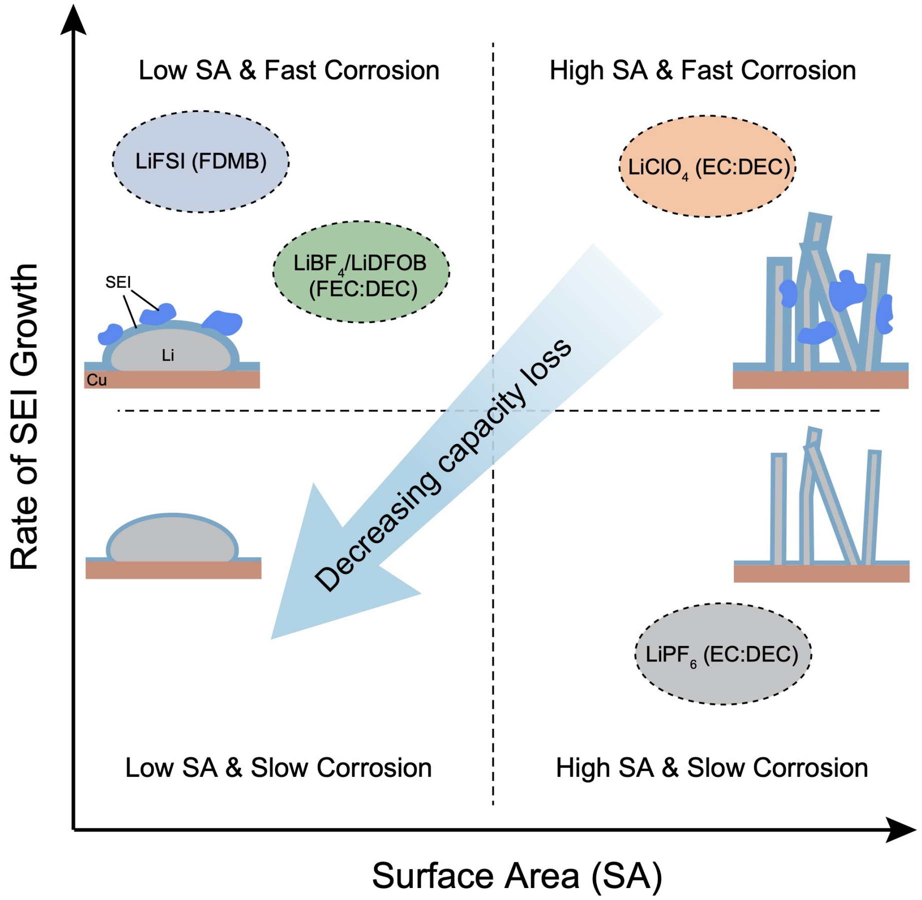
Fast SEI growth
Low SA

LiFSI (FDMB)



Fast SEI growth
Low SA

Electrolytes for anode-free Li metal batteries must simultaneously minimize surface area of Li and SEI growth



Responses to Previous Year Reviewers' Comments

The reviewers like the approach, the technical accomplishment and collaboration in this project. There is no major concern.

Collaboration and Coordination

Battery 500 PI's:
Jun Liu
Jie Xiao
Jason Zhang
Wu Xu
Stan Whittingham

SLAC/ Stanford University:
Prof. Zhenan Bao
Prof. Mike Toney
Prof. William Chueh
Prof. Reiner Dauskardt
Prof. Steven Chu
Prof. Jian Qin
Prof. Wah Chiu
Prof. Robert Sinclair
Prof. Paul McIntyre

Remaining Challenges and Barriers

- The best electrolyte and SEI structure are yet to be determined.
- The calendar ageing of Li metal batteries needs to be addressed.

Proposed Future Work

- To further develop approaches for 3D Li metal anodes with stable interfacial modification, nearly zero-volume change both globally and locally.
- To develop electrolytes to form stable SEI assisted by cryoEM study.
- To develop polymer coating layer to facilitate the formation of stable SEI.

Summary

- **Objective and Relevance:** The goal of this project is to develop stable and high capacity Li metal anodes and the full battery cells to enable high energy lithium metal-based batteries to power electric vehicles, highly relevant to the VT Program goal.

- **Approach/Strategy:** This project combines advanced nanomaterials design, synthesis, characterization, battery assembly and testing, and guided by cryogenic electron microscopy study.

- **Technical Accomplishments and Progress:** This project has produced many significant results, meeting milestones. They include identifying the key issues in lithium metal batteries, using rational materials design, synthesis, characterization and simulation. The results have been published in top peer-reviewed scientific journals. The PI has received numerous invitations to speak in national and international conferences.

- **Collaborations and Coordination:** The PI has established a number of highly effective collaborations.

- **Proposed Future Work:** Rational future plan has been proposed.