Operando Characterization of Lithium Plating and Stripping

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BATTERY 500 CONSORTIUM

Project ID: bat514

Overview

Timeline

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

Barriers

Barriers of batteries

- High cost (A)
- Low energy density (C)
- Short battery life (E)

Targets: cost-effective and high- energy electrode materials and batteries

Budget

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

Partners

- Collaboration
  - Battery 500 PI's
  - BMR program PI' s
  - DOE light sources

BATTERY 500 CONSORTIUM

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)

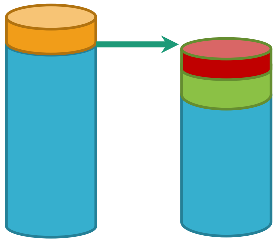
FY21
Q1 Compare new Li anode architecture with 50 micron Li anode using protocols for 350 Wh/kg cells (completed)
Q2, Measure solid or semisolid (oxides, polymer or composites) electrolyte performance using protocols for 350 Wh/kg cells (SLAC) (completed)
Q3, Characterizing Li metal-solid electrolyte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

Approach

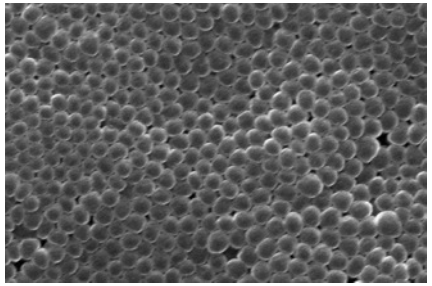
- Develop advanced diagnostic tools to monitor lithium plating and stripping, in particular, contributions to coulombic efficiency and morphology.
- Provide engineering guidance on electrolytes, additives, and cycling procedures for developing lithium-metal based batteries with 500 Wh/kg specific energy.
- Develop operando X-ray diffraction for deconvoluting contributions to coulombic efficiency during lithium plating and stripping.
- Develop operando grazing-incidence small-angle scattering and operando scanning probe microscopy to monitor morphology and microstructure during lithium nucleation and growth.

Technical Accomplishments and Progress

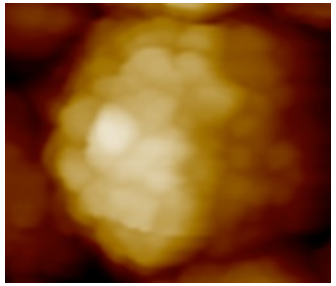
- What are the origins of poor performance (coulombic efficiency) in lithium metal?



- How does the SEI change the morphology of the lithium? And how can additives tune this behavior?

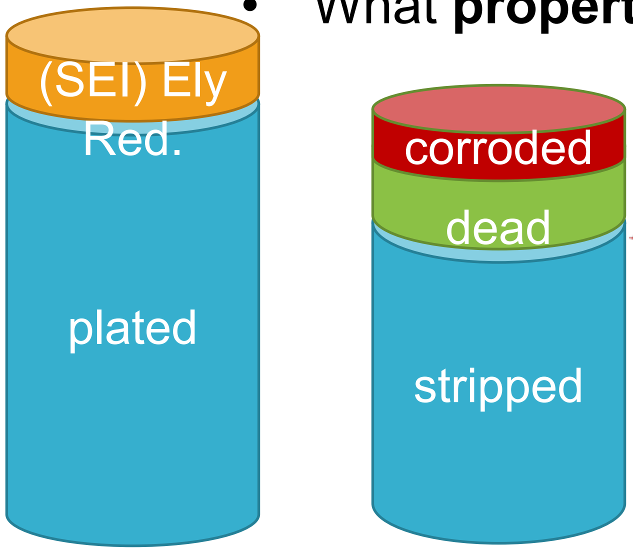


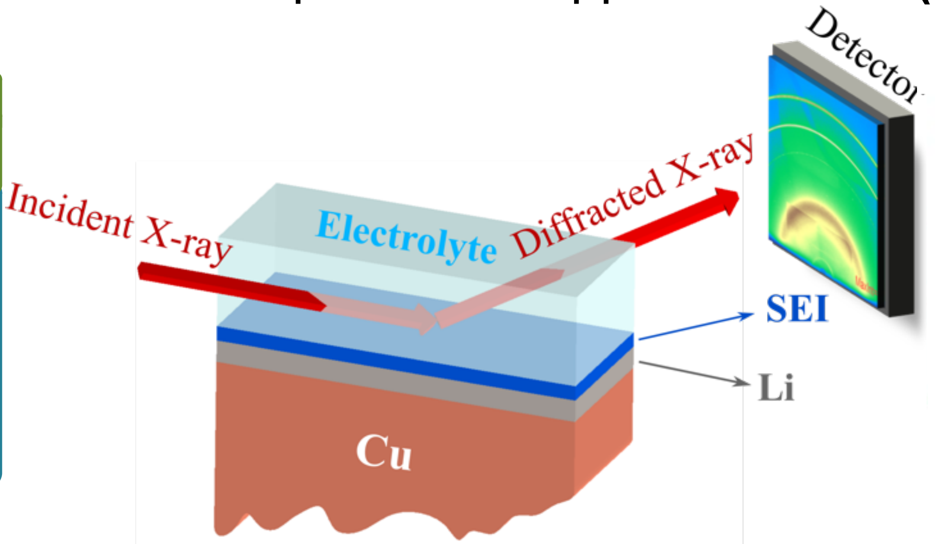
- How can the dynamics of nucleation processes be observed?

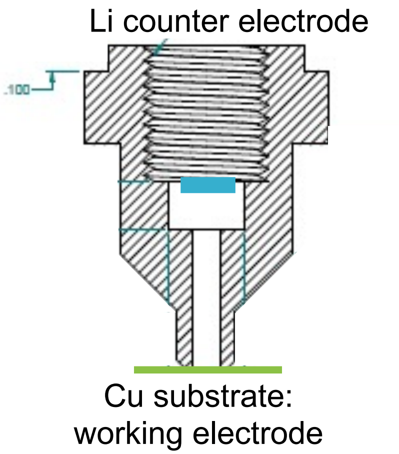


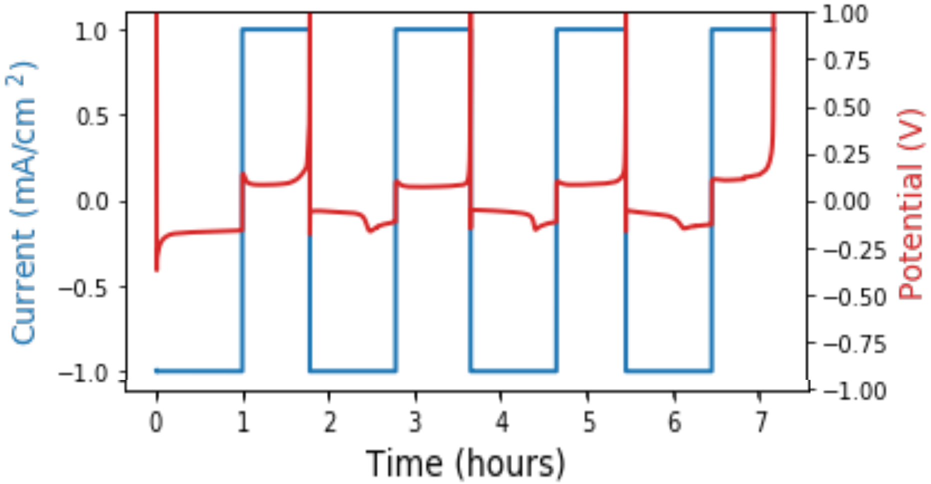
Technical Accomplishments and Progress:
Operando X-ray Diffraction as Quantitative Probe

- **How much capacity** is lost to electrolyte reduction, "dead" Li, corrosion?
- What **properties** make a protection approach more **(un)successful**?



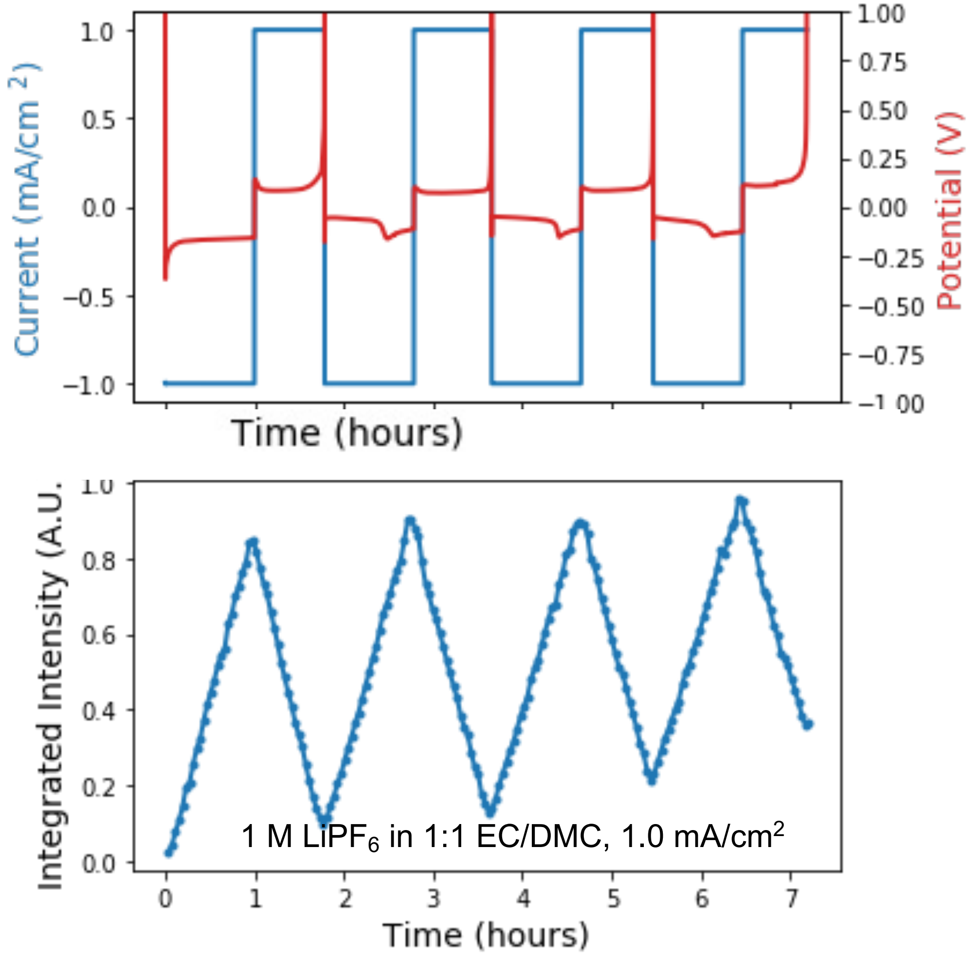




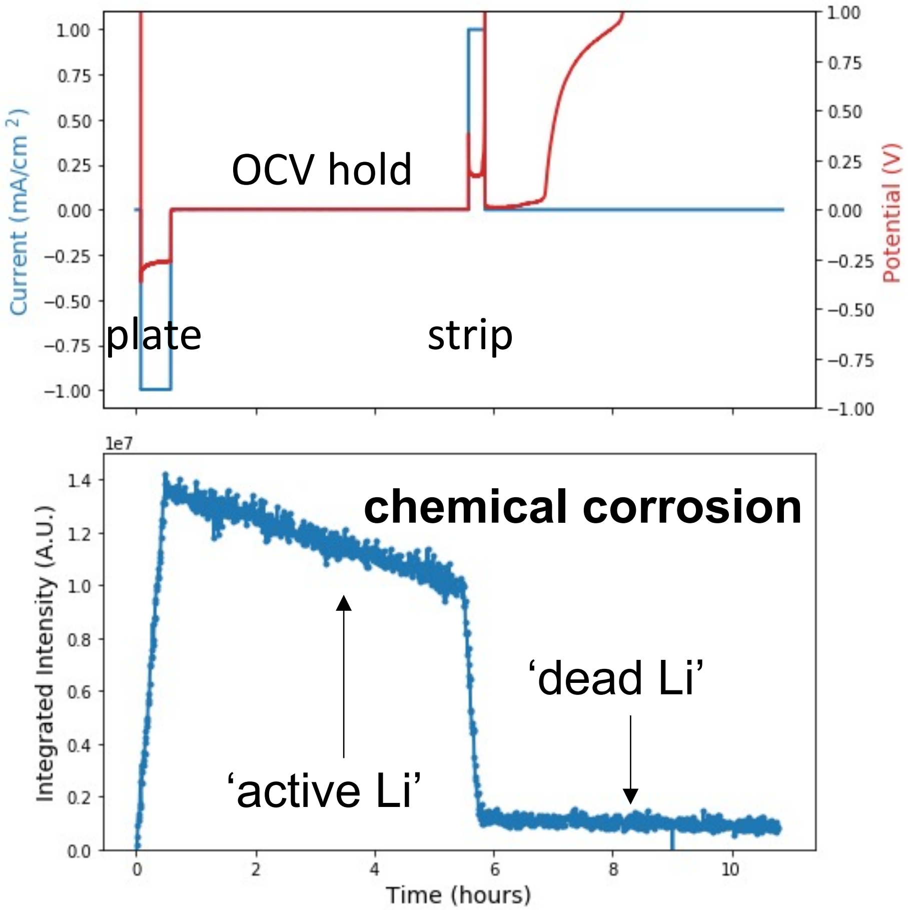


XRD is a technique that is sensitive to the structure – hence only to the Li in the sample and the intensity is reflective of the amount illuminated, therefore we can use it while plating and stripping (operando) to track the amount of lithium on the surface.

Technical Accomplishments and Progress:
Operando XRD of Li (110) During Plating/Stripping & Open Circuit

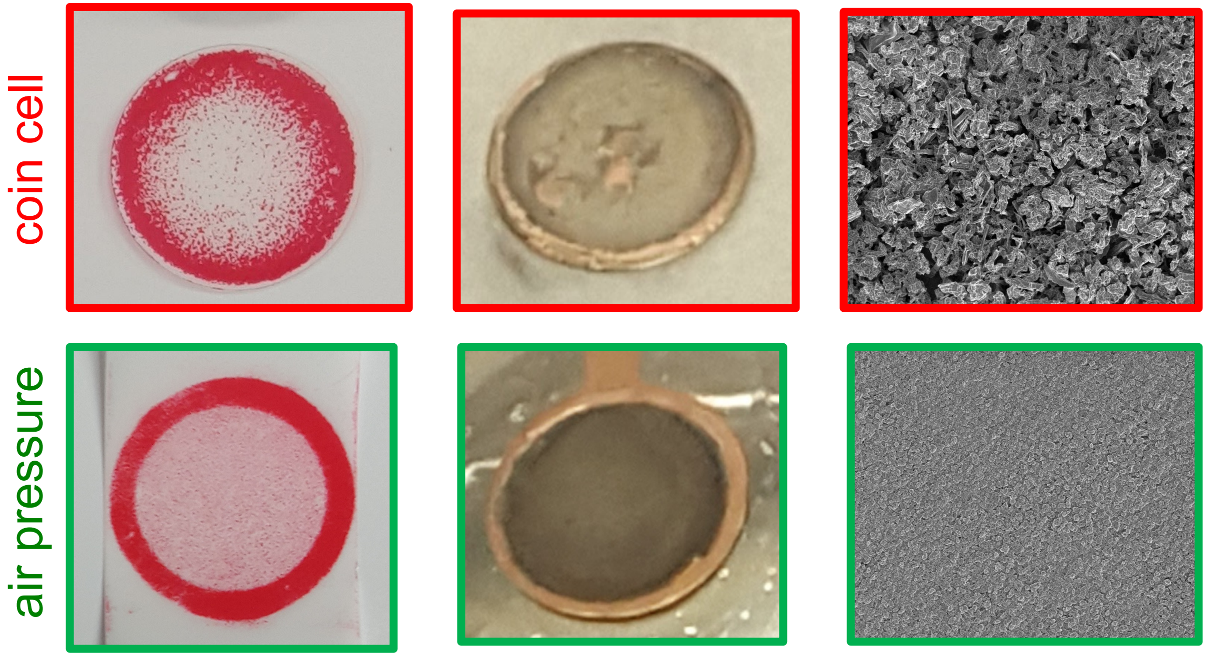


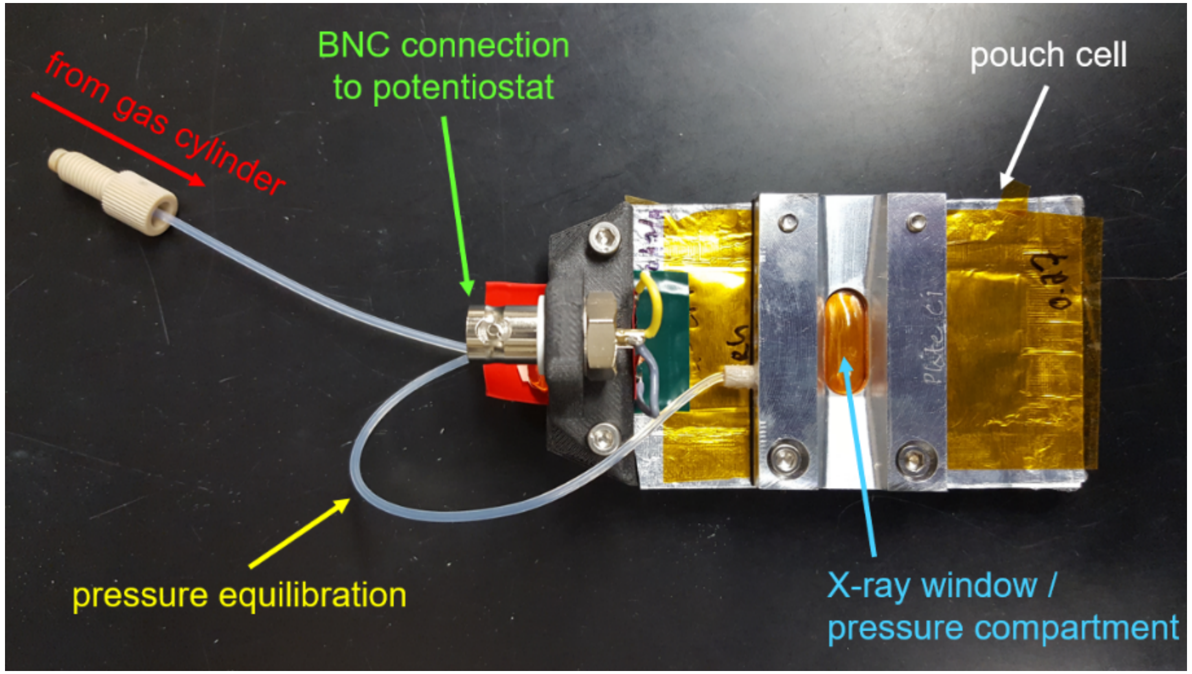
Correlation of electrochemical measurements with Li (110) peak area through 4 cycles. Observation of 'dead' Li formation



We observe chemical corrosion of both 'active' and 'dead' lithium, and extrapolate to find total corroded in cycle

Technical Accomplishments and Progress:
Uniformity of Applied Stack Pressure

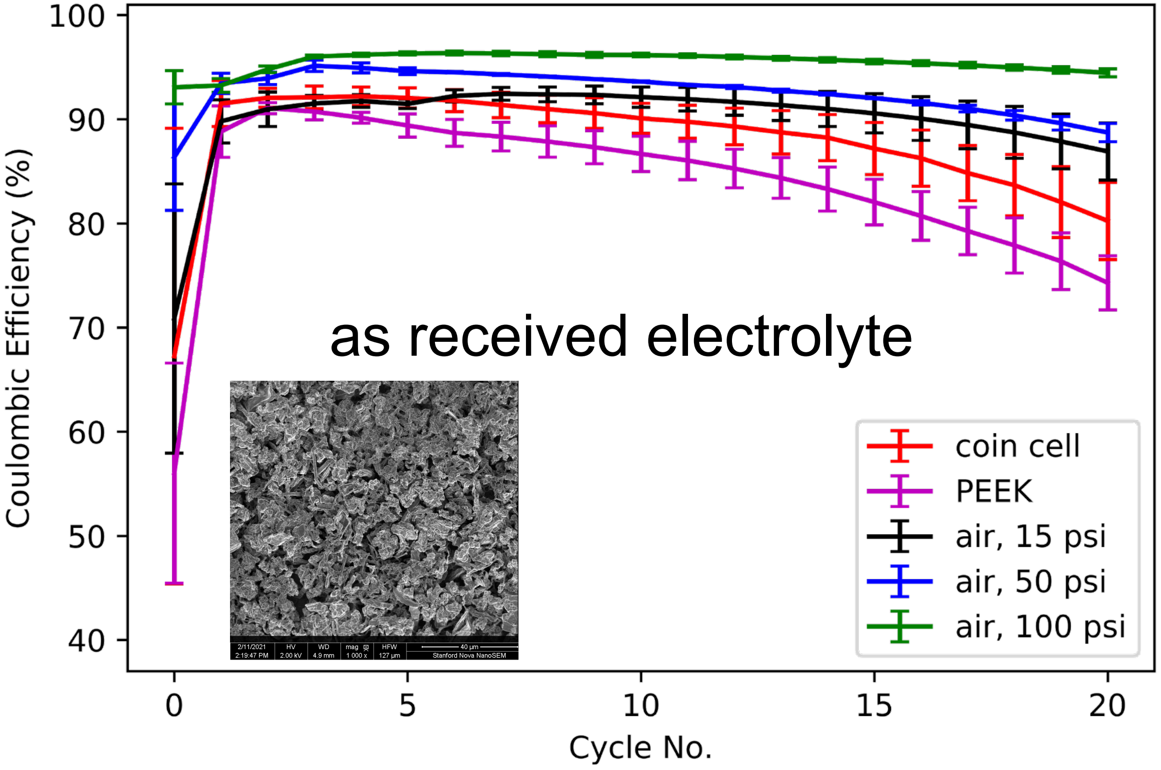


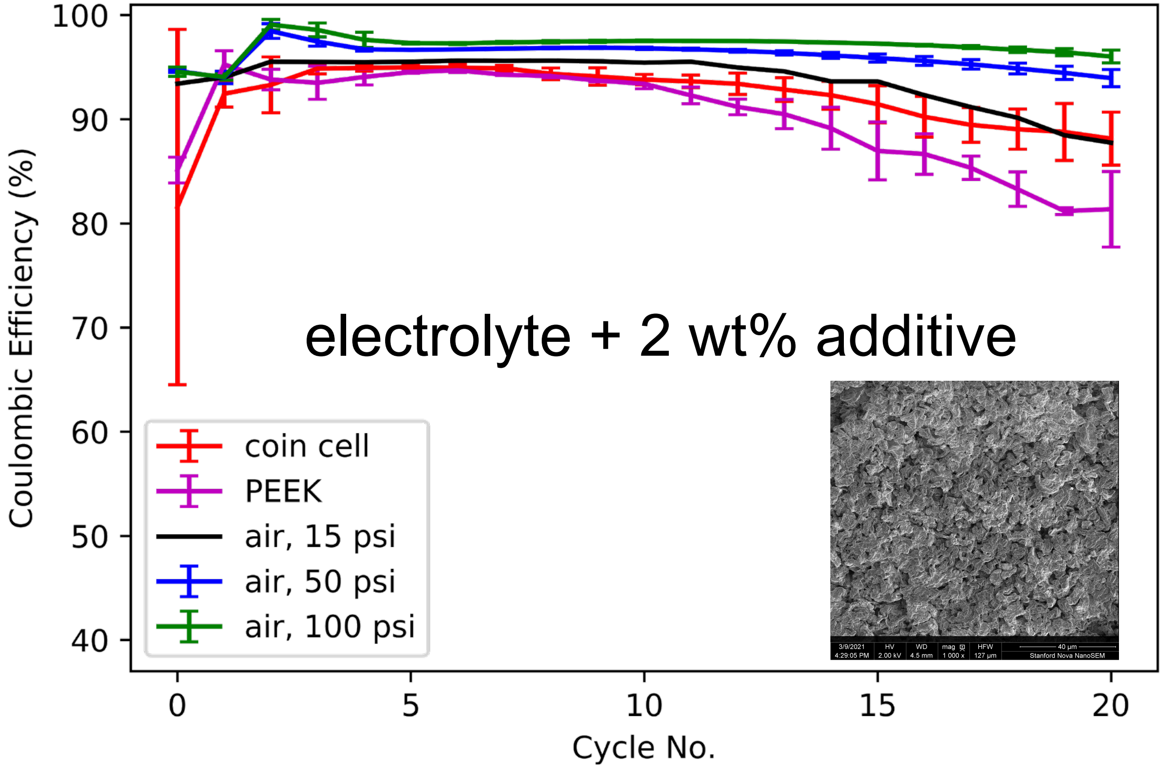


Pressure holder designed and built by Dr. Chris Takacs.

Gas bladder cell allows for highly precise application of uniform, conformal pressure

Technical Accomplishments and Progress:
Uniformity of Applied Stack Pressure

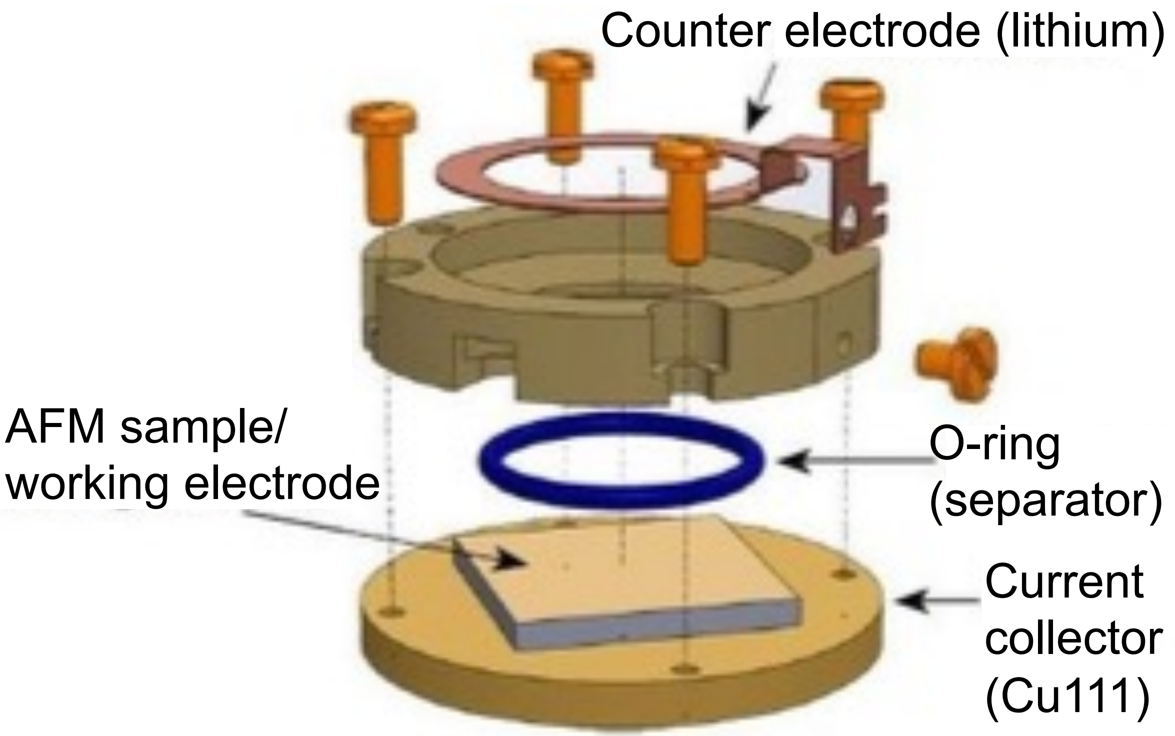




Performance enhancements from additives and stack pressure sum to yield the highest performing cells

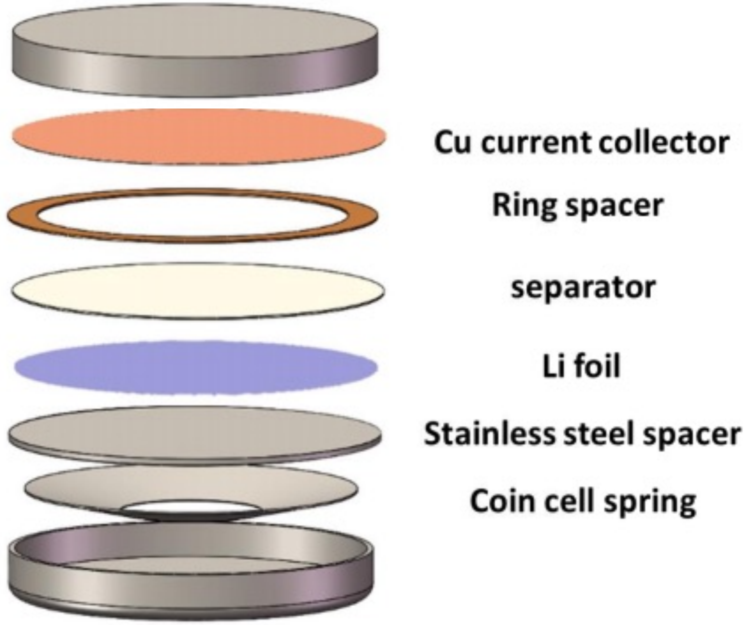
Technical Accomplishments and Progress:
AFM characterization of nucleation & growth

Electrochemical AFM cell



Asylum Research

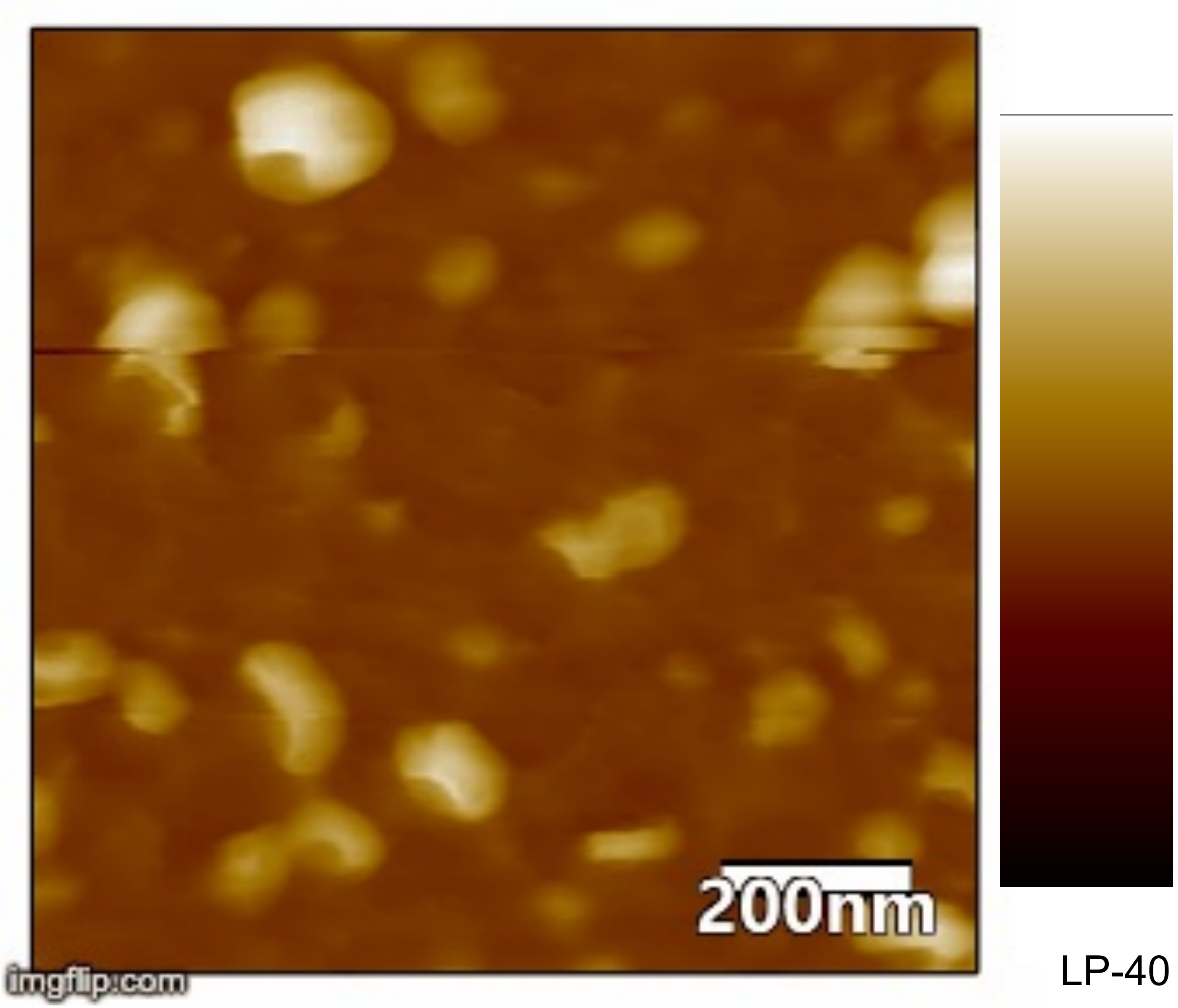
Pressure free cell for ex-situ comparisons

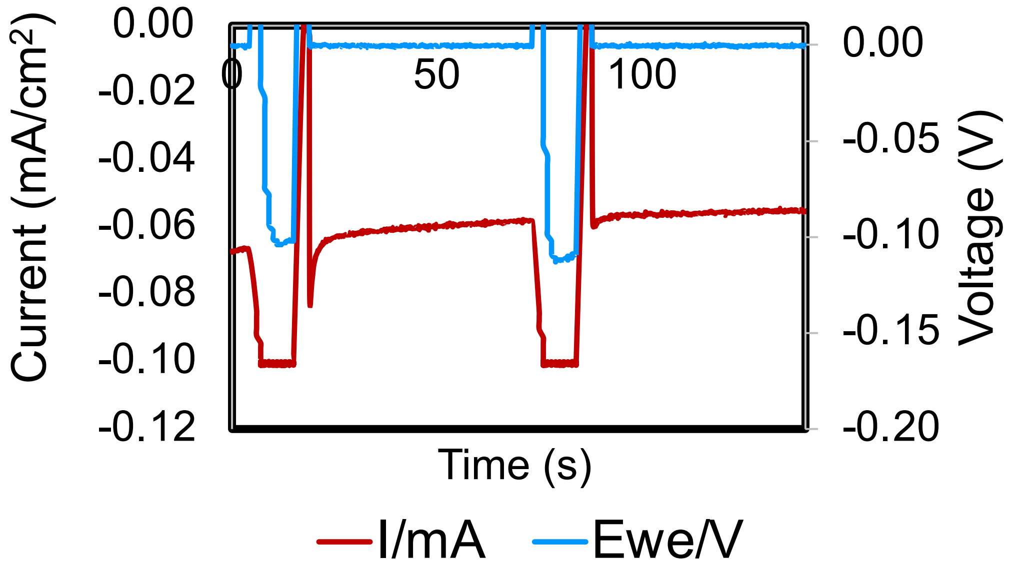


F Shi, et al. PNAS. 2017

Operando atomic force microscopy is a tool to probe SEI evolution and very early nucleation

Technical Accomplishments and Progress:
Nucleation during pulsed deposition

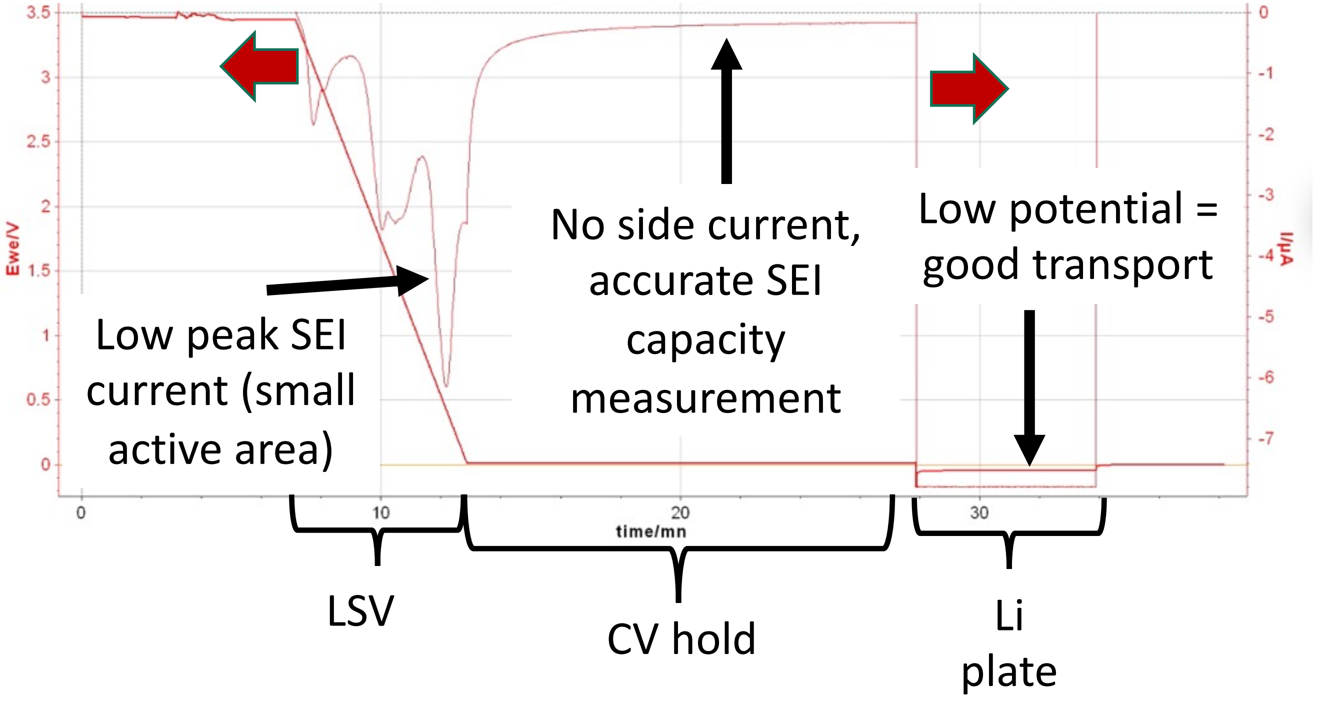




Nucleation during pulsed deposition proceeds heterogeneously between pulses, meaning each pulse leads to additional nuclei. Only a few select particles are active in pulsed growth at a given time → high local current fluxes → Likely due to nonuniform SEI passivation.

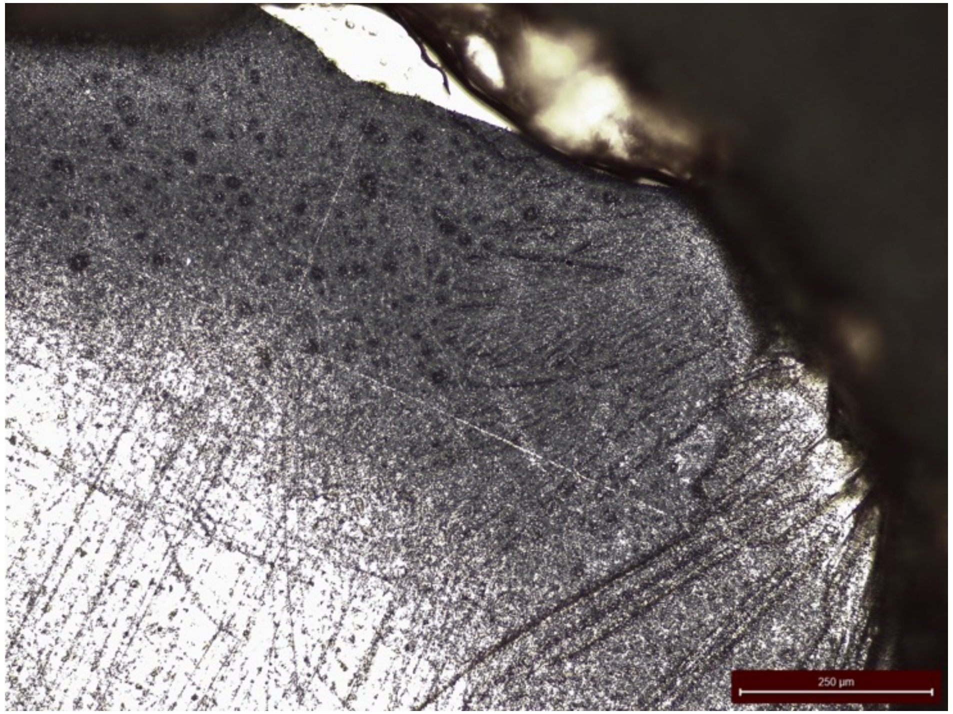
LP-40 Electrolyte, 1 μAh/cm^{-2} capacity per frame

Technical Accomplishments and Progress:
Greatly improved the uniformity of lithium plating & stripping in operando AFM



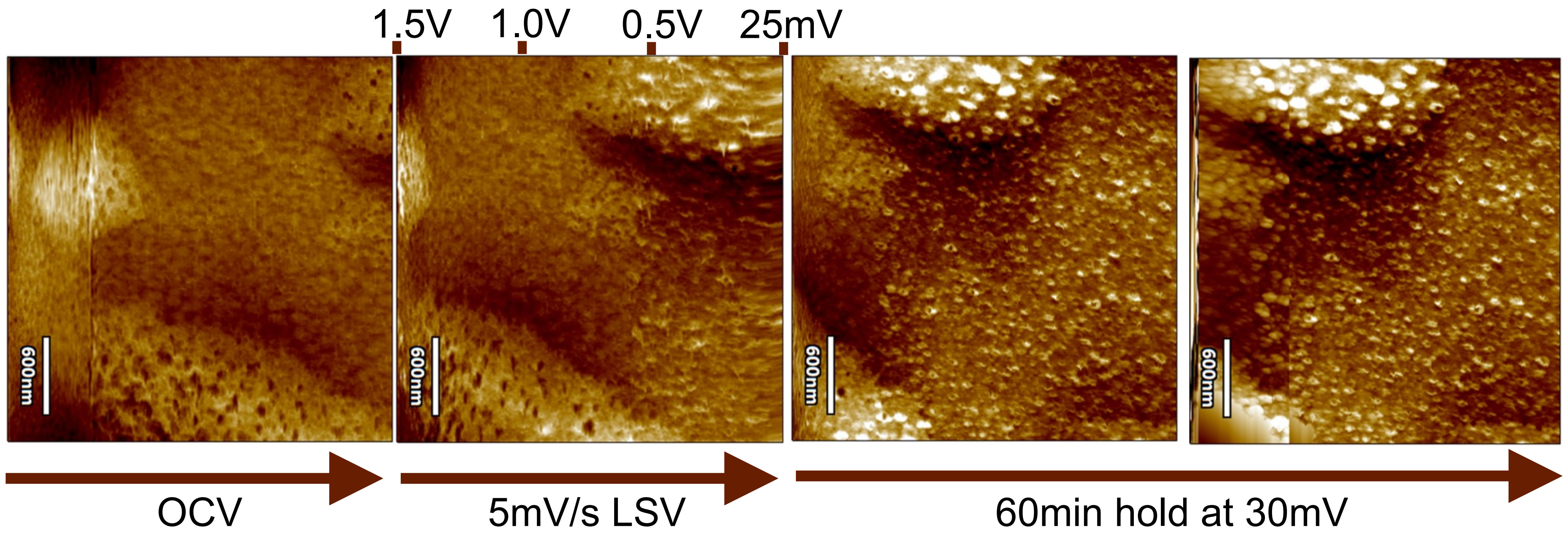
Electrochemistry from improved operando cell:

- 5mV/s voltage sweep
- 30min hold at 30mV
- 0.1mAh/cm^2 lithium plated at 1mA/cm^2



Optical imaging confirms uniform lithium deposition in active area

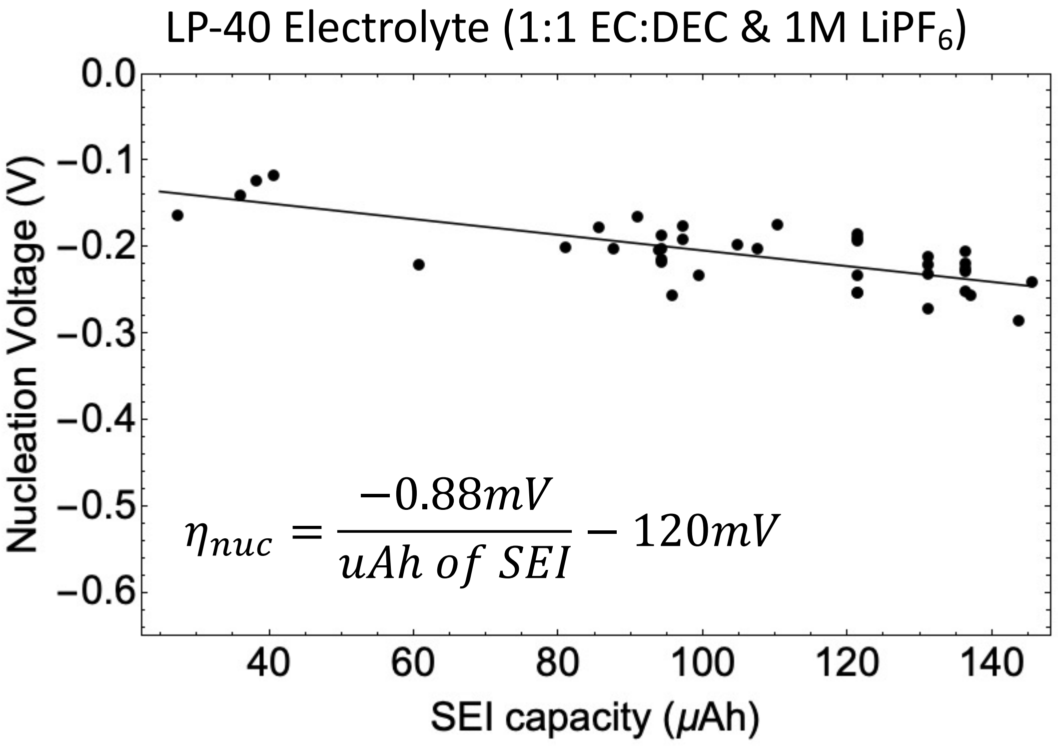
Technical Accomplishments and Progress:
Operando imaging of SEI formation pre-plating

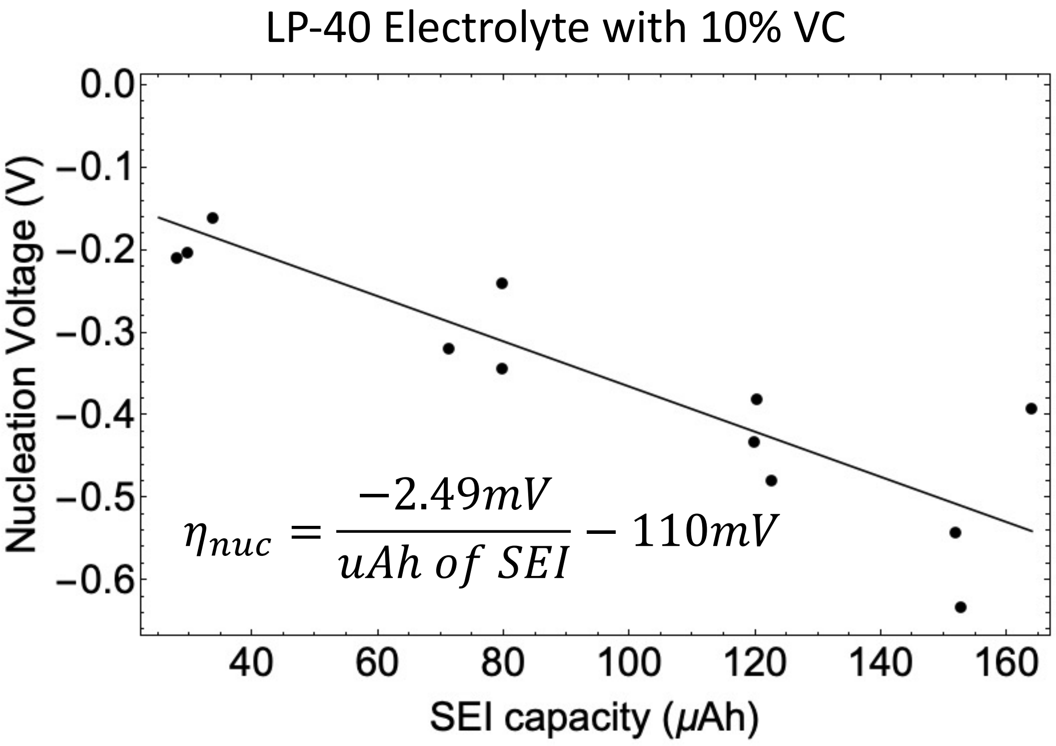


SEI morphology evolution is visible in test cell. Further results aim to show coupled SEI & Li metal morphology evolution

Technical Accomplishments and Progress: **Operando imaging of SEI formation pre-plating**

Nucleation peak height vs. SEI capacity





Hypothesis: strong correlation between pre-plating SEI and lithium plating overpotential

Responses to Previous Year Reviewers' Comments

None

Collaboration and Coordination

Battery 500 PI's:
Yi Cui
Jason Zhang, UW
Eric Dufek, INL
Ram Manthiram, UT Austin

DOE Users Facilities: Advanced Light Source, Lawrence Berkeley National Laboratory

Remaining Challenges and Barriers

- XRD measurement of lithium plating over many cycles remains challenging.
- Operando atomic force microscopy becomes challenging when the plated lithium is thick due to the rough microstructure.

Proposed Future Work

- Investigate lithium nucleation and growth dynamics as a function of charging protocol, providing the basis for optimizing charging protocol, especially at high rates.
- Investigate lithium stripping (morphology and efficiency) and its connection to plating.
- Probe how SEI thickness and chemistry affects the lithium plating & stripping dynamics, efficiency and morphology.

Summary

- We have successfully developed advanced diagnostic tools to monitor lithium plating and stripping, in particular, contributions to coulombic efficiency and morphology.
- We demonstrated operando X-ray diffraction for deconvoluting contributions to coulombic efficiency during lithium plating and stripping, as well as during calendar aging.
- Operando grazing-incidence small-angle scattering and operando scanning probe microscopy were employed to monitor morphology and microstructure during lithium nucleation and growth.
- The results are providing engineering guidance on electrolytes, additives, and cycling procedures for developing lithium-metal based batteries with 500 Wh/kg specific energy.