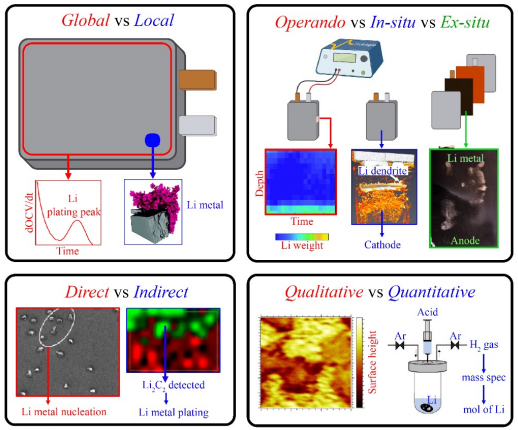
BAT457

XCEL
eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

eXtreme Fast Charge Cell Evaluation of Lithium-Ion Batteries (XCEL)

METHODS FOR THE DETECTION AND QUANTIFICATION OF LITHIUM PLATING



JOHANNA NELSON WEKER
SLAC National Accelerator Laboratory

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June 22, 2021
AMR, virtual

OVERVIEW

Timeline

- Start: October 1, 2017
- End: September 30, 2021
- Percent Complete: 94%

Barriers

- Cell degradation during fast charge
- Low energy density and high cost of fast charge cells

Budget

- Funding for FY20 – $5.6M

Partners

- Argonne National Laboratory
- Idaho National Laboratory
- Lawrence Berkeley National Lab
- National Renewable Energy Laboratory
- SLAC National Accelerator Lab
- Oak Ridge National Lab

Relevance

Impact

- Decrease charging time without sacrificing lifetime
- Connect Li plating to cell degradation mechanisms
- Identify and mitigate unfavorable Li plating to reduce capacity fade from extreme fast charging (XFC)

Objectives

- Develop approaches to accurately detect and quantify Li deposition during extreme fast charge conditions
- Link detection of onset of Li with cell performance, age, and local heterogeneity

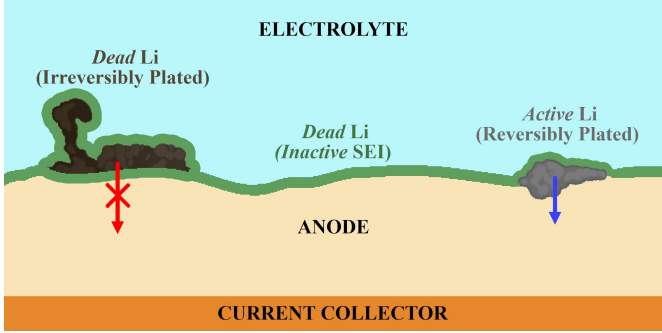
MILESTONES

High level Li detection related milestones in XCEL

Milestone	End Date	Status
1. Determine where the lost Li inventory is trapped using a combination of at least two Li detection techniques.	12/31/2020	Completed
2. Submit review paper on Li detection techniques which will outline where each technique is in terms of detection accuracy and correlations between multiple techniques.	12/31/2020	Completed
3. Connect “dead Li” to cycling age and determine if dead Li accelerates additional Li plating. Understand how intentional Li plating in the first few cycles affects future capacity fade during standard CCCV cycling.	6/30/2021	On Track
4. Identify if and what are the early warning signs of Li plating for different Li detection techniques. Identify which detection techniques that could be incorporated on a vehicle.	6/30/2021	On Track
5. Determine if the hero cell-1 plates less Li or later in life or SOC compared to R-II cells?	9/30/2021	On Track

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

Approach

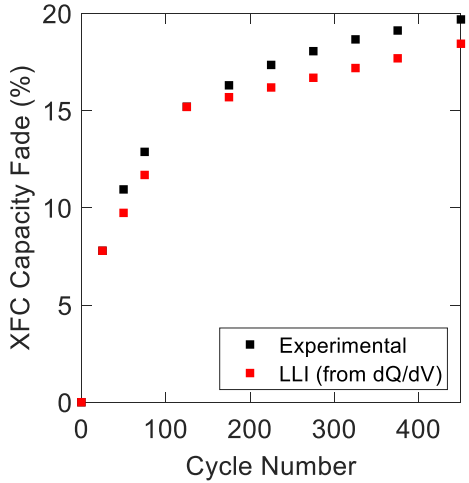


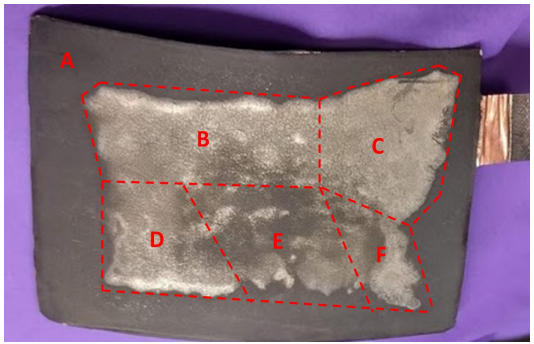
Leveraging different Li detection techniques to answer:

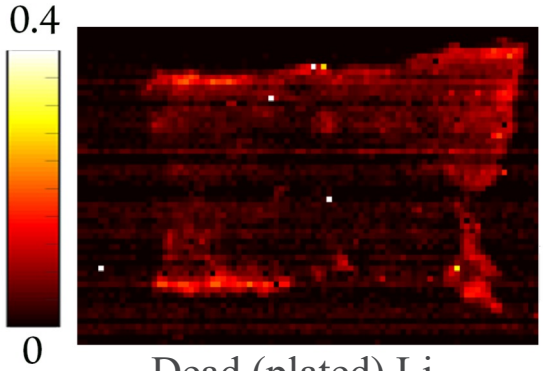
- Where is the lost Li inventory trapped?
  - Combine multiple detection techniques to gain holistic understanding of degradation processes during fast charge
- What *operando*, readily accessible techniques could be used for early detection?
  - Explore inexpensive, non-invasive detection & connect to modeling
- Will a small amount of Li plating result in irreversible damage contibuting to cell failure?

XRD quantification of dead Li

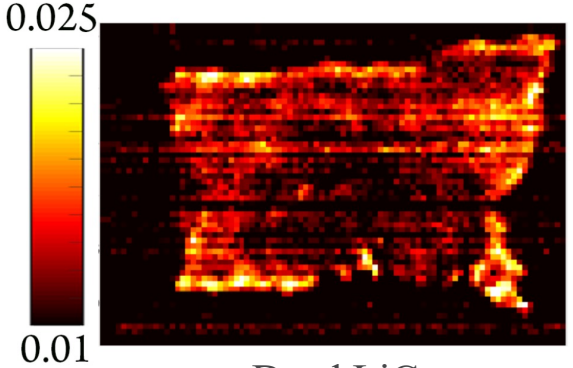
- Depth-averaged XRD gives ‘quantitative’ spatial maps of crystalline Li-containing species
- When summed up over the cell, we can get the total amount of such species over the cell







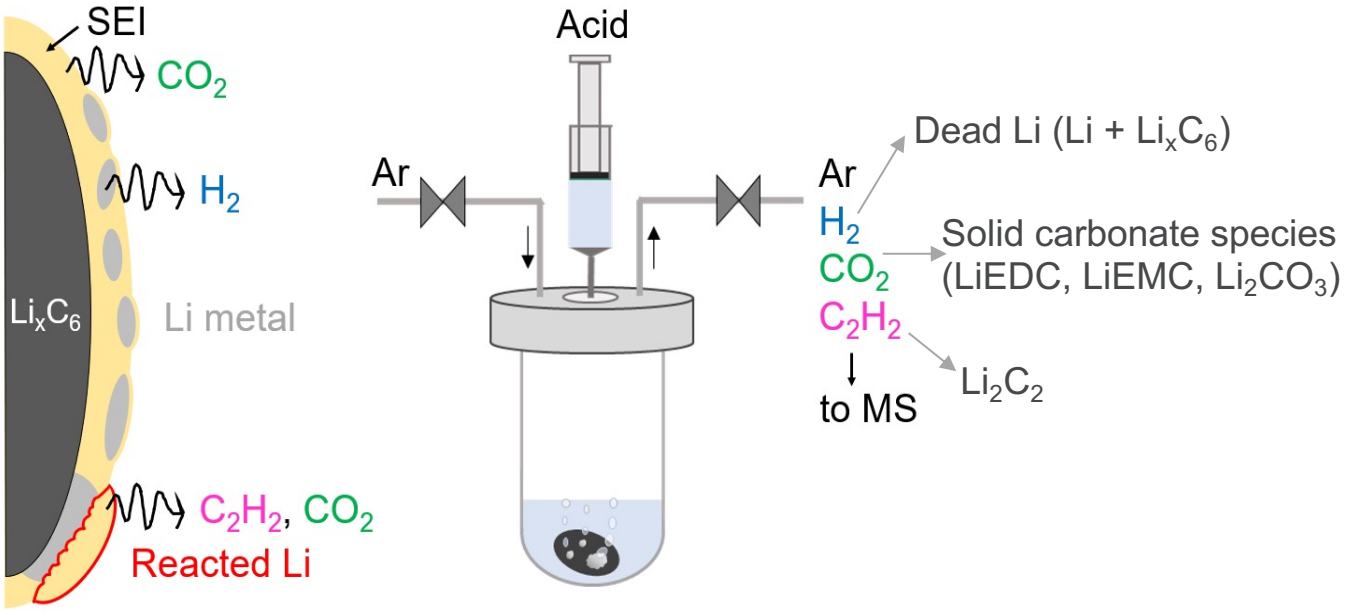
Dead (plated) Li
(µmol of Li)

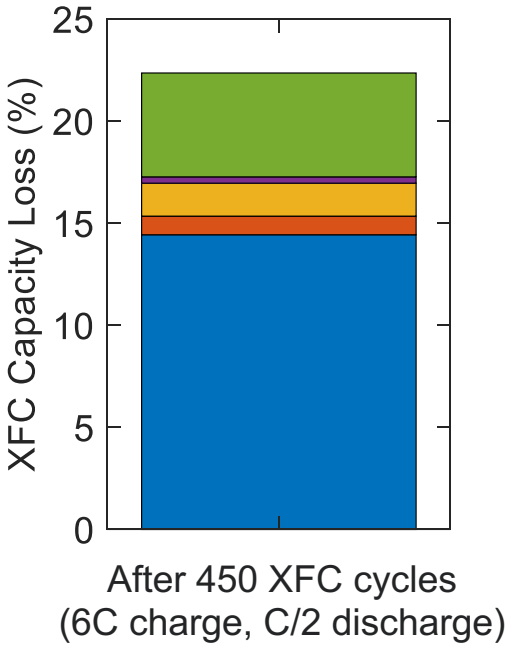


Dead LiC_6
(µmol of Li)

NMC532/Graphite Round 2 pouch cell after 450 XFC

Mass Spectrometry Titration (MST)

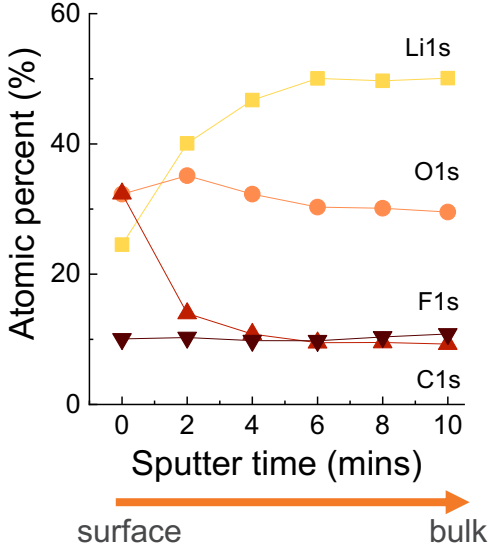


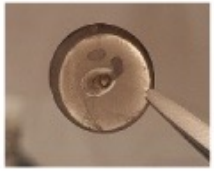


Graphite anodes from NMC532/Gr
Round 2 pouch cell after 450 XFC

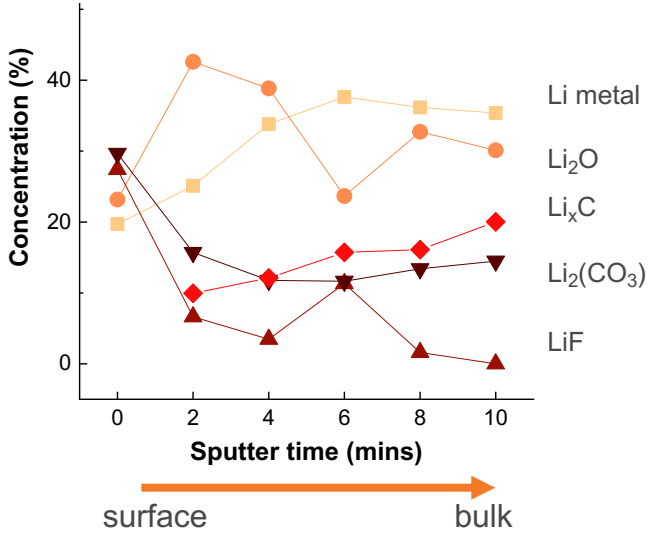
Other Li species – XPS depth profiling

Atomic concentration from surface to bulk





Detailed peak fitting of Li1s region



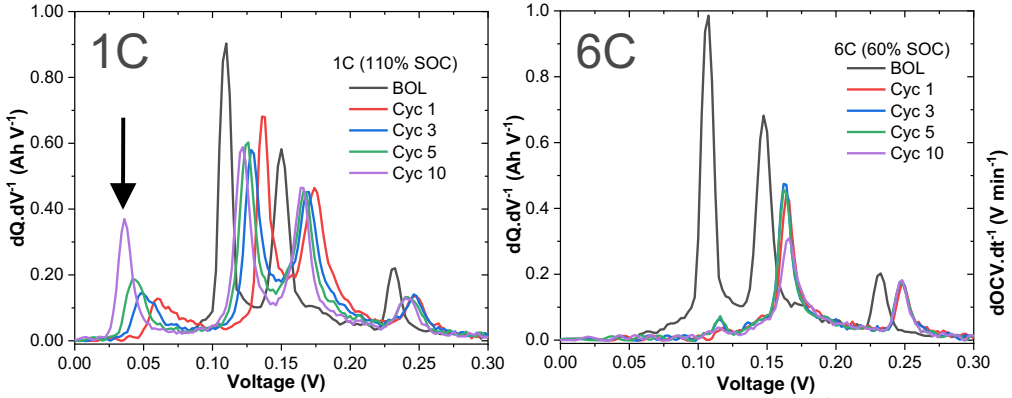
- Cannot compare same electrode as MST and XPS depth profiling are destructive
- But estimate of undetectable species (LiF, Li_2O, etc.) reasonable

Graphite anodes after 50 XFC (NMC532/Gr Round 2 coin cell)

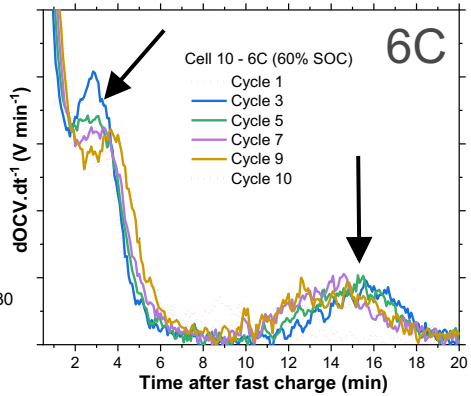
dQ/dV and dOCV sensitive to cycling conditions

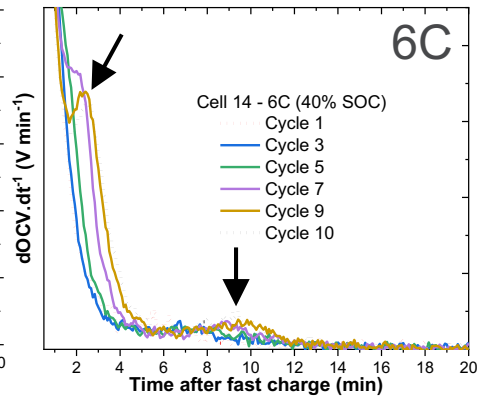
dQ/dV:
- reliable at low C-rates
- disappears at moderate/high rates

dOCV/dt:
- reliable at low & moderate C-rates
- signal highly variable at high C-rates and disappears after a few cycles



increasing C-rate

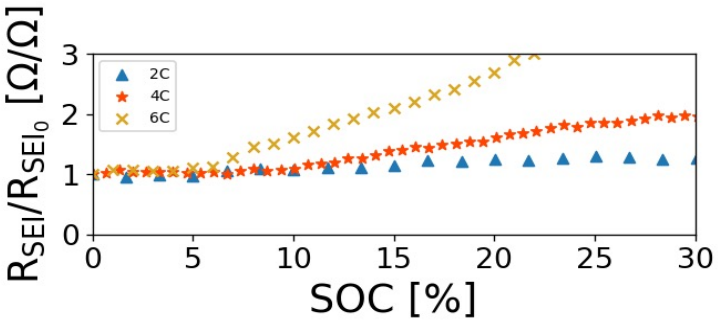


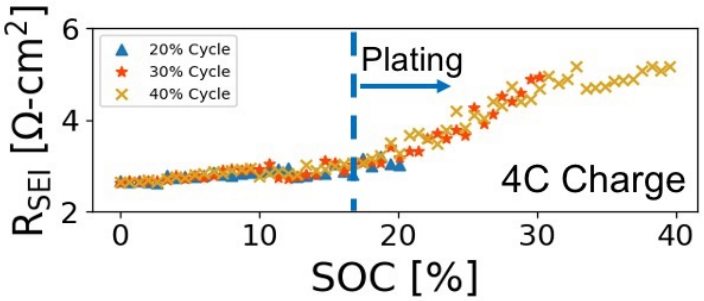


For confident detection, need multi-modal EC approach that includes modeling

Galvanostatic impedance

Measure impedance *during* fast charging

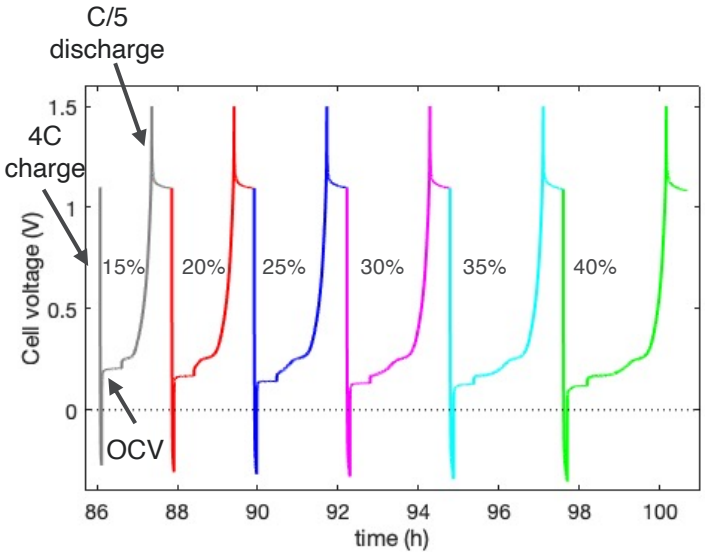




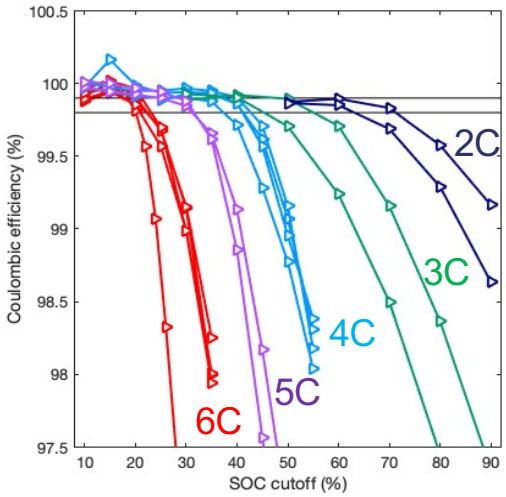
- Fast impendance scans (~6 s/scan) at up to 6C
- Increase in graphite solid electrolyte interphase resistance (R_{SEI}) indicates plating
- Cross-validation with MST suggests detection sensitivity: <0.5% of graphite
- Ongoing work:
  - Implement in 2 electrode full cells
  - Detection of plating in aged cells
  - Detection during CCCV (currently only CC)

SOC sweep protocol to detect onset with CE's

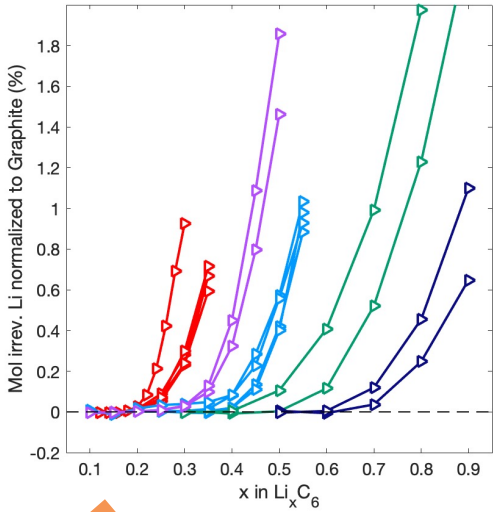
Graphite/Li coincell to determine Li plating onset during CC charging



Repeat for different C-rates



Normalized irrev. Li plating



Convert CE% to normalized irreversible Li plating

<u>Protocol overview</u>

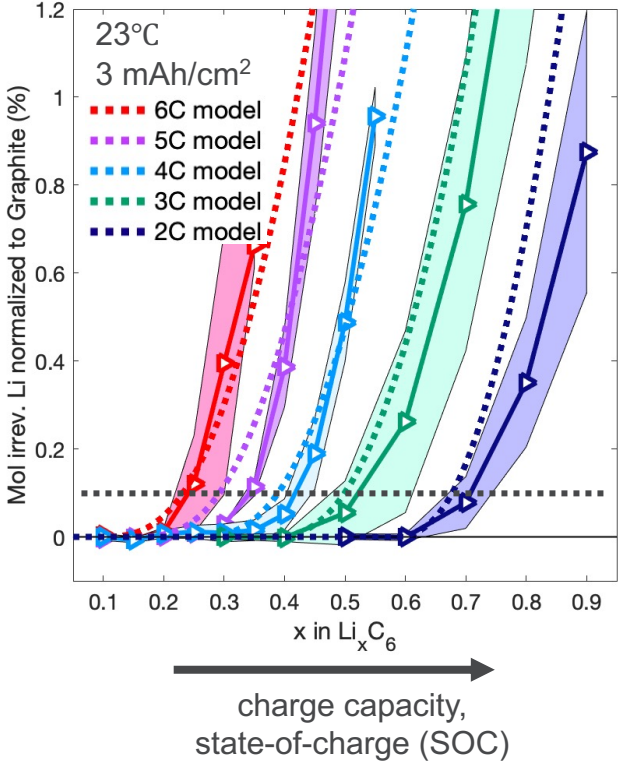
Three C/10 formation

Fast charge cycling at 5-10% increments

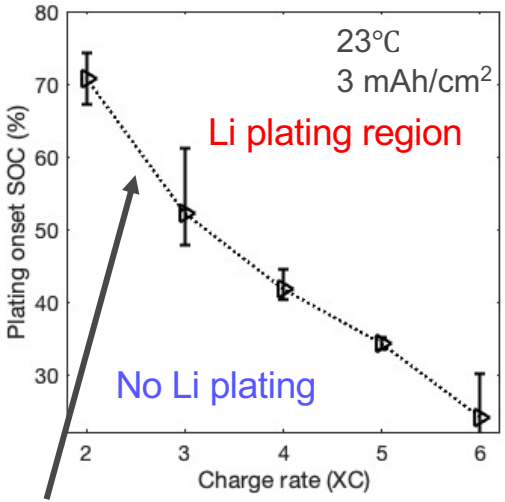
All C/5 deintercalation, OCV between steps

Li plating onset with CE experiments & modeling

Estimate irreversible Li plating from coulombic inefficiencies

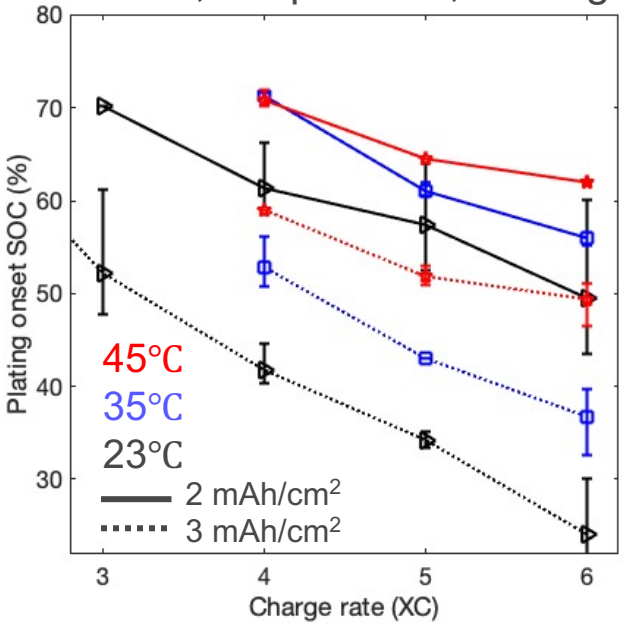


Mapping Li plating onset



Define 0.1 mol% as the onset

Onset as a function of: C-rate, temperature, loading

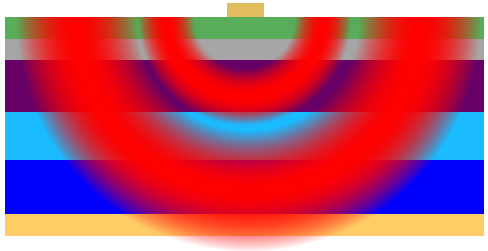


Model development will be invaluable for full-cell plating predictions

Map Li Concentration Gradient in Anode

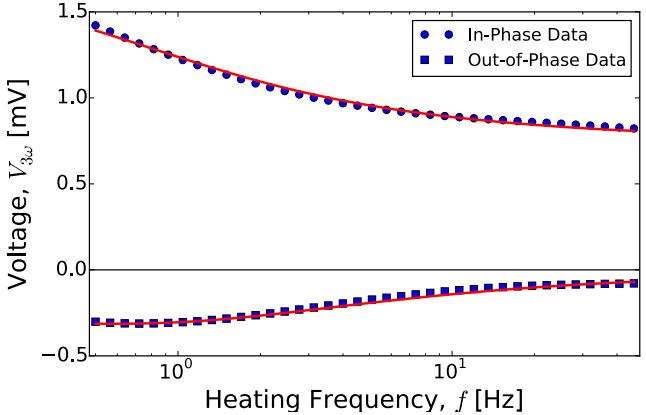
Stronger gradient precursor to Li plating

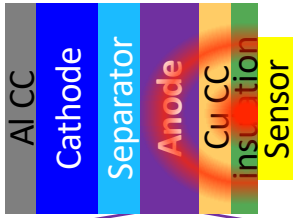
thermal wave sensor:

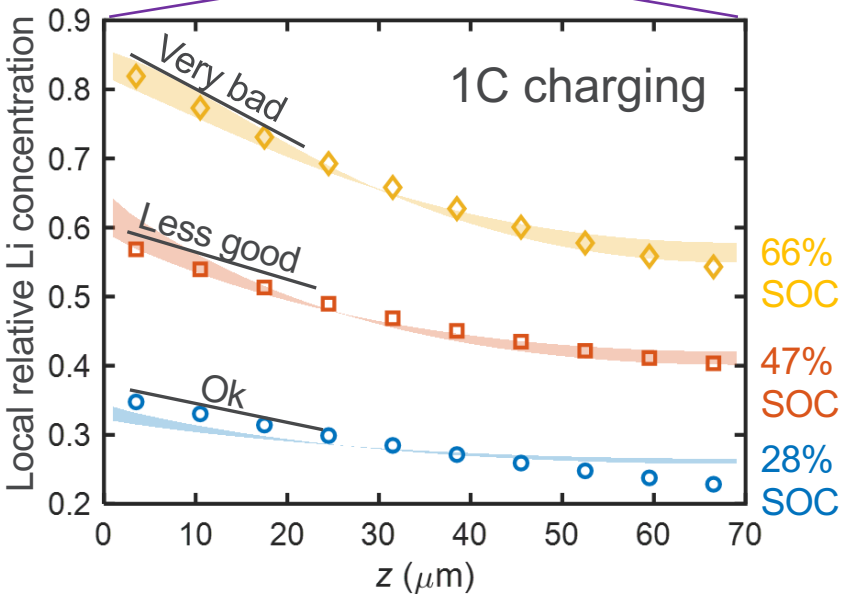


cross section view

Typically
0.01 Hz – 100 Hz





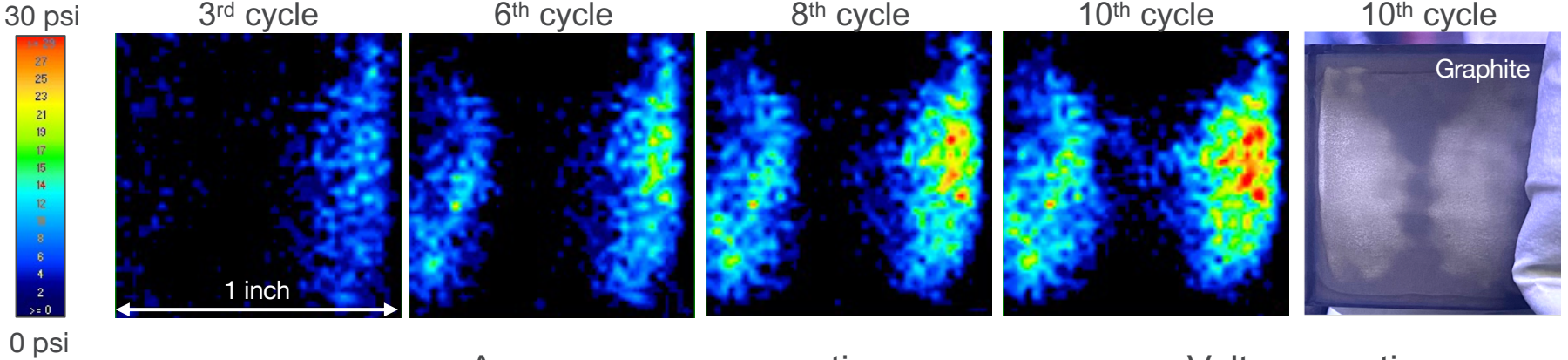


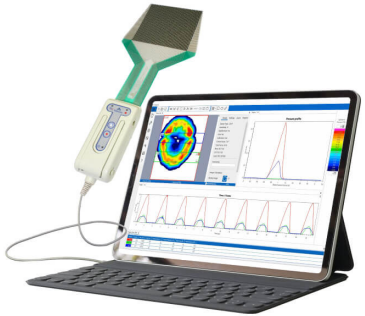
Points = sensor measurements

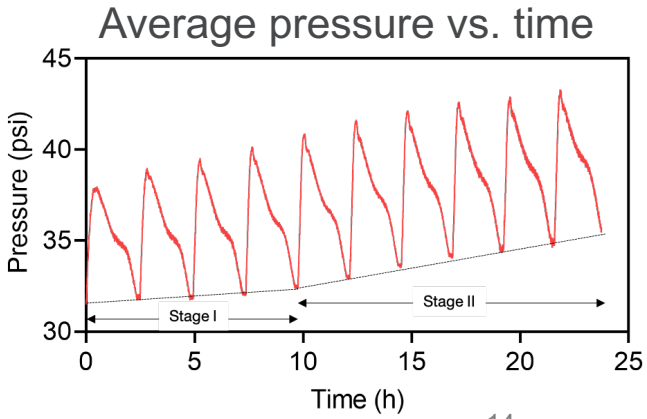
Shading = agnostic predictions from electrochemical simulations

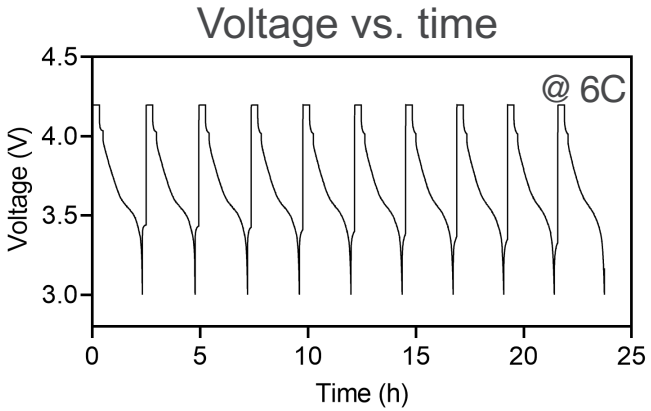
Pressure evolution with cycling

Pressure changes at discharged state correlate with dead Li









XCEL eXtreme Fast Charge Cell Evaluation of Lithium-ion Batteries

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Does Li plating create irreversible damage?

Preliminary electrochemical results for two cases studied

- Case 1: plate small amount of Li then cycle cell under “safe” (no plating) conditions
  - No additional Li is plated while cycling
  - No effect on long term capacity

- Case 2: repeatedly expose cell to plating conditions
  - Each cycle results in more irreversible plating per exposure

➢ **Preliminary conclusion**: small amounts of Li plating may not necessarily trigger cell failure

System: Coin-cells (no spring)
LFP vs. Round 1 graphite (N/P <<1)

Responses to previous year reviewers' comments

Not reviewed last year

COLLABORATION ACROSS LABS AND UNIVERSITIES

Argonne NATIONAL LABORATORY — Cell and electrode design and building, performance characterization, post-test, cell and atomistic modeling, cost modeling

INL Idaho National Laboratory — Performance characterization, failure analysis, electrolyte modeling and characterization, Li detection, charging protocols

BERKELEY LAB — Li detection, electrode architecture, diagnostics

NREL NATIONAL RENEWABLE ENERGY LABORATORY — Thermal characterization, life modeling, micro and macro scale modeling, electrolyte modeling and characterization

OAK RIDGE National Laboratory — Detailed Li plating kinetic models, SEI modeling

SLAC NATIONAL ACCELERATOR LABORATORY — Li detection, novel separators, diagnostics

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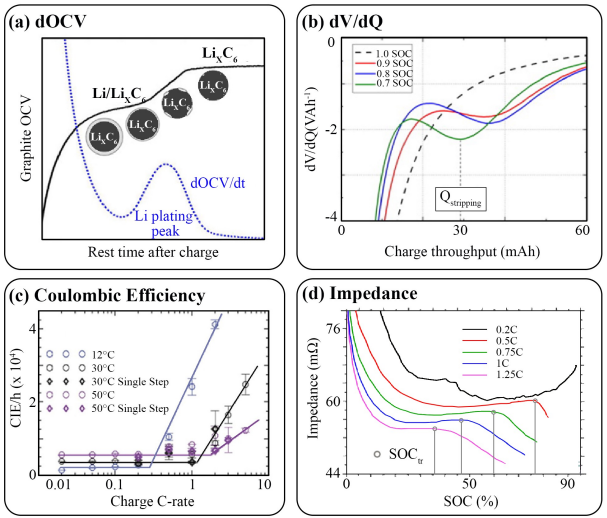
Remaining Challenges and Barriers

- Does the nature of lost Li inventory (metal, SEI, etc.) correlate to capacity fade or cycling conditions?
- How can we use models in combination with electrochemistry techniques as a reliable, readily-accessible, multimodal Li detection technique?
  - Should work with both new and aged cells
  - Should work under realistic charging conditions
- Can we find a reliable predictor of Li plating?
- How does Li plating (and stripping efficiency) evolve with battery age



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

Next steps

- Connect differences in SEI components and Li plating to capacity fade and cycle rate (XRD/MST analyses)
- Compare relative differences in SEI components with cycling temperature (30˚C vs. 45˚C) with XPS depth profiling
- Study reversibility of Li plating and Li_xC with XPS depth profiling and *in situ* XRD mapping
- Leverage models to extend the limitations of echem detection methods
- Quantify how much Li plating is acceptable before irreversible damage
- Compare Li plating conditions of “hero” cell compared to round 2 cells

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

Summary

- Identify and contrast approaches to accurately detect and quantify Li plating during extreme fast charge conditions resulting in a review paper
- Holistic approach to determine where the lost Li inventory is trapped
- Shown standard electrochemical techniques don't work in all cycling conditions
  - Need to combine techniques and support with robust modeling
- Small amounts of reversible Li plating does not contribute to long term capacity fade

CONTRIBUTORS AND ACKNOWLEDGEMENTS

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Charles Dickerson
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Matt Keyser
Michael Evans
Michael Toney
Molleigh Preefer
Nancy Dietz Rago
Ning Gao
Nitash Balsara
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Ryan Brow
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Sangwook Kim
Sean Lubner
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Shabbir Ahmed
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Susan Lopykinski
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Zhenzhen Yang

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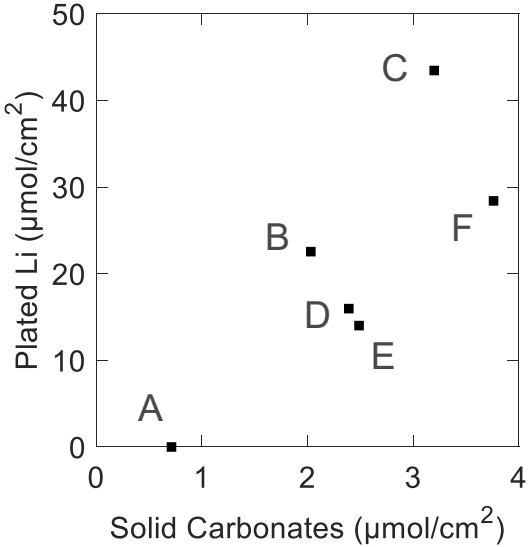
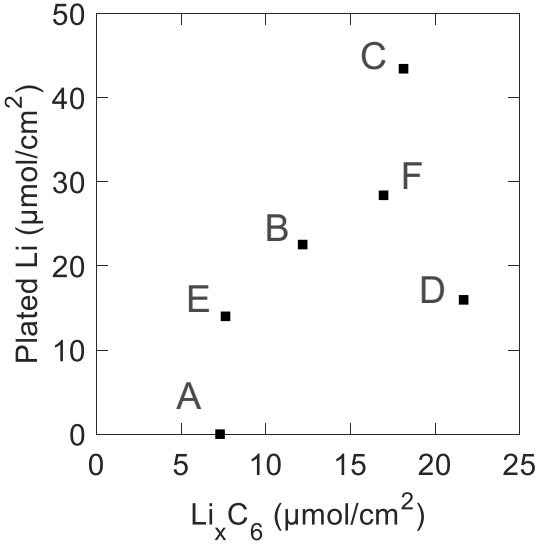
TECHNICAL BACKUP SLIDES

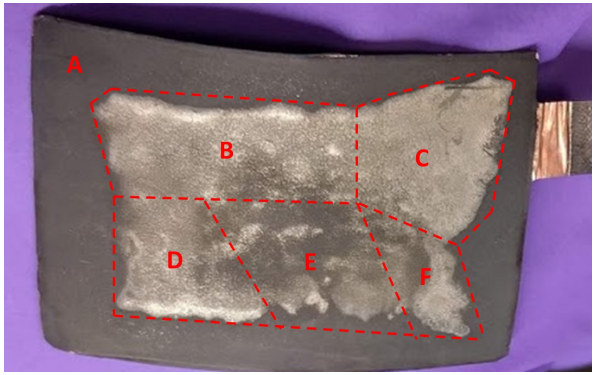
Local Analysis: XRD & MST



Thicker solid carbonate layer in areas with plating

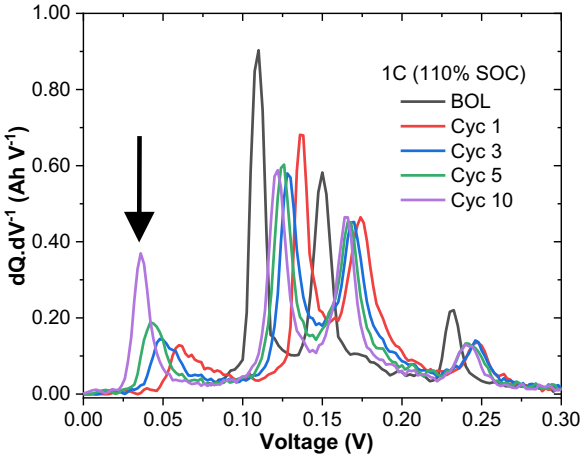


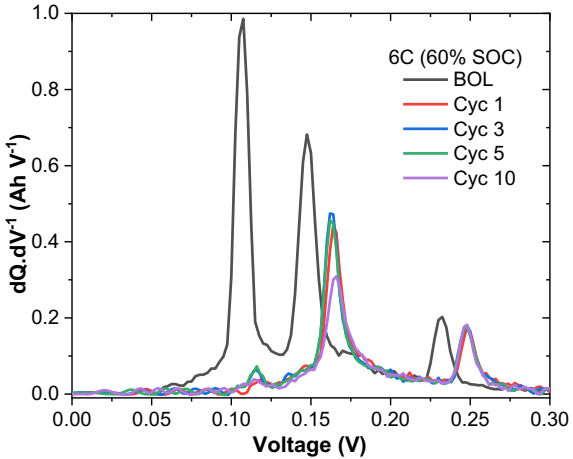
Li_xC_6 colocalized with plating

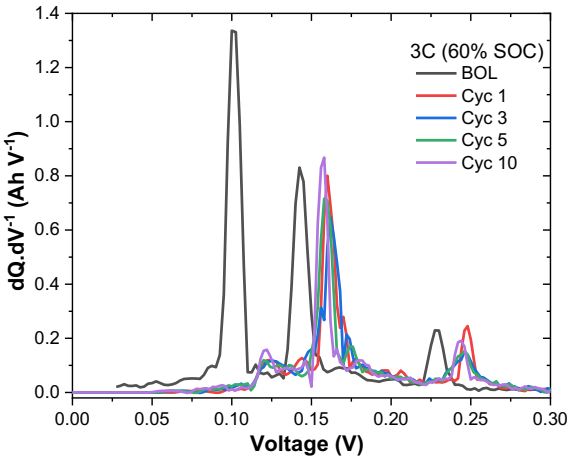


Ongoing work: Perform similar analyses on 3 additional electrodes with varying amounts of plating

LITHIUM PLATING DETECTION

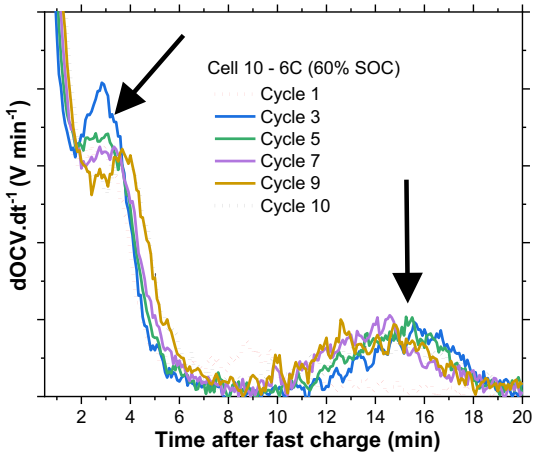


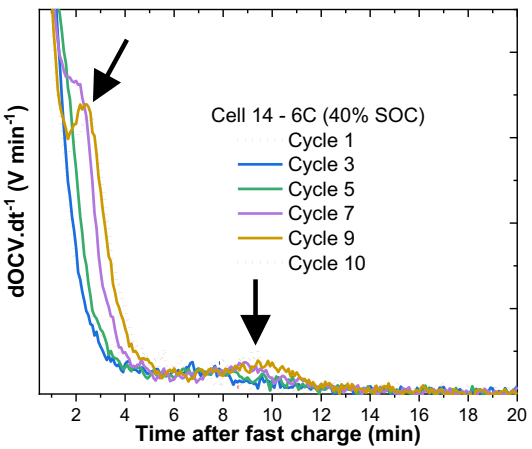


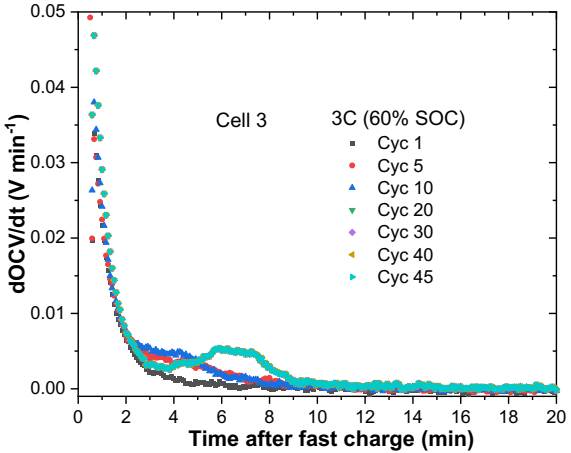


- Li plating detection with dQ/dV technique sensitive to cycling conditions
- Reliable at low C-rate conditions but disappears at moderate and high C-rate conditions even with Li plating

LITHIUM PLATING DETECTION



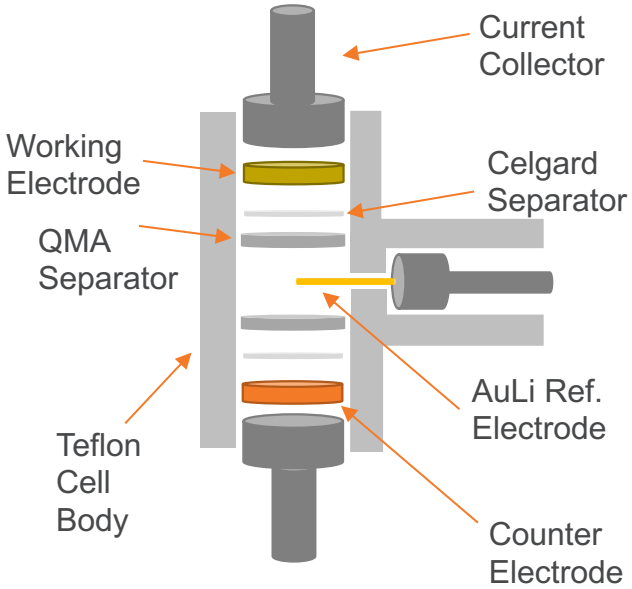




- Li plating detection with dOCV/dt technique sensitive to cycling conditions
- Reliable at low and moderate C-rate conditions
- High C-rate conditions makes signal highly variable and vanishes after few cycles
- Multi-modal EC techniques helps to improve Li plating identification and improves confidence in EC detection sensitivity and reliability

Galvanostatic impedance

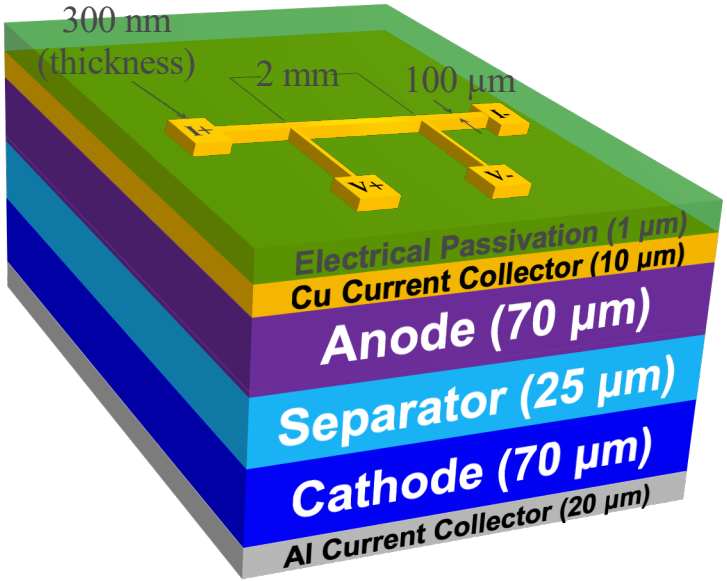
Modified Swagelok-type cell

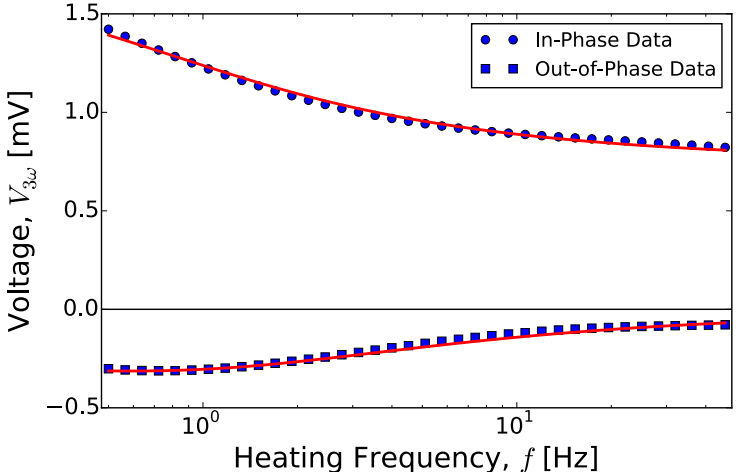


- Current work is in 3-electrodes cells
- We have also demonstrated that technique works, in principle, for 2-electrode full cells
- Implementing with CCCV cycling in future

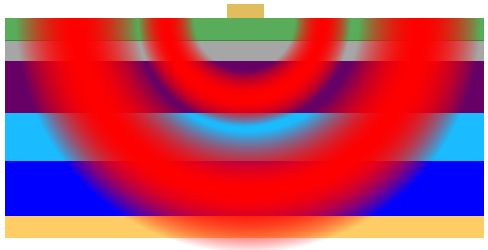
Thermal Wave Sensors

Thermal wave frequency controls measurement





Cross Section View



Typically
0.01 Hz – 100 Hz