Characterization and Modeling of Li-Metal Batteries: In situ and Operando Thermal Diagnostics of Interfaces

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Lawrence Berkeley National Lab (LBNL)

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Project ID: bat427

Overview

Timeline

- Project start: 10/01/2019
- Project end: 09/30/2022
- 25% complete

Budget

- Total project funding: $900k
- Funding for FY 2020: $300k

Barriers and Technical Targets

- Barriers addressed
  - Safety (diagnosis of dendrite growth and interface morphology change)
  - Performance & life (understanding transport and kinetic overpotential at the interfaces)

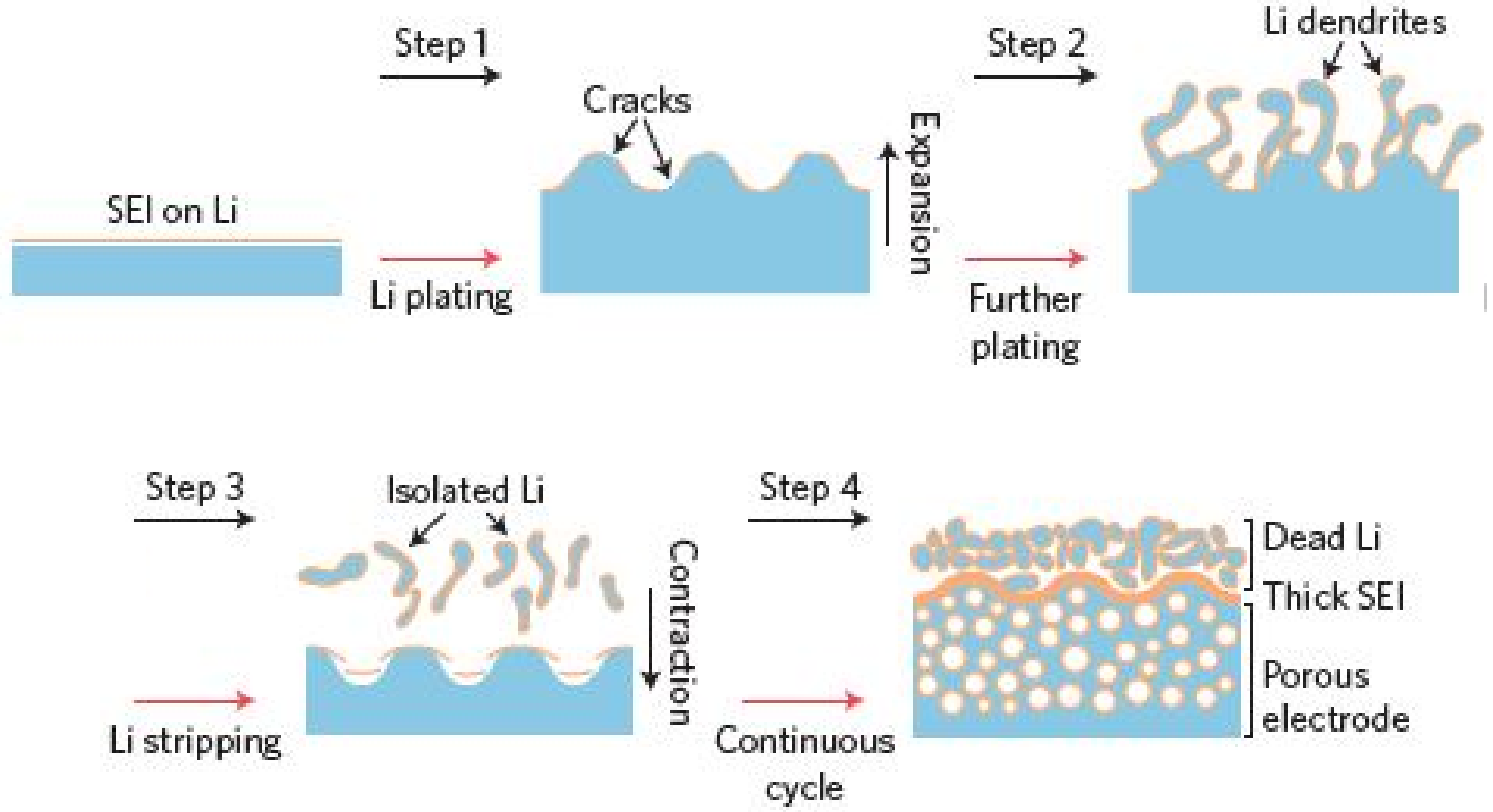
Relevance: Interface Problems in Batteries

Diagnostics of interface processes through thermal signatures will improve…

1) Safety: Operando detection of dendrite and interface morphology change

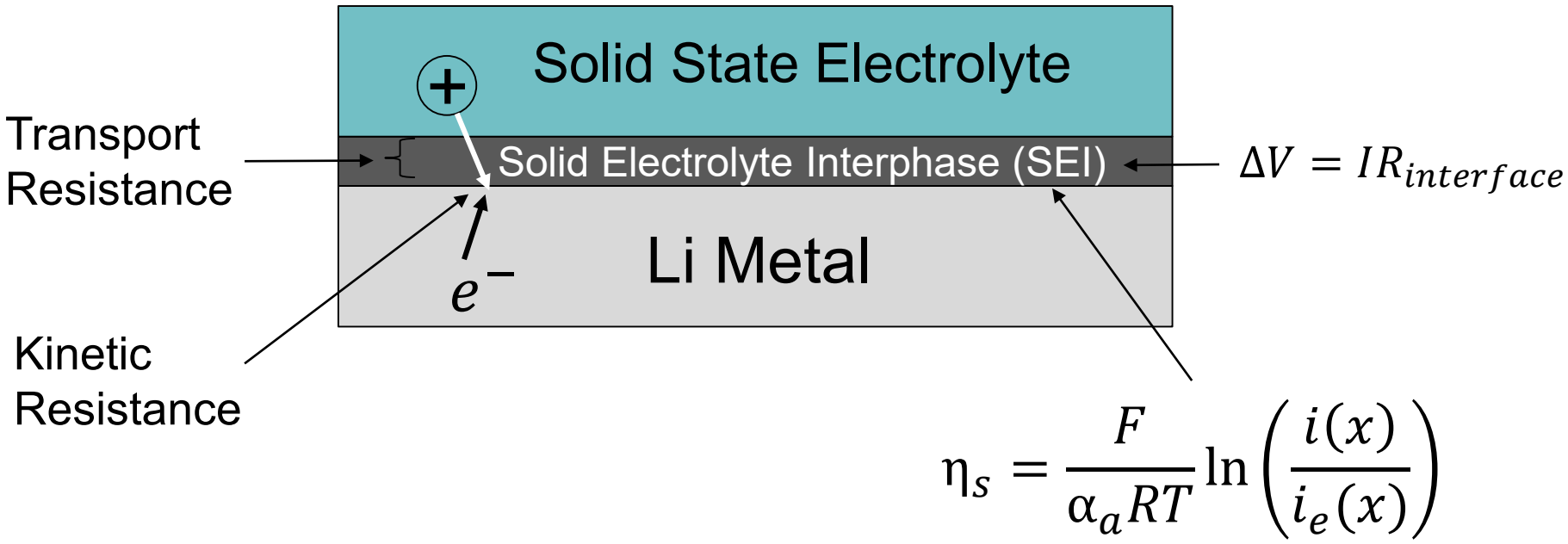
2) Performance: Understanding factors contributing to interface related transport and kinetic overpotential

Relevance: Dendrite formation and Morphology Change



D. Lin *et al.*, “Reviving the lithium metal anode for high-energy batteries,” *Nature Nanotechnology*, vol. **12**, pp. 194-206, 2017.

Relevance: Interface Transport and Kinetics



Milestones

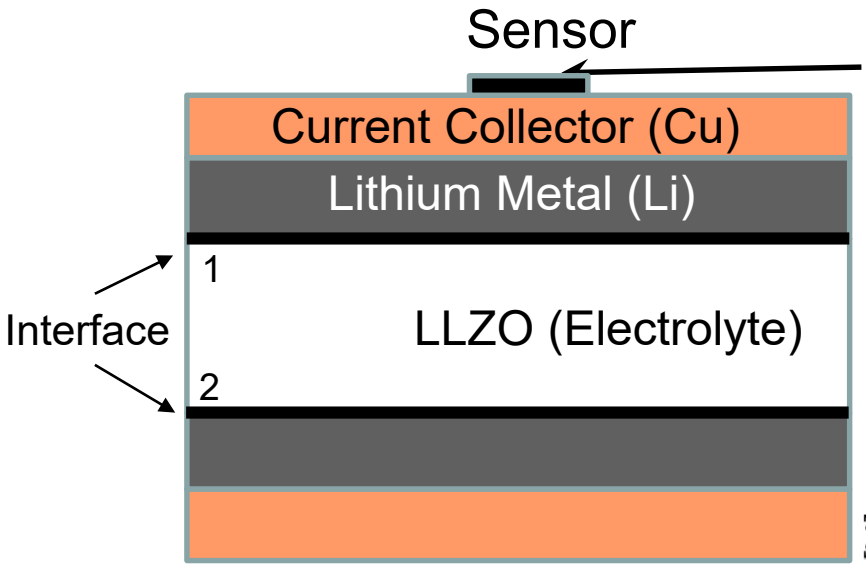
Quarter	Milestones & Go/No-Go	Status
Q3, FY20	Successful fabrication of functional 3-omega sensors	Complete
Q4, FY20	Measurement of thermal properties of individual components	Complete
Q1, FY21	Measurement of thermal contact resistance of buried interfaces	On Track
Q2, FY21	Measurement of thermal contact resistance post -cycling	On Track

Approach

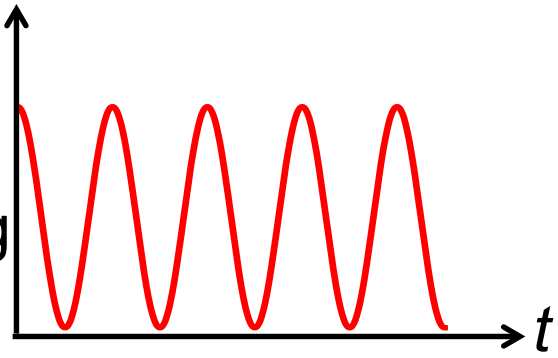
- Develop metrology that can measure thermal transport properties within a Solid State battery

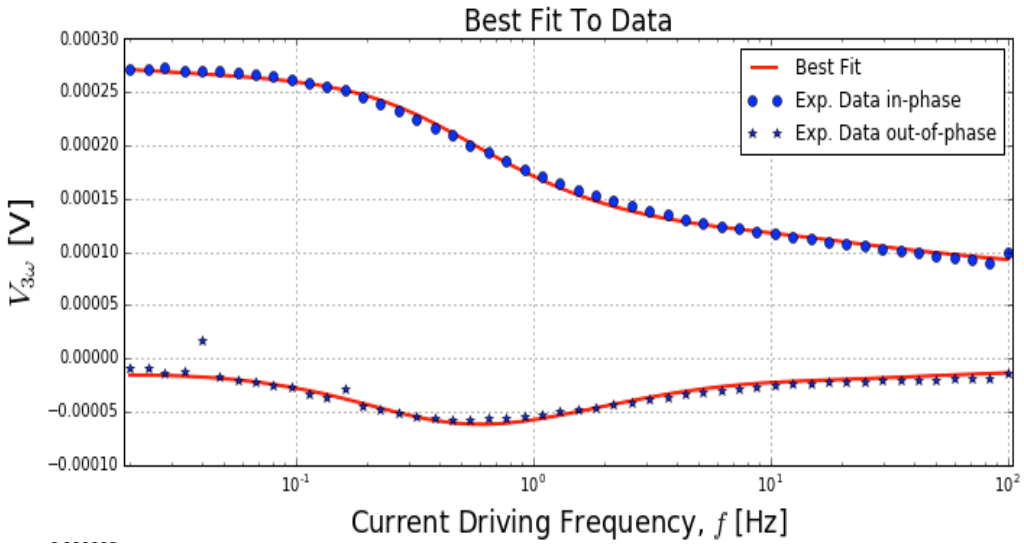
- Apply metrology to understand interface degradation, dendrite growth and interface electrochemistry

Approach: 3ω *Operando* Measurements



Periodic Joule Heating





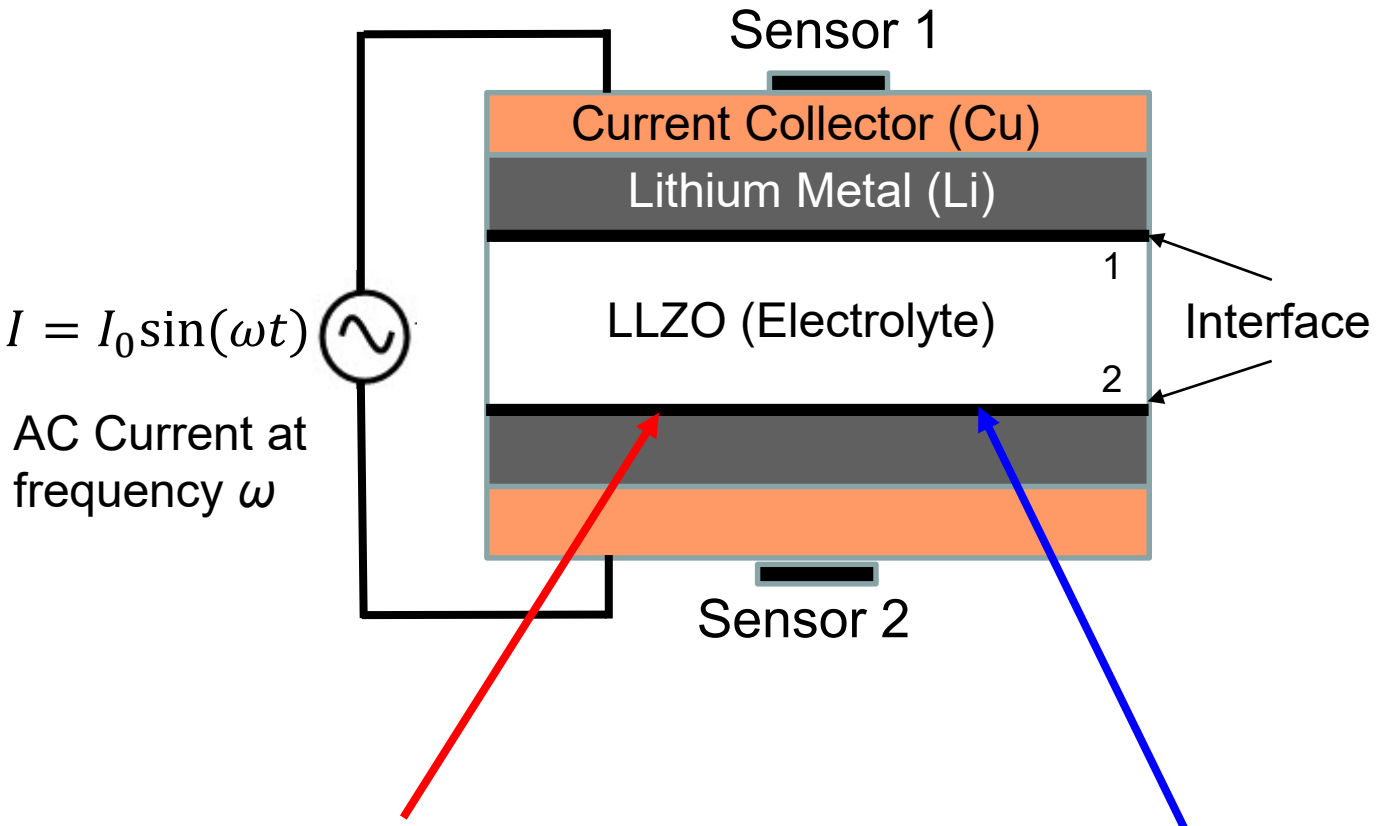
The "3ω Method"

Sensitive to **bottom** layers/interfaces

Sensitive to **middle** layers/interfaces

Sensitive to **top** layers/interfaces

Approach: Interface Resistance 4ω Method



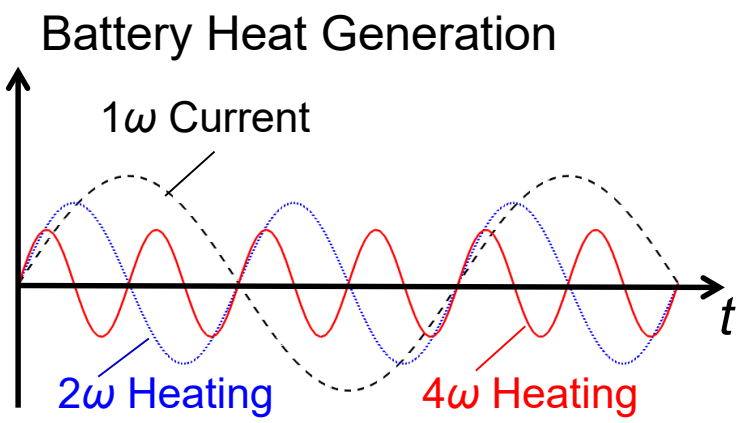
$$Q_{rxn} = A_s \frac{F}{\alpha_a RT} |i(x)| \ln\left(\frac{|i(x)|}{i_e(x)}\right)$$

2ω and 4ω Heat

$$Q_{transport} = I^2 R_{interface}$$

2ω Heat

Approach: Interface Resistance 4ω Method



Use different frequency components (ω) of heat signatures (Q) to isolate and measure electrochemical properties

- 2ω heat signature depends on interfacial resistance ($R_{interface}$ – transport properties)
- 4ω heat signature depends on exchange current density (i_e – kinetics properties)

Transport Heat

$$Q_{transport} = I^2 R_{interface}$$

$$\boldsymbol{Q_{transport,2\omega}} = \frac{-I^2}{2} R_{interface}$$

Measured by experiment

Properties we want to know

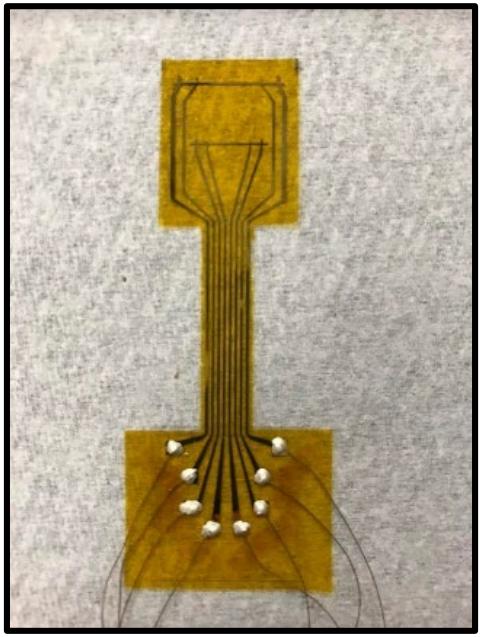
Reaction Heat

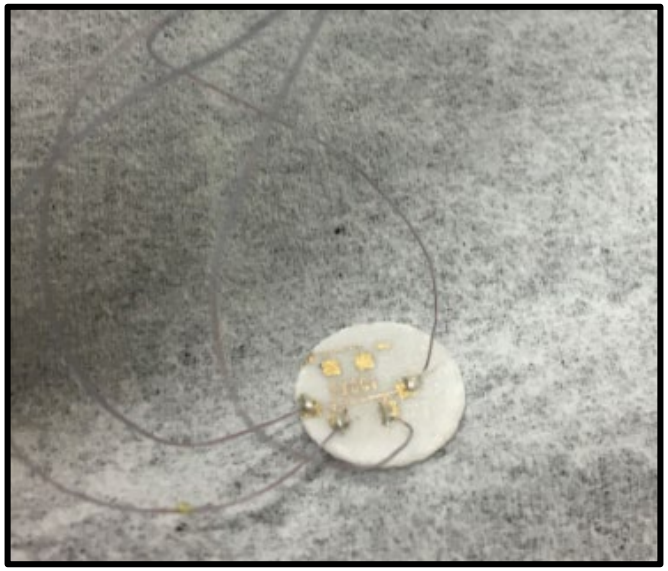
$$Q_{rxn} = A_s \frac{F}{\alpha_a RT} |i(x)| \ln\left(\frac{|i(x)|}{i_e(x)}\right)$$

$$\boldsymbol{Q_{rxn,4\omega}} = A_s \left((0.126 - 0.085\ln(a))\, A i_0 - 0.032 A \frac{i_0^3}{(a i_e)^2} \right)$$

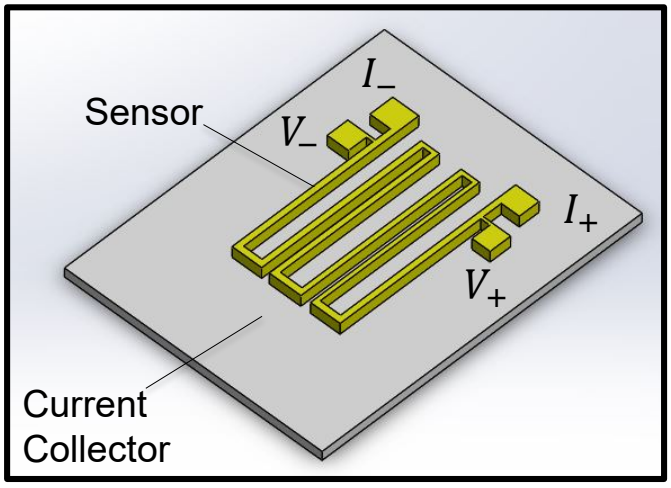
Approach: *Operando* Measurements

Anode Side Sensor





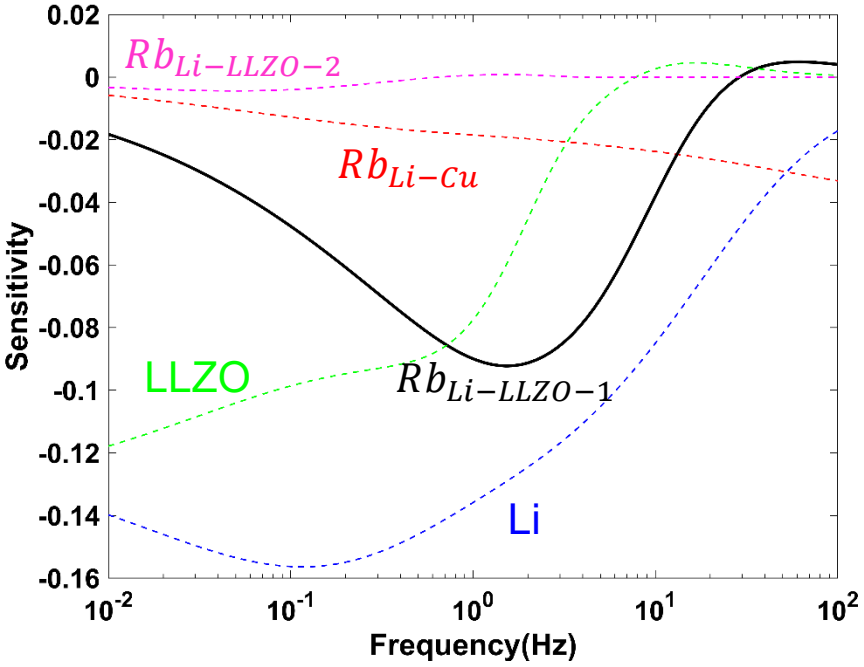
3ω on LLZO

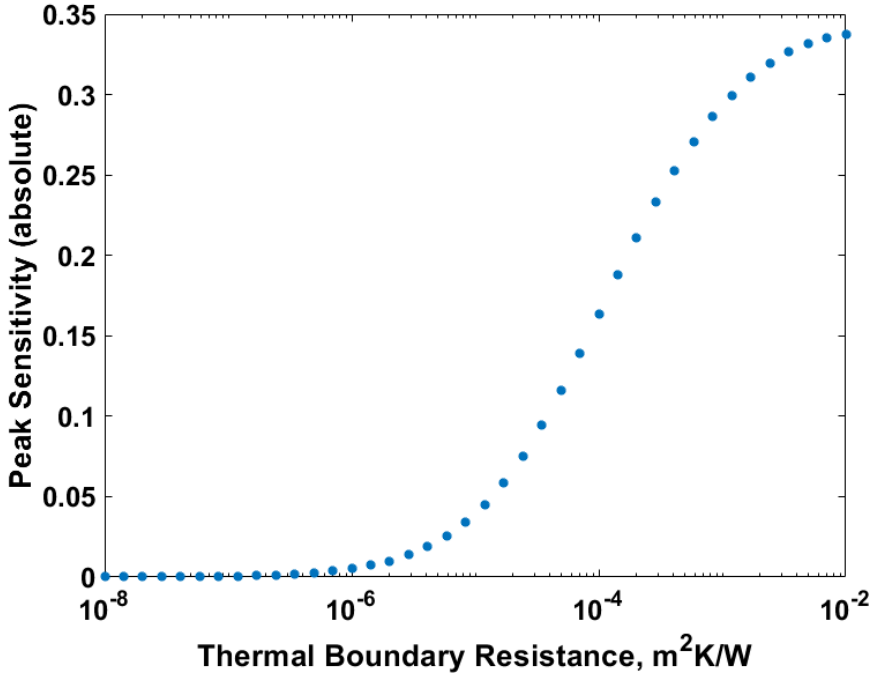


Resistance Sensor for 4ω

Technical Accomplishments and Progress

3ω Sensitivity Analysis

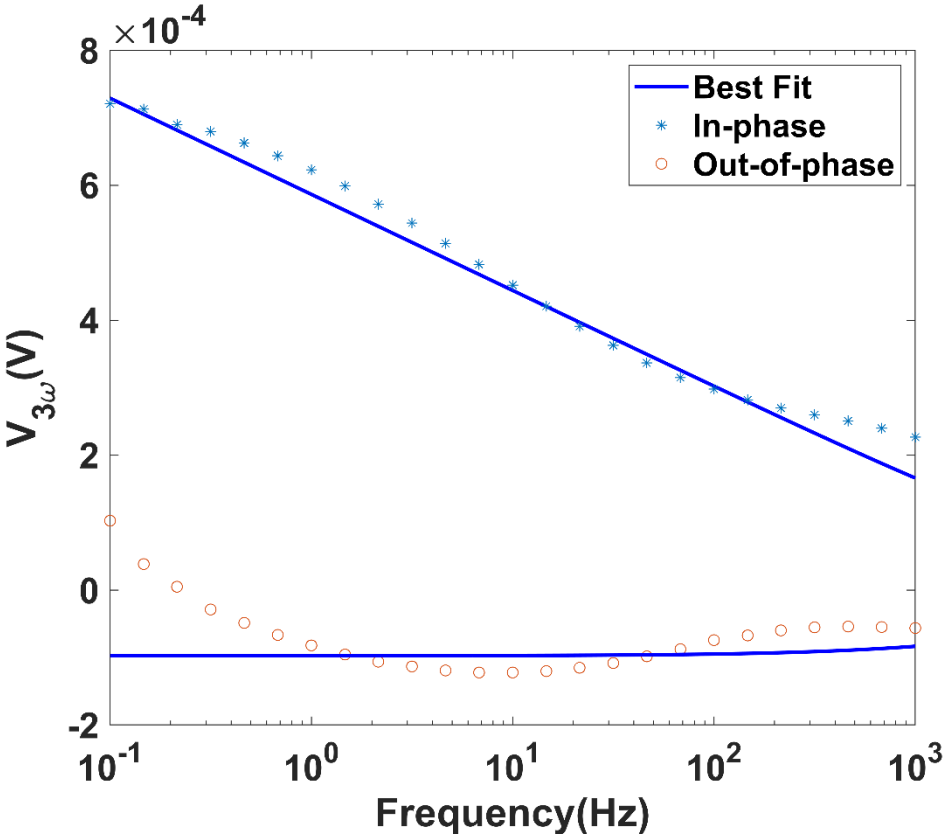


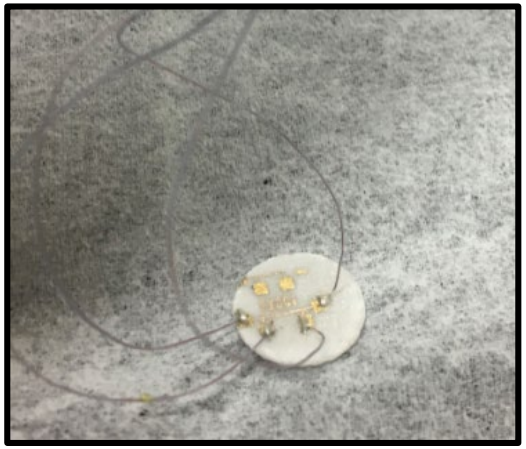


Thermal signal is the most sensitive to the interface between 1 Hz – 20 Hz. The peak absolute sensitivity increases as the value of the thermal interface resistance increases (interface degrades)

Technical Accomplishments and Progress

LLZO Thermal Properties

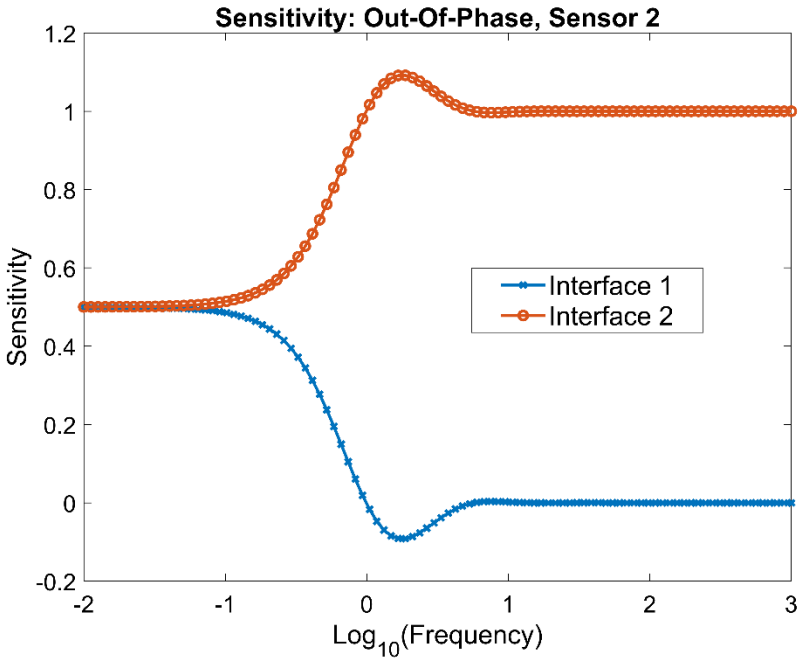




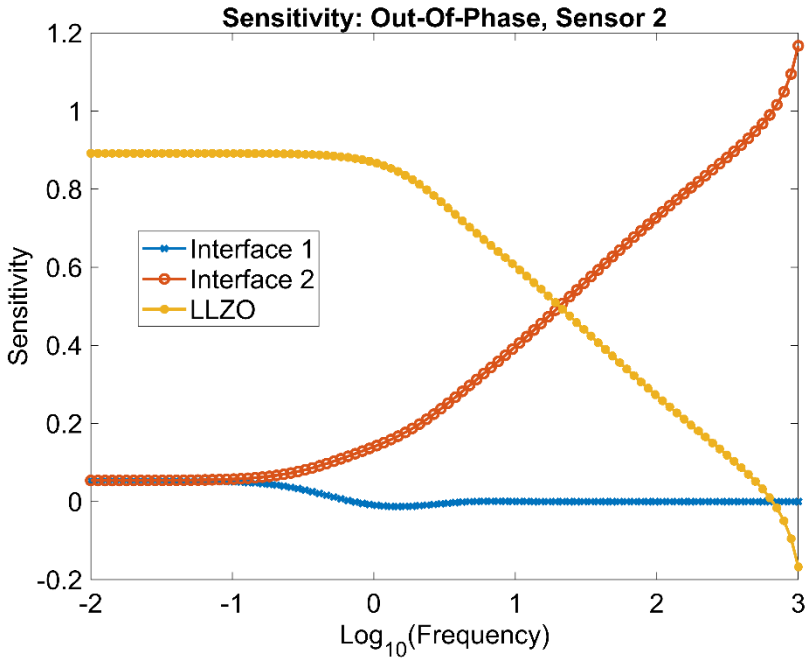
$$k_{LLZO} = 1.33\ W/mK, c_{p,\ LLZO} = 400\ J/kgK$$

Technical Accomplishments and Progress

4ω method Sensitivity Analysis



4ω Sensitivity



2ω Sensitivity

Both 4ω and 2ω signals are the most sensitive above 1Hz

Collaboration and Coordination

- The project does not have other collaborators

Remaining Challenges and Barriers

- Perform operando 3ω measurements on lithium symmetric solid state cells before and after cycling
- Modify the 3ω setup for 4ω measurements to extract the electrochemical information

Proposed Future Research

We are on track to meet the next two milestones, corresponding to the listed remaining challenges:

- Measurement of thermal contact resistance of buried interfaces
- Measurement of thermal contact resistance post -cycling

Additionally, we expect to be able to modify the 3ω metrology to be able to carry out the 4ω to accomplish:

- In-situ measurement of interfacial thermal properties
- Correlate electrochemical changes with 3-omega measurements

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

Summary

- Interface Phenomena such as dendrite growth, morphology change, charge transport resistance and kinetic overpotential can be probed using frequency dependent thermal metrology.

- Using the 3ω method, we plan to study dendrite growth and interface morphology and modify the 3ω method to 4ω method for studying interface transport and kinetics.

- We have measured the thermal properties of the solid state electrolyte and have completed the sensitivity analysis for both 3ω and 4ω methods.