Multidimensional Diagnostics of the Interface Evolutions in Solid-State Lithium Batteries

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Jun Lou, Hua Guo, Rice University

2021 DOE Vehicle Technologies Office Annual Merit Review
June 24, 2021

Project ID: bat489

Overview

Timeline

- Project start date: 10/1/2019
- Project end date: 3/31/2023
- Percent complete: 45%

Barriers

- Barriers addressed
  - Lack of tools to connect multiple techniques for characterization of battery components
  - Lack of joint techniques with desirable length scale, high-resolution and sensitivity for solid-state batteries

Budget

- Total project funding
  - $1.0 M from DOE
  - $250,000 cost share
- DOE Funding for
  - FY2020: $333,334
  - FY2021: $333,333

Partners

- PNNL, SLAC, NREL
- Rice, Brown
- Solid Power, Themo Fisher, Ampcera

Relevance

➢ **Objective**

- Develop an air-free vessel with an *in-situ* cell test platform connecting FIB-SEM tomography, ToF-SIMS, and in-SEM nanoindentation-based stiffness mapping for structural, chemical, and mechanical characterizations of solid-state Li batteries.
- Assess the influence of cell design and testing conditions (stacking pressure, current density, temperature *etc.*) on interface evolutions.

➢ **Impact**

- The consolidated diagnostic platform established in this work will provide insights to the failure mechanisms of solid-state Li batteries.

Milestones for FY20 and FY21

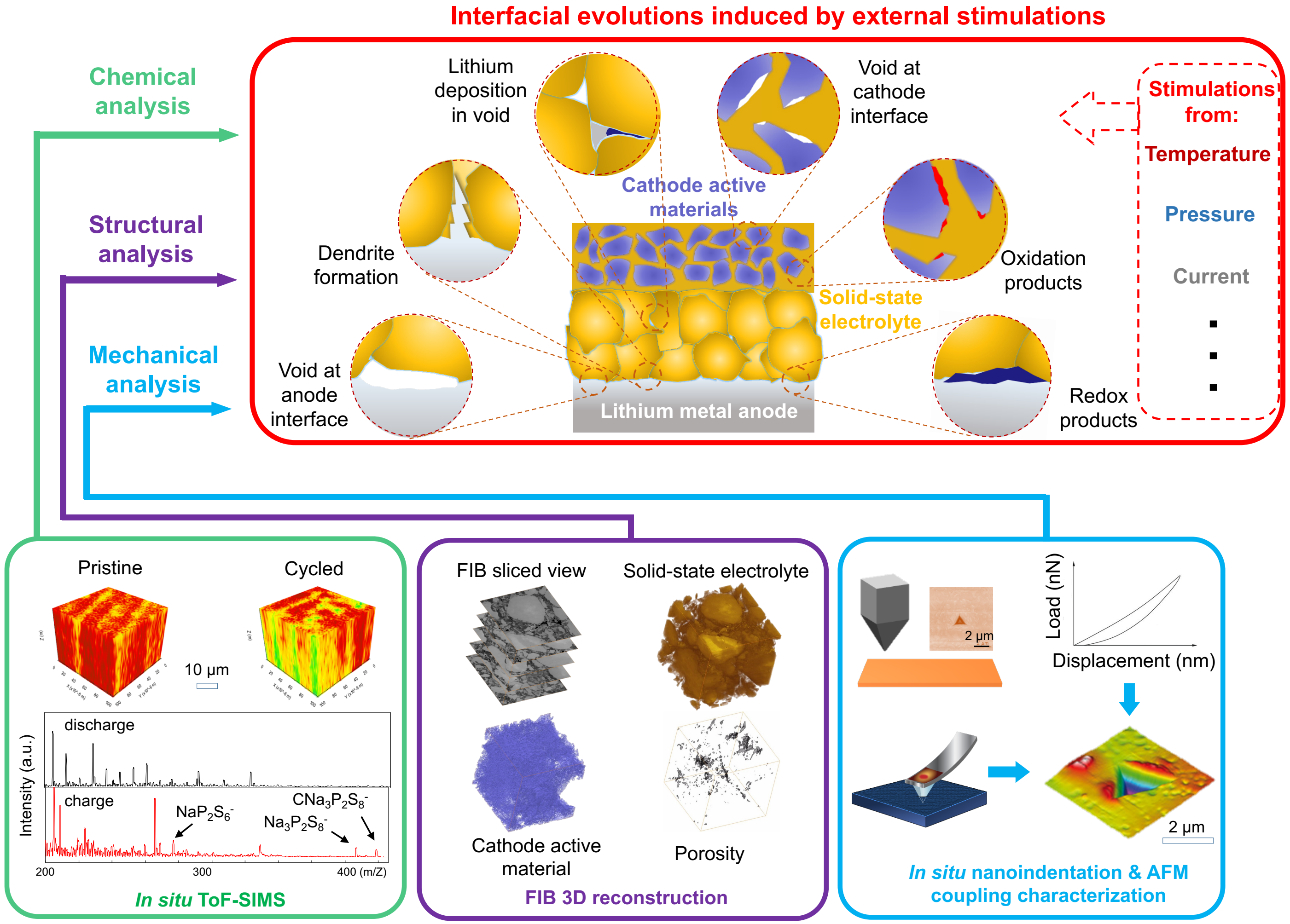
Tasks	Subtasks	Year 1				Year 2				Year 3			
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1	Development of electrochemical cells at multiple scales												
	1.1 Thin cell stacks development			1.1									
	1.2 Micro-cells development				1.2								
	1.3 Nano-cells development					1.3							
	1.4 Cell optimization and electrochemical benchmarking					1.4							
Task 2	Multiscale structural investigations of solid-state cells												
	2.1 Identification and quantification of interface structural features								2.1				
	2.2 Real-time monitoring of structural evolutions											2.2	
Task 3	Chemical analyses of electrolyte decomposition products at the interface												
	3.1 Composition and spatial distribution study									3.1			
	3.2 Real-time monitoring of the chemical products evolutions											3.2	
Task 4	Mechanical properties probing of solid-state cells												
	4.1 Selected region mechanical property probing										4.1		
	4.2 Real-time mapping of the mechanical property evolutions												4.2

Milestones for FY20 and FY21

Month/Year	Milestones and Go/No-Go Decisions	Status
Mar. 2020	**Solid-state thin-cell development** − Demonstrated uniform tape-cast 50 μm-thin solid electrolyte layers. Electrochemical performance of thin cells was comparable to the performance of bulk cells.	*Completed*
Jun. 2020	**Microcell development** − Microcell electrochemical performance was shown akin to thin cells, with in-situ optical and SEM measurements.	*Completed*
Feb. 2021*	**Nanocell development** − Demonstrated nanocell fabrication and preliminary in-situ characterization.	*Completed*
Mar. 2021	**Cell optimization and electrochemical benchmarking (GO/No-GO**) − Optimized cathode and anode chemistry for better performance. Optimized processing for reproducibility and cycling stability.	*Completed*
Jun. 2021	**Multiscale structural investigations** − Identify and quantify interface structural features	*On track*
Sept. 2021	**Composition and spatial distribution study** − Identify the interfacial reaction species and the spatial distribution of these species.	*On track*

* No-cost extension was requested and approved due to clean room facility shut-down during COVID.

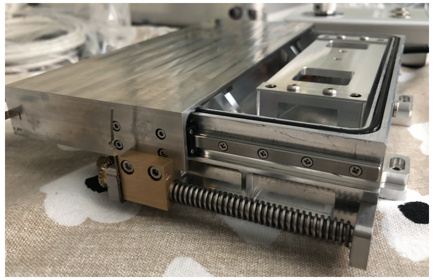
Approach



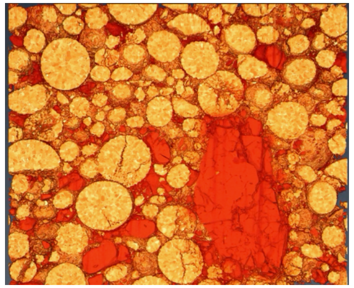
- Establish an air-free vessel with an *in-situ* cell test platform **connecting** FIB-SEM tomography, ToF-SIMS, and in-SEM nanoindentation-based stiffness mapping to
- Assess the influence of cell design and testing conditions on interface evolutions
- Better understanding the failure mechanisms of solid-state Li batteries.

Approach

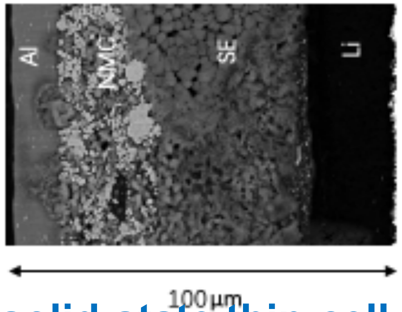
- Developed an air-free vessel to protect air-sensitive ASSBs and *in-situ* cell test platform for multimodal characterizations.
- Fabricated solid-state thin-cells (less than 100 µm) and nano-cells with electrochemical performance on par with their bulk-type counterparts.
- Realized electrochemical tests with precise temperature control, external pressure, and pressure monitoring of thin solid-state cells.
- Performed *ex-situ* structural, chemical, and mechanical characterizations of air-sensitive cells, either in vacuum or in inert atmosphere.



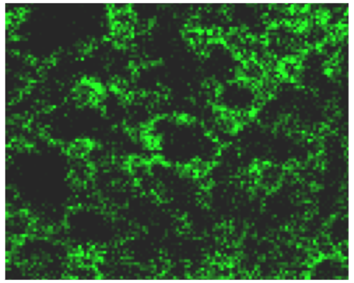
air-free vessel



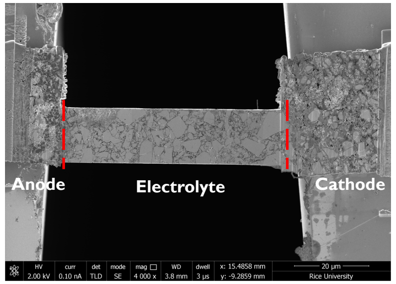
structural



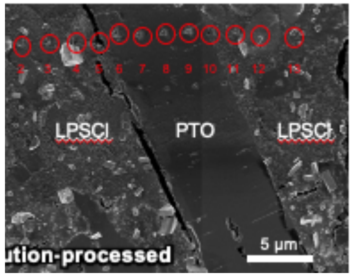
solid-state thin-cell



chemical

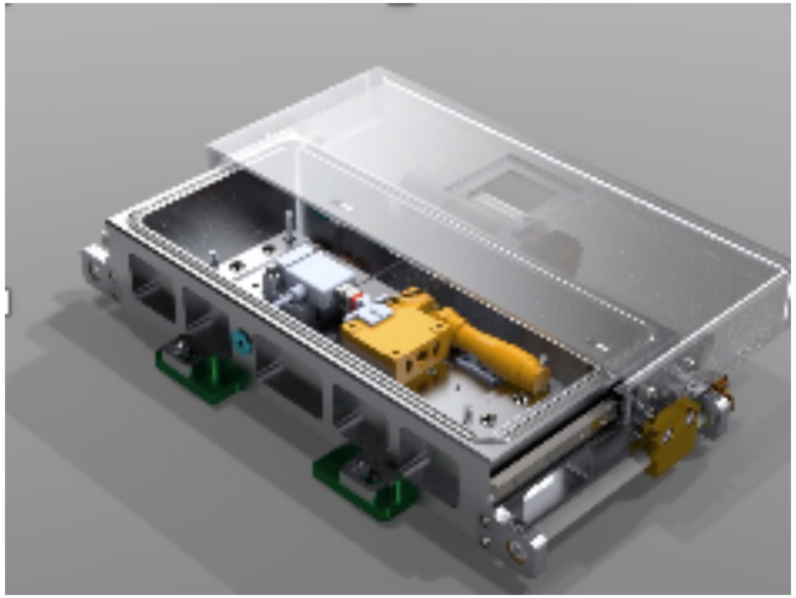


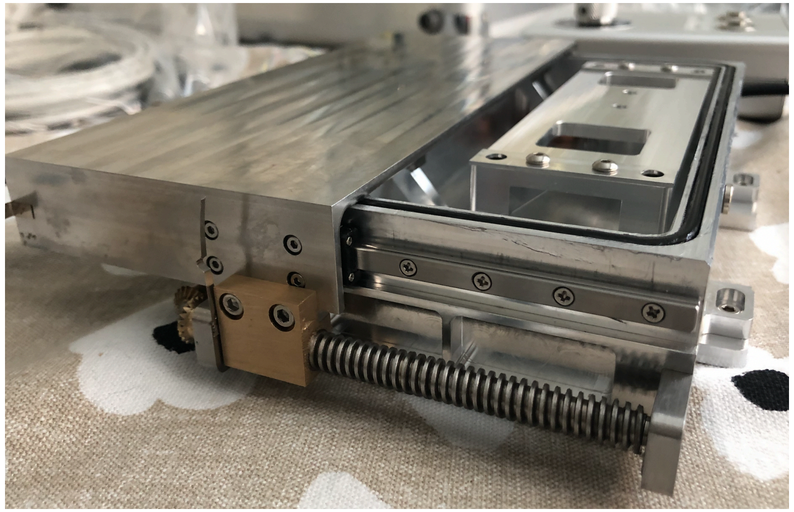
solid-state nano-cell



mechanical

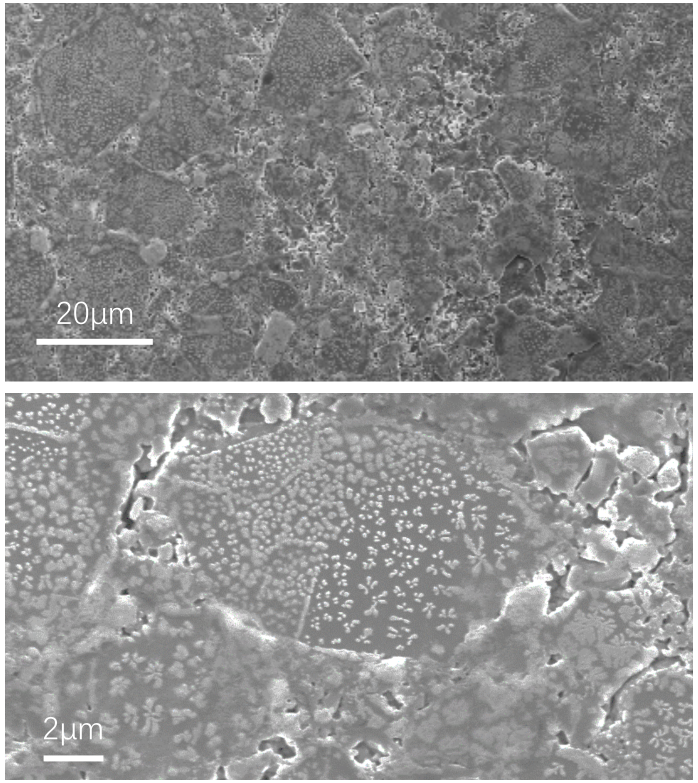
Accomplishments – Development of Air-free Transfer Vessel



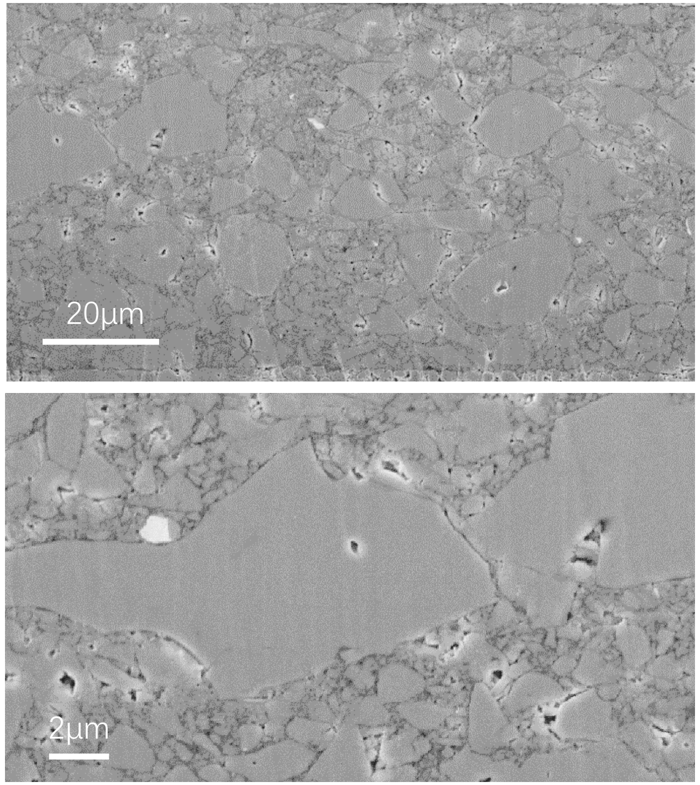


US patent application: 63042741

Li_6PS_5Cl exposure in air for 2 s



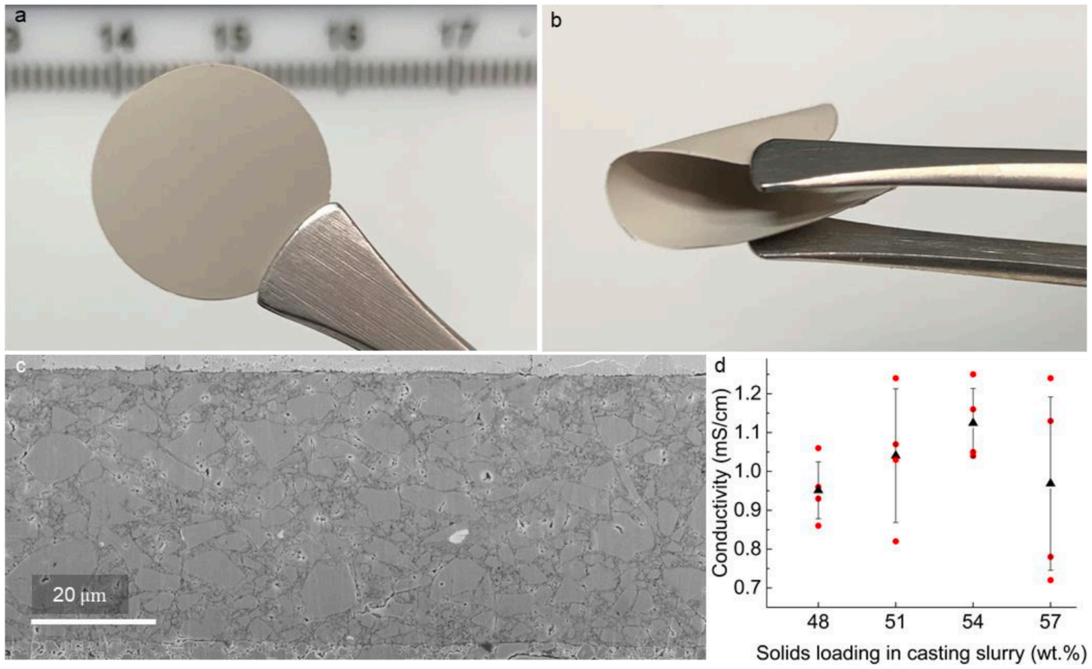
Li_6PS_5Cl protected in transfer vessel



The result shows the efficacy of air-free vessels in isolating the sample from atmosphere.

Accomplishments – Development of Thin Cells <100-μm Thick

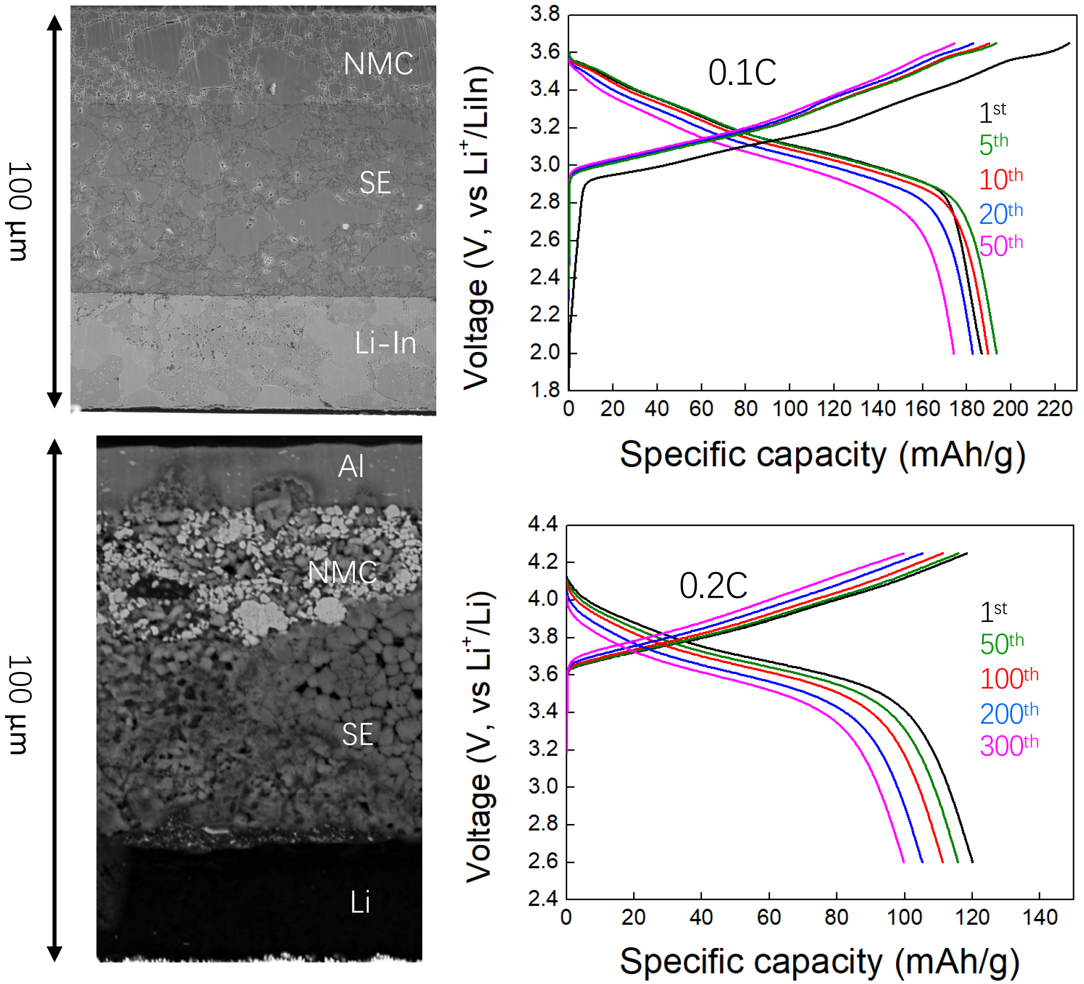
Tape-cast Li_6PS_5Cl solid electrolyte thin layer (~50 μm)



	Thickness (μm)	ASR (Ω cm²)	Conductivity (mS cm⁻¹)
This work	**55**	**5.0**	**1.12**
Bulk SE	700	62	1.10

Emley, Yao et al, *Materials Today Physics*, 2021, 18, 100397

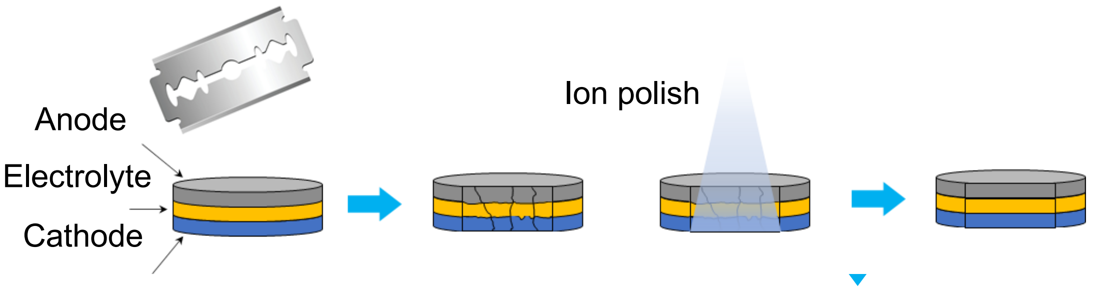
Thin Solid-State Cell (100 μm)

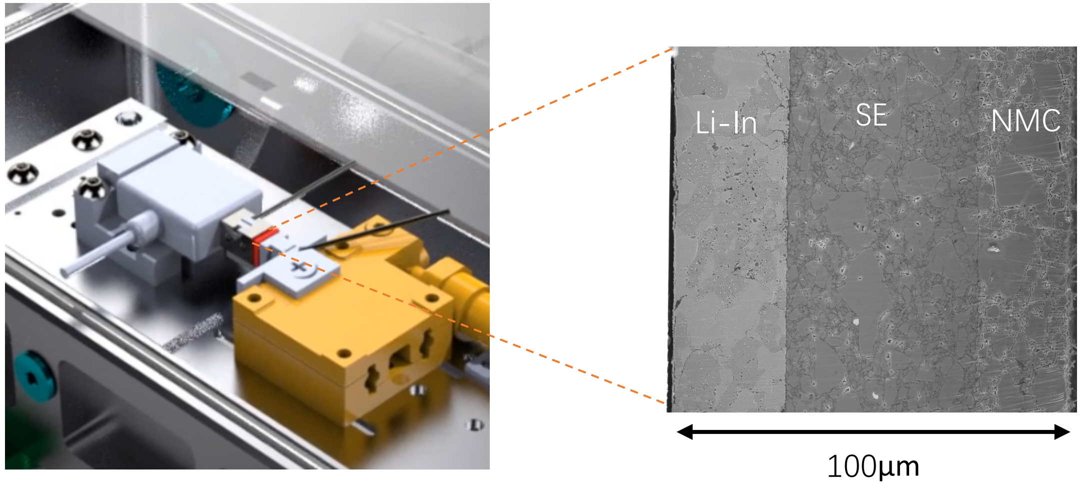


Wu, Fan, Yao et al, *in prep.*

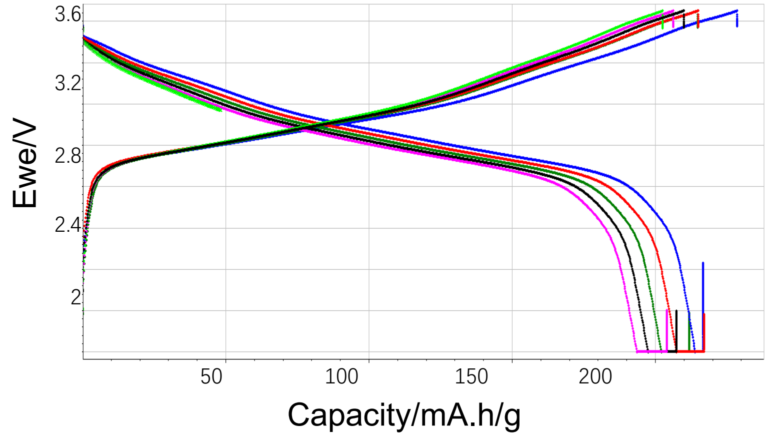
Accomplishments – Micro-Cells and *in situ* Cell Test Platform

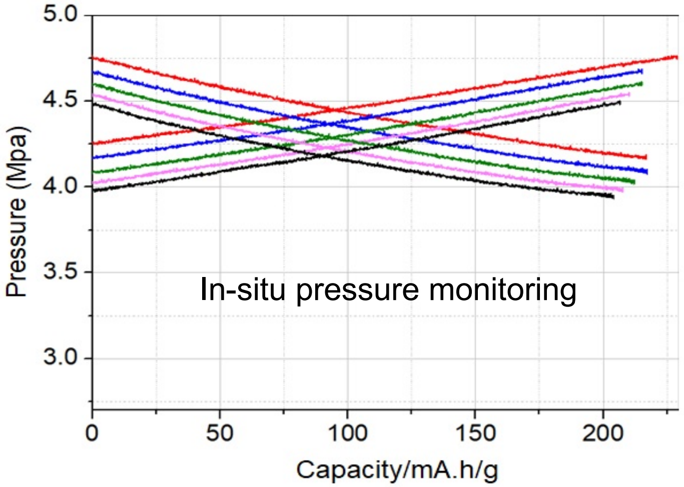
Micro-cell Preparation





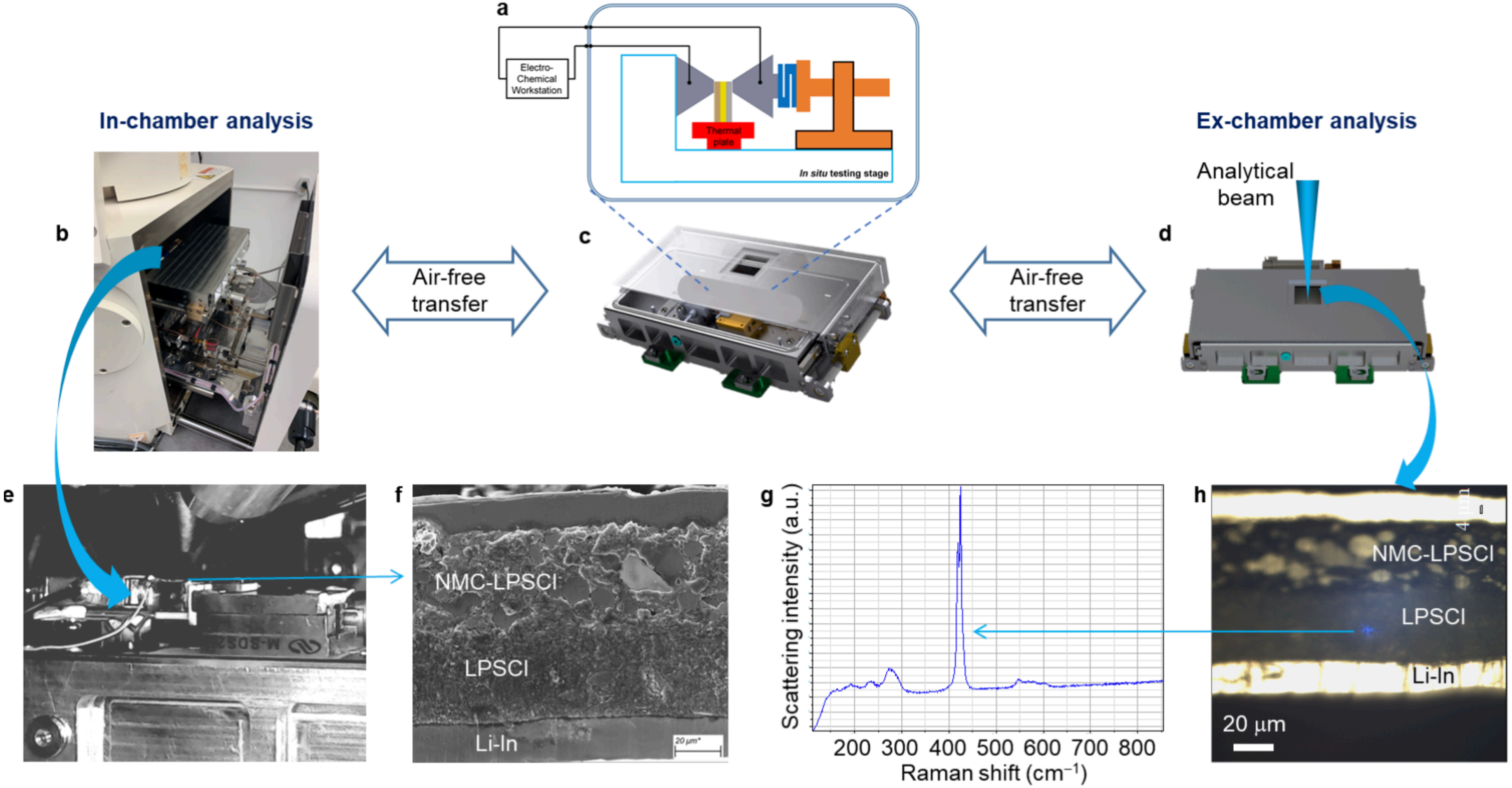
Cell size: 3mm*3mm*0.1mm





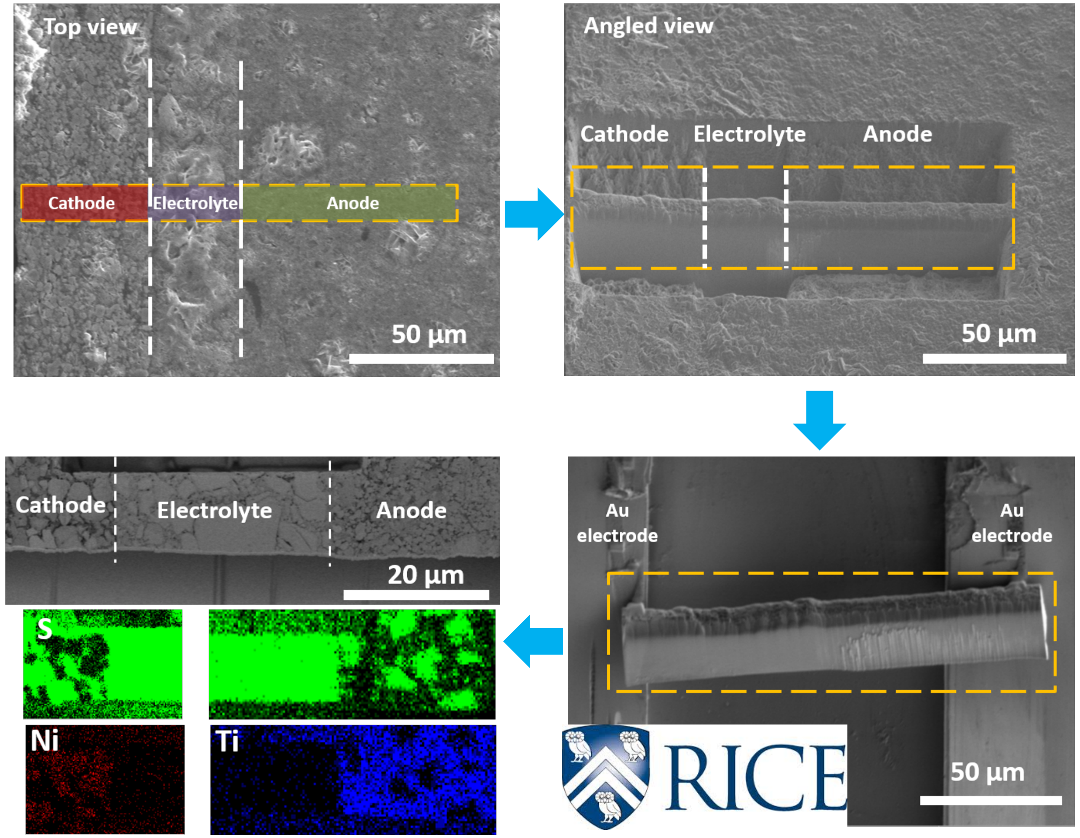
- **The platform equipped with micro-cell mount, heater, and pressure applier and sensor, has been optimized to deliver micro-cell performance comparable to bulk cells.**
- **Stacking pressure change can be monitored *in situ*.**

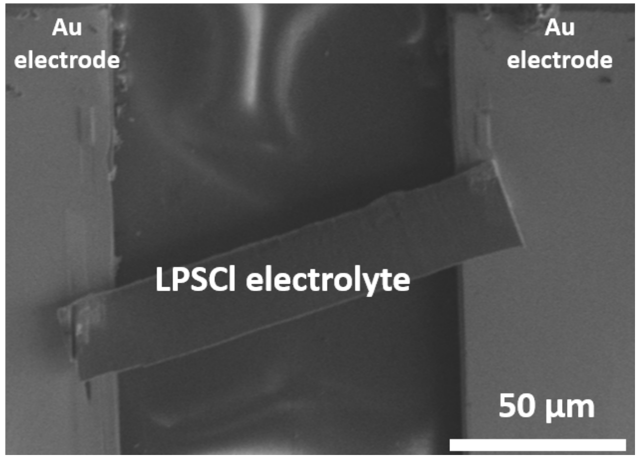
Accomplishments – Multimodal Characterization

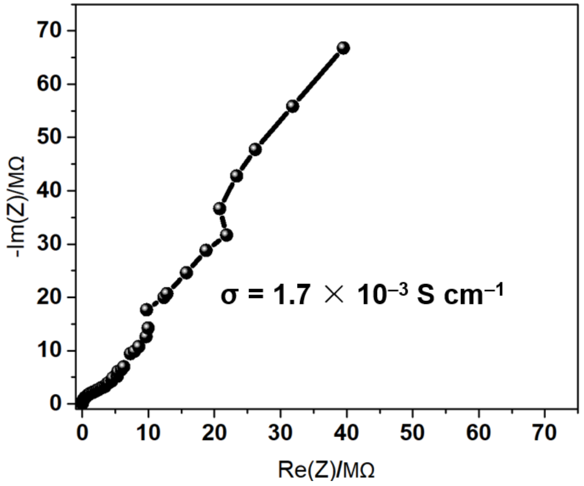


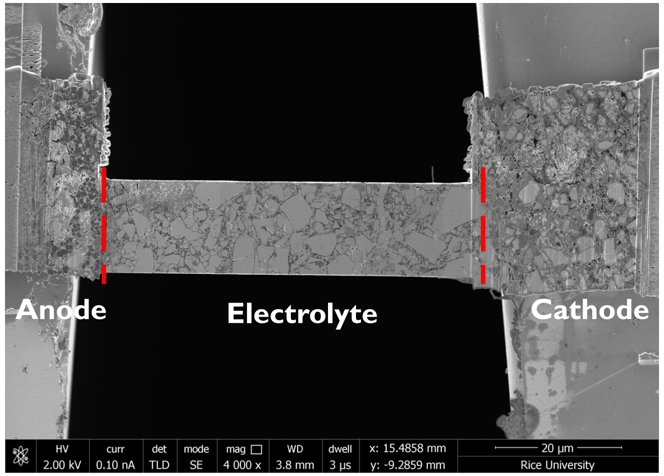
- **Multimodal measurements (SEM and Raman spectroscopy) for the same thin-cell at the same location.**

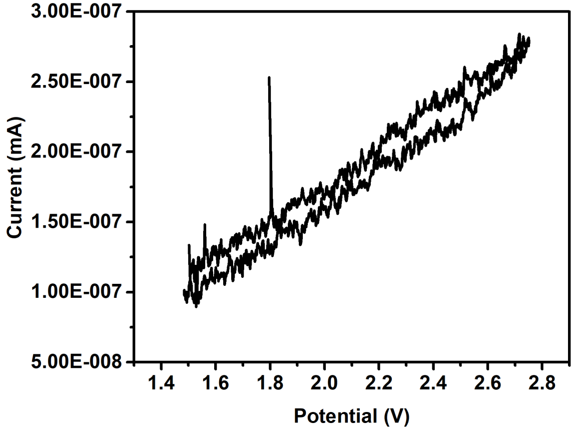
Accomplishments – Nano-cells





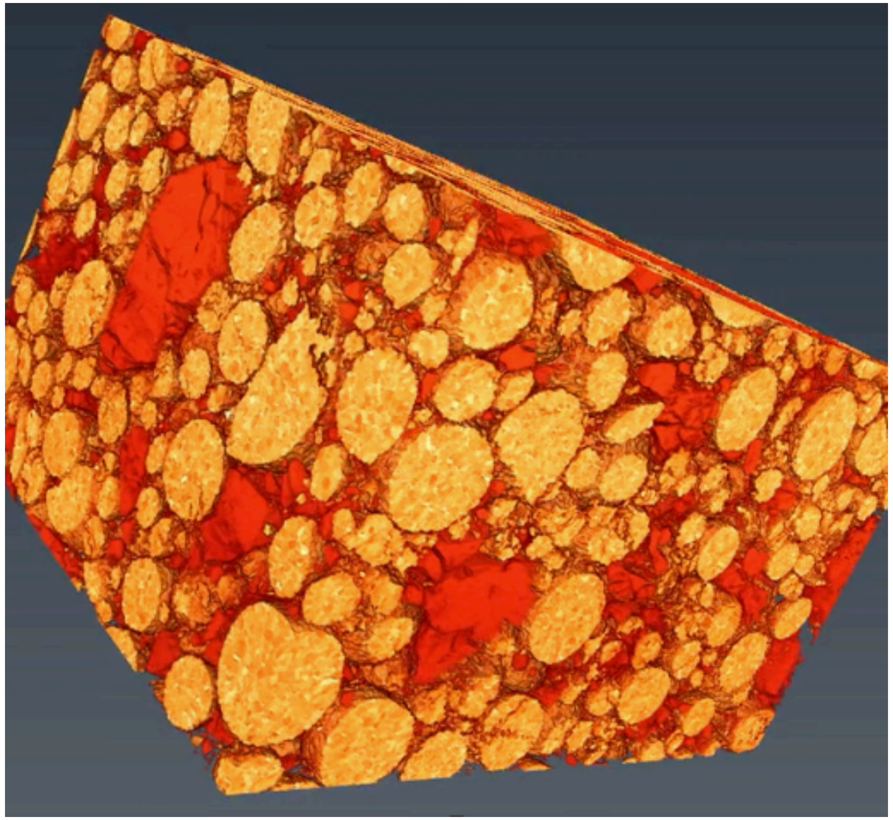






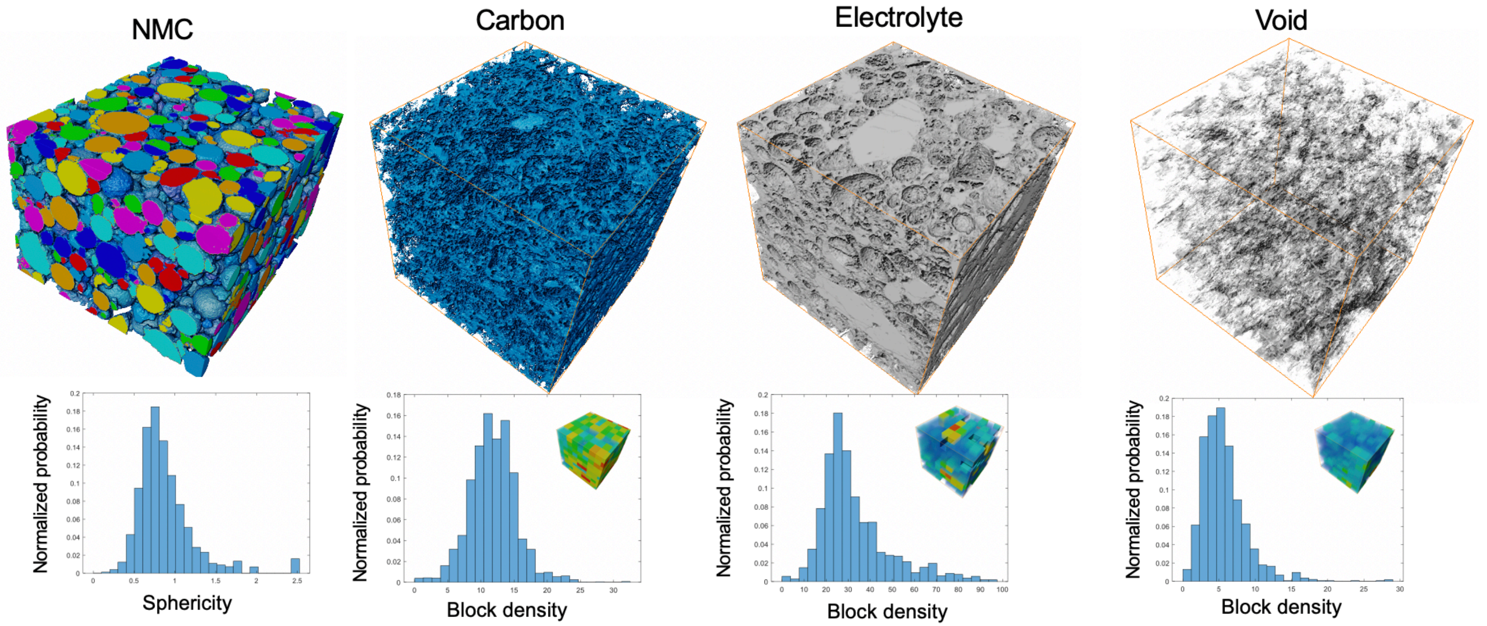
- **Ultra-low-current electrochemical upgrade is needed to operate nano-cells under realistic conditions**

Accomplishments – Structural Characterization



PFIB Volume: 100x100x50 μm^3

Dan Gostovic (ThermoFisher)

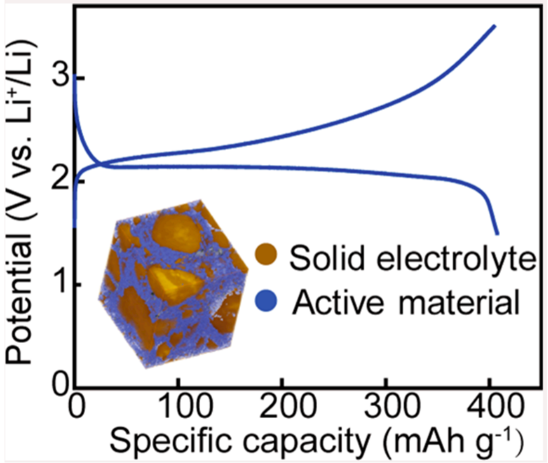


Yijin Liu (SLAC)

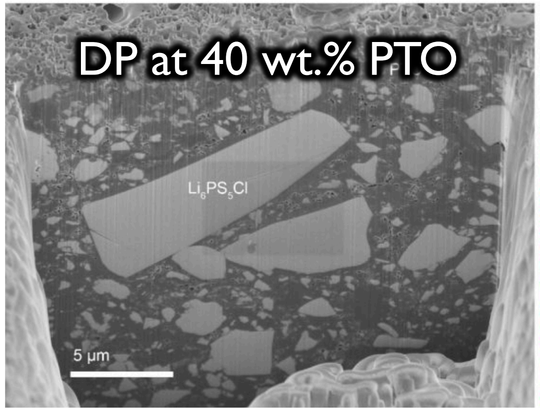
Material	Volume ratio (%)
NMC	49.72
Electrolyte	32.78
Carbon	11.80
Void	5.69

- **Plasma FIB reveals microstructure of cathode at desirable length scale and resolution.**
- **Machine learning-based image analysis provides info on porosity, tortuosity, volume ratio, and connectivity.**

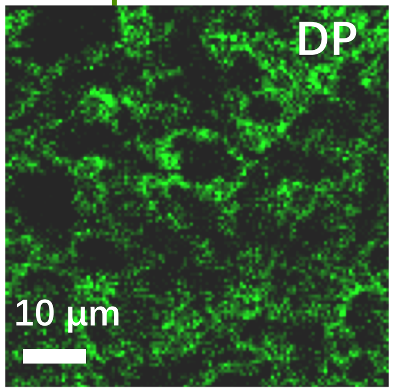
Accomplishments – ToF-SIMS for Chemical Characterization



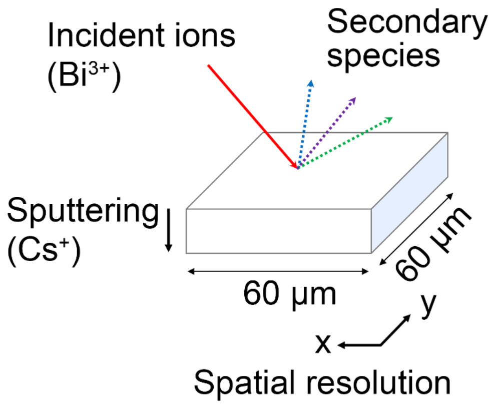
electrolyte-in-active material

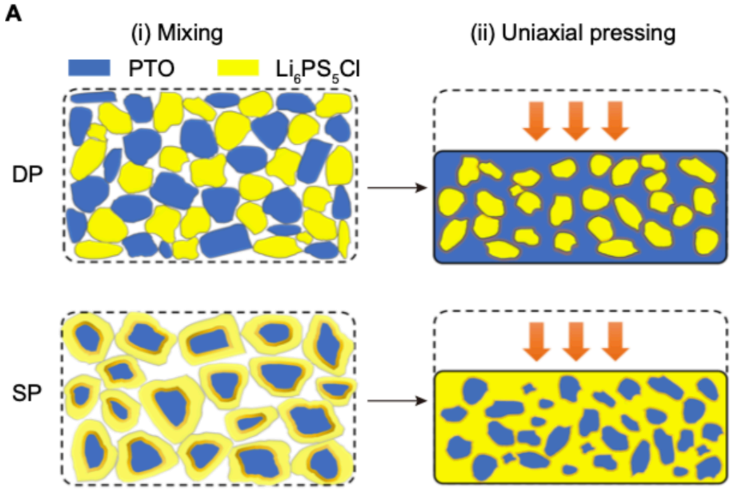


Cs$_2$LiC$_2^+$
Interphase-LixPTO



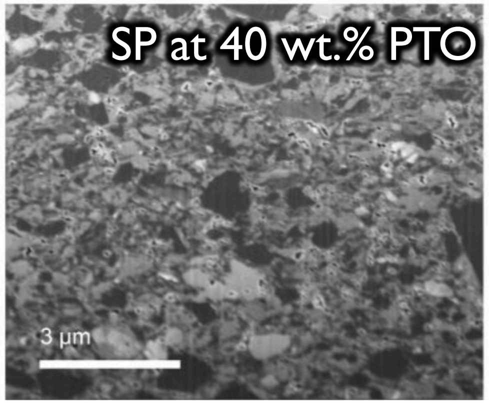
TOF-SIMS

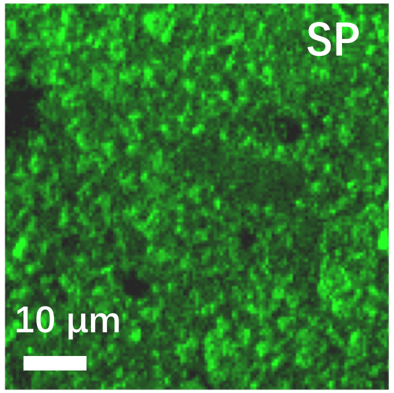


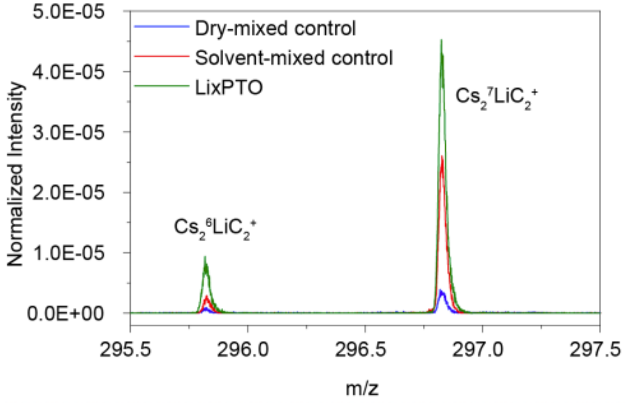


active material-in-electrolyte

$$PTO + Li^{+} + PS_4^{3-} \rightarrow Li_xPTO + Li{-}PS_n$$



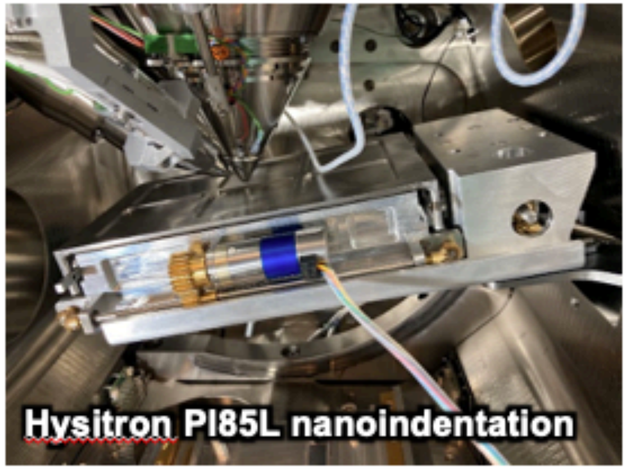


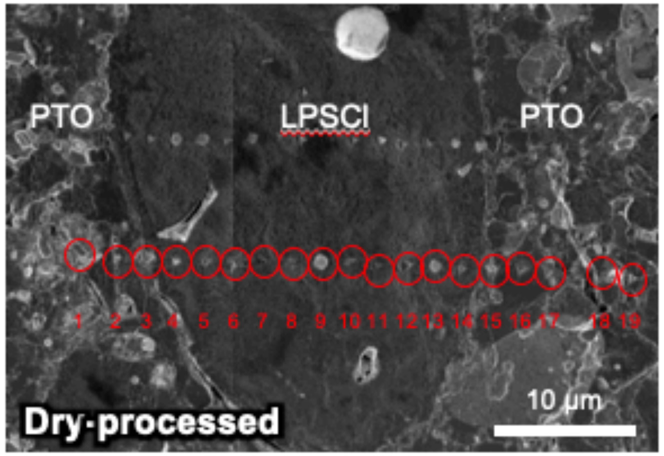


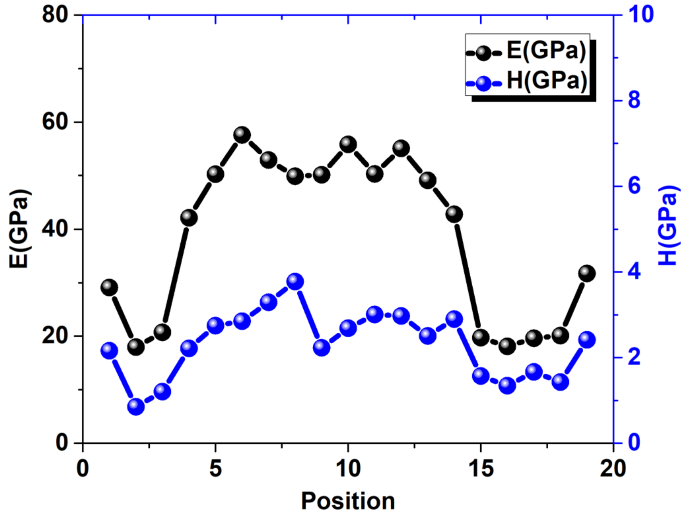
Zhang, Yao, et al. *Joule,* 2021, in press

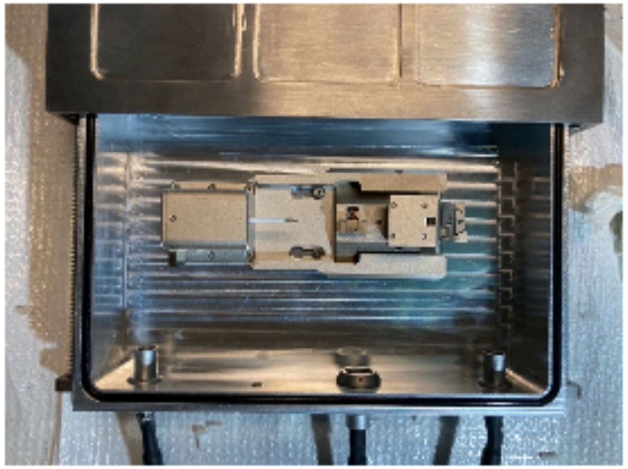
ToF-SIMS reveals chemical information of interfacial reaction products and spatial distribution.

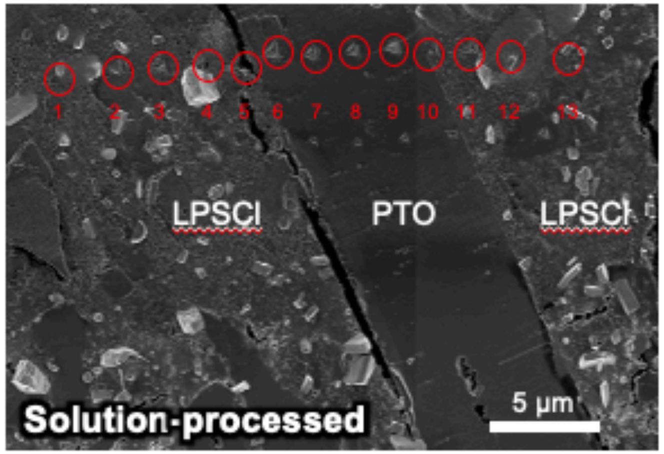
Accomplishment – Understanding origin of structure inversion

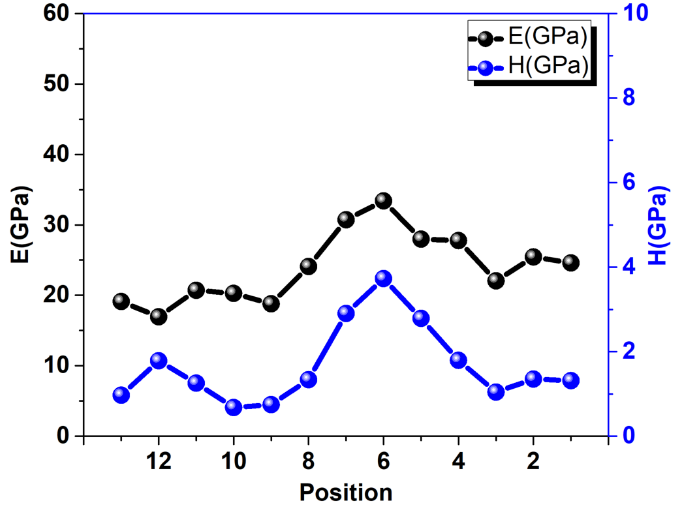












Nanoindentation reveals mechanical property changes of the PTO and LPSCl domains, which causes the structure inversion.

Responses to Previous Year Reviewers' Comments

No reviewer comments are available from previous year review on this project.

Collaboration and Coordination

- **Characterization**
  Dr. Jun Lou (Rice)
  Dr. Chongmin Wang (PNNL)
  Dr. Dan Gostovic (Thermo Fisher)
  Dr. Chunsheng Jiang (NREL)

- **Modeling**
  Dr. Yijin Liu (SLAC)
  Dr. Yue Qi (Brown)

- **Solid electrolyte and cell processing**
  Dr. Josh Buettner-Garrett (Solid Power)
  Dr. Ryan Du (Ampcera)
  Dr. Venkat Selvamanickam (UH)

Remaining Challenges and Barriers

- Complete equipment setup for *in-situ* characterization of micro-cells within SEM, nanoindentation, and ToF-SIMS chambers.

- Operate and characterize nano-cells under realistic conditions with the aid of the upgraded ultra-low-current electrochemical system.

- Multi-scale three-dimensional reconstruction of cell components to elucidate their microstructural features and correlation with cell performance.

- Develop automated analysis method for the analysis of ToF-SIMS data to identify intermediates relevant to electrode evolution.

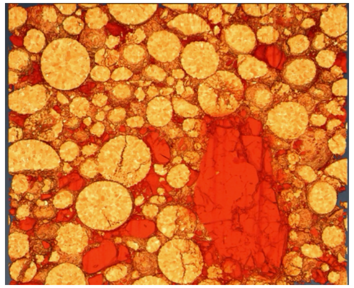
Proposed Future Research

We will conduct *ex-situ* characterizations of both electrodes and interfaces at various depth of discharge. (see milestones of FY21)

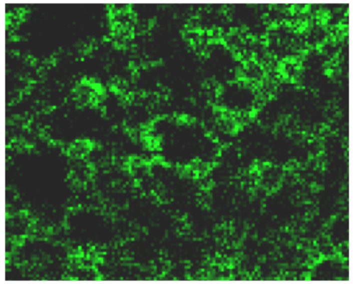
Task 2 – Multiscale structural investigations of solid-state cells
Subtask 2.1 – Identification and quantification of interface structural features for both cathode and anode at various cycles.

Task 3 – Chemical analysis of electrolyte decomposition products at the interface
Subtask 3.1 – Composition and spatial distribution study for both cathode and anode at various cycles.

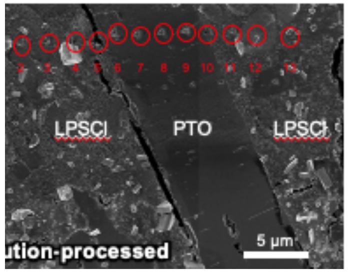
Task 4 – Mechanical properties probing of solid-state cells
Subtask 4.1 – Selected region mechanical property probing for both cathode and anode at various cycles.



structural



chemical

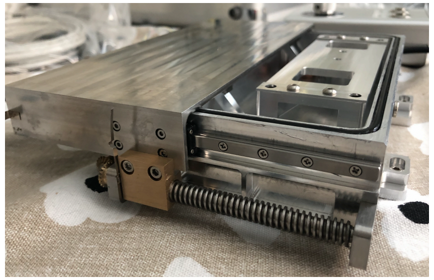


mechanical

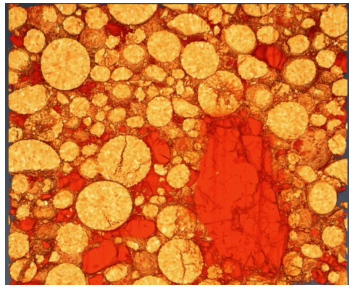
Any proposed future work is subject to change based on funding levels

Summary

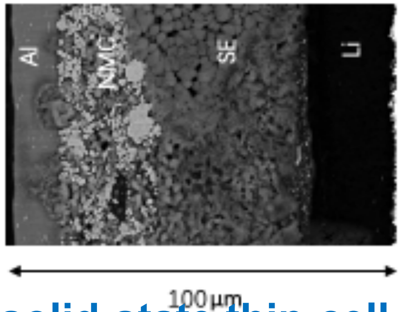
- Established air-free vessels to protect air-sensitive ASSBs and *in-situ* cell test platform for multimodal characterizations.
- Fabricated solid-state cells less than 100 µm and nano-cells with electrochemical performance on par with their bulk-type counterparts.
- Performed preliminiary *ex-situ* structural, chemical, and mechanical characterizations of air-sensitive ASSBs.



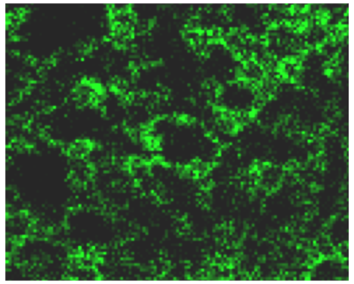
air-free vessel



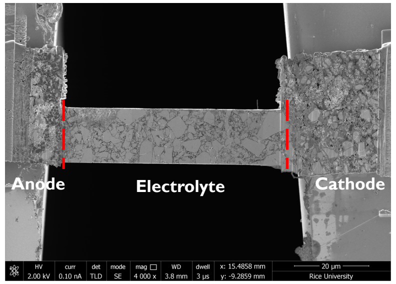
structural



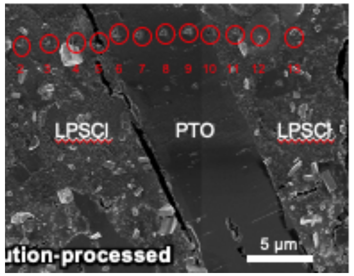
solid-state thin-cell



chemical



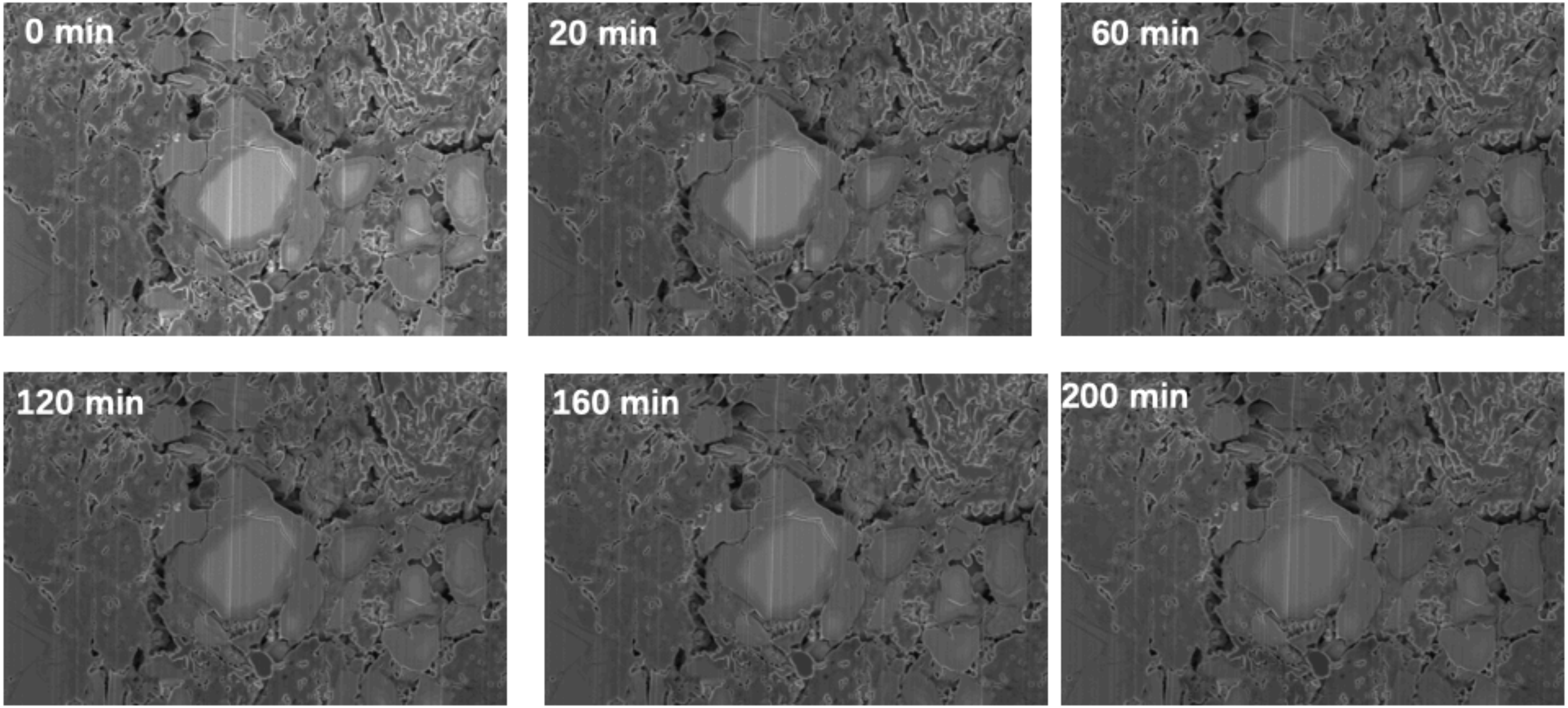
solid-state nano-cell



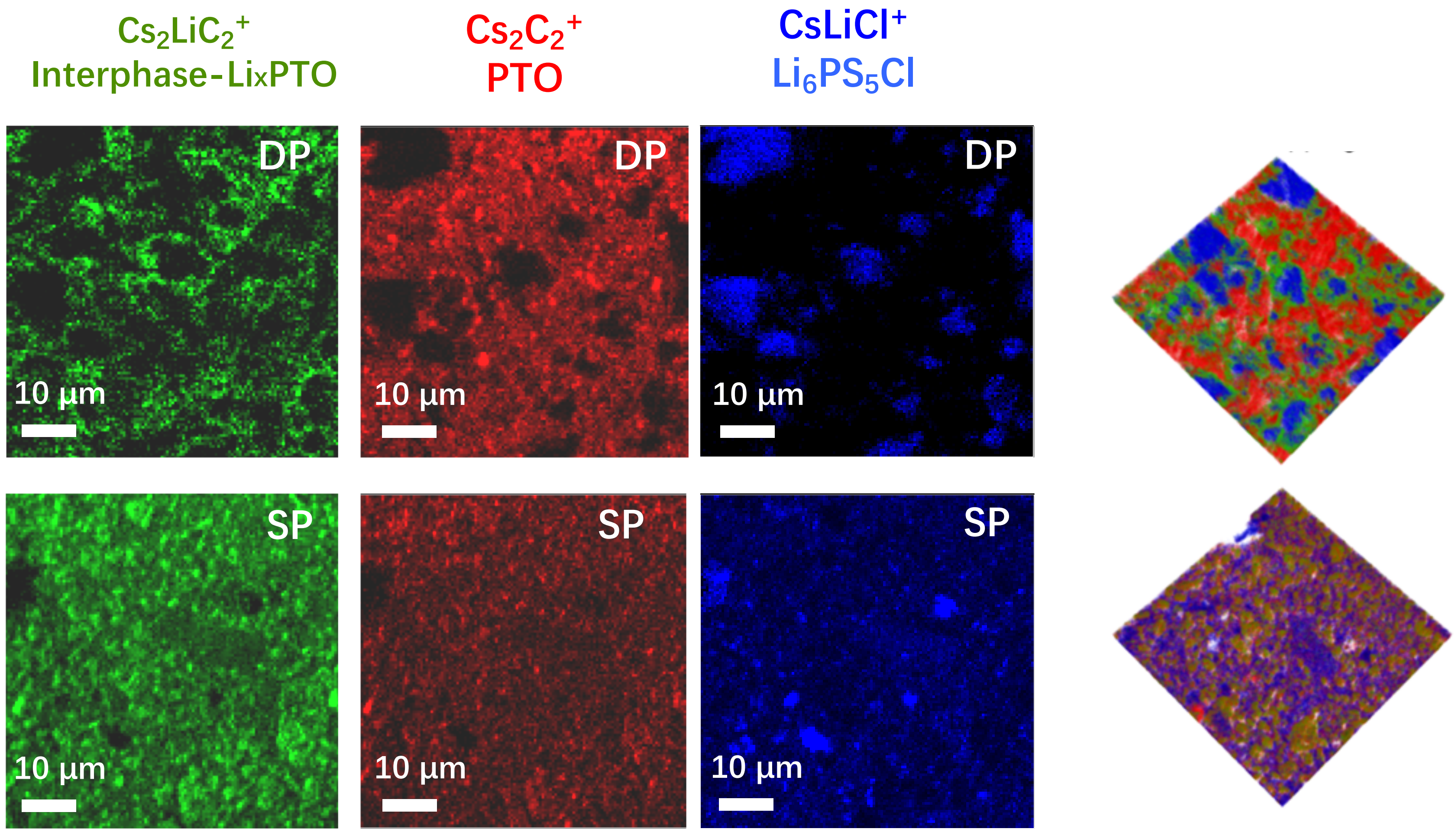
mechanical

Technical Backup Slides

In-operando SEM imaging of Nano-cells during CV test



ToF-SIMS for Interface Characterization



Accomplishment – Understanding origin of structure inversion