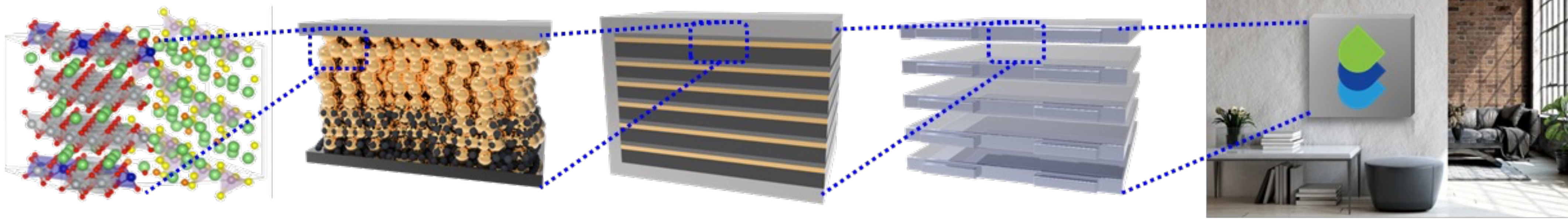
LESC
Laboratory for Energy Storage and Conversion



Scaling-Up High Energy Density Solid-State Batteries

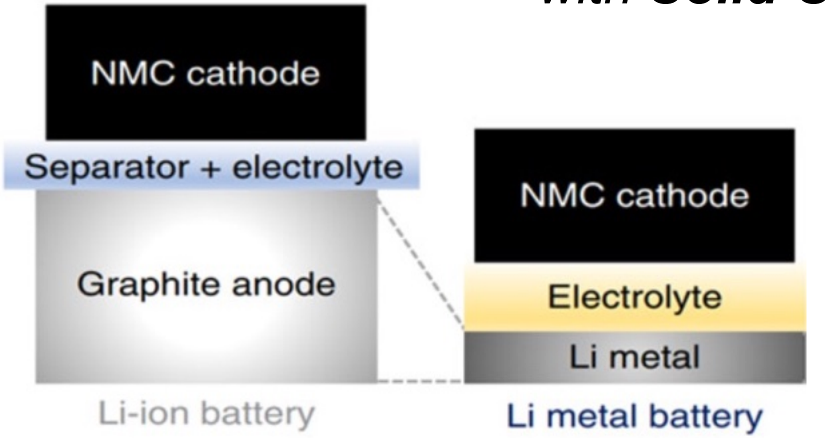
Y. Shirley Meng

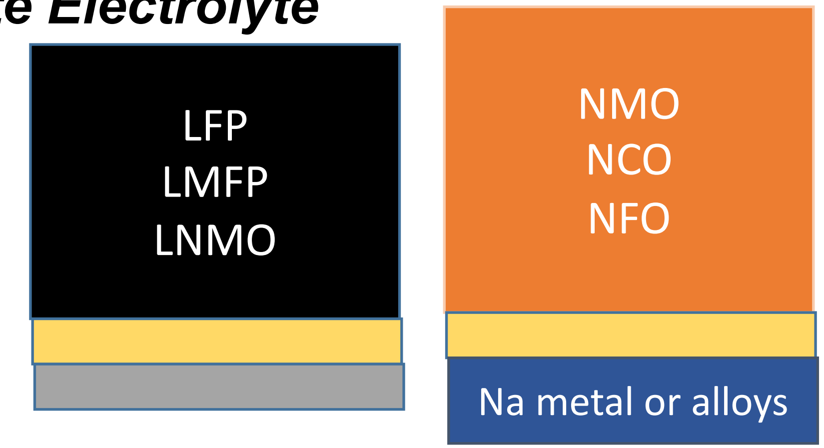
The University of Chicago & University of California San Diego
Argonne Collaborative Center for Energy Storage Science

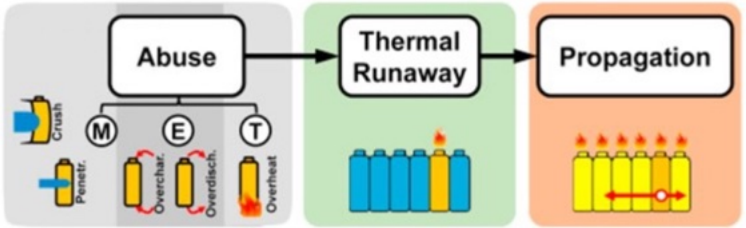
All Solid-State Batteries – Platform Technology

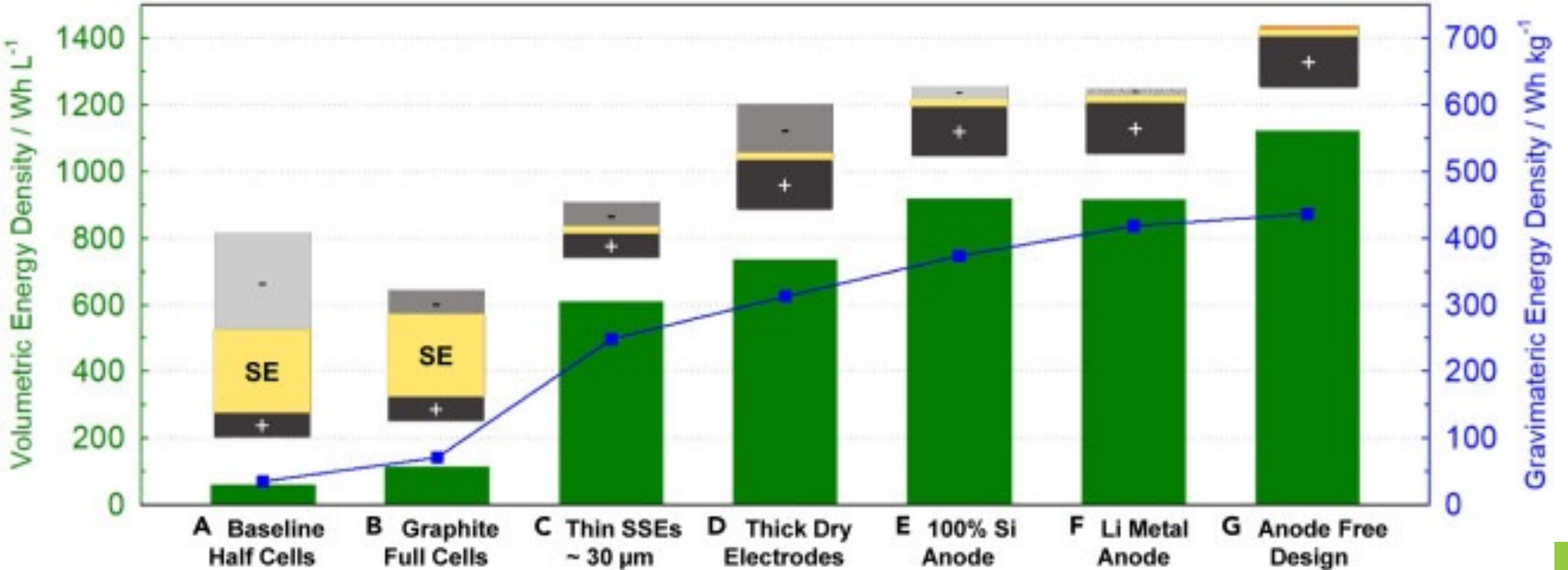
High-Energy-Density *and* ***Safe Batteries***

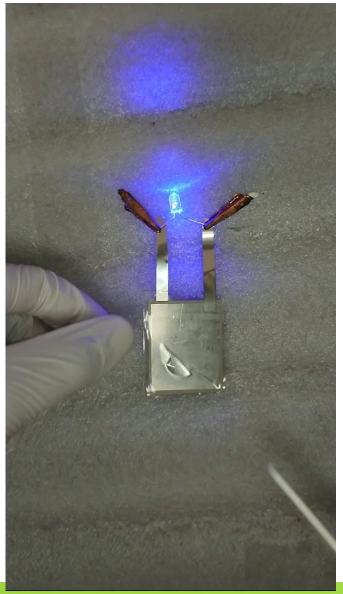
with ***Solid-State Electrolyte***











LGES – FRL Team Members

From Atom to System

Ong Kim Shpyrko Clement Meng Liu Chen

Computation
Modeling

Characterization
Novel Materials

Scalable
Processing

Devices
Prototyping

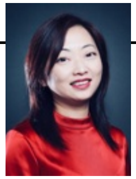
Recycling
Safety

Sustainable Power and Energy Center

LGES – UCSD Frontier Research Laboratory

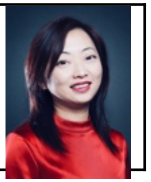
Scope & Areas of Collaboration

1. Materials	• Anode & Cathode strategy • Solid Electrolytes
2. Electrodes & Cells	• Dry Electrode Processing • Fabrication & Pouch Prototyping
3. Characterization	• Degradation/Interface Characterization • Electrochemical Diagnosis and Prognosis
4. Modeling	• Thermo-Mechanical-Electrochemical Modeling • Computational Materials Discovery Database

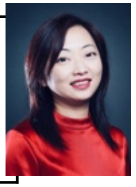






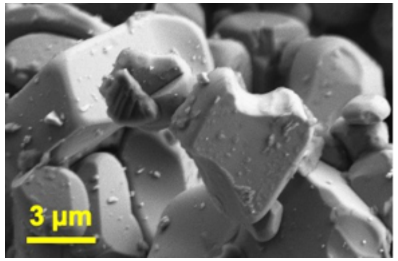




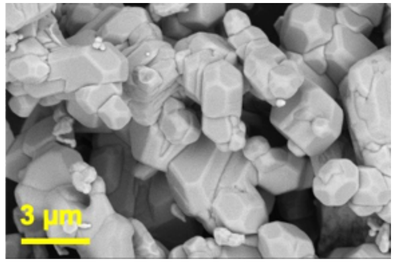

Interfacial Challenges and Strategies

Popular cathodes and their particle sizes, > 3µm

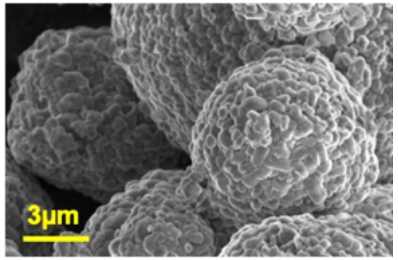
LCO



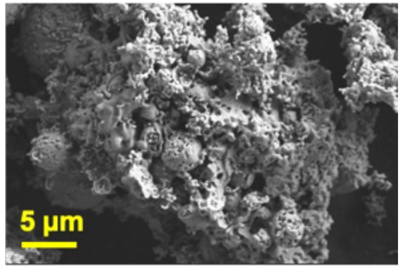
LMO



NMC811



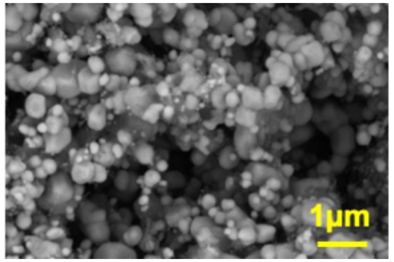
Uncoated LFP



Particle size reduction

Carbon coating (2 wt.%)

Carbon/ LFP

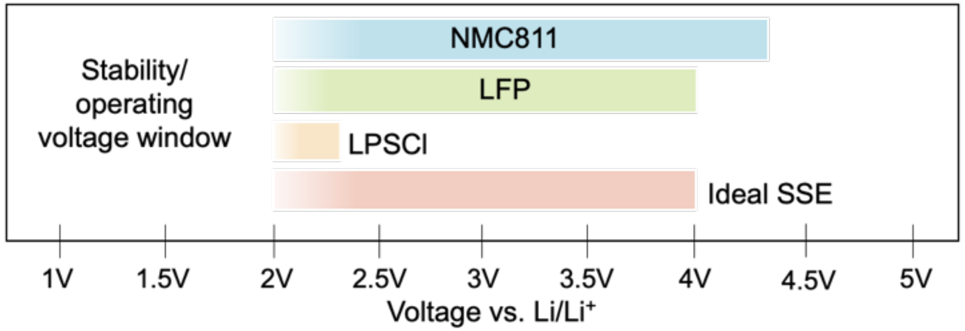


Poor electronic conductivity

- 1D Li^+ diffusion

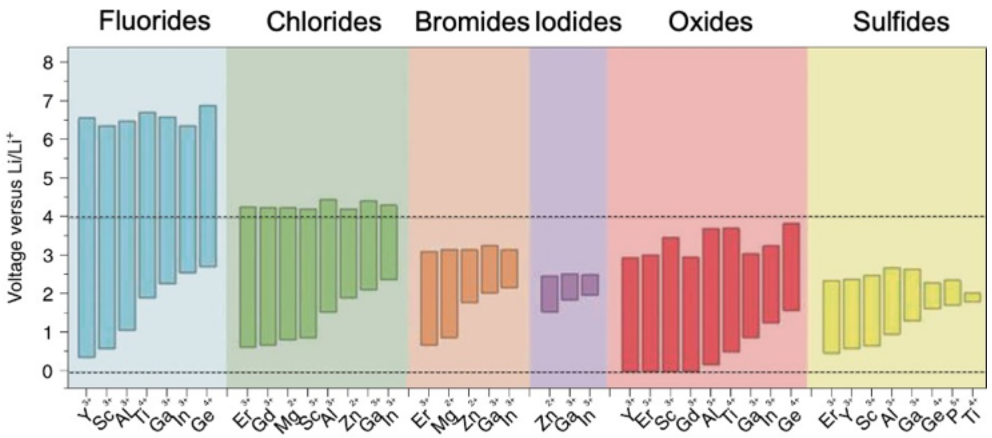
- Nanoscale
- Conductive interface

Sulfur Cathode Possible!!!



✓ Need an SSE that is stable to 4V (especially with carbon!)

✓ Need a compliant SSE that can provide intimate cathode/SSE contact (i.e. Li_6PS_5Cl)

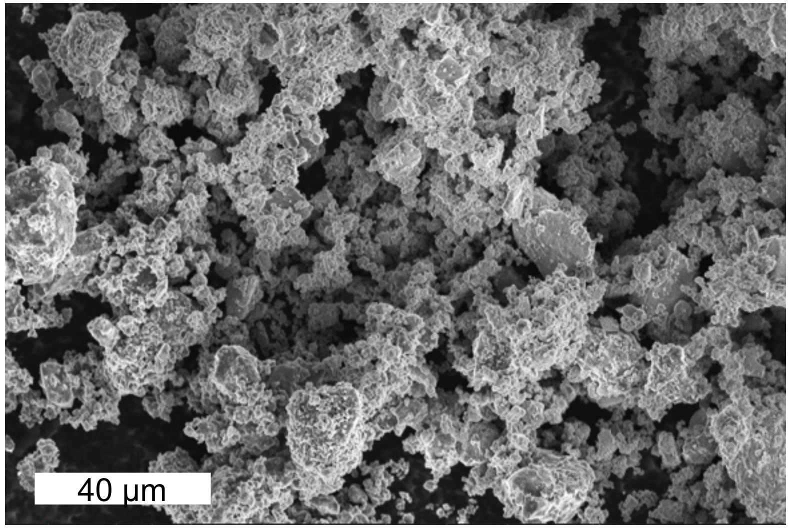


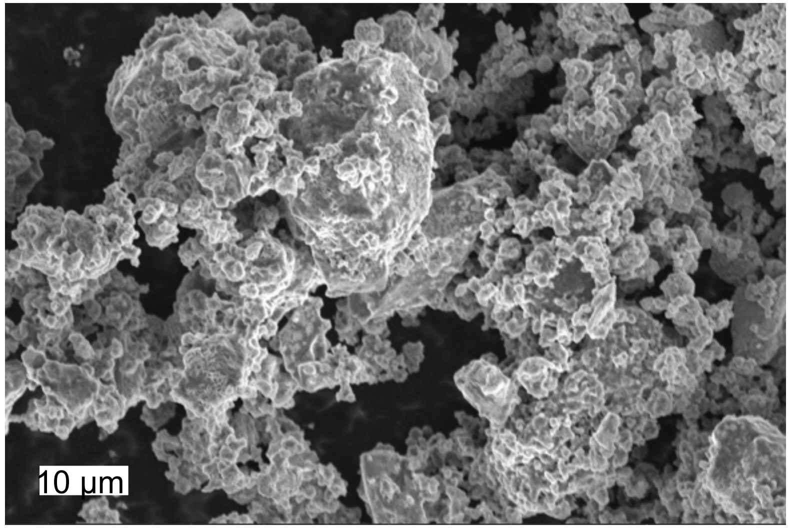
Tan et al. Nature Nanotechnology. Vol 15, 170-180 (2020)

- Chlorides are a good candidate for their oxidative stability and potential low-cost (i.e., Li_2ZrCl_6)

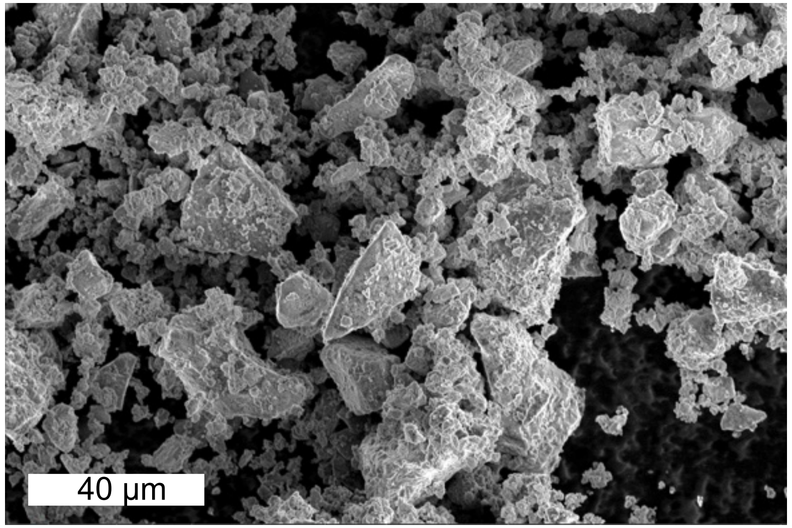
Why do We Choose Li_6PS_5Cl – Metric Ton Quantity

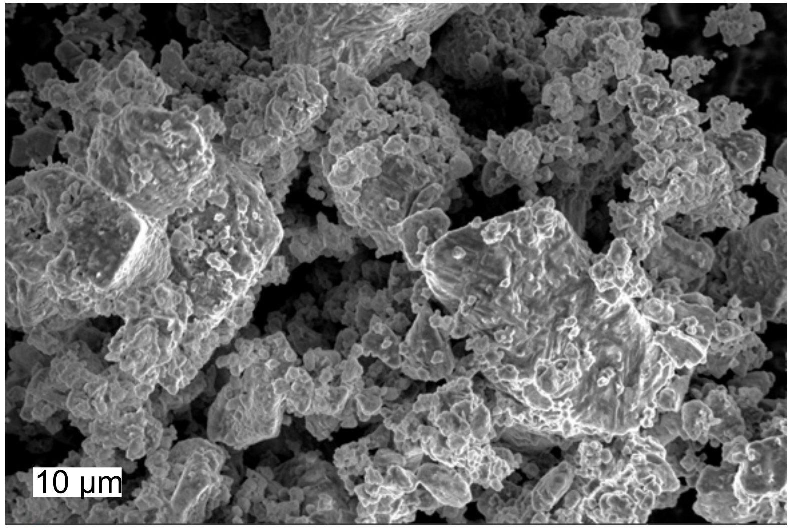
USA Supplier 1:



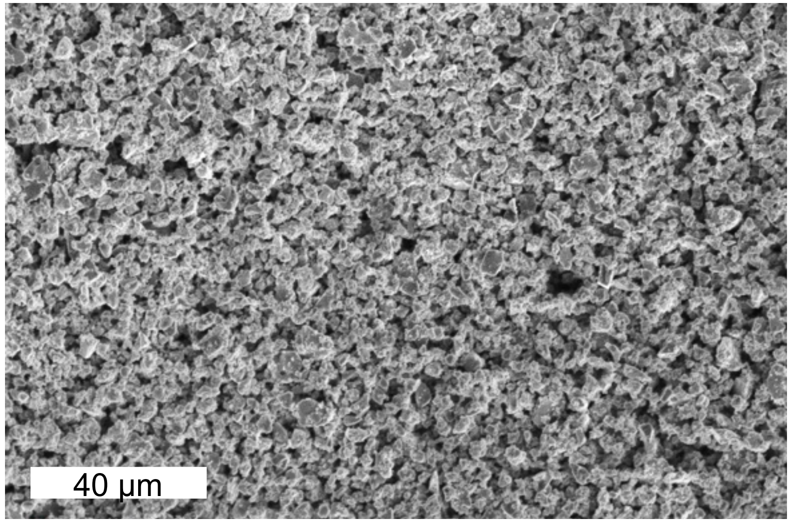


USA Supplier 2:

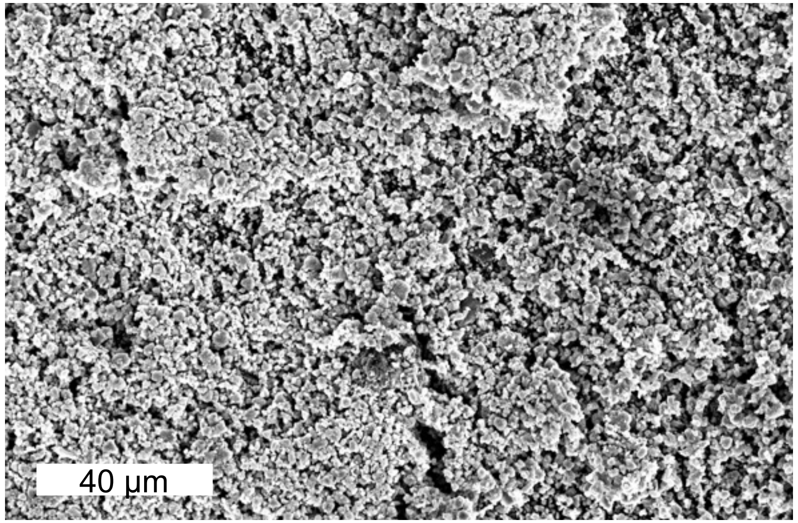




Japan Supplier 1



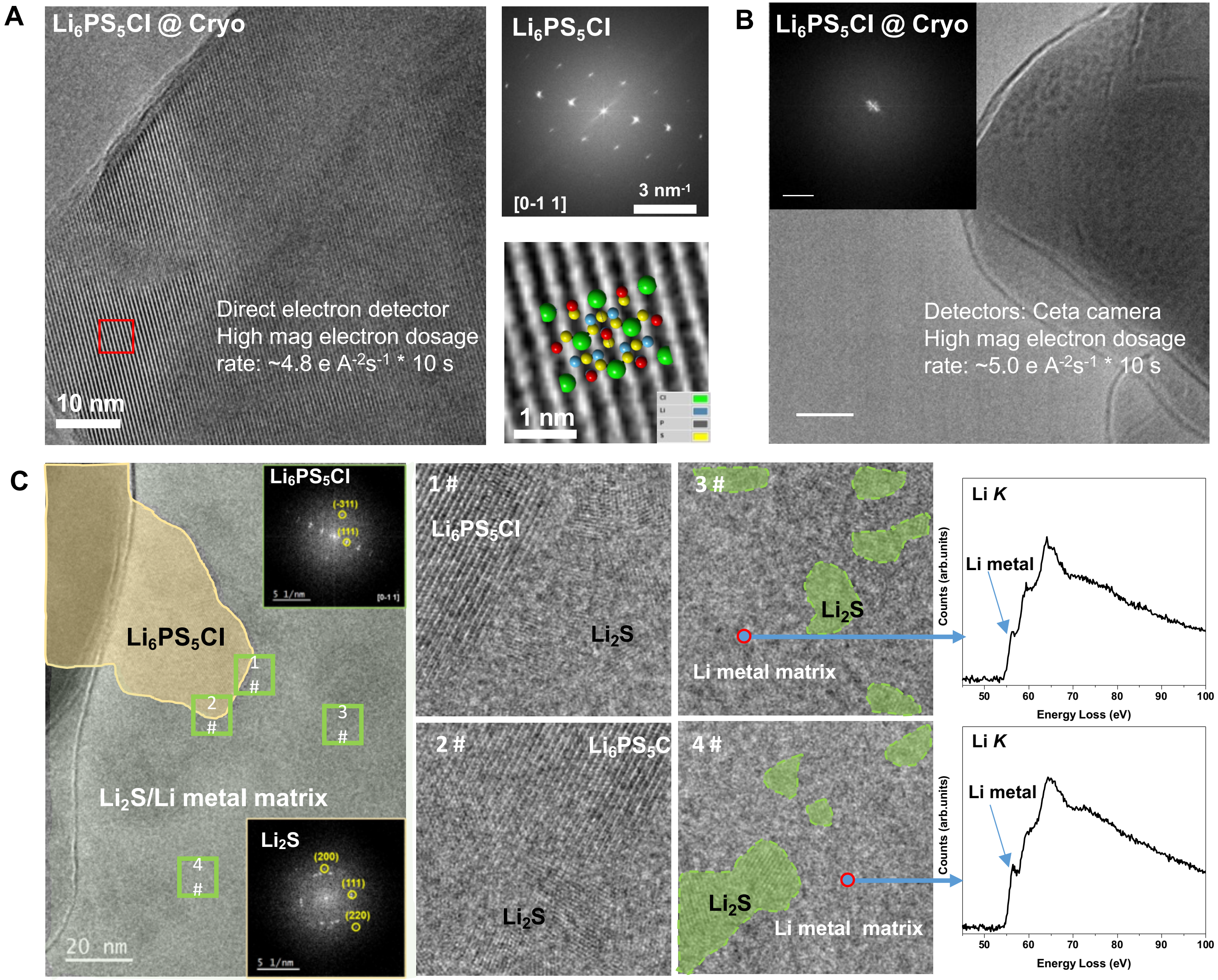
(A)



(B)

Necessity of Low Dose, DED and Special Holder

Unpublished data from Meng group – to be submitted in 2023



Magnification: 150 kx; Dosage rate: ~6.3 e $A^{-2}s^{-1}$ * 10 s

- LPSCl is super beam sensitive(melting and bubbling) even at Cryo temperature **(< 10 e $A^{-2}s^{-1}$, direct electron detector is required)!**
- **Cryo EM** will unlock the understanding of Solid-State Electrolytes, particularly glassy type

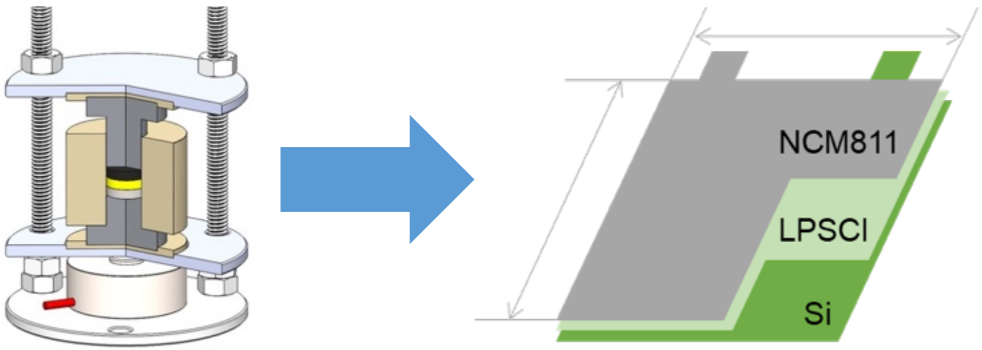
Supported by CRADA and LDRD

The PicoProbe is an advanced next generation analytical electron microscope which is the results of a multi-year CRADA at Argonne. This monochromated, aberration corrected, probe forming analytical electron microscope will harken the next generation of complementary characterization resource. It facilitates state-of-the-art correlative studies of the morphology, crystallography, elemental, chemical and electronic structure composition of soft and hard matter. Having the ability to operate between 30 and 300 keV, has probe sizes as small as 50 picometers. Combined with the worlds highest sensitivity detector for x-ray spectroscopy and the ZTwin lens, designed by Argonne, the Picoprobe enables unprecedented sensitivity and resolution for the characterization of hard and soft matter.

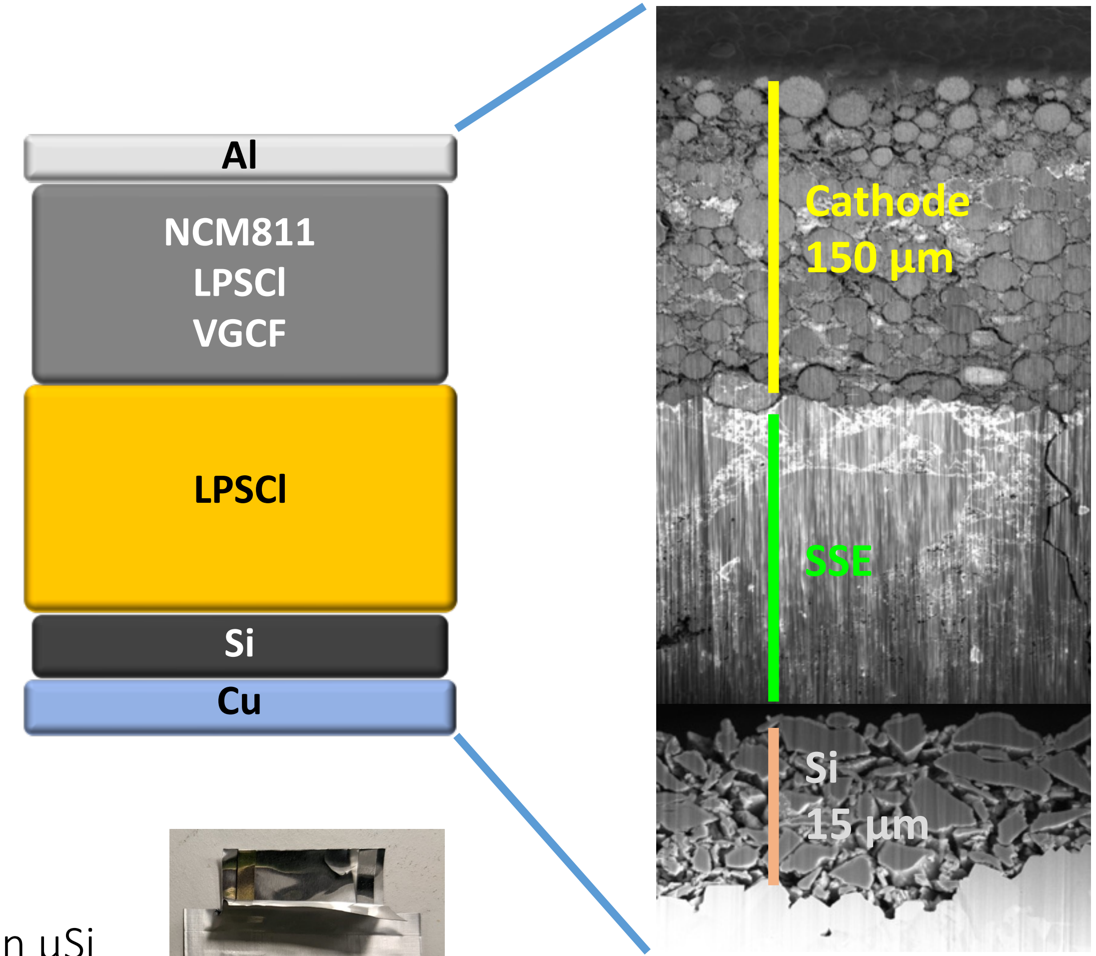
https://www.aps.anl.gov/AAEM/PicoProbe

Defining Cell Configuration

LGES-UCSD Frontier Research Laboratory



Requirements:	Pellet Type	Pouch Type
SSE Thickness	~ 700 µm	< 100 µm
Areal Loading	< 2 mAh cm^{-2}	4-6 mAh cm^{-2}
Cell Size	< 1 cm^2	> 10 cm^2
Stack Pressure	~ 50 MPa	< 5 MPa
Layers	1	≥1



- LPSCl is dry room compatible → Ready for pouch cells
- Setting key parameters for pouch demonstration based on µSi | LPSCl | NCM811

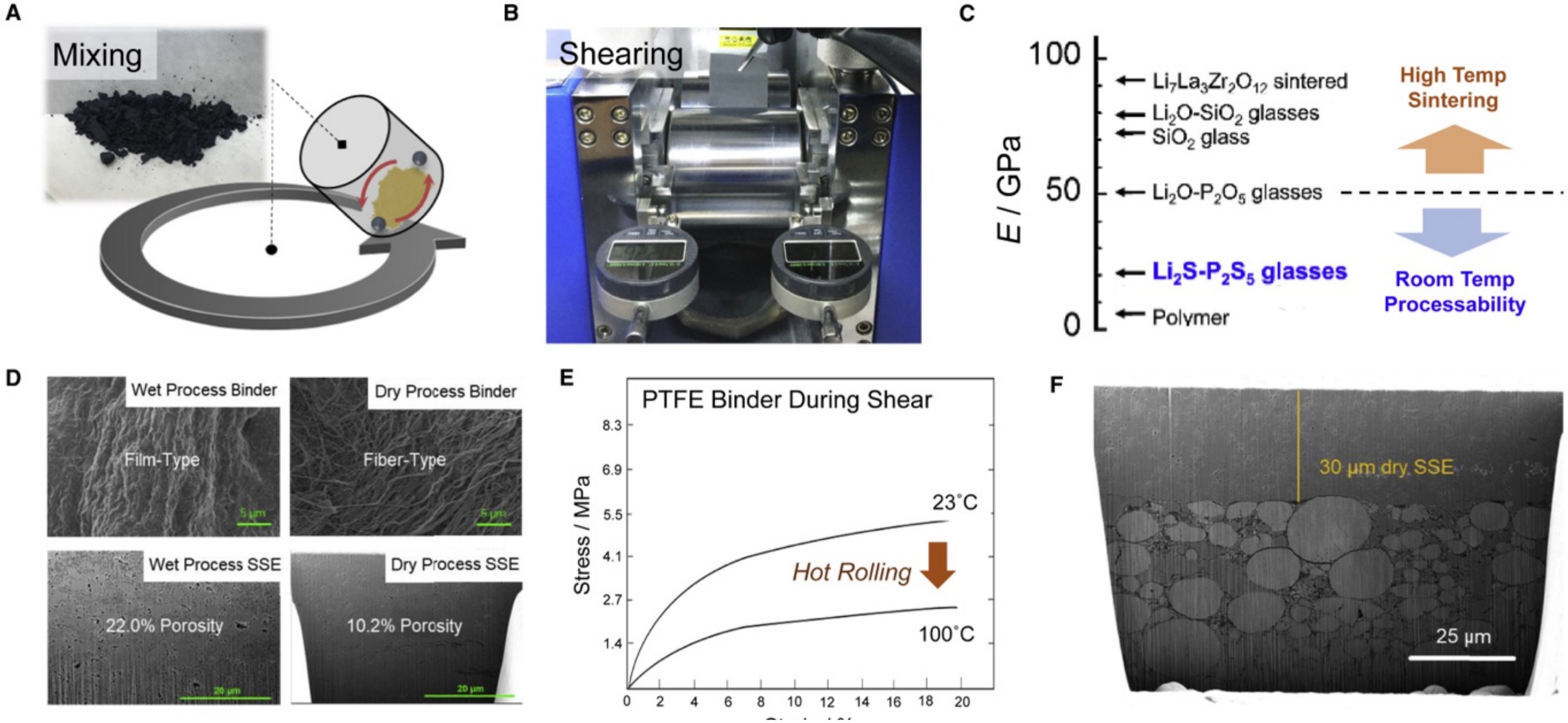
Single layer all-solid-state pouch cell

Unpublished data from Meng group

D. Tan, J. Jang and Y.S. Meng Joule 2022

https://doi.org/10.1016/j.joule.2022.07.002

Joule



Dr. Darren Tan

Dr. Jihyun Jang

Funded by

LG Energy Solution

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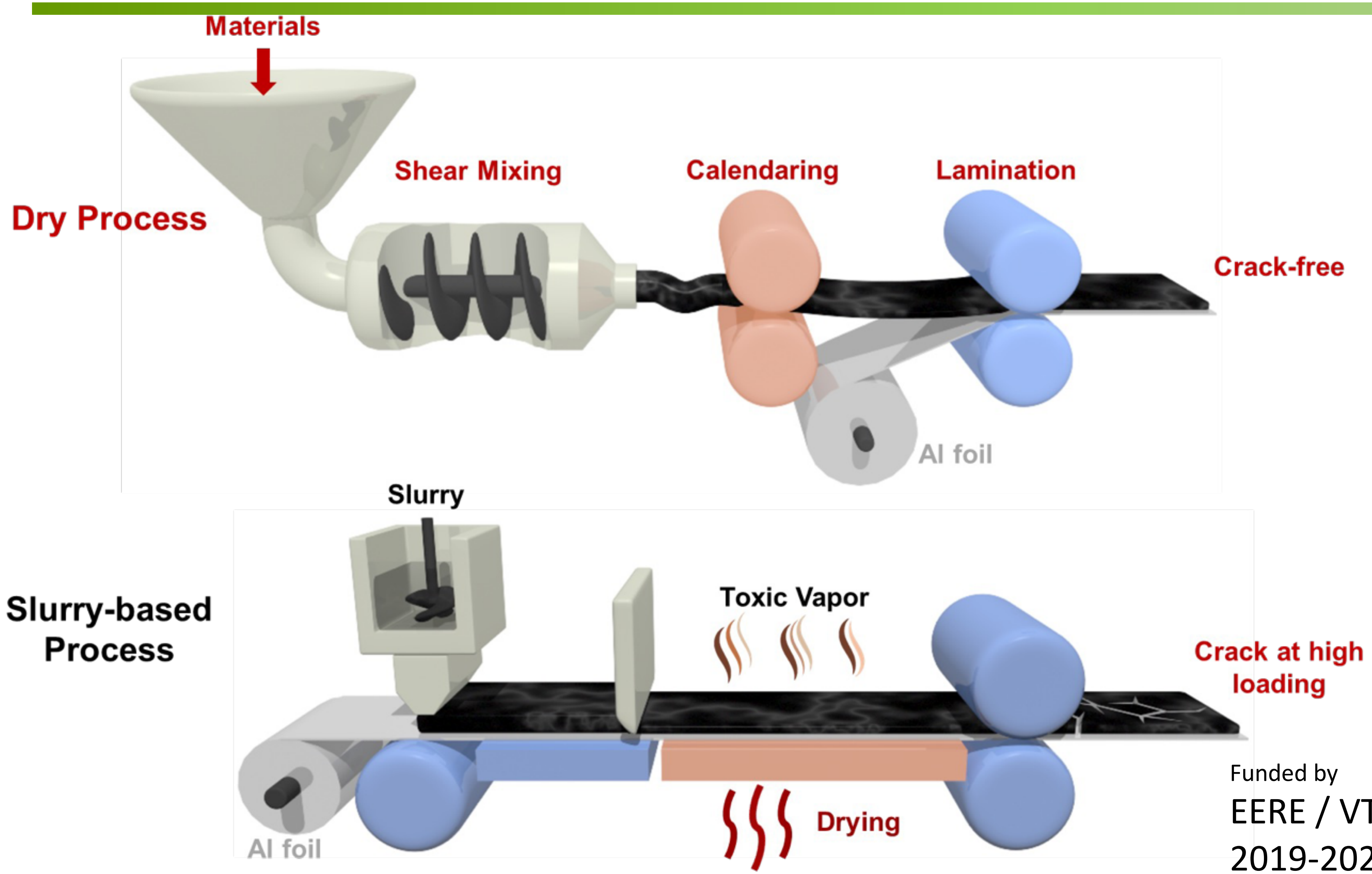
Slurry-based Method VS Dry Process



- Dry electrode method:
  - No solvent included
  - Easily achieve high mass loading without crack
  - Eliminate troublesome CB
  - More economical and simpler process

- Conventional slurry-based method:
  - Use of toxic NMP solvent
  - Lengthy drying process
  - Solvent recycling equipment
  - Cracks at high mass loading

Funded by
EERE / VTO and Tesla (Maxwell Technologies)
2019-2022

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Yao, Weiliang, *et al*. "A 5V-class Cobalt-free Battery Cathode with High Loading Enabled by Dry Coating." Energy & Environmental Science (2023).

Remaining Challenges

Li2S price needs to come down by 5X -10X
SSE particle size control must be done

Precursors

Processibility

Dry room compatibility - yes!
Dry processing – at scale!!!

Pressure reduction from 100MPa – 50MPa – 5MPa
Design SSB component and architecture

Pressure

Dry Room Compatibility Resolved

Y. Chen, M. A. T. Marple, D. H. S. Tan, S. Ham, B. Sayahpour, W. Li, H. Yang, J. B. Lee, H. J. Hah, E. A. Wu, J. Doux, J. Jang, P. Ridley, A. Cronk, G. Deysher, Z. Chen and Y. S. Meng, "[Investigating Dry Room Compatibility of Sulfide Solid-State Electrolytes for Scalable Manufacturing](#)", *J. Mater. Chem. A,* 2022, **10**, 7155 – 7164

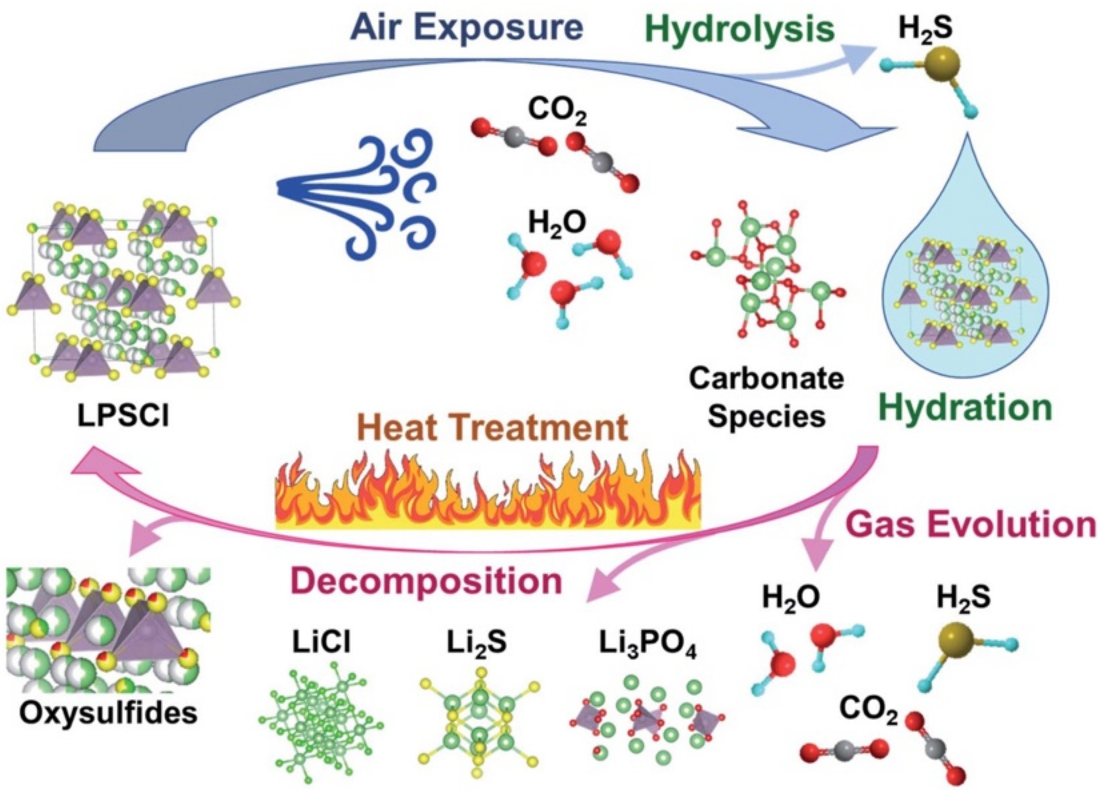
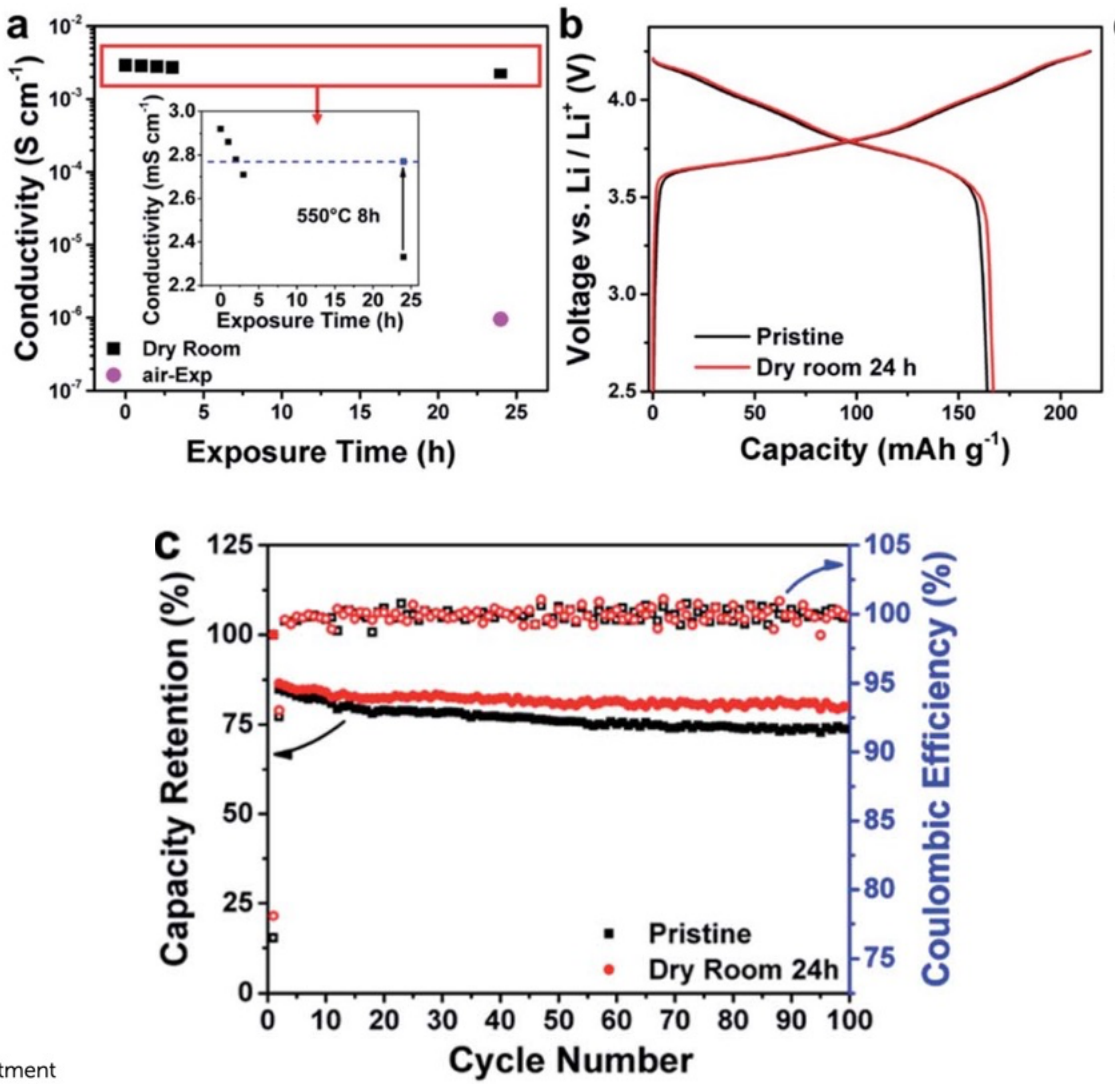
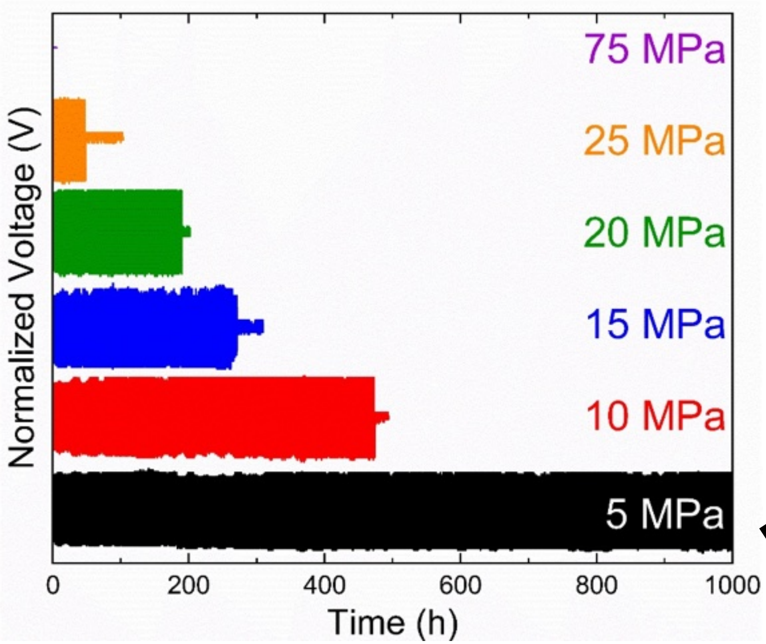


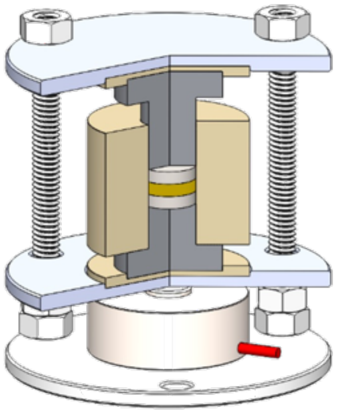
Fig. 1 Schematic of the chemical reactions that occur when Li_6PS_5Cl is exposed to ambient air and during the subsequent heat treatment process.



Stack Pressure Effect on Li Metal Anode

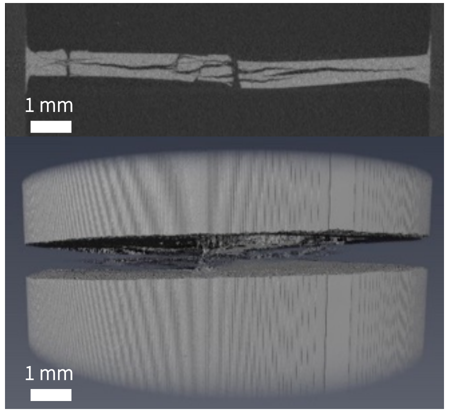
Li symmetric cells



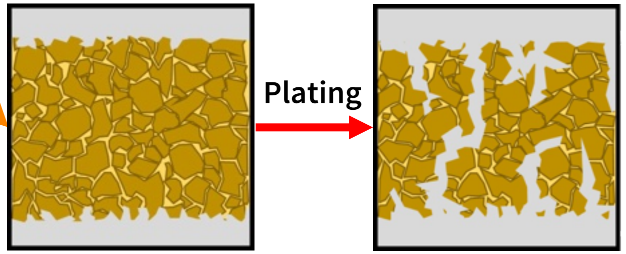


75 MPa

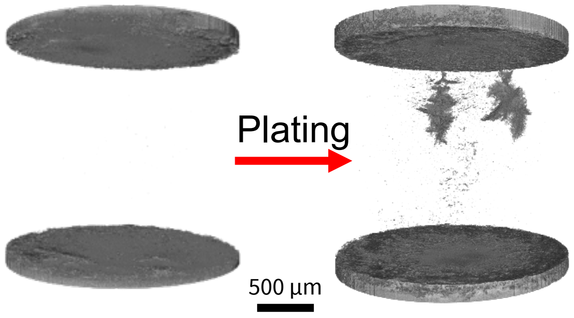
Mechanically induced short-circuit



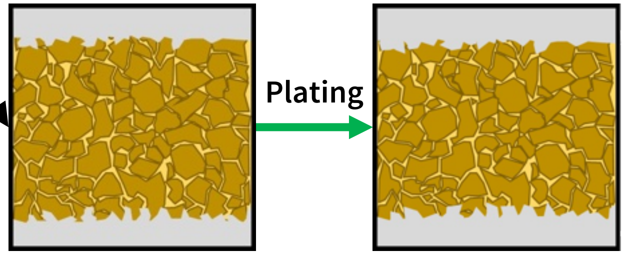
25 MPa



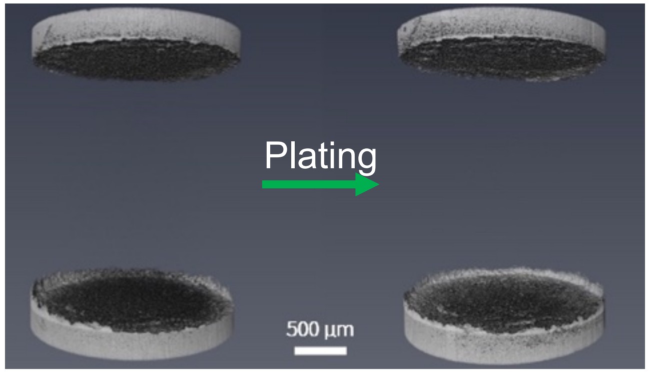
~ 48h: Plating short-circuit



5 MPa



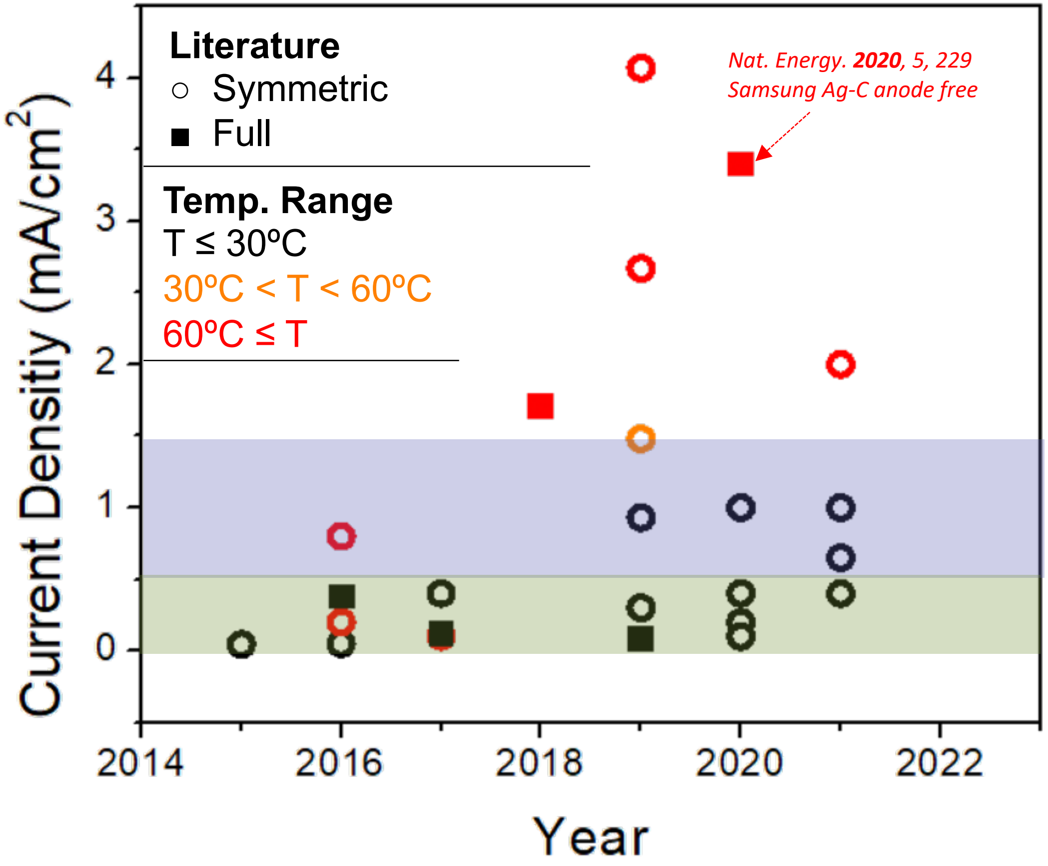
> 1000h: No short-circuit

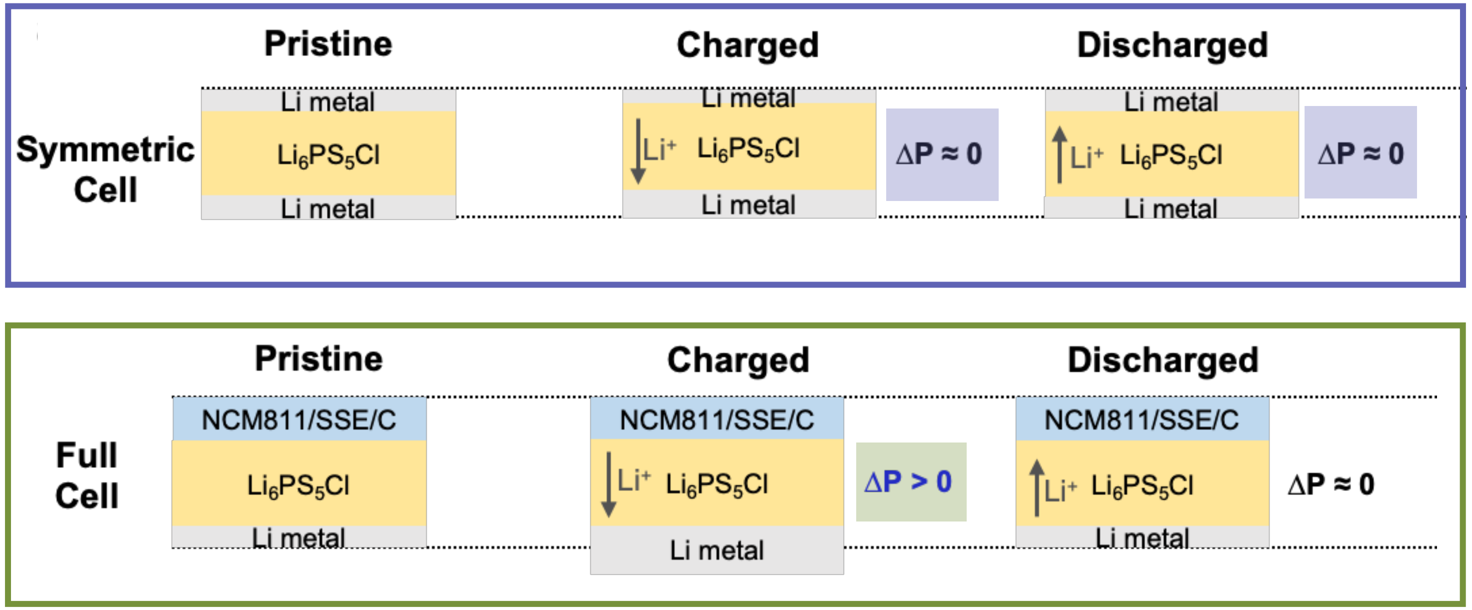


Doux, J.-M.; Nguyen, H.; Meng, Y. S. *et al.,* Stack Pressure Considerations for Room-Temperature All-Solid-State Lithium Metal Batteries. *Adv. Energy Mater. 10,* 1903253, **2020**.

Reported Critical Current Densities of Li Metal ASSB

Ham and Meng et al. *Energy Storage Material. 2023*



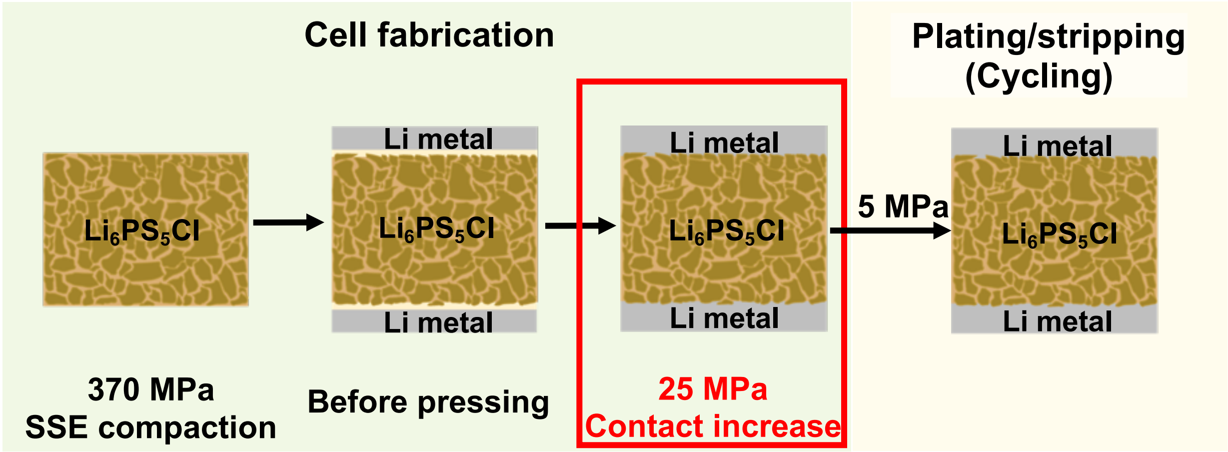


- Critical current density: Symmetric > Full
- Near room temperature full cell: < 1 mA/cm^2
- Pressure change: Symmetric < Full

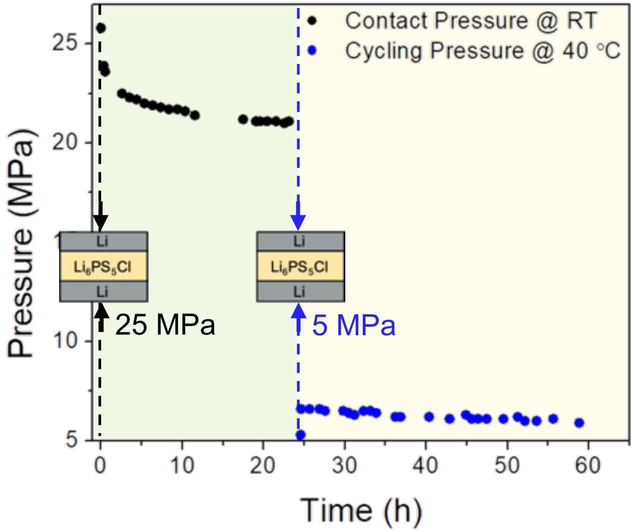
Li Metal Symmetric Cell: Cell Fabrication/Contact

Ham and Meng et al. *Energy Storage Material. 2023*

Li Metal Symmetric Cell Fabrication & Cycling Process



Pressure Monitoring of Li Metal Symmetric Cell



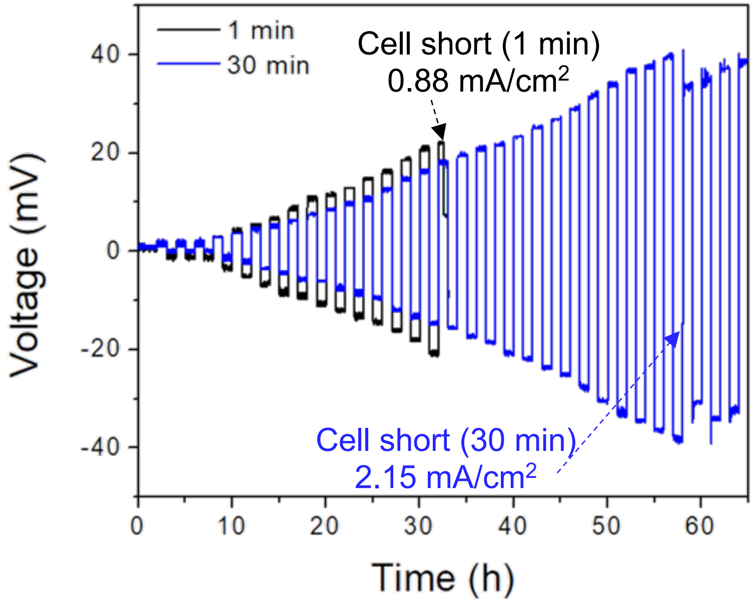
- Three different pressures applied during the fabrication/cycling process
  1. SSE compaction pressure = 370 MPa
  2. Contact pressure = 25 MPa
  3. Cycling pressure = 5 MPa

- Contact Pressure:
  Rapid drop during initial 30 min → Gradual decrease afterward
- Cycling (plating/stripping):
  No significant pressure change

Li Metal Symmetric cell: CCD/Failure

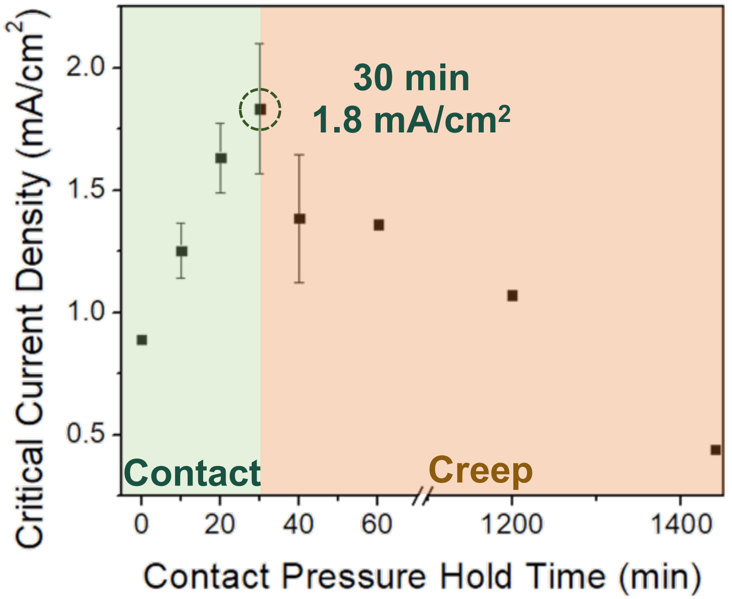
Ham and Meng et al. *Energy Storage Material. 2023*

Ramping Test of Different Contact Time Cells



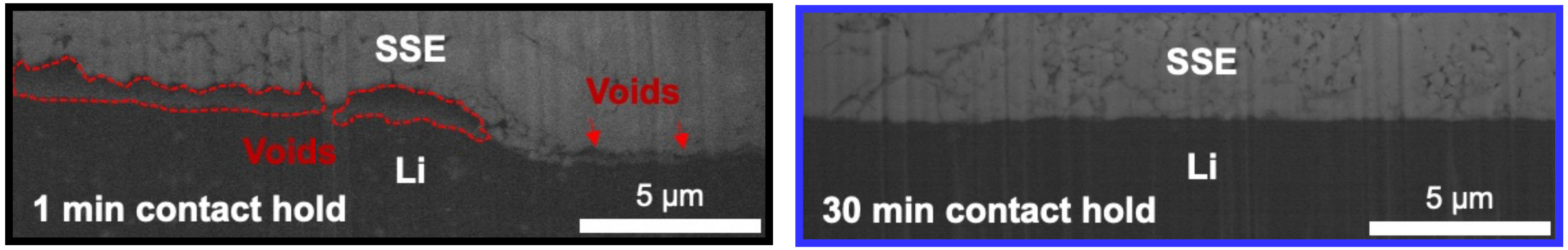
- Ramping test for CCDs of symmetric cells
- Higher CCD in 30 min contact hold sample

Ramping Test of Different Contact Time Cells



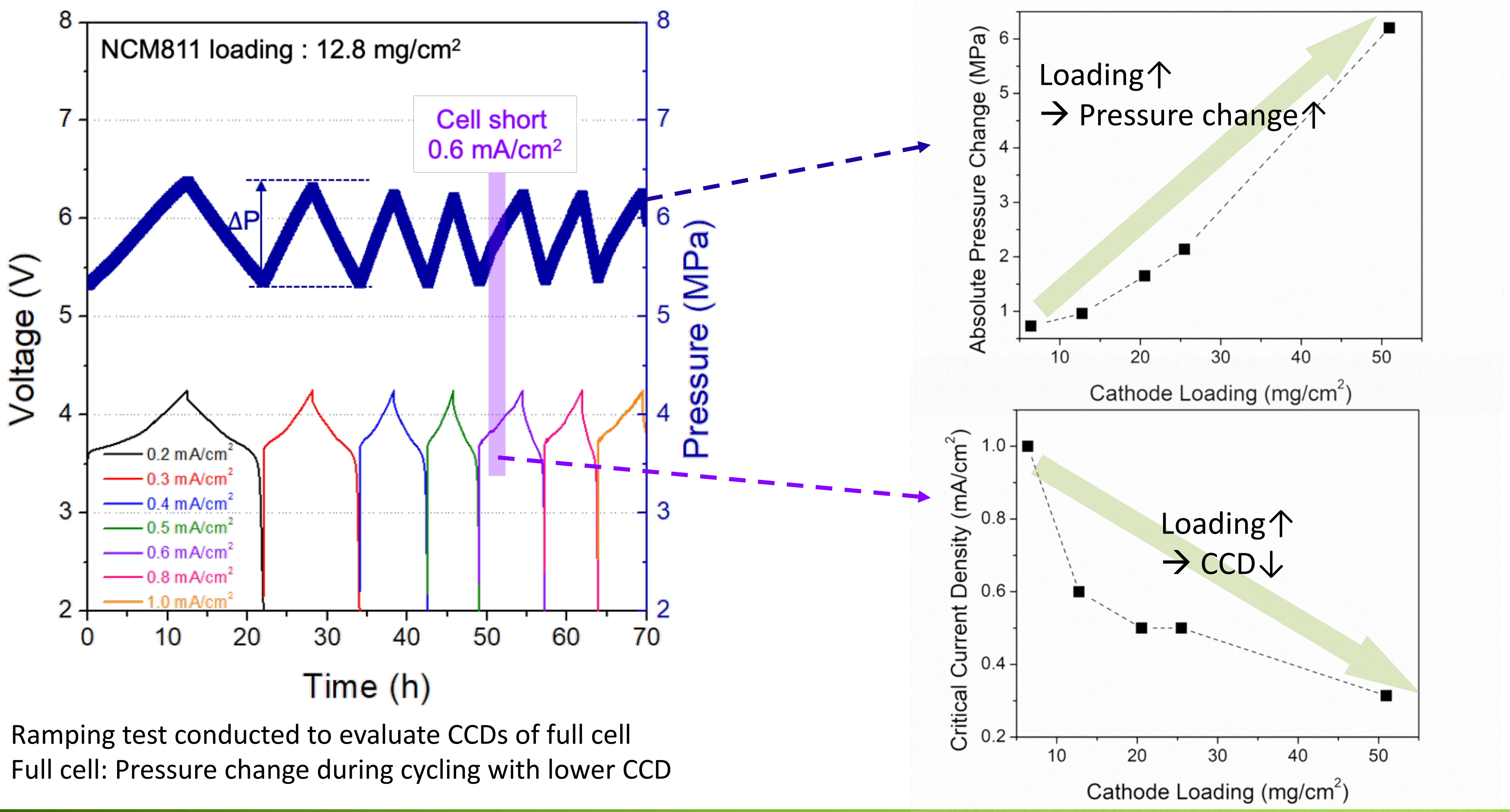
- CCD trends depending on contact hold time
- CCD increase until 30 min contact, decrease afterwards

Cryo-FIB/SEM : Direct observation of Li/SSE interface



Li Metal Full Cell: Pressure Dependence

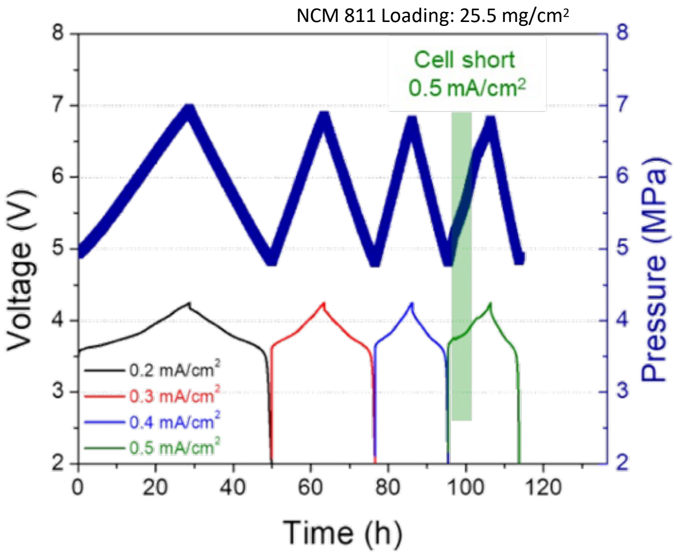
Ham and Meng et al. *Energy Storage Material. 2023*

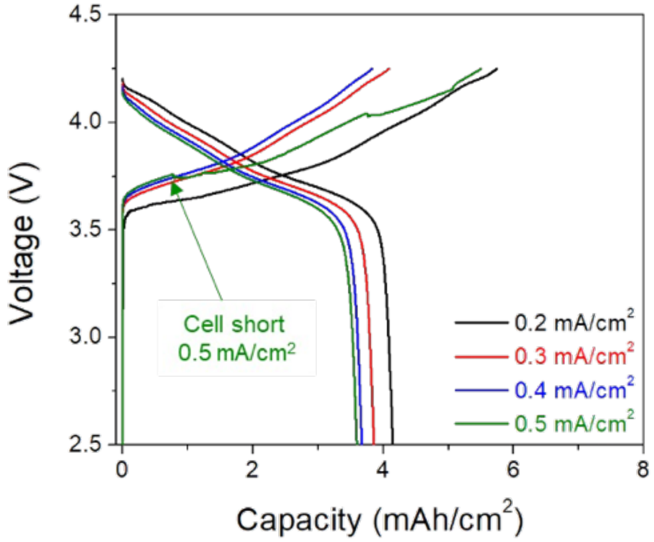


- Ramping test conducted to evaluate CCDs of full cell
- Full cell: Pressure change during cycling with lower CCD

Full Cell: Fixed Gap vs. Constant Pressure

Fixed gap

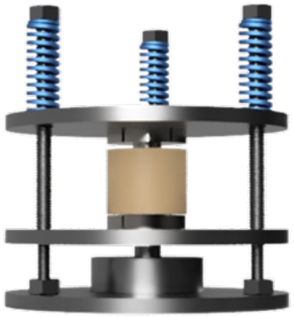


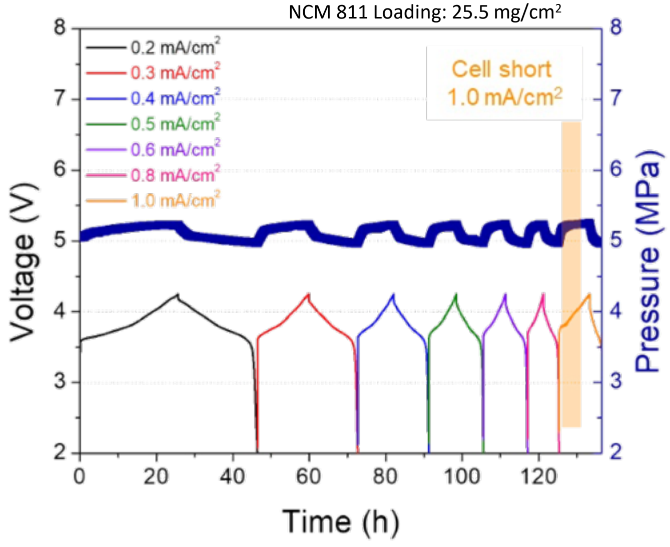


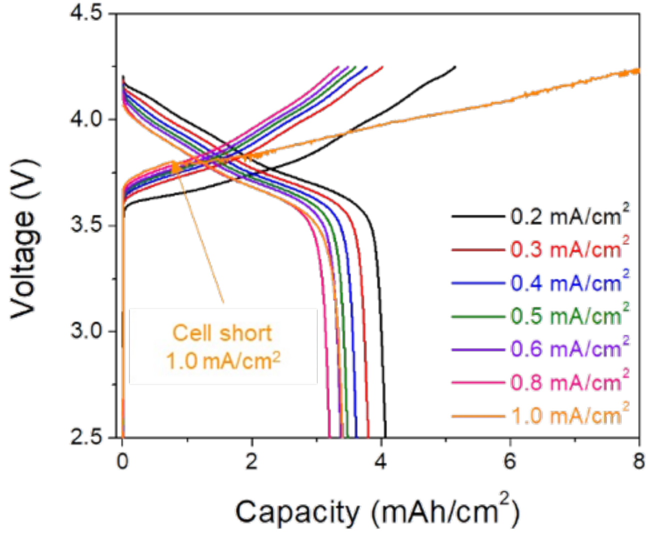
Lower pressure change and higher CCD in const pressure setup

Constant Pressure Set-up
for the volume change compensation

Constant pressure



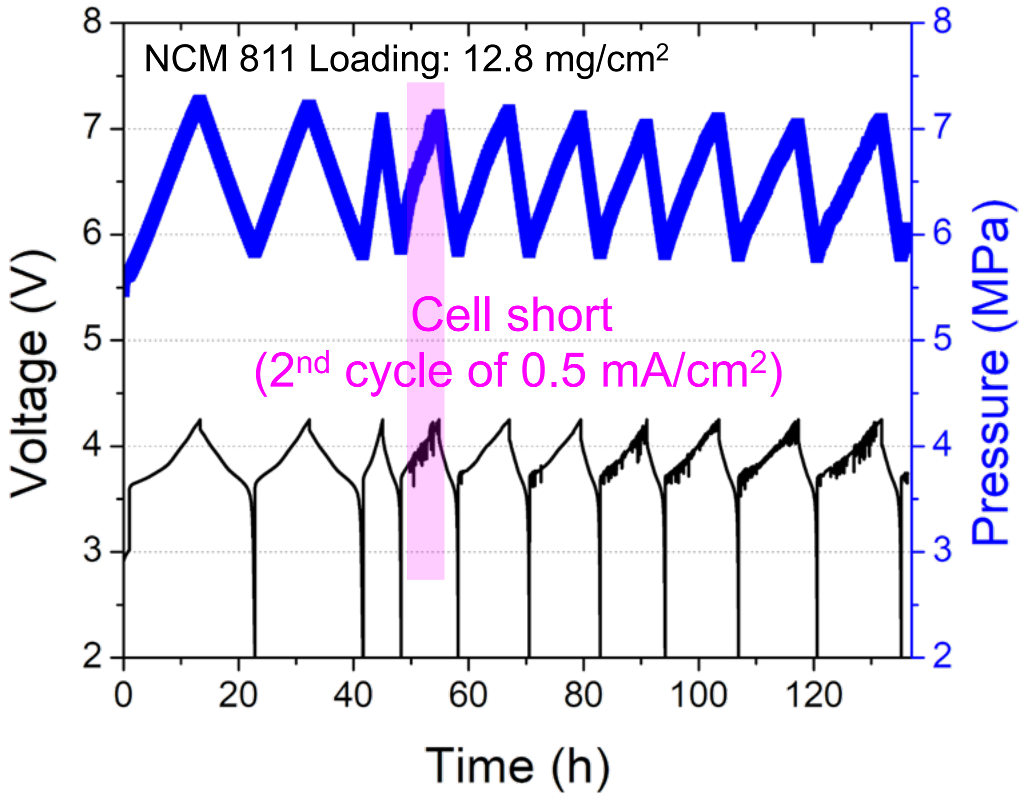




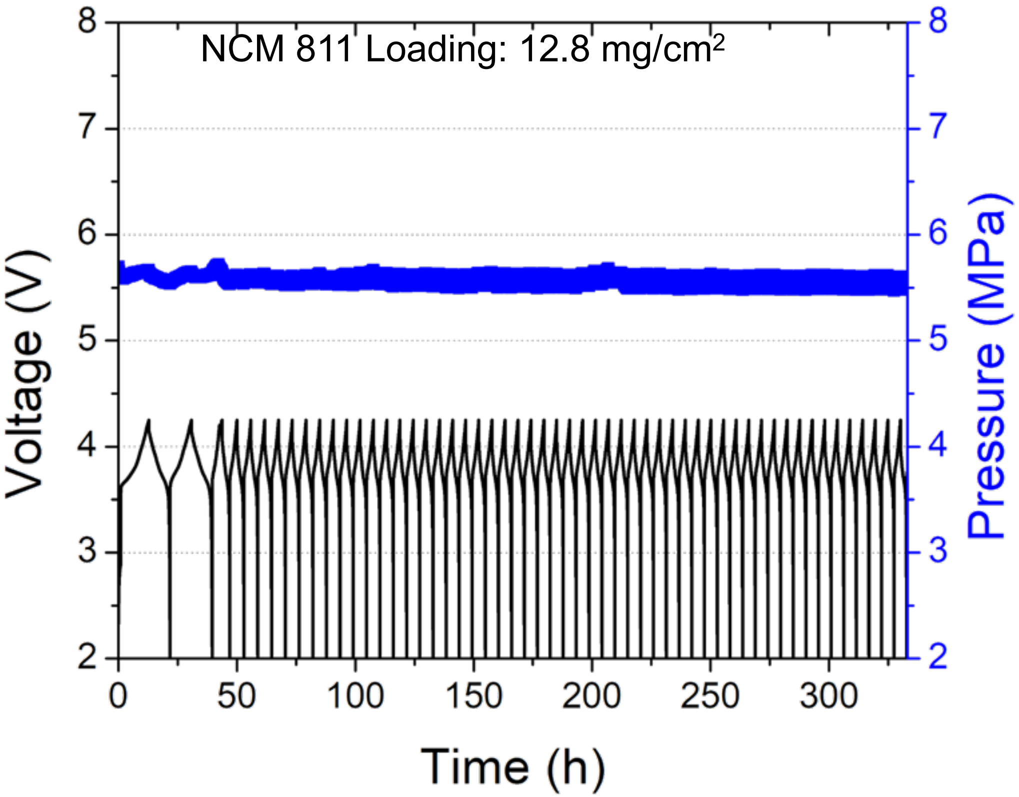
Long-term Cycling of Constant Pressure Setup

Ham and Meng et al. *Energy Storage Material. 2023*

Fixed gap



Constant pressure



LG Energy Solution

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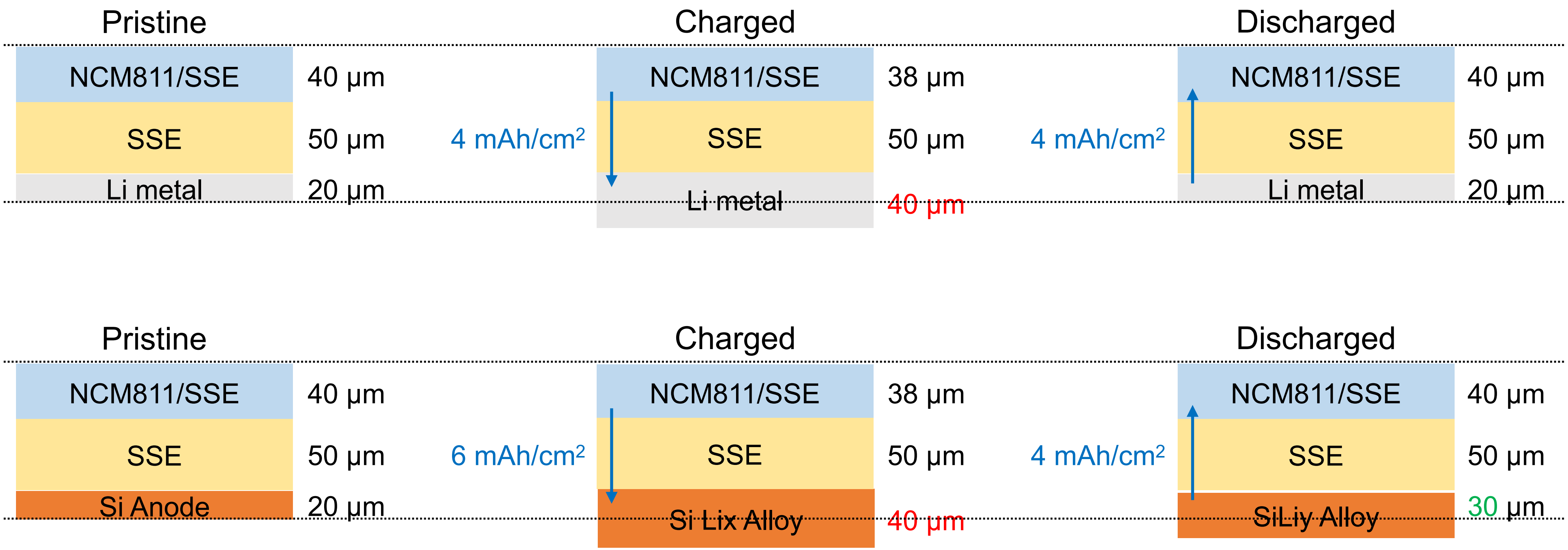
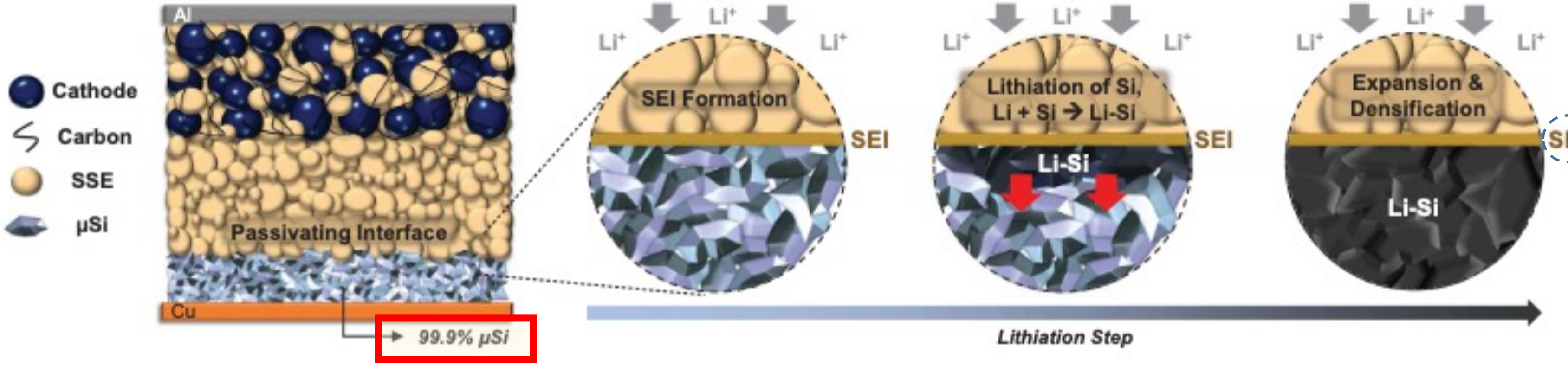
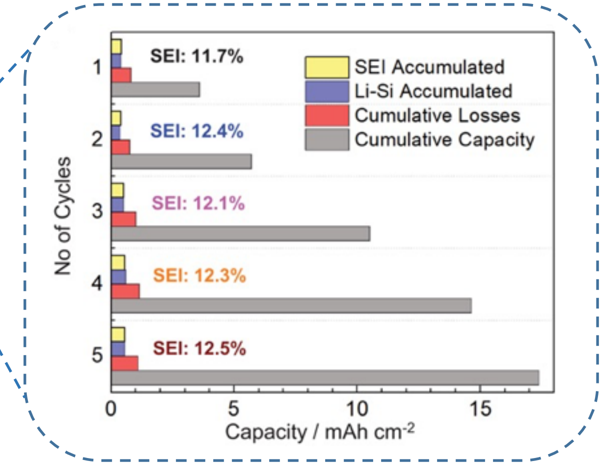
Si Has a Chance to Reduce Volume Changes

Volume expansion in full cell



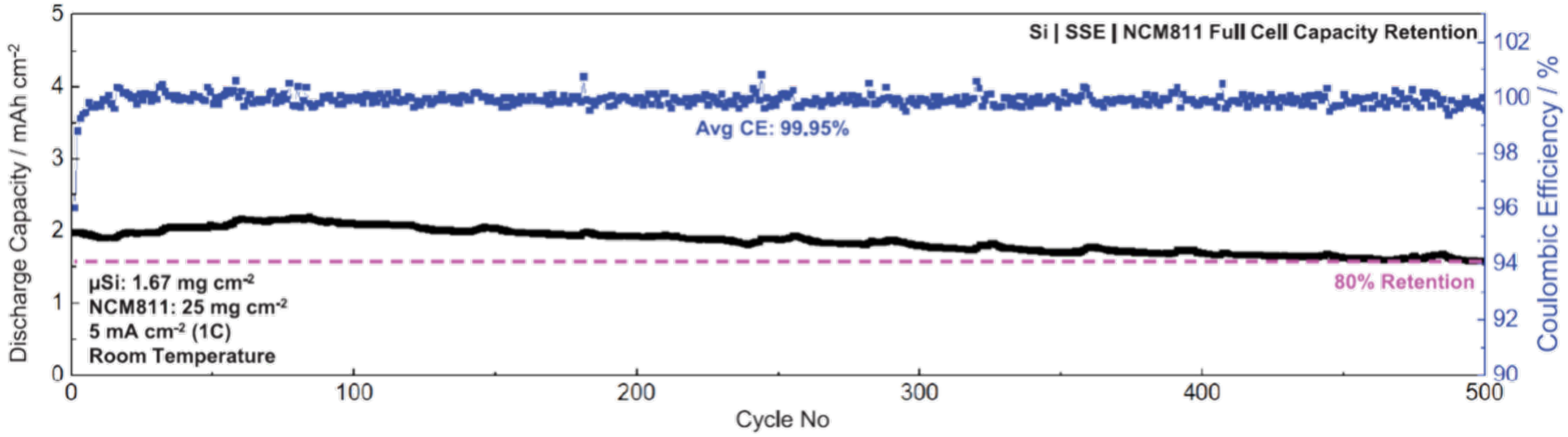
Si Anode Synergy in Solid-State Batteries



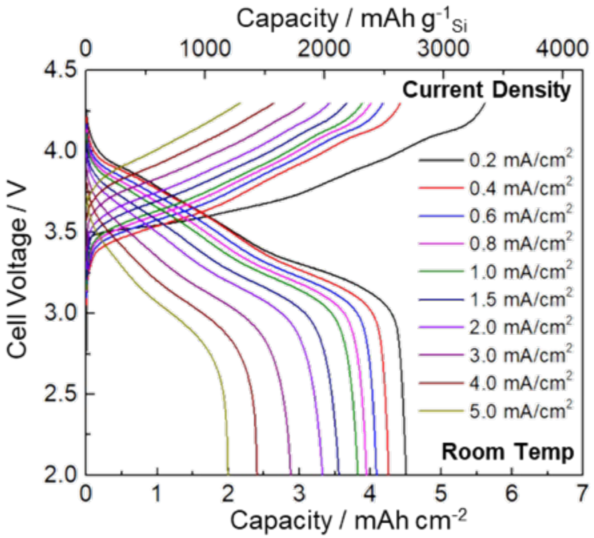


- Enable **99.9%** Si anode without carbon and solid electrolyte
- Inventory loss to the passivating SEI remained relatively constant
- Realized Si cycling >500 cycles

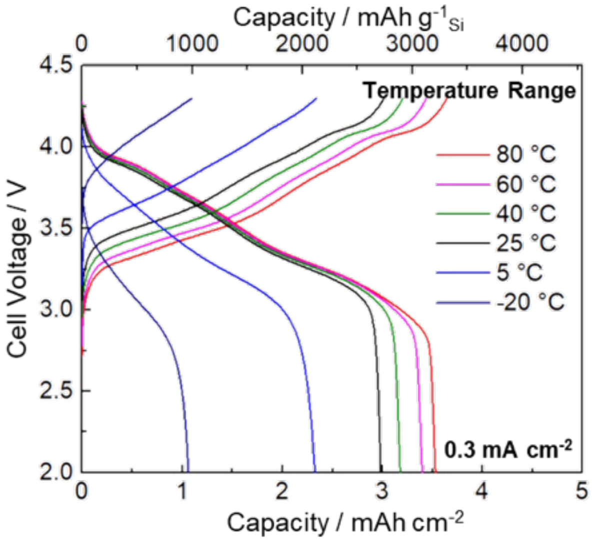
However, it is paramount to *improve the initial Coulombic efficiency (~76%)* to achieve high energy density all-solid-state batteries



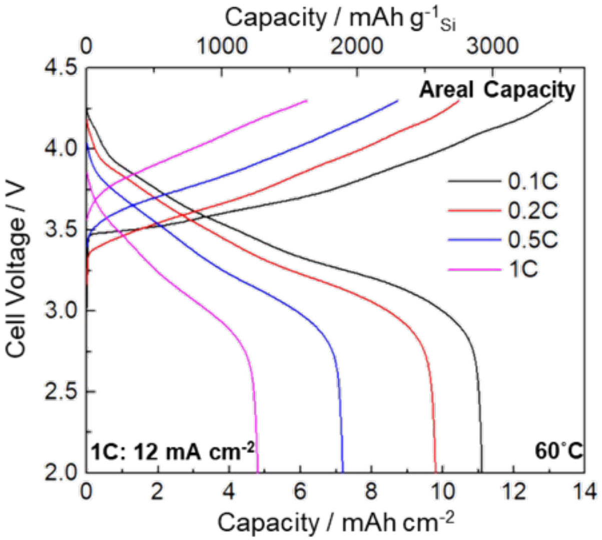
Electrochemical performance



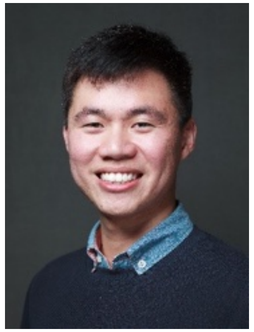
High Current Density



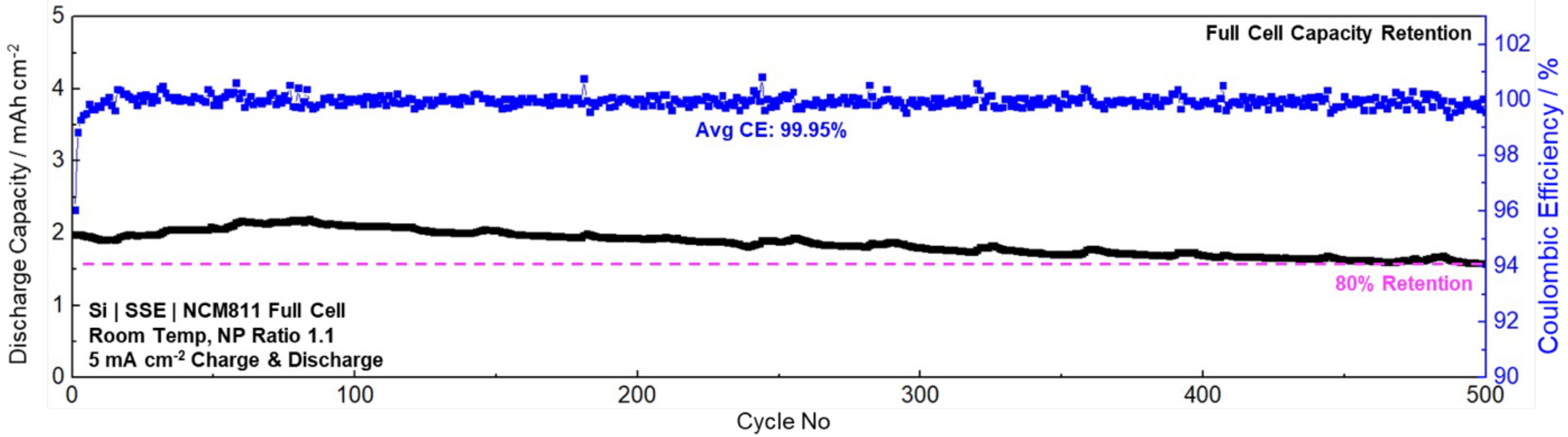
Wide Temperature Range



High Loading



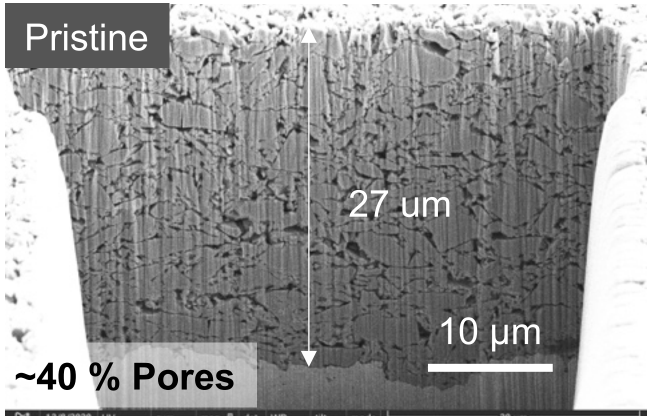
Dr. Darren Tan

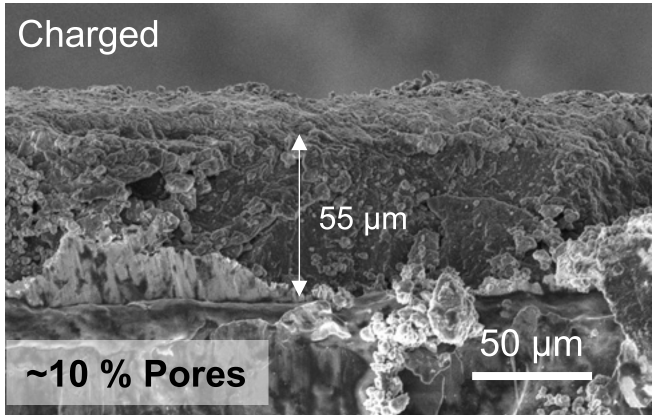


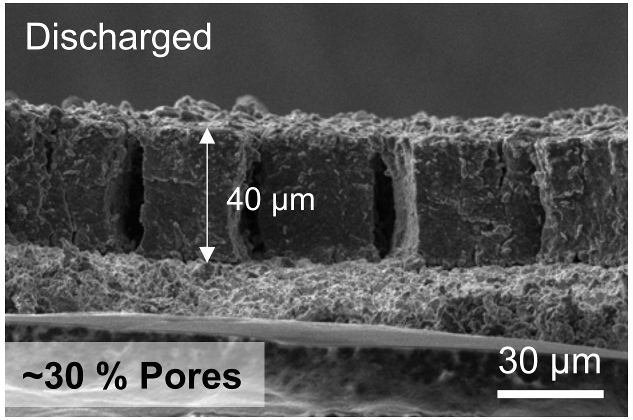
Tan, D.; Meng, Y. S. *et al.,* Carbon Free High Loading Silicon Anodes Enabled by Sulfide Solid Electrolytes for Robust All Solid-State Batteries. (*Science 2022*)

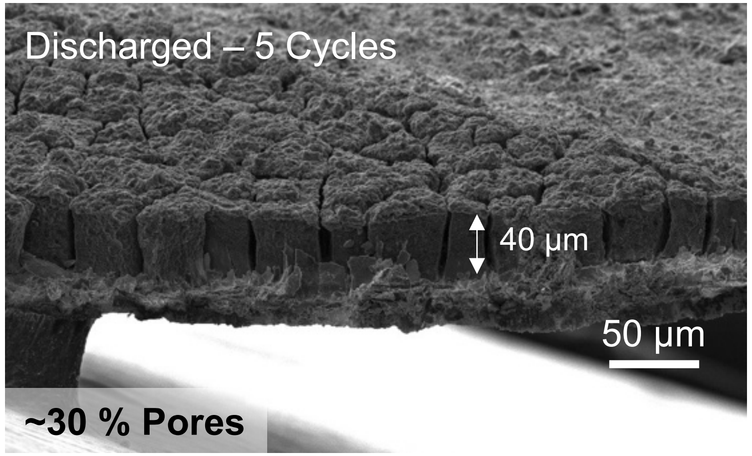
Porosity changes during cycling

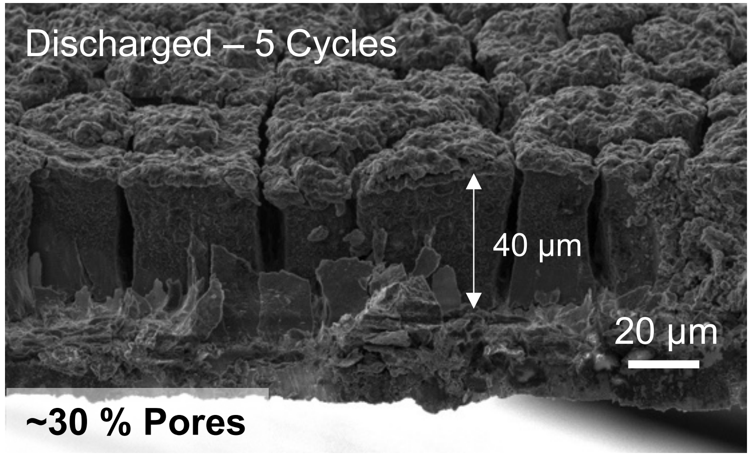
~3.8 mg cm^{-2} – 12 mAh cm^{-2}











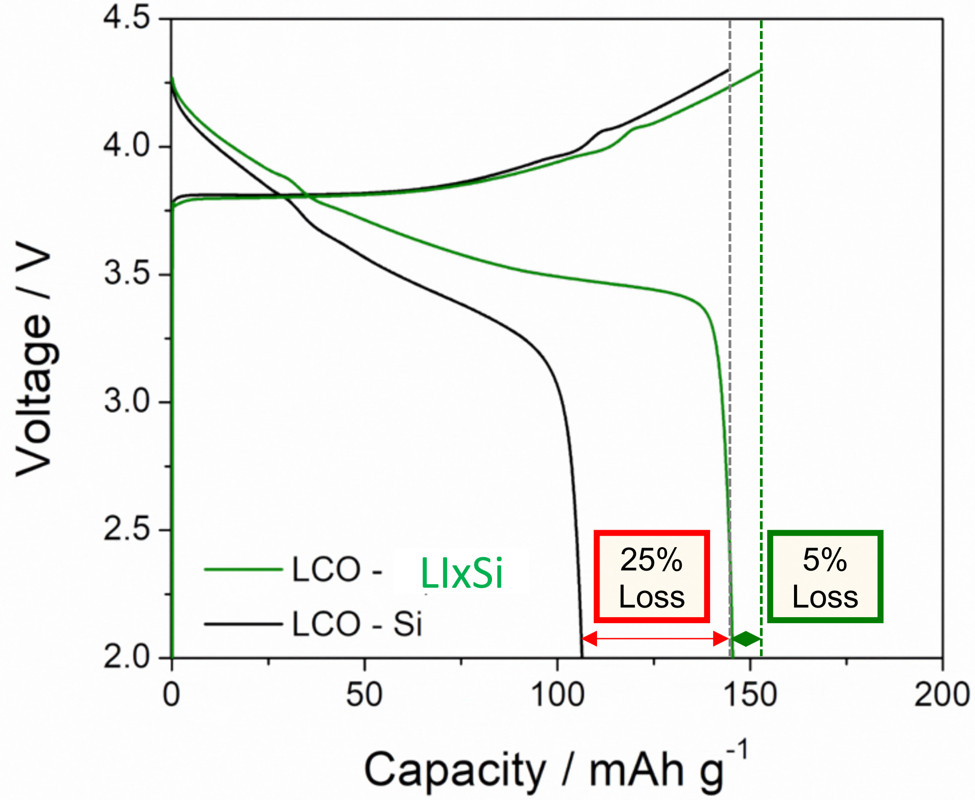
Tan, D.; Meng, Y. S. *et al.,* Carbon Free High Loading Silicon Anodes Enabled by Sulfide Solid Electrolytes for Robust All Solid-State Batteries. (*Science 2021*)

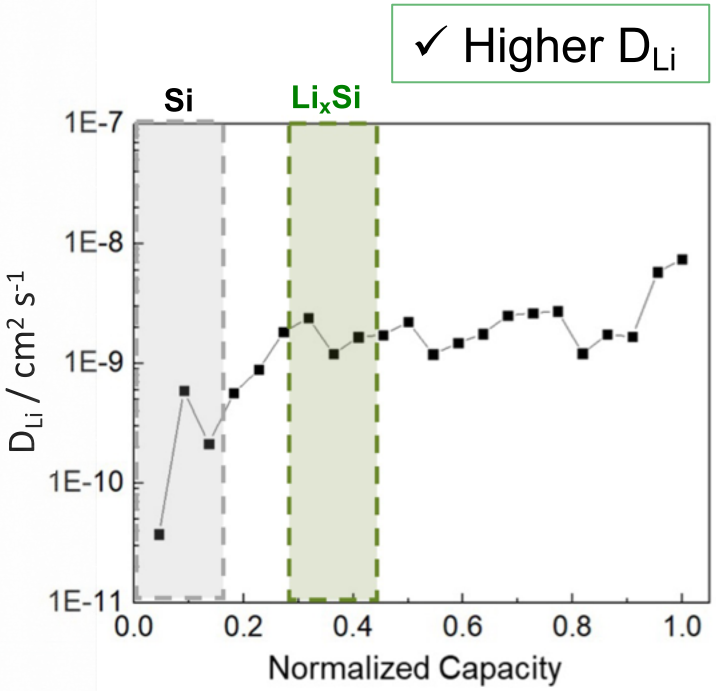
LG FRL - Anode Strategies

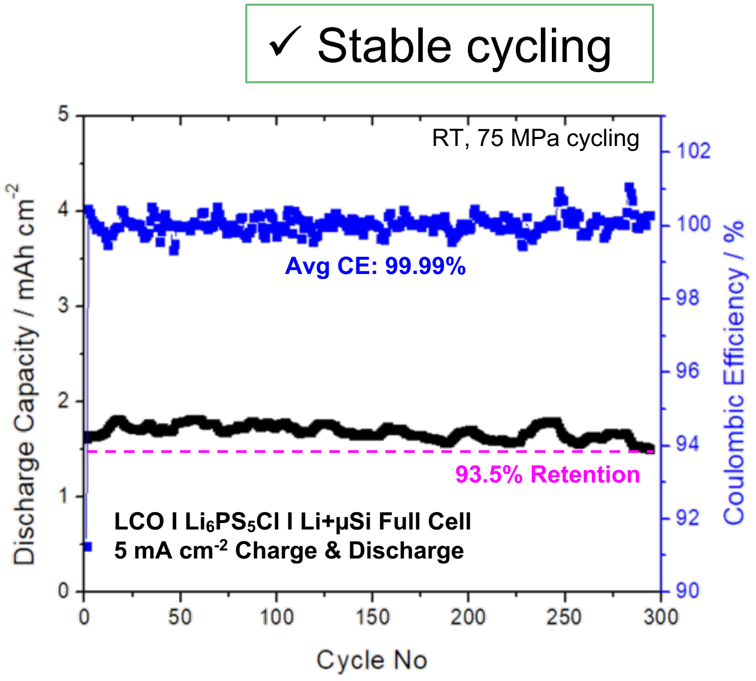
LGES-UCSD Frontier Research Laboratory

❑ 1^{st} Year Achievement

- Enhanced ICE
- Higher D_{Li} and stable cycling







So Yeon Ham et. al. To be Submitted 2023

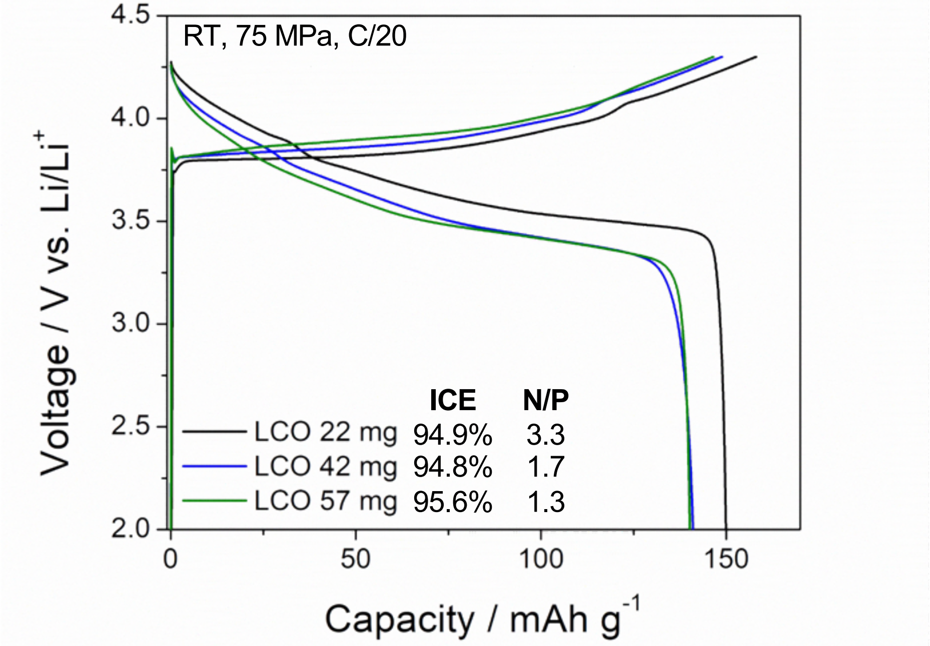
LGES-UCSD Frontier Research Laboratory

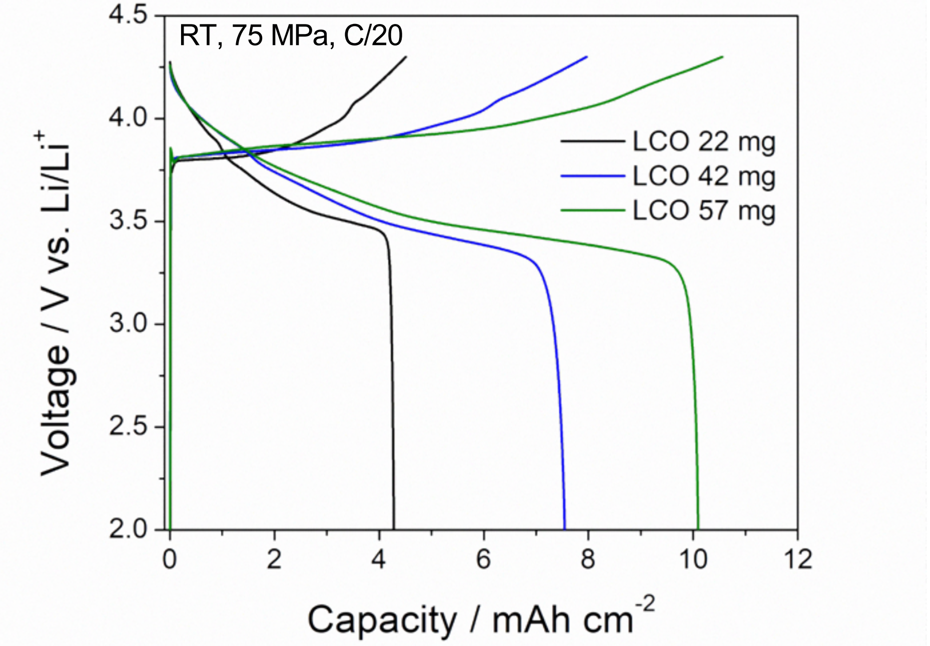
Prelithiation of Si – Unlock 10mAh/cm2 Capacity

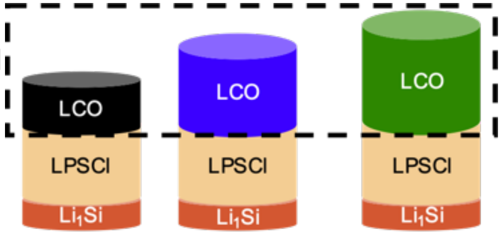
So Yeon Ham

Higher LCO loading cells by stacking dry films paired with 5 mg of lithiated Si (Li_1Si)

- Similar ICE for all loadings





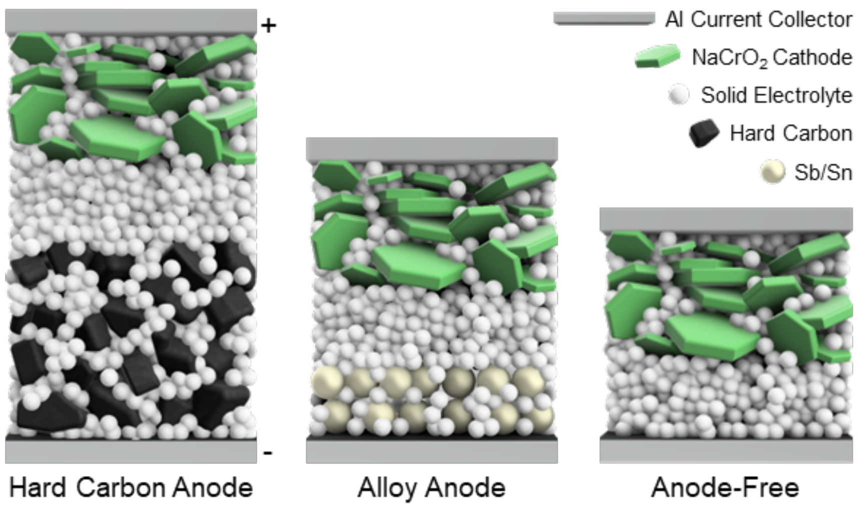


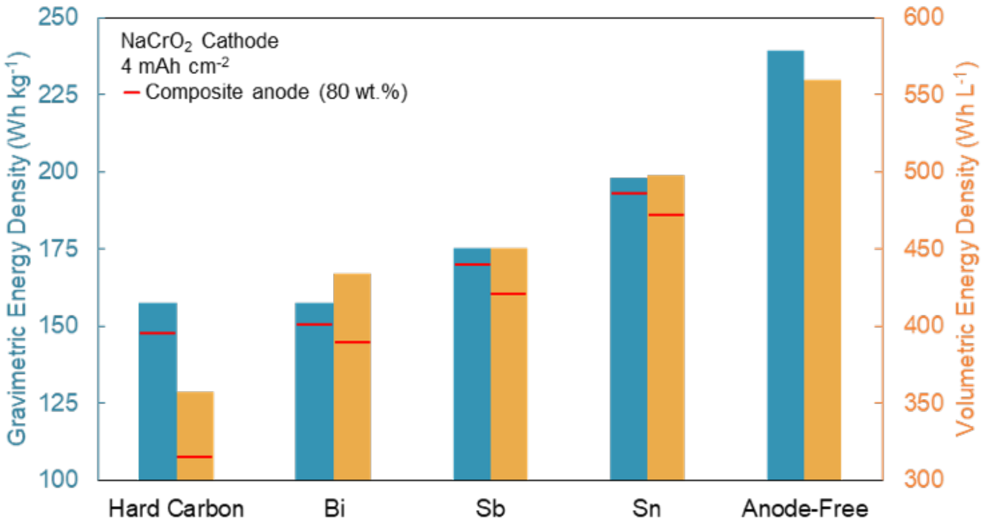
- Higher polarization for high loading but still achieved 140 mAh/g
- 5 mg lithiated Si enough for areal capacity of 10 mAh cm^{-2} discharge capacity

Ham *et al.*, "Effective prelithiation of micro-silicon in all-solid-state batteries", *Manuscript in preparation*

Anode Selection → Anode-Free Game Changing for Na ASSB

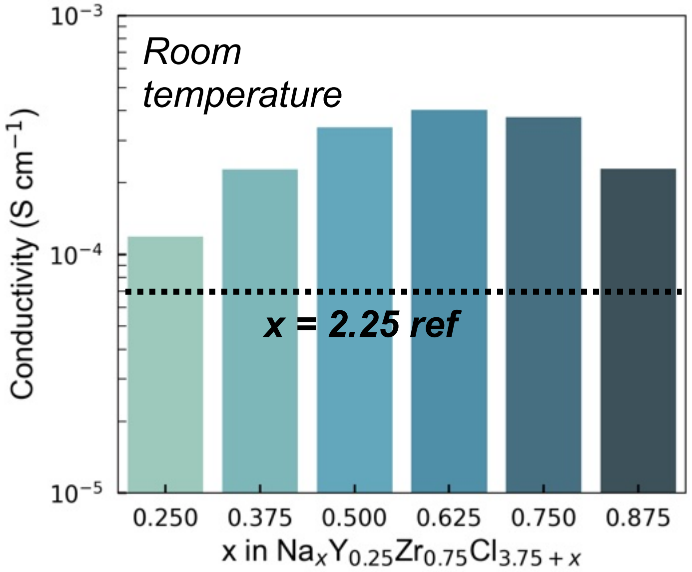
- "Anode-Free": Na/Li metal is directly deposited onto the current collector surface



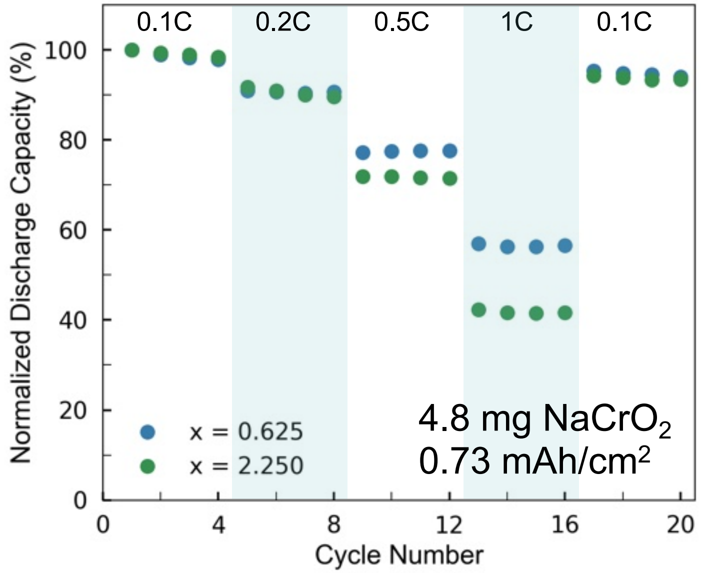


- Anode-Free can achieve significantly higher energy density
  - Zero weight and volume
  - Lowest reduction potential → highest cell voltage

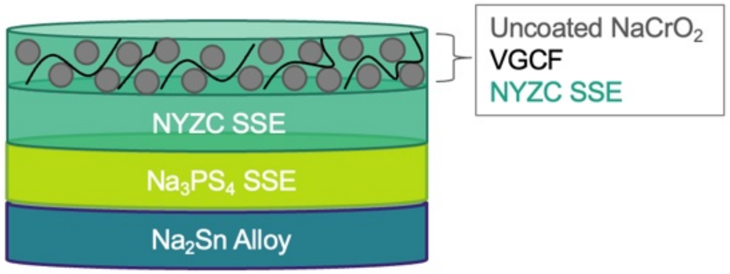
Improved Room Temperature NaASSB

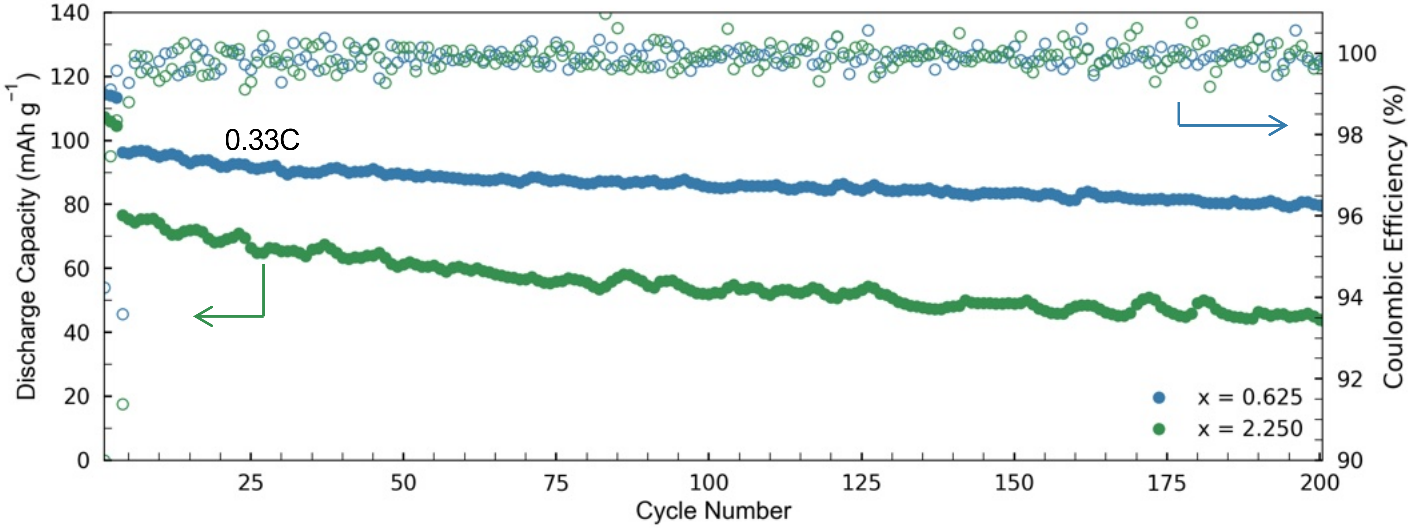


- Amorphous electrolyte → *Higher conductivity* → **improved capacity utilization** at room temperature
- Owed to *reduced crystallinity* → **free volume** & preferential population of **prismatic Na environments**



$Na_{2.25}Y_{0.25}Zr_{0.75}Cl_6$ (**x = 2.25**)
$Na_{0.625}Y_{0.25}Zr_{0.75}Cl_{4.375}$ (**x = 0.625**)



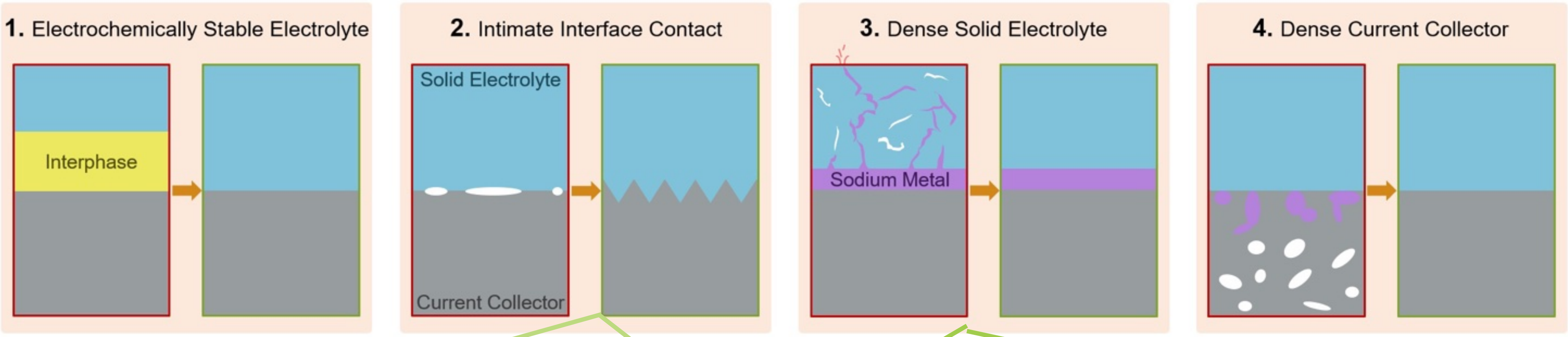


Ridley, Phillip, et al. "Glass-Ceramic Sodium-Deficient Chlorides with High Sodium-ion Conductivity." (Under Review 2023).

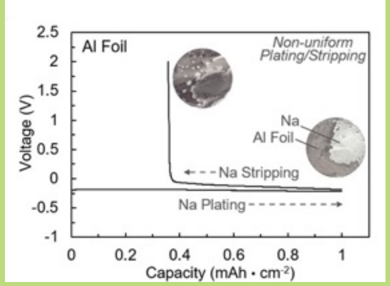
Patent Pending

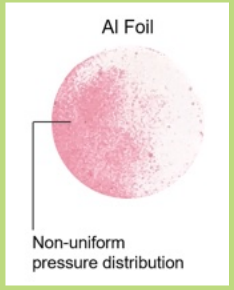
Anode-Free Solid-State Sodium S^3Batteries

Cell architecture criteria to realize an anode-free ASSB

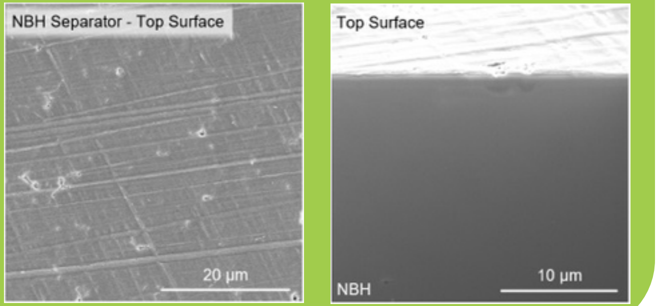


Poor interface contact





Dense morphology



Ability to deposit
40um Dense Sodium !!!

NSF 2010-now
Sodium Battery

Acknowledgements First

DOE VTO
Li Metal and Cathode Interfaces

DOE BES 2
LiPON SSB and Cryo EM

LG Energy Solution

LGES-UCSD Frontier Research Laboratory

Workflow design for battery
Next-gen Cryo EM for Energy and Quantum materials
Falcon Camera etc.

Sustainable Power and Energy Center

MTI KJ GROUP

Thermo Fisher SCIENTIFIC

Battery Prototyping

sdni San Diego Nanotechnology Infrastructure

nano3 SCIENCE ENGINEERING MEDICINE

IMRI UC IRVINE MATERIALS RESEARCH INSTITUTE

Solid State Battery Team at LESC group