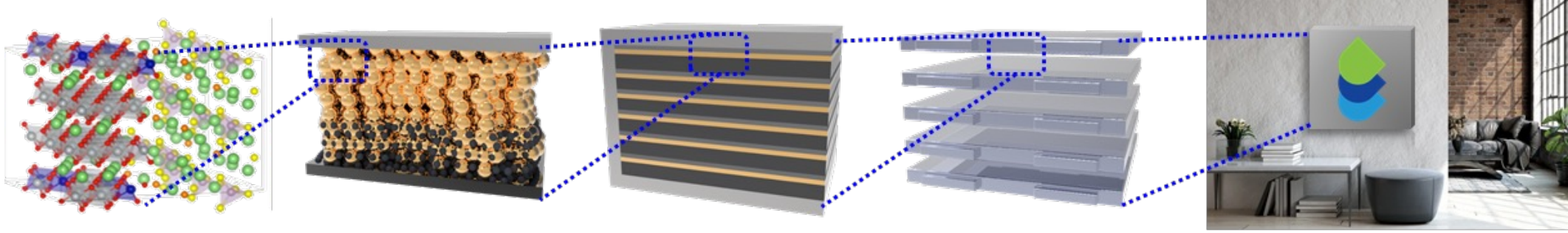
LESC
Laboratory for
Energy Storage and Conversion



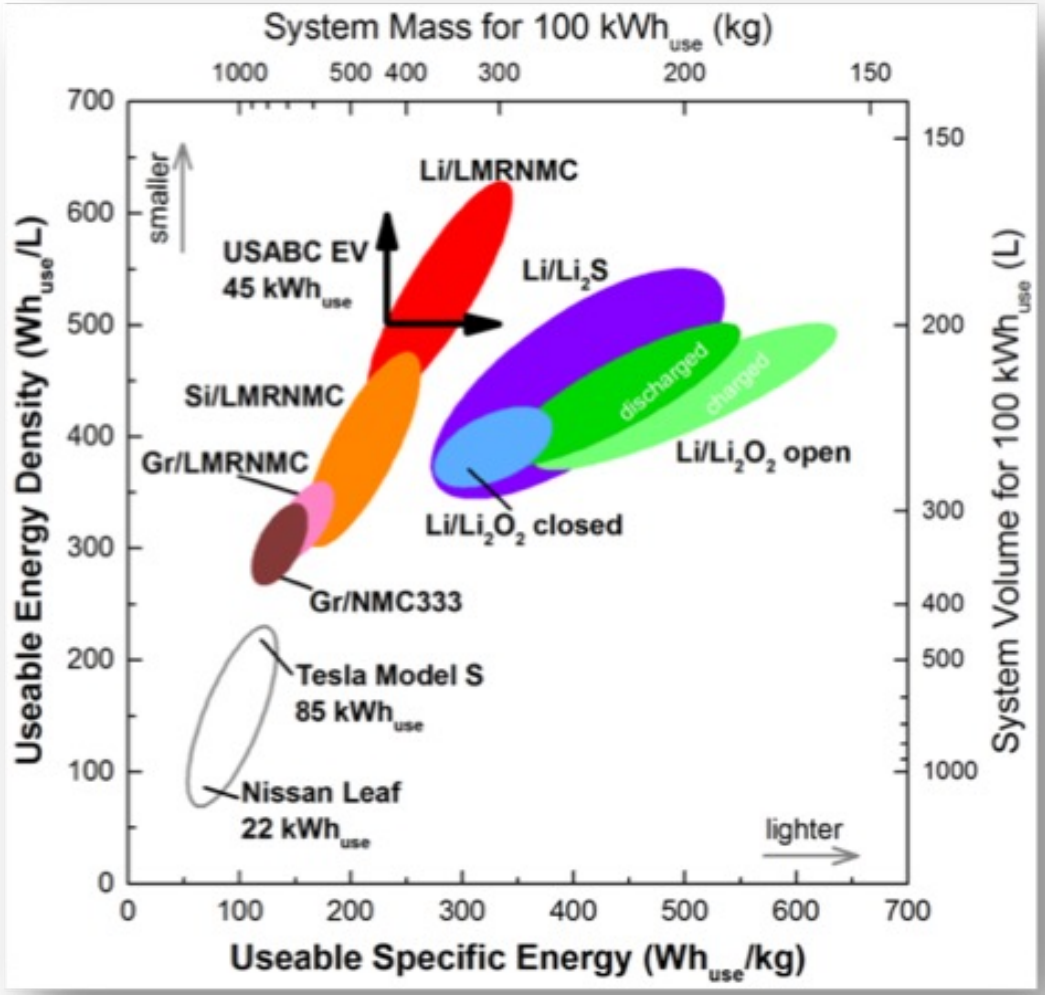
Understanding the Interphasial Phenomena in ALL SOLID State Batteries

Y. Shirley Meng

University of Chicago
University of California San Diego

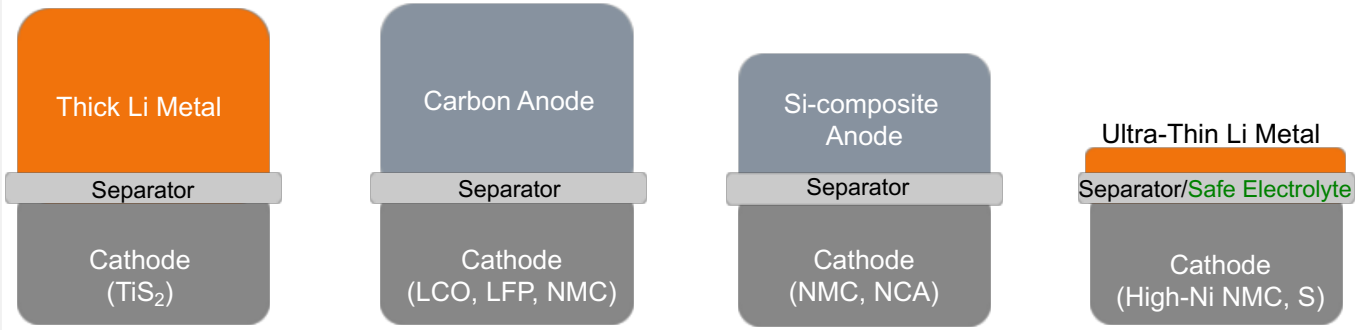
LIB will dominate, why bother with All Solid-State Battery?

What We have Achieved



Courtesy of Argonne National Lab

- **Tripled the Energy Density - 18650 Cylindrical Cell 1Ah → 3Ah**
- **Lowered the Cost 10 Times - 2005 (2000$/kWh) Today (<150$/kWh)**
- **Extended Cycle Life - 300 cycles to 3000 cycles deep DOD**
- **>1TWh/yr worldwide production capacity – will 10X Soon**
- **Recycling and Reuse of LiB - Happening!!!**



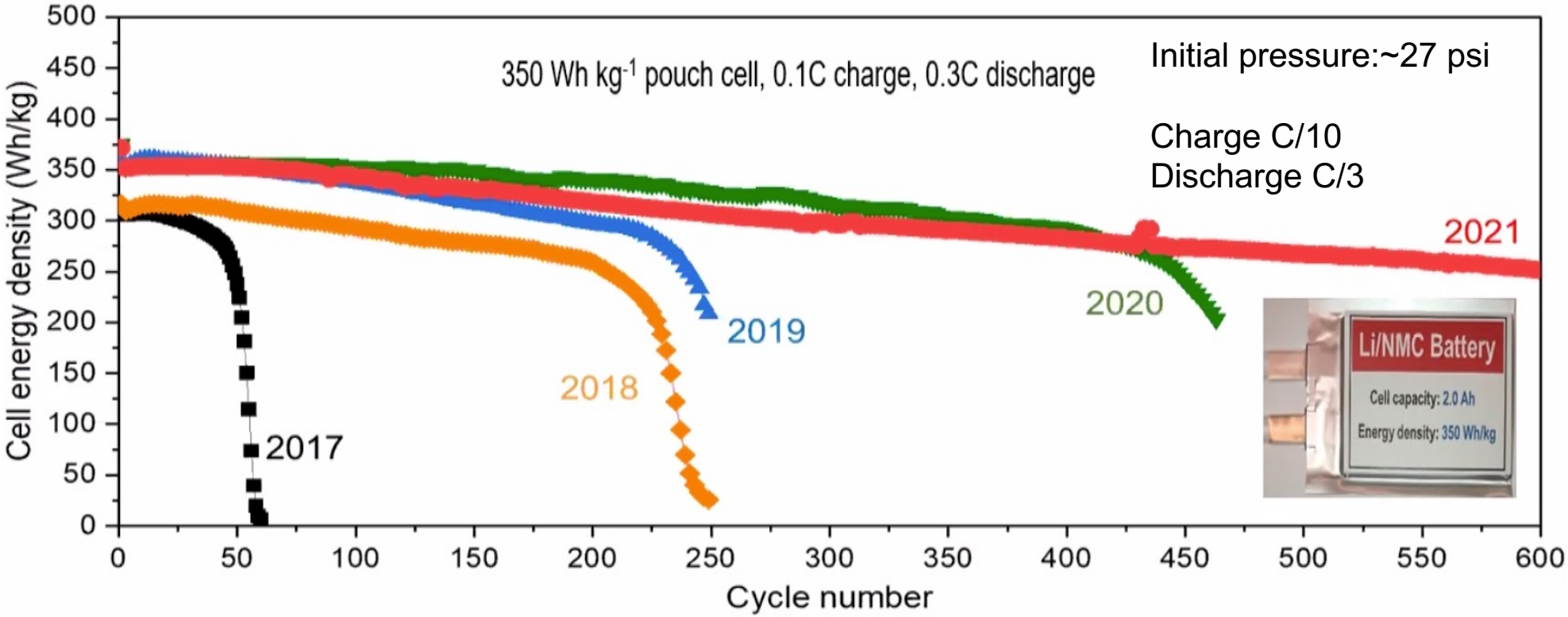
Gen 0
Li-Metal
100-200 Wh/kg
200-300 Wh/L
Dangerous

Gen 1
Li-ion
200-250 Wh/kg
600 Wh/L
Safe

Gen 2
Li-ion
250-300 Wh/kg
700 Wh/L
Safe

Gen 3
Li-Metal
400-500 Wh/kg
1200 Wh/L
Safe

Stable Cycling of 350 Wh/kg Li/NMC622 Pouch Cell



Commercialization

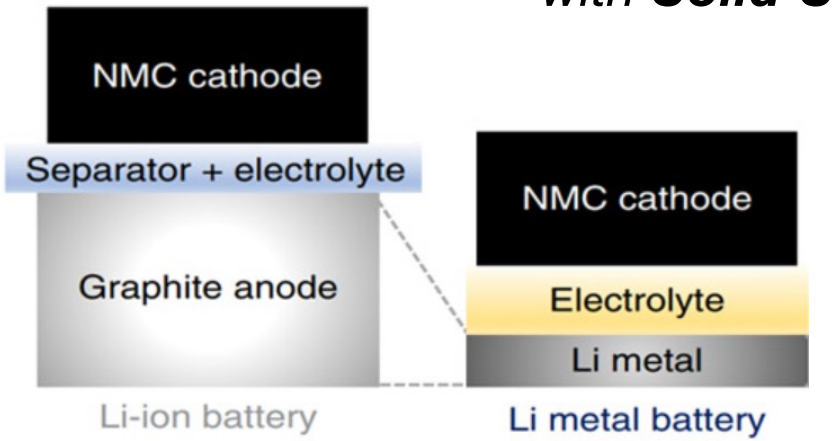
SES
Factorial
Cuberg
QuantumScape

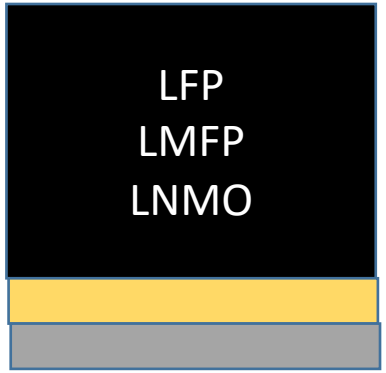
- Prototyping Li metal pouch cells demonstrate stable cycling: >550 cycles with 80% capacity retention (still under testing). Pouch cells are 2Ah in size and they can be produced by batches.
- A great platform to accelerate Batt500 innovation: electrode architecture, electrolyte, cell design, cell balance etc.
- Prototyping pouch cells were also shipped out for independent 3rd party validation.
- SAFETY – UNKNOWN - Risky for Startups to commercialize the technology at this point

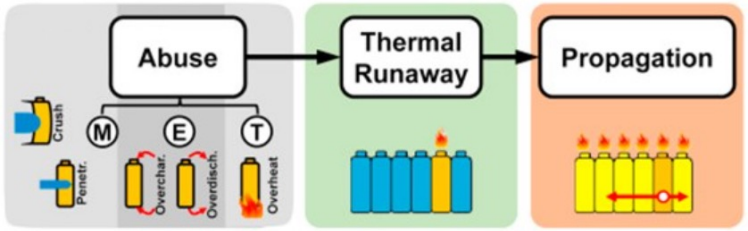
All solid-state batteries – Platform Technology

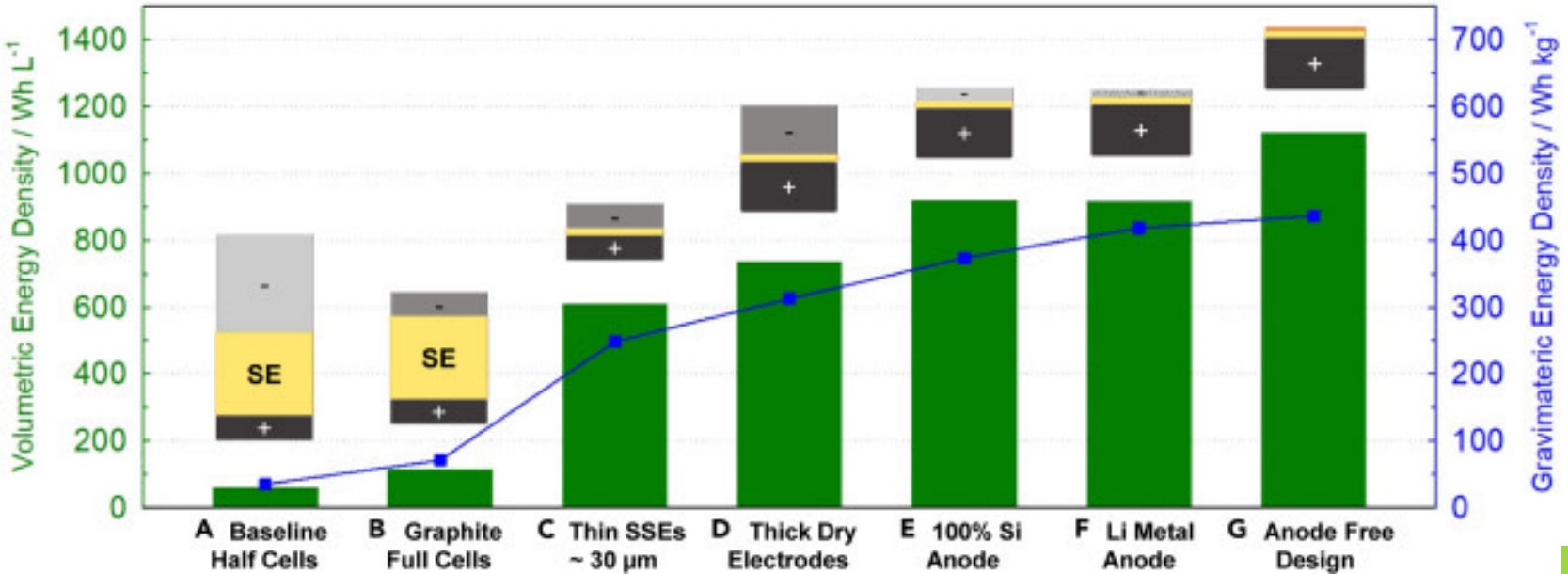
High-Energy-Density *and* ***Safe Batteries***

with ***Solid-State Electrolyte***









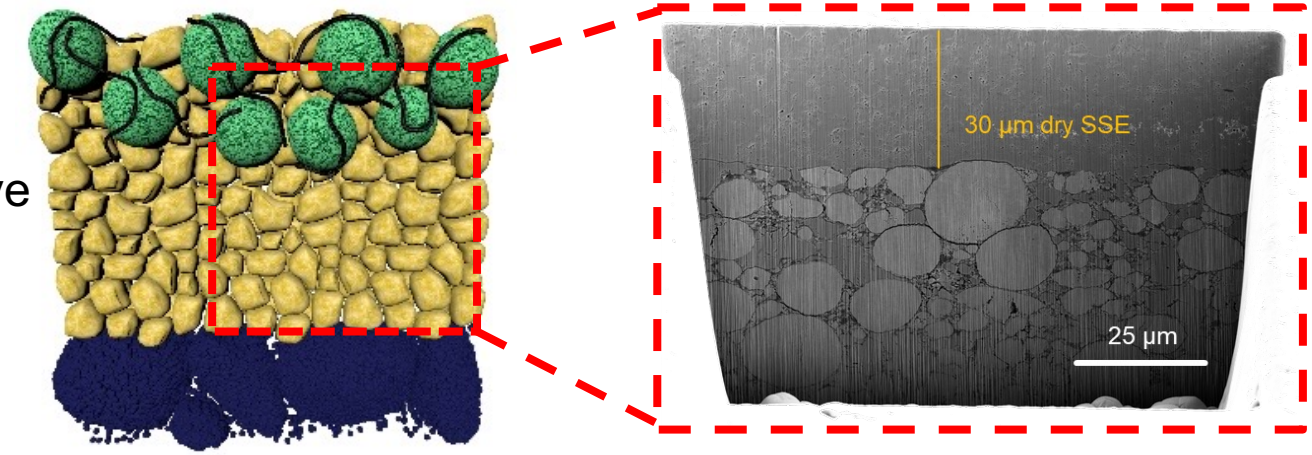
A Platform Technology Enabled by Green Manufacturing

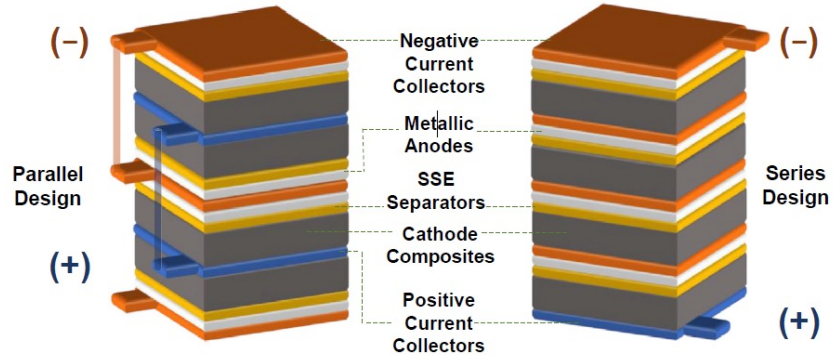
Cathode

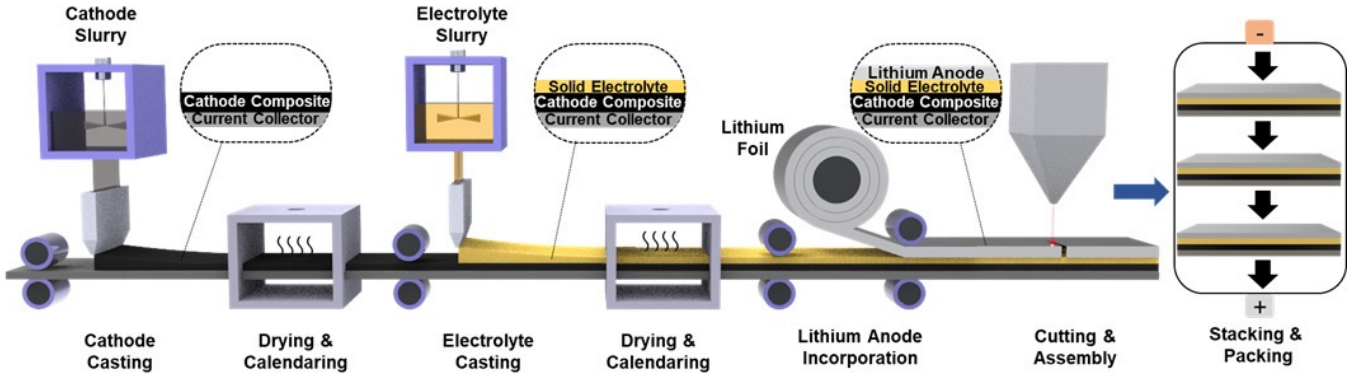
Carbon additive

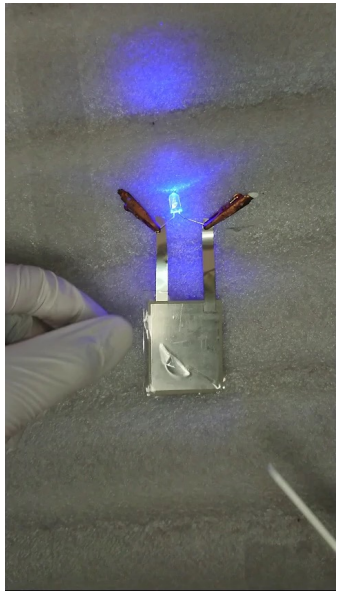
Electrolyte

Anode









Series (bi-polar) stacking:

- Reduces inactive materials components → increase energy density
- Higher overall voltage per cell

- Thin electrolyte film <30um
- High loading cathode >5mAh/cm2
- Stackable design – bipolar design
- Dry processing – green manufacturing

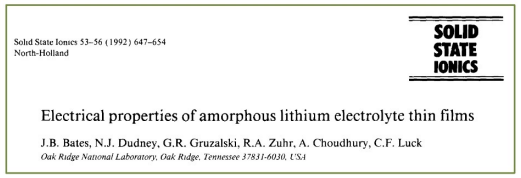
- Enhanced safety and abuse tolerance

When will All Solid-State Battery Will be Commercialized ?

Polymer based ones are already there!

A Brief (Long) History of LiPON

1992
Birth of LiPON


Solid State Ionics 53–56 (1992) 647–654
North-Holland

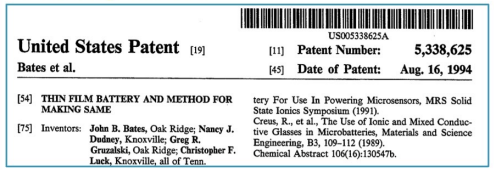
SOLID STATE IONICS

Electrical properties of amorphous lithium electrolyte thin films

J.B. Bates, N.J. Dudney, G.R. Gruzalski, R.A. Zuhr, A. Choudhury, C.F. Luck
Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6030, USA

Developed by Oak Ridge National Lab

1994
Filed patent


US005338625A

United States Patent [19]
Bates et al.

[11] **Patent Number: 5,338,625**
[45] **Date of Patent: Aug. 16, 1994**

[54] **THIN FILM BATTERY AND METHOD FOR MAKING SAME**

[75] Inventors: **John B. Bates**, Oak Ridge; **Nancy J. Dudney**, Knoxville; **Greg R. Gruzalski**, Oak Ridge; **Christopher F. Luck**, Knoxville, all of Tenn.

tery For Use In Powering Microsensors, MRS Solid State Ionics Symposium (1991).
Creus, R., et al., The Use of Ionic and Mixed Conductive Glasses in Microbatteries, Materials and Science Engineering, B3, 109–112 (1989).
Chemical Abstract 106(16):130547b.

Patent licensed to FrontEdge Technology (FET)

2000
Patent licensed to Cymbet

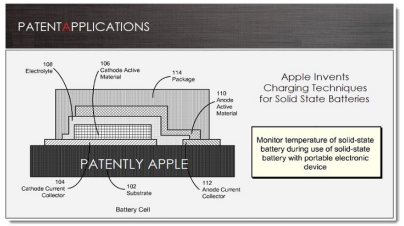
2001
Patent licensed to Oak Ridge Global Energy Solutions

2002
J.B Bates joined Oak Ridge Micro-Energy, Inc and served as director

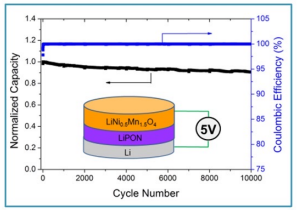
2009
ST Micro and FET started cooperation

2009
J.B. Bates resigned as CTO

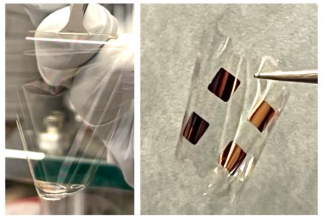
2013
Apple's patent on thin film battery



2015
LNMO/LiPON/Li full cell, 10000 cycles from N. Dudney's team



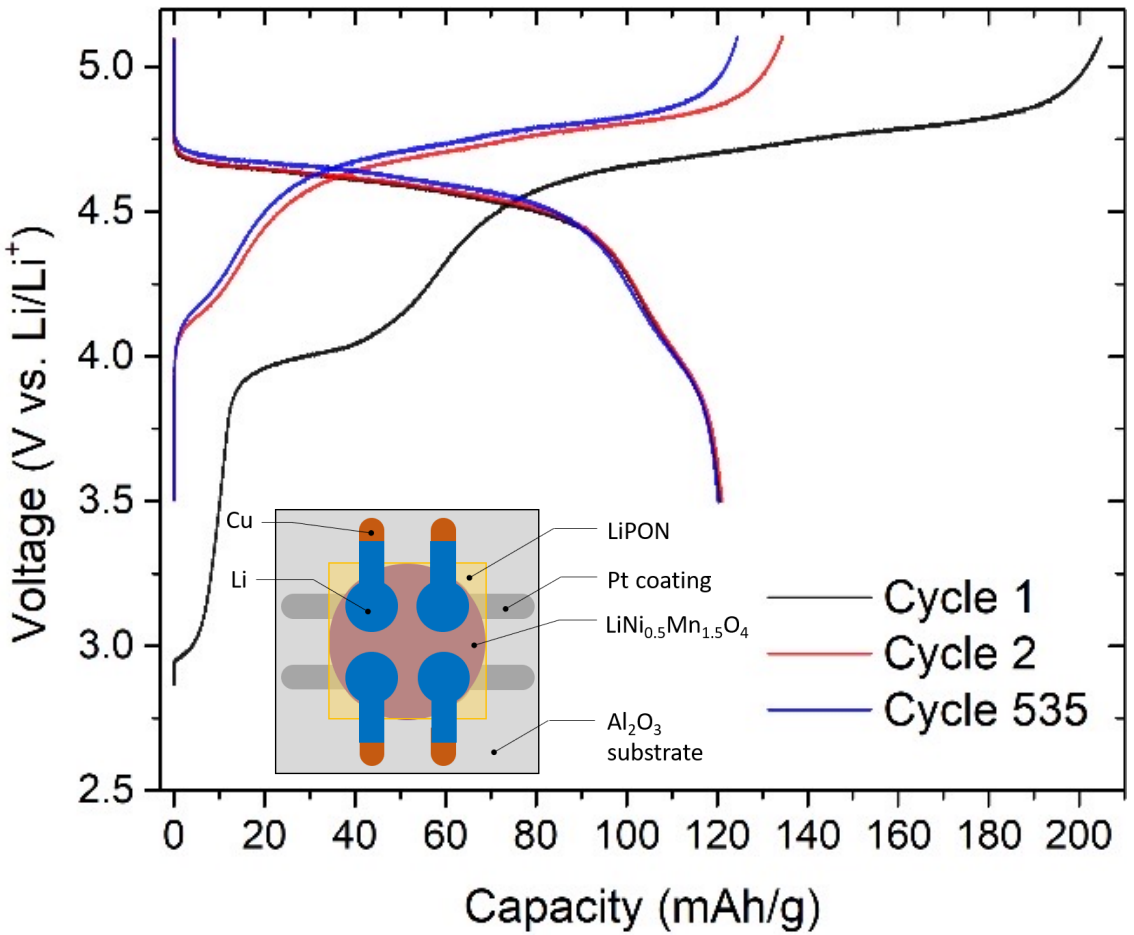
2022
Freestanding LiPON film produced in LESC

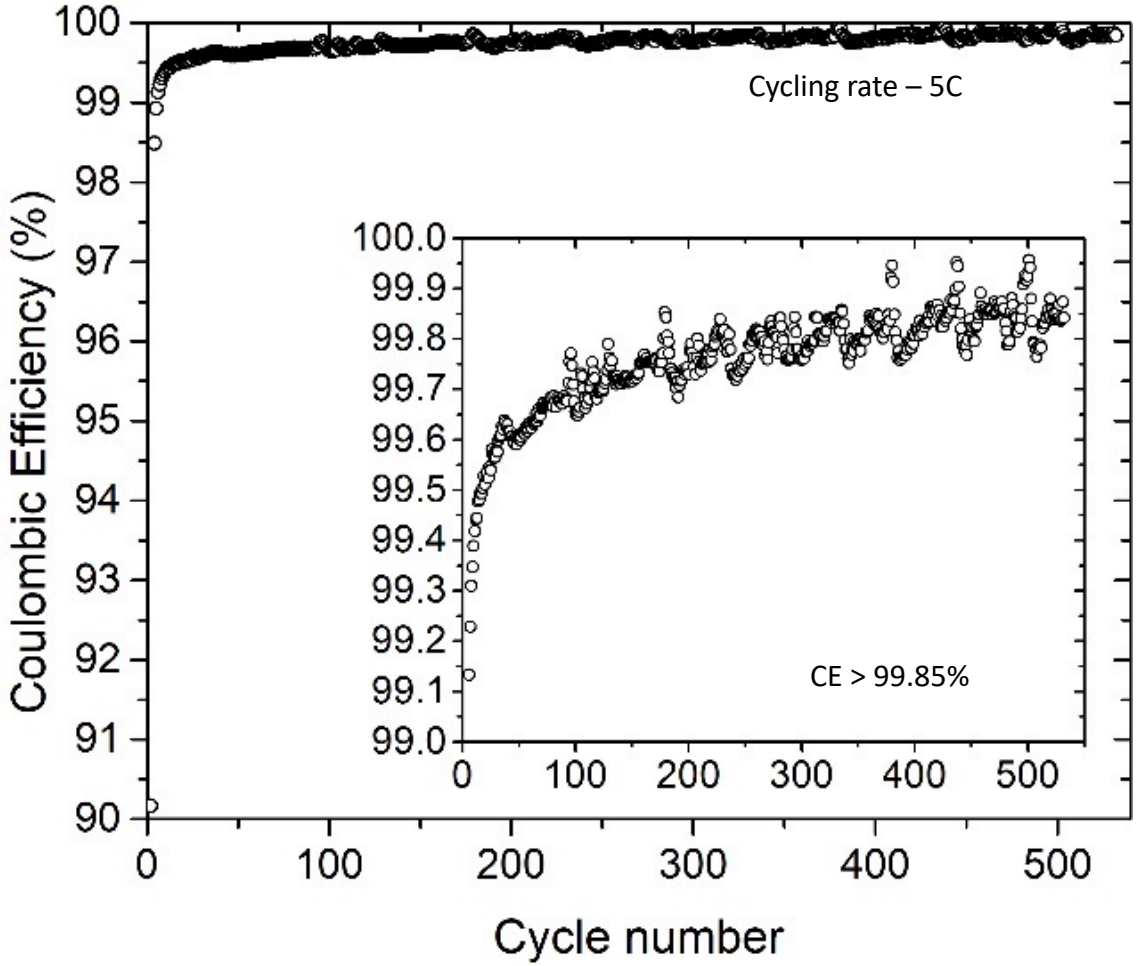


2023-
Next?

LiPON Enables Remarkable Battery Cyclability

Thin film full cell comprised of $LiNi_{0.5}Mn_{1.5}O_4$ high voltage cathode, LiPON and Li metal anode



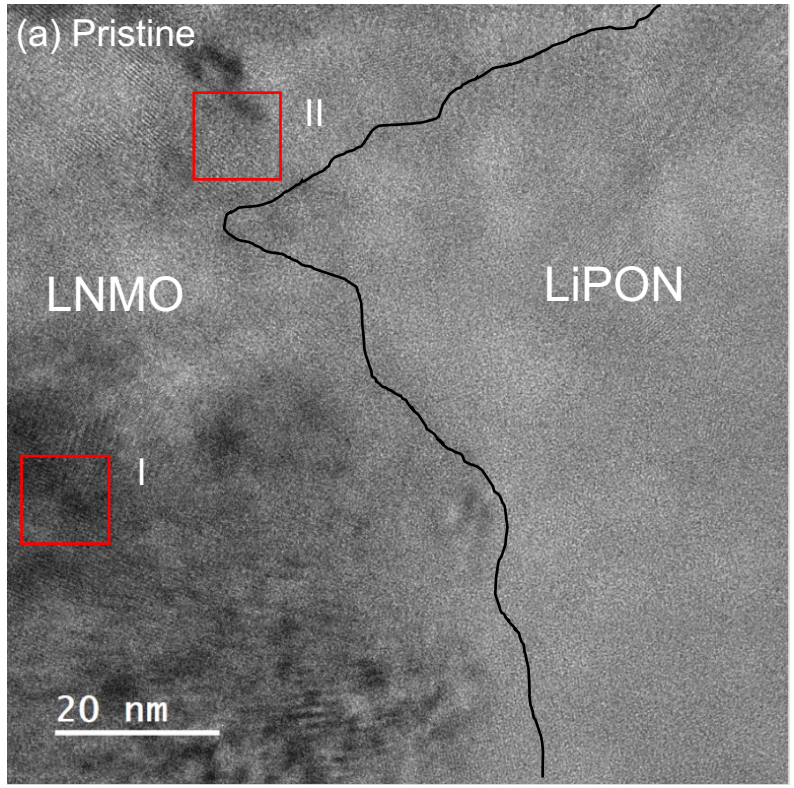


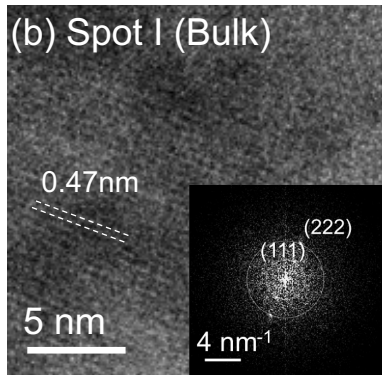
The **chemistry** of the electrode/electrolyte interfaces are more important than the **mesostructure**

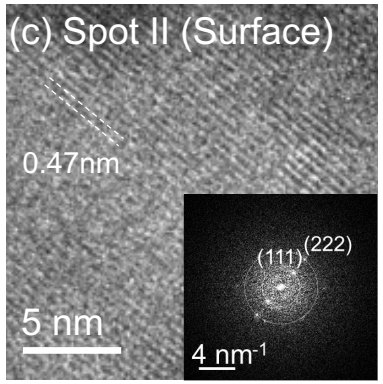
D. Cheng, T, A, Wynn, Y. S. Meng, et al., *Joule*, (2020), **4**, 1–17.

Cryo-EM unravels the stable cathode electrolyte interphase

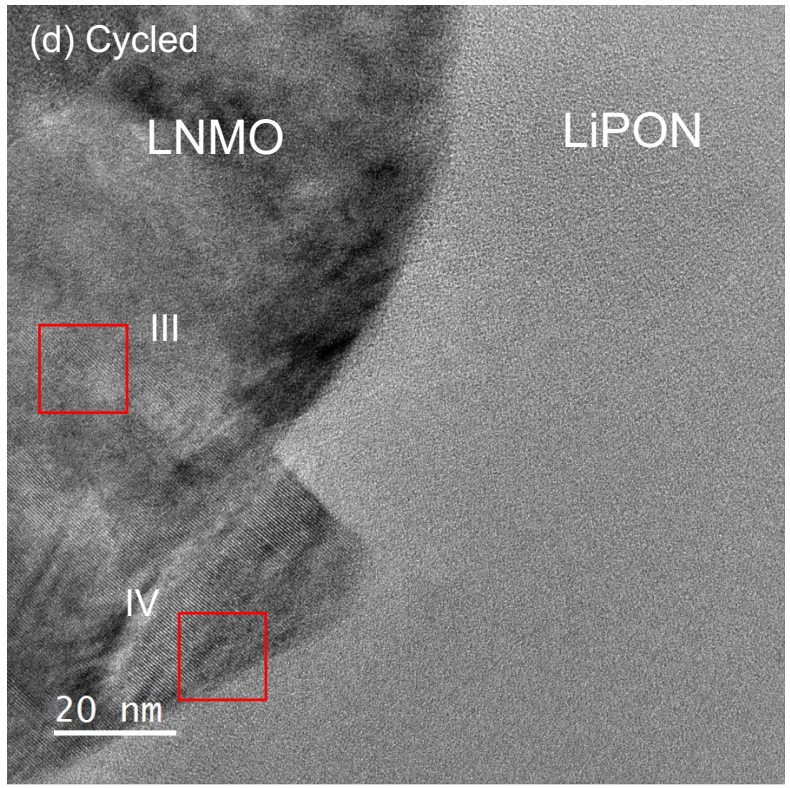
Pristine LNMO/LiPON interface

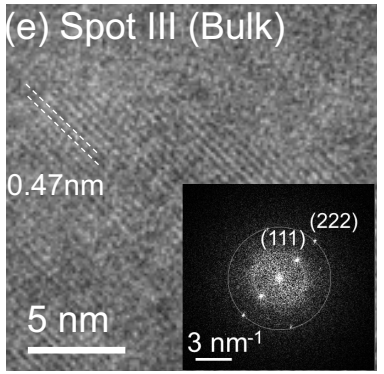


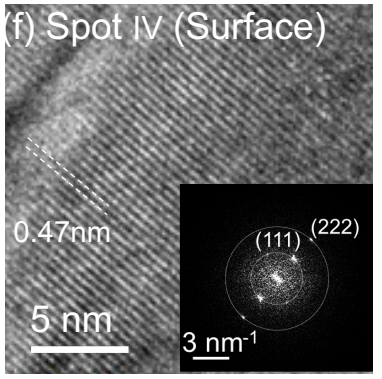




Cycled LNMO/LiPON interface





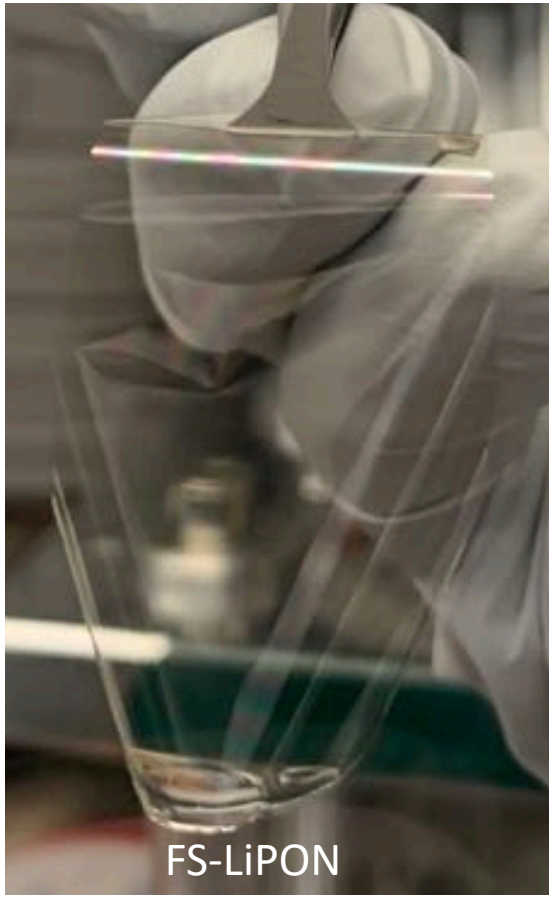


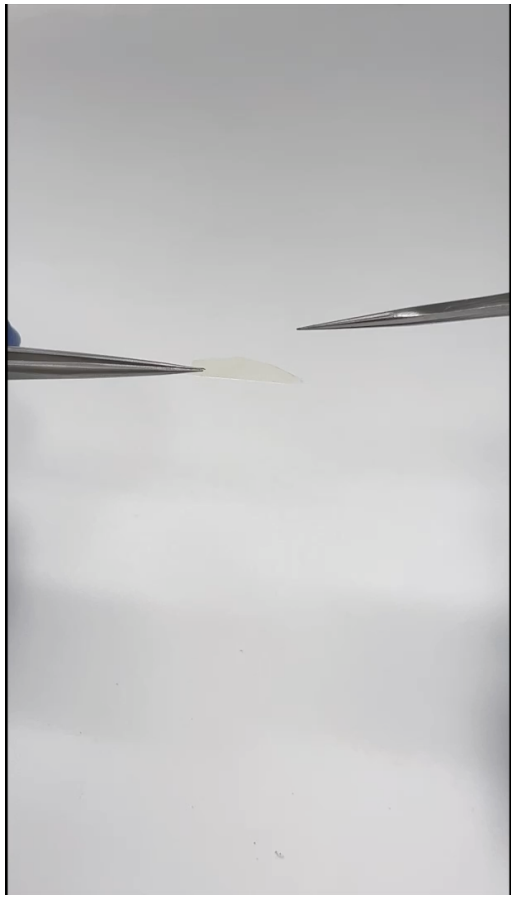
Most regions along LNMO/LiPON interface after >500 cycles shows no signs of cracking, delamination or decomposition.

R. Shimizu, D. Cheng, Y. S. Meng et al. *Adv. Energy Mater*. 2022, 2201119

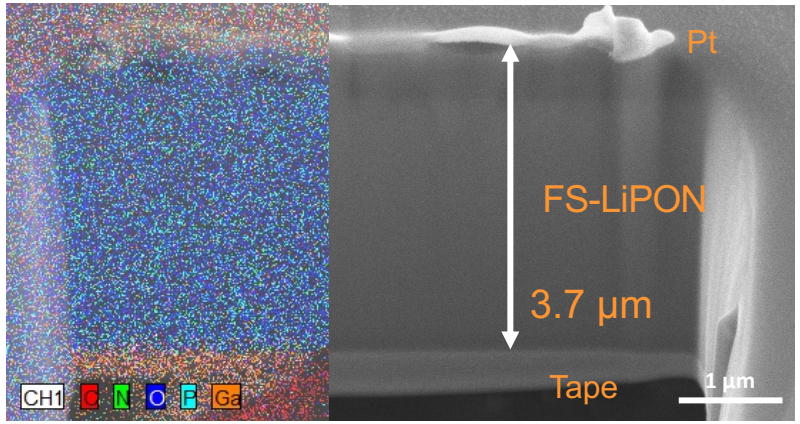
A unique form of LiPON thin film

Free-standing LiPON film

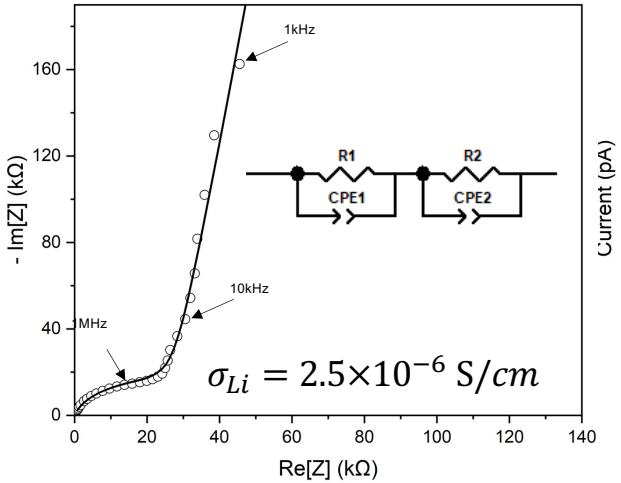


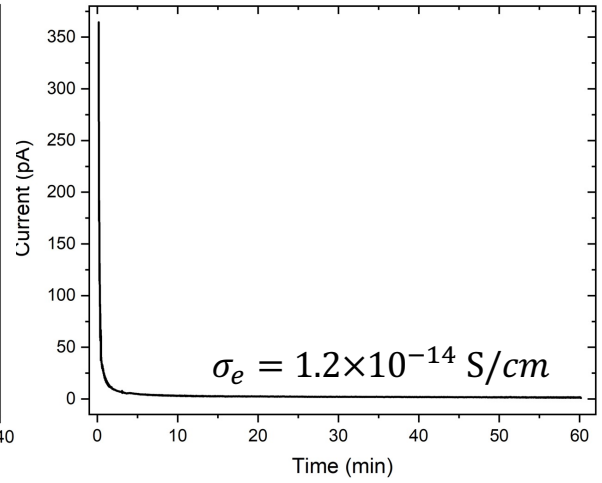


Fully dense solid-state electrolyte



Consistent Li/electron transport characteristic as LiPON



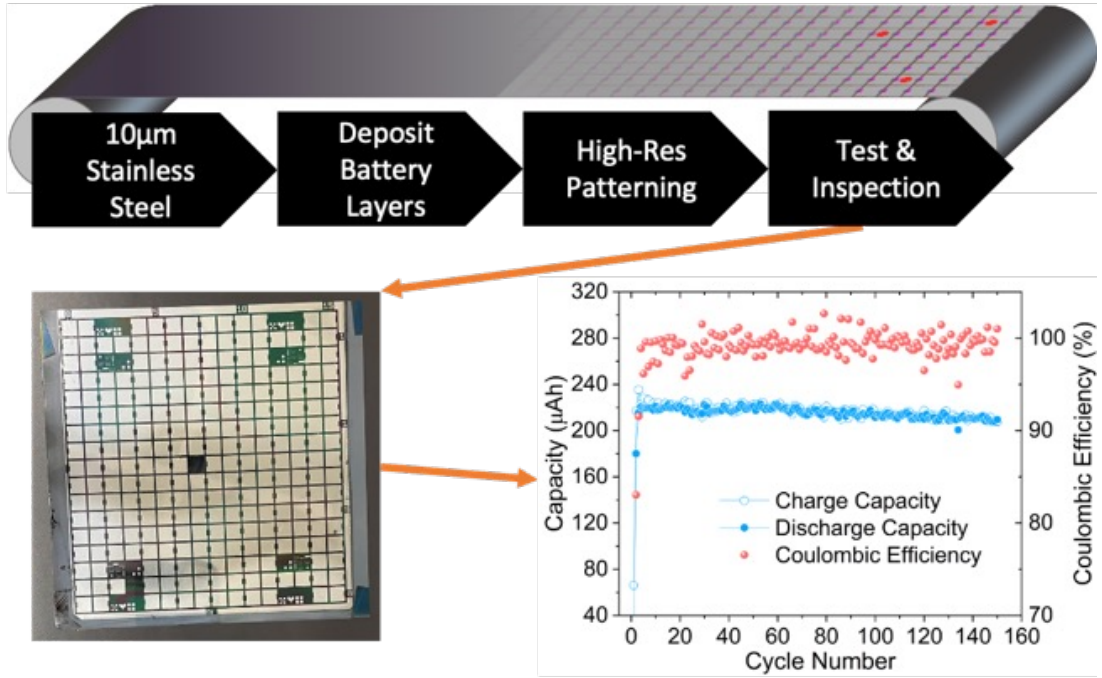


D. Cheng, Y. S. Meng et al. 2023, Just Accepted Nature NanoTech

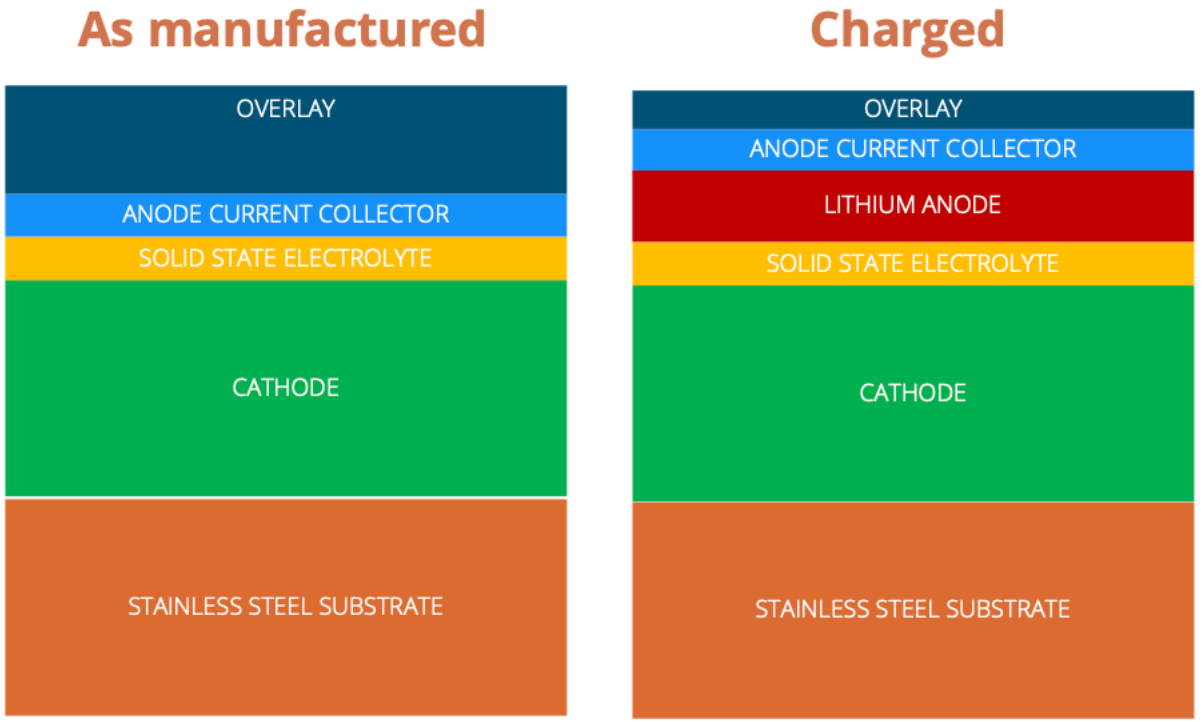
From Basic Science to Breakthrough Innovation

Enabled Free Standing LiPON Film
Pressure free dense Li plating

Thin Film Battery (Ensurge) – Anode Free Micro-Battery



ENSURGE

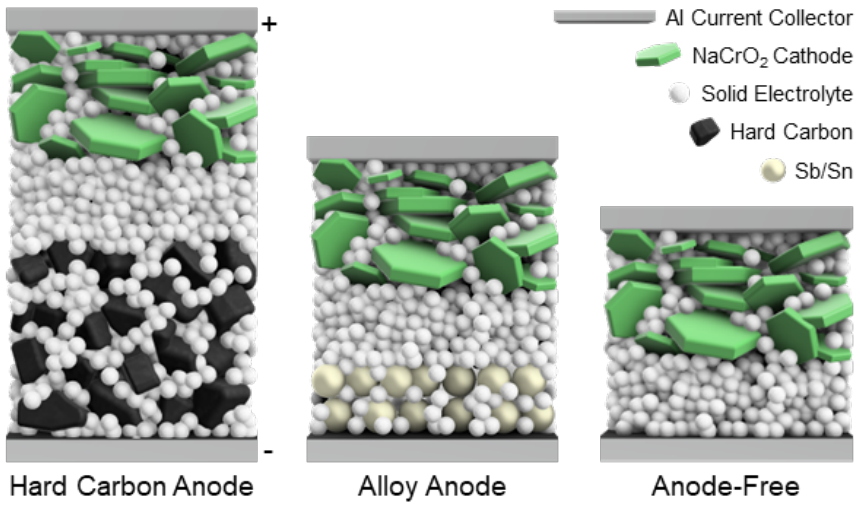


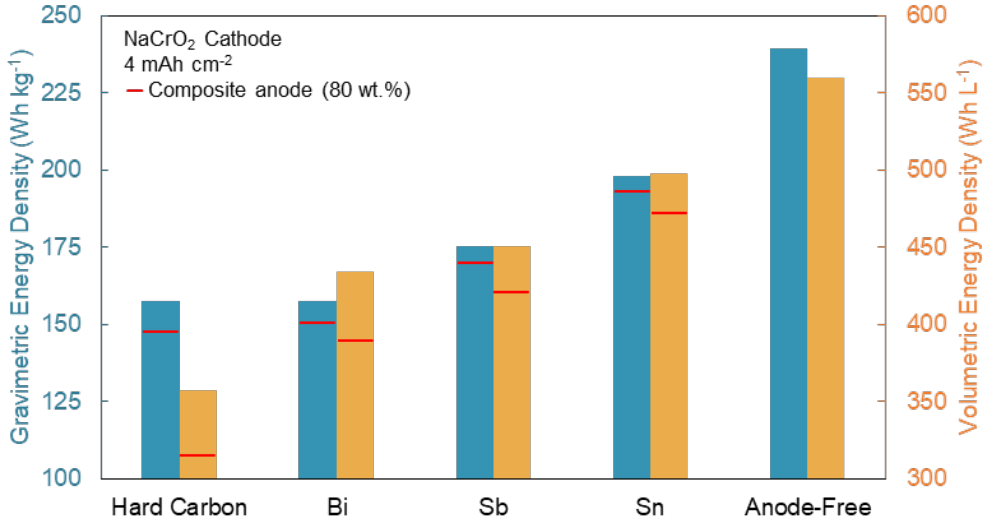
Unpublished data from Meng group

Please contact me if you would like an archived copy shirleymeng@uchicago.edu

Anode Selection → Anode-Free Game Changing for Na ASSB

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

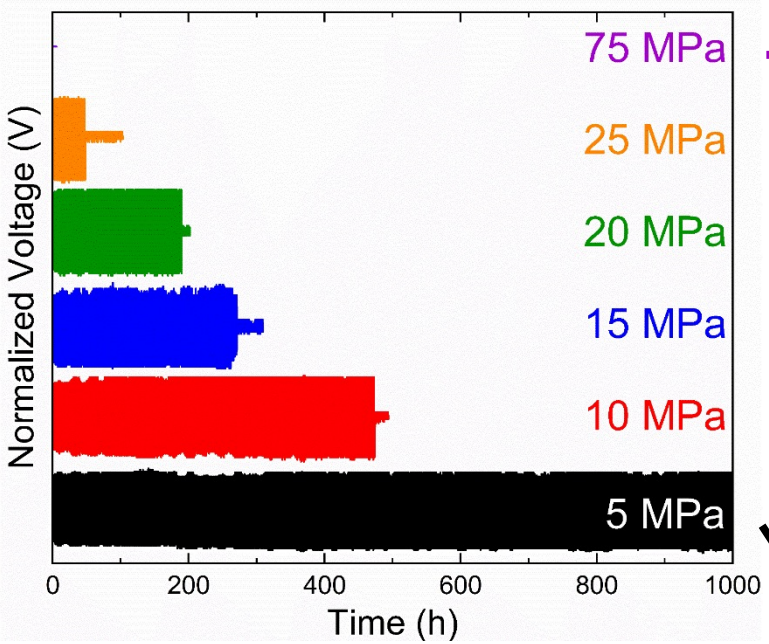


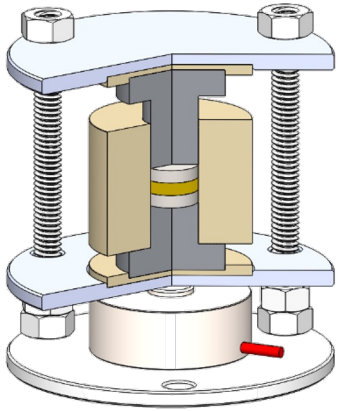


- Anode-Free can achieve significantly higher energy density
  - Zero weight and volume
  - Lowest reduction potential → highest cell voltage

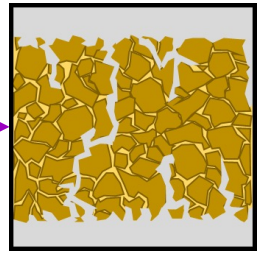
Stack pressure effect on Li metal anode

Li symmetric cells

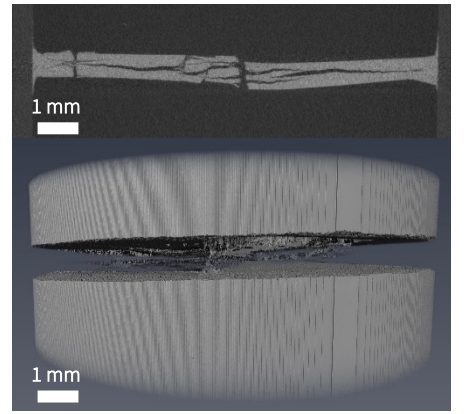




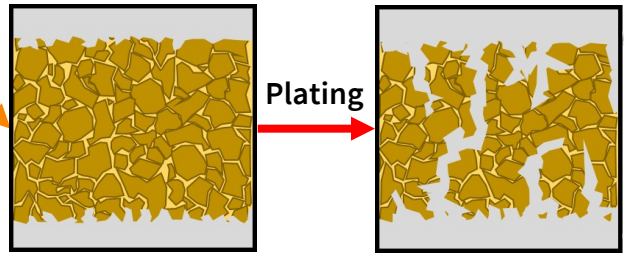
75 MPa



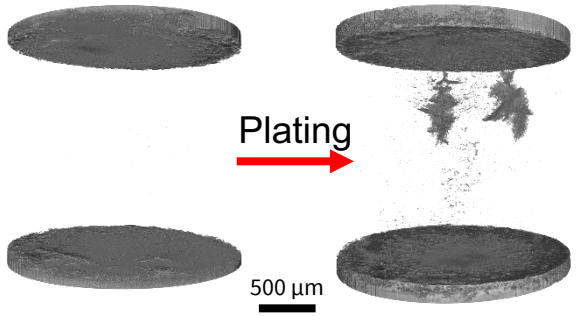
Mechanically induced short-circuit



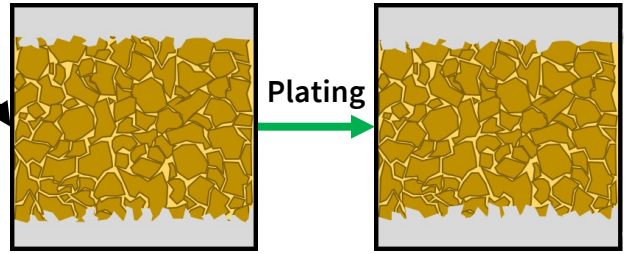
25 MPa



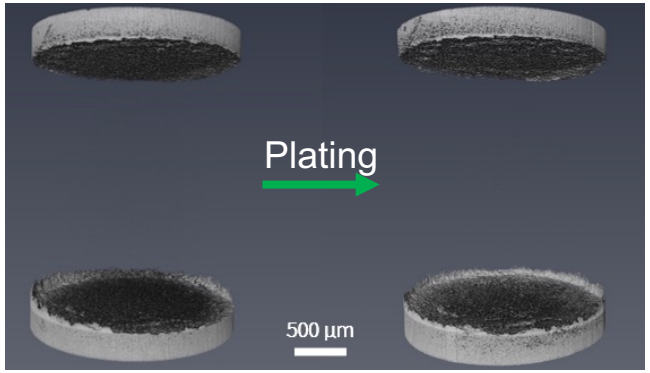
~ 48h: Plating short-circuit



5 MPa



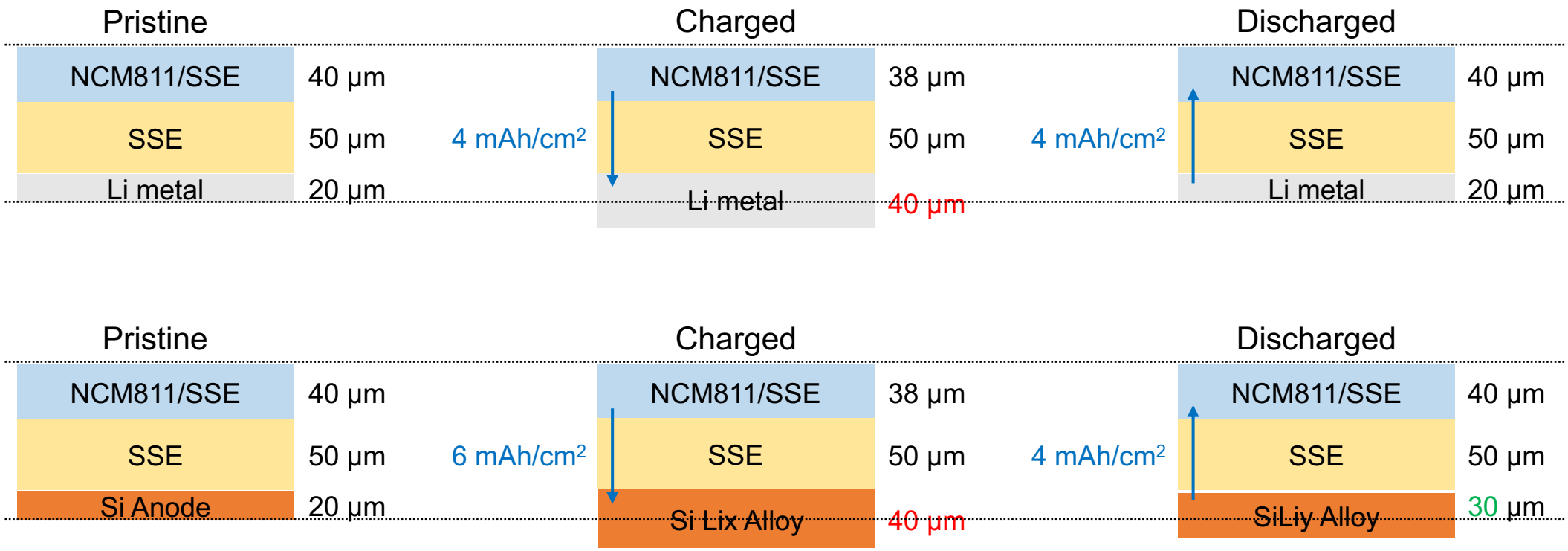
> 1000h: No short-circuit



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**.

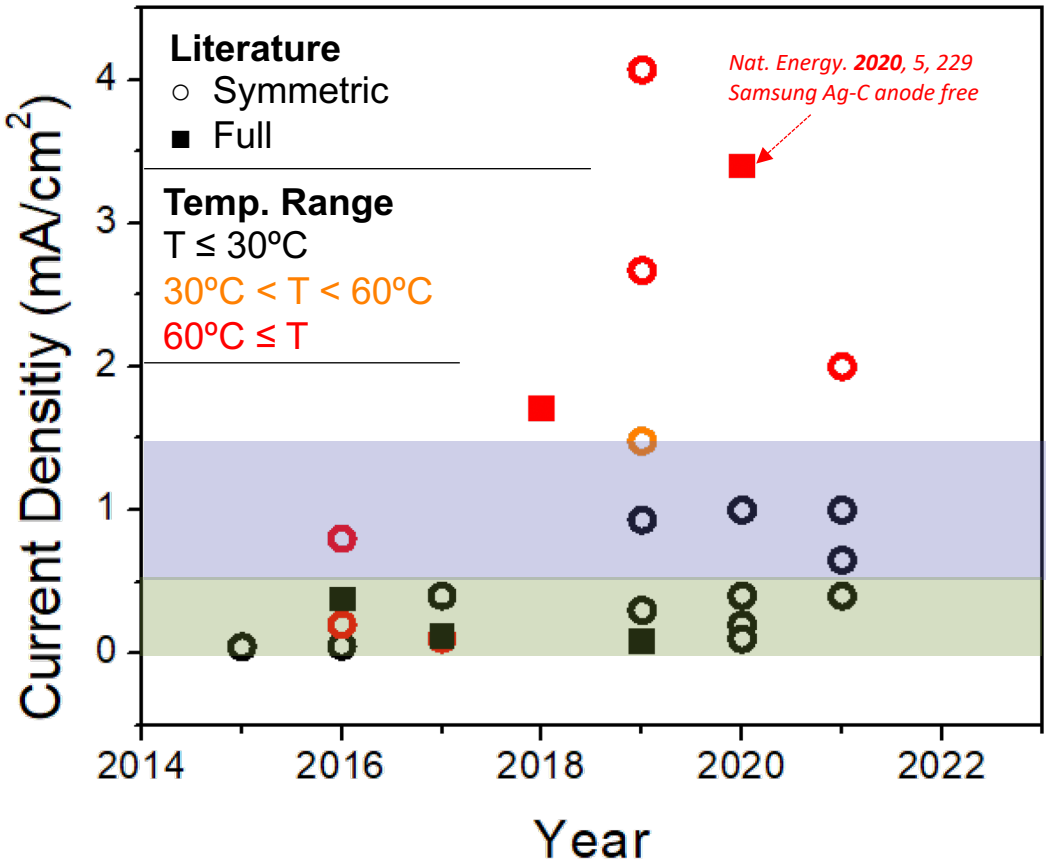
Conclusion / Future work

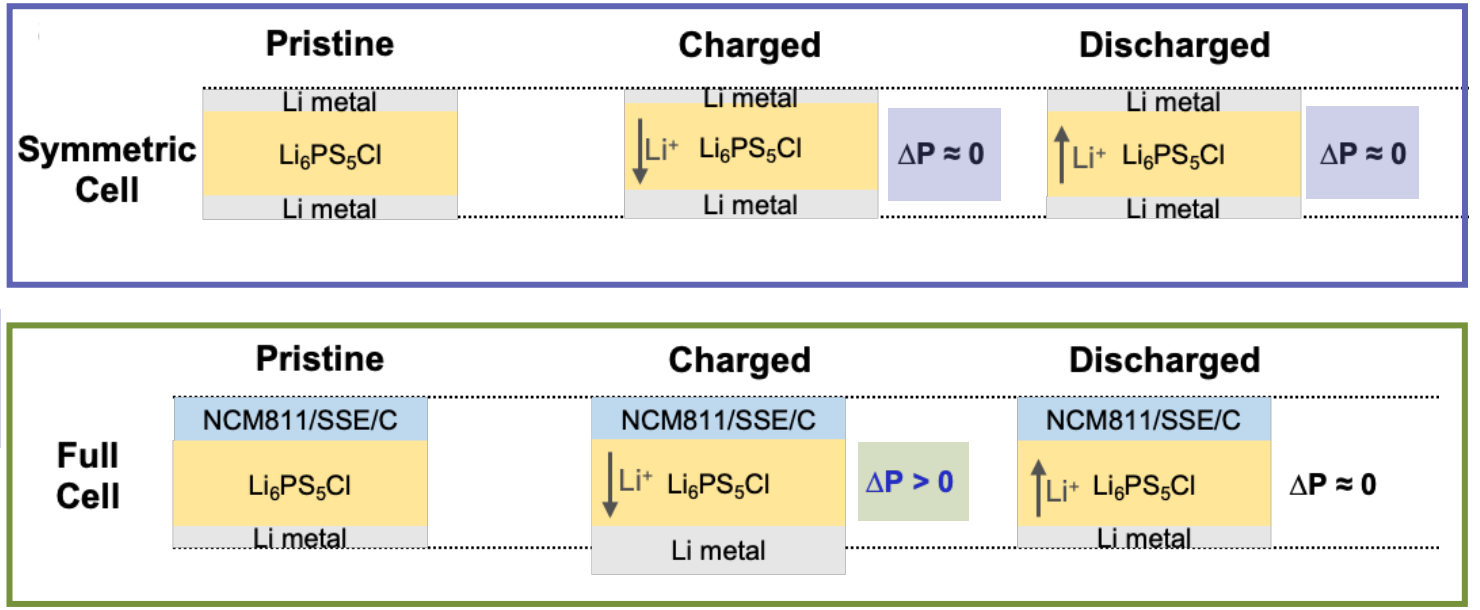
Volume expansion in full cell



→ Don't run away from the challenge! It is an Opportunity

Reported Critical Current Densities of Li Metal ASSB

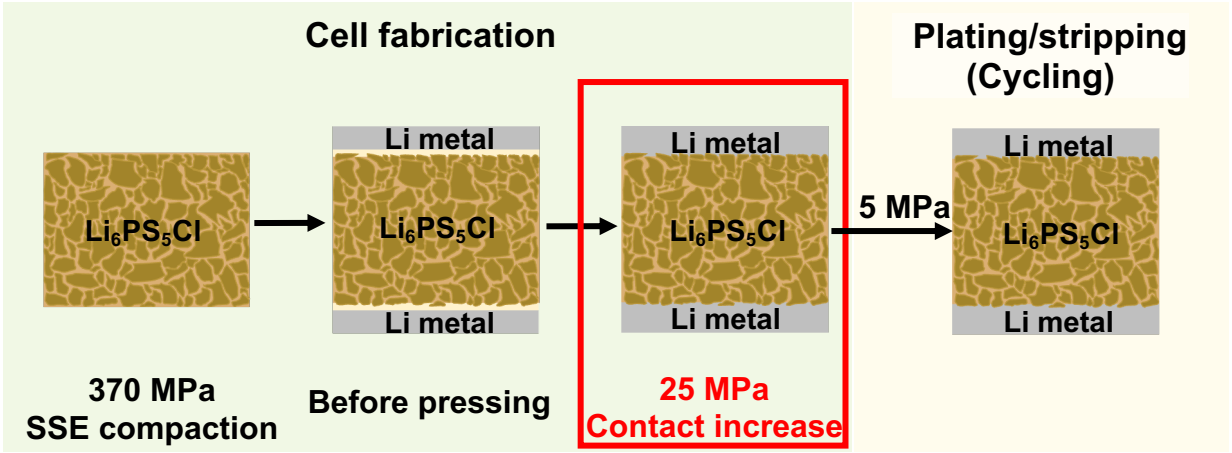




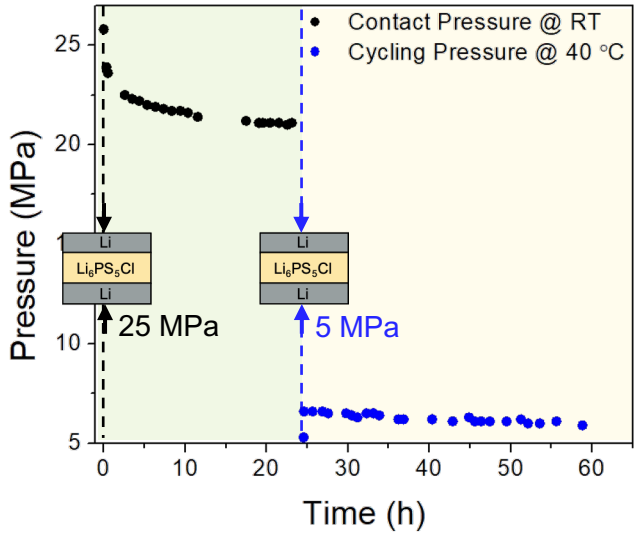
- Critical current density: Symmetric > Full
- Near room temperature full cell: < 1 mA/cm^2
- Pressure change: Symmetric < Full

Li Metal Symmetric Cell: Cell Fabrication/Contact

Li Metal Symmetric Cell Fabrication & Cycling Process



Pressure Monitoring of Li Metal Symmetric Cell

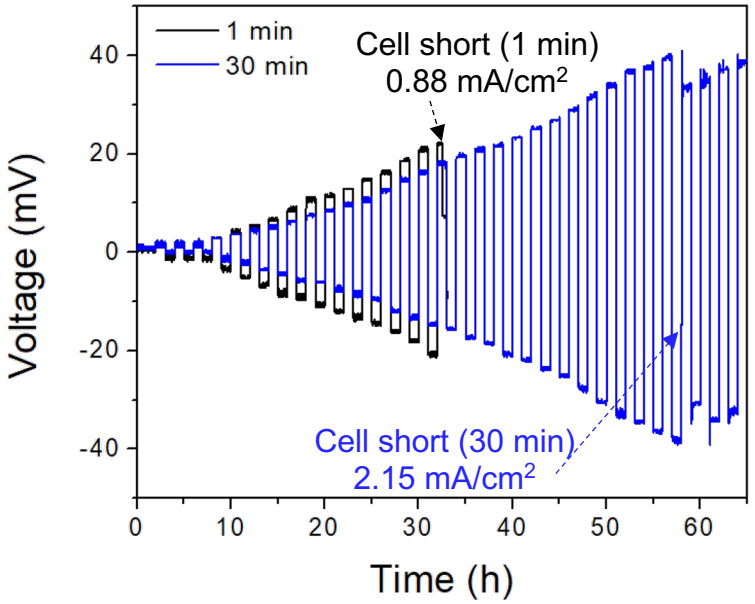


- Three different pressures applied during the fabrication/cycling process
  1. SSE compaction pressure = 370 MPa
  2. Contact pressure = 25 MPa
  3. Cycling pressure = 5 MPa

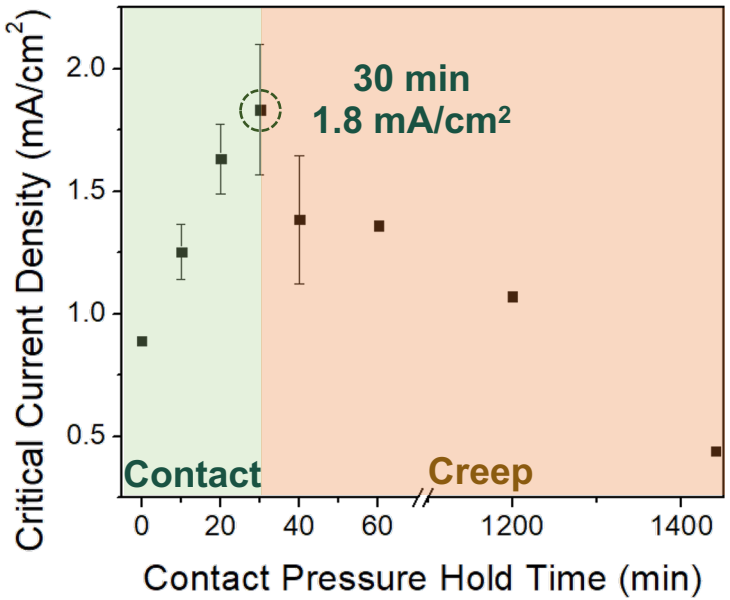
- Contact Pressure:
  Rapid drop during initial 30 min → Gradual decrease afterward
- Cycling (plating/stripping):
  No significant pressure change

Li Metal Symmetric cell: CCD/Failure

Ramping Test of Different Contact Time Cells



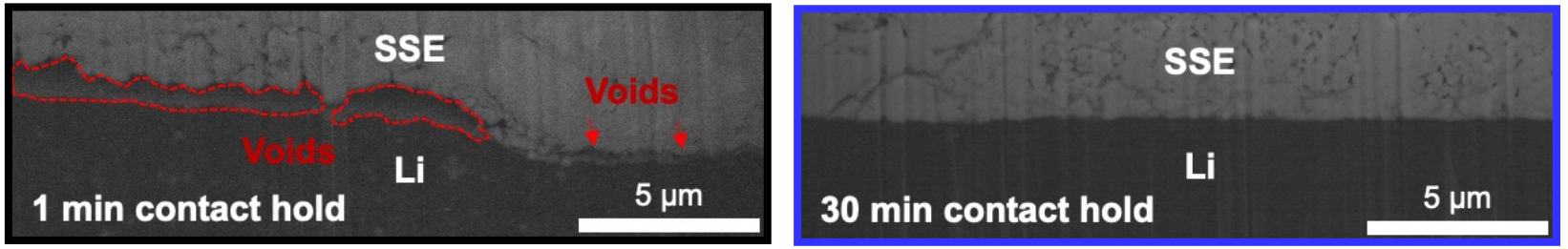
Ramping Test of Different Contact Time Cells



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

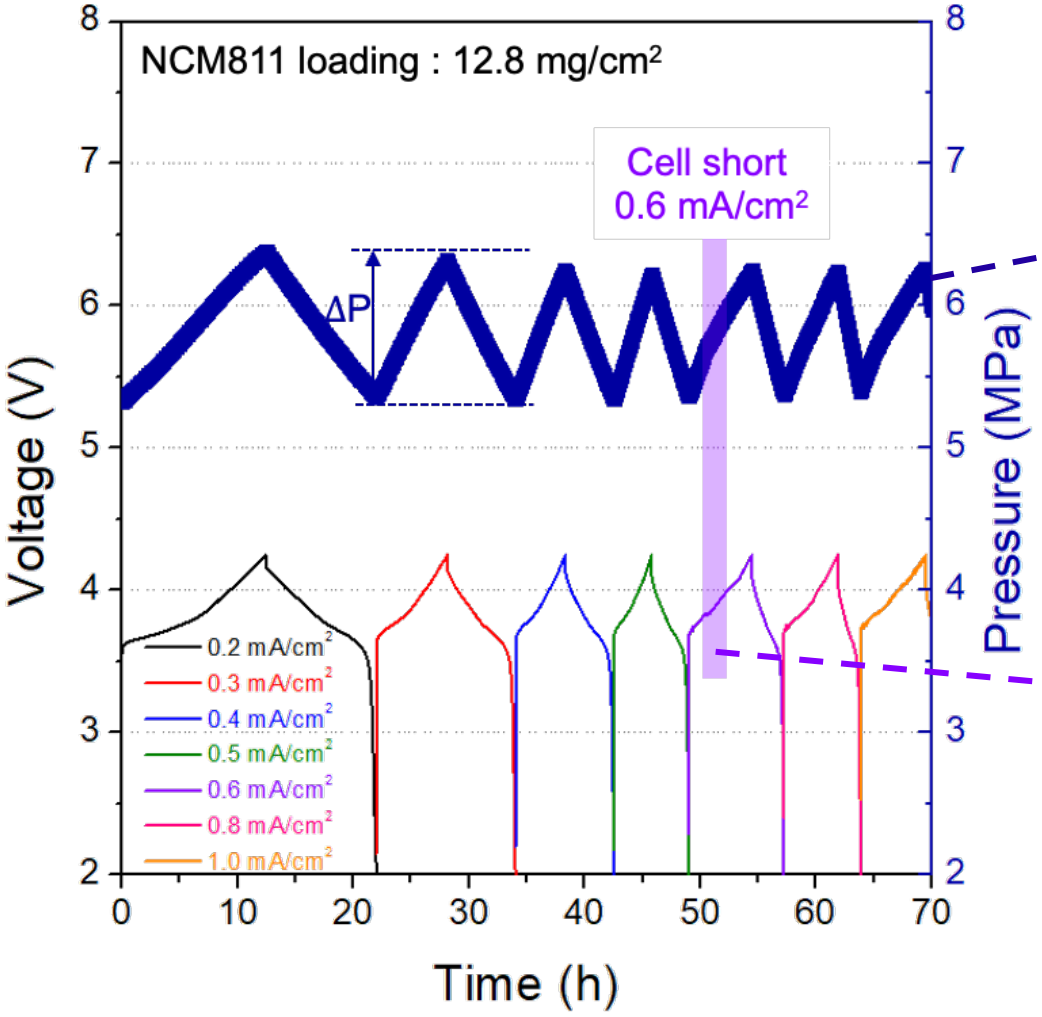
- CCD trends depending on contact hold time
- CCD increase until 30 min contact, decrease afterwards

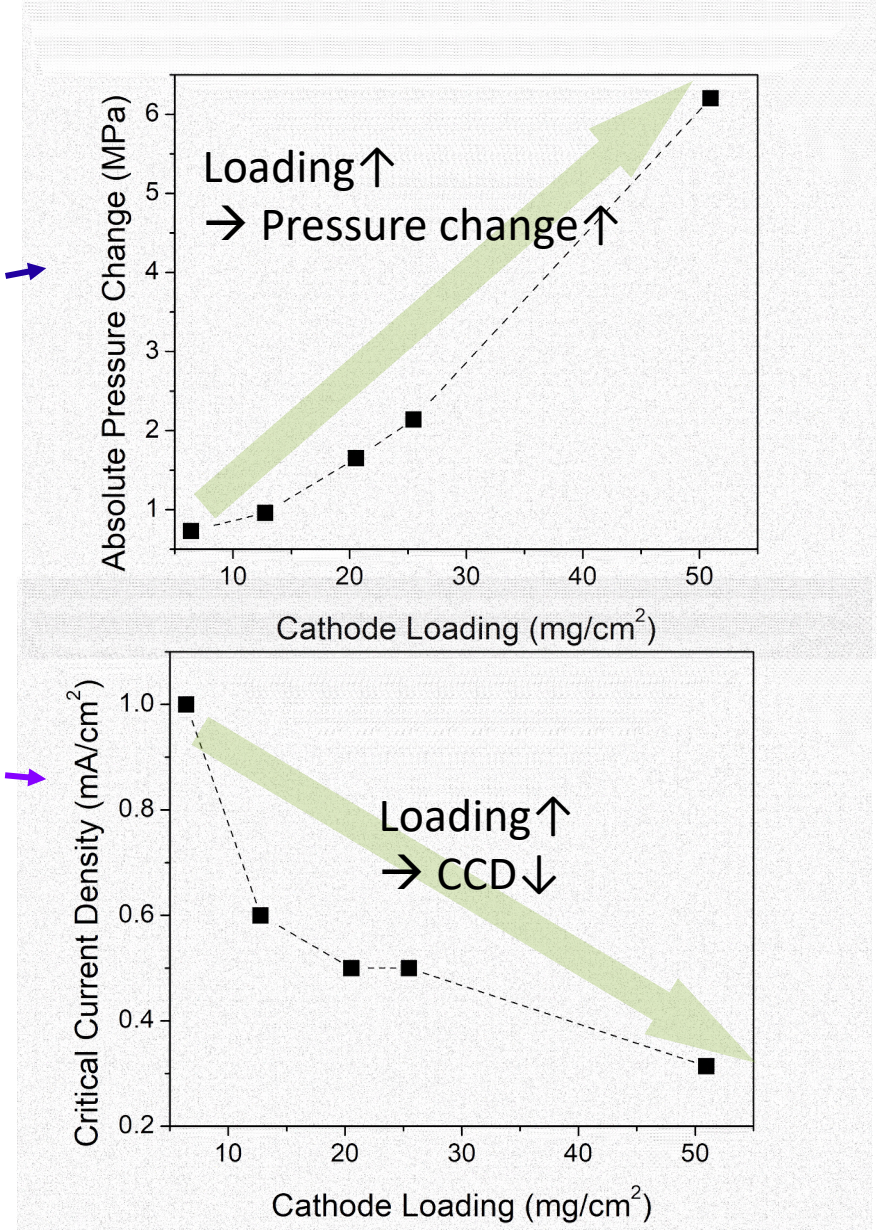
Cryo-FIB/SEM : Direct observation of Li/SSE interface



Ham et al. *Energy Storage Material. Under* revision

Li Metal Full Cell: Pressure Dependence



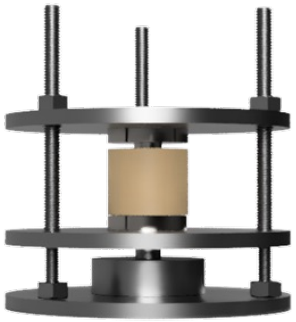


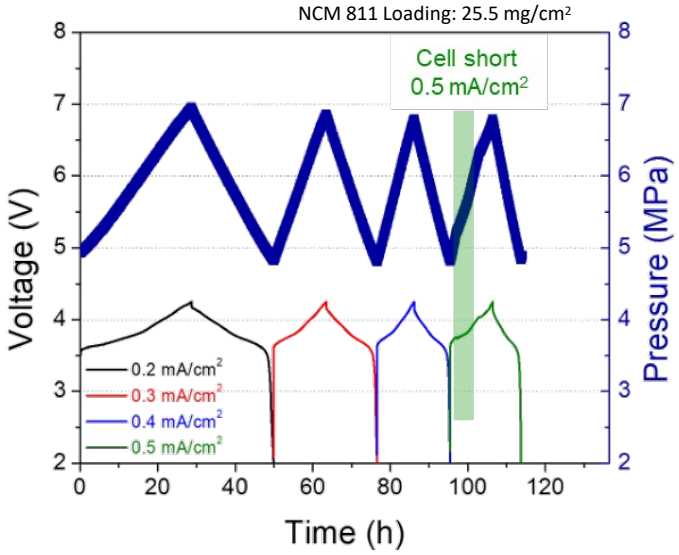
- Ramping test conducted to evaluate CCDs of full cell
- Full cell: Pressure change during cycling with lower CCD

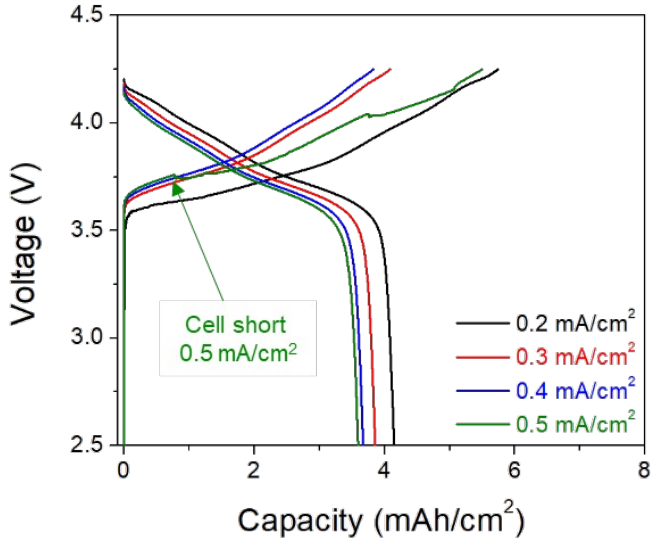
Full Cell: Fixed Gap vs. Constant Pressure


So Yeon Ham

Fixed gap



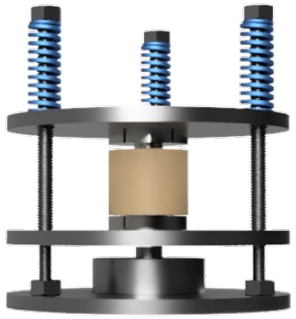


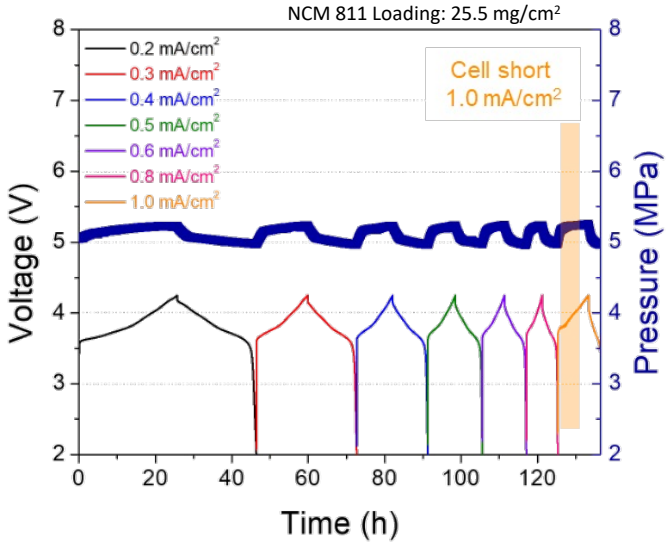


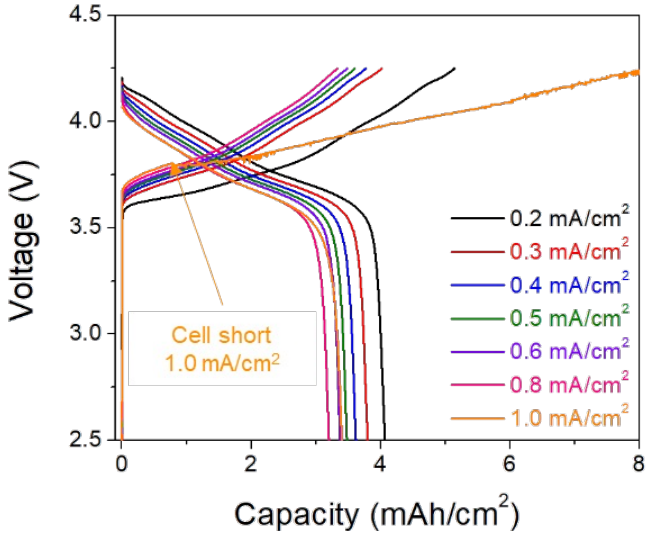
Lower pressure change and higher CCD in const pressure setup

Constant Pressure Set-up for the volume change compensation

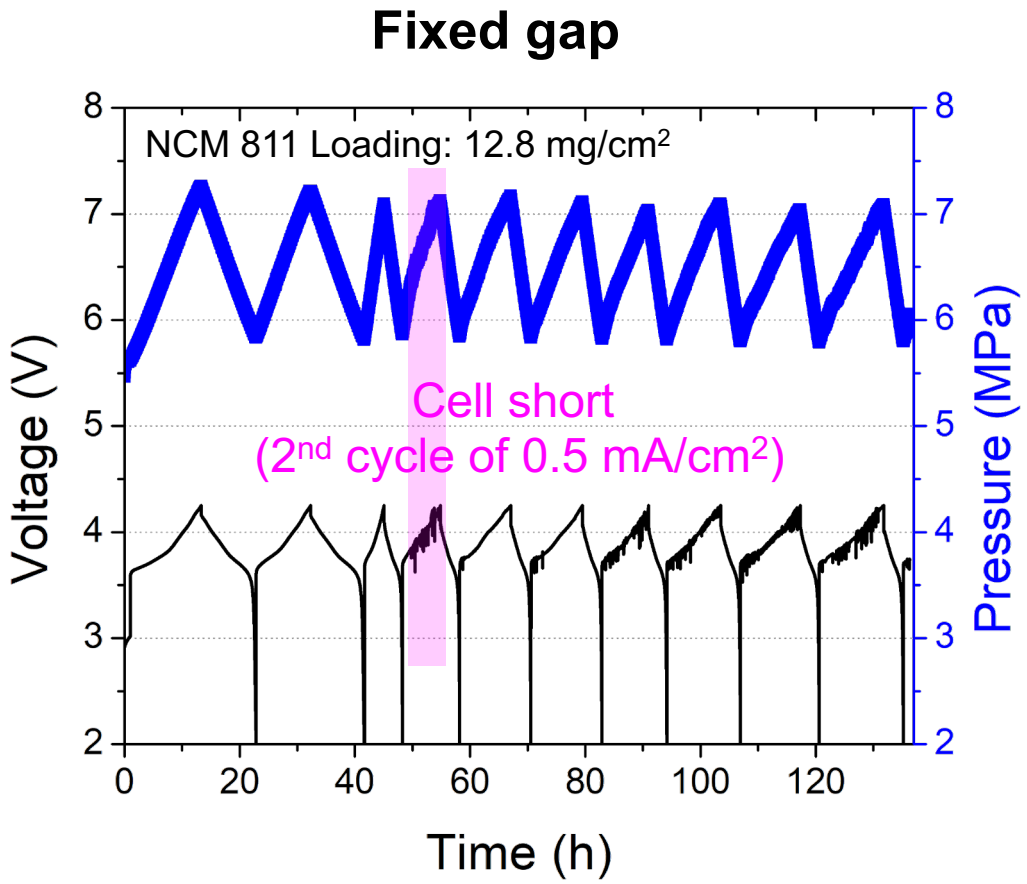
Constant pressure

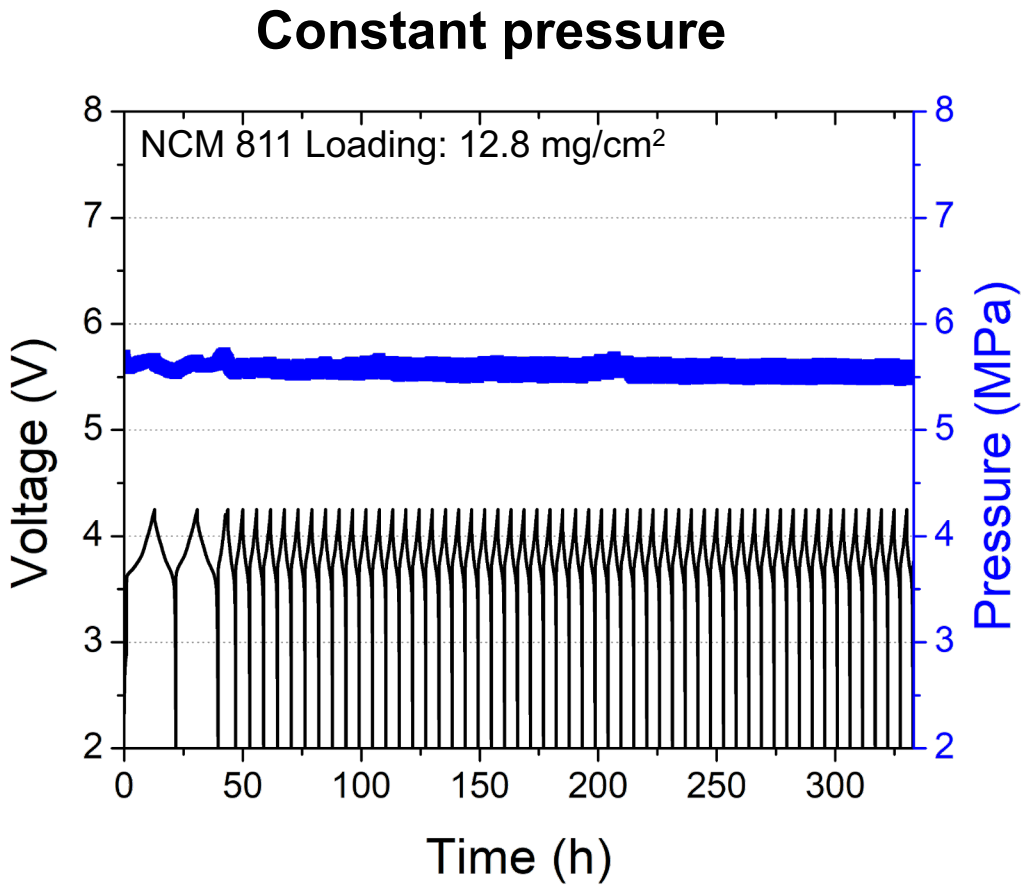






Long-term Cycling of Constant Pressure Setup





- 0.5 mA/cm^2 Long term cycling after two activation cycles
- Fixed gap: Shorted at 2nd cycle at 0.5 mA/cm^2
- Fixed gap: Cycled more than 50th cycle at 0.5 mA/cm^2

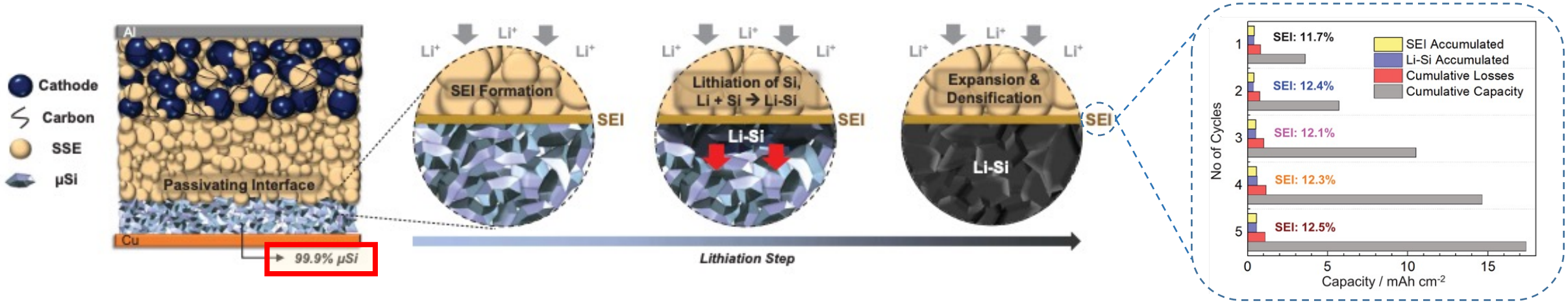
Ham et al. *Energy Storage Material. Under* revision

All-Solid-State-Li Metal Batteries:

- Elucidate CCD discrepancy between Li symmetric and full cell
- Li symmetric cell
  - Better contact enabled higher CCD
- Li full cell
  - Pressure change during cycling induce cell shorting
  - Constant pressure setup: Mitigate cell shorting

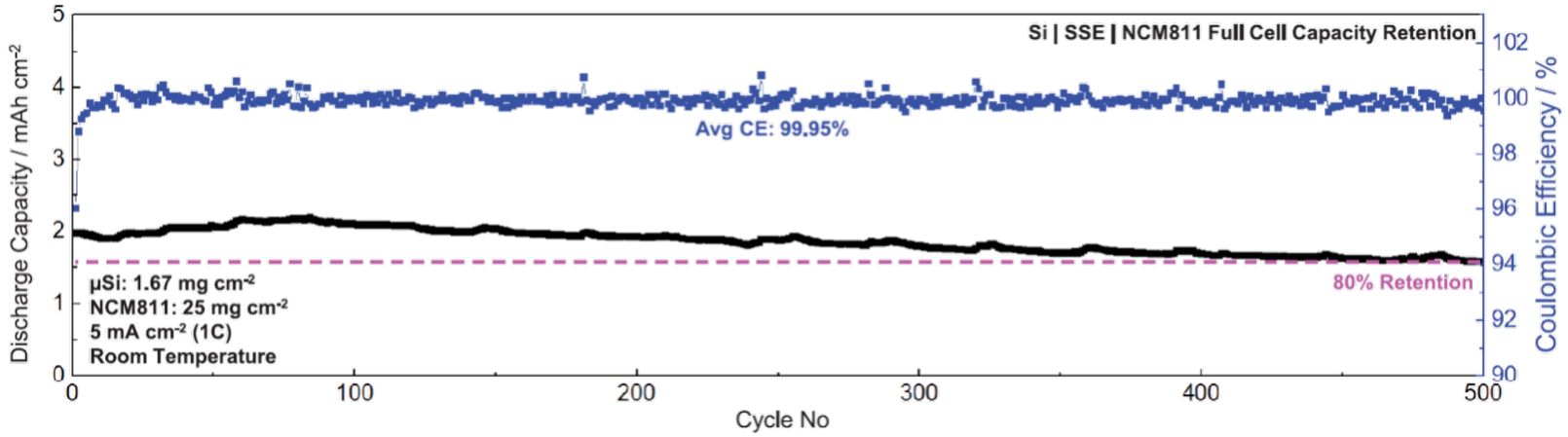
Ham et al. *Energy Storage Material. Under* revision
SSRN: https://ssrn.com/abstract=4213169 or http://dx.doi.org/10.2139/ssrn.4213169

Si Anode Synergy in Solid-State Batteries



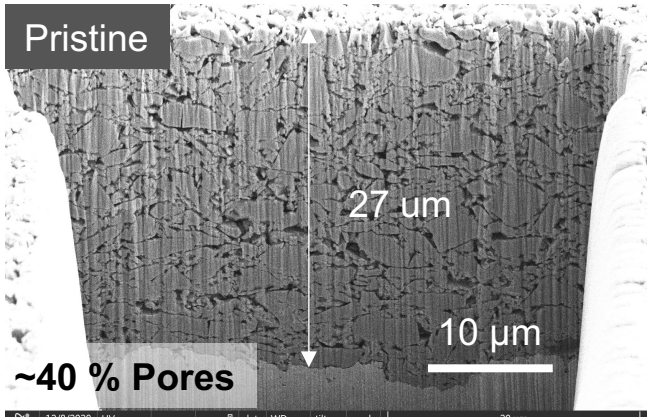
- Enable **99.9%** Si anode without carbon and solid electrolyte
- Inventory loss to the passivating SEI remained relatively constant
- Realized Si cycling >500 cycles

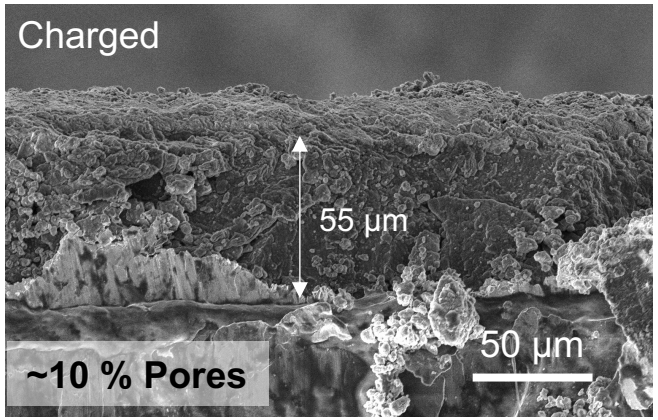
However, it is paramount to *improve the initial Coulombic efficiency (~76%)* to achieve high energy density all-solid-state batteries

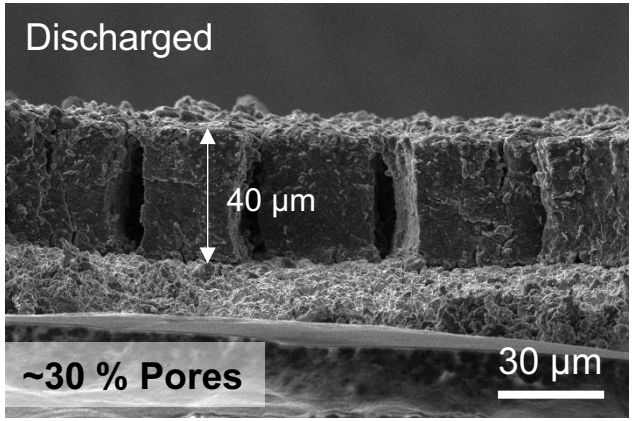


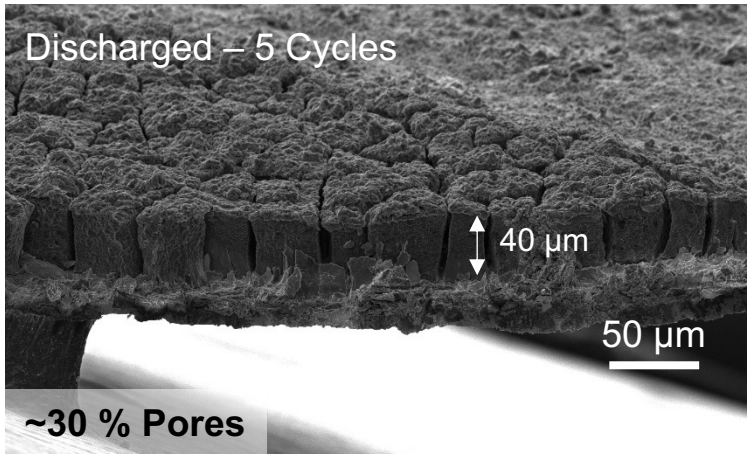
Porosity changes during cycling

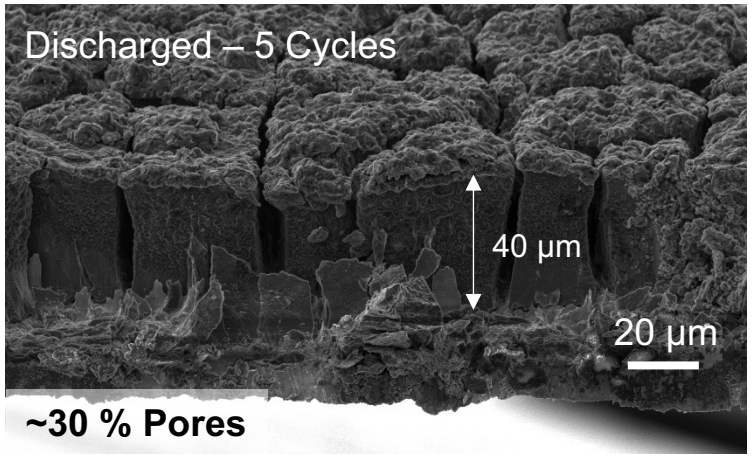
~3.8 mg cm^{-2} – 12 mAh cm^{-2}





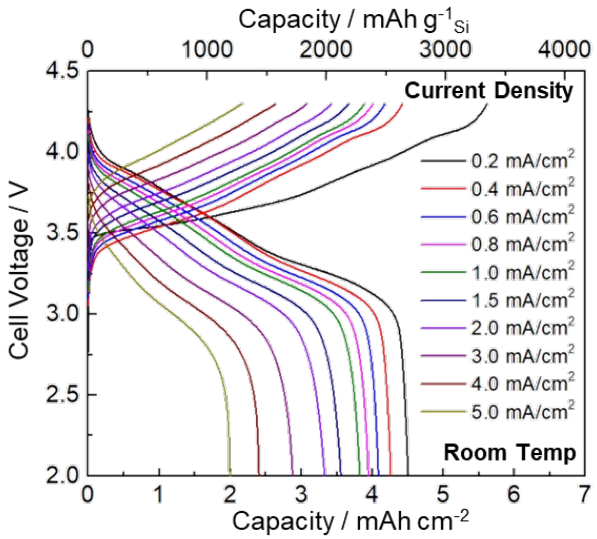




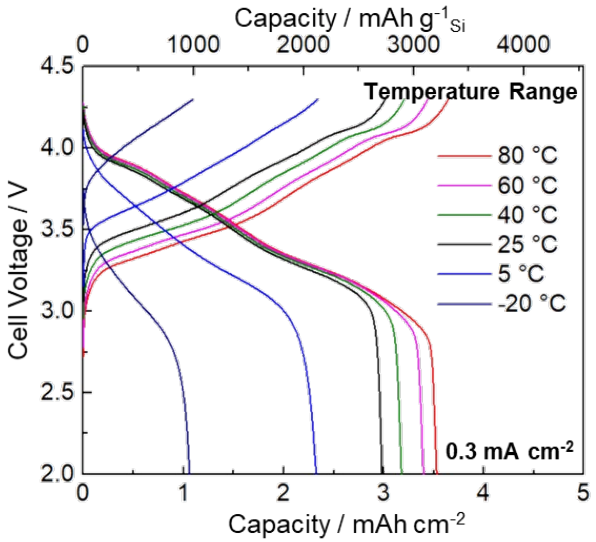


Tan, D.; Meng, Y. S. *et al.,* Carbon Free High Loading Silicon Anodes Enabled by Sulfide Solid Electrolytes for Robust All Solid-State Batteries. (*Science 2021*)

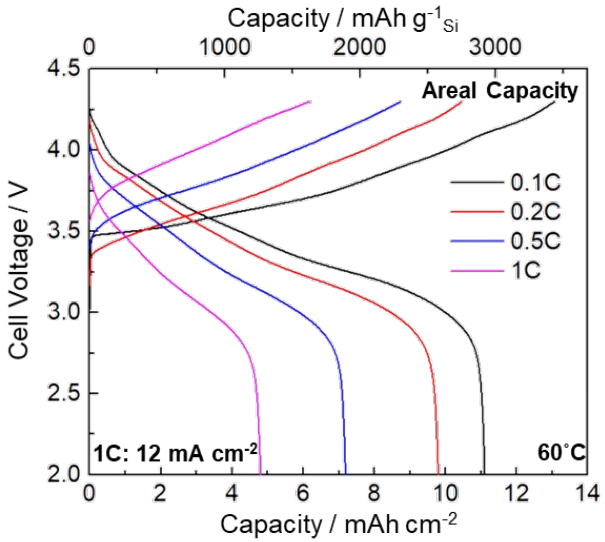
Electrochemical performance



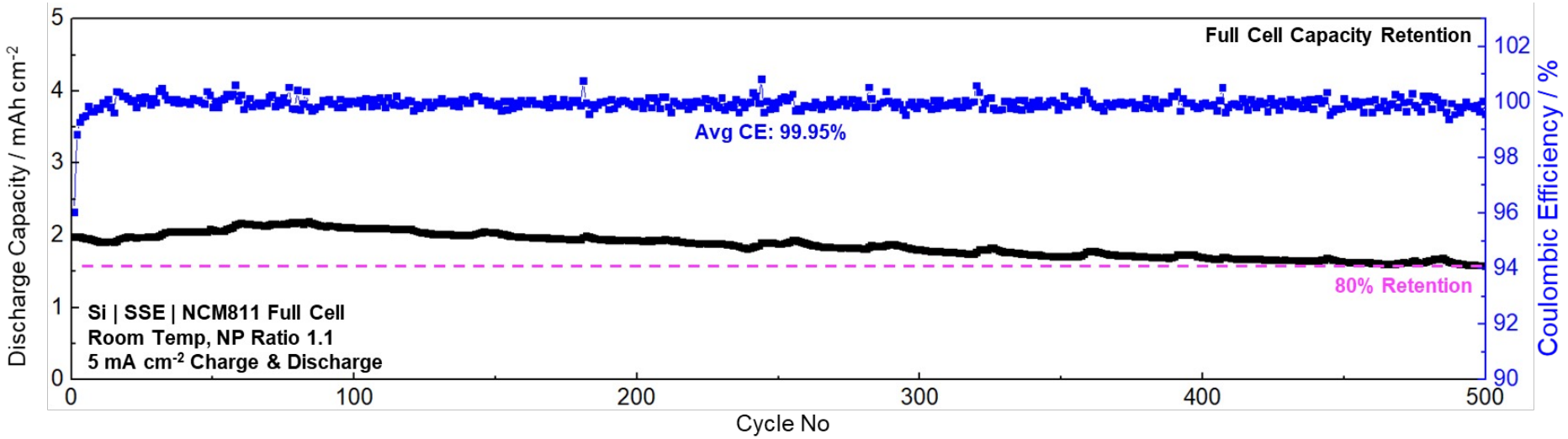
High Current Density

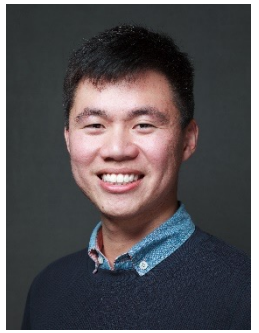


Wide Temperature Range



High Loading

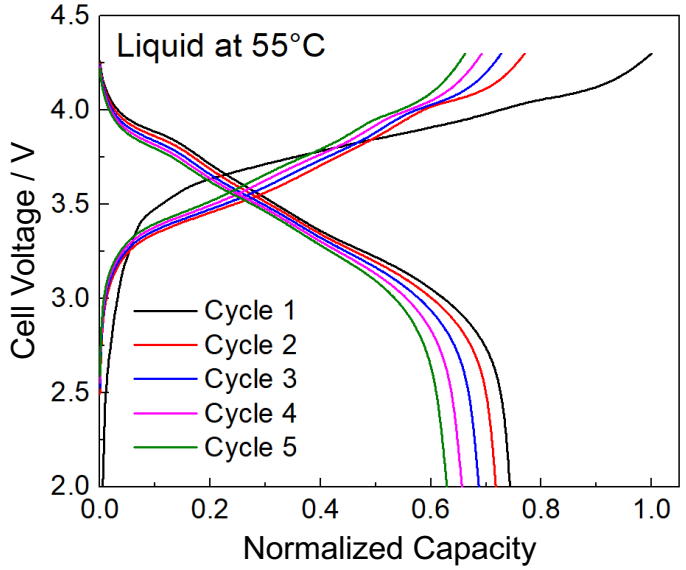


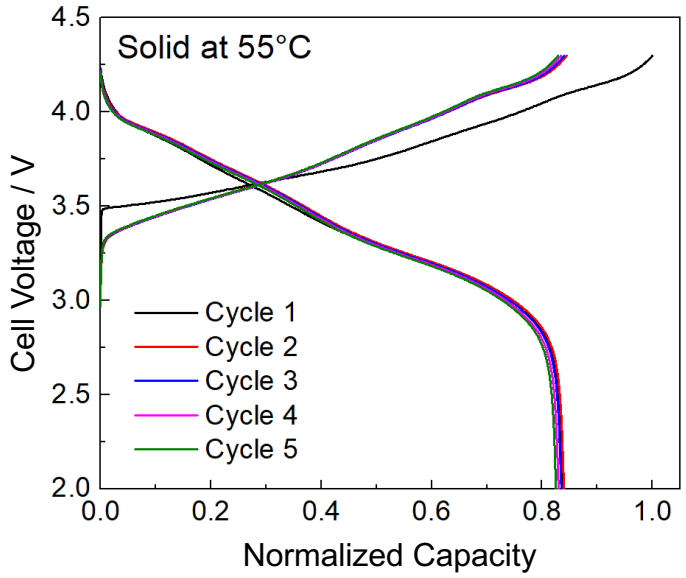


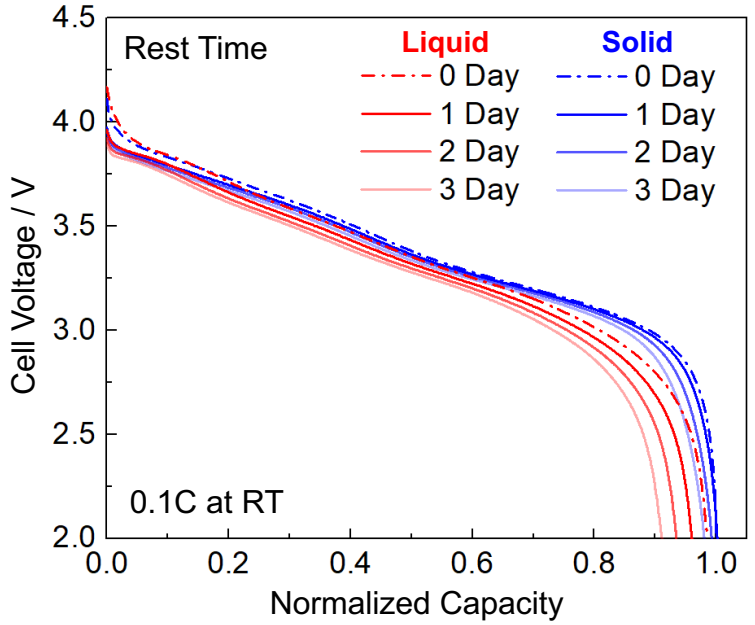
Dr. Darren Tan

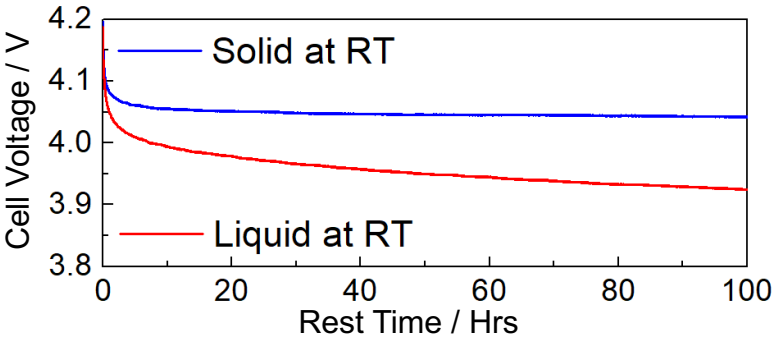
Tan, D.; Meng, Y. S. *et al.,* Carbon Free High Loading Silicon Anodes Enabled by Sulfide Solid Electrolytes for Robust All Solid-State Batteries. (*in review* - arXiv:2103.04230)

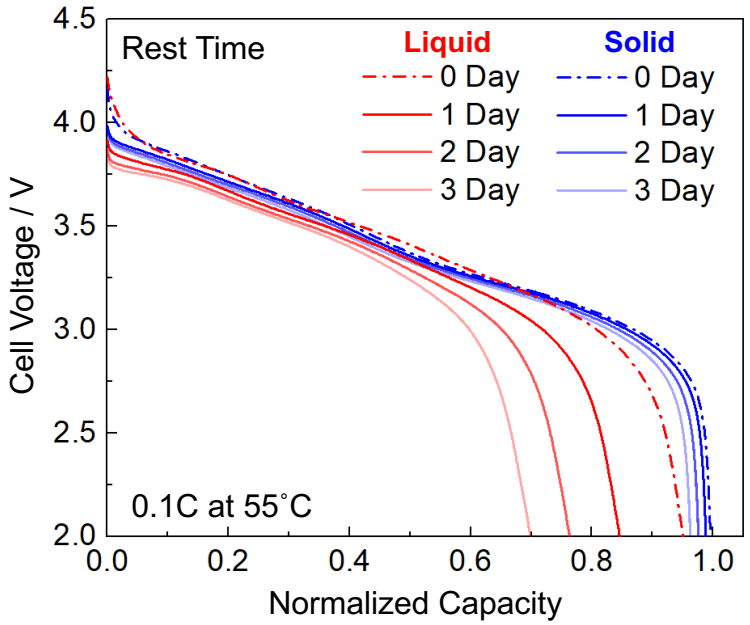
Passivating Interfaces – Extremely Stable

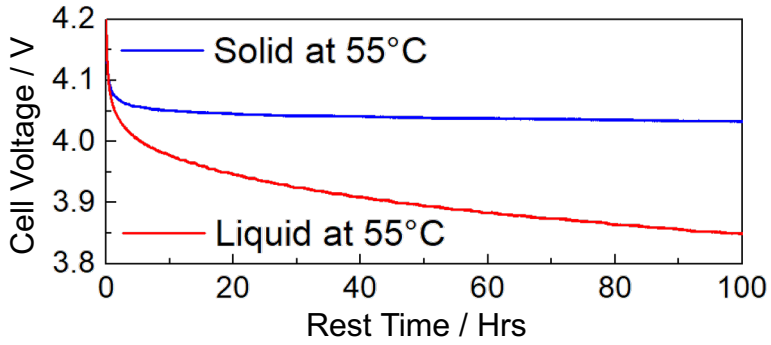










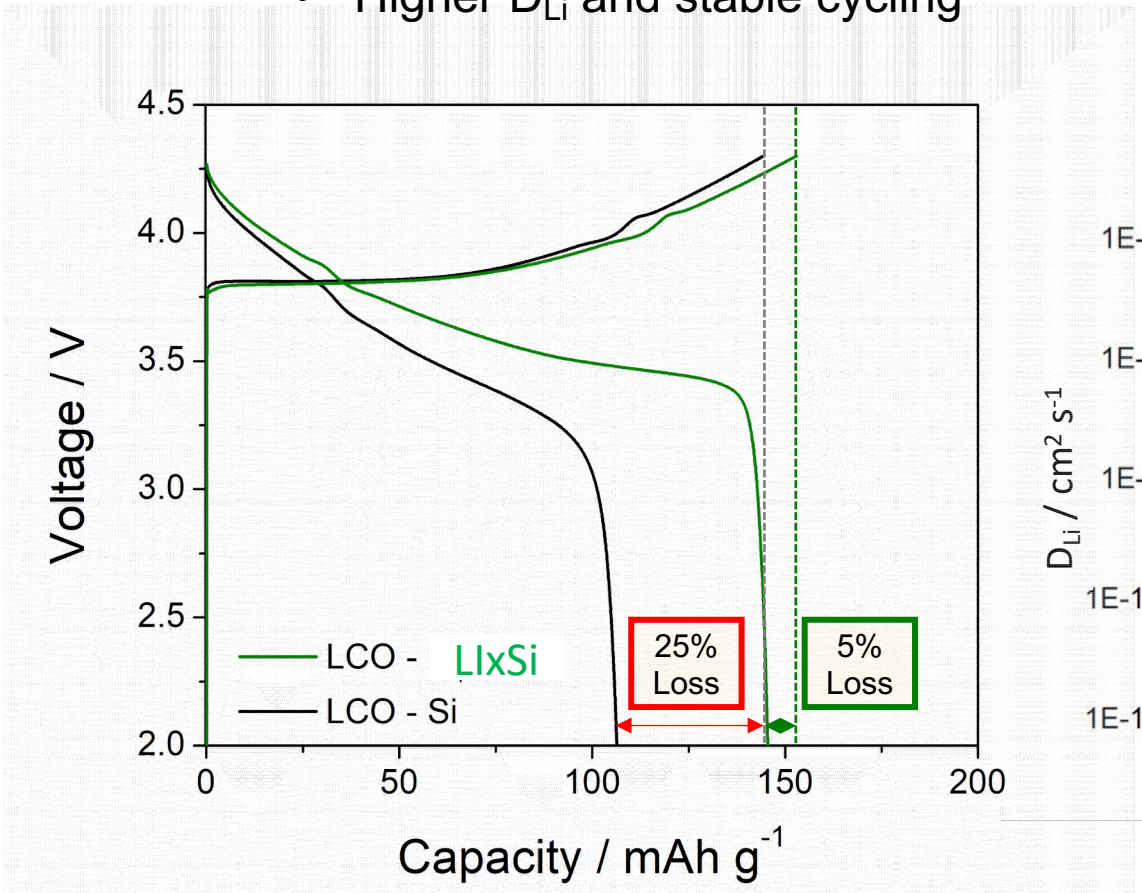


Tan, D.; Meng, Y. S. *et al.,* Carbon Free High Loading Silicon Anodes Enabled by Sulfide Solid Electrolytes for Robust All Solid-State Batteries. (*Science 2022)*

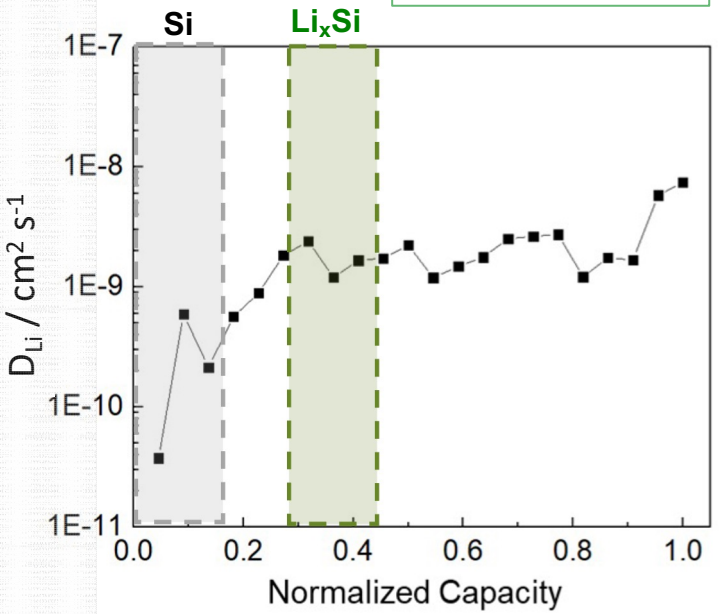
LG FRL - Anode Strategies

LGES-UCSD Frontier Research Laboratory

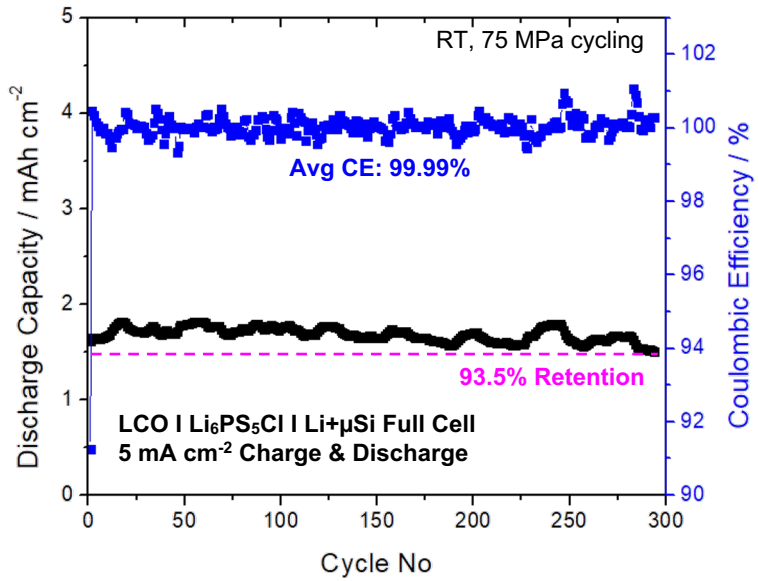
- 1st Year Achievement
  - Enhanced ICE
  - Higher D_{Li} and stable cycling



✓ Higher D_{Li}



✓ Stable cycling



So Yeon Ham et. al. To be Submitted 2023

Remaining Challenges

Precursors

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

Processibility

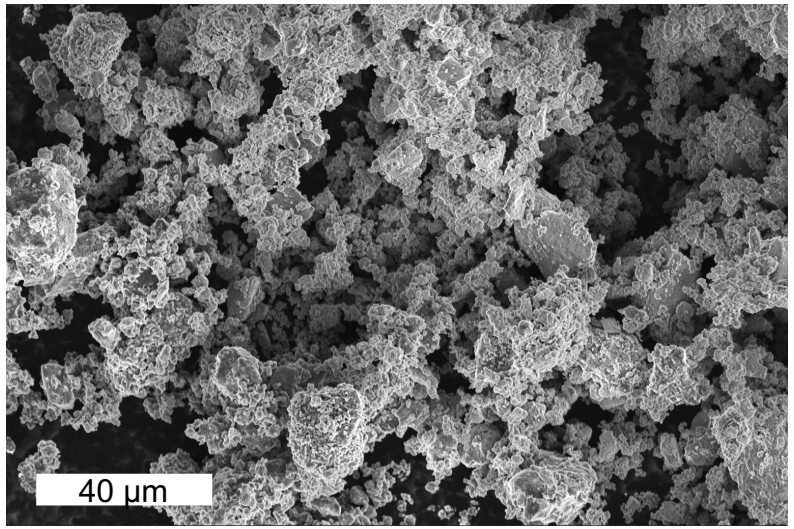
Dry room compatibility - yes!
Dry processing – at scale!!!

Pressure

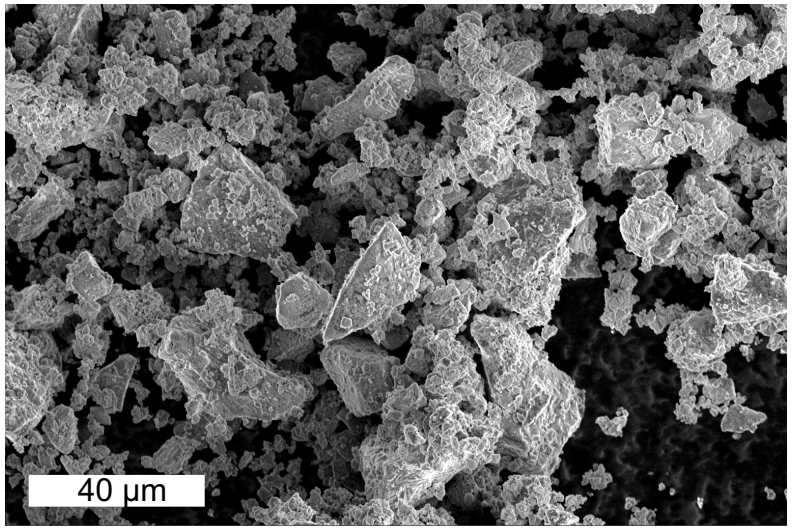
Pressure reduction from 100MPa – 50MPa – 5MPa
Making SSB structural component

Processing is the Key

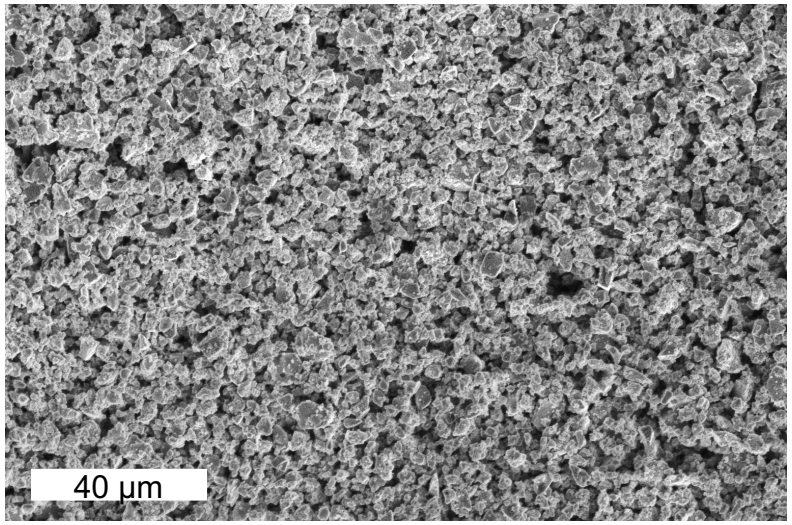
USA S1



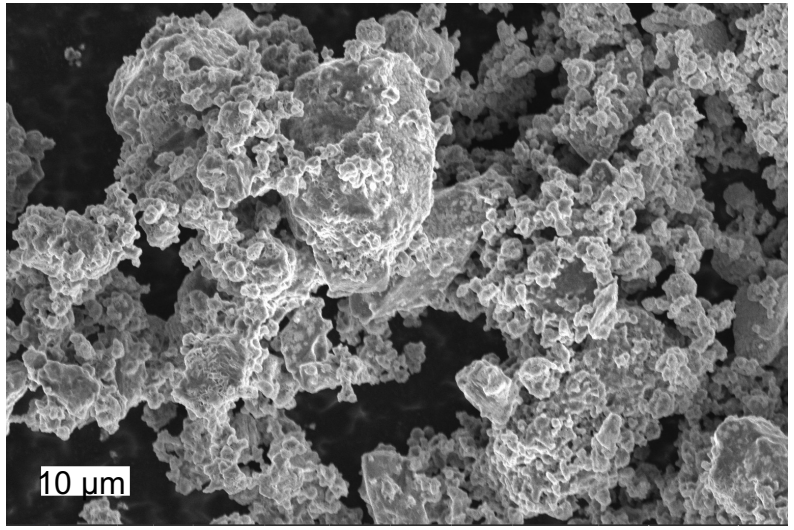
USA S2

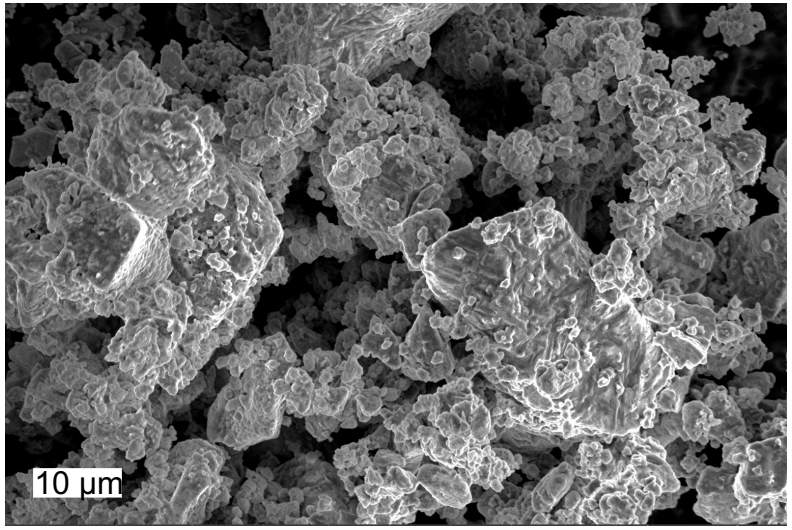


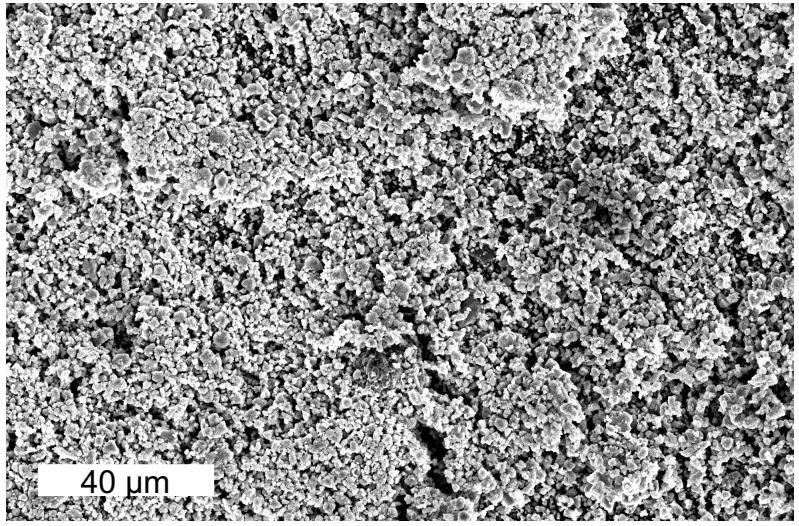
Japan S1



(A)







(B)

A Very Disturbing Paper…

CHEMISTRY OF MATERIALS

pubs.acs.org/cm Article

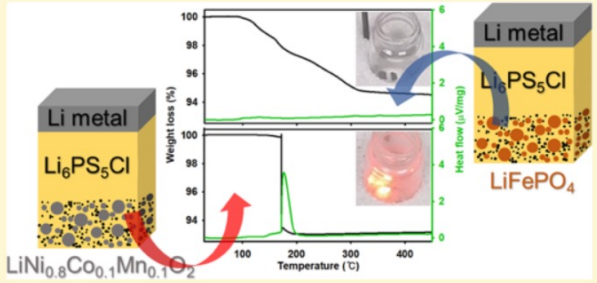
Thermal Runaway Behavior of Li_6PS_5Cl Solid Electrolytes for $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ and $LiFePO_4$ in All-Solid-State Batteries

Taehun Kim,‡ Kanghyeon Kim,‡ Seonghyun Lee, Gawon Song, Min Soo Jung, and Kyu Tae Lee*

Cite This: *Chem. Mater.* 2022, 34, 9159–9171 Read Online

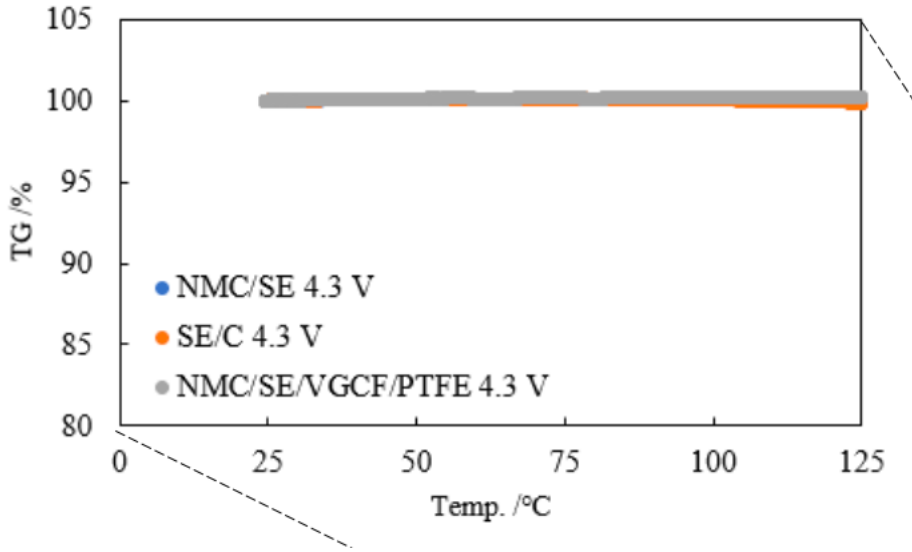
ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: All-solid-state batteries (ASSBs) have received much attention because of their high energy density and safety. However, the safety of argyrodite-type Li_6PS_5Cl (LPSCl)-based ASSBs is still not assured because their thermal stability has been assessed under selected mild conditions. Herein, we introduce the poor thermal stability of LPSCl with Ni-rich layered oxide cathode materials as the trigger of thermal runaway. The charged composite cathode pellets containing $Li_{1-x}Ni_{0.8}Co_{0.1}Mn_{0.1}O_2$ and LPSCl are explosively burned at 150 °C even in Ar. Moreover, the mechanical abuse gives rise to violent burning at room temperature. This is due to vigorous exothermic chemical reactions between delithiated $Li_{1-x}Ni_{0.8}Co_{0.1}Mn_{0.1}O_2$ and LPSCl. However, LPSCl with $LiFePO_4$ exhibits excellent thermal stability, such as no violent exothermic reactions even at 350 °C. This is because LPSCl is metastable with delithiated $Li_{1-x}FePO_4$. Moreover, $LiFePO_4$ shows excellent electrochemical performance, such as a high reversible capacity of 141 mAh g^{-1} and stable capacity retention over 1000 cycles, despite the fact that $LiFePO_4$ is known to be poorly electrochemically active for ASSBs. These findings provide fundamental insights to improve the thermal stability and electrochemical performance of LPSCl-based ASSBs.



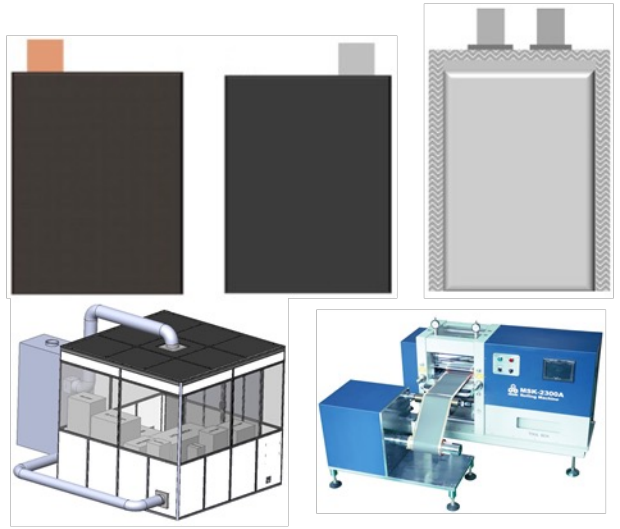
As a summary, I believe this paper is creating very specific scenarios to generate a NCM fire, and misinterpreting the cause as the SSE, which is not related to the ignition in the first place.

Dr. Darren Tan – CEO of UNIGRID



Data from work UC San Diego

Making ASSBs a Reality

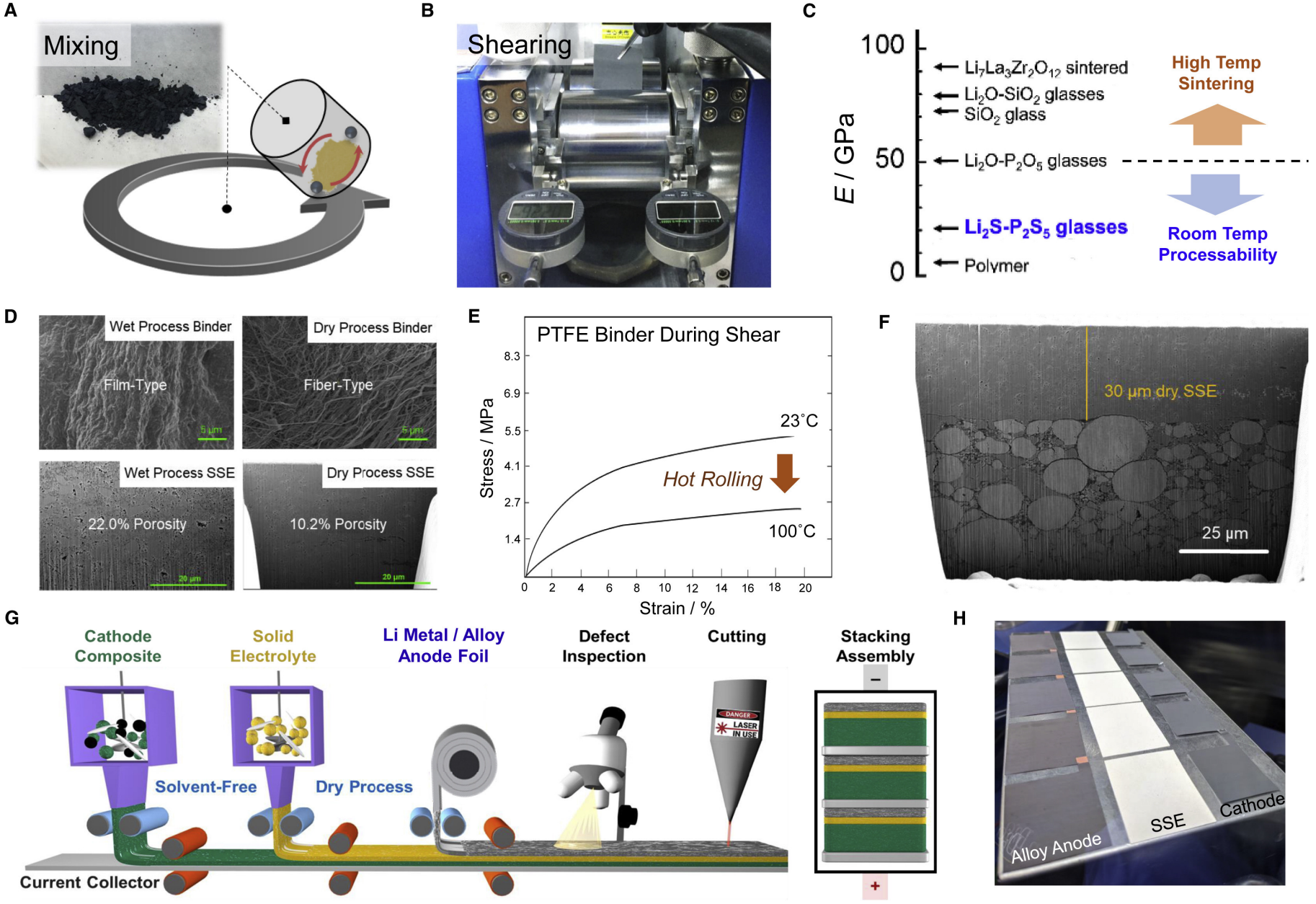


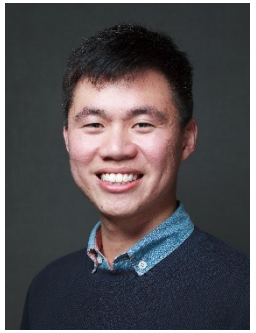
	Laboratory Research	Pilot Prototyping	Production Scale
Cell Size	0.001 to 1 Ah	0.1 Ah to 10 Ah	> 10 Ah Cells / kWh Packs
Methods	Manual – Glovebox Environments	Semi-Automated – Glovebox + Dry Room	Fully Automated – Large Footprint Dry Labs
Focus	Material Discovery & Screening	Chemistry & Design Validation	Cost & Throughput Optimization
Barriers	Access to Resources & Tools	Scalability & New Materials Supply Chain	Defect Elimination for Quality Control

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

Acknowledgements First

U.S. DEPARTMENT OF ENERGY
Office of Science

DOE BES 2012-now (Dr. Jane Zhu)
LiPON SSB and Perovskite SC and Memrisistive

ThermoFisher SCIENTIFIC

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

Sustainable Power and Energy Center

MIT KJ GROUP

LG Energy Solution
LGES-UCSD Frontier Research Laboratory

Battery Prototyping

sdni San Diego Nanotechnology Infrastructure

nano3 SCIENCE ENGINEERING MEDICINE

UC IRVINE MATERIALS RESEARCH INSTITUTE

Solid State Battery Team at my group