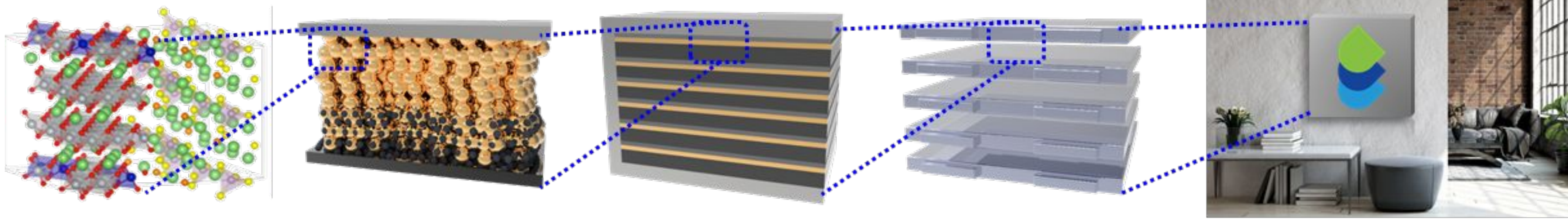
LESC
Laboratory for Energy Storage and Conversion

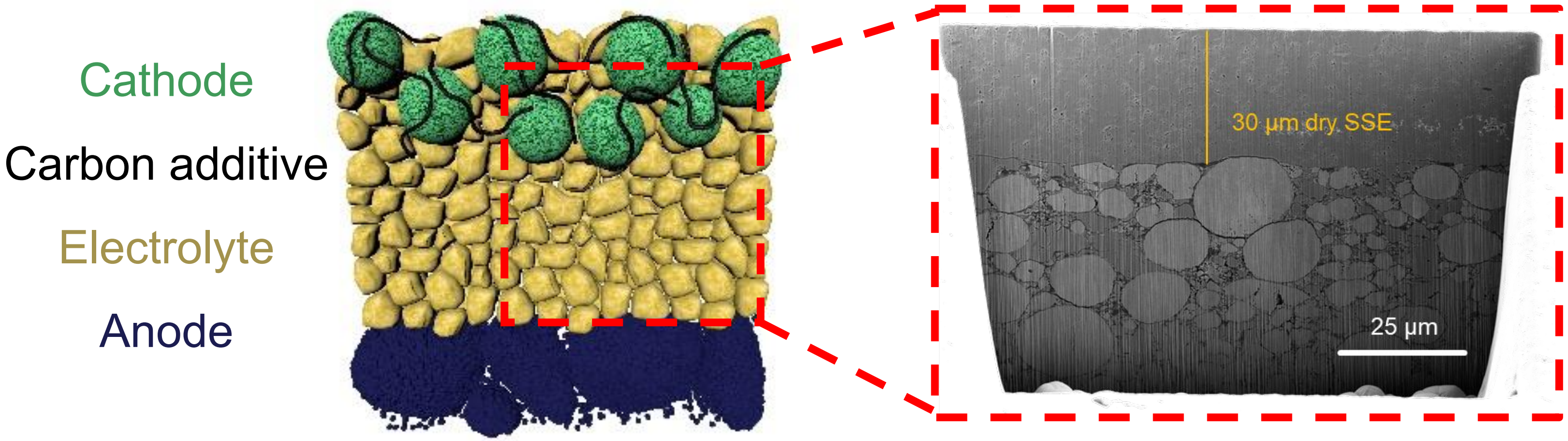


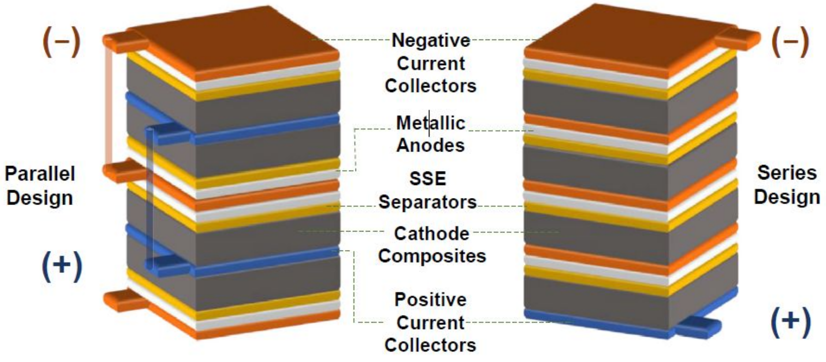
Enabling ALL-Solid State Battery Via Interfacial Science & Engineering

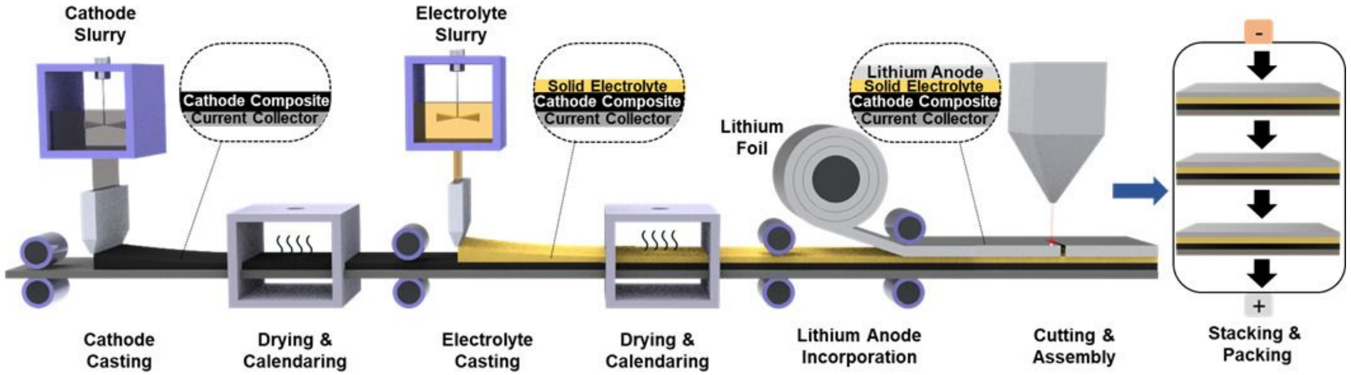
Y. Shirley Meng

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

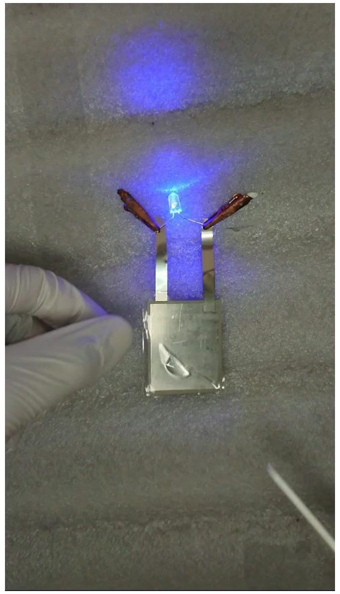
A Platform Technology Enabled by Green Manufacturing







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



Series (bi-polar) stacking:

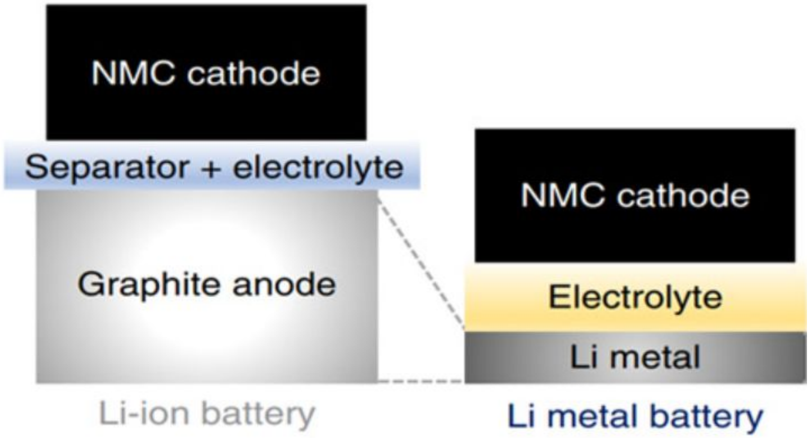
- Reduces inactive materials components → increase energy density
- Higher overall voltage per cell

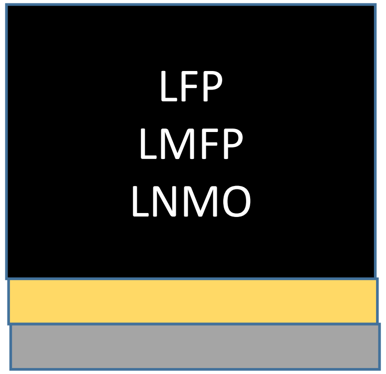
- Enhanced safety and abuse tolerance

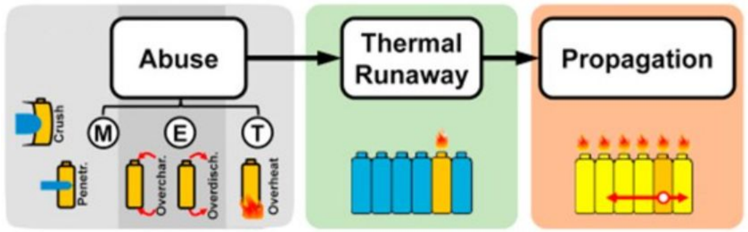
All solid-state batteries – Platform Technology

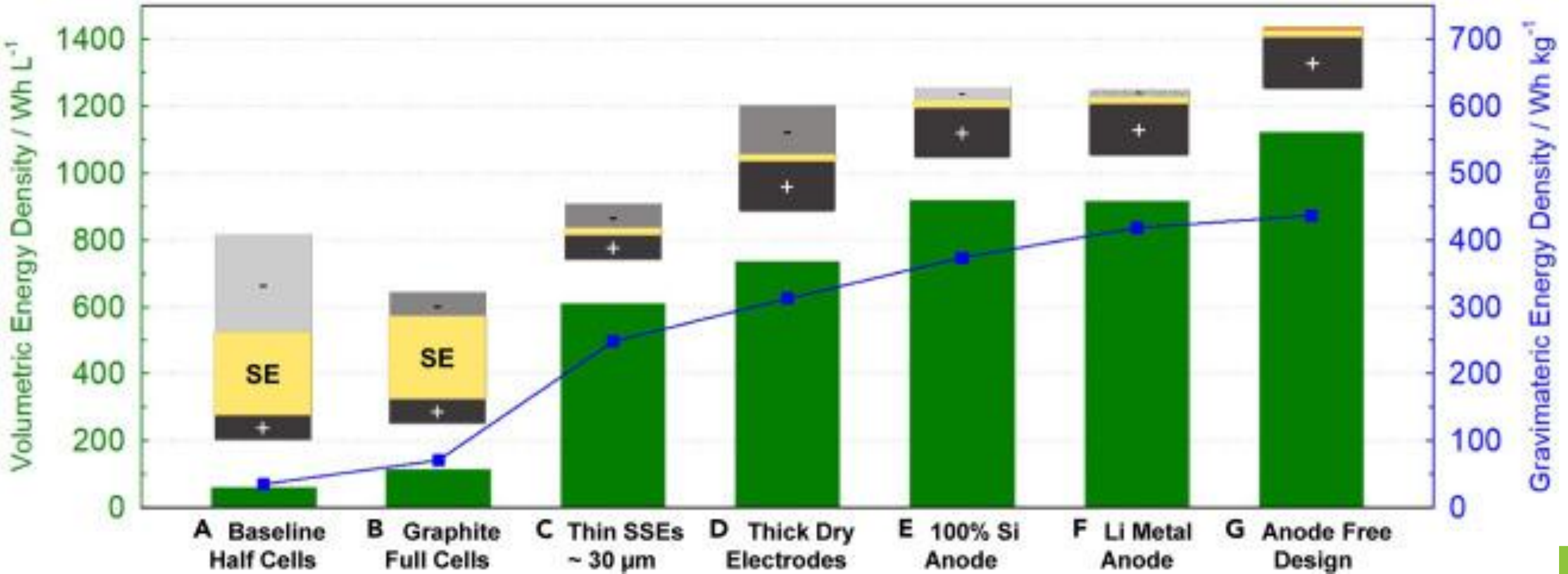
High-Energy-Density** and **Safe Batteries

*with **Solid-State Electrolyte***





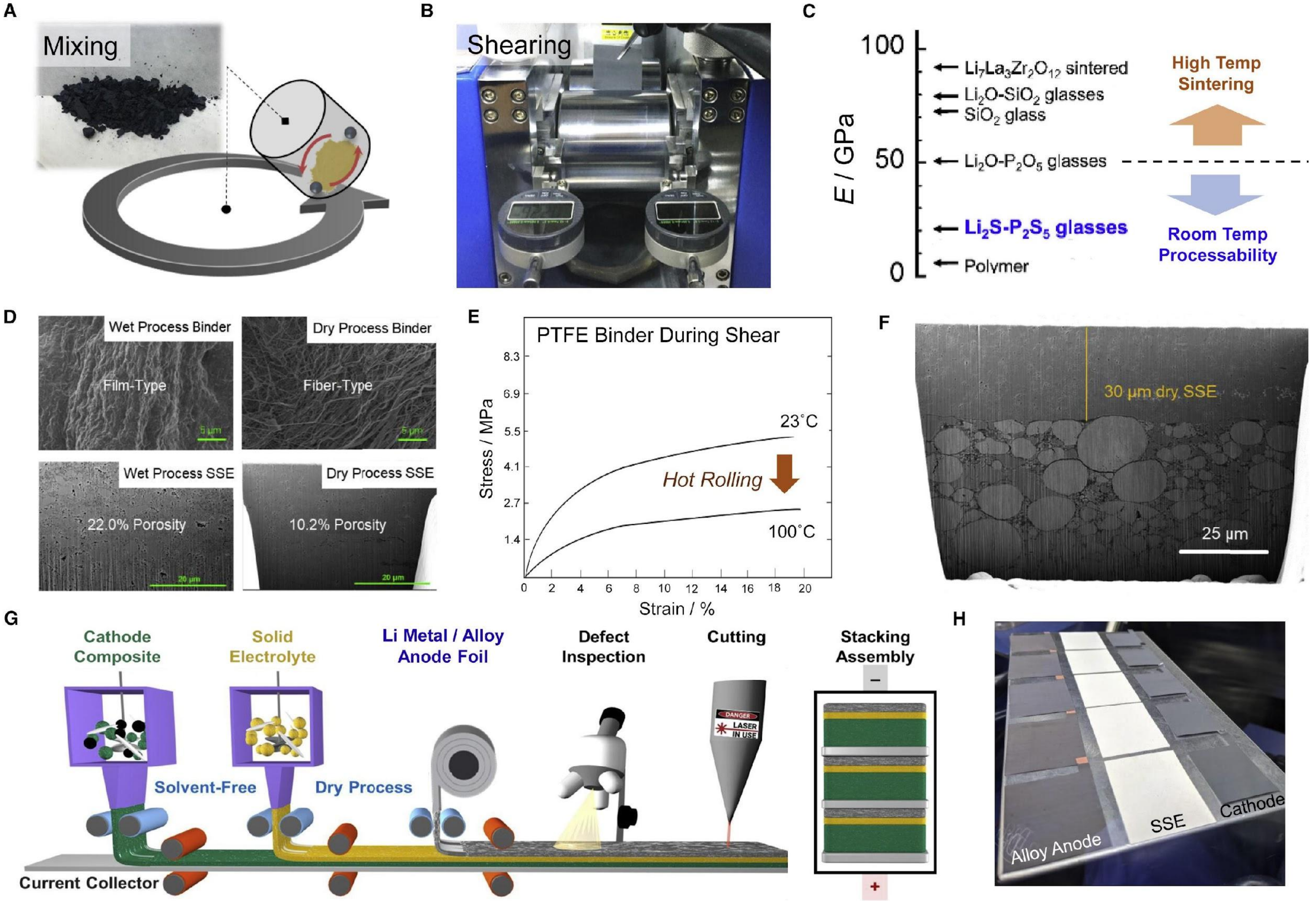


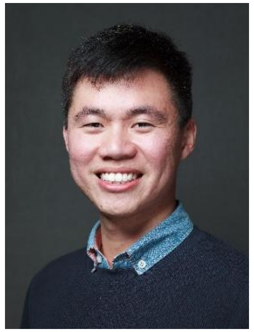


D. Tan, J. Jang and Y.S. Meng Joule 2022

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

Joule





Dr. Darren Tan

Dr. Jihyun Jang

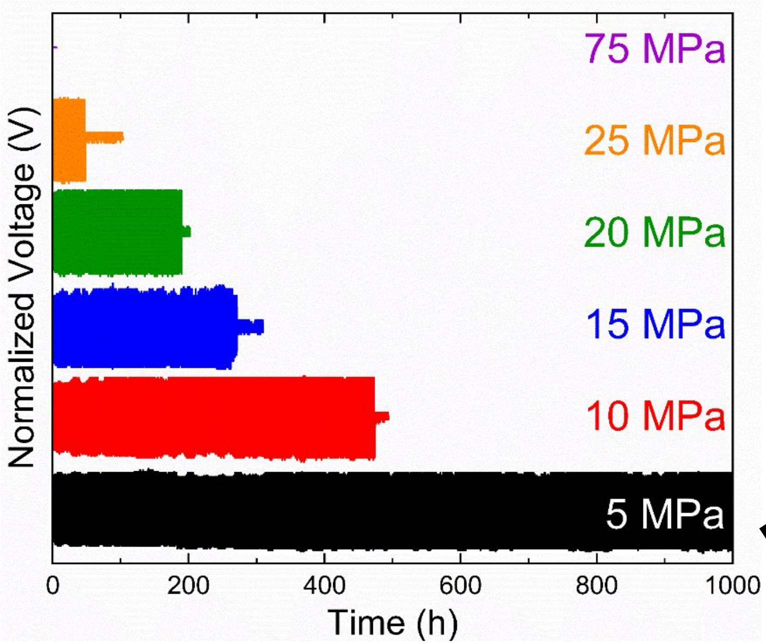
When will All Solid-State Battery Will be Commercialized ?

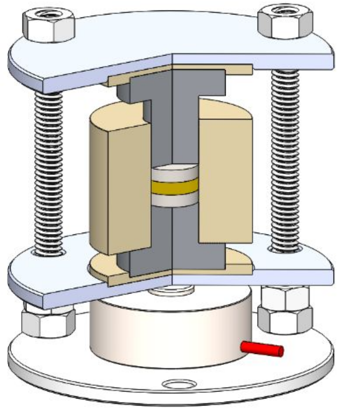
Polymer based ones are already there!

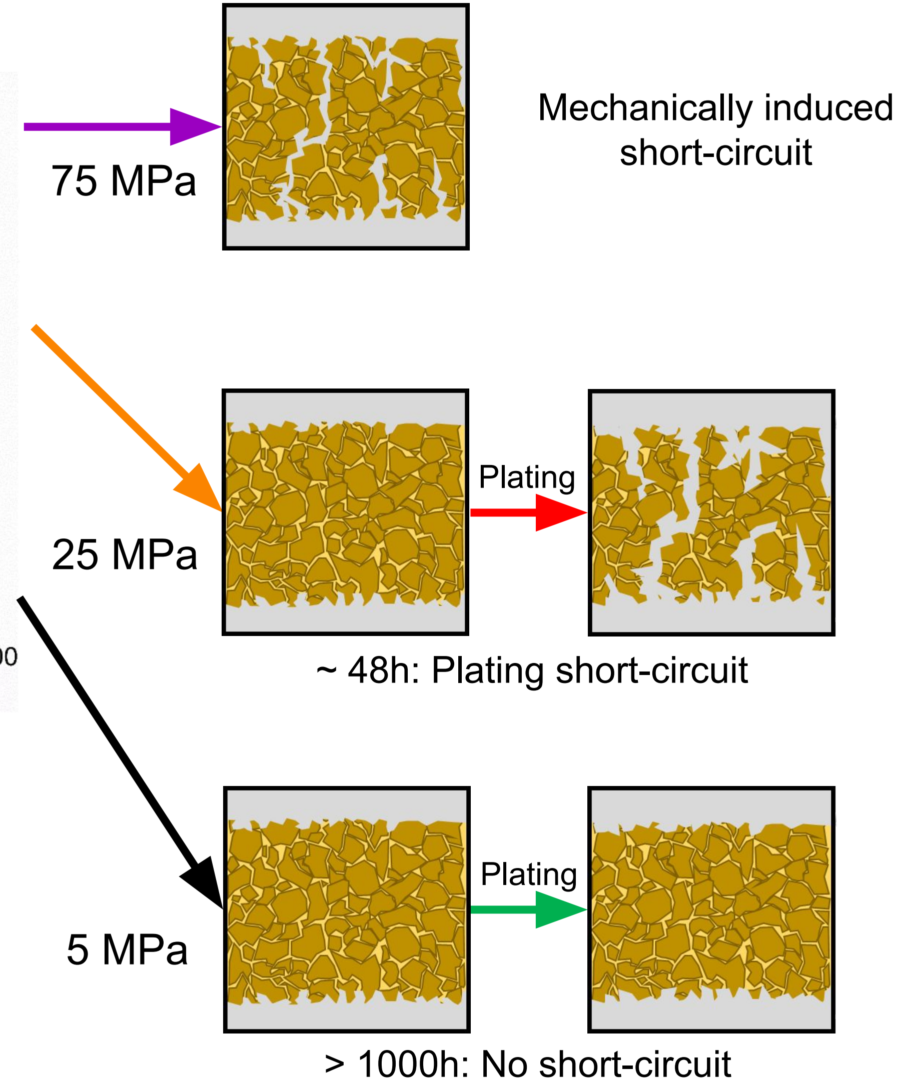
We are going for inorganic solids ☺️

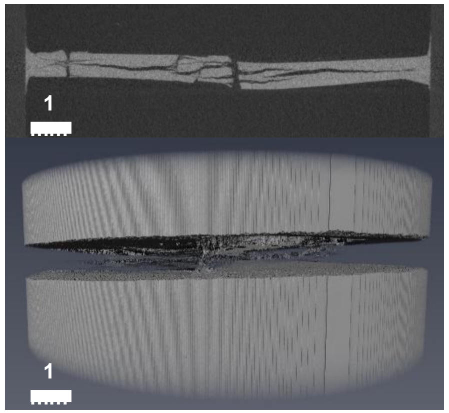
Stack pressure effect on Li metal anode

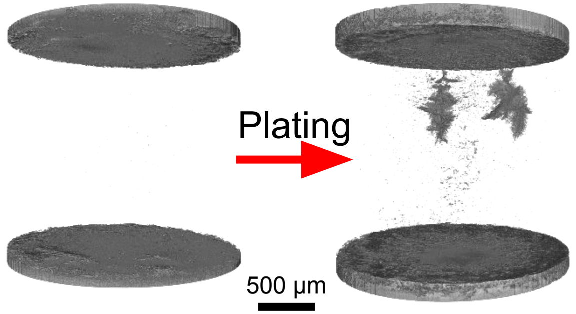
Li symmetric cells

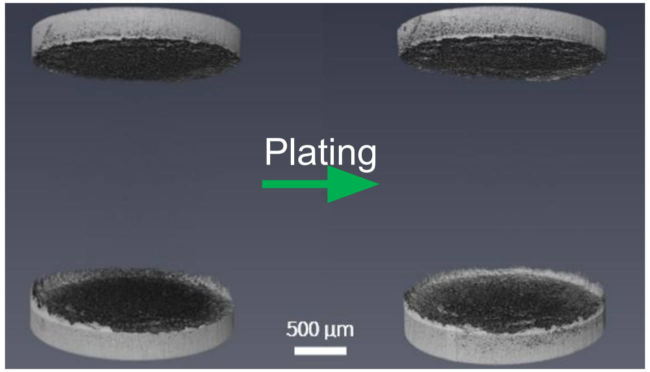






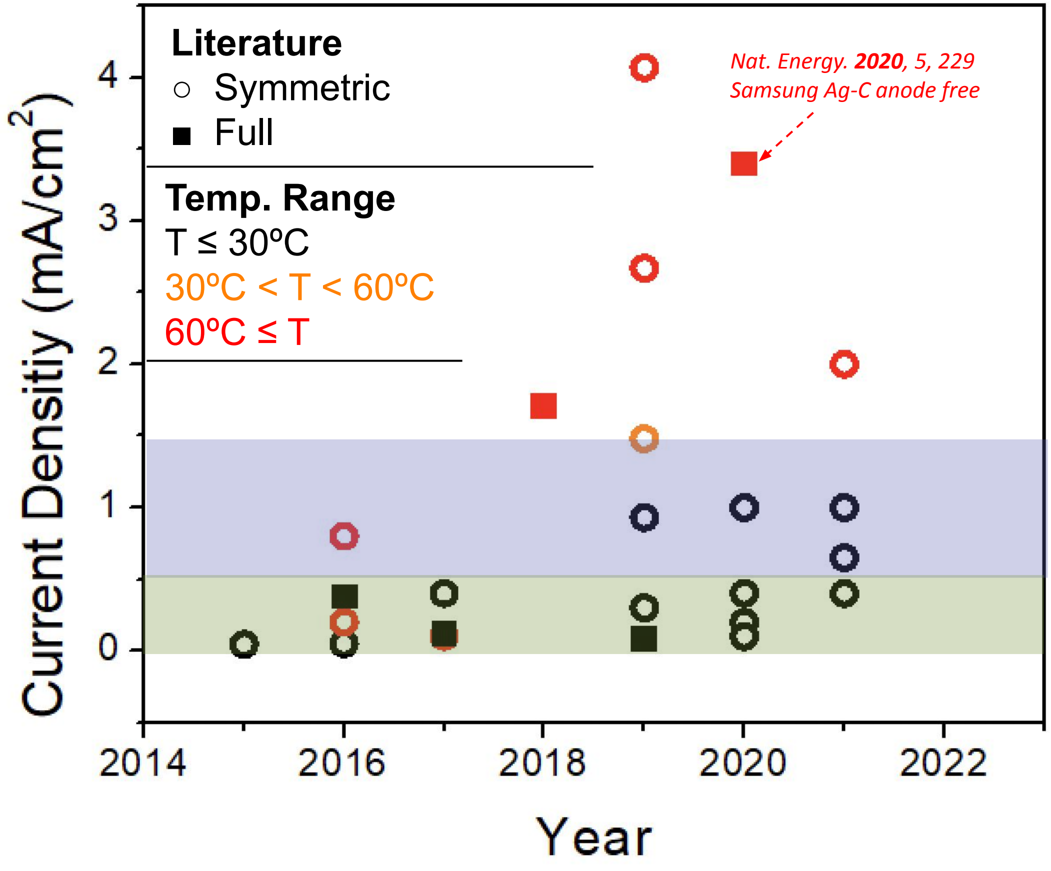


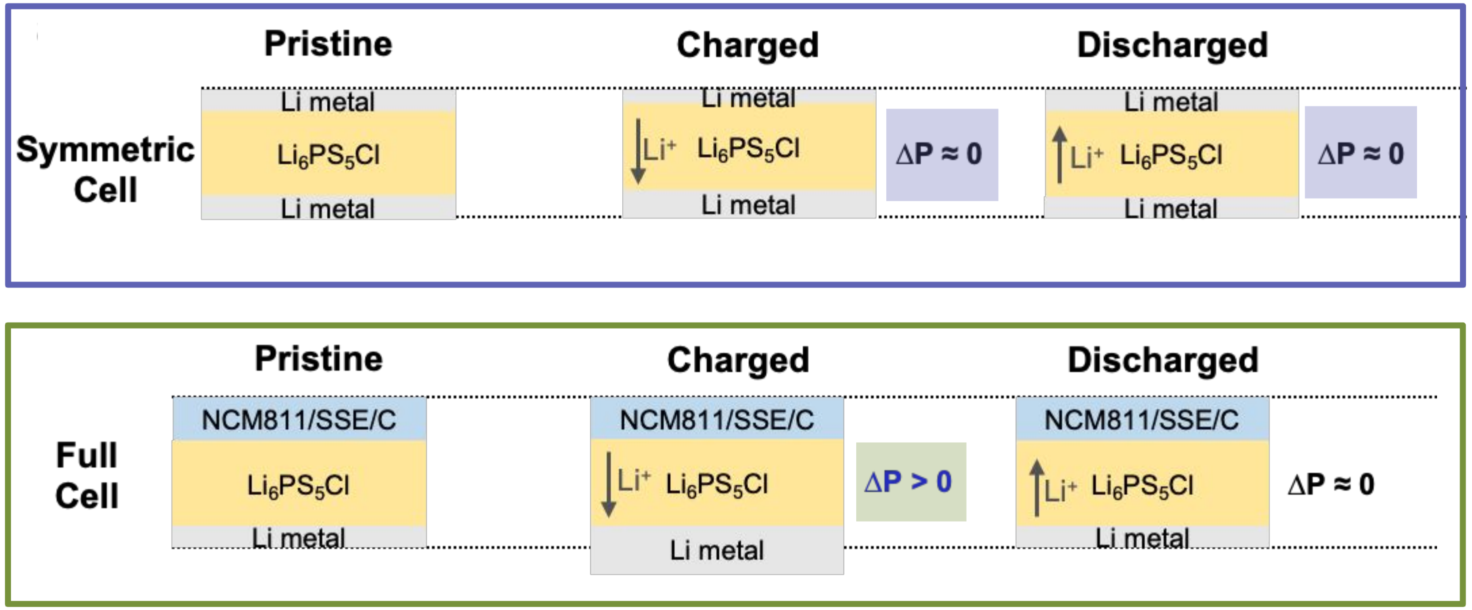




Doux, J.-M.; Nguyen, H.; Meng, Y. S. *et al.*, Stack Pressure Considerations for Room-Temperature All-Solid-State Lithium Metal Batteries. *Adv. Energy Mater. 10,* 1903253, **2020**.

Reported Critical Current Densities of Li Metal ASSB



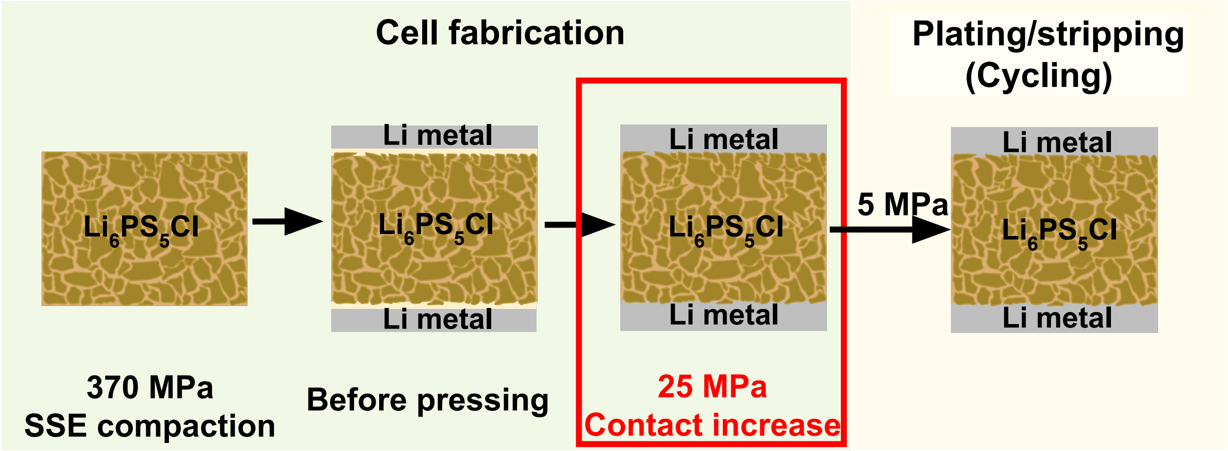


- Critical current density: Symmetric > Full
- Near room temperature full cell: < 1 mA/cm^2
- Pressure change: Symmetric < Full

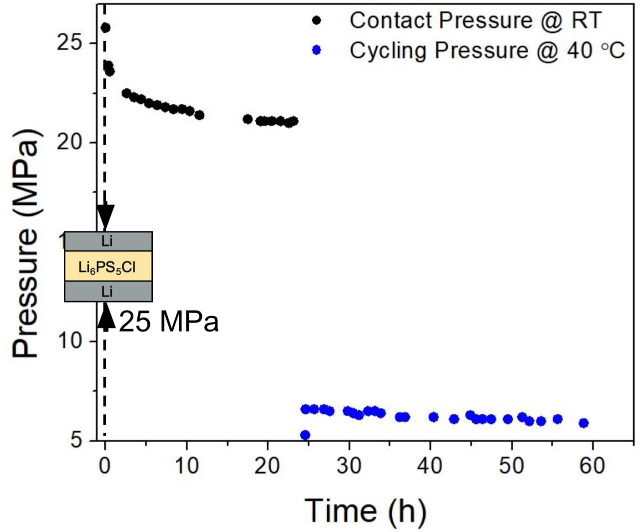
Ham et al. *Energy Storage Material. Under* revision

Li Metal Symmetric Cell: Cell Fabrication/Contact

Li Metal Symmetric Cell Fabrication & Cycling Process



Pressure Monitoring of Li Metal Symmetric Cell

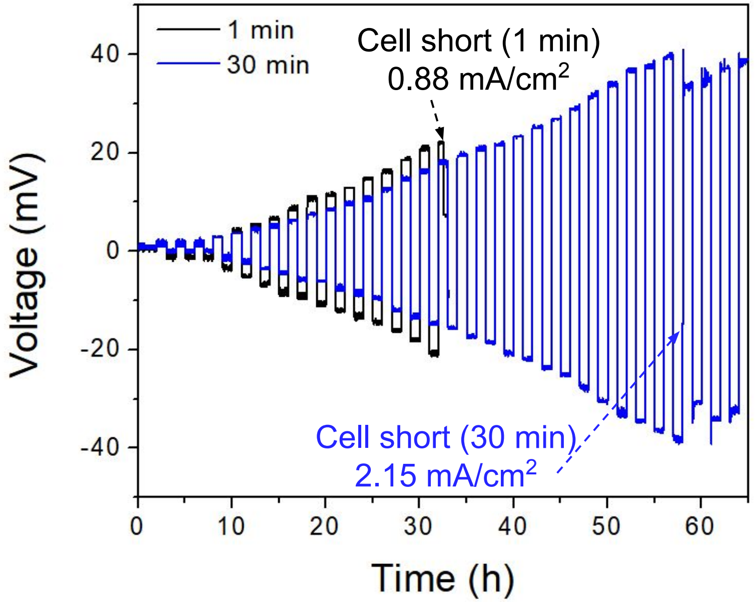


- Three different pressures applied during the fabrication/cycling process
  1. SSE compaction pressure = 370 MPa
  2. Contact pressure = 25 MPa
  3. Cycling pressure = 5 MPa

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

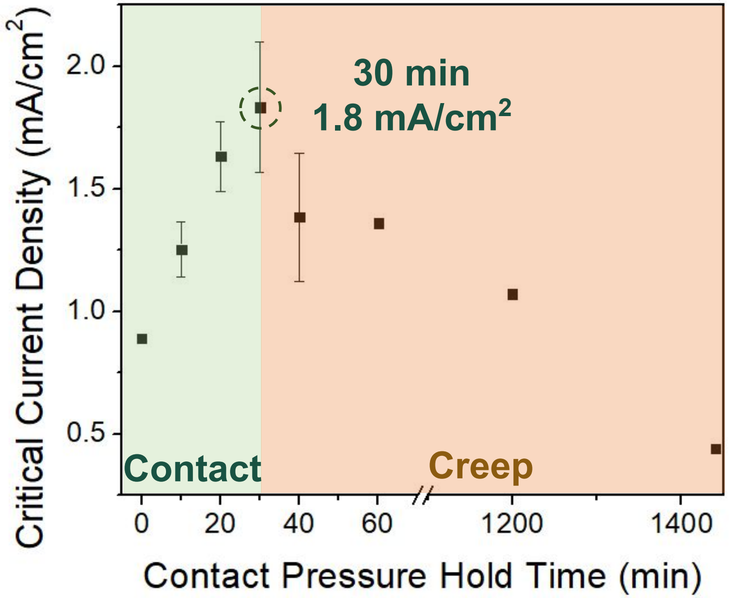
Li Metal Symmetric cell: CCD/Failure

Ramping Test of Different Contact Time Cells



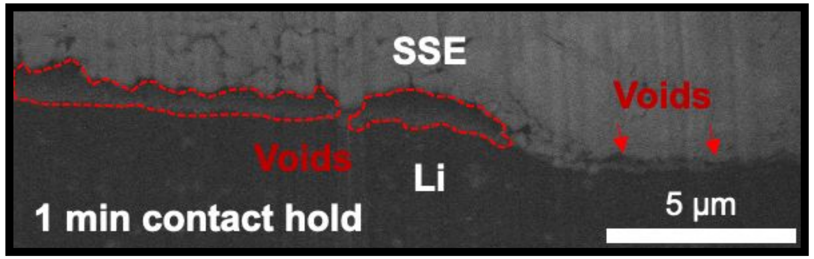
- Ramping test for CCDs of symmetric cells
- Higher CCD in 30 min contact hold sample

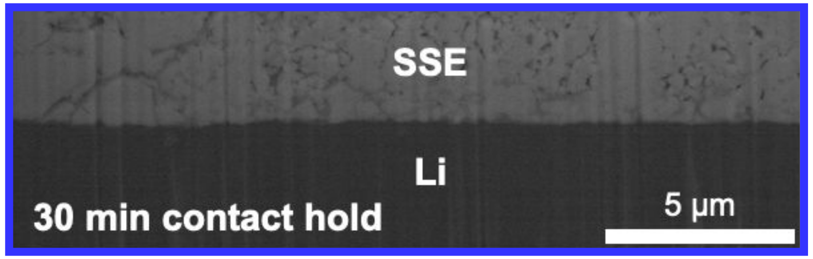
Ramping Test of Different Contact Time Cells



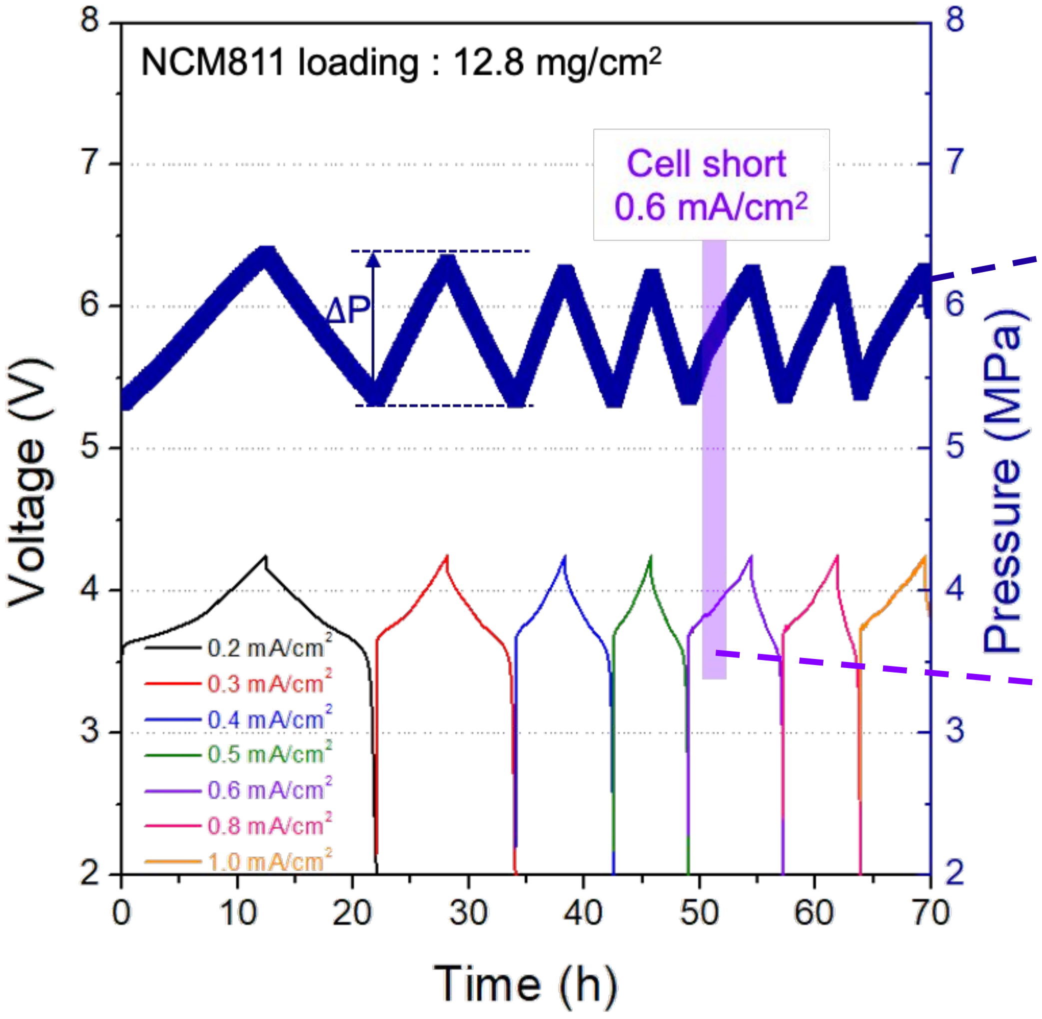
- CCD trends depending on contact hold time
- CCD increase until 30 min contact, decrease afterwards

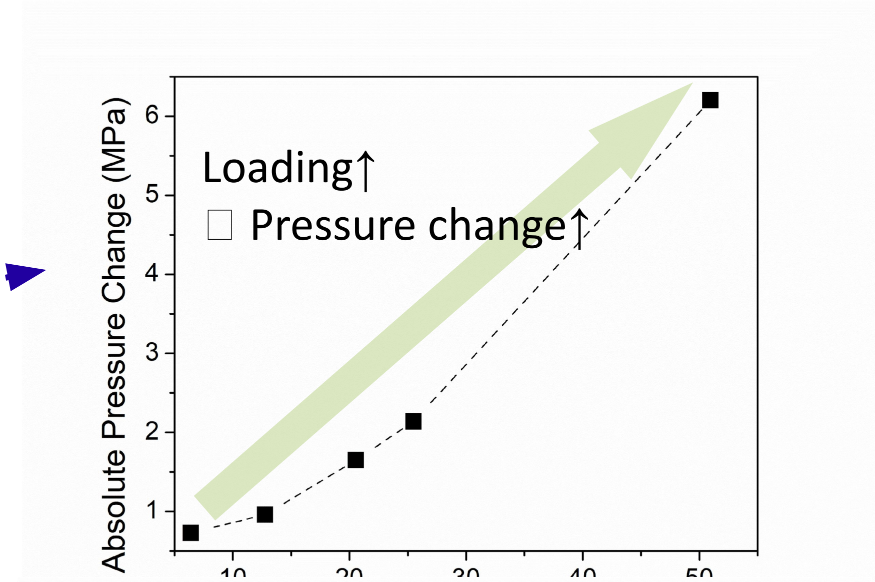
Cryo-FIB/SEM : Direct observation of Li/SSE interface

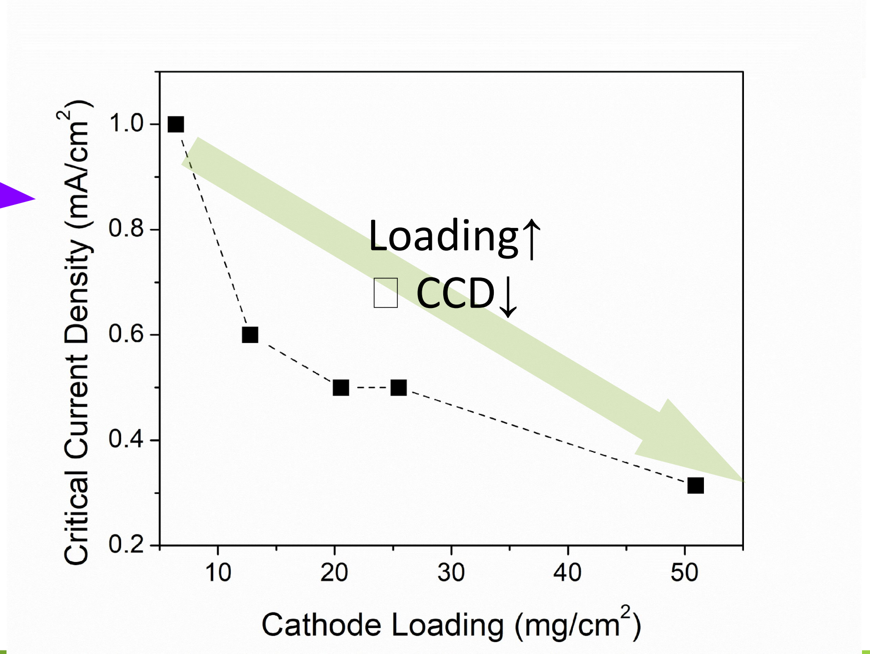




Li Metal Full Cell: Pressure Dependence





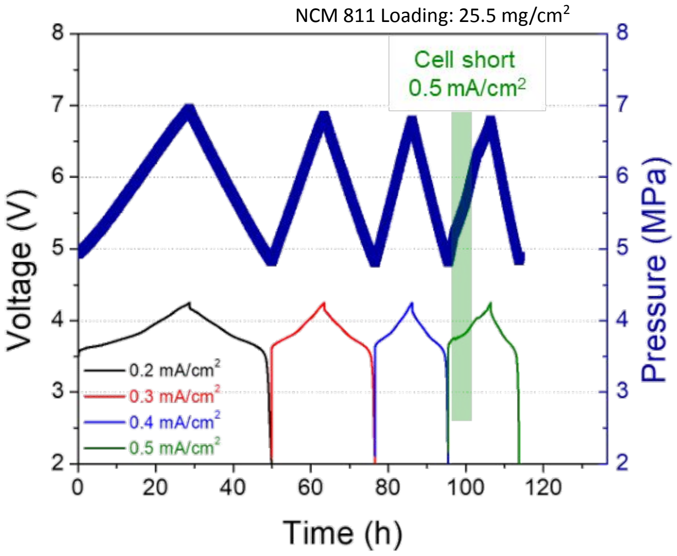


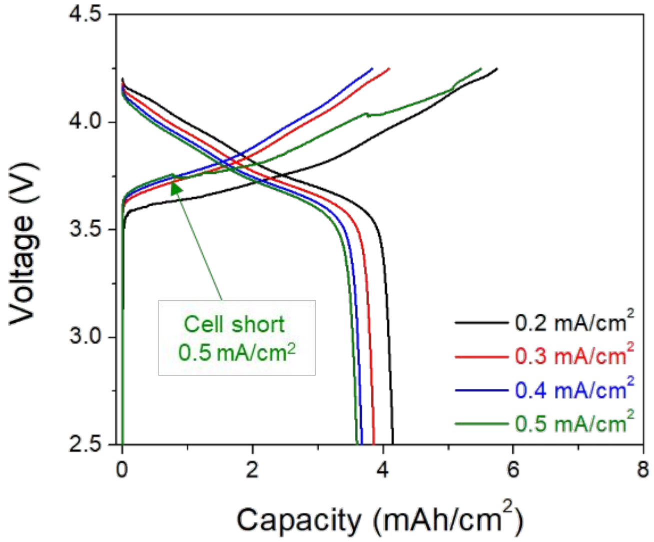
- Ramping test conducted to evaluate CCDs of full cell
- Full cell: Pressure change during cycling with lower CCD

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

Full Cell: Fixed Gap vs. Constant Pressure

Fixed gap

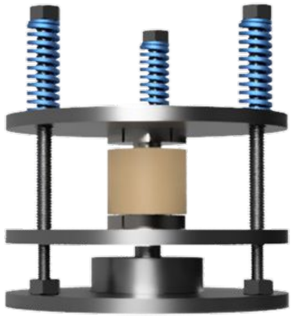


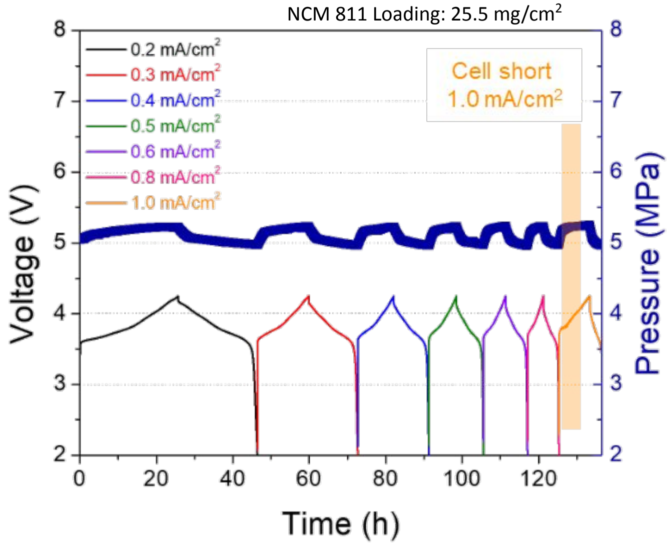


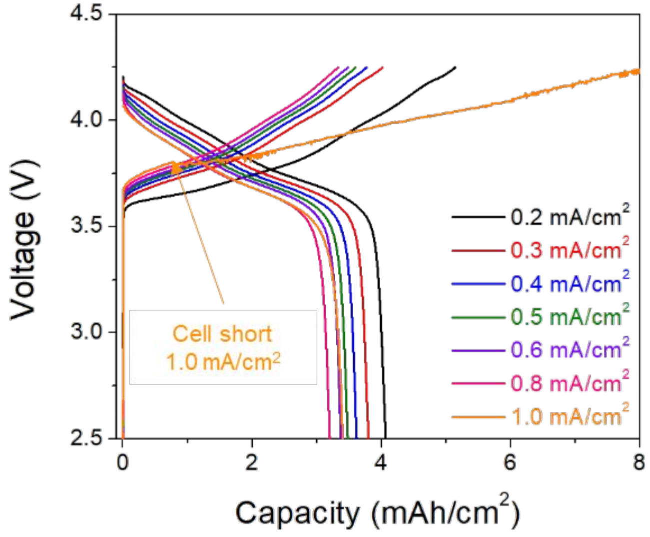
Lower pressure change and higher CCD in const pressure setup

Constant Pressure Set-up
for the volume change compensation

Constant pressure







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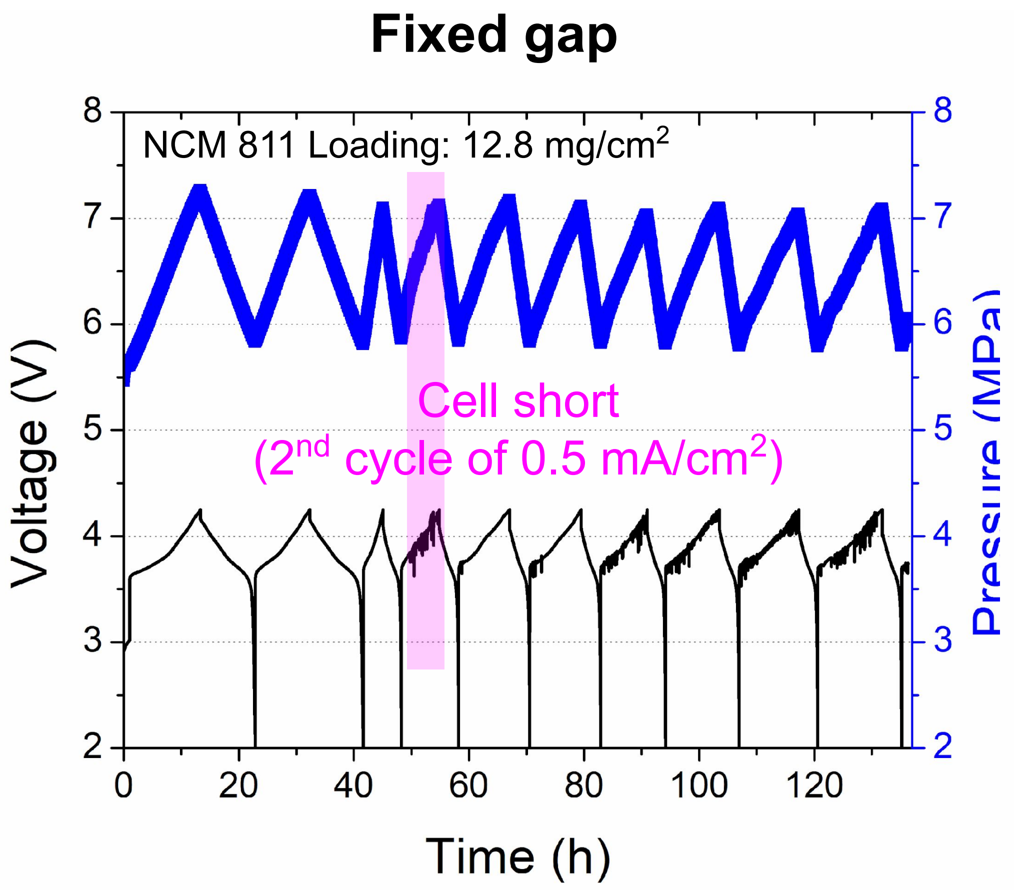
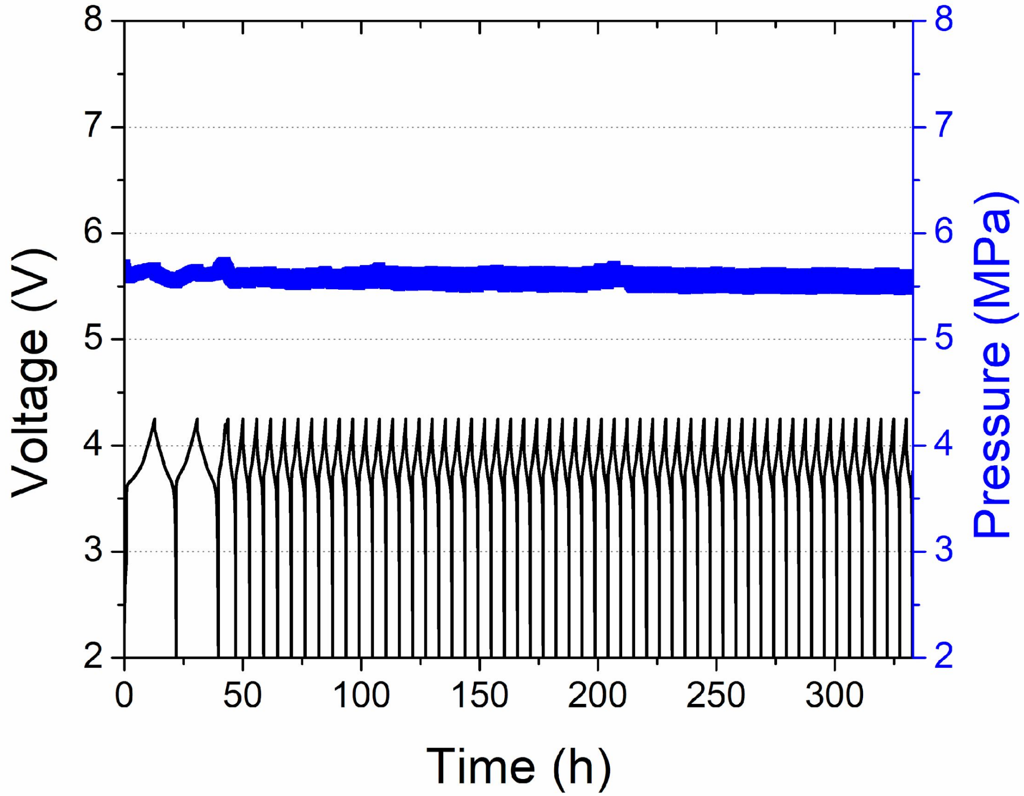
Long-term Cycling of Constant Pressure Setup





- 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

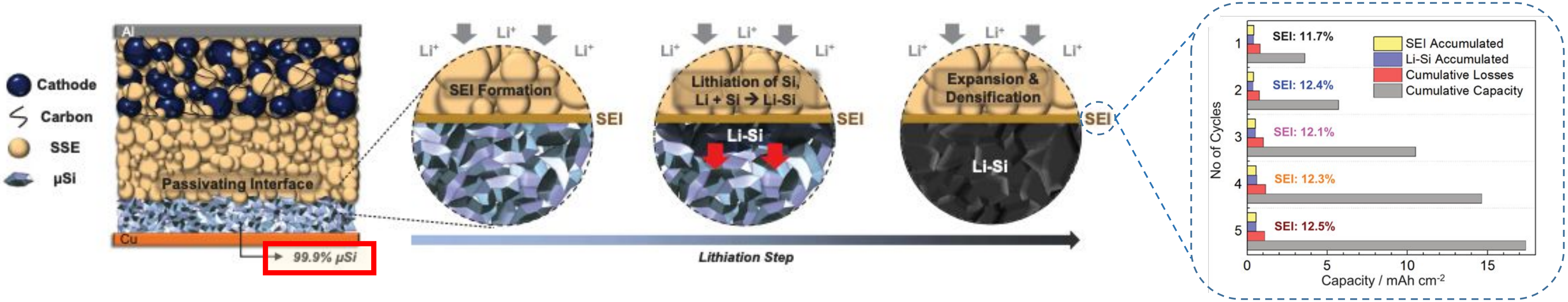
All-Solid-State-Li Metal Batteries:

- 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. 2023*

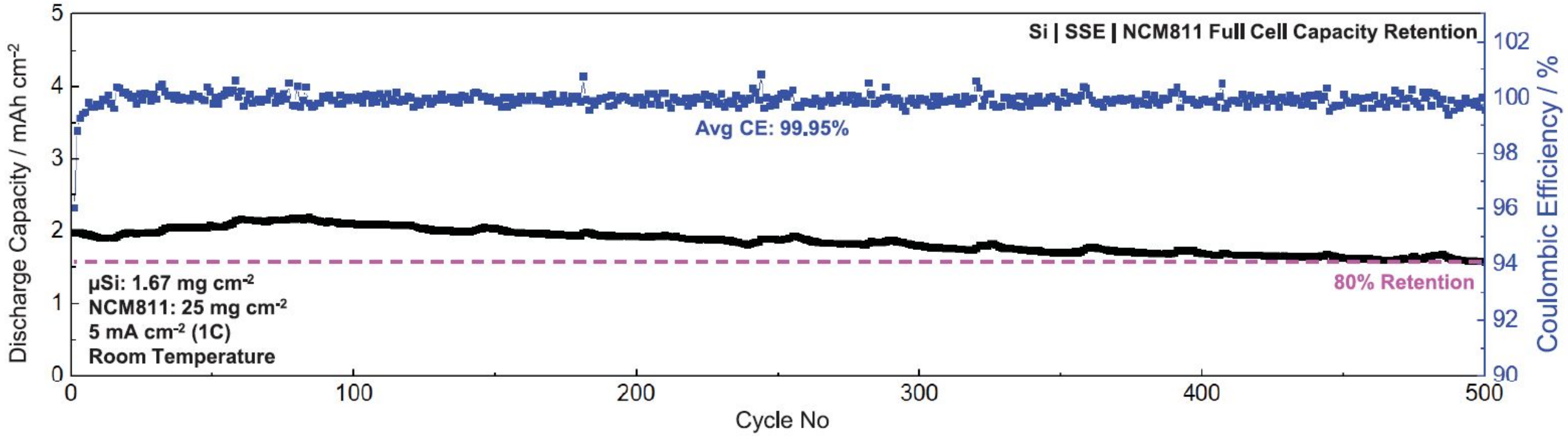
SSRN: https://ssrn.com/abstract=4213169 or http://dx.doi.org/10.2139/ssrn.4213169

Si Anode Synergy in Solid-State Batteries



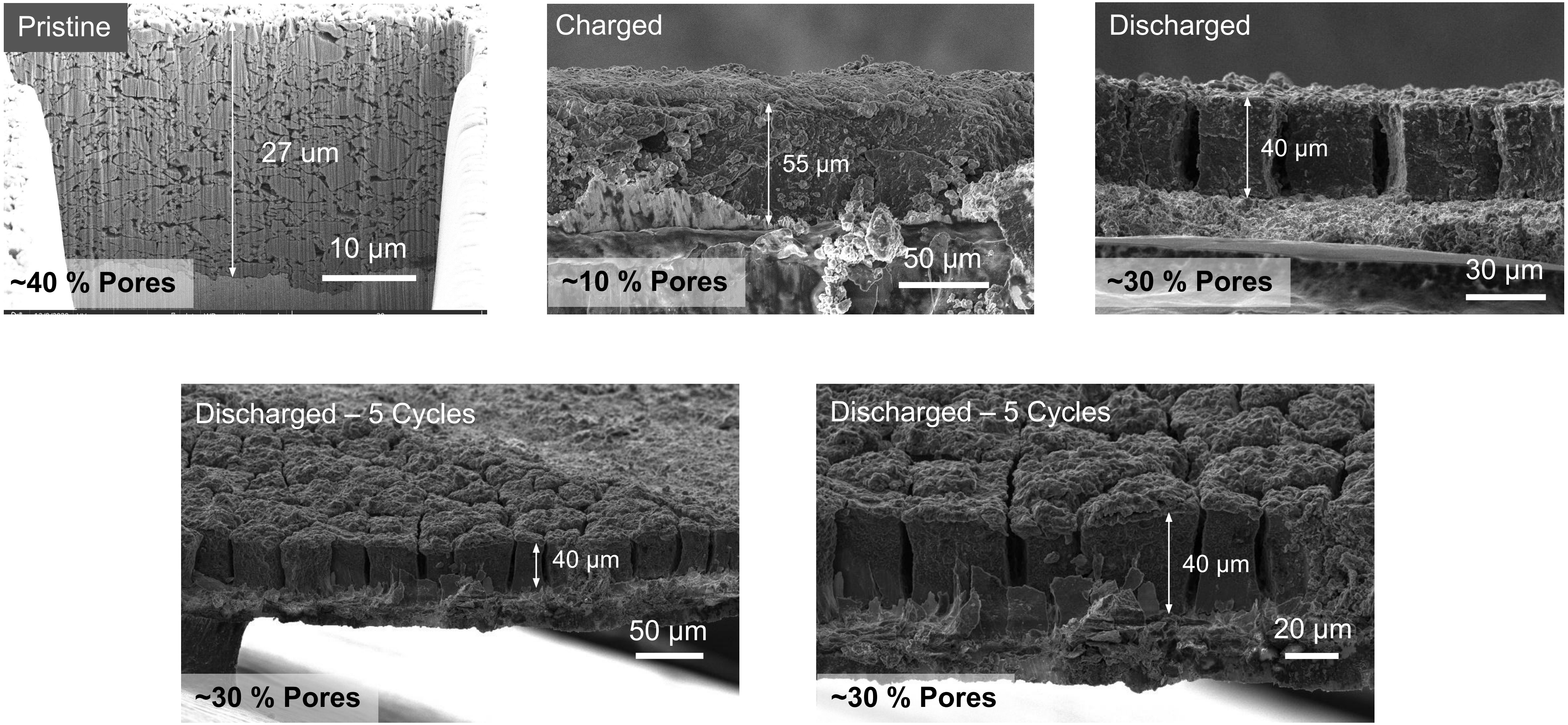
- Enable **99.9%** Si anode without carbon and solid electrolyte
- Inventory loss to the passivating SEI remained relatively constant
- Realized Si cycling >500 cycles

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



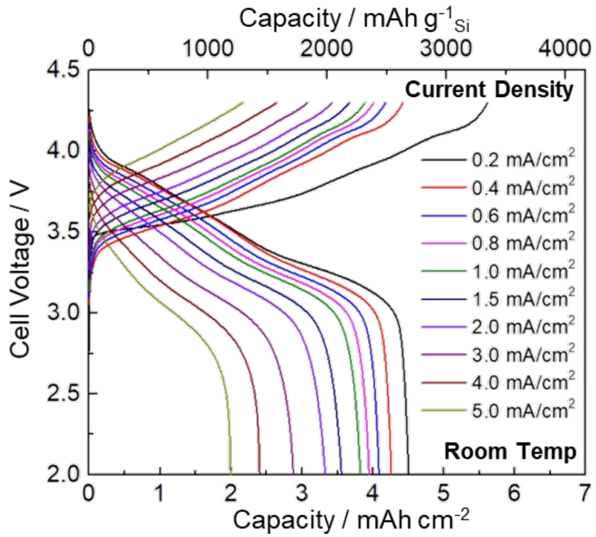
Porosity changes during cycling

~3.8 mg cm^{-2} – 12 mAh cm^{-2}

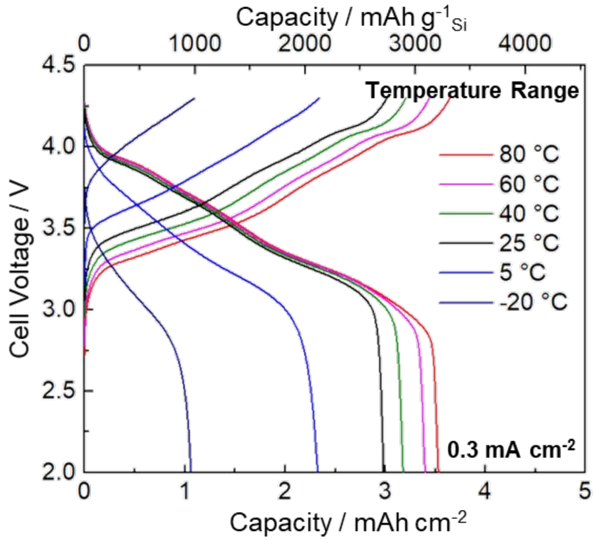


Tan, D.; Meng, Y. S. *et al.,* Carbon Free High Loading Silicon Anodes Enabled by Sulfide Solid Electrolytes for Robust All Solid-State Batteries. (*Science 2021*)

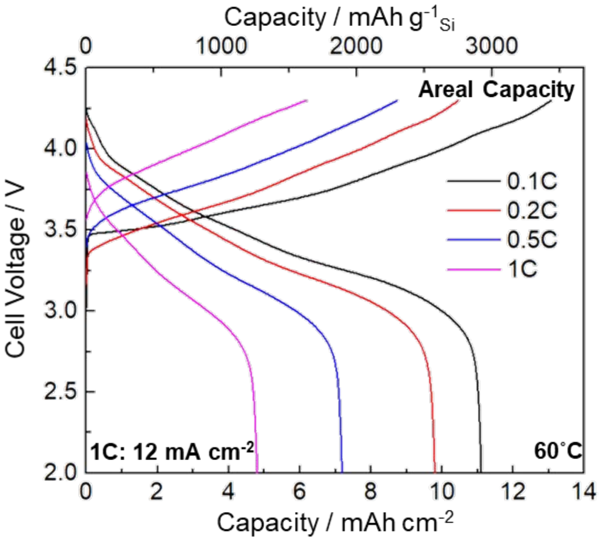
Electrochemical performance



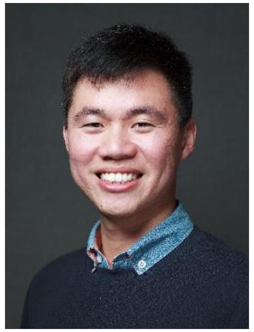
High Current Density



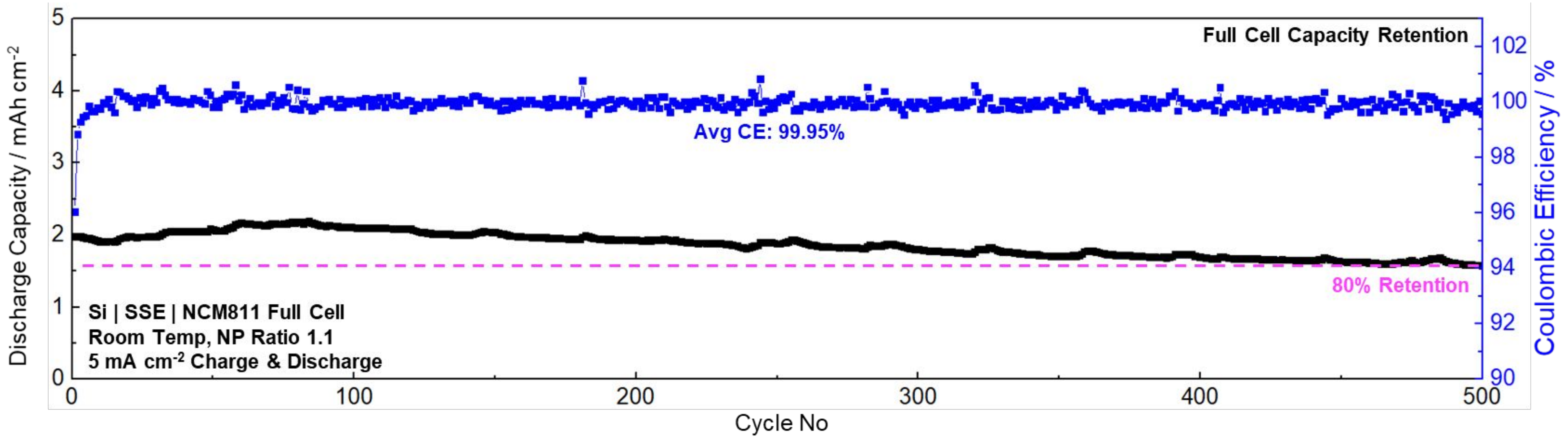
Wide Temperature Range



High Loading

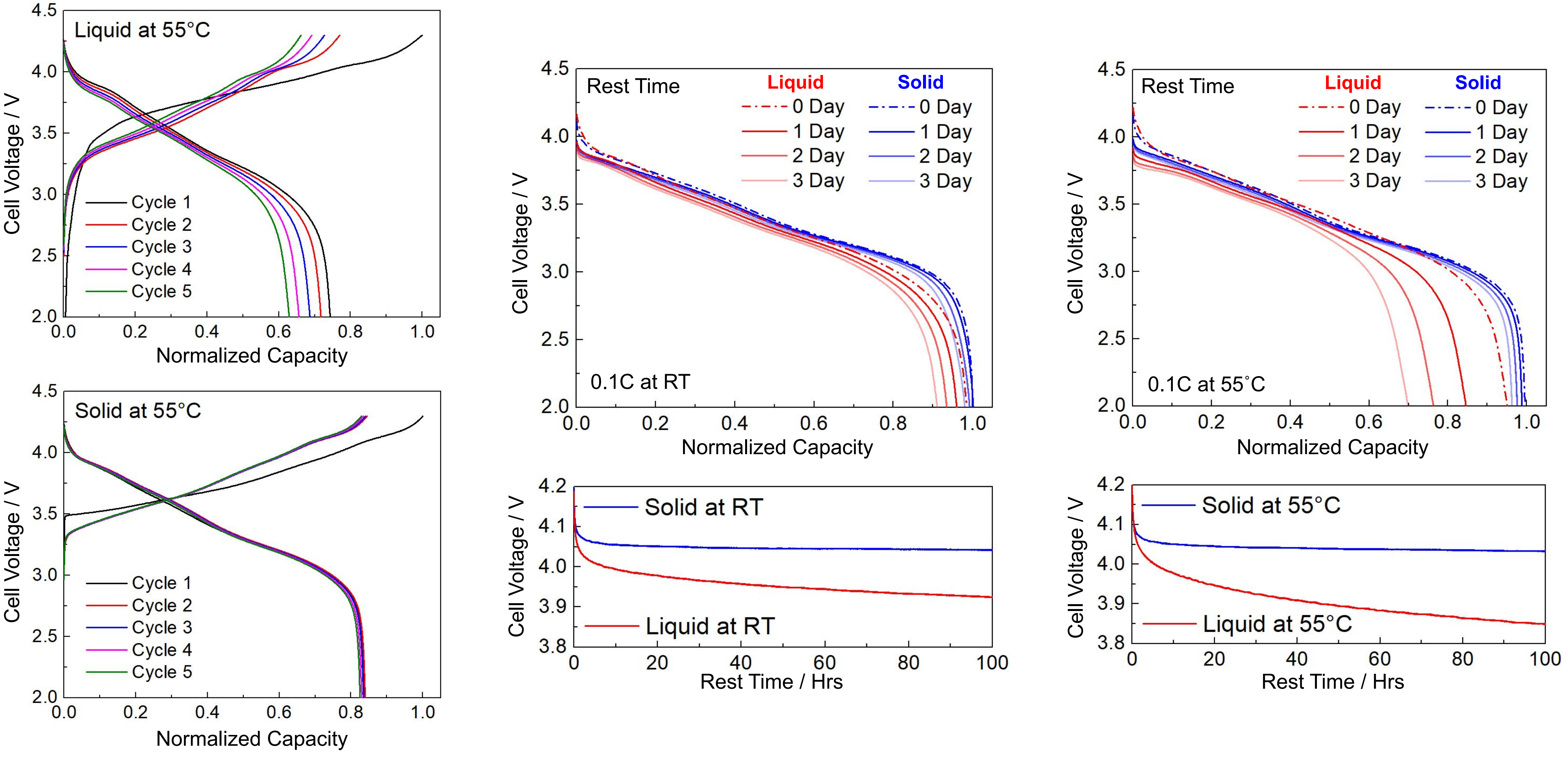


Dr. Darren Tan



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

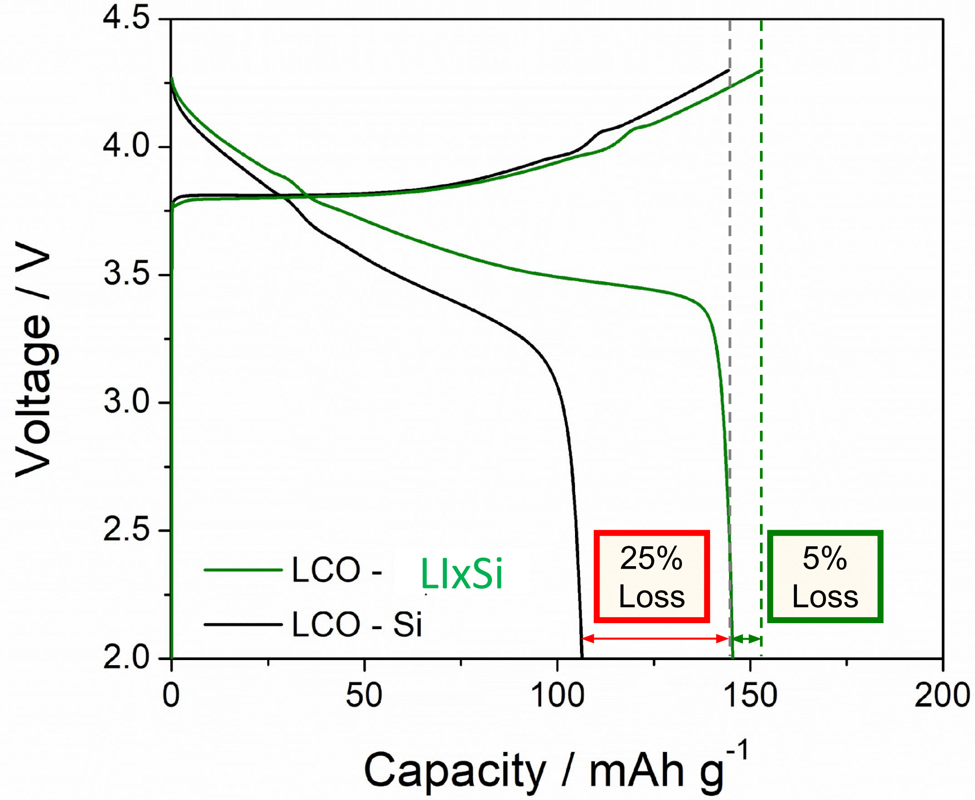


Tan, D.; Meng, Y. S. *et al.,* Carbon Free High Loading Silicon Anodes Enabled by Sulfide Solid Electrolytes for Robust All Solid-State Batteries. (*Science 2022)*

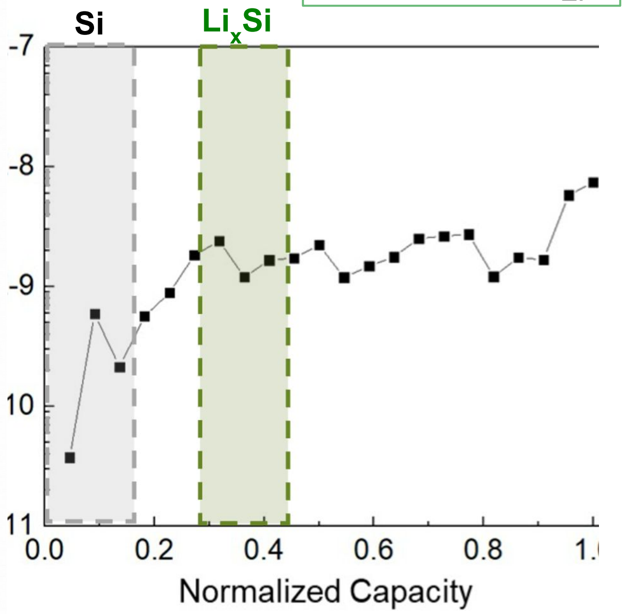
LG FRL - Anode Strategies

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

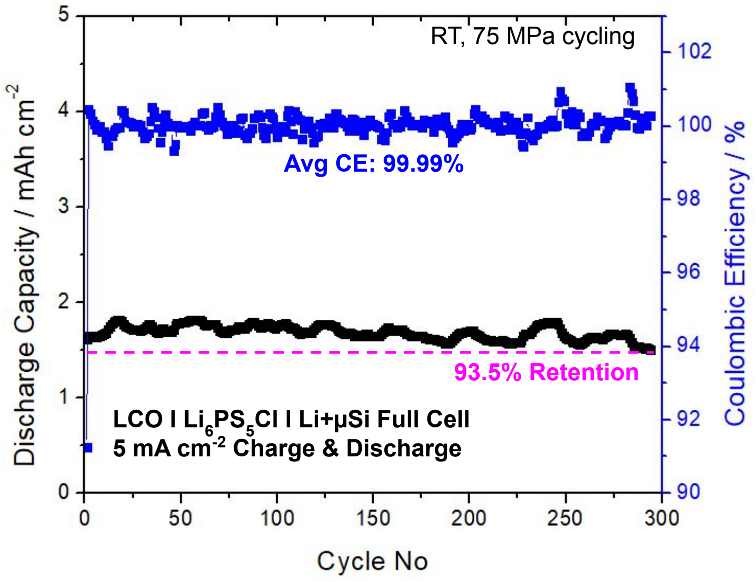
LGES-UCSD Frontier Research Laboratory



✔ Higher D_{Li}



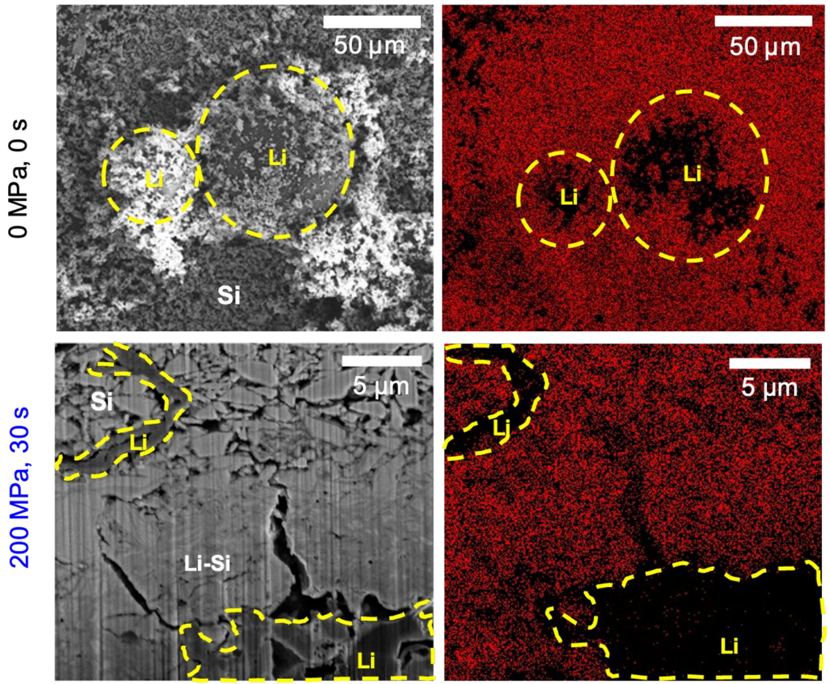
✔ Stable cycling



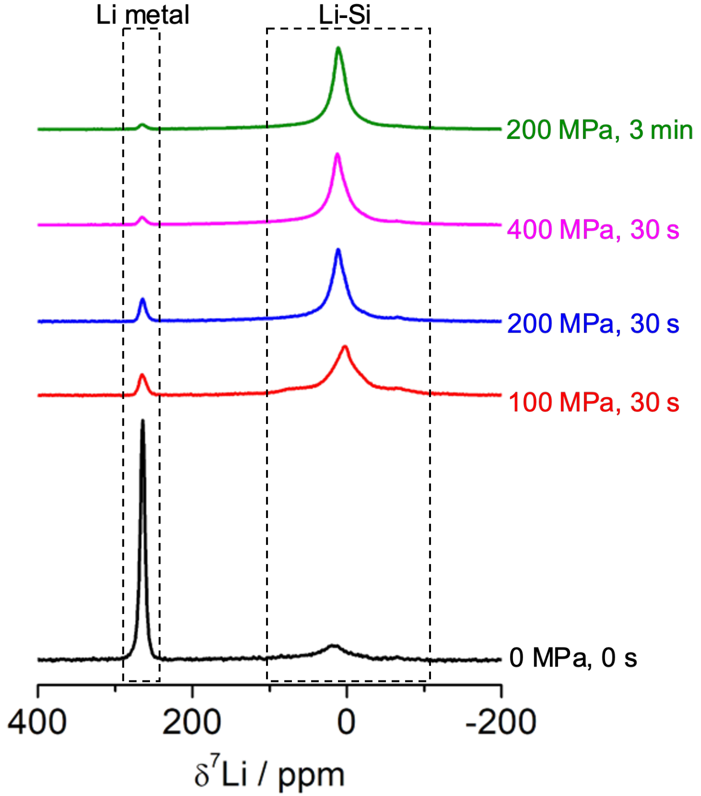
So Yeon Ham et. al. To be Submitted 2023

Prelithiation of Micro-Silicon via Pressurization

Morphology of Li_1Si
before and after pressurization



^{7}Li NMR of Li_1Si
before and after pressurization

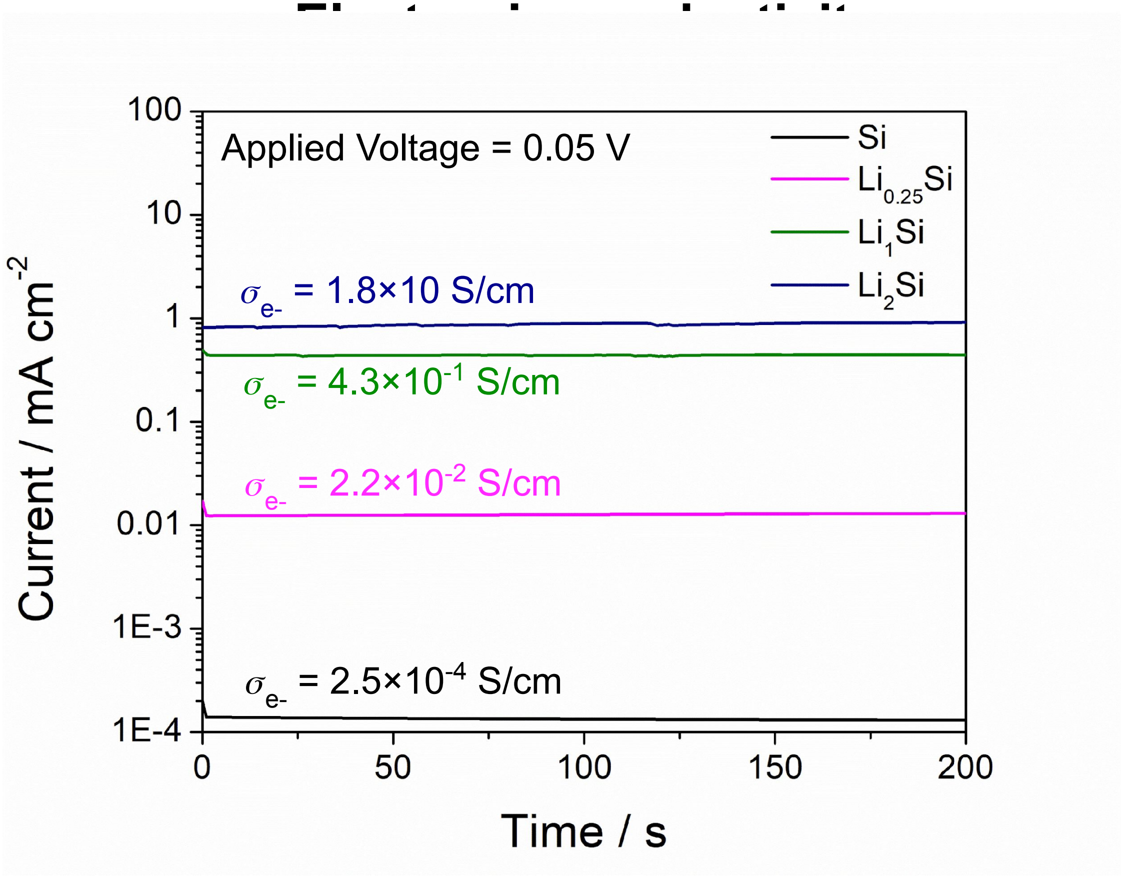


- **Li-Si formed after pressurization**
- Before pressurization: Preserved morphology of sphere stabilized lithium metal powder (SLMP) and micro-Si
- After pressurization: Li metal deformed and Li-Si phase

Nature Communications, under review (2023)

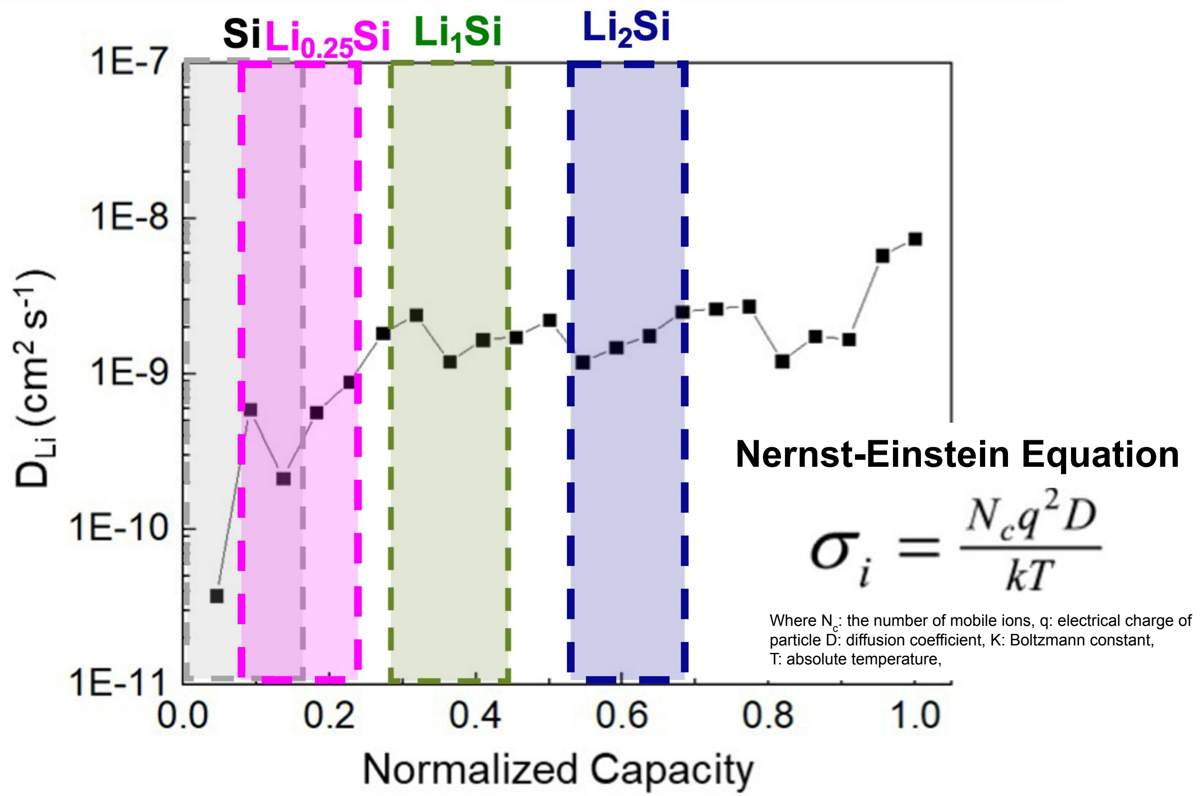
- Higher Li metal peak in unpressed (0 MPa, 0 s)
- **Longer pressurization time/higher pressure drives more Li incorporation**
- Pressurization converts nearly all Li metal to Li-Si

Physical Properties of Pure Si *and* Li_xSi



- **Higher Electronic conductivity**:
  Increase by orders of magnitude with more Li content

Ionic conductivity



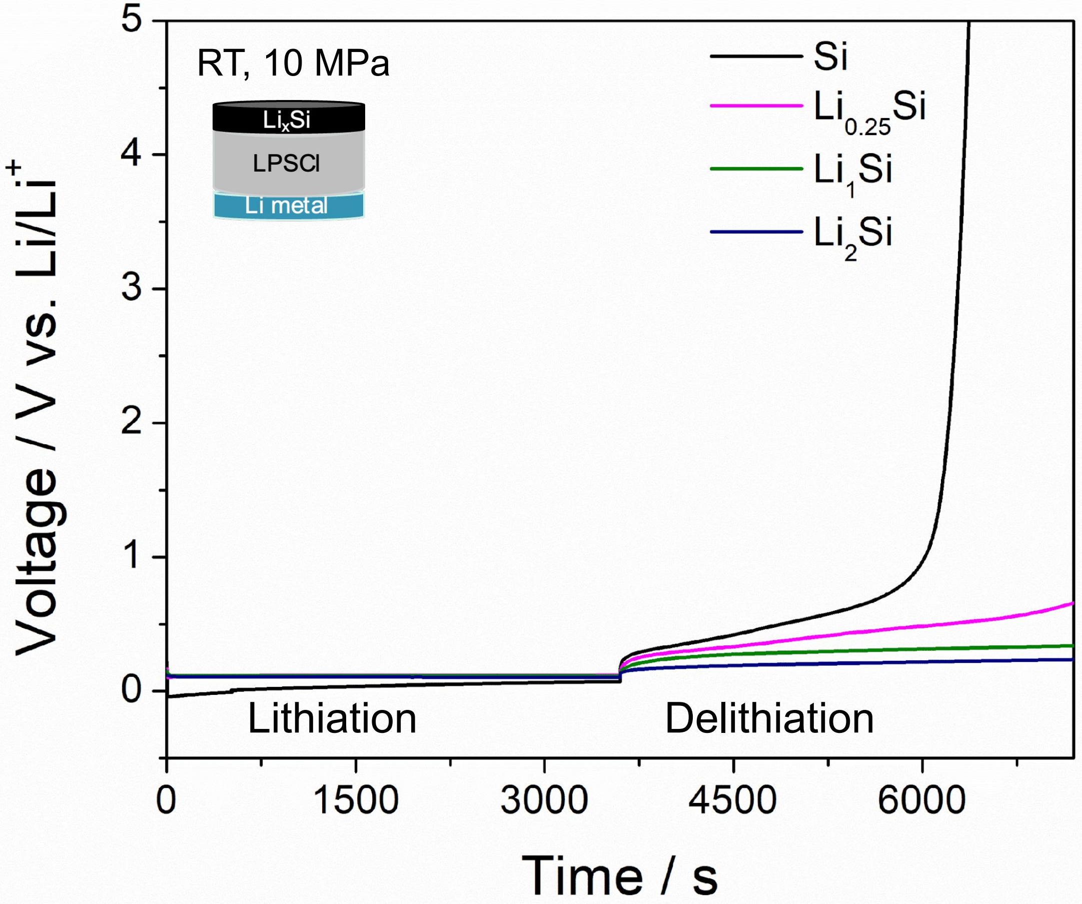
- Li^+ diffusivity in Si : Higher in higher SOC
- Prelithiation □ Faster Li^+ diffusion in Si
- **Higher ionic conductivity** increased by prelithiation

Nature Communications, under review (2023)

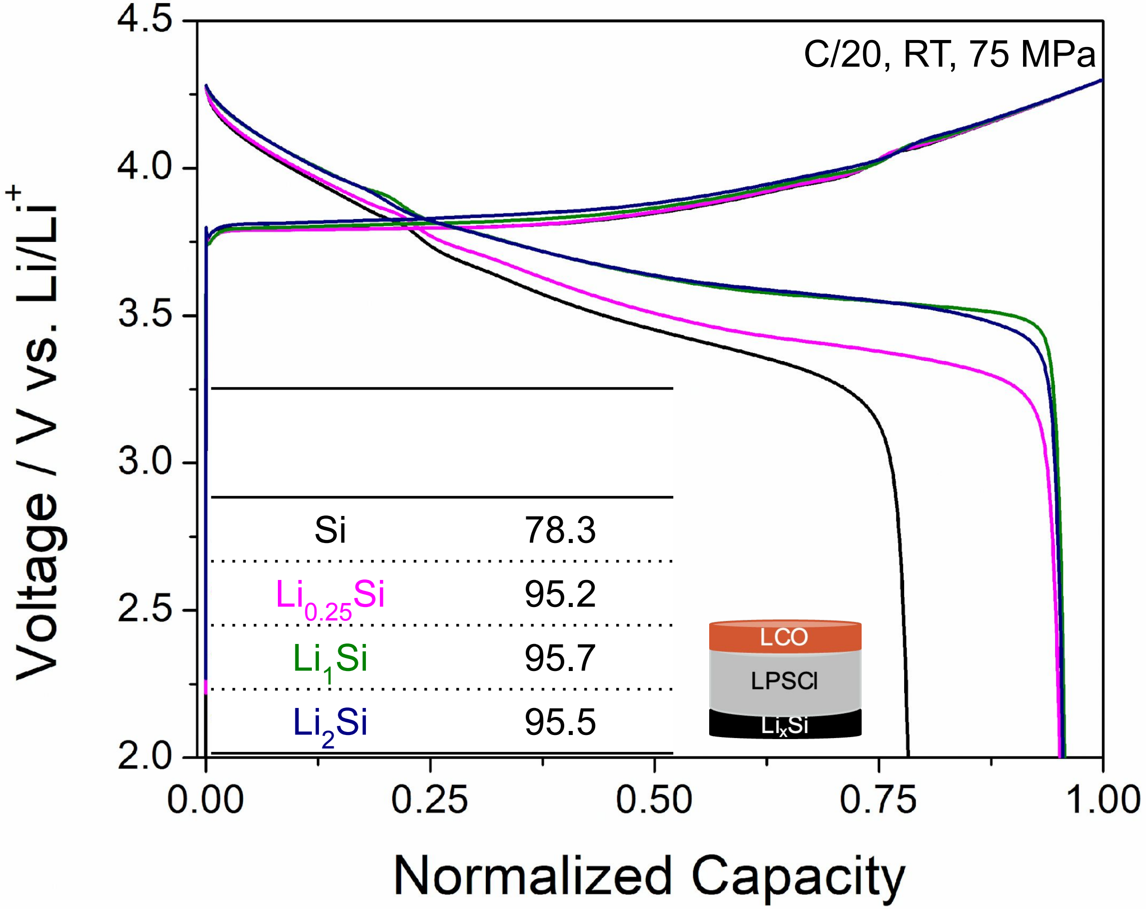
Li_xSi in Half- and Full-Cell

Nature Communications, under review (2023)

Half-Cell



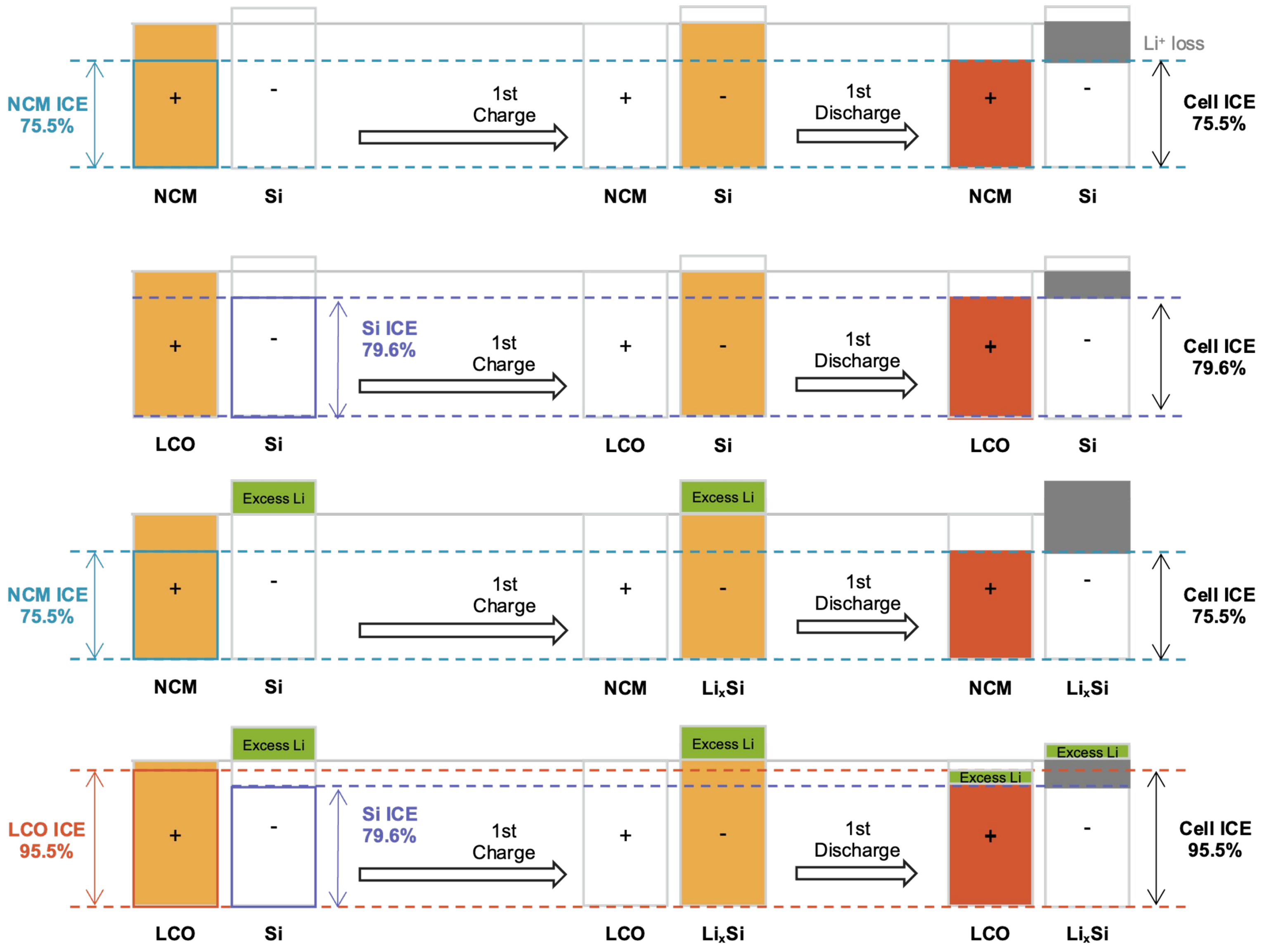
Full-Cell



- Lithiation: Similar overpotential
- Delithiation: Higher overpotential in less lithiated Li_xSi
- **Harder to delithiate Li_xSi depending on how much Li is in Si**

- Improved ICE in all lithiated Si, but converged to 95.5% after Li_1Si
- Li_1Si for remaining cell cycling experiments

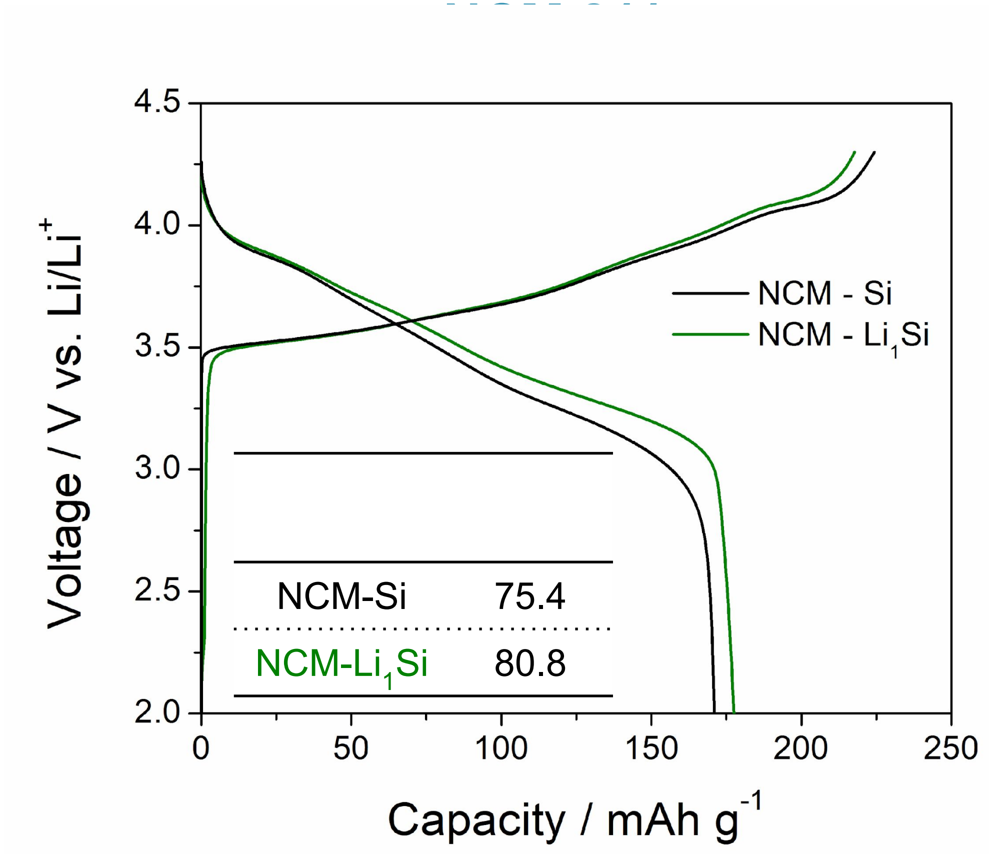
Prelithiation Driven Improvement: NCM *vs* LCO

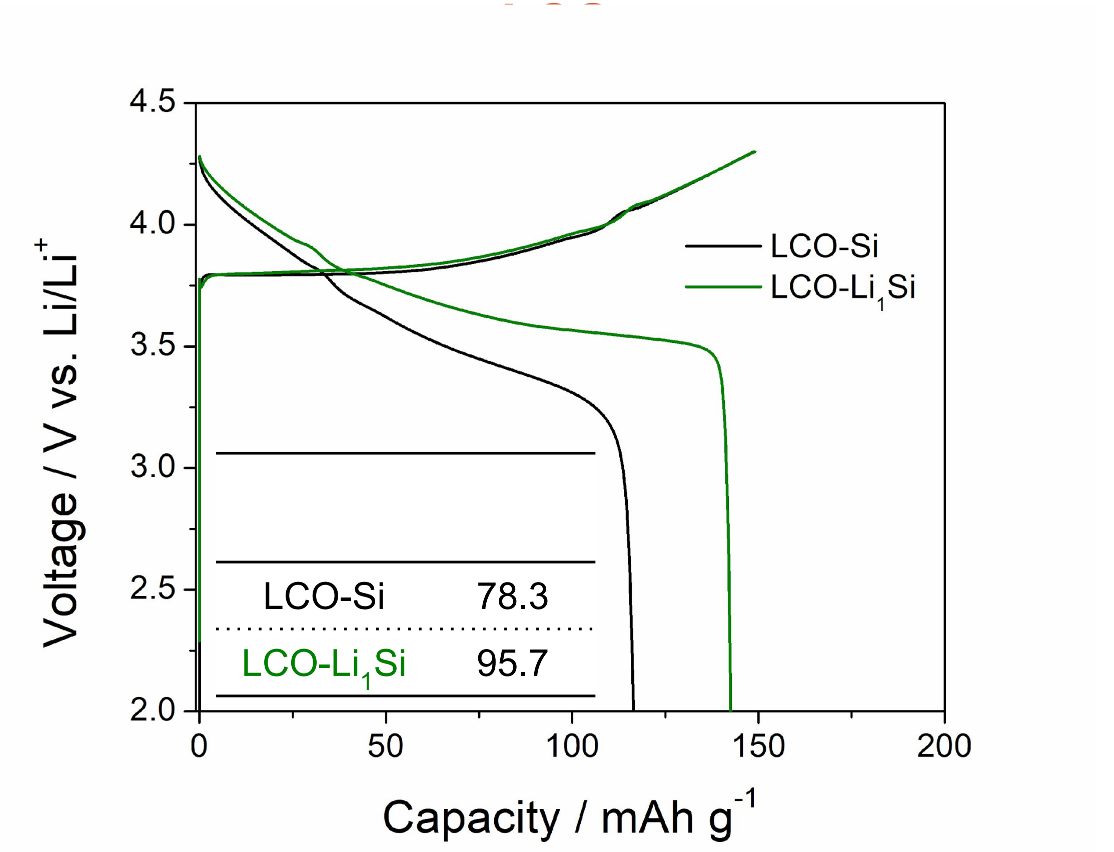


Nature Communications, under review (2023)

- Based on ICE of NCM, LCO, and Si (in the half-cell)
- Even with preithiation, NCM-LiSi ICE will be still limited by NCM ICE limit ***"Cathode Limit"***
- LCO-LiSi case: Higher ICE expected up to LCO ICE limit ***"Anode Limit"***

Prelithiation Driven Improvement: NCM *vs* LCO

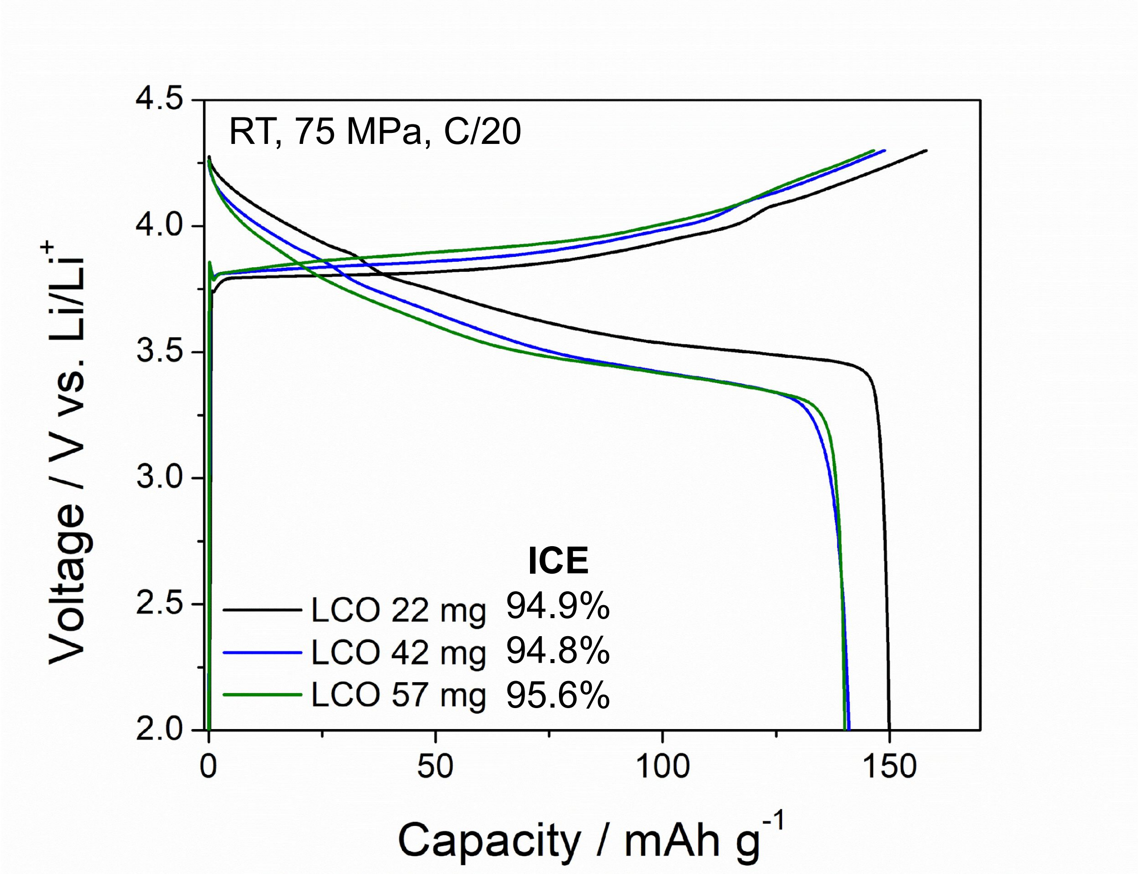


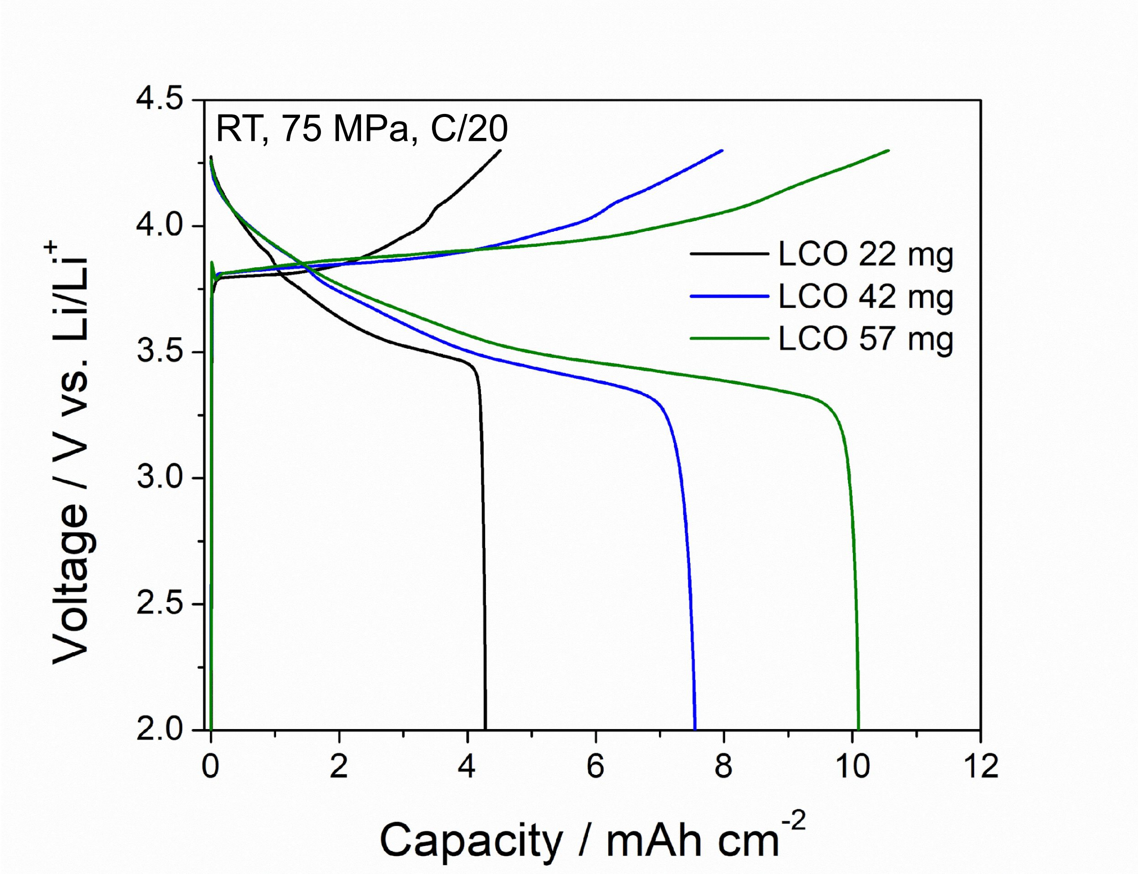


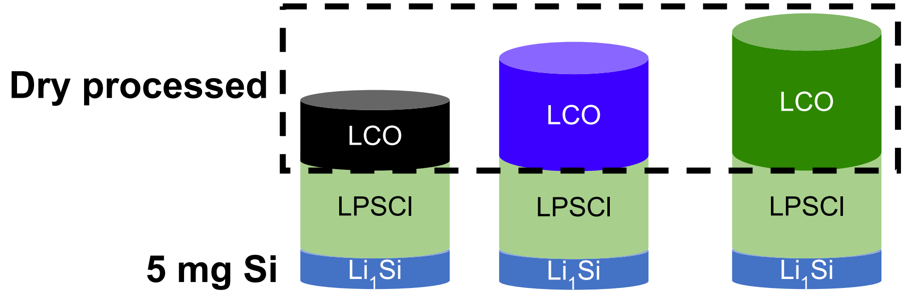
- With prelithiation, only LCO cell showed large ICE improvement
- NCM: limited by NCM ICE No further improvement from prelithiation
- **Prelithiation of anode is effective for “anode-limiting”**

Nature Communications, under review (2023)

Dry processed LCO – Li_1Si: High Loading Viability







- Similar ICE for all loadings
- Higher polarization for high loading but still achieved 140 mAh/g discharge capacity with areal capacity of more than 10 mAh cm^{-2} discharge capacity

- **Li_1Si (5 mg Si) could accommodate 10 mAh cm^{-2} capacity**

Remaining Challenges

Precursors

Li_2S 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 reduction from 100MPa – 50MPa – 5MPa
Making SSB structural component

Pressure

Solid State Fire ??!!

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

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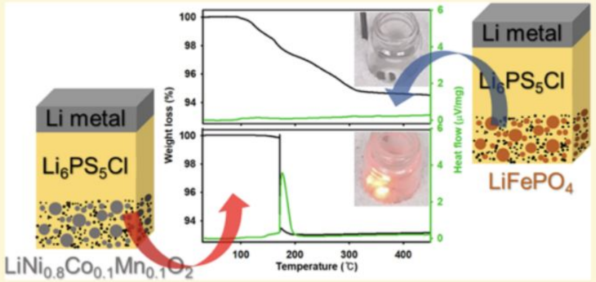
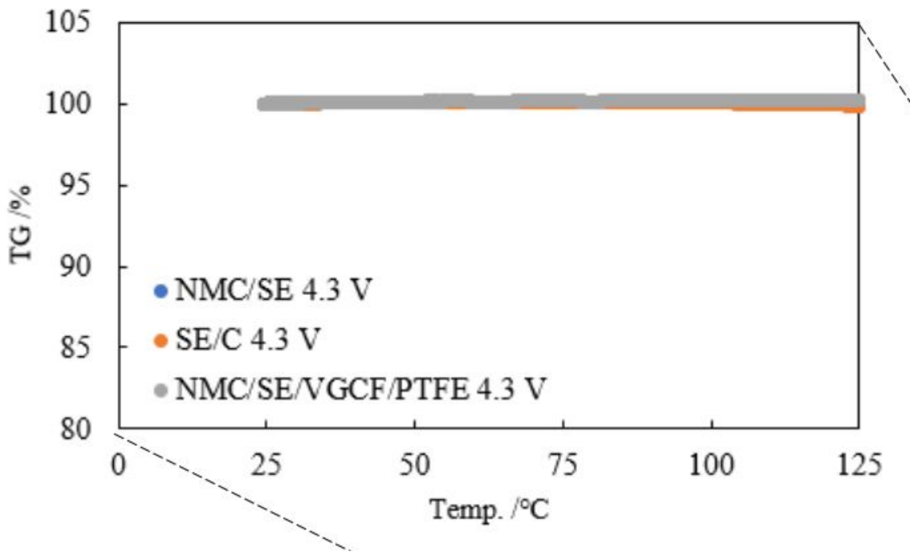


ABSTRACT: All-solid-state batteries (ASSBs) have received much attention because of their high energy density and safety. However, the safety of argyrodite-type Li_6PS_5Cl (LPSCl)-based ASSBs is still not assured because their thermal stability has been assessed under selected mild conditions. Herein, 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

LGES UCSD – FRL Team Members

Ong | Kim | Shpyrko | Clement | Meng | Liu | Chen

Computation Modeling

Characterization Novel Materials

Scalable Processing

Devices Prototyping

Recycling Safety

LG Energy Solution

Sustainable Power and Energy Center

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

Sustainable Power and Energy Center

MTI 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