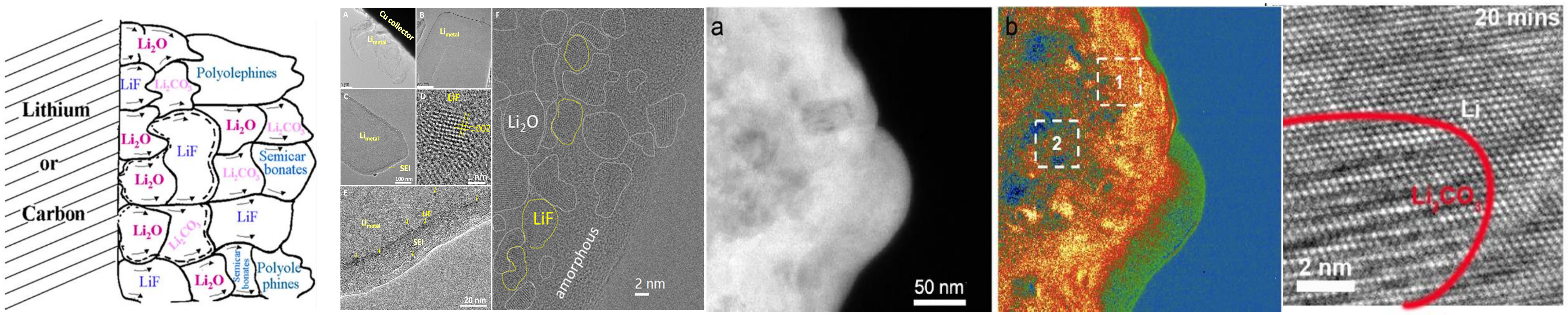


From atom to system – advanced characterization for lithium metal batteries

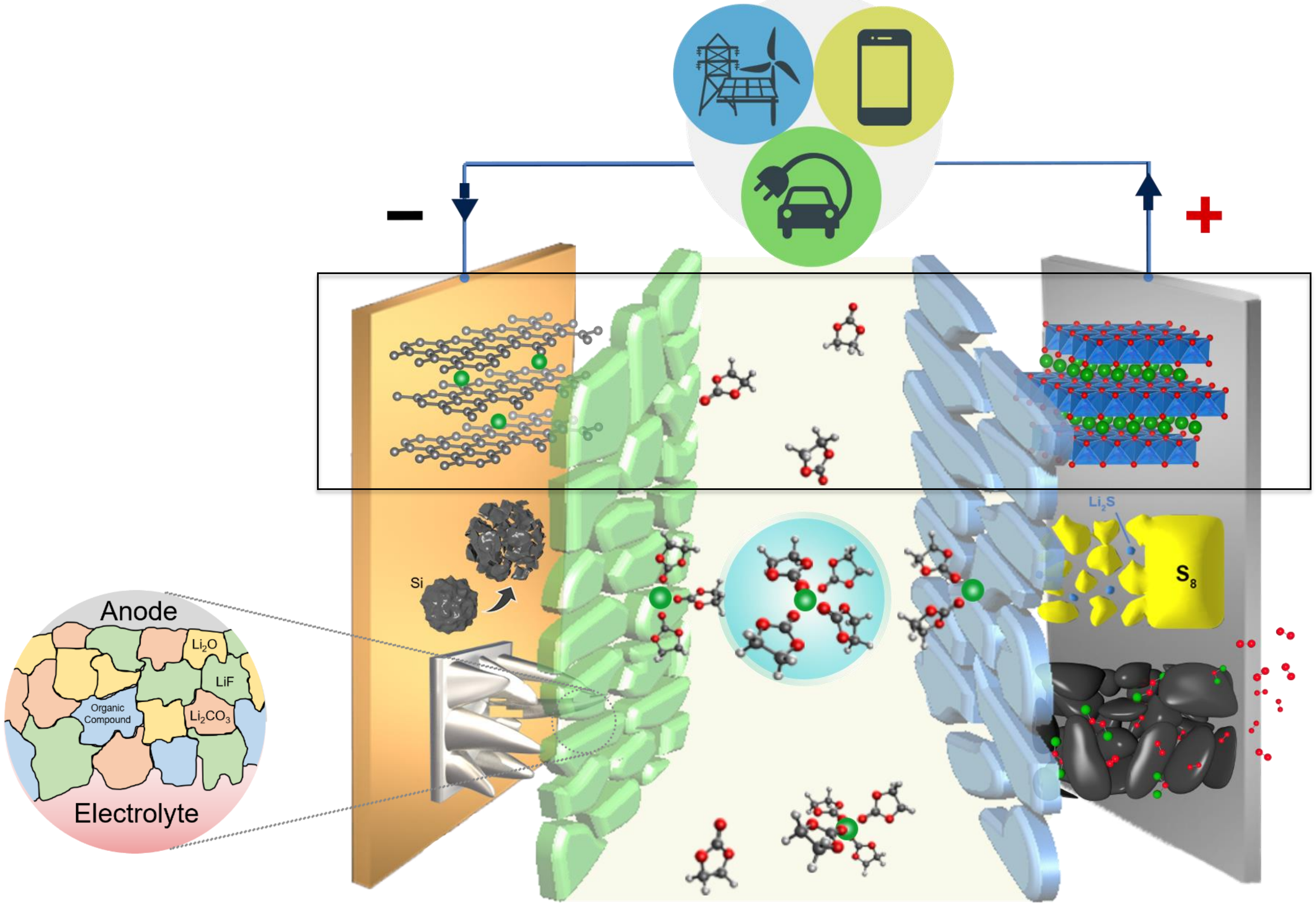
Ying Shirley Meng

Aachen, Germany 2023

UC San Diego · LESC · THE UNIVERSITY OF CHICAGO

Lithium Metal Battery - A More Complex “System”

Science Perspective – K. Xu V. Srinivasan and Y. S. Meng 2023



No longer Intercalation

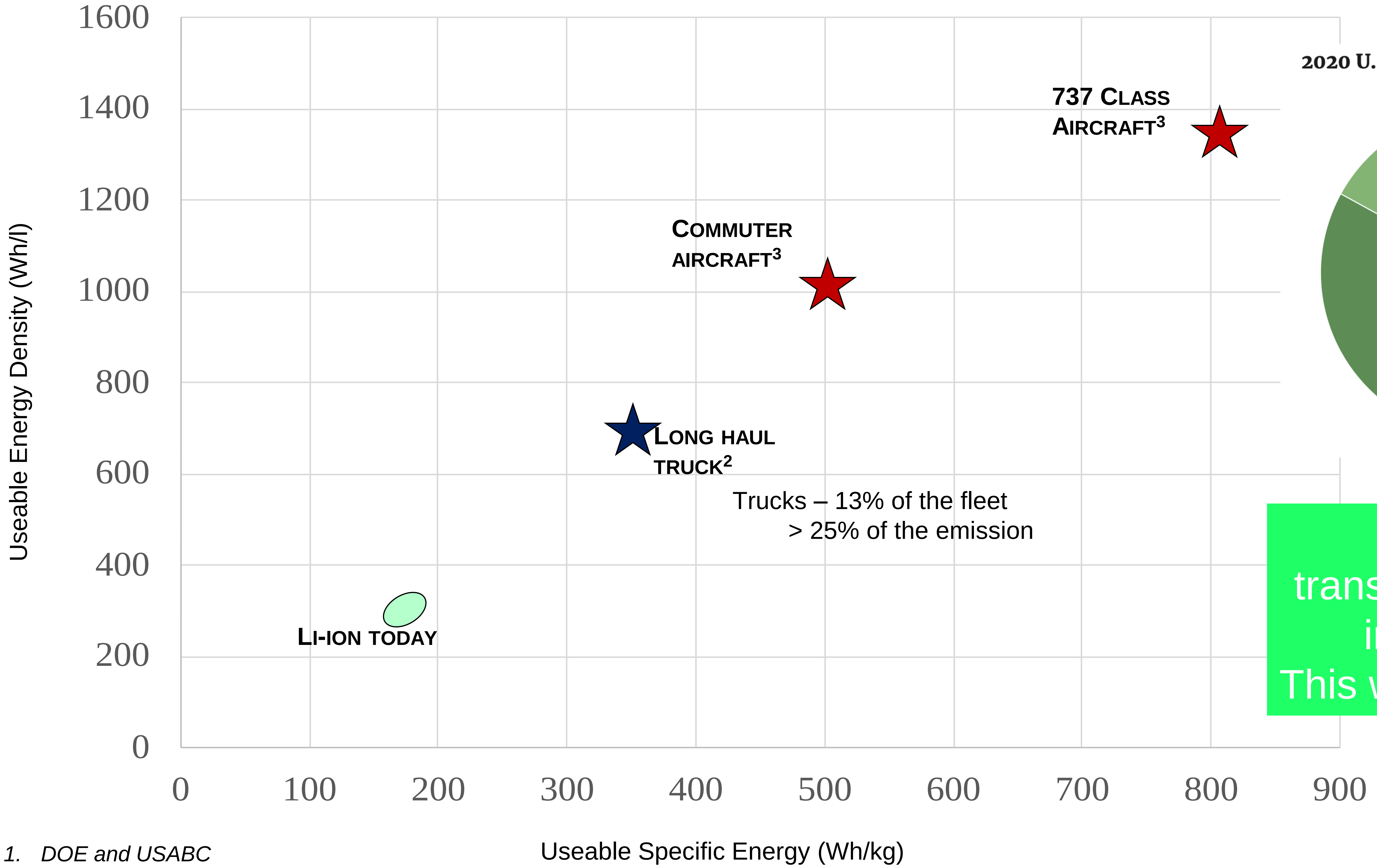
Dynamic Phenomena

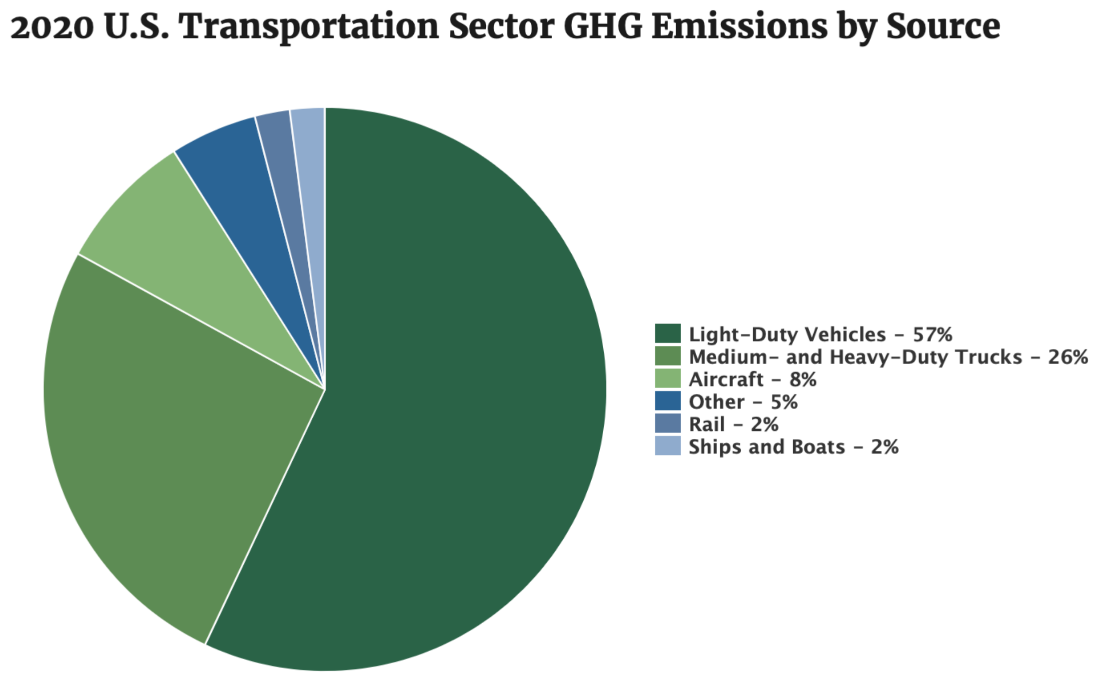
Volume changes
1mAh = 4.9um

Thermodynamically Closed System
>99.6% efficiency needed if excess Li

SEI – Life and Safety Differentiators

Why do We Need Even Higher Energy Density

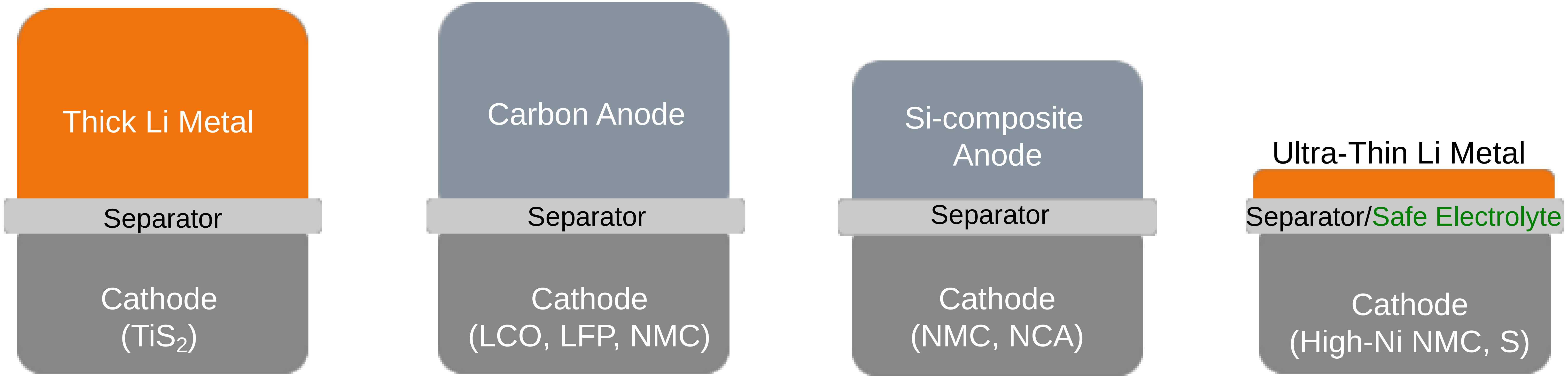




Deep decarbonization of transportation will require dramatic increase in energy density.
This will diversify the material needs

1. *DOE and USABC*
2. *ACS Energy Lett.* 2017, 2, 1669
3. *DOE-NASA electric aviation workshop*

Development of Li Metal Battery



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

The Innovation Center for Battery500 Consortium

Timeline

- Phase I: 2016-2021
- Phase II: 2022-2027

Budget

- Total Phase II: Over $75M
- Phase I funding: Over 50M

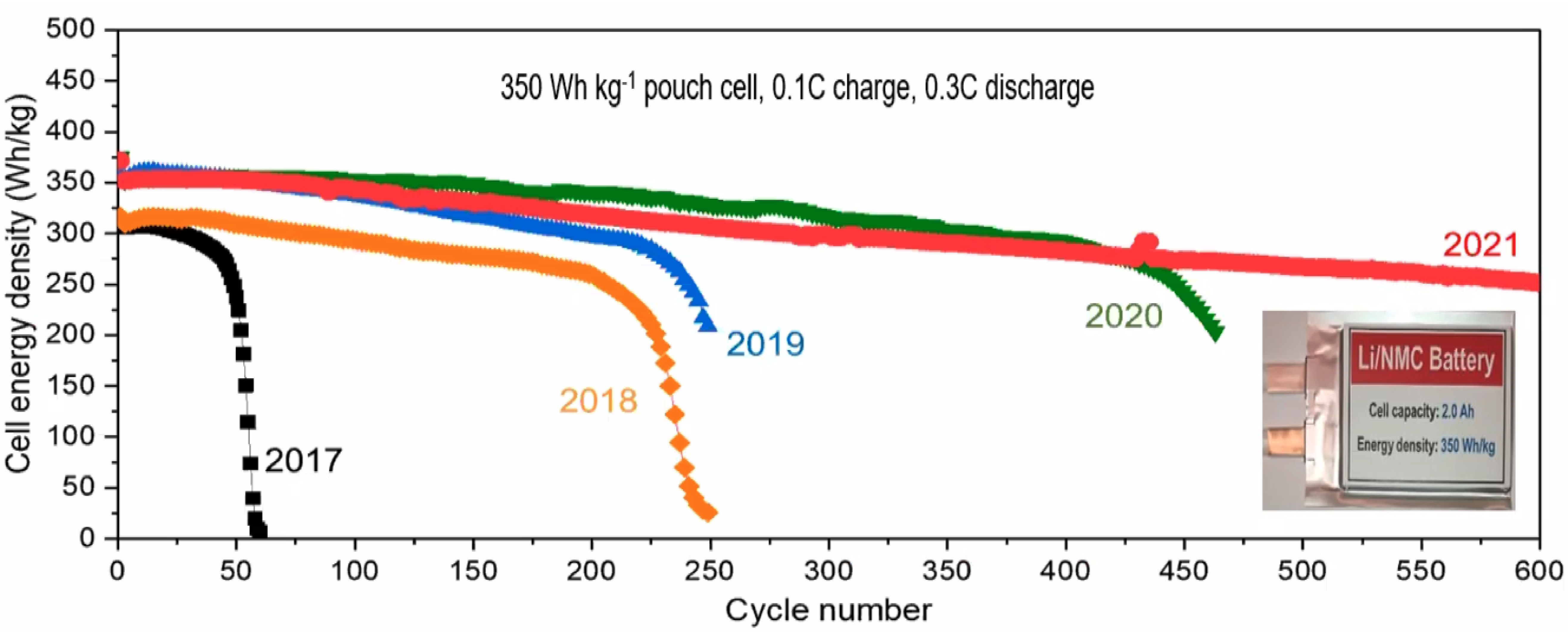
Goal

- Goal
  - Increasing the energy density of advanced lithium (Li) batteries beyond what can be achieved in today's Li-ion batteries is a grand scientific and technological challenge
  - 500 Wh kg and 1000 deep cycles

Partners

- Project lead: PNNL
- Team: Binghamton Univ., BNL, INL, GM, Penn State Univ., Stanford Univ./SLAC, Texas A&M, UC San Diego, Univ. of Maryland, Univ. of Pittsburgh, Univ. of Texas, Austin, Univ. of Washington
- Industry Advisory Board

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



2022 Data – 400Wh/kg 300 Cycles

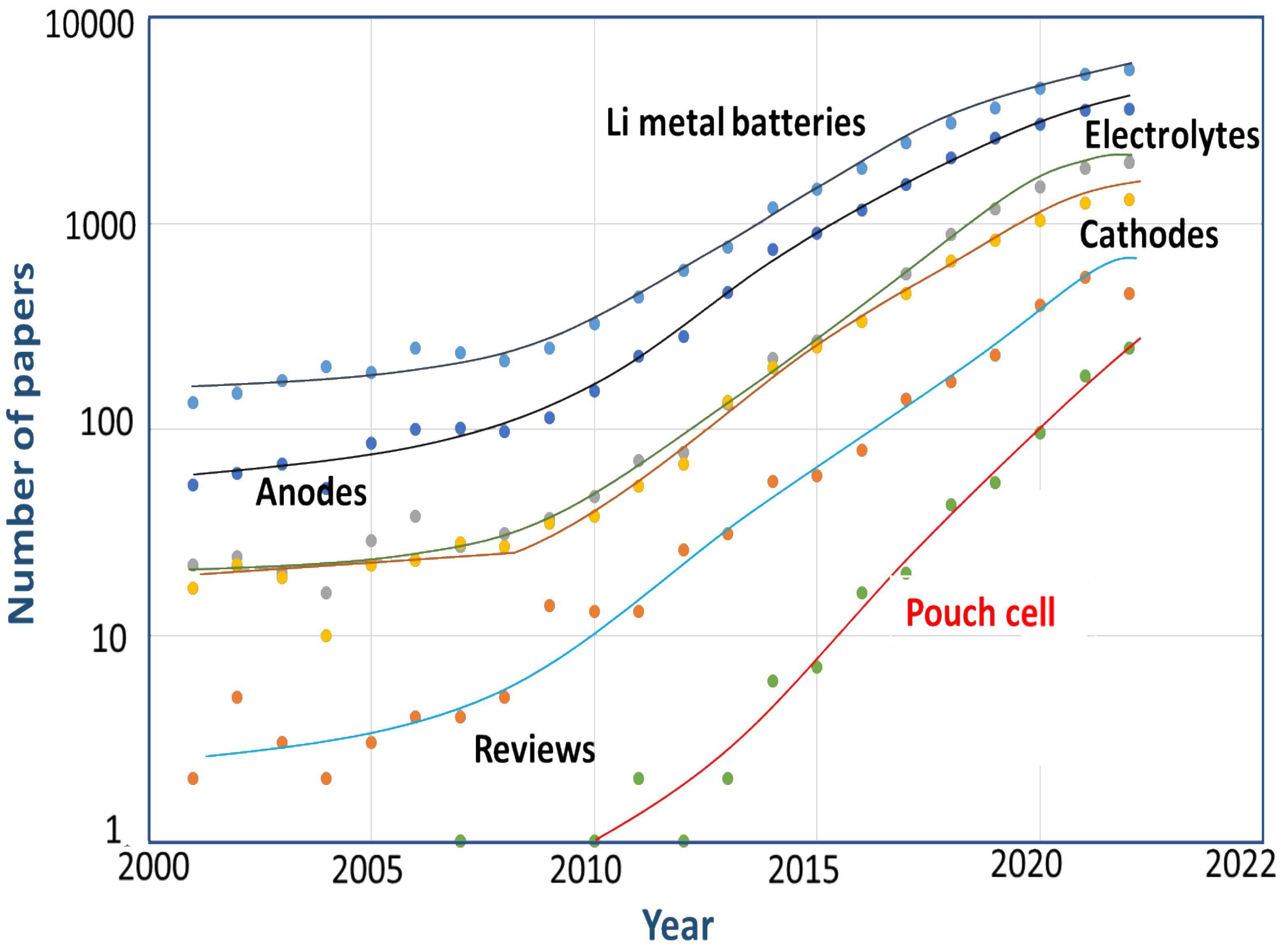
Initial pressure:~27 psi

Charge C/10
Discharge C/3

- 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

Number of papers published on Li metal and batteries

LMBW 2023
La Jolla



- **What have we learned in the last 5 years?**
- **What is the key problem to solve in the next 5 years?**

J. Liu et al, Battery500 perspective article: “Pathways for Practical High-Energy Long-Cycling Lithium Metal Batteries II.”

BATTERY 500 CONSORTIUM

Understanding How Materials Function

工欲善其事，必先利其器

- CONFUCIUS ~500BC

Spectroscopy
photons, x-ray, electron, NMR

Microscopy
SPMs, electrons, x-ray, near-field

Diffraction
X-ray, electrons, ions, neutrons

Novel Techniques and Methodologies
Characterization↔Detection

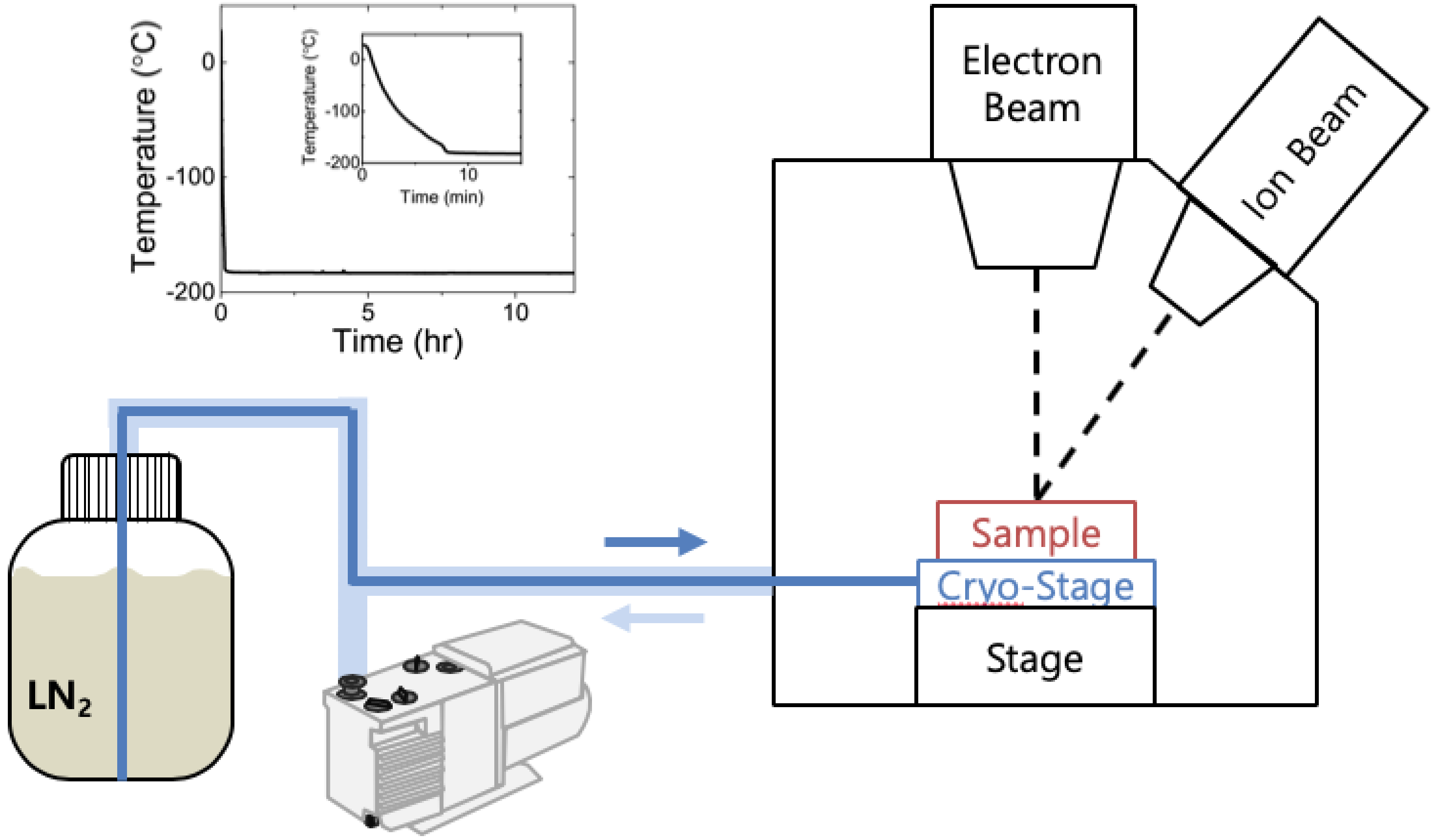
Materials
- Crystals and aritifcial structures
- Electrolytes (disordered structures)
- Phase transitions
- Electronic and magnetic properties

Target parameters
- *In situ* sensing/monitoring
- Spatial resolution:-> sub-Å , below diffraction limit,
- Time resolution → fsec
- Higher energy resolution

Interface
- Kinetics of surface phenomena
- (Meta)Stability of surface structures
- Competing processes, side-effects
- Transport and response functions

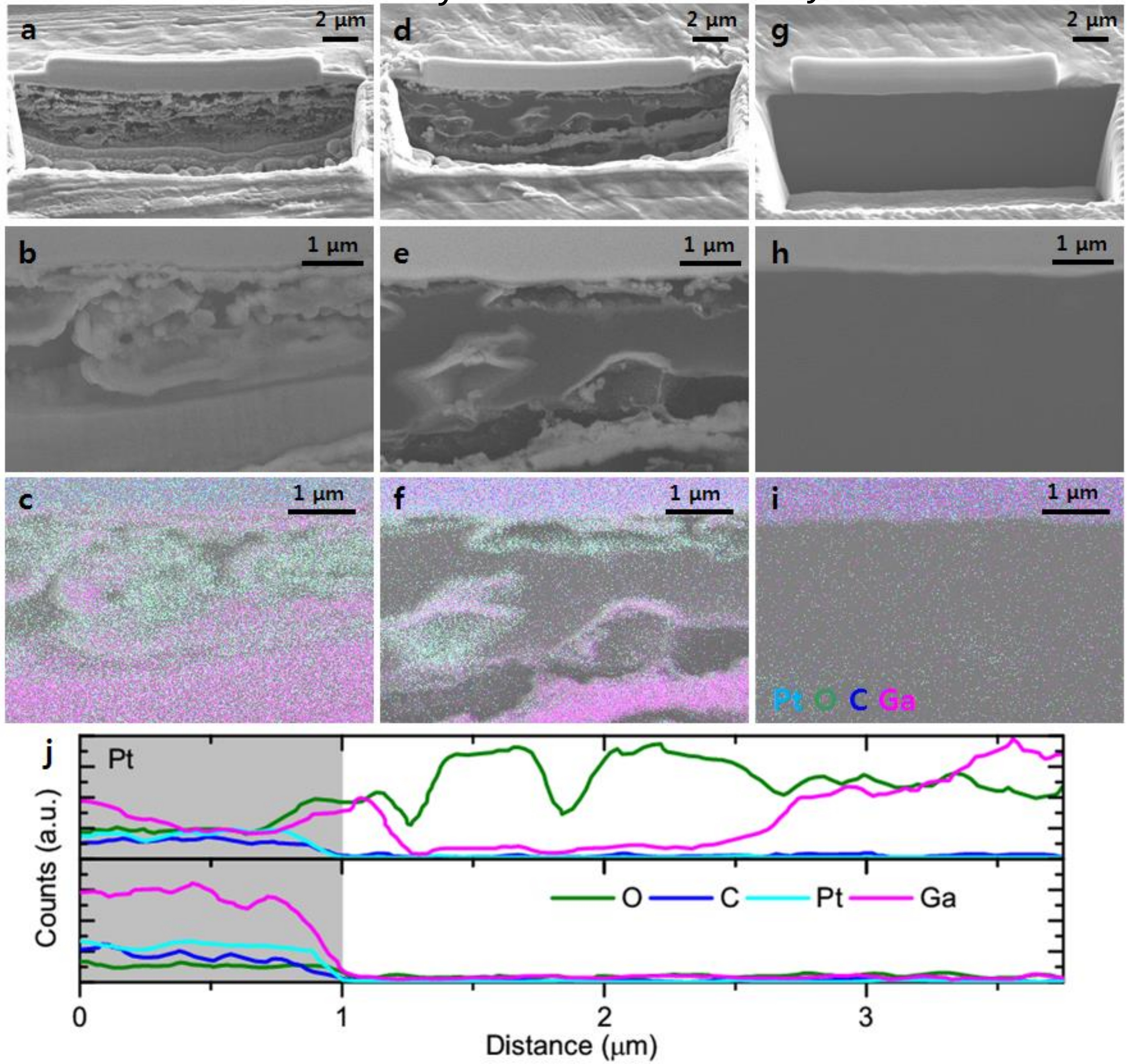
Cryo-FIB: Enabling Beam Sensitive Materials

J.Z. Lee, T.A. Wynn, Y.S. Meng, et al, ACS Energy Letters , 2019



Cryogenic focused ion beam (-170 ºC) shows notably reduced morphology change as well as reduced Ga^{+} implantation via EDS. Permits lift-out of lithium metal anode-based batteries.

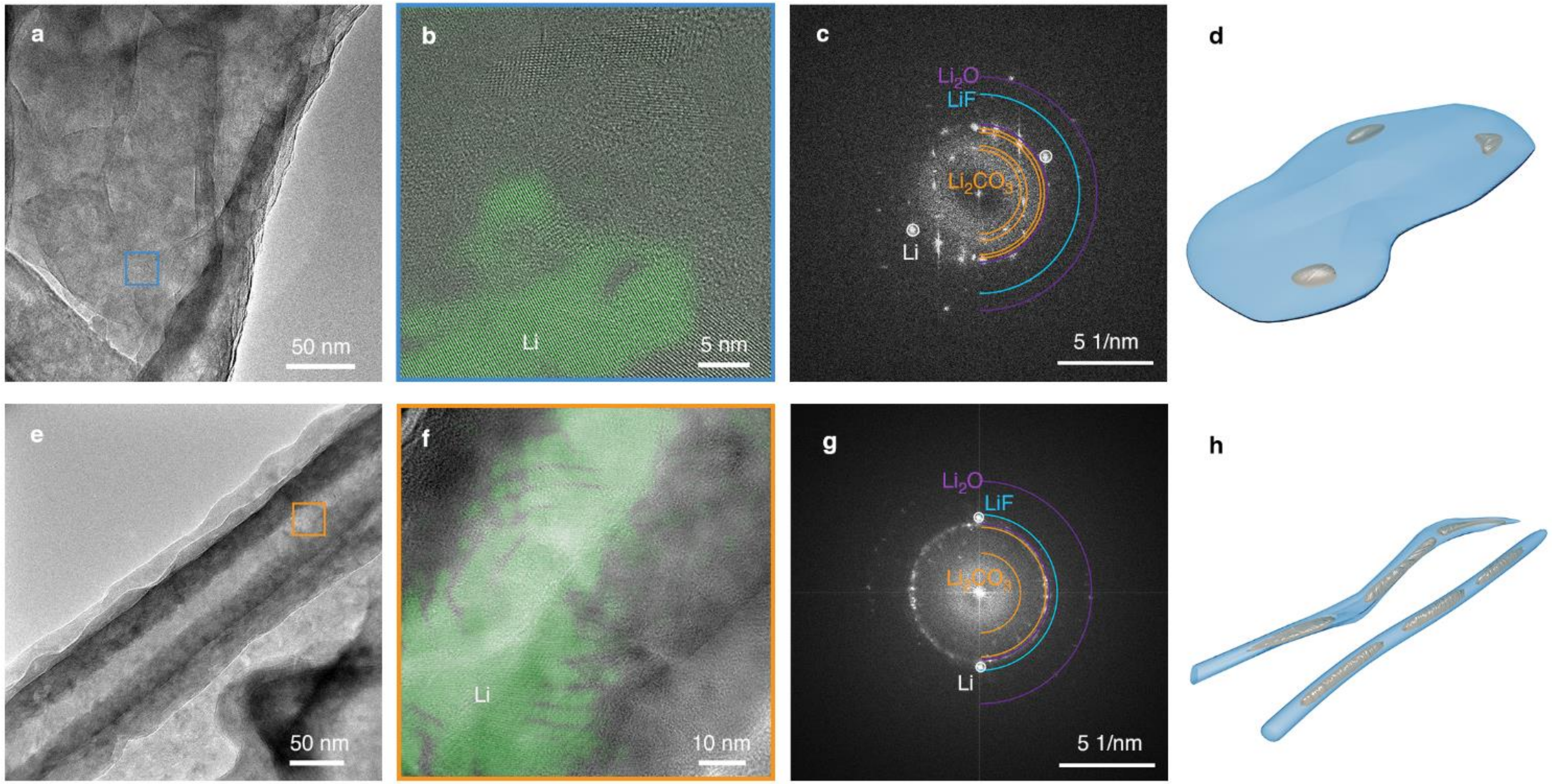
RT Cross-section RT Clean | RT Cross-section Cryo Clean | Cryo Cross-section Cryo Clean



Nanostructure of Inactive Li by Cryo-TEM

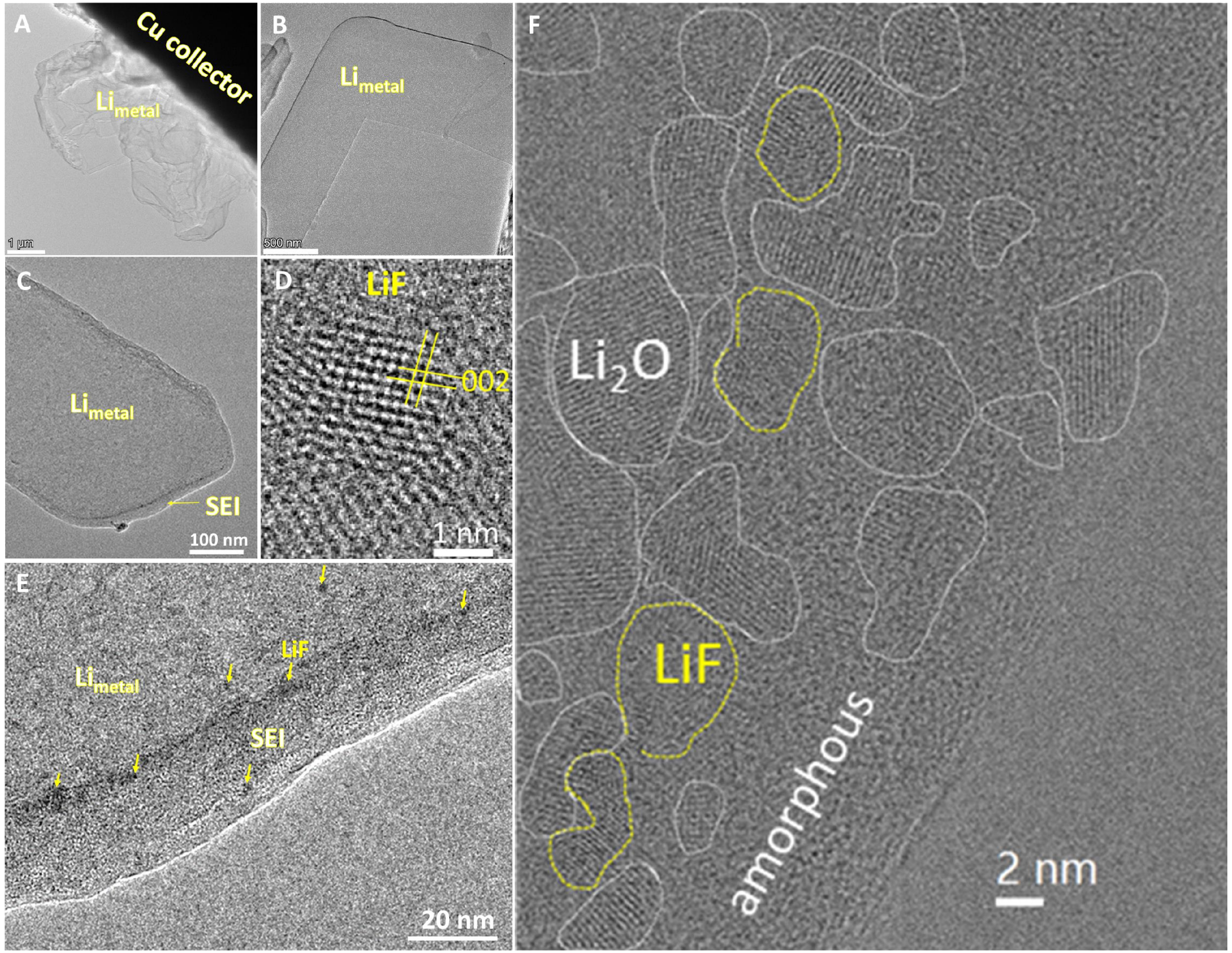
HCE

CCE



C. Fang, J. Li, Y.S. Meng *et al.*, "Quantifying Inactive Lithium in Lithium Metal Batteries", ***Nature* 572**, 511–515 (2019)

2D Cryo-TEM analysis of the plated Li flake and SEI



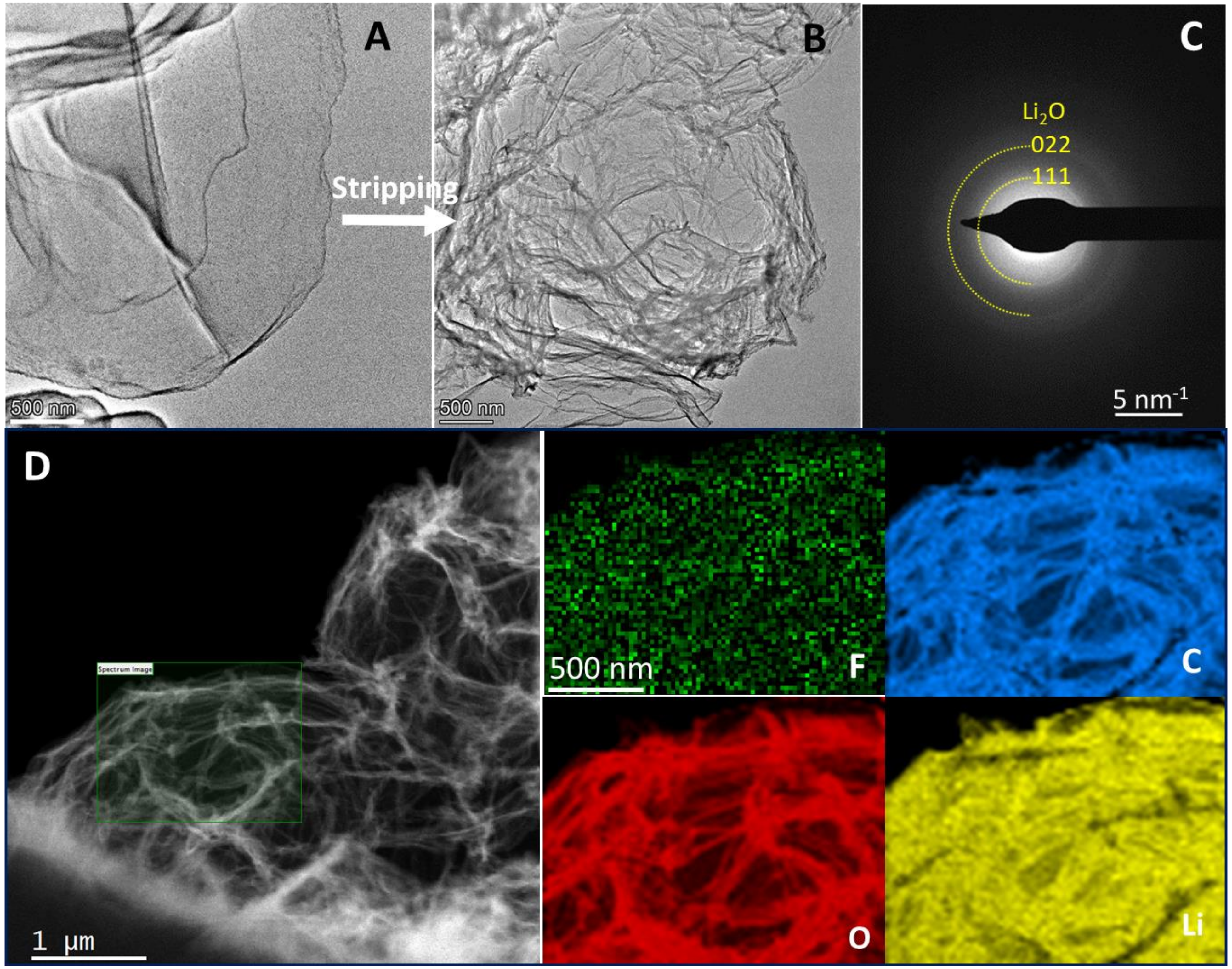
Cryo-TEM analysis of the plated Li flake and SEI formed using FEC additive after the 1st plating process.

A-C. Low-magnification cryo-TEM images showing plated Li metal and its SEI; **D**. HRTEM showing the LiF nanocrystal inside the SEI; **E**. Magnified local region showing the dark LiF nanocrystals (indicated by yellow arrows) inside the SEI; **F**. Distribution map of different phases in the SEI skin-layer.

The HRTEM images in panel D&F are acquired with electron dose rate ~8 e Å^{-2} s^{-1} for ~10s

Bin Hang … and Ying Shirley Meng, ***Matter, 2021***
DOI:https://doi.org/10.1016/j.matt.2021.09.019

2D Cryo-TEM and Cryo-STEM EELS analysis of the SEI



The morphology of the SEI after the first stripping cycle.

A Cryo-TEM image of the as-plated Li; **B** morphology of the remaining empty husks after first stripping cycle; **C** Electron diffraction of the remaining empty husks after Li stripping; **D** cryo-STEM image and EELS elemental maps (green: fluorine; blue: carbon; red: oxygen; yellow: Li) of the empty husks.

Bin Hang … and Ying Shirley Meng, ***Matter,2021***
DOI:https://doi.org/10.1016/j.matt.2021.09.019

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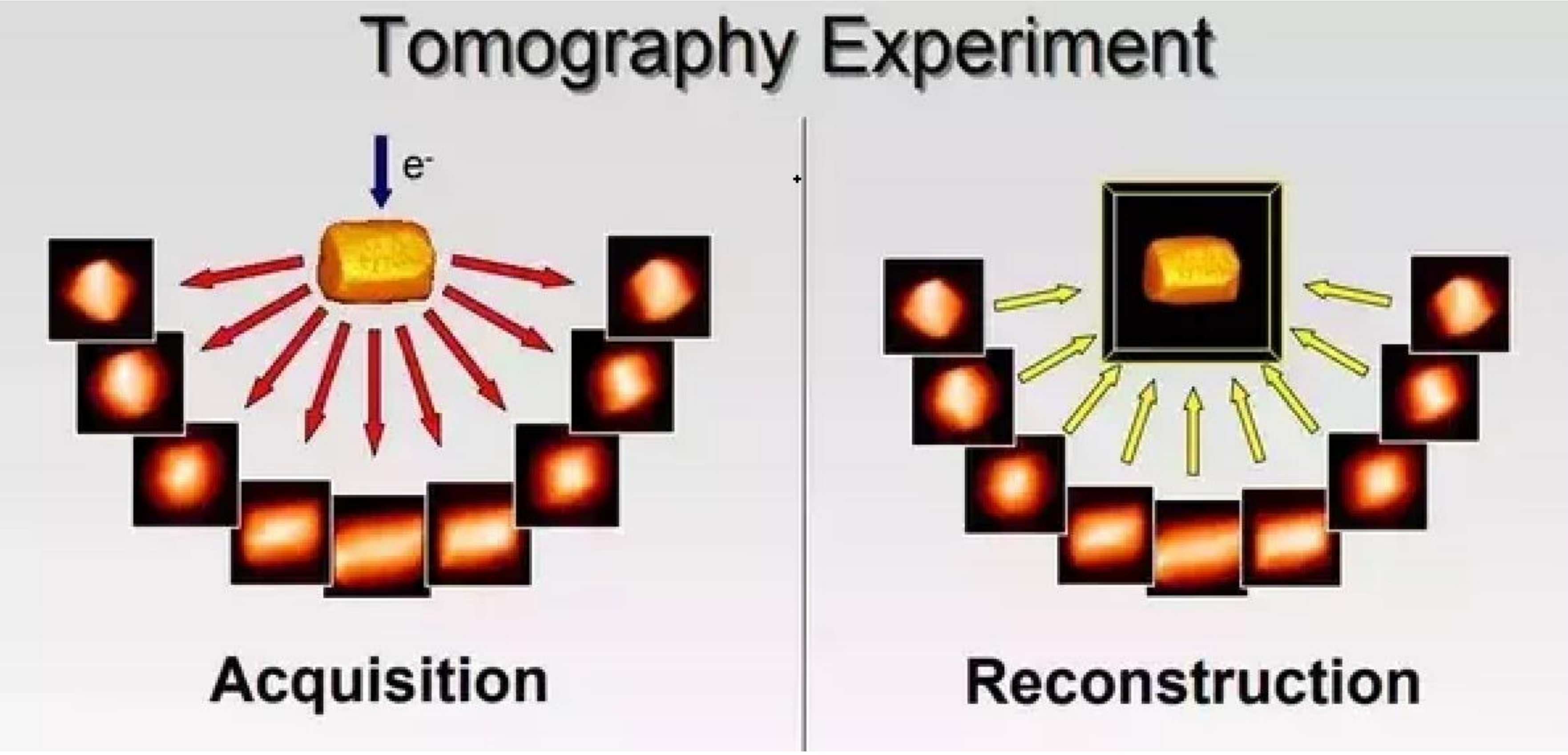
Why to study Li metal and SEI by Tomography



Any TEM or STEM image is a two-dimensional projection of a 3D specimen and this is a fundamental limitation.

The 3D Li morphology and distribution of SEI components matter !

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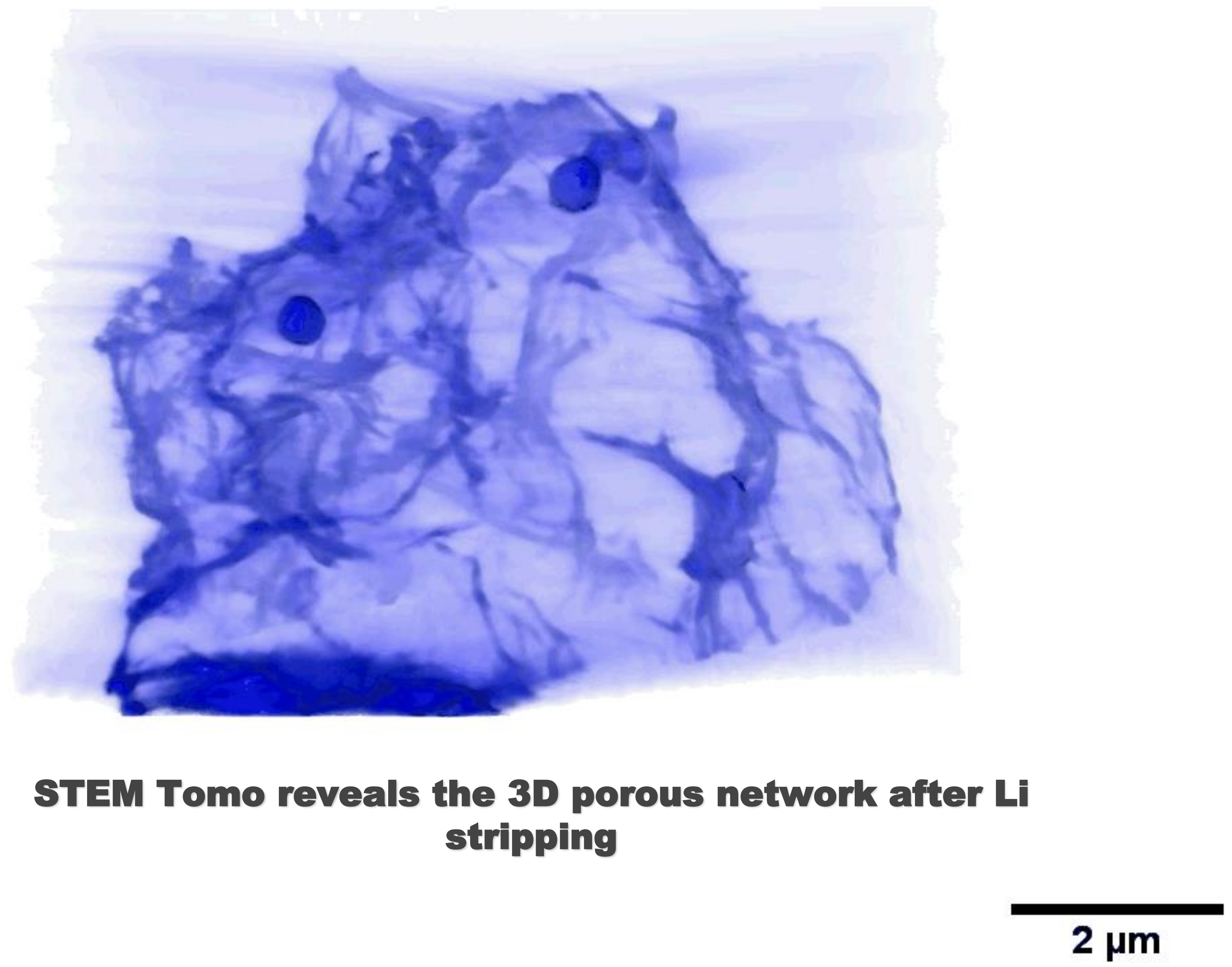
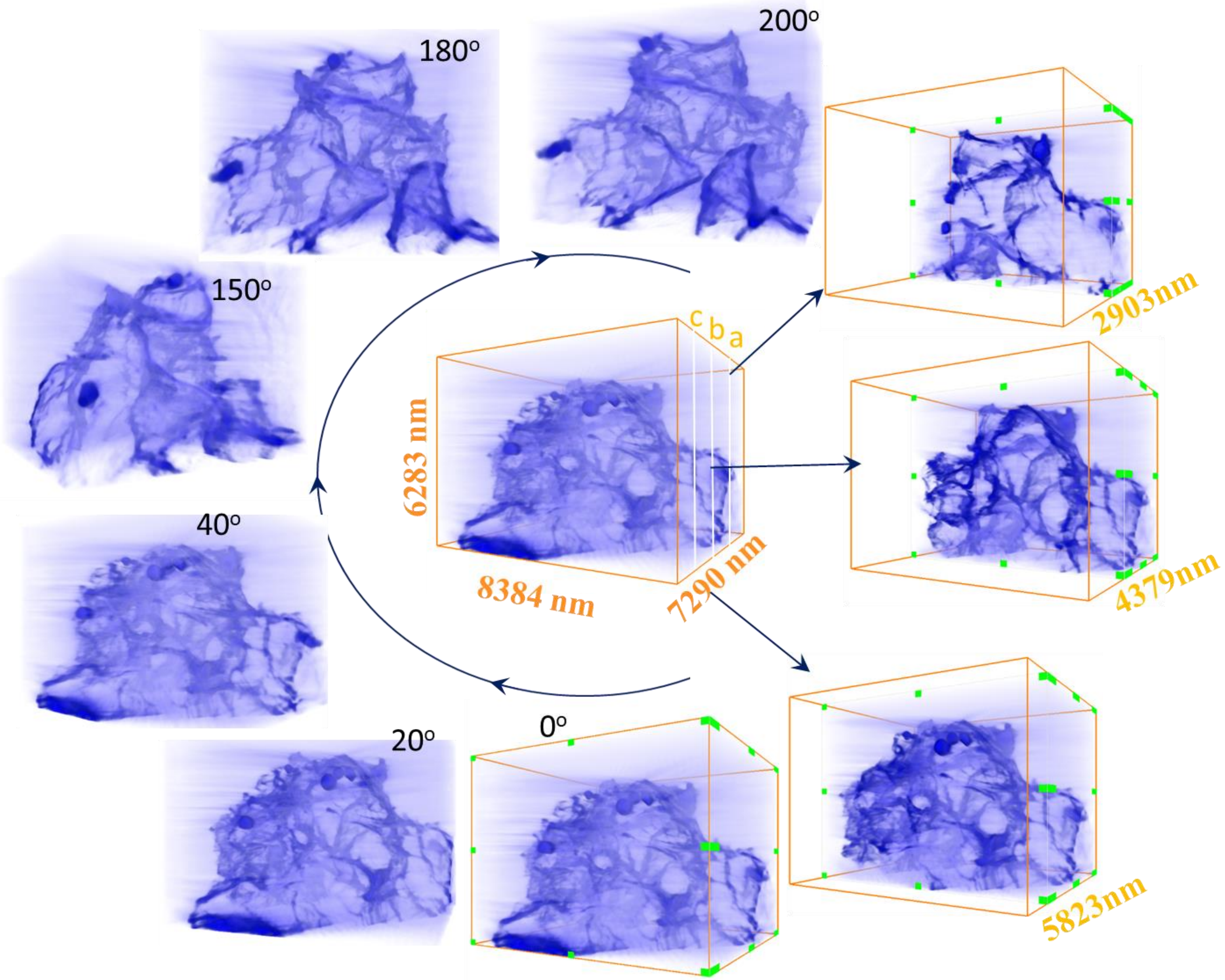
*Bin Hang … and Ying Shirley Meng, **Matter,2021***
DOI:https://doi.org/10.1016/j.matt.2021.09.019

3D STEM tomography reconstruction of SEI



STEM Tomo reveals the 3D porous network after Li stripping



STEM tomography reconstructed the 3D image of the SEI husk after Li stripping, illustrating the hollow, crumpled SEI structure.

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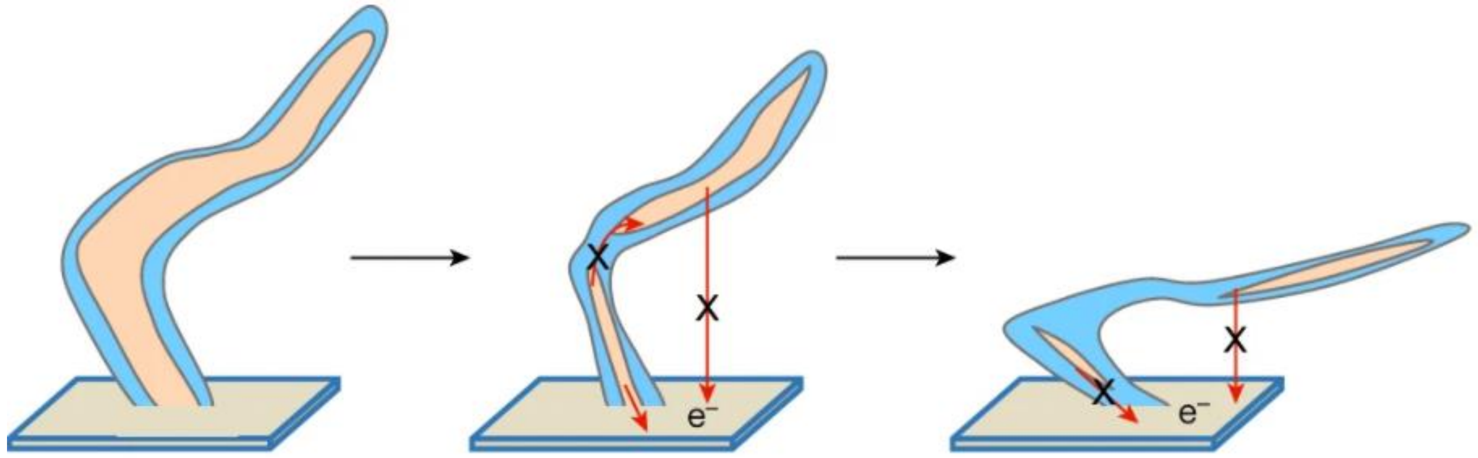
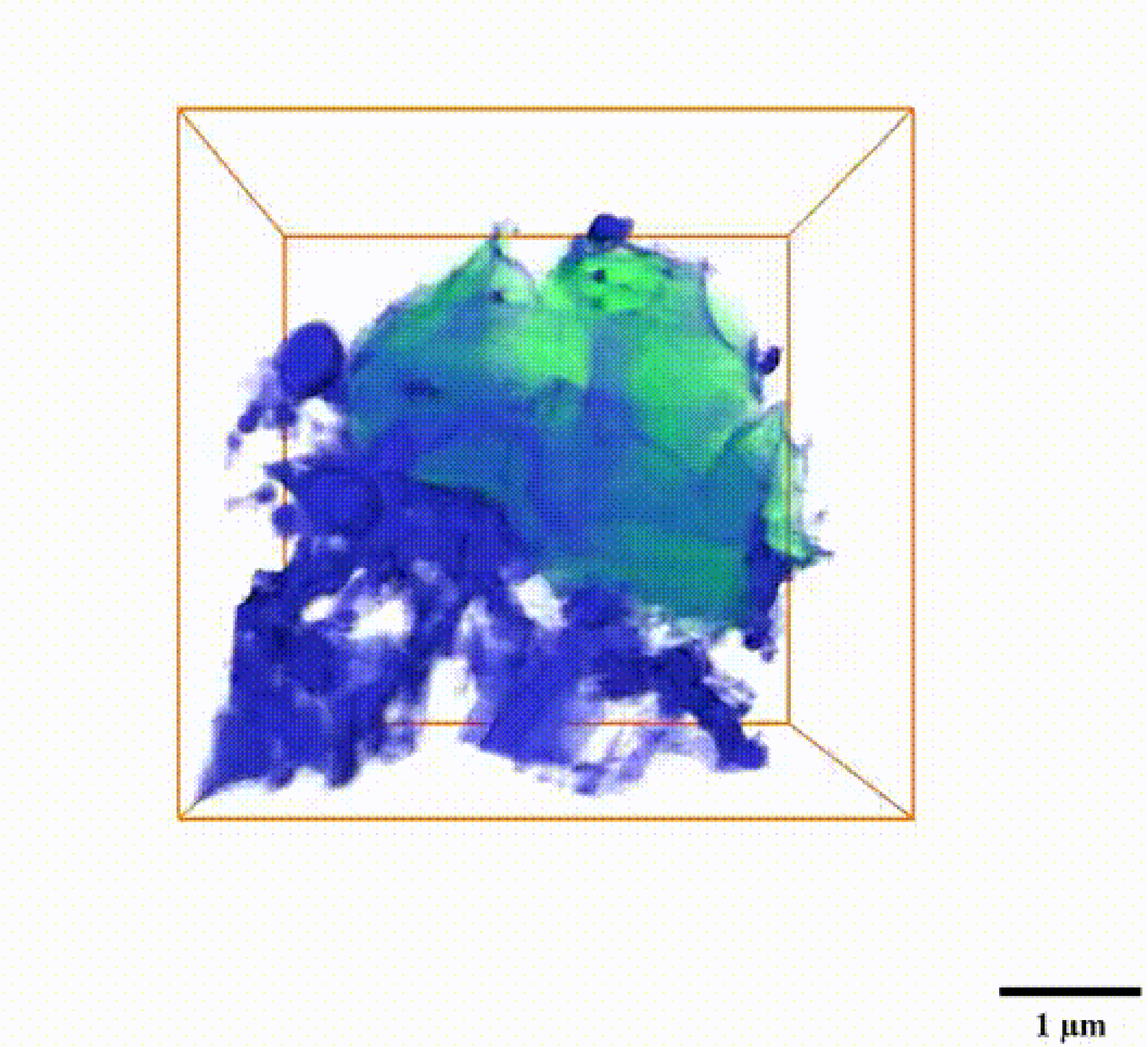
Bin Hang … and Ying Shirley Meng, ***Matter,2021***
DOI:https://doi.org/10.1016/j.matt.2021.09.019

3D STEM tomography of dead Li and SEI



Dead Li formation path

S. Y. Meng et al



Dendrite-type Li deposition results in large amounts of dead Li due to the cut off the electron conduction path (highlighted in green color) after Li stripping.

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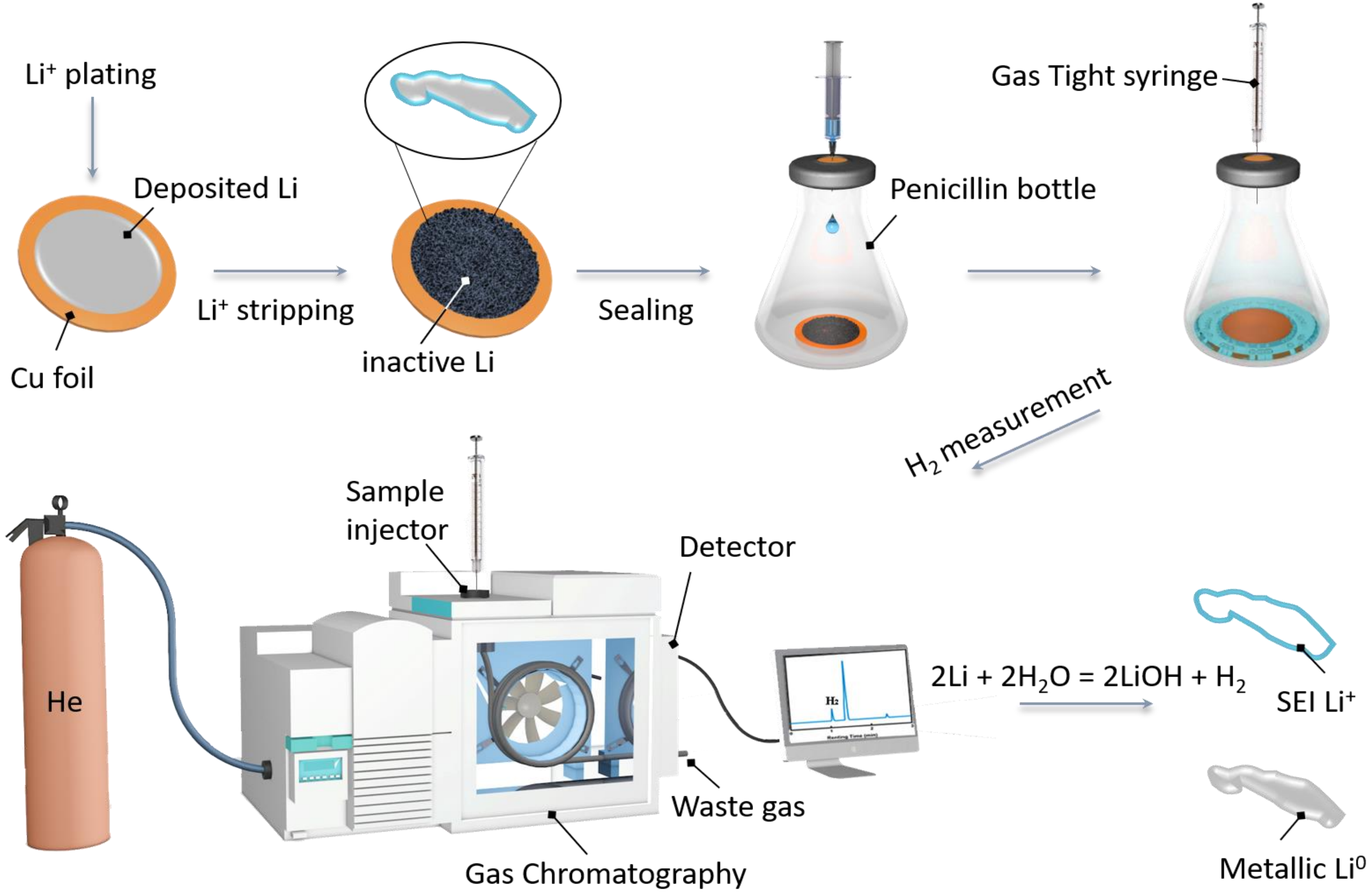
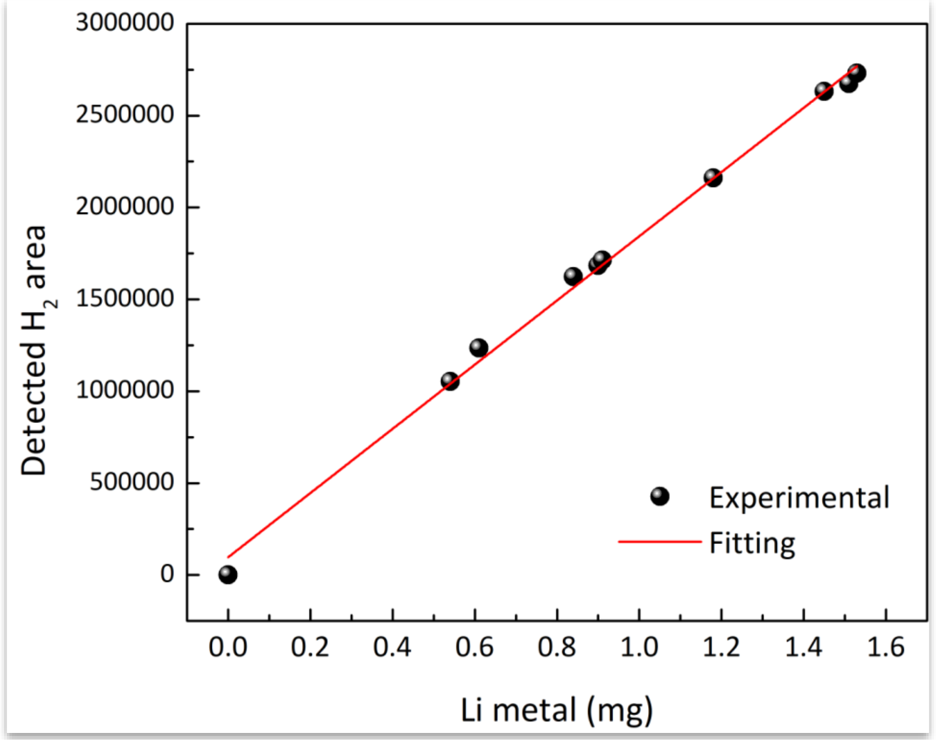
Bin Hang … and Ying Shirley Meng, ***Matter,2021***
DOI:https://doi.org/10.1016/j.matt.2021.09.019

Quantification of “Inactive” Metallic Li

A combination of H_2O **Titration** and **Gas Chromatography**



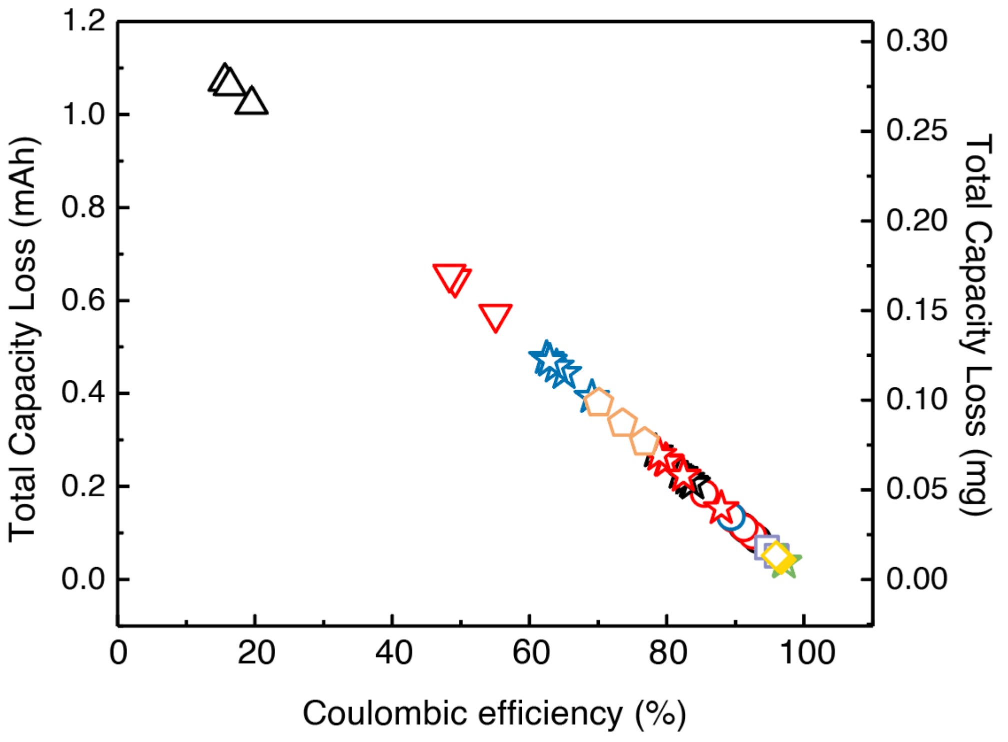
SEI component	Solubility in 100 mL H_2O
LiF	0.134 g (0.67 mg in 0.5 mL H_2O)
LiOH	12.8 g
$Li_2C_2O_4$	8 g
Li_2CO_3	1.29 g
Li_2O	$Li_2O + H_2O = LiOH$
CH_3Li	$CH_3Li + H_2O = LiOH + CH_4\uparrow$
ROLi	$ROLi + H_2O = LiOH + ROH$
$(CH_2OCO_2Li)_2$	$(CH_2OCO_2Li)_2 + H_2O = Li_2CO_3 + (CH_2OH)_2 + CO_2\uparrow$
$LiOCO_2R$	$2LiOCO_2R + H_2O = Li_2CO_3 + 2ROH + CO_2\uparrow$

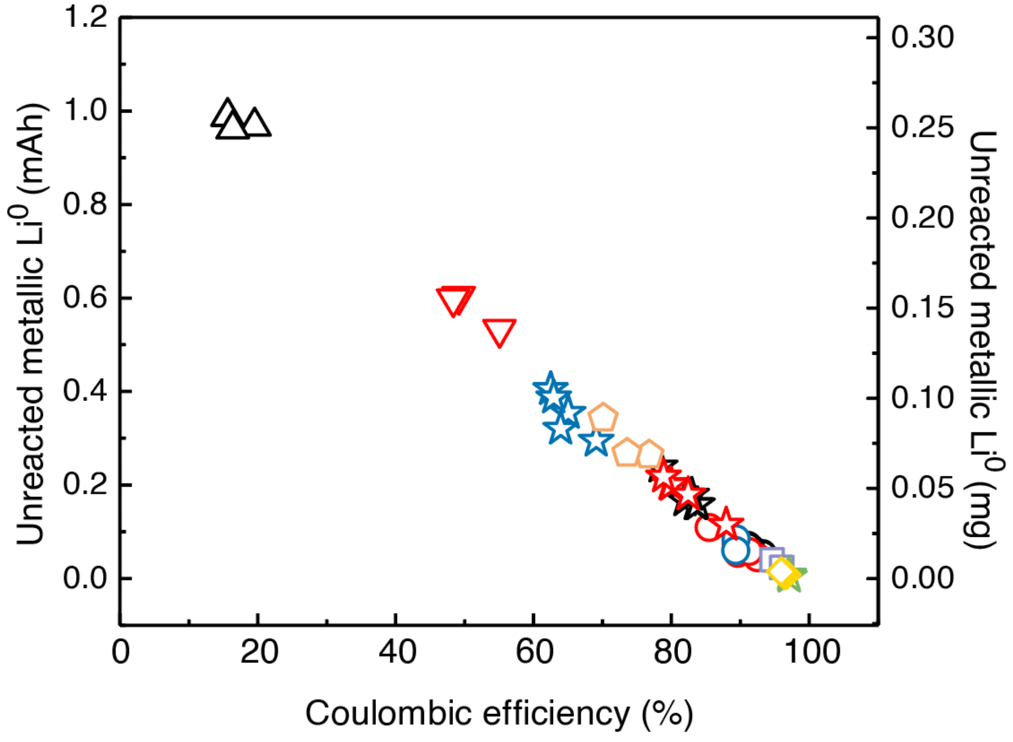


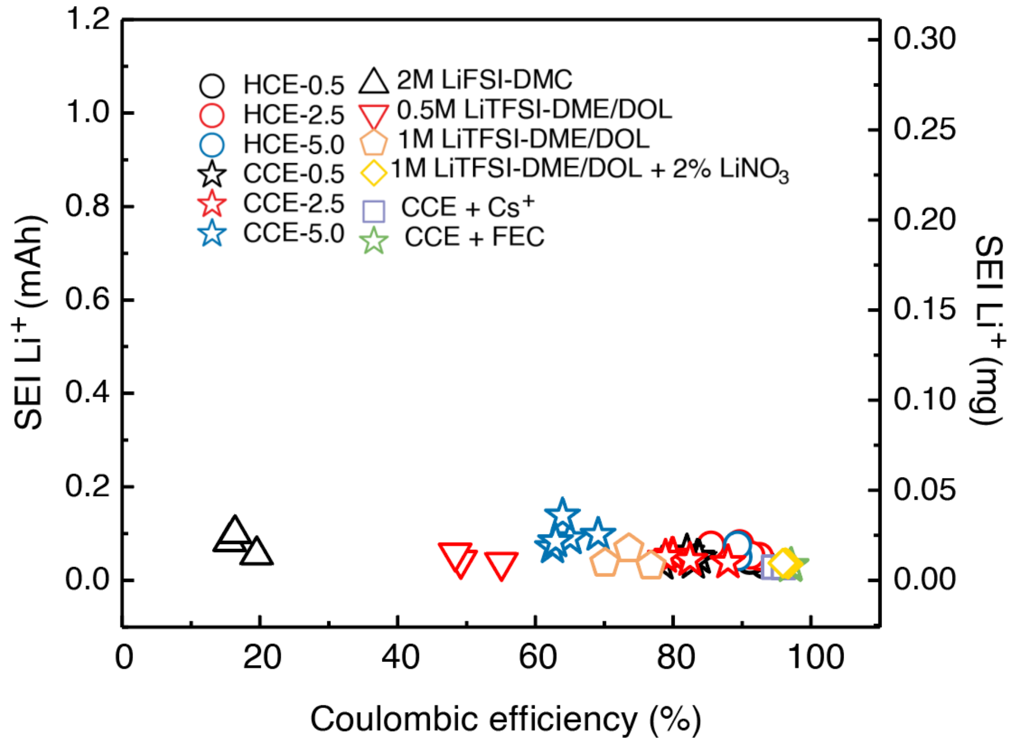
Detection limit is ug Li

Inactive Li^0 and Li^+ Quantification

Total capacity loss = **Metallic Li^0** + **SEI Li^+**







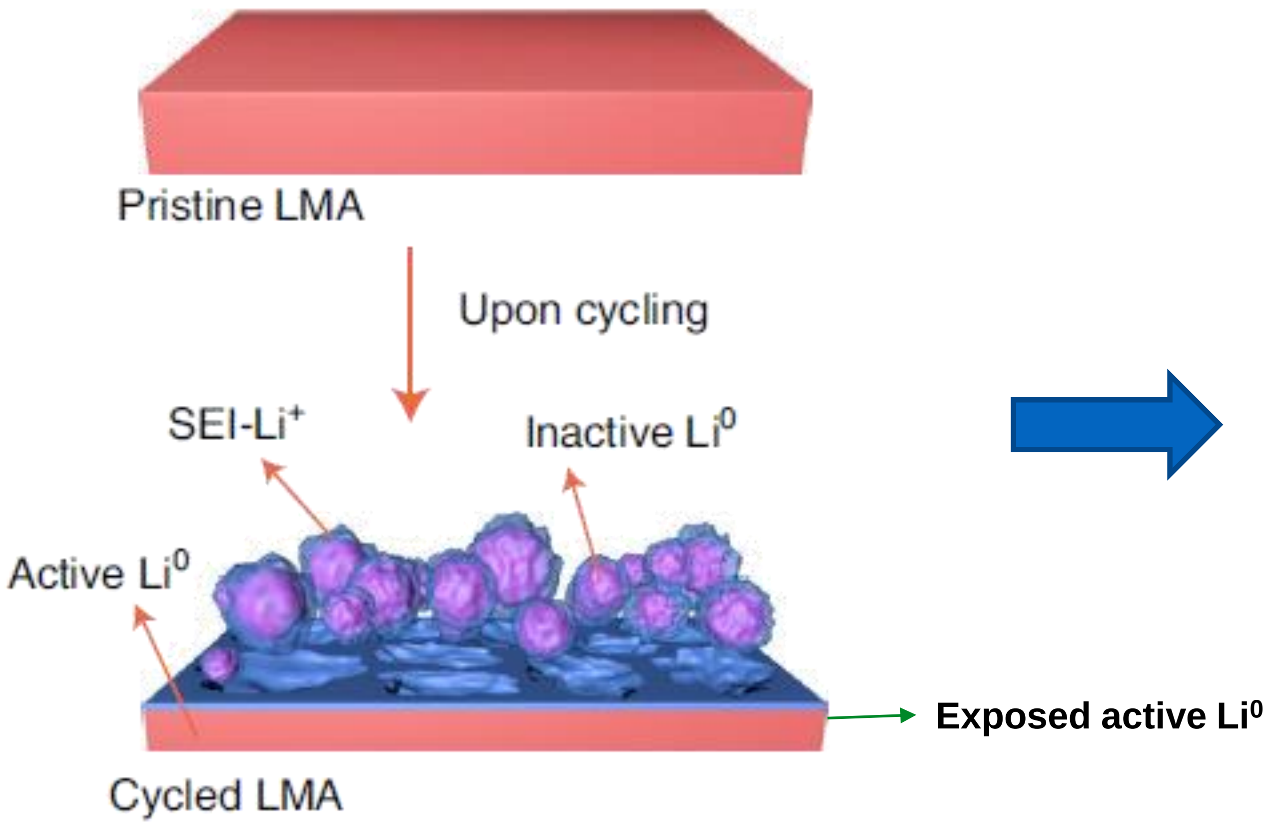
- Metallic Li^0 dominates the capacity loss
- SEI Li^+ amount keeps almost identical under all testing conditions

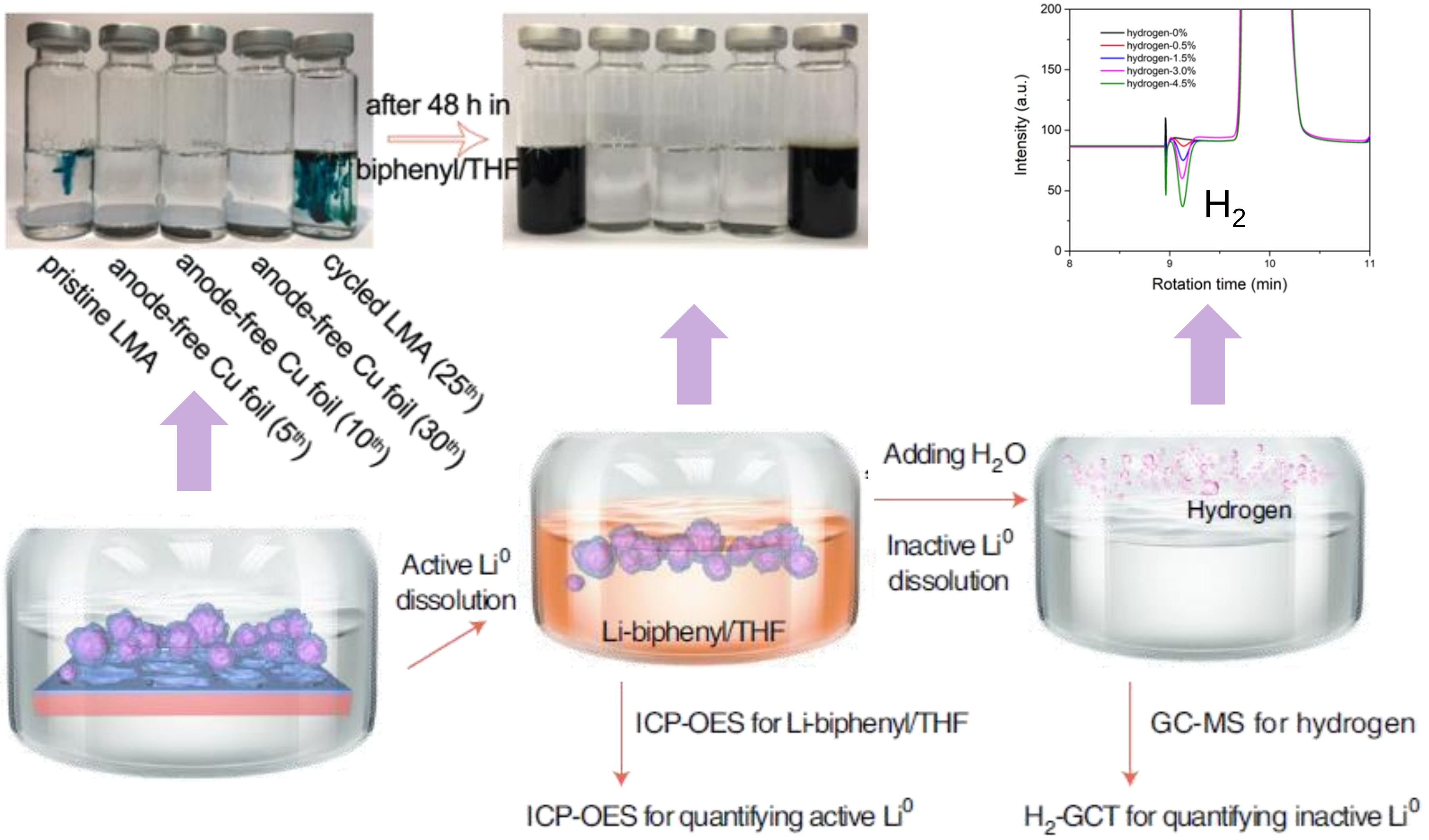
SEI is not the main reason for low Coulombic efficiency in Li metal batteries

C. Fang, J. Li, Y.S. Meng *et al.*, "Quantifying Inactive Lithium in Lithium Metal Batteries", ***Nature* 572**, 511–515 (2019)

Quantification active Li^0 vs. inactive Li^0

Cycled anode: **Li in anode**= SEI(Li^+)+ Inactive Li^0(Isolated by SEI)+ active Li^0

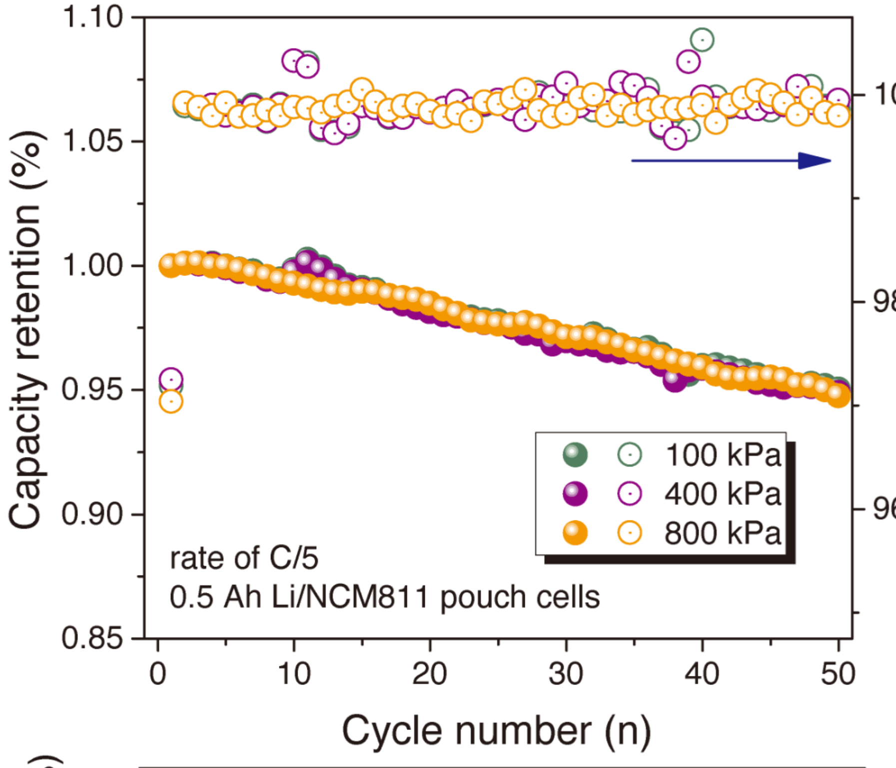


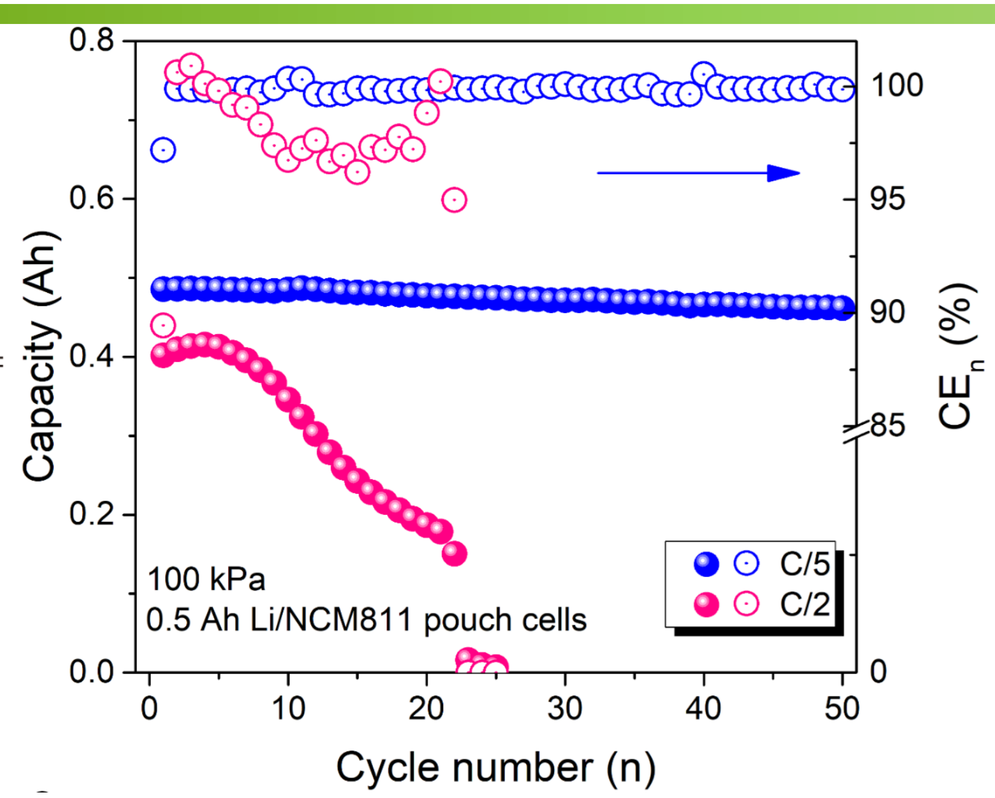


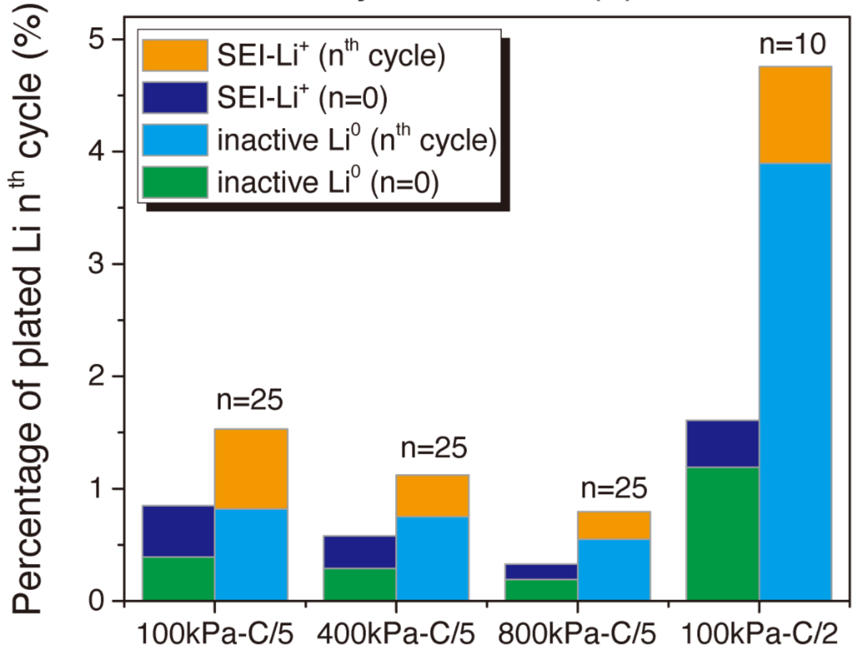
- A SEI stable solvent was introduced to only dissolve the active Li^0
- By controlling the reaction sequence the active Li^0 and inactive Li^0 can be differentiated.

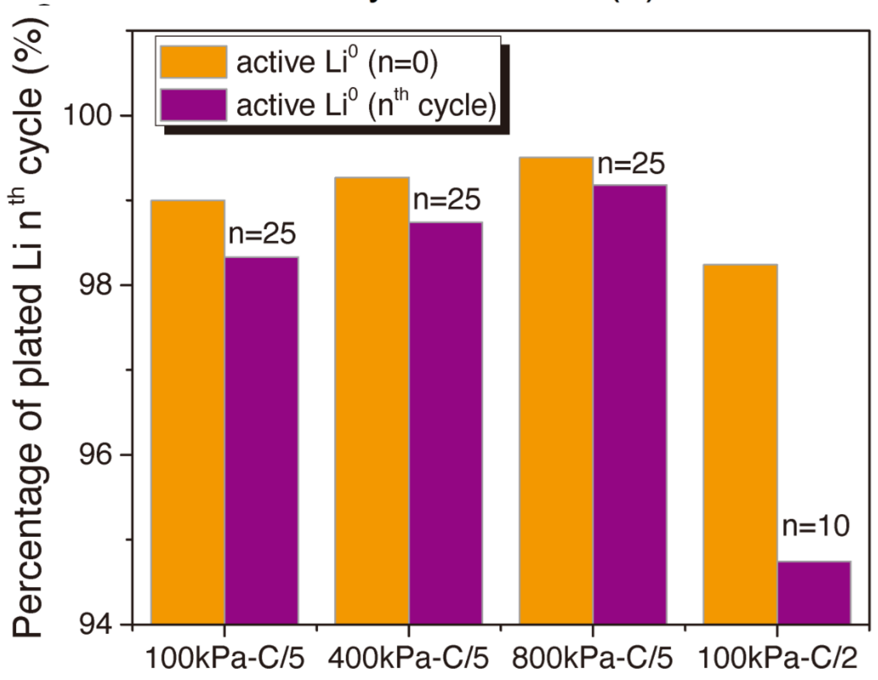
Deng, Wei, Xue Yin, Wurigumula Bao, Ying Shirley Meng et al. "Quantification of reversible and irreversible lithium in practical lithium-metal batteries." *Nature Energy* (2022): 1-11.

Quantify Li inventory loss in LMB



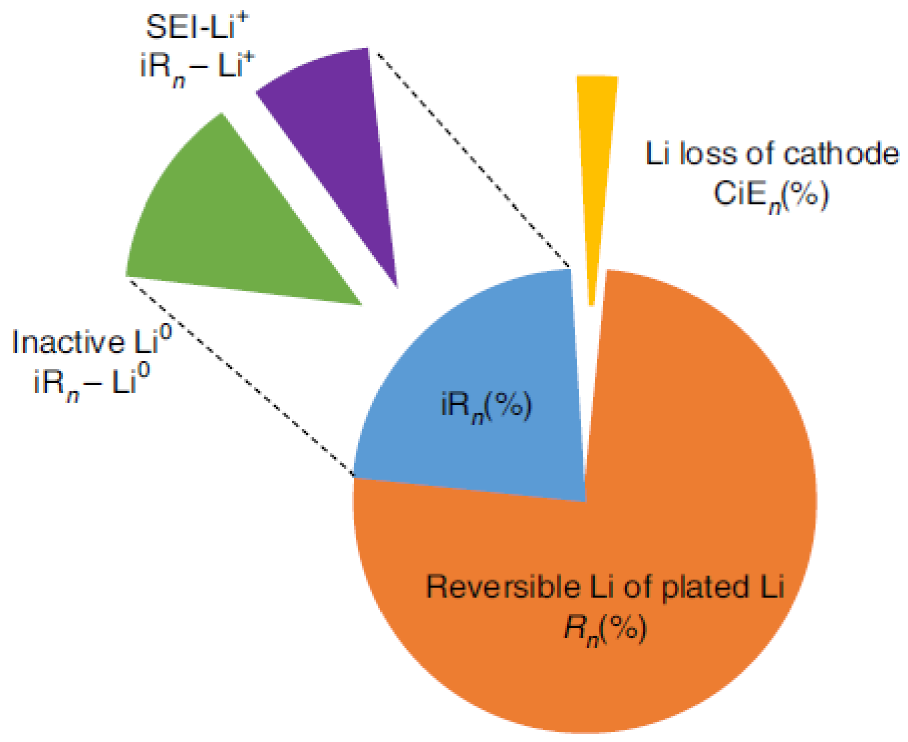






1.0 M $LiPF_6$ in FEC/EMC (in *vol.* ratio 1:5) N/P=2.6

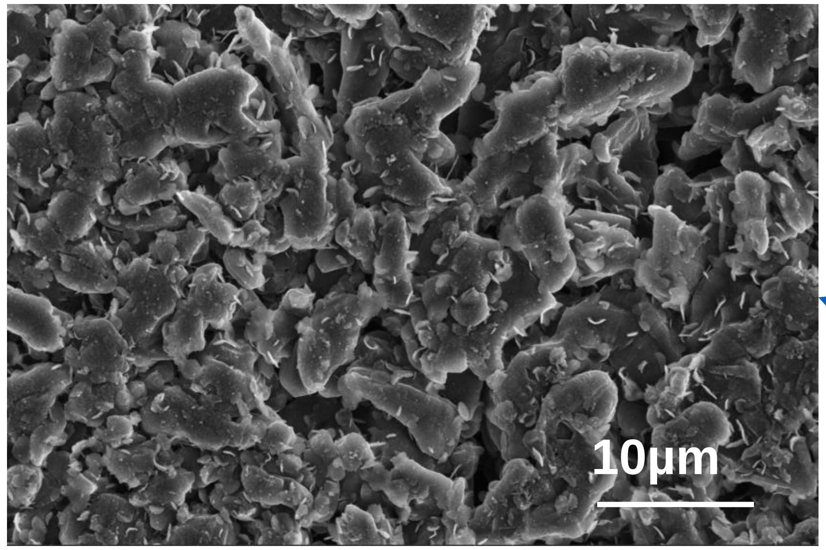
- Coulombic Efficiency could not reveal the true Li loss due to the compensation from excess Li.
- High C-rate cycling leads to even more inactive Li^0.
- Inactive Li^0 trapped by SEI is the main reason for active Li^0 inventory loss.

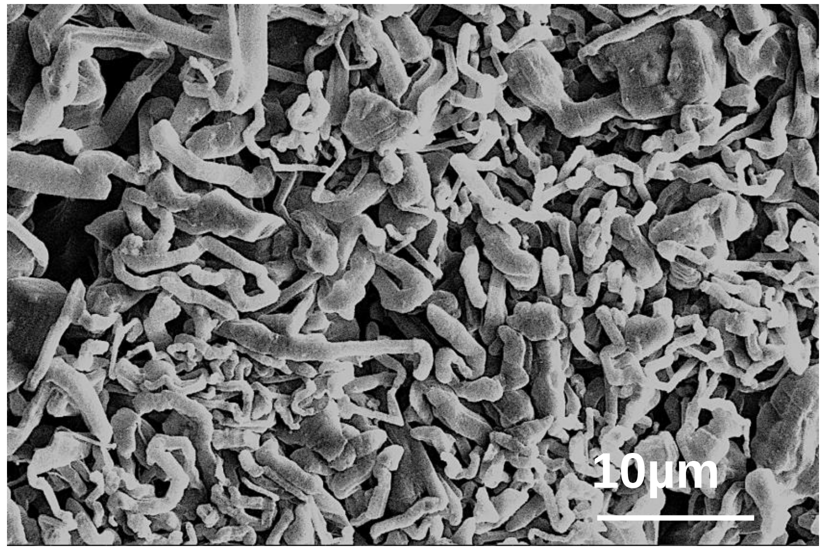


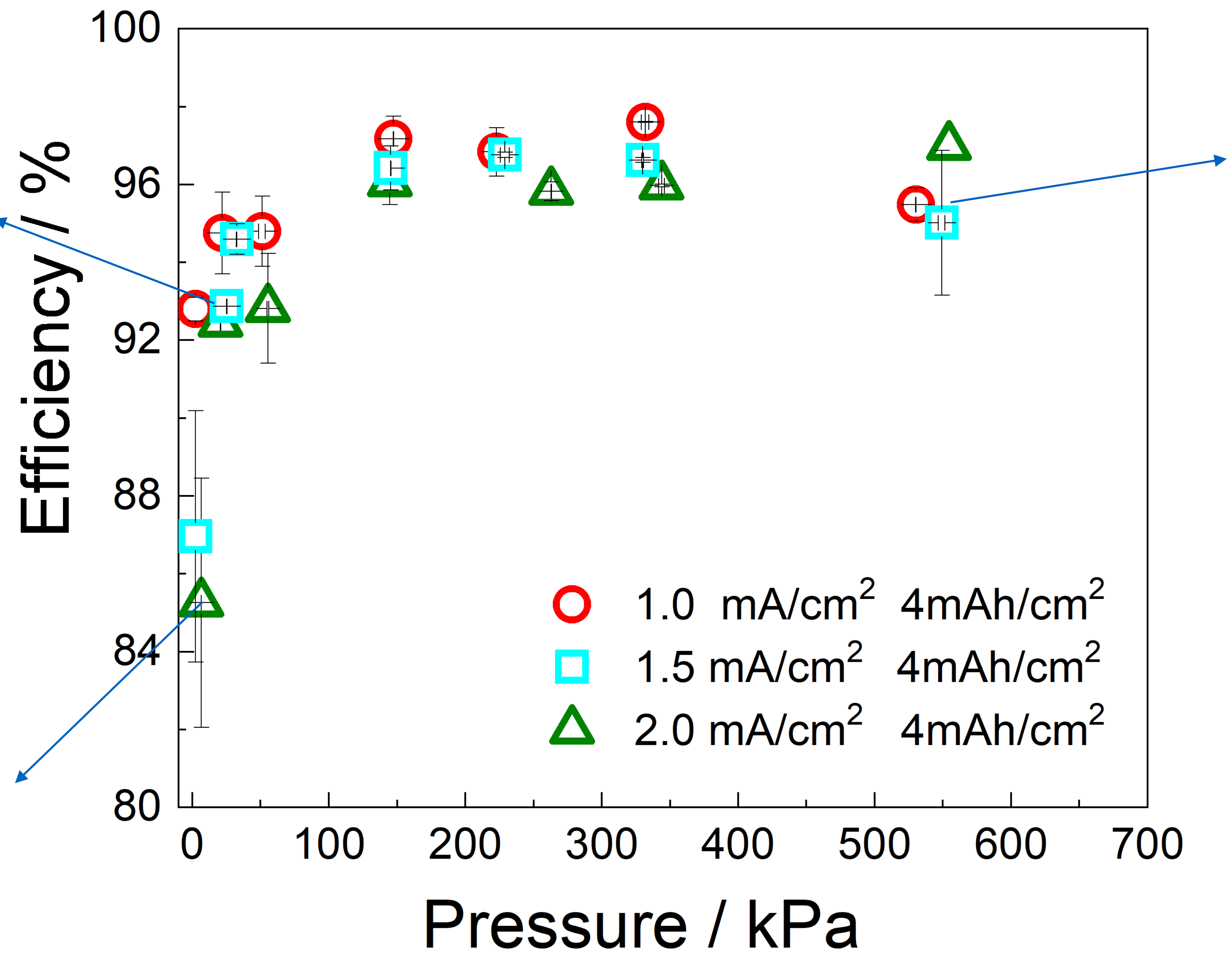
Reversibility and irreversibility of plated Li at *n*th cycle

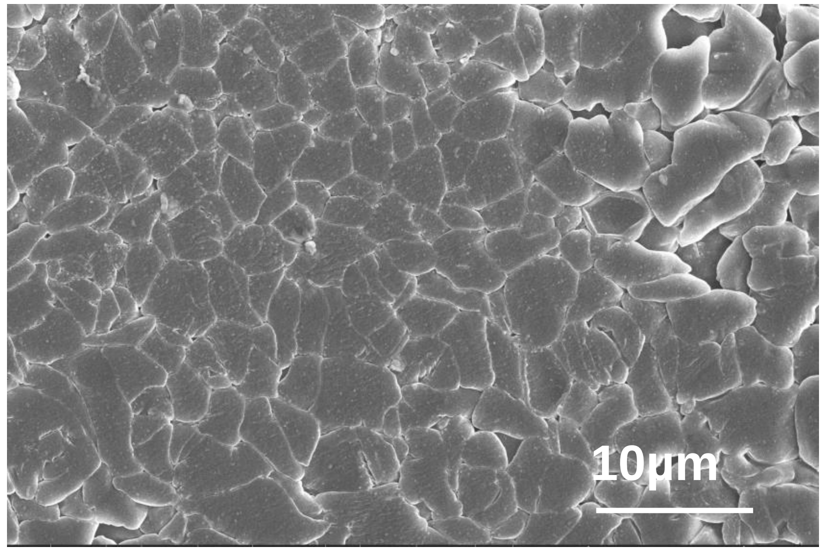
Deng, Wei, Xue Yin, Wurigumula Bao, Ying Shirley Meng et al. "Quantification of reversible and irreversible lithium in practical lithium-metal batteries." *Nature Energy* (2022): 1-11.

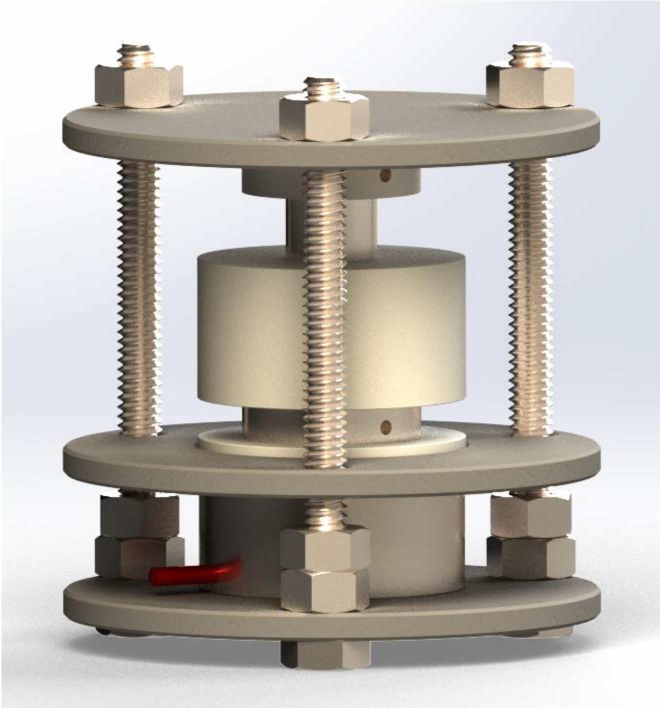
Trend of Pressure Effect on 1st Cycle CE











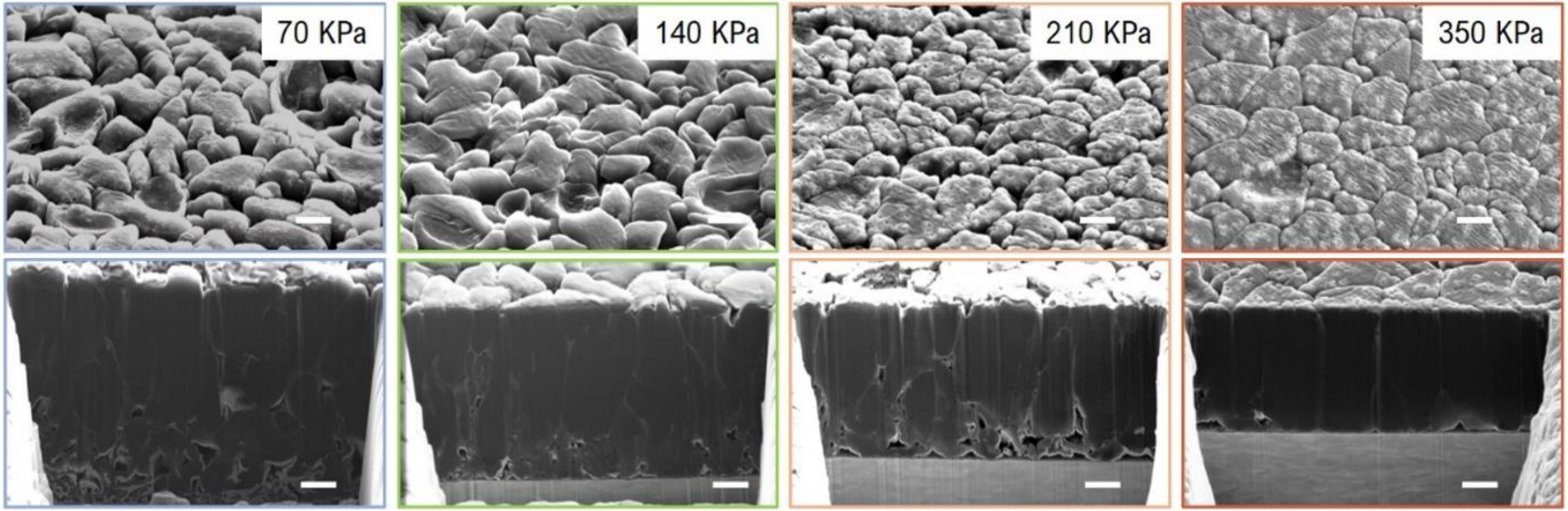
Pressure Control Setup

High concentration ether electrolyte

Top view SEM:
$2 mA/cm^2$; $4 mAh/cm^2$

- **0.1 kPa** resolution
- **50 μm thick Li foil** is used to minimize the Li deformation issue
- Minimum amount of electrolyte is used (~5μL)

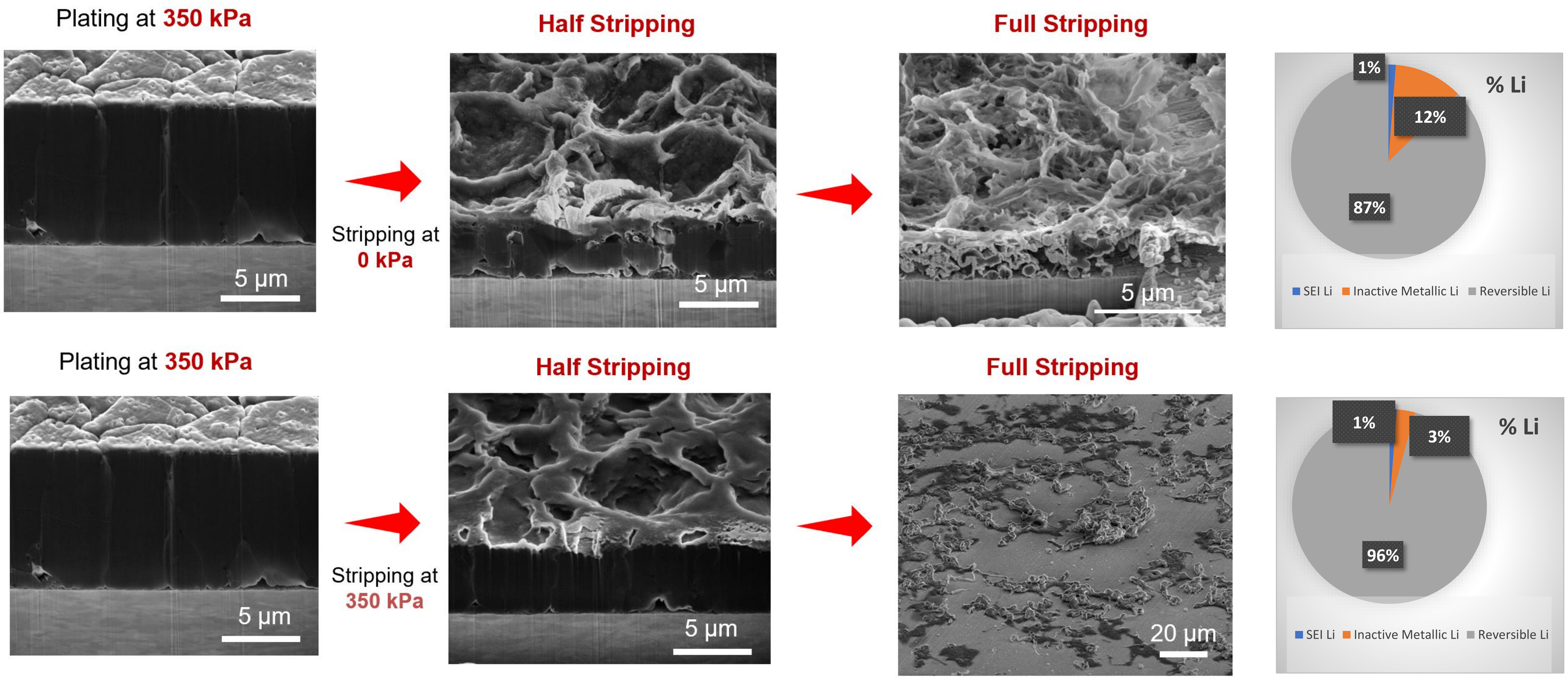
Pressure Effect on Plating Morphology



Top view and cross-sectional SEM images of Li plated under a range of pressure. Scale bar: 2µm

High concentration ether electrolyte
$2mA/cm^2$; $2mAh/cm^2$

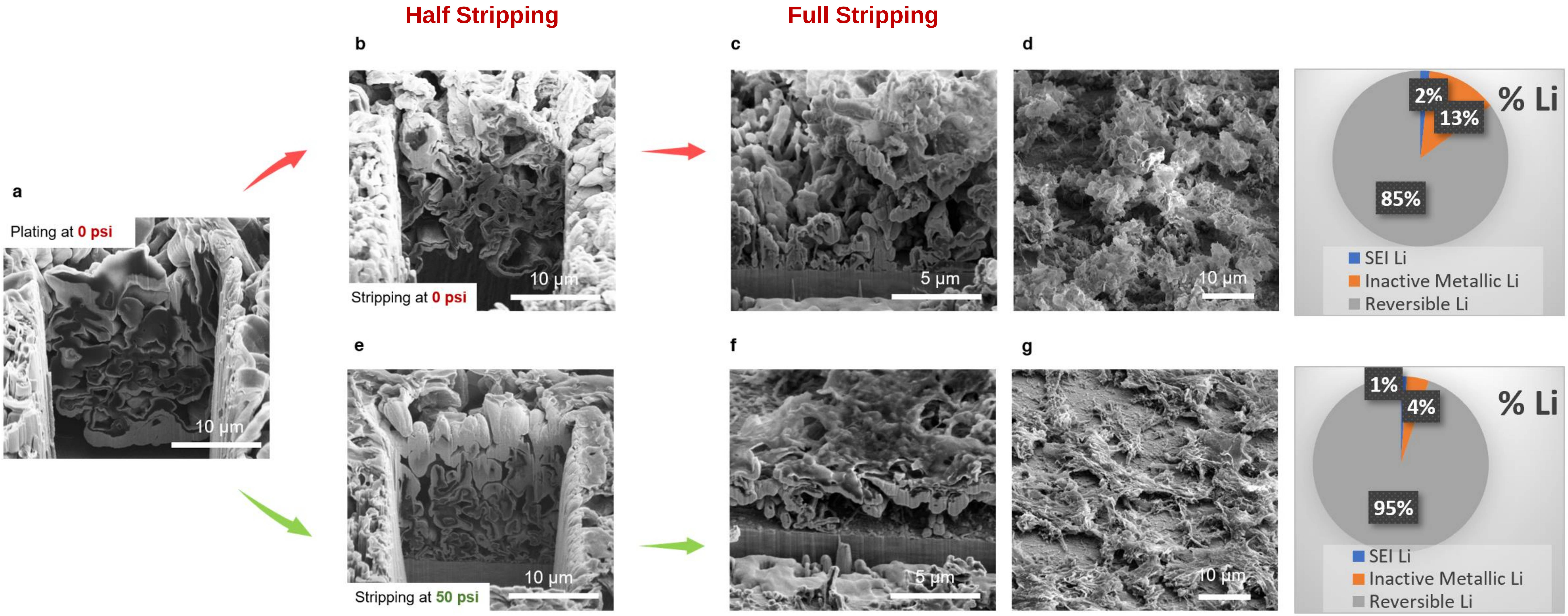
Pressure Effect on Stripping



High concentration ether electrolyte

$2mA/cm^2$; $2mAh/cm^2$

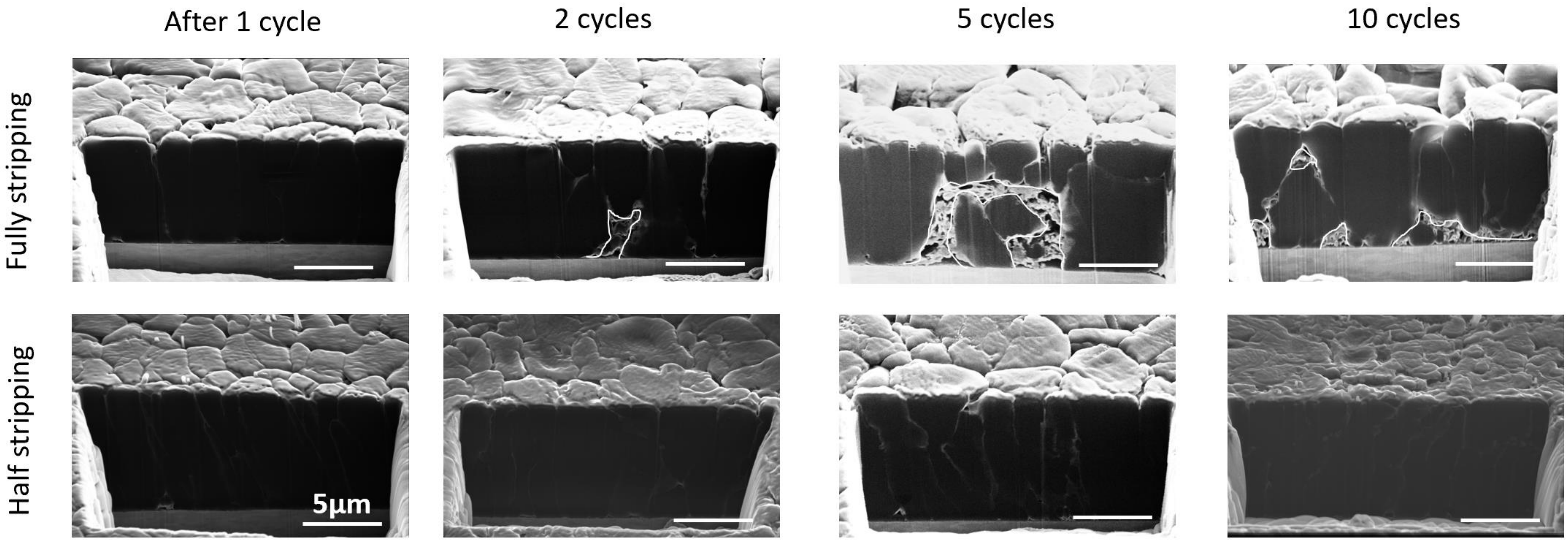
Pressure Effect on Stripping



High concentration ether electrolyte

2mA/cm^2; 2mAh/cm^2

Li Reservoir is a MUST for Anode-Free

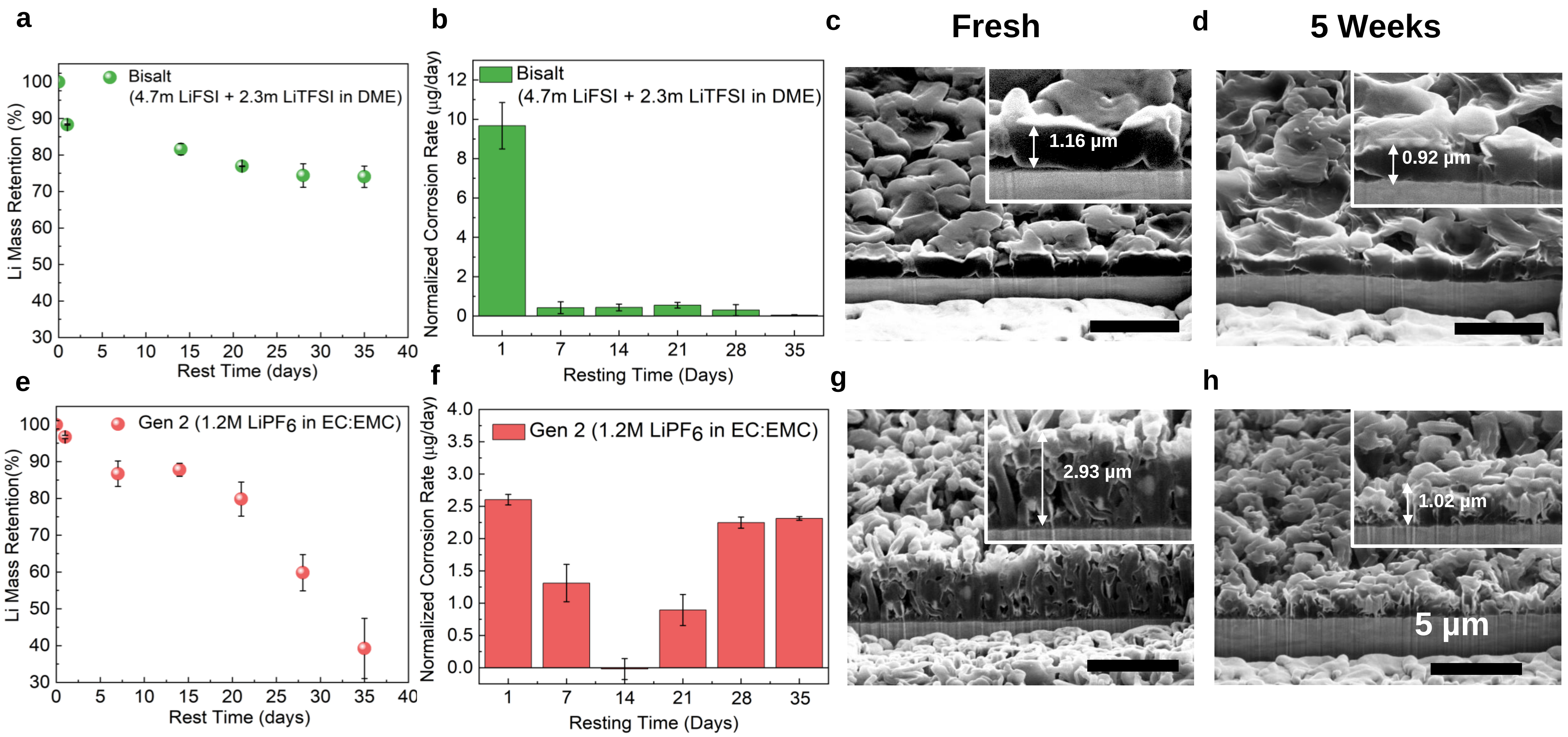


High concentration ether electrolyte

$2 mA/cm^2$; $2 mAh/cm^2$

C. Fang and Y. S. Meng et.al. – Nature Energy, 2021

Trend of Corrosion in Two Different Electrolytes



Mass retention and microstructure of Li metal. Li mass retention for Bisalt (a) and Gen2 electrolyte (e). Normalized corrosion rate of Li in Bisalt (b) and Gen2 electrolyte (f). Cryo-FIB/SEM cross section images after 0 days and 35 days in Bisalt (c, d) and (g, h) in Gen 2 electrolyte

- Corrosion test is done in two electrolyte systems, high concentration electrolyte (Bisalt) and carbonate electrolyte.
- The corrosion rate in the Bisalt is stabilized after 24 hours but not in the carbonate electrolyte.
- **There are two possible reasons for the different corrosion trend: 1) different SEI components; 2) different Li morphology.**

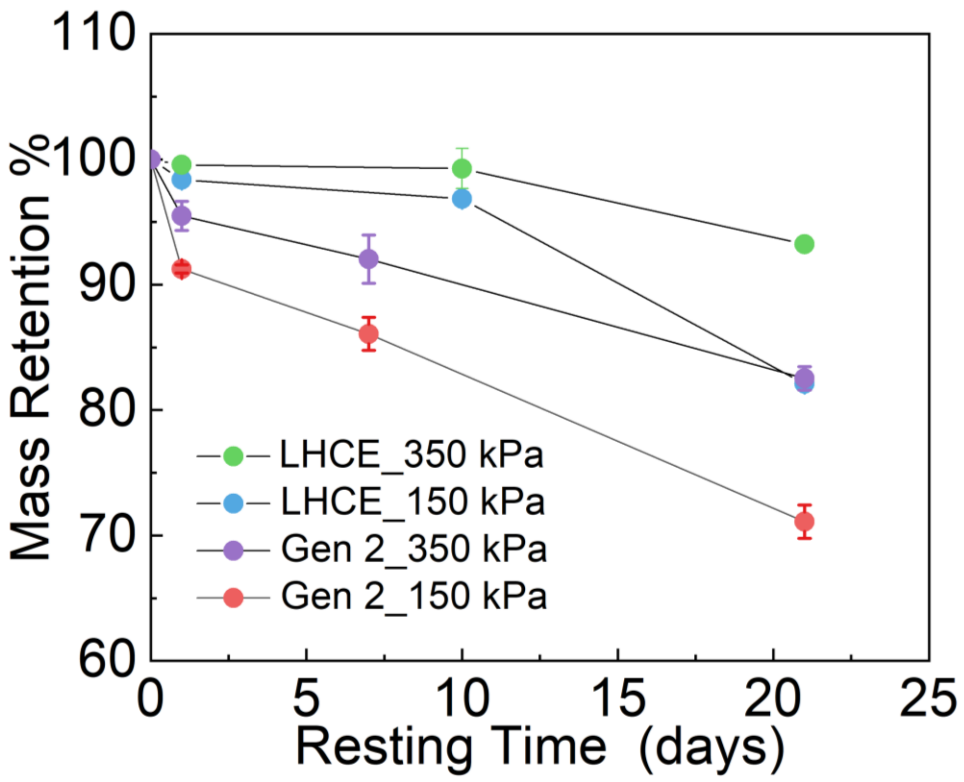
Protocol

•0.5 mA/cm^2; 0.5 hours; 0.25mAh/cm^2 50μL of electrolyte

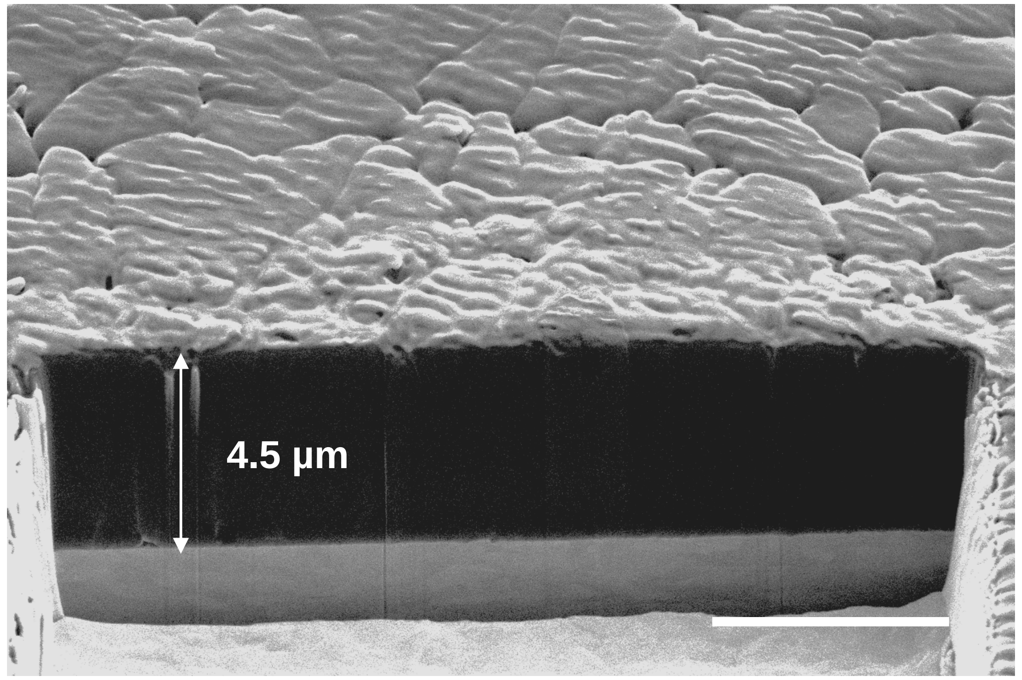
B. Lu and Y. S. Meng et.al. – Under Review 2022

Limited Li Corrosion with Dense Morphology

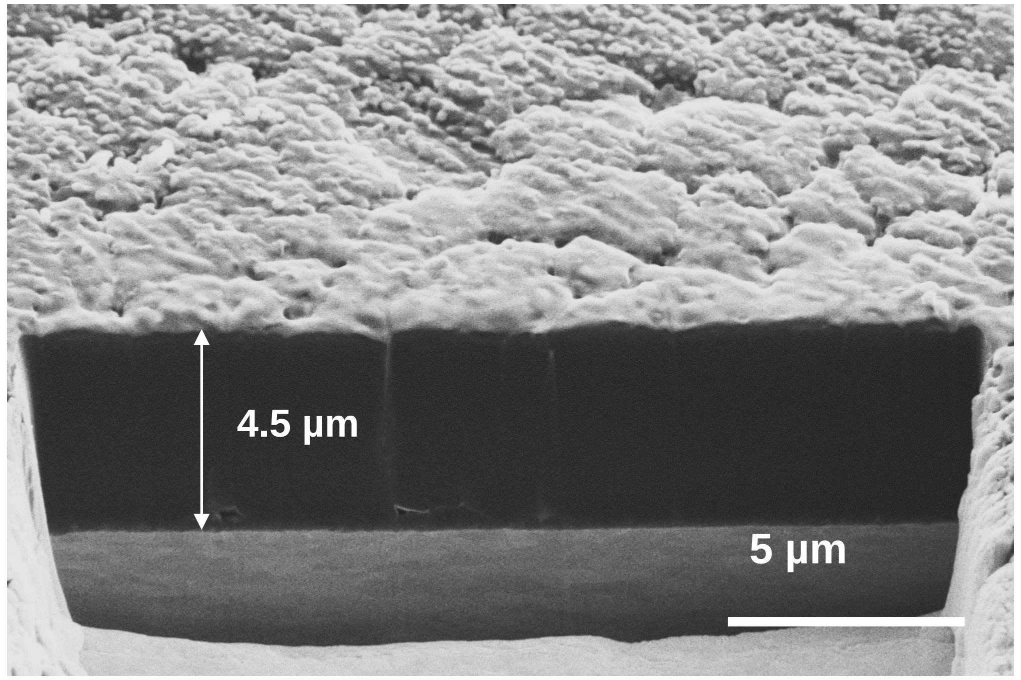
a



b LHCE Fresh 350 kPa



c LHCE 21 days 350 kPa

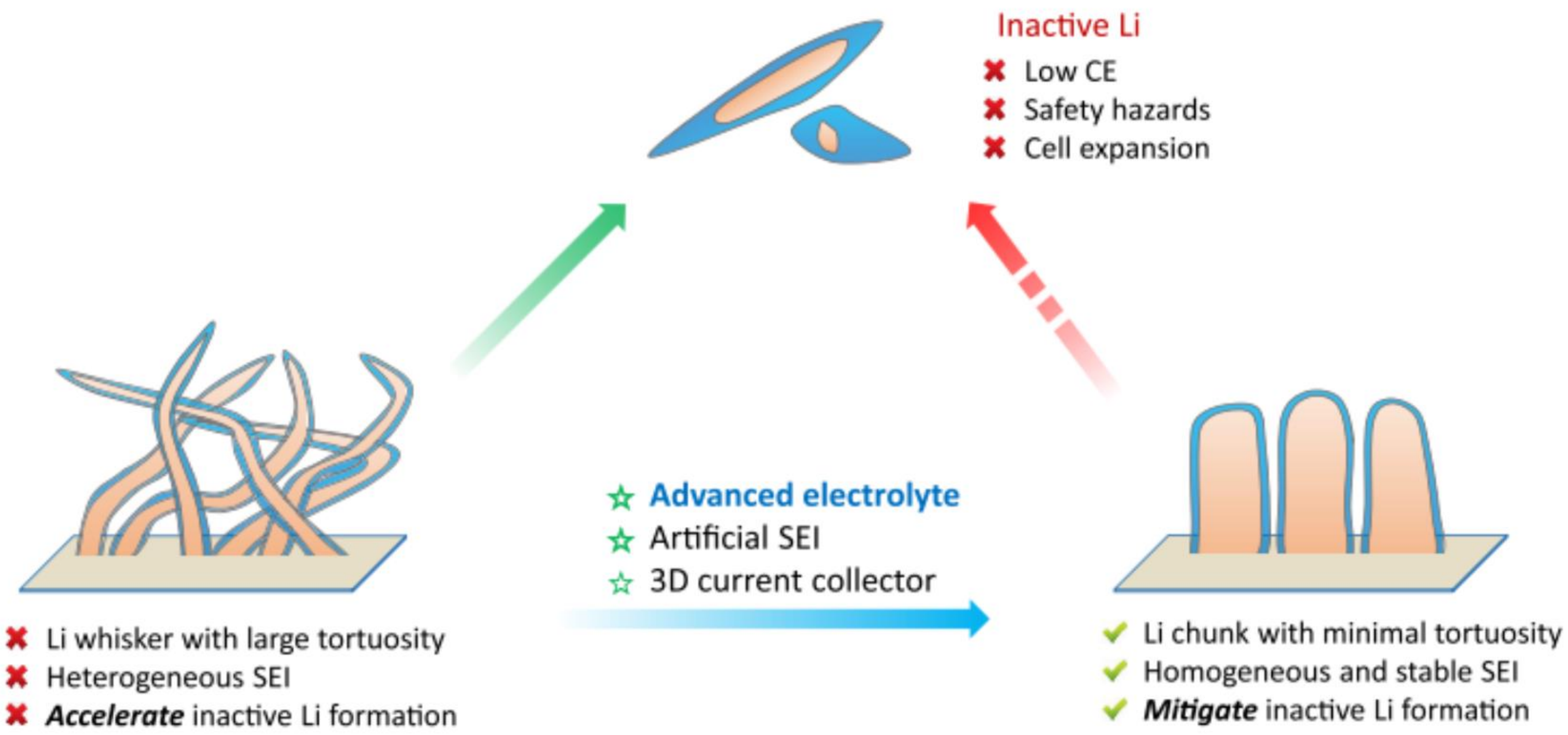


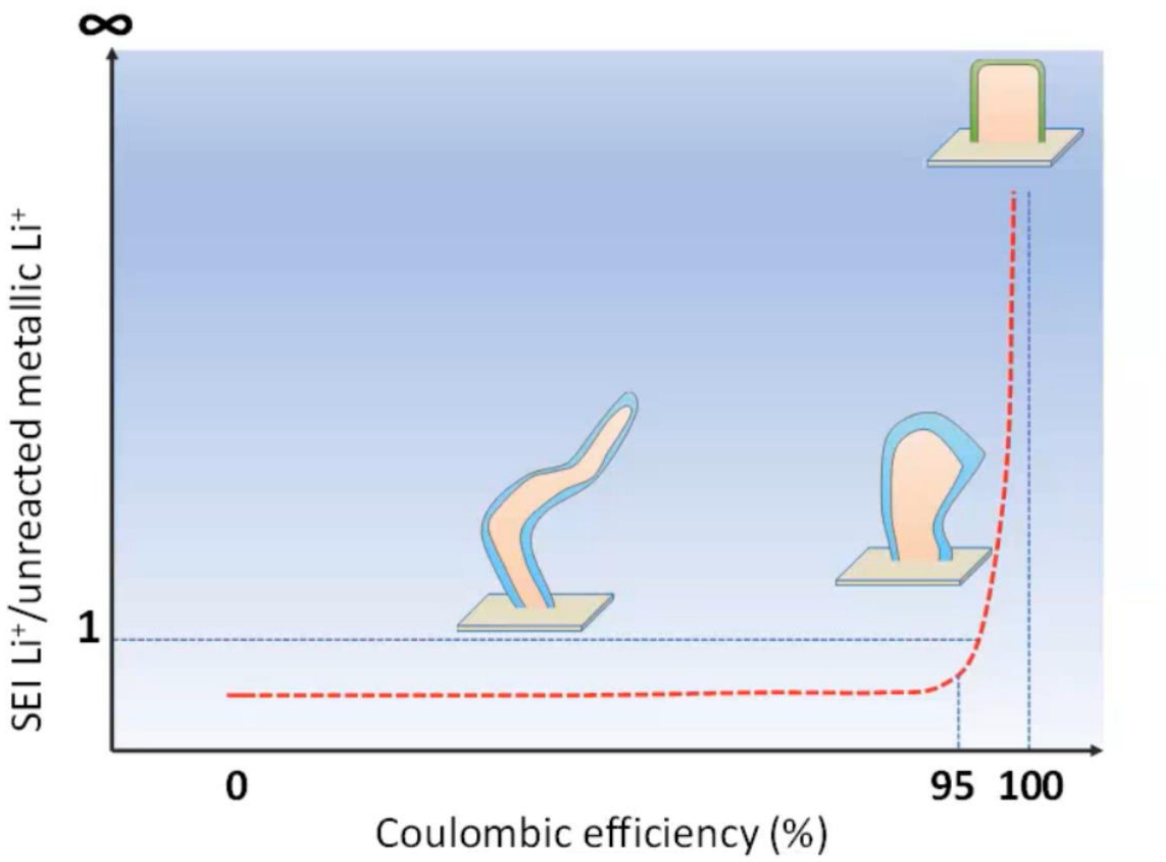
- Optimized stacked pressure and localized high concentration electrolyte (LHCE) are used to deposited near 100% dense Li.
- The resulting Li only experienced **less than 0.8% loss** of active material loss after 10 days of resting in flooded electrolyte.

0.5 mA/cm^2, plated 0.87 mAh/cm^2, Special Electrolytes Formulated by PNNL

B. Lu and Y. S. Meng et.al. – Under Review 2022

Lithium Metal Anode – Liquid or Solid Electrolytes





Tuning the electrochemical property of lithium metal - deposit DENSE Lithium

C. Fang, et al., Trends in Chemistry, May 2019, Vol. 1, No. 2

C. Fang, Y. S. Meng, et al. Nature 572, 511–515 (2019)

B. Lu , C. Fang and Y. S. Meng, 2022 under review

Possible to Invent More Electrolytes to Enable Metal Anodes

Prof. Betar Gallant and Prof. Yang Shao-Horn

DispatchDate: 22.09.2021 · ProofNo: 910, p.1

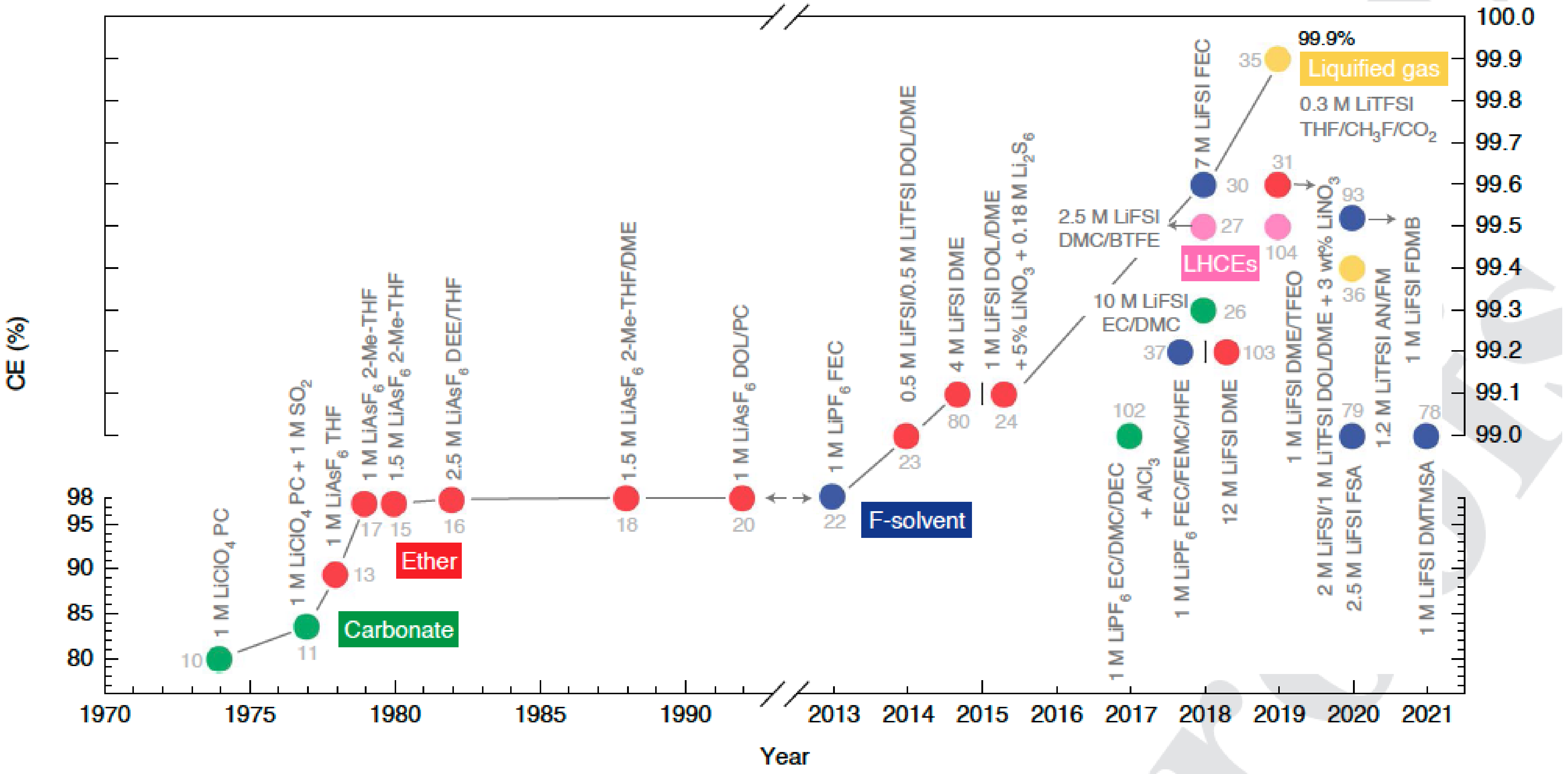
nature energy

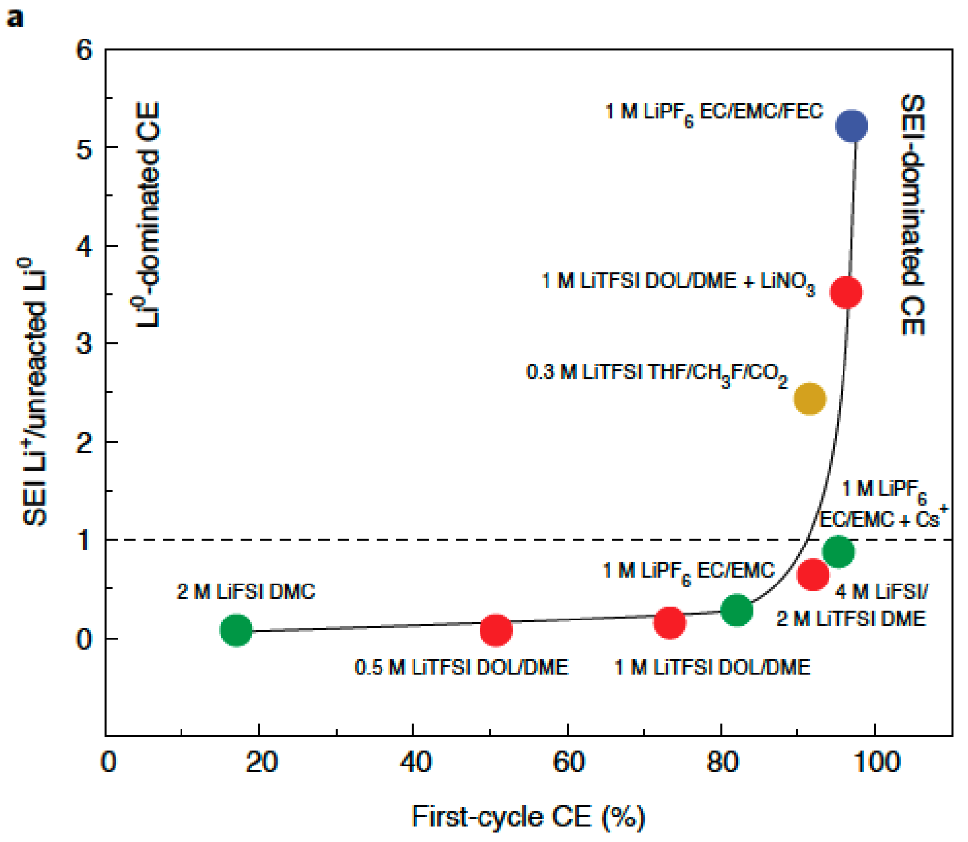
REVIEW ARTICLE

https://doi.org/10.1038/s41560-021-00910-w

Check for updates

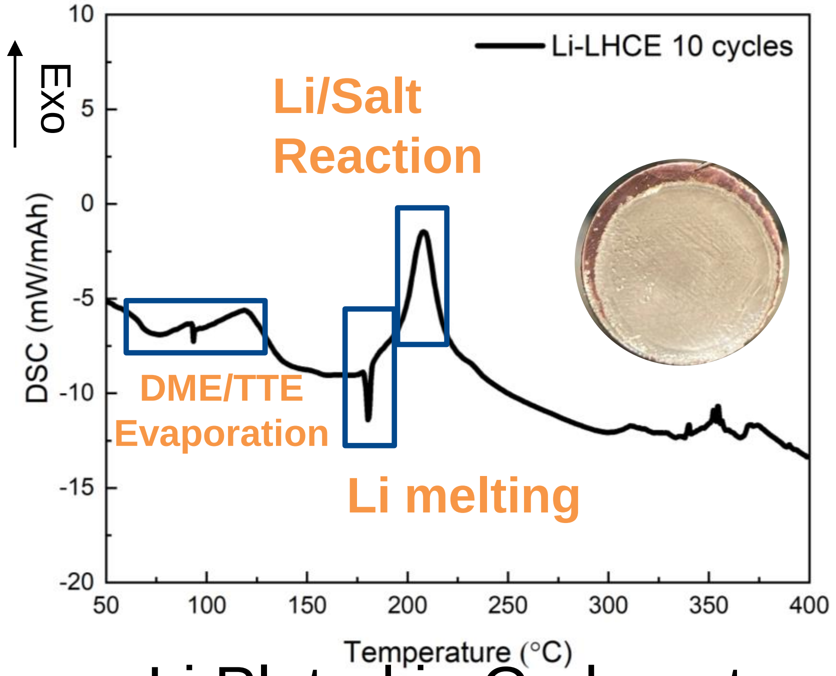
Moving beyond 99.9% Coulombic efficiency for lithium anodes in liquid electrolytes



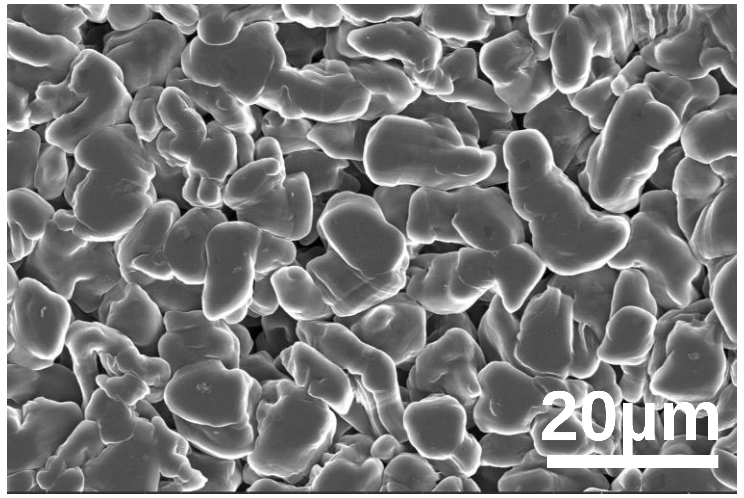


Li Metal Anodes in LHCE After 10 Cycles

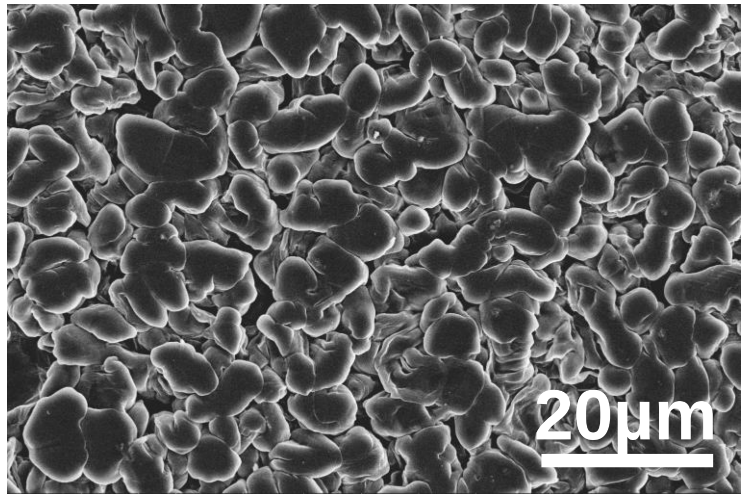
Li Plated in LHCE



After 1 cycle

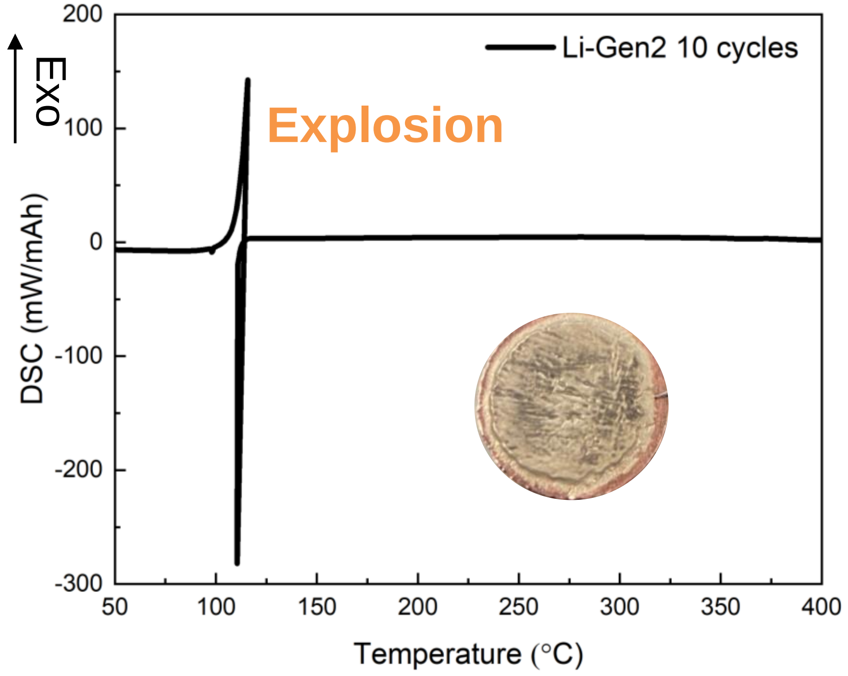


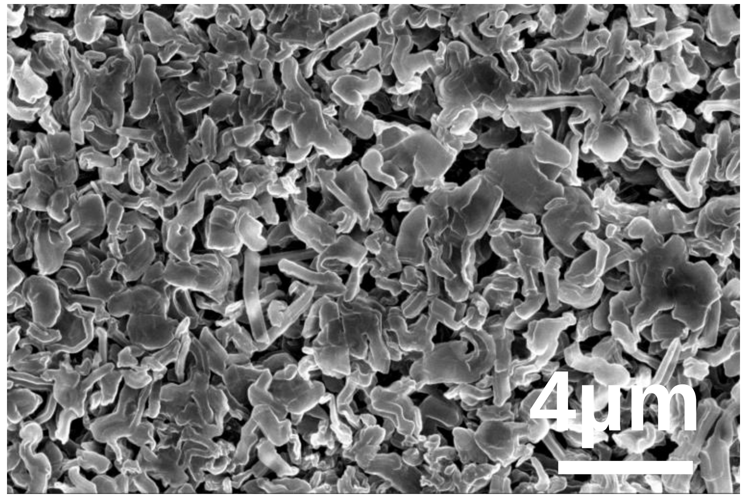
After 10 cycle

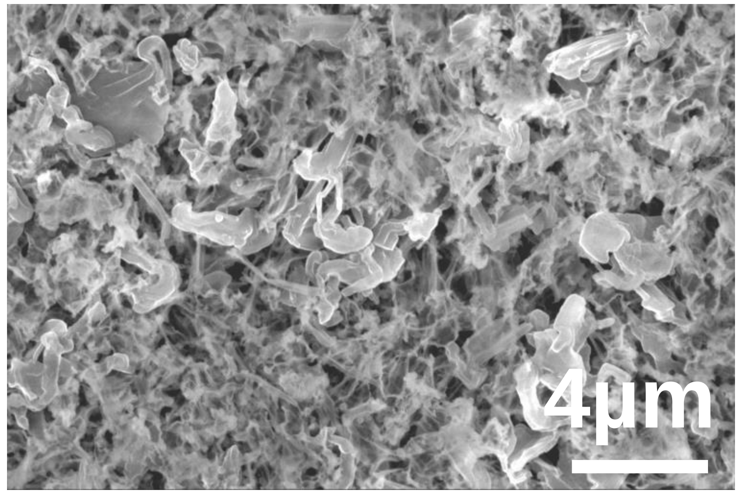


- There is no strong thermal response observed from the Li plated in LHCE after 10 cycles.
- The Li is still shinny even after 10 cycles. No inactive Li found on the electrode.

Li Plated in Carbonate





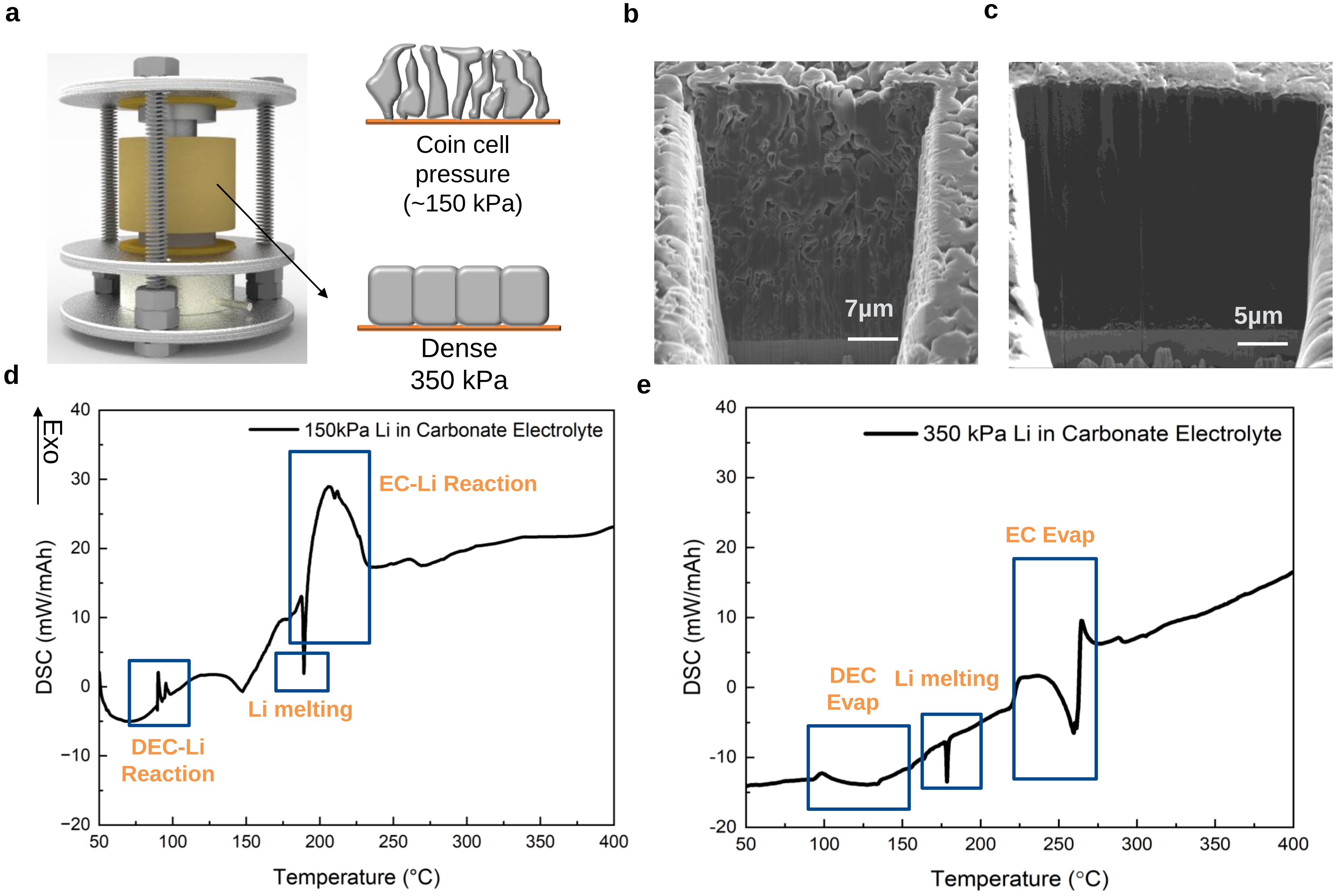


- The sample pan exploded during the DSC measurement for the Carbonate sample.
- There is a large amount of inactive Li accumulated on the electrode after cycling.

From 50 ℃ to 400 ℃, heating rate: 10 ℃/min, in N_2

Electrolyte: 1M $LiPF_6$ in EC:DEC with FEC
LiFSI:DME:TTE (1:1.2:3 molar ratio) 55μL
Cycling rate: C/20 Li metal plating rate: 0.5mA/cm^2

Pressure Effect on Li Reactivity

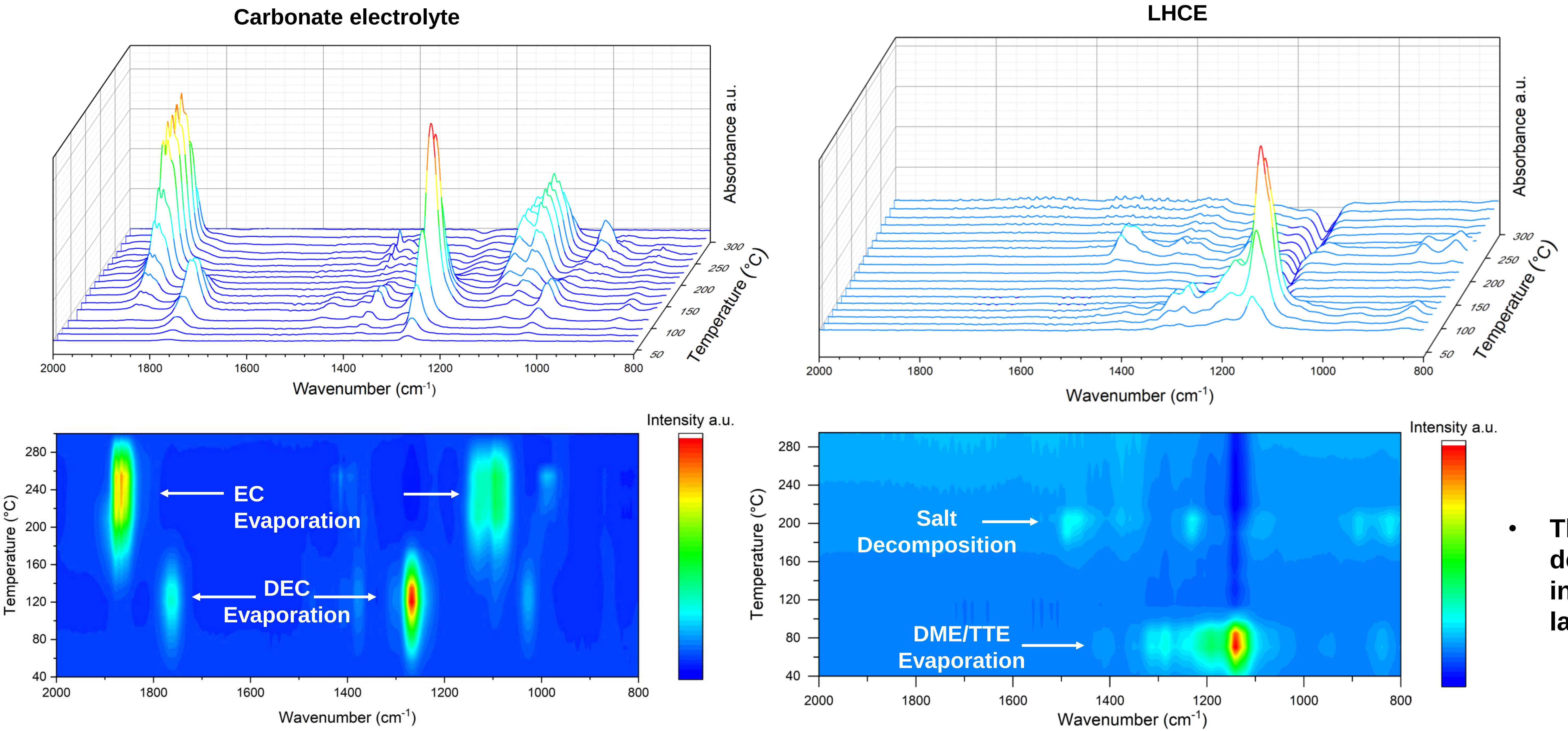


Optimized pressure can densify the Li and reduce the Li reactivity.

From 50 ℃ to 400 ℃, heating rate: 10 ℃/min, in N_2

Electrolyte: 1M $LiPF_6$ in EC:DEC with FEC
Cycling rate: C/20 Li metal plating rate: $0.5 mA/cm^2$

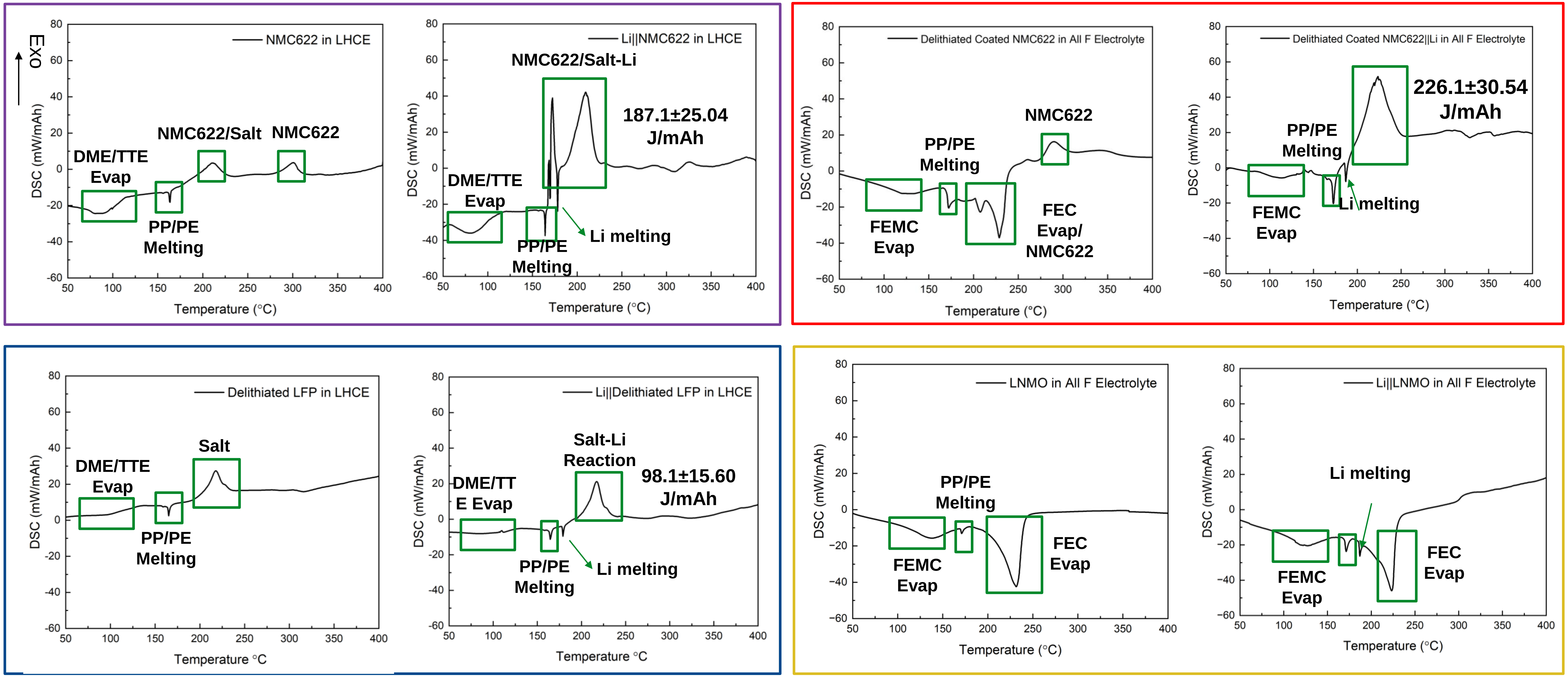
Gas Evolution during DSC by FTIR



- **The LiFSI decomposition in LHCE is a large issue.**

- 5mAh/cm^2 of Li is plated on Cu, with 1µL of electrolyte (E/S = 2.6).
- Electrolyte formula: 1M $LiPF_6$ in EC:DEC with FEC and LiFSI:DME:TTE (1:1.2:3 molar ratio)

Li Reactivity – Effects of Cathode

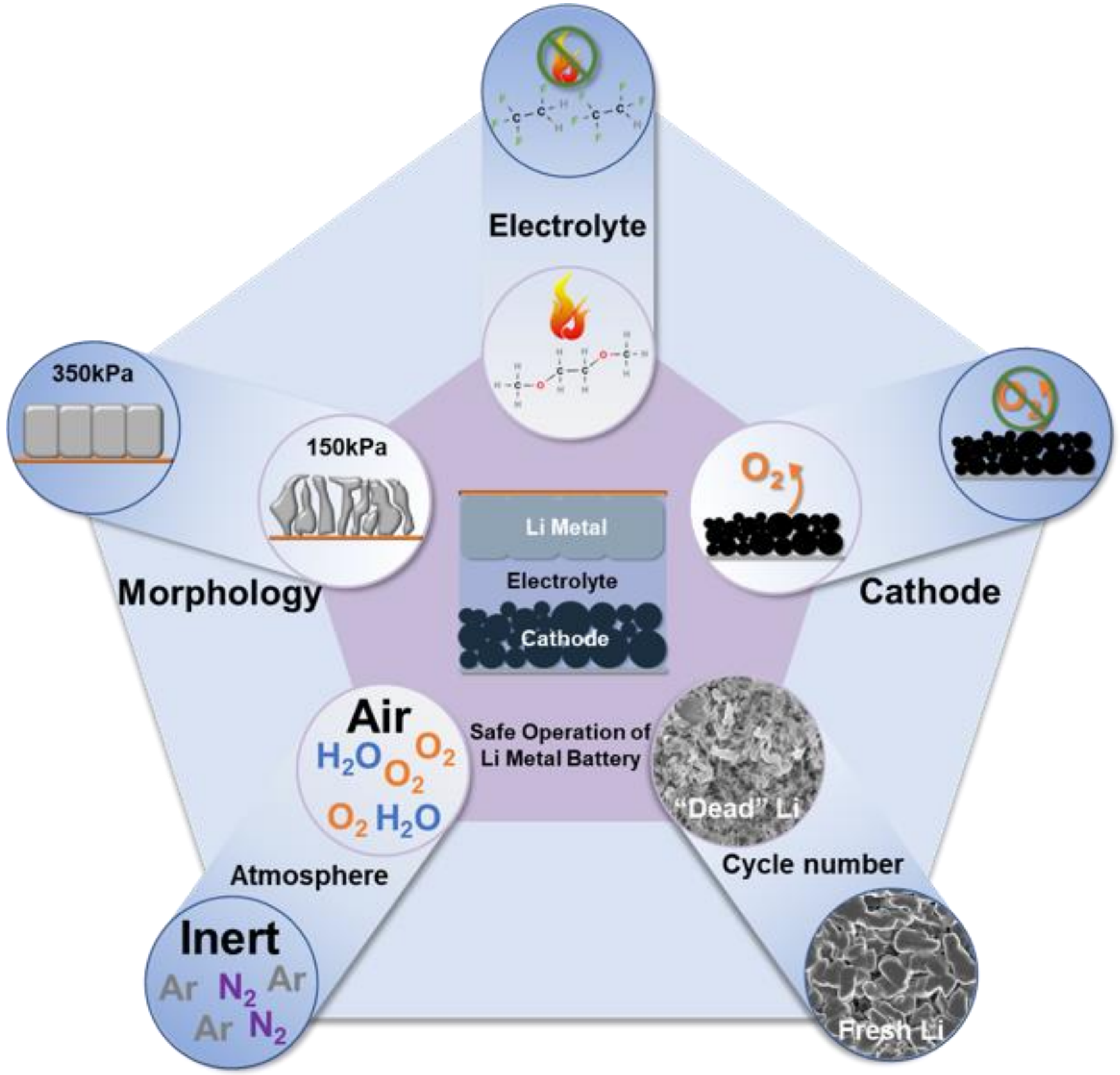


Electrolyte: 1M $LiPF_6$ in FEC:FEMC 3:7 by weight
LiFSI:DME:TTE (1:1.2:3 molar ratio)
Cycling rate: C/10 all at charged state

From 50 ℃ to 400 ℃, heating rate: 10 ℃/min, in Ar

Key Parameters in Controlling Li Metal Cell's Thermal Stability

B. Lu , W. Bao and Y. S. Meng, Submitted for publication 2023



Key parameters that need to be strictly controlled:

- **Li morphology**
- Needs external pressure to regulate the Li growth;
- Limits the contact surface area between Li and oxidants;
- **Electrolyte composition**
- Both Salts and Solvents are crucial parts
- Helps to obtain dense Li morphology
- Limits interaction with cathode
- **Cathode stability**
- High thermal stability
- Reduced oxygen release
- **Atmosphere**
- Limits the oxidation of cell components
- **Long-term cycling**
- Needs to maintain the dense morphology after long cycling

Remaining Challenges for Lithium Metal Battery

Laboratory for Energy Storage and Conversion

- Electrolyte design – **for cost / performance / safety** balance
- Pressure control – need out of box idea
- Lithium metal anode quality control – cost performance balance
- Quantify the reactivity after hundreds of cycles – how to do this safely and relevantly

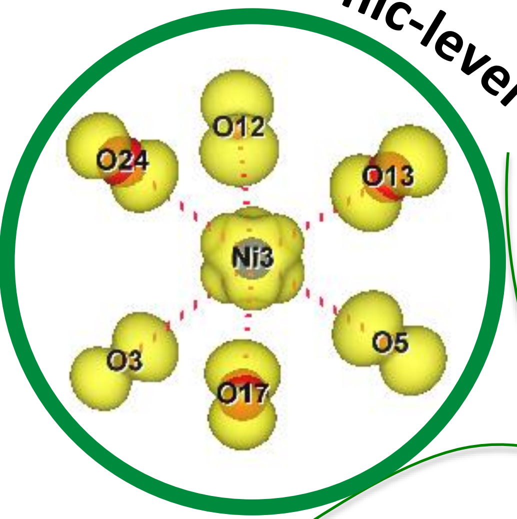
Workforce from Meng Group
2010 – 2022
24 + 8 Postdoctoral
32 + 14 Ph.D.
15 + 3 Master
25 + 6 Undergraduate

Prof. Shirley Meng and her team

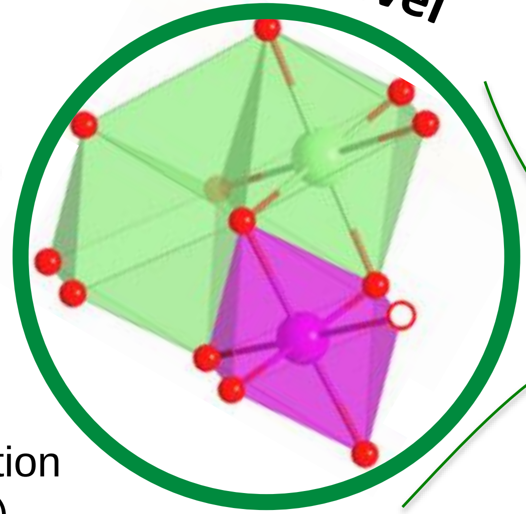
Science 2015
Science 2017 (**South 8 Technologies, Inc**)
Nature Energy 2018
Joule 2018, 2020
Nature 2019
Nature Nanotechnology 2020 (**Unigrid, LLC**)
Nature Materials 2020
Nature Energy 2021
Science 2021
Nature Energy 2022

Three Spun Out Startup Companies
Five Issue Patents and Four Pending

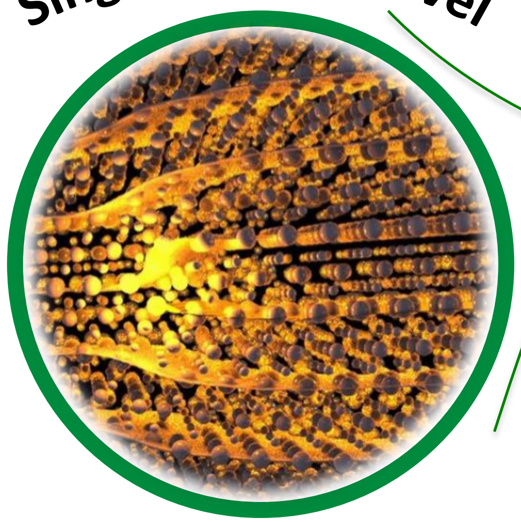
Electronic-level



Atomic-level

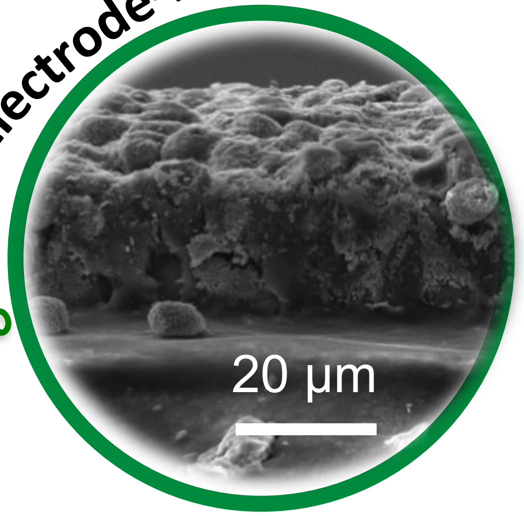


Single Particle-level



Meso-structure-level

Electrode-level



https://lescmeng.ai

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(including Maxwell / LG Energy Solutions / GM / SES / ThermoFisher Scientific / Umicore / Shell / UL / Chemours)

sdni San Diego Nanotechnology Infrastructure

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LESC Laboratory for Energy Storage and Conversion