Recent Progress in Cryogenic Electron Microscopy and Spectroscopy for Energy Materials

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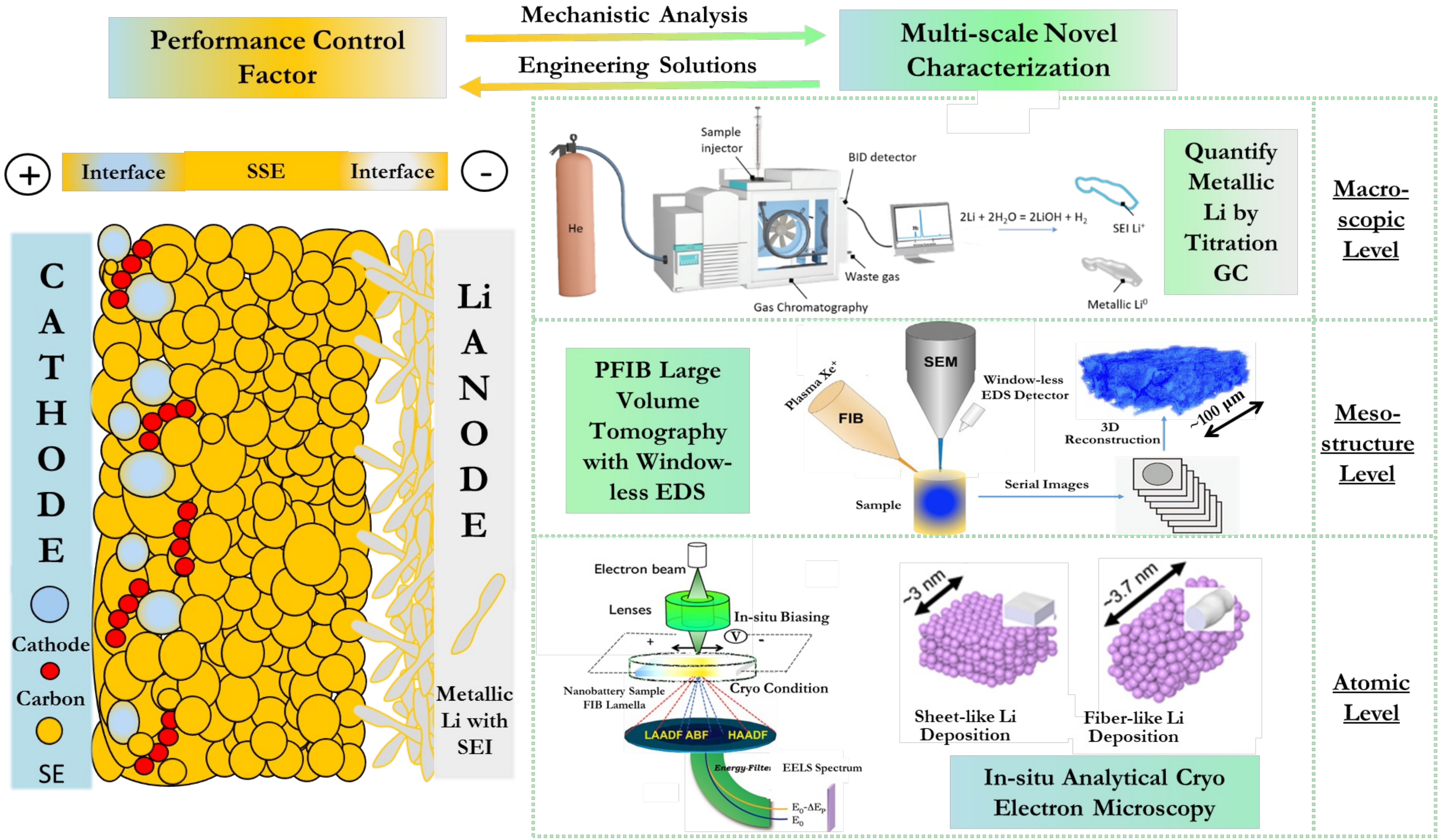
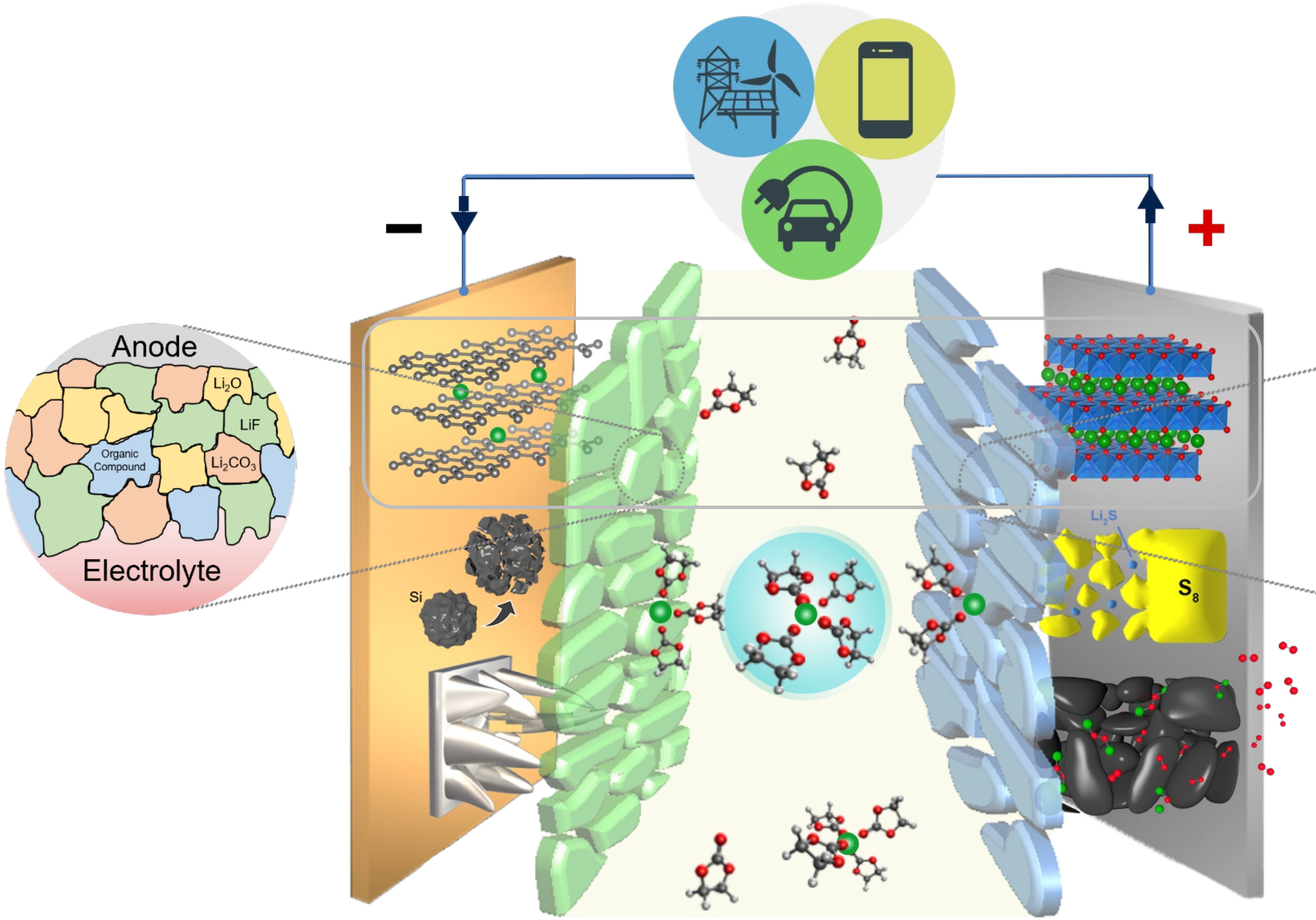
Overview of LESC Development Effort on Metrology



Lithium Ion/Metal Battery - A Complex “Living” System

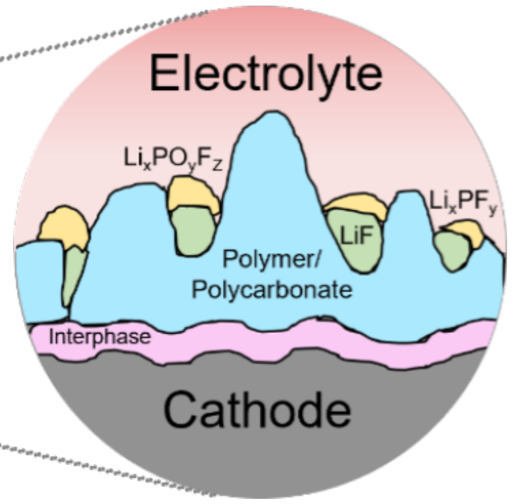
Perspective – K. Xu and Y. S. Meng



Moving Ions
(Chemical Bond)

Dynamic Phenomena

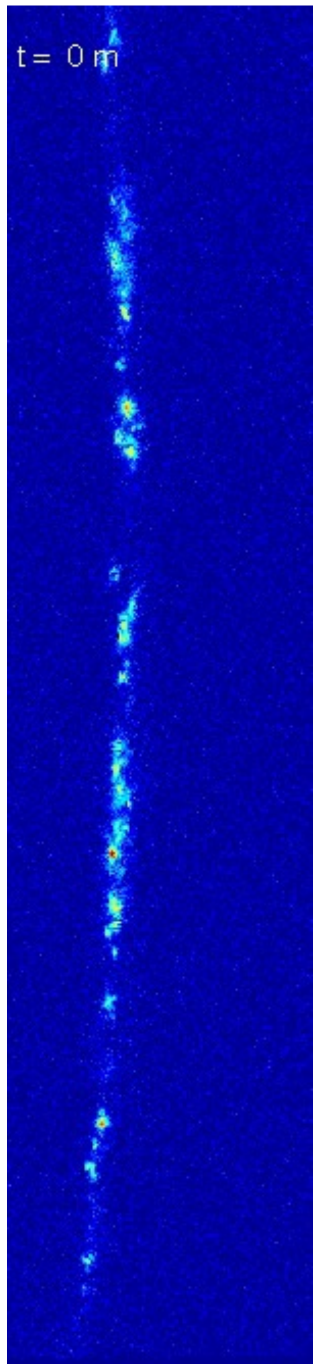
Strain - Fatigue



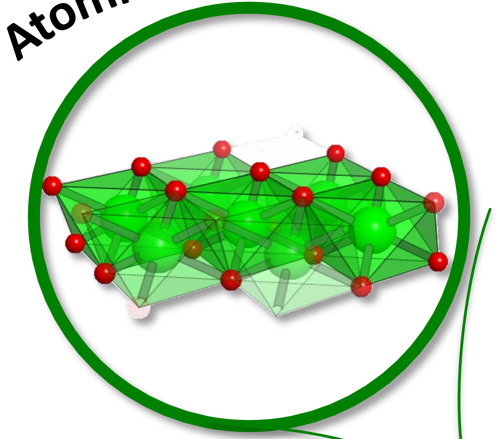
Thermodynamically Closed System 99.9% efficiency needed

SEI – Life and Safety Differentiators

Data from APS

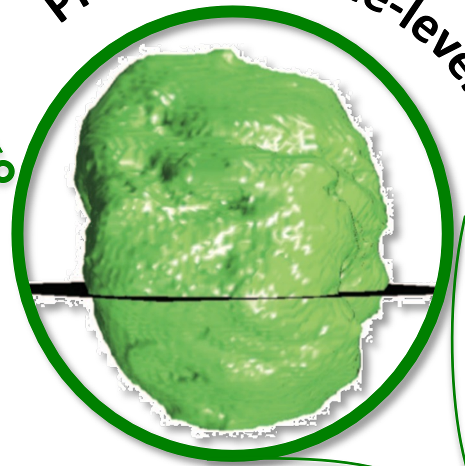


Multi-scale Multi-modal Characterization Platform



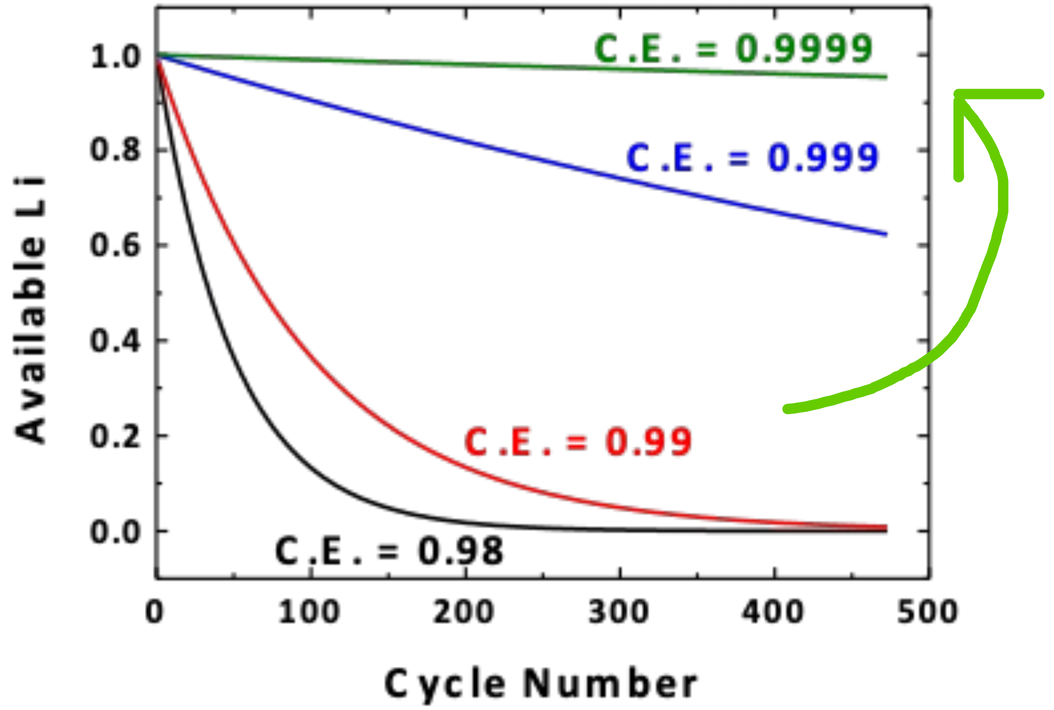
What changes in chemistry, structure & electronic state govern the bulk reaction?

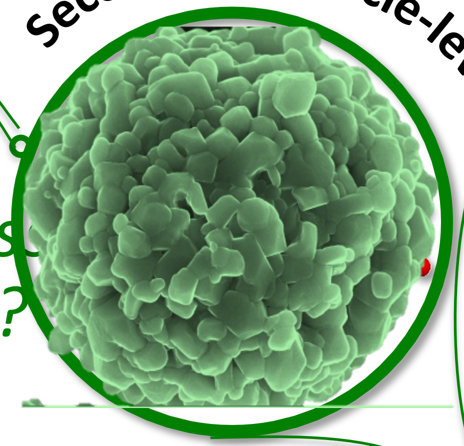
NMR, **STEM, ND, XRD**



How do transformations propagate within particles? From interfaces?

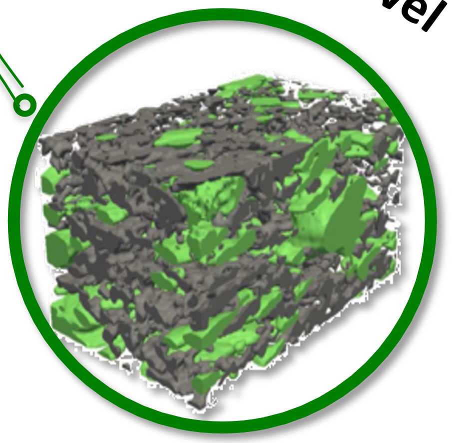
Strain & chemical mapping with **CXDI & X-ray microscopies and TEM/EELS**





How do reactions evolve across the electrode heterostructure?

Nano-SIMS, **Depth sensitive XRD and X-ray Tomography**



How to ensure fast e and mass transport through distance over 100um?

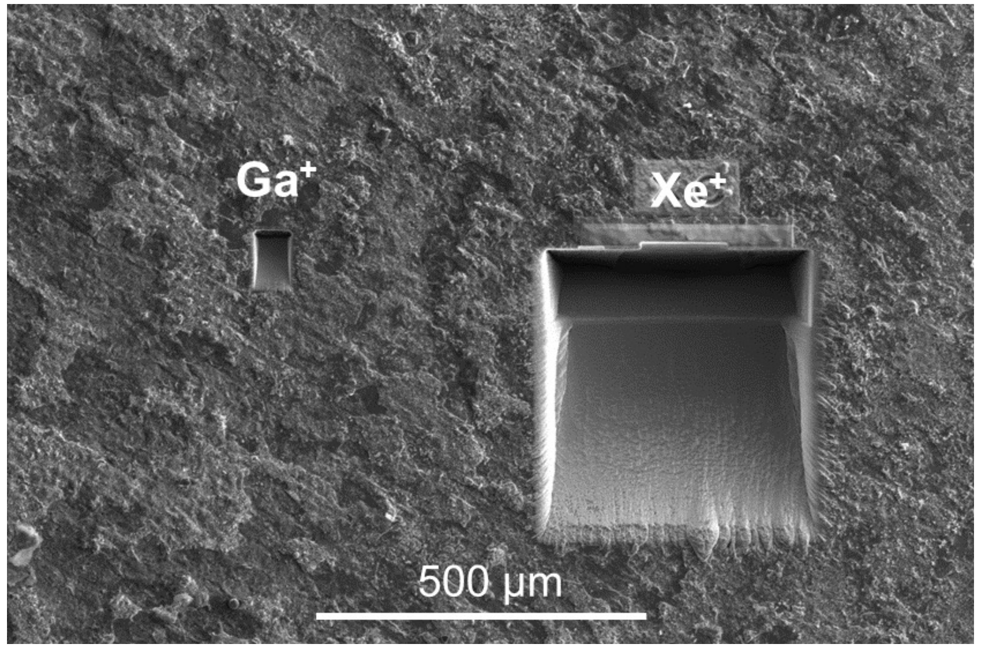
Xe- FIB, X-ray CT

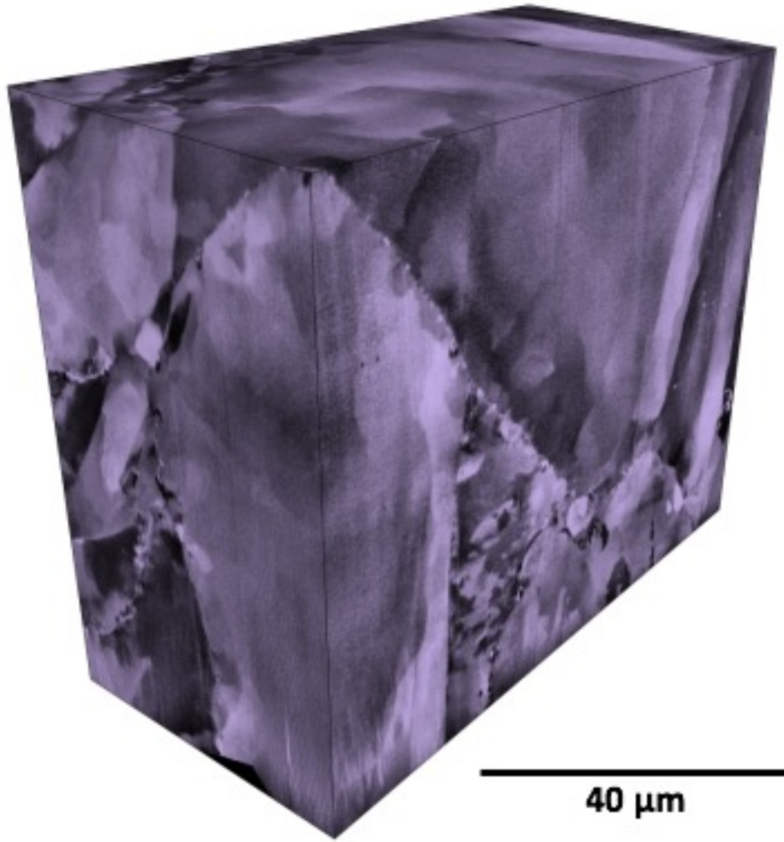
DOE BES Energy Frontier Research Center

Directors – 2009-2020
Prof. Clare P. Grey
Prof. M. Stanley Whittingham

NECCES
A DOE Energy Frontier Research Center

Quantitative Analysis of Large Volume Thick Electrode





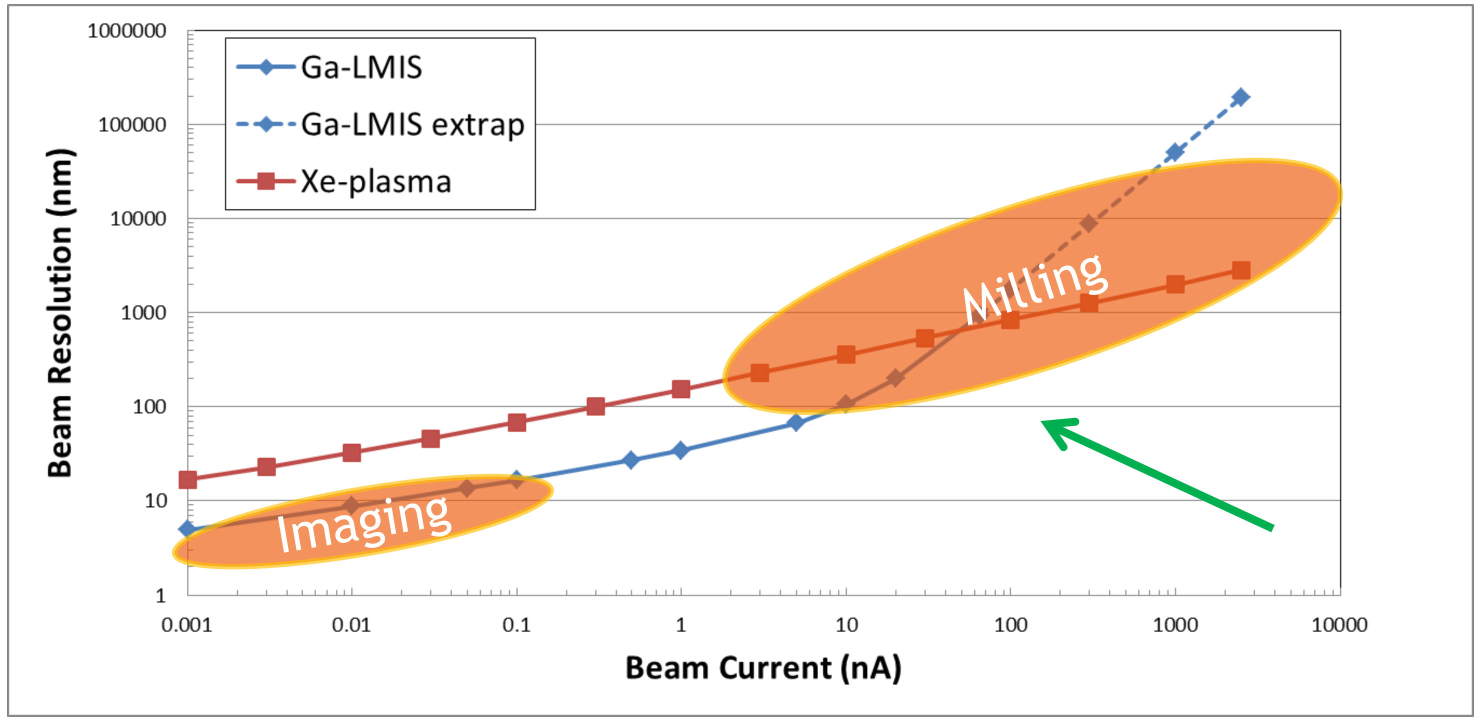
2500 nA

Xe+ PFIB

65 nA

Ga+ FIB

40 µm



- Both systems offer excellent ion beam performance;
- Gallium offers the lowest accelerating voltages (down to 500 V);
- Plasma offers the highest beam current (2.5 µA) and Ga-free milling.

Almost 40x more beam current

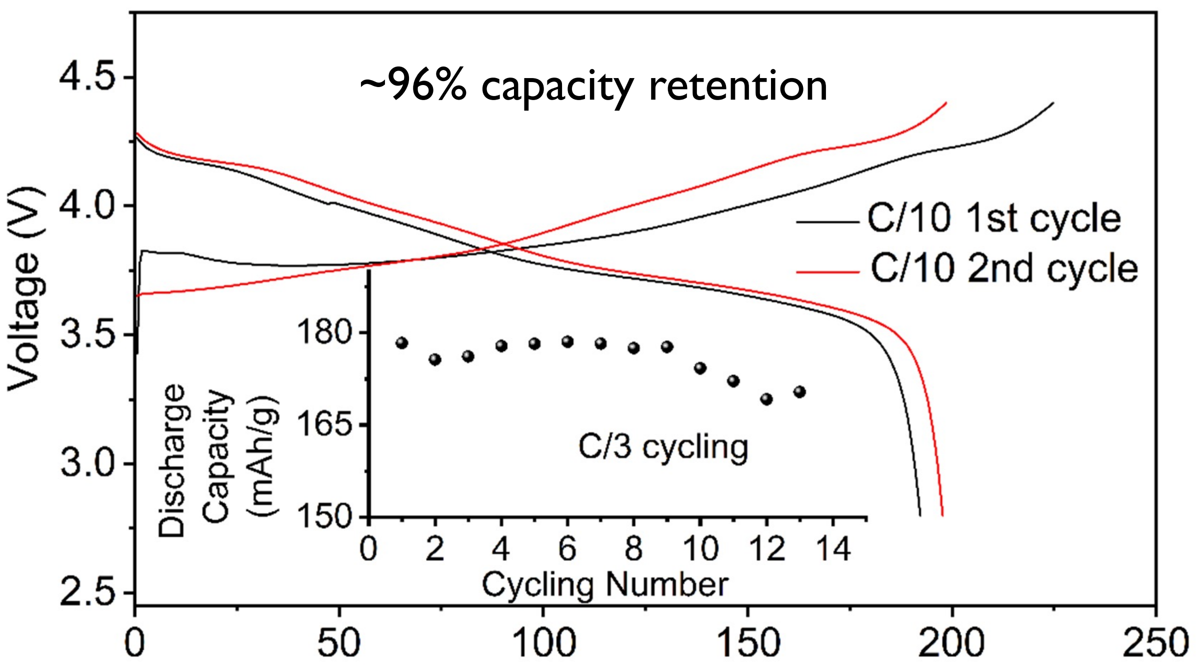
Credits to Thermo Fisher Scientific

M. Zhang, M. Chouchane, Y. S. Meng* et al., Joule, 2023, 7, 201

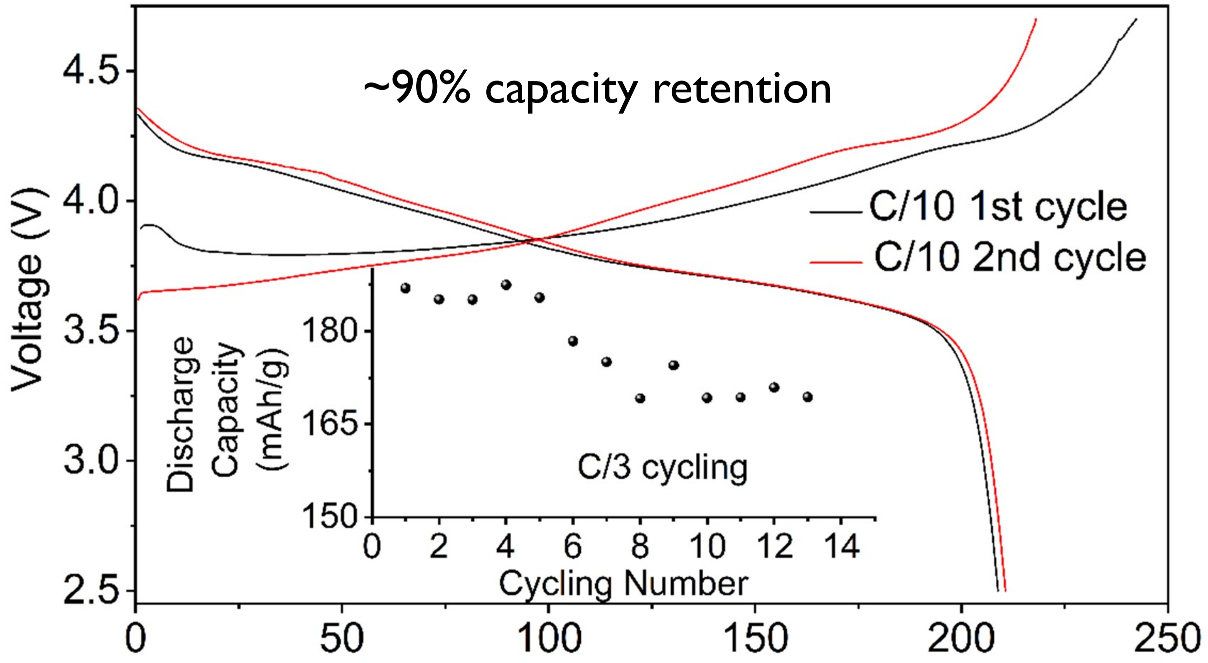
Different Component Volume Fraction of Cycled Electrode

EC Performance

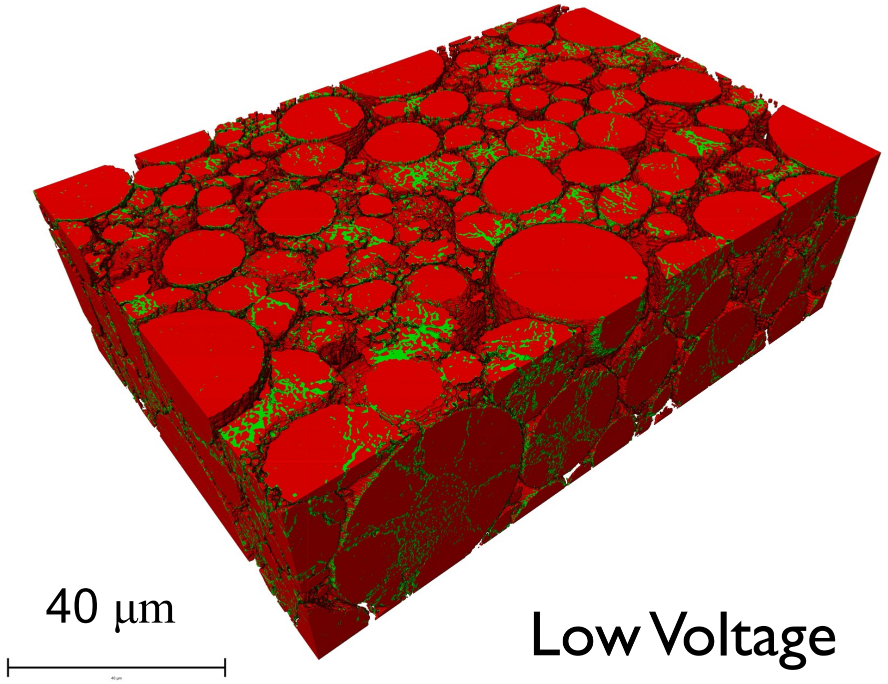
Charge and discharge between 4.4 and 2.8 V



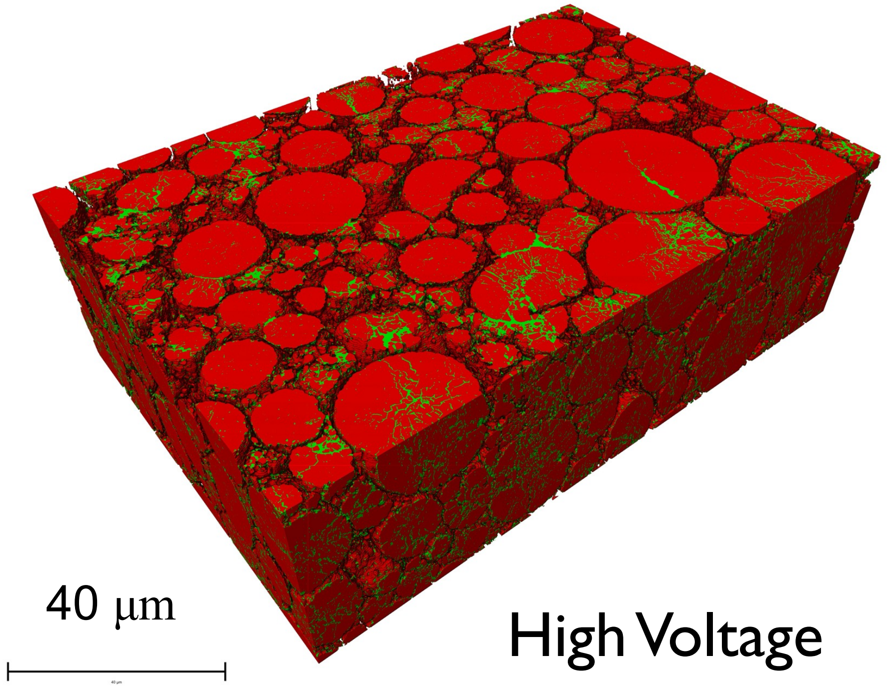
Charge and discharge between 4.7 and 2.5 V



Cracks + Particles



Low Voltage



High Voltage

M. Zhang, M. Chouchane, Y. S. Meng et al., Joule, 2023, 7, 201*

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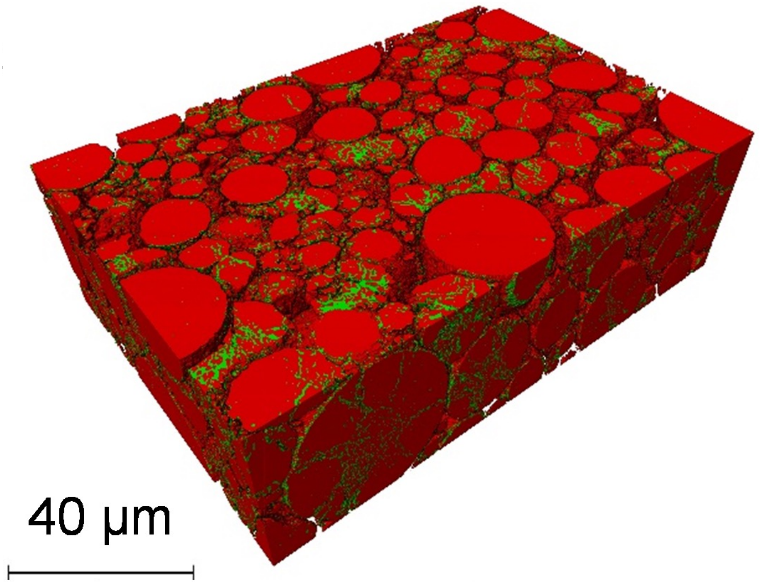
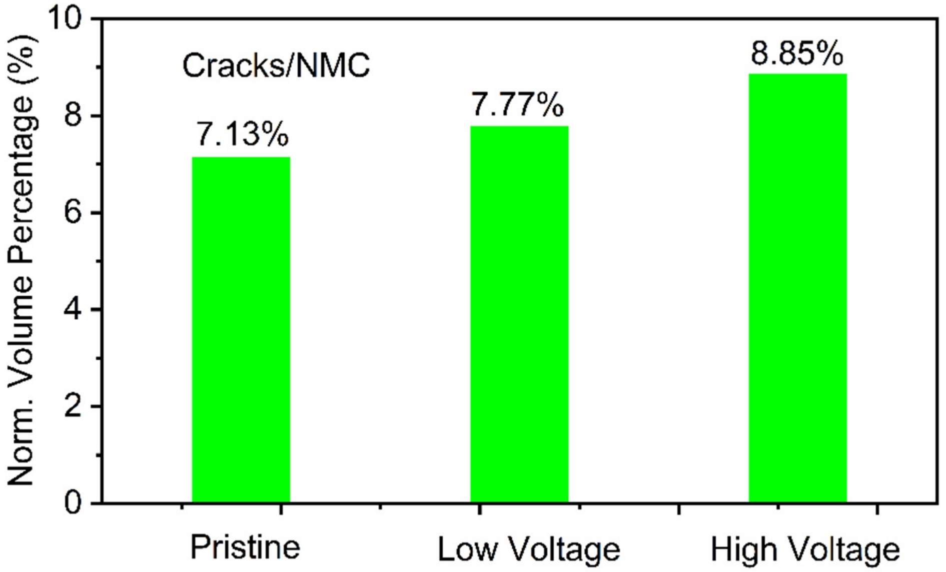
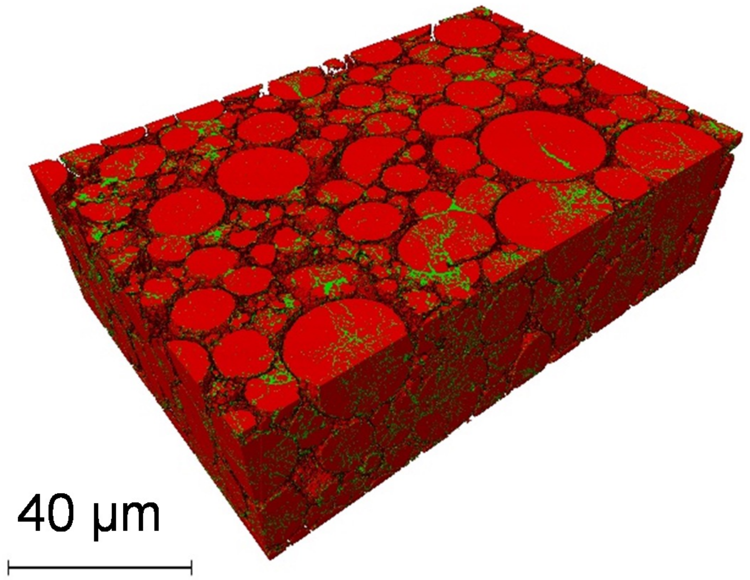
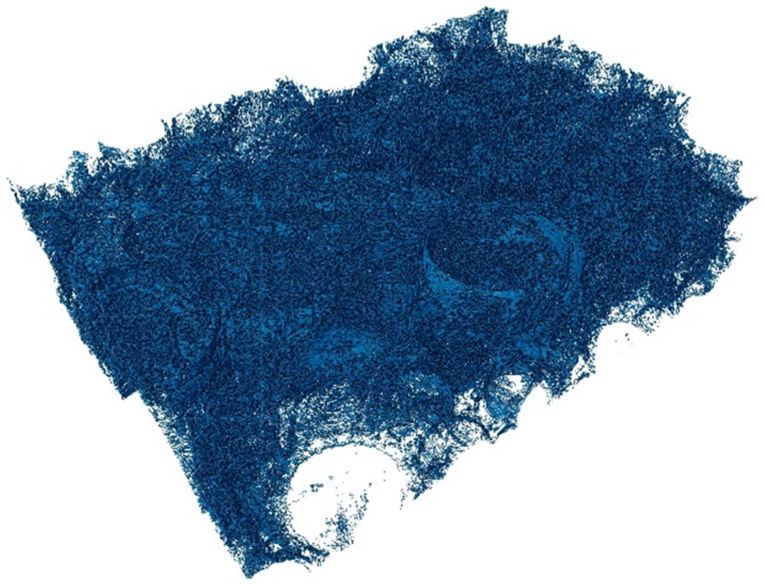
Laboratory for Energy Storage and Conversion

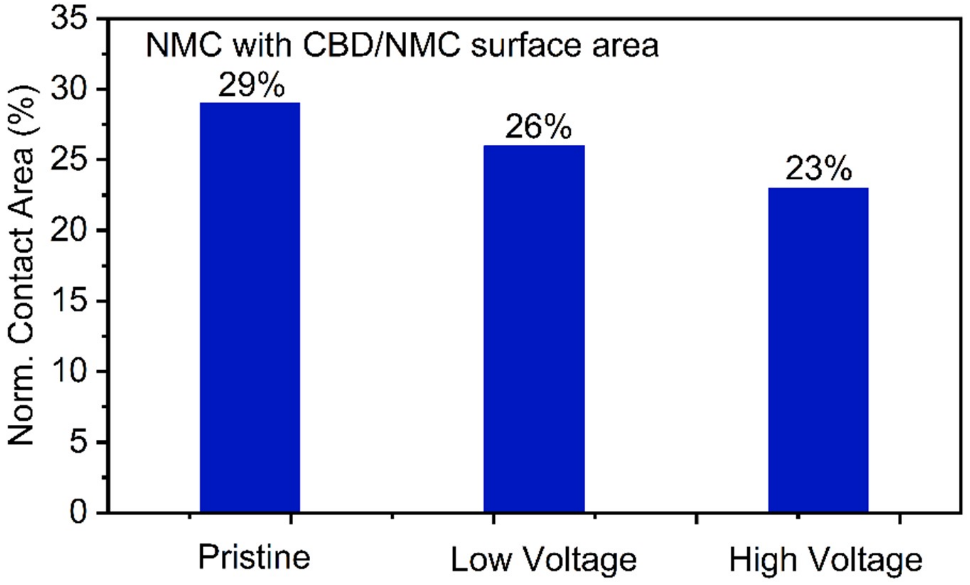
Different Component Volume Fraction of Cycled Electrode

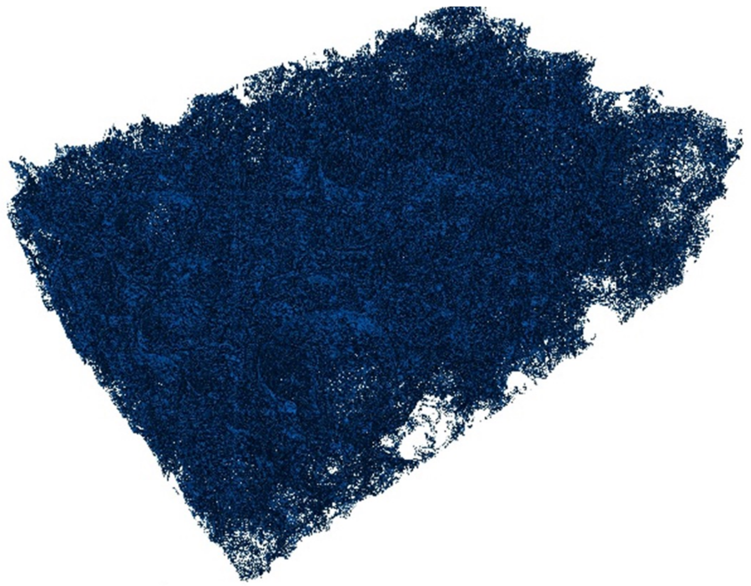










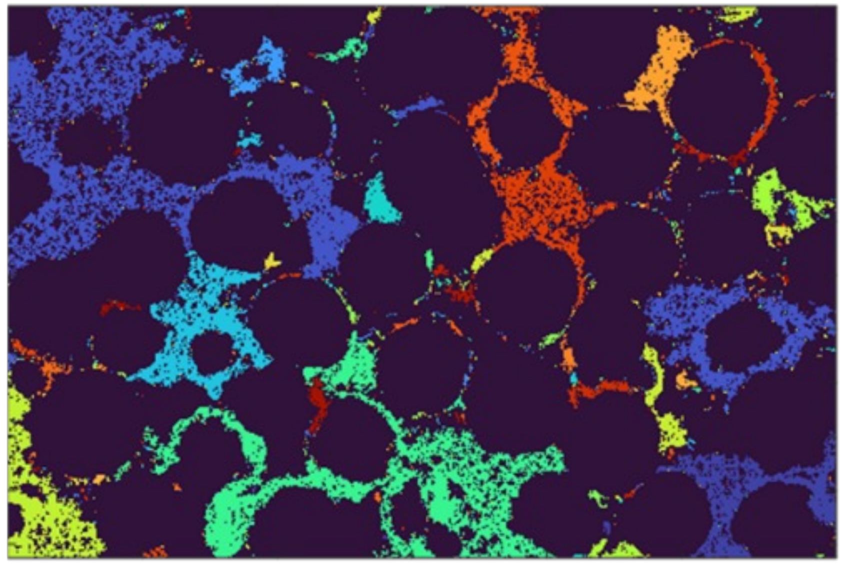


M. Zhang, M. Chouchane, Y. S. Meng[*] et al., Joule, 2023, 7, 201

Thick Electrode-Nanoscale Reaction Inhomogeneity

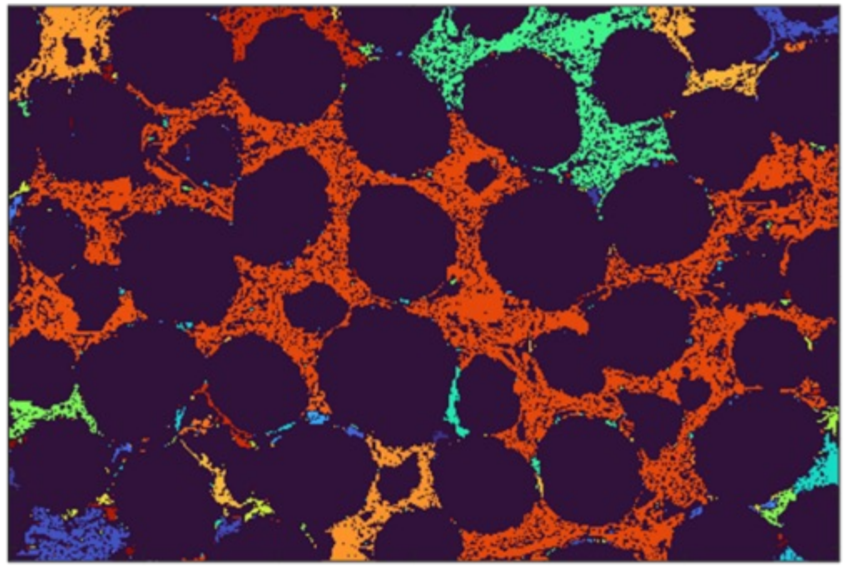
Slurry-LNMO

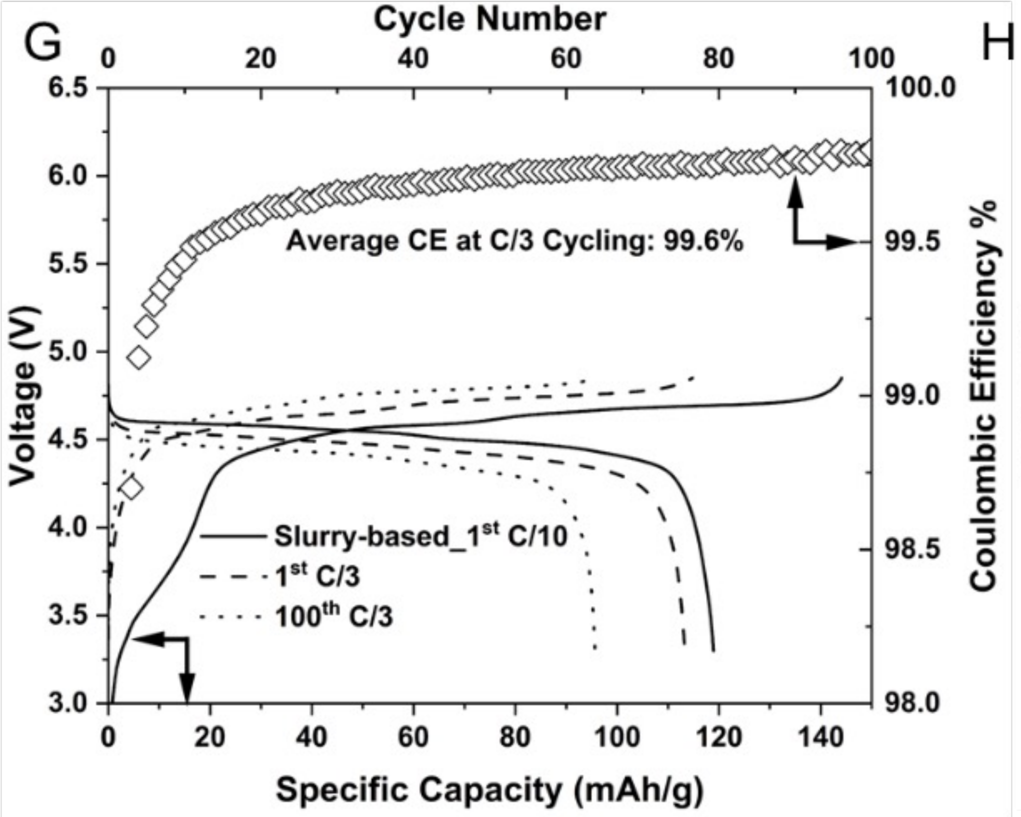
E

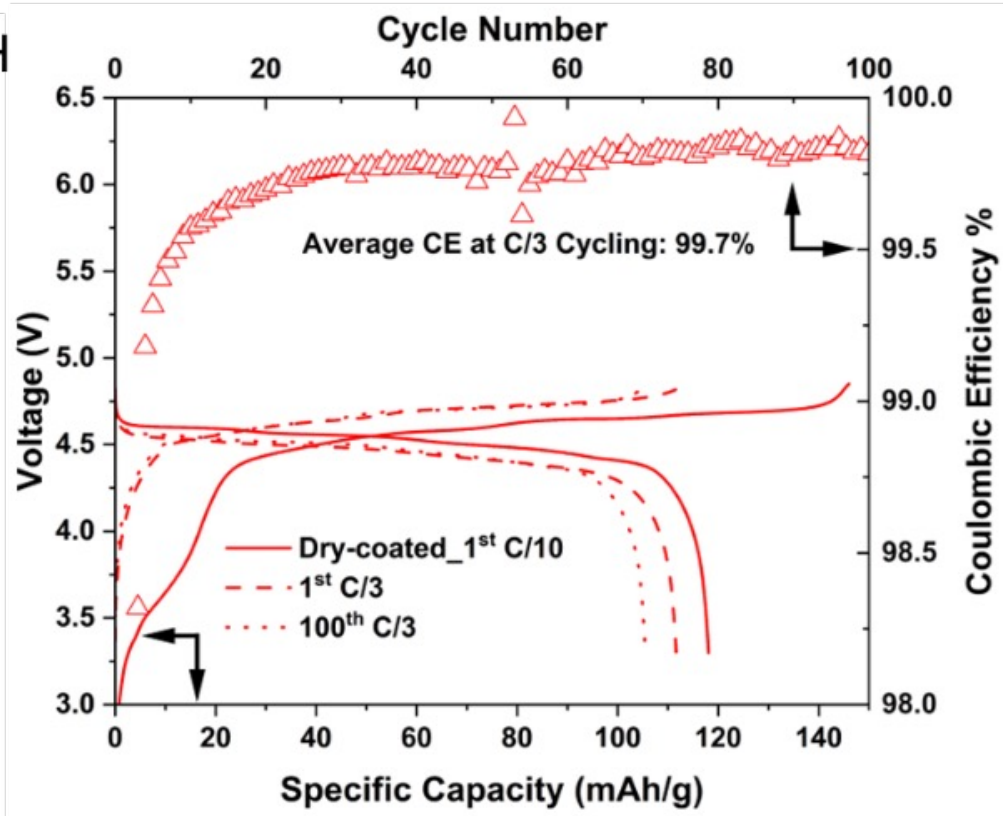


Dry-LNMO

F







- Based on the component segmentation, the CBD connectivity maps were built.
- The slurry-based method yields more disconnected CBD aggregates, represented by individual colors.
- The dry-LNMO full cell can achieve 94% capacity retention after 100 cycles, while slurry-based LNMO full cell can only deliver a capacity retention of 84%.

Cryo-EM for Li Metal Anode

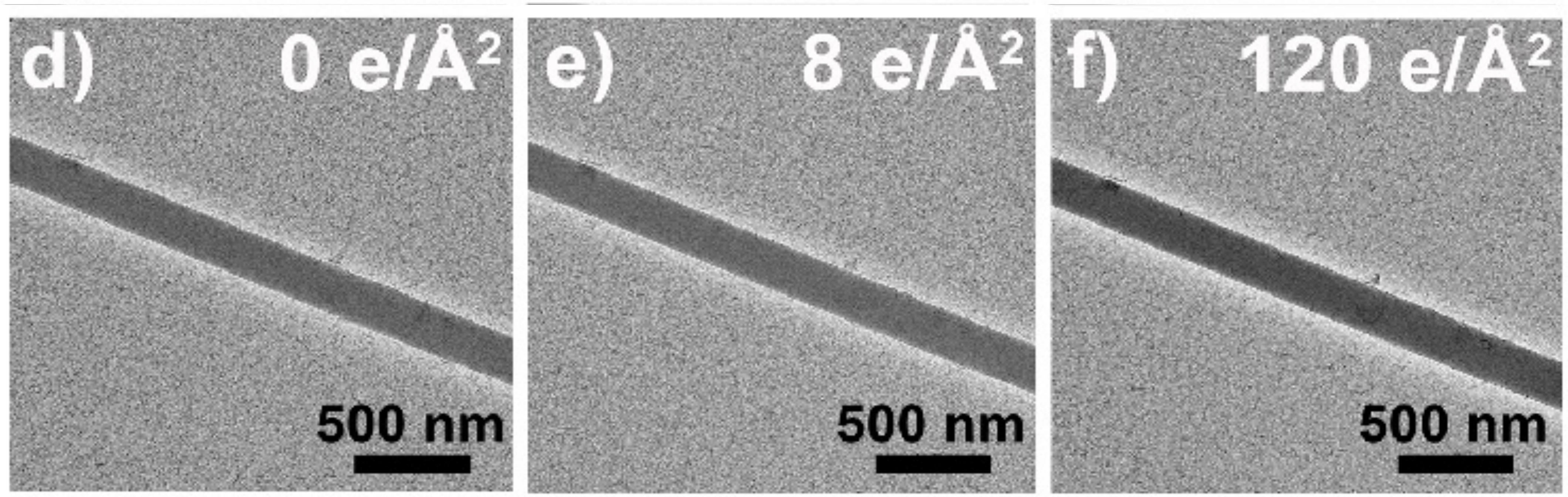
Grand Challenge - Li Metal Anode

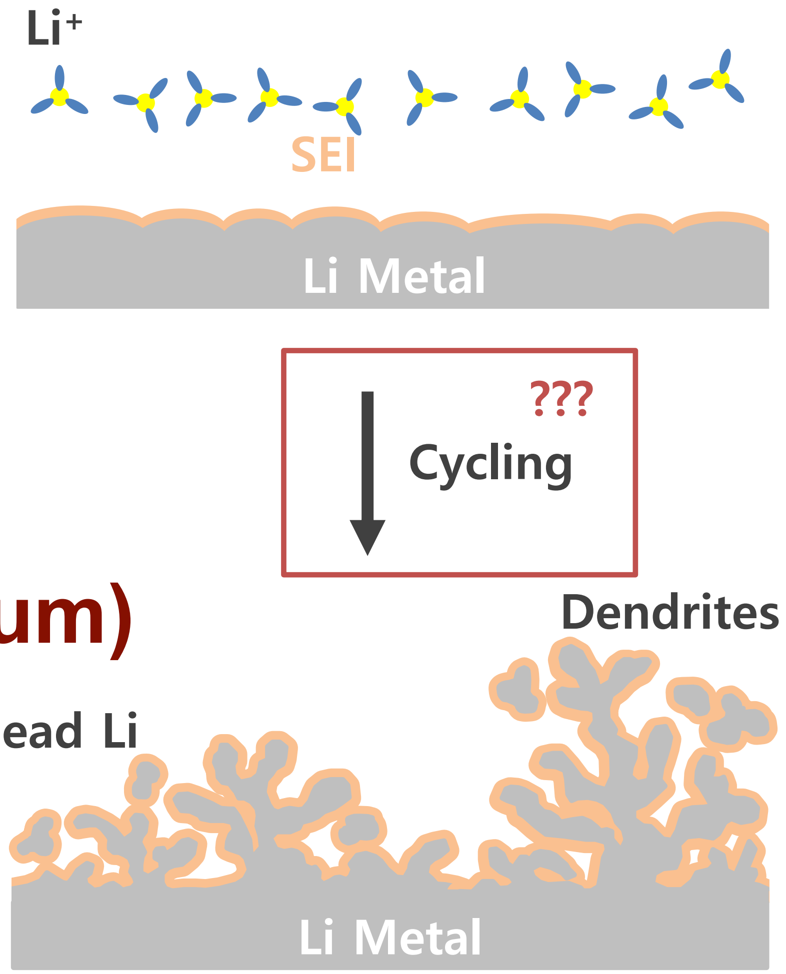
Knowledge Gaps:

1.What is the true CE ??? Depositing Li, Li_2O, Li_2CO_3, LiOH, LiF

2.Not all Li are the same - Li Foil, Vapor Deposited Li (VDLi)and Electrochemically Deposited Li (EDLi)

3.Substrate/Separator/Electrolyte (Avoid studying things in vacuum)



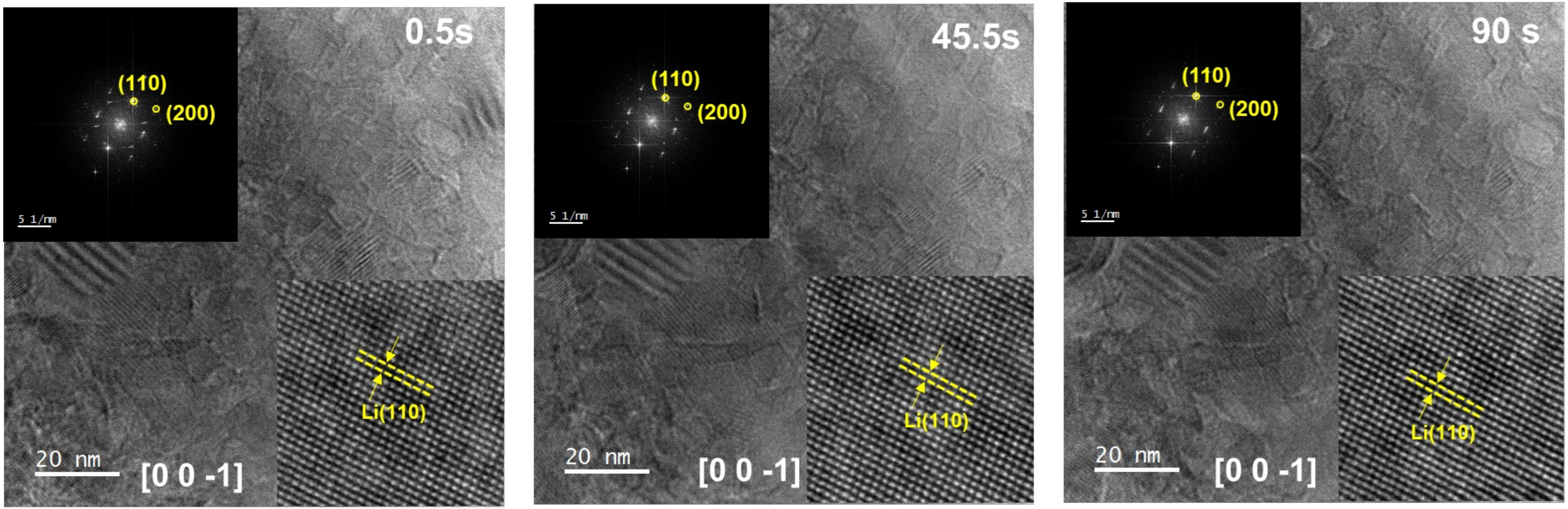


X. Wang, M. Zhang, and Y. S. Meng* et. al. Nano Letters 2017

S. Bai, M. Zhang*, Y. S. Meng* et al., 2023, in preparation

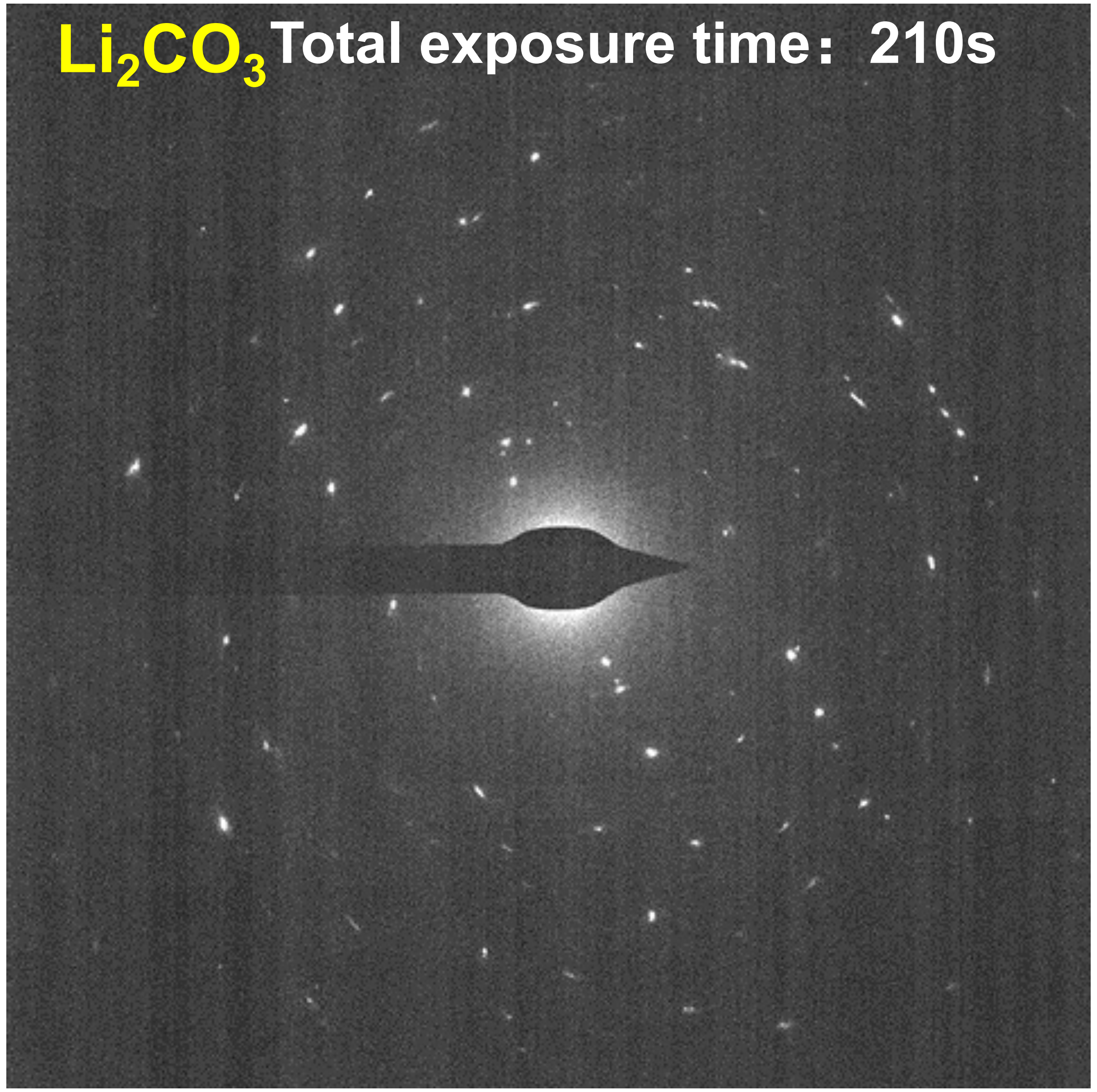
Room Temperature HRTEM for Pure Li Metal

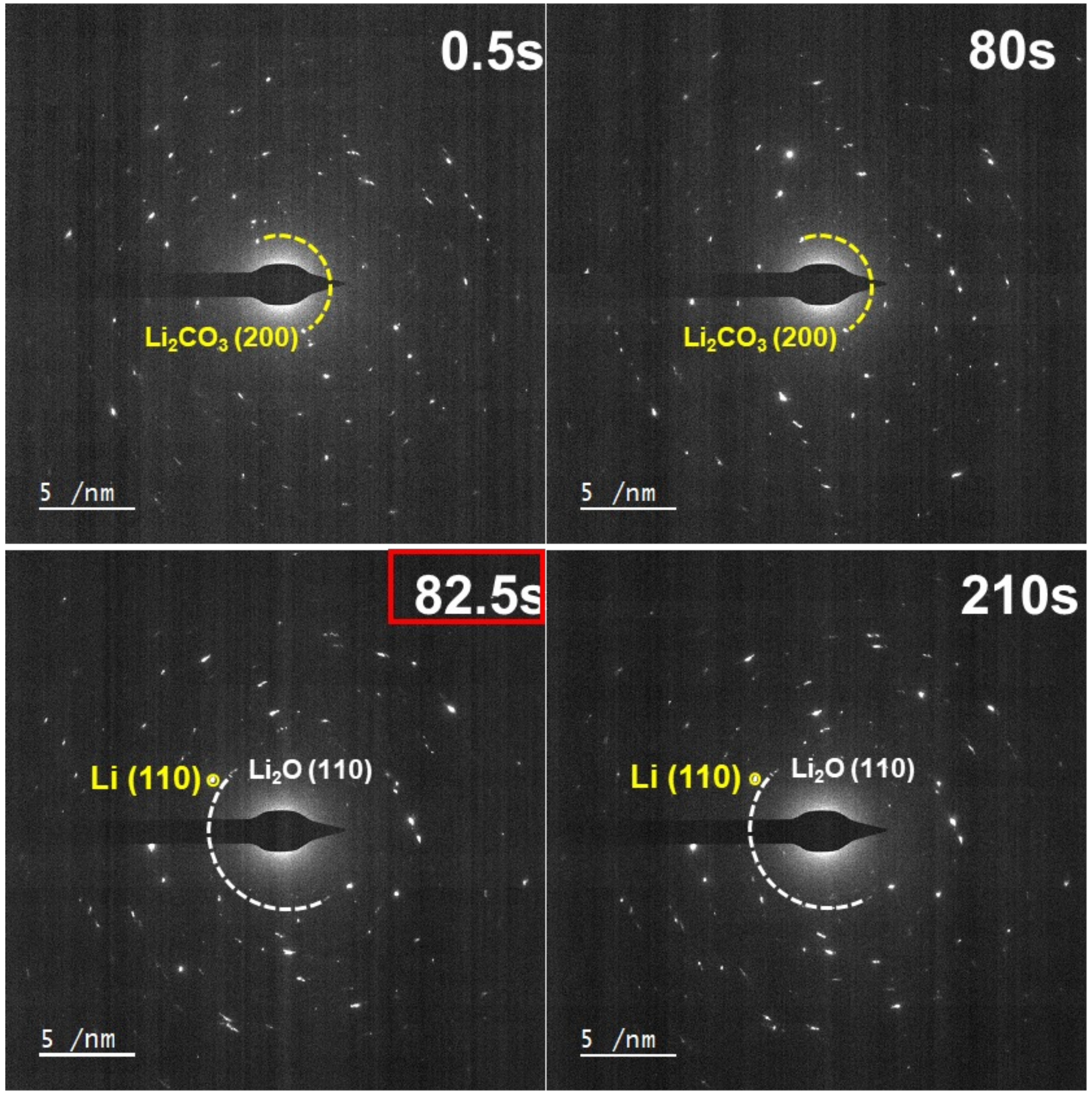
Li metal at RT @~10000 e $A^{-2}s^{-1}$



- Barely any lattice and morphology change after 90 s exposure.
- This observation is consistent with the recent publication where the authors successfully imaged Li metal growth from lithium compounds at room temperature.

Beam Damage for Li_2CO_3 at Room Temperature





Li_2CO_3 at RT @~1 e $A^{-2}s^{-1}$

- It is the SEI component (Li_2CO_3 in this example) which can be electron beam damaged at room temperature even with low beam dosage number.
- This observation justifies why cryo condition is necessary for the electrochemically deposited Li metal sample.

Comparison of Cryo-EM Protocols for Sample Transfer

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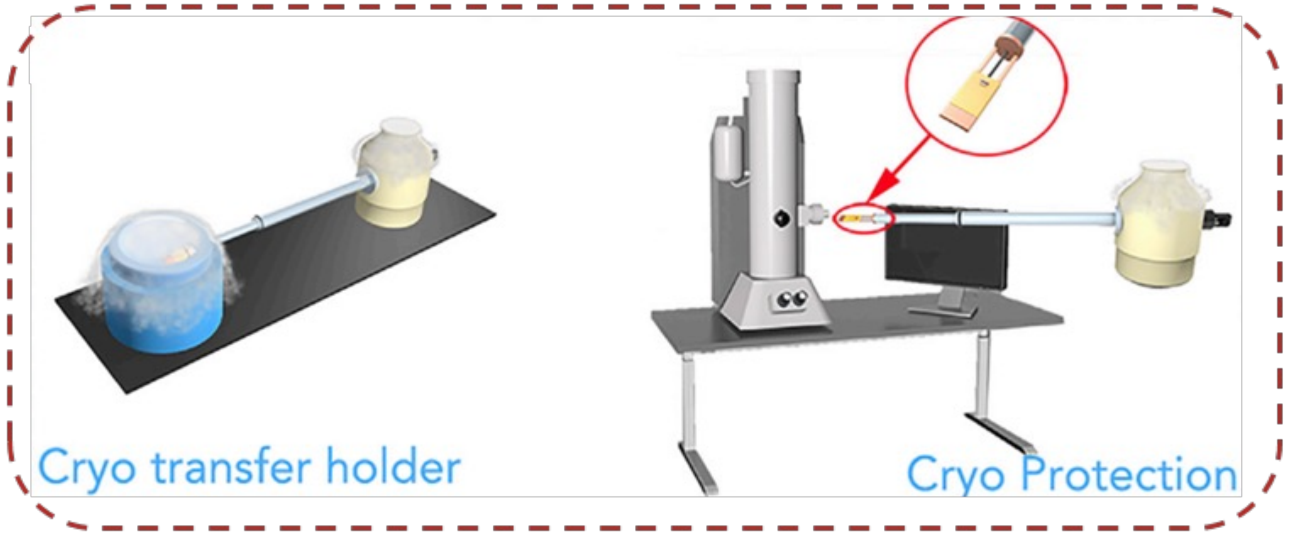
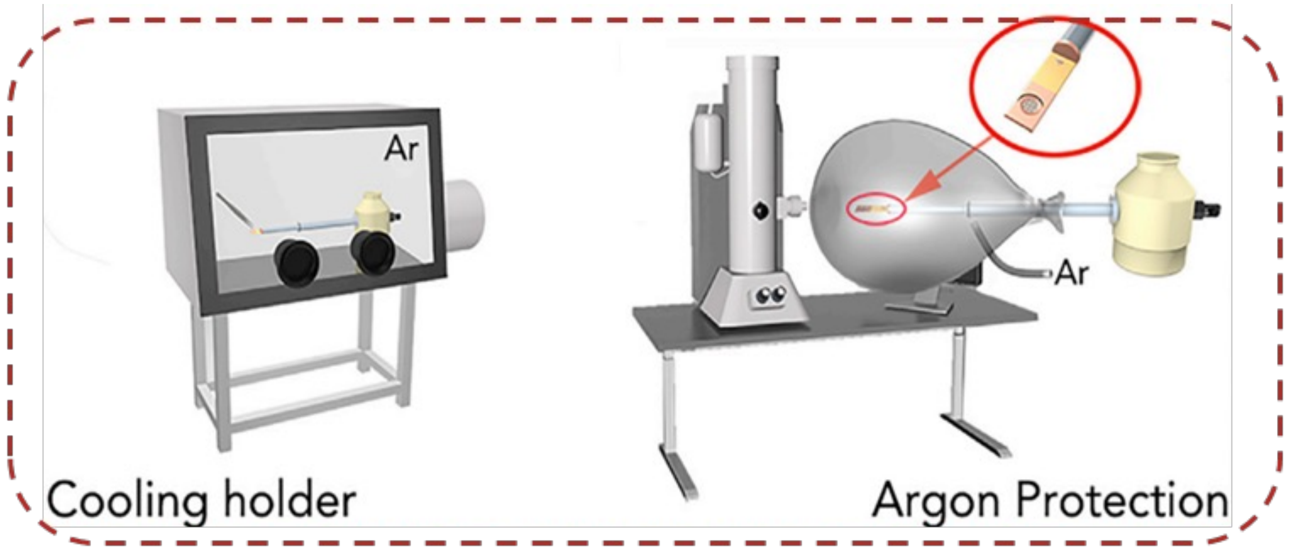
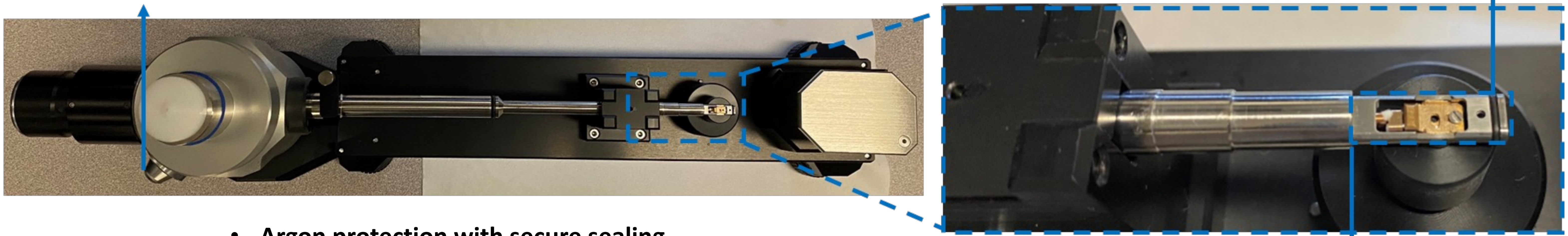




Connection for temperature control

O-ring seal



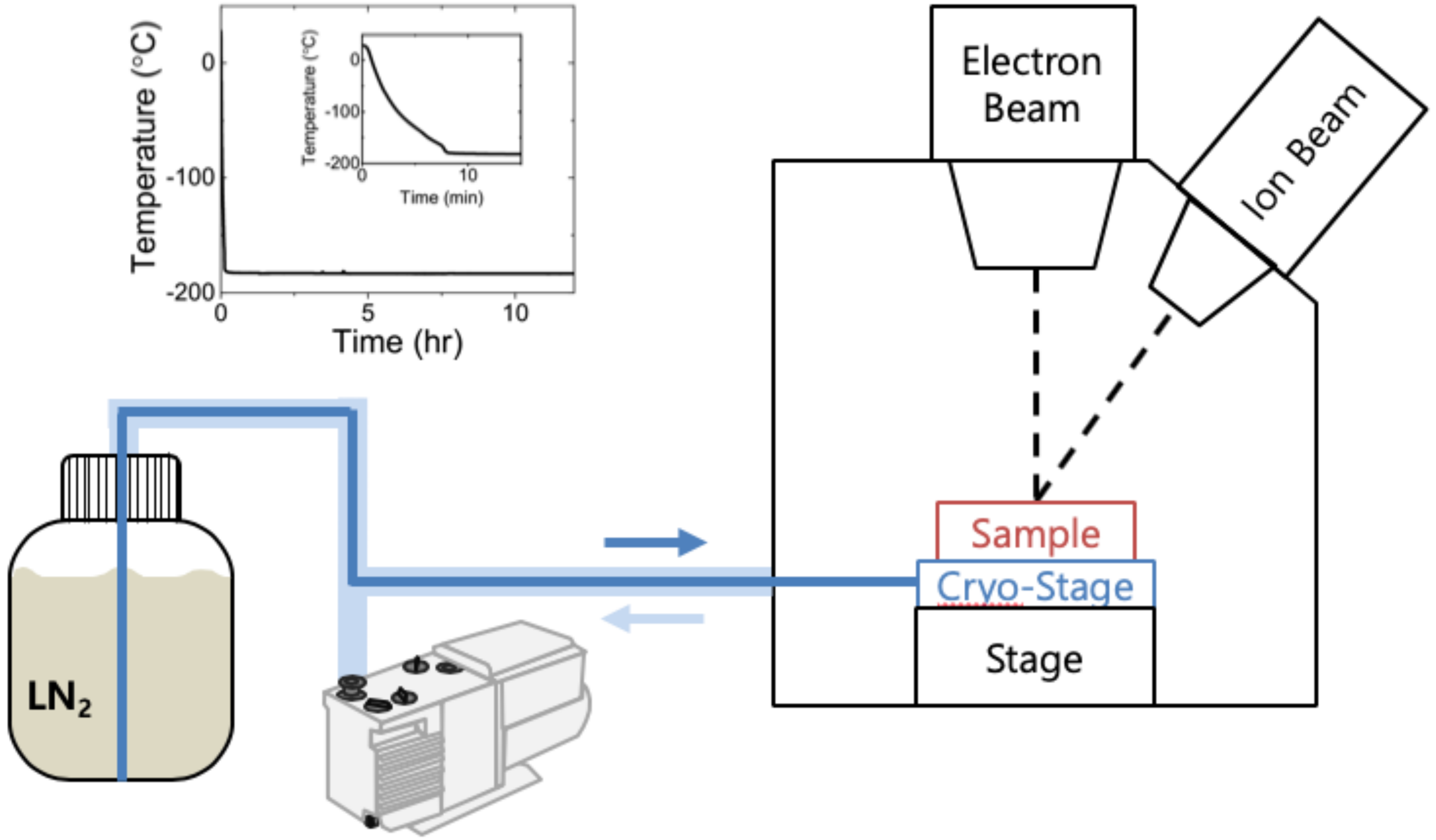
- **Argon protection with secure sealing**
- **No direct LN2 contact**
- **Double tilt capability**
- **Temperature monitor/control on both dewar and tip**

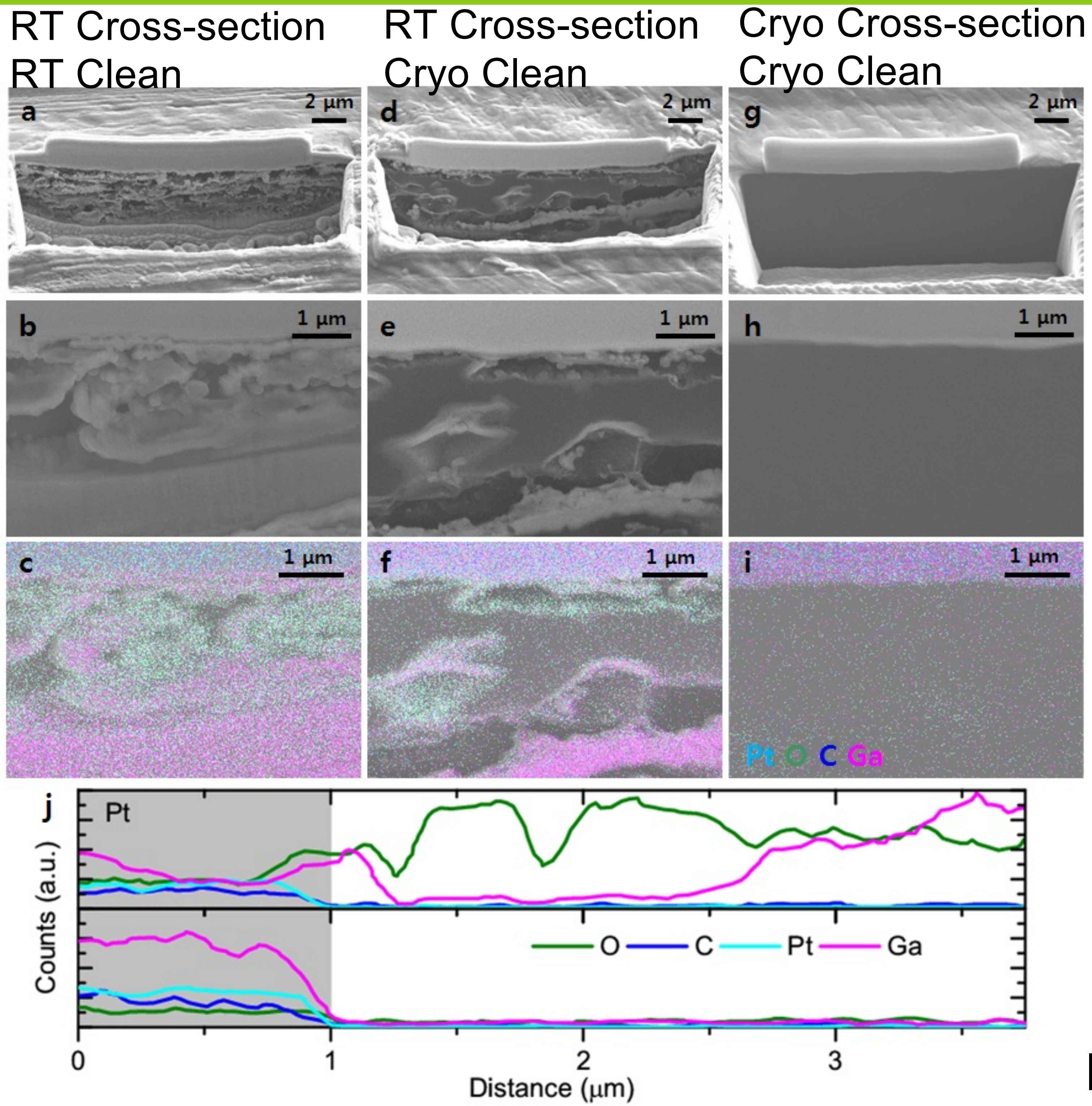
Mel-Build holder

The sample tip (dashed box) can be retraced inside the holder

ThermoFisher SCIENTIFIC

Cryo-FIB for Li Metal Anode



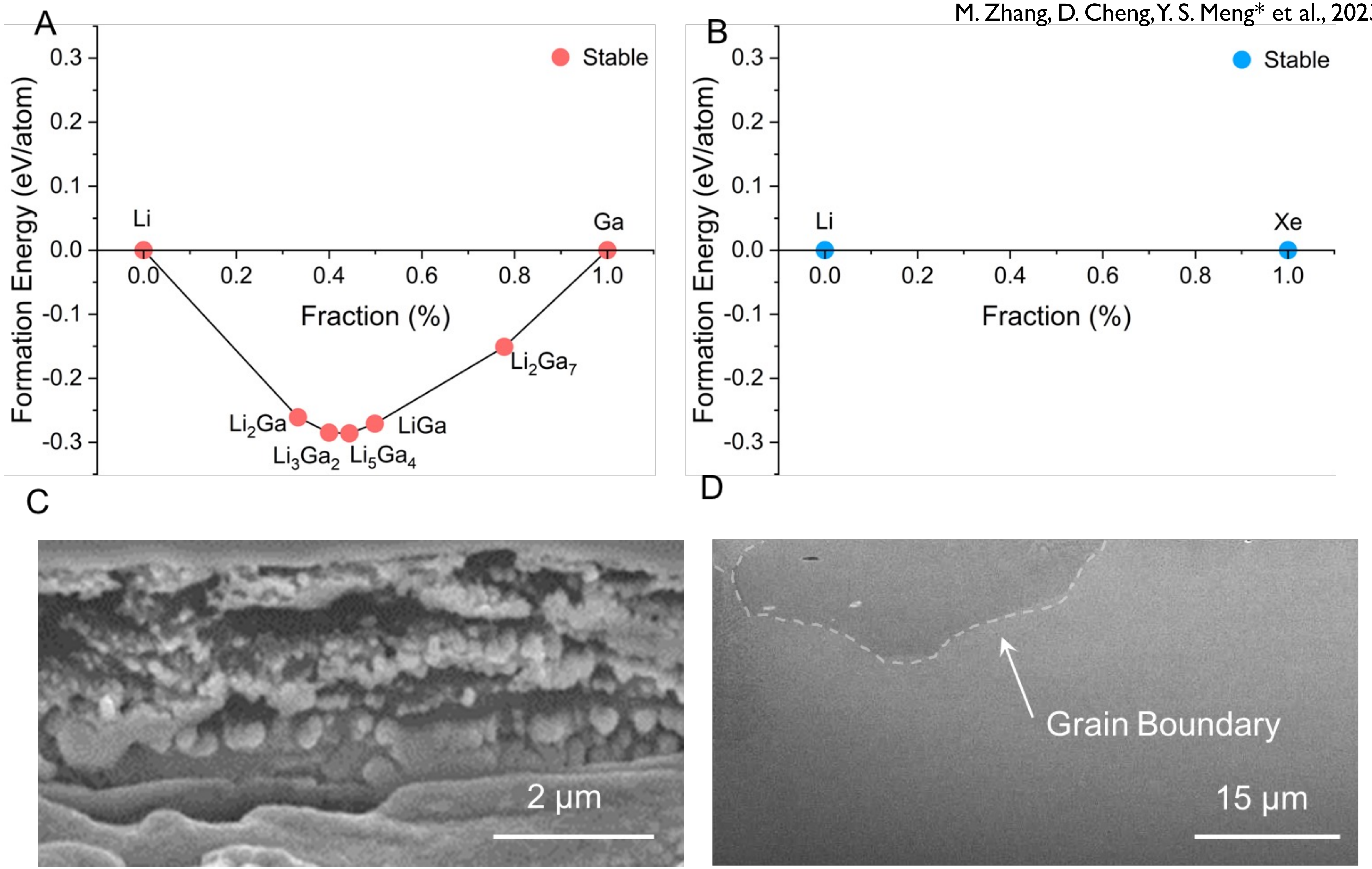


Cryogenic focused ion beam (-170 ºC) shows notably reduced morphology change as well as reduced Ga^+ implantation via EDS. Permits lift-out of lithium metal anode-based batteries.

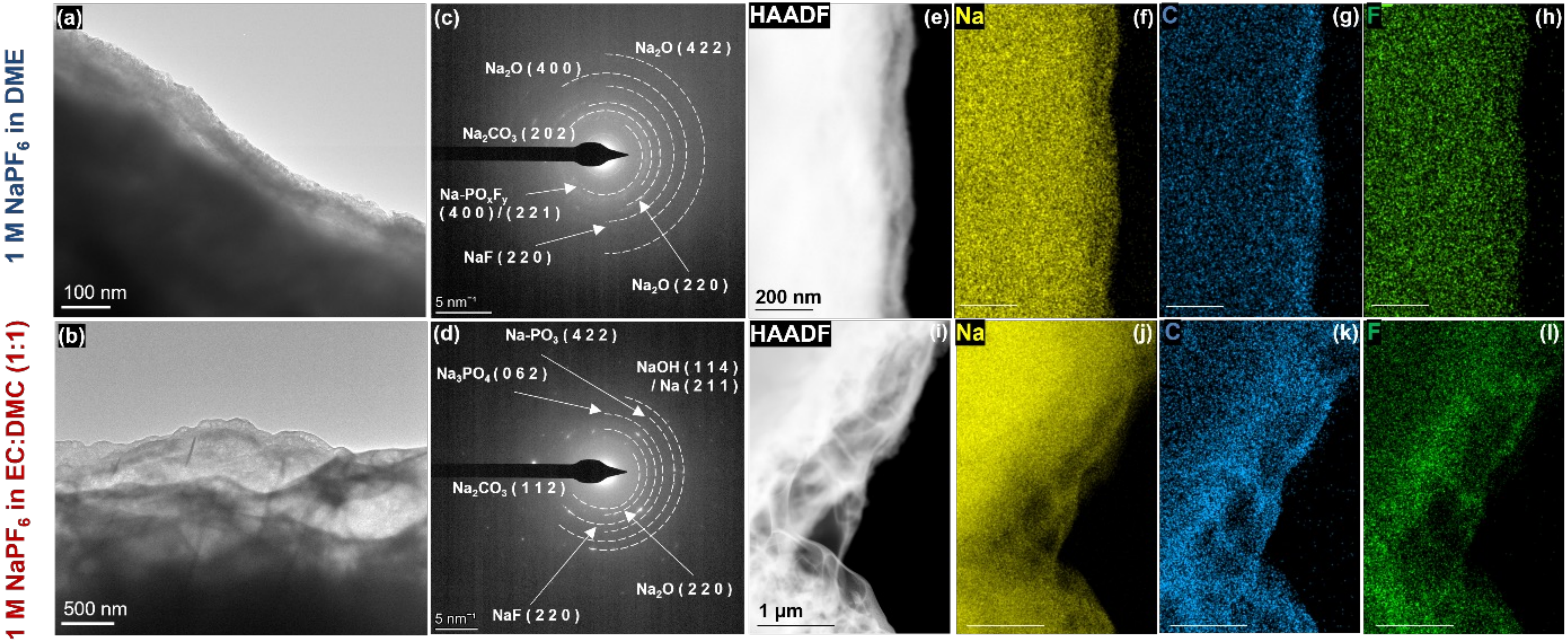
J.Z. Lee, T.A. Wynn, Y.S. Meng*, et al, ACS Energy Letters , 2019

PFIB for Li Metal Anode at Room Temperature

M. Zhang, D. Cheng, Y. S. Meng* et al., 2023, in preparation



Analysis of Na Metal Deposition

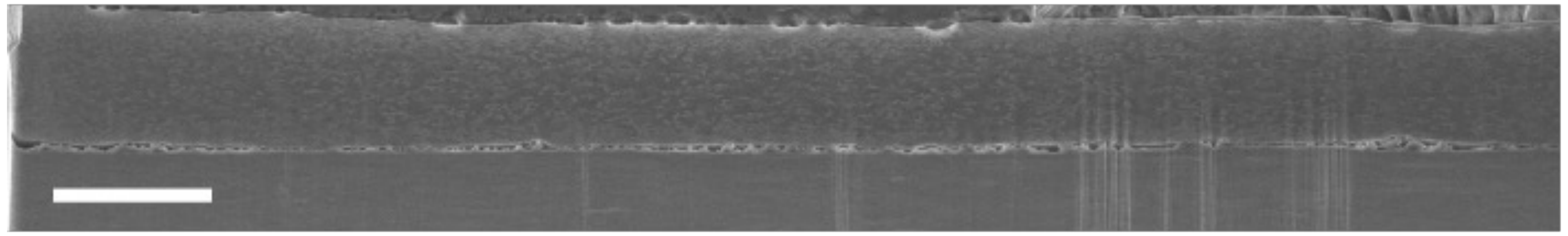


The cryo-STEM images on the SEI of the stripped sodium in (a) 1M $NaPF_6$ in DME, and (b) 1M $NaPF_6$ in EC:DMC (1:1).

B. Sayahpour, S. Bai, M. Zhang*, Y. S. Meng* et al., 2023, under review

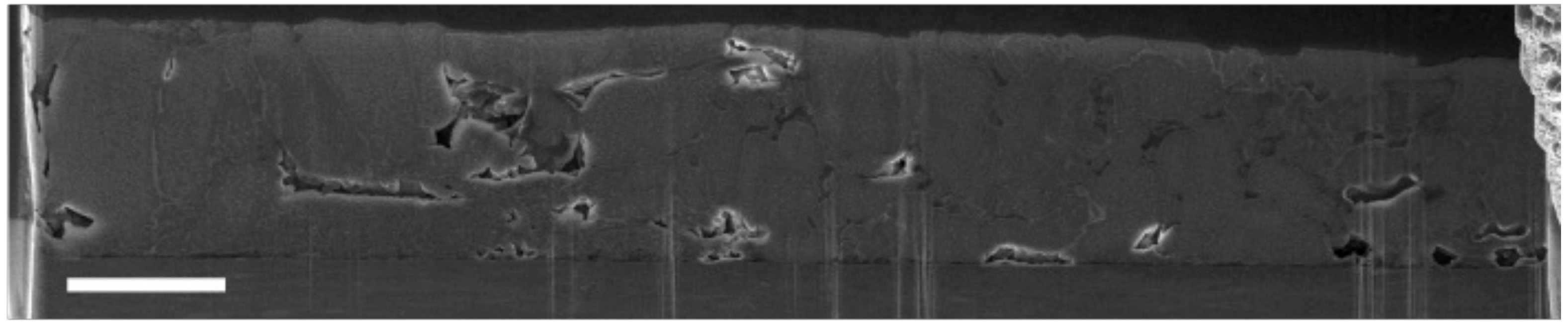
Na Metal Deposited via Different Electrolytes

(a) **1 M $NaPF_6$ in DME**



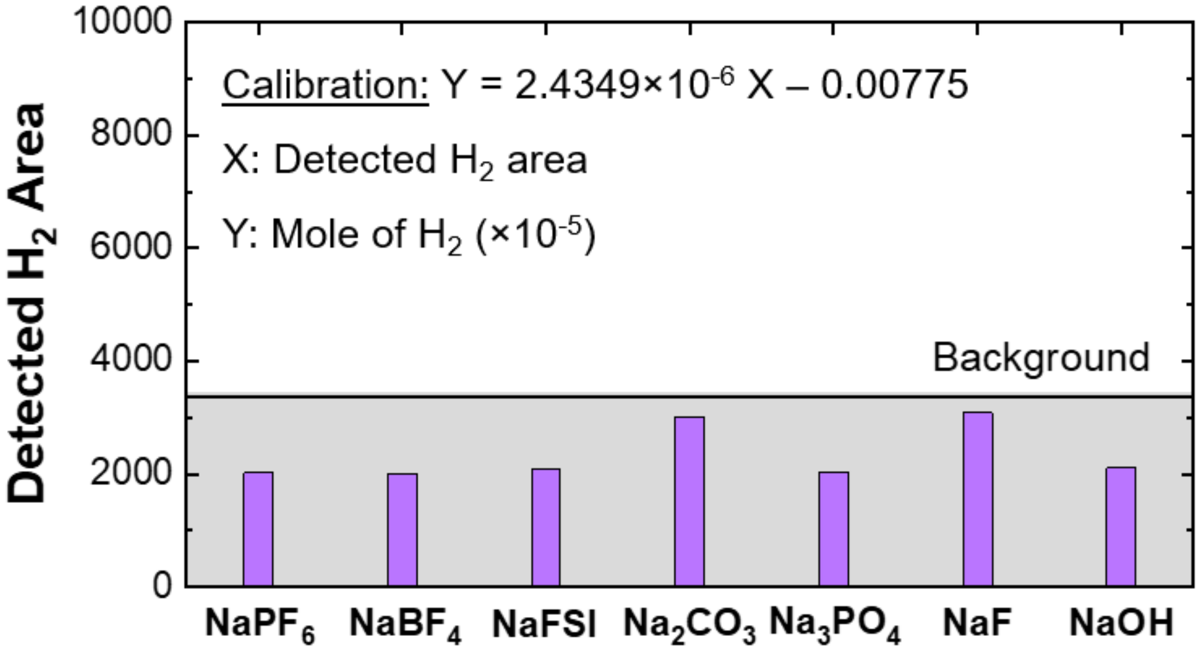
180 kPa

(b) **1 M $NaPF_6$ in EC:DMC (1:1)**



250 kPa

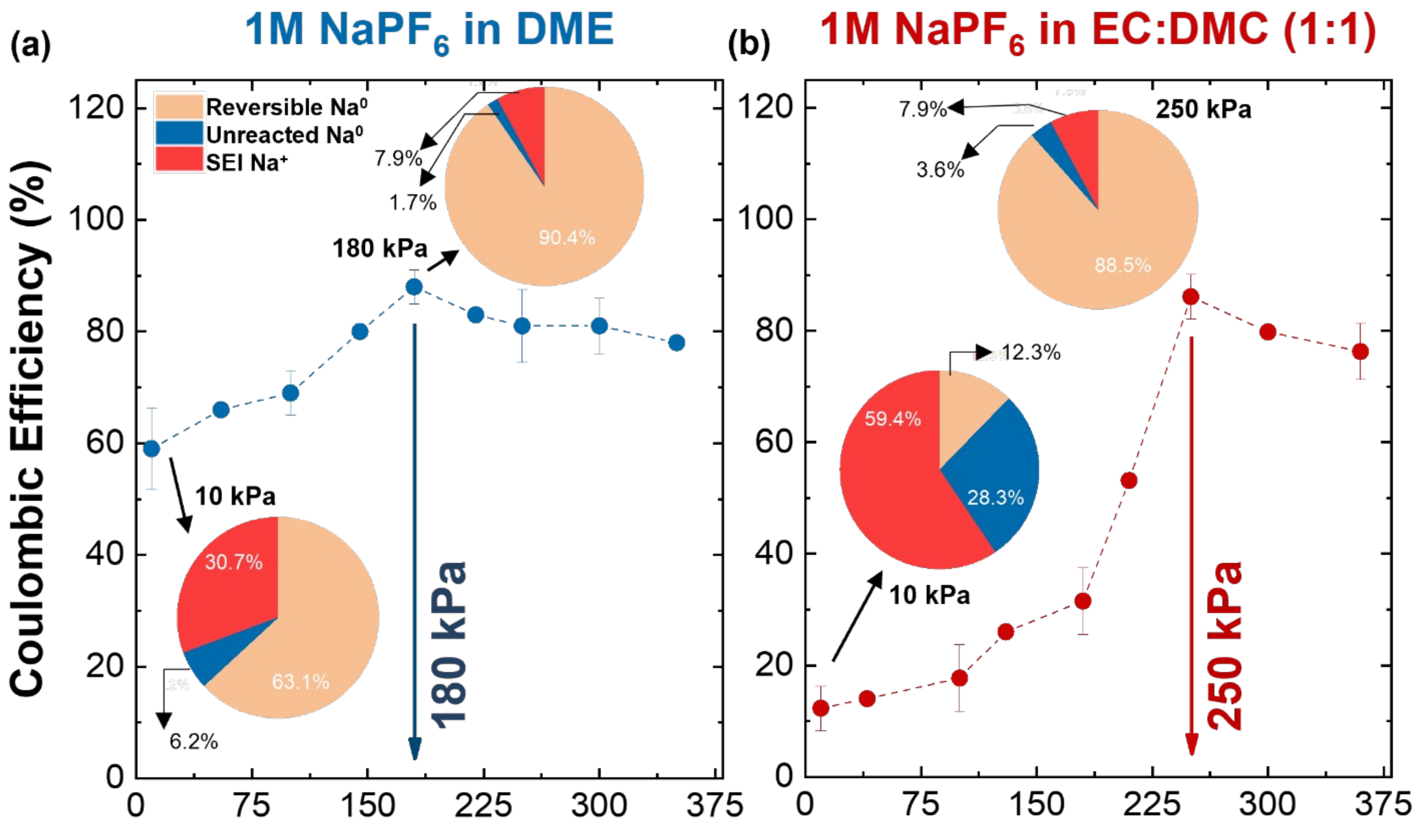
The sodium was plated at 0.5 mA/cm2 for 1 mAh/cm^2 on Al foil. The images are acquired under 5kV voltage and 0.2 nA current using a TLD detector. The scale bars are 10 μm.

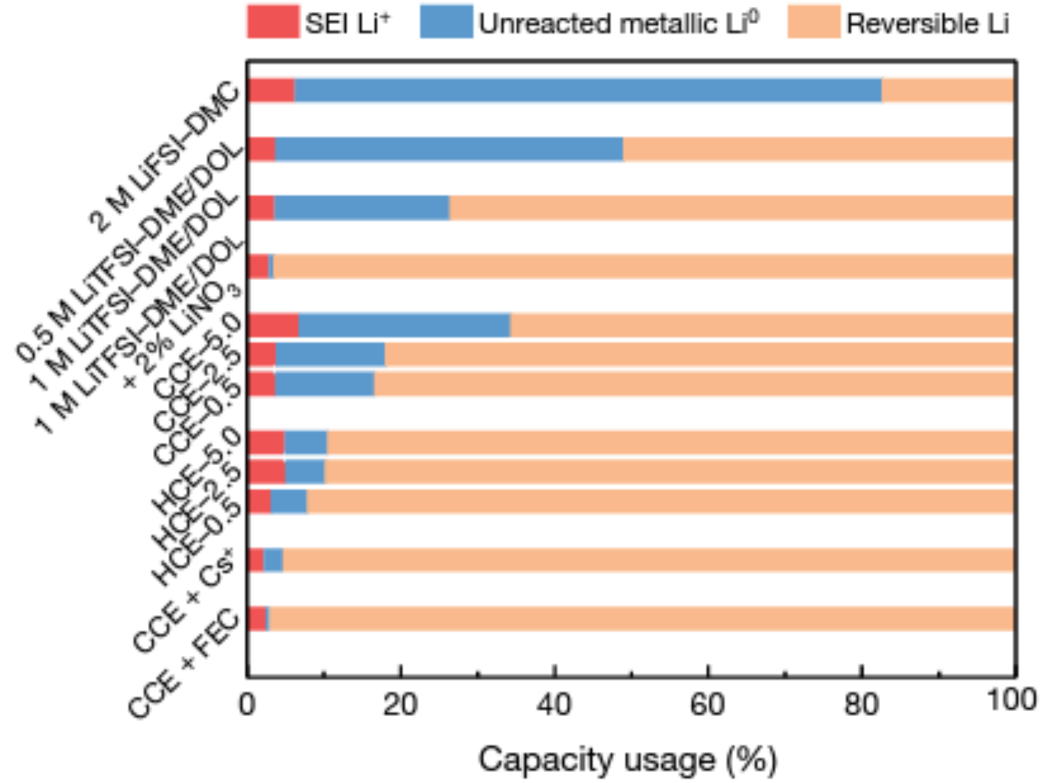


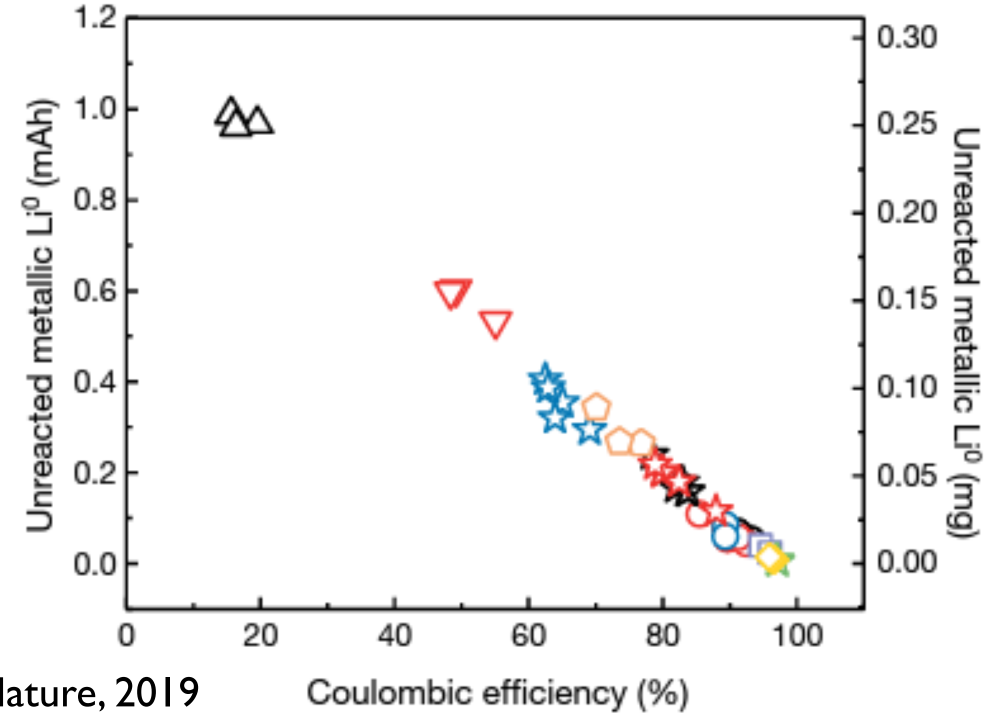
Standard	Detected H_2 Area
$NaPF_6$	2025
$NaBF_4$	2004
NaFSI	2100
Na_2CO_3	3013
Na_3PO_4	2037
NaF	3127
NaOH	2115

The controlled TGC experiment on standard commercial powders showed no hydrogen generation. This test was performed using ethanol as the solvent.

Quantification of the Na Inventory





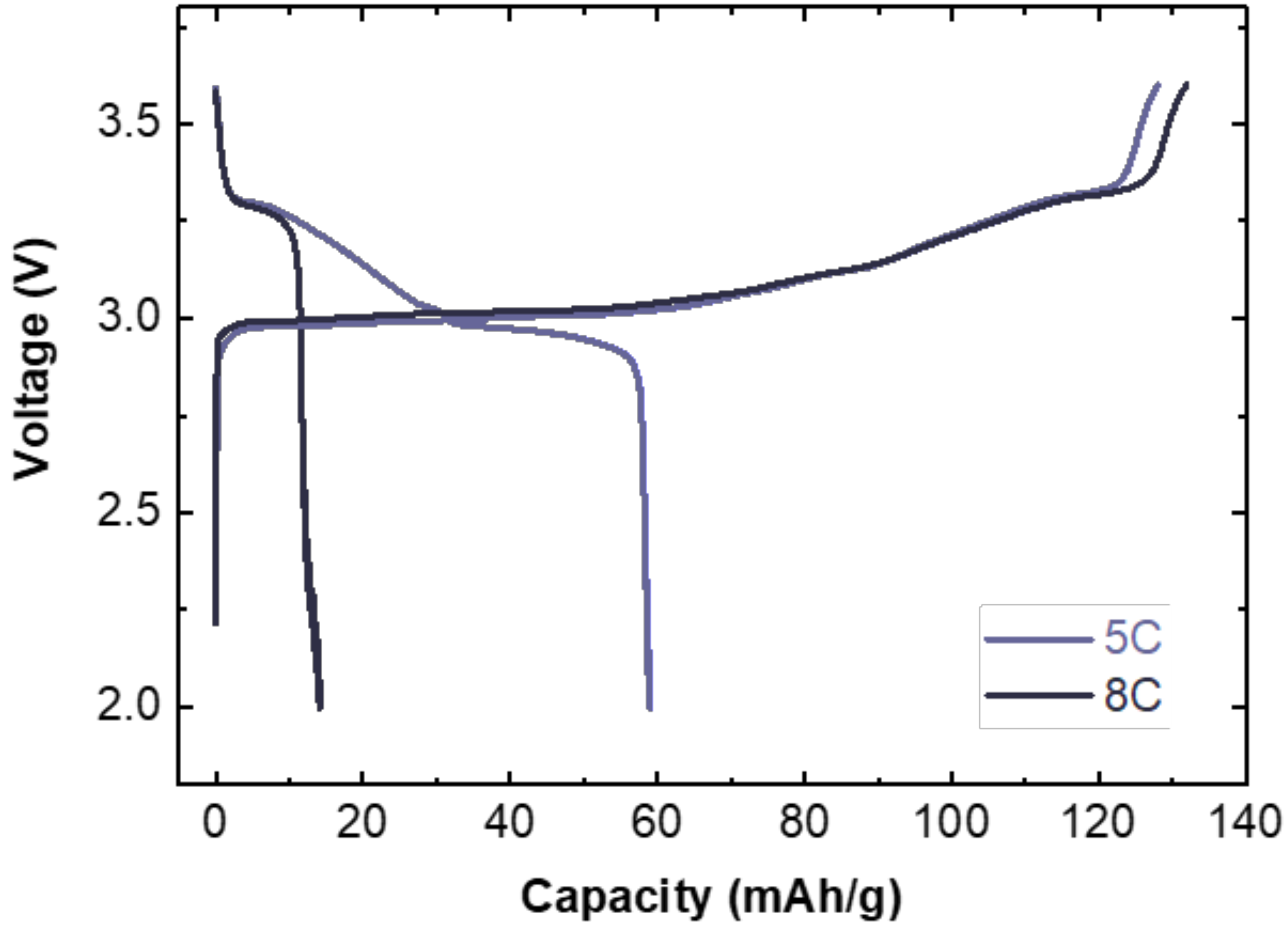


Baharak Sayahpour, et. al and Minghao Zhang, Ying Shirley Meng, "Quantitative Analysis of Sodium Metal Deposition and Interphase in Na Metal Batteries", *arXiv:2309.16006;* 2023

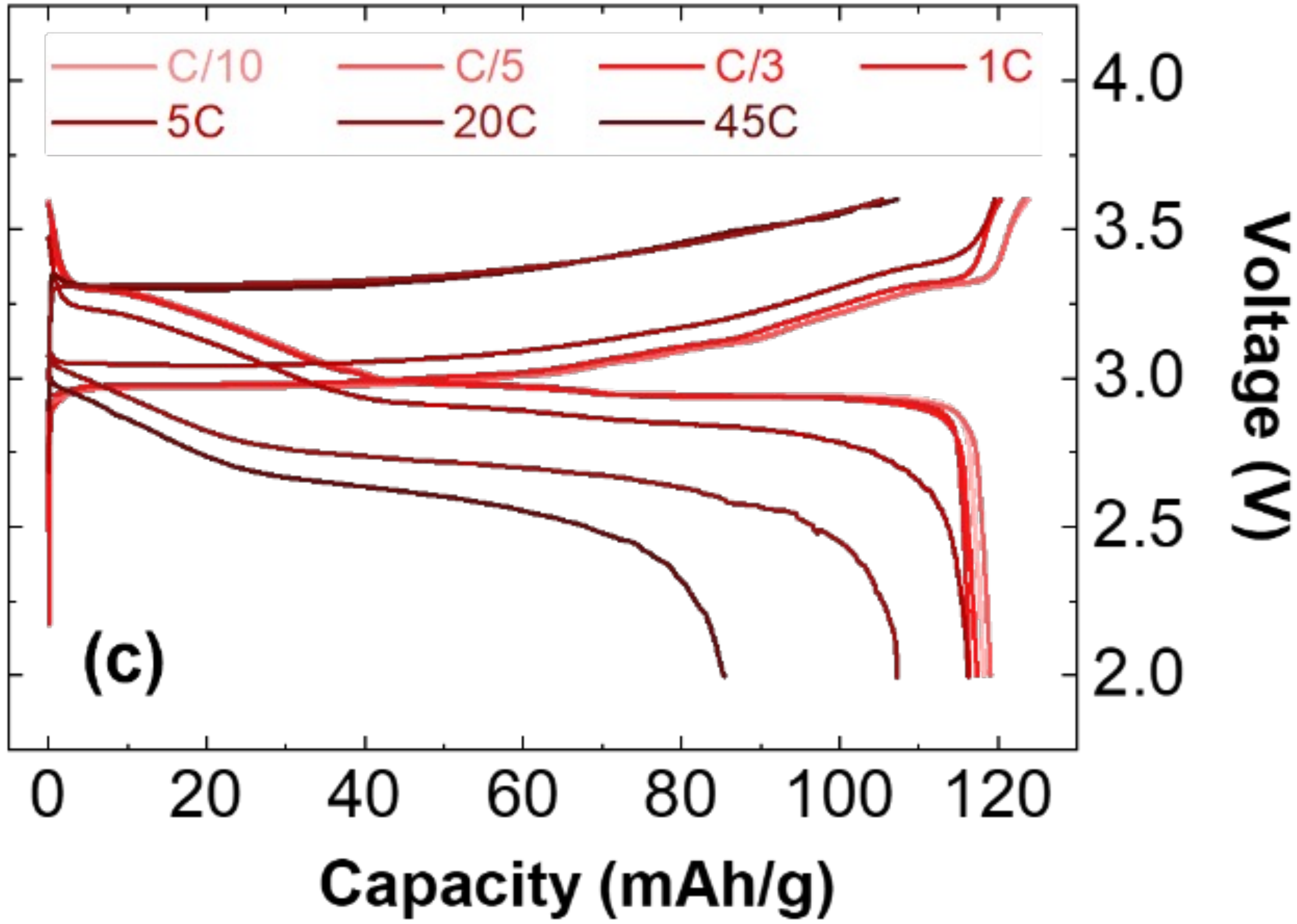
C. Fang, Y.S. Meng*, et al, Nature, 2019

Rate Capability of Na Metal Full Cell

$NaCrO_2$ as the cathode. The cells have controlled 100% excess of sodium inventory.



1M $NaPF_6$ in EC:DMC (1:1)

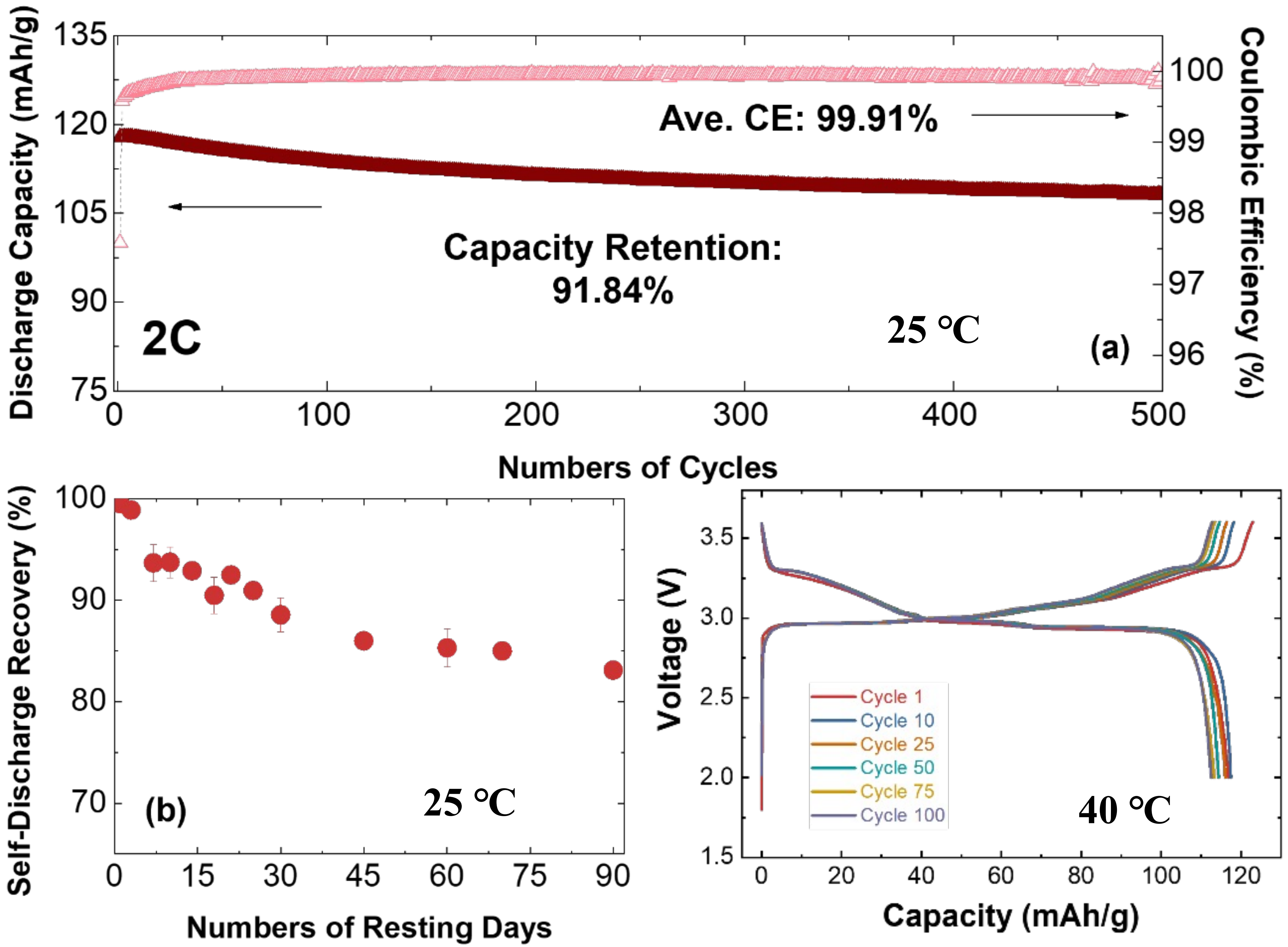


1M $NaPF_6$ in DME

Baharak Sayahpour, et. al and Minghao Zhang, Ying Shirley Meng, "Quantitative Analysis of Sodium Metal Deposition and Interphase in Na Metal Batteries", *arXiv:2309.16006;* 2023

Baharak Sayahpour, et. al and Minghao Zhang, Ying Shirley Meng, " Quantitative Analysis of Sodium Metal Deposition and Interphase in Na Metal Batteries", *arXiv:2309.16006;* 2023

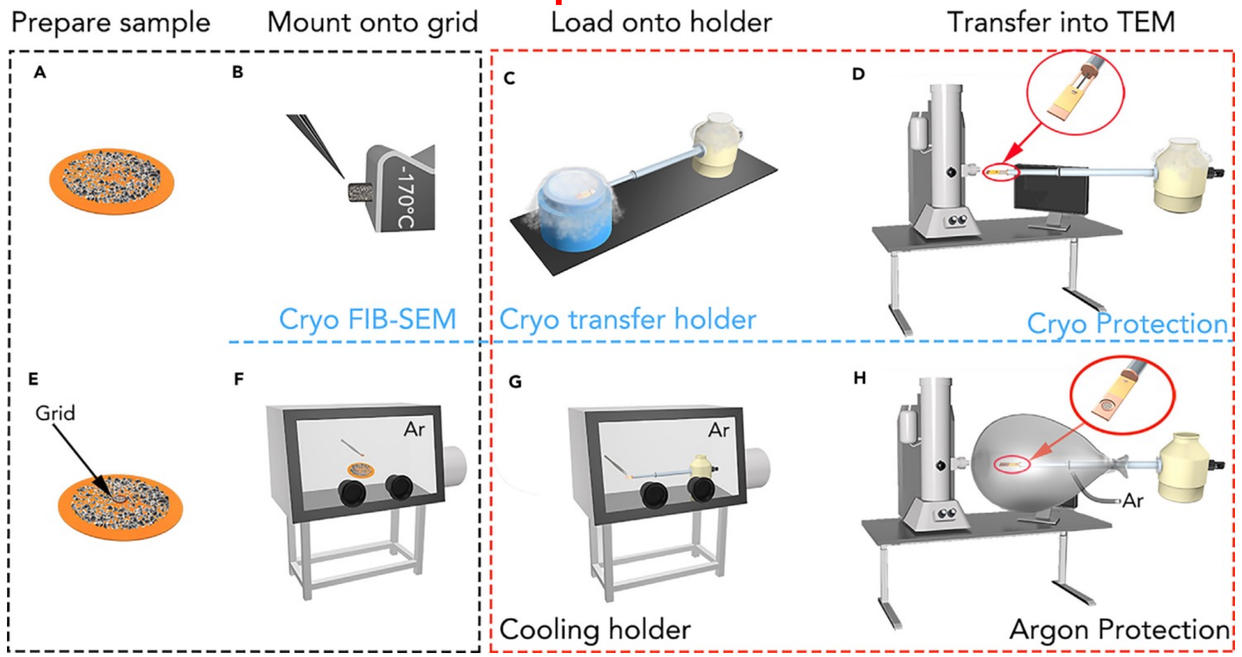
Cycling Stability of Na Metal Full Cell



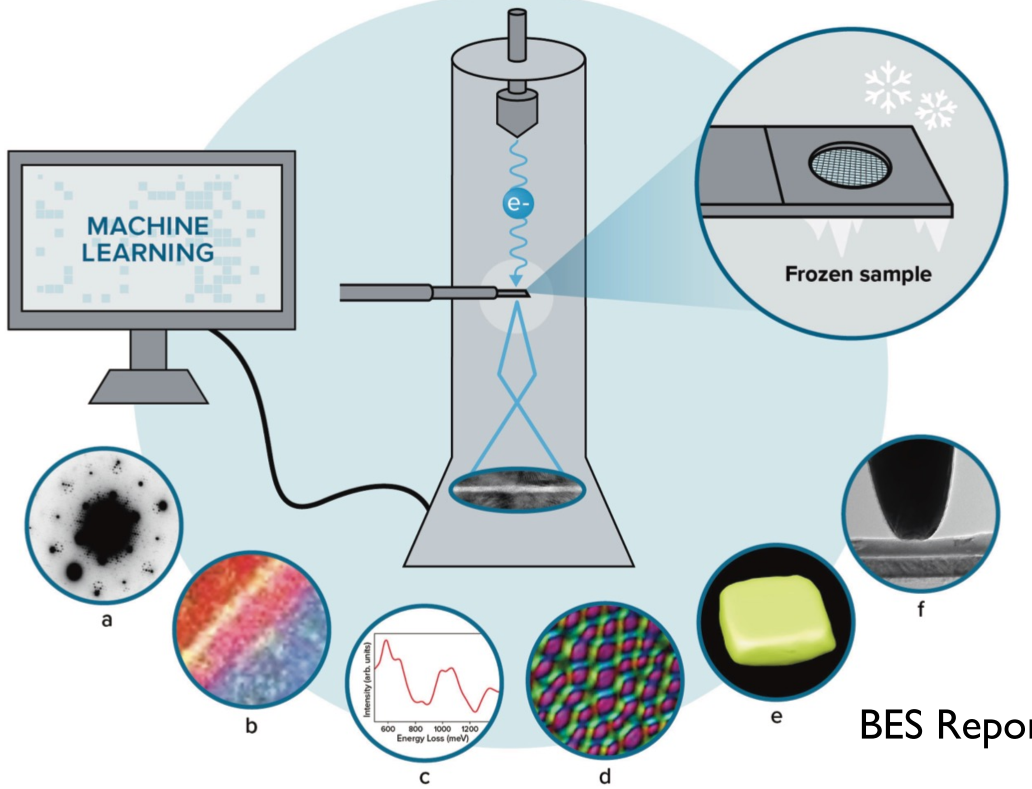
Cryogenic EM for Materials Science

X. Wang and Y.S. Meng, Joule, 2018

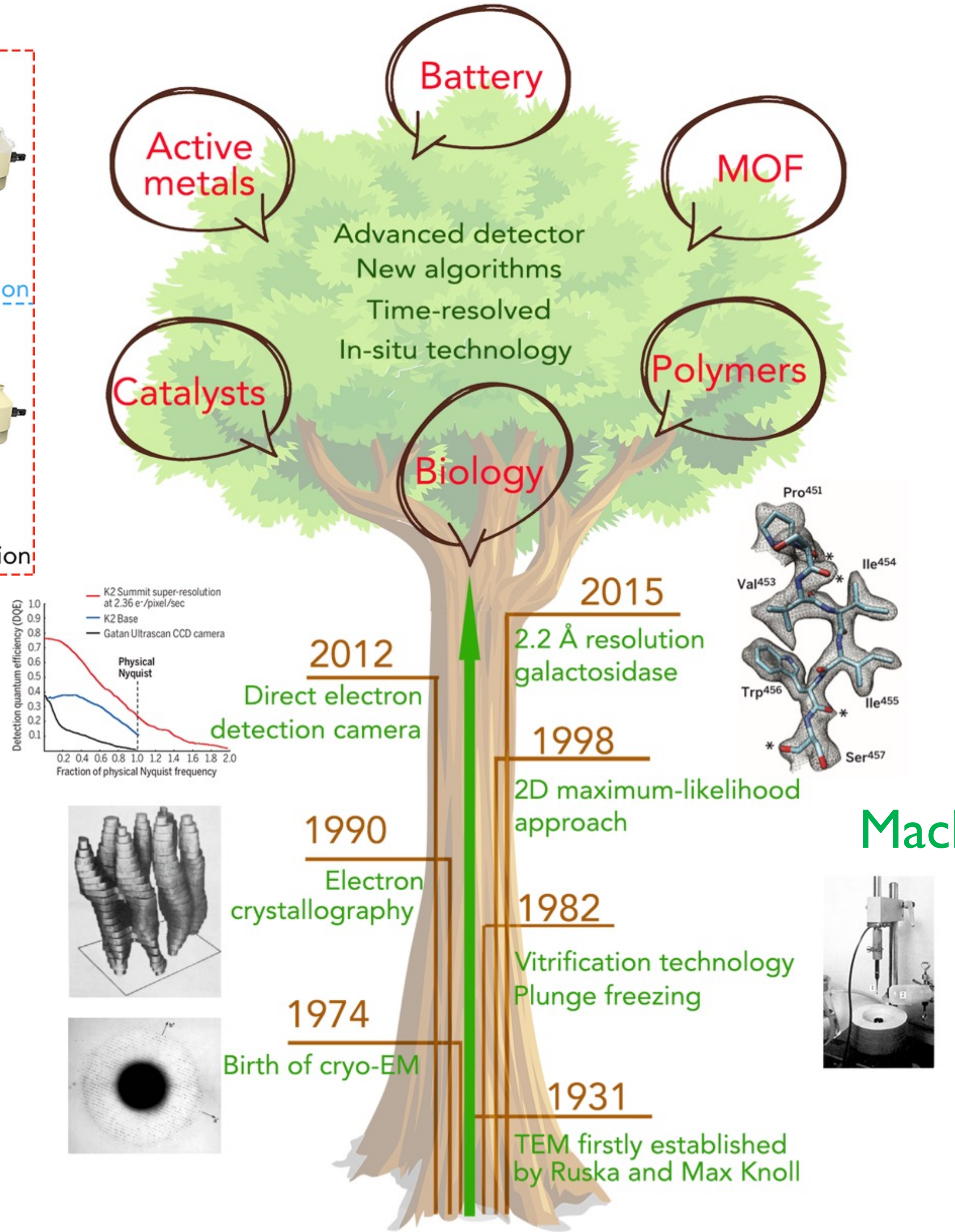
Work-Flow Optimization

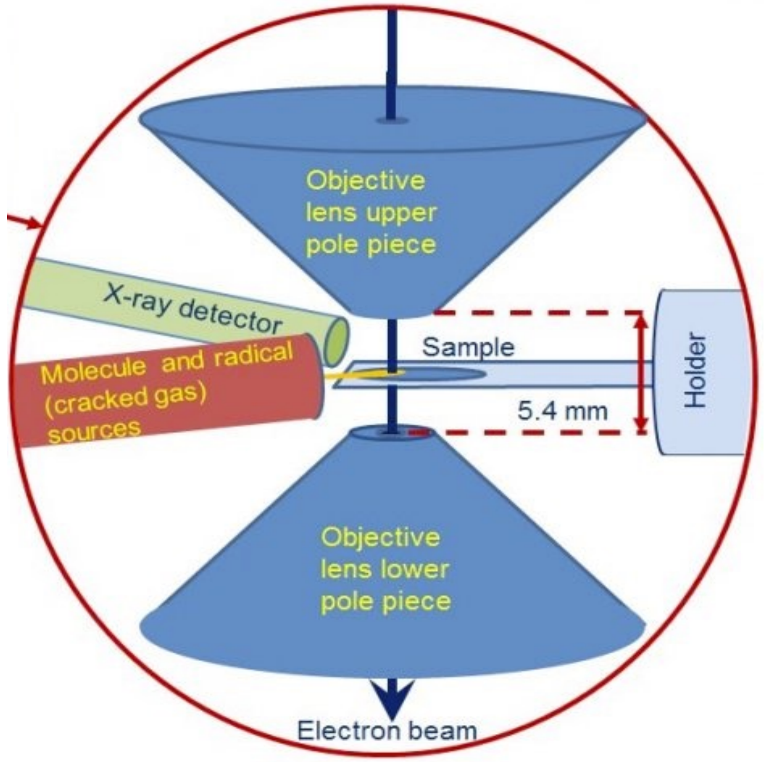


Operando In-Situ with Cryo



BES Report 2021

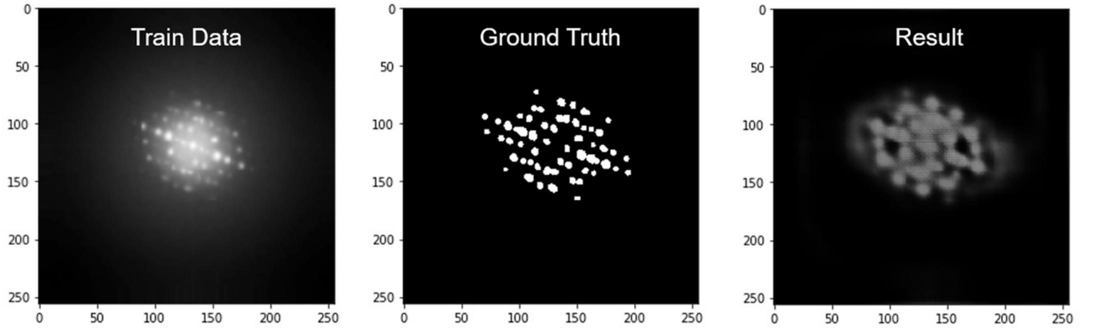




Pole Piece and Holder Innovation

Machine Learning of Data – Build Depository

Deep learning used to detect features in FFT image to tackle the noise issue



Collaborators and Funding

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Battery500 Consortium

Office of Vehicle Technologies DOE

BATTERY 500 CONSORTIUM

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THANK YOU

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