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Cryogenic EM of Lithium Metal Battery Aging and Failure Mechanisms

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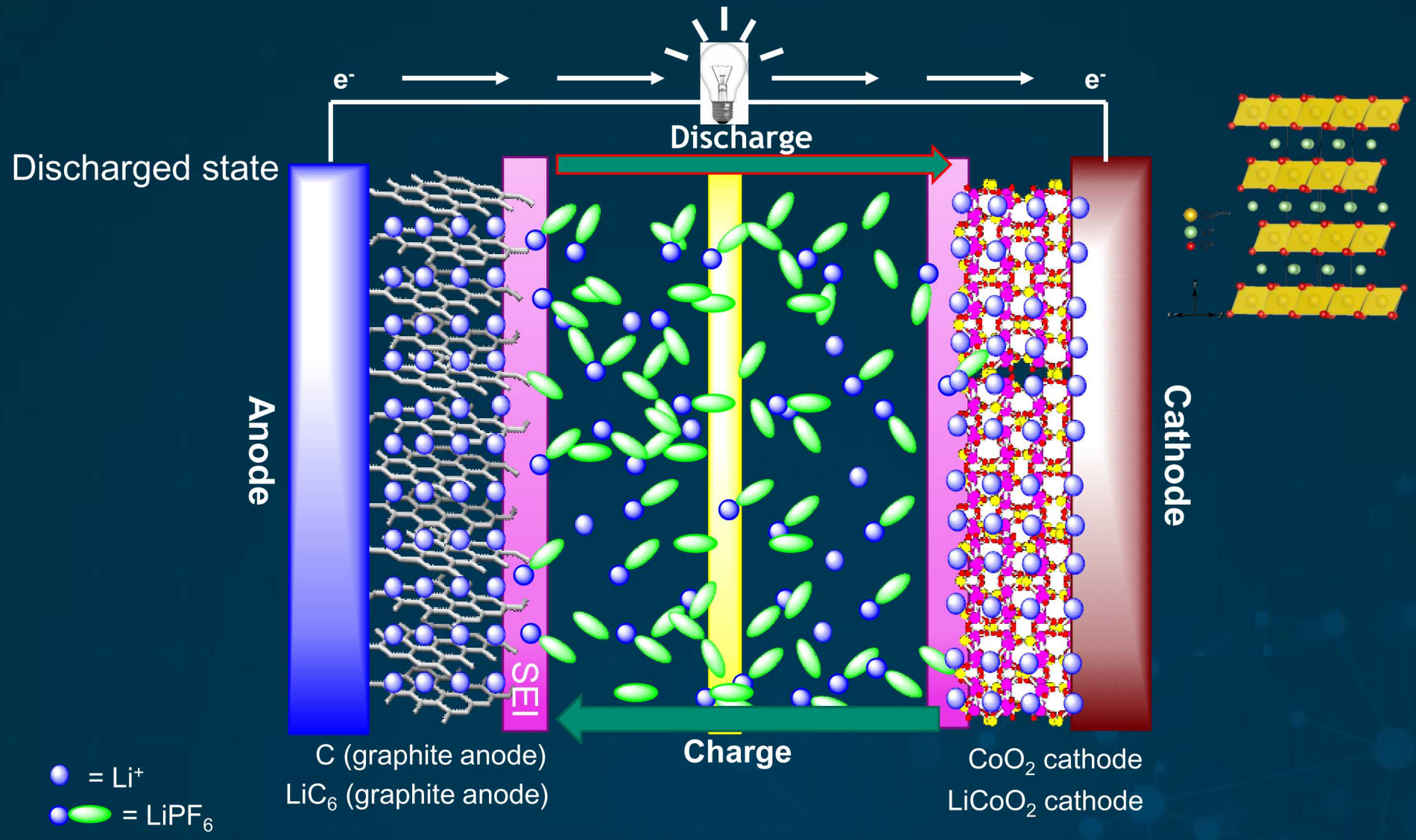
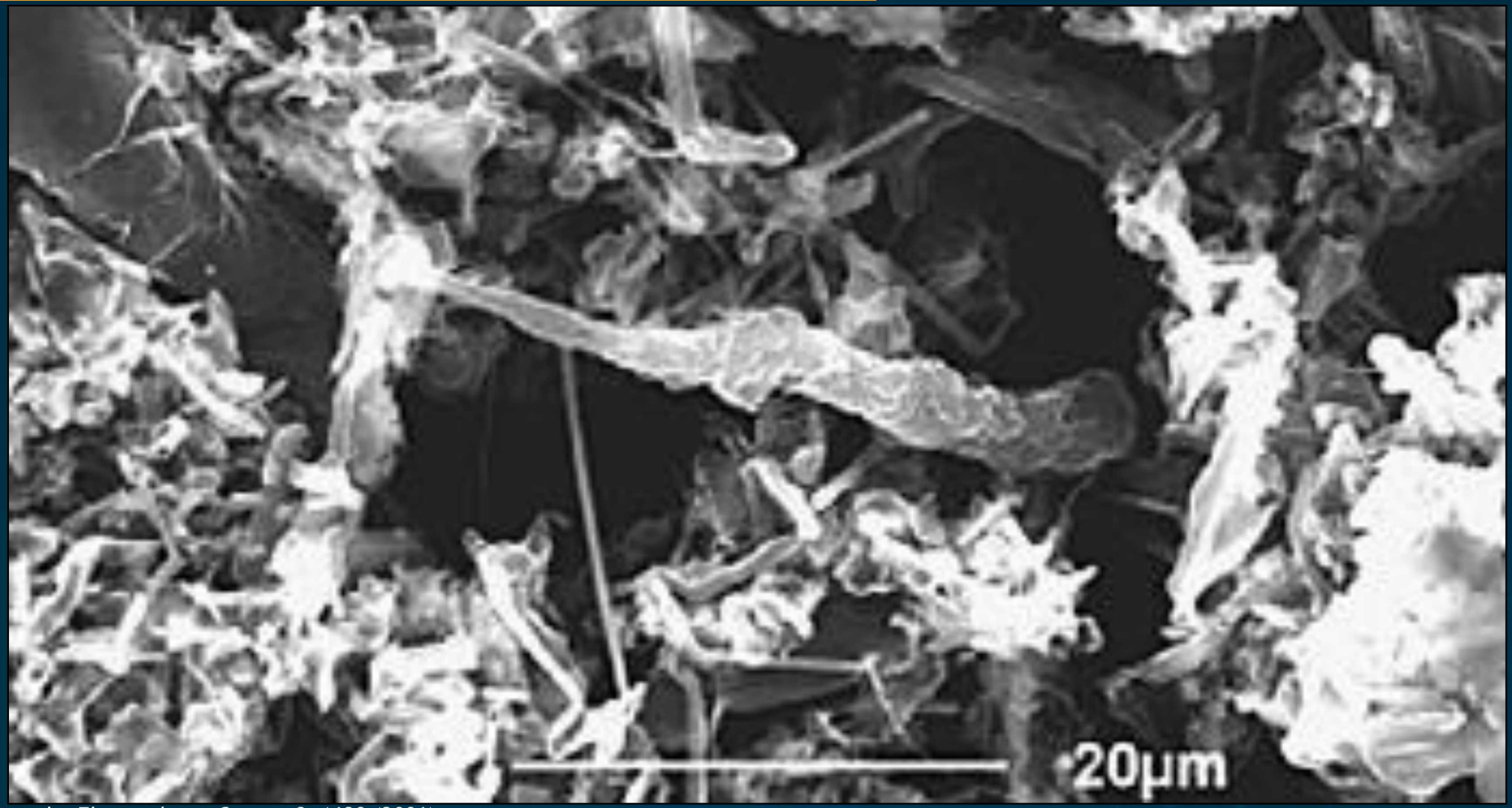
Current Graphite Li-Ion Batteries

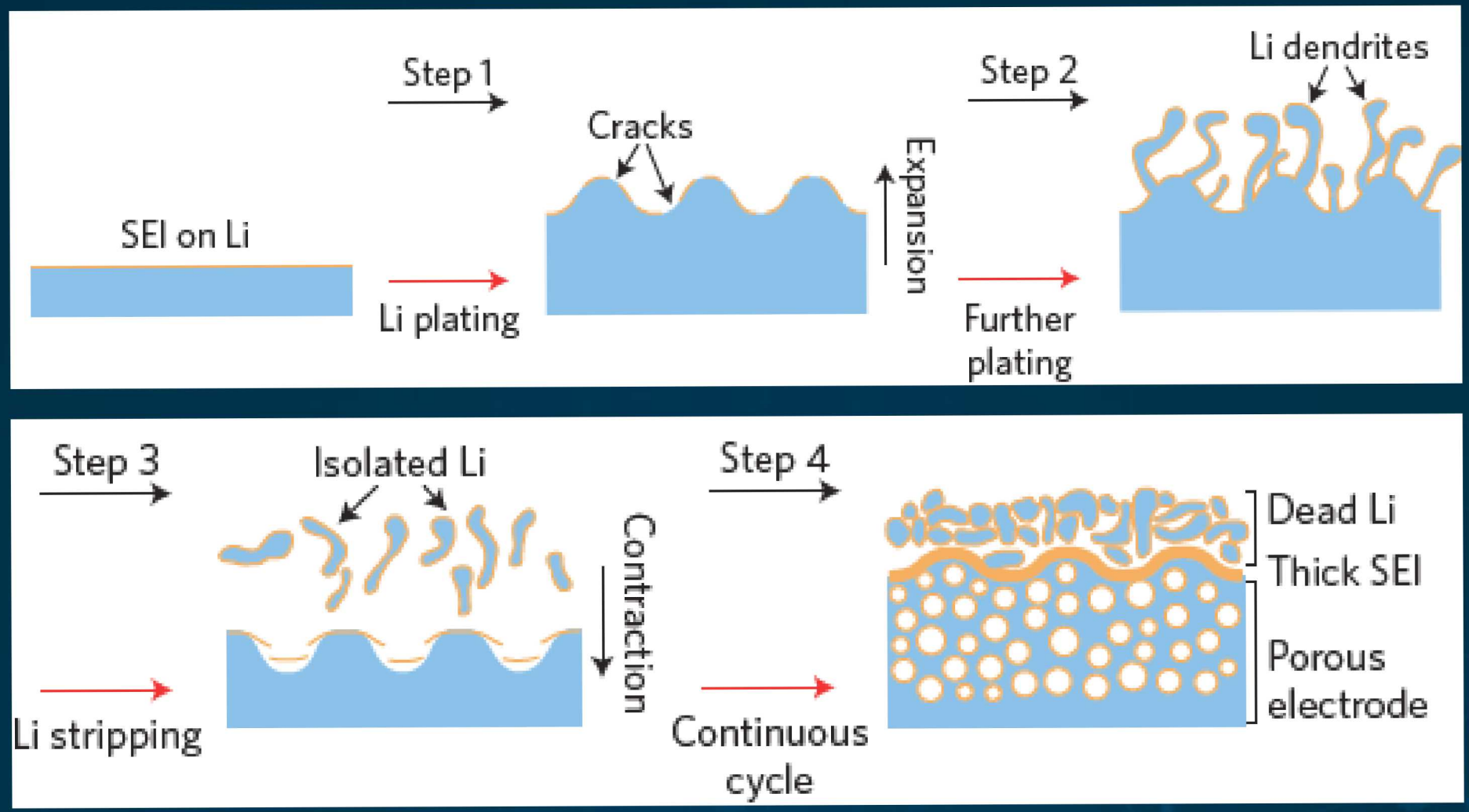


Mossy Electrodeposited Li



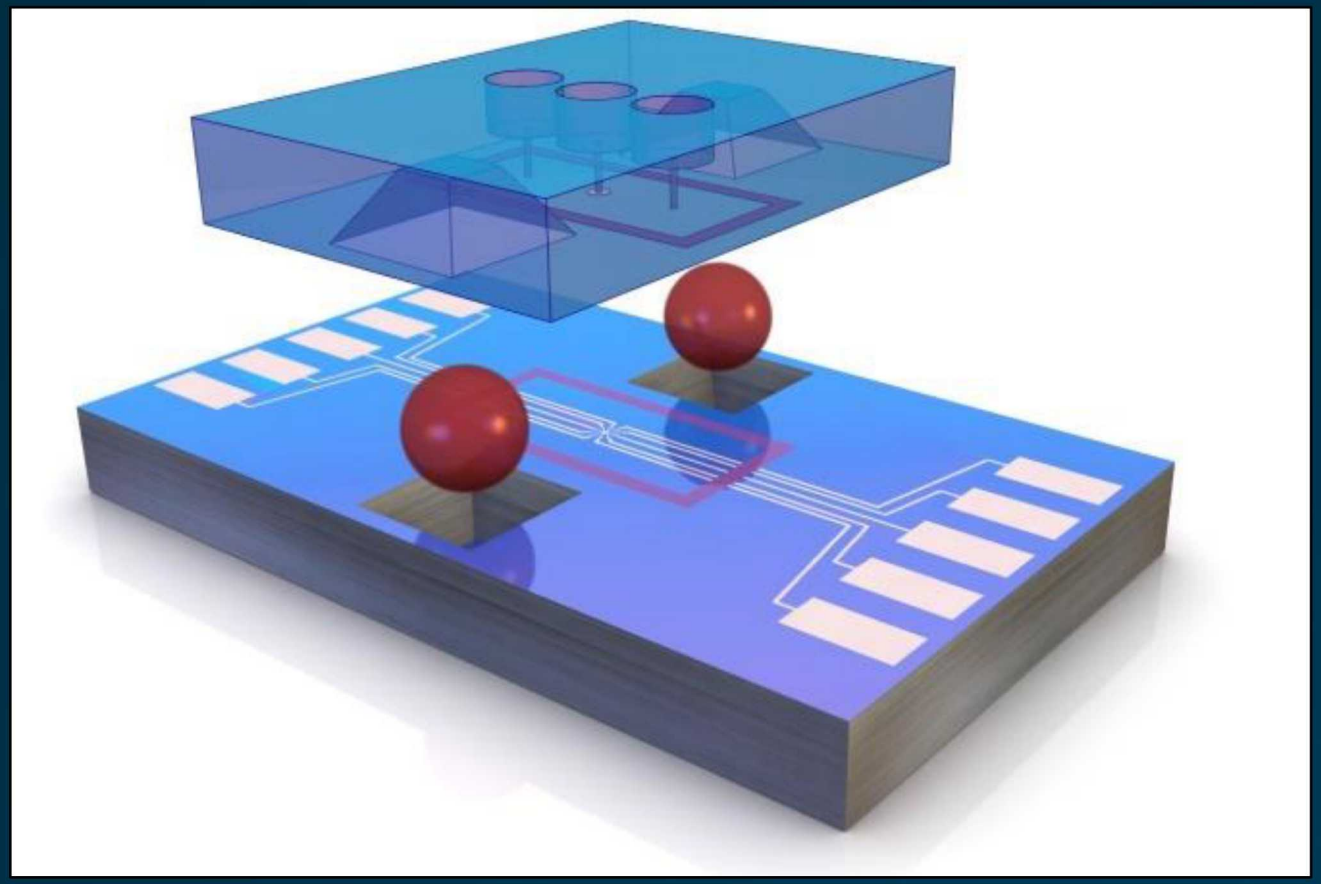
Gireaund et al., *Electrochem. Comm.* ***8***, 1639 (2006)

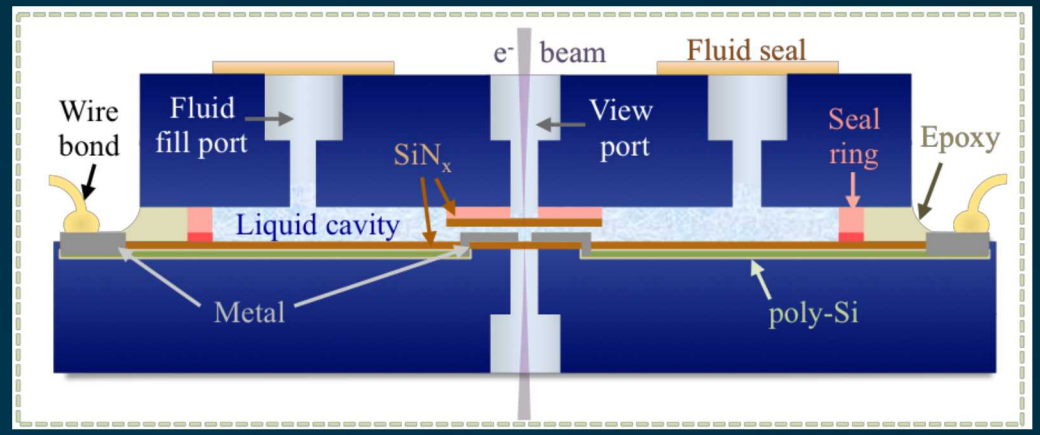
Proposed Mechanism for Li Capacity Loss

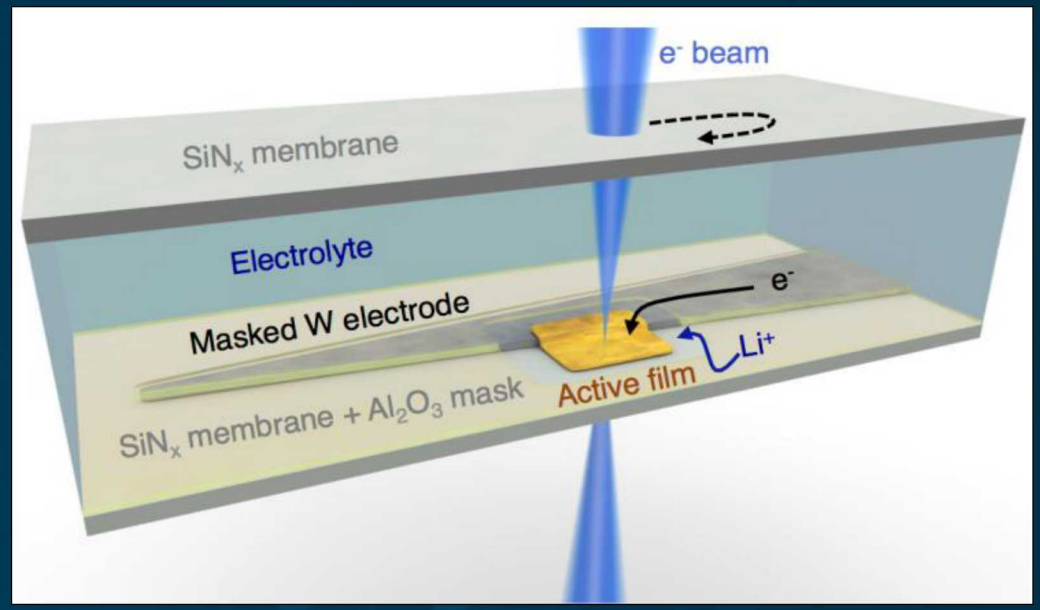


Lin et al. Nature Nanotech. **12**, 194 (2017)

High-Sensitivity Electrochemical TEM Platform

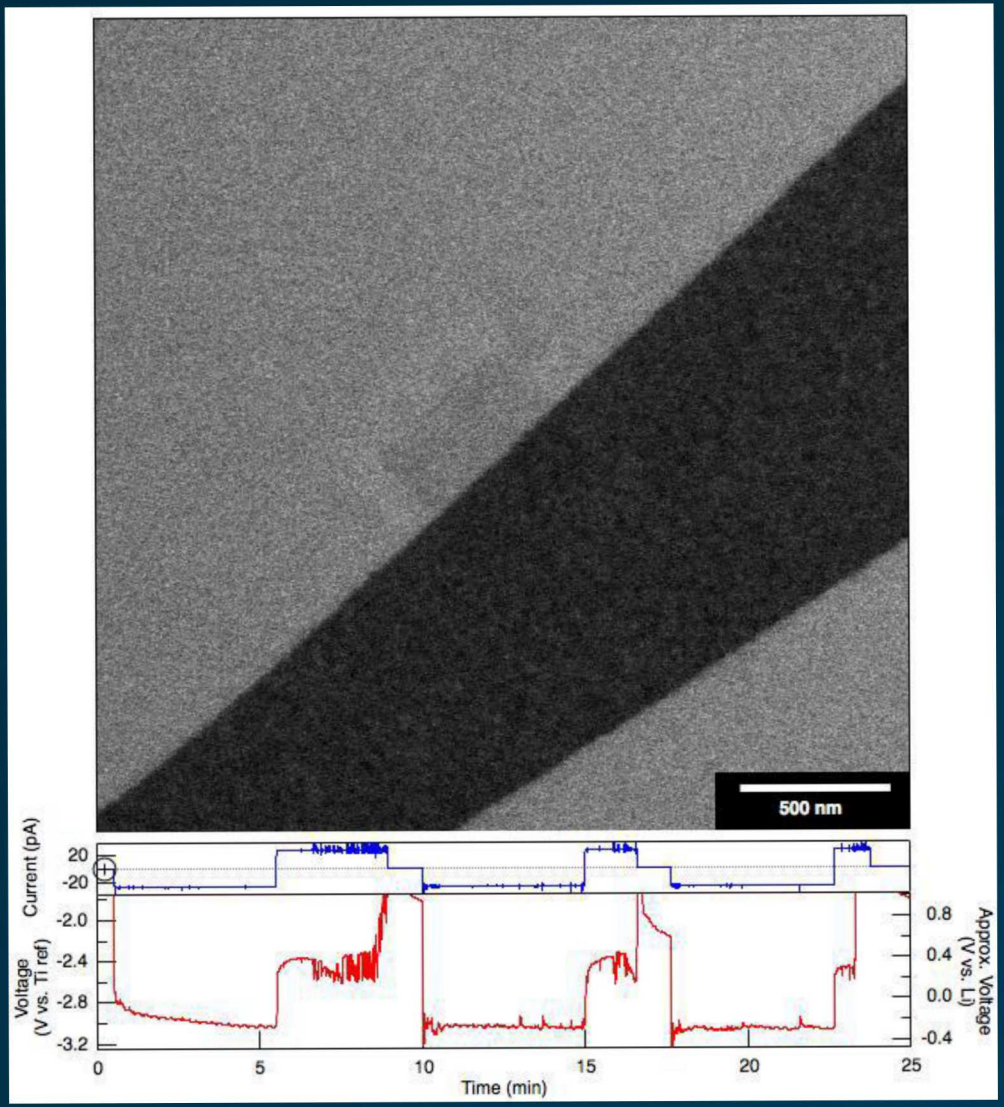


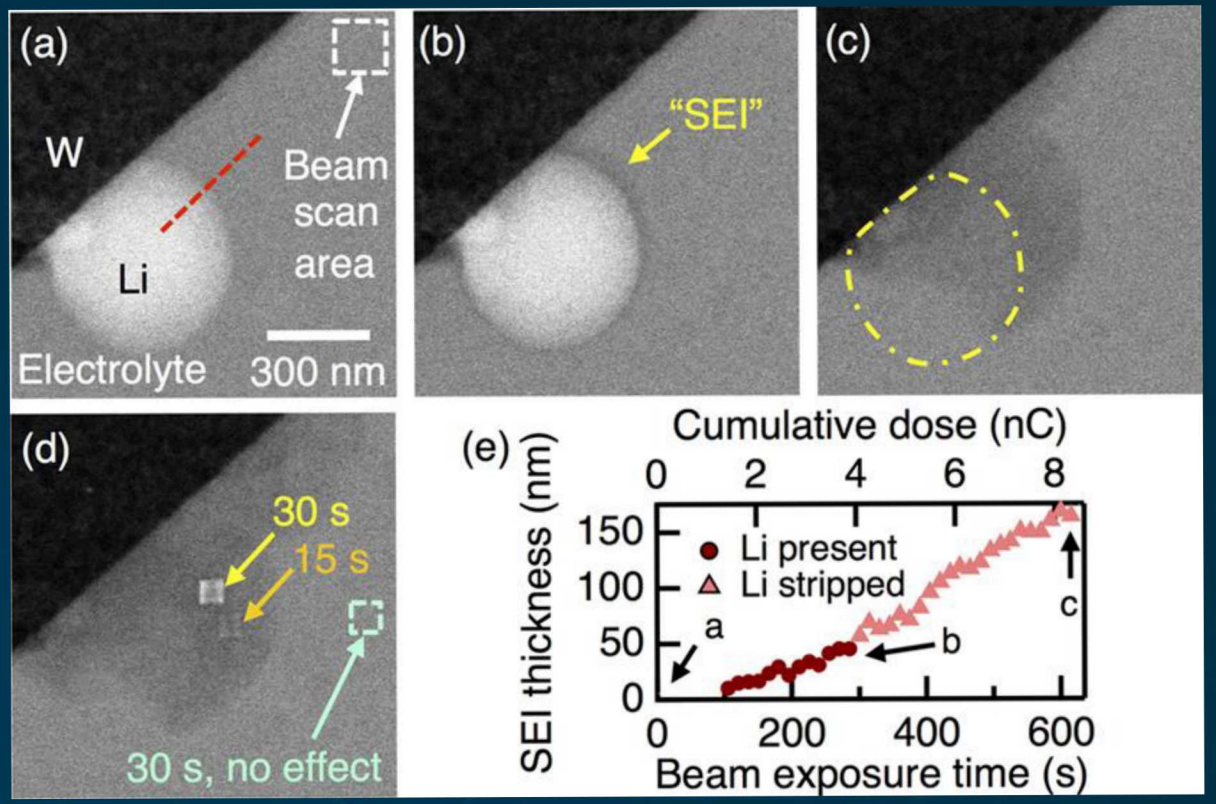




Leenheer et al. *J. MEMS* **24**, 1061 (2015)

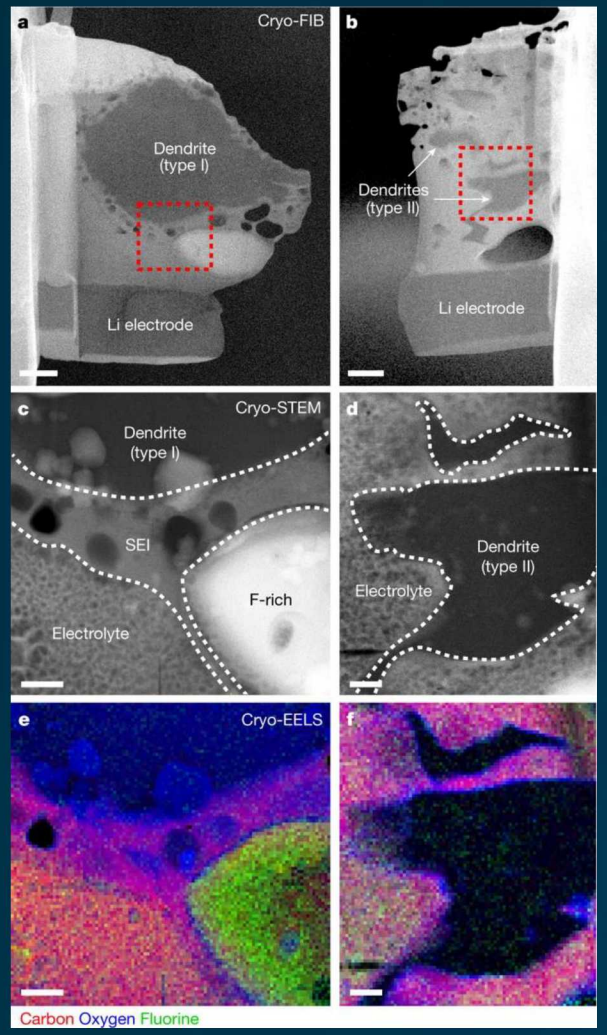
In-Situ STEM of Li Deposition/Dissolution





Leenheer et al. *ACS Nano* **9**, 4379 (2015)

Leica Inert Transfer for Cryo-FIB



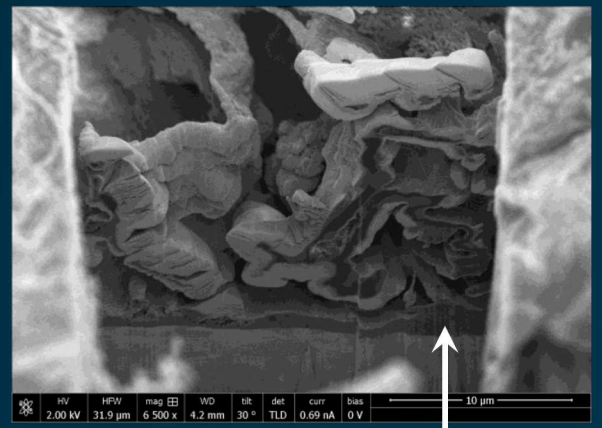
Zachman et al. *Nature* **560**, 345 (2018)

Looking at the Leaves

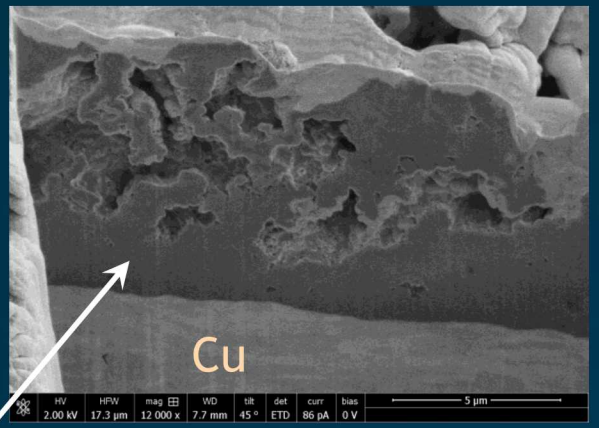
Lithium Metal 1st Deposition Cycle: Overview

Cross-Sectional View

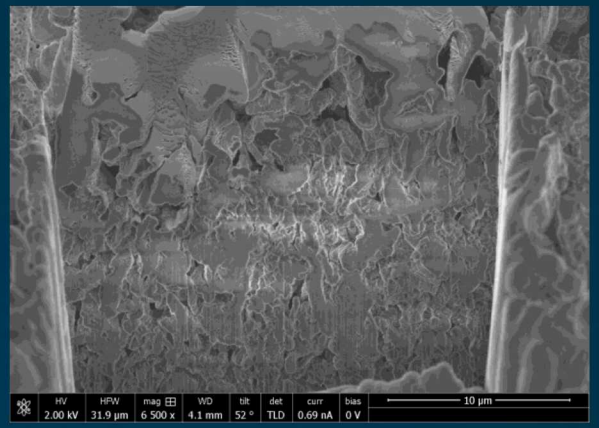
0 kPa



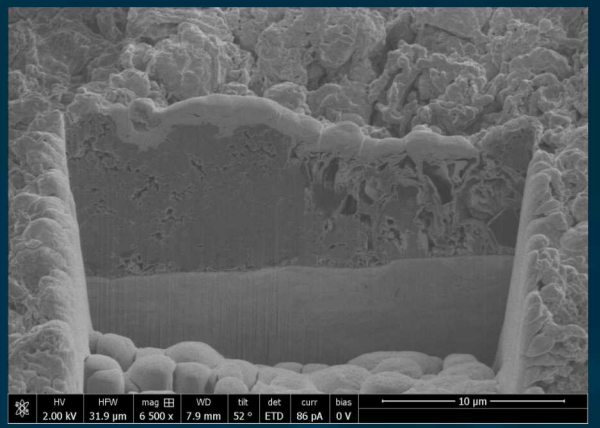
10 kPa



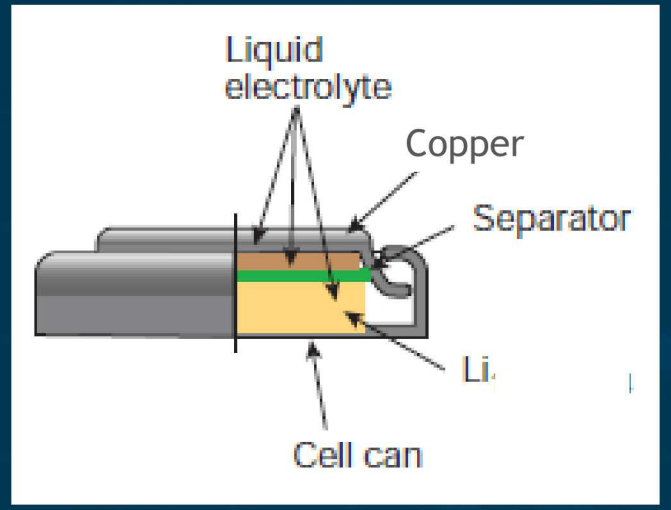
100 kPa



1,000 kPa

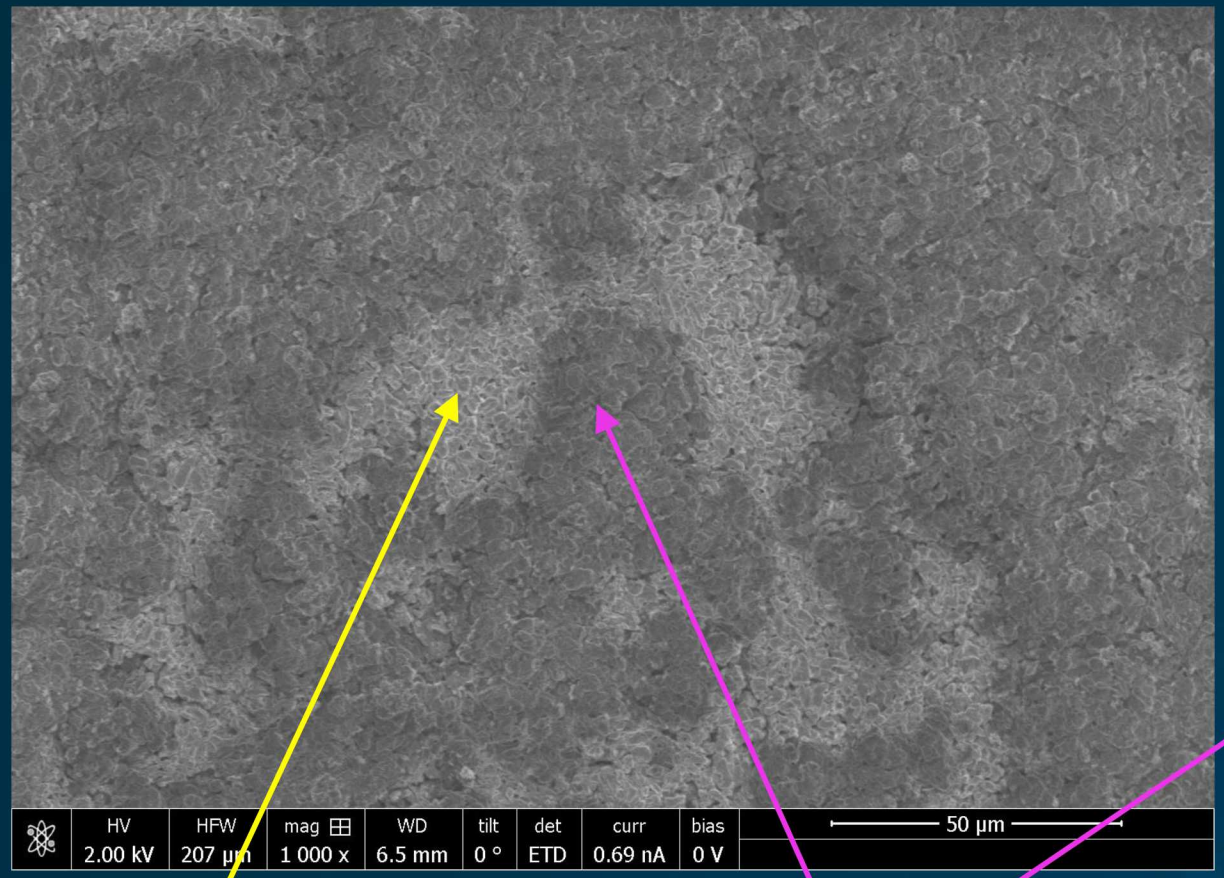


Lithium

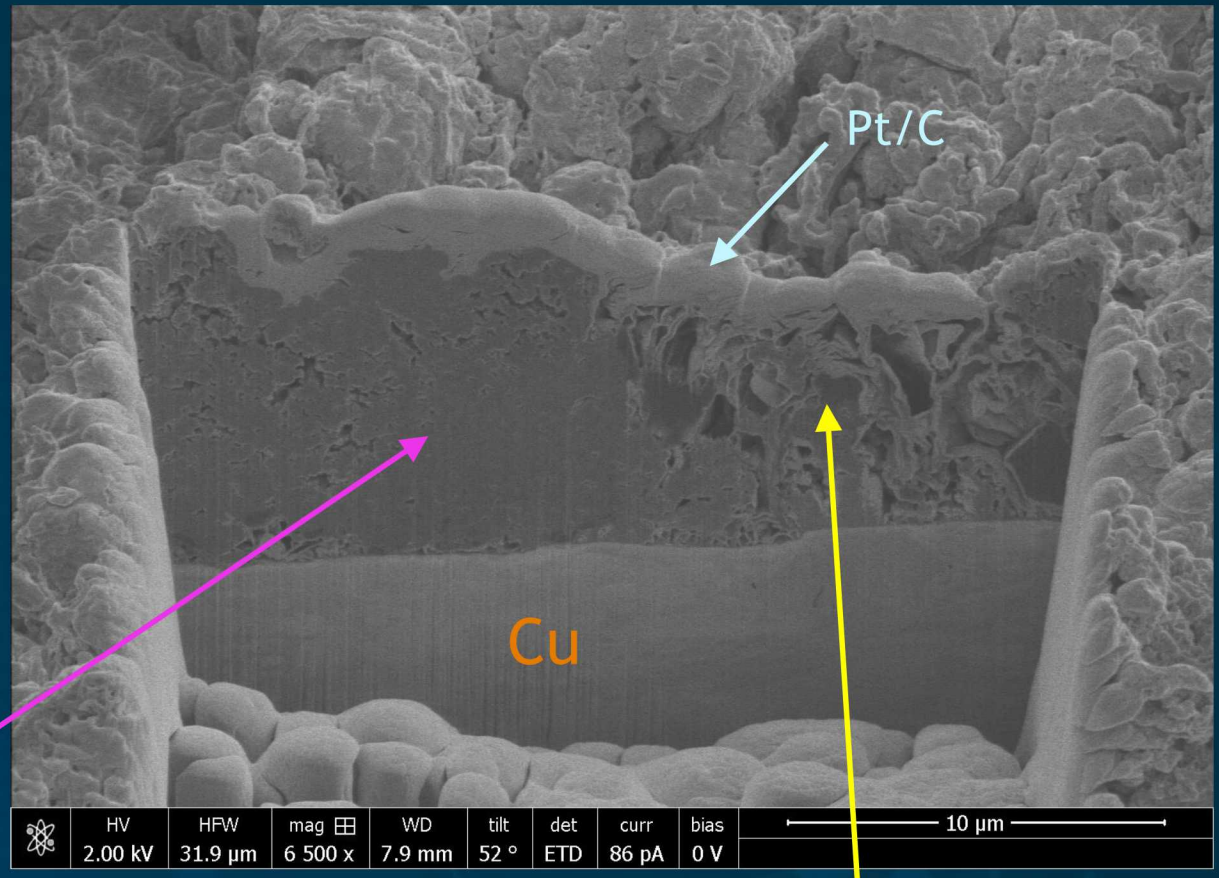


Lithium Metal 1st Deposition Cycle: 1,000 kPa

Low Magnification



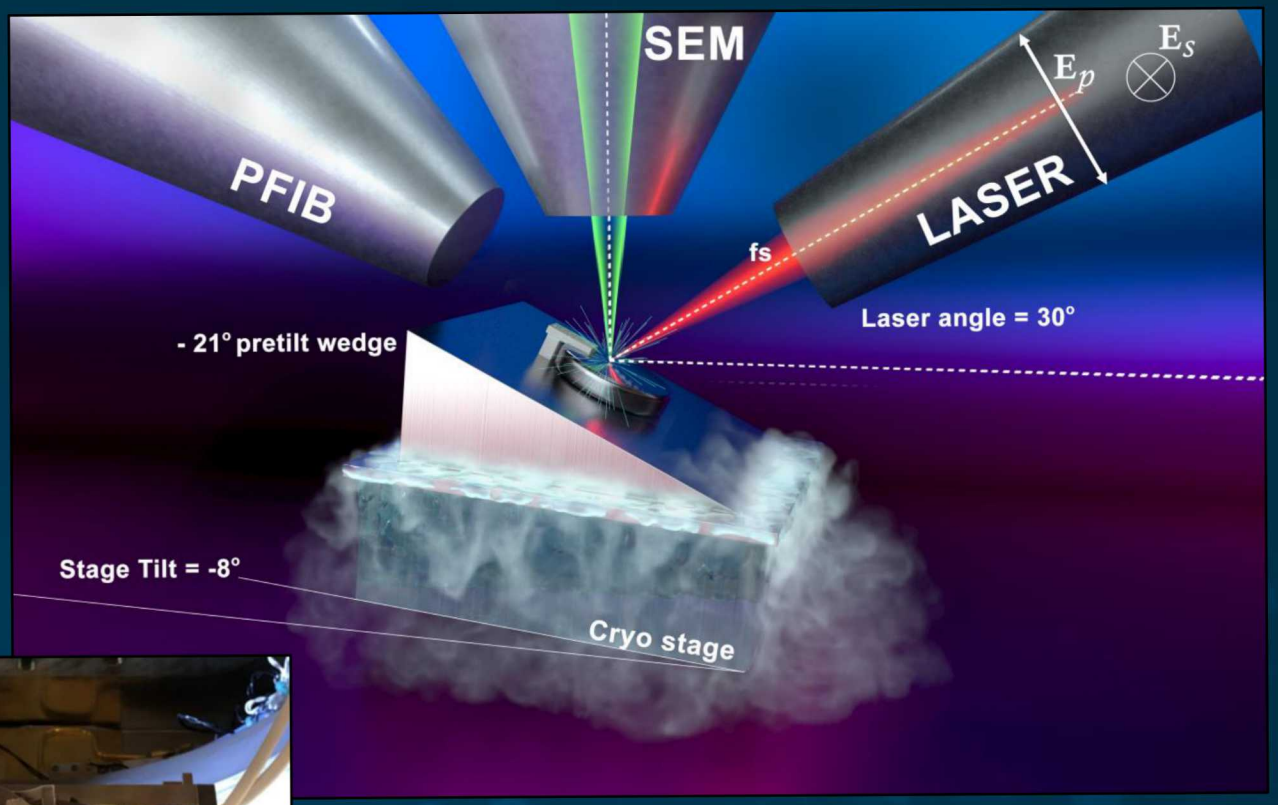
Cross-Sectional



Need to See the Forrest

TriBeam: fs Laser Plasma-FIB/SEM

Thermo Fisher Helios PFIB UXe Laser



1200x1200x1200 μm^3/hr

(**>15.000x** faster than FIB, or >1000μA)

TriBeam Bridges Characterization Length Scales

Region of Interest

Unserved space

30 mm 10 mm 3 mm 1 mm 300 µm 100 µm 10 µm 500nm <1nm

Macro CT

Micro CT

(P)FIB + fs-Laser

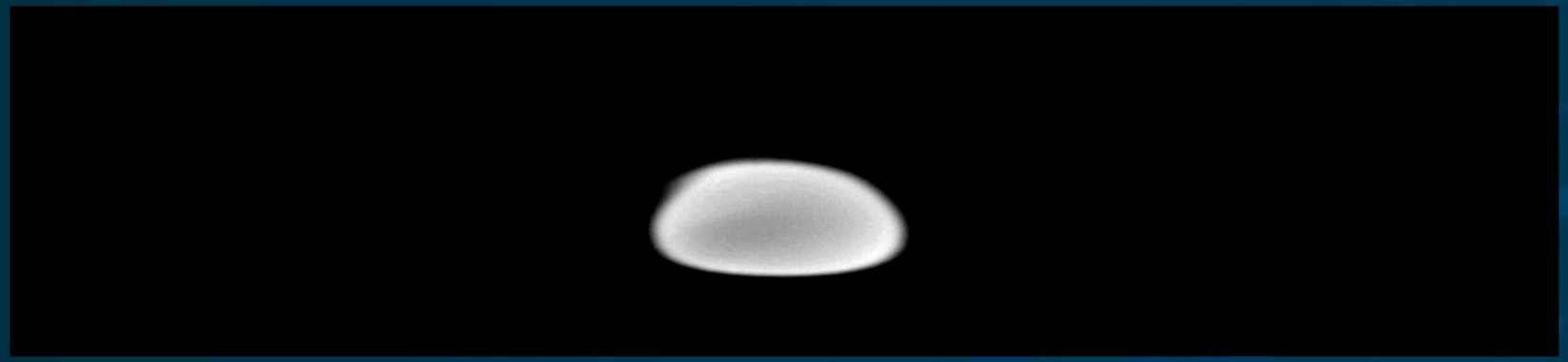
PFIB SnV (Xe+)

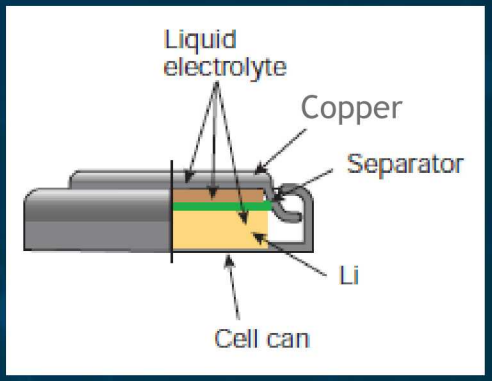
DB SnV (Ga+)

TEM Tomo

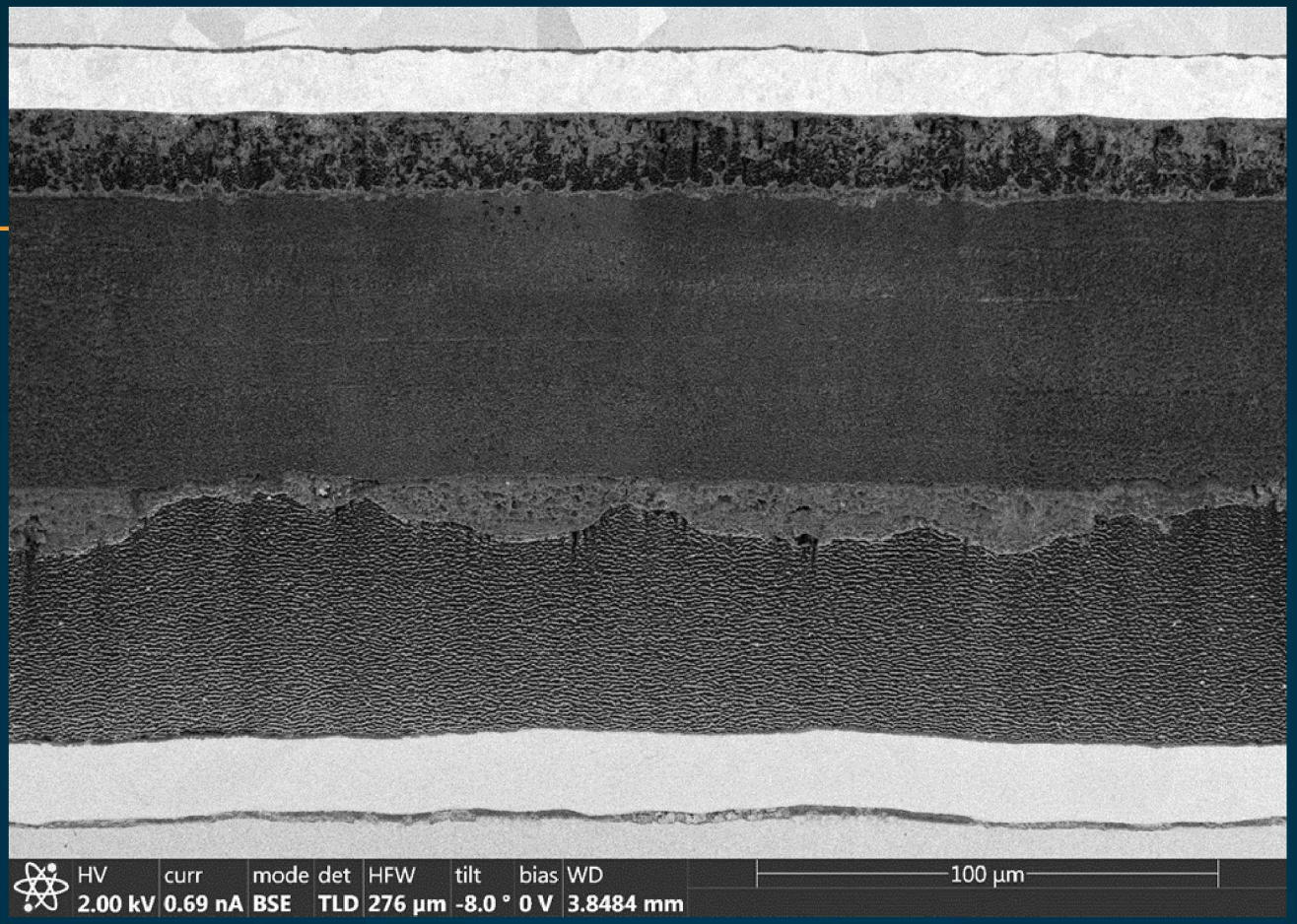
Spatial resolution

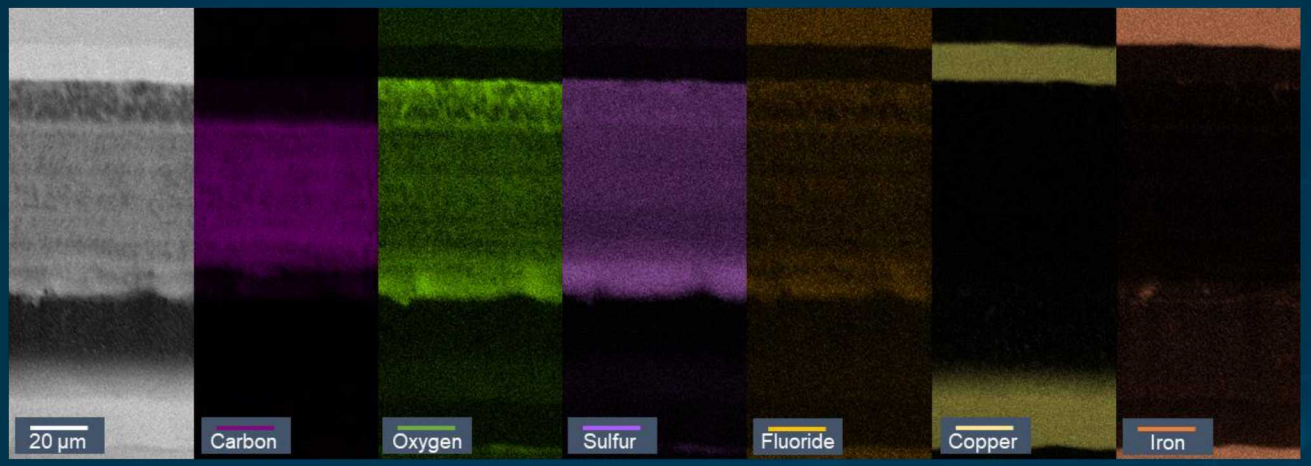
1 µm 1nm <1nm

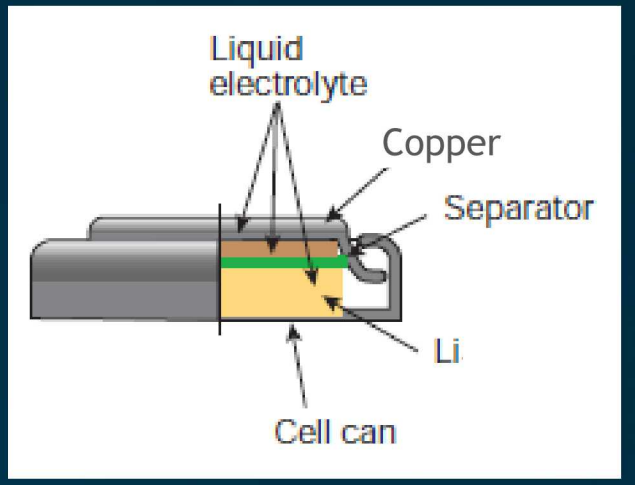




1st Li Plating

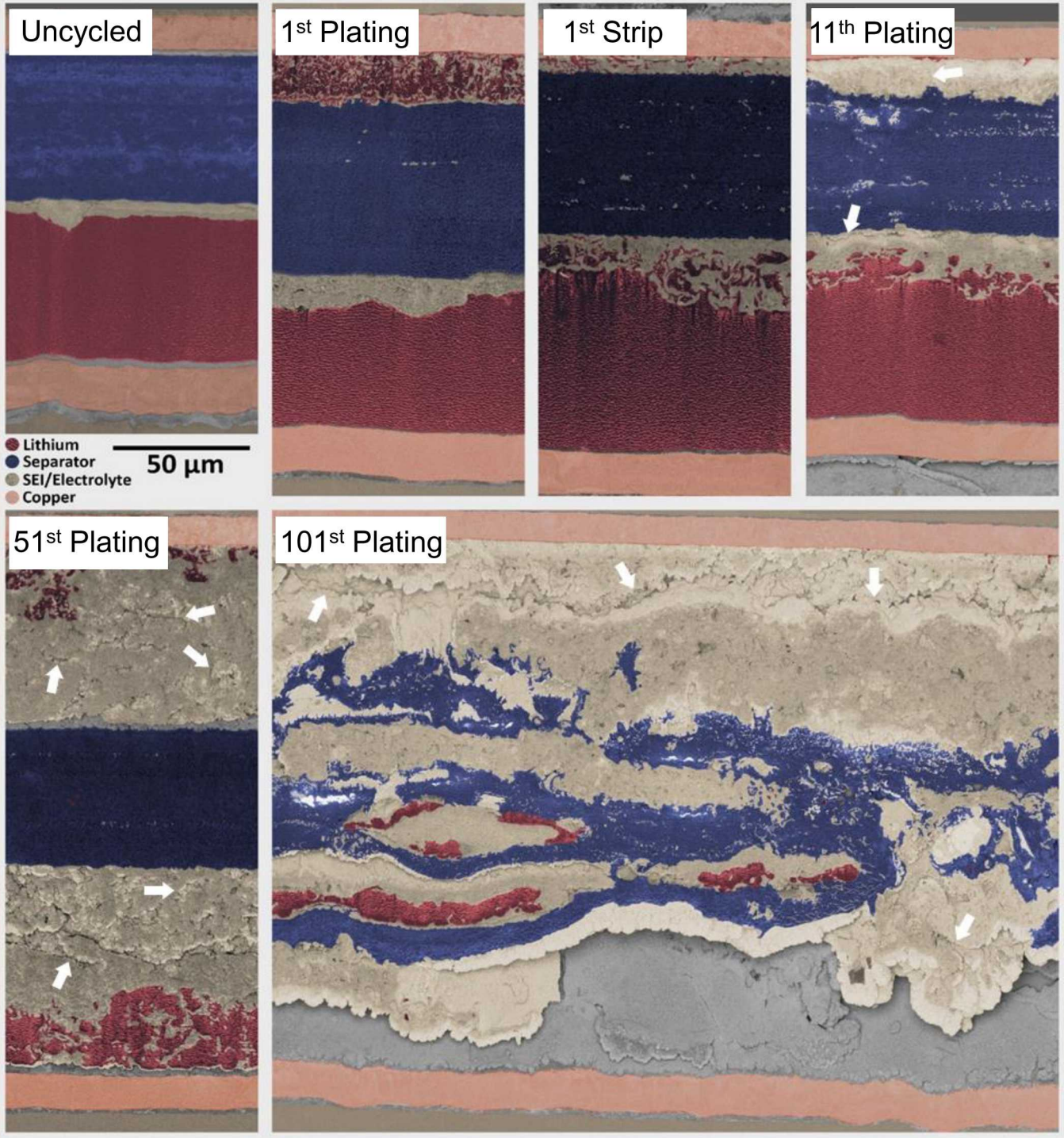






2.8 M LiFSI in DME
Two Celgard 2325 separators
Cycled at 1.88 mA/cm^2
Capacity: 1.88 mAh/cm^2

High Rate



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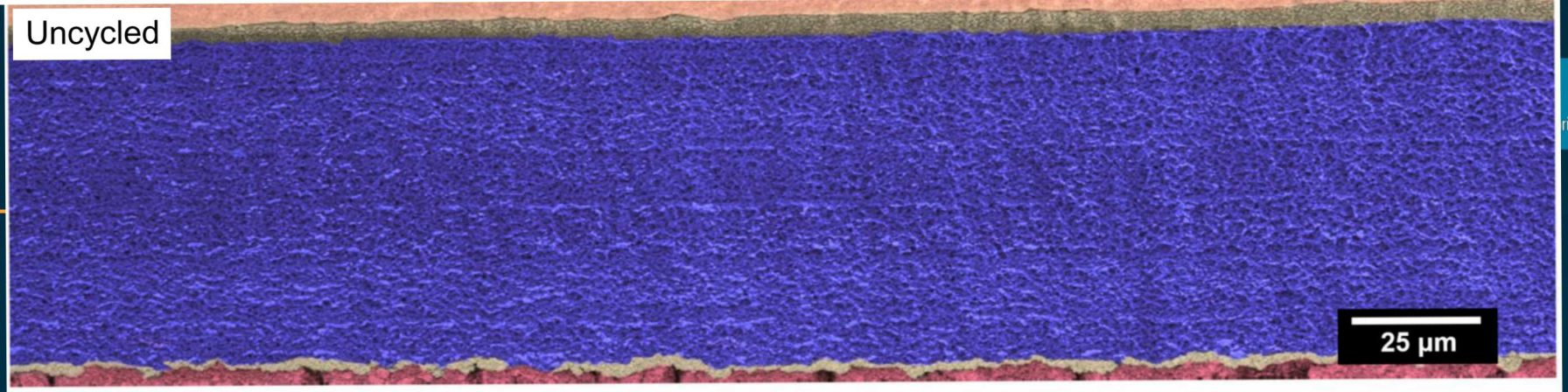
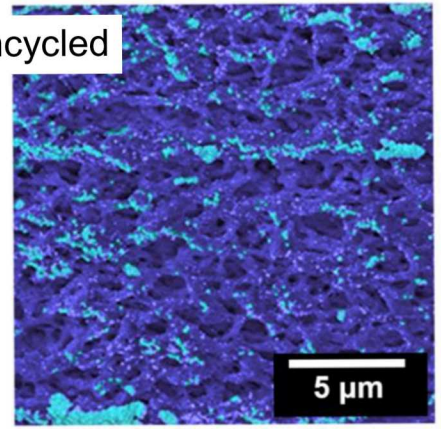
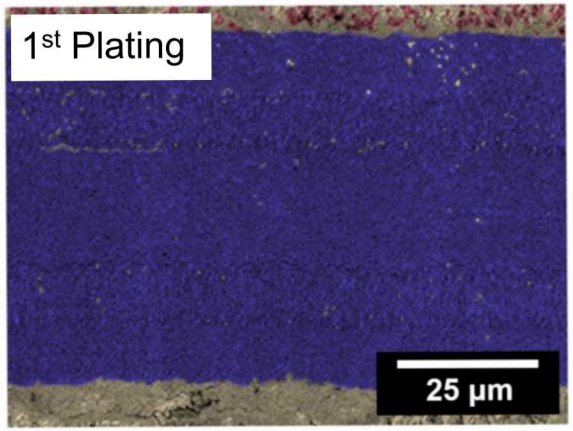
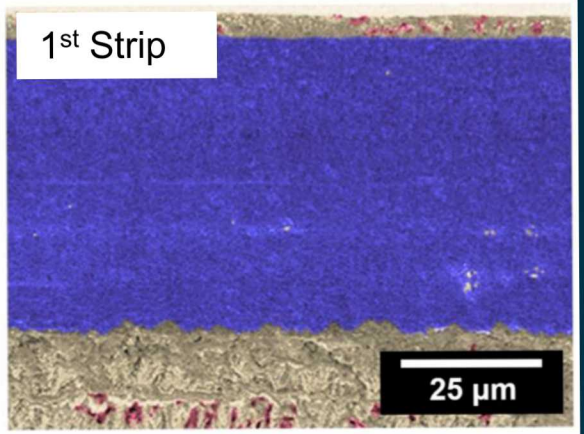
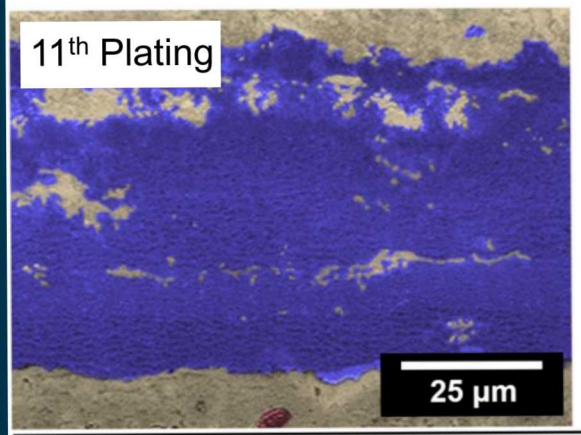
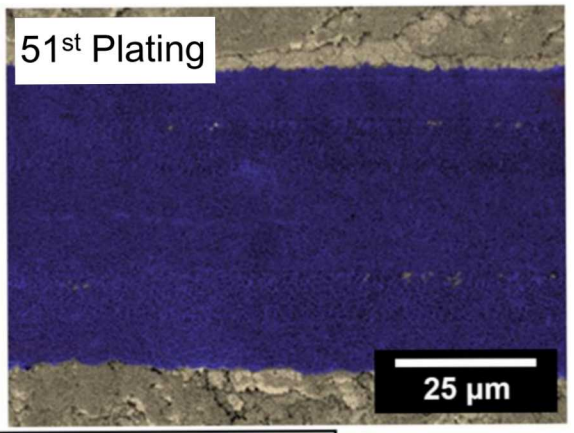

Uncycled
25 µm

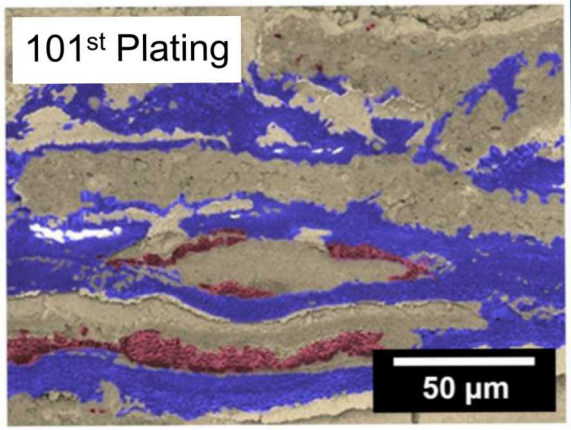

Uncycled
5 µm

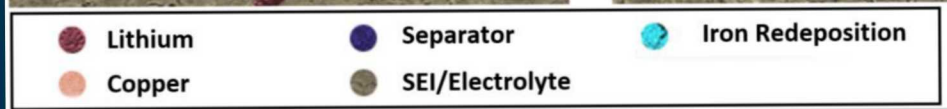

1st Plating
25 µm


1st Strip
25 µm

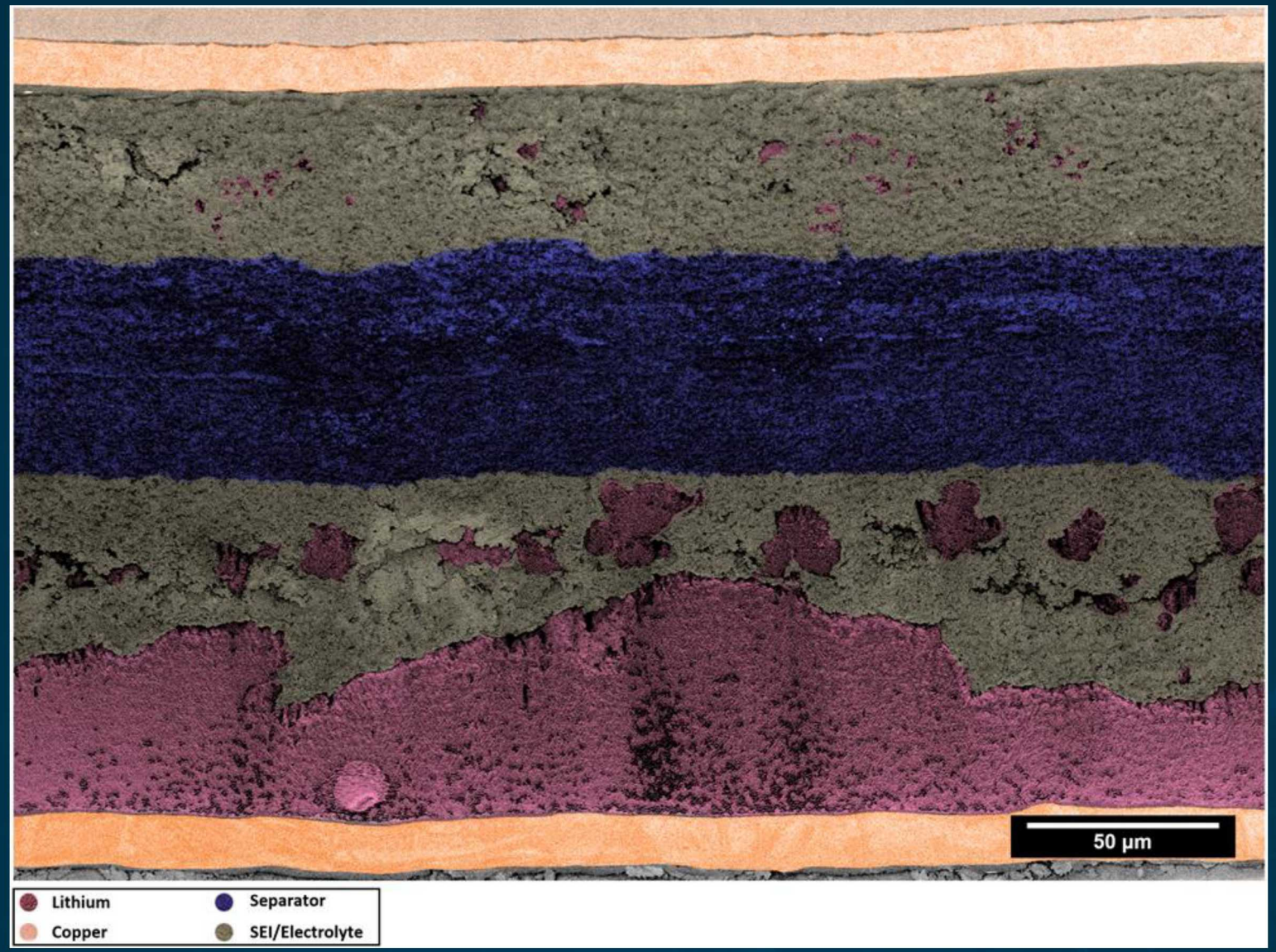

11th Plating
25 µm


51st Plating
25 µm


101st Plating
50 µm

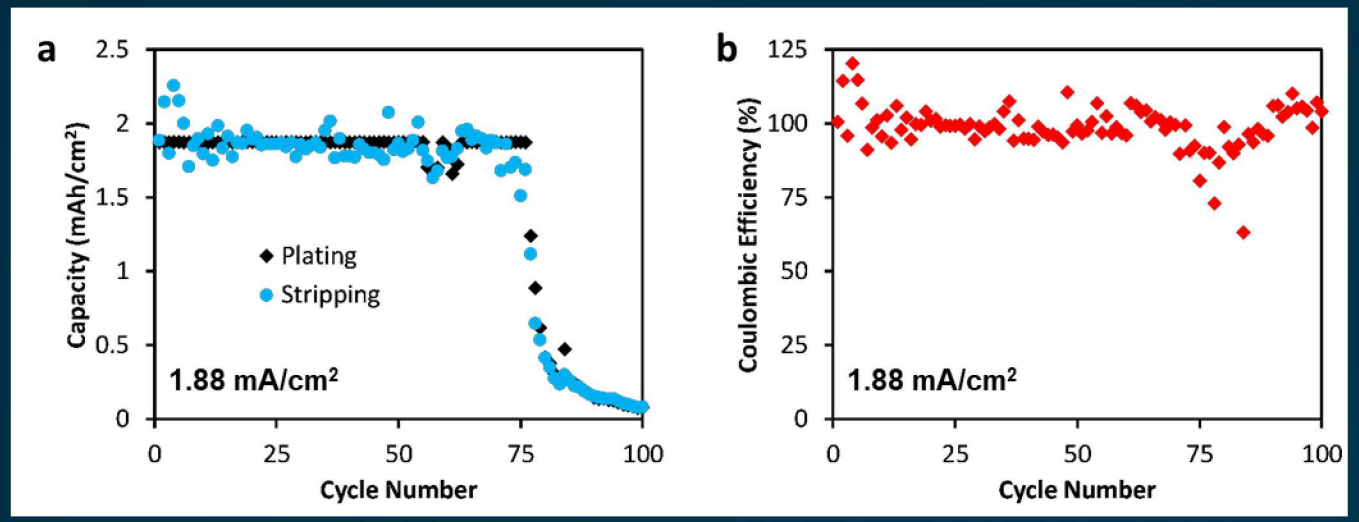

Lithium
Copper
Separator
SEI/Electrolyte
Iron Redeposition

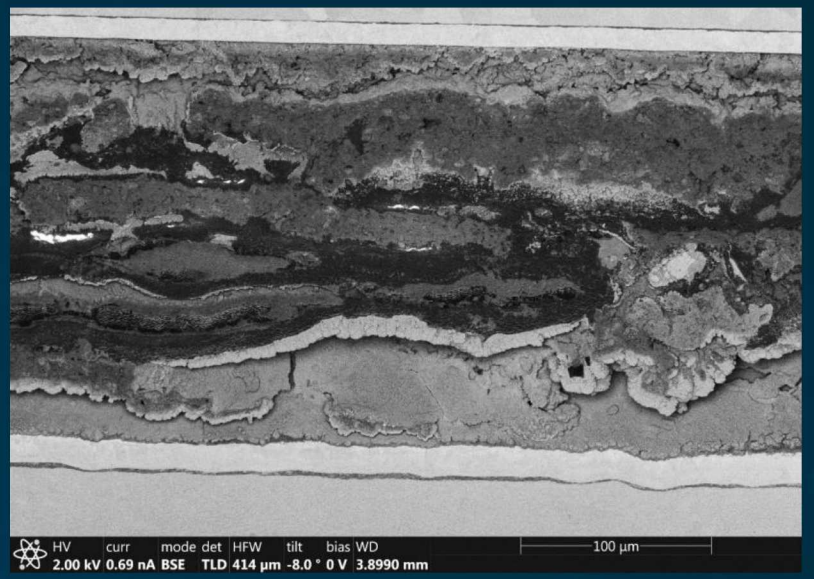
Low Rate Cycling: 101st Plating



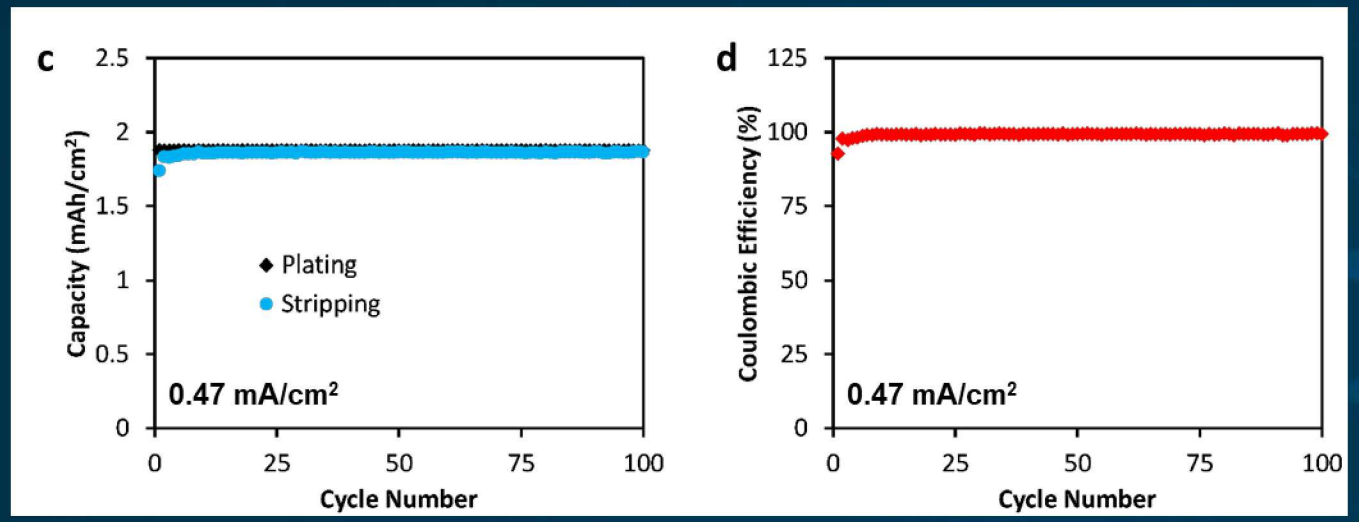
101st Li Plating in High *vs* Low Rate Cycling

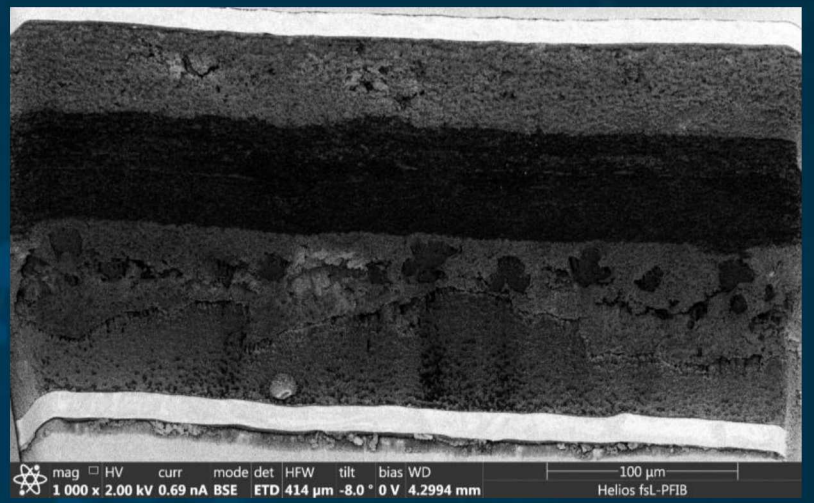
High Rate: 1.88 mA/cm²





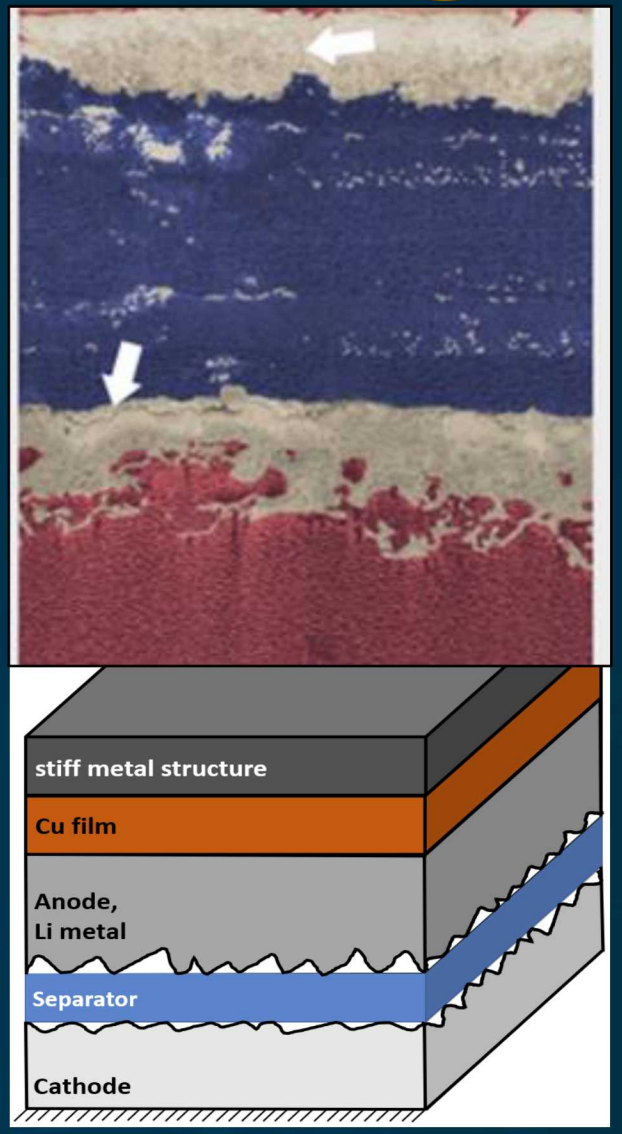
Low Rate: 0.47 mA/cm²





Conclusions

- Battery electrode interfaces are very heterogenous
- Cryogenic TriBeam characterization enables intact characterization of battery cross-sections
- Characterization of Li-metal battery electrodes after removal of the separator could lead to misinterpretations of the SEI/Li interface
- High-rate cycling of 2.8 M LiFSI in DME for two stacked Celgard 2325 separators found two failure mechanism that led to poor cycling performance:
  - SEI disfiguration of the Celgard separators
  - Cracks in SEI create reduced pathways for Li-ion transport through the battery stack
- Top down approach to characterizing solid electrolyte interphases from battery stacks



Zhang et al., *J Electro. Chem. Soc.* **166**(15) A3639 (2019).

Cryo-FIB at the Center for Integrated Nanotechnologies (CINT)

Dr. John Watt
watt@lanl.gov

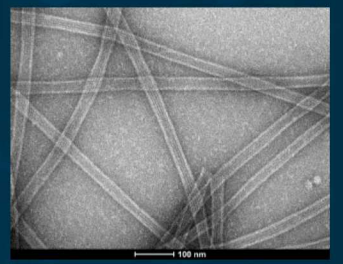
Sandia National Laboratories | Los Alamos NATIONAL LABORATORY EST. 1943

- Image materials and interfaces in their native solvated state across multiple length scales with minimal beam damage
- Biomacromolecules, polymers, nanoparticles, nanocomposites and their interfaces, and low-Z systems and interfaces

Vitrobot
Captures native, solvated state

Scios FIB/SEM
Analysis of surfaces & buried interfaces; 3D tomography

Leica Cryo SEM Stage
Includes cryo-FIB milling, lift out, and transfer to the TEM



Talos L120C CryoTEM
Dedicated low dose, low keV TEM for imaging of beam sensitive materials

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- Two proposal calls per year; proposals for short-term projects are accepted continuously
- Simple 2-page proposal
- Proprietary proposals for industry users

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- **In-Situ Characterization and Nanomechanics** – Developing and implementing world-leading capabilities to study the dynamic response of materials and nanosystems to mechanical, electrical, or other stimuli.
- **Nanophotonics & Optical Nanomaterials** – Synthesis, excitation, and energy transformations of optically active nanomaterials and collective or emergent electromagnetic phenomena (plasmonics, metamaterials, photonic lattices).
- **Soft, Biological & Composite Nanomaterials** – Synthesis, assembly, and characterization of soft, biomolecular, and composite nanomaterials that display emergent functionality.
- **Quantum Materials Systems** – Understanding and controlling quantum effects of nanoscale materials and their integration into systems spanning multiple length scales.

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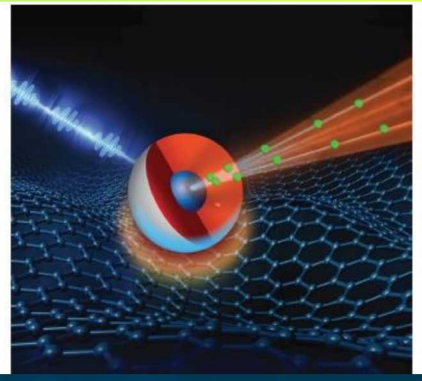

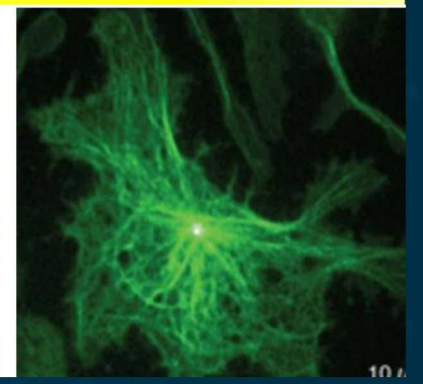

Acknowledgements

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science (OS) User Facility operated for the U.S. Department of Energy (DOE). Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

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