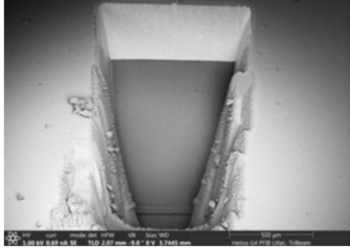
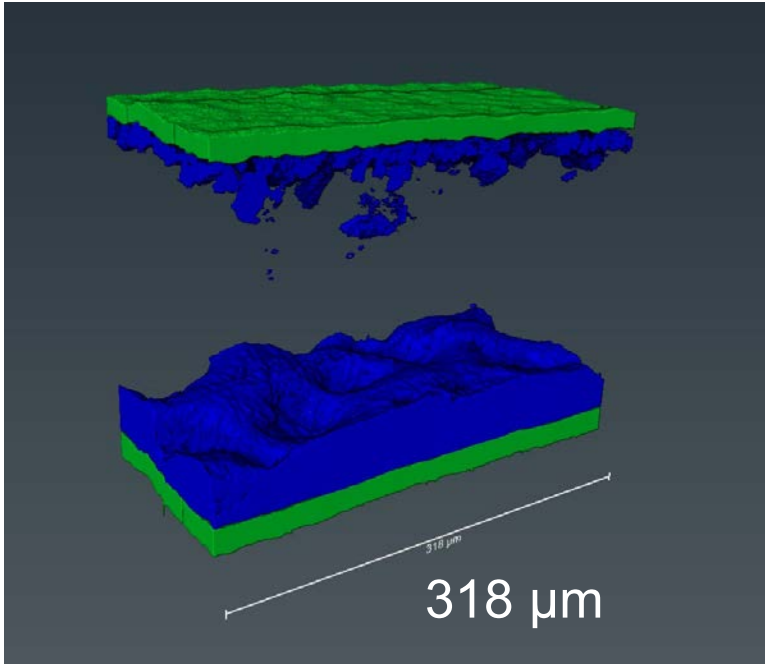


Cryogenic EM Across Length Scales for Li Metal Anode Batteries



Katherine L. Jungjohann

MRS Spring Meeting

April 12, 2023

Collaborators

Dr. Renae Gannon
Dr. Dave Johnson

Dr. Steven Randolph

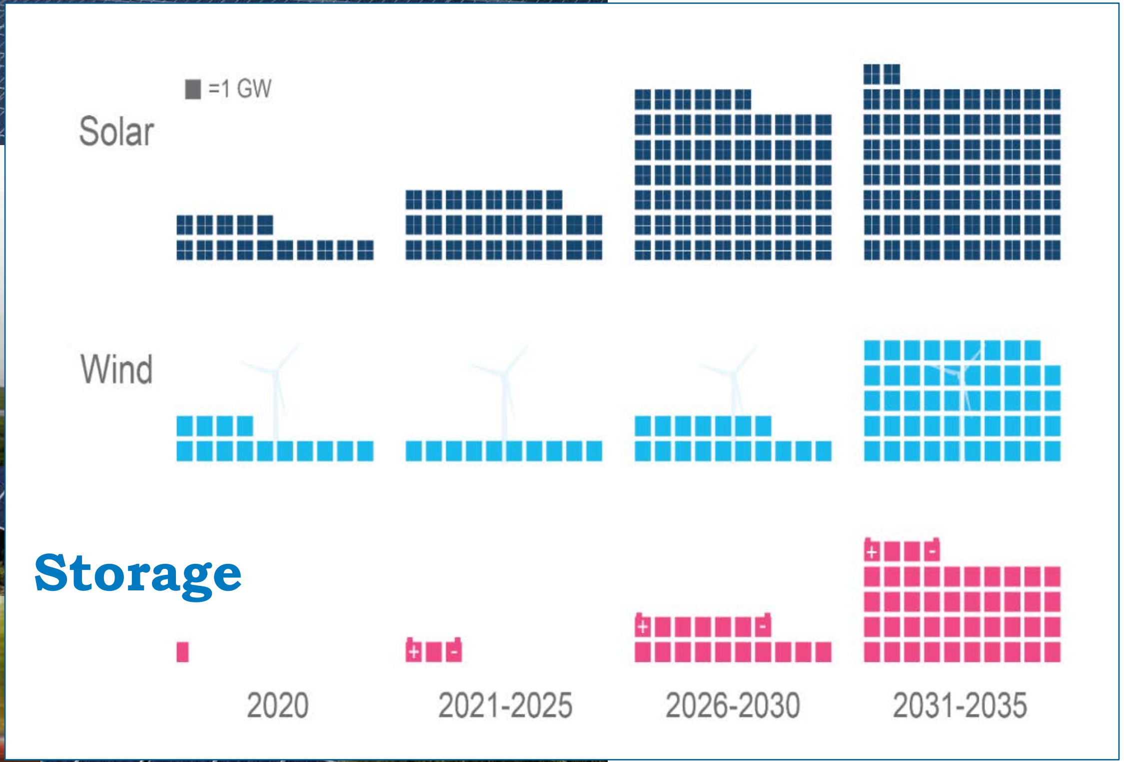
Dr. Katharine Harrison

Dr. Laura Merrill

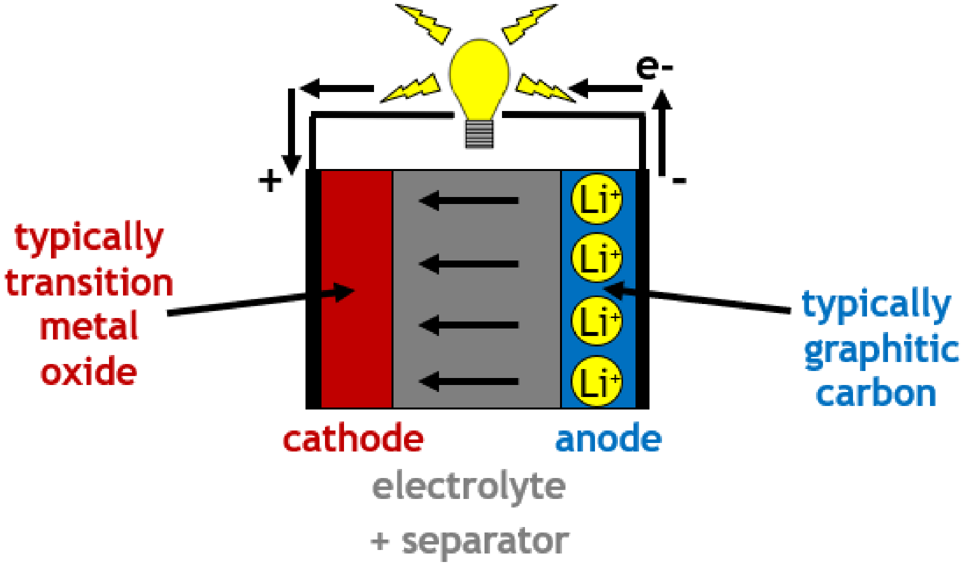

NREL
Transforming ENERGY

NREL Transforming ENERGY

Our Mission: Clean Energy Generation & Storage



Standard Li-Ion Batteries



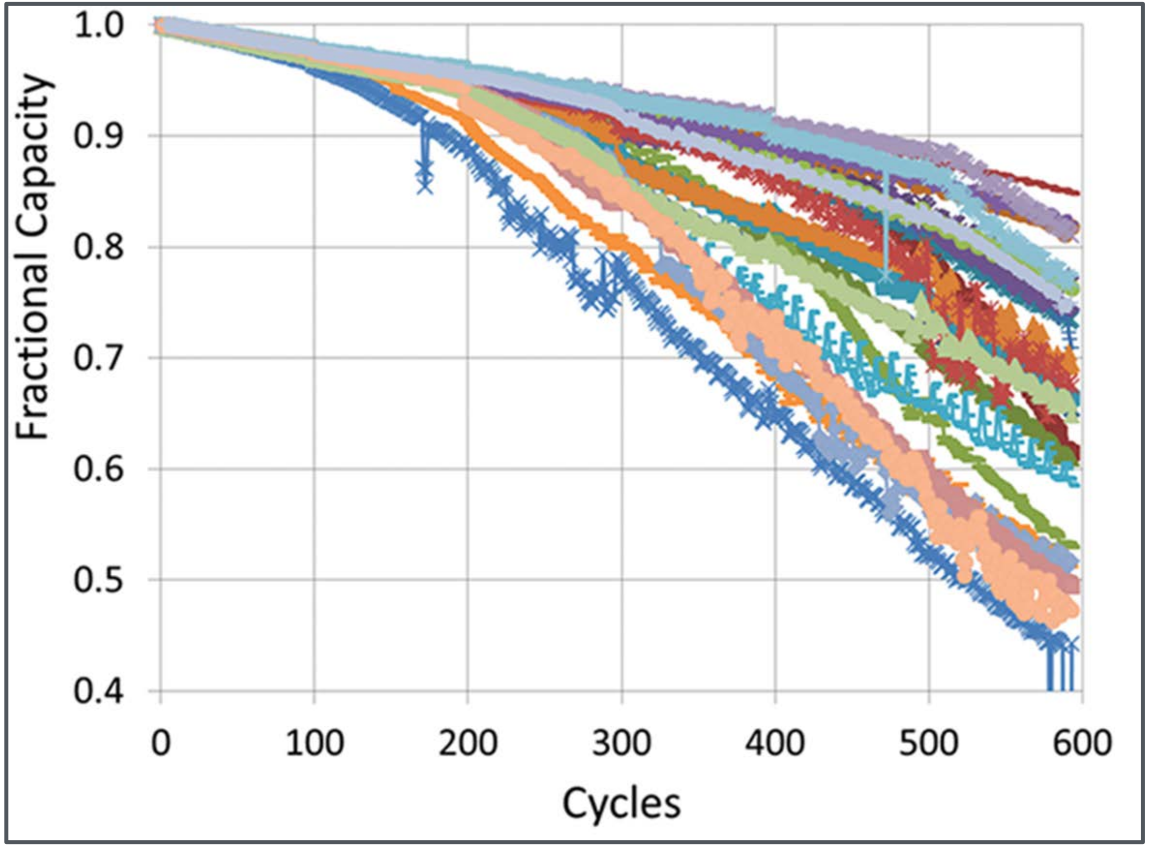
Discharging Battery

- Li^+ from the anode through the electrolyte and into the cathode
- e- move through the external circuit from the anode to the cathode (from - to + charge)

Variation on Performance of Identical Coin Cells

Storage

48 Batteries cycled to Failure

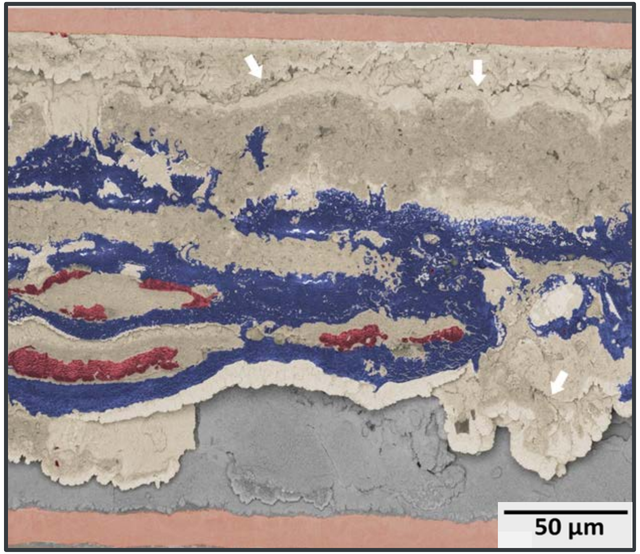


S. J. Harris, D. J. Harris and C. Li, J. Power Sources 342, 589 (2017)

Ideal Battery Characterization

Millimeter-to-Atomic Scale

Site-Specific: Structure – Composition – Chemistry – Bonding – Properties



What happened there?

Why did it happen there?

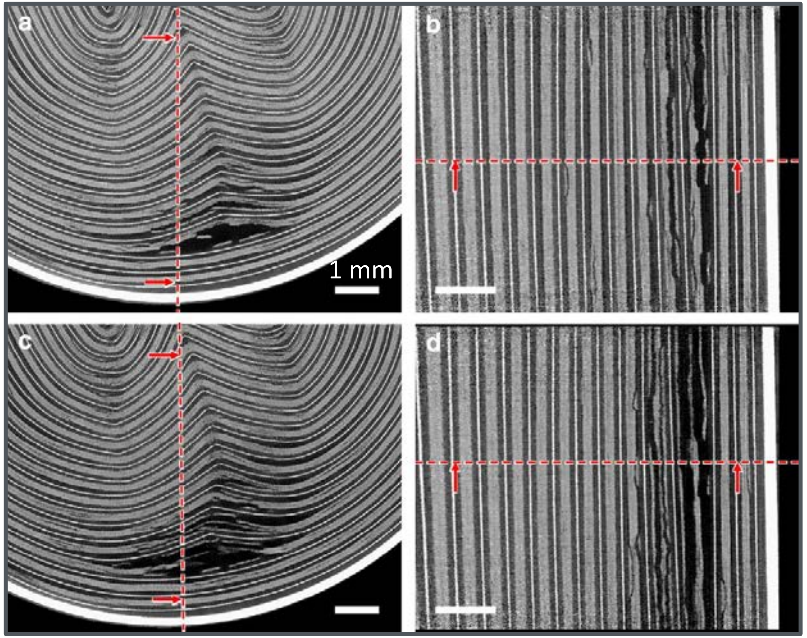
How likely is that happing over the entire electrode/cell?

What can we do about it?

Reality of Battery Characterization

Thermal Runaway

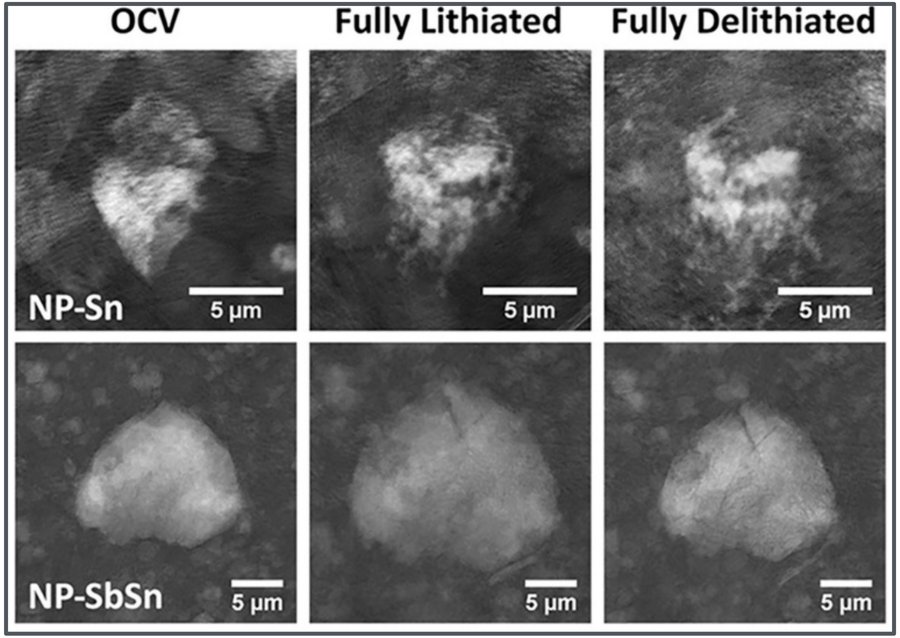
Operando Synchrotron X-ray Computed Tomography (CT)



Finegan et al. *Nat Commun 6, 6924 (2015)*

Nonporous Anode Charge Cycling

Operando Transmission X-ray Microscopy (TXM)



Lin et al. *ACS Nano 14, 14820 (2020)*

Millimeter-to-Atomic Scale

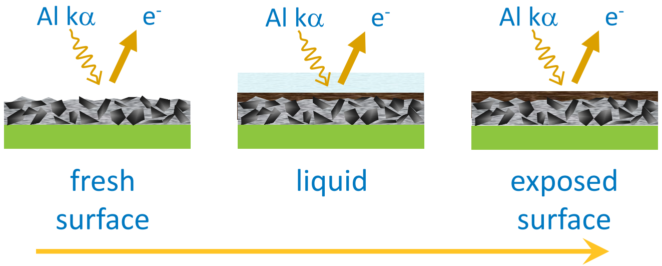
Site-Specific: Structure – Composition – Chemistry – Bonding – Properties

Reality of Battery Characterization

Specs ProvenX NAP-XPS

- XPS measurements on solids and liquid surfaces (~25 mbar)
- In situ heating/cooling
- Air-free transfer capability
- In-situ mass spectrometry

XPS in-situ solid|liquid interface measurements



In-situ and Operando XPS
Glenn Teeter
April 13, 8:15-8:45 am
Moscone Level 2, Rm 2006

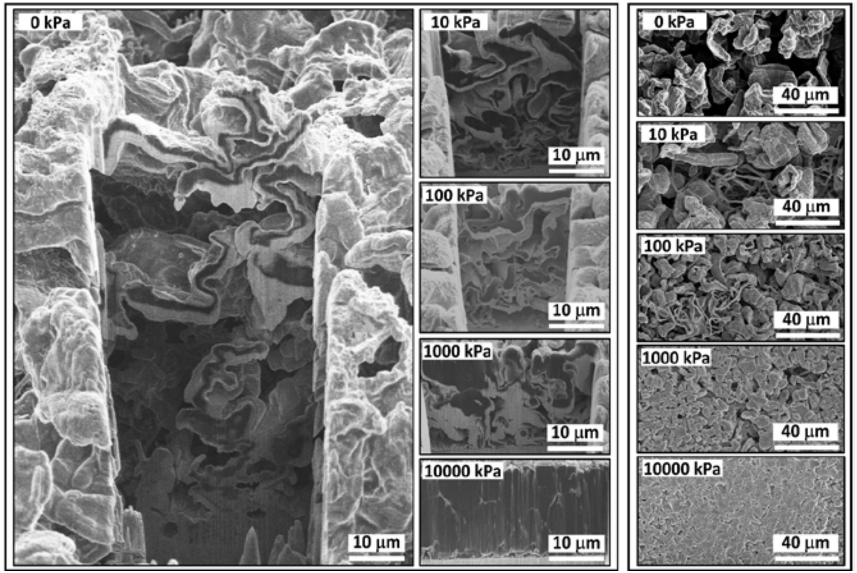
Millimeter-to-Atomic Scale

Site-Specific: Structure – Composition – Chemistry – Bonding – Properties

Reality of Battery Characterization

Controlled Pressure for Dense Li Deposits

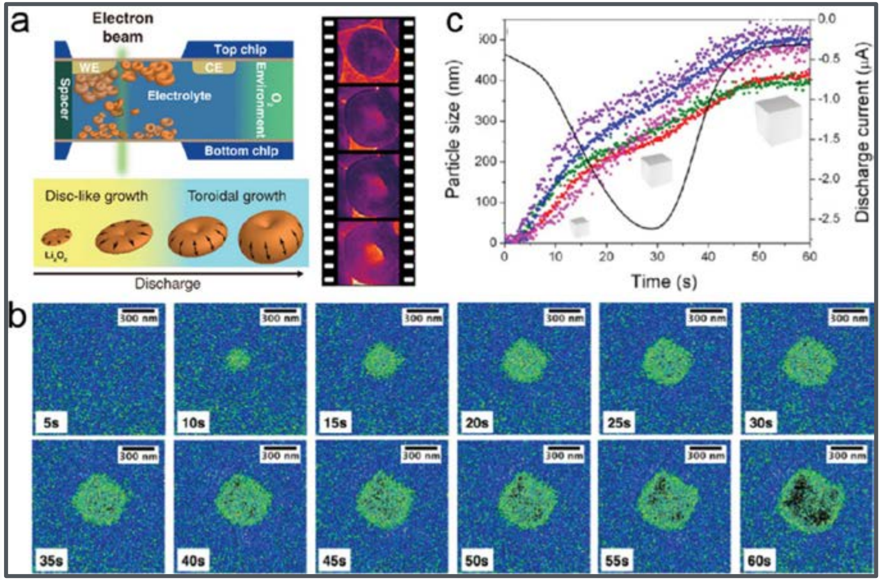
Cryo Focused Ion Beam / Scanning Electron Microscopy



Harrison et al., *ACS Appl. Mater. Interfaces 13, 31668 (2021)*

Electrochemical Growth of NaO_2 Nanocrystal

Operando Scanning Transmission Electron Microscopy (STEM)



Lutz et al. *Nano letters 18, 1280 (2018)*

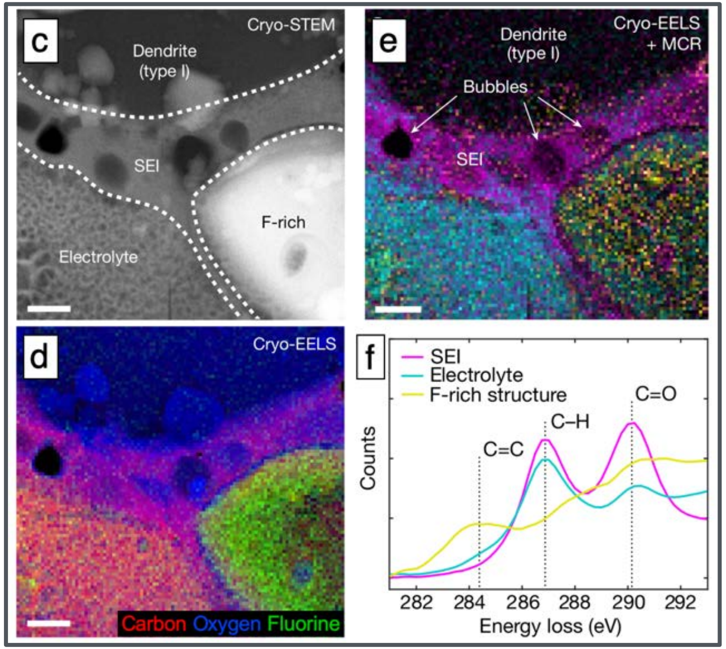
Millimeter-to-Atomic Scale

Site-Specific: Structure – Composition – Chemistry – Bonding – Properties

Reality of Battery Characterization

Electrode Electrolyte Interfaces

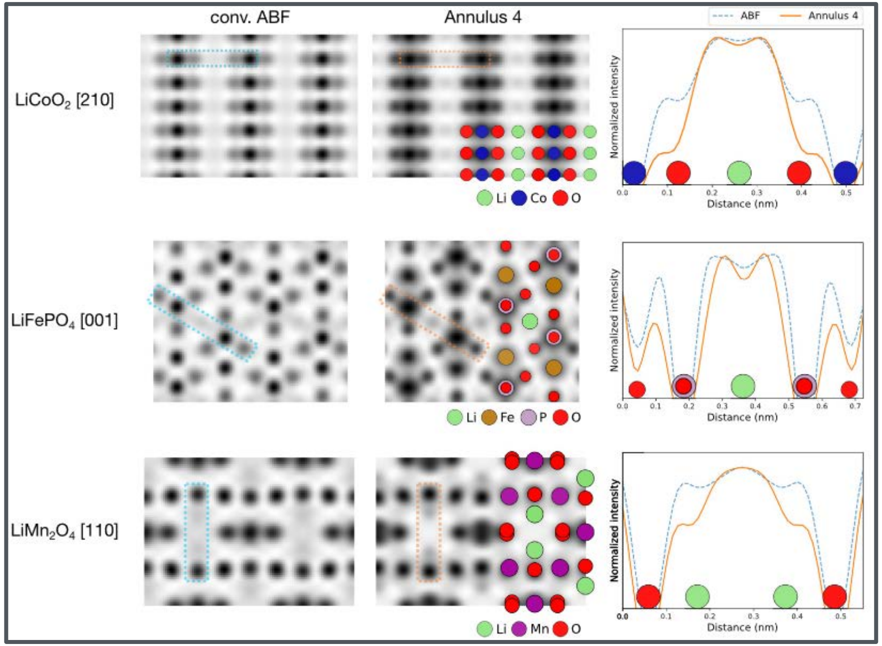
Cryo STEM & Electron Energy Loss Spectroscopy (EELS)



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

Imaging Light Elements in Cathodes

High-Resolution Scanning Transmission Electron Microscopy (STEM)

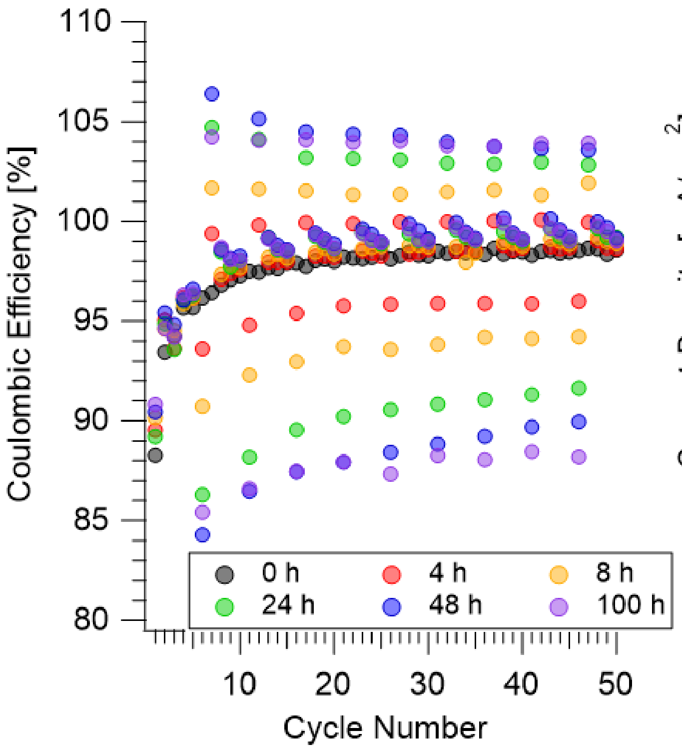


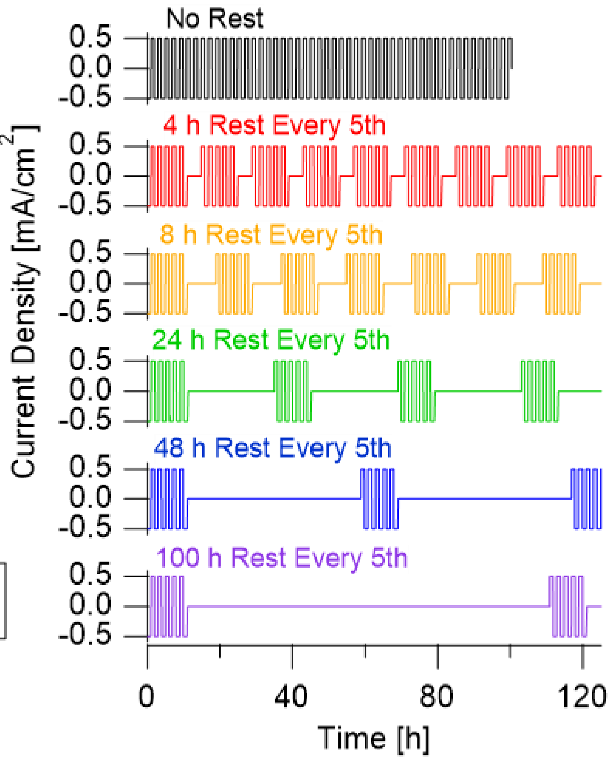
Ooe et al. *Ultramicroscopy 202, 148 (2019)*

Millimeter-to-Atomic Scale

Site-Specific: Structure – Composition – Chemistry – Bonding – Properties

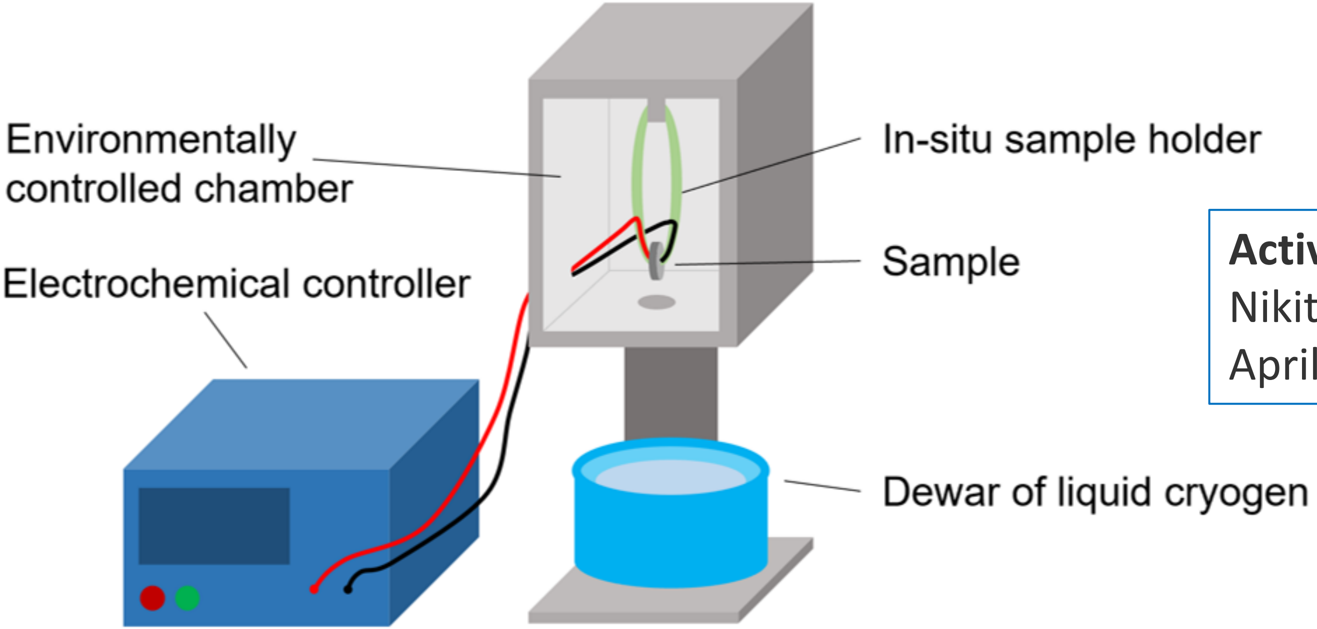
Interested in Active Electrode States





Merrill et al. *In Preparation (2023)*

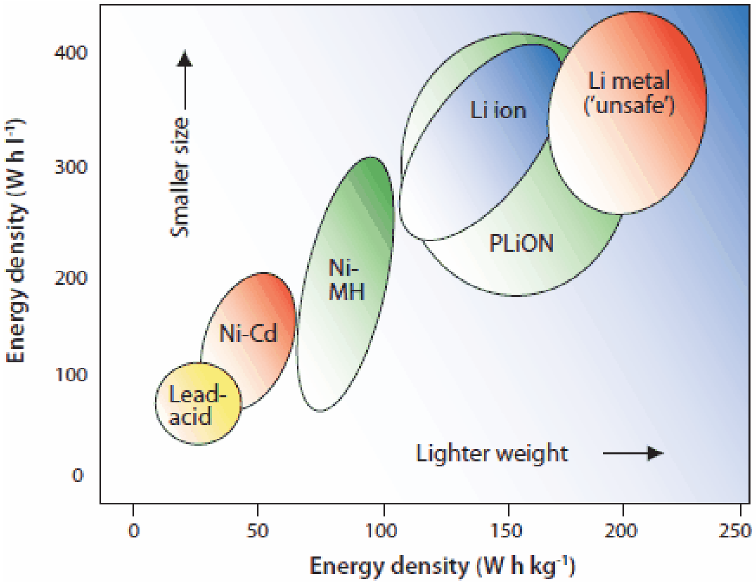
Interested in Active States



Dutta et al. Microsc. and Microanal. 28, 2162 (2022).

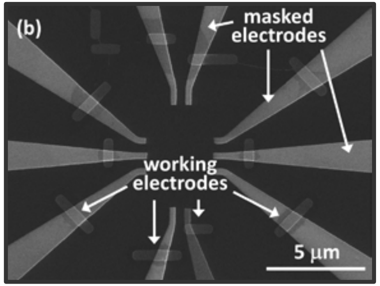
Active Battery Interfaces
Nikita Dutta
April 11, 2:15-2:45 pm

Value of Li-Metal Anodes & EM Characterization



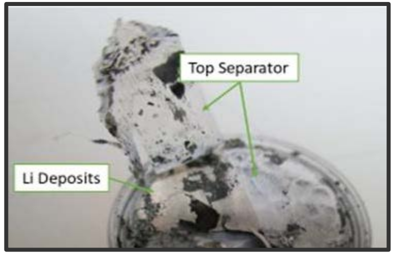
J.-M. Tarascon and M. Armand *Nature*
DOI: 10.1038/35104644

Electrochemical S/TEM



Nanoscale Electrodes

Ex-situ & Cryo SEM/FIB



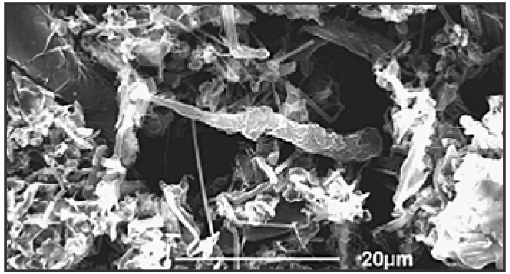
Individual Electrodes

Cryo Laser SEM/FIB

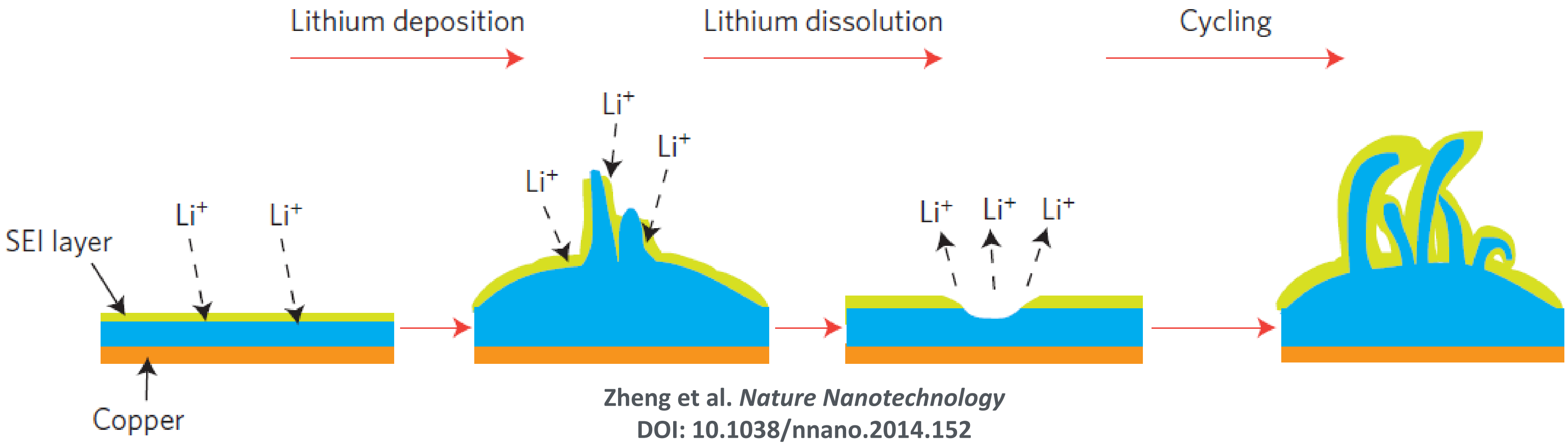
Coin cell

Rechargeable Li Metal: Chemical & Mechanical

- Uncontrolled morphology → many problems
  - Short circuits = fire
  - Excessive solid electrolyte interphase (SEI) = low Coulombic efficiency, high impendence, and Li consumption
  - Li gets stranded and disconnected = “dead” Li



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

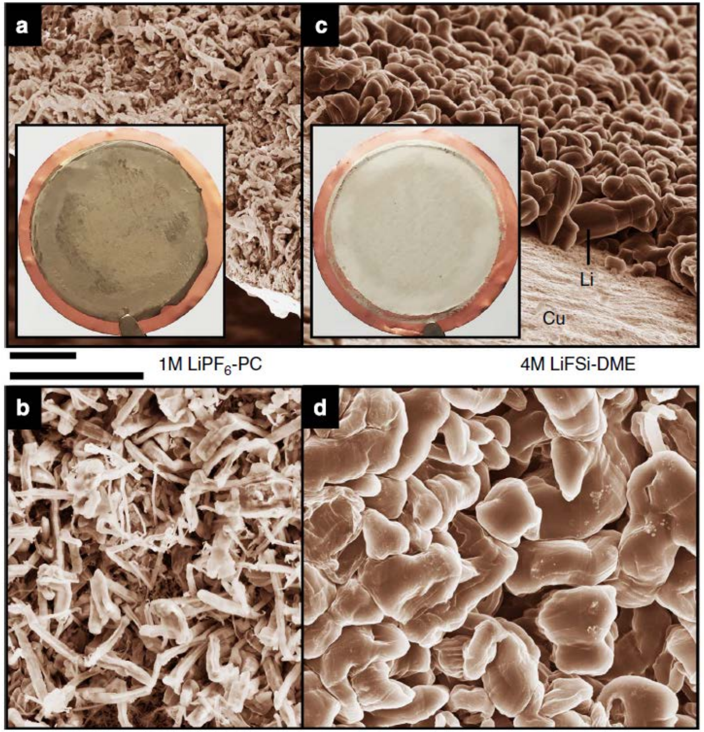


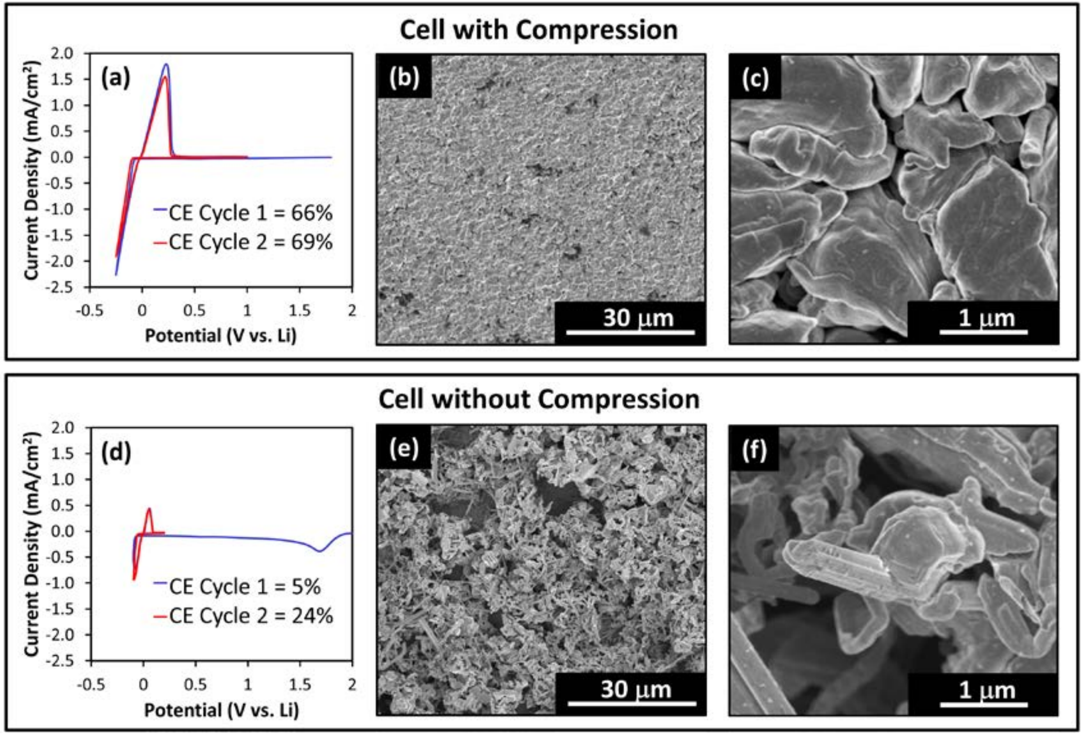
Zheng et al. *Nature Nanotechnology*
DOI: 10.1038/nnano.2014.152

Lithium Morphology Impacted by Contact Pressure

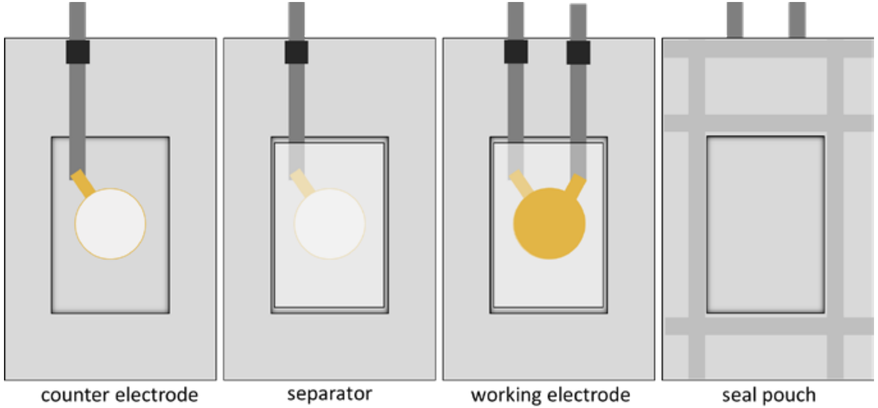
Qian et al. *Nature Communications* DOI: 10.1038/ncomms7362

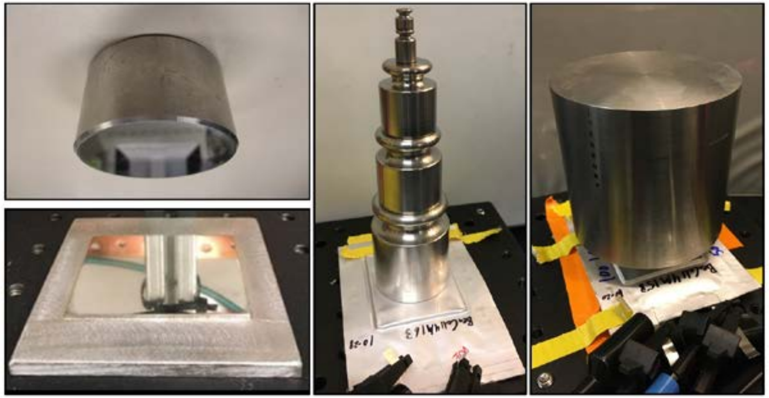
Harrison et al. *ACS Nano* 10.1021/acsnano.7b05513

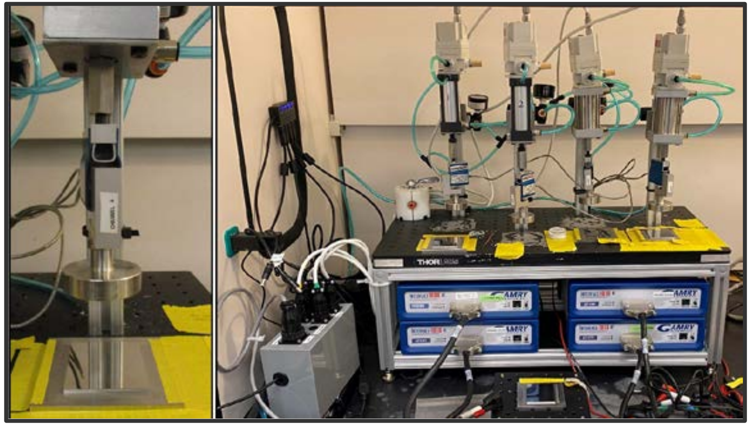


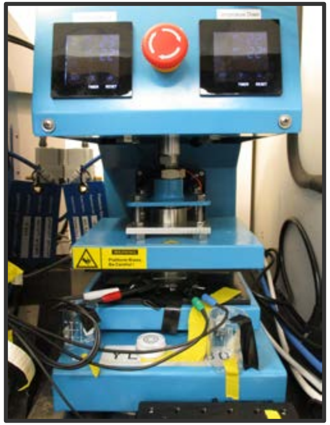


Controlled Pressure on Electrodeposited Li







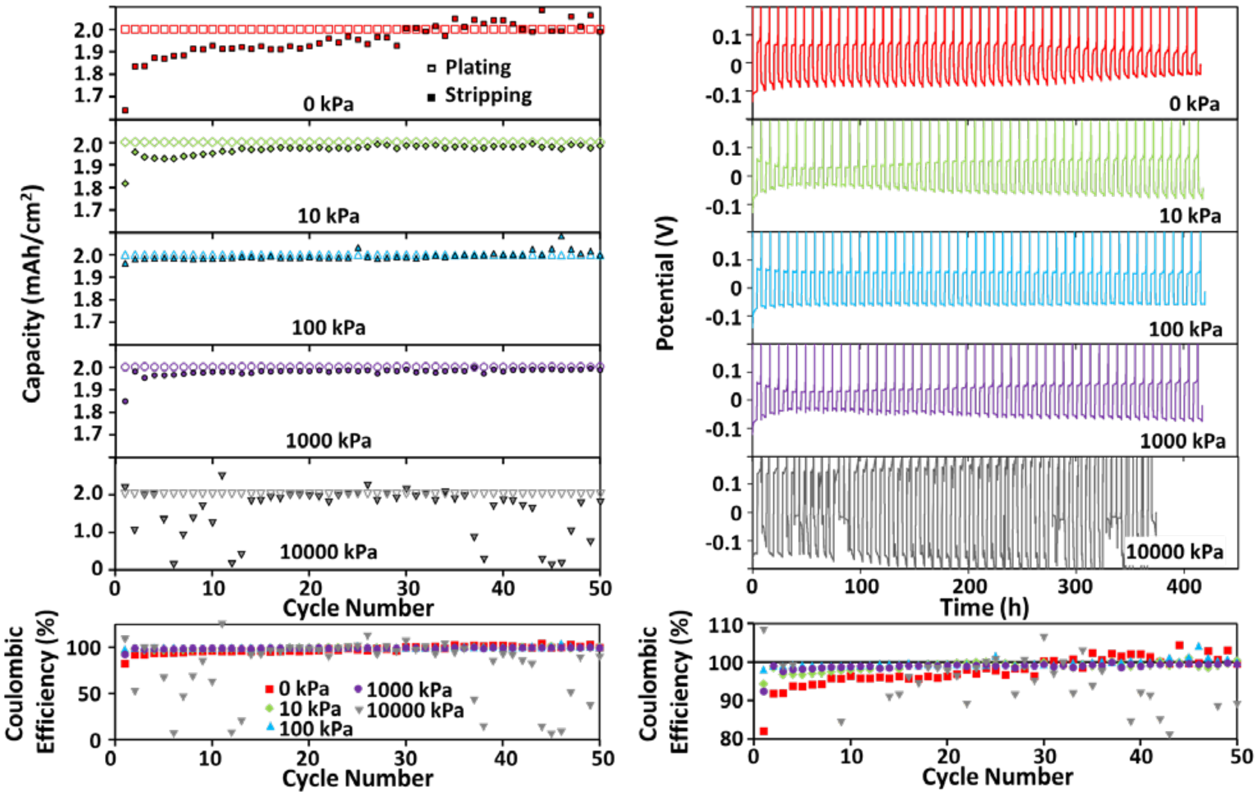


Sandia National Laboratories

Low Current: 0.5 mA/cm^2

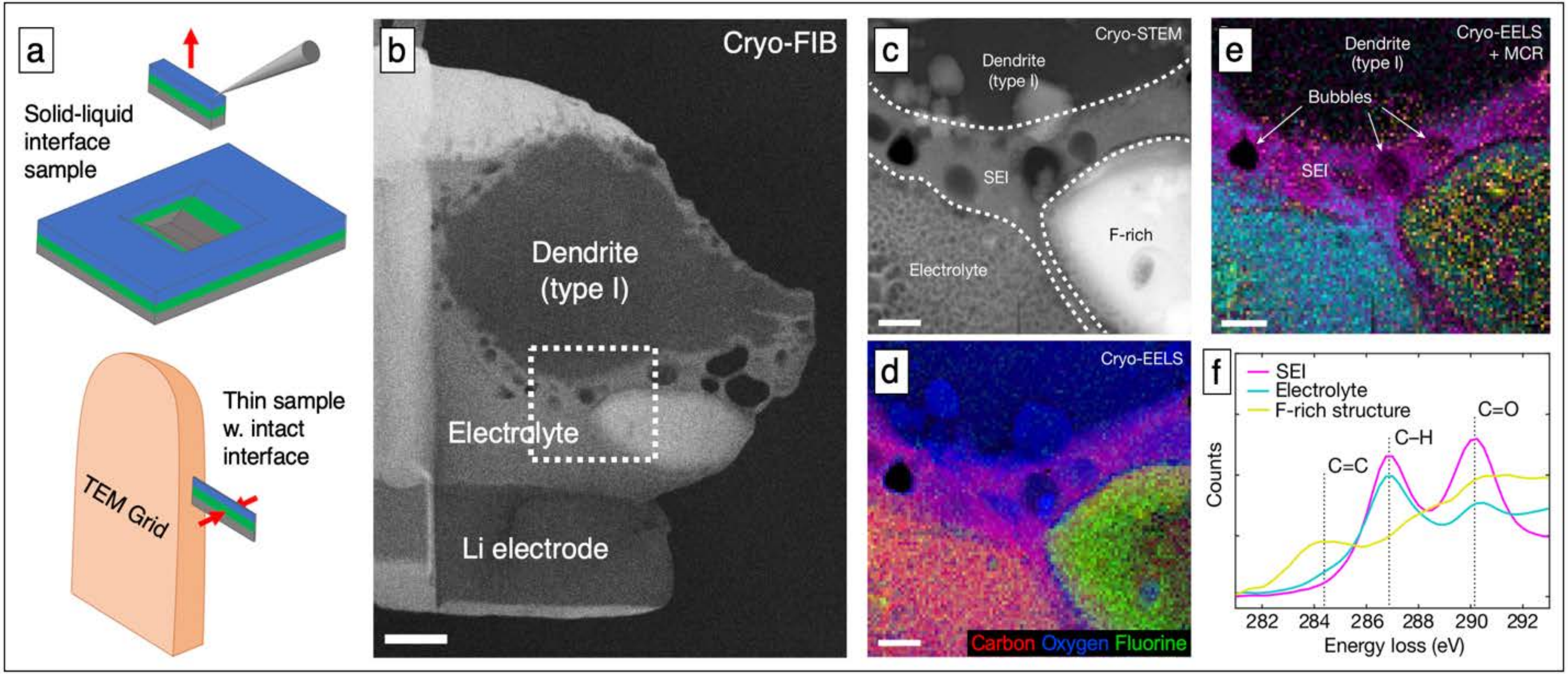
Effects of Pressure on Li Metal: Low Current

- Cycling stability generally increases with increasing pressure until 10,000 kPa
- 10,000 kPa is too high and causes increased overpotential and loss of cycling stability
- Transport might be limited locally at high pressure where pores can close
- CE generally improves with pressure but 100 and 1,000 kPa are similar



Harrison et al., ACS Appl. Mater. Interfaces 13, 31668 (2021)
DOI: 10.1021/acsami.1c06488

Cryogenic Scanning Transmission Electron Microscopy



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

Characterization: Cryogenic SEM/FIB & TEM

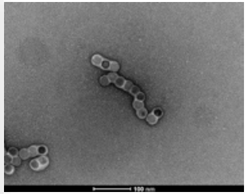
- **Plunge-freeze or slowly freeze coin cell battery electrodes**
- **Inert transfer from glovebox into cryo SEM/FIB**
- **Cross-sectioning in cryo SEM/FIB to observe electrodeposited Li metal**

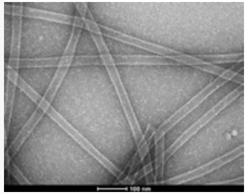
Dr. John Watt
watt@lanl.gov
cint.lanl.gov **or**
nsrcportal.sandia.gov

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

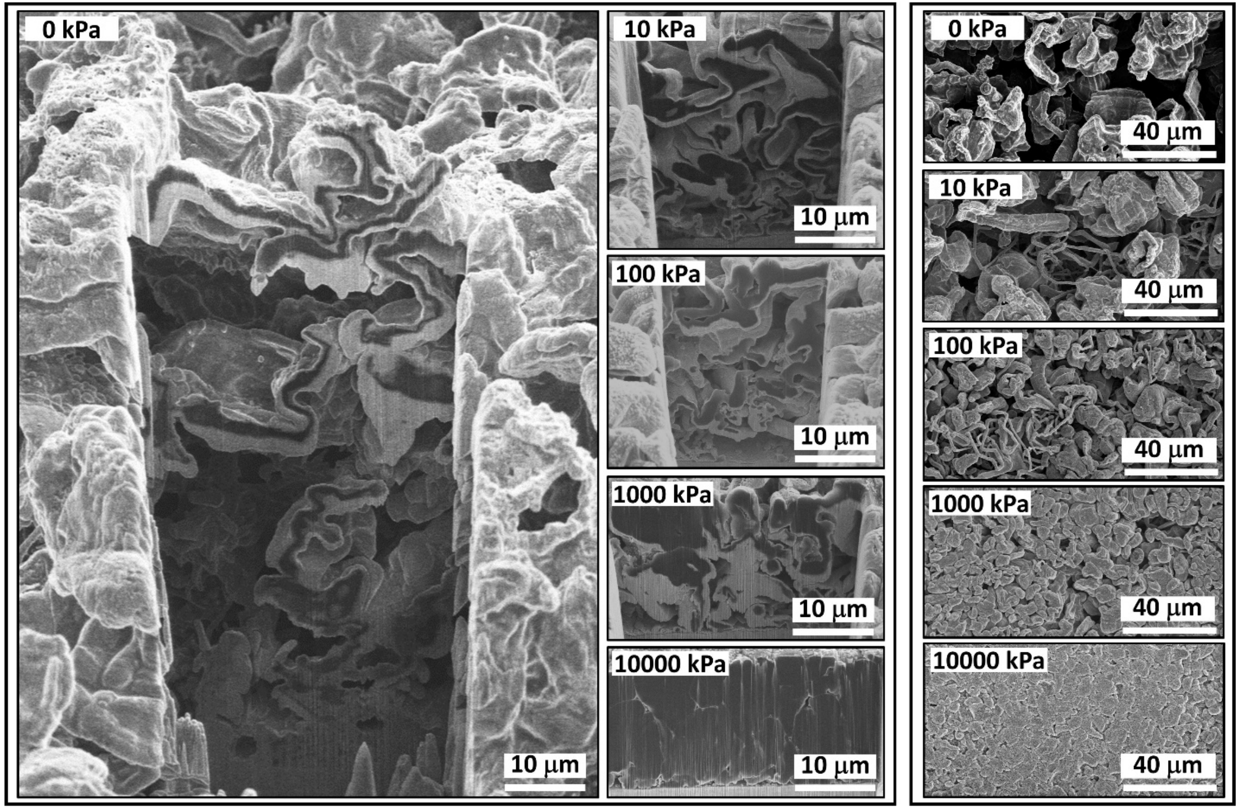
Low Current: 0.5 mA/cm^2

Pressure at Low Current: 1st Li Deposition Step

- Morphology improves drastically with pressure (even for 10000 kPa)

Pressure (kPa)	Average CE (%) First Cycle
0	82.3 ± 6.2
10	90.5 ± 4.1
100	97.5 ± 0.6
1000	93.6 ± 5.3
10000	106.2 ± 1.6

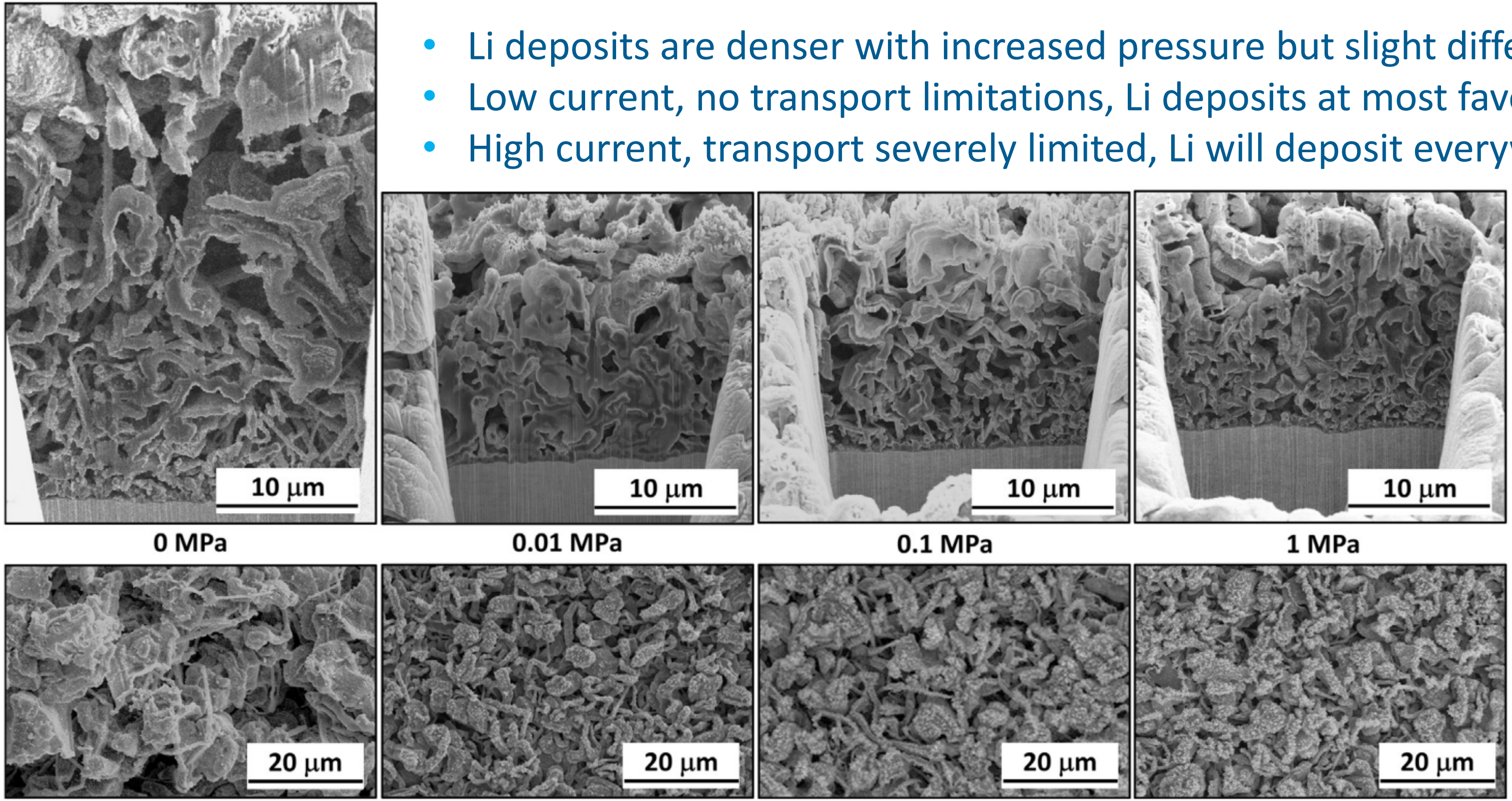
Pressure (kPa)	Thickness 1st Plating (μm)
0	91
10	33
100	30
1000	22
10000	17



Harrison et al., ACS Appl. Mater. Interfaces 13, 31668 (2021)
DOI: 10.1021/acsami.1c06488

Pressure at High Current: 1st Li Deposition Step

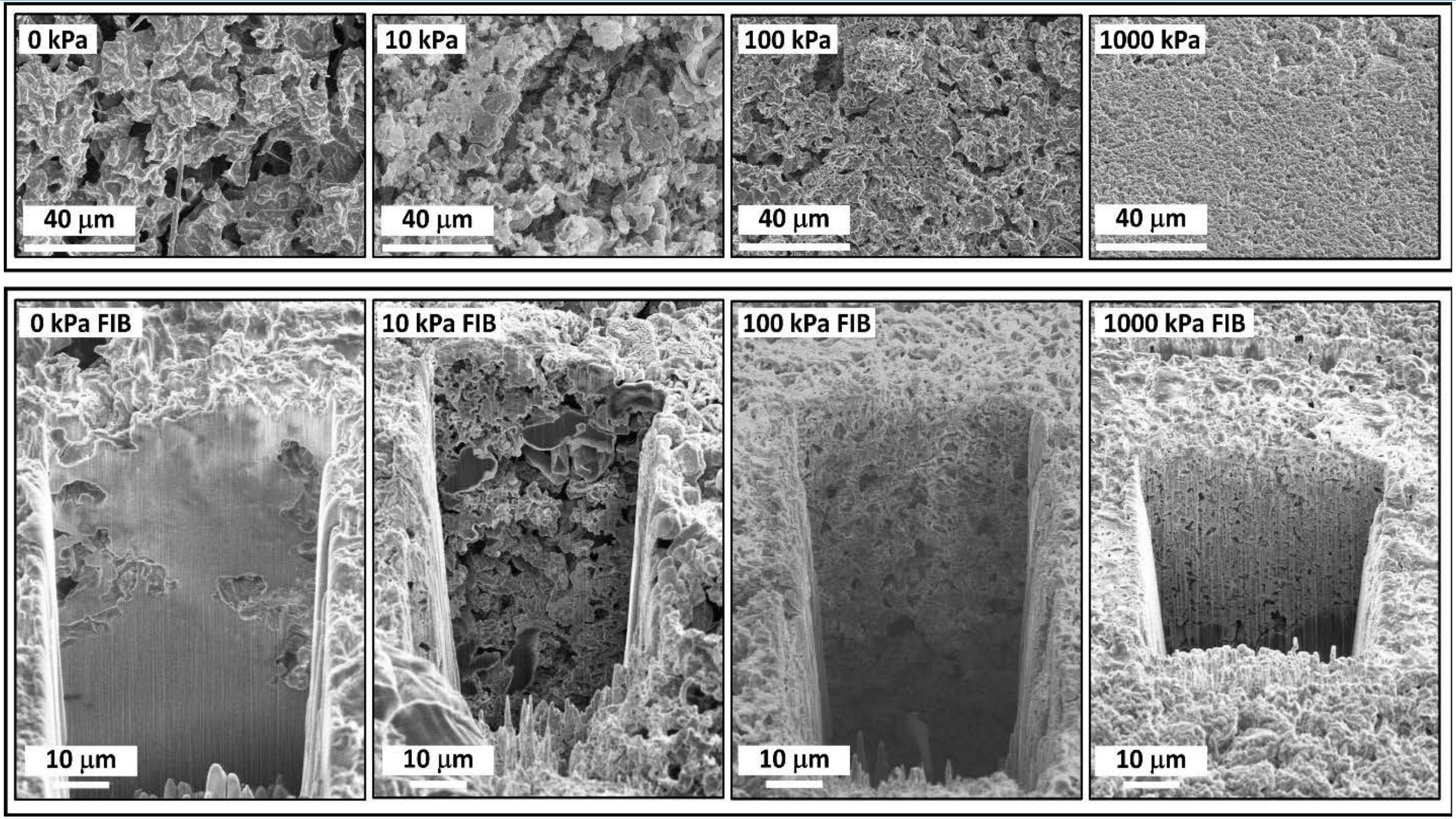
- Li deposits are denser with increased pressure but slight difference
- Low current, no transport limitations, Li deposits at most favorable sites
- High current, transport severely limited, Li will deposit everywhere



Harrison et al., iScience 24, 103394 (2021)
DOI: 10.1016/j.isci.2021.103394

Low Current: 0.5 mA/cm^2

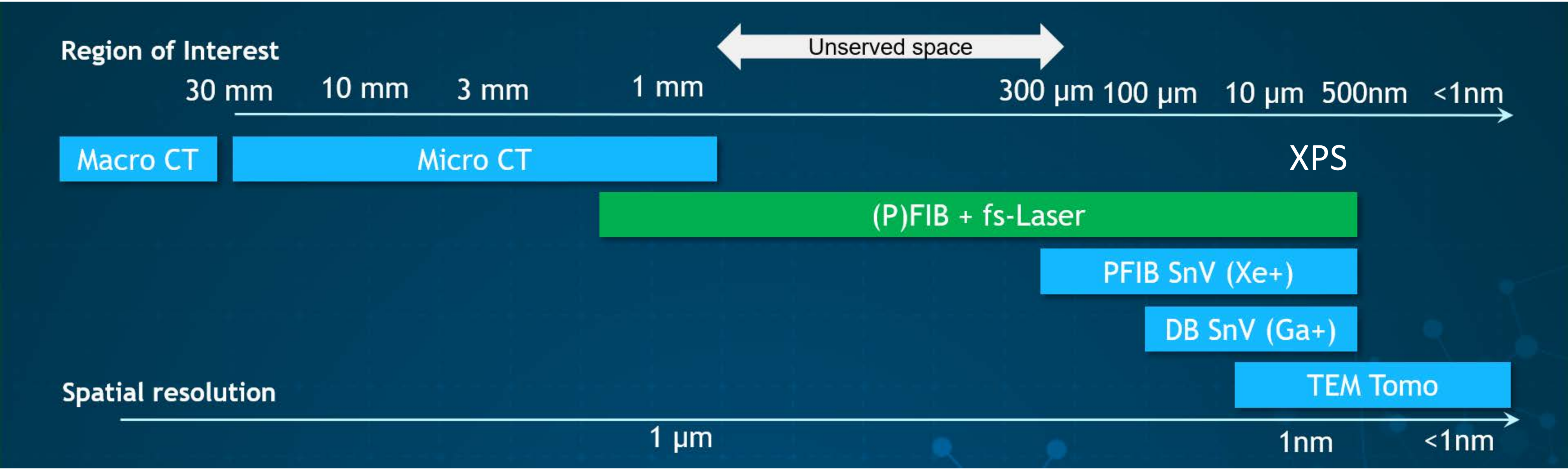
Pressure at Low Current: 51st Li Deposition Step



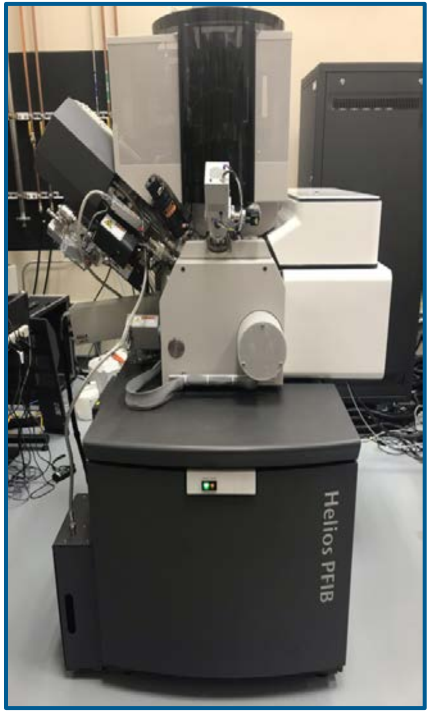
How to Achieve Ideal Battery Characterization?

Millimeter-to-Atomic Scale

Site-Specific: Structure – Composition – Chemistry – Bonding – Properties

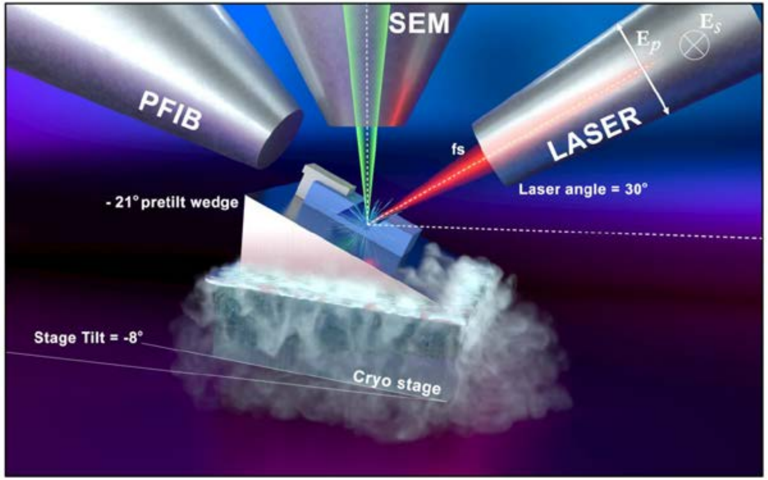


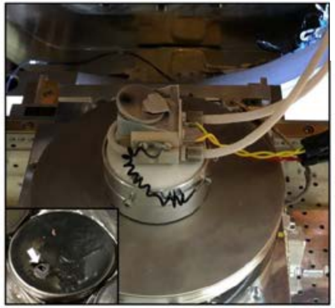
Cross-Sectioning without Battery Disassembly

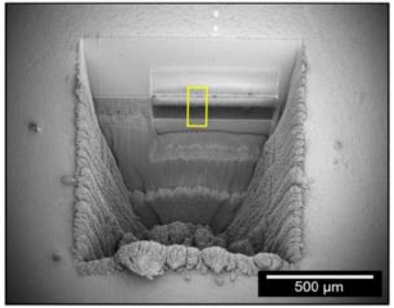


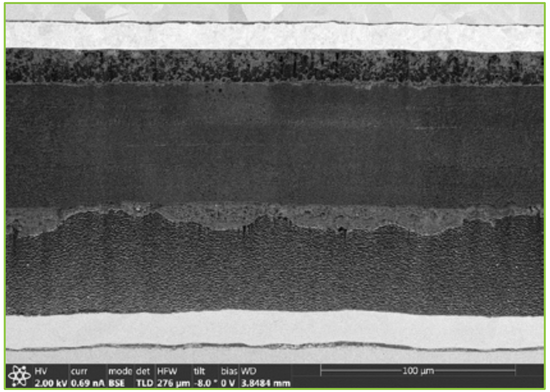
Helios Laser Plasma FIB

fs laser mills 15,000x faster than Ga-ion FIB

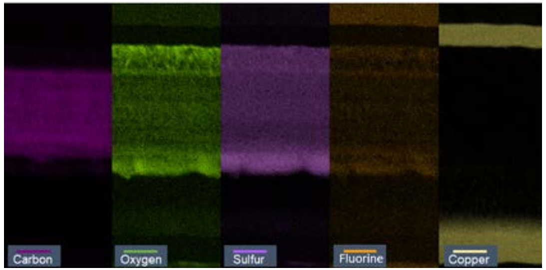






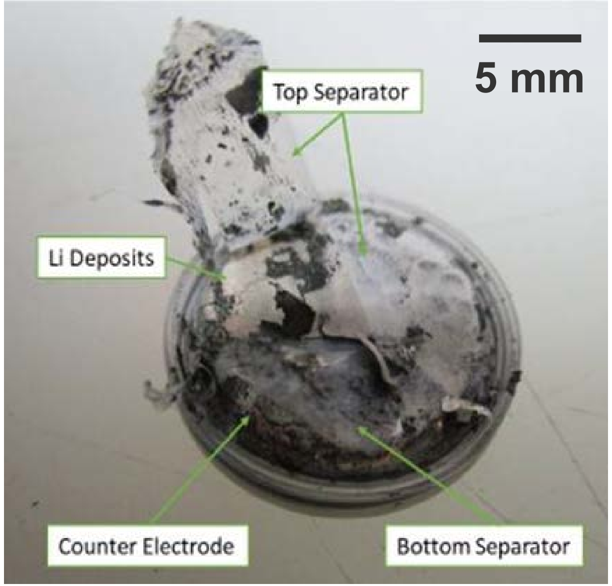


- Two Celgard 2325 Separators
- Li/SEI/electrolyte layers found



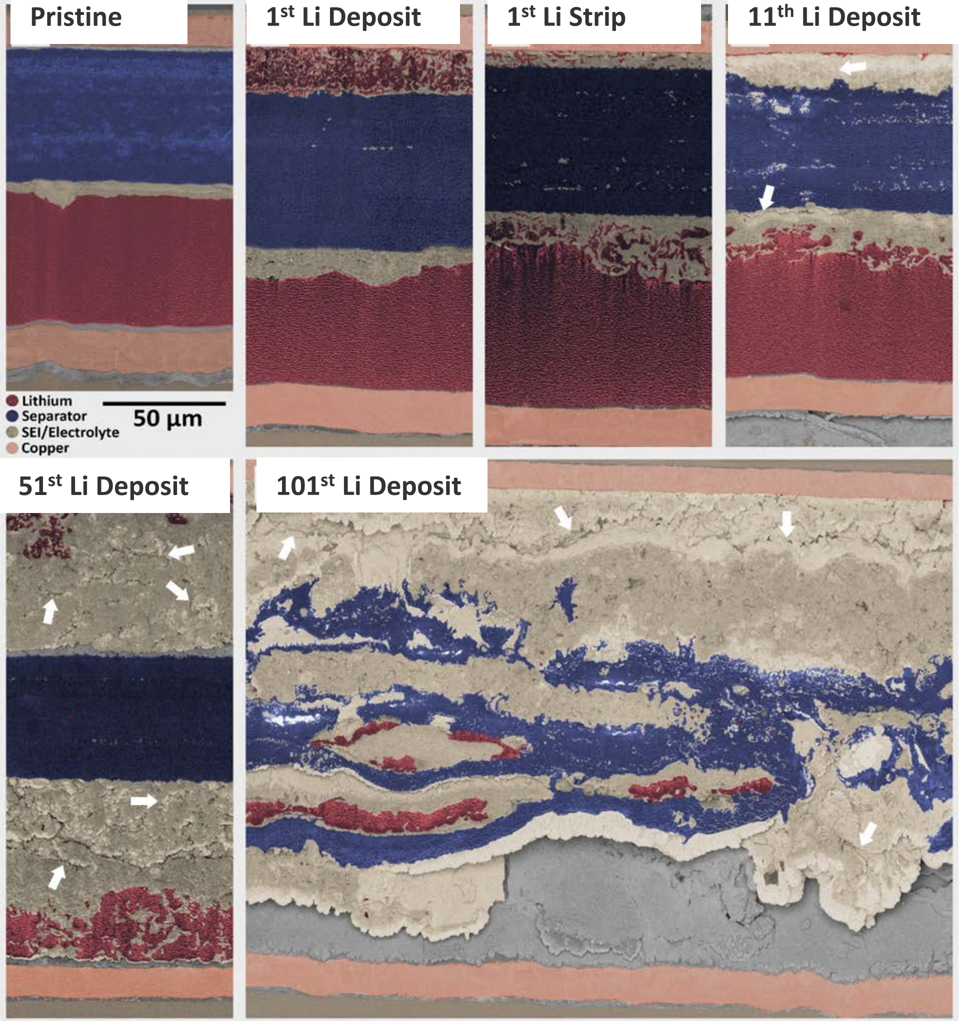
Jungjohann et al., ACS Energy Lett. 6, 2138 (2021)
DOI: 10.1021/acsenergylett.1c00509

Failure after Cycling



2.8 M LiFSI in DME
Two Celgard 2325 separators
Cycled at 1.88 mA/cm²
Capacity: 1.88 mAh/cm²

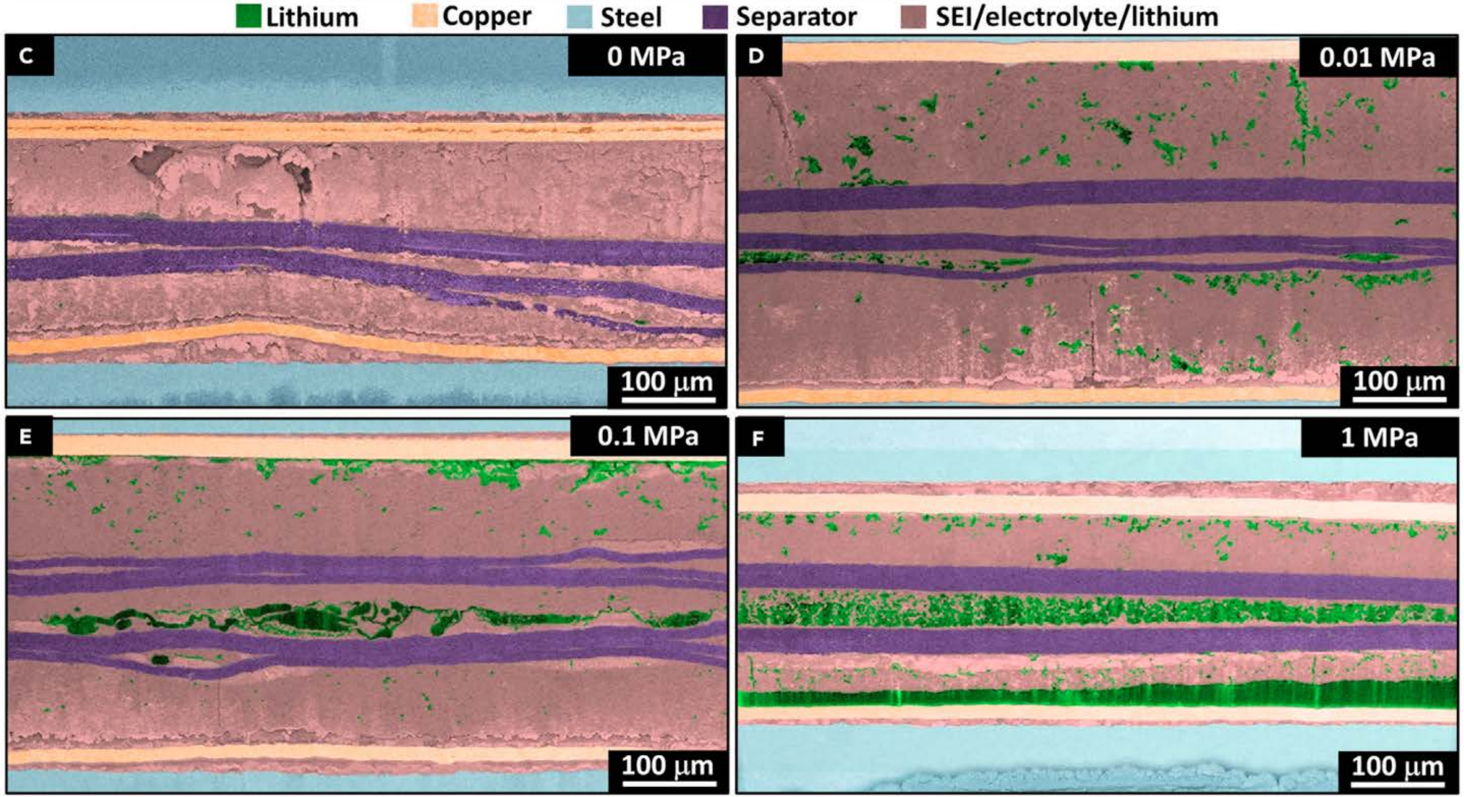
Jungjohann et al., ACS Energy Lett. 6, 2138 (2021)
DOI: 10.1021/acsenergylett.1c00509



High Current: 4 mA/cm^2

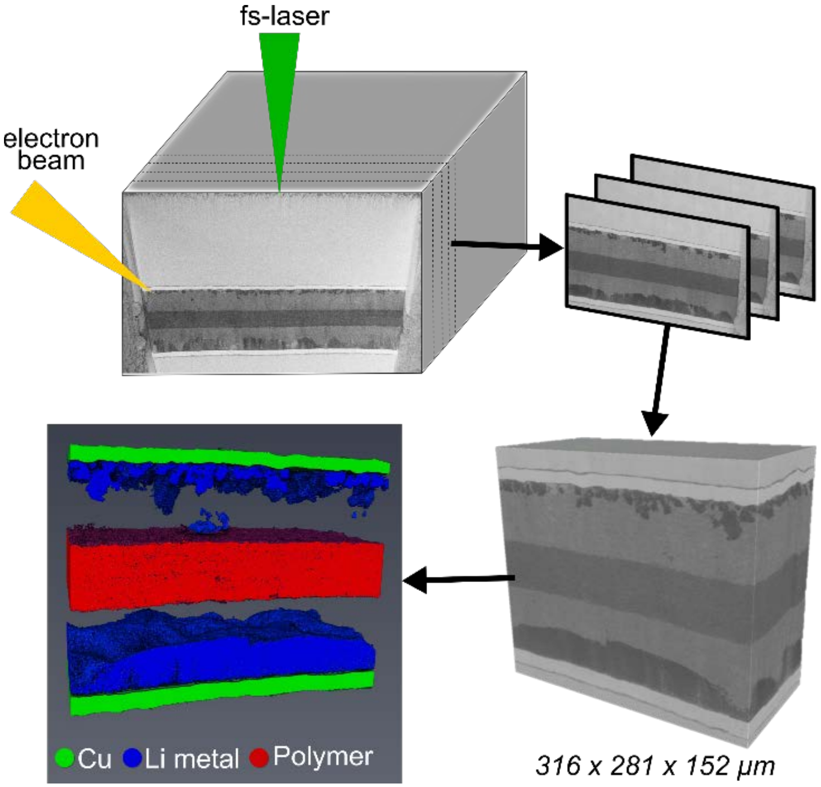
Pressure at High Current: 51st Li Deposition Step

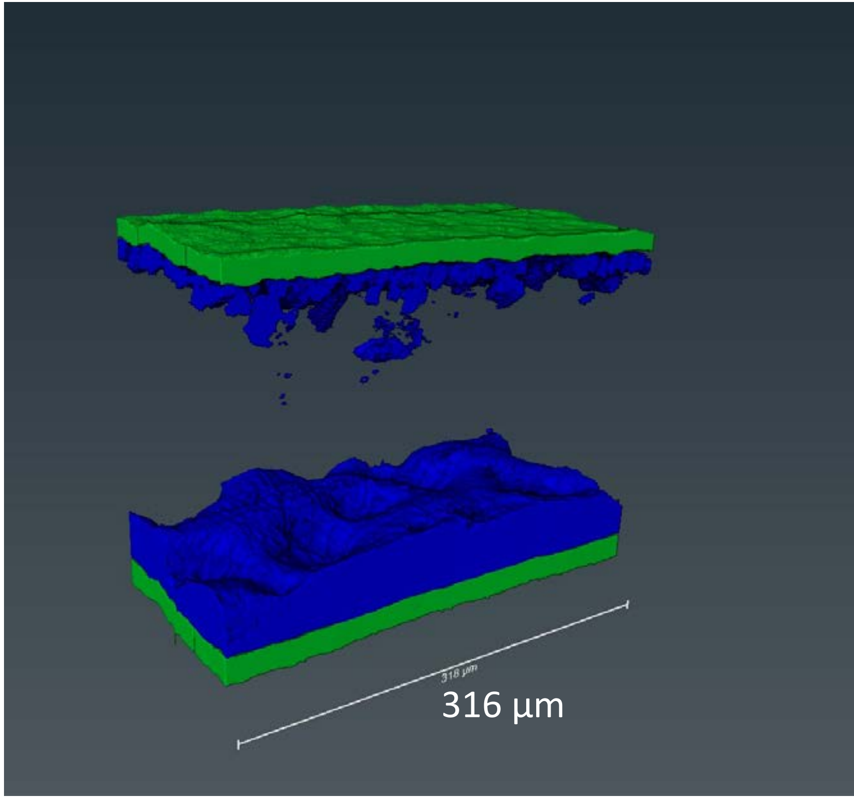
Pressure (MPa)	Thickness 51st Plating (μm)
0	189
0.01	318
0.1	274
1.0	188



Harrison et al., iScience 24, 103394 (2021)
DOI: 10.1016/j.isci.2021.103394

fs Laser Slice-N-View of Battery Stack

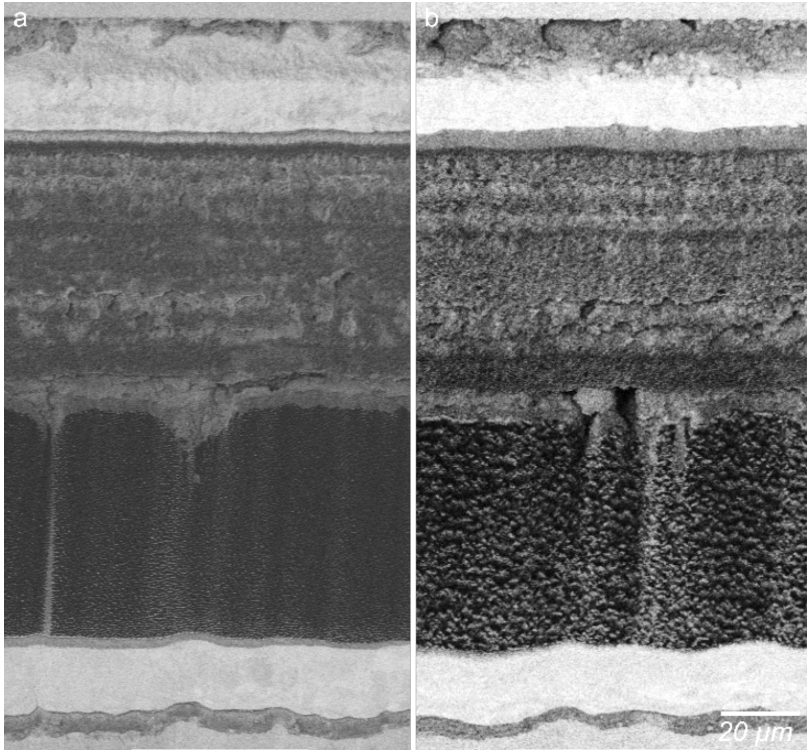




R. Gannon et al., (2023) In Preparation

fs Laser Wavelength Difference for Polishing

Pristine Li Metal Cell

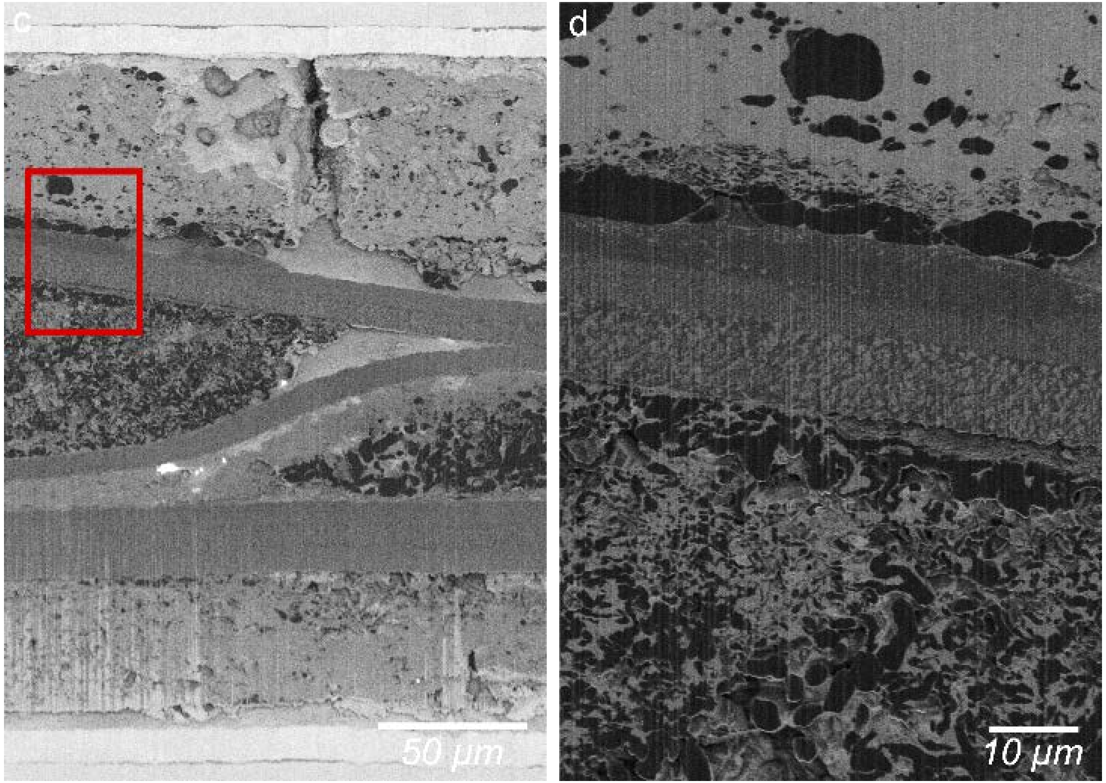


515 nm **1030 nm**

R. Gannon et al., (2023) In Preparation

Polishing with the Plasma FIB

101^{st} Cycle
Li Metal Cell



R. Gannon et al., (2023) In Preparation

How to Achieve Ideal Battery Characterization?

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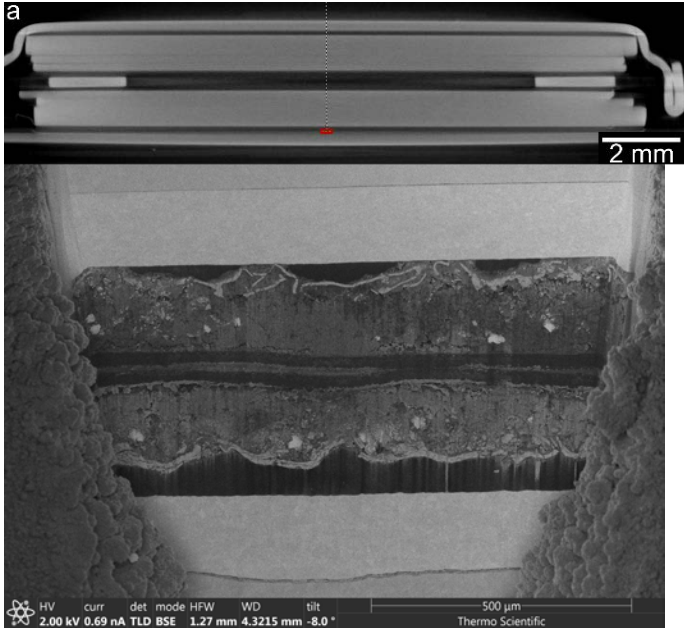
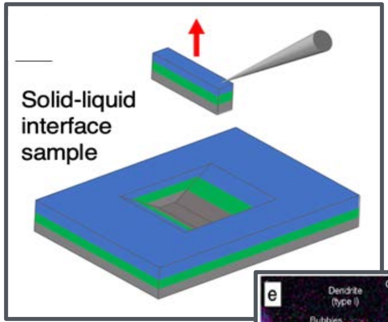
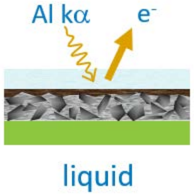
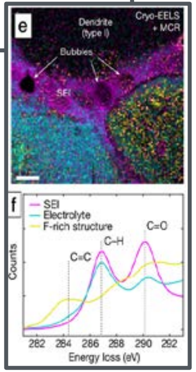








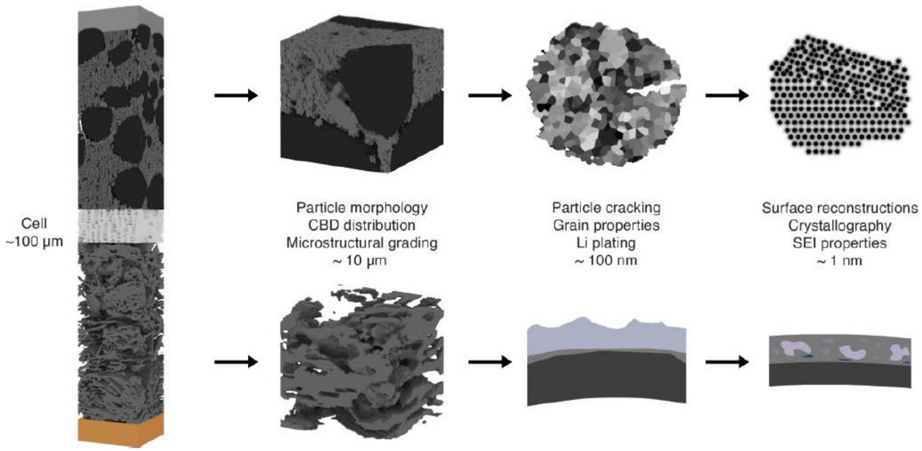
What happened there?

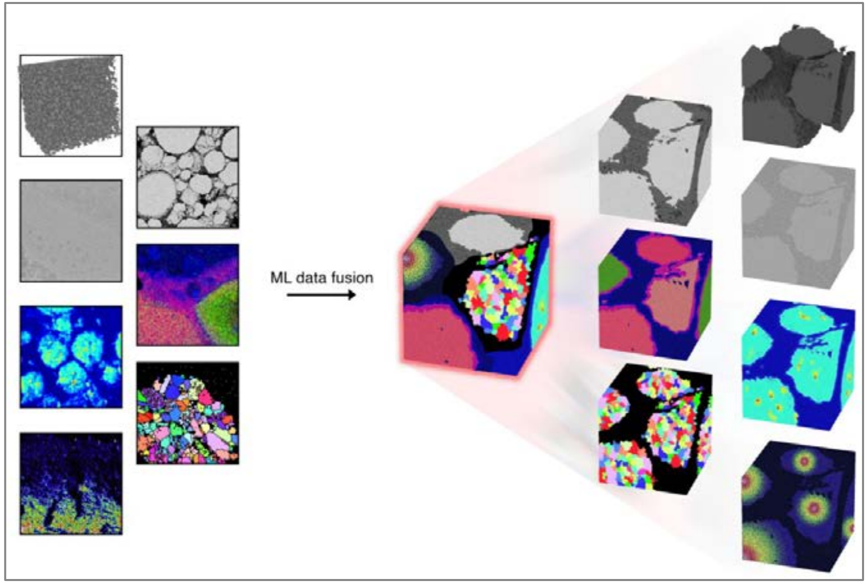
Why did it happen there?

How likely is that happing over the entire electrode/cell?

What can we do about it?

Machine Learning for Multimodal Data Cubes

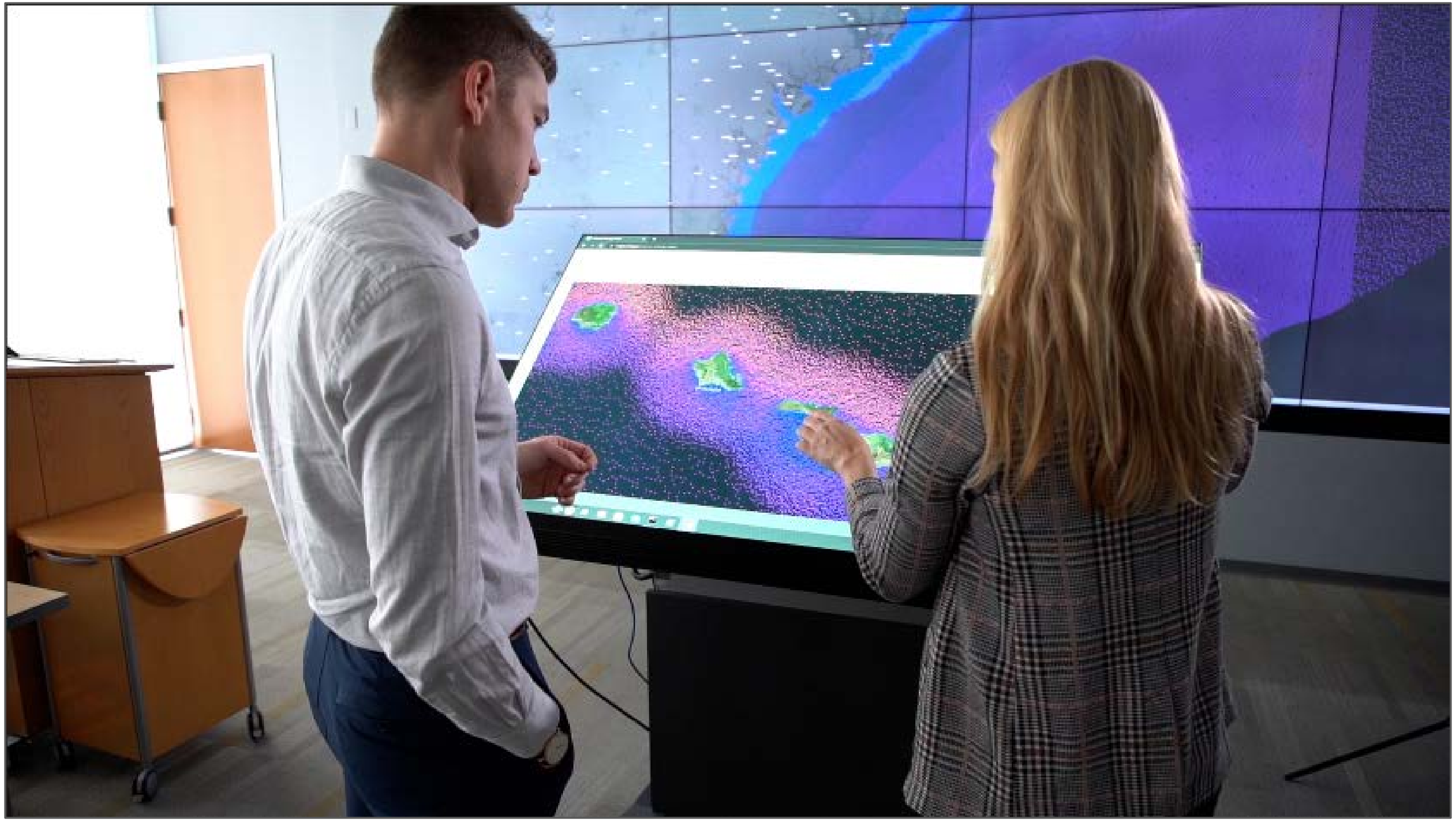




Imperial College London

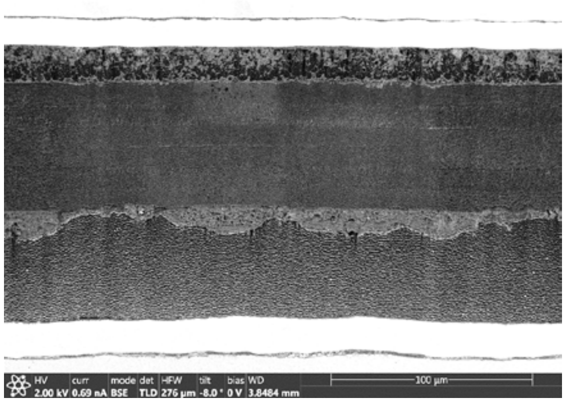
D. Finegan et al., ACS Energy Lett. 7, 12, 4368 (2022)

NREL Data Visualization Center



Conclusions

- Effects of pressure on Li cycling are often overlooked and can be significant
  - Pressure at low current density can improve:
    - Morphology
    - Cell-to-cell repeatability
    - Coulombic efficiency
  - Too much pressure ➡ transport problems (even at low current density)
  - Pressure at high current density impacts:
    - Li morphology
    - Pressure helps slow Li inventory loss



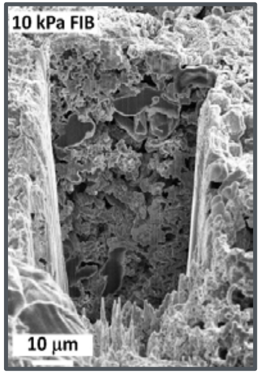
- Cryo laser PFIB can image intact coin cells without disassembly, characterization provides:
  - Structure of the separator-Li interface
  - Quantify Li inventory, Li morphology, cracking in SEI, and SEI thickness
  - Under high-rate cycling: Separators are damaged or destroyed
    - Li and SEI grow between separators and trilayers of separators

NREL Transforming ENERGY

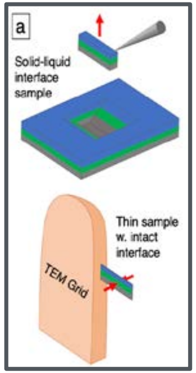
Summer 2024: Microscopy Investments

Laser PFIB

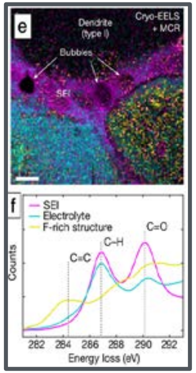
Inert-Transfer & Cryo PFIB

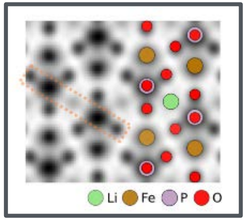


Inert-Transfer & Cryo Ga FIB



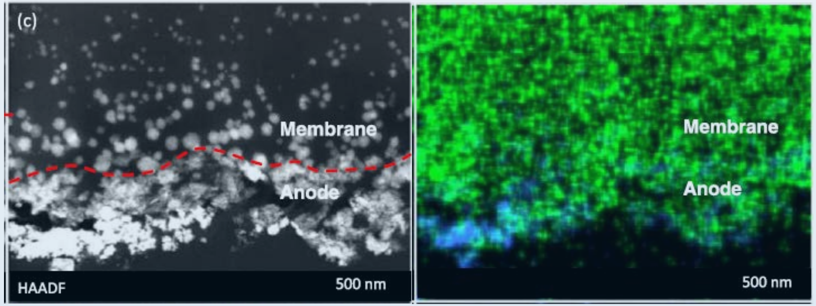
In-Situ & Cryo S/TEM



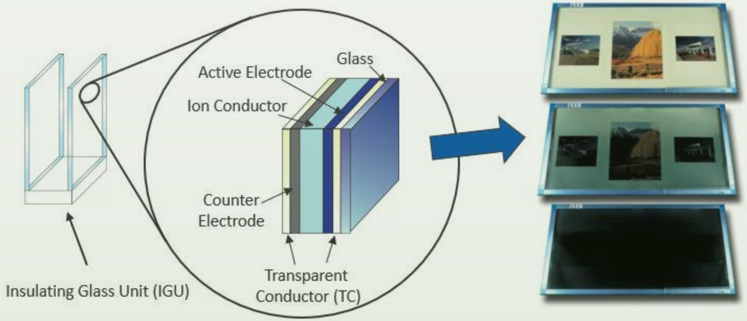


Degradation Science for Clean Energy Systems

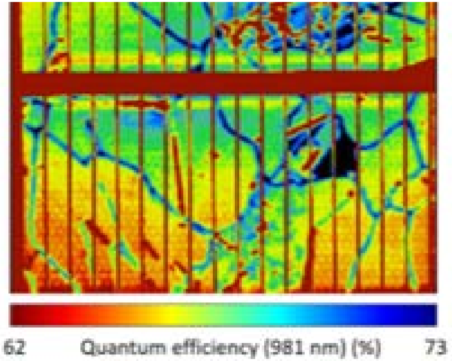
Electrolysis



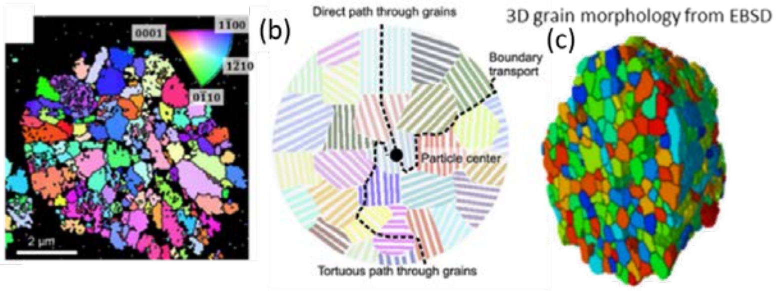
Electrochromic Windows



Solar Cells: Potential Induced Degradation



Energy Storage



Thank You!

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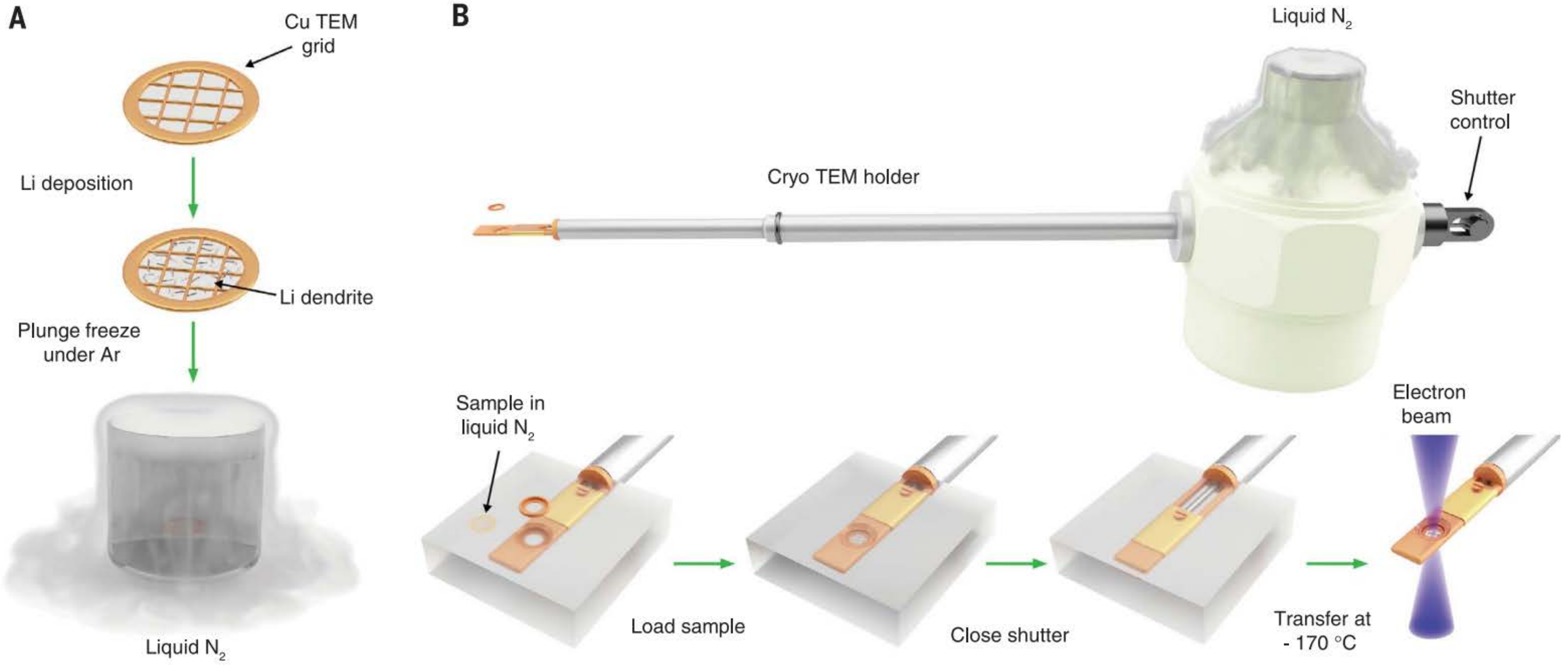
Cryogenic Transmission Electron Microscopy



Li et al., Science, 358, 506 (2017)