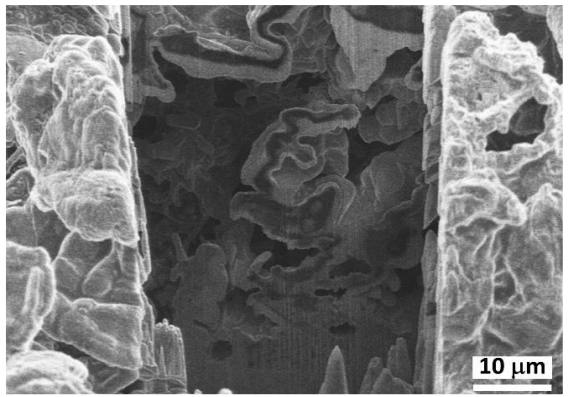
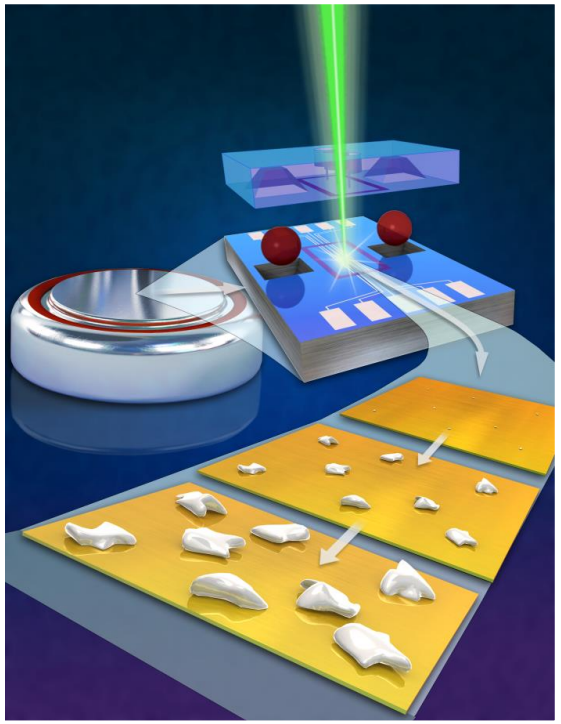
SAND2022-2384C

Nanoscale Characterization of Electrochemical-Mechanical Mechanisms with Electron Microscopy





Katherine Jungjohann

National Renewable Energy Laboratory

Formerly at Sandia National Laboratories

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About the Presenter

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Center for Integrated Nanotechnologies — CINT — Discovery, Performance, Integration, Education — Sandia, Los Alamos

Sandia National Laboratories

LDRD Laboratory Directed Research and Development

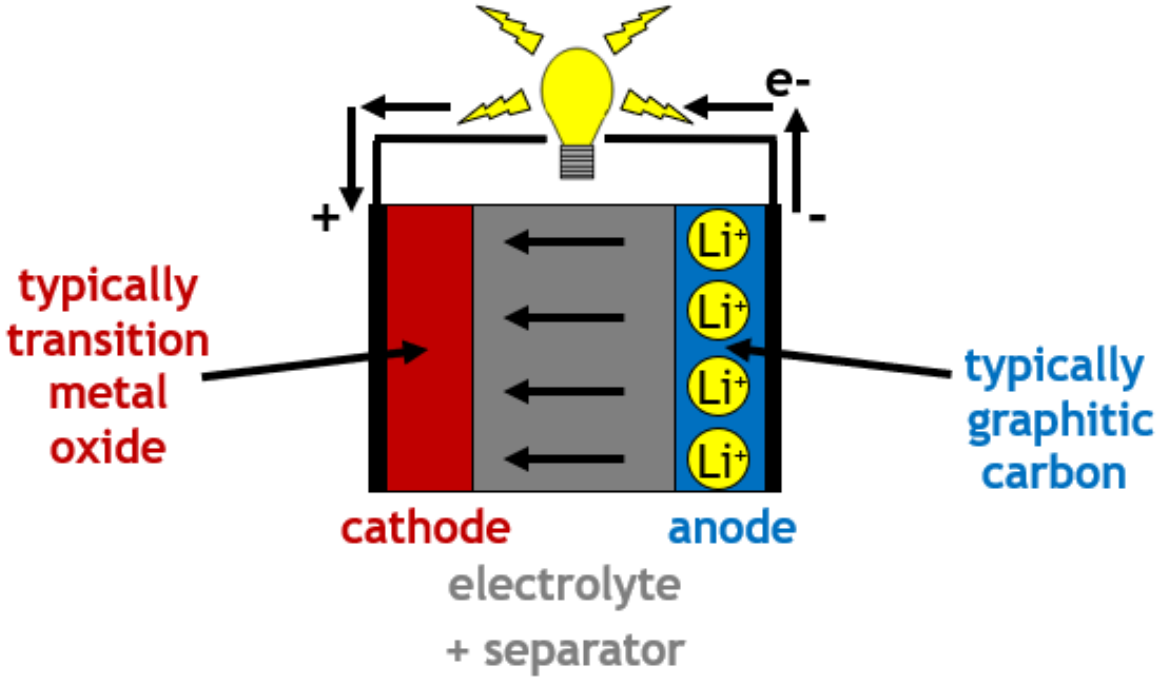
ThermoFisher SCIENTIFIC

NREL Transforming ENERGY

Lithium metal anodes can theoretically increase battery capacity b

10X

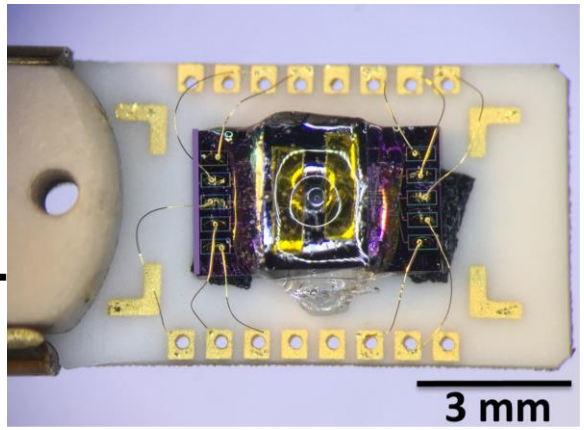
Traditional Li-Ion Batteries



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)

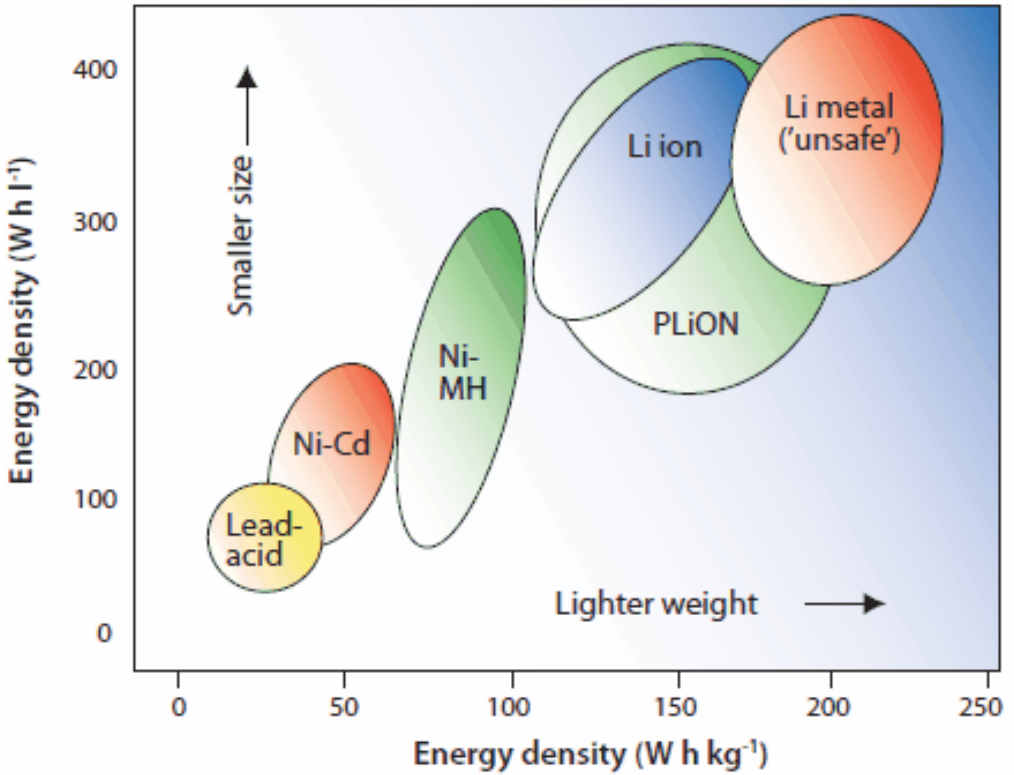
TEM cell
no pressure



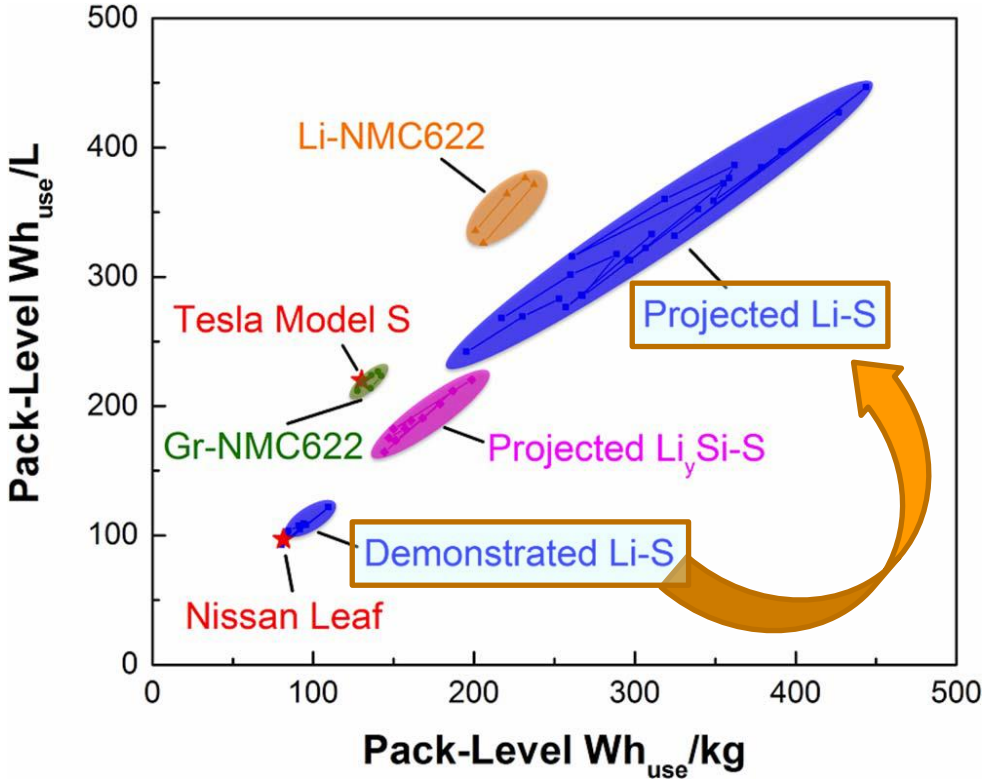
coin cell
spring pressure

pouch cells
external pressure

How Can We Improve Rechargeable Batteries?



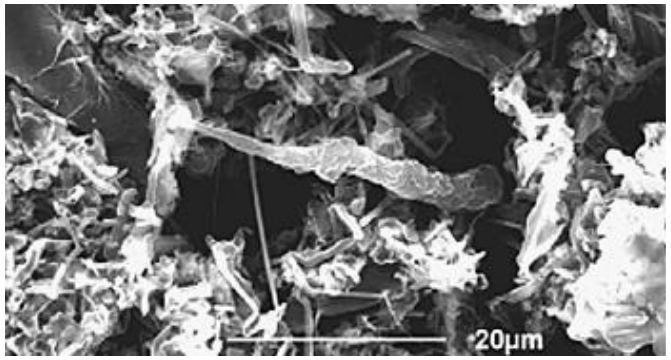
J.-M. Tarascon and M. Armand *Nature*
DOI: 10.1038/35104644



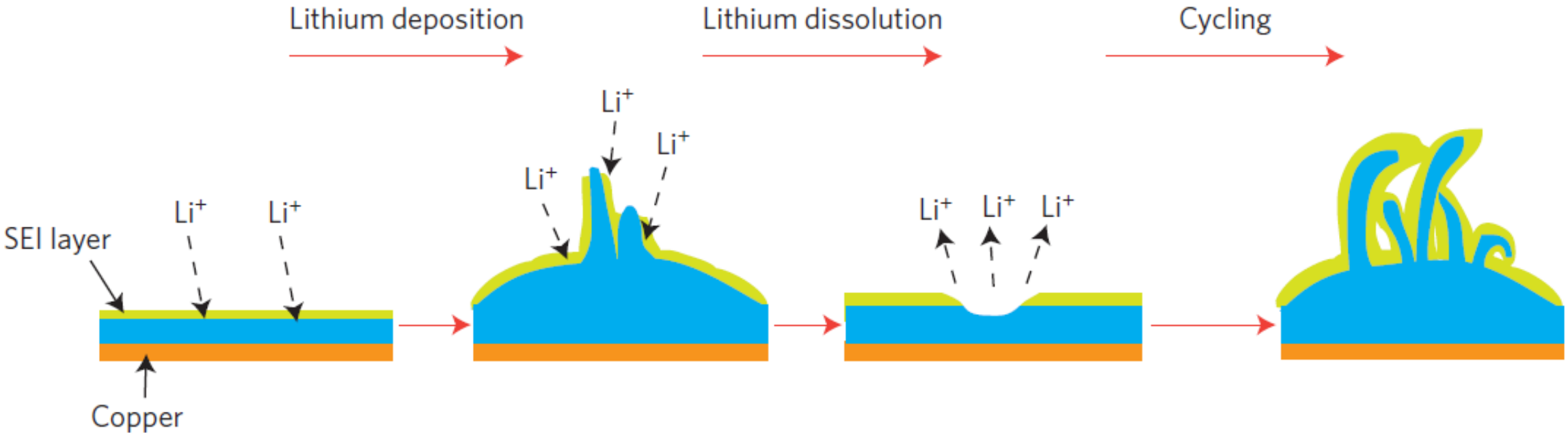
K.G. Gallagher et al. *J. Electrochem. Soc.*
DOI: 10.1149/2.0611506jes

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**

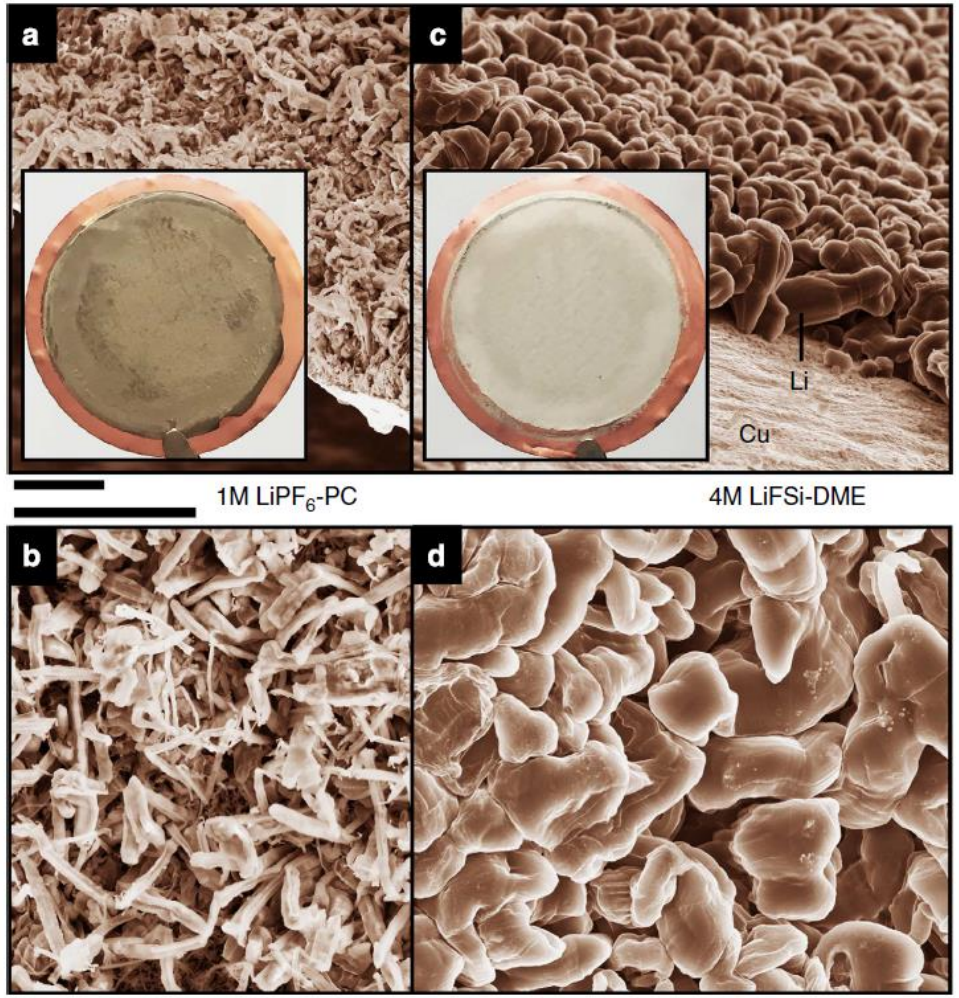


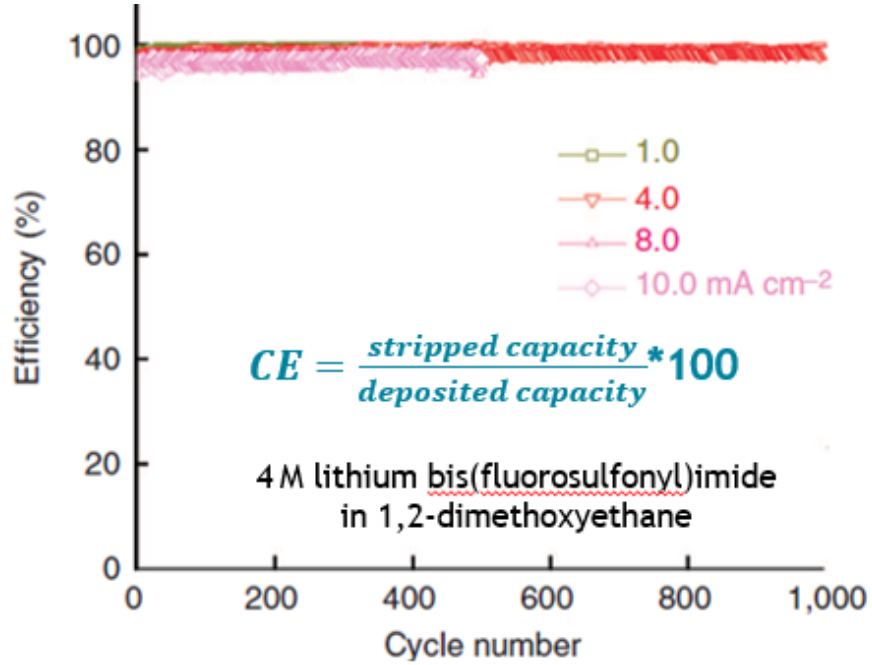
Gireaund et al., Electrochem. Comm. 8, 1639 (2006)

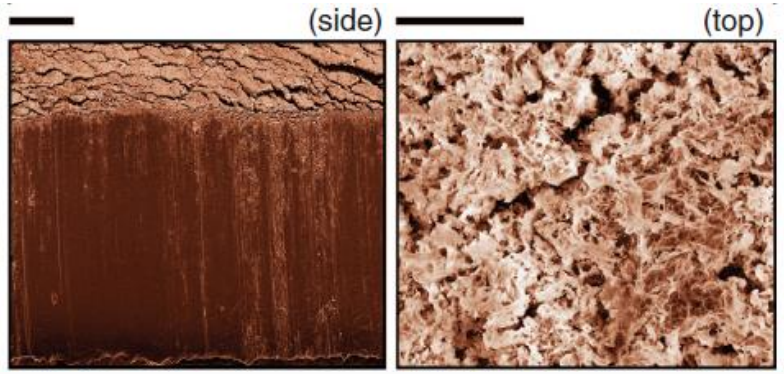


Lithium Self-Discharge and Prevention

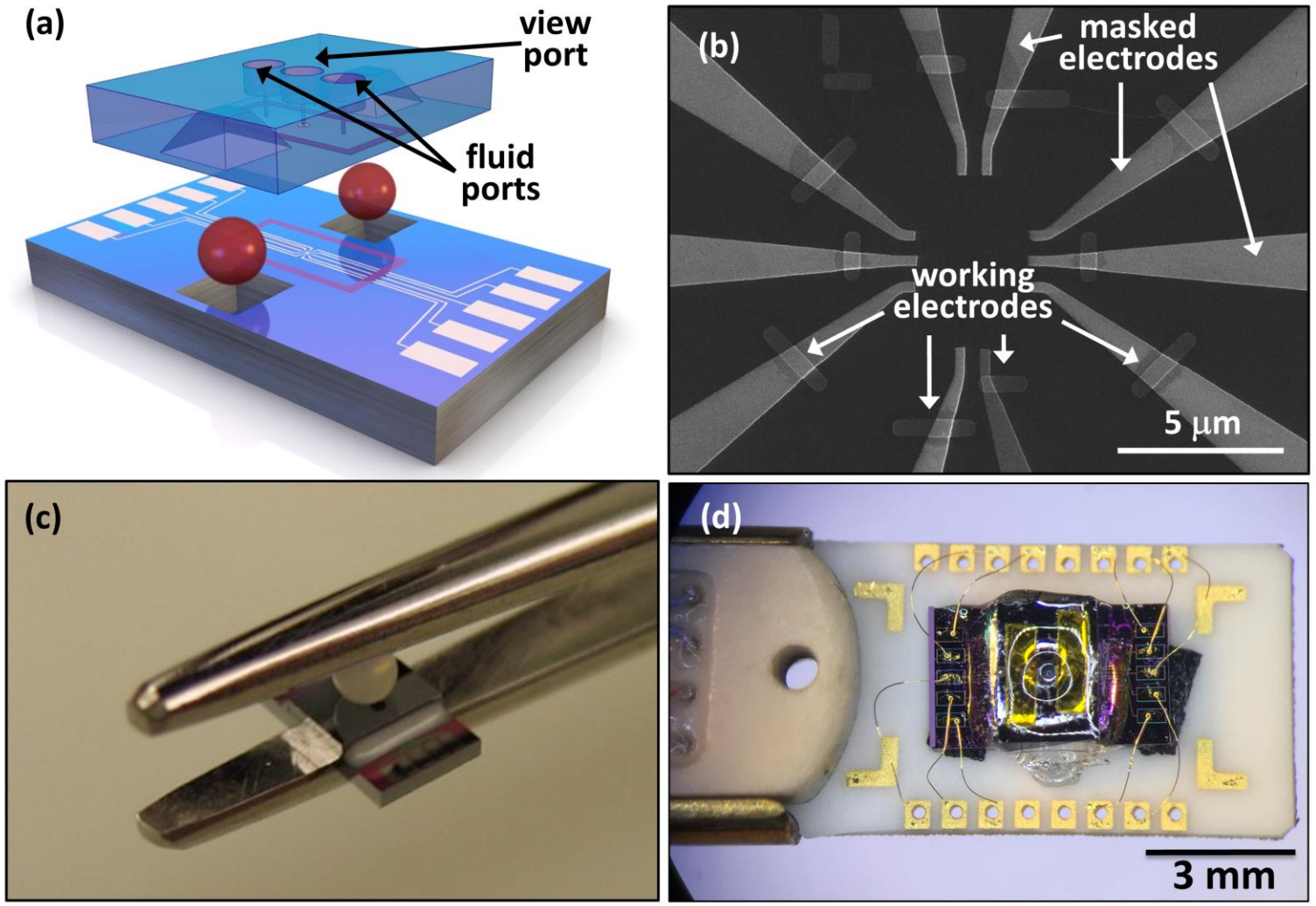
Qian et al. *Nature Communications* DOI: 10.1038/ncomms7362



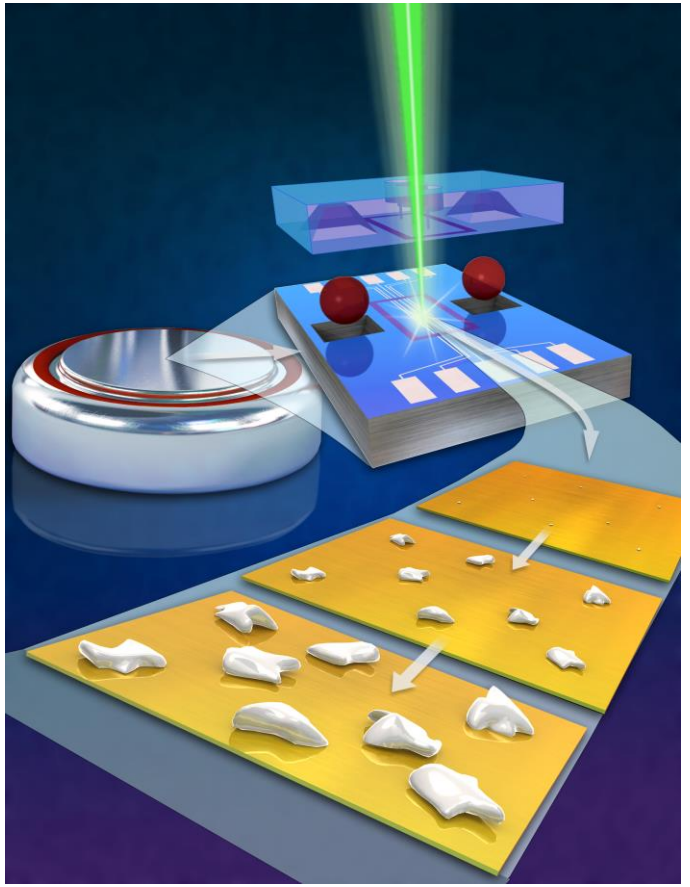




CINT's Electrochemical TEM Discovery Platform

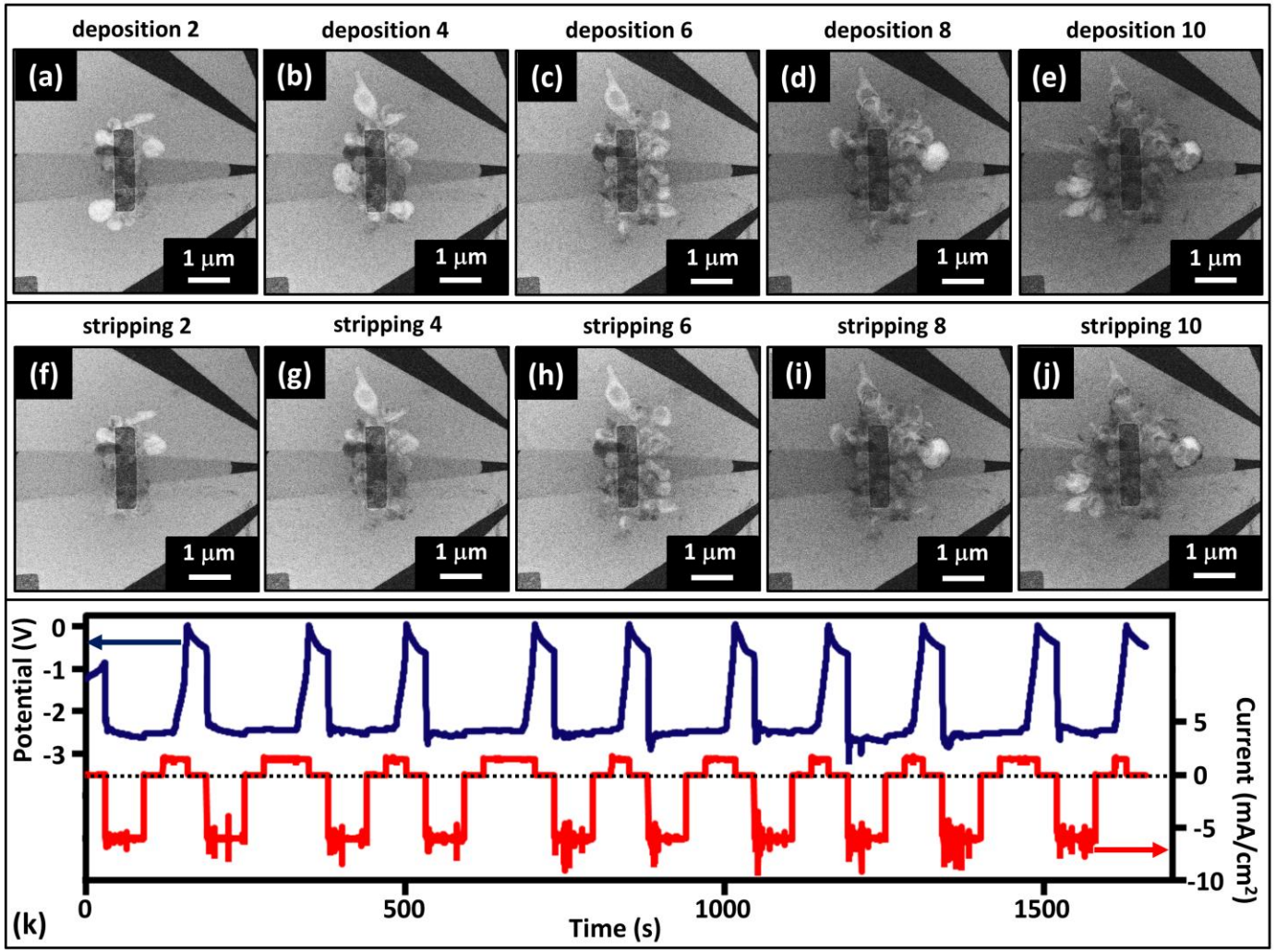


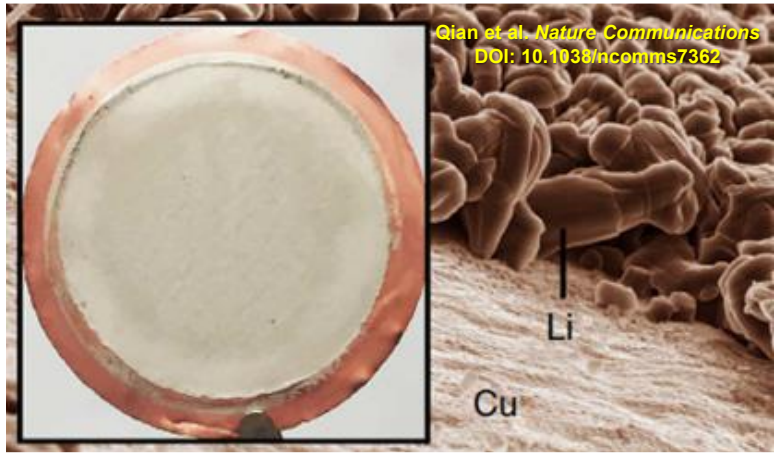
*planar electrodes on insulated chip surface with no separator



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

In-Situ Nanoscale Li Electrodeposition



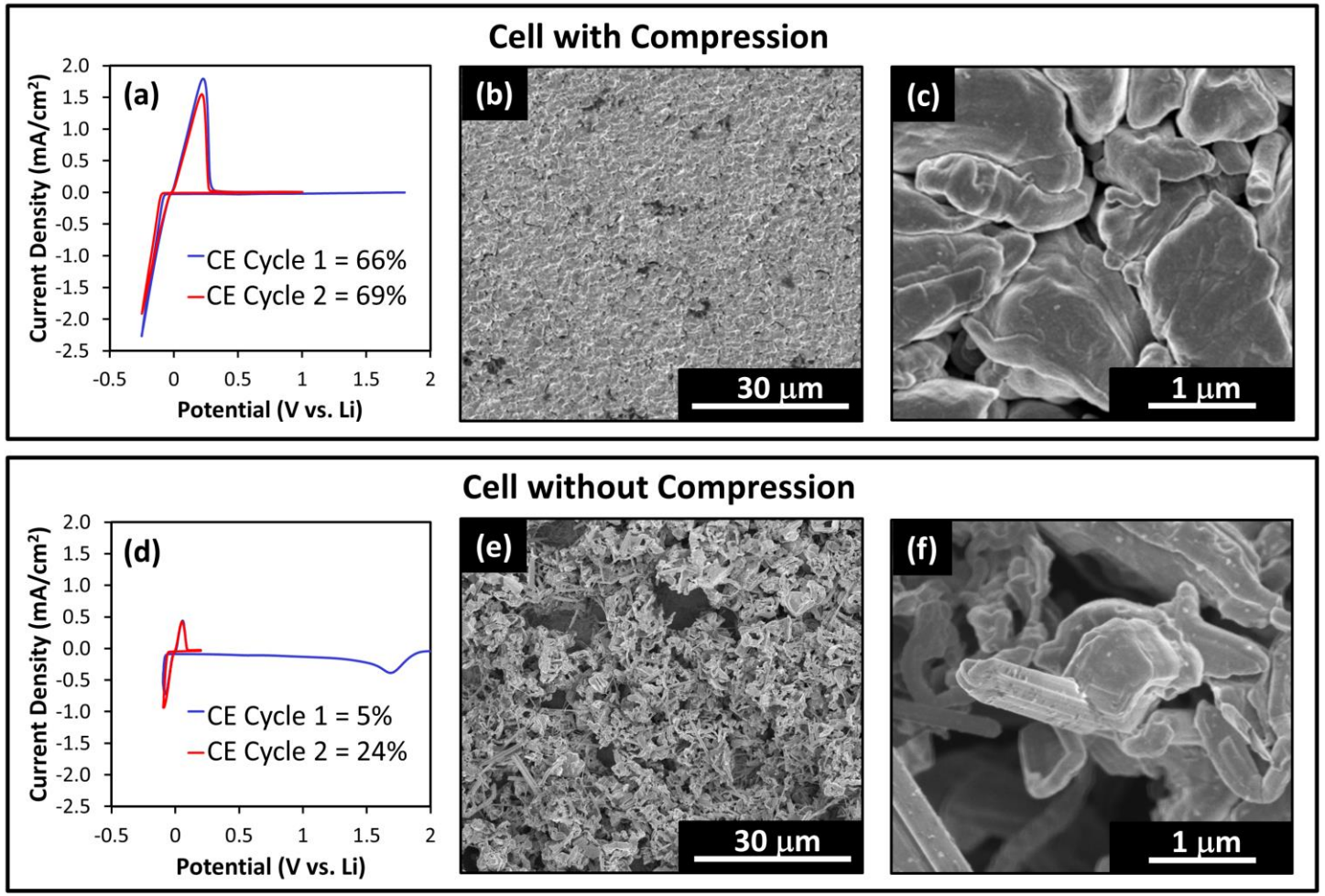


- **Morphology images after every deposition and stripping step (Li = white)**
- **CE VERY low (18% ± 9%)**
- **Widely varied morphology**

bright field imaging
WE = 60 nm Ni/5 nm Ti
deposit 6 mA/cm²
strip 1.5 mA/cm²
capacity = 0.1 mAh/cm²

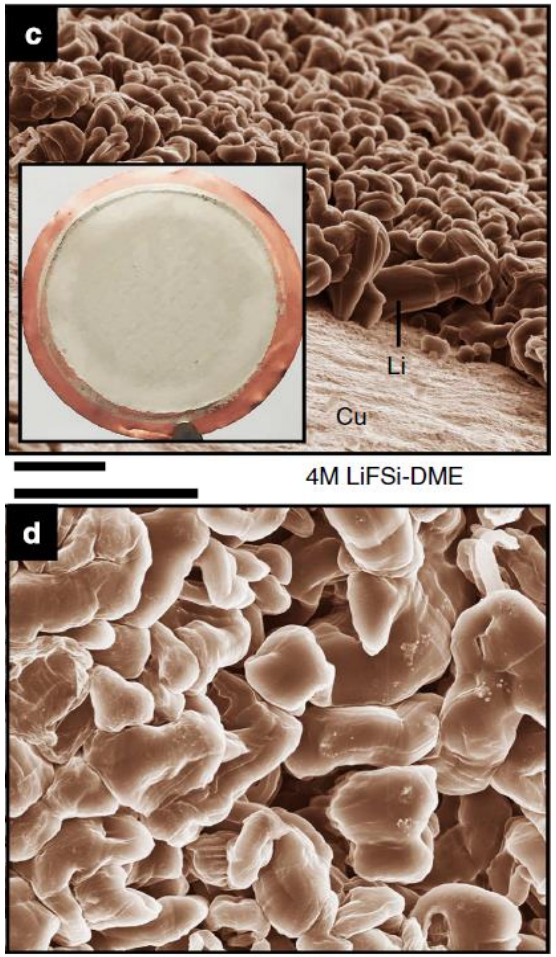
Harrison et al. *ACS Nano*
DOI: 10.1021/acsnano.7b05513

Applied Pressure Critical for High-Density Li



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

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



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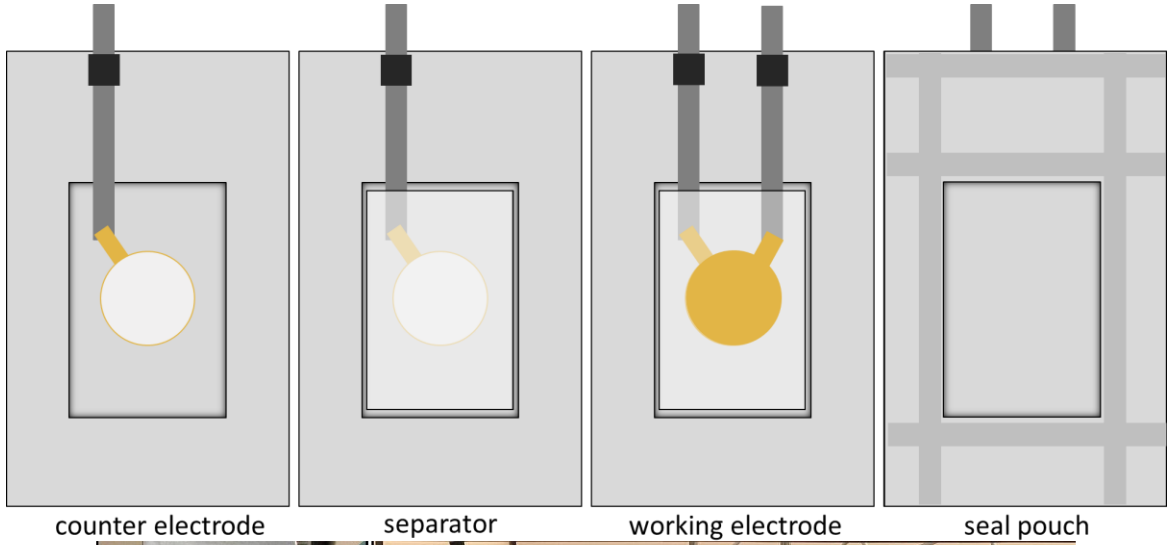
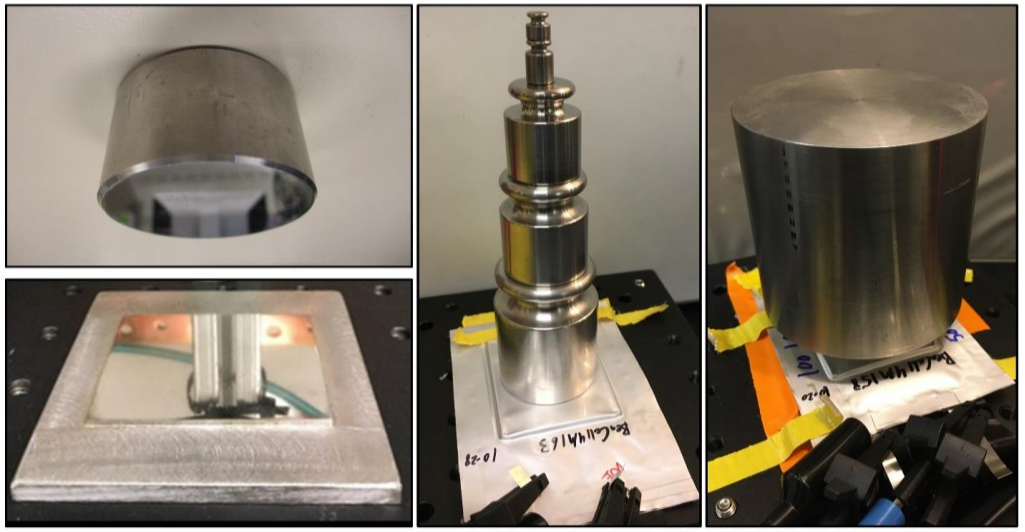
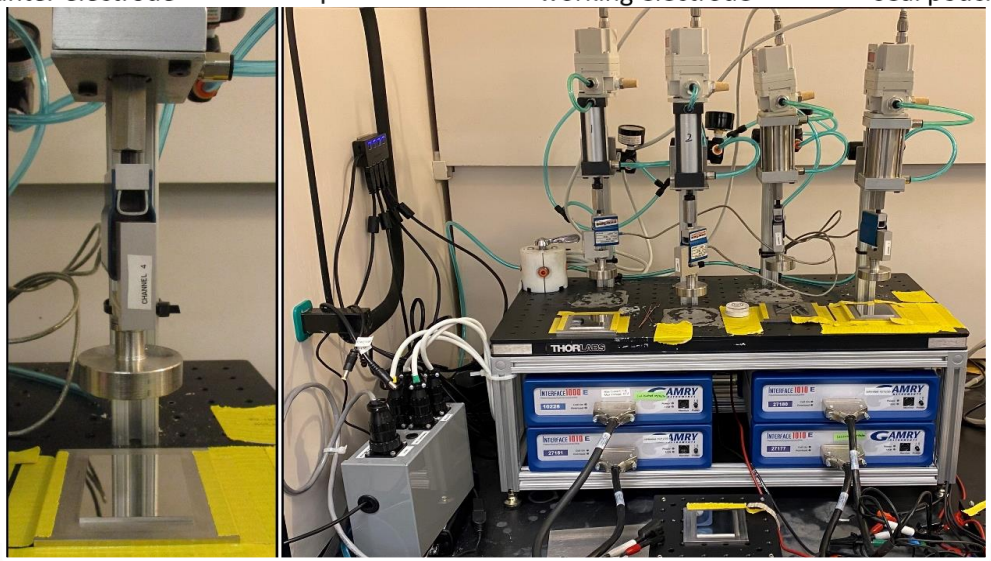
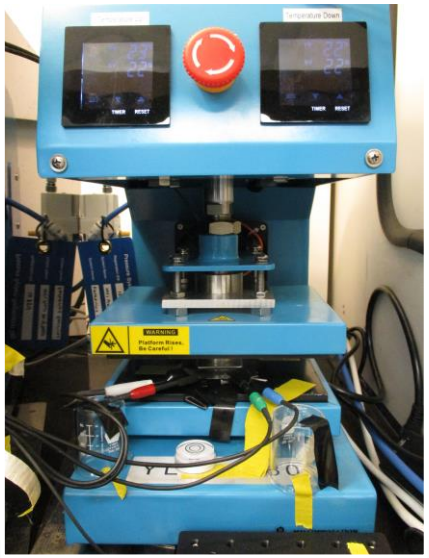
Controlled Pressure on Electrodeposited Li





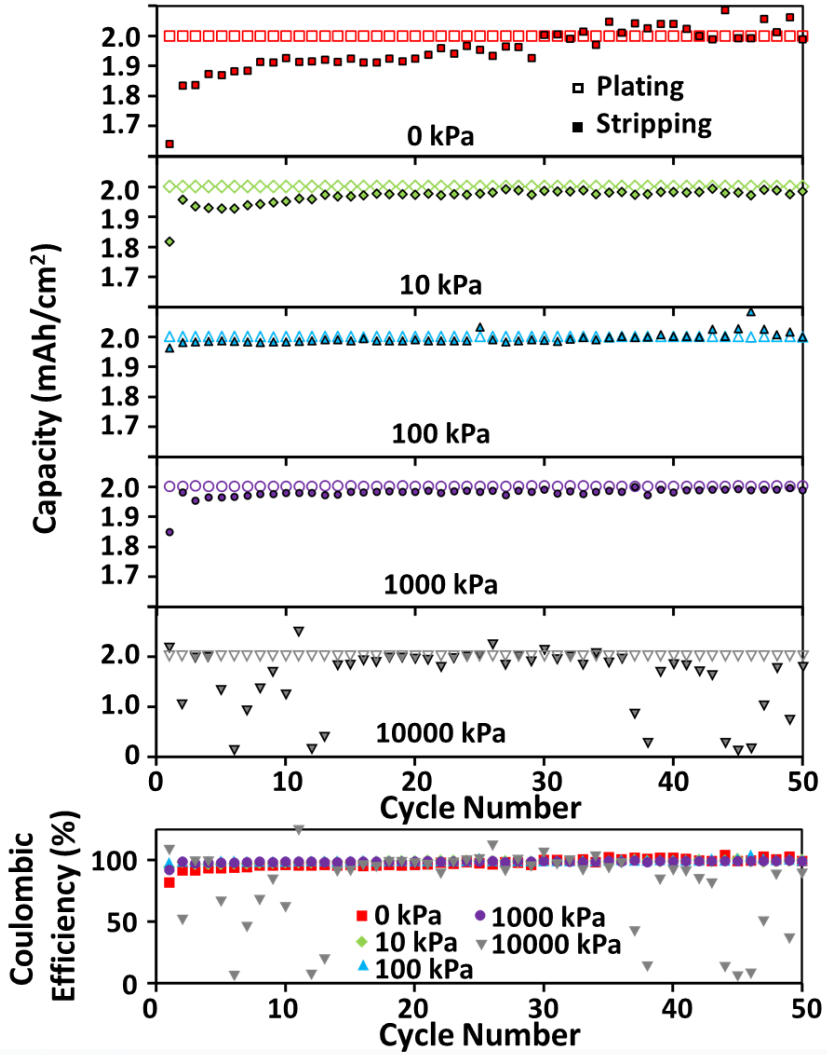


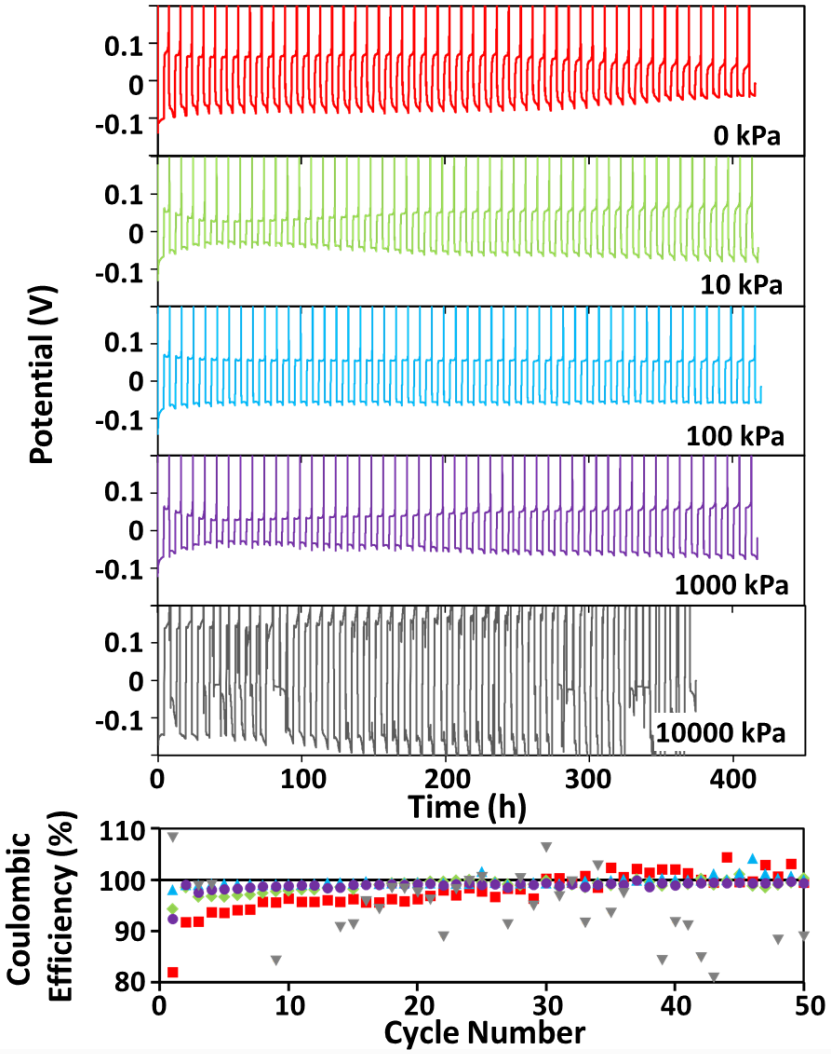


Effects of Pressure on Li Metal: Low Current

Low Current: 0.5 mA/cm^2

- 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

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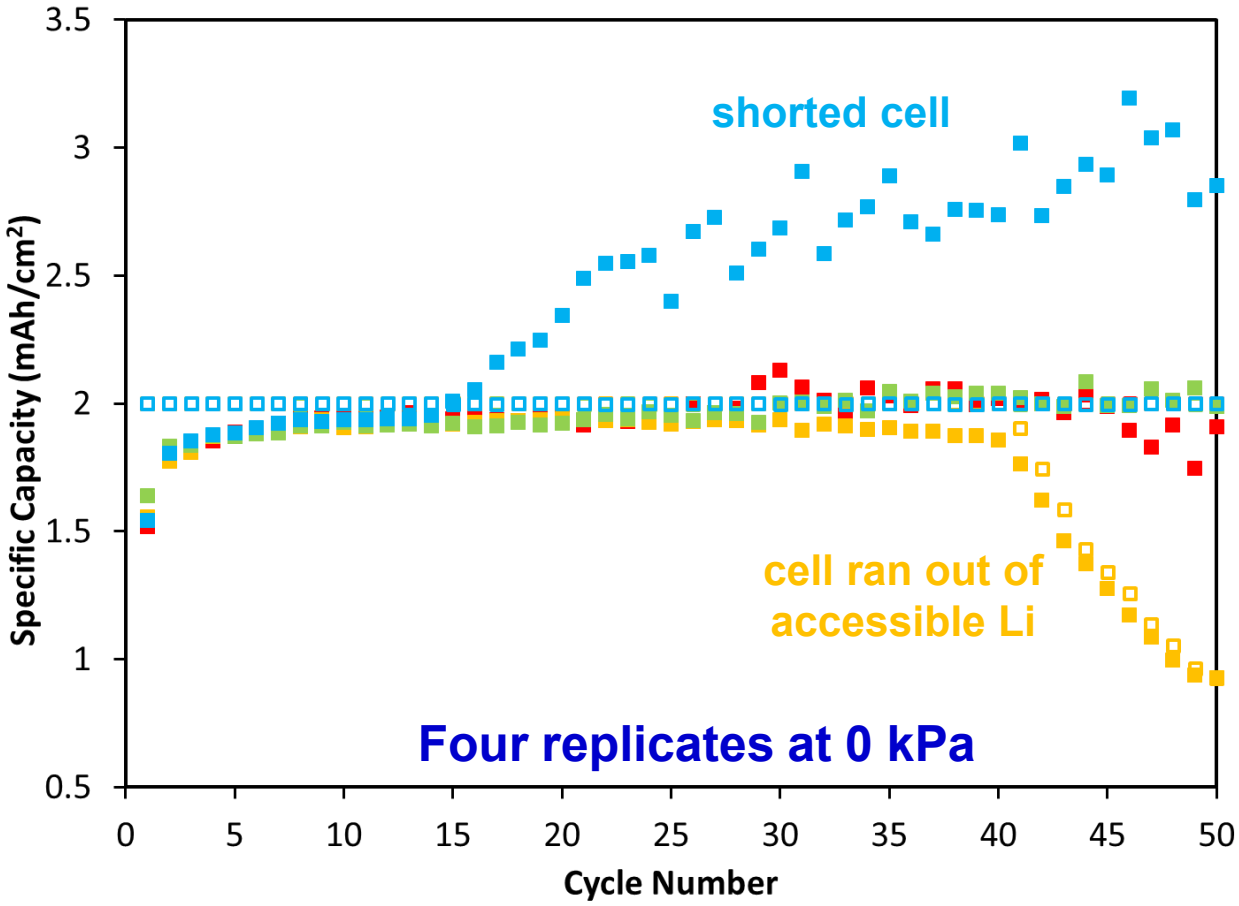
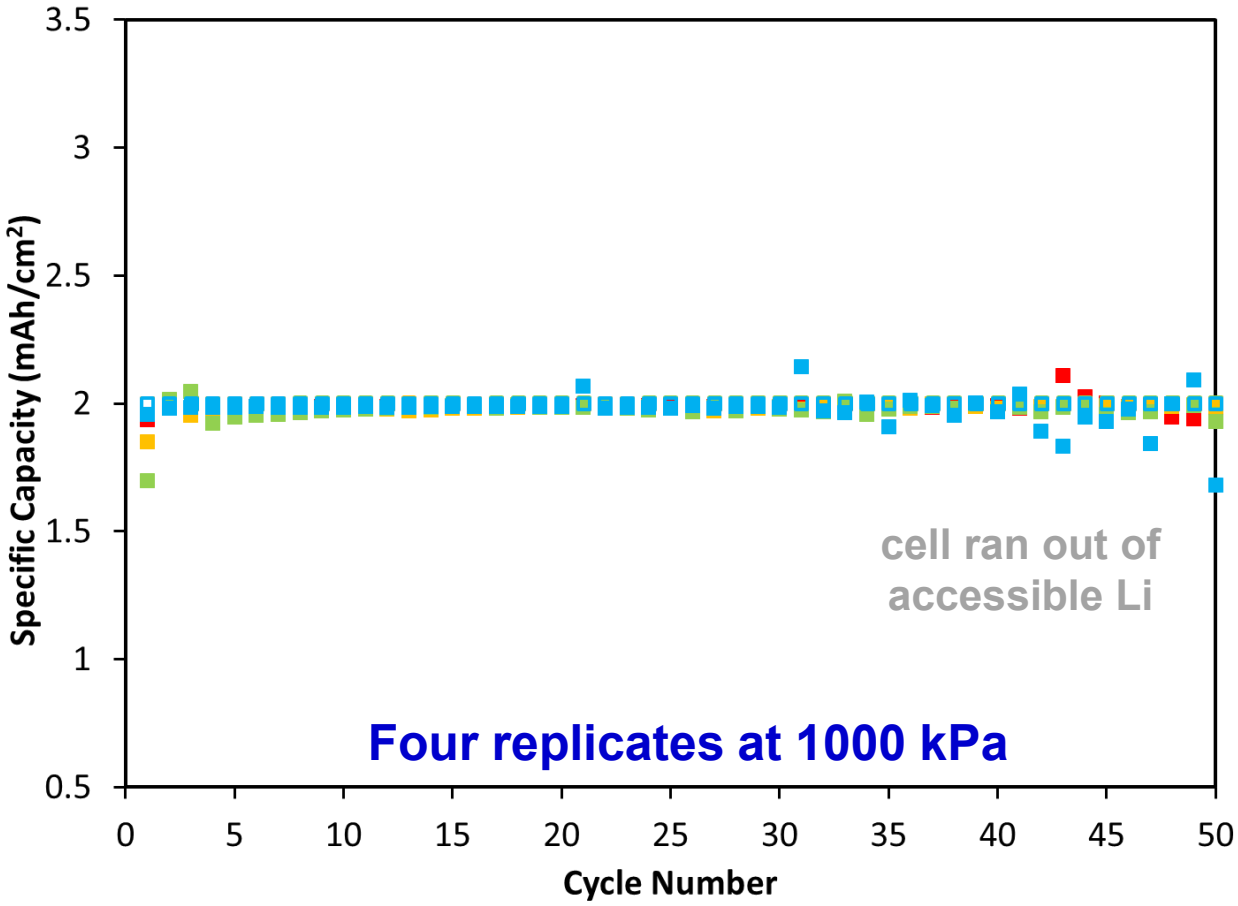
Effects of Pressure on Li Metal: Low Current

Low Current: 0.5 mA/cm^2





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

Characterization: Ex-Situ Cryogenic SEM

- 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

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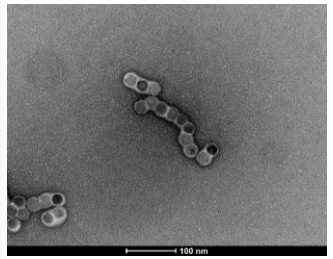
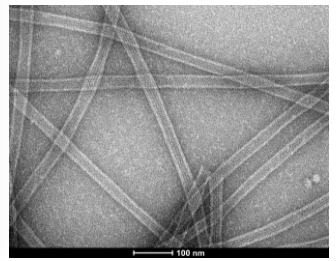




Vitrobot
Captures native, solvated state

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

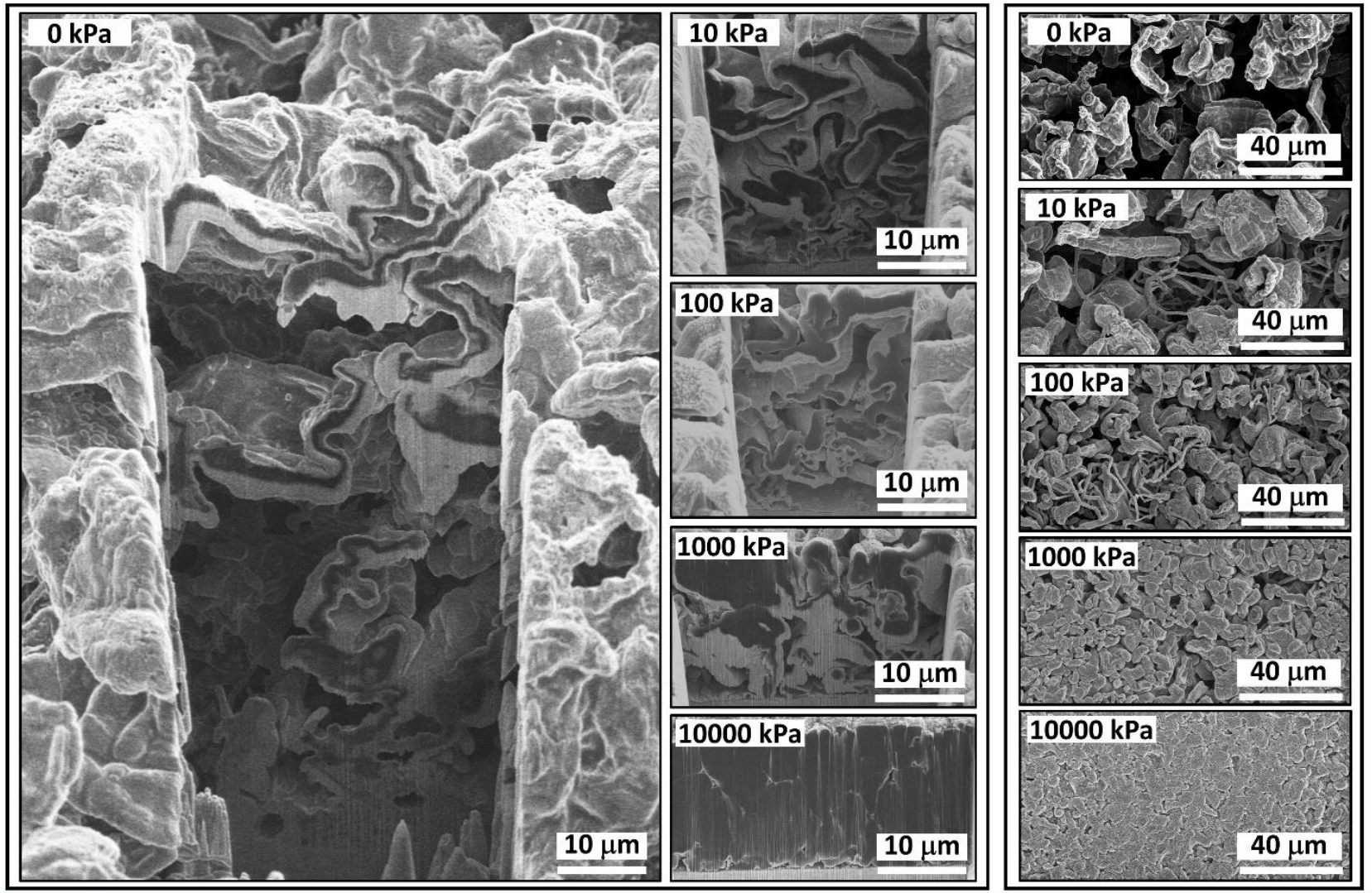
Pressure at Low Current: 1st Li Deposition Step

Low Current: 0.5 mA/cm^2

- **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 51st Plating (μm)
0	91
10	33
100	30
1000	22
10000	17

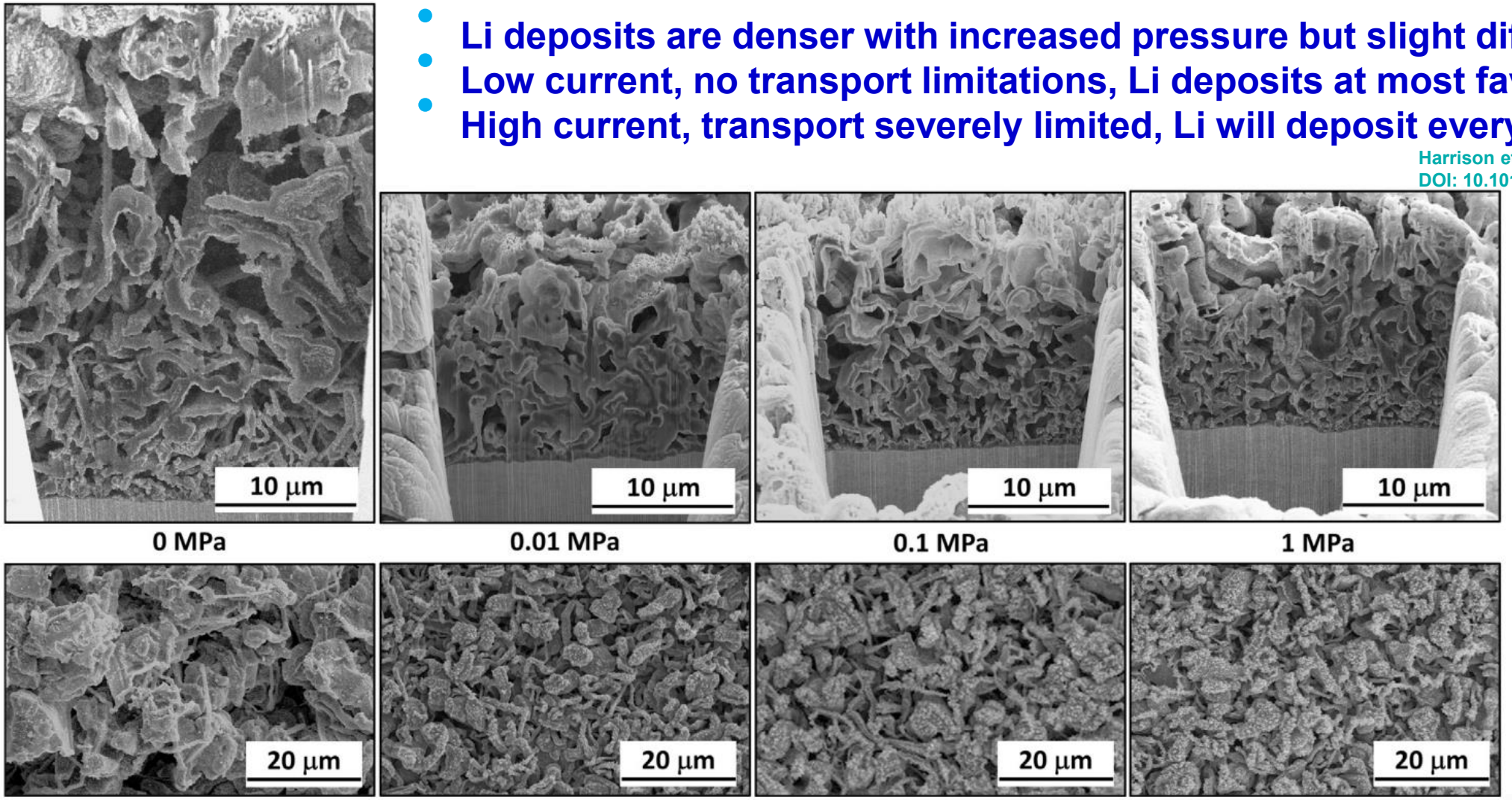


Harrison et al., *ACS Appl. Mater. Interfaces* 13, 31668 (2021).
DOI: 10.1021/acsami.1c06488

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



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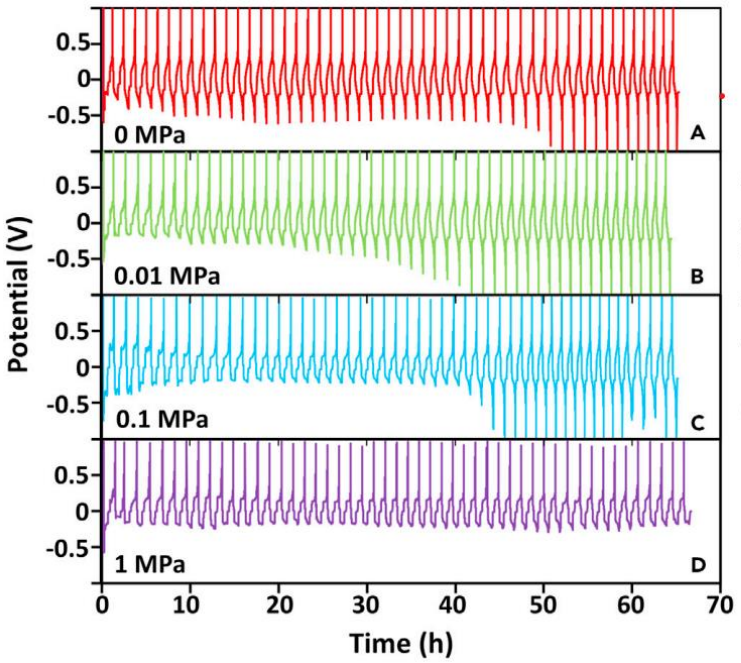
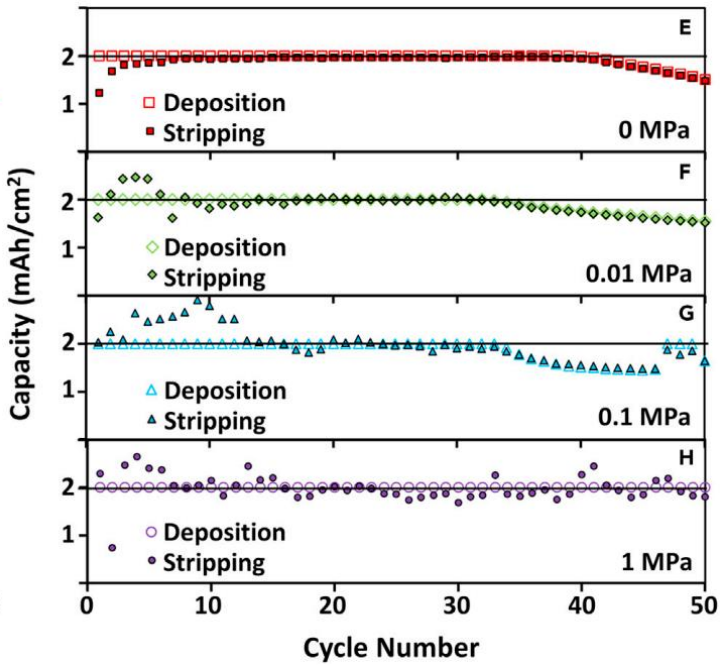
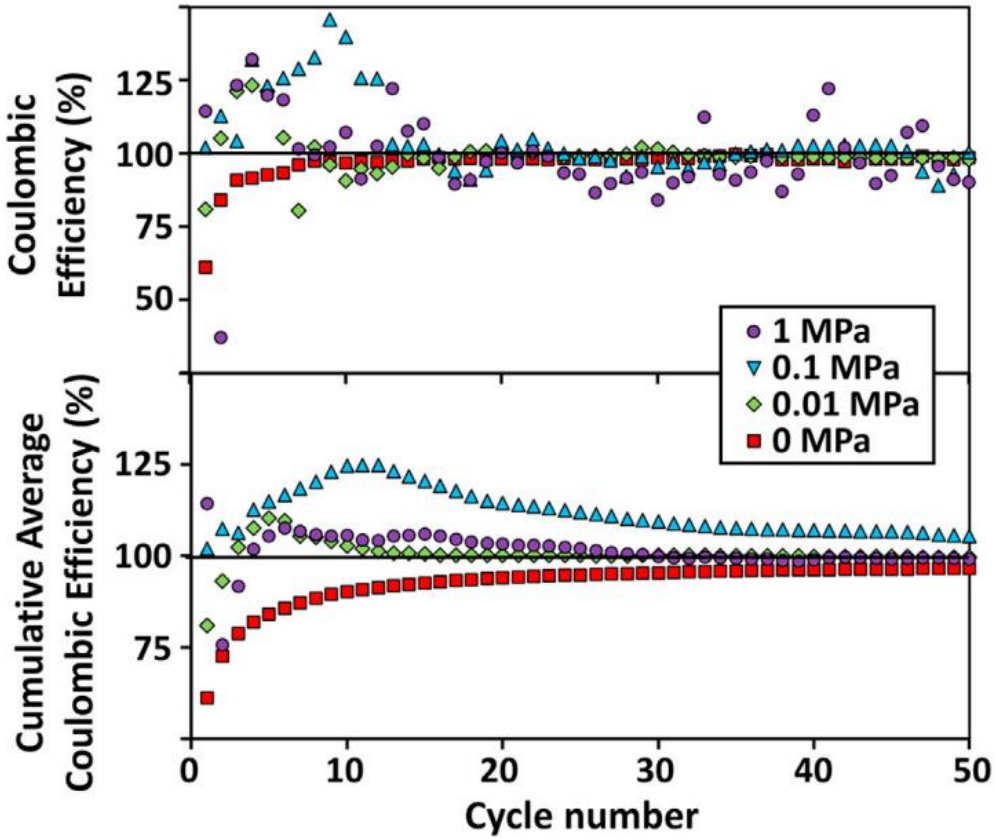
Effects of Pressure on Li Metal: High Current

High Current: 4 mA/cm^2

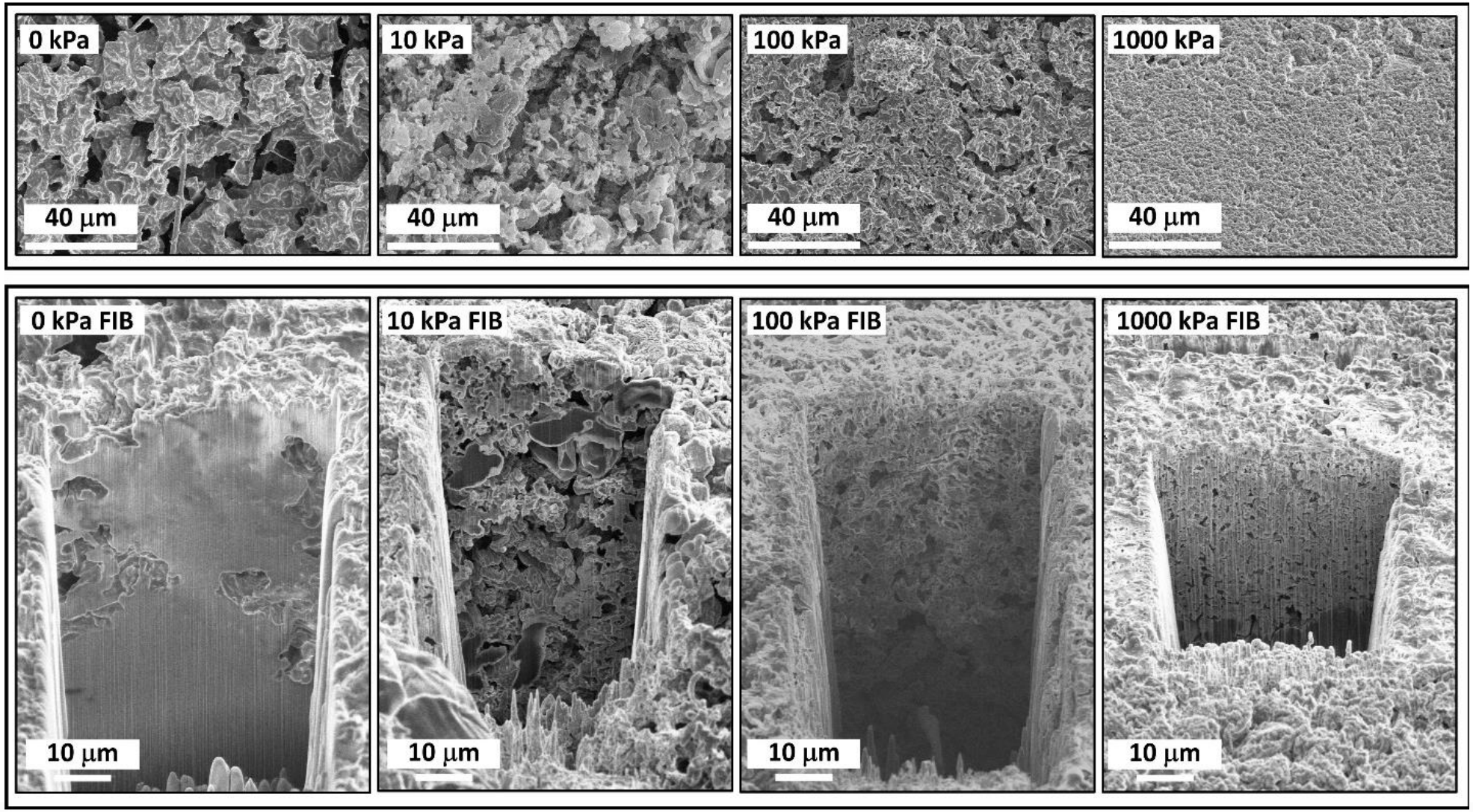






Harrison et al., *iScience 24*, 103394 (2021).
DOI: 10.1016/j.isci.2021.103394

Pressure at Low Current: 51st Li Deposition Step



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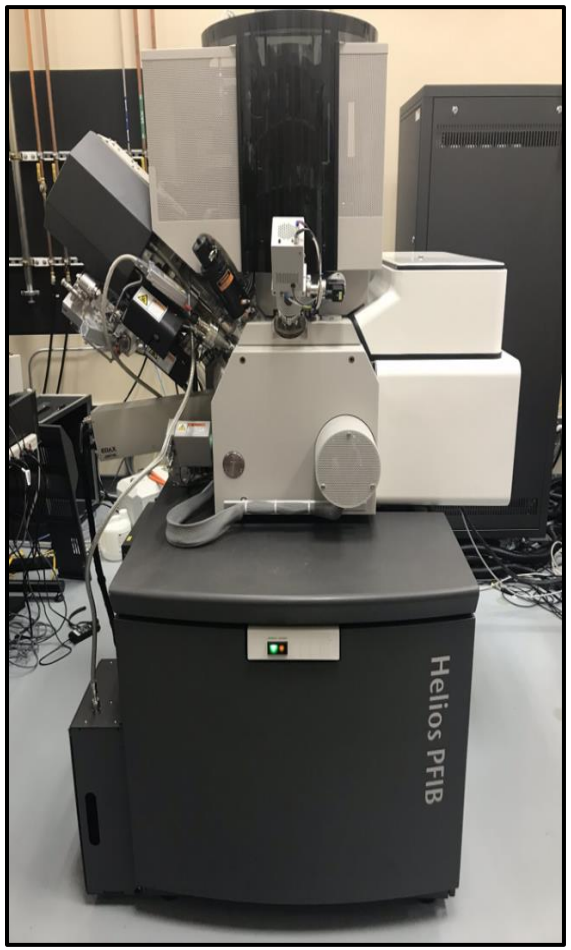
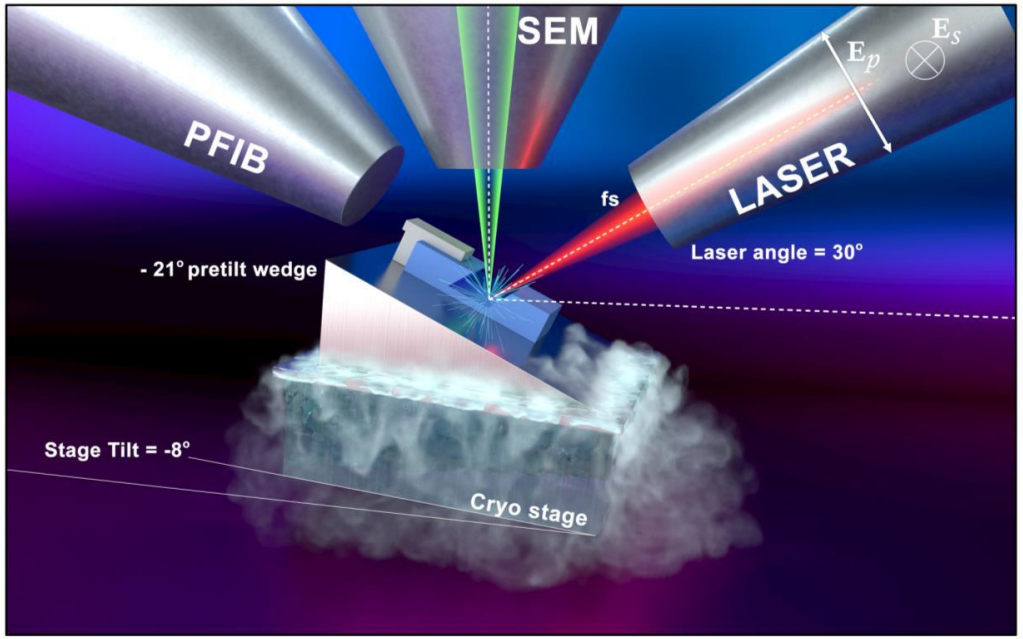
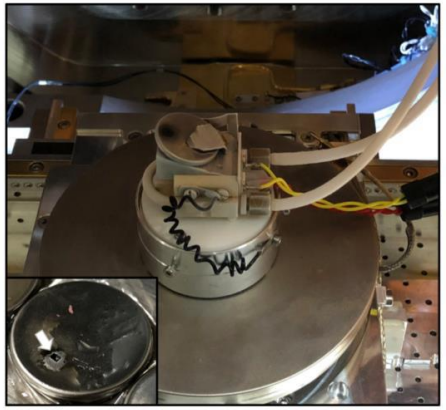
Cross-sectioning without Battery Disassembly

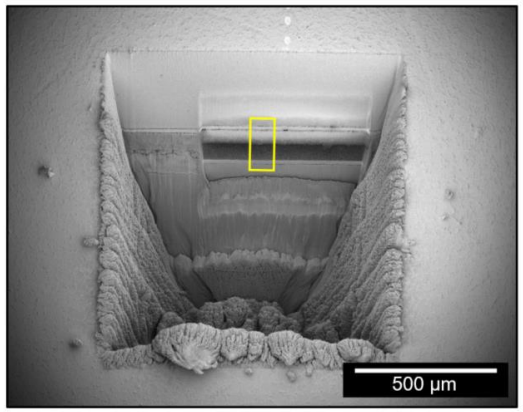


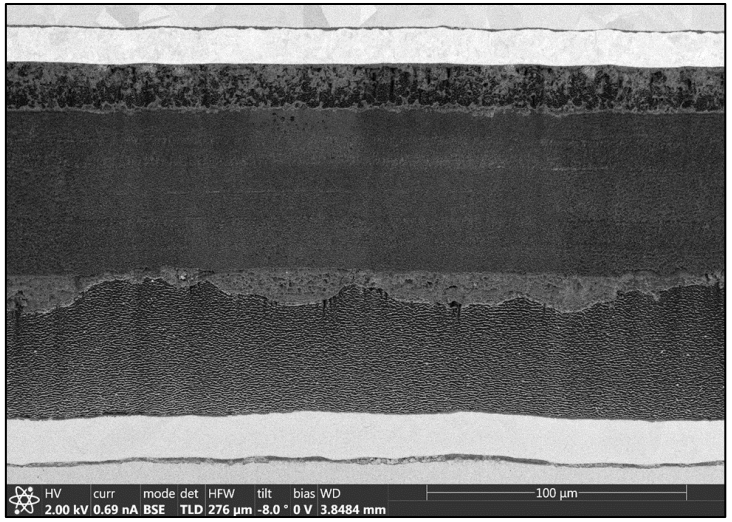
Helios Laser Plasma FIB

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

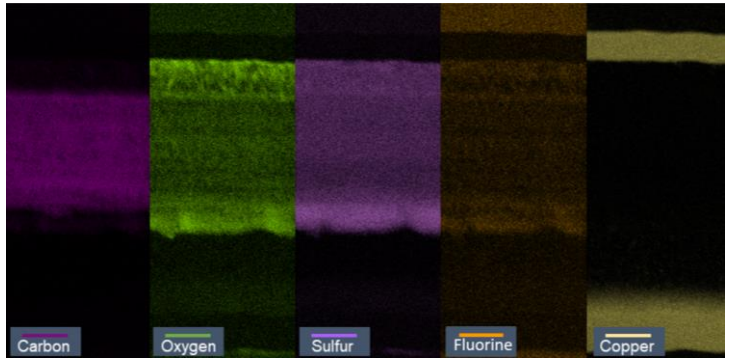








- Two Celgard 2325 Separators
- Li/SEI/electrolyte layers found



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

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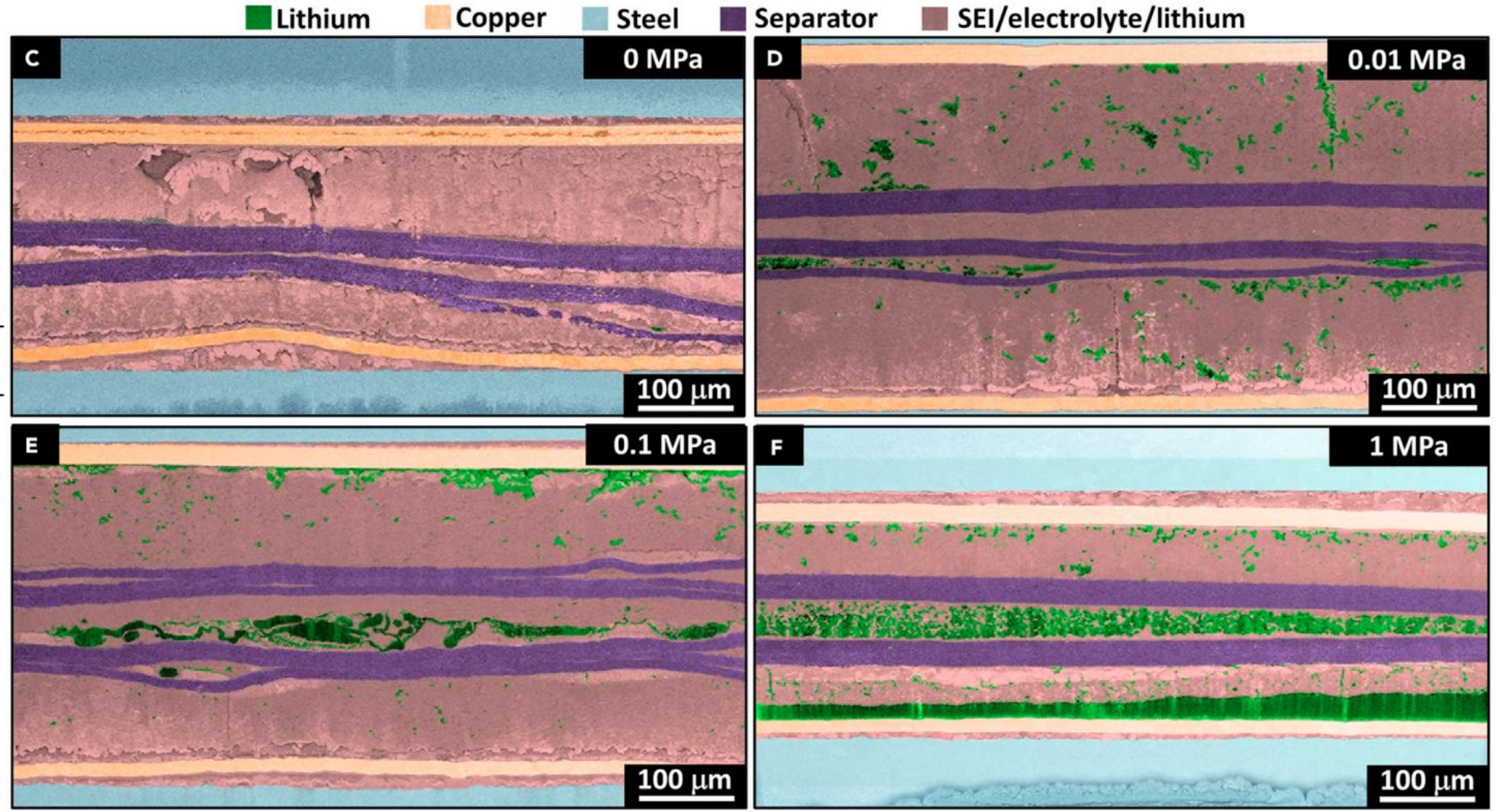
Pressure at High Current: 51st Li Deposition Step

High Current: 4 mA/cm^2

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

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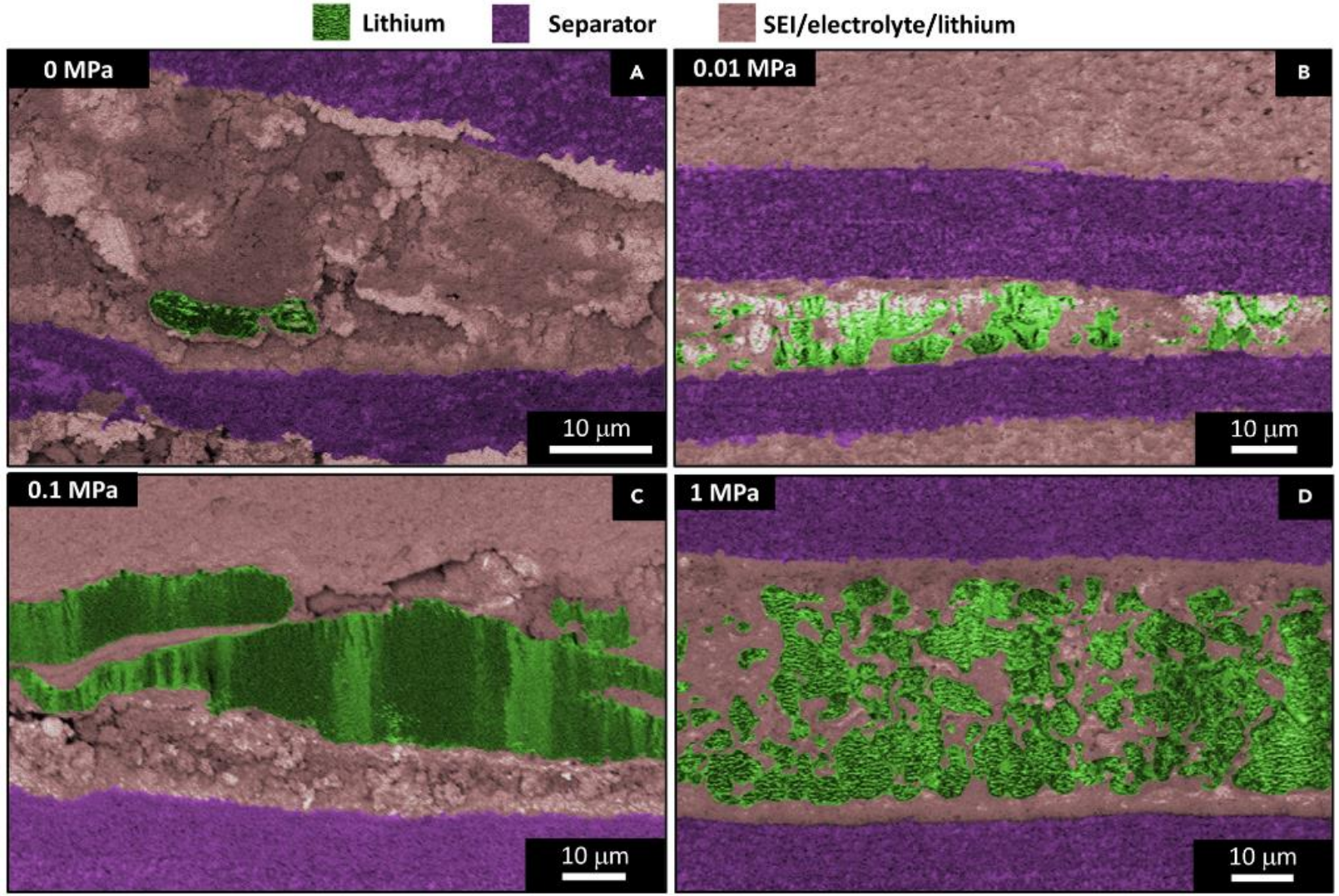
All Pressures: Li Deposition within Separator

High Current: 4 mA/cm^2



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

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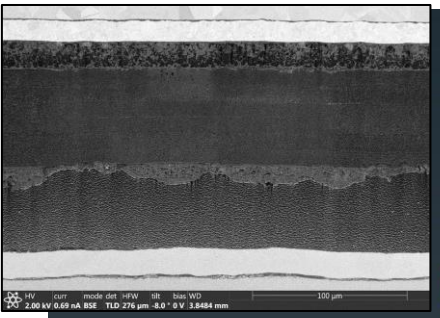
fs Laser Slice-N-View of Battery Stack



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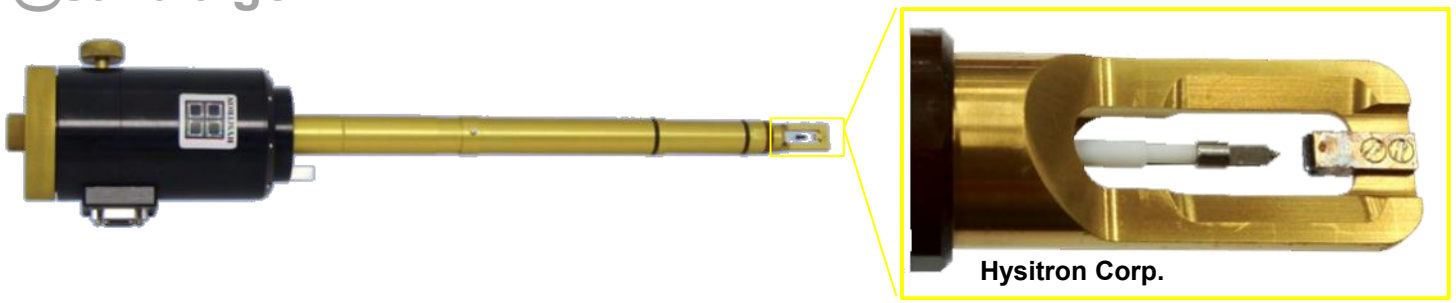
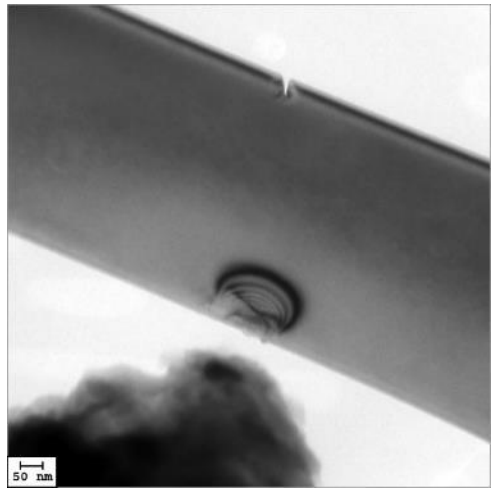
PI-95 Picoindenter in TEM

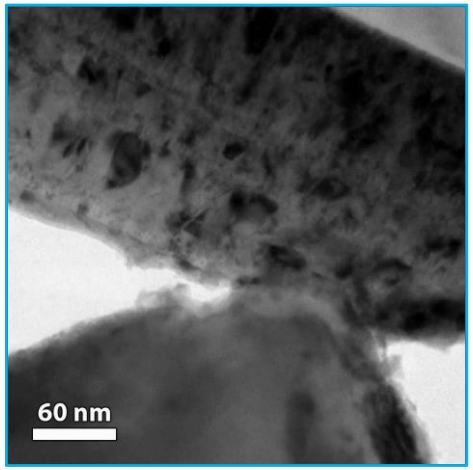
Dr. Khalid Hattar
khattar@sandia.gov



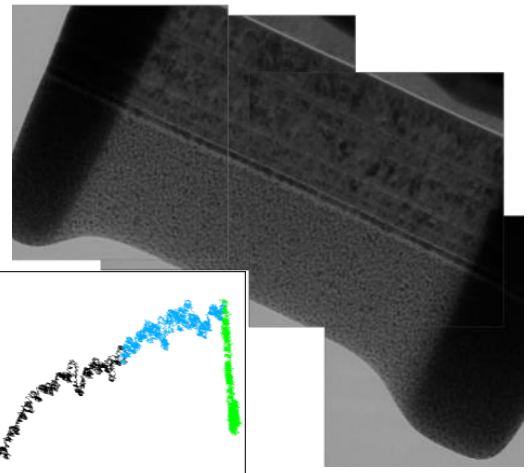
Notched Bar

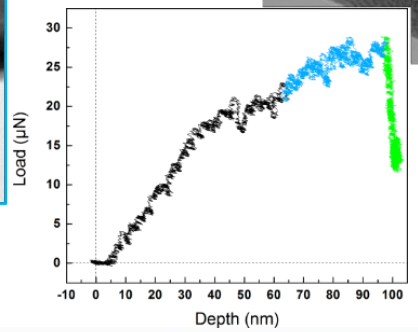


Nanoindentation

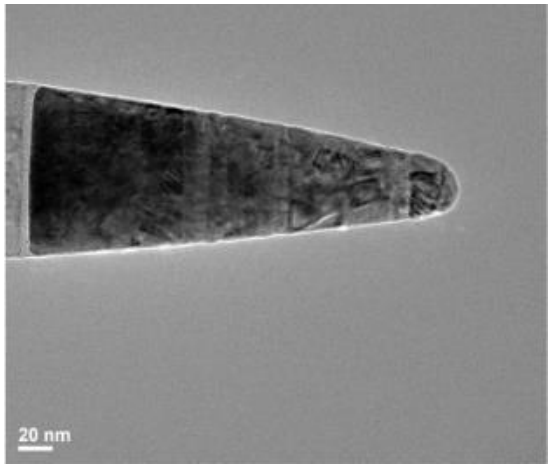


I Beams

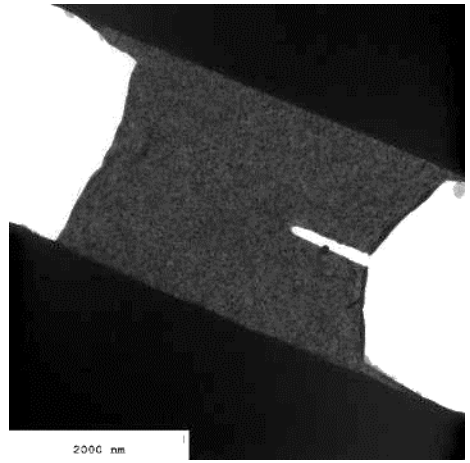




Nanopillars

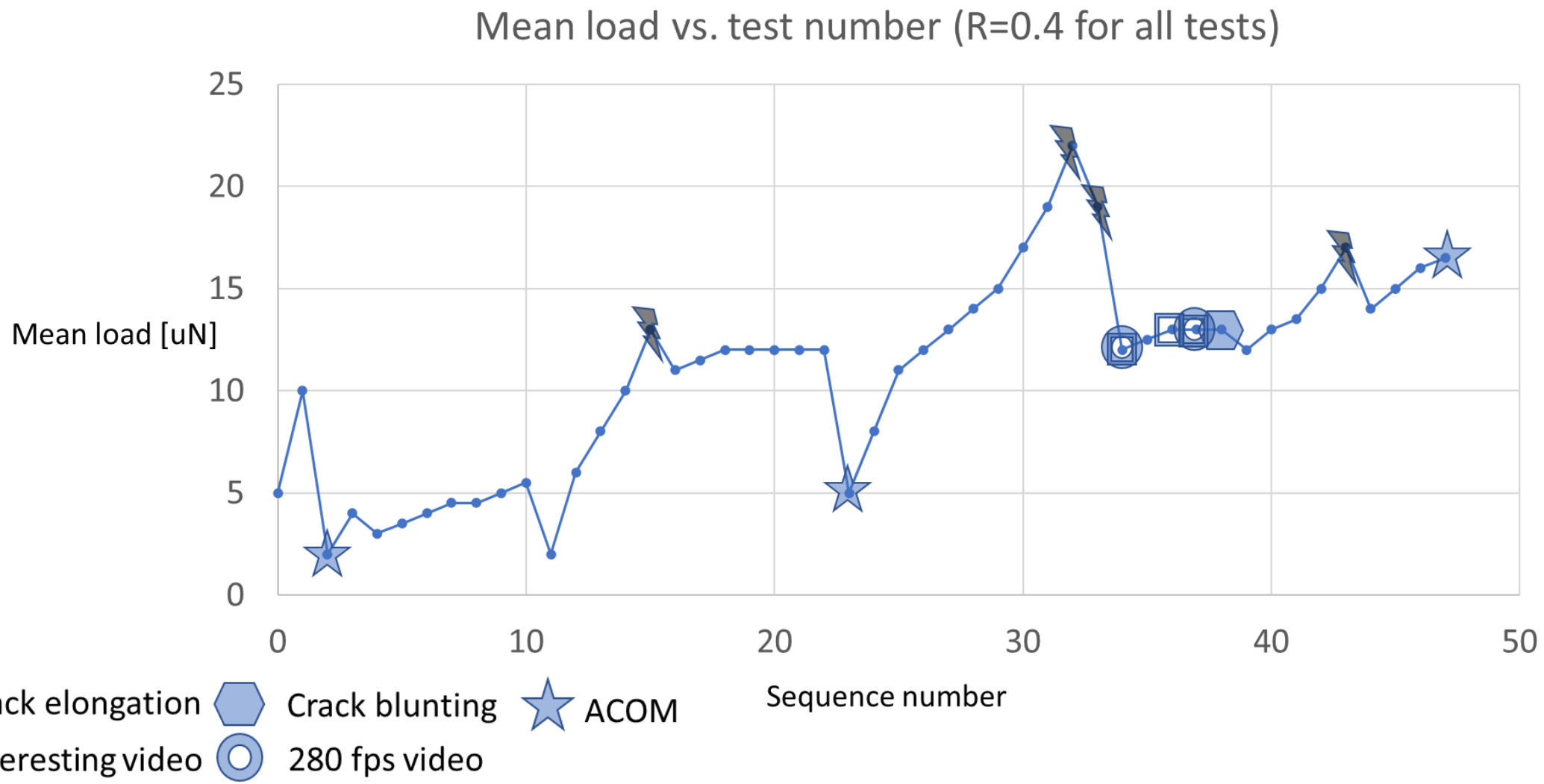


Notched Micro Tension Bars



Sandia National Laboratories

A6-2 Experiment



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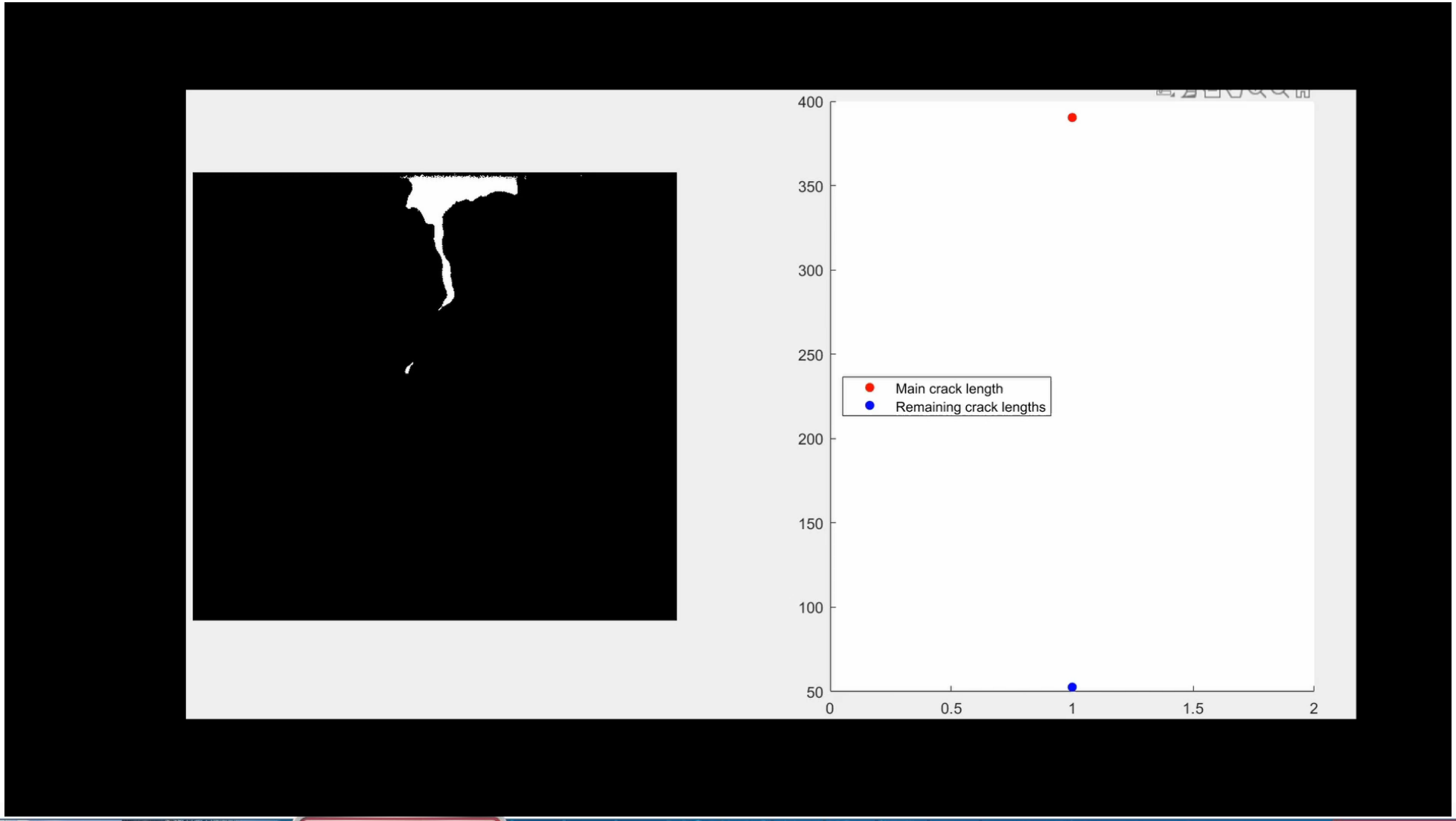
A6-2 Experiment



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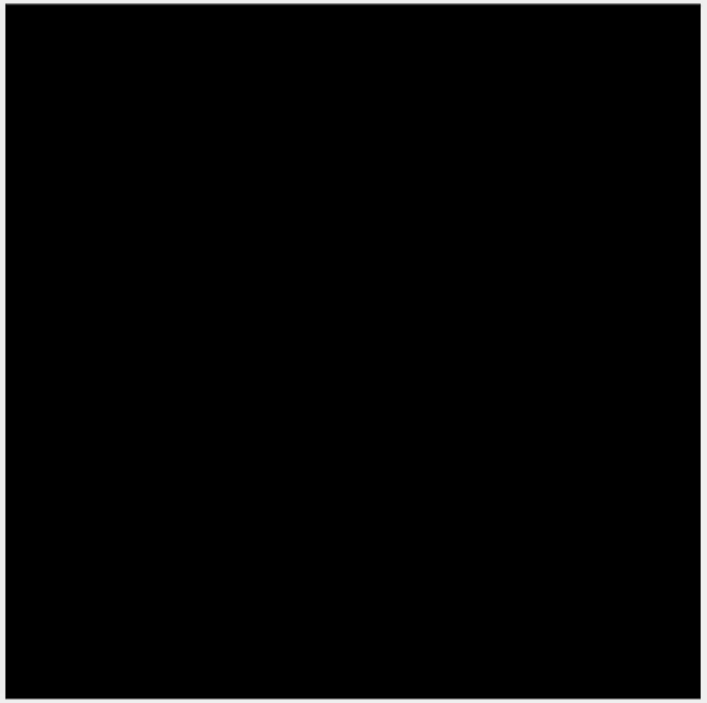
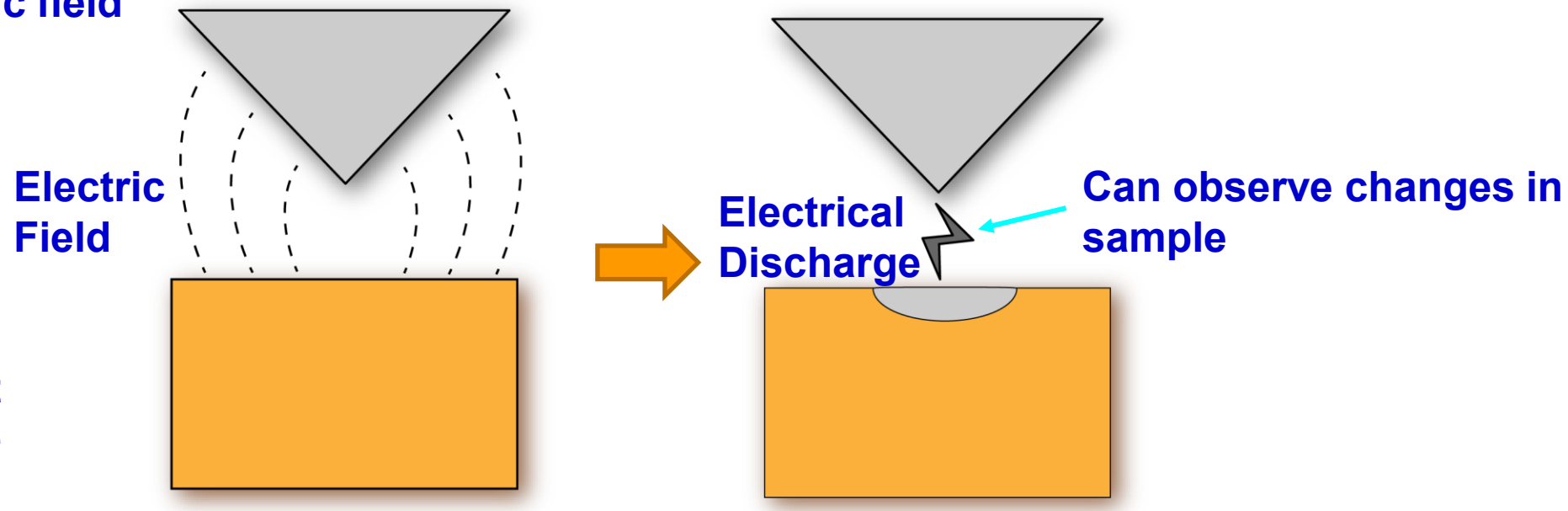
A6-2 Experiment



Future: Electrical-Mechanical TEM

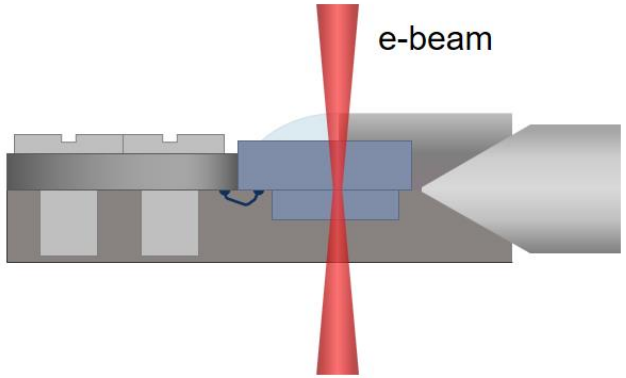
- Electromigration
- Electrical discharge
- Can combine with laser stimulus

Nanoindentation tip from PI-95 that applies the electric field

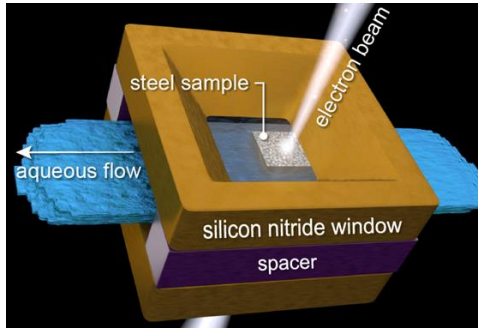


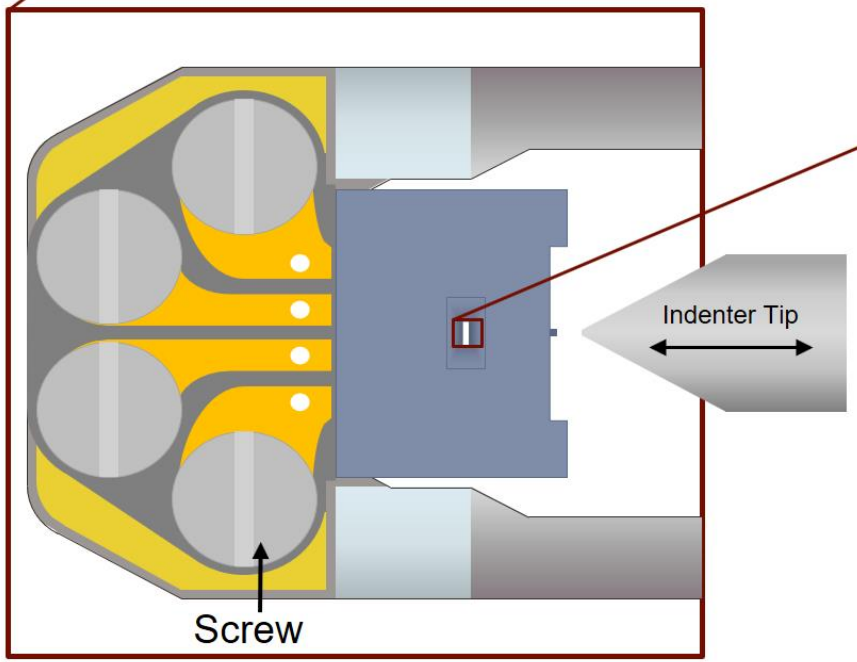
Sample can be at high temperature

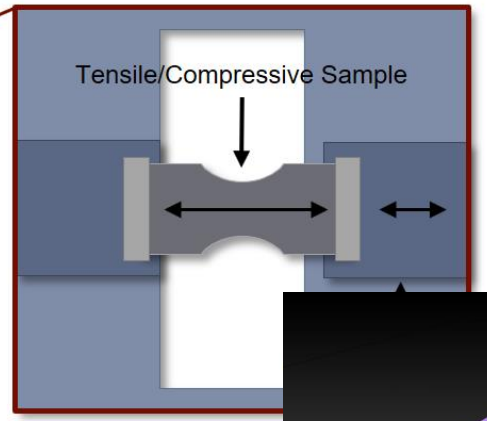
Future: Electrochemical-Mechanical TEM

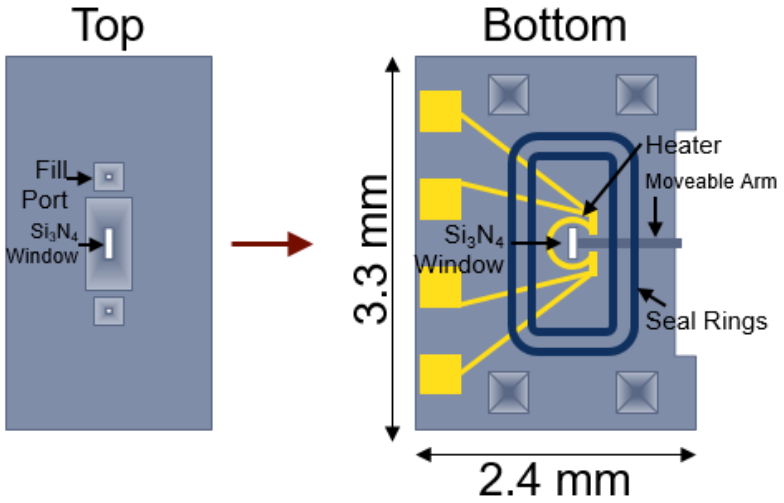


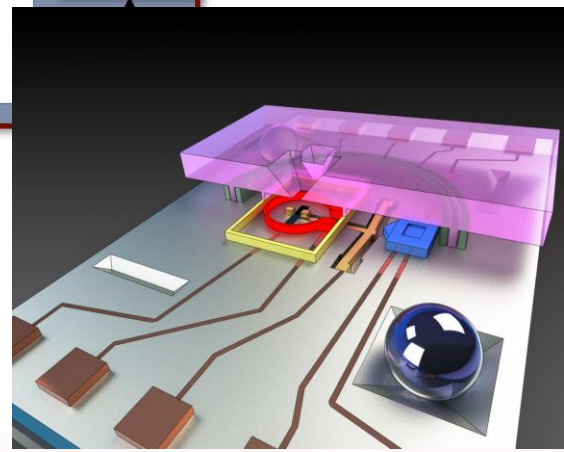
Hysitron PI-95 TEM PicoIndenter with 4 Electrical Leads











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Thank You! Questions?

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