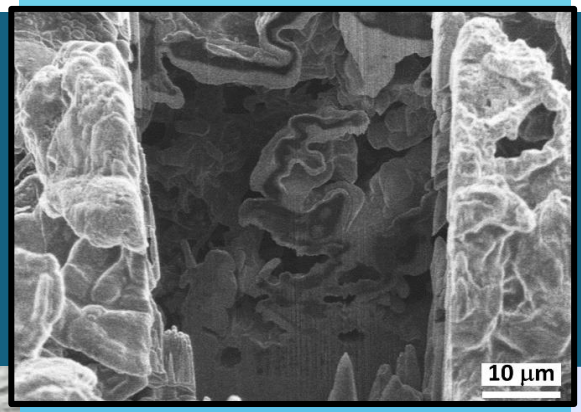
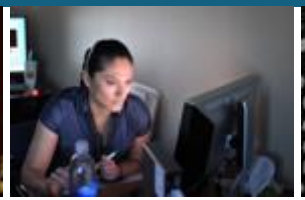
SAND2022-11200C

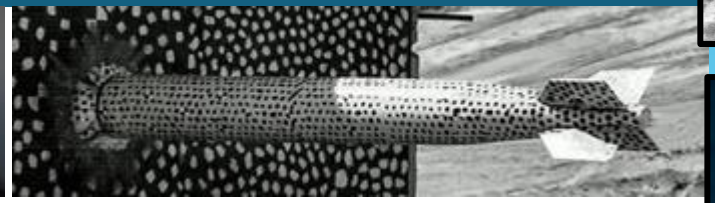
Sandia National Laboratories

Understanding lithium metal anodes in batteries through cryogenic focused ion beam and electron microscopy techniques

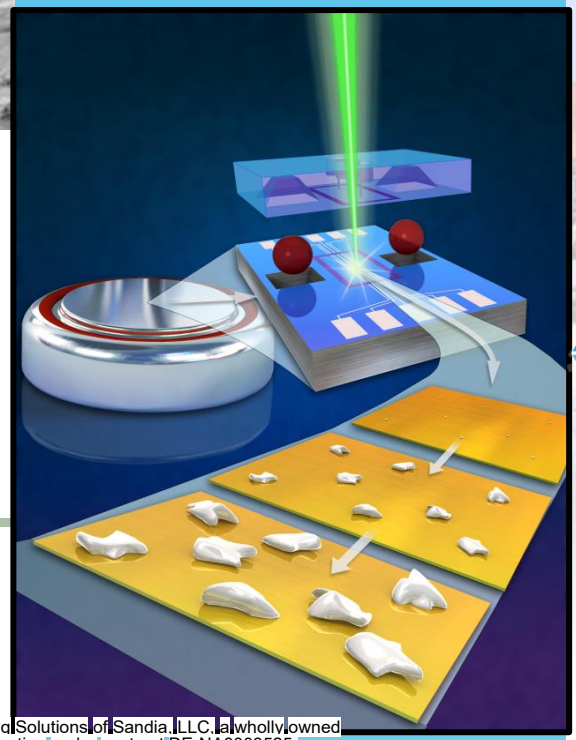


Supported in part by the Laboratory Directed Research and Development program at Sandia National Laboratories.





Molecular Foundry User Meeting
Lawrence Berkeley National Lab



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LDRD
Laboratory Directed Research and Development

U.S. DEPARTMENT OF ENERGY

NNSA

PRESENTED BY

Katharine Harrison, katharr@sandia.gov

Sandia National Laboratories

plus many excellent collaborators acknowledged throughout including several **microscopists** underlined and bolded

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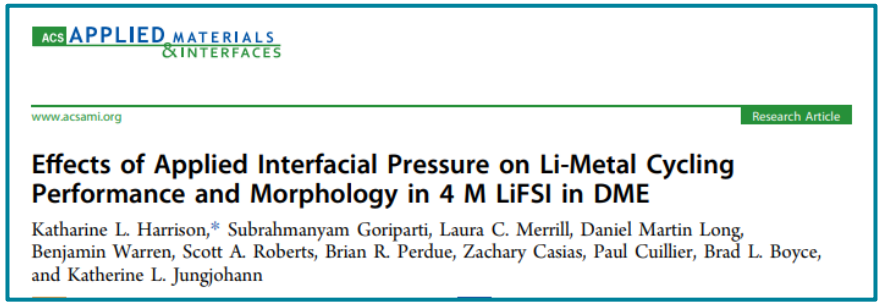
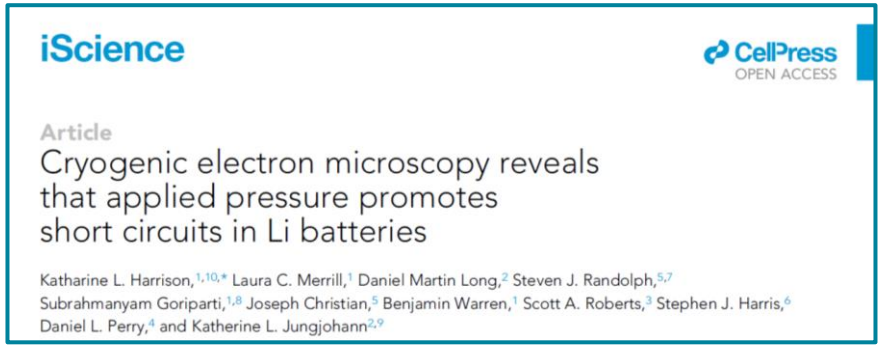
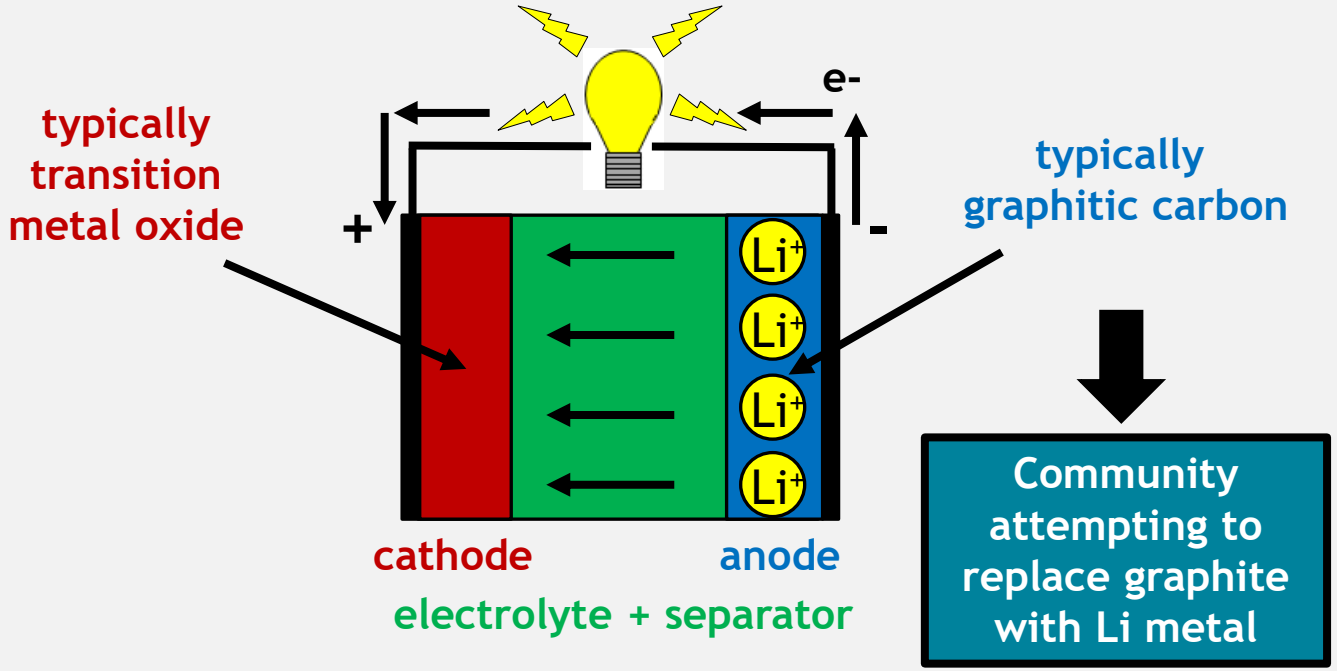
Outline

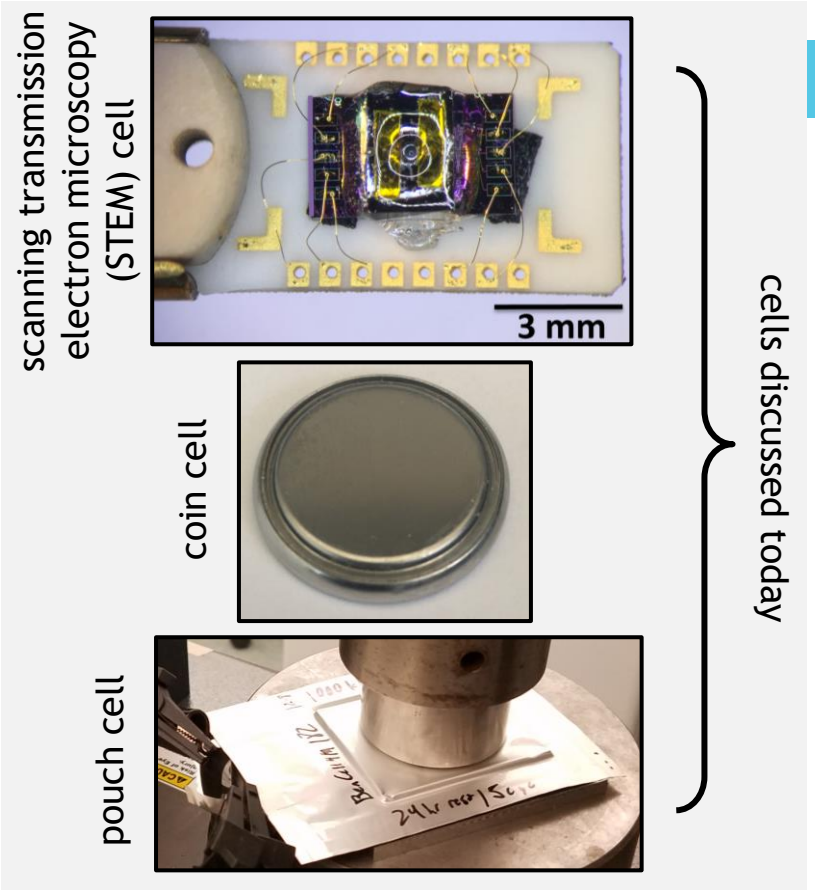
1. **Background and motivation**
2. In situ STEM of Li metal anode cycling
3. Cyro FIB/SEM reveals pressure effects on Li anodes at low current
4. Cryo FIB/SEM reveals pressure effects on Li anodes at high current
5. Cryo laser PFIB/SEM Li anode interfaces without cell disassembly
6. Cryo laser PFIB/SEM to understand volume expansion in Li anodes
7. In situ STEM to understand Li anode self discharge
8. Cyro FIB/SEM to understand self discharge of Li anodes





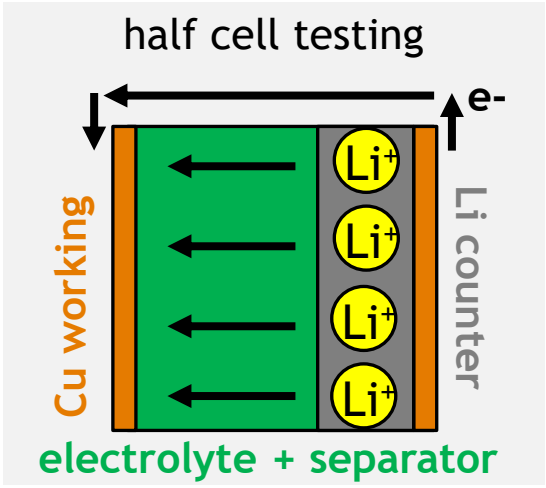
Replacing graphite anodes with Li metal anodes theoretically increases charge storage capacity 10x





Discharging Battery

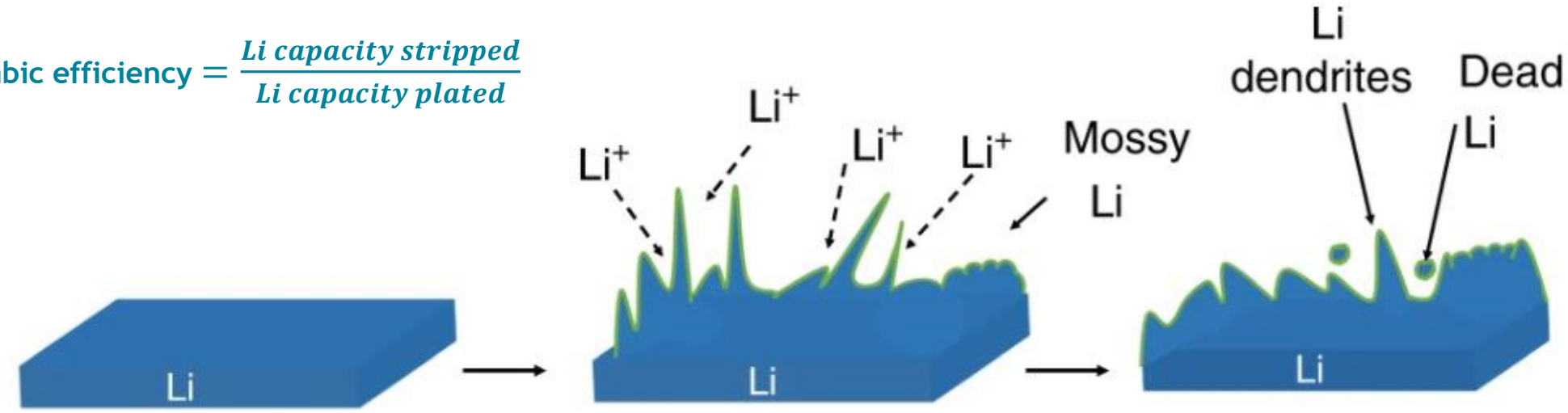
- Li^+ from the anode through the electrolyte and into the cathode
- e- move through the external circuit from the anode to the cathode (from - to + charge)



Why are rechargeable Li metal anodes difficult to commercialize?

- Mossy or dendritic morphology
  - Solid electrolyte interphase (SEI) = low Coulombic efficiency (CE), high impendence, Li consumption
  - Li gets stranded and disconnected = “dead” Li
  - Short circuits = fire
- Electrolyte selection improves this problem – focus on high concentrated electrolytes in this talk
- **Electron microscopy imaging is critically important to understand Li morphology evolution**

$$\text{Coulombic efficiency} = \frac{Li\ capacity\ stripped}{Li\ capacity\ plated}$$



Li starts like this

Li cycles to form this

Pathak et al. *Nature Communications*, 2020.
DOI: 10.1038/s41467-019-13774-2

Outline

Motivation = understand Li growth progression in high concentration electrolytes that improve Li morphology and CE

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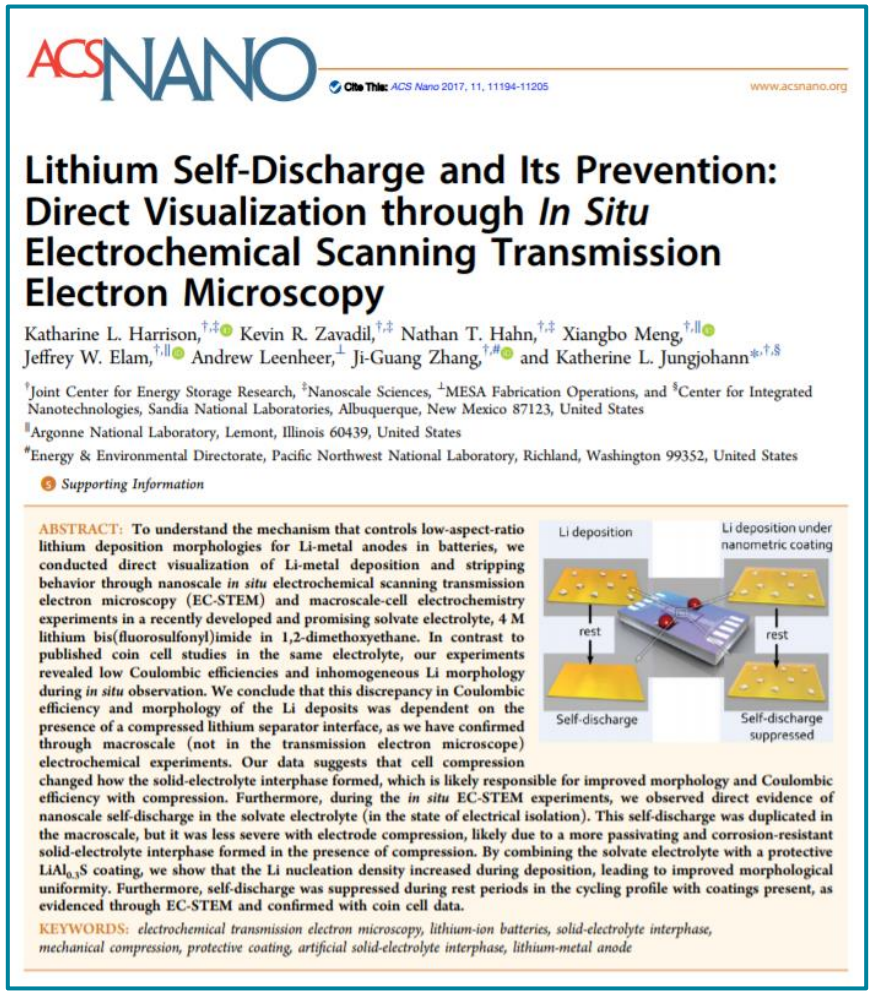

ACS NANO

Cite This: ACS Nano 2017, 11, 11194-11205 www.acsnano.org

Lithium Self-Discharge and Its Prevention: Direct Visualization through *In Situ* Electrochemical Scanning Transmission Electron Microscopy

Katharine L. Harrison,[†,‡] Kevin R. Zavadil,[†,‡] Nathan T. Hahn,[†,‡] Xiangbo Meng,[†,∥] Jeffrey W. Elam,[†,∥] Andrew Leenheer,[⊥] Ji-Guang Zhang,[†,#] and Katherine L. Jungjohann*[,†,§]

[†]Joint Center for Energy Storage Research, [‡]Nanoscale Sciences, [⊥]MESA Fabrication Operations, and [§]Center for Integrated Nanotechnologies, Sandia National Laboratories, Albuquerque, New Mexico 87123, United States

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Supporting Information

ABSTRACT: To understand the mechanism that controls low-aspect-ratio lithium deposition morphologies for Li-metal anodes in batteries, we conducted direct visualization of Li-metal deposition and stripping behavior through nanoscale *in situ* electrochemical scanning transmission electron microscopy (EC-STEM) and macroscale-cell electrochemistry experiments in a recently developed and promising solvate electrolyte, 4 M lithium bis(fluorosulfonyl)imide in 1,2-dimethoxyethane. In contrast to published coin cell studies in the same electrolyte, our experiments revealed low Coulombic efficiencies and inhomogeneous Li morphology during *in situ* observation. We conclude that this discrepancy in Coulombic efficiency and morphology of the Li deposits was dependent on the presence of a compressed lithium separator interface, as we have confirmed through macroscale (not in the transmission electron microscope) electrochemical experiments. Our data suggests that cell compression changed how the solid-electrolyte interphase formed, which is likely responsible for improved morphology and Coulombic efficiency with compression. Furthermore, during the *in situ* EC-STEM experiments, we observed direct evidence of nanoscale self-discharge in the solvate electrolyte (in the state of electrical isolation). This self-discharge was duplicated in the macroscale, but it was less severe with electrode compression, likely due to a more passivating and corrosion-resistant solid-electrolyte interphase formed in the presence of compression. By combining the solvate electrolyte with a protective $LiAl_{0.3}S$ coating, we show that the Li nucleation density increased during deposition, leading to improved morphological uniformity. Furthermore, self-discharge was suppressed during rest periods in the cycling profile with coatings present, as evidenced through EC-STEM and confirmed with coin cell data.

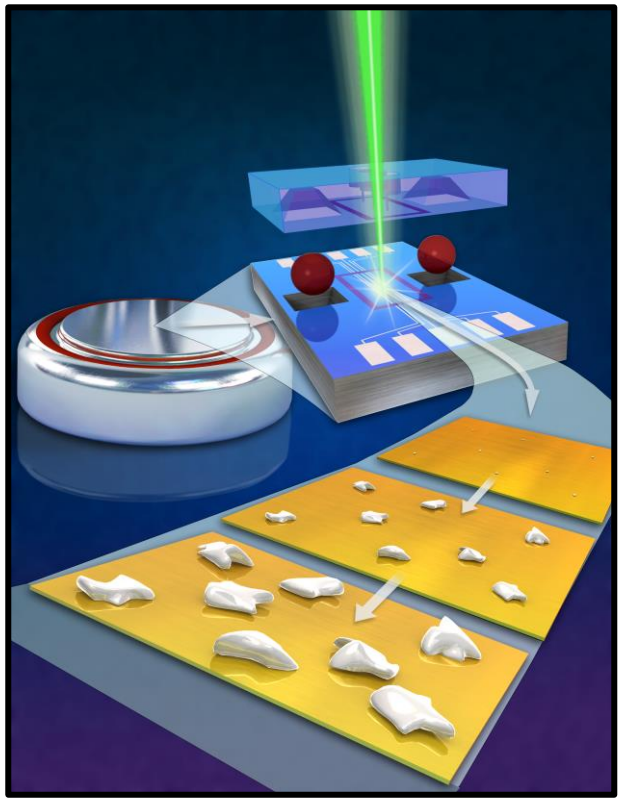
KEYWORDS: *electrochemical transmission electron microscopy, lithium-ion batteries, solid-electrolyte interphase, mechanical compression, protective coating, artificial solid-electrolyte interphase, lithium-metal anode*

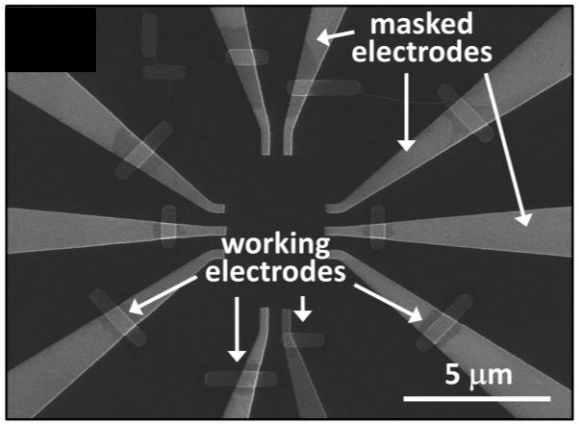
JCESR

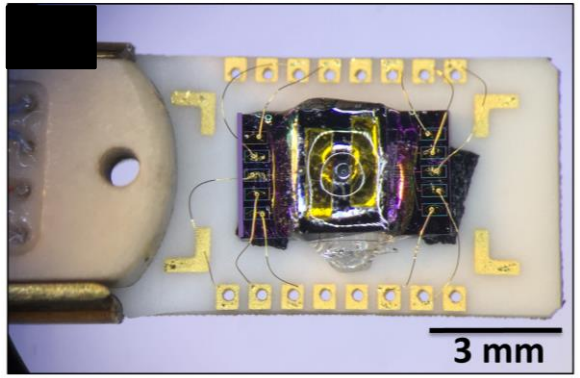
Center for Integrated Nanotechnologies — CINT — Sandia — Los Alamos — Discovery — Performance — Education — Integration

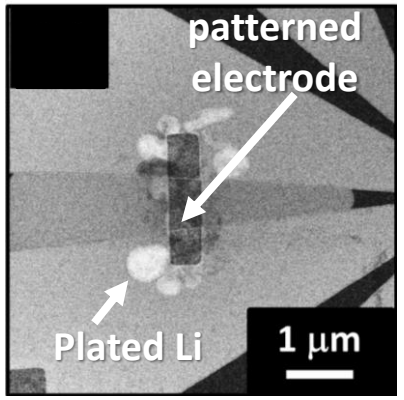
K.L. Harrison, K.R. Zavadil, N.T. Hahn, X. Meng, J.W. Elam, A. Leenheer, J.G. Zhang, and **K.L. Jungjohann**, 2017, Lithium self-discharge and its prevention: direct visualization through in situ electrochemical scanning transmission electron microscopy. *ACS nano*, 11(11), pp.11194-11205.

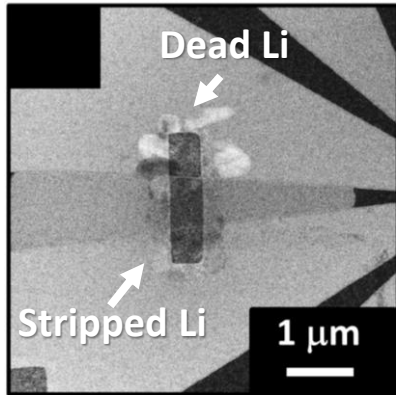
In situ electrochemical STEM revealed morphology that did not match coin cells, which we determined was due to lack of pressure in the in situ cell

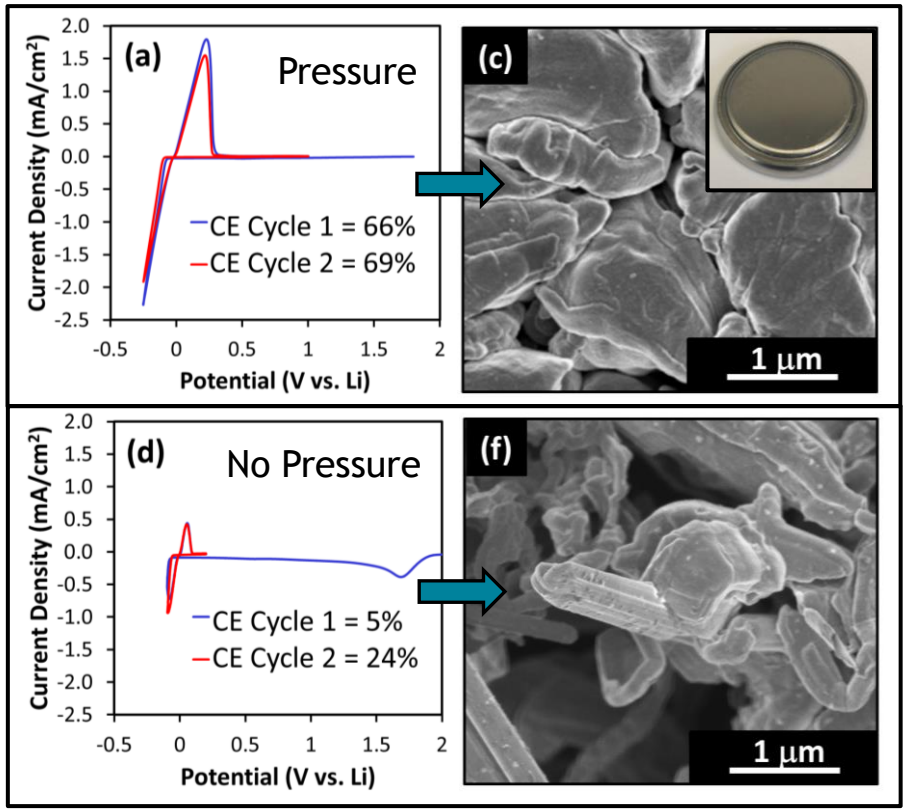












Harrison et al. *ACS Nano*
10.1021/acsnano.7b05513

- CE very low (18% ± 9%)
- Varied morphology
- Dead Li formation

- Applied pressure needed for high CE and favorable morphology
- Pressure cannot easily be replicated through in situ experiments

4 M lithium bisfluorosulfonyl imide in 1,2 dimethoxyethane = 4 M LiFSI in DME

Outline

Motivation = systematically study impact of pressure on Li metal anode cycling, using ex situ cryo FIB/SEM to understand morphology

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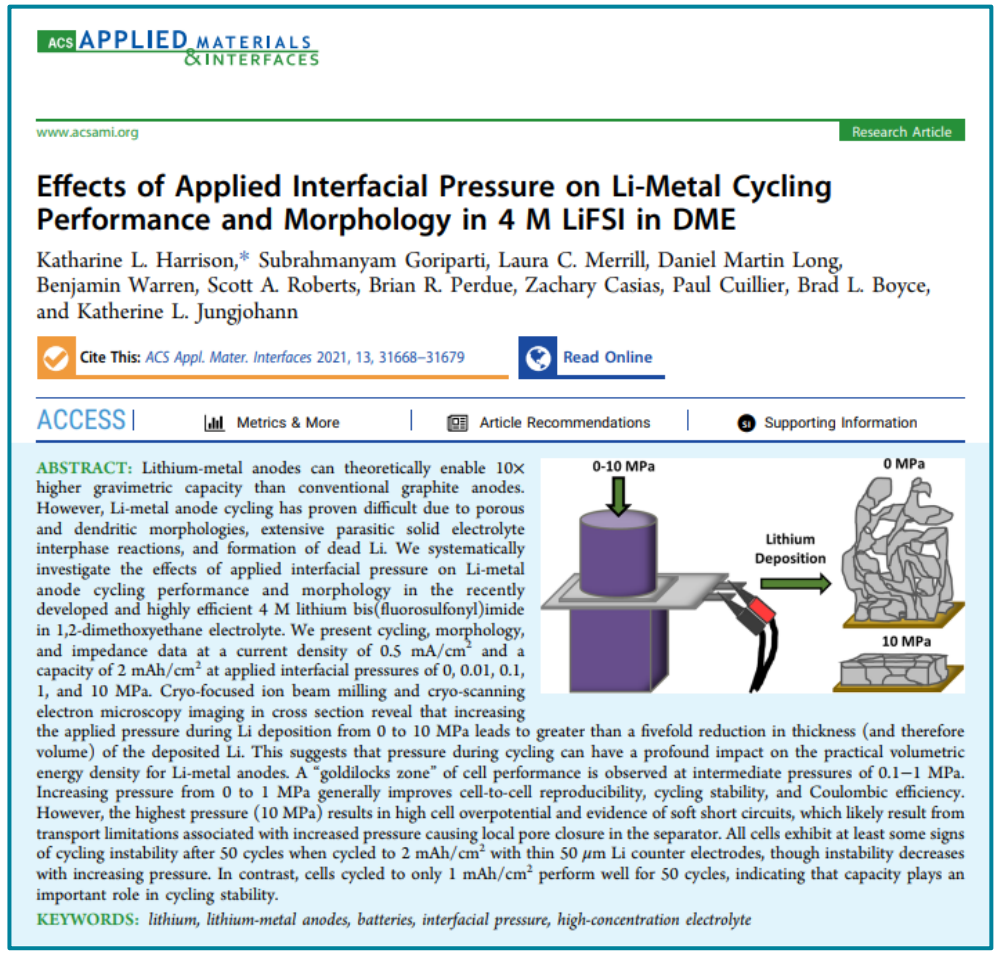
FIB = focused ion beam
SEM = scanning electron microscopy



ACS APPLIED MATERIALS & INTERFACES

www.acsami.org Research Article

Effects of Applied Interfacial Pressure on Li-Metal Cycling Performance and Morphology in 4 M LiFSI in DME

Katharine L. Harrison,* Subrahmanyam Goriparti, Laura C. Merrill, Daniel Martin Long, Benjamin Warren, Scott A. Roberts, Brian R. Perdue, Zachary Casias, Paul Cuillier, Brad L. Boyce, and Katherine L. Jungjohann

Cite This: *ACS Appl. Mater. Interfaces* 2021, 13, 31668−31679 Read Online

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ABSTRACT: Lithium-metal anodes can theoretically enable 10× higher gravimetric capacity than conventional graphite anodes. However, Li-metal anode cycling has proven difficult due to porous and dendritic morphologies, extensive parasitic solid electrolyte interphase reactions, and formation of dead Li. We systematically investigate the effects of applied interfacial pressure on Li-metal anode cycling performance and morphology in the recently developed and highly efficient 4 M lithium bis(fluorosulfonyl)imide in 1,2-dimethoxyethane electrolyte. We present cycling, morphology, and impedance data at a current density of 0.5 mA/cm^2 and a capacity of 2 mAh/cm^2 at applied interfacial pressures of 0, 0.01, 0.1, 1, and 10 MPa. Cryo-focused ion beam milling and cryo-scanning electron microscopy imaging in cross section reveal that increasing the applied pressure during Li deposition from 0 to 10 MPa leads to greater than a fivefold reduction in thickness (and therefore volume) of the deposited Li. This suggests that pressure during cycling can have a profound impact on the practical volumetric energy density for Li-metal anodes. A "goldilocks zone" of cell performance is observed at intermediate pressures of 0.1−1 MPa. Increasing pressure from 0 to 1 MPa generally improves cell-to-cell reproducibility, cycling stability, and Coulombic efficiency. However, the highest pressure (10 MPa) results in high cell overpotential and evidence of soft short circuits, which likely result from transport limitations associated with increased pressure causing local pore closure in the separator. All cells exhibit at least some signs of cycling instability after 50 cycles when cycled to 2 mAh/cm^2 with thin 50 μm Li counter electrodes, though instability decreases with increasing pressure. In contrast, cells cycled to only 1 mAh/cm^2 perform well for 50 cycles, indicating that capacity plays an important role in cycling stability.

KEYWORDS: *lithium, lithium-metal anodes, batteries, interfacial pressure, high-concentration electrolyte*

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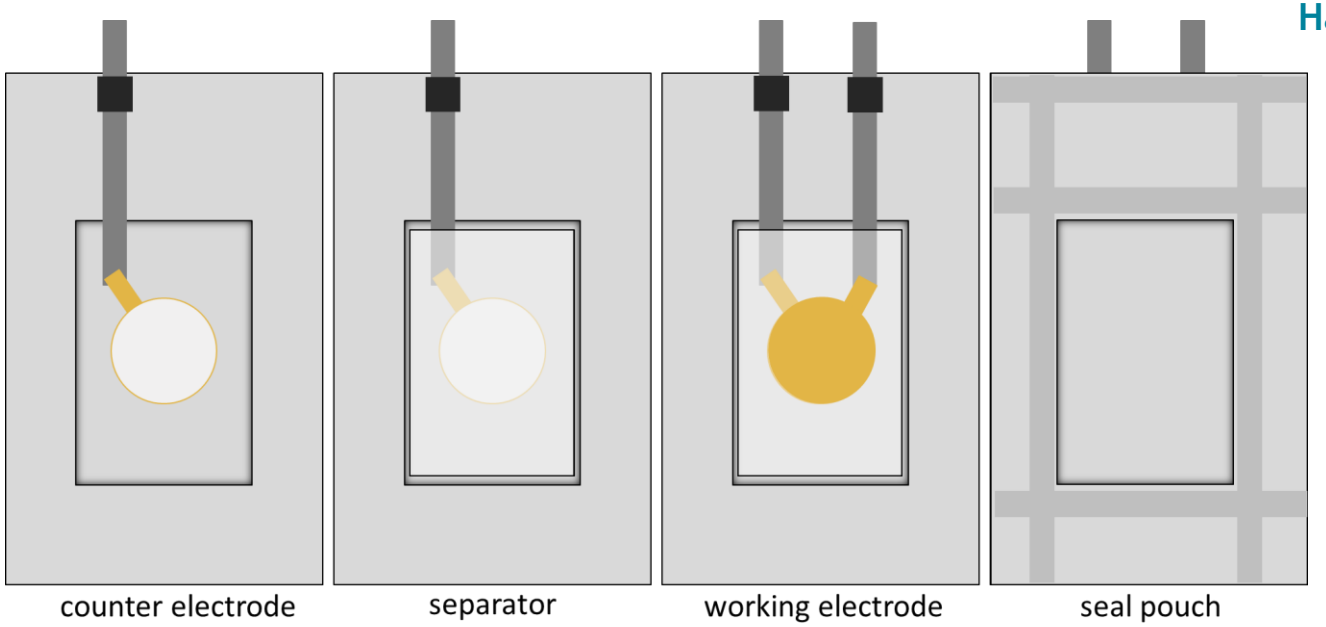
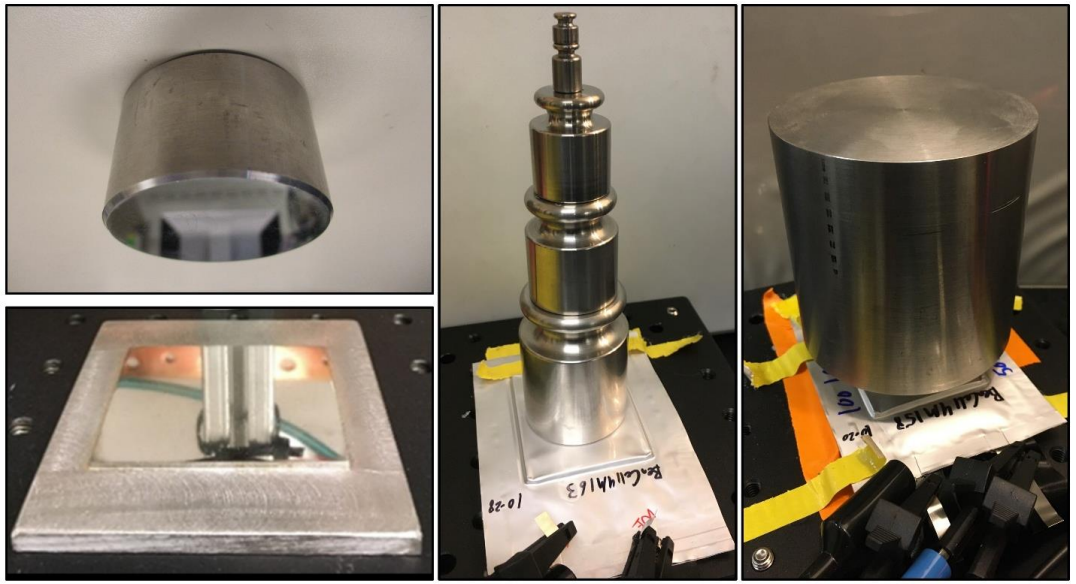
Center for Integrated Nanotechnologies — CINT — Discovery, Performance, Integration, Education — Sandia, Los Alamos

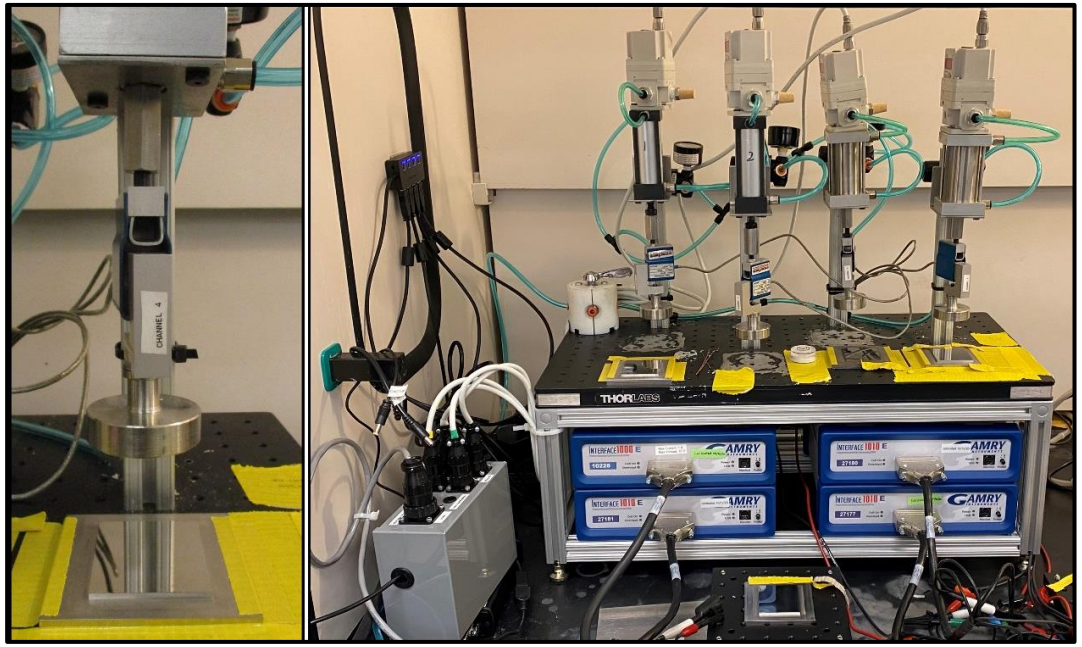
K.L. Harrison, S. Goriparti, L.C. Merrill, **D.M. Long**, B. Warren, S.A. Roberts, B.R. Perdue, Z. Casias, P. Cuillier, B.L. Boyce, and **K.L. Jungjohann**, 2021, Effects of applied interfacial pressure on Li-metal cycling performance and morphology in 4 M LiFSI in DME. *ACS Applied Materials & Interfaces*, *13*(27), pp.31668-31679.

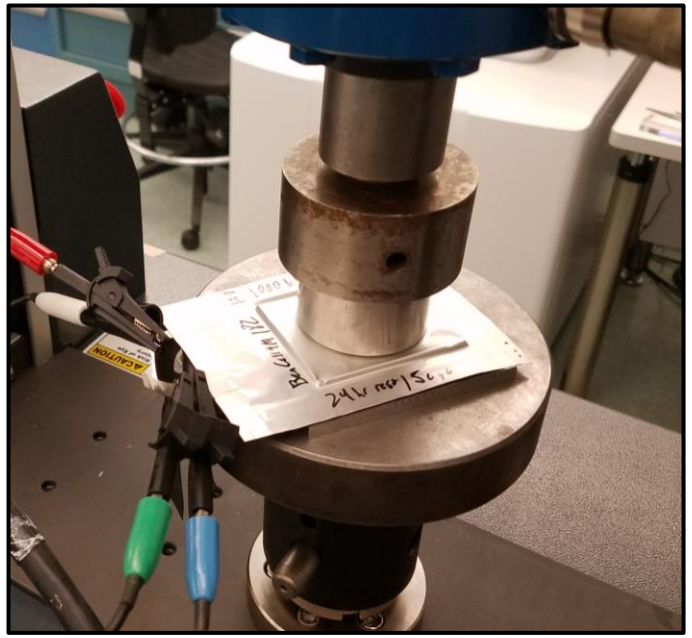
Systematically study effects of pressure on Li versus pouch Cu cells 0-10 MPa

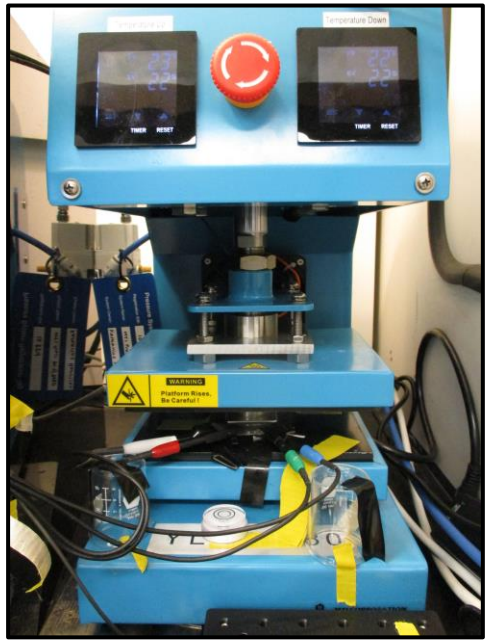
Harrison et al., *ACS App. Mat. & Int.*, 10.1021/acsami.1c06488











Cryogenic Ga^+ FIB and cryogenic SEM after one Li deposition on Cu reveals much denser deposits at high pressure, but CE suggests shorts at 10 MPa

Harrison et al., *ACS App. Mat. & Int.*, 10.1021/acsami.1c06488

- CE trends with morphology
- Higher than 100% CE in *1st cycle* at 10 MPa (pressure induced soft short circuits?)

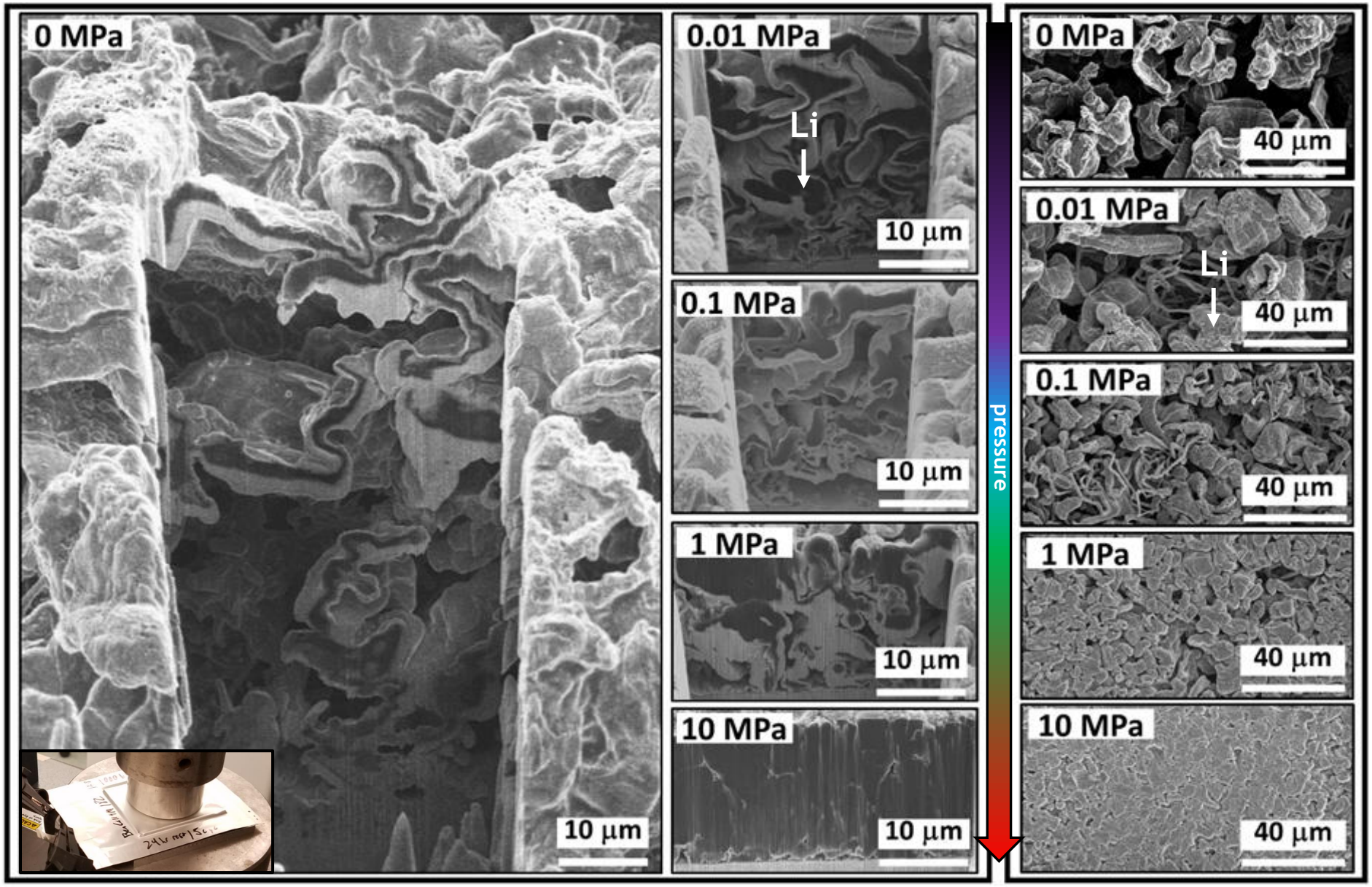
Pressure (MPa)	Average CE (%) First Cycle
0	82.3 ± 6.2
0.01	90.5 ± 4.1
0.1	97.5 ± 0.6
1	93.6 ± 5.3
10	106.2 ± 1.6

pressure

Pressure (MPa)	Thickness 1st Plating (mm)
0	91
0.01	33
0.1	30
1	22
10	17

pressure

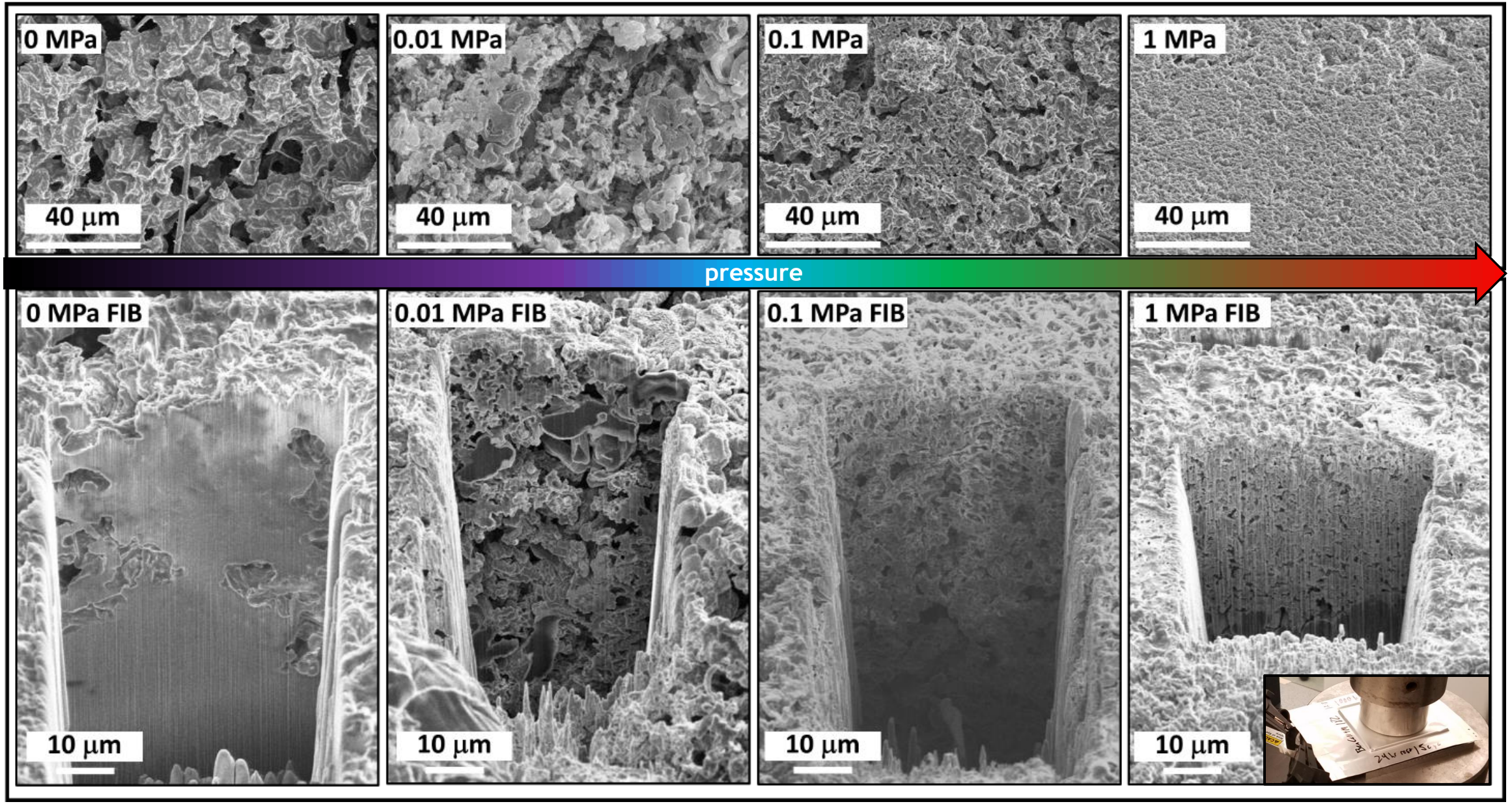
4 M LiFSI in DME
0.5 mA/cm²
2 mAh/cm²



Pressure still improves morphology after 51st Li deposition but we can't mill through

4 M LiFSI in DME, 0.5 mA/cm^2, 2 mAh/cm^2

Harrison et al., *ACS App. Mat. & Int.*, 10.1021/acsami.1c06488



Outline

Motivation = systematically study impact of pressure on Li anode cycling at high current where dendrites form, using ex situ cryo FIB/SEM to understand morphology

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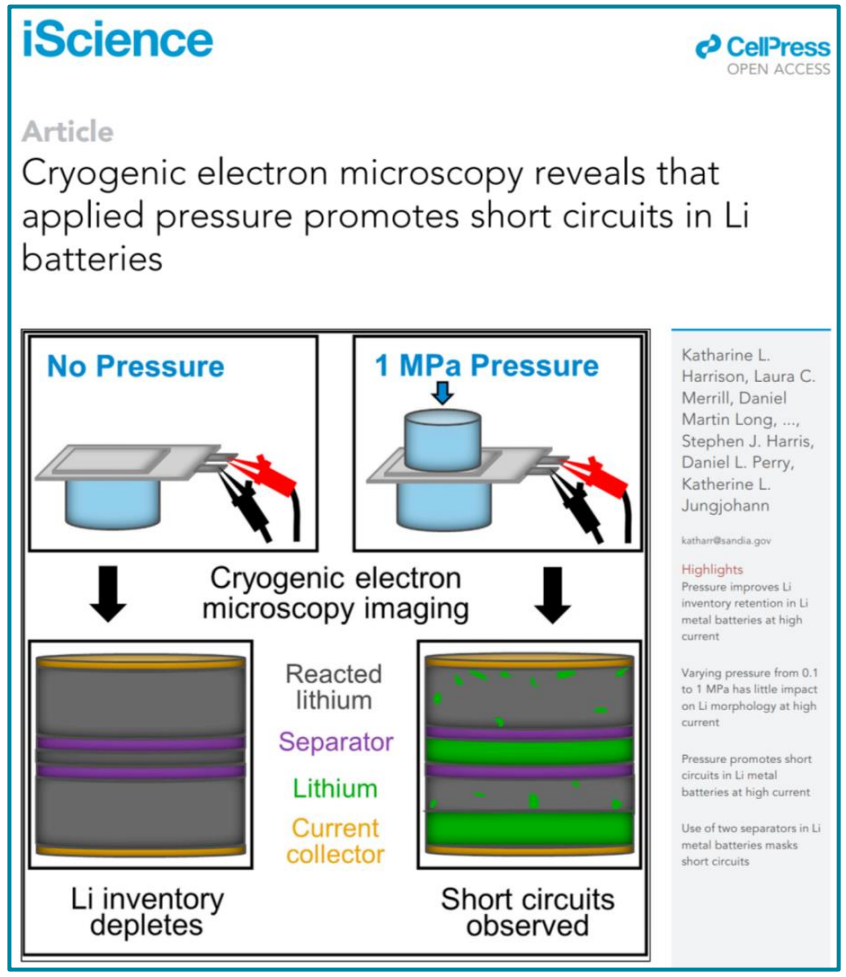

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K.L. Harrison, L.C. Merrill, **D.M. Long**, **S.J. Randolph**, **S.** Goriparti, **J. Christian**, B. Warren, S.A. Roberts, S.J. Harris, **D.L. Perry**, and **K.L. Jungjohann**, 2021, Cryogenic electron microscopy reveals that applied pressure promotes short circuits in Li batteries. *Iscience*, *24*(12), p.103394.

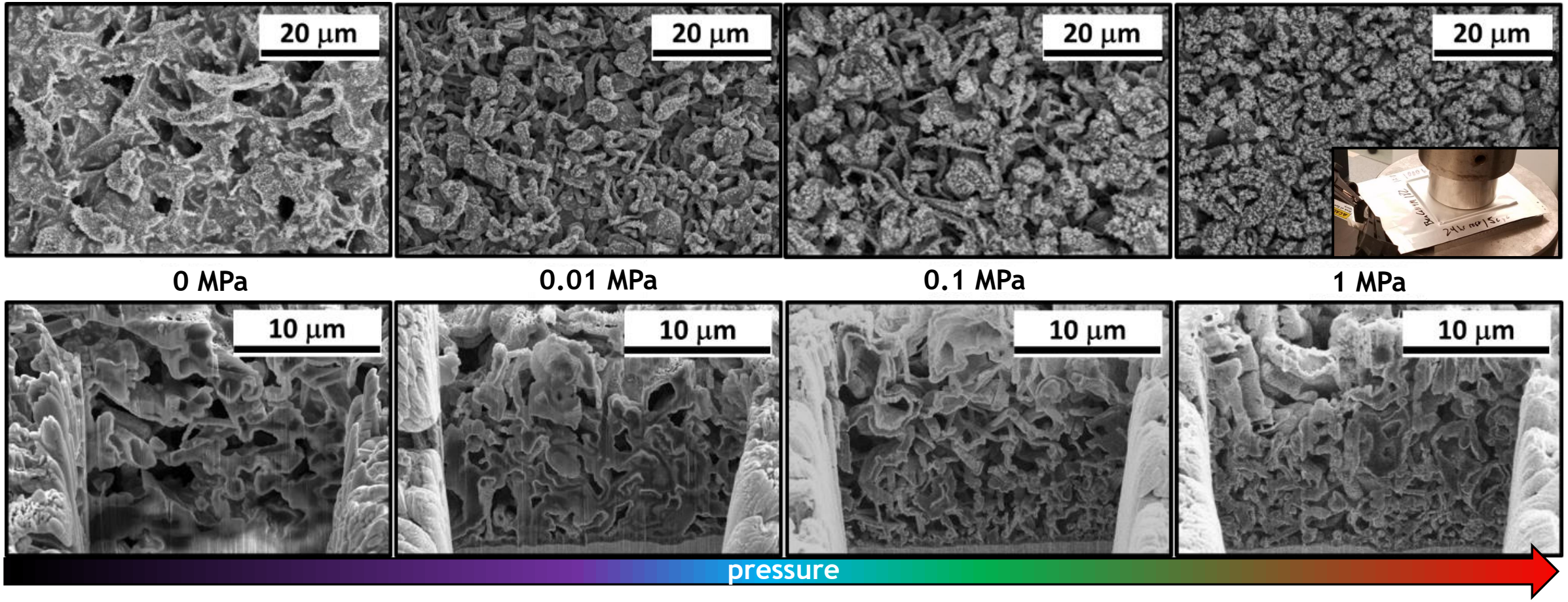
Li deposits at high current thinner and less dependent on pressure than low current

Harrison et al., *iScience*, 10.1016/j.isci.2021.103394

- 1st Li deposition at high current → little change from 0 to 1 MPa
- Low current, → Li can nucleate/grow at favorable sites because overpotentials small
  - Mechanical overpotential to displace pressurized interface larger than other overpotentials
- High current → overpotentials large so Li nucleates/grows everywhere
  - Mechanical overpotential small relative to other overpotentials so doesn't affect growth

Pressure (MPa)	Thickness 4 mA/cm² (μm)	Thickness 0.5 mA/cm² (μm)
0	varied	91
0.01	22	33
0.1	21	30
1	19	22

4 M LiFSI in DME, 2 mAh/cm²



Outline

Motivation = mill through entire electrode stack and image cross section to understand interfaces without destroying interfaces and evidence of dendrites

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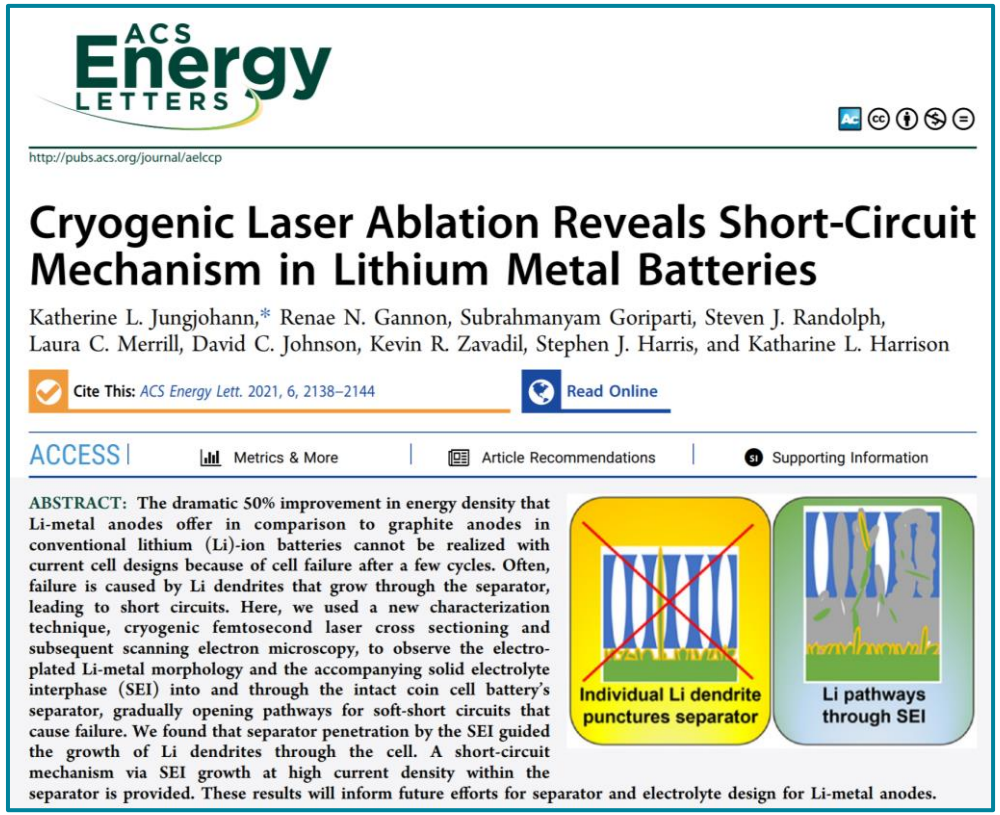
PFIB = plasma focused ion beam



ACS Energy LETTERS

http://pubs.acs.org/journal/aelccp

Cryogenic Laser Ablation Reveals Short-Circuit Mechanism in Lithium Metal Batteries

Katherine L. Jungjohann,* Renae N. Gannon, Subrahmanyam Goriparti, Steven J. Randolph, Laura C. Merrill, David C. Johnson, Kevin R. Zavadil, Stephen J. Harris, and Katharine L. Harrison

Cite This: *ACS Energy Lett.* 2021, 6, 2138–2144 | Read Online

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ABSTRACT: The dramatic 50% improvement in energy density that Li-metal anodes offer in comparison to graphite anodes in conventional lithium (Li)-ion batteries cannot be realized with current cell designs because of cell failure after a few cycles. Often, failure is caused by Li dendrites that grow through the separator, leading to short circuits. Here, we used a new characterization technique, cryogenic femtosecond laser cross sectioning and subsequent scanning electron microscopy, to observe the electroplated Li-metal morphology and the accompanying solid electrolyte interphase (SEI) into and through the intact coin cell battery's separator, gradually opening pathways for soft-short circuits that cause failure. We found that separator penetration by the SEI guided the growth of Li dendrites through the cell. A short-circuit mechanism via SEI growth at high current density within the separator is provided. These results will inform future efforts for separator and electrolyte design for Li-metal anodes.

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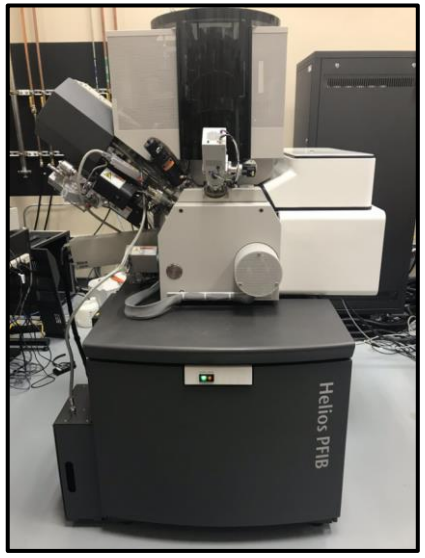
Center for Integrated Nanotechnologies CINT DISCOVERY PERFORMANCE INTEGRATION EDUCATION Sandia Los Alamos

K.L. Jungjohann, R.N. Gannon, S. Goriparti, S.J. Randolph, L.C. Merrill, D.C. Johnson, K.R. Zavadil, S.J. Harris, and K.L. Harrison, 2021, Cryogenic laser ablation reveals short-circuit mechanism in lithium metal batteries. *ACS Energy Letters*, 6(6), pp.2138-2144.

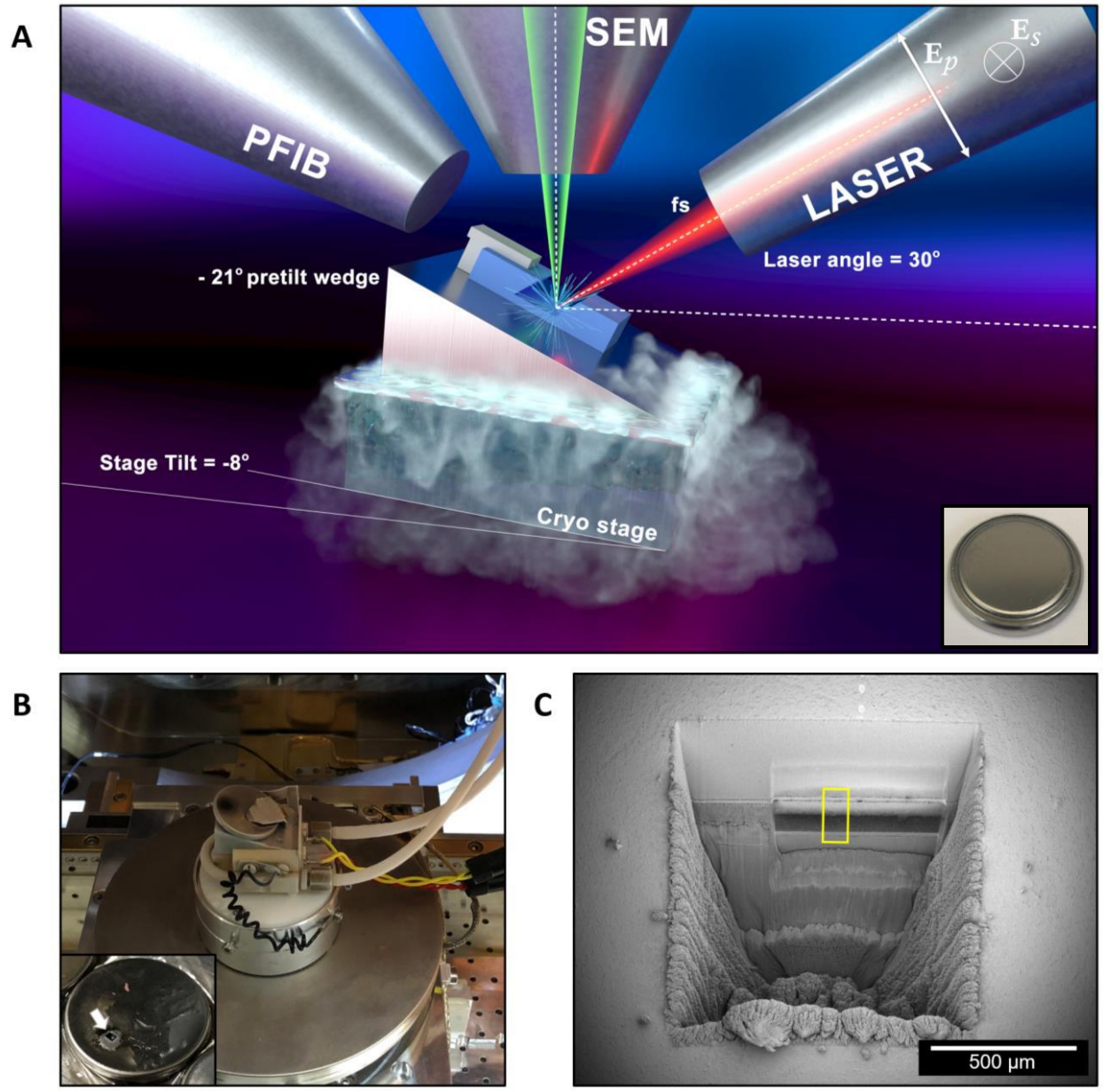
Used cryo laser PFIB to image interfaces without destroying them during cell disassembly

- ThermoFisher closely collaborated
- Cryo laser PFIB SEM (Helios 5)
- Freeze coin cell on cryo stage
- Mill through in tact coin cell
- 15000x faster than Ga^+ FIB
- Athermal milling to preserve Li



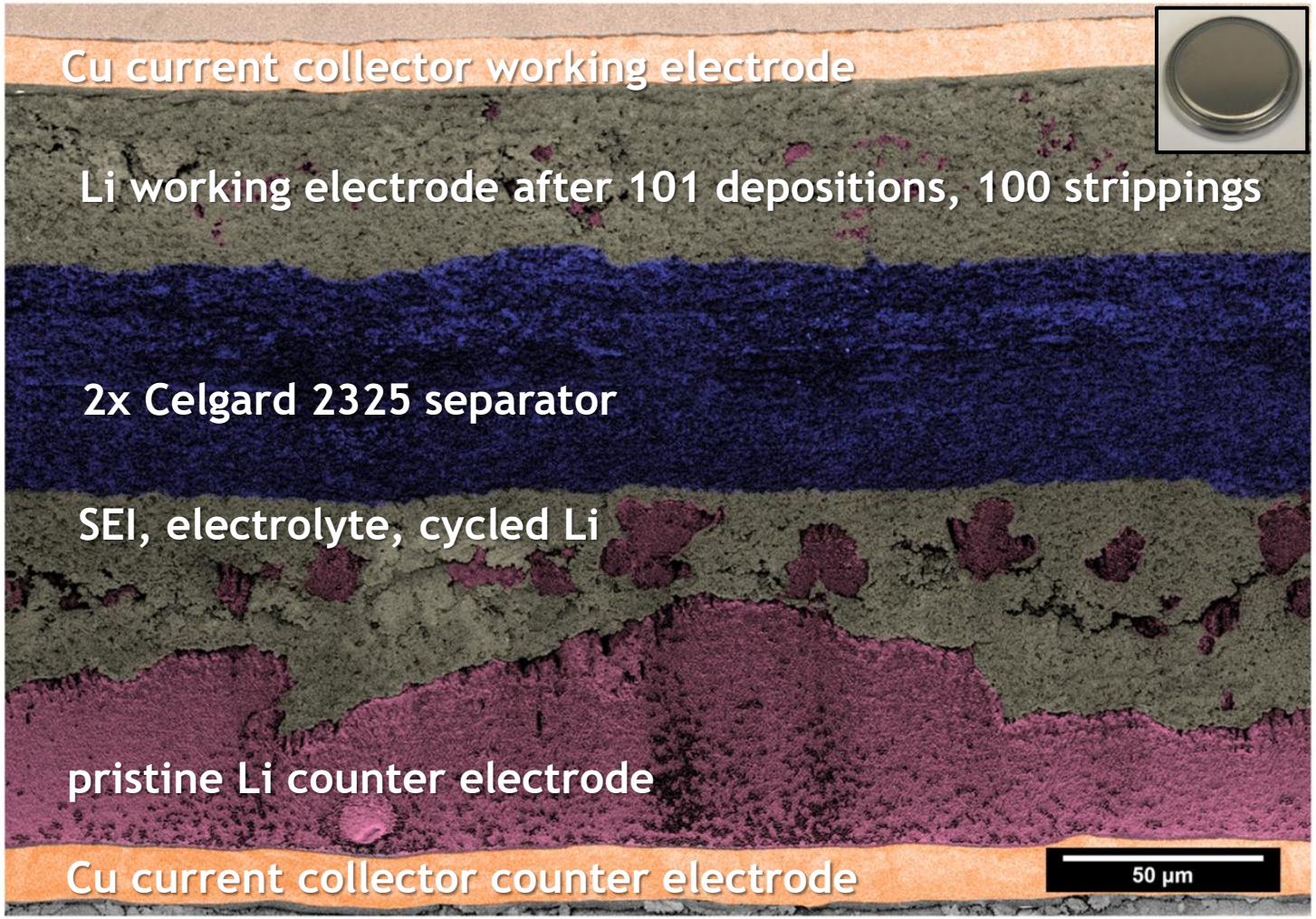
THANK YOU ThermoFisher!

Jungjohann et al., ACS Energy Letters,
10.1021/acsenergylett.1c00509



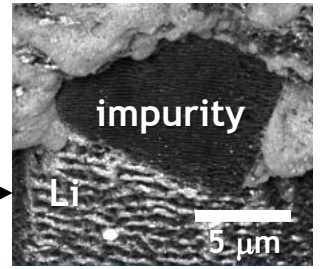
Laser PFIB/SEM shows well behaved Li cycling at low current after 101 cycles

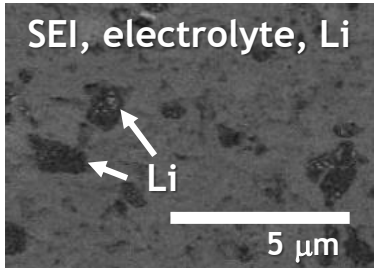
- Pristine Li remains at counter electrode and Celgard is in tact, but Li stripping is uneven
- Li deposits in small domains on working electrode with SEI and electrolyte interspersed

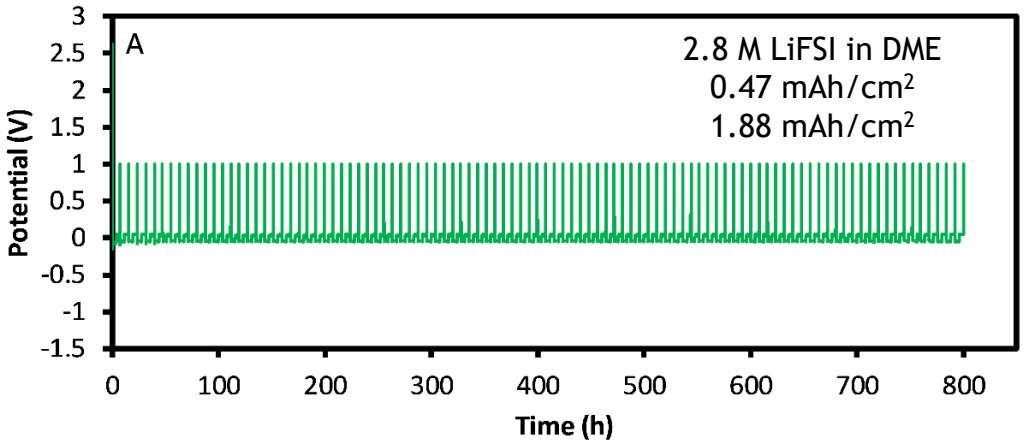


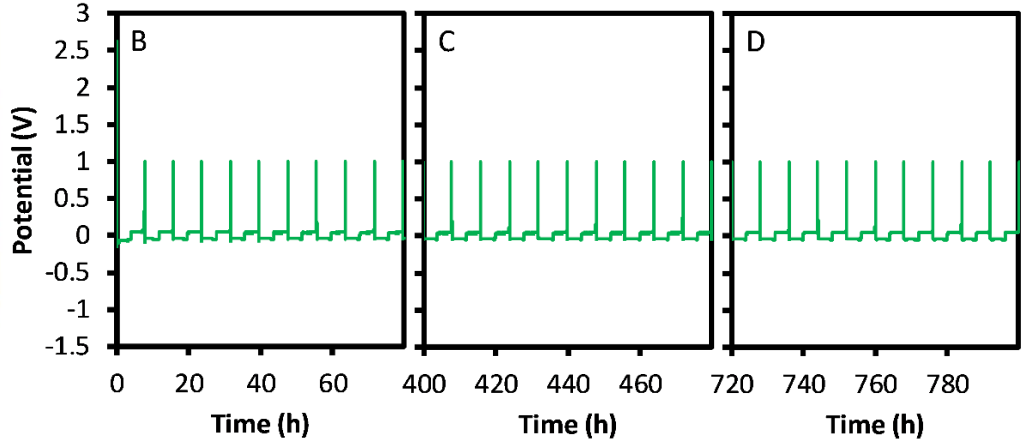
Jungjohann et al., ACS Energy Letters, 10.1021/acsenergylett.1c00509

laser induced pattern unique to Li



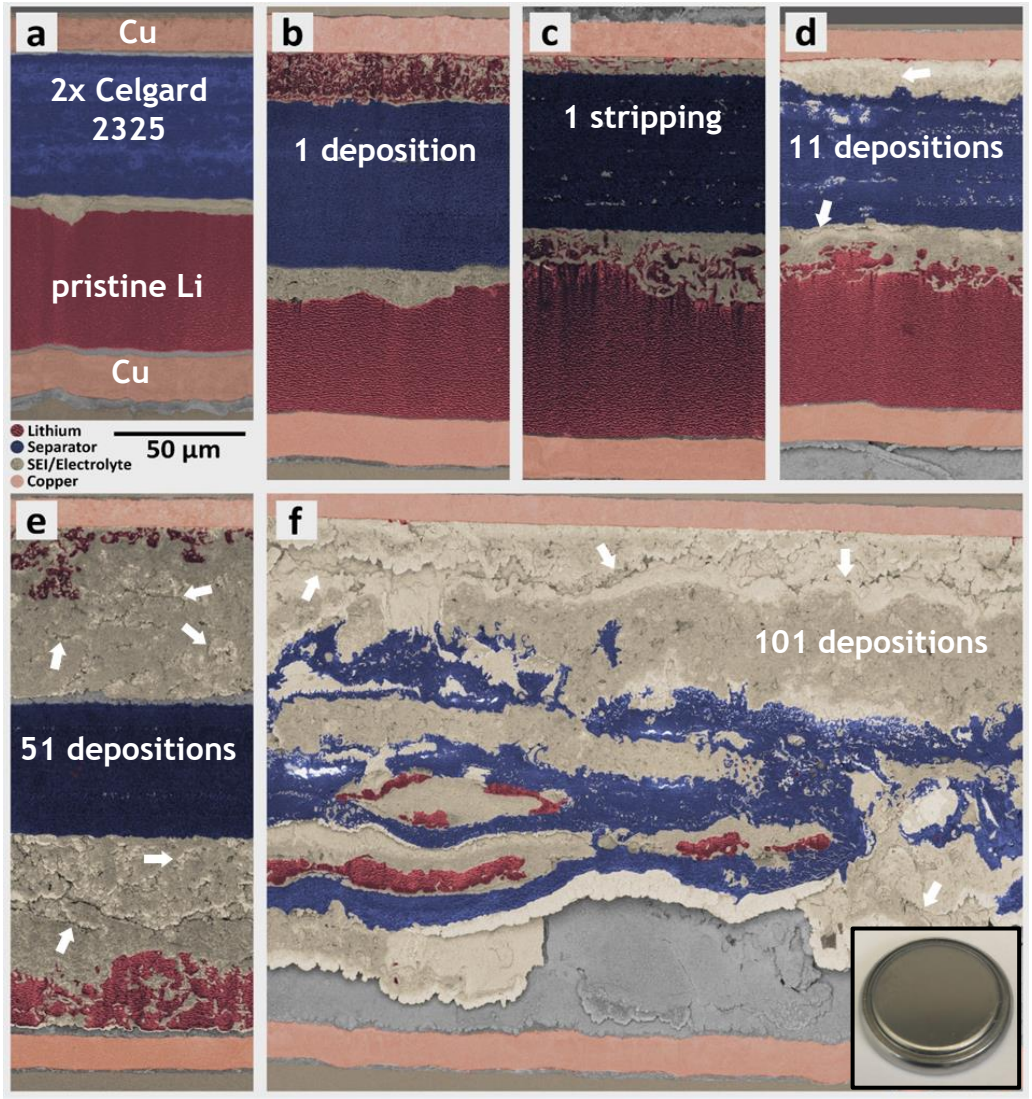




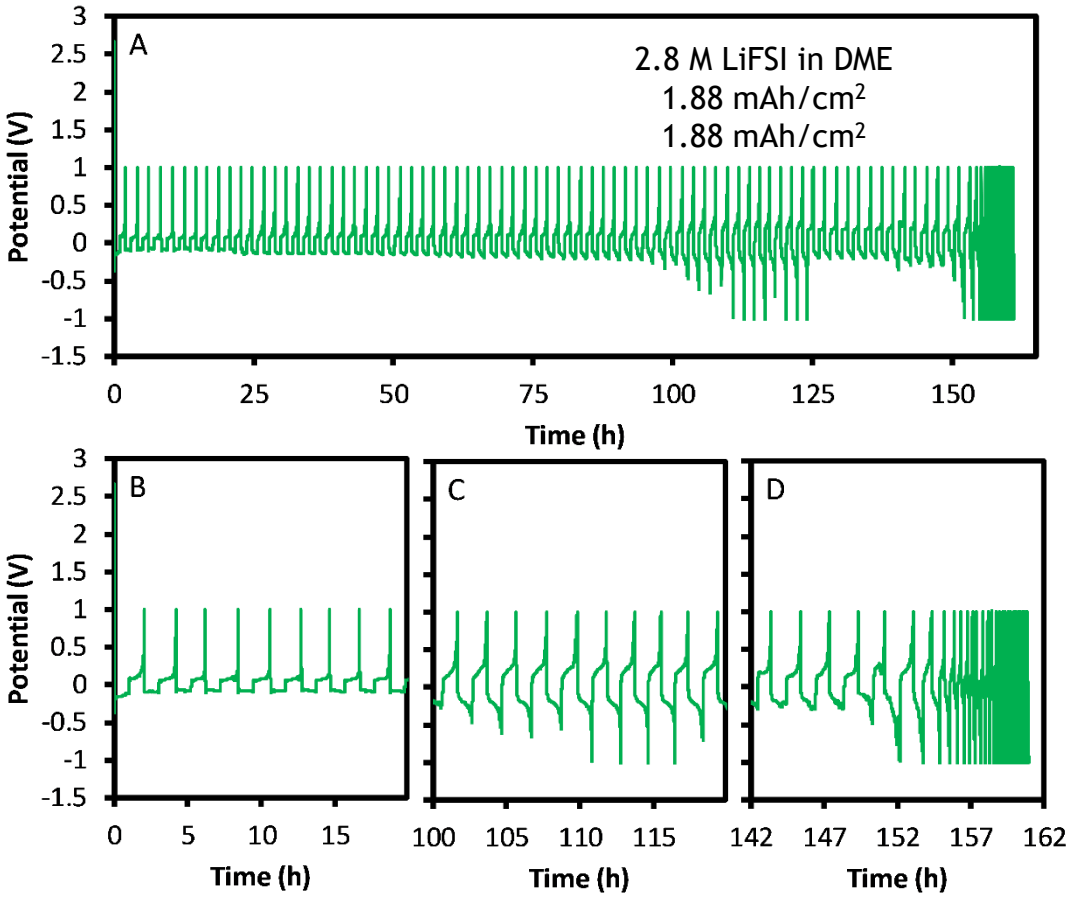


Laser PFIB/SEM shows separator completely destroyed after 101 cycles

- Growth of Li/SEI into the separator and eventually complete shredding of the separator
- Li growing into separator explains difficulty disassembling pouch cells at Li-separator interfaces



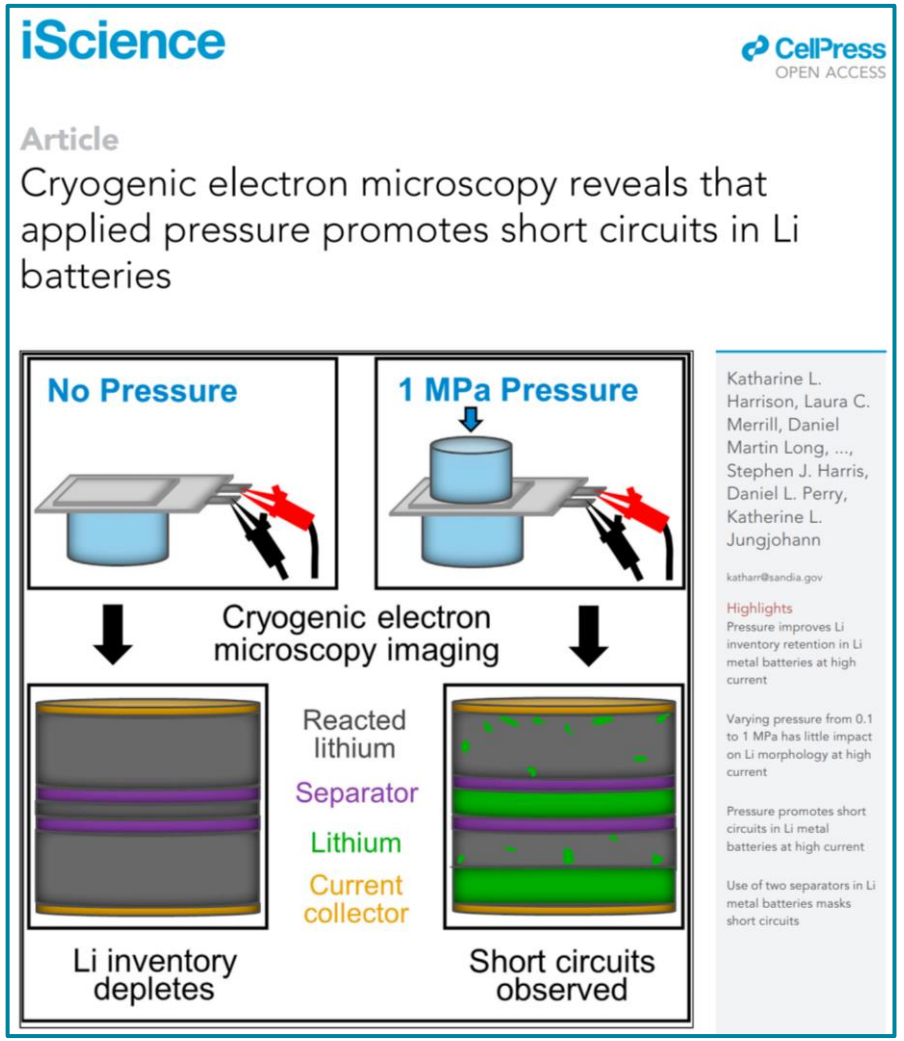
Jungjohann et al., ACS Energy Letters, 10.1021/acsenergylett.1c00509



Outline

Back to item 4 because now we demonstrated we can image interfaces without destroying them!!!

1. Background and motivation
2. In situ STEM of Li metal anode cycling
3. Cyro FIB/SEM reveals pressure effects on Li anodes at low current
4. **Cryo FIB/SEM reveals pressure effects on Li anodes at high current**
5. Cryo laser PFIB/SEM Li anode interfaces without cell disassembly
6. Cryo laser PFIB/SEM to understand volume expansion in Li anodes
7. In situ STEM to understand Li anode self discharge
8. Cyro FIB/SEM to understand self discharge of Li anodes



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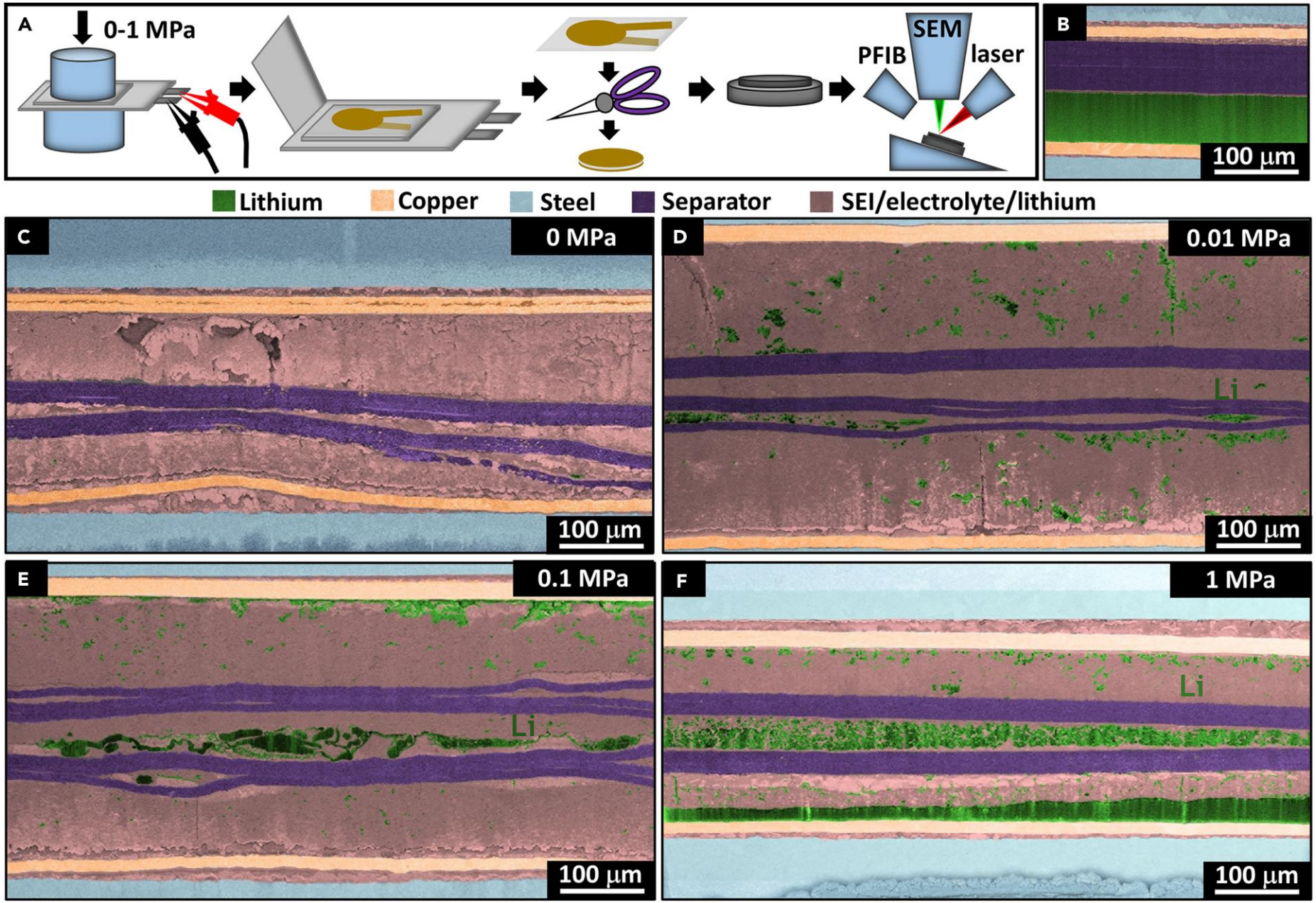
K.L. Harrison, L.C. Merrill, **D.M. Long**, **S.J. Randolph**, **S.** Goriparti, **J. Christian**, B. Warren, S.A. Roberts, S.J. Harris, **D.L. Perry**, and **K.L. Jungjohann**, 2021, Cryogenic electron microscopy reveals that applied pressure promotes short circuits in Li batteries. *Iscience*, *24*(12), p.103394.

Laser PFIB/SEM of stack after 51st deposition shows Li growing in separator

4 M LiFSI in DME
4 mAh/cm^2
2 mAh/cm^2

- Separator layers delaminate and fill with Li and SEI
- Increasing evidence of Li metal in separator as increase pressure
- Pressure exacerbates short circuits at high current rather than squashing dendrites



Harrison et al., *iScience*, 10.1016/j.isci.2021.103394

Outline

Motivation = understand and quantify volumetric capacity of Li metal anodes as a function of cycling

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8. Cyro FIB/SEM to understand self discharge of Li anodes

Understanding the Practical Capacity of the Lithium Metal Anode through Laser Plasma Focused Ion Beam Cross-Sectional Imaging

L.C. Merrill, R.N. Gannon, K.L. Jungjohann, S.J. Randolph, S. Goriparti, K.R. Zavadil, D. Johnson, K.L. Harrison

in preparation

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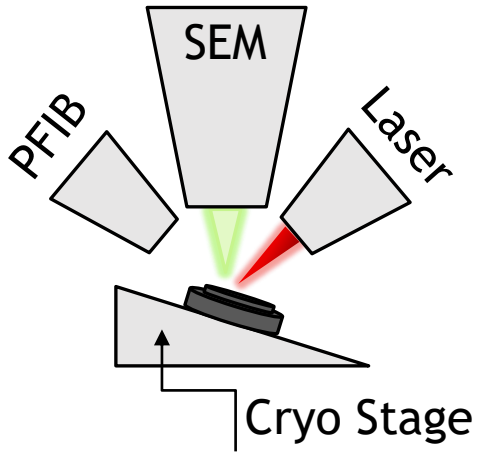
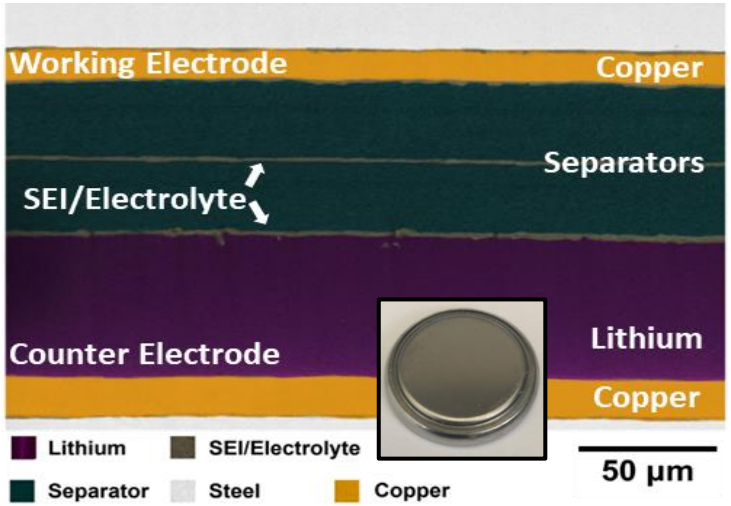


Pristine Coin Cell



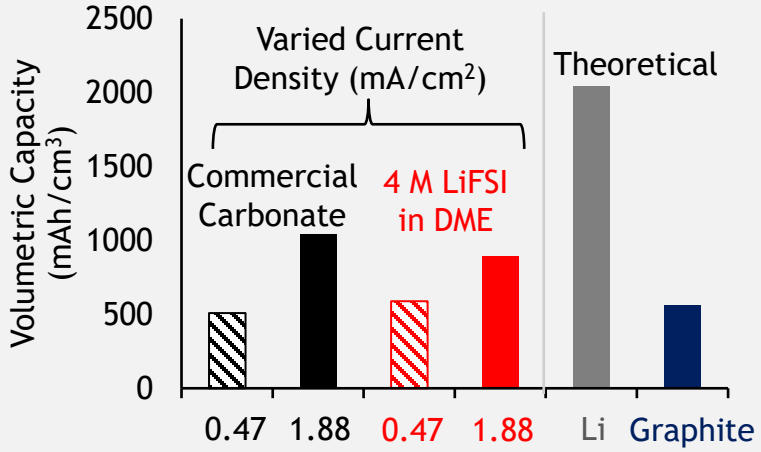
Li anode volumetric capacity similar or lower than graphite after first deposition and much lower than graphite after 101st deposition

Merrill et al., in preparation.

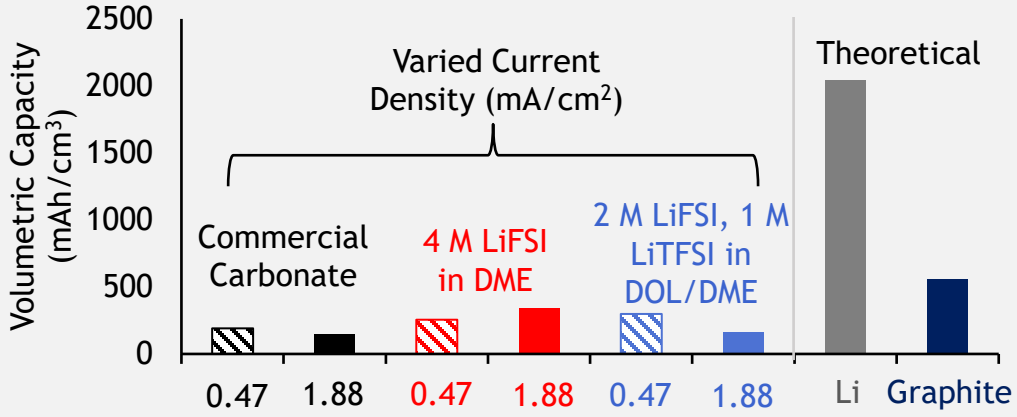
- Li has theoretically 10x higher gravimetric capacity than graphite
- Li does not deposit at theoretical density
- Li has lower practical volumetric capacity than graphite

DOL = 1,3-dioxolane
TFSI = bis(trifluoromethane)sulfonimide

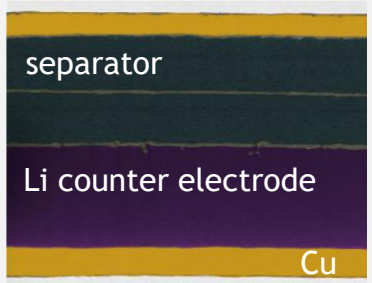
1 Deposition, 1.88 mA/cm², 1.88 mAh/cm²

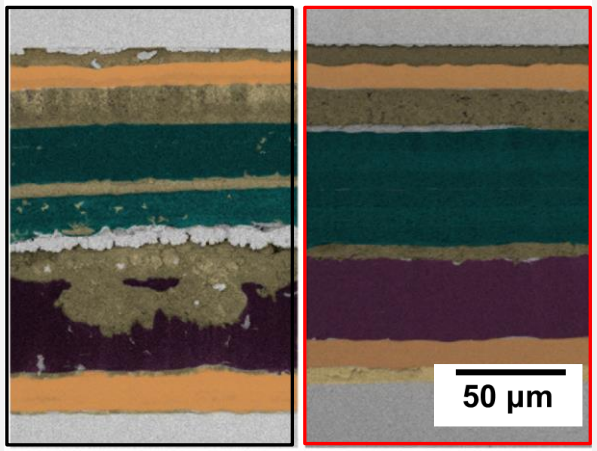


101st Deposition, 1.88 mA/cm², 1.88 mAh/cm²

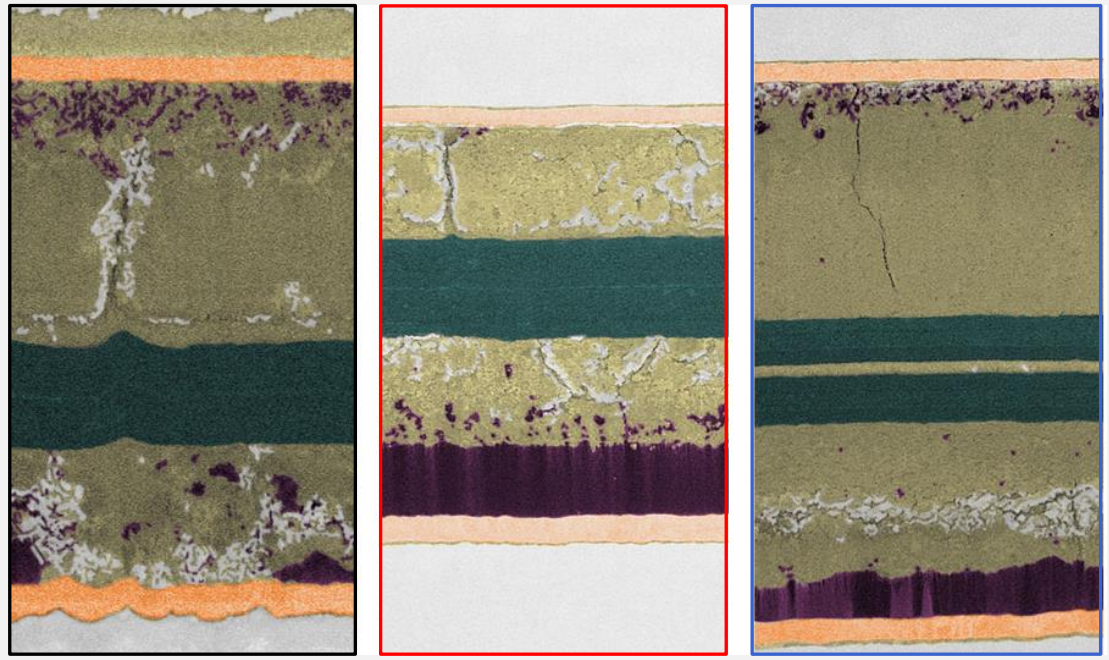


Pristine - No Cycling





Commercial Carbonate | 4 M LiFSI in DME



Commercial Carbonate | 4 M LiFSI in DME | 2 M LiFSI, 1 M LiTFSI in DOL/DME

Outline

Motivation = understand Li metal anode self discharge by directly visualizing what happens to the deposits when at rest

1. Background and motivation
2. **In situ STEM of Li metal anode cycling**
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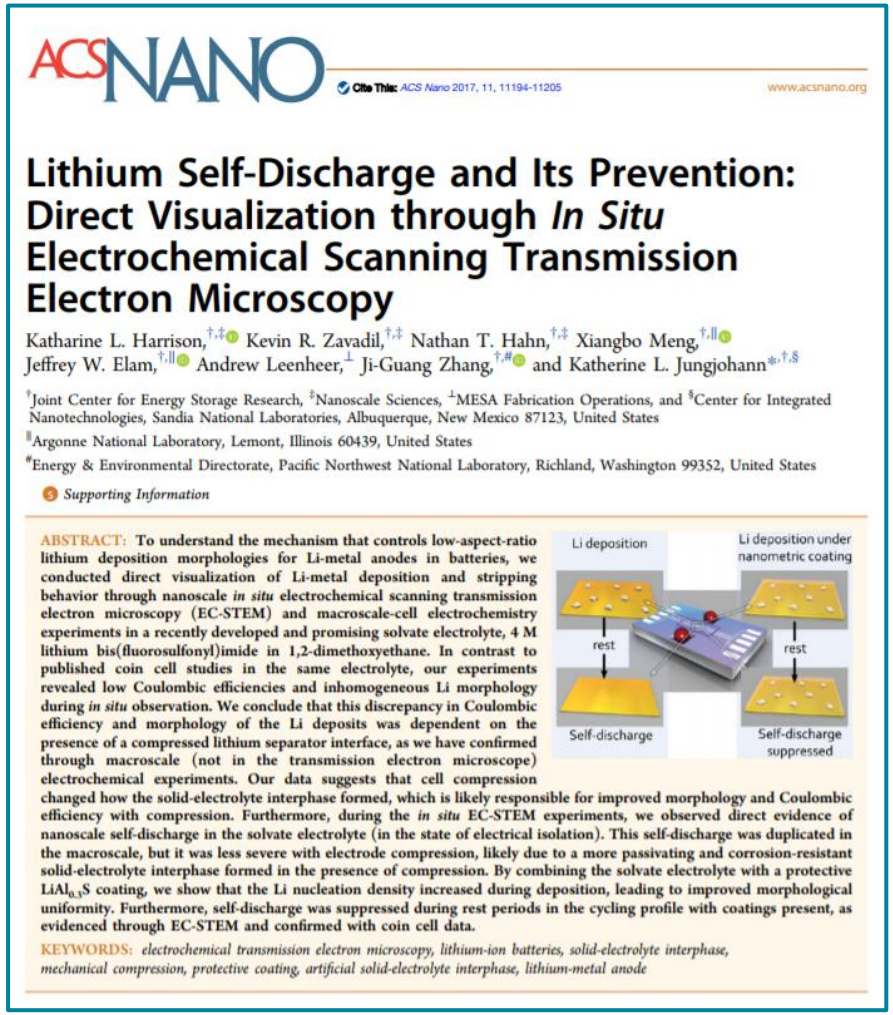

ACS NANO

Cite This: ACS Nano 2017, 11, 11194-11205 www.acsnano.org

Lithium Self-Discharge and Its Prevention: Direct Visualization through *In Situ* Electrochemical Scanning Transmission Electron Microscopy

Katharine L. Harrison,[†,‡] Kevin R. Zavadil,[†,‡] Nathan T. Hahn,[†,‡] Xiangbo Meng,[†,∥] Jeffrey W. Elam,[†,∥] Andrew Leenheer,[⊥] Ji-Guang Zhang,[†,#] and Katherine L. Jungjohann*[,†,§]

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[∥]Argonne National Laboratory, Lemont, Illinois 60439, United States

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Supporting Information

ABSTRACT: To understand the mechanism that controls low-aspect-ratio lithium deposition morphologies for Li-metal anodes in batteries, we conducted direct visualization of Li-metal deposition and stripping behavior through nanoscale *in situ* electrochemical scanning transmission electron microscopy (EC-STEM) and macroscale-cell electrochemistry experiments in a recently developed and promising solvate electrolyte, 4 M lithium bis(fluorosulfonyl)imide in 1,2-dimethoxyethane. In contrast to published coin cell studies in the same electrolyte, our experiments revealed low Coulombic efficiencies and inhomogeneous Li morphology during *in situ* observation. We conclude that this discrepancy in Coulombic efficiency and morphology of the Li deposits was dependent on the presence of a compressed lithium separator interface, as we have confirmed through macroscale (not in the transmission electron microscope) electrochemical experiments. Our data suggests that cell compression changed how the solid-electrolyte interphase formed, which is likely responsible for improved morphology and Coulombic efficiency with compression. Furthermore, during the *in situ* EC-STEM experiments, we observed direct evidence of nanoscale self-discharge in the solvate electrolyte (in the state of electrical isolation). This self-discharge was duplicated in the macroscale, but it was less severe with electrode compression, likely due to a more passivating and corrosion-resistant solid-electrolyte interphase formed in the presence of compression. By combining the solvate electrolyte with a protective $LiAl_{0.3}S$ coating, we show that the Li nucleation density increased during deposition, leading to improved morphological uniformity. Furthermore, self-discharge was suppressed during rest periods in the cycling profile with coatings present, as evidenced through EC-STEM and confirmed with coin cell data.

KEYWORDS: *electrochemical transmission electron microscopy, lithium-ion batteries, solid-electrolyte interphase, mechanical compression, protective coating, artificial solid-electrolyte interphase, lithium-metal anode*

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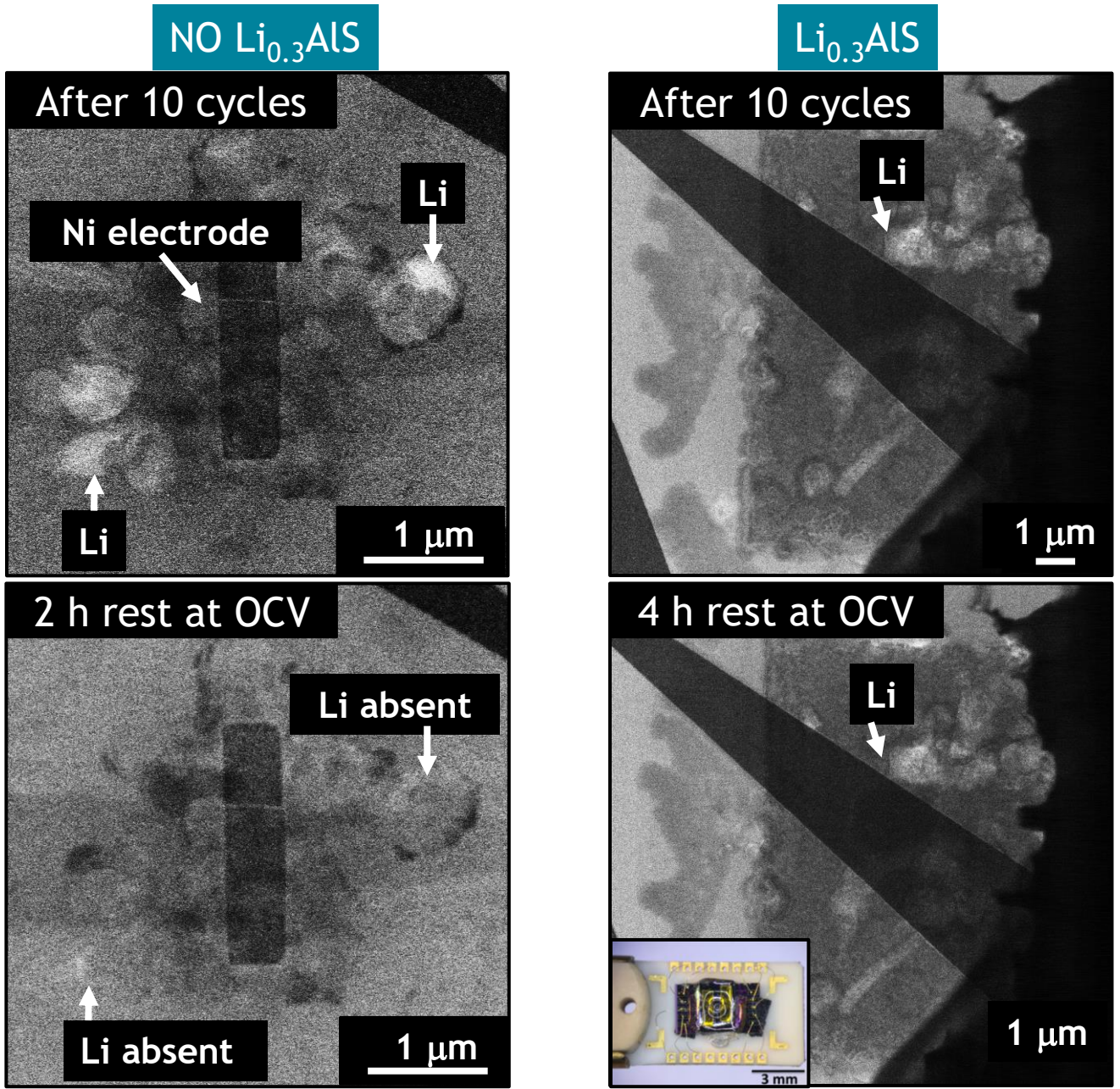
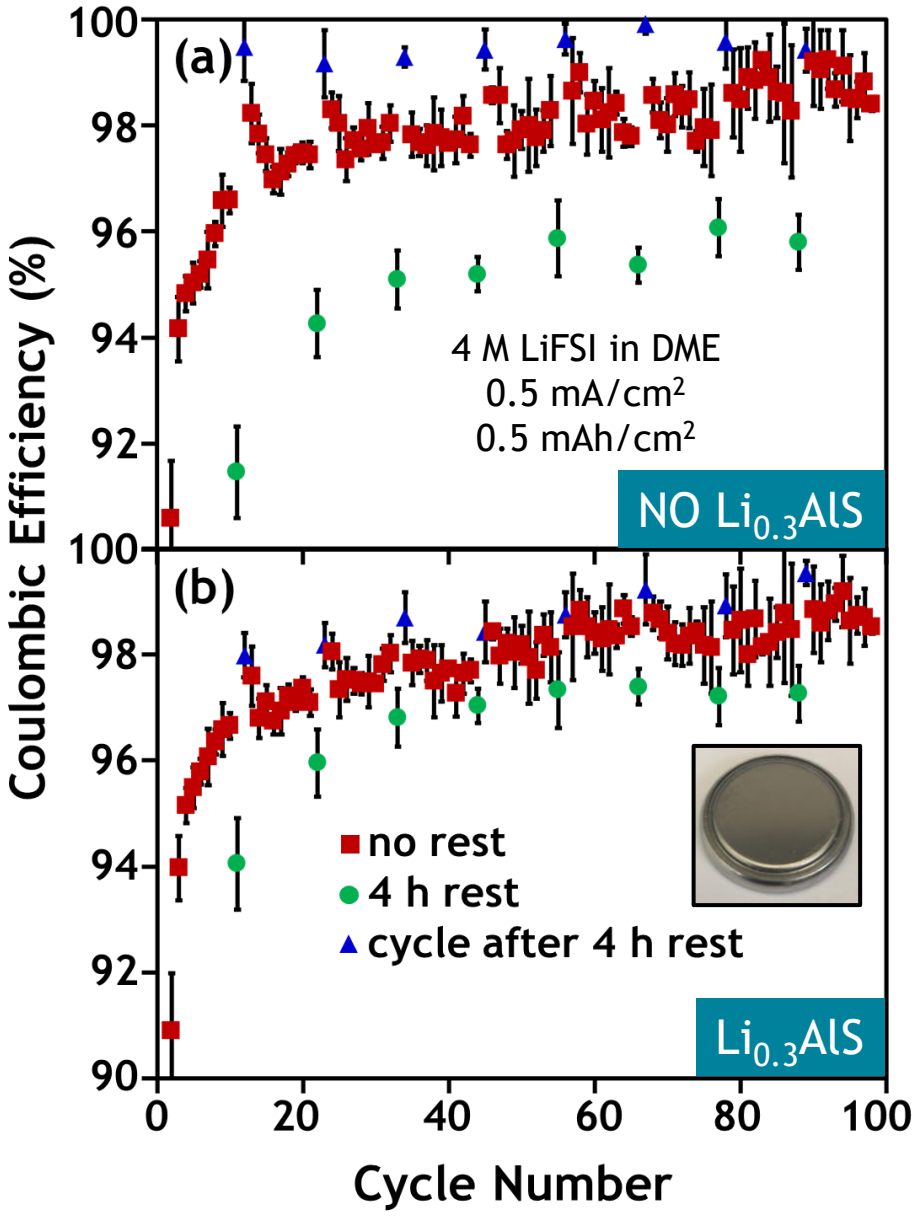
K.L. Harrison, K.R. Zavadil, N.T. Hahn, X. Meng, J.W. Elam, A. Leenheer, J.G. Zhang, and **K.L. Jungjohann**, 2017, Lithium self-discharge and its prevention: direct visualization through in situ electrochemical scanning transmission electron microscopy. *ACS nano*, 11(11), pp.11194-11205.

$Li_{0.3}AlS$ coating on current collector protects against Li self discharge

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





Outline

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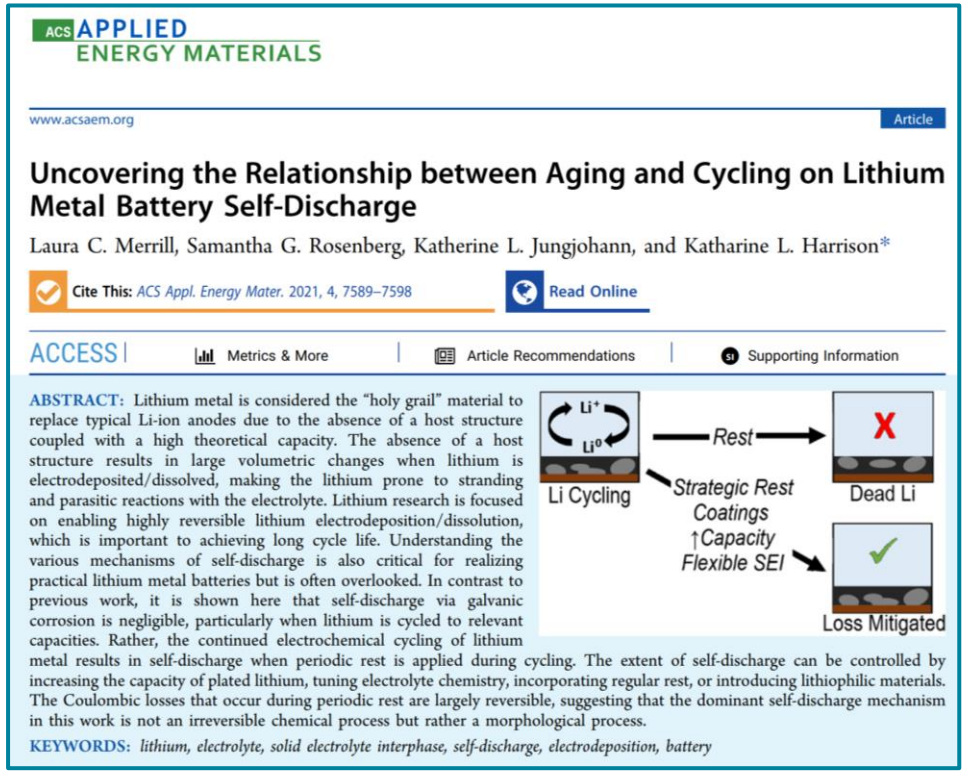
7. In situ STEM to understand Li anode self discharge
8. **Cyro FIB/SEM to understand self discharge of Li anodes**

Motivation = understand mechanisms of Li metal anode self discharge



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Uncovering the Relationship between Aging and Cycling on Lithium Metal Battery Self-Discharge

Laura C. Merrill, Samantha G. Rosenberg, Katherine L. Jungjohann, and Katharine L. Harrison*

Cite This: *ACS Appl. Energy Mater.* 2021, 4, 7589−7598 Read Online

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ABSTRACT: Lithium metal is considered the "holy grail" material to replace typical Li-ion anodes due to the absence of a host structure coupled with a high theoretical capacity. The absence of a host structure results in large volumetric changes when lithium is electrodeposited/dissolved, making the lithium prone to stranding and parasitic reactions with the electrolyte. Lithium research is focused on enabling highly reversible lithium electrodeposition/dissolution, which is important to achieving long cycle life. Understanding the various mechanisms of self-discharge is also critical for realizing practical lithium metal batteries but is often overlooked. In contrast to previous work, it is shown here that self-discharge via galvanic corrosion is negligible, particularly when lithium is cycled to relevant capacities. Rather, the continued electrochemical cycling of lithium metal results in self-discharge when periodic rest is applied during cycling. The extent of self-discharge can be controlled by increasing the capacity of plated lithium, tuning electrolyte chemistry, incorporating regular rest, or introducing lithiophilic materials. The Coulombic losses that occur during periodic rest are largely reversible, suggesting that the dominant self-discharge mechanism in this work is not an irreversible chemical process but rather a morphological process.

KEYWORDS: *lithium, electrolyte, solid electrolyte interphase, self-discharge, electrodeposition, battery*

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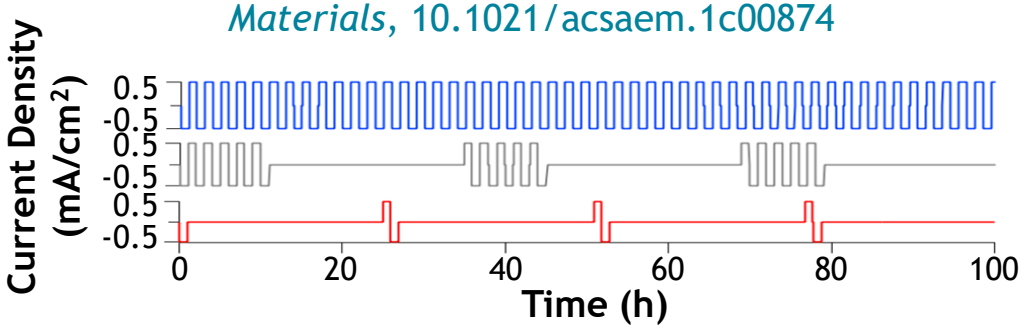
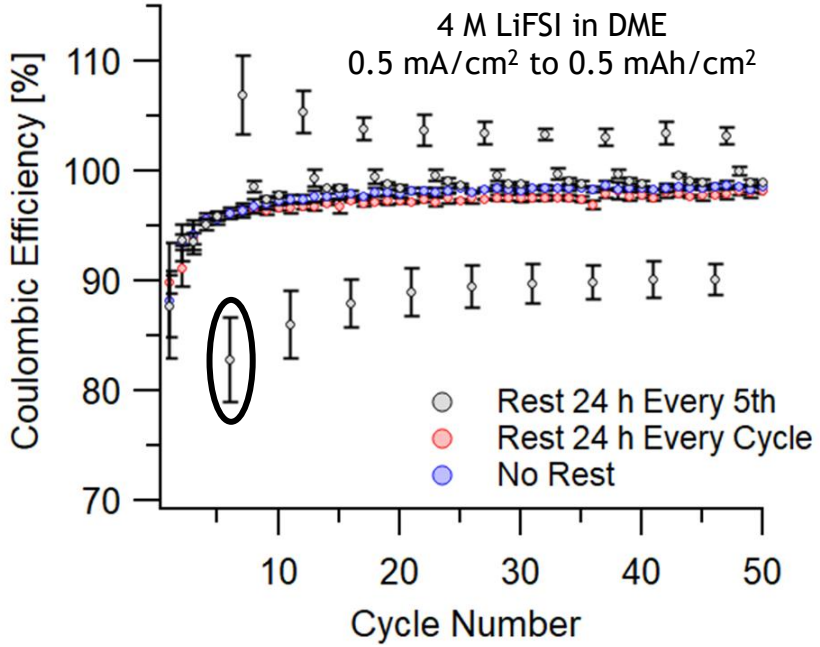
L.C. Merrill, S.G. Rosenberg, **K.L. Jungjohann**, and K.L. Harrison, 2021. Uncovering the Relationship between Aging and Cycling on Lithium Metal Battery Self-Discharge. *ACS Applied Energy Materials*, 4(8), pp.7589-7598.

Cryo FIB/SEM reveals less dead Li when rest applied after every deposition

Merrill et al., *ACS Applied Energy Materials*, 10.1021/acsaem.1c00874

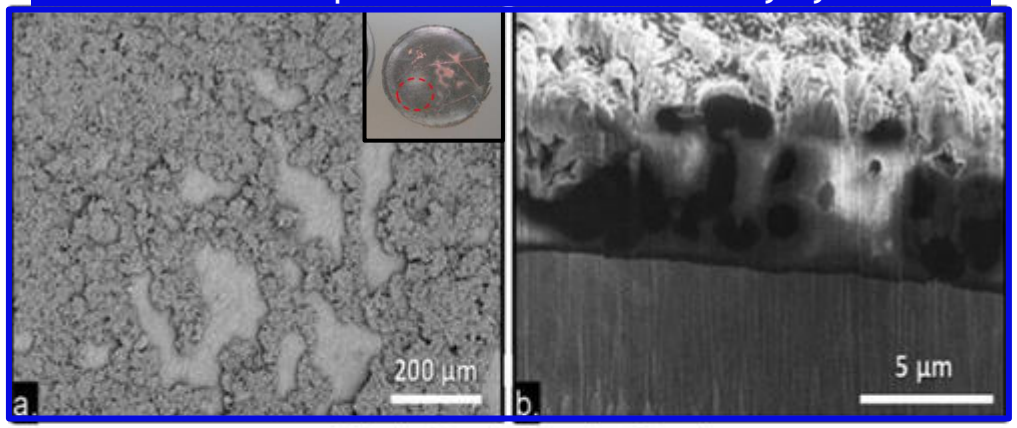




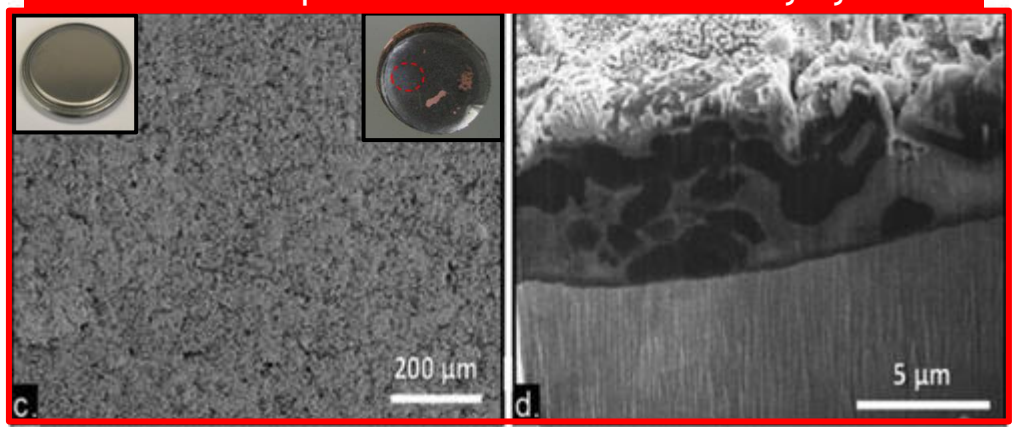
Average CE with Rest Every 5th Cycle: 97.4 %
Average CE without Rest: 97.6 %

- CE similar if cycle without rest or with 24 h rest every cycle
- Cycling Li with rest *only* every 5th cycle results in self-discharge
- Self-discharge is reversible (*not* irreversible galvanic corrosion)!
- Li is poorly adhered to current collector without rest
- Passive SEI deposits during rest and prevents dead Li

After 6th deposition - no rest after any cycle



After 6th deposition - 24h rest after every cycle



Conclusions and perspective on FIB and EM techniques to study Li anodes

- Focused ion beam and electron microscopy techniques are extremely important to understanding Li cycling and aging

- In situ electrochemical STEM enables real time visualization of Li deposits nucleating, growing, and corroding
  - Very time consuming and lots of preparation and failed experiments
  - Cells are difficult to design to exactly mimic battery designs and pressure is particularly difficult to replicate
  - May be better suited to Li-ion materials less dependent on pressure or alternative cell designs
  - Pressure plays an important role in morphology, Coulombic efficiency, and short circuits

- Ex situ cryo Ga^+ FIB and SEM enables high resolution imaging and sample washing enables easy viewing of Li grains
  - Morphological changes with pressure or during self discharge tests are very clearly visualized
  - Ex situ techniques require cell disassembly so evidence of dendrites at interfaces can be destroyed
  - Ga^+ FIB is very slow and only enables imaging small areas in cross section so there can be sampling problems and difficulty milling through thick samples

- Cryo laser PFIB/SEM enables fast athermal milling and imaging of large areas without disassembly (preserving interfaces)
  - This technique allows imaging of dendrites growing into separators in Li metal anodes to shed light on short circuits
  - Fast milling rates enable understanding of thickness changes with cycling to understand volumetric energy density
  - Cannot wash the electrodes so it is more difficult to distinguish frozen electrolyte from SEI and Li
  - Slice and view imaging possible to recreate 3D volume

THANK YOU FOR INVITING ME, FOR YOUR ATTENTION, AND THANK YOU TO MY SPONSORS AND COLLABORATORS!

Katharine Harrison, katharr@sandia.gov

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