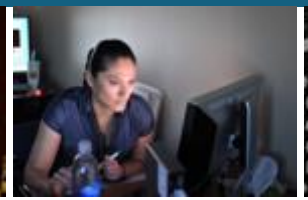
LDRD
Laboratory Directed Research and Development

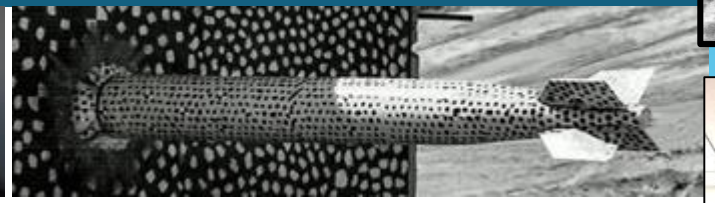
This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science and was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories

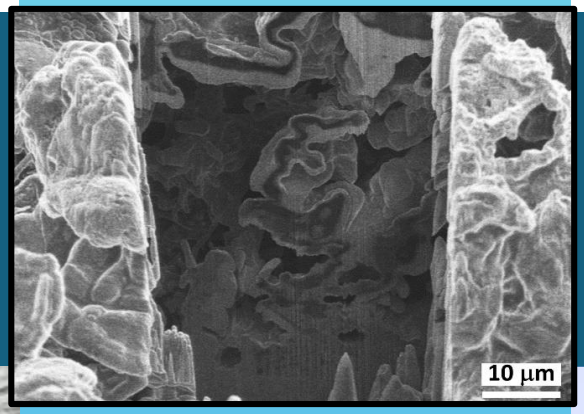
Sandia National Laboratories

SAND2021-4766C

The Effects of Applied Interfacial Pressure on Lithium Metal Cycling Behavior







Abstract ID: EN09.01.04
Session Date and Time: April 21, 2021
Presentation Time: 8:55-9:20 AM EDT
Symposium: EN09

PRESENTED BY

Katharine Harrison, katharr@sandia.gov

Sandia National Laboratories

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

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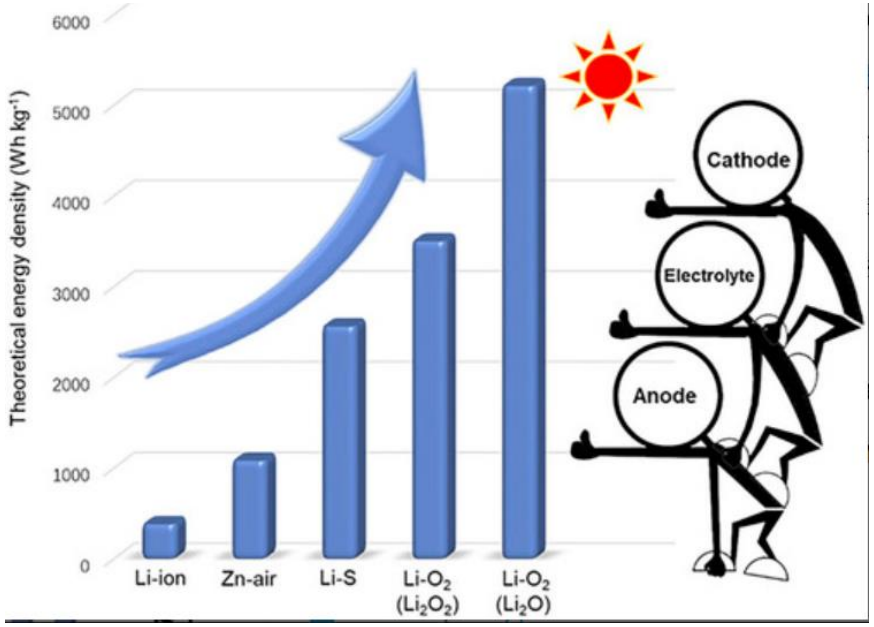
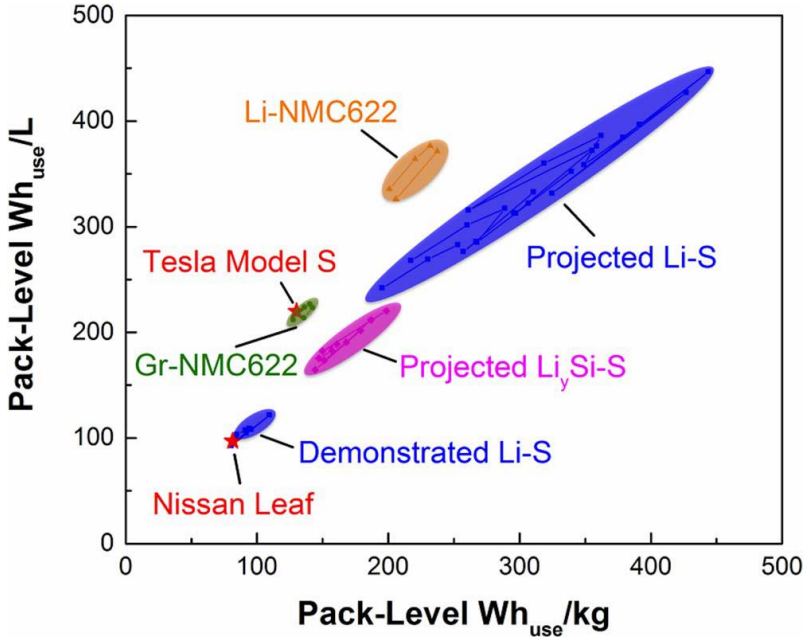
Motivation: energy density improves with conversion cathodes and Li anodes

- Current state of the art → lithium ion batteries
- Improvements → new electrode materials for Li-ion and new chemistries (Li-O_2, Li-S)
- Conversion cathodes depend on successful pairing with Li metal anodes



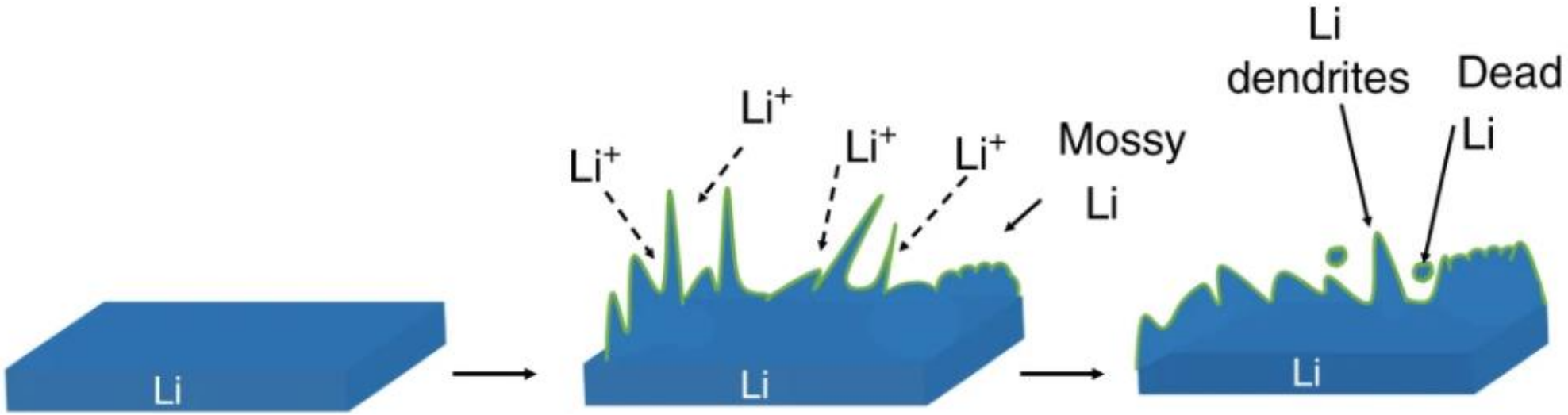
C. Wang et al. *APL Materials*, 2019
DOI: 10.1149/2.0611506jes



D. Eroglu et al. *J. Electrochem. Soc.*, 2015
DOI: 10.1149/2.0611506jes

Li metal anodes difficult to commercialize because of uncontrolled morphology

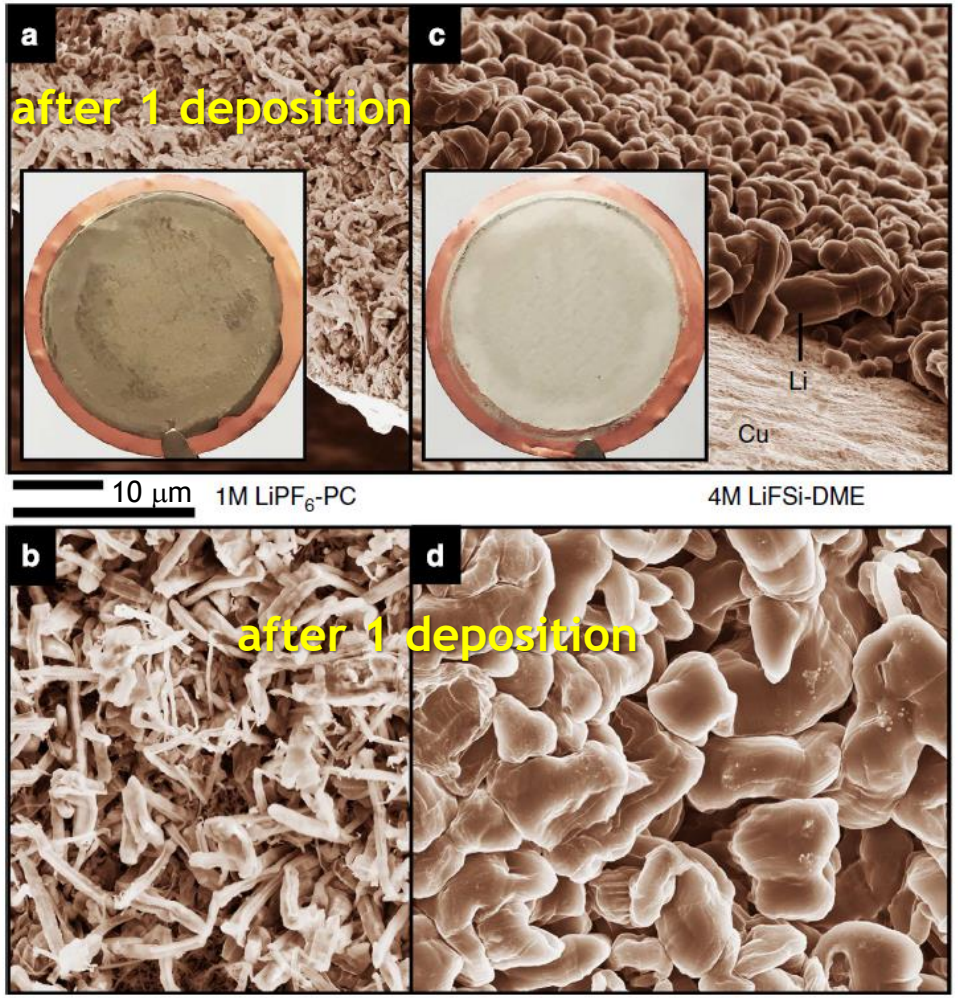
- Uncontrolled morphology
  - Short circuits and fire
  - Excessive solid electrolyte interphase (SEI)
  - Low Coulombic efficiency, dead Li, and high impendence
  - Volumetric energy density compromised by porous deposition morphologies

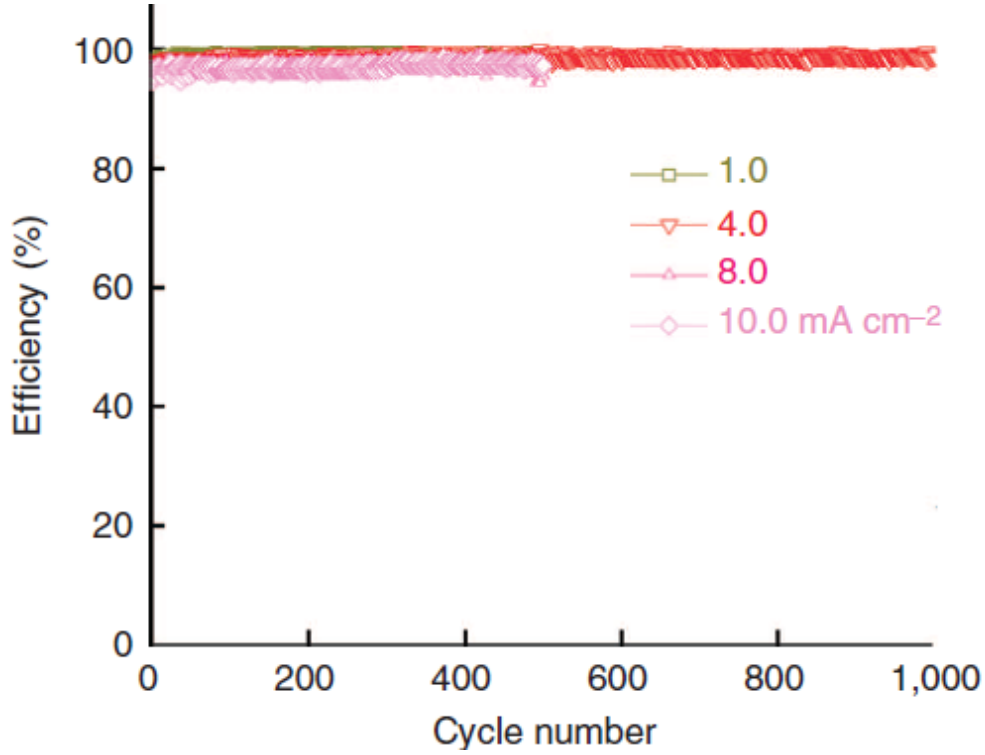


Pathak et al. *Nature Communications*, 2020.
DOI: 10.1038/s41467-019-13774-2

Alternative electrolytes and additives can improve Li metal anode cycling

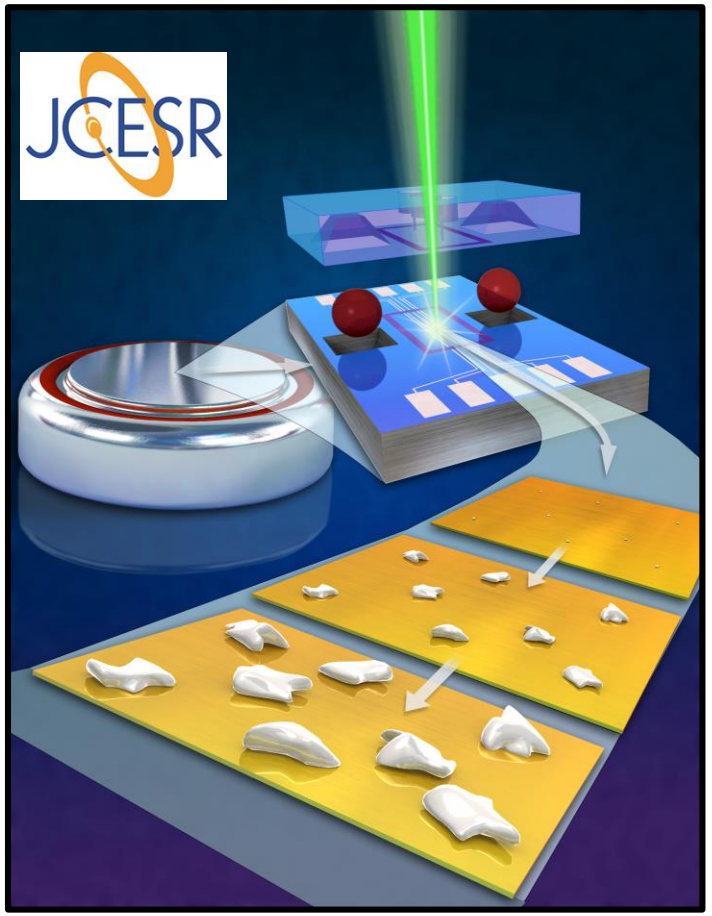
- Promising electrolyte: 4 M lithium bis(fluorosulfonyl)imide in 1,2-dimethoxyethane = 4 M LiFSI in DME

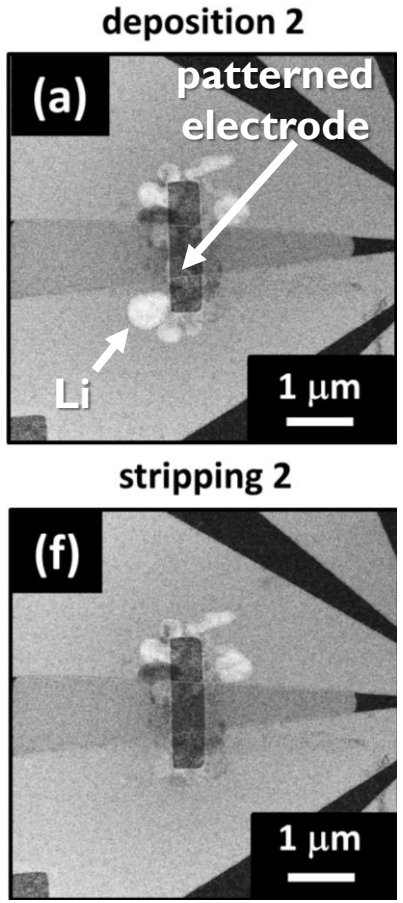




Qian et al. *Nature Communications*, 2015
DOI: 10.1038/ncomms7362

Prior work: in-situ electrochemical STEM did not match bulk experiments





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

K.L. Harrison, K.R. Zavadil, N.T. Hahn, X. Meng, J.W. Elam, A. Leenheer, J.G. Zhang, K.L Jungjohann, "Lithium Self-Discharge and Its Prevention: Direct Visualization through In Situ Electrochemical Scanning Transmission Electron Microscopy," (2017) *ACS Nano*, 11 (11), 11194-11205. 10.1021/acsnano.7b05513

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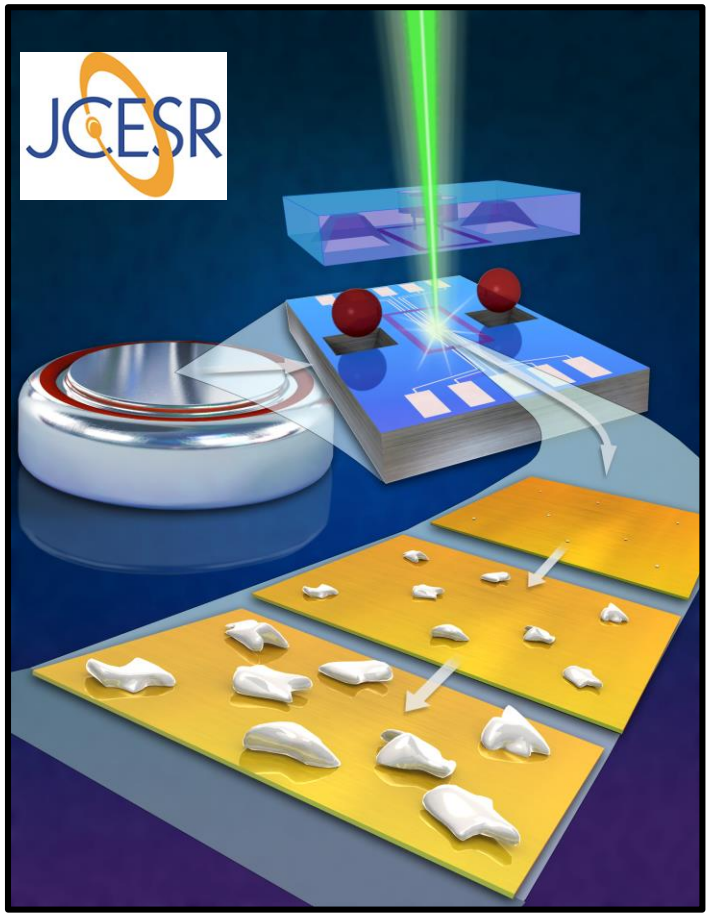

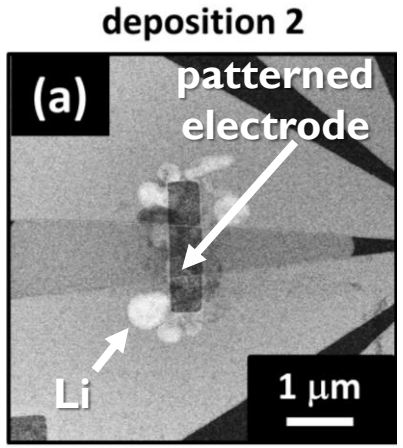

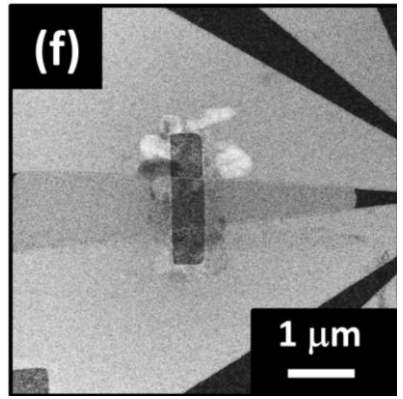

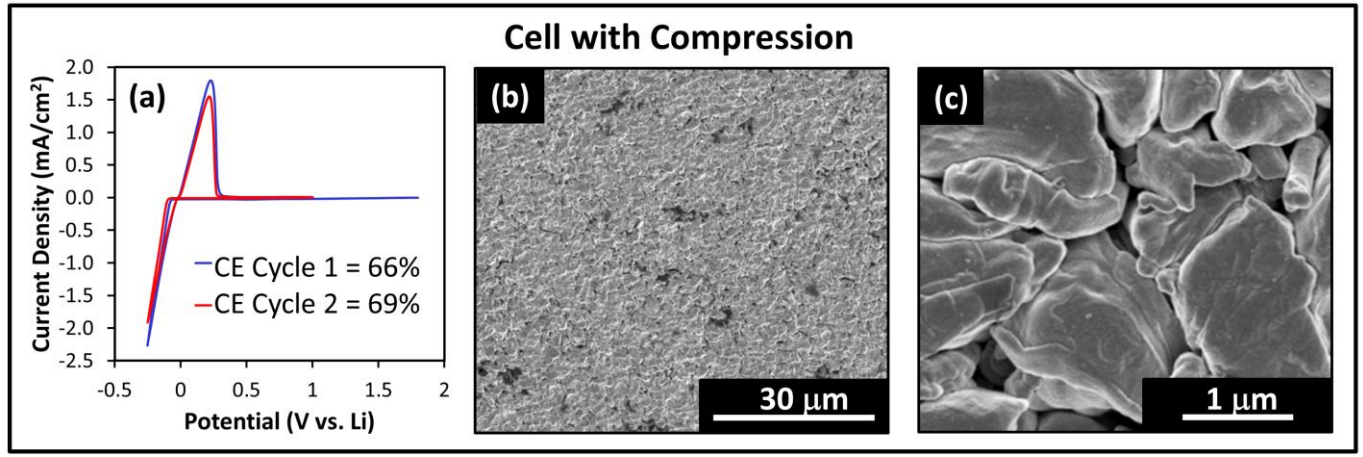

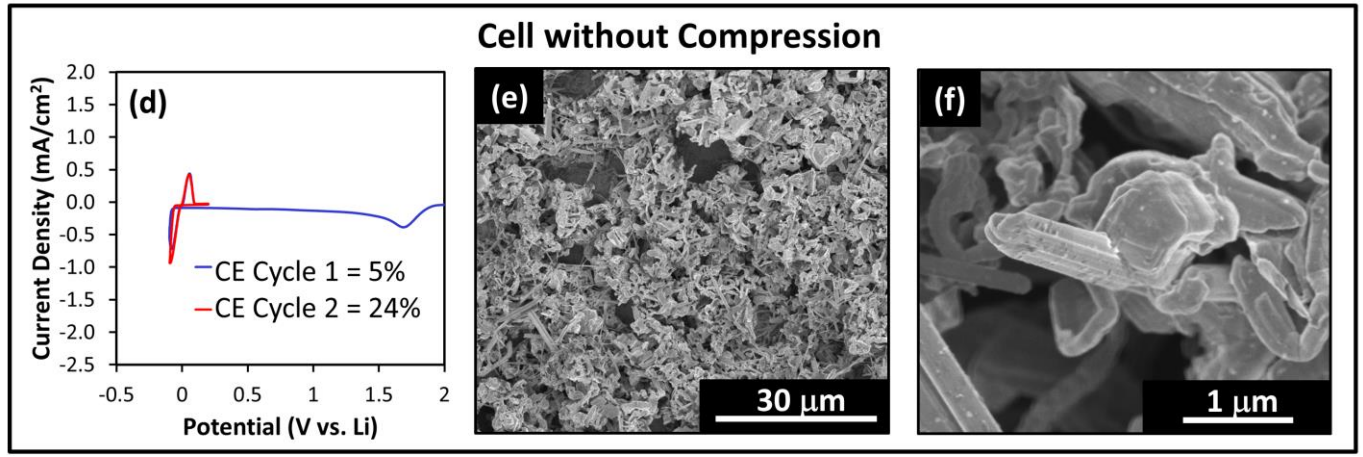

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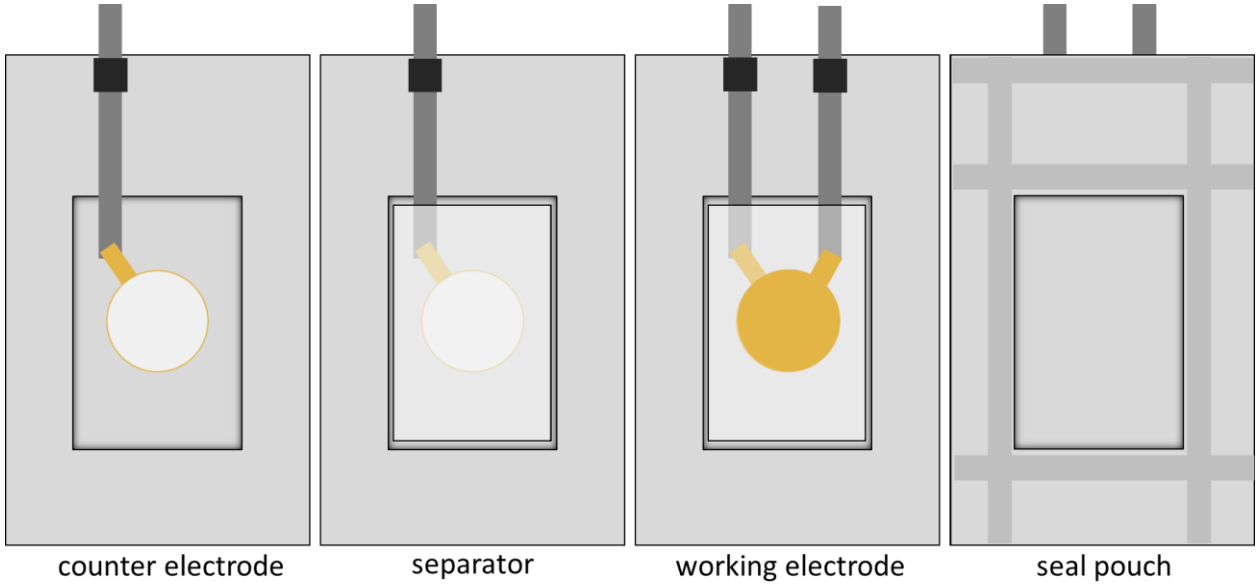
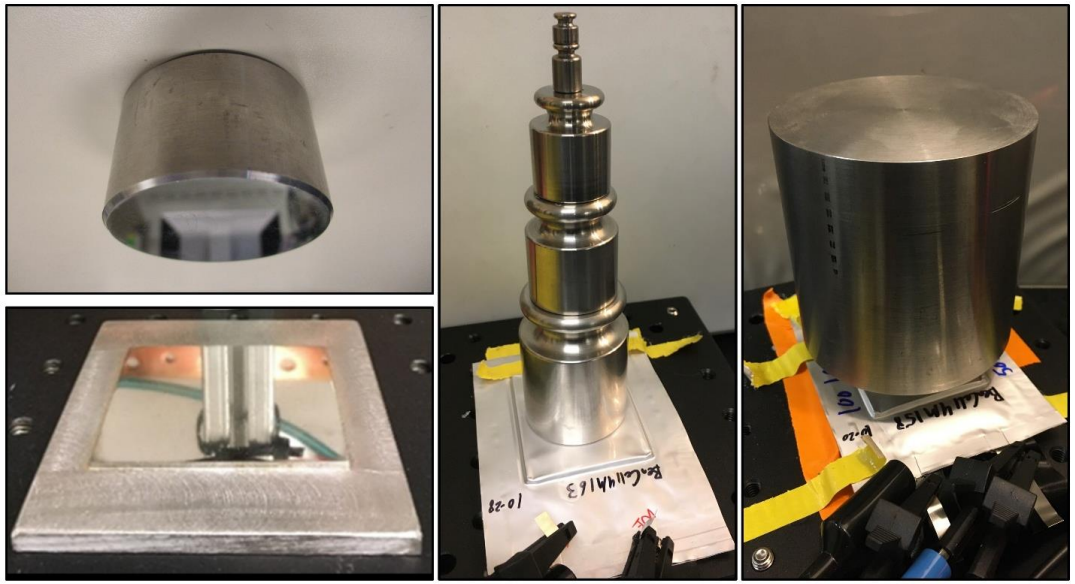
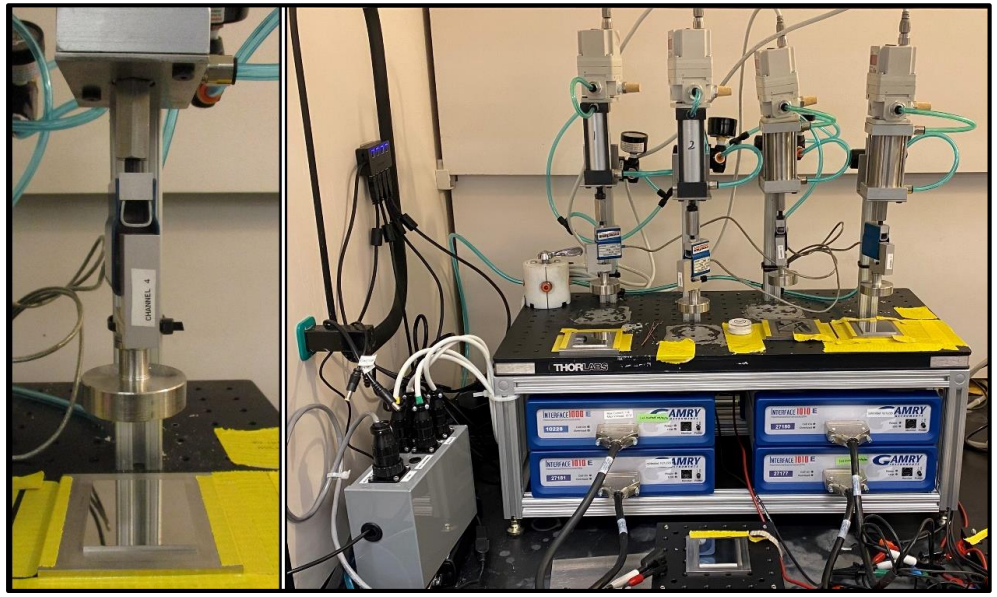
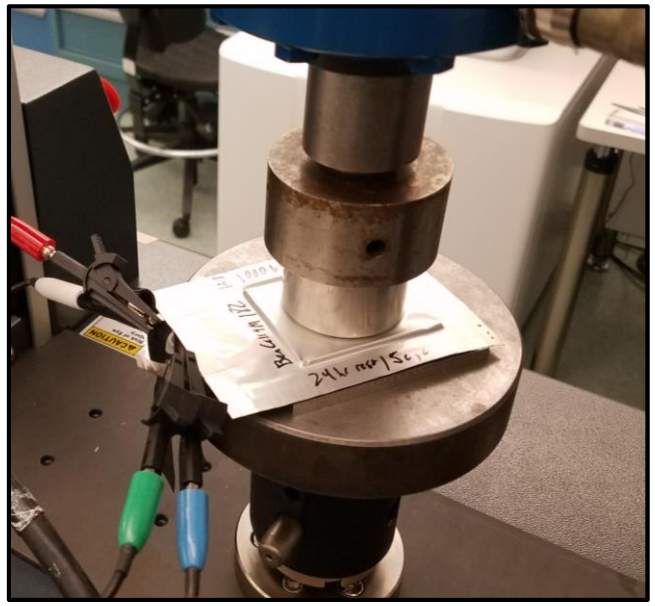
- Applied pressure important for high CE and favorable morphology
- Pressure cannot easily be replicated through in situ experiments

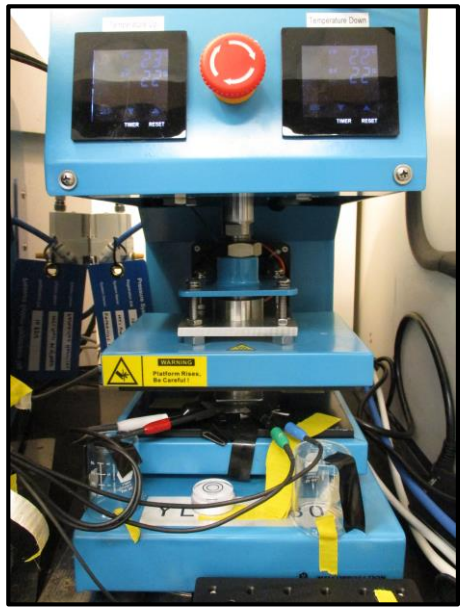
Systematic study: effects of pressure on Li versus Cu cells 0-10 MPa











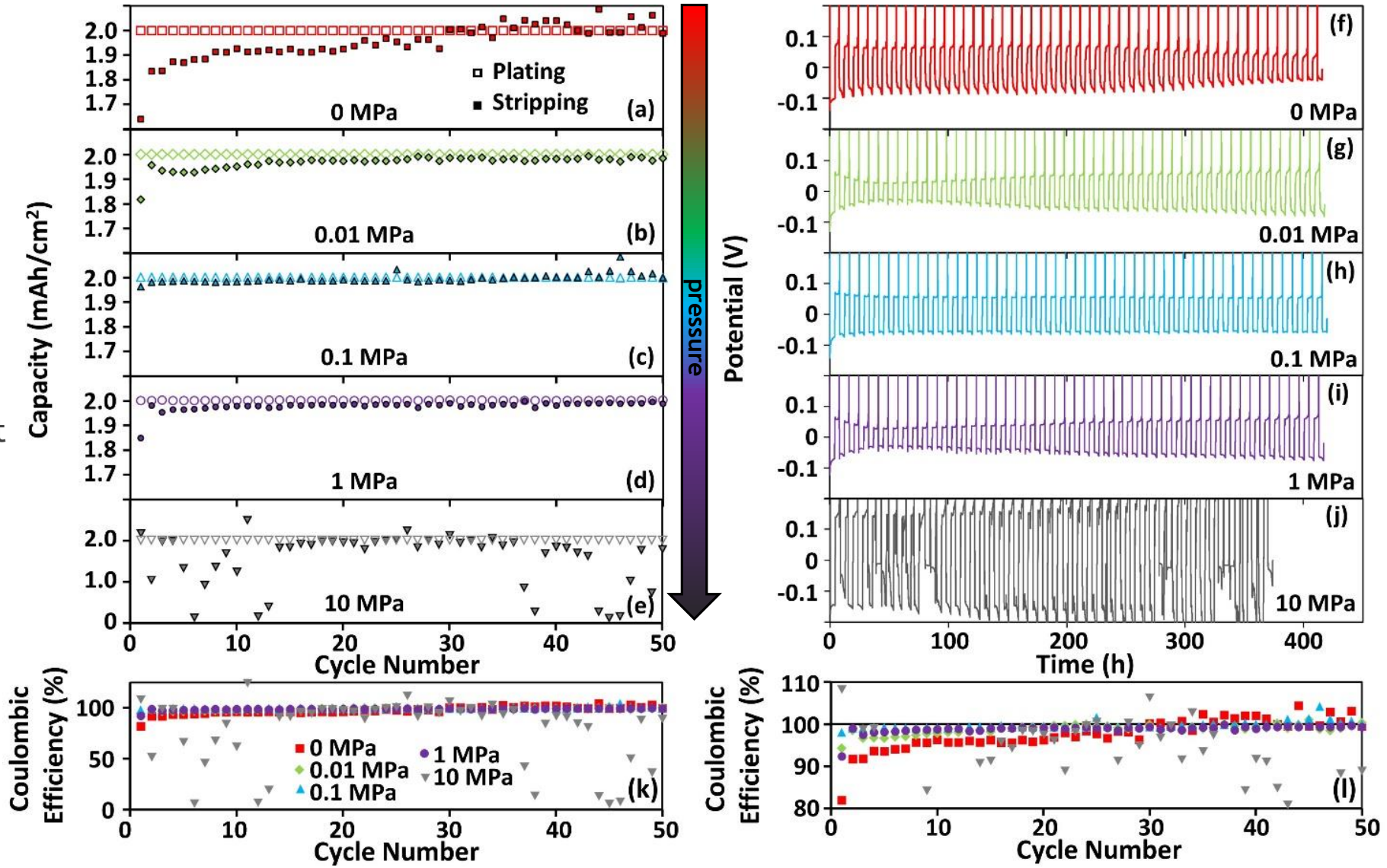
Harrison et al., The Effects of Applied Interfacial Pressure on Li Metal Cycling Performance and Morphology in 4 M LiFSI in DME, *submitted*.

Li cycling improves with pressure, but too much pressure degrades performance

0.5 mA/cm^2

Harrison et al., *submitted*.

- Cycling stability ↑ with ↑ pressure 0-1 MPa
- CE generally ↑ with pressure ↑
- 10 Mpa → cycling instability and increased overpotential
- 10 MPa: 7% loss in diffusivity
- Literature[1]: viscoelastic creep at 5 MPa → less uniform porosity
- Local electrolyte starvation at 10 MPa in regions with no pores?



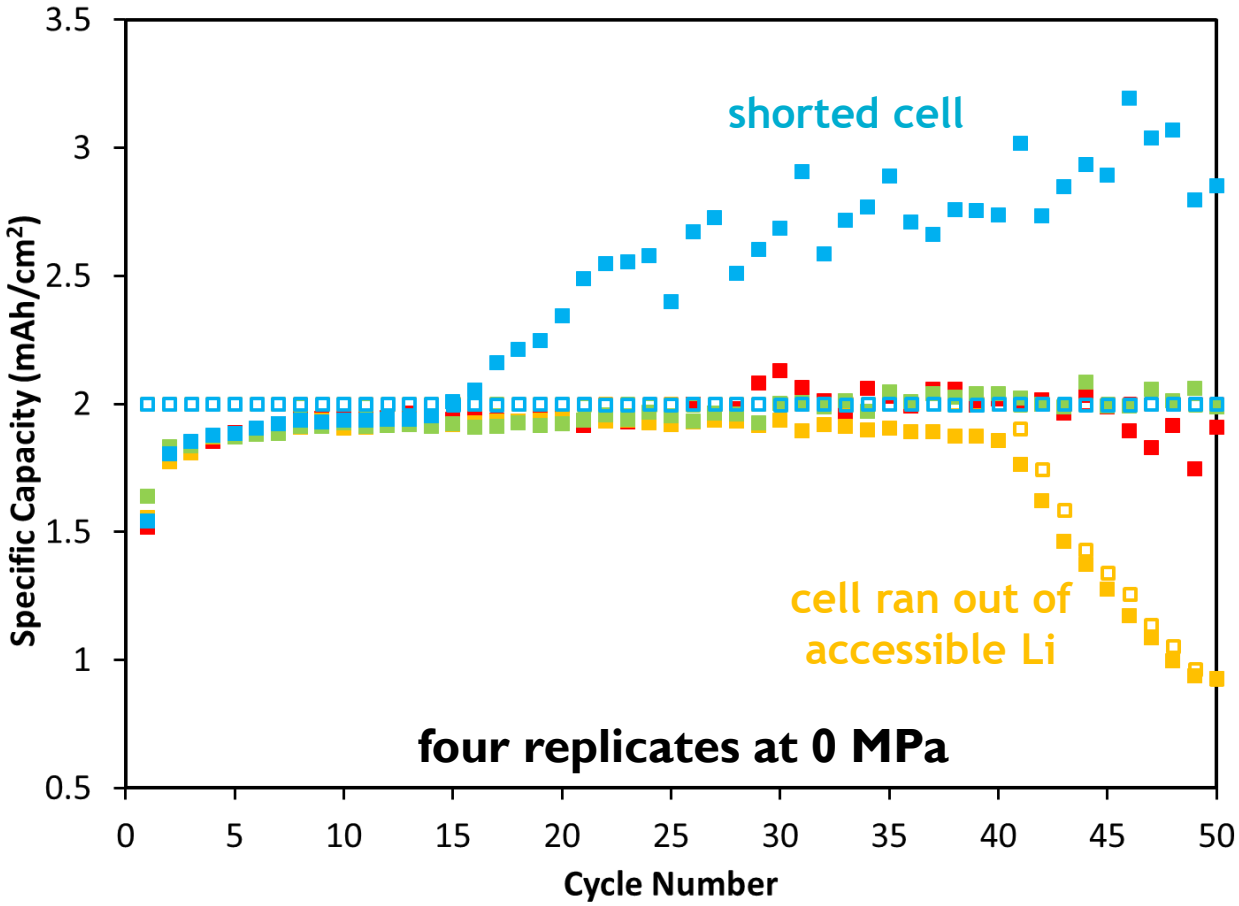
1. J. Cannarella, C.B. Arnold, *Journal of Power Sources*, ***2011*** 10.1016/j.jpowsour.2013.06.165

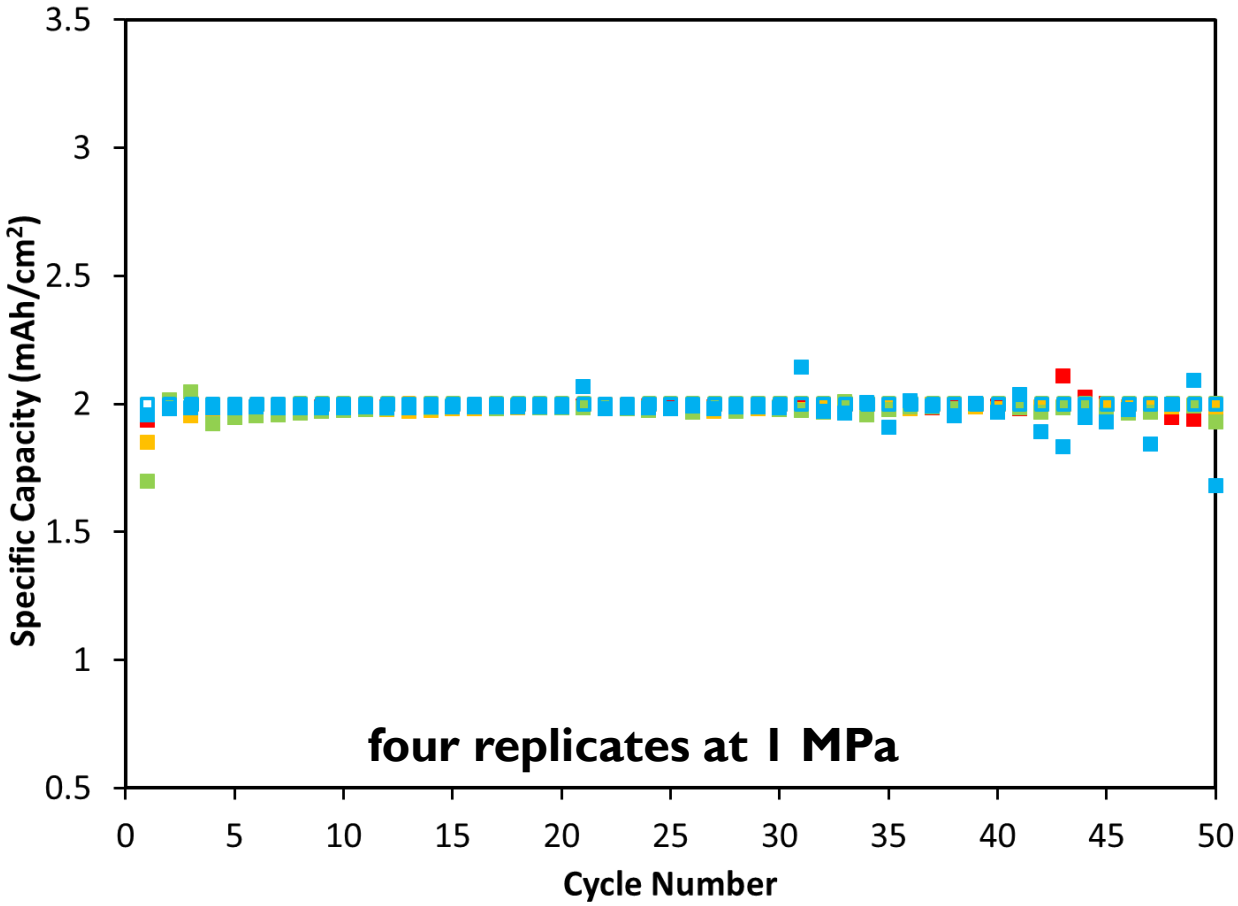
0.5 mA/cm^2

Moderate pressure drastically improves cell to cell repeatability

- 0 MPa cells → repeatability poor
- 0.1-1 MPa → repeatability much better
- 10 MPa → repeatability poor again (not shown)

Harrison et al., *submitted*.





Morphology improves drastically with pressure (even at10 MPa)

0.5 mA/cm^2

Harrison et al., *submitted*.

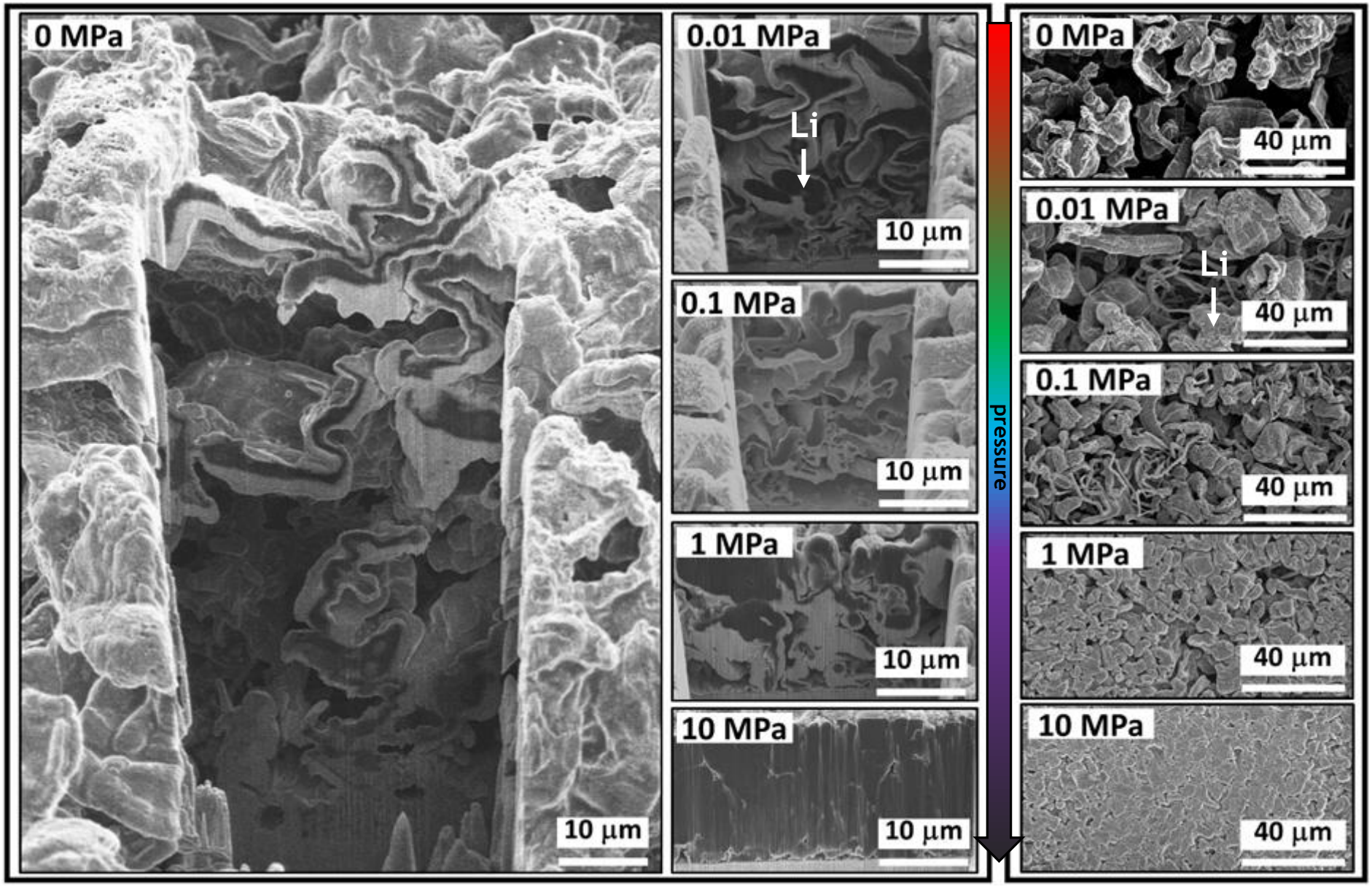
- Ex-situ cryo SEM after 1st Li deposition step
- 1st cycle CE trends with morphology
- Higher than 100% CE in *1st cycle* at 10 MPa (soft shorts?)

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

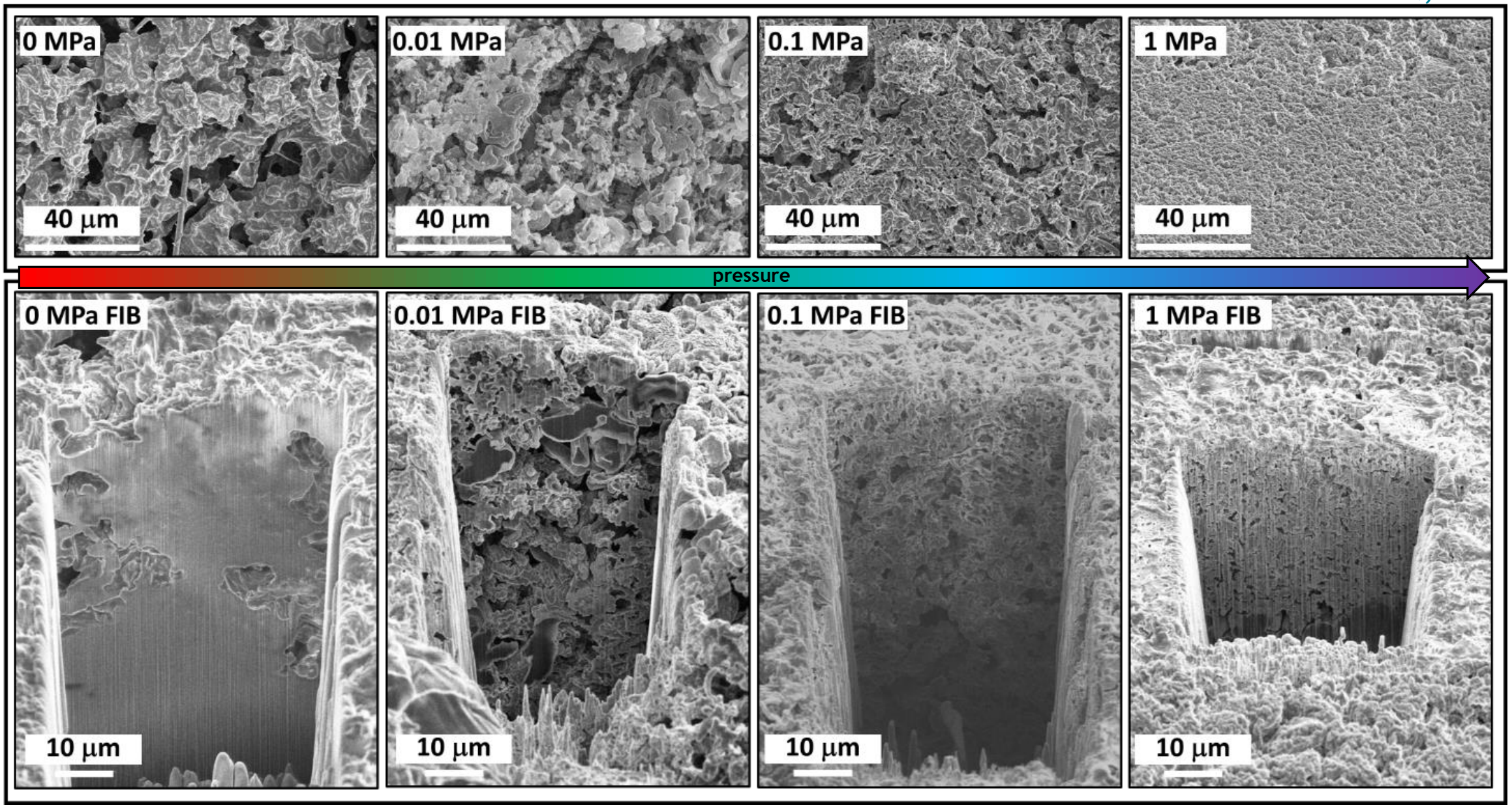
pressure



0.5 mA/cm^2

Similar morphology improvements after 51st Li depositions but thicker deposits

Harrison et al., *submitted*.

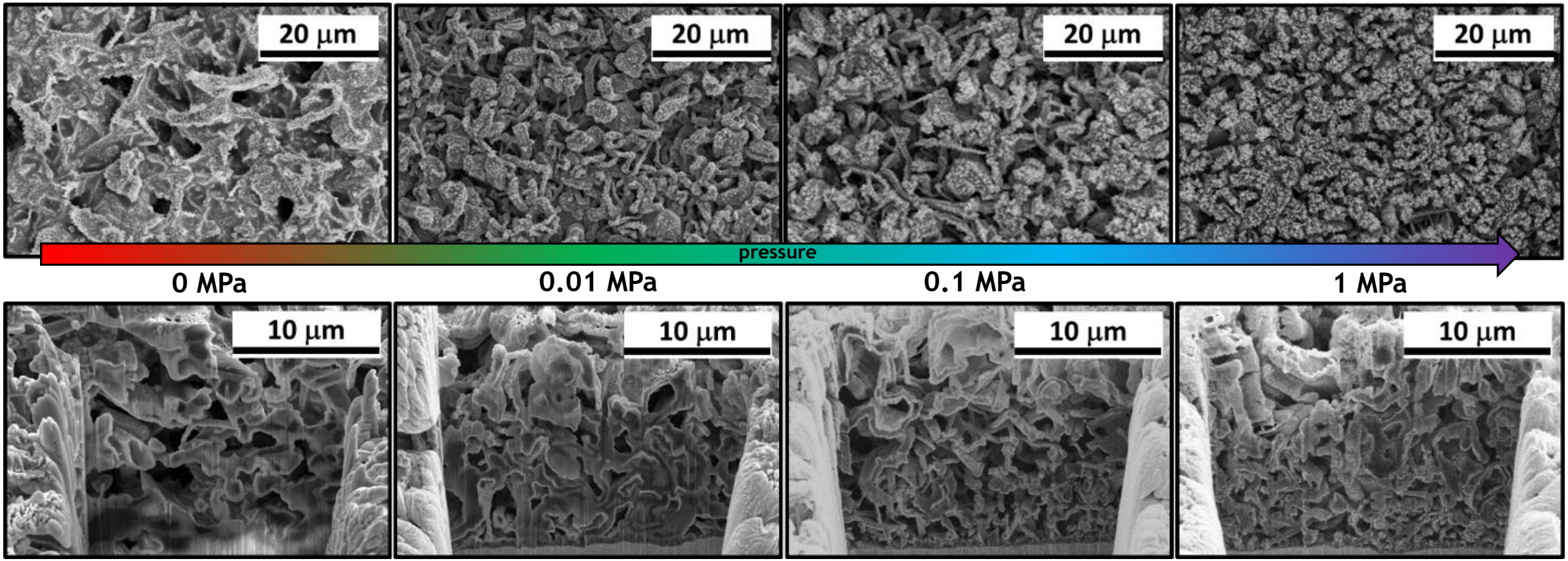


4 mA/cm^2

Li deposits at high current density less dependent on pressure than low current

Harrison et al., *in preparation*.

- Ex-situ cryo SEM of 1st Li deposition at high current density shows less change from 0 to 1 MPa
- At low current, Li can nucleate and grow at most favorable sites because overpotentials are small
  - Applied pressure gives rise to mechanical overpotential that affects growth because other overpotentials are small
- At high current, overpotential is large so Li nucleates/grows everywhere it can resulting in reasonably dense morphology
  - Mechanical overpotential from applied pressure is small relative to other overpotentials, so little effect on growth

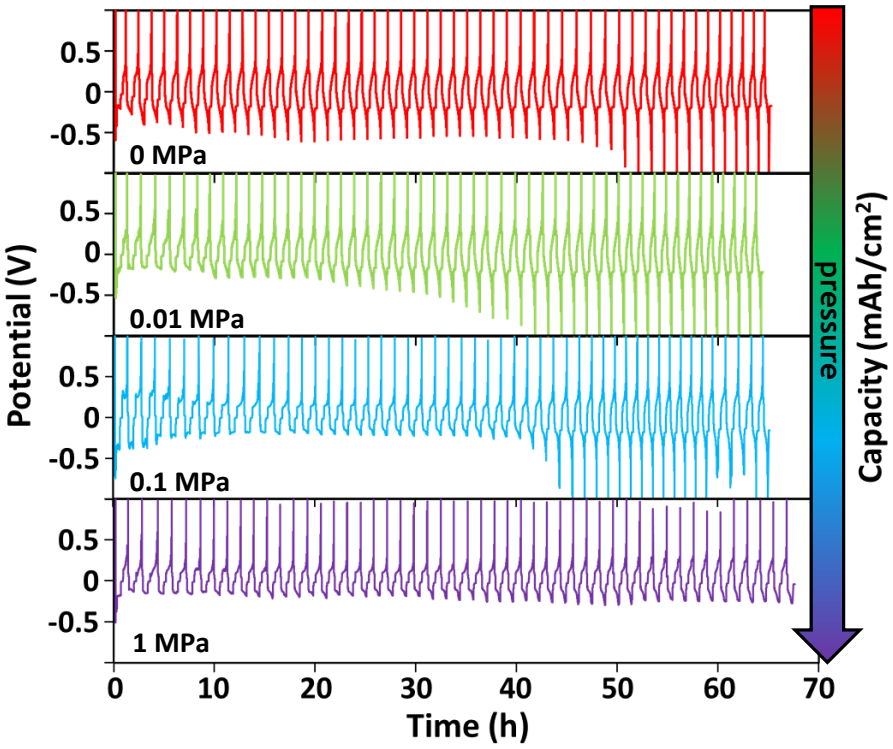


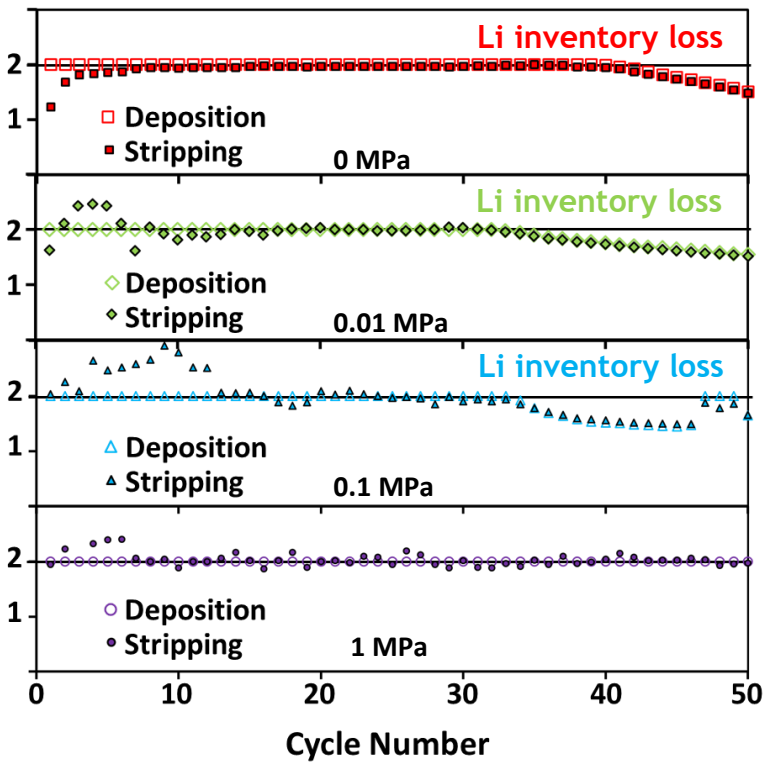
4 mA/cm^2

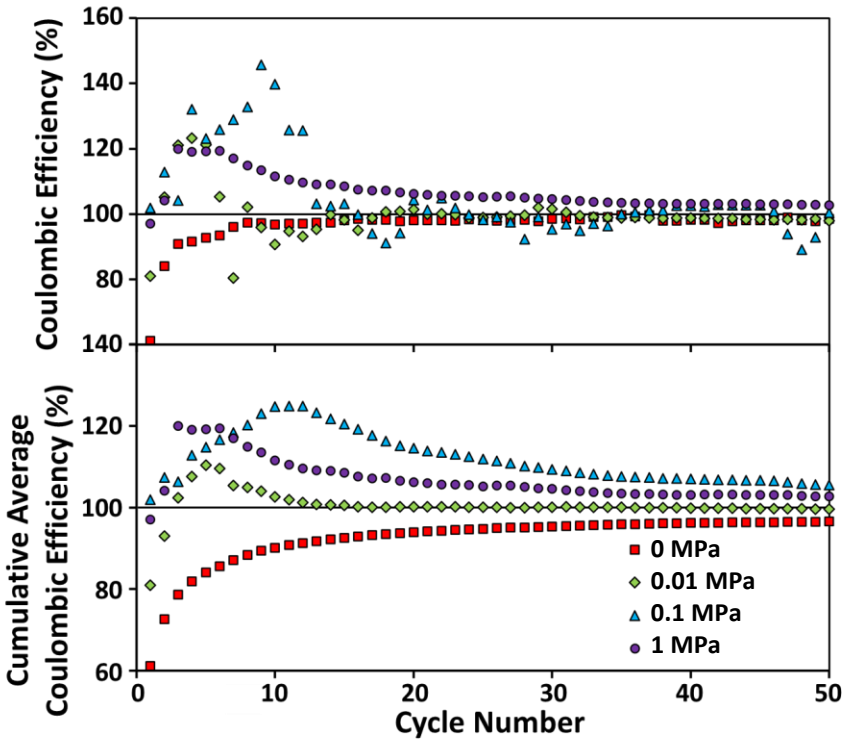
Pressure preserves Li inventory but may exacerbate shorts at high current density

Harrison et al., *in preparation.*

- Only1 MPa cells cycle Li to specified capacity for 50 cycles
- CE improves with pressure but lots of data points above 100% CE
- Average CE above 100% indicates short circuits or an unknown parasitic process during stripping
- Only the cells at 0 MPa show no evidence of shorts → does pressure exacerbate shorts?





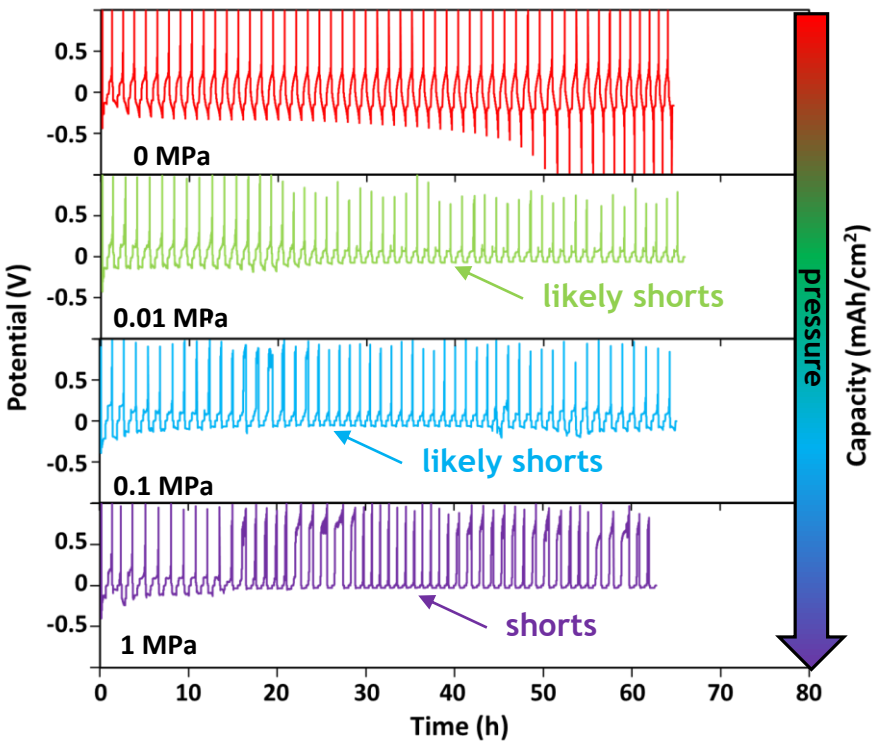


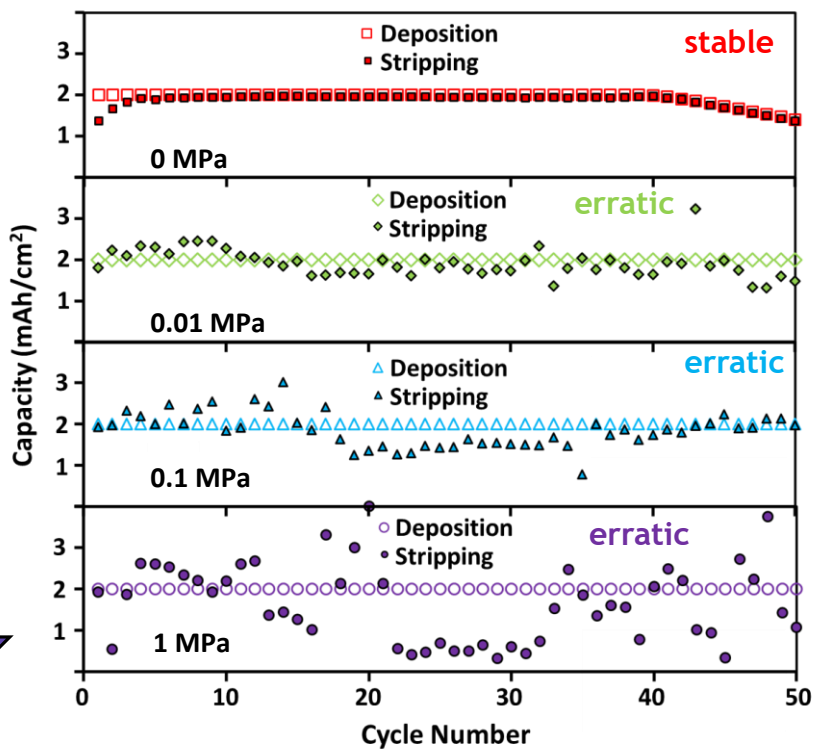
4 mA/cm^2

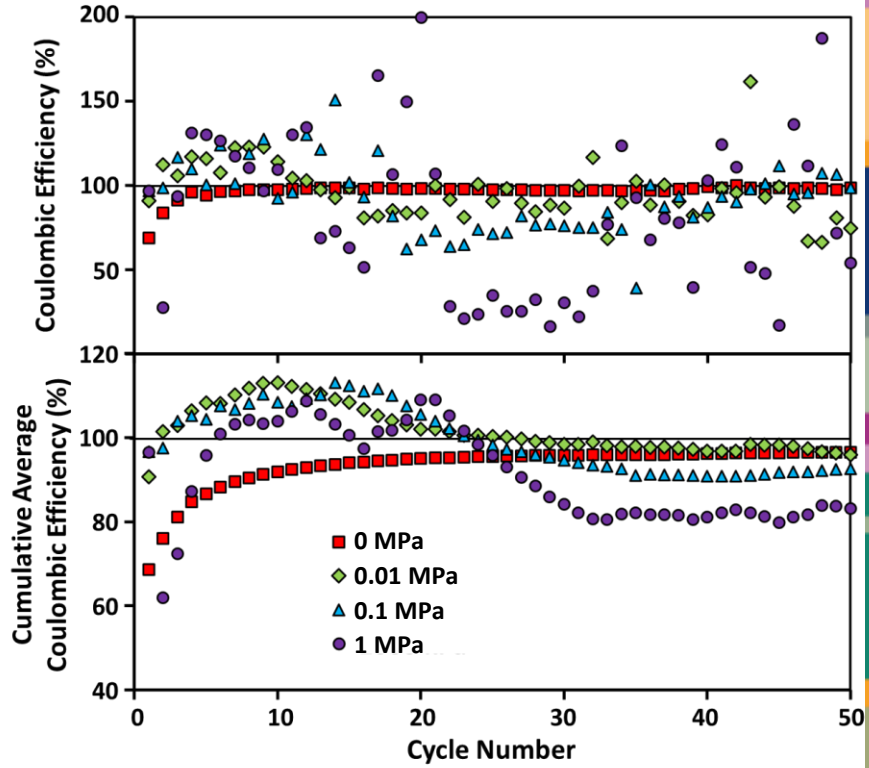
2 Celgard separators are a crutch – shorts more obvious with1 Celgard

Harrison et al., *in preparation*.

- 0 MPa → similar with one or two separators and still no signs of shorts
- 0.01, 0.1, and 1 MPa show signs of shorts → abrupt changes in overpotential, higher than 100% average CE
- Shorting most obvious for cells at 1 MPa → does pressure exacerbate shorts?
- If there are shorts, is the Li inventory less likely to deplete because not all current from charge transfer reactions?





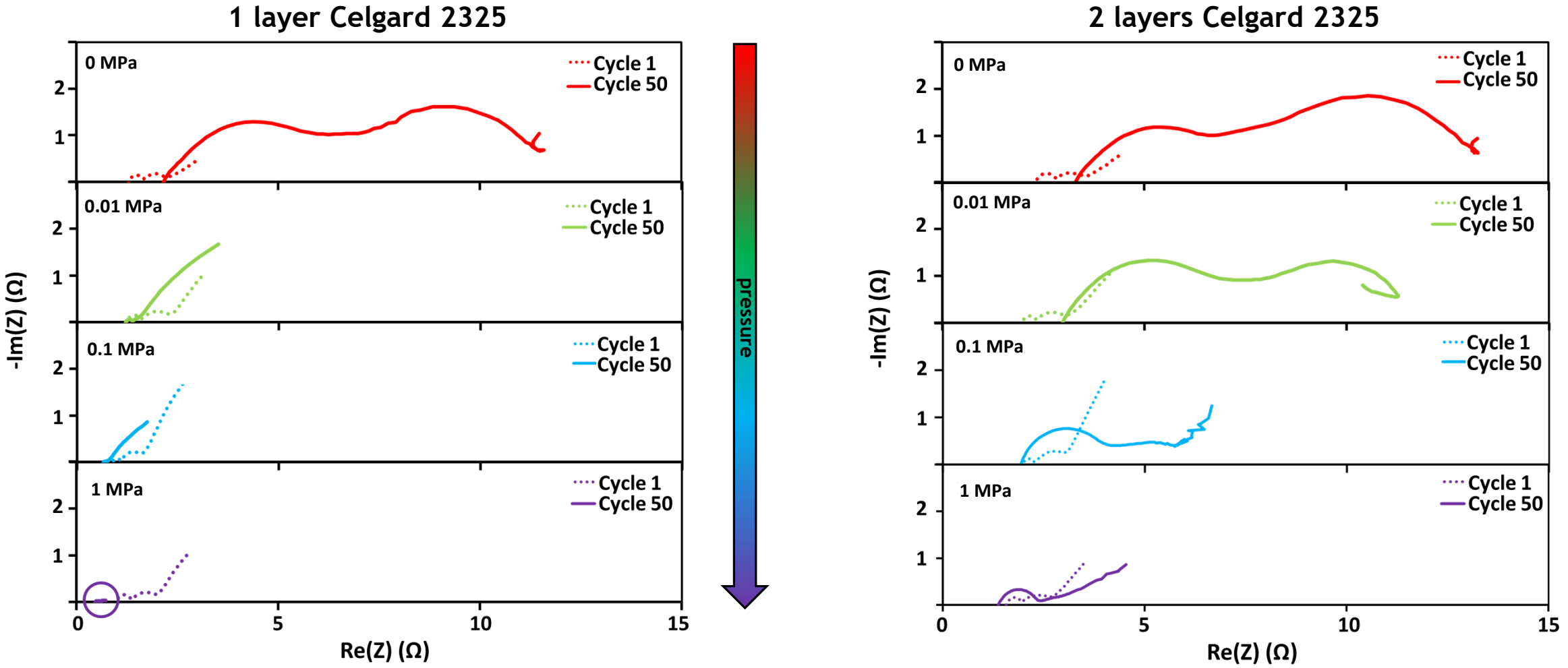


4 mA/cm^2

EIS further suggests short circuits occur more readily with one Celgard

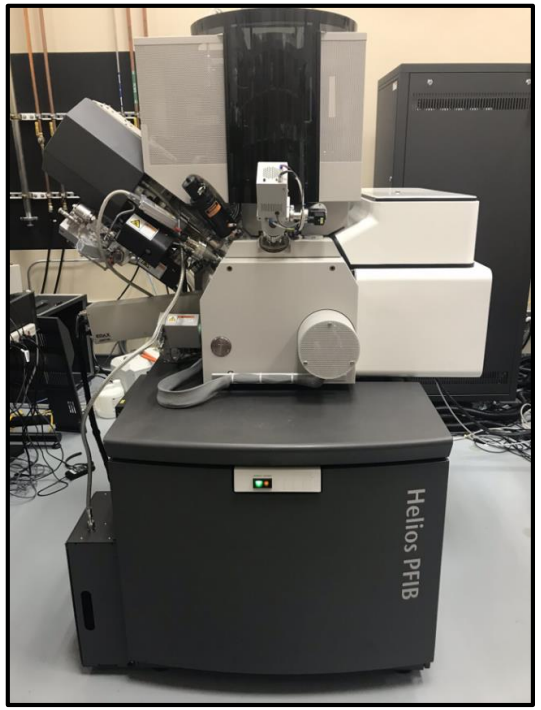
Harrison et al., *in preparation*.

- EIS spectra after one deposition similar with one or two Celgard
- EIS after deposition 50 → smaller semicircles with one Celgard than two and 1 MPa clearly shorted with one Celgard
- What happens in cells with 2 layers of Celgard 2325 that allows this difference in shorts? 2nd layer redirecting shorts?
- Cell disassembly after 50 cycles was difficult because electrode-separator interface stuck together



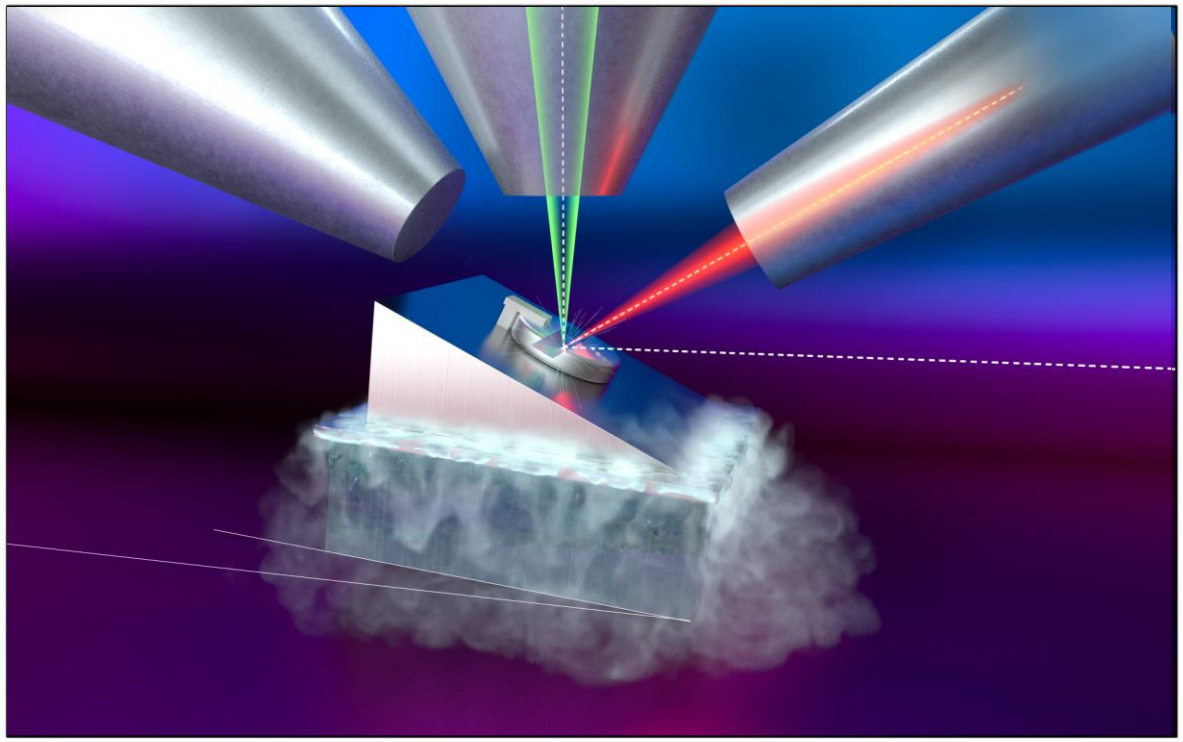
How can we image interfaces without destroying them by cell disassembly?

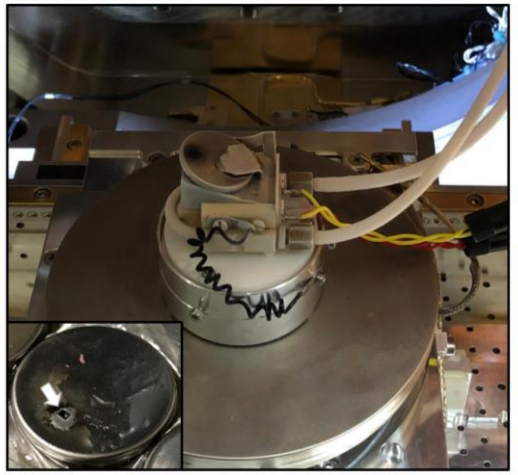
- Developed technique to mill through in-tact coin cells
- Cryo stage and athermal milling to preserve Li
- 15000x faster than Ga FIB

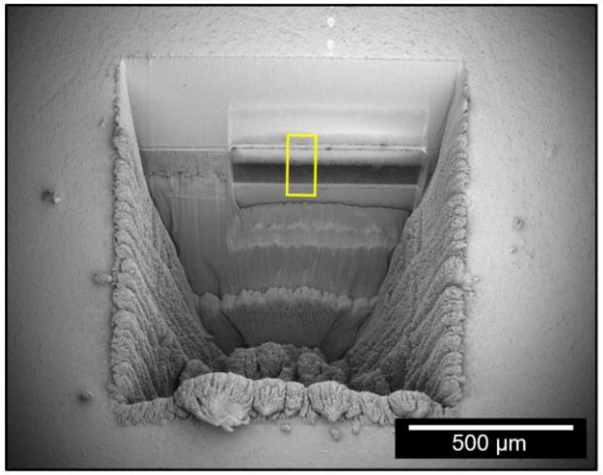


ThermoFisher laser Helios 5 PFIB SEM

For more information:
Abstract ID: EN08.08.01
Speaker: Katherine Jungjohann
Time: April 23, 5:15-5:40 PM EDT





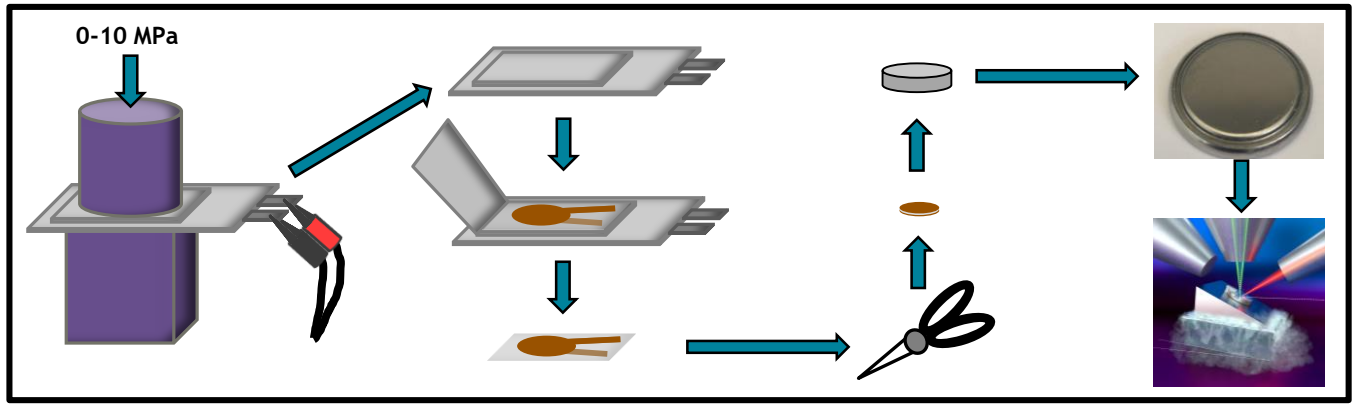


K.L. Jungjohann, R. Gannon, S. Goriparti, S. Randolph, L.C. Merrill, D. Johnson, K. Zavadil, S. Harris, K.L. Harrison, "Cryogenic Laser Ablation Reveals Short Circuit Mechanism in Lithium Metal Batteries," *submitted ACS Energy Letters*.

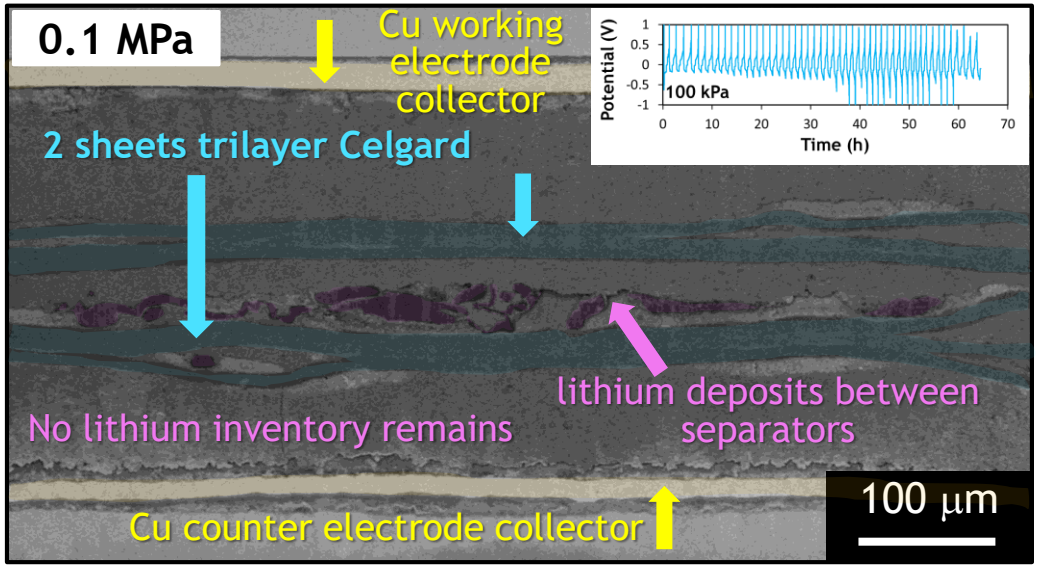
Laser PFIB SEM of stack after 51st deposition

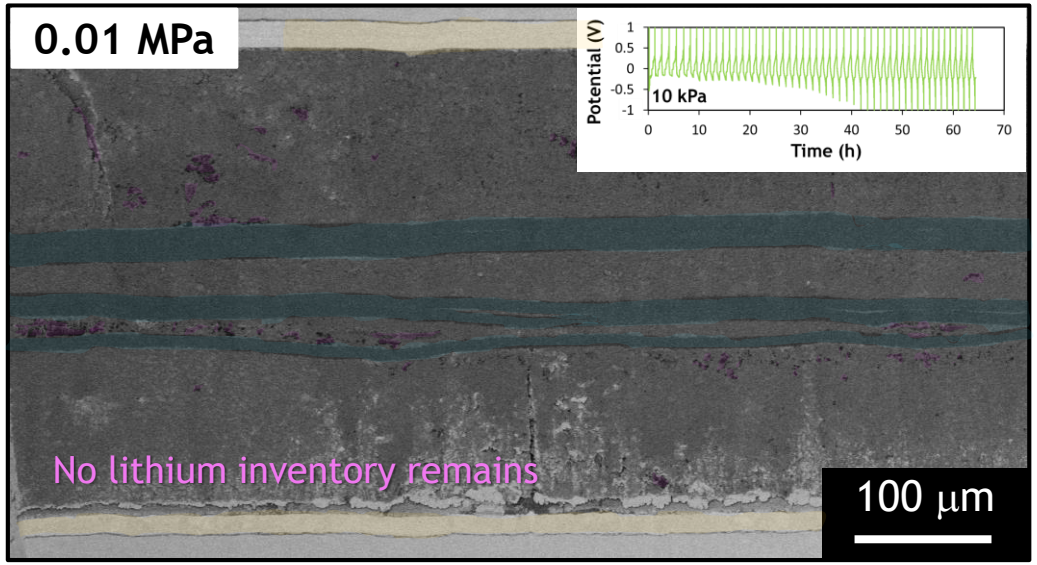
4 mA/cm²

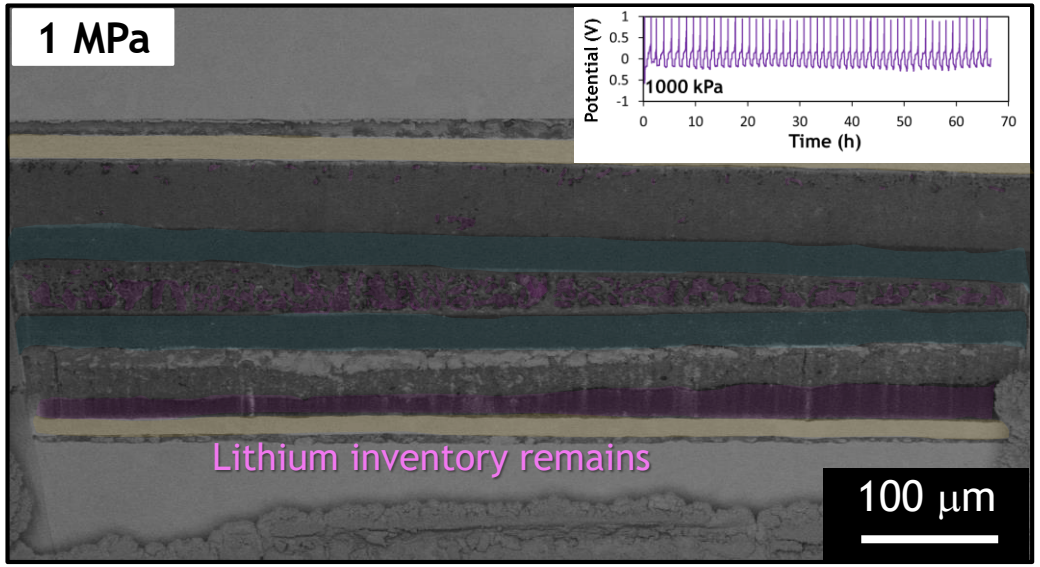
Harrison et al., *in preparation*.



- Celgard 2325 trilayers delaminate
- Large gaps form between the Celgard layers
- Li and SEI fill in between the separator

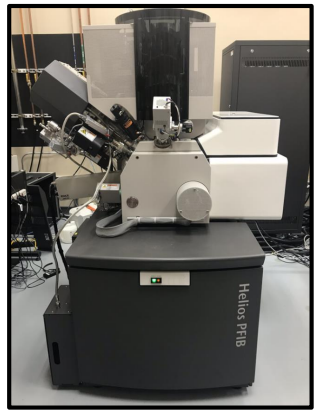


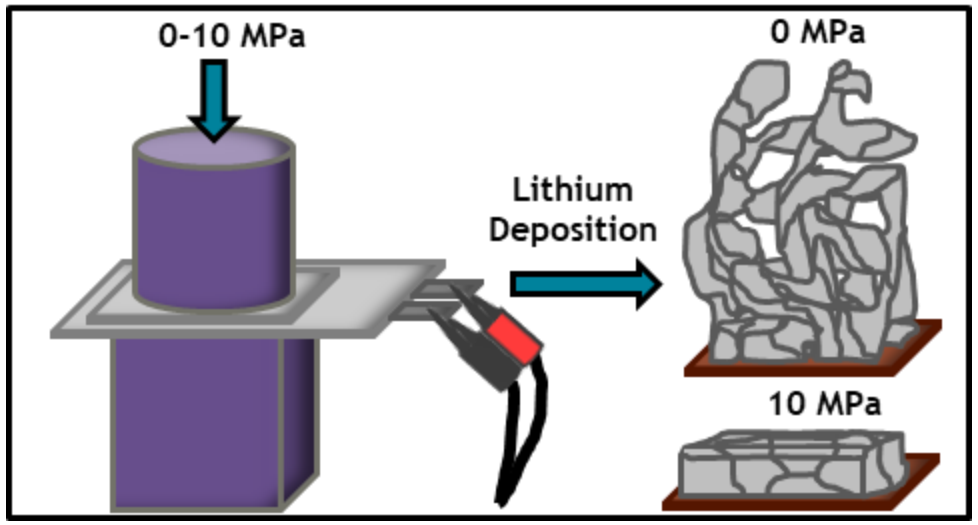




Conclusions

LDRD
Laboratory Directed
Research and Developmen





Low Current Density (0.5 mAh/cm^2)

- Increasing applied pressure from 0-1 MPa improves morphology, cell-to-cell repeatability, and CE
- Deposit thickness (and practical volumetric energy density) after one cycle varied by 5x from 0-10 MPa
- 10 MPa of applied pressure leads to transport problems even at low current density

High Current Density (4 mA/cm^2)

- Applied pressure has a more modest impact on morphology
- Soft short circuits likely at all pressures other than 0 MPa → does pressure exacerbate short circuits?
- Li inventory only available after 50 cycles at 1 MPa → pressure may slow inventory loss
- Use of two separators makes failure difficult to identify because shorts are redirected between layers

Thanks for your attention!

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