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Interfacial Pressure Improves Calendar Aging of Lithium Metal Anodes

Katharine L. Harrison (National Renewable Energy Lab)

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Spring MRS Meeting

04/24/2024 4:00-4:30 pm

katie.harrison@nrel.gov

Outline

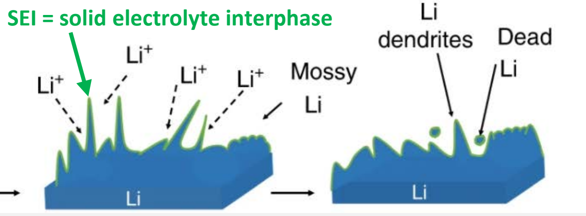
Motivation and initial studies evaluating Li metal anode calendar aging with and without coatings.

Motivation and initial studies evaluating applied pressure on Li anode cycling.

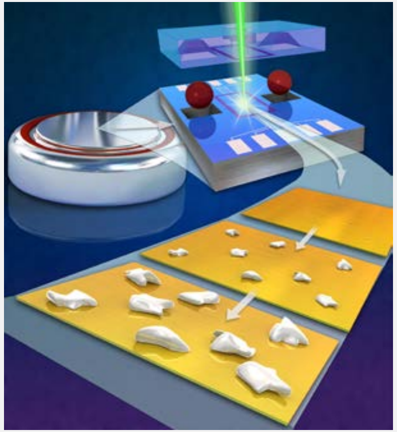
Study showing the impact of applied pressure with and without coatings on Li anode calendar aging.

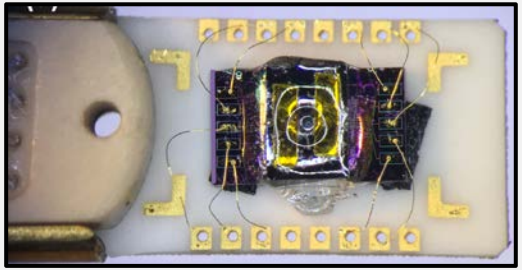
Motivating study: in situ electrochemical STEM reveals Li corrodes during calendar aging and aSEIs suppress Li corrosion

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



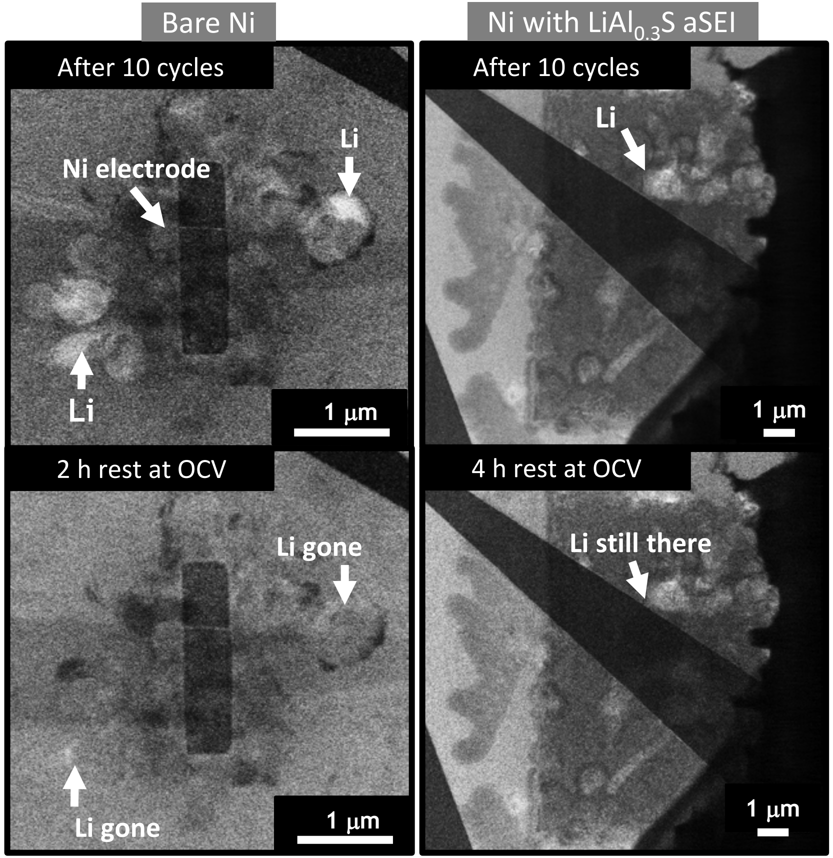
In situ electrochemical STEM to understand morphological evolution





Li corrodes without aSEI.

No corrosion with aSEI.

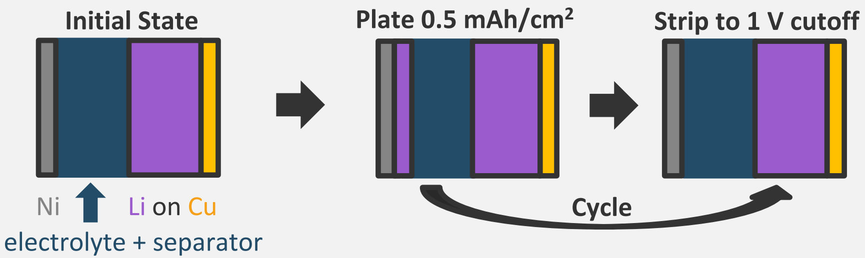


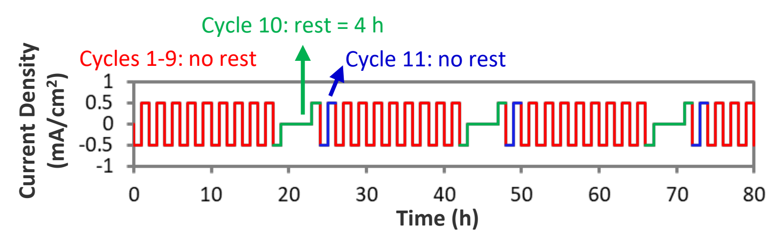
Harrison, Zavadil, Hahn, Meng, Elam, Leenheer, Zhang, Jungjohann, *ACS Nano*, 2017. DOI: 10.1021/acsnano.7b05513.

aSEI = artificial solid electrolyte interphase STEM = scanning transmission electron microscopy FSI = bis(fluorosulfonyl)imide DME = 1,2-dimethoxyethane

4 M LiFSI in DME

Motivating study: coin cells confirm Li loss during calendar aging but they show calendar aging in coin cells is at least partially reversible



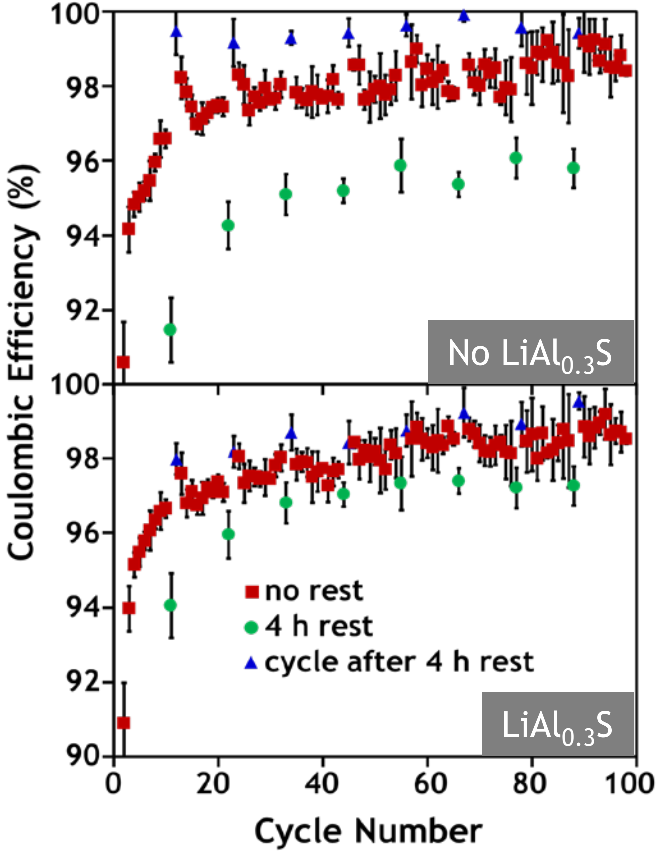


$$\mathrm{CE} = \frac{\text{electrostripped capacity}}{\text{electroplated capacity}} * 100\%$$

Calendar aging → capacity loss during rest.

Rest causes calendar aging on rest steps, suppressed by aSEI.

Capacity recovery after rest → reversible calendar aging.



Ni versus Li/Cu coin cell, 4 M LiFSI in DME, 0.5 mA/cm², 0.5 mAh/cm²

CE = Coulombic efficiency

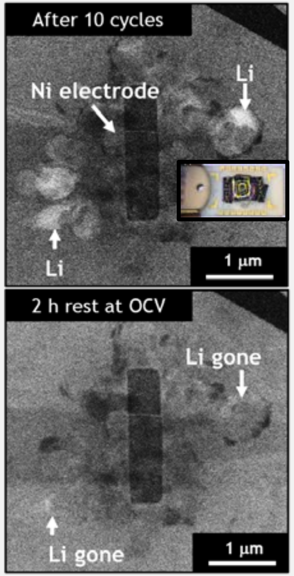
Harrison, Zavadil, Hahn, Meng, Elam, Leenheer, Zhang, Jungjohann, *ACS Nano,* 2017. DOI: 10.1021/acsnano.7b05513

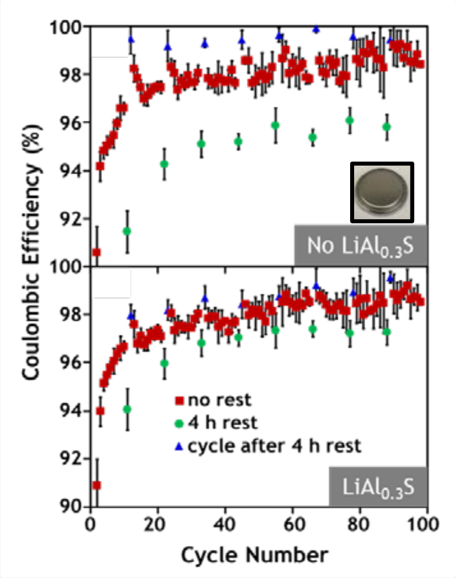
Galvanic corrosion explains corrosion in STEM experiments but not reversible capacity loss during aging in coin cell experiments

Kolesnikov et al., Adv. Energy Mat., 2020, 10, 2000017
DOI: 10.1002/aenm.202000017 (open access).

We expect galvanic corrosion to be irreversible.

Harrison, Zavadil, Hahn, Meng, Elam, Leenheer, Zhang, Jungjohann, *ACS Nano,* 2017. DOI: 10.1021/acsnano.7b05513



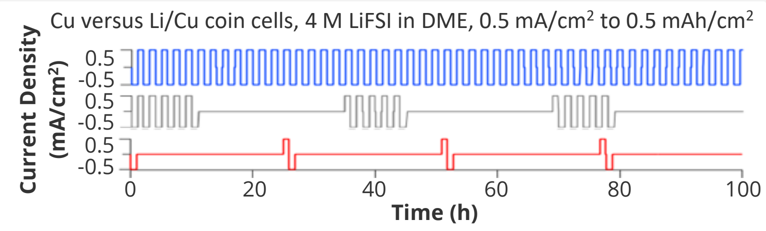


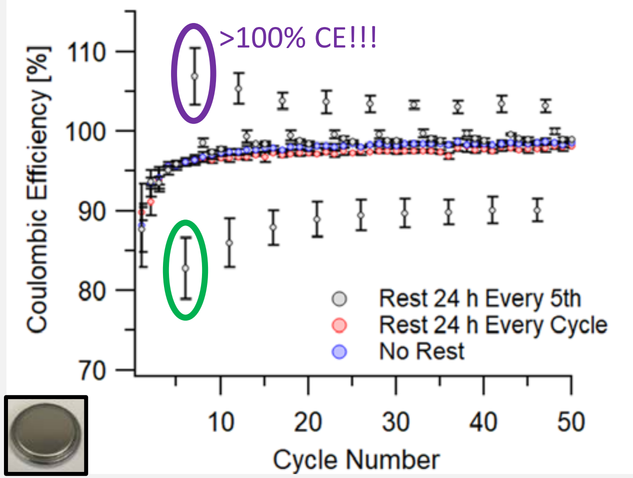
galvanic corrosion explains behavior

reversibility not explained by galvanic corrosion

We were motivated to understand this reversible calendar aging phenomenon!

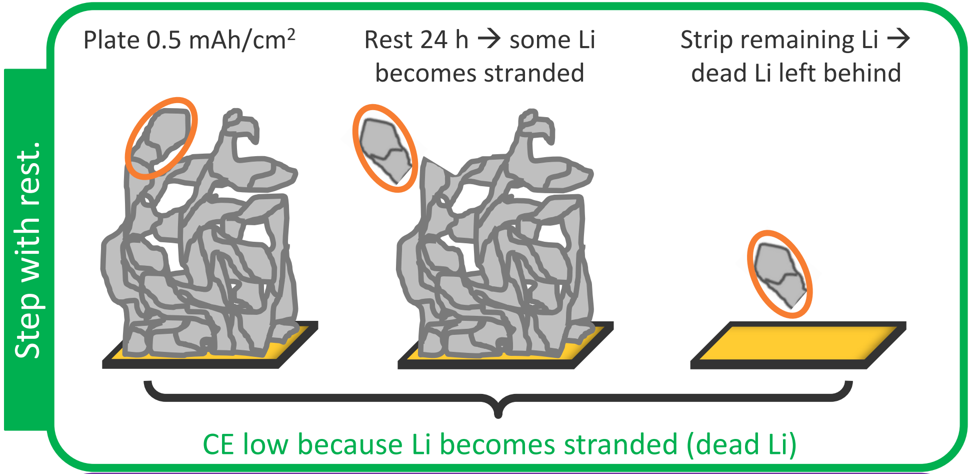
Intermittent calendar aging leads to largely reversible capacity losses because losses are due to dead Li formation during rest and reattachment during cycling

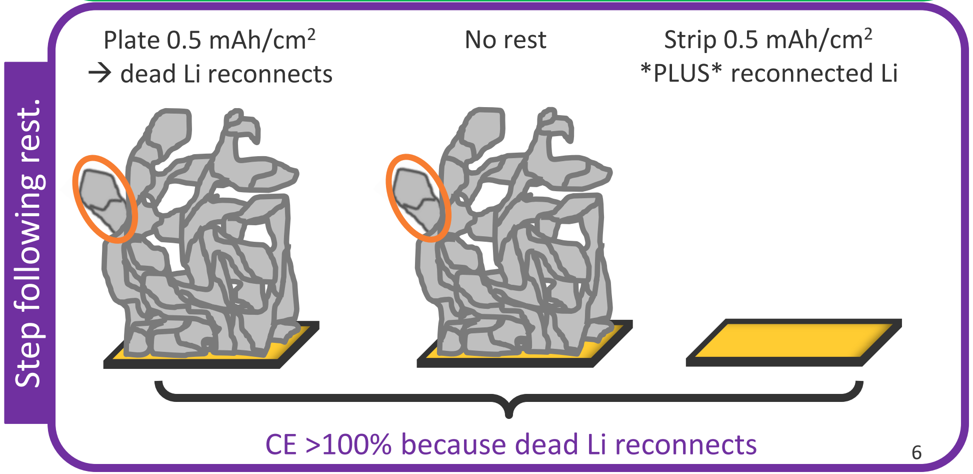




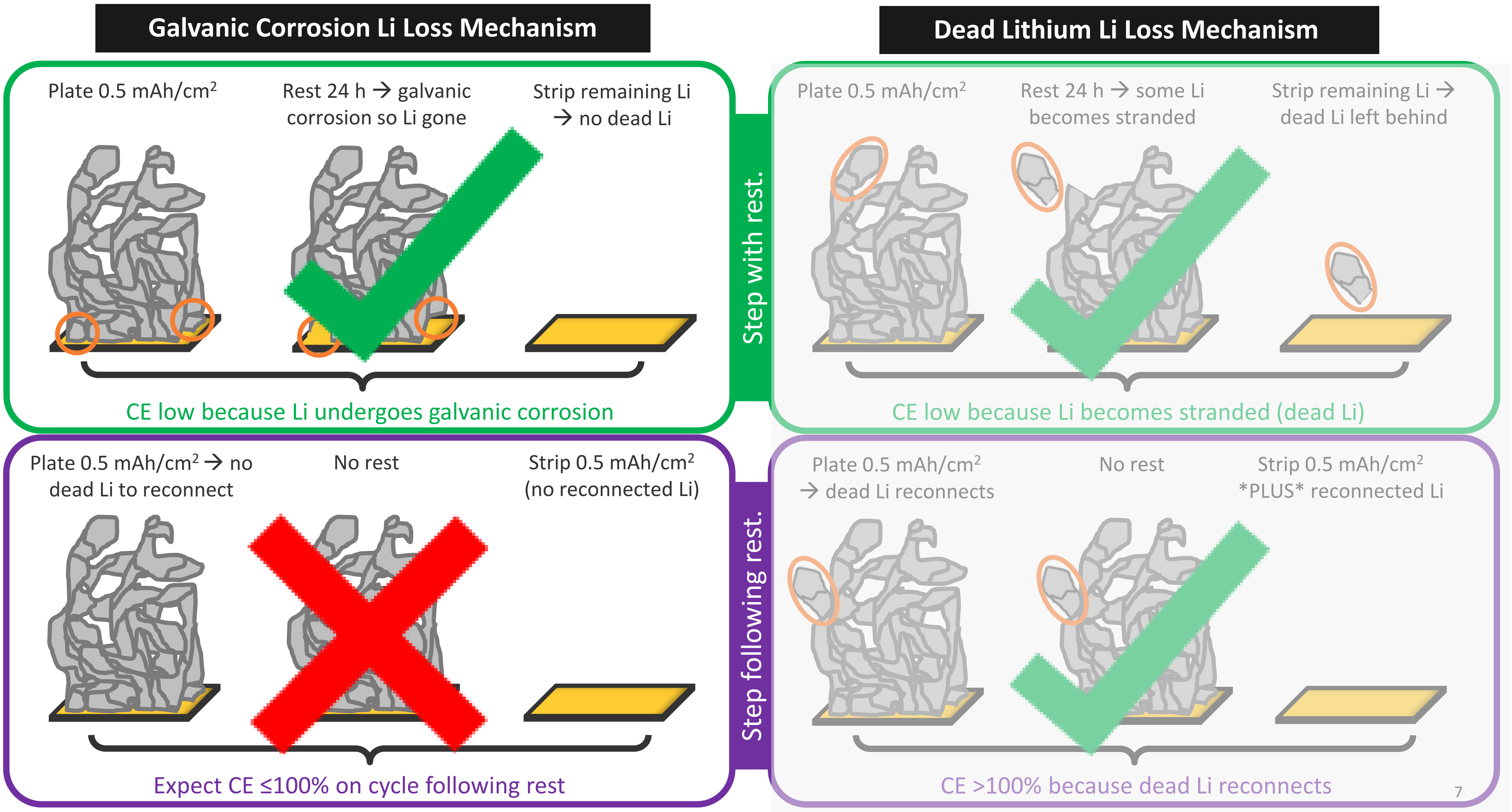
Average CE → 97.4±0.2% 97.6±0.1% 97.0±0.1%

Dead Li formation consistent with reversible losses.





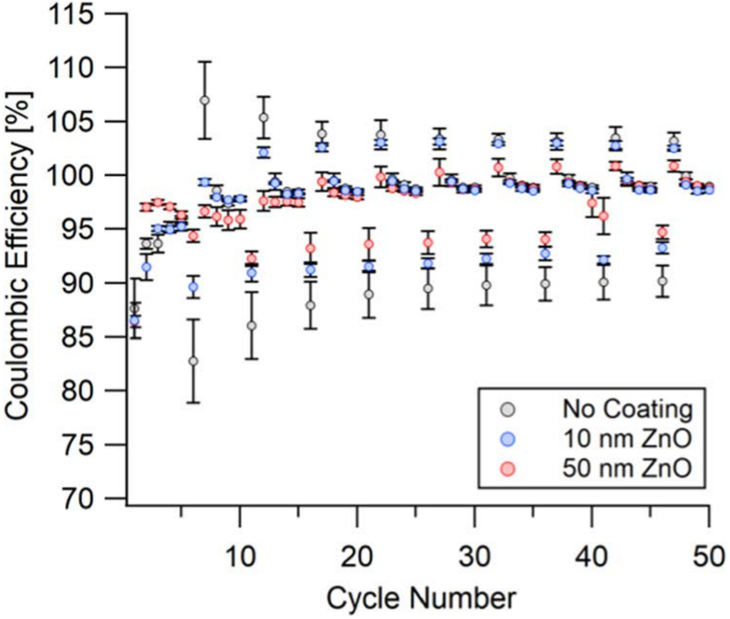
Merrill, Rosenberg, Jungjohann, Harrison, *ACS App. Energy Mater.*, 2021. DOI: 10.1021/acsaem.1c00874.

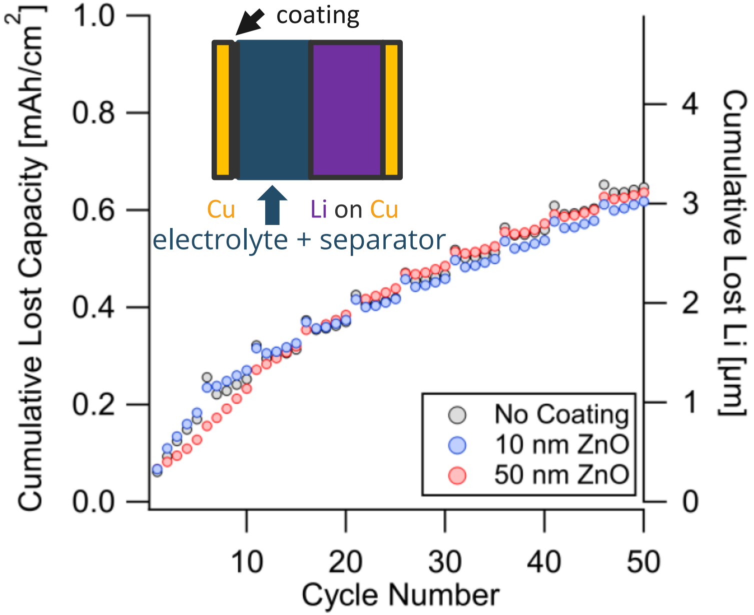


Galvanic Corrosion Li Loss Mechanism
Dead Lithium Li Loss Mechanism
Plate 0.5 mAh/cm^2
Rest 24 h → galvanic corrosion so Li gone
Strip remaining Li → no dead Li
CE low because Li undergoes galvanic corrosion
Step with rest.
Plate 0.5 mAh/cm^2
Rest 24 h → some Li becomes stranded
Strip remaining Li → dead Li left behind
CE low because Li becomes stranded (dead Li)
Plate 0.5 mAh/cm^2 → no dead Li to reconnect
No rest
Strip 0.5 mAh/cm^2 (no reconnected Li)
Expect CE ≤100% on cycle following rest
Step following rest.
Plate 0.5 mAh/cm^2 → dead Li reconnects
No rest
Strip 0.5 mAh/cm^2 *PLUS* reconnected Li
CE >100% because dead Li reconnects

ZnO coatings can improve adhesion and decrease losses during intermittent calendar aging rest steps

Cu or ZnO-coated Cu versus Li/Cu coin cells, 4 M LiFSI in DME, 0.5 mA/cm² to 0.5 mAh/cm², 24 h rest every 5th cycle





after deposition 6 (no aging steps)

Li deposit bare Cu

Li deposit ZnO-coated Cu

ZnO-coated Cu decreases losses during intermittent calendar aging cycles, but overall cumulative capacity loss is similar to bare Cu.

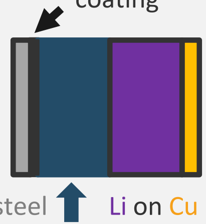
ZnO coatings appear to improve adhesion of the Li to the current collector, which likely reduces dead Li formation during aging.

Merrill, Rosenberg, Jungjohann, Harrison, *ACS App. Energy Mater.*, 2021. DOI: 10.1021/acsaem.1c00874.

ZnO & Al_2O_3 aSEIs are passivating but LiF aSEI is not passivating

Motivated to understand if common aSEIs and coatings impact calendar aging by guiding morphology evolution or through passivation.

10 nm LiF, ZnO, Al_2O_3 on steel



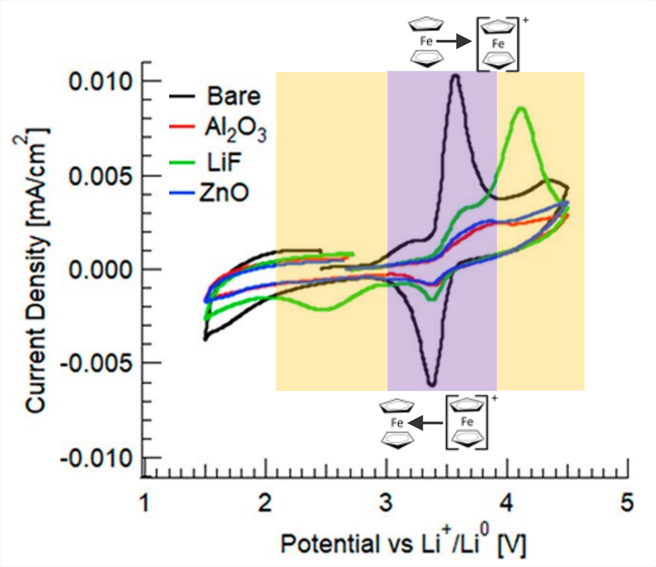
1 M LiTFSI and 5 mM ferrocene in tetraglyme

ZnO and Al_2O_3 coatings are passivating but LiF is not.

LiF often touted as ideal SEI component, but DFT calculations shows LiF grains leak electrons.[1]

LiF: smaller peak splitting
Facile electron transfer process

LiF: larger peak splitting
Slow electron transfer process

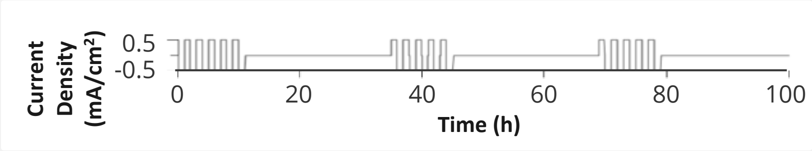


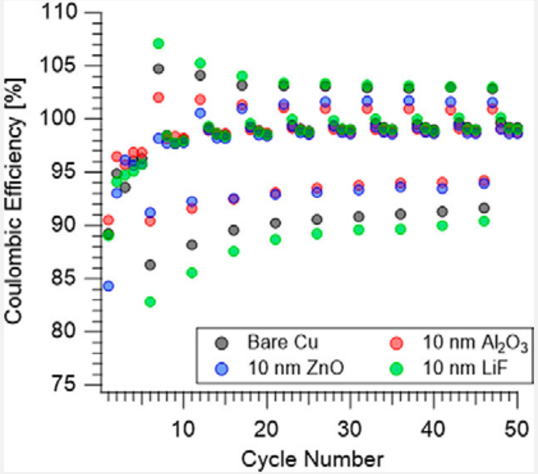
Merrill, Long, Small, Jungjohann, Leung, Bassett, Harrison, *J. Phys. Chem. C*, 2021. DOI: 10.1021/acs.jpcc.2c05385.

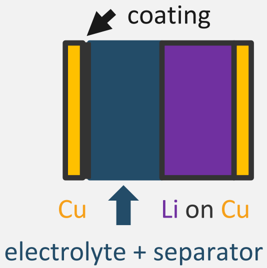
1. DFT: Smeu and Leung, 2021. Phys. Chem. Chem. Phys., 23(5), pp.3214-3218)

DFT: density functional theory

ZnO & Al_2O_3 suppress calendar aging losses because they promote Li growth morphology less prone to Li stranding (but LiF does not)

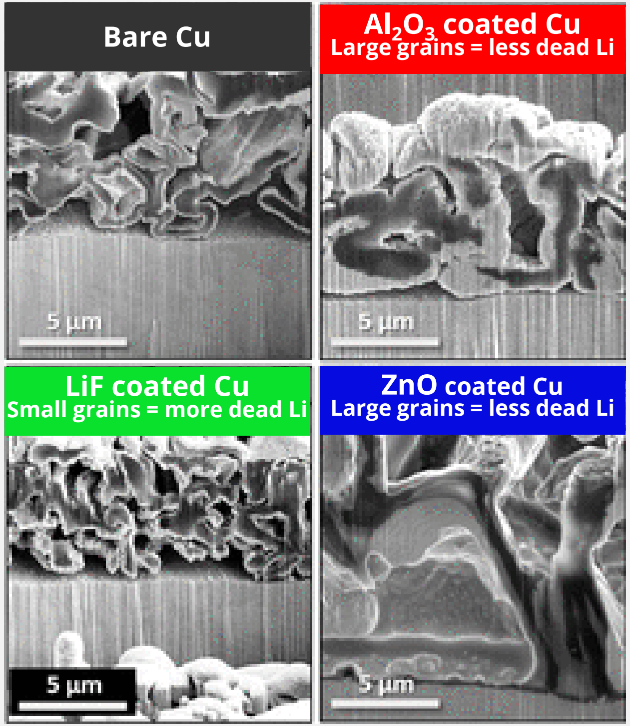






4 M LiFSI in DME
0.5 mA/cm² to 0.5 mAh/cm²
24 h rest every 5th cycle
Cu or coated Cu versus Li/Cu coin cells

Passivation can't explain LiF behavior (Cu even less passivating).

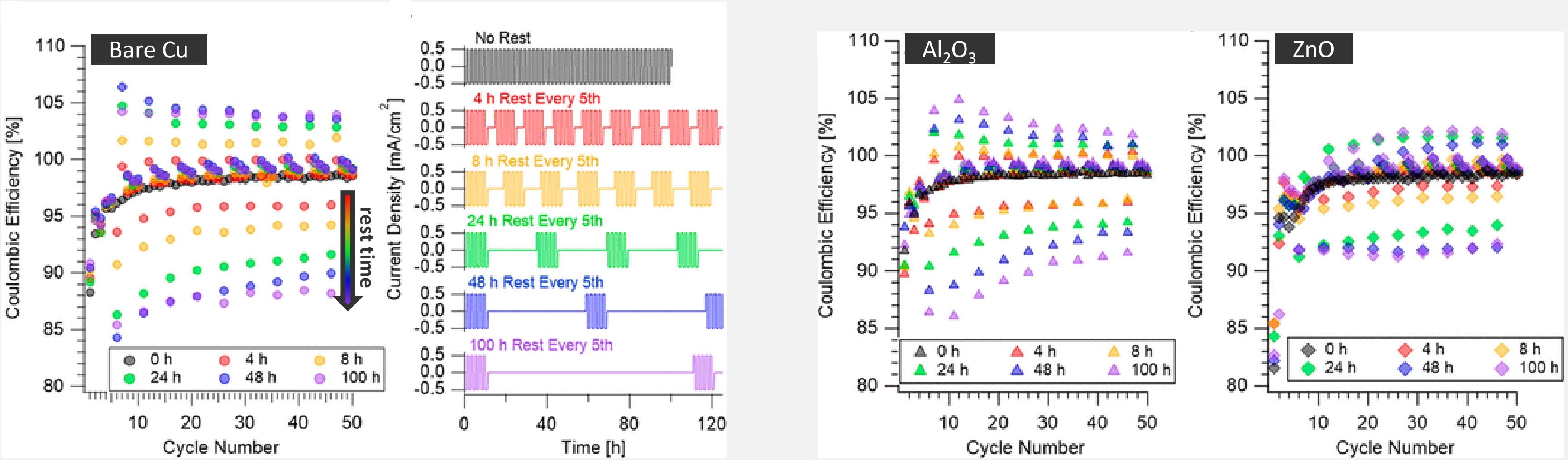


Coatings that guide morphology to larger grain sizes exhibit less loss during aging steps.

Merrill, Long, Small, Jungjohann, Leung, Bassett, Harrison, *J. Phys. Chem. C*, 2021. DOI: 10.1021/acs.jpcc.2c05385.

At longer rest times, calendar aging remains largely reversible and aSEIs continue to suppress calendar aging losses moderately

Calendar aging increases with rest time but not linearly (loss after 100 h rest ~3x larger than after 4 h rest → *not 25x*).



Average CE similar with and without rest → losses during rest reversible → reversibility consistent with Li stranding as major mechanism.

	CE (%), 0 h rest	CE (%), 4 h rest	CE (%), 8 h rest	CE (%), 24 h rest	CE (%), 48 h rest	CE (%), 100 h rest
Bare	97.6	97.7	97.7	97.8	97.7	97.4
ZnO	97.4	97.6	97.6	97.5	97.0	97.3
Al_2O_3	97.9	97.8	97.9	97.9	97.7	97.7

Merrill, Long, Small, Jungjohann, Leung, Bassett, Harrison, *J. Phys. Chem. C.*, 2021. DOI: 10.1021/acs.jpcc.2c05385.

Cu or coated Cu versus Li/Cu coin cells
4 M LiFSI in DME, 0.5 mA/cm² to 0.5 mAh/cm²

Outline

Motivation and initial studies evaluating Li metal anode calendar aging with and without coatings.

- Intermittent calendar aging after Li deposition leads to capacity loss during the rest.
- Coatings can partially mitigate calendar aging by directing morphology to decrease dead Li.
- ZnO is the most promising coating in terms of reducing calendar aging.
- The aging is largely reversible, indicating it is related to dead Li formation and reattachment.

Motivation and initial studies evaluating applied pressure on Li anode cycling.

Study showing the impact of applied pressure with and without coatings on Li anode calendar aging.

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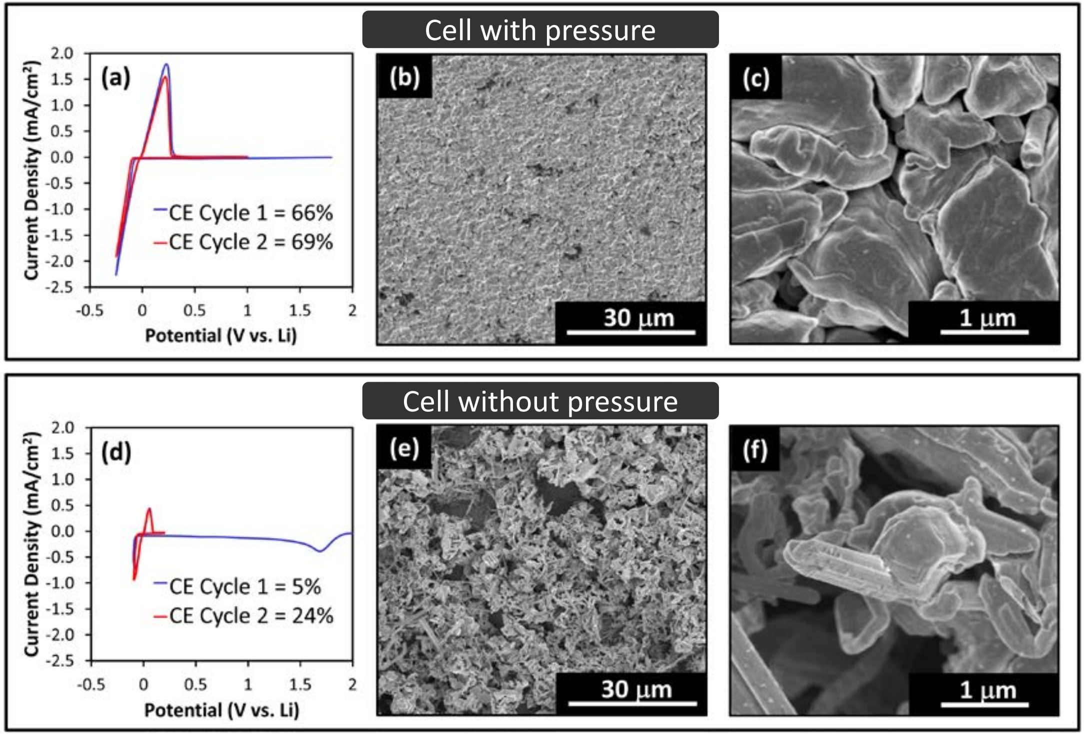
Bulk electrochemical experiments in 4 M LiFSI DME on Cu current collectors show applied pressure critical to high CE and favorable morphology

Applied pressure is very important for controlling Li morphology evolution.



Harrison, Zavadil, Hahn, Meng, Elam, Leenheer, Zhang, Jungjohann, *ACS Nano,* 2017. DOI: 10.1021/acsnano.7b05513.

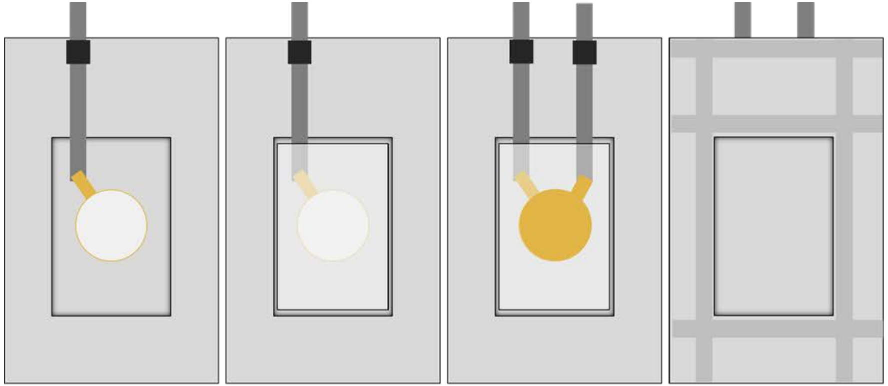
Cu versus Li half cell, scan rate = 10 mV/s, Li deposition for SEM @ 1 mA/cm^2, capacity 0.4 mAh/cm^2

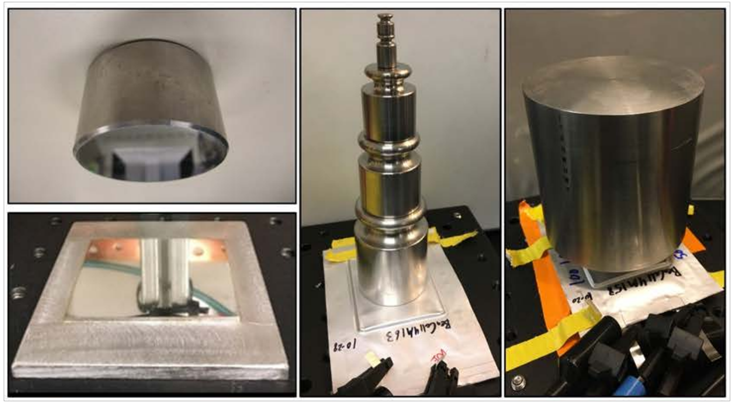
Systematically studied effects of pressure on Li versus Cu pouch cells 0-10 MPa

Cu

Li on Cu

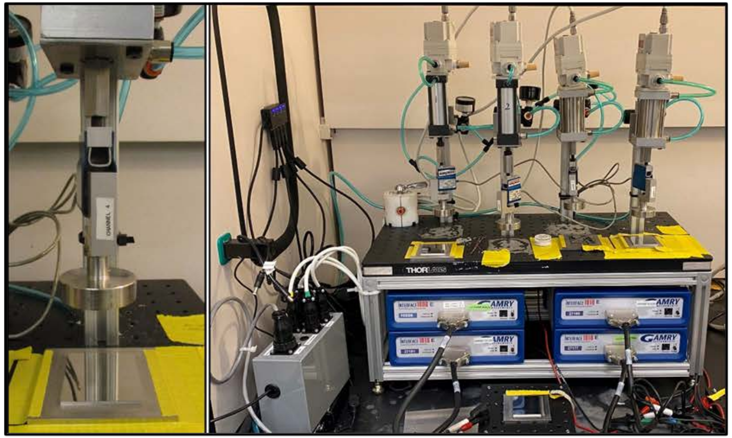
electrolyte +
separator





4 M LiFSI in DME
0.5 mA/cm^2 to 2 mAh/cm^2
continuous cycling (no aging)

0, 0.01. 0.1, 1, 10 MPa



Harrison, Goriparti, Merrill, Long, Warren, Roberts, Perdue, Casias, Cullier, Boyce, Jungjohann, *ACS App. Mat. & Int.,* 2021. 10.1021/acsami.1c06488.

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

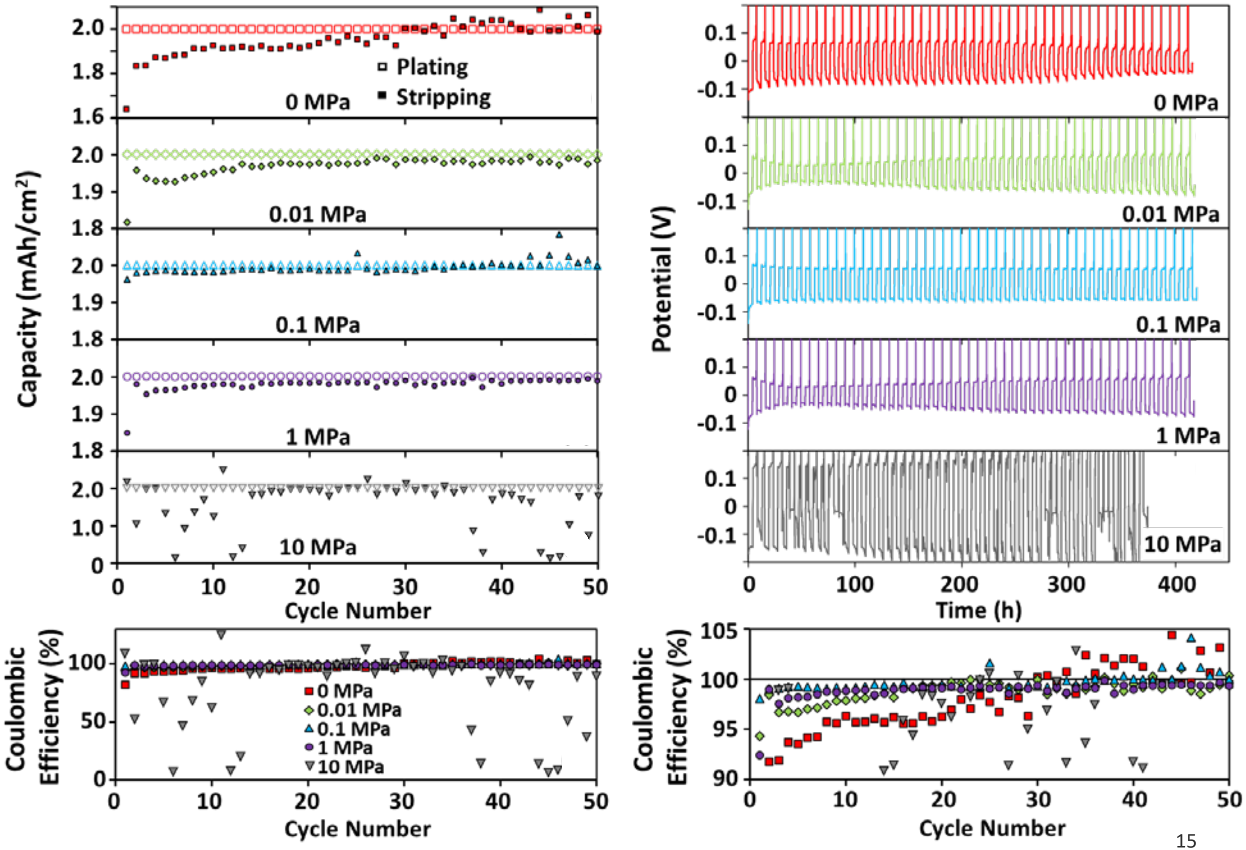
4 M LiFSI in DME
2 mAh/cm^2, 0.5 mA/cm^2
continuous cycling (no aging)

Cycling stability generally increases with increasing pressure until 10 MPa.

CE generally improves with pressure but 0.1 and 1 MPa similar.

10 MPa → increased overpotential and loss of cycling stability.

Transport limited locally at high pressure where pores can close.



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Cryo FIB/SEM after 1st Li deposition step – pressure improves morphology

SEM = scanning electron microscopy
FIB = focused ion beam

CE trends with morphology, likely due to less dead Li.

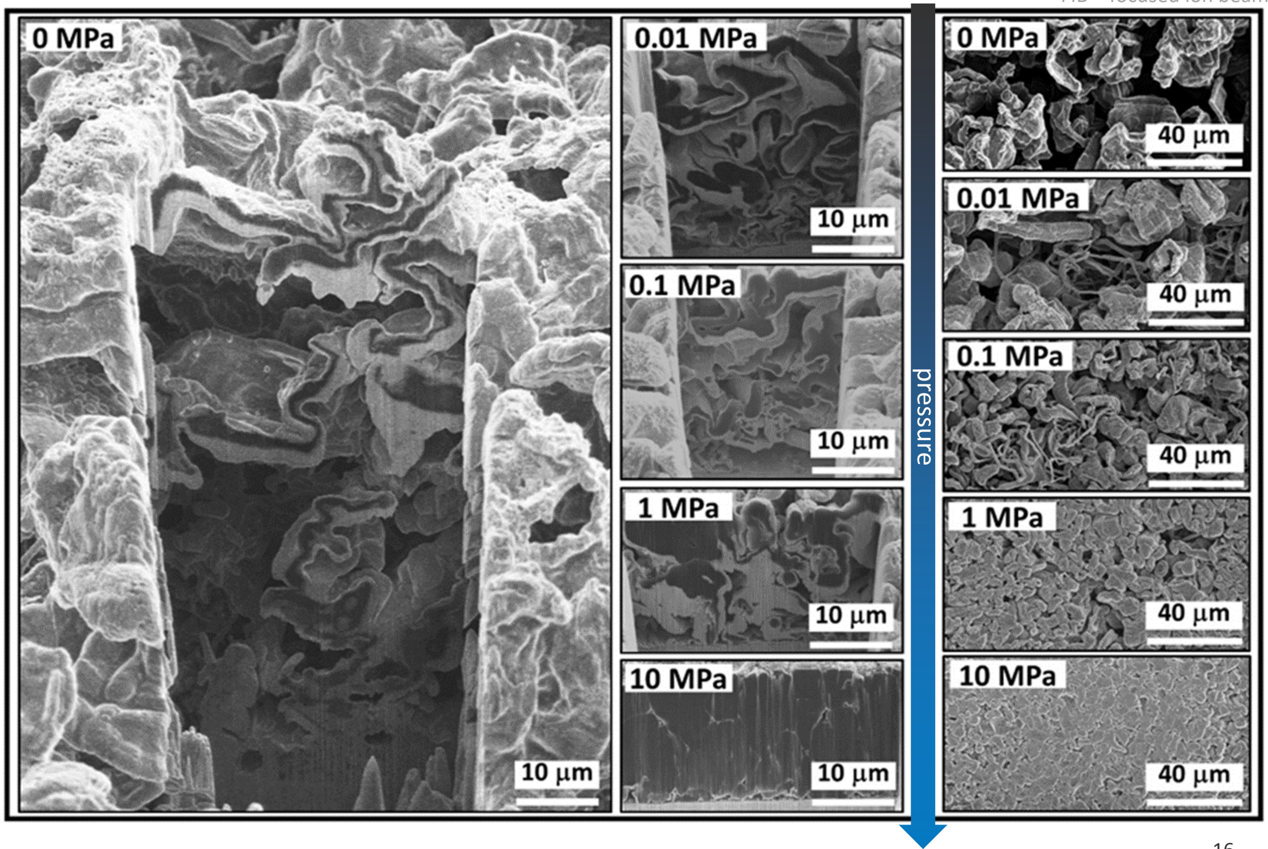
Pressure (MPa)	Thickness 1st Plating (µm)
0	91
0.01	33
0.1	30
1	22
10	17

pressure

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

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



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- The aging is largely reversible, indicating it is related to dead Li formation and reattachment.

Motivation and initial studies evaluating applied pressure on Li anode cycling.

- Applied pressure leads to higher CE and more stable, repeatable cycling performance.
- Too much pressure leads to erratic cycling behavior, transport limitations, and short circuits.
- Applied pressure leads to significantly denser Li deposits with more favorable morphology.
- Applied pressure likely improves cycling by decreasing surface area and reducing dead Li.

Study showing the impact of applied pressure with and without coatings on Li anode calendar aging.

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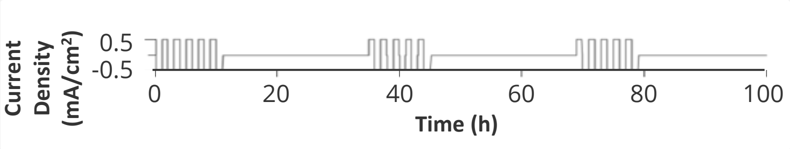
Study showing the impact of applied pressure with and without coatings on Li anode calendar aging.

Coin cells with intermittent calendar aging show much less capacity fade during rest when cycled to higher and more relevant capacity

Aging work in previous slides was in coin cells with 0.5 mAh/cm^2 capacity.

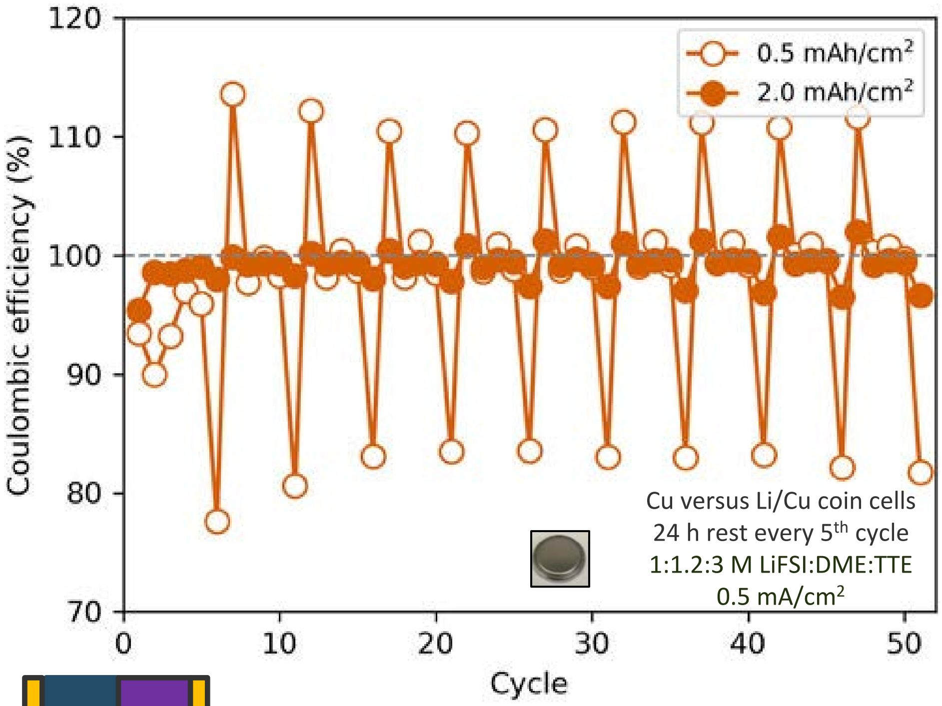
Applied pressure work in previous slides was in pouch cells with 2 mAh/cm^2 capacity.

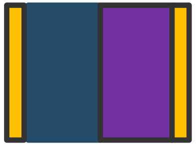


Coin cells show much less capacity loss during calendar aging tests with 2 mAh/cm^2 compared to 0.5 mAh/cm^2.

2 mAh/cm^2 chosen here because more relevant.

1:1.2:3 M LiFSI:DME:TTE here instead of 4 M LiFSI in DME in previous studies discussed.

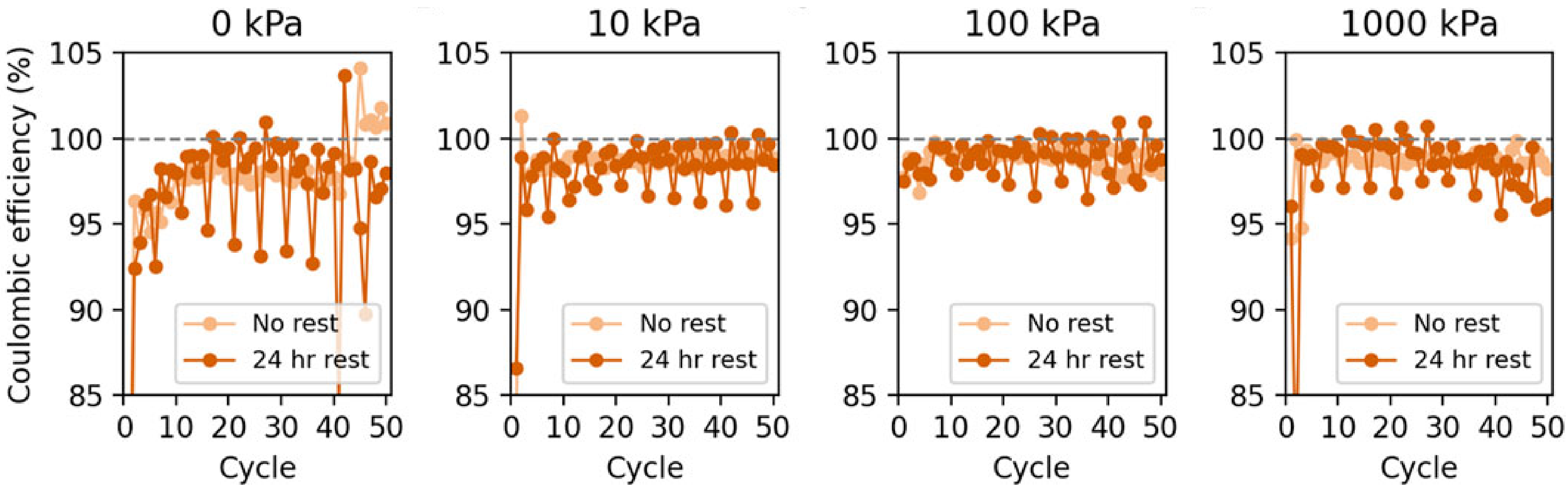




TTE = 1,1,2,2-tetrafluoroethyl 2,2,3,3-tetrafluoropropyl ether

Bassett, Small, Long, Merrill, Warren, Harrison. *Frontiers in Batt. and Electrochem.*, 2023. DOI: 10.3389/fbael.2023.1292639.

Applied pressure in pouch cells cycled to 2 mAh/cm^2 decreases capacity loss during intermittent calendar aging



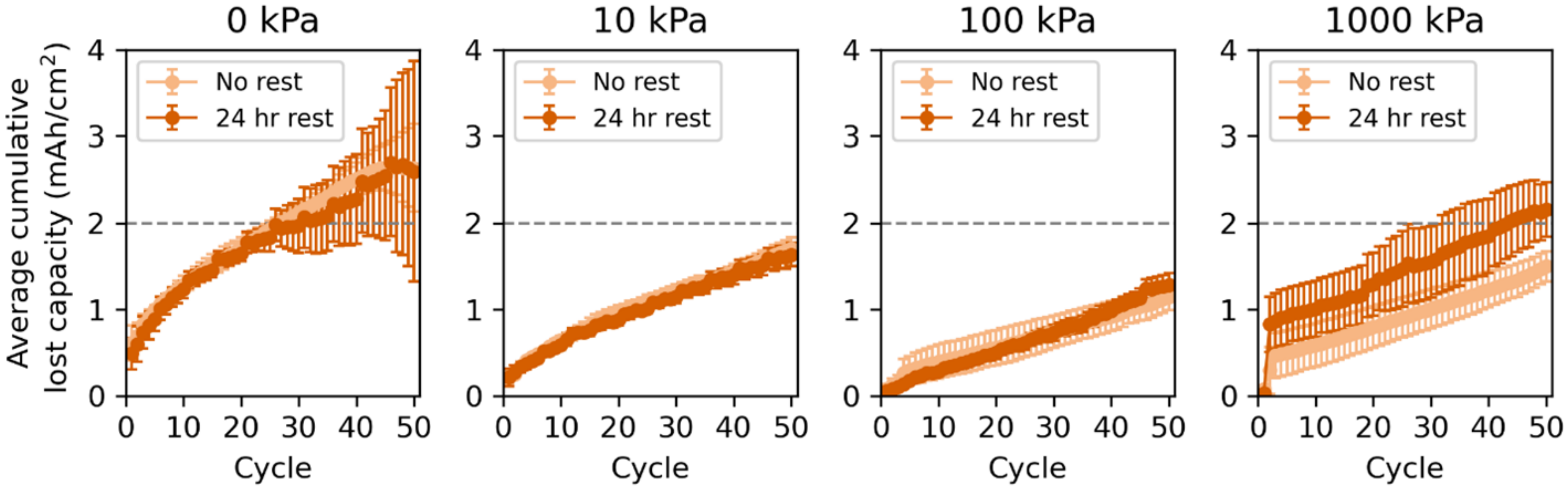
Much lower losses in calendar aging steps at 10 kPa compared to 0 kPa, more subtle changes 10-1000 kPa.

Increased applied pressure reduces losses during calendar aging steps due to suppression of dead Li formation with pressure.

Cu versus Li/Cu pouch cells
24 h rest every 5th cycle
1:1.2:3 M LiFSI:DME:TTE
0.5 mA/cm^2 to 2 mAh/cm^2

Bassett, Small, Long, Merrill, Warren, Harrison. *Frontiers in Batt. and Electrochem.*, 2023. DOI: 10.3389/fbael.2023.1292639.

Average cumulative capacity loss shows that 100 kPa is the optimal pressure and generally losses during rest are reversible



Pressure (kPa)	Cu No Rest	Cu 24 h Rest
0	97.4±0.5	97.0±1
10	98.1±0.1	98.4±0.2
100	98.9±0.2	98.7±0.1
1000	98.5±0.2	97.8±0.3

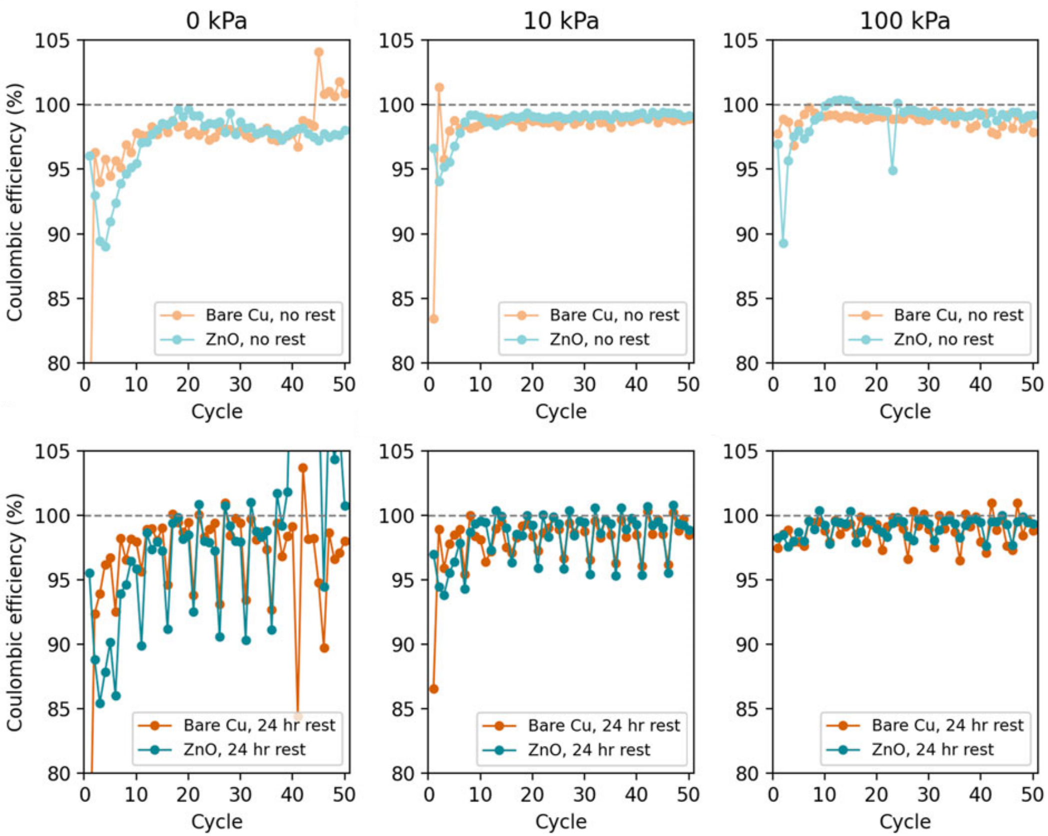
100 kPa exhibits the lowest cumulative loss.

Cumulative losses in cells with intermittent calendar aging steps are similar to cells without aging steps (except at 1000 kPa).

Bassett, Small, Long, Merrill, Warren, Harrison. *Frontiers in Batt. and Electrochem.*, 2023. DOI: 10.3389/fbael.2023.1292639.

Cu versus Li/Cu pouch cells
24 h rest every 5th cycle
1:1.2:3 M LiFSI:DME:TTE
0.5 mA/cm² to 2 mAh/cm²

ZnO coating provides slight improvements in calendar aging at 100 kPa but not at 0 or 10 kPa



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24 h rest every 5th cycle
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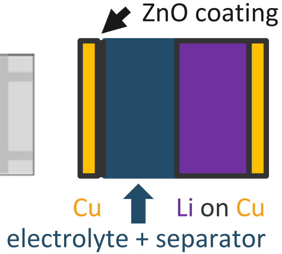
0.5 mA/cm^2 to 2 mAh/cm^2



Pressure improves cycling with and without aging.

At low pressure, performance is similar with and without ZnO coatings (unlike previous slides).

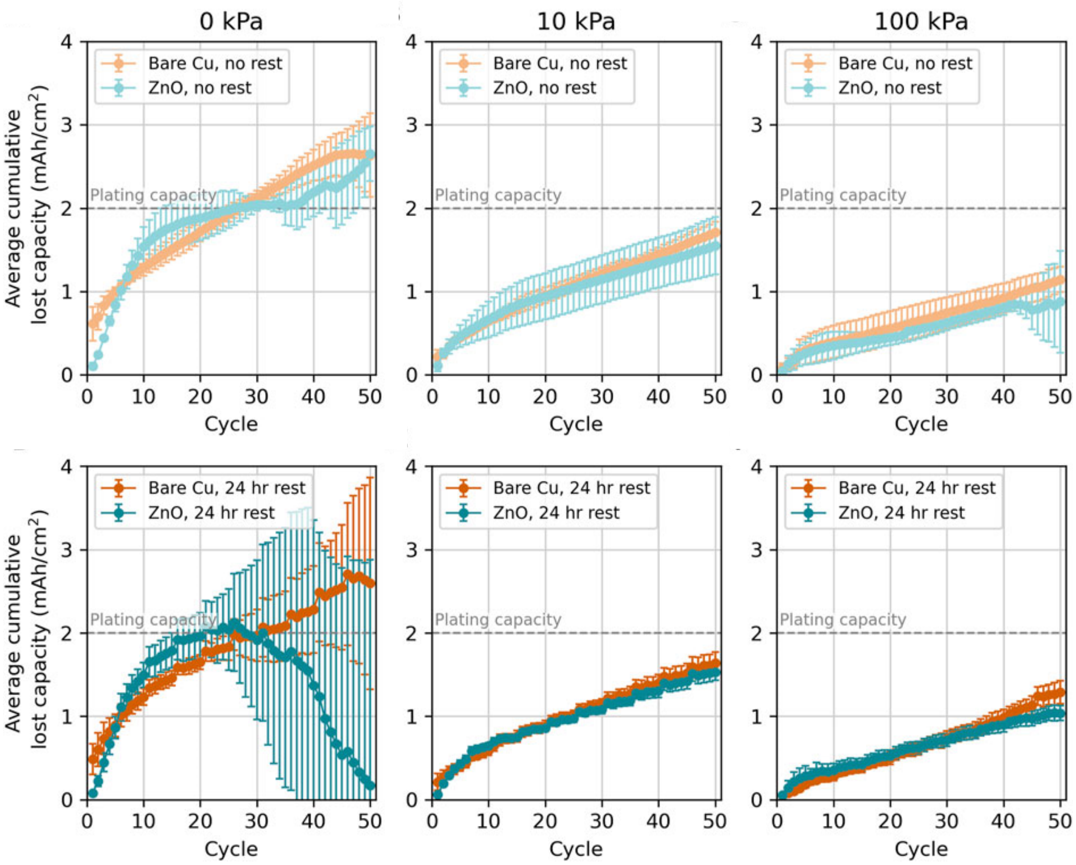
At 100 kPa, ZnO may slightly reduced losses.

Previous slides → ZnO *clearly* reduced losses at rest.

- 0.5 mAh/cm^2 coin versus 2 mAh/cm^2 pouch.
- 10 nm ZnO thickness may need optimization.
- 4 M LiFSI in DME versus 1:1.2:3 LiFSI:DME:TTE.

Bassett, Small, Long, Merrill, Warren, Harrison. *Frontiers in Batt. and Electrochem.*, 2023. DOI: 10.3389/fbael.2023.1292639.

Cumulative capacity loss lowest in cells cycled at 100 kPa and no difference between cells with and without ZnO coating



Pressure (kPa)	Cu No Rest	Cu 24 h Rest	ZnO No Rest	ZnO 24 h Rest
0	97.4±0.5	97.0±1	97.4±0.3	100.0±3
10	98.1±0.1	98.4±0.2	98.5±0.4	98.5±0.1
100	98.9±0.2	98.7±0.1	99.1±0.6	99.0±0.1

Cumulative capacity loss lowest for 100 kPa cells with and without intermittent aging.

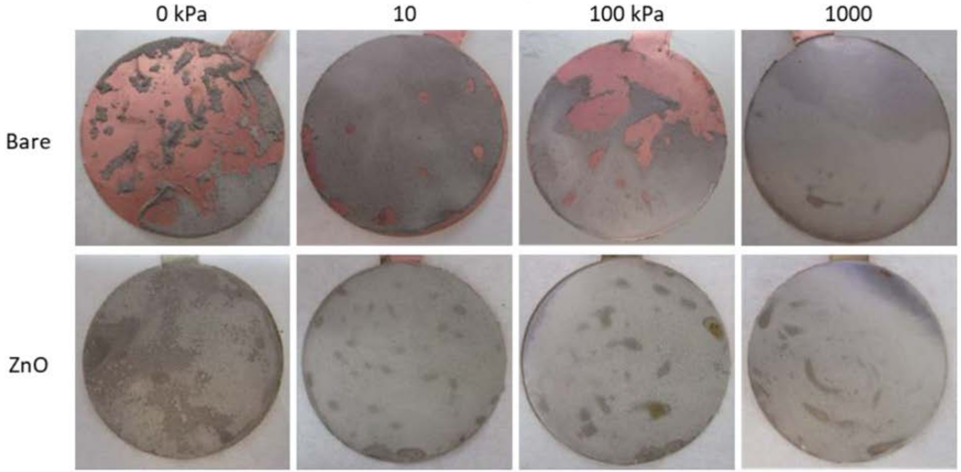
ZnO does not significantly reduce cumulative capacity loss compared to uncoated Cu.

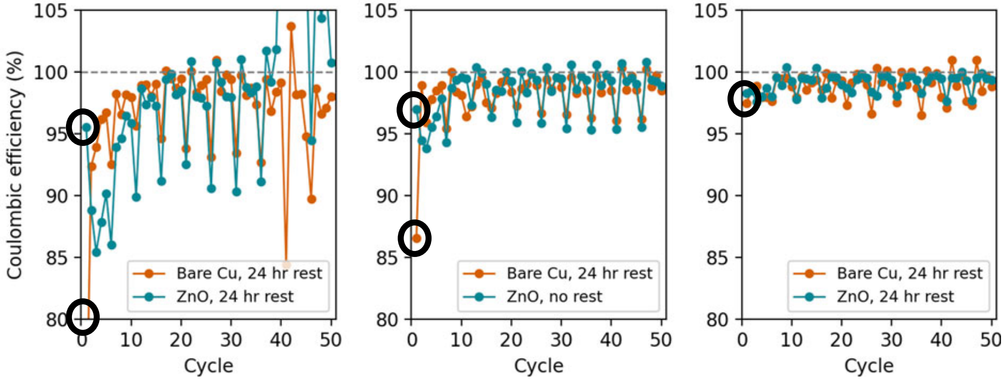
ZnO cells with continuous cycling and those with intermittent calendar aging similar.

Cu or coated Cu versus Li/Cu pouch cells
24 h rest every 5th cycle
1:1.2:3 M LiFSI:DME:TTE
0.5 mA/cm^2 to 2 mAh/cm^2

Bassett, Small, Long, Merrill, Warren, Harrison. *Frontiers in Batt. and Electrochem.*, 2023. DOI: 10.3389/fbael.2023.1292639.

After one Li deposition, pressure and ZnO tend to improve adhesion





Pressure generally improves adhesion of Li to Cu on the first deposition from 10-1000 kPa.

ZnO also improves adhesion, which likely reduces dead Li formation.

Better adhesion and less dead Li likely explain why the cycle 1 CE is generally higher in cells with ZnO coatings, especially at low pressures.

Cu or coated Cu versus Li/Cu pouch cells
24 h rest every 5th cycle
1:1.2:3 M LiFSI:DME:TTE
0.5 mA/cm^2 to 2 mAh/cm^2

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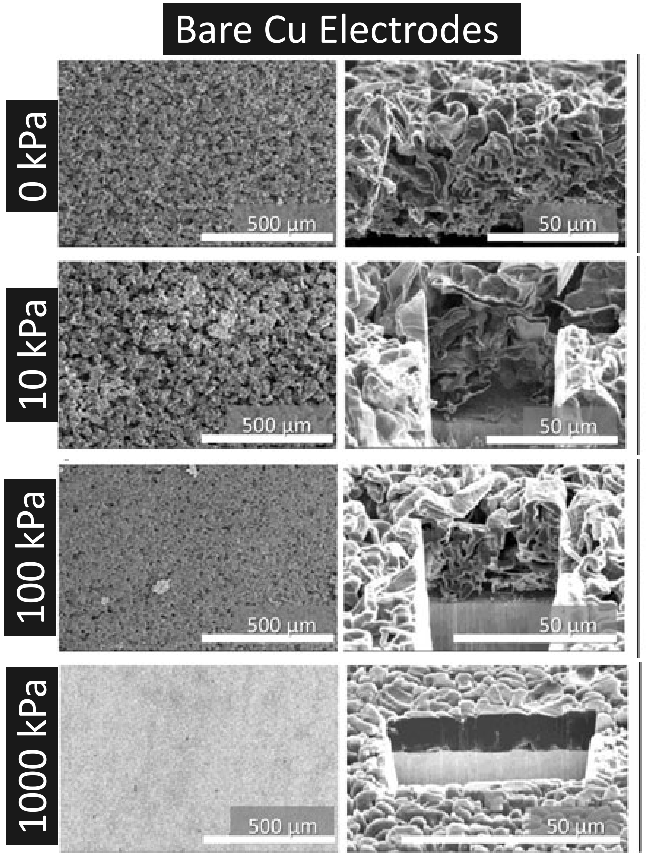
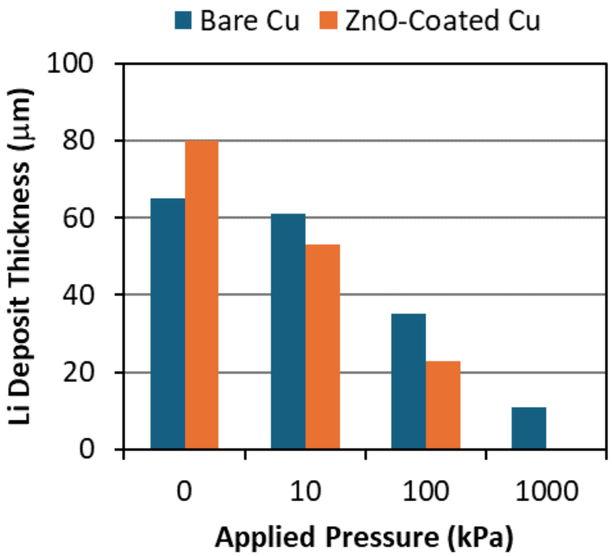
Cryo FIB/SEM after one Li deposition



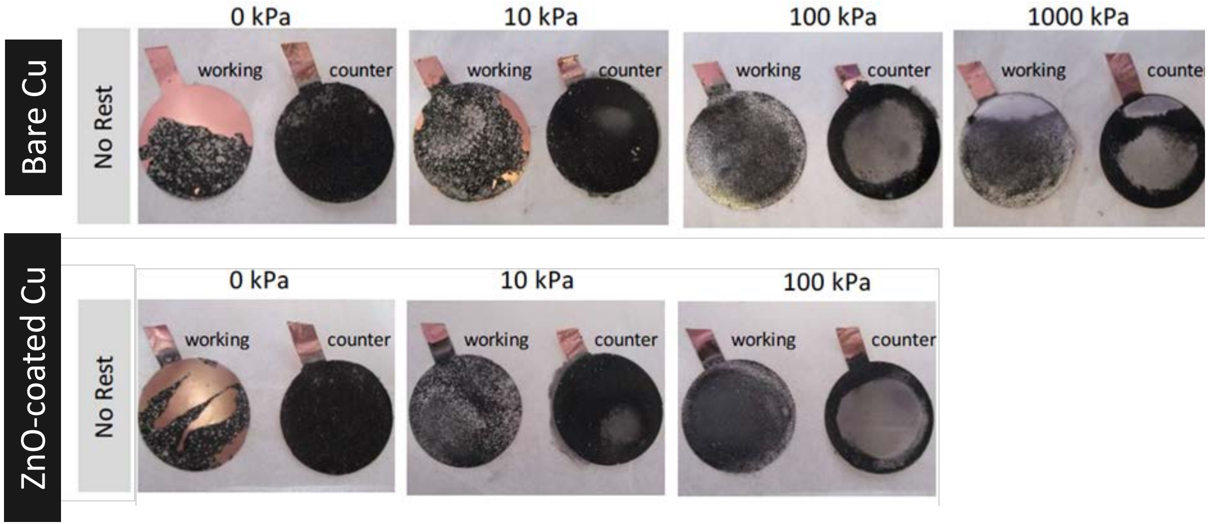


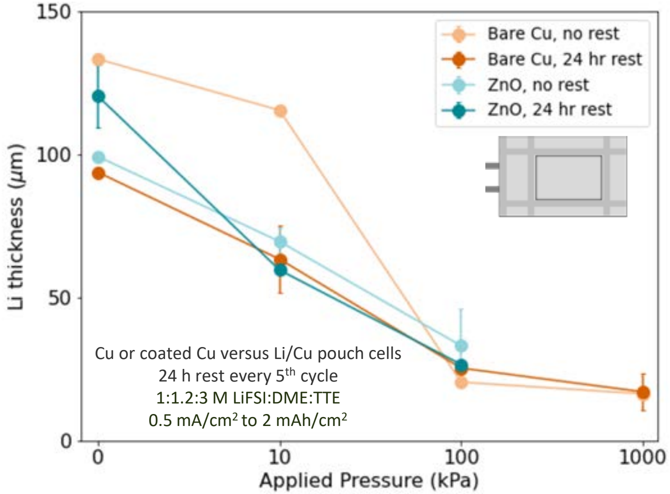
Morphology becomes denser and more uniform with higher pressure.

ZnO improves uniformity and density except at 0 kPa.

Bassett, Small, Long, Merrill, Warren, Harrison. *Frontiers in Batt. and Electrochem.*, 2023. DOI: 10.3389/fbael.2023.1292639.

Cell disassembly images and Li deposit thickness after 50 cycles





Pressure continues to improve adhesion after 50 cycles.

Adhesion slightly better with ZnO but pressure more important.

Deposit thickness decreases as pressure increases regardless of whether ZnO-coated or bare Cu is cycled.

Pressure decreases dead Li, leading to less capacity loss during aging steps.

Bassett, Small, Long, Merrill, Warren, Harrison. *Frontiers in Batt. and Electrochem.*, 2023. DOI: 10.3389/fbael.2023.1292639.

Conclusions

Motivation and initial studies evaluating Li metal anode calendar aging with and without coatings.

- Intermittent calendar aging after Li deposition leads to capacity loss during the rest.
- Coatings can partially mitigate calendar aging by directing morphology to decrease dead Li.
- ZnO is the most promising coating in terms of reducing calendar aging.
- The aging is largely reversible, indicating it is related to dead Li formation and reattachment.

Motivation and initial studies evaluating applied pressure on Li anode cycling.

- Applied pressure leads to higher CE and more stable, repeatable cycling performance.
- Too much pressure leads to erratic cycling behavior, transport limitations, and short circuits.
- Applied pressure leads to significantly denser Li deposits with more favorable morphology.
- Applied pressure likely improves cycling by decreasing surface area and reducing dead Li.

Study showing the impact of applied pressure with and without coatings on Li anode calendar aging.

- Increased cycling capacity leads to much lower losses during intermittent aging steps.
- ZnO coatings have little impact on loss during rest steps in pouch cells cycled to 2 mAh/cm^2.
- 100 kPa leads to lower cumulative losses than other pressures (with and without aging).
- Average CE and cumulative losses are the same at a given pressure with and without aging.
- Losses during aging steps are reversible, consistent with dead Li formation and reattachment.

Thank you!

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

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- Joint Center for Energy Storage Research for initial pressure and in situ TEM aging studies

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