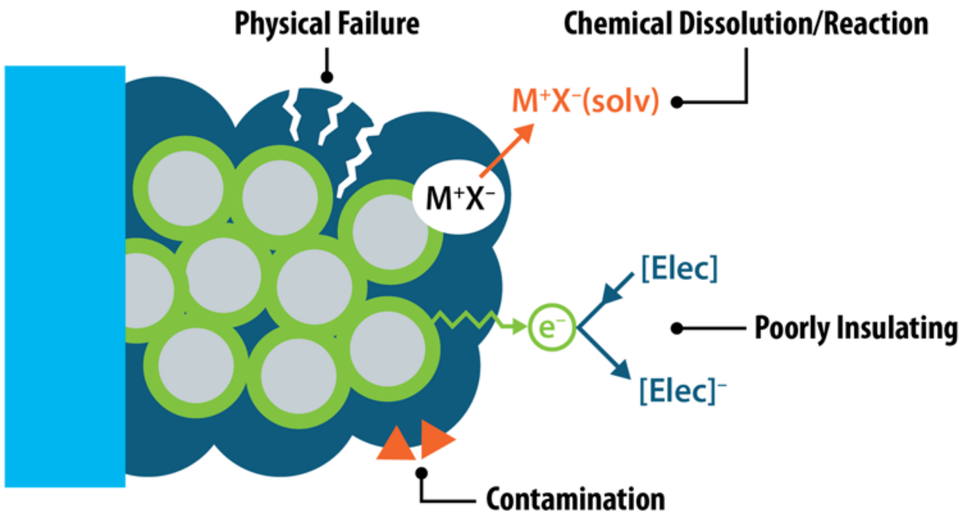
U.S. DEPARTMENT OF ENERGY'S (DOE) VEHICLE TECHNOLOGIES OFFICE (VTO) 2024 ANNUAL MERIT REVIEW (AMR)

“This presentation does not contain any proprietary, confidential, or otherwise restricted information”

THE SILICON CONSORTIUM PROJECT: MECHANICAL PROPERTIES OF SILICON ANODES



PI: ANTHONY BURRELL

PRESENTER: KATHARINE HARRISON
Mechanical Characterization
National Renewable Energy Laboratories

Project ID: bat499
Presentation Date: 06/06/2024
Presentation Location: Washington DC

NREL/PR-5K00-89362

(PH)EV = (plug in hybrid) electric vehicles, USABC = United States Advanced Battery Consortium

OVERVIEW

Timeline

- October 1st 2020 - September 30st 2025.
- Percent complete: 73%

Budget

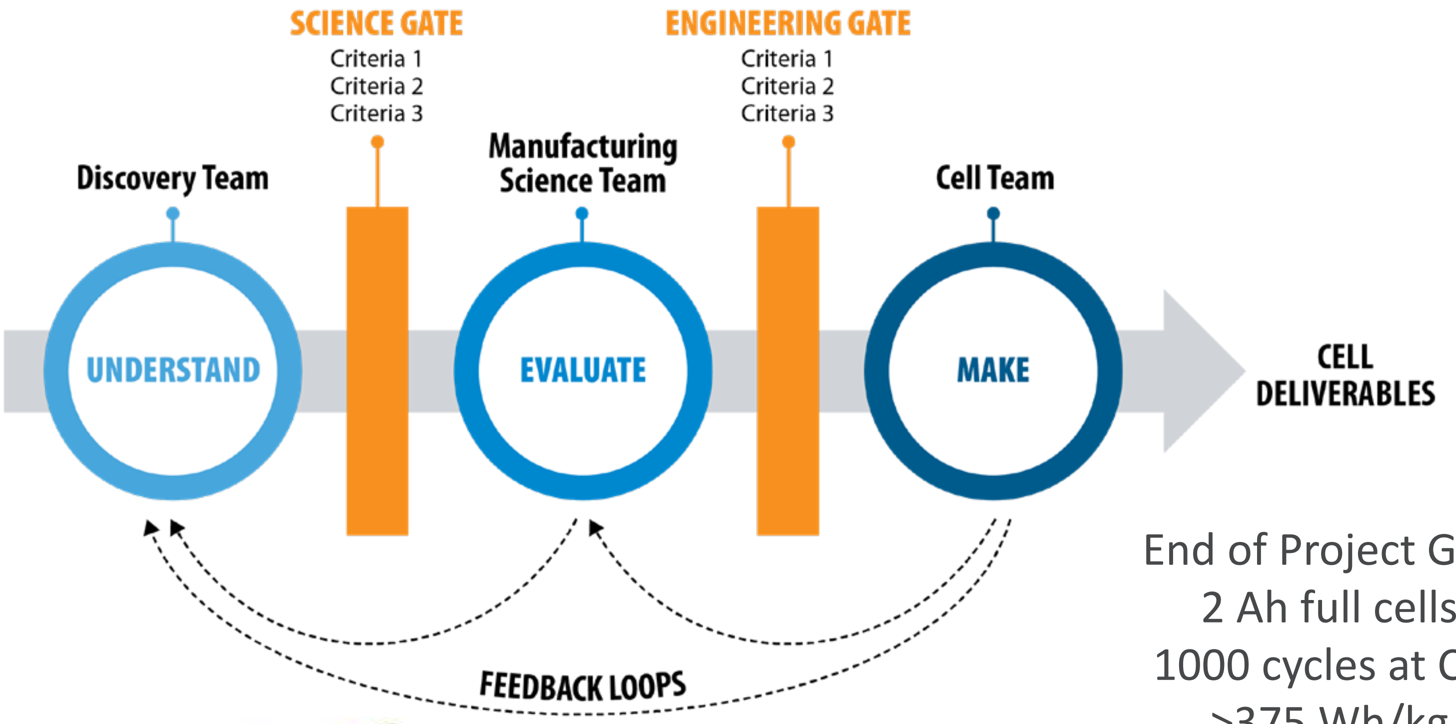
- Total Project Funding: $37500
- Funding for FY23: $7500K
- Funding for FY24: $7500K

Partners

- Project Lead: NREL

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals. Specifically targeting the development of calendar life in silicon anode.
  - Cost, Performance and Safety

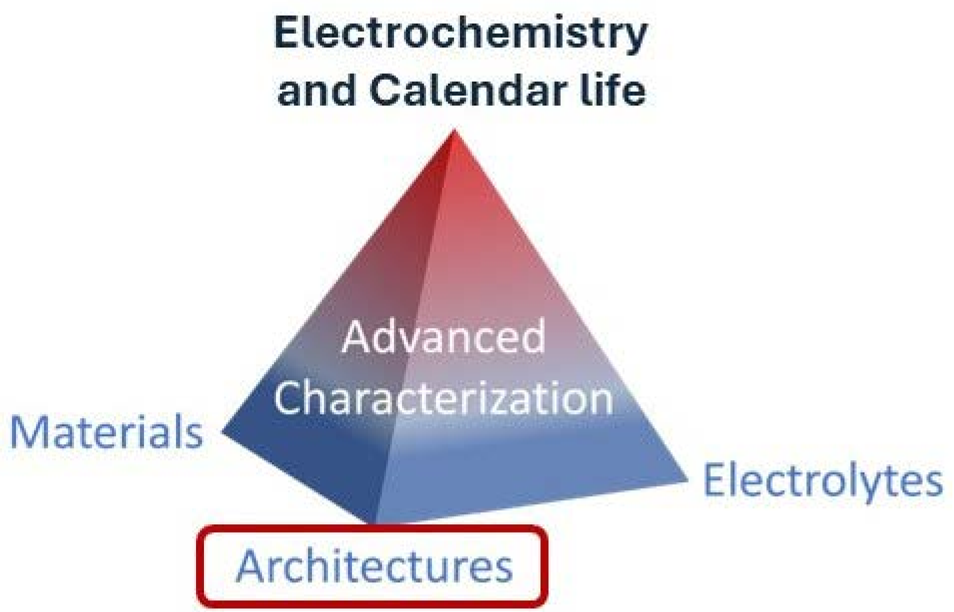


End of Project Goal
2 Ah full cells
1000 cycles at C/3
>375 Wh/kg
>750 Wh/L
calendar life >10 years

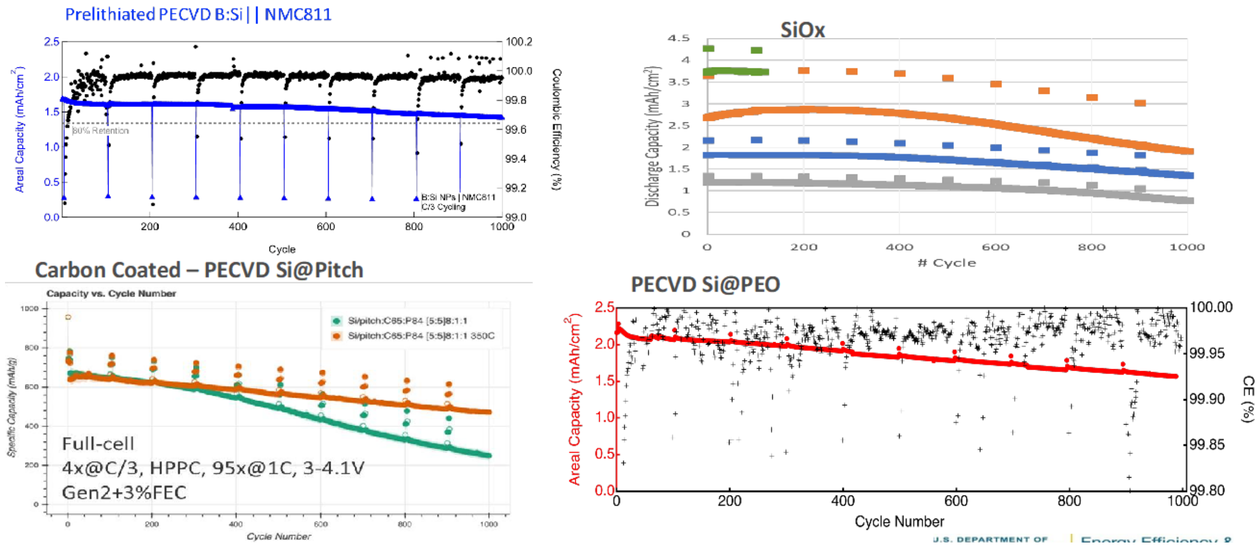
THRUST TASKS, RESOURCES, AND COLLABORATION

Budget

- Funding for FY23: $7500K
- Funding for FY24: $7700K



Several SCP systems have achieved cycle life metric



Calendar Life is the Focus

Resources
- Suite of facilities 7 national labs
- People
- Protocols
- Regular meetings

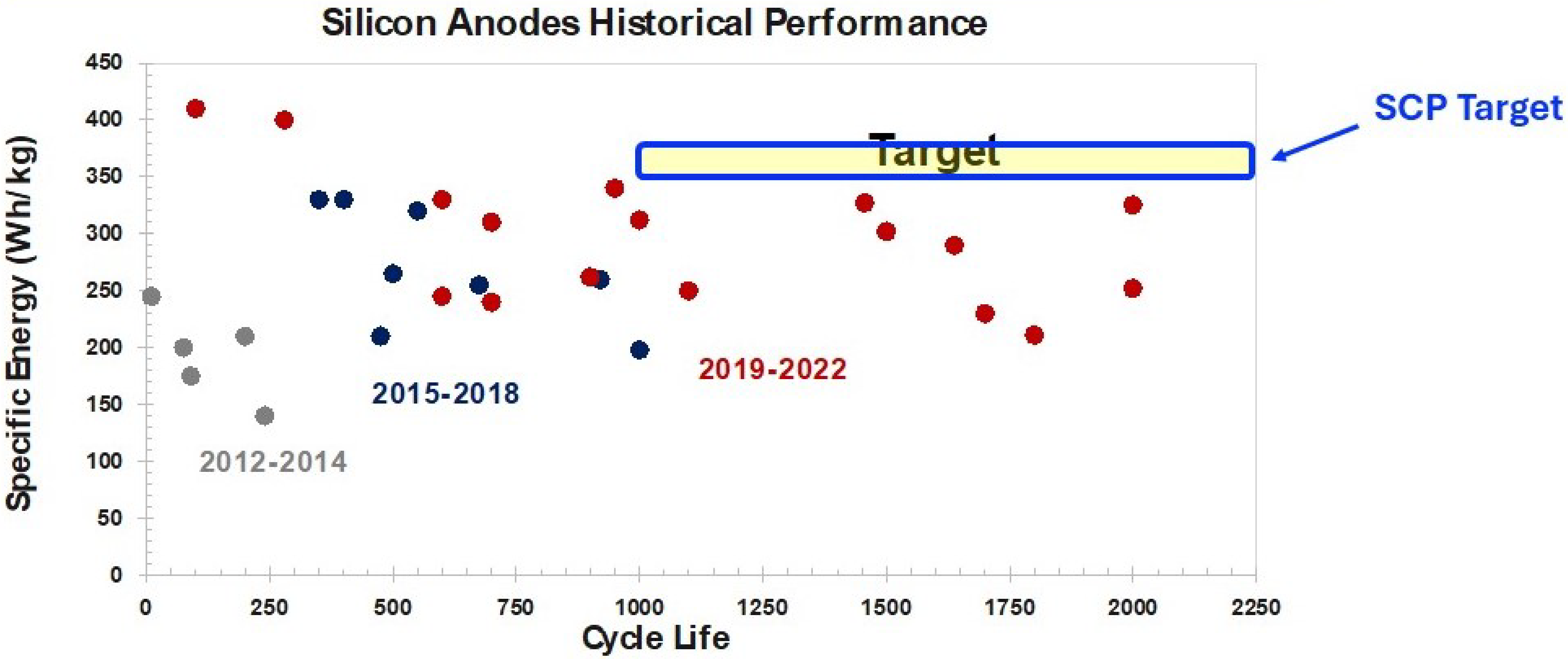
NREL Transforming ENERGY · Sandia National Laboratories · Berkeley Lab · Oak Ridge National Laboratory · Argonne National Laboratory · Pacific Northwest National Laboratory · INL Idaho National Laboratory

SCP = Si Consortium Project

RELEVANCE

Si consortium project goal is to understand calendar life limitations in Si anodes and demonstrate long cycle life, long calendar life, and high energy density cells.

Targets	Challenges
• 1,000+ mAh/g & 350+ Wh/kg • 10 years & 1000 cycles	• Large first-cycle irreversible loss • Low cycle and calendar life / High capacity fade



Reproduced from: B. Cunningham, US DOE VTO AMR 2023 *bat343_cunningham_2023_o.pdf*

MILESTONES

Q1 Prepare and ship new baseline PEO-PECVD anodes at ≥ 1.5 mAh cm^2 areal loading with a total electrode area of at least 1 m^2 to the whole team.

Q2 Define at least three new electrolyte compositions designed to increase calendar life for PEO-PECVD based cells and evaluate them for 1000 cycles at C/3.

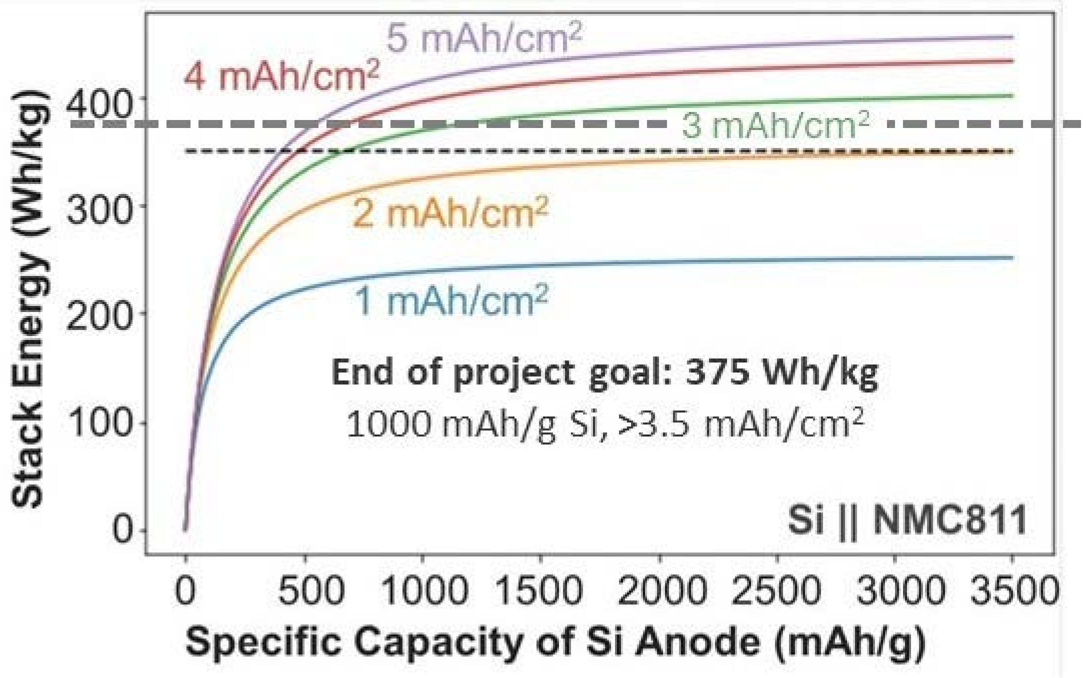
Q3 Define prelithiation protocol and conditioning conditions for PEO-PECVD silicon anodes and cells.

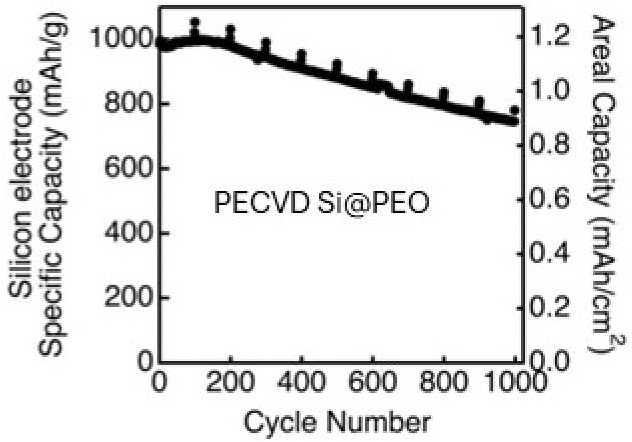
Q4 Go/No Go Develop and implement methods that reduce the time needed for calendar life prediction to less than 15 months.

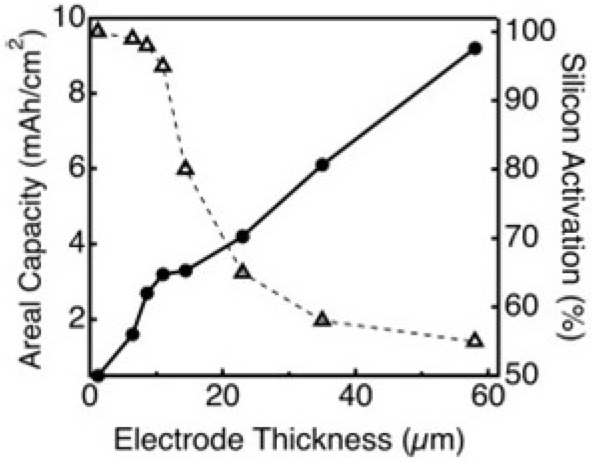
Q4 Propose at least two hypothesis that identify mechanistic causes that result in diminished calendar life for silicon-based cells.

PEO = polyethylene oxide
PECVD = plasma enhanced chemical vapor deposition

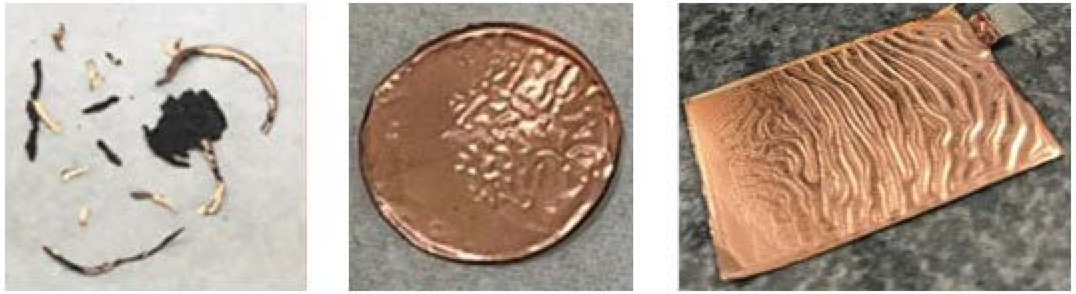
OBJECTIVES: ARCHITECTURE THRUST







- Si capacity over 1000 mAh/g → diminishing energy returns.
- High loading needed for high specific energy.
- High loading → transport and mechanical problems.



Si@pitch with PI binder 4 mAh/cm²　Si@PEO with PI binder 2-3 mAh/cm²　SiO_x with PI binder 4.5 mAh/cm²

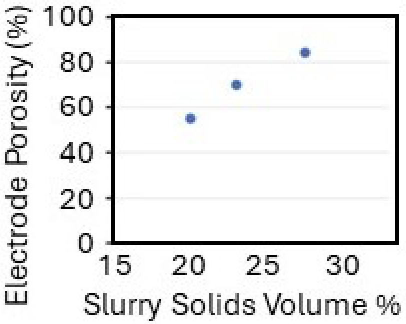
Architecture Thrust Objectives

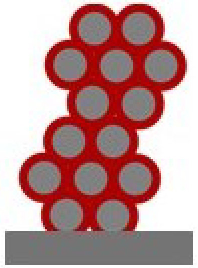
- Develop electrode architectures that enable high loading silicon electrodes capable of enabling 375 Wh/kg that cycle 1000 times at C/3.
- Understand whether electrode architecture impacts calendar aging.

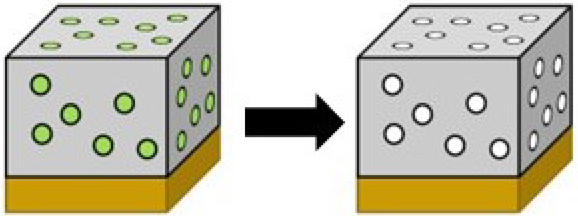
NMC811 = $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$
PI = polyimide

APPROACH: ARCHITECTURE THRUST

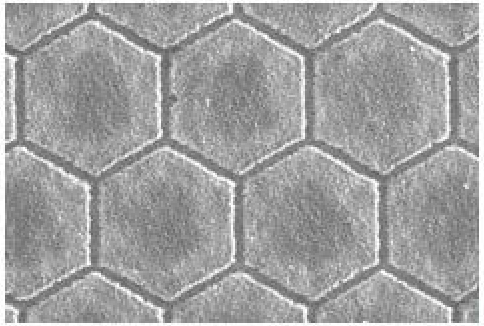
Develop electrode architectures to enable high loading electrodes and high specific energy at C/3 for 1000 cycles
Understand how electrode architecture impacts cycle life and calendar life

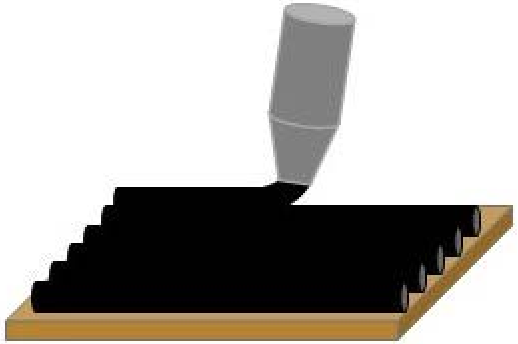




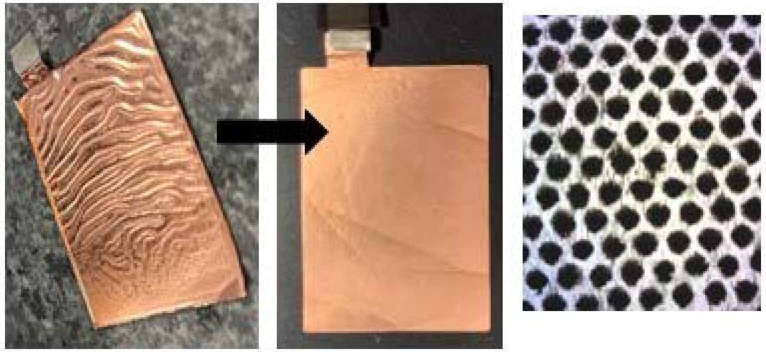


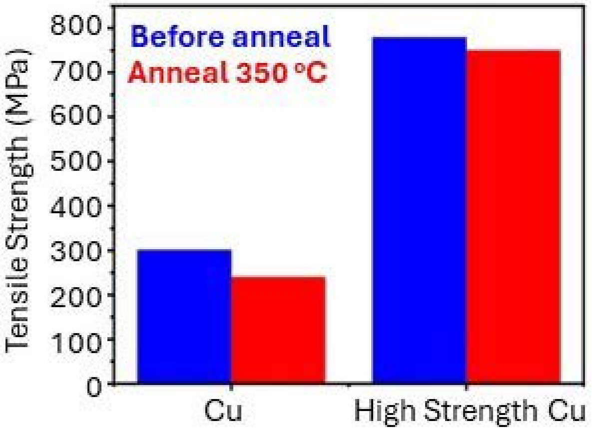
Introduce porosity in high loading electrodes to:
1. Improve transport and decrease stress by generating space for expansion.
2. Decrease stress by decreasing binder at the current collector.



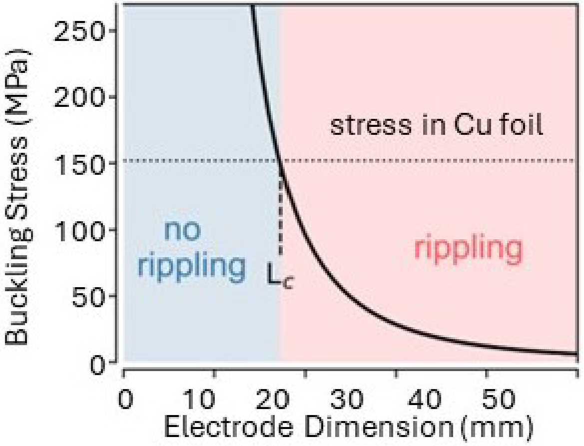


Introduce macroscopic porosity for facile wetting and electrolyte transport as well as stress relief.





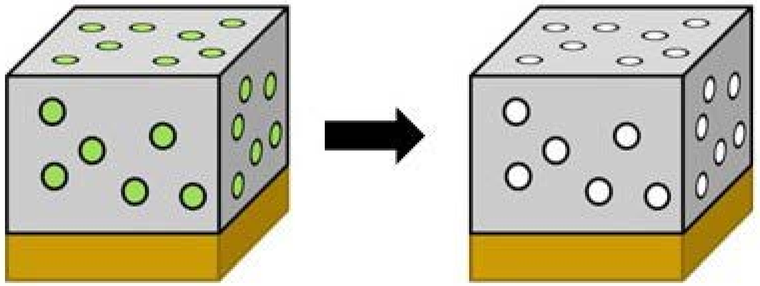
Alternative current collectors, current collector processing, and tuning interfacial adhesion to reduce stress at the interface.

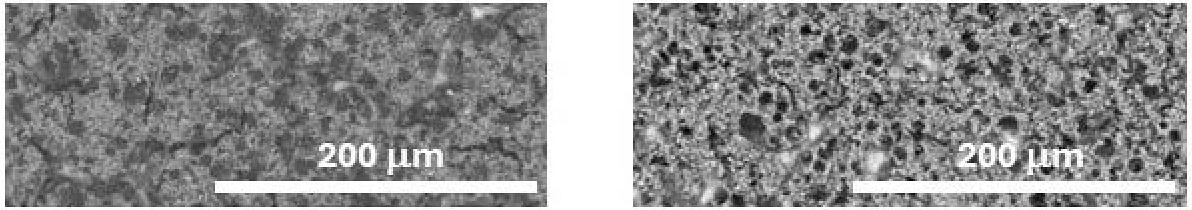


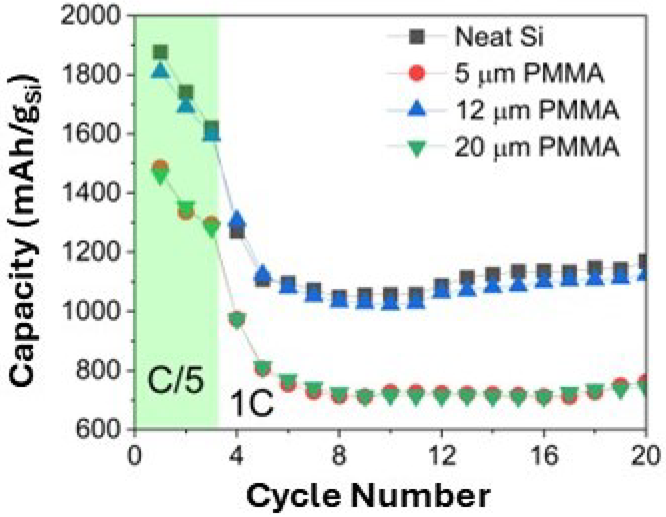
Modeling

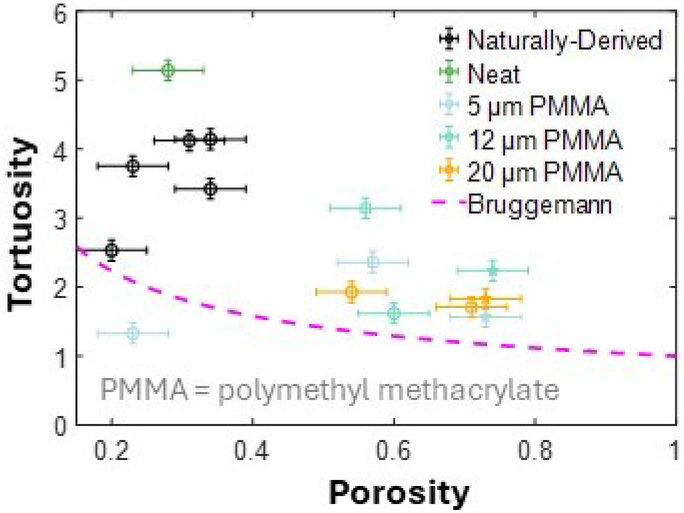
Characterization

POROSITY CAN BE CONTROLLED IN MILLED SILICON ELECTRODES









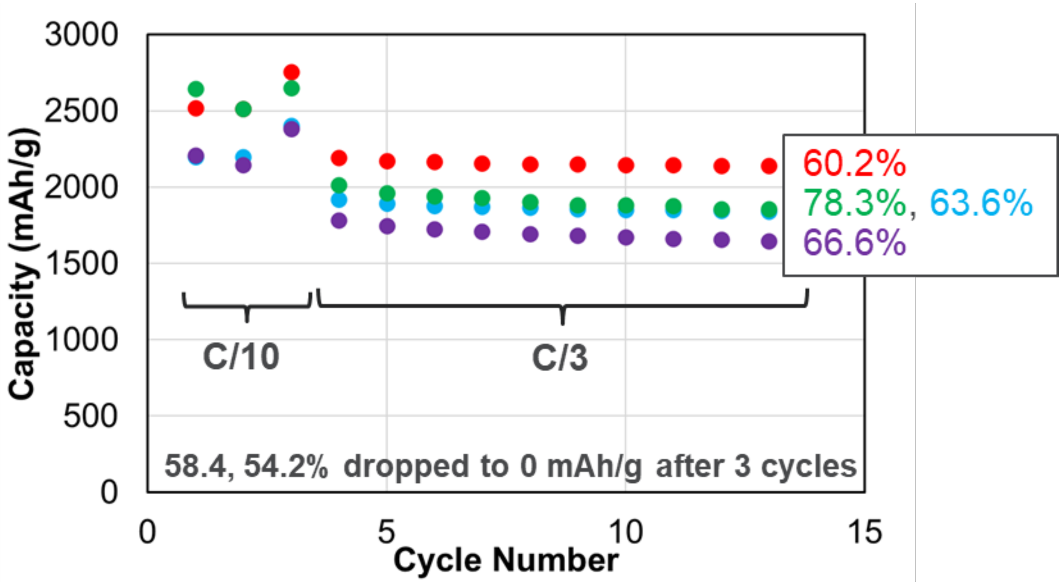
- Fugitive phase removal increases large scale porosity and reduces tortuosity but does not improve cycling performance.

Roll jack Si in NMP/PI (varied solids ratios)

↓

Add carbon black and roll jack →

80% milled Si, 10% carbon, 10% PI

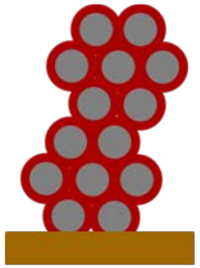


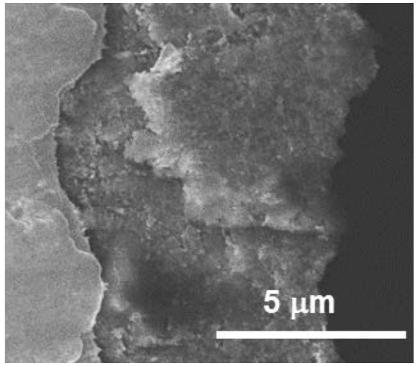
- Porosity can also be varied by changing solids loading.
- This likely smaller scale porosity impacts cycling.

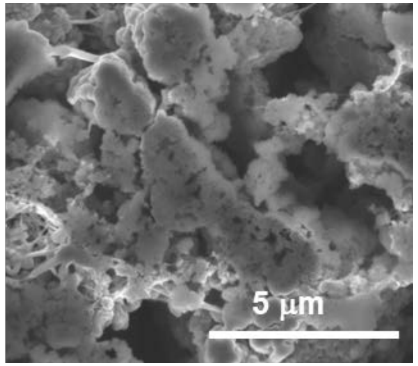
MAKING PROGRESS TOWARDS PECVD SI ELECTRODES WITH HIGHER POROSITY

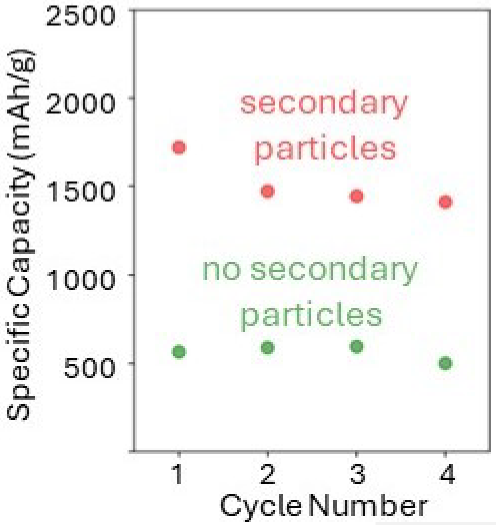
PECVD Si@polyPMI

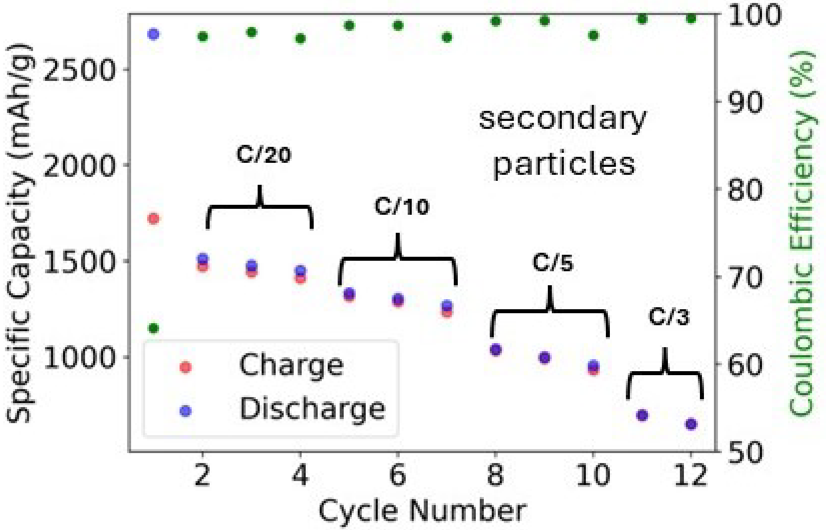
- Secondary particles enable porous electrodes.
- Capacity 2.5x higher with than without secondary particles.





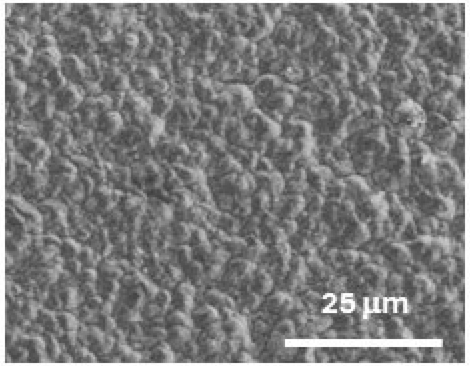


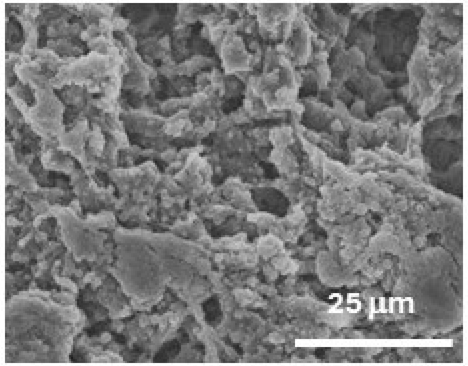


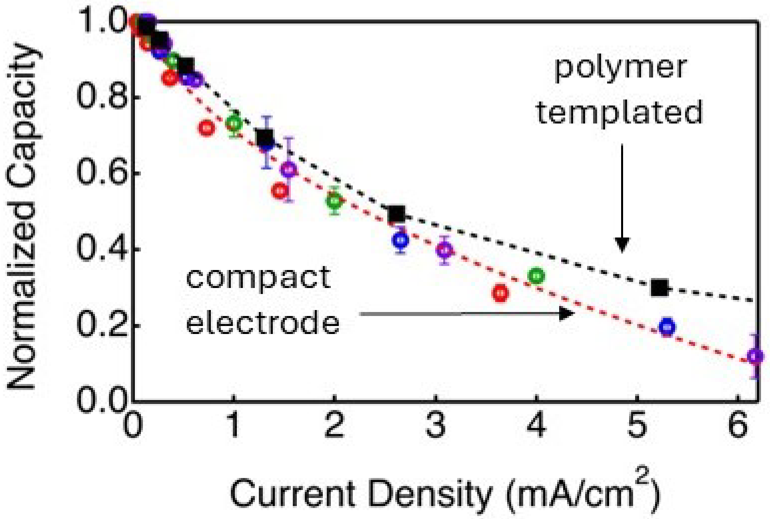


PECVD Si@PEO

- Polymer templating enables porous electrode.
- McMillan number virtually unchanged.





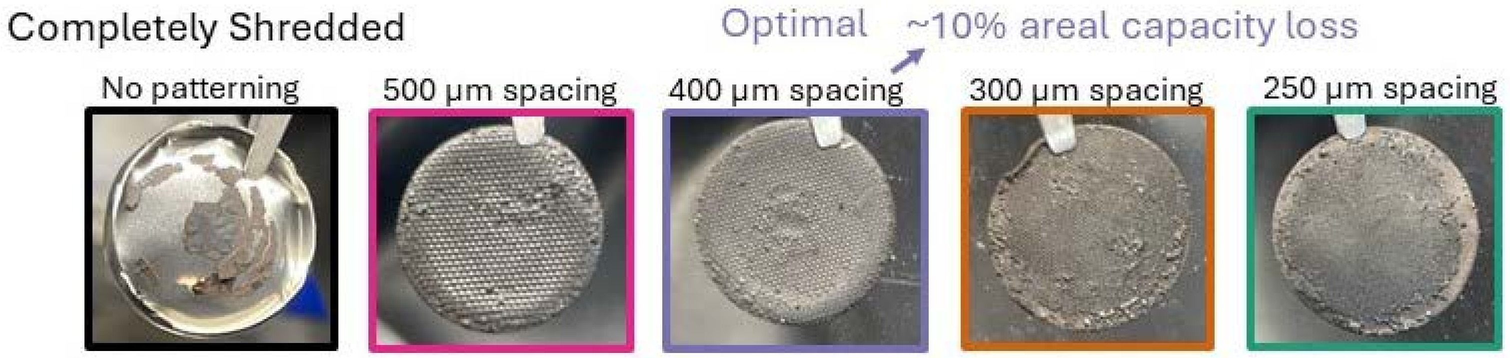


PolyPMI = polyphenylmethanimine

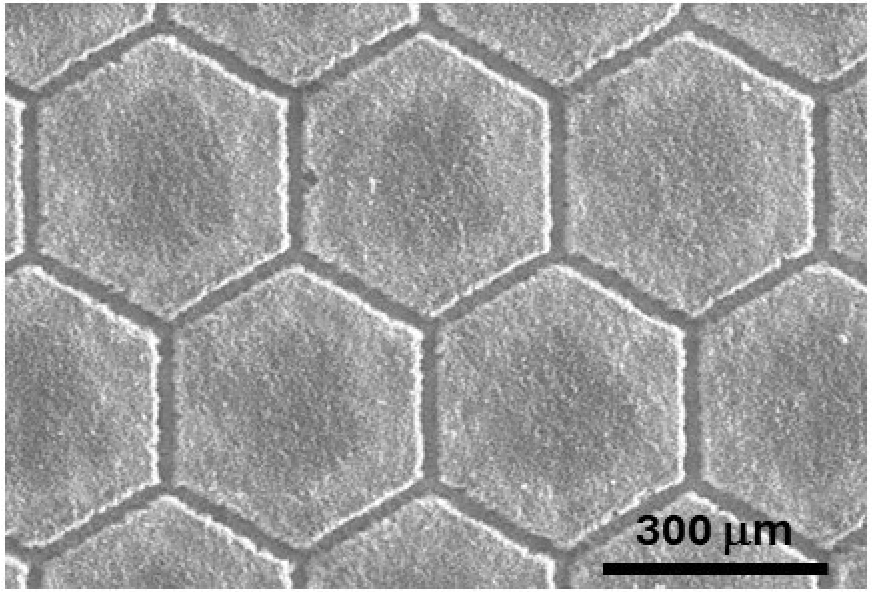
- Succeeded in increasing porosity but more improvement in rate capability is needed.
- Hypothesize that even smaller scale porosity (mesopores?) should be targeted.

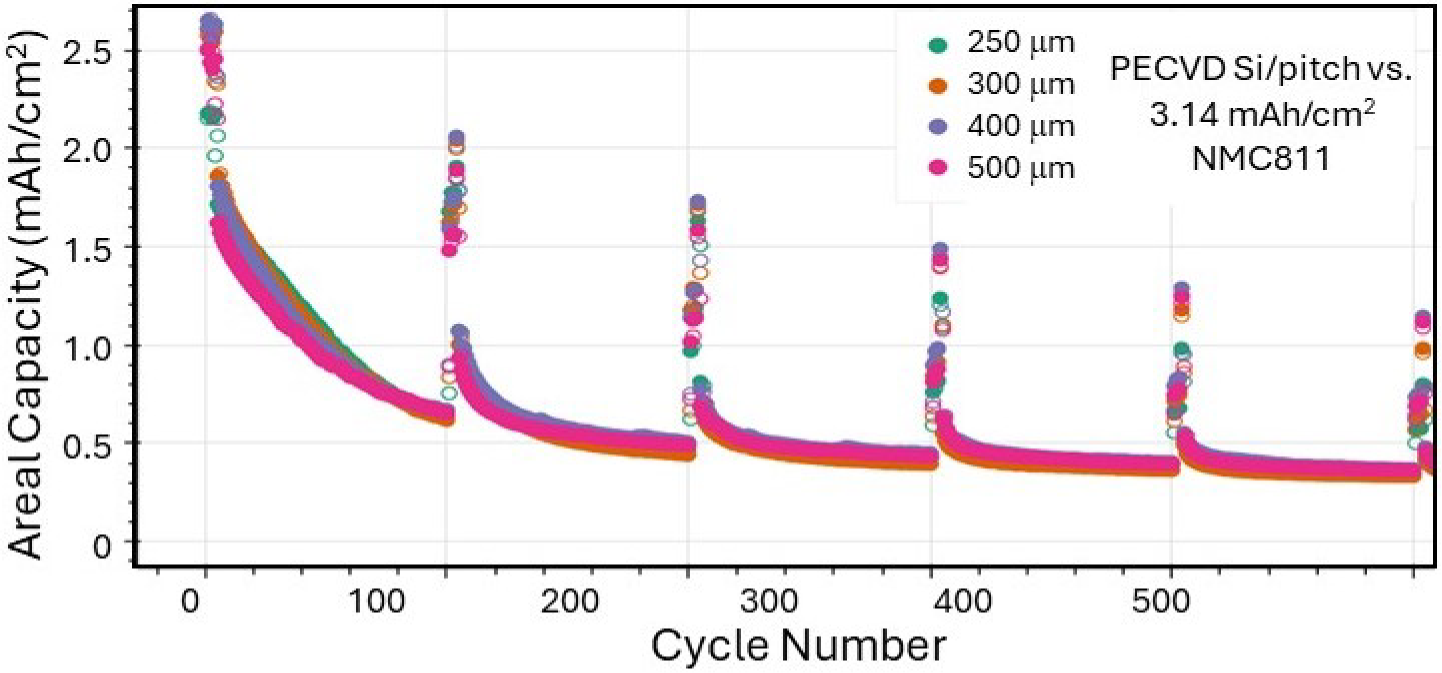
LASER PATTERNING OF PECVD SI ELECTRODES RELIEVES STRESS

- Laser ablation mitigates shredding!
- High loading Si/pitch electrodes still exhibit severe capacity fade in full cells after patterning.
- Current collector shredding is not the only degradation mechanism and smaller scale porosity is likely needed.

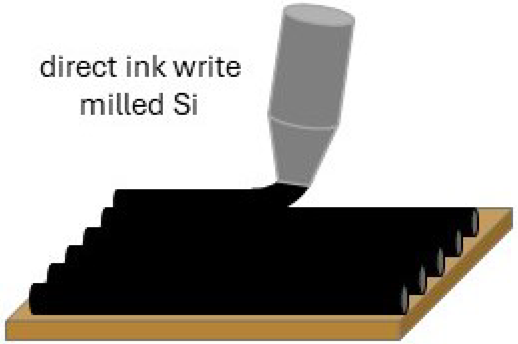


4-5 mAh/cm^2 hex-patterned electrodes after 3x cycles 10-750 mV vs Li

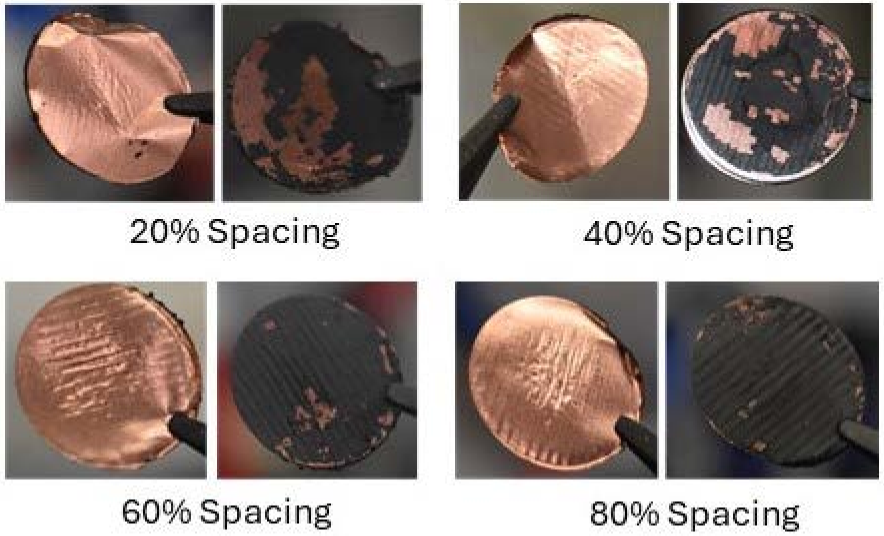


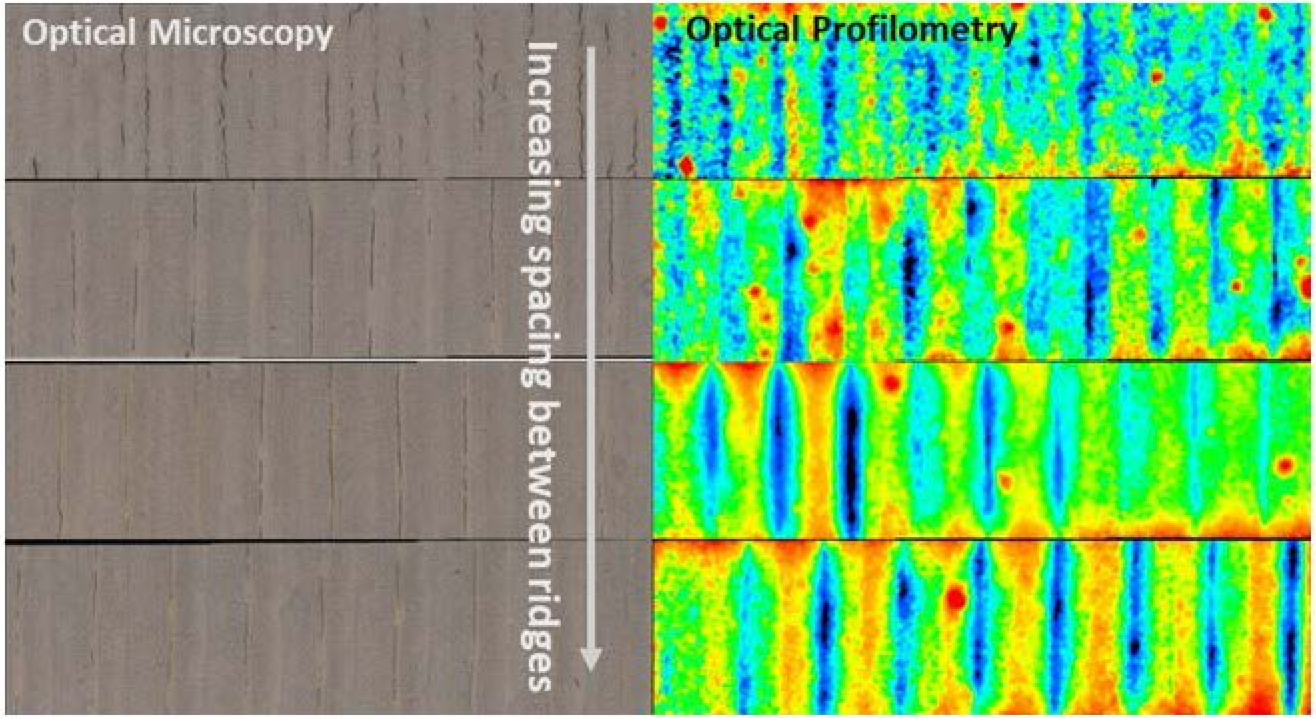


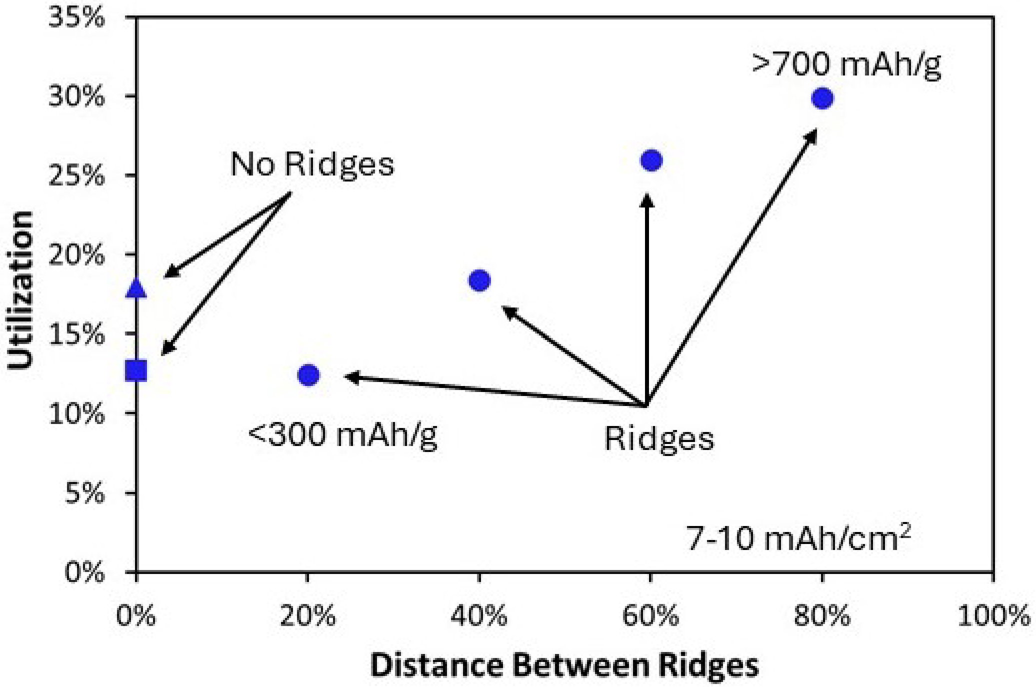
ADDITIVELY MANUFACTURED RIDGED ARCHITECTURES RELIEVE STRESS IN MILLED SI



- Milled Si utilization increases with ridge spacing in preliminary high loading ridged electrodes.
- Likely improves wetting/transport through ridges.
- Increased ridge spacing leads to decreased delamination → ridges provide stress relief.
- Needs further optimization to improve utilization.
- Some delamination still apparent with ridges.





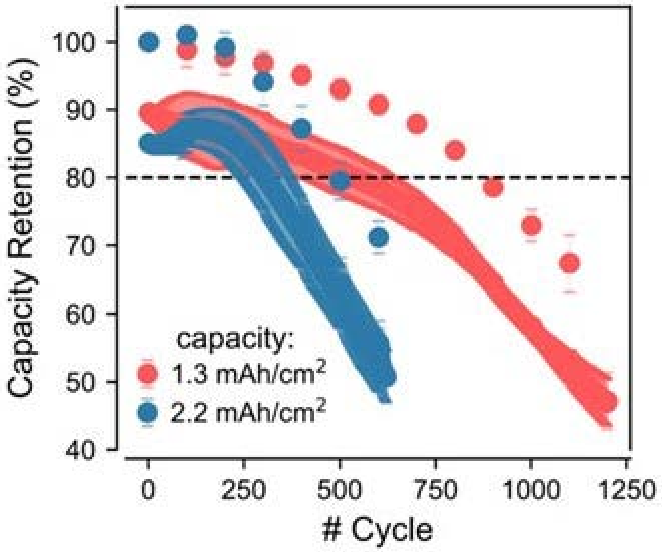


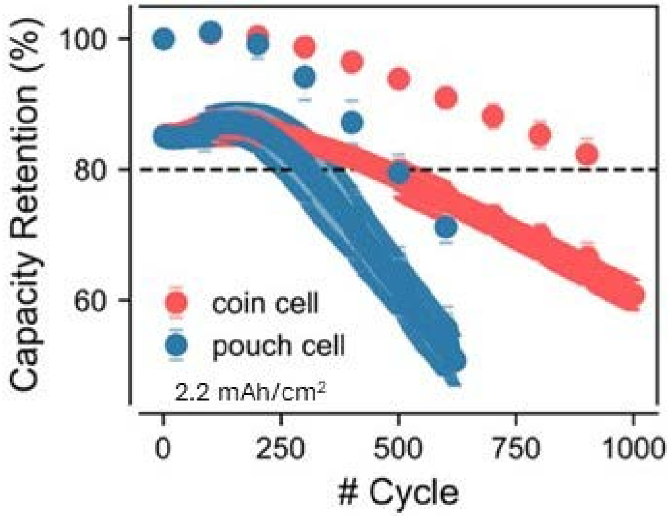
WRINKLING PROBLEMS ARE SIZE AND LOADING DEPENDENT

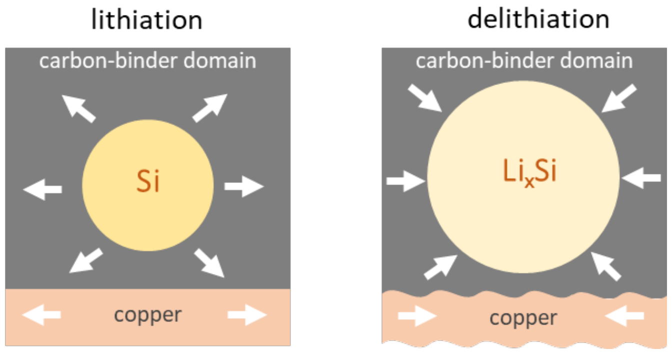
- Capacity fade increases with increased loading.
- Higher areal loading = increased wrinkling.

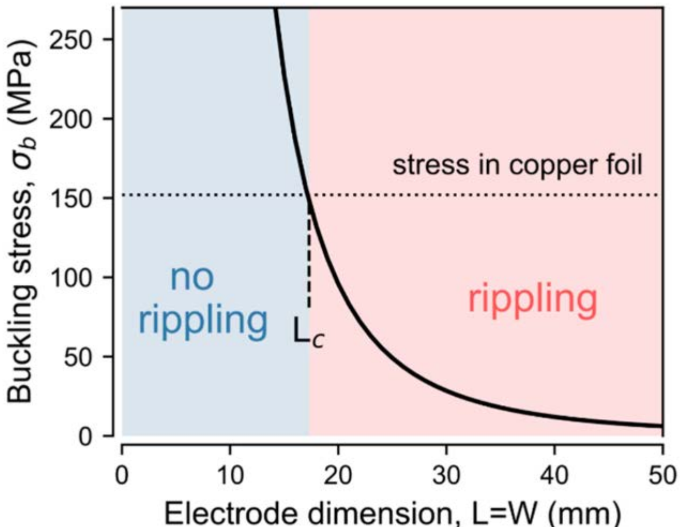
- Capacity fade worse in pouch than coin cells.
- Larger electrode area = increased wrinkling.

- Modeling confirms that critical buckling stress to wrinkle increases with size.
- Higher loading likely directs more stress to the current collector.









Showed data left column at previous annual merit review.

70% SiO_x, 10% C45, 20% PI
NMC811 cathode, 30 psi

1.2 mAh/cm^2

2.3 mAh/cm^2

Rodrigues, M.T.F., Rajendran, S., Trask, S.E., Dunlop, A.R., Singh, A., Allen, J.M., Weddle, P.J., Preimesberger, J.I., Coyle, J., Colclasure, A.M. and Yang, Z., 2023. Cell-format-dependent mechanical damage in silicon anodes. ACS Applied Energy Materials, 6(18), pp.9243-9248.

BINDER MODIFICATIONS IMPROVE FY23 Q4 MILESTONE CELLS BUT FAIL AT 400 CYCLES

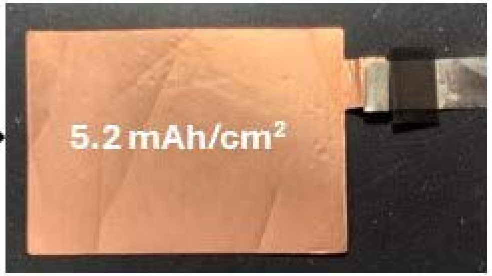
- ~2.4 Ah SiO_x-graphite/NMC811 multi-layer pouch cells.
  - 5.05 mAh/cm^2 initial capacity per side.
  - Cycled to 4.18 V in gen2+3% FEC.
  - Prelithiation offsets initial capacity loss but no reservoir.
  - PI replaced with aqueous PAA to minimize wrinkling.
  - % binder tuned for optimal adhesion (no sliding).
- Li plating on wrinkles may cause sudden drop.
- Gassing when add more electrolyte supports Li plating.

stretching / wrinkling

60% SiO_x, 17% graphite, 3% C45, 20% PI binder

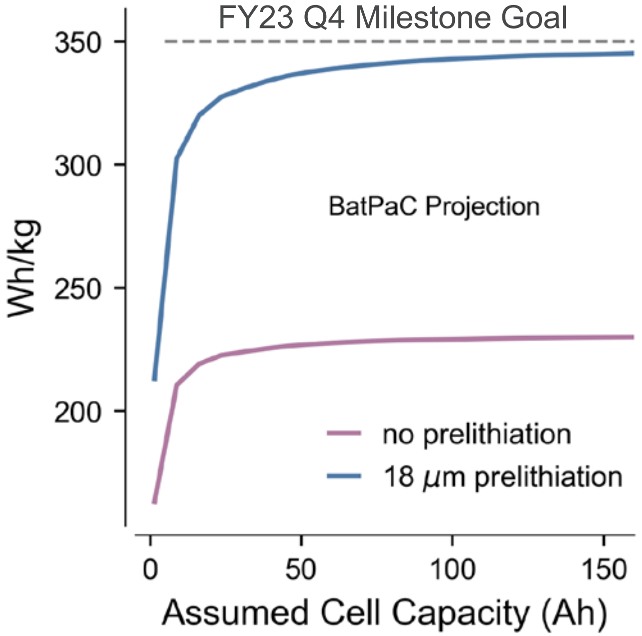
coating slides beyond Cu

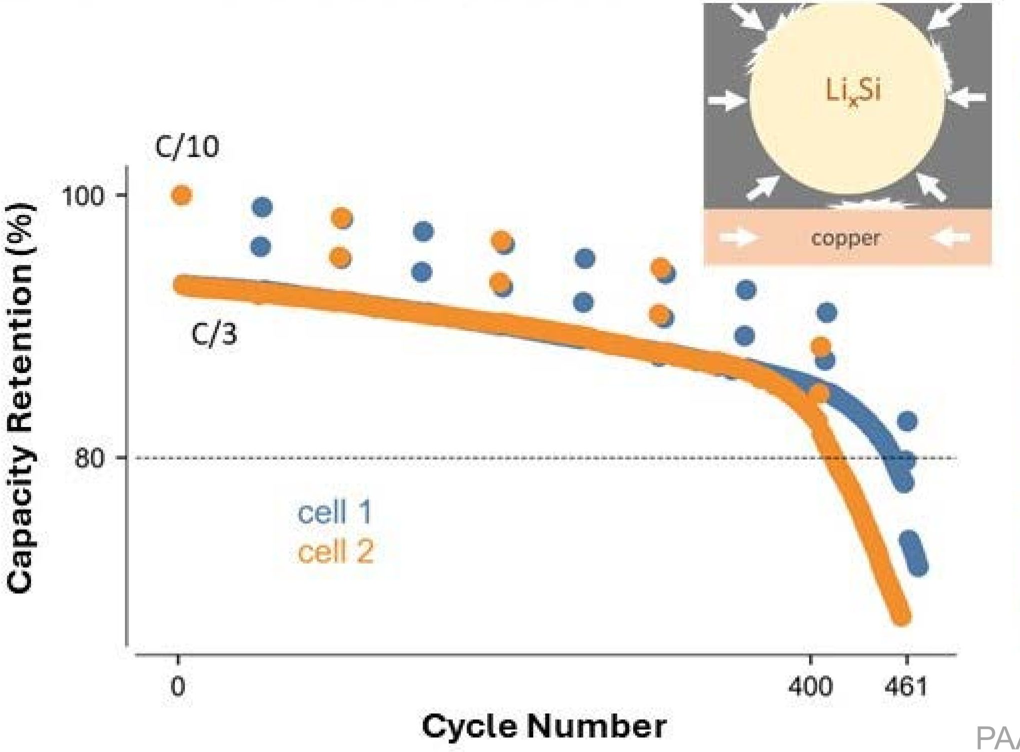
70% SiO_x 19% graphite, 1% SWCNT, 1% CMC, 9% PAA



no stretching / wrinkling

70% SiO_x, 16% graphite, 1% SWCNT, 1% CMC, 12% PAA

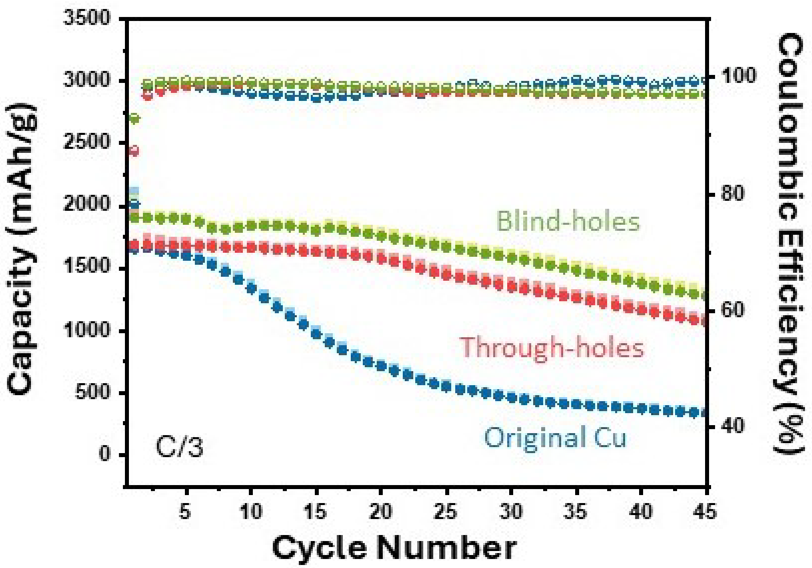




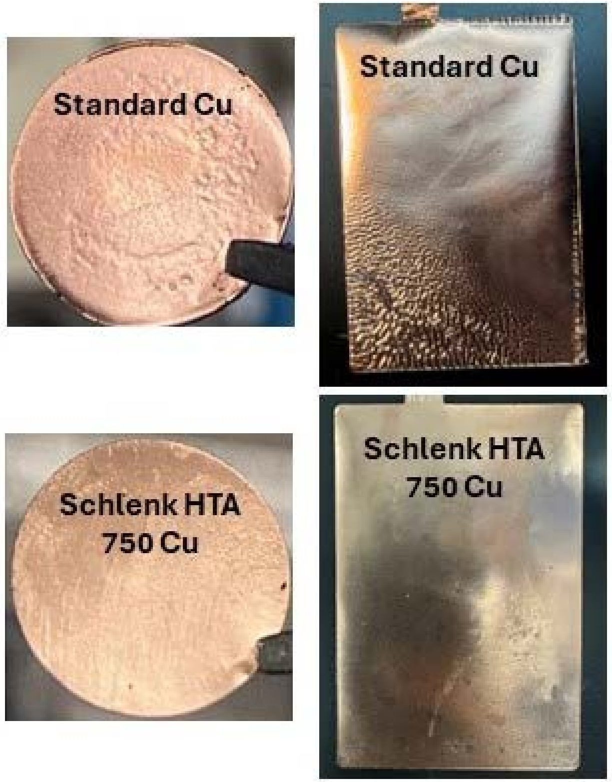
SWCNT = single walled carbon nanotubes
PAA = polyacrylate, FEC = fluoroethylene carbonate
C45 = carbon, CMC = carboxylmethycellulose

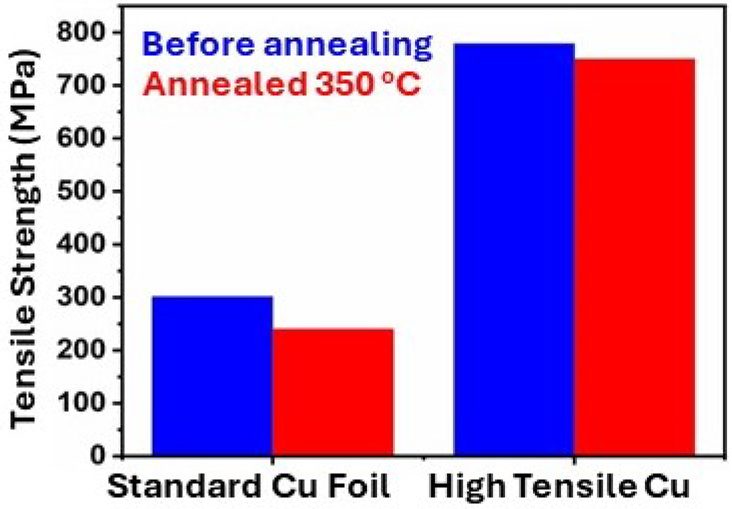
CURRENT COLLECTOR MODIFICATION SHOWS PROMISE FOR IMPROVING INTERFACIAL STRESS

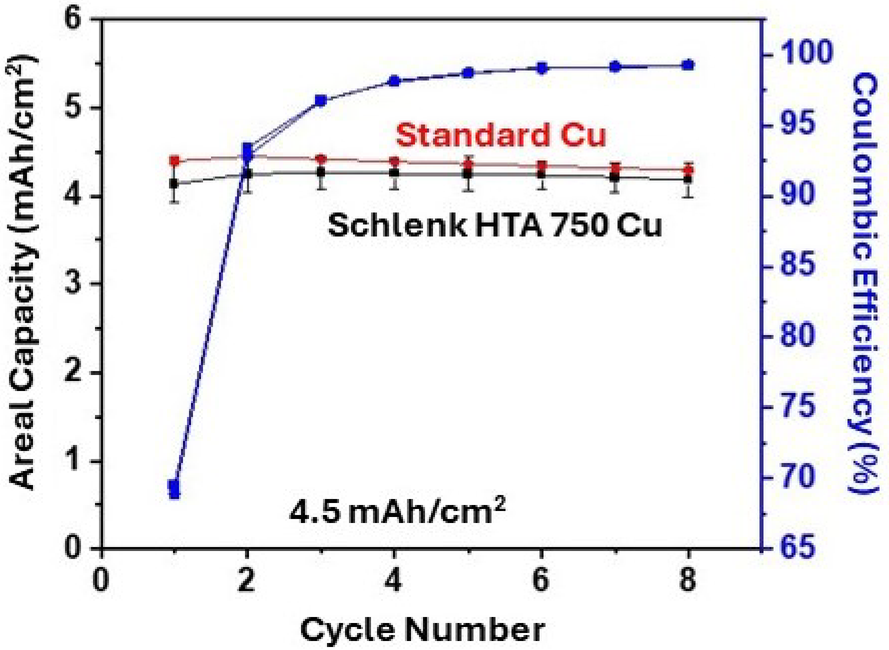
- Laser ablating patterns in Cu current collector leads to cycle life improvement.
- Demonstrated thus far with milled Si at relatively low loading (~1-1.5 mAh/cm^2) and 20 μm thick Cu.



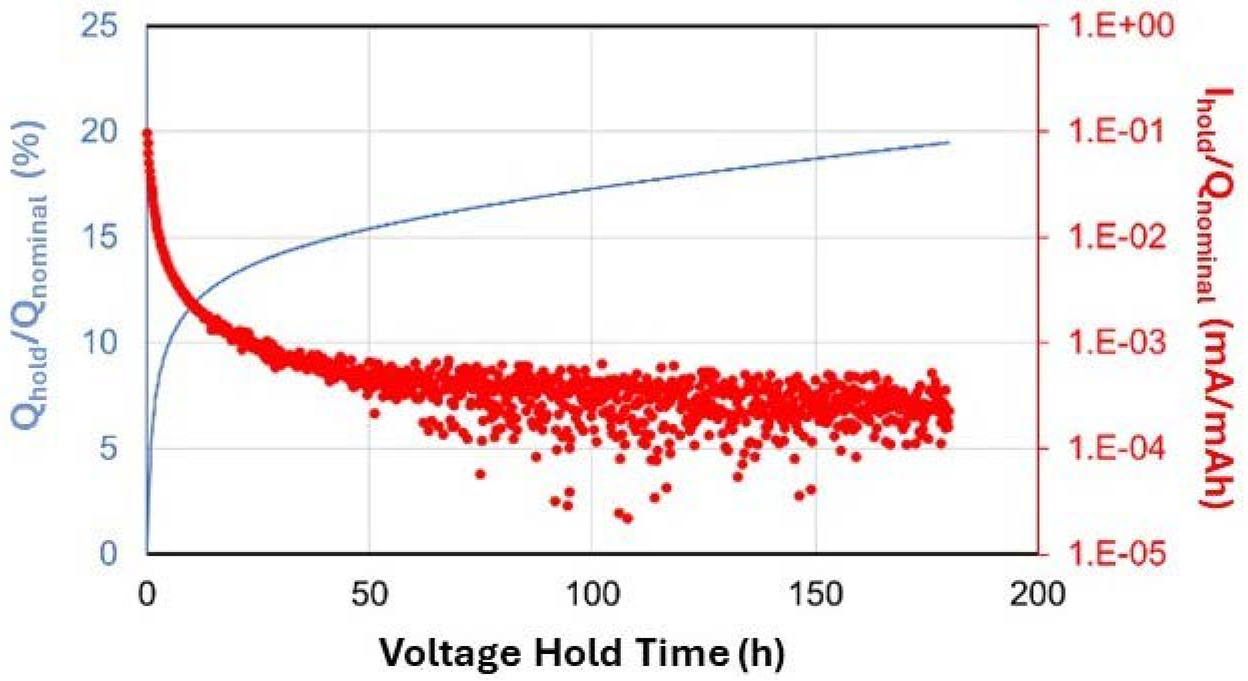
- Schlenk foils (HTA product series) have higher tensile and yield strength than standard copper foil.
- Milled Si electrodes on Schlenk foil do not wrinkle after initial cycling in coin or pouch cells, unlike conventional Cu.

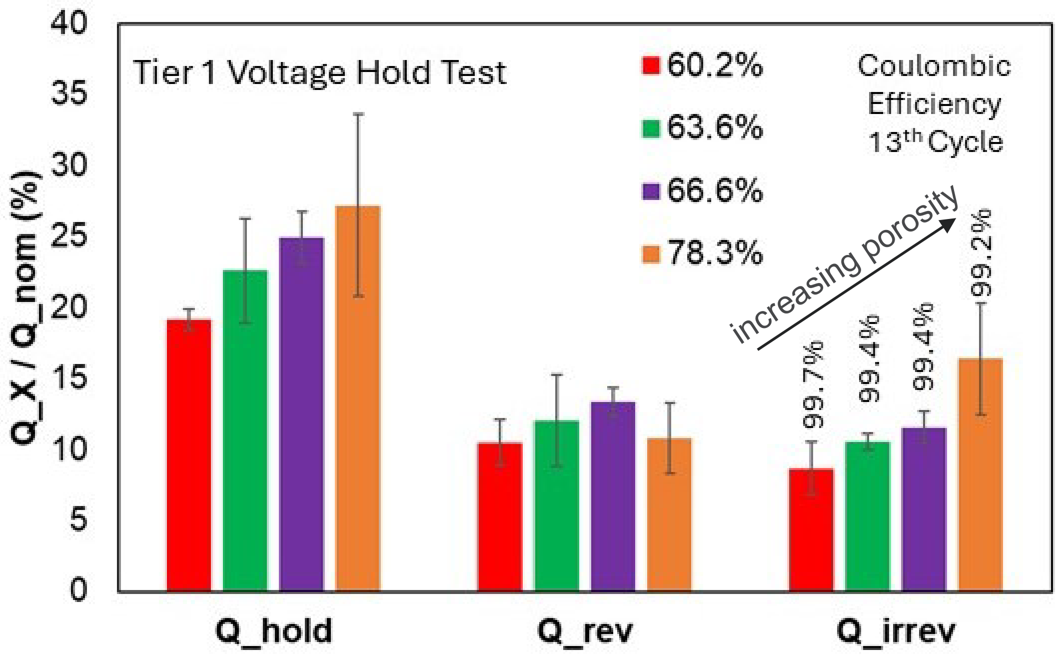




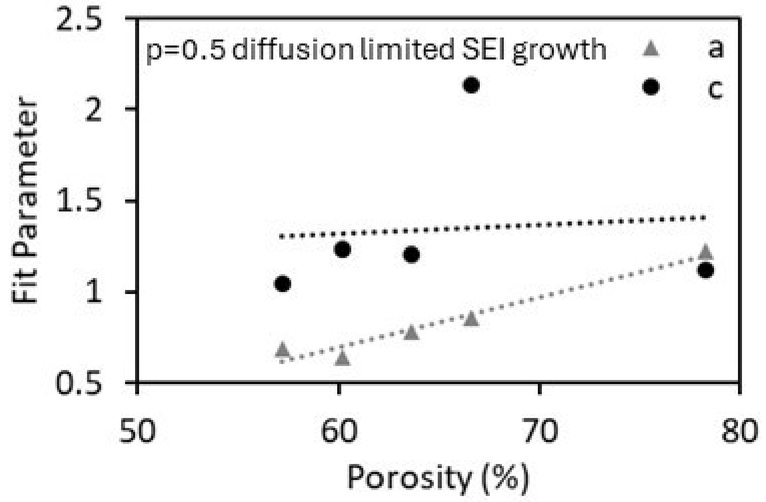


VARIED POROSITY ELECTRODES USED TO SHOW POROSITY MAY AFFECT CALENDAR AGING





$$Q_{hold}(t) = Q_{rev}(t) + Q_{irrev}(t) = \frac{Q_{rev}^{final}(c + t_{final})t}{t_{final}(c + t)} + at^p$$



- Irreversible capacity loss increases with increasing porosity.
- Increasing <u>a</u> suggests faster SEI growth with increasing porosity.
- Erratic **c** values with increasing porosity suggest that reversible lithiation timescales are not strongly correlated to porosity.
- Irreversible capacity loss during voltage hold reasonably correlated with Coulombic efficiency.

RESPONSES TO FY22 REVIEWERS COMMENTS

…**microcalorimetry results were inconsistent with the electrochemical test results**, probably because microcalorimetry was not done under realistic cell operating conditions.

- New microcalorimetry data shows SEI does not stabilize on Si and reference performance tests (RPT) cause spikes in parasitic heat.
- SEI does stabilize on graphite in the same test.
- New variable RPT tests do confirm that more frequent RPTs degrade calendar aging quicker but not when RPTs occur once per month.
- **Mechanical SEI disruption during an RPT is not the dominant calendar aging mechanism for Si, but it does contribute.**
- SEI on Si is less passivating than on graphite even without the contribution from RPTs.

…clear that **additional electrode structural optimization is needed**… includes the areas of **other binder candidates**.
…might be helpful to **consult with industrial materials suppliers**…potentially **most beneficial in the binder system**, but could also extend to the selection of **current collector materials** (e.g.: copper/nickel composites) and **conductive additives**.
…could be helped by collaboration on **optimizing the non-active materials components**.

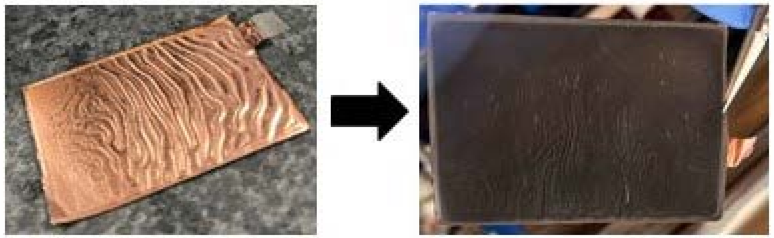
- **Have begun examining other binders (PAA) but so far non-aqueous binders are most compatible with synthesized Si materials.**
- Have been considering using more than one binder to tune adhesion and cohesion.
- **We have begun examining alternative current collector materials (high tensile strength Cu) and have a few more in mind.**
- Non-active material components other than the binder are also under testing, described more in our materials presentation (Neale BAT498).

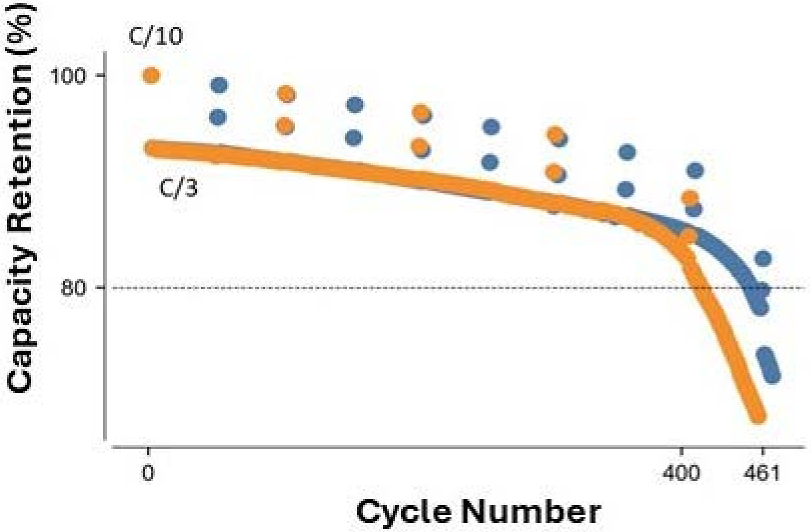
…hopefully more insights can be gained to help **understand the degradation mechanisms caused by the many parameters** identified by the team, such as, Si material, electrode manufacturing conditions, electrochemical aging/cycling protocols, pouch versus coin cells, and size and loading of the electrodes.
…more detailed **characterization of the mechanical properties, at various stages of calendar aging and cycle number,** would be necessary to understand degradation mechanisms.

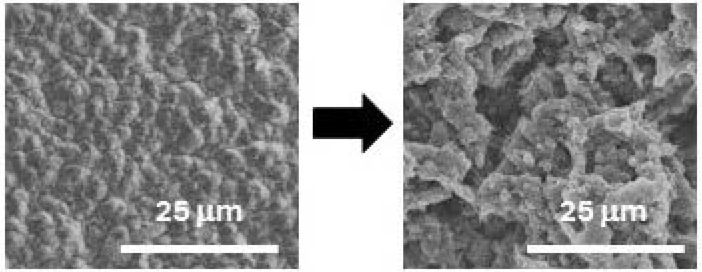
- We have gained some insight regarding how degradation mechanisms are impacted by these parameters but certainly have more to do.
- **Disassembly/characterization at varied cycle number is a great suggestion, though this is only useful after major issues like shredding in early cycles have been mitigated (which we have shown can be mitigated in some systems).**

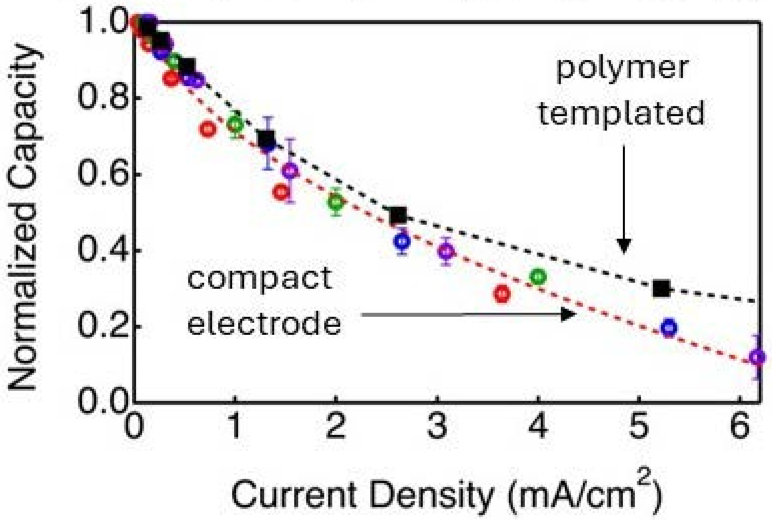
REMAINING CHALLENGES AND BARRIERS FOR ARCHITECTURE

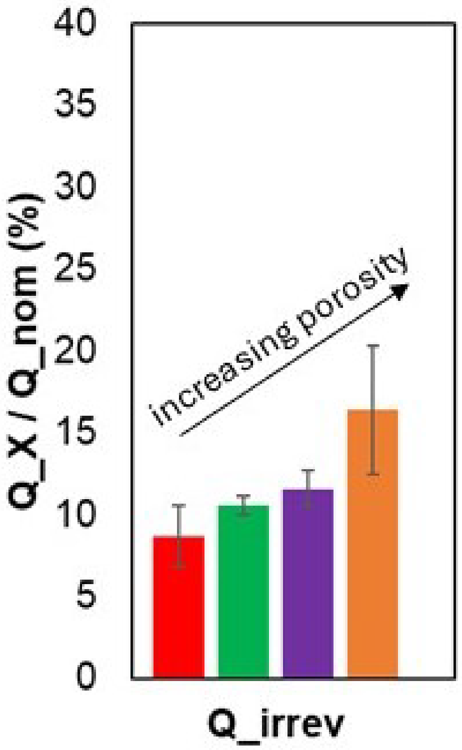
- Slurry modifications have greatly improved cycle life in 2 Ah cells, but more optimization is still needed.
- Porosity introduction has been partly successful, but high loading PECVD Si is still transport limited.
- Need more testing to understand impact of electrode architecture on calendar aging.





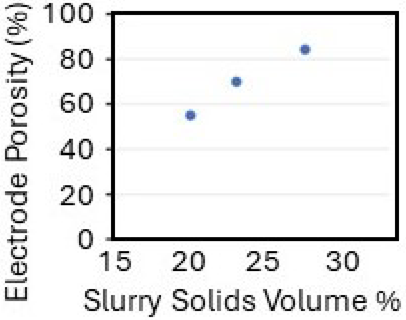


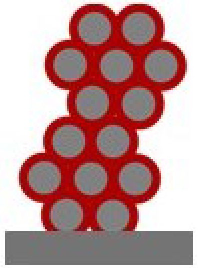


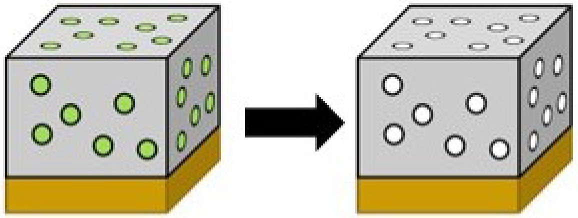


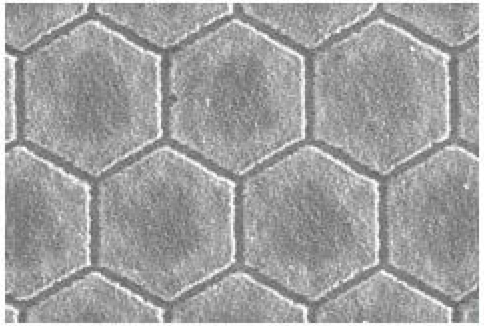
PROPOSED FUTURE RESEARCH – TWEAKS TO APPROACH

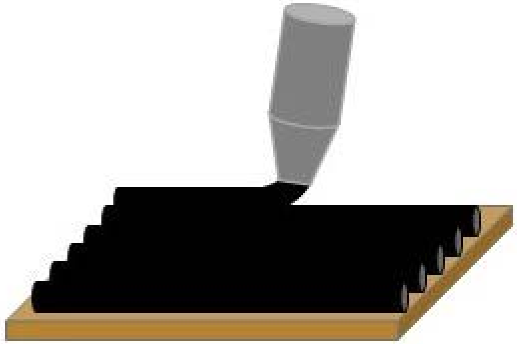
Develop electrode architectures to enable high loading electrodes and high specific energy at C/3 for 1000 cycles
Understand how electrode architecture impacts cycle life and calendar life.





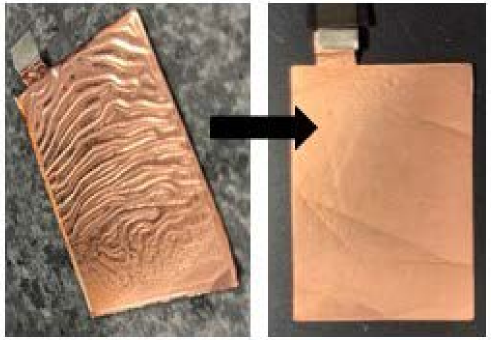


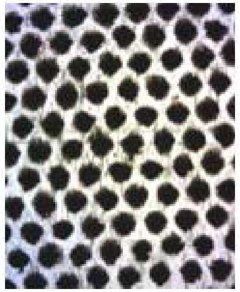


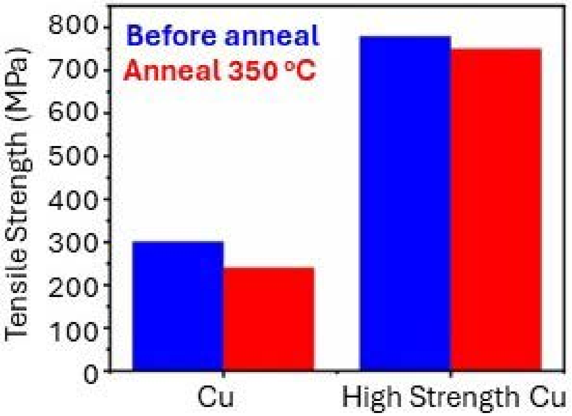


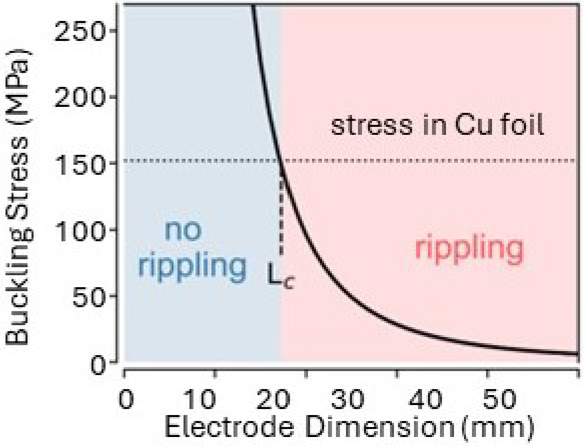
Continue developing methods that introduce **small length scale porosity** for transport and stress relief to improve cycling of high loading electrodes but **focus on understanding whether architecture impacts calendar aging.**

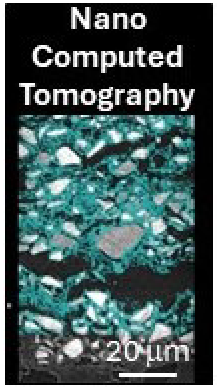
Macroscopic porosity hypothesized **too large to solve transport limitations in PECVD Si** but can still help with wetting and stress relief and will particularly **use for SiO_x.**











Continue utilizing high strength current collectors and **translate milled Si results to PECVD Si electrodes and 2 Ah cell builds.**

Modeling/characterization as needed to understand porosity.

Any proposed future work is subject to change based on funding levels.

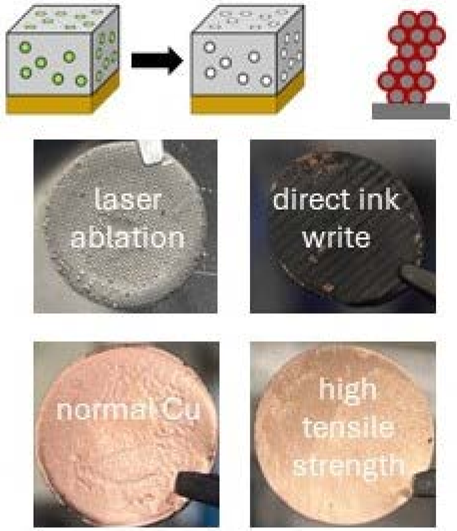
SUMMARY: ARCHITECTURE THRUST

Problems

- 375 Wh/kg cells require high loading electrodes (3-5 mAh/g) rather than high utilization.
- Stress in high loading Si electrodes leads to delamination, wrinkling, and shredding.
- Wrinkling is size and loading dependent, so pouch cells are more affected by stresses.
- High loading also impedes transport, particularly in dense PECVD electrodes.

Progress

- Porosity can be manipulated by solids loading, fugitive phases, polymer templating, and formation of secondary particles comprised of nanoparticle Si.
- Macroscale porosity can be generated by laser ablation and additive manufacturing of ridged electrode architectures to relieve stress at the current collector interface.
- Current collector stresses can also be mitigated by tuning binder selection and content, modifying the current collector, or by utilizing high tensile strength current collectors.
- **Architecture may impact calendar aging.**



Next Steps

- Translate successful mitigations to PECVD Si systems and integrate successful mitigations into pouch cells.
- **Understand impact of porosity on calendar aging with more rigorous (Tier 3) testing.**

COLLABORATION AND COORDINATION WITH OTHER INSTITUTIONS

Support for this work from the Office of Vehicle Technologies, DOE-EERE, is gratefully acknowledged – Nicolas Eidson, Carine Steinway, Thomas Do, and Brian Cunningham,

Baris Key
Sohyun Park
Zhengcheng Zhang
Joseph Kubal
Devashish Salpekar
Brian Ingram
Steve Trask
Avi Gargye
Zhenzhen Yang
Glenn Teeter
Jaclyn Coyle
Juliane Preimesberger

Rachel Korkosz
Eric Dufek
Jack Deppe
Kevin Gering
Bumjun Park
Mauresh Savargaonkar
Robert Kostecki
Tony Burrell
Kae Fink
Ryan Tancin
Mike Carroll
Jae Ho Kim
Eric Allcorn
Megan Diaz

Ankit Verma
Petter Weddle
Bertrand Tremolet de Villers
Kae Fink
Ryan Tancin
Mike Carroll
Jae Ho Kim
Zoey Huey
Chun-Sheng Jiang
Jasmine Tabatabai
John Westgard
Qian Huang
Josey McBrayer

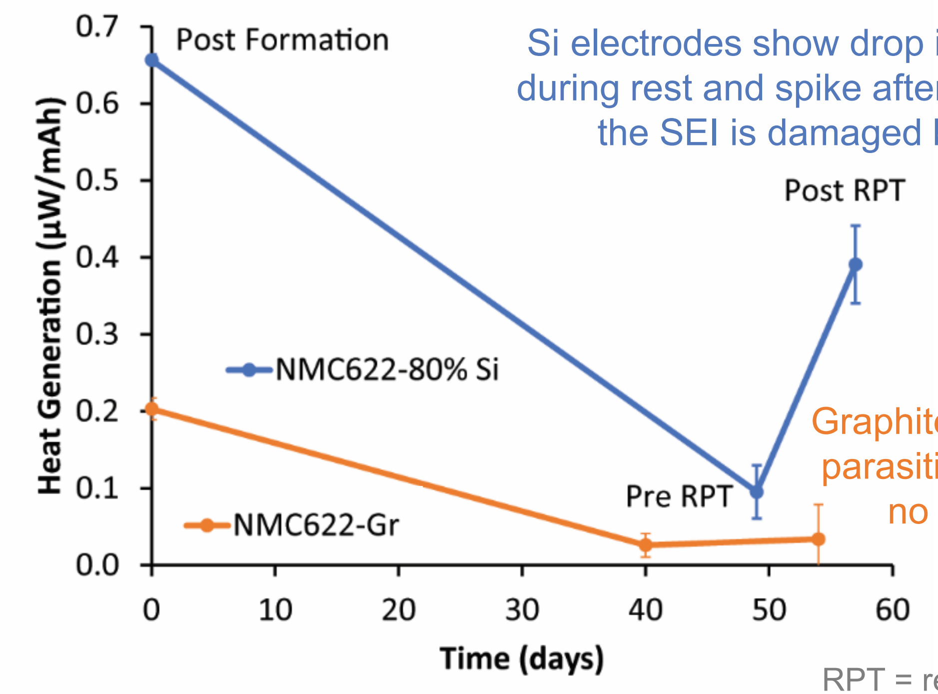
Francois Usseglio-Viretta
Donal Finegan
Max Schulze
Matt Keyser
Pashupati Adhikari
Pallavi Sundaram
John Farrell
Nina Prakash
Trevor Martin
Jackson Pope
Erika Hunting
Lydia Meyer

Anton Tomich
Alison Dunlop
Marco Tulio Fonseca Rodrigues
Wenquan Lu
Evelyna Wang
Fulya Dogan Key
Lily Robertson
Daniel Abraham
Andrew Jansen
Nate Neale
Katie Harrison
Andrew Colclasure

Jack Vaughey
Chris Johnson
Tyler Sweet
Gabe Veith
Beth Armstrong
Khryslyn Arano
Amanda Musgrove
Robert Sacci
Steven Lam
Jie Xiao
Chongmin Wang
Joseph Quinn

TECHNICAL BACKUP SLIDES

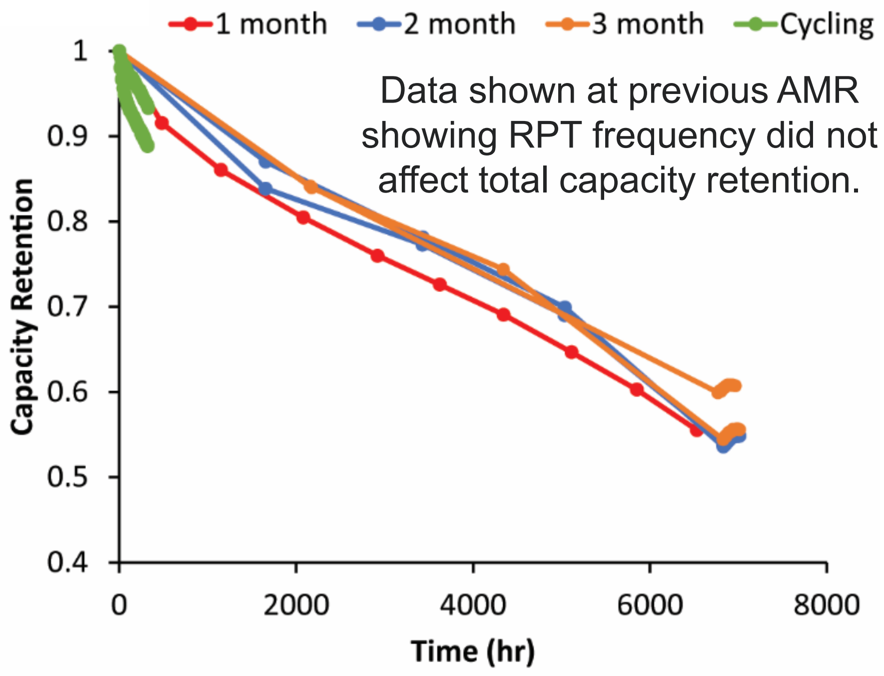
TECHNICAL BACKUP SLIDE 1: REVIEW RESPONSE ABOUT ISOTHERMAL MICROCALORIMETRY (IMC) DISAGREEING WITH ELECTROCHEMISTRY

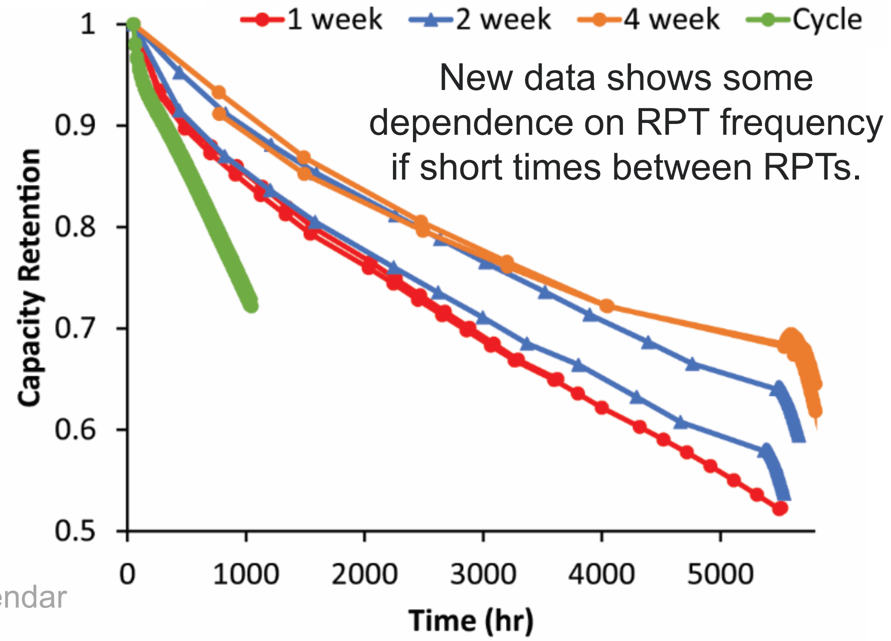


Graphite electrodes show much lower parasitic heat than Si electrodes and no large spike after the RPT.

RPT = reference performance test

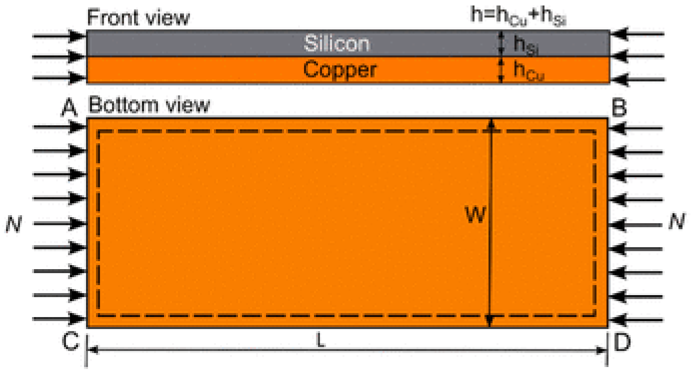
- IMC suggests Si SEIs are damaged by RPTs, causing parasitic heat due to passivation loss.
  - This seemed inconsistent with the previous AMR variable RPT data showing that RPT frequency did not affect capacity retention after aging (top right).
  - New data with more frequent RPTs show a dependence on RPT frequency (bottom right).
- IMC also suggests Si SEI is less passivating at all data points than graphite.
  - This passivation problem is likely a larger contributor than the SEI damage after an RPT.





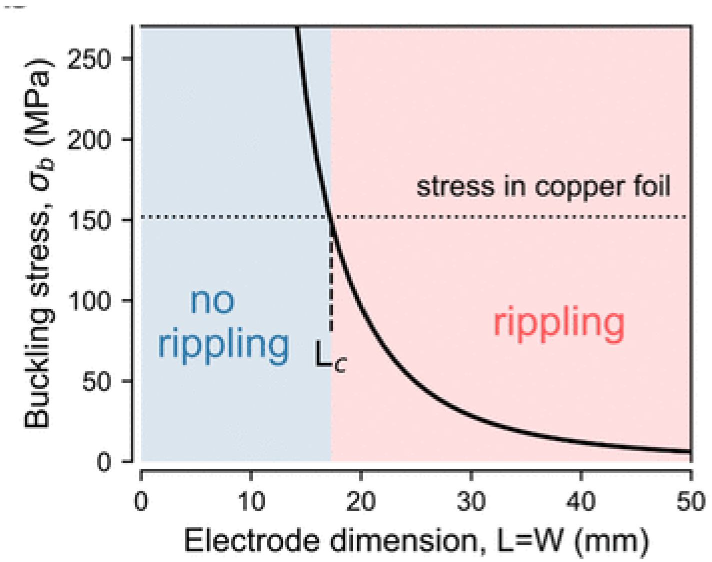
McBrayer, J.D., Harrison, K.L., Allcorn, E. and Minteer, S.D., 2023. Chemical contributions to silicon anode calendar aging are dominant over mechanical contributions. *Frontiers in Batteries and Electrochemistry*, 2:1308127.

TECHNICAL BACKUP SLIDE 2: MODELING DETAILS FOR BUCKLING STRESS



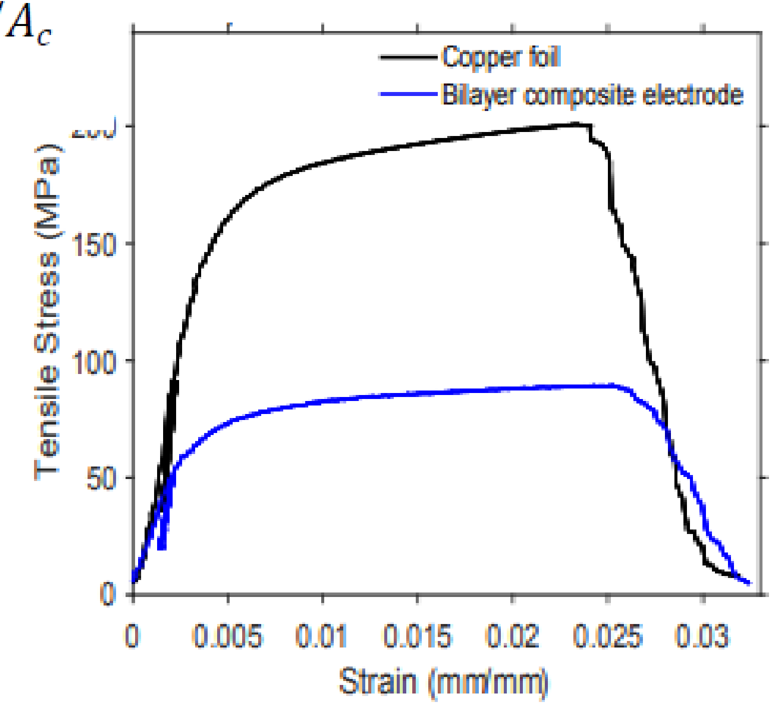
Modified couple stress theory of thin bilayer plate of Si and Cu

- Uniaxial compressive load.
- Displacement field based on Kirkoff thin plate theory.
- Buckling stress is the stress required to create ripples.
- Measured modulus of Si-Cu thin bilayer composite to be 43 GPa.
- Assume Poisson ratio 0.3.
- Yield strength Cu 152 MPa.
- Si electrode is 80% milled Si, 10% PI binder, 10% carbon.



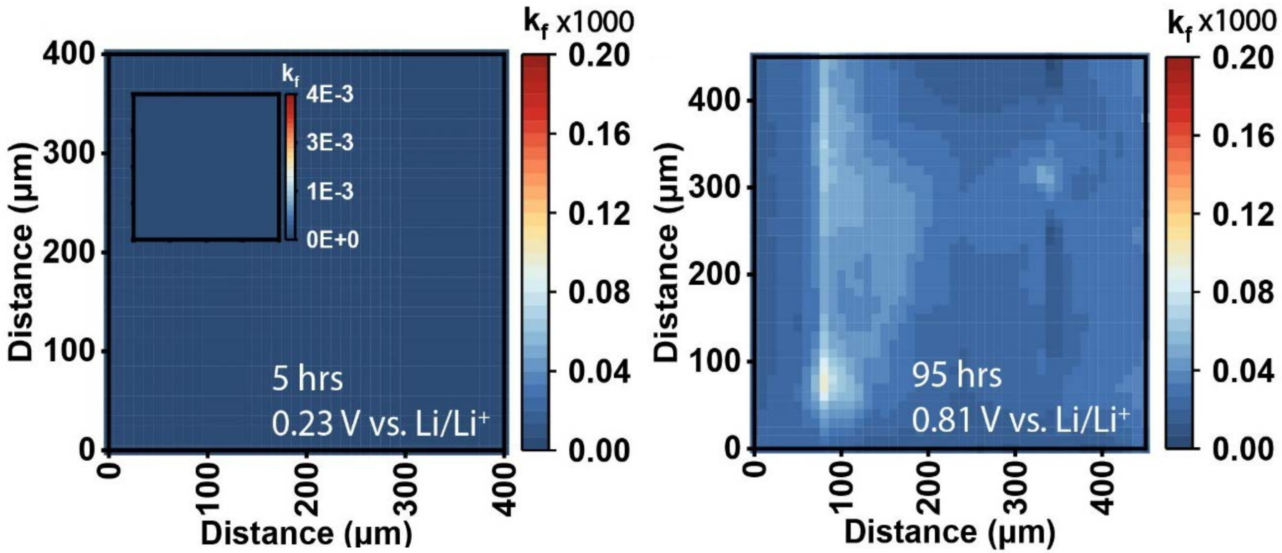
$$\sigma_b = \left(D + l^2 G h\right)\left(\frac{L}{m\pi}\right)^2\left[\left(\frac{m\pi}{L}\right)^2 + \left(\frac{n\pi}{W}\right)^2\right]^2 / A_c$$

σ_b = Buckling stress
D = flexural rigidity
l = intrinsic length scale = $h_{Cu}/3$
G = Lamè constant
h = $h_{Cu}+h_{si}$ = 11 + 14 µm
L = thin plane length
m = number half sine waves in x direction = 5
n = number half sine waves in y direction = 1
W = thin plane width
A_c = Wh

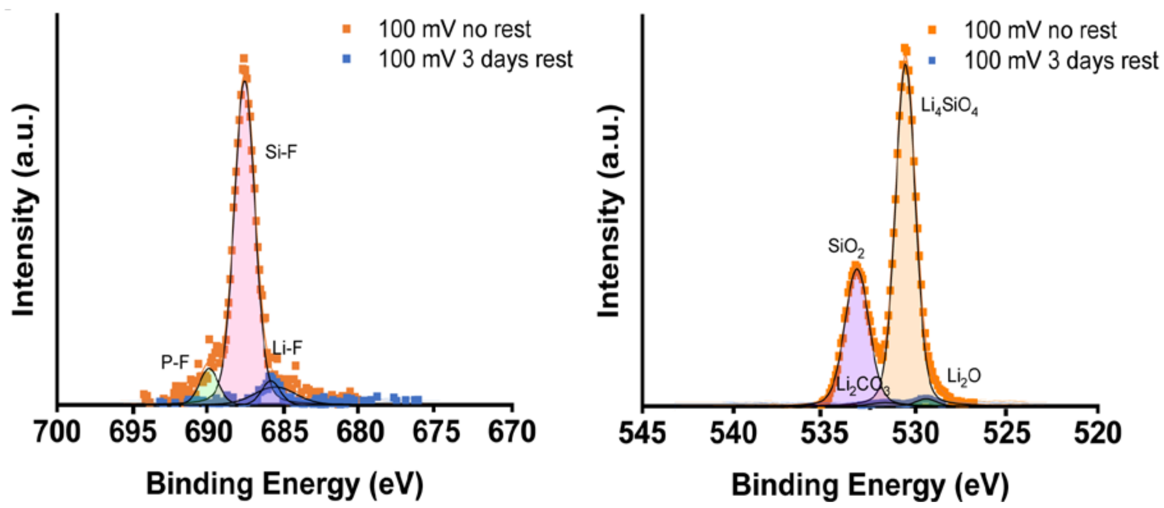


Rodrigues, M.T.F., Rajendran, S., Trask, S.E., Dunlop, A.R., Singh, A., Allen, J.M., Weddle, P.J., Preimesberger, J.I., Coyle, J., Colclasure, A.M. and Yang, Z., 2023. Cell-format-dependent mechanical damage in silicon anodes. ACS Applied Energy Materials, 6(18), pp.9243-9248.

TECHNICAL BACKUP SLIDE 3: WHY ARCHITECTURE MAY IMPACT CALENDAR AGING



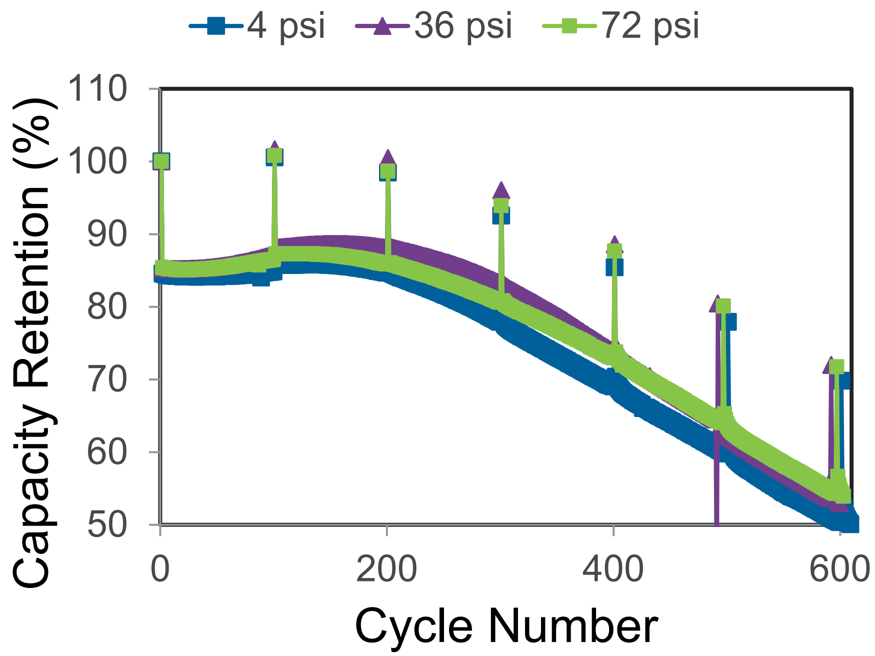
SECM shows that Si passivation decreases during calendar aging following formation, which is consistent with SEI dissolution.



Passivation loss correlates with much lower SEI signals after calendar aging (blue) than before calendar aging (orange).

- SEI components typically have low solubility in organic electrolytes, but the dissolved amount would be dictated by total electrolyte volume available, local pore size near the SEI surface, and tortuosity because it affects diffusion.
- SEI may also delaminate or become porous so that it no longer can passivate.
- If SEI dissolves, porosity may impact the rate of dissolution and ultimately the calendar aging rate.

TECHNICAL BACKUP SLIDE 4: APPLIED PRESSURE DOES NOT SOLVE WRINKLING



Cell Details

- SiO_x vs. NMC811
- 3 – 4.06 V
- Gen2 + 3% FEC
- 1x C/10, HPPC, 99x1C, loop
- ~950 mAh/g_{SiOx+C}
- Prelithiation to 600 mV

Beginning of life

- 150 mAh/g_{NMC}
- 950 mAh/g_{SiOx+C}
- 2.17 mAh/cm^2
- 3.6 V ASI ~22.7 $\Omega\ cm^2$

4 psi = 28 kPa
36 psi = 248 kPa
72 psi = 496 kPa

HPPC = hybrid pulse power characterization
ASI = area specific impedance

TECHNICAL BACKUP SLIDE 5: ADDITIONAL RESPONSES TO REVIEWS

What was not as clear to the reviewer was how this work overlaps with the electrode structure development work in the adjacent projects. The reviewer clarified that this is important to note since this project does not just address mechanical characterization of the electrode but also steers electrode design.

- CAMP is involved in this project, so we are taking advantage of their knowledge/participation in adjacent projects to guide electrode design.
- BAT 232 from 2023 AMR focused on development of high loading electrodes for other materials but many lessons.
  - General rules that apply to all material systems are difficult to develop.
  - Solvent content needs to be optimized and optimization changes with carbon type and amount.
  - Carbon additives and their aggregation can be critical for porosity.
  - Mixing order matters.

The reviewer noted the excellent collaborations and said that it would be better if the team included industrial collaboration as well. The reviewer mentioned that collaborations are mainly among the National Labs, and that it may be helpful to expand collaborations to include experts on characterization of mechanical behavior of Si-electrodes to help solve mechanical damages especially in high loading Si cells. The reviewer suggested that it may be helpful to expand external collaborations to strengthen mechanical characterization. The reviewer added that this may help determine which of the many hypothetical parameters are important in affecting the calendar and cycle life of Si-containing electrodes.

- Transitioned this thrust away from a focus on mechanical characterization.
- While there are a lot of techniques we could add, the mechanical degradation is clear (delamination, shredding, wrinkling).
- With 1.5 years left in the project, we are focusing on mitigation by architecture design rather than characterization at this stage.

The reviewer stated that future work is clearly defined, and that large format cells (i.e., 3-5Ah) are recommended for study on gas generation and stability. The reviewer clarified that in coin cells, it is not possible to observe gas generation.

- We agree with the reviewer that we will likely not be able to detect gas in coin cells and small scale pouch cells.
- Our targets are 2 Ah cells so we will not likely fabricate 3-5 Ah cells in this project and we may only see limited gassing in 2 Ah cells.
- We note that sometimes gassing is observed in 2 Ah cells (slide 14) so gassing can still be used to infer degradation in extreme cases.