Achieving Stable Cycling Performance of Silicon Anode for LIB by Optimized Electrochemical Pre-Lithiation

Advanced Battery Power conference
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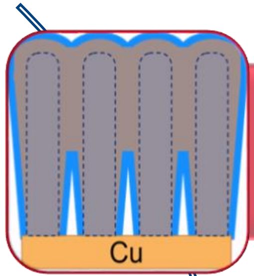
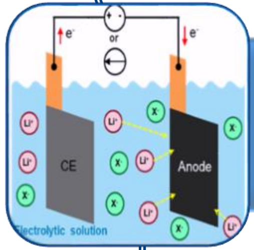
GREEN SPEED
JARA Jülich Aachen Research Alliance
JÜLICH Forschungszentrum | HELMHOLTZ-INSTITUTE MÜNSTER
ISEA Power Electronics and Electrical Drives
CARL Center for Ageing, Reliability and Lifetime Prediction of Electrochemical and Power Electronic Systems
RWTH AACHEN UNIVERSITY

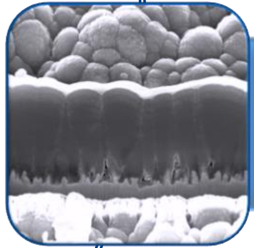
Outline



Silicon (Si) as Next-Gen Anode Materials for LIB



Challenges: Pre-Lithiation for Pure Si



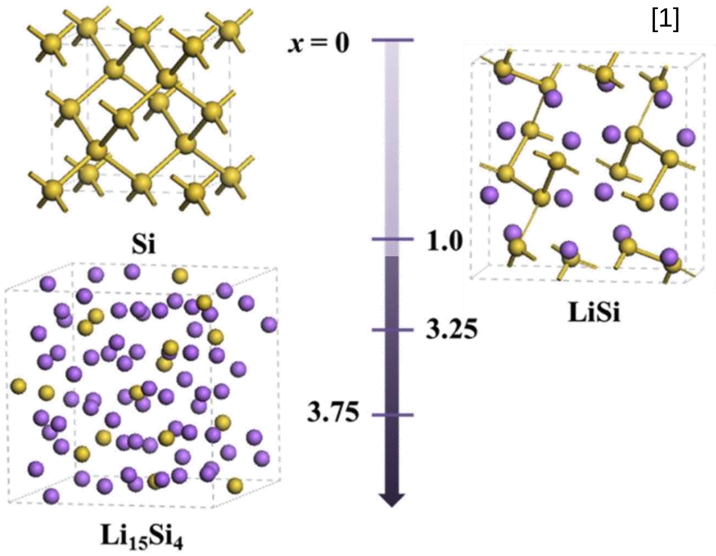
Experimental Results: Initial Performance

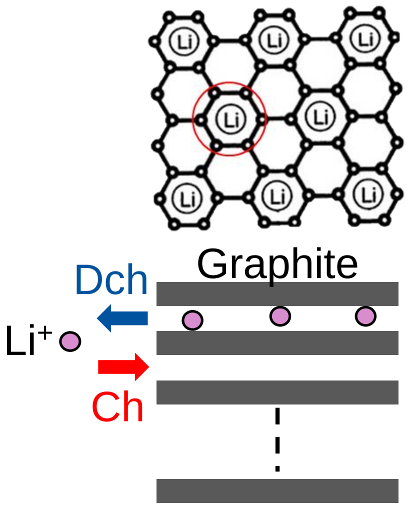
Experimental Results: Cycle Performance

Background - Silicon as Promising Anode Active Material

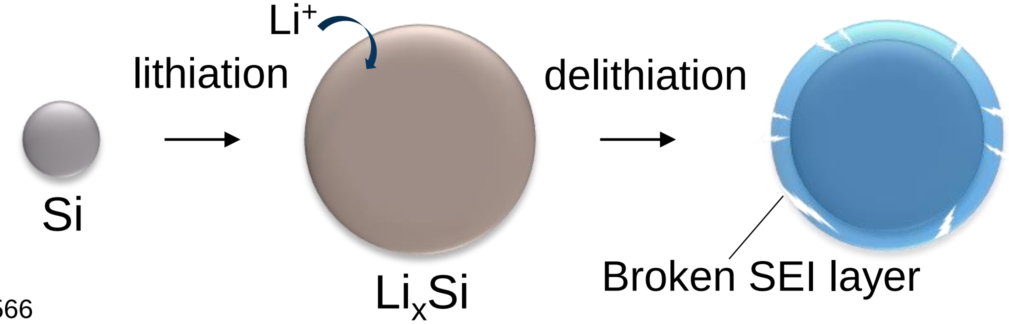
- **Role of silicon (Si) in battery evolution: why Si?**
  - Theoretical capacity

Graphite:	**LiC_6**	~372 mAh/g
Si:	**$Li_{15}Si_4$**	~3,579 mAh/g





- **Key challenges in Si anodes:**
  - **Large volume change (~300%)** during lithiation/delithiation
  - Mechanical stress leading to **particle pulverization**
  - The formation of solid electrolyte interphase **(SEI)** consumes lithium (Li), **irreversible capacity loss**
  - SEI instability



[1] J. Moon *et al.*, J. Power Sources 328 (2016) 558-566

Structural Solutions for Si Anodes

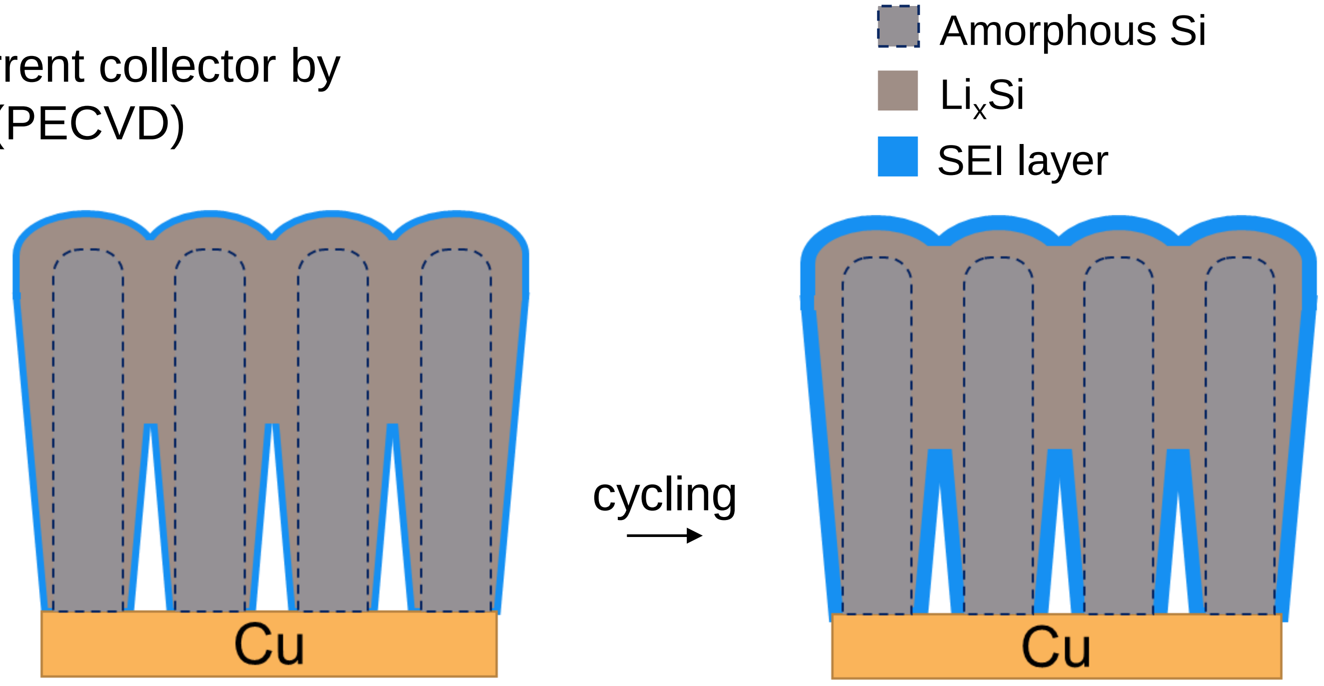
Advanced Si structures: Si nanowires, porous Si, and composite materials

SEI stabilization: coating technologies and material engineering, binders

- Pure Si Anode (dry-coating)
  - Amorphous Si growing on the copper (Cu) current collector by plasma-enhanced chemical vapor deposition (PECVD)
  - Sponge-like-columnar structure
  - Remains mechanically stable when lithiated
  - Significantly reduced cell thickness

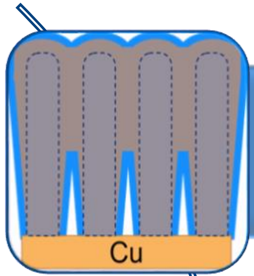
greenSPEED
EU project

Project partner: LeydenJar
Pure Si anode



Pure Si Anode cross-section

Outline



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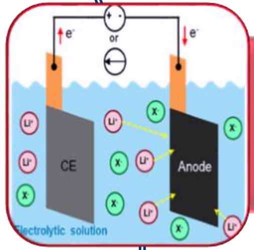

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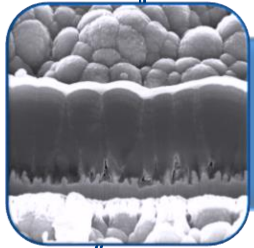

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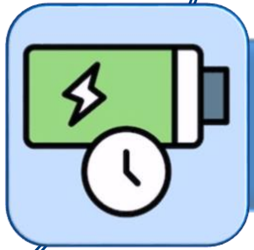
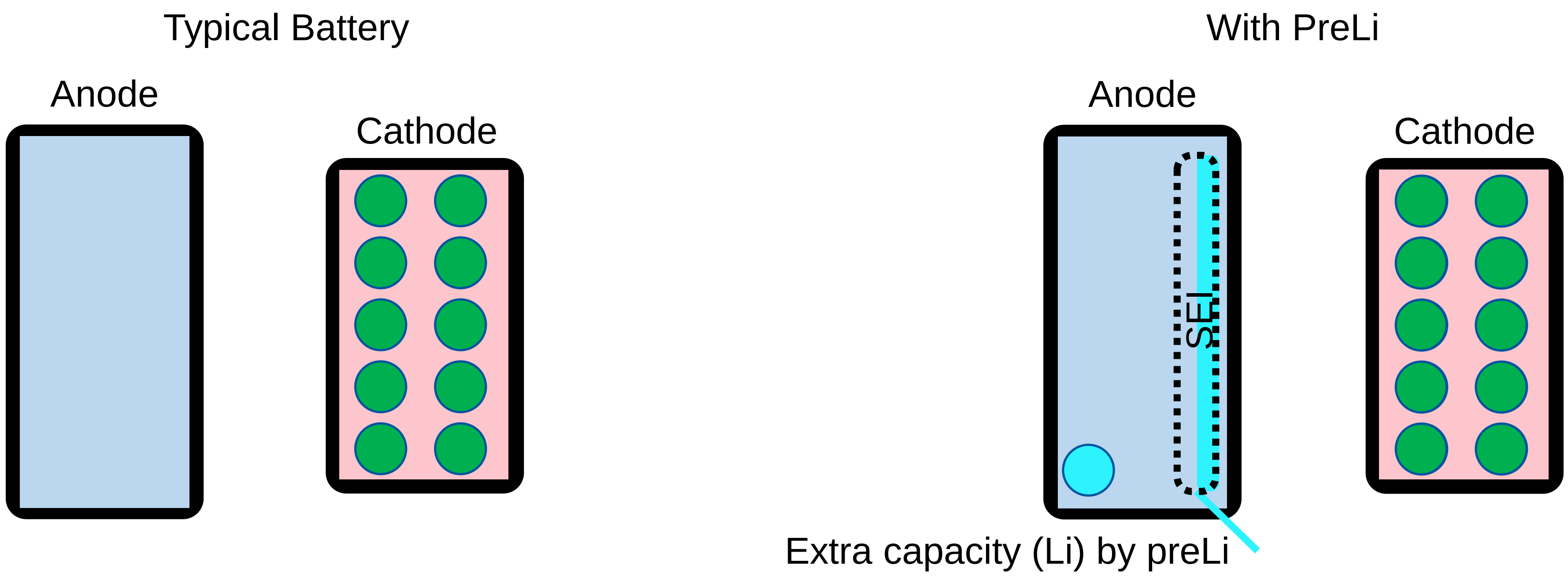


Experimental Results: Cycle Performance

Pre-Lithiation (PreLi) as a Solution[2]

- **Addressing Li loss**:
  PreLi is designed to mitigate **Li loss** during SEI formation, thereby enhancing initial coulombic efficiency (ICE) and overall cycling performance.



[2] X. Y. Yue, et al., Adv. Mater. (2022) 34, 2110337

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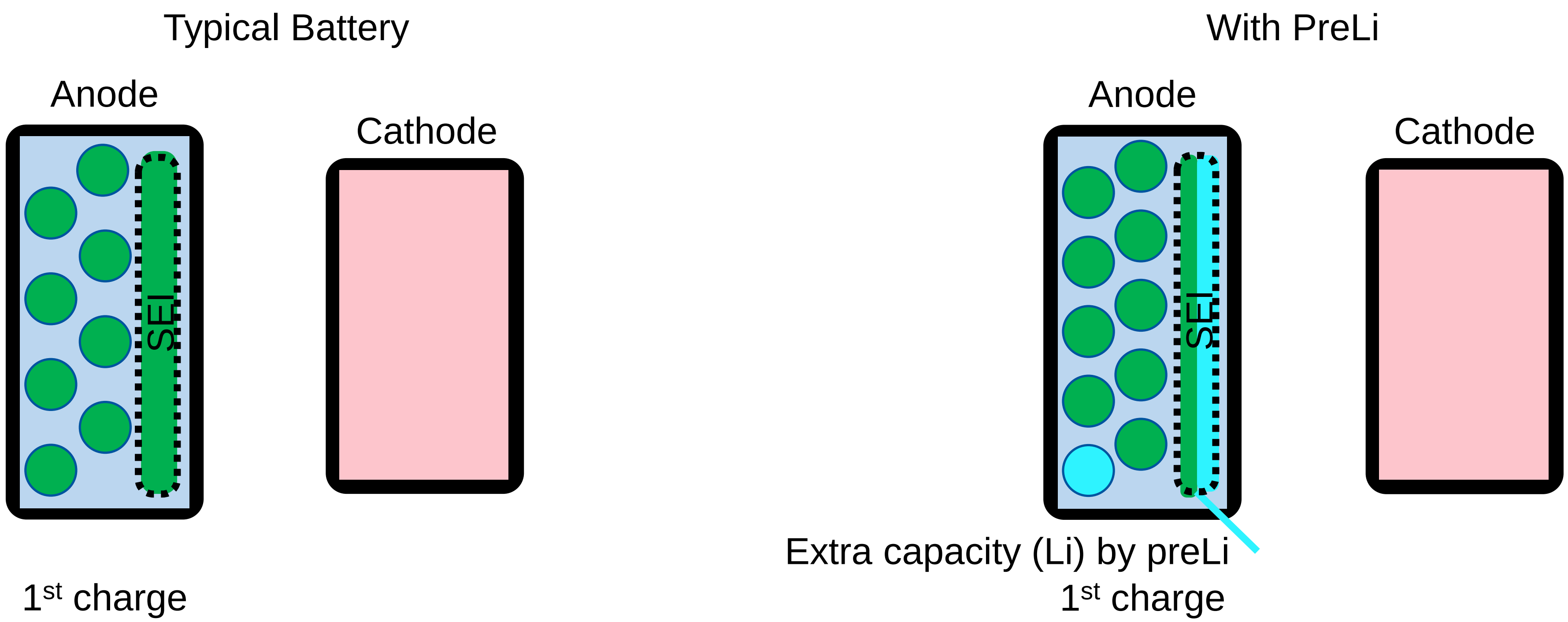

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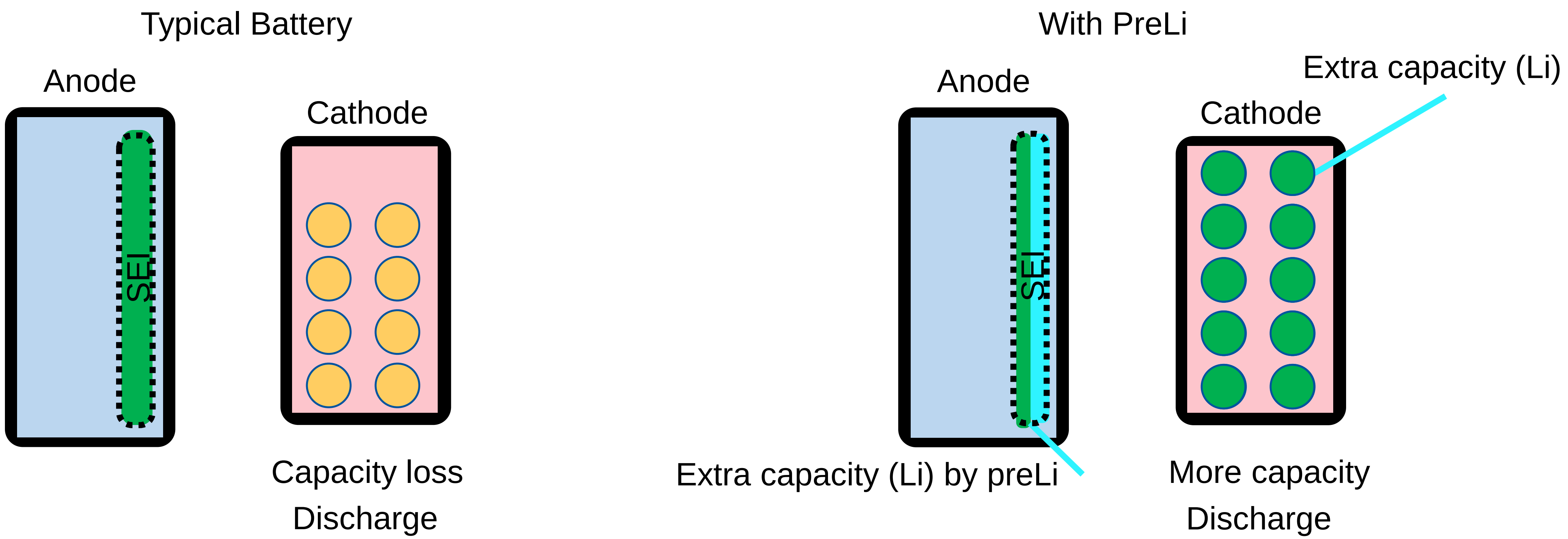

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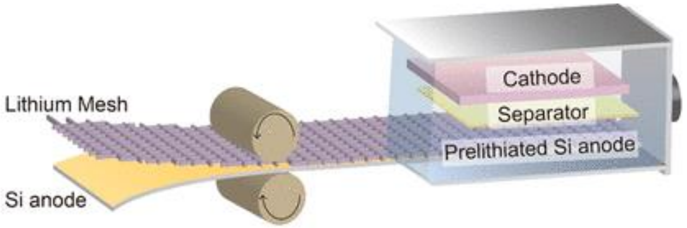
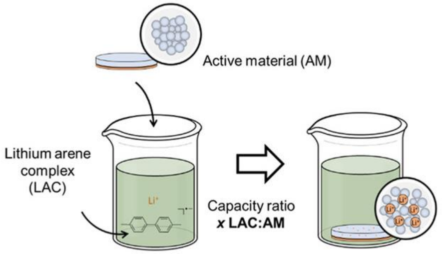
PreLi Methods

1. Mechanical PreLi[3]



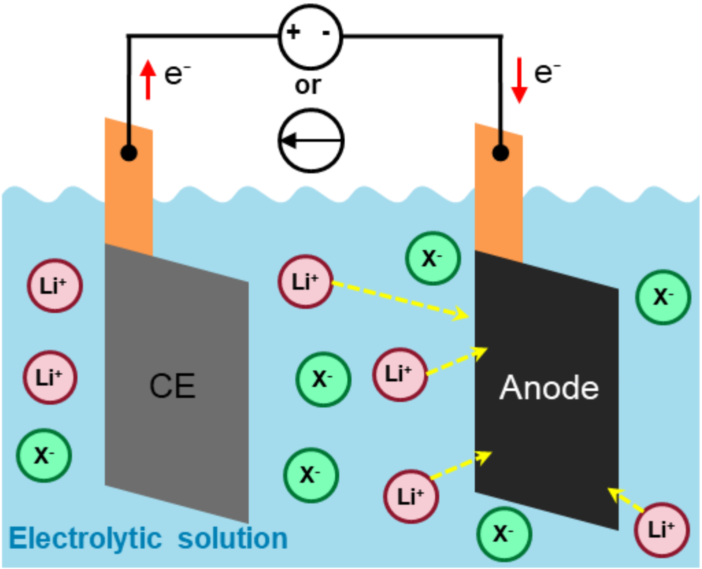
Mechanical PreLi (direct contact with Li)

2. Chemical PreLi[4]



Chemical PreLi (anode into chemical)

3. **Electrochemical PreLi**
   Safer, scalable, and efficient for SEI pre-formation



Electrochemical PreLi

[3] Y. Yang, *et al.,* Nano Lett., 23 (2023) 5042−5047 https://doi.org/10.1021/acs.nanolett.3c00859
[4] L. Frankenstein, *et al*., Adv. Energy Sustainability Res., 5 (2024) 2300177

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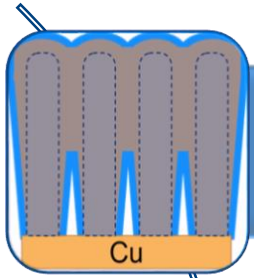

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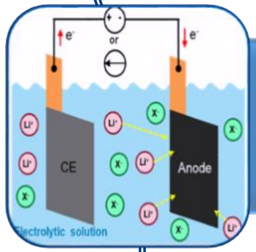

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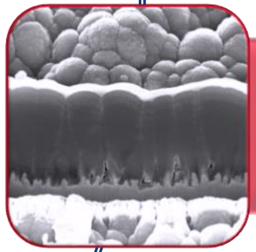
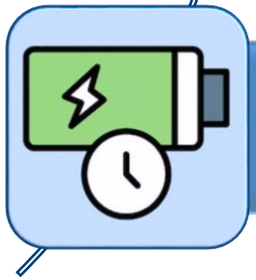


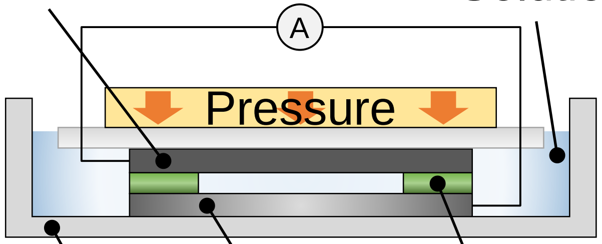
Experimental Results: Initial Performance



Experimental Results: Cycle Performance

Electrolytic-Bath PreLi

- Condition: Dried-atmosphere-controlled environments, crucial for handling Li
- Electrolyte: Organic Li-salted solvent
- Li metal of the counter-electrode was replaced by graphite
- Size: 5 x 8 cm^2
- Anode coating: Single-sided
- Cell type: Coin cell



Pristine Si

Electrolytic-Bath PreLi

Curly anode
tension of the coating

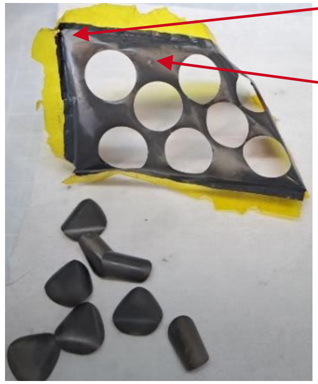
Electrolytic-Bath PreLi

Full cell: pure Si (4.8 mg/cm^2)|| NMC622 (3.5 mAh/cm^2)
Carbonate base electrolyte

Results
- Coulombic efficiency (**CE**)
- Cycle-life performance
- Electrochemical impedance spectroscopy (**EIS**)
- Focused ion beam-scanning electron microscopy (**FIB-SEM**)

Pristine Si

Electrolytic-Bath PreLi



Nonlithiated area

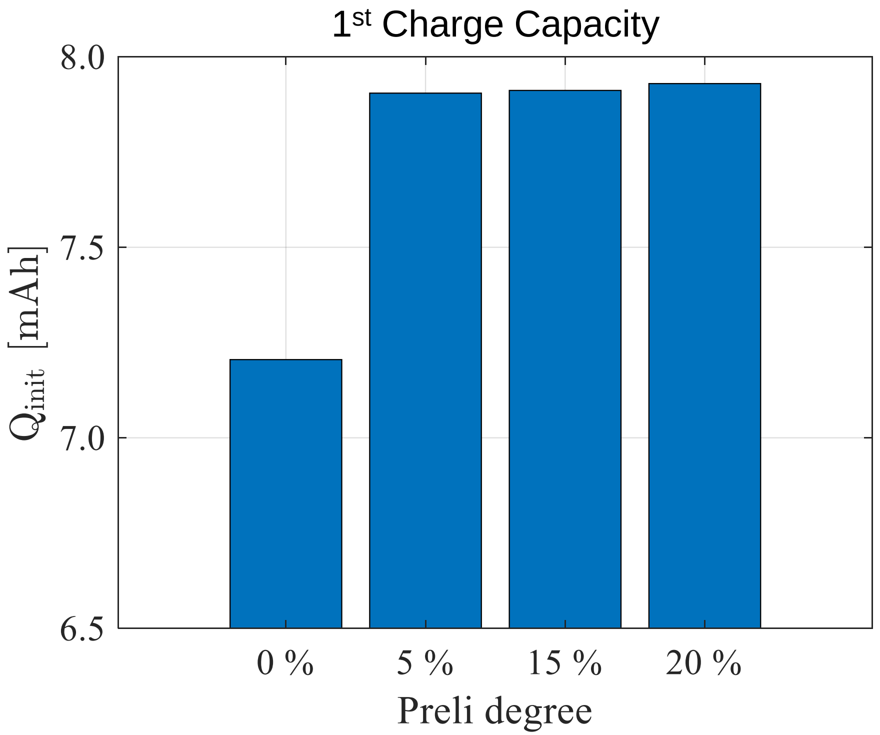
Lithiated area

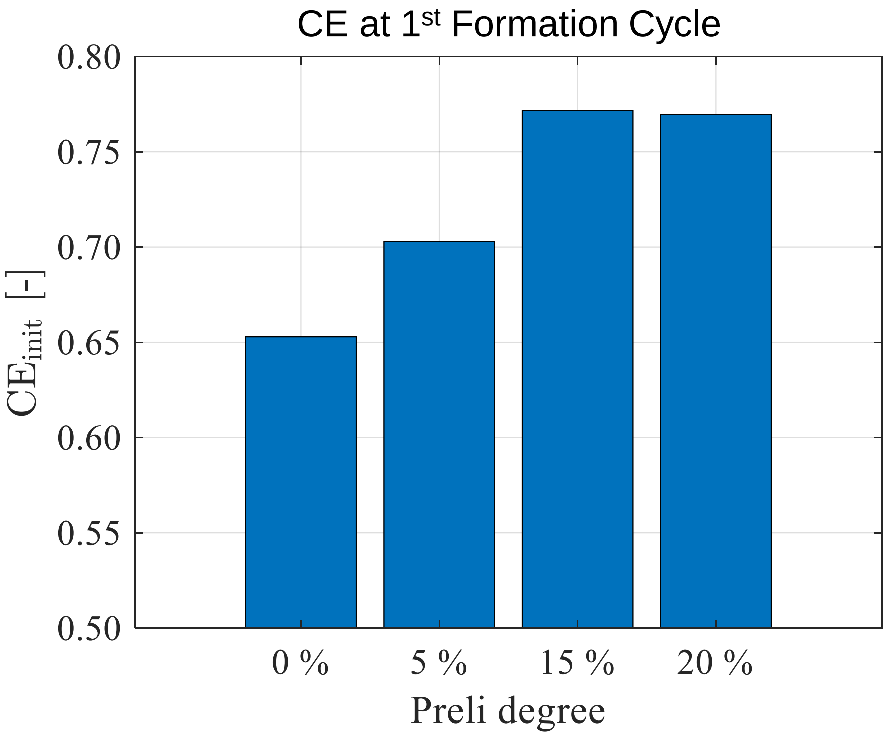
Curly anode
tension of the coating

Initial capacity and ICE during Formation

Full cell: pure Si || NMC622, carbonate base electrolyte
Formation: 1st cycle 0.01 C CCCh10 h, 0.1 C CCCh/Dch 2.5-4.2 V
2nd cycle 0.2 C CCCh/Dch 3-4.2 V

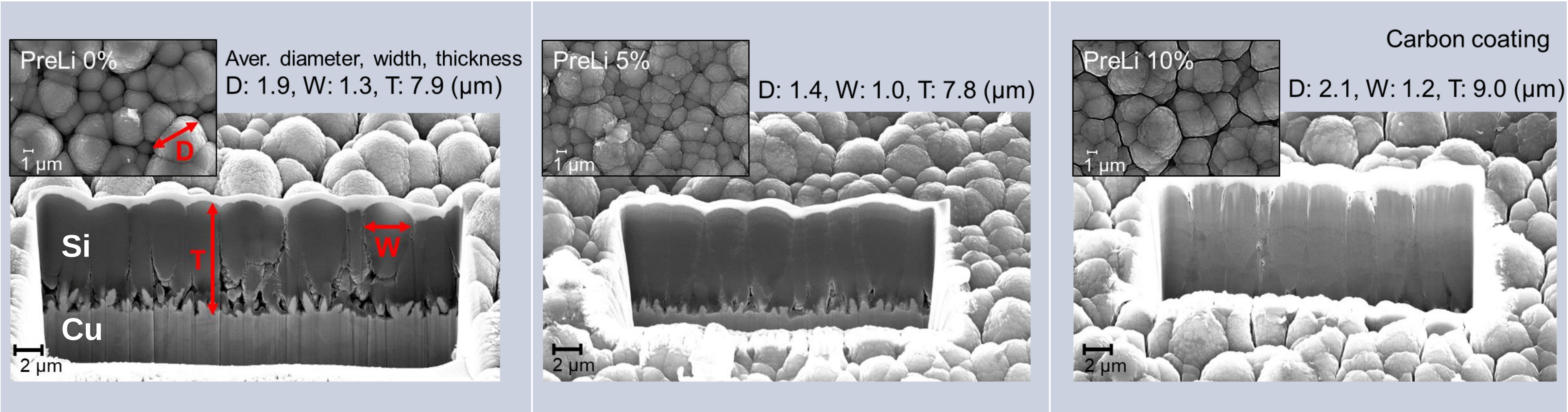
- **Higher Initial Capacity**: Prelithiated anodes show slightly increased first-cycle charge capacity.
- **Performance Boost**: More Li did not lower capacity; it may enhance performance.
- **Stable SEI**: PreLi helped SEI formation, reducing lithium loss and improving battery longevity.
- **CE Improvement**: Coulombic efficiency rose with up to 15% preLi degree.





Focused Ion Beam - Scanning Electron Microscopy (FIB-SEM)

Without preLi	PreLi 5%	PreLi 10%



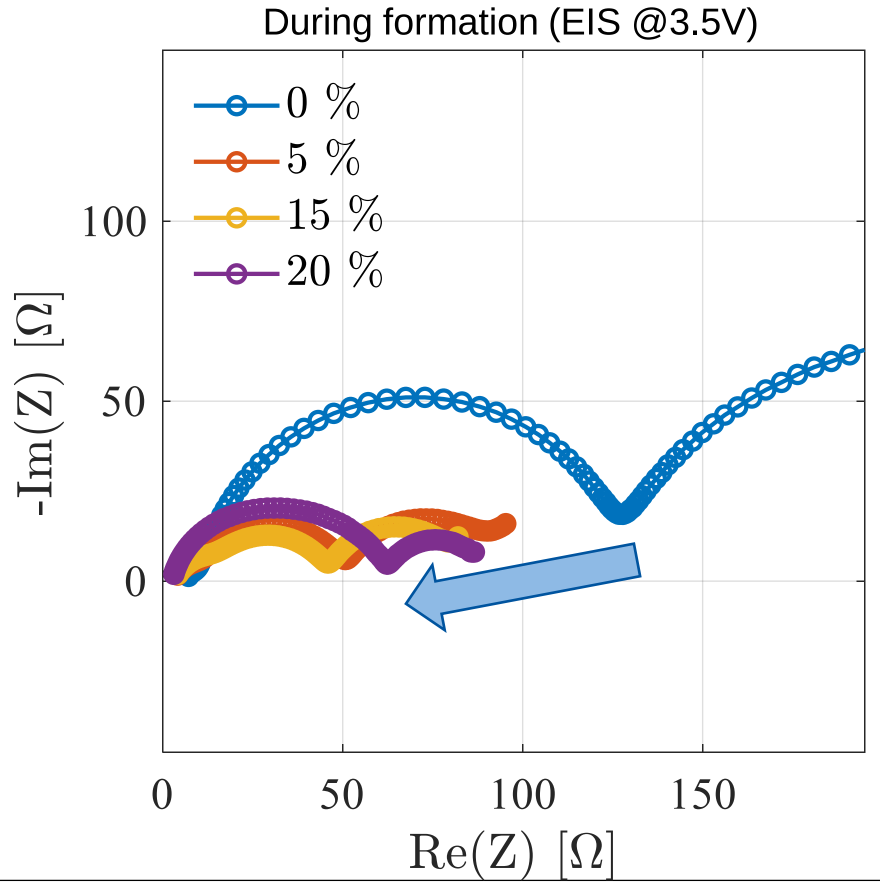
The structure change of the anode surface and cross-section with preLi were observed and compared.

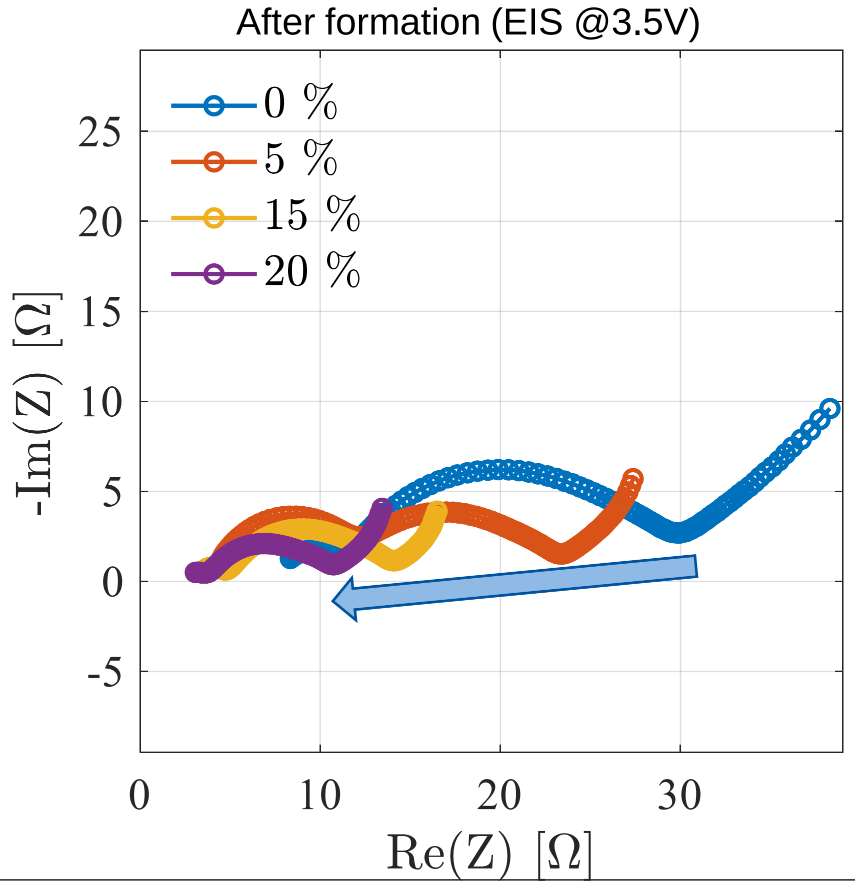
- □ The spaces between particles decreased as the preLi dosage increased.
- □ PreLi 5%: Instead of delamination, a greater contact between Si/Cu was observed.
- □ PreLi 10%: Thickness expansion and surface cracking occurred.
- □ A higher preLi degree causes greater expansion of the particles, resulting in increased stress on the anode.

Electrochemical Impedance Spectroscopy (EIS) – Coin cell (Electrolytic-Bath PreLi)

- The resistance improved because of the subsequent Li for SEI layer by preLi.
- PreLi demonstrated lower resistance even after formation.
- At 20% preLi, kinetics improved after the formation stage.

Full cell: pure Si || NMC622
Carbonated electrolyte
100 kHz – 80 mHz





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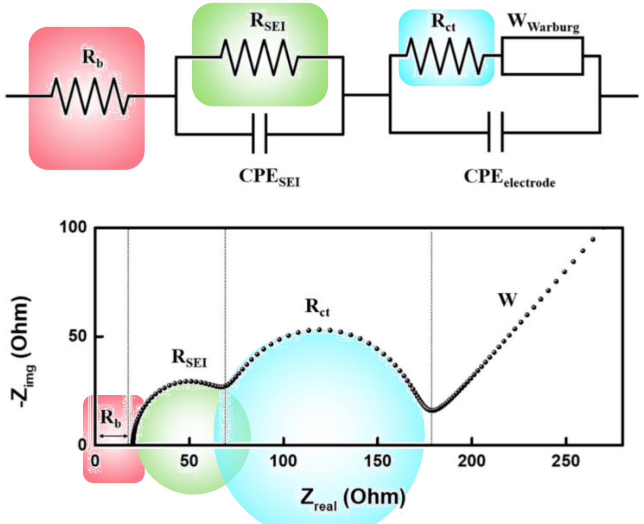
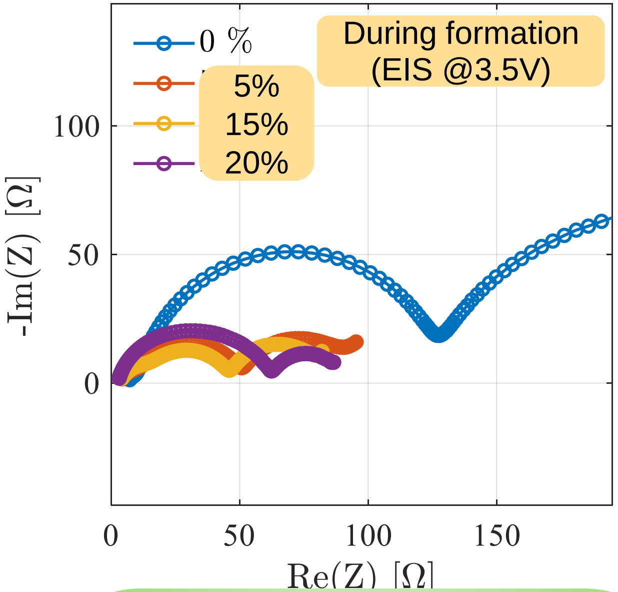
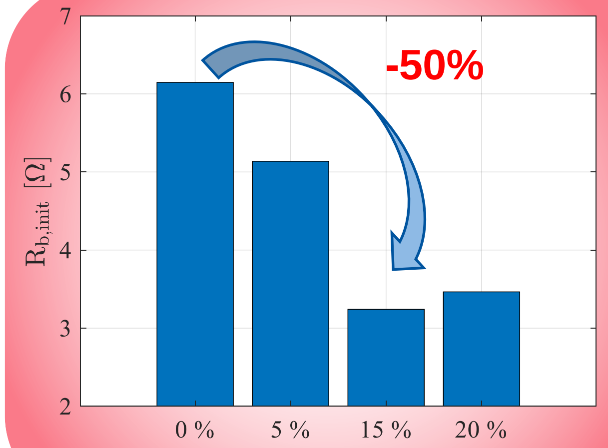


Image: Journal of Electrochemical Science and Technology

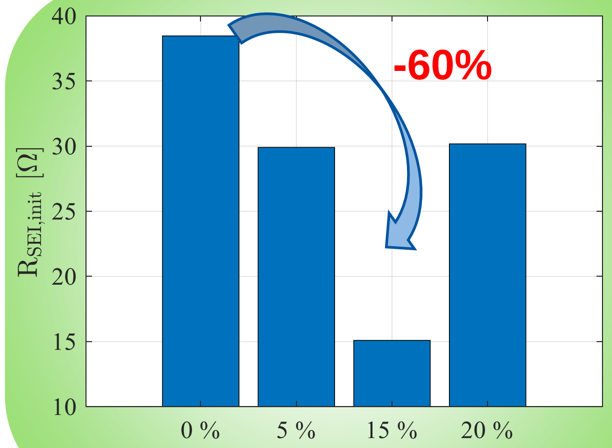


- The equivalent circuit model corresponds to the EIS Nyquist plot.
- Initial resistances showed improvement up to 15% preLi

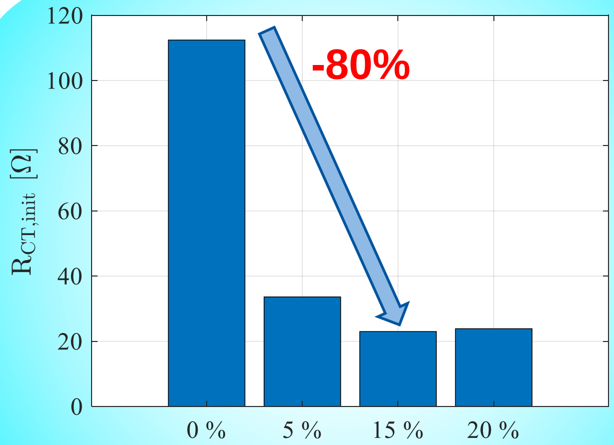
Full cell: pure Si || NMC622
Carbonated electrolyte
100 kHz – 80 mHz



Bulk Resistance (R_b)



SEI Resistance (R_{SEI})



Charge Transfer Resistance (R_{ct})

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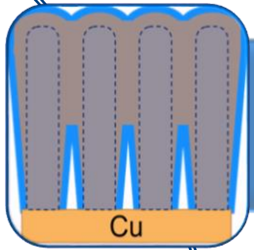

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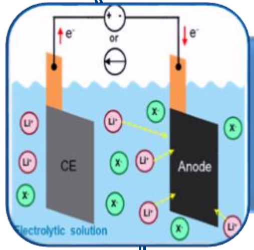

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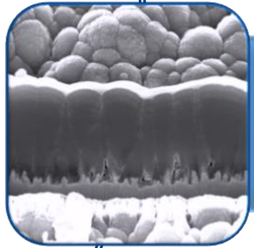

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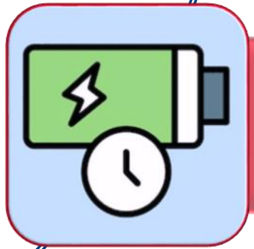
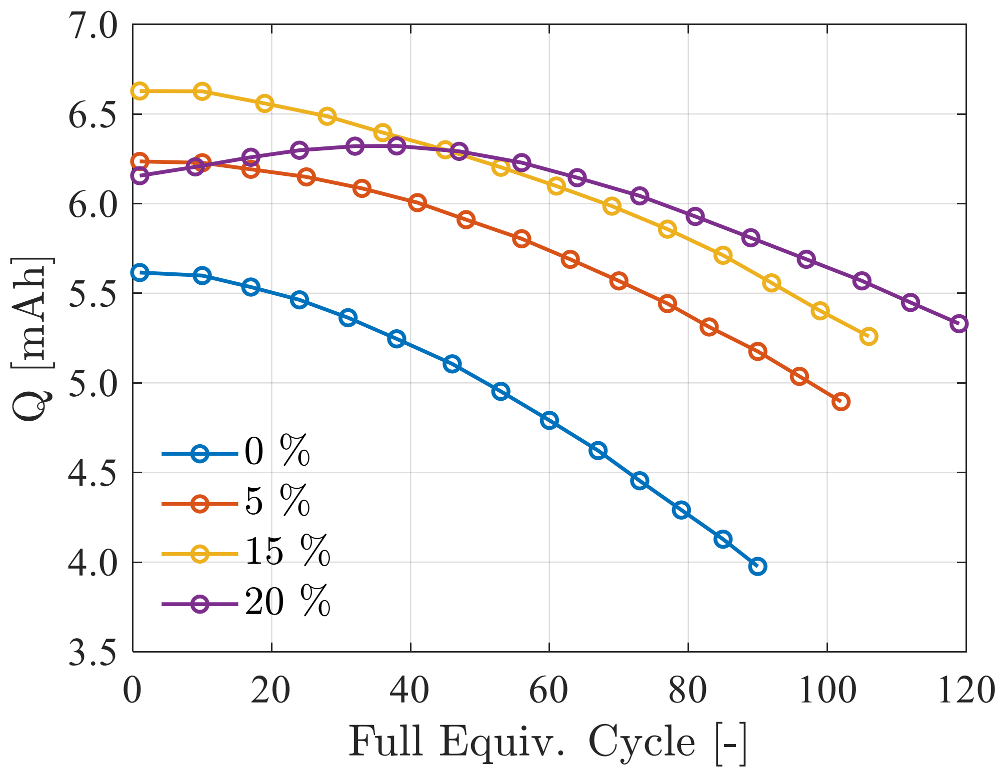


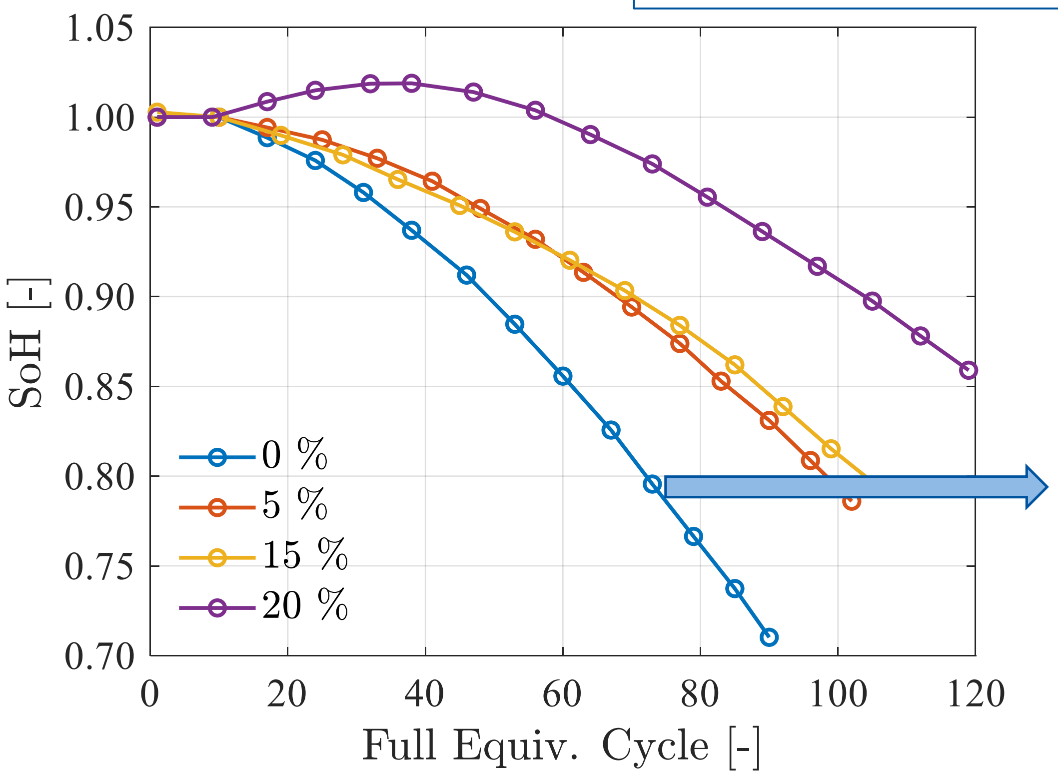
Experimental Results: Cycle Performance

Cycle Performance

- The initial capacity increased according to the Li dosage up to 15% preLi degree.
- Higher preLi degree improved cycling stability, trapped Li reactivated.
- With preLi, cells last significantly longer compared to without preLi

Full cell: pure Si || NMC622
Carbonated electrolyte
0.5 C CCCV Ch/ CC Dch, rest 30 min

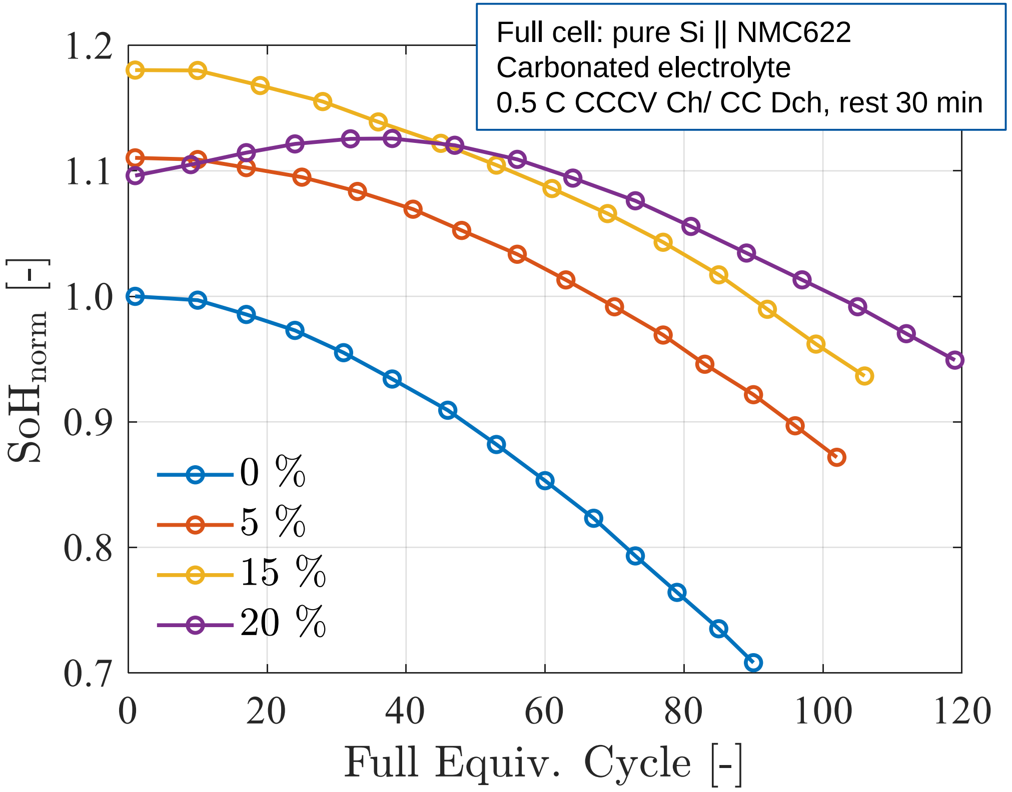


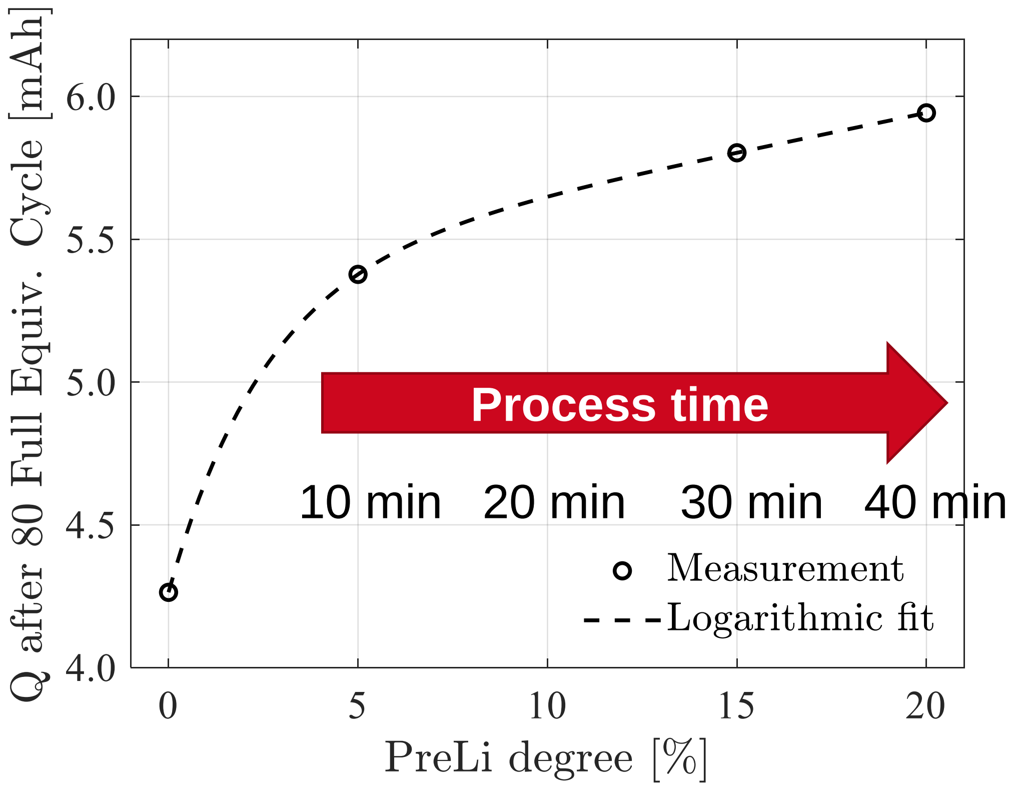


Degradation

- Normalized SoH is calculated based on the capacity without preLi
- After 80 full equiv. cycles, a logarithmic fit can be observed, with 5% as the optimum balance

☺Scaling up with the same current density ☹Increasing mass loading or preLi degree





Summary

- **Challenges:**
  - The precise control of the lithiation amount can still be discussed.
  - Reducing process time with optimum preLi protocol would be the key.
- **Current Progress:**
  - Dry-coated pure Si anode can be applied for the preLi.
  - Optimum preLi degree in initial and cycle performance were investigated.
- **Industrial Implications:**
  - Collaboration with industry to explore larger-scale manufacturing (greenSPEED)
  - Methods developed in coin cells can be **replicated at pouch-cell scale.**
- **Next Steps:**
  - Transitioning from experimental setups to pilot-scale production
  - Optimizing the preLi protocol to make the process faster and more efficient

Thank you for your attention

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