Elucidating the Effect of Pre-lithiation of Silicon Dominant Anodes on the Full Cell Performance

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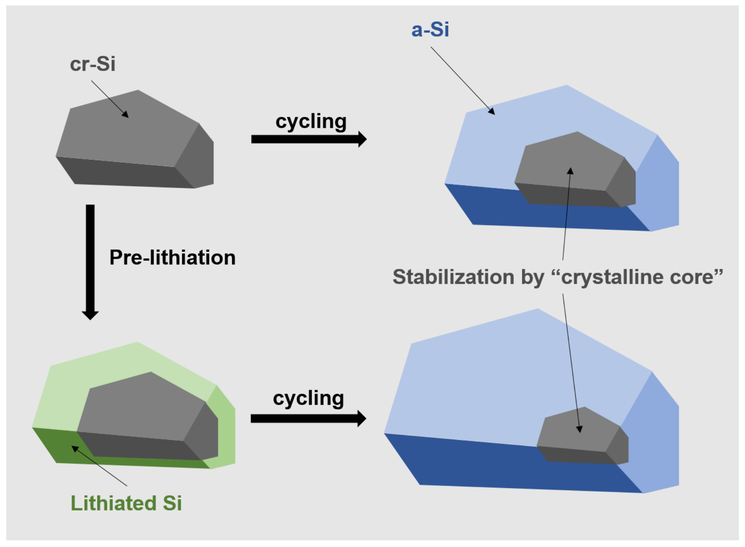
1 Motivation

- Over the last few years, there has been a **high interest in improving the energy density** of lithium-ion batteries (LIBs) in order to increase the driving range of battery electric vehicles. On a material level, silicon is a promising anode active material candidate due to its high theoretical capacity of 3579 mAh g^{-1} (~ten-fold higher than graphite with 372 mAh g^{-1}).[1]
- However, the lifetime of silicon based LIBs is limited by its intrinsic volume expansion of +300 % upon lithiation.[2] This leads to rupturing of the passivating solid-electrolyte interphase (SEI), particle cracking, and loss of electronic contact.
- Jantke *et al.* proposed the concept of **partial utilization of µm-sized crystalline silicon**, where only one-third of the theoretical capacity is used for (de)lithiation. Thereby, a crystalline core remains, and the volume expansion on the particle-level is reduced to approximately +100 %.[3]
- Further, it was shown that irreversible losses during the formation and upon cycling can be compensated by **pre-lithiation of the silicon anode**, which increases the lifetime significantly.[4,5]



2 Experimental Setup

Scope:

- In this study, we investigated a promising cell chemistry for high-energy density applications, containing a **Si-dominant** anode and a cathode based on a **Co-free lithium- and manganese-rich NMC**

Pre-lithiation in coin half-cell:

- As the reference cells show a poor capacity retention, the Li-inventory was systematically increased by **electrochemical pre-lithiation** to elucidate aging phenomena in the full-cells

Half-cell:

Anode:
69.9 % Si, 19.9 % Graphite, 8 % Li-PAA, 2 % C_{65} and 0.2 % Na-CMC

Counter electrode:
Lithium metal disc

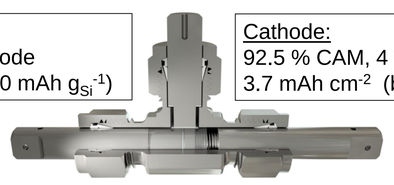
1) Lithiation at *C*/10 to 300, 600 or 900 mAh g_{Si}^{-1}

2) Disassembly and harvesting of the silicon anodes

Full-cell:

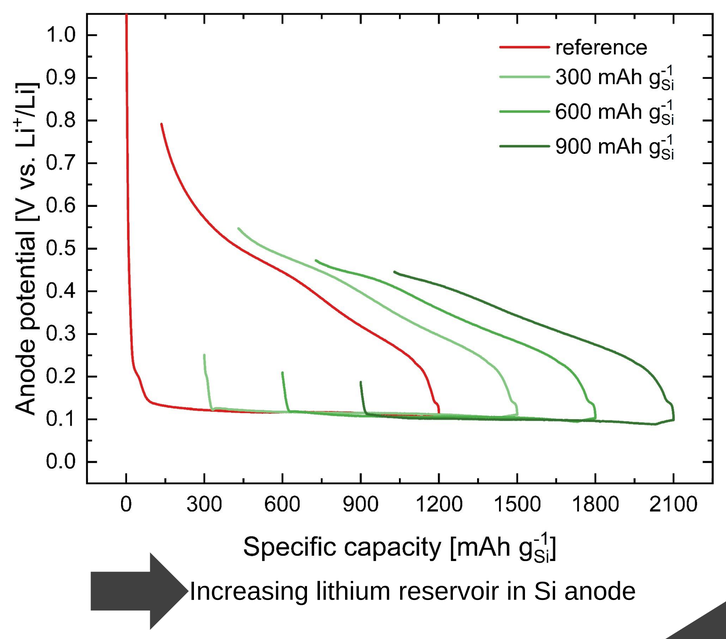
Lithum metal reference

Anode:
Pristine or pre-lithiated Si anode
3.7 mAh cm^{-2} (based on 1200 mAh g_{Si}^{-1})



Cathode:
92.5 % CAM, 4 % C65 and 3.5 % PVDF
3.7 mAh cm^{-2} (based on 250 mAh g_{CAM}^{-1})

2 glass fiber separators
90 µl 1 M $LiPF_6$ in FEC:DEC (1:4; v:v)



3 Cell Aging

Procedure:

Activation:	2.0 – 4.7 V | 1x 0.1*C*
Cycling:	2.0 – 4.5 V | 45x 0.5*C*
Check-Up:	2x 0.1*C*, DCIR at 3.7 V for 1 s, 2x 0.5*C*|2*C*

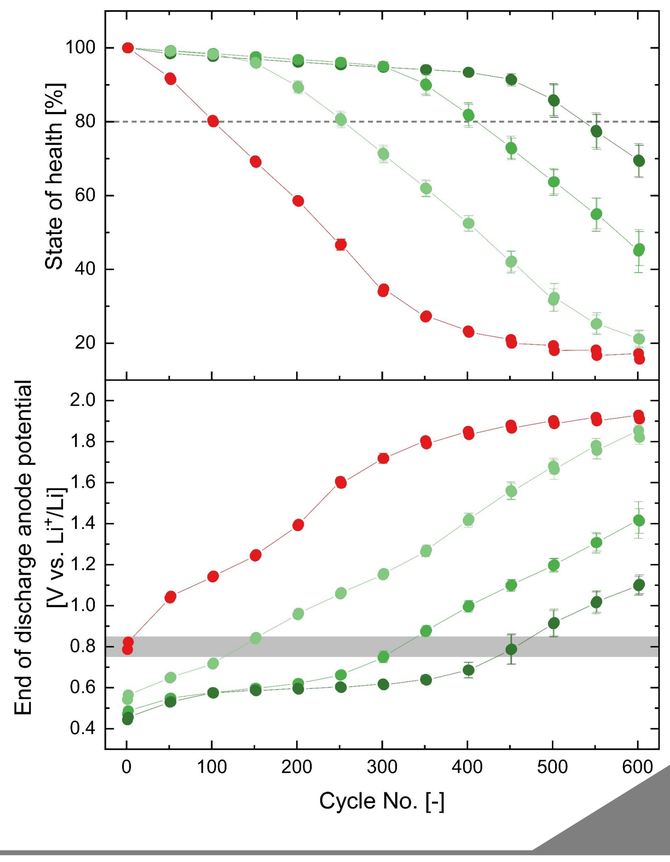
Cycling:

- Rapid capacity fading for reference (80 %SOH after ~100 cycles)
- Improved lifetime for pre-lithiated cells

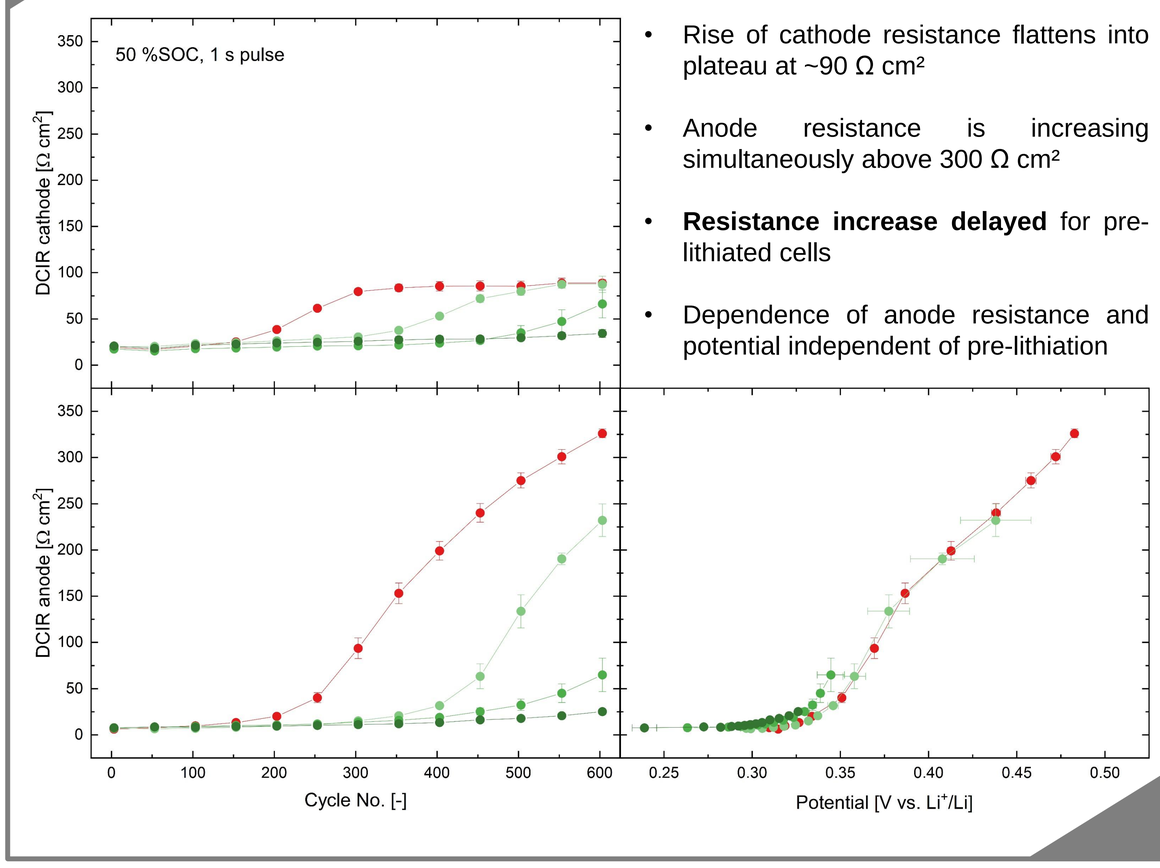
End of discharge potential:

- Increasing EoD potential over aging.
- ➢ Consumption of Li-reservoir
- Lower EoD anode potential for pre-lithiated cells and delayed increase for higher degree of pre-lithiation

Loss of lithium inventory is the dominating aging mechanism



4 Resistance Analysis



- Rise of cathode resistance flattens into plateau at ~90 Ω cm²
- Anode resistance is increasing simultaneously above 300 Ω cm²
- **Resistance increase delayed** for pre-lithiated cells
- Dependence of anode resistance and potential independent of pre-lithiation

5 Conclusion

- Rise in end of discharge anode potential reveals **loss of lithium inventory** as dominating aging mechanism
  - ➢ Stable cycling below 800 mV vs. Li^+/Li
- Lifetime can be **successively improved** by electrochemical pre-lithiation
  - ➢ + 150 cyc. for every 25 % pre-lithiation
- Higher resistance increase for anode compared to cathode
  - ➢ Both are dependent on Li-inventory
- Anode resistance **mainly influenced by the degree of lithiation** rather than cycle number

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References

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