

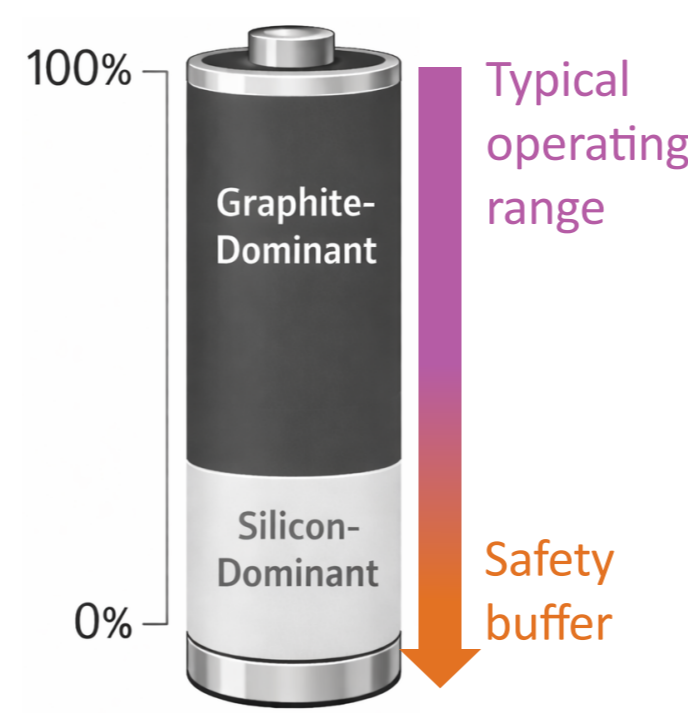
Enormous Increase in the Lifetime of Lithium-Ion Batteries with Silicon-Graphite Blend Electrodes by Partial Use of Silicon

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Motivation and Introduction

- ▶ Adding silicon to graphite anodes increases the energy density, but leads to **higher degradation** due to volume expansion of silicon of over 300% [1].
- ▶ Silicon is **predominantly used at low full-cell SOC**s due to the higher potential vs Li/Li⁺ of silicon compared to graphite [2].
- ▶ In mobile applications, especially flight applications, the cells are **rarely completely discharged** as the low SOC region serves mainly as a safety buffer.
- ▶ Avoiding fully delithiation of silicon reduces aging. However, correlation between usage of silicon capacity and additional aging is not known yet.



Main findings

- ▶ **Partial use of silicon** capacity does not lead to increased aging of the full-cell up to a certain threshold (1/3 of its capacity), using only 2/3 of the silicon capacity still at least doubles lifetime compared to full usage (disch. to 0% SOC).
- ▶ With increasing degree of usage of silicon both loss of active silicon and loss of lithium increase in a **strongly nonlinear way**.
- ▶ **Sporadic usage of silicon** does not lead to strong additional aging.
- ▶ Two cell types with different silicon contents show **transferability** of the results to cells with different silicon contents.

Test matrix

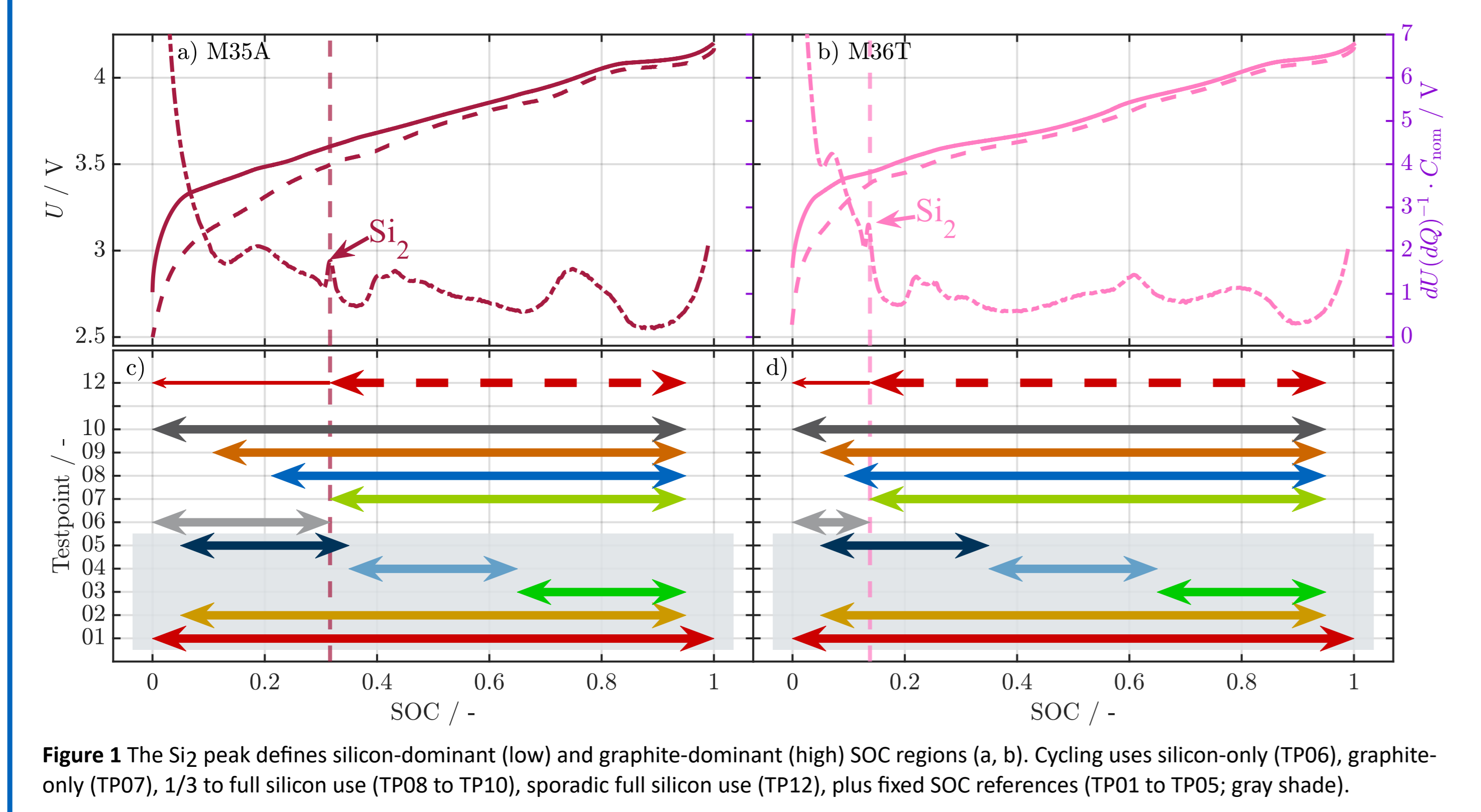


Figure 1 The Si₂ peak defines silicon-dominant (low) and graphite-dominant (high) SOC regions (a, b). Cycling uses silicon-only (TP06), graphite-only (TP07), 1/3 to full silicon use (TP08 to TP10), sporadic full silicon use (TP12), plus fixed SOC references (TP01 to TP05; gray shade).

Experimental

- ▶ A total of **63 cells** were cyclically aged over 1600 equivalent full cycles (EFC), additional 144 cells were calendar aged as reference.
- ▶ Two 18650 cell types with different silicon contents, namely **Molicec M35A** and **LG M36T** were used. Cyclic aging was done with C/2 CCCV for charge and discharge.
- ▶ The anodic capacity provided by silicon is **~30% for the M35A** (~8 wt% SiO_x) and **~15% for the M36T** (~3 wt% SiO_x).
- ▶ Based on the Si₂-peak in the DV of the discharge pOCV, the SOC is split into a **silicon-dominant region** (low SOC) and a **graphite-dominant region**.
- ▶ Cyclic tests are performed at fixed SOC (TP01 to TP05) as reference.
- ▶ To quantify impact of partial silicon use, cells are cycled starting from 95% SOC in the graphite-dominant region (TP07) and then using one third, two thirds, or all of silicon capacity (TP08 to TP10).
- ▶ **Occasional use** of silicon (19 cycles TP07; one cycle TP10) to show path dependency of silicon usage (TP12).
- ▶ **Degradation mode analysis (DMA)** separating silicon and graphite losses [3].
- framework available at <https://github.com/tum-ees/DegradationModeAnalysis>

Impact of (partial) silicon usage

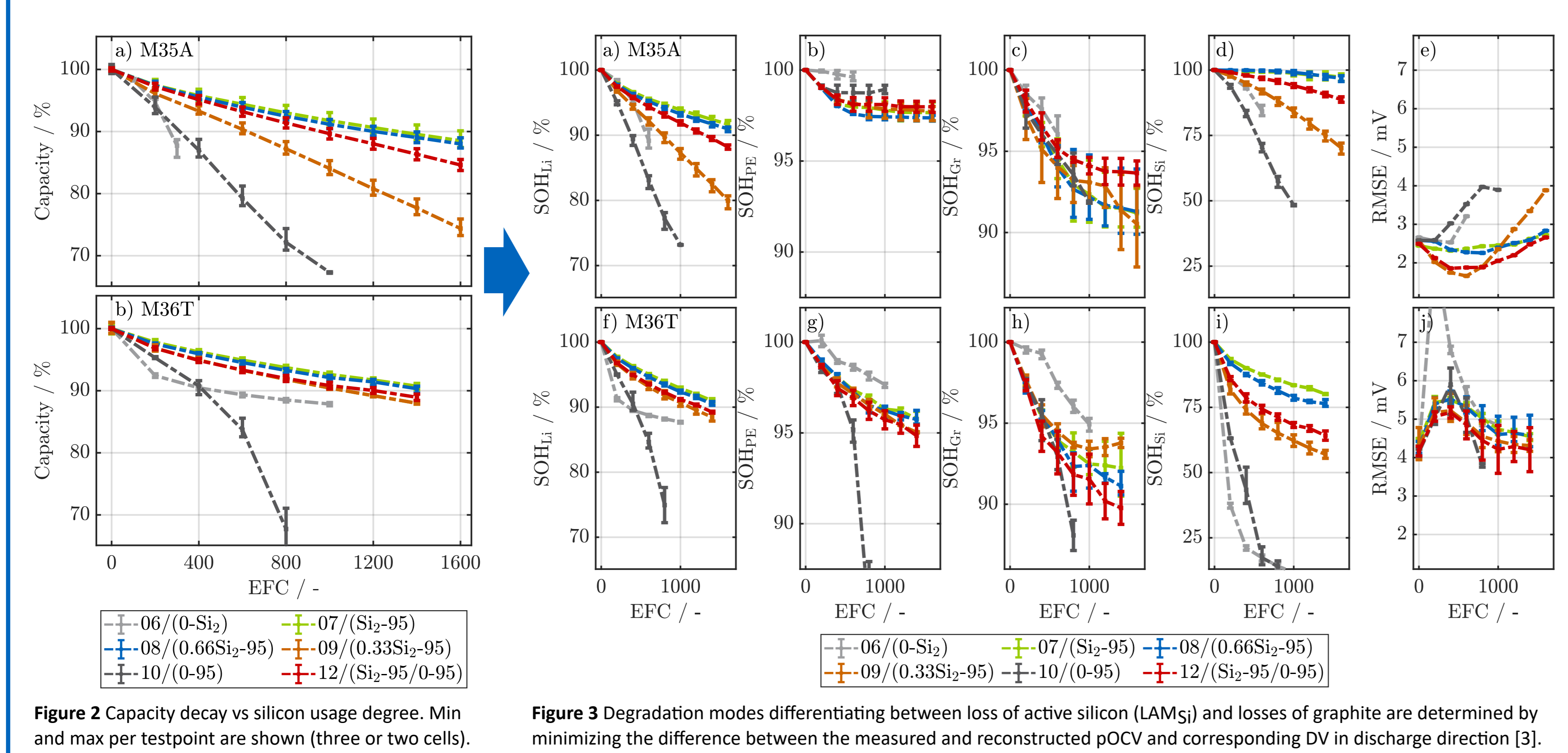


Figure 2 Capacity decay vs silicon usage degree. Min and max per testpoint are shown (three or two cells).

Figure 3 Degradation modes differentiating between loss of active silicon (LAM_{Si}) and losses of graphite are determined by minimizing the difference between the measured and reconstructed pOCV and corresponding DV in discharge direction [3].

Parameterization

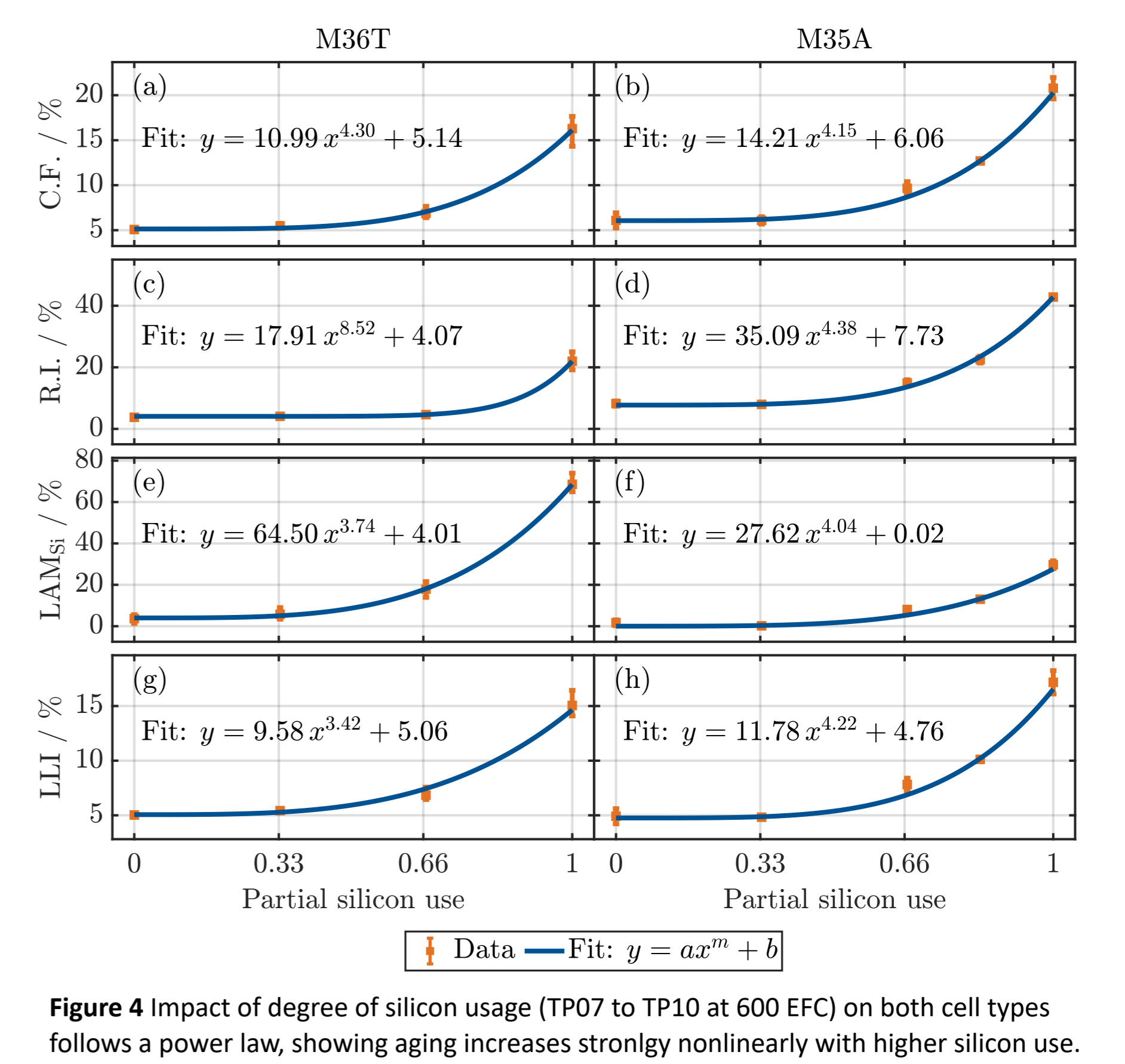


Figure 4 Impact of degree of silicon usage (TP07 to TP10 at 600 EFC) on both cell types follows a power law, showing aging increases strongly nonlinearly with higher silicon use.

Resistance increase

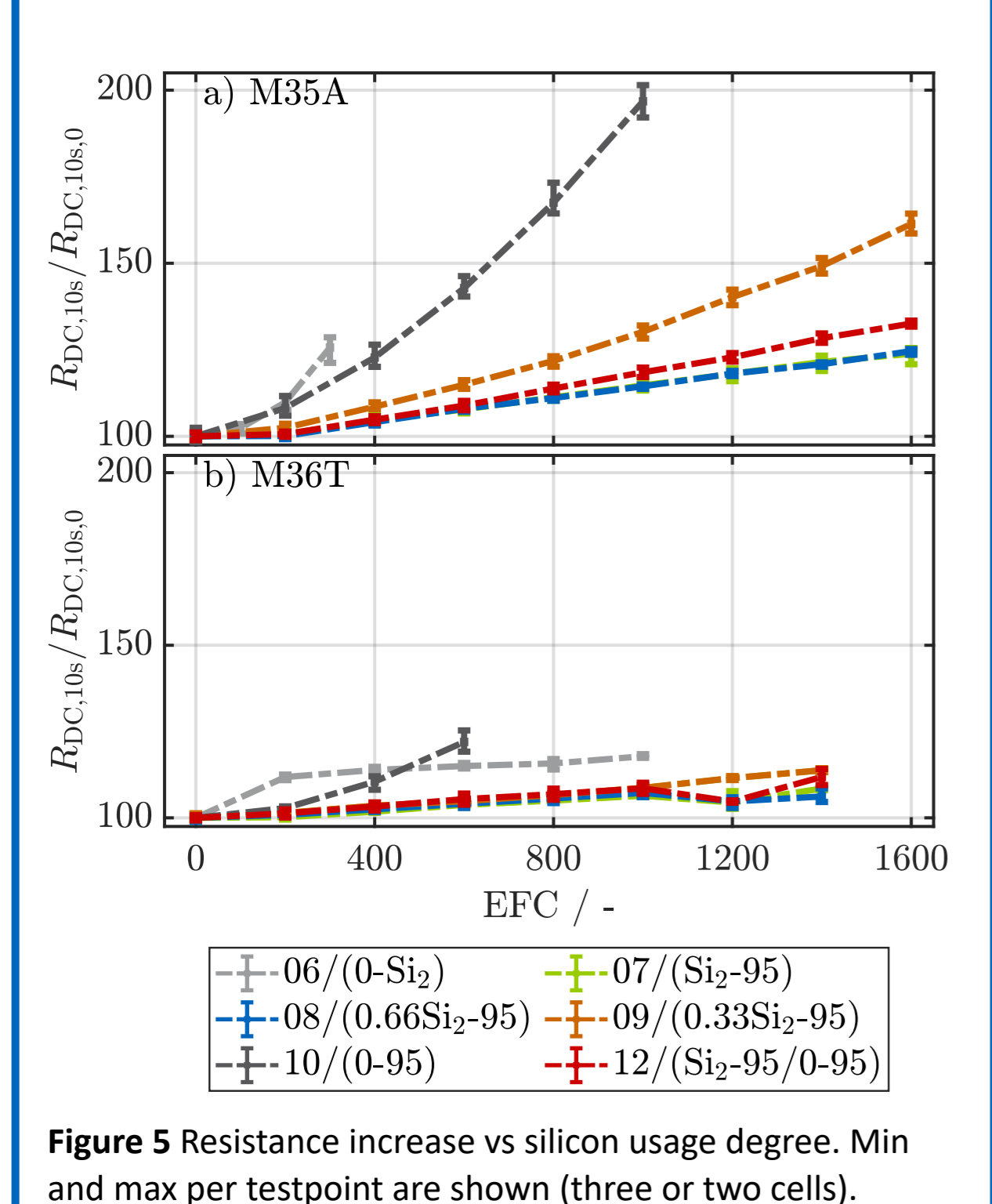


Figure 5 Resistance increase vs silicon usage degree. Min and max per testpoint are shown (three or two cells).

Reference tests

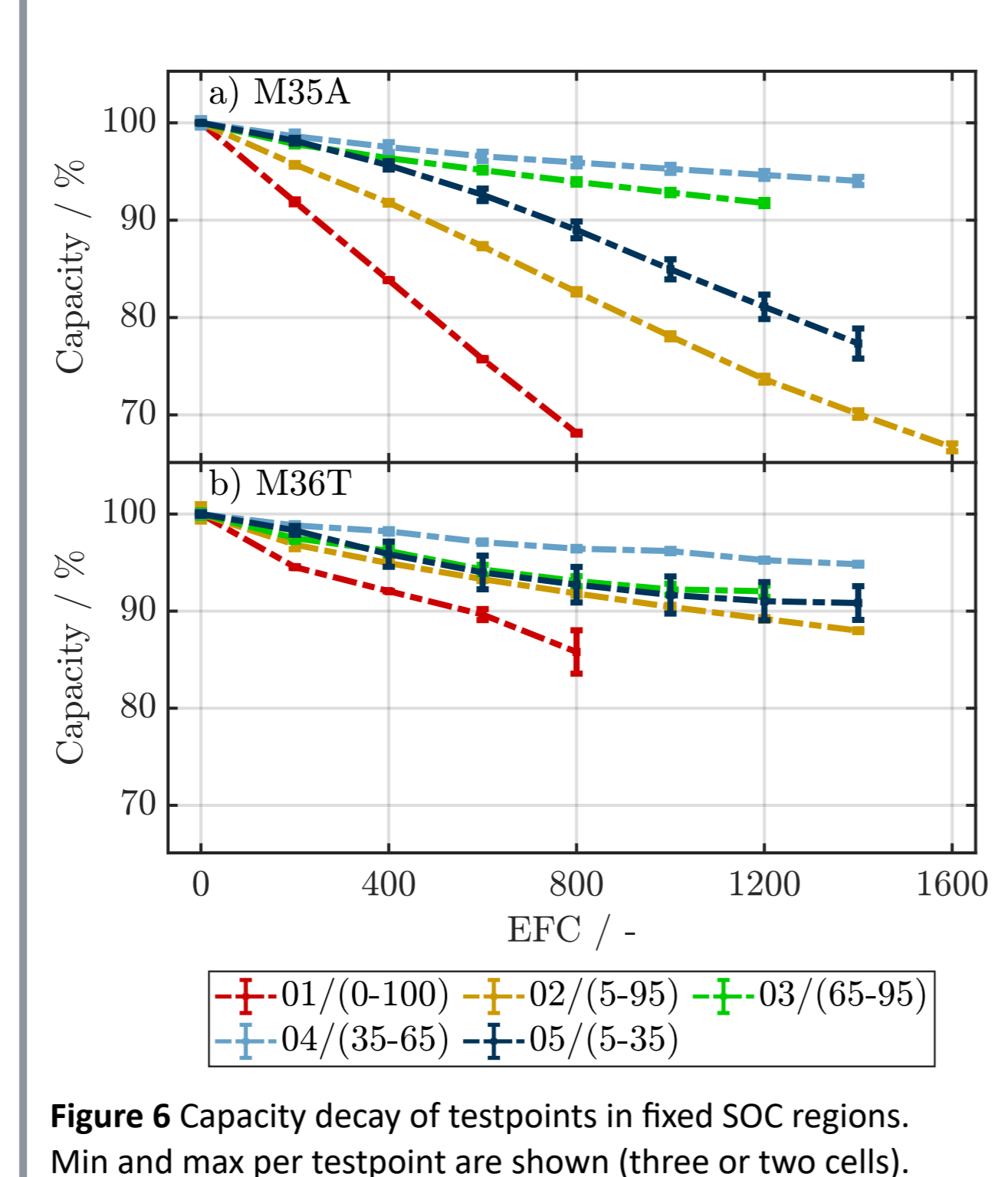


Figure 6 Capacity decay of testpoints in fixed SOC regions. Min and max per testpoint are shown (three or two cells).

Discussion

- ▶ Two cell types with different silicon contents confirm **transferability to other silicon contents**.
- ▶ **Using only part of the silicon capacity** strongly reduces aging: 1/3 silicon capacity usage adds negligible fade (TP08 vs TP07), while using 2/3 of silicon capacity (TP09, 10-95% SOC for M35A, 5-95% SOC for M36T) still doubles lifetime vs full discharge (TP10).
- ▶ As silicon use increases, **capacity fade rises nonlinearly**. DMA links it to added LLI with strong LAM_{Si} driving the fade.
- ▶ Capacity fade, LAM, and LLI scale with silicon capacity use via a power law in **both cell types with similar exponents** (here shown for 600 EFC).
- ▶ **Sporadic discharge** (each 20th cycle) to end-of-discharge voltage does not lead to strong additional LLI or LAM.

Outlook

- ▶ Parameterization will be used for more **precise modeling** of aging of LIBs with silicon-containing anodes in PyBaMM.

Supported by:



on the basis of a decision by the German Bundestag

References

- [1] Kirkaldy, N.; Samieian, M. A.; Offer, G. J.; Marinescu, M.; Patel, Y. Lithium Ion Battery Degradation: Measuring Rapid Loss of Active Silicon in Silicon Graphite Composite Electrodes. *ACS Applied Energy Materials* **2022**, *5*, 13367–13376. doi: 10.1021/acsaem.2c02047
- [2] Ai, W.; Kirkaldy, N.; Jiang, Y.; Offer, G.; Wang, H.; Wu, B. A Composite Electrode Model for Lithium Ion Batteries with Silicon Graphite Negative Electrodes. *Journal of Power Sources* **2022**, *527*, 231142. doi:10.1016/j.jpowsour.2022.231142.
- [3] Rehm, M.; Natterer, J.; Eizenhammer, J.; Guenther, M.; Korkmaz, C.; Roehrer, F.; Jossen, A. How to determine the degradation modes of lithium-ion batteries with silicon-graphite blend electrodes. *Preprint* **2025**, doi:10.2139/ssrn.5958815.

Acknowledgements

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