

Explaining the Voltage Hysteresis and Slow Relaxation of Silicon Nanoparticles with a Chemo-Mechanical Particle-SEI Model

Lukas Köbbing, Arnulf Latz, Birger Horstmann

German Aerospace Center (DLR), Wilhelm-Runge-Straße 10, 89081 Ulm, Germany

Helmholtz Institute Ulm (HIU), Helmholtzstraße 11, 89081 Ulm, Germany

Ulm University, Faculty of Natural Sciences, Albert-Einstein-Allee 47, 89081 Ulm, Germany

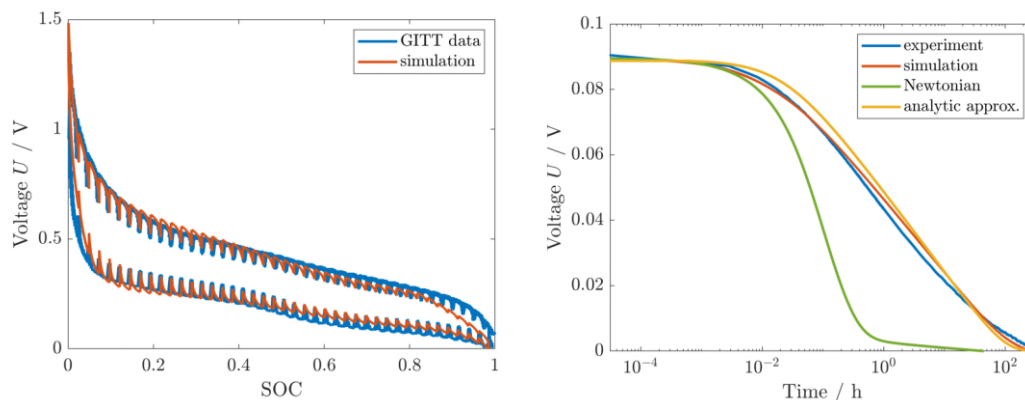
lukas.koebbing@dlr.de

Silicon is widely considered to be a promising next-generation anode material, primarily due to its remarkably high theoretical capacity. Furthermore, silicon is an abundant, cheap, and widely spread material. However, a major challenge for the commercialization of silicon anodes is the significant voltage hysteresis reducing efficiency and leading to detrimental heat generation during fast-charging. Additionally, the hysteresis causes an unclear state-of-charge (SOC) to voltage relation impeding precise SOC estimation.

The voltage hysteresis behavior of silicon anodes is addressed in literature with three different arguments: phase transformations, plastic flow of silicon, and slow diffusion. These approaches can interpret the voltage hysteresis of crystalline silicon, thin films, and large anode particles, respectively. Nevertheless, we show that they cannot explain the hysteresis observed for silicon anodes consisting of amorphous nanoparticles, the relevant material for next-generation lithium-ion batteries.

Our investigation highlights the chemo-mechanical interplay between the silicon nanoparticle and the covering Solid-Electrolyte Interphase (SEI) as the underlying cause for the significant voltage hysteresis. The SEI, a thin passivating layer, forms on negative electrode particles due to electrolyte decomposition [1]. In the case of silicon particles, the volume changes during lithiation and delithiation result in massive strains and plastic deformation occurring within the SEI [2]. Our chemo-mechanical particle-SEI description successfully replicates the observed open-circuit voltage hysteresis in experiments and aligns with the Plett model [3]. Moreover, our visco-elastoplastic SEI model reproduces the voltage difference between slow cycling and the relaxed open-circuit voltage. In our recent work, we show that a sophisticated mechanical model explains the slow voltage relaxation observed for silicon nanoparticles as well as the observed C rate dependence [4].

To conclude, we explain the voltage hysteresis and the slow voltage relaxation of silicon nanoparticles with a visco-elastoplastic particle-SEI model and discuss options to mitigate the size of the voltage hysteresis. This detailed physical understanding can improve the performance of all-silicon anodes and contribute to their commercialization.



[1] Köbbing, L.; Latz, A.; Horstmann, B. *J. Power Sources* **2023**, DOI: 10.1016/j.jpowsour.2023.232651.

[2] Kolzenberg, L.; Latz, A.; Horstmann, B. *Batter. Supercaps* **2022**, DOI: 10.1002/batt.202100216.

[3] Köbbing, L.; Latz, A.; Horstmann, B. *Adv. Funct. Mater.* **2024**, DOI: 10.1002/adfm.202308818.

[4] Köbbing, L.; Latz, A.; Horstmann, B. *ArXiv* **2024**, DOI: 10.48550/arXiv.2408.01106.