Chemo-Mechanical Core-Shell Model Explaining the Silicon Voltage Hysteresis and Long-Term Relaxation

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Silicon is considered as next-generation anode material for lithium-ion batteries owing to the tenfold increase in theoretical capacity compared to graphite anodes. However, beneath the significant volume expansion of silicon during lithiation, the silicon voltage hysteresis represents a major challenge for the commercial use. The hysteresis causes a reduced efficiency, detrimental heat generation, and complicates the state-of-charge estimation. Our contribution elucidates the reason of the voltage hysteresis phenomenon and identifies approaches to overcome the related limitations.

We developed a chemo-mechanical model accounting for the interaction between active silicon and a surrounding inactive phase in a core-shell geometry. The shell can be considered as solid-electrolyte interphase (SEI), inactive silicon domains, or silicon oxide. The volume changes of the active silicon during cycling cause significant stresses inside the shell, resulting in pronounced degradation [1]. Simultaneously, the visco-elastoplastic shell implies stress to the silicon particle, impacting the chemo-mechanical potential. Therefore, our model reproduces the experimentally observed silicon voltage hysteresis during cycling and after short-term relaxation [2]. Moreover, a recent improvement of our mechanical model allows to describe the long-term, logarithmic voltage relaxation over weeks [3]. Hence, our modeling approach reproduces the observed silicon voltage hysteresis and relaxation consistently. In addition, we derived a reduced hysteresis model, which outperforms the empirical Plett model in terms of physical interpretability and voltage predictions during relaxation.

In conclusion, we explain the silicon voltage hysteresis and long-term relaxation with a visco-elastoplastic core-shell model. Our physical understanding supports the improvement of the performance and state estimation of pure silicon anodes desired for future applications.

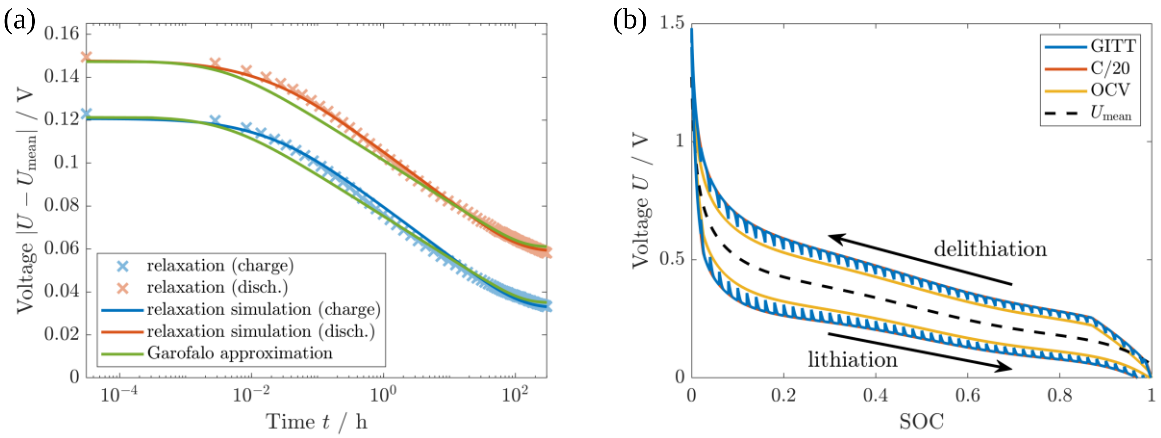

Figure 1: (a) Long-term voltage relaxation in simulation and experiment. (b) Voltage hysteresis during cycling and after relaxation predicted by the reduced hysteresis model. Reprinted from Ref. [3].

References:
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