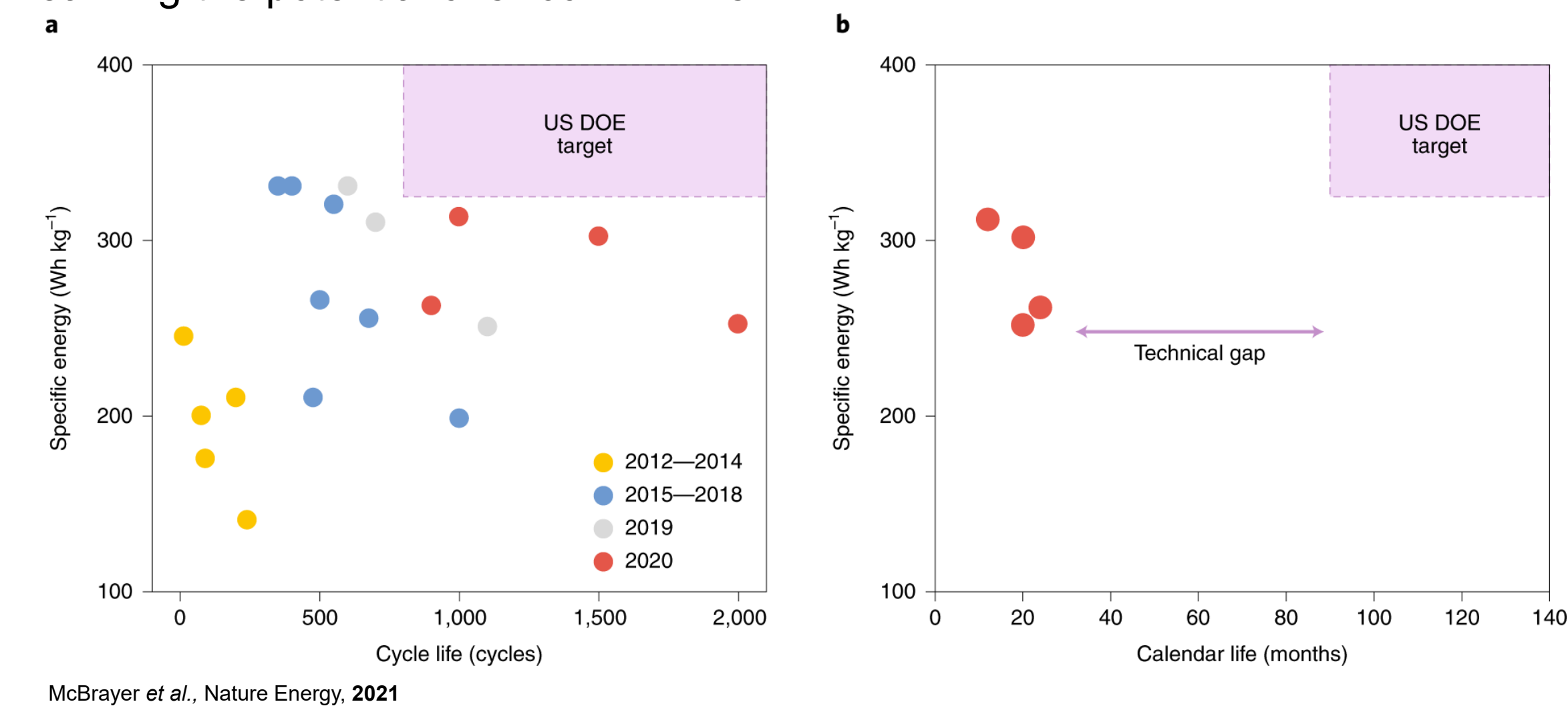
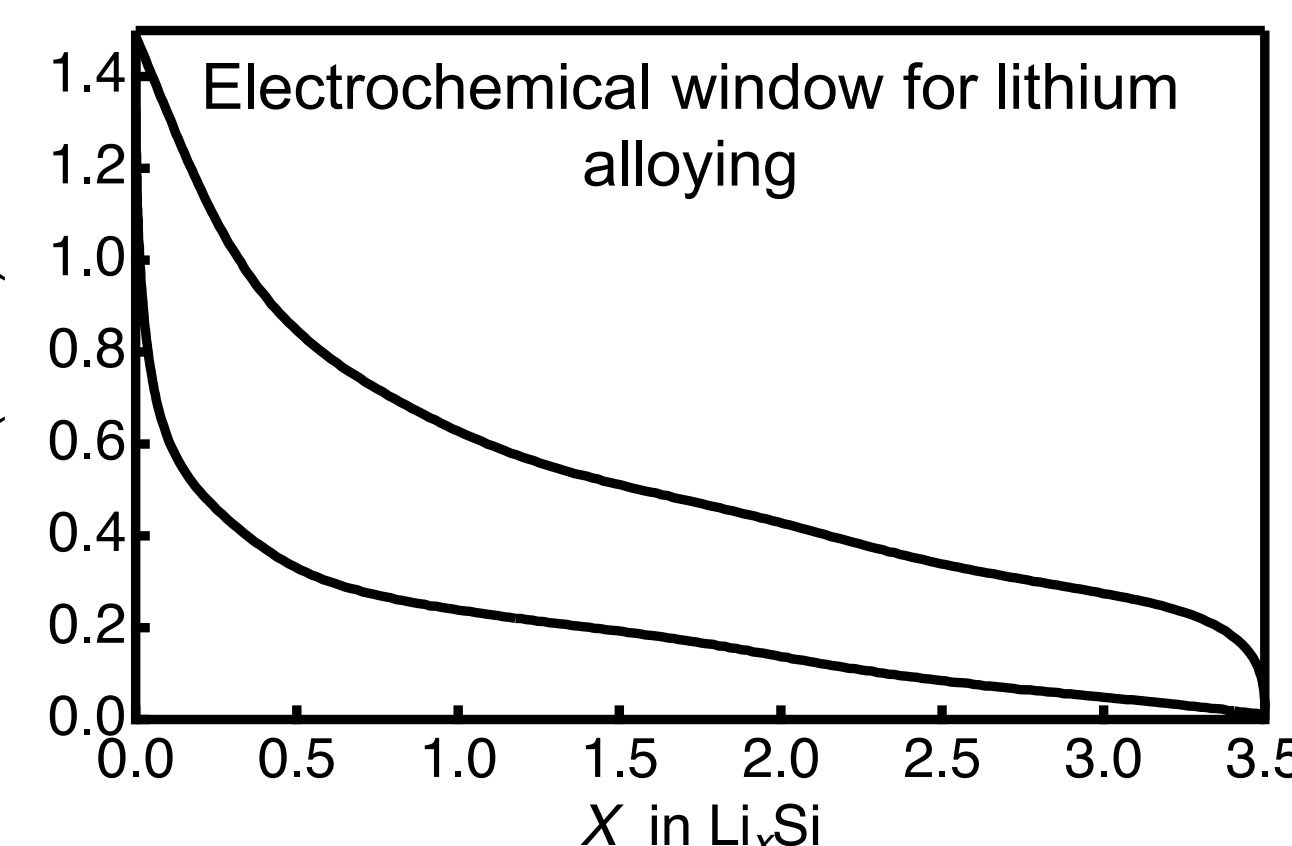


Introduction

Chemical reactivity of silicon-based Li-ion battery electrodes has kept the high energy density material from making a large impact on Li-ion batteries. Specifically, the degradation that occurs over time (calendar-life) is *the* central challenge to realizing the potential of silicon in LIBs.

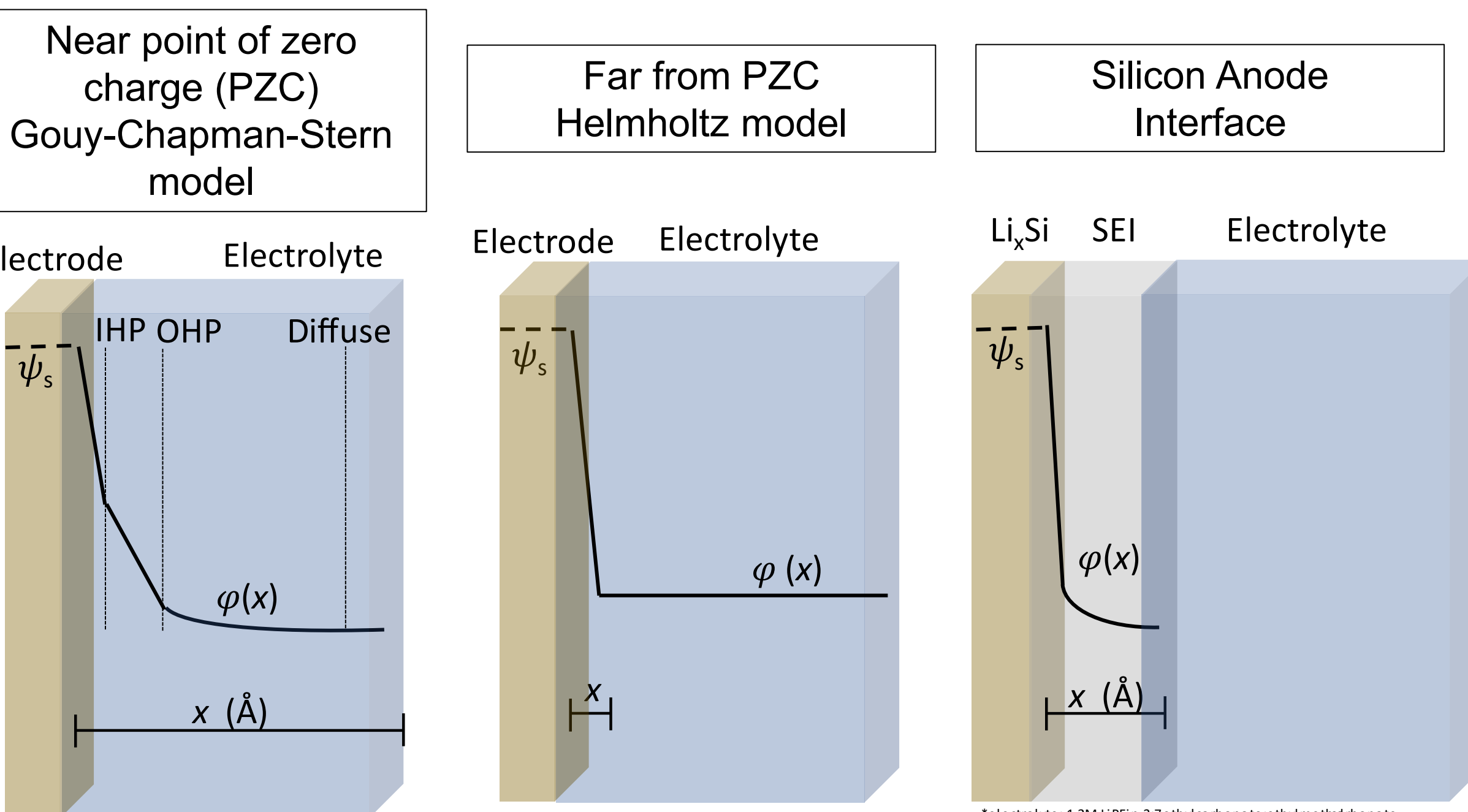


To realize the entire capacity of silicon, the voltametric range of silicon is 1.49V to (0.01 – 1.5V vs Li). Within this broad range, silicon, and its interface cycles between Si^0 and $\text{Li}_{3.5}\text{Si}$. We hypothesize that within this voltage range, the SEI passivation is reduced at certain potentials which can be understood through classical electrochemical interface theory.



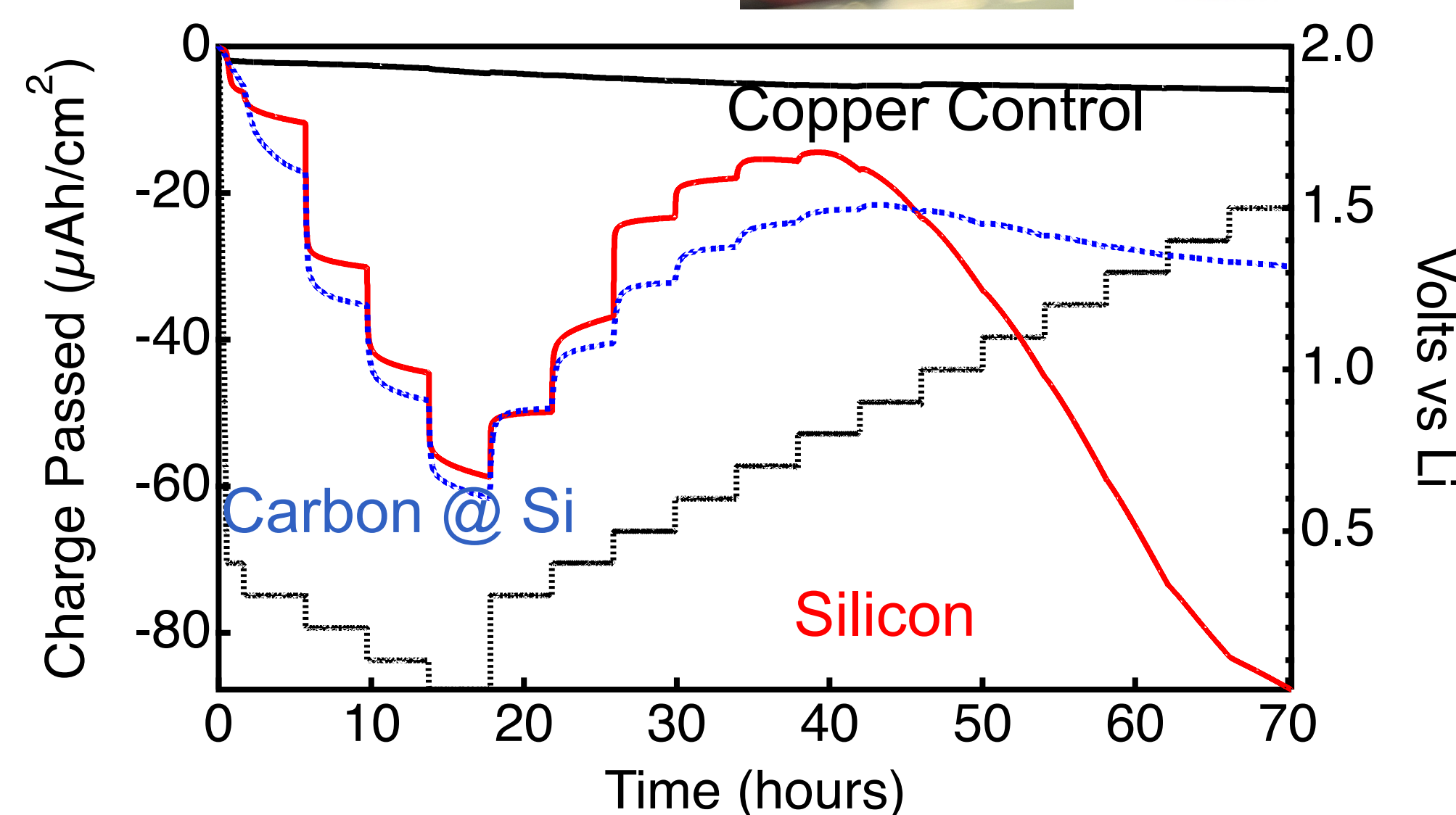
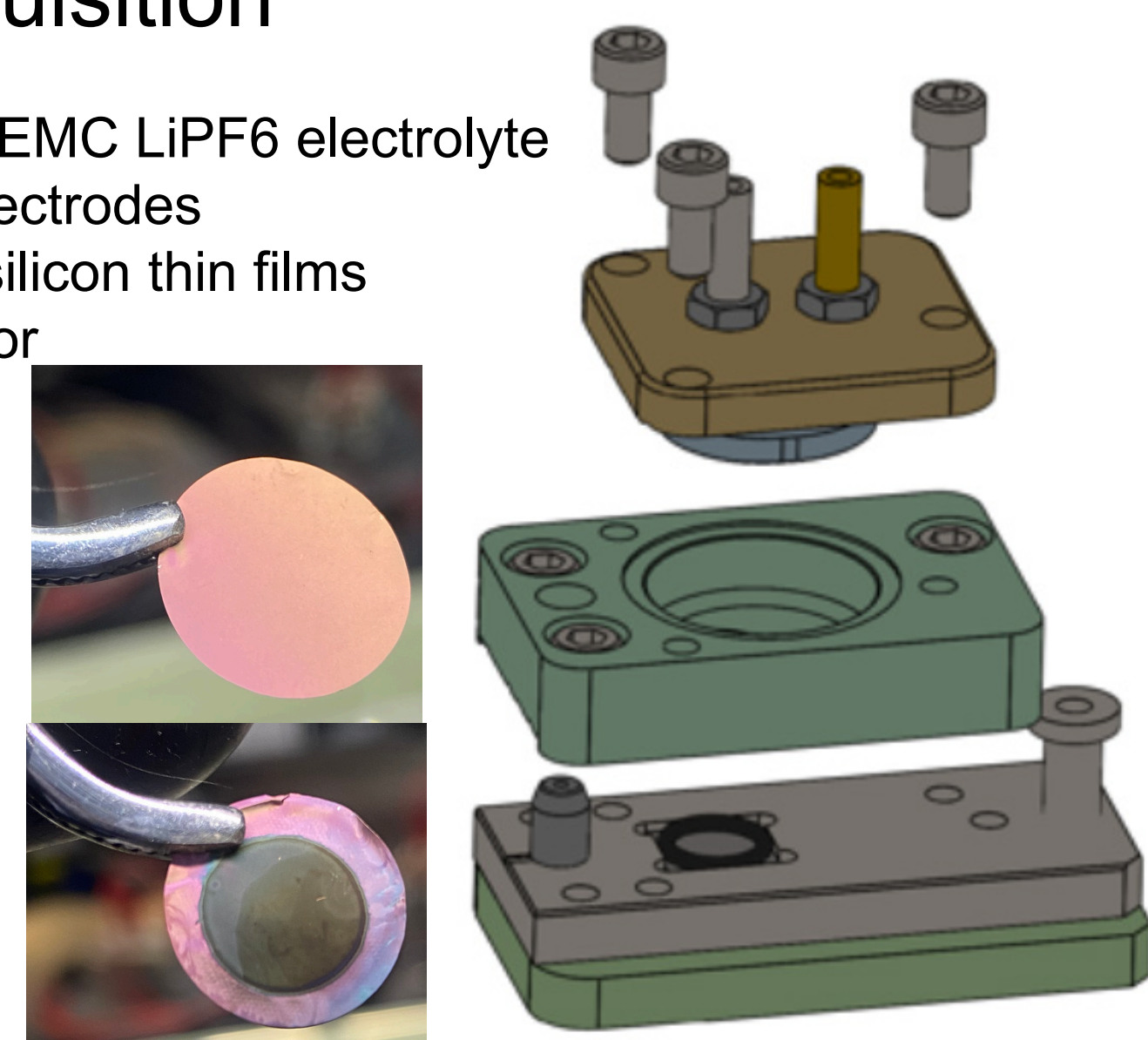
Approach

Use the traditional Gouy-Chapman-Stern model of electrochemical interfaces to understand complex silicon anode interface at different states of charge.

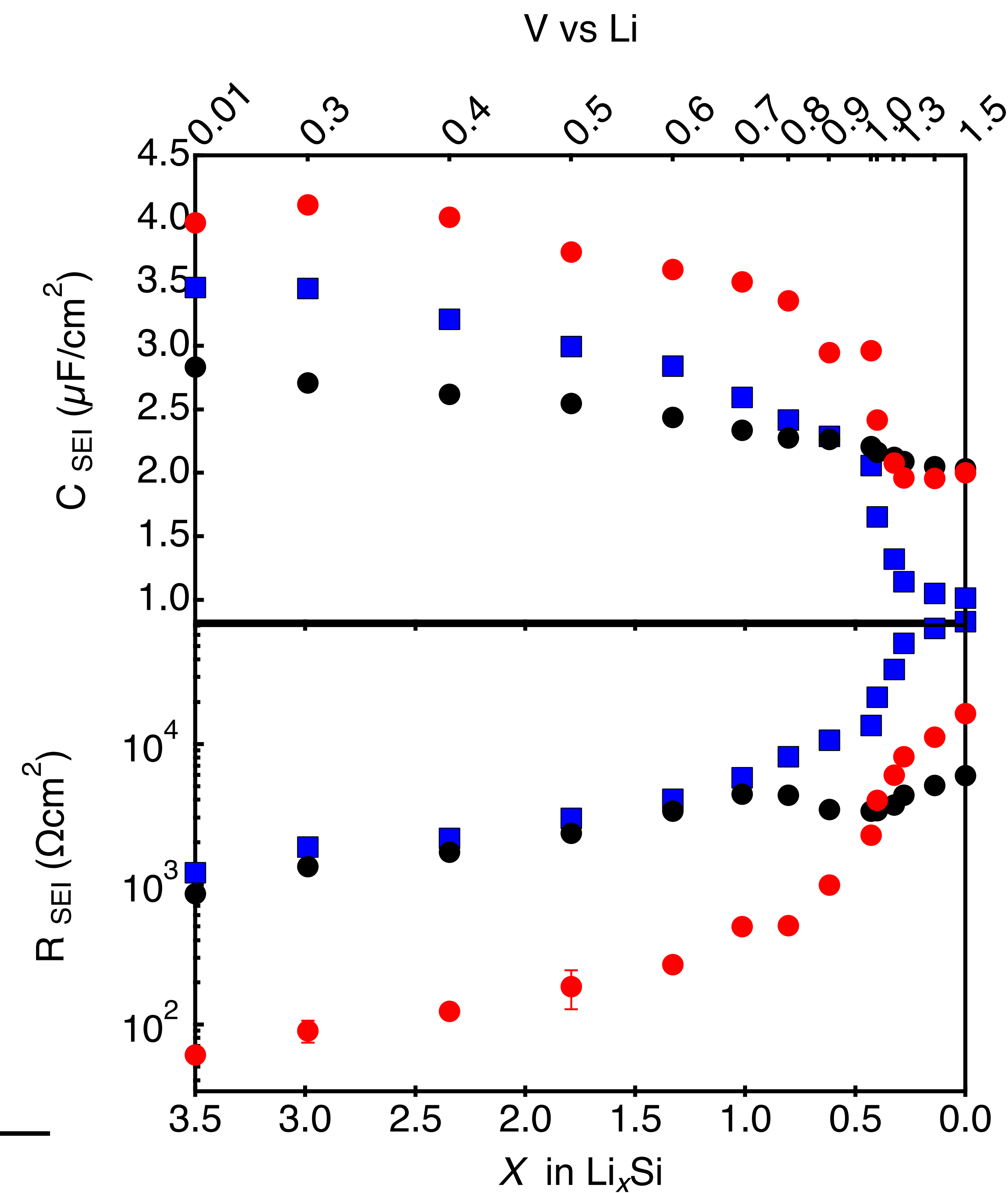
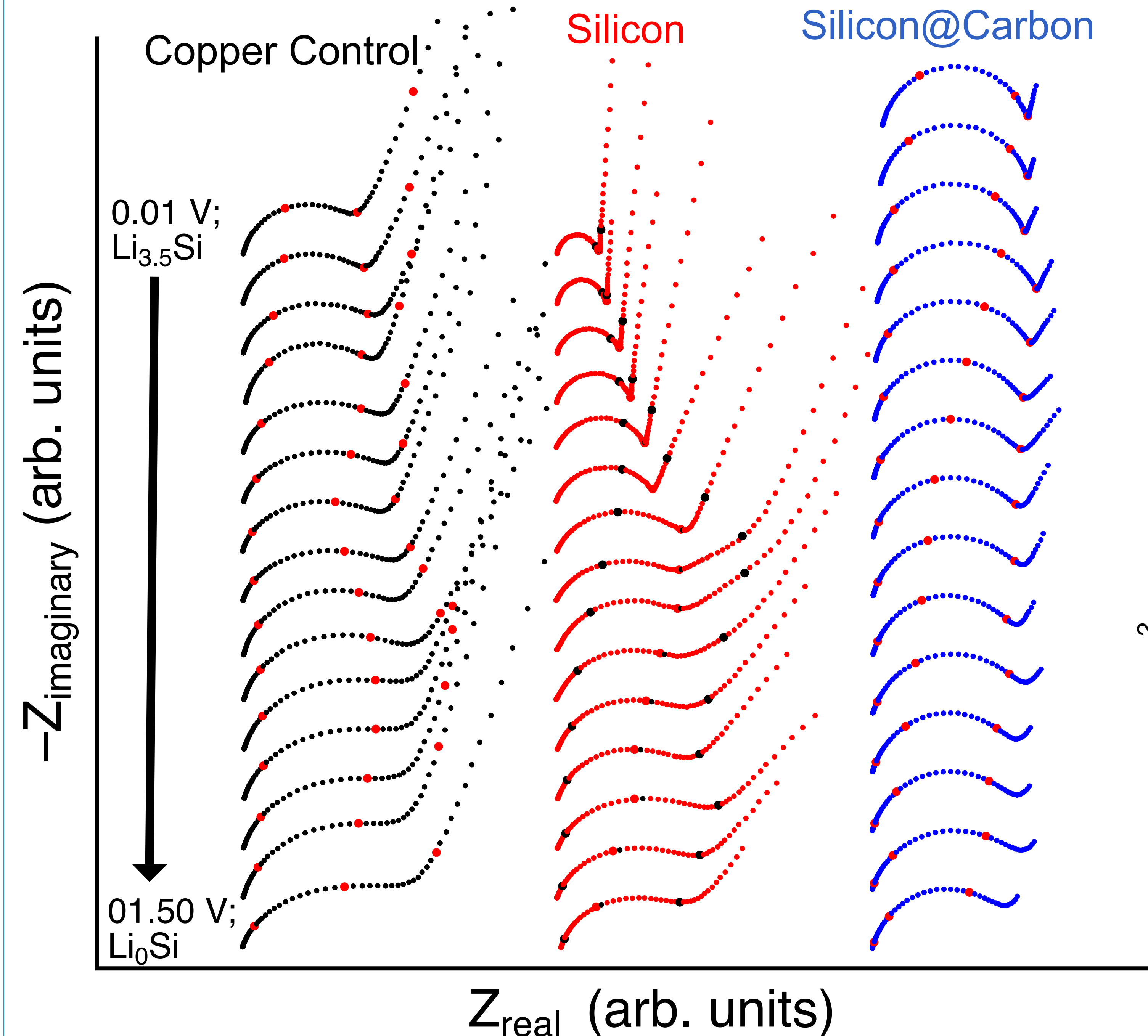


Experiment and data acquisition

- Three electrode cell with flooded EC:EMC LiPF6 electrolyte
- Lithium counter and reference electrodes
- 50nm thick silicon or carbon-coated silicon thin films sputtered onto copper current collector
- Potential swept between 1.5 and 0.01V (standard range for lithiation)
- Potential held every 100 mV for 4 hours to reach equilibrium (reflective conditions)
- Three EIS spectra collected at the end of potential hold
- Frequency range 1Mhz – 10mHz

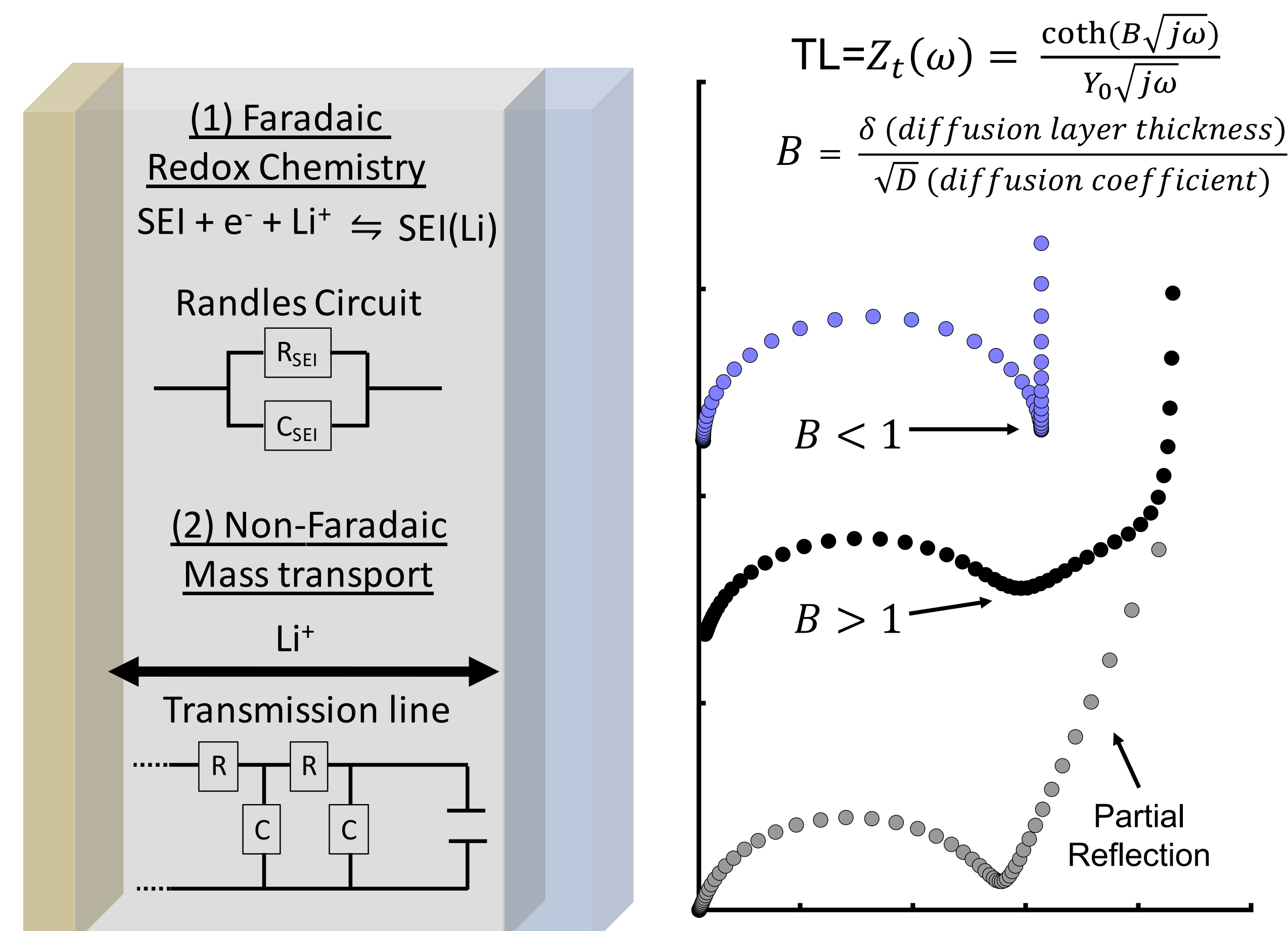


Results and Analysis



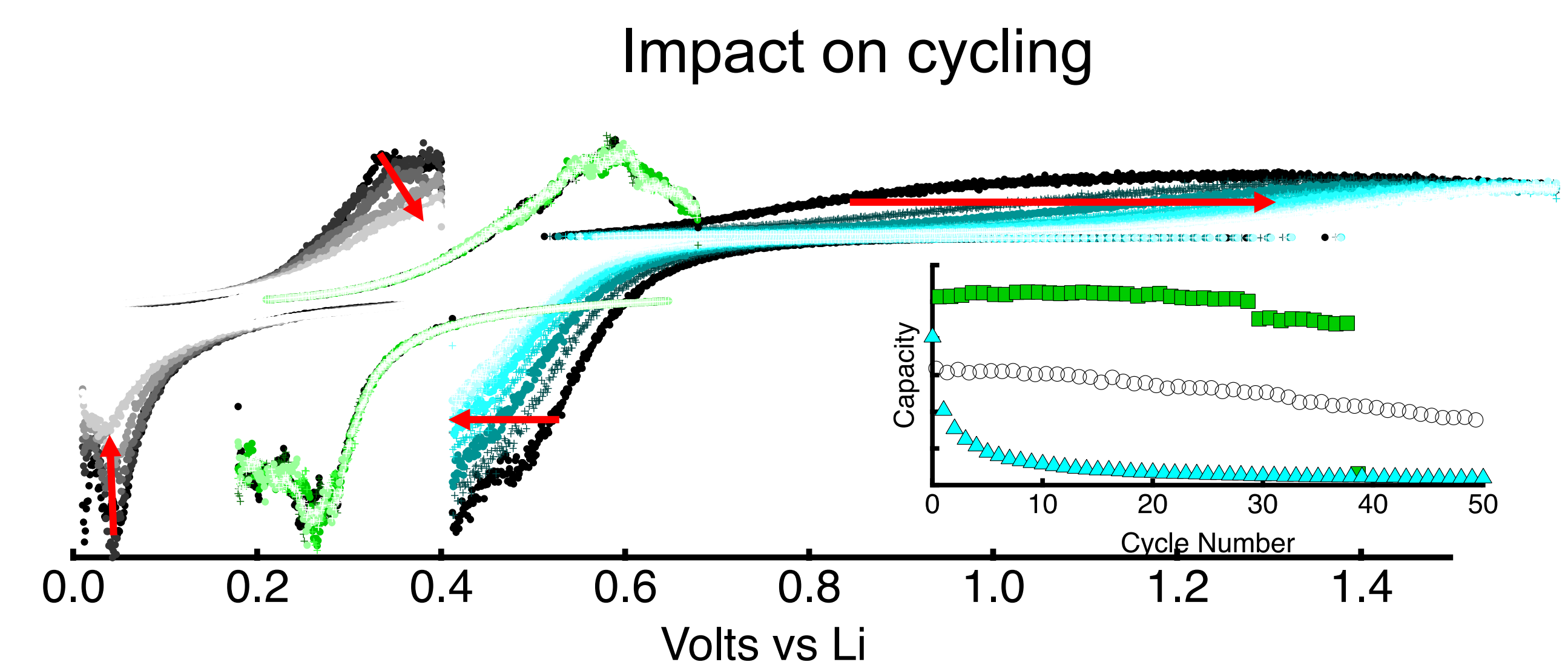
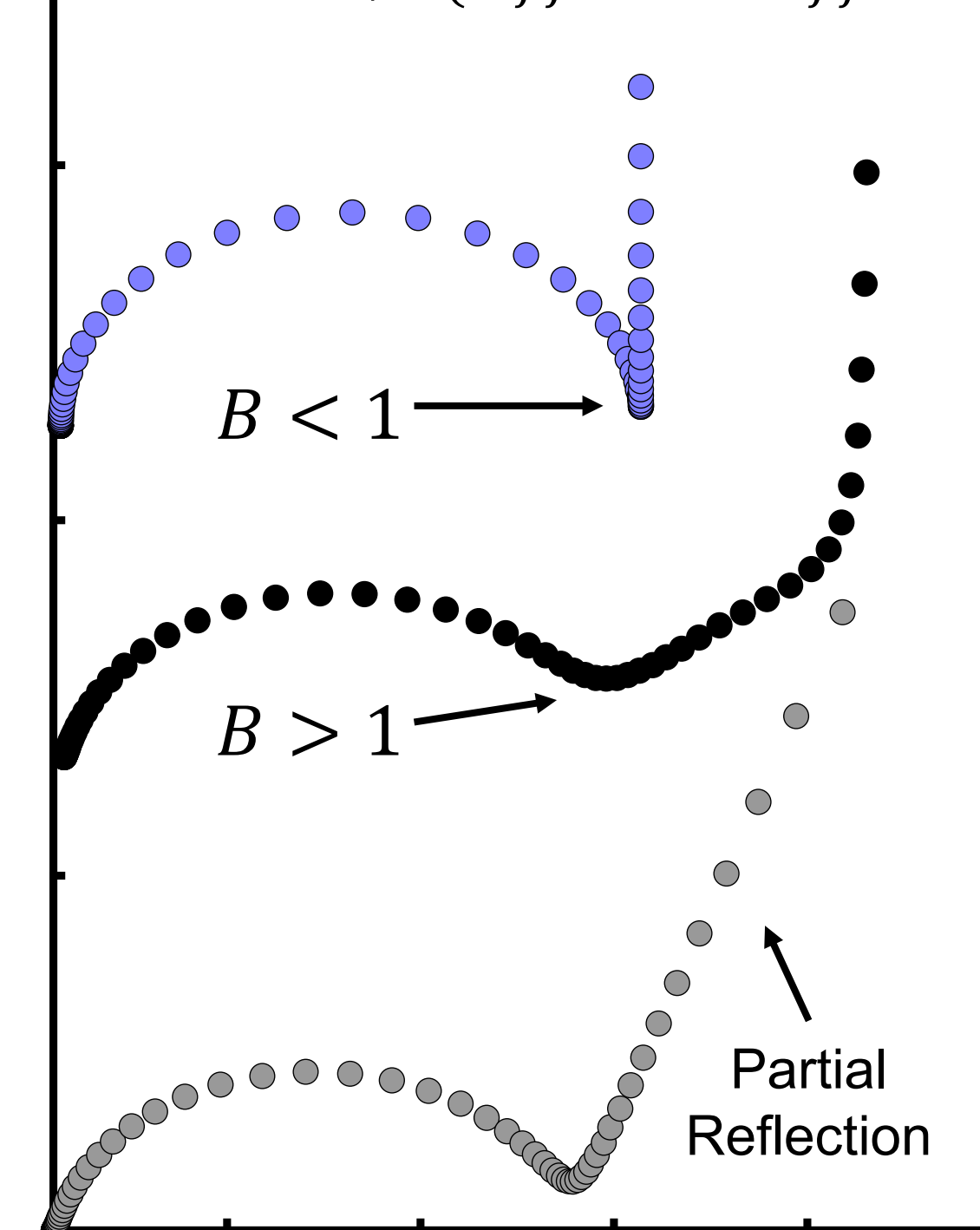
- Inflection point in C_{SEI} at $\sim 0.8V$ or $\text{Li}_{0.5}\text{Si}$
- Si@Carbon displays same inflection point as Si electrode at $\text{Li}_{0.5}\text{Si}$
- Shape reflects 'U-shape' found near the PZC
- The silicon interface still dominates the electrostatic profile at the Si@Carbon electrode.**

Electrochemical Impedance Spectroscopy of a redox active thin film at a reflective boundary.

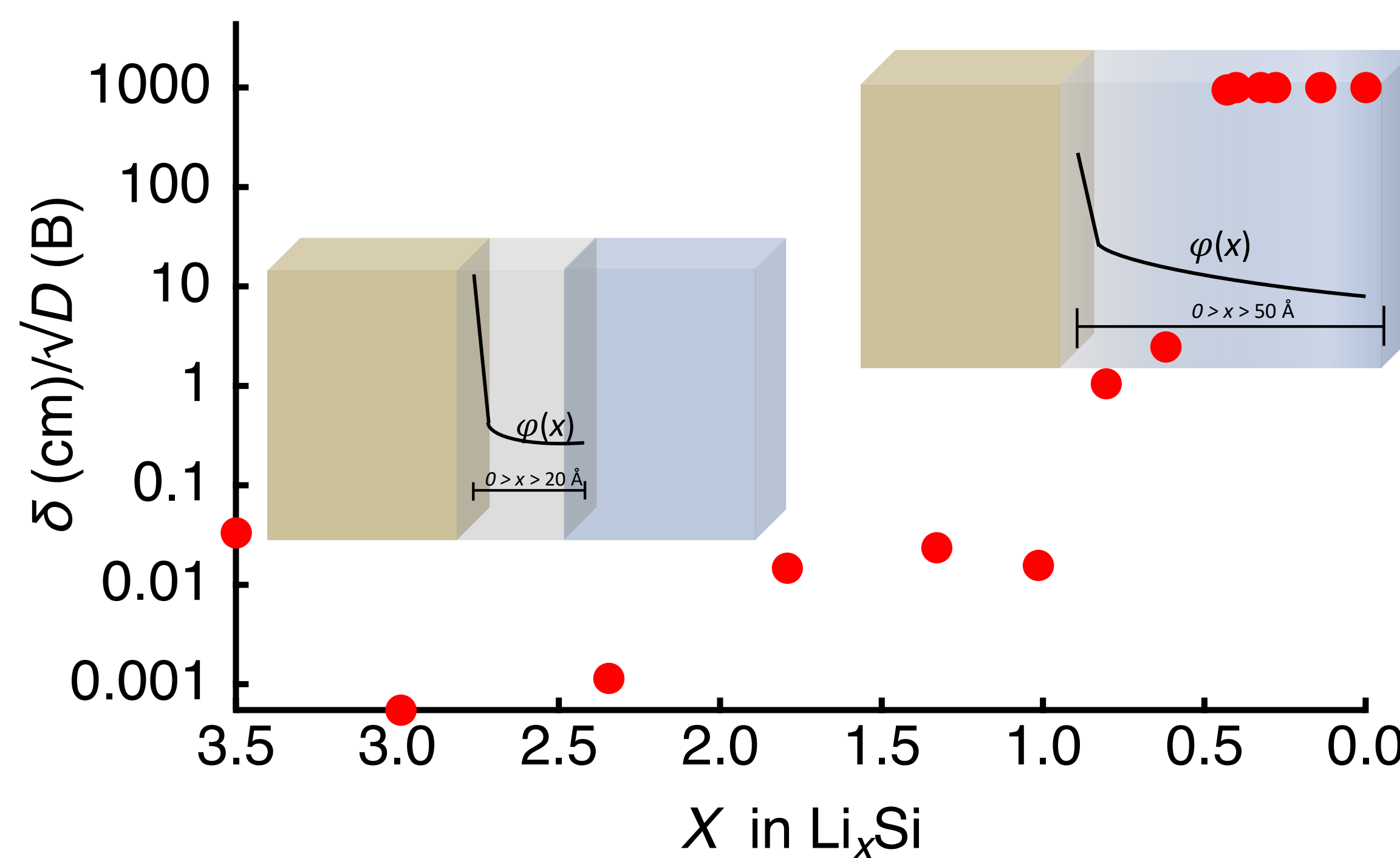


$$TL = Z_t(\omega) = \frac{\coth(B\sqrt{j\omega})}{Y_0\sqrt{j\omega}}$$

$$B = \frac{\delta \text{ (diffusion layer thickness)}}{\sqrt{D} \text{ (diffusion coefficient)}}$$



- Half cells cycled between different voltages**
- Low voltage cycle range has a large impedance gain
- High voltage range has loss of capacity and impedance gain
- Mid voltage range has stable cycling



Conclusions

Classical models of the electrochemical interface can be applied to complex and dynamic electrodes to understand important mechanisms that are relevant to device-level phenomena like calendar aging or cycle life. Here, we show that negative alloy electrodes with wide electrochemical windows cannot be assumed to have static interfaces throughout all states of charge. Under high states of charge, the interface –including the solid electrolyte interphase– has characteristics that resemble a highly polarized electrode far from the point of zero charge. Under these conditions, the interface can be understood through the Helmholtz model. At lower states of charge, the interface capacitance decreases and the space charge layer length increases. This transformation resembles a metal electrode approaching the point of zero charge which is understood through the Gouy-Chapman-Stern-Grahame model of the electrochemical interface. This transformation happens at both silicon and carbon-coated silicon interfaces. From voltage-limited cycling experiments, in the limit of the diffuse double layer, the silicon electrode impedance rises significantly in the first few cycles. This rise is related to the continuous electrochemical reduction of electrolyte components from an interface that is not electronically screened from the electrolyte. In other words, an electrode interface for batteries should resemble a 'Helmholtz-like' structure.