Computational Modeling of the Formation and Mechanical Instability of SEI on Silicon Electrodes

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Introduction

Silicon (Si) is considered to be a promising anode material for Lithium ion batteries (LIBs). In this work, we develop sophisticated computational models to study: (i) diffusion induced mechanical deformation during the (de)lithiation process of Si anodes; (ii) the formation and mechanical instability of solid electrolyte interphase (SEI) on Si anodes.

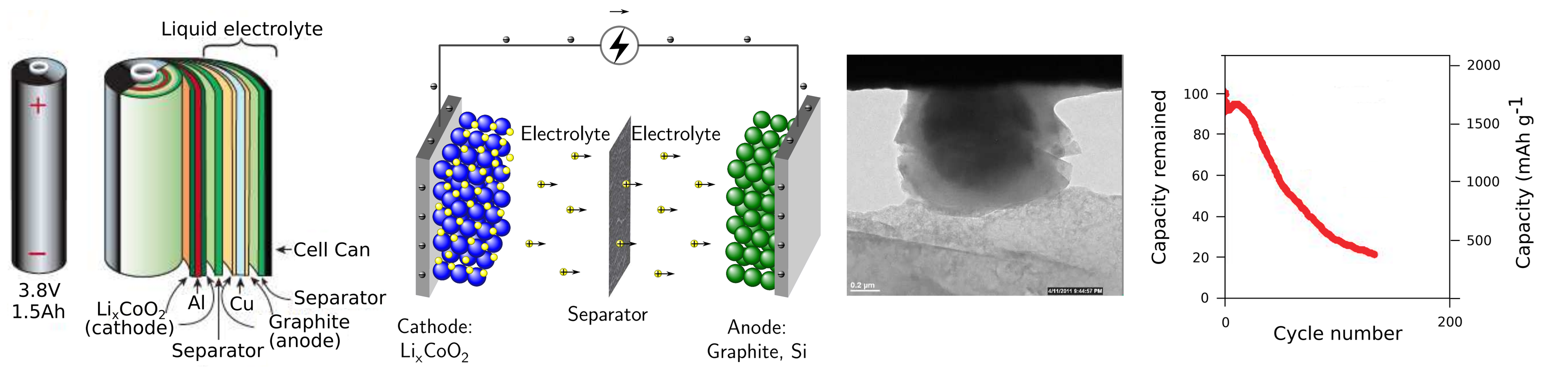


Figure: Illustration of the internal structure of LIBs, diffusion induced fracture of Si nanoparticle anode, and the poor cyclic performance of Si nanowire anodes.

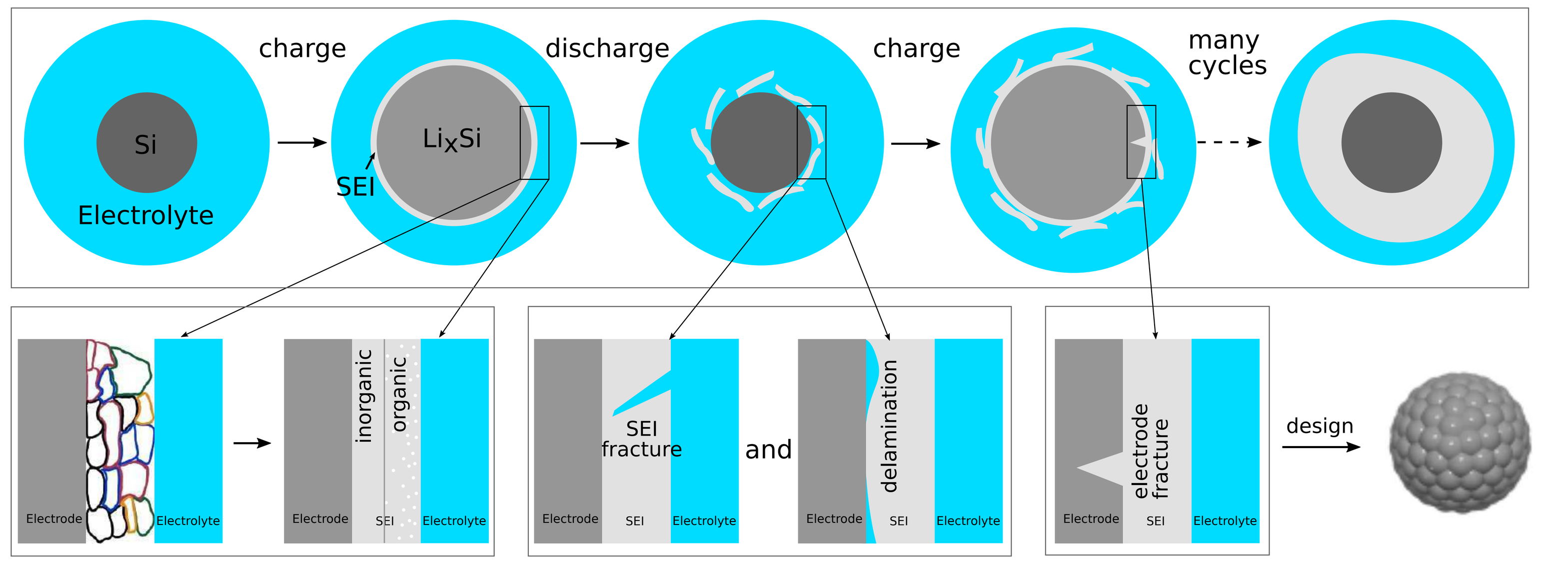


Figure: Illustration of (i) the complex structure of the SEI layer; (ii) the formation and mechanical instability of the SEI layer, which is crucial to the cyclic performance of Si based LIBs.

Research goals:

- propose a reaction controlled diffusion model to study two phase lithiation of Si anodes.
- develop an electro-chemo-mechanical coupled model to study diffusion induced large deformation and fracture for both Si anodes and SEI layers.
- propose a reaction based growth model for the SEI layer.
- study the cyclic performance of LIBs by investigating the mechanical instability of the SEI layer.

Electro-Chemo-Mechanical Coupled Model

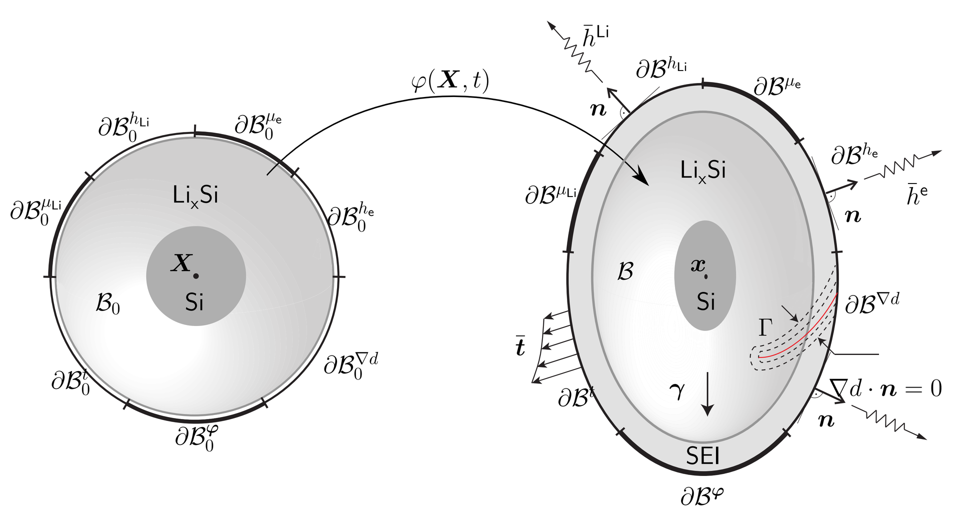


Figure: Illustration of the undeformed (left) and deformed (right) configuration of the electro-chemo-mechanical coupled initial boundary value problem with the corresponding boundary conditions.

In this electro-chemo-mechanical coupled model, we have four primary unknowns: displacement field $\{\boldsymbol{\varphi}\}$, chemical potential for Li $\{\mu_{\mathrm{Li}}\}$, chemical potential for the electrolyte $\{\mu_{\mathrm{e}}\}$, and the damage field $\{d\}$. The boundary conditions are given in Figure 3.

For **Si anodes**, we have $\{\boldsymbol{\varphi},\ \mu_{\mathrm{Li}},\ d\}$ as the primary unknowns. We consider a multiplicative decomposition of the deformation gradient

$$\boldsymbol{F} = \boldsymbol{F}^e \boldsymbol{F}^c \boldsymbol{F}^p \quad \text{with} \quad \boldsymbol{F}^c = J_c^{1/3}\boldsymbol{1}, \quad J_c = 1 + \Omega(c_{\mathrm{Li}} - c_{\mathrm{Li}_0}).$$

For **SEI Layer**, we have $\{\boldsymbol{\varphi},\ \mu_{\mathrm{Li}},\ \mu_{\mathrm{e}},\ d\}$ as the primary unknowns. We focus on the inner dense inorganic layer and assume that the SEI growth is controlled by the diffusion and reaction of the electrolyte. We further assume that the formed SEI is homogeneous. We consider a multiplicative decomposition of the deformation gradient

$$\boldsymbol{F} = \boldsymbol{F}^e \boldsymbol{F}^g \quad \boldsymbol{F}^g = \boldsymbol{1} + g(c_{\mathrm{e}}, V_a)\boldsymbol{N} \otimes \boldsymbol{N}$$

where $\boldsymbol{F}^g$ describes the volumetric growth of the SEI. The growth parameter g is computed as

$$g = \int_{t_0}^{t} v_0 \cdot k(c_e)\, dt = \int_{t_0}^{t} v_0 \cdot k_0\, c_e \exp\left(-\frac{\alpha F}{RT} V_a\right)\, dt$$

where V_a is the electric potential on the anodes, which is computed from the Li chemical potential based a Butler-Volmer kinetic relationship. We have four governing equations for this electro-chemo-mechanical coupled problem

(*i*)	$\mathrm{Div}[\partial_{\boldsymbol{h}^e}\psi \boldsymbol{F}^{-T}] + \rho_0 \boldsymbol{\gamma} = \boldsymbol{0}$	balance of linear momentum
(*ii*)	$\dot{c}_{Li} + \mathrm{Div}[\partial_{\ _{Li}}\phi^{Li}_{\mathrm{diff}}] = 0$	species conservation for Li
(*iii*)	$\beta^f + \partial_d \psi = 0$	damage equation
(*iv*)	$\dot{c}_e + \mathrm{Div}[\partial_{\ _e}\phi^{e}_{\mathrm{diff}}] + k(c_e) = 0$	species conservation for the electrolyte.

Results

Lithiation of Si Nanopillar

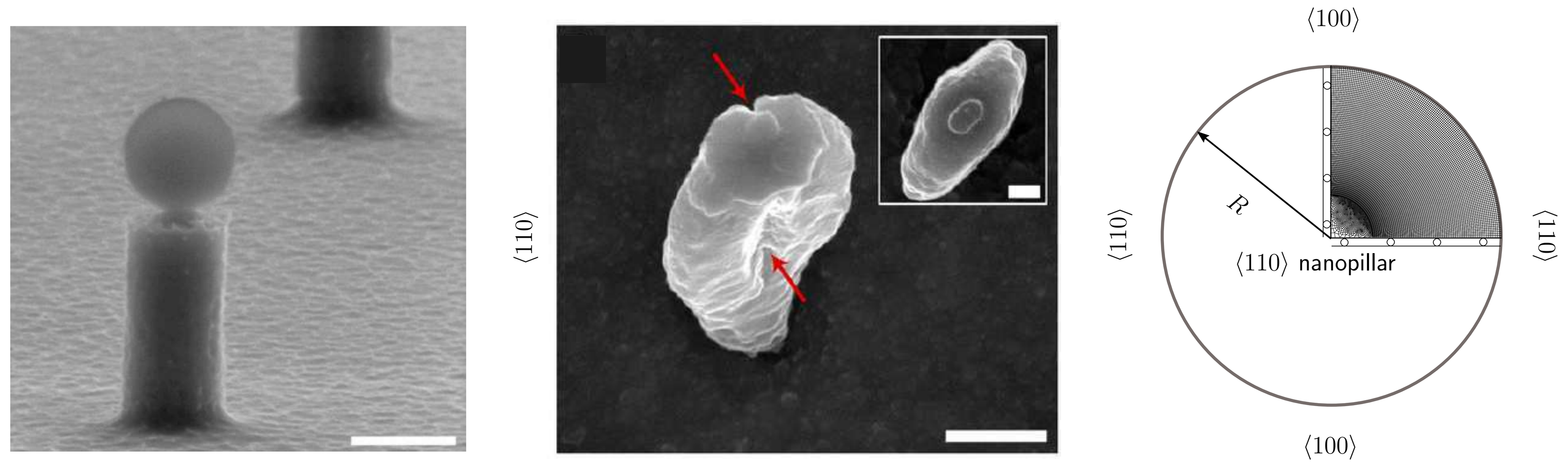


Figure: Si nanopillar: illustration of the initial shape of crystalline Si nanopillar (left), the lithiated Si nanopillar with and without crack (middle), and the numerical simulation setup (right).

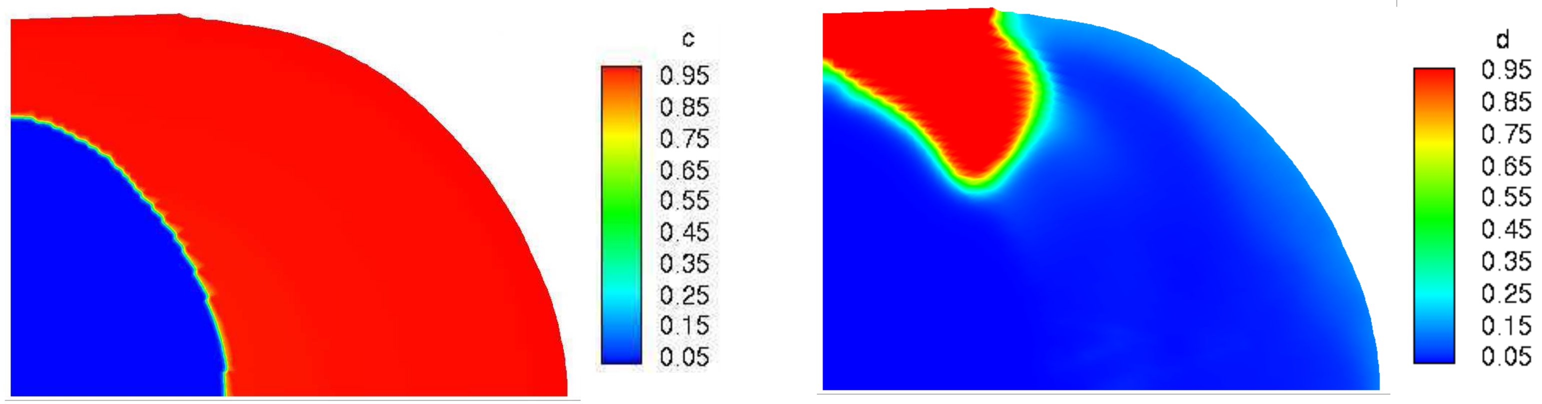


Figure: Si nanopillar: the Li concentration (left) and the damage field (right) for the lithiated Si nanopillar. Diffusion induced anisotropic deformation is attributed to the different reaction rates in different crystalline directions.

Formation of SEI layer

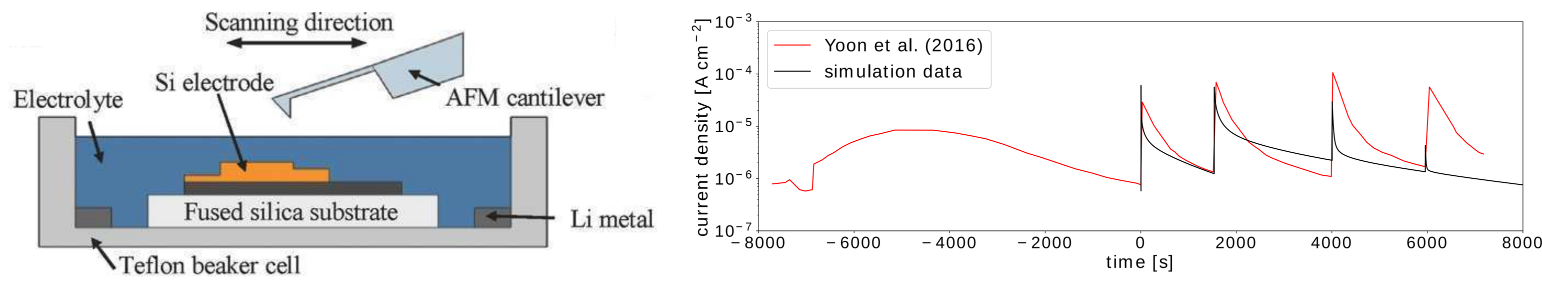


Figure: SEI formation: illustration of the experimental setup for Si thin film half cell (left) and the current density output from numerical results compared with the experimental results.

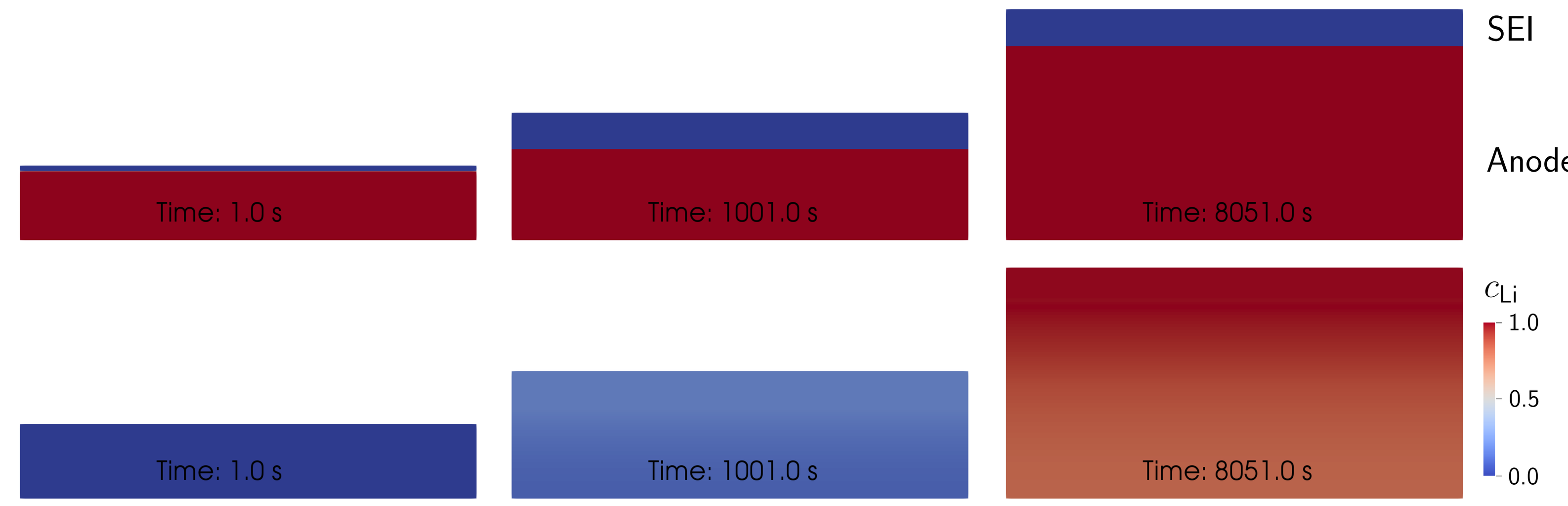
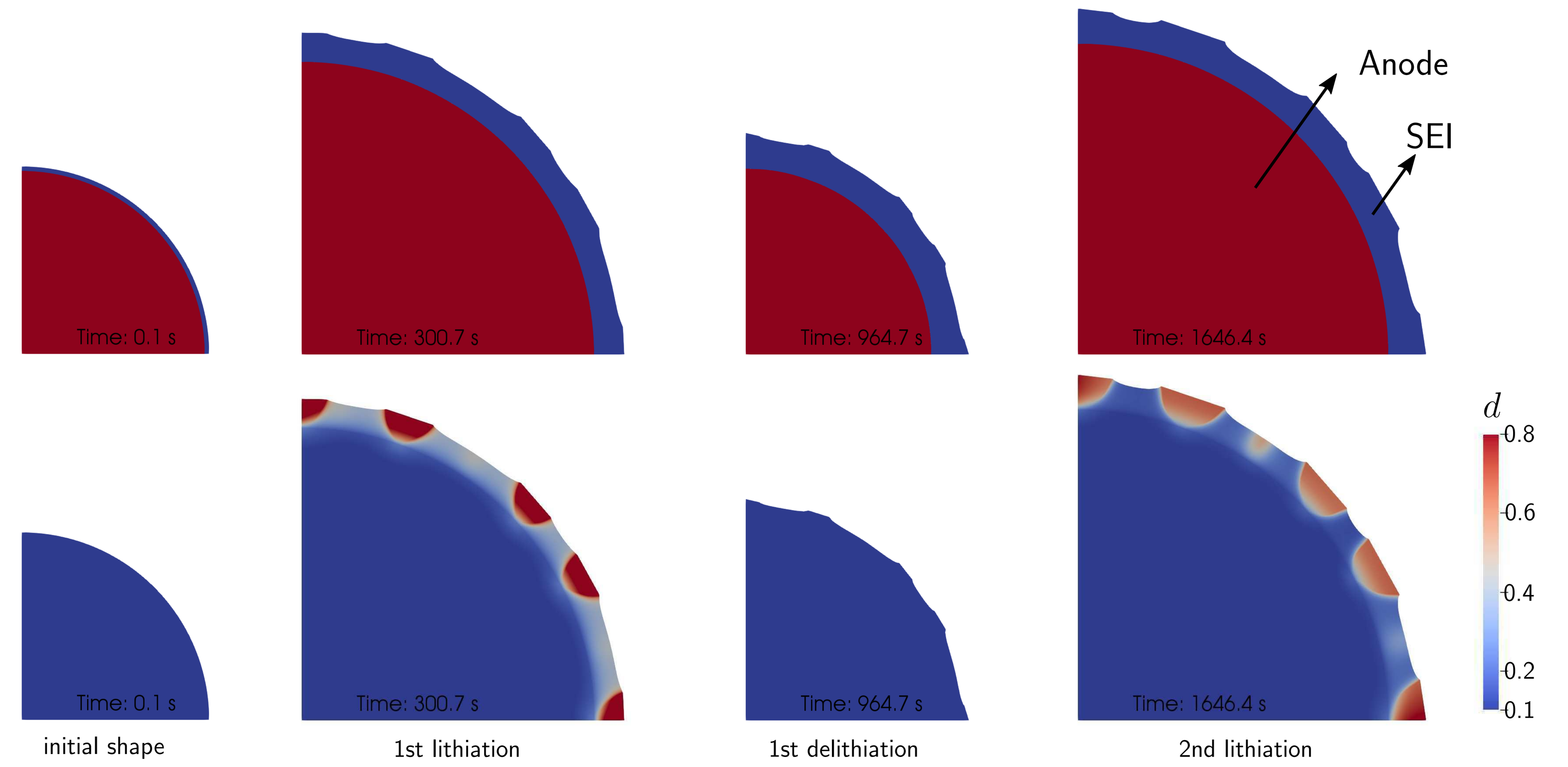


Figure: SEI formation: formation of SEI on Si thin film anode (upper) and Li concentration distribution (bottom) at different time steps. The Si thin film anode has an initial geometry of 200 nm×30 nm. The SEI forms rapidly during the initial lithiation stage and remains unchanged during the rest lithiation process.

Cyclic performance of Si based LIBs



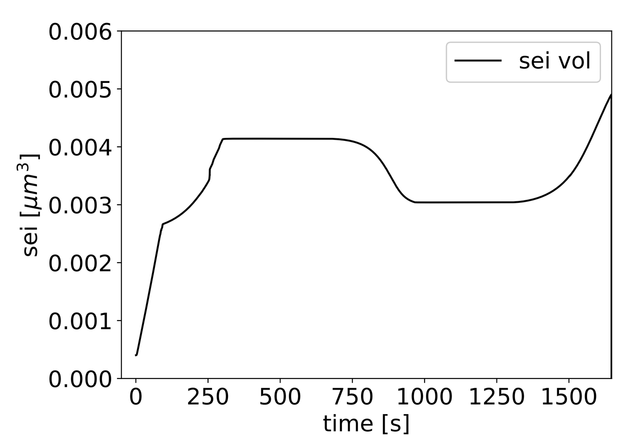


Figure: Cyclic performance: formation of SEI on Si circular anode at different (de)lithiation stages (1st row), the damage field in the SEI layer at different (de)lithiation stages (2nd row), and the evolution of the total amount of SEI (left). Because of the cracks formed in the SEI, the electrotype can be exposed to the electrode. Thus chemical reaction will happen and new SEI will form to heal the crack. A plasticity-like internal parameter is introduced to account for this healing phenomenon at the end of each lithiation stage. The total amount of SEI is computed from the simulation, which can be used to predict the capacity loss of each (de)lithiation cycle.

Future Work

- Conduct systematically parameter study to better understand SEI formation mechanism.
- Investigate the delamination mechanism of the SEI layer during (de)lithiation cycles.
- Use this fully coupled computational model to design high performance Si anodes with stable SEI.

References

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