Simulation of SEI Formation: Revealing SEI Morphology

Fabian Single[1,2], Tobias Schmitt[1,2,3], Arnulf Latz[1,2,3], and Birger Horstmann[1,2]

Helmholtz Institute Ulm Electrochemical Energy Storage

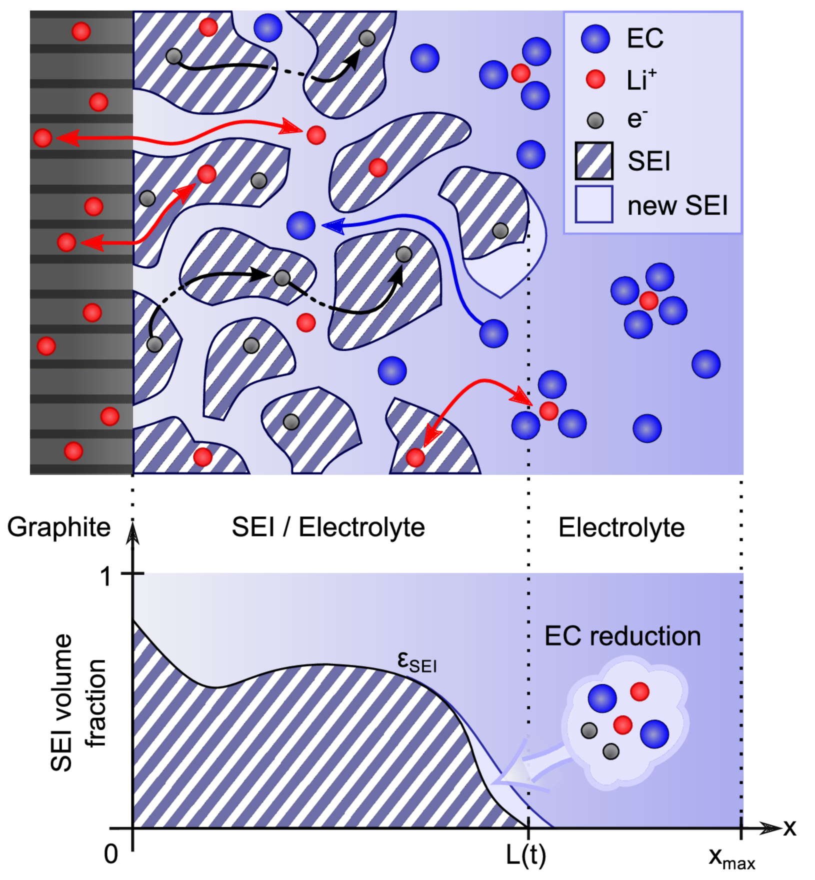
Federal Ministry of Education and Research

Li-EcoSafe

[1] German Aerospace Center, Institute of Engineering Thermodynamics, Pfaffenwaldring 38-40, 70569 Stuttgart, Germany.
[2] Helmholtz Institute Ulm for Electrochemical Energy Storage (HIU), Helmholtzstraße 12, 89081 Ulm, Germany.
[3] University of Ulm, Institute of Electrochemistry, Albert-Einstein-Allee 47, 89081 Ulm, Germany.

Introduction

- Modeling growth of nano-porous SEI
- 1D model perpendicular to electrode
- Transport of electrons and solvent [2-4]
  - Electrons in solid SEI
  - Binary electrolyte in pores, e.g., EC/DMC
- Two electrolyte reduction reactions and two SEI components



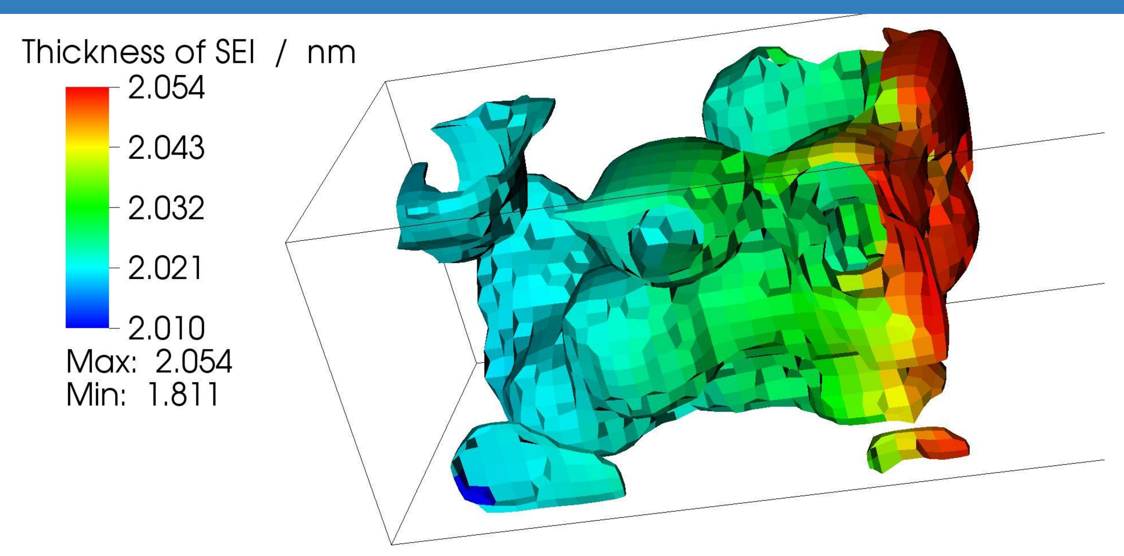
SEI Growth Model

- SEI volume fraction evolution along an axis perpendicular to the electrode surface
  $$\partial_t \varepsilon_1 = V_1 \dot{s}_1 \qquad \partial_t \varepsilon_2 = V_2 \dot{s}_2$$
- Solvent diffusion and convection in the electrolyte phase (binary mixture)
  $$\partial_t(\varepsilon c_i) = -\mathrm{div}\left(j_{\mathrm{D},i} + j_{\mathrm{C},i}\right) - \dot{s}_i$$
- Electron conduction within the solid SEI phase
  $$0 = -\mathrm{div}\left(j_{\mathrm{elec}}\right) - F\dot{s}_i$$
- Convection velocity from incompressibility ($V_i^{\mathrm{solv}} c_i = 1$)
  $$\mathrm{div}\, v = \sum\left(2V_i - \nu_i V_i^{\mathrm{solv}}\right)\dot{s}_i$$

Bruggeman relation	Flux densities
• $\boldsymbol{D} = \varepsilon^{\beta} D_{\mathrm{Bulk}}$ • $\boldsymbol{\sigma} = (1-\varepsilon)^{1.5}\sigma_{\mathrm{Bulk}}$	• $\boldsymbol{j}_{\mathrm{D},i} = -D \cdot \mathrm{grad}\, c_i$ • $\boldsymbol{j}_{\mathrm{C},i} = c_i v$ • $\boldsymbol{j}_{\mathrm{elec}} = -\sigma \cdot \mathrm{grad}\Phi$

- Solvent reduction: ν_i **Solvent**$_i$ + 2 e$^-$ + 2 Li$^+ \rightleftharpoons$ **SEI**$_i$
  $$\dot{s}_i = A(\varepsilon)\Gamma \frac{k_B T}{h} \exp\left(\frac{-E_A}{k_B T}\right)\left(c_i / c_i^0\right)^{\frac{\nu_i}{2}} 2\sinh\left(\frac{RT}{F}\eta_i\right),$$
  $$\eta = -\left(\Phi - \Phi_i^0\right) + \nu_i \ln\left(\frac{c_i}{c_i^0}\right)$$
- Specific surface area
  $$A(\varepsilon) = \frac{1}{a_0}(1-\varepsilon)\left(\varepsilon + \frac{a_0^2}{6}\frac{\partial^2 \varepsilon}{\partial x^2}\right)$$

3D Electrode Simulation

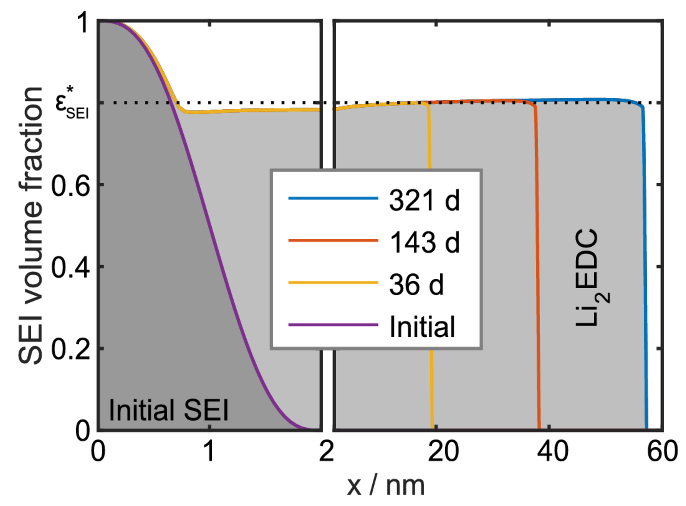


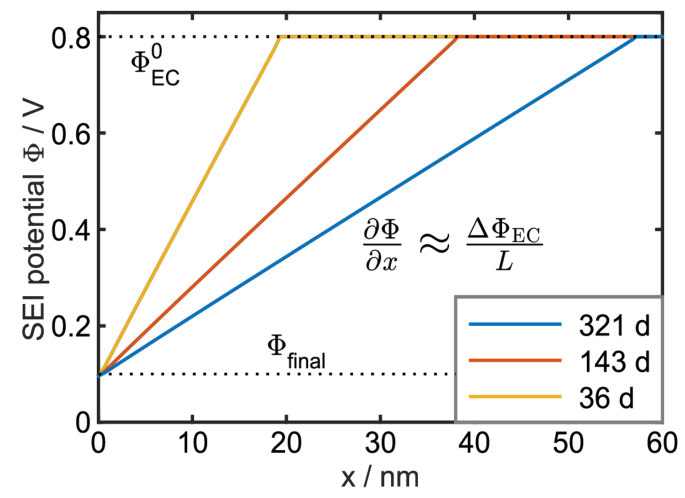
- BEST: 3D transport in porous electrodes [5]
  - Implementing SEI growth model on the graphite surface
  - Prediction of inhomogeneous SEI thickness
- Understanding intercalation through SEI and lithium loss

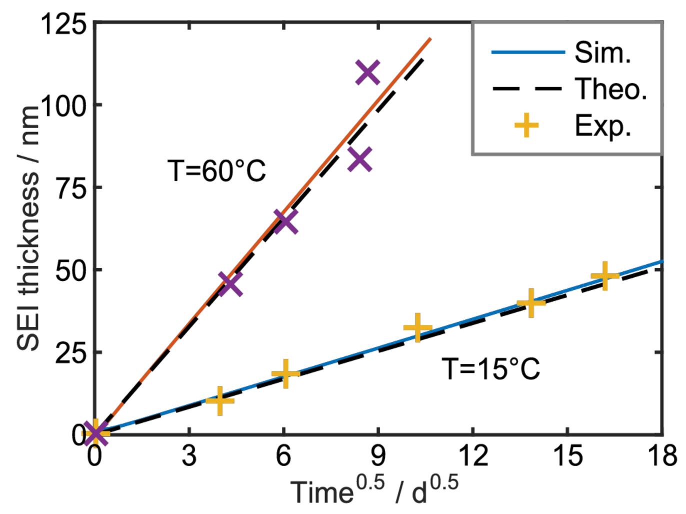
Results: Inert Co-Solvent

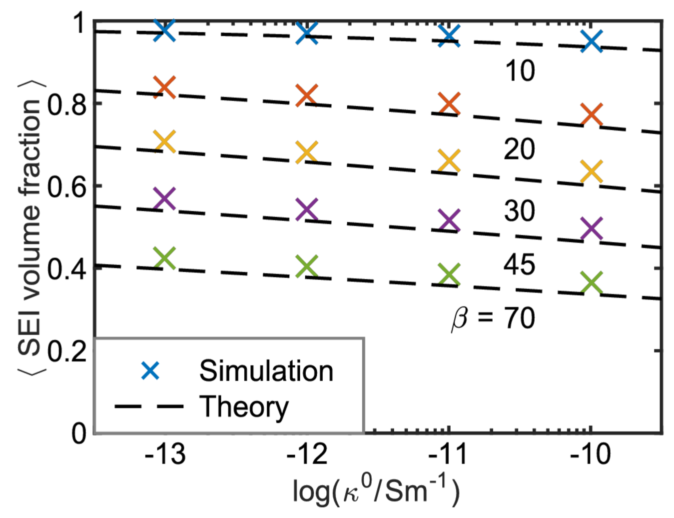
- Formation of porous SEI
- SEI porosity $\varepsilon^* = 1 - \varepsilon^*_{\mathrm{SEI}}$ nearly constant
- SEI thickness grows with $\sqrt{t}$

$$L(t) \approx \sqrt{\frac{V_1 \varepsilon_{\mathrm{SEI}}^{0.5} \sigma_{\mathrm{Bulk}} \Delta\Phi_1}{2F}}\sqrt{t}$$









- Electronic conductivity from fit to experiment [1,2]
  - $\sigma_{\mathrm{Bulk}} = 0.3$ pS/m at T=15°C
  - $\sigma_{\mathrm{Bulk}} = 4.5$ pS/m at T=60°C
- Analytic expression for porosity ε^*

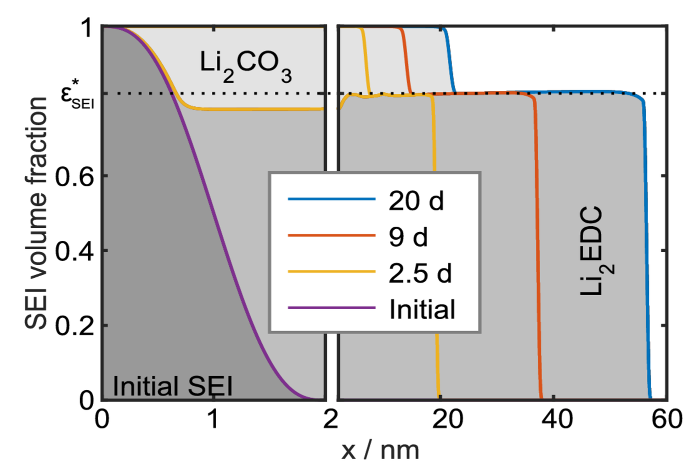
$$\sigma(\varepsilon^*) = D(\varepsilon^*)\frac{F^2 c_1^0}{RT}\left(\frac{1}{2} + \beta\frac{1-\varepsilon^*}{\varepsilon^*}\right)$$

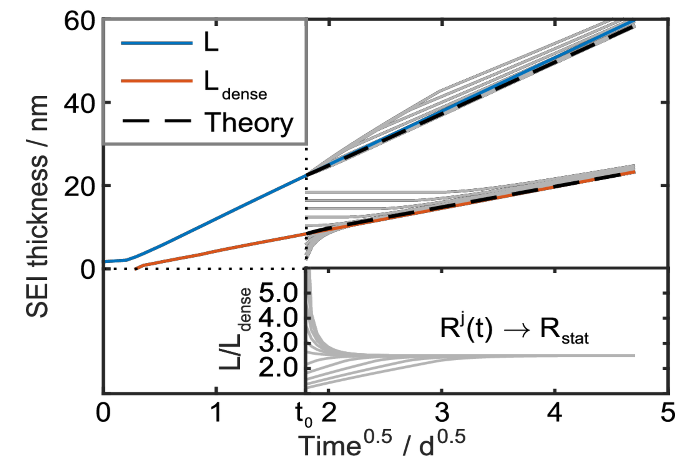
Results: Active Co-Solvent

- Dual-layer morphology
  - Co-Solvent reduction at low voltages near electrode
  - Dense inner layer
  - Porous outer layer
- $R = L/L_{\mathrm{dense}}$ quickly converges to parameter dependent R_{stat}

$$\frac{\Delta\Phi_2}{\Delta\Phi_{\mathrm{diff}}} R_{\mathrm{stat}}^2 - \left(\frac{\Delta\Phi_2}{\Delta\Phi_{\mathrm{diff}}} + \varepsilon_{\mathrm{SEI}}^{*1.5}\right)$$

$$\cdot\, R_{\mathrm{stat}} = \varepsilon^* \varepsilon_{\mathrm{SEI}}^{*0.5}\frac{V_1}{V_2}$$





Conclusions and Outlook

- SEI thickness: electron transport
- SEI porosity: solvent and electron transport
- Dual-layer morphology for two reduction mechanisms
- 3D simulation of inhomogeneous SEI during battery cycling
- SEI deformation from transformation reaction

References

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[4] Shi, S. et al. *J. Am. Chem. Soc.* **134** (37), 15476–15487 (2012).
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birger.horstmann@dlr.de