Modeling SEI Formation and Morphology

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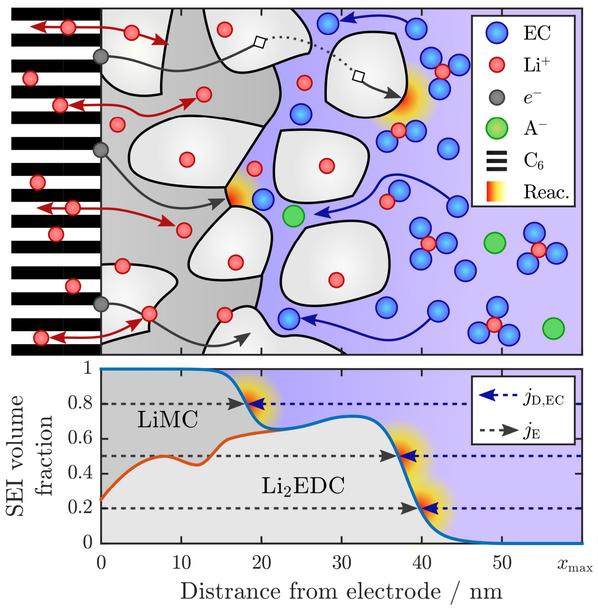
Introduction

- Modeling growth of nano-porous SEI
- 1D model, model axis perpendicular to electrode
- Transport of electrons and solvent [1-3]
  - Electrons: solid SEI
  - Binary electrolyte in pores, EC/DMC 3:7
- Up to two electrolyte reduction reactions forming different SEI compounds



SEI Growth Model

- SEI volume fraction evolution along an axis perpendicular to the electrode surface
  $$\partial_t \varepsilon_i = V_i \dot{s}_i - \mathrm{div}(\varepsilon_i \tilde{v})$$
- Solvent diffusion and convection in the electrolyte phase (binary mixture)
  $$\partial_t(\varepsilon c_i) = -\mathrm{div}\left(j_{\mathrm{D},i} + j_{\mathrm{C},i}\right) - \nu_i \dot{s}_i$$
- Electron conduction within the solid SEI phase
  $$0 = -\mathrm{div}(j_{\mathrm{E}}) - F\dot{s}_i$$
- Convection velocity from incompressibility $\left(V_i^{\mathrm{solv}} c_i = 1\right)$
  $$\mathrm{div}\, v = \sum\left(2V_i - \nu_i V_i^{\mathrm{solv}}\right)\dot{s}_i$$
- Solid convection
  $$\mathrm{div}\, \tilde{v} = \alpha(\varepsilon)\, \dot{\varepsilon}_{\mathrm{SEI,C}}/\varepsilon_{\mathrm{SEI}}$$

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

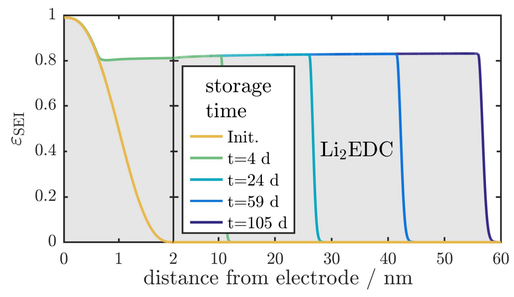
- Butler-Volmer: $\dot{s}_i = A(\varepsilon)\Gamma \frac{k_B T}{h} \exp\left(\frac{-E_A}{k_B T}\right)\left(c_i/c_i^0\right)^{\frac{\nu_i}{2}} 2\sinh\left(\frac{RT}{F}\eta_i\right)$

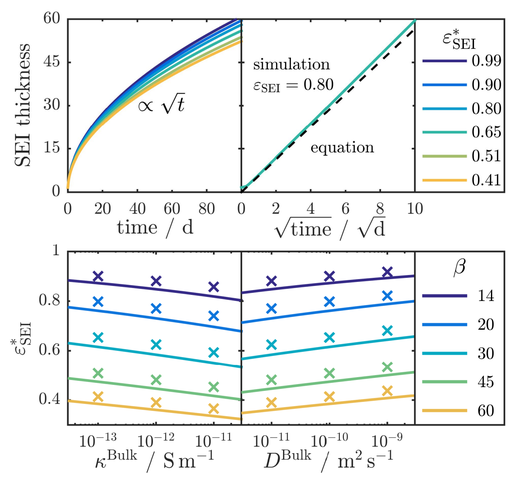
$$\eta_i = -\left(\Phi - \Phi_i^0\right) + \nu_i \ln\left(\frac{c_i}{c_i^0}\right)$$

- Specific surface area: $A(\varepsilon) = \frac{1}{a_0}\varepsilon\left(\varepsilon_{\mathrm{SEI}} + \frac{a_0^2}{6}\frac{\partial^2 \varepsilon}{\partial x^2}\right)$

Simulations: Inert Co-Solvent

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





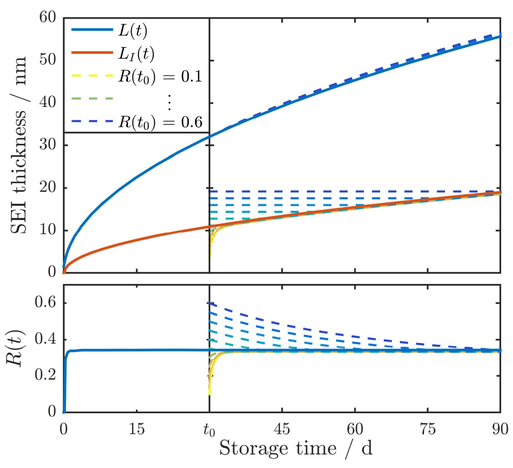
$$L(t) \approx \sqrt{V_1 \kappa^* \Delta\Phi_1 / 2F\varepsilon^*_{\mathrm{SEI}}}\sqrt{t}$$

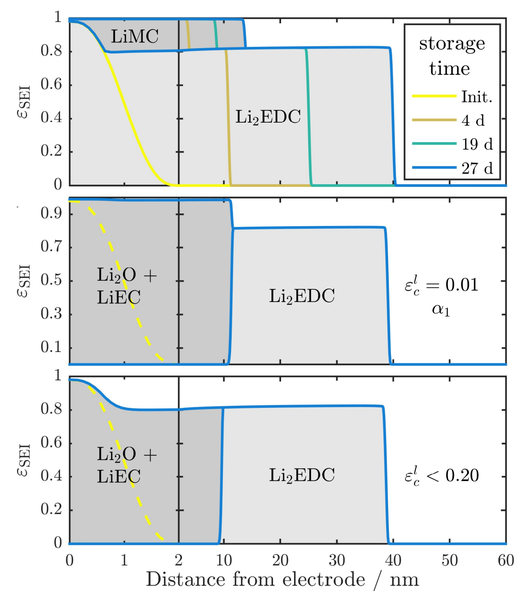
- Electronic conductivity from fit to experiment [1,2]
  $$\sigma_{\mathrm{Bulk}} = 0.3 - 4.5\,\mathrm{pS/m}$$
- Analytic expression for porosity
  $$\frac{\kappa^*}{D^*} = \frac{F^2 c_1^0}{RT}\left(\frac{1}{2} + \beta\frac{1-\varepsilon^*}{\varepsilon^*}\right)$$

Simulations: Dual-Layer SEI

- Second reduction reaction
  - Active co-solvent
  - Conversion of Li_2EDC

➡ **Dual-layer SEI**



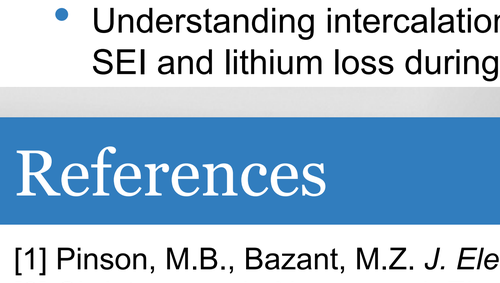


- Inner and outer layer thickness (L_I and L) are related

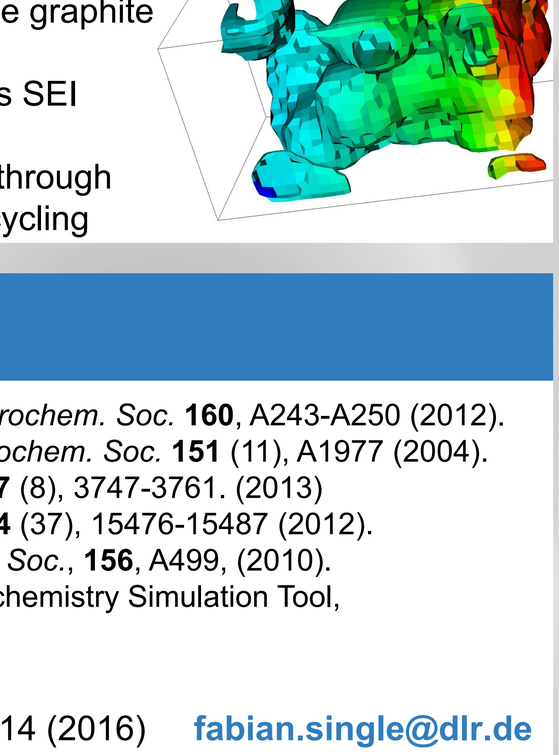
$$R(t) = \frac{L_I(t)}{L(t)} \to R_{\mathrm{stat}}$$

Simulations: Self-Shaping SEI

- Assumption: SEI porosity is a material property
  - Set porosity with $\alpha(\varepsilon)$



- Reaction interface inside the SEI, located at $x = \tilde{R}\cdot L$
- **Both transport mechanisms contribute**
- $\tilde{R} = \left(1 + \frac{D^*}{\kappa^*}\frac{Fc}{\Delta\Phi}\right)^{-1}$, $L(t) \propto \sqrt{\frac{\kappa^* t}{\tilde{R}}}$



3D Electrode Simulation

- BEST: 3D transport simulation with porous electrodes [6]
- Simple SEI growth model on the graphite surface
  - Prediction of inhomogeneous SEI thickness
  - Understanding intercalation through SEI and lithium loss during cycling

References

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[5] Liu, P., Wang et al. *J. Electrochem. Soc.*, **156**, A499, (2010).
[6] ITWM, BEST - Battery and Electrochemistry Simulation Tool, http://itwm.fraunhofer.de/BEST

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