Modeling Graphite Surfaces: Lithium Plating & Solid Electrolyte Interphase

E^2 Fliegen

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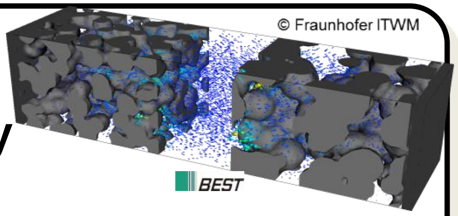
Birger Horstmann, Fabian Single, Simon Hein, Tobias Schmitt, Arnulf Latz

Helmholtz Institute Ulm for Electrochemical Energy Storage

- Center of Excellence for research in electrochemical energy storage
- Started in Jan. 2011
- New building on University Ulm campus for 80 scientists (July 2014)
- DLR battery modeling activities are integrated into HIU

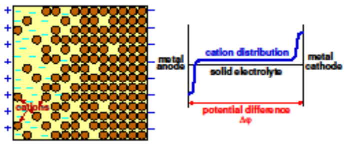
Computational Electrochemistry - HIU Theory III

Li-ion batteries: Elektrochemistry and transport



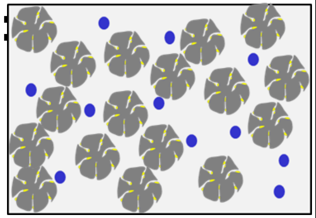
Research on structures and processes
Research on degradation and safety

Solid Electrolytes: Interfaces and transport



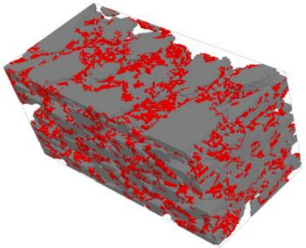
Theory development and application

Metal-Sulfur Batteries: Redox-chemistry and transport



Evaluation of novel battery concepts

Metal-Air Batteries: Multi-phase transport and electrochemistry



Lattice-Boltzmann, battery concepts, and interfaces

DLR
HIU Helmholtz Institute Ulm Electrochemical Energy Storage

Dreamliner Battery

- **Heat generation due to internal short circuit**
- Three possible causes were isolated
  - **Lithium metal deposition**
  - Contamination from production
  - Damaged Separator

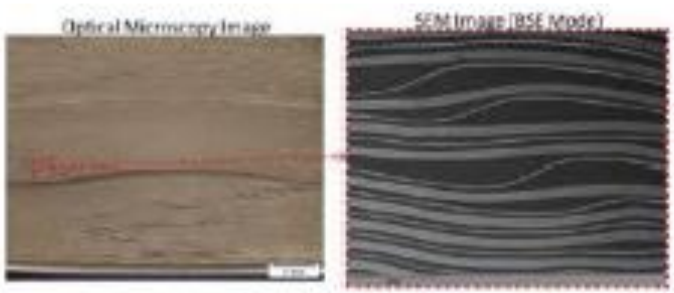


Fig. 2.11.6.9-3: Gaps in Electrodes

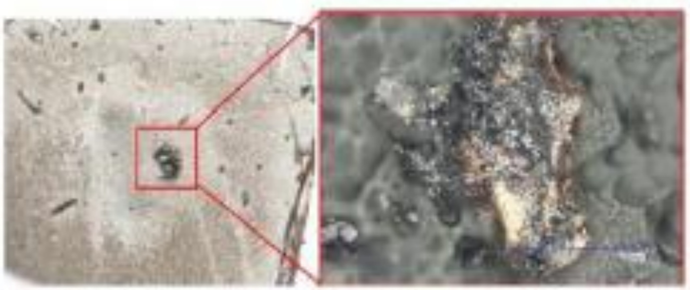
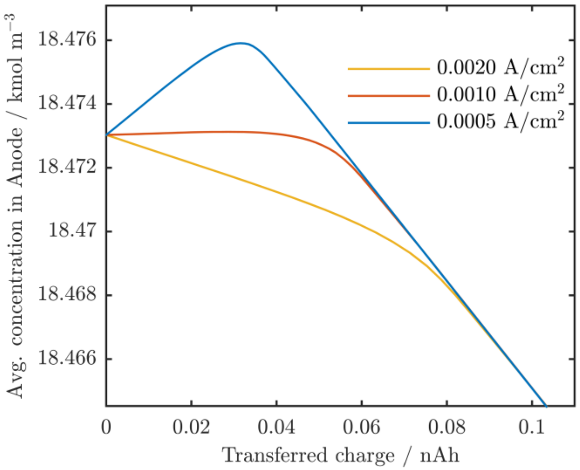


Fig. 2.11.6.9-2: Copper Particle Discovered on Separator

Pictures from NTSB and JTSB report

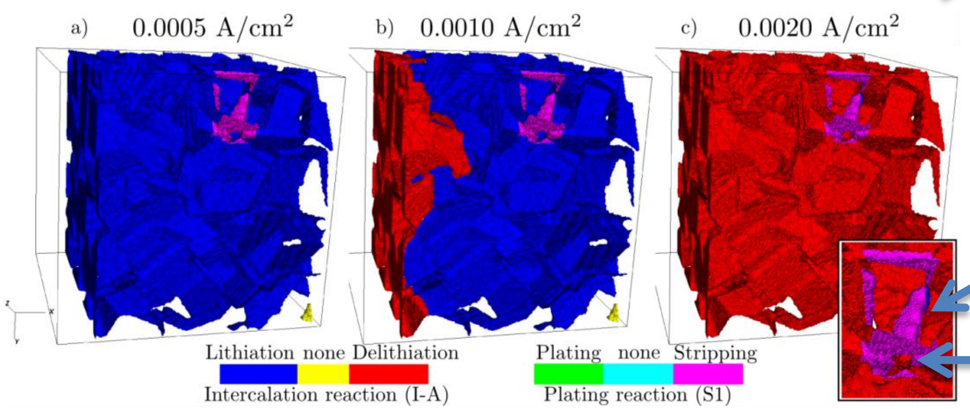
3D Electrode: Lithium Plating and Stripping

- Electrochemical simulations in **3D microstructures**
- Charge: Plating
  - **Metallic lithium forms on graphite**
- Discharge: Stripping
  - Metallic lithium dissolves
  - Depending on applied current, graphite is lithiated during stripping



Average lithium concentration in graphite

Applied current increases



Intercalation close to plated lithium

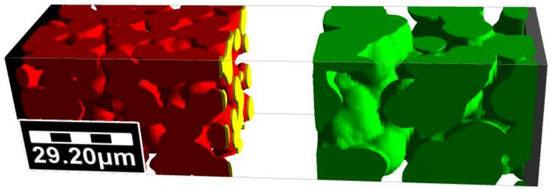
Plated lithium

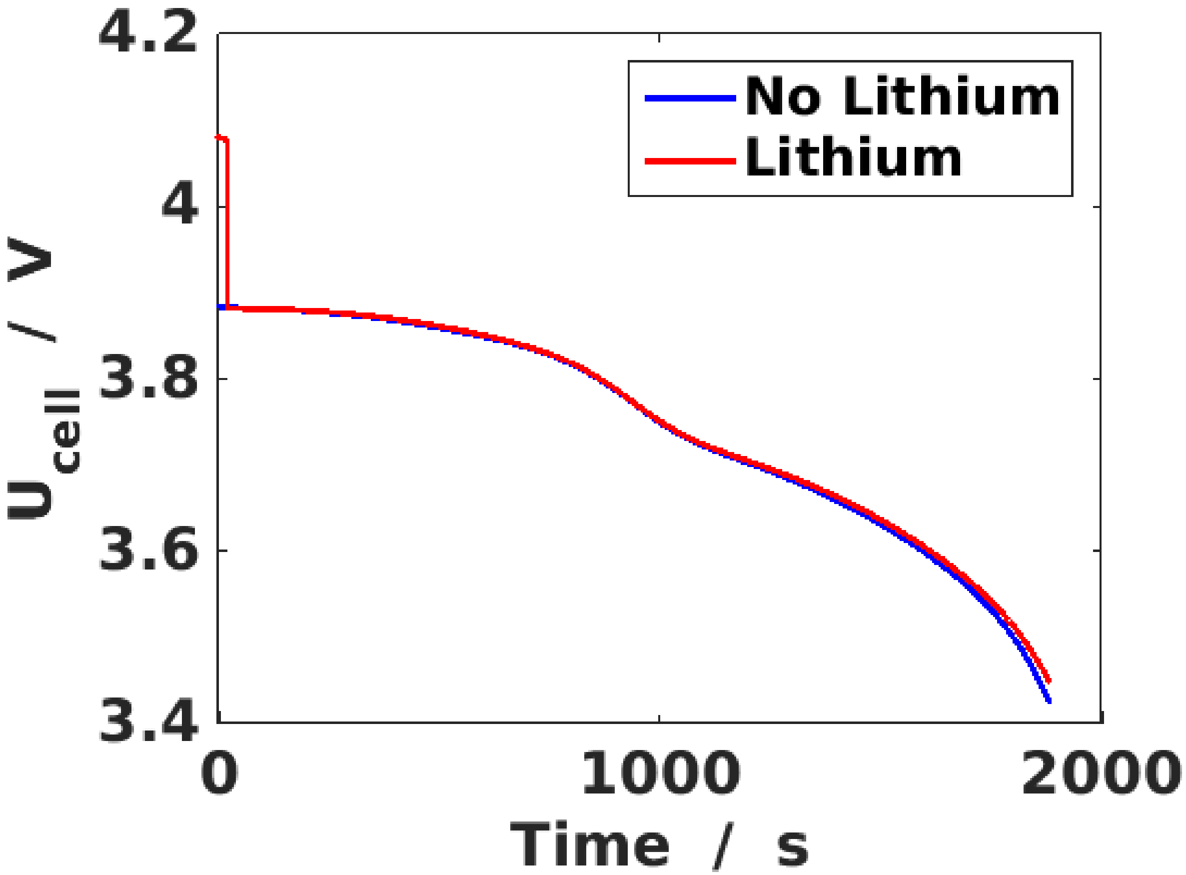
Reaction rate during discharge for various currents (SOC: 0.02 nAh)

S. Hein and A. Latz, Electrochimica Acta, accepted

3D Electrode: Lithium Stripping During Discharge

- Impact on cell voltage: **discharge plateau** = lithium amount





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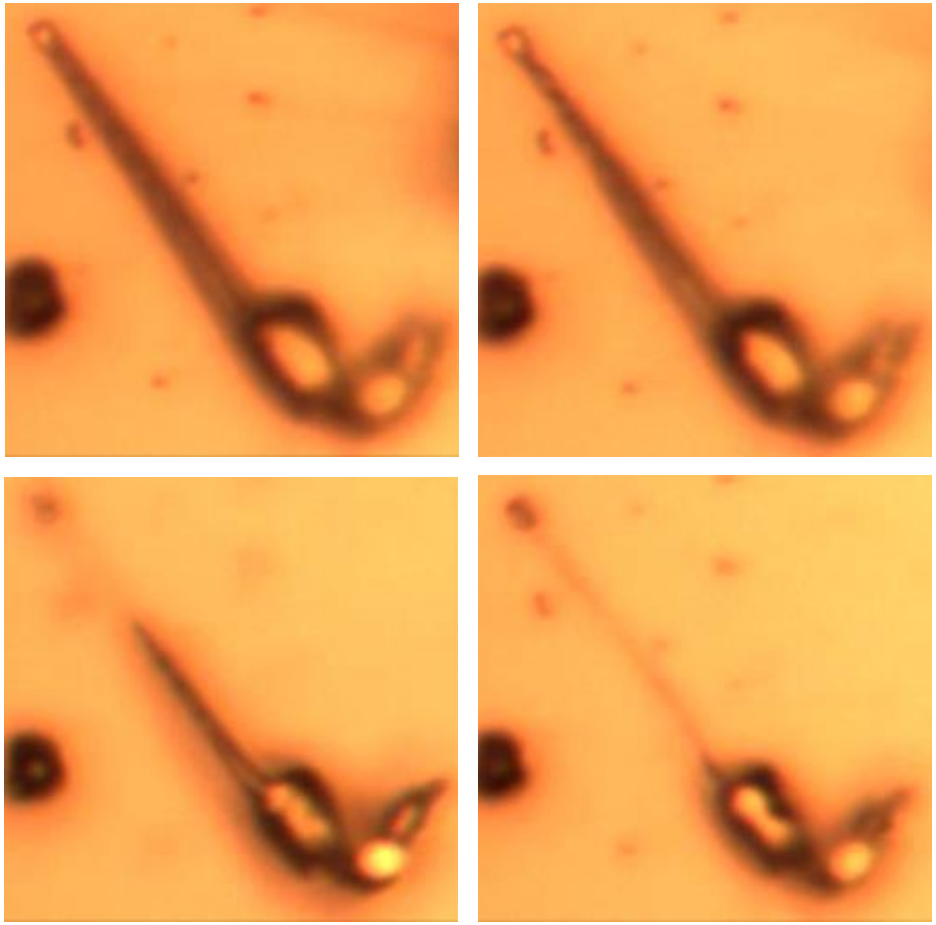
Experiment: Lithium Dendrites

Jens Steiger, Dominik Kramer,
Rainer Mönig,

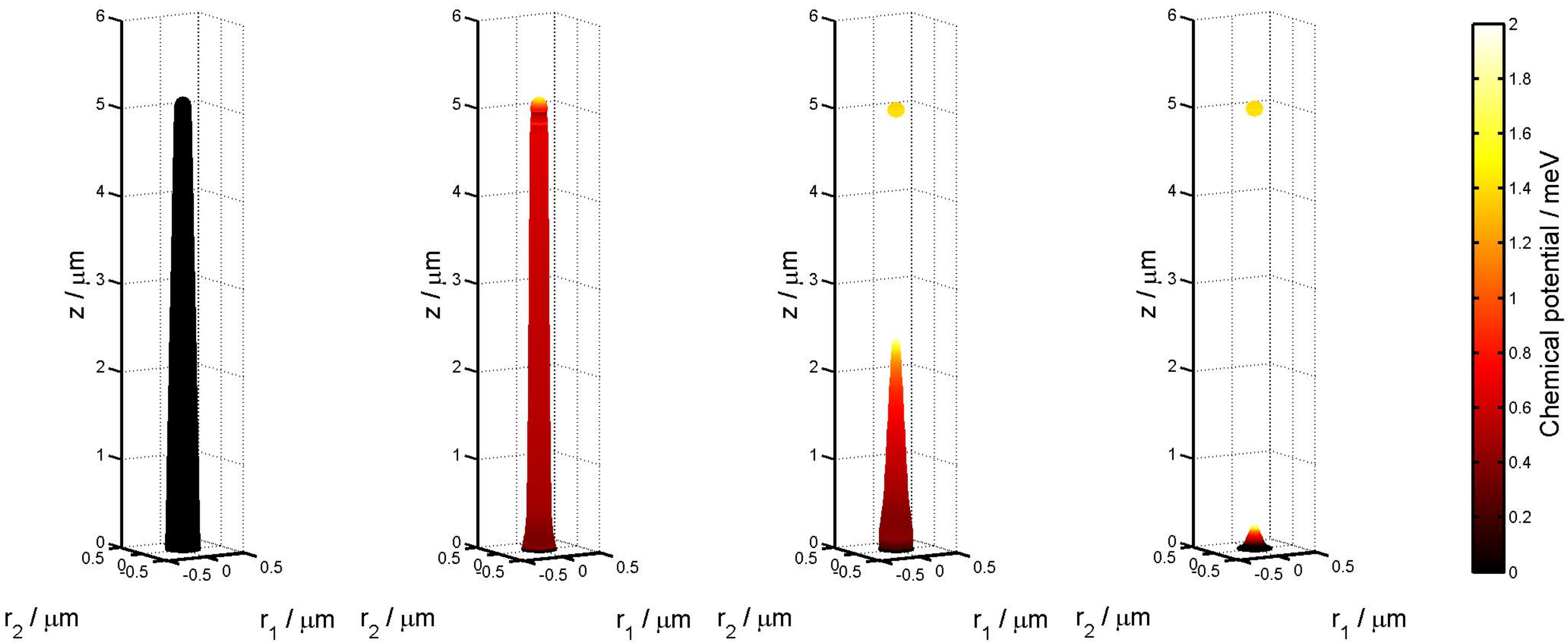
J. Power Sources **261**, 112 (2014).

- Dissolution of lithium dendrites
  - EC:DMC 50:50; 1M $LiPF_6$
  - SEI visible
  - **Droplet** at tip does not dissolve
- Explanations
  - Defect material at tip
  - **Surface tension + Bond to SEI**



Simulation: Lithium Droplet Formation

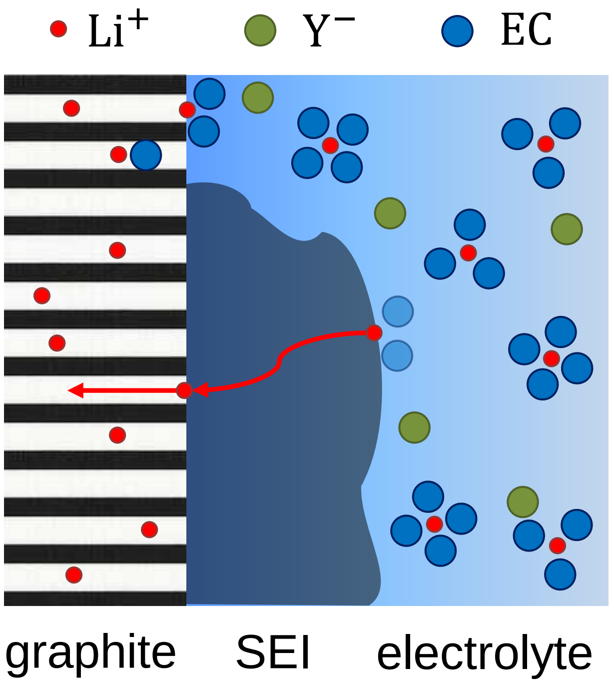
- Droplet formation (Rayleigh-Jeans instability) for
  - **Thin dendrites**, large wavelength fluctuations $2\pi r > \lambda$
  - **Small currents** compared to exchange current $J \ll J_{00}$



Motivation: Solid Electrolyte Interphase (SEI)

Formation

- Reduction of electrolyte, e.g.
  Ethylene Carbonate (EC)
  $2\mathrm{EC} + 2\mathrm{Li}^+ + 2\mathrm{e}^- \rightleftharpoons (\mathrm{CH_2OCO_2Li})_2 + \mathrm{R}$



SEI advantages

- Almost **no further electrolyte reduction**
- Protection of graphite from exfoliation
- Increase in mechanical stability of graphite

SEI disadvantages

- Li^+ ion consumption
- **Continous growth → capacity fade**
- Increase in impedance

Reviews on SEI composition:

- Agubra, V. a., & Fergus, J. W. *Journal of Power Sources* **268**, 153–162 (2014).
- Verma, P., Maire, P., & Novák, P. *Electrochimica Acta* **55**(22), 6332–6341 (2010).

SEI Modeling - Literature Review

Current Models

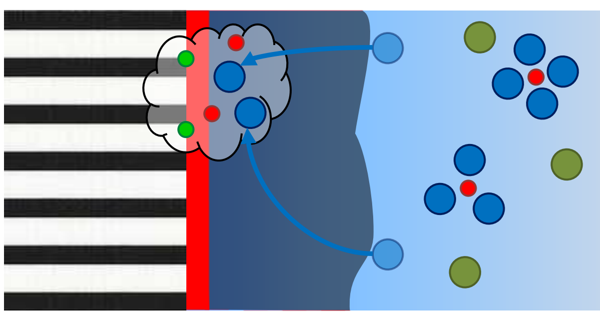
- **Homogeneous** composition
- **Single** transport mechanism
- Fast reaction kinetics
- Single reaction interface

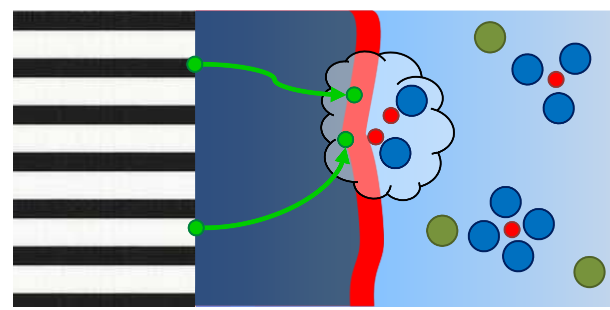
transport-limited growth

$$L(t) \propto \sqrt{t}$$

Solvent/anion diffusion:
- Pinson, M.B. & Bazant, M.Z. *Journal of the Electrochemical Society* **160**, A243-A250 (2012).
- Ploehn, H.J., Ramadass, P. & White, R.E. *Journal of The Electrochemical Society* **151**, A456 (2004).

Electron conduction:
- Christensen, J. & Newman, J. *Journal of The Electrochemical Society* **151**, A1977 (2004).





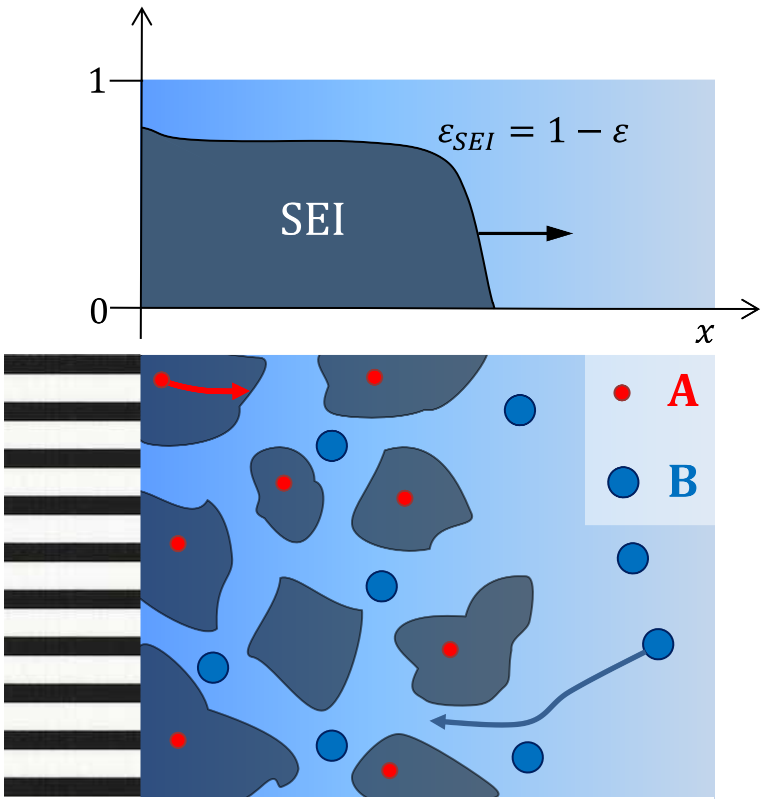
Li^+ Y^- EC e^-

graphite SEI electrolyte

Modeling Concept

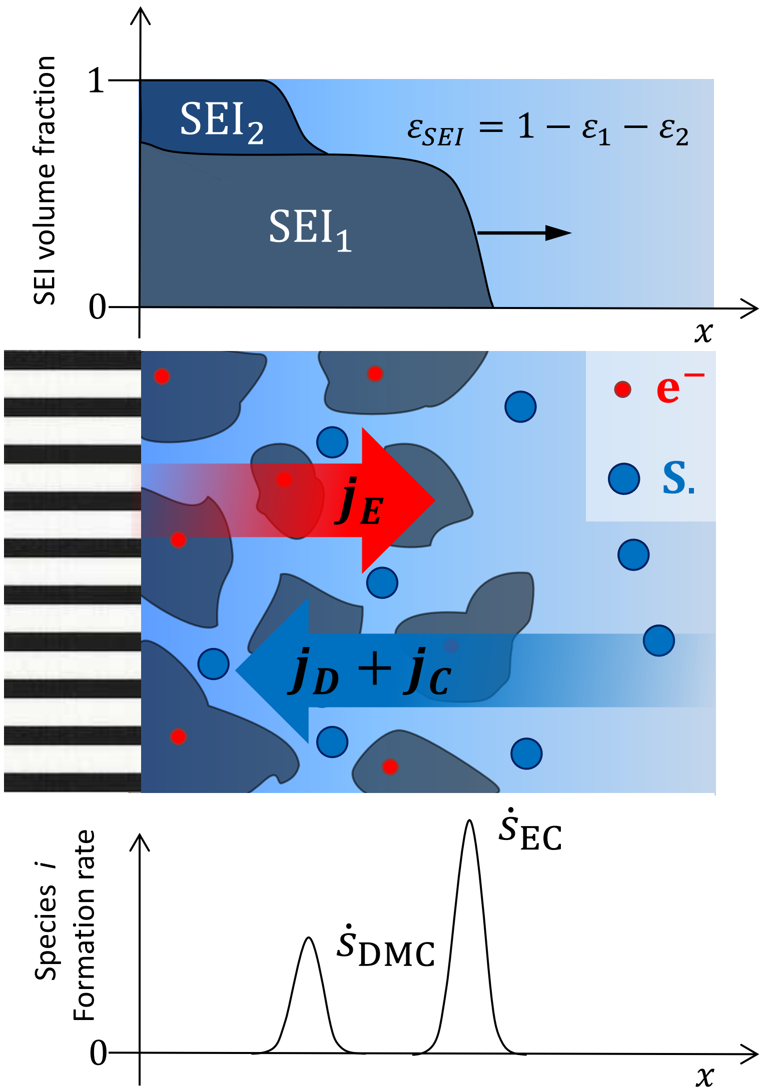
Assumptions & Properties

- **1D model**
- Transport of **all educts** (e^- + Solvent)
- Nano **porous SEI**
  - e^- restricted to SEI
  - Solvent restricted to pores
- Binary solvent mixture (EC/DMC)
- Two SEI components



Model Overview

SEI	Electrons, e^- Ohm's law: $j_\mathrm{E} = \sigma \nabla \Phi$
Electrolyte	Solvent (S.) EC/DEC • Diffusion, Fick´s law $j_\mathrm{D} = D \nabla c$ • Convection $j_\mathrm{C} = c\boldsymbol{v}$ (incompressible fluid)
Formation Rate	$\dot{s}_i \propto \sinh(\tilde{\eta}), \quad i = \mathrm{EC/DMC}$ $\tilde{\eta} = \max(0, \eta)$ $\eta = \frac{z}{2}\frac{\mathrm{RT}}{\mathrm{F}}\left(\Phi - \Phi_i^0\right) + \ln\frac{c_i}{c_i^0}$



Model Overview

Incomp. fluid

Convection velocity

Transport

SEI phase $\sigma = (1-\varepsilon)^{1.5}\boldsymbol{\sigma}_{\mathrm{Bulk}}$

Electrolyte phase $D = \varepsilon^{\boldsymbol{\beta}}\boldsymbol{D}_{\mathrm{Bulk}}$

Mass balance equations

Reactions

$\dot{\boldsymbol{s}}_{\boldsymbol{1}} = \mathrm{Li_2EDC}$ formation rate

$\dot{\boldsymbol{s}}_{\boldsymbol{2}} = \mathrm{Li_2CO_3}$ formation rate

$\varepsilon_1, \varepsilon_2, c_{\mathrm{EC}}, \Phi, v$

Bruggeman

Drive evolution

$$\frac{\partial \varepsilon_i}{\partial t} = V_i \dot{\boldsymbol{s}}_{\boldsymbol{i}}$$

Porosity profile: $\varepsilon_{SEI} = 1 - \varepsilon_1 - \varepsilon_2$

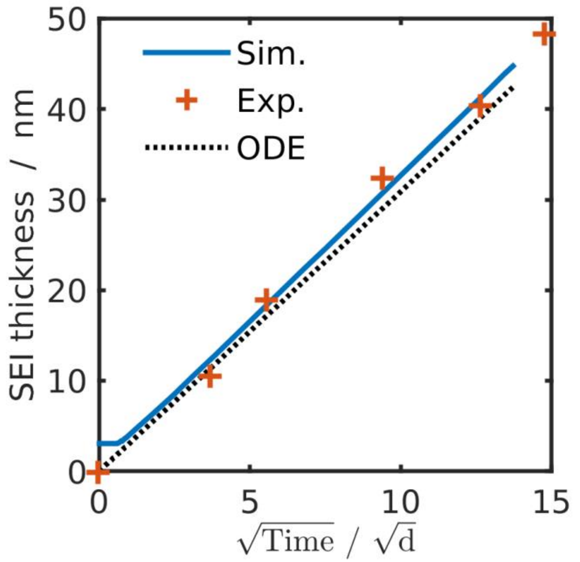
ε_i = Volume fraction of SEI species i

SEI Formation: Single Reduction Reaction

$\sqrt{t}$-growth is observed

Transport parameter fit

- Choose $\beta = 25$
- Fit $\boldsymbol{\sigma}$ to experimental data (15°C)
  $\Rightarrow \boldsymbol{\sigma \approx 0.3\ \mathrm{pS/m}}$

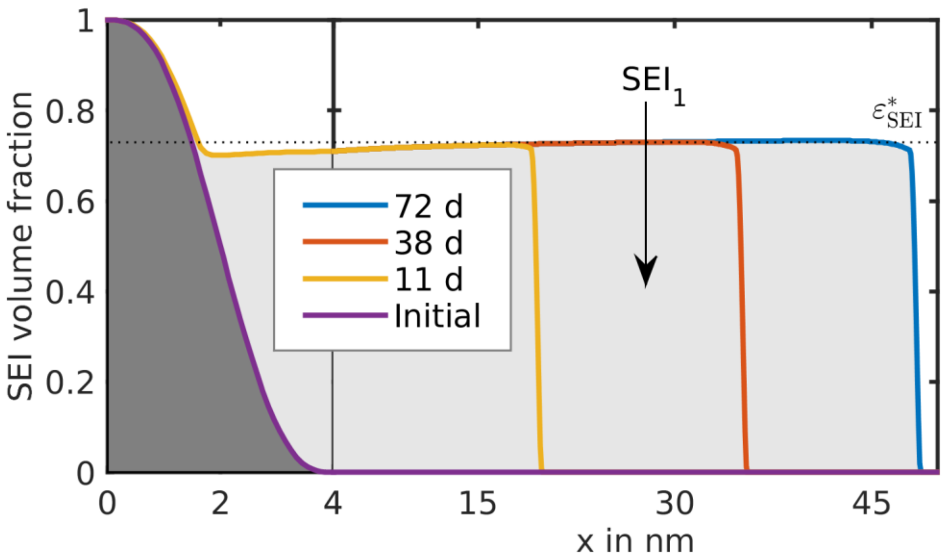


Bulk SEI has **homogeneous porosity**
$\Rightarrow$ Analytic estimation of thickness:

$$\dot{L} = V_{\mathrm{SEI}}\, j_{\mathrm{E}}/2F \propto L^{-1}$$

$$\Rightarrow \boldsymbol{L(t) = \alpha\sqrt{t}}$$

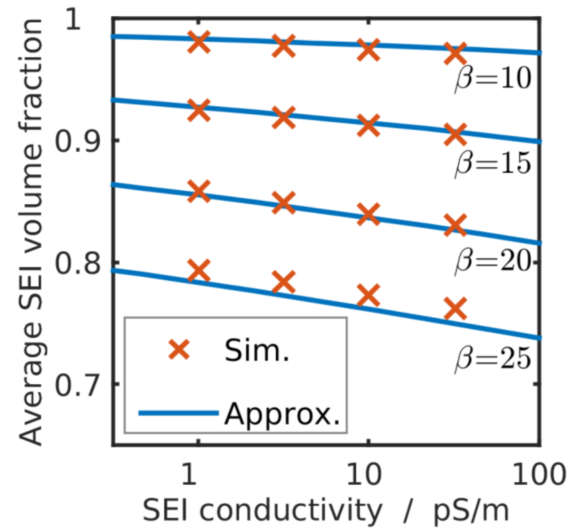
$$\alpha = \sqrt{\varepsilon_{\mathrm{SEI}}^{*1/2} V_{\mathrm{SEI}} \boldsymbol{\sigma} \Delta\Phi / F}$$



Data from:

- Liu, P., Wang et al. *Journal of The Electrochemical Society*, **156**, A499, (2010).
- Pinson, M.B. & Bazant, M.Z. *Journal of the Electrochemical Society* **160**, A243-A250 (2012).

SEI Porosity: Single Reduction Reaction



$\varepsilon^* = 1 - \varepsilon^*_{SEI}$ depends on

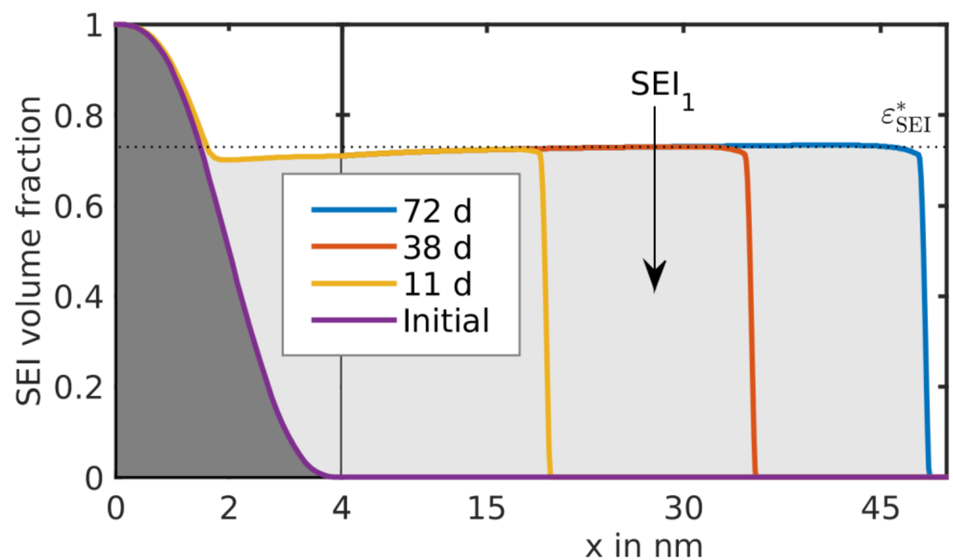
- transport parameters σ and D
- Bruggeman coefficient β

Analytical expression can be derived from:

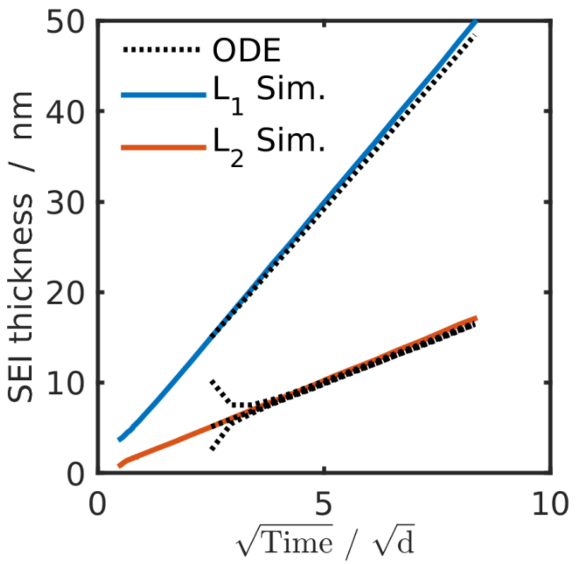
$$\frac{d\varepsilon(t, L(t))}{dt} = \frac{\partial \varepsilon}{\partial t} + \underbrace{\frac{\partial \varepsilon}{\partial L}}_{\varepsilon'} \frac{dL}{dt}$$

Approximation for $\varepsilon^* \rightarrow 1$

$$\varepsilon^* \approx \left(\frac{\sigma RT}{c_{EC} D F^2}\right)^{\frac{1}{\beta - 1}}$$



Two Reduction Reactions



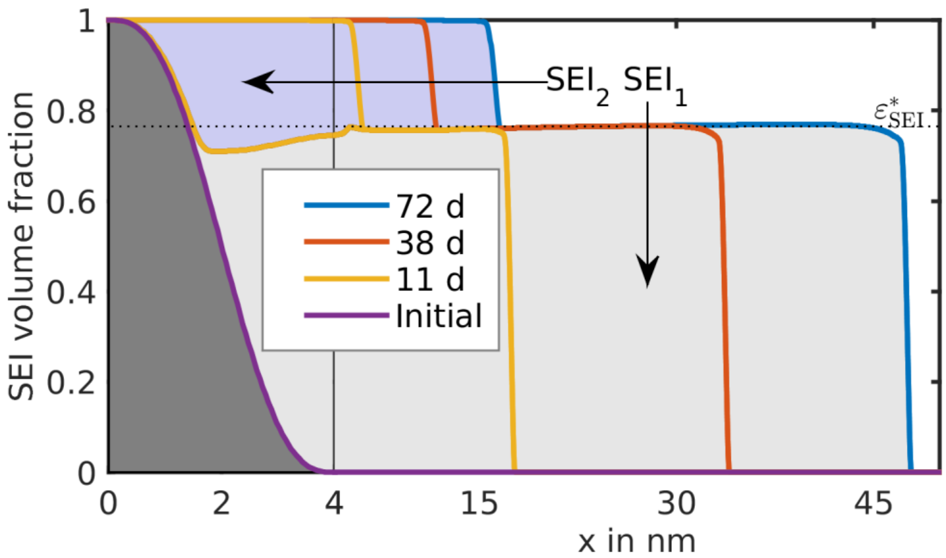
Second SEI species closes pores

- **dense layer**
- L_1 total SEI thickness
- L_2 thickness of dense layer

Transport limited approximation for dual+layer system:

$$\dot{L}_1 = V_{\text{SEI},1} \frac{j_{\text{E,porous}}}{2F\varepsilon^*_{\text{SEI}}}$$

$$\dot{L}_2 = V_{\text{SEI},2} \frac{\left(j_{\text{E,dense}} - j_{\text{E,porous}}\right)}{F\left(1 - \varepsilon^*_{\text{SEI}}\right)}$$

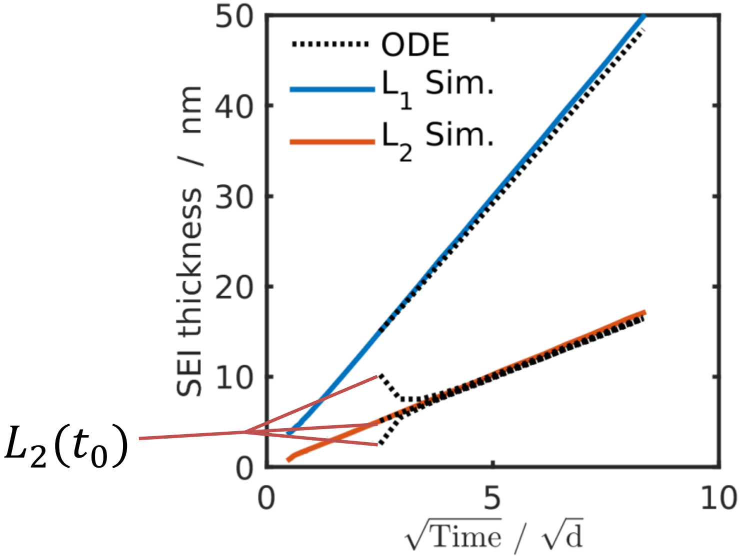


Two Reduction Reactions

Observation:

- Ratio $R = L_1/L_2$ converges fast
- Solution independent of initial value $L_2(t_0)$!
- ODE has analytic solution with $R = const.$

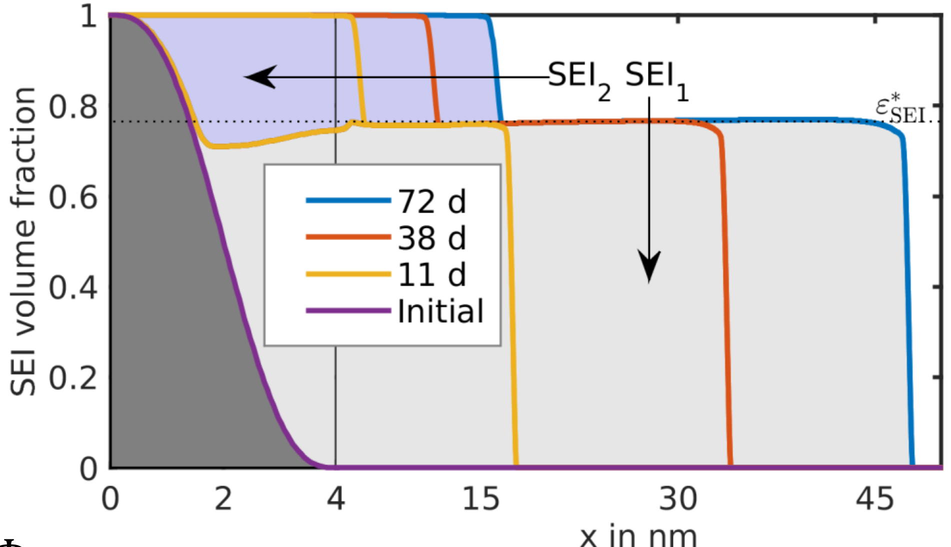
  $\Rightarrow \boldsymbol{L_1(t) = \tilde{\alpha}\sqrt{t}}$



Find stationary R:

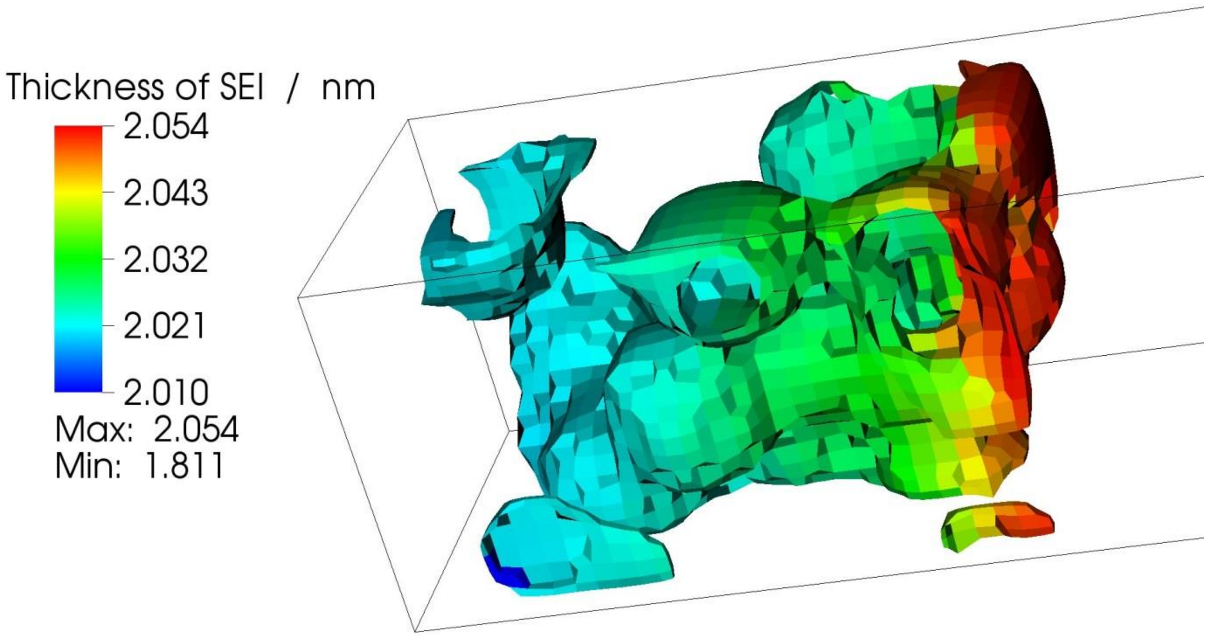
$$\frac{dR}{dt} = \frac{\dot{L}_1}{L_2^2} - \frac{L_1\dot{L}_2}{L_2} = 0$$

$$\frac{\Delta\Phi_1}{\Delta\Phi_2}R^2 - \left(\frac{\Delta\Phi_1}{\Delta\Phi_2} + \varepsilon_{\mathrm{SEI}}^{*1.5}\right) - \varepsilon^*\varepsilon_{\mathrm{SEI}}^*\frac{V_1}{V_2} = 0$$



$\Delta\Phi_1 = \Phi_1^0 - \Phi_2^0, \qquad \Delta\Phi_2 = \Phi_2^0 - \Phi_{\mathrm{electrode}}$

3D Electrode: SEI Formation



- BEST: 3D transport in porous electrodes

$$\frac{\mathrm{d}L}{\mathrm{d}t} = \frac{\sqrt{\varepsilon_{\mathrm{SEI}}^{*}}\, V_{\mathrm{SEI}}\, \sigma_{\mathrm{Bulk}}}{2F} \cdot \frac{\Phi_{\mathrm{SEI}}^{0} - \Phi_{\mathrm{anode}} + \mu_{\mathrm{el}}^{\mathrm{Li}}}{L}$$

  - Implementing SEI growth model on the graphite surface
  - Prediction of **inhomogeneous SEI thickness**
- Understanding intercalation through SEI and lithium loss

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Conclusion

- Modeling dendrite dissolution
    - Droplet formation for pure lithium metal
    - **Rayleigh-Jeans** instability on lithium surface
    - **Binding to SEI** inhibits dissolution of dendrite tip

- Novel SEI modeling
    - SEI phase transport → **growth rate**
    - SEI + electrolyte phase transport → **porosity**

- BEST: **3D electrolyte transport simulation**
    - Voltage fluctuations affect lithium plating and stripping
    - Inhomogeneous SEI formation

Li-EcoSafe

GEFÖRDERT VOM
Bundesministerium für Bildung und Forschung

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Thank you!