Modeling Graphite Surfaces: Lithium Plating & Solid Electrolyte Interphase

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• 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
Dreamliner Battery

• Heat generation due to internal short circuit

• Three possible causes were isolated
  • Lithium metal deposition
  • Contamination from production
  • Damaged 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

![Diagram showing 3D Electrode: Lithium Plating and Stripping](image)

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

- Reaction rate during discharge for various currents (SOC: 0.02 nAh)
- Average lithium concentration in graphite

Intercalation close to plated lithium

Applied current increases

Plated lithium

"DLR.de/tt  •  Folie 5"
3D Electrode: Lithium Stripping During Discharge

- Impact on cell voltage: discharge plateau = lithium amount
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)
  \[ 2\text{EC} + 2\text{Li}^+ + 2\text{e}^- \rightleftharpoons (\text{CH}_2\text{O}\text{CO}_2\text{Li})_2 + \text{R} \]

SEI advantages
• Almost no further electrolyte reduction
• Protection of graphite from exfoliation
• Increase in mechanical stability of graphite

SEI disadvantages
• Li$^+$ ion consumption
• Continuous growth \(\rightarrow\) capacity fade
• Increase in impedance

Reviews on SEI composition:
SEI Modeling - Literature Review

Current Models

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

\[ L(t) \propto \sqrt{t} \]

**Solvent/anion diffusion:**

**Electron conduction:**
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

| SEI | Electrons, $e^-$  
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<td>Ohm’s law: $j_E = \sigma \nabla \Phi$</td>
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### Electrolyte

| Solvent (S.) EC/DEC | Diffusion, Fick’s law $j_D = D \nabla c$  
|---------------------|------------------|
|                     | Convection $j_C = c \nu$  
|                     | (incompressible fluid) |

### Formation Rate

| Formation Rate | $\dot{s}_i \propto \sinh (\tilde{\eta})$, $i = \text{EC/DMC}$  
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<td>$\tilde{\eta} = \max(0, \eta)$</td>
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<td>$\eta = \frac{z RT}{2 F} (\Phi - \Phi_i^0) + \ln \frac{c_i}{c_i^0}$</td>
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\[ \varepsilon_{SEI} = 1 - \varepsilon_1 - \varepsilon_2 \]
Model Overview

Transport

SEI phase
\[ \sigma = (1 - \varepsilon)^{1.5} \sigma_{\text{Bulk}} \]

Electrolyte phase
\[ D = \varepsilon^\beta D_{\text{Bulk}} \]

Mass balance equations

Reactions
\[ \dot{s}_1 = \text{Li}_2\text{EDC formation rate} \]
\[ \dot{s}_2 = \text{Li}_2\text{CO}_3 \text{ formation rate} \]

\[ \partial_i \varepsilon_i \partial t = V_i \dot{s}_i \]

Porosity profile:
\[ \varepsilon_{SEI} = 1 - \varepsilon_1 - \varepsilon_2 \]
\[ \varepsilon_i = \text{Volume fraction of SEI species } i \]

Convection velocity
Incomp. fluid

Bruggeman

Drive evolution

\[ c_{EC}, \Phi, \nu \]
**SEI Formation: Single Reduction Reaction**

\( \sqrt{t} \)-growth is observed

**Transport parameter fit**

- Choose \( \beta = 25 \)
- Fit \( \sigma \) to experimental data (15\(^\circ\)C)

\( \Rightarrow \sigma \approx 0.3 \text{ pS/m} \)

Bulk SEI has **homogeneous porosity**

\( \Rightarrow \) Analytic estimation of thickness:

\[ \dot{L} = \frac{V_{SEI} j_E}{2F} \propto L^{-1} \]

\[ \Rightarrow L(t) = \alpha \sqrt{t} \]

\[ \alpha = \sqrt{\frac{\varepsilon_{SEI}^{1/2} V_{SEI} \sigma \Delta \Phi}{F}} \]

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**Data from:**
SEI Porosity: Single Reduction Reaction

\(\varepsilon^* = 1 - \varepsilon_{SEI}^*\) depends on
- transport parameters \(\sigma\) and \(D\)
- Bruggeman coefficient \(\beta\)

Analytical expression can be derived from:

\[
\frac{d\varepsilon(t, L(t))}{dt} = \frac{\partial \varepsilon}{\partial t} + \frac{\partial \varepsilon}{\partial L} \frac{dL}{dt}
\]

Approximation for \(\varepsilon^* \rightarrow 1\)

\[
\varepsilon^* \approx \left( \frac{\sigma RT}{C_{EC}DF^2} \right)^\frac{1}{\beta-1}
\]
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:

\[
\dot{L}_1 = V_{SEI,1} \frac{j_{E,\text{porous}}}{2F \epsilon_{SEI}^*}
\]

\[
\dot{L}_2 = V_{SEI,2} \frac{(j_{E,\text{dense}} - j_{E,\text{porous}})}{F(1 - \epsilon_{SEI}^*)}
\]
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 $R = const.$

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

Find stationary $R$:

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

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

$$\Delta \Phi_1 = \Phi_1^0 - \Phi_2^0, \quad \Delta \Phi_2 = \Phi_2^0 - \Phi_{\text{electrode}}$$
3D Electrode: SEI Formation

- BEST: 3D transport in porous electrodes
  \[
  \frac{dL}{dt} = \frac{\sqrt{\varepsilon_{\text{SEI}}^{*}} V_{\text{SEI}} \sigma_{\text{Bulk}}}{2F} \cdot \frac{\Phi_{\text{SEI}}^{0} - \Phi_{\text{anode}} + \mu_{\text{el}}^{\text{Li}}}{L}
  \]
  - Implementing SEI growth model on the graphite surface
  - Prediction of inhomogeneous SEI thickness
- Understanding intercalation through SEI and lithium loss
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

Thank you!