Solid Electrolyte Interphase: Theory and Experiment

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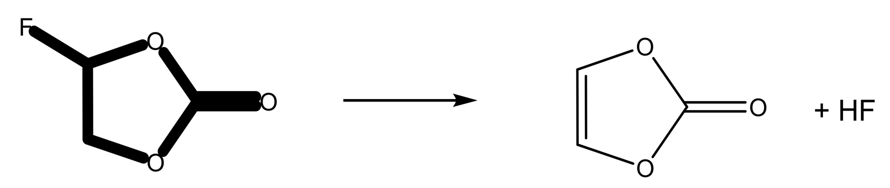
Solid Electrolyte Interphase (SEI)

- Film formation on graphite anode
  - **Reduction product** of electrolyte
  - SEI slows down further electrolyte reduction
  - **Continued capacity fade** / Increase in impedance
- Challenges in Experiment and Theory
  - Complex **chemical composition**
  - SEI morphology: **porosity** / dual-layer structure
  - Limiting **transport process**

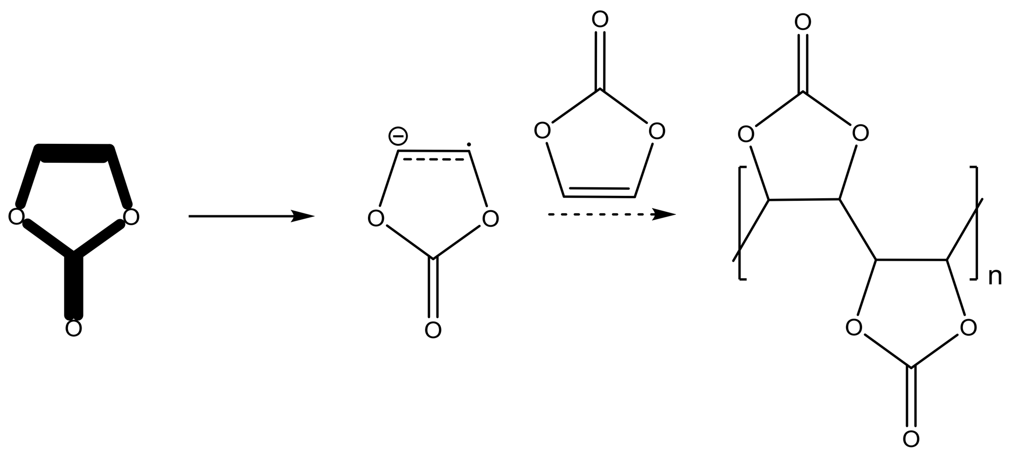
Experiment

- Graphite vs. Li/Li+
- Electrolyte: EC:DEC 3:7 wt.-%. 1 M $LiPF_6$
- Additive: Fluoroethylene carbonate (FEC), 2 wt.-%

Reaction of FEC[1]:



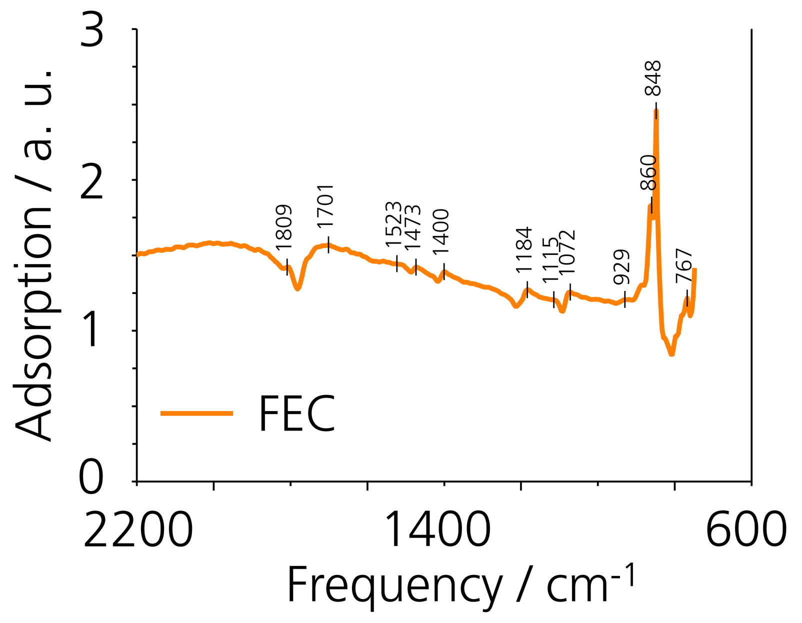
Splitting from HF



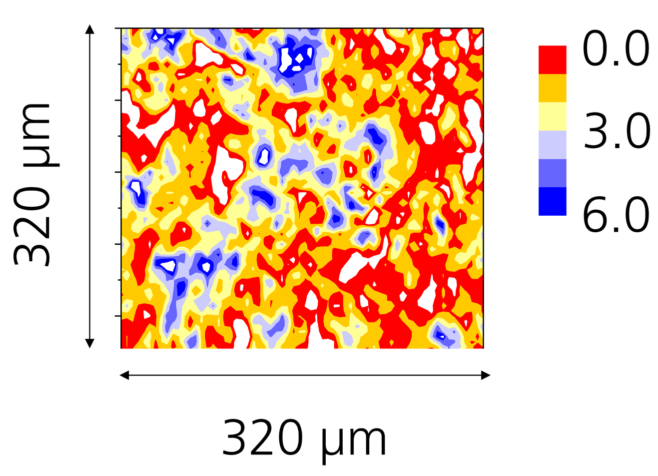
Electrochemically induced radical polymerization

Results:

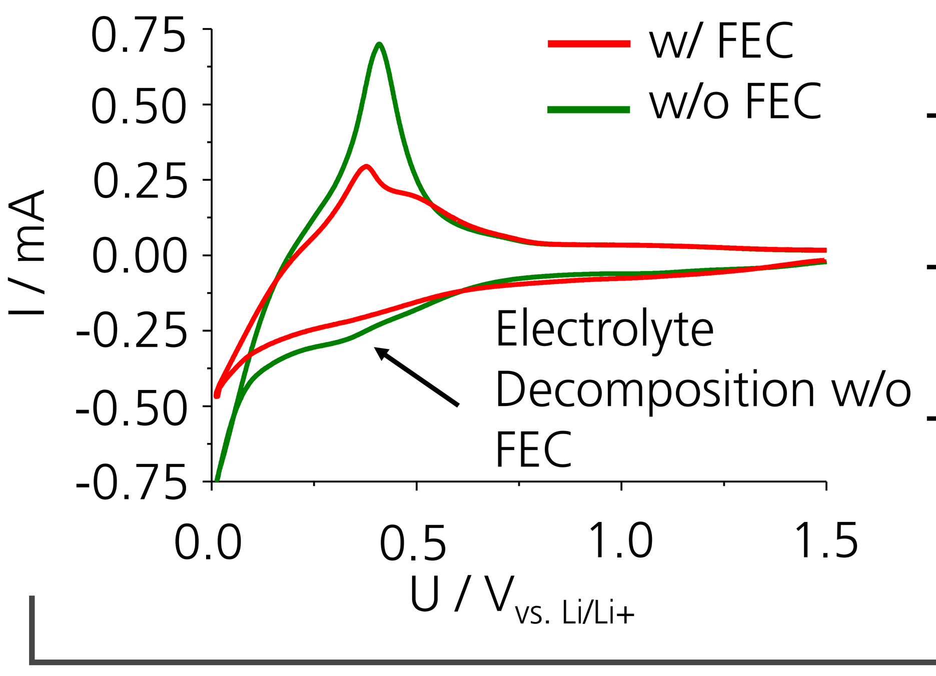
Fourier Transform Infrared Spectroscopy



Peak area
1200-1116 cm-1



Cyclovoltammetry

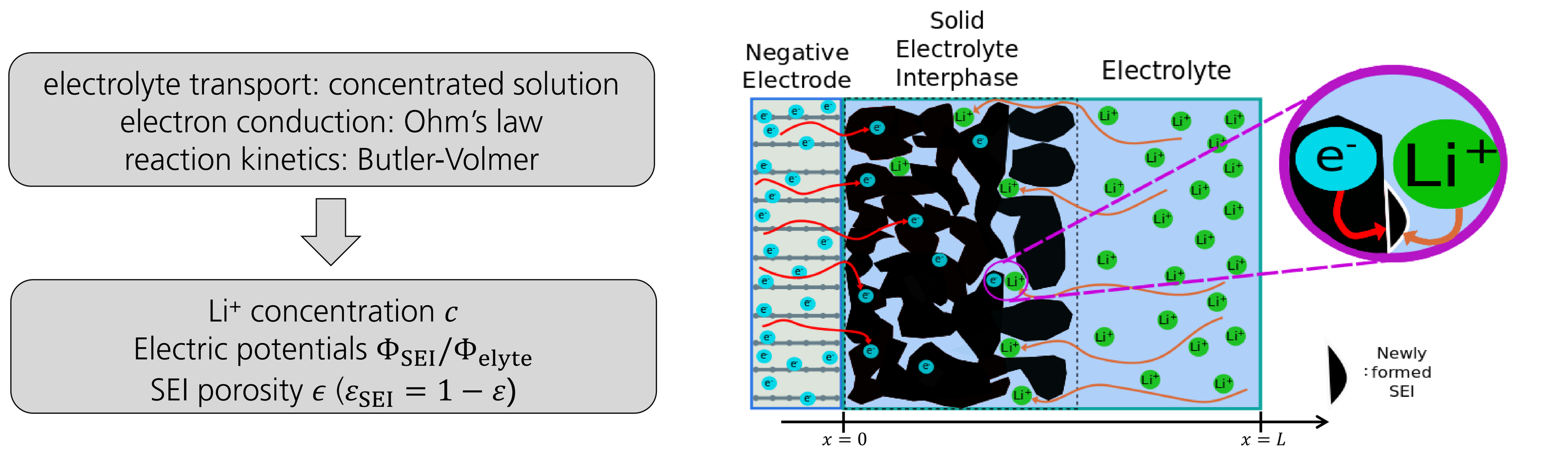


Conclusion:

- VC is reduced earlier than the electrolyte (CV)
- A stable film on the anode side is formed
- Further electrolyte decomposition is prevented
- Homogeneity of SEI-layer verified with space-resolved FTIR

Modeling Scheme

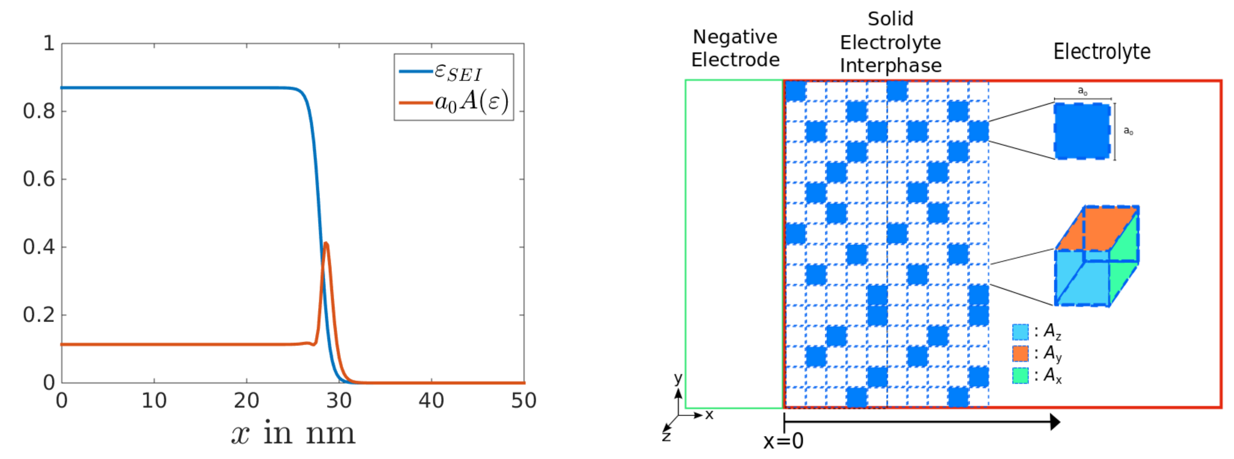
- 1D mesoscopic continuum model on electrode surface
  - Simple SEI chemistry: Li_2CO_3
  - Electrolyte conductivity in **nanopores** $\sigma^{eff} = \epsilon^{\beta}\sigma$ with large empirical Brugemann coefficient β



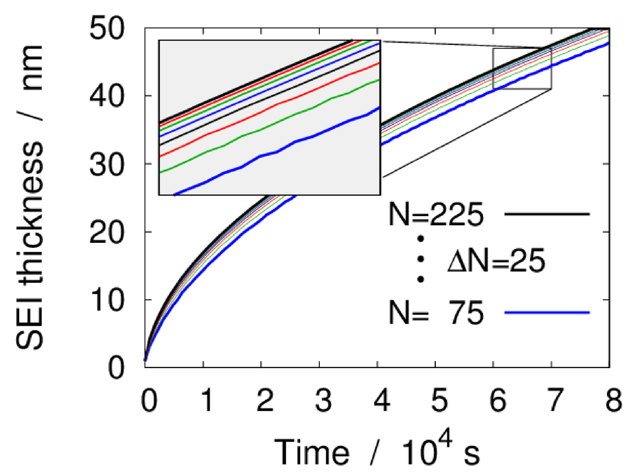
- **Specific Surface Area** of porous SEI

$$A(\varepsilon) = \frac{6}{a_0}\varepsilon(1-\varepsilon) - a_0\varepsilon\frac{\partial^2\varepsilon}{\partial x^2}$$

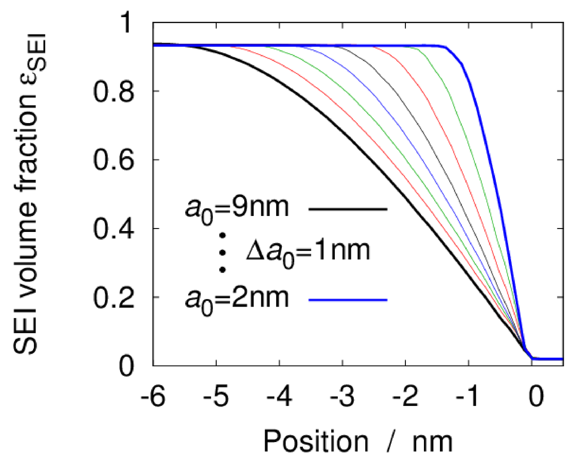
  - Elementary cubes of size a_0^3 filled with probability ε_{SEI}



Simulation and Discussion

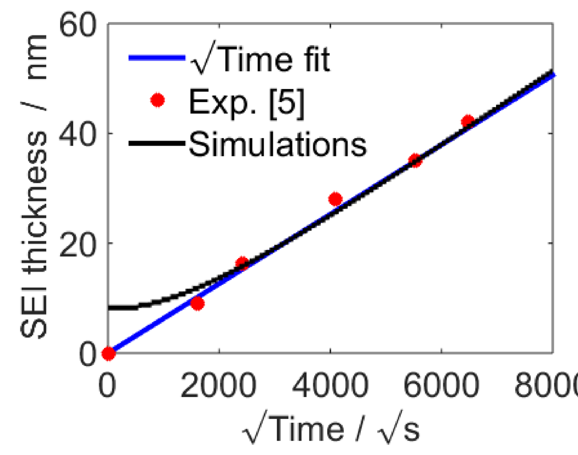


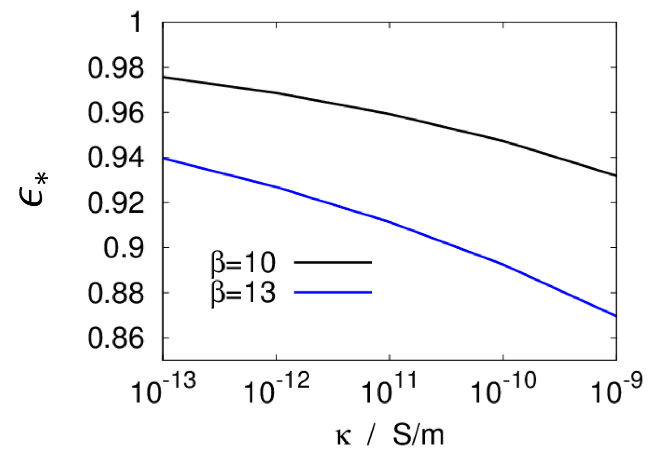
- Numerical stability
- Front width scales with a_0



- **Thickness** growth with $\sqrt{t}$ due to electron conductivity ($\kappa \approx 10^{-12}$S/m)

$$\frac{dL}{dt} = \frac{\Phi'\kappa(1-\varepsilon(L))^{1.5}}{2F}(1-\varepsilon(L))V^M$$





- **Constant porosity** ϵ_* due to balance with electrolyte transport ($\beta \approx 10$)

$$\beta\epsilon_*^{\beta-1}\sigma \approx (1-\epsilon_*)^{2.5}\kappa$$

Literature

[1] S. S. Zhang, J. Power Sources 162 (2006) 1379.
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Li-EcoSafe
ZSW
DLR
HIU Helmholtz Institute Ulm Electrochemical Energy Storage

BMBF Projekt (03X4636A): Li-EcoSafe - Entwicklung kostengünstiger und sicherer Lithium-Ionen-Batterien