Institute of
Technical Thermodynamics

Theoretical Aspects of Lithium Plating and dendrite dissolution in 3D electrodes

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Microscopy of Lithium Dendrite Dissolution

In situ light microscopy study on electrodeposition of lithium and the onset of dendritic growth

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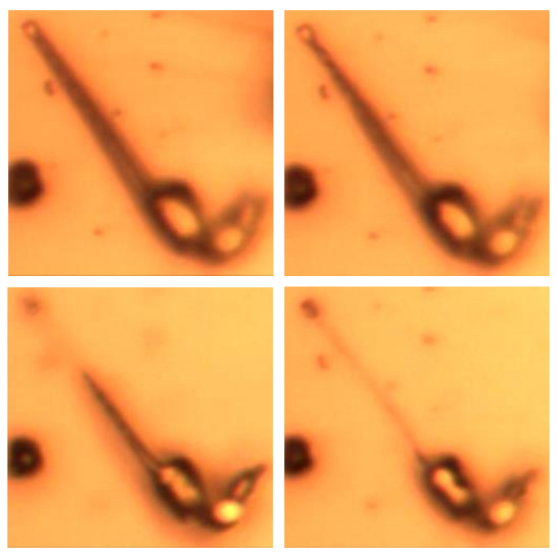
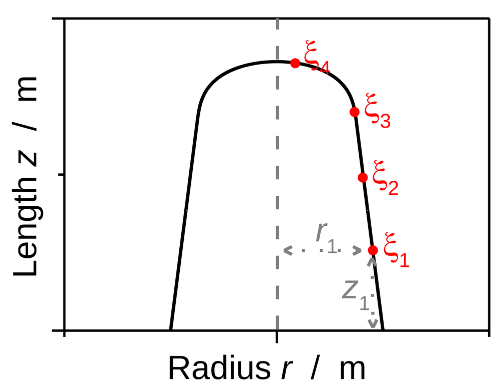
- Experiment
  - EC:DMC 1:1; 1M $LiPF_6$
  - SEI visible
  - **Droplet formation at tip**
- Hypotheses
  - Surface energies: SEI / Li
  - Defect material at tip



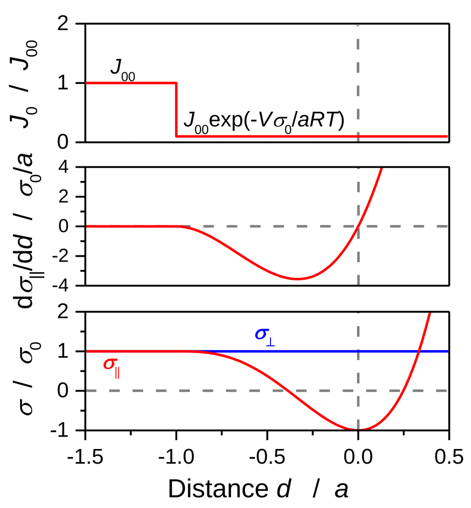
Model for Rayleigh-Jeans Instability

- Modeling methodology[1]
  - Axial symmetry (z, r) plane
  - Surface markers ξ_i



- **Butler-Volmer** reaction rate[2,3]

$$J(\xi) = J_0\left(e^{-\frac{0.5F\Delta\Phi}{RT}} - e^{\frac{\mu(\xi)}{RT}} e^{\frac{0.5F\Delta\Phi}{RT}}\right)$$



- Non-equilibrium Gibbs energy

$$G = \int \sigma \, dA = \int g \, dz$$

- Variational chemical potential

$$\mu = \frac{V}{2\pi r}\frac{\delta G[r]}{\delta r} = \frac{V}{2\pi r}\left(\frac{\partial g}{\partial r} - \frac{\partial}{\partial z}\frac{\partial g}{\partial \frac{\partial r}{\partial z}}\right)$$

- **Surface energy** (d distance, α angle Li-SEI)

$$\sigma(d, \alpha) = \sigma_\perp \cdot \sin^2(\alpha/2) + \sigma_{||}(d) \cdot \cos^2(\alpha/2)$$

- **Young-Laplace** chemical potential $\mu = \mu_{Li} + \mu_{SEI} + \mu_\Delta$

standard Li surface

$$\mu_{Li} = V\frac{\sigma_{||} + \sigma_\perp}{2}\left(\frac{1}{R^1} + \frac{1}{R^2}\right)$$

bond-breaking SEI-Li

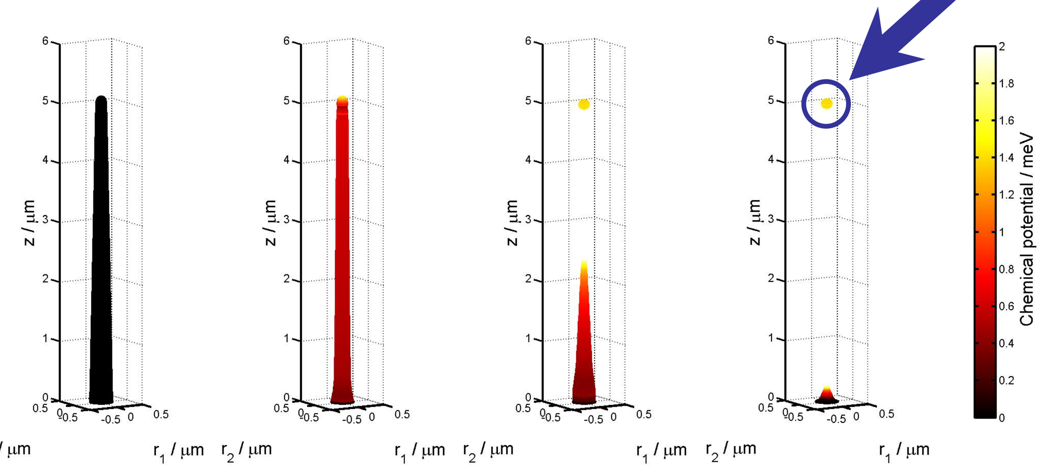
$$\mu_\Delta = V\frac{d\sigma_{||}}{dd}\cos^2(\alpha/2)$$

chemical bond SEI-Li

$$\mu_{SEI} = V\frac{\sigma_{||} - \sigma_\perp}{2}\left(\frac{1}{d + R_0^1} + \frac{1}{d + R_0^2}\right)$$

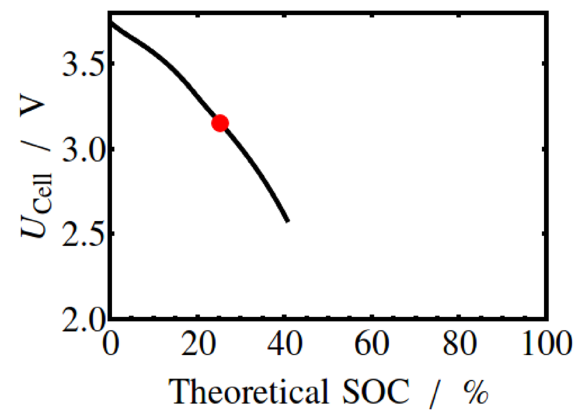
Simulation of Droplet Formation

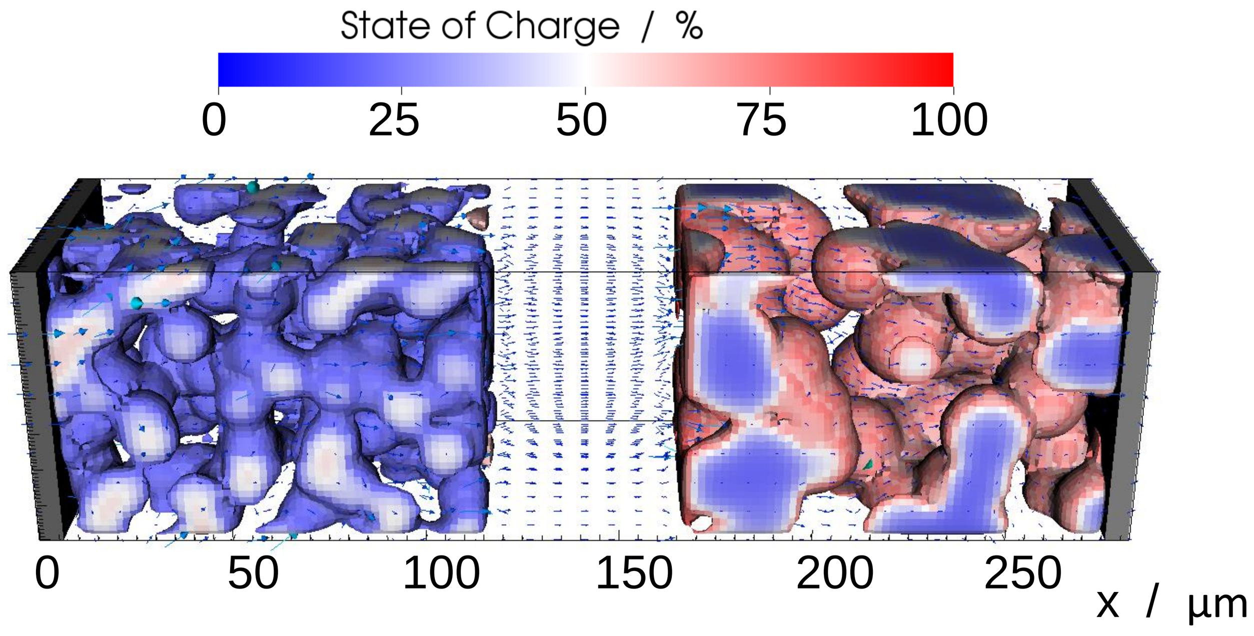
- Requirements
  - **Thin dendrites** ($r < \lambda/2\pi$ fluctuation wavelength)
  - **Small currents** ($J \ll J_{00}$ exchange current)
- Droplet formation for pure lithium metal.
- **Binding to SEI** inhibits dissolution of tip.



Modeling Framework

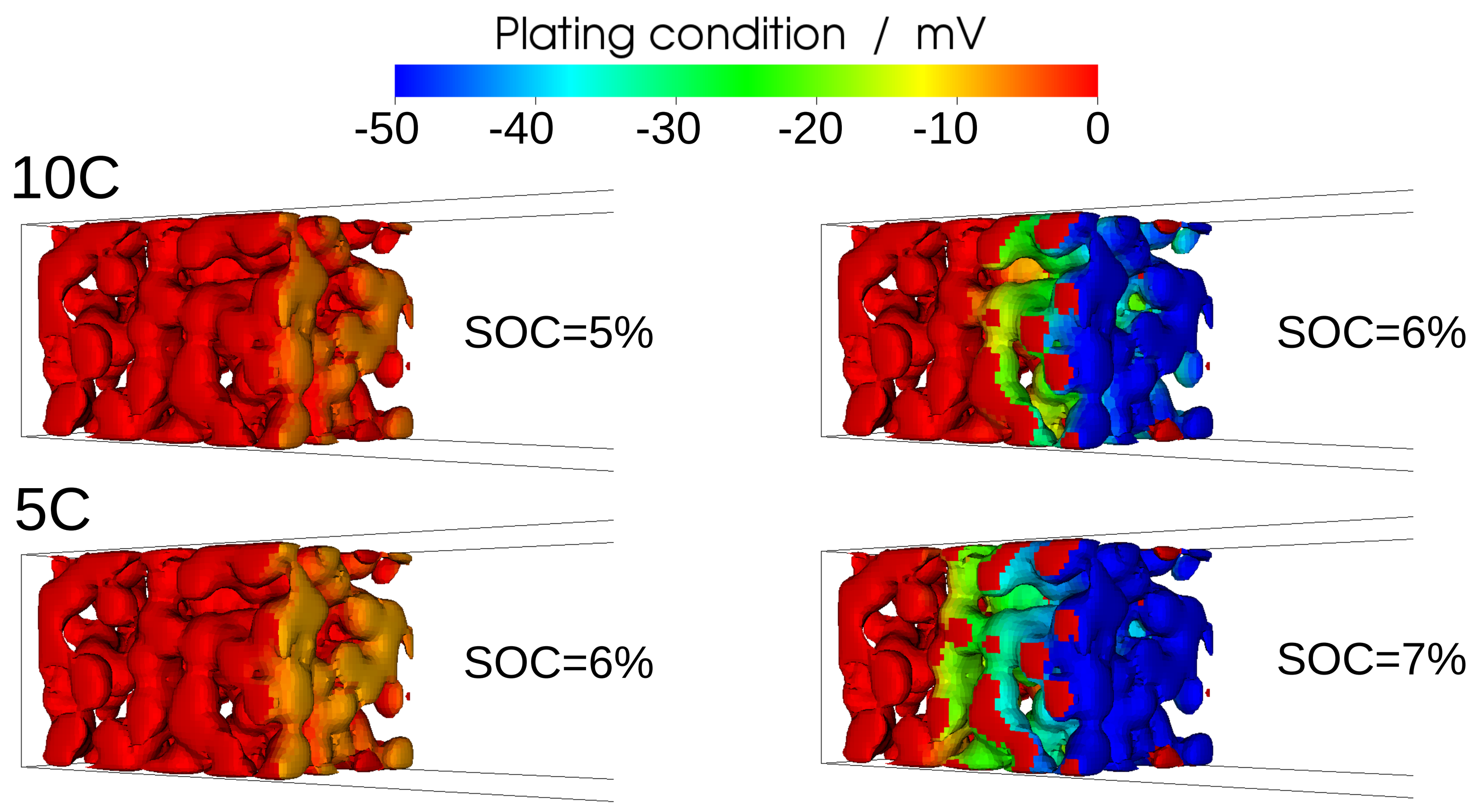
- Thermodynamically consistent 3D transport model[4]
  - Concentrated solution theory in electrolyte
  - Fick's diffusion in solid particles
  - Electric conduction
- Development of simulation tool **BEST – Battery and Electrochemical Simulation Tool**[5]
- Example: lithium ion battery[6-8]
  - Anode: Graphite Li_xC_6
  - Cathode: $LiMn_2O_4$
  - Electrolyte: $LiPF_6$, EC:DMC 3:7
  - Discharge rate: 1C





Thermodynamic Condition for Lithium Plating

- Plating on graphite electrode[9]
  - Necessary condition $\Phi_{solid} - \varphi_{elyte} = \eta + U_0^{an} \le 0$



- Results
  - **Plating starts at anode-separator interface**
  - Agreement with experiments[10]
  - Outlook: growth of metallic lithium phase

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