Simulation of lithium plating in electrode microstructures

Institute of Engineering Thermodynamics

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Lithium Plating

- Formation of metallic lithium on negative electrode surface:

$$Li^+ + e^- \rightleftharpoons Li^o$$

- Plating thermodynamically possible if [1,2]:

$$\Phi_{\text{solid}} - \varphi_{\text{elec}} < 0$$

- Plating condition:

$$\eta_{\text{So/El}} + OCV_{\text{solid}}(SoC) < 0$$

1D+1D Model

- Based on Arora et al. [3]
- Lithium plating and stripping
- No intercalation of plated lithium into active particle
- Deposition current in negative electrode

$$i_d = i_{d,0}(c_e) \cdot \left(\mathrm{f(r_{Li})} \cdot \exp\left(\frac{\alpha_a \cdot F \cdot \eta_d}{R \cdot T}\right) - \exp\left(-\frac{\alpha_c \cdot F \cdot \eta_d}{R \cdot T}\right)\right)$$

$$\eta_d = \Phi_s - \varphi_e - i_d \cdot R_{film}$$

$$f(r_{Li}) = \begin{cases} 1 & r_{Li} > r_{min} \\ r_{Li}/r_{min} & r_{Li} \leq r_{min} \end{cases}$$

- Film resistance

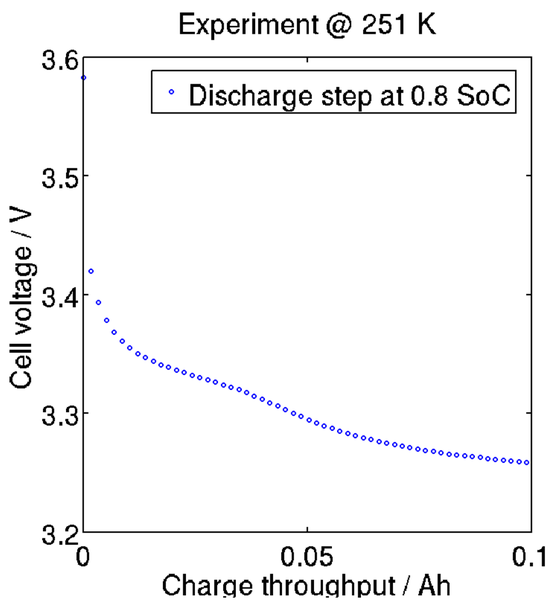
$$R_{film} = R_{SEI} + \frac{r_{Li}}{\sigma_{Li}}$$

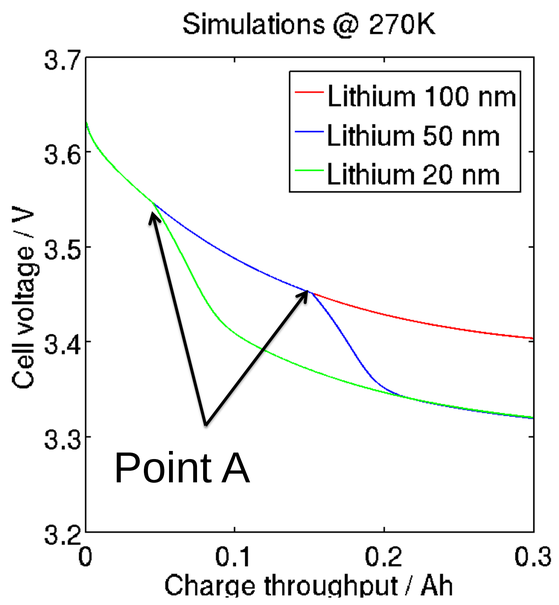
- Film Growth

$$\frac{\partial\, r_{Li}}{\partial\, t} = -\frac{i_d \cdot M_{Li}}{\rho_{Li} \cdot F}$$

Comparison between Experiment and Simulation [4]

- Experiments on commercial cylindrical 26650-type cells
- LFP + Graphite
- Charge and discharge at low temperatures





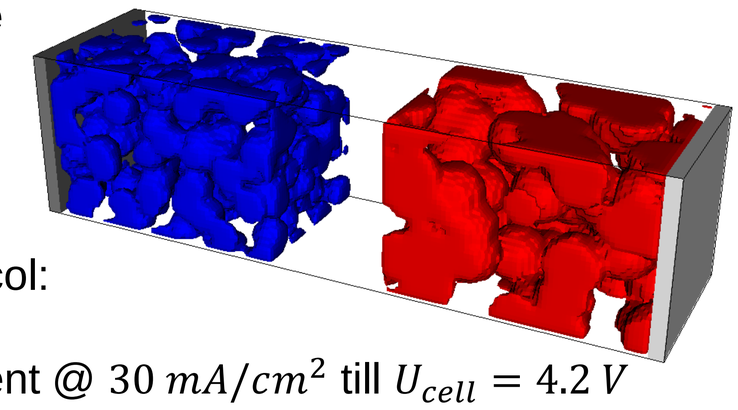
- Plateau in cell voltage due to lithium stripping
- Point A: Indication that most of the lithium is stripped
- Shape of Plateau: Kinetics of stripping

- No SEI-formation allowed
- Temperature dependence of OCP unknown

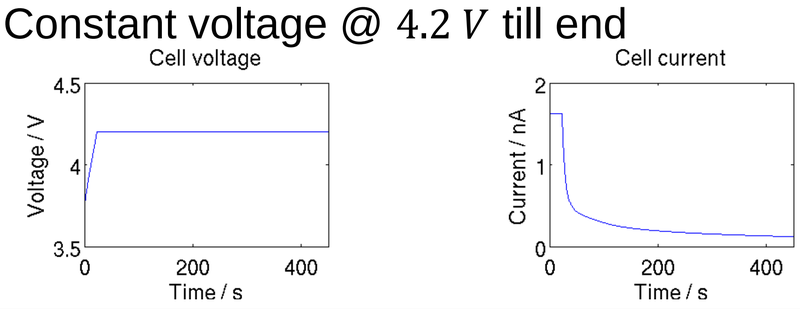
3D Model

- Based on Latz et al. [5]
- Software framework BEST [6]

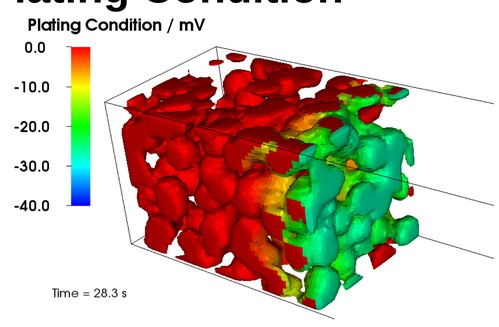
3D Microstructure



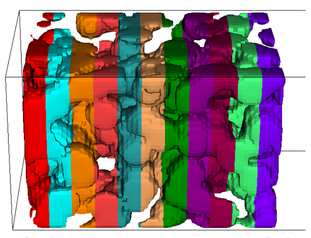
- Blue: Graphite
- Red: LMO
- Void: $LiPF_6$ (EC:DMC 3:7)
- Operation protocol:
  - $T = 298\ K$
  - Constant current @ $30\ mA/cm^2$ till $U_{cell} = 4.2\ V$
  - Constant voltage @ $4.2\ V$ till end



Plating Condition



- First fulfilled at Separator/Anode interface



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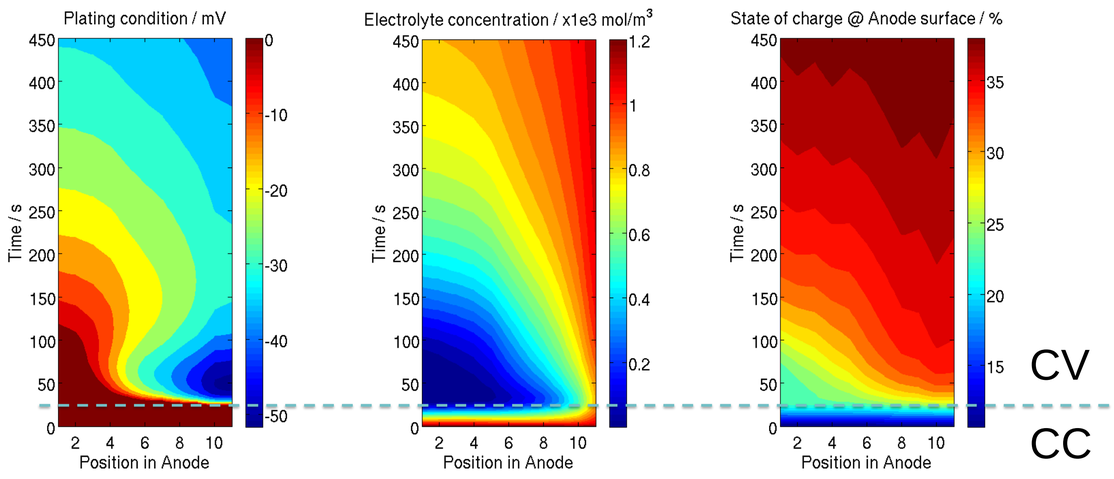
- Subdivide Anode for analysis:



- Plating condition fulfilled at RT
- Li-Diffusion in Elyte hinders advancing of plating front:
  - Li-Depletion in Elyte → No further change of SoC
  - Li-Diffusion in solid lowers SoC on Surface
  - Li-Diffusion in Elyte → Advancing of plating front

[1] N. Legrand, B. Knosp, P. Desprez, F. Lapicque, and S. Raël, *J. Power Sources*, **245**, 208 (2014).
[2] A. M. Colclasure and R. J. Kee, *Electrochim. Acta* **55** (28), 8960 (2010).
[3] P. Arora, M. Doyle, and R. E. White, J. Electrochem. Soc. **146**, 3543 (1999)
[4] M. Petzl and M. A. Danzer, J. Power Sources **254**, 80 (2014).
[5] A. Latz and J. Zausch, J. Power Sources **196**, 3296 (2011).
[6] ITWM, BEST, www.itwm.fraunhofer.de/best

Knowledge for Tomorrow

DLR Deutsches Zentrum für Luft- und Raumfahrt German Aerospace Center

HIU Helmholtz Institute Ulm Electrochemical Energy Storage

ZSW

Federal Ministry of Education and Research

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