Institute of Engineering Thermodynamics

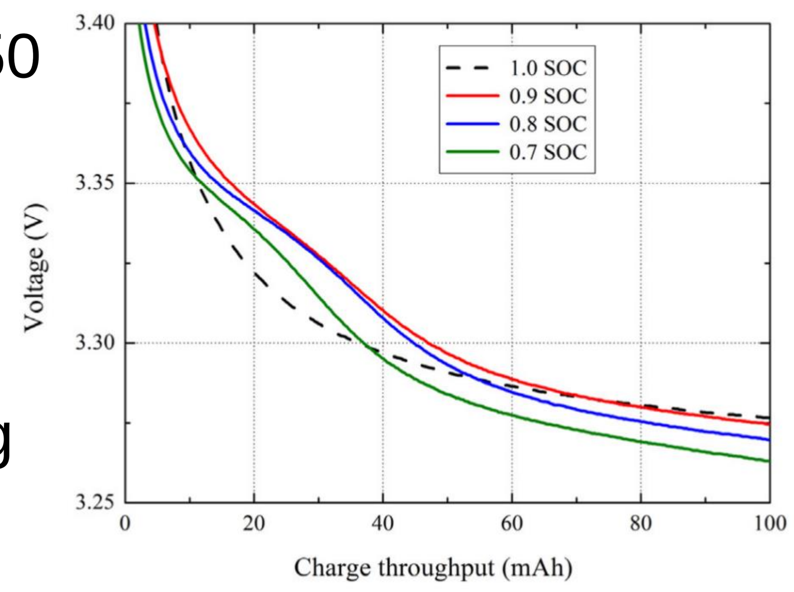
Simulation of Lithium Plating and Stripping during low temperature operation of Li-ion Battery

Simon Hein[1,2,3], Mathias Petzl[2], Michael A. Danzer[2,4], and Arnulf Latz[1,2,3]

[1] German Aerospace Center, 70569 Stuttgart, Germany
[2] Helmholtz Institute Ulm, 89081 Ulm, Germany
[3] University of Ulm, 89081 Ulm, Germany
[4] Center for Solar Energy and Hydrogen Research Baden-Württemberg (ZSW), 89081 Ulm, Germany

Experiments[1]

- Commercial cylindrical 26650 -type cells
- LFP + Graphite
- Charge and discharge at low temperatures
- Indication of lithium stripping in discharge curve
- Reversible and irreversible lithium plating



Voltage profile of discharge steps (Fig. 2 in [1])

Model and Simulation

- 1D+1D Model [2,3]
- Lithium plating and stripping
- No intercalation from lithium metal to active particle

$$\epsilon_e \frac{d\langle c_e\rangle}{d\,t} = \nabla\left(D_e^{eff}\nabla\langle c_e\rangle\right) + \frac{a\cdot i_1}{F}\cdot(1-t_+)$$

$$0 = \nabla\left(\kappa_e^{eff}\nabla\langle\varphi_e\rangle\right) + \frac{t_+-1}{F}\cdot R\cdot T\cdot\nabla\left(\kappa_e^{eff}\cdot\nabla(ln\langle c_e\rangle)\right) + a\cdot i_2$$

$$\frac{d\,c_s}{d\,t} = \frac{1}{r^2}\cdot\nabla_r\left(D_s\cdot r^2\cdot\nabla_r c_s\right)$$

$$0 = \nabla\left(\sigma_s^{eff}\nabla\langle\Phi_s\rangle\right) - a\cdot i_4$$

- Deposition current in negative electrode

$$i_{dep} = i_{dep,0}\cdot\langle c_e\rangle^{\alpha_{dep,c}}\cdot$$
$$\left(f(r_{Li})\cdot\exp\left(\frac{\alpha_{dep,a}\cdot F}{R\cdot T}\cdot\eta_{dep}\right) - \exp\left(-\frac{\alpha_{dep,c}\cdot F}{R\cdot T}\cdot\eta_{dep}\right)\right)$$

$$\eta_{dep} = \langle\Phi_s\rangle - \langle\varphi_e\rangle - i_{dep}\cdot R_{film}$$

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

- Intercalation current in negative electrode

$$i_{int} = 2\cdot i_{int,0}\cdot\sqrt{\langle c_e\rangle}\cdot\sqrt{c_s\cdot(c_{s,max}-c_s)}\cdot\sinh\left(\frac{F\cdot\eta_{int}}{2\cdot R\cdot T}\right)$$

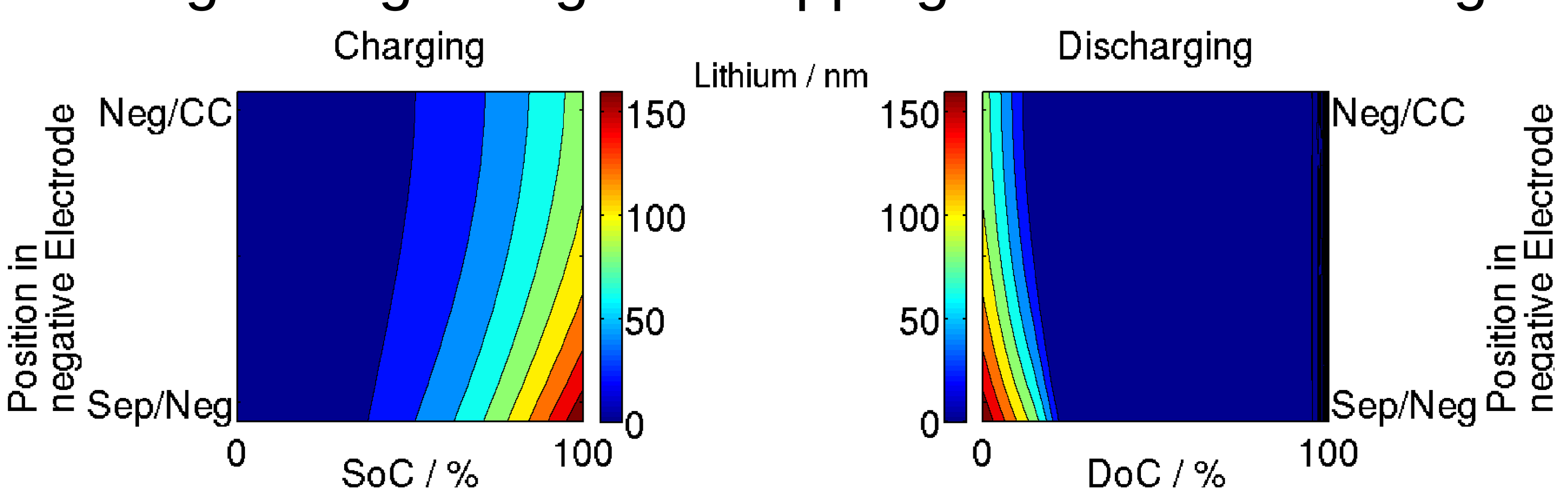
$$\eta_{int} = \langle\Phi_s\rangle - \langle\varphi_e\rangle - U_0 - i_{int}\cdot R_{film}$$

- Film resistance

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

Lithium Plating

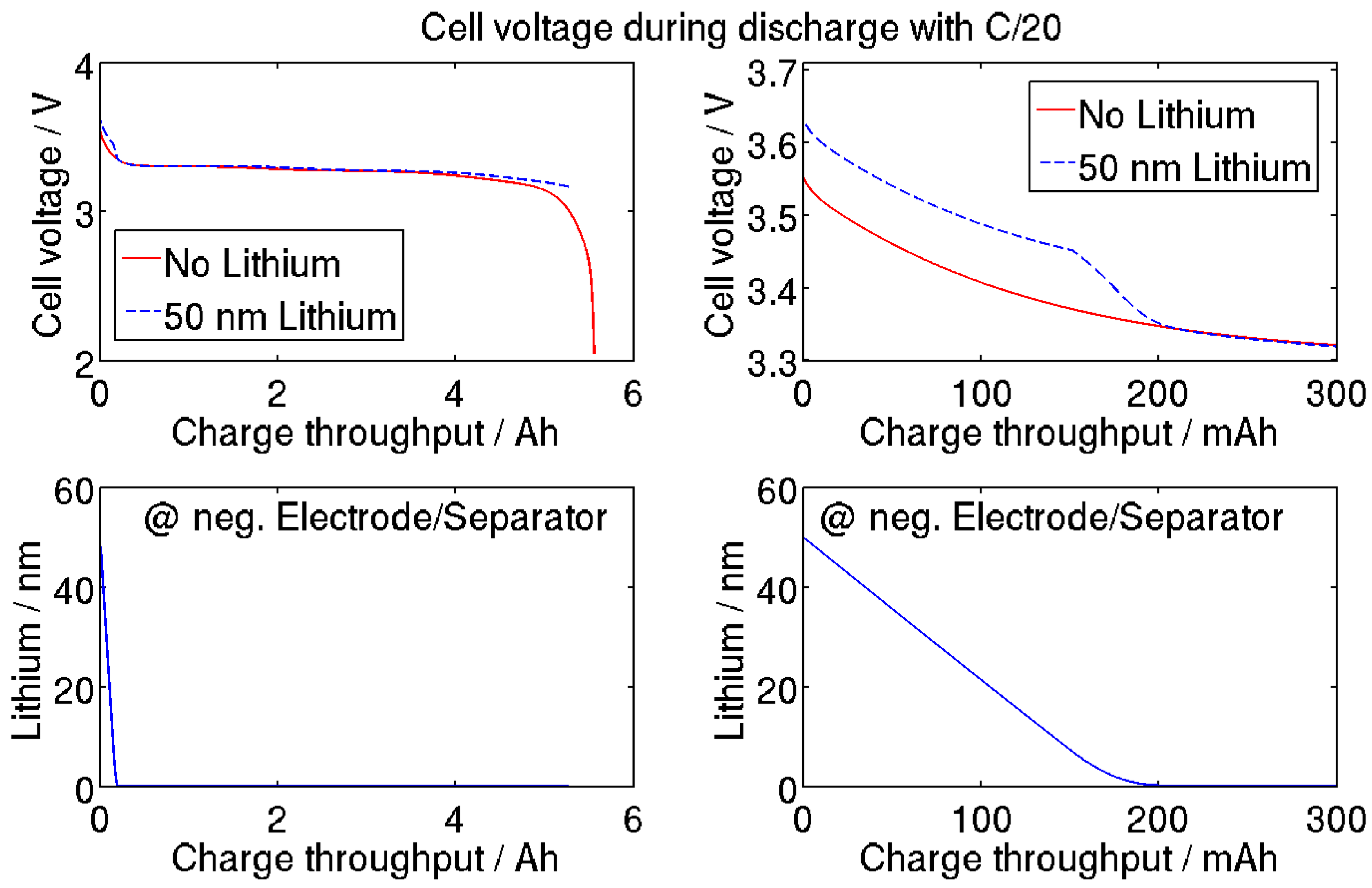
- 1C charge, 1C discharge at 270K
- Plating during charge & Stripping at start of discharge



- Plating is strongest at interface between negative electrode and separator
- Agreement with Experiments[4]

Influence of Lithium Stripping on Cell voltage

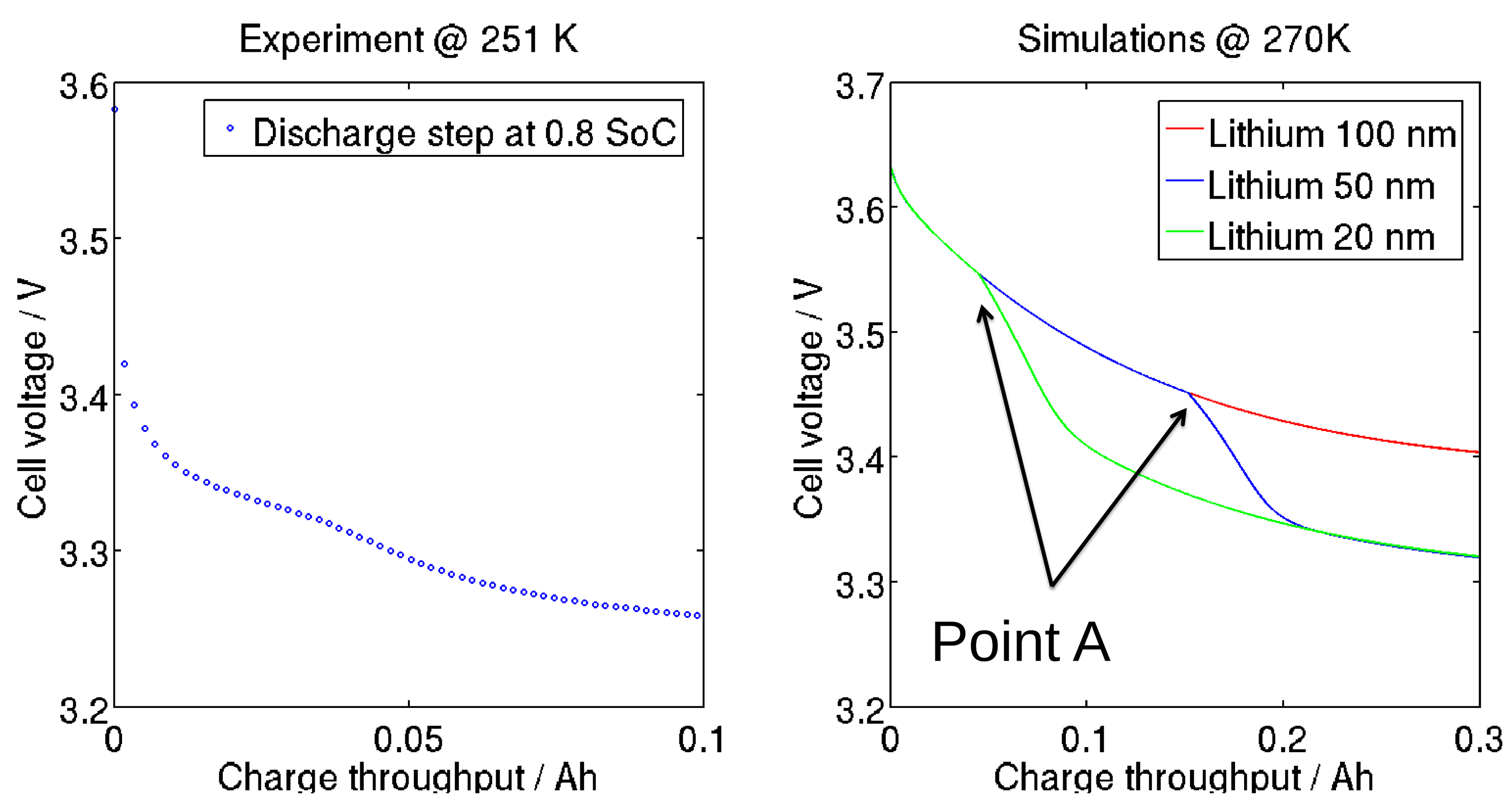
- Discharge simulation at C/20 @ 270K and 50 nm Li
- Cell voltage higher during lithium stripping



- All lithium stripped during the first 200 mAh / 2400s
- During stripping negative electrode at const. potential

Comparison between Experiment and Simulation

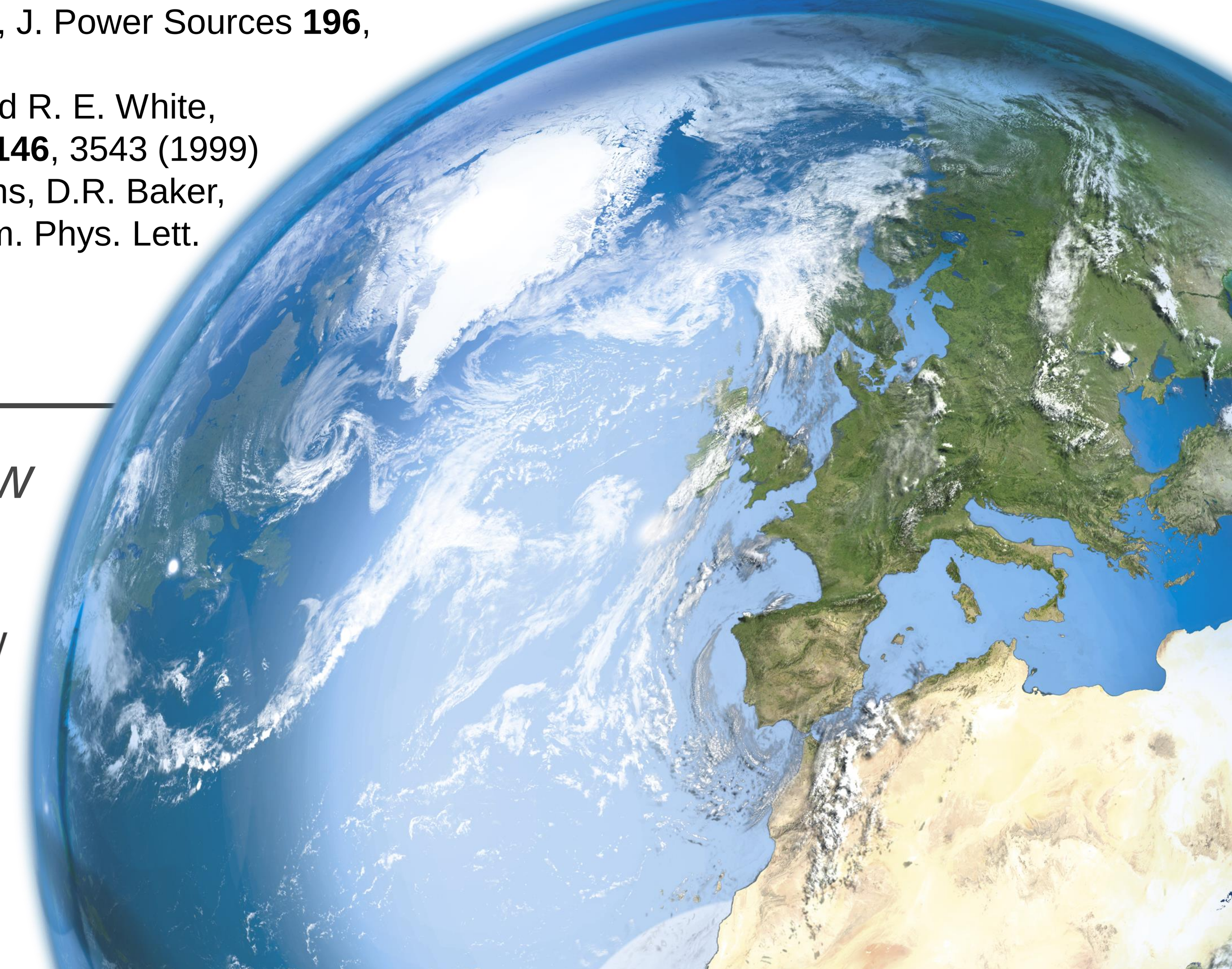
- Simulation at 270K with 100/50/20 nm Lithium



- 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
- Exact material of negative electrode unknown
- Temperature dependence of OCP unknown

[1] M. Petzl and M. A. Danzer, J. Power Sources **254**, 80 (2014).
[2] A. Latz and J. Zausch, J. Power Sources **196**, 3296 (2011).
[3] P. Arora, M. Doyle, and R. E. White, J. Electrochem. Soc. **146**, 3543 (1999)
[4] S.J. Harris, A. Timmons, D.R. Baker, and C. Monroe, Chem. Phys. Lett. **485**, 265 (2010).



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