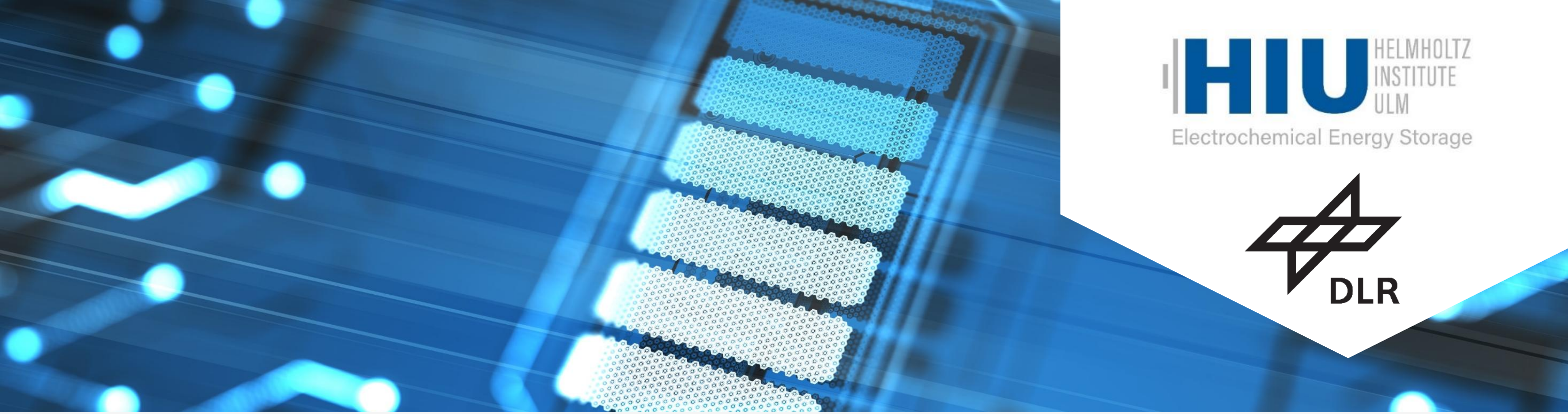


Lukas Köbbing, Arnulf Latz, Birger Horstmann

From Stress to Voltage – Modeling the Hysteresis and Slow Relaxation of Silicon Anodes

14th HIU Biennial Meeting 2025

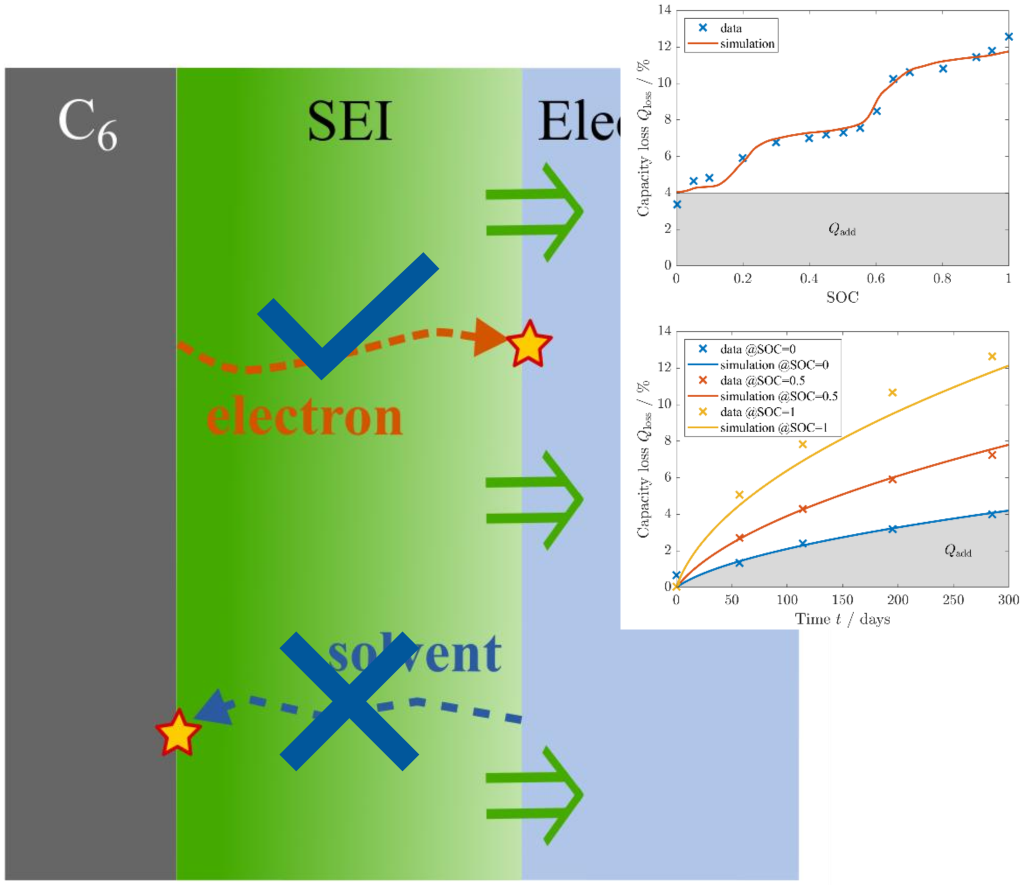
Solid-Electrolyte Interphase (SEI)

$$2\mathrm{Li}^{+} + 2\mathrm{e}^{-} + 2\mathrm{EC} \rightarrow \mathrm{Li_2EDC} + \mathrm{R}$$

Hinders electrolyte decomposition
➢ **Enables** lithium-ion batteries

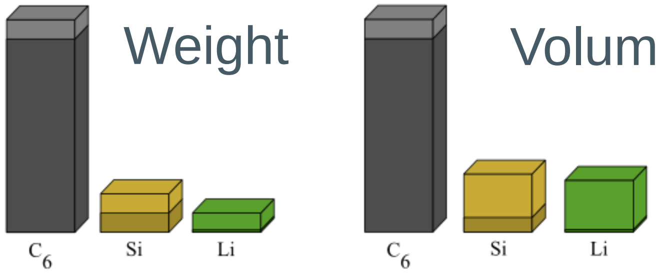
Consumes cyclable lithium
➢ Capacity **fade**

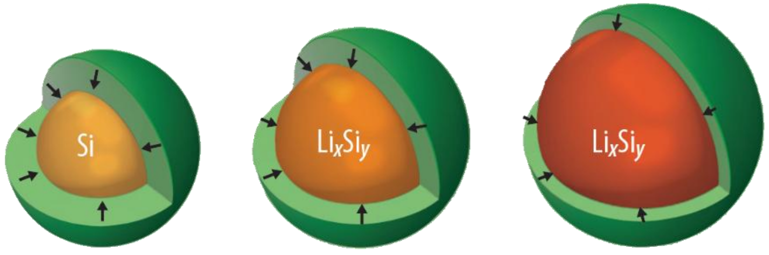
SEI covers anode particles
➢ **Core−shell structure**



Motivation

Silicon shows 10x higher capacity…

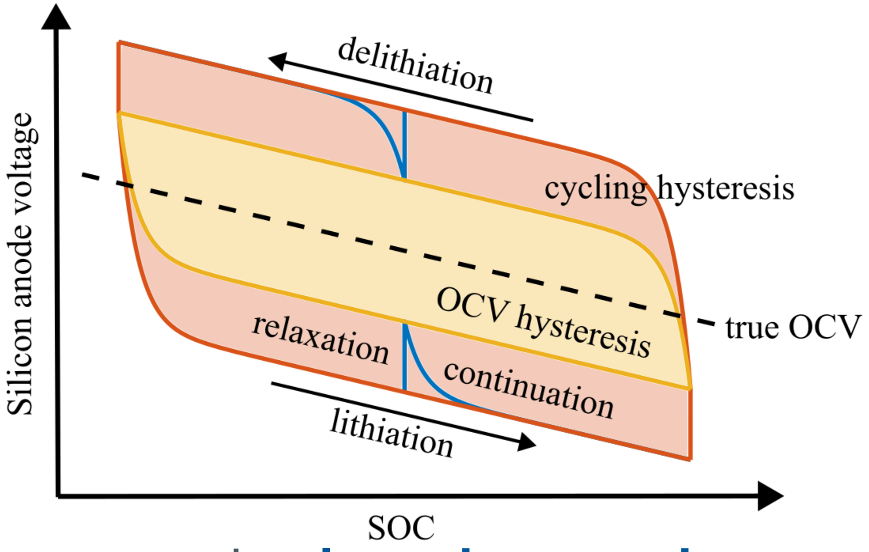




… but 300% volume expansion…

Drawbacks:

- Imprecise SOC
- Heat generation
- Reduced efficiency



Reason:

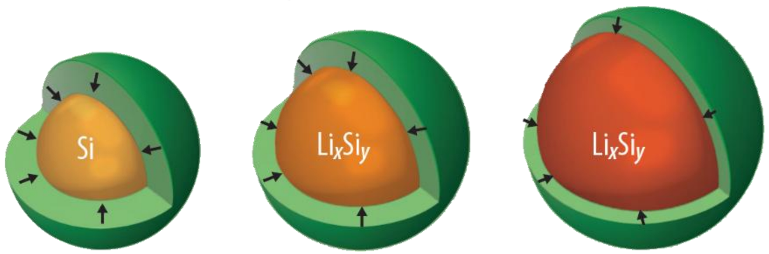
?

… and **voltage hysteresis**.

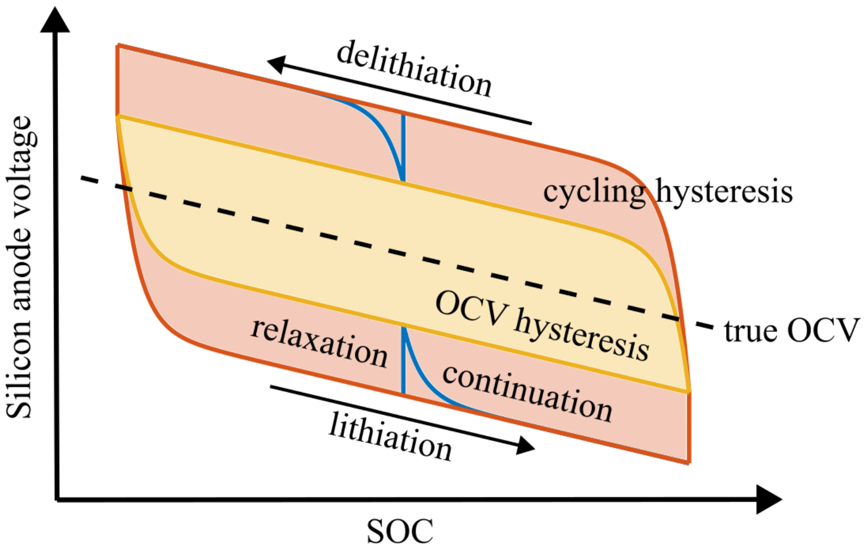
L. Köbbing, A. Latz, B. Horstmann, *Physik Journal* **2024**, 23 (5), 28-34.

Hypothesis: Chemo-Mechanical Coupling

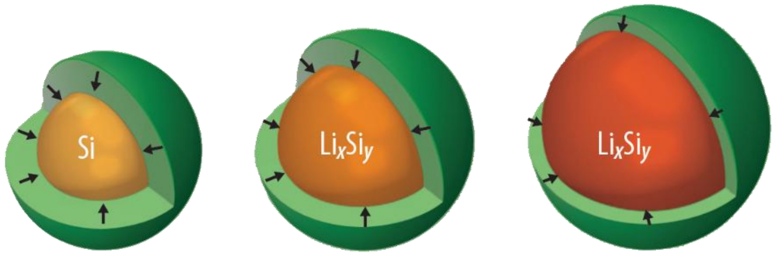
Core-Shell Structure



Voltage Hysteresis



Thermodynamic Consistent Model



Deformation: $\mathbf{F} = \mathbf{F}_{\mathrm{pl}}\mathbf{F}_{\mathrm{el}}\mathbf{F}_{\mathrm{ch}}$

Free energy:

$$\rho_0\varphi = -\int_0^{c_{\mathrm{Li},0}} FU_0\left(c'_{\mathrm{Li},0}\right)dc'_{\mathrm{Li},0} + \frac{1}{2}\left(\lambda\left(\mathrm{tr}(\mathbf{E}_{\mathrm{el}})\right)^2 + 2G\mathrm{tr}\left(\mathbf{E}_{\mathrm{el}}^2\right)\right)$$

Combining 1st and 2nd law:

Constitutive equations

$$\mu_{\mathrm{Li}} = \frac{\partial\rho_0\varphi}{\partial c_{\mathrm{Li},0}} = -FU_0 - \frac{v_{\mathrm{Li}}}{3\lambda_{\mathrm{ch}}^3}\mathbf{P}:\mathbf{F}$$

$$\mathbf{P} = 2\mathbf{F}\frac{\partial\rho_0\varphi}{\partial\mathbf{C}} = \lambda_{\mathrm{ch}}^{-2}\mathbf{F}\mathbf{F}_{\mathrm{pl}}^{-\mathrm{T}}\mathbf{F}_{\mathrm{pl}}^{-1}\left(\lambda\mathrm{tr}(\mathbf{E}_{\mathrm{el}})\mathbf{Id} + 2G\mathbf{E}_{\mathrm{el}}\right)$$

Entropy production

$$R = -\vec{N}_{\mathrm{Li},0}\nabla_0\mu_{\mathrm{Li}} + \mathbf{M}:\mathbf{L}_{\mathrm{pl}} + \mathbf{P}_{\mathrm{visc}}:\dot{\mathbf{F}} \geq 0$$

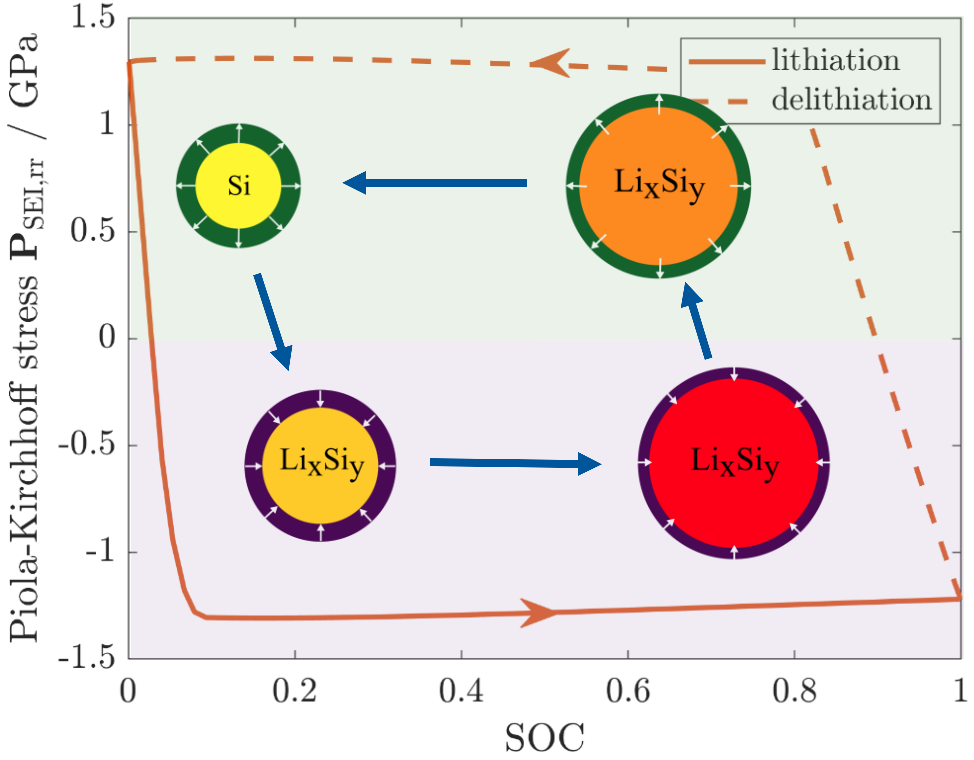
OCV $\quad U = U_0 + \frac{v_{\mathrm{Li}}}{3F\lambda_{\mathrm{ch}}^3}\mathbf{P}:\mathbf{F}$

ODEs

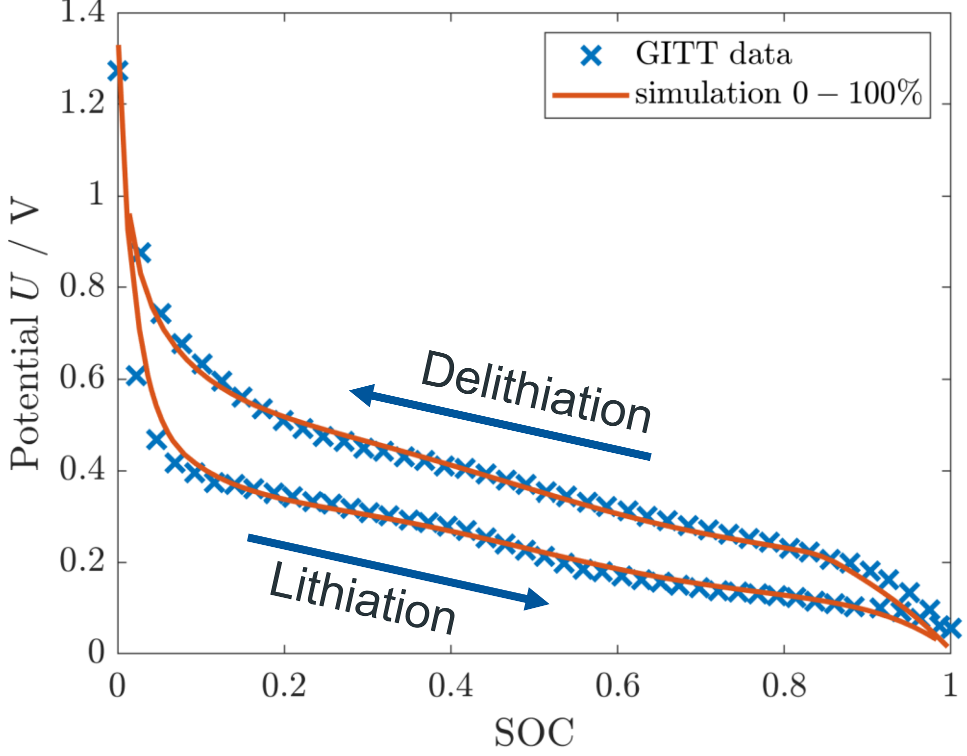
$$\begin{cases} \dot{c}_{\mathrm{Li},0} = -\nabla_0\cdot\vec{N}_{\mathrm{Li},0} \\ \nabla_0\cdot\mathbf{P} = 0 \\ \mathbf{L}_{\mathrm{pl}} = \phi\frac{\partial f}{\partial\mathbf{M}} \end{cases}$$

Elastoplastic SEI: OCV Hysteresis

SEI stress during cycling



OCV: $U = U_0 + \frac{v_{\mathrm{Li}}}{3F\lambda_{\mathrm{ch}}^3}\mathbf{P}:\mathbf{F}$

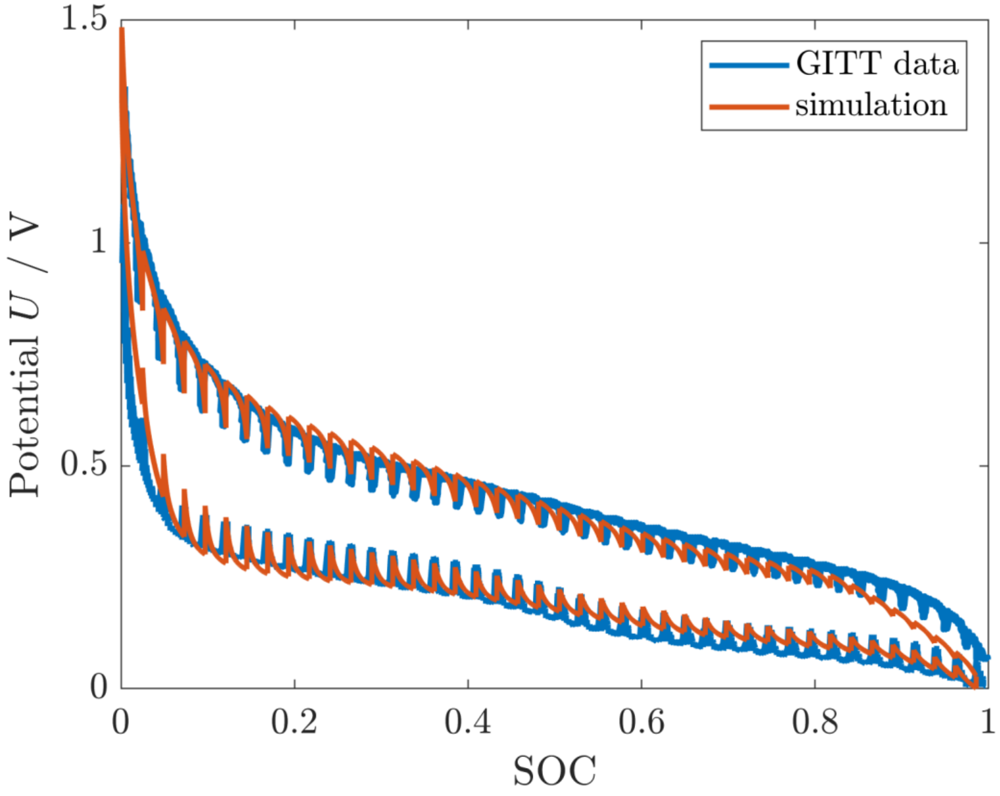


Plastic flow causes stress hysteresis

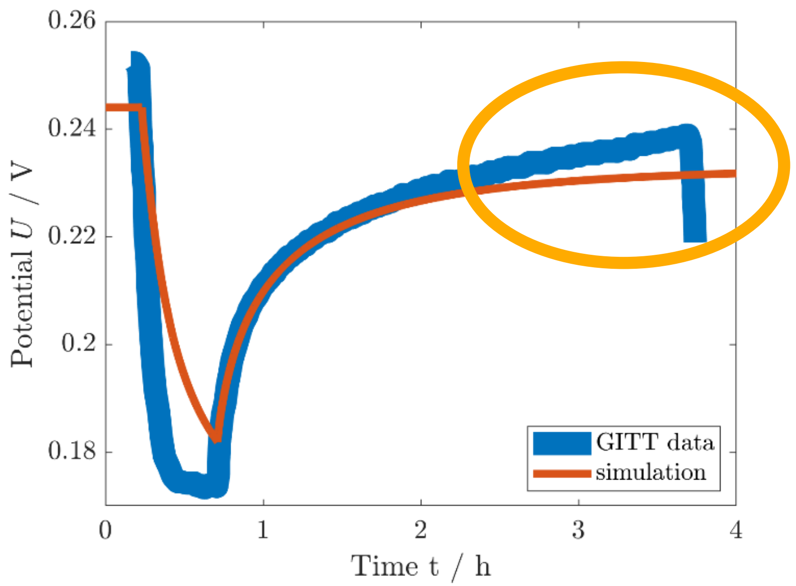
L. Köbbing, A. Latz, B. Horstmann, *Adv. Funct. Mater.* **2024**, 34, 202308818.
Exp. data: K. Pan, F. Zou, M. Canova, J. Kim, *J. Power Sources* **2019**, 413, 20-28.

Visco-Elastoplastic SEI: GITT Procedure

Enlarged hysteresis for small currents



➢ **Voltage profile** of GITT pulse reproduced

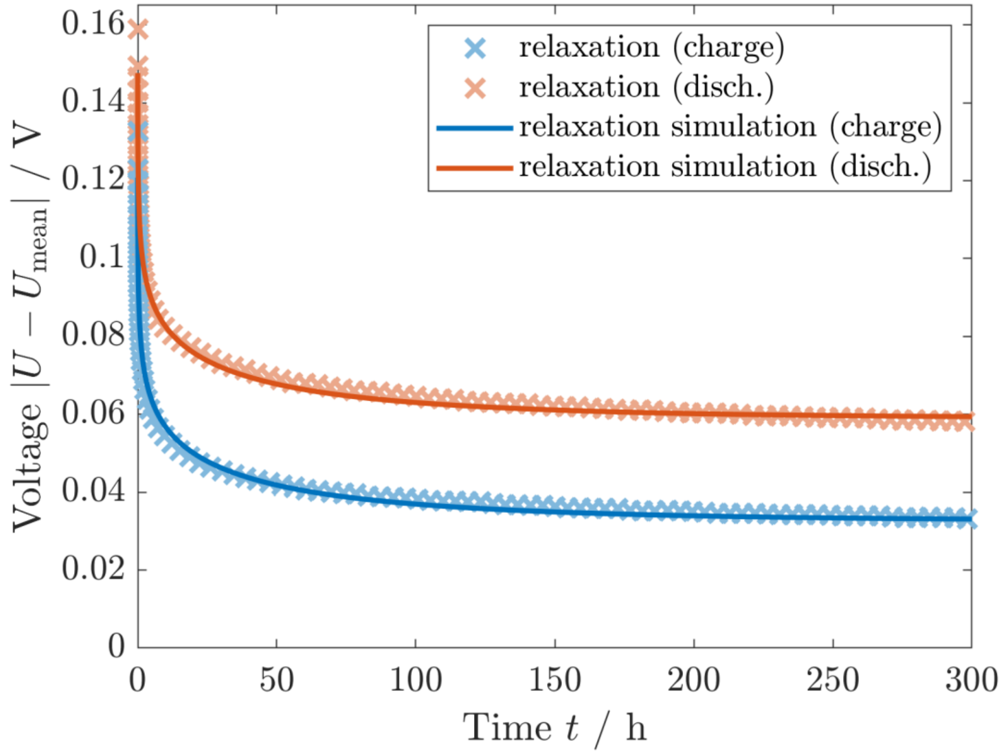


➢ **SEI viscosity** explains **GITT profile**

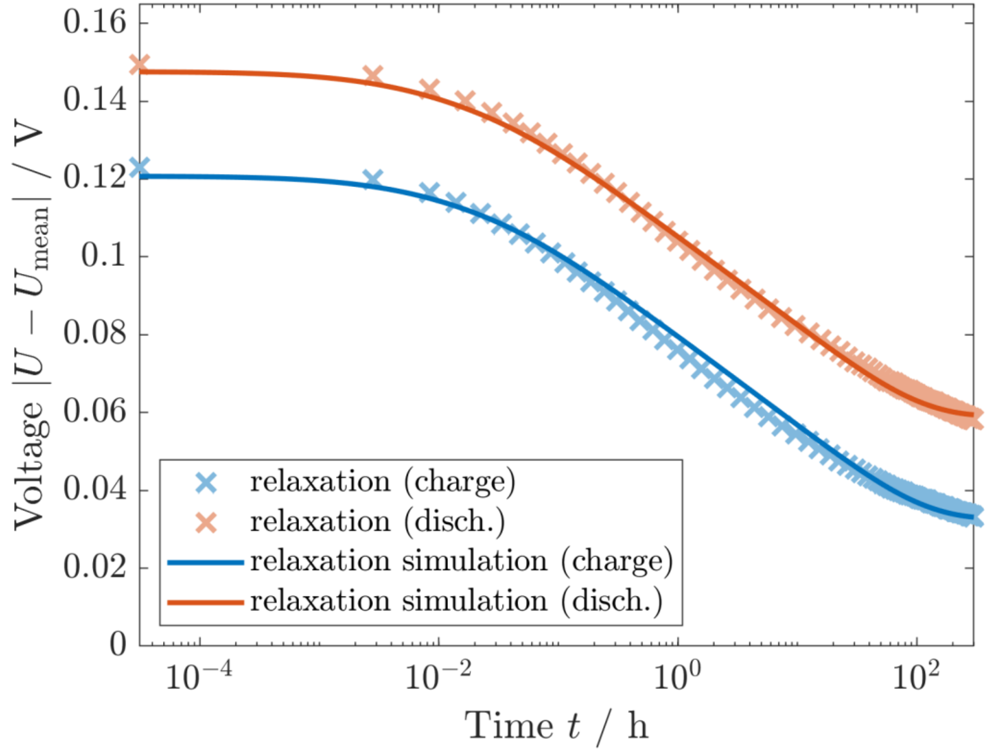
L. Köbbing, A. Latz, B. Horstmann, *Adv. Funct. Mater.* **2024**, 34, 202308818.
Exp. data: K. Pan, F. Zou, M. Canova, J. Kim, *J. Power Sources* **2019**, 413, 20-28.

Logarithmic Silicon Voltage Relaxation

Voltage relaxation



Logarithmic plot



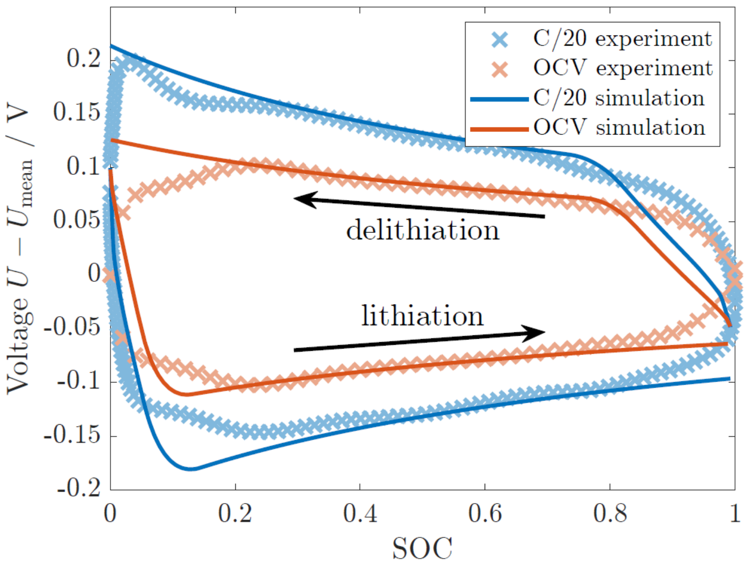
Viscosity: $\sigma_{\mathrm{Garofalo}} = \sigma_{\mathrm{ref}} \operatorname{asinh}(\tau \dot{\mathrm{E}})$

➢ **Model fits logarithmic trend**

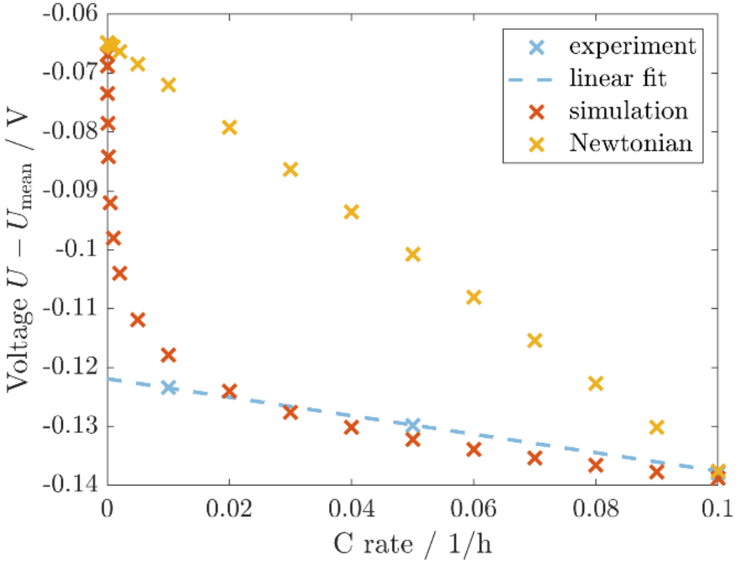
L. Köbbing, Y. Kuhn, B. Horstmann, *ACS Appl. Mater. Interfaces* **2024**, *16* (49), 67609–67619.
Exp. data: D. Wycisk, G. K. Mertin, M. Oldenburger, O. v. Kessel, A. Latz, *J. Energy Storage* **2024**, *89*,111617.

Consistency with other Hysteresis Phenomena

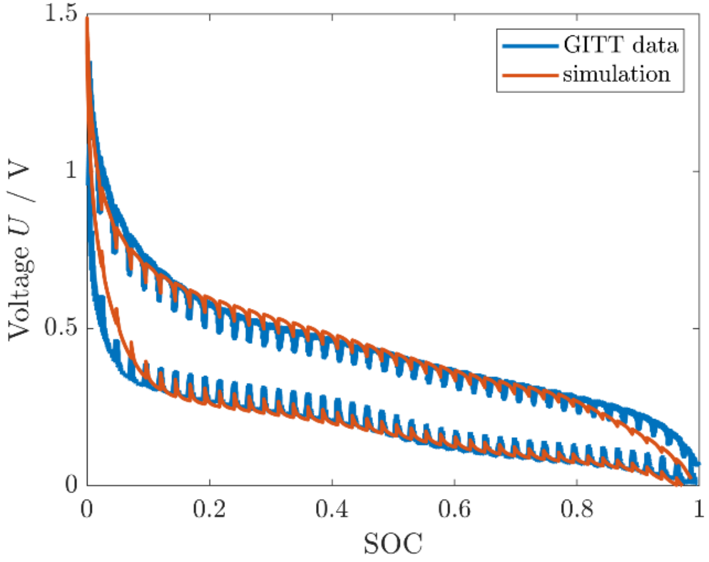
Hysteresis



C rate dependence



GITT procedure



➢ **Garofalo viscosity model describes hysteresis phenomena consistently**

L. Köbbing, Y. Kuhn, B. Horstmann, *ACS Appl. Mater. Interfaces* **2024**, *16* (49), 67609–67619
Exp. data: D. Wycisk, G. K. Mertin, M. Oldenburger, O. v. Kessel, A. Latz, *J. Energy Storage* **2024**, *89,*111617.
Exp. data: K. Pan, F. Zou, M. Canova, Y. Zhu, J.-H. Kim, *J. Power Sources* **2019**, *413,* 20–28.

Reduced Chemo-Mechanical Hysteresis Model

Voltage: $U = U_0 + \Delta U_{\mathrm{ee}} + \Delta U_{\mathrm{ev}}$

Elasto-plasticity

I

$$\frac{\mathrm{d}\,\Delta U_{\mathrm{ee}}}{\mathrm{d}t} = \begin{cases} -E_{\mathrm{shell}} \dfrac{2 v_{\mathrm{Li}}^2}{3F\lambda_{\mathrm{ch}}^7} \dot{c}_{\mathrm{Li}}, & \text{if } f < 0 \\ \sigma_{\mathrm{Y,shell}} \dfrac{\alpha v_{\mathrm{Li}}^2}{F\left(1+\alpha\lambda_{\mathrm{ch}}^3\right)^2} \left|\dot{c}_{\mathrm{Li}}\right|, & \text{otherwise} \end{cases}$$

Viscosity

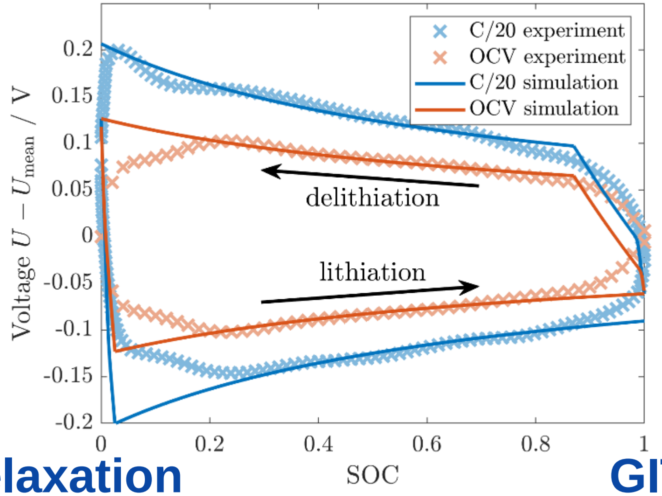
II

$$\frac{\mathrm{d}\,\Delta U_{\mathrm{ev}}}{\mathrm{d}t} = -\frac{E_{\mathrm{core}} v_{\mathrm{Li}}}{\tau F \lambda_{\mathrm{ch}}^2} \sinh\left(\frac{\alpha\lambda_{\mathrm{ch}}^3 F \Delta U_{\mathrm{ev}}}{\sigma_{\mathrm{ref}} v_{\mathrm{Li}}}\right) - \frac{E_{\mathrm{core}} v_{\mathrm{Li}}^2}{3\lambda_{\mathrm{ch}}^3} \dot{c}_{\mathrm{Li}}$$

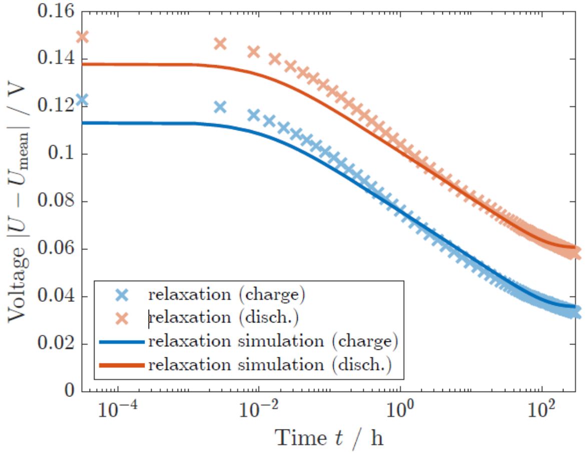
with $\alpha = \frac{1}{2}\left(\frac{R_{\mathrm{core}}}{L_{\mathrm{shell}}} - 1\right)$

and $f = -\operatorname{sgn}(\dot{c}_{\mathrm{Li}})\left(1+\alpha\lambda_{\mathrm{ch}}^3\right)\frac{F\Delta U_{\mathrm{ee}}}{v_{\mathrm{Li}}\sigma_{\mathrm{Y,shell}}} - 1$

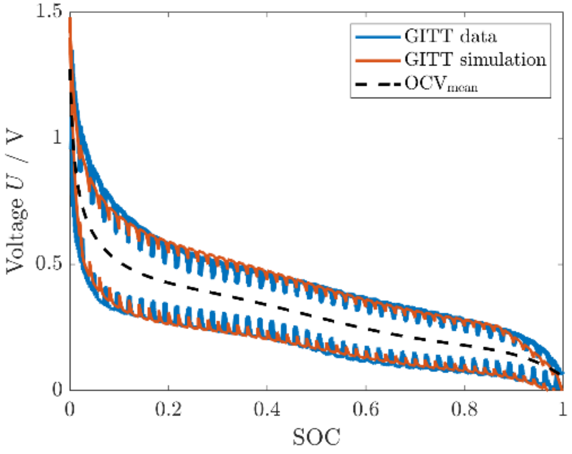
Hysteresis



Relaxation



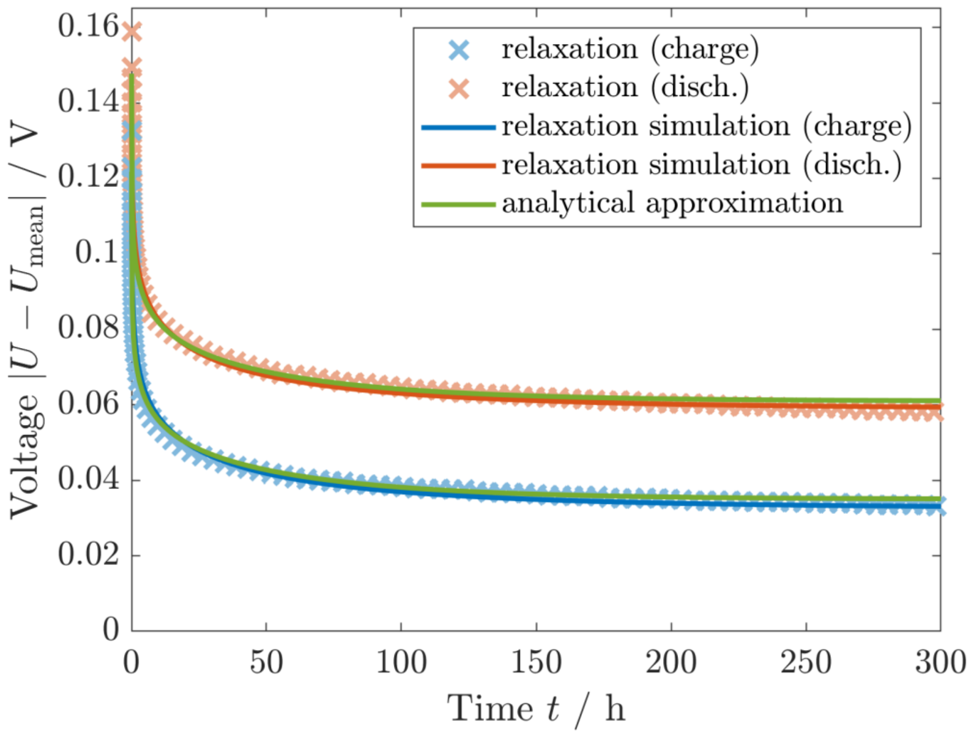
GITT



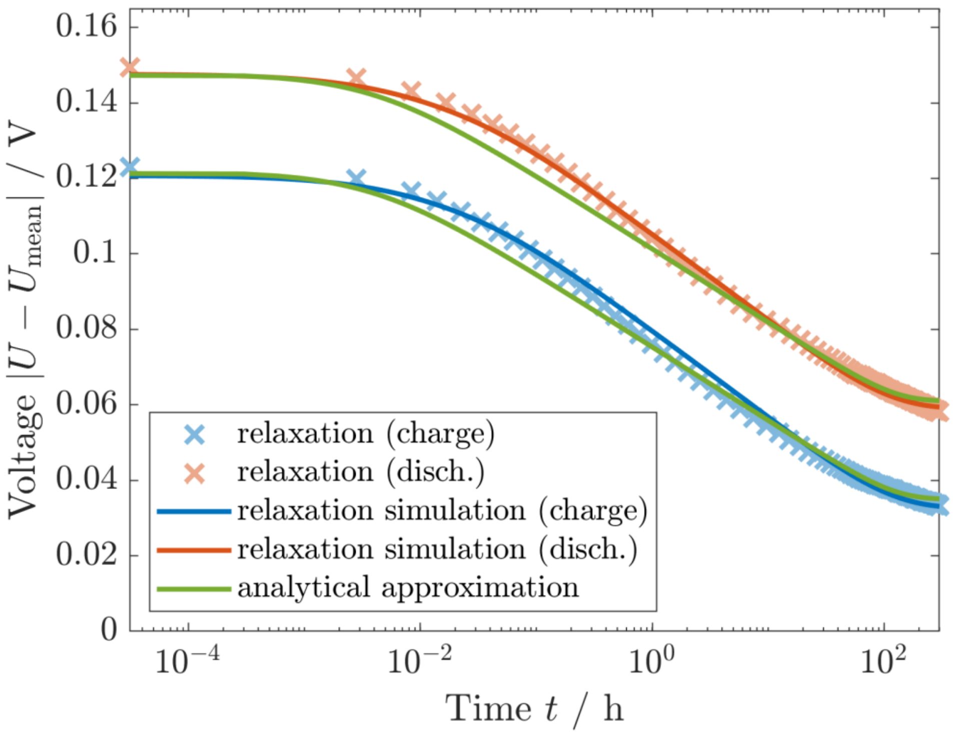
Analytical Approximation: Voltage Relaxation

Voltage relaxation in time: $$\Delta U_{\text{ev}} = \frac{2 v_{\text{Li}} \sigma_{\text{ref}}}{\alpha_{\text{red}} F \lambda_{\text{ch}}^3} \operatorname{atanh}\left(C \cdot \exp\left(-\frac{E_{\text{core}} \alpha_{\text{red}} \lambda_{\text{ch}}}{\tau \sigma_{\text{ref}}} t \right)\right)$$

Voltage relaxation



Logarithmic plot

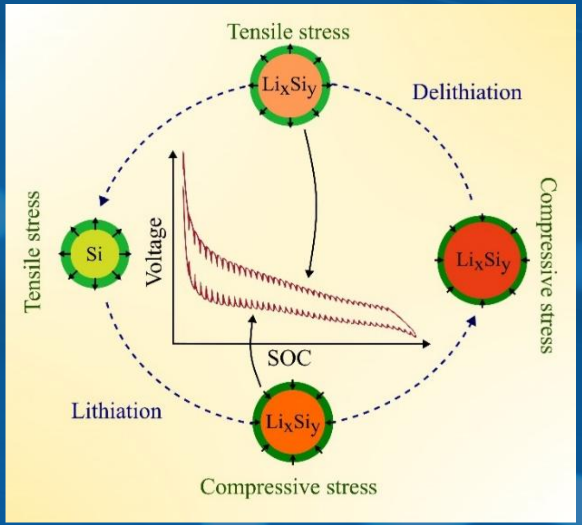


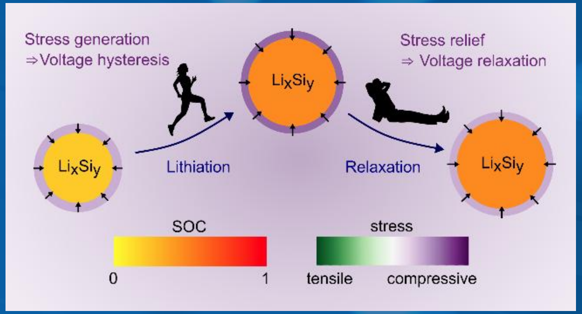
L. Köbbing, Y. Kuhn, B. Horstmann, *ACS Appl. Mater. Interfaces* **2024**, *16* (49), 67609–67619

Conclusion

- **SEI on silicon:** Chemo-mechanical core-shell model
- **Elastoplastic shell:** OCV hysteresis of Si nanoparticles
- **Visco-elastoplastic shell:** reproduces voltage relaxation
- **Reduced hysteresis model** for easy voltage estimations

➢ **Soft but passivating SEI might reduce the OCV hysteresis**





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R. Schoof, L. Köbbing, A. Latz, B. Horstmann, W. Dörfler, *Batter. Supercaps* **2025**, *8* (5), *202400604*.