Dependence of SEI growth on state-of-charge and cycling conditions

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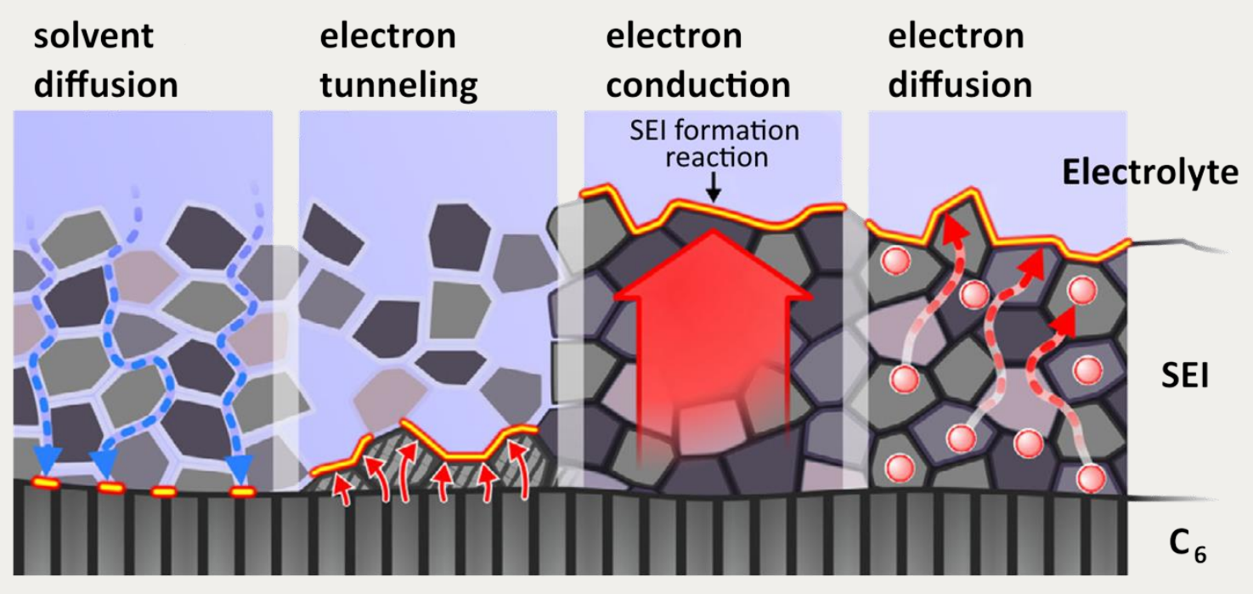
MOTIVATION AND AIM

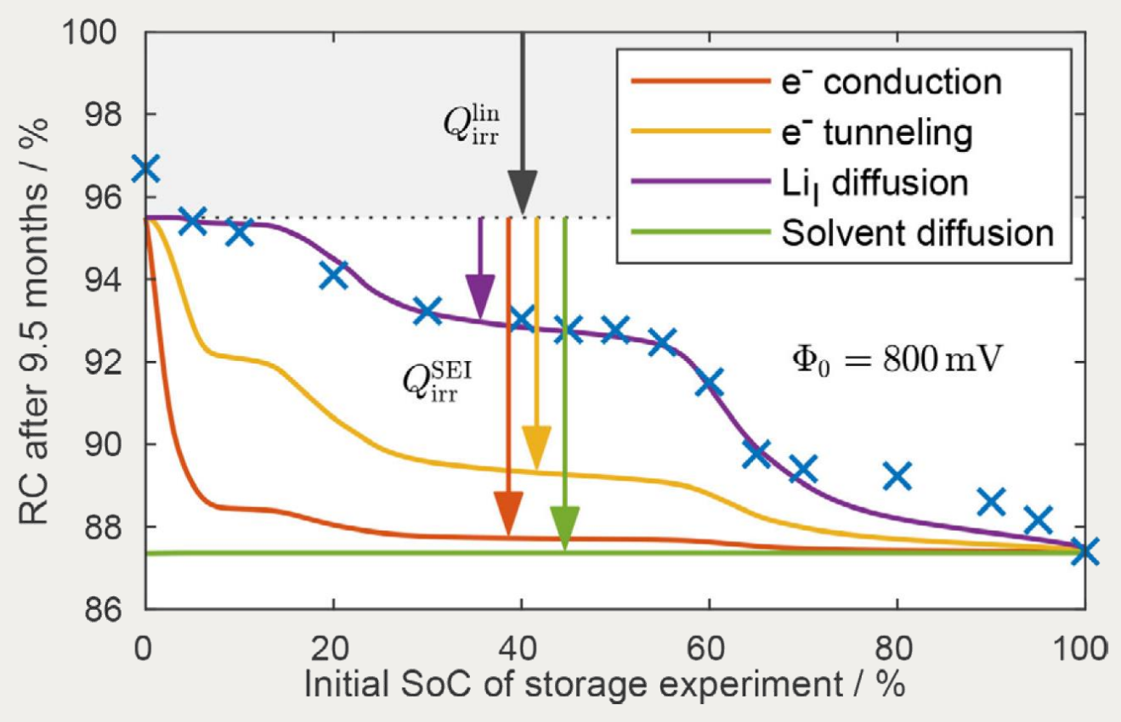
- The **SEI and SEI growth** is crucial but not fully understood.
- The relevant **transport mechanisms are** still under debate [1].
- **Electron diffusion** vs. solvent diffusion as growth mechanism.
- Coupling of **chemical, electrical, and mechanical effects.**

SEI GROWTH DURING BATTERY STORAGE [2]

Mechanisms in the literature

- Solvent diffusion
- Electron tunneling
- Electron conduction
- Electron diffusion through localized states





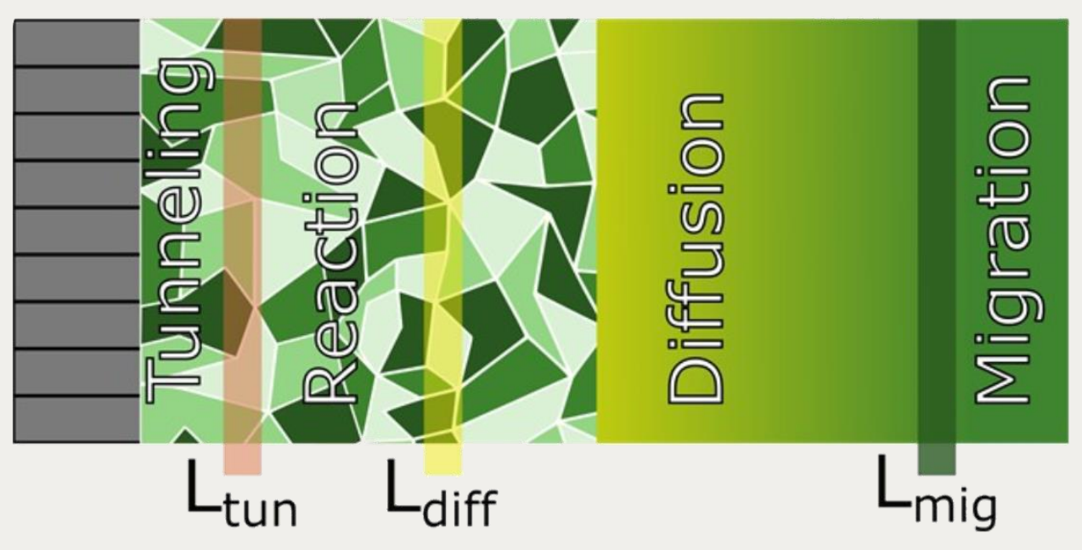
Electron / Li interstitial diffusion

- Validation with capacity fade during calendar aging
- **Explains SOC dependence**
- Other mechanisms fail

SEI GROWTH DURING BATTERY CYCLING

Local overpotential: $\tilde{\eta}_{\mathrm{SEI}} = \frac{F}{RT}\left(\eta_{\mathrm{int}} + U_0 + \frac{\mu_{\mathrm{Li},0}}{F}\right)$

Growth regimes [4]



- If $L_{\mathrm{app}} \ll L_{\mathrm{diff}}$

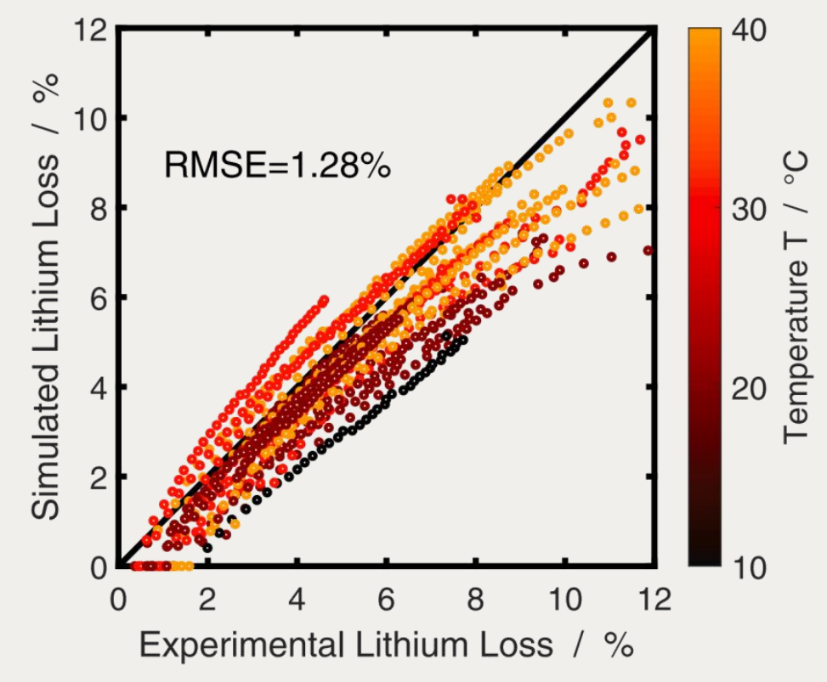
  $$L_{\mathrm{SEI}} = \frac{v_{\mathrm{SEI}}}{F} j_{\mathrm{SEI},0} e^{-\alpha_{\mathrm{SEI}}\tilde{\eta}_{\mathrm{SEI}}} \cdot t$$

- If $L_{\mathrm{diff}} \ll L_{\mathrm{app}} \ll L_{\mathrm{mig}}$

  $$L_{\mathrm{SEI}} = L_{\mathrm{tun}} + \sqrt{2 v_{\mathrm{SEI}} c_{\mathrm{Li},0} D e^{-\tilde{\eta}_{\mathrm{SEI}}} \cdot t + \left(L_{\mathrm{SEI},0} - L_{\mathrm{tun}}\right)^2}$$

- If $L_{\mathrm{mig}} \ll L_{\mathrm{app}}$

  $$L_{\mathrm{SEI}} = \frac{v_{\mathrm{SEI}} c_{\mathrm{Li},0} D F j_{\mathrm{int}}}{2RT\kappa_{\mathrm{Li}^+,\mathrm{SEI}}} e^{-\tilde{\eta}_{\mathrm{SEI}}} \cdot t$$

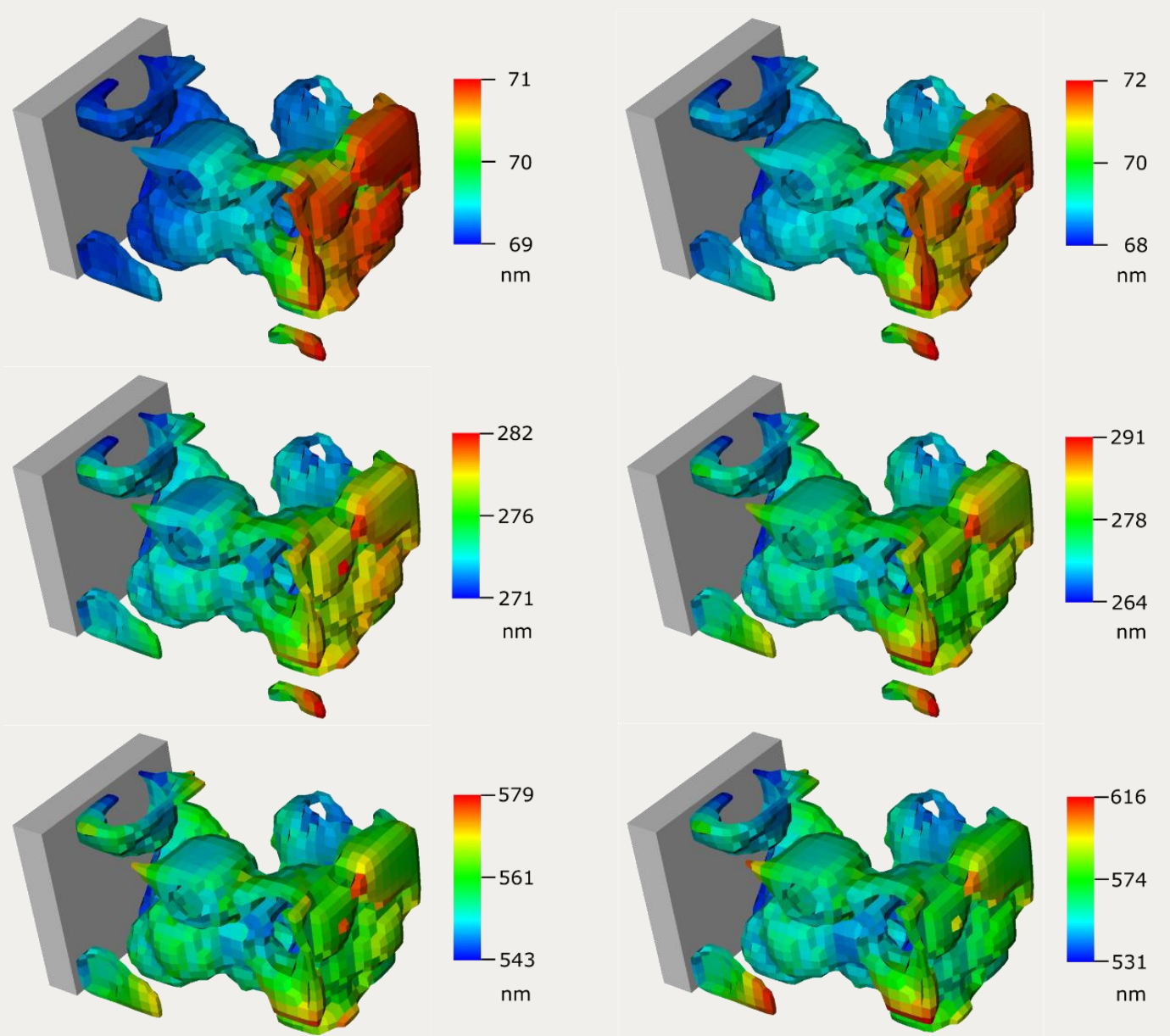


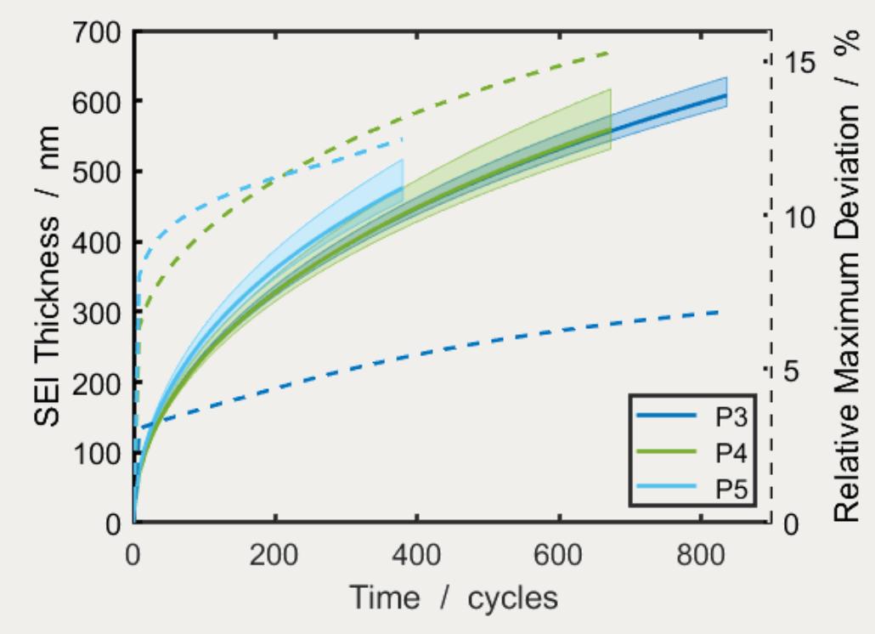
Validation with automotive cells [5]

- Excellent agreement at moderate temperature
- Additional degradation mechanism at low temperature

Inhomogeneous SEI growth in 3D simulation [6]

- Local overpotential determines SEI growth rate





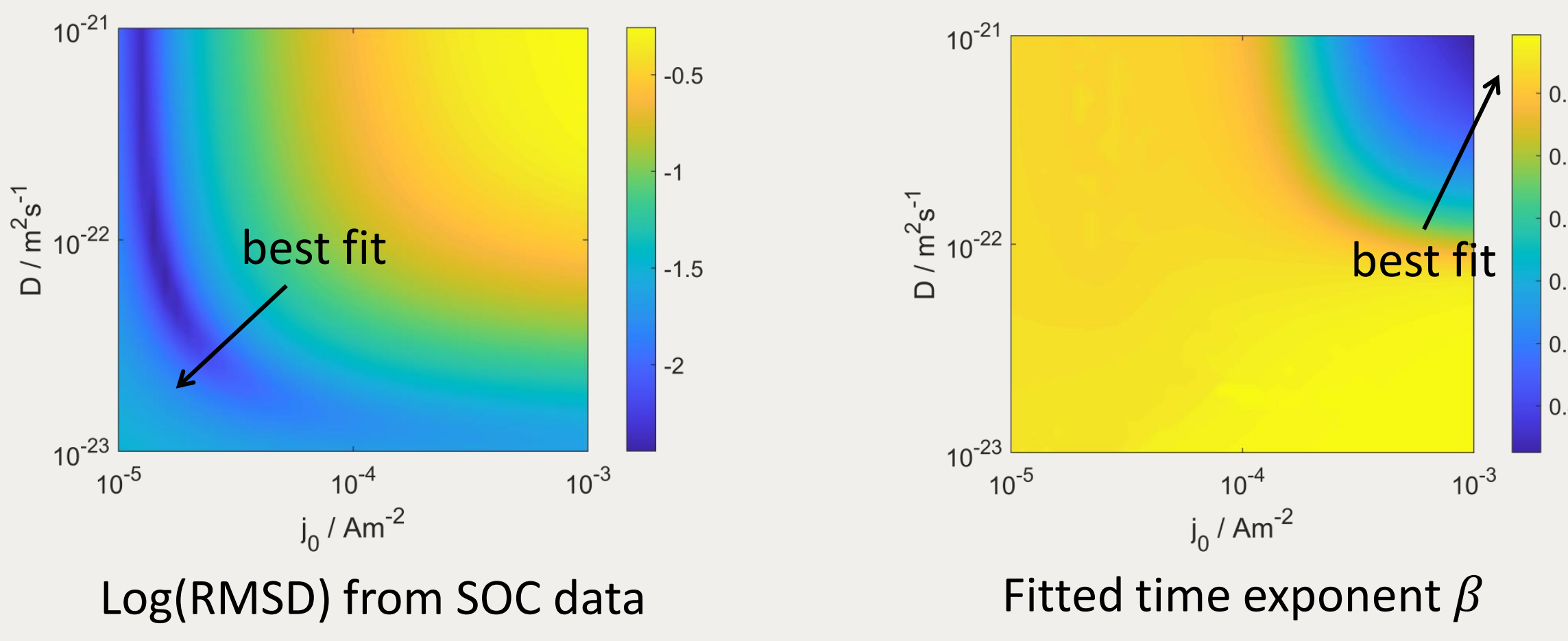
COMPARISON WITH SOLVENT DIFFUSION

Theory of SEI growth

- Reaction and diffusion: $\partial_t \tilde{L}_{\mathrm{SEI}} = \frac{v j_0}{F L_{\mathrm{SEI},0}} \cdot \frac{e^{-(1-\alpha)\tilde{U}_0} - e^{\alpha\tilde{U}_0 - \tilde{U}_{\mathrm{SEI}}}}{1 + \frac{j_0 L_{\mathrm{SEI},0}}{F D c_{\mathrm{EC},\infty}} e^{-(1-\alpha)\tilde{U}_0}\tilde{L}_{\mathrm{SEI}}}$

SOC dependence of calendar aging

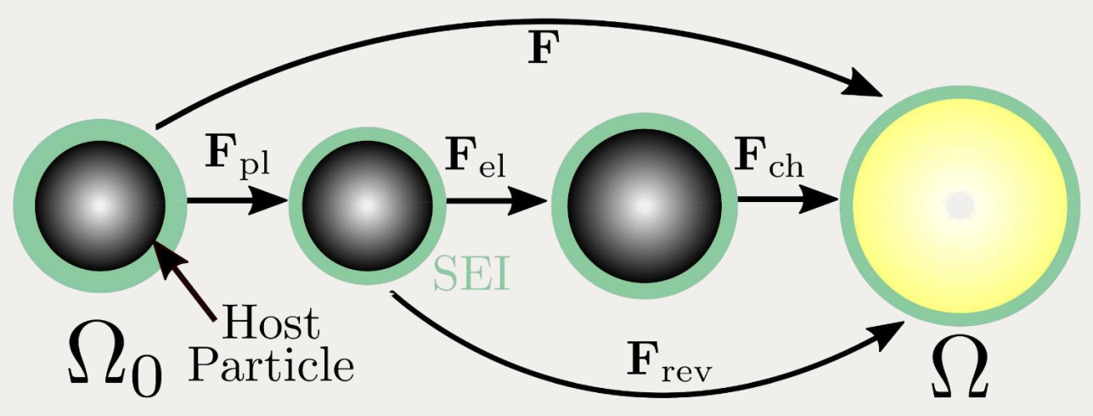
➢ **Either SOC dependence or $t^{0.5}$ reproduced**



Log(RMSD) from SOC data

Fitted time exponent β

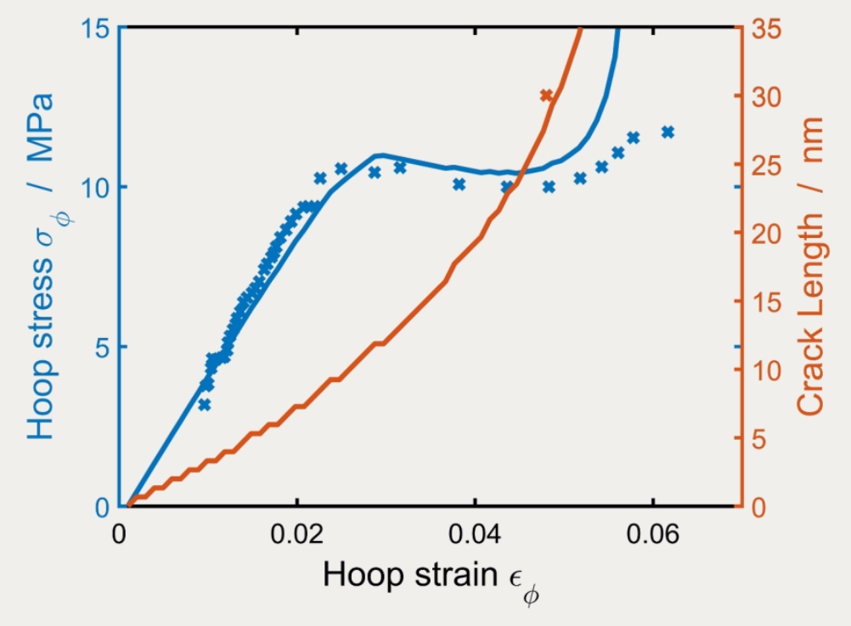
SEI MECHANICS [7]



- Silicon particle deforms chemically $\mathbf{F}_{\mathrm{ch}}$ and elastically $\mathbf{F}_{\mathrm{el}}$
- **SEI** deforms plastically $\mathbf{F}_{\mathrm{pl}}$ and elastically $\mathbf{F}_{\mathrm{el}}$, SEI failure
- Mechanics and chemistry coupled *via* free energy density

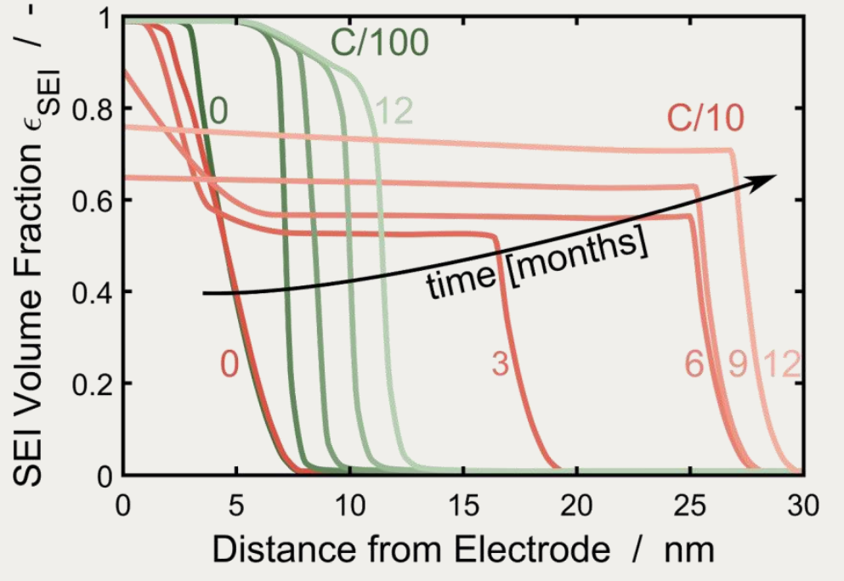
$$\psi = c_{\mathrm{Li,max}}[\mu_{\mathrm{Li}}^0 \tilde{c}_{\mathrm{Li}} + RT(\tilde{c}_{\mathrm{Li}} \ln \tilde{c}_{\mathrm{Li}} + (1-\tilde{c}_{\mathrm{Li}})\ln(1-\tilde{c}_{\mathrm{Li}}))] + \frac{1}{2}\mathbf{E}_{\mathrm{el}} : \mathbb{C}\,\mathbf{E}_{\mathrm{el}}$$

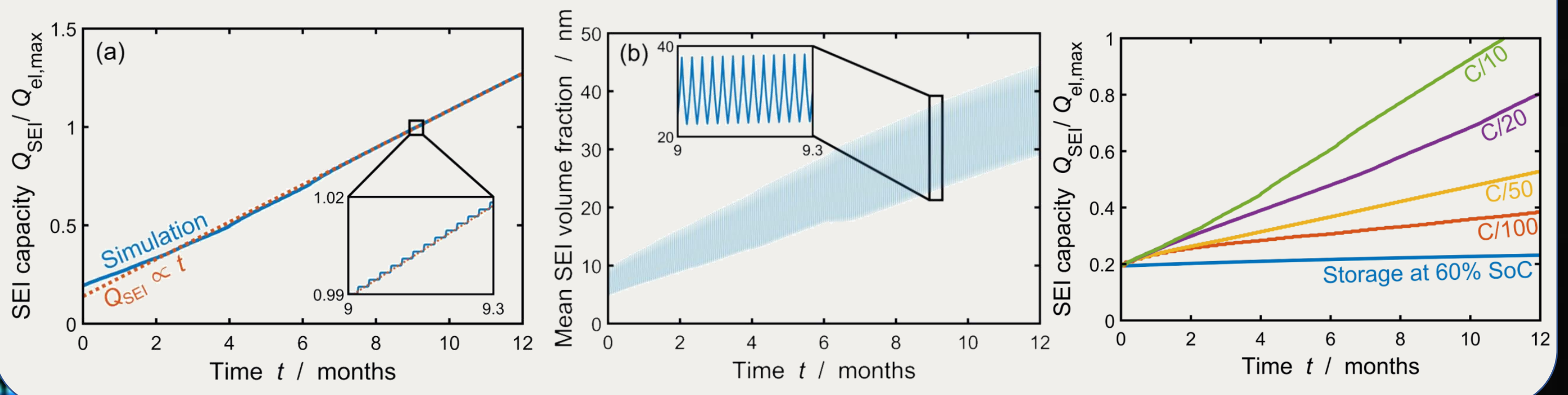
Parameterization



- Dual layer SEI
- SEI thickness oscillates
- Growth transition sfrom $L_{\mathrm{SEI}} \propto t^{0.5}$ to $L_{\mathrm{SEI}} \propto t^1$

Cracking and healing





SUMMARY

- **Electron diffusion** through localized states can explain **SOC dependence** and **heterogeneous SEI growth** in electrodes.
- Different **SEI growth regimes** during battery cycling validated with experimental data.
- **Solvent diffusion** can **not** describe the SOC dependence **and** $t^{0.5}$
- SEI deformation and cracking determines capacity fade of silicon electrodes.

References

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