Dendrite Formation in Batteries: Dead Lithium and Thermodiffusion

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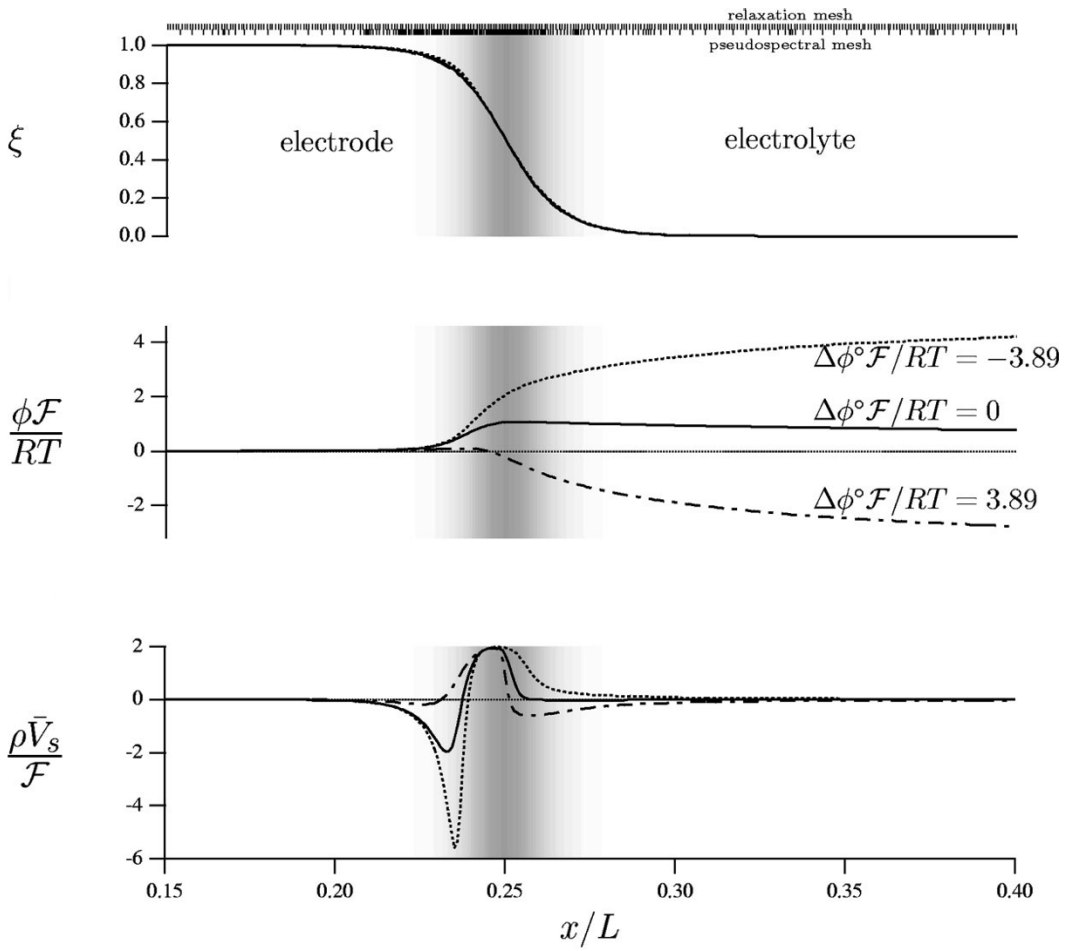
Naval Research Laboratory

Phase Field methods and length scales

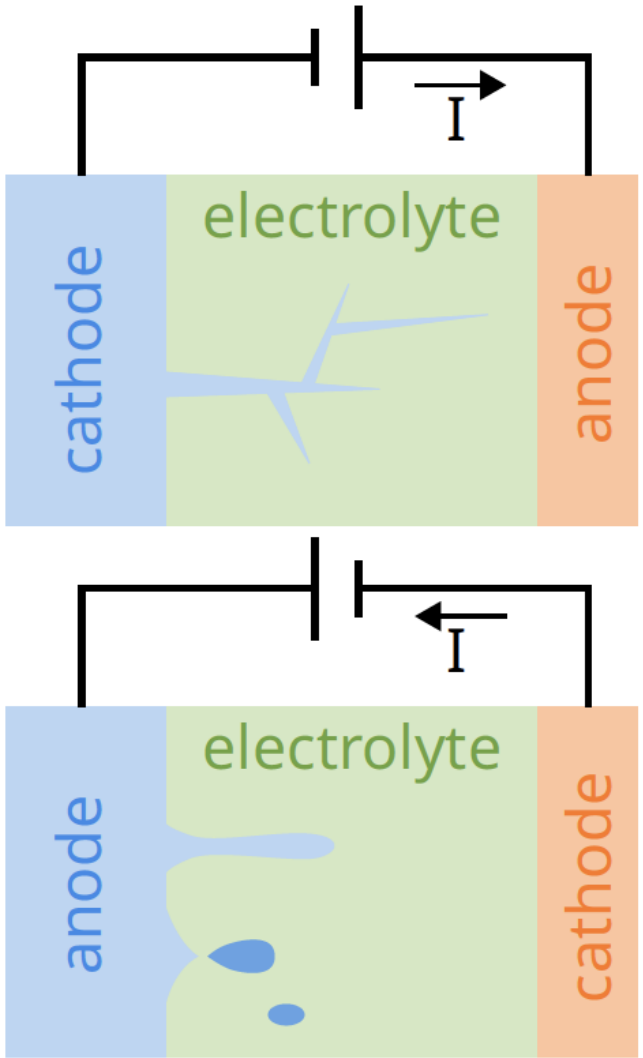
At the smallest length scale, explicit treatment of the electrolyte-electrode interface

Guyer, Jonathan E., William J. Boettinger, James A. Warren, and Geoffrey B. McFadden. "Phase field modeling of electrochemistry. I. Equilibrium." *Physical Review E* 69, no. 2 (2004): 021603.



- Explicit treatment of electrons, anions and electrolyte
- Reproduces Gouy-Chapman and Debye-Huckel theories
- The differential capacitance, surface charge agree with existing theories
- Similar approach for oxides: Sherman, Q. C., and P. W. Voorhees. "Phase-field model of oxidation: Equilibrium." *Physical Review E* 95, no. 3 (2017): 032801.

Li-metal batteries



Challenges of Li metal electrode

- Safety
- Short lifetime

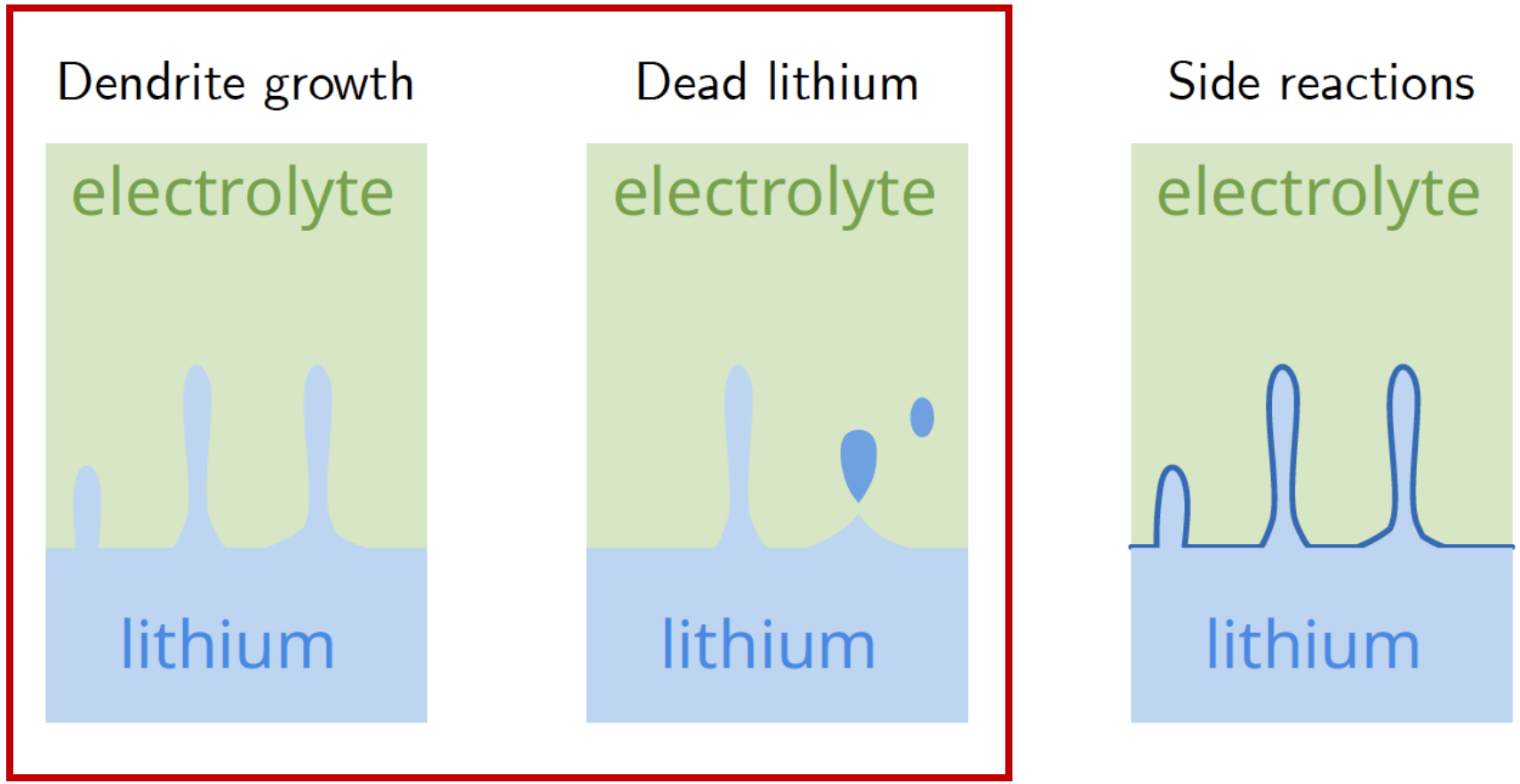
Main causes

- Dendrite formation
- Dead Li formation

Goal

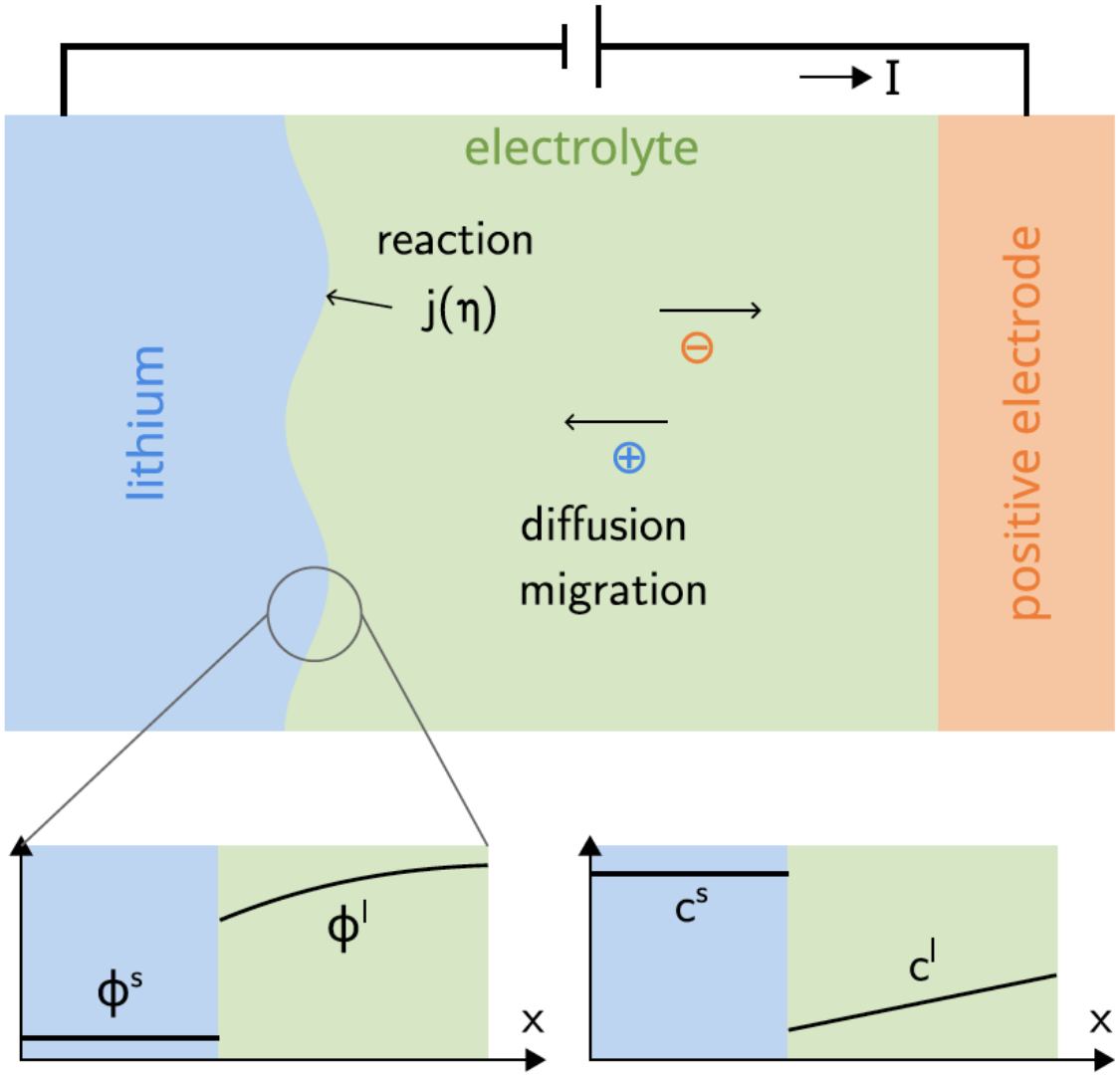
- Model formation of dendrite and dead Li
- Understand **degradation mechanism**

Degradation of Li-metal batteries



Evolving interface & topological changes $\Rightarrow$ Phase field method

Battery system is complex



Physical Processes

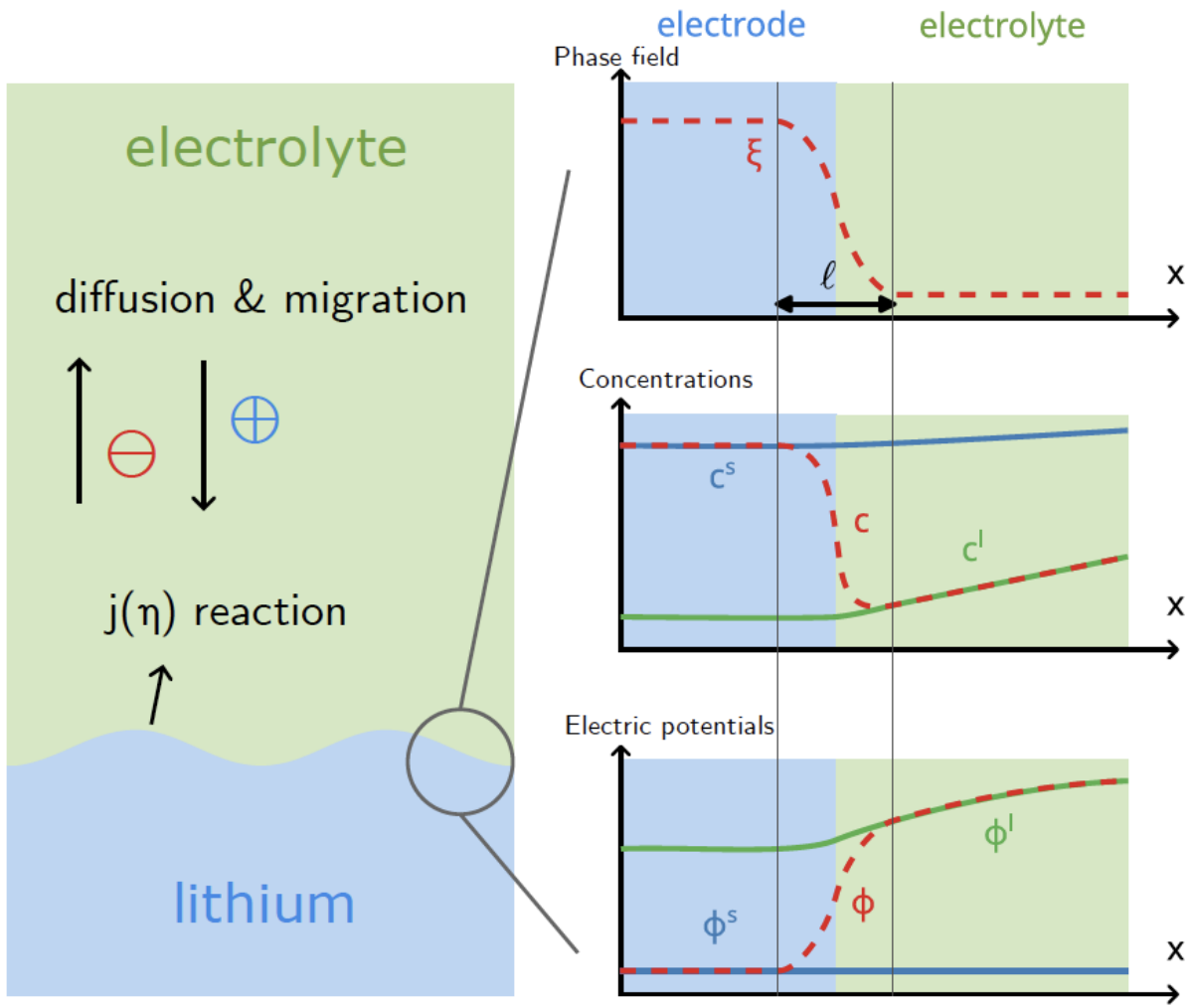
- Ion transport: diffusion & migration
- Interfacial reactions (nonlinear)
- Interface discontinuities

Goal

Develop a General Phase Field Model

- General applicability
- Multiphysics coupling
- General reaction kinetics
- General thermodynamics
- Quantitative predictions

Phase field model: State variables



Variables to describe the system state

- ξ phase field
- c_i concentration
- ϕ electric potential
- other relevant physical fields: $\vec{u}, T, \cdots$

Helmholtz free energy

$$\mathcal{F}(\xi, c_i, \phi^s, \phi^l, \cdots)$$

Phase Field method

$$f^{\alpha} = \underbrace{\sum_i \mu_i c_i}_{\text{chemical}} + \underbrace{\rho\phi - \frac{1}{2}\vec{D}\cdot\vec{E}}_{\text{electrical}} - \underbrace{\vec{j}\cdot\vec{A} + \frac{1}{2}\vec{H}\cdot\vec{B}}_{\text{magnetic}} + \underbrace{\frac{1}{2}\sigma : \epsilon}_{\text{mechanical}} + \cdots$$

Total energy of the system (ξ is the phase field variable)

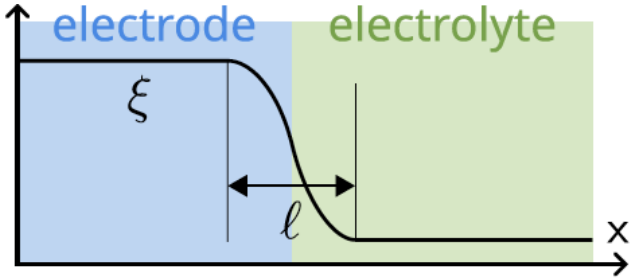
$$F = \int_V \underbrace{\frac{1}{2}\kappa|\vec{\nabla}\xi|^2 + mg(\xi)}_{\text{interfacial energy}} + \underbrace{\sum_{\alpha} p_{\alpha}(\xi) f^{\alpha}}_{\text{bulk energy}} \, dV$$

Second law of thermodynamics (isothermal)

$$\frac{dF}{dt} \leqslant 0 \qquad \text{this gives constitutive laws}$$

RE García et al. Acta Mater (2004)

Phase field model: Derive evolution equations



Total energy of the system

$$\mathcal{F}(\xi, c_i, \phi^s, \phi^l) = \int \underbrace{\frac{1}{2}\kappa|\vec{\nabla}\xi|^2 + mg(\xi)}_{\text{interfacial energy}} + \underbrace{p(\xi)\bar{f}^s(c_i^s, \phi^s) + (1-p(\xi))\bar{f}^l(c_i^l, \phi^l)}_{\text{bulk energy}} \, dV$$

Second law of thermodynamics

driving force, flux

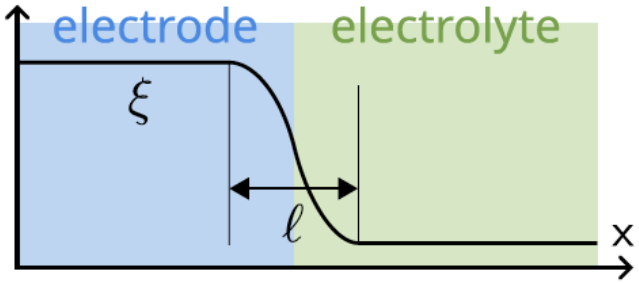
$$\frac{d\mathcal{F}}{dt} = \int \frac{\delta\mathcal{F}}{\delta\xi}\frac{\partial\xi}{\partial t} + \sum_i \vec{\nabla}\frac{\delta\mathcal{F}}{\delta c_i}\cdot\vec{J}_i + \sum_\alpha \frac{\delta\mathcal{F}}{\delta\phi^\alpha}\frac{\partial\phi^\alpha}{\partial t} dV \leqslant 0$$

$$\frac{\delta\mathcal{F}}{\delta\xi}\frac{\partial\xi}{\partial t} \leqslant 0, \qquad \vec{\nabla}\frac{\delta\mathcal{F}}{\delta c_i}\cdot\vec{J}_i \leqslant 0, \qquad \frac{\delta\mathcal{F}}{\delta\phi^\alpha} = 0$$

$\mathcal{F}$: Helmholtz free energy of system, ξ: phase field parameter, p: interpolation function

J. Zhang, A.F. Chadwick, and P.W. Voorhees. *Journal of The Electrochemical Society* 170, no. 12 (2023): 120503.

Phase field model



Second law of thermodynamics

$$\frac{\delta \mathcal{F}}{\delta \xi} \frac{\partial \xi}{\partial t} \leqslant 0,$$

Define variational overpotential

$$\eta = \frac{V_m}{F} \frac{\delta \mathcal{F}}{\delta \xi}$$

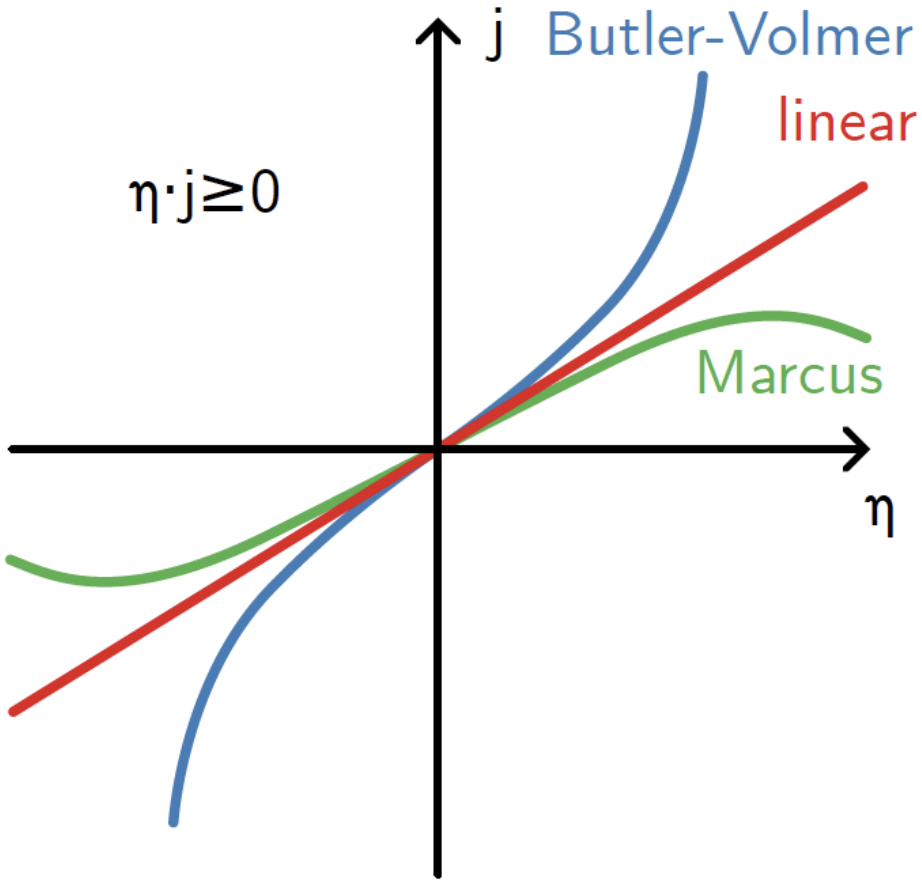
Evolution of the phase field

$$\frac{\partial \xi}{\partial t} = -\frac{V_m}{6F\ell} j(\eta)$$

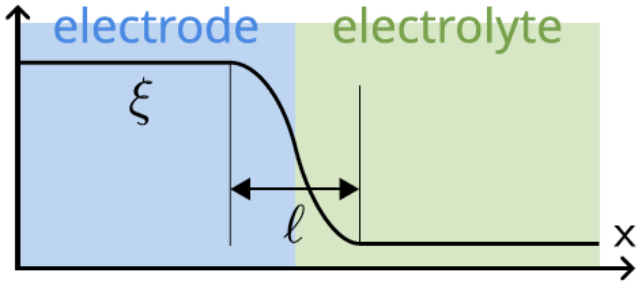
Second law requires

$$j(\eta)\, \eta \geqslant 0$$

Phase field model



Our model works for any general reaction kinetics



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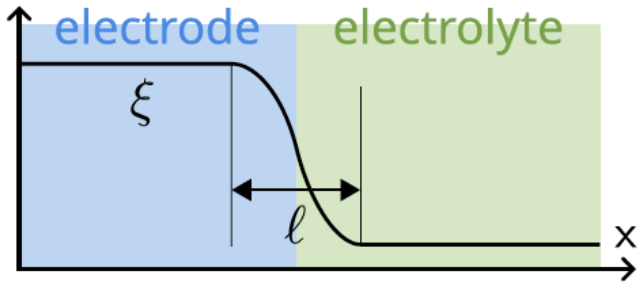
Phase field model



For ideal solution

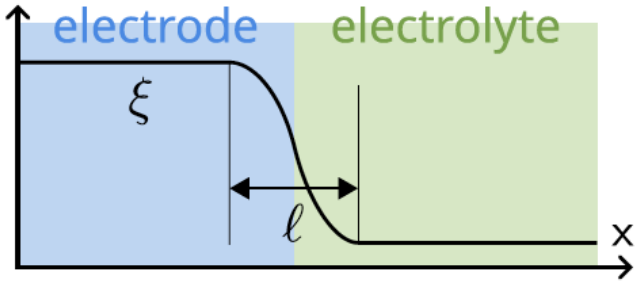
$$\eta = \frac{V_m}{F}\frac{\delta \mathcal{F}}{\delta \xi} = \frac{V_m}{F}\underbrace{\left(m g'(\xi) - \kappa \vec{\nabla}^2 \xi\right)}_{\text{interfacial energy}} + p'(\xi)\underbrace{\left(E^{\ominus} + \phi^s - \phi^l + \frac{RT}{F}\ln\frac{c_+^s}{c_+}\right)}_{\text{activation overpotential}}$$

Classical definition (sharp interface)

$$\eta = \frac{V_m}{F}\sigma\mathcal{H} + E^{\ominus} + \phi^s - \phi^l + \frac{RT}{F}\ln\frac{c_+^s}{c_+^l}$$

$\mathcal{F}$: Helmholtz free energy of system, ξ: phase field parameter, p: interpolation function

Phase field model



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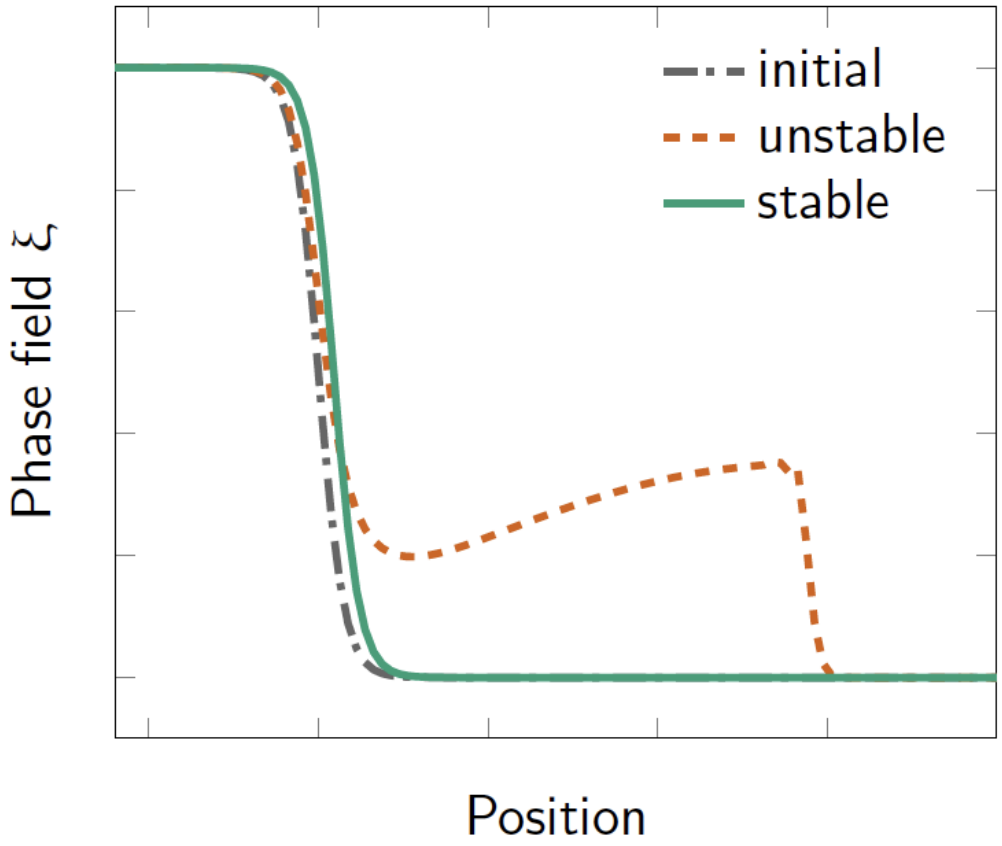
Classical d

We assumes a Helmholtz double layer

More complex double layer models: a multiscale approach

$\mathcal{F}$: Helmholtz free energy of system, ξ: phase field parameter, p: interpolation function

Challenge for quantitative modeling



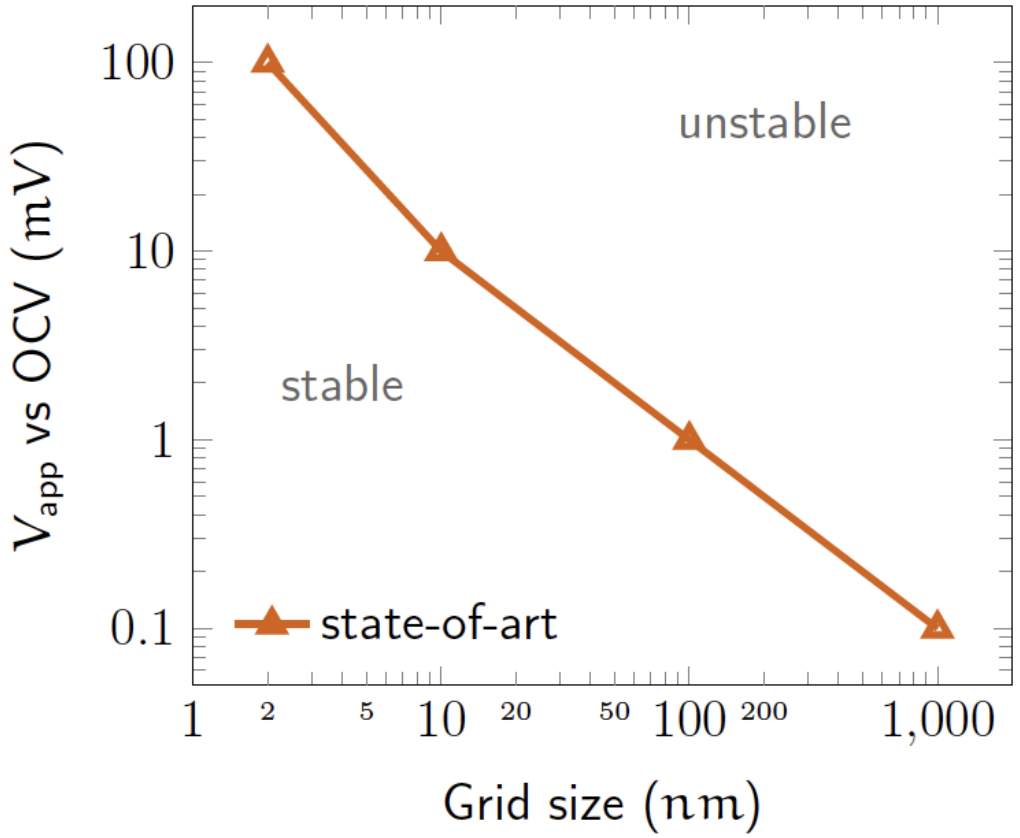
System with

- Electrode: Li metal
- Electrolyte: 1M $LiPF_6$ in EC

System size: 100 μm

Interface is no longer stable

Challenge for quantitative modeling



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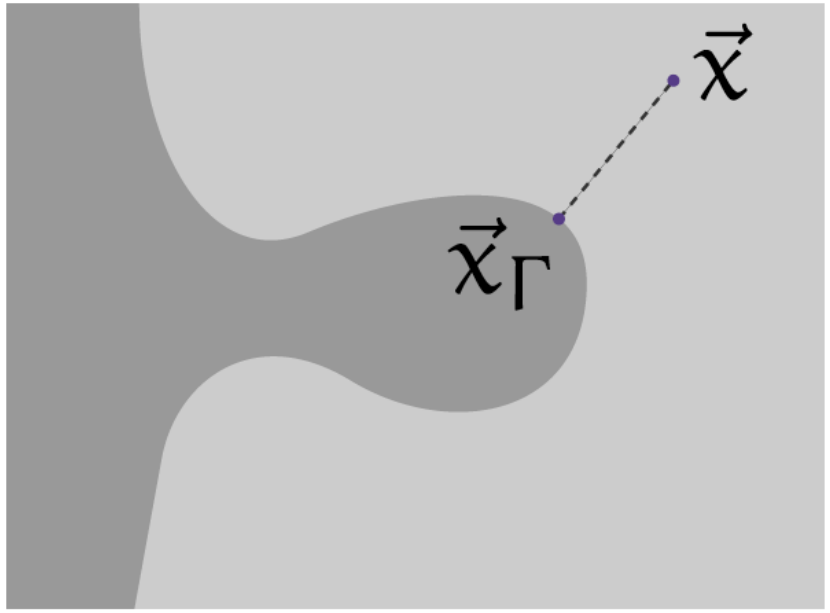
Driving force extension

2D and 3D



How to solve the problem?

▲ A constant η_a has no stability issue

Extend the activation overpotential:

$$\mathcal{P}(\eta_a(\vec{x}, t)) = \eta_a(\vec{x}_\Gamma, t)$$

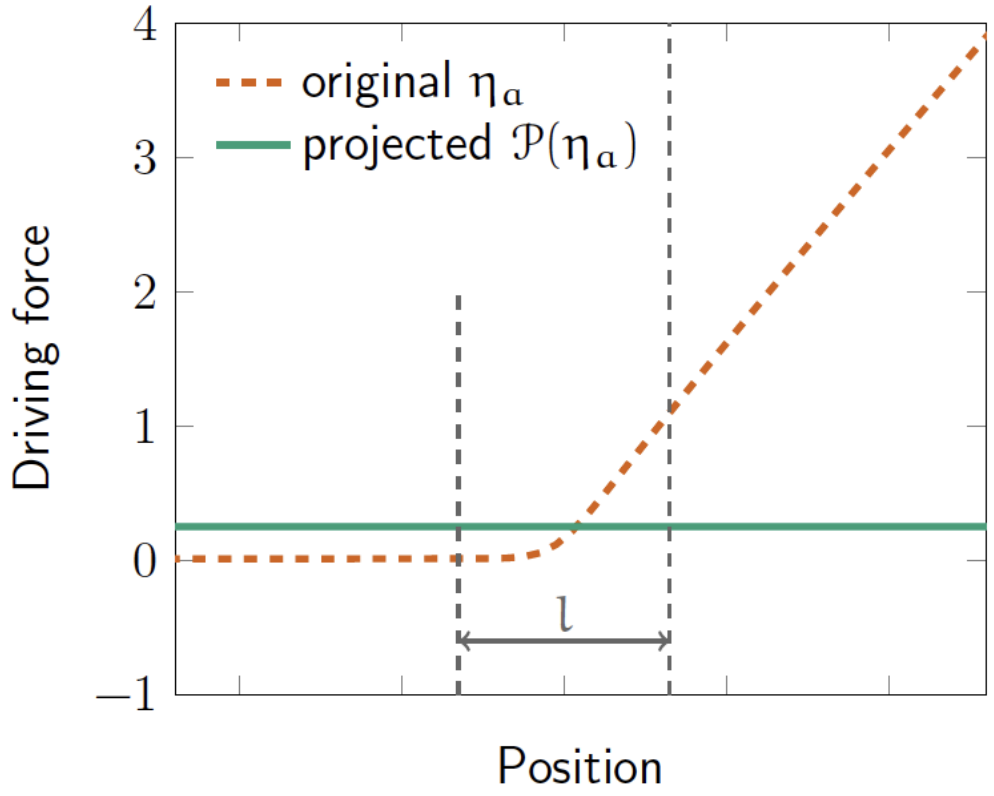
Introduce a simple modification:

$$\eta = -\frac{V_m}{F}\frac{6\sigma}{l}\left(l^2\vec{\nabla}^2\xi - \frac{g'(\xi)}{2}\right) + p'(\xi)\mathcal{P}(\eta_a)$$

Fast marching method

J. Zhang, A.F. Chadwick, D.L. Chopp, and P.W. Voorhees. *npj Computational Materials* 9, no. 1 (2023): 166.

Driving Force Extension



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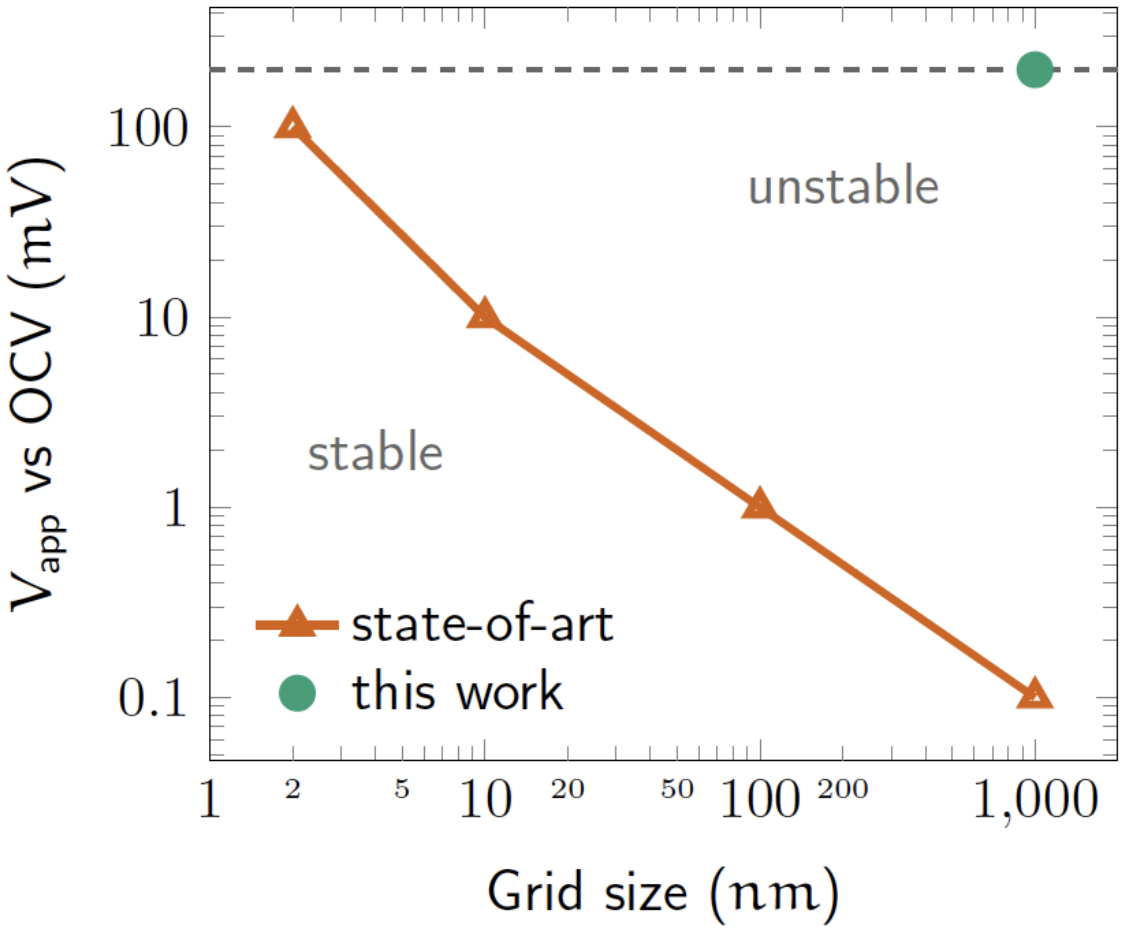
Driving force extension



For a problem in d-dimension,
Timestep

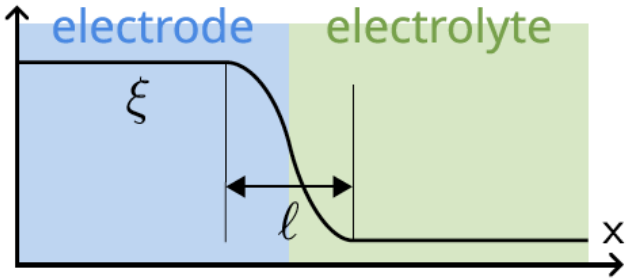
$$\Delta t = \frac{\Delta x^2}{2dD^l}$$

Computational cost

$$\text{time} \propto \left(\frac{1}{\Delta x}\right)^{2+d}$$

Example:
increase Δx by a factor of 1000,
reduce time by a factor of 10^{12} for 2D
reduce time by a factor of 10^{15} for 3D

Phase field model: Summary



$p = 1$: electrode, $p = 0$: electrolyte

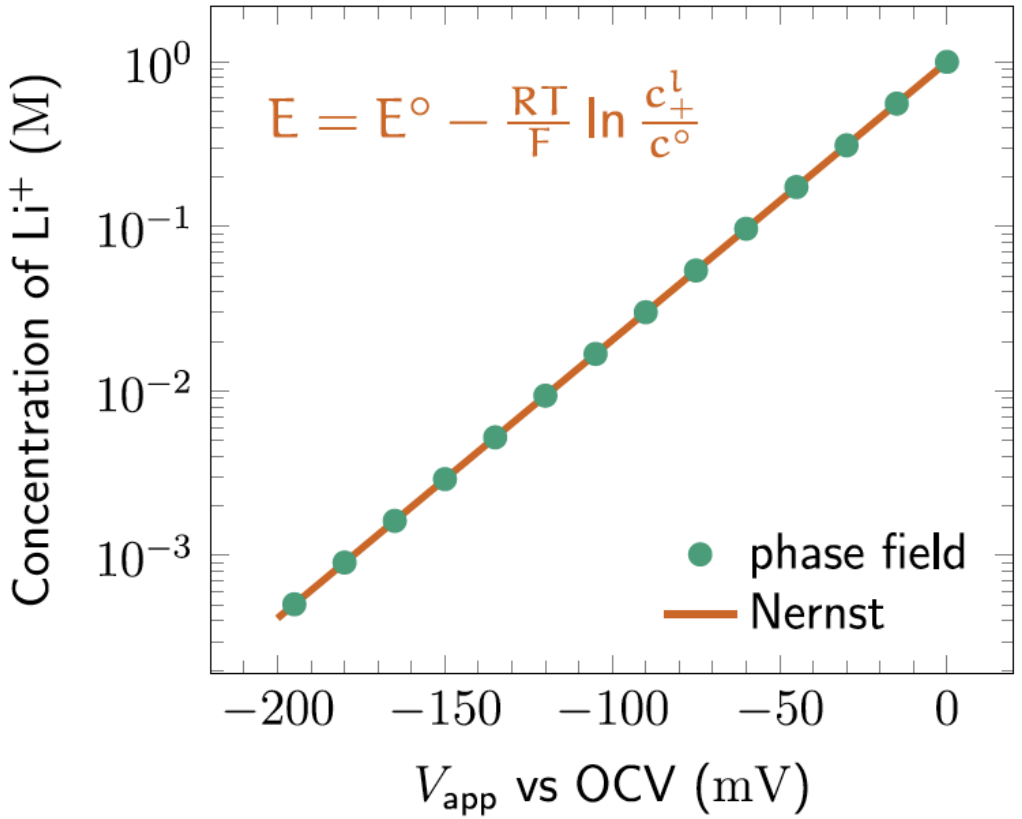
State variables: ξ, c, ϕ^l, ϕ^s

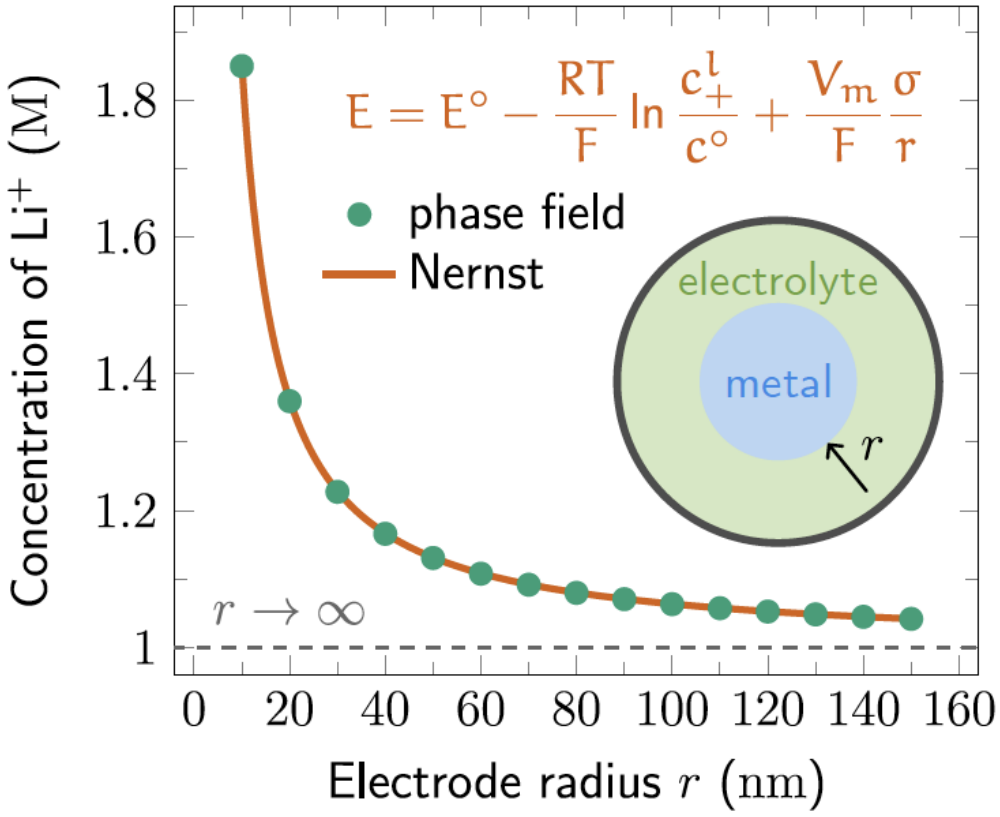
$$\begin{cases} \dfrac{\partial \xi}{\partial t} = \dfrac{V_m}{6\ell F} j(\eta) \\ \dfrac{\partial c}{\partial t} = \vec{\nabla} \cdot (M \vec{\nabla} \tilde{\tilde{\mu}}) \\ \vec{\nabla} \cdot \left((1 - p(\xi)) \vec{i}^{\,l}_{ion} \right) = p'(\xi) F c^s \dfrac{\partial \xi}{\partial t} \\ \vec{\nabla} \cdot \left(p(\xi) \vec{i}^{\,s}_{e} \right) = -p'(\xi) F c^s \dfrac{\partial \xi}{\partial t} \end{cases}$$

1. Reaction kinetics
2. Mass conservation
3. Ionic charge conservation
4. Electrical charge conservation

$\mathcal{F}$: Helmholtz free energy of system, ξ: phase field parameter, p: interpolation function

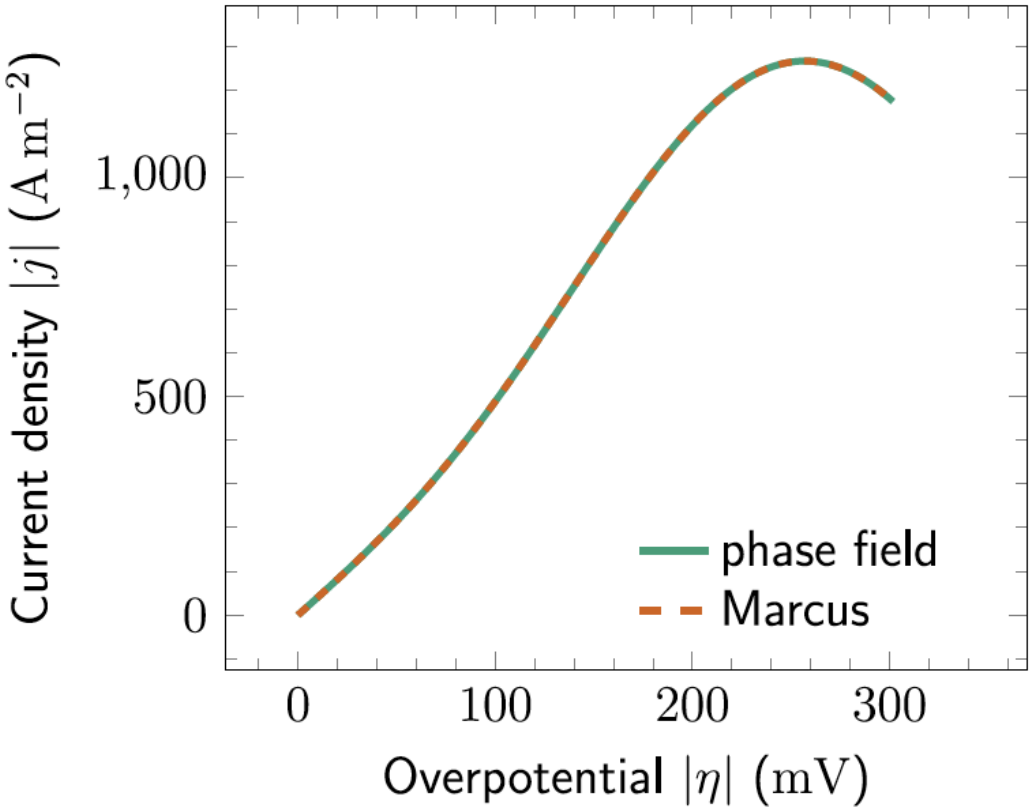
Model verification: Equilibrium

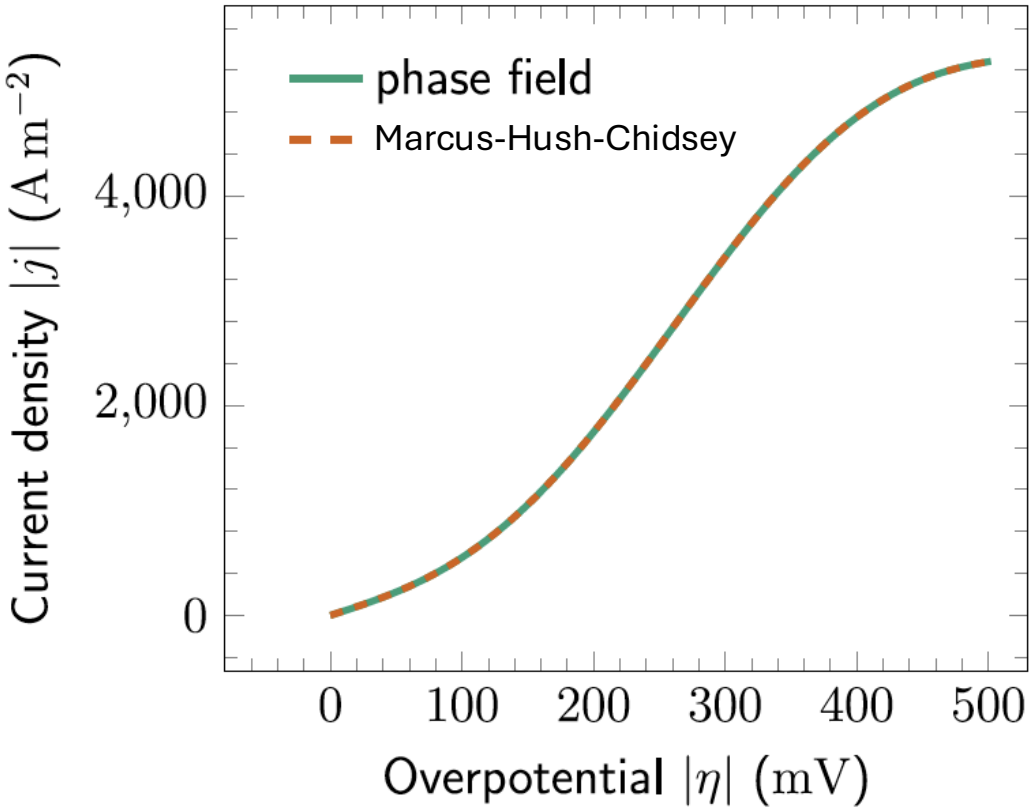




Excellent agreement with classical electrochemical theory

Model verification: Reaction kinetics





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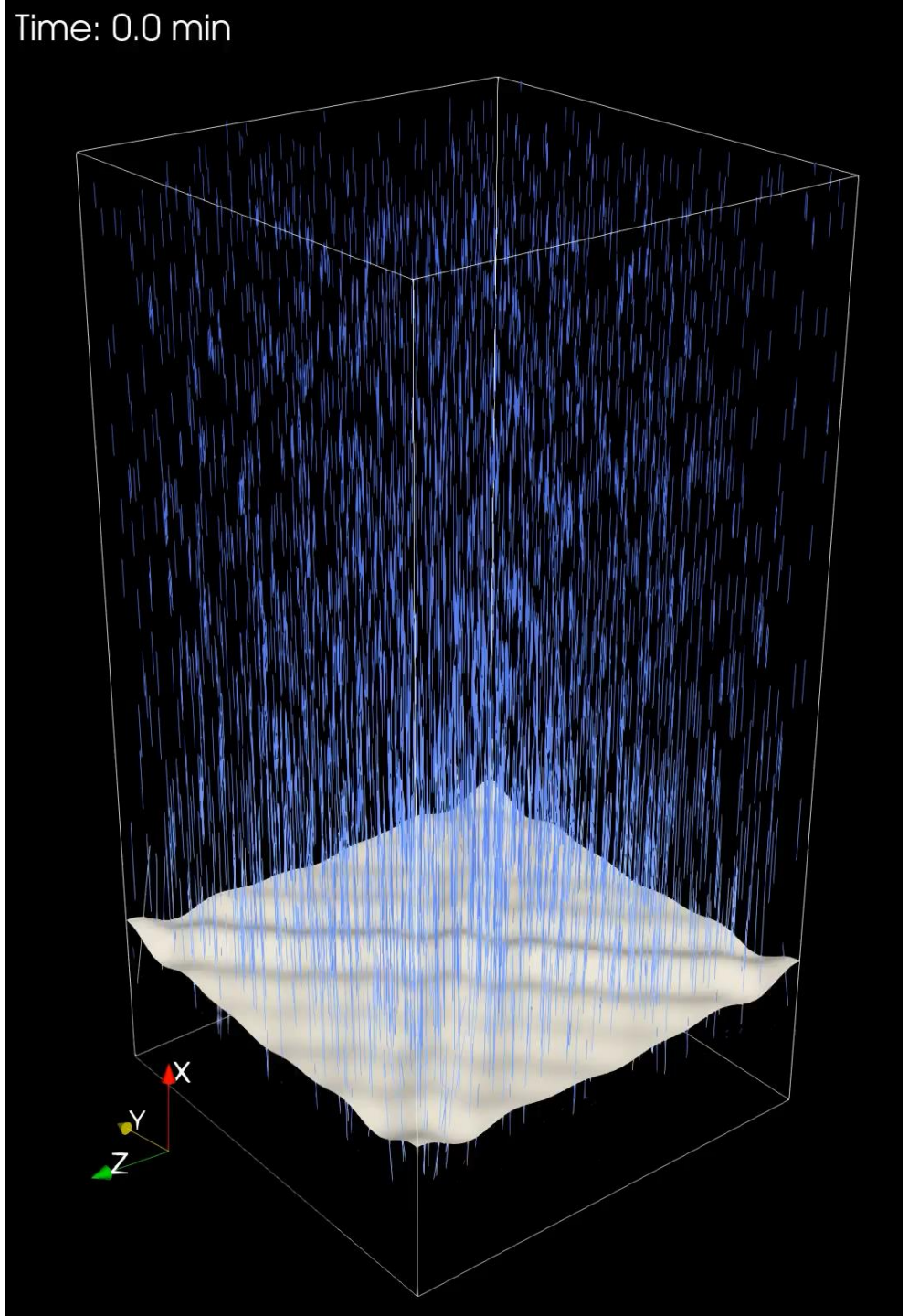
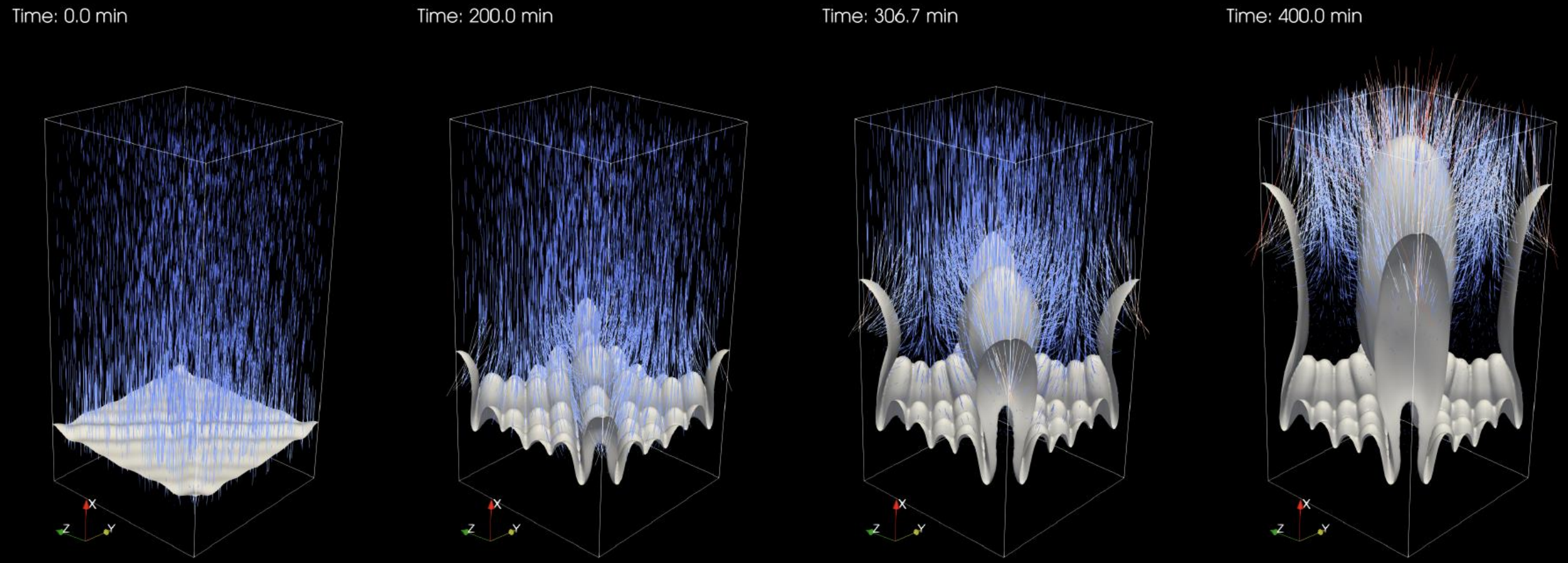

Time: 0.0 min
X
Y
Z

Lithium dendrite growth



Applied voltage: $-100\mathrm{m}V$ vs $\mathrm{Li}|\mathrm{Li}_+$

Concentration at start: 1M

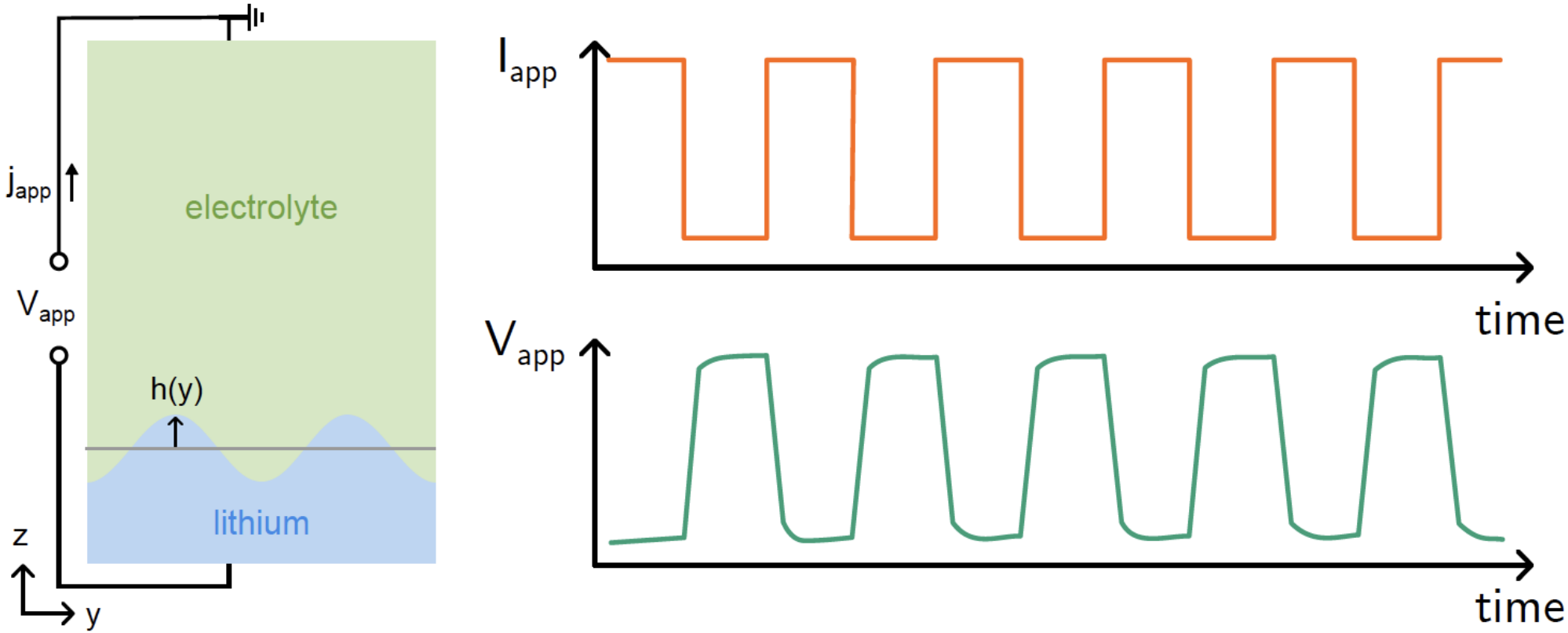
Domain size: 64 μm x 64 μm x 128 μm

Anode: Li metal

Electrolyte: PEO

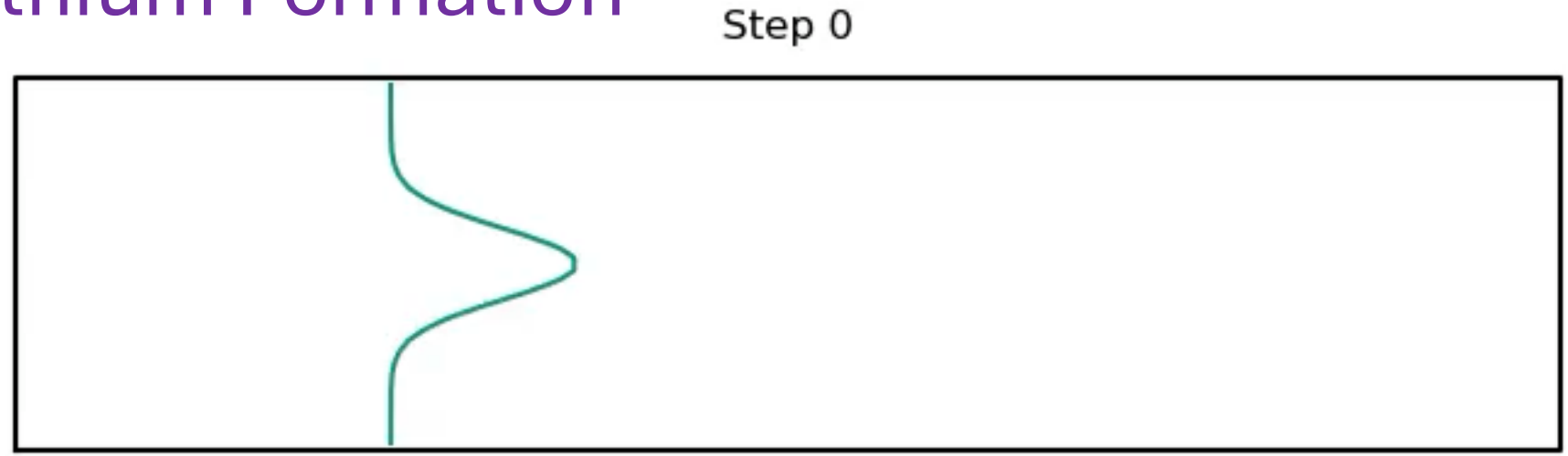
Computational time with 52 cores: 12 days

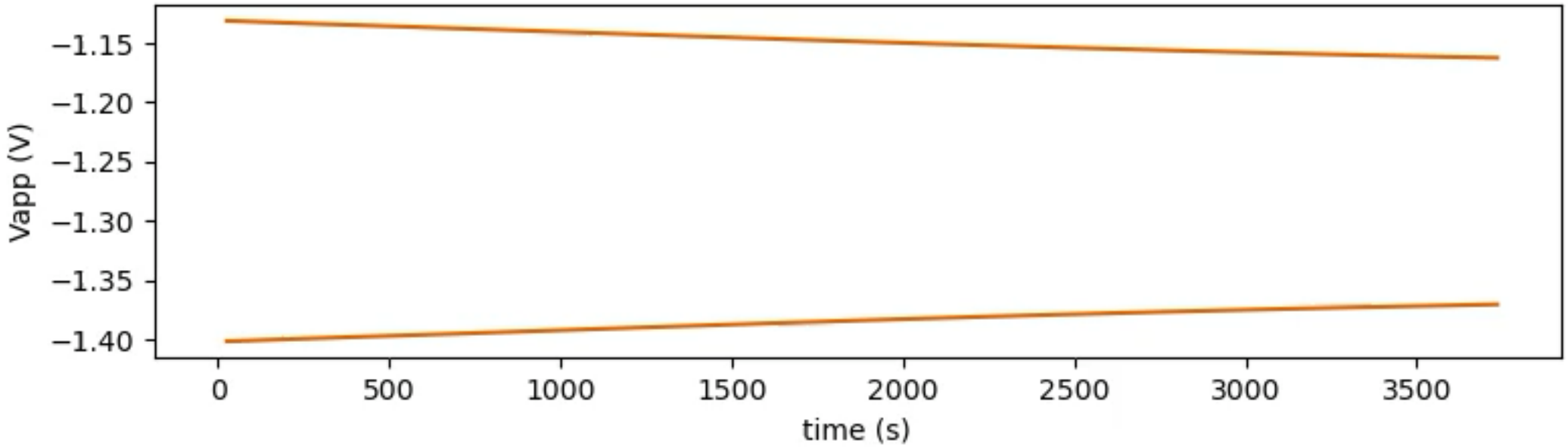
Dead Lithium Formation



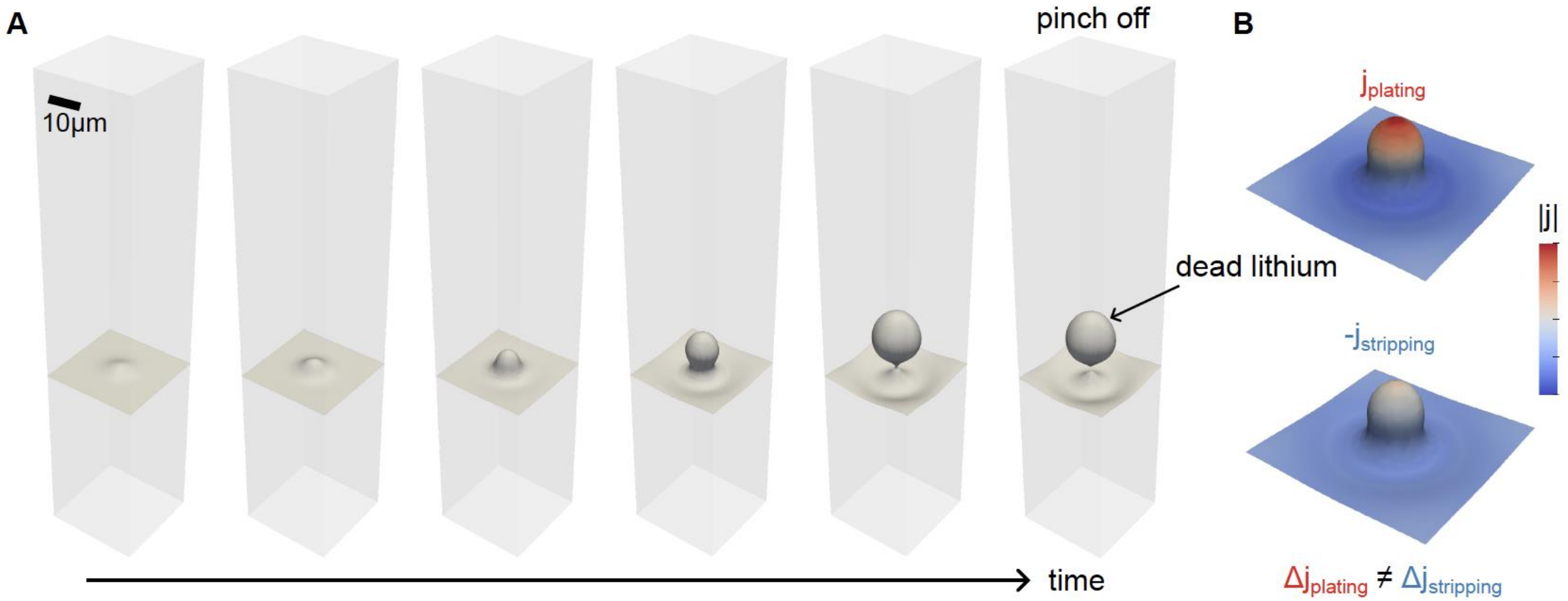
Zhang, Chadwick, Voorhees, Cell Rep Phys Sci (2025) 102360

Dead Lithium Formation



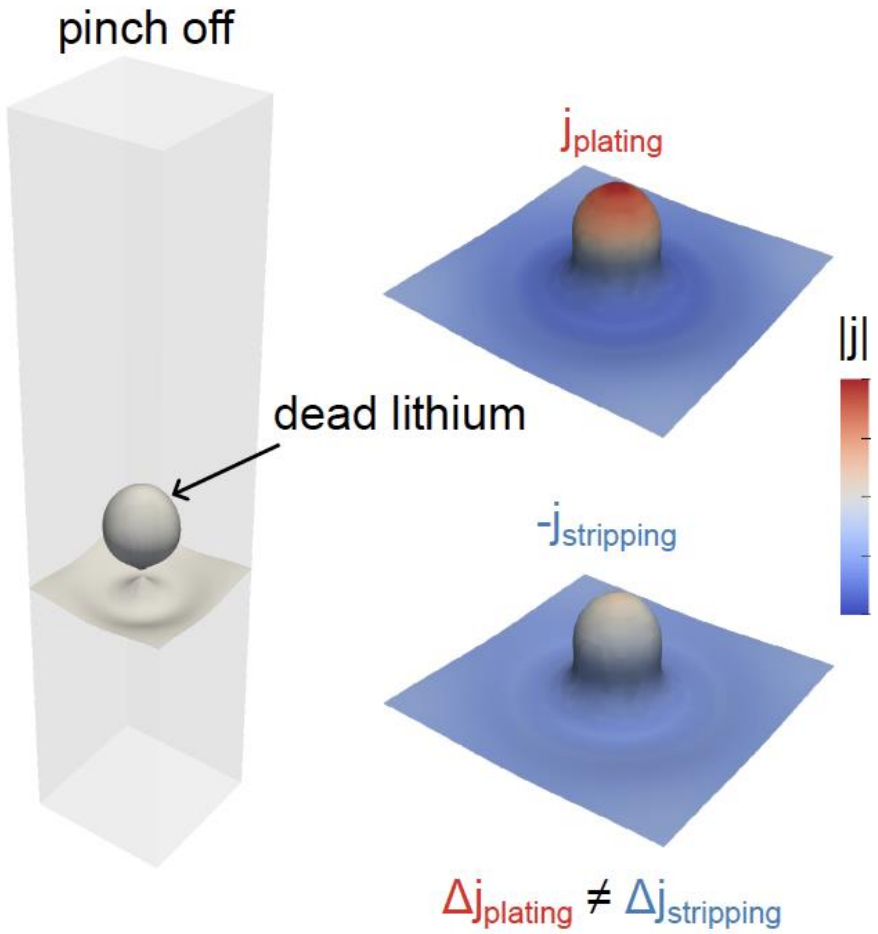


Dead Lithium Formation



Dead Li forms because plating and stripping currents are not symmetric

Dead Lithium Formation

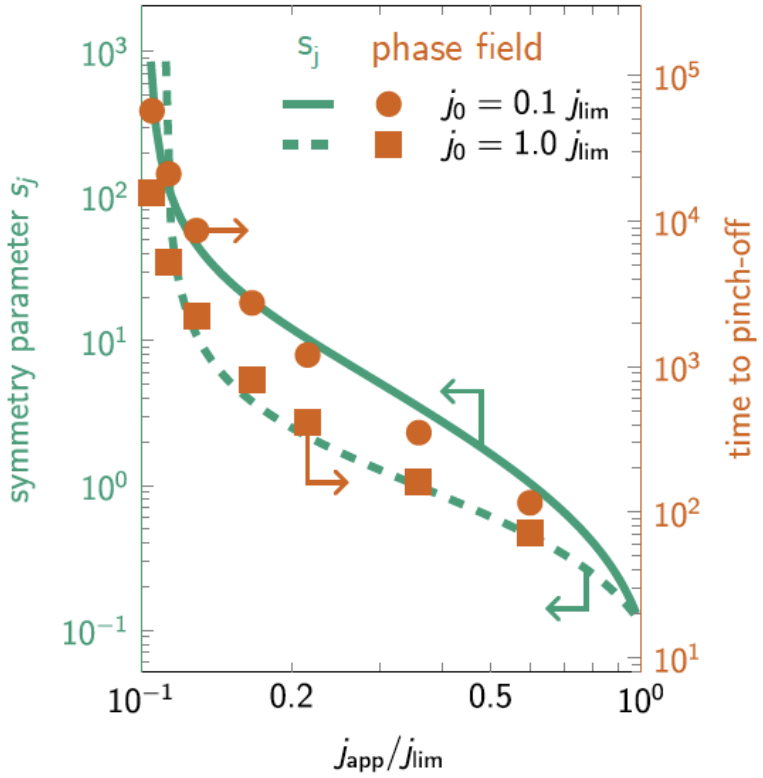


Define a symmetry parameter

$$s_j = \frac{j_{app}}{\Delta j_{plating} + \Delta j_{stripping}}$$

- $s_j = +\infty$: symmetric (no dead Li)
- $s_j > 0$: formation of dead Li
- $s_j < 0$: no dead Li

Dead Lithium Formation



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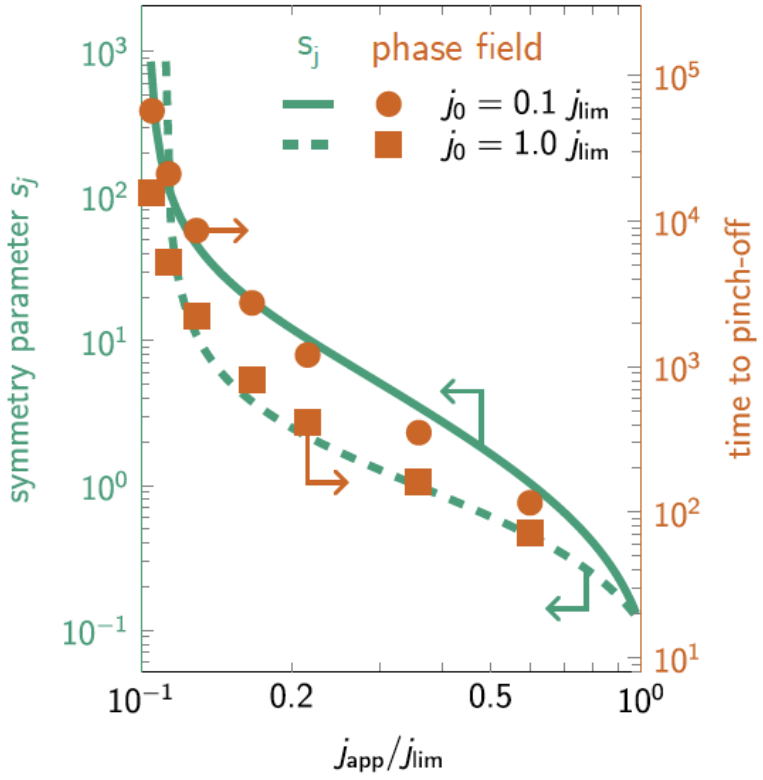

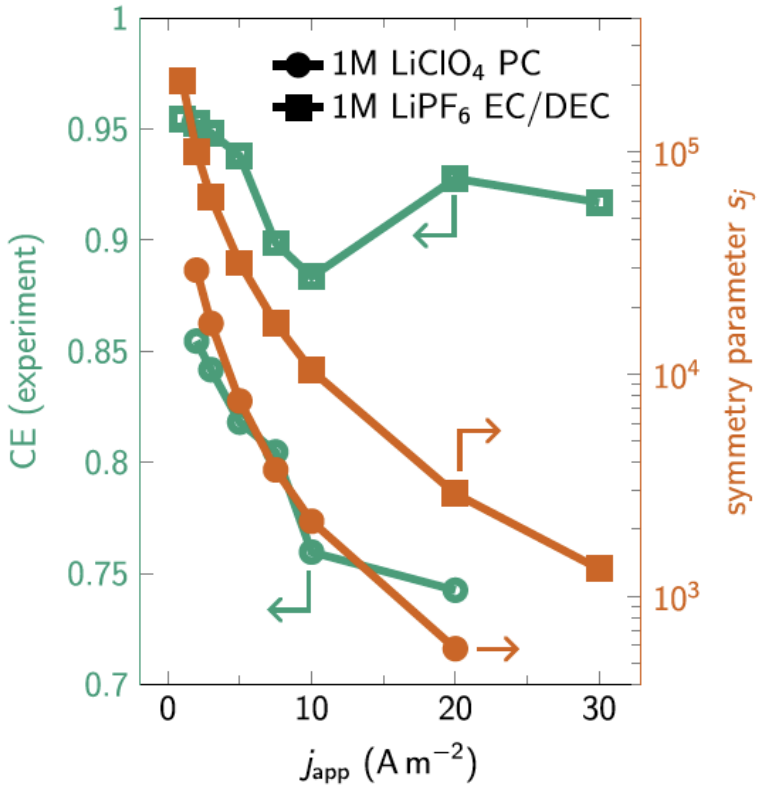

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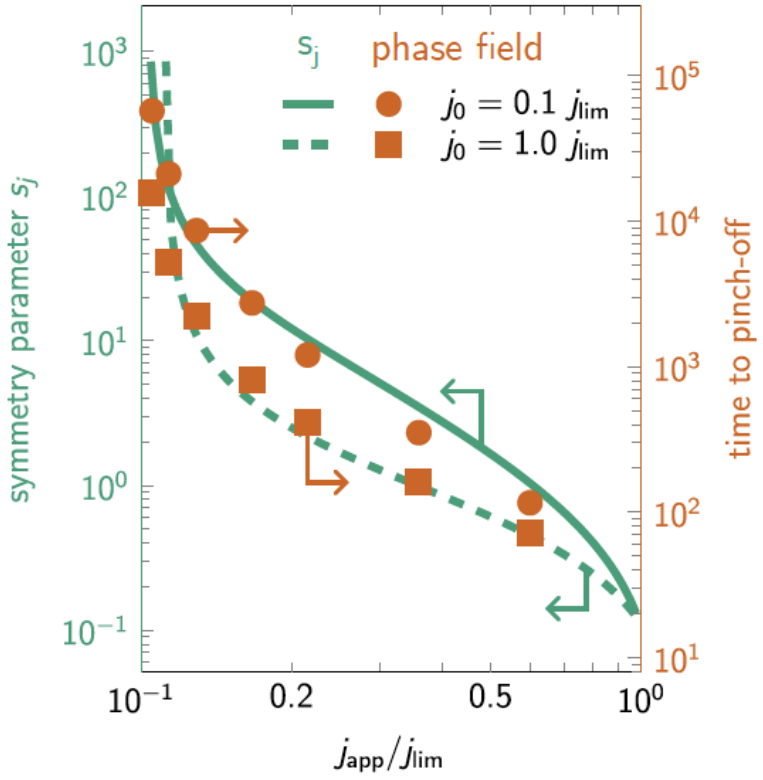
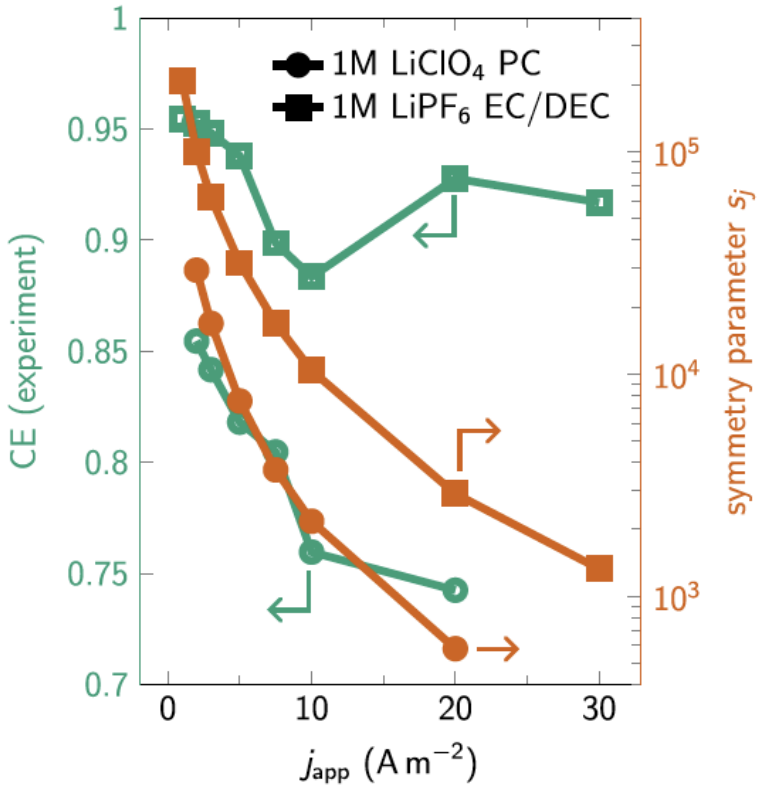
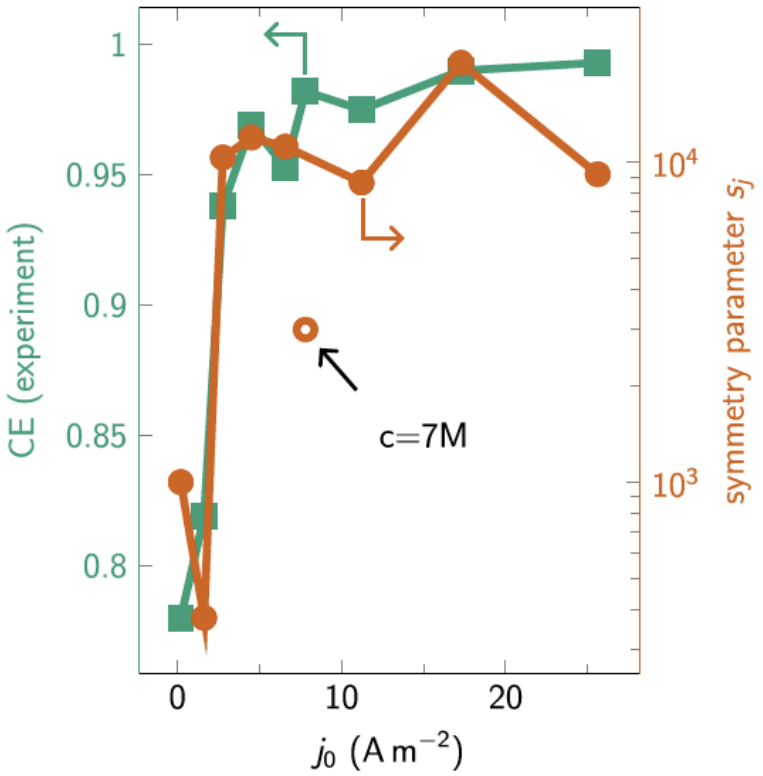


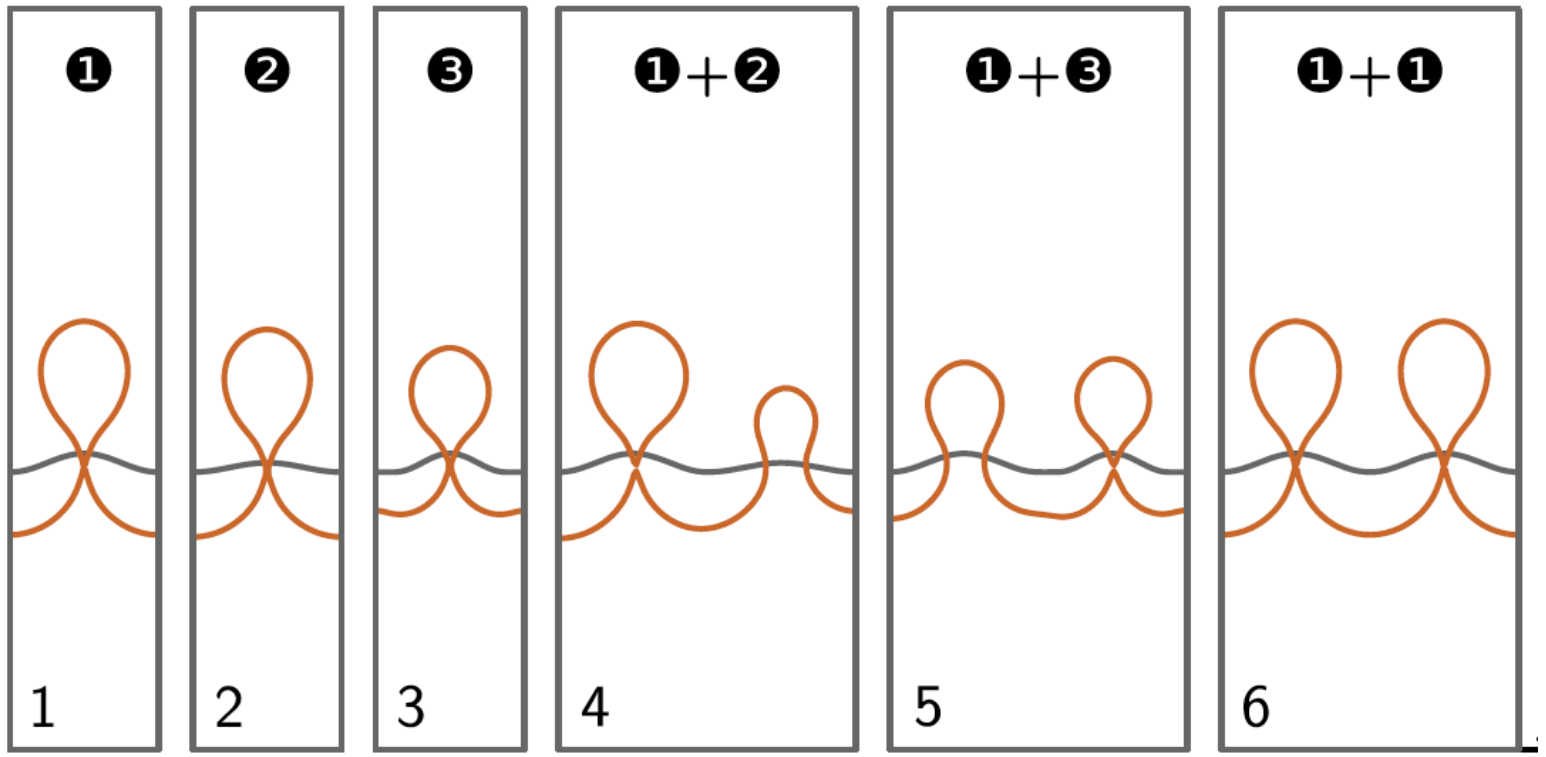


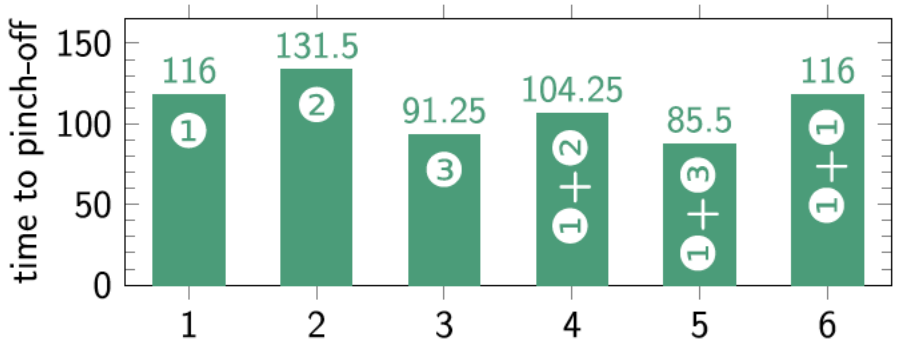


Good correlation between phase field, s_j, and experimentally measured CE!

Dead Lithium Formation

Effect of nonlinear perturbations and initial shape of the interface



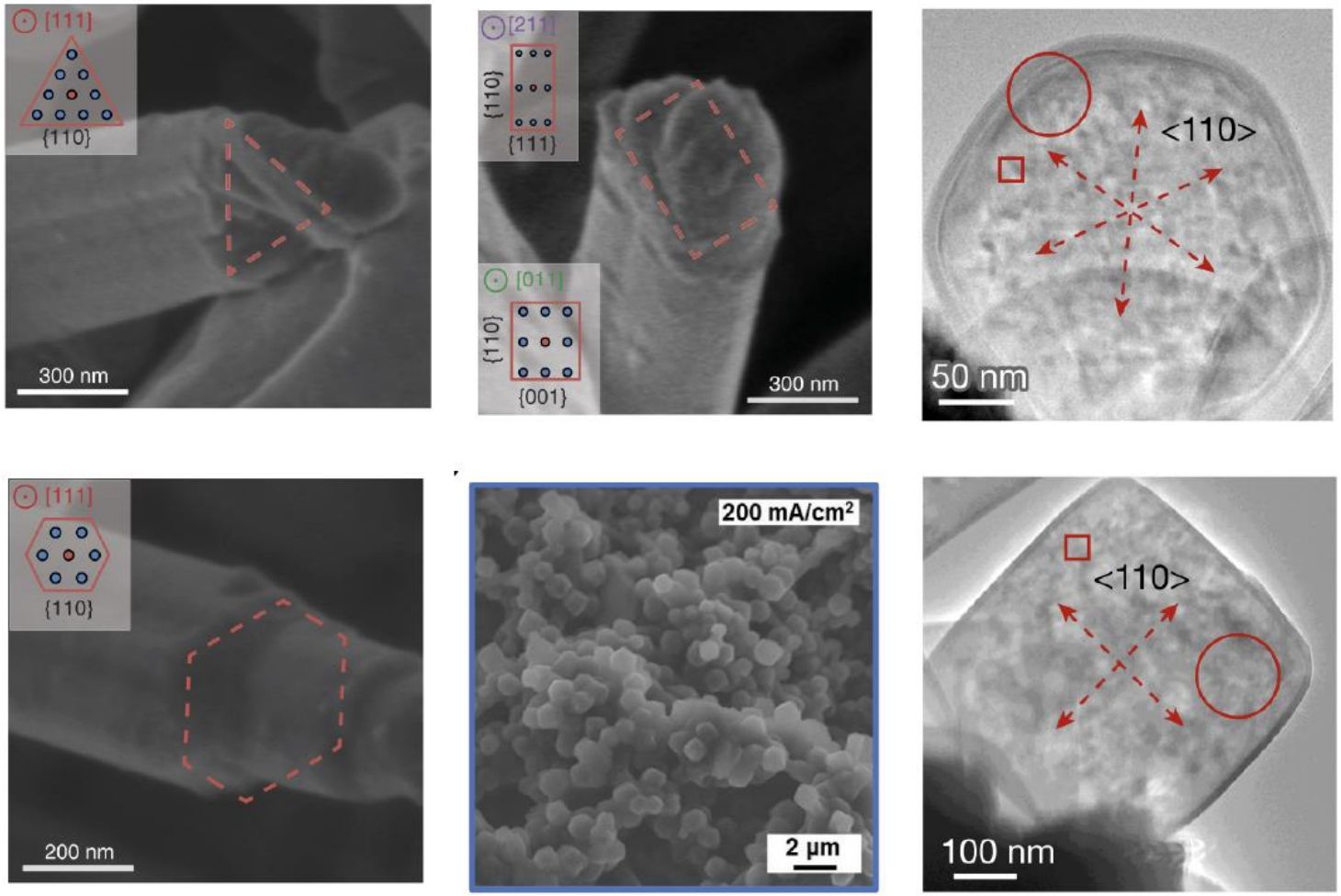


Dead Li formation: strategies

Reduce the non-symmetry between charging and discharging

- Keep concentration far from depletion
- Slow charging and slow discharging
- High electrolyte concentration
- High electrolyte diffusivity/conductivity
- Asymmetric reaction kinetics

Dead Lithium Formation With Anisotropy



Li, Science 2017; Yuan, Nature 2023

Dead Lithium Formation With Anisotropy

Butler-Volmer

$$j(\eta) = j_0(\hat{n}) \left(e^{-\alpha \frac{F\eta}{RT}} - e^{(1-\alpha) \frac{F\eta}{RT}} \right)$$

Overpotential

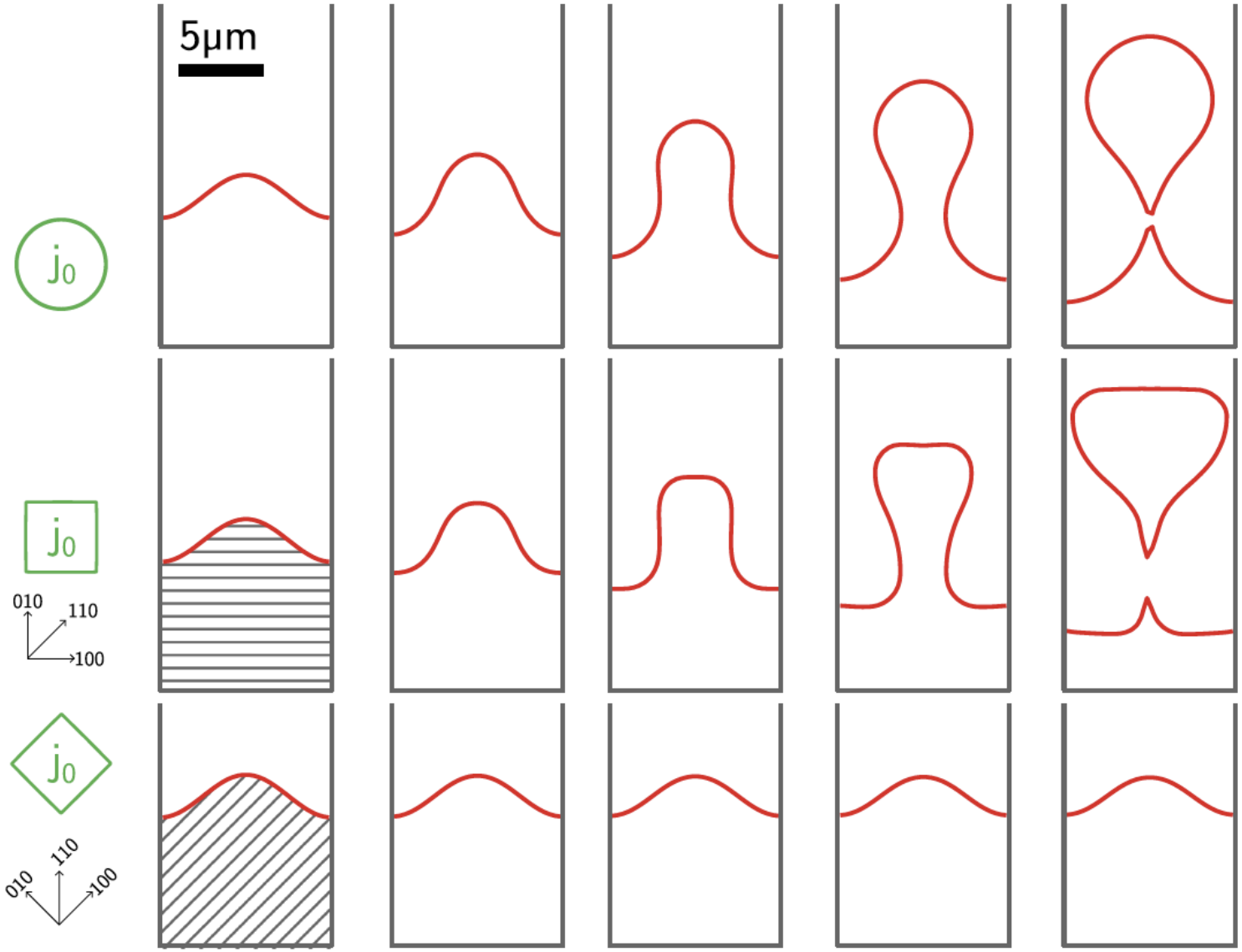
$$\eta = E^{\ominus} + \phi^s - \phi^l + \frac{RT}{F} \ln \frac{c_+^s}{c_+^l} + \frac{V_m}{F} \sigma(\hat{n}) \mathcal{H}$$

- Interfacial energy anisotropy: $\sigma(\hat{n})$
- Kinetic anisotropy: $j_0(\hat{n})$

Both anisotropy can affect the morphology!

$\hat{n}$ interface normal, σ interfacial energy, $\mathcal{H}$ curvature, j_0 exchange current density

Dead Lithium Formation With Anisotropy



Consider anisotropy

Examine the effect of lithium orientation on cycling behavior

(110) plane parallel to the electrode surface

$\Rightarrow$ suppress dead Li

Dendrite Suppression by Thermodiffusion

- Symmetric cells with fixed temperature differences, cell lifetime improves when the warmer electrode is charged first.
- Small changes in temperature across a cell, on the order of 1K, can promote or suppress dendrite formation (Carter, R.; Love, C. T. ACS Appl. Mater. Inter. 2018, 10, 26328–26334)
- How can such a small change in temperature matter?
  - A 1K difference across a 10 μm thick separator can lead to a temperature gradient of 10^5 K/m.

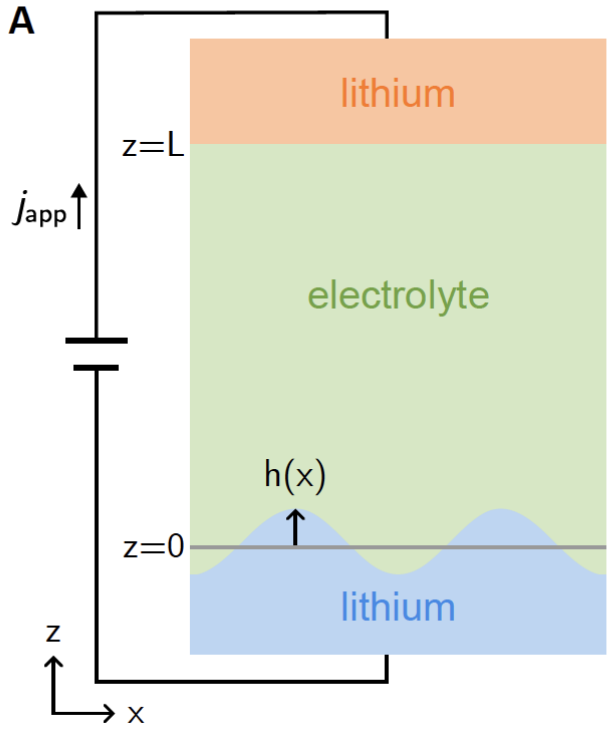
The effects of thermal gradients on the mass and charge transport in the electrolyte by Soret and Seebeck effects

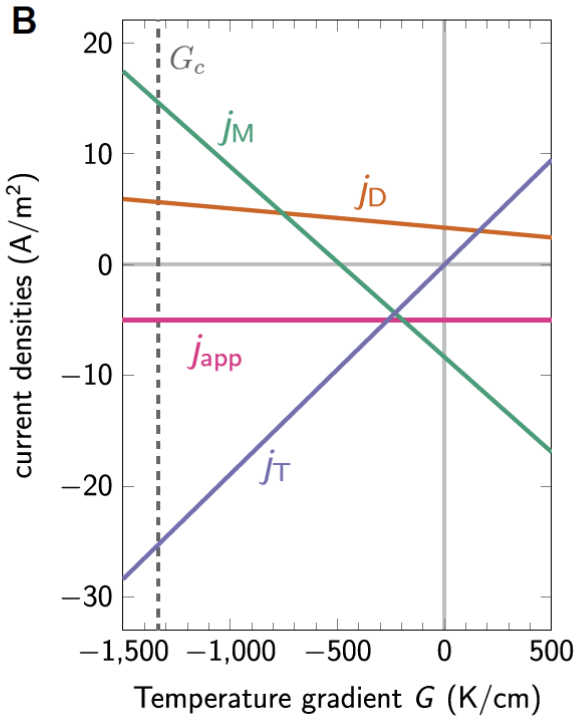
Alexander F. Chadwick, Jin Zhang, Michael W. Swift, David L. Chopp, Michelle D. Johannes, and Peter W. Voorhees, submitted

Dendrite Suppression by Thermodiffusion

$$\frac{\partial c}{\partial t} = \nabla \cdot (D_s \nabla c) + \nabla \cdot (D_s S_{\mathrm{T}} c \nabla T) - \frac{\nabla t_+ \cdot \vec{j}_{\mathrm{ion}}}{F},$$

$$\vec{j}_{\mathrm{ion}} = -\kappa \nabla \phi - \kappa S_{\mathrm{ion}} \nabla T + \frac{F D_s (1 - 2t_+)}{2t_+(1 - t_+)} \nabla c.$$





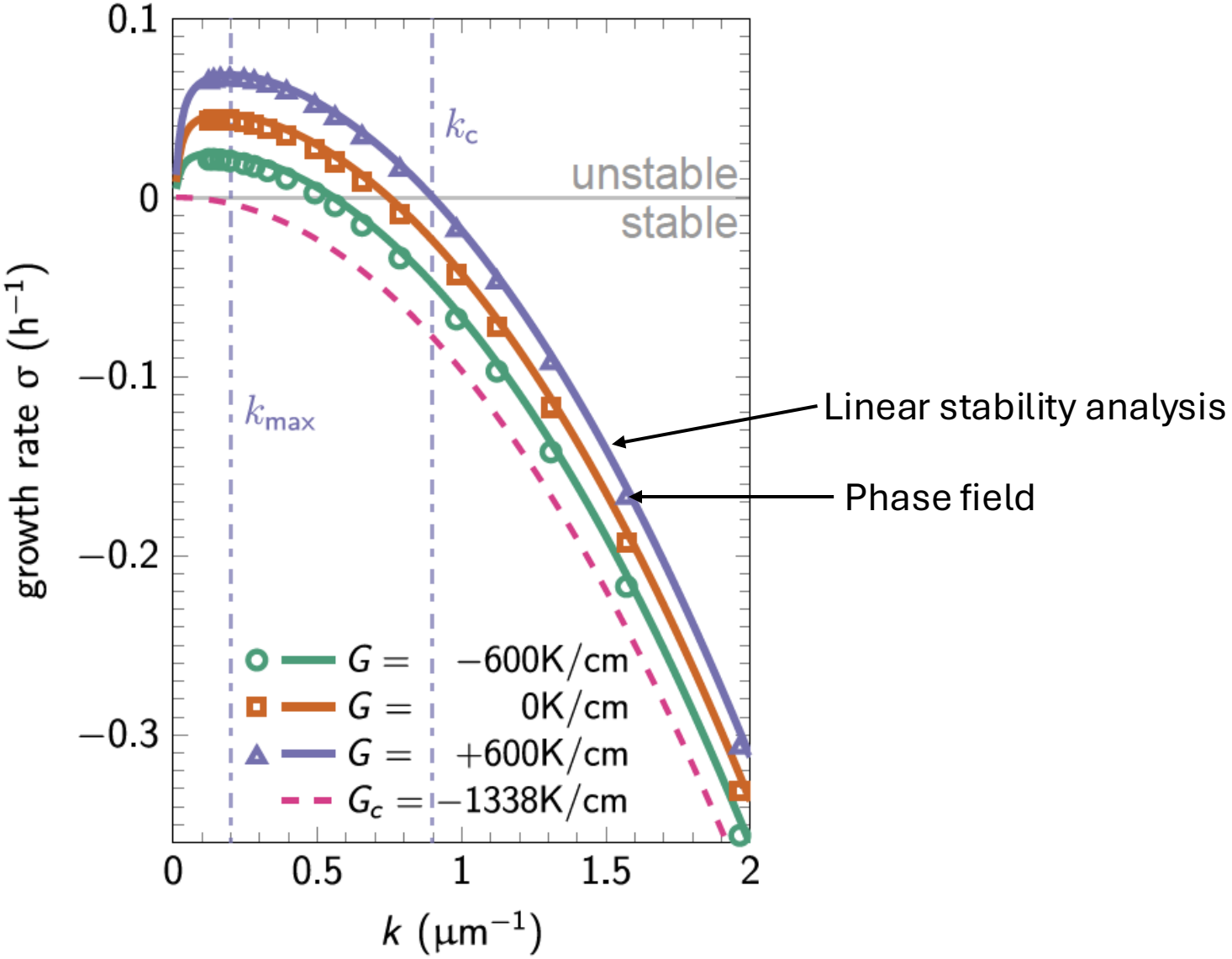
- Additional fluxes are in included in the phase field model with the driving force extension method
- Sharp interface model was used for a linear stability analysis
- Temperature- and concentration-dependent diffusivities were calculated with molecular dynamics

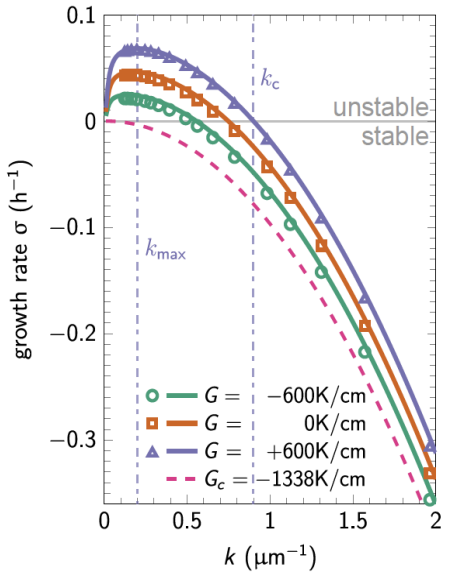
Dendrite Suppression by Thermodiffusion

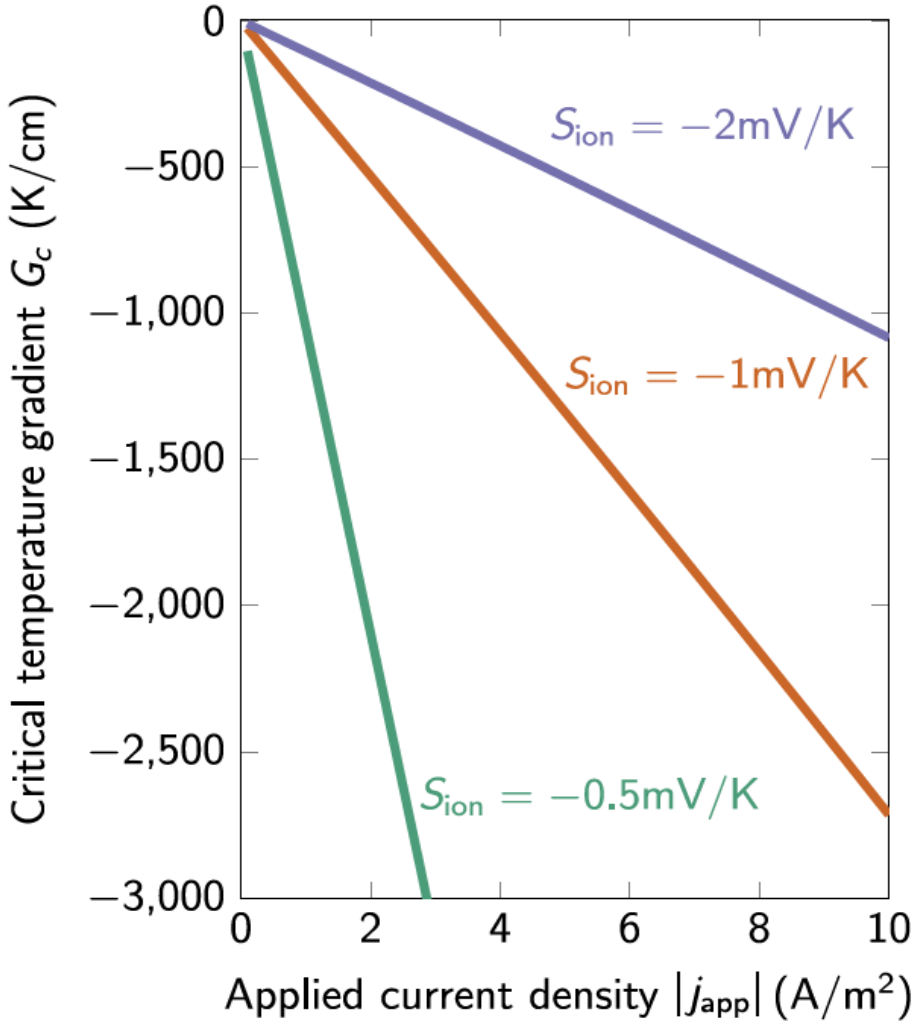
Linear stability analysis

$$h(x,t) = \varepsilon \hat{h} e^{ikx+\sigma t}$$

Both the phase-field model and linear stability theory predicts that thermodiffusion can suppress dendrite growth with an applied thermal gradient

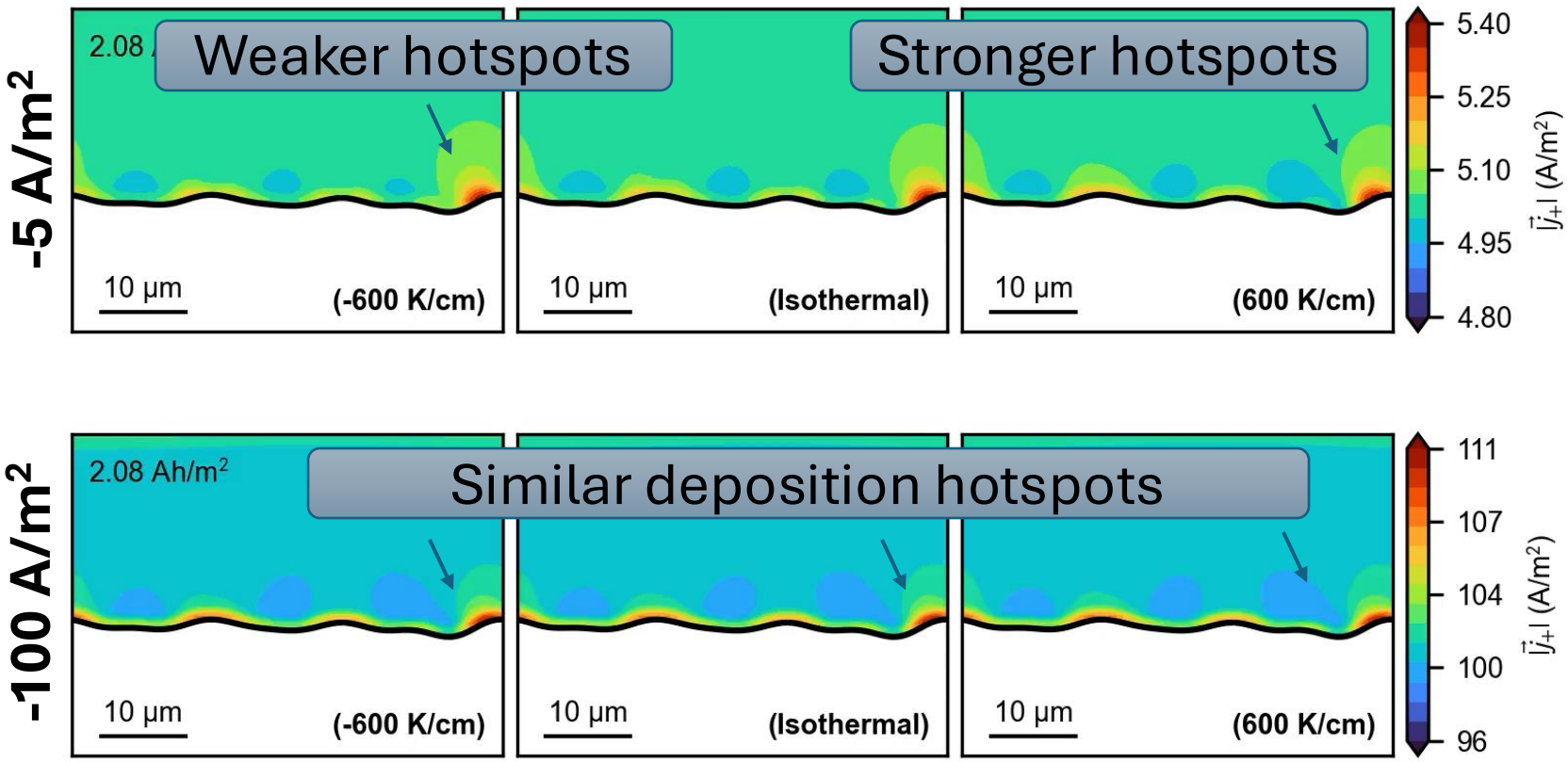






Dendrite suppression by thermal gradients is most effective during slow charging and least effective during fast charging, consistent with experiments

Dendrite Suppression by Thermodiffusion



Note: simulations are in a moving reference frame

- For small currents, thermal gradient can significantly affect dendrite growth
  - Lifetime can be extended even without complete suppression
- Smaller impact for large currents

$$G_c \propto -j_{\text{app}}$$

Chadwick et al., *submitted*.

Conclusions

- General phase field model for electrochemical processes
- A mapping method to use realistic materials parameters
- Asymmetry of the charge and discharge cycles are key in the dead lithium formation process
- Thermal gradients can carry a significant portion of current in a battery due to thermodiffusion
- There is a critical value of externally applied thermal gradient that suppresses dendrite formation
- The directional dependence between G and the applied current has practical implications in battery thermal design