

Supplemental Information for

Thermal Relaxation of Lithium Dendrites

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In principle, the electric potential field, ϕ , should be obtained by solving Gauss's law. However, since electroneutrality is a valid approximation throughout the electrolyte up to the thin depletion boundary, and ion-ion electrostatic interactions are screened out by counter ions because the Debye length under present conditions ($\lambda_D = 0.27 \text{ nm}$) is smaller than the average interionic separation ($R_{ij} = 1.2 \text{ nm}$), Gauss's equation approximately reduces to Laplace's equation. Since temperature profile is also described by Laplace's equation, we define a generic parameter U as follows:

$$U = [\phi(x,y), T(x,y)] \quad (\text{SE1})$$

where x and y are coordinates parallel and normal to the cathode. Hence we have:

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$$\frac{\partial^2 U}{\partial x^2} + \frac{\partial^2 U}{\partial y^2} = 0$$

(SE2)

with the following boundary conditions:

$$U(x,0) = [V_-, T_-] \quad (\text{SE3})$$

$$U(x,L) = [V_+, T_+] \quad (\text{SE4})$$

because the high electrical and thermal conductivities of Li^0 ensure that the surface of cathodic electrodeposits is equipotential and isothermal at $[V_-, T_-]$ at all times. To ensure a smooth surface, the equipotential surface extends slightly beyond the bonding radius of Li^0 at $(1.3 r_+)$.

$$U_{\text{dendrite}} = U_{\text{cathode}} \quad (\text{SE5})$$

We solved (SE2) using a finite difference method in a (280 x 280) grid defined by equation (SE6) [1]:

$$U_{i,j} = \frac{1}{4}(U_{i+1,j} + U_{i-1,j} + U_{i,j+1} + U_{i,j-1}) \quad (\text{SE6})$$

Periodic boundary conditions (PBC) were assumed in the x direction. i.e., every Li^+ exiting the domain from right/left boundaries enters from the opposite side. The electric field was obtained numerically as:

$$E_{i,j} = - \frac{\phi_{i+1,j} - \phi_{i-1,j}}{2\Delta x} i - \frac{\phi_{i,j+1} - \phi_{i,j-1}}{2\Delta y} j \quad (\text{SE7})$$

We further considered that the overpotential for Li^+ reduction is so small that Li^+ should be reduced with unit probability once it reaches the cathode within $1.3 r_+$ at the applied potentials.

The temperature distribution can be also obtained from E2. Since the conductivity of the polymethyl-methacrylate separators is significantly lower than the metal collectors ($\alpha_{Li,Cu} \gg \alpha_{PMMA}$), we assume that the heat within the cell flows along the y-coordinate normal to the electrodes. So we have:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial y^2} \quad (\text{SE8})$$

Also since the time scale of temperature relaxation is much faster than ion transport, we will assume a quasi-steady state distribution throughout, that is, temperature profiles are time independent, hence:

$$\frac{\partial^2 T}{\partial y^2} = 0 \quad (\text{SE9})$$

The imposed boundary conditions are:

$$\begin{cases} T(0) = T_- \\ T(L) = T_+ \end{cases} \quad (\text{SE10})$$

Therefore, we obtain a linear temperature distribution between anode and cathode, which is independent of the solvent thermal conductivity:

$$T(y) = \frac{T_+ - T_-}{L} x + T_- \quad (\text{SE11})$$

Figure 1 shows the distributions of normalized temperature, $|T|$, defined by SE12:

$$|T| = \frac{T - T_+}{T_- - T_+} \quad (\text{SE12})$$

as a function of normalized height y/L over convex and concave regions of Li^0 electrodeposits. The concave/convex morphology has been imitated by a sinusoidal function during one period and the higher curvatures have been approximated with higher sin powers.

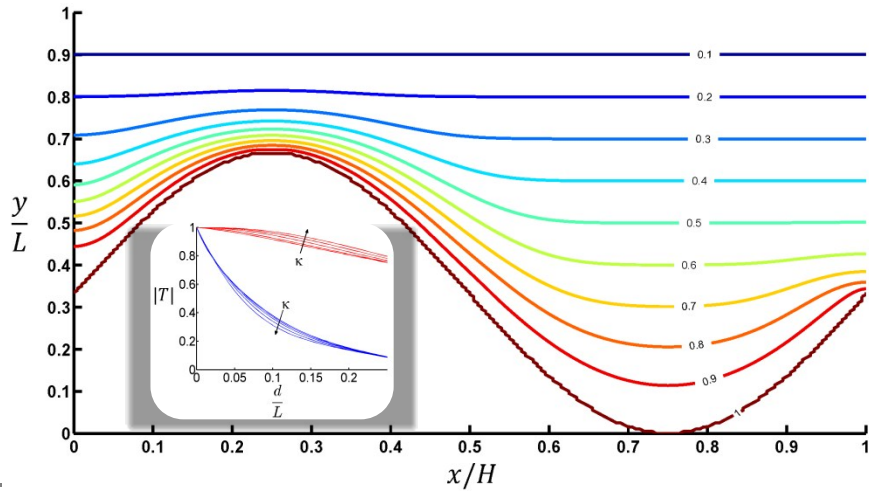


Figure S1 - Normalized temperature distribution over convex and concave regions as function of normalized cell height (y/L) and width (x/H). Inset: $|T'|$ normal gradients to the electrodes over convex (blue traces) and concave (red traces) regions as function of increasing positive and negative curvatures κ , respectively.

[1] R. J. LeVeque, *Finite difference methods for ordinary and partial differential equations: steady-state and time-dependent problems* (Siam, 2007).