Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Information for

Thermal Relaxation of Lithium Dendrites

Asghar Aryanfar[1*], Daniel J. Brooks[2], Boris V. Merinov[2], William A. Goddard III[2], Agustin J. Colussi[1*] and Michael R. Hoffmann[1]

[1]Linde Center for Global Environmental Science; [2]Materials & Process Simulation Center, California Institute of Technology, Pasadena, CA 91125, U.S.A.

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 ($\lambda_D = 0.27\ nm$) is smaller than the average interionic separation ($R_{i,j} = 1.2\ nm$), 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:

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

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

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[*] Corresponding Authors: AA: aryanfar@caltech.edu, AJC: ajcoluss@caltech.edu

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

(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 ($1.3\ r_+$).

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

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:

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial y^2} \tag{SE8}$$

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:

$$\frac{\partial^2 T}{\partial y^2} = 0 \tag{SE9}$$

The imposed boundary conditions are:

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

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

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

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

$$|T| = \frac{T - T_+}{T_- - T_+} \tag{SE12}$$

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.

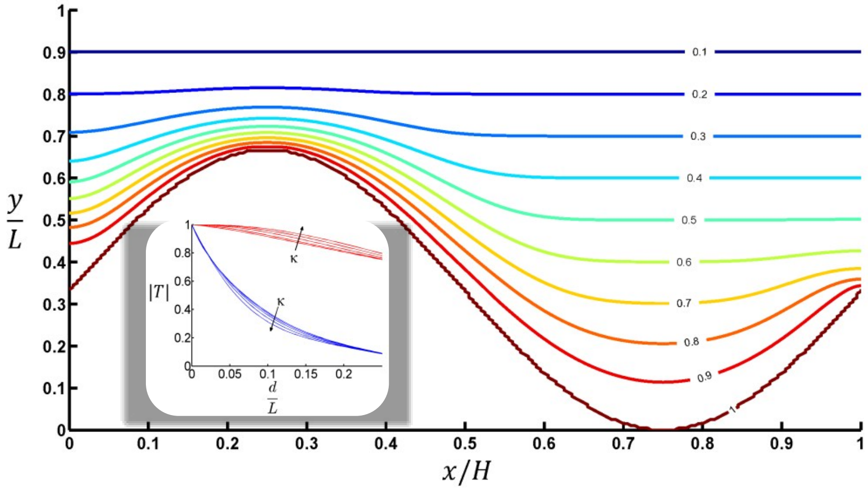

Figure S1 - Normalized temperature distribution over convex and concave regions as function of normalized cell height (*y/L*) and width (*x/H*). Inset: $|T|$ normal gradients to the electrodes over convex (blue traces) and concave (red traces) regions as function of increasing positive and negative curvatures κ, respectively.

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