Supporting Information for
Dynamics of Lithium Dendrite Growth and Inhibition - Pulse Charging
Experiments and Monte Carlo Calculations

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**Experimental Details:**

The cell separator was crafted from an acrylic plate by means of universal ILS9 laser cutter and interelectrode distance was precision-machined to 1/8”. Current collectors were machined from copper rod alloy 110 (1” dia.) with protrusion of compatible with separator depression for an effective sealing. The cathode current collector was threaded (1/32” dia.) for electrolyte injection. Ring gaskets (9/16” ID, 5/8” OD) were chopped out from silicone rubber sheet (McMaster-Carr, Plain Back, 0.02” thick). All cell components were washed with deionized water and isopropyl alcohol and dried under vacuum at 60°C for 48 hours and were transferred to argon-filled glovebox (H₂O, O₂ < 0.5 ppm).

Lithium foil (Aldrich, 99.9% on trace metal basis) 0.38 mm thick was punched (5/8” dia.) to be used as electrode. The counter lithium electrode was punched (1/32” dia.) in the middle for later electrolyte injection. Lithium oxide layers were scraped out via a sharp blade and dimethyl carbonate (DMC). The clean electrodes were flattened by being rolled via a glass tube. Both electrodes were intercalated in the separator. Wave disc springs (McMaster-Carr, high-carbon steel, 0.413” ID, 0.622” OD, 0.006” thick) were planted after electrodes to fill the possible gap in fabrication. Silicone rubber rings were laid between current collectors and separator to provide airtight sealing. The components were sandwiched with insulated screws. The electrolyte was injected into the cell afterwards and the hole was plugged through a small screw lined with Teflon tape.

Lithium perchlorate (Aldrich, battery grade, 99.99% trace metal basis) was dried for 24 hours in a vacuum oven at 100°C and dissolved in propylene carbonate (Aldrich, 99.7% Anhydrous) and 1 molar lithium perchlorate in propylene carbonate was synthesized through stoichiometric mixing to be used as electrolyte.

The demo cell was fabricated with representative electrodes and electrolyte and was cycled with the rate of 1mA/cm² and C/5, for 400 cycles inside the glovebox and for the most of the period, stable voltage regime was recorded without drying out the liquid electrolyte. The small voltage and current variations are attributed to lithium electrode surface reorganization to different morphologies.

Multiples cells were fabricated and subsequently charged with Bio-logic instruments (SP-50, VSP) and Neware battery tester (BTS-5V10mA, Shenzhen, China). The cells were flushed in perimeter via isopropyl alcohol after each experiment for dendrite measurements and various morphologies of dendrites were observed (Fig. 1').
Fig. 1’: Observed dendrites reach the counter electrode and short the cell.

**Modeling Details:**

We assumed following considerations to mimic the experimental conditions rather than the assumptions indicated in the main text:

I. We have assumed periodic boundary conditions (PBC) in x and y directions. Hence, every Li\(^+\) exiting the domain boundaries automatically enters the domain from the opposite side. i.e.

\[
\forall \, x, \, y:\begin{cases} 
\text{if } x > \alpha \Rightarrow x := x - \alpha, \\
\text{if } y > \alpha \Rightarrow y := y - \alpha
\end{cases}
\]

where \(\alpha\) is the square domain dimension.

II. For mimicking the electrolyte concentration in the experiment, we set the number of free ions in the model such that the average interionic distances would be close. In the 1 M LiClO\(_4\) in PC, the average interionic distance is 11.8 Å. Setting the same initial interionic distance for the model, we obtain the maximum number of free ions as \((166.7/11.8 + 1)^{\ast}2 = 229\). As dendrites advance into the electrolyte, the free domain becomes smaller and, therefore, in order to preserve the average interionic distance the number of free ions should decrease as well. Accordingly, we chose such number at 50,
which is also computationally affordable. We verified that the trends predicted by our calculations do not change upon slight variations in the number of free ions.

III. We define *maximum transition time* as the mean time it takes for ions to diffuse through the largest distance in the cell. The diffusion distance is defined as:

\[ \Delta x = \sqrt{2Da} \]  

(E1')

From Table 1, the modeling domain length is 166.7Å. We scaled down the diffusion coefficient to maintain close transition times between experiments and our model. Setting \( D = 1.4 \times 10^{-14} \text{m}^2/\text{s} \) gives the maximum transition time as 9.9 ms. For the experiments, we first obtain the distance in the vicinity of the electrode the considerable variations in the concentrations occur (Chazalviel, 1990). Setting \( D = ((3.64 \times 8.09 \times 10^{-12} - 3.175 \times 10^{-1} - 3 \times 16/(32 \times 1.30 \times 10^{-1} - 23 \times 300 \times 1000 \times 6.02 \times 10^{23}))^{1/2} \approx 1.8 \mu m \)

and hence we obtain the maximum transition time as 4.36 ms which is in the same order as the corresponding modeling parameter.

IV. About 2% of simulations shorted the counter electrode during simulations. In those cases, we stopped the run and analyzed the dendrite measurements from the obtained dendrite until then. The average number of attached atoms in those simulations was 540 (versus 600 in normal condition).

The dendritic growth during charge is the result of gradients in electrochemical potential parameters such as electrostatic field around the equipotential electrode surface, diffusion coefficient and mobility of solvent (Bard, 1980) as well as electrode surface morphology (Aurbach, Zinigrad, Cohen, & Teller, 2002).

Let the position of each Li\(^+\) at time \( t \) and \( (t + \Delta t) \) be \( r_i(t) \) and \( r_i(t + \Delta t) \), respectively. During the interval \( \Delta t \), Li\(^+\) ions will perform random walks due to collisions with the solvent and/or migration under the applied electric field. In such case we obtain (E3).

The value for the diffusion coefficient employed in the simulations corresponds to the measured current flow of lithium cations in propylene-carbonate based solutions (Nimon & Churikov, 1996) and mobility is calculated from Einstein-stokes equation (Table 1).

When a Li\(^+\) ion comes within \( d_{out} \) of a Li\(^0\) on the surface or dendrite, it attaches to the structure. In this case, it is pushed a distance \( d_{out} \) from nearby atoms becomes a Li\(^0\) atom on the dendrite. We define the dendrite equipotential surface as points within a distance \( r_{surface} \) of Lithium atoms attached to the electrode. To ensure a smooth surface, \( r_{surface} \) is taken to be slightly larger than the radius of a Lithium atom \( (1.3r_0) \) and is considered as the same potential as dendrite. The Li\(^+\) fails to attach if there is no electron provided in the electrode/dendrite surface. In the rare case where the Li\(^+\) is still too close to an atom after pushes, it is
returned to its position one time-step before it approached the Li\textsuperscript{0}. Every time a Li\textsuperscript{+} is annihilated as Li\textsuperscript{0} at the dendritic sites and lithium electrode surface, another lithium ion is added randomly in a thin layer at the top of the domain.

Although the experiments were done in galvanostatic condition, we observed a stable voltage regime mostly in the range of 3.5V and 4.5V. Hence, we did the simulations based on equivalent potentiostatic condition. Since the computational domain is much smaller, we have set a much less voltage. Therefore we assign the boundary conditions as the following

\[
\begin{align*}
\Phi_{anode} &= V_- \\
\Phi_{cathode} &= V_+
\end{align*}
\]

(E2’)

(E3’)

When the electrode is off, we have:

\[
\Phi_{anode} = \Phi_{cathode}
\]

(E4’)

Thus, there would be no electrostatic field in the cell domain.

We reasonably assume the Solid Electrolyte Interphase (SEI) is composed of sufficient lithium metal atoms and the electrical conductivity holds between electrode surface and dendrite, therefore we have:

\[
\Phi_{dendrite} = V_-
\]

(E5’)

The Poisson equation describing the potential distribution Li\textsuperscript{+} transport as follows (Bard, 1980):

\[
\frac{\partial^2 \Phi}{\partial x^2} + \frac{\partial^2 \Phi}{\partial y^2} = \frac{-\rho (z_c C_c - z_a C_a)}{\varepsilon_r \varepsilon_0}
\]

(E6’)

\[\Phi\] is the potential, \(\rho\) is the charge density and \(\varepsilon_r\) and \(\varepsilon_0\) are vacuum and relative electrolyte permittivity, \(z_c, z_a\) are cationic and anionic valence numbers and \(C_c\) and \(C_a\) are cationic and anionic concentrations.

The potential field alternatively can be obtained by iterating the following equation using finite difference method (LeVeque, 2007):

\[
\Phi_{ij} = \frac{\Phi_{i+1,j} + \Phi_{i-1,j} + \Phi_{i,j+1} + \Phi_{i,j-1} - 4 \Phi_{ij}}{\Delta x^2 + \Delta y^2}
\]

(E7’)

The finite difference method runs as follows:

1. Impose an arbitrary potential in any point in the inter-electrode space. The simplest case is uniform distribution from \(V_-\) to \(V_+\).
2. Apply neighbor-based discrete Poisson relation to each point until the values in all space converge to a constant value or the errors between two subsequent iterations becomes smaller than the acceptable assigned voltage error.

The electrostatic field can be numerically calculated as:
The large electrostatic field occurs specially at the dendrite tip and in the vicinity of attachment is the main contributor to deposition and dendrite growth (Liu et al., 2011).