S1. Supplementary Visualization Cell Information

Figure S1. Schematic representation of the visualization cell used to capture portions of main text Figures 1 and 7 as well as Videos 1, 2, 3, and 4.

S2. Supplementary Information on Testing of LiPF₆

Figure S2. Voltage profile for visualization cell with a separator cycled in LiPF₆ cycled for 100 cycles a) and a higher resolution view of cycles 97-100 b). The characteristic “peaking” behavior is obvious for each half cycle. The corresponding video is shown in Video 4.

Figure S2 shows how voltage profiles reach a more consistent shape for each half cycle as increasing cycles are carried out. This has been well documented in our previous work.¹
Figure S3. Voltage profile of a Li-Li symmetric cell where the first six half cycles were cycled for 7.5 min. Subsequent half cycles were cycled for longer periods of time. In a) the longer cycle was a sequence of cycling at either 1 mA/cm$^2$ or 5 mA/cm$^2$ for 15 s followed by a rest period of 30 s. For a more detailed view see b). This sequence was carried out until the amount of time under galvanostatic conditions was 45 min. In c) the cell was cycled at 2 mA/cm$^2$; the first 4 half cycle were 7.5 min and the subsequent 2 half cycles were for 45 min.

Figure S3 shows that the shape of the voltage profile is not due to capacitive effects. Comparing a) with c) reveals that the overpotential and peak position are identical for the same amount of charge passed. This can be clearly seen for the second peak, associated with electrodissolution from the bulk, where that peak appears after ~420 mC/cm$^2$ (for the 1 mA/cm$^2$ graph) of charge was passed and at an overpotential of ~150 mV regardless of the interrupted current.

Figure S3c also shows that the position of the dissolution peak shifts toward later time once sufficient Li has been deposited during the previous half cycle. This can be observed by comparing the 5$^{th}$ and 6$^{th}$ half cycles. Since only 900 mC/cm$^2$ were passed during the 4$^{th}$ half cycle the peak associated with dissolution from the bulk occurs close to that point (~840 mC/cm$^2$). However, after 5400 mC/cm$^2$ was passed during the 5$^{th}$ half cycle, that same peak appears after ~5000 mC/cm$^2$ in the 6$^{th}$ cycle. This supports the discussion provided in the main text.

Additionally, the part of figure S3c labeled (i) shows how pitting evolves once all the active Li sites are removed from the dendrites during the 5$^{th}$ half cycle. The portion labeled (ii) shows the length of plating during the 6$^{th}$ half cycle.
Figure S4. Comparison of voltage traces for various geometries

Figure S4 shows that regardless of cell geometry and other variables, the “peaking” behavior is very consistent. This type of behavior has also been observed in many previous reports.1-4

S3. Supplementary Information on the Numerical Model
S3.1. Governing Equations
The numerical approach in this study is based on previously described methods for simulating the dynamics of electrochemical systems.5-9 The mass fluxes of the electrolyte species are described by the 1D Nernst-Planck equation (Equation (1) in main text). This mass flux includes contributions from diffusion and migration. The diffusivity is dependent upon the concentration of the electrolyte species, and the values are taken from the experimental data obtained by Valoen et al.10 There are several approaches that have been employed in the literature to describe the electrostatic potential, including electroneutrality,11-13 continuity of the current,12-14 the displacement current equation,5-7 and the Poisson equation8,9,15, which is the approach adapted for this model (Equation (2) in the main text).

For this work, the model uses a 1D domain where the boundaries correspond to the surfaces of the lithium electrodes, initially located at \(x = 0\) and \(x = L\). These interfaces are allowed to move independently, and the velocity of each electrode surface may be calculated as:

\[
v_{el} = \frac{i\Omega_{Li}}{F}
\]  

(S1)

where \(v_{el}\) is the electrode surface velocity, \(i\) is the current density (as measured per unit projected area of the electrode), and \(\Omega_{Li}\) is the molar volume of metallic lithium.14 Over the course of a half cycle, the electrode surfaces only move a small distance relative to the electrode separation, and we therefore neglect convection in the electrolyte. The time-based evolution of the electrolyte species concentrations is described by a continuity equation:

\[
\frac{\partial c_i}{\partial t} = -\frac{\partial i_i}{\partial x}
\]  

(S2)

where \(t\) is the time. The boundary conditions for the species concentrations and the electrostatic potential are given in Table S1, with the extra boundary condition on the electrostatic potential at \(x = L\), which is necessary to prevent the Poisson-Nernst-Plank (PNP) equations from becoming ill-posed.
At each electrode, the applied current is assumed to be governed by Butler-Volmer kinetics, for which the current-overpotential relationship may be written as: \(^{5,9,13,16}\)

\[
i = Fk^0 \left[ c_{Li} \exp \left( \frac{(1 - \beta)F}{RT} \eta \right) - c_{Li+} \exp \left( - \frac{\beta F}{RT} \eta \right) \right]
\]  

(S3)

where \(k^0\) is the standard heterogeneous rate constant, \(\beta\) is the charge transfer symmetry coefficient, \(c_{Li} = 1/\Omega_{Li}\) is the surface concentration of metallic lithium, and \(c_{Li+}\) is the surface concentration of lithium ions. The overpotential, \(\eta\), may be further rewritten as:

\[
\eta = E_{el} - \phi_0 - E^0'\tag{S4}
\]

where \(E_{el}\) is the electrode potential, \(\phi_0\) is the electrostatic potential, and \(E^0'\) is the formal potential of the electron transfer reaction.\(^{5,9,17}\) To capture the effects of the electrode morphology and the SEI layer, two modifications are made to Equation (S3). First, the right hand side is multiplied by \(\gamma\), which is a measure of the roughness of the electrode surface. This coefficient is calculated as the ratio of the total surface area including deposits relative to the surface area of the electrode if it was perfectly flat. The second modification is that \(k^0\) becomes dependent upon the extent to which the electrode is covered in deposits. In this model, we assume that the reaction kinetics is faster on the deposits than on the bulk electrode, which may be attributed to differences in the SEI layer. The SEI layer on the deposits may be thinner and/or more defective than that on the bulk electrode, or it may have an entirely different chemical composition, leading to the higher reaction rate.\(^{18}\) The assumption of different kinetics between the deposit and the bulk may be expressed as:

\[
k^0_{\text{eff}} = \theta_{\text{fast}}k^0_{\text{fast}} + (1 - \theta_{\text{fast}})k^0_{\text{slow}}
\]  

(S5)

where \(\theta_{\text{fast}}\) is the fraction of the surface area with fast kinetics, and \(k^0_{\text{fast}}\) and \(k^0_{\text{slow}}\) are the rate constants for the deposit surface and the bulk electrode surface, respectively. The modified current-overpotential relationship is therefore:

\[
i = \gamma Fk^0_{\text{eff}} \left[ c_{Li} \exp \left( \frac{(1 - \beta)F}{RT} \eta \right) - c_{Li+} \exp \left( - \frac{\beta F}{RT} \eta \right) \right]
\]  

(S6)

which accounts for the effects of the electrode morphology and the SEI layer. Note that this current density is defined per nominal area of the electrode (i.e., the area if the electrode is flat). This form of the modified current-overpotential relationship is similar to one previously used in the simulation of the electrodeposition and electrodissolution of magnesium\(^{15}\). Integrating Equation (S6) in time results in the deposited charge per nominal area, \(\Gamma_{\text{dep}}\):

\[
\Gamma_{\text{dep}}(t) = - \int_0^t \frac{i(t)}{F} dt \tag{S7}
\]

To mathematically describe the values of both \(\gamma\) and \(\theta_{\text{fast}}\), it is necessary to make some assumptions about the geometry of the lithium deposits. We assume that the deposits grow as an array of uniform hemispheres, and that the hemispheres may begin to impinge and then eventually merge (see Figure S5). This assumption is consistent with the observations of Stark et al.\(^{19}\) The volume of the hemispherical deposit (with radius \(r\)), \(V_d\), may be calculated by solving the following integral in the x-y plane:

\[
V_d = \iint (r^2 - x^2 - y^2)^{1/2} \, dx \, dy \tag{S8}
\]

The surface area of the deposit, \(A_d\) may be calculated by solving:

\[
A_d = \iint \left( \frac{r^2}{(r^2 - x^2 - y^2)^{1/2}} \right)^{1/2} \, dx \, dy \tag{S9}
\]

Table S1. Boundary conditions for the PNP equations. The extra boundary condition on the electrostatic potential prevents the equations from becoming ill-posed.

| Quantity          | \(x = 0\) (EL-a) | \(x = L\) (EL-b) |
|-------------------|------------------|------------------|
| \(c_{Li}^+\)      | \(j_{Li}^+ = i/F\) | \(j_{Li}^+ = i/F\) |
| \(c_{Li}^-\)      | \(j_{Li}^- = 0\)  | \(j_{Li}^- = 0\)  |
| \(\phi\)          | \(\frac{\partial \phi}{\partial x} = 0\) | \(\frac{\partial \phi}{\partial x} = 0, \phi(L) = 0\) |
and the uncovered area of the electrode, $A_{e}^u$ may be calculated by solving:

$$A_{e}^u = A_{e}^n - \int (r^2 - x^2)^{1/2} \, dx$$  \hspace{1cm} (S10)

where $A_{e}^n$ is the nominal area of the electrode. The bounds of the integrals depend upon the extent of the hemispherical deposit and whether it has impinged on its neighbors. The volume per nominal area of the electrode is then related to $\Gamma_{dep}$. With Equations (S16) and (S17), it is possible to calculate both $\gamma$ and $\theta_{fast}$:

$$\gamma = \frac{A_d + A_{e}^u}{A_{e}^u}$$  \hspace{1cm} (S11)

$$\theta_{fast} = \frac{A_d}{A_d + A_{e}^u}$$  \hspace{1cm} (S12)

and the values of these two quantities may be related to the deposited charge per nominal area via Equation (S8).

In order to include its effect in the model, it is necessary to define the effective Coulombic efficiency. We follow a definition similar to those in the literature:\textsuperscript{20}

$$CE = \frac{\text{mass of dissolved Li from prev. deposits}}{\text{mass of deposited Li to prev. deposits}}$$  \hspace{1cm} (S13)

In the visualization cell, it is clearly observed that electrochemically dead lithium forms during dissolution. However, for simplicity, the model does not explicitly track the amount of dead lithium that has formed, but we assume that a less-than-unity Coulombic efficiency would result in an apparently faster dissolution of the deposited lithium as some lithium is converted to dead lithium and does not contribute to the current. Thus, the Coulombic efficiency is incorporated as an effective multiplier of the applied current density during electrodissolution:

$$i_{\text{eff}} = i \frac{1}{CE}$$  \hspace{1cm} (S14)

where $i_{\text{eff}}$ is the effective applied current density during electrodissolution. This increased current only occurs at the electrode that is currently being dissolved. In addition, we assume that lithium may only be dissolved from the bulk electrode once the deposited lithium layer has been removed. The effective velocity of the electrode/electrolyte interface during electrodissolution is then given by:

$$v_{\text{el}}^{\text{eff}} = v_{\text{el}} \frac{1}{CE}$$  \hspace{1cm} (S15)

where $v_{\text{el}}^{\text{eff}}$ is the effective velocity of the electrode/electrolyte interface, which is greater than the theoretical velocity when the Coulombic efficiency is less than unity.

**Figure S5.** Schematic showing the modeled approximation of lithium deposits as a uniform square array of hemispheres that grow and eventually impinge during electrodeposition and that contract and separate during electrodissolution. In reality, the dendritic growth result in porous structure, which behaves similarly to the model due to screening.

**S3.2. Numerical Methods**

For this study, a backward-implicit finite difference method (FDM) was employed to discretize and solve the governing equations. The model domain was initially discretized using a cell-centered grid of 100 grid points that were evenly spaced between the electrodes. An additional ghost point was placed outside each edge of the computational domain to ensure centering of the boundary conditions. A detailed schematic of a portion of the grid is shown in Figure S6. The boundaries are allowed to move over time with the velocities $v_{\text{el}}^{\text{left}}$ and $v_{\text{el}}^{\text{right}}$. To ensure that the edge of the computational domain (excluding the ghost zone) remains at the midpoint between the ghost point and the first point within the computational domain, these points are moved at the
same velocity. As a result, the size of the second cell from the edge cell changes as deposition or dissolution occurs. To prevent this cell from becoming too large, it was divided into two if it became larger than $1.5 \Delta x^0$, where $\Delta x^0$ is the initial grid spacing. Likewise, if a cell became smaller than $0.5 \Delta x^0$, it was merged with its neighbor to maintain numerical accuracy. A typical backward-implicit stencil was found to not conserve the mass of the system, and thus the following discretization was employed for equation (S2):

$$c_j^{n+1} \Delta x_j^{n+1} + \Delta t (J_j^{n+1} - J_j^{-n+1}) = c_j^n \Delta x_j^n$$  \hspace{1cm} (S16)

where the superscript $n$ refers to the current time step, the subscript $j$ refers to the grid point, $\Delta x_j^b = x_j^b - x_{j-1}^b$ is the difference in the cell boundary positions of the grid point, $\Delta t$ is the time step size, and $J_j^+$ and $J_j^-$ are the fluxes in and out of the cell at positions $x_j^b$ and $x_{j-1}^b$, respectively. The overall FDM was second order in space and first order in time.

![Figure S6. A schematic depiction of the cell-centered grid used for the finite difference discretization employed by the model. The variable $x_j$ denotes the locations of the cell center for grid point $j$, and $x_j^b$ denotes the location of the boundary between grid points $j$ and $j + 1.$](image)

The discretization of Equations (1), (2), and (S2) with N grid points in the computational domain results in a system of $3(N+2)$ nonlinear equations with $3(N+2)$ unknown variables, $c_{Li^+}$, $c_{PF_6}$, and $\phi$, associated with each grid point (including the ghost points). The system of equations may be solved simultaneously using the Newton-Raphson method, the details of which may be found in References.7,8 The Newton-Raphson method is also employed when adding a grid point in the refinement scheme. The values of the concentrations and electrostatic potentials are known on either side of the refined cells, and the remaining unknown quantities may be calculated by assuming that mass is conserved and that the mass flux at one of the boundaries of the cell to be refined remains constant during the refinement process. When two cells are merged, the concentration of the new cell is calculated from the conservation of mass alone. The electric potential of each electrode is calculated separately from the PNP equations by solving Equation (S6). The difference between $E_{el}^{left}$ and $E_{el}^{right}$ is the cell voltage. The deposited charge per unit surface area, $\Gamma_{dep}$, is calculated by integrating the applied current density with respect to time. To improve the computational performance, a lookup table was used to interpolate $r$ and $\theta_{fast}$ for a given value of $\Gamma_{dep}$. This lookup table was generated by numerically evaluating Equations (S8)-(S12) from a lower radius bound of $r = 0$ to an upper bound of $r = R_{dep}^{max}$ in increments of $\Delta r$. The nominal electrode area was calculated based on a center-to-center deposit spacing, $d_{deposit}$. For all portions of the model that use the Newton-Raphson method, the iteration was performed until the residuals were less than a tolerance $10^6 \epsilon_m \left(2.22 \times 10^{-10} \right)$, which is smaller than the truncation error of the finite difference approximation, where $\epsilon_m$ is machine precision for double precision floating point arithmetic. To avoid instances where the residual never reached the tolerance, the grid refinement scheme employed an adaptive tolerance that would increase by one order of magnitude if the Newton-Raphson method failed to converge within 10,000 iterations.

**S4. Model Results**

Table S2 contains values of the parameters that were used for the simulation of the visualization cell. The initial concentrations of Li$^+$ and PF$_6^-$ ($c_{Li^+}^{init}$ and $c_{PF_6}^{init}$), the nominal diffusivity, the solvent dielectric constant, and the charge transfer symmetry coefficient were parameterized from available data.10,22-25 The deposit
spacing is chosen such that it is of a similar order of magnitude as may be observed in the video data. The rate constants and effective Coulombic efficiency were determined by visually fitting the simulated voltage trace to the experimental data. For each cycle from 1 to \( n_{\text{cyc}} \), the applied current density was first held positive for \( t_{\text{on}}^{+} \), followed by a rest period \( t_{\text{off}} \), then held negative for \( t_{\text{on}}^{-} \), and lastly a final rest for \( t_{\text{off}} \). In order to compare with the experimental data, the simulation results are plotted without the rest period unless otherwise indicated.

**Table S2. Parameter values used for simulation of potentiometric behavior in the visualization cell.**

| Parameter | Value | Ref. |
|-----------|-------|------|
| \( c_{\text{nominal}} \) | \( 1.0 \times 10^{-2} \) mol/cm\(^2\) | |
| \( c_{\text{init}} = c_{\text{init}} \) | \( 0.5 \times 10^{-2} \) mol/cm\(^2\) | 10 |
| \( D_{\text{nominal}} \) | \( 3.208 \times 10^{-4} \) cm\(^2\)/s | 10 |
| \( \Omega_{d} \) | 13.0 cm\(^2\)/mol | |
| \( \varepsilon_{s} \) | 16.8 | 22-24 |
| \( T \) | 300 K | |
| \( l \) | 5.0 mA/cm\(^2\) | |
| \( t_{\text{on}} = t_{\text{on}}^{-} \) | 900 s | |
| \( t_{\text{off}} \) | 30 s | |
| \( n_{\text{cyc}} \) | 5 | |
| \( \beta \) | 0.5 | 25 |
| \( \varepsilon^{0} \) | 0.0 V | |
| \( k_{\text{fast}} \) | \( 3.5 \times 10^{-8} \) cm/s | |
| \( k_{\text{slow}} \) | \( 9.0 \times 10^{-8} \) cm/s | |
| CE | 80 % | |
| \( L \) | \( 7.5 \times 10^{-2} \) cm | |
| \( x_{\text{rat}} \) | \( 1.0 \times 10^{-3} \) cm | |
| \( \delta t \) | \( 1.0 \times 10^{-3} \) s | |
| \( \Delta r \) | \( 1.0 \times 10^{-4} \) cm | |
| \( d_{\text{depos}} \) | \( 2.4 \times 10^{-3} \) cm | |
| \( \varepsilon_{m} \) | \( 2.22 \times 10^{-16} \) | |

**S4.1. Effect of changing \( k_{\text{fast}}^{0} \)**

Using the same parameters as in Table S2, two additional simulations were performed: one with \( k_{\text{fast}}^{0} = 9.0 \times 10^{-8} \) cm/s and one with \( k_{\text{fast}}^{0} = 3.5 \times 10^{-7} \) cm/s. The first two cycles of these two simulations are plotted in Figure S7 along with the first two cycles of the simulation from Table S2. It can be observed that as \( k_{\text{fast}}^{0} \) is reduced from the largest value, the trough between the first and second voltage peak becomes shallower. The model therefore predicts that the size and shape of the trough between the double peaks in the voltage depends upon the effects of the SEI layer and the electrode morphology. When \( k_{\text{fast}}^{0} = k_{\text{slow}}^{0} = 9.0 \times 10^{-8} \) cm/s, the cell voltage is nearly uniform throughout the half cycle; the small variation is due to the change in morphologies.
Figure S7. The first two cycles of simulations with values of $k_{\text{fast}}$ from $9.0 \times 10^{-8}$ cm/s (equal in value to $k_{\text{slow}}^0$) to $3.5 \times 10^{-6}$ cm/s (the value necessary to match the experimental visualization cell data) are shown. As the value of $k_{\text{fast}}^0$ decreases, the depth of the trough between the double peaks in the cell voltage becomes shallower until it disappears completely.

S4.2. Concentration Profiles in the Electrolyte
Using the parameters in Table S2, simulations were performed to obtain the concentration profiles of Li$^+$ ions in the electrolyte over time. The results of these simulations are plotted in Figure S8 for fourteen different times. It is observed that the concentration of Li$^+$ ions is never depleted at either electrode surface. Thus, it is expected that transport-limited behavior is not dominant in the observed voltage trace. The small electrode separation and the lack of separator in the visualization cell likely contribute to this result.

Figure S8. Simulated concentration profiles of Li$^+$ ions across the visualization cell during (left) the first half-cycle, (center) the first rest cycle, and (right) the second half cycle, demonstrating the transient and pseudo steady-state behavior of the mass transport. The concentration is never depleted at either electrode surface (the edges of the domain in each plot), and thus the observed voltage trace is not expected to be dominated by transport-limited behavior.

S4.3. Isolated Electrode Overpotentials
With the numerical model, it is possible to explicitly track the overpotentials associated with each electrode as well as the potential drop across the electrolyte, similar to the three electrode measurements shown in main text Figure 3. The results from the numerical model are displayed in Figure S9. It can be observed that the electrode undergoing deposition in a given half-cycle features the initial voltage peak, and the electrode undergoing dissolution is the source of the second voltage peak. By contrast, the potential drop across the electrolyte remains relatively constant throughout a given half-cycle, indicating that it is not a dominant feature in the total voltage trace. This strongly resembles main text Figure 3.
Figure S9. The simulated overpotentials of EL-a and EL-b, as well as the simulated potential drop across the electrolyte for the first two cycles. In a given half cycle, the electrode undergoing deposition (initially EL-b) is the source of the initial voltage peak, while the electrode undergoing dissolution is the source of the second voltage peak.

It is observed in Figure S9 that the overpotential at each electrode is not centered about 0 V as might initially be expected. However, this offset can be readily explained by examining the governing equations. If Equation (S6) is solved for when there is no net current density, the resting electrode potential is obtained:

\[ E_{el} = \frac{RT}{F} \ln \left( \frac{c_{Li}^{i+}}{c_{Li}} \right) + \phi_0 + E^0 \]  

(S17)

As an example, we first consider the behavior of EL-b. The formal potential is 0 V for all of the simulations, and at \( x = L \) (EL-b) the electrolyte potential has been pinned to 0 V. From the data presented in Figure S8, the Li\(^+\) concentration ranges from around \( 0.3 \times 10^{-3} \) mol/cm\(^3\) at the end of deposition to around \( 0.7 \times 10^{-3} \) mol/cm\(^3\) at the end of dissolution. Within this concentration range, the electrode potential spans from approximately \(-143\) mV after deposition to \(-121\) mV after dissolution, which correspond to the observed offsets. Because both EL-a and EL-b are offset by roughly equal potential values, their individual contributions are negated in the total voltage trace. If a reference electrode was explicitly included in the numerical model, then it would also have an offset potential within this range. Therefore, the measured electrode overpotentials relative to the reference electrode would be centered approximately around 0 V.

S5. Supplementary Information About General Framework

To provide a visual aid and a qualitative explanation of the observed voltage profile behavior, a general framework is presented in the main text (please see Equations (5) to (9)). We start by considering the Gibbs free energy and Butler-Volmer (BV) kinetics for a symmetric cell where 1) Li can be stripped from either the dendrites (labeled by ‘den’) or the bulk (Figure S10a) and 2) Li can be deposited on previously active sites (labeled by ‘grow’) or nucleate on new sites (labeled by ‘nuc’), as shown in Figure S10b.

Figure S10. Schematic representation of difference in activation barriers between a) the anodic (electrodissolution) processes of Li removal from either dendrites (labeled by ‘den’) or the bulk (labeled by ‘bulk’) and b) the cathodic (electrodeposition) processes involving nucleation (labeled by ‘nuc’) and growth (labeled by ‘grow’).

If we start with conditions were dendrites exist on one electrode and relatively small pits on the other, then \( \theta_{den} > 0 \) and \( \theta_{grow} = 0 \). Since we assume that \( \Delta G_{bulk} > \Delta G_{den} \) (and therefore \( k^0_{den} > k^0_{bulk} \)) and that \( \theta_{den} > \theta_{bulk} \), \( I_{den} \) will dominate Equation (6) in the main text. Also, since \( \theta_{grow} = 0, I_{grow} = 0 \), for which Equation (6) may be simplified as:

\[ I_{cell} = I_{den} = I_{nuc} \]  

(S18)

The reaction pathway at this point during the cycle can be observed schematically in Figure 5a in the main text. Here the exchange current densities are given by:

\[ i_{0den} = F c_{den} f e^{-\Delta G_{den}/RT} \]  

(S19)
\[ i_{\text{nuc}} = F c_{\text{nuc}} f e^{-\Delta G_{\text{nuc}}/RT} \]  

From Figure S10, it can be observed that \( i_{\text{nuc}} \) will be much smaller than \( i_{\text{den}} \) due to its large activation barrier. For the initial decay in \( V_{\text{cell}} \), \( \delta \eta_{\text{cathode}} \gg \delta \eta_{\text{anode}} \), and therefore the observed decay is due primarily to the cathodic half reaction, which may be expressed as:

\[
\delta V_{\text{cell}} \approx \delta \eta_{\text{cathode}}
\]

As time progresses, \( Z_{\text{grow}} \) decreases, causing a transition between reaction pathways on the cathode from nucleation to growth, until \( I_{\text{nuc}} \) becomes negligible and \( I_{\text{grow}} \) dominates the cathodic processes (See Scheme 2a main text). This occurs while \( \theta_{\text{den}} \) on the anode is not close to zero, meaning the anodic current is dominated by dissolution from dendrites (main text Figure 5b). At this point, \( \delta V_{\text{cell}} \) has significant contributions from both the anode and the cathode.

As \( \theta_{\text{den}} \) approaches zero, \( Z_{\text{den}} \) increases, and eventually becomes similar in magnitude to \( Z_{\text{bulk}} \). At this point, a transition occurs in reaction pathways at the anode from \( I_{\text{den}} \) to \( I_{\text{bulk}} \) (The unshaded region of main text Figure 5). Once \( \theta_{\text{den}} \approx 0 \), \( Z_{\text{bulk}} \ll Z_{\text{den}} \), and \( I_{\text{bulk}} \) is the dominant current contribution at the anode (See Scheme 2a main text). The exchange current densities at this point can be expressed as:

\[
I_{\text{o bulk}} = nF C_{\text{bulk}} f e^{-\Delta G_{\text{bulk}}/RT} \\
I_{\text{o grow}} = nF C_{\text{grow}} f e^{-\Delta G_{\text{grow}}/RT}
\]

Here, the change in anodic overpotential will dominate the change in cell polarization, \( V_{\text{cell}} \), such that:

\[
\delta V_{\text{cell}} \approx \delta \eta_{\text{anode}}
\]

which is seen graphically in figure 5c in the main text.

As the cycling process continues, pits form on the anode as Li is dissolved from the bulk. Consequently, fractures occur in the surface layers, resulting in a transition in reaction pathways at the anode surface to pitting, Figure 5d of the main text. The pitting also causes an increase in \( \theta_{\text{pit}} \), which results in a continued decrease in \( Z_{\text{pit}} \), causing a decrease in overpotential at the anode until polarity is switched.

\[ i_{\text{pit}} = F c_{\text{pit}} f e^{-\Delta G_{\text{pit}}/RT} \]

\[ Z_{\text{pit}} \]

\[ \delta V_{\text{cell}} \approx \delta \eta_{\text{anode}} \]

Figure S11. Voltage traces for coin cells cycled in LiPF\(_6\) at current densities of .5, .75, 1, 2, 5, 10 mA/cm\(^2\)

Voltage trace signature have been shown to be true over a range of practical current densities. Figure S11 shows that the peaking behavior is observed at current densities stretching from .5 mA/cm\(^2\) to 10 mA/cm\(^2\)
Figure S12. The effect of current density on dendrite nucleation in 1M LiPF$_6$. a) Electrochemical voltage traces at various current densities and the corresponding micrograph for b) 1mA/cm$^2$ c) 2 mA/cm$^2$ and d) 5 mA/cm$^2$.

Additionally, Figure S12 shows the effect of different current densities on nucleation. From this data it can be clearly observed that the cell polarization increases with current density as expected. It can also be seen in Figure S12a that the initial voltage trace decays more rapidly at higher current densities. This can be linked to difference in morphology observed in Figure S12b-d. At 1mA/cm$^2$ dendrites are larger and more widely spaced, while as current density is increased dendrites become relatively smaller and closer together. The more rapid decay in initial cell polarization at higher current densities is consistent with a faster increase in surface area for the smaller and more closely spaced dendrites that form after nucleation occurs.

S6. Effect of Electrolyte and Cell Performance on Voltage Profiles

Figure S13. Voltage traces for the different electrolytes studied in this work. Due to the small cell polarization for the LiTFSI, a magnified portion of the voltage profile is shown to the right.

Figure S13 reveals the lower cell polarization to drive dissolution and deposition for both the LiFSI and LiTFSI electrolytes. The LiTFSI, in particular, requires a very low overpotential. While the initial decrease in voltage during a half-cycle for the LiFSI is almost negligible, it is more well defined in the LiTFSI.
Figure S14. Time-dependent EIS measurements for the LiPF₆, LiFSI and LiTFSI electrolyte systems. a) Growth of impedance as a function of time for the different electrolyte systems b) EIS spectra after 30 seconds of contact with fresh Li c) a magnified view of the EIS spectra shown in b). The other graphics show a schematic representation of how ether-based electrolytes decrease the energy barriers of d) nucleation and e) dissolution from the bulk.

EIS measurements were taken to measure the growth rate of the various electrolytes (Biologic VSP). These measurements where taken from 500kHz to 1Hz. After making the cell, a very small amount of Li was immediately plated (~1.6 µC/cm²) to create freshly plated Li. An EIS measurement was taken right away and subsequently measured every 2min for a total of 100 min.

Additionally, Figure S14 shows a schematic representation of how the SEI kinetics depend on the electrolyte system. Energy barriers associated with lithium electrode dissolution and electrodeposition vary depending on the nature of the electrode/electrolyte interactions. For example, in the LiTFSI/LiFSI systems a less resistive SEI forms on the surface of the electrodes. This lower magnitude of impedance can greatly change the effective rate constant of the system (See modeling discussion above). When comparing either the LiTFSI or LiFSI with LiPF₆, the ratio of the ‘slow’ and ‘fast’ effective rate constants differ significantly. This is shown schematically in Figure S14d/e, where the difference between energy barriers associated with the LiTFSI electrolyte is much smaller. As a result, simultaneous contributions the ‘slow’ and ‘fast’ processes occur in the LiTFSI electrolyte. This creates greater separation between the local minimum and local maximum in the voltage trace. During later cycles in the LiTFSI system, the peak shifts towards later times in the half-cycle (i.e. more charge being passed).
Figure S15. Schematic depicting the modified version of the average Coulombic efficiency (aCE) method proposed by Aurbach et al.26 a) Initial setup of the cell. Starting from this point, the cells were cycled at 1 mA/cm² such that 3.6 C/cm² of charged were passed during each of the galvanostatic half cycles. b) During the final cycle all of the Li was dissolved from one electrode and plated onto the other. The amount of Li lost to SEI formation or through dead/detachment of Li can then be calculated and divided by the number of cycles to determine an aCE value.

A mathematical description of the aCE as shown in figure S15 is given below:

\[
\text{aCE} = \frac{Q_c - (Q_i + Q_c \times x) - Q_r}{Q_c} \quad (S25)
\]

where \(Q_c\) is the length of charge for each half cycle, \(Q_i\) is the initial amount of charge stored in Li on the Li-Cu laminate, \(Q_r\) is the amount of charge remaining on the electrode after cycling, and \(N\) is the number of cycles.

S7. Effect of Electrolyte on Morphology in SEM

Figure S16. SEM images taken for the three different electrolyte systems after 2 full electrochemical cycles. The top row of images shows morphological difference at high magnification, revealing the different size and density of dendrite
coverage. The bottom row of images at low magnification shows the difference in uniformity surface coverage for each system.

From Figure S16 it can be observed at high magnification (5 μm field of view) the dendritic structures for each system are remarkable similar. At lower magnification the differences in the systems become more pronounced, highlighting the importance of the optical length scale. While it is expected that the presence of a separator and compression from coin cell crimping will cause dendrite agglomeration and some differences in morphology, the observed trends are generally the same as observed in the visualization cell. The LiPF₆ electrolyte exhibits large dendrites more spaced apart with fewer regions that have agglomerated together. However, for both the LiFSI and LiTFSI more densely packed, agglomerated dendrites are observed. These general trends fit well with the information presented in the main text.

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