Electronic Supplementary Information:

Lithium Dendrite Growth Mechanisms in Polymer Electrolytes and

Prevention Strategies

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Computational Methodology

To estimate whether a dendritic protrusion will grow into a complete dendrite or not, the reaction current at the peak (i_{peak}) and the valley (i_{valley}) is determined. The magnitude of reaction current is calculated using the modified version of the Butler-Volmer equation^{1, 2}. This relation has contributions from mechanical stress, concentration and potential within both lithium metal and electrolyte. Hence, it is necessary to solve for the mechanical deformation, potential distribution and concentration profile within both lithium and electrolyte phases. In the present work, PEO-based electrolytes have been considered because of their ability to potentially suppress the growth of lithium dendrites. Since, elastic-plastic deformation of lithium metal and PEO-based electrolyte is a common phenomenon, a proper nonlinear stress-strain relation has been used to calculate the generation of stress³⁻⁶. Lithium ion concentration-dependent conductivity of the polymer electrolyte has been taken into account⁷. However, a fixed value of lithium ion diffusivity within the electrolyte phase has been used here. This leads to easier estimation of the limiting current density. In the present analysis, primary current induced by potential gradients, secondary current induced by electrode kinetics, and tertiary current induced by concentration gradients have been taken into consideration⁸. Detailed descriptions of these governing differential equations, along with the appropriate boundary conditions, are given below.

Starting from a relaxed (stress-free) configuration of the lithium metal and dendritic protrusion, the electrolyte phase has been lowered into contact with the lithium metal⁹. The bottom of the lithium region has been kept fixed. This constraint induces compressive force within the lithium metal, electrolyte phase, and the newly-deposited dendritic protrusion. Depending on the stress generated during the compression process, plastic deformation within

both lithium metal and electrolyte is possible. Plasticity of lithium combined with a very stiff separator leads to a modified protrusion height^{10, 11}. Symmetric boundary conditions have been applied on the left and right sides of the domain, constraining the displacement along the horizontal (x) direction and allowing for free movement along the vertical (z) direction.

Schematic representations of the lithium/electrolyte domain considered in the present analysis are provided in Figure S1. The mesh for the undeformed lithium metal is shown in Figure S1(a). No deformation in either the x or z directions is allowed at the bottom of this domain: $u_x(x, z = 0) = 0$ and $u_z(x, z = 0) = 0$. Symmetric boundary conditions are applied on the left and right boundaries of the domain. Deformation along the x-direction has been constrained $\left(u_{x}|_{left and right} = 0\right)$ and free movement along the z-direction is allowed. To reproduce the dendritic protrusion at the lithium electrolyte interface, sinusoidal displacement is applied at the top of the lithium metal according to $u_z = A\cos(\omega x)$. Unconstrained deformation along the x-direction has been allowed at the top surface. In literature, the sizes of dendritic protrusions range from nanometers to microns¹²⁻¹⁴. The present work takes A = 400nm and $\omega = 10^6 m^{-1}$. The deformed geometry of lithium metal with the dendritic protrusion has been shown in Figure S1(b). Since the dendritic protrusion is expected to be initially in a stress-free relaxed condition, all the stresses within the deformed lithium metal are taken to be zero⁹. The initial distance between the peak and the valley of the dendritic protrusion is approximately 800nm. Next, the electrolyte is placed on top of lithium metal, as schematically demonstrated in Figure S1(c). Since PEO-based polymer electrolytes are strong candidates for application in solid electrolyte batteries, PEO has been used as the electrolyte material in the present study. As shown in Figure S1(d), the electrolyte is pushed into full contact with the lithium surface. Symmetric boundary conditions

are applied on the left and right side of the computational domain, and the bottom surface of the lithium is fixed. This induces compressive stress within the lithium metal as well as the electrolyte domain. Depending on the magnitude of stress, both phases can display elastic-plastic deformation. Due to plastic deformation within lithium metal, the height of the dendritic protrusion reduces to 580*nm* in the presence of PEO-based polymer electrolytes. Hence, the presence of solid electrolyte not only generates a compressive stress field around the dendritic protrusion, but also decreases the protrusion height through plastic deformation.

Growth of a dendritic protrusion depends on its electrolyte environment. Any fluctuation that occurs within the polymer electrolyte far away from the lithium nucleus does not have any significant impact on its growth. In addition, the variation in electrolyte-salt concentration vanishes as we move away from the dendrite tip in the x-dimension. For an 800nm high dendritic protrusion, the concentration variation vanishes within $2\mu m - 3\mu m$. This is evident from the concentration contour plot in Figure 3(b) within the main manuscript and the concentration contour maps in the supplementary section (explained later in the Results section). Hence, simulation of the polymer-electrolyte near the protrusion should be sufficient to understand its growth. In the present study, we use the $6\mu m$ thick polymer-electrolyte layer in order to reduce the computation complexity. At the top of the $6\mu m$ thick electrolyte layer, the salt concentration is uniform, and no impact of the dendritic protrusion is observed. Therefore, the exact value of the separator thickness has little impact on the simulation results, except in the definition of the limiting current.

Finally, the concentration and potential within lithium metal and polymer electrolyte have been solved on the computational domain demonstrated in Figure S1(e). The reaction current at the lithium-electrolyte interface has been estimated from the modified Butler-Volmer equation.



Figure: S1. Demonstration of multiple domains used in this computational analysis. (a) The undeformed domain of lithium metal. (b) Deformed lithium metal when subjected to a sinusoidal deformation of $u_z = A\cos(\omega x)$ at the top surface. The bottom of lithium metal has been kept fixed. The right and left sides are allowed to deform along the y-direction and fixed along the x-direction. (c) Deformed lithium metal and undeformed electrolyte on top of it. This serves as the initial condition for estimating the magnitude of stress evolution within lithium metal and electrolyte during development of a dendritic protrusion. (d) Deformed lithium metal and electrolyte completely touching each other. Initial relaxed condition of lithium metal and subsequent compressive force applied on top of the lithium and electrolyte domain where concentration and potential distributions are calculated. Influx of lithium ions occurs at the top of the electrolyte region. The bottom boundary of the lithium metal serves as a current collector. Reaction current at the electrolyte-lithium interface has been estimated using the Butler-Volmer equation. Symmetric boundary conditions have been imposed on the left and right sides, implemented as zero flux.

The effect of mechanical stress has been incorporated within the exchange current density term. Influx of lithium ions occurs at the top of the electrolyte region. The bottom surface of the lithium metal serves as a current collector. Symmetric boundary conditions have been implemented at the left and right boundaries through the application of zero current and zero ion flux.

Electrochemical equations: Charge transfer in solid lithium can be captured by making the divergence of current equal to zero along with the conductivity of lithium¹⁵:

$$\vec{\nabla} \cdot \left(\boldsymbol{\sigma}_{Li} \vec{\nabla} \boldsymbol{\phi}_s \right) = 0 . \tag{S1}$$

Here, ϕ_s is the potential in the solid lithium phase, σ_{Li} is the conductivity of lithium and $\overline{\nabla}$ is the gradient operator. No variation in the out-of-plane direction has been considered in the present problem. Here, a scalar value of σ_{Li} has been assumed. Since the conductivity of lithium is multiple orders of magnitude larger than the electrolyte phase¹⁶, variation in potential within the lithium metal is negligible and it remains very close to zero. Current entering the lithium metal adjacent to the electrolyte phase can be estimated using the Butler-Volmer equation, which has been discussed in the main text (see Eq. (2)). On the other end, which is adjacent to the current collector, outflow of current is assumed to be equal to the applied current density:

$$-\sigma_{Li}\bar{\nabla}\phi_s = i_{applied} \,. \tag{S2}$$

Potentials are calculated relative to that at one particular point on the bottom boundary. On the left and right boundaries, at which symmetric boundary conditions are applied, there is zero current density.

The electric potential in the lithium phase follows Ohm's law¹⁵. The current is determined from the potential gradient and conductivity of metallic lithium. In the electrolyte phase, charge is carried by migration as well as the diffusion of ionic species⁸. Hence within the

electrolyte region, both the ohmic current and the diffusion-induced current must be taken into account⁸. The convective transport of lithium ions within electrolyte can be neglected⁸. In the electrolyte phase, charge is carried by migration of ions as well as diffusion of ionic species. Hence, while modeling the charge transfer within the electrolyte, both the ohmic current and the diffusion-induced current must be taken into account¹⁵.

$$\vec{\nabla} \cdot \left(\kappa_{PEO} \vec{\nabla} \phi_e + \kappa_{D,PEO} \vec{\nabla} \ln \left(c_e \right) \right) = 0$$
(S3)

Here, ϕ_e indicates the potential and c_e signifies the concentration of lithium ions within the polymer electrolyte phase. The conductivity for the PEO-based polymer electrolyte is a scalar quantity (κ_{PEO}), but varies with the concentration of lithium ions (c_e) within the electrolyte. The conductivity for the PEO-based polymer electrolyte (κ_{PEO}) is a scalar quantity that varies with the concentration of lithium ions (c_e) within the electrolyte. The conductivity for the PEO-based polymer electrolyte (κ_{PEO}) is a scalar quantity that varies with the concentration of lithium ions (c_e) within the electrolyte according to the following relation⁷:

$$\kappa_{PEO} = 3.801 \times 10^{-4} c_{e} - 2.169 \times 10^{-7} c_{e}^{2} + 3.112 \times 10^{-11} c_{e}^{3}$$
(S4)

This value of concentration-dependent conductivity of PEO has been estimated at an elevated temperature (90°C). The magnitude of the diffusion-induced conductivity ($\kappa_{D,PEO}$) is estimated from concentrated solution theory, and given by the form⁸:

$$\kappa_{D,PEO} = \frac{2RT\kappa_{PEO}}{F} \left(t_{Li^+} - 1 \right) \left(1 + c_e \frac{\partial \ln f_{\pm}}{\partial c_e} \right).$$
(S5)

Here, R indicates the universal gas constant, T is the ambient temperature in Kelvin scale, F indicates the Faraday constant, t_{Li^+} signifies the transference number within the electrolyte phase, and f_{\pm} is the mean molar activity coefficient for the electrolyte salt. A constant value for the lithium transference number (t_{Li^+}) and $\frac{\partial \ln f_{\pm}}{\partial c_e}$ has been assumed in the present study^{17, 18}.

Flow of current at the lithium electrolyte interface is estimated from the Butler-Volmer equation (see Eq. (2) in the main text). At the other end, inflow of current is assumed to be equal to the applied current density:

$$-\left(\kappa_{PEO}\vec{\nabla}\phi_e + \kappa_{D,PEO}\vec{\nabla}\ln(c_e)\right) = i_{applied}.$$
(S6)

The two sides, with symmetric boundary conditions, are subjected to zero flux of current (similar to the lithium metal).

Reduction of lithium ions occurs at the lithium-electrolyte interface (see Eq. (1) in the main text), and the newly generated lithium metal gets deposited on top of the anode. The exact magnitude of the reaction current is estimated form the nonlinear Butler-Volmer equation. In the present context, a modified version of the Butler-Volmer relation has been adopted to incorporate the impact of mechanical stress within the charge transfer process. The expression for the reaction current density has been provided as Eq. (2) of the main text.

Diffusion of lithium within the electrolyte phase has been modeled using the Stefan-Maxwell equations⁸. The parameter, transference number, indicates the current carried by a particular species. Since the electrolyte of lithium ion battery consists of only two charged species, the lithium cation carries some portion of the applied current and the anions transports the remaining current. The total influx of lithium is represented by $j_{LI^+}\left(=\overset{i_{applied}}{F}\right)$, of which the amount $t_{LI^+}j_{LI^+}$ gets transported by migration and the remaining amount $(1-t_{LI^+})j_{LI^+}$ diffuses through the electrolyte.

At the lithium/polymer interface, no formation of a solid-electrolyte-interphase (SEI) layer has been modeled, and the two adjacent regions are assumed to be in perfect contact. The governing equation describing the diffusion of lithium ions within the electrolyte phase has been

derived from concentrated solution theory⁸. The following equation is used to estimate concentration profile within the electrolyte phase⁸:

$$\frac{\partial c_{e}}{\partial t} = \vec{\nabla} \cdot \left(D_{e} \left(1 - \frac{d \ln c_{0}}{d \ln c_{e}} \right) \nabla c_{e} \right).$$
(S7)

Here, t indicates time, c_0 denotes the solvent concentration and D_e signifies the diffusivity of lithium within the electrolyte phase. In the present context, for PEO-based polymer electrolyte systems, the solvent concentration depends weakly on the electrolyte concentration, which indicates that $(d \ln c_0/d \ln c_e) \approx 0^{19}$. Diffusion of lithium within the electrolyte has been assumed to be isotropic; hence a scalar value of the diffusion coefficient is sufficient. The magnitude of diffusivity (D_e) has been assumed to be constant and independent of lithium ion concentration. Under the assumption of zero bulk velocity of the electrolyte, and a constant value of the cation transference number, the governing equation for lithium-ion diffusion simplifies to:

$$\frac{\partial c_e}{\partial t} = \vec{\nabla} \cdot \left(D_e \vec{\nabla} c_e \right). \tag{S8}$$

At the top of the domain, the influx of lithium ions within the electrolyte phase is modeled as:

$$-D_e \overline{\nabla} c_e = \left(1 - t_{Li^+}\right) \cdot j_{Li^+} = \left(1 - t_{Li^+}\right) \cdot \frac{l_{applied}}{F}.$$
(S9)

At the lithium-electrolyte interface, the outflow of lithium ions can be approximated as:

$$-D_e \bar{\nabla} c_e = \left(1 - t_{LI^+}\right) \cdot \frac{i_{BV}}{F}.$$
(S10)

At the side boundaries, symmetric boundary conditions suggest that there is zero flux of lithium ions. The initial concentration of lithium ions within the electrolyte phase has been taken to be

 $c_e(t=0)=c_{e,0}$. The kinetic and transport parameters used in the simulation are also given in Table: I.

Mechanics equations: The quasistatic equilibrium equation solved to estimate the hydrostatic and deviatoric stresses within the lithium metal could be written as²⁰:

$$\vec{\nabla} \cdot \underbrace{\sigma}_{\underline{x}} = 0. \tag{S11}$$

Here, $\overline{\nabla}$ indicates the gradient operator and $\underline{\sigma}_{\underline{z}}$ is the second order stress tensor. In this article, the vector/tensor and indicial notations have been used interchangeably. While using the indicial notation, implicit summation over the repeated indices have been assumed. Also the body force and inertia terms have been neglected. The total stress tensor (σ_{ij}) has been divided into deviatoric (s_{ij}) and hydrostatic $(\sigma_{kk} = \sigma_{11} + \sigma_{22} + \sigma_{33})$ components:

$$\sigma_{ij} = s_{ij} + \frac{1}{3}\sigma_{kk}\delta_{ij} \,. \tag{S12}$$

Here, δ_{ij} indicates the Kronecker delta function. Another stress measure, usually known as the effective stress (σ_{eff}) , must be defined here for usage in the theory of plasticity:

$$\sigma_{eff} = \sqrt{\frac{3}{2}} s_{ij} s_{ij} . \tag{S13}$$

If the effective stress exceeds the yield strength of the material, plastic deformation occurs. Under the assumption of small-strain (ε_{ij}) , the strain-displacement kinematic relation is given as:

$$\mathcal{E}_{ij} = \frac{1}{2} \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} \right).$$
(S14)

Here, \bar{u} and \bar{x} represents the displacement and position vector, respectively. The linear elastic stress-strain constitutive relations are given in terms of the shear modulus (G) and Poisson's ratio $(v)^{20}$:

$$\sigma_{ij} = 2G\varepsilon_{ij} + \frac{2\nu G}{1 - 2\nu}\varepsilon_{kk}\delta_{ij}.$$
(S15)

During plastic deformation, the stress-strain constitutive relation must be modified in a consistent fashion to achieve faster convergence (the modified constitutive relation for elastic-plastic deformation is shown later as Eq. (S22)).

Appropriate modeling of the elastic-plastic deformation of both lithium metal and the polymer electrolyte phase must be conducted to obtain the correct stress field around the dendritic protrusion. To appropriately model the elastic-plastic deformation of both lithium metal and the polymer electrolyte phase, the yield function has been defined as^{20, 21}:

$$F\left(\sigma_{ij},\varepsilon_{ij}\right) = \sigma_{eff}\left(\sigma_{ij}\right) - \sigma_{y}\left(\varepsilon_{pl}\right) = 0.$$
(S16)

Here, F is the yield function, which satisfies F < 0 at all times, σ_{ij} is the stress tensor, σ_{y} indicates the yield strength and ε_{pl} is the equivalent plastic strain. When the material deforms plastically, $F(\sigma_{ij}, \varepsilon_{pl}) = 0$. Hence, during plastic deformation²²:

$$dF = 0 = \frac{\partial F}{\partial \sigma_{ij}} d\sigma_{ij} + \frac{\partial F}{\partial \varepsilon_{pl}} d\varepsilon_{pl}.$$
(S17)

Due to the small-strain small-displacement assumption, the total strain tensor (ε_{ij}) can be characterized as the summation of elastic strain (ε_{ij}) and plastic strain (ε_{ij}) tensors:



Figure: S2. Schematic diagram of the experimental setup and computational mesh used to obtain the elastic-plastic stress-strain curves for lithium metal and PEO-based polymer electrolyte. (a) Schematic diagram of the experimental setup, where one end of the sample is kept fixed. Point load is applied at the other end through a stiff support, which tries to emulate the application of uniformly distributed load according to the St. Venant's principle. (b) Schematic diagram of the mesh used in the computational study. The zero-displacement boundary conditions at the bottom and the left sides of the sample and the uniformly distributed load at the top surface have also been depicted here. The axis system considered in this study is also shown.

$$\varepsilon_{ij} = \varepsilon_{ij}^{e} + \varepsilon_{ij}^{p} \,. \tag{S18}$$

The change in equivalent plastic strain $\left(\Delta \varepsilon_{pl}\right)$ can be written in terms of the change in plastic strain $\left(\Delta \varepsilon_{ij}^{p}\right)^{21}$:

$$\Delta \varepsilon_{pl} = \sqrt{\frac{2}{3}} \Delta \varepsilon_{ij}^{\ p} \Delta \varepsilon_{ij}^{\ p} \ . \tag{S19}$$

For both lithium metal and polymer electrolyte, the magnitude of the yield stress (σ_y) changes according to an isotropic strain hardening law, which has been provided later as Eq. (S20).

For both lithium metal and polymer electrolyte, the magnitude of the yield stress (σ_y) changes according to an isotropic strain hardening law²²:

$$\sigma_{y} = \sigma_{0} + H\varepsilon_{pl}^{m}.$$
 (S20)

Here, σ_0 is the initial yield strength, *H* indicates the hardening modulus and *m* denotes the hardening exponent. These are material-specific parameters and their values will be different for metallic lithium and PEO polymer-based electrolyte systems. To obtain the values of initial yield strength (σ_0), hardening modulus (*H*) and hardening exponent (*m*), a comparison of theoretical predictions with experimental results has been conducted. The experimental stress-strain curves, adopted from literature, were obtained by applying uniaxial tension on a sample, as demonstrated in Figure S2(a)^{3, 5}. The bottom of the experimental sample was assumed to remain attached to a base support. A point load was applied at the top of another rigid support, which ensures uniform load distribution to the sample according to St. Venant's principle. To simulate similar uniaxial tension behavior on the computational domain, the boundary and loading

conditions adopted have been demonstrated in Figure S2(b). The roller boundary condition at the bottom and the left side ensures the absence of spurious constraints.

At the molecular scale, elasticity is characterized as stretching of the atomic and molecular bonds²². No rearrangement of atoms or molecules occurs during the elastic deformation, which also ensures reversibility under mechanical unloading²². On the other hand, plastic deformation is always accompanied with atomic or molecular rearrangements inside the material²². Even though the same nonlinear mathematical expression has been used for modeling the plasticity and strain hardening observed in lithium and polymer electrolyte, the mechanisms behind plastic deformation in lithium metal and polymers are very different. In metallic lithium, formation and propagation of dislocations results in plastic flow of the material²³. Each dislocation produces a stress field around itself²³. Accumulation of many dislocations increases the strength of the stress field. Formation and movement of new dislocations become difficult due to the presence of this enhanced internal stress field²². Hence, more external force needs to be applied to create new dislocations and move existing ones. This leads to the strain hardening observed in lithium metal during plastic deformation²². However, plastic deformation in PEOtype semi-crystalline polymers occurs through the elongation of amorphous chains and reorientation of crystalline blocks²⁴. Energy required to reorient and reorganize the molecular blocks manifests as strain hardening in the macroscopic scale²⁴.

During lithium deposition, if the stresses within the lithium metal or polymer electrolyte are lower than their yield strengths, the materials deform purely elastically. As soon as the effective stress within the material exceeds its yield limit, the material starts to deform plastically, and the linear elastic stress-strain relation becomes inapplicable²². When a material is in the plastic regime, determination of the actual stress magnitude is conducted using the "radial-

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return" algorithm. The different steps associated with the calculation of the stress term is listed below^{20, 22}:

- 1. Calculate incremental strain estimated from displacement according to Eq. (S14): $\Delta \varepsilon_{ii}$
- 2. Estimate incremental trial stress $(\Delta \sigma_{ij}^{trial})$ using the elastic constitutive matrix (C_{ijkl}^{e}) defined in Eq. (S15): $\Delta \sigma_{ij}^{trial} = C_{ijkl}^{e} \Delta \varepsilon_{kl}$.
- 3. Calculate total trial stress for this time step (σ_{ij}^{trial}) using stress at previous step (σ_{ij}^{n}) : $\sigma_{ij}^{trial} = \sigma_{ij}^{n} + \Delta \sigma_{ij}^{trial}$
- 4. Estimate the trial deviatoric stress $\left(s_{ij}^{trial}\right)$ from Eq. (S12).
- 5. Estimate the trial effective stress $\left(\sigma_{eff}^{trial}\right)$ from Eq. (S13).
- 6. If the trial effective stress is smaller than the yield stress $(\sigma_{eff}^{trial} < \sigma_y)$, the material is in elastic domain. On the contrary, if the trial effective stress is greater than the yield stress, the material is in plastic domain $(\sigma_{eff}^{trial} > \sigma_y)$.
- 7. If the material is in elastic domain, then the trial stress (σ_{ij}^{trial}) is the final stress (σ_{ij}^{n+1}) for the present time step (n+1), which can also be written as: $\sigma_{ij}^{n+1} = \sigma_{ij}^{trial}$.
- 8. If the material is in the plastic domain, estimate the direction tensor: $\hat{n}_{ij} = \frac{3}{2} \cdot \frac{S_{ij}^{trial}}{\sigma_{eff}^{trial}}$.
- 9. The incremental elastic-plastic stress tensor $(\Delta \sigma_{ij})$ can be estimated by using Eq. (S17) (for detailed description please refer to Section 6.3 in Ref. ²⁵):

$$\Delta \sigma_{ij} = C^{e}_{ijkl} \left(\Delta \varepsilon_{kl} - \frac{\hat{n}_{ab} C^{e}_{abcd} \Delta \varepsilon_{cd}}{\hat{n}_{ab} C^{e}_{abcd} \hat{n}_{cd} + Hm \varepsilon^{m-1}_{pl}} \hat{n}_{kl} \right).$$
(S21)

- 10. For elastic-plastic deformation, the stress at the end of present step is calculated by adding incremental stress $(\Delta \sigma_{ij})$ to the stress of previous step (σ_{ij}^{n}) , which is explicitly written as: $\sigma_{ij}^{n+1} = \sigma_{ij}^{n} + \Delta \sigma_{ij}$.
- 11. The final step is the estimation of elastic-plastic tangent modulus (C_{ijkl}^{ep}) , which is used to calculate the stiffness matrix and subsequently the displacement vector mentioned in the first step:

$$C_{ijkl}^{ep} = \begin{cases} C_{ijkl}^{e} & \text{if } \sigma_{eff}^{trial} < \sigma_{y} \\ C_{ijkl}^{e} - \frac{\left(C_{ijab}^{e} \hat{n}_{ab}\right) \left(\hat{n}_{mn} C_{mnkl}^{e}\right)}{\hat{n}_{ab} C_{abcd}^{e} \hat{n}_{cd} + Hm \varepsilon_{pl}^{m-1}} & \text{if } \sigma_{eff}^{trial} \ge \sigma_{y} \end{cases}$$
(S22)

12. Steps 1 through 11 are continued until the force vector converges, according to the criterion $\left(\sqrt{\sum \left(\bar{f}_{k+1}^{n+1} - \bar{f}_{k}^{n+1}\right)^{2}} / \sqrt{\sum \left(\bar{f}_{k+1}^{n+1}\right)^{2}}\right) \le 10^{-6}$. Here, \bar{f}_{k}^{n+1} is the elemental force vector at (n+1) time step and k iterations. The summation is conducted over all the

elements within the domain.

Through successful implementation of the radial-return algorithm, the correct magnitudes of stress within the lithium metal as well as polymer electrolyte have been estimated.

The initial stress state of lithium metal significantly influences the reaction kinetics at the lithium-polymer interface. Monroe and Newman assumed the existence of tensile stress within the lithium metal, prior to cell assembly². Under this assumption of "pre-stressed" lithium and under purely linear elastic deformation, prevention of dendrite growth is possible only if the

shear stiffness of electrolyte is two times larger than that of lithium metal². However, this assumption of pre-stressed lithium suggests dendrite growth even at very low rates of operation⁹, which does not match most experimental reports. An initially relaxed state of lithium (prior to cell assembly) was found to give results in line with typical experimental observations and has been adopted in the present analysis⁹.

From the correct values of the stress tensor, the exact mechanical stress-induced electrochemical potential can be estimated from Eq. (3) (in the main text). To estimate the contribution of the surface energy into the electrochemical potential, the local curvature has to be measured. In the 2D computational domain, the local curvature κ has been calculated in a piecewise fashion according to the following formula²⁶:

$$\kappa(x) = \frac{\partial^2 z}{\partial x^2} \cdot \left[1 + \left(\frac{\partial z}{\partial x}\right)^2 \right]^{-3/2}$$
(S23)

where z(x) represents the vertical position of the lithium-electrolyte interface. Substituting this expression of electrochemical potential from Eq. (3) into the Butler-Volmer expression given in Eq. (2), the local reaction current density can be obtained. Depending on the concentration, potential and stress profiles, the magnitude of reaction current density changes along the x-direction.

Results

Based on the developed computational technique, it is possible to estimate the potential and concentration distribution within the polymer electrolyte at different applied current densities.



Figure: S3. Potential and concentration contour plots within the electrolyte at three different applied current densities. (a, c, e) Potential contours at applied current densities of 1%, 50% and 90% of the limiting current. (b, d, f) Concentration contour plots at applied current densities of 1%, 50% and 90% of the limiting current. Gradients in both potential and concentration are large at higher current densities.

Figures S3(a), S3(c) and S3(e) demonstrate the potential contours around the dendritic protrusion for three different current densities of 1%, 50% and 90% of the limiting current. Potential within the electrolyte is almost zero for low current operation (see Figure S3(a)). However, as the current density increases, potential gradients between the protrusion peak and valley emerge. The concentration profiles at three different current densities of 1%, 50% and 100% of the limiting current are shown in Figure S3(b), S3(d) and S3(f), respectively. At lower magnitudes of applied current, almost uniform concentration is observed. For higher applied current densities, significant concentration gradients between the peak and the valley evolve. This variation is concentration influences the reaction current distribution in a two-fold fashion:

- 1. Electrolyte salt concentration differences impacts the local conductivity, which in turn affects the potential distribution⁷.
- 2. The reference exchange current density $(i_{0,ref} = Fk_a^{\alpha_c} (k_c c_e)^{\alpha_a})$ also depends on the local concentration of electrolyte salt¹⁵.

Propensity of growth of a dendritic protrusion is estimated from the ratio of reaction current density at the protrusion peak over that at the valley⁹. Since the variation in concentration and potential around the dendritic protrusion is more pronounced at higher current densities, the possibility of dendrite growth also increases close to the limiting current. Due to the extremely high conductivity of lithium metal, the solid phase potential remains almost close to zero¹⁶. Since the deposition of lithium occurs at the lithium-polymer electrolyte interface, no transport of lithium occurs within the metal. Hence, neither potential nor concentration profiles within the lithium metal has been demonstrated in the contour plots.

Evolution of stress within the lithium metal and the polymer electrolyte has a significant impact on the overall reaction current density².



Figure: S4. Contour plot of stress evolution within the lithium metal and polymer electrolyte system. (a) When the shear modulus of the electrolyte phase is significantly smaller than that of lithium $(G^{Electrolyte} < 10^{-4} \cdot G^{Lithium})$, effective stress that evolves within both lithium and electrolyte are much smaller than the corresponding yield strength. This leads to only elastic deformation of both lithium and electrolyte. (b) For PEO polymer based electrolyte, the shear modulus is approximately two orders of magnitude smaller than lithium metal $(G^{Electrolyte} ~ 10^{-2} \cdot G^{Lithium})$. This leads to significantly larger values of effective stress within the metal and polymer. The yield strength of lithium is almost half of PEO-based polymer. The effective stress in lithium exceeds the yield limit in certain locations. But the effective stress in electrolyte stays well below its yield strength, which is supposed to result in only elastic deformation of the PEO polymer.

The magnitude of the effective stress (calculated from Eq. (S13)) determines whether plastic deformation occurs or not. If the effective stress exceeds the yield limit of the material, it deforms plastically. Figure S4 demonstrates the distribution of effective stress within the lithium metal and polymer electrolyte. For relatively soft electrolytes with shear modulus multiple orders of magnitude smaller than that of lithium $(G^{Electrolyte} < 10^{-4} \cdot G^{Lithium})$ (shown in Figure S4(a)), the effective stress is significantly smaller than the yield limit. However, as the electrolyte modulus increases to something equivalent to that of PEO-based polymers, the effective stress within both lithium metal and polymer electrolyte increase. As shown in Figure S4(b), the effective stress in the lithium exceeds its yield strength. However, the effective stress in the electrolyte is smaller than its yield limit. Hence, plastic deformation is supposed to occur within lithium metal, but only elastic deformation is observed in the polymer electrolyte. This plastic deformation of lithium metal combined with elasticity of electrolyte leads to significantly reduced height of the dendritic protrusion¹¹.

Evolution of plasticity within lithium metal and the polymer electrolyte governs the actual height of the dendritic protrusion to a significant extent. For very low modulus electrolytes (shown in Figure S5(a)), only elastic deformation occurs within both the lithium metal and polymer electrolyte. As the electrolyte modulus increases to that of PEO-based polymer (see Figure S5(b)), the effective stress in lithium exceeds its yield limit, and plastic deformation is observed there. However, the effective stress in electrolyte remains below the yield strength, and it experiences only elastic deformation. Similar stress evolution was also observed in Figure S4(b). Finally, for extremely high shear modulus of the polymer (see Figure S5(c)), both lithium and electrolyte experience plastic deformation. This variation in evolution of plasticity has a significant impact on the overall protrusion height (H).



Figure: S5. Plasticity contour plots for three different values of electrolyte shear modulus. Dark blue region indicates elastic deformation and light green region denotes evolution of plasticity. The white space has been drawn on the electrolyte region at the interface with the lithium to visually differentiate between the lithium metal and polymer-based electrolyte domain. (a) For very low magnitude of electrolyte shear modulus ($G^{Electrolyte} \sim 10^{-5} G^{Lithium}$), the effective stress within lithium and electrolyte region remains well below their corresponding yield limits. Hence, only elastic deformation is observed. (b) For electrolyte shear modulus equivalent to that of PEO-based polymer ($G^{Electrolyte} \sim 7.7 \times 10^{-3} G^{Lithium}$), plastic deformation occurs within lithium metal, but the electrolyte deforms elastically. (c) For higher shear modulus of the electrolyte ($G^{Electrolyte} \sim 2G^{Lithium}$), plasticity evolves within both lithium and the electrolyte region. This variation in elastic and plastic deformation of lithium and polymer electrolyte impacts the height of the dendritic protrusion, and subsequently its propensity to grow.

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