Supplementary Information for

Concentration Polarization and Metal Dendrite Initiation in

Isolated Electrolyte Microchannels

Youngju Lee^a, Bingyuan Ma^a, and Peng Bai^{a,b,*}

^a Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, 1 Brooking Dr, St. Louis, MO 63130, USA.

^b Institute of Materials Science and Engineering, Washington University in St. Louis, 1 Brooking Dr, St. Louis, MO 63130, USA.

*Correspondence to: pbai@wustl.edu

Estimation of the penetration current density



Figure S1. Example images of penetrated separators and solid electrolytes, which were analyzed to derive the penetration area and penetration current density. (a) Ceramic-coated polymer separator with liquid electrolyte. (1.0M LiPF₆ in EC/DMC) (b) Glass fiber separator with liquid electrolyte.¹ (c) LLZTO ceramic electrolyte.² (d) Polymer electrolyte.³

Several images of the penetrated separators or solid electrolytes were analyzed. The images were either from our experimental results (Fig. S1a) or from literature (Fig. S1b-d). These include systems containing liquid electrolyte and porous separator,¹ ceramic separator,^{2,4,5} and polymer

separators.^{3,6,7} The images were processed with ImageJ software to derive the ratio of the penetrated area (which appears as the black dots in the images) and the area of the electrode. For the cases that this method was not applicable, as the case of cross-sectional images from the polymer electrolytes (Fig. S1d), the length of the dendrite tip was measured and was used to calculate the penetration area. The exact area of the electrodes was often not given for the cross-sectional images, and rough estimations of the thickness (~ 1mm) and length of the electrode (4-10 mm) were done for the calculation.

Equations used in the COMSOL model

This section explains the equations and the boundary condition used in the COMSOL model. The Nernst-Plank equation describes the concentrations of ions within an electrolyte system under the effects of diffusion, convection, and migration:⁸

$$\frac{\partial c_i}{\partial t} = F u_i Z_i \nabla \cdot (c_i \nabla \phi) + D_i \nabla \cdot (\nabla c_i) - \nabla \cdot (c_i \nu)$$
(S1)

where c_i is the concentration of the species i, D_i is its diffusivity, Z_i is its charge number, u_i is its mobility, \emptyset is the electric potential, F is the Faraday constant, and v is the velocity of the fluid.

For a binary electrolyte, the expression can be converted into a simpler form by using the ambipolar diffusivity (apparent diffusivity), which includes the effect of migration.⁹ The ambipolar diffusivity, D_{amb} , can be defined as

$$D_{amb} = \frac{D_{+}D_{-}Z_{+} - D_{+}D_{-}Z_{-}}{D_{+}Z_{+} - D_{-}Z_{-}}$$
(S2)

where D and Z are the diffusivity and charge number of the corresponding ions.

Using D_{amb} , the Nernst-Plank equation now takes the following form:

$$\frac{\partial c}{\partial t} + \nabla \cdot (cv) = D_{amb} \nabla \cdot (\nabla c)$$
(S3)

which has the form of the convection-diffusion equation. If the velocity of the fluid is assumed to be zero, the equation now becomes the classical diffusion equation with the following form:

$$\frac{\partial c}{\partial t} = D_{amb} \nabla \cdot (\nabla c) \tag{S4}$$

In our COMSOL model, this diffusion equation form was used. "Transport of the Diluted Species Study" module of the software was used with a diffusion equation,

$$\frac{\partial c_{Li}}{\partial t} + \nabla \cdot J_{Li} = 0 \tag{S5}$$

and

$$J_{Li} = -D_{amb} \nabla c_{Li} \tag{S6}$$

where J_{Li} is the flux of Li ions. As mentioned earlier, migration is already included in the ambipolar diffusivity term, and no convection condition was assumed. For the boundary condition for both electrodes, Li ion dissolution/deposition can be represented by the electrode surface coupling boundary condition, described by

$$R_{Li} = \frac{\nu_{Li}j}{nF} \tag{S7}$$

where v_i is the stoichiometric coefficient (1 for Li), n is the number of a participating electron in the reaction, *j* is the current density, and R_{Li} is the number of reacted Li ions per unit area per unit time. At the electrode surface,

$$-n \cdot J_{Li} = n \cdot D_{Li} \nabla c_{Li} = R_{Li} = \frac{j}{F}$$
(S8)

where *n* is the normal vector. Since generally $D_{Li} \neq D_{amb}$, the relation between the two diffusivities,

$$D_{Li} = \frac{D_{amb}}{t_a} \tag{S9}$$

can be used with the transference number t_a (0.62 for LiPF₆ in EC/DMC).

Table S1. Parameters and constants used in the COMSOL simulations

Faraday constant	Li metal Density	Molar mass of Li	Li ion diffusivity
96485.33 [C/mol]	0.534 [g cm ⁻³]	6.941 [g mol ⁻¹]	$3.0E-6 [cm^2 s^{-1}]$

Table 1 summarizes the parameters and constants used in the COMSOL simulation. Porosity, calculated from the operando optical microscope images and the amount of total charge passed,

was in the range of $0.95 \sim 0.99$, and we used the porosity value in this range that best fitted our experimental results in the COMSOL model. Unless otherwise noted, Li ion diffusivity of 3E-6 cm² s⁻¹ was used in simulations. For certain simulated cases, an advancing electrode front due to Li deposition was considered, using the deformed geometry function that COMSOL software provides. A prescribed normal mesh velocity was set, and the velocity was controlled by the amount of Li metal being deposited per unit time. The expression used for the volume increase due to Li deposition was calculated as follows:

$$\Delta V = \frac{IM}{F\rho\varepsilon_M} \tag{S10}$$

where ΔV is the increase of volume each second, I is the total current, M is molar mass, F is the Faraday constant, ρ is the density of the lithium, and ε_M is the porosity of the Li metal deposition. The normal mesh velocity for the advancing electrode front boundary, v, was expressed as

$$v = \frac{\Delta V}{A} \tag{S11}$$

where *A* is the transient cross-sectional area calculated from the location of the advancing electrode surface within the defined geometry.

Limiting current density and the steady-state concentration profile in converging channels



Figure S2. (a) COMSOL model calculated limiting current densities for varied Li ion diffusivities. (b-c) Lengthwise distribution Li ion concentration values in a straight channel (b) and converging channel (c) at a different time. In both cases, limiting current density was applied. The steady-state

concentration profile was derived both analytically and numerically, while the transient profiles were derived only numerically. L=5 mm for (a-c).

As much as the accurate prediction of Sand's time has been emphasized, the accurate derivation of the limiting current density is also important since it is directly related to the maximum current density that can be used in the system.¹⁰ The limiting current density for the converging or the straight channels with a fixed electrode front can be solved analytically with the steady-state assumption as explained in more detail in the later section (S12-22). However, the advancing electrode front makes it infeasible to analytically derive the limiting current density, so a numerical method was used for the advancing front case.

Analytically and numerically derived values of the limiting current density were compared in Figure S2a. The limiting current density for the converging channels with the fixed electrode front, which was calculated both numerically and analytically, showed a linear relation with the diffusivity, but with a gentler slope than the straight channel case. This relationship is clearer when comparing the two analytical solutions for each case (S16 and 18). This difference is due to the delayed diffusion and thus a faster depletion caused by the converging channel. Even for the cases with both a converging channel and an advancing electrode front, the relationship between diffusivity and the limiting current density remains linear, as shown in Fig. S2a. This result has practical significance since even for a converging channel where the Sand equation is no longer valid, the diffusivity can still be determined by measuring the limiting current density, provided that an electrolyte with the known diffusivity is used as a reference. Meanwhile, an increase in porosity, and thus a faster electrode movement, led to a steeper slope (Fig. S2a). Again, the

advancing electrode front delayed the ion depletion, so more current density was needed before transport-limitation can be reached. One additional point to note is that for the converging channel, the steady-state concentration profile was not linear (Fig. S2b), unlike the diffusion process inside a straight channel (Fig. S2c).

Analytical solution for a steady-state concentration profile and limiting current density

This section describes the derivation of the analytical solution for a steady-state concentration profile and limiting current density. For straight channels without considering the growth-induce movement of the electrode, the following linear diffusion equation needs to be solved for the analytical solution:

$$\frac{\partial c_i}{\partial t} = D_{amb} \frac{\partial^2 c_i}{\partial x^2}$$
(S12)

At steady-state, the left term becomes zero and the following boundary conditions can be used:⁸

At
$$x = 0$$
 (at the center), $c_i(0) = c_0$ (S13)

At
$$x = L$$
 (at the electrode surface), $c_i(L) = 0$ (S14)

At
$$x = L$$
 (at the electrode surface), $\frac{D_{amb}}{t_a} \left[\frac{\partial c_i}{\partial x} \right]_{x=L} = -\frac{j}{nF}$ (S15)

Note that the transference number is used in the boundary condition S15 because only the cation is being consumed at the electrode surface. Solving the equation with the boundary conditions gives the concentration profile at steady-state, which is a straight line (Fig. S2b), as well as the limiting current density, described by the following expression:

$$j_{lim} = -\frac{D_{amb}F2c_0}{t_a - L}$$
(S16)

For the diffusion process within a curved geometry where the cross-sectional area of the electrode changes with x, the Fick-Jacobs equation can be used as a governing equation:^{11–13}

$$\frac{\partial p_i(x,t)}{\partial t} = \frac{\partial}{\partial x} DA(x) \frac{\partial}{\partial x} \left(\frac{p_i(x,t)}{A(x)} \right)$$
(S17)

Where *D* is the diffusivity of the ion inside electrolyte, A(x) is the cross-sectional area at point *x*, and $p_i(x,t)$ is the cross-sectional integration of concentration so that $p_i(x,t)/A(x) = c_i(x,t)$. Note that the concentration is assumed to vary only along the x-axis.

The same boundary conditions as above can be applied, and the limiting current density now has the following expression:

$$j_{lim} = -\frac{D_{amb}F}{t_a} \left[\frac{\partial c_i}{\partial x}\right]_{x=L}$$
(S18)

The analytical solution for a curved wall with a catenary profile (r = a * cosh(x/a) - b), a = 70.640 mm and b = 70.595 mm) can be solved as follows.

From the equation S17, at steady-state, the following equation obtains:

$$0 = \frac{\partial}{\partial x} \left(A(x) \frac{\partial c_i}{\partial x} \right)$$
(S19)

Due to the catenary wall profile, the area can be expressed as

$$A(x) = \pi (a * \cosh(x/a) - b)^2$$
(S20)

Using equation S19 and 20 and by integrating twice with the boundary condition S13-15, the following expression can be derived:

$$a\alpha \left(\frac{2b\tan^{-1}\left(\frac{(a+b)tanh\left(\frac{x}{2a}\right)}{\sqrt{a^2 - b^2}}\right)}{(a^2 - b^2)^{\frac{3}{2}}} + \frac{a\sinh\left(\frac{x}{a}\right)}{(a-b)(a+b)(a\cosh\left(\frac{x}{a}\right) - b)} \right) \\ c_i(x) = \frac{\pi}{\alpha} + \beta$$
(S21)

where $\alpha = -0.0039$ and $\beta = 1000$ are the constants of integration.

The limiting current density, from equation S18, can be expressed as

$$j_{lim} = -\frac{D_{amb}F \ \alpha}{t_a \ A(L)}$$
(S22)

Analytical derivation of the Sand's time in curved channels

This section describes the derivation of the analytical solution for the Sand's time in curved channels. For the case of curved geometry, the Fick-Jacobs equation (S17) should be solved.

Equation S17 can be rearranged to the following form:

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + D \frac{dA(x) \, \partial c}{A(x) dx \partial x}$$
(S23)

For the special case of $A(x) = A_0 exp^{[in]}(bx)$, where A_0 and b are constants, the equation S23 can be simplified as the following form, which has a similar form to convection-diffusion equation:

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c}{\partial x^2} + b D \frac{\partial c}{\partial x}$$
(S24)

With the change of variable, $\xi = x + bDt$, the equation can be further simplified to diffusion equation form,

$$\frac{\partial c(\xi,t)}{\partial t} = D \frac{\partial^2 c}{\partial x \xi^2}$$
(S25)

The initial and boundary conditions are as the following:

$$c(\xi, t = 0) = c_0 \tag{S26}$$

$$c(\xi \to \infty, t) = c_0 \tag{S27}$$

$$c(\xi = 0, t > 0) = 0 \tag{S28}$$

Note that $\xi = 0$ is the location of the electrode surface.

For the surface reaction, the following flux balance relation can be established:

$$D\frac{\partial c(\xi = 0, t > 0)}{\partial \xi} = \frac{I(t)}{nFA}$$
(S29)

where I(t) is current, *n* is the number of a participating electron in the reaction, *F* is the faraday constant, and *A* is the surface area of the electrode. Using the Laplace transform with initial and boundary conditions, along with the flux balance relationship, the analytical solution can be found as the following:

$$c(\xi,t) = c_0 - \frac{(1-t_+)I}{nFAD} \left[2\sqrt{\frac{Dt}{\pi}} exp\left(-\frac{\xi^2}{4Dt}\right) - \xi \, erfc\left(\frac{\xi}{2\sqrt{Dt}}\right) \right]$$
(S30)

Substituting back to x and putting x = 0 and c(0,t) = 0 gives the following relation between the Sands time (t_s) and current density (*J*):

$$2\sqrt{\frac{t_s}{D\pi}}\exp\left(-\frac{b^2Dt_s}{4}\right) - bt_s \operatorname{erfc}\left(\frac{b\sqrt{Dt_s}}{2}\right) = \frac{c_0 nF}{J(1-t_+)}$$
(S31)

The relationship between curvature and the scaling exponents



Figure S3. (a) Adjusted values of fitted A(x) plotted against the distance from the electrode surface. The adjustment was done by dividing A(x) values with A_0 , for the fitted equations of $A(x) = A_0 \exp(bx)$. The values of the exponents remain the same as the scalar b of the fitted equations, showing that b-values are directly related to the changing rate of A(x), which also represents the extent of the channel wall curvature. (b) The values of the area changing rate b

plotted against the varied interelectrode distance. (c) Scaling exponent values plotted against the area changing rate b. The changing rate b and the Scaling exponent showed a monotonic relationship, suggesting a monotonic relationship between the channel wall curvature and the scaling exponent values.



Limiting current density and the steady-state concentration profile in expanding channels

Figure S4. (a) Configuration of the geometry used in the simulations for expanding channels. (b) Limiting current density values with varied Li ion diffusivities, compared between different channel configurations. Expanding channel and the advancing electrode front increased the limiting current density significantly. (c) Lengthwise distribution Li ion concentration values in expanding channel at a different time. L=3.5 mm for (b-c).

Sand's time in expanding channels with varying metal porosity



Figure S5. (a) Mathematically simulated ion concentration at the advancing electrode front with varying metal porosity, inside expanding channels. The equation used for the varying metal porosity (ε_M) was $\varepsilon_M = -79.08 * exp(-J/4.72) + 0.9783$, where J is the current density. The resulting porosity was nearly constant initially for the higher current densities, then decreased rapidly at the current densities below 50 mA cm⁻², which was close to the experimentally observed trend. For the case of 80 mA cm⁻², the depletion did not occur if the porosity was fixed at the initial value, but the rapid decrease of porosity resulted in depletion. (b) Logarithmic plot of experimental and simulated Sand's time versus current densities obtained within expanding channels. Calculated Sand's time from the model with varying metal porosity was extended compared to the model with fixed porosity, especially for the lower current densities resulting in more negatively deviated scaling exponent closer to the experimental value. For the simulations, $\varepsilon_M = 0.978$ was used for constant porosity case while $\varepsilon_M = -79.08 * exp(-J/4.72) + 0.9783$ for the varying porosity case.

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