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Complete List of Authors:	Parekh, Mihir; The Pennsylvania State University College of Engineering, Mechanical Engineering Rahn, Christopher; The Pennsylvania State University College of Engineering, Department of Mechanical Engineering	
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## Reducing dendrite growth in lithium metal batteries by creeping Poiseuille and Couette flows

Mihir N. Parekh<sup>a,\*</sup>, and Christopher D. Rahn<sup>a</sup>

<sup>a</sup>Department of Mechanical Engineering, The Pennsylvania State University, University Park, Pennsylvania 16802, USA

### Abstract

Dendrites in lithium metal batteries grow due to instabilities during metal electrodeposition. This paper derives analytical models for electrodeposition with creeping Poiseuille and Couette flows parallel to the two electrodes. The models predict that creeping electrolyte flow parallel to the surface of metal electrode increases the stability of lithium plating by reducing the dendrite growth rate. Moreover, parallel flow reduces the curvature of dendrites leading to flatter electrodeposits, so the dendrites are less likely to penetrate the separator or fracture the Solid Electrolyte Interphase (SEI). For the same average flow rate, Poiseuille flow can be upto two times more stabilizing than Couette flow. However, parallel flows must be many orders of magnitude higher than normal flows for similar reduction in instability. It is also not possible to completely stabilize the metal electrode with creeping parallel flows.

**Keywords**: Lithium metal battery; Dendrite; Poiseuille flow; Couette flow; Stability; Perturbation

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<sup>\*</sup>Corresponding author

 $<sup>\</sup>mathit{Email}$  addresses: mzp523@psu.edu (Mihir N. Parekh), cdr10@psu.edu (and Christopher D. Rahn)

#### 1. Introduction

Rechargeable batteries with lithium, sodium, magnesium, and zinc metallic anodes are potentially low cost and energy dense. Lithium Metal Batteries (LMBs), for example, are amongst the highest performing cells due to their high volumetric and gravimetric energy densities [1]. Lithium electroplating during charging, however, often leads to dendrite growth. Solid Electrolyte Interphase (SEI) cracking around dendrite tips due to excessive tensile stress promotes further dendrite growth and leads to the production of dead Li [2] and rapid capacity deterioration. Dendrite growth can also lead to internal short circuits, fires and explosions. To make LMBs viable, dendrite growth must be reduced and, if possible, eliminated.

Chazelviel [3] studies the role of mass transport limitations and ion depletion at dendrite tips in dendrite growth. The high concentration gradient and large electric field at dendrite tips promotes excessive plating and leads to ion depletion. Nishikawa *et al.* [4], experimentally investigate the effects of mass transfer on dendrite growth. Local effects often govern dendrite growth in LMBs as dendrites grow even before Sand's time [5] and at current densities lower than the limiting current densities [6, 7, 8]. Inhomogeneous and mossy Li growth during initial stages of plating leads to electrolyte confinement, so local effects play a role [9]. Wood *et al.* [10] study galvanostatic electrodeposition in Li/Li symmetric cells with insitu video operando microscopy and relate voltage response to the electrodeposition process.

Dendrite growth rate depends on the applied overpotential and is initiated only at overpotentials above a critical overpotential [11]. Akolkar calculates dendrite growth rate under pure activation control [12]. Temperature gradients can al-

ter dendrite morphoology [13] and temperature affects the kinetics of dendrite growth due to Arrhenius temperature dependent diffusion [14]. Jana *et al.* [8] couple stress driven and transport limitation driven dendrite growth models and identify various regimes of dendrite growth. Pressure [15] and charging patterns have been shown to reduce dendrite growth [16, 17, 18].

Stability analysis has often been used to study the problem of electrodepsotion. Barkey *et al.* [19] use stability analysis to study copper electrodeposition on a rotating cylinder. Chen *et al.* [20] show the importance of reacting ion concentration, concentration gradient, migration within the diffusion layer and diffusion layer thickness in governing the morphological instability during electrodeposition. Sundstrom *et al.* [21] and Tikekar *et al.* [22] study the stability of electrodeposition processes and show that the competing effects of surface tension and electrode curvature govern dendrite growth. Their analyses predict a maximum in the curve of dendrite growth rate versus wavelength of sinusoidal perturbations. Khoo *et al.* [23] use transient linear stability analysis and show that surface conduction in charged nanopores can potentially eliminate dendrites.

Maraschky *et al.* [24] show that increasing thickness of SEI layer which leads to ion depletion at the electrode surface is the main cause of dendrite growth. They extend their work and further explore the effect of temperature on transport through SEI layer [25] as it is tied to dendrite growth. Unstable SEI layers may lead to the production of dead Li and decreased coulombic efficiency and capacity [26]. Unstable SEI layer can also lead to dendrite growth. So, stabilizing the SEI is another method to control dendrite growth. Using electrolyte additives [27, 28, 29, 30] and protective layers on the lithium metal electrode

[31, 32] are ways to stabilize the SEI. Uniform metal ion flux [33, 34] reduces the concentration gradients at dendrite tips and suppresses dendrite growth. Using 3D porous structured anodes with large number of polar groups [35] or 3D mixed ion-electron conductors [36] can reduce the local plating current density and suppress dendrite growth. Anodes made of polymer brushes with lithiophilic functional groups [37] experience homogeneous lithium nucleation and dendrite-free plating. Homogeneous, localized or gradient distributed lithium ion flux [38] can potentially eliminate dendrites. Sharp dendrites that grow at current densities higher than bulk limiting current density can penetrate through nanoporous ceramic separators and may lead to internal short circuit [39]. Root-growing mossy lithium at current densities below bulk limiting current density can be stopped by nanoporous ceramic separators [40]. Rehnlund *et al.* [41] stress upon the importance of electrolyte concentration in controlling dendrite growth.

Magnetic stirring of the electrolyte [42], Lorentz force [43], and electrokinetic pumping through a sponge like structure [44] enhance mass transport and reduce dendrite growth. Electrolyte replenishment due to vortex formation near dendrite tips can change dendrite morphology from straight to mossy [45].

Experimental evidence [45, 46, 47] shows that electrolyte flow can reduce dendrite growth. Parekh *et al.* [48, 49] show that electrolyte flow normal to a porous lithium metal electrode can eliminate dendrite formation during electroplating. Huang *et al.* [50] experimentally study the effects of acoustic streaming of electrolyte on dendrite growth. In this paper, for the first time we study analytically the effects of electrolyte flows parallel to the electrode on dendrite growth. Using a first order stability analysis technique, similar to the one used

by Tikekar *et al.* [22] and Parekh *et al.* [48], this paper calculates the dendrite growth rate as a function of flow rate and current density.

#### 2. Governing Equations

Figure 1 shows a schematic diagram of a Li metal cell with advective electrolyte flow parallel to the electrodes. Poiseuille flow and Couette flow have the parabolic and linear velocity profiles shown in Fig. 1a and Fig. 1b, respectively. Poiseuille flow may be generated by externally pumping the electrolyte through the inter-electrode gap using a pressure gradient in the  $\mathbf{X}$  direction. Couette flow can be generated by relative horizontal motion of the two electrodes.

With Couette and Poiseuille flow being parallel to the electrode, diffusion is the main ion transport mechanism. The time scale for an ion to move from one electrode to the other may be given by  $L^2/D_c$ , where L is the inter-electrode distance and  $D_c$  is the diffusivity of cations. For the parameters listed in 1, this time is 40 s. Typically batteries take around an hour to charge and thus, 40 s is negligible compared to the timescale of charging process. Moreover, electrolyte flow is assumed to be creeping flow and so it is quasistatic. In case of Couette flow, the creeping flow assumption means that flow has negligible transients and tracks the relative motion of the two electrodes. So, the relative motion can be periodic in nature without a steady drift of one electrode relative to the other.

A charging current density  $\tilde{J}(X,T)$  transports Li<sup>+</sup> ions from the positive electrode at Y = -0.5L to the Li metal electrode at Y = 0.5L where they plate and change the thickness of the anode over time T. In both cases, electrolyte flow is parallel to the electrode, so diffusion is the main mechanism for lithium ion transport from the counter-electrode to the lithium metal electrode. Assuming quasi-steady state gives

$$\nabla \cdot \mathbf{N_c} = 0, \tag{1}$$

where

$$\tilde{\mathbf{N}}_{\mathbf{c}} = -D_c \nabla \tilde{C}_c - \mu_{0c} F \tilde{C}_c \nabla \tilde{\Phi} + \tilde{C}_c \tilde{\mathbf{V}}$$
(2)

is the cation flux where F is Faraday's constant, D is diffusivity,  $\mu_0$  is electric mobility,  $\tilde{C}(X, \mathbb{Z}, T)$  is concentration,  $\tilde{\Phi}(X, \mathbb{Z}, T)$  is electrostatic potential, and subscript c indicates cation parameters. The anion flux

$$\tilde{\mathbf{N}}_{\mathbf{a}} = -D_a \nabla \tilde{C}_a + \mu_{0a} F \tilde{C}_a \nabla \tilde{\Phi} + \tilde{C}_a \tilde{\mathbf{V}}$$
(3)

is governed by

$$\nabla \cdot \tilde{\mathbf{N}}_{\mathbf{a}} = 0, \tag{4}$$

where subscript a indicates anion parameters. Neglecting the small double layer region, we assume electroneutrality, so

$$\tilde{C}_c = \tilde{C}_a.$$
(5)

The flow field is described by continuity

$$\nabla \cdot \mathbf{V} = 0, \tag{6}$$

and the creeping flow equation

$$-\nabla \tilde{P} + \mu \nabla^2 \tilde{\mathbf{V}} = 0, \tag{7}$$

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where  $\mu$  is the dynamic viscosity of the electrolyte,  $\tilde{P}(X, Z, T)$  is the pressure, and  $\tilde{\mathbf{V}}(X, Z, T)$  is the electrolyte velocity.

The normal anion flux at the lithium metal electrode is assumed to be zero. So,

$$\tilde{\mathbf{N}}_{\mathbf{a}} \cdot \tilde{\mathbf{n}}|_{\tilde{H}_c} = 0, \tag{8}$$

where  $\tilde{H}_c$  is the location of lithium metal electrode,  $\tilde{\mathbf{n}}$  is the unit vector in a direction normal to the lithium metal electrode surface, and  $()|_{\tilde{H}_c}$  means evaluated at the growing surface  $\tilde{H}_c$ . The rate of electrodeposition per unit surface area of the metal electrode is given by

$$\frac{\partial \tilde{H}_c}{\partial T} = \left( v_m \tilde{\mathbf{N}}_{\mathbf{c}} \cdot \tilde{\mathbf{n}} \right) |_{\tilde{H}_c},\tag{9}$$

where  $v_m$  is the molar volume of Li. Introducing the non dimensional variables,  $\tilde{\mathbf{n}}_{\mathbf{c}} = \frac{\tilde{\mathbf{N}}_{\mathbf{c}}L}{D_cC_0}$ ,  $\tilde{\mathbf{n}}_{\mathbf{a}} = \frac{\tilde{\mathbf{N}}_{\mathbf{a}}L}{D_aC_0}$ ,  $Pe = \frac{V_0L}{D_c}$ ,  $Re = \frac{\rho V_0L}{\mu}$ ,  $\tilde{p} = \frac{\tilde{P}L^2}{\mu D_c}$ ,  $\tilde{\mathbf{v}} = \frac{\tilde{V}}{V_0}$ ,  $\tilde{\phi} = \frac{\tilde{\Phi}F}{RT}$ ,  $\tilde{c}_c = \frac{\tilde{C}_c}{C_0}$ ,  $\tilde{c}_a = \frac{\tilde{C}_a}{C_0}$ ,  $z = \frac{Z}{L}$ ,  $x = \frac{X}{L}$ ,  $M = (\frac{Dc}{Da} + 1)Pe$ ,  $\tilde{h}_c = \tilde{H}_c/L$ , and  $t = \frac{v_m D_c C_0 T}{L^2}$  in Eqs. 1-9 produces

$$\nabla \cdot \tilde{\mathbf{n}}_{\mathbf{c}} = 0, \tag{10}$$

$$\nabla \cdot \tilde{\mathbf{n}}_{\mathbf{a}} = 0, \tag{11}$$

$$\nabla \cdot \tilde{\mathbf{v}} = 0, \tag{12}$$

$$-\frac{\nabla \tilde{p}}{RePe} + \frac{\nabla^2 \tilde{\mathbf{v}}}{Re} = 0, \tag{13}$$

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$$\tilde{\mathbf{n}}_{\mathbf{c}} = -\nabla \tilde{c}_c - \tilde{c}_c \nabla \phi + \tilde{\mathbf{v}} \tilde{c}_c P e, \qquad (14)$$

$$\tilde{\mathbf{n}}_{\mathbf{a}} = -\nabla \tilde{c}_a + \tilde{c}_a \nabla \tilde{\phi} + \tilde{\mathbf{v}} \tilde{c}_a (M - Pe), \qquad (15)$$

$$\tilde{c}_c = \tilde{c}_a,\tag{16}$$

$$\tilde{\mathbf{n}}_{\mathbf{a}} \cdot \tilde{\mathbf{n}}|_{\tilde{h}_c} = 0, \tag{17}$$

$$\tilde{c}_{c} = \tilde{c}_{a}, \qquad (16)$$

$$\tilde{\mathbf{n}}_{\mathbf{a}} \cdot \tilde{\mathbf{n}}|_{\tilde{h}_{c}} = 0, \qquad (17)$$

$$\frac{\partial \tilde{h}_{c}}{\partial t} = \tilde{\mathbf{n}}_{\mathbf{c}} \cdot \tilde{\mathbf{n}}|_{\tilde{h}_{c}}, \qquad (18)$$

where  $C_0$  and  $V_0$  are the average concentration and velocity, respectively. The electrochemical energy of the cation at the metal boundary is

$$\Psi_c(X, \tilde{H}_c, T) = \Psi_c^0 + RT_0 \ln(\tilde{C}_c(X, \tilde{H}_c, T)) + F\tilde{\Phi}(X, H_c, T),$$
(19)

where  $\Psi_c^0$  is the standard electrochemical energy for the electrolyte, R is the universal gas constant,  $T_0$  is the operating cell temperature. We assume fast kinetics, and neglect activation overpotential, which is typically small for batteries [22]. The electrochemical energy in the metal electrode is

$$\Psi_m(X,T) = \Psi_m^0 + \gamma v_m K(X,T) + F \tilde{\Phi}_m(X,T), \qquad (20)$$

where  $\gamma$  is the surface tension at the electrode-electrolyte interface,  $\Psi^0_m$  is the standard electrochemical energy for the electrode, K is the curvature, and  $\Phi_m(X,T)$  is the electrostatic potential at the metal electrode surface.

Assuming equilibrium at the metal electrode surface gives

$$\tilde{\Phi}_m = \frac{\Psi_c^0 - \Psi_m^0}{F} + \frac{RT_0}{F} \ln(\tilde{C}_c(X, \tilde{H}_c, T)) - \frac{\gamma v_m K(X, T)}{F} + \tilde{\Phi}(X, \tilde{H}_c, T).$$
(21)

For charging the cell, an overpotential

$$\tilde{E}_0 = \tilde{\Phi}(X, -L/2, T).$$
(22)

is applied at the counter -electrode. Substituting the non-dimensional variables k = KL,  $\tilde{\phi}_m = F\tilde{\Phi}_m/(RT_0) - 6.91$ ,  $\psi_c^0 = \Psi_c^0/(RT_0)$ ,  $\beta = \gamma v_m/(RT_0L)$ , and  $\psi_m^0 = \Psi_m^0/(RT_0)$ , and  $\tilde{e}_0 = \frac{\tilde{E}_0F}{RT_0}$  we obtain the non-dimensional equations

$$\tilde{\phi}_m = \psi_c^0 - \psi_m^0 + \ln(\tilde{c}_c(x, \tilde{h}_c, t)) - \beta k(x, t) + \tilde{\phi}(x, \tilde{h}_c, t),$$
(23)

and

$$\tilde{\phi}(x, -0.5, t) = \tilde{e}_0. \tag{24}$$

#### 3. Base Case Solutions

For the base case, uniform plating and fully developed conditions are assumed, so  $\tilde{J}(X,T) = J$ ,  $\tilde{c}_c(x,z,t) = c_c(z)$ ,  $\tilde{c}_a(x,z,t) = c_a(z)$ ,  $\tilde{\phi}(x,z,t) = \phi(z)$ ,  $\tilde{e}_0(x,z,t) = e_0$ ,  $\tilde{\mathbf{v}}(x,z,t) = v(z)\hat{\mathbf{i}}$ , and  $\tilde{h}_c(x,t) = h_c(t)$ , where J is the charging current density. J/F is the cation flux in the z direction, where F is Faraday's constant. The anion flux in the z direction is assumed to be zero. Substituting these expressions into Eqs. 14-18 and 24, setting k = 0 for the planar electrode in the base case, using the boundary conditions  $c_a(z = -0.5) = c_{a0}$ , and  $\phi(z = 0.5) = 0$ , and starting with the initial condition  $h_c = 0.5$  gives the base case solutions

$$c_c = c_{a0} - j(z+0.5)/2, \tag{25}$$

$$\phi = e_0 + \ln\left(\frac{c_{a0} - j(z+0.5)/2}{c_{a0}}\right),\tag{26}$$

$$c_{a0} = 1 + j/4, h_c = 0.5 - jt, e_0 = \ln\left(\frac{1+j/4}{1-j/4}\right),$$
(27)

where  $j = \frac{JL}{FD_cC_0}$ .

Using a no slip boundary condition at the counter electrode gives

$$\tilde{v}(-0.5) = 0.$$
 (28)

A no slip boundary condition at the metal electrode gives

$$\tilde{v}(\tilde{h_c}) = 0, \tag{29}$$

for Poiseuille flow and

$$\tilde{v}(\tilde{h_c}) = 2, \tag{30}$$

for Couette flow.

Using these boundary conditions leads us to the following solutions

$$v = 1.5 - 6z^2, \tag{31}$$

and

$$v = 2z + 1, \tag{32}$$

for Poiseuille and Couette flows. respectively.

Figures 2a, 2b, and 2c show the concentration, electrostatic potential, and electric field profiles at 2 different electrostatic potentials using the parameters for a lithium metal cell listed in Tab. 1. The base case solutions are independent of flow rate because the concentration and velocity profiles are assumed to be fully developed. While the concentration and electrostatic potential decrease from the positive electrode to the metal electrode, the electric field increases to its maximum at the negative electrode. Higher electrostatic potential implies higher current which requires higher electric field and concentration gradient [22]. The current density depends on applied electrostatic potential as shown in Fig. 3. As the applied electrostatic potential increases, current density also increases.

#### 4. Stability analysis

To determine whether the flat deposition of the base case is stable, we perturb the metal surface with an infinitesimally small sinusoid

$$\tilde{h_c} = h_c + h'_c exp(\sigma t) exp(ikx),$$
(33)

where k,  $h'_c$  and  $\sigma$  are the non-dimensional wavenumber, non-dimensional amplitude, and non-dimensional exponential growth rate, respectively. The wavenumber equals  $2\pi/\lambda$  where  $\lambda$  is the wavelength. The perturbations grow and decay exponentially fast for  $\sigma > 0$  and  $\sigma < 0$ , respectively. Curvature of the perturbed surface concentrates the electric field lines and increases the ionic concentration gradient near the plating surface. Thus, plating on the perturbation tip is a function of curvature and wavenumber (k). We assume that no electrodeposition occurs on the positive electrode, so it is not perturbed. We assume that concentration, electrostatic potential, and current density are also sinusoidally perturbed:

$$\tilde{c_c} = c_c + c'_c exp(\sigma t) exp(ikx), \qquad (34)$$

$$\phi = \phi + \phi' exp(\sigma t) exp(ikx), \tag{35}$$

$$\tilde{j} = j + j' exp(\sigma t) exp(ikx), \qquad (36)$$

where  $c'_c$ ,  $\phi'$ , and j' are the non-dimensional perturbation amplitudes in cation concentration, electrostatic potential, and current density, respectively. Perturbation analysis of Eq. 23 gives

$$\frac{c_c'(0.5)}{c_c(0.5)} + \frac{1}{c_c(0.5)} \frac{dc_c}{dz}(0.5)h_c' + \phi'(0.5) + \frac{d\phi}{dz}(0.5)h_c' = -\beta h_c' k^2.$$
(37)

In an infinitesimally small region very close to the lithium metal electrode surface, v' = 0, where v' is the normal component of velocity perturbation. So, the normal component of anion flux has only diffusion and migration terms. Substituting v' = 0 and subtracting the base case from Eq. 17, and using electroneutrality gives  $\phi' = \frac{c'_e}{c_c}$ . This functional form is only valid in an infinitesimally small region close to the lithium metal electrode where v' = 0. Using this functional form for  $\phi'$  yields

$$\phi'(0.5) = \frac{c'_c(0.5)}{c_c(0.5)} \tag{38}$$

The electrolyte velocity is perturbed according to

$$\tilde{\mathbf{v}} = v\hat{\mathbf{i}} + v'\hat{\mathbf{k}}exp(\sigma t)exp(ikx) + u'\hat{\mathbf{i}}exp(\sigma t)exp(ikx).$$
(39)

Pressure in the electrolyte will also have first order sinusoidal perturbations given by

$$\tilde{p} = p + p' exp(\sigma t) exp(ikx).$$
(40)

Substituting Eqs. 39, and 40 in Eqs. 12, and 13 gives

$$iku' + \frac{dv'}{dz} = 0,$$
 (41)

$$-ikp' + Pe\left(\frac{d^2u'}{dz^2} - k^2u'\right) = 0,$$
(42)

$$-\frac{dp'}{dz} + Pe\left(\frac{d^2v'}{dz^2} - k^2v'\right) = 0.$$
(43)

No slip and no penetration at both electrodes provides boundary conditions

$$u'(-0.5) = 0,$$
 (44)  
 $v'(-0.5) = 0,$  (45)

$$v'(-0.5) = 0, (45)$$

$$v'(0.5 + h'_c) = 0. (46)$$

For Couette flow,

$$u'(0.5 + h'_c) = -2h'_c \tag{47}$$

and for Poiseuille flow,

$$u'(0.5 + h'_c) = 6h'_c. (48)$$

At the perturbed lithium metal electrode surface  $(z = 0.5 + h_c), u'$  is non-zero to satisfy the no slip boundary conditions. This is because, as per the base case, v(0.5) = 0, but at the perturbed lithium metal electrode surface  $(z = 0.5 + h'_c)$ , v is non-zero. Solving Eqs. 41-43, eliminating p' and using boundary conditions 44-46 gives u' and v'.

Eqs. 36 and 18 imply

$$\sigma h'_c = 2 \frac{dc'_c}{dz} (0.5 + h'_c) - Mv'(0.5 + h'_c)c_c(0.5 + h'_c).$$
(49)

Solving Eqs. 41-43, and 49 using the boundary conditions 44-46 and 37 produces perturbation growth rate as a function of wavenumber.

Figures 4 and 5 show the variation of non-dimensional perturbation growth rate as a function of non-dimensional wavenumber at a given electrostatic potential and various flow rates in the creeping flow regime for Poiseuille and Couette flows, respectively.

For a fixed charging electrostatic potential and current density, perturbation growth rate attains a maximum with increasing wavenumber and then reduces. This is due to the competing effects of enhanced concentration gradient at dendrite tips and large energy required for electrodeposition on curved surfaces. For wavenumbers higher than a critical wavenumber, the perturbation growth rate is negative, indicating stable plating.

In the creeping flow regime, increasing the flow rate reduces the perturbation growth rate, the critical wavenumber, and the wavenumber at which maximum perturbation growth rate is obtained. The parallel flow rates are very high compared to the Pe = 1 flow required for stable, dendrite-free plating with uniform normal flow [48]. This is expected because the stabilizing effect for normal flow

with porous electrodes comes from the increased contribution of advective flux at the Li metal electrode in the base case [48], whereas only the velocity perturbations contribute to stability in case of parallel flow. Also, unlike normal flows, creeping parallel flows cannot completely stabilize ( $\sigma < 0$  for all k > 0) electrodeposition.

Figure 6 shows the variation of  $\sigma$  with k for a fixed flow rate at two different charging electrostatic potentials for both Poiseuille and Couette flow. Higher charging electrostatic potentials implies higher charging current which leads to a larger dendrite growth rate. Fig. 4 shows that at both  $e_0 = 2$  and  $e_0 = 4$ , Poiseuille flow stabilizes electrodeposition better than Couette flow. This possibly arises from the larger magnitude of u' at the metal electrode surface for Poiseuille flow than for Couette flow, as is evident from Eqs. 47 and 48. Although v' = 0 at the lithium metal electrode surface, for both Poiseuille and Couette flow, larger u' at the lithium metal electrode implies larger v' near the lithium metal electrode surface. The stabilizing effect of flow mainly arises from the normal velocity perturbations v', so larger v' near the lithium metal electrode surface for Poiseuille flow implies lesser perturbation growth rate.

#### 5. Discussion

Parekh *et al.* [48, 49], have shown that normal flow towards a porous or perforated lithium metal electrode helps eliminate dendrites. Zheng *et al.* [51] experimentally show that dendrites in zinc electrodeposition on a rotating disk electrode can be eliminated at higher rotation rates. Thus, normal flow towards a non-porous metal electrode also can eliminate dendrites. This paper, for the first time, shows that creeping Poiseuille and Couette flows parallel to the electrode can significantly reduce dendrite growth. Since, electrolyte velocity can be represented by a combination of velocities normal and parallel to the metal electrode, creeping flow in general, helps stabilize or reduce the instabilities in plating. Increasing the flow rate beyond the creeping flow regime, however, may lead to increased dendrite growth as observed experimentally by Huang *et al.* [50].

We do not explicitly account for breakage and reformation of SEI. SEI breakage typically occurs due to large volume change associated with plating and stripping Li from under the SEI or excessive tensile stress at the dendrite tips. This can lead to inhomogeneities in the SEI layer, which can initiate dendrites. At the dendrite tips, SEI may fail under excessive tensile stress [2] which depends on curvature. For the sinusoidal perturbations that we consider in this study, the dendrite tip curvature is proportional to the amplitude and the square of the wavenumber. Parallel flows reduce the dendrite growth rate and shift maximum growth rate to smaller curvatures, so dendrite growth is slower and flatter, reducing the potential for SEI breakage.

Maraschky *et al.* have shown that transport through the SEI layer is an important factor that can affect the onset of dendrite growth in lithium metal batteries. The thickness of SEI layer is often very small compared to the interelectrode gap and hence any change of diffusion coefficient within the SEI layer would have a negligible effect. It is important to note that the linear stability analysis technique used in this paper is similar to the techniques used for studying ramified deposits of zinc, copper, and silver that do not have SEI. The origin of dendrite growth in such metals is a electrohydrodynamic instability [52]. Moreover, zinc dendrites grow only at current densities larger than the limiting current density [51].

Typically pouch cells have a porous separator to electronically insulate the two electrodes from each other and this will impede the proposed electrolyte flow and ionic diffusion. For both Poiseuille and Couette flow, ion diffusion would be slowed by the separator but this can be accommodated within the current model by reducing the diffusivity constant.

For Poiseuille flow, the presence of a porous separator increases the pressure required to pump the electrolyte through the inter-electrode gap but the flow profile is unchanged. For Couette flow, the flow profile depends on whether the separator is shearing or translating relative to one of the electrodes. For a porous separator that fills almost the entire gap, the velocity profile would be unchanged but the force required to move the electrode would increase. However, for a separator that is moving as a rigid body, the velocity profile would be different.

#### 6. Conclusion

This paper shows that creeping electrolyte flow parallel to the lithium metal electrode can reduce dendrite growth. Dendrites will grow at a slower rate and be flatter, so they will be less likely to penetrate the separator or fracture the SEI. Parallel flows must be several orders of magnitude higher than normal flows for similar reduction in instability. It is also not possible to completely stabilize electrodeposition with creeping flow parallel to the lithium metal electrode. For the same average flow rate, Poiseuille flow can be upto two times more stabilizing than Couette flow.

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Figure 1: Schematic diagram of the lithium metal cell with (a) Poiseuille flow and (b) Couette flow.



Figure 3: Electrostatic potential versus current

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Figure 4: **Poiseuille flow:** Non-dimensional growth rate versus non-dimensional wavenumber at  $e_0 = 1$ , Pe = 0 (bold), Pe = 3E3 (dashed), Pe = 3E4 (dotted)



Figure 5: Couette flow: Non-dimensional growth rate versus non-dimensional wavenumber at  $e_0 = 1$ , Pe = 0 (bold), Pe = 3E3 (dashed), Pe = 3E4 (dotted)





Figure 6: Non-dimensional growth rate versus non-dimensional wavenumber at Pe = 3E4,  $e_0 = 2$  for Poiseuille flow (solid),  $e_0 = 2$  for Couette flow (dotted),  $e_0 = 4$  for Poiseuille flow (dashed), and  $e_0 = 4$  for Couette flow (dashed-dotted).

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Property	Value
$C_0$	1 M
$T_0$	300 K
L	$20 \ \mu m$
$D_a$	$4E - 10 \ m^2 s^{-1} \ [22]$
$D_c$	$10^{-11} m^2 s^{-1} [14]$
F	$96500 \ Cmol^{-1}$
R	$8.314 \ Jmol^{-1}K^{-1}$
$\gamma$	$1.716 \ Nm^{-1} \ [22]$
$\mu_c$	$D_c/(RT_0) \ mols^{-1}N^{-1}$
$\mu_a$	$D_a/(RT_0) \ mols^{-1}N^{-1}$
$v_m$	$1.33E - 5 \ molm^{-3}$ [22]
$\mu$	4.152E - 3 Pas
$\rho$	$1300 \ kgm^{-3}$

Table 1: Parameters used in the model