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Permalink

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Journal

Journal of The Electrochemical Society, 166(15)

ISSN

0013-4651

Authors

Zhang, Xin
Wang, Q Jane
Harrison, Katharine L
[et al.](#)

Publication Date

2019

DOI

10.1149/2.0701914jes

Peer reviewed

Rethinking How External Pressure Can Suppress Dendrites in Lithium Metal Batteries

Xin Zhang¹, Q. Jane Wang^{1,*}, Katharine L. Harrison^{2a}, Katherine Jungjohann^{2b},
Brad L. Boyce^{2b}, Peter M. Attia³, Stephen J. Harris^{4,*}

1. Mechanical Engineering Dept., Northwestern University, Evanston, IL 60208
2. Nanoscale Sciences and ^aCenter for Integrated Nanotechnologies, ^bSandia National Laboratories, Albuquerque, New Mexico, 87123
3. Dept. of Materials Science and Engineering, Stanford University, Stanford, CA 94305
4. Materials Science Div., Lawrence Berkeley National Lab, Berkeley, CA 94720

*Corresponding Authors: Q. Jane Wang, qwang@northwestern.edu, Stephen J. Harris, sjharris@lbl.gov

ABSTRACT

Lithium metal anodes are critical enablers for high energy density next generation batteries, but they suffer from poor morphology control and parasitic reactions. Recent experiments have shown that an external packing force on Li metal batteries with liquid electrolytes extends their lifetimes by inhibiting the growth of dendritic structures during Li deposition. However, the mechanisms by which pressure affects dendrite formation and growth have not been fully elucidated. For example, beneficial pressure effects have been observed even for thin polymer separators whose mechanical properties are not expected to be able to hinder dendrite growth. In this paper we offer an explanation for how dendrite growth can be inhibited when the cell is subjected to an external load, even with a relatively soft separator. We carried out a three-dimensional contact mechanics model based on the semi-analytical method for tracking Li surface and sub-surface stresses for a pouch cell architecture with realistically (micron-scale) rough electrode surfaces subjected to a packing force. Our work shows that the picture normally used to understand dendrite penetration, where micron-scale Li metal protrusions press conformally against a separator, is oversimplified. At the larger, sub-mm scales studied here, contact between the Li metal and the separator/cathode is highly heterogeneous and far from conformal for surfaces with realistic roughness: the load is carried at a relatively small number of the tallest asperities, while the rest of the Li surface feels no force at all. Yet, dendrite growth is suppressed over the entire Li surface. To explain this observation, we suggest that (1) local contact stresses can be high enough (tens of MPa) at the peaks of Li protrusions (incipient dendrites) so that incremental Li^+ ions avoid plating there; and (2) creep ensures that Li protrusions are gradually flattened. These mechanisms cannot be captured in micron-scale analyses of dendrite growth.

1. INTRODUCTION

Using lithium (Li) metal anodes is a focus of next-generation batteries due to their high capacity [1-3]. However, the development of Li-metal batteries with liquid electrolytes, the focus of this work, has encountered a number of problems [4-6], such as loss of active Li (loss of capacity) as the Li reacts with the (liquid) electrolyte; and formation and growth of Li protrusions (commonly referred to as dendrites), which results in “dead” Li. Li protrusions can also penetrate through the separator and cause a short circuit [3, 7-11], potentially resulting in a fire [12].

A number of experimental observations [5, 13-16] have shown that applying an external mechanical force on a Li metal pouch cell with a liquid electrolyte can inhibit dendrite growth, thereby reducing capacity loss and improving safety. To understand this behavior, analytical and numerical studies have been undertaken to describe the influence of local mechanical stresses on dendrite initiation and growth, including phase field models[17, 18], which study dynamics at the interfaces between the electrolyte and dendrites; surface-tension models [19-22], which study the conditions for dendrite initiation and growth velocity in liquid electrolytes; Brownian statistical models [23-26], which analyze the morphology evolution of deposited species; and the Chazalviel electromigration-limited model [9, 27-29], which considers that dendrite initiation is induced by an electrodeposition process.

The most widely used model for understanding how mechanical forces inhibit dendrite growth is that proposed by Monroe and Newman [20, 30]. This model assumes that a growing Li protrusion (incipient dendrite) under a given current density pushes against a polymer electrolyte or separator such that they are in perfect (conformal) contact, and it calculates minimum mechanical properties of the polymer such that dendrites cannot penetrate through it. Srinivasan et al. [31] have recently proposed an extension of this model and applied it to soft gel, polymer, and ceramic electrolytes. The model, which focuses on the shear strength of the electrolyte, has met with only limited success. For example, ceramic solid electrolytes, with sufficient shear modulus to prevent dendrites according to the model, suffer from defects and grain boundaries that are susceptible to dendrite penetration,

demonstrating the importance of considering real rather than ideal model systems. Furthermore, even glass solid electrolytes with no grain boundaries suffer from dendrite penetration [32-36]. Similarly, dendrite suppression with soft separators under an external load[16] would also seem to violate its predictions.

Most of the work mentioned above has focused on the influence of local mechanical stresses at the particle or micron scale, an understanding of which is clearly necessary for analyzing growth of Li protrusions. However, because of Li metal's modest yield strength and tendency to creep, its mechanical behavior cannot be fully captured with a micron- or sub-micron-scale analysis. To our knowledge, there have been no investigations of the effects of spatial heterogeneity [10, 37] on the mechanical contact stresses that are generated when macroscopic external pressures are applied to electrodes with realistic (rough at the micron-scale) surfaces. As we show below, stresses caused by micron-sized asperities at one location can affect the stress field over thousands of square microns.

Theoretical work aimed at accounting for spatial heterogeneity in pressure must consider the nature of the cell architecture, including modeling the contacts for a realistically rough cathode. (The cathode porosity, generally near 30% for commercial cathodes, ensures that its surface is rough.) A significant level of roughness is inevitable on the Li metal as well[11, 16, 38, 39], which can add to the complexity of the stress field.

In this work, we ask how an external pressure can inhibit dendrite growth in lithium metal batteries, even in the absence of a stiff polymer electrolyte or separator. Our approach is to model the mechanics of a single electrode pair under conditions similar to those used by Dahn et al [16]. In those experiments, a Cu foil current collector supported by a rigid structure served as the negative electrode upon which Li metal was deposited during the charge step. We used that work to guide our modeling because the experiment was well characterized and because it showed a beneficial effect of pressure, even for a thin separator whose mechanical properties would not have been expected[20, 31] to inhibit dendrite growth according to the Monroe-Newman model.

We consider the Li-separator and cathode-separator interfaces to be contact interfaces (where stresses are calculated), while the interface between the Cu foil and the Li metal is considered as an internal material interface. Contact interfaces involving rough surfaces can be modeled by using semi-analytical methods (SAMs) built on core analytical solutions and supported by efficient numerical approaches, including the conjugate gradient method (CGM) [40] and the fast Fourier transform (FFT) method [41, 42]. SAMs have been used for solving numerous contact problems, such as magnetoelastic contacts [43-45], elastoplastic contacts [46-49], and contact involving rough surfaces [50-53]. Derivation of the core analytical solutions, in terms of displacements and stresses, is essential for developing a contact model and simulating the surface interactions in such structures. Here we use a SAM-based analysis to model a single electrode pair. By carrying out the analysis in 3D, we can properly capture long-range effects of rough surfaces.

We emphasize that these are mechanics calculations carried out at the sub-mm scale. We are not trying to account for non-mechanical (*e.g.*, electrical, chemical, transport) effects on dendrite formation; or for *any* effects—mechanical or otherwise—at the 1-micron scale or smaller. Furthermore, we are not investigating how dendrites penetrate separators; we are focusing on understanding why an external pressure can inhibit dendrite growth in the absence of a stiff separator.

2. FORMULATION FOR 3D CONTACTS OF LI-SEPARATOR-CATHODE INTERFACES

2.1 Problem description

Figure 1 illustrates the 3D structure of a Li metal pouch cell with a single electrode pair. A liquid electrolyte fills the pores, shown in white. We assume that, since there is essentially 100% pore connectivity in commercial electrodes[54] and separators[55], excess electrolyte can be locally squeezed out under any local load—ultimately, to the edges of the pouch, as is the case for gases [56]—so that for purposes of these calculations we assign a zero modulus to these regions and ignore their contribution to the local pressure, even though the pores always remain filled with electrolyte. The Poiseuille equation predicts that for a pressure differential of 1 atm, an electrolyte

viscosity of 2 cp[57], and a pore diameter of 0.1 μm , electrolyte can flow through the electrode or the separator in less than 1 second, supporting this assumption.

Rectangular Cartesian coordinates (x, y, z_{Li}) , (x, y, z_{Cath}) and (x, y, z_{Cu}) are introduced with the positive z_{Li} axis oriented into the depth direction (or the vertical direction) of the Li metal, the positive z_{Cath} axis oriented into that of the cathode, and the positive z_{Cu} axis oriented into that of the copper, as shown in Figure 1. Such a contact problem is completely general subject to the following considerations:

- During the charge cycle, the thickness of the Li metal increases from 2 μm to 18 μm , corresponding to an incremental 3.3 mAh[16]. Simultaneously, the external load increases. We treat the copper foil plus its supporting structure as a half space, where any effects from the far side of the supporting structure is ignored. The elastic modulus of the copper foil on the rigid support is taken to be that of copper.
- The separator is treated as continuous body whose only important property is its elasticity. (See below for additional discussion.)
- The cathode is treated as a rigid body because the elastic moduli for all commercial cathode particles are much larger (> 100 GPa) than those of the contact partners—a polypropylene separator (~ 0.22 GPa[58, 59]) and Li metal. The binder can be relatively soft, but we assume that the calendaring process, which occurs at very high pressures before assembly, has made the cathode much more rigid (jammed) in compression than the separator and the Li metal. (Calendaring, a process carried out for commercial electrodes, can reduce the porosity by up to a factor of 2[60], with the compressive forces used in calendaring limited by the fracture strength of the particles[61, 62].) Our analysis assumes a calendared electrode in order to make it relevant to real-world systems.
- The lengths of the system, L_c in the x and y directions, are taken to be infinite relative to the separator thickness h_{sep} (13.5 μm).

2.2 Interfacial conditions

2.2.1 Li-Separator (Li-Sep) interfacial conditions.

We introduce a 3D rough surface profile $s_{Li}(x, y)$ of the Li as a function of lateral coordinate variables x and y . The Li-Sep interfacial condition (i.e. $z_{Li} = z_{Sep} = 0$) for the vertical displacements can be expressed as,

$$u_{Li,z}(x, y, 0) + u_{Sep,z}(x, y, 0) = -s_{Li}(x, y) + g_{Li-Sep}(x, y) + \delta_{Li-Sep}, \quad (1)$$

where $u_{Li,z}(x, y, 0)$ and $u_{Sep,z}(x, y, 0)$ are the surface vertical displacement components of the Li and the separator, respectively, $g_{Li-Sep}(x, y)$ is the gap between the Li and the separator, and δ_{Li-Sep} is the relative rigid-body motion between Li and the separator.

Due to the roughness of the Li surface, the contact and non-contact regions between Li-Sep interface are complementary to each other, in which the contact region Γ_{Li-Sep} is subjected to contact pressure p (in the Li-Sep interface). Hence, the contact condition for pressure distributions can be written as,

$$\begin{aligned} p(x, y) > 0 \ \& \ g_{Li-Sep}(x, y) = 0, \ \forall (x, y) \in \Gamma_{Li-Sep}, \\ p(x, y) = 0 \ \& \ g_{Li-Sep}(x, y) > 0, \ \forall (x, y) \notin \Gamma_{Li-Sep}, \end{aligned} \quad (2)$$

where the overall mechanical equilibrium condition for the packing force W in the modeled region, must satisfy

$$\int_{\Gamma_{Li-Sep}} p(x, y) dx dy = W. \quad (3)$$

The surface stresses in the Li and separator at the Li-Sep interface (i.e. $z_{Li} = z_{Sep} = 0$) can be written as,

$$\sigma_{Li,zx}(x, y, 0) = 0, \ \sigma_{Li,zy}(x, y, 0) = 0, \ \sigma_{Li,zz}(x, y, 0) = -p(x, y), \quad (4)$$

$$\sigma_{Sep,zx}(x, y, 0) = 0, \ \sigma_{Sep,zy}(x, y, 0) = 0, \ \sigma_{Sep,zz}(x, y, 0) = -p(x, y), \quad (5)$$

where $\sigma_{zx}(x, y, 0)$ and $\sigma_{zy}(x, y, 0)$ are the surface shear stress components, and $\sigma_{zz}(x, y, 0)$ is the surface normal stress.

2.2.2 Separator-Cathode interfacial conditions.

Surface roughness was measured for a commercial LiFePO₄ (LFP) cathode harvested from a dry A123 20Ah pouch cell using a Bruker Dektak XT Stylus Profilometer. We take this surface to be representative of commercial, calendered cathodes. A 1000 μ m x 1000 μ m region was interrogated with a 1 μ m spacing,

averaging over any structures at the sub-micron scale in order to study forces at the sub-mm scale. The surface profile is considered as a 3D function of lateral coordinate variables x and y , *i.e.* $s_{Cath}(x, y)$. In the presence of a packing force W , the cathode surface asperities penetrate into the separator, deforming it. The vertical displacement $u_{Sep,z}$ of the separator at the Sep-Cath interface (*i.e.* $z_{Sep} = h_{Sep}$) can be written as,

$$u_{Sep,z}(x, y, h_{Sep}) = -s_{Cath}(x, y) + g_{Sep-Cath}(x, y) + \delta_{Sep-Cath}, \quad (6)$$

where $g_{Sep-Cath}(x, y)$ is the gap between the separator and the cathode, and $\delta_{Sep-Cath}$ is the relative rigid-body motion between the separator and cathode.

Due to the roughness of the cathode surface, contact and non-contact regions in the Sep-Cath interface are complementary, where the contact region $\Gamma_{Sep-Cath}$ is subjected to deformation constraints q (caused by cathode asperities). Hence, the contact condition for deformation constraints q can be written as,

$$\begin{aligned} q(x, y) = s_{Cath}(x, y) - \delta_{Sep-Cath} \quad \& \quad g_{Sep-Cath}(x, y) = 0, \quad \forall (x, y) \in \Gamma_{Sep-Cath}, \\ q(x, y) = 0 \quad \& \quad g_{Sep-Cath}(x, y) > 0, \quad \forall (x, y) \notin \Gamma_{Sep-Cath}. \end{aligned} \quad (7)$$

Due to the lack of bonding at the Sep-Cath interface (*i.e.* $z_{Sep} = h_{Sep}$), the shear stresses on the separator at the Sep-Cath interface vanish,

$$\begin{aligned} \sigma_{Sep,zx}(x, y, h_{Sep}) &= 0, \\ \sigma_{Sep,zy}(x, y, h_{Sep}) &= 0. \end{aligned} \quad (8)$$

The overall mechanical equilibrium condition for the normal stress at the Sep-Cath interface must satisfy

$$\int_{\Gamma_{Sep-Cath}} |\sigma_{Sep,zz}(x, y, h_{Sep})| dx dy = W. \quad (9)$$

2.2.3 Li-Cu interfacial conditions.

Following the experiments of Dahn et al.[16], we assume an initial 2 μm thick Li film that is perfectly bonded to the Cu; Li metal is added during the charge step. Displacements at the Li-Cu interface (*i.e.* $z_{Li} = h_{Li}$ and $z_{Cu} = 0$) are

$$\begin{aligned} u_{Li,x}(x, y, h_{Li}) &= u_{Cu,x}(x, y, 0), \\ u_{Li,y}(x, y, h_{Li}) &= u_{Cu,y}(x, y, 0), \\ u_{Li,z}(x, y, h_{Li}) &= u_{Cu,z}(x, y, 0), \end{aligned} \quad (10)$$

2.3 Displacement and stress solutions

The boundary-value problem described by Eqs. (1-10) can be handled by a fast Fourier transform (FFT)-based numerical process, if the Fourier-transformed solutions of displacements and stresses at the Cu-Li and the separator-rigid cathode systems are analytically solvable.

The Fourier-transformed elastic displacements and stress solutions for the Cu-Li metal system can be found in [42], also provided in the Supplementary Information S1. The Fourier transformed displacements and stresses for the separator-rigid cathode system can be obtained starting from the Lamé-Navier equations using the Papkovitch–Neuber potentials and by considering the interfacial conditions Eqs. (5-8). Solutions and derivation details are also presented in the Supplementary Information S2.

2.4 FFT-based elastic-perfectly-plastic contact modeling

In the FFT-based numerical process, the contact information (*e.g.* pressure, contact stress) and profiles of the Li and cathode surfaces are taken as discrete data from an infinite sequence along the x and y directions. A representative portion, $L_c \times L_c$, in the $x - y$ plane is selected as the physical domain, assuming that $L_c \times L_c$ is one period of the whole structure, as shown in Figure 2. This means the overall information, including surface features, loading conditions, and mechanical behaviors, are taken as periodically repeated from those in the representative $L_c \times L_c$.

To operate the FFT-based algorithm, the solutions in section 2.3 need to be obtained in the form of frequency response functions (FRFs) by the continuous convolution and FFT (CC-FT) algorithm [63]. The details of CC-FT algorithm are given in the Supplementary Information S3. The contact simulation was written in Fortran, involving the CC-FT algorithm [63] and the conjugate gradient method (CGM) [40]. The details of the contact algorithm and a flow diagram are given in the Supplementary Information S4.

In most elastic-perfectly-plastic contact models involving rough surfaces, when yield occurs at the surface of materials, we can simply truncate the contact pressure peaks at the material hardness, which is about 3 times the yield strength σ_Y . As shown in [64], the accuracy of the pressure calculation when using such a truncation

treatment increases with decreasing material yield strength, indicating that truncation for Li, which has a low yield strength, should be acceptably accurate.

In the following numerical computation, the physical representative domain of $L_c \times L_c$ was discretized with a 400×400 subset grid in the x and y directions, where the periodic length of the modeled interface is set to $L_c = 400 \mu\text{m}$, and the spatial resolution is $1 \mu\text{m}$. At this size, the major features of the surface are included, and CPU times for these 3D calculations are reasonable. We assume that the Li is elastic-perfectly-plastic for these low to moderate strain rates[65].

To calculate the Li subsurface stresses, the Li was discretized with 200 grid points in the z direction. The spacing of these grid points depended on the subsurface stress gradients. The macroscopic external pressure is calculated by $P = W/(L_c \times L_c)$ where W is the total packing force applicable to this representative domain.

Experiment shows that under low pressures, plated Li can be porous [13], while deposition at higher pressure can lead to a denser material. In the Dahn et al. experiments [16], run at a current density of 0.6 mA/cm^2 , a Li metal thickness increase of $\sim 250 \mu\text{m}$ was measured during deposition in their multi-electrode-pair cell, compared to a calculated thickness increase of $254 \mu\text{m}$. This calculation explicitly assumed that the plated Li was fully dense at 0.534 g/cm^3 . (No account was taken of any volume change in their cathode, but we have measured the crystallographic volume change of their cathode material to be less than 1% upon delithiation[66].) The agreement, to within about 2% between the calculated and measured thickness increase, argues that the plated Li in their high-pressure experiments was reasonably close to fully dense.

There is considerable discussion in the literature over the appropriate value to use for the yield stress of Li metal. Low values for bulk Li have been measured [67, 68] in the range of 0.41 to 0.89 MPa. However, more recent work has shown that the yield stress depends strongly on the size of the Li structure [69, 70]. Images from deposition at high pressure [16] show Li structures roughly in the range 1 to $10 \mu\text{m}$, corresponding to yield stress values [69] in the range of 10 to 100 MPa. Therefore,

we have performed calculations for the three values, 0.66, 10 and 100 MPa, shown in Table 1.

3. RESULTS

3.1 Model properties and verification

The cathode surface profile is shown in Figure 3(a). As expected, the measured roughness of this commercial (calendered) electrode is low. The surface roughness of Li metal varies dramatically[38], within each cycle and from cycle to cycle. Rather than trying to capture the full range of possible Li surfaces in our calculations, we will consider 2 cases: a perfectly smooth Li surface and a surface with a sinusoidal form, $s_{Li}(x, y) = A_0 \cos(2\pi x/\lambda) \cos(2\pi y/\lambda)$ where we have taken $A_0 = 1.0\mu\text{m}$ and $\lambda = 40\mu\text{m}$, Figure 3(b), as an example. Each peak may be considered as a model Li protrusion (incipient dendrite). Although such an assumption is clearly idealized, we believe that by analyzing simple surfaces, we can obtain a semi-quantitative understanding of local stresses and their distributions for a range of realistic conditions.

When the separator thickness h_{sep} approaches infinity, the coefficients in Eq. Eq. (S2.16) become $C = -1/\alpha$, $\bar{C} = 0$, $D = (1 - 2\nu_{sep})/\alpha^2$, and $\bar{D} = 0$. Therefore, the Fourier-transformed displacement in Eq. Eq. (S2.8) yields $\tilde{u}_{sep,z} = (1 - \nu_{sep})\tilde{p}/(\mu_{sep}\alpha)$, which is identical to the classical solutions to a half-space given in [41], confirming that the Fourier-transformed solutions with their coefficients Eqs. (S2.6-S2.14, S2.16) are correctly calculated for this case. In order to further verify the CC-FT based numerical modeling, we compare the term, $\delta_{sep-cath} - u_{sep,z}$, at the separator-cathode interface with the cathode surface profile, s_{cath} , of Figure 3(a), for the problem of a large macroscopic external pressure $P = 1,585\text{kPa}$, a Li thickness $h_{Li} = 18\mu\text{m}$, and the Li surface profile s_{Li} of Figure 3(b). For such a large external pressure, the calculation shows no gap between the separator and the cathode. As shown in Figure 3(c), $\delta_{sep-cath} - u_{sep,z}$ calculated from the present numerical model agrees well with the surface profile s_{cath} , consistent with the interfacial condition given in Eq. (6).

3.2 Contact stress calculation

3.2.1 Smooth Li

Figures 4 and 5 plot the Li surface stress contours ($x - y$ section), and Li subsurface von Mises stress contours ($y - z$ section) for a smooth Li surface with yield strengths of $\sigma_Y = 0.66\text{MPa}$, 10MPa and 100MPa , corresponding to Li structures of “very large,” $\sim 10\mu\text{m}$, and $\sim 1\mu\text{m}$, respectively [69]. In the experiments[16], the packing pressure increased with Li thickness h_{Li} , and we modeled 3 cases taken from their Table 1, where $(P, h_{Li}) = (744\text{ kPa}, 2\mu\text{m})$, $(1,205\text{ kPa}, 11\mu\text{m})$, and $(1,585\text{ kPa}, 18\mu\text{m})$. Our calculation results show no gaps between the separator and the cathode at these very high pressures, which means the surfaces are conformal, and the entire separator-cathode interface carries load. On the other hand, the Li-separator interface is not conformal. Red, green, and yellow regions in Figures 4(a) and 5(a) show areas where there is contact between the separator and the Li, while the blue regions denote regions where the stress is zero (no contact). Thus, all of the load is supported by taller asperities. Figure 5(c) shows the gap thickness between the Li and the separator where white regions show where the gap is zero, denoting the contact areas. The maximum gap is between 0.5 and 0.6 microns for the case of $(P, h_{Li}) = (744\text{kPa}, 2\mu\text{m})$. The gap volumes are 2×10^4 , 1.3×10^4 , and $9 \times 10^3 \mu\text{m}^3$, for $(P, h_{Li}) = (744\text{kPa}, 2\mu\text{m})$, $(1,205\text{kPa}, 11\mu\text{m})$, and $(1,585\text{kPa}, 18\mu\text{m})$, respectively. The surface stress reaches its maximum value of 1.98MPa , which is $3\sigma_Y$, at most contact points. The von Mises stress values indicate that subsurface regions below the contact points are plastically deformed.

For a yield strength of $\sigma_Y = 10\text{MPa}$, corresponding to Li structures near $10\mu\text{m}$ [69], the fraction of the area in contact A_p is reduced because the larger yield strength allows contact asperities to carry more load. The peak surface stress for this case is 25MPa , below its maximum value of $3\sigma_Y = 30\text{MPa}$. The peak von Mises stress is 6.66MPa , lower than yield strength, so that no plastic yielding occurs inside the Li metal. The stresses for a yield strength of $\sigma_Y = 100\text{MPa}$ ($1\mu\text{m}$ Li structures) are identical to those for $\sigma_Y = 10\text{MPa}$.

3.2.2 Rough Li

Figures 6, 7, and 8 plot the Li surface stress contours ($x - y$ section), and Li subsurface von Mises stress contours ($y - z$ section) for the “rough” (*i.e.*, sinusoidal with an amplitude of $1 \mu\text{m}$) Li surface of Figure 3(b). For the low yield strength case, $\sigma_Y = 0.66\text{MPa}$, the surface stress either reaches its maximum value of 1.98MPa or is 0. Most of the subsurface Li below the contact points is plastically deformed, highlighted by red regions. The surface and sub-surface stresses for $\sigma_Y = 10\text{MPa}$, Figure 7, are plastic only near some of the contact points. For $\sigma_Y = 100\text{MPa}$, Figure 8, the contact points can carry larger loads without plasticity. The largest surface stress is 40MPa , too low for plastic deformation. These results show that Li protrusions (incipient dendrites) are exposed to significant compressive contact stresses (up to tens of MPa) by the time they are only $1 \mu\text{m}$ tall.

Figure 9 shows how the smooth (a) and sinusoidal (b) Li surfaces deform against the cathode for external pressures of $P = 744, 1,205, \text{ and } 1,585 \text{ kPa}$. The cathode surface profile along the y direction (for $x = 0$) from Figure 3(a) is also plotted as a dotted line for comparison. For a smooth Li surface, asperity peaks of the rigid cathode surface penetrate into the separator, as described by interfacial condition Eq. (6). As expected, corresponding convex crests appear on the separator surface at the Li-separator interface. For the sinusoidal surface, direct contacts between the Li asperities and separator become stronger, so that the Li stress distribution is dominated by details of the Li surface profile for this example.

3.2.3 Lighter loads

The previous calculation results show that for an external pressure of $P = 744 \text{ kPa}$ or greater, the cathode surface is completely conformal with the soft separator. Figure 10(a) plots the surface contact stresses on Li for lighter external pressures of $P = 100, 200, \text{ and } 300 \text{ kPa}$, and a Li thickness of $h_{Li} = 10 \mu\text{m}$. We have preliminary experimental data showing that suppression of Li protrusions may occur in this pressure range. For such pressures, which are of more practical interest, there are gaps between the separator and cathode, shown in red, green, and yellow regions in Figure 10(b). Separator-cathode gap maps for the rough Li case are identical to those

for smooth Li case. Figure 11 plots the fraction of the area in contact as a function of the external pressure, for both the Li-separator and separator-cathode interfaces. When the external pressure is 500kPa, the whole cathode interface is in contact with the separator, while only 12.6% of the Li is in contact with the separator.

4. DISCUSSION

We first point out two important properties of the separator. (1) Although we are treating the separator as a homogeneous solid, in fact it is highly heterogeneous, with pores that penetrate through it. The smaller in-plane dimension of the pores is typically about 100 nm[55], ~2 orders of magnitude smaller than the contact regions seen in Figure 5. Thus, from a mechanical point of view, treating the separator as homogeneous is a reasonable approximation at the scale of interest here. (2) Assuming that all of the separator pores are filled with electrolyte, Li⁺ ions can diffuse through the separator for purposes of plating or stripping just as readily in contact regions as in non-contact regions (but see discussion below).

Numerous factors, including external pressure, charging rate, separator properties, electrolyte chemistry, and temperature can impact the growth of Li protrusions (incipient dendrites) during charging. In the absence of constraints, protrusions tend to grow for electrical and transport reasons, a positive feedback process that can lead to dendrite growth[11]. In this work we focus on the mechanical aspects at larger (sub-mm) scales. One effect of these macroscale interactions is to distribute the load in complex patterns that depend on the surface roughness of the electrodes. These stress fields do depend on mechanical properties of the separator, but in a manner different from that discussed by Monroe and Newman[20, 30, 31].

Our analysis at sub-mm length scales shows that even under high packing forces, most of the Li metal surface is not in contact with the separator (unless we use a presumably unrealistically low[69, 70] Li yield strength of < 1 MPa). We note that previous work has assumed, implicitly or explicitly, that contact between the separator and the lithium metal is conformal, so that any protrusion that starts to form would be

subject to being “squashed” by is an extremely stiff separator. Whatever the validity of this picture at micron or sub-micron scales, our results indicate that the mechanics involved in pressurizing a Li metal cell should also take larger scales into account.

The primary question we must ask with respect to our analysis is: In the absence of a stiff separator[20], and in the absence of physical contact over most of the Li surface (Figure 5), how can we understand the experimental observation that an external pressure can impede growth of Li protrusions over the full surface? We will offer two hypotheses that may, singly or in combination, explain the observations. We will also propose possible experimental tests of these hypotheses.

4.1 Asperities

During the charging step, a total of 15.9 μm of Li was deposited on a 2 μm thick Li metal film[16]. Our calculations show that stresses at asperity contacts can exceed the average (macroscale) pressure by as much as 2 orders of magnitude, if we use the recent measurements for the yield strength[69, 70]. We hypothesize that there will be a tendency for Li ions to avoid plating in regions with such high stresses because an incremental Li atom deposited on the surface of a region under load is at higher energy than one deposited on a surface that is not feeling any load. In general, depositing on the regions that are supporting the external load requires local $P\Delta V$ mechanical work to lift the cathode by 15.9 microns[71]. These processes can lead to local deposition overpotentials on the order of several mV at local stresses of tens of MPa[36]. For this reason, we suggest that there will be a tendency to plate in regions of lower stress, ultimately allowing the most-stressed regions to partially unload. This process will tend to homogenize the stress field and flatten the Li, but only until the stress effects at asperities are small compared to effects of electrochemistry and transport [11], at which point this mechanism will no longer operate. Similarly, new protrusions may form and grow during plating, leading to new asperity contacts, until the stresses there become high enough so that plating moves elsewhere. This picture differs qualitatively from the Monroe-Newman model in that we are not focusing on properties of the separator that are needed to prevent dendrite growth, and we are not specifying a particular local current density. Instead,

we are focusing on longer-range heterogeneity in local contact stresses that encourages a more uniform Li plating.

We next address the possibility, ignored up to this point, that protrusions can grow as nanoscale dendrites through the separator pores. There is evidence that at these modest current densities (well below the limiting current), dendrite growth through nanoscale pores does not occur. Monroe and Newman's Figure 12 [20] shows that the initial dendrite radius is around 0.4 microns at the limiting current and larger than 1 micron at lower currents, compared to a pore size of 0.1 microns in the separator. Supporting their calculation, TEM images show[14] that incipient dendrites quickly attain a tip radius of curvature greater than 1 micron. Cui et al[72] also found that Li deposited directly under a separator has a large radius of curvature. Additionally, Bazant et al[11] showed that the tips of mossy lithium, the form that grows at low current densities, have large radii of curvature. Most important, they showed that mossy dendrites do not penetrate small pores, although their work did not involve any external pressure. In order to test our asperity picture, we suggest performing a ^6Li - ^7Li isotope experiment using TOF-SIMS[73, 74], where ^6Li is deposited under pressure on a ^7Li substrate. To the extent that asperity contact stress plays a role and that separator pores can be ignored, we should see an initial (before all of the gaps have been filled) patchy spatial distribution of ^6Li and ^7Li that statistically resembles a contact stress map analogous to Figure 5.

4.2 Creep of Li

It has recently been demonstrated[65, 75, 76] that creep plays a critical role in understanding the mechanics of Li metal. Unfortunately for the purposes of our analysis, most creep work has examined more-or-less pure Li metal[65, 70, 75, 76]. This has a different overall composition from the Li that is plated in an electrochemical environment, which incorporates significant amounts of SEI. Because the presence of stiff SEI could change the mechanical properties of Li, we are not convinced that it is useful at this time for us to carry out quantitative calculations involving creep of electrodeposited Li.

Nevertheless, we expect, qualitatively, that creep can play an essential role in

determining Li morphology, especially at long times. Once a mechanical situation such as that shown in Figure 5 is created, Li metal will begin to creep away from regions of high stress to regions of low stress during intervals (which could be many hours) such as after charging but before discharging, or even during a slow charge. Thus, creep will also tend to smooth out Li metal surfaces and homogenize stress over time scales on the order of hours[65]. This possibility can be tested by rapidly charging multiple cells under identical electrochemical and pressure conditions. The cells can then be held at rest, opened at appropriate intervals, and examined *ex-situ* to see if the Li surfaces flatten (relax) with time in a statistical sense.

In contrast to the Monroe-Newman model, we do not specify a local (micron-scale) current density. Instead, our picture assumes that Li will plate wherever its energy is lowest. Since Li in asperity contact with even a soft separator is at relatively high energy, our picture says that Li will tend to plate elsewhere, while protrusions that are in contact with the separator will slowly melt away via creep. Thus, in our picture, specific mechanical properties of the separator, such as a high shear modulus ($\gg 1$ GPa[20, 36, 76]), are not required in order for dendrite growth to be inhibited, in agreement with observation [16]. These processes cannot be captured unless stress heterogeneity at greater than micron-scale is recognized.

4.3 Possible Additional Effects on Dendrite Growth

Experiment shows that growth of Li protrusions/dendrites depends on electrolyte chemistry[16, 72, 77, 78]. One possible contributing factor is that the relatively stiff SEI films could act as reinforcements for the plated Li, forming Li/SEI composites that have higher yield stresses and lower creep rates than pure Li, as suggested by the work of Cheng et al.[79]. If SEI mechanical properties are different for different electrolytes, we can rationalize the observed dependence on electrolyte chemistry.

The creep picture could provide a contributing factor for why dendrites are more likely to grow at high current densities, since if dendrite formation is fast compared to characteristic creep times, then creep cannot play its role.

4.4 Approximations, Assumptions, and Limitations

Our analysis is subject to a number of approximations, assumptions, and

limitations, foremost of which is that we are considering only static mechanical effects. We recognize that a dynamic analysis will ultimately be necessary, but we expect mainly quantitative changes, rather than qualitative changes, for such an analysis.

4.4.1 Viscoelastic and viscoplastic deformation of the separator

Viscoelastic and viscoplastic deformation of the nanoporous polypropylene separator may further enhance the effective flattening of the Li-separator interface and corresponding uniformity of stress state. This is because creep deformation of the separator might collapse the pore network, inhibiting ion transport through the separator while enhancing plating in contact-free or low-stress locations. Such an effect has been documented in conventional Li-ion batteries and has been suggested as a mechanism for mechanically-induced capacity fade [80, 81]. Indeed, scanning electron images of stress-induced separator pore collapse show that the collapse is spatially heterogeneous – an effect that may be attributable to the heterogeneous asperity contact. Such behavior could be confirmed experimentally with two complementary experiments: (1) a rigid countersurface (e.g. sapphire) with different levels of surface roughness (from polishing or from lithography), can be loaded against separators and the subsequent spatial pore density can be measured via a scanning electron microscope as in [80]; and (2) a separator can be uniformly compressed to achieve various fractions of collapse, and its ionic transport properties can be measured.

4.4.2 Pressurization of the electrolyte

Key assumptions in the present analysis include that the electrolyte escapes freely from contacting regions of the interface during deformation, and that there is no poroelastic transfer of stress through the liquid. These approximations should be good, especially at low contact pressures, given the apparent connectivity in gaps shown in Figure 5. Yet in this figure, there are some islands of contact gap even at low contact pressure, and the degree of percolation deteriorates further at higher pressures. Subsequent creep of the Li or separator could further reduce percolation pathways and increase the possibility of pressurization of trapped electrolyte. Even without fully trapped electrolyte, the Poiseuille equation indicates that electrolyte

pressurization may become significant for pathways below tens of nm. Under these circumstances, an internal hydrostatic pressure and smoothing of the stress distribution in the underlying Li may occur. One way to evaluate the contribution of electrolyte pressurization would be to evaluate stress-induced separator pore collapse with and without electrolyte present. Like the experiment described in the previous section, the counterface could be a nondeformable smooth solid such as sapphire, eliminating the complexity of rough Li surfaces. If the electrolyte is trapped, it will suppress pore collapse leading to larger pores in the electrolyte-containing separator compared to the dry separator. Assuming that pore collapse is suppressed to some extent, the degree of pore collapse can be used in conjunction with the properties of the separator to estimate the effective pressure sustained in the electrolyte.

4.4.3 Li properties

Li metal was treated as an elastic-perfectly-plastic material, which is valid[65] for low strain rates ($\leq 3 \times 10^{-4} s^{-1}$). Analyses that includes strain-hardening behavior, relevant for high strain rates[65], may show significant effects during fast charging.

It may be possible to use true, evolving Li surfaces, rather than the idealized Li surfaces analyzed here, once data along these lines[38] is available for cells under pressure

5. CONCLUSIONS

A 3D contact model has been developed for understanding the Li surface and sub-surface stresses at a sub-mm scale for electrodes with realistically rough surfaces and under a packing force. Our results reveal that contact between the Li metal and the separator is far from conformal, even under high external pressures. The fact that moderate (hundreds of kPa or less) pressure inhibits growth of Li protrusions for thin separators with modest shear moduli[16] argues against the ability of the Monroe-Newman model to explain dendrite suppression[36] with external pressure—at least for these experiments. Instead, we suggest that asperity contact stress and creep can promote flatter surfaces as local current densities adjust to pressure heterogeneities. Surface flattening will be limited to conditions where surface stress

effects are significant compared to the transport and electrochemical effects that tend to enhance dendrite growth.

We conclude with two suggested takeaways, based on our calculations. (1) While pressurizing a cell retards dendrites, it does not appear that overpressurizing provides additional benefits. (2) Conformal contact is not necessary to limit dendrite growth, but flatter cathodes may provide improved improved inhibition of dendrites and a longer cell life.

ACKNOWLEDGMENTS

The authors would like to acknowledge Prof. Y.T. Cheng of University of Kentucky and Prof. Brian Sheldon of Brown University for valuable discussions. S.J.H. was supported by the Assistant Secretary for Energy Efficiency, Vehicle Technologies Office of the US Department of Energy under the Advanced Battery Materials Research Program. K.L.H, K.L.J., and B.L.B were supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

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