Current limit diagrams for dendrite formation in solid-state electrolytes for Li-ion batteries

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Abstract

We build upon the concept that nucleation of lithium dendrites at the lithium anode-solid state electrolyte interface is instigated by the higher resistance of grain boundaries that raises the local electro-chemical potential of lithium, near the lithium-electrode. This excess electro-chemo-mechanical potential, however, is reduced by the mechanical back stress generated when the dendrite is formed within the electrolyte. These parameters are coalesced into an analytical model that prescribes a specific criterion for dendrite formation. The results are presented in the form of current limit diagrams that show the “safe” and “fail” regimes for battery function. [A higher conductivity of the electrolyte can reducedendrite formation.](#)

Keywords: Li-ion batteries, solid state electrolytes, dendrite formation

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Introduction

Solid-state electrolytes are attractive because, unlike conventional organic liquid electrolytes, they are nonflammable, and can remain stable in contact with Li metal, which may then be used directly as anodes. However, the solid electrolytes must have high ionic, and low electronic conductivity [1-3], and they must be chemically stable against the Li anode and cathode. Among the candidate materials cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO) possesses high ionic conductivity, ~ 0.1 to 1 mS cm^{-1} [4,5], and, it is stable with respect to Li-metal [6-9].

A high shear modulus is yet another desirable feature to oppose dendrite formation during charging. Monroe and Newman suggest that the shear modulus of the solid-electrolyte should be at least twice that of Li metal [10]. The shear modulus of cubic LLZO is approximately 60 GPa, while Li metal has a modulus of ~ 4 GPa [11]. However, dendrite formation has been observed in cubic LLZO at current densities $> 0.5 \text{ mA cm}^{-2}$ [8,9,12-17]. Dendrite formation is independent of composition, having been observed in LLZO doped with Al or Ta or Nb [8,13-15]. The relative density of the electrolyte should also play a role; however, dendrites do not appear to form if the density $> 93\%$ [16,17]. It has been suggested that a higher grain boundary resistivity, relative to the crystal matrix, could account for dendrite formation [8,15]. It is fair to conclude that at present we do not have a model that adequately describes dendrite formation in terms of the mechanical *and* electrical properties of LLZO.

Here, we propose such an analytical model based on the electro- chemo-mechanical potential of lithium at interfaces [18], where the interfacial stress and the electrical potential are combined into a unified description of the chemical potential. A comparison of this potential with the standard potential of lithium (the lithium-metal electrode) is then used to analyze the nucleation of Li dendrites just ahead of the electrolyte –Li metal anode interface. The results are presented in the form of current limit diagrams that show “safe” and “fail” regimes in terms of the ionic conductivity of the electrolyte and the interfacial stress. They are in fair agreement with experiment.

The Approach

The approach for analyzing the nucleation of Li-metal dendrites at grain boundaries of the electrolyte is described in Fig. 1 [19,20].

Fig. 1. Nucleation is analyzed in terms of the difference in the Gibbs free energy of the supersaturated state (State I) and the state where the supersaturation is relieved by the growth of a precipitate. The barrier to nucleation exists because surface energy opposes the “supersaturation” driving force. For subcritical embryos which have a high surface to volume ratio, the interfaces dominate the difference in the free energy. The volume term overwhelms the surface energy term when the embryo becomes larger than a critical size.

Consider the difference in the Gibbs free energy of two states. State I contains a supersaturation of Li, having an electro-chemo-mechanical potential μ_{Li}^* . In State II an embryo of lithium-metal has formed at the grain boundary; here Li has the reference potential of pure lithium which is given by μ_{Li}^o . The excess chemical potential, $\Delta\mu_{Li}^* = \mu_{Li}^* - \mu_{Li}^o$, provides the driving force for the nucleation of a precipitate of Li-metal. The force opposing nucleation arises from the excess surface energy created by the embryo; this consists of the difference between the energy of the metal-electrolyte interface with a specific energy of γ , minus the energy of the grain boundary of the electrolyte which no longer exists when the embryo is created. The specific energy of the grain boundary is called γ_{gb} . The two quantities are related by the contact angle, θ , defined in Fig. 1

$$\cos \theta = \frac{\gamma_{gb}}{2\gamma} \quad (1)$$

The difference between the Gibbs free energies of the two states in Fig. 1, defined as $\Delta G = G_{II} - G_I$, is then

$$\Delta G = -(\Delta\mu_{Li}^* n_v) r^3 F_v(\theta) + \gamma r^2 F_s(\theta) - \gamma_{gb} r^2 F_b(\theta) \quad (2)$$

Here $(\Delta\mu_{Li}^* n_v)$ is the energy gained (per unit volume) when the supersaturated Li precipitates into metallic lithium. n_v is the number of atoms of Li per unit volume. The volume of the nucleus is given by $r^3 F_v(\theta)$; r is the radius of curvature of the embryo interface. The function F_v is calculated from geometry and is given by

$$F_v(\theta) = \frac{2\pi}{3} (2 - 3\cos\theta + \cos^3\theta) \quad (3)$$

The other two terms in Eq. (2) are related to the change in the interfacial energies; they scale as r^2 ; the positive value is given by the increase in the new surface that is created, and the negative by the grain boundary area that has been eliminated. The magnitudes of these terms are defined by the functions F_s and F_b , which are again obtained from geometrical analysis. They are

$$F_s(\theta) = 4\pi(1 - \cos\theta) \quad (4)$$

and

$$F_b(\theta) = \pi \sin^2 \theta \quad (5)$$

A plot of ΔG vs. r will show a maximum, which is the critical condition for nucleation. Differentiating Eq. (2) with respect to r and equating to zero yields the height of the free energy barrier to nucleation, ΔG_c , and the position of this maximum, r_c , which specifies the critical radius. They are given by

$$r_c = \frac{2\gamma\Omega_{Li}}{\Delta\mu_{Li}^*} \quad (6)$$

and

$$\Delta G_c = \frac{r_c^3 F_v(\theta) \Delta \mu_{Li}^*}{2 \Omega_{Li}} \quad (7)$$

Note that the number of Li atoms per unit volume are related to the volume per lithium atom in the electrolyte, Ω_{Li} , that is

$$n_v = \frac{1}{\Omega_{Li}} \quad (8)$$

The probability of nucleation is then given by $\exp(-\Delta G_c / k_B T)$, where k_B is the Boltzmann constant. A formal calculation of the nucleation probability is not worthwhile at this juncture since many parameters in the above equations are not known. We resort to the general experience in nucleation kinetics, which is that embryos are able to grow to the critical size within realistic time scales when the number of atoms in the critical nucleus ranges from 1,000 to 10,000 [21,22]. The physical volume of the embryo is given by $r_c^3 F_v(\theta)$. Therefore the value for r_c will depend on θ . This plot for lithium atoms, which have an atomic volume of $2.2 \times 10^{-29} \text{ m}^3$ (calculated using the atomic weight of 7 g mol^{-1} and a density of 0.53 g cm^{-3}), is given in Fig. 2. The magnitude for the contact angle is not known. Using a typical number for metals in ceramics of $\theta = 30^\circ$ [23], we find from Fig. 2 that a reasonable value for the critical radius is equal to $r_c = 10 \text{ nm}$, which is used for the analysis in the following section.

Fig. 2. Nucleation kinetics can be visualized in terms of the number of atoms that must aggregate, climbing up hill towards the top of the energy barrier, to create an embryo that becomes supercritical. Generally the number of atoms in the embryo of a critical size ranges from 1,000 to 10,000 atoms to achieve nucleation within realistic time spans. The radius of curvature of the critical nucleus is related to this number of atoms through the contact angle as described in Fig. 1.

The Model

The electrical current flowing through the electrolyte passes through the grain boundary and the matrix as if they are resistive elements in series, as illustrated in Fig. 3.

Fig. 3. Far within the electrolyte the discontinuities in the electrical potential due to the difference between the ionic conductivities of the grain boundary and the grain matrix, conform to the average electrical field through the thickness of the electrolyte. It is assumed that the grain boundary has a higher resistance as compared to the grain matrix.

The average field through the electrolyte, Γ , is then equal to the sum of the voltage drop across the grain boundary, ΔV_B , and across the grain matrix, ΔV_d , divided by the grain size, d . They are related to the resistivity of the grain boundary, ρ_B , and of the grain matrix, ρ_d , as follows

$$\Delta V_B = j \rho_B \delta_B \quad (9)$$

and

$$\Delta V_d = j \rho_d d \quad (10)$$

Here, j is the current density. δ_B is the effective boundary width and d is the grain size.

Note in Fig. 2 that away from the Li electrode the electric field, Γ , is uniform although the potential experiences discontinuities at the grain boundaries. If this discontinuity occurs close to the Li-metal electrode, it can raise the local electrochemical potential of Li relative to μ_{Li}^o (the reference potential of Li-metal). This effect is illustrated in Fig. 3, where the grain boundary is at a distance d' from the metal electrode, where $d' < d$. The local electrical potential at the grain boundary can then become negative, which as derived below

Fig. 4. The voltage drop across the interface that is in close proximity of the Li electrode can produce an overpotential that provides the driving force for nucleation of dendrites.

can increase the local electrochemical potential of Li at the grain boundary, $\mu_{Li}^*(d')$. In the analysis below we refer to it simply as μ_{Li}^* . It is related, in part, to the potential drop at the grain boundary, ΔV , as defined in Fig. 4. By inspection we write that

$$\Delta V = \frac{j(\rho_B \delta_B + \rho_d d)}{d} d' - j \rho_B \delta_B \quad (11)$$

Setting,

$$\alpha = \frac{d'}{d}, \quad (12)$$

Eq. (11) becomes,

$$\Delta V = j \rho_d d' - j \rho_B \delta_B (1 - \alpha) \quad (13)$$

Next, we wish to relate ΔV to the local electrochemical potential of Li at $z = d'$. We begin by enforcing equilibrium between lithium atoms, lithium ions and electrons

$$Li = Li^+ + e \quad (14)$$

where e is the charge on an electron (it is a negative quantity, and equal in magnitude to the charge carried by one electron). The excess electrochemical potential of Li at the grain boundary, $\Delta\mu_{Li} = (\mu_{Li} - \mu_{Li}^0)$ is then given by

$$\Delta\mu_{Li} = \Delta\mu_{Li^+} + \Delta\mu_e \quad (15)$$

As shown in Fig. 5 the forward flux of Li-ions (this is achieved by the formation of a space charge of positive Li ions next to the grain boundary), which must remain equal to the current density, requires that

$$\Delta\mu_{Li^+} = j\rho_d d' |e| \quad (16)$$

where $|e|$ represents the positive charge on the Li-ion.

Fig. 5. The nucleation barrier is analyzed by considering the difference in the Gibbs free energy of the supersaturated state on the left (State I), and the state where Li has formed a precipitate at the expense of the supersaturation (State II). The precipitate produces a mechanical compressive traction which must be overcome to form the precipitate. As in classical theory, nucleation is opposed by the interfacial energies that are formed by the embryo.

The chemical potential of the electrons at the grain boundary relative to the standard potential at the metal electrode is related to Eq. (13) by

$$\Delta\mu_e = e\Delta V = -|e|[j\rho_d d' - j\rho_B \delta_B(1-\alpha)] \quad (17)$$

Substituting from Eqns (16) and (17) into (15) we have that

$$\Delta\mu_{Li} = j\rho_B \delta_B(1-\alpha)|e| \quad (18)$$

Note that α , given by Eq. (12) is less than unity. When it is equal to unity then there is no driving force for the precipitation of Li at the grain boundary.

The insertion of a Li embryo into the grain boundary, as shown in Fig. 5 creates a back stress which will oppose nucleation. In other words it will reduce the electrochemical driving force for nucleation as given by Eq. (18). The back stress is expressed as a normal traction at the metal-ceramic interface, since any shear traction will be relaxed quickly by the diffusion of Li along the interface [24]. The mechanical energy associated with this traction has two parts, (i) the mechanical strain energy induced in the surrounding matrix, and (ii) the work done to add a lithium atom to the embryo, at the interface, in presence of the

compressive traction. The strain energy per unit volume is equal to $\frac{\sigma^2}{2E}$ where σ is the stress in the matrix. This stress is maximum at the interface and declines moving away from the interface into the matrix. Therefore it is always less than the normal traction at the interface. The normal traction at the interface is written as σ_n (it is defined to have a positive sign when the traction is tensile).

The second contribution to the mechanical energy is equal to the work done by the surroundings to insert one Li atom at the interface. It is given by $-\sigma_n \Omega_{Li}$. In comparison the strain energy per atom, within the matrix is $\leq \frac{\sigma_n^2}{2E} \Omega_{Li}$, where E is the elastic modulus of the matrix. Since σ_n must be less than the fracture stress of the ceramic, σ_F , which for a brittle material is expected to be much less than the E , we find that the magnitude of the strain energy term is smaller than $-\sigma_n \Omega_{Li}$ by a factor of at least $\frac{\sigma_n}{2E}$, and is therefore insignificant in comparison to it. We disregard the strain energy term, and assume that the change in chemical potential is given by $-\sigma_n \Omega_{Li}$. This mechanical work can be converted into an electrical potential by enforcing the equation which has been derived and shown to be

experimentally confirmed in Ref. [18]. Applying it to Li^+ , which has a charge number of unity, that equation becomes

$$|e| \Delta V_{mech} = \sigma_n \Omega_{Li} \quad (19)$$

Note that σ_n is a negative quantity since the interface traction is compressive.

The magnitude of σ_n , which is the compressive traction, also called the back stress that is produced at the interface of the embryo, is related to the fracture stress of the ceramic electrolyte. The question arises how it can be that a compressive traction, σ_n , can produce fracture which requires a tensile force. The answer is that a flaw will experience a tensile force normal to its plane, when a compressive load is applied parallel to the plane of the flaw. It follows that the magnitude of σ_n cannot exceed the fracture stress of the electrolyte, which we call $|\sigma_F|$. Therefore

$$|e| \Delta V_{mech} = -|\sigma_F| \Omega_{Li} \quad (20)$$

Combining Eqns (18) and (20) we have the total driving force for the nucleation of Li precipitates at the boundary

$$\Delta \mu_{Li}^* = j \rho_B \delta_B (1 - \alpha) |e| - \sigma_F \Omega_{Li} \quad (21)$$

where the magnitude notation for the fracture stress is now omitted. Combining Eqns (6) and (21) we obtain the final condition for the “SAFE” condition when dendrite formation becomes unlikely. It obtains when the total driving force, $\Delta \mu_{Li}^*$, is insufficient to overcome the energy barrier for nucleation

$$j \rho_B \delta_B (1 - \alpha) |e| \leq \frac{2\gamma \Omega_{Li}}{r_c} + \sigma_F \Omega_{Li} \quad (22)$$

Note that $j \rho_B \delta_B$ is equal to the potential drop across the interface. In a highly conducting grain boundary the potential drop becomes negligible and dendrite formation is avoided. A higher fracture stress increases the right hand side of the equation, making dendrite formation less likely. Similarly a lower current density reduces the magnitude of the left hand side, again reducing the chance of dendrite formation.

Response
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comment
(1)

Current Limit Diagrams for Dendrite Formation

We now develop current limit diagrams that can display the “safe” and “fail” regimes graphically in terms of the (i) the critical current density, which if exceeded, causes dendrites to form, (ii) the ionic conductivity of the electrolyte, and (iii) the mechanical resistance to fracture. They are written as j in units of mA cm^{-2} , $(1/\rho)$ in units of mS cm^{-1} , and σ_F in MPa. The diagrams are based upon the inequality in Eq. (22).

Most parameters in the above equation are reasonably well known, except for $\rho_B \delta_B$. Since the model is based upon the grain boundary having a much higher resistivity than the grain matrix, we approximate that the overall resistivity of the electrolyte is determined substantially by the grain boundaries. The overall resistivity, ρ is written as

$$\rho d = \rho_B \delta_B + \rho_d d \quad (23)$$

$$\rho_B \delta_B = f \rho d \quad (24)$$

where

$$f = (1 - \frac{\rho_d}{\rho}) \quad (25)$$

Combining Eqs (22, (23), and (24) we obtain

$$j(f \rho d)(1 - \alpha)|e| \leq \frac{2\gamma \Omega_{Li}}{r_c} + \sigma_F \Omega_{Li} \quad (26)$$

The critical condition for nucleation is obtained by enforcing the equal-to sign in Eq. (26), which then gives the critical current density, j^* , for dendrite formation,

$$j^* = \frac{(2\gamma \Omega_{Li} / r_c) + \sigma_F \Omega_{Li}}{f d (1 - \alpha)|e|} \cdot \frac{1}{\rho} \quad (27)$$

Therefore, a high conductivity (lower ρ) increases the tolerance for a higher current density.

Response
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(2)

In Eq. (27) the parameter f , prescribed by (25), is a measure of the contribution of the grain matrix resistivity to the total resistivity. If grain boundary resistivity is dominant then $\rho_d \gg \rho$ and $f \rightarrow 1$. If on the other hand grain boundary resistivity is negligible (relative to the grain matrix), then $f \rightarrow 0$. Since Eq. (26) specifies the “safe” condition, it is always satisfied if $f = 0$. The most demanding condition for avoiding dendrite formation occurs when $f = 1$.

The parameter α is the proximity factor which measures how close a grain boundary is to the Li metal interface, as a fraction of the grain size. If $\alpha = 1$ then the grain boundary is at a distance equal to the grain size from the Li-metal interface, and dendrite nucleation becomes unlikely. At the other extreme, $\alpha = 0$ means that a grain boundary exists very close to the Li-metal interface; it gives the lowest value for the critical current density.

We construct the current limit diagrams with the condition that $\alpha = 0$ and 0.5 , and then consider two different values for $f = 0.5$ and 1.0 . The greatest probability for dendrite formation is predicted for the case $\alpha = 0$, and $f = 1$. For the other parameters we substitute

$$d = 5 \mu\text{m}$$

$$|e| = 1.6 \times 10^{-19} \text{ Coulombs}$$

$$\gamma = 0.5 \text{ J m}^{-2}$$

$$r_c = 10 \text{ nm (as described in the previous section)}$$

$$\Omega_{Li} = 2.2 \times 10^{-29} \text{ m}^3$$

$\sigma_F = 30 \text{ MPa, to } 100 \text{ MPa}$ (which is a reasonable range for the fracture stress of functional ceramics).

The transition from safe to fail regime is obtained from Eq. (27), that is, by calculating the critical current density for different values of $(1/\rho)$, and of σ_F . Current densities above these values are predicted to nucleate dendrites. Lesser values spell safe operation of the battery. The results are shown graphically in Fig. 6.

Fig. 6. Current limit diagrams that display how the current density, the ionic conductivity of the electrolyte, and the fracture stress of the ceramic interact to limit battery performance as determined by dendrite formation. The parameter f represents the grain boundary resistance (relative to the crystal matrix), while α expresses the proximity to the Li-metal interface. A high grain boundary resistance and closer proximity to the metal increases the chance of dendrite formation.

The maps in Fig. 6, show how the critical values for the current density vary with the ionic conductivity of the electrolyte. Since these values depend on the fracture stress, graphs for $\sigma_F = 30$ MPa and 100 MPa are shown. A lower fracture stress increases the probability of dendrite formation. The safe region also contracts if the grain boundary is closer to the Li-metal interface (a smaller value for α). A higher grain boundary resistance (a higher value for f) also increases the chance of dendrite formation. However, the most noticeable feature

of the diagrams is that a high ionic conductivity of the electrolyte is expected to reduce the chance of dendrite formation.

Experiments with LLZO, usually doped with Al_2O_3 , often show dendrite induced failure at $\sim 0.5 \text{ mA cm}^{-2}$ when the ionic conductivity of the electrolyte lies in the $0.2 - 0.5 \text{ mS cm}^{-1}$ range [8], with about equal contributions from grain boundaries and the crystal matrix (that is $f \approx 0.5$); this is the case considered in Fig. 6(b).

Response
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(3)

In most instances the dendrites inevitably form at current densities that exceed 1 mA cm^{-2} , at ionic conductivities that are less than 1 mS cm^{-1} in tests carried out at room temperature [12,16,17]. The diagrams in Fig. 6 suggest that dendrites should have formed at conductivities that are about an order of magnitude lower, or stated the other way, the cell should have tolerated current density one order of magnitude higher at a conductivity of 1 mS cm^{-1} . The most likely reason for this discrepancy lies in the value for γ , the interfacial energy between the ceramic and the metal, which has been assumed to be 500 mJ m^{-2} . The presence of Li^+ in the electrolyte can be expected to reduce the interfacial energy with lithium metal. Excellent agreement with experiment would have been obtained if the interfacial energy were to be set equal to 50 mJ m^{-2} .

The influence of temperature on survival has been reported in [9]. The critical current density rises from 0.05 mA cm^{-2} at 30°C to 20 mA cm^{-2} at 160°C , presumably because the conductivity rose with temperature. The grain boundary conductivity in these specimens, which were prepared by a rapid hot-pressing technique, was also only about 10% of the total conductivity. These results generally agree with the predictions from the present analysis that higher ionic conductivity, and lower grain boundary resistance reduces the chance of dendrite formation.

Discussion

In order for the dendrites to form in front of the Li electrode, the electrochemical potential of Li must rise above the reference potential of the lithium-metal. The higher resistance of the grain boundaries, relative to the grain matrix, can raise the local electrochemical potential of lithium. When the boundary is in the proximity of the Li-metal electrode the potential can rise above the reference potential, thereby providing a driving force for nucleating a Li

precipitate in front of the solid-electrolyte – metal interface. The back stress generated by the formation of the precipitate however, opposes the nucleation of a dendrite. The analysis presented here combines both contributions into an electro-chemo-mechanical potential[18]. This excess potential is then integrated into the analysis of a nucleation barrier for [dendrite formation](#).

The final result is expressed in [Eq. \(26\)](#) and [Eq. \(27\)](#) in terms of parameters that are related to battery performance, namely, the current density, the ionic conductivity of the electrolyte, and the ability of the electrolyte to resist fracture. The interplay between these parameters is used to construct current limit diagrams that prescribe the safe and fail regimes in a graphical representation, shown in Fig. 6. The predictions from the performance maps are credible though they somewhat underestimate the values for the electrolyte specific conductivity for causing failure at current densities of about 1-2 mA cm⁻². [The estimate of the current limit is brought into better agreement by recognizing that interfacial energy of the electrolyte with Li-metal could be one order of magnitude lower than assumed in the present analysis, that is 50 mJ m⁻² instead of 500 mJ m⁻².](#)

There remains the question of the dendrite growing directly from the Li-metal into the electrolyte. A protuberance from the surface of the lithium metal will concentrate the local current density which can promote its growth. We analyze this problem according to the model described in Fig. 7. The bump on the surface has a width at its tip given by w , while the distance of the tip from the nominal lithium surface is h , that is the incipient dendrite has

Fig. 7. The concentration of the current density at the tip of a protuberance on the surface of the Li-metal anode. Its intensity depends on the aspect ratio of the “bump”, which can then raise the local Li potential because of interfacial area specific resistance.

an aspect ratio of (h/w) , which is the strength of the “singularity” that can [promote local growth of the lithium dendrite](#). The iso-current and iso-potential contours (they are normal to one another) are shown schematically in Fig. 7. The current density becomes concentrated near the tip of the bump; its magnitude, j_{int} , using the St. Venant’s principle, may be written as

$$j_{\text{int}} = j \frac{h}{w} \quad (25)$$

where j is the average current density flowing through the electrolyte. The driving force for the growth of lithium is $\Delta\mu_{\text{Li}}$. We write it in terms of $\Delta\mu_{\text{Li}^+}$ and $\Delta\mu_e$ as described by Eq. (15). Since growth occurs at the metal surface and since a metal must be at an equipotential, we have that

$$\Delta\mu_e = 0 \quad (26)$$

The potential step at the interface, $\Delta\mu_{Li^+}$, is related to the interfacial area specific resistance in units of Ohms cm^2 , or k_{int} by $\Delta\mu_{Li^+} = |e| k_{\text{int}} j_{\text{int}}$, which combined with Eq. (26) and Eq. (15) gives

$$\Delta\mu_{Li} = |e| k_{\text{int}} j_{\text{int}} \quad (27)$$

Adding the back stress, σ_F , which will oppose dendrite growth, using the same procedure as before give the excess potential of Li at the interface to be

$$\Delta\mu_{Li}^{\text{int}*} = |e| k_{\text{int}} j \frac{h}{w} - \sigma_F \Omega_{Li} \quad (29)$$

For the incipient dendrite (in the form of a protuberance) to grow it is required that

$$\Delta\mu_{Li}^{\text{int}*} > 0 \quad (30)$$

that is

$$\sigma_F \Omega_{Li} < |e| k_{\text{int}} j \frac{h}{w} \quad (31)$$

Assuming that $\sigma_F = 100\text{MPa}$, the voltage equivalent of the left hand side in Eq. (31) is equal to 13.7 mV. Assuming the aspect ratio of the protuberance to be about unity, and a current density of 1 mA cm^{-2} , we find that the dendrite can be expected to grow if $k_{\text{int}} > 13.7\Omega\text{cm}^2$.

It still remains to address how the dendrites grow once they are nucleated. Their growth rate will be determined not by the fracture strength, but instead by the *fracture toughness* of the ceramic electrolyte. The dendrite can be expected to grow quickly since its aspect ratio will increase as it grows, and from Eq. (29), so will the local potential of Li. The back stress must now be replaced by the stress-intensity factor and the height of the dendrite, a problem which has yet to be addressed.

There still remains a caveat that surface diffusion will seek to smooth out the irregularities in the surface of the lithium metal anode by surface diffusion. The rate of this smoothing effect scales as the fourth power of the wavelength of the undulations in the shape of the interface [25], and can occur at physically meaningful rates at temperature in the range

of $0.5T_M$ to $0.75T_M$ of the metal. At room temperature (300 K) Li is at $0.67T_M$; therefore it is quite likely that any protuberance in the metal surface will be smoothed out by diffusion, even if the battery is idle. However, such a process can occur only if the Li metal is not strongly bonded to the electrolyte, since otherwise the change in the shape of the interface will be constrained by the metal-electrolyte interface. (Interestingly, if the interface is weakly adherent then smoothing can open up cavities at the Li-electrolyte interface with obvious consequences – this problem of de-adhesion remains to be analyzed).

Summary

The nucleation and growth of dendrites from the lithium metal-solid state electrolyte is analyzed in terms of the local electro-chemo-mechanical potential of Li that develops either from the high local (ionic) resistivity of grain boundaries or from physical irregularities in the shape of the Li interface. This local excess potential, written as $\Delta\mu_{Li}^*$, is reduced by the back stress and increased by the local electrical resistance of grain boundaries or by the concentration of current at a protuberance in the lithium metal surface.

The grain boundary resistance model invokes the nucleation of Li metal embryos just ahead of the interface. The analysis of this problem, leads to current limit diagrams illustrated in Fig. 6. [They agree with experiments to within an order of magnitude in terms of the critical current density for dendrite nucleation.](#)

The model assumes that the back stress, which opposes nucleation, is equal to the effective fracture stress of the electrolyte. It is assumed to be equal to 100 MPa. The fracture occurs by the tensile stress created at the surface of a defect such as a pore when the electrolyte presses against the Li-metal precipitate. Thus while the normal traction at the interface is compressive it creates an equal tensile stress in the orthogonal direction which can cause fracture.

In the other case we consider the growth of a protuberance at the lithium interface by the concentration of current density. In this instance the interface area specific resistance, as well as the aspect ratio of the protuberance become the limiting parameters. It is estimated that a protuberance can grow if the interfacial charge transfer resistance is greater than approximately $14 \text{ } \Omega\text{cm}^2$.

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List of Figures

1. Nucleation is analyzed in terms of the difference in the Gibbs free energy of the supersaturated state (State I) and the state where the supersaturation is relieved by the growth of a precipitate. The barrier to nucleation exists because surface energy opposes the “supersaturation” driving force. For subcritical embryos which have a high surface to volume ratio, the interfaces dominate the difference in the free energy. The volume term overwhelms the surface energy term when the embryo becomes larger than a critical size.

2. Nucleation kinetics can be visualized in terms of the number of atoms that must aggregate, climbing up hill towards the top of the energy barrier, to create an embryo that becomes supercritical. Generally the number of atoms in the embryo of a critical size ranges from 1,000 to 10,000 atoms to achieve nucleation within realistic time spans. The radius of curvature of the critical nucleus is related to this number of atoms through the contact angle as described in Fig. 1.

3. Far within the electrolyte the discontinuities in the electrical potential due to the difference between the ionic conductivities of the grain boundary and the grain matrix, conform to the average electrical field through the thickness of the electrolyte. It is assumed that the grain boundary has a higher resistance as compared to the grain matrix.

4. The voltage drop across the interface that is in close proximity of the Li electrode can produce an overpotential that provides the driving force for nucleation of dendrites.

5. The nucleation barrier is analyzed by considering the difference in the Gibbs free energy of the supersaturated state on the left (State I), and the state where Li has formed a precipitate at the expense of the supersaturation (State II). The precipitate produces a mechanical compressive traction which must be overcome to form the precipitate. As in classical theory, nucleation is opposed by the interfacial energies that are formed by the embryo.

6. Current limit diagrams that display how the current density, the ionic conductivity of the electrolyte, and the fracture stress of the ceramic interact to limit battery performance as determined by dendrite formation. The parameter r represents the grain boundary resistance

(relative to the crystal matrix, while α expresses the proximity to the Li-metal interface. A high grain boundary resistance and closer proximity to the metal increases the chance of dendrite formation.

7. The concentration of the current density at the tip of a protuberance on the surface of the Li-metal anode. Its intensity depends on the aspect ratio of the “bump”, which can then raise the local Li potential because of interfacial area specific resistance.