Mechanism of Lithium Metal Penetration through Inorganic Solid Electrolytes

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Li deposition is observed and measured on a solid electrolyte in the vicinity of a metallic current collector. Four types of ion-conducting, inorganic solid electrolytes are tested: Amorphous 70/30 mol% Li$_2$S-P$_2$S$_5$, polycrystalline β-Li$_2$PS$_4$, and polycrystalline and single-crystalline Li$_6$La$_3$ZrTaO$_{12}$ garnet. The nature of lithium plating depends on the proximity of the current collector to defects such as surface cracks and on the current density. Lithium plating penetrates/infiltrates at defects, but only above a critical current density. Eventually, infiltration results in a short circuit between the current collector and the Li-source (anode). These results do not depend on the electrolytes shear modulus and are thus not consistent with the Monroe–Newman model for “dendrites.” The observations suggest that Li-plating in pre-existing flaws produces crack-tip stresses which drive crack propagation, and an electrochemomechanical model of plating-induced Li infiltration is proposed. Lithium short-circuits through solid electrolytes occur through a fundamentally different process than through liquid electrolytes. The onset of Li infiltration depends on solid-state electrolyte surface morphology, in particular the defect size and density.

1. Introduction

The ever-increasing demand for mobile energy storage has led to extensive development of lithium-ion batteries due to their exemplary performance, energy density, and cycle life. However, safety concerns have prompted the need for alternative materials while preserving benefits. Furthermore, vast improvements in energy density may be achieved with lithium metal anodes owing to their high gravimetric capacity (3869 mA h g$^{-1}$) and low density (0.534 g cm$^{-3}$). However, adoption of rechargeable lithium metal batteries has been unsuccessful thus far due to safety concerns associated with short circuits that occur when Li dendrites grow through the liquid electrolyte during the charging process. Although several approaches have reduced dendrite formation, to date the phenomenon has not been avoided under all relevant conditions.

Nonflammable inorganic solid electrolytes, paired with Li metal anodes, could result in high energy density yet safe rechargeable lithium batteries. As reviewed by Takada, inorganic solid electrolytes have now been widely studied, but are not yet commercialized. Monroe and Newman have suggested that dendrite growth during the plating process may be suppressed if the liquid electrolyte is replaced with a Li-ion conducting solid electrolyte of a sufficiently high shear modulus. According to this criterion, numerous inorganic solid electrolytes should be able to suppress dendrite formation. However, multiple research groups have recently reported cases where ceramic solid electrolytes paired with a Li metal anode experience a short circuit.
event[21–27] Several attempts to suppress the shorting via solid electrolyte composition alterations and electrode/solid electrolyte interfacial modifications have been made,[24,28–31] but with limited success. Only in thin film batteries have Li metal negative electrodes paired with inorganic solid electrolytes (e.g., LiPON) been able to avoid dendrite penetration over extended cycling.[32] The reasons for this difference in behavior between bulk and thin film batteries are not understood. As pointed out in two recent reports,[33,34] similar short circuit events were investigated in Na-ion conducting solid electrolytes in liquid Na batteries in the 1970–1980s.[35–42] In these cases, the short circuit event was attributed to stresses created by molten sodium metal plating into cracks within the solid electrolyte bulk, resulting in crack propagation and eventual failure.

Thus, the mechanism by which short circuit events occur in all-solid-state Li-ion batteries is unclear. Here, a novel technique is employed to monitor lithium metal penetration into solid-state electrolytes (SSEs) during electrodeposition, using four different SSEs: (1) amorphous 70/30 mol% Li2S-P2S5, (2) polycrystalline β-Li3PS4, (3) polycrystalline Li6La3ZrTaO12 garnet, and (4) single-crystalline Li8La2ZrTaO12 garnet. The surface defect population of these SSEs was intentionally varied, through surface treatments as well as internal microstructure. These experiments made it possible to identify both similarities and differences between lithium penetration phenomena in the different SSEs. A chemo-mechanical model is also developed to evaluate the stresses generated in a sharp flaw during electrodeposition of Li metal. The experimental results and analytical model together allow an interpretation of the mechanism of Li metal penetration into inorganic SSEs.

2. Results and Discussion

The experimental apparatus used in this work is shown schematically in Figure 1. A solid electrolyte pellet is placed in contact with Li metal foil at the bottom surface and with a metal electrode at the top surface. The top electrode is a spring-loaded contact to a brass or gold electrode. Galvanostatic experiments are conducted with an applied potential that transports lithium metal penetration into the SSEs during electrodeposition, using four different SSEs: (1) amorphous 70/30 mol% Li2S-P2S5, (2) polycrystalline β-Li3PS4, (3) polycrystalline Li6La3ZrTaO12 garnet, and (4) single-crystalline Li8La2ZrTaO12 garnet. The surface defect population of these SSEs was intentionally varied, through surface treatments as well as internal microstructure. These experiments made it possible to identify both similarities and differences between lithium penetration phenomena in the different SSEs. A chemo-mechanical model is also developed to evaluate the stresses generated in a sharp flaw during electrodeposition of Li metal. The experimental results and analytical model together allow an interpretation of the mechanism of Li metal penetration into inorganic SSEs.

Figure 1. Schematic of apparatus for Li plating on a metal electrode in contact with a solid electrolyte.
In the first instance where the electrode tip is in contact with the as-fractured LPS surface, the sequence of images in Figure 2a–d show that lithium metal deposits on the surface of the LPS and gradually propagates laterally from the electrode contact point. No cracking or surface degradation of the LPS was evident, and the cell did not short-circuit during the experiment.

However, when the electrode was placed in contact near the precracked area, there is no evidence of lithium accumulation on the surface of the LPS under the same galvanostatic conditions (0.8 μA). Instead, as seen in Figure 2e–h, cracks formed and extended into the sample as the experiment progressed. In Figure 2f, the extension and opening of the metal-filled crack is indicated by the outlined box. We interpret that the progressive crack opening is driven by the electroplating of lithium metal into one or more sharp flaws (Griffith flaws) at the surface of the SSE, despite the low yield strength of lithium metal (0.5 MPa), which might otherwise suggest that it should be able to flow and deposit on the surface.

Similar experiments were then conducted on single-crystal Li₃La₂ZrTaO₁₂ garnet (LLZTO) samples. The ionic conductivity of the sample was measured via EIS to be 0.2 mS cm⁻¹ (Figure S1, Supporting Information). The crystal structure and phase purity have been confirmed via XRD experiments. Having seen the impact of surface defects on lithium metal penetration in glassy LPS, the surface of the LLZTO crystal was subjected to two different polishing schemes in order to vary the severity of surface flaws. In one instance, the single crystal was ground using 400 grit SiC abrasive paper, producing a microscopically rough surface with widespread fracture features, as seen in Figure 3a. To obtain a surface with much finer defect size, a highly polished single-crystal surface was also prepared, as shown in Figure 3b. This surface was prepared by polishing LLZTO single-crystal samples with successively finer abrasive papers, culminating in a final polish with 50 nm alumina paste. Atomic force microscope (AFM) scans of the two surfaces are shown in Figure 3a,b, respectively. The root-mean-square (rms) roughness of the rough surface is 200 nm, and that of the polished surface is 4 nm (each obtained for a scan size of 10 μm × 10 μm). However, of greater importance are the largest flaws on the respective surfaces. It has been shown that during surface grinding of brittle materials, subsurface damage is produced that extends to a maximum depth determined by several factors, including the size distribution of particles (the largest particles bearing most of the load) and the normal force while grinding. The maximum damage depth for standard abrasives is observed to range from one to several times the mean particle size. Since the ANSI 400 grit specification corresponds to a D50 particle size of 22 μm, it is reasonable to assume that LLZTO surfaces ground with this grit size have surface cracks extending 30–50 μm into the SSE. SEM images of the surface support this assumption (Figure 3c,e). The largest flaws on the highly polished surface were found, using SEM, to be polishing scratches of ≈0.4 μm width, shown in Figure 3d,f, but possibly deeper. Thus, for these two surfaces, we assume the largest surfaces flaws to be in the range of 30–50 μm and 0.4–1 μm, respectively.

Gold electrodes were then sputtered onto the samples, under which lithium metal is electrodeposited during galvanostatic testing. Because gold readily alloys with lithium metal, it has a
negligible nucleation barrier (overpotential) for lithium plating at the inception of the experiment. This allows our experiment to test the subsequent crack growth and lithium penetration process. Constant current densities of 0.01, 0.1, 0.5, 1, and 5 mA cm$^{-2}$ (the area being that of the sputtered gold electrode) were applied in a stepwise sequence, with each step lasting for 15 min. The cells reached a short-circuit state in all cases during the 1 or 5 mA cm$^{-2}$ steps, with no apparent correlation in short-circuit conditions with surface roughness. (Four experiments were conducted on the rough surface and nine experiments on the smooth surface.) The absence of any clear differentiation in the current density at which crack propagation occurs for the rough and smooth suggests that both surfaces contain defects of sufficient severity to be “supercritical” under present electrodeposition conditions.

An example of the sequence of crack formation and propagation at 5 mA cm$^{-2}$ current density (based on the gold electrode area) on LLZTO polished to 50 nm surface finish, is shown using in situ optical microscopy in Figure 4a–d. The galvano-static current was applied for 15 min, passing a total charge of ≈2 µA h, which corresponds to a Li-plated volume of ≈1 × 10$^6$ µm$^3$. Figure 4c captures a moment about halfway through the experiment when a crack (white silhouette) has grown from under the gold electrode into the field of view. The crack then extends further as Li-plating continues (Figure 4d). A second example, conducted at lower current density of 1 mA cm$^{-2}$, is shown.
During real-time observation, cracks could be observed propagating into the SSE away from the gold electrode. The dark contrast reflections in the image correspond to cracks filled with electrodeposited lithium metal. In the inset figure in Figure 5b, one such lithium-filled crack is shown after the single crystal was polished to half its initial thickness of 3 mm. Since multiple cracks were created under the sputtered gold electrode, the specific crack responsible for the short circuit was not identified. These results conducted on the polished LLZTO show at practical current densities (1 and 5 mA cm\(^{-2}\)), lithium metal penetration can occur from an electrode-SSE interface with starting defect size as small as \(\approx 1 \mu m\).

Polycrystalline SSE samples were next investigated. Galvanostatic lithium deposition was conducted, using the configuration of Figure 1, onto a densely pressed polycrystalline \(\beta\)-Li\(_3\)PS\(_4\) sample. The ionic conductivity of the sample was measured via EIS to be 0.2 mS cm\(^{-1}\) (Figure S1, Supporting Information). XRD confirmed that the sample is single-phase \(\beta\)-Li\(_3\)PS\(_4\) (Figure S2a, Supporting Information). As shown in Figure 6a–c, the \(\beta\)-Li\(_3\)PS\(_4\) powder was cold-pressed into a pellet at 700 MPa.

![Figure 4](image-url) **Figure 4.** a–d) Optical microscopy images of a polished single crystal of LLZTO (4 nm rms roughness) with sputtered gold electrode during galvanostatic deposition of lithium metal beneath the gold electrode at 5 mA cm\(^{-2}\) current density. Uniform plating behavior appears to take place until a crack is observed to propagate (white silhouette).

![Figure 5](image-url) **Figure 5.** a) Optical microscopy image of a single-crystal LLZTO polished with 50 nm particle size polishing media sample, after deposition of the gold electrode. Scratches on the gold film are due to positioning of the contact probe. b) After lithium deposition at 1 mA cm\(^{-2}\) to short circuit, cracks are clearly visible. In the inset, a crack is still clearly visible when the sample has been polished to half its original thickness. The dark background in (b) is the reflection of lithium metal filling the cracks.
uniaxial pressure, after which it was translucent in appearance. The surface of the pellet appeared smooth in optical microscopy (Figure 6a), but SEM imaging revealed fine sub-micrometer-scale pores or cracks at the surface (Figure 6e). A current of 4 µA was passed through the cell, corresponding to a high current density of \( \approx 50 \, \text{mA cm}^{-2} \) based on the tip electrode area (lithium metal deposition rate of \( \approx 500 \, \text{µm}^3 \, \text{s}^{-1} \)). The duration of the experiment for which data are shown in Figure 6 is 2 min, resulting in \( \approx 0.13 \, \text{µA h} \) of charge passed equivalent to \( \approx 6 \times 10^4 \, \text{µm}^3 \) of plated lithium metal. Upon inspection, it was clear that the majority of lithium deposition occurred within the bulk of the \( \beta\)-Li\(_3\)PS\(_4\) pellet and not on the surface, as can be seen in Video S1 (Supporting Information). Figure 6d shows, in transmission optical microscopy, that the lithium metal deposition occurs in a characteristic branching pattern.

After the galvanostatic experiment, the \( \beta\)-Li\(_3\)PS\(_4\) pellet was fractured to expose the lithium metal network shown in Figure 6d. Scanning electron microscopy was used to record images of the fracture surface using secondary electrons (Figure 7a,b,d) and backscattered electrons (Figure 7c), respectively. The sample in Figure 7a–c experienced air exposure for <1 min, while the sample in Figure 7d was transported in a vacuum-operated transfer box.\(^{[44]}\) This transfer box is designed to be sealed while in the glove box under high purity argon at 1 atm pressure, but to spontaneously open in the SEM chamber when the vacuum reaches a critical value. In Figure 7a–c, the LPS has a more rounded appearance, which we attribute to volume-expansive surface reactions that occurred upon exposure to air. This feature is absent in Figure 7d, suggesting that the transfer box has served the intended function. The lithium metal in these images is readily identified in two ways. First, each of the secondary electron images show the fracture features characteristic of a ductile phase, namely, elongated filaments that are necked down at the tips where they have separated from the opposing surface. This ductile phase must be lithium metal rather than LPS, given the low measured fracture toughness of LPS (0.23 MPa m\(^{1/2}\)).\(^{[46]}\) Second, a comparison between the secondary electron images and the backscattered electron image in Figure 7c shows that the phase corresponding to the ductile fracture features has very low backscattered electron contrast, as expected from lithium metal. Between the branches of lithium metal are seen polycrystalline aggregates of \( \beta\)-Li\(_3\)PS\(_4\) particles. The electrodeposited lithium metal has propagated in a cellular manner, along pore channels, grain boundaries, or both. A recently published study shows similar cellular lithium metal penetration through Al-doped LLZO,\(^{[26]}\) although in that instance the penetration appears to follow most grain boundaries rather than isolating polycrystalline aggregates as in the present instance.

In the current experimental design, the cell impedance is dominated by the solid electrolyte layer. An advantage of this design, from the viewpoint of experimental diagnostics, is that the ohmic resistance of the cell can be used to monitor in situ the growth and penetration of a lithium metal network through the solid electrolyte. Before a short-circuit occurs due to complete lithium metal penetration, there is typically a decrease in cell resistance as the lithium metal network advances through the solid electrolyte. We took advantage of this behavior and conducted a series of experiments to electrically monitor lithium metal penetration under varying electrodeposition conditions.

Figure 6. a–c) Lithium metal deposition at high current density (\( \approx 50 \, \text{mA cm}^{-2} \)) propagates into densely pressed polycrystalline \( \beta\)-Li\(_3\)PS\(_4\) from a brass tip electrode. d) Viewed in transmission optical microscopy, the lithium metal network shows a branching pattern. e) The starting as-pressed surface of the \( \beta\)-Li\(_3\)PS\(_4\) polycrystal exhibits sub-micrometer (\( \approx 200 \, \text{nm} \) length scale) cracks or pores.
In one such experiment, the cell voltage under galvanostatic conditions was monitored as a function of time, using polycrystalline $\beta$-Li$_3$PS$_4$ and LLZTO as solid electrolytes (Figure 8a). The ionic conductivity of the polycrystalline LLZTO sample was measured via EIS to be $0.16 \text{ mS cm}^{-1}$ (Figure S1, Supporting Information). The sample was confirmed to have a single garnet phase using XRD (Figure S2b, Supporting Information). Under a constant current of $2 \mu\text{A}$, which is $\approx 25 \text{ mA cm}^{-2}$ initial current density based on tip area, the lithium deposition rate is $\approx 250 \mu\text{m}^3\text{s}^{-1}$. For both LPS and LLZTO, there is an initial rapid drop of the cell voltage over a few minutes. Concurrent with this voltage decrease, rapid propagation of the lithium network was observed in the $\beta$-Li$_3$PS$_4$ pellet via optical microscopy. After $\approx 5 \text{ min}$ (0.16 $\mu\text{A h}$ charge passed, $8 \times 10^4 \mu\text{m}^3$ of plated Li), the cell voltage stabilized, and at the same time, growth of the lithium network appeared to have stopped. Continuing the experiment to 15 min (0.48 $\mu\text{A h}$ charge passed, $24 \times 10^4 \mu\text{m}^3$ of plated Li) did not result in a short-circuit of the cell. Even after 24 h of the experiment (data not shown, 46 $\mu\text{A h}$ charge passed, $1.15 \times 10^7 \mu\text{m}^3$ of plated Li), a cell short-circuit was not observed. Similar behavior was observed with the polycrystalline LLZTO (Figure 8a). A plausible interpretation of the cell voltage stabilization is that the lithium metal network branching during growth decreases the local current density at the filament tips to a value below a critical current density necessary for propagation. The sharp stepwise decrease in the cell voltage at about 4 min is attributed to preferential Li plating inside a newly formed crack aligned with the thickness direction of the LLZTO crystal.

Thus, in a second experiment, we first allowed the cell voltage to stabilize via galvanostatic discharge, then ramped the current density in order to observe whether there is a critical current density at which the lithium metal network again propagates (as indicated by cell voltage). Figure 8b shows these results. Two cells of the same kind, again using $\beta$-Li$_3$PS$_4$ and polycrystalline LLZTO as solid electrolytes, were first subjected to galvanostatic conditions of 2 $\mu\text{A}$ for 2 h. Based on the experiments in Figure 8a, this is well beyond the duration needed to establish steady state. Then, the current was increased at a constant rate of $0.025 \mu\text{A s}^{-1}$, while measuring the cell voltage. Based on the current and resistance at the start of the ramp, the ohmic resistance in the absence of any change in the sample should follow the straight dashed lines in Figure 8b. The data for the two cells (solid curves), however, show in each case a negative deviation from linearity at a critical value of current, which is $\approx 9 \mu\text{A}$ for the polycrystalline LPS sample and $\approx 15 \mu\text{A}$ for the polycrystalline LLZTO. We attribute this behavior to renewed penetration of the solid electrolyte occurring as the current density at the leading asperities of the lithium metal network reaches a critical value, although the specific local value of current density is not easily established given the extensive crack branching.

Finally, experiments were conducted to compare the effects of unidirectional deposition with the cyclic deposition that would be experienced in a rechargeable battery. Using the polycrystalline LLZTO, a constant current of 2 $\mu\text{A}$ (25 mA cm$^{-2}$) was again applied, but the direction of the current was frequently reversed, as shown in Figure 8c. The cell experienced a short-circuit after only seven cycles (14 h), while under...
unidirectional deposition (Figure 8a), no short-circuit occurs even after 24 h. The net deposition of lithium metal in the cycled case, based on the difference in time under positive and negative current, is 5 µAh, corresponding to 2.5 × 10⁶ µm³ of Li metal, which is about an order of magnitude smaller compared to the unidirectional deposition case. Perhaps more critically, a comparison of the results in Figure 8b,c indicates that galvanostatic cycling has lowered the critical current density at which metal deposition advances through the solid electrolyte, since short-circuiting occurs in Figure 8c under only 2 µA. Factors that could be responsible for this behavior include localized thermodynamic and kinetic effects, stress distribution in the solid electrolyte, and subcritical mechanical damage ahead of the filament tip.

2.1. Electrochemomechanical Model of Lithium Metal Penetration

It is clear that in the present experiments, phenomena other than that proposed by Monroe and Newman, control the formation and propagation of lithium metal through the solid electrolyte. They suggested that perturbations during Li deposition that lead to dendrite formation can be suppressed if a solid electrolyte with a sufficiently high shear modulus (about twice that of Li, which has shear modulus of 4.2 GPa) is used instead of a liquid electrolyte. In the present case, the shear modulus for LPS, 8.3 GPa, is just about twice that of Li metal, while that for the oxide garnet, 61 GPa, is more than tenfold higher and vastly exceeds the criterion. The present...
results instead point to a mechanism based on the propagation of surface flaws, and suggest that electrodeposition of metal within a surface crack can induce crack opening and advancement, despite the low shear modulus and yield strength (0.5 MPa\textsuperscript{[46]} of lithium. Indeed, it is unclear whether the term “dendrite” applies to such metal penetration structures, given the metallurgical definition of a dendrite as originating from the kinetically determined amplification of an interfacial perturbation.\textsuperscript{[50–52]} A suitable chemo-mechanical model must be able to explain lithium metal propagation in the present solid electrolytes under a wide range of surface conditions, ranging from a highly polished single crystal to polycrystals containing microscopic pores as well as grain boundaries. The observation of a critical current density, seen here as well as in other studies,\textsuperscript{[34,53]} must also be explained.

We assume that lithium metal plating is initiated on the electronically conductive metal electrode that is the source of electrons, and grows to fill any space between the current collector and the SSE. If there are pores or cracks on the solid electrolyte surface, lithium metal deposition will first fill those flaws, both because the overpotential is low, needing to only overcome surface and interfacial energies, and because the electric field concentration is increased at any asperity penetrating into the SSE. Once the flaw is completely filled, mechanical stresses within the metal and SSE are expected to rise as lithium metal continues to plate. In order to determine the extent of stress build up, an analytical model is here developed, based on a simplified geometry of a Li filament within a typical inorganic solid electrolyte, and is shown in Figure 9.

Taking a cue from the experimental observations of lithium metal filled cracks, the filament thickness (y-direction) is assumed to be constant (here, \( \approx 300 \) nm) and small compared to its length (x-direction) and width (z-direction). Employing a plain strain analysis, the equilibrium stress condition on an infinitesimal volume element inside the Li filament leads to the following 1D relationship between the stress gradient in the x-direction and the shear stress

\[
\frac{\partial \sigma_{xx}}{\partial x} = 2 \frac{\tau}{h} \tag{1}
\]

where \( \sigma_{xx} \) is the stress in the x-direction, \( h \) is the filament thickness, and \( \tau \) is the shear stress on the surface. To evaluate \( \tau \), the frictional coefficient between lithium and the solid electrolyte is required, along with the yield strengths of the solid electrolyte and lithium. For simplicity, however, it is assumed that the solid electrolyte is rigid and the shear stress at the surface is proportional to the normal force, such that \( \tau = \mu \sigma_{yy} \), where \( \mu \) is the friction coefficient. Thus, Equation (1) becomes

\[
\frac{\partial \sigma_{xx}}{\partial x} = 2 \frac{\mu}{h} \sigma_{yy} \tag{2}
\]

A relationship between \( \sigma_{xx} \) and \( \sigma_{yy} \) is required to solve Equation (2). Under the assumption that Li is only plated at the filament tip (\( x = 0 \)), material compression behind the tip (\( x > 0 \)) induces a Poisson expansion which is constrained by the surrounding solid electrolyte such that \( \sigma_{yy} = \nu \sigma_{xx} \) (both stresses are compressive), where \( \nu \) is the Poisson ratio. Far away from the filament tip the stress is zero. Solving for \( \sigma_{xx} \) in Equation (2) with this condition gives

\[
\sigma_{xx} = \sigma_0 e^{-\frac{2\mu x}{h}} \tag{3}
\]

where \( \sigma_0 \) is the stress at the filament tip, namely, the maximum value of \( \sigma_{xx} \). Note that \( \sigma_0 \) is a function of the amount of Li plated on the filament. From Equation (3) we obtain a characteristic filament length scale, \( \lambda = h/2\mu \nu \). The analysis leading to Equation (3) assumes that the filament length significantly exceeds \( \lambda \) (i.e., by setting the stress to zero far away from the tip). Stress build-up will thus be less severe when the filament length is shorter than this length. With a filament thickness \( h \) of 300 nm and typical values for \( \mu \) and \( \nu \) of 0.5 and 0.3, respectively, \( \lambda = 1 \) \( \mu m \). The growing cracks in the experiments, as seen in Figures 2, 3, 4, 5, 6, 7, are much longer than \( \lambda \) and satisfy the high aspect ratio assumed in obtaining Equation (3). In shallower flaws the boundary condition at infinity is not valid. Under these conditions, the pressure build-up at the crack tip may be able to displace Li metal out of the flaw (to the left in Figure 9) in an extrusion-like process.

What then determines the value of the hydrostatic stress \( \sigma_0 \)? It has a maximum value, \( \sigma_{0,\text{max}} \), that is thermodynamically determined by the overpotential, \( \Delta \Phi \), at which the lithium metal is plating

\[
\sigma_{0,\text{max}} \equiv \frac{F}{V_m} \times \Delta \Phi \tag{4}
\]

\( F \) is Faraday’s constant and \( V_m^{\text{li}} \) is the molar volume of lithium metal (13 cm\(^3\) mol\(^{-1}\)). This relationship shows that even a relatively small overpotential can lead to substantial stress. For example, an overpotential of \( \Delta \Phi = 10 \text{ mV} \) corresponds to \( \sigma_{0,\text{max}} \approx 75 \text{ MPa} \). We now have a basis for relating electrical driving force to mechanical failure. With a uniform internal stress, \( \sigma \), inside of the flaw, linear elastic fracture mechanics gives the following criterion for crack extension

![Figure 9. Simplified schematic of a Li filament in a solid electrolyte matrix. The arrows at the rounded end of the filament depict the applied pressure from the Li metal (and are also present along the length of the filament), and the arrows along the side show shear tractions due to friction along this interface. The model predicts a maximal stress at the filament tip that decays along the length of the filament from the tip backward. Note that the actual filaments that were observed have a much higher aspect ratio than what is shown here, and that the crack extension model is based on an atomically sharp tip. The thickness of the filament in the y-direction, \( h \), was observed to be \( \approx 300 \) nm for extended cracks in the experiments.

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\( F \) is Faraday’s constant and \( V_m^{\text{li}} \) is the molar volume of lithium metal (13 cm\(^3\) mol\(^{-1}\)). This relationship shows that even a relatively small overpotential can lead to substantial stress. For example, an overpotential of \( \Delta \Phi = 10 \text{ mV} \) corresponds to \( \sigma_{0,\text{max}} \approx 75 \text{ MPa} \). We now have a basis for relating electrical driving force to mechanical failure. With a uniform internal stress, \( \sigma \), inside of the flaw, linear elastic fracture mechanics gives the following criterion for crack extension
Here, $\sigma_{\text{IC}}$ is the fracture toughness, which has been measured to be $0.23$ MPa m$^{1/2}$ for glassy LPS and $1.25$ MPa m$^{1/2}$ for polycrystalline LLZO. From theory, the geometric factor, $\gamma$, of the surface crack shape is taken to be $1.12$. Setting $\sigma_{\gamma \pi a} = \sigma$ yields a limiting case where the uniform internal stress is assumed equal to the maximum hydrostatic stress expressed in Equation (4). In this situation note that there is no deviatoric component to the stress tensor and thus the low yield stress of lithium metal is not relevant (i.e., plastic flow will not occur). While this simplification is not valid for the initial stress build-up at the tip that is shown in Figure 9, continuing lithium addition to a static crack should cause the internal stress to approach the hydrostatic limit as long as the aspect ratio is high enough to minimize the stress-relaxation effects near the surface (e.g., the extrusion-like process mentioned above). For this limiting case, Figure 10 plots the corresponding minimum overpotential, $\Delta \Phi$, as a function of the flaw size, $a$, for LPS and LLZTO. Also plotted are the maximum stresses, $\sigma_{\gamma \pi a}$, both quantities decrease with an inverse square root dependence on the crack length.

Comparing the results of the model to present experimental conditions, the glassy LPS sample with introduced flaws of $\approx 25$ µm depth should exhibit crack extension for stresses $>25$ MPa, which corresponds to an overpotential of $>3.1$ mV. In our galvanostatic experiments, the total voltage drop at current density of $1$ mA cm$^{-2}$ is $\approx 0.4$ V, the majority of which is due to SSE resistance. The required overpotential for crack propagation is only $\approx 1\%$ of this value, and should be easily reached. For the LLZTO single crystals, the surface defect sizes of $30$–$50$ and $0.4$–$1$ µm correspond to critical overpotentials of $12$–$16$ and $135$–$85$ mV, respectively. The polycrystalline LPS has surface defects of $\approx 0.2$ µm width (Figure 6e) but likely greater depth, including the possibility of continuous multigrain junctions. Assuming $\approx 1$ µm deep flaws, propagation should occur at only $\approx 16$ mV overpotential. Thus for three of the four experimental cases considered here the predicted overpotentials are relatively small and easily reached in galvanostatic experiments at current densities above the values of $1$–$5$ mA cm$^{-2}$ at which crack propagation is observed. The higher overpotential for the polished LLZTO specimen is also plausible, and here it is quite possible that the actual threshold value is somewhat lower because of the inherent challenges associated with estimating the maximum flaw size for the polished surface. Precise measurement of the plating overpotential is experimentally challenging since there are several potential drops within the cells to be resolved. Nonetheless, our analysis suggests that relatively small overpotentials are sufficient to create lithium-plating stresses that are sufficient to propagate lithium metal filaments via Griffith-like crack extension through brittle solid electrolytes.

3. Summary and Conclusions

The growth of lithium metal filled cracks through four types of solid electrolytes, glassy LPS, $\beta$-Li$_3$PS$_4$, polycrystalline and single-crystal LLZTO, was studied using galvanostatic electrolysis experiments coupled with in situ and ex situ microscopy. An electrochemomechanical model for growth of lithium-filled cracks was developed. For current densities up to $5$ mA cm$^{-2}$, only the as-fractured surface of glassy LPS has lithium metal deposition at the surface alone, without penetration of the solid electrolyte. All other surfaces of LPS and LLZTO studied exhibit defects, the maximum initial sizes of which are directly observed or deduced. Electrodeposition of lithium at these surfaces is accompanied by the filling, and then propagation, of lithium metal filled cracks, even at highly polished surfaces of LLZTO with $4$ nm rms roughness (but occasional $0.4$–$1$ µm deeper flaws). The experimental results and electrochemomechanical model suggest that above a critical current density, the Li plating overpotentials, and corresponding mechanical stresses, reach values sufficiently large to extend surface defects, which subsequently can also form more complex networks. Thus, the prevailing failure mechanism in brittle solid electrolytes is Griffith-like, and differs from the amplification of kinetic perturbations at the metal interface that results in dendrite growth in liquid electrolytes. The results suggest that the shear-modulus criterion proposed by Monroe and Newman for prevention of dendrites is not the determining factor for typical high modulus, brittle inorganic electrolytes. It is suggested that stabilization of inorganic solid electrolyte interfaces against lithium metal penetration will require scrupulous attention to minimize interfacial defects.

4. Experimental Section

Synthesis: Experiments were conducted on four types of solid electrolytes, amorphous $70/30$ mol% Li$_2$S-P$_2$S$_5$ (glassy LPS), polycrystalline $\beta$-Li$_3$PS$_4$, polycrystalline and single-crystal Li$_6$La$_3$ZrTaO$_{12}$ garnets (LLZTO). The glassy LPS sample was synthesized using
Li$_3$S (Alfa Aesar, 99.9%) and P$_2$S$_5$ (Sigma Aldrich, 99%) in a ratio of 70/30 mol%, mixed in an argon-filled glove box and sealed in a carbon-coated quartz ampoule under house vacuum. The ampoule was then heated at 750 °C for 2 h in a preheated furnace, followed by quenching in ice water. β-Li$_3$P$_2$S$_5$ powder was synthesized via a wet chemical procedure described in ref. [35]. The powder (≈200 mg) was then cold-pressed into a pellet of 10 mm diameter and ≈1 mm thickness under a uniaxial pressure of 700 MPa. Polycrystalline LLZTO was synthesized by a high-temperature sintering route described in ref. [56]. The single-crystal LLZTO sample was grown by the Czochralski method directly from the melt. The starting materials, Li$_2$CO$_3$ (99%, Merck), La$_2$O$_3$ (99.99%, Aldrich), ZrO$_2$ (99.0%, Aldrich), and Ta$_2$O$_5$ (99.99%, Aldrich) were dried, mixed in a stoichiometric ratio with 10 wt% excess of Li$_2$CO$_3$, then polycrystalline/single-crystal LLZTO samples were pressed into contact. The pellet was then melted in an iridium crucible by RF-induction heating using a 25 kW microwave generator. An iridium rod was used as a seed for crystal growth within a nitrogen gas atmosphere. 1.5 mm h$^{-1}$ and 10 rpm were the seed pulling and rotation rates, respectively. The transparent crystal was then cut into 3 x 3 x 3 mm cuboidal LLZTO samples.

In order to prepare the LLZTO samples for electrodeposition experiments, the surfaces were first lapped using 400 grit size SiC abrasive paper. In order to produce the most highly polished surfaces used in this study, the sample was then sequentially polished using successively finer abrasives: SiC abrasive paper of 400, 1000, 2000, and 4000 grit size. Finally, the sample was polished using alumina abrasive pastes of 1 μm and 50 nm particle size. All samples were then sonicated for 5 min in deionized water to remove polishing debris, following which gold electrodes were sputtered onto the polished surfaces.

Characterization of Material Properties: For ionic conductivity measurements, previously described β-Li$_3$P$_2$S$_5$ pellet was sandwiched between two stainless steel (SS) current collectors to prepare a SS/β-Li$_3$P$_2$S$_5$/SS cell. EIS measurements were conducted at room temperature using a Solartron 1400/1470E cell test system, whereas the sinusoidal voltage amplitude was set to 10 mV and the frequency was swept from 1 MHz to 100 Hz. Single and polycrystalline LLZTO samples were prepared for ionic conductivity measurements by depositing a 10 nm thick Ti layer on the pellets followed by a 200 nm thick Pt electrode. EIS experiments were then performed using a Novocontrol Alpha analyzer, wherein the sinusoidal voltage amplitude was set to 10 mV and the frequency was swept from 5 MHz to 100 Hz. XRD patterns for β-Li$_3$P$_2$S$_5$ and polycrystalline LLZTO samples were obtained using a PANalytical X’Pert Pro multipurpose diffractometer and a Siemens D8 diffractometer, respectively. Both diffractometers were equipped with a Cu Kα radiation source.

Experimental Setup and Characterization: Li plating experiments were performed in an Ar-filled glove box. The apparatus consisted of a lithium metal disk counter electrode upon which the β-Li$_3$P$_2$S$_5$ and polycrystalline/single-crystal LLZTO samples were pressed into contact. The irregularly shaped glassy LPS sample was embedded in a β-Li$_3$P$_2$S$_5$ powder matrix to which the Li disk was attached. The top surface of the samples was contacted with a spring loaded brass tip electrode (≈50 μm radius, ≈1 N spring load), except in case of the single-crystal LLZTO sample with a sputtered gold electrode where a tungsten wire (50 μm radius, ≈1 N spring load), except in case of the single-crystal LLZTO sample with a sputtered gold electrode where a tungsten wire (50 μm radius, ≈1 N spring load) was used instead.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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