A New General Paradigm for Understanding and Preventing Li Metal Penetration through Solid Electrolytes

Yue Qi[1], Chunmei Ban[2]*, and Stephen J. Harris[3]

[1] School of Engineering, Brown University, Providence, RI, 02912, USA

[2] Mechanical Engineering, University of Colorado Boulder, Boulder, CO, 80309, USA

[3] Energy Storage Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Abstract

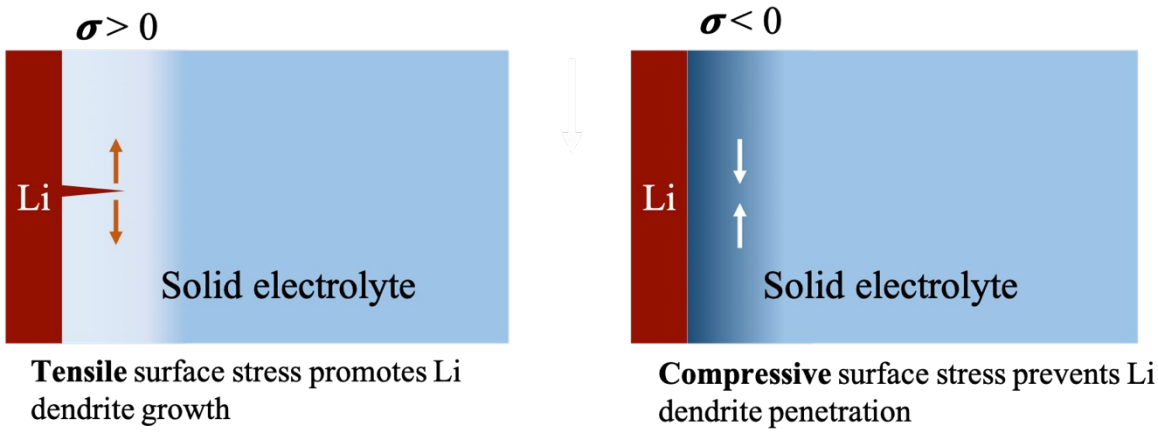
The use of lithium (Li) or sodium (Na) metal anodes together with highly ion-conductive solid electrolytes (SEs) could provide batteries with a step improvement in volumetric and gravimetric energy densities. Unfortunately, these SEs face significant technical challenges, in large part because Li and Na dendrites can penetrate through the SEs, leading to short circuits. The ability of such a soft material (Li or Na metal) to penetrate through a ceramic is surprising from the point of view of models widely used in the Li battery field.

We introduce a concept, new to the battery field, for preventing penetration of lithium dendrites through SEs by putting the SE surfaces into a state of residual compressive stress. For a sufficiently high compressive stress, cracks have difficulty forming, and cracks that do form are forced to close, inhibiting dendrite penetration. This approach is widely used to solve commercially important stress corrosion cracking problems in metals and static fatigue problems in ceramics and glasses (e.g., Gorilla Glass). However, the technique will not be useful for SEs if

* Correspondence: chunmei.ban@colorado.edu

the Li ion transport rate through a SE is substantially reduced when the SE is in compression. Our molecular dynamics calculations for Li ion transport through a common SE demonstrate that the introduction of even very high residual compressive stresses (~10 GPa) has only a modest effect on Li ion transport kinetics, suggesting that the approach is viable and capable of providing a new paradigm for developing high-performance and mechanically stable SEs.

TOC Graphic



Introduction

The use of Li or Na metal negative electrodes (anodes) could provide a substantial increase in the gravimetric and volumetric energy density for Li batteries. However, their use in high capacity rechargeable batteries has been precluded, in large part, because of the growth of Li filaments (loosely called "dendrites").[1] The filaments provide surfaces for degradation reactions, and they may become electrically isolated. Dendrite penetration into solid electrolytes, which occurs readily,[2] can induce mechanical failure and fracture of solid electrolytes, and if the dendrites

reach the positive electrode, they will cause a short circuit, potentially leading thermal runaway or fire.[3-8]

The battery community has taken several approaches to addressing the dendrite penetration problem.[9,10] Monroe and Newman and followers proposed an electrochemical-mechanical model in which Li metal with a small protrusion (proto-dendrite) is pressed conformally, or nearly conformally, against a solid polymer separator.[11-13] They found that a sufficiently high separator shear modulus, could prevent penetration. However, neither suppression of dendrite penetration in liquid electrolyte cells under moderate stack pressures,[14,15] nor penetration through solid electrolytes with very high shear moduli—cases that do not involve solid polymer separators—can be readily explained with this paradigm.[2,16] We attribute this discrepancy to a combination of the model not incorporating Li creep; ignoring internal defects in the solid electrolyte; and assuming near-conformal contact, which is not realized for interfaces between Li metal and either thin commercial separators or solid electrolytes under commercially feasible pressures.[14,16] It is important to note that because only a small fraction of the Li metal and solid electrolyte surfaces are in physical contact[16], GPa-level hydrostatic pressures in Li cannot[17] build up against SEs because Li rapidly relaxes, by deformation and creep, into non-contact regions that may be at a considerable distance from the contact point. Even if contact is conformal inside cracks, Li will still be readily squeezed out of the crack at the dendrite's base if the hydrostatic pressure climbs to or above the Li hardness, given the very high sensitivity of the creep rate to stress.[18] We note that the MPa-level stresses that are possible are too small to affect the plating reaction,[14] while GPa-level compressive stresses could significantly inhibit plating.[17] Thus, we believe that contact mechanics between Li and a solid electrolyte cannot be properly modeled on

a scale of a single penetrating dendrite. In addition, internal defects, such as pores, cracks, and grain boundaries in solid electrolytes can trap electrons and nucleate metallic Li, even ahead of the Li-metal front.[19]

Chemical and physical modifications to the Li-separator interface, such as introduction of nanostructures or coatings or by modification of the electrolyte,[20-34] have seen some success in inhibiting dendrite growth, while other approaches have focused on developing new solid electrolytes and special Li hosts or on controlling the temperature.[35,36,37,38] Nevertheless, to date there are no commercially available high capacity rechargeable Li metal batteries that operate at current densities comparable to those in liquid electrolytes, in significant part because of the dendrite penetration problem. This Perspective proposes a new paradigm for eliminating dendrite-induced short circuits.

A New Approach to Suppress Lithium-Dendrite Penetration of SEs

Our proposed approach is based on an analogy to stress corrosion cracking (SCC),[39-42] which has been studied and largely solved in the corrosion field. SCC occurs when the surface of a component is chemically (usually electrochemically) attacked at a defect or heterogeneity.[43] The result is the formation or extension of an incipient crack that can grow if and only if the crack tip is in a sufficiently high state of tension. Thus, SCC crack growth occurs under the combined effect of a chemical reaction plus local tensile stresses that are above some threshold value but below the level required for fast crack propagation.[44,45] SCC has led to catastrophic results, such as the collapse of the Silver Bridge across the Ohio River. In that case, local rusting led to stress corrosion cracks that followed grain boundaries in the steel.[46,47] Although SCC is often thought of

as occurring primarily in metals, it can also occur in glasses, ceramics, and quartz, where the process is known as static fatigue.[48-53]

Since the attacking medium in SCC is usually water, shear strength[11,12] plays no role, so the fact that soft Li metal penetrates through hard ceramic solid electrolytes is not surprising if SCC is the mechanism.[11,12] Furthermore, high hydrostatic pressures in the Li are not required, since the SCC driving force comes from chemical reactions in regions of tensile stress in the solid electrolyte rather than from pressure. The proposed analogy between water penetration and Li metal penetration is visualized in **Figure 1**, which shows stainless steel that has been attacked by water via SCC,[54] where intergranular cracks were observed during aging at 550 ˚C, **Figure 1(a).** The formation of chromium carbides along the grain boundaries, which is facile at elevated temperature, results in creation of a chromium-depleted region, exacerbating the susceptibility to intergranular corrosion when tensile stresses are present. **Figure 1c** shows intergranular penetration of LLZO by Li metal, forming dendrites as the cracks propagate.[2] As illustrated in **Figures 1b** and **1d**, both processes involve corrosive/electrochemical environments together with the presence of heterogeneities,[43] including grain boundaries, contaminants, or precipitates. We suggest that, in analogy with SCC, local residual tensile stresses promote Li dendrite penetration

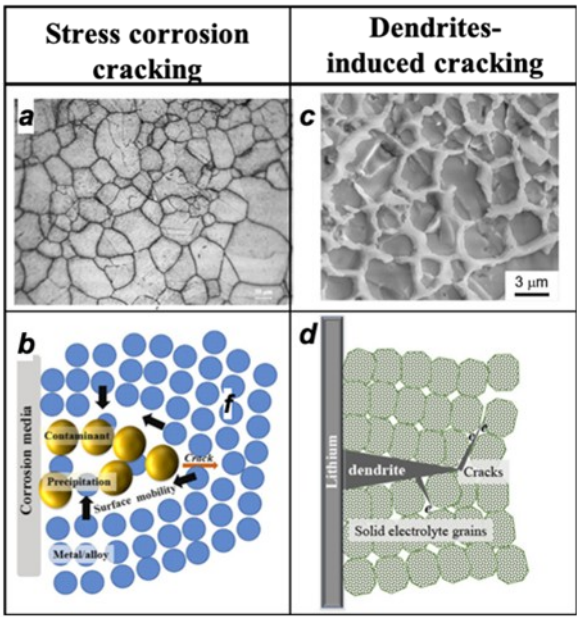


Figure 1: SEM images of (a) intergranular cracking in stainless steel (b) the intergranular penetration of LLZO by Li. Schematic of (c) SCC propagation and (d) lithium penetration into LLZO.

via crack propagation. Detailed modeling demonstrates how tensile stresses and crack propagation interact in secondary NMC particles.[55]

An approach that often solves SCC problems is putting the surface into a state of residual compressive stress. For example, the crack resistance of Gorilla Glass is due to exchanging smaller sodium atoms near the surface with larger potassium atoms.[56]

We are not aware of any spatially resolved surface stress measurements in solid electrolytes, although residual tensile stresses above 100 MPa in LLZT were observed from SPS processing.[57] Experiment shows that when tensile, such stresses can result in highly brittle products.[58] Local tensile residual stresses can also be generated from heterogeneities as well as from machining or polishing.[59-62] Thus, solid electrolytes may be readily susceptible to an analog of SCC (or static fatigue) as well as to brittle fracture.

However, the analogy between solving SCC and solving Li dendrite penetration is imperfect because a solid electrolyte must also maintain sufficient ionic conductivity after the compression is introduced, a factor that is irrelevant for something like Gorilla Glass. Previous work has shown that internal stresses can have a significant impact on ionic conductivity, and it is possible that putting the solid electrolyte into compression could substantially hinder ion mobility.[63-69]

Evaluation of the Impact of Stress on Li Diffusion

To evaluate the effect of a hydrostatic compressive stress on Li diffusion kinetics, molecular dynamics (MD) simulations were performed as described in the Methods section. Results are shown in **Figure 2(a)**, which were calculated at 1100K to accelerate the diffusion process. The

Li self-diffusivity D in LLZO was fitted to the linear region of the root mean square distance (RMSD) vs simulation time. The diffusivity was then plotted as a function of the average hydrostatic pressure.

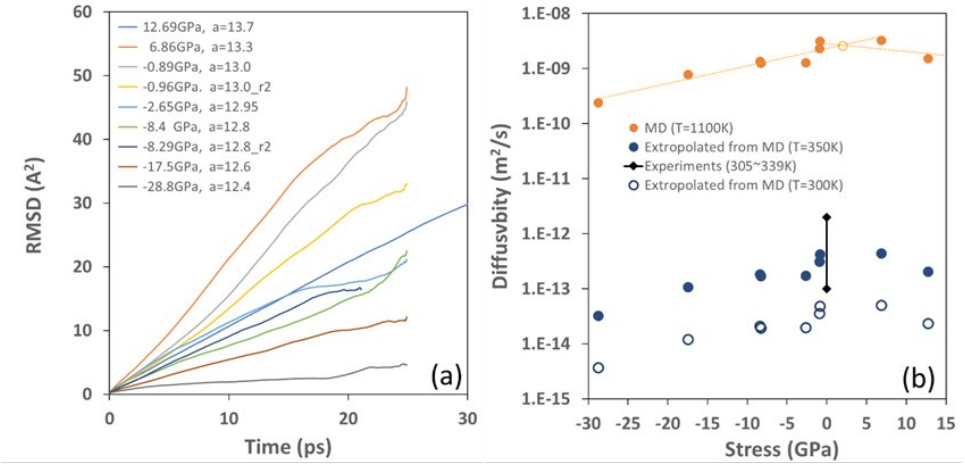


Figure 2. (a) Simulated average Li RMSD vs. simulation time with varying lattice parameters. (b) Li self-diffusivity as a function of stress (positive stress means tension). The dotted lines fitting the diffusivity with positive and negative slopes intersect at 2 GPa and a peak stress of 2.6 x10^{-9} m^2/s.

Simulation results at 1100K (orange dots, **Figure 2(b)**) show a peak diffusivity of 2 GPa tensile stress. In order to compare to experiments at room temperature, the simulated diffusivity was extrapolated to 300K (blue circles) and 350k (blue dots) based on the experimentally measured activation energy of 0.38 eV, a value that is insensitive to strain, according to density functional theory (DFT) calculations.[70,71] The solid blue dots, **Figure 2(b),** show that the simulated/extrapolated room temperature Li diffusivity at zero stress is ~0.5×10^{-13} m^2/s, which is within the range of experimental values, $0.1-2\times10^{-12}$ m^2/s[70], supporting the MD simulation results. It is not surprising to see that Li diffusivity peaks around 2 GPa tensile stress because fast ionic conductivity in LLZO is enabled by low-barrier concerted ion migrations, which are triggered by the strong ion-ion Coulomb interactions at unique ion configurations. While compression shrinks the free volume available for Li ion mobility, high tension may reduce the Coulomb interactions required for fast ion conductivity.

Although the Li diffusivity decreases under compression, even at 10 GPa compression the diffusivity is still 40% of its value at zero stress. This difference is even less than the variation of the experimental data at zero stress. Consistent with our results, we note that the experimentally measured Li ion conductivity in LLZO showed minimal changes under compressive residual stresses between 12.5 MPa and 50 MPa.[72] This observation can be generalized to other solid electrolyte systems. Famprikis et al.[73] recently summarized the activation volume, the change of activation barrier to pressure, for cation conduction in many solid electrolytes. Depending on the diffusion carrier (vacancy or interstitial), the activation volume is either positive or negative. All values (1.7±1.4 cm^3/mol) lead to 0.017±0.014 eV activation energy change with a pressure of 1 GPa. For the commonly used lithium solid electrolytes, less than 5% impedance and 0.01 eV activation energy change were reported in mechanically strained LiPON;[74] less than 0.02~0.05 eV migration barrier change was reported up to a 4% of strain in $Li_{10}GeP_2S_{12}$ and in LLZO.[67,71,75,71,76] The only exception and discrepancy reported is that the Li migration barrier in Li $Li_{10}GeP_2S_{12}$ is much higher under compression than tension.[75] Therefore, we conclude that even very large compressive stresses will not have a large impact on Li ion diffusion over short distances in most of the solid electrolytes.

Methods for Applying Compressive Stress

As mentioned above, SCC can occur only when the surface is in tension, so a highly successful and widely used strategy for preventing SCC has been to put the component's surface into a state of residual compression. If this residual compressive stress is high enough, cracks are difficult to form or grow, and cracks that exist are forced to close. Among the most widely used techniques to introduce a surface residual compressive stress in metals is shot peening,[77-80] which is a cold

164 working process where large numbers of small hard particles (metallic, ceramic, or glass)
165 impinge on the component with sufficient force to deform it plastically and put the surface into
166 compression.[81,82] For brittle materials such as ceramics and glasses, other techniques have been
167 developed for commercial application. Among them are laser shock peening (LSP), which can
168 yield compressive stresses of up to 500 MPa in aluminum oxide;[83] ion implantation;[84,85] and ion
169 exchange[49,86] (which is used to make Gorilla Glass).[49,56,86] The latter techniques can introduce
170 compressive residual stresses as high as 10 GPa in aluminum oxide, although much lower
171 stresses are appropriate for metals, typically half the yield stress.[85] We next consider each of
172 these approaches, except for shot peening, for use with LLZO.

173 LSP introduces laser plasma-driven shock-waves into a material, typically using a plasma-
174 confining medium (e.g., glass or water) to increase the peak pressure of the shock wave. A
175 sacrificial layer is often used to protect the treated sample from laser ablation. Shukla et al.
176 demonstrated that their LSP-treated a-Al_2O_3 had a biaxial compressive residual stress of several
177 hundred MPa that extended to a depth of up to 1.2 mm from the surface.[83]

178 Ion exchange has also been used to introduce compressive stresses at the surface, typically by
179 exchanging alkali (or sometimes alkaline-earth) ions in the original glass/glass-ceramic with
180 larger ones from a molten salt bath.[87] The introduction of large ions near the surface induces a
181 volume increase, generating a compressive stress in the ion-exchange region. The final
182 mechanical properties are dependent on the stress level at the surface and the depth of
183 penetration of the larger ions.

Unfortunately, the use of these strengthening strategies for preventing Li dendrite penetration through solid electrolytes face potentially severe constraints. In the case of ion exchange, only a limited selection of ions can be introduced. Also, ion exchange strongly favors the exchange of monovalent ions—replacing the Li in this case—whose removal will inhibit Li ion mobility in the exchanged region. While LSP avoids these problems, it may create heterogeneous surface damage that could increase the interface resistance; it can also create local tensile stresses.[83] Furthermore, the range of stresses introduced by LSP, up to hundreds of MPa, is much lower than what is possible with other techniques.

The preferred alternative, in our estimation, is ion implantation, which can be used to introduce residual surface compressive stresses with control of stress level, depth profile, crystallinity, and chemistry in the near-surface region (10 to 1,000 nm). It has been used commercially for decades to strengthen polymers, glasses and ceramics in order to solve stress corrosion cracking (SCC) or static fatigue problems, but it has not been applied to SEs, to our knowledge. An advantage of ion implantation is the large number of chemical, structural, and physical states that can be created, including metastable non-equilibrium states, for nano/mesoscale tailoring the surface structure of SEs.

Energetic implanted ions can include transition metal ions, halide ions, rare gas ions, and even lithium ions, which can modify the surface structure—including creating local disorder—leading new mechanical properties for solid electrolytes, as illustrated schematically in **Figure 3**. With its control of dopant species, concentration, and spatial distribution

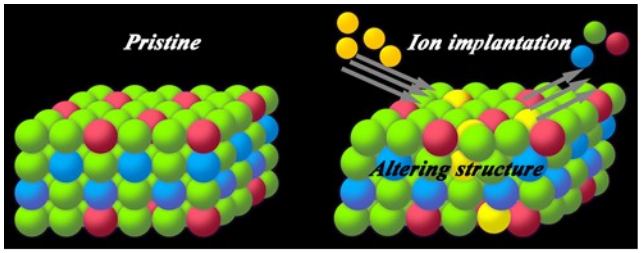


Figure 3: Schematic of using ion implantation to alter structure of solid electrolytes.

(implantation depth), ion implantation has also been widely used in modifying electronic properties of semiconductors for the microelectronics industry, as well as strengthening of metals and non-conducting ceramics.[88] Recent work has shown a positive impact of using ion beam modification on the ionic conductivity of polymer electrolyte films due to increased charge carries and dielectric constant.[89] Implantation can amorphize the implanted region, but the fact that both crystalline and glassy SEs transport Li ions[7,58] suggests that this issue may not be severe. Implantation also changes the chemical identity of the implanted region.[7] Effects of typical implanted doses (less than 1%) on Li ion conductivity will be studied in future work. Minimizing the thickness of the implanted region may ameliorate these issues. Since monovalent ions tend to be mobile, we will concentrate our efforts on polyvalent ions for implantation. Of course, any polishing treatment to remove surface contaminants would have to be performed before implantation.[90]

Finally, we note that introduction of compressive residual surface stresses is expected to make any material, including SEs, less brittle and, thus, easier to handle in a commercial environment. We expect that implantation of solid electrolytes will enable materials with properties that can be optimized for batteries as well as for a wide variety of other applications.

Conclusion and Perspective

In summary, inspired by successful work on stress corrosion cracking, we have proposed a new paradigm for inhibiting dendrite penetration through solid electrolytes: we suggest putting the SE surfaces into a state of residual compressive stress in order to inhibit the short circuits—initiating either at the Li surface or from within the SE—that accompany dendrite penetration. We have

performed MD simulations to demonstrate that the introduction of even very high (~10 GPa) hydrostatic compressive stresses in LLZO has only a modest impact on Li diffusion kinetics, enabling our proposal. In addition to inhibiting dendrite penetration in solid electrolytes, compressive stresses on the order of GPa will improve their fracture toughness and will tend to suppress lithium nucleation in the compressed region inside of solid electrolytes because of an increased overpotential. While there are a number of techniques that can be used commercially to introduce compressive residual stresses, we suggest that ion implantation will be the most useful for this purpose, as it may provide a new avenue for developing controllable, high-performance and stable solid electrolytes.

METHODS

A periodic cubic cell of $Li_{24}La_{24}Zr_{16}O_{96}$ was simulated using GULP software and implemented in Materials Studio with a force-field including the long-range Coulombic potential, the short-range Buckingham potential, and a core–shell polarizable potential for O atoms following the parameters provided in.[91] The simulation cell length was varied from 12.4 Å to 13.7 Å, and the root mean square displacement (RMSD) of Li^+ ions was tracked during NVT (fixed cell) dynamics.

AUTHOR CONTRIBUTIONS

S.J.H. and C. B. proposed the idea and concepts. Y.Q. did the calculations. All authors contributed equally to the writing of the manuscript.

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518 **Figure Legends**

519 **Figure 1:** Comparison between the intergranular cracks caused by SCC and Li intergranular
520 penetration into LLZO. Surface morphology of SCC propagation and the intergranular
521 penetration of LLZO by Li are shown in (a) and (c), respectively. Reprint with permission from
522 ref. 2 and 54. Copyright 2017 Elsevier. Schematic illustration of the SCC propagation and
523 lithium penetration into LLZO is shown in (b) and (d).
524

525 **Figure 2:** (a) Simulated average Li RMSD vs. simulation time with varying lattice parameters.
526 (b) Li self-diffusivity as a function of stress (positive stress means tension). The dotted lines
527 fitting the diffusivity with positive and negative slopes intersect at 2 GPa and a peak stress of 2.6
528 $x10^{-9}$ m^2/s.
529

530 **Figure 3:** Schematic of using ion implantation to alter structure of solid electrolytes.

531