

Perspective

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Challenges in Lithium Metal Anodes for Solid State Batteries

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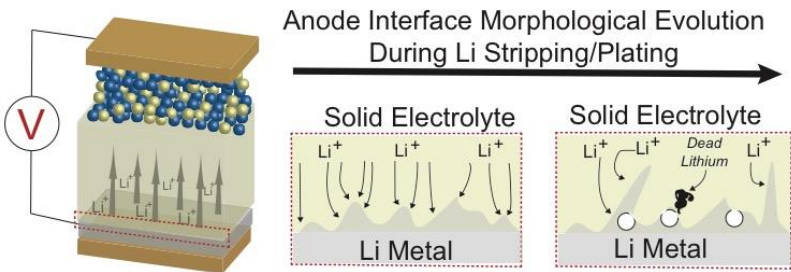
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ABSTRACT

In this perspective, we highlight recent progress and challenges related to the integration of lithium metal anodes in solid-state batteries. While prior reports have suggested that solid electrolytes may be impermeable to lithium metal, this hypothesis has been disproven under a variety of electrolyte compositions and cycling conditions. Herein, we describe the mechanistic origins and importance of lithium filament growth and interphase formation in inorganic and organic solid electrolytes. Multi-modal techniques that combine real and reciprocal space imaging and modeling will be necessary to fully understand non-equilibrium dynamics at these buried interfaces. Currently, most studies on lithium electrode kinetics at solid electrolyte interfaces are completed in symmetric Li-Li configurations. To fully understand the challenges and opportunities afforded by Li metal anodes, full-cell experiments are necessary. Finally, the impacts of operating conditions on solid state batteries are largely unknown with respect to pressure, geometry, and break-in protocols. Given the rapid growth of this community and diverse portfolio of solid electrolytes, we highlight the need for detailed reporting of experimental conditions and standardization of protocols across the community.

TOC GRAPHICS



There is considerable interest in replacing graphite anodes in rechargeable batteries with Li metal due to its high theoretical capacity (3860 mAh/g) and large negative potential (-3.06 vs. NHE)¹. However, Li metal is prone to unstable side reactions, leading to solid electrolyte interphase (SEI) and dendrite formation when in contact with most liquid electrolytes. These side effects can lead to considerable safety concerns and a loss of efficiency. Solid electrolytes that are chemically stable against Li metal may be able to suppress these negative effects. However, there remain several unknown aspects to the nature of ion transport and kinetics at Li-metal|solid-electrolytes (Li-metal|SE) interfaces. For future adoption, it is critical to understand Li-metal|SE interfaces to mitigate Li filament formation, achieve reliable power densities, and maintain a high Coulombic efficiency over the cycling lifetime.

Controlling the morphology of Li metal during electrochemical stripping and plating processes at Li-metal|SE interfaces is necessary for the realization of energy-dense Li-metal solid-state batteries (SSBs)²⁻⁴. Li metal SSBs could potentially increase energy density and reduce space and weight requirements (Fig. 1a).⁵ However, achieving $>10 \text{ mAh cm}^{-2}$ cumulative capacity plated at failure, $>3 \text{ mA cm}^{-2}$ plating current density, $>3 \text{ mAh cm}^{-2}$ per cycle areal capacity, and $>80\%$ fraction of Li passed per cycle are all necessary at the device level to displace the current state-of-the-art graphite anodes.⁴ Few reports come close to these targets because Li metal is prone to interfacial instabilities and significant volume changes. This perspective summarizes the recent progress in understanding Li metal|SE interfaces for SSBs, with the goal of ultimately controlling factors such as Li filament growth and interfacial reaction/delamination during electrochemical cycling. The mechanistic origins of lithium filament growth in SEs is discussed with respect to interphase formation and lithium mechanics. Next, the perspective highlights state-of-the-art characterization tools equipped to observe Li|SE interfaces and discusses future needs, including

techniques that provide complementary chemical and structural information. Finally, the paper concludes with a discussion of frontiers in modeling and remaining open questions in the quest for Li-metal SSBs (Fig. 1a).

Lithium Penetration through Solid Electrolytes. Graphite has been the standard anode material for decades because reactive Li metal can lead to dendrite formation, short-circuits, and fires. Concentration gradients across a cell can create excess charge at an interface (local space charge) and induce instabilities (e.g. dendrites). The term ‘Li dendrite’ broadly describes the formation of a wide range of non-planar/branched metal morphologies, and may not accurately describe the complex mechanisms involved in SEs (Fig. 1b). Li filaments through SEs plague SSBs, leading to a loss of efficiency and cell failure. Understanding the nature of this growth is imperative for next generation SSBs.

The current density at which a Li filament propagates across a SE is known as the critical current density (CCD). The magnitude of the CCD is important because it dictates the power density of a cell. Low CCDs are generally ascribed to iR losses that emerge as a result of interfacial impedances between the SE and the electrodes. These interfacial impedances are largely governed by chemical, electrochemical, and mechanical stability issues at interfaces. Deconvoluting these loss mechanisms and interpretation of CCD measurements can be challenging because SEs may be susceptible to ‘soft shorts’ that can go undetected in symmetric cell experiments that utilize thick lithium metal ($>30\ \mu\text{m}$).⁴ Furthermore, the CCD is dependent on cell stack pressure and plating capacity and thus it is necessary to report detailed experimental conditions (e.g. Li metal thickness and stack pressure) to accurately interpret data.³ Recently, Sakamoto and co-workers described a new terminology, critical stack pressure, which highlights the pressure dependency in CCD measurements.³ This parameter is an important additional metric for evaluating Li electrode

properties at SE interfaces. Pores in Li metal formed during electrochemical dissolution (stripping) and uneven Li^+ transport at anode-electrolyte interfaces may be origins for dendrite nucleation⁶⁻⁸. A nominal stack pressure can aid in mitigating pore formation during Li stripping. However, Li filament growth and propagation occurs upon Li plating. When these occur simultaneously in Li-Li cells, the pressure will significantly affect CCD. However, it is unclear exactly how these effects will translate to full cells, where plating and stripping are independent processes. Further work is necessary to resolve differences between whole cell and symmetric experiments.

Li filament growth at a solid polymer electrolyte (SPE) interface is dependent on the electrolyte's transference number, the electrolyte's mechanical properties, and Li metal impurities (Fig. 1c). Ionic transport in SPEs (for example, polyethylene oxide (PEO)) mimics the transport characteristics of liquid electrolytes and can be accurately described by the concentrated solution theory for binary electrolytes based on the Onsager-Stefan-Maxwell formalism⁹. Thus, current flux is a consequence of ion transport under both concentration and potential gradients in the polymer electrolyte, with a transference number of the cation being less than unity.⁸ Consequently, the CCD

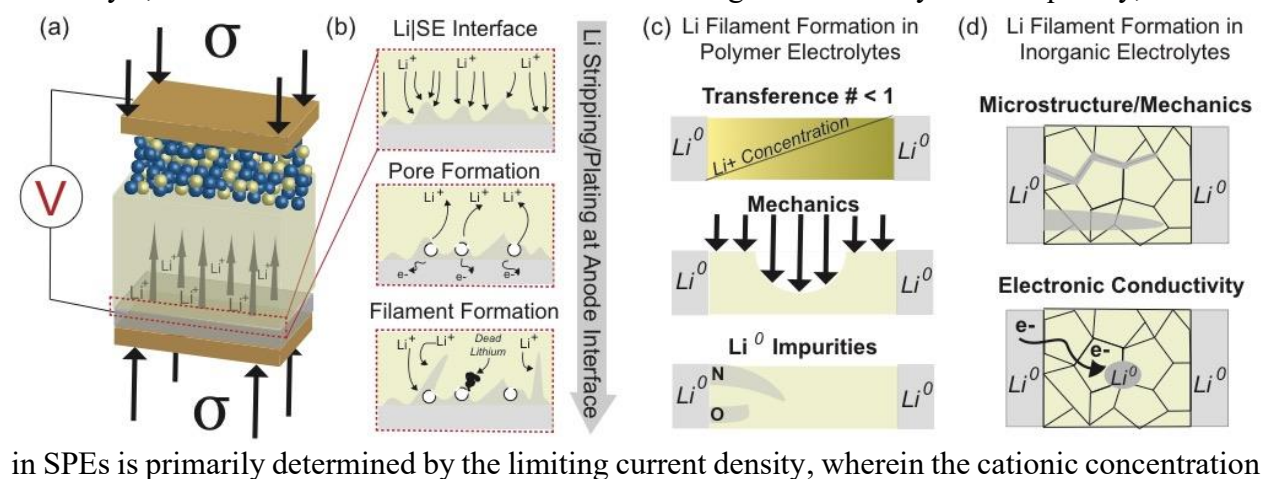


Figure 1 Li-metal solid-state battery architecture. To achieve adequate rate performance, pressure (σ) is applied to the cell (a). The morphology of the interface governs local ionic flux, pore formation in the Li-metal upon stripping and Li filament growth (b). Li filament growth in a polymer solid electrolyte is governed by electrolyte mechanics, transference number, and the presence of interfacial impurities (c). Li filaments in inorganic SEs are attributed to electronic conductivity, microstructural properties, and interfacial contact (d).

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3 goes to zero at Sand's time, engendering unmitigated dendritic growth.¹⁰ Sand's time is inversely
4 proportional to the square of the anionic transference number, and thus single-ion solid conducting
5 SEs (inorganic or polymer) are theoretically stable against Li filament growth.¹¹⁻¹² However, a
6 large number of single-ion conducting polymers have been developed without significant
7 improvements to the CCD.¹²⁻¹³
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16 Monroe and Newman predicted that if the shear modulus of a SPE exceeded 6 GPa, Li
17 filaments could not penetrate the SPE.⁶ Recent work by the Balsara group has shown that
18 improving the modulus can increase the CCD, especially at high temperatures, but it cannot
19 entirely eliminate Li filament formation.¹⁴⁻¹⁷ Thus, neither the mechanical properties nor the
20 transference number of the SE can fully determine the growth of Li filaments through SPEs. In
21 models such as the Monroe and Newman model, Li is assumed to be pure, which may not be fully
22 representative of the interfacial composition. X-ray imaging has shown that Li metal surface
23 impurities (Li_2O , Li_3N , or Li_2CO_3) can cause inhomogeneities in the local current density and
24 promote the nucleation of Li protrusions (Fig. 1c).¹⁸⁻²⁰ Thus, while increasing the elastic modulus
25 and transference number of SPEs is critical, the purity of the Li metal source and surface may play
26 a significant role on Li penetration at high current densities. Pre-treatment strategies may be
27 necessary for integration of Li metal.²¹
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44 Single ion conducting inorganic SE (glass and/or ceramic) have distinctly different failure
45 mechanisms than SPEs (Fig. 1d). Metal filament formation has been attributed to physical and/or
46 microstructural properties of the SE, Li metal|SE interfacial contact, and/or electronic properties
47 of the electrolyte (Fig. 1d).²² Pioneering work on solid state Na beta-alumina batteries revealed
48 two modes for Na filament formation. Mode 1 describes filament formation and propagation with
49 respect to SE microstructural features (grain boundaries, voids, scratches, etc.). This failure mode
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is based on Griffith's theories of fracture mechanics, and was used to derive an empirical relationship for the critical current density of a Na beta-alumina system²²,

$$i_{crit} = \left[\frac{\pi(1 - \nu^2)F\gamma_{eff}^2}{8 V_m E \eta} \right] \left(\frac{c^2}{l^3} \right)$$

where ν is Poisson's ratio, F is Faraday's constant, γ_{eff} is the surface energy, V_m is the molar volume of Na, E is Young's modulus, η is the Na viscosity, $2c$ is the crack width, and l is the crack length. In simpler terms, the CCD is determined by the aspect ratio of surface defects (c^2/l^3) such as voids, scratches or cracks, the wetting of the alkali metal to the solid electrolytes (γ_{eff}) and the mechanical properties of the electrolyte. Temperature also plays a key role as this will directly affect the surface wetting (γ_{eff}) and viscosity of the alkali metal (η). Previously, it was shown that heating and constant pressure enable improved contact, lower interfacial resistances, and higher critical current densities²³. In contrast, Mode 2 describes how the electronic properties of the SE governs filament growth.²⁴⁻²⁵ During operation, Na beta-alumina changes colors as the electronic conductivity of the material changes. When the SE is electrically conductive, Na can deposit within the SE and act as a nucleation site for filament growth. These two growth modes provide valuable insights into the driving mechanism for filament propagation in Li SEs. Recent research with Li metal strongly suggests that Li filament propagation is analogous to that of the Na metal filament propagation.

Parallels between Na and Li filament growth mechanisms can be drawn from a series of reports by Porz and Swamy.²⁶⁻²⁷ Porz et al.²⁶ studied Li filament formation and growth in a wide

range of inorganic solid electrolytes ($\text{Li}_7\text{La}_4\text{Zr}_2\text{O}_{12}$, crystalline $\beta\text{-Li}_3\text{PS}_4$, and lithium thiophosphate glasses). Their work demonstrates that lithium filaments prefer to grow through cracks and defects and that plating-induced lithium infiltration can take place in pre-existing microstructural flaws. Later work by Swamy et al. observed that lithium filaments preferentially grew at the electrode edge in grain-boundary free, single-crystal LLZO. Preferential Li growth at the electrode edge, rather than at engineered defects, reveals that filament formation can be driven by local electric-field hot spots. This current focusing leads to preferential Li deposition and results in enhanced mechanical stresses at these locations. Another recent paper by Westover et al.²⁸ corroborates the role that current focusing and surface flaws (e.g. grain boundaries) play on filament propagation. Li filaments demonstrated preferential growth at artificial Lipon-Lipon interfaces and completely avoided the bulk electrolyte. Li filament penetration along the interface is attributed to current focusing, the presence of Li_2CO_3 defects, and the interfacial mechanical properties. All of these factors can contribute to the relatively wide spread in reported CCD values for Li-metal SSBs. There is currently a crucial need for unified, standard operating protocols (ramp rate, current hold duration, etc.) and standard cell architectures for CCD measurements for effective comparison across the community.

Although the most well studied mechanism for Li filament penetration is Mode 1 (microstructure, defect, etc.) a recent paper by Han *et al.*²⁹ highlighted Mode 2 (electronic conductivity) mechanisms. *In situ* neutron depth profiling experiments revealed increases in Li metal content within the SE (Lipon, LLZO, and $\beta\text{-Li}_3\text{PS}_4$) during electrochemical cycling. Increases in Li content within the SE suggests that local depositions of Li metal can occur within the bulk SE (Fig. 1d). These deposits can act as nucleation sites for filament growth and can cause a short circuit. Electron microscopy³⁰ and x-ray tomography³¹ results also showed isolated Li

deposits that supporting this finding. It has been hypothesized that the SE electronic conductivity is responsible for these localized Li deposits,³² however, recent theoretical studies suggest that local reduction of La or Zr at the grain boundaries³³ or electrons trapped at surface defects may drive deposition events.³⁴ Further research is needed to fully understand this mechanism, or combination of mechanisms, and to guide the development of materials and engineering solutions that enable high CCDs at room temperature.

Aside from SE properties, the mechanical properties of the lithium metal anode also play an important role in Li filament formation in SEs. Recent studies of the bulk mechanical response of Li metal have demonstrated that power-law creep is the dominant deformation mechanism over a wide range of strain rates and temperatures.³⁵⁻³⁶ These results help contextualize the evolution of mechanical stresses as Li is plated out at a solid-electrolyte surface from a viscous-flow perspective. The coupled relationships between current density and strain rate directly impact stress accumulation at the solid-solid interface. This has significant implications for the model of Porz et. al.,²⁶ where extrusion of Li metal out of structural heterogeneities on the SE surface will contribute to the current-density dependence of mechanical failure of the SE.

Furthermore, both nano-indentation³⁷⁻³⁸ and micro-pillar compression³⁹ experiments have reported that lithium can support significantly higher stresses when confined to small length scales. Using nano-indentation, Herbert et al. observed a change in the underlying deformation mechanism as a function of indentation depth.³⁸ At shallow indentation depths, self-diffusion dominated the flow and at deeper depths shear-driven dislocation motion was the primary deformation mechanism. Within the diffusive flow regime, the pressure that Li is capable of supporting was found to be significantly higher than the bulk yield stress and strongly dependent on the strain rate, which is directly impacted by the current density. Both of these results

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3 have implications for the propagation of Li filaments within solid-state electrolytes. More research
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5 is needed to understand the role that Li metal mechanics plays on filament formation and growth.
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7 In particular, improved knowledge regarding Li purity (especially at the SE interface), Li
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9 mechanical properties, and how the morphology and microstructure of Li metal change during
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11 electrochemical cycling is needed.
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16 ***Interphase Formation and Engineered Interfaces.*** Solid electrolyte redox stability depends on
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18 the alignment of the solid electrolyte's valence and conduction bands relative to the Li chemical
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20 potential (μ_{Li+}) and decomposition thermodynamics.⁴⁰⁻⁴¹ Thus, most SEs will form an interphase
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22 at Li metal due to redox reactions. The formation of interphase layers between Li and SEs has
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24 widespread consequences for the operation of SSBs. Many SEs under consideration are unstable
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26 in contact with Li metal, and the evolution of the reacted interphase is expected to be dependent
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28 on its transport properties⁴²⁻⁴⁴ An interphase that conducts both ions and electrons (a mixed
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30 conductor) will continue to grow with time due to direct electrochemical reaction occurring at the
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32 SE. An interphase that conducts only ions and not electrons could grow to a stable thickness, which
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34 would ideally result in a passivating layer that enables long-term stability. An interphase with
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36 insufficient ionic conductivity, however, will cause increased impedance. Finally, for stability in
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38 contact with Li metal, the interphase must prevent atomic Li diffusion from the Li anode to the
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40 SE, which is challenging given the relatively high diffusion rate of Li in many materials.
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47 The chemo-mechanics of interphase formation and growth have important ramifications
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49 for battery operation. Li insertion and microstructural transformation during interphase growth
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51 causes the evolution of mechanical stress both within the interphase and within the SE⁴⁵⁻⁴⁶. In SE
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53 materials where the interphase grows to be relatively thick, such stresses can be large enough to
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55 mechanically fracture the SE. Fracture of $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) caused by interphase
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growth was recently monitored with *in situ* X-ray imaging, and it was found that this mechanical degradation was the primary cause of increased cell impedance, rather than the transport properties of the interphase itself⁴⁷. The chemo-mechanics of interphase formation is also important in the context of electrochemical deposition and stripping of Li metal, but this topic has received less attention to date. For instance, stress within the interphase or in the SE near the Li metal interface could alter diffusion barriers and pathways for Li ions. Furthermore, local variations in interphase morphology could lead to stress non-uniformities that may locally alter the potential, which could impact Li deposition/stripping and lead to the formation of Li filaments or dendrites⁷. The interrelationship between interphase growth and Li deposition/stripping mechanics thus requires dedicated investigation by the community. To date, there have been two primary approaches to mitigating interphase effects: (1) engineering the lithium metal and/or (2) engineering an interfacial layer material (e.g. interlayer).

One promising approach toward engineering the anode is through controlled alloying. Li-rich alloys (e.g., Si, Sn, Al, Mg, In, etc.) may play an important future role in SSBs. Such materials have received significant attention as high-capacity anodes for liquid-based Li-ion batteries, and are now being integrated in small quantities into commercial graphite anodes to boost capacity⁴⁸. In SSBs, they could be useful either as interfacial layers or as anode active materials. In principle alloy materials can experience greater diffusion coefficients than pure lithium. Recently, Li-Mg alloys were used to maintain interfacial contact and increase Li utilization with no external applied pressure in SSBs⁴⁹. Furthermore, Li-In alloys were shown to be chemically stable against Li₃PS₄ when the alloy remained in the two-phase region (In)-InLi⁵⁰. As described previously, the mechanical properties of Li metal (e.g., creep behavior) may not be sufficient to avoid delamination and pore formation at high current densities²⁻³. The addition of Li-alloy interfacial

layers in contact with Li metal anodes could allow for tuning of their mechanical and Li transport properties, which could aid in maintaining uniform interfacial contact at the SE interface. The use of high-capacity Li alloys as anodes instead of Li metal is another potential route that could lead to high-energy SSBs. Many Li alloys may be more stable in contact with SEs due to their higher potentials compared to the Li/Li⁺ redox couple⁵⁰. However, further research needs to be carried out to understand the properties and structure of interphases between SEs and Li alloys, especially as delithiation kinetics and Li diffusivities at the interface will be different in alloys compared to pure Li metal.

Engineered interfacial layers between Li metal and SEs can aid in improving cell performance. Much of the work in this area has focused on reducing interfacial impedance and improving physical contact between Li and the SE. The two primary routes to achieve these goals involve either introducing a physical interlayer or controlling the surface chemistry of a specific material (electrode or electrolyte).^{21, 51} Interfacial layers (interlayers), such as polymer coatings, can act as a barrier film to decrease chemical decomposition at solid|solid interfaces during electrochemical cycling and to promote uniform Li deposition/stripping.⁵² Several coating strategies are reported within the literature. A soft and flowable coating can prevent the formation of cracks or pinholes in the SEI layer.⁵³ A highly elastic coating can regulate interface uniformity by exerting high strength at high-strain areas.⁵⁴ Additionally, a polymer coating with chemistries that can mitigate the reactivity between the electrolyte and Li is beneficial.⁵⁵⁻⁵⁷ These coatings are formed either *ex situ* or *in situ*. Other strategies include adding a very soft polymer layer underneath the current collector and Li instead of in between Li and the SE. The soft polymer layer can effectively diminish the plating stress and prevent stress-driven dendrite growth.⁵⁸

Besides interfacial layers, another strategy in which ceramic ion conductors are combined with polymer ion conductors to form hybrid membranes has been shown to enable more compliant and tunable interfaces.⁵⁹⁻⁶⁰ In the hybrid approach, the ceramic SE could provide high a mechanical modulus and high ionic conductivity, and the polymer electrolyte could provide ease of manufacturability as well as improved adhesion and stability with the electrodes⁶¹. However, this approach requires careful design and proper processing methods to be able to take the advantage of the advantageous properties of both the polymer and the ceramic.⁶¹⁻⁶⁴ In particular, the interface between the polymer and the ceramic electrolytes needs to be optimized.⁶⁵⁻⁶⁶

Alternatively, it may be feasible to design the SE to decompose into a beneficial interphase without the need for an additional interlayer. Ideally, such engineered interphases would prevent (electro)-chemical reaction between the SE and Li while still allowing for Li-ion transport. This requires materials that conduct ions, block electrons, and are (kinetically) stable in contact with Li. While a variety of polymers, ceramics, and even metals have been reported to improve the stability of reactive SEs^{35, 67-68}, characterizing the atomic structure of the interphase that forms upon cycling is challenging, and further efforts are necessary to elucidate the interphase evolution in the presence of such protection layers.

Ultimately, strategies to mitigate deleterious interphase formation need to be extended to roll-to-roll (R2R) scales⁶⁹⁻⁷¹. Li metal forms a passivating surface film (even in dry environments), and this film can lead to a high interfacial resistance that can result in cell degradation. High interfacial resistance must be minimized during manufacturing, if large Li metal foils are used in place of traditional anodes. Vapor deposition or melt processing techniques can be used to create a uniform layer of Li metal on top of the SE or interfacial layers⁷². However, depositing Li metal in this manner can drive up manufacturing costs. These costs may be offset by the inclusion of a

smart manufacturing environment, where inline quality control and environmental monitoring are used to reduce manufacturing defects and increase overall cell yield. In addition to manufacturing, the electrode architecture, cell design, and packaging must be re-engineered for future SSBs while considering the implications for both manufacturing and high-performance cells.

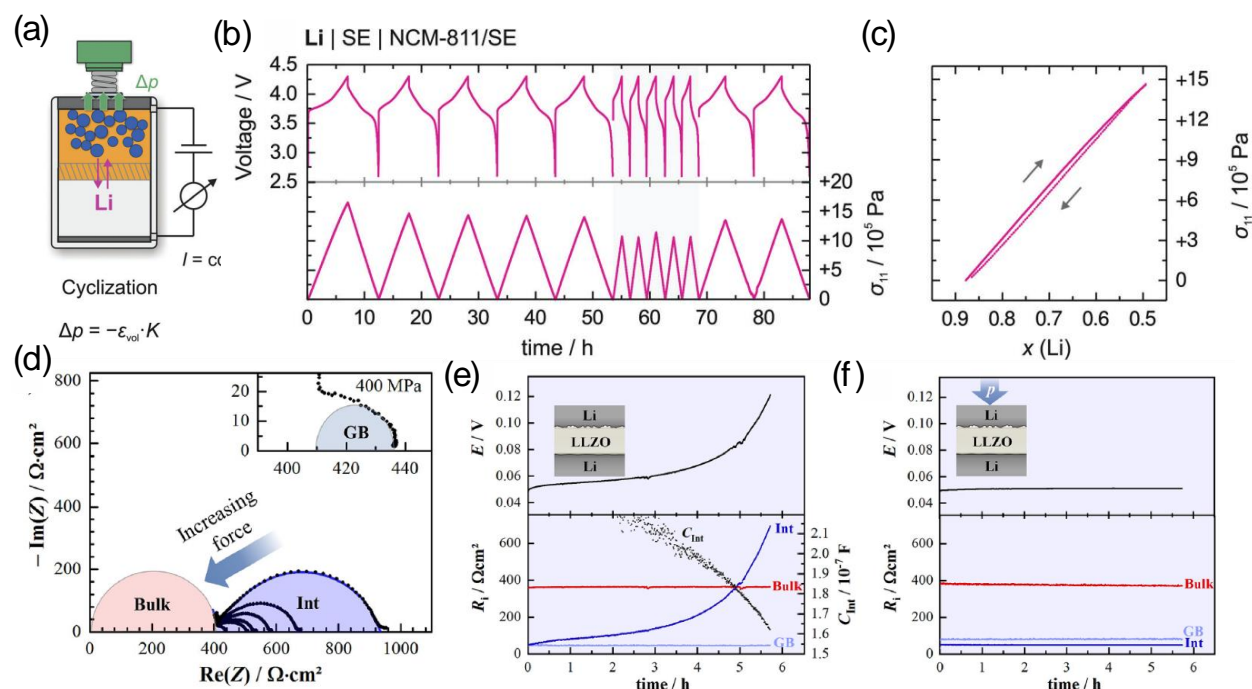


Figure 2: a) Schematic of a measurement setup for pressure-monitoring during solid-state battery operation⁷³. b-c) Volume expansion and contraction of the lithium metal anode during cycling results in large pressure changes and pressure oscillations⁷³. Reproduced by permission of The Royal Society of Chemistry. d) Pressure-dependent impedance response of Li/LLZO/Li cells. At high enough pre-forming pressure, the interface resistance between Li and LLZO can be mitigated. However, while preformation is necessary, unless there is a constant applied pressure on the cell contact loss will occur during stripping experiments. Hence, high pressures are needed for pre-formation, however, some external pressure is still needed to avoid pore formation⁷⁴. d)-f) are reprinted with permission from reference ⁷⁴.

Pressure during operation and formation in a solid-state battery. SSBs rely on intimate contact

between solid phases, i.e. the active material and the SE, as well as possible additives (Fig. 2a).

Charging and discharging leads to volume changes in the anode and cathode active materials. In the case of the anode, the volumetric expansion can be up to 300% for extreme cases such as pure silicon, and even graphite undergoes volume expansion of approximately 10% upon full lithiation.

The pressure oscillations due to volume change of a Li metal anode in a thioSSB are shown in

Figure 2b and 2c, in which solid-solid contacts will exhibit localized stresses. These local tensile stresses lead to cracking and bending of SSBs if no external pressure is used, ultimately resulting in contact loss and poor battery performance. Thiophosphate-based SEs are generally softer and more elastic ($K/G > 1.75$, where K is the bulk modulus and G is the Shear modulus in GPa) than other inorganic solid electrolytes (e.g. LLZO). The elasticity of the SE will be important for decreasing fracture events in all-inorganic cathodes⁷³ and will likely affect the critical state pressure.

Applying pressure to the SSB often occurs in two steps. First, high pressure (which may also be accompanied by an elevated temperature) can be applied during cell fabrication to initially contact all components. Subsequently, a lower external pressure is used during cycling to avoid contact loss³. The initial pressure required for formation depends on the mechanical properties of the SE and active materials, as well as the interfacial wetting properties with the Li anode. In contrast, the external pressure during cycling only counteracts the detrimental volume changes. Figure 2d-f show an example of these different scenarios. When using an Li/LLZO/Li cell, the interface resistance between Li and LLZO decreases and ultimately becomes negligible at 400 MPa of an external pre-forming pressure⁷⁴. However, when using the Li/LLZO/Li cell during stripping experiments, a reduced pressure of 35 MPa is sufficient to retain good contact and prevent void formation and morphological instabilities during stripping.⁷⁴ For polymer electrolytes, a decrease in interfacial impedance has also been observed with increasing stack pressure, until a “critical stack pressure” is reached⁷². Overall, the needed pressure conditions during forming, the maintenance of stack pressure under different operation conditions, and the implications of these needed pressures on manufacturing concerns are still open questions.

Diagnostics and Characterization Tools for Li|SE Interfaces. Diagnostics tools and characterization techniques that can probe sub-surface phenomena are critical to improve our understanding of the mechanistic origins of Li filament growth and degradation pathways at solid|solid interfaces (Fig. 3). There are different opportunities for different characterization techniques with respect to: (1) technique spatial and temporal resolution, (2) sample preparation and experiment characteristic length scale, and (3) working environment. There are also several mechanisms and processes that occur at different length scales within a battery, and the resolution of the technique (both temporal and spatial) provides boundaries for experiments. Finally, the experimental working environment can introduce transient and non-equilibrium conditions, especially if the technique is destructive.

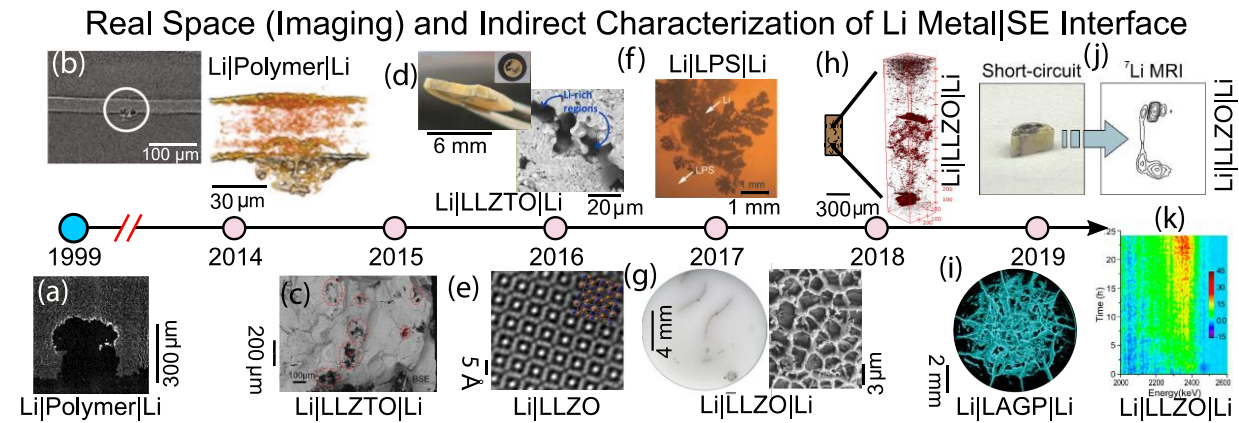


Figure 3. Timeline of imaging and characterization of Li-metal|SE interfaces Optical techniques (a) (Copyright 1999, Elsevier) and x-ray tomography (b) reveal morphology of Li filaments at a polymer SE interfaces (Reprinted by permission from Springer Nature: Nature Materials, copyright 2013¹⁹). Ex situ Scanning electron microscopy revealed sub-surface deposition in inorganic electrolytes (c,d) (Copyright 2015, Elsevier and reproduced with permission from⁷⁵). Transmission electron microscopy experiments reveal structural transformation at LLZO interfaces in contact with Li metal. Reproduced with permissions from⁷⁶. Optical techniques demonstrate dendritic growth β -Li₃PS₄ polycrystals (Copyright 2017, Wiley) (f). Lithium metal extruding out of intergranular regions (g) in LLZO (Copyright 2015, Elsevier) and microstructural representation of Li metal forming in pores from x-ray tomography experiments (h) (Reproduced with permissions from³¹). Large mechanical fracture of LAGP solid electrolyte (i) and evidence of lithium penetration across a LLZO electrolyte imaged with NMR (j) (Reproduced with permissions from⁷⁷). Neutron depth profiling enabling tracking of lithium at sub-surface regions in a SE (k) (Reproduced with permissions from⁷⁸). Figure reproduced from 18-19, 26, 31, 47, 75, 77-80

Over the last several years, there has been considerable interest in characterizing physical and chemical transformations at solid|solid interfaces that contribute to interfacial evolution and

metal filament formation over a wide range of time and length scales^{26, 75, 79}. While the theoretical basis for the formation of passivating interphases is clear from the previous discussion, the actual structure, chemistry, and transport properties of interphases that form on the variety of SSE materials are largely unknown⁸¹. Recently, SE chemical decomposition pathways when in contact with Li was discerned using *in situ* x-ray photoelectron spectroscopy (XPS) experiments⁸²⁻⁸⁴ and *ex situ* scanning electron and optical microscopy has revealed filament formation within the bulk SE (Fig. 3a-d,f,g). *In situ* transmission microscopy (TEM) (Fig. 3e) has also revealed important information about interfacial chemical and structural changes.^{52, 76, 81} In cubic LLZO, for instance, a few-nanometer region near the interface converts to the tetragonal phase due to Li insertion⁷⁶. The NASICON-type LAGP material was found to react and amorphize in contact with Li⁸¹, with none of the thermodynamically-predicted compounds observed via diffraction. Solid-state nuclear magnetic resonance (NMR) spectroscopy has been employed to gain an understanding of the composition⁸⁵ of amorphous decomposition products present at electrode|electrolyte interfaces and how these species impact Li ion transport in SSBs⁸⁶. Expanding the use of other *in situ/operando* techniques well-suited to characterizing amorphous phases will enable the investigation of structural changes in a wider variety of SE materials. Due to the highly heterogeneous and dynamic nature of interphase formation it is desirable to couple theory and computation with characterization to aid in experimental interpretation and decrease experimental uncertainty. This is key to understanding interphase dynamics and will also inform the engineering of artificial interphases with beneficial properties.

Beyond interphase characterization, there is a considerable need to understand meso-scale material transformations (delamination, filament growth, etc.). NMR techniques are powerful tools for understanding Li microstructural growth and Li-ion dynamics within SSBs⁷⁵. ⁷Li NMR is able

to distinguish between ^7Li resonances from the bulk Li electrode and Li microstructures (filaments and/or dead Li)⁸⁷. Furthermore, ^7Li NMR combined with magnetic resonance imaging (MRI) can enable 3D spatial tracking of Li filament growth using ^7Li chemical shift imaging (CSI). Marbella et al. used *ex situ* ^7Li CSI to correlate Li microstructural growth with instabilities in galvanostatic cycling⁷⁷ (Fig. 3j). These experiments showed heterogeneity at both interfaces, suggesting the formation of local “hot spots” during Li stripping and deposition. While the imaging dimension in these experiments is limited to approximately 300 μm , NMR can provide additional chemical resolution as well as enable *in situ/operando* experimentation. Recently, *in situ* 3D ^7Li MRI experiments enabled tracking of local Li concentration gradients within the bulk of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS)⁸⁸. These experiments directly corroborated increases in interfacial resistances with Li concentration depletion at the anode interface. NMR will continue to play a crucial role in SSB characterization due to the unique ability of NMR to identify disordered structural features⁸⁹ that are often present at interfaces, as well as to monitor Li ion dynamics⁹⁰.

X-ray computed tomography (XCT), like 3D ^7Li MRI, is also a 3D imaging technique, but can achieve higher spatial resolutions of <1 μm (micro-XCT) and <50 nm (nano-XCT). Synchrotron XCT can be leveraged to carry out non-destructive, *in situ/operando* measurements due to fast acquisition times (Fig. 3i-j)^{15, 17, 19, 31}. The key drawback of this technique is the lack of chemical specificity towards Li. Thus, only indirect observation of filament growth can be achieved. Neutron depth profiling (NDP) (Fig. 3k) is another tool to investigate Li metal deposits near the anode|electrolyte interface. NDP is a near-surface analysis technique that employs cold neutrons to excite Li to emit alpha particles and protons which are subsequently detected³. NDP is a non-destructive tool that can offer insight into Li concentrations near the interfacial region with

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3 μm -level resolution. However, NDP is currently limited in its ability to track deposition within the
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5 bulk and in its ability to track local structural characteristics.
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8 Most of the characterization techniques used to investigate chemical, physical/mechanical,
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10 and microstructural transformations at Li|SE interfaces have focused on a singular aspect of the
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12 system. Experimental results have conclusively shown a strong co-dependence between material
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14 transformations and electrochemical performance. Thus, it is vital to pursue multi-modal
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16 characterization in order to achieve complementary datasets on coupled phenomena. Coupling
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18 techniques like atomic force microscopy with spectroscopy can provide simultaneous information
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20 regarding mechanical, structural, and chemical properties. Synchrotron techniques also offer high
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22 versatility in terms of combining techniques to probe multiple phenomena at varying length scales;
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24 for example, transmission X-ray microscopy coupled with x-ray absorption near edge structure
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26 (XANES), or microtomography coupled with X-ray diffraction/absorption spectroscopy.
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28 *Operando* optical video microscopy can be synchronized with voltage signatures during cycling,
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30 to provide insights into electrochemical signatures of Li filament propagation⁷². In the future,
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32 *operando* and *in situ* measurements coupled with theory and computation will continue to offer
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34 new insights into the dynamic, coupled phenomena occurring in these systems.
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40 **Modeling.** Advanced modeling of SSBs is critical for the interpretation of experiments, probing
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42 transport mechanisms, and describing the phenomenological origin of interfacial transformations.
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44 Mechanical stresses at the Li|SE interface are intrinsic to SSBs, which point toward adopting rigid
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46 barriers as a possible strategy for dendrite mitigation. The complexities of ion transport in the
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48 electrolyte, reaction kinetics, and mechanics due to stress generation at the Li|SE interface need to
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50 be understood to correlate with changes in SSB performance (Fig. 4a). Transport behavior in
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52 all-inorganic and all-polymer electrolytes has been explored at the continuum scale, yet
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formulations for stress-induced modifications to ion transport have yet to be identified. The effects of stress on transport in the SE are likely important, which may be analogous to stress effects on Li diffusion during intercalation events.⁹¹ Accurate experimental determination of ionic conductivity as a function of external pressure as well as transport properties are necessary for building effective models for all inorganic or polymer SSBs. Furthermore, *operando* and *in situ* experimentation which combines real space imaging techniques with electrochemistry and transport measurements will aid in the development of accurate meso-scale models (Fig. 4b-d). While transport mechanisms at the continuum level are well understood for homogenous SEs, less is known about transport in hybrid composite SEs. The ion transport behavior in inorganic/polymer composites is complex and provides a rich design space to explore and optimize.^{63-64, 92} Developing a molecular-scale understanding of ion transport at the interface of polymer-ceramic composites could help to develop high-performing composite electrolytes that can manifest the benefits of inorganic and polymeric materials.⁹² Recently, effective mean field theory (EMFT) approaches combined with experimentally obtained ionic conductivity measurements were used to map ion transport pathways in hybrid SEs.⁶³ While EMFT provides a pathway for discerning between anionic and cationic transport pathways at complex inorganic/organic interfaces, it does not include solvation/desolvation mechanisms and polymer physics. Advanced modeling and experiments are necessary to deconvolve transport mechanisms between polymer and ceramic ion conductors.

Monroe and Newman proposed the first model of stress-kinetics coupling by correlating the exchange current density from Butler-Volmer kinetics at the Li-polymer interface with the electrochemical potential change through interfacial hydrostatic/deviatoric stresses and molar volume mismatch.⁶⁻⁷ Furthermore, linear elastic perturbation analysis on a static metal-polymer

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3 system incorporating the stress-kinetic formulations was used to determine a threshold shear
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5 modulus of SEs for stable deposition, precluding transport effects. Barai and Srinivasan extended
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7 this model to incorporate transport, plastic Li deformation, and external pressure effects.^{8, 93} Model
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9 reformulation for inorganic SEs to delineate stability regimes, as well as accounting for the
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11 polycrystalline microstructure of the SE, has been explored as well.^{11, 94-96} First-principles studies
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13 have also proposed a mechanism for Li metal penetration through polycrystalline solid electrolytes
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15 based on grain boundary softening.⁹⁷ However, studies have yet to ascertain a singular root cause
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17 of the CCD observed across all classes of inorganic electrolytes, whether single crystal or
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19 polycrystalline. Recently, Griffith's theory based on linear elastic fracture mechanics has been
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21 proposed to understand the mechanism of lithium metal penetration through inorganic solid
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23 electrolytes, correlating the lithium plating overpotential to the surface defect size and fracture
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25 toughness of the electrolyte.²⁶ This theory gives contrasting results to the Monroe-Newman model;
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27 high Young's modulus solid electrolyte metal is associated with lower CCDs through higher
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29 magnitudes stress-based crack opening. It is the authors' opinion that a reconciliation of the two
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31 theories can be achieved through incorporation of pertinent interfacial physics to the models,
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including chemical/mechanical wettability and contact/fracture mechanics resulting from inherent interfacial surface roughness.

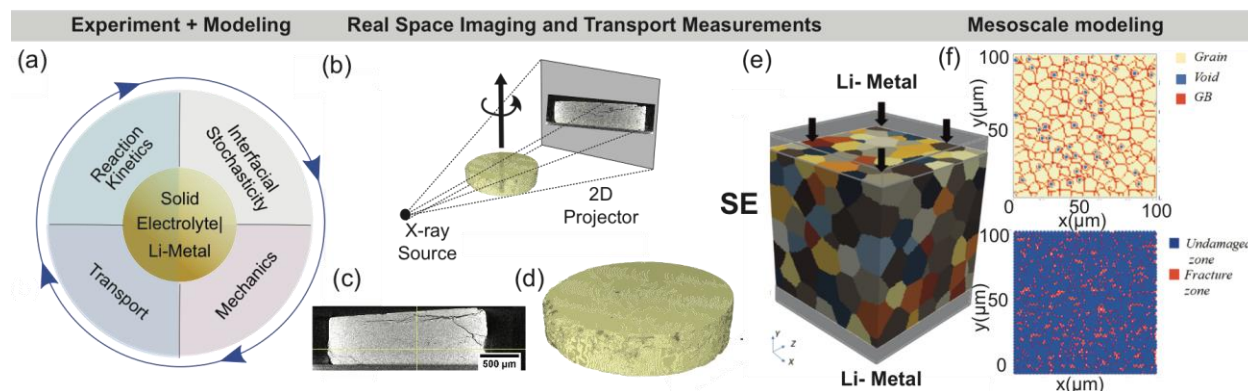


Figure 4. Advanced mesoscale models that combine experimentally obtained properties (transport, kinetics, interfacial properties, and mechanics) are necessary for discerning fundamental transformations in all solid state batteries (a). Operando experiments that combine real space imaging techniques (b-d) can provide a basis for modeling domains (Reproduced with permissions from⁹⁸). Non-equilibrium meso-structural transformation are important for building effective models. Schematic of polycrystalline SE sandwiched between Li metal electrodes in symmetric cell configuration with (e) corresponding microstructure phase map consisting of grains, voids and grain boundaries (GB), and (f) damage map exhibiting fracture concentration along the grain boundaries with electrodeposition under the constrained configuration.

It is imperative to note that there is an ongoing debate in the scientific community with regards to the molar volume inside the inorganic solid electrolyte. Zero molar volume has been reported for LLZO in literature based on negligible volumetric change with Li^+ incorporation, alongside a wide range of values for different SEs.⁹⁴⁻⁹⁵ Ahmad *et al.* has delineated the stability regime of inorganic solid electrolytes as a function of solid electrolyte to Li metal molar volume and shear modulus ratio and has shown that inorganic solid electrolytes with low molar volume and high shear moduli ratios (such as LPS or LLZO) are prone to current instabilities.¹¹ A bridge needs to be built between the molecular scale definitions of molar volume with those used in continuum models; in particular, there is a lack of consensus as to whether to correlate molar volume to the cationic/anionic radii or to consider it as an inherent part of the crystal structure.

Detailed insights into the performance of SSBs through modeling requires a dynamic model that is capable of temporal tracking of deposition/stripping at the interface which includes the interactions emanating from elastic-plastic stresses, ion transport, and electrochemistry. Furthermore, incorporation of chemical (surface tension) and mechanical wettability (external pressure), imperfect contact/peeling, and microstructural heterogeneities (e.g., voids, grains, grain boundaries for a polycrystalline electrolyte) into the modeling paradigm will help elucidate the scenarios that limit performance (Fig. 4e-f). The presence of an interphase/interlayer between the metal and SE will add to the model complexity, requiring stresses and transport to be solved in an additional layer, while accounting for characteristics of the layer (brittle/ductile deformation, Maxwell/Ohm transport law, Butler-Volmer/Tafel kinetics etc.). First-principles studies catalyzed by machine learning approaches will also be useful in rapid estimation of the transport, mechanical and thermodynamic properties of the SE materials⁹⁹. First-principles atomistic calculations utilizing density functional theory catalyzed by machine learning approaches will also be useful in rapid estimation of the transport (ionic conductivity/diffusivity), mechanical (stiffness tensor), kinetic (exchange current density) and thermodynamic (molar volume) properties of the SE materials⁹⁹. In literature, density functional theory has proven useful in estimating the ionic conductivity and Young's modulus of both amorphous and polycrystalline solid electrolyte materials¹⁰⁰⁻¹⁰¹. Our conjecture and proposition is that dynamic mesoscale interactions¹⁰²⁻¹⁰³, including the interplay between reaction kinetics, interfacial stochasticity, transport, and mechanics, are essential to provide fundamental mechanistic insights into Li-metal-based SSBs (Fig. 4e).

Outlook and Future Directions. To date, the majority of work on Li filament formation in SSBs has focused on characterizing Li plating/stripping in Li/Li symmetrical cells. Interfacial

phenomena that are key to filament nucleation and growth may differ substantially in full cells, emphasizing the need to expand these characterization techniques to more realistic systems. Furthermore, the formation of heterogeneous interphases can lead to stress non-uniformities that impact the local accumulation of stripping and/or deposition products. While there are many potential pathways toward mitigating lithium filaments (e.g. Li alloys, pressure, SE strength), maintaining uniform contact between the electrode and SE is paramount. Characterization and control over the atomic structure of the interphase will be important for addressing chemo-mechanical challenges at solid|solid interfaces. Advanced techniques that combine real and reciprocal space experimental techniques with modeling may provide a means for probing the variety of length scales that exist in a solid-state battery at realistic temporal and spatial length scales. There is also an emerging need for standardization of experimental methods across the community. Communication of protocols and operating conditions (Li metal thickness, temperature, pressures, etc.) will be paramount for interpretation of results within this rapidly growing community, with the ultimate goal of achieving lithium – solid electrolyte interfaces for solid-state battery operation.

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Quotes:

1. The term ‘Li dendrite’ broadly describes the formation of a wide range of non-planar/branched metal morphologies, and may not accurately describe the complex mechanisms involved in SEs (Fig. 1b). Li filaments through SEs plague SSBs, leading to a loss of efficiency and cell failure. Understanding the nature of this growth is imperative for next generation SSBs.

2. The chemo-mechanics of interphase formation is also important in the context of electrochemical deposition and stripping of Li metal, but this topic has received less attention to date.
3. Experimental results have conclusively shown a strong co-dependence between material transformations and electrochemical performance. Thus, it is vital to pursue multi-modal characterization in order to achieve complementary datasets on coupled phenomena. Coupling techniques like atomic force microscopy with spectroscopy can provide simultaneous information regarding mechanical, structural, and chemical properties.
4. Developing a molecular-scale understanding of ion transport at the interface of polymer-ceramic composites could help to develop high-performing composite electrolytes that can manifest the benefits of inorganic and polymeric materials