Electro-Chemo-Mechanical Challenges and Perspective in Lithium Metal Batteries

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Abstract

The development of next-generation batteries, utilizing electrodes with high capacities and power densities requires a comprehensive understanding and precise control of material interfaces and architectures. Electro-chemo-mechanics plays an integral role in the morphological evolution and stability of such complex interfaces. Volume changes in electrode materials and the chemical interactions of electrode/electrolyte interfaces result in non-uniform stress fields and structurally-different interphases, fundamentally affecting the underlying transport and reaction kinetics. The origin of this mechanistic coupling and its implications on degradation is uniquely dependent on the interface characteristics. In this review, the distinct nature of chemo-mechanical coupling and failure mechanisms at solid-liquid interfaces and solid-solid interfaces is analyzed. For lithium metal electrodes, the critical role of surface/microstructural heterogeneities on the solid electrolyte interphase (SEI) stability and dendrite growth in liquid electrolytes, and on the onset of contact loss and filament penetration with solid electrolytes is summarized. With respect to composite electrodes, key differences in the microstructure-coupled electro-chemo-mechanical attributes of intercalation- and conversion-based chemistries are delineated. Moving from liquid to solid electrolytes in such cathodes, we highlight the significant impact of solid-solid point contacts on transport/mechanical response, electrochemical performance, and failure modes such as particle cracking and delamination. Lastly, we present our perspective on future research directions and opportunities to address the underlying electro-chemo-mechanical challenges for enabling next-generation lithium metal batteries.

Keywords

lithium metal batteries, solid-state batteries, electro-chemo-mechanics, solid-solid point contacts, microstructure, solid-solid interfaces, anode stability, particle cracking, delamination, contact stresses, transport, reaction kinetics.

1. Introduction

Lithium-ion batteries (LIBs) are at the forefront of the energy storage technology for portable electronic devices and are poised to play a pivotal role in vehicle electrification [1, 2]. Tremendous research efforts are being made towards developing next-generation batteries that can meet the ever-increasing demands for energy and power densities[3]. In this regard, replacing conventional graphite anode with the lithium metal anode, owing to its low material density (0.534 g cm^{-3}) and high theoretical capacity (3860 mAh g^{-1}), holds the potential to surpass the theoretical limits of the conventional LIBs[4-7]. However, several fundamental challenges need to be addressed for the stable and safe operation of lithium metal batteries. With organic liquid electrolyte, repeated charging and discharging results in severe volume changes of lithium which leads to the rupture of solid electrolyte interphase (SEI), uncontrolled lithium dendrite growth and ultimately short circuit[8, 9]. In addition, high reactivity of lithium metal with liquid electrolyte causes unwanted side reactions leading to lower Coulombic efficiency due to the loss of lithium inventory and even thermal runaway under extreme circumstances[10, 11]. Inorganic solid electrolytes (SEs), due to their mechanical rigidity and non-flammability, promise to alleviate these safety and performance issues, thus rendering solid-state batteries (SSBs) as a promising candidate for enabling next-generation energy storage systems[12-14]. Because of the high cationic transference number, solid electrolytes also overcome the concentration polarization problem prevalent in liquid electrolytes[15]. Despite such underlying advantages, progress towards commercialization of solid-state batteries is rife with several electro-chemo-mechanical challenges pertaining to both lithium metal anode and solid-state cathode[16, 17].

Key components of the solid-state battery comprise of solid-state composite cathode, lithium metal anode (or composite anode), and solid electrolyte separator. Unlike liquid electrolyte systems, where liquid electrolyte fully wets the electrode active material surface, electrochemically active area and electronic/ionic percolation pathways in solid-state batteries are limited due to inherent solid-solid point contacts[18]. In addition, these solid-solid point contacts result in severe internal stresses during the electrochemical operation due to volume changes of the electrode materials[19]. Thus, chemo-mechanics play a more critical role in solid-state batteries as compared to the conventional LIBs where liquid electrolytes, owing to their inherent nature, can easily accommodate the volume changes and act to relieve the electrochemically induced strains.

Although solid electrolytes are expected to suppress lithium dendrite growth, several studies have reported lithium metal penetration and short circuit in solid-state batteries[20-22]. Several factors such as the presence of grain and grain boundaries in the solid electrolyte microstructure[21, 23-26], surface defects[27, 28], plastic flow of lithium[29, 30], unstable evolution of the interface[31, 32] have been proposed to be responsible for such failure. Presence of heterogeneities such as grain and grain boundaries and surface defects result in heterogeneous transport and reaction kinetics leading to preferential stripping and plating during electrochemical operation[33-36]. In addition, due to the distinct mechanical properties of the grain and grain boundaries, preferential metal penetration along the grain boundaries of solid electrolyte have been observed[37]. Contact loss during stripping due to incomplete replenishment of lithium results in increase in the overpotential at anode-solid electrolyte interface[38, 39]. The subsequent plating on the remaining contact points leads to the current focusing and instigates the morphological instability, metal penetration and mechanical failure[32]. Contact loss and plating behavior at the anode- solid electrolyte interface are strongly dependent on the mechanical properties of the lithium and solid electrolyte, stack pressure, operating temperature, and current density[40-43]. Depending on the molar volume of lithium in solid electrolyte and lithium metal anode, stress-driven reaction and transport also govern the interface stability[44]. Non-zero electronic conductivities of $Li_7La_3Zr_2O_{12}$ and Li_3PS_4 solid electrolytes have been observed to be responsible for isolated deposition in the solid electrolytes, which can exacerbate the problem of short circuit in solid-state batteries[45, 46]. Furthermore, inherent cathode microstructural stochasticity can also lead to heterogeneous reaction distribution at the anode- solid electrolyte interface, thus affecting the anode stability[47].

Mechanical and chemical properties of the constituent elements of the solid-state battery play a significant role in dictating the electro-chemo-mechanical interactions and stability of the solid-solid interfaces. For instance, the decomposition of solid electrolyte is a strong function of the stresses and mechanical constraints present within the solid-state battery[48]. The Young's modulus of the solid electrolyte and cathode active material govern the interfacial active area and severity of the solid-solid point contacts[49-51]. These interfacial characteristics directly affect the transport and reaction signatures within the composite cathode[49]. Surface adhesion energy is another important property which controls the delamination behavior at the solid-solid interfaces[52-54]. Delamination leads to an increase in both reaction and transport resistances, thus contributing towards performance decay[55-57]. Owing to the large stresses developed within the active material and solid electrolyte phases, stress-driven overpotential and transport can affect the utilization of the composite electrodes[17, 58]. Depending on the fracture threshold, stresses can result in fracture within active material and solid electrolyte particles leading to longer lithium transport pathways[59-61]. Replacing intercalation-type composite cathodes with conversion-type cathodes such as sulfur promise to enhance the energy density of solid-state batteries[62-64]. However, several electro-chemo-mechanical challenges exist as sulfur cathodes undergo severe volume changes and microstructure evolution during electrochemical cycling[65-68].

Overall, the development of lithium metal batteries having either liquid electrolyte or solid electrolyte is plagued with several electro-chemo-mechanical challenges. Due to such myriad issues concerning the safety and stability of the lithium metal batteries, deep understanding of the electro-chemo-mechanical interactions and their implications on the electrochemical performance is paramount. In this review, we discuss the recent advancements and future opportunities towards practical application of lithium metal anode batteries and shed light on the mechanistic understanding of various electro-chemo-mechanical interactions within such systems. Having a stable solid electrolyte interphase (SEI) is the key to preventing lithium dendrite growth and enabling lithium metal batteries with liquid electrolytes. To this end, we elucidate how the mechanical properties of SEI, transport and morphological heterogeneities, applied pressure, and exchange current density play a critical role in lithium metal anode stability. Thereafter, we shed light on the key mechanisms that lead to metal penetration and interfacial contact loss in solid-state batteries. Here, the role of mechanical properties of lithium and solid electrolyte, structural heterogeneities such as grain and grain boundaries and surface defects are discussed in detail. We also annotate the potential of anode-free batteries along with the chemo-mechanical challenges associated with such systems. Moreover, we discuss the intricate coupling between mechanics and electrochemical stability of solid-solid interfaces and its role in prevention of lithium dendrites.

Highlighting the critical pain points of solid-solid point contacts in intercalation-based solid-state cathodes, the role of solid electrolyte rigidity in dictating these point contacts and its implications on transport and reaction signatures are discussed. Mechanistic origins of interfacial delamination, its dependence on the volume-change characteristics of the cathode material and its impact on electrochemical performance is delineated. The role of stress-driven overpotential and transport in the context of solid-state electrodes and its critical implications on electrode utilization are discussed. Owing to the severe stresses generated in solid-state batteries, cracking of active material particles poses a critical bottleneck. Thus, mechanistic implications of fracture of the constituent elements in solid-state batteries (including high-capacity anodes such as Si, Sn) on the underlying lithium transport is expounded and fracture mitigation strategies are delineated.

Conversion-based cathodes such as sulfur have a potential to further enhance the energy density of the lithium metal batteries. However, several chemo-mechanical challenges stemming from the high-volume expansion of cathode, polysulfide shuttling, and transport limitations need to be overcome to realize the true potential of lithium-sulfur batteries. To this end, fundamental challenges pertaining to liquid and solid electrolyte-based lithium-sulfur batteries are discussed. In addition, design strategies to achieve enhanced cycling and rate performance are presented.

Lastly, we present our perspective on potential opportunities and research directions for enabling lithium metal batteries. This review provides fundamental insights into the electro-chemo-mechanical challenges associated with various interfaces in lithium metal batteries with liquid and solid electrolytes and gives directions for future research towards achieving the true potential of these energy storage systems.

2. Lithium metal anode

2.1. Challenges for lithium metal anodes in liquid electrolytes

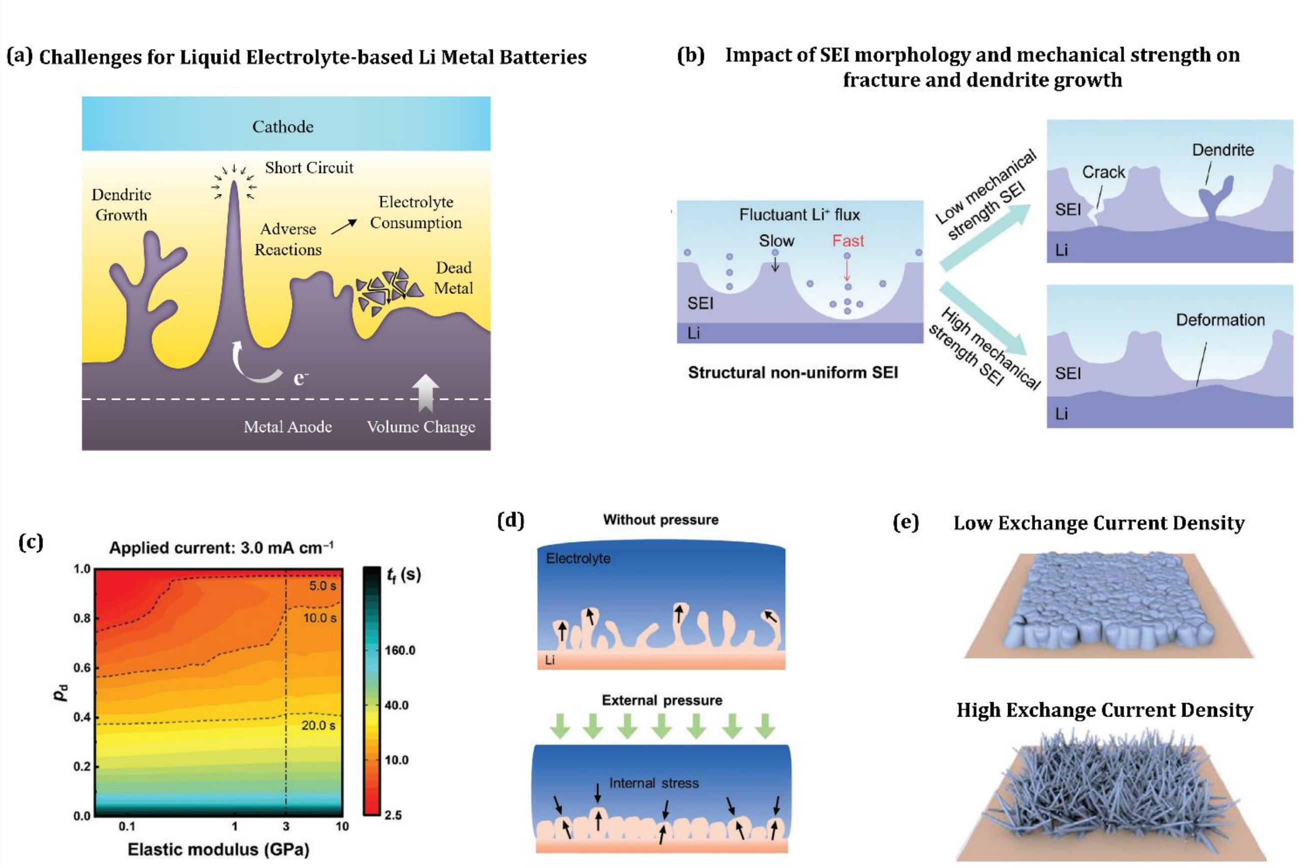


Figure 1. (a) Overview of the mechanistic challenges for lithium metal anode in liquid electrolytes. (Recreated with permission from [4]. Copyright 2017 American Chemical Society.) (b) Schematic illustration of the impact of solid electrolyte interphase (SEI) morphology and mechanical strength on SEI fracture and dendrite growth. (Reproduced with permission from [69]. Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.) (c) Effect of structural heterogeneity and mechanical strength on the onset of mechanical instability (Reproduced with permission from [69]. Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.) Critical role of (d) external pressure (Reproduced with permission from [70]. Copyright 2021 Wiley-VCH GmbH.) and (e) exchange current density (Reproduced with permission from [71]. Copyright 2021 Wiley-VCH GmbH) on the electrodeposition morphology.

While lithium metal holds irrefutable potential in enabling next-generation batteries with higher energy densities than lithium-ion batteries, the successful realization of lithium-metal batteries faces various fundamental challenges [4, 9, 72-76]. A majority of these challenges (Figure 1(a)) are linked to the highly reactive nature of lithium, causing electrolyte reduction and formation of a passivating solid electrolyte interphase (SEI) on its surface[77-81]. The SEI typically consists of multiple organic and inorganic components and can potentially exhibit non-uniformities with respect to structure, transport, mechanics and morphology.[82-84] The large volume changes of the lithium anode can result in significant mechanical stresses and hotspots, leading to mechanical rupture of the SEI.[85, 86] The resulting growth of dendrites through such cracks can expose fresh lithium to the electrolyte (Figure 1(b)) and cause further decomposition of the electrolyte and consumption of the lithium reservoir.[70] Analogously, the reduction of anode volume during stripping triggers further breakdown of the SEI, while also leading to the formation of 'dead' metal strands.[87-90] The accumulation of a dead metal layer above the lithium anode leads to ion transport limitations and a reduction in cell capacity with cycling.[10] Overall, the stability of the lithium metal anode is influenced by an interconnected set of electrochemical, transport, mechanical and morphological factors, which are predominantly governed by the chemical reactivity of lithium with the electrolyte, SEI characteristics and the electrochemical growth behavior of lithium.

2.1.1. Chemo-mechanical interactions and heterogeneity at lithium interfaces in liquid electrolytes

Structural uniformity, ionic transport and mechanical properties of the solid electrolyte interphase (SEI) play a critical role in determining its chemo-mechanical interactions with the lithium metal and subsequent failure pathways during repeated electro-dissolution and deposition.[91-97] Importantly, non-uniform SEI morphology results in heterogeneous ionic flux, eventually leading to uneven electrodeposition as shown in Figure 1(b). The presence of chemical inhomogeneities in the SEI can alter the transport behavior and reaction distribution, further exacerbating the occurrence of dendrites.[98-100] Driven by the presence of various spatial heterogeneities including defects, protrusions and pits, the morphological growth of the lithium metal exhibits a strong coupling with the mechanical response of the SEI. Recently, the joint influence of structural uniformity and elastic modulus of the SEI on the onset of mechanical failure was examined[69] as shown in Figure 1(c). Interestingly, it is inferred that the onset time of mechanical failure is predominantly dictated by the structural uniformity of the SEI, while the elastic modulus of the SEI has a lesser impact on the failure onset time beyond a certain critical value. Thus, improving the structural uniformity of the SEI is a more crucial design consideration, as opposed to targeting a significantly large mechanical strength [69]. In a related study, Liu *et al.*[86] evaluated the role of ionic conductivity and mechanical strength of the SEI on the resulting mechanical stress distribution and electrodeposition morphology. It was concluded that a lower ionic conductivity of SEI results in stress hotspots due to localized electrodeposition. Such stress hotspots affect not only the mechanical stability of SEI but also the reaction kinetics at the interface. Thus, an optimal SEI regime would include the consideration of a sufficient Young's modulus and ionic conductivity.[86, 101-103] Although most of the chemo-mechanical interactions between the SEI and lithium anode appears to be driven by the volume expansion of lithium, the interface behavior can also be accompanied by potential swelling of the SEI.[104] This can alter the mechanical stresses during the electrochemical growth of lithium, limit the amount of electrolyte in the battery and affect ionic transport within the SEI. The degree of SEI swelling is dependent on the electrolyte chemistry and exhibits a direct correlation with the electrochemical performance of the battery.[104]

In addition to aspects such as electrolyte composition, solid electrolyte interphase (SEI) chemistry and surface morphology that intrinsically impact the chemo-mechanical interactions, the role of external conditions such as pressure has been shown to play an important role in modulating the stress fields and plating behavior.[70, 105] For instance, external pressure can alter the progression of electroplated morphologies and regulate the shape of dendrite toward a smooth and dense morphology (Figure 1(d))[70]. However, the application of higher pressures can have an adverse effect on the mechanical stability of the system. External pressure in liquid electrolyte cells can also influence the nucleation behavior[106, 107], SEI structure[80, 108], surface self-diffusion characteristics[109-112] and the propensity for dead metal formation[89, 113]. Thus, a delicate balance between the beneficial range of external pressures and the elastic modulus of the electrolyte,[69, 82, 114] while considering factors such as lithium surface profile[100] (e.g., defects) and SEI properties[103], needs to be delineated. The precise control of external pressure is an important step to achieve stable electrodeposition and dissolution under operational extremes such as fast charging and low temperatures in lithium-metal batteries.[70, 105] Identifying an optimal combination of external conditions[105, 114-118] (e.g., pressure, temperature) and various electrode/electrolyte modification strategies such as interface coatings[119, 120], host architectures[121-123] and electrolyte additives[124, 125] could be important toward attaining the desired rate performance and areal capacities in lithium-metal batteries.[126]

While there has been tremendous research progress in lithium-metal batteries over the past decade, there is still scope for enhancing our fundamental understanding of the underlying electro-chemo-mechanical interactions. For instance, exchange current density has been identified as a critical kinetic characteristic affecting the nucleation and growth behavior[71] (Figure 1(e)); however, the role of external pressure and stress fields on the exchange current density of liquid-electrolyte/electrode interfaces still needs to be examined. In addition, the correlation between stress fields, SEI structure and the ionic transport response within the SEI should be comprehensively understood. The implications of metal-SEI interactions and mechanical stress on the nucleation at metal anode interfaces still requires fundamental interrogation. Such underpinning mechanisms should also be mapped to the plating/stripping morphology, Coulombic efficiency and cycle life. Through a synergy of external (e.g., pressure) and internal modulators (e.g., SEI chemistry/structure), exploiting the electro-chemo-mechanical coupling at the metal/SEI/electrolyte interfaces would be critical in tailoring stable reaction landscapes and homogenous electrochemical growth in lithium-metal batteries.

2.2. Chemo-mechanical challenges for lithium metal anode in solid-state batteries

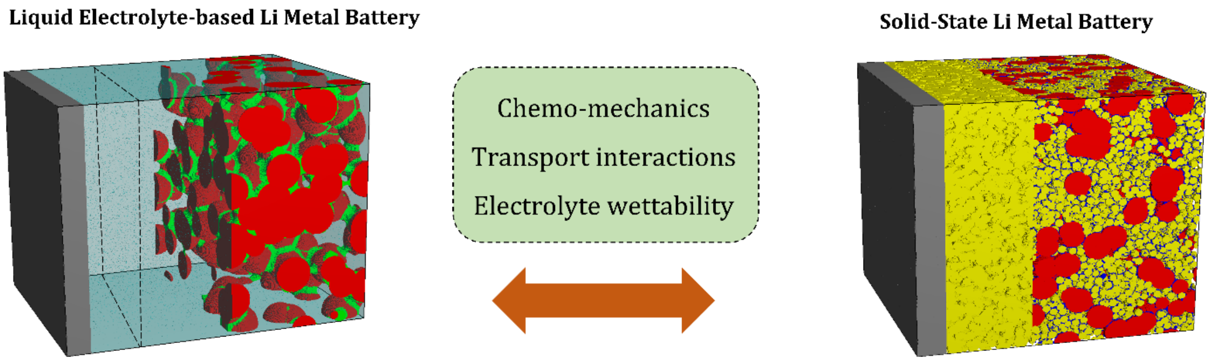


Figure 2. Schematic illustration of liquid and solid electrolyte-based lithium metal battery. The stability of lithium metal anodes in liquid and solid electrolytes is distinctly influenced by fundamental differences pertaining to the chemo-mechanical interactions, ionic transport and electrolyte wettability.

In recent years, solid electrolytes have garnered significant research attention and are considered to be potential enablers of the lithium metal anode[14, 127, 128]. The development of solid-state batteries has received tremendous focus, primarily due to the various theoretical advantages that solid electrolytes offer over their liquid counterparts[13, 129]. Driven by a combination of beneficial attributes such as mechanical rigidity, limited concentration gradients and non-flammability, solid-state batteries are believed to hold the ability to address the performance and safety challenges encountered with liquid electrolytes[15, 130, 131]. The mechanical characteristics of the solid-solid interface at the anode and the microstructural heterogeneity underlying the solid electrolyte and Li leads to a distinct set of chemo-mechanical interactions and challenges, culminating in various degradation and failure pathways[24, 31, 39, 42, 45, 132-141]. While the failure mechanism in solid and liquid electrolytes share mechanistic commonalities such as the role of heterogeneities in the lithium metal surface (e.g., grain boundaries, defects), there are critical differences with respect to the electrolyte wettability, transport interactions and chemo-mechanical response (Figure 2). Driven by these underpinning aspects, this section discusses the various modes of electrochemical and mechanical instability that manifest at the lithium-solid electrolyte interface.

2.2.1. Challenges in oxide-based solid-state batteries

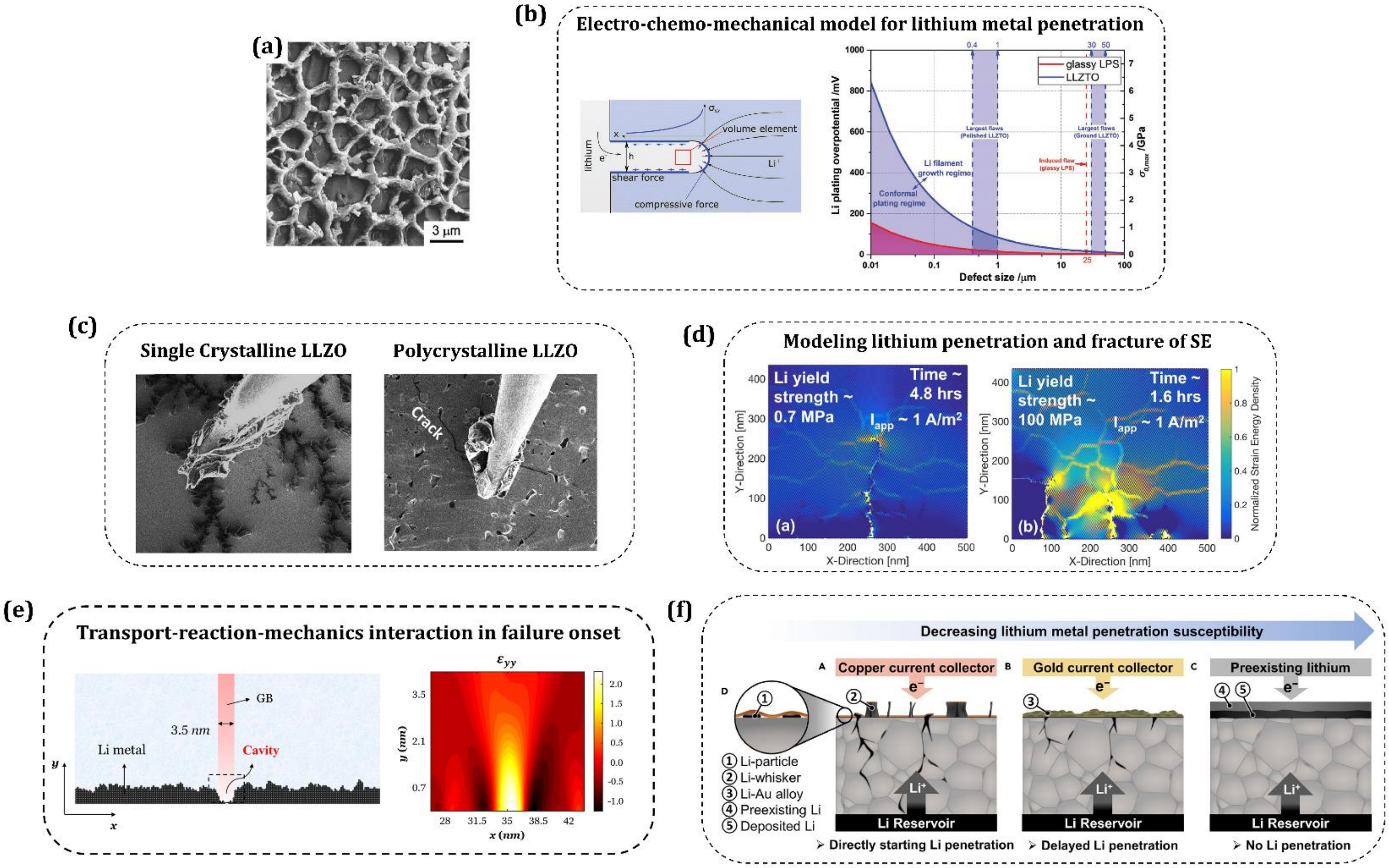


Figure 3. (a) SEM image showing lithium metal penetration along the grain boundaries of cycled $Li_7La_3Zr_2O_{12}$ (LLZO). (Reproduced with permission from [21]. Copyright 2016 Elsevier Ltd.) (b) Electro-chemo-mechanical model proposed by Porz *et al.*[28] to predict lithium metal penetration within the solid electrolyte as a function of plating overpotential and defect size. (Reproduced with permission from [28]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.) (c) SEM image depicting lateral lithium growth and electrochemically induced fracture in single crystalline and polycrystalline LLZO during electrodeposition of lithium. (Reproduced with permission from [142]. Copyright 2020 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.) (d) Model proposed by Barai *et al.*[143] to predict fracture and metal penetration within LLZO-based solid electrolytes. (Reproduced with permission from [143]. Copyright 2020 The Electrochemical Society.) (e) Lithium metal penetration into the solid electrolyte and mechanical stability is related to the transport-reaction-mechanics interactions at the grain boundary-lithium metal junctions[23]. (Reproduced with permission from [23]. Copyright 2021 Wiley-VCH GmbH.) (f) Lithium plating behavior observed by Krauskopf *et al.*[137] using copper current collector, gold current collector and pre-existing dense lithium layer. (Reproduced with permission from [137]. Copyright 2019 Elsevier Inc.)

Several recent studies have reported lithium metal penetration within different solid electrolytes leading to short circuit in solid-state batteries[21, 82, 132, 142, 144, 145]. Lithium metal penetration within solid electrolytes was first observed by Cheng *et al.*[21] where lithium metal propagated intergranularly through the LLZO grain boundaries (see Figure 3(a)) which resulted in the short circuit during cycling. Similarly, Porz *et al.*[28] observed that lithium deposition preferentially occurs on the pre-existing surface defects of the solid electrolyte. This results in a Griffith-like failure mechanism where the defects are first filled with lithium and subsequently crack formation and propagation occurs which is fundamentally different from the dendrite growth observed in liquid electrolyte systems. Along with the experimental study, this work proposed an electro-chemo-mechanical model (Figure 3(b)) which suggests that the plating behavior is strongly dependent on the plating overpotential and the defect size. In other words, for a particular defect size, above a critical current density, the plating overpotential and the corresponding mechanical stresses are large enough for a crack to form and propagate through the solid electrolyte. From the above discussion, it is clear that deposition behavior and interface stability are strongly dictated by the microstructural characteristics of the solid electrolyte such as grain boundaries, surface defects and interface morphology[14, 146]. Since the defect size is the outcome of the system design and processing conditions, future investigations should focus on understanding the manufacturing methods, and establishing a systematic correlation to the defect attributes and mechanical properties of the solid electrolyte and Li.

The plating behavior and failure mechanism was further investigated by Krauskopf *et al.*[142] for single crystalline (large grain size) and polycrystalline (small grain size) LLZO solid electrolyte. For single crystal LLZO, lateral and dendrite-like growth of lithium was observed along the surface of LLZO after applying a high negative overpotential (-10 V) as shown in Figure 3(c). This lateral growth mode resulted in a short circuit as lithium reached the counter electrode. Such deposition behavior of lithium indicates ion transport limitation within the solid electrolyte[147, 148]. On the other hand, for polycrystalline LLZO, grain boundaries and surface defects within the solid electrolyte microstructure resulted in the formation of cracks which propagated to the counter electrode causing a short circuit (Figure 3(c)). It is noted that this type of failure for polycrystalline LLZO occurred at much lower overpotential ($|\eta| < 1\mathrm{V}$) as compared to the single crystalline LLZO. These results further emphasize the importance of solid electrolyte microstructural characteristics in the stability of solid-solid interfaces in solid-state batteries. In addition to the solid electrolyte microstructural features, mechanical properties of lithium metal such as yield strength, creep, and viscoplastic deformation have a strong influence on lithium filament growth through the solid electrolyte[143]. Lithium metal with higher yield strength has been found to produce severe fracture in LLZO solid electrolyte in a short amount of time as shown in Figure 3(d).

Reaction heterogeneity at the lithium metal-solid electrolyte interface derived from the distinct ion transport characteristics of the grain and grain boundaries of the LLZO solid electrolyte has been examined in recent works[23]. To this end, a highly conductive grain boundary can lead to preferential deposition at the grain boundary-lithium metal interface. On the other hand, less conductive grain boundaries compared to the grains can lead to preferential deposition at the grain-lithium metal interface as shown in Figure 3(e). Such heterogeneous deposition results in localized stress hotspots leading to fracture in the solid electrolyte microstructure. Apart from the distinct ion transport features, dissimilar mechanical properties of the grain and grain boundaries also has significant influence on the failure onset and the nature of filament growth within the solid electrolyte[37]. To mitigate the deleterious implications of heterogeneous deposition at the lithium metal- solid electrolyte interface, activating lithium self-diffusion and plastic flow (from high deposition sites to the low deposition sites) via modulating the operating temperature and stack pressure is proposed[23]. In addition, employing grain boundaries-free solid electrolytes (e.g., amorphous LLZO) can help homogenize the interfacial reactions and mitigate the metal penetration[149].

To increase the energy density of lithium-ion batteries as well as to reduce manufacturing costs, there has been a tremendous increase in research efforts for anode-free systems[150-153]. However, there are many fundamental challenges that need to be addressed in this regard. For instance, preventing the loss of lithium due to side reactions and preserving Coulombic efficiency over a large number of cycles is crucial[154]. In addition, plating in anode-free batteries is observed to be more heterogeneous as compared to the lithium metal anode batteries (see part A and part C of Figure 3(f))[137]. Thus, understanding lithium nucleation and deposition behavior on the current collector is important as it is directly related to the interface stability[112, 155-157]. Heterogeneous lithium metal nucleation has been observed on the Cu current collector which leads to metal penetration into the solid electrolyte as represented in Figure 3(f). Also, the contact loss between current collector and solid electrolyte exacerbates this scenario due to current focusing. To achieve stable interfaces, strategies such as employing an alloy-forming interlayer like Au and Ag can enable homogeneous plating owing to the reduction in the nucleation overpotential (see part B of Figure 3(f))[158, 159]. Moreover, utilization of carbon interlayers can also help in achieving uniform plating as carbon provides efficient transport pathways for lithium as well as helps in reducing the nucleation overpotential[160].

2.2.2. Challenges in sulfide-based solid-state batteries

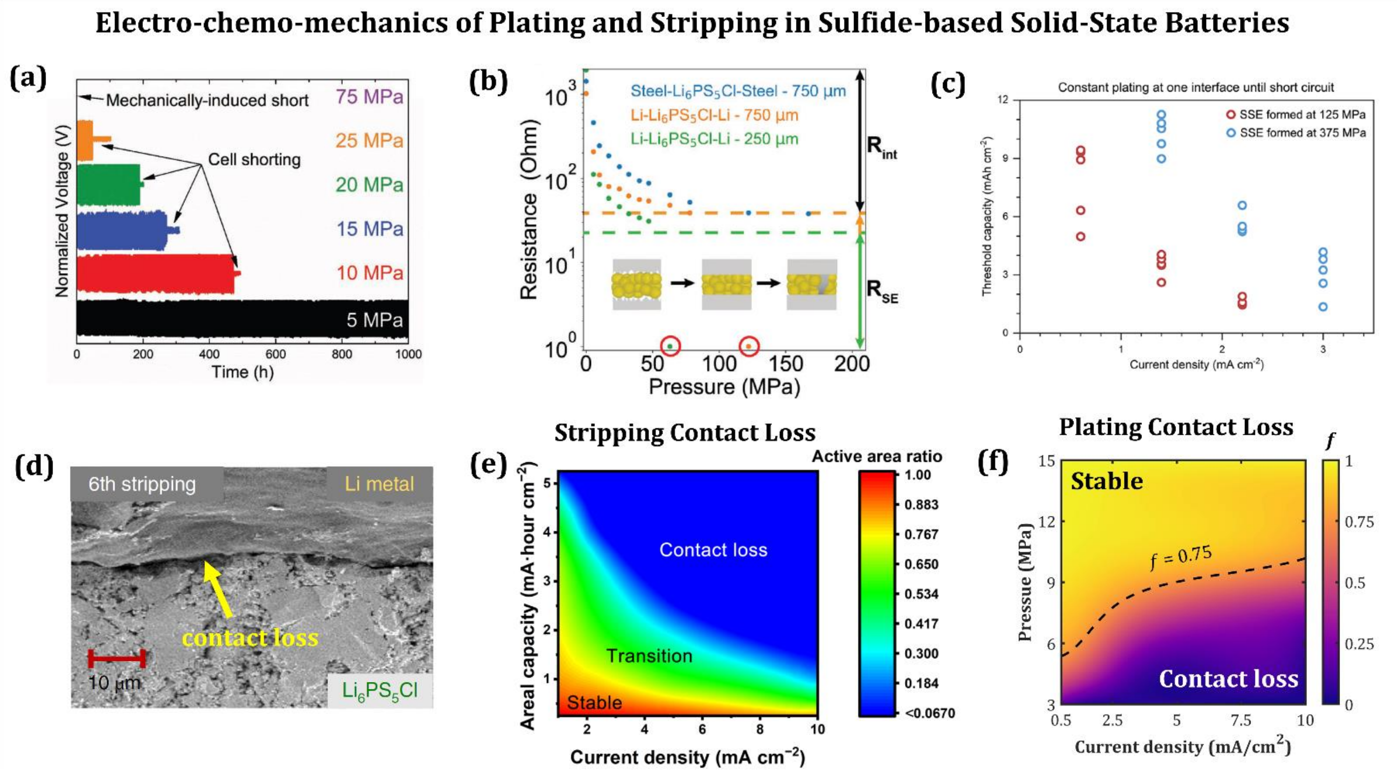


Figure 4. (a) Normalized voltage as a function of time for Li | Li_6PS_5Cl | Li symmetric cell during plating and stripping at different stack pressures. (Reproduced with permission from [144]. Copyright 2019 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.) (b) Cell resistance as a function of stack pressure for M | Li_6PS_5Cl | M symmetric cell (M = Li or stainless steel). (Reproduced with permission from [145]. Copyright 2021 Wiley-VCH GmbH.) (c) Capacity obtained until short circuit during plating at different current densities and fabrication pressure. (Reproduced with permission from [161]. Copyright 2022 American Chemical Society.) (d) SEM cross-sections after sixth stripping showing substantial contact loss at the Li metal-solid electrolyte interface. Reproduced with permission from [32]. Copyright 2019 Springer Nature Limited.) (e) Contact loss at the Li metal-$Li_7P_3S_{11}$ solid electrolyte interface as a function of areal capacity and current density. (Reproduced with permission from [162]. Copyright 2022 American Association for the Advancement of Science) (f) Quantification of the contact loss observed during plating at Li metal-Li_6PS_5Cl interface as a function of applied pressure and current density. (Reproduced with permission from [163]. Copyright 2022 Wiley-VCH GmbH.)

Similar to the oxide-based solid-state batteries, failure mechanisms like short circuit and contact loss have been observed in sulfide based solid-state batteries[32, 144, 145, 161]. However, owing to their lower Young's modulus, sulfide-based solid electrolytes are more sensitive towards externally applied pressures. In particular, higher applied pressures have often been reported to cause cell failure due to short circuit (Figure 4(a))[144]. On the other hand, lower applied pressure results in increased interfacial resistance due to insufficient contact between Li metal and solid electrolyte (Figure 4(b))[145]. Thus, an optimal range of operating pressures is critical towards ensuring good rate and cycling performance of the solid-state batteries. Increased plasticity and creep of Li at higher pressures drives Li to the counter electrode through the pores, grain boundaries, defects, and cracks present within the solid electrolyte microstructure causing short circuit. In this regard, solid electrolyte fabrication process can play a vital role in alleviating this problem. For instance, a recent study[161] showed that a sulfide-based solid-state battery with fabrication pressure of 375 MPa delivers higher capacity (until short circuit) as compared to a solid-state battery with 125 MPa fabrication pressure as shown in Figure 4(c). Higher fabrication pressure results in densified solid electrolyte microstructure with relatively lower pores and defects, thereby suppressing Li metal penetration.

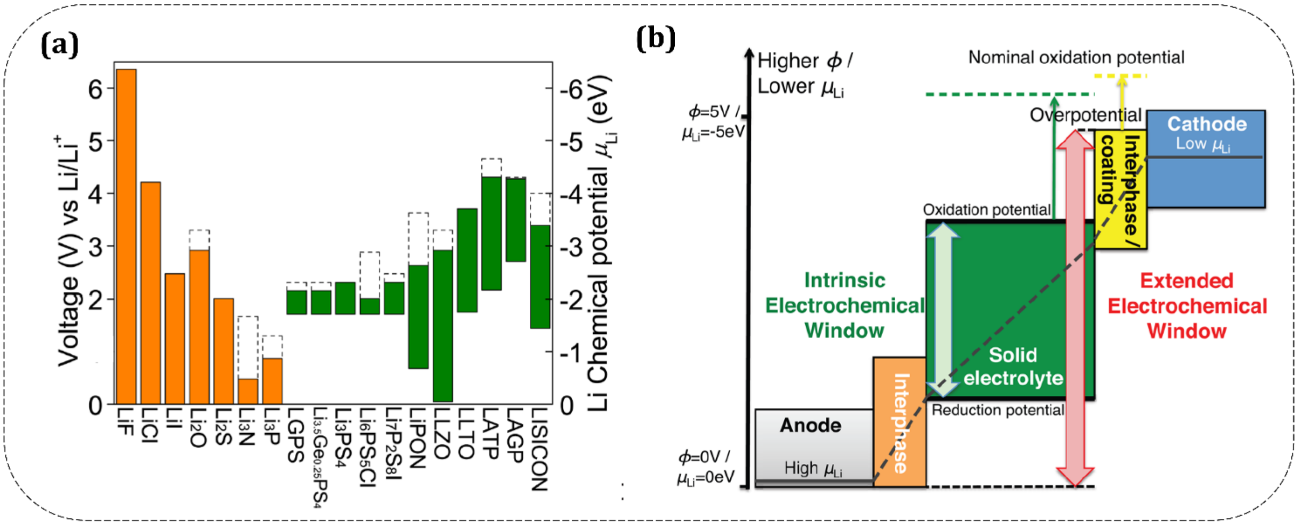
In addition to the external pressure, Li metal-solid electrolyte interface characteristics such as surface roughness[164], contact/non-contact distribution[40], and presence of solid electrolyte grain and grain boundaries[23] also influence the Li metal penetration and short circuit behavior during plating. For example, non-uniform interface profile can lead to uneven electric field gradients, resulting in reaction heterogeneity at the interface. The presence of interfacial voids (or non-contact sites) and grain and grain boundaries can result in preferential lithium deposition and eventual fracture of solid electrolyte microstructure.

During stripping, dissolution of the Li metal results in contact loss at the Li metal-solid electrolyte interface (Figure 4(d))[32]. Recent studies have observed severe contact loss at the Li metal-solid electrolyte interface, especially at high capacities and current densities (Figure 4(e))[162]. Such severe contact loss can result in the formation of point contacts at the interface leading to a sharp overpotential rise. Thus, maintaining sufficient contact during stripping is paramount for efficient battery performance. In this regard, mechanisms such as Li self-diffusion, plasticity and creep can assist in replenishing the interfacial voids formed during stripping. Increasing applied pressure can make these mechanisms more effective towards stabilizing the interface. However, this may not be the best strategy as it may lead to short circuit during plating as discussed earlier. Thus, strategies such as utilizing interlayers or composite anodes (consisting of Li metal and carbon nanotubes)[165] which can provide fast self-diffusion kinetics of Li to fill the interfacial voids are being explored. It is worth noting that if the interfacial voids are not replenished, the contact loss during stripping can result in the current focusing during subsequent plating[32]. This can lead to rapid metal penetration and cell failure due to short circuit. Moreover, a recent study [163] has also observed contact loss during plating as shown in Figure 4(f), which originates from the gap formation due to non-uniform deposition heights of Li metal at the anode-solid electrolyte interface. These failure mechanisms such as contact loss and short circuit due to solid electrolyte fracture and metal penetration need to be addressed in order to achieve fast charging in solid-state batteries. Moreover, electrochemical stability at the electrode-electrolyte interfaces also plays an important role in electro-chemo-mechanical coupling in solid-state batteries, which has been discussed in detail in the next section.

In addition to the experimental and computational studies discussed above, machine learning based studies have also been performed to analyze the stability of the anode-solid electrolyte interface[166-169]. Owing to the large number of potential solid electrolyte candidates, machine learning approaches can be very useful to predict potential solid electrolyte materials which exhibit stable solid-solid interfaces with the lithium metal anode. For example, a recent study[169] performed machine learning-based computational screening of over 12000 inorganic solids based on their abilities to suppress the dendrite growth at the lithium metal anode-solid electrolyte interface. This study found 20 interfaces with six different solid electrolytes that could enable dendrite suppression at the anode-solid electrolyte interface. Key features common in these solid electrolytes include anisotropy based on crystallographic orientation and mechanical softness.

2.3. Role of mechanics in electrochemical stability and its application towards anode stability

Electrochemical Stability of Solid Electrolytes in Solid-State Battery



Electrochemical Stability-Based Design Strategy for Preventing Lithium Dendrites

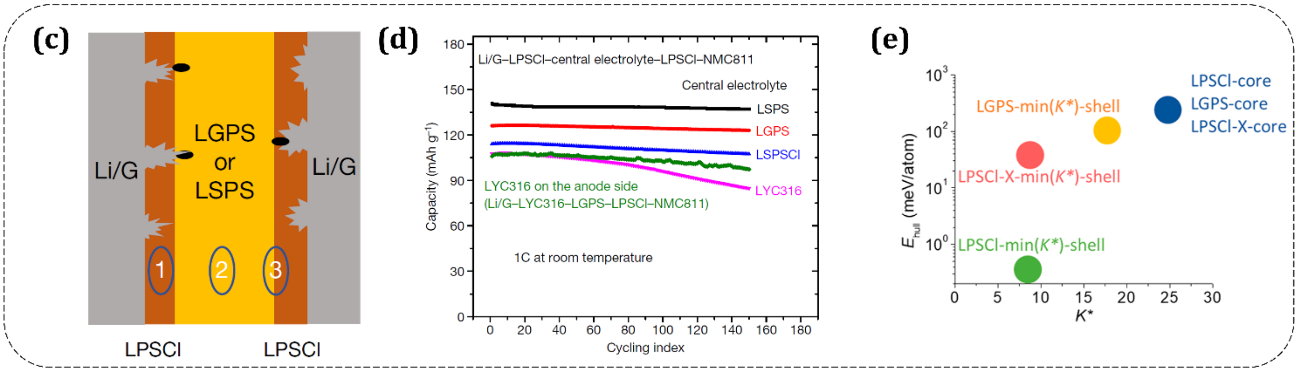


Figure 5. (a) Electrochemical stability window of various solid electrolytes and decomposition products. Dotted lines denote the oxidation potential required to fully delithiated the material. (Reproduced with permission from [68]. Copyright 2015 American Chemical Society.) (b) Schematic illustration of the electrochemical window and the Li chemical potential profile across various components of the solid-state battery. Potential difference across the interphases accounts for the chemical potential gaps between the solid electrolyte and electrodes within solid-state battery[68]. (c) Schematic of the multilayer design strategy where less stable solid electrolyte is sandwiched between more stable solid electrolyte to prevent the growth of lithium dendrites. (Reproduced with permission from [48]. Copyright Springer Nature Limited 2021.) (d) Cycling performance at 1 C-rate with different solid electrolytes as the central electrolyte demonstrating versatility of the multilayer design strategy[48]. (e) Critical modulus, K^*, and decomposition energy, E_{hull}, for a few representative solid electrolyte compositions. (Reproduced with permission from [170]. Copyright 2022 American Chemical Society) Both K^* and E_{hull} play a critical role in dictating solid electrolyte's behavior towards Li dendrite prevention.

2.3.1. Electrochemical stability in solid-state batteries

In addition to having favorable mechanical conditions which can prevent Li penetration and contact loss at the electrode-solid electrolyte interfaces, having good electrochemical stability at these interfaces is equally important. Figure 5(a) presents the electrochemical stability window of different solid electrolytes and their decomposition products with Li metal[68]. Most of the solid electrolytes have narrow electrochemical stability window, meaning, they are not thermodynamically stable either with the Li metal anode or the solid-state cathode. In particular, sulfide-based solid electrolytes have a narrower stability window as compared to the oxide-based solid electrolytes. At the Li metal anode-solid electrolyte interface, solid electrolyte materials are reduced to form decomposition products (e.g., LiF, LiI, Li_2O, Li_2S, Li_3P, Li_3N, etc) or solid electrolyte interphase (SEI). As shown in Figure 5(a), most of these decomposition products are stable at 0V and thus avoid further decomposition at the Li metal anode-solid electrolyte interface. This passivation mechanism is the result of the electronic insulation property of the SEI products and is essential for the stable and efficient operation of the solid-state battery. However, solid electrolytes like $Li_{10}GeP_2S_{12}$ (LGPS), $Li_{0.33}La_{0.56}TiO_3$ (LLTO), $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) and $Li_{1.5}Al_{0.5}Ge_{1.5}(PO_4)_3$ (LAGP) form electronically conductive products with the Li metal and thus, do not form a stable interphase, resulting in the rapid rise of internal resistances. In addition to the electronic insulation, a stable SEI should also exhibit low thickness for minimal interfacial resistances and good ionic conductivity to facilitate efficient ionic transport across the SEI. Similar to the Li metal anode-solid electrolyte interface, most of the solid electrolytes remain unstable at the cathode-solid electrolyte interface[171, 172] and thus are oxidized to form decomposition products. Moreover, these products result in a significant rise of overpotential at the cathode-solid electrolyte interface, resulting in performance decay. Various coating materials such as $LiNbO_3$, $LiTaO_3$, Li_2SiO_3, $Li_4Ti_5O_{12}$, and Li_3PO_4 [173-175]have been proven vital for the electrochemical stability of the solid-solid interfaces in solid-state battery. Overall, SEI and coating layers having favorable kinetic and transport attributes provide a bridge between the electrode and solid electrolyte to form stable interfaces (Figure 5(b)).

2.3.2. Anode stability via modulating interface stabilities

Recently, researchers have shown that the different interface stabilities of solid electrolyte materials can be leveraged to prevent the growth of lithium dendrites. In this regard, *Ye* and *Li*[48] proposed a multilayer design strategy where a less-stable solid electrolyte is sandwiched between more stable solid electrolytes as illustrated Figure 5(c). While the stable solid electrolyte in contact with Li metal ensures better reaction kinetics via lower overpotential, it cannot prevent the penetration of Li metal towards the counter electrode (Figure 5(c)). On the other hand, decomposition of the less-stable solid electrolyte after coming in contact with the penetrated Li metal results in filling of the cracks and gaps within the solid electrolyte microstructure and prevents the further growth of the Li dendrites. In other words, the decomposition of the less-stable solid electrolyte acts as a 'concrete' and inhibits the Li dendrite penetration, thereby improving both the rate and cycling performance of the solid-state batteries. Figure 5(d) shows the cycling performance of the solid-state batteries at 1C with different solid electrolytes as the central electrolyte. Relatively unstable solid electrolytes such as $Li_{9.54}Si_{1.74}(Pb_{0.9}Sb_{0.1})_{1.44}S_{11.7}Cl_{0.3}$ (LSPS) and LGPS show a better cycling performance when used as central electrolyte. A stable solid electrolyte (e.g., Li_3YCl_6 (LYC316)) cannot assist in filling up the cracks within solid electrolyte microstructure and thus promotes Li dendrite penetration and capacity fade.

2.3.3. Role of mechanics

Electro-chemo-mechanics play a strong role in dictating the above-mentioned ability of solid electrolyte decomposition process to prevent the penetration of Li dendrites. The Gibbs energy of the decomposition reaction is a strong function of the mechanical parameters such as internal stresses and mechanical modulus[176]. In particular, Gibbs energy for a reaction (with positive reaction-induced strain) decreases in its absolute value with increase in the mechanical constrictions. Here, Gibbs energy of reaction refers to the change in Gibbs energy that takes place when a reaction occurs. Thus, owing to the strong mechanical interactions due to solid-solid point contacts within the solid-state battery, internal stresses can increase significantly during solid electrolyte decomposition and in reverse can affect the further decomposition of the solid electrolyte. Previous studies have shown that the decomposition of solid electrolyte can be totally suppressed if the local effective modulus, K_{eff}, is greater than a critical threshold modulus, K^*.[170] Here, K^* corresponds to the effective modulus where the Gibbs energy for the decomposition reaction becomes zero, that is, the mechanical constrictions are just enough to stop the decomposition of the solid electrolyte. In an electrochemical operation, mechanical constraints at a local solid electrolyte decomposition site increase dynamically, which leads to an increase in the local effective modulus. When the effective modulus reaches a critical value (K^*), the solid electrolyte decomposition at that site is stopped. Thus, to stop the decomposition of solid electrolyte as early as possible by utilizing the mechanical constriction effect, it is necessary to have a low value of the critical modulus (K^*). Such effect can not only prevent the excess decomposition of the solid electrolyte but also allow us to leverage the solid electrolyte decomposition in filling up of the cracks and defects present within the solid electrolyte microstructure. Such dynamic filling of the cracks can potentially suppress the Li dendrite penetration and prevent short circuit, thus contributing towards longer cycle life of the solid-state battery. In addition to a low critical modulus, a sufficiently high decomposition energy is also required for this effect to be efficient. Hence, critical modulus and decomposition energy are key solid electrolyte parameters which can dictate its ability towards enabling the above-mentioned dynamic stability within solid-state batteries[170]. With such an approach, the electrochemical stability window of the solid electrolytes can be significantly improved and brought to the normal operating range of the solid-state battery (0 - 4.5 V). Figure 5(e) shows the critical modulus and decomposition energy for some representative solid electrolyte materials. Using machine learning, *Wang et al.*[170] predicted the compositions of the solid electrolyte materials (LPSCl-X-min(K^*)-shell ($Li_{7.4}P_{0.5}S_{2.3}Cl_{2.2}$) and LGPS-min($K^*$)-shell ($Li_{14.2}Ge_{0.9}P_{1.8}S_8$)) which can exhibit favorable critical modulus and decomposition energy so that they can be used as the central electrolyte in the multilayer configuration for successful prevention of the growth of Li dendrites (Figure 5(e)). Electro-chemo-mechanical coupling of such battery designs is intricately dependent on the solid electrolyte microstructure, mechanical properties, transport and kinetic properties of the decomposition products, fabrication and operating pressures, and temperature.

3. Intercalation-based solid-state electrodes

3.1. Implications of solid-solid point contacts on reaction and transport interactions

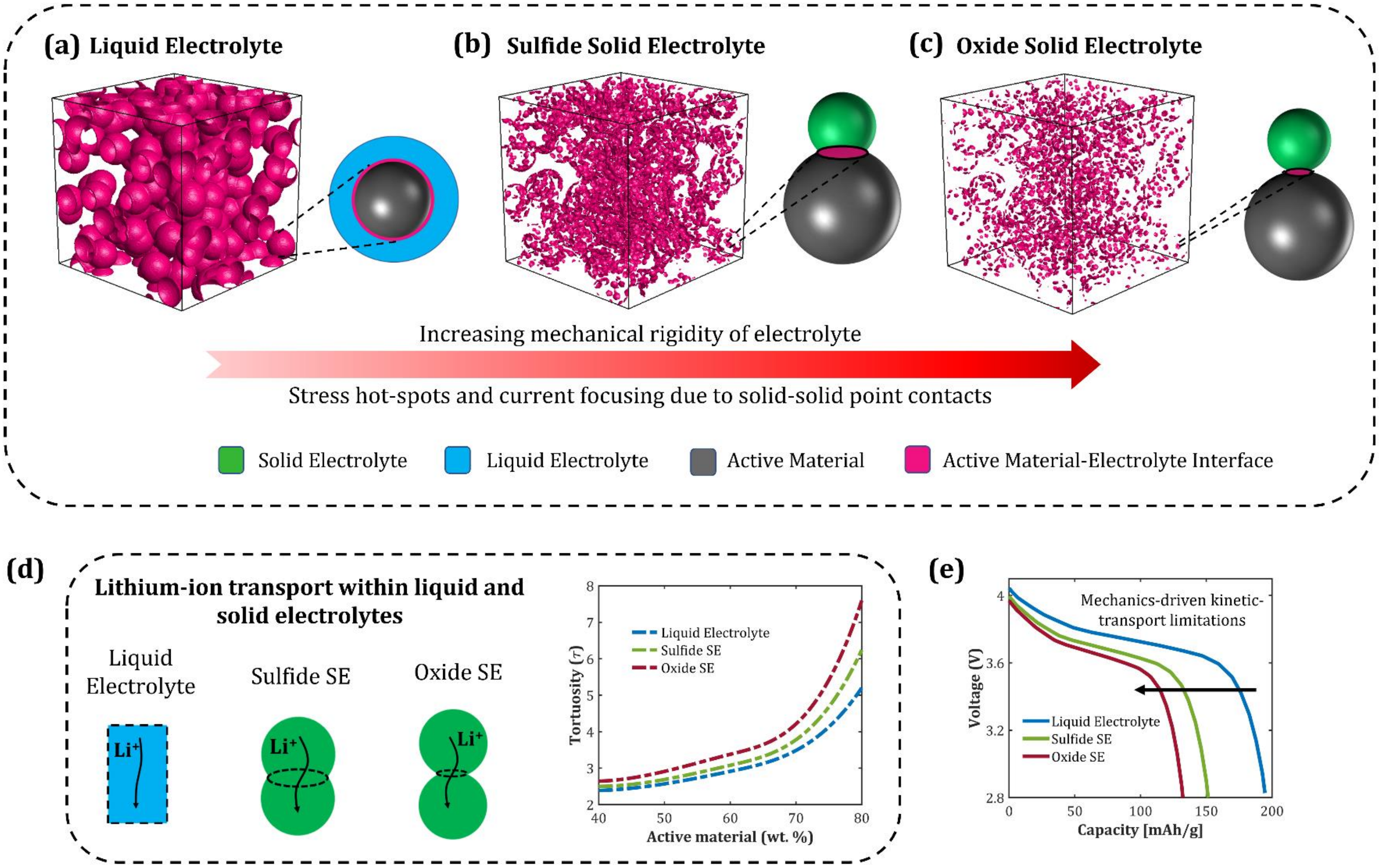


Figure 6. Three-dimensional electrode-level and particle-level representation of the cathode-electrolyte interface for (a) liquid electrolyte, (b) sulfide-based solid electrolyte, and (c) oxide-based solid electrolyte. Liquid electrolyte fully wets the active material particle surface resulting in conformal interfacial contact. Increasing mechanical rigidity of electrolyte leads to severe solid-solid point contacts resulting in stress hot-spots and current focusing within the cathode microstructure. (c) Effect of mechanical behavior of electrolyte on the ionic tortuosity and percolation pathways for liquid electrolyte, sulfide and oxide-based solid electrolytes. (e) Impact of electrolyte mechanical behavior-driven kinetic-transport limitations on the battery performance.

The cathode microstructure is composed of stochastic arrangement of its constituent phases, namely, active material, electrolyte, carbon additives, and binders. While interfacial contact between active material and electrolyte governs the reaction signatures, contact between solid electrolyte particles dictate the ionic percolation pathways within solid-state battery cathodes[177]. Mechanical properties of active material and solid electrolyte play a critical role in dictating these intrinsic interfaces within the cathode microstructure. Thus, mechanical behavior of the active material and electrolyte intricately governs the kinetic and transport signatures within the cathode, thus having a significant impact on the battery performance[178, 179].

Figure 6(a) shows the three-dimensional representation of electrode-level and particle-level interfacial contact between the active material and liquid electrolyte within the cathode microstructure. Intimate interfacial contact between the active material and liquid electrolyte is maintained throughout the battery operation as liquid electrolyte fully wets the active material surface. This results in uniform electrochemical reactions and lithium intercalation within the active material particles. However, achieving perfect interfacial contact between active material and solid electrolyte within solid-state battery cathodes is challenging owing to the solid-solid point contacts between particles (Figures 6(b) and 6(c))[18]. Presence of such point contacts between active material and solid electrolyte particles leads to stress hot-spots and kinetic heterogeneity resulting in current focusing, increased overpotential and lower active material utilization[47, 49, 180, 181]. Moreover, unlike liquid electrolytes, where pore phase contributes towards continuous ionic percolation pathways, presence of voids and solid-solid point contacts between solid electrolyte particles results in additional ion transport resistance within solid electrolyte phase via increased tortuosity (as shown in Figure 6(d)) and current constriction[18, 182, 183]. Thus, presence of solid-solid interfaces contributes to both reaction and transport limitations within solid-state battery cathodes. Such limitations can exacerbate at high active material loading cathode designs owing to the increased ionic tortuosity (Figure 6(d)) and limited active material coverage by solid electrolyte phase[184]. Severity of such reaction and transport limitations is strongly related to the mechanical properties of solid electrolytes. As sulfide-based solid electrolytes (Young's modulus of 8-20 GPa) are relatively softer as compared to the oxide-based solid electrolytes (Young's modulus of 150-200 GPa), they can easily deform and achieve better solid-solid contact than oxide-based solid electrolytes[185]. Thus, mechanics-driven reaction-transport limitations are more severe in oxide-based solid electrolytes as compared to sulfide-based solid electrolytes (Figures 6(b) and 6(c)). Figure 6(e) shows the representative comparison on how mechanics-driven kinetic-transport limitations affect the electrochemical performance of solid-state batteries with sulfide and oxide-based solid electrolytes as compared to liquid electrolyte systems[186]. From the observed electrochemical signatures, it is clear that achieving intimate contact between active material-solid electrolyte and solid electrolyte-solid electrolyte particles within composite cathodes is crucial for attaining enhanced performance of solid-state batteries.

Researchers have adopted various strategies to improve the interfacial contact within solid-state battery cathodes such as cold pressing, active material coating and high temperature sintering[187]. Enhanced interfacial contact in cathodes with sulfide-based solid electrolytes can be achieved simply by cold-pressing, owing to their malleable nature and lower Young's modulus[51]. However, achieving such intimate contact in cathodes with oxide-based solid electrolytes requires high temperature sintering, which has been observed to result in unwanted side reactions leading to solid electrolyte decomposition, formation of ion-blocking and electron-blocking phases, etc.[188]. Such deleterious interactions can result in a steep rise in the interfacial resistances and often lead to performance decay of solid-state batteries. In this regard, active material coatings have been proven to be an efficient strategy to avoid unwanted reactions in both oxide and sulfide-based solid electrolyte systems.

3.2. Interfacial delamination at solid-solid interfaces

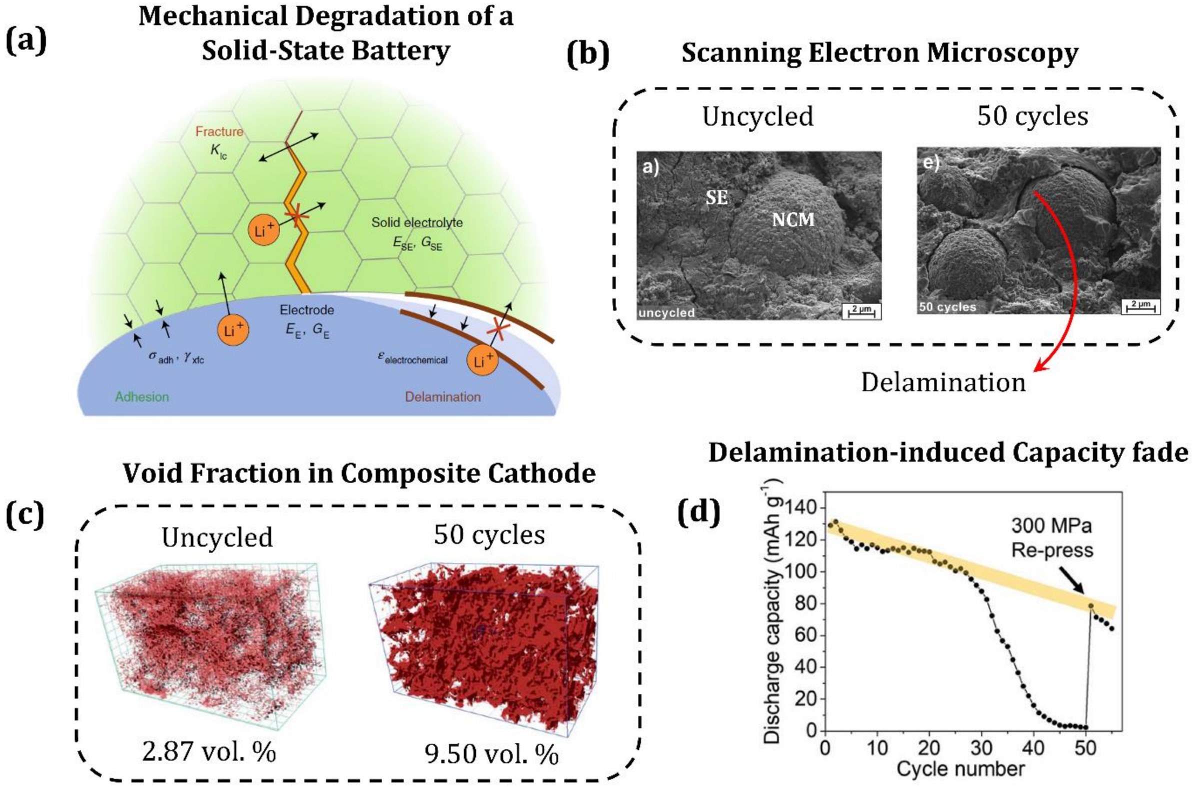


Figure 7. (a) Schematic demonstration of various modes of mechanical degradation occurring at the cathode-solid electrolyte interface within solid-state batteries. (Reproduced with permission from [52]. Copyright 2019 Springer Nature Limited) (b) Scanning electron micrographs of the composite cathode consisting of NMC811 and β-Li_3PS_4 at uncycled state and after 50 cycles at discharged state, respectively. (Reproduced with permission from [186]. Copyright 2017 American Chemical Society.) While the uncycled state shows intimate contact between active material and solid electrolyte, severe delamination is observed after 50 cycles. (c) Increase in voids from 2.87 vol. % to 9.5 vol. % within composite cathode from the uncycled state to the discharge state after 50 cycles indicates interfacial contact loss due to delamination. (Reproduced with permission from [189]. Copyright 2020 The Royal Society of Chemistry.) (d) Discharge capacity of the solid-state battery as a function of cycle number where pressure of 300 MPa was reapplied after 50 cycles. (Reproduced with permission from [189]. Copyright 2020 The Royal Society of Chemistry.) With the application of pressure, two modes of capacity fade, namely, chemical degradation and mechanical degradation can be distinctly quantified.

Lithiation and delithiation of active material particles during electrochemical operation results in their cyclical volume expansion and contraction[190]. Such volume changes within the composite cathodes result in significant stress fluctuations during charging and discharging processes which often manifest into several modes of mechanical degradation such as fracture in active material and solid electrolyte particles, and interfacial delamination (Figure 7(a))[52]. Fractures within active material and solid electrolyte particles affect the lithium diffusivity and ionic transport, respectively. Fracture onset is mostly related to the fracture toughness of the material and the local defect size and thus, are among the most important mechanical parameters in addition to mechanical modulus which dictate the interface stability and cycling performance of the solid-state batteries. While fracture toughness is the intrinsic material property, defect sizes within the material strongly depends on the manufacturing processes. Interface delamination leads to hindrance in ionic transport across interfaces as well as increase in the interfacial resistance causing overpotential rise and thus, capacity fade[56]. Interface delamination is majorly related to the surface adhesion energy between the participating materials as schematically illustrated in Figure 7(a). Interfacial chemical energy, mechanical energy and electrical energy intricately contribute to the surface adhesion and thus, a multi-dimensional and multi-disciplinary approach is needed to get the mechanistic understanding of the interface delamination[191]. In addition, side reactions such as electrolyte decomposition and formation of cathode-electrolyte interphase (CEI) add intricacies into the fundamental analysis of interface delamination[192]. Moreover, the role of binder in sustaining the interfacial contact between active material and solid electrolyte particles is another important aspect that should be considered[193]. With multiple factors governing the interface delamination, a multi-scale computational approach may show promise in obtaining quantitative insights into the mechanisms that dictate delamination-induced performance decay in solid-state batteries.

Several experimental efforts have been made to understand the implications of delamination-induced contact loss in solid-state batteries. Figure 7(b) shows the scanning electron micrographs of composite cathode consisting of NMC811 active material and β-Li_3PS_4 solid electrolyte at uncycled state and after 50 cycles at discharged state[186]. Uncycled state shows intimate contact between active material and solid electrolyte as active material particles are well embedded in the solid electrolyte phase. After 50 cycles, contact loss between active material and solid electrolyte phase is clearly seen from Figure 7(b) which can be attributed to the volume changes of active material particles during electrochemical operation. Figure 7(c) also corroborates the contact loss mechanism by depicting the volume % of voids present within the composite cathode in the pristine state and after 50 cycles[189]. With subsequent cycling, voids were observed to be generated near the periphery of the active material particles, directly correlating it to the contact loss and capacity fade. An interesting mechanistic insight that Shi *et. al.*[189] presented through their work is that the voids were found to be concentrated on one side of the active material particle, rather than uniformly distributed around the active material surface. Such a phenomenon may lead to severe transport limitations due to longer transport pathways in both solid electrolyte (lithium-ion transport) and active material (lithium diffusion) phases. Moreover, current focusing due to accumulation of the interfacial contact points may also lead to severe kinetic limitations due to overpotential rise. Such heterogeneities due to asymmetric contact loss can also have significant implications on lithium diffusion and electrochemical reactions due to non-uniform stress distribution, which will be discussed in detail in the subsequent section.

In addition to active material-solid electrolyte contact loss due to volume changes in active material, chemical degradation can also contribute substantially to the capacity fade over cycling[194, 195]. In Figure 7(d), discharge capacity of a solid-state battery is shown as a function of cycle number, where 300 MPa of pressure is reapplied after 50 cycles and the subsequent discharge capacity is obtained[189]. From the results shown in Figure 7(d), two modes of capacity fade, namely, mechanical degradation and chemical degradation can be distinctly quantified. It is also noted that, both the modes contribute significantly to the performance decay and thus, research focus should be given on mitigating both mechanical and chemical degradation within composite cathodes of solid-state batteries.

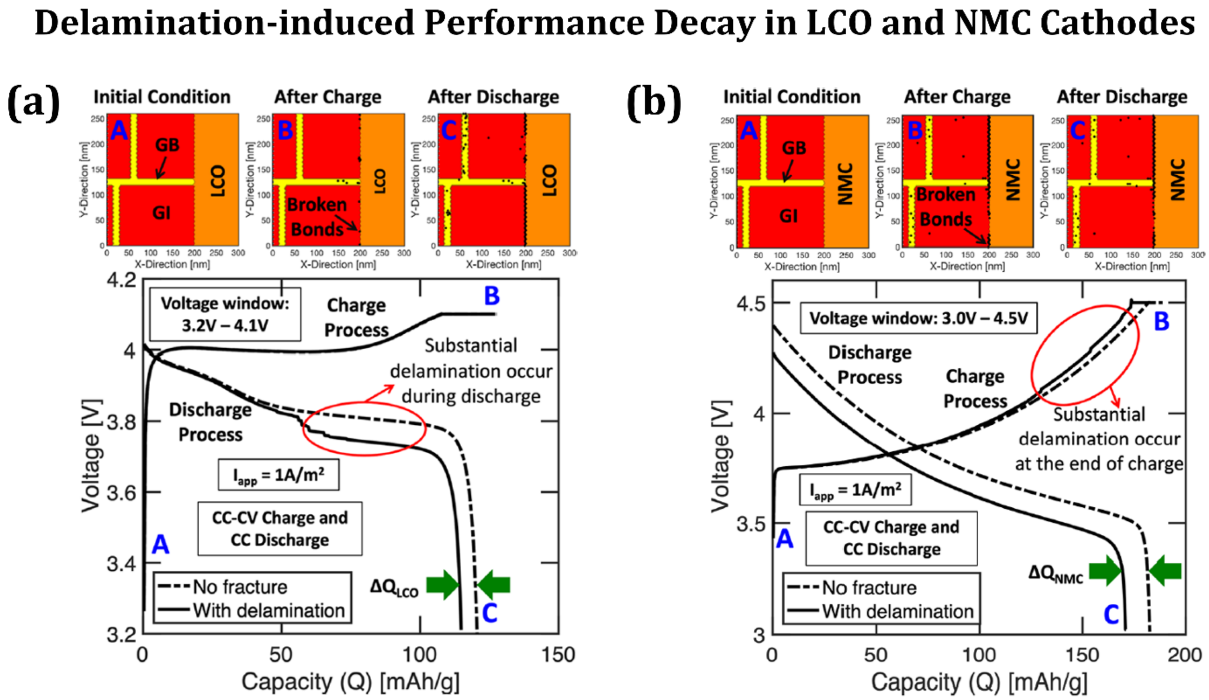

Delamination-induced Performance Decay in LCO and NMC Cathodes

Figure 8. Comparison between the electrochemical performance signatures with and without the interfacial delamination for (a) LCO and (b) NMC cathodes, respectively. (Reproduced with permission from [56]. Copyright 2021 American Chemical Society.) LCO and NMC cathodes exhibit distinct delamination behavior owing to the negative and positive partial molar volume of lithium, respectively, which manifests into distinct performance signatures.

Different cathode materials show different volume-change characteristics during charging and discharging operation based on the partial molar volume of lithium. For instance, NMC cathodes exhibit positive partial molar volume of lithium, meaning, the NMC particles expand upon lithiation and contract upon delithiation. On the other hand, LCO cathodes exhibit negative partial molar volume of lithium, that is, LCO particles shrink and expand during lithiation and delithiation, respectively which has been illustrated ahead in Figure 9(c). Figures 8(a) and 8(b) shows the effect of delamination on the electrochemical signature of LCO and NMC cathodes, respectively[56]. During the first charging operation, negligible contact loss is observed for LCO cathodes as active material particles expand during charging (delithiation), thus experiencing compressive stresses. Whereas substantial delamination is observed during the subsequent discharge operation. As LCO particles contract during discharge (lithiation), tensile stresses are generated at the active material-solid electrolyte interface. As soon as stresses exceed the fracture threshold of the active material-solid electrolyte interface, delamination occurs, contributing towards performance decay. Unlike LCO cathodes, significant delamination is observed in NMC cathodes during the first charge itself, owing to the tensile stresses generated because of active material shrinkage, thus resulting in capacity fade. Even if further delamination is negligible during subsequent discharge operation, reduced capacity is observed due to already existing contact loss from the previous charging step. It is worth noting that most of the delamination in NMC cathodes occurs towards the end of first charge. As a result, lowering the upper cut-off voltage can serve as a potential strategy to minimize the delamination induced performance decay in solid-state batteries, thus improving the capacity retention over multiple cycles[56, 196]. Since the grain boundaries of solid electrolyte are usually softer than the grains, increasing the number of grain boundaries near the active material-solid electrolyte interface (to accommodate for the volume changes of active material) by reducing the grain size can be another strategy to minimize the contact loss between active material and solid electrolyte.

3.3 Implications of solid-solid contact stress on electrochemical performance

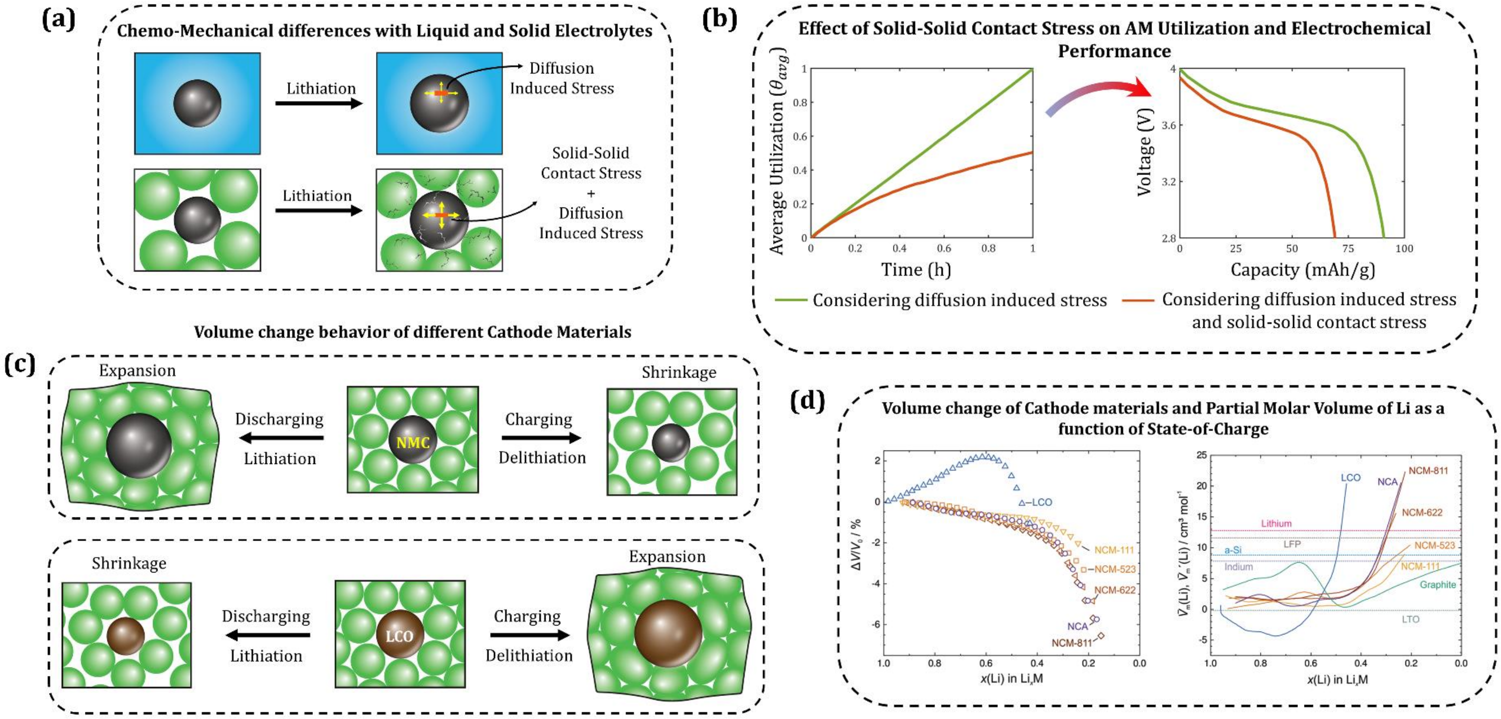


Figure 9. (a) Fundamental differences underlying the chemo-mechanical interactions in cathodes with liquid and solid electrolytes. (b) Representative comparison of the active material utilization and the electrochemical performance signature with and without considering the solid-solid contact stresses in active material particles of composite cathodes. (c) Schematic demonstrating the distinct behavior of NMC and LCO particles during charging (delithiation) and discharging (lithiation) owing to the positive and negative partial molar volumes of lithium for NMC and LCO particles, respectively. (d) Relative volume change of the cathode materials and the partial molar volume of lithium in the cathode materials obtained as a function of state-of-charge. (Reproduced with permission from [61]. Copyright 2018 The Royal Society of Chemistry.)

In Figure 9(a), a schematic illustration depicts the fundamental differences underlying chemo-mechanical interactions in cathodes having liquid electrolyte and solid electrolyte, respectively. Liquid electrolytes, owing to their inherent nature, can easily accommodate the lithiation-delithiation induced volume changes of active material particles. Due to weak mechanical interactions between active material particles and liquid electrolyte, the active material surface which is in contact with liquid electrolyte is almost at a stress-free state during the entire electrochemical operation. However, in solid-state battery cathodes, solid-solid point contacts between particles lead to high magnitude of stresses in both active material and solid electrolyte particles. Moreover, expansion and contraction of active material particles result in severe stress fluctuations within the system[19, 61]. Thus, in addition to the diffusion induced stress, contact stresses play a significant role in dictating the kinetic and transport signatures in solid-state cathodes (Figure 9(a))[17, 197]. Hence, critical understanding of the mechanistic role of electro-chemo-mechanical coupling underlying solid-state cathodes and its implications on the battery performance is paramount.

Insertion of lithium in active material particles gives rise to the diffusion induced stresses which in return regulate the lithium diffusion in active material particles. In addition, lithiation induced volume expansion results in severe solid-solid contact stresses, thus furthering the effect of stress on lithium diffusion[58, 198]. Solid-state diffusion of lithium considering the effect of stress can be mathematically expressed as follows:

$$\frac{\partial c_s}{\partial t} = \nabla.\left[D(c_s, \sigma_h)\left(\nabla c_s - \frac{\Omega_{Li} c_s}{RT} \nabla \sigma_h\right)\right] \tag{1}$$

Here, c_s is the lithium concentration, D is the diffusion coefficient, Ω_{Li} is the partial molar volume of lithium, σ_h is the hydrostatic stress, R is the universal gas constant and T is the temperature. It is worth noting that the diffusion coefficient, D, depends on both stress state and lithium concentration. Previous studies have shown that stresses can not only slow down the diffusion of lithium in active material particles, but also completely arrest the lithiation process under extreme circumstances, resulting in severe under-utilization of active material particles within the electrode and subsequent capacity fade (Figure 9(b))[198].

Stresses also impact the reaction kinetics at the active material-solid electrolyte interfaces. Mathematical expression for Butler-Volmer kinetics with the stress effect is given as follows[199]:

$$i_{BV} = Fk_a^{\alpha_c}(k_c c_{SE})^{\alpha_a}\exp\left(\frac{\alpha_a \Delta\mu_{e^-}}{RT}\right)\left(\exp\left(\frac{\alpha_a F\eta}{RT}\right) - \exp\left(-\frac{\alpha_c F\eta}{RT}\right)\right) \tag{2}$$

Here, F is the Faraday's constant, k_a and k_c are the anodic and cathodic reaction rate constants, α_a and α_c are the anodic and cathodic transfer coefficients, c_{SE} is the lithium concentration in the solid electrolyte, and η is the electrical overpotential. $\Delta\mu_{e^-}$ denotes the electrochemical potential change due to the mechanical stresses and is expressed as follows[43, 199]:

$$\Delta\mu_{e^-} = -\frac{1}{2}(\Omega_{Li} + \Omega_{Li^+})\left(-\gamma\kappa + e_n \cdot \left(\left(\tau_d^{Elec} - \tau_d^{SE}\right)e_n\right)\right) + \frac{1}{2}(\Omega_{Li} - \Omega_{Li^+})(\Delta p^{Elec} + \Delta p^{SE}) \tag{3}$$

where, Ω_{Li} and Ω_{Li^+} are the partial molar volumes of lithium and lithium ions, respectively, γ denotes the surface energy, κ is the mean interface curvature, τ_d^{Elec} and τ_d^{SE} are the interfacial deviatoric stress tensors for electrode and electrolyte, and Δp^{Elec} and Δp^{SE} are the pressure terms evaluated as $\Delta p^{Elec} = -\frac{\sigma_{kk}^{Elec}}{3} = -\sigma_h^{Elec}$ and $\Delta p^{SE} = -\frac{\sigma_{kk}^{SE}}{3} = -\sigma_h^{SE}$, respectively. As seen from Eq. (1-3), reaction-transport interactions within the solid-state batteries intricately depend on parameters such as hydrostatic stresses, partial molar volumes of lithium (in electrode) and lithium ions (in electrolyte), shear moduli and interface morphology.

The above-mentioned electro-chemo-mechanical coupling needs to be investigated separately for each electrode chemistry owing to their distinct mechanical response. For example, a prior study[200] showed that, for a molar volume ratio, $\nu = \frac{\Omega_{Li^+}}{\Omega_{Li}}$, of 3.85, stable electrodeposition at the lithium metal anode-solid electrolyte interface can be obtained if the shear modulus of solid electrolyte is greater than two times the shear modulus of lithium metal. Another study specific to high-capacity anode materials (e.g., Si and Ge) revealed that as the lithiation generates core shell structure (non-lithiated crystalline core and lithiated amorphous shell), internal stresses within such system contribute to the reduction of both lithium diffusivity and reaction rate[198]. Under extreme circumstances, stresses can completely arrest the lithiation process resulting in severe under-utilization of active material particles within the electrode and subsequent capacity fade (Figure 9(b)).

While the effect of stresses on the reaction kinetics and transport has been extensively studied in the context of anodes (especially lithium metal anodes), their mechanistic implications for solid-state cathodes still need further attention. As active material particle are surrounded by grains and grain boundaries of solid electrolyte, another active material particles, carbon additives, binders and voids, stress heterogeneity within the active material particle due to such non-uniform mechanical interactions at the surface can have significant impact on the above-mentioned stress-driven reaction kinetics and transport. As mentioned in the earlier section, distinct volume change behavior of LCO and NMC cathode active material particles (Figures 9(c-d)) leads to distinct stress evolution signatures during charging and discharging. As a result, stress-driven kinetics and transport will have distinct dynamics in LCO and NMC cathodes. In addition, the contact loss between the active material and solid electrolyte due to the cyclical volume changes will lead to significant increase in the internal stresses at the solid-solid point contacts, thereby influencing the reaction-transport interactions[197]. Also, the electro-chemo-mechanical implications of dynamic change in the partial molar volume of lithium within the intercalation-based active material during lithiation and delithiation processes (Figure 9(d)) still need to be explored in detail[61].

3.4. Particle cracking and mitigation strategies

3.4.1. Computational methods to study fracture in electrode particles

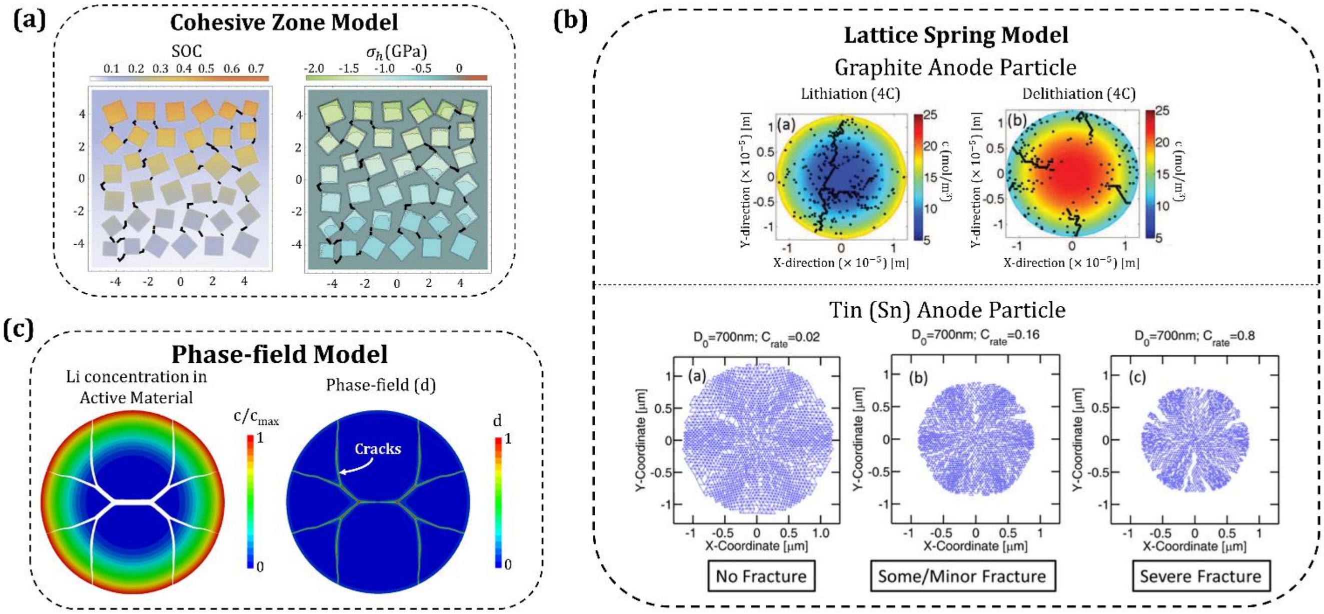


Figure 10. (a) Mechanical damage in the solid electrolyte obtained using the cohesive zone model. (Reproduced with permission from [59]. Copyright The Royal Society of Chemistry 2017.) (b) Crack formation and propagation within the graphite and tin anode particles captured using the lattice spring model. (Reproduced with permissions from [201, 202]. Copyright 2013 and 2016 The Electrochemical Society.) (c) Crack propagation within active material particles modeled using the phase field model where the phase field parameter is solved as a function of time to obtain the crack evolution. (Reproduced with permission from [203]. Copyright 2016 Elsevier Ltd.)

In addition to the mechanics-driven kinetic and transport limitations and delamination within the composite electrodes of solid-state batteries, fracture within active material and solid electrolyte phases contributes significantly to the capacity decay. Fracture leads to longer lithium diffusion pathways within active material particles, whereas in solid electrolyte phase it leads to higher tortuosity for lithium-ion transport[204]. Bucci *et al.*[59] used a cohesive zone model to capture the mechanical degradation in the solid electrolyte phase caused by the intercalation-induced volume expansion of electrode particles (Figure 10(a)). It was shown that the mechanical properties of active material and solid electrolyte phases as well as the microstructural attributes such as particle morphologies play a significant role in determining the onset and propagation of the fracture within the solid electrolyte. Volume expansion of the active material particles lead to not only compressive but also tensile stresses at the specific locations within the solid electrolyte matrix. Fracture is initiated and propagated as the tensile stresses exceed the fracture threshold of the solid electrolyte material.

Extensive computational efforts have been made to study the crack initiation and propagation in active material particles in liquid electrolyte systems using different approaches such as lattice spring[202] and phase field models[203, 205] (Figures 10(b-c)). In lattice spring formulation, the active material particle domain is discretized into spring elements, with each element having the mechanical properties of the active material. If the strain energy in the stretched spring element exceeds the fracture threshold, the spring element is broken, and crack is generated. In Figure 10(b), crack propagation behavior in a graphite anode particle is shown for lithiation and delithiation processes. During lithiation, compressive and tensile stresses are generated near the active material surface and center, respectively. As a result, central cracks are formed during the lithiation process. On the other hand, delithiation results in tensile stress near the periphery of the active material particle, while compressive stress is generated at the center of the particle. Hence, peripheral cracks are formed during the delithiation process. The lattice spring model has also been used to study the effect of two-phase diffusion and creep on mechanical degradation in high-capacity anode particles as shown in Figure 10(b)[201]. Lithium transport within Sn anode particles occurs via two phase diffusion mechanism (experiments have also revealed the presence of multiple phases during lithiation in high-capacity anode particles[206]). Two phase front separates the Li-rich and Li-poor phases within the particle, thus resulting in a sharp jump in the lithium concentration. Two-phase diffusion results in large strain inhomogeneity between the two phases which exacerbates the fracture within the Sn particles. On the other hand, stress relaxation due to creep at lower charging rates has been found to mitigate the mechanical degradation in Sn particles. As charging rate is increased, insufficient time for creep-driven stress relaxation results in severe fracture.

Evolution of crack within an active material particle has also been studied using the phase field model, where the phase field parameter is dynamically solved which provides a quantitative measure of the mechanical degradation within the particle as a function of space and time (Figure 10(c)). Unlike in liquid electrolyte systems, where diffusion induced stress is the most important factor dictating the fracture evolution in active material particles, solid-solid constraints being a dominating factor in solid-state composite electrodes, fracture behavior in solid electrolyte systems can be significantly different. Thus, the above-mentioned modeling capabilities can be useful to study the fracture response of active material particle and its correlation with the intrinsic and extrinsic conditions (presence of voids, binder, and active material, microstructural attributes such as grain and grain boundaries of solid electrolyte, mechanical properties, stack pressure, etc.).

3.4.2. Fracture mitigation strategies

Fracture results in penetration of liquid electrolyte within microcracks of the active material particles. Exposing fresh active material surface to the electrolyte leads to the loss of lithium inventory via new solid electrolyte interphase (on anode side) and cathode electrolyte interphase (on cathode side) formation. However, due to the increase in electrochemically reactive sites, fracture leads to enhancement in the reaction kinetics in conventional lithium-ion batteries with liquid electrolyte. On the other hand, in solid-state batteries, as solid electrolyte cannot seep into the microcracks of the active material particles, reaction sites remain almost the same. Thus, owing to the exacerbated lithium diffusion within active material particles and unaltered reaction sites, fracture can have more severe implications on the electrochemical performance in solid-state batteries as compared to their liquid counterparts[204].

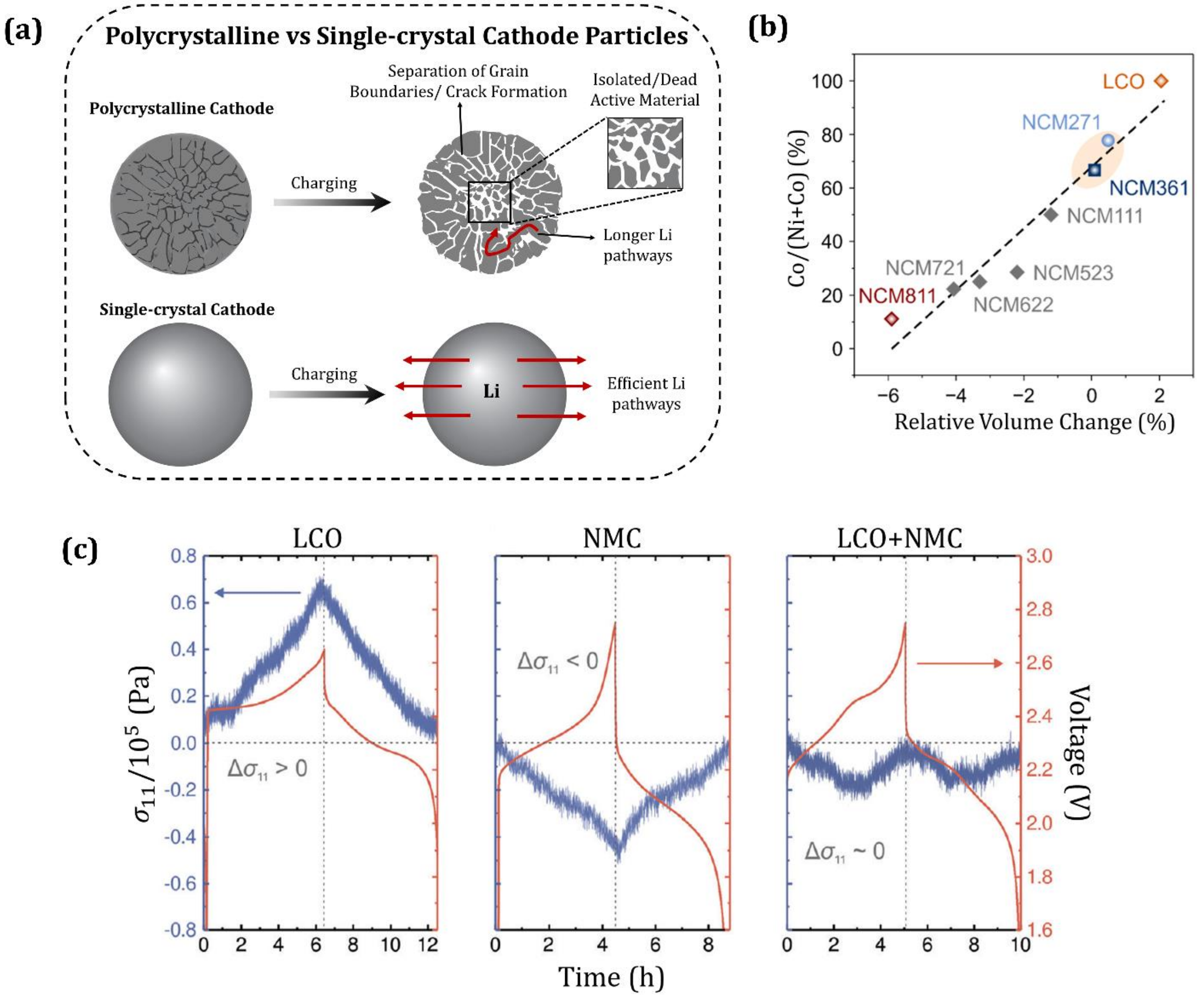


Figure 11. (a) Schematic illustration of the underlying differences between polycrystalline and single crystal cathode particles during electrochemical operation. (b) Molar ratio of Co/ (Ni + Co) and the corresponding relative volume change for various cathode active materials (Reproduced with permission from [207]. Copyright 2019 American Chemical Society). (c) Stress mitigation by utilizing two different active materials (NMC and LCO) exhibiting positive and negative partial molar volume of lithium, respectively. (Reproduced with permission from [61]. Copyright 2018 The Royal Society of Chemistry.)

Employing single crystal cathode particles is a potential strategy to enhance the performance and endurance of both solid-state batteries and conventional lithium-ion batteries as single crystal cathode particles can potentially avoid the fracture and improve lithium diffusion due to the absence of grain boundaries[208]. For instance, solid-state batteries with single crystal NMC532 have shown 6-14 times higher lithium diffusivity than polycrystalline NMC532 as well as significant improvement in performance, especially at higher applied current densities[209]. Utilizing polycrystalline cathode particles in solid-state batteries not only results in longer lithium diffusion pathways[210], but also results in dead active material as fracture along the grain boundaries can potentially lead to loss of contact as shown in Figure 11(a). Dead active material cannot participate in either electrochemical reactions, lithiation, or electronic percolation and thus resulting in direct capacity fade.

Researchers have considered various approaches to mitigate internal stresses in solid-state composite electrodes. Recently, Strauss *et al.*[207] proposed the design of quasi-zero-strain NMC cathode materials to minimize the volume changes of cathode active material in solid-state batteries. Figure 11(b) shows the plot of molar ratio of Co/(Ni + Co) and the corresponding relative volume change for various cathode active materials. Here, linear fitting using the available experimental data, potential zero-strain cathode materials (NMC361 and NMC271) were identified and experimentally tested. Quasi-zero strain cathode active materials can potentially mitigate the deleterious effects such as delamination-induced contact loss, fracture in active material and solid electrolyte phases, thus ensuring consistently efficient transport and kinetics over a number of cycles. In regard to the stress mitigation in solid-state batteries, a recent study has also proposed the utilization of both NMC and LCO cathode particles in the composite electrode (Figure 11(c))[61]. As NMC and LCO exhibit positive and negative partial molar volume of lithium, respectively, expansion of NMC and simultaneous contraction of LCO during lithiation results in reduced stresses, thus minimizing mechanical degradation of active material and solid electrolyte within the electrode.

4. Electro-chemo-mechanical challenges with conversion-based (sulfur) cathode

High theoretical promise of lithium-sulfur (Li-S) batteries (theoretical specific capacity of 1672 mAh g^{-1} for elemental sulfur), low cost and abundance of sulfur in earth's crust make them a potential candidate for next-generation energy storage systems[62]. However, due to several fundamental challenges such as polysulfide shuttle effect, kinetic and transport limitations due to surface passivation and pore blockage, respectively and high-volume expansion (~ 80%) during cycling, full potential of Li-S batteries is yet to be realized[211]. Several experimental and computational efforts are being made towards mechanistic understanding and enhancing the performance and cyclability of Li-S batteries.

4.1. Challenges in liquid electrolyte-based Li-S battery

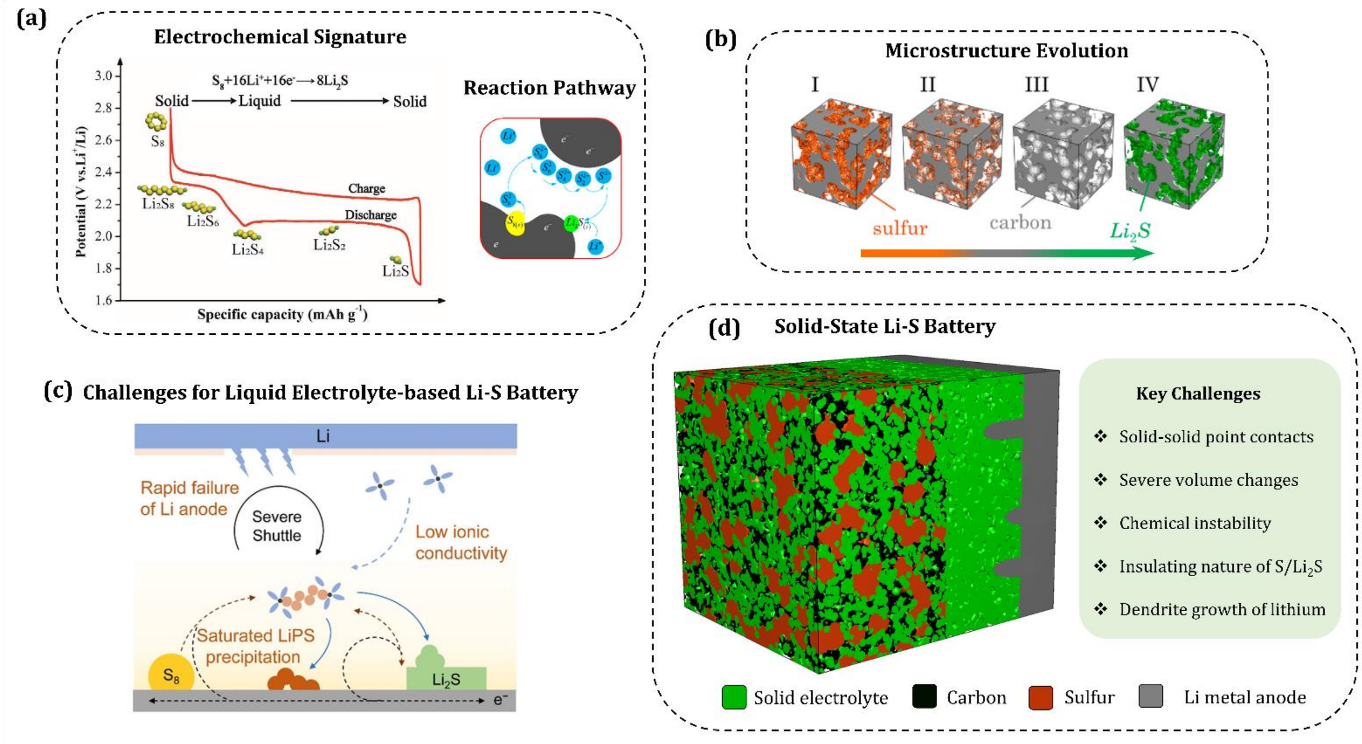


Figure 12. (a) Representative charge/discharge signature of the Li-S battery along with the schematic of corresponding reaction pathway[212, 213]. (b) Schematic representation of the microstructure evolution of sulfur cathode during discharge operation[214]. (c) Schematic illustration of the challenges for liquid electrolyte-based Li-S battery[211]. (d) Schematic illustration of the solid-state lithium-sulfur battery and list of associated electro-chemo-mechanical challenges. (Reproduced with permission from [211, 212, 214] . Copyright 2017, 2018 and 2020 American Chemical Society.) (Reproduced with permission from [213]. Copyright 2017 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.)

During the discharge operation, sulfur ($S_{8(s)}$) dissolves in the electrolyte to form $S_{8(l)}$ and undergoes a multistep electrochemical reduction process where the long-chain polysulfides (PSs) get converted to the short-chain PSs ($S_{8(l)} \rightarrow S_8^{2-} \rightarrow S_6^{2-} \rightarrow S_4^{2-} \rightarrow S_2^{2-} \rightarrow S^{2-}$) as shown by the reaction pathway in Figure 12(a)[212]. Short-chain PSs then react with the incoming lithium-ions from anode to form Li_2S precipitate, which results in 80% volume expansion as compared to solid $S_{8(s)}$. The schematic representing the microstructure evolution during discharge is represented in

Figure 12(b). Dissolution and precipitation induced volume changes within the cathode microstructure generate internal stresses which leads to fracture and cracking in the constituent phases, and subsequent capacity fade[65]. As Li_2S is ionically/electronically insulating, precipitation leads to reduction in the electrochemically active area, resulting in the overpotential rise. Interfacial energies of Li_2S-carbon and Li_2S-Li_2S interfaces play a crucial role in determining the severity of this kinetic limitation. The lower interfacial energy of Li_2S-carbon interface leads to preferential precipitation on the carbon surface (film-like deposition), leading to severe reduction in the active area and capacity fade. On the other hand, preferential precipitation on already existing precipitate (finger-like deposition) ensures sufficient availability of the active area for electrochemical reactions[212]. Increase in the volume of precipitate over the cell operation results in pore blockage, leading to increased tortuosity for ionic transport, which adds transport limitations to the system. Moreover, dissolution of multiple PSs in the electrolyte negatively affects the ionic conductivity of the electrolyte, causing extra rise in the internal resistances[214]. Transport and kinetic resistances arising from the surface passivation, pore blockage and reduction in the electrolyte conductivity contributes to dramatic capacity fade, especially at higher charging rates and sulfur loadings[215]. All these challenges pertaining to liquid electrolyte-based Li-S battery are schematically represented in Figure 12(c).

4.2. Solid-state Li-S batteries

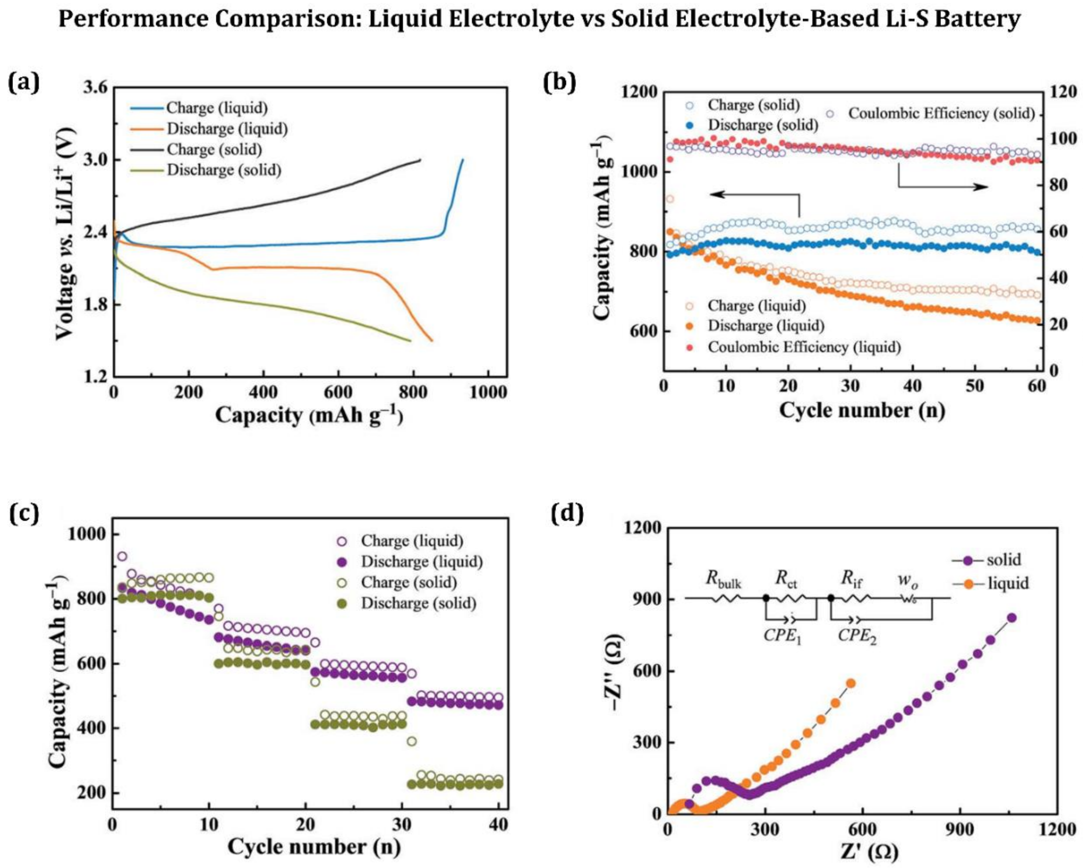


Figure 13. Comparison of (a) charge-discharge signatures, (b) cycling performance, (c) rate performance, and (d) internal resistances between liquid and solid electrolyte-based Li-S battery. (Reproduced with permission from [216]. Copyright The Royal Society of Chemistry 2017.)

Towards mitigating the safety concerns regarding liquid electrolytes (due to their intrinsic inflammable nature) and permanently eliminating the polysulfide shuttle effect, solid-state Li-S batteries have attracted tremendous research efforts[62]. Figures 13(a-d) presents a systematic comparison of the electrochemical performance of the liquid and solid electrolyte-based Li-S batteries[216]. Two plateaus are observed in the discharge curve of the liquid electrolyte-based Li-S battery in Figure 13(a), one around 2.3V and the second around 2.1 V. This corresponds to the multi-step reduction process of S_8 to Li_2S. On the other hand, no plateaus are observed in the discharge profile of a solid electrolyte-based Li-S battery which signifies the direct conversion of S_8 to Li_2S without the intermediate PSs. Thus, solid-state Li-S battery holds potential to solve the issues related to the polysulfide shuttling in liquid electrolyte-based Li-S battery. Elimination of the polysulfide shuttling improves the cycling performance and coulombic efficiency in solid-state Li-S battery as shown in Figure 13(b). However, solid-solid point contacts present in solid-state Li-S battery results in higher interfacial and transport resistance, thus limiting the rate performance (Figures 13(c-d)). Also, solid-solid mechanical interactions within the composite electrode render the implications of high-volume expansion more critical in solid-state Li-S batteries as compared to the liquid electrolyte-based Li-S batteries. Solid-solid point contacts lead to limited active area and percolation pathways, and the surface passivation during the electrochemical operation can exacerbate this scenario[66]. High-volume expansion can result in fracture within solid electrolyte further affecting the ionic percolation pathways. Cyclical expansion and contraction can lead to the development of compressive and tensile stresses at the carbon-solid electrolyte interface, leading to the interfacial delamination and contact loss. Such contact loss increases the kinetic overpotential and hinders the sulfur utilization, resulting in capacity fade. The kinetic limitation can further exacerbate in the later stages due to the ionic/electronic insulating nature of Li_2S. In addition, The role of stress-driven transport and reaction kinetics can be critical and needs to be explore in solid-state Li-S systems[17]. Moreover, stress heterogeneity arising due to non-uniform Li_2S deposition and its implications on transport and kinetic interactions and mechanical degradation need to be considered to further the mechanistic understanding of electro-chemo-mechanical coupling in solid-state Li-S batteries. Schematic representation of the solid-state Li-S battery is shown in Figure 12(d) along with the list of key challenges discussed above.

4.3. Strategies towards performance enhancement of solid-state Li-S batteries

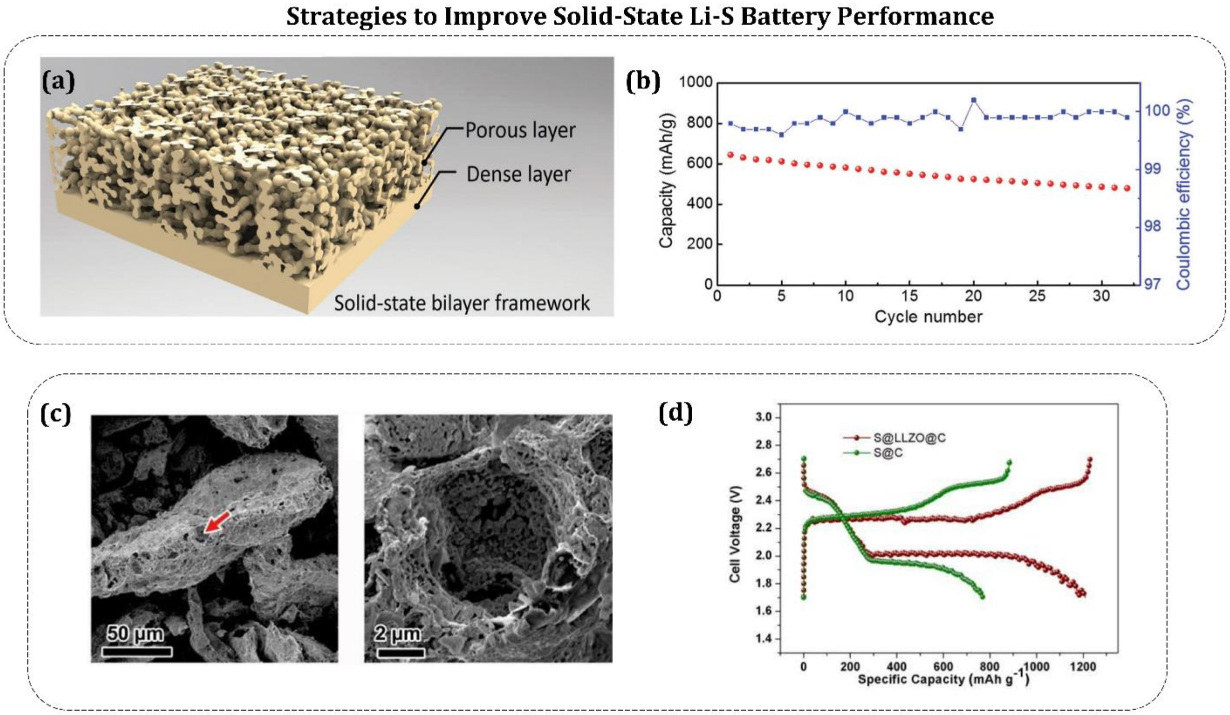


Figure 14. (a) Schematic of a three-dimensional bilayer garnet solid electrolyte framework for high energy density and performance of solid-state Li-S battery. (Reproduced with permission from [217]. Copyright The Royal Society of Chemistry 2017.) (b) Cycling performance of the solid-state Li-S battery employing 3D bilayer solid electrolyte framework[217]. (c) SEM images of LLZO nanoparticles-decorated porous carbon foam (LLZO@C) which acts as host for sulfur and also provide efficient electronic/ionic transport pathways within cathode microstructure[218]. (d) Comparison of the electrochemical performance of the proposed S@LLZO@C cathode with a typical S@C cathode. (Reproduced with permission from [218]. Copyright 2017 American Chemical Society)

To mitigate the deleterious effects derived from the internal stresses, special attention needs to be given on the design and architectural aspects of solid-state cathodes. In this regard, recent studies have shown promise of both high capacity and long cycle life for solid-state lithium-sulfur batteries using various methods as shown in Figure 14(a-d)[217, 218]. Researchers proposed employing a three-dimensional bilayer solid electrolyte framework which consists of a thin dense solid electrolyte layer on the anode side and a thick, porous solid electrolyte layer on the cathode side[217] (Figure 14(a)). Dense layer prevents the growth of lithium dendrites as well as the diffusion of polysulfides towards the anode. On the other hand, a porous solid electrolyte layer acts as the host for the carbon additive and the cathode active material. As shown in Figure 14(b), the proposed battery design showed promising cycling performance and Coulombic efficiency. In another study[218], LLZO nanoparticle-decorated carbon foam was synthesized by the one step facile Pechini sol-gel method. The porous LLZO/C matrix (Figure 14(c)) served as the hosts for the cathode active material as well as improves the electronic/ionic transport pathways. The proposed S/LLZO/C cathode showed enhanced performance when compared with a typical S/C cathode (Figure 14(d)). Other strategies such as *in situ* synthesis of Li_2S-C nanocomposites[219], controlling particle size and cut-off voltages[196], yolk-shell nanoarchitecture with internal void spaces[220], and carbon nanotube-sulfur composite cathode[221] have also been explored to enhance the performance of solid-state Li-S batteries. In addition to the challenges pertaining to the sulfur cathodes, dendrite growth, contact loss and interfacial instability on the anode side also pose safety and performance issues which are similar to those discussed in the previous sections.

5. Summary and perspective

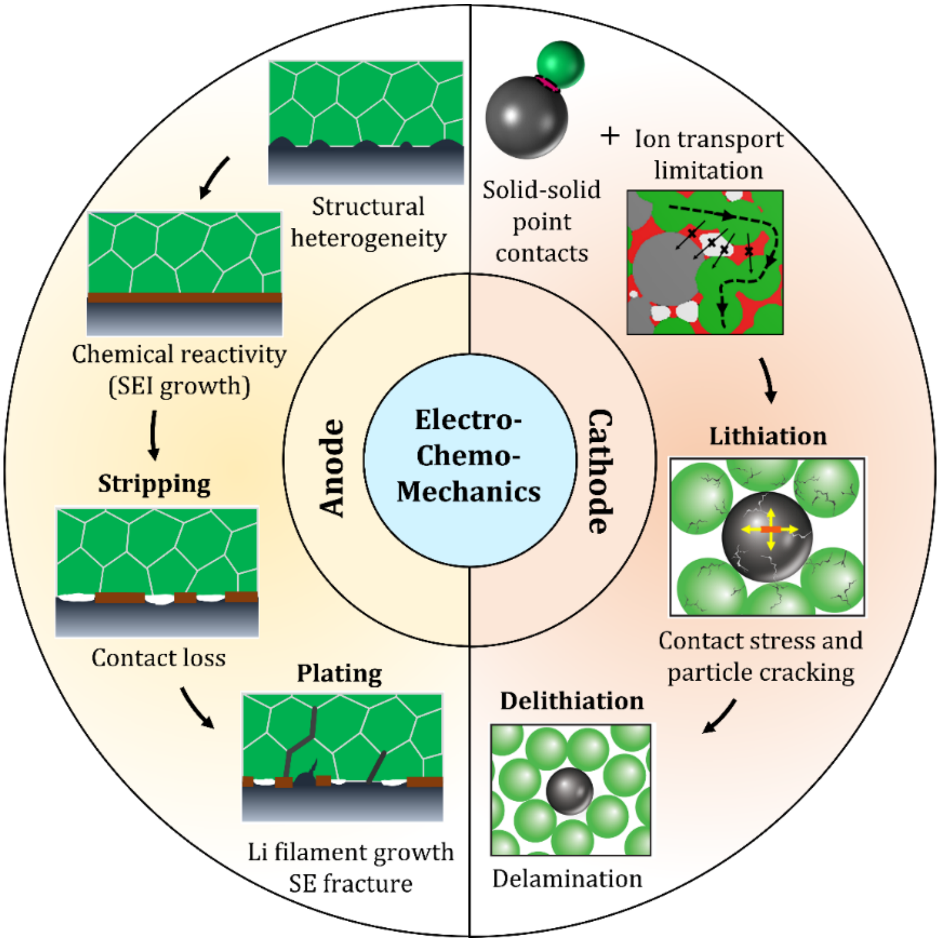


Figure 15. Key mechanisms pertaining to the electro-chemo-mechanical interactions in solid-state batteries. Structural heterogeneities such as presence of grain and grain boundaries and surface defects, chemical reactivity of lithium with solid electrolyte, contact loss during stripping and filament growth during plating are the main challenges with lithium metal anode. Whereas, solid-solid point contact, ion transport limitation, particle cracking, and delamination are the main issues with solid-state cathode.

The pursuit of high energy and power density energy storage systems demands the development of lithium metal batteries. However, realizing the true potential of lithium metal batteries is predicated on addressing several electro-chemo-mechanical challenges which affect their safety and performance. As discussed in this review, for safe and stable operation of lithium metal batteries with liquid electrolyte, solid electrolyte interphase (SEI) stability and suppression of lithium dendrites is paramount. In this regard, mechanical and transport properties of the SEI play a crucial role. solid-state batteries are a promising alternative to enable lithium metal anodes owing to the mechanical rigidity and thermal stability of the solid electrolytes. However, utilization of solid electrolytes comes with several other electro-chemo-mechanical challenges pertaining to both cathode and anode. Lithium filament growth and contact loss during plating and stripping respectively impact the interface stability on the anode side where metal penetration along the grain boundaries and surface defects of the solid electrolyte can result in short circuit and failure of the solid-state batteries. On the other hand, in the solid-state cathode, solid-solid point contacts, chemical instability, interface delamination and particle cracking severely affect the reaction and transport signatures. These key challenges pertaining to the solid-state batteries are summarized in Figure 15. In the following section, the perspective and the future outlook for lithium metal batteries has been discussed with a separate focus on the anode and the cathode.

Anode: Unstable solid electrolyte interphase (SEI) in lithium metal batteries with liquid electrolyte can have severe consequences such as dendrite growth, formation of dead lithium, lower coulombic efficiency, and short circuit. Thus, achieving stable SEI in lithium metal batteries with liquid electrolyte is critical. Several factors such as SEI morphology, chemical composition, mechanical properties, SEI-induced transport and reaction heterogeneities play a very important role in dictating the SEI stability. In this regard, achieving smooth interface, uniform lithium deposition and dissolution has been proposed to be very effective in maintaining stable SEI[69]. However, achieving uniform reactions over a large number of cycles is very challenging, thus demanding serious research efforts towards deeper understanding of the electro-chemo-mechanical interactions in lithium metal batteries with liquid electrolytes.

On the other hand, addressing the issues of contact loss, unstable interface evolution, metal penetration leading to short circuit, and chemical instability is vital for employing lithium metal anodes in solid-state batteries. Heterogeneities such as rough interface morphology (dictated by the surface roughness of solid electrolyte and lithium metal), presence of grain and grain boundaries and surface defects have observed to result in current focusing, localized lithium nucleation (during plating) and preferential contact loss (during stripping). Minimizing these interfacial heterogeneities is crucial towards achieving stable electrochemical reactions at the anode-solid electrolyte interface. Utilization of single crystal SE particles instead of polycrystalline particles has been proposed to minimize the interface heterogeneities and increase resistance against metal penetration[142]. Researchers have also proposed utilization of the amorphous solid electrolyte materials (e.g., amorphous LLZO) to eliminate heterogeneities arising due to the presence of grain and grain boundaries[149, 222]. Enhancing vacancy diffusion in the lithium metal anode for complete replenishment of lithium at the interface is crucial. In this regard, utilization of materials exhibiting faster diffusion pathways for lithium such as carbon nanotubes or efficient mixed ionic-electronic conductor (MIEC) can prevent the contact loss during stripping[165, 223]. Investigating lithium’s mechanical properties, especially plasticity and creep, and its implications on the contact loss and filament growth behavior is necessary. Insufficient plasticity and creep of lithium can result in contact loss and formation of solid-solid point contacts at the anode-solid electrolyte interface. Whereas excessive plasticity and creep can ease the metal penetration through the solid electrolyte microstructure leading to short circuit. As these mechanical (and transport) properties are strongly dependent on the stack pressure[144] and temperature[224], controlling the extrinsic modulators is very crucial for the anode stability. Along similar lines, as internal resistances (particularly within the cathode) can result in significant self-heating of the battery, understanding its implications on the electro-chemo-mechanical interactions and the anode stability is critical[225, 226]. Recently, incorporation of interlayers (carbon interlayers, alloy forming Ag/Au interlayers) have shown promising results on the deposition behavior at lithium metal anode[158, 160, 227]. Enhanced transport characteristics of such interlayers and their ability to reduce the nucleation overpotential can assist in achieving uniform electrodeposition. However, deeper understanding of the underlying mechanisms and the electro-chemo-mechanical interactions is still needed. Recent developments have also highlighted the potential of anode-free solid-state batteries as they can exceptionally increase the energy densities[150]. However, chemo-mechanical challenges such as heterogeneous lithium nucleation and deposition, contact loss, metal penetration still exist. In this regard, deeper mechanistic insights into the role of current collector, solid electrolyte microstructure and interlayers in dictating the electro-deposition and dissolution behavior are required.

Cathode: To address the transport and reaction limitations due to inherent solid-solid point contacts in the solid-state cathodes, enhancement in ionic/electronic percolation pathways in critical[18, 228]. In this regard, optimal proportion of the constituent phases, namely, cathode active material, solid electrolyte, carbon additives and binder is important to ensure sufficient active area, low tortuosity for the ionic and electronic transport. Particle sizes and morphologies of the active material and solid electrolyte also play an important role in dictating the active area and percolation pathways[229]. Approaches such as bimodal and trimodal particle size distribution can be effective in minimizing the void space present in composite cathode, thus ensuring better solid-solid contact and lower tortuosity[230]. Chemical stability of the solid-solid interface is very crucial for minimizing the interfacial resistances, maintaining stable operation and high coulombic efficiency over a large number of cycles. In this regard, developing coating layers for various solid electrolytes and cathode materials is critical towards reducing the interfacial resistances and preventing unwanted chemical reactions. Similarly, discovering new solid electrolyte materials exhibiting high ionic conductivity, good chemical stability with the active material interfaces, favorable mechanical properties for good solid-solid contact is important. Atomistic studies using approaches like DFT, and Ab initio molecular dynamic (AIMD) coupled with machine learning-based prediction of the potential solid electrolyte materials can be very impactful in the development of high energy and power density batteries.

To avoid interface delamination, adhesion between the participating interfaces should be strong so that it can withstand the strain fluctuations occurring during the electrochemical cycling. In this regard, the role of binder is critical in governing the adhesion between constituent phases of the composite cathode, thus choosing a chemically stable and adhesive binder is necessary. Studies have also observed that the carbon-based conductive additives used in cathode composite result in accelerated capacity fade and enhanced generation of SE decomposition products[231]. Thus, appropriate morphologies and surface coatings for conductive additives should be systematically developed to minimize such deleterious reactions. Also, efforts should be directed towards minimizing these electrochemically inactive phases (carbon additives and binder) which can also assist in improving the energy density of solid-state batteries[232].

Recently, significant research efforts are being taken to develop zero-strain cathode materials to minimize internal stresses generated within the composite cathode during electrochemical operation[233]. For instance, researchers proposed NCM271 and NCM361 cathode materials to exhibit almost zero strains[207]. Successful development of such zero-strain cathode materials can alleviate multiple electro-chemo-mechanical issues such as interface delamination, particle cracking, stress-driven overpotential, etc. and contribute to the direct improvement in the stability and the cyclability of solid-state batteries. Another potential strategy to minimize the internal stresses due to solid-solid contacts is to have an appropriate stoichiometric blend of cathode materials exhibiting positive and negative partial molar volumes of lithium (e.g., NMC and LCO, respectively)[61, 185]. In such set up, when one cathode material expands due to lithiation/delithiation, the other shrinks and ensures minimal stress generation in the battery. However, investigating the chemical instabilities of such co-existing cathode materials in solid electrolyte matrix is necessary. To prevent active material particle cracking, single crystal cathode particles should be favored over polycrystalline cathode particles since particle cracking can lead to problems like longer lithium transport pathways and dead active material[234, 235]. Lastly, the cathode materials with well-defined crystal structure show inherent anisotropy. Lithium diffusion and interfacial kinetics of such active materials are highly dependent on their crystallographic orientation since the crystal structures consist of ion-diffusing and ion-blocking facets [236-238]. Appropriate orientation of such active material particles can help in enhancing the lithium transport, thus enabling fast charging and high energy density solid-state batteries.

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Conflict of Interest

There are no conflicts to declare.

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