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# Silver-carbon interlayers in anode-free solid-state lithium metal batteries: Current development, interfacial issues, and instability challenges

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## ABSTRACT

As an interlayer between the anode and the electrolyte of the all-solid-state lithium metal batteries (ASSLMBs), the silver-carbon (Ag-C) nanocomposite has been reported to significantly increase the energy density and cycle rate of solid-state lithium metal batteries. Ag-C interlayers serve as mixed ionic-electronic conductor that conducts both Li<sup>+</sup> ions and electrons and lithium storage capacity. Unfortunately, it was unclear how the Ag-C interlayer regulated lithium plating and stripping. Moreover, the structural and chemical instabilities between the interlayer and the electrolyte, within the interlayer, or beneath the interlayer on lithium substrate are likely to cause cell failure. In this review, we discuss interfacial issues and summarize recent progress in solution strategies for ASSLMBs, with a specific focus on the use of a silver-carbon (Ag-C) nanocomposite interlayer in anode-free setups. Based on the Li transport kinetics among the Ag-C interlayers, the interfacial configurations of Ag-C interlayers are classified as either exterior or internal. The review concludes with a discussion of the perspectives and future prospects, allowing for the improvement of interlayer techniques for solid-state batteries.

## 1. Introduction

Since their commercial introduction in the 1990s, Lithium-Ion Batteries (LIBs) have experienced rapid expansion in portable electronics, electric vehicles, smart grid storage, and other fields [1]. However, as the demand for high energy and power density batteries increases, the limitations of current commercial LIBs, consisting of a graphite anode, liquid electrolyte (LE), and intercalation cathode, become more apparent. The cell level energy density of these batteries is currently around 260 Wh Kg<sup>-1</sup> [2], and is expected to approach its theoretical limit soon [3–5]. In consideration of future needs, U.S. Department of Energy's Battery500 consortium aims to boost the battery's specific energy to 500 Wh Kg<sup>-1</sup> [6]. Lithium metal anode is one promising approach to achieve high energy density due to its low redox potential (-3.04 V) and high theoretical capacity (3862 mAh g<sup>-1</sup> vs. 372 mAh g<sup>-1</sup> for graphite) among all feasible anode materials [7–12]. Furthermore, compared with flammable liquid electrolyte (LE), solid electrolyte (SE)

is a better match for Li metal anode because of 1) potentially wider Electrochemical window enabling the use of high voltage cathode, 2) better resistance to Li filament due to its rigid nature [13,14], and 3) non-flammable nature [15-20]. Therefore, the all-solid-state lithium metal batteries (ASSLMBs), which combines Li metal anode with solid electrolyte is a good alternative to LIBs due to the resulting higher energy density. Furthermore, ASSLMB offers improved safety compared to traditional LIBs due to the use of non-flammable solid electrolyte [21] as opposed to flammable liquid electrolyte [22,23]. This could potentially reduce the requirement for thermal management or safety components in the battery pack, ultimately resulting in an increase in volumetric and gravimetric energy density at the pack level. Despite these potentials, solid-state batteries have several practical challenges such as side reaction between lithium and electrolyte, inhomogeneous lithium deposition, unstable interfacial contact, etc., leading to premature cell failure [24-26]. In recent years, anode-free cell configurations have gained attention for their potential to improve the stability of solid-state

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batteries. Such configurations exclude a lithium metal anode during cell assembly, relying solely on the cathode as the source of lithium [27]. Samsung, for example, recently reported the use of an Ag-C nanocomposite interlayer in a pouch-type anode-free solid-state cell, which achieved a bulk energy density of >900 Wh L<sup>-1</sup> and demonstrated stable cycling for more than 1000 cycles, with an average Coulombic efficiency (CE) of >99.8% [27]. This superior electrochemical CE, and cyclability is believed to be established by Ag-C nanocomposite interlayer. In addition to superior electrochemical performance, anode free configurations are beneficial from the perspective of processing due to the absence of excess lithium [28–30].

The metal-carbon (M - C) nanocomposite interlayer permits uniform ion flux between the anode and electrolyte contact, leading to uniform plating and stripping. The effect of pore size [31], particle surface property, use of different metal nanoparticles [32], and binders [33] on the performance of M - C interlayer has been investigated in prior research. However, a comprehensive understanding on the working mechanism of M - C interlayer remains elusive [34,35]. In addition, there is a lack of in-depth discussion on the anode/electrolyte interface evolutions with the presence of composite interlayer [36–41]. Therefore, it is necessary to bridge the understanding of interfacial effects from lithium anode to anode-free solid-state batteries (AFSSBs) and extend this knowledge to understand in-depth working mechanism of M – C composite interlayer in AFSSBs.

In this review, an emphasis is placed on the anode-electrolyte interface of anode-free solid-state batteries employing sulfides or oxides as solid electrolyte. We first discuss the prevalent interfacial issues in ASSLMB, such as dendrite formation, interfacial morphological instability, high interfacial impedance, *etc.*, and explore the underlying mechanisms of these challenges. Regarding the M - C interlayer in the ASSLMB with anode-free configuration, we classify the complex interface configurations among the interlayer into extrinsic and intrinsic interfaces based on their nature and location. With this unique perspective, we then discuss the role of mixed ion and electron conducting (MIEC) network and porous structure in M - C interlayer in facilitating uniform deposition and stripping. Finally, we offer future perspectives and challenges of the M - C interlayer for the promotion of ASSLMB.

# 2. Interfacial effects

In solid-state cells, the use of solid components in the cathode, electrolyte, and anode layers leads to multiple interfaces due to the stacked configuration. The rigid solid-solid contact at these interfaces, unlike dynamic mechanism in liquid electrolyte, could result in mechanical issues such as poor contact, gaps and even cracks during electrochemical cycling [42-44]. The nature of these interfaces has a significant impact on the final performance of the battery, including the energy density, cyclability, rate capability, CE, etc. Various processes occur at the anode side of a battery during operation, such as interphase formation and growth due to SE decomposition with Li, mechanochemical contact loss due to volume change during cycling, current constriction, resulting deposition hotspots due to poor contact, and lithium diffusion through Coble creep [45]. Understanding these processes in detail is crucial for developing better solution strategies to improve battery performance, as they play a critical role in cell performance. Moreover, these interfacial processes are interdependent in nature, all occurring simultaneously during the electrochemical cycling of the battery. For example, volume change at the anode during lithium plating/stripping can lead to contact instability at the Li/electrolyte interface, such as void formation and even anode delamination at high current densities (>3 mAh cm $^{-2}$ ) [46–48]. The loss of contact raises the barrier for lithium transport, which consequently increases interfacial resistance and results in a rapid decay in capacity and deposition hotspots resulting dendritic formation [49-51]. Furthermore, most inorganic solid electrolytes form an interphase layer upon contact with Li,

which has been confirmed both theoretically and experimentally [52–54]. This interphase layer formation, in addition to contact loss, leads to a parabolic growth of interphase resistance in solid-state batteries [53,54]. The interfacial stability is essential in AFSSBs since there is no extra lithium available to compensate for losses. These losses mainly occur due to the formation of interphase and dead lithium, referring to inaccessible lithium metal that does not contribute to battery capacity. Thus, optimizing interfacial stability is critical in AFSSBs to prevent rapid and irreversible loss of cell capacity caused by these lithium losses [55].

# 2.1. Types of interfaces and their nature

Several interfaces existing in a cell can be categorized into two types i.e., extrinsic, and intrinsic interfaces based on their location, which is schematically shown in Fig. 1. Here, we define extrinsic interface as the boundary between two different layers in a cell such as boundary between lithium anode and electrolyte. In this type of interface, Li<sup>+</sup> flux passes through a 2D surface, which has numerous pathways formed by solid-solid particle contacts of these two layers. Due to the difference in chemical, transport, and mechanical property of the combining layers, complex electro-chemo mechanical effects are observed during plating and stripping at this interface. Having an in-depth understanding of these effects and their dependance on different factors will allow us to modify the interface for uniform plating and stripping processes. Similarly, we define intrinsic interface as the interface that exists within an interlayer. A lot of research has recently been done on anode-free batteries with porous interlayers and MIEC materials. For such type of cells, the intrinsic interface is formed with 3D network of MIEC pathways. This network of electronic and ionic conduction pathways intersects at different nodes, which can potentially serve for reduction. In summary, extrinsic interface exists at a boundary between two different layers whereas intrinsic interface exists within a layer, specifically interlayer.

## 2.1.1. Extrinsic interface

As defined in previous section, the extrinsic interface is a boundary between different layers in a cell. This interface is characterized with interphase layer, which forms mainly at Li/electrolyte interface, and mechanical contact condition. Most solid electrolytes, such as LGPS  $(Li_{10}GeP_2S_{12})$  [56], argyrodite  $Li_6PS_5X$  (X = Br, Cl) [54], glassy  $Li_2S-P_2S_5$ , perovskite-type LLTO [52], etc., are unstable with highly reduced Li metal and results in interphase layer called solid electrolyte interphase (SEI) at Li metal and electrolyte interface. This SEI layer, in most case, has much lower ionic conductivity than bulk electrolyte and therefore acts as a barrier to ion transport limiting the rate capability of a battery. For example, Li<sub>2</sub>S which is primary phase of SEI for LGPS,  $Li_2S-P_2S_5$  and  $Li_6PS_5X$  (X = Cl, Br, I) has ionic conductivity of only 10 nS cm<sup>-1</sup> [53] which is much smaller than bulk electrolyte conductivity. Additionally, the consumption of limited lithium during interphase formation can lead to a reduction in the capacity of anode-free configuration as the lithium is limited and its loss in each cycle may not be compensated [27,57]. Poor interfacial contact is another interfacial issue associated with extrinsic interface which affects lithium deposition and striping behavior. This poor contact can be due to two main reasons including 1) in as-assembled cell due to rough solid electrolyte surfaces or poor fabrication [58,59], and 2) contact loss which occurs during the plating/stripping process causing pore formation at interface. This insufficient contact can result in current constriction and plating hotspots during electrodeposition [60]. The formation of lithium dendrites is largely attributed to poor contact at the interface between lithium and electrolyte, which leads to an uneven distribution of current and subsequent dendrite formation [59,61]. In addition, the work of adhesion (work required to open the interface) among anode-interlayer, and interlayer-electrolyte interfaces play an important role in determining the morphology and location of lithium deposits [45]. Increased fabrication pressure could result in a higher adhesion work between the



**Fig. 1.** Schematic of extrinsic and intrinsic interfaces. Figures on left show Li ion transport pathway through both interfaces. Intrinsic interface has a 3D web-like pathway for Li ion transport whereas Extrinsic interface is more like 2D surface with numerous parallel Li<sup>+</sup> transport pathways. (A colour version of this figure can be viewed online.)

electrolyte and the interlayer; this high adhesion work at the electrolyte-interlayer interface prevents lithium deposition and pushes it towards the anode CC-interlayer interface.

The interfacial issues related to extrinsic interface mainly include unstable interphase layer, poor interfacial contact, dendrite propagation, and contact loss during cycling. These issues are mainly due to mechanical and chemical incompatibility of solid electrolyte and Li metal layers, which can be solved by implementing interlayers and coatings. We will be discussing these solution strategies in our later sections.

#### 2.1.2. Intrinsic interface

The intrinsic interface, as defined earlier, exists inside an interlayer. For instance, carbon (C) and Ag particle contacts in Ag-C interlayer to form a 3D network of ionic and electronic conduction pathways, a.k.a., MIEC network [27]. In addition to MIEC 3D network, the porous structure inside the interlayer is important to be considered while investigating lithium deposition behavior. During dynamic plating/stripping, changes in volume can occur for both C and Ag particles within the interlayer. These changes can affect the contact between particles, leading to induced stress and possible mechanical instability at the intrinsic interface. This phenomenon is similar to what is observed at the extrinsic interface, where volume changes can also result in mechanical instability. For instance, Ag particles undergo large volume change during alloying/de-alloying process, and this induces local stress and degrades the electrode's integrity during repeated charge/discharge process [62,63]. In addition to mechanical integrity, the deposition behavior is also affected by induced stress due to stress-induced overpotential. The induced stress due to volume expansion affects deposition behavior by changing overall nucleation overpotential [64] and this directly affects where and when deposition occurs inside the interlayer. We will discuss these interfacial effects on lithium nucleation and deposition in details in Section 2.3.

For the electrochemical reduction to happen, both the ion and electron should meet at a point. Therefore, the 3D network of MIEC pathways will increase the effective area for lithium reduction. The electronic conductivity of Ag-C MIEC network is much larger than ionic conductivity, reduction mostly occurs at extrinsic (interlayer/electro-lyte) interface. However, the lithium deposition was observed at anode/ interlayer interface. This implies that lithium diffuses through the porous interlayer. In another research, the lithium deposition in a porous interlayer was observed to be improved with smaller average pore size [45]. This implies that the Li movement through the interlayer is achieved through diffusional Coble creep [45,65]. This illustrates the

dependence of Li plating/stripping behavior on both the extrinsic and intrinsic interfaces.

## 2.2. Factors affecting the nature of interface

To optimize battery performance, it is important to understand the factors that govern the type of interface and the associated interfacial processes. In this section, we will explore some of the key factors that influence the nature of the interface. By examining how these factors affect the resulting interface, we can effectively control interfacial effects. Some critical factors that determine the nature of the interface include the type of solid electrolyte, the architecture of the battery, and the type of CC.

#### 2.2.1. Architecture of anode-free solid-state cell

Depending on the architecture of anode-free solid-state cell, the nature and complexity of interfaces varies, which consequently affects the Li deposition behavior. For instance, conventional Li anode solid-state batteries have only extrinsic interface, and the Li deposition occurs directly at Li-electrolyte extrinsic interface. This type of direct deposition inherently results in numerous interfacial problems in ASSLMB. As shown in Fig. 2a, the anode free solid-state cell setup with Ag-C nanocomposite interlayer [27] has a combination of extrinsic and intrinsic interfaces (Fig. 1). This results in separating the location of Li reduction and deposition which improves the deposition and stripping processes achieving high cyclability (Fig. 2b). Similarly, the deposition behavior in anode free cells with the similar type of interlayer utilizing carbon nanoparticles [32], carbon tubules [65], 3D anode host with Nickel (Ni) nanoparticles [31], etc., has also been studied in detail. In another type of setup, anode-free configuration with 3D ion conductive framework (Fig. 2c) was found to have better Li deposition behavior and full cell stability due to increased Li-ion reduction area [66]. Furthermore, the deposition behavior was observed to be improved by modifying intrinsic interface by coating amorphous carbon [67], and carbon nanotubes [68]. Sakamoto et al. studied an anode-free solid-state cell configuration (Fig. 2d) with bare CC setup [57], where Li deposits directly on CC-electrolyte extrinsic interface. This type of direct deposition resulted in non-uniform plating/stripping behavior, which is similar to cells with lithium metal anode, and results in premature cell failure due to Li dendrite penetration. Recently, McDowell et al. demonstrated that these type of Li-free cells (with bare CC at anode side) are more prone to Li filament growth and short circuiting as compared to Li-excess cells [69, 70]. In another study, Li<sub>2</sub>Te-Cu | LPSCl | NMC anode free cell with modified Cu CC was studied. The extrinsic interface in this cell setup was



**Fig. 2.** (a) Schematic of an AFSSB with  $\text{LiNi}_{0.90}\text{Co}_{0.05}\text{Mn}_{0.05}\text{O}_2$  (NMC) cathode (areal capacity >6.8 mAh cm<sup>-2</sup>), Li<sub>6</sub>PS<sub>5</sub>Cl (LPSCl) solid electrolyte (SE) and an Ag–C nanocomposite layer at initial discharged state and charged state. (b) Cycling performance and CE of the Ag–C|SSE|NMC prototype pouch cell (0.6 Ah) are plotted against the cycle numbers. A constant current mode with the charge/discharge rate of 0.5 C/0.5 C was applied (voltage window, 2.5–4.25 V versus Li/Li<sup>+</sup> at 60 °C). The areal capacity loading of the (NMC) cathode was 6.8 mAh cm<sup>-2</sup> (1 C) [27]. (c) Schematic for the process of Li plating and stripping in the 3D Li-ion-conductive host, where the upper layer is filled with the Li source and the lower layer is empty with Cu deposited on the bottom [66]. (d) Schematic of a discharged "Li-free" configuration. Here, the current collector (CC) material is assumed to be Cu [57]. (A colour version of this figure can be viewed online.)

modified to make it more lithophilic, which reduced overpotential during electro dissolution/deposition and improved CE [71]. All of above examples demonstrates that nature and complexity of interfaces in solid-state batteries vary depending on its architecture, which in turn affects the plating and stripping mechanism. Consequently, the solutions for different battery architectures also differ. For instance, in bare CC architecture, solutions focus on modifying the CC surface to increase its lithophilicity. Whereas in porous interlayer architecture, solutions aim to improve Li diffusion through the porous structure by optimizing pore size and modifying the intrinsic interface with metal nanoparticles.

## 2.2.2. Type of electrolyte

As discussed in previous sections, the extrinsic interface at anode side is almost always characterized by an interphase layer except the case of LLZO. Whether it's an anode-free or Li metal anode configuration, there will be either Li anode or deposited Li in contact with electrolyte. Even in the anode-free solid-state cell with interlayer, interphase layer forms at the electrolyte-interlayer interface. Commonly used solid electrolyte are thermodynamically unstable with highly reductive Li metal and forms an interphase layer [72,73] and this has been both theoretically predicted and experimentally confirmed [52-54]. In this review, we are only discussing about inorganic solid electrolytes, which can be broadly categorized into oxides and sulfides [74]. The reactivity of electrolyte with lithium can be predicted with Electrochemical Stability Window (ESW), which is defined as stability of a electrolyte material against reactions that contain transfer of atoms of the mobile species, e.g., Li-atoms [75]. ESW's of some of the solid electrolytes are illustrated in Fig. 3a. If the chemical potential of an electrode (*i.e.*  $\mu_{Li}$ ) is beyond the ESW of electrolyte, an interphase layer will form at the interface as illustrated in Fig. 3b. For example, the ESW of LPSCl is 1.7-2.3V which means that reduction will occur at voltages below 1.7 V vs. Li/Li<sup>+</sup> where oxidation will start at 2.3V. This stability window of electrolyte can be calculated either theoretically using Density Functional Theory (DFT) calculations [76] or experimentally with cyclic voltammetry (CV)



**Fig. 3.** Stability of anode-electrolyte interfaces. (a) Electrochemical windows of different SEs (green bars) and binary lithium compounds (orange bars) and the interfacial stability range of lithium chemical potential (dashed bars). (b) The mechanism of interfacial stability by reducing the chemical potential of lithium atom in the SEI [72]. (c) Types of interfaces between Li metal and SSE. Type 1: Non-reactive and thermodynamically stable interface; Type 2: Reactive and mixed conducting interphase; Type 3: Reactive and metastable SEI. (d-f) *In-situ* XPS analysis of the LGPS/Li interface: (d) Schematic illustration of the *in-situ* XPS experiment. (e) Impedance of the Li/LGPS/Li symmetric cell, which shows impedance increasing with time. (f) XPS spectra (S 2p, Ge 3d, and P 2p/Ge 3p) recorded during deposition of 31 nm lithium metal on the LGPS. With the increase of the decomposition time, the LGPS decomposed into Li<sub>2</sub>S, Li<sub>3</sub>P, and Ge or Li<sub>15</sub>Ge<sub>4</sub> [52]. (A colour version of this figure can be viewed online.)

measurements [15]. Based on the type of interphase formed, Wenzel et al. studied interphase formation with *in-situ* photoelectron spectroscopy (Fig. 3d–f) and classified the Li-electrolyte interfaces into three types as shown in Fig. 3c [52], including Type I: A thermodynamically stable interface where no SEI forms, Type II: A reactive and unstable interface where the SEI layer continuously grows with formation of mixed conducting interphase (MCI) [53,77], and Type III: A reactive but kinetically stable interface with mainly ion conducting interphases. Therefore, the type of SEI layer formed at this extrinsic Li-electrolyte interface depends primarily on the type of solid electrolytes.

A study by Wu et al. observed the role of a stable interphase layer at Li-Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO) and Li-Li<sub>1+x</sub>Ti<sub>2-x</sub>Al<sub>x</sub>(PO<sub>4</sub>)<sub>3</sub> (LATP) interfaces on controlling lithium dendrite growth and found that the formation of an electronically insulating and ionically conducting interphase layer helps in reducing lithium dendrite growth at the interface [78]. The garnet type cubic (LLZO) upon contact with lithium forms a thin layer (6 nm) of tetragonal LLZO [79], which avoids further reduction of cubic LLZO and creates a stable interphase layer (Type III). Similarly, several in-situ X-ray photoelectron spectroscopy (XPS) measurements [53,80,81] have confirmed the thermodynamic instability of sulfide SEs such as  $Li_7P_3S_{11}$ , Li<sub>3</sub>PS<sub>4</sub>, Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> with lithium and predicted their primary interphase products to be Li<sub>2</sub>S and Li<sub>3</sub>P, which formed a stable and passivating SEI layer with Li, as shown in Fig. 3b. The argyrodite type Lithium argyrodites were also reported to be reduced to stable SEI layer consisting of Li<sub>3</sub>P, Li<sub>2</sub>S and LiX. This stabilized SEI layer (Type III) with argyrodite LPSCl resulted in improved CE [82]. Whereas with LGPS, due to formation of electronically conducting interphases, SEI layer is observed to grow continuously resulting in unstable Type II interface [83]. While thermodynamics determines whether SEI layer forms or not, the further reduction of interface depends on the kinetic factor which is primarily the conductive properties of SEI [72,84,85]. The formation, growth and composition of interphase layers depend on both thermodynamic factors (electrolyte's ESW) and kinetic factors (conductivity of SEI layer), and both should be considered together as simulations show that under kinetic control, thermodynamically unfavorable compounds may form. The kinetically stable interphase layer that forms at interfaces enables a cell to operate wider voltage range as illustrated in Fig. 3c. Therefore, the electrochemical stability of interface depends primarily on the type of electrolyte and determines the type of interphase formed and hence interfacial stability. In addition to electrochemical stability of SE, the SE surface property and microstructure also affects the interface nature.

Porz et al. investigated the effect of SE surface's defect size and density on lithium dendrite growth and crack propagation. By developing a model, they examined the relationship between lithium deposition overpotential and stress-crack propagation with defect size on different inorganic electrolytes and found that the minimum overpotential and crack-extension stress decreases with defect size with inverse square root dependence. This was consistent with their experimental results that correlates surface roughness of solid electrolyte with resulting Critical Current Density (CCD) [86]. When the applied/localized current density exceeds the critical CCD, which represents the specific current density at which lithium dendrites initiate formation during battery operation. To avoid failure, batteries should operate below the CCD, albeit at the expense of limiting their performance. In addition to surface defects, the microstructure or grain size of electrolyte also affects the deposition behavior. In LLZO, it was observed that lithium tends to move along the boundaries between grains [87]. This is likely because the grain boundaries in LLZO have higher ionic conductivity than the bulk material, which causes current to focus on these locations. Similarly, the softer grain boundary regions are found to reduce the evolving stress at the interface and locally decreases kinetic charge transfer overpotentials during plating [88]. In a study, Cheng et al. found that the SSE with smaller grain size resulted in lower interfacial resistance and helped achieve better cycling performance [89]. Moreover, several other experimental observations have confirmed the increased CCD with a smaller average grain size [90–92].

Chen et al., based on their observation, suggested that eliminating grain boundary from polycrystalline LLZO could increase CCD [87,93]. The impact of grain size, however, is not entirely understood because, in another study, it was shown that larger grain size in LLZO led to an increase in the CCD [94].

Unlike oxide, which exhibit well-defined grain boundaries due to their crystalline nature, sulfide solid electrolytes (SEs) are glassyceramic nature and have less well-defined grain boundaries. As a result, the effect of grain boundaries on CCD is less pronounced in sulfides compared to oxides. Wang et al. investigated cycling and rate performance of crystalline vs. glassy lithium thiophosphate (LPS) electrolyte using several compositions. They observed that in all compositions, CE, cycling performance, rate performance was better for glassy LPS [95]. This result indicates that absence of well-defined grain boundaries in glassy SE enabled electrolytes to resist lithium dendrite penetration better. Sulfide-based SEs commonly used in solid-state batteries (SSBs) are glassy-ceramic nature so still have some grain boundaries but not as much as in polycrystalline or ceramic oxides [96]. However, lithium penetration through sulfides is still observed. In a study, lithium growth was observed along grain boundaries of  $\text{Li}_2\text{S-P}_2\text{S}_5$ electrolyte layer, leading to crack formation and short circuiting of cells [97]. Similarly, grain size of sulfide SE also affect the resulting CCD of cell. Singh et al. conducted a study where the particle size of cold-pressed Li<sub>6</sub>PS<sub>5</sub>Cl pellets was varied, resulting in small-grain and large-grain samples. The larger grain sample exhibited a lower CCD compared to the small-grain sample. This was attributed to the higher surface roughness in the large-grain sample, promoting current focusing on the interface and thereby increasing the likelihood of lithium filament growth. Conversely, the small-grain samples exhibited an increased critical current density (CCD) due to a stress-shielding effect. This effect was attributed to the higher density of grain boundary triple junctions in the small-grain samples, which enhanced the material's fracture toughness (K<sub>IC</sub>) and resulted in improved resistance to lithium penetration [98]. Moreover, a study found that sulfides have lower grain boundary resistance compared to oxides [99]. This suggests that the impact of grain boundaries on current focusing on the interface is reduced in sulfides, resulting in a lower likelihood of lithium filament formation compared to oxides. In addition to the microstructure, mechanical properties such as Young's modulus (rigidity) of SE is also determining factor as it affects the mechanical stability and contact condition of interface. The mechanical stability of interface is important to be considered as mechanical failure such as fractures could result in contact loss and block Li<sup>+</sup> ion transport [50].

Although the rigid nature of electrolyte is beneficial for suppressing dendrites, very high rigidity constrains volumetric/morphological changes occurring at interface, and results in induced stress during cycling. This induced stress might give rise to cracks, and even delamination and thereby reduces the contact area at interfaces [46,100]. This greatly affects the charge transfer kinetics at interface. The charge transfer resistance can increase by at least an order of magnitude due to the inhomogeneous contact at the Li-electrolyte interface [101–104]. For instance, oxide SEs' rigidity and brittleness lead to poor physical contact at the interface, which increases interfacial charge transfer resistance and results in a substantially lower CCD (0.5 mA cm<sup>-2</sup>) for dendritic growth [105-109]. In addition to that, oxides such as perovskite-type LLTO require high temperature sintering during their synthesis to reduce grain boundary resistance [110]. On the other hand, sulfides which are relatively softer than oxides are mechanically robust, and form better interfacial contact even without high temperature sintering during fabrication. However, achieving low porosity in LPSCL sulfide SE and thereby increasing resistance to lithium filament propagation through the SE requires a sufficiently high fabrication pressure [111]. In an electro-chemo-mechanical model, it was suggested that SE with Young's modulus > 15 GPa are more likely to get microcracking. This model further supports that the problem of cracking is more severe in oxide electrolytes which has high Young's modulus (LATP, LLTO,

LLZO has 115, 193, and 150 GPa, respectively) [112]. A common solution approach for this poor contact resulting from rigid SE is to improve the electrolyte's surface wettability to lithium metal by applying a thin, lithophilic coating. This will be discussed in detail in Section 3.2.

# 2.3. Interfacial effect on plating and stripping behavior

In the anode-free battery configurations, the performance of battery is mainly determined by the efficiency of plating/stripping process. An ideal and uniform plating/stripping process reduces the amount of dead lithium, which improves CE, also problems such as contact loss and dendrite formation are minimized and ultimately this will result in stable cycling of battery. Therefore, understanding the relationship between interface nature and corresponding plating and stripping behavior can guide us to better solution strategies.

#### 2.3.1. Plating and stripping behavior in solid-state batteries

The absence of excess lithium in AFSSBs demands high reversibility during cyclic plating and stripping processes for high-capacity retention [113,114]. However due to poor contact and non-uniform interphase layer thickness, the lithium plating occurs at limited area and increases localized current density, generating hotspots for dendrite growth. This results in rapid decay of capacity in anode free setup and even premature failure of the cell. Recently, Lewis et al. discovered a unique degradation mechanism in sulfide-based anode free cells using cryo-focused ion beam (FIB) and ex-situ synchrotron tomography. They observed that non-uniform lithium plating and stripping caused local depletion of lithium in some areas at the end of stripping process, reducing the electrochemically active area. This led to an increase in local current density and the formation of voids during stripping, as well as filament growth during subsequent plating. As a result, anode free cells experience more dendrite growth than cells with a lithium metal anode [70]. This study highlights the importance of plating/stripping process in the final performance of anode free cell. For a highly reversible plating and

stripping, a uniform ion flux is required at the interface, which requires an intimate interfacial contact and a stable interphase layer at anode side interface.

Kasemchainan et al. have proposed three diffusion mechanisms that regulate lithium plating and stripping in SSBs, including 1) lithium ion migration (J<sub>Li+ migration</sub>) from anode to SE which depends on the local current density, 2) lithium atom self-diffusion (JLi diffusion) in bulk Li, which is constant at constant temperature and pressure, and 3) lithium metal creep (J<sub>Li creep</sub>), which depends on applied stack pressure [61]. The balance among this diffusion mechanism is required to maintain stable morphology at Li-electrolyte interface during plating/stripping. The lithium atom self-diffusion ( $J_{Li\ diffusion}$ ) in bulk lithium metal is through the vacancy and adatom diffusion (Fig. 4a). The vacancies, which are created at the interface due to dissolution, must move away from interface to maintain good contact at Li-electrolyte interface. These vacancies may be annihilated at dislocations, grain boundaries or diffuse further into the metal bulk [40]. The morphological stability is attained only if vacancy diffusion is in local equilibrium with the injection rate of vacancies, which is the rate of lithium dissolution. In the conditions of  $J_{Li+\ migration} > J_{Li\ diffusion} + J_{Li\ creep}$  , voids forms resulting in progressive loss of contact during stripping as illustrated in Fig. 4b [58,115–117]. During the subsequent plating, limited contact can result in high current density and the formation of deposition hotspots. This, in turn, may lead to the development of lithium dendrites (Fig. 4c). [118]. Schmalzried and Janek [119] developed a kinetic model to estimate critical anodic current density, below which the morphological stability at Li-electrolyte interface could be attained [119]. Based on this model, a critical current density of 10–100  $\mu$ A cm<sup>-2</sup> for lithium metal electro dissolution was estimated [58]. This rough estimate is way smaller than practically required current densities which is in the range of few mA cm<sup>-2</sup>. This indicates that the morphological instability at Li-electrolyte interface is mainly due to the limited diffusion of lithium atoms in the bulk metal. Moreover, Wang et al., by using in-situ NDP observed lithium plating/stripping process at the Li-garnet and Li-carbon nanotube (CNT) interface as illustrated in Fig. 4d and e. This research demonstrates the



**Fig. 4.** Schematic illustration of lithium stripping and plating at two different levels of current density. (a) Schematic of the different mechanisms that facilitate charge transfer at the lithium metal anode under anodic load: i) if the local current density does not exceed the vacancy diffusion limit in the metal, the interface remains structurally stable. ii) and iii) If the externally applied local current density exceeds the diffusion limit, vacancies supersaturate and accumulate to form pores near the interface, which will grow and lead to increasing contact loss. Herein, adatom diffusion of the metal pore surface may cause a second, higher diffusion limit. iv) If external pressure is applied, pores will be annihilated because of plastic deformation of the lithium metal and contact loss is restricted [58]. (b and c) Schematic of lithium/LPSCl interface cycled at an overall current density above the critical current for stripping. Sequence from pristine interface to void formation upon stripping to lateral growth of thin lithium film across electrolyte surface to formation of occluded voids [61]. (d) *In-situ* NDP characterization setup, and (e) result for interfacial diagnosis [120]. (A colour version of this figure can be viewed online.)

diagnostic potential of *in-situ* non-destructive testing in predicting short circuits [120]. This *in-situ* technique helped better understand the dynamic plating/stripping process at the electrolyte-Li metal interface. In later sections, we will discuss how the diffusion of lithium and lithium creep can be improved with the use of porous interlayer to achieve a stable anode side interface.

## 2.3.2. Interfacial effect on lithium transport

The lithium transport through an interface in solid state battery is affected by mainly two factors: the nature of interphase layer and the contact condition. The formation of an interphase layer, which generally has lower ionic conductivity than solid electrolyte, blocks/hinders both the Li-ion transport and charge transfer across the interface [121,122]. As a result, the interface acts as the major bottleneck for Li<sup>+</sup> transport in solid-state batteries [123,124]. In several studies, addition of electronically insulating, ionically conducting artificial layer at interface has been observed to improve lithium transport across the interface thereby reducing interfacial resistance and enhancing high-rate capabilities [125,126]. In addition, ionic transport at the interface with solid electrolyte possesses more challenges due to rigid and solid-solid nature of contact as compared to liquid electrolyte system. Yu et al. observed reduction in Li-ion transport across Li<sub>6</sub>PS<sub>5</sub>Br-Li<sub>2</sub>S interface after cycling. This was reported due to both contact loss and increase in activation energy that attributed to ion-resistive interphase formation at the interface [123].

Several experiments have observed a rapid increase in interfacial resistance during the stripping process. In addition, as symmetric cells are cycled progressively, an increase in overpotential is also observed. This phenomenon could be attributed to gradual loss of contact leading to increased local current density, as illustrated in Fig. 4b [61,127], and continuous decomposition of the electrolytes resulting in thicker SEI layer. Such a continuous decomposition upon contact with lithium is observed in most sulfide electrolytes [72,83,128]. Poor contact is common in brittle and rigid oxide electrolytes than sulfides [108]. During cycling, the effective contact area between the electrode and the

electrolyte may be reduced due to the formation of passivating layers or due to the dissolution of the electrode material. This reduction in interfacial contact creates current constriction, where the current focuses and pass-through discrete contact points as illustrated in Fig. 5a [129]. As a result of current constriction, the ion flux is channeled, leading to an increase in local current density in certain regions of the electrode. This increased current density can lead to a higher overpotential for charge transfer. In addition to poor contact and interphase layer, the presence of grain boundaries, contamination layers and surface defects of Solid electrolyte near the interface also affects ion transport (Fig. 5b). Even for ideally contacted interface, the deviating ion conductivity and mechanically softer nature of grain boundary regions could cause current focusing [88,89]. This is consistent with the observed preferential growth of lithium through grain boundaries [87]. Therefore, the nature of the interface plays a significant role in Li-ion transport. In addition to lithium transport, lithium nucleation is also necessary for lithium plating to occur, and we will discuss this in detail in the next section.

## 2.3.3. Interfacial effect on nucleation

During plating process, the nucleation occurs when chemical potential of lithium ( $\mu_{Li}$ ), which is given by Equation (1), exceeds standard chemical potential of lithium metal ( $\mu_{Li}^{0}$ ). This overshoot in chemical potential ( $\mu_{Li}$ - $\mu_{Li}^{0}$ ), which acts as the driving force for lithium nucleation, should overcome nucleation overpotential for heterogeneous nucleation to occur at interface such as CC-electrolyte interface or inside the interlayer in anode free configurations. Moreover, the chemical potential of lithium in anode or Li<sup>+</sup> in solid electrolyte could also be modified by normal stress and strain energy [130,131]. The mechanical forces such as induced stresses were found to affect the lithium nucleation process in heterogeneous plating at solid-solid interface [132].

$$\mu_{\mathrm{Li}} = \mu_{\mathrm{Li}+} + \mu_{\mathrm{el}} \tag{1}$$

The nucleation kinetics dependence on surface characteristics of SE has been studied in detail [133]. Surface characteristics such as defects,



**Fig. 5.** Origin of non-uniform ion flux and induced uneven deposition (a) Schematic representation of the Li|LLZO interface showing a few contact points as origin of constriction and the resultant bending of the current lines at the interface, which is the basis of the applied theory. At higher external forces, the contact spots increase their area because of the plastic deformation of the softer material (*i.e.*, lithium). The arrows schematically indicate current lines. Equipotential lines are shown as red dotted lines [58]. (b) Schematic illustration of the origin of inhomogeneous current distribution at the solid electrolyte/anode interface [40]. (c-e) lithium nucleation and plating dynamics in dependence of the overpotential (calculations based on a liquid electrolyte system): (c) influence of the overpotential on the nucleation energy barrier, (d, e) number and size of lithium nuclei dependence of the overpotential [137]. (f) Uneven electrolyte surface induces local concentration of Li<sup>+</sup> flux and thus filamentary lithium growth. Schematic description of lithium redistribution through the gold layer and lithium nucleation [134]. (A colour version of this figure can be viewed online.)

protrusions, non-uniform interphase layer thickness, and impurities at the interface can cause inhomogeneous current distribution, which acts as a hotspot for lithium dendrite nucleation during plating [129]. Krauskopf et al. also found that lithium plating behavior at CC-electrolyte interface is mainly affected by the microstructure of the SE surface. They performed electrodeposition experiment on CC-LLZO interface that have limited chemical inhomogeneities, and observed the preference of lithium nucleation on fractures or structural defects [133]. Similar observation was seen at Li-LLZO interface, the defects on the LLZO acted as deposition hotspots resulting in filamentary lithium growth. In the same study, the authors probed lithium deposition on different substrates with the use of Atomic Force Microscope (AFM) and found that deposition morphology was significantly affected by the geometry of electrolyte's surface [134]. Furthermore, the nucleation overpotential also affects the density and uniformity of lithium deposition [135,136]. Pei et al. studied the effect of nucleation overpotential on lithium nucleation and growth at the nanoscale level and found that the nucleation energy barrier increases with overpotential, which in turn reduces the size and increases the density of lithium nuclei as illustrated in Fig. 5 c-e. Moreover, the nucleation barrier and overpotential is found to increase with galvanostatic current density [137]. These findings indicate that lithium nucleation and growth can be tailored by adjusting the overpotential through optimizing the charge/discharge condition or the micro-/nanostructures at anode. Moreover, deposition substrate with metals such as Au, Ag, and Zn that have higher solubility of Li, have been found to have lower nucleation overpotential for lithium deposition [134,138]. Kim et al. coated LLZO electrolyte surface with an Au layer to form an interlayer matrix which facilitated more uniform lithium precipitation compared to an uncoated interface. Previously, they observed that, without the Au layer, surface defects on the LLZO electrolyte resulted in localized areas of high electric fields, causing a concentrated Li<sup>+</sup> flux. These areas act as persistent "hotspots" where lithium deposition occurs, leading to the growth of filamentary lithium structures (Fig. 5f) [134]. Moreover, Ag coating layer has been found to facilitate more homogeneous lithium plating compared to Au layer due to higher diffusion coefficient of Li-Ag alloys [139]. Also, Liu et al. demonstrated the benefits of using lithophilic Mg metal nanoparticles as seeds for controlled nucleation resulting for uniform and dendrite free lithium deposition in liquid electrolyte [140]. Later, in anode free setup with M - C nanocomposite interlayer, the effect of using different metal nanoparticles was investigated [32]. They found that, with Ag nanoparticles in M - C interlayer, the cycle performance and capacity retention was excellent. This was ascribed partially to lower nucleation overpotential offered by Ag particles resulting in uniform deposition of lithium on the CC [27]. Therefore, inclusion of metal layer or particles at interface can influence nucleation kinetics and can be utilized to achieve more uniform and controlled layer-by-layer lithium deposition. All these studies indicate that lithium nucleation is highly affected by the surface property of SE and deposition substrate and this effect can to be tailored for a controlled and uniform lithium deposition.

### 3. Solutions for interfacial issues

As discussed in the previous sections, anode-side interfacial issues mainly result from mechanical and chemical incompatibilities, renders in poor cell performance such as low cyclability, low CE, high interfacial impedance, *etc.* Therefore, to improve the cell performance, the primary work should be focused on addressing these interfacial incompatibilities. In this section, we will discuss solution strategies including electrolyte modification, interlayers, and coatings to effectively stabilize the anode-side interface and improve cell performance. In general, these strategies aim to reduce interfacial impedance, improve mechanical contact, and promote uniform ion flux through the interface. The solution strategies will be classified based on their working mechanism and each strategy will be discussed in detail to provide a better understanding of their functioning. This knowledge can guide future efforts to develop more effective solution strategies.

# 3.1. Selection and modification of electrolyte

The type of solid electrolyte is a determining factor that dictates the nature of interface, specifically extrinsic interface between Lielectrolyte, and thereby affects the lithium plating and stripping behaviors. Here we will be outlining some criteria for the selection of appropriate electrolyte and some modification strategies for electrolyte's bulk and surface chemistry to change interface nature and improving cycling performance of a cell.

The selection of electrolyte is a crucial step which directly affects the final performance of a cell. Based on the general understanding, there are four main criteria for solid electrolyte selection for stable interface: 1) High ionic conductivity( $>0.1 \text{ mS cm}^{-1}$ ) at room temperature [141], 2) Stable interphase formation with lithium metal, 3) Sufficient strength and minimum defects to inhibit dendrite formation, and 4) Affordable raw materials and good processability for large scale production [142]. In general, sulfides SEs such as thio-LISICON (LGPS) [21],  $Li_6PS_5X$  (X = Cl, Br, I) [143-147], and glassy Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> [148] have higher room temperature ionic conductivity (typically  $>10^{-3}$  S cm<sup>-1</sup>), better mechanical flexibility but low electrochemical stability as compared to oxides. Metals containing sulfides such as LGPS, react with lithium and form SEI layer with intermetallic phases, which are electronically conductive, resulting in a continuously growing interphase layer [83]. To solve this issue, Kanno et al. developed Ge free LGPS and observed stable interphase layer with improved CE in first cycle [21]. Argyrodite type LPSCl/Br, in addition to high ionic conductivity, forms stable and passivating interface with lithium [149] which makes them a suitable choice for SSBs. This kinetically stable interface with lithium is due to the formation of halide-based decomposition product such as LiCl [54, 150,151]. Similarly, most oxide electrolytes which include garnets (e.g., LLZO), perovskites (e.g., LLTO), NASICON (e.g., LATP), and LiPON are thermodynamically unstable with lithium and form interphase layer. Among these, LLZO has the lowest reduction potential of 0.05V against Li/Li<sup>+</sup> and forms highly stable interphase layer with lithium [15,152]. This superior stability with lithium makes garnet type LLZO a suitable option for AFSSBs setup and therefore several types of anode-free setup have been tested with LLZO [57], Li7La2.75Ca0.25Zr1.75Nb0.25O12 (LLCZN) [66], etc. On the other hand, NASICON type LATP and perovskites type LLTO, which both contain unstable Ti<sup>4+</sup> ion forms mixed conducting phases upon reacting with lithium and results in unstable (Type II) interphase layer [52,77,153]. The underlying reason for better stability of LLZO is the high activation barrier required to break strong M - O bond resulting in kinetic stability with lithium. As a result, for sulfides such as LGPS, the oxygen substitution resulted in Li<sub>10</sub>GeP<sub>2</sub>S<sub>11.7</sub>O<sub>0.3</sub>, which was observed to have improved stability with lithium metal and higher ionic conductivity. Similarly, doping metal-sulfide (MoS<sub>2</sub>) in Li<sub>2</sub>S-P<sub>2</sub>S<sub>5</sub> glassy sulfide resulted in Li<sub>7</sub>P<sub>2 9-</sub>  $S_{10,85}Mo_{0,01}$ , which was observed to have lower interfacial resistance with lithium as compared to Li<sub>7</sub>P<sub>3</sub>S<sub>11</sub> [154]. Additionally, doping ZnO in Li<sub>3</sub>PS<sub>4</sub> resulted in the synthesis of Li<sub>3.06</sub>P<sub>0.98</sub>Zn<sub>0.02</sub>S<sub>3.98</sub>O<sub>0.02</sub>, which was observed to have better stability with lithium resulting in a capacity retention of 81% after 100 cycles compared to 31% for bare LPS [155]. Davis et al. used multi-modal operando analysis to compare SEI formation and lithium plating in different sulfide SSEs in an anode-free configuration [82]. They found that the LPSCl interface stabilized after SEI formation, allowing for lithium metal deposition, while the LGPS interface did not stabilize, and the SEI continued to grow. The authors concluded that the transition from SEI formation to lithium plating is a critical factor in determining CE in anode-free SSBs. This study demonstrates the importance of stability of solid electrolyte on the final performance of anode-free cell.

In terms of processibility, sulfides, in general, are better than oxides. Sulfides can be prepared by simply slurry casting whereas oxides must be sintered, which complicates large scale continuous production [142]. Moreover, the ability of SEs to be formed into thin layer is also an important selection criterion as a thin SE layer helps improve energy density of a cell. Researchers has achieved 30um of layer thickness for LPSCl by slurry casting [27], 25  $\mu$ m of LLTO by tape casting and subsequent sintering [156]. Also, oxides have better electrochemical stability with Li, higher fracture toughness and Young's modulus than sulfides. However, lithium dendrites can still grow through oxide SEs at current density lower than 1 mAh cm<sup>-2</sup>, which is due to lithium deposition concentrating at surface defects where dendrite starts to form.

Besides selection of electrolyte, surface modification of electrolyte is also an effective strategy to stabilize the interface. For instance, LLZO upon exposure to ambient air develops a surface layer of Li<sub>2</sub>CO<sub>3</sub> and LiOH, This layer alters the wettability of LLZO and leads to insufficient contact and high resistance when combined with lithium [93,157–159]. Several approaches can address this issue. One method involves enhancing the air stability of LLZO through elemental doping [160]. Another approach is to eliminate the impurity layer itself by subjecting LLZO to furnace heating at approximately 700 °C with carbon [161]. Alternatively, the layer can be removed by polishing it off [158,162] before incorporating into the cell. Moreover, Goodenough's group claimed that this impurity layer can also be from at internal grain boundaries and can be prevented by incorporating LiF during the synthesis step of electrolyte [163]. In another study, Wu et al. modified LLZO surface by filling the microstructure with Si nanoparticles through polishing, these Si form Li-Si alloy when contacted with lithium layer and stabilized the interface thereby suppressing lithium dendrites [78]. In another example, the Li-LLZT interface was modified by introducing Li<sub>3</sub>PO<sub>4</sub> to Garnet type Li<sub>6.5</sub>La<sub>3</sub>Zr<sub>1.5</sub>Ta<sub>0.5</sub>O<sub>12</sub> (LLZTO) surface to produce a self-limiting Li<sub>3</sub>P interphase, which stabilized the interface with its high ionic conductivity [163]. In another interesting study, Wachsman et al. used 3D printing technique to draw a micrometer-level 3D pattern on LLZO surface, which effectively increased areal contact between lithium and electrolyte [164].

#### 3.2. Implementing coatings

Even with careful selection and modification of solid electrolyte, the Li-electrolyte extrinsic interface is unstable due to chemical and mechanical incompatibilities and therefore results in high interfacial impedance. This can be solved by introducing a thin and uniform coating, which is electrochemically compatible with both lithium and electrolyte, to physically separate these two layers at extrinsic interface. Moreover, the coating material, with its lithophilic nature, improve interfacial contact due to better lithium wettability of coatings.

Several classes of coatings have been implemented and studied including oxides, metals, carbon, polymers, and lithium phosphates, etc. as illustrated in Fig. 6. Similarly, coatings such as SnF<sub>2</sub> [165], Cu<sub>3</sub>N [166], ZnO [167], Al<sub>2</sub>O<sub>3</sub> [168], and SnO [169] etc., can be used to form artificial SEI layer as they form Li-ion conducting phases like LiF, Li<sub>3</sub>N, Li<sub>2</sub>O, LiAl<sub>5</sub>O<sub>8</sub> upon contact with lithium (Fig. 6a, b, c). These phases protect SEs from direct contact with highly reductive lithium as they are electrochemically stable with lithium metal as illustrated in Fig. 3b and avoid thick interphase formation while maintaining good ion conductivity through the interface. Oxide coatings such as ZnO on LLZO is found to improve Li-LLZO contact and thereby reduce interface resistance. lithium upon contact with ZnO forms Li-Zn alloy, this alloying process improves lithium diffusion through the metal oxide layer and hence makes it lithophilic [167,170]. Similar mechanism is observed with Al<sub>2</sub>O<sub>3</sub> [171–173] on garnet-type LLCZN and on thio-LISICON-type LGPS [168], where Li-Al-O phase with high lithium diffusivity was formed upon lithiation. Metal coatings, such as aluminum (Al), and Ag-sputtered Li7La2.75-Ca0.25Zr1.75Nb0.25O12 garnet can enhance wettability and lithium diffusion by forming alloys with lithium, resulting in a significant reduction in interfacial resistance. For example, depositing a 20 nm Al layer on LLCZN garnet created a lithophilic surface that formed a Li-Al alloy upon contact with lithium, reducing the interfacial resistance from 950  $\Omega$  cm<sup>2</sup> to 75  $\Omega$  cm<sup>2</sup> [174]. Meanwhile, Ag-sputtered LLCZN garnet demonstrated seamless interfacial contact with the Li metal anode, forming a Li-Ag alloy during cycling and exhibiting a seven-fold reduction in interfacial resistance after 150 cycles compared to the pristine garnet [175]. Similarly, Ge coating applied to the surface of NASICON-type LAGP via sputtering improved Li-ion transfer by improving the electrolyte surface wettability with lithium and reducing LAGP decomposition [176,177]. Similar alloying mechanism is observed to reduce interfacial resistance with other metal coatings such as Mg [178], Au [59], In Ref. [179], and non-metals such as Si [78,108] and boron nitride [180] coatings. A thin 5-10 nm coating of boron nitride (BN) on LATP(Li1.3Al0.3Ti1.7(PO4)3) surface avoided the reduction of electrolyte (Fig. 6d) by blocking electron transport while allowing ions to permeate as illustrated in Fig. 6e. However, the alloying mechanism of these types of coatings has kinetic limitation due to



**Fig. 6.** Modification of the interface with different coatings (a) SEs such as LLZO are kinetically stable with lithium metal and do not wet with lithium metal due to a surface energy mismatch, which results in interfacial gaps between LLZO and lithium metal. (b) Lithophilic coatings are applied on LLZO surface by PLD, or ALD methods followed by (c) heating with lithium metal. The Lithophilic coating is activated by heating in inert environment (such as Argon) where diffusion and chemical reactions between the lithophilic layer and lithium metal occur to form a stable, ionically conductive interface [39]. (d) An LATP pellet gets reduced upon contact with lithium metal forming reaction products which are electronically and ionically conductive and thus incapable of stopping the continuous reduction of LATP. (e) An artificial boron nitride (BN) film is chemically and mechanically robust against lithium and electronically isolates LATP from lithium but still provides stable ionic pathways when infiltrated by PEO or liquid electrolyte [180]. (f) Schematics to illustrate the lithium anode stripping/plating behaviors with the amorphous carbon nanocoating. The carbon coating presents both electron and ion conductive capability which connects the electron-conductive-only current collector and ion-conductive garnet electrolyte. The lithium metal is dispersed uniformly during cycling to inhibit the formation of porous and layered dead lithium metal [67]. (g) Schematic of the SnS<sub>2</sub> coating onto the LLZTO pellet. (h) Simple schematic of the CCD improvement by SnS<sub>2</sub> coating [182]. (A colour version of this figure can be viewed online.)

limited chemical diffusion of lithium in the alloy and thereby can't sustain practical current densities in the range of several mA cm<sup>-2</sup>. A study showed that Li-Mg alloy with 10 at% of Mg is only able to maintain conformal interface at low current densities and temperatures above 80  $^{\circ}$ C is required to meet advanced battery requirements of 10 mA cm $^{-2}$ current density [181]. In another study, Zhou et al. coated the garnet-type LLZTO with SnS2 (as shown in Fig. 6g). This resulted in an improved CCD of the symmetric cell, indicating better inhibition of lithium dendrites. During lithiation, an in-situ conversion reaction occurs between SnS2 and Li, leading to the formation of Li-Sn alloy and Li<sub>2</sub>S. The composition of the interlayer formed *in-situ* can be continuously altered as the current density changes, providing a uniform electric field and smooth pathways for Li<sup>+</sup> transport at the interface, thus suppressing lithium dendrites (Fig. 6h) [182]. Recently, Wang et al. demonstrated the development of a stable LPSCl electrolyte-CC interface in an anode-free cell. This was achieved by tuning the wettability of Cu CC through the use of a Tellurium (Te) coating. Unlike other coatings such as Mg, Sn, SnS<sub>2</sub>, and In, which undergo reversible alloying/dealloying during cycling, the Li<sub>2</sub>Te alloy formed after initial lithiation was found to be electrochemically stable. This stability prevented the volume change associated with reversible alloving/de-alloving, making it a more advantageous approach than other reversible alloving methods [71].

Another class of coatings include solid electrolytes, which are stable with lithium. This thin electrolyte coatings can effectively prevent main electrolyte's decomposition. For instance, Li<sub>3</sub>N coated on garnet type LLZT pellet through plasma enhanced chemical vapor deposition resulted in stable plating/stripping behavior and was observed to have reduced interfacial resistance [183]. This was mainly due to high lithium ion conductivity and excellent lithium wettability of Li<sub>3</sub>N coating [184]. In another example, lithium phosphate (LiH<sub>2</sub>PO<sub>4</sub>) layer was formed by a simple *in-situ* chemical reaction at the LGPS-Li interface. This layer effectively prevented electrolyte reduction by utilizing its high ionic conductivity and low electronic conductivity, resulting in a full cell with a long cycle life and high capacity [185].

Likewise, different forms of carbon such as amorphous, graphite, and graphene oxide can be used as coatings to stabilize Li-electrolyte interface. In the 3D porous framework of garnet-type electrolyte, amorphous carbon nanocoating at the anode side was observed to promote homogeneous plating by introducing electron conducting pathways (Fig. 6f). The carbon coating, due to its electron and ion conducting capabilities, helps homogenize lithium deposition, facilitates electron transport, and expands the locations for Li-ion reduction. This results in reduced nucleation overpotential during lithium plating and improved stability at the lithium-electrolyte interface [67]. Feng et al. deposited amorphous C layer via vapor deposition on LLZTO surface to improve its stability with air and lithium wettability and thereby observed reduction in interfacial resistance. Moreover, higher CCD was achieved with low graphitized carbon (LGC), as it achieved faster lithiation than high graphitized carbon (HGC) because of more Li<sup>+</sup> transport pathways resulting from its amorphous structure [186]. In another example,  $Li_7P_3S_{11}$  particle was coated with graphene oxide (GO) layer, which avoided the reduction of electrolyte upon contact with lithium. The reduced GO, which formed due to reduction by Li, helped in improving homogeneous growth and cycling stability [182]. Shao et al. drew a graphite based soft interfacial layer on LLZTO surface. Upon lithiation, the graphite formed LiC<sub>6</sub> which has good ionic and electronic conductivity. Moreover, the soft graphite improved mechanical contact at the interface, which resulted in a uniform distribution of ion flux through the interface and improved interfacial stability [187].

While selecting a coating, it is important to consider its mechanical properties, as coating material needs to accommodate volume and morphological changes that occurs during plating/stripping and thereby avoid crack formation and dendrite growth. Previously discussed oxides such as Al<sub>2</sub>O<sub>3</sub> and ZnO, which have high Young's modulus, could easily form cracks due to large stress induced by lithium deposition. These

cracks will act as hotspots for lithium dendrite nucleation and growth. In anode-free LIBs, softer polymer coatings such as polyethylene oxide (PEO) was observed to provide good interfacial compatibility and stable cycling in anode-free LIBs [188]. Similar coatings can also be used in solid electrolytes. For example, PEO-based electrolyte coating on NASICON type SE was found to reduce interfacial resistance significantly, which resulted in stable stripping/plating voltage profile with lower voltage polarization [189]. Moreover, Goodenough et al. applied a flexible polymer coating on both sides of LATP electrolyte to form a sandwich geometry (polymer | LATP | polymer) and demonstrated a high CE of 99.9% and a cycle life of 640 cycles at room temperature [190]. Similarly, LiPON layer formed by sputtering on LATP is also demonstrated to form a passivation layer upon reacting with lithium and achieved better interfacial stability with reduced dendritic growth [191].

In summary, coatings applied to the anode side of lithium-ion SSBs serve two primary functions: enhancing lithophilicity at the interface to improve interfacial contact and reduce resistance, and preventing direct contact of the SE with lithium to decrease SE decomposition. Consequently, these coatings effectively reduce Li<sup>+</sup> consumption during the initial cycle, leading to an increase in the initial coulombic efficiency. However, most coatings, such as metals and oxides, undergo in-situ conversion reactions with the lithium anode or deposited lithium and thereby can have a negative impact on the initial coulombic efficiency if the transformation is irreversible in nature. For instance, coatings like SnF2, SnO, and Cu3N undergo in-situ reaction generating phases such as LiF, Li<sub>3</sub>N, and Li<sub>2</sub>O. Unfortunately, these in-situ conversion reactions are not entirely reversible. A specific example is the Te coating mentioned earlier, where the resulting in-situ formed Li2Te alloy is irreversibly bound [71]. When such coatings are applied to anode-free cells, which lack excess lithium on the anode side, the initial coulombic efficiency decreases due to lithium consumption resulting from these irreversible in-situ conversion reactions. On the other hand, coatings that employ alloying-dealloying processes, such as those using Mg, SnS<sub>2</sub>, and Ag, exhibit a predominantly reversible nature. This means that the alloyed lithium formed during charging returns to the cathode upon discharging, minimizing its impact on the initial coulombic efficiency. In summary, while certain coatings lead to irreversible in-situ conversion reactions that affect the initial coulombic efficiency, coatings employing reversible alloying-dealloying mechanisms have a lesser impact on the initial coulombic efficiency.

Although coatings are effective in reducing interfacial impedance and improving stability at the Li-electrolyte interface, they have limitations in terms of the resulting cyclability, rate capability, and other performance compared to current LIBs performance. Additionally, many of the coating techniques used, such as atomic layer deposition, magnetron sputtering, plasma-enhanced chemical vapor deposition, and electrospinning, are time-consuming and expensive, adding complexity and cost to the battery manufacturing process. Therefore, it is essential to explore a solution strategy that is more effective, easier to implement, and cost-effective.

## 3.3. Implementing interlayers

To ensure long-lasting capacity retention through hundreds of cycles, it is important for AFSSBs to possess high CE and reversibility in lithium plating/stripping process. However, inherent unstable interface between solid electrolyte and lithium results in premature cell failure due to inhomogeneous lithium deposition, unstable interfacial contact, and side reactions [24–26]. Despite their high mechanical strength, solid electrolytes can still suffer from dendritic lithium growth and internal short circuits. These issues stem from surface inhomogeneity, leading to uneven local current densities and deposition hotspots [133,192,193]. This risk of premature cell failure due to the interfacial issues can be circumvented by implementing a M - C interlayer, which promotes uniform plating/stripping and physically separates lithium

electrodeposition from the electrolyte [27,32,194]. In liquid electrolyte system, 3D electronic conductive networks with increased effective area have been demonstrated to promote uniform lithium deposition and reduced dendritic propagation by reducing local current density [68, 195-198]. However, the lack of fluidity in solid electrolytes makes it challenging to create adequate Li<sup>+</sup> conductive channels within a 3D electron-conducting network. Therefore, incorporating a MIEC 3D network in the interlayer of a solid electrolyte system is essential. In a separate study conducted by Chen et al., they found that incorporating a porous interlayer made of MIEC-type carbon tubules with a diameter of approximately 100 nm facilitated rapid lithium transport through interface-diffusional Coble creep along the MIEC-Li boundary (as shown in Fig. 7a) [65]. This creep deformation occurs below the yield strength and thereby increased the lithium diffusion and enhanced the kinetics of lithium dissolution, which, in turn, reduced the stress that develops at the interface during lithium plating. Consequently, this approach helped prevent cell failure due to crack formation at the interface. Moreover, the porous framework provided by the interlayer acts as a host structure for lithium deposition to accommodate volumetric changes and relieve stress during dynamic plating/stripping process [190]. Such interlayers can effectively homogenize lithium deposition and stripping thereby prevents dendrite formation, contact loss, reduces side reaction between lithium and SE, and ultimately improve capacity retention, rate capability, and cyclability.

Ion conductive materials such as Li<sub>3</sub>N [183,203], and LiF [203] can also be used as interlayer to protect SEs against lithium due to their low electronic conductivity [204]. In a study, a mixture of organic/inorganic composite interlayer (PVDF-HFP/CuF<sub>2</sub>) was used to stabilize the interface between a PEO-based solid electrolyte and lithium [205]. The reaction between CuF<sub>2</sub> and lithium resulted in *in-situ* formation of LiF,

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which effectively stabilized the SE-Li interface and suppressed the formation of dendrite morphology [206,207]. Moreover, the flexible polymer component of the interlayer was also effective in accommodating volume change over cycles. The combination of excellent elasticity and strong adhesion (by LiF) with lithium ensured the structural stability of the interlayer during the dynamic plating and stripping of lithium. In another interesting study, Lee et al. implemented a multi-interlayer consisting of lithophilic (Ag) and electron-blocking (LiF) layer (as illustrated in Fig. 7b) and observed low interfacial resistance and improved lithium dendrite suppression. By controlling the transport of both  $\mathrm{Li}^+$  ions and e–, this interlayer enabled a full cell with outstanding cycling performance, achieving over 3000 cycles at high current density (2C or 1 mA cm<sup>-2</sup>) and high CCD (3.1 mA cm<sup>-2</sup>) recording one of the highest performances for lithium metal SSBs [199]. Similar type of electron blocking and ion permeating amorphous LiPON interlayer (Fig. 7c) has been demonstrated to improve interfacial stability between LPSCL electrolyte and lithium anode and thereby resulting in very high CCD of 4.1 mA cm $^{-2}$  [200]. Similarly, Xiong et al. demonstrated a novel approach to stabilize the LAGP-Li metal interface by implementing a highly ion-conductive quasi-solid hybrid paste interlayer consisting of LAGP nanoparticles and an ionic liquid electrolyte. This interlayer improved interface stability by physically separating the LAGP electrolyte from the lithium metal anode to prevent electrolyte decomposition. Additionally, the interlayer's fast Li-ion conductivity helped better regulates Li-ion flux (Fig. 7d) [201].

Several studies have observed 3D MIEC framework to be the preferable host for lithium metal to enhance the contact area, reduce Lidiffusion distance, and counteract the expected volume change [31,50, 169,202]. Xiong et al. used solid state lithium naphthalenide as a plastic monolithic mixed conducting interlayer (PMMCI) at garnet SE-Li



**Fig. 7.** Implementing interlayer for improved lithium plating/stripping (a) Schematic process of creep-enabled lithium deposition/stripping in an MIEC tubular matrix with a geometry of (h, W, w), where Coble creep dominates via interfacial diffusion along the MIEC/Li<sub>bcc</sub> incoherent interface. MIEC tubules are shown as red, with white arrows indicating the free movements of electrons( $e^-$ ) and lithium ions (Li<sup>+</sup>);  $\alpha$ ,  $\beta$  and  $\gamma$  are Li<sub>bcc</sub> drops that are still recoverable [169]. (b) Schematic illustrations of the interface between lithium metal and garnet-type solid electrolyte with interfacial design coupling with lithophilic and electron-blocking interlayers. The schemes at the bottom show enlarged views of the interface [199]. (c) i. Schematic of a poor interfacial contact between LPSCI SSE and a lithium metal electrode. ii. FIB-SEM cross-section image of the interface between the un-coated LPSCI SSE and lithium metal. The LPSCI SSE without a LiPON coating has poor interfacial contact with the lithium metal electrode. The bottom-right inset is the digital photo of a droplet of molten lithium forming a ball on the surface of the LPSCI pellet. iii. Schematic of the improved wetting behavior of a coated LPSCI SSE with the lithium metal anode. iv. FIB-SEM cross-section image of the interface between the liPON coated LPSCI SSE over the whole imaged area. The bottom-right inset is the digital photo of superior wetting behavior of liquid lithium on the LiPON-coated LPSCI SSE [200]. (d) Schematic diagram of the role of LAGP-IL interlayer based on polymer electrolyte. LFP: LiFePO<sub>4</sub> cathode, PEO: poly (ethylene oxide) electrolyte [202]. (A colour version of this figure can be viewed online.)

interface and achieved a high cyclability for 500 h at 1 mA cm $^{-2}$ . This interlayer not only improved contact between lithium anode and the garnet electrolyte, but also provided ordered layered MIEC frameworks for easy transportations of both Li-ion ( $\sigma_{\rm Li+}=4.38\times10^{-3}~{\rm S~cm^{-1}})$  and electrons ( $\sigma_{e^-} = 1.01 \times 10^{-3} \text{ S cm}^{-1}$ ). Consequently, the interlayer greatly improved interfacial charge transfer kinetics and enabled dendrite free lithium plating/stripping at high current density [208]. Zhang et al., employed a 3D MIEC interlayer comprising a Cu nanowire network coated with Sn/Ni alloy (Cu@SnNi) to facilitate fast Li + ion transport between the lithium metal anode and LiFePO<sub>4</sub> cathode. The Cu@SnNi interlayer, as illustrated in Fig. 7e, allowed Li<sup>+</sup> ions to flow through the lithiated Sn/Ni alloy layer, while electrons flowed through the Cu nanowires, creating a MIEC network that enabled homogenous electron/ion flux distribution. This resulted in excellent rate capability (133 mAh  $g^{-1}$ , 2 C; 100 mAh  $g^{-1}$ , 5 C) and good cycling stability (87% capacity retention after 200 cycles at 1 C). In contrast, the cell lacking the interlayer exhibited lower rate performance (117 mAh  $g^{-1}$ , 2 C; 60 mAh  $g^{-1}$ , 5 C) and a shorter cycling life (short circuit after 30 cycles at 1 C) [202].

Several researchers have found that using a M - C composite interlayer, as illustrated in Fig. 8, can significantly improve the overall CE and cycling of a cell over hundreds of cycles. In a recent study by Samsung, 5-10 µm thick Ag-C nanocomposite interlayer (in weight ratio of 1:3) was placed between SE and anode side CC (Fig. 2a) [27]. The Ag-C interlayer only accounted for 5-10% of the total capacity, causing most of the lithium to precipitate out at the CC-interlayer interface. The full-cell incorporating this interlayer demonstrated a high energy density (>900 Wh  $L^{-1}$ ), an average CE of 99.8%, and a long cycle life exceeding 1000 cycles with 2 MPa applied stack pressure at 60 °C. Suzuki et al. subsequently explored the effect of incorporating different metals, including Ag, Sn, Al, Zn, and Ni, in the M - C composite interlayer (Fig. 8a). They found that adding Ag nanoparticles significantly improved both rate capability and capacity retention, resulting in an 86% retention rate after 700 cycles with 4 MPa applied stack pressure at 60 °C (Fig. 8b) [32]. This improved performance with Ag nanoparticles could be ascribed to high lithium diffusivity in Li-Ag alloys [139] resulting in fast redistribution of lithium inside Ag-layer and lower

nucleation overpotential for lithium deposition once Li-Ag alloy layer is oversaturated with lithium. Lithiated carbon demonstrates excellent electron and Li-ion conductivity (ranging from  $10^{-11}$  to  $10^{-6}$  cm<sup>2</sup> s<sup>-1</sup>) [209]. Consequently, when the M – C nanocomposite interlayer, which consists of interconnected NPs of metal and carbon, is lithiated, it forms a network of MIEC pathways. This MIEC network plays a vital role in facilitating e<sup>-</sup> and Li<sup>+</sup> transport through the interlayer. Moreover, the porous structure within the M - C interlayer facilitates lithium diffusion mainly via Coble creep. In a recent study, researchers observed pore size-dependent lithium deposition behavior in a 3D porous Ni nanoparticle anode, finding improved lithium deposition in smaller pores and identifying diffusional Coble creep as the mechanism for lithium movement through the porous structure [31]. Consequently, the carbon and Ag coated Ni particle anode host resulted in initial discharge capacity of 2 mA cm<sup>-2</sup> and average CE of 99.47% for 100 cycles (with 5 MPa applied stack pressure at 45 °C). Later, the same group of researchers verified similar pore size-dependent lithium deposition behavior with C and Ag-C porous interlayers, noting that smaller pores enabled lithium deposition at the CC-electrolyte interface, resulting in improved cyclability during repeated lithium deposition and stripping [45]. Besides pore size, they investigated the impact of temperature, scaffold material, and surface modification of the interlayer with Ag nanoparticles on lithium deposition behavior. Coating the surface of carbon spheres with Ag resulted in denser and more homogeneous lithium deposition, believed to be due to improved lithium diffusion through lithophilic Ag and Li-Ag alloys. In their investigation, the researchers also examined the impact of adhesion work at extrinsic interfaces on the location of lithium deposits. They found that with sufficiently strong adhesion at the SE-interlayer interface, lithium deposits at the interlayer-CC interface [45]. Moreover, Spencer-Jolly et al. examined the effectiveness of an Ag-graphite composite interlayer with LPSCl electrolyte. Their results showed that the addition of Ag to the graphite interlayer did not substantially inhibit dendrite growth, at applied current>=2.5 mA cm<sup>-2</sup> (with 2 MPa stack pressure at 60 °C) lithium metal starts to plate at interlayer-SE interface leading to dendritic growth and cell failure. However, Ag addition to graphite interlayer facilitated more uniform lithium plating and stripping thereby



**Fig. 8.** Modification of the interface using M - C interlayer (a) Schematic Fig. of ASSB with CB-based anode. (b) Discharge capacity retention and CE of ASSB with Ag-, Zn-, Sn-, and Al/CB-based anodes. Condition of cycle test was 3 mA cm<sup>-2</sup> for CC mode for both charge and discharge [32]. (c) 3D graphic of elastic recovery during lithiation and delithiation of Ag particles. Electrochemical impedance spectroscopy (EIS) plots of the all-solid-state half-cells with Spandex and polyvinylidene fluoride (PVDF) binders. (d) before cycling, and (e) after 20 charge–discharge cycles [33]. (A colour version of this figure can be viewed online.)

enabling better cyclability. The study found that dendrite suppression was primarily influenced by lithium diffusion in graphite and suggested integrating carbon with higher lithium diffusivity could enhance rate capability in carbon-based composite interlayers [210].

The performance of an anode-free cell depends not only on the contact condition at the extrinsic interface but also on the intrinsic interface. In a study by Oh et al., the effect of a destabilized intrinsic interface of an interlayer on the cell performance was examined [33]. The destabilization was caused by severe volume expansion of Ag particles in Ag-C nanocomposite interlayer, which they resolved by replacing PVDF binder with an elastic polymer binder called "spandex" (Fig. 8c, d, e). This helped maintain intimate contact between carbon and Ag particles, creating a stable intrinsic interface, and improving charge-discharge reversibility and long-term cyclability. Additionally, they observed decreased porosity with the spandex binder, which reduced trapped lithium and further improved initial reversibility. These studies demonstrate the effectiveness and potential of porous M -C interlayers in regulating the deposition and stripping of Li, highlighting their potential for practical applications. Moreover, researchers have also developed a 3D porous framework of garnet-type electrolyte to promote uniform deposition by increasing effective anode interfacial area and reduce local current density [66]. However, due to lack of electronic pathways into the porous structure, the deposition of lithium was not uniform in this cell [156]. Later the same group of researchers coated one side of the porous layer with amorphous carbon, they enhanced the electronic conductivity of the porous garnet layer, forming a 3D MIEC framework (Fig. 6f). This led to an increased effective area of the Li-garnet interface, allowing for uniform lithium deposition and stripping [67].

Multiple studies have demonstrated the significant impact of stack pressure on the cyclability of lithium metal all-solid-state batteries (ASSBs) [211,212]. Maintaining an appropriate stack pressure is crucial to prevent contact loss at the lithium/solid electrolyte (SE) interface. However, excessive pressure can lead to mechanically induced lithium penetration and short circuit the cell [211]. To address this dilemma, interlayers have emerged as a solution. These interlayers enhance lithium diffusion, reducing the required pressure for achieving flux balance and interface stability, thus ameliorating pressure-induced lithium penetration. For example, the incorporation of an Ag-C interlayer facilitates lithium diffusion through diffusional Coble creep at the Li/SE interface. This improvement in lithium diffusion promotes morphological stability, enabling the cell to operate at a low stack pressure of 2 MPa while achieving high cyclability of over 1000 cycles at a relatively high current density of 3.2 mAh  $cm^{-2}$ . Interestingly, this Ag-C interlayer even enables full cell cycling without applied stack pressure at a low rate of 0.05C (0.34 mA cm<sup>-2</sup>) [27]. Likewise, Su et al. demonstrated that using a LiPON interlayer between the Li metal anode and LPSCL electrolyte increased the critical current density (CCD) to 4.1 mA  $cm^{-2}$  [200]. By implementing this interlayer, they were able to enhance CCD and reduce the required stack pressure to 4.6 MPa at 30 °C. Thus, the application of interlayers reduces the necessary applied pressure for a stable interface by promoting lithium diffusion, preventing void generation and deposition hotspots, and consequently increasing CCD.

Temperature is an additional factor that influences the morphological stability at the interface, alongside applied pressure. Both diffusional and displacive (dislocation) creep deformation mechanisms are sensitive to temperature variations. Furthermore, the applied current density also plays a role in determining the morphological stability at the lithium-solid electrolyte (Li-SE) interface, thereby affecting cyclability. However, it is worth noting that not all research papers provide clear information about these parameters, making it challenging to draw direct comparisons between different types of interlayers and coatings. To enable effective comparisons and promote standardized reporting, the implementation of a uniform protocol for evaluating and reporting interlayer performance becomes necessary in future research endeavors. Such a protocol would provide a consistent framework for assessing the influence of temperature, applied pressure, current density, and other relevant factors on the performance of interlayers and coatings. A new parameter called critical interphase overpotential (CIOP) was introduced in a recent study for an effective comparison of different interlayers or interphase quality in solid electrolytes. CIOP represents the required overpotential for lithium dendrites to penetrate the interphase or interlayer. Unlike CCD, CIOP is an intrinsic property of the interphase or interlayer and is independent of engineering parameters such as applied pressure, electrolyte thickness, and lithium plating/stripping conditions and therefore can serve as a better performance metric than CCD for interlayer design and selection. In the same study, the LPSCL electrolyte was coupled with Li2NH-Mg as interlayer, resulting in an observed increase in CIOP from 9 mV to 222.9 mV. This increased CIOP value represents better dendrite suppression capability of the artificially coated interlayer (Li<sub>2</sub>NH-Mg) as compared to interphase formed at bare LPSCL and lithium interface. This study shows a superior capability of the Li<sub>2</sub>NH-Mg interlayer to suppress dendrite formation and potentially improve cyclability and rate capability [213].

### 4. Conclusion and outlook

This review summarizes the recent developments in anode-free solidstate batteries. The anode-free configuration enables theoretical highest energy density in any given forms of the cathodes due to the full utilization of the lithium metal as anode active material, which is solely plated from the cathode. An Ag-C composite interlayer was employed in the anode-free configuration for the regulation of lithium metal plating and stripping during the cycling. Researchers announced that the multilayer pouch-cell anode-free solid-state battery with high energy density and long cycling life is implemented by adding Ag-C interlayer [27].

Nevertheless, despite the recent advances of anode-free solid-state batteries enabled by Ag-C composites, the scientific and technological challenges in implementing interlayer in solid-state cells, as well as the barriers in fundamentally understanding the operation mechanisms of the Ag-C interlayer, impeded the further development of interlayer approaches. We outlined below several perspectives for future investigations.

## 4.1. In-situ diagnosis

As indicated in Section 3, the complicated evolutions of lithium transport in the MIEC-type Ag-C interlayer necessitate in-depth diagnostics conducted under realistic battery operation conditions to quantify the coupled properties. The *in-situ* diagnosis will provide fundamental insight into research gaps including the natures of lithium transport within the Ag-C structure, the processes of lithium diffusion within silver (Ag) particles, and the intermediate and metastable phase of Ag particles during lithium diffusion, thereby guiding the development of improved interlayer designs for solid-state batteries.

#### 4.2. Binder-assisted sheet-type interlayer fabrication

From a practical perspective, the design of thinner interlayers in the anode-free configuration is advantageous for increasing the mass loading in the cathode, hence permitting larger energy densities. Scaleup manufacturing of sheet-type Ag-C interlayer typically needs the presence of polymer binders; however, their insulative nature has detrimental effects on charge transport kinetics. In addition, existing knowledge on the binder effects in typical liquid-based lithium-ion batteries do not necessarily apply to solid-state batteries. By using a polymer binder, the Li<sup>+</sup> transport kinetics among internal interface and external interfaces of the Ag-C interlayer will be reshuffled. Consequently, novel slurry-coating strategies are sought for scalable Ag-C interlayer technologies.

## 4.3. Noble-metal-free interlayers

The usage of Ag metal in the Ag-C interlayer contradicts with the efforts to move away from key metals in high-volume production of batteries, especially in the case of low Ag abundance in the Earth's crust (75 ppb). However, interlayers with non-noble metals such as Zn, Al, Sn, and Ni performed worse than their Ag-containing counterparts [27,32]. Non-noble-metal alternatives to Ag are not immediately obvious due to the lack of a comprehensive understanding of the working mechanism of the Ag-C interlayer; consequently, it is essential to define interlayer design guidelines and develop noble-metal-free alternatives as the interlayers for all-solid-state batteries.

# Author contributions

Conceptualization, Z.F., W.Z, and F.R.; writing—original draft preparation, S.R., C.W., F.W., S.R.; writing—review and editing, S.R. and Z.F.; supervision, Z.F., Y.Y. All authors have read and agreed to the published version of the manuscript.

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## Declaration of competing interest

Z.F. and Y.Y. have equity interest in Solid Design Instruments LLC. Y. Y. has equity interest in LiBeyond LLC. Their relationship with Solid Design Instruments LLC has been reviewed and approved by the University of Houston in accordance with its conflict of interest policies.

## Data availability

No data was used for the research described in the article.

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