Solid Electrolytes in Solid-State Battery Technology

Subjects: Others

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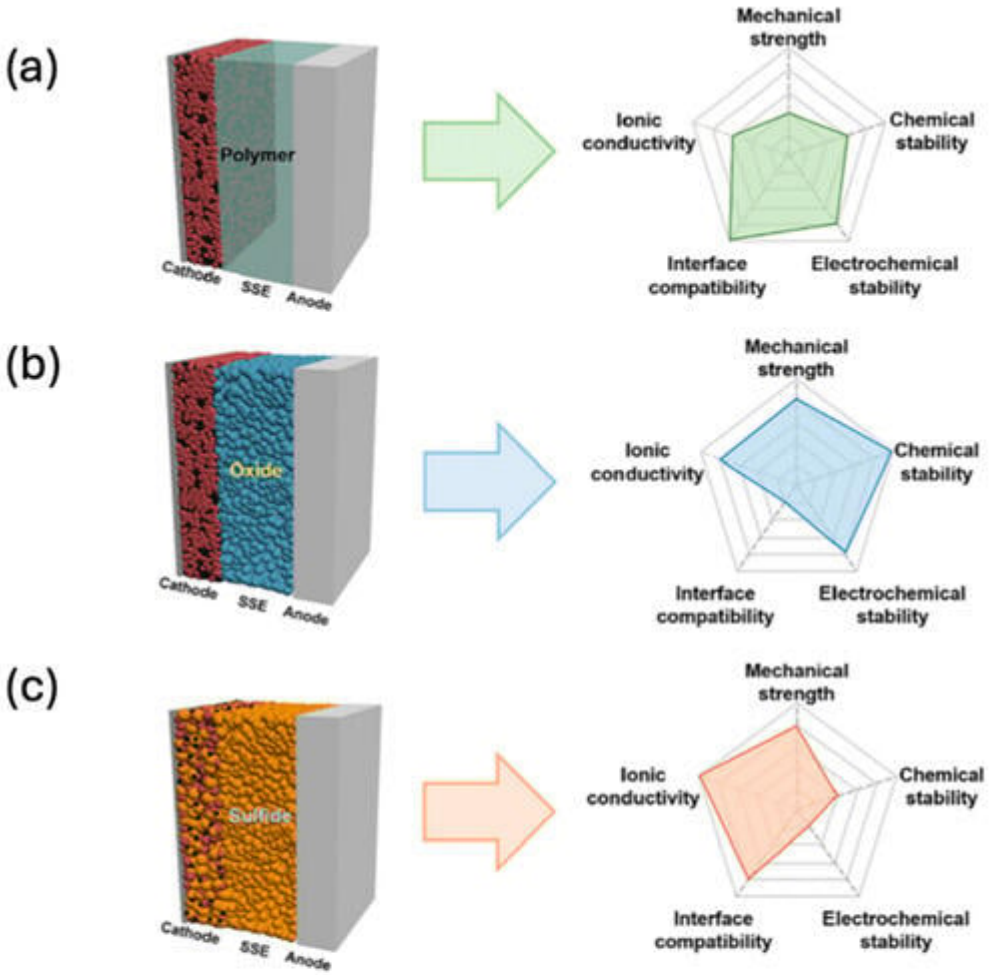
The evolution of energy storage technologies has been pivotal in advancing contemporary technological capabilities, significantly contributing to the development of sustainable energy systems. Historically, energy storage has undergone various phases of innovation, each enhancing the efficiency, safety, and environmental impact. A notable transition is occurring towards solid-state energy storage, exemplified by the development and implementation of solid-state batteries (SSBs). This shift is driven by two main factors: the recognition of the limitations in traditional energy storage systems, particularly those using liquid electrolytes, like in lithium-ion batteries (LE-LIBs), and substantial progress in materials science, introducing novel materials and fabrication techniques vital for solid-state energy storage systems

solid-state batteries cathode materials energy density energy electrolytes

1. Introduction

The gradual shift to solid electrolytes has been influenced by the prior development of conventional lithium (Li) batteries, which have traditionally employed liquid electrolytes.

The attributes of solid-state electrolytes, such as ionic conductivity, stability, and ease of processing, vary considerably across different classes, each presenting unique strengths and limitations. The research of Liang et al. [1] on the advancements and future potential of different solid electrolyte types for use in solid-state batteries offers a thorough insight into their categorization. Illustrations depicting the diverse types of SEs, along with a review of their essential properties, like mechanical strength, ionic conductivity, interface compatibility, and chemical and electrochemical stability, are shown in **Figure 1**a–c. Additionally, **Figure 1**d illustrates the distinct challenges faced by each type of SSE [1].


(a)
Polymer
Cathode
SSE
Anode
Mechanical strength
Chemical stability
Electrochemical stability
Interface compatibility
Ionic conductivity
(b)
Oxide
Cathode
SSE
Anode
Mechanical strength
Chemical stability
Electrochemical stability
Interface compatibility
Ionic conductivity
(c)
Sulfide
Cathode
SSE
Anode
Mechanical strength
Chemical stability
Electrochemical stability
Interface compatibility
Ionic conductivity

(d)

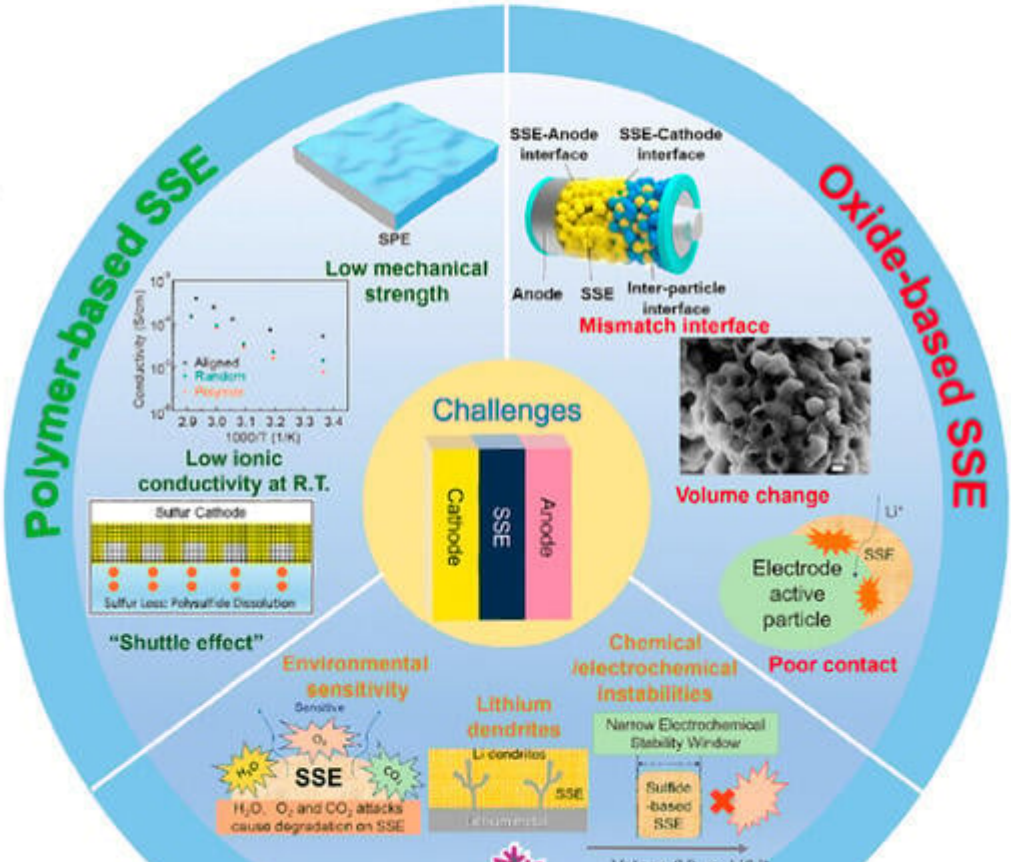

Polymer-based SSE
Oxide-based SSE
SPE
Low mechanical strength
Low ionic conductivity at R.T.
Sulfur Cathode
Sulfur Loss: Polysulfide Dissolution
"Shuttle effect"
SSE-Anode interface
SSE-Cathode interface
Anode
SSE
Inter-particle interface
Mismatch interface
Volume change
Electrode active particle
SSF
Poor contact
Challenges
Cathode
SSE
Anode
Environmental sensitivity
Sensitive
SSE
H2O, O2 and CO2 attacks cause degradation on SSE
Lithium dendrites
Li dendrites
SSE
Chemical /electrochemical instabilities
Narrow Electrochemical Stability Window
Sulfide -based SSE

Figure 1. Comparison of SSBs using polymer (**a**), oxide (**b**), and sulfide (**c**) SSEs; and the challenges for SSBs depending on the SSEs used (**d**). Reprinted with permission from ref. [1]. Copyright 2022, Elsevier.

The range of cell designs enabling these electrolytes is as varied as the materials themselves. Consequently, an extensive array of SSLBs is being concurrently developed in both academic and industrial research settings. The different types of SSEs are categorized as follows:

- Oxide Electrolytes: LIPON, NASICON, and Garnet Type;
- Sulfide Electrolytes: LPS and Argyrodites;
- Polymer Electrolytes;
- Halide Electrolytes;
- Composite Electrolytes;
- Hybrid Solid–Liquid Electrolytes.

Each type of SSE is further elaborated upon in the respective sections, providing an in-depth understanding of their unique properties and applications.

2. Oxide Electrolytes

2.1. LIPON

Lithium phosphorus oxynitride (LiPON) represents a unique glassy phase within the category of oxide-based solid electrolytes. Its chemical formula, denoted as LixPOyNz, adheres to the principle of charge neutrality, with stoichiometric coefficients satisfying the equation x = 2y + 3z − 5. The initial development of LiPON glass solid-state electrolytes dates back to the 1970s at Oak Ridge [2], exhibiting an ionic conductivity of approximately 2 × 10^{-3} mS cm^{-1}. The fabrication of these amorphous LiPON glasses typically employs magnetron sputtering, utilizing a lithium orthophosphate target in a nitrogen plasma atmosphere. Nevertheless, the process of physical vapor deposition for these materials is both time and energy intensive, limiting their use to thin-film applications rather than large-format solid-state electrolytes. LiPON finds practical use in the production of microbattery cells, often paired with a $LiCoO_2$ cathode and a lithium-metal anode, specifically for low-power applications. Its implementation in larger format pouch cells is currently impractical. The most widespread applications of LiPON in the market are in the realm of microbatteries, such as those used in medical devices. Recent advancements have seen the production of LiPON bulk glasses with varying nitrogen contents, achieved through the ammonolysis of $LiPO_3$ melts [3][4]. LiPON is particularly significant in the field of thin-film solid electrolytes due to its key characteristics. It boasts a broad electrochemical window (0–5.5 V) against lithium metal and demonstrates electrochemical stability, enduring thousands of cycles without the formation of lithium dendrites [5]. Furthermore, LiPON possesses

relatively high ionic conductivity (around 2×10^{-6} S cm^{-1}) and extremely low electronic conductivity (approximately 8×10^{-14} S cm^{-1}) at room temperature [5]. The electrolyte is compatible with various electrode materials. Due to its amorphous nature, LiPON benefits from isotropic conduction properties and the ability to form mechanically stable, flexible thin films [6]. Notably, it maintains structural integrity without cracking even under volume changes in the cathode. Other studies highlight LiPON thin films' intriguing mechanical properties [7], particularly their resistance to microscale cracking through densification and shear flow, enhancing their commercial appeal. On the downside, the active loading of the cathode in these systems is around 0.5 mg cm^{-2}, significantly lower than that of commercial liquid electrolyte lithium-ion batteries. Additionally, the production costs for thin-film microbatteries are relatively high. However, beyond its use as a solid electrolyte, LiPON is also gaining attention as a particle coating to stabilize high-voltage cathodes [8][9].

2.2. NASICON

NASICON, an acronym for "Sodium Super-Ionic Conductor", describes a class of ceramic materials characterized by an orthorhombic crystal structure (see **Figure 2**) [10] that facilitates the easy movement of ions, particularly sodium ions. Originating from the concept of sodium-conducting oxides, NASICON materials have evolved to encompass a wider range of ion-conducting applications, including in solid-state batteries where sodium is replaced with lithium. During the early 1990s, researchers began investigating NASICON-type oxides [11][12][13], focusing on compounds with the formula $Li_{1+x}A_xTi_{2-x}(PO_4)_3$ (LATP), where 'A' represents elements such as Al, Cr, Ga, Fe, In, La, Sc, and Y. The ionic conductivity of these materials is influenced by several factors, including the concentrations of alkali and titanium [14], as well as the grain size. Lithium salt concentration, in particular, plays a critical role in modifying the ionic conductivity, with higher lithium salt levels up to 20% enhancing the conductivity and achieving single-phase material [15]. However, challenges arise when there is an inadequate mixing of aluminum and titanium, leading to the formation of a secondary phase ($AlPO_4$) which acts as a resistive layer, thereby reducing the ionic conductivity [16]. Through controlled synthesis, the morphology and grain size of these materials can be manipulated, significantly affecting their ionic conductivity [17]. The primary focus of LATP research has been its application in batteries with a bulk layer structure, achieving ionic conductivities of about 1 mS cm^{-1}. A subsequent development was the discovery of $Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) [18], a new material in this category. NASICON-type LATP solid-state electrolytes offer several advantages, such as excellent stability in ambient atmospheres, which minimizes processing environmental requirements. They exhibit the highest ionic conductivity among oxide materials and remain stable in the presence of high-potential (5 V) cathodes. Additionally, these materials require relatively low sintering temperatures between 600 and 700 °C, further reducible to below 400 °C with process optimization [19][20].

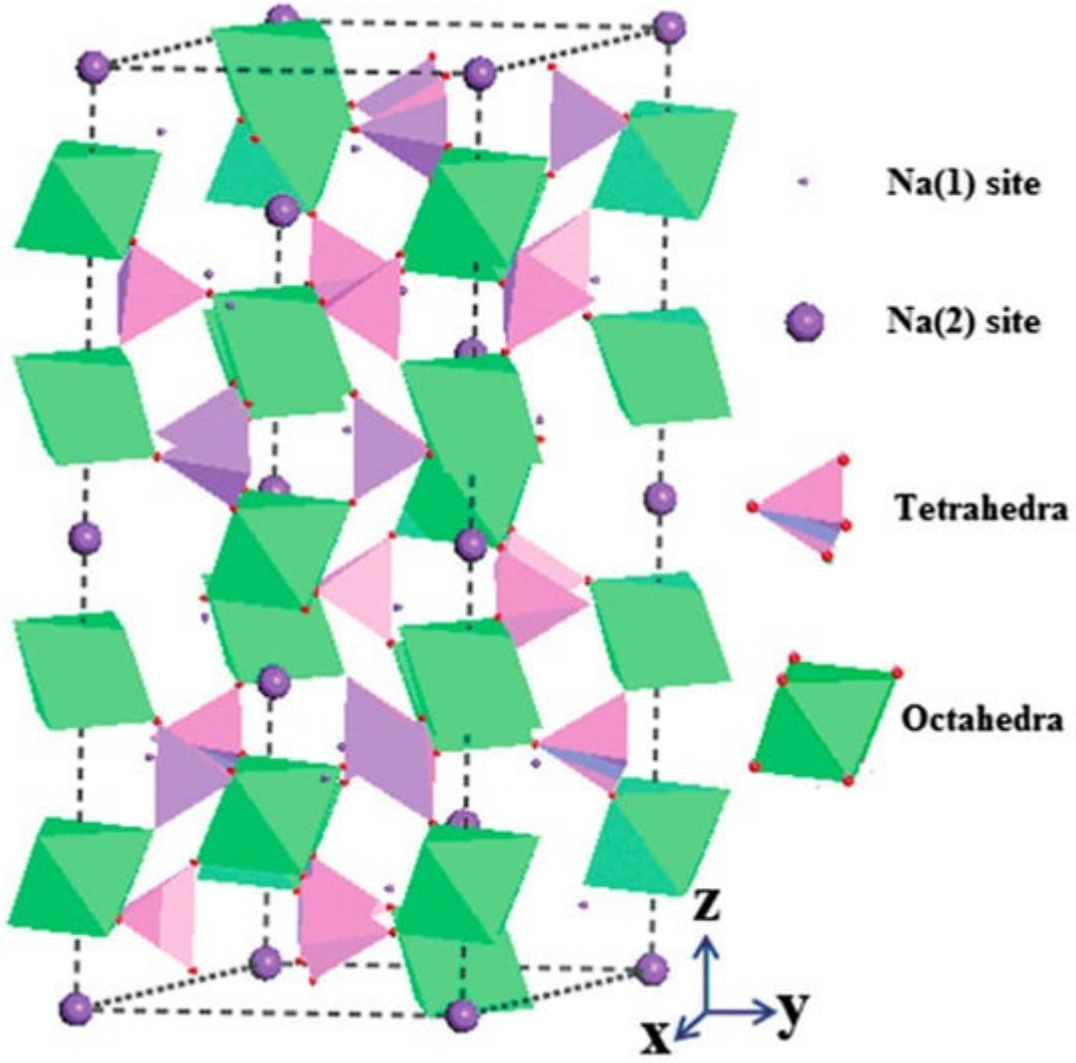


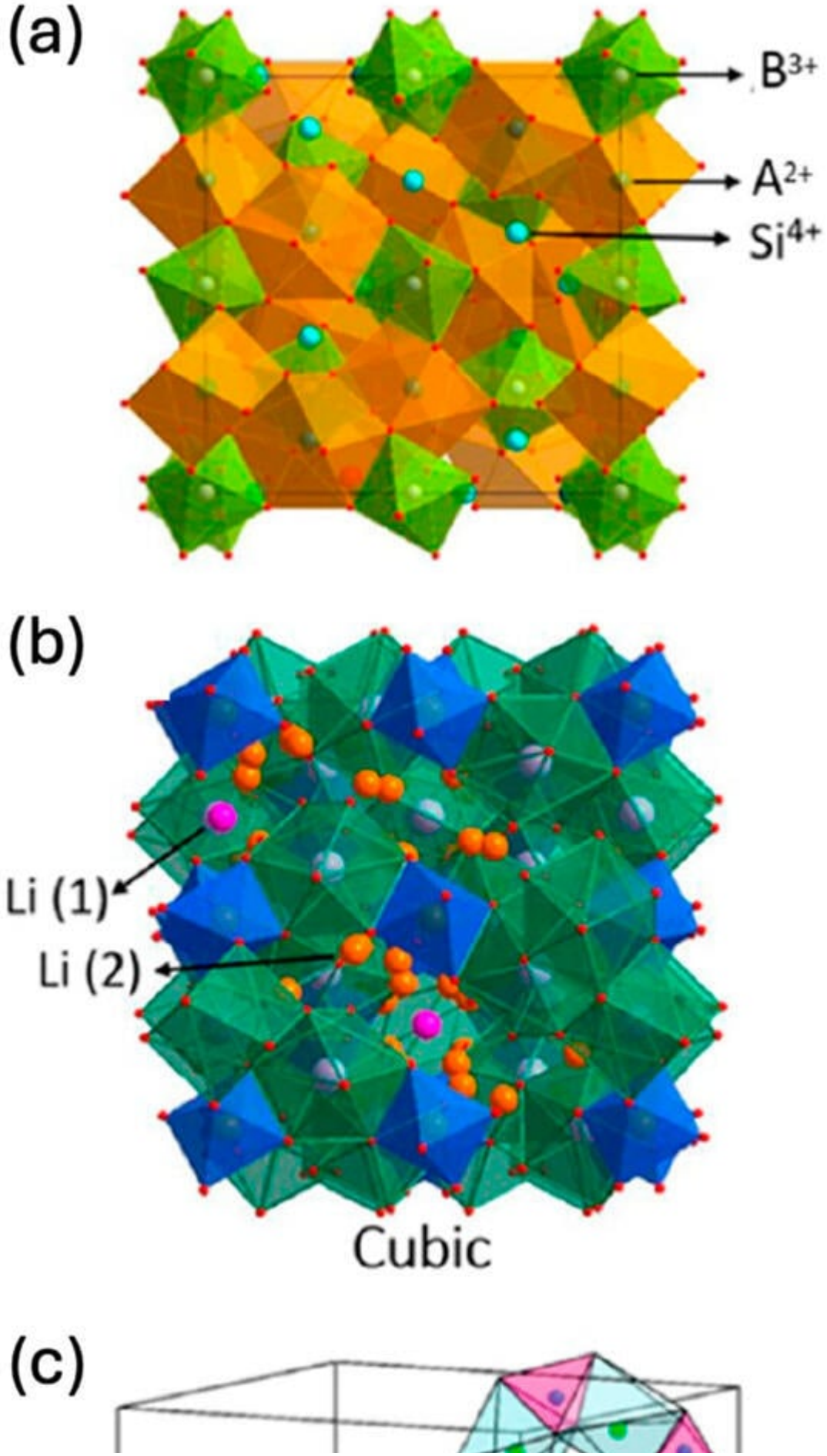
Figure 2. Schematic representation of the $Na_3V_2(PO_4)_3$ crystal structure with a NASICON framework. Reprinted with permission from ref. [10]. Copyright 2014, Royal Society of Chemistry.

Despite these benefits, LATP faces challenges, particularly in its interaction with lithium-metal anodes [11][21][22]. Enhancements in these solid electrolytes are focused on introducing interlayers to mitigate interfacial impedance, prevent dendrite nucleation, and protect the electrolyte from side reactions [14]. A potential solution involves using LAGP barrier layers to prevent direct contact with the lithium metal and facilitate stable redox reactions. However, LAGP's long-term stability against lithium metal is limited, and it incurs higher costs due to the inclusion of germanium. Compared to garnet-type and perovskite-type oxides, NASICON-type oxides display the least thermal resistance. Notably, in certain experimental setups, thermal runaways have been observed with LAGP and LATP at onset temperatures around 300 °C [19][23].

2.3. Garnet-Type

The garnet-type solid electrolyte $Li_7La_3Zr_2O_{12}$ (LLZO) is increasingly recognized as a leading contender for use in solid-state batteries due to its high ionic conductivity and impressive electrochemical stability. The initial studies on Li-conduction in $Li_5La_3M_2O_{12}$ were reported in 2003 [24], demonstrating an ionic conductivity of about 10^{-6} mS cm^{-1}

at 25 °C. The development of the electrolyte $Li_6ALa_2Ta_2O_{12}$ (A = Sr, Ba) [25] marked a significant improvement, enhancing the ionic conductivity to 4 10^{-2} mS cm^{-1} at 22 °C and introducing a new category of garnets. Further refinement led to the formulation of $Li_7La_3Zr_2O_{12}$ (LLZO), with a cubic atomic structure (see **Figure 3**), achieving ionic conductivities around 1 mS cm^{-1} [26]. This advancement was underpinned by an understanding of the fundamental transport properties of Li-diffusion paths in the material [27]. Recent developments in LLZO research have explored the impact of varying lithium contents on Li-conduction [28], the existence of two different polymorphs of LLZO (cubic and tetragonal) [29], and the effects of introducing dopants into the LLZO crystal structure [30]. Current efforts in LLZO garnet development are centered on diverse doping strategies targeting the Li, La, or Zr sites, with some of the highest conductivities recorded at approximately 1 mS cm^{-1} at room temperature [31]. The key benefits of garnet-type electrolytes include a high Li-ion conductivity (approximately 10^{-3} S cm^{-1} at 25 °C), a broad electrochemical stability window (around 6 V vs. Li^+/Li) [32], and a robust chemical stability against Li metal [33][34]. They also exhibit strong mechanical properties, with a high shear modulus that theoretically helps prevent Li dendrite formation [35][36]. However, challenges persist with lithium dendrite formation, often occurring along grain boundaries or within porous areas [37], and high interfacial resistance in Li/garnet interfaces leading to uneven Li distribution [38] and weak mechanical strength at grain boundaries [39].


(a)
B3+
A2+
Si4+
(b)
Li (1)
Li (2)
Cubic
(c)

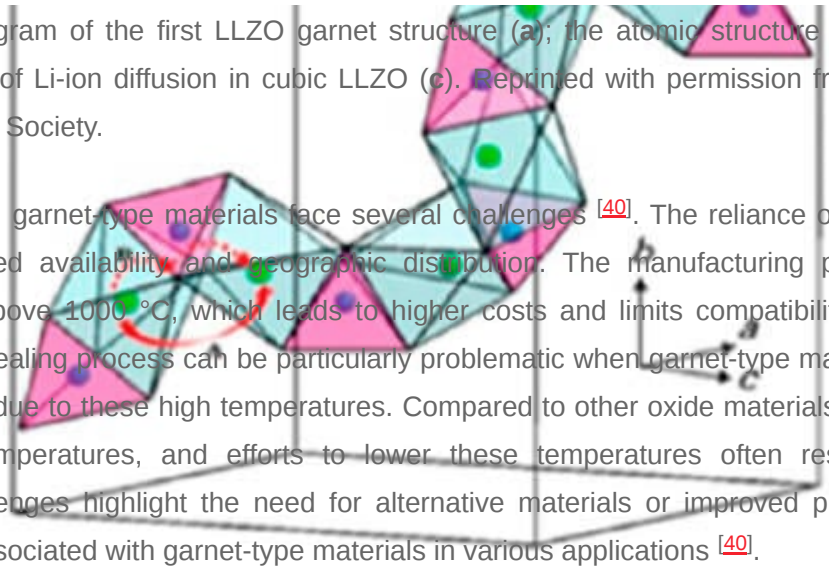


Figure 3. Schematic diagram of the first LLZO garnet structure (**a**); the atomic structure of cubic $Li_7La_3Zr_2O_{12}$ (LLZO) (**b**); the pathway of Li-ion diffusion in cubic LLZO (**c**). Reprinted with permission from ref. [25]. Copyright 2021, American Chemical Society.

Despite their advantages, garnet-type materials face several challenges [40]. The reliance on lanthanum (La) is a concern due to its limited availability and geographic distribution. The manufacturing process requires high sintering temperatures above 1000 °C, which leads to higher costs and limits compatibility with some cathode active materials. The annealing process can be particularly problematic when garnet-type materials are paired with cathode active materials due to these high temperatures. Compared to other oxide materials, garnet-types require the highest sintering temperatures, and efforts to lower these temperatures often result in reduced ionic conductivity. These challenges highlight the need for alternative materials or improved processing methods to mitigate the limitations associated with garnet-type materials in various applications [40].

3. Sulfide Electrolytes

Sulfide solid electrolytes encompass a range of compounds primarily composed of lithium and sulfur, and can include additional elements, like phosphorous, silicon, germanium, or various halides. These materials are highly regarded in the domain of solid-state ceramic electrolytes due to their exceptional ionic conductivity. This conductivity is often comparable to, or even surpasses, that of traditional organic liquid electrolytes [41][42][43][44]. The standout conductivity of sulfides, relative to oxides, is attributed to the properties of sulfur atoms. Sulfur atoms are softer and more polarizable than oxygen atoms, leading to a reduced interaction with lithium ions and thereby increasing their mobility. Sulfide-based electrolytic substances also boast notable malleability and ductility, beneficial for cold-press manufacturing methods that circumvent expensive high-temperature sintering. Under high pressure, these materials can form extremely dense layers with minimal grain boundary resistance. This characteristic enhances electrode–electrolyte contact, reducing the formation of lithium dendrites. Overall, sulfide-based electrolytes demonstrate promising qualities, such as effective ionic conductivity, reduced interfacial resistance with electrodes, and lower production costs. These features position them as leading candidates in the field of inorganic solid electrolyte materials. Noteworthy among these electrolytes are glass–ceramic lithium thiophosphate (LPS) and argyroditic glasses, which are explained in further detail.

3.1. LPS

LPS electrolytes (glass–ceramics and glasses), are derived from the binary mixture xLi_2S $(100\text{-}x)P_2S_5$, where 'x' represents the molar percentage [45][46]. Within this category, the $75Li_2S\text{-}25P_2S_5$ composition, known as 75:25 LPS, has been extensively studied due to its superior ionic conductivity of 0.28 mS cm^{-1} at room temperature, and its greater thermal stability compared to other glass types [47].

The production of LPS glass–ceramics involves the annealing of LPS glasses at specific temperatures, leading to their partial crystallization. This crystallization process generally reduces the Li^+ ion conductivity, but this can be mitigated by altering the material composition [48]. For instance, in the Li_2S–P_2S_5–P_2S_3 ternary system, introducing

a minor amount of P_2S_3 into the Li_2S–P_2S_5 base, improves the conductivity of the resultant glass–ceramics [49]. Additionally, in the binary LPS system, superionic crystalline phases develop during the annealing of metastable compositions with x ≥ 70. The most effective glass–ceramic is produced by crystallizing the 70:30 LPS mixture, resulting in the formation of a $Li_7P_3S_{11}$ superionic crystalline phase with remarkably high ionic conductivity, up to 17 mS cm^{-1} [46]. The Li-P-S compound group has the advantage of being synthesized at low temperatures (below 300 °C) and can be sintered at room temperature [41]. However, caution is necessary during the synthesis and cell assembly stages due to its reactivity with air and moisture, which can lead to the emission of toxic hydrogen sulfide (H_2S) gas [50][51].

3.2. Argyrodites

The initial discovery of these sulfide-based electrolytes can be traced back to the compound argyrodite Ag_8GeS_6 [52]. Substituting silver (Ag) with lithium (Li) led to the formation of lithium-based argyrodites, specifically Li_6PS_5X (where X represents Cl, Br, and I) [52], as depicted in **Figure 4**. There has been significant research and development in the field of argyrodites. For instance, the chlorine variant of argyrodite, Li_6PS_5Cl, demonstrates a lithium-ion conductivity of approximately 2 mS cm^{-1} at ambient temperature [53]. This conductivity rate can be enhanced through various substitutions, such as in $Li_{5.5}PS_{4.5}Cl_{1.5}$, which shows a conductivity rate of nearly 9 mS cm^{-1} at room temperature [54].

Argyrodites are increasingly recognized as one of the leading candidates for solid-state electrolyte materials in commercial applications. However, key challenges include overcoming interface resistances, poor mechanical strength, and managing decomposition at the solid electrolyte (SSE)–electrode interface [55].

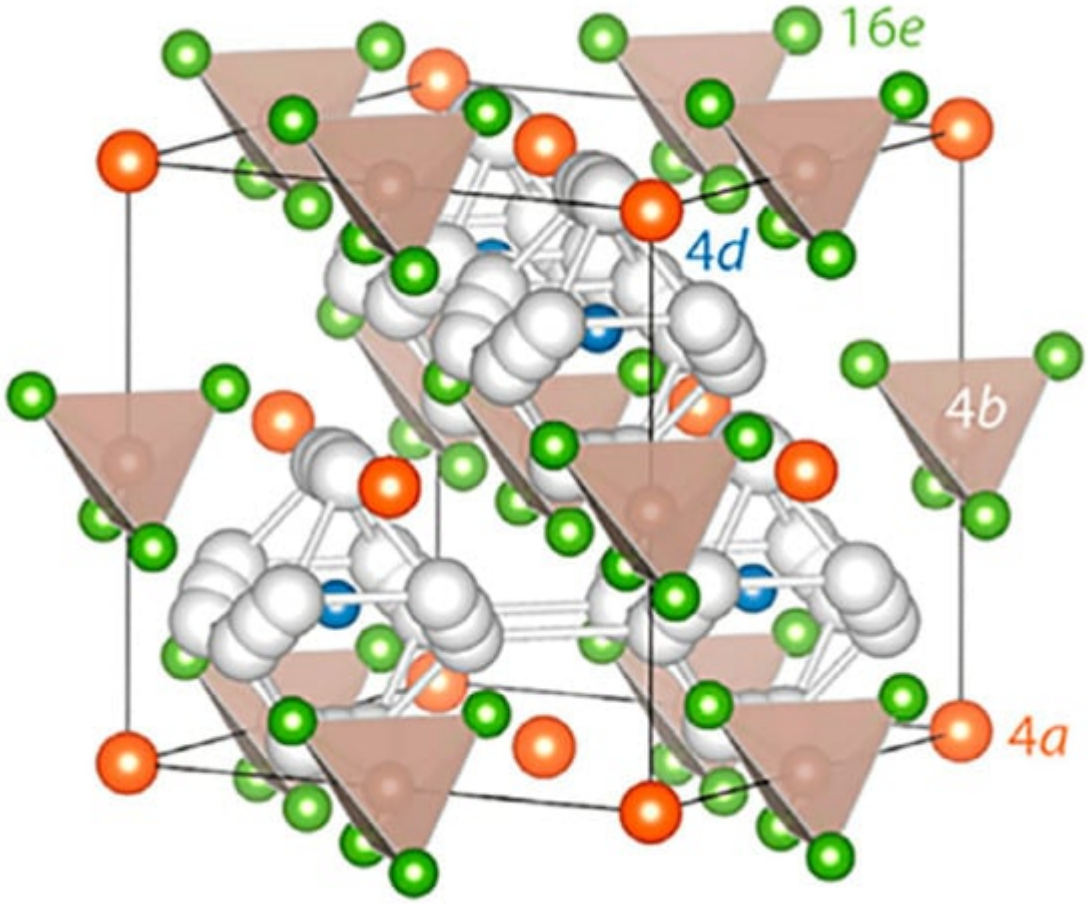


Figure 4. The crystal structure of Li-based argyrodites. Reprinted with permission from ref. [56]. Copyright 2023, John Wiley & Sons.

4. Polymer Electrolytes

Polymer solid electrolytes (PEs) serve as a transitional technology, bridging the gap between liquid electrolytes and solid-state alternatives. These polymers are composed of repeating units, or monomers, forming extensive molecular chains. Each polymer-based solid electrolyte is characterized by a polymer framework that encapsulates dissolved lithium salts, with the electrochemical behavior governed by the polymeric chain, facilitating Li^+ ion movement within the solid structure. PEs closely resemble liquid electrolytes in their semicrystalline or completely amorphous nature at room temperature, making them suitable for battery applications [57].

PEs are comprised of three primary components: an organic polymer matrix, lithium salt, and various additives, including inorganic functional materials. The matrix plays a crucial role in maintaining the structural and mechanical integrity of the electrolyte system [58]. Essential attributes of the polymer matrix include the mechanical robustness, ionic conductivity, and stability, both thermally and chemically, alongside its ability to dissolve lithium salts [59][60][61]. Choosing the appropriate polymer for the matrix is vital due to the varying mechanical, thermal, and chemical properties of different polymers. Common polymers used include polyethylene oxide (PEO), polyvinylidene fluoride (PVDF), and polyethyleneimine (PEI) [59]. In PEO-based electrolytes, the preferred lithium salt is $LiN(CF_3SO_2)_2$,

also known as LiTFSI. This salt is favored for its effectiveness in reducing the crystallinity of PEO, thereby enhancing the ionic conductivity within the polymer–salt matrix [62]. Important characteristics for lithium salts include low lattice energy to facilitate ion-pair separation, along with chemical and thermal stability, and cost-effectiveness. Certain novel lithium salts have shown conductivity greater than 1 mS cm^{-1} when combined with PEO at ambient temperature [63][64].

Additives in PEs are utilized to enhance the mechanical properties or to inhibit the crystallization of the polymer–salt matrix, particularly at lower temperatures, thus promoting greater ionic conductivity. For instance, nanofillers are advantageous in increasing salt dissociation, minimizing anion movement [65], and enhancing interface stability with the lithium anode. Active nanofillers, like γ-$LiAlO_2$, aid in lithium-ion conduction, while passive fillers, such as Al_2O_3, SiO_2, or carbon particles, have diverse roles [66][67].

Ionic liquids, molten salts with a melting point below 100 °C, such as PyrxTFSI [68], show promise in enhancing ionic conductivity, and mechanical and thermal stability in polymer–salt complexes. Although their high cost poses a challenge for widespread use, these liquids contribute significantly to the stability of the solid electrolyte interface (SEI) on electrodes, thus reducing gas generation and the interface area. While further optimization to reduce interfacial resistance is required, ionic liquids are considered a promising direction for significant improvements in the performance of polymer electrolytes in the medium term.

Efforts to improve the relatively low ionic conductivity of polyethylene at room temperature have been extensive. Research has focused on methods like diminishing polymer crystallization by adding inorganic fillers. **Figure 5** [69] offers a concise overview of the evolution of polymer electrolytes. Poly(ethylene oxide) [60] has been the most studied polymer in this context due to its ability to coordinate its multiple oxygen atoms with Li-ions, effectively facilitating ion conduction within the matrix. Ion transport primarily occurs in PEO's amorphous regions via the polymer chains. These chains are crucial for both ion conductivity and the mechanical properties of the material. It has been observed that adjusting the proportion of two different liquid crystalline monomers, each with varying methylene chains linked to a rigid core and terminal acrylate groups, can significantly enhance PEO's electrochemical properties [70]. This adjustment creates efficient ion transport channels in the porous polymer network, improving both the structural integrity and ion conductivity.

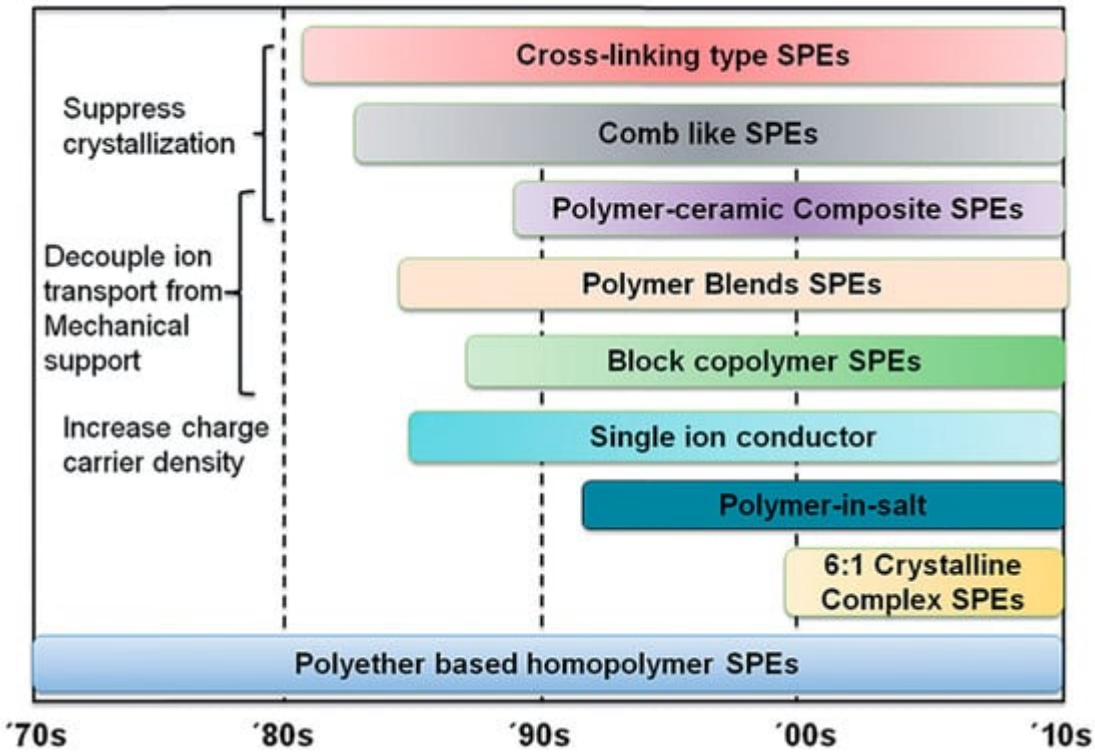


Figure 5. Overview of the evolution of solid polymer electrolytes over the past forty years. Reprinted with permission from ref. [69]. Copyright 2015, Royal Society of Chemistry.

However, PEO's high crystallinity at room temperature impedes polymer segmental motion and Li-ion movement, leading to relatively low conductivity (approximately 10^{-8} to 10^{-5} S cm^{-1} at room temperature) [71]. Additionally, the mechanical weakness of PE in its solid state is insufficient to physically block the hazardous penetration of lithium dendrites at elevated temperatures or high current densities, a crucial aspect for industrial or commercial applications. To overcome these challenges, additives are employed to boost the ionic conductivity and polymeric design strategies have been explored [72] to enhance the mechanical strength (see **Figure 6**).

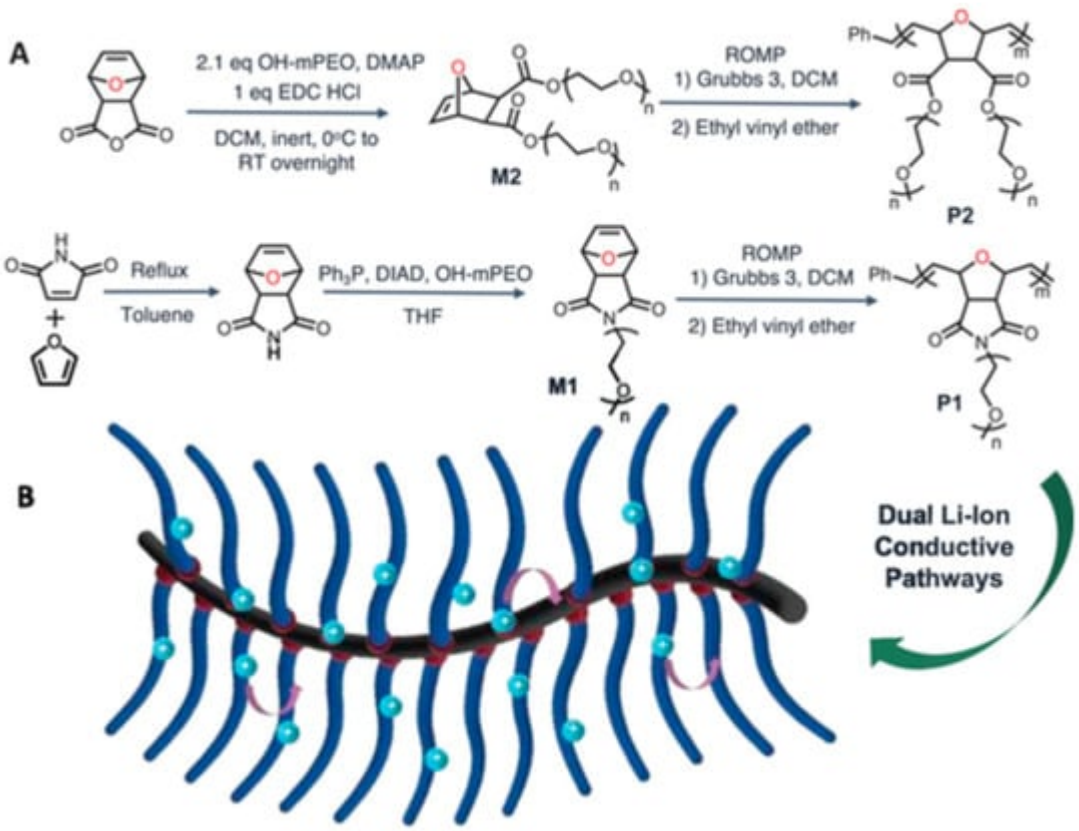


Figure 6. Synthesis of bottlebrush-type polymers (**A**) and a diagram illustrating bottlebrush polymer electrolytes (**B**), highlighting the dual movements of Li-ions. Reprinted with permission from ref. [72]. Copyright 2023, John Wiley & Sons.

In summary, polymeric materials offer several advantageous features, including low flammability, ease of processing, and electrochemical stability. They provide better mechanical resilience to electrode deformation compared to liquid alternatives and allow for more flexible interfacial contact with electrodes than other solid-state options. Despite these benefits, important areas for improvement remain, such as increasing Li-ion conductivity (enhancing Li-ion transport number) to counteract polarization caused by anion migration and bolstering the mechanical strength to prevent lithium metal dendrite formation.

5. Halide Electrolytes

Halide solid-state electrolytes are considered top contenders for advancing all-solid-state battery technology, largely due to the unique chemical attributes of halogen anions [73]. Key advantages include the weaker coulombic interaction between monovalent halogen anions and lithium ions, leading to faster Li-ion transport and higher ionic conductivity [74][75]. Additionally, the larger ionic radii of halogen anions result in longer ionic bond lengths, which are expected to enhance ion mobility and deformability [74]. Another benefit is the higher electrochemical redox potential of halide anions, particularly fluorine and chlorine, contributing to greater oxidative stability [76]. Despite these promising features, halide SSEs, explored since the 1930s, initially faced challenges like low ionic conductivity at room temperature, limiting their widespread application [76]. Metal halide superionic conductors, with

a general formula of Li_3MX_6 (where M is a trivalent rare-earth metal, and X is F, Cl, Br, or I), typically have a crystallographic structure based on the LiX matrix [77]. This structure is achieved through doping with M elements and forming vacancies. The stability of these structures depends on the close contact between cations and anions, governed by their ionic radii, polarity, and packing styles. For fluoride SSEs, most structures form a $LiMF_4$ phase due to the radius ratio of M^{3+}/F^- being greater than 0.73. While fluoride SSEs offer a wide electrochemical window, their ionic conductivity at room temperature is generally low [77]. In contrast, chloride, bromide, and iodide superionic conductors usually form a stable Li_3MX_6-type structure with MX_6 octahedral coordination, as their radius ratio falls between 0.41 and 0.73 [77]. Understanding the relationship between structure and performance is key, especially for fluoride SSEs, which require more research to enhance their ionic conductivity. Among the limitations of metal halide superionic conductors, a notable issue is their high sensitivity to moisture due to significant hygroscopicity [78]. This leads to the absorption of water molecules from the environment, resulting in their degradation. In a study by Wang et al. [79], the air stability of Li_3InCl_6 and Li_3YCl_6 was investigated, particularly focusing on their degradation mechanisms when exposed to air. Li_3InCl_6 showed a faster water absorption rate compared to Li_3YCl_6, but Li_3YCl_6 absorbed more water overall due to $InCl_3$'s higher solubility than YCl_3. The stability of these compounds is influenced by their exposure area to air. Additionally, it was found that Li_3InCl_6 partially reacts with H_2O, while some of it absorbs moisture to become hydrated [80]. The study also indicated that, in dry conditions with low humidity, the ionic conductivity decay of Li_3InCl_6 is slow, suggesting its potential integration in SSB manufacturing in controlled dry environments.

Different synthesis methods, like mechanochemical and wet-chemistry synthesis, have gained prominence in the field of solid-state electrolytes (SSEs), particularly due to their scalability and potential for mass production [81][82]. These methodologies are critical in overcoming some of the common production barriers in SSE development. The challenges in this domain are multifaceted, with moisture sensitivity and anode instability being prominent issues. To mitigate these problems, innovative solutions like atomic layer deposition coatings and interface buffers have been introduced [81]. These advancements are crucial for enhancing the stability and efficacy of SSEs in high-energy-density applications.

The development of fluoride-based halide solid-state electrolytes (SSEs) is a significant area of focus, considering their potential to enable high-capacity batteries [83]. The pursuit of environmentally friendly and cost-effective synthesis routes is also pivotal for the advancement and commercialization of these materials. Addressing moisture sensitivity and anode instability remains a critical challenge, underscoring the need for continued research and innovation in this field. The evolution of SSEs towards addressing these key areas will be instrumental in realizing their full potential in next-generation energy storage technologies.

6. Composite Electrolytes

Ceramic fast-ion conductors are known for their high ionic conductivities, which exceed 10^{-4} S cm^{-1} [41][73]. However, they face significant challenges in processing and exhibit poor chemical and mechanical properties at the electrode/electrolyte interfaces. These limitations pose a considerable constraint on their practical application in battery technology. In contrast, polymer electrolytes are advantageous due to their flexibility and ease of

processing. Nonetheless, they are limited by low ionic conductivities at room temperature, generally falling within the range of 10^{-6} to 10^{-7} S cm^{-1} [84]. This low conductivity substantially affects their utility in battery applications.

The combination of these two elements—ceramic fast-ion conductors and polymer electrolytes—into what is termed composite electrolytes (CEs) represents a promising approach that aims to capitalize on the synergistic benefits of both components, effectively overcoming their individual drawbacks [85]. By selecting the right ceramic filler and polymer, CEs can be customized to improve their overall performance in solid-state batteries [85].

CEs can be broadly categorized into two primary types [86]: (a) those composed of inorganic nanoparticle/polymer combinations (INPCs) and (b) those made up of inorganic nanofiber/polymer structures (INFPCs). In the realm of INPC solid electrolytes, the incorporation of inorganic nanofillers, like SiO_2, Al_2O_3, and TiO_2, into polymer matrices has been a focal point of research [87]. The rationale behind this approach lies in the enhancement of the mechanical strength, ionic conductivity, and interfacial stability in the resulting polymer solid electrolytes [88]. A critical element in these composites is the role of the particle size of the inorganic fillers in influencing the electrolyte's ionic conductivity. It has been observed that smaller particles are more beneficial, acting as solid plasticizers at the nanoscale [89]. This role plays a crucial part in preventing the crystallization of the polymer matrices, thereby facilitating improved ionic transport within the composite. Moreover, the surface area of these nanoparticles, dependent on their size and quantity, is clearly related to the interfacial conductivity of the composites. Thus, the proportion of nanoparticles to polymer is a key factor in adjusting the ionic conductivity of these composite electrolytes. In this context, a notable example of INPC research is exemplified by the study conducted by Wang et al. [90]. This study was designed to assess the impact of different nanoparticle types on the ionic conductivity of polyethylene oxide/lithium perchlorate (PEO/$LiClO_4$)-based composite solid electrolytes. The nanoparticles evaluated included $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP) as an active filler, and titanium dioxide (TiO_2) and silica nanoparticles as passive fillers. The findings from this research indicated a superior cation transport in composites containing LATP compared to those with passive fillers, like TiO_2 or silica. Notably, in certain scenarios, such as the composite formulated with 10 wt.% LATP nanoparticles, the ionic conductivity achieved was remarkable, reaching 1.7×10^{-4} S cm^{-1}. This study underscores the significant role that the type of nanoparticle filler can play in enhancing the ionic conductivity of composite solid electrolytes.

Although there has been progress in developing INPC electrolytes, their ionic conductivities are not high enough for advanced lithium batteries that require high energy and power. A major problem with these composites is that Li^+ ions have to move through many particle junctions, which slows down their movement. In response to this challenge, a second type of composite electrolyte has emerged, known as an inorganic nanofiber/polymer composite (INFPC), which uses nanofibers instead of nanoparticles. By incorporating a continuous network of inorganic nanofibers into the polymer matrix, the number of junctions is significantly reduced, leading to smoother and uninterrupted pathways for ionic transport. This not only provides steady channels for Li^+ ions but also prevents the polymer from crystallizing, improving the breakdown of lithium salts and enhancing ion movement within the composite. Liu et al. [91] successfully incorporated electrospun lithium lanthanum titanate ($Li_{0.33}La_{0.557}TiO_3$ or LLTO) nanowires into a polyacrylonitrile (PAN)–$LiClO_4$ polymer composite. These evenly spread LLTO nanowires created a three-dimensional network for ion conduction within the polymer, greatly

increasing ionic conductivity, which was mainly due to the quick movement of ions along the surfaces of these ceramic nanowires. Similarly, Fu et al. [92] created a composite with garnet-type $Li_{6.4}La_3Zr_2Al_{0.2}O_{12}$ (LLZO) nanofibers and PEO. These LLZO nanofibers, recognized for their high ionic conductivity and stability, were merged into the PEO matrix, forming a continuous network for lithium-ion conduction, and demonstrating high ionic conductivity.

7. Hybrid Solid Electrolyte–Liquid Electrolyte

In solid-state batteries, SEs are confronted with significant challenges, notably their relatively low ionic conductivity at ambient temperatures [93]. This impediment hampers efficient ion transport, undermining the overall performance of the battery. Compounding this issue, SEs often struggle to maintain robust interfacial contact with electrodes [94]. This inadequate contact can lead to increased resistance, negatively impacting battery efficiency. The interface between SEs and electrodes is critical; poor interfacial compatibility can result in uneven current flow and localized material degradation [94]. Additional concerns include dendrite formation, mechanical instabilities, and chemical reactivity at the electrolyte–electrode interface [95]. Addressing these challenges, the concept of hybrid solid–liquid electrolyte (SLE) systems emerge as a promising solution. These systems blend the high ionic conductivity of liquid electrolytes (LEs) with the structural integrity and safety offered by SEs. The goal is to create a synergistic effect: the liquid component mitigates interfacial resistance, enhancing ion transport, while the solid matrix contributes to overall stability and safety [96]. This innovative approach is anticipated to curb the issues of dendrite formation and mechanical stability, which are prevalent in conventional electrolytes. In general, the advantages offered by these hybrid SLE systems are multifaceted. Incorporating a liquid component within the solid electrolyte matrix leads to enhanced ionic conductivity, particularly beneficial at lower temperatures, thus optimizing the battery's performance [96]. Furthermore, this hybridization fosters more efficient interfacial contact with the electrodes, ensuring a more consistent current distribution and minimizing the risk of localized degradation. The mechanical robustness of these systems also surpasses that of pure liquid electrolytes, significantly reducing the risks associated with leakage and flammability [96]. By amalgamating the benefits of both solid and liquid electrolytes, hybrid SLE systems stand out as a highly promising avenue for advancing the development of safer and more effective solid-state batteries. In this regard, the study by Vivek et al. [97] focused on how the water content and other additives affect the formation and resistance of solid–liquid electrolyte interfaces (SLEIs) in Ohara Li_2O–Al_2O_3-TiO_2-P_2O_5 (LATP) glass solid electrolytes and different lithium liquid electrolytes. They found that adding water to the liquid electrolytes can significantly lower the resistance to ion conduction at the solid/liquid interface [97]. The analysis revealed that SLEIs are composed of a mix of inorganic and organic compounds, similar to those in solid electrolyte interphases (SEIs). The research suggests potential benefits of using solvent additives in hybrid electrolyte systems to reduce resistance, although the exact mechanisms behind this effect are not yet fully understood [97]. In other study by Gupta et al. [98], the role of additives and lithium salts in liquid electrolytes was analyzed using Ta-doped Li_7-$La_3Zr_2O_{12}$ garnet oxide (LLZTO) and acetonitrile as a solvent. The study focused on lithium salts, like LiTFSI, LiBOB, and $LiPF_6$, exposing LLZTO to these salt solutions and monitoring the impedance. It was found that all systems displayed increasing interfacial resistance over time, with significant variations among different salt systems [98]. Further analysis using X-ray photoelectron spectroscopy indicated chemical reactions between

LLZTO and the salts, influencing the solid–liquid electrolyte interface (SLEI) formation. The study concluded that the formation of the SLEI is predominantly driven by the lithium salts in the LE rather than the solvent [98]. Hatz et al. [99] investigated the stability of the sulfide superionic conductor tetra-Li_7SiPS_8 (LiSiPS) against a range of solvents, spanning from protic polar to aprotic nonpolar types. They found that, while LiSiPS remains stable in aprotic solvents, it decomposes into oxygen-substituted thiophosphates in water and into oxygen-substituted thioethers in alcohols [99]. The study also revealed that LiSiPS maintained high ionic conductivity in solvents, such as p-xylene, anisole, and acetonitrile. Additionally, LiSiPS was shown to be capable of tolerating up to 800 ppm of residual water in solvents, with anisole used to demonstrate this resilience.

In summary, hybrid solid–liquid electrolytes offer a promising approach to addressing the issues of interfacial and cell resistance that have limited the effectiveness of solid electrolytes in supplanting traditional liquid ones. While these hybrid systems hold potential for use in future energy storage devices, several obstacles still need to be overcome to fully realize their applicability. Continued research and development could significantly enhance their viability as a practical solution.

8. Progress, Challenges, and Prospects in Solid Electrolytes

The field of solid electrolytes has seen significant strides due to innovations in materials and fabrication methods. Researchers have been exploring a variety of new materials, including ceramics, polymers, and composites, for their potential in solid-state batteries. These materials offer advantages like better stability and safety compared to traditional liquid electrolytes. Advances in fabrication methods have also been pivotal. Techniques such as thin-film deposition, sintering, and advanced lithography have enabled the production of solid electrolytes with improved structural integrity and enhanced electrochemical properties. Particularly, within the realm of oxide and sulfide electrolytes, it is only the oxide class that provides comparatively broad electrochemical stability windows, facilitating their use with high-voltage cathodes to achieve batteries with enhanced power and energy densities [100]. Nonetheless, oxide-based solid electrolytes encounter a trio of significant obstacles: their inherent brittleness and suboptimal mechanical characteristics, a constrained compatibility with prevailing cathode chemistries, and a tendency to have greater densities than other electrolyte categories, impacting the net gravimetric energy density adversely. Notably, these solid electrolytes need to be fabricated as slender ion-conducting layers and as ceramic separators for electrodes in SSBs [100]. Nevertheless, the method of thin-film growth presents serious challenges in SSBs. Planar thin-film batteries (TFBs) are significantly constrained in terms of total capacity due to the relatively limited electrode volume available for energy storage [101]. This limitation arises from the impracticality of utilizing thicker electrode films to increase capacity because of kinetic constraints. In contrast, traditional battery designs allow for an increase in electrode volume and, correspondingly, in capacity by enhancing the overall thickness of the slurry-coated particle composite layer [101]. This enhancement leads to an increase in the active material's "mass-loading". In such designs, the electrolyte solution infiltrates the porous composite electrode layer, while an electronic additive, like carbon black, ensures electronic connectivity throughout the electrode [101]. To enhance the storage capacity of TFBs without making the electrode films thicker, it is possible to carry out the deposition of the battery components onto a specially structured substrate, thereby expanding the surface area available for energy

storage [101]. The design of 3D TFBs hinges on two key factors: the area enhancement factor (AEF), which is the ratio of the 3D structure's effective surface area to its footprint area, and the open volume of the 3D substrate, which is the space available for the battery stack. A higher AEF means more capacity per unit of footprint, but there is a trade-off with the open volume, as a larger open volume could reduce the AEF [101]. This concept is clarified in the diagram shown in **Figure 7**.

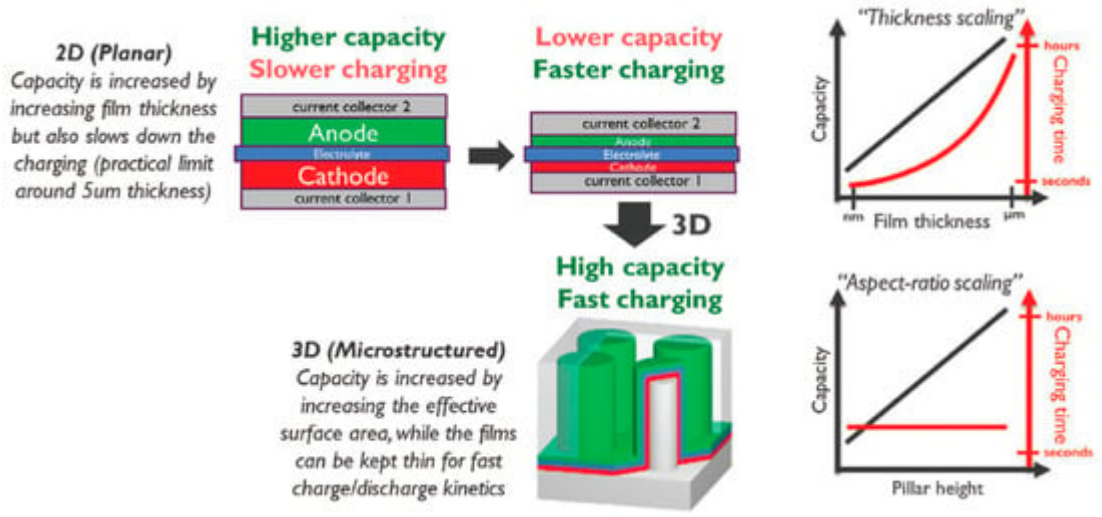


Figure 7. TFBs (planar) and 3D TFBs properties. Reprinted with permission from ref. [101]. Copyright 2019, Advanced Materials Interfaces.

Advances in thin-film techniques have been significant in recent years. Thus, in contrast to the complexity of 3D TFB systems, Sahal et al. [102] had recently investigated the development of a novel SSE using a perovskite-structured material: polycrystalline lithium lanthanum titanate, $Li_{0.3}La_{0.56}TiO_3$ (LLTO). This development aimed to address the common limitations in current SSEs, especially in terms of energy density and processability. LLTO was synthesized through a rapid, high-throughput, open-air process, completed in just one minute [102]. The resulting material consisted of polycrystalline LLTO, with selectively retained crystalline precursor phases and exceptional mechanical properties, such as flexibility and high fracture toughness. These characteristics were attributed to the enhancement in the grain boundaries and a reduction in the crystallinity, resulting from the ultrafast processing method [102].

Other advanced solid-state electrolyte (SSE) manufacturing procedures, such as sintering, have been extensively studied in recent years. In this regard, Li et al. [103] explored the development of a NASICON-type $Na_3Zr_2Si_2PO_{12}$ (NZSP) ceramic electrolyte utilizing NaBr-assisted sintering. This process improved the electrolyte's ionic conductivity and its compatibility with the anode, demonstrating the effectiveness of the NaBr sintering aid in lowering sintering temperatures and achieving a denser NZSP structure, leading to enhanced electrical performance and mechanical strength [103]. In another study, Lin et al. [104] developed a cleaning method and a low-temperature sintering process that allowed for the synthesis of $Li_{0.33}La_{0.55}TiO_3$ (LLTO) with good ionic conductivity and phase stability. Generally, the common element across sintering methods for SSE fabrication is the utilization of high temperatures. However, despite the existence of procedures that significantly lower the treatment

temperature [103][104], there is a pressing need to aim for more ambitious goals involving substantially lower treatment temperatures [31]. Alternatively, methods that curtail lengthy processing times are required, as extended processing can lead to severe Li loss and the formation of secondary phases that modify the overall behavior of the material, impacting its porosity and ionic conductivity. In this regard, Ramos et al. [105] developed an innovative ultrafast sintering method using a CO_2 laser in combination with a heating stage. This technique proved effective in rapidly densifying $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ (LLZTO) films, which are typically challenging to densify with conventional furnace sintering methods. The approach was characterized by several notable aspects, including a significant reduction in lithium loss due to the rapid sintering process, anisotropic shrinkage behavior that considerably reduced the film thickness, and a wave-like surface topology that enabled 3D interfacial contacts with electrode materials. The LLZTO films produced through this new procedure exhibited high density (>95%) and high conductivity (0.26 mS cm^{-1} at 25 °C), making this synthesis method highly promising for future developments in SSBs.

In addition to the already described solid-state electrolyte (SSE) synthesis procedures, nanolithography has emerged as an interesting option that has been extensively developed in recent years. Stereolithography (SLA) uses a laser to cure photosensitive resins layer by layer, producing parts with very high resolution [106]. However, the choice of materials is limited to those that can be photocrosslinked. This technique has enabled the synthesis of some SSEs, particularly solid polymer electrolytes (SPEs), inorganic solid electrolytes (ISEs), and composite solid electrolytes (CSEs) [107][108][109]. Another procedure similar to SLA is digital light processing (DLP) [110], which uses a digital light projector to cure photosensitive resins. DLP can print faster than SLA, as it cures an entire layer at once, making it suitable for scalable production. However, like SLA, it is limited to photopolymerizable materials. SLA and DLP methods allow for the creation of microstructures that can enhance the performance of solid electrolytes, such as by creating shorter lithium-ion transport paths or improving the interfacial contact between the electrolyte and the electrodes [106]. Regardless of their complexity, these techniques could potentially become a means of custom SSE fabrication for highly specific applications in the future.

In light of the diverse synthesis strategies for solid-state electrolytes (SSEs) discussed earlier, the researchers recognize a broad spectrum of approaches, each offering unique benefits and facing distinct challenges. Some of these processes, however, confront specific hurdles, such as effectively manufacturing SSEs sensitive to air and moisture, achieving high-resolution in the manufacturing process, and tackling various post-treatment complications. These challenges underscore the complexity and precision required in the field of SSE manufacturing. Moreover, it is important to note that, while these advanced techniques present novel opportunities, they also bring forth issues, such as compatibility with existing materials and scalability for industrial applications. This suggests that a one-size-fits-all approach may not be feasible, and a more tailored strategy might be necessary for different types of SSEs. Given these considerations, a potentially promising direction could be the integration of these modern synthesis techniques with more traditional methods. Such a hybrid approach might combine the strengths of both advanced and conventional practices, potentially leading to more robust, efficient, and versatile manufacturing processes. This integration could enable the utilization of the precision and customization offered by newer methods while leveraging the established reliability and scalability of traditional

manufacturing processes. As a preliminary reflection, this integration not only seems desirable but might also be essential in advancing the field of SSE manufacturing towards more practical and wide-ranging applications.

In addition to experimental techniques for preparing SSEs, it is essential to emphasize the importance of complementary tools to purely experimental approaches, such as simulation techniques [111]. In this regard, computational chemistry stands as a pivotal tool in the realm of material science, particularly in the advancement and development of new materials for use as solid-state electrolytes (SSEs) [112]. This field has seen a variety of SSEs, encompassing polymers, oxides, sulfides, and halides. Among these, sulfide-based SSEs are distinguished for their markedly higher ionic conductivities in comparison to alternatives like organic polymers, oxides, and halides, positioning them as particularly promising candidates for next-generation battery technologies [113]. The role of computational chemistry extends beyond mere identification and classification of materials. It plays a critical role in the study and simulation of the dynamical properties of these electrolytes, which is essential for understanding and optimizing their performance [114][115]. This involves a detailed statistical analysis of ion diffusion events within these materials. By quantifying key parameters, such as ionic diffusivity, ionic conductivity, and the activation energy barriers, computational studies provide deep insights into the fundamental mechanisms that govern the behavior of SSEs. Moreover, these computational approaches enable researchers to model and predict the performance of these materials under various conditions, thus aiding in the design of more efficient and effective electrolytes. This theoretical understanding is instrumental in guiding experimental efforts, helping to streamline the process of material development and optimization. Furthermore, computational chemistry facilitates the exploration of the interactions between different components of solid-state batteries, such as the interface between the SSE and the electrodes. Understanding these interactions is crucial for improving the overall stability and efficiency of the batteries. In summary, computational chemistry is not just a tool for material discovery but is integral to the comprehensive understanding and refinement of SSEs. Its applications span from the atomic-level analysis of material properties to the practical considerations of battery design and performance, making it an indispensable component of modern material science research in the field of energy storage.

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