

Review

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Review

Advancements and Challenges in Solid-State Battery Technology: An In-Depth Review of Solid Electrolytes and Anode Innovations

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Abstract: The primary goal of this review is to provide a comprehensive overview of the state-of-the-art in solid-state batteries (SSBs), with a focus on recent advancements in solid electrolytes and anodes. The paper begins with a background on the evolution from liquid electrolyte lithium-ion batteries to advanced SSBs, highlighting their enhanced safety and energy density. It addresses the increasing demand for efficient, safe energy storage in applications like electric vehicles and portable electronics. A major part of the paper analyzes solid electrolytes, key to SSB technology. It classifies solid electrolytes as polymer-based, oxide-based, and sulfide-based, discussing their distinct properties and application suitability. The review also covers advancements in anode materials for SSBs, exploring materials like lithium metal, silicon, and intermetallic compounds, focusing on their capacity, durability, and compatibility with solid electrolytes. It addresses challenges in integrating these anode materials, like interface stability and lithium dendrite growth. This review includes a discussion on the latest analytical techniques, experimental studies, and computational models to understand and improve the anode-solid electrolyte interface. These are crucial for tackling interfacial resistance and ensuring SSBs' long-term stability and efficiency. Concluding, the paper suggests future research and development directions, highlighting SSBs' potential in revolutionizing energy storage technologies. This review serves as a vital resource for academics, researchers, and industry professionals in advanced battery technology development. It offers a detailed overview of materials and technologies shaping SSBs' future, providing insights into current challenges and potential solutions in this rapidly evolving field.

Keywords: solid-state batteries; cathode materials; energy density

1. Introduction

1.1. Contextualizing the Shift to Solid-State Energy Storage

The development of energy storage technologies has been crucial for advancing contemporary technological capabilities, significantly contributing to the evolution of sustainable energy systems [1,2]. Throughout history, energy storage has undergone different phases, each marked by innovations that progressively improved the efficiency, safety, and environmental impact of these systems. Currently, we are observing a notable transformation in this field — a shift towards solid-state energy storage. This transition, highlighted by the development and deployment of solid-state batteries (SSBs), represents not only a technological advancement but also addresses the increasing global demand for more efficient, safer, and environmentally friendly energy solutions [3–5].

This shift is driven by two primary factors. First, there is a growing recognition of the limitations inherent to traditional energy storage systems, especially those using liquid electrolytes, such as the used in lithium-ion batteries [6,7]. These limitations encompass concerns about safety, energy density, and long-term stability. Second, there has been substantial progress in the field of materials

science, offering new avenues to surmount these limitations [6]. The emergence of novel materials and innovative fabrication techniques has been crucial in the exploration and development of solid-state energy storage systems [5].

SSBs are at the forefront of this technological shift [8]. Contrary to their liquid-based counterparts, SSBs use solid electrolytes, which may offer higher energy densities—a vital attribute for applications spanning from consumer electronics to electric vehicles [5]. Additionally, the solid-state configuration inherently reduces many safety risks associated with liquid electrolytes, such as leakage and flammability [8]. This feature is significant in the context of large-scale energy storage where safety is of utmost importance. Furthermore, solid electrolytes could enable the use of more chemically stable and durable electrode materials, thereby enhancing the lifespan and efficiency of the batteries [9].

In this review, our goal is to emphasize the transition from liquid-based systems to solid-state ones, outlining the technological and scientific developments that have driven this change. We will explore key factors prompting this shift, including the growing need for more efficient energy storage across various sectors, the limitations of existing technologies, and the advancements in materials science enabling this evolution. While this review covers a broad range of complex systems, our aim is to provide a thorough understanding of the paradigm shift in energy storage technologies. We focus on the most pertinent concepts and lay the groundwork for discussing the materials and mechanisms that shape the current and future landscape of solid-state energy storage systems.

1.2. The Constraints of Liquid Electrolyte Lithium-Ion Batteries

In the changing landscape of energy storage technologies, liquid electrolyte lithium-ion batteries (LE-LIB) have become the predominant choice, powering everything from portable electronic devices to electric vehicles [10]. Their widespread adoption can be attributed to their high energy density, relatively good cycle life, and decreasing cost due to economies of scale [11]. However, as we venture into an era where the demands on energy storage are more stringent, the limitations of LE-LIBs become increasingly pronounced [9,10]. The constraints of LE-LIBs are multifaceted, encompassing safety, performance, and environmental concerns. The liquid organic electrolytes used in these batteries are flammable, posing significant safety risks such as thermal runaway—a condition where the battery's internal temperature and pressure rise to the point of combustion [12]. This risk is exacerbated by the potential for dendrite formation during the charging process, which can lead to short circuits and, consequently, fires or explosions [12,13]. Performance limitations also present a considerable challenge. The ionic conductivity of liquid electrolytes is highly temperature-dependent, which can result in reduced battery performance in extreme temperature conditions [10]. At low temperatures, the increased viscosity of the electrolyte can lead to a marked decrease in conductivity, while high temperatures can cause the electrolyte to degrade [10]. This degradation not only impairs the battery's performance over time but also limits its lifespan. Moreover, the reliance on liquid electrolytes restricts the choice of electrode materials to those that are stable within the electrolyte's operating window. This limitation hinders the development of high-voltage cathodes and anodes that could potentially increase the energy density of the battery [14,15]. The compatibility of the electrolyte with the electrode material is a critical factor in the stability and capacity retention of the battery, and finding suitable combinations of materials remains a significant challenge.

The environmental impact of LE-LIBs is another area of concern [16]. The extraction of lithium, cobalt, and other raw materials has substantial environmental and social implications [17]. Additionally, the liquid electrolytes often contain volatile organic compounds (VOCs), which have a high global warming potential and can present health hazards if not handled properly [16]. The end-of-life disposal of LE-LIBs poses further environmental challenges, as the recycling processes for these batteries are not yet fully sustainable or economical [16].

In light of these constraints, there is a growing interest in alternative energy storage materials and technologies that can overcome the limitations of LE-LIBs. SSBs emerge as a promising candidate, offering the potential for higher safety, improved performance across a wider temperature range, and better environmental compatibility [18,19]. The transition to solid-state electrolytes in SSBs could

enable the use of more reactive electrode materials, further increasing the energy density and expanding the operating voltage window [20].

1.3. Advancements and Concepts of Solid-State Batteries (SSBs)

Solid-state batteries (SSBs) represent a significant advancement in energy storage technology, marking a shift from liquid electrolyte systems to solid electrolytes. This change is not just a substitution of materials but a complete re-envisioning of battery chemistry and architecture, offering improvements in efficiency, durability, and applicability [19]. At the core of SSBs are solid electrolytes made of ceramic, polymer, glass, or sulfide materials, facilitating lithium-ion transport between the anode and cathode without the risks associated with liquid electrolytes, such as volatility and combustibility [19]. This solid medium not only enhances safety but also allows for the use of lithium metal as an anode, offering a higher theoretical capacity and a stable interface that prevents dendritic growth [21].

The solid-state design of SSBs leads to a reduction in the total weight and volume of the battery, eliminating the need for certain safety features required in liquid electrolyte lithium-ion batteries (LE-LIBs), such as separators and thermal management systems [4,19]. This compactness is particularly beneficial for electric vehicles (EVs), where space and weight savings are crucial. Additionally, solid electrolytes in SSBs are more stable and degrade less under cycling conditions, contributing to a longer lifespan and slower decline in battery capacity over time [9]. Research in this field has led to the discovery of materials with exceptional ionic conductivities, rivaling or surpassing those of liquid counterparts [9].

The manufacturing processes for SSBs have also evolved, with new techniques ensuring uniformity and quality in large-scale production [22,23]. This scalability is vital as the demand for advanced energy storage systems increases with global electrification efforts [24,25]. In terms of sustainability, SSBs have a more environmentally friendly lifecycle, with solid components being generally more stable, less reactive, and potentially less hazardous than the volatile organic compounds in liquid electrolytes [27–29].

The fundamental principle of SSBs lies in replacing the conventional liquid electrolyte with a solid one, transforming the battery's structure for enhanced performance and safety [28]. The solid electrolyte functions similarly to its liquid counterpart in traditional batteries but is made from non-flammable materials that facilitate ionic conduction while preventing short-circuiting [28]. The interaction between the solid electrolyte and electrodes is crucial, as any incompatibility can lead to increased resistance and decreased performance [29]. The possibility of using lithium metal as an anode in SSBs mitigates risks associated with dendrite formation and unlocks the potential for higher energy density [21,30]. The design of SSBs also allows for a more compact and versatile form factor, suitable for integration into various devices [21,30]. The solid electrolyte must be both ionically conductive and mechanically robust, adding complexity to the design of SSBs [31].

In summary, the development of SSBs is a transformative leap forward, redefining the boundaries of energy storage with an innovative and superior alternative that aligns with contemporary and future energy requirements.

1.4. Advantages Relative to Conventional Battery Technologies

SSBs represent a new era in energy storage, bringing with them a suite of advantages over traditional LE-LIBs. These advantages are not merely incremental improvements but rather transformative features that redefine the capabilities of battery technology. Broadly speaking, the main advantages could be summarized as:

Enhanced Safety: The most important advantage of SSBs is their improved safety profile. The absence of flammable liquid electrolytes in SSBs dramatically reduces the risk of fires and explosions, a concern that has been a lingering shadow over LE-LIBs [20]. This safety feature is particularly crucial in applications where battery failure can have dire consequences, such as in electric vehicles and large-scale energy storage systems.

Increased Energy Density: SSBs offer the potential for higher energy densities compared to LE-LIBs. This is partly due to the possibility of using lithium metal anodes, which have a higher capacity than the graphite anodes typically used in LE-LIBs [30]. Additionally, the more compact design of SSBs, devoid of the bulky ancillary components required for liquid electrolyte management, contributes to an overall reduction in cell size, allowing for more efficient use of space and, consequently, higher energy storage per unit volume [31,32].

Longer Lifespan: The solid electrolytes in SSBs are less prone to degradation compared to liquid electrolytes, which tend to break down over time and under thermal stress [20,23]. This inherent stability of solid electrolytes contributes to a longer lifespan for SSBs, reducing the frequency of battery replacement and, in the long run, diminishing the environmental and economic impact of battery disposal [33].

Operational Stability Across Temperature Extremes: SSBs demonstrate superior performance stability across a wide range of temperatures [34]. Unlike liquid electrolytes, whose ionic conductivity can vary significantly with temperature, solid electrolytes maintain consistent performance in both high and low-temperature environments [18,34]. This trait enhances the reliability of SSBs in various climatic conditions, making them suitable for a broader range of applications.

No Leakage or Drying Out: The solid-state nature of these batteries inherently eliminates the risk of electrolyte leakage, an issue that can affect LE-LIBs and lead to reduced performance and safety risks. Additionally, solid electrolytes do not dry out over time, a common problem in some types of LE-LIB, especially under high temperature conditions [35].

Flexibility in Design: The absence of liquid components in SSBs offers greater flexibility in battery design. This allows for the development of batteries in shapes and sizes that were previously unfeasible, opening up new possibilities for the integration of batteries into a wide array of products and devices, including wearable electronics and uniquely designed electric vehicles [36].

Environmental Sustainability: From an environmental perspective, SSBs present a more sustainable option. The reduction in the use of toxic and volatile components, typical in liquid electrolytes, translates to a lower environmental risk during both the production and disposal phases [20,37]. Moreover, the longer lifespan of SSBs reduces the frequency of battery replacement, thereby decreasing the overall environmental footprint of battery usage.

In essence, the advantages of SSBs over conventional technologies are based on their unique construction and material properties, which confer superior safety, higher energy density, longer service life, temperature resistance, design flexibility and environmental sustainability. These benefits collectively position SSBs as a critical technology in the future landscape of energy storage solutions.

1.5. Technological Hurdles in the Adoption of Solid-State Batteries

Despite the significant advantages that SSBs offer, their widespread adoption faces several technological challenges. Overcoming these obstacles is crucial to the transition from laboratory-scale prototypes to commercially viable products.

Interface Stability: One of the main challenges of SSBs is to achieve stable interfaces between the solid electrolyte and the electrodes. Unlike LE-LIBs, where the liquid electrolyte can easily conform to the electrode surfaces, in SSBs, the rigid nature of the solid electrolyte can cause poor contact, creating high interfacial resistance [38]. This problem is exacerbated during cycling, as volume changes across the electrodes can further degrade the interface. Ensuring a stable, low-resistance interface is critical for efficient ion transport and overall battery performance.

Manufacturing Complexity and Scalability: SSBs production involves complex manufacturing processes that are currently challenging to scale. Fabricating thin, defect-free layers of solid electrolyte and ensuring perfect contact with the electrodes requires precision engineering and control [39]. Scaling these processes to mass production while maintaining quality and consistency is a significant obstacle that needs to be overcome for SSBs to be commercially viable.

Material Selection and Cost: Finding suitable materials for solid electrolytes that offer high ionic conductivity, mechanical strength, and stability is a major challenge. Many of the promising solid

electrolyte materials are expensive or difficult to synthesize in large quantities, impacting the cost-effectiveness of SSBs [40]. Furthermore, the quest for compatible electrode materials that can work efficiently with these solid electrolytes adds another layer of complexity [40,41].

Solid Electrolyte Brittleness: Many solid electrolytes, particularly ceramic-based ones, are brittle, posing challenges in handling and durability. This brittleness can lead to cracks and mechanical failure, especially under the stress of repeated loading and unloading cycles [42]. It is crucial to develop solid electrolytes with adequate mechanical properties to withstand these stresses.

Lithium Dendrite Formation: While SSBs reduce the risk of dendrite formation compared to LE-LIBs, it is not entirely eliminated, especially when using lithium metal anodes. The formation of lithium dendrites can still occur, potentially leading to short-circuiting and battery failure [43]. Addressing this issue requires a deep understanding of the conditions that promote dendrite growth and the development of strategies to mitigate it.

Thermal Management: Although SSBs are inherently safer and more stable at high temperatures, their thermal management is still a concern, especially in high-power applications like electric vehicles [44]. The solid electrolyte's ability to dissipate heat is less efficient compared to liquid electrolytes. Designing SSBs that can effectively manage heat during rapid charge-discharge cycles is crucial for maintaining performance and ensuring longevity [44].

Limited Understanding of Solid Electrolyte Behavior: The behavior of solid electrolytes under various conditions is not as well understood as that of liquid electrolytes [45]. The lack of comprehensive models that accurately predict the behavior of ions in solid matrices limits the ability to innovate and improve the performance of SSBs. Investing in fundamental research to deepen the understanding of solid electrolytes is essential for advancing SSB technology.

In summary, while SSBs offer a promising future for energy storage, addressing these technological obstacles is imperative for their successful market integration. These challenges span materials science, manufacturing, and the fundamental understanding of solid-state electrochemistry, and each requires dedicated research and innovation to overcome.

2. Solid Electrolytes: The Heart of Solid-State Batteries

The gradual shift to solid electrolytes has been influenced by the prior development of conventional lithium (Li) batteries, which have traditionally employed liquid electrolytes. To provide a comparison, Table 1 displays some of the most widely used electrolytes along with the most significant characteristics of both types. Solid-state electrolytes (SSEs) are generally classified into two main categories: organic and inorganic. The primary varieties within these categories include ceramic oxides, sulfides, and salt-complexed polymers. Two types of hybrid categories, composite electrolytes and solid-liquid electrolytes, are notably gaining attention in the industry. These hybrid electrolytes, under active research and development, show substantial potential for future commercial applications. They are particularly appealing for their potential to enhance ionic conductivity, improve inter-electrode contact, and offer greater mechanical strength.

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. [46] 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 1a–c. Additionally, Figure 1d illustrates the distinct challenges faced by each type of SSEs [46].

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

- 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.

Table 1. Ionic conductivities (σ) of some representative liquid and solid electrolytes. Adapted with permission from refs. [47,48], Copyright 2018 and 2022, Elsevier.

	σ (S cm ⁻¹)	
Liquid Electrolytes	0.6 M LiBOB in DMMP	4 x 10 ⁻³
	1 M LiTFSI in DMMEMP	2 x 10 ⁻³
	1.0 M LiPF6 in FEC/FEMC/HFE (2:6:2 wt.)	5.1 x 10 ⁻³
	1 M LiPF6 in FEC/DMC/EMC/HFPM (2:3:1:4 vol.)	8.5 x 10 ⁻³
	1 M LiBOB in GBL/F-EPE (70:30 wt.)	5.5 x 10 ⁻³
	1 M LiPF6 in EC/DEC/DMC (1:1:1).5% PFPN	11.3 x 10 ⁻³
	2.2 M LiFSI in TEP	1.3 x 10 ⁻³
	3.5 M LiFSI in FEC/TFEC (3:7 vol.)	1.2 x 10 ⁻³
	1.2 M LiFSI in TEP/BTFE (1:3 mol.)	1.3 x 10 ⁻³
Solid Electrolytes	Perovskite, NASICON, LISICON, garnet	10 ⁻⁵ - 10 ⁻³
	Li2S-P2S5	10 ⁻⁸ - 10 ⁻³
	Li10GeP2S12	10 ⁻³
	LIPON	10 ⁻⁷
	LATP, LAGP	10 ⁻⁴ - 10 ⁻³
	PEO	10 ⁻⁴ - 10 ⁻³
	TFSI	10 ⁻⁶ - 10 ⁻³

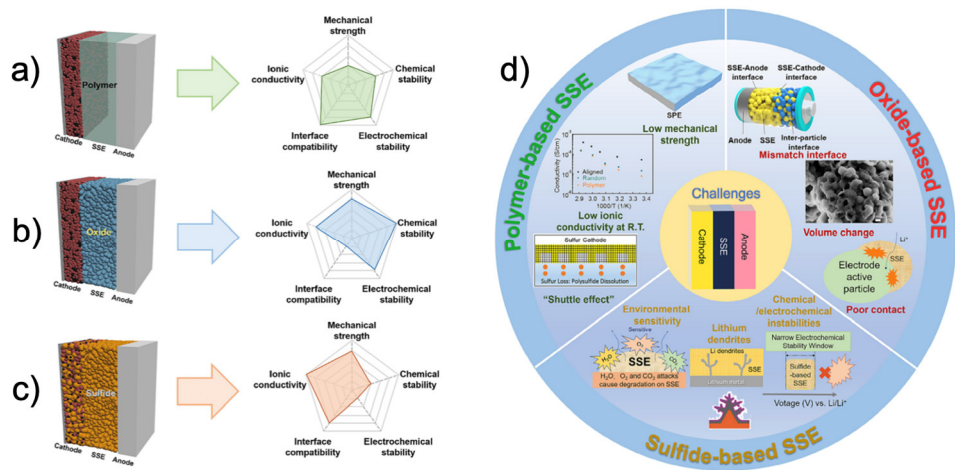


Figure 1. Comparison of SSBs using polymer (a), oxide (b), and sulfide (c) SSEs; and challenges for SSBs depending on the SSEs used. Reprinted with permission from ref. [46], Copyright 2022, Elsevier.

2.1. Oxide Electrolytes

2.1.1. LIPON

Lithium Phosphorus Oxynitride (LiPON) represents a unique glassy phase within the category of oxide-based solid electrolytes. Its chemical formula, denoted as $\text{Li}_x\text{PO}_y\text{N}_z$, 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 [49], exhibiting an ionic conductivity of approximately $2 \times 10^{-3} \text{ mS cm}^{-1}$. 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 [50,51]. 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 [52]. Furthermore, LiPON possesses relatively high ionic conductivity (around $2 \times 10^{-6} \text{ S cm}^{-1}$) and extremely low electronic conductivity (approximately $8 \times 10^{-14} \text{ S cm}^{-1}$) at room temperature [52]. 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 [53]. Notably, it maintains structural integrity without cracking even under volume changes in the cathode. Other studies highlight LiPON thin films' intriguing mechanical properties [54], 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 [55,56].

2.1.2. NASICON

NASICON, an acronym for "Sodium Super-Ionic Conductor," describes a class of ceramic materials characterized by an orthorhombic crystal structure (see Figure 2) [57] 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 [58–60], focusing on compounds with the formula $\text{Li}_{1+x}\text{A}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (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 [61], as well as 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 conductivity and achieving single-phase material [62]. However, challenges arise when there is inadequate mixing of aluminum and titanium, leading to the formation of a secondary phase (AlPO_4) which acts as a resistive layer, thereby reducing ionic conductivity [63]. Through controlled synthesis, the morphology and grain size of these materials can be manipulated, significantly affecting their ionic conductivity [64]. 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 $\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$ (LAGP) [65], 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 600–700 °C, further reducible to below 400 °C with process optimization [66,67].

Despite these benefits, LATP faces challenges, particularly in its interaction with lithium metal anodes [58,68,69]. Enhancements in these solid electrolytes are focused on introducing interlayers to mitigate interfacial impedance, prevent dendrite nucleation, and protect the electrolyte from side reactions [61]. 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 [66,70].

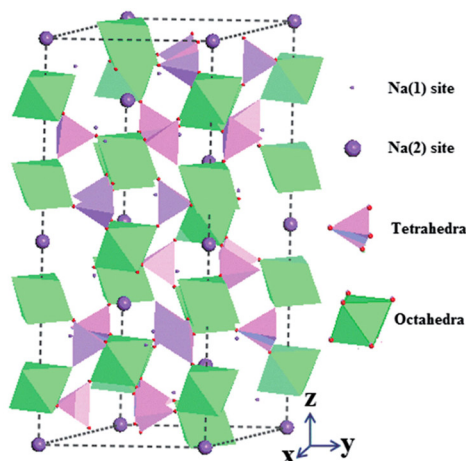


Figure 2. Schematic representation of the $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ crystal structure with a NASICON framework. Reprinted with permission from ref. [57], Copyright 2014, Royal Society of Chemistry.

2.1.3. Garnet Type

Garnet-type solid electrolyte $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (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 $\text{Li}_5\text{La}_3\text{M}_2\text{O}_{12}$ were reported in 2003 [71], demonstrating an ionic conductivity of about $10^{-6} \text{ mS cm}^{-1}$ at 25 °C. The development of the electrolyte $\text{Li}_6\text{Ala}_2\text{Ta}_2\text{O}_{12}$ (A=Sr, Ba) [72] marked a significant improvement, enhancing ionic conductivity to $4 \times 10^{-2} \text{ mS cm}^{-1}$ at 22 °C and introducing a new category of garnets. Further refinement led to the formulation of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), with a cubic atomic structure (see Figure 3), achieving ionic conductivities around 1 mS cm^{-1} [73]. This advancement was underpinned by an understanding of the fundamental transport properties of Li-diffusion paths in the material [74]. Recent developments in LLZO research have explored the impact of varying lithium content on Li-conduction [75], the existence of two different polymorphs of LLZO (cubic and tetragonal) [76], and the effects of introducing dopants into the LLZO crystal structure [77]. 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 [78]. Key benefits of garnet-type electrolytes include high Li-ion conductivity (approximately $10^{-3} \text{ S cm}^{-1}$ at 25 °C), a broad electrochemical stability window (around 6 V vs Li^+/Li) [79], and robust chemical stability against Li metal [80,81]. They also exhibit strong mechanical properties, with a high shear modulus that theoretically helps prevent Li dendrite formation [82,83]. However, challenges persist with lithium dendrite formation, often occurring along grain boundaries or within porous areas [84], and high interfacial resistance in Li/garnet interfaces leading to uneven Li distribution [85] and weak mechanical strength at grain boundaries [86].

Despite their advantages, garnet-type materials face several challenges [87]. 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 [87].

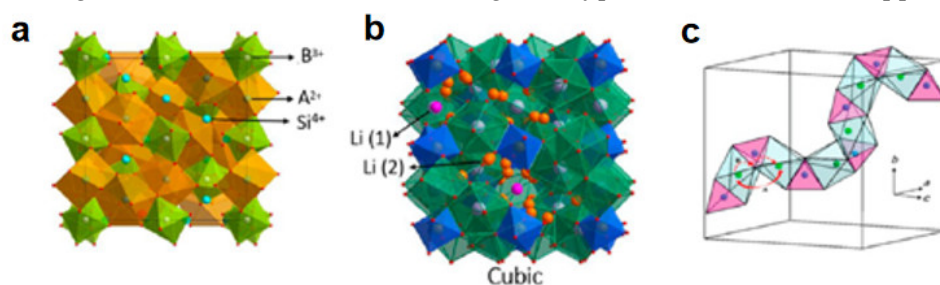


Figure 3. Schematic diagram of the first LLZO garnet structure (a); Atomic structure of cubic Li₇La₃Zr₂O₁₂ (LLZO) (b); and the pathway of Li-ion diffusion in cubic LLZO (c). Reprinted with permission from ref. [72], Copyright 2021, American Chemical Society.

2.2. 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 [88–91]. 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.

2.2.1. LPS

LPS electrolytes (glass-ceramics and glasses), are derived from the binary mixture $x\text{Li}_2\text{S} (100-x)\text{P}_2\text{S}_5$, where 'x' represents the molar percentage [92,93]. Within this category, the 75Li₂S-25P₂S₅ 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 [94].

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 [95]. For instance, in the Li₂S-P₂S₅-P₂S₃ ternary system, introducing a minor amount of P₂S₃ into the Li₂S-P₂S₅ base improves the conductivity of the resultant glass-ceramics [96]. Additionally, in the binary LPS system, superionic crystalline phases develop during the annealing of metastable compositions with $x \geq 70$. The most effective glass-ceramic is produced by crystallizing the 70:30 LPS mixture, resulting in the formation of a Li₇P₃S₁₁ superionic crystalline phase with remarkably high ionic conductivity, up to 17 mS cm⁻¹ [93]. 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 [88]. 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 (H₂S) gas [97,98].

2.2.2. Argyrodites

The initial discovery of these sulfide-based electrolytes can be traced back to the compound Argyrodite Ag_8GeS_6 [99]. Substituting silver (Ag) with lithium (Li) led to the formation of Lithium-based Argyrodites, specifically $\text{Li}_6\text{PS}_5\text{X}$ (where X represents Cl, Br, I) [99], as depicted in Figure 4. There has been significant research and development in the field of Argyrodites. For instance, the Chlorine variant of Argyrodite, $\text{Li}_6\text{PS}_5\text{Cl}$, demonstrates a lithium-ion conductivity approximately 2 mS cm^{-1} at ambient temperature [100]. This conductivity rate can be enhanced through various substitutions, such as in $\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$, which shows a conductivity rate of nearly 9 mS cm^{-1} at room temperature [101].

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 [102].

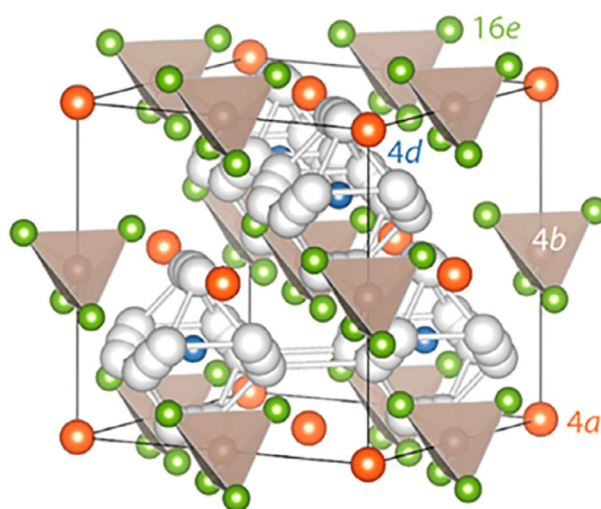


Figure 4. The crystal structure of Li-based argyrodites. Reprinted with permission from ref. [103], Copyright 2023, John Wiley & Sons.

2.3. Polymer Electrolytes

Polymer solid electrolytes (PE) 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 semi-crystalline or completely amorphous nature at room temperature, making them suitable for battery applications [104].

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 [105]. Essential attributes of the polymer matrix include mechanical robustness, ionic conductivity, and stability both thermally and chemically, alongside its ability to dissolve lithium salts [106–108]. 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) [106]. In PEO-based electrolytes, the preferred lithium salt is $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, 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 [109]. 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 [110,111].

Additives in PEs are utilized to enhance 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 [112], and enhancing interface stability with the lithium anode. Active nanofillers like $\gamma\text{-LiAlO}_2$ aid in lithium-ion conduction, while passive fillers such as Al_2O_3 , SiO_2 , or carbon particles have diverse roles [113,114].

Ionic liquids, molten salts with a melting point below 100°C such as PyrTFSI [115], show promise in enhancing ionic conductivity, 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 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 [116] offers a concise overview of the evolution of polymer electrolytes. Poly(ethylene oxide) [107] 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 [117]. This adjustment creates efficient ion transport channels in the porous polymer network, improving both the structural integrity and ion conductivity.

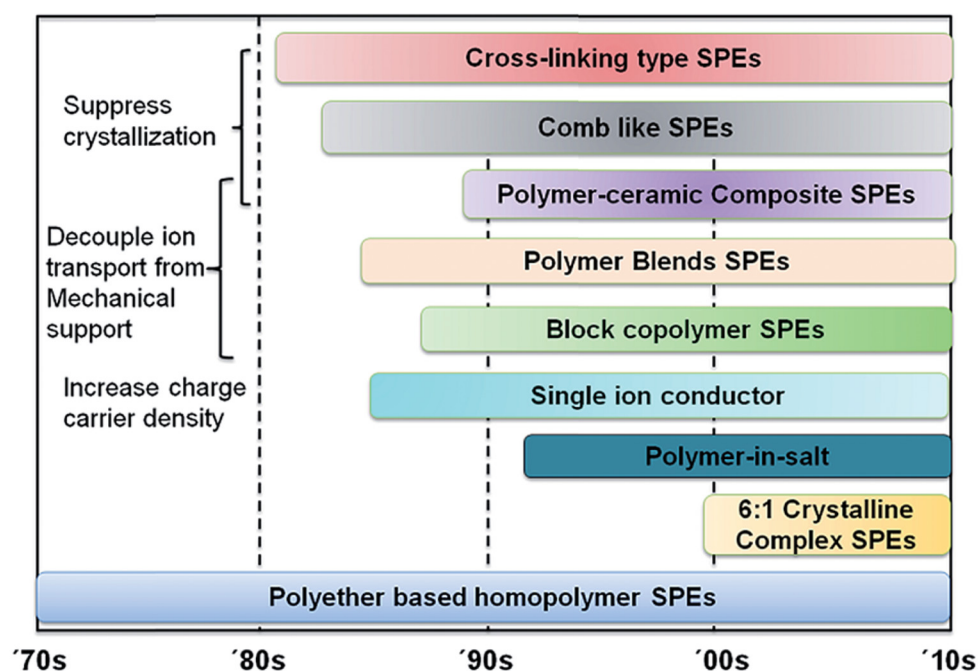


Figure 5. Overview of the evolution of solid polymer electrolytes over the past forty years. Reprinted with permission from ref. [116]. Copyright 2015, Royal Society of Chemistry.

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 $10^{-5} \text{ S cm}^{-1}$ at room temperature) [118]. 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 ionic conductivity and polymeric design strategies have been explored [119] to enhance mechanical strength (see Figure 6).

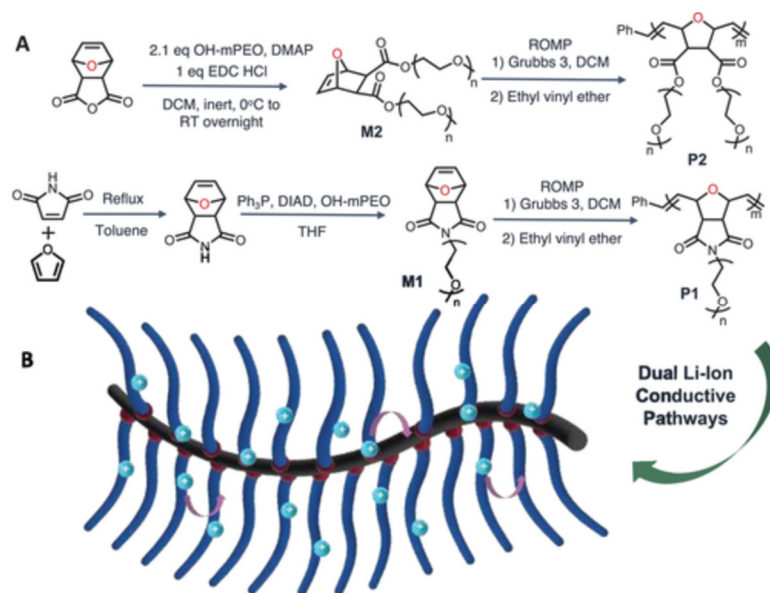


Figure 6. Synthesis of bottlebrush type polymers (a), and diagram illustrating bottlebrush polymer electrolytes, highlighting the dual movements of Li-ions. Reprinted with permission from ref. [119]. Copyright 2023, John Wiley & Sons.

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 mechanical strength to prevent lithium metal dendrite formation.

2.4. Composite Electrolytes

Ceramic fast-ion conductors are known for their high ionic conductivities, which exceed 10^{-4} S cm^{-1} [88,120]. 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} [121]. 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 [122]. By selecting the right ceramic filler and polymer, CEs can be customized to improve their overall performance in solid-state batteries [122].

CEs can be broadly categorized into two primary types [123]: a) those composed of inorganic nanoparticle/polymer combinations (INPC), and b) those made up of inorganic nanofiber/polymer structures (INFPC). In the realm of INPC solid electrolytes, the incorporation of inorganic nanofillers like SiO₂, Al₂O₃ and TiO₂ into polymer matrices has been a focal point of research [124]. The rationale behind this approach lies in the enhancement of mechanical strength, ionic conductivity, and

interfacial stability in the resulting polymer solid electrolytes [125]. 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 [126]. 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.* [127]. This study was designed to assess the impact of different nanoparticle types on the ionic conductivity of polyethylene oxide/lithium perchlorate (PEO/LiClO₄) based composite solid electrolytes. The nanoparticles evaluated included Li_{1.3}Al_{0.3}Ti_{1.7}(PO₄)₃ (LATP) as an active filler, and titanium dioxide (TiO₂) 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 TiO₂ or silica. Notably, in certain scenarios, such as the composite formulated with 10 wt.% LATP nanoparticles, the ionic conductivity achieved was remarkable, reaching $1.7 \times 10^{-4} \text{ S cm}^{-1}$. 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 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.* [128] successfully incorporated electrospun lithium lanthanum titanate (Li_{0.33}La_{0.557}TiO₃ or LLTO) nanowires into a polyacrylonitrile (PAN)-LiClO₄ 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.* [129] created a composite with garnet-type Li_{6.4}La₃Zr₂Al_{0.2}O₁₂ (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.

2.5. Hybrid Solid Electrolyte-Liquid Electrolyte

In solid-state batteries, SEs are confronted with significant challenges, notably their relatively low ionic conductivity at ambient temperatures [130]. 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 [131]. 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 [131]. Additional concerns include dendrite formation, mechanical instabilities, and chemical reactivity at the electrolyte-electrode interface [132]. Addressing these challenges, the concept of hybrid solid-liquid electrolyte (SLE) systems emerges 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 [133]. 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 [133]. 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 [133]. 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.* [134] focused on how water content and other additives affect the formation and resistance of solid-liquid electrolyte interfaces (SLEIs) in Ohara $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{P}_2\text{O}_5$ (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 [134]. 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 [134]. In other study by Gupta *et al.* [135] the role of additives and lithium salts in liquid electrolytes was analyzed using Ta-doped $\text{Li}_7-\text{La}_3\text{Zr}_2\text{O}_{12}$ 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 [135]. 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 SLEI is predominantly driven by the lithium salts in the LE rather than the solvent [135]. Hatz *et al.* [136] investigated the stability of the sulfide superionic conductor tetra-Li SiPS_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 [136]. 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 tolerate 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.

2.6. 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 [137]. 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 [137]. 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 [138]. 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 [138]. 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 [138]. 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 [138]. 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's a trade-off with open volume, as larger open volume could reduce AEF [138]. This concept is clarified in the diagram shown in Figure 7.

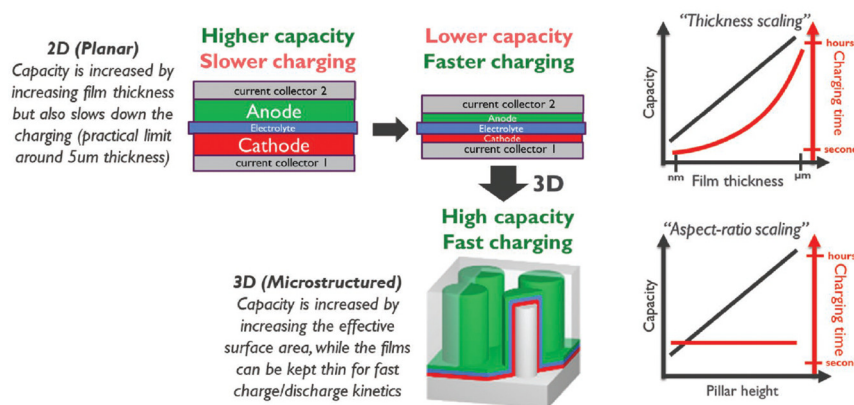


Figure 7. TFBs (planar) and 3D TFBs properties. Reprinted with permission from ref. [138], Copyright 2019, Advanced Materials Interfaces.

Advances in thin-film techniques have been significant in recent years. Thus, in contrast to the complexity of 3D TFB systems, Sahal *et al.* [139] had recently investigated the development of a novel SSE using a perovskite-structured material: polycrystalline lithium lanthanum titanate, $\text{Li}_{0.3}\text{La}_{0.56}\text{TiO}_3$ (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 [139]. 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 of grain boundaries and a reduction in crystallinity, resulting from the ultrafast processing method [139].

Other advanced solid-state electrolyte (SSE) manufacturing procedures, such as sintering, have been extensively studied in recent years. In this regard, Li *et al.* [140] explored the development of a NASICON-type $\text{NaZr}_2\text{Si}_2\text{PO}_{12}$ (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 [140]. In another study, Lin *et al.* [141] developed a cleaning method and a low-temperature sintering process that allowed for the synthesis of $\text{Li}_{0.33}\text{La}_{0.55}\text{TiO}_3$ (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 [140,141], there is a pressing need to aim for more ambitious goals involving substantially lower treatment temperatures [78]. 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. [142] developed an innovative ultrafast sintering method using a CO₂ laser in combination with a heating stage. This technique proved effective in rapidly densifying Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (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 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 [143]. However, the choice of materials is limited to those that can be photo-crosslinked. This technique has enabled the synthesis of some SSEs, particularly solid polymer electrolytes (SPEs), inorganic solid electrolytes (ISEs), and composite solid electrolytes (CSEs) [144–146]. Another procedure similar to SLA is digital light processing (DLP) [147], 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 [143]. 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, we 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 [148]. 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) [149]. 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 [150]. 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 [151,152]. 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.

3. Anode Innovations in Solid-State Batteries

3.1. Importance of Anode Material in Solid-State Batteries (SSBs)

The anode in solid-state batteries (SSBs) plays a vital role in determining important performance parameters like energy density, safety, lifespan, and the ability to support fast charging cycles. SSBs have attracted considerable attention in the search for next-generation energy storage systems, as they have the potential to surpass conventional lithium-ion batteries (LIBs) in terms of safety and energy density [19]. The development of innovative anode materials is driven by the desire to leverage the inherent advantages of SSBs, such as the elimination of flammable liquid electrolytes and the possibility of utilizing high-capacity lithium metal anodes with a theoretical capacity of 3860 mAh g⁻¹ [19,153].

For SSBs, the ideal anode should demonstrate a high theoretical capacity, allowing for greater energy storage per unit of mass. Additionally, it should have a low electrochemical potential relative to lithium to ensure a high cell voltage, resulting in higher energy output. Excellent electronic conductivity is crucial for efficient electron transfer during battery operation, improving the rate capability. Structural stability is another critical attribute, as the anode material needs to withstand volume changes during lithium intercalation and deintercalation without significant degradation, which could otherwise shorten the battery's lifespan [154].

Current research efforts are focused on exploring materials like silicon, tin, and various alloys, which exhibit promising properties such as high capacity and compatibility with solid electrolytes. However, challenges such as volume expansion and the formation of an unstable solid electrolyte interphase (SEI) persist, demanding further innovation in material science and engineering [153]. Developing a robust SEI is particularly important in SSBs as it can prevent dendrite growth, improving safety and enabling the use of lithium metal anodes.

Transitioning from traditional liquid electrolyte-based LIBs to SSBs with advanced anode materials is a complex task, as the interface between the anode and solid electrolyte must remain intact and conductive throughout the battery's lifespan. This is essential to maintain the ion transport properties crucial for the battery's operation [154]. Hence, meticulous selection and optimization of materials are necessary to ensure compatibility with the solid electrolyte and create a stable interface.

3.2. Anode Material Selection for SSBs

In the domain of SSBs, lithium metal anodes have emerged as a primary focus, owing to their high specific capacity and low anodic potential, as identified in reference [155]. This combination grants them a significantly superior energy density when compared to conventional graphite anodes. The work of Aktekin *et al.* [155] marks a critical advancement in this area. They introduced a novel electrochemical method to evaluate electrolyte side reactions on active metal electrodes' surfaces, a key factor in incorporating lithium metal anodes into SSBs. Their innovative approach (see Figure 8), involving an anode-free stainless steel | Li₆PS₅Cl | Li cell configuration, not only deepens our understanding of dendritic lithium growth but also enables the examination of various electrolytes and current collectors. These elements are essential for the stability of lithium metal anodes in SSBs.

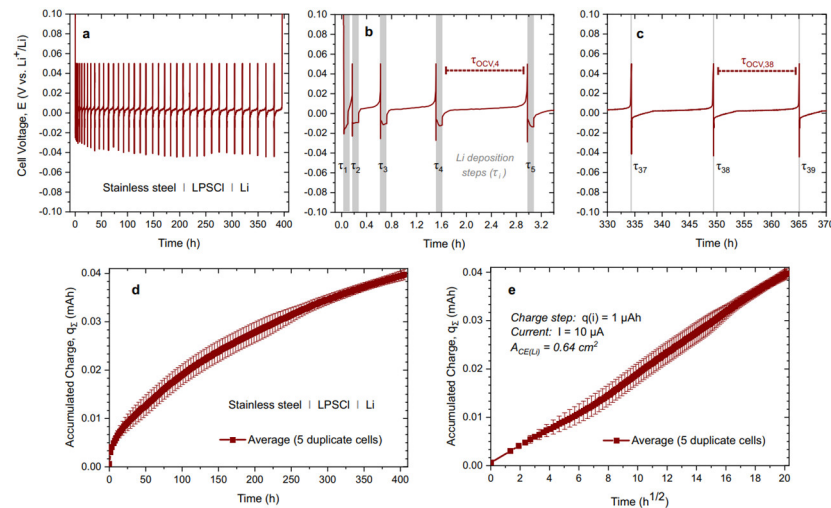


Figure 8. Results of the Coulometric Titration Time Analysis (CTTA) are presented. (a) The performance of LPSCl solid electrolyte in a stainless steel | LPSCl | Li cell setup at a temperature of 25 °C and pressure approximately 13 MPa is depicted. The potential profiles during specific, zoomed-in time intervals from an early phase (b) and a later phase (c) of the experiment are illustrated. The durations of the constant current lithium deposition stages (i.e., lithium titration) are highlighted in gray. The periods between each lithium deposition step represent Open Circuit Voltage (OCV) resting states ($\tau_{\text{OCV},i}$). The cumulative capacity over time is graphically represented as a function of time in (d) and as a function of the square root of time in (e). Reprinted with permission from ref. [155], Copyright 2023, Nature Communications).

A primary challenge in using lithium metal anodes is the formation of lithium dendrites during cycling, leading to potential short circuits and battery failure, as noted in reference [156]. This dendritic growth, along with chemical and electrochemical instability and chemo-mechanical expansion, creates significant barriers to the commercialization of SSBs. To address these issues, Yao and colleagues [156] concentrated their research on designing solid-state electrolytes that operate at reduced temperatures. Their findings suggest that lower operational temperatures in SSBs can greatly improve the stability and effectiveness of lithium metal anodes, thereby reducing the risks associated with dendrite formation and other instabilities.

The challenges associated with lithium metal anodes in SSBs have seen remarkable progress, as demonstrated by Kalnaus *et al.* [2]. They emphasized the vital role of mechanical factors in solid-state batteries. Their research illuminates the significant impact of mechanical properties on the performance and reliability of lithium metal anodes. Their detailed analyses shed light on optimizing mechanical rigidity in solid electrolytes and lithium transference number ($t(\text{Li}^+) \approx 1$), aiming to curb lithium dendrite growth. This research is instrumental in understanding the mechanical interactions at the anode-electrolyte interface, providing insights into enhancing the stability and safety of SSBs with lithium metal anodes.

In the broader context of anode development, alloy anodes, composed of lithium alloyed with elements like silicon, tin, or aluminum, are known for their increased capacity relative to traditional anodes [157]. These anodes can host a larger quantity of lithium ions, resulting in enhanced capacity. They also show improved cycling stability compared to pure lithium anodes. However, these anodes face significant volume changes during lithiation and delithiation cycles, causing mechanical stress and potential degradation of the anode material. This issue represents a critical limitation for their practical application in SSBs [157–159].

Recent research, including that of Huang *et al.* [157], has focused on overcoming these challenges, particularly the issue of volume expansion. Their study into the electrochemical stability of silicon as an anode material in SSBs, while highlighting its potential to address key challenges such as dendrite formation and morphological instability, represents a significant contribution to this field. Despite silicon's approximately tenfold greater specific capacity compared to graphite, its application as an anode in post-lithium-ion batteries faces considerable challenges. Cui and colleagues [159] investigated the compatibility of silicon with various solid electrolytes, finding that a hydride-based solid electrolyte exhibited superior stability. This enabled a solid-state Si anode with a record high initial Coulombic efficiency of 96.2%.

Another significant advancement in this area is the research focusing on aluminum-foil anodes [158]. This investigation (see Figure 9) revealed that using aluminum-foil anodes could limit volume expansion during lithiation to the normal direction of the foil, significantly enhancing electrode cyclability. By leveraging metallurgical principles like thermodynamics, elastic strain, and diffusion, this approach facilitated unidirectional volume-strain circumvention. The aluminum (Al) anode, as rolled, is directly assembled, and its electrode reaction involves partial lithiation of the Al matrix. This forms a lithiated layer which develops a columnar-porous structure, serving as active material in subsequent cycles. The cycling performance with a LiCoO_2 cathode shows no significant degradation over 120 cycles. Investigations into the Al anodes' surfaces and cross-sections post initial lithiation and after repeated cycles confirm the integrity of both active and current-collector layers [158]. The findings highlighted the importance of the appropriate hardness of the matrix and a certain tolerance to off-stoichiometry in the resultant intermetallic compound for achieving this effect.

Since Sony commercialized the graphite anode in 1991, carbon-based anodes have been a key focus of research, identified as promising candidates for lithium-ion batteries (LIBs) and "post lithium-ion batteries" like sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs) [160,161]. These batteries, while sharing similar components and electrochemical reaction mechanisms in carbon materials, exhibit significant differences in their electrochemical storage behaviors. The exploration of carbon anode materials, such as graphite, graphene, soft carbon, and hard carbon, continues to be a priority for enhancing their electrochemical performance [160,161].

In recent research, Yan *et al.* [161] developed a hard-carbon-stabilized Li-Si alloy anode for all-solid-state Li-ion batteries (ASSBs), demonstrating its potential for practical applications. This innovative anode effectively suppresses lithium dendrite growth and manages significant volume expansion. The anode was synthesized through a press-induced reaction between a Si-contained film and Li foil, leading to improved cycling stability and electrochemical performance.

Continued research and development in this field are crucial to address the challenges associated with carbon-based anodes, such as enhancing their stability and electrochemical performance. Persistent exploration and innovative approaches are vital for advancing solid-state battery technologies [160,161].

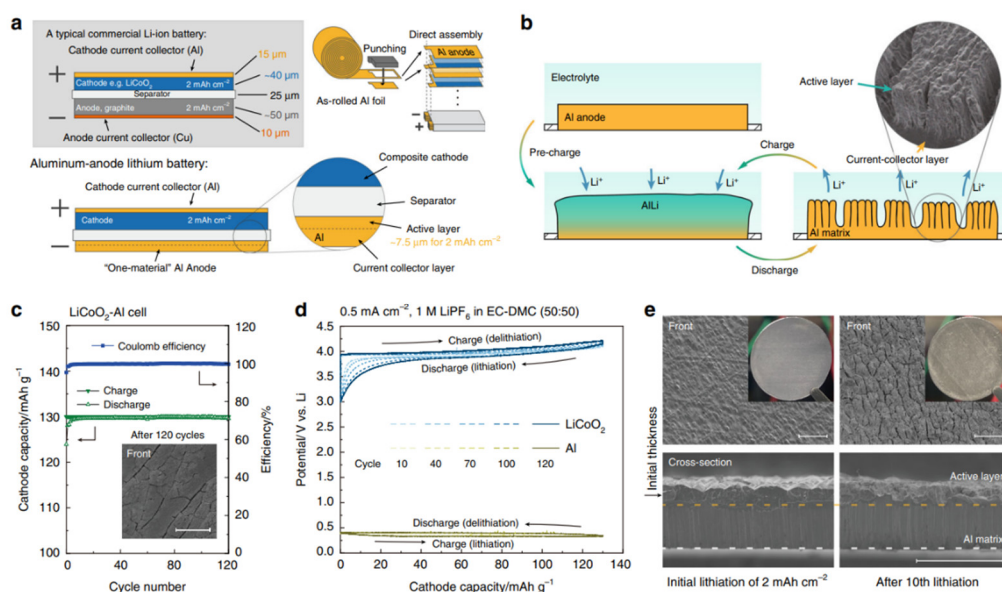


Figure 9. Exploring the use and efficacy of an Al-anode in lithium batteries. (a) Comparison of Al-anode and traditional Li-ion battery structures. (b) Electrode reaction and structure development in Al anode. (c) Cycling performance of Al anode with LiCoO₂ cathode. Inset: SEM image post 120 cycles. (d) Stable potential profiles across various cycles. (e) Surface and cross-section post-lithiation. SEM scale bars: 100 μm. Reprinted with permission from ref. [158], Copyright 2020, Nature Communication.

3.3. Overcoming Anode Challenges

3.3.1. Prevention of Dendritic Lithium Formation

Addressing dendritic lithium formation is critical for enhancing the performance and safety of ASSBs. Lithium metal dendrites significantly contribute to the degradation and failure of these batteries. Li, Tchelepi, and Tartakovsky's research [162] accentuates the effectiveness of materials like Ag, Al, Sn, and the antiperovskite superionic conductor Li₃S(BF₄)_{0.5}Cl_{0.5} in stabilizing electrodeposition and mitigating dendrite growth. Supported by experimental data, this research directs attention towards identifying novel buffer materials compatible with specific electrolytes.

Singh *et al.* [163] proposed a method to stabilize anodes in solid-state batteries by manipulating the microstructure of lithium metal. Their research reveals that fine-grained polycrystalline lithium metal anodes can address pore formation issues during stripping by leveraging the microstructural dependence of creep rates. This finding is crucial for anode-free solid-state batteries, where the microstructure and mechanical state of lithium are key.

Another study [164] delved into deposition-type lithium metal anodes, proposing a method for dendrite suppression. This research suggests enhancing the discharge capacity of all-solid-state batteries through active stack pressure control or hot pressing of binder-inclusive anodes and separators. This strategy emphasizes the importance of maintaining robust mechanical contact throughout the cycling process, paving the way for future commercial applications of ASSBs.

3.3.2. Enhancement of Anode/Electrolyte Contact

Enhancing anode-electrolyte contact remains a central challenge, attracting significant research interest. Deng *et al.* [165] introduced a gradient composite polymer solid electrolyte (GCPE), synthesized via a UV-curing polymerization method. This approach tackles both suboptimal interfacial contact and complex manufacturing processes, common hurdles in solid-state battery applications. The GCPE, with a high-Li_{6.4}La₃Zr_{1.4}Ta_{0.6}O₁₂ (LLZTO)-content side and an LLZTO-deficient side, offers high oxidation resistance and excellent interfacial contact with the Li metal

anode, promoting uniform Li deposition and enhanced performance, as demonstrated by the low-voltage hysteresis potential and extended cycle life in symmetric Li//Li cells [165].

Deysher *et al.* [166] emphasized the importance of selecting suitable solid electrolytes for stable anode-electrolyte interfaces in sodium all-solid-state batteries. They explored various solid electrolytes – chloride, sulfide, and borohydride – using advanced characterization techniques like FIB-SEM imaging, XPS, and electrochemical impedance spectroscopy (see Figure 10). Their findings indicate that interface stability is influenced by both the intrinsic electrochemical stability of the solid electrolyte and the passivating nature of interfacial products formed during cycling. This study highlights the criticality of material selection for stable cycling performance in sodium all-solid-state batteries.

Cao *et al.* [167] presented a novel approach to enhance lithium stripping efficiency in anode-free solid-state lithium metal batteries (ASLMBs). They implemented a conductive carbon felt elastic layer that autonomously adjusts pressure on the anode side, ensuring consistent lithium-solid electrolyte contact. This method not only improved initial Coulombic efficiency but also significantly enhanced cycling stability, offering a practical solution to lithium stripping inefficiencies in ASLMBs [167].

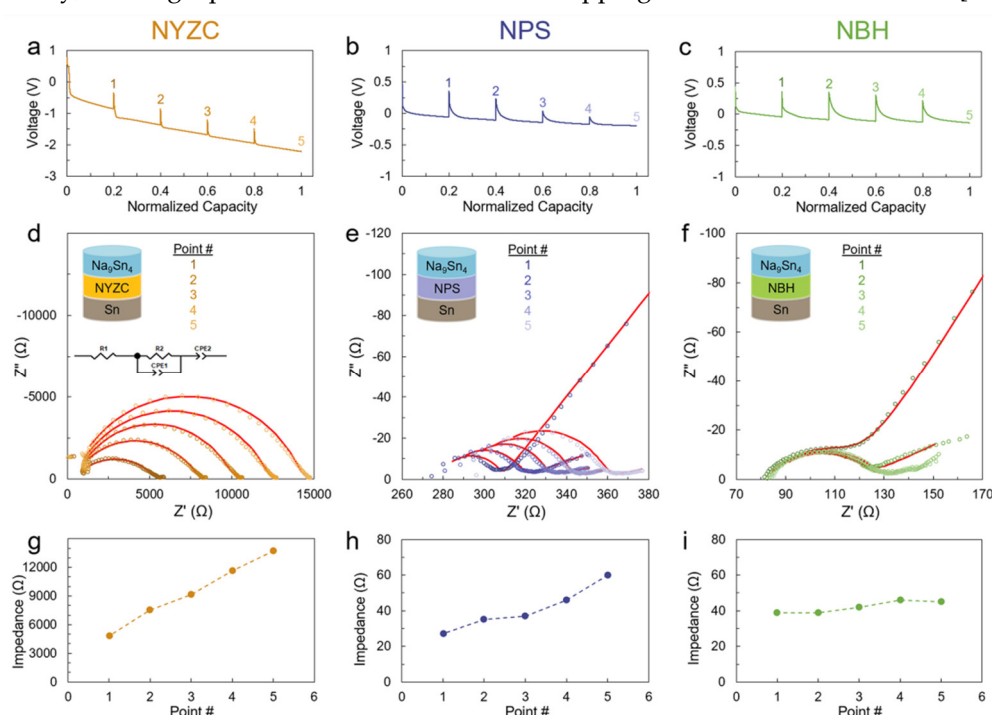


Figure 10. Voltage profiles for Na₉Sn₄ | SSE | Sn half cells employing (a) NYZC, (b) NPS, and (c) NBH electrolytes, cycled at a current density of 0.16 mA cm⁻². The increase in impedance during Sn sodiation in Na₉Sn₄ | SSE | Sn half cells using (d) NYZC, (e) NPS, and (f) NBH electrolytes is documented. The escalation of interfacial impedance during sodiation for (g) NYZC, (h) NPS, and (i) NBH, as interpreted from the EIS fitting outcomes, is also illustrated. Reprinted with permission from ref. [166], Copyright 2022, ACS Applied Materials & Interfaces.

3.3.3. Augmentation of Anode Life Cycle and Efficiency

Recent research in SSBs, particularly regarding anodes, has made significant strides in improving their life cycle and efficiency. Wu *et al.* [168] addressed challenges in anode-free Li-metal batteries (AFLBs), which suffer from issues like accumulative Li dendrites and dead Li, leading to reduced lifetimes and Coulombic efficiency. They introduced effective electrolyte additives, specifically LiAsF₆ and FEC, substantially enhancing the cycle life and average Coulombic efficiency of NCM || Cu AFLBs. This approach resulted in a capacity retention of about 75% after 50 cycles and an average Coulombic efficiency of 98.3% over 100 cycles, attributed to the additives' role in stabilizing Li deposition and solid electrolyte interphase (SEI) formation.

Other researchers [169] implemented an interface re-engineering strategy to address chemical stability issues between $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) and Li metal in all-solid-state lithium batteries. They developed a LiH_2PO_4 protective layer on the Li anode surface, significantly enhancing the stability of LGPS with Li metal. This advancement led to a stable polarization voltage over 950 hours at 0.1 mA cm^{-2} and a remarkable cycle life, with a reversible discharge capacity of 131.1 mAh g^{-1} at the initial cycle and 113.7 mAh g^{-1} at the 500th cycle under 0.1 C. This study not only improved cycle life but also provided insights into the stability mechanisms between LGPS and the Li anode.

Lastly, Humana and their team [170] focused on characterizing anodes for lithium-ion batteries, emphasizing the importance of properties like energy density, cycle life, safety, and environmental compatibility. They explored commercial carbon and shungite carbon in anodes, demonstrating effective activation processes and high-rate discharge capability. Their study highlighted the potential of these materials in achieving high discharge capacity values, significantly contributing to the overall efficiency and life cycle of lithium-ion batteries.

3.4. Anode Enhancement Techniques

3.4.1. Surface Modification and Coating

In the evolving landscape of solid-state battery technology, integrating lithiophilic layers for anode enhancement represents a pivotal advancement, as illustrated in the seminal work of Wang *et al.* [171]. This research outlines the development of a stable, anode-free all-solid-state battery (AF-ASSB) using a sulfide-based solid-electrolyte (argyrodite $\text{Li}_6\text{PS}_5\text{Cl}$). The novelty of this research lies in the strategic alteration of lithium metal's wetting characteristics on a copper current collector. The creation of a 1 μm lithiophilic Li_2Te layer on the collector resulted in a significant reduction of electro-deposition/electrodissolution overpotentials, enhancing the Coulombic efficiency (CE). This modification enabled an electrodeposition of lithium beyond 70 μm , surpassing the Li foil counter-electrode's thickness. The modified collector not only improved the initial CE to 83% at 0.2C but also consistently maintained a cycling CE above 99%, emphasizing the critical role of lithiophilicity in AF-ASSBs.

García-Calvo *et al.* [172] explored the potential of copper foil as an anode current collector in anode-free batteries (AFB) with solid electrolytes. Their investigation into copper foil surface modifications, using composite layers of carbon and metal nanoparticles (Ag, Sn, Zn), aimed to address the reversibility challenges in the lithium-plating/stripping process. The study's thorough analysis of these modifications on the electrochemical performance of solid-state anode-free pouch cells, which utilized a PEO electrolyte and a LiFePO_4 cathode, provided essential insights into the electrochemical behavior of these modified surfaces. This research underscores the significance of surface modifications in optimizing the anode-electrolyte interface, thereby enhancing overall battery performance.

Xia *et al.* [173] investigated the stability of lithiophilic modification layers in the context of long-term cycling for anode current collectors in all-solid-state anode-free lithium batteries. Their research specifically addressed the failure mechanisms of a silver lithiophilic modified layer in liquid electrolytes. The study revealed that the primary failure mode was the formation of a solid electrolyte interface on the Ag surface and the detachment of silver particles during cycling. The introduction of Ag between the solid electrolyte (LiCPON) and the current collector enabled long-term cycling of all-solid-state Li/Cu half cells with high Coulombic efficiency (see Figure 11). This study provides insights into the design of stable electrolyte/anode interfaces, emphasizing the importance of evaluating and optimizing lithiophilic layers for enhanced performance in all-solid-state anode-free lithium batteries.

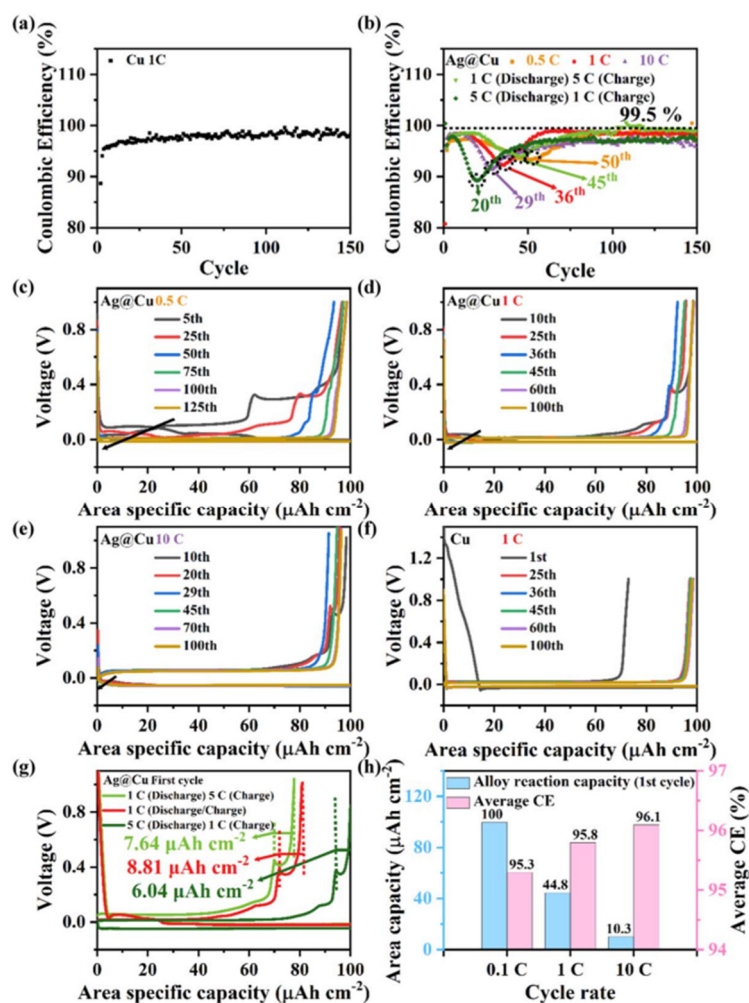


Figure 11. Analyzing the electrochemical characteristics of Li/Cu (Ag@Cu) half cells in 6M LiFSI/DME at a density of $100 \mu\text{Ah cm}^{-2}$ across various current rates (where 1C equals $100 \mu\text{A cm}^{-2}$). (a) Presents the Coulombic Efficiency (CE) of Li/Cu half-cell. (b) Illustrates the CE of Li/Ag@Cu half cells at different current rates. (c–e) Show the voltage profiles for Li/Ag@Cu half cells at varying current rates. (f) Depicts the voltage profiles for Li/Cu half-cell at a rate of 1C. (g) Details the voltage profiles from the initial cycle featuring varying charge and discharge current densities. (h) Displays the alloy reaction capacity from the first cycle and the average CE across cycles until the CE reaches its minimum value. Reprinted with permission from ref. [173], Copyright 2023, Journal of The Electrochemical Society.

3.4.2. Nanoengineering for Improved Performance

Nanoengineering has emerged as a critical technique for enhancing anode materials in solid-state batteries. Fuchs *et al.* [174] demonstrated the potential of carbon nanotubes (CNTs) in composite anodes comprising lithium metal. This study highlighted the transformation of dissolution kinetics from 2D to 3D in the anode, crucial for maintaining contact with the solid electrolyte and facilitating lithium transport. The incorporation of CNTs not only enhanced effective diffusion within the anode but also significantly improved the discharge capacity, achieving over 20 mAh cm^{-2} at $100 \mu\text{A cm}^{-2}$ without external stack pressure. This research underscores the potential of nanoengineering in optimizing the mechanical and electrochemical properties of anodes for practical solid-state battery applications.

Another group [175] presented an innovative approach, focusing on the modification of anode interfaces in molten sodium batteries. They developed a nanoparticle-decorated porous carbon structure on β'' -alumina solid-state electrolytes, significantly improving the wetting behavior of

molten sodium. The interface, engineered through a simple heat treatment process, formed a stable, low-resistance interface, enabling the battery to sustain nearly 6000 cycles. This modification not only reduced the lead content in the anode interface but also opened avenues for replacing toxic lead with environmentally benign materials like tin. The success of this technique in creating a high-performance anode interface is a testament to the effectiveness of nanoengineering in enhancing solid-state battery technologies.

Liu *et al.* [176] provided insights into nanoengineering at the anode/solid-state electrolyte interface in ASSBs. By coating the anode with a nanolithium niobium oxide layer and optimizing post-annealing treatment, they significantly improved the capacity and rate capability of the ASSBs. This nano-engineered layer effectively suppressed the decomposition of the sulfide solid-state electrolyte and stabilized the anode/SSE interface, highlighting the critical role of nanoengineering in designing high-performance anode materials for ASSBs.

3.4.3. Formation of Protective Layers

The advancement of protective layers on anodes marks a significant step in improving the efficiency and lifespan of batteries. Wang *et al.* [177] showcased an innovative method by establishing an *in situ* ion-conducting protective layer on lithium metal anodes in all-solid-state sulfide-based lithium metal batteries (see Figure 12). Utilizing a spin-coating technique, they employed a blend of polyacrylonitrile (PAN) and fluoroethylene carbonate (FEC). This layer effectively managed lithium deposition and bolstered interface stability, resulting in augmented discharge capacity and prolonged battery life. These findings illuminate the crucial role of protective layers in elevating anode performance.

Addressing the hurdles encountered by alloy anodes in ASSBs, Fan and their team [178] adopted a mechanically prelithiated aluminum foil as an anode. This anode demonstrated superior lithium conduction kinetics and stable interfacial compatibility with sulfide electrolytes. This strategy not only enhanced cycling stability but also maintained high capacity over numerous cycles, thus underscoring the efficacy of protective layers in mitigating issues like substantial volume changes and poor interfacial stability in alloy anodes.

Additionally, Huang *et al.* [179] conducted a review of anode-free solid-state lithium batteries, emphasizing the need to address inefficiencies in lithium plating and stripping. The review presents various strategies, including protective layer formation, to optimize performance and prolong battery life. This comprehensive analysis highlights the pivotal role of protective layers in enhancing the durability and efficiency of solid-state batteries.

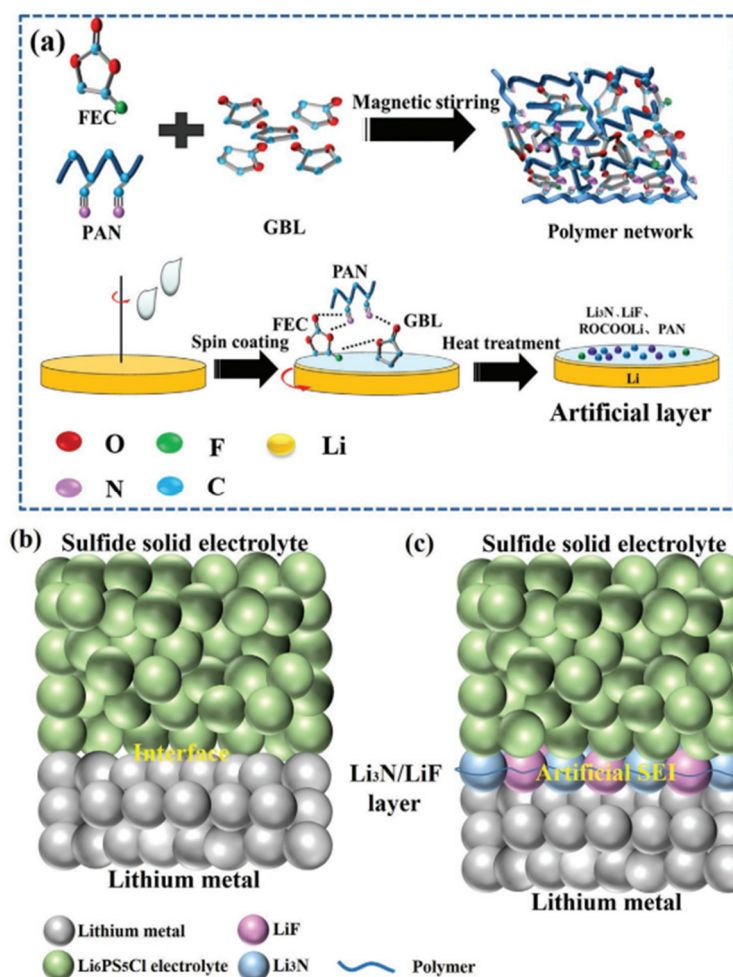


Figure 12. (a) Illustrative representations of the formation of a protective layer on the Li metal anode. (b) Interface of Li/LiPS₅Cl. (c) Altered interface featuring a consistent, slender Li₃N/LiF interphase layer resulting from the interplay between Li, PAN, and FEC. Reprinted with permission from ref. [177], Copyright 2021, Advanced Materials Interfaces.

4. The Convergence of Solid Electrolytes and Anodes

4.1. Designing for Synergy between Anodes and Solid Electrolytes

The integration of solid electrolytes with anodes in SSBs marks a significant evolution in energy storage technologies, addressing key safety and performance challenges inherent in traditional lithium-ion systems. For instance, the work of Miao *et al.* [180] offers a critical assessment of the interface engineering between inorganic solid-state electrolytes and electrode materials. Despite the impressive ionic conductivity of many solid-state electrolytes, their performance often suffers due to suboptimal interfaces with electrodes. This research highlights the importance of enhancing interfacial compatibility and stability. It also emphasizes the need to mitigate dendritic lithium formation, which is crucial for achieving high-performance cells. The study comprehensively evaluates recent advancements in improving the electrode/electrolyte interface, which includes optimizing components and innovatively designing the architecture of bulk anodes, electrolytes, and cathodes.

Banerjee *et al.* [41] explore the unique characteristics of interfaces and interphases in ASSBs with inorganic solid electrolytes. They observe a transition in the primary bottleneck in ASSBs from lithium-ion diffusion within the electrolyte to challenges like low Coulombic efficiency, suboptimal power performance, and reduced cycling life due to increased resistance at interfaces. This study illuminates the complex nature of these interfaces, which encompasses aspects like physical contact,

grain boundaries, and a spectrum of chemical and electrochemical reactions. A deep understanding of the composition, distribution, and electronic and ionic properties of these interfaces is imperative for the design of stable interfaces. The research also reviews the application of conformal coatings to prevent side reactions and emphasizes the significant role of mechanical behavior at these interfaces.

Wu and colleagues [5] provide a detailed review of the current status and future directions of ASSBs, focusing especially on batteries with lithium metal anodes, sulfide-based solid-state electrolytes, and Ni-rich layered transition metal oxide cathodes. They identify lithium dendrite growth at the anode or within the solid electrolyte as a major risk factor for cell failure. The study also notes that interfacial resistance increases due to electrolyte decomposition and the formation of interfacial voids at both cathode–electrolyte and anode–electrolyte interfaces, leading to gradual capacity fading. This review offers a comprehensive look at the latest research progress in ASSBs and provides perspectives on future research directions, emphasizing the importance of understanding and addressing the challenges at the interfaces of these components.

4.2. Analytical and Experimental Insights into Solid Electrolyte-Anode Pairings

The interaction between solid electrolytes and anodes in SSBs is a crucial research domain, offering insights into optimizing battery performance and longevity. Wu *et al.* [181] investigated the interaction between sodium anodes and sulfide-based solid electrolytes, like Na_3SbS_4 (NAS) and Na_3PS_4 (NPS), in ASSBs. Despite their high ionic conductivities at ambient temperatures, these electrolytes show instability with Na metal. Their study reveals that capacity fade and cell failure in ASSBs predominantly result from chemical reactions at the Na anode and solid-state electrolyte interface, exacerbated by electrochemical cycling (see Figure 13). The Na-solid electrolyte interphase (SSEI), composed of Na_2S and Na_3Sb for NAS, is identified both computationally and experimentally, displaying mixed ionic and electronic-conducting properties. This composition fosters SSEI growth, increasing cell impedance and reducing performance and cycle life. The study highlights the importance of SSE compatibility with both anodes and cathodes for enhancing the electrochemical properties and practicality of Na-based ASSBs.

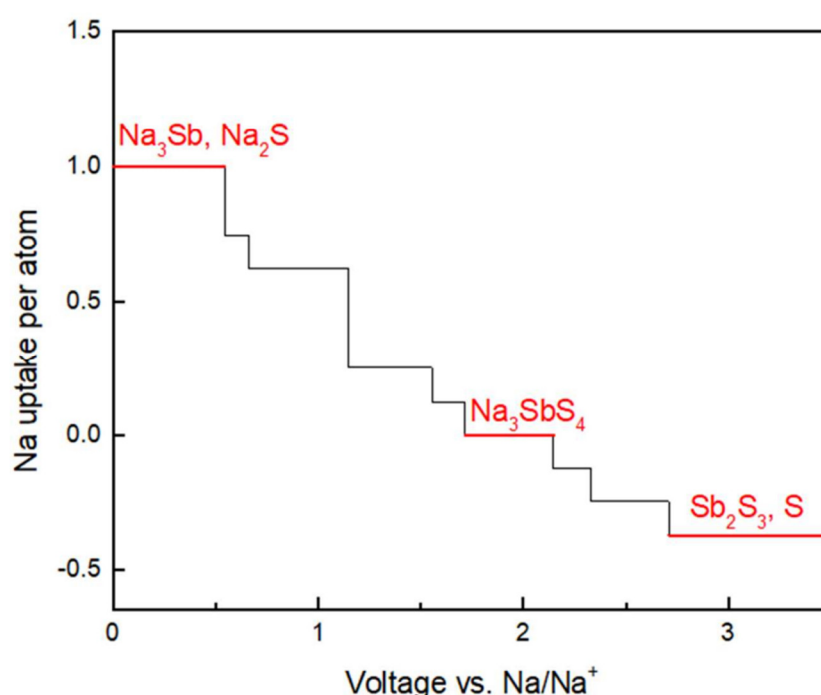


Figure 13. Grand potential phase stability diagrams for Na_3SbS_4 are presented. In the anodic or low voltage area, Na_3SbS_4 experiences a reduction reaction and absorbs Na, while in the cathodic or high voltage zone, it undergoes oxidation and releases Na. The compounds shown on the plot represent

the predicted phase equilibria in their respective regions. Reprinted with permission from ref. [181], Copyright 2018, ACS Applied Materials & Interfaces.

Another research group [182] contributes a comprehensive review of the fundamentals, structures, thermodynamics, chemistries, and electrochemical kinetics of solid electrolyte interphase (SEI) necessary for reversible anodes in SSBs. This review provides theoretical and experimental insights into metal nucleation, deposition, and stripping for the reversible cycling of metal anodes. It discusses ion transport mechanisms and the latest solid-state electrolytes (SEs) for high-performance cells. The challenges and strategies for integrating SEs, anodes, and cathodes in large-scale SSBs are addressed, focusing on aspects like physical/chemical contacts, space-charge layers, interdiffusion, lattice mismatch, dendritic growth, and thermal instability. This comprehensive review underscores recent innovations in anode interface chemistries developed by SEs, comparing monovalent and multivalent cation carriers in various battery types.

Moreover, Gao *et al.* [183] present a study focusing on nanometer-thin solid-state electrolyte/electrode interfaces in ASSBs. Their work underscores the importance of understanding these interfaces to achieve efficient and safe ASSBs. Employing a multiscale framework that combines Density Functional Theory (DFT), reactive force field, and continuum scale approaches with surface and electrochemical techniques, they elucidate the structural origin of interfacial resistance, degradation mechanisms, and lithium-ion transport mechanisms at cathode interfaces under different conditions. This hybrid experimental and computational approach is pivotal in designing highly compatible and stable electrolyte/electrode interfaces, extending to other energy conversion and storage devices.

Complementing advanced characterization and analysis techniques, Li *et al.* [184] delved into advanced methods for understanding dynamic processes in LIBs. Their research emphasized the importance of investigating batteries across different length and time scales, using *in situ* and *operando* methods. The review discusses insertion and conversion electrode materials, underscoring the necessity of these techniques to enhance understanding of battery operation, degradation, and failure mechanisms. This foundational research is crucial for future developments in battery technology in the coming years.

4.3. Computational Approaches in Predicting and Enhancing Performance

The integration of computational methods in the development of solid electrolytes and anodes for solid-state batteries is a rapidly evolving field, where these approaches are crucial in predicting and enhancing performance. In the context of ASSBs, pursuing high-performance solid-state electrolytes (SEs) is essential. Yang and his team [185] underscore the importance of understanding transport mechanisms and electrochemical properties of fast sodium-ion conductors at an atomic level. Advanced computational tools are instrumental in exploring functional materials for SEs, significantly contributing to the rapid advancement of ASSBs. This study emphasizes the vital role of computational studies, working in tandem with experimental efforts, in expediting the development of high-performance sodium-ion SEs.

The review by Dutra and Dawson on antiperovskite solid electrolytes for solid-state batteries (SSBs) [186] is a deep dive into the potential of these materials, which offer high ionic conductivity and are well-suited for use with various metal anodes like Si, Li, or Sn. Their review goes beyond the basics, delving into the computational design of these electrolytes. This involves advanced techniques like high-throughput screening for novel compositions, understanding synthesizability, exploring doping effects, and leveraging machine learning (ML) to predict properties like ionic conductivity. Pu *et al.* [187] propose an interactive visualization system for experts to select suitable ML models and to comprehensively understand and explore prediction results. Validated through case studies and lab experiments, this system demonstrates the effectiveness of ML in predicting ionic conductivity for solid-state electrolytes. It exemplifies the transformative impact of computational approaches in materials science, particularly in the context of solid electrolytes and anodes for solid-state batteries. In this regard, Wang *et al.* [188] conducted comprehensive studies on the SEI in LIBs,

utilizing methods ranging from electronic structure calculations to mesoscale modeling. Their research focused on the thermodynamics and kinetics of electrolyte reduction reactions and examined how the properties of SEI were affected by electrolyte design, impacting battery performance. Additionally, their work included the development of artificial SEI layers and identified potential future research directions in the field. Similarly, in the case of cathodes, Xiao *et al.* [189] explored the use of computational methods to identify suitable cathode coating materials for SSBs. Their study emphasized the potential of polyanionic oxide coatings, due to their optimal electrochemical and chemical stability while maintaining ionic conductivity. The research examined phase stability, electrochemical and chemical stability, and ionic and electronic conductivity of various materials, once again demonstrating the effectiveness of computational approaches in advancing SSB technology.

5. Conclusions and Forward Look

In this comprehensive review, we thoroughly examine the evolution of SSBs, highlighting their transition from traditional liquid electrolyte lithium-ion batteries (LIBs). This shift mirrors the increasing demand for safer, more efficient, and durable energy storage solutions. A primary focus is the integration of solid electrolytes with anodes and cathodes, which significantly influences battery performance and safety, offering enhanced energy density and stability over traditional batteries.

The paper delves into the challenges and advancements at the interfaces between solid electrolytes and electrode materials. These interfaces are crucial for the functionality and efficiency of SSBs, with initial concerns centered on lithium-ion diffusion. Advances in understanding and improving the interactions at these solid-solid interfaces have been notable, with the work of researchers like Miao *et al.* and Banerjee's team providing valuable insights into interface engineering, highlighting the importance of compatibility and stability for battery performance and lifespan.

The interaction between solid electrolytes and anodes is also a key research area. Studies explore the dynamics between various anodes, such as sodium, and sulfide-based solid electrolytes, revealing that capacity fade and cell failure often stem from chemical reactions at the interfaces. This underscores the importance of selecting solid electrolytes that are chemically stable with both anodes and cathodes.

Furthermore, computational studies have become vital for understanding transport mechanisms at an atomic level, crucial for designing efficient solid electrolytes and electrode materials. These models are increasingly relied upon for material design, particularly anti-perovskite solid electrolytes known for their high ionic conductivity and stability.

The review also highlights the need for deeper considerations for common anode materials in SSBs. The stability of the anode in a solid-state environment is essential for maintaining the integrity of the solid electrolyte and preventing degradation. The thermal properties of these anode materials must be compatible with the solid electrolyte to maintain consistent performance across temperatures. The intricacies of the anode-solid electrolyte interface need fine-tuning for minimal resistance and maximal ionic conductivity, influencing the overall battery architecture. This includes weight, size, and design flexibility considerations for practical device integration. These factors are key for the successful application of materials in SSBs, marking a departure from their roles in conventional liquid electrolyte batteries. This holistic approach, combining computational design with material stability and interface optimization, is vital in advancing SSBs, showcasing a significant evolution from traditional liquid electrolyte batteries.

In conclusion, this review not only encapsulates the significant strides made in the field of solid-state batteries but also sets a forward-looking perspective. It underscores the ongoing need for research in enhancing the interfaces of solid electrolytes and electrodes and highlights the potential of computational methods in advancing material design. The continued exploration and development in these areas are essential for realizing the full potential of solid-state batteries, paving the way for more sustainable and efficient energy storage solutions in the future.

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Conflicts of Interest: The authors declare no conflict of interest.

List of Acronyms

AEF	Area enhancement factor
AF-ASSB	Anode-free all-solid-state battery
AFB	Anode-free battery
ASSB	Anode/solid-state electrolyte interface
DLP	Digital light processing
DME	Dimethoxyethane
EV	Electric vehicle
FEC	Fluoroethylene carbonate
GCPE	Gradient composite polymer solid electrolyte
INPC	Inorganic nanoparticle/polymer combination
INFPC	Inorganic nanofiber/polymer structure
ISE	Inorganic solid electrolyte
LAGP	$\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3$
LATP	$\text{Li}_{1+x}\text{A}_x\text{Ti}_{2-x}(\text{PO}_4)_3$ (where ‘A’ represents Al, Cr, Ga, Fe, In, La, Sc, or Y)
LE-LIB	Liquid electrolyte lithium-ion battery
LGPS	$\text{Li}_{10}\text{GeP}_2\text{S}_{12}$
LiFSI	Lithium bis(fluorosulfonyl)imide
LiPON	Lithium phosphorus oxynitride
LiTFSI	$\text{LiN}(\text{CF}_3\text{SO}_2)_2$
LLTO	$\text{Li}_{0.33}\text{La}_{0.557}\text{TiO}_3$
LLZO	$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$
LLZTO	$\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$
LPS	Glass-ceramic lithium thiophosphate
NAS	Na_3SbS_4
NASICON	Sodium super-ionic conductor
NPS	Na_3PS_4
NZSP	$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$
PAN	Polyacrylonitrile
PE	Polymer solid electrolyte
PEO	Polyethylene oxide
PVDF	Polyvinylidene fluoride
SEI	Solid electrolyte interphase
SLEIs	Solid-liquid electrolyte interfaces
SLA	Stereolithography
SSE	Solid-state electrolyte
SSLB	Solid-state lithium battery
SSBs	Solid-state batteries

TFBs
VOCPlanar thin-film battery
Volatile organic compound

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