

REVIEW

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Strategies for Obtaining High-Performance Li-Ion Solid-State Electrolytes for Solid-State Batteries

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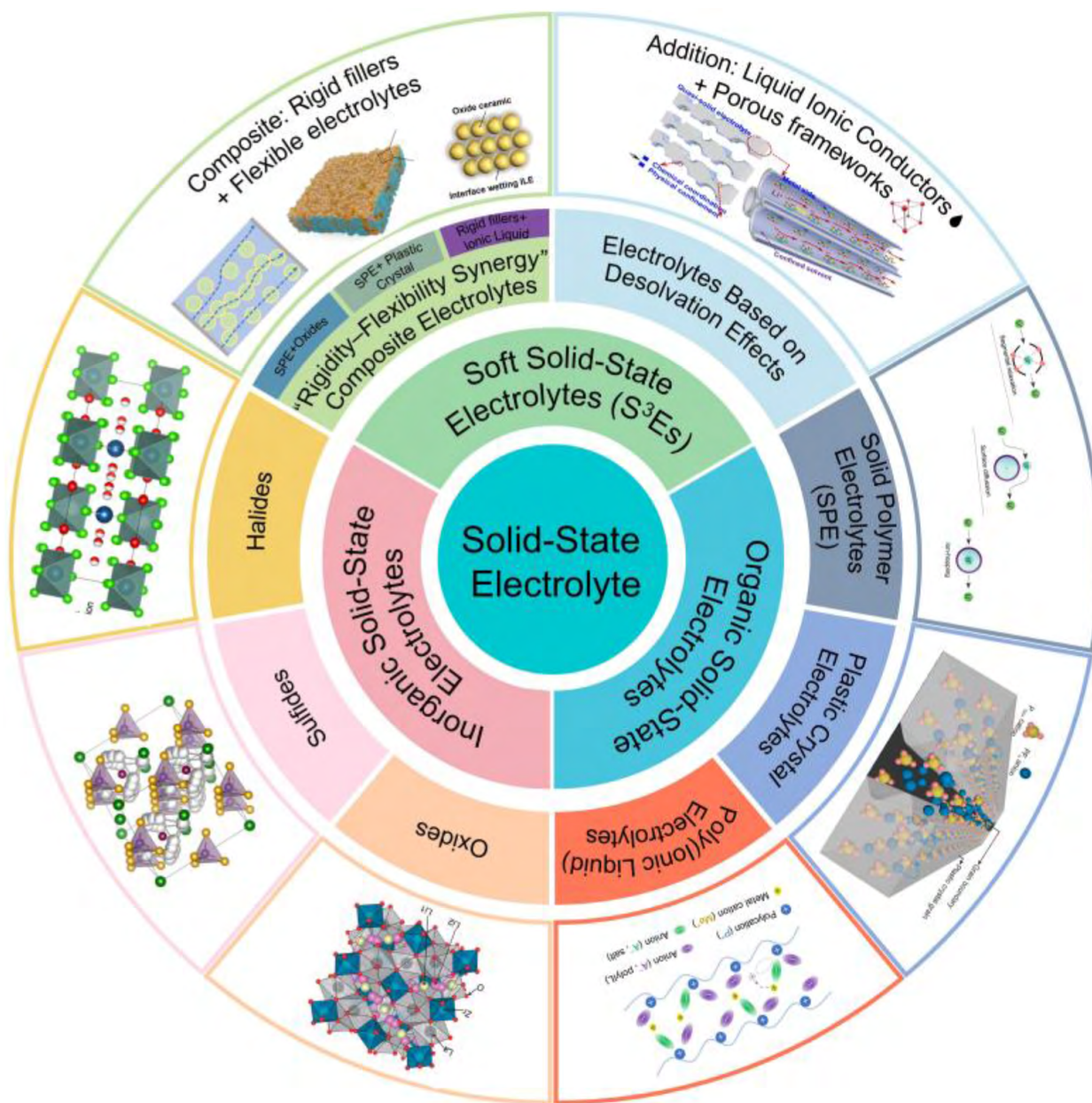
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Abstract

With the widespread adoption of lithium-ion batteries (LIBs), safety concerns associated with flammable organic electrolytes have become increasingly critical. Solid-state lithium batteries (SSLBs), with enhanced safety and higher energy density potential, are regarded as a promising next-generation energy storage technology. However, the practical application of solid-state electrolytes (SSEs) remains hindered by several challenges, including low Li^+ ion conductivity, poor interfacial compatibility with electrodes, unfavorable mechanical properties and difficulties in scalable manufacturing. This review systematically examines recent progress in SSEs, including inorganic types (oxides, sulfides, halides), organic types (polymers, plastic crystals, poly(ionic liquids) (PILs)), and the emerging class of soft solid-state electrolytes (S^3Es), especially those based on “rigid-flexible synergy” composites and “ Li^+ -desolvation” mechanism using porous frameworks. Critical assessment reveals that single-component SSEs face inherent limitations that are difficult to be fully overcome through compositional and structural modification alone. In contrast, S^3Es integrate the strength of complementary components to achieve a balanced and synergic enhancement in electrochemical properties (e.g., ionic conductivity and stability window), mechanical integrity, and processability, showing great promise as next-generation SSEs. Furthermore, the application-oriented challenges and emerging trends in S^3E research are outlined, aiming to provide strategic insights into future development of high-performance SSEs.

Keywords: Solid-state electrolytes; Solid-state batteries; Soft solid-state electrolytes; Lithium-ion conductivity; Interface compatibility

1. Introduction

Lithium-ion batteries (LIBs) have become the dominant energy storage technology for portable electronics, electric vehicles, and grid-scale applications owing to their high energy density and long cycle life [1–3]. However, their reliance on flammable and volatile carbonate-based electrolytes raises significant safety concerns, particularly under thermal abuse conditions where LIBs are prone to catching fire and burning [4]. Furthermore, conventional LIBs face intrinsic energy density limitation due to the low theoretical capacity of graphite anodes ($372 \text{ mAh}\cdot\text{g}^{-1}$). In contrast, Li metal anode offers an order-of-magnitude higher theoretical capacity ($3860 \text{ mAh}\cdot\text{g}^{-1}$), rendering it a promising alternative for next-generation high-energy-density batteries. Nevertheless, the practical implementation of Li metal anode remains hindered by its poor cycling stability and uncontrollable dendritic growth in liquid electrolytes [5–7]. To overcome these challenges, solid-state lithium batteries (SSLBs) have emerged as a viable solution, offering enhanced safety and higher energy density potential [8]. By replacing flammable liquid electrolytes with non-flammable solid-state electrolytes (SSEs), SSLBs mitigate thermal runaway risks while enhancing electrochemical stability [7, 9, 10]. Additionally, SSEs with high mechanical modulus serves as a robust physical barrier against lithium dendrite penetration, significantly improving cycling performance [11, 12]. Consequently, the shift from liquid to solid-state electrolytes is widely regarded as a pivotal strategy to overcome the safety and energy density limitations of conventional LIBs [13].

As the core component of SSLBs, an ideal SSE should simultaneously satisfy multiple critical

requirements: high ionic conductivity (σ) but negligible electronic conductivity, a wide electrochemical stability window, appropriate mechanical strength, excellent chemical stability, favorable interfacial compatibility, and environmentally sustainable manufacturing processes. SSEs are broadly categorized into inorganic and organic types based on their composition and structure. Inorganic SSEs primarily include oxides, sulfides, and halides, while organic SSEs mainly contain polymers, plastic crystals and poly(ionic liquid)s, etc. Oxide-based electrolytes (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ and $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$) demonstrate relatively high room-temperature σ ($\sim 10^{-3} \text{ S}\cdot\text{cm}^{-1}$) along with exceptional thermal and chemical stability [14, 15]. However, their excessively high Young’s modulus ($>100 \text{ GPa}$) results in limited particle contact points, leading to substantial interfacial resistance at both electrolyte-electrolyte and electrolyte-electrode interfaces [16]. Sulfide-based SSEs (e.g., $\text{Li}_7\text{P}_3\text{S}_{11}$ and $\text{Li}_6\text{PS}_5\text{Cl}$) present distinct advantages, including lower Young’s moduli ($<35 \text{ GPa}$) for better interfacial contact [17], and remarkably high σ ($\sim 10^{-2} \text{ S}\cdot\text{cm}^{-1}$) due to low Li^+ migration barriers [18–20]. Nevertheless, their narrow electrochemical stability window ($1.7\text{--}2.5 \text{ V vs. Li}^+/\text{Li}$) limits compatibility with conventional electrodes [21, 22], while their extreme sensitivity to moisture and polar solvents demands rigorous environmental control throughout material synthesis, electrode processing, and cell assembly [23]. Halide SSEs (e.g., Li_3InCl_6 and Li_2ZrCl_6) combine moderate mechanical properties with good oxidative stability, making them particularly compatible with high-voltage cathodes [24–27]. Yet, their instability against lithium metal anodes and similar hygroscopic nature pose major challenges for practical use [28, 29]. From a manufacturing standpoint, integrating inorganic

SSEs into existing LIB production lines remains difficult, often requiring substantial process redesign and specialized infrastructures. In contrast, organic SSEs, primarily represented by polymer systems, such as polyethylene oxide (PEO), polyvinylidene fluoride (PVDF), and polyacrylonitrile, present superior process compatibility with conventional battery manufacturing [30]. The polymer SSEs also provide advantages like lightweight, flexibility, and roll-to-roll processability [30, 31]. However, low room-temperature σ ($<10^{-4}$ S·cm $^{-1}$), limited Li $^{+}$ transference number ($t_{Li^{+}}$), and inadequate mechanical strength are major obstacles for their practical application [32, 33].

Overall, each SSE has its own merits and drawbacks, and no single SSE can fully meet the requirements of SSBs. The inherent limitations of single-component SSEs are difficult to be overcome, even with efforts in chemical modification and structural optimization. This has spurred the development of soft solid-state electrolytes (S ^{3} Es) through innovative multi-phase coupling designs. S ^{3} Es uniquely combine the compliance of soft materials with robustness of rigid components, exhibiting more balanced properties in ionic conductivity, mechanical strength, and interfacial adaptability, and therefore receiving considerable attention. The SSEs are achieved primarily through two approaches: (1) incorporation of rigid nanofillers (e.g., oxides) into flexible polymer, plastic crystal, or ionogel matrices to create rigid-flexible synergistic composites [34–38], in which the flexible components provide excellent interfacial conformity, while the fillers enhance mechanical strength and promote Li $^{+}$ transport; (2) designing Li $^{+}$ -desolvation electrolytes using porous frameworks that immobilize solvent molecules while allowing efficient Li $^{+}$ transport [39–42]. Despite promising results, key challenges remain, including achieving uniform component distribution, optimizing multi-phase interfacial stability, and developing scalable fabrication methods.

This review systematically examines recent progress in SSEs, with emphasis on material innovations, interfacial challenges, and scalable manufacturing. We critically evaluate single-component SSEs (inorganic and organic-based) in terms of σ , stability, mechanical properties, and interfacial issues, identifying key bottlenecks for SSLB development. Subsequently, special emphasis is placed on S ^{3} Es, including rigid-flexible synergistic composites and Li $^{+}$ -desolvation systems, with detailed discussion on their mechanical reinforcement and ion transport mechanisms. Finally, we outline application-oriented challenges and emerging trends in S ^{3} E research, aiming to provide strategic insights for the rational design of next-generation SSEs.

2. Ion Transport Mechanisms and Key Characteristics of Solid-State Electrolytes

Solid-state batteries offer higher safety and energy density compared to traditional lithium-ion batteries. Structurally, they consist of a composite cathode, a solid electrolyte layer, and an anode. The solid electrolyte presents in the composite cathode, the electrolyte layer and in certain anodes serve to establish fast Li $^{+}$ transport pathways. Inorganic solid electrolytes exhibit excellent ionic conductivity at room temperature; for instance, sulfide-based electrolytes can achieve conductivities in the range of 10^{-3} to 10^{-2} S·cm $^{-1}$. The conduction of Li $^{+}$ in these materials is a solid-state process governed by lattice dynamics and defect chemistry [43]. Key elements for this process include mobile Li $^{+}$ carriers, continuous migration pathways with suitable energy barriers, and a sufficient concentration of available vacant or interstitial sites. When Li $^{+}$ ions acquire enough energy, they overcome lattice energy barriers and hop into adjacent vacant sites. Polymer solid electrolytes generally show relatively low room-temperature σ , typically around 10^{-6} to 10^{-4} S·cm $^{-1}$, and often require operation above 60 °C to reach practically useful levels ($>10^{-3}$ S·cm $^{-1}$). The conduction of Li $^{+}$ in polymer electrolytes occurs primarily through segmental motion in amorphous regions [44]. The polymer chains in these regions are highly flexible, allowing Li $^{+}$ ions to coordinate with polar groups (such as the ether oxygen –C–O–C– in PEO) and dissociate under an electric field. Directional migration is facilitated by conformational rearrangements and inter-chain hopping of polymer segments. Ion transport in soft solid electrolytes, including Li $^{+}$ -desolvating electrolytes and “rigidity-flexibility synergy” composites, is more complex. In these systems, conduction may occur through multiple components and along their interfaces. A common strategy involves immobilizing mobile species such as anions or solvent molecules to promote selective Li $^{+}$ transport.

The ionic conductivity of solid electrolytes is typically measured using pellets or membranes. Oxide electrolytes, which have high Young’s modulus, are often processed by cold pressing under high pressure (~300–400 MPa) followed by high-temperature sintering to achieve dense structures. Sulfide and halide electrolytes can generally be pelletized by cold pressing alone, without sintering. Polymer electrolytes are commonly fabricated into membranes via solution casting or hot pressing. Symmetric cells are then assembled by sandwiching the electrolyte between blocking electrodes under controlled pressure. Electrochemical impedance spectroscopy (EIS) is used to measure ionic conductivity.

Table 1. Summary of inorganic solid-state electrolytes.

Type	Material	Conductivity (S·cm ⁻¹ , 25 °C)	Advantage	Disadvantage
Oxide	LISICON Li ₁₄ Zn(GeO ₄) ₄ NASICON LiTi ₂ (PO ₄) ₃ Perovskite LiLaTiO ₃ Garnet Li ₃ La ₃ Zr ₂ O ₁₂	10 ⁻⁵ –10 ⁻³	• High chemical and thermal stability • Good mechanical strength	• Poor interface contact • Expensive large-scale production
Sulfide	Glass Li ₂ S-P ₂ S ₅ LGPS-type Li ₁₀ GeP ₂ S ₁₂ Argyrodite Li ₆ PS ₅ Cl	10 ⁻³ –10 ⁻²	• High conductivity • Excellent interfacial adaptability	• Low chemical stability • Sensitive to moisture • Narrow electrochemical stability window
Halide	Crystalline Li ₃ InCl ₆ Amorphous LiTaOCl ₄	10 ⁻⁴ –10 ⁻²	• Good mechanical strength and interfacial adaptability • High electrochemical oxidation voltage	• Low chemical stability • Sensitive to moisture • Unstable with lithium metal

Besides ionic conductivity, the electrochemical stability window is another essential property of solid electrolytes. It is commonly evaluated using linear sweep voltammetry (LSV) with lithium as the counter electrode in a mixture containing a large proportion of conductive additive. Generally, oxide and halide electrolytes exhibit higher oxidation stability, whereas polymer electrolytes tend to show better reduction stability.

Interfacial stability is also critical in practical solid-state batteries. The rigid nature of solid/solid interfaces makes it difficult to form and maintain seamless contact; limited physical contact is prone to reconstruction due to structural changes or stress evolution in either phase. Applying external pressure is often necessary to stabilize the interface. Oxide-based cells usually require high-temperature sintering to reduce interfacial resistance and typically need to be operated under an applied pressure of several to tens of MPa. Sulfide and halide systems are generally processed under several hundred MPa and operated under tens to hundreds of MPa. In contrast, flexible polymer electrolytes only require applied pressures ranging from 0.1 to several MPa.

3. Inorganic Solid-State Electrolytes

Inorganic solid-state electrolytes used in SSBs are primarily classified into oxide-, sulfide-, and halide-based materials. Table 1 provides a summary of typical inorganic SSEs, highlighting their key characteristics. In the following sections, we will discuss in detail the properties and recent advancements in oxide-, sulfide-, and halide-based SSEs.

3.1. Oxide electrolytes

3.1.1. Structures and characteristics

Oxide-based SSEs primarily include LISICON-type, NASICON-type, perovskite-type, and garnet-type materials. Among LISICON-type electrolytes, Li₁₄Zn(GeO₄)₄ is a representative compound formed as a solid solution of Li₄GeO₄ and Zn₂GeO₄ (Fig. 1a) [45]. Its framework is composed of interconnected [Li₁₁Zn(GeO₄)₄]³⁻ units, with excess Li⁺ occupying octahedral interstitial sites. At elevated temperatures, the relatively weak Li–O bonds facilitate Li⁺ migration within planar layers, enabling σ of 1.3×10^{-4} S·cm⁻¹ at 300 °C [46]. Another LISICON derivative, Li_{3.5}Si_{0.5}P_{0.5}O₄, formed by combining Li₄SiO₄ and Li₃PO₄, exhibits enhanced Li⁺ content and more interstitial sites, which contribute to improved conductivity [47]. However, its room-temperature σ ($\sim 10^{-7}$ S·cm⁻¹) remains too low for practical application. In addition, the presence of reducible elements, such as Zn and Ge, leads to poor chemical stability when it is in contact with metallic lithium.

The NASICON-type structure, originally developed for sodium-ion conductors with the general formula Na_{1+x}Zr_{2-3-x}P_xSi_xO₁₂ (Fig. 1b), features a 3D framework composed of corner-sharing [PO₄] tetrahedra and [ZrO₆] octahedra [48]. Sodium ions (Na⁺) migrate through interconnected channels along the C-axis, resulting in high σ [49]. Lithium-substituted NASICON analogs, such as LiTi₂(PO₄)₃ and LiGe₂(PO₄)₃, exhibit lower Li⁺ mobility due to stronger Li–O bonds. Partial substitution of Ti⁴⁺ or Ge⁴⁺ with smaller Al³⁺ ions reduces the size of the metal-oxygen polyhedra, elongates Li–O bonds, and improves Li⁺ transport. As a result, compounds, such as Li_{1+x}Al_xTi_{2-x}(PO₄)₃ (LATP) and Li_{1+x}Al_xGe_{2-x}(PO₄)₃

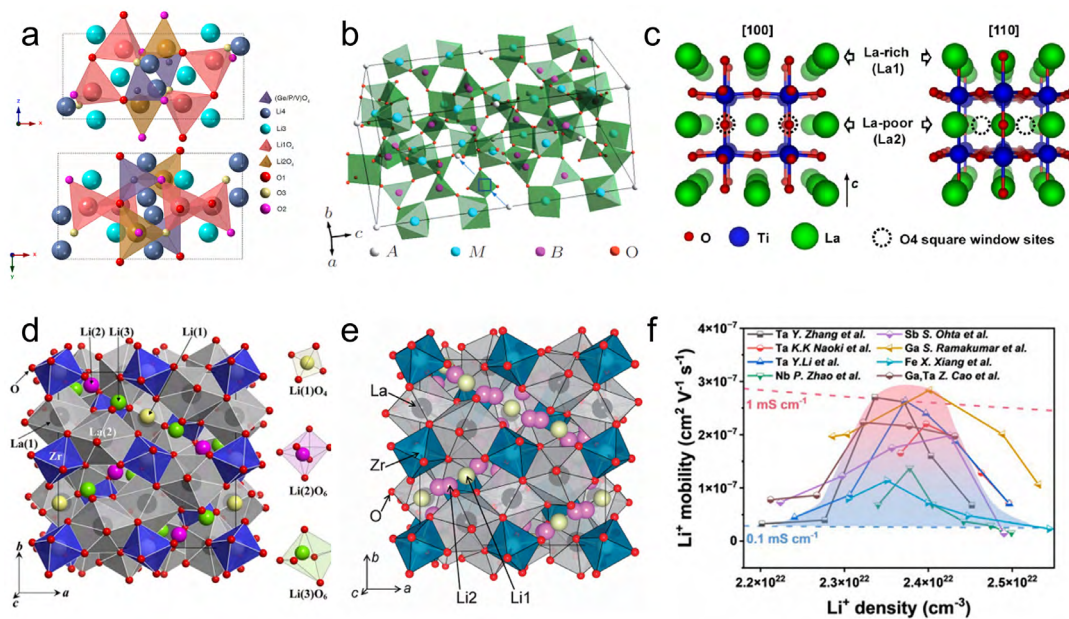


Fig. 1. Crystal structures of representative oxide-based solid electrolytes: (a) LISICON-type. Reproduced with permission from ref. [52]. Copyright 2019 American Chemical Society. (b) NASICON-type. Reproduced with permission from ref. [53]. Copyright 2021 Elsevier B.V. (c) LLTO. Reproduced with permission from ref. [54]. Copyright 2013 American Chemical Society. (d) Tetragonal LLZO. Reproduced with permission from ref. [55]. Copyright 2009 Elsevier Inc. (e) Cubic LLZO. Reproduced with permission from ref. [56]. Copyright 2011 The Chemical Society of Japan. (f) Li^+ mobility vs. Concentration. Reproduced with permission from ref. [57]. Copyright 2024 Elsevier B.V.

(LAGP), achieve room-temperature σ in the range of 10^{-4} - 10^{-3} S·cm $^{-1}$, with optimized sintering conditions pushing values toward $\sim 10^{-3}$ S·cm $^{-1}$ [49, 50]. NASICON-based electrolytes are valued for their high conductivity, stability in humid environments, and wide electrochemical stability window (~ 7 V *vs.* Li/Li $^{+}$). However, the susceptibility of Ti $^{4+}$ and Ge $^{4+}$ to reduction at the lithium-metal interface restricts their broader applicability [49–51].

Perovskite-type SSEs adopt the general formula ABO_3 , where A-site cations typically include Ca, Sr, or La, and B-site cations are often aluminum (Al) or titanium (Ti). Among these, $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ (LLTO) is a widely studied Li^+ conductor. In LLTO, Li^+ and La^{3+} share the A-site positions within a structure composed of corner-sharing TiO_6 octahedra (Fig. 1c). The large ionic radius of La^{3+} generates a high concentration of A-site vacancies, facilitating bulk σ up to $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ at room temperature. However, the presence of alternating La-rich and La-deficient domains leads to vacancy ordering and spatial heterogeneity, which disrupts uniform Li^+ transport and impedes overall ion migration [58]. Furthermore, the thermodynamic instability of the cubic phase results in phase coexistence with tetragonal, hexagonal, or rhombohedral structures, which increases grain boundary resistance and reduces total σ [59]. In addition, Ti^{4+} is prone to reduction upon contact with lithium metal, limiting the compatibility of LLTO with

lithium-metal anodes and constraining its practical application in SSBs.

Garnet-type SSEs, generally expressed as $A_3B_2(XO_4)_3$, feature A, B, and X cations occupying eight-, six-, and four-fold coordinated sites, respectively. Early garnet systems, such as $Li_5La_3M_2O_{12}$ (M = tantalum (Ta) or niobium (Nb)), demonstrated low σ ($\sim 10^{-5}$ S·cm $^{-1}$) [60]. Substitution of M with zirconium (Zr) led to the development of LLZO, which achieves improved σ up to 3×10^{-4} S·cm $^{-1}$. LLZO exists in tetragonal (Fig. 1d) and cubic (Fig. 1e) polymorphs at room temperature; the tetragonal phase exhibits poor σ ($\sim 10^{-6}$ S·cm $^{-1}$), while the cubic phase offers σ that is two orders of magnitude higher [61, 62]. In the cubic structure, the $[La_3Zr_2O_{12}]^{7-}$ framework accommodates Li^+ ions in 24d tetrahedral and 96h octahedral interstitial sites [63]. Stabilization of this high-conductivity cubic phase at ambient temperature is achieved through aliovalent doping at the Li and Zr sites, which also increases the concentration of lithium vacancies and enhances ion transport. Optimal σ is typically observed when the lithium content is maintained between 6.2 and 6.6 (Fig. 1f) [57]. LLZO ceramics are readily processable, chemically stable against lithium metal, and exhibit room-temperature σ approaching 10^{-3} S·cm $^{-1}$, along with a wide electrochemical stability window exceeding 4 V. These favorable properties position LLZO as a leading candidate for next-generation solid-state lithium

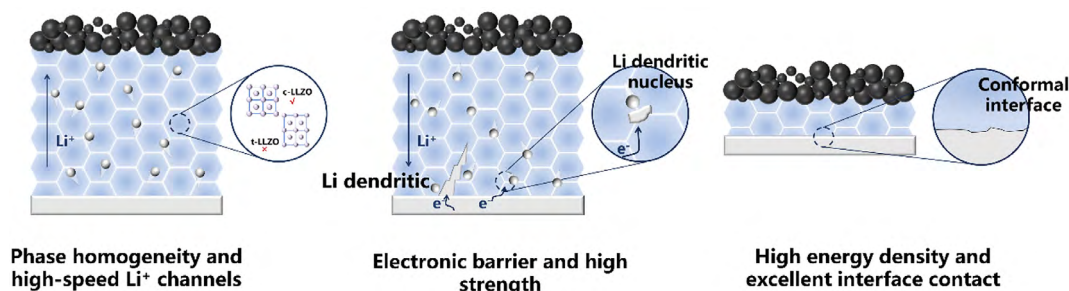


Fig. 2. Key challenges of LLZO in SSBs.

batteries [64]. The following discussion will focus on the key challenges and recent advancements related to LLZO-based electrolytes.

3.1.2. Challenges of garnet-Type solid electrolytes

Despite their favorable characteristics, garnet-type LLZO electrolytes encounter several critical limitations (Fig. 2). At room temperature, LLZO exists in both tetragonal and cubic phases, with the tetragonal structure exhibiting poor Li^+ conductivity. Therefore, stabilizing its phase in pure cubic form is essential for consistent performance. Lithium dendrite formation remains a significant challenge. Although high σ contributes to dendrite suppression, effective mitigation also requires low electronic conductivity and high mechanical strength to prevent electron leakage and dendrite penetration. Moreover, the presence of heavy elements and the necessity for thick ceramic layers result in a significant increase in weight and substantial reduction in energy density of SSBs. Consequently, minimizing thickness and weight of LLZO-based electrolytes is considered a critical step toward their commercial deployment in SSB technologies.

Undoped LLZO exhibits σ up to $3 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ when stabilized in the cubic phase, while the tetragonal phase shows significantly lower σ of $\sim 10^{-6} \text{ S}\cdot\text{cm}^{-1}$ due to distinct Li^+ transport mechanisms. In the tetragonal structure, Li^+ ions are ordered and migrate through a concerted hopping process with high diffusion barriers. Conversely, the cubic phase features disordered Li^+ occupancy across 24d tetrahedral and 96h octahedral sites, facilitating a transition from collective to single-ion migration and reducing energy barriers. In addition, the symmetry transformation from $I4d$ to $I3d$ introduces extra diffusion pathways (48e-12a/b-48e), further improving Li^+ mobility [65]. Li^+ conductivity is governed by the mobility, concentration, and charge of Li^+ ions; however, these parameters often exhibit trade-offs. For instance, excessive Li content may lower mobility due to increased site occupancy. Optimal conductivity is achieved at Li stoichiometries

between 6.2 and 6.6 [57]. To reach this range and enhance electrochemical performance, aliovalent doping and optimized sintering protocols are applied to stabilize the cubic phase, increase sublattice disorder, and maximize the concentration of mobile Li^+ ions.

Enhancing σ is essential for efficient battery operation, as it improves rate capability and reduces energy loss during cycling. Equally important is the suppression of Li dendrite formation to maintain stable performance and prevent internal short circuits. Studies have shown that electronic conductivity and mechanical strength, both of which are strongly influenced by grain boundary properties, and play critical roles in dendrite suppression. In LLZO, grain boundaries possess an electronic bandgap approximately 3.7 V lower than that of the grain interiors, resulting in relatively high electronic conductivity ($\sim 10^{-8} \text{ S}\cdot\text{cm}^{-1}$), which is significantly greater than that of NASICON-type electrolytes ($\sim 10^{-10} \text{ S}\cdot\text{cm}^{-1}$) [66, 67]. This elevated electronic conductivity facilitates electron leakage along grain boundaries, promoting Li dendrite nucleation within the electrolyte. Furthermore, grain boundaries are mechanically weaker regions where dendrites tend to propagate. The intrinsic fracture toughness of LLZO is approximately $0.96 \text{ MPa}\cdot\text{m}^{1/2}$, which is considerably lower than that of conventional ceramics ($\sim 2 \text{ MPa}\cdot\text{m}^{1/2}$), further increasing susceptibility to mechanical failure [68]. Therefore, reducing electronic conductivity and enhancing mechanical strength, particularly at grain boundaries, are critical strategies for mitigating dendrite growth, and improving the safety and durability of LLZO-based solid-state Li-metal batteries.

Electrolyte thickness plays a critical role in determining the energy density of SSBs. Huang et al. [69] demonstrated that electrolyte thickness must be reduced below $\sim 25 \mu\text{m}$ to achieve battery energy densities exceeding $400 \text{ Wh}\cdot\text{kg}^{-1}$. However, early studies on LLZO primarily focused on bulk ceramic electrolytes with thickness exceeding $500 \mu\text{m}$, emphasizing densification, ionic and electronic conductivity, and

electrode interface compatibility. In comparison, LLZO-polymer composite thin films exhibit improved interfacial conformability, facilitating stable and well-adhered interfaces with electrodes. This reduces interfacial resistance and enhances Li^+ transport. Therefore, the development of thin-film LLZO electrolytes is considered essential for practical implementation, offering a promising pathway toward scalable, high-energy-density SSB systems.

3.1.3. Innovative solutions to critical issues

The cubic phase of LLZO is metastable and requires aliovalent doping at Li and Zr sites to stabilize the structure and disrupt Li ordering, thereby enabling high σ . Microstructural optimization is also critical and can be achieved through tailored sintering protocols, such as precise control of Li_2O partial pressure [64], along with advanced densification methods including spark plasma sintering (SPS) [70], hot isostatic pressing (HIP) [71], atmospheric plasma spraying (APS) [72], and ultrafast high-temperature sintering (UHS) [73]. These approaches are essential for promoting dense grain connectivity and mechanical integrity. To mitigate Li dendrite penetration, the incorporation of second-phase materials has been employed to reduce electronic conductivity and enhance mechanical strength. In addition, ferroelectric materials have shown potential to facilitate uniform Li deposition due to their intrinsic electric fields. Addressing LLZO's low energy density requires

the fabrication of thin-film electrolytes to minimize thickness and improve volumetric energy density. Organic-inorganic composite films further enhance interfacial conformability and mechanical compatibility, supporting the development of scalable and high-performance SSB systems.

Entropy-driven stabilization of the cubic LLZO structure is commonly achieved through elemental doping, which promotes single-ion conduction. The Zr site serves as the primary target, with Ta and Nb being the most frequently used dopants. Both elements stabilize the cubic phase, although Ta-doping has been shown to result in higher σ ($\sim 10^{-3} \text{ S}\cdot\text{cm}^{-1}$) [64]. As demonstrated by M. D. Johannes et al. [88], at a Li vacancy concentration of 0.5, Ta substitution elongates the Li–O bond length, facilitating Li^+ migration and enhancing conductivity (Fig. 3a). At the Li site, Al, gallium (Ga), and iron (Fe) are typical dopants. Ga^{3+} doping at concentrations above 0.07 molar ratio induces a phase transition from $\text{Ia}\bar{3}\text{d}$ to $\text{I}\bar{4}3\text{d}$ [89], introducing additional Li^+ migration pathways and achieving conductivity up to $2.06 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ (Fig. 3b). By contrast, Al^{3+} doping does not alter the crystal structure but occupies sites that partially obstruct Li^+ transport, leading to lower conductivity compared with Ta doping [90] (Fig. 3c). Fe^{3+} doping is limited due to the valence instability of Fe^{3+} in contact with Li metal. Doping at the lanthanum (La) site with smaller cations results in a lattice without phase transformation, which reduces Li^+ mobility and decreases σ . The

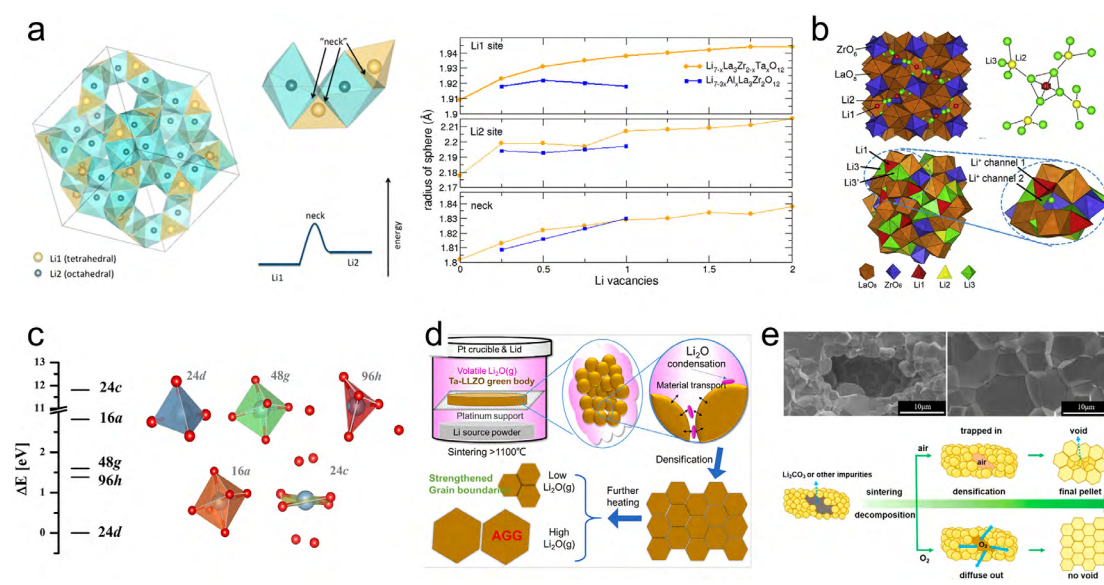


Fig. 3. (a) Variation of Li^+ ionic radius with lithium vacancy concentration. Reproduced with permission from ref. [88]. Copyright 2015 American Chemical Society. (b) Crystal structure and Li^+ transport path in c-LLZO (space group $\text{I}\bar{4}3\text{d}$). Reproduced with permission from ref. [91]. Copyright 2020 Elsevier Ltd. (c) Coordination polyhedra surrounding Al^{3+} at the 24d, 48g, 96h, 16a, and 24c sites, and their site preference energies. Reproduced with permission from ref. [90]. Copyright 2014 American Chemical Society. (d) Mechanism of Li_2O partial pressure regulation during sintering. Reproduced with permission from ref. [64]. Copyright 2019 Elsevier B.V. (e) O_2 -assisted sintering principle for densification enhancement. Reproduced with permission from ref. [92]. Copyright 2020 American Chemical Society.

Table 2. Representative physical properties of various doped LLZO systems.

Component	Sintering condition	$\sigma_{\text{total}} (\times 10^{-4} \text{ S}\cdot\text{cm}^{-1}, 25^\circ\text{C})$	Ea (eV)	Ref.
Undoped				
$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$	1230 °C $\times$ 36 h, CPS	3	0.34	[74]
Li sites				
$\text{Li}_{6.55}\text{Ga}_{0.15}\text{La}_3\text{Zr}_2\text{O}_{12}$	1075 °C $\times$ 12 h, CPS	20.6	N/A	[75]
$\text{Li}_{6.25}\text{Al}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$	1150 °C $\times$ 10 min, FAST	5.7	0.3	[76]
$\text{Li}_{6.25}\text{Fe}_{0.25}\text{La}_3\text{Zr}_2\text{O}_{12}$	1230 °C $\times$ 6 h, CPS	13.8	0.28	[77]
Zr sites				
$\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Nb}_{0.25}\text{O}_{12}$	1200 °C $\times$ 36 h, CPS	8	0.31	[78]
$\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$	1250 °C $\times$ 1 min, CPS	10	N/A	[64]
$\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.7}\text{W}_{0.3}\text{O}_{12}$	1100 °C $\times$ 36 h, CPS	7.89 (30 °C)	0.45	[79]
$\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Mo}_{0.25}\text{O}_{12}$	1230 °C $\times$ 4 h, CPS	3.4	0.43	[80]
$\text{Li}_{6.5}\text{La}_3\text{Zr}_{1.75}\text{Te}_{0.25}\text{O}_{12}$	1100 °C $\times$ 15 h, CPS	1.02	0.41	[81]
$\text{Li}_6\text{La}_3\text{Ta}_{1.5}\text{Y}_{0.5}\text{O}_{12}$	1100 °C $\times$ 6 h, CPS	1.62	N/A	[82]
$\text{Li}_6\text{La}_3\text{SnNbO}_{12}$	1130 °C $\times$ 12 h, CPS	0.35	0.503	[83]
$\text{Li}_6\text{La}_3\text{SnTaO}_{12}$	1130 °C $\times$ 12 h, CPS	0.42	0.498	[83]
$\text{Li}_{6.6}\text{La}_3\text{Zr}_{1.6}\text{Sb}_{0.4}\text{O}_{12}$	1100 °C $\times$ 24 h, CPS	7.7	0.34	[84]
$\text{Li}_{7.1}\text{La}_3\text{Zr}_{1.9}\text{Cr}_{0.1}\text{O}_{12}$	1230 °C $\times$ 16 h, CPS	5.2	0.39	[85]
La sites				
$\text{Li}_{6.6}\text{La}_{2.6}\text{Ce}_{0.4}\text{Zr}_2\text{O}_{12}$	1050 °C $\times$ 1 h, HIP	0.144	N/A	[86]
$\text{Li}_7\text{La}_{2.6}\text{Sm}_{0.4}\text{Zr}_2\text{O}_{12}$	1200 h $\times$ 18 h, CPS	0.6	0.40	[87]
$\text{Li}_7\text{La}_{2.6}\text{Dy}_{0.4}\text{Zr}_2\text{O}_{12}$	1200 h $\times$ 18 h, CPS	1.6	0.35	[87]
$\text{Li}_7\text{La}_{2.9}\text{Er}_{0.1}\text{Zr}_2\text{O}_{12}$	1200 h $\times$ 18 h, CPS	1.0	0.22	[87]
$\text{Li}_7\text{La}_{2.9}\text{Yb}_{0.1}\text{Zr}_2\text{O}_{12}$	1200 h $\times$ 18 h, CPS	1.5	0.18	[87]

CPS: Conventional pressureless sintering; FAST: field-assisted sintering; HIP: hot isostatic pressing.

effects of various doping strategies on sintering conditions, ion conductivity, and activation energy are summarized in Table 2.

LLZO sintering is hindered by abnormal grain growth due to high sintering activity at elevated temperatures. Conventional pressureless sintering has been shown by Huang et al. [64] to achieve up to 98% relative density by precisely controlling the Li_2O partial pressure within platinum (Pt) crucibles (Fig. 3d). Both excessive and insufficient Li_2O vapor pressures negatively impact densification and microstructural uniformity. Shen et al. [92] demonstrated that near-full densification can be achieved by sintering in an oxygen atmosphere, which allows oxygen to diffuse out of pores before their closure, unlike nitrogen that becomes trapped during air sintering (Fig. 3e). Advanced densification techniques, such as

spark plasma sintering, hot isostatic pressing, aerosol spray pyrolysis, and Joule heating rapid sintering, have been employed to further increase LLZO density, approaching theoretical values. A radar diagram comparing various sintering methods in terms of temperature, duration, thickness, relative density, cost, and Li loss is presented in Fig. 4.

When exposed to air, LLZO reacts with H_2O and CO_2 , forming alkaline residues (Li_2CO_3 and LiOH) on its surface. These residues impede Li^+ transport and may promote lithium dendrite growth. Although high-temperature treatment can decompose these surface layers, it often causes lithium loss and the formation of poorly conductive secondary phases [93]. To overcome this limitation, Wang et al. [94] developed a high-temperature thermal pulse technique that rapidly heats LLZO to 1250 °C within less than

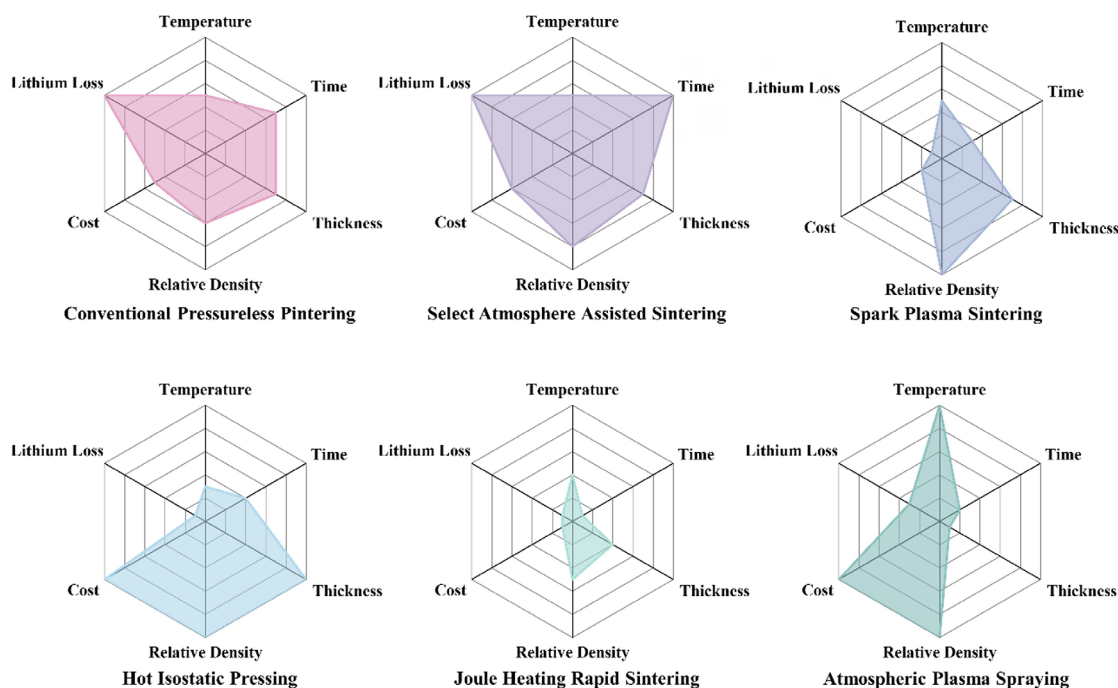


Fig. 4. Radar charts comparing temperature, time, thickness, relative density, cost, and lithium loss of LLZO across different sintering methods.

2 s, effectively removing residues while avoiding lithium evaporation and phase degradation. This treatment increased the ionic conductivity of LLZO from approximately $1.6 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ to $3.2 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$. Alternatively, acid treatment offers a low-temperature approach for residue removal. For example, Huo et al. [95] showed that immersing $\text{Li}_{6.4}\text{La}_3\text{Zr}_{1.4}\text{Ta}_{0.6}\text{O}_{12}$ in 1 M HCl for 30 s effectively eliminates surface contaminants. Care must be taken to control the treatment duration to prevent damage to the LLZO structure. Consequently, milder acids such as citric acid, phosphoric acid, and polyacrylic acid have also been explored for the removal of surface residues [96, 97].

As electronic conductivity and mechanical strength in LLZO are predominantly influenced by grain boundary characteristics, grain boundary engineering is essential for suppressing electron leakage and enhancing structural integrity. Zheng et al. [98] introduced Li_2TiO_3 into $\text{Li}_{6.75}\text{La}_3\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12}$ (LLZTO), which transforms Li_2TiO_3 into LaTiO_3 at high temperatures and localizes at grain boundaries (Fig. 5a). This modification reduces electronic conductivity and improves grain bonding, resulting in a critical current density of $1.8 \text{ mA}\cdot\text{cm}^{-2}$. Similarly, You et al. [67] incorporated Li_3TaO_4 and Zr_3O phases at grain boundaries, enhancing both electrical insulation and mechanical strength (Fig. 5b). Biao et al. [99] added Li_3AlF_6 , which reacts to form LiAlO_2 and doped LLZO-LLZOF phases at grain boundaries. These phases suppress LiC_x formation and reduce bulk

electronic conductivity, thereby inhibiting dendrite nucleation (Fig. 5c). In addition, Xiong et al. [100] embedded ferroelectric BaTiO_3 at grain boundaries, generating localized internal electric fields that promote uniform Li deposition, presenting a promising strategy for mitigating dendrite growth (Fig. 5d).

Bulk ceramic electrolytes often exhibit low energy densities due to their considerable thickness, while reducing their thickness in films typically compromises mechanical integrity. Therefore, an optimized balance between mechanical robustness and minimal thickness is necessary. Common architectural strategies include dense single-layer, multilayer, and single-layer porous ceramics. Kim et al. [101] fabricated an LLZO ceramic film with a thickness of $\sim 74 \mu\text{m}$ using a tape casting method (Fig. 6a). The LLZO surface was coated with silver (Ag), combined with an Ag-C composite interlayer through cold isostatic pressing and subsequently bonded to a Li metal anode and paired with an NCM333 cathode. This configuration enabled the assembly of a pouch cell that maintained stable over 800 cycles at $1.6 \text{ mA}\cdot\text{cm}^{-2}$, highlighting the practical viability of LLZO ceramic films in SSB applications. Building on single-layer membrane designs, Wachsmann et al. [102] introduced porous layers on both sides of a dense LLZO core, doped with elements such as Nb, Nd, Cr, and Ce. This doping strategy enhanced the electronic conductivity of the porous LLZO regions by 3–4 orders of magnitude (Fig. 6b). The resulting mixed ionic-electronic conductivity

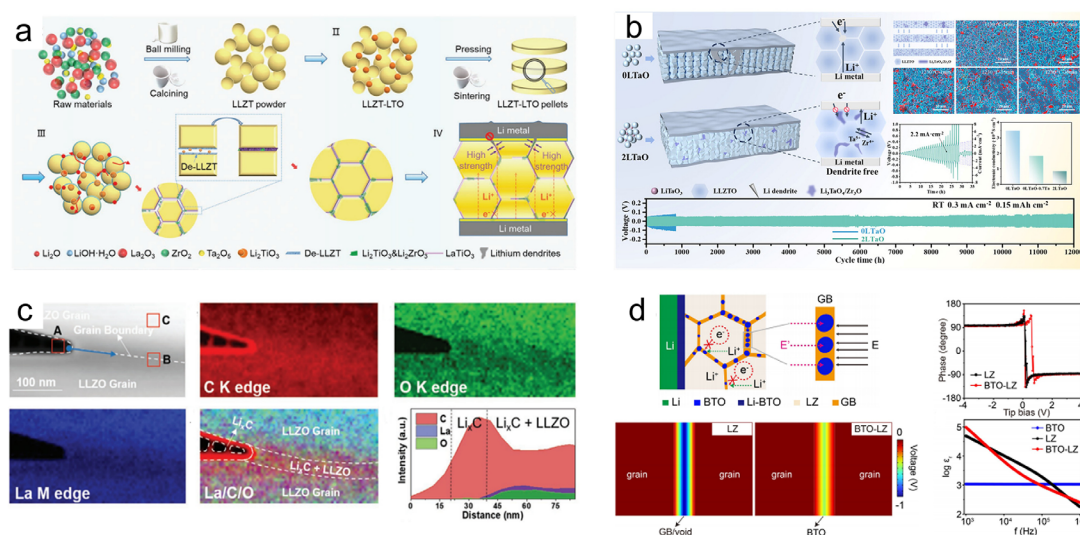


Fig. 5. Grain boundary engineering strategies for LLZO: (a) LaTiO_3 modification. Reproduced with permission from ref. [98]. Copyright 2022 John Wiley and Sons. (b) $\text{Li}_2\text{TaO}_4/\text{Zr}_2\text{O}_3$ phases. Reproduced with permission from ref. [67]. Copyright 2025 American Chemical Society. (c) Formation of conductive Li_xC species. Reproduced with permission from ref. [99]. Copyright 2023 John Wiley and Sons. (d) BaTiO_3 -modified electric-field-guided lithium deposition. Reproduced with permission from ref. [100]. Copyright 2024 The Royal Society of Chemistry.

enabled controlled Li deposition and stripping within porous layers. Symmetric Li cells employing this porous-dense-porous configuration achieved critical current densities up to $100 \text{ mA}\cdot\text{cm}^{-2}$, significantly surpassing previously reported values. However, the solid-solid interfaces with electrodes remained rigid, limiting interfacial adaptability. To overcome this, Wen et al. [103] developed a $12\text{-}\mu\text{m}$ porous LLZO scaffold that served as a framework for *in-situ* polymerization, forming a dual-continuous phase composite electrolyte with conformal and flexible interfaces (Fig. 6c). This composite exhibited σ of $1.19 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ and t_{Li^+} of 0.83. When integrated into a pouch cell with an NCM83 cathode ($4 \text{ mAh}\cdot\text{cm}^{-2}$) and a $50\text{-}\mu\text{m}$ Li anode, the system delivered high energy densities of $376 \text{ Wh}\cdot\text{kg}^{-1}$ and $1186 \text{ Wh}\cdot\text{L}^{-1}$.

3.1.4. Development outlook

Oxide-based SSEs offer high σ and excellent mechanical strength, making them strong candidates for inhibiting Li dendrite growth. Among them, garnet-type LLZO electrolytes are particularly notable for their favorable properties and superior chemical stability. In this review, the structures and performance characteristics of various oxide SSEs have been examined, with a focused analysis of the critical challenges associated with LLZO and the advanced strategies developed to overcome them.

Nonetheless, several fundamental challenges remain unresolved, including the establishment of robust and reproducible synthesis protocols for LLZO, the precise control of the balance between electronic

and ionic conductivities, and the inherent trade-off between energy density and mechanical strength of the electrolyte. To further meet the practical requirements of solid-state LIBs with high energy density and safety, the following areas warrant continued and focused investigation:

1) To enable stable LLZO fabrication, a comprehensive set of rigorous and quantitative standards must be defined, encompassing precursor purity, synthesis temperature, humidity regulation, atmospheric conditions, and processing protocols. Establishing such criteria is essential for ensuring the consistent production of high-quality LLZO, which is critical for scalable manufacturing and systematic performance evaluation.

2) Although doping and second-phase composite strategies are commonly employed to reduce electronic conductivity, challenges remain. Fluorine doping tends to suppress both ionic and electronic conductivities, while the introduction of second phases often impedes grain boundary ion transport despite limiting electron leakage. Consequently, the development of novel methods that selectively reduce electronic conductivity without sacrificing σ is urgently required and should be a focus of future research.

3) The inherent trade-off between energy density and mechanical strength presents a significant challenge. Despite recent progress, a comprehensive solution that simultaneously achieves high energy density, strong interfacial compatibility, and mechanical robustness has yet to be realized. Advancing thin-film electrolyte systems that preserve conformal

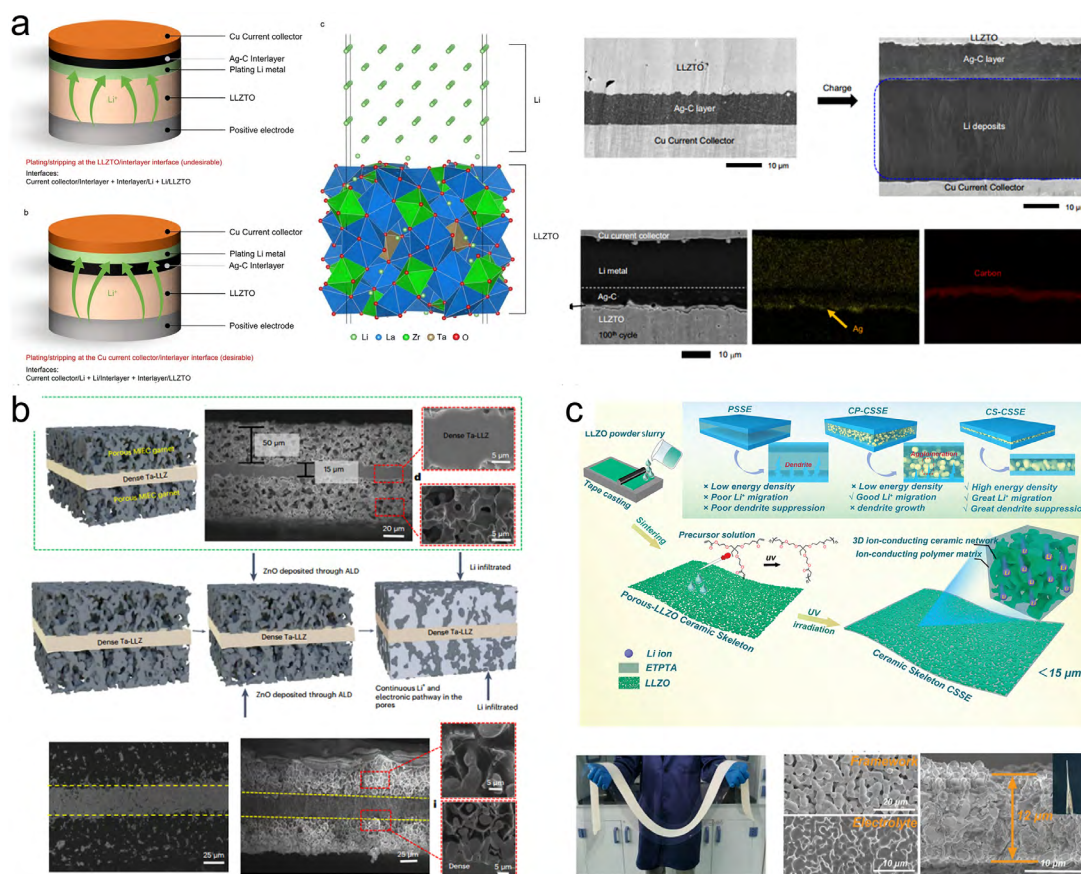


Fig. 6. Interface engineering strategies for LLZO: (a) Ag-C-modified LLZO thin film and cell cross-section. Reproduced with permission from ref. [101]. Copyright 2023 Springer Nature. (b) Porous layer-assisted multilayer LLZO symmetric cell. Reproduced with permission from ref. [102]. Copyright 2023 Springer Nature. (c) Organic-inorganic composite electrolyte structure and morphology. Reproduced with permission from ref. [103]. Copyright 2023 John Wiley and Sons.

interfaces and structural integrity under high-rate cycling is a key priority for future research.

3.2. Sulfide electrolytes

3.2.1. Structures, characteristics and conduction mechanisms

Sulfide electrolytes have emerged as highly promising candidates for all-solid-state Li batteries due to their distinctive intrinsic properties. In comparison to oxide and polymer-based solid electrolytes, sulfide systems offer several notable advantages. They exhibit high Li^+ conductivities in the range of 10^{-3} – $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at room temperature, comparable to or exceeding those of conventional liquid electrolytes [104], attributed to their low migration energy barriers and wide ion transport pathways. Moreover, sulfide electrolytes possess a low Young's modulus, typically below 30 GPa, which enables deformation under moderate external pressure [105]. This mechanical softness facilitates to improve solid-solid interfacial contact and allows densification via cold pressing.

In addition, their exceptional room-temperature processability eliminates the need for high-temperature sintering, simplifying manufacturing process and reducing production costs.

Based on their crystalline states, sulfide electrolytes are categorized into glassy, glass-ceramic, and crystalline types. Alternatively, classification by chemical composition divides them into binary and ternary sulfides. Each category exhibits distinct characteristics in terms of structural order, ion migration mechanisms, formability, and application compatibility.

Glassy sulfide electrolytes are typically binary systems synthesized using Li_2S as the Li source, combined with precursors such as P_2S_5 , B_2S_3 , SiS_2 , or GeS_2 . Among these, the Li_2S - P_2S_5 system is the most representative. These materials lack long-range structural order and consist of amorphous random networks without well-defined ion migration pathways. Li^+ transport occurs through random hopping between available sites, requiring the overcoming of local energy barriers. As a result, their σ is strongly temperature-dependent, exhibiting thermally activated

behavior. Due to the absence of directional lattice channels, ion conduction in glassy sulfide electrolytes is generally isotropic and characterized by relatively high activation energies, typically in the range of 0.3–0.4 eV or higher [106].

Glass-ceramic electrolytes are synthesized by applying controlled heat treatment to glassy materials, inducing partial crystallization and forming composites composed of both crystalline and amorphous phases. Their structure consists of metastable crystalline particles, typically on the nanometer or micrometer scale, uniformly dispersed within an amorphous matrix. The crystalline regions offer ordered lattice frameworks with continuous Li^+ migration channels, enhancing σ . The amorphous phase contributes flexible interfaces, reduces grain boundary resistance, and mitigates structural cracking. As a result, glass-ceramic electrolytes combine the high conductivity of crystalline materials with the processability of amorphous systems, often exhibiting superior overall performance compared with either pure glassy or crystalline counterparts. For example, heat treatment of $\text{Li}_2\text{S-P}_2\text{S}_5$ systems can induce the formation of thio-LISICON II or $\text{Li}_7\text{P}_3\text{S}_{11}$ phases, significantly increasing σ .

Crystalline sulfide electrolytes possess highly ordered lattice structures with well-defined Li^+ migration channels. Among these, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS)-type and argyrodite-type electrolytes ($\text{Li}_6\text{PS}_5\text{X}$, where $\text{X} = \text{Cl}, \text{Br}, \text{or I}$) are the most widely studied and representative systems. LGPS adopts a tetragonal structure consisting of interconnected GeS_4^{4-} and PS_4^{3-} tetrahedra, forming a framework in which Li^+ occupies interstitial sites (Fig. 7a) [107]. This structure provides one-dimensional fast ion transport along the c -axis, enabling low activation energy diffusion (~ 0.2 – 0.25 eV). The room-temperature σ of LGPS can reach $10^{-2} \text{ S}\cdot\text{cm}^{-1}$, ranking among the highest for crystalline sulfide electrolytes. In addition, LGPS exhibits compositional flexibility, allowing partial substitution of Ge with more cost-effective elements such as Si or Sn without significantly reducing conductivity [109, 110]. Argyrodite-type electrolytes have a cubic structure composed of PS_4^{3-} tetrahedra, sulfide anions (S^{2-}), and halide ions (X^-), with Li^+ occupying structural voids (Fig. 7b) [108]. These ions migrate through a three-dimensional network, enabling nearly isotropic conduction. The halide species (Cl^- , Br^- , or I^-) strongly influence the structure and transport properties. Among them, $\text{Li}_6\text{PS}_5\text{Cl}$ is particularly notable for its high conductivity (10^{-3} – $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ at room temperature), enhanced air stability, and good processability. Further improvements can be achieved by controlling the degree of disorder at Li and halide sites to optimize ion transport pathways. Crystalline sulfide

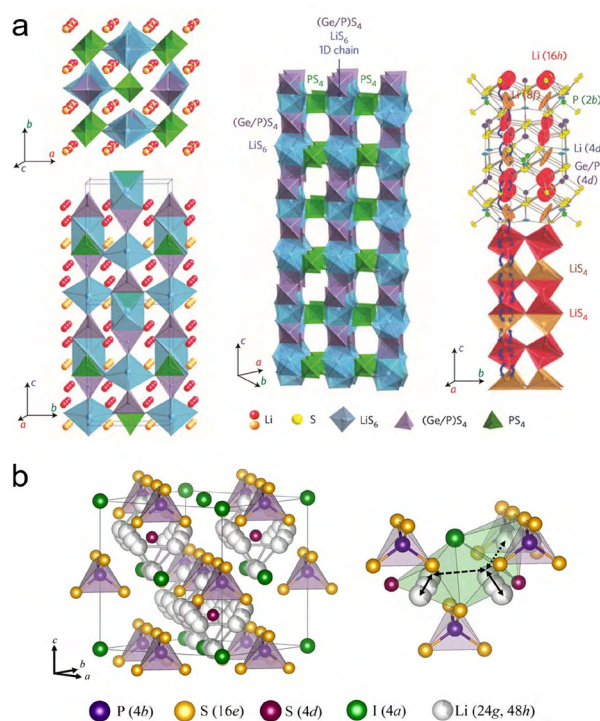


Fig. 7. (a) Crystal structure and Li^+ migration pathways of $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$. Reproduced with permission from Ref. [107]. Copyright 2011, Springer Nature. (b) Crystal structure and Li^+ migration pathways of argyrodite-type electrolyte ($\text{Li}_6\text{PS}_5\text{I}$). Reproduced with permission from Ref. [108]. Copyright 2018, American Chemical Society.

electrolytes exhibit the highest intrinsic σ among sulfide categories. However, their brittleness, complex fabrication, and large grain boundary impedance remain key limitations. Therefore, careful tuning of structural order, channel geometry, and cation disorder is essential to enhance their overall performance.

3.2.2. Synthesis methods and their advantages and limitations

The performance of sulfide electrolytes is strongly influenced by the synthesis method. An optimized preparation process determines not only the crystallinity and phase purity but also significantly affects σ and interfacial stability. Currently, the primary synthesis approaches include solid-state reactions, mechanical ball milling, and wet chemical methods, each offering distinct characteristics and advantages.

The solid-state reaction is one of the most established and widely used methods for synthesizing sulfide electrolytes. In this approach, precursors such as Li_2S and P_2S_5 are mixed in stoichiometric ratios and heated to promote a complete reaction, followed by rapid cooling to form the solid electrolyte. However, high-temperature sintering often causes volatilization of Li and sulfur (S), leading to impurity phases that reduce material purity. To address this, reactions

are typically conducted in vacuum-sealed quartz tubes. The combination of pre-pressing, vacuum sealing, and controlled high-temperature treatment helps minimize volatilization. Using hot-press sintering, glass-ceramic electrolytes based on the $\text{Li}_2\text{S-P}_2\text{S}_5$ system have achieved ionic conductivities up to $1.7 \times 10^{-2} \text{ S}\cdot\text{cm}^{-1}$, demonstrating excellent ion transport properties [111]. Similar solid-state synthesis methods apply to high-conductivity ternary sulfide electrolytes. For example, the LGPS can be synthesized by reacting Li_2S , GeS_2 , and P_2S_5 at 550°C , followed by slow cooling, yielding conductivities exceeding $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ [107]. Argyrodite electrolytes, such as $\text{Li}_6\text{PS}_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$), can also be produced by solid-state methods; however, these often require extended heating durations, with some processes involving annealing time of up to two weeks, resulting in lengthy synthesis cycles.

Mechanical ball milling provides a simpler, low-temperature synthesis route that has become increasingly important in the preparation of sulfide electrolytes. This method includes intense particle collisions and diffusion reactions, enabling the formation of amorphous electrolytes at room temperature without the need for high-temperature equipment. It applies to both binary and ternary systems. For example, $\text{Li}_2\text{S-P}_2\text{S}_5$ electrolytes synthesized solely by ball milling typically exhibit ionic conductivities in the range of 10^{-4} – $10^{-3} \text{ S}\cdot\text{cm}^{-1}$. Combining ball milling with post-treatment processes such as annealing or hot pressing significantly improves crystallinity and interparticle contact, thereby enhancing σ . In the case of the $70\text{Li}_2\text{S-30P}_2\text{S}_5$ system, σ can reach $8.6 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ following ball milling and hot-press sintering [112]. Similarly, for chlorine-rich argyrodite electrolytes ($\text{Li}_{5.5}\text{PS}_{4.5}\text{Cl}_{1.5}$), conductivity increases from $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ after initial ball milling to $8 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ upon annealing [113]. Despite its advantages, mechanical ball milling has limitations, including a labor-intensive process, long processing time, and the risk of introducing metallic impurities due to high-energy impacts. In addition, electrolytes synthesized via this method often require further annealing to achieve optimal performance. Therefore, ball milling and solid-state reaction methods are considered complementary, and their combination can reduce synthesis time while improving material properties.

Wet chemical synthesis has emerged as a promising approach for preparing sulfide electrolytes. This method utilizes a liquid solvent as the reaction medium, enabling uniform dispersion and reaction of precursors. Electrolyte powders are typically obtained through solvent evaporation or precipitation, producing fine particles with controlled morphology and size. The process is relatively simple, flexible,

and well-suited for large-scale manufacturing. For instance, Liu et al. pioneered the liquid-phase synthesis of sulfide electrolytes using tetrahydrofuran (THF) to synthesize $\beta\text{-Li}_3\text{PS}_4$ [114]. Subsequent studies refined solvent systems (e.g., THF/ethanol mixtures), reaction durations, and drying conditions, yielding $\text{Li}_6\text{PS}_5\text{Cl}$ electrolytes with conductivities up to $3.9 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ [115]. Wet chemical synthesis also offers advantages for scalable production and thin-film fabrication. However, several limitations remain. Common solvents, including THF, acetonitrile, and toluene, are often toxic and environmentally hazardous. Residual solvents or by-products may form non-conductive phases at grain boundaries, degrading σ . In addition, electrolytes produced via wet chemical routes typically require post-synthesis annealing to enhance crystallinity and performance, and they often lag behind solid-state or ball-milled counterparts in overall electrochemical properties.

3.2.3. Major challenges and mitigation strategies

Although sulfide electrolytes offer excellent σ , interfacial adaptability, and ease of processing, several intrinsic limitations hinder their large-scale implementation and long-term stability. Among these, poor air stability is a major concern. Sulfide materials readily react with atmospheric moisture, producing hydrogen sulfide (H_2S) gas and compromising the structural integrity of the electrolyte, which leads to reduced σ . Exposure to carbon dioxide (CO_2) further exacerbates degradation by forming insulating lithium carbonate (Li_2CO_3) phases through reactions with lithium-containing byproducts, such as LiOH or Li_2S . These interfacial byproducts increase resistance and accelerate performance decline. Even minor fluctuations in humidity or CO_2 levels during ball milling, storage, or cell assembly can cause substantial variations in material quality (Fig. 8a) [116]. Therefore, enhancing intrinsic moisture resistance or mitigating water reactivity through surface coatings and compositional modifications has become a key research direction. The incorporation of oxide components and the development of sulfur-oxygen coexisting phases have been shown to improve moisture tolerance. In addition, fluorination treatments and dense protective surface coatings have demonstrated effectiveness in retarding air-induced degradation of sulfide electrolytes [117].

Besides air stability, solvent stability is another critical factor limiting the practical use of sulfide electrolytes. In composite electrode fabrication, slurry-casting techniques necessitate direct contact of electrolyte with solvents. However, sulfide electrolytes are generally unstable in polar solvents, which often results in structural degradation and a marked decline in σ

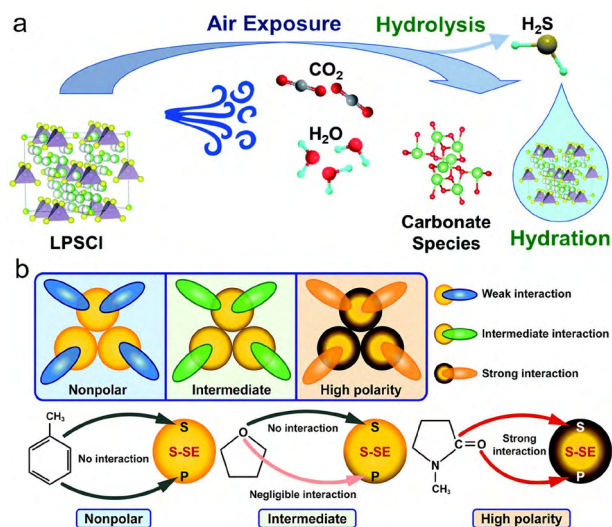


Fig. 8. (a) Chemical reactions of sulfide solid electrolytes upon exposure to ambient air. Reproduced with permission from Ref. [116]. Copyright 2022, Royal Society of Chemistry. (b) Compatibility of sulfide solid electrolytes and solvents of varying polarity and possible nucleophilic attack mechanisms. Reproduced with permission from Ref. [118]. Copyright 2022, Royal Society of Chemistry.

(Fig. 8b). This instability arises from nucleophilic attacks by solvent molecules containing electron-rich atoms (e.g., nitrogen or oxygen) on electrophilic centers such as P^{5+} in the sulfide structure. Such interactions disrupt key structural units, including PS_4^{3-} and $P_2S_7^{4-}$, forming degradation products with low σ . In addition, S^{2-} may react with electrophilic carbon atoms in carbonate-based solvents, further accelerating deterioration [118]. These solvent-induced reactions not only compromise the electrochemical performance of sulfide electrolytes but also severely restrict their compatibility with wet-processing techniques.

To improve solvent stability of sulfide electrolytes, several strategies have been developed. Firstly, selecting low-polarity solvents, such as THF or toluene (TOL), helps reduce chemical reactivity due to their low nucleophilicity. Secondly, applying protective surface layers, such as lithium fluoride (LiF) coatings or polymer membranes, physically separate the electrolyte from solvents, effectively suppressing degradation reactions. Thirdly, compositional modifications through elemental doping with elements such as oxygen, fluorine (F), or antimony (Sb) enhance the intrinsic structural stability of the electrolyte and reduce its chemical reactivity. For example, Zhao et al. demonstrated that partial substitution of P with Sb and S with Cl stabilized the crystal structure and improved resistance to solvent-induced degradation in TOL environments [119]. In addition, process optimization, such as controlling solvent evaporation rates and minimizing contact time, can reduce residual

solvent content and its impact on σ . These combined strategies can improve solvent compatibility, supporting broader application and large-scale manufacturing of sulfide-based solid electrolytes.

Beyond air and solvent stabilities, electrochemical stability is a critical limitation for the practical use of sulfide electrolytes. Theoretical calculations show that their electrochemical stability window is considerably narrower than that of oxide or halide electrolytes (Fig. 9a) [120]. This narrow window makes sulfide electrolytes susceptible to oxidative decomposition at high voltages and reductive degradation at low voltages, leading to the formation of interfacial byproducts that are electronically insulating and ionically resistive. These interfacial degradation layers increase interfacial resistance, deplete active Li, and lead to capacity fading. Such effects are especially severe when sulfide electrolytes are paired with Li anodes and high-voltage cathodes, such as $LiNi_xCo_yMn_zO_2$ (NCM) or $LiNi_xCo_yAl_zO_2$ (NCA) (Fig. 9b and c) [121, 122].

Notably, side reactions between sulfide solid electrolytes and Ni-rich cathodes can generate substantial heat, increasing the risk of thermal runaway [123]. The evolution of gases and subsequent cross-talk reactions driven by these gases play a critical role in initiating battery thermal failure. When the potential exceeds 4.5 V, Ni-rich cathodes release O_2 , and surface carbonate species decompose into CO_2 [124]. This released O_2 then reacts with the sulfide solid electrolyte, producing SO_2 and releasing a significant amount of heat [125]. Tu et al. [126] systematically investigated the reaction mechanisms between O_2 and sulfide solid electrolytes, demonstrating that both elevated temperatures and higher fabrication pressures intensify these exothermic side reactions.

To address these challenges, several strategies have been developed. These include modifying the electrolyte's intrinsic electronic structure through elemental doping, constructing heterogeneous interfaces to improve redox stability, and introducing stable buffer layers between the electrolyte and electrodes to prevent direct chemical interactions. Furthermore, designing new sulfide electrolyte systems with intrinsically wider electrochemical stability windows is considered essential for mitigating decomposition and improving long-term battery performance.

Interfacial challenges are prevalent throughout the practical application of sulfide electrolytes. Unlike liquid electrolytes, sulfide SSEs often encounter interfacial reactions, poor electrode contact and delamination resulting from volume changes during cycling. Although sulfide electrolytes possess a relatively low Young's modulus, mechanical stress can still accumulate during extended cycling due to electrode

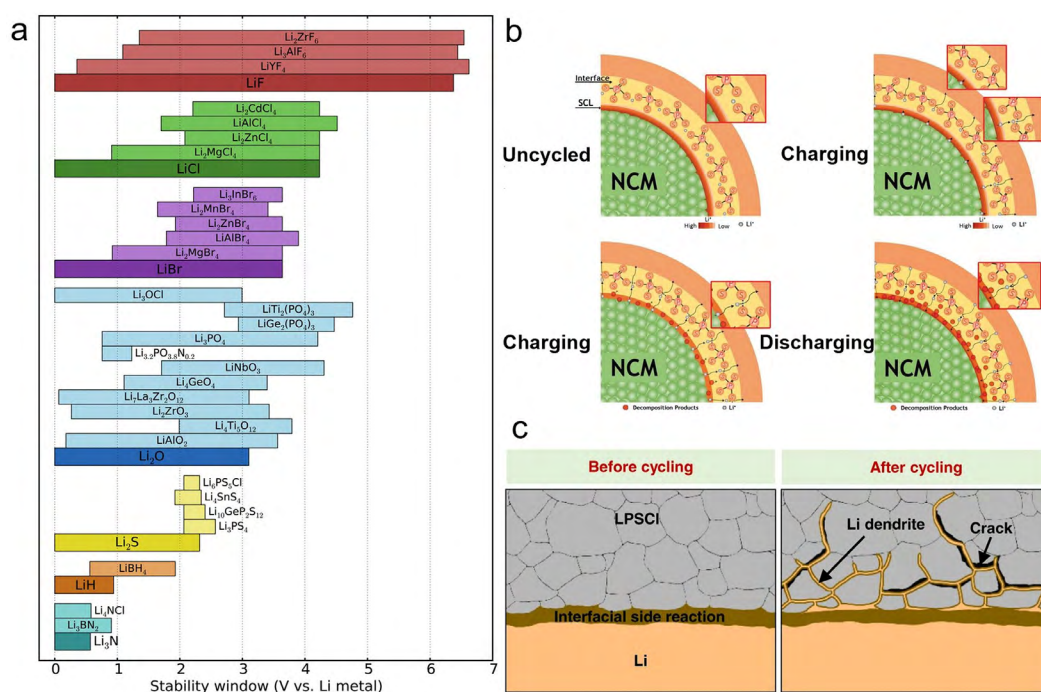


Fig. 9. (a) Electrochemical stability ranges of different electrolyte materials. Reproduced with permission from Ref. [120]. Copyright 2016, American Chemical Society. (b) Interfacial evolution between sulfide electrolytes and oxide cathodes. Reproduced with permission from Ref. [121]. Copyright 2020, Wiley-VCH. (c) Interfacial evolution between sulfide electrolytes and lithium metal anodes. Reproduced with permission from Ref. [122]. Copyright 2021, Springer Nature.

expansion and contraction. This stress accumulation may cause microcracks and voids at the interface, leading to increased electrochemical polarization and accelerated capacity fading. To mitigate these issues, two main approaches have been explored. The first one is design of nanostructures and optimization of particle morphology to improve interfacial conformity between electrodes and electrolytes. The second one is leveraging techniques including *in-situ* interfacial reactions, surface pretreatment and surface modification with adaptive interfacial layers (e.g., Li_3PO_4 or LiNbO_3 coatings) to reduce interfacial resistance [127]. In addition, maintaining moderate external pressure during battery operation has also been demonstrated to be effective in preserving interfacial integrity and delaying mechanical failure.

Cost and raw material availability also present practical barriers to the widespread adoption of sulfide electrolytes. For instance, although the LGPS system demonstrates excellent electrochemical performance, its dependence on germanium, which is both expensive and scarce, significantly limits its commercial viability. As a result, ongoing research is focused on identifying more abundant and cost-effective alternatives, such as silicon or tin, and on developing sulfide electrolyte systems that do not rely on rare metals. In addition, the production of

high-purity lithium sulfide (Li_2S), a critical precursor, remains complex and costly. This continues to hinder scalable manufacturing. Despite these issues, rapid research progress is being made. Improvements in air and solvent stabilities, the expansion of electrochemical windows, enhanced interfacial compatibility, and reductions in material costs are all contributing to the advancement of sulfide-based solid electrolytes toward large-scale commercial applications.

3.2.4. Development outlook

Sulfide electrolytes, due to their high σ and excellent interfacial adaptability, are considered leading candidates for all SSB applications. However, several critical challenges must be addressed before large-scale implementation:

1) At the material level, the narrow electrochemical stability window is a challenge. Sulfide electrolytes must prioritize three essential attributes: broad electrochemical stability, high chemical inertness, and robust thermodynamic stability. Although current sulfide electrolytes exhibit ionic conductivities comparable to those of conventional liquid electrolytes, their limited oxidative tolerance at high voltages and insufficient reductive stability against Li metal remain significant limitations. To overcome these drawbacks, efforts should be directed toward stoichiometric

optimization, controlled elemental doping, lattice defect engineering, and the design of multi-component composite systems to further enhance intrinsic material performance. Moreover, the discovery of new sulfide electrolyte candidates is expected to accelerate through the integration of high-throughput computational screening with machine learning, enabling shorter development cycles and increased research efficiency.

2) On the application front, interfacial instability and system integration remain persistent challenges. The use of Li metal anodes, which is crucial for achieving high energy density, continues to be hindered by chemical and electrochemical degradation at the electrolyte–anode interface. To address these limitations, future research should emphasize interfacial engineering strategies, such as *in-situ* formation of stable interphases, the development of self-healing interfaces, and the application of advanced surface modification techniques. Furthermore, the integration of nanoscale structural control with flexible material design is expected to mitigate microcrack formation and suppress dendrite growth, thereby enhancing cycling stability over extended operation.

3) Cost reduction is critical for enabling the industrial-scale deployment of sulfide electrolytes. Commercial viability can only be achieved if material costs are brought within practical limits. Currently, essential precursors such as high-purity Li_2S are costly, and their synthesis involves complex, high-cost processes that constrain large-scale adoption. Consequently, future research should prioritize the development of environmentally friendly, cost-effective, and scalable synthesis routes for these materials. In addition, the limited air stability of sulfide electrolytes significantly contributes to elevated production costs. Their synthesis and handling still require glove boxes or high dew point drying rooms, impeding manufacturing scalability and automation. Improving the air stability of sulfide electrolytes would ease processing constraints and markedly lower overall production expenses.

In conclusion, the advancement of sulfide-based SSEs presents both significant opportunities and persistent challenges. Continued progress will depend on integrated efforts across theoretical modeling, experimental validation, material optimization, and structural engineering. Interdisciplinary collaboration, cross-team innovation, and sustained investment in research will remain essential. With the development of high-performance materials and the maturation of interfacial engineering strategies, sulfide-based all-solid-state Li batteries are anticipated to transition from laboratory-scale research to commercial-scale deployment, positioning them as a leading solution

for next-generation electric vehicles and advanced energy storage systems.

3.3. Halide electrolytes

3.3.1. Main characteristics and challenges

Halide electrolytes have garnered significant research interest owing to their distinctive halogen anion chemistry, which offers several compelling advantages. First, the weaker electrostatic interactions between monovalent halogen anions and Li^+ enable enhanced ionic conductivity compared to divalent chalcogen (S/O) based systems. Second, the larger ionic radii of halogens promote bond elongation and increase polarizability, thereby facilitating Li^+ migration while simultaneously improving material plasticity. Third, the pronounced ionic character of halide compounds confers exceptional stability under ambient atmospheric conditions and at elevated temperatures. These advantageous characteristics establish halide electrolytes as a highly promising material class for next-generation solid-state battery applications.

Research on halide SSEs dates back to the 1930s [117], but early efforts were hindered by their low σ , typically below $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at room temperature. A resurgence of interest occurred in 2018 when Li_3YCl_6 and Li_3YBr_6 were reported by Panasonic Corporation, achieving conductivities close to $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ [118]. Subsequent advancements have further improved σ to nearly $10^{-2} \text{ S}\cdot\text{cm}^{-1}$ [119–121], establishing halide SSEs as promising candidates for SSBs. Despite these advances, three major challenges persist: 1) Low conductivity in cost-effective compositions. Halide SSEs based on abundant elements (e.g., Zr, Al, Fe) still exhibit insufficient ionic conductivity for practical applications; 2) Poor stability. Both chemical and electrochemical stabilities remain inadequate, particularly under ambient air exposure, upon contact with Li metal anodes and with high-voltage cathodes; 3) Processing constraints. The incompatibility of halide SSEs with conventional solvents and binders during electrode fabrication poses a barrier to scalable manufacturing, impeding their implementation in practical SSBs.

To overcome these challenges, significant research efforts have been devoted to enhancing ionic conductivity, improving chemical/electrochemical stability, and optimizing electrode manufacturing compatibility. The following sections provide a comprehensive discussion of these advances.

3.3.2. Enhancing ionic conductivity

Ionic conductivity, a critical performance metric for halide electrolytes, has seen remarkable

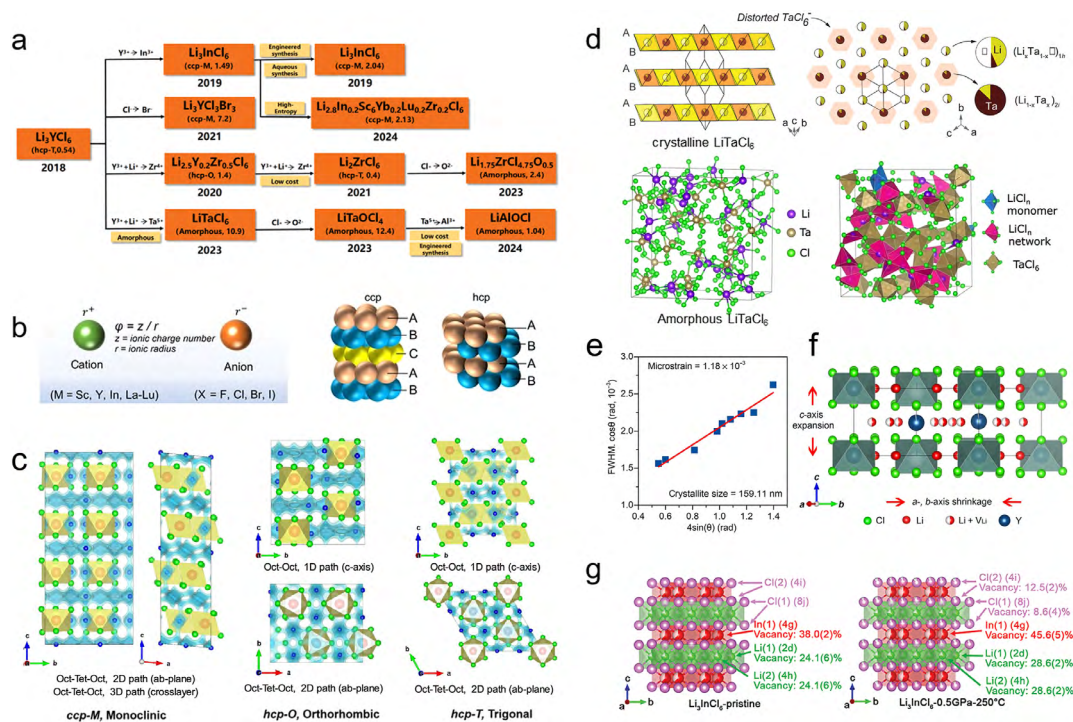


Fig. 10. (a) Evolution of σ , structure, and composition in halide electrolytes from Li_3YCl_6 . (b) Schematic of conventional cation (M), anion (X), ionic potential, and hcp/ccp packing arrangements Reproduced with permission from ref. [143]. Copyright 2022 American Association for the Advancement of Science. Reproduced with permission from ref. [133]. Copyright 2024 Springer Nature. (c) Crystal structures derived from hcp/ccp packing, with Li (blue), Cl (green), MCl_6 polyhedra (yellow), and Li^+ transport channels (light blue). Reproduced with permission from ref. [131]. Copyright 2020 American Chemical Society. (d) Crystalline and amorphous structures of LiTaCl_6 . Reproduced with permission from ref. [138]. Copyright 2024 John Wiley and Sons. Reproduced with permission from ref. [139]. Copyright 2024 John Wiley and Sons. (e) Microstrain from size confinement. Reproduced with permission from ref. [144]. Copyright 2024 American Association for the Advancement of Science. (f) Structural changes in Li_3YCl_6 via ammonium-assisted wet synthesis. Reproduced with permission from ref. [144]. Copyright 2024 American Association for the Advancement of Science. (g) Li vacancy fraction in Li_3InCl_6 after cold vs. hot pressing. Reproduced with permission from ref. [142]. Copyright 2024 John Wiley and Sons.

improvements through structural engineering and compositional tuning. State-of-the-art materials including LiTaCl_6 [128], LiTaOCl_4 [129], and $\text{Li}_3\text{GdCl}_3\text{Br}_3$ [130] have achieved room-temperature conductivities exceeding $10 \text{ mS}\cdot\text{cm}^{-1}$, rivaling conventional liquid electrolytes (Fig. 10a). These advancements stem from following three primary strategies.

Crystal Structure Tailoring. The Li^+ migration energy barrier can be effectively reduced through crystal structure tailoring, thereby enhancing ionic conductivity. Halide electrolytes typically adopt the general formula $\text{Li}_\alpha\text{MX}_\beta$ (where M is a non-lithium metal cation and X is a halide anion). In this system, the ionic potential ($\varphi = Z/r$), defined as the charge number (Z) divided by the ionic radius (r), plays a key role in governing interionic interactions and atomic packing, thereby determining the resulting crystalline phase. Hexagonal close packing (hcp) produces in trigonal (hcp-T) and orthorhombic (hcp-O) phases, while cubic close packing (ccp) yields a monoclinic (ccp-M) structure (Fig. 10b and c). These crystal types exhibit distinct Li^+ transport behaviors: hcp-T and hcp-O structures support restricted 1D diffusion along the

c-axis and 2D migration in the ab-plane, whereas the ccp-M phase enables multidimensional Li^+ conduction through interconnected 2D and 3D pathways. The ccp-M over hcp-T structure offers a substantially lower Li^+ migration barrier compared with the hcp-T and hcp-O phases, making it the most favorable configuration for fast ion transport [131, 132]. To enhance σ , phase transitions from hcp-T to hcp-O and ultimately to ccp-M can be induced by tuning the ionic potential [133]. This structural transformation is achieved through 1) cation substitution, such as $\text{Li}_3\text{YCl}_6(\text{hcp-T}) \rightarrow \text{Li}_3\text{InCl}_6(\text{ccp-M})$ [135]; 2) anion substitution, such as $\text{Li}_3\text{YCl}_6(\text{hcp-T}) \rightarrow \text{Li}_3\text{YCl}_6\text{Br}_3(\text{ccp-M})$ [136]; and 3) partial substitution with high-valent cations, such as $\text{Li}_3\text{YCl}_6(\text{hcp-T}) \rightarrow \text{Li}_{2.5}\text{Y}_{0.5}\text{Zr}_{0.5}\text{Cl}_6(\text{hcp-O})$ [137]. Furthermore, ccp-M structures enable high-entropy design through multi-cation substitution, creating chemical disorder that promotes Li^+ redistribution and 3D diffusion. For example, Li_3InCl_6 ($2.13 \text{ mS}\cdot\text{cm}^{-1}$) shows enhanced conductivity when being modified to $\text{Li}_{2.8}\text{In}_{0.2}\text{Sc}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2}\text{Zr}_{0.2}\text{Cl}_6$.

Amorphization Strategy. Amorphization can disrupt long-range order and facilitate the formation of

dynamic Li^+ conduction networks, while lowering grain boundary resistance. For example, crystalline LiTaCl_6 [138] with an hcp-T framework composed of TaCl_6 and LiCl_6 octahedra (Fig. 10d), exhibits a conductivity of only $5.98 \times 10^{-5} \text{ mS}\cdot\text{cm}^{-1}$. However, its amorphous counterpart with disordered TaCl_6 units and LiCl_n ($n \leq 6$) oligomeric/polymeric networks [128, 139], shows a significantly improved σ up to $10.95 \text{ mS}\cdot\text{cm}^{-1}$. This is because the enhanced low-frequency vibrational coupling between Ta–Cl and Li–Cl bonds activate a dynamic 3D migration pathway. Moreover, oxygen incorporation can further modify the coordination environment by converting MCl_x polyhedra into mixed $\text{MO}_y\text{Cl}_{x-y}$ units, promoting amorphization and weakening Li^+ – MCl_x interactions, thereby accelerating Li^+ transport. This approach has successfully enhanced conductivity in systems like $\text{LiTaCl}_6 \rightarrow \text{LiTaOCl}_4$ and Li_2ZrCl_6 [140] $\rightarrow \text{Li}_{1.75}\text{ZrCl}_{4.75}\text{O}_{0.5}$ [141] (Fig. 10a).

Synthesis/Structure Optimization. The ionic conductivity (σ) of halide electrolytes exhibits significant dependence on synthesis methodologies and post-treatment conditions, which collectively influence crystallographic ordering, defect concentration, and interfacial connectivity across multiple length scales. Comparative studies reveal that ammonium-assisted wet-chemical synthesis of Li_3MCl_6 ($\text{M} = \text{Sc}, \text{Y}, \text{Er}$) produces submicron-sized crystallites ($\sim 500 \text{ nm}$), in contrast to the larger grains obtained through conventional mechanical milling and solid-state synthesis routes [118, 145, 146]. This nanoscale morphology generates substantial microstrain and induces anisotropic lattice distortion (Fig. 10e), manifesting as c-axis elongation concomitantly with a- and b-axis contraction in hcp-T structured materials (Fig. 10f). Such structural modifications effectively expand interlayer spacing, thereby facilitating enhanced Li^+ conduction within the ab-plane for both Li_3YCl_6 and Li_3ErCl_6 systems. In contrast, Li_3ScCl_6 with a ccp-M structure exhibits a low ionic conductivity due to the steric hindrance of contracted interlayer space to Li^+ migration [147]. Post-synthesis thermal treatment, specifically hot pressing, effectively enhances Li^+ transport properties in Li_3InCl_6 through three synergistic mechanisms: (1) generation of additional cationic vacancies (Fig. 10g), (2) lattice expansion, and (3) grain boundary consolidation. This multifactorial optimization results in a dramatic conductivity enhancement, with hot-pressed samples achieving $\sigma = 4.4 \text{ mS}\cdot\text{cm}^{-1}$, representing a 6.3-fold improvement over cold-pressed specimens ($0.695 \text{ mS}\cdot\text{cm}^{-1}$) [142].

3.3.3. Improving electrochemical stability

The electrochemical stability window represents a critical parameter for evaluating the intrinsic stability

of halide electrolytes, as it defines the safe operation voltage range of SSBs. The oxidation limit of halide electrolytes is largely determined by the electronegativity of the X, while the reduction limit is primarily influenced by the electronegativity of the central metal cation (M). First-principles calculations have systematically mapped the thermodynamic stability windows of various Li–M–X systems (Fig. 11a) [145], demonstrating that chloride-based electrolytes combine high σ with oxidation potentials exceeding 4 V (*vs.* Li^+/Li). This intrinsic property makes them highly compatible with conventional layered oxide cathodes. Current strategies to expand the electrochemical stability window have predominantly employed elemental substitution approaches, which have shown remarkable success in improving oxidative stability for high-voltage cathode applications. Nevertheless, these materials remain intrinsically limited by the redox activity of M-site cations, as evidenced by only modest enhancements in reduction stability. This fundamental constraint continues to challenge the thermodynamic stability of Li–M–X halide electrolytes when paired with lithium metal anodes.

The electrochemical stability window of $\text{Li}_{3-x}\text{Er}_{1-x}\text{Zr}_x\text{Cl}_6$ demonstrates a systematic expansion with reduced Zr substitution (decreasing x value), exhibiting a proportional decrease in reduction potential coupled with an increase in oxidation potential [150]. This cation substitution effect shows remarkable transferability across different systems, as evidenced by analogous behavior observed in Zr-substituted Li_3LuCl_6 (Fig. 11c) [146]. Notably, the introduction of multiple M-site cations generates two synergistic effects: (1) increased configurational entropy and (2) local structural distortions. These combined effects yield three significant benefits: (i) reduced activation energy for ionic transport, (ii) enhanced ionic conductivity (σ), and (iii) suppressed Cl^- oxidation kinetics, collectively contributing to improved oxidative stability (Fig. 11d and e) [147]. Compared to metal cation effects, the electronegativity of the X exerts a more dominant influence on the oxidation potential of halide electrolytes. Substitution with highly electronegative F^- substantially enhances oxidative stability (Fig. 11f). Conversely, oxygen incorporation in Li_2ZrCl_6 elevates oxidation potential while concurrently reducing reduction potential (Fig. 11g). This anomalous behavior originates from dual structural modifications: (1) altered Zr^{4+} coordination environments ($\text{Cl}^- \rightarrow \text{mixed Cl}^-/\text{O}^{2-}$) and (2) oxygen-induced crystallinity reduction [141].

3.3.4. Elevating interfacial stability

The integration of halide electrolytes into SSBs requires rigorous assessment of intrinsic material

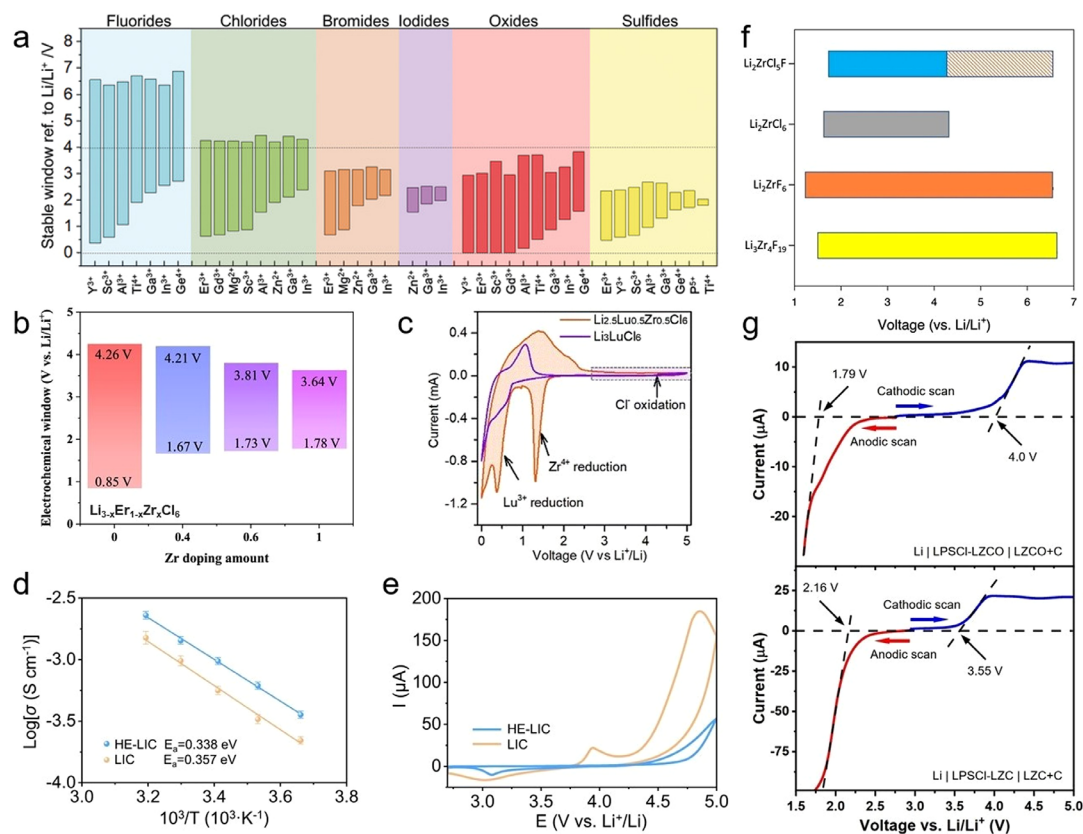


Fig. 11. (a) Theoretical electrochemical stability windows of Li-M-X ternary halide, oxide, and sulfide electrolytes. Reproduced with permission from ref. [145]. Copyright 2019 John Wiley and Sons. (b) Electrochemical window variation of $\text{Li}_{3-x}\text{Er}_{1-x}\text{Zr}_x\text{Cl}_6$ with increasing x. Reproduced with permission from ref. [148]. Copyright 2022 American Chemical Society. (c) CV curves of Li_3LuCl_6 before and after Zr substitution. Reproduced with permission from ref. [146]. Copyright 2023 The Royal Society of Chemistry. (d) Temperature-dependent σ and (e) Electrochemical window of high-entropy vs. pristine Li_3InCl_6 . Reproduced with permission from ref. [147]. Copyright 2024 Springer Nature. (f) Theoretical stability window of Li_2ZrCl_6 before and after F substitution. Reproduced with permission from ref. [149]. Copyright 2023 Springer Nature. (g) Linear sweep voltammetric curves of Li_2ZrCl_6 before and after O substitution. Reproduced with permission from ref. [141]. Copyright 2024 Springer Nature.

properties and interfacial compatibility, particularly with electrodes and other solid-state components. Interfacial chemical stability with cathodes can be evaluated using reaction energy as a predictive metric. Theoretical calculations reveal that chloride-based electrolytes exhibit lower reaction energies ($<100 \text{ meV}\cdot\text{atom}^{-1}$) with cathodes compared with sulfide electrolytes ($>300 \text{ meV}\cdot\text{atom}^{-1}$) (Fig. 12a), suggesting enhanced thermodynamic compatibility. However, the reactivity between chloride electrolytes and $\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$ (NCM) cathode materials increases with Ni content. Furthermore, the state of charge (SOC) of NCM cathodes also significantly affects interfacial stability. Calendar aging studies demonstrate that pairing NCM811 ($\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$) with Li_3InCl_6 accelerates degradation at low SOC, leading to more pronounced capacity loss compared to high SOC conditions (Fig. 12b). This degradation stems originate from interfacial $\text{Li}^+/\text{In}^{3+}$ cation exchange, which triggers reductive decomposition of Li_3InCl_6 ($\text{In}^{3+} \rightarrow \text{In}^0$)

and In^{3+} diffusion into Li sites within the NCM811 structure, thereby compromising Li^+ transport [150]. To address these issues, two main approaches have been proposed: 1) enhancing the intrinsic redox stability of halide electrolytes via elemental substitution or high-entropy engineering [131, 151], and 2) implementing interfacial protection layers. For example, a Li_3PO_4 coating applied to Li-rich cathodes via atomic layer deposition and annealing (Fig. 12c) effectively suppresses both Li_3InCl_6 oxidation and cathode degradation, enabling stable cycling within a wide voltage window of 2.0–4.8 V (Fig. 12d) [152].

Li-M-X-type halide solid electrolytes exhibit relatively high reduction potentials ($\geq 0.6 \text{ V vs. Li}^+/\text{Li}$), rendering them intrinsically incompatible with silicon or lithium metal anodes. Hence, interlayer electrolytes or passivation strategies are essential to stabilize the anode interface. Although sulfide-based interlayers are widely employed with silicon anodes, they remain susceptible to interfacial side reactions and lithium dendrite penetration when coupled with

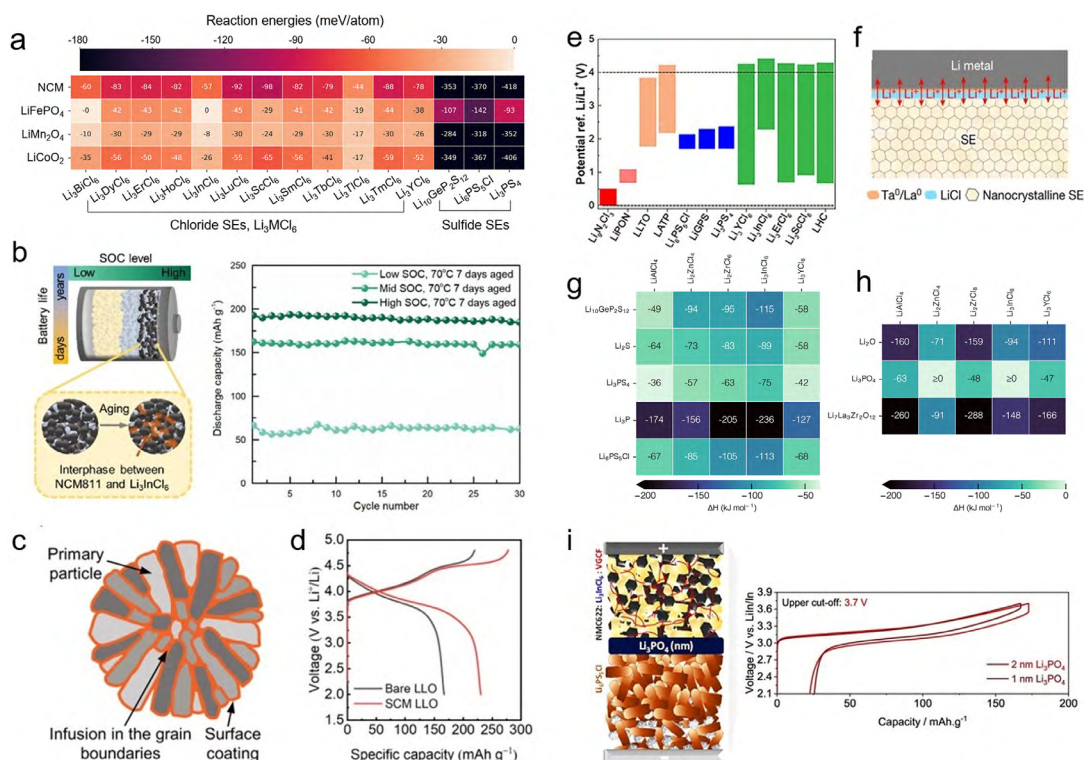


Fig. 12. (a) Calculated reaction energies between chloride/sulfide solid electrolytes and cathode materials. Reproduced with permission from ref. [131]. Copyright 2020 American Chemical Society. (b) Aging schematic and electrochemical performance of NCM811/Li₃InCl₆ composite cathodes at various states of charge. Reproduced with permission from ref. [150]. Copyright 2023 John Wiley and Sons. (c) Infusion-plus-coating architecture with Li₃PO₄ infused into grain boundaries and coated on particle surfaces. (d) Initial charge/discharge curves of the bare LLO vs. Li-rich cathodes with Li₃PO₄ treatment. Reproduced with permission from ref. [152]. Copyright 2023 John Wiley and Sons. (e) Theoretical electrochemical windows of Li₉N₂Cl₃ and other electrolytes. Reproduced with permission from ref. [153]. Copyright 2023 American Association for the Advancement of Science. (f) Interfacial layer products at the Li/Li_{0.388}Ta_{0.238}La_{0.475}Cl₃ interface. Reproduced with permission from ref. [156]. Copyright 2023 Springer Nature. (g, h) Calculated reaction enthalpies between chloride and sulfide/oxide electrolytes or their decomposition products. Reproduced with permission from ref. [157]. Copyright 2024 American Chemical Society. (i) Schematic of Li₃PO₄ nanolayer between Li₃InCl₆ and Li₆PS₃Cl and corresponding cycling performance with a 2-nm layer. Reproduced with permission from ref. [158]. Copyright 2022 American Chemical Society.

lithium metal. Notably, anion-dominated nitride solid electrolytes, such as $\text{Li}_9\text{N}_2\text{Cl}_3$ [153], $\text{Li}_{2.5}\text{N}_{0.5}\text{S}_{0.5}$ [154], and $\text{Li}_7\text{N}_2\text{I}\cdot 0.5\text{LiOH}$ [155], have shown exceptional compatibility with Li metal anodes. Lacking reducible cationic species, these materials demonstrate ultra-low reduction potentials approaching 0 V (*vs.* Li^+/Li) (Fig. 12e), positioning them as ideal interlayers for dual-electrolyte configurations in Li metal batteries. Integration of halide electrolytes with such nitrides has enabled all-solid-state Li metal batteries with extended cycle life and enhanced interfacial stability [153]. Alternatively, in-situ formation of passivation layers through self-limiting interfacial reactions provides a viable stabilization strategy. For example, symmetric $\text{Li}/\text{Li}_{0.388}\text{Ta}_{0.238}\text{La}_{0.475}\text{Cl}/\text{Li}$ cells develop an interfacial LiCl layer (Fig. 12f), which kinetically suppresses further Ta^{5+} reduction. This passivation effect enables stable cycling for over 5000 h [156].

Interlayer electrolytes can effectively isolate halide electrolytes from reactive anodes; however,

this introduces a new interface between the halide and interlayer electrolytes. The interfacial chemical stability between chloride-based and sulfide/oxide-based solid electrolytes has been assessed using reaction enthalpy calculations (Fig. 12g and h) [157]. Notably, the widely adopted Li_3InCl_6 and $\text{Li}_6\text{PS}_5\text{Cl}$ bilayer configuration exhibits a significantly negative reaction enthalpy, indicating poor interfacial compatibility. This theoretical prediction has been experimentally confirmed through decomposition product analysis, which reveals the formation of InS_x compounds, such as In_2S_3 and LiInS_2 [150, 157]. In contrast, the $\text{Li}_3\text{InCl}_6|\text{Li}_3\text{PO}_4$ interface exhibits a reaction enthalpy of zero, suggesting thermodynamic stability. Consequently, the application of a nanoscale Li_3PO_4 passivation layer at the $\text{Li}_3\text{InCl}_6|\text{Li}_6\text{PS}_5\text{Cl}$ interface (Fig. 12i) has been shown to effectively suppress interfacial reactions, resulting in 92.3% capacity retention over 400 cycles [158]. These findings highlight the critical importance of

rational interface engineering, including optimized electrolyte pairing and interphase/interlayer design, for improving the long-term cycling performance of halide-based all SSBs.

3.3.5. Enhancing solvent compatibility

The chemical stability of halide electrolytes against solvents critically governs the performance of slurry-processed electrolytes and composite cathodes, which are essential for large-capacity all-solid-state pouch cells. Chemical compatibility can be categorized by solvent polarity as follows.

High-polarity Lewis base solvents, such as dimethylformamide and N-methyl-2-pyrrolidinone, possess strong dipolar moments that can facilitate the dissolution of halide electrolytes. However, their lone pair electrons readily participate in nucleophilic reactions with high-valent central cations (e.g., In^{3+} , Zr^{4+}) in halide electrolytes [159, 160]. These reactions cause irreversible structural degradation and conductivity loss, even after solvent removal and annealing [160–162]. By contrast, protic solvents high-polarity, such as anhydrous ethanol (EtOH) and deionized water (H_2O), can dissolve Li_3InCl_6 without nucleophilic degradation and therefore, the crystal structure and σ of Li_3InCl_6 can be fully restored after solvent removal and annealing, [160]. However, Li_2ZrCl_6 behaves differently. It suffers irreversible nucleophilic reactions in both Lewis base solvents (e.g., N-methyl-2-pyrrolidinone (NMP) and protic solvents (e.g., H_2O), yielding LiCl impurities and reducing σ to $<10^{-10} \text{ S}\cdot\text{cm}^{-1}$ [161, 162]. These findings emphasize that, besides solvent polarity, the chemical nature of halide electrolytes must be carefully considered when selecting solvent systems for slurry processing.

Low- and non-polar solvents with weak dipolar moments, typically show limited solubility and reactivity to halide electrolytes. Nevertheless, structural degradation and conductivity loss persist in some cases. For example, Li_2ZrCl_6 are dissolved partially in o-xylene (3.64%) and toluene (TOL, 0.53%), yet post-processing forms LiCl impurity and causes structural collapse, reducing σ to $3 \times 10^{-10} \text{ S}\cdot\text{cm}^{-1}$ [161]. In contrast, solvents like dibromomethane (DBM, a nonpolar solvent) and TOL/chlorobenzene (PhCl , low-polarity) induce minimal damage. DBM dissolves only trace amounts of Zr ($<9.9 \text{ ppm}$) from Li_2ZrCl_6 and causes no observable phase change after solvent removal [161]. Similarly, Li_3InCl_6 is particularly insoluble in TOL and PhCl , and fully retains its σ post-treatment [160]. These results suggest that effective solvent screening must prioritize structural/property preservation and minimize irreversible reactions to ensure compatibility.

3.3.6. Development outlook

To advance the practical application of halide electrolytes, future research should focus on three key areas: enhancing ionic conductivity, broadening the electrochemical stability window, and improving electrode-electrolyte interfacial compatibility.

While advanced halide electrolytes, such as LiTaOCl_4 and $\text{Li}_3\text{GdCl}_3\text{Br}_3$, exhibit high ionic conductivities ($>10 \text{ mS}\cdot\text{cm}^{-1}$), and materials like Li_3InCl_6 demonstrate excellent air stability and compatibility with aqueous-phase synthesis, their widespread deployment remains constrained by the high cost of rare metals. In contrast, recently reported materials such as LiAlOCl offer lower cost and potential for kilogram-scale production but exhibit moderate ionic conductivity ($\sim 1 \text{ mS}\cdot\text{cm}^{-1}$) and poor air stability. To address cost-related challenges, future studies should leverage advanced computational approaches—including deep learning and intelligent algorithm frameworks [163, 164]—to design superionic and air-stable halide electrolytes composed of earth-abundant and inexpensive elements such as Zr, Al, and Fe. This strategy is expected to accelerate the discovery and scalable development of high-performance halide-based materials. Moreover, under high-voltage operation ($>4.3 \text{ V}$), halide electrolytes face additional challenges, including intrinsic oxidative decomposition and interfacial degradation, which hinder their integration with high-voltage cathodes (e.g., Li-rich manganese-based oxides) [152]. Encouragingly, emerging systems such as high-entropy halide electrolytes and oxyhalides (e.g., LiAlOCl) have demonstrated promising stability and compatibility at elevated voltages, offering viable pathways toward next-generation high-energy-density solid-state batteries (SSBs). Moreover, the fabrication of halide electrolyte membranes and composite cathodes requires significant advancement. Studies have shown that even low-polarity or nonpolar solvents can degrade the ionic conductivity (σ) of halide electrolytes, posing a major limitation for wet-process manufacturing of halide solid-state electrolyte (HSSE) membranes and all-solid-state battery devices [165]. Overcoming this challenge will require enhancing the chemical stability of halide electrolytes against solvent exposure to preserve ionic conductivity during processing. For dry-process fabrication, further optimization of halide electrolyte particle size distribution and mechanical properties is essential. Achieving uniform, dense, and mechanically robust HSSE membranes and composite electrodes is critical to meet the stringent integration demands of practical SSB systems.

In conclusion, although halide electrolytes offer distinct advantages for all-solid-state battery systems,

major challenges remain in materials development, processing methodologies, and device-level integration. Continued progress in these areas is essential to unlock substantial performance gains and enable the large-scale commercialization of halide-based all-solid-state batteries.

4. Organic Solid-State Electrolytes

4.1. Solid polymer electrolytes

4.1.1. Characteristics, classification, structures, and conduction mechanisms

Solid polymer electrolytes (SPEs) have attracted considerable attention for SSBs owing to their flexibility, low density, and processability [166–168]. SPEs generally comprise a polymer matrix that facilitates Li^+ transport and a lithium salt providing ionic charge carrier. They are classified into various types based on their polymer matrices, including polyether-based [169, 170], polyacrylate-based [171], PVDF-based [172], polycarbonate-based [173], polyurethane-based [174], polyacrylonitrile-based systems [175]. Among existing systems, polyether-based electrolytes remain the most prevalent system for SSB applications and are thus selected as the primary focus in this review to discuss recent advances in SPE development.

Fig. 13 illustrates microscopic ion transport mechanisms in conventional polyether-based SPEs. In amorphous region, Li^+ ions coordinate with ether oxygen atoms on polyether chains via Lewis acid–base

interactions. Li^+ migrates through a continuous “complexation–decomplexation” process, both within and between polymer chains, enabled by the polymer segmental motion (Fig. 13a) [167, 176]. By contrast, Li^+ transport is largely restricted in the crystalline regions of semicrystalline SPEs due to immobilized polymer segments (Fig. 13b). These crystalline spherulites impede ionic conduction by disrupting percolation pathways in the amorphous matrix, significantly reducing conductivity [167]. In well-defined crystalline complexes, however, Li^+ migration can occur via hopping between adjacent sites (Fig. 13c) [167].

4.1.2. In-situ polymerized polyether-based solid polymer electrolytes

Conventional polyether-based SPEs are typically fabricated using *ex-situ* methods such as solution casting [177], electrospinning [178], and phase inversion [179]. However, these approaches often result in poor electrode-electrolyte interfacial contact, leading to high interfacial resistance. *In-situ* polymerization has emerged as an effective strategy to address this issue by enabling direct electrolyte formation within the battery cell, thereby enhancing interfacial adhesion and reducing resistance [180].

A representative example is poly(1,3-dioxolane) (PDOL), which exhibits considerable promise for SSBs due to its favorable lithium metal compatibility and straightforward synthetic route [181]. Dioxolane (DOL), the monomer of PDOL, can be polymerized through either electrochemical or electrophilic pathways. In battery systems, such polymerization can be

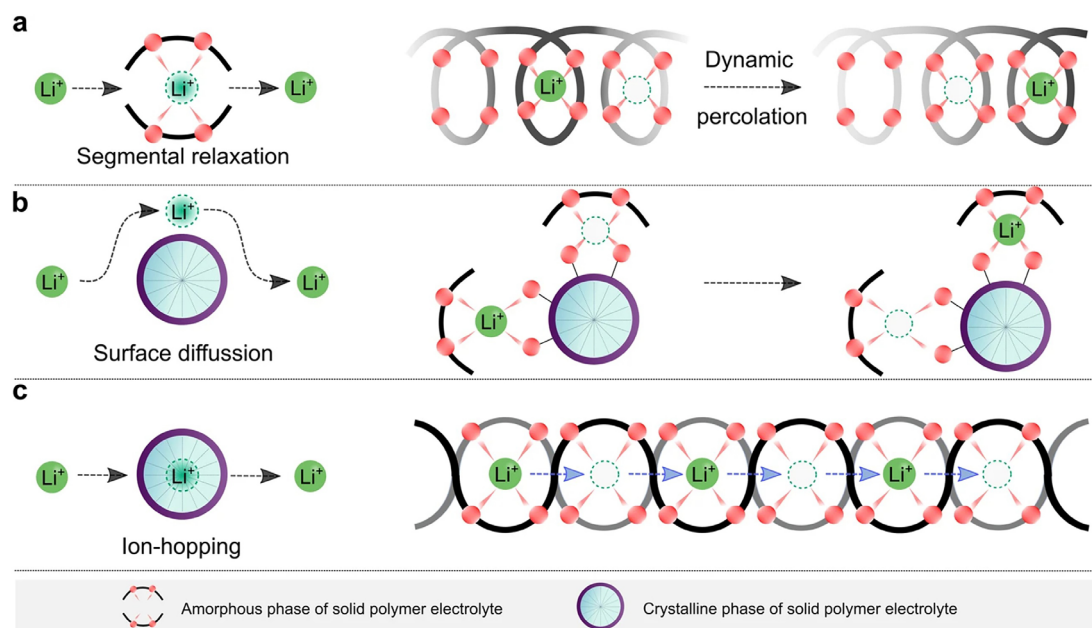


Fig. 13. Schematic of Li^+ conduction mechanisms in polyether-based SPEs. (a) Fully amorphous phase. (b) Mixed amorphous-crystalline phase. (c) Crystalline phase. Reproduced with permission from ref. [167]. Copyright 2024 Springer Nature.

triggered under controlled potentials, by specific lithium salts, or via acidic additives, making DOL highly suitable for *in-situ* electrolyte fabrication.

Electrochemical polymerization is a simple and feasible approach. By introducing a DOL-containing electrolyte into a cell and applying a potential above 3.5 V (vs. Li/Li⁺), DOL polymerization can be initiated [182]. Kong et al. [183] prepared a precursor solution of 1 mol·L⁻¹ LiTFSI in a DOL/DME (2:1 by mass) mixture, which was assembled between LiCoO₂ cathodes and lithium metal anodes. The DOL polymerization was induced by cycling the cell at increasing current densities from 20 to 500 mA·g⁻¹. Results showed that higher current densities (e.g., 500 mA·g⁻¹) significantly enhanced the conductivity of the resulting PDOL electrolyte, delivering cycling performance comparable to conventional carbonate-based lithium-ion batteries. Nevertheless, since electrochemical polymerization mainly occurs near the electrode surface, issues such as poor spatial uniformity of the polymer layer and residual unreacted DOL remain challenging.

Alternatively, electrophilic ring-opening polymerization occurs when the oxygen atom in DOL is protonated or attacked by Lewis acids. Lithium salts such as LiPF₆ [184], LiBF₄ [185], LiDFOB [186], and LiFSI [187] are commonly used initiators that react with trace water to generate proton acids, facilitating DOL polymerization. Multivalent cations including Mg²⁺ [188] and Al³⁺ [189] can also directly initiate the reaction. Organic Lewis acids represent another class of effective initiators. For example, Xiang et al. [190] employed tris(pentafluorophenyl)borane (TB) to trigger DOL polymerization. With only 3 wt% TB, 89% of DOL was converted into polymer, yielding an SPE with a high room-temperature ionic conductivity of 1.16 mS·cm⁻¹ and enabling stable lithium metal cycling for over 2000 h.

In summary, *in-situ* polymerization significantly improves the interfacial compatibility of polyether-based SPEs. However, challenges such as incomplete monomer conversion, limited ionic conductivity at room temperature, and insufficient oxidative stability remain. Future efforts should focus on developing novel initiators (e.g., organic Lewis acids) to enhance conversion efficiency, and exploring copolymerization strategies with other monomers to improve the high-voltage stability of polyether-based SPEs for practical applications.

4.1.3. Key challenges and mitigation strategies

Low σ remains a primary obstacle to the practical implementation of SPEs. Conventional PEO-based SPEs typically exhibit low σ (10⁻⁷–10⁻⁶ S·cm⁻¹) and Li⁺ transference number ($t_{\text{Li}^+} \approx 0.1$ –0.2) at room temperature,

restricting their use in SSBs [166, 191–193]. To address this limitation, extensive efforts have focused on enhancing σ , primarily by reducing polyether crystallinity, as ion transport occurs predominantly in the amorphous phase. This is commonly achieved through copolymerization or crosslinking with amorphous polymers [167, 194–197]. For instance, a triblock copolymer electrolyte comprising a modified linear PEO central block and two polystyrene (PS) lateral blocks was synthesized via controlled radical polymerization by Bouchet et al. [198]. In this structure, uniformly distributed chemical defects reduce the stereoregularity of the PEO chains, thereby lowering both the melting temperature and crystallinity of SPEs. This yielded $\sigma = 1.3 \times 10^{-5}$ S·cm⁻¹ at 60 °C with $t_{\text{Li}^+} > 0.85$ [176]. Encouraged by this result, various polyether-based copolymers have been proposed to enhance σ , including polyurethane-based multi-block networks [199, 200], and PEO-dimethylsiloxane block copolymers [201]. Hyperbranched polyethers have also been employed to increase polymer free volume, which effectively reduce crystallinity and improves ionic conductivity [202–204]. More recently, Chen et al. designed an alternating copolymer with periodically arranged anionic and PEO [205]. This molecular configuration promoted homogeneous Li⁺ distribution, enhanced Li⁺-anion dissociation, and inhibited ion aggregation. Consequently, it enabled a cooperative PEO-Li⁺-anion migration mechanism, achieving $\sigma \approx 4.0 \times 10^{-5}$ S·cm⁻¹ at 30 °C. This alternative sequence strategy offers a promising direction for advancing SPE performance.

The Li⁺ solvation structure in SPEs, arising from the short- and long-range dipole-ion interactions, plays a critical role in determining σ . Strong coordination between Li⁺ and ethylene oxide (EO) units impedes ion mobility. Thus, weakening Li⁺-polymer interactions while maintaining sufficient salt dissociation capacity is essential [205–207] to improve the ionic conductivity. Poly(tetrahydrofuran) (PTHF), structurally similar to PEO but with a lower ether oxygen density, exhibits reduced Li⁺-polymer coordination strength [208]. Crosslinked PTHF (xPTHF), synthesized by Bao et al. [209], demonstrated weaker Li⁺ binding, which achieved a higher t_{Li^+} (0.53) and superior σ compared with xPEO-based SPEs at room temperature. Similarly, keto-carbonyl-based polymers have been explored for their ability to dissociate Li salts while maintaining weak Li⁺ coordination [210–212]. In addition, non-conductive polymer segments can be introduced to create locally concentrated solvation zones, thereby increasing local ion concentration around the PEO chains and weakening ion-polymer interactions [213, 214]. The anion structure of the Li salt also significantly influences Li⁺ solvation.

By tailoring anions to interact with polymer chains via covalent bonding [198, 215], Lewis acid-base interactions [215, 216], or hydrogen bonds [217–220], anion mobility can be restricted, facilitating the Li⁺ migration. For instance, Yan et al. [220] developed selectively fluorinated aromatic lithium salts (SFALS), in which fluorinated benzene rings form hydrogen bonds with ether oxygens in PEO chains. This design reduces Li-polyether interactions while strengthening Li⁺-anion coordination. As a result, PEO-based SPEs incorporating SFALS achieve a Li⁺ conductivity of $3.81 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ at 60 °C [218, 221, 222].

The limited oxidative stability of polyether-based electrolytes significantly restricts their application in high-voltage SSBs. For instance, PEO-based SPEs exhibit an oxidative decomposition potential of $\sim 3.9 \text{ V}$ vs. Li/Li⁺ [223]. Both $-\text{C}-\text{O}-\text{C}-$ and $-\text{OH}$ groups within the PEO structure undergo oxidation under elevated voltages [224–226]. To extend the electrochemical stability window, antioxidant functional groups have been engineered into polyether matrices [170, 227]. Yang et al. [170] reported that substituting $-\text{OH}$ with $-\text{OCH}_3$ improved the oxidative stability of PEO to 4.3 V. Cui developed a cyano-functionalized SPE through copolymerization of 2-cyanoethyl acrylate and poly(ethylene glycol) methyl ether acrylate, enhancing interfacial compatibility with high-voltage cathodes. The electron-deficient $-\text{C}\equiv\text{N}$ group preferentially interacts with LiCoO₂ during charging, thereby suppressing the oxidative decomposition of EO segments. Consequently, LiCoO₂/Li cells using this SPE maintained 80.7% capacity after 500 cycles at 4.4 V and 60 °C, and 93.5% retention after 100 cycles at 4.5 V under 0.05 C conditions [228]. Fluorination has also been employed to enhance oxidative resistance, as the electron-withdrawing nature of fluorine stabilizes the polymer backbone and mitigates oxidative chain degradation. This approach has enabled various fluorinated polymer electrolytes with improved high-voltage performance [229–232].

4.1.4. Development outlook

SPEs represent promising candidates for SSBs. Despite decades of research addressing their intrinsic limitations and developing new polymer systems, several critical challenges must still be addressed for large-scale commercialization.

A key issue lies in the need for the simultaneous enhancement of σ and mechanical robustness. Most SPEs exhibit ionic conductivities below $10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which remain insufficient for practical applications. Conversely, those SPEs that achieve σ comparable to liquid electrolytes often suffer from poor mechanical properties. This trade-off arises because σ is typically improved by reducing the glass transition

temperature (T_g) of the polymer matrix, which compromises structural integrity. Therefore, innovative strategies must be developed to concurrently optimize both ionic transport properties and mechanical performance in SPE systems.

The interfacial compatibility of SPEs with both anodes and high-voltage cathodes must be addressed in a coordinated manner. Strategies designed to enhance the cathode-electrolyte interface often compromise the stability of the anode interface, a challenge that is often emphasized in the literature. For instance, the cyano group in polyether-based SPEs enhances the cathode interface but reacts unfavorably with Li metal, deteriorating the anode interface. Bilayer or multi-layer SPEs can improve bipolar interface compatibility but introduce new internal interfaces. Therefore, optimizing both interfaces cooperatively remains a key challenge.

From a practical standpoint, the interfacial wettability of SPEs on thick electrodes is critical for SSB performance and safety. Poor wettability impairs rate capability and compromises thermal stability. Studies have shown that PEO-based SPEs fail to adequately infiltrate and passivate the primary particles within polycrystalline NMC811, due to limited interfacial wettability [233]. Consequently, the thermal stability of NMC811 is significantly degraded when paired with PEO-based SPEs.

In addition, smart SPEs represent a promising direction for enhancing the safety of SSBs. For instance, temperature-responsive electrolytes can delay short circuits by initiating thermal radical polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGA) [234]. Other smart SPEs form densely crosslinked networks at elevated temperatures, suppressing the diffusion of Li⁺ and active gases [235]. However, these systems must not compromise electrochemical performance. Therefore, ensuring interfacial stability remains a fundamental requirement for the practical development of smart SPEs.

4.2. Plastic crystal electrolytes

4.2.1. Characteristics and classification

Plastic crystal electrolytes (PCEs) constitute a distinct class of solid-state electrolytes derived from plastic crystalline materials that simultaneously exhibit long-range structural order and liquid-like molecular dynamics. This unique combination arises from the facile reorientational and translational motions of constituent molecules or ions within a periodically arranged lattice, enabling efficient ion transport. PCEs offer notable advantages, including high room-temperature σ ($>10^{-4} \text{ S}\cdot\text{cm}^{-1}$), wide electrochemical stability window ($>5 \text{ V}$ vs. Li⁺/Li),

and low cost [236, 237], making them attractive for room-temperature SSB applications. Structurally, PCEs are categorized as molecular (*e.g.*, those using succinonitrile (SN) as the solvent) or ionic (based on ionic crystals). Due to the phase behavior of plastic crystals, which are liquid at elevated temperatures, PCEs can be prepared by simply melting the crystals and incorporating lithium salts and additives. This method makes PCEs particularly suitable for large-scale manufacturing.

4.2.2. Conduction mechanisms and novel design of PCEs

SN-based PCEs, as typical molecular PCEs, exhibit ionic conductivities up to $3.4 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ with the addition of 5 wt.% lithium bis(trifluoromethanesulfonylamide) (LiTFSI). Li^+ transport proceeds via translational hopping, facilitated by molecular/ionic reorientation dynamics [237–243]. Geirhos et al. [244] demonstrated that adding glutaronitrile (GN) to LiPF_6/SN increases ionic conductivity by nearly three orders of magnitude. This improvement is attributed to the “revolving-door” mechanism [238, 240, 245], wherein GN molecules create transient pathways for Li^+ hopping between coordination sites, enhancing ion migration [243].

Similarly, the movement of Li^+ ions in ionic plastic crystal matrices is driven by the dynamic motion of surrounding cations and anions. Structural imperfections in crystalline solids [246], such as vacancies, interstitial defects, dislocations [245], and grain boundaries, create accessible sites that facilitate ion migration. Vacancies enable Li^+ migration via vacancy-assisted hopping between adjacent lattice sites (Fig. 14b), while dislocations and grain boundaries form extended conduction pathways where aggregated lattice defects act as channels for Li^+ transport [243]. However, excessive Li^+ concentration in ionic PCEs can adversely affect σ by inducing the formation of less-conductive secondary phases [247, 248]. To address this, a novel class of silylsulfate-based plastic crystal salts has been developed, including $\text{Li}_4\text{Si}(\text{SO}_4)_4$, $\text{Li}(\text{CH}_3)_3\text{SiOSO}_3$, $\text{Li}(\text{OCH}_3)_3\text{SiOSO}_3$, and $\text{Li}(\text{OCH}_2\text{CH}_3)_3\text{SiOSO}_3$ [237, 249], which act as single-cation conductors and achieve high ionic conductivities of up to 10 mS cm^{-1} at room temperature. These single Li^+ -conducting materials represent a promising avenue for developing high-performance ionic PCEs. In addition, Ai et al. developed an ionic PCE based on 1-ethyl-1-methylpyrrolidinium bis(fluorosulfonyl)imide, which attained a notable conductivity of $0.36 \text{ mS}\cdot\text{cm}^{-1}$ at -110°C when assisted by mild solvation with methyl acetate (Fig. 14c and d) [250, 251]. These findings highlight that tuning the Li^+ solvation structure represents an effective strategy for enhancing σ of ionic PCEs.

4.2.3. Major challenges and corresponding strategies

The limited compatibility of PCEs with anodes remains a major constraint to their practical deployment. For example, SN-based PCEs exhibit high reactivity with Li metal, where the terminal cyano groups undergo polymerization at the anode surface. This interfacial reaction significantly increases the electrode-electrolyte impedance and severely reduces battery lifespan. To address this, Cui proposed a dual-anion SN-based PCE system using LiTFSI and LiDFOB (D-DES) [254]. In this system, coordination and hydrogen bonding between Li salts and SN limit the direct interaction between Li metal and nitrile groups. The anions act as film-forming agents, modifying the interface, and promoting rapid Li^+ transport and uniform Li nucleation. As a result, Li|Li symmetric cells demonstrated over 10,000 h of stable cycling with $5 \text{ mAh}\cdot\text{cm}^{-2}$ Li capacity, while $\text{LiCoO}_2|\text{Li}$ full cells retained over 70% capacity after 500 cycles at 4.7 V. Similarly, the addition of 1,3,2-dioxathiolane-2,2-dioxide (DTD) into SN-based PCEs improved compatibility with the Na anode [255]. Strong hydrogen bonding between S=O groups of DTD and the α -H of SN enhanced SN's stability in the presence of Lewis basic anode environments. The involvement of DTD in the Na^+ solvation sheath reduced the coordination number of SN, facilitating the formation of a robust, gradient inorganic-rich interphase. As a result, $\text{Na}_3\text{V}_2(\text{PO}_4)_3|\text{Na}$ cells retained 82.8% capacity after 800 cycles at 25°C and 86.3% after 100 cycles at 60°C . Long-term cycling of ionic PCEs in Li/Li symmetric cells at current densities above $0.01 \text{ mA}\cdot\text{cm}^{-1}$ has remained challenging. Shekibi reported that $[\text{C}_2\text{mpyr}][\text{BF}_4]$ -based ionic PCEs enabled stable Li plating/stripping over 124 cycles at $0.1 \text{ mA}\cdot\text{cm}^{-2}$ and 70°C [256]. Recently, organic plastic-crystal Li salts have emerged as novel ionic PCEs [257], functioning simultaneously as Li^+ sources and solid-state ion conductors. Wang introduced dilithium (1,3-diethyl-4,5-dicarboxylate) imidazole bromide ($[\text{C}_2\text{eim}(\text{COOLi})_2][\text{Br}]$) as an ionic plastic-crystal electrolyte, achieving σ of $>10^{-3} \text{ S}\cdot\text{cm}^{-1}$. Li|Li symmetric cells using this electrolyte demonstrated excellent long-term cycling at a high current density of $1 \text{ mA}\cdot\text{cm}^{-2}$.

4.2.4. Development outlook

Plastic crystals (PCs), characterized by their ordered crystalline structure coupled with liquid-like molecular dynamics, demonstrate significant potential as SSEs. Among them, SN-based PCEs have been widely investigated due to their high σ and excellent voltage tolerance. Their large-scale implementation in SSBs is anticipated once the compatibility issues with lithium metal anodes are resolved. Recently, organic plastic-crystal Li salts have emerged as a new class

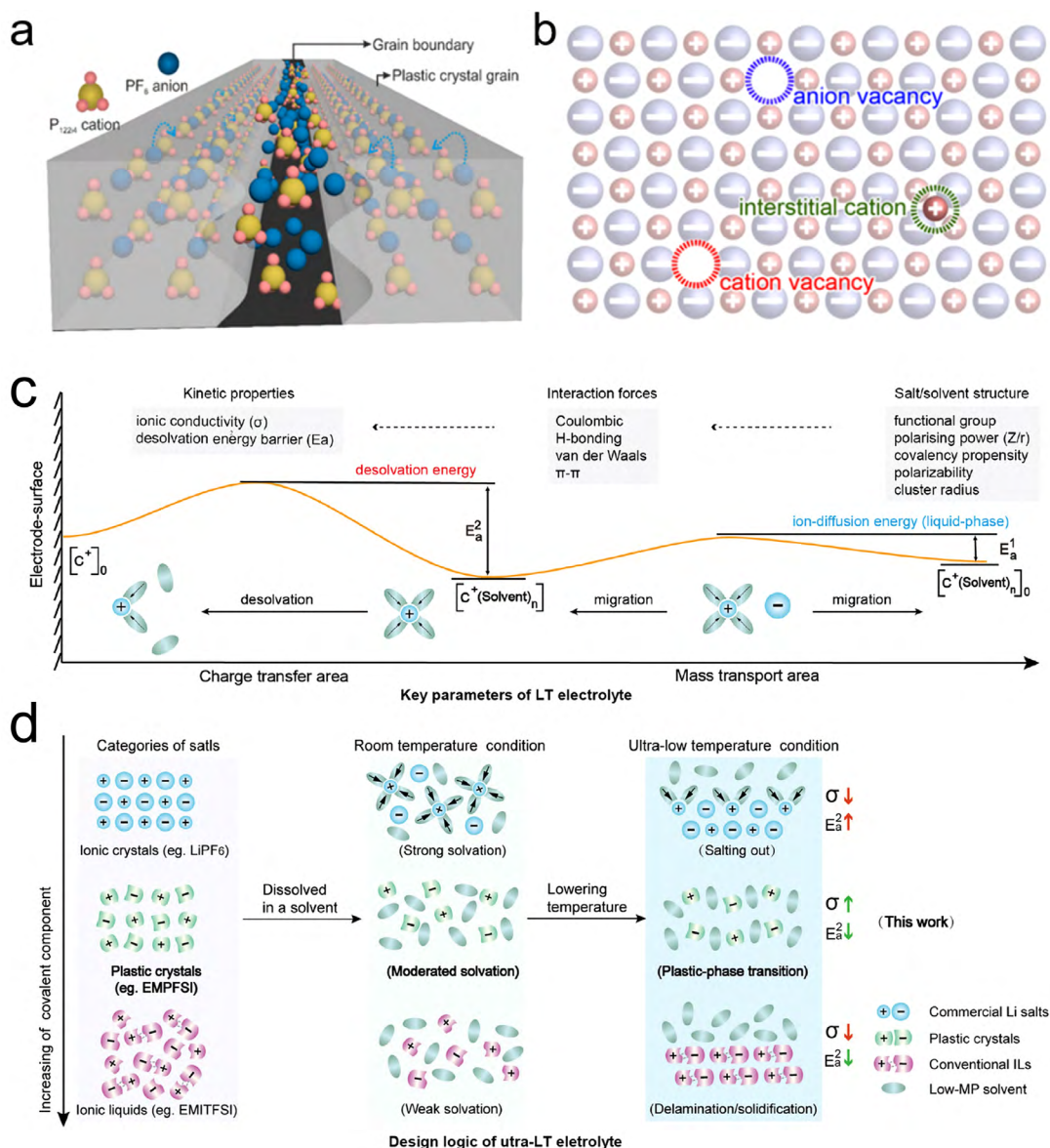


Fig. 14. (a) Schematic of phase structure and ion transport in diethyl(methyl)(isobutyl) phosphonium hexafluorophosphate. Reproduced with permission from ref. [252]. Copyright 2021 American Chemical Society. (b) Illustrations of imperfections in ionic PCEs, such as point defects. Reproduced with permission from ref. [253]. Copyright 2024 Elsevier Inc. (c) Key parameters affecting low-temperature battery performance include ion diffusion and desolvation energy. (d) Design strategy for fast-ion-conductor electrolytes based on ionic plastic crystal compounds. Reproduced with permission from ref. [251]. Copyright 2024 John Wiley and Sons.

of PCEs, demonstrating ultra-high σ ($>10^{-3} \text{ S}\cdot\text{cm}^{-1}$) and representing a promising direction for future development. Advancements are expected through the establishment of molecular design principles to guide ion transport. Initial studies have begun to explore the relationship between chemical structure and ion dynamics in ionic PCEs [253]. However, these materials remain in early research stages, with insufficient understanding of their interfacial compatibility with electrodes, currently impeding their practical implementation.

4.3. Poly(ionic liquid) electrolytes

4.3.1. Characteristics and classification

Poly(ionic liquid)-based electrolytes (PILEs) refer to electrolytes that utilize poly(ionic liquids) (PILs) as the polymer matrix. PILs are distinctive ionomers synthesized by polymerizing ionic liquid (IL) monomers, incorporating cationic, anionic, or both ionic species into the polymer backbone, while the counterions remain mobile. PILEs offer several advantages, including good processability, non-volatility, non-flammability, mechanical robustness, tunable

ionic structures, and enhanced space-charge layer effects [258]. Their preparation methods are similar to those of SPEs, encompassing both *in-situ* polymerization and *ex-situ* techniques. Based on their composition, PILEs are generally categorized into PIL-based gel polymer electrolytes (GPEs) and PIL-based solid polymer electrolytes (SPEs).

4.3.2. Conduction mechanisms and fabrication methods

PILEs exhibit unique ion transport mechanisms, wherein PILs form microporous channels facilitating Li^+ migration between electrodes [259]. When formulated as gel polymer electrolytes (GPEs) with organic electrolytes, PILEs achieve high ionic conductivity (σ) due to the dominance of liquid-phase ion transport. Forsyth *et al.* demonstrated the adaptability of PILs in GPEs and proposed a structural diffusion mechanism for metal ions. In this mechanism, rapid reconfiguration of the metal ion coordination cage is essential for enhancing diffusivity (Fig. 15). The formation of a molten salt-like region within the PIL matrix further enables efficient metal ion diffusion, provided that the salt binding energy remains moderate [260]. A PIL incorporating imidazolium cations positioned distantly from the main polymer chain was designed to enhance ionic transport in PIL-based GPEs [261]. This material was synthesized by

grafting 1-aminopropyl-3-methylimidazole bis(trifluoromethanesulfonyl)imide (APMImTFSI) into glycidyl methacrylate. The resulting polymer features a branched backbone bearing positive charges, which interact strongly with TFSI⁻ anions through Coulombic forces. The immobilized TFSI⁻ anions establish continuous pathways for the Li^+ and MEMP⁺ cations transport, thereby enhancing ionic mobility within the GM-GPE. As a result, the PIL-based GPE incorporating $0.3 \text{ mol}\cdot\text{L}^{-1}$ LiTFSI/N-methyl-N-methoxyethyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide achieves a high ambient σ of $4.3 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$.

In PIL-based SPEs, ion transport predominantly depends on the polymer's inherent conduction properties. Although ion-conducting groups within the polymer matrix offer transport sites, Li^+ mobility is often hindered by polymer crystallinity and strong ion-polymer interactions [262, 263]. In addition, the Li^+ solvation structure significantly affects σ [264]. Strong anion- Li^+ interactions or weak cation-anion binding can increase the Li^+ migration activation energy, thereby reducing conductivity. To mitigate these limitations, a PIL-based SPE was developed using polydiallyldimethylammonium bis(fluorosulfonyl)imide (PDADMAFSI) blended with LiFSI. Molecular dynamics simulations revealed that FSI⁻ is cooperatively coordinated by both Li^+ and the polymer

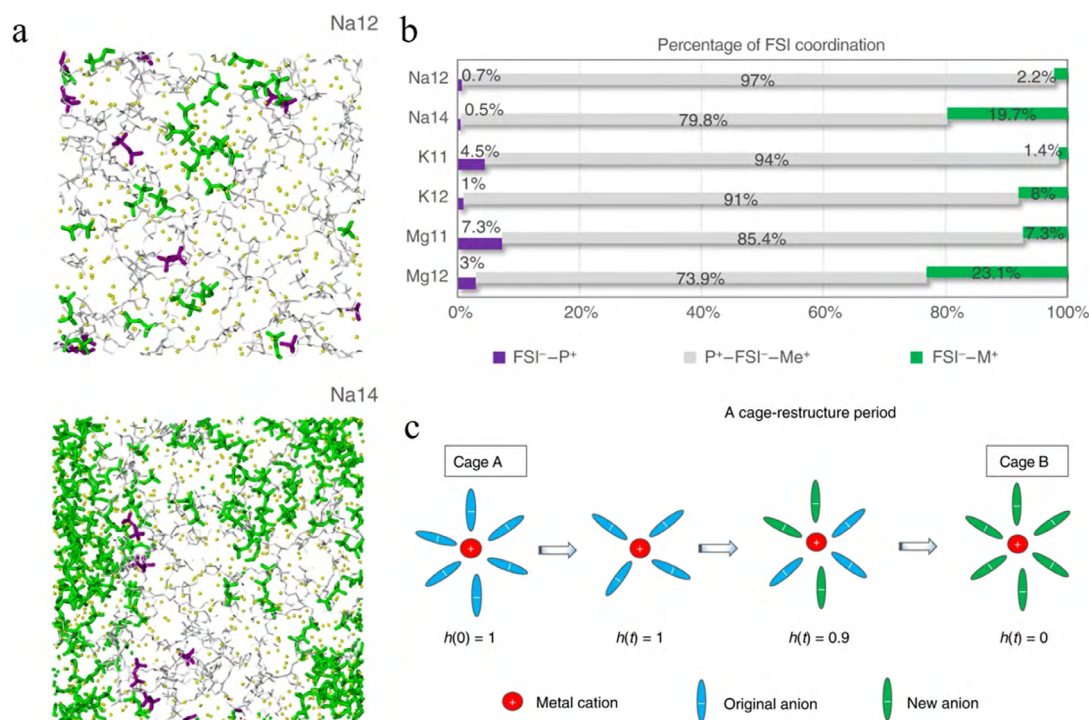


Fig. 15. (a) Equilibrium snapshots of Na_{12} and Na_{14} systems. (b) Distribution of FSI⁻ anions among three coordination states across six PIL systems. (c) Illustration of cage-restructuring and corresponding coordination state function $h(t)$. Reproduced with permission from ref. [260]. Copyright 2022 Springer Nature.

backbone [265]. Notably, interactions between the polycation (N^+) and FSI^- facilitated LiFSI dissociation. At an optimal N^+ to LiFSI ratio of 1.5, the resulting SPE achieved a maximum σ of $0.7 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ at 80°C with $t_{Li}^+ = 0.56$.

4.3.3. Major challenges and corresponding strategies

Low σ remains the primary limitation of PIL-based SPEs. Building on earlier studies, Forsyth enhanced conductivity by incorporating a high salt concentration of lithium (fluorosulfonyl) (trifluoromethanesulfonyl) imide (LiTFSI) into PDADMAFSI. As salt content increased, ion transport behavior shifted from decoupled (1:2) to coupled (1:8) with polymer dynamics, influencing T_g . Despite the high salt concentration, σ remained stable, and t_{Li}^+ reached 0.8. Further tuning of the anion ratio while maintaining 90 mol% saturation improved conductivity to $9.0 \times 10^{-5} \text{ S}\cdot\text{cm}^{-1}$ and t_{Li}^+ to 0.81 at 80°C [266, 267]. In addition, Segalman et al. developed semicrystalline zwitterionic SPEs that decouple ion motion from polymer segmental dynamics via self-assembled ion-conductive domains [268]. Weak ion-ion interactions promoted Li salt dissociation and Li^+ transport. Ion size also influenced ionic distribution. These SPEs achieved a high Li^+ conductivity of $1.6 \text{ mS}\cdot\text{cm}^{-1}$ and t_{Li}^+ of ~ 0.6 – 0.8 . These approaches offer practical pathways for enhancing the conductivity of PIL-based SPEs.

4.3.4. Development outlook

Current research indicates that PIL-based GPEs achieve high σ and show promise for SSB applications. However, safety concerns regarding residual liquid-phase components require further investigation. Despite various strategies to enhance σ of PIL-based SPEs, they still fall short of meeting the performance requirements for SSBs. Therefore, low σ remains the primary challenge for their practical deployment.

Beyond bulk conductivity, PILs offer a promising platform for addressing interfacial challenges in SSBs. For instance, Bao et al. demonstrated that the type of cations in PILs can regulate Li^+ deposition on Li metal anodes [269, 270]. By forming an electrostatic shield on the anode surface, concentrated Li deposition on the heterogeneous regions can be suppressed, enabling more uniform deposition under high current densities. This was achieved by incorporating cations into the polymer backbone or pendant groups, creating an electrostatically active coating without relying on free cations. Additionally, decoupling Li^+ transport from polymer segmental mobility has emerged as a critical strategy for enhancing ion transport kinetics.

5. Soft Solid-State Electrolytes (S^3E)

5.1. Quasi-solid electrolytes based on MOF/COF desolvation effects

5.1.1. Desolvation effect of MOF/COF

Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have attracted growing interest in alkali metal SSEs due to their intrinsic porosity and high surface area [271]. Recently, quasi-solid electrolytes leveraging the MOFs/COFs desolvation effects have emerged as a key research focus [272–276]. In conventional MOF/COF-based electrolytes, liquid electrolytes are confined within nanopores, where the solvation structure of Li^+ is primarily dominated by solvent-separated ion pairs with weakly coordinated solvent molecules (Fig. 16b). These solvated species are susceptible to decomposition upon contact with Li metal or high-voltage cathodes, leading to interfacial degradation and battery performance decline (Fig. 16a) [277, 278]. To overcome this limitation, Chang et al. [272] pioneered “desolvation” quasi-solid electrolytes. Their work demonstrates that the sub-nanometer pores of MOFs/COFs can selectively strip solvent molecules from the solvated Li^+ ions, transforming solvent-separated ion pairs into contact ion pairs (CIPs) [277]. This desolvation intensifies Li^+ -solvent-anion interactions, forming a solvation structure with improved oxidative stability and expanded electrochemical window (Fig. 16c) that outperforms traditional organic SSEs [277].

In desolvated quasi-solid electrolytes, Li^+ transport primarily follows a solvent-assisted hopping mechanism, similar to that in conventional MOF/COF-based SSEs [274]. Sub-nanometer pore confinement induces partial desolvation of Li^+ , yielding a contracted solvation structure that accommodates more TFSI $^-$ anions in the solvation sheath. Concurrently, Li^+ interacts with O atoms in the MOF/COF framework, leading to preferential aggregation of Li^+ around these sites and generating a non-uniform distribution. The synergistic effects of desolvation and Li^+ -framework interactions collectively impede the mobility of both ionic species. Nevertheless, the TFSI $^-$ anion experiences stronger steric hindrance during migration compared to Li^+ due to its larger ionic radius [274]. Consequently, an elevated t_{Li}^+ is observed in desolvated quasi-solid electrolytes. Nonetheless, the detailed Li^+ transport mechanism and its governing factors in these systems remain to be thoroughly investigated.

5.1.2. Preparation methods of desolvated quasi-solid electrolytes

Due to the mismatch between the size of solvated cations and the sub-nanometer pores of MOFs or

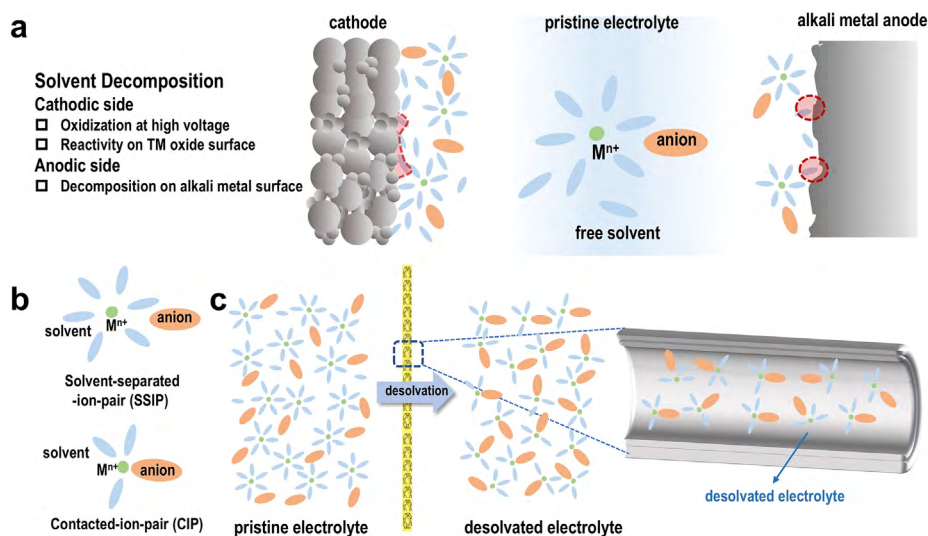


Fig. 16. (a) Solvent-induced decomposition issues in conventional electrolytes for lithium-metal batteries. Reproduced with permission from ref. [278]. (b) Solvation structures of alkali metal ions in electrolytes. (c) Desolvation effect of MOF/COF and schematic of quasi-solid-state 55 electrolyte architecture. Reproduced with permission from ref. [277]. Copyright 2024 John Wiley and Sons.

COFs, spontaneous diffusion is insufficient for forming desolvated electrolytes. In addition, the higher thermodynamic stability of solvated cations relative to their desolvated counterparts necessitates external driving forces to initiate desolvation [279]. Chang et al. [272] applied an external electric field by cycling a Li||Li symmetric cell containing a Cu-paddle-wheel-based $\text{Cu}_3(\text{BTC})_2$ (nicknamed Cu-BTC, where BTC $\equiv$ benzene 1,3,5-tricarboxylate) and PVDF composite membrane filled with $1 \text{ mol} \cdot \text{L}^{-1}$ LiTFSI/PC electrolyte. This approach triggered sustained desolvation within the pores over 10 cycles. Alternatively, Zhu et al. [273] prepared a quasi-solid electrolyte by impregnating $0.5 \text{ mol} \cdot \text{L}^{-1}$ LiTFSI in SN into a ZIF-69 membrane and removing residual solvents through prolonged soaking and multiple vacuum-drying steps. However, both the electric field-driven activation and the multi-step drying process are complex and unsuitable for large-scale production. Therefore, the development of efficient and scalable preparation techniques remains a critical challenge in the advancement of desolvated quasi-solid electrolytes.

5.1.3. Research progress on desolvated quasi-solid electrolytes

Chang et al. [272] were the first to utilize the desolvation effect of MOF materials in SSEs by employing CuBTC MOF as the matrix and $1 \text{ mol} \cdot \text{L}^{-1}$ LiTFSI in PC as the liquid electrolyte to fabricate a quasi-solid electrolyte. This electrolyte exhibited a high oxidation potential of 5.4 V, and enhanced thermal stability with confined electrolyte decomposition onset at $\sim 200^\circ\text{C}$ (Fig. 17a and b). Attenuated total reflectance Fourier

transform infrared spectroscopy and Raman spectroscopy were employed to confirm the formation of stable Li^+ -PC-TFSI $^-$ coordination complexes within MOF pores. XPS analysis of the cycled NCM811 cathode revealed that the coordination between Li^+ and PC effectively suppressed the decomposition of PC, resulting in negligible cathode-electrolyte interphase (CEI) formation. Furthermore, the Li||Li symmetric cell using this quasi-solid electrolyte exhibited a smooth Li metal surface after cycling, demonstrating its capability to inhibit dendrite formation and mitigate side reactions. Chang et al. [272] identified two types of liquid electrolytes confined within the MOF pores (Fig. 17d): physically confined electrolytes capable of exiting the pores to wet the cathode, and physicochemical confined electrolytes that remain trapped and immobilized. This dual confinement maintains stable ion conduction during electrochemical cycling. The NCM811||Li pouch cell assembled with this quasi-solid electrolyte delivered 300 stable cycles at 90°C (Fig. 17c), demonstrating excellent electrochemical performance.

Zhu et al. [273] extended the application of liquid electrolytes to nitrile-based systems, which are generally incompatible with Li metal. Succinonitrile (SN), known for its thermal stability and oxidation resistance, is limited by its reactivity with Li [280]. By leveraging the desolvation effect within ZIF-69 MOF nanopores, Zhu et al. engineered a quasi-solid SN-ZIF-69 electrolyte with an oversaturated structural configuration, effectively resolving the interfacial incompatibility between SN and lithium metal electrodes. This electrolyte exhibited an electrochemical

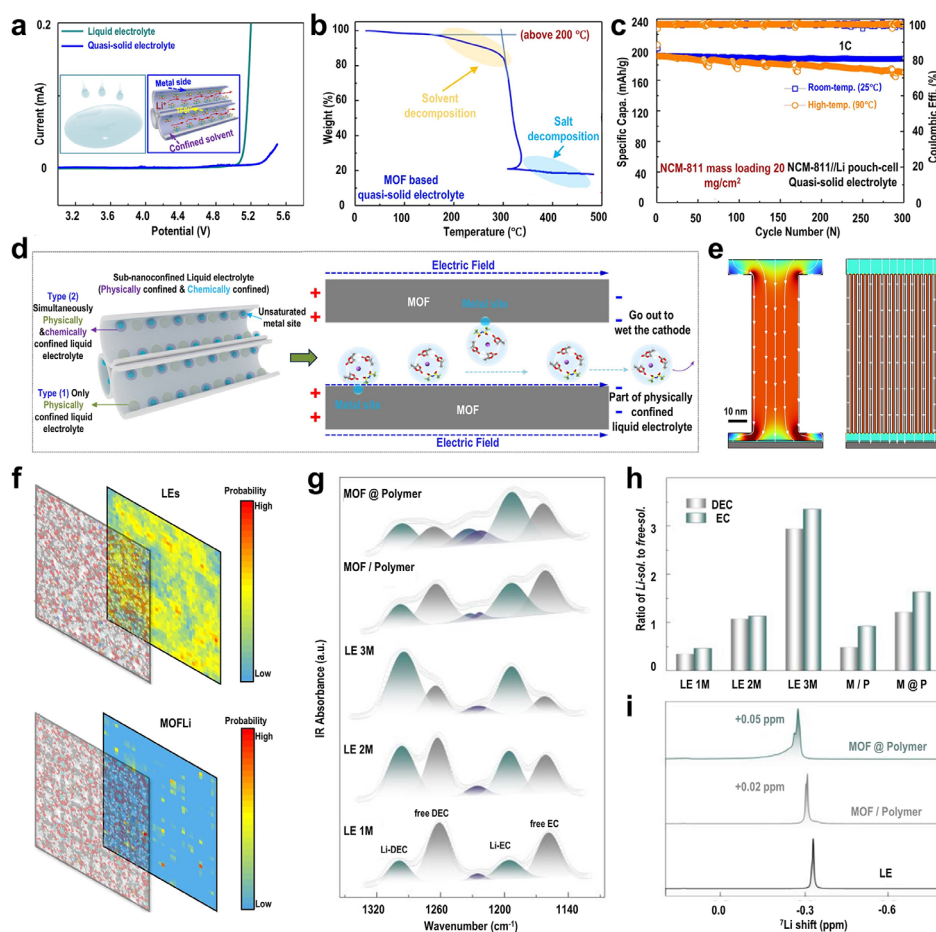


Fig. 17. (a) Linear sweep voltammetric curves of two electrolytes with an inset showing schematic configurations. (b) Thermal gravimetric analyzer (TGA) curve of the MOF-based quasi-solid electrolyte. (c) Cycling performance of NCM-811/Li pouch cell using the quasi-solid electrolyte. (d) Schematic of electrolyte types in MOF channels and their working mechanism. Reproduced with permission from ref. [272]. Copyright 2021 Springer Nature. (e) Finite element method simulations of ion flux in PE membrane with LE and MOFLi QSEs. (f) Final snapshot and Li^+ distribution from molecular dynamics simulations of LE and MOFLi. Reproduced with permission from ref. [274]. Copyright 2024 Springer Nature. (g) FT-IR spectra of LE (1 mol·L⁻¹, 2 mol·L⁻¹, and 3 mol·L⁻¹), MOF/Polymer, and MOF@Polymer films. (h) Solvate species distribution from FT-IR fitting. (i) Li NMR spectra of LE, MOF/Polymer, and MOF@Polymer films. Reproduced with permission from ref. [275]. Copyright 2025 John Wiley and Sons.

stability window of 5.4 V, a high t_{Li}^+ of 0.67, and σ of $1.37 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$. The $\text{Li}||\text{Li}$ symmetric cell achieved stable cycling for 1600 h at 0.25 mA·cm⁻² and 400 h at 0.5 mA·cm⁻². The findings by Zhu et al. and Chang et al. underscore the advantages of desolvated quasi-solid electrolytes, including enhanced thermal stability, broad electrochemical stability windows, high σ , and expanded compatibility with various liquid electrolyte systems.

Chen et al. [274] developed a Janus quasi-solid electrolyte (MOFLi/MSLi QSEs) incorporating UiO-66 MOF particles, mesoporous silica (MS) and PVDF-HFP, and systematically investigated the ion transport mechanism and Li^+ flux regulation. Finite element method simulations (Fig. 17e) demonstrated that the nanoporous structure of MOFLi/MSLi QSEs homogenizes Li^+ flux, promoting uniform Li

deposition and suppressing dendrite growth. Molecular dynamics simulations (Fig. 17f) showed that oxygen atoms in the MOFs and MS coordinate with Li^+ , leading to preferential localization of Li^+ around these O sites within the pores. Mean square displacement analysis confirmed that the limited pore size of MOFs and strong interactions with O atoms impede the diffusion of both Li^+ and TFSI⁻. Owing to its larger ionic radius, TFSI⁻ encounters greater diffusion resistance, thereby increasing t_{Li}^+ of the quasi-solid electrolyte. Furthermore, Feng et al. [275] demonstrated that the dispersion uniformity of MOF particles within the polymer matrix markedly influences the desolvation effect. In MOF@polymer systems, MOFs are more uniformly distributed than in conventional MOF/polymer blends, resulting in a continuous microstructure. This homogeneous distribution facilitates a

Li^+ solvation configuration resembling that of highly concentrated electrolytes, and enhances the chemical interactions between Li^+ and MOFs (Fig. 17g–i).

Beyond MOFs, COFs have also shown considerable promise. Lin et al. [276] developed a quasi-solid electrolyte by incorporating TpPa-2 COF nanosheets with acrylonitrile and poly(ethylene glycol) dimethacrylate (PEGDMA). The resulting electrolyte (HGPE/TpPa-2) exhibited a high t_{Li^+} of 0.57 and an extended electrochemical window of 4.8 V, providing a viable material option for the design of high-performance SSEs.

In addition to MOFs/COFs, alkali metal aluminosilicate zeolites with sub-nanometer pores have also been utilized for electrolyte desolvation. In contrast to MOFs/COFs, zeolites demonstrate superior structural rigidity, higher thermal stability, and enhanced chemical stability. Their cost-effectiveness and wide availability further underscore their potential applicability in desolvation processes. Research indicates that zeolites can encapsulate species within their porous frameworks [281]. The acidic sites present on zeolites effectively adsorb solvent molecules and anions, thereby facilitating the desolvation process [282]. Moreover, zeolites can be transformed into lithiated variants via cation exchange. Once lithiated, they act as efficient Li^+ conductors, enabling solid-state Li^+ transport [283, 284]. For instance, Yang et al. [285] incorporated 3A zeolite powder into a PVDF-based solid electrolyte. The zeolite effectively adsorbed residual free N,N-dimethylformamide molecules, reducing their interaction with Li^+ ions. This adjustment modified the solvation structure of the electrolyte and extended the electrochemical stability window of PVDF from 3.7 V to 4.6 V. Consequently, $\text{Li}||\text{NCM811}$ cells exhibited stable over 250 cycles with a cutoff voltage of 4.5 V. As a result, the $\text{Li}||\text{NCM811}$ cell exhibited stable for 250 cycles at a cutoff voltage of 4.5 V.

5.1.4. Challenges and outlook for desolvated quasi-solid electrolytes

Despite notable progress in enhancing the electrochemical performance of MOF/COF-based desolvated quasi-solid electrolytes, critical challenges persist. The current fabrication methods exhibit prohibitive complexity that impedes scalable manufacturing and practical implementation. In addition, the transport kinetics of alkali metal cations within confined pore environments are not yet fully understood and require further research. Another key issue is the trade-off between σ and mechanical strength, which requires strategic resolution. Future research priorities should encompass: (i) Elucidating Li^+ transport mechanisms in nanoconfined architectures; (ii) Developing scalable and energy-efficient fabrication

protocols; (iii) Designing novel MOF/COF materials with topologically optimized pore structures. These concerted efforts are essential to advance high-performance electrolytes for next-generation high-energy-density battery systems.

5.2. “Rigidity-flexibility synergy” composite electrolytes

To address the limitations of inorganic and organic SSEs, a “rigid-flexible synergistic” strategy has been developed. This approach integrates flexible organic ionic conductors with rigid organic/inorganic fillers to construct composite solid-state electrolytes (CSEs). In these systems, flexible ionic conductors, such as SPEs, PCEs, and ionic liquid electrolytes (ILEs), primarily contribute to σ and interfacial conformability. Rigid components, including polymers, inorganic nano-oxides, and porous organic or inorganic frameworks, are incorporated to enhance mechanical strength. Based on their composition, CSEs can be classified into the following types: nano-oxide-polymer composite electrolytes (NO-SPEs), plastic crystal-polymer solid-state electrolytes (PCE-SPEs), ionogel-based electrolytes, and polymer-inorganic-organic multi-component composite solid-state electrolytes (PIO-CSEs) (Fig. 18). Each type will be discussed in the subsequent section.

5.2.1. Nano-oxide-polymer composite electrolytes

NO-SPEs are primarily composed of SPEs and inorganic nano-oxides with high specific surface areas. These nano-oxides play a key role in improving the mechanical strength, σ , and t_{Li^+} of the composite electrolyte. Based on their functional roles, nano-oxide fillers in NO-SPEs are classified as either inert or active fillers. Inert fillers typically include nano-oxide ceramics such as SiO_2 [286], TiO_2 [38], Al_2O_3 [38, 287], and ZrO_2 [288], which do not conduct Li^+ . When dispersed within the SPE matrix, these fillers act as cross-linking centers through physical or chemical interactions, disrupting the ordered arrangement of polymer chains and reducing crystallinity. In addition, the acidic surface sites of inert fillers interact with Li salts to promote dissociation and immobilize anions. This dual effect leads to improvements in both mechanical strength and σ of NO-SPEs. As early as 1998, the Core team demonstrated this concept by introducing an inert TiO_2 into a PEO-based electrolyte. This approach suppressed room-temperature recrystallization, increased σ by three orders of magnitude, and raised t_{Li^+} to 0.6 (Fig. 19a) [38]. Subsequent studies demonstrated that the surface chemistry of nano-oxide fillers plays a critical role in the performance of NO-SPEs. It was observed that acidic Al_2O_3 fillers significantly enhanced both the conductivity

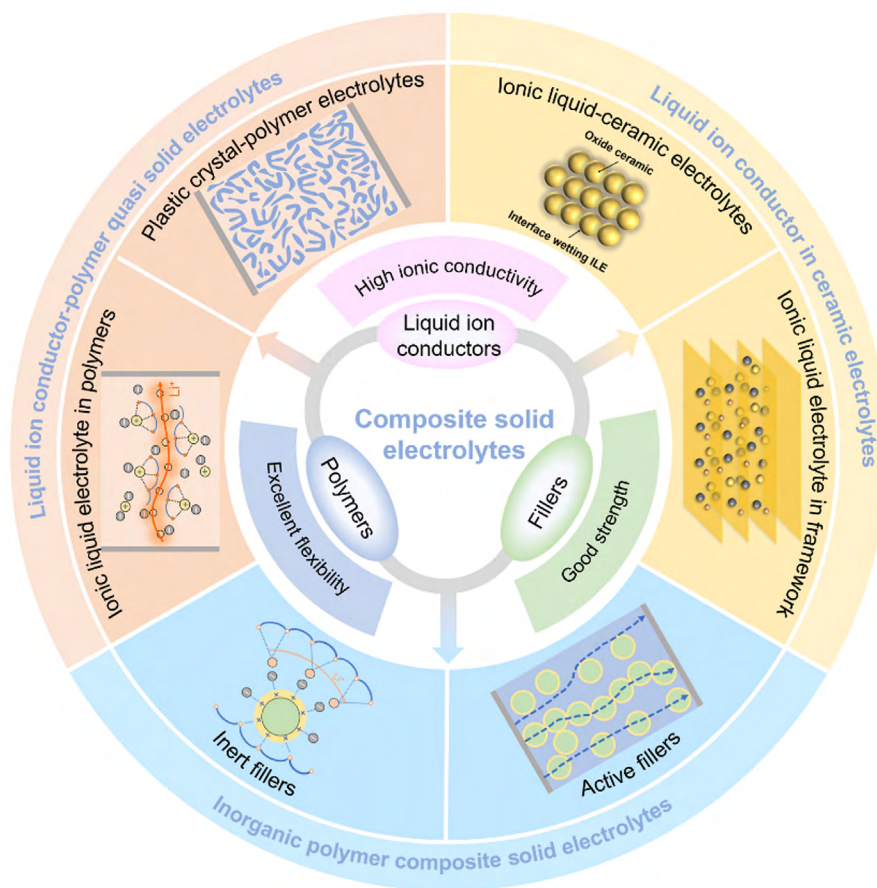


Fig. 18. Schematic illustration of the compositions of different composite electrolytes.

and t_{Li}^+ of PEO-based electrolytes, whereas alkaline Al_2O_3 had minimal effect [287]. Zhao et al. [289] prepared oxygen vacancy-rich SiO_2 nanosheets by doping with V_2O_5 , resulting in a NO-SPE with a room-temperature σ of $3.82 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ and t_{Li}^+ of 0.66 (Fig. 19b). In addition to surface chemistry, the dielectric properties of nano-oxide fillers also influence NO-SPE performance. Dielectric materials, such as BaTiO_3 [290] and $\text{Li}_{0.33}\text{Ti}_{0.02}\text{Ni}_{0.68}\text{O}$ [291], can become polarized under an external electric field, attracting Li^+ and anions to opposite poles of the filler. This polarization effect facilitates Li salt dissociation, thereby enhancing σ .

Active fillers primarily consist of oxide solid electrolytes with intrinsic Li^+ conductivity. Unlike inert ceramics, these fillers contribute directly to ion transport by providing solid-phase Li^+ conduction pathways. However, constructing continuous ion-conducting networks is hindered by high interfacial resistance and the agglomeration of nano-oxide electrolytes. For instance, Hu et al. [292] compared inert ZrO_2 and active LLZTO fillers in polyacrylonitrile (PAN)/ LiClO_4 electrolytes, finding that the conductivity enhancement from LLZTO was only 1.7%

over ZrO_2 -filled systems (Fig. 19c). To reduce interfacial resistance, Guo's team removed high-resistance Li_2CO_3 layers on LLZTO surfaces using poly(propylene carbonate) (PPC) (Fig. 19d), resulting in a NO-SPE with a room-temperature conductivity of $3.4 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which was 3.4 times greater than that of untreated LLZTO composite (Fig. 19e) [293]. To address agglomeration, Shi et al. [294] engineered $\text{Li}_{0.33}\text{La}_{0.56}\text{TiO}_{3-x}\text{-BaTiO}_3$ nanowires (Fig. 19f), which formed a continuous 3D Li^+ transport network in a PVDF matrix (Fig. 19g). This approach elevated σ to $8.2 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ and enabled Li metal batteries to maintain stable for 1500 cycles.

The development of high-performance NO-SPEs relies on regulating the structure and surface properties of nano-oxides, strengthening their synergy with SPE matrices, and constructing efficient Li^+ transport pathways. For inert oxide fillers, particular emphasis should be placed on engineering surface Lewis acidity to optimize interactions with both Li salts and polymer chains. By contrast, oxide solid electrolyte fillers require interface optimization and uniform dispersion to maximize their inherent σ . Furthermore, the incorporation of multiple

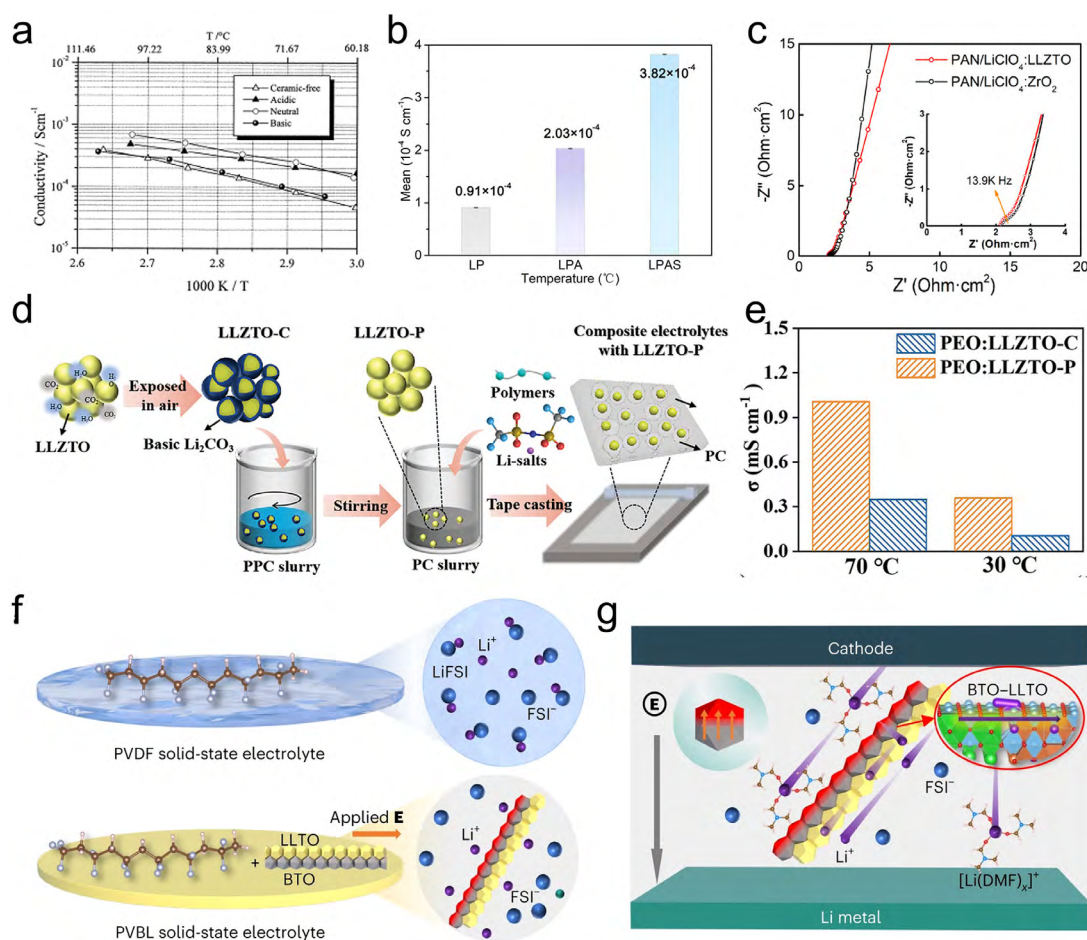


Fig. 19. (a) Arrhenius plots of ceramic-free $\text{P(EO)}_{20}\text{LiSO}_3\text{CF}_3$ and $\text{P(EO)}_{20}\text{LiSO}_3\text{CF}_3 + 10 \text{ wt\% Al}_2\text{O}_3$ above the PEO crystallization temperature. Reproduced with permission from ref. [287]. Copyright 2001 Elsevier Science Ltd. (b) Ionic conductivity of SPEs with oxygen-vacancy-rich layered SiO_x . Reproduced with permission from ref. [289]. Copyright 2024 John Wiley and Sons. (c) Nyquist plots of NO-SPEs using fillers with varying σ (LLZTO vs. ZrO_2). Reproduced with permission from ref. [292]. Copyright 2020 American Chemical Society. (d) Schematic of PPC-treated LLZTO preparation and resulting composites and (e) Ionic conductivity comparison. Reproduced with permission from ref. [293]. Copyright 2024 John Wiley and Sons. (f) Illustration of Li salt states in PVDF and PVBL matrices [294]. (g) Schematic of Li salt dissociation and Li^+ transport via coupled BTO-LLTO in PVBL electrolyte. Reproduced with permission from ref. [294]. Copyright 2023 Springer Nature.

functional fillers, such as plasticizing, dielectric, or fast-ion-conducting oxides, or the design of multi-functional nano-oxides presents a promising strategy to enhance σ , mechanical strength, and interfacial stability simultaneously.

5.2.2. Plastic crystal-polymer solid-state electrolytes

PCE-SPEs primarily consist of SPEs integrated with immobilized PCEs. Within these systems, PCEs serve two key functions: acting as plasticizers to reduce polymer crystallinity and enhance σ of the polymer matrix, and contributing their inherent solid-phase ionic pathway to improve the overall σ and t_{Li}^+ . Due to the soft and flexible nature of both components, PCE-SPEs generally exhibit excellent interfacial conformability, enabling conformal contact to reduce interfacial resistance.

SN, a representative PCE, has been widely utilized in composite SSEs due to its high σ , broad plastic crystal temperature range, and excellent oxidative stability. For example, Lee et al. [295] developed an SN-based composite solid electrolyte by integrating SN with butylacrylate (BA) and poly(ethylene glycol) diacrylate (PEGDA) copolymers (Fig. 20a). The resulting SN-polymer composite solid electrolyte (SN-SPE) exhibited a high σ of $1.1 \times 10^{-3} \text{ Scm}^{-1}$ at room temperature and t_{Li}^+ of 0.75. In this system, the crosslinked polymer network provided mechanical support, while the embedded SN built a continuous ion-conduction pathway. Further investigations demonstrated that the performance of SN-SPEs is strongly affected by the composition and architecture of the composite. Increasing the SN content enhanced σ by improving ion transport channels but

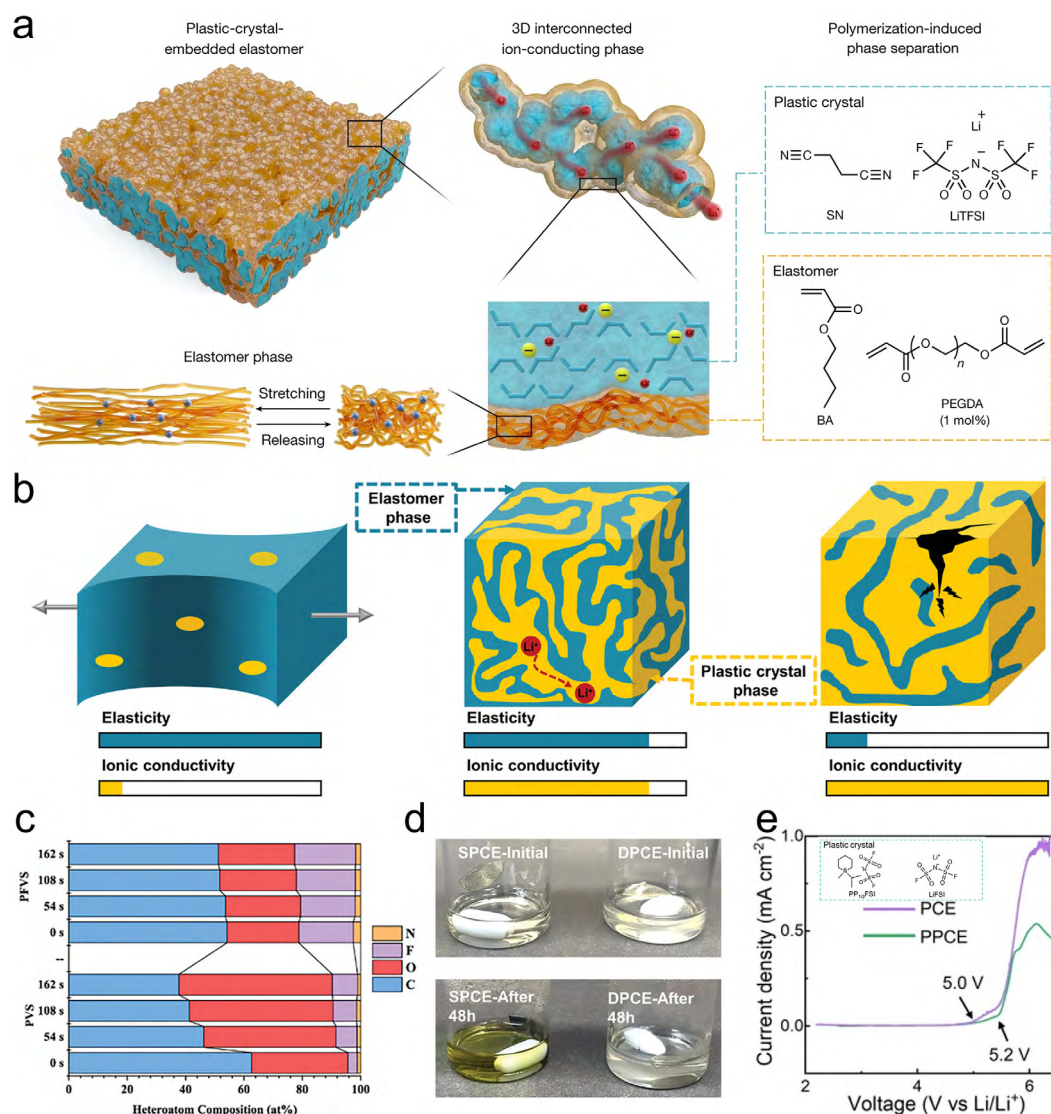


Fig. 20. (a) Design and structure schematic of SN-SPE. Reproduced with permission from ref. [295]. Copyright 2022 Springer Nature. (b) Three schematic cases show structure–property relationships in PCEs by volume phase ratio. Reproduced with permission from ref. [296]. Copyright 2022 John Wiley and Sons. (c) Atomic concentrations in PFVS (fluorinated skeleton). Reproduced with permission from ref. [297]. Copyright 2024 John Wiley and Sons. (d) Photographs of SN-PCEs before and after 48-h Li metal soaking at 70 °C with LiBOB. Reproduced with permission from ref. [300]. Copyright 2023 John Wiley and Sons. (e) Linear sweep voltammetric curves of Li/IPCE-SPE/SS cells at 0.1 mV·s⁻¹ at 25 °C. Reproduced with permission from ref. [301]. Copyright 2024 Elsevier B.V.

compromised mechanical strength (Fig. 20b) [296]. However, SN tends to undergo severe interfacial side reactions with Li metal. To mitigate this issue, two interfacial stabilization strategies have been developed. One approach involves incorporating fluorinated polymer frameworks to enhance the interfacial chemical stability of SN-SPEs with Li metal [297, 298]. For instance, Sun et al. introduced fluorine-containing functional groups into the polymer chains, promoting the formation of a stable, dense LiF-rich interphase on the Li surface (Fig. 20c). This interphase effectively suppressed undesirable reactions between

Li and SN, enabling stable cycling over 4000 h in Li/Li symmetric cells. Another approach involves directly adding film-forming additives into SN-SPEs, such as fluoroethylene carbonate [295], lithium di-fluoro(oxalato)borate (LiDFOB) [299], and lithium bis(oxalato)borate (LiBOB) [300], which are capable to enhance interface stability and battery performance. For instance, Sun et al. [300] incorporated LiBOB into SN-SPE, effectively suppressing interfacial side reactions between Li and SN (Fig. 20d). As a result, Li/Li symmetric cells demonstrated stable cycling for over 1200 h.

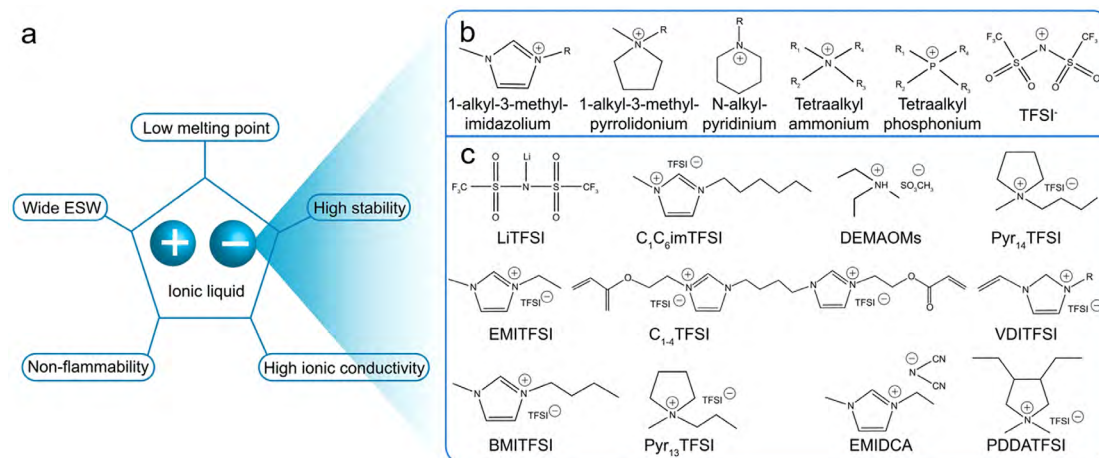


Fig. 21. (a) Advantages of ILs. (b) Structures of typical organic cations and anions. (c) Representative IL structures used in ionogels. Reproduced with permission from ref. [307]. Copyright 2022 John Wiley and Sons.

Beyond conventional SN-SPEs, increasing attention has been directed toward ionic plastic crystal polymer electrolytes. By selecting suitable ionic plastic crystals and compatible polymer matrices, Li salts can be dissolved to form electrochemically stable ionic plastic crystal polymer electrolytes. Yang et al. [301] developed an IPCE-SPE using a highly concentrated LiFSI/methyl isopropyl piperidinium (PP₁₃FSI) ionic plastic crystal combined with poly(ethyl acrylate). The use of chemically stable piperidinium cations and film-forming FSI⁻ anions enabled the electrolyte to achieve a wide electrochemical stability window of 5.2 V (*vs.* Li⁺/Li) and excellent compatibility with Li metal (Fig. 20e). Li/Li symmetric cells assembled with this electrolyte achieved stable cycling for up to 2500 h.

Although PCE-SPEs exhibit synergistic enhancement in σ and interfacial compatibility, their practical application remains limited by inherent phase separation and insufficient mechanical strength. These limitations can be addressed through multiscale structural engineering strategies. For instance, incorporation of inorganic fillers or construction of fibrous reinforcement networks can improve mechanical stability. In addition, modifying polymer matrices with polar functional groups can enhance interfacial compatibility between polymer-plastic crystal phases while facilitating the formation of continuous ion transport pathways. Through these approaches, high-performance composite electrolytes with superior structural integrity and electrochemical performance can be achieved.

5.2.3. Ionogel-based electrolytes

Ionogel-based electrolytes have attracted considerable interest as promising candidates for

next-generation SSBs due to their distinctive solid-liquid synergistic properties. These electrolytes typically consist of ILs confined within organic or inorganic gel matrices, which provide mechanical support and continuous ion transport pathways. Ionogels offer several advantages, including non-flammability, negligible volatility, and a broad electrochemical stability window (Fig. 21a), thereby eliminating the risks of leakage and flammability associated with conventional liquid electrolytes [302–304]. Compared with SPEs, ionogels exhibit superior σ and reduced interfacial impedance [305]. Furthermore, their electrochemical and mechanical properties can be effectively tuned by modifying the IL composition and tailoring the pore structure of the gel matrix (Fig. 21b and c) [306]. Therefore, ionogel-based electrolytes, guided by a rigid-flexible synergistic design, are regarded as core candidates for high-safety, wide-temperature-range SSBs.

Numerous ionogel-based electrolytes exhibit exceptional σ at room temperature, often surpassing 1 mS·cm⁻¹. This conductivity is primarily governed by the intrinsic viscosity of the IL, salt concentration, matrix content, and temperature. In nanoscale inorganic ionogels, the interaction between the gel matrix and ILs significantly influences ion transport. Nanomaterials with high specific surface areas strengthen IL-matrix interactions, promoting Li salt dissociation and increasing carrier concentration. This nanoscale effect serves as an effective strategy to enhance t_{Li}^{+} in ionogel electrolytes [308–312]. Typically, inert inorganic ceramics such as TiO₂ [313], SiO₂ [314], and BaTiO₃ [315] are employed as structural frameworks in ionogels. Although these ceramics do not exhibit intrinsic Li⁺ conductivity, they enhance the ion transport by modulating the behavior of ILEs through

surface interactions. For example, Ahn et al. [315] demonstrated that the high dielectric constant of BaTiO₃ facilitates anion adsorption from the ILE, thereby promoting Li⁺ migration. The resulting inorganic ionogels demonstrated σ of $1.3 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ and enabled stable cycling of LiCoO₂ cathodes at 80 °C. Zhang et al. [316] reported an enhanced ion transport by integrating aminated vermiculite with ILE. Through nanoconfinement and hydrogen bonding, anions were immobilized within vermiculite nanosheets, elevating t_{Li}^+ to 0.89. The phase separation was also effectively mitigated in the ionogel. Furthermore, it was found that functionalized matrices are capable of improving the ILEs' conductivity beyond their intrinsic level. For instance, an ionogel formulated with epoxy-functionalized SiO₂ and N-propyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide (Py13-TFSI)/LiTFSI achieved a conductivity of $1.91 \text{ mS}\cdot\text{cm}^{-1}$ at 30 °C, exceeding that of the pure ILE [314]. In another approach, inorganic solid electrolytes such as LLZO [317], LPS [318], and LGPS [318] have been utilized as hosts, with ILEs introduced to enhance interfacial wetting and reduce grain boundary resistance. To address the limited ion transport caused by the rigidity and poor interparticle connectivity of LLZO, Kim et al. [317] incorporated ILEs to form a conformational ionic shell around LLZO particles. This configuration improved interfacial ion conduction, yielding an inorganic ionogel with a conductivity of $4.0 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$. Lithium metal batteries employing this electrolyte maintained stable for over 150 cycles. Sulfide-based solid electrolytes, such as LPS and LGPS, have also been investigated as inorganic hosts to improve the conductivity of inorganic ionogels. Although these sulfides typically exhibit high reactivity with polar organic solvents, Jung et al. [318] successfully incorporated the solvated IL electrolyte Li(G3)TFSI into LPS and LGPS matrices. The strong coordination between the ether oxygen groups in G3 and Li⁺ effectively suppressed undesirable reactions with sulfides, ensuring chemical compatibility. Owing to the high σ and superior interfacial wetting capability of Li(G3)TFSI, the resulting Li-In/LiFePO₄ SSB delivered a specific capacity of $144 \text{ mAh}\cdot\text{g}^{-1}$.

In polymer-matrix ionogels, the polymer network can be engineered to enhance Li⁺ transport. ILEs typically contain mobile cations (e.g., imidazolium, pyrrolidinium, piperidinium). When incorporated into polymer matrices, these cations interact with polar functional groups to release Li⁺ from the polymer chains while simultaneously suppressing polymer crystallinity [319]. For instance, poly(vinylidene fluoride-trifluoroethylene-chlorotrifluoroethylene) [P(VDF-TrFE-CTFE), or PTC] has been employed as a framework material in ionogel electrolytes. Unlike

PVDF, PTC exhibits lower cation adsorption energy due to its tailored polarity, reducing interference with Li-hopping sites. Furthermore, its higher dielectric constant enhances the dissociation of Li-anion clusters, promoting uniform Li⁺ transport across different domains. In another example, a zwitterion-based copolymer matrix was synthesized via copolymerization of trimethylolpropane ethoxylate triacrylate (ETPTA) and 2-methacryloyloxyethylphosphorylcholine (MPC), a typical zwitterion. Interactions between Li⁺ and both TFSI⁻ and MPC form a coordination shell, reducing the Li⁺ desolvation energy barrier. This dual coordination significantly improved room-temperature σ , reaching $4.4 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ [320]. However, conventional ILs typically exhibit high viscosities ($\approx 10^6 \text{ mPa}\cdot\text{s}$), which are several orders of magnitude greater than those of common organic solvents [321]. This elevated viscosity significantly limits both σ and t_{Li}^+ in traditional ILEs and their composites, thereby hindering their practical use.

To address these limitations, the concept of solvated IL electrolytes has recently emerged and gained considerable attention. These electrolytes are formulated by dissolving Li salts, such as LiTFSI, in solvents with strong coordination ability toward Li⁺, such as tetraethylene glycol dimethyl ether (G4) or triethylene glycol dimethyl ether (G3). In such systems, most solvent molecules are coordinated with Li⁺, effectively reducing the number of free solvent molecules. Consequently, the electrolyte exhibits similar physicochemical characteristics with ILEs, including low volatility, non-flammability, high thermal stability, and broad electrochemical stability windows. Compared with traditional ILEs, these solvated systems exhibit significantly lower viscosity, higher σ ($> 1 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$), and improved t_{Li}^+ ($t_{\text{Li}}^+ \approx 0.5$). In addition, their relatively low cost makes them attractive alternatives for ILEs. For instance, Yan et al. [322] developed a polymer-matrix ionogel electrolyte by incorporating Li(G4)TFSI-LiBOB into a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) matrix. This ionogel exhibited a high room-temperature σ of $2.18 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ and t_{Li}^+ of 0.86. When applied in a Li/LiFePO₄ semi-SSB, the system delivered a specific capacity of $143.2 \text{ mAh}\cdot\text{g}^{-1}$ and retained 95.9% of its capacity after 500 cycles at 0.5 C under ambient conditions.

Ionogel-based electrolytes are mainly prepared by four methods: sol-gel, physical mixing, solvent-assisted, and *in-situ* polymerization. Sol-gel method is commonly used for inorganic-matrix ionogels, such as SiO₂-, TiO₂-, and ZrO₂-based systems (Fig. 22). The physical mixing method directly mixes prepared inorganic particles or polymers with ILs and Li salts. It is simple, low cost, and suitable for

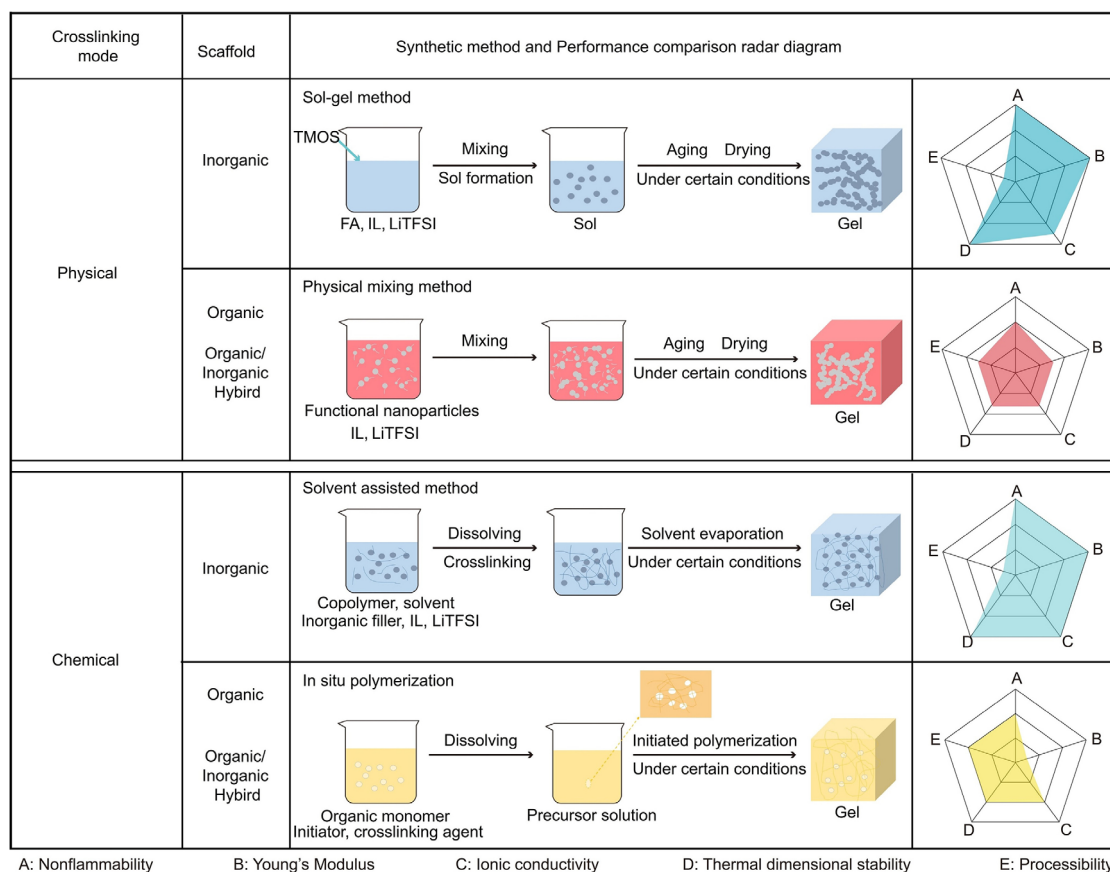


Fig. 22. Preparation methods and properties of ionogel-based electrolytes: sol-gel, physical mixing, solvent-assisted, and in-situ polymerization. Reproduced with permission from ref. [307]. Copyright 2022 John Wiley and Sons.

inorganic-based ionogels. The compatibility between ILs and the host material affects the film-forming quality. The physical cross-linking in ionogel-based electrolytes depends on weak molecular interactions, such as hydrogen bonding and van der Waals forces, resulting in low mechanical strength and poor thermal stability. The thermal-assisted method is suitable for systems where ILs are incompatible with the matrix. In this method, the weak physical interaction between polymers leads to the formation of a cross-linked macromolecular gel structure (Fig. 22). This approach can preserve complex gel architectures and achieve ultra-high toughness (elongation >1000%) or high ion content (>80%). However, the multi-step of swelling-exchange-drying process increases procedural complexity. *In-situ* polymerization is used for fabricating polymer-matrix ionogels and is favored for its simplicity, efficiency, and low cost [323, 324]. Common polymer matrices include PEO [325–328], PVDF, polybutyl acrylate (PBA) [329], and polymethyl methacrylate (PMMA) [330–334].

Balancing mechanical strength and σ persists as a key challenge in ionogel electrolytes. Conventional

systems generally suffer from low mechanical strength with fracture strengths typically below 1 MPa, and exhibit a trade-off between σ and mechanical integrity. For example, highly cross-linked networks improve mechanical properties but disrupt continuous ion transport pathways, reducing conductivity (typically $<10^{-3} \text{ S}\cdot\text{cm}^{-1}$). To address this issue, Chen et al. designed an ionogel-based electrolyte with enhanced strength and stretchability by introducing a micro-segregated structure comprising a crystalline hard phase of poly(N-isopropylacrylamide) and an amorphous soft phase of poly(acrylic acid). This system exhibited a fracture strength of 11.73 MPa, a strain of 473%, and a toughness of $28.09 \text{ MJ}\cdot\text{m}^{-3}$ [335]. Similarly, Zhang et al. [336] developed supramolecular ionogels using 2 wt% 12-hydroxyoctadecanoic acid as a low-molecular-weight gelator, achieving high σ ($\sim 10^{-3} \text{ S}\cdot\text{cm}^{-1}$) and a thermally reversible gel-to-sol transition.

Poor interfacial compatibility with anodes presents another major challenge for ionogel-based electrolytes. When ionogel-based electrolytes contact with a Li metal anode, severe parasitic interfacial reactions often occur. Introducing a high concentration of

alkali metal salts into ILs has been shown to effectively suppress Li dendrite formation [337–341]. *In-situ* gelation also offers an effective strategy to enhance interfacial contact by forming the gel directly at the electrode surface [267, 324, 342], thereby improving interfacial compatibility. However, the compatibility of ionogel-based electrolytes with graphite and silicon-based anodes remains poor, significantly restricting their application in LIBs. Therefore, it is crucial to systematically investigate the compatibility mechanisms between ionogel-based electrolytes and various anode materials, and to develop targeted modification strategies.

Although considerable progress has been achieved in the development of ionogel-based electrolytes, several critical issues remain that must be addressed in future research:

1) As highlighted, the large surface area of nanoscale matrices enhances σ . To fully exploit this advantage, the interactions between Li^+ and nanoscale matrices must be thoroughly characterized and quantitatively correlated with the physical and electrochemical properties of ionogels.

2) Mechanical robustness and potential leakage of liquid-phase ILEs are pressing concerns. Addressing these challenges requires the incorporation of high-strength, porous skeleton materials to improve mechanical integrity and liquid retention capacity.

3) Although ionogels are inherently non-flammable, their safety performance in practical battery configurations has not been systematically investigated. Key concerns regarding their thermal stability in conjunction with high-nickel layered cathodes and Li metal anodes, as well as the role of their flash point-free nature to safety enhancement remain unknown. Elucidating these electrochemical-thermal coupling mechanisms at multi-phase interfaces should be a central focus of future research.

4) The implementation of ionogel-based electrolytes in high-temperature SSBs represents a promising research frontier. For instance, LiFePO_4 half-cells incorporating a SiO_2 reinforced EMIM-TFSI/LiTFSI ionogel demonstrated excellent rate capability at 125 °C ($\sim 140 \text{ mAh}\cdot\text{g}^{-1}$ at 1 C and $\sim 100 \text{ mAh}\cdot\text{g}^{-1}$ at 12 C) [343]. More recently, an hexagonal BN-based EMIM-TFSI/LiTFSI ionogel enabled the stable cycling of LiFePO_4 half-cells at 10 C and 175 °C, with 90% capacity retention over 100 cycles [344], representing the highest operating temperature reported for rechargeable SSBs. These advances establish ionogels as enablers of lithium battery functionality in previously inaccessible thermal regimes. Nevertheless, systematic investigation of long-term cycling stability under extreme temperatures remains imperative in future works.

5.2.4. Multi-component composite solid-state electrolytes

Polymer-inorganic-organic multi-component composite solid-state electrolytes (PIO-CSEs) represent an emerging material class engineered to integrate the synergistic advantages of SPE, nano-inorganic fillers, and organic liquid electrolytes, such as high-concentration electrolytes, PCEs, or ILEs. This multicomponent architecture is intended to synergistically enhance the comprehensive performance of SSEs to meet the stringent requirements of next-generation batteries. In this system, the SPE functions as a flexible matrix, providing mechanical support and a continuous ion-conducting network. The role of nano-inorganic fillers is to reduce polymer crystallinity, enhance Li^+ transport, and reinforce mechanical strength. Meanwhile, the incorporated organic electrolytes function as plasticizers and interfacial wetting agents, further boosting σ and improving electrode-electrolyte interface conformability.

Recent advancements in PIO-CSE research have shown significant progress. Kyeong-Seok et al. [345] developed a flexible and safe PIO-CSE by incorporating cationic polymers, $\text{TiO}_2/\text{SiO}_2$ -doped Al_2O_3 nanoparticles, and high-concentration liquid electrolytes (Fig. 23a). The electrolyte achieved a high t_{Li}^+ of 0.91 (Fig. 23b), attributed to anion immobilization by cationic groups in the polymer and acidic sites on the nano-oxide surfaces, as well as the plasticizing effects of both the nano-oxides and the liquid electrolytes. In another study, Lei et al. [346] used ILE as an interfacial wetting agent to enhance Li^+ transport at the interface between $\text{Li}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ and SPE. The resulting PIO-CSE achieved σ of $8.3 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ and t_{Li}^+ of 0.81 (Fig. 23c). Pouch cells assembled with this electrolyte, a Li-metal anode, and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode exhibited excellent cycling stability, high rate performance, and strong safety under mechanical abuse conditions, including bending, folding, cutting, and nail penetration (Fig. 23d and e).

Despite the superior comprehensive performance of multicomponent PIO-CSEs, the inclusion of multiple components and complex interfacial phases increases system complexity. Therefore, enhancing PIO-CSEs' performance necessitates joint consideration of structural stability and component compatibility. This may be achieved by employing porous framework materials to reinforce interactions among polymers, liquid electrolytes, and the framework surface, as well as leveraging the confinement effect of porous structures to attain ordered component distribution and structural stability. For example, Lanceros et al. [347] constructed a composite electrolyte using natural zeolites as the framework, combined with ILE and PVDF-HFP. Interactions between PVDF-HFP,

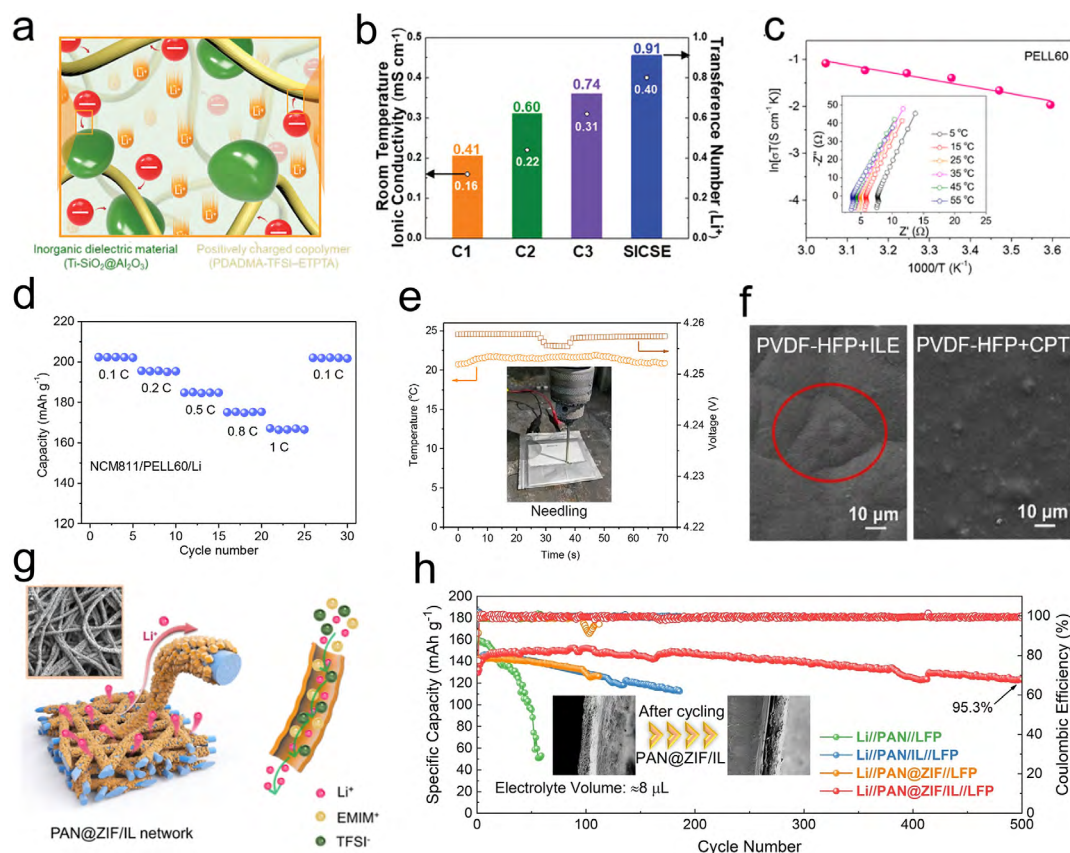


Fig. 23. (a) Ion transport mechanism in PIO-CSE [345]. (b) Room-temperature (σ) and Li^+ transference number (t_{Li^+}) of the PIO-CSE and controls (C1–C3). Reproduced with permission from ref. [345]. Copyright 2021 John Wiley and Sons. (c) EIS and Arrhenius plots of PIO-CSE [346]. (d) Rate performance of NCM811/PIO-CSE/Li cells [346]. (e) Nail penetration test with voltage and temperature profiles. Reproduced with permission from ref. [346]. Copyright 2024 American Chemical Society. (f) SEM images of PVDF-HFP + ILE and PVDF-HFP + CPT with representative spherulites. Reproduced with permission from ref. [347]. Copyright 2021 American Chemical Society. (g) Electrochemical process and ion transport in PIO-CSE [348]. (h) Cycling performance of Li||LFP cells at 0.1 and 1 C at 25 °C. Reproduced with permission from ref. [348]. Copyright 2023 John Wiley and Sons.

ILE, and zeolite surfaces, along with the micro/nano-pore storage capacity of zeolites, effectively suppressed the formation of spherulitic polymer microcrystals and prevented ILE leakage (Fig. 23f). The electrolyte achieved a room-temperature σ of $1.9 \times 10^{-4} \text{ S cm}^{-1}$ and remained thermally stable up to 300 °C. Moreover, MOFs, which possesses high specific surface area, multiple cation sites, tunable pore sizes, and functional surface groups, have been widely applied in composite SSEs. Zhang et al. [348] developed a 3D porous MOF/polymer electrolyte membrane incorporating ILE (Fig. 23g). This membrane demonstrated a room-temperature Li^+ conductivity of $8.17 \times 10^{-4} \text{ S cm}^{-1}$ and t_{Li^+} of 0.82. A Li/LiFePO₄ battery employing this membrane delivered a reversible capacity of $\sim 140 \text{ mAh g}^{-1}$ at 1.0 C with 95.3% capacity retention after 500 cycles (Fig. 23h).

PIO-CSEs integrate the strengths of multiple components to overcome the limitations of single component SSEs, establishing themselves as

high-performance alternatives. However, challenges including interfacial complexity and phase separation remain unresolved. These challenges can be mitigated by engineering the pore channels and surface chemistries of porous framework materials. Through confinement effects, component compatibility can be improved, offering an effective strategy to enhance the structural and interfacial stabilities of PIO-CSE systems.

5.2.5. Challenges and outlook for rigid-flexible synergy composite

Despite notable progress in CSEs, key challenges persist. Conventional NO-SPEs often fail to exhibit adequate room-temperature σ for practical applications. Although incorporating mobile-phase fast ionic conductors, such as ILEs or PCEs, can improve conductivity and interfacial compatibility, these additions typically weaken mechanical integrity and introduce risks of liquid-phase leakage. A promising strategy

involves embedding solid-state micro/nanoporous fillers to immobilize mobile ionic conductors within the CSE matrix. These fillers offer abundant surface sites to interact with polymer functional groups, promoting Li^+ release, while their internal pore structure traps anions and residual solvents. This design enables the formation of multi-channel pathways that facilitate fast Li^+ migration. Consequently, a rigid-flexible synergistic CSE system with both high t_{Li^+} (>0.6) and σ ($>10^{-3} \text{ S}\cdot\text{cm}^{-1}$) can be achieved, warranting further investigation.

6. Conclusions and Perspectives

SSEs, as essential components of SSBs, have attracted considerable attention in recent years. From the perspective of material systems, current research primarily focuses on three material categories: inorganic SSEs (including oxides, sulfides, halides), polymer electrolytes, and composite systems. Oxide electrolytes, such as garnet-type (e.g., $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$) and NASICON-type (e.g., $\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$), exhibit high room-temperature σ ($>10^{-3} \text{ S}\cdot\text{cm}^{-1}$) along with excellent thermal and electrochemical stability [349]. However, their inherent rigidity often results in poor solid-solid interfacial contact. Although surface modifications and particle downsizing can reduce grain boundary resistance, high-temperature sintering remains necessary to achieve sufficient interfacial adhesion [350]. Sulfide electrolytes (e.g., $\text{Li}_6\text{PS}_5\text{Cl}$, Li_3PS_4) demonstrate high σ (10^{-2} – $10^{-3} \text{ S}\cdot\text{cm}^{-1}$) and favorable deformability. Nevertheless, their practical application is hindered by poor air stability and interfacial degradation during cycling. Strategies such as oxygen doping [351], protective coatings [117] (e.g., LiF on $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$), or elemental substitution [119] (e.g., Sb for P) have been explored to enhance air stability. However, these approaches lead to compromised ionic conductivity, presenting a fundamental trade-off between stability and performance. Halide electrolytes (e.g., Li_3InCl_6 , Li_2ZrCl_6) are promising due to their moderate Young's modulus and excellent electrochemical oxidation stability ($>4.2 \text{ V}$), enabling compatibility with high-voltage cathodes. Recent advances in high-entropy doping (e.g., $\text{Li}_{2.8}\text{In}_{0.2}\text{Sc}_{0.2}\text{Yb}_{0.2}\text{Lu}_{0.2}\text{Zr}_{0.2}\text{Cl}_6$), ccp-M structuring, and amorphization have achieved conductivities exceeding $10^{-3} \text{ S}\cdot\text{cm}^{-1}$ [147, 352–354]. Despite these merits, halide electrolytes face two critical challenges: (1) poor interfacial compatibility with anodes and (2) chemical instability in humid environments and organic solvents. Polymer electrolytes, particularly polyethylene oxide (PEO)-based systems, offer advantages in flexibility and processability, making them attractive for flexible electronics. Nonetheless,

their low room-temperature σ (typically $<10^{-3} \text{ S}\cdot\text{cm}^{-1}$) limits practical adoption. Approaches such as grafting, copolymerization, cross-linking, and blending have been employed to increase the amorphous content and improve Li^+ mobility. Additionally, modifications to Li salts and copolymer unit structures have also been applied to weaken Li^+ coordination and enhance t_{Li^+} [166, 191–193]. Despite these efforts, dry polymer electrolytes typically achieve conductivities of only $\sim 10^{-4} \text{ S}\cdot\text{cm}^{-1}$, which remains inadequate for commercial viability.

While optimizing individual material components has demonstrated limited success in meeting practical application requirements, recent research has shifted toward a multi-dimensional co-design approach for composite electrolytes. This paradigm integrates complementary material systems to simultaneously achieve balanced properties including: (1) high ionic conductivity (σ), (2) broad electrochemical stability window, (3) excellent electrode-electrolyte interfacial compatibility, (4) appropriate mechanical strength, (5) environmental tolerance, and (6) cost-effectiveness. Among various approaches, the development of solid-solid-solid electrolytes (S^3Es) has emerged as particularly promising. S^3Es uniquely combine the advantages of different material classes, exhibiting superior interfacial conformity and processability compared to inorganic solid-state electrolytes (SSEs), while offering enhanced ionic conductivity and mechanical robustness relative to polymer-based SSEs. Current research highlights two key design strategies for advanced S^3Es : 1) “Rigid-Flexible Synergy” Design. This approach combines soft ionic conductors (e.g., polymers, plastic crystals, or ionogels) with mechanically robust inorganic or organic nanostructured materials to achieve optimal performance balance [38]; 2) “ Li^+ -Desolvation” Electrolyte Systems. These systems immobilize solvent molecules within the nanoconfined pores of porous framework materials (e.g., MOFs, COFs), effectively addressing critical challenges including solid electrolyte interphase (SEI) instability and lithium dendrite formation [39–42].

Building on these fundamental strategies, we identify four particularly promising material configurations for next-generation S^3Es : plastic crystal-polymer composites, ionogel-organic framework (MOF/COF) composites, nano-inorganic Li^+ ion conductor-polymer composites, and complementary multi-component hybrid systems. These architectures demonstrate exceptional potential for developing novel S^3Es with the following characteristics: ultra-light-weight design, balanced high mechanical strength and flexibility, elevated Li^+ transference numbers ($t_{\text{Li}^+} > 0.6$), high ionic conductivity ($\sigma > 10^{-3} \text{ S}\cdot\text{cm}^{-1}$) and excellent interfacial stability. The rational design and

optimization of these composite systems represent a critical pathway toward practical implementation of high-performance S³Es.

Future breakthroughs in S³Es necessitates synergistic progress in four interconnected domains: fundamental material innovation, battery architecture optimization, scalable manufacturing techniques, and advanced characterization methodologies.

1) Material Innovation: Critical challenges in S³E include interfacial incompatibility and phase separation during long-term cycling. These issues stem from repulsive interactions between rigid fillers and flexible polymer matrices, mismatches in thermal expansion coefficients, and Li⁺ electrochemical potential gradients. Such mismatches induce localized interfacial stress and ionic transport bottlenecks, promoting phase separation. Atomic-scale interfacial engineering of rigid fillers, through strategies such as directional surface grafting or *in-situ* polymer modification, combined with core-shell heterostructure designs, can establish graded interfaces that enhance compatibility and promote continuous Li⁺ transport. Utilizing the thermodynamic responsiveness and tunable nanostructure of flexible electrolytes enables the creation of stress-adaptive composite systems. Introducing reversible dynamic bonds (e.g., disulfide, coordination, or π - π interactions) into 3D interpenetrating networks allows for self-healing of cycling-induced damage, thereby relieving local stress concentrations. Strengthening interfacial interactions between components further reduces the free energy of mixing, enhancing phase stability. Moreover, topological protection of Li⁺ transport pathways, achieved by exploiting spatial confinement and interfacial coupling between rigid inorganic frameworks and flexible electrolytes (e.g., Li⁺-desolvation electrolytes), effectively mitigates interfacial instability caused by volume deformation.

2) Battery Architecture Optimization: The interfacial compatibility of S³E with both cathodes and anodes remains a significant limitation. While plastic crystal-polymer composite electrolytes (e.g., SN-based) offer a wide electrochemical stability window and excellent wettability, they are prone to decomposition at the Li metal interface. Conversely, nano-oxide-polymer composite (e.g., PEO-based) exhibits favorable stability with Li anodes but lacks sufficient oxidative stability at the cathode interface. Incorporating trace amounts of liquid interfacial wetting agents can improve interfacial contact and reduce resistance within the S³E system. In addition, constructing multi-layered S³E architectures enables targeted interfacial optimization. For instance, a bilayer electrolyte comprising a plastic crystal-polymer composite on the cathode side and a PEO-based nano-oxide-polymer composite on the anode side can achieve

dual compatibility by tailoring interfacial properties for each electrode.

3) Scalable Manufacturing Techniques: The structural complexity of S³E presents significant challenges for achieving uniform dispersion of multicomponent materials and precise microstructural control during large-scale fabrication. To address this, *in-situ* optical monitoring should be integrated with machine learning-driven process optimization to guide manufacturing based on multi-physics field coupling. Techniques, such as roll-to-roll continuous coating, *in-situ* curing, and solvent-induced self-assembly, can be employed to enable green, intelligent, and high-efficiency production. These approaches facilitate the scalable fabrication of large-area, ultra-thin electrolyte films suitable for industrial applications.

4) Advanced Characterization Methodologies: Establishing standardized evaluation systems is essential for advancing S³E research and commercialization. This includes a consistent method for assessing electrolyte performance, such as σ , t_{Li}^+ , electrochemical stability window, and interfacial compatibility, as well as quantifying dendrite suppression through metrics such as critical current density and symmetric cell cycle life. In addition, defining quality control specifications for large-scale manufacturing, including electrolyte film porosity, thickness tolerance, and uniformity, is critical for industrial viability.

In conclusion, S³E offers promising avenues for advancing SSB technology. Realizing their full potential will require coordinated efforts across material innovation, structural design, fundamental mechanical research, and scalable manufacturing to achieve breakthroughs in interfacial stability, cycle durability, and practical application.

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Conflicts of interest

Xin-Ping Ai is the Associate Editor-in-Chief of Journal of Electrochemistry and was not involved in the editorial review or the decision to publish this article. All authors declare that there are no competing interests.

Author contribution

Yi-Cheng Deng: Writing – original draft (Equal); Zichang You: Writing – original draft (Equal); Geng-Zhong Lin: Writing – original draft (Equal); Guo Tang: Writing – original draft (Equal); Jing-Hua Wu: Writing – original draft (Equal); Zhi-Min Zhou: Writing – original draft (Equal); Xiang-Chun Zhuang: Writing – original draft (Equal); Li-Xuan Yang: Writing – original draft (Equal); Zhen-Jie Zhang: Writing – original draft (Equal); Zhao-Yin Wen: Writing – review & editing (Equal); Xia-yin Yao: Writing – review & editing (Equal); Chang-Hong Wang: Writing – review & editing (Equal); Qian Zhou: Writing – review & editing (Equal); Guang-Lei Cui: Writing – review & editing (Equal); Ping He: Writing – review & editing (Equal); Hui Li: Writing – review & editing (Equal); Xin-Ping Ai: Writing – review & editing (Lead).

Data availability

This review does not involve the use of primary data. All information is based on previously published studies.

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对电化学十大科学问题之三“如何获得满足固态电池应用需求的高性能碱金属离子固体电解质?”的深度思考——

获得满足固态电池应用需求的高性能锂离子固体电解质策略

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摘要:

随着锂离子电池 (LIBs) 在便携式电子产品、电动汽车和电网储能领域的广泛应用, 因可燃液态有机电解质所引起的电池安全问题受到越来越多的关注。固态锂电池 (SSLBs) 凭借其高安全性和高的能量密度潜力, 被视为下一代储能技术的重要方向。然而, 固态电解质 (SSEs) 的实际应用仍面临诸多挑战, 包括离子电导率低、与电极界面相容性差、机械性能不理想, 以及规模化制备困难等。如何获得满足应用需求的高性能锂离子固体电解质呢? 为回答这一科学问题, 本文系统梳理了近年来 SSEs 的研究进展, 涵盖无机类 (氧化物、硫化物、卤化物)、有机类 (聚合物、塑性晶体、聚离子液体) 以及新兴的软固态电解质 (S³Es) 类。分析表明, 单组分 (无机、有机) 固态电解质存在固有局限性, 且仅通过成分和结构调整难以完全克服。相比之下, 软固态电解质, 特别是基于“刚-柔协同”复合策略和借助多孔框架实现“Li⁺去溶剂化”机制的 S³Es 体系, 能够通过整合互补组分的优势, 在电化学性能 (如离子电导率与电化学稳定窗口)、力学性能及可加工性方面实现协同提升, 展现出作为下一代 SSEs 的巨大潜力。此外, 本文还进一步探讨了 S³Es 面向实际应用所面临的关键挑战及新兴研究趋势, 旨在为高性能 SSEs 的未来发展提供战略性见解。

关键词: 固态电解质; 固态电池; 软固态电解质; 离子电导率; 界面稳定性