

Bulk Na⁺ Transport and Interfacial Stability in Inorganic Solid Electrolytes for All-Solid-State Sodium-Metal Batteries

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Cite This: *ACS Energy Lett.* 2026, 11, 4854–4877

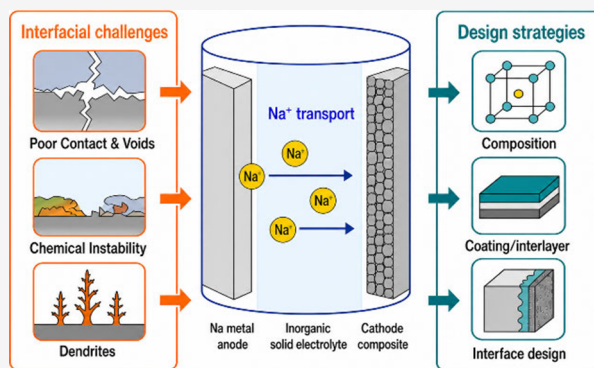
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ABSTRACT: All-solid-state sodium-metal batteries (ASS-SMBs) are promising for safe, sustainable energy storage, but their advancement requires solid electrolytes that combine fast bulk Na⁺ transport with stable interfaces, two factors that are intrinsically coupled. This review presents a descriptor-based perspective on sodium-ion conduction across major inorganic electrolyte families, including oxides, sulfides, halides, anti-perovskites, and complex hydrides. We emphasize how crystal structure, defect chemistry, lattice dynamics, and grain-boundary characteristics govern migration pathways, transport heterogeneity, and interfacial evolution. We then examine the origins of key interfacial challenges, such as space-charge effects, contact loss, interphase instability, and dendrite initiation and relate them to bulk transport descriptors across different electrolyte systems. Finally, we summarize current design and interface-engineering strategies and propose cross-family design rules for developing practical inorganic solid electrolytes for ASS-SMBs.



Sodium-based batteries are attracting increasing attention as cost-effective and resource-abundant alternatives to Li-ion batteries for large-scale energy storage.^{1,2} Within this broad class, all-solid-state sodium-metal batteries (ASS-SMBs) are particularly attractive because metallic sodium provides a low redox potential of −2.71 V versus SHE and a high theoretical specific capacity of 1166 mAh g^{−1}.³ Compared with hard-carbon-anode solid-state sodium-ion batteries, which typically deliver practical energy densities of approximately 160 Wh/kg, Na-metal configurations offer a more direct route toward higher energy density.⁴ However, realizing this advantage requires solid electrolytes that simultaneously provide fast Na⁺ transport, chemical/electrochemical stability, and robust interfacial compatibility with Na metal.

Inorganic solid electrolytes are central to ASS-SMBs because they combine high ionic conductivity with non-flammability, good thermal stability, and, in principle, sufficient mechanical strength to suppress dendrite penetration.⁵ However, the use of a rigid solid electrolyte does not remove the challenges of the sodium metal anode; instead, it shifts them to the Na-metal/solid-electrolyte interface, where solid–solid contact is inherently susceptible to poor wettability, high interfacial resistance, and mechanical degradation during repeated plating/stripping.^{5,6}

Unlike conventional reviews that organize inorganic sodium solid electrolytes primarily by crystal structure, chemical family, or isolated performance metrics, this review adopts a descriptor-based framework that links structure/defects, Na⁺ transport, interfacial stability, and cell-level performance. The central value

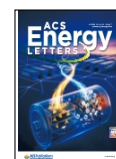
of this framework is that it identifies transferable descriptors across different electrolyte families, including mobile-ion concentration, defect chemistry, migration barriers, bottleneck geometry, lattice softness/polarizability, chemical disorder, grain-boundary characteristics, and transport heterogeneity. These descriptors govern not only intrinsic Na⁺ conductivity but also transport heterogeneity, space-charge formation, interphase evolution, contact stability, and dendrite tolerance. By connecting these bulk and interfacial descriptors within a unified mechanistic chain, this framework enables cross-family comparison and provides design guidance that extends beyond material-specific conductivity optimization. The aim of this review is therefore not only to summarize representative electrolyte families, including Na-β/β'-Al₂O₃, NASICON, sulfides, anti-perovskites, halides, and complex hydrides, but also to extract cross-family design rules that connect materials descriptors to device-relevant behavior. On this basis, we first discuss fundamental ion-transport mechanisms and interfacial issues, survey the structural features and conduction modes of major inorganic sodium solid electrolytes, and finally summarize strategies to improve conductivity and interfacial stability,

Received: April 4, 2026

Revised: May 16, 2026

Accepted: May 22, 2026

Published: June 22, 2026



together with future directions toward practical ASS-SMBs (Figure 1).

TRANSPORT DESCRIPTORS AND TRANSPORT-INTERFACE COUPLING

Single-Ion and Cooperative Na⁺ Transport

Na⁺ transport in solid electrolytes proceeds through thermally activated jumps between lattice sites and is governed by point defects and the local migration energy landscape.⁷ Defect chemistry controls the concentration of mobile carriers, whereas migration barriers determine the intrinsic resistance to ion hopping.⁵ In crystalline solids, Na⁺ transport generally occurs through vacancy-, interstitial-, or interstitialcy-type pathways, depending on site connectivity and defect distribution (Figure 2a). The temperature dependence of ionic conductivity (σ) can be described by a modified Arrhenius relationship:

$$\sigma = \frac{A}{T} e^{-E_a/k_B T} \quad (1)$$

where k_B is the Boltzmann constant, T is the temperature, and A is the pre-exponential factor, and E_a is the activation energy.

While Na⁺ transport has long been described in terms of independent single-ion hopping, recent studies indicate that concerted migration can play an important role in many sodium conductors. In Na-rich or strongly interacting sublattices, excess Na⁺ ions may occupy higher-energy sites and migrate cooperatively by displacing neighboring ions, leading to partial cancellation of migration barriers (Figure 2b). Such correlated multi-ion motion can lower the effective activation barrier and significantly enhance ionic conductivity.⁷ This mechanism is particularly prominent in densely packed or strongly interacting Na⁺ sublattices and provides an important design principle for developing fast sodium-ion solid electrolytes.

Structural and Chemical Descriptors Governing Na⁺ Mobility

Anionic Frameworks and Bottleneck Dimensions

The mobility of Na⁺ ions is strongly governed by the topology of the anionic framework, which defines both the connectivity of stable/metastable sites and the geometry of accessible migration pathways. Recent studies show that fast sodium-ion transport is favored in frameworks that provide structurally equivalent, facet-sharing pathways with relatively low migration barriers, as exemplified by bcc-like anion arrangements (Figure 3a).²

A key geometric parameter is the bottleneck size, namely the triangular channel formed by neighboring anions through which Na⁺ migrates (Figure 3b). For Na⁺, larger bottlenecks generally reduce steric and electrostatic constraints and lower migration barriers, whereas smaller bottlenecks impede migration and increase transport resistance.⁸ Because bottleneck size is determined by crystal geometry, it can be tuned only indirectly through chemical substitution or lattice modification.

Beyond static structure, dynamic anion units can also facilitate Na⁺ migration through rotationally or vibrationally assisted pathway opening.² As illustrated in Figure 3c–e, anion

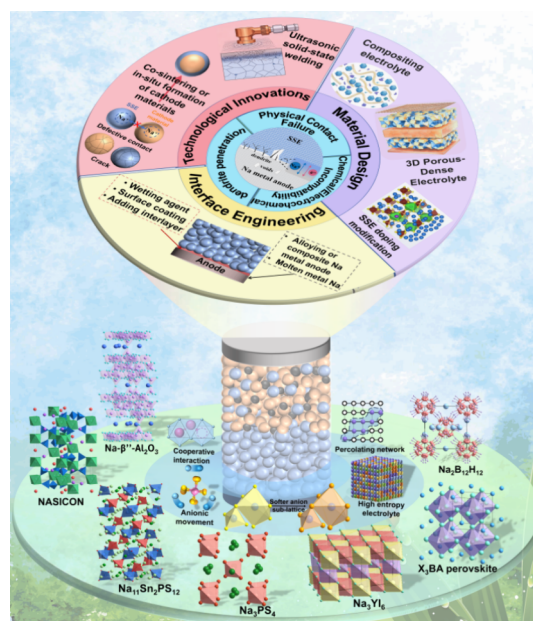


Figure 1. Schematic funnel diagram illustrating the convergence of material design and interface engineering to mitigate contact failure, chemical instability, and mechanical degradation in representative inorganic solid electrolytes for ASS-SMBs.

migration, local vibration, and rotational motion can all modulate the local energy landscape, particularly when their frequencies are comparable to those of the migrating Na⁺ ions.^{9,10} These mechanisms have been observed in systems containing dynamic anionic units such as [SbS₄]^{3−} and B_xH_y.^{11,12} Although the detailed coupling mechanisms remain under debate, dynamically active anionic frameworks represent a promising route for designing high-conductivity sodium solid electrolytes.⁹

Lattice Dynamics and Chemical Disorder

The migration-energy landscape of sodium ions is governed not only by crystal geometry but also by lattice dynamics and the nature of Na–anion interactions. In particular, softer anionic frameworks generally correlate with lower migration barriers and higher ionic conductivity because weaker and more deformable Na–anion bonding facilitates ion hopping.⁷ As shown in Figure 4a, highly polarizable anions can weaken Na–anion interactions and thereby reduce the energetic cost of migration. However, this effect is not universally beneficial, since excessive lattice softening may also lower the pre-exponential factor and offset gains in conductivity.⁸

Chemical disorder provides another important route for enhancing Na⁺ mobility. In highly ordered lattices, ion transport is often limited by an uneven site-energy landscape and restricted local dynamics.¹⁵ By contrast, disorder introduced through doping, mixed-anion substitution, or rotationally active frameworks can disrupt long-range order, broaden the distribution of accessible sites, and promote more favorable migration pathways (Figure 4b).¹³ More generally, disorder can flatten the local energy landscape and create networks of energetically similar neighboring sites, enabling percolative Na⁺ transport (Figure 4c–e). This idea is particularly relevant to high-entropy

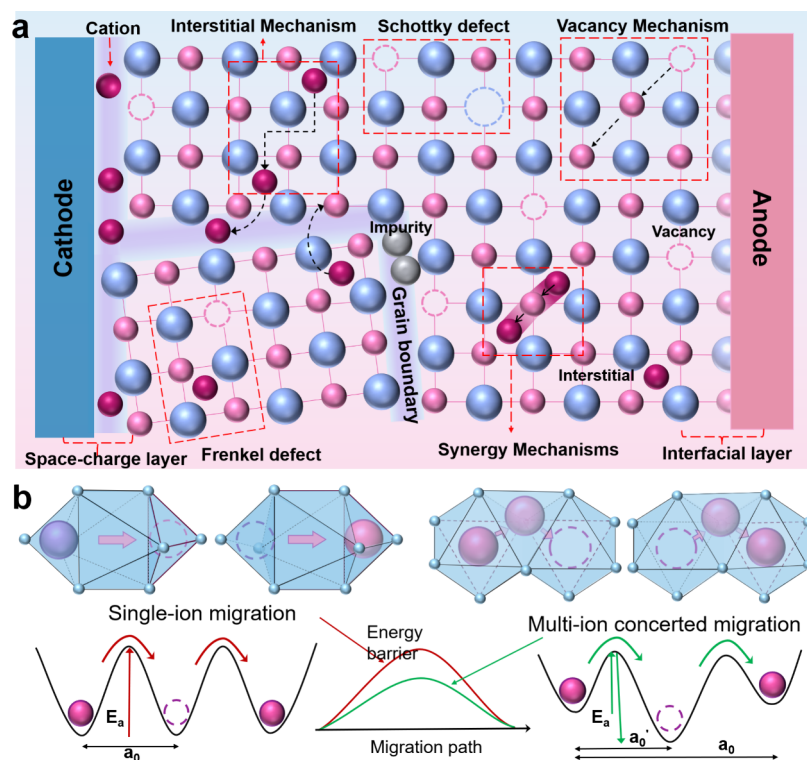


Figure 2. (a) Schematic illustration of point defects, Na^+ migration pathways, and grain and grain-boundary structures in solid electrolytes.⁸ Adapted with permission from ref 8. Copyright 2023 Royal Society of Chemistry. (b) Conceptual diagram of the energy barriers required for single-ion diffusion and concerted multi-ion migration.⁷ Adapted from ref 7. Available under a CC-BY 4.0. Copyright 2017 Springer Nature.

electrolytes, where multi-element substitution may enhance transport by increasing local distortion and site-energy overlap, although the underlying mechanisms remain insufficiently understood.¹⁴

FROM BULK TRANSPORT TO INTERFACIAL DEGRADATION

The performance of ASS-SMBs critically depends on the integrity of the electrode/electrolyte interface. However, interfacial degradation does not arise independently of the electrolyte bulk; rather, it reflects how bulk transport characteristics manifest once ion transport is subjected to interfacial and microstructural constraints.¹⁶ Defect chemistry determines the concentration and stability of mobile Na^+ carriers, while migration barriers govern the intrinsic resistance to ion hopping. These barriers are further modulated by lattice dynamics and chemical disorder, which together shape the local transport landscape.^{6,17} For example, in soft lattices, dynamic structural motions may transiently lower migration barriers and facilitate Na^+ transport, whereas chemical disorder can introduce spatial fluctuations in local transport kinetics. Consequently, even electrolytes with similar average ionic conductivities may exhibit markedly different degrees of transport heterogeneity. At the electrode–electrolyte interface, such heterogeneity can produce nonuniform Na^+ flux, local overpotential buildup, current focusing, and stress concentration, thereby accelerating pore formation, dendrite nucleation, and interfacial degradation.¹⁸ Thus, interfacial failure is closely connected

to the same structural and chemical descriptors that govern bulk Na^+ transport.

Space-Charge Layers and Transport Heterogeneity

For polycrystalline ceramic solid electrolytes, grain boundaries (GBs) are critical to both ionic transport and interfacial stability.¹⁹ Compared with the bulk, GBs often exhibit higher migration barriers and can also act as sites of local stress accumulation, thereby promoting mechanical degradation and, in some cases, facilitating sodium penetration and dendrite formation.²⁰ A common origin of this transport resistance is the formation of space-charge layers at GBs, where local charge imbalance alters the concentration of mobile Na^+ carriers and produces grain-boundary regions with reduced ionic conductivity.¹⁹ The carrier concentration within this layer significantly influences overall GB conductivity, which can be quantitatively expressed as:

$$\sigma_{\text{gb}} = \frac{C_b}{C_{\text{gb}}} \frac{L_b}{R_{\text{gb}} S} \quad (2)$$

where L_b is the electrode spacing, R_{gb} is the grain-boundary resistance, S is the electrode area, and C_b and C_{gb} are the bulk and GB capacitances, respectively.²¹

Importantly, the carrier concentration in the grain-boundary region, C_{gb} , is not independent of the bulk but is determined by the same defect-formation equilibria that govern the bulk carrier concentration, C_b . The space-charge potential, and thus C_{gb} ,

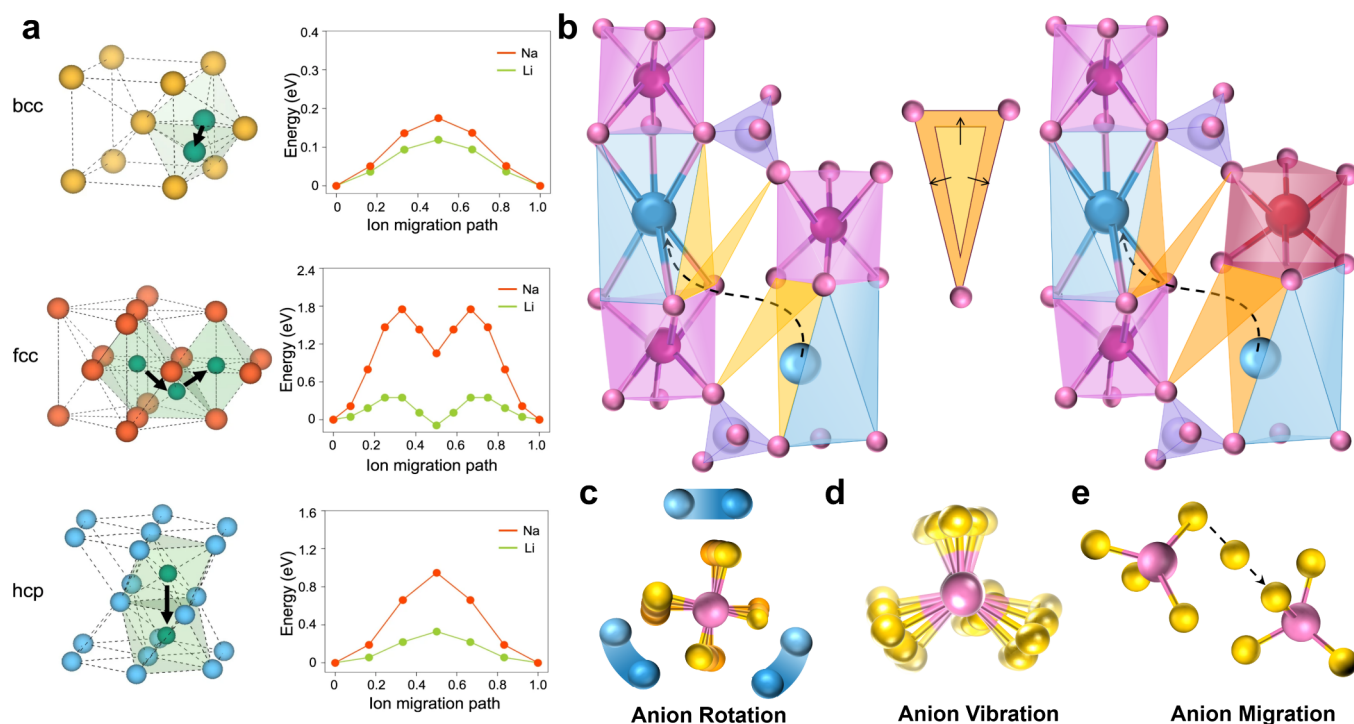


Figure 3. Schematic representation of the structural factors affecting sodium-ion migration. (a) Simulated diffusion paths (left) and corresponding energy profiles (right) of individual lithium and sodium ions migrating through different fixed anion sublattices: body-centered cubic (bcc) S^{2-} , face-centered cubic (fcc) O^{2-} , and hexagonal close-packed (hcp) Cl^- anion sublattices.² Reproduced from ref 2. Available under a CC-BY 4.0. Copyright 2023 Springer Nature. (b) Conceptual diagram showing the impact of bottleneck size on Na⁺ migration efficiency.⁸ Adapted with permission from ref 8. Copyright 2023 Royal Society of Chemistry. (c–e) Three representative modes of anionic group dynamics that can enhance Na⁺ mobility: (c) rotational motion, (d) local vibrational displacement, and (e) translational migration.⁹ Adapted with permission from ref 9. Copyright 2022 Royal Society of Chemistry.

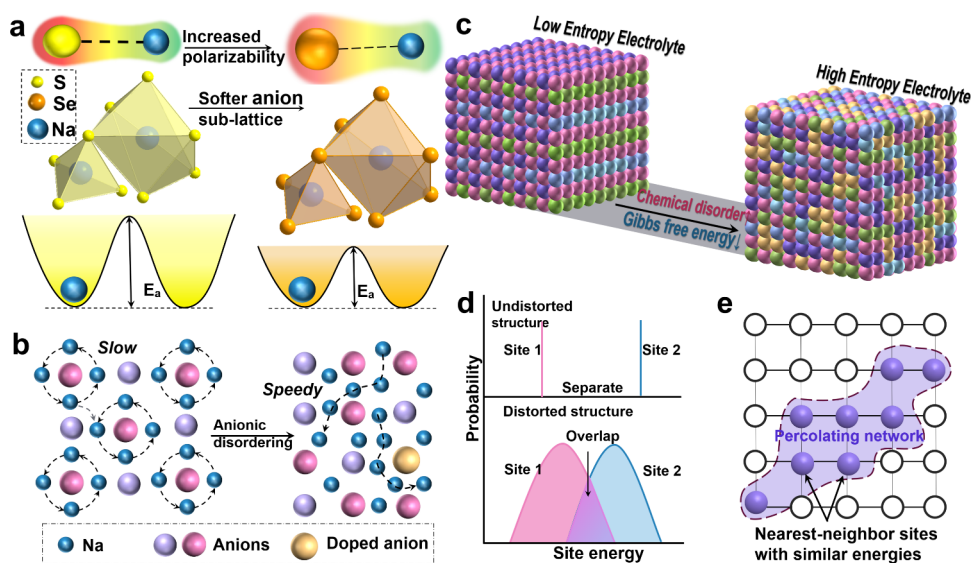


Figure 4. Schematic representation of the chemical factors affecting sodium-ion transport. (a) Increased anion polarizability weakens Na–anion interactions and lowers migration barriers. (b) Anion disorder disrupts long-range ordering and can facilitate ion transport.¹³ Adapted with permission from ref 13. Copyright 2024 Springer Nature. (c) High-entropy strategy introducing multiple cation species to enhance configurational entropy and induce local lattice distortions. (d) Local structural distortion leads to overlapping site energy levels, reducing energy barriers for ion hopping. (e) Formation of percolation pathways composed of energetically similar neighboring sites (purple circles), enabling fast and continuous Na⁺ ion migration.¹⁴ Reproduced with permission from ref 14. Copyright 2022 American Association for the Advancement of Science.

depends sensitively on the local defect chemistry.²¹ As a result, electrolytes with similar bulk conductivities can still display very different grain-boundary resistances if their defect chemistries respond differently to the broken periodicity at grain boundaries. High bulk ionic conductivity alone does not guarantee interfacial stability because local defect distributions and transport heterogeneity govern local Na⁺ accumulation and interfacial evolution.

This principle can be seen by comparing different material families. The overall influence of grain boundaries on Na⁺ transport in sulfide Na₃PS₄ is markedly smaller than in oxides. The tetragonal phase of Na₃PS₄ exhibits a total ionic conductivity of $3.39 \times 10^{-3} \text{ S cm}^{-1}$ at 25 °C, with grain-boundary contributions being nearly negligible compared to bulk transport.²² In contrast, in NASICON-type oxides, Na_xZr₂Si_xP_{3-x}O₁₂ typically exhibits a bulk Na⁺ conductivity of $5\text{--}6 \times 10^{-3} \text{ S cm}^{-1}$ at RT; however, the high formation energy of Na vacancies at grain boundaries creates a depletion layer that impedes ion transport in these regions, resulting in a final conductivity limited to approximately $0.1 \times 10^{-3} \text{ S cm}^{-1}$.²³ This comparison demonstrates that the same bulk transport descriptors could translate into very different grain-boundary behaviors depending on the local chemical environment and the nature of the space-charge layer. Bulk conductivity alone therefore cannot be used to predict low grain-boundary resistance or stable interfacial behavior.⁵

Pore Formation and Sodium Dendrites

Unlike liquid electrolytes, rigid solid–solid contacts in SSEs are prone to interfacial voids and contact loss, which hinder Na⁺ transport, increase impedance, and cause current constriction.¹⁸ On the cathode side, repeated Na⁺ insertion/extraction induces anisotropic lattice strain and localized stress. On the anode side, when stripping current exceeds Na vacancy diffusion in the metal, vacancies accumulate at the interface and coalesce into voids, raising local field and current density to promote dendrite growth.¹⁷

Importantly, the critical current density (CCD) is not an intrinsic material constant, but a practical parameter determined by the interfacial current distribution, which is itself strongly influenced by the bulk transport properties of the SSE. When the electrolyte exhibits anisotropic ionic conduction or heterogeneous grain-boundary transport, local chemical potential gradients become steeper, which lowers the practical CCD even when the average bulk conductivity remains high. Such transport heterogeneity can promote localized sodium deposition during plating and sodium depletion during stripping.²⁴ Once interfacial voids form, they further intensify the local electric field, creating a positive feedback loop that accelerates dendrite nucleation and growth. This mechanistic picture helps explain why SSEs with similar bulk conductivities can display markedly different dendrite tolerance: interfacial stability is governed not only by average conductivity but also by the spatial heterogeneity of ion transport.²⁵

Thermodynamic Instability and Transport-Induced Degradation

The degradation of the Na/SSE interface can arise from two fundamentally distinct origins, and distinguishing them is essential for rational electrolyte design. One is thermodynamic instability of SSEs, which is commonly discussed in terms of the electrochemical stability window (ESW) of the electrolyte.

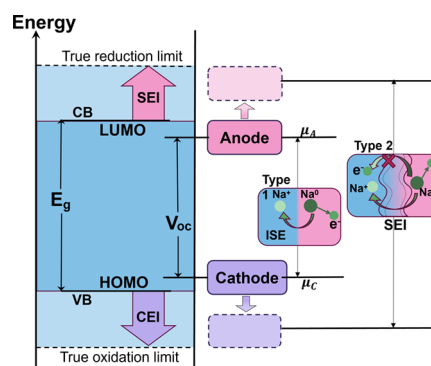


Figure 5. Schematic illustration of the ESW of solid electrolyte. μ_A and μ_C refer to the energy levels of the anode and cathode, respectively. LUMO and HOMO represent the lowest unoccupied and highest occupied molecular orbitals of the SE, respectively. V_{oc} refers to the open-circuit voltage of the cell. Type 1 corresponds to a thermodynamically stable interface, whereas Type 2 represents a kinetically stable interface.⁸ Adapted with permission from ref 8. Copyright 2023 Royal Society of Chemistry.

Schematically, this can be understood from alignment between the electrode chemical potentials (μ) and the electronic structure of the electrolyte, more generally represented by its reduction and oxidation limits.²⁶ The thermodynamically stable interface (Type 1, Figure 5) is expected when the anode chemical potential (μ_A) remains below the reduction limit of the SSE and the cathode chemical potential (μ_C) remains above its oxidation limit, thereby preventing spontaneous electron or hole transfer across the interface. Conversely, the kinetically stable interface (Type 2, Figure 5) occurs when either μ_A exceeds the reduction limit or μ_C falls below the oxidation limit; interfacial redox reactions become thermodynamically allowed. In such cases, the actual interfacial behavior depends strongly on the nature of the decomposition products. If the reaction products form an electronically insulating but ionically conducting solid-electrolyte interphase (SEI), further decomposition may be kinetically suppressed, and the interface can exhibit apparent stability under practical operating conditions.⁸ If they form a mixed ion-electron conducting (MIEC) layer, electrons continue to flow, and the reaction proceeds unchecked.²⁶

Reported ESW values should be interpreted with caution because the experimentally observed stability window can depend strongly on the measurement configuration rather than reflecting an absolute material constant.²⁶ Experimental studies show that measurement parameters strongly affect the apparent ESW of solid electrolytes. For Na₃PS₄, an inert working electrode like gold or stainless steel yields a broad 0–5 V window, but using sodium metal as the reference electrode at 0.1 mA cm⁻² causes rapid decomposition.²⁵ Cyclic voltammetry reveals that different scanning modes, working electrode materials, or two-electrode versus three-electrode configurations give different oxidation and reduction limits. A two-electrode setup often produces a wider window because it cannot clearly separate Faradaic currents from capacitive contributions.²⁷ For NASICON-type oxides, increasing the scan rate from 0.1 to 1 mV s⁻¹ in cyclic voltammetry causes a shift of several hundred millivolts in the observed anode decomposition onset point, as the faster scan rate exceeds the kinetic reaction rate of the decomposition products at the interface. Conversely, a slower scan rate ($\leq 0.01 \text{ mV s}^{-1}$) brings the conditions closer to

equilibrium and narrows the observation window as it approaches the thermodynamic limit.²⁷ These findings confirm that reported ESW values are not absolute material constants but condition-dependent parameters. Any reported stability metric must therefore be accompanied by a full description of the measurement conditions.²⁵

A second and fundamentally different origin of failure is transport-induced interfacial degradation, which does not necessarily require any chemical reaction between sodium and the electrolyte. Instead, it arises from spatially non-uniform ion transport, local current concentration, void formation, and dendrite propagation. In practice, interfacial stability is therefore governed by the coupled effects of chemical reactivity and transport heterogeneity.¹⁸ For example, even a thermodynamically unstable electrolyte may remain temporarily protected if it forms a passivating interphase that is both electronically blocking and mechanically intact. However, if transport heterogeneity generates localized current concentrations, the associated stress can fracture this interphase, expose fresh electrolyte, and reactivate interfacial decomposition.¹⁶ Conversely, an electrolyte with relatively transport uniformity may still fail if it is thermodynamically unstable and forms an MIEC interphase. Thus, the practical stability of an ASS-SMB emerges from the coupled evolution of chemical reactivity and transport heterogeneity.¹⁷

SOLID ELECTROLYTES

Oxide Solid Electrolytes: Na- β / β'' -Al₂O₃

Na- β / β'' -Al₂O₃ (BASE) is one of the classical sodium-ion solid electrolytes and remains an important oxide reference system for understanding the relationship between crystal structure, anisotropic transport, and interfacial stability.²⁸ As illustrated in Figure 6a, Na- β -Al₂O₃ adopts a hexagonal layered structure, whereas Na- β'' -Al₂O₃ has a rhombohedral framework with

larger conduction space and higher vacancy concentration, leading to much higher in-plane Na⁺ conductivity, reaching 0.2–0.4 S cm⁻¹ at RT.²⁹ However, the β'' phase is also more sensitive to moisture, thermal decomposition, and mechanical degradation, so practical systems often rely on β / β'' mixed phases to balance conductivity with processability.

Na⁺ transport in Na- β -Al₂O₃ proceeds within the conduction planes through an interstitial-pairing mechanism involving symmetry-related sites (Figure 6b).³⁰ Cation substitution can further tune the local charge environment and Na⁺ occupancy in these planes. In general, lower-valent dopants such as Li⁺ or Mg²⁺ can enhance conductivity by increasing Na⁺ population in the conduction layers, whereas excessive doping may induce phase segregation and degrade both conductivity and mechanical stability.³¹

Processing and mechanical constraints are also important for β -alumina electrolytes. Conventional solid-state sintering typically requires temperatures above 1600 °C, which can induce sodium volatilization, grain coarsening, and reduced β'' -phase content, whereas lower-temperature routes such as microwave-assisted synthesis and Spark plasma sintering (SPS) can improve densification control and reduce Na loss.^{6,32} At the same time, the intrinsic brittleness of β -alumina (fracture toughness $\sim$ 2–3 MPa m^{1/2}) makes it susceptible to microcracking under stack pressure, highlighting the importance of lower-temperature processing and mechanically toughened architectures for practical application.³

More broadly, studies on BASE in classical molten-Na battery systems also offer broader design principles that remain highly relevant to present-day solid-state sodium batteries. In particular, the practical performance of β'' -alumina is strongly influenced not only by its intrinsic Na⁺ conductivity but also by sodium wetting, interfacial contact retention, and the mechanical response of the Na/electrolyte interface. Earlier

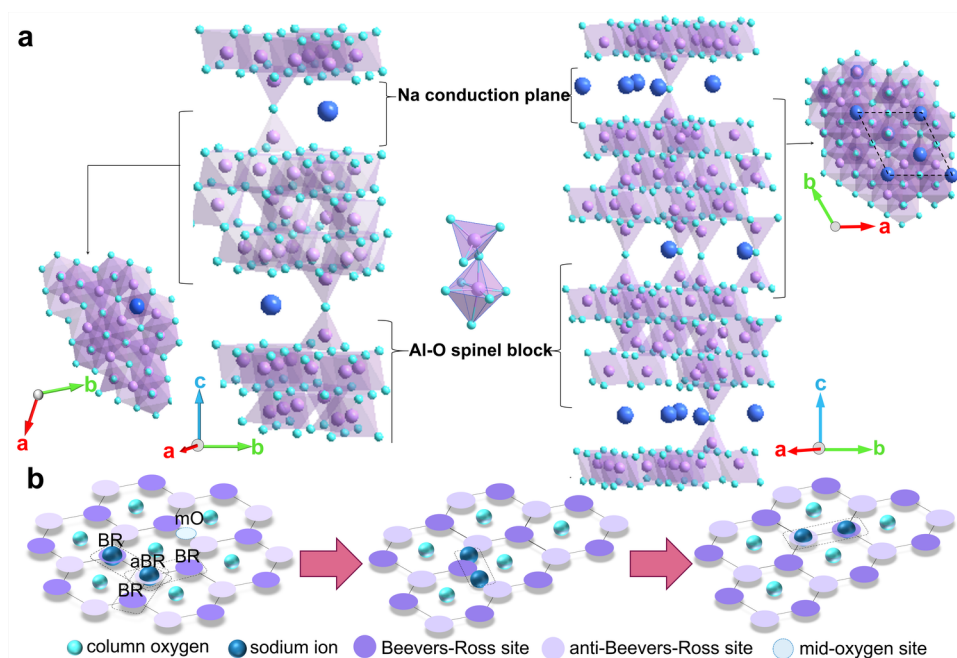


Figure 6. (a) Crystal structures of Na- β -Al₂O₃ (left) and Na- β'' -Al₂O₃ (right). (b) Schematic illustration of Na⁺ migration within the conduction planes.³⁰ Adapted with permission from ref 30. Copyright 1979 Elsevier.

studies on Na–S, ZEBRA, and related BASE-based systems showed that insufficient Na wetting at reduced temperature readily increases interfacial resistance and promotes contact failure, whereas improved sodiophilicity can markedly lower the contact barrier and extend stable cycling.³³ More recent interface-engineering studies further show that wetting-promoting interlayers, elastic interfacial architectures, and locally deformable contact phases can suppress void formation, homogenize Na⁺ flux, and improve tolerance against dendritic growth.³⁴ These observations indicate that, even for a classical oxide electrolyte such as β -alumina, practical interfacial stability is governed not by bulk conductivity alone but by the coupled effects of transport uniformity, sodium affinity, contact mechanics, and interphase evolution. In this respect, β -alumina provides a useful bridge between traditional molten-Na batteries and modern solid-state sodium systems and highlights design principles that are also relevant to NASICON, sulfide, and halide electrolytes.

Oxide Solid Electrolytes: NASICON Electrolytes

In contrast to the two-dimensional Na⁺ conduction in β -alumina, NASICON (Na Super Ionic Conductor) offers a highly efficient three-dimensional ion transport network. NASICON-type electrolytes with the general formula $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ (NZSP) consist of corner-sharing ZrO_6 octahedra and $(\text{Si}, \text{P})\text{O}_4$ tetrahedra, forming interconnected migration channels for fast Na⁺ transport. Depending on Na content, Si/P ratio, and temperature, NZSP can adopt rhombohedral or monoclinic polymorphs (Figure 7a). The rhombohedral phase ($R\bar{3}c$) is generally stabilized at low ($x < 2.8$) and high ($x > 3.2$) Na contents, whereas the monoclinic phase is favored at intermediate compositions ($2.8 < x < 3.2$) at RT.³⁸ In the rhombohedral structure, Na⁺ occupies crystallographically distinct Na sites, including Na1 sites with antiprismatic oxygen coordination and Na2 sites with more distorted coordination environments involving both ZrO_6 and XO_4 units.³⁹ Increasing Na content and Si substitution redistribute Na⁺ among these sites and can induce Na-site splitting during the monoclinic transformation, thereby modifying the topology of the Na⁺ migration network.³⁵

From a transport perspective, the ionic conductivity of NASICON is primarily governed by several coupled descriptors, including the Na⁺/vacancy ratio, Na-site connectivity, oxygen bottleneck geometry, and the migration-barrier landscape. An optimal balance between mobile Na⁺ carriers and vacant sites is required because excessive vacancies reduce carrier concentration, whereas excessive Na⁺ occupancy can increase electrostatic repulsion and hinder long-range diffusion. Near the optimized NZSP composition, the Na⁺ energy landscape becomes flatter, enabling lower-barrier migration.³⁹ In addition to isolated single-ion hopping, cooperative Na⁺ migration can further reduce the effective activation barrier when local Na⁺ configurations and vacancy distributions are favorable (Figure 7b,c).³⁵ The triangular oxygen bottlenecks formed between ZrO_6 octahedra and PO_4/SiO_4 tetrahedra are therefore critical structural descriptors because their size and distortion directly regulate Na⁺ mobility.³⁶

Compositional regulation is a primary strategy for optimizing bulk Na⁺ transport in NASICON electrolytes. Aliovalent doping can regulate the Na⁺/vacancy ratio and carrier concentration (Figure 7e), while isovalent or multivalent substitution can modify bottleneck geometry and facilitate Na⁺ migration

(Figure 7d).^{36,37} These effects indicate that the conductivity enhancement in NASICON-type electrolytes is not governed by carrier concentration alone but by the coupled optimization of Na⁺ occupancy, vacancy availability, bottleneck geometry, and local framework flexibility.

Processing and microstructural control constitute a separate but equally important requirement for translating favorable bulk transport into practical cell performance. Recent reviews and interface-focused studies show that the practical behavior of NZSP cannot be understood from bulk conductivity alone, but must be considered in terms of the coupled effects of defect chemistry, grain-boundary composition, microstructure, and Na-metal interfacial stability.^{18,40} Processing-induced heterogeneity, including Na/P volatilization, secondary phases, grain-boundary segregation, pore formation, and surface contamination, can substantially alter both effective Na⁺ transport and local interfacial chemistry.^{19,41} Consequently, NZSP electrolytes with similar nominal bulk conductivities may still exhibit markedly different Na wettability, interfacial resistance, critical current density, and metal-filament tolerance. Recent studies further show that regulating composition, Na–O affinity, grain-boundary chemistry, or biphasic microstructure can improve bulk transport while stabilizing the Na/NZSP interface.^{41–44}

These processing-related challenges are further coupled with the intrinsic mechanical and densification characteristics of NASICON electrolytes. NASICON has moderate moduli (56–96 GPa) but low fracture toughness (1–1.5 MPa m^{1/2}), making it prone to microcracks and grain-boundary defects.⁴⁵ Their densification is also strongly processing-dependent: conventional sintering above 1200 °C can achieve 96–98% relative density but often at the cost of sodium volatilization and secondary-phase formation, whereas cold sintering at 350–375 °C under ≈ 360 MPa offers a lower-temperature route.⁴⁶ Therefore, practical NASICON processing must balance densification, secondary-phase control, grain-boundary chemistry, mechanical integrity, and stack-pressure management.

Sulfide Solid-State Electrolytes: Na_3PS_4

Na_3PS_4 is the prototypical sodium thiophosphate electrolyte and serves as a foundational platform for understanding the transport chemistry of sulfide solid electrolytes. As shown in Figure 8a, it is built from isolated $[\text{PS}_4]^{3-}$ tetrahedra and can adopt tetragonal, cubic, and orthorhombic polymorphs depending on temperature. In general, the higher-symmetry cubic and high-temperature phases exhibit greater Na⁺ disorder and better ionic transport than the low-temperature tetragonal phase, making Na_3PS_4 a representative example of how structural flexibility and phase evolution influence conductivity in sulfide electrolytes. The low-temperature tetragonal α -phase shows poor ionic conductivity (4.17×10^{-6} S cm⁻¹ at 50 °C) because its Na⁺ migration pathways are relatively discontinuous.⁴⁷ Upon heating above 261 °C, it transforms into the cubic β -phase, where lattice expansion and Na-site displacement promote higher Na⁺ mobility and raise the RT conductivity to $\sim 2 \times 10^{-4}$ S cm⁻¹.⁴⁸ At still higher temperatures (> 500 °C), the orthorhombic γ -phase exhibits further unit-cell expansion, stronger $[\text{PS}_4]^{3-}$ tetrahedral dynamics, and greater Na⁺ disorder, resulting in an additional increase in conductivity, from $\sim 40 \times 10^{-3}$ to $\sim 400 \times 10^{-3}$ S cm⁻¹.⁴⁹

The transport behavior of Na_3PS_4 is closely associated with the soft thiophosphate lattice, defect chemistry, and anion

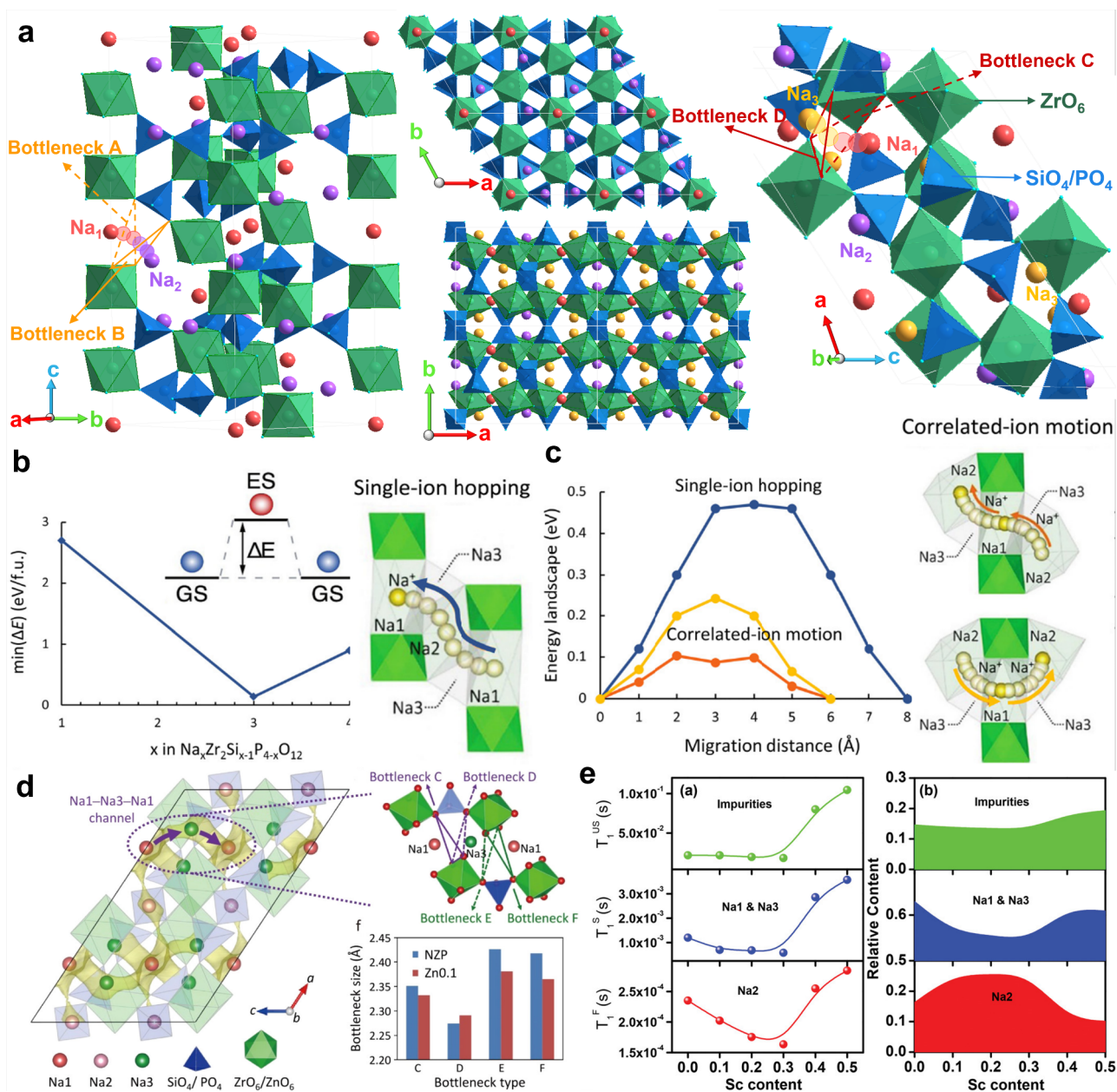


Figure 7. (a) Crystal structures of NZSP illustrating the rhombohedral phase and the monoclinic phase, with Na⁺ conduction channels embedded within the 3D MO₆-XO₄ framework. (b, c) Schematic illustrations of the optimal Na⁺/vacancy ratio and cooperative Na⁺ migration in NASICON.³⁵ Reproduced with permission from ref 35. Copyright 2020 Wiley-VCH. (d, e) Representative analyses of bottleneck geometry and Na-site evolution in composition-modified NASICON electrolytes.^{36,37} (d) Reproduced with permission from ref 36. Copyright 2020 American Chemical Society. (e) Reproduced with permission from ref 37. Copyright 2021 Wiley-VCH.

dynamics. Compared with oxide frameworks, the weaker Na–S interactions and higher polarizability of sulfide anions create a softer energy landscape that facilitates Na⁺ migration and reduces the transport penalty at grain boundaries.⁴⁹ In addition, vacancy formation and local structural disorder can markedly enhance conductivity by activating long-range hopping pathways, while soft-mode vibrations and tetrahedral motions further lower migration barriers (Figure 8b,c).⁵¹ Representative studies also show that aliovalent or isovalent substitution can improve Na₃PS₄ by tuning vacancy concentration, local

symmetry, and bottleneck geometry, although the detailed effect depends strongly on dopant chemistry and defect distribution.⁵⁰

Compositional substitution provides an effective route to tune these descriptors. Heterovalent cation substitution (e.g., Ca²⁺) introduces Na vacancies and stabilizes the conductive cubic phase (Figure 8d); tetravalent substitution at P⁵⁺ sites (Sn⁴⁺, Ge⁴⁺, etc.) widens diffusion channels.^{52,54} Anion substitution provides another effective route: replacing S²⁻ with halides lowers the migration barrier while largely preserving the host framework, and Cl-doped Na_{3-y}PS_{4-x}Cl_x reaches

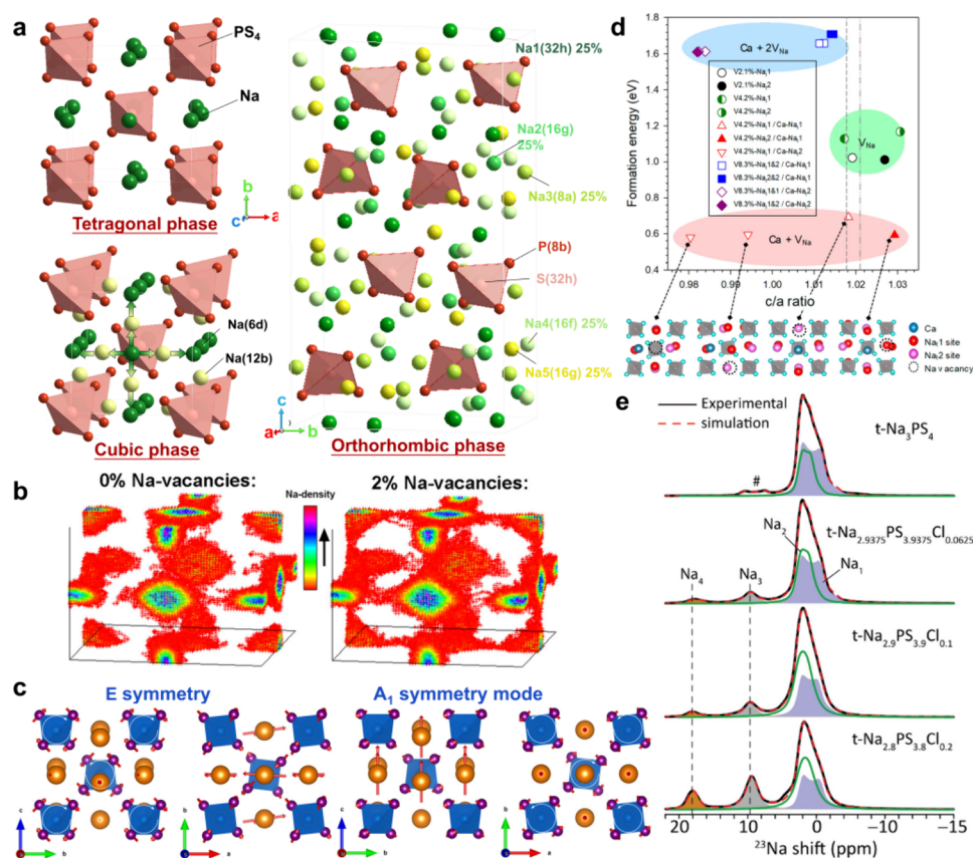


Figure 8. (a) Tetragonal, cubic, and orthorhombic polymorphs. (b) MD-simulated Na^+ distributions in pristine and vacancy-containing Na_3PS_4 .⁵⁰ Reproduced with permission from ref 50. Copyright 2016 American Chemical Society. (c) DFT-calculated soft modes related to Na^+ migration and tetrahedral tilting.⁵¹ Reproduced from ref 51. Available under a CC-BY 4.0. Copyright 2022 American Chemical Society. (d) Formation energy as a function of c/a ratio, Ca doping, and Na-vacancy concentration.⁵² Reproduced with permission from ref 52. Copyright 2018 American Chemical Society. (e) ^{23}Na solid-state MAS NMR analysis of defect evolution in $\text{t-Na}_{3-x}\text{PS}_{4-x}\text{Cl}_x$ ($x = 0, 0.0625, 0.1, \text{ and } 0.2$) electrolytes.⁵³ Reproduced with permission from ref 53. Copyright 2019 Wiley-VCH.

conductivities of $1.96 \times 10^{-3} \text{ S cm}^{-1}$, consistent with the emergence of highly mobile Na sites revealed by ^{23}Na solid-state NMR (Figure 8e).⁵³ Softer isovalent units (Sb^{5+} , Se^{2-}) further enlarge bottlenecks and lower activation energies.^{6,55}

However, the same descriptors that promote fast Na^+ transport also introduce stability constraints. In Na_3PS_4 , the soft and highly polarizable thiophosphate framework facilitates Na^+ transport, but it also increases sensitivity to air/moisture exposure and can promote interfacial reactions with metallic sodium and oxide cathodes.⁴⁹ Therefore, Na_3PS_4 illustrates an important feature of sulfide SSEs: high conductivity is often achieved through soft bonding, high anion polarizability, and defect disorder, but these features must be balanced against environmental tolerance and interfacial stability.

Sulfide Solid-State Electrolytes: $\text{Na}_{10}\text{MP}_2\text{S}_{12}/\text{Na}_{11}\text{M}_2\text{PS}_{12}$ ($\text{M} = \text{Ge}, \text{Sn}, \text{Si}$)

The $\text{Na}_{10}\text{GeP}_2\text{S}_{12}/\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ family represents a high-conductivity class of sulfide electrolytes with three-dimensional diffusion networks. Compared with simpler thiophosphate frameworks, these materials provide more highly connected Na^+ pathways and can achieve substantially higher ionic conductivity, making them important model systems for understanding fast Na^+ transport in sodium sulfides.⁵⁸

In $\text{Na}_{10}\text{MP}_2\text{S}_{12}$, alternating MS_4 and PS_4 tetrahedra generate a three-dimensional Na^+ diffusion network (Figure 9a). Partially occupied Na1 and Na3 tetrahedral sites form chain-like channels along the c -axis, while vacancy-containing regions and distorted Na coordination environments provide interchain connections.⁵⁶ Molecular dynamics simulations indicate that Na^+ transport is primarily facilitated by cooperative migration along the Na1/Na3 chains, together with interchain hopping through these cross-linked vacancy-containing regions. This structural topology highlights the importance of partial site occupancy, vacancy distribution, and cross-linked channel connectivity in enabling long-range Na^+ transport.

Increasing the Sn:P ratio from 1:2 to 2:1 produces the distinct tetragonal phase $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ ($I4_1/acd$, Figure 9b). In this structure, Na^+ ions occupy five octahedral sites, with partial vacancy at the Na1 and Na2 sites, forming critical cross-links within a highly connected three-dimensional migration network. These partially vacant sites connect diffusion pathways along both the c -axis (Na4–Na1–Na3–Na1) and the ab -plane (Na4–Na2–Na4), supporting long-range Na^+ transport (Figure 9c). In addition, the Na6 gap site provides an auxiliary pathway between Na1 and Na2, further increasing the connectivity of the migration network and enhancing vacancy-assisted transport (Figure 9d).⁵⁷

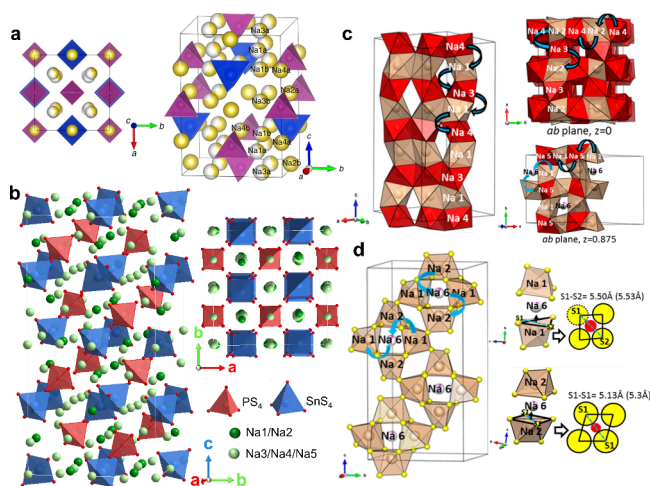


Figure 9. (a, b) Crystal structure of $\text{Na}_{10}\text{SnP}_2\text{S}_{12}$ and distribution of Na sites.⁵⁶ Reproduced from ref 56. Available under a CC-BY 4.0. Copyright 2016 Springer Nature. (c) View of the Na^+ ion diffusion channel of $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ along the c -axis, $z = 0$ and $z = 0.87$ in the ab -plane. (d) Auxiliary channel of Na6 at the interstitial site of $\text{Na}_{11}\text{Sn}_2\text{PS}_{12}$ with its coordination environment and bottleneck size.⁵⁷ Reproduced with permission from ref 57. Copyright 2018 American Chemical Society.

The transport behavior of this family is governed by polyanion chemistry, anion softness, Na-site connectivity, vacancy distribution, and cooperative migration. Dynamic rotational motion of $[\text{PS}_4]^{3-}$ tetrahedra can transiently enlarge local pore size and promote Na^+ mobility,¹¹ while $\text{Na}_{11}\text{Sn}_2\text{PSe}_{12}$ achieves $2.15 \times 10^{-3} \text{ S cm}^{-1}$ at RT when Na vacancies are distributed more uniformly over six sites.⁵⁹ Similarly, Sn^{4+} or Ge^{4+} substitution in $\text{Na}_{11+x}\text{Sn}_2\text{P}_{1-x}\text{M}_x\text{S}_{12}$ expands the lattice and lowers the migration barrier, with Sn substitution producing the more pronounced effect.⁶⁰ These results show that conductivity optimization cannot be guided by a simple compositional rule but requires coordinated tuning of polyanion electronegativity, bonding character, anion size, vacancy distribution, and channel geometry.

More broadly, sulfide electrolytes illustrate a descriptor-level design constraint for inorganic SSEs. The same soft, highly polarizable, and defect-tolerant frameworks that flatten the Na^+ migration energy landscape and enable room-temperature densification can also narrow the stability margin against moisture, Na metal, and mechanical loading. As a result, high bulk ionic conductivity does not necessarily translate into stable ASS-SMB operation. For example, $\text{Na}_{11}\text{Sn}_2\text{PSe}_{12}$ exhibits high RT conductivity but undergoes reductive decomposition against Na metal to form Sn and Na_2Se .⁵⁹ The low elastic modulus of sulfide electrolytes, typically approximately 20–30 GPa, also facilitates densification by uniaxial cold pressing without high-temperature sintering,¹⁸ but this mechanical softness increases susceptibility to creep deformation and pressure-induced short circuiting under excessive stack pressure.⁶¹ Their low fracture tolerance further makes practical processing sensitive to macroscopic defects and particle agglomeration, requiring powder uniformity and phase purity.⁵⁵ Therefore, sulfide SSE design should not aim solely at maximizing ionic conductivity. Instead, lattice

softness, anion polarizability, defect chemistry, environmental tolerance, mechanical reliability, and Na-metal interfacial stability should be treated as coupled descriptors and optimized within the same design space.

Halide Electrolytes

Halide solid electrolytes are of growing interest in ASS-SMBs because they combine relatively favorable oxidative stability with potential compatibility with high-voltage cathodes. Compared with sulfides and oxides, halide anions (Cl^- , Br^- , I^-) generally provide weaker Coulombic interactions with Na^+ and can support more open migration frameworks, making them promising candidates for cathode-side solid electrolytes.¹⁵ These materials generally follow the formula Na_nMX_m (M = transition/rare-earth metal; X = halogen), and their crystal structures are jointly determined by the identity and size of M^{3+} and X^- ions.⁶² In the representative Na_3MX_6 family, phase stability and Na^+ migration topology are mainly governed by the ionic-radius ratios t_{AX} and t_{MX} (Figure 10b).¹⁵

For Na_3MCl_6 , the preferred phase (Figure 10d) evolves systematically with the radius of M^{3+} : small cations such as Cr^{3+} favor the trigonal $P\bar{3}1c$ phase, large cations such as Y^{3+} and most lanthanides stabilize the trigonal $R\bar{3}$ phase, and intermediate-sized cations such as Sc^{3+} and Yb^{3+} tend toward the monoclinic $P2_1/n$ phase.⁶⁴ In Na_3MBr_6 , the larger Br^- radius lowers the $t_{\text{AX}}/t_{\text{MX}}$ ratio, broadens the stability range of the $R\bar{3}$ phase, and also enables smaller M^{3+} ions to remain stable in the $P\bar{3}1c$ phase.¹⁵

Na^+ transport in these halides is highly structure-sensitive. In the trigonal $P\bar{3}1c$ phase, represented by Na_3CrCl_6 , Na^+ migrates from Na1 to Na2 through intermediate octahedral and tetrahedral interstitial sites (Figure 10a), with activation energies of ~ 0.34 – 0.41 eV.^{63,64} In the trigonal $R\bar{3}$ and $R\bar{3}$ phases, migration along the c -axis can proceed directly through octahedral–octahedral pathways, whereas diffusion in the ab plane requires an octahedral–tetrahedral–octahedral process; because tetrahedral interstitial sites are destabilized by repulsion from surrounding MX_6 octahedra, c -axis transport is generally more favorable, and the migration barriers are correspondingly lower (Figure 10c).⁶³ By contrast, the monoclinic $P2_1/n$ phase, exemplified by Na_3ErCl_6 , supports three-dimensional diffusion but typically exhibits higher barriers of ~ 0.49 – 0.60 eV.⁶⁴ For iodides, Na_3MI_6 usually adopts the monoclinic C_2/m phase (Figure 10b), in which Na^+ migration mainly follows octahedral–tetrahedral–octahedral pathways.

The mechanical and processing behavior of halide electrolytes depends strongly on their phase state and crystal structure. Crystalline halides such as Na_3YCl_6 exhibit relatively low and anisotropic Young's moduli (18.36–27.02 GPa) and can undergo stress-induced phase transformation under compression, accompanied by $\sim 3.4\%$ volume expansion.⁶⁵ By contrast, amorphous halides offer distinct processing advantages: their grain-boundary-free structure and viscoelastic response enable plastic flow and cold densification, while in some cases also improving ionic transport.⁶⁶ These results show that, for halide electrolytes, practical performance depends not only on transport and oxidative stability but also on how phase state and synthesis route determine deformability and densification behavior.

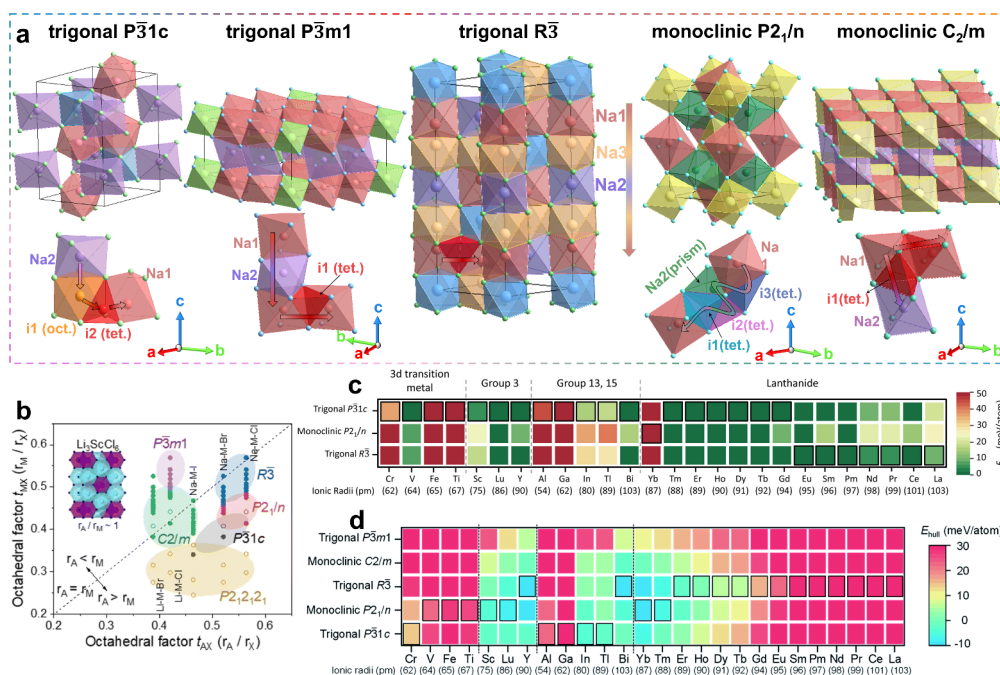


Figure 10. (a) Typical crystal structures and Na⁺ migration motifs in Na-based halides. (b) Octahedral coefficients used to predict preferred structure types in Na halides.¹⁵ Reproduced with permission from ref 15. Copyright 2022 Royal Society of Chemistry. (c, d) Convex-hull thermograms illustrating the preferred stabilizing phases of Na₃MBr₆ and Na₃MI₆, respectively.^{63,64} (c) Reproduced with permission from ref 63. Copyright 2022 American Chemical Society. (d) Reproduced with permission from ref 64. Copyright 2021 Royal Society of Chemistry.

Anti-Perovskite Electrolytes

Anti-perovskite solid electrolytes (X₃BA; X = cation, A, B = anions) have emerged as a structurally versatile platform following the discovery of high Li⁺ conductivity in Li₃OCl (>1 × 10^{−3} S cm^{−1} at RT).⁶⁷ Both perovskites and anti-perovskites adopt cubic frameworks (space group *Pm* 3̄ *m*), although distortions can occur depending on composition and thermodynamic conditions. For Na-based anti-perovskites, cubic-phase stability is evaluated using a modified tolerance factor $t = (r_{\text{B}} + r_{\text{Na}})/\sqrt{2}(r_{\text{A}} + r_{\text{Na}})$, with cubic symmetry generally stabilized within $t = 0.8$ – 1 .⁶⁸ In contrast to ABX₃ perovskites, anti-perovskites feature an inverted coordination environment in which the B anion occupies the octahedral center, Na⁺ resides at the vertices, and the A anion is located at the face centers, giving rise to distinct electrostatic landscapes and transport pathways (Figure 11a).

Na⁺ transport in anti-perovskites is predominantly vacancy-mediated (Figure 11b), typically associated with Schottky defect pairs (e.g., V_{Na}–V_{Cl}), while Frenkel defects contribute only at high defect concentrations.⁶⁹ Migration occurs through triangular bottlenecks formed by two B-site and one A-site anions (Figure 11d), making the activation barrier highly sensitive to bottleneck geometry and local electrostatic interactions. Beyond 3D cubic frameworks, layered Ruddlesden–Popper (RP)-type anti-perovskites introduce anisotropic transport (Figure 11c), where in-plane Na⁺ migration proceeds via vacancy hopping, whereas cross-layer diffusion requires gap-assisted migration regulated by anion polarization.⁷⁰

The intrinsically low conductivity of sodium anti-perovskites originates from limited mobile-carrier concentration and high native defect-formation energies, necessitating deliberate defect

engineering. Aliovalent doping and non-stoichiometric design can effectively introduce Na vacancies (Figure 11e(i)). For example, Mg²⁺ or Ca²⁺ doping in Na₃OCl generates mobile vacancies with relatively low dopant–vacancy binding energies (~0.25 eV), whereas trivalent dopants (e.g., Al³⁺) tend to form immobile vacancy clusters that hinder transport.⁷⁴ Similarly, anion substitution (e.g., Cl[−]/Br[−]/I[−]) can simultaneously tune vacancy concentration and lattice parameters, although excessive substitution may induce secondary phases or thermal instability.⁶⁹ Optimized co-doping strategies, such as Na_{2.9}Sr_{0.05}OBr_{0.6}I_{0.4}, demonstrate the importance of balancing defect concentration and structural stability, achieving conductivities above 10^{−2} S cm^{−1} at 200 °C (Figure 11e(ii)).⁷¹

Beyond defect concentration, lattice dynamics and bottleneck geometry are key descriptors of Na⁺ transport. Increasing anion size and polarizability expands diffusion bottlenecks and softens the lattice, thereby lowering migration barriers (Figure 11fg).^{72,73} For example, I[−] or S^{2−} substitution enlarges the triangular bottleneck and reduces activation energy, while hydride-based systems benefit from highly polarizable H[−]-induced lattice softening, achieving conductivities up to 1.0 × 10^{−3} S cm^{−1}.⁷² Cluster-based anti-perovskites further introduce a “paddle-wheel” mechanism, in which rotational disorder of anionic groups (e.g., [BH₄][−], [BF₄][−]) dynamically reshapes migration pathways and reduces energy barriers, with activation energies as low as ~0.2 eV predicted in stabilized phases (Figure 11h).¹⁰ However, excessive cluster size or disorder can destabilize the lattice and increase migration barriers, highlighting the need to balance rotational freedom and structural integrity.⁷⁵

Anti-perovskites offer an attractive low-temperature processing advantage because they can, in principle, be densified by melt casting at relatively low temperatures (~300 °C), rather than by

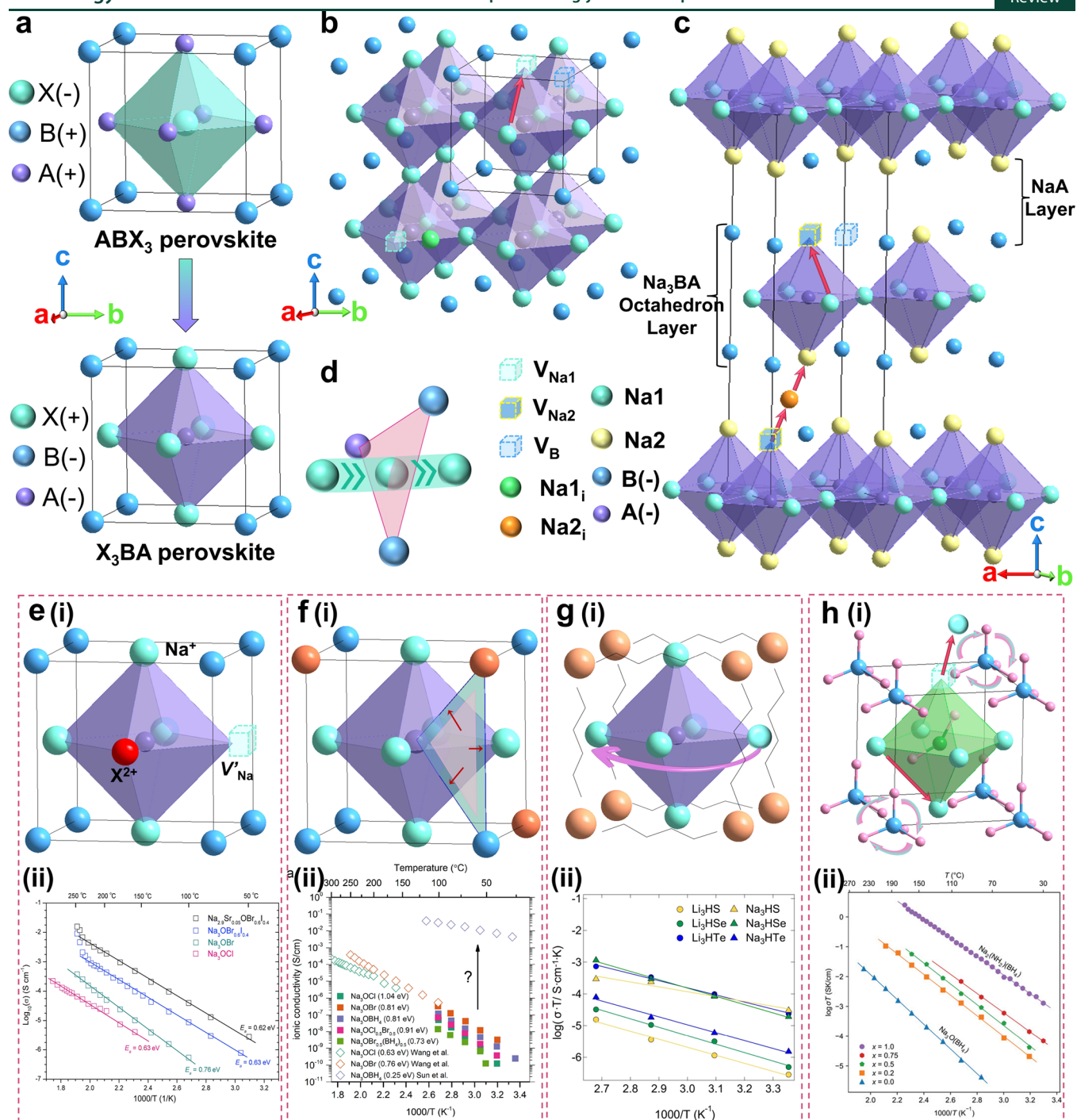


Figure 11. (a) Schematic structure of chalcocite and anti-perovskite, where “+” denotes cations and “−” denotes anions. (b) Schematic of the 3D structure of X_3BA anti-perovskite and the ion transport mechanism. (c) Schematic diagram of the 2D layered structure of Ruddlesden–Popper (RP) phase Na_4BA_2 anti-perovskite and the ion transport mechanism. (d) Schematic diagram of Na^+ ion transport through the A–B–A triangular bottleneck. (e) High-valent cation doping: (i) schematic of the doping mechanism; (ii) Arrhenius plots of anti-perovskite SSEs synergistically modulated by halogen-ion size difference and Sr^{2+} heterovalent doping.⁷¹ Reproduced with permission from ref 71. Copyright 2015 Elsevier. (f) Mixed-anion regulation of ion-channel bottlenecks: (i) schematic of anion mixing effects on channel structure; (ii) ionic conductivity and activation energy as functions of A-site anion radius in several anti-perovskite SSEs.⁷² Reproduced with permission from ref 72. Copyright 2020 Elsevier. (g) Lattice softening via highly polarizable anions: (i) schematic of the lattice softening mechanism; (ii) Arrhenius plots of anti-perovskite hydride SSEs with different structures.⁷³ Reproduced from ref 73. Available under a CC-BY 4.0. Copyright 2021 Springer Nature. (h) Cluster rotation coupled with Na^+ migration: (i) schematic of the coupling process; (ii) ionic conductivity of $Na_{3-x}O_{1-x}(NH_2)_x(BH_4)$ as a function of Na^+ vacancy and $[NH_2]^-$ cluster concentration at various temperatures.¹⁰ Reproduced with permission from ref 10. Copyright 2022 Wiley-VCH.

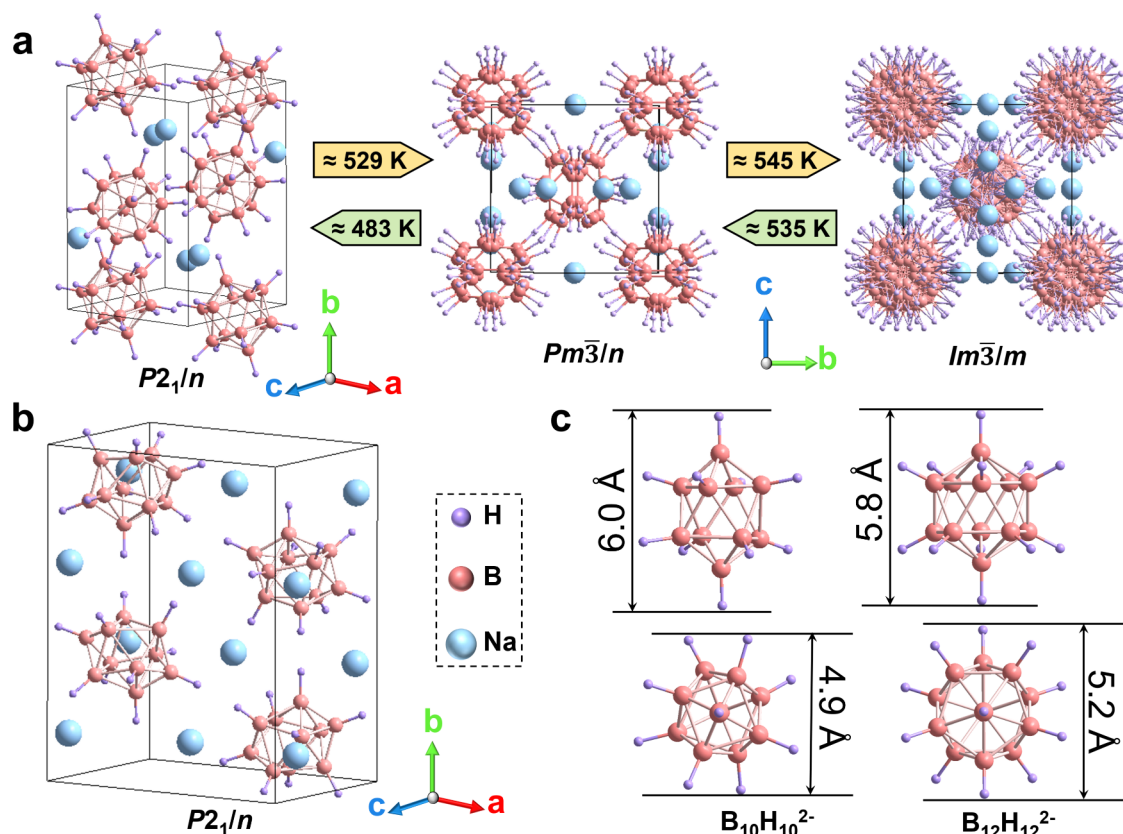


Figure 12. (a) Schematic representation of the structure of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ at RT and of the structure undergoing a phase transition at elevated temperatures, with a gradual increase in the number of sites that Na^+ may occupy and the degree of anionic reorientation disorder; (b) schematic representation of the structure of $\text{Na}_2\text{B}_{10}\text{H}_{10}$ at RT; (c) geometry of the $[\text{B}_{10}\text{H}_{10}]^{2-}$ and $[\text{B}_{12}\text{H}_{12}]^{2-}$ anions in side and top views and the corresponding sizes.⁷⁷ Adapted with permission from ref 77. Copyright 2014 Wiley-VCH.

high-temperature ceramic sintering. Their elastic properties are also compositionally tunable; for example, Na_3OCl and Li_3OBr exhibit Young's moduli of 60.2 and 92.8 GPa, respectively, indicating that larger ions can reduce the elastic modulus.⁷⁶ However, grain boundaries are likely to remain a critical weakness, as they can introduce both transport barriers and local mechanical softening, leading to effective conductivities substantially below those of the grains.²⁰ Practical development of sodium anti-perovskites will therefore require low-temperature densification, strict moisture control, and grain-boundary engineering to stabilize both transport and mechanical response.

Complex Hydrides

Composite hydride SSEs, composed of metal cations (e.g., Na^+ , Li^+) and complex anions (e.g., $[\text{BH}_4]^-$, $[\text{B}_{10}\text{H}_{10}]^{2-}$, $[\text{B}_{12}\text{H}_{12}]^{2-}$, etc.), have garnered attention owing to their wide electrochemical windows, high thermal stability, and mechanical softness. However, their cage-like anionic frameworks often impose strong steric constraints, leading to high Na^+ migration barriers and limited ionic conductivity at RT. Typical examples include $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}$, whose structures and anion geometries are illustrated in Figure 12a–c.

$\text{Na}_2\text{B}_{12}\text{H}_{12}$ adopts a monoclinic crystal structure ($P2_1/n$) at RT, where icosahedral $[\text{B}_{12}\text{H}_{12}]^{2-}$ anions form a relatively rigid framework with Na^+ occupying tetrahedral sites (Figure 12a). Upon heating, $\text{Na}_2\text{B}_{12}\text{H}_{12}$ undergoes a first-order phase transition to a partially ordered $Pm\bar{3}n$ symmetric structure

($\sim 256\text{ }^\circ\text{C}$) and fully disordered cubic phases ($Im\bar{3}m$, $>387\text{ }^\circ\text{C}$), accompanied by increased Na-site disorder and reduced site occupancy.⁷⁸ This transition dramatically enhances anion reorientation dynamics, with hopping rates increasing by nearly two orders of magnitude, as revealed by ^1H NMR and neutron scattering.⁷⁹ The resulting orientational disorder, coupled with increased vacancy availability, broadens migration pathways and enables superionic conduction. A similar mechanism operates in another typical closed borohydride, $\text{Na}_2\text{B}_{10}\text{H}_{10}$, which transforms to a disordered fcc phase at a lower temperature ($\sim 360\text{ K}$), where anisotropic distortion of the $[\text{B}_{10}\text{H}_{10}]^{2-}$ cluster optimizes Na^+ diffusion pathways (Figure 12b,c).⁷⁷

A defining feature of these materials is the strong coupling between anion dynamics and Na^+ transport. Sodium-based hydrides can outperform their lithium counterparts in ionic conductivity because the larger Na^+ ion expands the lattice and facilitates the reorientation of $[\text{B}_{12}\text{H}_{12}]^{2-}$ clusters. These anion dynamics are strongly coupled to the lowering of the effective migration barrier. When cluster reorientation is restricted, Na^+ diffusion decreases dramatically, confirming that anion dynamics enable fast ion transport.⁸⁰

Despite these advantages, practical application is hindered by the high temperatures required to activate superionic phases. For example, $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{10}\text{H}_{10}$ exhibit high conductivities ($>0.1\text{ S cm}^{-1}$) only at elevated temperatures ($>200\text{ }^\circ\text{C}$).⁷⁷ To address this limitation, several strategies have been developed to stabilize disordered phases and enhance room-temperature

transport.⁷⁷ Carbon substitution (e.g., NaCB₁₁H₁₂, NaCB₉H₁₀) weakens Na–anion interactions and significantly lowers phase transition temperatures, enabling high conductivity near or at RT.¹² Open-cage (nido) borohydrides and mixed-anion systems introduce lattice frustration, suppress long-range ordering, and stabilize dynamically disordered frameworks.⁸¹

From a processing perspective, mechanochemical methods such as ball milling can introduce structural disorder and stabilize high-temperature phases at ambient conditions, leading to conductivity enhancements of several orders of magnitude (e.g., $\sim 0.01 \text{ S cm}^{-1}$ for Na₂B₁₂H₁₂).⁸² Surface oxidation and composite strategies (e.g., polymer blending) further improve ionic transport by generating interfacial defects and enhancing Na⁺ mobility, with conductivities up to $1.6 \times 10^{-3} \text{ S cm}^{-1}$ at 45 °C.⁸³

Complex hydrides are also distinguished by exceptionally low elastic moduli (8–25 GPa) and high compressibility (bulk modulus $\sim 14 \text{ GPa}$), which allow dense pellets to be obtained by cold pressing at moderate pressures ($\sim 265 \text{ MPa}$) without high-temperature sintering.⁸⁴ Their practical behavior is nevertheless strongly pressure-dependent: for Na₄(CB₁₁H₁₂)₂ (B₁₂H₁₂), increasing stack pressure up to 35 MPa lowers interfacial resistance, whereas pressures above 70 MPa induce short circuits through Na filament propagation; under the optimal pressure window, a room-temperature CCD of 0.6 mA cm^{-2} can be achieved.⁸⁵ This combination of mechanical compliance, low-temperature processability, and pressure-sensitive interfacial stability makes complex hydrides attractive for applications where rigid ceramic contacts would otherwise be limiting.

CROSS-FAMILY COMPARISON AND SHARED DESCRIPTORS

To enable a more standardized cross-family comparison, representative inorganic solid-state electrolytes for sodium batteries are summarized in Table 1. This table compares the most consistently reported bulk transport, electrochemical, and processing-related metrics across the major electrolyte families, including β -alumina, NASICON-type oxides, sulfides, halides, anti-perovskites, and complex hydrides.

Beyond benchmark comparison, the descriptor-based framework reveals how the same descriptors, such as lattice softness, can simultaneously benefit transport and cause interfacial issues. Soft sulfides and hydrides lower Na⁺ migration barriers and improve grain-boundary permeability but suffer from higher reactivity, moisture sensitivity, and creep. Rigid oxides (e.g., Na- β / β' -Al₂O₃, NASICON) offer chemical robustness, yet are prone to grain-boundary carrier depletion, local bottlenecks, and brittle failure. Halides occupy an intermediate position. Their polarizable anion frameworks can support Na⁺ migration, whereas their interfacial behavior remains sensitive to local structural response and interphase chemistry.^{86,87} More broadly, defect chemistry, migration barriers, lattice softness, grain-boundary characteristics, and transport heterogeneity jointly govern bulk conductivity, interphase evolution, stress accumulation, and dendrite initiation. Therefore, high bulk conductivity alone does not guarantee stable cell performance; only by optimizing transport uniformity, interphase chemistry, and chemo-mechanical compatibility together can realistic design rules be established.

Defect chemistry and microstructural heterogeneity further couple bulk transport to interfacial stability.⁴⁰ As a result, electrolytes with similar bulk ionic conductivities can still show

markedly different grain-boundary resistance and Na-metal compatibility. This contrast becomes even more pronounced when microstructural heterogeneity and mechanical response are considered because local variations in grain-boundary chemistry, porosity, phase distribution, or stiffness can readily produce transport heterogeneity, local stress concentration, and distinct interfacial reaction pathways.⁸⁸ Practical stability is therefore governed not by bulk conductivity alone but by the coupling among transport uniformity, local defect chemistry, and interfacial evolution in each electrolyte system.⁶²

INTERFACE ENGINEERING STRATEGIES

Interface engineering in ASS-SMBs should not be viewed as a set of isolated post-synthetic remedies but rather as targeted interventions on the same descriptors that govern bulk transport and interfacial degradation. In this sense, interface engineering strategies can be understood according to the bottlenecks they address: defect chemistry and carrier distribution, migration barriers and transport heterogeneity, grain-boundary composition and contact loss, chemo-mechanical stress accumulation, and interphase reaction pathways. The approaches summarized below, including doping/composition modulation, structural and processing design, and surface/interlayer engineering, therefore act not only by lowering interfacial resistance but also by reshaping Na⁺ flux distribution, stabilizing local chemistry, and mitigating the coupled transport–mechanical origins of failure.

Doping and Composition Modulation

Doping and composition modulation are the most direct strategies for linking interface engineering to the descriptor-based framework introduced in Transport Descriptors and Transport-Interface Coupling section.¹⁷ Their primary function is not merely to improve conductivity but to regulate carrier concentration, defect equilibria, migration bottlenecks, lattice softness, and grain-boundary chemistry in a coordinated manner. Because these descriptors also determine local Na⁺ flux distribution, interphase formation, and chemo-mechanical stability at interfaces, composition control can simultaneously influence bulk transport and interfacial behavior.⁵ In this sense, aliovalent substitution, framework tuning, and local bond-strength engineering should be viewed as intrinsic interface-design strategies rather than bulk-property optimization alone.

In NASICON electrolytes, composition control tunes the Na⁺/vacancy ratio, bottleneck dimensions, grain-boundary transport, and interfacial chemistry with Na metal.⁴⁰ For example, Lu-doped Na_{3.3}Zr_{1.7}Lu_{0.3}Si₂PO₁₂ exhibits a critical current density of up to 1.4 mA cm^{-2} and over 4800 h of stable cycling in Na symmetric cells.⁹³ Research indicates that when F-doped Na₃Zr₂Si₃PO₁₂ materials are combined with a Na₃V₂(PO₄)₃ cathode and a small amount of NaF additive, the full cell maintains a high discharge capacity of 85.9 mAh g^{-1} after 100 cycles at a 0.5 C rate.⁹⁴

In sulfide electrolytes, doping regulates lattice softness, local bonding, air stability, and mechanical robustness at the Na interface. For Na₃PS₄-based systems, this regulation is especially important because sulfur's strong affinity for oxygen makes Na₃PS₄ highly moisture sensitive and its narrow stability window further restricts practical application.²⁵ Targeted aliovalent doping offers one route to address these issues. For example, Ca²⁺ incorporation strengthens Ca–S interactions, suppresses

Table 1. Cross-Family Benchmark Comparison of Representative Inorganic Solid-State Electrolytes for Sodium Batteries, Summarizing Key Transport, Electrochemical, and Processing-Related Metrics, including Ionic Conductivity, Activation Energy, Relative Density, Electrochemical Stability Window (ESW), and Synthesis Method where Available

electrolyte family	representative materials	ionic conductivity	activation energy (eV)	relative density (%)	ESW	synthesis method	ref
β -Alumina	Na- β'' -Al ₂ O ₃	1.6	0.41	/	/	SM	89
	Na- β'' -Al ₂ O ₃ (0.25 wt % NiO, Li ₂ O-stabilized)	66 (350 °C)	0.17	98.7%	/	SM + HT	90
NASICON	Na _{1.67} Mg _{0.67} Al _{9.33} GaO ₁₇	0.92 (30 °C)	/	97.2%	~6.0 V vs Na ⁺ /Na ⁺ (CV, Au/electrolyte/Na, 1 mV/s)	SM	28
	Na ₃ Zr ₂ Si ₂ PO ₁₂	0.19	0.34	/	0–5 V vs Na ⁺ /Na ⁺ (CV; Au/SSE/Na; 0.05 mV/s)	SM	91
	Na ₃ Zr _{1.95} Mg _{0.05} Si ₂ PO ₁₂	3.5	0.25	/	0–4.5 V vs Na ⁺ /Na ⁺ (CV; Au/SSE/Na; 0.1 mV/s)	BM + SM	92
	Na ₃ Zr ₂ Si ₂ P _{0.6} O ₁₂	5	0.32	95%	/	SA-SSR	93
	Na ₃ Zr ₂ Si ₂ PO ₁₂ + 0.7 mol NaF	1.41	0.33	94.6%	4.95 V vs Na ⁺ /Na ⁺ (CV/LSV, Au/SSE/Na; 0.2 mV/s)	SM	94
sulfides	Na ₃ PS ₄	0.2	0.28	/	0–5 V vs Na ⁺ /Na ⁺ (CV; Na/SSE/stainless steel; 5 mV/s)	BM	48
	Na _{2.9} PS _{3.95} Se _{0.05}	0.12	0.23	/	–0.5 to 5 V vs Na ⁺ /Na ⁺ (CV; Na/SSE/C; 5 mV/s)	LM + HT	95
	Na _{2.730} Ca _{0.133} PS ₄	0.94	0.49	/	0.5–2.5 V vs Na ⁺ /Na ⁺ (CV, Ti/SSE/Na ₃ Sn; 5 mV/s)	SM	52/59
	Na _{1.1} Sn ₂ PS ₆ Se ₁₂	2.15	0.28	/	1.22–2.65 V vs Na ⁺ /Na ⁺ (CV; Na/SSE/stainless steel; 0.5 mV/s) (60 °C)	SM + slow cooling	59
	Na _{1.08} Sn _{1.9} PS _{1.8}	0.67	0.307	80%	0–5 V (Na/SSE/Na; 0.1 mV/s) (80 °C)	GM + HT	96
anti-perovskite	Na _{1.15} Sh ₂ Sb _{0.5} Ti _{0.5} S ₁₂	1.01	0.27	/	0.3–2.7 V vs Na ⁺ /Na ⁺ (CV, Na/SSE/stainless steel; 1 mV/s)	SM + annealing	97
	Na ₃ OBr	0.0028 (110 °C)	0.68	/	0–1.8 V vs Na ⁺ /Na ⁺ (DFT)	SM	70/88
	Na ₄ Ol ₂	0.0025 (110 °C)	0.646	/	0–1.6 V vs Na ⁺ /Na ⁺ (DFT)	SM	70/88
halide	Na _{2.9} Sr _{0.05} OBr _{0.04} I _{0.4}	1.9 (200 °C)	0.62	/	/	SM	71
	Na ₃ OBH ₄	4.4	0.25	/	/	SM	75
	Na ₃ YBr ₆	0.028	0.36	/	1.43–3.35 V vs Na ⁺ /Na ⁺ (LSV; Na/N ₂ , ₉ PS _{3.5} Cl _{0.1} /SSE + C; 1 mV/s)	SM + BM	98
	NaYbZrCl _{0.75}	0.066	0.37	/	4.1 V vs Na ₂ Sn/Na ⁺ (CV; Na ₂ Sn/Na ₃ PS ₄ /SSE + C; 0.1 mV/s)	BM	99
	crystalline NaTaCl ₆	0.06	0.41	/	2.5–4.0 V vs Na _{1.5} Sn ₄ (LSV; Na _{1.5} Sn ₄ /Na ₃ PS ₄ /SSE + carbon black; 0.1 mV/s)	BM	100
complex hydrides	amorphous NaTaCl ₆	4	0.3	/	/	BM	100
	Na ₂ B ₁₀ H ₁₀	10 (110 °C)	0.47	95%	/	BM	77
	NaCB ₁₁ H ₁₂	120 (110 °C)	0.22	94%	/	BM	12
	oxidized Na ₂ B ₁₂ H ₁₂ ·20 wt % SiO ₂	1.3	0.51	/	5.2 V vs Na ⁺ /Na ⁺ (LSV; Na/SSE/Na; 10 μ V/s)	BM	101
	Na ₄ (CB ₁₁ H ₁₂) ₂ (B ₁₂ H ₁₂)	0.9 (20 °C)	/	/	0–6.5 V (CV; Na/SSE/Pt; 0.1 mV/s)	BM + HT	81

^aNotes: Unless otherwise specified, ionic conductivity and electrochemical windows were measured at room temperature. ^bThe ESW values measured in experiments are influenced by test conditions (such as electrode materials, scan rate and current thresholds); the figures listed here are taken from the literature and do not necessarily represent the thermodynamic limits of the material. ^cGM, SM, LM, BM, HT, and SA-SSR denote gas-phase, solid-state reaction, liquid-phase, ball milling, heat treatment, and solution-assisted solid-phase reaction methods, respectively.

sulfur migration, inhibits the formation of detrimental Na_2S , and improves interfacial mechanical integrity by enhancing the tensile strength and deformation resistance of Na_3PS_4 (Figure 13a).¹⁰²

In halide electrolytes, composition modulation is closely tied to interfacial stability because it reshapes both local transport pathways and the reduction/oxidation chemistry at the Na metal or cathode interface.¹⁵ For example, fluorinated $2\text{NaF}\cdot\text{ZrCl}_4$ strengthens $\text{Zr}\text{--}\text{F}$ bonding, weakens $\text{Na}\text{--}\text{F}$ interactions, and increases the RT conductivity to $2.35 \times 10^{-4} \text{ S cm}^{-1}$, while the fluorine-rich interfacial layer suppresses Cl^- oxidation and other side reactions (Figure 13b). This enables a $\text{NaNi}_{1/3}\text{Fe}_{1/3}\text{Mn}_{1/3}\text{O}_2$ base full cell to retain 81.1% capacity after 600 cycles over 1.9–4.3 V.¹⁰³

Physical Treatment and Structural Design

Physical treatment and structural design mainly target the geometric and mechanical origins of interfacial degradation. From the perspective of the descriptor-based framework in Transport Descriptors and Transport-Interface Coupling section, these approaches act by improving contact retention, reducing current constriction, suppressing pore formation, and mitigating chemo-mechanical stress accumulation during Na plating/stripping. Their importance lies in the fact that even when bulk transport is favorable, local transport heterogeneity can still emerge if the electrode/electrolyte interface is mechanically unstable, poorly conformal, or structurally inhomogeneous.

At the Na metal interface, contact loss leads to current concentration and void formation. Ultrasonic welding can improve Na/NASICON contact by forming dense interfacial bonding, enabling 90% capacity retention after 900 cycles at RT. (Figure 13c).¹⁰⁴ At the cathode/electrolyte interface, structural integration strategies reduce interfacial discontinuities and tortuous ionic pathways while minimizing thermally induced phase degradation. Conventional high-temperature sintering causes sodium volatilization and degradation of active materials, whereas spark plasma sintering (SPS) offers a lower-temperature route. For example, co-sintered $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ and $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ at 900 °C via SPS produced monolithic solid-state cells with improved interfacial integration.¹⁰⁷ However, this temperature remains high for scalable manufacturing. Chemical mechanical solution creep sintering technology further lowers the processing to 375 °C, suppressing impurity formation, and yields ternary composite electrodes with densities above 85%.¹⁰⁸ However, excessive densification may reduce the structural tolerance to electrode volume changes during cycling, thereby promoting particle fracture, impairing ion transport, and increasing polarization.

Structural engineering can also redistribute Na^+ flux and relieve interfacial stress by introducing porous, conformal, or hierarchical pathways for ion transport. For example, a porous Na_3PS_4 framework impregnated with phase-change polymer forms a three-dimensional NSS/PPP composite (Figure 13d), which enables the $\text{TiS}_2|\text{3D-NSS/PPP SCE}|\text{Na}$ cell to deliver an initial specific capacity of 170 mAh g^{-1} at a current density of 50 mA g^{-1} , with excellent capacity retention over 550 cycles.¹⁰⁵ Solution-based surface coating provides another effective route: coating Na_3PS_4 onto Mo_6S_8 particles improves Na^+ /electron transport and increases the density of active interfacial sites, allowing the battery to retain 52 mAh g^{-1} after 500 cycles at 60 °C.¹⁰⁹

Surface Modification and Interphase Construction

Surface modification and interlayer construction are the most direct strategies for manipulating interphase chemistry and local Na^+ flux at solid–solid interfaces. Within the framework established in Transport Descriptors and Transport-Interface Coupling section, these approaches mainly address three coupled bottlenecks: poor wetting/contact, electronically or ionically unfavorable interphases, and transport heterogeneity that leads to local current concentration and dendrite propagation. By introducing functional interlayers onto electrode or electrolyte surfaces, these methods reshape local Na^+ flux, improve sodium affinity and interfacial conformity, and suppress chemically or electronically unfavorable reaction pathways.

Metal and Alloy Interlayers. Metallic or alloy-forming interlayers are mainly used to improve sodium affinity, reduce contact angles, and homogenize interfacial Na^+ flux, thereby suppressing current hotspots and dendrite initiation. The low hardness and weak wettability of sodium metal are the primary reasons for its poor contact with rigid SSEs. In the BASE system, metal-based interfacial layers can enhance the affinity of liquid or softened Na toward the BASE surface.¹¹⁰ This design reduces the Na contact angle from 90 to 35°, enhances Na^+ wettability, and simultaneously provides porous space to buffer deposition-induced stress. As a result, the corresponding Na/BASE/Na symmetric cell maintained stable cycling for more than 1000 h at 1 mA cm^{-2} .

For the NASICON system, metal modification proves equally effective for improving Na-metal interfacial compatibility. A ZnO-modified NASICON surface exhibits enhanced sodium wettability, suppressed dendrite growth, and markedly reduced interfacial impedance.¹¹¹ Further structural optimization can be achieved by combining compositional tuning with interfacial coating. A three-dimensional $\text{Zn}^{2+}/\text{Mg}^{3+}$ co-doped $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ coated with tin oxide was designed with a porous–dense–porous trilayer architecture (Figure 13e), which improves interfacial compatibility while blocking electrode diffusion.¹⁰⁶ This structure delivers a critical current density of 40 mA cm^{-2} and a cumulative cycled capacity of 10.8 Ah cm^{-2} without external pressure.

Polymer Interlayers and Composite Electrolyte. Polymer and composite interlayers mainly improve interfacial compliance, buffer volume changes, and maintain ionic continuity across chemically or mechanically mismatched interfaces. In Na-metal solid-state batteries, polymer-based interlayers can enhance wettability, reduce impedance, and suppress direct parasitic reactions. For example, a polydopamine (PDA)-modified NZSP surface forms an amphiphilic interfacial layer that improves Na-metal contact, enabling stable cycling of a $\text{Na|PDA-coated NZSPNVP}$ cell.¹¹²

Beyond polymer-based composite strategies, multilayer electrolyte architectures provide another effective route to balance electrochemical stability and chemical compatibility. For example, a double-layer electrolyte design, in which Na_3PS_4 serves as a protective interlayer on $\text{Na}_{11}\text{Sn}_2\text{SbS}_{11.5}\text{Se}_{0.5}$, effectively suppresses direct reactions between sodium metal and the less stable sulfide electrolyte, extends the electrochemical window to 5 V, and markedly improves full-cell cycling stability and capacity retention.¹¹³ More generally, dual-layer combinations of chloride and sulfide electrolytes can couple the superior

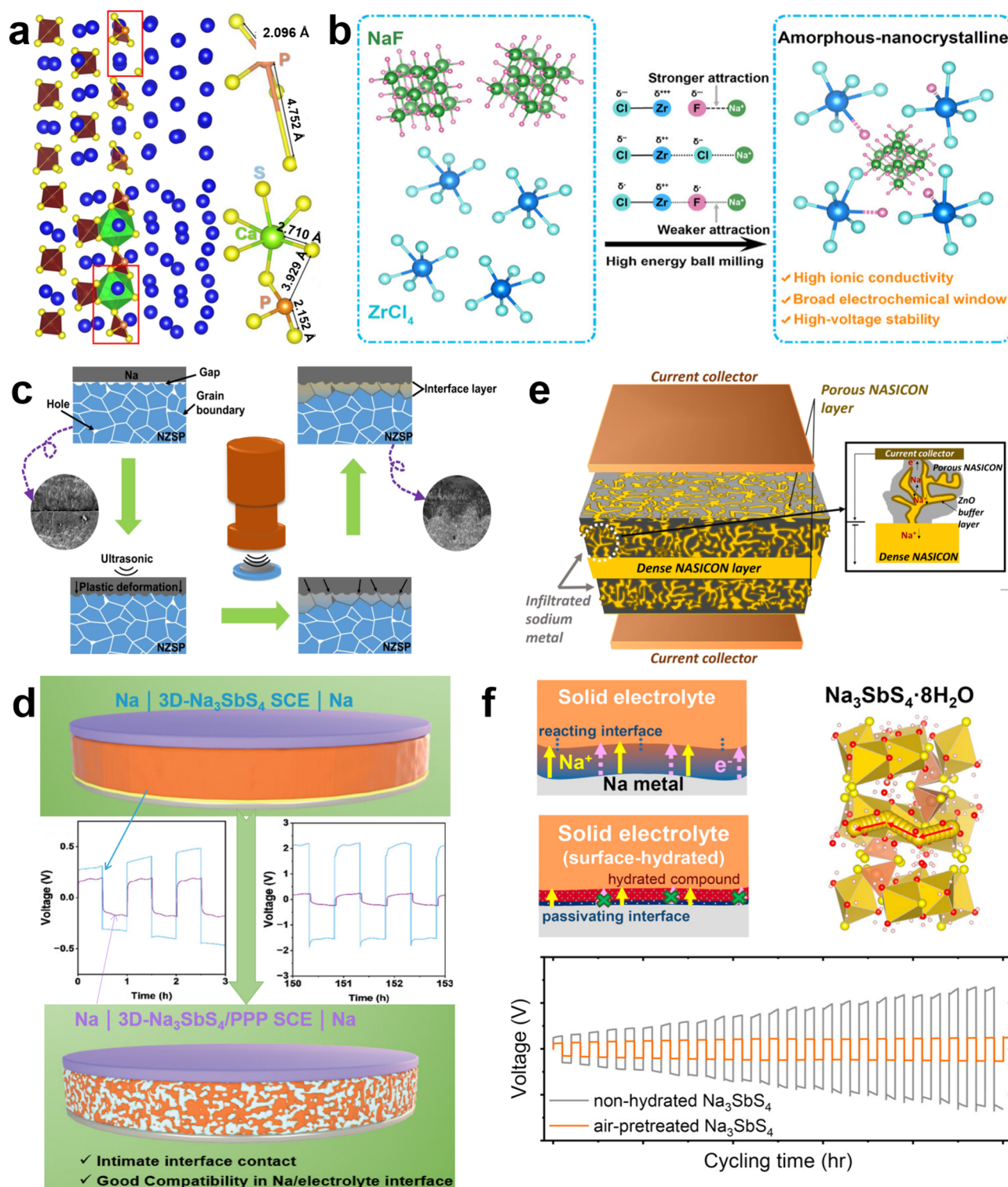


Figure 13. (a) Optimized interfacial structures of Na-Na₃PS₄ and Na-Ca_{0.125}Na_{2.75}PS₄, P-S and Ca-S bond lengths are shown schematically.¹⁰² Reproduced with permission from ref 102. Copyright 2023 Elsevier. (b) Schematic illustrating how F doping enhances Zr-F bonds while weakening Na-F interactions, improving both ionic conductivity and voltage stability in halide SSEs.¹⁰³ Reproduced with permission from ref 103. Copyright 2025 American Chemical Society. (c) Schematic showing improved Na/NZSP interfacial contact via an ultrasonic solid-state welding method.¹⁰⁴ Reproduced with permission from ref 104. Available under a CC-BY 4.0. Copyright 2021 Springer Nature. (d) Schematic of a Na symmetric battery using porous Na₃SbS₄ particles and 3D-Na₃SbS₄/PPP SCE, with cycling performance at a 0.1 mA cm⁻² current density.¹⁰⁵ Reproduced with permission from ref 105. Copyright 2024 Wiley-VCH. (e) Schematic of Na⁺ migration in a Zn/Mg co-doped, ZnO-coated NASICON trilayer symmetric cell during stripping.¹⁰⁶ Reproduced with permission from ref 106. Copyright 2024 Royal Society of Chemistry. (f) Cycling performance of Na/Na₃SbS₄/Na cells with and without surface hydration pretreatment at a current density of 0.1 mA cm⁻², and a schematic representation of the conductivity of the interface layer.¹⁶ Reproduced with permission from ref 16. Copyright 2019 Cell Press.

Table 2. Quantitative Comparison of Representative Interfacial Performance Metrics for Inorganic Solid-State Electrolytes in Sodium Batteries, Summarizing Electrolyte Family, Representative Material, Interfacial Strategy, Test Conditions, Electrolyte Thickness, Area-Specific Resistance (ASR), Critical Current Density (CCD), and Corresponding References

electrolyte family	representative materials	interfacial strategy ^a	test conditions (temperature, stack pressure)	electrolyte thickness (mm)	ASR ^b (Ω cm ²)	CCD ^b (mA cm ⁻²)	ref.
β -Alumina	Na- β "-Al ₂ O ₃	unprocessed	RT, 3.4 MPa	1.4	19,909	0.3	89
		high-temperature heat treatment	RT, 3.4 MPa	1.4	8	12	
		3D cross-linking carbon fiber with Sn particle coating	RT	0.8	6.6	1.3	31
		unprocessed	30 °C 0.14 MPa	0.8	38	0.4	28
NASICON	Na _{1.67} Mg _{0.67} Al _{10.33} O ₁₇ Na _{1.67} Mg _{0.67} Al _{9.33} GaO ₁₇	unprocessed	30 °C 0.14 MPa	0.8	16	0.8	
		unprocessed	65 °C	1	4000	0.15	91
		formation of interface layer in situ	65 °C	1	400	0.25	
		CPMEA polymer sandwich	65 °C	/	1000	0.2	114
sulfide	Na _{3.4} Zr ₂ Si _{2.4} P _{0.6} O ₁₂ Na ₃ PS ₄ Na ₃ PS _{3.85} O _{0.15}	unprocessed	60 °C 100 MPa	1	4.1	1.8	93
		unprocessed	RT	/	3000		115
		unprocessed	60 °C, 7 MPa	/	416		116
		Na ₃ PS _{3.4} O _{0.6} Na ₃ PS _{3.85} O _{0.15} Na ₃ PS _{3.4} O _{0.6} tri-layer	60 °C, 7 MPa	/	10	2.3	
complex hydride	Na ₂ B ₁₂ H ₁₂ + NaHF ₂ oxidized Na ₂ B ₁₂ H ₁₂ + 20 wt %SiO ₂	formation of interface layer in situ	30 °C	0.5		0.55	77
		unprocessed	RT	0.4–0.6		0.8	101

^aNotes: Unless otherwise specified, the reported values correspond to symmetric Na/electrolyte/Na-type cells or closely related interfacial test configurations used in the cited studies. ^bASR and CCD values are strongly dependent on cell design, measurement protocol, temperature, stack pressure, electrolyte thickness, and interfacial treatment. Therefore, the values listed here should be interpreted as representative literature benchmarks rather than intrinsic material constants.

high-voltage stability of the former with the high ionic conductivity of the latter, offering a promising strategy for solid-state sodium batteries that require both high energy density and long cycle life.⁴

In Situ Interphase Construction. In situ interphase formation offers a distinct route to stabilize interfaces by converting the initial chemical reactivity into a passivating and transport-compatible interphase, rather than allowing uncontrolled decomposition to continue. In this approach, the interfacial chemical environment is deliberately regulated so that decomposition preferentially yields electronically insulating but ionically functional products, thereby improving long-term stability.¹⁷ For example, exposure of Na₃SbS₄ to air leads to the formation of Na₃SbS₄·8H₂O, which reacts with sodium metal to generate insulating NaH and Na₂O interphases. These passivation products suppress the formation of electronically conductive decomposition species such as Na₃Sb and thereby mitigate interfacial side reactions (Figure 13f).¹⁶

Taken together, these interface engineering strategies can be understood as targeted interventions on the descriptor-level origins of interfacial failure. Whether through defect regulation, structural/contact design, or interphase construction, their common purpose is to reshape Na⁺ flux distribution, stabilize local chemistry, and mitigate the coupled transport–mechanical bottlenecks discussed in Transport Descriptors and Transport-Interface Coupling section. To place these strategies on a more quantitative footing, representative interfacial performance metrics reported across major electrolyte families are summarized in Table 2, including ASR, CCD, and the associated testing conditions. This comparison further shows that practical interfacial behavior is highly sensitive to interfacial design and measurement configuration and therefore cannot be inferred from bulk conductivity alone. Interface engineering should therefore be viewed not as an independent add-on but as the practical extension of the bulk–interface coupling framework.

DEVICE-LEVEL COMPARISON ACROSS ELECTROLYTE FAMILIES

To further connect electrolyte properties to practical cell requirements, Table 3 summarizes the major device-relevant constraints and trade-offs across the principal inorganic solid-state electrolyte families for sodium batteries. In addition to transport and interfacial considerations, this comparison highlights thickness constraints, areal capacity, stack pressure, operating temperature windows, mechanical properties, Na-metal compatibility, and the resulting implications for practical energy density and manufacturability.

As shown in Table 3, mechanical and processing factors are first-order determinants of practical solid-state battery performance. Oxides offer high stiffness and chemical robustness but often require high-temperature densification and are prone to brittle fracture.^{17,32} Sulfides are more deformable and easier to densify but are more sensitive to creep and pressure-induced short circuiting.^{55,117} Halides occupy an intermediate position, combining attractive transport and oxidative stability with continuing challenges in densification and scalable integration.^{62,66,118} Emerging systems such as anti-perovskites and complex hydrides highlight the benefits of low-temperature processability and mechanical compliance but still face transport and interfacial limitations.^{75,76,84,85} Overall, electrolyte selection must consider not only ionic conductivity but also processability, mechanical compatibility, and practical cell integration.

SUMMARY AND OUTLOOK

ASS-SMBs are promising candidates for next-generation energy storage because they offer the prospect of improved safety with high energy density. In this review, we have examined sodium-ion transport mechanisms and interfacial challenges across major inorganic solid electrolyte families, including oxides, sulfides, halides, anti-perovskites, and complex hydrides. Across

Table 3. Cross-Family Comparison of Representative Inorganic Solid-State Electrolyte Families for Sodium Batteries, Summarizing Device-Relevant Constraints and Practical Trade-Offs, including Thickness, Areal Capacity, Stack Pressure, Operating Temperature Window, Moisture Stability, Na-Metal Compatibility, Mechanical Properties, Energy-Density Implications, and Key Advantages and Challenges

electrolyte family	device-relevant parameters	oxides	sulfides	halides	anti-perovskites	complex hydrides
thickness constraint (nm)	0.1–1	0.5–1.5	0.5–1.5	0.5–1.5	0.3–1.0	0.3–1.0
areal capacity (mAh cm ⁻²)	0.1–3.0	0.1–1	0.1–1	0.1–1.5	0.1–0.5	0.1–0.5
stack pressure (MPa)	1–400	100–300	100–300	100–400	100–400	1–400
operating temperature window (°C)	–20–350 °C	–20–100 °C	–20–100 °C	–20–100 °C	100–300 °C	25–100
moisture stability	excellent	low	low	low	moderate	moderate
Na-metal compatibility	good	poor	poor	poor	good	good
fracture toughness (MPa m ^{1/2})	1.0–2.5	0.2–0.5	0.2–0.5	0.3–0.8	0.5–1.0	0.2–0.5
Young's modulus range (GPa)	70–280	10–25	10–25	6–15	20–80	8–20
energy-density implications	suitable for high-voltage cathodes, but high interfacial resistance limits its practical application	often requires a low-voltage anode or the use of a protective interphase; energy density is limited	high room-temperature ionic conductivity; soft and deformable; pressure-assisted densification	compatible with high-voltage cathodes, supporting high-energy-density designs	the current energy density contribution is limited and requires further optimization	compatible with medium-voltage cathodes; its light weight helps improve energy density
key advantages	high oxidative stability; wide temperature range; mature ceramic processing routes	high room-temperature ionic conductivity; soft and deformable; pressure-assisted densification	high room-temperature ionic conductivity; soft and deformable; pressure-assisted densification	wide electrochemical window; good compatibility with high-voltage cathodes	structural flexibility; tunable ion-transport channels; low-temperature processability	good Na-metal compatibility; low weight; high deformability; low elastic modulus
key challenges	high synthesis temperature, interfacial instability; brittle nature	narrow electrochemical window; air sensitivity; manufacturing cost	narrow electrochemical window; air sensitivity; manufacturing cost	moisture sensitivity; unstable interface with Na metal; possibly expensive precursors	complex synthesis; interfacial instability	high phase-transition temperature; low room-temperature ionic conductivity

these systems, a common message emerges: atomic-scale ion migration is closely linked to interfacial ion distribution, chemo-mechanical response, and electrochemical stability. Bulk transport and interfacial degradation should therefore be viewed as coupled manifestations of the same structural and chemical descriptors.

Looking forward, several opportunities clearly transcend individual electrolyte classes. First, pathway engineering through defect control offers a general route to regulate carrier concentration, migration barriers, and transport heterogeneity across different inorganic electrolytes. Such control can improve not only bulk conductivity but also grain-boundary transport and local interfacial stability, although it must be balanced against lattice distortion, secondary phase formation, and unfavorable local chemistry.

Second, interface-aware electrolyte design will be essential. Practical stability depends not simply on high ionic conductivity but on the coupled evolution of bulk transport, interphase chemistry, wetting/contact behavior, and mechanical response. As a result, electrolytes with similar bulk conductivities may still behave very differently in real cells if they differ in transport uniformity, grain-boundary chemistry, or interfacial reaction pathways.

Third, manufacturing-compatible electrolyte architectures are needed to translate materials advances into practical devices. Low-temperature densification, scalable coating strategies, robust composite electrodes, and pressure-efficient contact technologies can help preserve both transport performance and interfacial stability while reducing volatilization, parasitic reactions, and contact loss. Different electrolyte families may be advantageous for different use cases: oxides favor chemical and mechanical stability but often require higher-temperature processing; sulfides offer high conductivity and deformability but face challenges in moisture-controlled fabrication; halides are promising for high-voltage systems but still require progress in cost, environmental stability, and cell-level integration. More broadly, cathode, anode, and electrolyte design should be treated as a coupled problem rather than optimized independently.

Further progress will also rely on closer integration of computation, advanced characterization, and scalable processing. Computational, data-driven, and machine-learning approaches can accelerate the identification of promising chemistries and transport descriptors, while in situ and operando methods remain indispensable for resolving the dynamic interfacial processes that govern degradation and failure. Taken together, effective electrolyte design requires structure/defects, transport, interface, and processing constraints to be optimized together rather than in isolation.

Although substantial challenges remain, advances in defect-controlled transport, interface-aware materials design, and scalable electrolyte architectures are likely to define the next stage of progress and move inorganic solid electrolytes closer to reliable, high-performance sodium solid-state batteries.

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■ ACKNOWLEDGMENTS

This research was supported by the Guangxi Natural Science foundation (No.2025GXNSFBA069588), the Guangxi Key Research and Development Program (No. GuikeAB25069467), the National Natural Science Foundation of China (Nos. 22205017, 22090043, 22090042, 22479074, 22475096, 22561160129, and U25A20628), the National Key R&D Program of China (2020YFA0406202), the Beijing-Tianjin-Hebei Fundamental Research Cooperation Project (No. B2024202090), the CNPC Innovation Found (No. 2024DQ02-0311), the Guilin University of Technology Research Startup Project (NO. RD2400002912), the Equipment Pre-Research and Ministry of Education Joint Fund (8091B02052407), the Fundamental Research Program Key Project of Jiangsu Province (BK20253008), the Science and Technology Major Project of Jiangsu Province (BG2024013), the Scientific and Technological Achievements Transformation Special Fund of Jiangsu Province (BA2023037), the Academic Degree and Postgraduate Education Reforming Project of Jiangsu Province (JGKT24_C001), the Key Core Technology Open Competition Project of Suzhou City (SYG2024122), the Open Research Fund of Suzhou Laboratory (SZLAB-1308-2024-TS005), the Chenzhou National Sustainable Development Agenda Innovation Demonstration Zone Provincial Special Open Competition Project (2023sfq11, 2025sfq38), and the Fundamental Research Funds for the Central Universities and Nanjing University International Collaboration Initiative (020514380354). The authors are also grateful to Guangxi BaGui Scholars Special Funding.

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