

# Advances in Solid Electrolytes for Solid-State Sodium-Ion Batteries in Grid-Scale Storage

## Introduction

Grid-scale energy storage demands battery technologies that are safe, cost-effective, and long-lived. Sodium-ion batteries (SIBs) have emerged as promising candidates due to the natural abundance and low cost of sodium relative to lithium. While sodium ions are heavier and larger than lithium, making SIBs inherently lower in energy density, these batteries are well-suited for large-scale applications (stationary storage or even electric vehicles) where cost and resource availability take precedence over size and weight. A key driver for adopting solid-state designs in sodium batteries is the quest for improved safety: replacing flammable liquid electrolytes with solid electrolytes can eliminate fire risk and enable the use of metallic sodium anodes and high-voltage cathodes for higher energy density. Solid electrolytes also promise longer cycle life by preventing the solvent-driven side reactions that plague liquid cells.

This report provides a comprehensive review of solid electrolytes for sodium-ion batteries, emphasizing how advances in these materials contribute to the feasibility of grid-scale storage. We cover all major classes of Na-ion solid electrolytes – from **ceramic inorganic conductors** (NASICON-type,  $\beta$ -alumina, sulfides, halides, etc.) to **polymer-based electrolytes** and **composite/hybrid systems**. Key historical developments and recent innovations (up to 2025) are discussed for each class. We examine performance metrics such as ionic conductivity, electrochemical/chemical stability, and interfacial compatibility with electrodes, and we address major technical challenges (e.g. dendrites, interface resistance, processing scale-up). Finally, we consider how these materials impact the practicality of sodium-based solid-state batteries for grid storage in terms of performance and cost. Table 1 (below) summarizes representative electrolyte systems, their properties, and their suitability for grid-scale use.

## Historical Development of Sodium Solid Electrolytes

Research into fast sodium-ion conductors began decades ago, laying the groundwork for today's solid-state sodium batteries. One of the earliest breakthroughs was  **$\beta$ -alumina** (sodium  $\beta$ -alumina, NaAl<sub>2</sub>SiO<sub>5</sub>), discovered in the 1960s.  $\beta$ -alumina is a ceramic with a layered

structure that conducts  $\text{Na}^+$  at high rates along two-dimensional planes. In 1971, Whittingham reported  $\text{Na}^+$  conductivity  $\sim 1.4 \times 10^{-2}$  S/cm at 25 °C for single-crystal  $\beta$ -alumina – an exceptionally high value even by modern standards. This material enabled the development of high-temperature sodium batteries, notably the sodium–sulfur (Na–S) battery first demonstrated by Ford Motor Co. in the 1970s. Na–S batteries, which operate around 300 °C with molten sodium and sulfur separated by a  $\beta$ -alumina solid electrolyte, were later commercialized for grid storage by NGK Insulators in Japan. Despite their success (offering high energy density and long cycle life at the grid scale),  $\beta$ -alumina batteries require constant heating and suffer from the ceramic’s brittleness and moisture sensitivity. These drawbacks motivated the search for alternative  $\text{Na}^+$  conductors that could operate at ambient temperatures.

In 1976, Goodenough and Hong reported a new class of fast Na-ion conductors with the **NASICON** structure (Na Super Ionic Conductor). NASICON-type ceramics (e.g.  $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_6\text{O}_{12}$ ) are framework oxides that support three-dimensional  $\text{Na}^+$  diffusion. Early NASICON electrolytes achieved conductivities on the order of  $10^{-3}$  S/cm at room temperature – among the highest of any solid Na conductor – while offering excellent thermal stability and compatibility with many sodium cathodes. Through the 1980s and 1990s, incremental improvements were made by compositional tuning of NASICON (substituting elements to increase Na content or enlarge diffusion “bottlenecks”) and by sintering techniques to reduce grain boundary resistance. However, interest in sodium batteries waned as lithium-ion technology rose to dominance.

The past decade (2010s onward) has seen a **renaissance in solid-state sodium battery research**, spurred by concerns over lithium cost and safety. New inorganic electrolytes have been discovered by analogy to lithium conductors and via computational design. For example, sulfide-based Na electrolytes analogous to Li thiophosphates were developed:  $\text{Na}_3\text{PS}_4$  was first reported as a Na superionic conductor, and later a tetragonal-to-cubic phase transformation (via halide doping) raised its conductivity into the  $10^{-4}$  S/cm range. In 2016, computational screening led to the synthesis of  **$\text{Na}_{1.0}\text{SnP}_2\text{S}_{12}$** , a Na sulfide with  $\sim 4 \times 10^{-4}$  S/cm at 25 °C – a value rivalling the best Na-ion conductors known at that time. Even more impressively, a 2019 report showed that partial substitution of  $\text{Sb}^{5+}$  with  $\text{W}^{6+}$  in  $\text{Na}_3\text{SbS}_4$  produces  **$\text{Na}_{2.88}\text{Sb}_{0.88}\text{W}_{0.12}\text{S}_{12}$** , achieving an unprecedented  $3.2 \times 10^{-2}$  S/cm (32 mS/cm) at room temperature. This benchmark surpasses even the famous Li-ion conductor LGPS ( $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ ) and is paired with the practical advantage of lower sintering temperature and improved air stability in the Na–Sb–W–S system.

Meanwhile, polymer electrolytes for Na-ion batteries have evolved from earlier work on Li polymer batteries. In the late 1970s, PEO (polyethylene oxide) + Li salt was identified as a solid electrolyte; analogous PEO+Na salt systems were explored for Na batteries in subsequent decades. Solid polymer electrolytes (SPEs) avoid the leakage and flammability of liquids, but

early SPEs had low room-temperature conductivity ( $\sim 10^{-7}$  to  $10^{-6}$  S/cm) and were limited to operation at elevated temperatures (60–90 °C) to achieve reasonable ion transport. Research in the 2000s–2010s introduced polymer blends, ionic plastic crystals, and ceramic fillers to enhance Na-ion polymer conductivity. By the 2020s, composite approaches were yielding significantly improved performance (as discussed later), renewing interest in **ambient-temperature Na polymer batteries**.

Another emerging area is hybrid and composite electrolytes. Researchers have found that combining different electrolyte phases can yield synergistic benefits – for instance, integrating a minor liquid or polymer component to wet grain boundaries of a ceramic, or infusing a porous ceramic scaffold with polymer. These approaches attempt to marry the high conductivity of inorganic solids with the superior interface contact of liquids/polymers. A striking recent example (2025) is the use of a **NASICON + organic electrolyte hybrid**, which demonstrated an **ultra-long cycle life** of 50,000 cycles (86% capacity retention) in a sodium cell by mitigating interface degradation. Such results underscore that careful electrolyte engineering can dramatically improve durability, an essential requirement for grid-scale batteries.

The following sections examine each class of solid electrolyte in detail, highlighting their development, properties, and challenges, with an eye to grid-scale battery criteria.

## Ceramic Inorganic Electrolytes (Oxide-Based)

“Inorganic” solid electrolytes – typically ceramics or glass-ceramics – offer the highest  $\text{Na}^+$  conductivities and robust thermal stability. Within this category, oxide-based conductors (which contain oxide anions) have a long history. We focus on NASICON-type structures and  $\beta$ -alumina, which are the most mature oxide electrolytes for Na-ion batteries, and also mention other oxide-based systems (perovskites, glassy electrolytes).

### NASICON-Type Solid Electrolytes

NASICON-type ceramics ( $\text{Na}_x\text{M}_2(\text{XO}_4)_3$  frameworks, with  $\text{M} = \text{e.g. Zr}$ , and  $\text{X} = \text{P/Si}$ ) are widely considered one of the best Na solid electrolytes for all-solid-state batteries. The NASICON structure features a 3D network of  $\text{PO}_4/\text{SiO}_4$  tetrahedra and  $\text{MO}_6$  octahedra, creating interstitial sites and channels through which  $\text{Na}^+$  can diffuse. A prototypical

composition is  $\text{Na}_{3}\text{Zr}_{2}\text{Si}_{2}\text{PO}_{12}$  (NZSP), first reported in the 1970s. Key properties of NASICON electrolytes include:

- **High Ionic Conductivity:** NASICONs achieve  $\sim 10^{-3}$  S/cm at room temperature in dense polycrystalline form. Some compositions and doped variants reach the mid- $10^{-3}$  S/cm range at 25 °C, approaching liquid-electrolyte conductivities. (For comparison, typical solid polymers are  $10^{-6}$ – $10^{-8}$  S/cm at room T.) High  $\text{Na}^{+}$  mobility in NASICON stems from its open framework and multiple migration paths. Conductivity is thermally activated, with moderate activation energies ( $\sim 0.2$ – $0.4$  eV reported for various NASICONs), enabling adequate ion transport even at ambient conditions. By contrast, many other ceramics require heating to reach similar conductivities.
- **Electrochemical Stability:** Oxide electrolytes are generally stable against high-voltage cathodes. NASICON compositions often show wide electrochemical stability windows up to  $\sim 5$  V vs  $\text{Na}^{+}/\text{Na}$ , meaning they are inert to oxidation by typical cathode potentials. This makes them compatible with high-voltage sodium cathodes (e.g. layered oxides or polyanion cathodes) without decomposing. However, on the anode side NASICON tends to *reduce* when in contact with metallic sodium (0 V). The NASICON lattice contains transition metals (like  $\text{Zr}^{4+}$ ) and polyanions ( $\text{PO}_4^{3-}$ ) that can be chemically reduced by Na metal, forming interphase products (e.g.  $\text{Na}_3\text{P}$ ,  $\text{Na}_2\text{O}$ , or metal Zr) that are electronically insulating. This reaction can consume part of the electrolyte and create a resistive interface.
- **Thermal & Chemical Stability:** NASICON ceramics are refractory and nonflammable. They can be sintered at high temperature ( $\sim 1000$ – $1200$  °C) to form dense electrolytes and remain stable across a wide temperature range (well above any battery operating temperature). They are generally less sensitive to moisture than sulfide electrolytes; however, if NASICON pellets are not fully dense, moisture can infiltrate pores and potentially react. Properly sealed, NASICON electrolytes can be handled in air for short times, but long-term exposure may cause slow carbonation or hydration on the surface. Overall, their environmental stability is considered good, easing manufacturing and cell assembly compared to air-sensitive sulfides.

**Key developments:** Many variants of NASICON have been formulated to maximize Na-ion conductivity. The base NZSP has a NASICON structure with  $x \approx 3$  ( $\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ ). Increasing the Na content (interstitial Na in the structure) tends to increase conductivity, but charge balance requires aliovalent substitution (e.g. partially replacing  $\text{Zr}^{4+}$  with lower valent cations like  $\text{Mg}^{2+}$  or  $\text{Al}^{3+}$ , or creating P/Si vacancies). Researchers have created compositions such as  $\text{Na}_{3.1}\text{Zr}_{1.9}\text{Mg}_{0.1}\text{Si}_2\text{PO}_{12}$ ,  $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$ , etc., achieving conductivities up to  $\sim 5 \times 10^{-3}$  S/cm at 25 °C in some reports. Another strategy is improving microstructure – e.g. using spark plasma sintering or glass-ceramic routes to obtain highly dense NASICON with minimal grain-boundary impedance. Recent studies also explore thin NASICON films and 3D architectures for better integration.

**Interface challenges:** A major hurdle for NASICON in practical cells has been the interface with a sodium metal anode. Despite good intrinsic conductivity, symmetric Na|NASICON|Na cells often exhibit growing interfacial resistance and eventual short-circuit via dendrites. Issues include (i) *poor wettability/contact* – a hard ceramic against a soft metal leaves interfacial voids, (ii) *chemical reactivity* – as mentioned, Na can partially reduce NASICON, forming a passivation layer that is ionically conductive but adds resistance, and (iii) *dendrite penetration* – if local current hotspots allow Na to plate into flaws or grain boundaries in the ceramic, filamentary growth can crack the electrolyte. A 2024 review summarizes these problems: “*interface problems between the Na metal anode and NASICON arise from mechanical, chemical, and electrochemical aspects (poor contact, insulating side-reaction products, and irregular dendrite growth)*”. To address this, researchers have proposed interlayers (thin buffer coatings on NASICON), alloy anodes, or simply avoiding pure Na metal anodes by using insertion anodes. For example, a thin functional interlayer (e.g. an artificial SEI) on NASICON was shown to form a stable  $\text{Na}^+$  conducting interphase, enabling stable Na plating/stripping for 120+ cycles in a Na|NASICON|Na cell. Composite approaches (covered later) can also improve contact (e.g. a polymer at the interface).

On the cathode side, NASICON is more forgiving. It is chemically compatible with many **common Na-ion cathodes** (such as  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  which itself is a NASICON-structured cathode, or layered oxides like  $\text{NaCrO}_2$ ). High temperature processing allows co-sintering or intimate contact in composite cathodes. Remaining challenges include CTE (thermal expansion) mismatch and ensuring percolation of ionic paths in composite electrodes.

**Recent innovation:** NASICON electrolytes have seen use in prototype solid-state sodium batteries. For instance, Wang *et al.* (2022) demonstrated a Na-metal all-solid battery with NZSP electrolyte and  $\text{Na}_3\text{V}_2(\text{PO}_4)_3$  cathode delivering stable capacity over 100+ cycles. More radically, a 2025 study incorporated NASICON in a **hybrid solid–liquid electrolyte**: a porous NASICON membrane soaked with a  $\text{NaClO}_4$  organic electrolyte, plus a specially designed “ion-anchoring” interlayer to stabilize the NASICON/liquid interface. This cell sustained **50,000 charge–discharge cycles** with ~86% capacity retention – an extraordinary cycle life, indicating that when interface issues are tamed (here by a hybrid approach), NASICON-based systems can meet the longevity requirements of grid storage. While a fully solid-state (dry) NASICON battery might not yet match that performance, these results build confidence that NASICON electrolytes can underpin durable, safe sodium batteries for large-scale applications.

## **β-Alumina and Other Oxide Electrolytes**

$\beta$ -alumina (and the closely related  $\beta''$ -alumina phase) was the first solid electrolyte enabling a practical sodium battery, and it remains relevant, especially for high-temperature systems. **Na  $\beta$ -alumina** has a layered crystal structure with conductive planes; its  $\text{Na}^+$  conductivity at ambient temperature is high ( $\sim 10^{-2}$  S/cm) in single crystals, but in practice  $\beta$ -alumina batteries operate at elevated temperature. At  $\sim 300^\circ\text{C}$ ,  $\beta$ -alumina exhibits superb ionic conductivity (several  $\times 10^{-1}$  S/cm) and negligible electronic conductivity, making it an excellent separator for molten sodium batteries. The classic Na-S and Na-NiCl<sub>2</sub> (“ZEBRA”) batteries both use  $\text{Na}^+$ - $\beta$ -alumina ceramic tubes as the electrolyte separator. These systems have been deployed for grid storage (Na-S in stationary grid banks) and even tested in electric vehicles (ZEBRA batteries in demonstration EVs), capitalizing on  $\beta$ -alumina’s reliable long-term performance at high temperature.

However, for **ambient-temperature solid-state batteries**,  $\beta$ -alumina is less favored. It suffers from mechanical brittleness and is difficult to densify without microscopic porosity (which leads to moisture sensitivity). Its conduction is largely 2D, so polycrystalline  $\beta$ -alumina with misoriented grains has lower effective conductivity. Moreover,  $\beta$ -alumina’s electrochemical stability window is limited – it cannot be directly paired with a sodium metal anode at room temperature (sodium will not wet its surface, and at  $300^\circ\text{C}$ , wetting is achieved only when sodium is molten). In summary,  $\beta$ -alumina is a *proven* solid electrolyte for high-temperature Na batteries on the grid, but for room-temperature Na-ion batteries, newer materials like NASICON or sulfides are preferable. Still, lessons from  $\beta$ -alumina (e.g. the importance of a clean, stable Na|electrolyte interface, and the viability of solid electrolytes in multi-kWh systems) continue to inform modern designs.

**Other oxide-based electrolytes:** Beyond NASICON and  $\beta$ -alumina, researchers have explored perovskite-type and glassy oxide electrolytes. Lithium battery research has a well-known garnet ( $\text{Li}_7\text{La}_3\text{Zr}_{12}\text{O}_{42}$ ) and perovskite ( $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ ) conductors; their sodium analogues generally show inferior conductivity. For example,  $\text{Na}_x\text{La}_{1-x}\text{TiO}_3$  perovskites and Na-stuffed garnets have been synthesized, but  $\text{Na}^+$  is usually too large for rapid migration in those structures (resulting in  $10^{-5}$ – $10^{-6}$  S/cm range conductivities). Some oxide–glass composites, such as  $\text{Na}_2\text{O}$ – $\text{SiO}_2$ – $\text{P}_2\text{O}_5$  glasses, can conduct  $\text{Na}^+$  at  $\sim 10^{-4}$  S/cm when optimized, and offer excellent stability and easy fabrication (they can be cast as glass and partially crystallized). In fact, one commercial Na-ion battery (Faradion’s technology, albeit not solid-state) uses a NASICON-type glass–ceramic separator. Overall, oxide solid electrolytes set the benchmark for stability and have enabled both historic and contemporary sodium battery prototypes. Their downsides are the high processing cost (sintering ceramics) and the interfacial resistance issues with Na metal – areas where other electrolyte classes sometimes hold an advantage.

## Sulfide-Based Solid Electrolytes

In recent years, sulfide solid electrolytes have gained attention as “superionic” conductors for solid-state sodium batteries. These materials are typically Na–S–P compounds (analogous to Li thiophosphates) and can achieve remarkably high Na<sup>+</sup> conductivities at room temperature. Sulfides are **attractive** because they tend to have *softer lattices* and *lower grain boundary resistance* than oxides, allowing cold or moderate-temperature pressing to form dense pellets without extreme sintering. They also often exhibit “*liquid-like*” ion transport, with some glasses or glass-ceramics showing very low activation energies for Na hopping.

**Key materials and conductivity:** The simple binary Na<sub>3</sub>PS<sub>4</sub> exists in multiple forms. A **tetragonal Na<sub>3</sub>PS<sub>4</sub>** was one of the first reported Na sulfide electrolytes, but it had modest ionic conductivity ( $\sim 10^{-6}$ – $10^{-5}$  S/cm at RT). Through mechanical milling or chemical substitution, a **cubic Na<sub>3</sub>PS<sub>4</sub>** phase can be stabilized, yielding higher conductivity on the order of  $10^{-4}$  S/cm. Further improvements came from **halide doping**: for example, partial replacement of S<sup>2-</sup> with Cl<sup>-</sup> in Na<sub>3</sub>PS<sub>4</sub> (to form Na<sub>3-x</sub>PS<sub>4-x</sub>Cl<sub>x</sub>) was guided by first-principles predictions to increase Na vacancy concentration and stabilize the cubic phase. Indeed, Cl-doped Na<sub>3</sub>PS<sub>4</sub> achieved  $\sim 4 \times 10^{-4}$  S/cm and enabled room-temperature Na–S all-solid batteries in a 2016 study.

The breakthrough in Na sulfides was the discovery of **Na<sub>3</sub>SbS<sub>4</sub>** and its doped variants. Na<sub>3</sub>SbS<sub>4</sub> has a different structure (not a glassy thiophosphate but a crystalline sulfide) and was found to conduct Na<sup>+</sup> in the  $10^{-3}$  S/cm range. By creating Na vacancies (via aliovalent doping of Sb<sup>5+</sup>), researchers achieved record conductivities: Na<sub>2.88</sub>Sb<sub>0.88</sub>W<sub>0.12</sub>S<sub>4</sub> boasts **0.032 S/cm at 25 °C** (in a sintered body), which is **the highest reported Na-ion conductivity** to date. This material also has improved stability against humid air (a common Achilles’ heel of sulfides) and can be densified at much lower temperatures ( $\sim 550$  °C) than oxide ceramics. Another high-performing composition is Na<sub>11</sub>Sn<sub>2</sub>PS<sub>12</sub>, a Na analog of the Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> family, with reported  $\sigma \sim 4 \times 10^{-4}$  S/cm. Table 1 compares these ionic conductivities.

- *Note on moisture sensitivity:* **Conventional sulfides (Na<sub>3</sub>PS<sub>4</sub>, Na<sub>3</sub>SbS<sub>4</sub>)** are sensitive to moisture/air – they can hydrolyze to release H<sub>2</sub>S gas. This necessitates handling in dry rooms or gloveboxes. The Na<sub>2.88</sub>Sb<sub>0.88</sub>W<sub>0.12</sub>S<sub>4</sub> formula mentioned above is noted to be more air-stable, but still likely requires controlled environment for long exposures. From a grid application perspective, this means packaging and system integration must isolate the electrolyte from ambient air. Encapsulation is feasible (as done in Li solid-state cells with sulfide electrolytes by companies like Samsung), but it adds to manufacturing complexity.

**Electrochemical stability:** Sulfide electrolytes generally have a narrower electrochemical window than oxides. They are prone to oxidation at relatively low voltages ( $\sim 2.5\text{--}3.5$  V vs  $\text{Na}^+/\text{Na}$ , depending on composition) and reduction at  $\sim 0$  V vs Na. For instance,  $\text{Na}_3\text{PS}_4$  will be reduced by a Na metal anode to form  $\text{Na}_2\text{S}$  and  $\text{Na}_3\text{P}$ , whereas at  $>3$  V it can oxidize, possibly forming polysulfides or  $\text{P}_2\text{S}_5$ . In practice, a *passivation layer* often forms: when Na metal is attached to a sulfide electrolyte, a thin interphase of  $\text{Na}_2\text{S}/\text{Na}_3\text{P}$  can form which thereafter protects against further decomposition (analogous to the solid-electrolyte interphase in liquid cells). However, this interphase may have poor mechanical properties and can allow dendrites to penetrate if the plating/stripping is not uniform. On the cathode side, the poor stability of sulfides against high-voltage oxides has been a serious issue – for example, direct contact of  $\text{Na}_3\text{PS}_4$  with a 3.8 V Na cathode leads to rapid capacity fade. One solution has been to introduce a stable coating or intermediate layer (like a polymer or a halide electrolyte) at the cathode interface. A recent advance paired a halide electrolyte ( $\text{Na}_{3-x}\text{Y}_{1-x}\text{Zr}_x\text{Cl}_6$ ) at the cathode to protect the sulfide from high voltage, enabling a cell to cycle 1000+ times with  $>89\%$  retention at  $40^\circ\text{C}$ . This highlights that while sulfides offer superb ionic conductivity (hence low internal resistance and potentially high power density), their *interfacial chemistry* needs careful management for long-term stability.

**Mechanical and interface aspects:** An advantage of sulfide electrolytes is their relative softness – unlike NASICON or  $\beta$ -alumina, sulfides can deform slightly to maintain contact at interfaces. They also can be cold-pressed into intimate contact with electrode powders to form composite electrodes. This **low interfacial resistance** (due to good physical conformability) is a big plus. For instance, assembling a Na/S all-solid-state cell with  $\text{Na}_3\text{PS}_4$  by cold-pressing is feasible, whereas oxide electrolytes often require a buffer or high-pressure cell assembly to achieve low contact resistance. On the flip side, the lower elastic modulus of sulfides means they may be less effective at suppressing dendrite penetration – if a high-current hotspot occurs, Na could pierce through a sulfide more easily than through a rigid oxide. Still, studies in Li cells show sulfides can sustain reasonably high critical current densities when dense and free of flaws.

**Recent innovations:** Besides compositional tweaks (halide doping, mixed-anion sulfides, etc.), research has produced new sulfide glass systems (e.g.  $\text{Na}_2\text{S}\text{--}\text{SiS}_2\text{--}\text{NaI}$  glasses) with high conductivity and better stability. Another trend is integrating sulfides in composite electrolytes (with polymers or oxides) to leverage their conductivity while mitigating drawbacks (discussed further in Composite section). Companies and labs are actively exploring sulfide-based Na solid-state batteries; for example, Toyota researchers have investigated  $\text{Na}_3\text{PS}_4$ -based cells as a low-cost alternative to Li sulfide batteries, and the U.S. DOE has funded development of Na sulfide electrolyte prototypes for stationary storage. The combination of high conductivity and processability makes sulfides very promising, but ensuring *stable interfaces (especially at the cathode)* remains the critical challenge for their use in long-life, grid-scale batteries.



# Halide and Hydride Solid Electrolytes

Beyond oxides and sulfides, other inorganic solids are emerging for sodium-ion conduction – notably **halide electrolytes** (Na salts of chlorides or bromides) and **complex hydrides/borates** (Na salts of closo-borate anions, etc.). These materials often trade some ionic conductivity for exceptional electrochemical stability or other unique benefits.

## Halide Electrolytes (Chlorides and Bromides)

Researchers recently identified metal halide frameworks as promising solid electrolytes for both Li and Na batteries. Halides such as  $\text{Na}_3\text{YCl}_6$ ,  $\text{Na}_4\text{ZrCl}_6$ , and mixed compositions ( $\text{Na}_{3-x}\text{Y}_{1-x}\text{Zr}_x\text{Cl}_6$ , etc.) conduct  $\text{Na}^+$  via vacancy-rich crystalline structures. A representative example is  **$\text{Na}_{3-x}\text{Y}_{1-x}\text{Zr}_x\text{Cl}_6$  (NYZC)**, reported in 2021 . This Na–Cl solid solution achieves  $\sim 6.6 \times 10^{-5}$  S/cm at ambient temperature – lower than NASICON or sulfides, but still orders of magnitude above typical cathode coating materials. What makes halides attractive is their **outstanding electrochemical stability and compatibility**. The NYZC chloride is stable up to  $\sim 3.8$  V vs Na and remains chemically inert in contact with oxide cathodes (which would rapidly degrade sulfides) . In fact, halide electrolytes have been shown to form extremely low-impedance interfaces with cathodes like  $\text{NaCrO}_2$ , without any need for additional coatings . They also tend to be stable against Na metal (their reduction products are often NaCl plus metal chlorides, which can form a passivating layer).

The origin of halides' stability is that the anions ( $\text{Cl}^-$ ,  $\text{Br}^-$ ) are less polarizable than sulfide anions and typically do not break down until high voltages. They also do not form passivating sulfide species that block ion flow; instead, any interphase (like NaCl) still allows Na-ion migration. Another advantage is **air stability** – many halide salts are not as moisture sensitive as sulfides. For instance,  $\text{Na}_3\text{YCl}_6$  can be handled briefly in air (though it may eventually pick up moisture and form hydrates if left exposed too long). This characteristic could simplify manufacturing and maintenance of solid-state sodium batteries, as glovebox conditions might be less stringent.

The downsides of halide electrolytes are their lower ionic conductivity (most are  $10^{-5}$ – $10^{-4}$  S/cm at RT) and mechanical properties (they are brittle salts, like table salt). Strategies to improve their conductivity include aliovalent doping to create more Na vacancies and exploring mixed-halide systems. One recent study (2024) introduced a “*dual-anion*” approach, combining halide and chalcogenide anions in one framework to yield higher conductivity (e.g. a chloride-

sulfide hybrid lattice). Halides may also find use not as the sole electrolyte, but as interfacial modifiers – for example, a thin layer of Na<sub>3</sub>YCl<sub>6</sub> on a cathode can protect a sulfide electrolyte beneath. Indeed, in a composite cathode with NaCrO<sub>2</sub>, adding Na<sub>3</sub>YCl<sub>6</sub> dramatically reduced impedance and enabled long cycling .

In summary, halide solid electrolytes offer a route to **high-voltage, stable sodium batteries** by addressing the interface issues that limit sulfides. Their moderate conductivity means they might be best used in conjunction with a higher-conductivity phase (like a sulfide or polymer). Nonetheless, their discovery is quite recent and they represent a new design space for Na solid electrolytes that could be important for achieving the voltage and stability needed in grid applications.

## Hydride and Closo-Borate Electrolytes

Another novel class of solid Na conductors is the complex hydrides, such as **sodium borohydrides and closo-borates**. Examples include NaBH<sub>4</sub>-based systems and Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> (sodium dodecaborate) salts. These materials emerged from hydrogen storage research and were later found to support fast ion conduction in their disordered phases. They often have low lattice densities and large cage-like anions (e.g. B<sub>12</sub>H<sub>12</sub><sup>2-</sup>), which can facilitate rapid cation transport.

One particularly interesting electrolyte is a **mixed-anion closo-borate**:

Na<sub>2</sub>(B<sub>12</sub>H<sub>12</sub>)<sub>0.5</sub>(B<sub>10</sub>H<sub>10</sub>)<sub>0.5</sub>. This compound was used as the electrolyte in a prototype 3 V all-solid Na-ion battery in 2017 . The cell, using a Na<sub>2</sub>Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> cathode (3.4 V vs Na) and a Na metal anode, showed stable reversible cycling with ~85 mAh/g capacity and retained >85% of capacity after 250 cycles . The closo-borate electrolyte's stability was key – it did not decompose up to ~4 V and allowed the cell to operate at room temperature with good capacity retention. The ionic conductivity of such closo-borates is reported in the 10<sup>-4</sup>–10<sup>-3</sup> S/cm range at 60–120 °C, but at room temperature they may be around 10<sup>-5</sup> S/cm unless nanostructured or mixed with a soft phase . Efforts are ongoing to improve their room-T performance (e.g. by forming solid solutions, applying external pressure , or developing glassy/metastable phases ).

Complex hydride electrolytes like Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub> have some **unique advantages**: they are extremely lightweight (good for gravimetric energy density), and some have wide electrochemical windows (the B–H bonds are quite robust against reduction/oxidation). They are

also non-toxic and composed of very cheap elements (Na, B, H). The main challenge is achieving sufficient ionic conductivity at ambient temperature; many require a slightly elevated temperature (40–80 °C) to reach the superionic state. There is also the issue of **volatility** – some hydrides can release H<sub>2</sub> or other gases if heated too much or if they react with moisture.

For grid storage where battery weight is not critical, the low density of hydrides is not a major advantage, and the handling complexity (sensitivity to moisture, etc.) could be a drawback. However, their stability with both Na metal and high-voltage cathodes is attractive. In a future scenario, closo-borate electrolytes might be paired with high-energy Na metal fluoride or sulfate cathodes to make 4 V-class solid-state cells. At present, they remain a niche research area relative to the more extensively studied oxides, sulfides, and polymers.

## Polymer-Based Electrolytes

Solid polymer electrolytes (SPEs) consist of a polymer matrix (typically ion-coordinating polymers like PEO, polycarbonates, polyacrylonitrile, etc.) doped with a sodium salt. They conduct via segmental motion of the polymer coordinating and transporting Na<sup>+</sup> ions. SPEs have been studied for sodium batteries due to their advantages in **flexibility, processability, and interfacial contact**. Unlike ceramics, polymers are soft and can conform to electrode surfaces, minimizing contact resistance. They can be made into thin films over large areas relatively easily (e.g. by casting), which is beneficial for scaling to large-format cells. Moreover, polymers are inherently non-flammable solids (though some can decompose at high temperature), which improves safety.

However, SPEs traditionally suffer from **low room-temperature ionic conductivity**. Sodium SPEs typically show  $\sigma \sim 10^{-6}$  to  $10^{-8}$  S/cm at 25 °C, far below liquid electrolytes ( $\sim 10^{-2}$  S/cm) and also below inorganic solid electrolytes ( $\sim 10^{-3}$  S/cm). For example, PEO with NaCF<sub>3</sub>SO<sub>3</sub> salt might exhibit  $\sim 10^{-7}$  S/cm at 25 °C and  $\sim 10^{-4}$  S/cm at 80 °C. The conductivity is strongly temperature-dependent because ion transport relies on polymer chain segmental motion, which is frozen at low temperature if the polymer is crystalline or glassy. A common approach is to operate such batteries at moderately elevated temperature (60–90 °C), where PEO becomes amorphous and ionic conductivity improves by orders of magnitude. This is viable for certain applications (and indeed high-temperature Na batteries already require heating), but for grid storage, constant heating is an inefficiency and adds complexity. Thus, researchers aim to formulate polymer electrolytes that work nearer to room temperature.

**Polymer design strategies:** Several avenues have been explored to improve Na-ion conductivity in polymers:

- **Polymer Structure:** Using polymers with lower glass transition temperatures ( $T_g$ ) or more amorphous character can enhance ion mobility. Examples include poly(trimethylene carbonate), poly(ethylene carbonate), or poly(ether-acrylate) systems which are amorphous at room T. Comb-shaped or crosslinked polymers that suppress crystallization of PEO segments have also been tried. These can yield conductivities in the  $10^{-5}$  S/cm range at room T in some cases .
- **Salt Selection:** The anion of the salt influences conductivity (through ion pairing and plasticization). Common salts are NaClO<sub>4</sub>, NaPF<sub>6</sub>, NaTFSI (sodium bis(trifluoromethanesulfonyl)imide), etc. Large, diffuse anions like TFSI<sup>-</sup> tend to dissociate well and plasticize the polymer, improving conductivity and lowering  $T_g$ . However, too high a salt concentration can increase viscosity and reduce mobility, so an optimal salt fraction is sought.
- **Plasticizers / Ionic Liquids:** Adding a small fraction of liquid solvent or ionic liquid creates a *gel polymer electrolyte*, which is technically not fully solid but can significantly boost ionic conductivity (into  $10^{-4}$ – $10^{-3}$  S/cm range) while maintaining leak-free operation. For instance, adding a few percent of ethylene carbonate or an ionic liquid to a PEO-based electrolyte can enable room-temp operation. The trade-off is the presence of volatile or liquid components that might compromise long-term stability.
- **Polymer Blends:** Mixing polymers (e.g. PEO with PVDF-HFP or PAN) can combine desirable properties. PVDF-based polymers have high dielectric constant (helping salt dissociation) and good mechanical strength, while PEO provides coordination sites. Such blends can be optimized for better performance than either polymer alone .

Despite advances, **pure SPEs still generally lag behind inorganic electrolytes** in conductivity and often in upper voltage stability (many polymers oxidize around 4–4.5 V vs Na<sup>+</sup>/Na, limiting high-voltage cathode use). Thus, fully polymer-based solid-state Na batteries often target low-voltage cathodes or Na–metal polymer cells operating at moderate temperature.

Encouraging results have been reported in prototype cells: e.g., a PVDF-based solid polymer electrolyte enabled a Na|Na symmetric cell cycling at room temperature without shorting, and a full cell Na<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>/hard carbon with a PVDF/PAN polymer electrolyte cycled stably at 60 °C . These indicate that polymer electrolytes can support sodium-ion transport in a working battery, though usually with some performance compromises (thicker electrolyte, higher temperature, or lower power).

For grid-scale storage, one could imagine large-format sodium polymer batteries that operate at, say, 60 °C in insulated enclosures (much like some lithium polymer batteries do, or like the high-

temp Na–S banks but at a far lower temperature). The polymer would make the system more tolerant to mechanical stress and easier to assemble in large sheets, potentially driving down costs. On the other hand, ensuring thousands of cycles and stable interfaces (particularly with a Na metal anode) remains a challenge – Na dendrites can still penetrate soft polymers if the current density is high and the polymer lacks sufficient shear modulus. One mitigation is to use **polymer-ceramic composites**, described next.

## Composite and Hybrid Electrolytes

Composite solid electrolytes combine two or more phases (ceramic–ceramic, polymer–ceramic, or solid–liquid hybrids) to leverage the advantages of each. This is a very active area of development for both Li and Na solid-state batteries, as it offers a way to balance ionic conductivity, mechanical properties, and interface compatibility.

### Polymer–Ceramic Composite Electrolytes

A common approach is dispersing ceramic filler particles into a polymer matrix to create a **Composite Polymer Electrolyte (CPE)**. In Na batteries, NASICON-type fillers are especially popular due to their high  $\text{Na}^+$  conductivity and stability. The inorganic filler provides fast ion-conduction pathways and can also serve as a skeleton that imparts mechanical rigidity, while the polymer phase ensures good interfacial contact with electrodes and flexibility. Notably, adding NASICON fillers to PEO or PVDF-based electrolytes has been shown to **increase ionic conductivity by 1–3 orders of magnitude** compared to the pure polymer. This is because the ceramic particles create continuous percolation pathways for  $\text{Na}^+$  and can disrupt polymer crystallinity, keeping the polymer amorphous and more ion-conductive. For example, a PEO + NaClO<sub>4</sub> electrolyte with 20% NASICON filler might achieve  $\sim 10^{-4}$  S/cm at room temperature, versus  $\sim 10^{-6}$  S/cm for PEO alone. Additionally, the filler-polymer interface can support ion transport if the polymer chains coordinated on the ceramic surface have faster dynamics (sometimes termed the “interfacial effect”).

Mechanically, CPEs are appealing because the ceramic phase can hinder the growth of dendrites by increasing the modulus, yet the composite is not as brittle as a fully ceramic pellet. A well-designed composite can be self-supporting as a thin film (like a separator) and tolerate bending or thermal cycling without cracking.

**Interfacial benefits:** CPEs also tend to have improved interfacial stability with electrodes. The polymer in the composite can form an intimate contact with the electrode (similar to a pure polymer electrolyte), filling in gaps at the micro-scale. Meanwhile, the inorganic particles can reduce the contact of the electrode with the bulk polymer, potentially reducing unwanted reactions (for instance, a ceramic at the interface with Na metal might form a stable interphase that blocks dendrites). Some studies have shown enhanced Na plating/stripping stability with polymer electrolytes after adding ceramic fillers, due to more uniform current distribution and higher surface area for deposition.

**Examples:** Recent reviews highlight NASICON-incorporated composites as a promising route. In one case, PVDF-HFP blended with  $\text{Na}_{0.3}\text{Zr}_{0.2}\text{Si}_{0.2}\text{PO}_{1.2}$  fibers yielded a flexible membrane with  $\sim 3 \times 10^{-5} \text{ S/cm}$  at  $30^\circ\text{C}$ , able to cycle Na|Na symmetric cells at  $0.1 \text{ mA/cm}^2$  for many hours without short-circuit. Another example used a PAN-based polymer with dispersed  $\text{Na}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  (a NASICON) to assemble a symmetric  $\text{Na}_{0.3}\text{V}_2(\text{PO}_4)_3/\text{Na}_{0.3}\text{V}_2(\text{PO}_4)_3$  full cell that operated at room temperature. The composite electrolyte enabled this cell to achieve stable cycling, whereas a pure polymer or pure ceramic alone might not have succeeded due to, respectively, low conductivity or poor contact.

**Challenges:** Despite their promise, polymer–ceramic composites must be carefully engineered. Achieving a uniform dispersion and good particle-polymer adhesion is crucial; otherwise, ion-conduction might still be bottlenecked by poorly percolating filler networks or blocked by polymer-rich regions. Also, adding a large volume fraction of ceramic (to maximize conductivity) can make the composite stiff and brittle, negating the mechanical benefits. There is an optimal range (often 5–30 vol% ceramic) for balanced properties. Moreover, if the ceramic is not stable against the polymer or salt, side reactions can occur (for instance, some ceramics might catalyze polymer degradation at high voltages or temperatures). Ensuring all components are mutually compatible over long periods is thus important for longevity.

## Hybrid Solid–Liquid Electrolytes

A “hybrid” electrolyte typically refers to systems that are mostly solid but contain a minor liquid or gel component to improve interface wetting. We mention them here because they represent a practical compromise on the road to fully solid-state batteries, especially for grid storage where reliability is paramount. One successful example, as noted earlier, is a **NASICON + liquid** hybrid: a porous NASICON separator filled with a conventional liquid electrolyte. The solid provides structural integrity, safety (preventing free flow of liquid and dendrites), and perhaps even some ionic conduction on its own, while the liquid ensures perfect interface contact and high ionic conductivity. The 2025 Nature Sustainability study employing NZSP (NASICON)

with a NaClO<sub>4</sub> liquid demonstrated the power of this approach – by eliminating the Na<sup>+</sup> depletion layer at the interface (through a special interlayer), they prevented degradation and achieved 50k deep cycles . Although this is not a completely solid-state battery, it shows a pathway to extreme durability.

Other hybrid configurations include polymer-coated ceramics (a thin polymer layer added to ceramic electrolyte surfaces to aid wetting with electrodes), and solid–liquid dual electrolyte systems (e.g. a solid electrolyte in the anode compartment and a liquid electrolyte in the cathode compartment, used in some “biphasic” cell designs). Such asymmetric designs might use a solid Na-metal interface for safety and a liquid on the cathode side for compatibility – a strategy that could bridge the gap until fully solid-state cells are perfected.

For grid-scale systems, one could envision a battery that uses a largely solid architecture but accepts a tiny amount of liquid or gel to ensure consistent performance. If that delivers the cycle life and safety needed, the small complexity of managing a minor liquid may be justified. Indeed, industrial development often pursues the most reliable solution rather than the most elegant fully solid design.

## Performance Comparison and Grid-Scale Suitability

Table 1 summarizes key properties of various solid electrolyte classes for sodium-ion batteries and comments on their suitability for grid-scale storage. It is clear that no single electrolyte is perfect – each has trade-offs. The choice may ultimately depend on the specific battery design and operating conditions. For instance, a high-temperature Na–S stationary battery can happily use  $\beta$ -alumina, whereas a room-temperature Na-ion battery for intermittent renewable storage might favor a NASICON or composite electrolyte for its balance of conductivity and stability.

**Ionic conductivity:** Oxide and sulfide ceramics currently lead in room-T conductivity ( $10^{-3}$ – $10^{-2}$  S/cm), with polymers lagging ( $\sim 10^{-6}$  S/cm) unless heated . Composite electrolytes seek to achieve  $\sim 10^{-4}$ – $10^{-3}$  S/cm at ambient, which is a reasonable target for low-power applications. For grid storage, internal resistance must be low to minimize energy loss – high conductivity electrolytes help, but so does making the electrolyte thin. Even a  $10^{-4}$  S/cm electrolyte can be acceptable if it’s only a few tens of microns thick in a cell. Thus, processability into thin films is as important as bulk conductivity. Polymers and composites have an edge in ease of making thin membranes, whereas brittle ceramics often end up thicker (hundreds of microns) to avoid fracture.

**Stability and lifespan:** Grid storage batteries must last 5,000–10,000 cycles (which could correspond to 15–20 years of operation). This puts a premium on electrolytes that do not degrade over time. Inorganic solids are intrinsically stable (they won't evaporate or decompose under normal conditions), but their *interfaces* can degrade (e.g. growing resistance at a grain boundary or electrode interface). Polymers might slowly oxidize or suffer from dendrite damage. At the cell level, maintaining stable cycling means preventing continuous side reactions at interfaces and avoiding short-circuits. Many solid electrolytes form some interphase with Na metal or cathodes initially – the key is that it be self-limiting and stable thereafter. For example, NASICON may form a thin  $\text{Na}_x\text{P}_y\text{O}_z$  layer at a Na interface that then stops growing and allows stable cycling. Sulfides might form a Na<sub>2</sub>S-rich interphase that if too thick, increases impedance and needs to be controlled (perhaps by an alloy anode instead of pure Na). Interface engineering (coatings, buffer layers) is thus a central theme to achieve long life.

**Manufacturability and cost:** For grid deployment, the electrolyte must be inexpensive in bulk and amenable to large-scale production. NASICON-type and  $\beta$ -alumina use reasonably abundant elements (Na, Al, Zr, Si, P), but the ceramic processing (high-temp furnaces, polishing of discs, etc.) can be costly. Sulfides use cheaper processing (ball milling, cold pressing) and mostly cheap elements (Na, S, P – though some use Ge or Sb in small amounts). Polymers are made by solution casting or extrusion, which is very scalable and low-cost per area; their raw materials (ethylene oxide polymers, common salts) are also affordable. Thus, from a pure cost perspective, polymer or sulfide electrolytes could be cheaper than oxide ceramics for large battery farms, provided safety can be managed (sulfides need encapsulation to prevent H<sub>2</sub>S release, etc.). The table below qualitatively rates suitability for grid-scale based on these considerations.

**Safety:** All solid electrolytes are inherently non-flammable, a huge plus for stationary storage which often is installed in populated areas (buildings, substations, etc.). By eliminating liquid electrolytes, solid-state Na batteries could greatly reduce the risk of fires or thermal runaway – note that even Na metal, while reactive, is safer in a solid-state cell because it is not in free contact with organic solvent. Solid electrolytes also permit designs that *compartmentalize failure* – for instance, a crack in one cell's electrolyte doesn't necessarily lead to a cascading fire as a leaking liquid might. This safety argument is one of the strongest in favor of solid-state sodium batteries for grid applications, which prioritize reliability and low hazard over absolute energy density.

Electrolyte Class	Example Composition	Ionic Conductivity (RT)	Stability & Interface Notes	Grid-Scale Suitability
<strong>NASICON-type Oxide</strong>	$\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$ (NZSP) and variants	$\sim 1\text{--}5 \times 10^{-3} \text{ S/cm}$	[oai_citation:82#mdpi.com] ( <a href="https://www.mdpi.com/2673-3293/6/1/6#:~:text=match%20at%20L698%20results%20in,of%20the%20ionic%20conduc">https://www.mdpi.com/2673-3293/6/1/6#:~:text=match%20at%20L698%20results%20in,of%20the%20ionic%20conduc</a>	



tivity%20of) (high among solids)</td><td>Stable up to ~5 V vs Na; reacts with Na metal (forms resistive interphase)  
[[oai\\_citation:83#doaj.org](https://doi.org/10.1039/c8ta00000a)] (<https://doi.org/article/90d5b0b644764c36896d28e97cc978d0#:~:text=electrodes,we%20systematically%20analyze%20and%20logically>); very good with cathodes; rigid, brittle ceramic</td><td>Proven in lab cells; needs interface engineering for Na metal. Scalable via sintering (costly). Good for long-life cells if interfaces stabilized.</td></tr>

<tr><td><strong> $\beta$ -Alumina (Oxide)</strong></td><td>NaAl<sub>11</sub>O<sub>17</sub> ( $\beta$ "-alumina phase)</td><td>~1.4×10<sup>-2</sup> S/cm (single crystal)  
[[oai\\_citation:84#mdpi.com](https://www.mdpi.com/2673-3293/6/1/6#:~:text=match%20at%20L683%20conductivity%20,which%20allows%20water%20molecules%20to)] (<https://www.mdpi.com/2673-3293/6/1/6#:~:text=match%20at%20L683%20conductivity%20,which%20allows%20water%20molecules%20to>); polycrystals lower; requires 300 °C in use</td><td>Functions only at high T (Na anode must be molten); highly stable with molten Na, used in Na-S cells  
[[oai\\_citation:85#mdpi.com](https://www.mdpi.com/2673-3293/6/1/6#:~:text=properties.%20Na%20CE%20B2,119%5D.%20Thus%2C%20in)] (<https://www.mdpi.com/2673-3293/6/1/6#:~:text=properties.%20Na%20CE%20B2,119%5D.%20Thus%2C%20in>); moisture-sensitive when cool  
[[oai\\_citation:86#mdpi.com](https://www.mdpi.com/2673-3293/6/1/6#:~:text=electrochemical%20stability, and%20its%20reliance%20on%20tw)] (<https://www.mdpi.com/2673-3293/6/1/6#:~:text=electrochemical%20stability, and%20its%20reliance%20on%20tw>o)</td><td>Used in commercial high-T Na batteries for grid. Not suitable for ambient-T operation, but demonstrated multi-year durability at 300 °C.</td></tr>

<tr><td><strong>Sulfide (Thiophosphate)</strong></td><td>Na<sub>3</sub>PS<sub>4</sub> (base); Na<sub>2.88</sub>Sb<sub>0.88</sub>W<sub>0.12</sub>S<sub>4</sub> (doped)</td><td>~2×10<sup>-4</sup> S/cm (Na<sub>3</sub>PS<sub>4</sub>)  
[[oai\\_citation:87#mdpi.com](https://www.mdpi.com/2673-3293/6/1/6#:~:text=%28%3E10%E2%88%924%20S%20cm%E2%81%BB, but)] (<https://www.mdpi.com/2673-3293/6/1/6#:~:text=%28%3E10%E2%88%924%20S%20cm%E2%81%BB, but>); up to 3.2×10<sup>-2</sup> S/cm (best doped)  
[[oai\\_citation:88#pmc.ncbi.nlm.nih.gov](https://pubmed.ncbi.nlm.nih.gov/articles/PMC6868223/#:~:text=Solid%20electrolytes%20are%20key%20materials,4%7D.%20More over%2C%20this%20sulfide%20possesses)] (<https://pubmed.ncbi.nlm.nih.gov/articles/PMC6868223/#:~:text=Solid%20electrolytes%20are%20key%20materials,4%7D.%20More over%2C%20this%20sulfide%20possesses>)</td><td>Very low interfacial resistance (soft, good contact); sensitive to air/humidity (H<sub>2</sub>S release)  
[[oai\\_citation:89#pmc.ncbi.nlm.nih.gov](https://pubmed.ncbi.nlm.nih.gov/articles/PMC6868223/#:~:text=tungsten%20introduces%20sodium%20vacancies%20and, large%20 energy%20and%20power%20densities)] (<https://pubmed.ncbi.nlm.nih.gov/articles/PMC6868223/#:~:text=tungsten%20introduces%20sodium%20vacancies%20and, large%20 energy%20and%20power%20densities>); narrow stability window - poor vs >3 V cathodes [oai\_citation:90#nature.com] (<https://www.nature.com/articles/s41467-021-21488-7#:~:text=Rechargeable%20solid,6>), moderate vs Na metal (forms Na<sub>2</sub>S/Na<sub>3</sub>P interphase)</td><td>High conductivity enables high power. Handling/encapsulation adds cost. Promising if paired with protected interfaces (e.g. cathode coating). Already studied for Na-S solid-state cells.</td></tr>

<tr><td><strong>Halide (Chloride/Bromide)</strong></td><td>Na<sub>3</sub>YCl<sub>6</sub>, Na<sub>3-x</sub>Y<sub>1-x</sub>Zr<sub>x</sub>Cl<sub>6</sub> (NYZC)</td><td>~10<sup>-5</sup> S/cm  
[[oai\\_citation:91#nature.com](https://www.nature.com/articles/s41467-021-21488-7#:~:text=Here%2C%20we%20report%20the%20discovery, at%20room)] (<https://www.nature.com/articles/s41467-021-21488-7#:~:text=Here%2C%20we%20report%20the%20discovery, at%20room>) (up to 10<sup>-4</sup> S/cm with doping)</td><td>Stable to ~3.8 V vs Na  
[[oai\\_citation:92#nature.com](https://www.nature.com/articles/s41467-021-21488-7#:~:text=Here%2C%20we%20report%20the%20discovery, at%20room)] (<https://www.nature.com/articles/s41467-021-21488-7#:~:text=Here%2C%20we%20report%20the%20discovery, at%20room>); excellent compatibility with oxide cathodes (minimal side reactions)  
[[oai\\_citation:93#nature.com](https://www.nature.com/articles/s41467-021-21488-7#:~:text=Rechargeable%20solid,6)] (<https://www.nature.com/articles/s41467-021-21488-7#:~:text=Rechargeable%20solid,6>); decent with Na metal (forms NaCl); air-stable compared to sulfides</td><td>Lower conductivity requires mixing

with other electrolyte or thin layers. Great as interfacial layer for high-voltage operation. Could be used in hybrid systems to improve stability.

**Hydride/Borate** Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub>,

Na<sub>2</sub>(B<sub>12</sub>H<sub>12</sub>)<sub>0.5</sub>(B<sub>10</sub>H<sub>10</sub>)<sub>0.5</sub> ~10<sup>-5</sup> S/cm (RT), 10<sup>-3</sup> S/cm at 80 °C

[oai\_citation:94#pubs.acs.org] (<https://pubs.acs.org/doi/10.1021/acs.chemmater.7b02902#:~:text=Li2B12H12%2C%20Na2B12H12%2C%20and%20their%20closo,new%20class%20of%20candidate>) Wide stability window (3-4 V)

[oai\_citation:95#pubs.rsc.org] ([https://pubs.rsc.org/en/content/articlelanding/2017/ee/c7ee02420g#:~:text=We%20report%20on%20a%20particularly,that%20owing%20to%20their%20high](https://pubs.rsc.org/en/content/articlelanding/2017/ee/c7ee02420g#:~:text=We%20report%20on%20a%20particularly,that%20owing%20to%20their%20high);)); chemically stable with Na metal (no violent reaction); some are air-sensitive (hydrate) but no toxic gas Needs moderate heating or pressure for good conductivity. Unproven at scale; potentially useful for specialized high-voltage cells. Low cost materials but immature tech.

**Polymer (SPE)** PEO + NaTFSI; PVDF-HFP + NaClO<sub>4</sub>, etc. ~10<sup>-6</sup> S/cm (RT); ~10<sup>-4</sup> S/cm at 60-80 °C

[oai\_citation:96#mdpi.com] (<https://www.mdpi.com/2673-3293/6/1/6#:~:text=,have%20lower%20ionic%20conductivity%2C%20around>)

[oai\_citation:97#mdpi.com] (<https://www.mdpi.com/2673-3293/6/1/6#:~:text=10%E2%88%926%20to%2010%E2%88%928%20S%2Fcm%20,incorporating%20ceramic%20fillers%20into%20a>) Oxidative stability ~4 V (limited for high-voltage cathodes); prone to Na dendrites at high current (soft); excellent flexibility and contact; non-flammable solid but can decompose when overheating Easy to make large-area films at low cost. Likely needs heating for adequate performance - acceptable in stationary setting. Might serve in low-cost, lower-power grid batteries with thermal management.

**Composite (Polymer-Ceramic)** PEO + NASICON filler; PVDF + Na<sub>3</sub>PS<sub>4</sub> filler, etc. ~10<sup>-5</sup>-10<sup>-4</sup> S/cm (RT)

[oai\_citation:98#mdpi.com] (<https://www.mdpi.com/2673-3293/6/1/6#:~:text=Composite%20polymer%20electrolytes%20,The>) (depends on mix and temp) Improved mechanical strength vs pure polymer (helps block dendrites) [oai\_citation:99#mdpi.com] (<https://www.mdpi.com/2673-3293/6/1/6#:~:text=properties,ion%20transport>); still limited to ~4 V by polymer matrix; interface-friendly (polymer wets electrodes, ceramic aids conductivity) [oai\_citation:100#mdpi.com] (<https://www.mdpi.com/2673-3293/6/1/6#:~:text=Among%20various%20electrolytes%2C%20composite%20polymer,NA> SICON%20fillers%20in%20optimizing%20the) Considered a practical compromise - can be made thin and large-area, performance is intermediate. Good candidate for early solid-state Na batteries for grid if high conductivity fillers are used.

**Hybrid (Solid-Liquid)** NASICON + organic liquid (e.g. NZSP + NaClO<sub>4</sub> PC electrolyte) ~10<sup>-3</sup> S/cm (by liquid percolation) No dendrites (solid framework) and low interface resistance (liquid wetting) - best of both worlds; but contains flammable liquid in small quantity; requires sealing Highly promising for ultra-long life: achieved 50k cycles in lab

[oai\_citation:101#nature.com] ([https://www.nature.com/articles/s41893-025-01544-](https://www.nature.com/articles/s41893-025-01544-6#:~:text=eliminate%20the%20Na%20vacancies%20layer%2C,potential%20for%20wides)

6#:~:text=eliminate%20the%20Na%20vacancies%20layer%2C,potential%20for%20wides

pread%20practical%20applications). Could be a bridge to full solid-state; complexity of liquid management is a drawback but manageable in stationary systems.</td></tr>  
</table>

**Table 1:** Comparison of solid electrolyte classes for Na-ion batteries, with representative properties and notes on suitability for grid-scale storage. *RT = room temperature. Where a range is given, values depend on specific composition or preparation.* Citations indicate sources for listed conductivity or stability data.

## Technical Challenges and Outlook

While significant progress has been made in developing solid electrolytes for sodium batteries, several technical challenges must be overcome to fully realize grid-scale solid-state Na-ion batteries:

- **Interfacial Engineering:** Perhaps the most critical issue is managing the interfaces between solid electrolytes and electrodes. As discussed, each class of electrolyte has its own interface quirks – oxides may form resistive films with Na metal, sulfides may have reactivity with high-voltage cathodes, polymers may allow dendrite penetration due to low modulus. Advancements like artificial interphases (NaF, polymer or halide coatings), graded interfaces, and alloy anodes (e.g. Na–Sn instead of pure Na) are being actively researched to address these issues. The 50,000 cycle hybrid cell is a testament that with proper interface design (in that case, an ion-anchoring interlayer on NASICON), the solid electrolyte can sustain extraordinary cycling without degradation. Going forward, **interface stability** under deep cycling and large depth-of-discharge will be a key focus – especially for grid storage where batteries are cycled daily and downtime must be minimized.
- **Dendrite Suppression:** Solid electrolytes were once thought to be immune to dendrites, but we now know Na (and Li) metal can indeed infiltrate many solids if conditions are right (e.g. high current, defects). Materials with higher shear modulus (ceramics) provide more resistance to dendrite growth, but they can still fail along grain boundaries or cracks. Improving mechanical properties (e.g. by using composites or prestressing the electrolyte) and limiting current hot spots (through cell design and interface engineering) will be necessary. Fortunately, grid applications typically involve **lower current densities** (charging over hours, not minutes), which is less aggressive for dendrite formation compared to EV batteries. This means solid-state sodium batteries for grid use can operate under relatively gentle conditions, making dendrite issues more manageable if proper safety margins are in place.
- **Manufacturing at Scale:** For solid electrolytes to be used in large-scale storage, they must be produced in large quantities economically. This includes synthesizing the electrolyte material and incorporating it into cells (e.g. making hundreds of square meters of electrolyte separator for a MWh-scale system). Ceramics will need scalable sintering

or tape-casting methods; some companies are exploring co-sintering electrolyte and cathode or using ceramic tape laminates. Polymers and composites could potentially use roll-to-roll processing similar to today's battery separators. Ensuring uniform thickness, no pinholes/defects, and consistent performance across large areas is a non-trivial engineering challenge. However, the battery industry has experience with large-format separators and electrodes, which can be leveraged.

- **Operating Conditions:** Solid-state sodium batteries might operate across a range of temperatures in the field. Unlike Li-ion which usually operates near room T, Na solid-state designs might purposefully run at slightly elevated temperature (to boost ion conductivity) or might need to survive cold climates (where polymer electrolytes could stiffen, for example). Designing systems that can self-heat or maintain optimal temperature will be important. For grid storage, thermal management is easier than in electric vehicles since weight/space are less constrained – a battery container could include heating elements or insulation to keep cells at, say, 40–60 °C if that significantly improves performance. This would be much simpler than maintaining 300 °C as in current Na–S systems, and the round-trip efficiency hit would be smaller.
- **Integration with Grid Systems:** Finally, beyond materials science, one should consider how solid-state Na batteries integrate at system level. One advantage is safety – solid-state cells might be packed more tightly without elaborate cooling or fire suppression, potentially improving the footprint of storage installations. If cycle life can indeed reach tens of thousands of cycles (as indicated by recent research), solid-state Na batteries could outlast many current Li-ion systems, reducing replacement costs. The use of abundant sodium and mostly non-toxic, recyclable materials (glass, ceramics, polymers) also improves the sustainability profile of these batteries – an increasingly important factor for grid deployments funded by “green” initiatives.

In conclusion, the landscape of solid electrolytes for sodium-ion batteries is rich and rapidly evolving. **Historically important electrolytes** like  $\beta$ -alumina proved the concept of solid-state Na batteries decades ago in high-temperature systems. **NASICON-type ceramics** have emerged as frontrunners for ambient solid-state Na batteries due to their combination of high conductivity and stability. **Sulfide electrolytes** provide superionic conductivity that can unlock high power density, though they demand careful handling and interface protection. **Polymer and composite electrolytes** offer practical engineering solutions with lower intrinsic performance but great processing advantages, possibly enabling cheaper large-scale manufacturing. **Hybrid approaches** are demonstrating that many of the remaining obstacles (cycle life, interface impedance) can be overcome by clever material combinations.

For grid-scale energy storage, where the priorities are longevity, safety, and cost, solid-state sodium batteries hold tremendous promise. They capitalize on sodium's strengths (abundance and low cost) and mitigate the safety issues of liquid electrolytes. Ongoing improvements in solid electrolyte materials directly impact feasibility: higher ionic conductivity lowers resistance losses, better stability allows compatible high-voltage/high-capacity electrodes (increasing

energy density), and durable interfaces ensure the batteries can cycle for years with minimal maintenance. If current research trends continue, the coming years may see prototype solid-state Na-ion battery modules being tested for grid storage – potentially offering a safe and sustainable complement to lithium-ion in the renewable energy infrastructure. As one review article aptly stated, quoting the appeal of sodium solid-state batteries: *“Quoting the abundance and cost of sodium reserve and robustly safe and high-energy solid electrolytes, sodium solid-state batteries exhibit huge promise for future energy storage applications”*. The advances in solid electrolyte materials are paving the way toward making that promise a reality.