Solid-Electrolyte Advances Enabling Grid-Scale Sodium-Ion Storage

1. Introduction:

The increasing integration of intermittent renewable energy sources, such as wind and solar power, into the electrical grid necessitates the development of robust and efficient grid-scale energy storage solutions to ensure a stable and reliable power supply.[1] The inherent variability of these renewable sources requires energy storage systems capable of capturing excess power during peak generation and releasing it when demand is high or generation is low. While lithium-ion batteries (LIBs) have become a dominant technology in various energy storage applications, their widespread use in grid-scale deployments faces challenges related to the cost and availability of lithium resources, as well as safety concerns associated with the flammable liquid electrolytes commonly employed.[4] The geographical concentration of lithium reserves creates vulnerabilities in the supply chain and contributes to price volatility, prompting the exploration of alternative battery technologies. Furthermore, the flammability of liquid electrolytes poses a significant safety risk, particularly in large-scale stationary energy storage systems.

Sodium-ion batteries (SIBs) have emerged as a promising alternative to LIBs, primarily due to the abundance and lower cost of sodium.[4] Sodium is a readily available element found in seawater and mineral deposits, making its extraction less energy-intensive and geographically constrained compared to lithium. This inherent advantage translates to potentially lower raw material costs for SIBs, making them an economically attractive option for large-scale energy storage. Although SIBs generally exhibit a lower energy density compared to LIBs, they possess significant potential for stationary applications such as grid energy storage, where cost and cycle life are often more critical performance parameters than energy density.[6] Grid storage systems are typically stationary installations, allowing for larger and heavier battery packs, thus shifting the focus towards minimizing the cost per unit of stored energy and maximizing the number of charge-discharge cycles the battery can endure.

The incorporation of solid-state electrolytes (SSEs) into sodium-ion batteries offers the potential for significant advancements in both safety and performance, particularly for grid-scale applications.[4] By replacing the flammable liquid electrolytes used in conventional batteries with non-flammable solid materials, the risk of fire and explosion is substantially reduced. This enhanced safety profile is particularly crucial for large-scale deployments where safety is paramount. Furthermore, SSEs can potentially enable the use of sodium metal anodes, which possess a high theoretical capacity, thereby offering a pathway to achieving higher energy densities in SIBs.[4] Sodium metal has a much higher theoretical energy storage capacity than the carbon-based anodes typically used in SIBs with liquid electrolytes. However, sodium metal is highly reactive with liquid electrolytes and tends to form dendrites during charging and discharging, which can lead to short circuits. Solid electrolytes have the potential to suppress dendrite formation and facilitate the stable use of sodium metal anodes. This report aims to provide a comprehensive review of the recent progress in solid electrolytes for sodium-ion batteries, focusing on their properties, performance, and suitability for grid-scale energy storage. The discussion will encompass various types of SSEs, the key factors enabling their advancements, the challenges that remain to be addressed, and the future research directions in this rapidly evolving field.

2. Advantages of Solid-State Sodium Batteries for Grid-Scale Energy Storage:

The utilization of solid-state electrolytes in sodium-ion batteries presents several compelling advantages that make them particularly attractive for grid-scale energy storage applications. One of the most significant benefits is the enhanced safety compared to traditional batteries that rely on flammable liquid electrolytes.[8]The elimination of these volatile liquids drastically reduces the risk of fire and explosion, a critical consideration for large-scale stationary installations where a high density of energy storage is required. Grid-scale battery systems often comprise a multitude of interconnected cells, and a single cell failure in a liquid electrolyte system can propagate to adjacent cells, potentially leading to thermal runaway and catastrophic events. Solid electrolytes, being non-flammable solids, inherently mitigate this risk. Moreover, many SSEs exhibit non-volatile characteristics and greater thermal stability, allowing for safer operation across a broader temperature spectrum.[8] This improved thermal stability can simplify the design of thermal management systems in grid storage facilities, potentially leading to reductions in both cost and complexity. Traditional batteries with liquid electrolytes often require active cooling or heating to maintain optimal performance and safety within a limited temperature range. The physical robustness of solid electrolytes also contributes to enhanced safety and longevity by providing resistance to leakage and rupture, which are common failure modes in liquid electrolyte systems.[8] Leaks can lead to performance degradation and safety hazards, while ruptures can result in the release of flammable and corrosive liquids. The solid nature of SSEs effectively eliminates these concerns, contributing to more reliable and durable battery systems for grid applications.

Solid-state sodium batteries also offer the potential for higher energy density and extended cycle life, which are crucial for the economic viability and long-term operation of grid storage systems.[4] The ability of SSEs to enable the use of high-capacity sodium metal anodes can lead to higher energy densities compared to conventional SIBs that utilize carbonaceous anodes. While cost and cycle life are primary considerations for grid storage, achieving higher energy density can be advantageous in scenarios where space is limited or longer discharge durations are required. Furthermore, solid electrolytes can offer greater resistance to wear and degradation compared to liquid electrolytes, potentially resulting in a longer lifespan and a higher number of charge-discharge cycles. The stable interface formed between the solid electrolyte and the electrodes can minimize undesirable side reactions and structural degradation that typically limit the lifespan of batteries employing liquid electrolytes. Impressively, research into hybrid electrolytes has even demonstrated the potential for exceptionally long cycle life, with one study reporting a hybrid electrolyte system capable of sustaining 50,000 cycles.[15] This extended cycle life is particularly beneficial for grid storage applications that demand frequent charging and discharging over many years.

The thermal stability of certain SSEs can also translate to a wider operating temperature range for solid-state sodium batteries.[8] This allows for operation at higher temperatures without electrolyte decomposition, potentially simplifying thermal management strategies. A wider operating temperature range can enhance the flexibility and resilience of grid storage systems in diverse environmental conditions, reducing the need for complex and energy-intensive temperature control systems.

A key driver for the development of sodium-ion batteries, including their solid-state variants, is the cost-effectiveness and abundance of sodium resources.[4] The readily available nature of sodium translates to lower raw material costs, making SSSBs a potentially more economical option for large-scale energy storage compared to LIBs, which rely on more scarce and geographically concentrated lithium resources. Moreover, the production of sodium from sources like soda ash supports environmentally friendly practices, avoiding the energy-intensive and potentially damaging processes often associated with lithium mining.[7] This enhanced sustainability profile further adds to the appeal of SSSBs for grid-scale deployment.

Considering the specific demands of stationary energy storage, the current limitations of SIB energy density compared to LIBs are less of a concern.[6] For grid storage, the ability to store and discharge large amounts of energy over extended periods and withstand numerous charge-discharge cycles are paramount. The inherent cost-effectiveness and the potential for long cycle life offered by SSSBs make them particularly well-suited for these requirements. Furthermore, the scalability of sodium-ion battery technology makes it suitable for the large-scale energy storage deployments necessary for grid applications.[2] Grid storage projects often necessitate massive battery installations with capacities ranging from megawatt-hours to gigawatt-hours. The abundance of sodium resources and the potential for cost-effective manufacturing are crucial factors in achieving this level of scalability.

3. Recent Advances in Solid Electrolytes for Sodium-Ion Batteries:

Significant progress has been made in the development of various types of solid electrolytes for sodium-ion batteries, each with its unique characteristics and potential for grid-scale applications.

3.1 Inorganic Solid Electrolytes:

Among inorganic solid electrolytes, oxide-based materials have been extensively investigated. NASICON (Na Super Ion Conductor) type electrolytes, particularly $Na_3Zr_2Si_2PO_{12}$ (NZSP), have shown high ionic conductivity, with recent advancements in manufacturing techniques such as solution-assisted solid-state reaction, spark plasma sintering, and sol-gel reduction enabling conductivities as high as approximately

2 mS cm^{-1}.[16] The structural flexibility of NASICON materials allows for compositional modifications to further enhance the transport of sodium ions.[14] Researchers are also actively addressing the challenge of high interfacial resistance between NASICON electrolytes and electrodes through strategies like doping the electrolyte and employing wetting agents such as polyvinyl-based polymers, which have demonstrated ionic conductivities of 1.31 mS cm^{-1}.[16] β-alumina is another well-known oxide electrolyte that has been historically used in high-temperature sodium-sulfur batteries. Current research focuses on improving its room-temperature performance by increasing the content of the more conductive β″-Al_2O_3 phase and through ion doping.[14]However, challenges remain in preventing the formation of sodium dendrites at room temperature when using β-alumina.[17]

Sulfide-based solid electrolytes have garnered considerable attention due to their exceptionally high ionic conductivity, often surpassing that of oxide-based electrolytes at room temperature. Examples include Na_3PS_4 and $Na_{11}Sn_2P_2S_{12}$.[14] These materials also offer advantages such as lower synthesis temperatures, superior mechanical properties like ductility, and good contact with electrodes.[14] Various doping strategies, such as doping Na_3PS_4 with calcium or chlorine and Na_3SbS_4 with tungsten or molybdenum, have proven effective in further enhancing their ionic conductivity.[14] A key limitation of traditional sulfide electrolytes is their sensitivity to air and moisture. However, recent advancements have led to the development of more air-stable sulfide electrolytes, such as tungsten-doped Na_3SbS_4.[14] Surface modification of sulfide electrolytes with oxysulfide glass has also been explored as a means to improve interface stability and cycling performance in all-solid-state sodium batteries.[16] Despite these advancements, the inherent sensitivity to water and the relatively narrow electrochemical stability window of sulfide electrolytes remain areas requiring further research.[17]

Halide-based electrolytes represent another promising class of inorganic solid electrolytes. The discovery of ion conductors like Na_3<0xE2><0x82><0x8B>$_xY_1$<0xE2><0x82><0x8B>$_xZr_xCl_6$ (NYZC) with high electrochemical stability up to 3.8 V against Na/Na^+ and good chemical compatibility with oxide cathodes marks a significant advancement in this area.[16] These materials exhibit high ionic conductivity attributed to abundant sodium vacancies and a cooperative rotation mechanism within their structure, leading to low interfacial impedance and excellent cycling performance in full cells.[16]

Borohydride-based electrolytes, with their unique cage-like structures, have also emerged as promising candidates, exhibiting high ionic conductivity even at low temperatures. For instance, a combination of $NaB_{11}H_{14}$ and $Na_2B_{12}H_{12}$ has achieved a conductivity of 4 mS cm^{-1} at 20 °C.[14] Recent developments include hydroborate-based electrolytes that demonstrate not only high ionic conductivity but also a high transference number and a wide electrochemical stability window of up to 6 V.[14]

Antiperovskite-based electrolytes, such as Na_3OBr and Na_4OI_2, represent a relatively new class of inorganic solid electrolytes that have shown improved ionic conductivity.[14] Theoretical studies suggest that these materials possess low activation energies for sodium ion migration, indicating their potential for high performance.[14]

P-2-type layered oxide electrolytes, such as $Na_2M_2TeO_6$, offer an alternative to NASICON electrolytes, featuring a layered structure that facilitates two-dimensional migration of sodium ions.[14] Doping these materials with elements like magnesium, nickel, gallium, and calcium has been shown to increase sodium ion concentration and enlarge the pathways for ionic transport, leading to improved ionic conductivity. Notably, gallium-doped $Na_2Zn_2TeO_6$ has demonstrated particularly high conductivity at ambient temperatures. Furthermore, increasing the interlayer spacing in these structures has been identified as a crucial factor in enhancing ionic conductivity.[14]

3.2 Organic Solid Electrolytes:

Organic solid electrolytes, including solid polymer electrolytes (SPEs), gel polymer electrolytes (GPEs), and plastic crystal electrolytes (PCEs), offer distinct advantages such as mechanical flexibility and ease of processing.[17] However, SPEs typically suffer from low ionic conductivity at room temperature. To address this, researchers are exploring various strategies such as copolymerization, the addition of plasticizers like ionic liquids, and the incorporation of fillers like inorganic nanoparticles and metal-organic frameworks.[17] Examples of SPEs under investigation include those based on PEO, PVDF, and even biodegradable polymers like carboxymethyl cellulose.[17] GPEs represent an intermediate state between solid and liquid electrolytes and often exhibit higher ionic conductivity than SPEs. PEO-based GPEs with cross-linked structures and immobilized liquid electrolytes have shown excellent performance, including high ionic conductivity and stability with sodium metal anodes.[17] Similarly, PVDF-HFP-based and PAN-based GPEs have demonstrated promising results.[17] Innovative designs such as 3D ion conductive networks and in-situ polymerized electrolytes are also being explored to further enhance the performance of GPEs.[17] PCEs are a newer class of organic solid electrolytes that can achieve high ionic conductivity at room temperature due to their unique crystal structures. Succinonitrile (SCN) is a prominent example, reaching conductivities up to 1×10^{-3} S cm^{-1} [[17]. To improve their mechanical strength, PCEs are often combined with polymer matrices, resulting in plastic crystal polymer electrolytes (PCPEs) that exhibit both good mechanical properties and ionic conductivity.[17]Organic ionic plastic crystals (OIPCs) are also being investigated as potential PCEs.[17]

3.3 Hybrid Electrolytes:

Hybrid electrolytes, which combine the benefits of both inorganic and organic electrolytes, are being actively explored to achieve improved performance and stability in solid-state sodium batteries.[4] These hybrid systems aim to leverage the high ionic conductivity and mechanical strength of inorganic electrolytes with the good interfacial contact and processability of polymer electrolytes. Examples include Na_2ZnSiO_4-based electrolytes [6], composite electrolytes consisting of a polymer matrix and an oxide electrolyte filler [16], and hybrid solid–liquid electrolytes.[15] Notably, a hybrid electrolyte composed of $Na_3Zr_2Si_2PO_{12}$ (NZSP) and a liquid electrolyte has demonstrated exceptional cycle life, sustaining 50,000 cycles with minimal capacity fade.[15] This highlights the potential of hybrid electrolyte approaches to meet the demanding requirements of grid-scale energy storage.

Table 1: Comparison of Key Properties of Different Types of Solid Electrolytes for Sodium-Ion Batteries

Electrolyte Type	Example Materials	Ionic Conductivity at RT (S cm^{-1})	Electrochemical Stability Window (V vs. Na/Na^+)	Notable Recent Advancements	Key Remaining Challenges	Snippet IDs
NASICON	$Na_3Zr_2Si_2PO_{12}$ (NZSP)	Up to ~2 x 10^{-3}	Potentially wide	Improved conductivity through novel synthesis; strategies to reduce interfacial resistance	High interfacial resistance	14
β-alumina	Na–β-Al_2O_3, Na–β″-Al_2O_3	~6.3 x 10^{-4}	-	Improved room-temperature conductivity; ion doping	Preventing sodium dendrite formation at RT	14
Sulfide	Na_3PS_4, $Na_{11}Sn_2P_2S_{12}$, Na_3SbS_4	Up to ~10^{-2}	Narrow	High conductivity; improved air stability through doping; surface modification for interface stability	Sensitivity to water; narrow electrochemical stability window	14

Halide	Na$_3$<0xE2><0x82><0x8B>$_x$Y$_1$<0xE2><0x82><0x8B>$_x$Zr$_x$Cl$_6$ (NYZC)	High	Up to 3.8	High ionic conductivity; good compatibility with oxide cathodes; excellent cycling performance	Further research needed	16
Borohydride	$NaB_{11}H_{14}$, $Na_2B_{12}H_{12}$, $Na_3B_{24}H_{23}$-$5Na_2B_{12}H_{12}$	Up to ~4 x 10^{-3}	Up to 6	High conductivity at low temperatures; wide electrochemical stability window	Further research needed	14
Antiperovskite	Na_3OBr, Na_4OI_2	Improved	-	Improved ionic conductivity; low activation energies for Na^+ migration	Relatively new; further research needed	14
P-2-Type Layered Oxide	$Na_2M_2TeO_6$ (M = Ni, Co, Zn, Mg)	Enhanced	-	Conductivity enhancement through doping; enlarged interlayer spacing	Further research needed	14
Solid Polymer (SPE)	PEO, PVDF, CMC	Typically low at RT	Varies	Copolymerization; addition of plasticizers and fillers	Low ionic conductivity at room temperature	17

Gel Polymer (GPE)	PEO-based, PVDF-HFP-based, PAN-based	Higher than SPEs	Varies	Cross-linked structures; immobilized liquid electrolytes; high ionic conductivity and stability with Na metal anodes	Potential for leakage of liquid component	[17]
Plastic Crystal (PCE)	Succinonitrile (SCN)	Up to ~10^{-3}	Varies	High ionic conductivity at room temperature	Mechanical weakness	[17], S_B 18
Hybrid (e.g., solid-liquid)	NZSP + liquid electrolyte	-	-	Exceptionally long cycle life demonstrated	Interface stability between solid and liquid components	[15]

Note: RT = Room Temperature

4. Key Enabling Factors and Advancements:

Several key strategies and recent developments have significantly contributed to the advancements in solid electrolytes for sodium-ion batteries. Enhancing the ionic conductivity of these materials is a primary focus. Doping inorganic electrolytes with ions of different valences or sizes can create vacancies in the crystal lattice or modify the pathways for ion transport, leading to improved conductivity.[14] Similarly, structural modifications aimed at widening the bottlenecks that hinder ion movement and increasing the density of mobile ions have proven effective.[14] For polymer electrolytes, incorporating plasticizers increases the flexibility of the polymer chains, facilitating ion movement, while adding fillers, especially conductive ones, can create pathways for ion transport within the polymer matrix.[17] Furthermore, the development of novel synthesis techniques for inorganic electrolytes, such as solution-assisted methods and spark plasma sintering, has enabled the production of denser materials with reduced grain boundary resistance, which significantly improves ionic conductivity.[16]

Widening the electrochemical stability window of solid electrolytes is another crucial aspect for enabling high-energy-density batteries. Surface coatings applied to sulfide electrolytes can prevent their decomposition at high voltages, allowing for the use of higher voltage electrode materials.[16] The discovery and development of new electrolyte materials, such as borohydrides and halides, which inherently possess wider stability windows, also represent significant progress.[14] Additionally, doping strategies have been employed in oxide electrolytes to enhance their stability at high potentials.[14]

Mitigating the interfacial resistance between solid electrolytes and electrodes is essential for achieving high-performance solid-state batteries. Surface modifications of solid electrolytes can improve their contact with electrode materials, facilitating more efficient ion transport.[16] The use of interlayer materials, such as ionic liquids or thin buffer layers, between the electrolyte and electrodes can also help to reduce resistance and prevent unwanted reactions at the interface.[16] The formation of a stable solid electrolyte interphase (SEI) layer at the electrode/electrolyte interface is crucial for long-term performance, preventing continuous decomposition of the electrolyte.[6] In the case of oxide electrolytes, incorporating wetting agents like polyvinyl-based polymers has been shown to enhance interfacial contact, leading to improved performance.[16]

Suppressing the formation of sodium dendrites, particularly when using sodium metal anodes, is critical for the safety and longevity of solid-state sodium batteries. Employing mechanically strong electrolytes that can physically resist dendrite penetration is one approach.[4] Modifying the electrode-electrolyte interface to promote uniform sodium deposition during charging can also prevent the formation of dendrite initiation sites.[17] In solid polymer electrolytes, specific polymer architectures are being investigated for their ability to inhibit dendrite growth.[17] Furthermore, the use of a graphene layer to enhance interfacial contact and suppress dendrite growth in NASICON electrolytes has shown promising results.[10]

5. Challenges and Future Directions for Grid-Scale Application:

Despite the significant progress in the field of solid-state sodium batteries, several challenges remain that need to be addressed to enable their widespread application in grid-scale energy storage. Developing scalable and cost-effective methods for synthesizing solid electrolyte materials and fabricating large-format solid-state sodium batteries is a major hurdle.[9] Many promising solid electrolytes are currently synthesized using complex and expensive laboratory-scale techniques. Transitioning to mass production at a competitive cost requires the development of simpler, more scalable, and economically viable manufacturing processes. Furthermore, optimizing these processes to ensure consistent quality and performance of solid-state batteries at the large scales required for grid storage is crucial.[9] Variations in material properties or interface quality can lead to inconsistent performance and potential failures in large battery systems.

The long-term stability and performance of solid-state sodium batteries under the demanding operating conditions of grid storage need to be thoroughly evaluated.[4] Grid storage batteries will be subjected to high cycle rates, deep discharges, and a wide range of temperatures over their operational lifetime. Understanding and mitigating the degradation mechanisms that occur in solid electrolytes and at the electrode-electrolyte interfaces over extended periods is essential for ensuring the long-term reliability and economic viability of these systems.[8]

Further research is needed to develop solid electrolytes with even higher ionic conductivity, particularly at room temperature, to meet the power requirements of all potential grid applications.[8] While significant progress has been made, achieving conductivities comparable to or exceeding those of liquid electrolytes across a wider temperature range remains a key goal. Continued efforts are also required to improve the interfacial compatibility between solid electrolytes and various electrode materials to minimize resistance and enhance overall battery performance.[4] The interface remains a critical factor limiting the performance of solid-state batteries.

Future research directions should focus on exploring novel solid electrolyte materials with unique structures and properties that could lead to significant breakthroughs in performance.[14] This includes investigating new chemical compositions and crystal structures that may offer superior ionic conductivity, wider electrochemical stability windows, or better interfacial compatibility. The development of advanced characterization techniques is also crucial for gaining a deeper understanding of the fundamental mechanisms of ion transport and interface phenomena in solid-state sodium batteries.[16] Such insights will be invaluable in guiding the design and development of improved materials and devices. Finally, a significant research focus should be on overcoming the challenges associated with the use of sodium metal anodes in all-solid-state sodium batteries to achieve higher energy densities for grid-scale applications where it would be advantageous.[4]

6. Conclusion:

In conclusion, significant advancements have been made in the development of solid electrolytes for sodium-ion batteries, encompassing various material types including oxides, sulfides, halides, borohydrides, and organic polymers. These advancements have led to notable improvements in ionic conductivity, electrochemical stability, and the mitigation of interfacial resistance and dendrite formation. The inherent advantages of solid-state sodium batteries, such as enhanced safety, the potential for long cycle life, and the cost-effectiveness and abundance of sodium resources, position this technology as a promising alternative to lithium-ion batteries for grid-scale energy storage. While challenges related to scalability, long-term stability, and further performance enhancements remain, the ongoing research efforts and the potential for future breakthroughs suggest a bright outlook for the role of solid-state sodium batteries in revolutionizing grid-scale energy storage and enabling a more sustainable energy future.