

Application of Solid Polymer Electrolytes for Solid-State Sodium Batteries

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Abstract. Rechargeable sodium-ion batteries have become more attractive because of its advantages such as abundant sodium resources and lower costs compared to traditional lithium-ion batteries. In keeping with the future development of high-capacity secondary batteries, solid-state batteries, which use solid electrolytes instead of liquid organic electrolytes, are expected to overcome the challenges of traditional lithium-ion batteries in terms of energy density, cycle life and safety. Among various electrolytes, polymer matrices have great potential and application in flexible solid-state sodium batteries, as they can form large molecular structures with sodium salts, exhibit low flammability and excellent flexibility. But there are still challenges including low ionic conductivity, poor wettability, electrode/electrolyte interface stability and compatibility, which can limit battery performance and hinder practical applications. The preparation, benefits, and drawbacks of polymer-based solid-state sodium batteries (SSBs) are examined in this article based on an overview of solid electrolytes from the perspectives of polymer-based sodium battery materials, solid polymer electrolytes, and composition polymer electrolytes. Finally, it provides insights into the challenges and potential developments for polymer-based solid-state sodium batteries in the future.

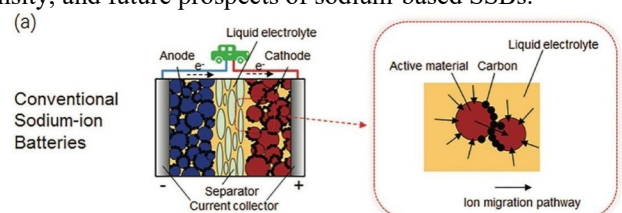
1 Introduction

As the depletion of conventional fossil fuels, advanced energy storage systems (ESSs) will be a viable option for reducing emissions and resolving the existing issue of environmental pollution. Due to its high energy ratio, high dependability, and environmental friendliness, electrochemical energy storage devices, one of the representations of clean energy, are widely utilized in portable electronic items and electric cars. Lithium-ion batteries (LIBs) have dominated the industry for the past few decades, however as the market need increases, LIBs will experience escalating costs and resource problems. The traditional LIBs will inevitably experience side reactions during the charge and discharge process because they use an organic liquid electrolyte. Additionally, the battery cycle process of electrolyte volatilization, leakage, and other phenomena will result in an irreversible attenuation of the battery capacity, which will affect the service life of the battery. A different battery that is less expensive and has more resource reserves is therefore required at this time.

Rechargeable Na-ion batteries (NIBs) are appropriate for widespread deployment because they have a low cost and abundant supply of sodium resources, and their electrochemical energy storage mechanism is comparable to that of LIBs. Sodium metal has the qualities like high-specific capacity and an excellently low standard reduction potential. However, there are still many issues, particularly in liquid electrolyte batteries

where uneven deposition during charging results in dendrite sodium growth [1-3]. It is currently challenging to improve the energy and power density of liquid electrolyte sodium ion batteries at the moment, because the formation of dendrites has the ability to pierce the battery diaphragm and result in a short circuit.

Using a new electrolytic medium in place of a liquid electrolyte is a better way to stop dendrite formation. Another option is provided by solid-state batteries (SSBs), which have better energy and power densities and enhanced safety. Negative electrodes, positive electrodes, electrolytes, and diaphragm materials typically make up NIBs employing solid electrolytes (Fig. 1). The solid electrolyte can be used as both electrolyte and separator [4, 5]. We will provide an overview of the electrode materials used in SSBs in this review. Section 3 provides a thorough analysis of polymer-based sodium-ion SSEs, including information on the ionic conducting mechanism. Section 4 describes the stability of interface, safety, energy and power density, and future prospects of sodium-based SSBs.



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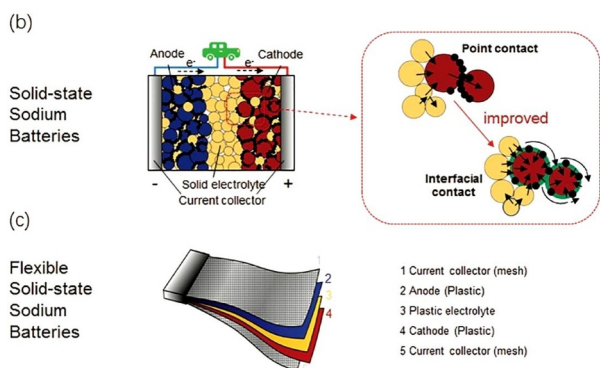


Fig. 1. a) examples of standard OLEs, namely the organic liquid electrolytes, b) typical illustration of ISEs, inorganic solid electrolytes, and c) matrix of solid polymer/plastic electrolytes (SPEs) used in traditional Na-ion battery (NIB, with the liquid electrolytes), the latter is the solid sodium batteries. There has been a lot of interest in the electrode electrolyte contact layer [6, <https://onlinelibrary.wiley.com/doi/abs/10.1002/aenm.201703012>].

2 Typical solid-state electrolytes

There are three main kinds of solid electrolytes: solid polymer electrolytes (SPEs), composite polymer electrolytes (CPEs), and inorganic solid electrolytes (ISE). SPEs have the ability to build macromolecular structures, exhibit low flammability, and exhibit good flexibility, giving them significant competitive advantages [6, 7]. SPEs based on the fusion of polyethylene oxide (PEO) and sodium salt are currently the subject of in-depth research in solid sodium-ion batteries [8-10], although SPEs have a reduced ionic conductivity at room temperature (RT) of 10^{-6} - 10^{-8} S/cm. In order to improve ion conductivity, researchers have developed composite polymer electrolytes (CPE) by adding ceramic additives [11-14]. By using this technique, the polymer body is given additional amorphous regions to improve ion transport. Although ISEs typically have strong mechanical strength and high ionic conductivity (10^{-3} S/cm), there are many problems like high cost and complicated production that call for further optimization.

The conductivity of sodium-based solid electrolytes (SSEs) is a crucial factor to evaluate solid-state sodium batteries under 20 °C. The conductivity of a few examples existing SSEs is shown in Fig. 2. But actually, these materials were not found to be highly conductive under 20 °C, not even at liquid electrolyte level (red ellipses), have been discovered to have high ionic conductivity. In comparably low temperature ranges, ISEs demonstrate stronger ionic conductivity than polymer electrolytes. Recent studies have revealed the potential for solid electrolytes to form in the Na superconductor structure (NASICON) $\text{Na}_{3.3}\text{La}_{0.3}\text{Zr}_{1.7}\text{Si}_2\text{PO}_{12}$ composite electrolyte possess a high ion conductivity at 25 °C [16]. The current state of sodium ion solid electrolytes, primarily SPEs and CPEs, will be discussed in this part, along with their distinctive ion transport methods and possible fundamental features.

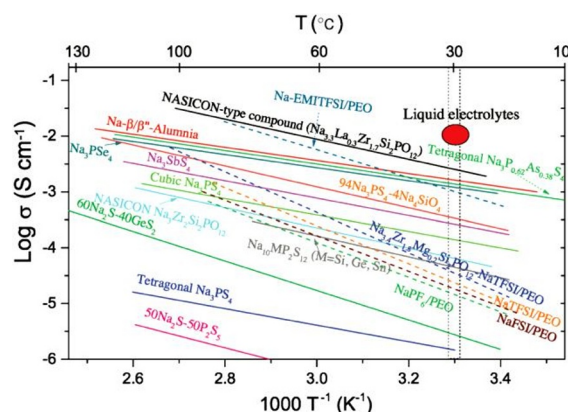


Fig. 2. Several representative sodium based solid electrolyte ion conductivity. The dashed portion represents twenty degrees, and liquid electrolyte is the red ellipse [6, <https://onlinelibrary.wiley.com/doi/abs/10.1002/aenm.201703012>].

2.1 Electrolytes of solid polymer

Polymer electrolytes are mainly formed by dissolving metal salts in the polymer body [7-9]. Alkaline ions in polymer chains can undergo ion migration, yet, they also highly depend on temperature [10-12].

With a good flexibility, Polymer electrolytes can compensate for changes in electrode volume. Therefore, they have great potential for use in flexible SSBs [13]. At present, PEO, polymethyl methacrylate (PMMA), polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC), polyepoxypropane (PPOX), polyacrylonitrile (PAN) and polyvinyl alcohol (PVA) are the polymer matrices commonly used in SSEs. PEO is the most common of them. It has a wider commercial application because its ethylene oxide segment and ether oxygen atom are flexible [8,9,13,16-19].

2.1.1 Ion transport mechanism

Polar groups (-O-, -N-, -S-, C=O, C=N) is crucial in the dissolution of sodium salts. To be honest, a greater dielectric strength of the polymeric matrix helps to dissociate inorganic salts. Ion transport in SPEs mainly takes place in the amorphous region of the polymer body, resulting in ion conductivity [8-10]. Na^+ ions are initially located at sites that coordinate with polymer polar groups (such as the -O- group in PEO). Under the action of an electric field, the segmental motion of the molecular chain induces the free volume of Na^+ ion migration. Afterwards, sodium ions jump from one site to the neighbouring active site along the long chain, causing ion transport [6, 11, 19].

In addition, it is also possible for ion transport to occur in the quiescent and ordered circumstances of the polymer body, for example lithium ions can remove from one position to another position in channel of the PEO₆: LiXF_6 (X=P, As, Sb) crystalline polymer electrolyte. Nevertheless, ion transport in SSEs is almost impossible because of lack of precise structure-property patterns.

2.1.2 PEO electrolyte

PEO dissolved alkali metal salts were first discovered in 1973 and first use in solid-state batteries in 1979 [22, 23]. In 1988, the first SPEs based on PEO of Na-batteries were officially created. This measure dissolves sodium chlorate in PEO. Since this, the SPEs of $\text{NaN}(\text{SO}_2\text{F})_2$, (NaFSI) and $\text{NaN}(\text{SO}_2\text{CF}_3)_2$ (NaTFSI)-PEO were found to exhibit high conductivity at normal temperature [11, 12, 17]. At the moment, other sodium salts are used for research in such area, such as NaPF_6 , NaSCN , NaBF_4 , 2,3,4,5-tetra sodium cyanate (NaTCP) [5, 10-13]. NaTFSI is a relatively promising of these salts because it has a high ionic conductivity. It is reported that at room temperature, the SPE of NaTFSI-PEO is more conductive than the SPE of NaFSI-PEO [11]. Precisely speaking, ionic conductivity decides largely by the amount of free Na^+ ; NaTFSI salts are more soluble in PEO with more mobile ions than NaFSI salts [14].

2.2 Composite polymer electrolyte

To further improve the ionic conductivity of SPE, several strategies have been employed, including polymer cross-linking, mixing, copolymerizing, softening agents, inorganic fillers, and liquid electrolyte doping, to achieve the preparation of composite polymer electrolytes (CPEs) [4,10,16-18]. CPEs can provide high ionic conductivity, and also have good flexibility, chemical/thermal stability. Experiments have shown that polymer crosslinking, blending and copolymerisation are better for improving ionic conductivity. For example, at 60 °C, the ion conductivity of CPEs with NaClO_4 -PEO doped with nano-sized TiO_2 is 2.63×10^{-4} S/cm, higher than that of SPEs without titanium dioxide (1.35×10^{-4} S/cm) [13]. In addition to the simple mechanical mixing of inorganic fillers with polymer matrices, a method for in-situ growth of monodisperse silica-polymer electrolytes has also been raised. This synthetic method promotes more chemical bondings between inorganic fillers and polymer chains, leading to increased amorphous regions and ionic conductivity. ILs have always been considered as ideal electrolyte additives due to their high ionic conductivity, high thermal stability, and low flame fluidity [19-21]. What is more, SiO_2 nanoparticles were grafted with PEG to form SiO_2 -PEG negative ion and Na^+ salt (SiO_2 anion), respectively, the epoxy resin SiO_2 anion and EP- SiO_2 -PEG negative ion CPEs were obtained by dissolving these two molecules in a matrix of PEO and polyethylene glycol dimethyl ether [11], the ionic conductivity of these two CPEs obtained at room temperature is about 10^{-5} S/cm, while at the same Na^+ concentration, the ion conductivity of the EP- SiO_2 -PEG anion is higher, which may be due to the inhibition of high concentration polarisation by highly delocalised anionic sulfonamide groups. This also indicates that some appropriate optimizations can promote the birth of high-performance polyethylene with high ionic conductivity and good mechanical properties. Therefore, CPEs have the ability to improve ion

conductivity and their electrochemical and mechanical properties.

Furthermore, the gel polymer electrolyte, which is consist of organic electrolyte solution mixed with polymer matrix, can be regarded as the midbody between typical liquid and dry solid polymeric electrolytes, and has a high ion conductivity at RT, approximately 10^{-3} S/cm. This electrolyte reduces the risk of liquid electrolyte leakage, usually has higher safety. The sodium type perfluorosulfonic acid ionic polymer gel electrolyte membrane expanded by non-aqueous solvents such as ethylene carbonate and propylene carbonate has been used as the electrolyte and separator of NIB [15, 16]. This electrolyte has good mechanical and thermal stability. Research shows that ionic monomer on perfluorosulfonic acid has a high ion exchange capacity, can provide ion sites, decrease the crystallization of the membrane, and increase the absorption capacity of the unit weight of the membrane to solvents. In recent years, high-order multi ion fluid-based solid electrolytes have been prepared with high security LIBs and NIBs [25]. By exploiting the properties of polyionic liquids and the pros of in situ synthesis methods, it provides high ion conductivity for solid material applications. Adding filler particles to GPEs is a better approach to improve their mechanical strength and electrochemical performance [21].

3 Typical solid-state electrolytes

SSBs are viewed as a promising replacement for liquid electrolyte batteries with the potential for widespread use. But basic research and related technologies are still in their infancy and require further advancement. Currently, consideration must be given to issues such as power density interface effects, safety issues, etc. The most important of these concerns, which is connected to the transferring of charge and the therefore straightly influence the performance of SSBs in electrochemistry, is not only the interface effect of electrodes but also the materials of solid electrolyte. A prognosis on the future development of SSBs will be provided in this part, along with a discussion of certain considerations for the aforementioned elements separately.

3.1 Issues about power density of SSBs

The desirable quality of solid-state batteries is high energy density. The materials of electrode with high-voltage and high-capacity have a lot of developing potential due the wide window of voltage and extraordinary mechanical qualities. High-energy solid-state batteries work best with sodium metal anodes that have high capacity and low potential. Although the majority of SSEs have strong mechanical properties and can, to some extent, inhibit the formation of Na dendrites, their thermodynamic instability to metallic Na frequently results in several side reactions that lead to catastrophic mechanical failures. As a result, a variety of methods can be used to modify the Na negative anode, including building a three-dimensional framework to prevent the

anode's volume from changing, creating an artificially slim SEI layer on the surface of anode in situ, alloying the sodium metal with other elements to enhance the stability of the anode [17-25]. Future testing based on SSEs are still necessary, but the aforementioned technique considerably improved the conditions of both carbonate and ether metal sodium negative anodes and the development of dendrite become less at the processing cycles of plating and stripping. It is also desirable to use cathode materials with the qualities of high-capacity/high-voltage to achieve higher energy densities, such as polyanionic-structured materials or the anionic redox composites to constitute the cathodes of high capacity. However, it is still requireable for more research and development on the dendrites of metal and the stability of chemistry and electrochemistry. Power density is a crucial factor in determining how quickly SSBs charge and discharge. High power density requires both high ionic conductivity and good interfacial contact between components. Unfortunately, the power densities of all the reported Na-based SSBs are low and need to be improved.

3.2 Effect of the interface between electrodes

The optimum electrolyte-electrode interface should have excellent ionic conductivity, sufficient mechanical strength, and acceptable compatibility. Effective formation of an ionically conductive layer and facilitation of the charge transfer process are characteristics of good wetting. It is challenging to generate an efficient ion-conducting layer in situ when using ISEs like Na- β/β'' alumina and NASICON since they are ineffective with electrode materials. Despite having better ion conductivity at high temperature conditions, batteries cannot perform well. As a result, it is crucial to create an interfacial wetting layer in Fig. 4 using techniques including the addition of ionic liquid or the other treatment like polymer infiltration. Also, the in-site/ex-situ treatment of heating is also available [16, 18, 20]. Different It is true that polymer-based electrolytes and sulfide electrolytes can create a soft contact with electrodes, have strong ionic conductivity, and produce good battery performance. Long-term cycling, however, can be harmed by their lack of mechanical strength or poor electrochemical stability. Long-term cycling will result in poor compatibility and high interfacial resistance due to the electrode material's significant volume change and the production of by-products [9, 10, 13, 14, 22, 25]. SSBs with the ISEs such as Na- β'' -alumina and NASICON has been stated that they show excellent long-term stability and can even withstand 10 thousand cycles. But due to their low interfacial compatibility with electrode materials, it is typically planned to add a tiny amount of ionic liquid to artificially create an appropriate interfacial wetting layer. Although polymer-based electrolytes have strong interfacial compatibility, their long-term performance is constrained by poor interfacial and electrochemical stability. Long-term performance requires a stable interface since it not only accounts for the electrode's

volume change but also prevents side effects from occurring, albeit achieving this is still difficult. For instance, an under-oxidation process typically takes place when solid-state electrolytes made up of sulfide come into contact with sodium metal, resulting in the formation of insulating sodium sulfide and sodium phosphide, which will result in high interfacial resistance and subpar performance [17]. A sulfide that is extremely stable to metallic sodium is therefore necessary. For the three layers of solid electrolyte interface (SEI), stable interface (stable), and the mixed conductive interface (MCI), may naturally or artificially form between the materials of electrolyte and the electrode during the initial charge-discharge process [17]. For these three interfacial layers, a constant, high ionic conductivity is required.

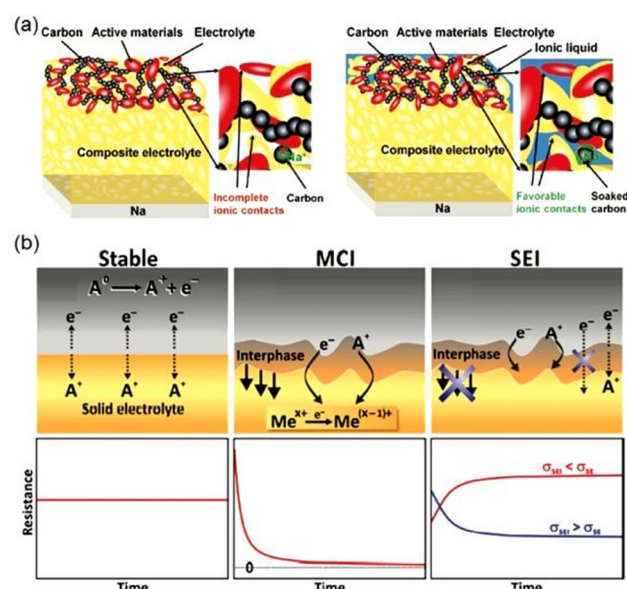


Fig. 3. a) SSBs of “Cathodic/SSEs/Sodium anode” and “Catal/IWL/SSE/Sodium Anode” illustration. The moist layer of the interface can be made up of by the addition of ionic liquid, the penetration of polymer, and the thermal treatment of the site. b) There are three mostly available interfaces between the electrolyte and the electrode material: the first is stable interface, solid electrolytes interface (SEI) and the hybrid conduction interface (MCI). The corresponding resist [6, <https://onlinelibrary.wiley.com/doi/abs/10.1002/aenm.201703012>].

3.3 Safety

Due to the solid electrolytes currently used that are not flammable, one of the main goals in the development of new SSEs will be making solid-state batteries which is highly safe. In addition, using sodium metal to produce negative anode in solid-state sodium batteries poses the greatest safety risk, second only to the electrolyte itself. Large amounts of sodium metal must be handled with extraordinary caution in large-scale manufacture due to its severe sensitivity to oxygen and water. And when handled or stored incorrectly, it might catch fire or even blow up like the lithium metal that is currently in use. However, if the sealed battery sustains damage, the Na metal negative anode will come into direct touch with it

or be exposed to moist air, which could have disastrous effects. How to minimize the drawbacks and maximize the benefits in solid-state batteries is still a challenging issue that needs more investigation. Although a final solution hasn't yet been suggested, some potential plans, like the creation of protective layers to improve interfacial stability and the use of 3D structures to reduce volume changes, may in some cases present promising chances for using metallic Na as a negative anode. To promote practical applications, more pertinent research must be done as solid-state sodium battery technology is still in its initial stage.

4 Conclusion

Solid-state sodium battery is a milestone in the development of batteries, and the electrolytes will be the critical factor and promising materials which influence the capability of SSBs. Different kinds of materials for electrolytes will make great influence on the properties of SSBs, such as energy and power density, Coulombic efficiency, specific capacity, etc. However, there are still some challenges and downsides including short cycle life, low energy density, large size, etc. SSBs' performance and uses are significantly influenced by the materials of electrode and techniques of battery manufacture and optimizing the preparation procedure. Rational application techniques are essential to obtain these solutions in systems of batteries for commercial implementation. Additionally, future advancements at the laboratory level ought to place more emphasis on this issue. As a new energy storage technology, SSBs will offer great development potential and will play a big role in the future energy sector.

Authors Contribution

All the authors contributed equally and their names were listed in alphabetical order.

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