Research and Development Status of Solid-State Batteries

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Abstract. Batteries, as a widely used energy storage device, have become an important component in the development of modern society. However, traditional liquid batteries face a number of security challenges, energy density and lifespan, and the development of new battery technologies is urgently needed. As an emerging battery technology with high energy density, safety advantages and long lifespan, solid-state batteries (SSB) have obtained much attention worldwide. This paper first introduces the basic working principle of batteries. Batteries use chemical reactions to convert chemical energy into electrical energy, and realize the energy output by the flow of electrons through the movement of ions in the electrolyte. SSB differ from conventional liquid batteries in that they use solid-state materials, such as ceramics or polymers, for the electrolyte, which provide high ionic conductivity. Second, this paper will examine the current SSB development, in which domestic and foreign research institutions and enterprises have conducted extensive and continued to research SSB. They are committed to improving the battery preparation process, optimizing the battery assembly structure, and developing new solid-state electrolyte (SSE) materials. This paper then explores the fundamental technologies related to SSE, which are a critical aspect in the advancement of SSB. Recently, scientists have suggested a range of solid-state electrolyte materials possessing elevated levels of ionic conductivity, including oxides, sulfides, and polymers. Lastly, the advantages and challenges of SSB are analyzed in this paper. Greater safety, higher energy density, and longer lifespan are offered by SSB in comparison to traditional liquid batteries. Nonetheless, challenges regarding the conductivity of the solid-state electrolyte, selection of electrode material, and battery manufacturing costs still need to be addressed by SSB. In summary, SSB as an innovative energy storage solution have great development potential and broad application prospects. Future research and technological innovation will further promote the application and commercialization of SSB in energy storage.

Keywords: Solid-State battery, solid-state electrolyte, sulfide electrolyte, oxide electrolyte, polymers electrolyte.

1. Introduction

In recent years, there has been a shift in focus among scientists towards advancing novel energy batteries in order to achieve carbon peak and carbon neutralization goals. This shift is driven by the increasing global demand for energy, as traditional liquid electrolyte batteries are unable to meet the growing energy demands due to their drawbacks such as liquid leakage, combustion, and overheating. Therefore, there is a need to develop battery technologies with higher energy density, improved safety, and longer lifespan to address this challenge. SSB, which utilize solid state materials as electrolytes, have emerged as promising alternatives. These batteries offer advantages such as higher thermal stability and vibration resistance, and can provide higher energy density and improved safety, making them suitable for current social development needs. The development of new materials and advancements in preparation technology have further propelled the progress of SSB technology. This enables researchers to synthesize, design, and optimize SSE, electrode materials, and other components, thereby advancing the study of SSB.

In terms of research significance, the study of SSB has multiple academic, economic and social significance. From the academic point of view, the research and development of SSB can promote the advancement of battery science and technology and expand the research directions and methods in the field of batteries. This will help promote the development of related fields such as materials science, chemistry and physics. In addition, the research and application of SSB technology will also promote the development of electric vehicles, energy storage and renewable energy and other fields.

From an economic perspective, the research and application of SSB technology will promote the development of electric vehicles, energy storage and renewable energy, etc., bringing new business opportunities and jobs. At the same time, SSB technology can also improve the competitiveness and market share of the battery industry, contributing to the country's economic development. From a social perspective, the research and application of SSB technology will promote the popularization of electric vehicles and the transformation of energy structure. Promoting the use of electric vehicles and the adoption of SSB technology can reduce dependence on limited fossil energy, reduce air pollution, improve environmental quality, and create a more sustainable society. In addition, the application of SSB in areas such as micro-electronic devices, medical equipment and wearable devices will bring convenience and innovation to people's lives, contributing to the development of the country and the improvement of people's livelihood.

Therefore, this paper aims to explore the recent progress in SSB research, encompassing the development status, SSE, as well as their advantages and disadvantages. The advancements in SSB research hold significant potential to deliver safer and more efficient energy storage solutions for diverse applications, including electric vehicles, consumer electronics, and grid-level energy storage

2. Solid Batteries

2.1. Operating Principle

SSB are a new type of battery technology whose operating principle is based on a solid electrolyte dominating ion transport. Typically, a SSB consists of two electrodes (anode and cathode) and a solid electrolyte layer in between. During the charging process, current flows from an external power source through the anode, resulting in the oxidation of ions in the anode material and the release of electrons. These electrons flow through the external circuit to the cathode, completing the charging reaction. During discharge, a load in the external circuit absorbs electrons, driving the migration of ions from the anode, passing through the solid electrolyte layer, to the cathode. At the cathode, the ions react with a reducing agent (e.g., oxygen) to release electrons. These electrons again through the external circuit flow back to the anode to complete the discharge reaction. Because this sort of battery uses SSE, they offer higher ion transfer rates, greater safety and durability than traditional liquid electrolytes. At the same time, SSB can also use high energy density materials, providing higher energy density and battery performance. As a result, SSB are widely regarded as next-generation candidates of high-performance battery technology.

2.2. Development Status

SSB represent a new form of energy storage technology that utilizes a solid electrolyte, which distinguishes them from conventional batteries that rely on liquid or gel electrolytes. The use of SSE is a defining characteristic that distinguishes SSB from traditional lithium batteries. As a result, many domestic and international automakers, research and development institutions, and battery suppliers are actively engaged in the development and large-scale production of next-generation all-solid-state electric vehicle batteries. For example, Asahi Kasei of Japan has made important breakthroughs in solid-state oxide electrolyte materials and introduced high-performance SSB products. Top research institutions such as Stanford University has also devoted themselves to SSB research and have achieved some important theoretical and experimental results. In China, SSB research has also made some progress. The Chinese Academy of Sciences, Peking University and other universities and research institutions have actively conducted research on SSB and published a number of papers with international impact. In addition, Chinese electric vehicle manufacturers and materials companies have also begun research and development in the field of SSB, and are counting on the commercialization of SSB. Table 1 summarizes recent advances in SSB research in China, Europe, America and Japan.

Table 1. The current development status of SSB both domestically and internationally

Country and area	Achievements
China	A solid-state lithium battery composed of lithium zirconium oxychloride and high-nickel ternary cathode can stably cycle more than 2000 times in an environment with room-temperature conditions under the condition of fast charging in 12 minutes.
Europe and America	USA has developed a novel processing technology for solid-state electrolyte, which exhibits a conductivity approximately 1000 times higher than traditional processes in an environment with room-temperature conditions and more than 10 times higher at elevated temperatures.
Japan	Japan has developed a SSE with high ionic conductivity and stability, achieving a capacity of over 20 milliamperes per square centimeter electrode.

2.3. Applications

SSB offer vast applications across multiple industries, with electric vehicles standing out as a significant area of potential. Additionally, SSB provide a promising solution for portable electronics by offering higher energy density and improved performance, leading to extended battery life in smartphones, laptops, and other portable devices. Furthermore, SSB hold the potential to revolutionize energy storage in the renewable energy sector. They can efficiently store electricity generated from renewable sources such as solar or wind power, ensuring a stable and reliable power supply when needed. Moreover, SSB find relevance in aerospace and satellite technology, owing to their high energy density and enhanced thermal stability. These features make them ideal for lightweight, reliable power sources during space exploration missions.

In conclusion, SSB possess the transformative potential to drive advancements in various industries, including new energy vehicle, portable electronic devices, storage of renewable energy sources, and aerospace applications. Embracing SSB technology paves the way towards a cleaner and more sustainable future.

3. Solid Electrolytes

SSE are materials used in energy storage devices such as batteries and supercapacitors and are characterized by their solid form, high ionic conductivity and chemical stability. SSE offer greater safety, a wider operating temperature range and longer cycle life than traditional liquid electrolytes. SSE are synthesized and prepared by a variety of methods, including sol-gel, solid-phase, and copolymerization methods. Ionic conductivity is an important indicator for evaluating the performance of SSE, which can be assessed by conductivity testing. At the same time, SSE also need to have good mechanical stability and interfacial compatibility with electrode materials. SSE have a wide range of applications in the field of energy storage. They can be used in devices such as lithium-ion batteries, solid-state batteries, and all-solid-state supercapacitors to achieve high-capacity, high-security energy storage and conversion. In addition, SSE can be used in flexible electronics, sensors and electrochemical catalysis.

Solid electrolytes are typically inorganic materials, such as sulfides (e.g., Li_2S) [1], oxides (e.g., Al_2O_3, ZrO_2), and polymers (e.g., Polyvinylidene fluoride) [2]. These materials exhibit high ion conductivity. Currently, major institutions are particularly focused on the following three types of solid electrolytes, ranked according to their ion conductivity: sulfides > oxides > polymers [3]. Fig 1 and Table 2 show the characteristics of different types of solid electrolytes.

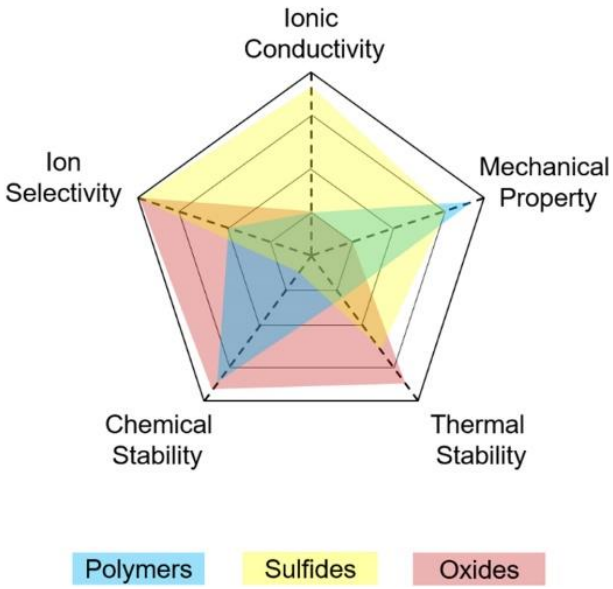


Figure 1. Solid electrolyte characteristics comparison.
https://kns.cnki.net/KXReader/Detail?invoice=SmykikHtT1aBVvRtSEgU5YhaWUJIKjHvrVqYBy3kX2iUdcISf3KEI1Fsm6BGCk9bKq%2BabKQ4CxGKb6kgHZEeblConW8r7ce2CxyaCatkQVB9bbpMMUBr1XyYQ%2FKhLilkeXQKyM6aW5DcOYQxZlOm7OZh7PP5cMitBNkFEoDXtM4%3D&DBCODE=CJFD&FileName=ZJTY202219027&TABLEName=cjfdlast2022&nonce=ED76E57D1BA04E9C8EF0537FAC334500&TIMESTAMP=1691998202585&uid=

Table 2. Solid electrolyte characteristics comparison [4].

Types	Ionic conductivity / (S/cm)	Advantages	Disadvantages
Sulfide	1×10^{-7}~1×10^{-3}	High ionic conductivity, wide electrochemical window, good scalability and versatility	Poor oxidation stability, sensitive to water, Sensitive to air, in which it can decompose into toxic gases, inducing safety problems.
Oxide	1×10^{-5}~1×10^{-3}	High thermal stability, good mechanical strength, rich material selection.	Poor contact with the electrode interface, resulting in high interfacial impedance. Easy reduction at low potential leads to the decrease of lithium-ion conductivity.
Polymers	Below 1×10^{-5}	Stable with metal lithium, flexible and easy to operate.	In an environment with room-temperature conditions, the lithium-ion conduction rate will be lower due to the restricted movement of molecular chain segments and lower conductivity.

3.1. Sulfide Solid Electrolytes

Sulfide SSE are a class of SSE based on sulfide materials with many beneficial features and promising applications. First, it has high ionic conductivity, which enables fast ionic transport, helps to increase the charge/discharge rate and energy density of the battery, and reduces the internal resistance of the electrolyte. Second, it typically has a wide electrochemical stabilization window and can withstand higher voltages and current densities. This allows solid state batteries to achieve higher operating voltages and power densities and maintain stability over a longer lifespan. At the same time, the sulfide solid-state electrolyte is more stable to common chemicals such as oxygen, water, and air, which allows for less interaction with the environment and electrolyte depletion. This helps to improve the safety and long-term stability of solid-state batteries. And sulfide SSE have better performance over a wide temperature range. They not only show good ionic conductivity in an environment with room-temperature conditions, but also can work at high or low temperatures to

adapt to the needs of different applications. Therefore, it is widely investigated for use in energy storage fields. In addition, they can be used in applications such as solid-state electrolysis of water for hydrogen production and solid-state electrochemical sensors.

Compared with the other two solid electrolytes, sulfide solid electrolytes have higher ionic conductivity, which can reach the level of liquid electrolytes. However, most sulfide solid electrolytes can react with moist air, and their chemical stability is poor, so it is difficult to develop.

According to the number of elements, sulfide solid electrolytes can be divided into binary system and ternary system. Sulfide solid electrolytes have high ionic conductivity in an environment with room-temperature conditions, about 10^{-4} S/cm ~ 10^{-2} S/cm, among which $Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ demonstrates the highest ionic conductivity, ranging up to 25 mS/cm in an environment with room-temperature conditions [5, 6].

3.1.1. Binary sulfide solid electrolyte

The binary sulphide solid electrolyte is represented by x Li_2S-(100-x) P_2S_5, which has simple composition and high ionic conductivity, so it is a kind of sulfide solid electrolyte which is expected to realize industrialization. Among them, Li_3PS_4 (x = 75) has been studied most widely. The results show that L_3PS_4 has three kinds of crystalline phases, including α phase β phase and γ phase. The ionic conductivity of different crystal phases varies greatly, among which the ionic conductivity of β-Li_3PS_4 can reach 10^{-4} S/cm [7].

The remarkable comprehensive properties of binary sulfide solid electrolytes make them highly promising. However, to achieve practical application viability, continual enhancement is required in terms of ionic conductivity and chemical stability of the materials. Fig. 2 illustrates the effort of SSE in binary systems with varying Li_2S concentrations.

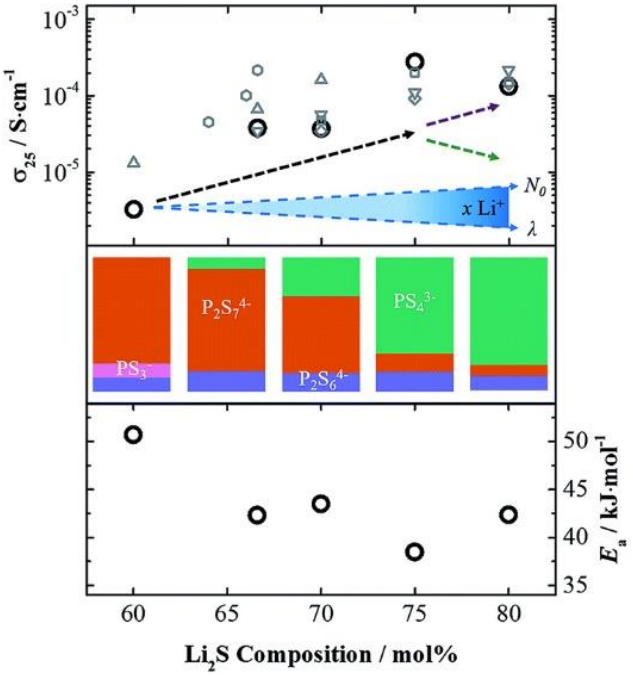


Figure 2. The effort of SSE in binary systems with varying Li_2S concentrations. https://kns.cnki.net/KXReader/Detail?invoice=SmykikHtT1aBVvRtSEgU5YhaWUJIKjHvrVqYBy3kX2iUdcISf3KEI1Fsm6BGCk9bKq%2BabKQ4CxGKb6kgHZEeblConW8r7ce2CxyaCatkQVB9bbpMMUBr1XyYQ%2FKhLilkeXQKyM6aW5DcOYQxZlOm7OZh7PP5cMitBNkFEoDXtM4%3D&DBCODE=CJFD&FileName=ZJTY202219027&TABLEName=cjfdlast2022&nonce=ED76E57D1BA04E9C8EF0537FAC334500&TIMESTAMP=1691998202585&uid=

3.1.2. Ternary sulfide solid electrolytes

The ternary sulphide solid electrolyte is a Li_2S-P_2S_5-P_2S_5 solid electrolyte prepared by introducing other sulfides instead of part of P_2S_5 on the basis of the binary system, in which M_xS is transition

metal sulfides such as GeS_2, SiS_2, Al_2S_3, and SnS. The conductivity of sulfide solid electrolyte in ternary system is generally above 10^{-3} S/cm, which is significantly higher by one or two orders of magnitude compared to the binary system. It is a kind of solid electrolyte with industrial prospect [8].

3.2. Oxide Solid Electrolytes

Oxide SSE are solid electrolytes based on oxide materials with high ionic conductivity and chemical stability, which are widely used in solid state batteries, sensors, electrochemical synthesis and electrochemical energy storage. They can be categorized into single oxide, double oxide and composite oxide electrolytes. Common single oxide electrolytes include lithium oxide, sodium oxide, etc., double oxide electrolytes such as zirconium oxide, titanium oxide, etc., and composite oxide electrolytes consist of two or more oxides, such as zirconium oxide doped mendelevium oxide and lithium oxide doped aluminum oxide. Furthermore, they have high ionic conductivity and can achieve high ionic transport rates in an environment with room-temperature conditions; at the same time, oxide SSE have good thermal and chemical stability, and can withstand high temperatures and strong acidic and alkaline environments; in addition, the solid-state nature of the oxide SSE allows for greater flexibility in the design of battery structures. Meanwhile, this sort of electrolyte is widely used in the field of SSB. In addition, oxide SSE can be used to prepare sensors, such as oxygen sensors, humidity sensors and so on. At the same time, oxide SSE also have potential applications for electrochemical synthesis and electrochemical energy storage.

Oxide solid electrolyte has high ionic conductivity and good stability, but it has the problems of large particle rigidity and poor contact. At present, the conductivity of oxide electrolytes in terms of ions. is generally 10^{-6} ~ 10^{-3}S/cm, which mainly includes Perovskite structure, NASICON and Garnet structure.

3.2.1. Perovskite structure

The ABO_3 structure is used to represent the perovskite arrangement, which consists of two cations and various oxygen defects. In this structure, A is typically used to represent a larger cation, often a rare earth element such as Nd, whereas B is used to denote a smaller cation, typically a transition metal ion like Al [9]. Among the known solid electrolytes, the Lanthanum titanate lithium (LLTO) system is recognized for its exceptional lithium-ion conduction speed.

3.2.2. NASICON structure

NASICON was initially suggested by Xie, who discovered that a Na superionic conductor ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) could be synthesized through the substitution of some phosphorus in $NaZr_2(PO_4)_3$ with silicon [10]. The resulting compound with a similar structure was named NASICON, with the chemical formula $AM_2(PO_4)_3$. In comparison to perovskite electrolytes, NASICON exhibit both high ionic conductivity and chemical stability, making them a highly promising choice for solid electrolyte systems in lithium batteries.

3.2.3. Garnet structure

The general chemical formula of garnet solid electrolyte can be expressed as $Li_{3+x}A_3B_2O_{12}$ [9]. It has garnered increasing attention because of its significant ionic conductivity and expansive electrochemical window. The ionic conductivity is about 10^{-6} ~ 10^{-5} S/cm in an environment with room-temperature conditions [4].

3.3. Polymers Solid Electrolytes

Polymer electrolytes are more suitable for mass production due to their own advantages of good flexibility, ease of processing and low cost. At present, the most studied are polyethers, polycarbonates, polyamides, polysiloxanes, polyacrylates and so on. Based on the type of conducting ions, polymer electrolytes can be divided into 2 main categories: bi-ionic polymer electrolytes and mono-ionic polymer electrolytes.

Bi-ionic polymer electrolytes comprising of a polymer matrix and a binary lithium salt in which both anions and cations are mobile. The cation (Li^+) is usually less mobile than its counterpart, the anion, because the movement of the anion is strongly coupled to the movement of the Lewis base site in the polymer matrix. Mono-ionic polymer electrolytes immobilize the anion on the polymer backbone or provide an anion receptor and only Li^+ migrates. During the charging and discharging process of Li-ion batteries, anions accumulate on the electrode surface to form a concentration gradient because only Li^+ is exchanged between the electrode and the electrolyte. In general, bi-ionic polymer electrolytes have enhanced ionic conductivity, while mono-ionic polymer electrolytes possess enhanced Li^+ migration numbers [11].

4. Advantages and Challenges

SSB, as an emerging energy storage technology, offer many advantages and some potential challenges.

To begin with, SSB possess superior safety features in contrast to traditional lithium-ion batteries that employ liquid or gel electrolytes. SSE are less prone to leakage or the occurrence of fires, effectively reducing the safety risk of batteries at high temperatures or under violent collisions. Secondly, SSB have greater energy density. SSE have a higher ionic conductivity, allowing the battery to store more energy in the same volume or weight, thus providing longer range or use time. In addition, SSB take less time to charge. Due to the better ionic transport properties of SSE, batteries can be charged and discharged more quickly, improving energy storage efficiency and charging speed.

Nevertheless, SSB face certain obstacles at present. For instance, the current production cost of SSB remains relatively elevated. Electrolyte materials' development and production processes are still being improved, and more investment and technological breakthroughs are needed to reduce production costs. Second, the long-term durability of SSB in high-temperature environments still needs further improvement. High-temperature environments may lead to degradation of solid-state electrolyte materials and decrease in battery performance, limiting their reliability and durability in specific applications.

In summary, SSB, as a technology with great potential, have the advantages of higher safety, greater energy density, and shorter charging time. However, continued research and innovation are still needed to address the challenges in terms of their cost, stability, etc., in order to commercialize them and promote them to a wider range of applications.

5. Conclusion

Taken together, SSB, a highly promising battery technology, hold enormous potential in the realm of energy storage. They operate by utilizing SSE, and in comparison, to conventional lithium-ion batteries, SSB provide superior levels of safety, energy density, and charging efficiency. Currently, researchers worldwide are actively promoting SSB development technology and have made significant progress. Many countries and enterprises have increased their research and development investment in the technology and achieved a series of breakthrough results. These efforts have not only pushed the commercialization of SSB technology, but also provided safer and more efficient energy storage solutions for electric vehicles, consumer electronics and grid-level energy storage. SSE, being a vital constituent of SSB, exhibit exceptional ion transportation characteristics and enhanced chemical stability, serving as the fundamental basis for the realization of SSB. Nonetheless, the technology of SSB still encounters various obstacles and hurdles. Among them, cost and stability are current issues that need to be addressed urgently. Reducing manufacturing costs, increasing production efficiency, and improving the stability of batteries in high-temperature environments are key directions for future research. Overall, SSB, as an energy storage technology with great potential, provide an important support for sustainable development and the realization of carbon neutrality goals. Through further research and technological innovation, it is believed that SSB will gradually

become an important technology in the field of energy storage in the future, creating more environmentally friendly and reliable energy solutions for mankind.

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