Challenges and Future of the Industrialization Development of Solid-State Batteries

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Abstract. With the explosive growth of China's electric vehicle industry, make an urgent demand for high-performance energy storage devices. Currently, the performance development of mainstream liquid lithium-ion batteries has significant shortcomings and is no longer able to fully meet the higher standards of the market. Solid-state batteries are regarded as the most promising next-generation electrochemical energy storage technology. This article systematically analyzes the technical advantages, challenges and future development trends of solid-state batteries. Research has found that the most core advantage of solid-state batteries lies in their extremely high safety and the potential to achieve high energy density, in addition to having a longer cycle life. However, its industrialization still faces many severe challenges, such as the unsatisfactory electrolyte materials, and high impedance and side reactions at the solid-solid interface, and the high manufacturing cost also restricts its development. This study indicates that solid-state batteries are a promising but highly challenging technology.

1 Introduction

In recent years, China's electric vehicle industry has witnessed explosive growth. Coupled with the expansion of demand in areas such as portable electronic devices and large-scale energy storage, there is an urgent need for high-performance energy storage devices. Currently, the battery supply system is no longer fully capable of meeting the market's higher standards for driving range, fast charging capacity, and safety performance. Among the current commercial energy storage technologies, liquid lithium-ion batteries hold a dominant position, and their technological maturity and electrochemical energy storage efficiency are beyond doubt. However, the performance development of liquid lithium-ion batteries has approached the theoretical limit and there are significant shortcomings like：During the charging and discharging process, gas generation and leakage are prone to occur, and under extreme conditions, thermal runaway may be triggered. In high-temperature environments, organic electrolytes are prone to decomposition, and at the same time, lithium metal anodes (or lithium ion intercalation and deintercalation processes) are prone to lithium dendrite precipitation. All these problems can lead to battery failure and seriously restrict its application in scenarios with high safety requirements [1]. Against this backdrop, solid-state

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batteries, as a new generation of energy storage technology, offer a better solution to meet the aforementioned high requirements.

Solid-state batteries, with their inherent characteristics, fundamentally avoid the risks of liquid electrolyte leakage and combustion, while significantly enhancing battery thermal stability and offering extremely high safety. In addition, solid electrolytes can effectively isolate the direct interference between the positive and negative electrodes and suppress the side reactions at the interface between the active material and the electrolyte. This feature directly addresses the core pain point of poor long-term cycle stability of traditional liquid lithium-ion batteries, providing key support for extending battery life [2]. Solid-state batteries can better meet the demands of electric vehicles for long range, large-scale energy storage and long cycles, and have huge application potential.

Based on the above background, this paper aims to systematically analyze the technical advantages and development challenges of solid-state batteries. This paper aims to provide a theoretical framework and reference basis for the material screening and interface design of solid-state batteries, promoting the resolution of safety and energy density bottlenecks faced by high-performance energy storage devices, and having positive significance for promoting the development of electrochemical energy storage and other fields

2 The basic structure of solid-state batteries

Solid-state batteries are mainly composed of four parts: the positive electrode, the negative electrode, the solid electrolyte, and the current collector. The most significant difference between solid-state batteries and liquid batteries is that solid-state batteries use a fully solid-state electrolyte layer to replace the liquid electrolyte and porous separator in liquid batteries. This has fundamentally changed its structure, endowing solid-state batteries with intrinsic safety. Solid-state electrolytes are the core component of solid-state batteries, mainly including ceramic oxides, sulfides and composite polymers. Mixed electrolytes, composite electrolytes and solid-liquid electrolytes have received particular attention from the industry. Secondly, the most closely watched part of solid-state batteries is the negative electrode, which is the most promising aspect of solid-state batteries. It is divided into compatible anodes, which continue to use graphite or silicon-carbon, and revolutionary anodes, which directly use metallic lithium as the anode. The theoretical capacity of lithium metal anodes is more than ten times that of graphite anodes, enabling solid-state batteries to have a higher energy density.

3 The technical advantages of solid-state batteries

3.1 Extremely high security

Traditional liquid batteries use flammable organic liquids such as carbonates. When thermal runaway occurs, these solvents will vaporize, catch fire or even explode. But the Solid-state batteries use non-flammable inorganic solid electrolytes such as ceramic glass or high-temperature resistant polymer electrolytes. These electrolytes themselves are not flammable, fundamentally removing the "fuel source" inside the battery and thus achieving intrinsic safety. The reaction temperature between the liquid electrolyte and the lithium anode the start reaction temperature usually 60-120 ℃, while that between the oxide electrolyte and the lithium anode is higher than 250 ℃. And solid electrolytes may slow down the reaction between electrode materials and electrolytes. This phenomenon will slow down the increase in battery temperature and prevent the acceleration of exothermic reactions that could lead to thermal runaway [3].

3.2 Extremely high energy density potential

All-solid-state batteries have the potential to achieve higher energy density compared with lithium-ion liquid batteries. Solid-state batteries offer the possibility of using lithium metal anodes with higher capacity, thereby significantly enhancing the overall energy density of solid-state batteries. In addition, solid-state batteries are more compact in design, eliminating the large auxiliary components required for liquid electrolyte management, reducing the overall size of the battery and effectively utilizing space, thereby achieving higher energy storage per unit volume [4]. At present, the volume and mass energy densities of liquid lithium ions are as high as 770 Wh/L and 260 Wh/kg respectively. According to the solid-state battery roadmap, it is estimated that the battery-grade mass energy density of emerging solid-state batteries can reach 350 to 500 Wh/kg [5].

3.3 Longer cycle life

Compared with the irreversible and persistent side effects between liquid organic electrolytes and highly active electrodes, especially high-voltage cathodes and lithium metal anodes. Solid electrolytes such as inorganic ceramics and oxide electrolytes have a wider electrochemical window, higher chemical stability, and significantly reduced side reactions with electrode materials, which slows down the rate of capacity attenuation. In addition, solid-state batteries have a more stable solid-solid interface. Compared with the dynamic and unstable SEI film existing at the solid-liquid interface in liquid batteries, once a stable solid-solid interface layer is formed in a solid-state battery, its structure is not prone to continuous changes. It avoids the repeated generation and destruction of the interface during the loop process, which is conducive to long-term cycling. Moreover, solid-state batteries have high-temperature thermal stability, are not prone to decomposition, and can maintain structural stability at higher temperatures.

4 The challenges faced by solid-state batteries in achieving industrialization

4.1 Solid electrolyte

Although solid electrolytes are safer than liquid electrolytes, but there are significant differences among different categories in terms of ionic conductivity, chemical stability, preparation process and cost, different advantages and limitations. The following will introduce the mainstream solid electrolytes.

4.1.1 Lithium-based electrolytes

Lithium-based electrolytes, as a kind of superionic conductor, can allow ions to pass through quickly, thus having high ionic conductivity and enabling rapid charging. In addition, its internal resistance is very low, which can generate greater power. It also has the advantages of batteries being stackable without interfering with each other and having a long service life. However, a very small number of materials have the limitation of low ionic conductivity. The conductivity of lithium solid electrolytes of oxides is usually less than 1mS/cm. In addition, there are disadvantages such as mechanical stiffness and the need for sintering to achieve good contact [6].

4.1.2 Sulfide electrolyte

Its representative materials include LPS, LGPS, etc. Sulfide electrolytes have an extremely high ionic conductivity, even exceeding that of liquid electrolytes. Among them, glass-ceramic sulfide solid electrolytes (SSEs) and crystalline sulfide solid electrolytes have been proven to have the highest conductivity in all-solid-state batteries. In particular, Li7P3S11 demonstrated a performance as high as 0.0042S/cm. However, their most serious drawback is that they are extremely sensitive and unstable in the air, and are prone to generating highly toxic and flammable hydrogen sulfide gas [7]. And when in contact with the high-voltage positive electrode, it is prone to oxidation, forming a high-impedance layer. This places extremely high demands on the production process and battery safety.

4.1.3 Oxide electrolytes

Oxide electrolytes are as brittle as ceramic sheets and are difficult to process into dense and ultrathin electrolyte layers. It poses significant challenges in terms of handling and durability. And these brittleness points, especially under repeated charge and discharge cycles, can lead to cracks and mechanical failures [4]. And the overall conductivity of oxide electrolytes is low.

4.1.4 Polymer electrolytes

Polymer electrolytes are a transitional technology that Bridges the gap between liquid electrolytes and solid electrolytes. It is very similar to liquid electrolytes at room temperature, having semi-crystalline or non-fully shaped properties. Although polymer electrolytes can more flexibly contact the electrode interface compared with other solid electrolytes, and have the characteristics of low flammability, easy processing and electrochemical stability [4]. Although some polymer electrolytes have relatively high electrical conductivity, they still face the problem of low ionic conductivity at room temperature and need to be heated above 60 degrees Celsius to function normally, which seriously limits their application scenarios. Moreover, it has poor antioxidant capacity and cannot be matched with high-voltage cathode materials, which limits the energy density.

4.2 Solid-solid interface issues

Although solid-state batteries have made significant progress in improving the conductivity of solid-state electrolytes， but the high interface impedance and interface side reactions faced by the solid-solid interface severely limit the battery performance. The solid-solid interface is the most challenging technical problem for solid-state batteries on the road from the laboratory to industrialization. It has an essential difference from the "solid-liquid" interface of traditional liquid batteries. The problems and challenges it faces can mainly be divided into two aspects: interface physics and interface chemistry.

4.2.1 Interface physics

The interface physical problems are mainly manifested in lithium dendrite puncture and high interface impedance. In traditional lithium-ion batteries, the growth of lithium dendrites may pass through the separator, causing short circuits. People initially expected that solid electrolytes could resist dendrite punctures due to their high mechanical rigidity, but recent reports suggest that metallic lithium can penetrate solid electrolytes. Even at lower current densities, this risk occurs in all solid electrolytes [8]. Compared with liquid electrolytes, the physical contact between solid electrolytes and electrodes is usually poorer. In addition, during the charge and discharge cycles, the electrode material undergoes repeated volume expansion and contraction, resulting in the loss of the effective contact surface between the electrode and the electrolyte. This unstable solid-solid contact interface will seriously impede the cross-interface transport of lithium ions, thereby causing a rapid decline in the battery's cycle performance [9].

4.2.2 Sulfide electrolyte

Interfacial chemistry problems. The voltage will change sharply in the interface area. Then due to the existing voltage difference, the anode will drive the mobile cations into the electrolyte. Meanwhile, the mobile cations are driven towards the cathode. Due to the lower dielectric constant of solid electrolytes, they exhibit more obvious volume polarization. This leads to intensified rearrangement in solid-state batteries, causing the solid-state electrolyte to react with the electrodes, forming a lithium-rich interface phase at the anode and a lithium-poor interface phase at the cathode [8]. It causes problems such as battery performance decline and shortened lifespan.

4.3 The problem of large-scale production

4.3.1 Material level

The material cost is high. Many high-performance solid electrolytes such as LLZO and LGPS contain rare and expensive elements like Ge, Ta, and La. The material is unstable and the processing environment is harsh. Like sulfide electrolytes are extremely sensitive to air, water, etc. When they come into contact with water, they will produce highly toxic hydrogen sulfide gas. This means that the entire production process of the battery (from synthesis, transportation, coating to battery packaging) must be carried out in a fully Dry Room or a glove box filled with inert gas, and the equipment investment and operating costs are extremely high.

4.3.2 Technological process challenges

Such as the difficulties faced in the manufacturing of solid-solid interfaces. For instance, the challenge faced in the manufacturing of solid-solid interfaces lies in how to achieve uniform, dense and low-impedance solid-solid contact between electrodes and electrolytes on large-scale production lines. The preparation of electrolytes is difficult. So far, no electrolyte material has been discovered that integrates high electrochemical performance, stable interface, high mechanical strength and moderate flexibility, as well as excellent physical and chemical properties, and is highly practical and economical.

4.3.3 Insufficient supply chain and equipment

Liquid lithium-ion batteries have a highly mature and large-scale equipment supply chain. The supply chain for solid-state batteries has almost started from scratch, with both material suppliers and equipment suppliers still in the early stages. Moreover, almost all the production equipment for traditional liquid batteries currently available cannot be directly applied to the production of solid-state batteries, and dedicated equipment needs to be developed anew. Moreover, due to the complex process, sensitive materials, and it is an emerging technology, the yield rate during the production process is a major challenge.

5 Outlook

5.1 Material innovation: multi-system composite design

To develop the next-generation electrolyte materials, it is necessary to break through the limitations of a single system and integrate the advantages of different materials through composite design. For instance, the lithium-filled garnet oxide electrolyte with the formula LLZO not only features a high ionic conductivity range of 10-4 to 10-3 SCM-1, but also has an electrochemical window as high as 6V. In addition, when lithium metal is used as the anode, LLZO is stable, which solves the major problem of the reaction between the electrolyte and the lithium metal anode [10].

5.2 Interface control: stable interface phase design

The current interface protection scheme using "cathode active material coating" has limitations—Although the coating can reduce some electrolyte decomposition, it will introduce an additional potential drop and cannot completely inhibit the mutual diffusion and chemical decomposition between the electrolyte and the electrode. In the future, the focus should be on researching "functional interface phase design". By means of in-situ reactions, artificial interface layers (such as Li_3PO_4, LiF-based coatings), etc., interface phases with ionic conductivity, chemical stability and mechanical compatibility are constructed to fundamentally solve the problems of interface impedance and side reactions.

6 Conclusion

This article systematically analyzes the core advantages, industrialization bottlenecks and breakthrough directions of solid-state batteries as the next-generation energy storage technology. After in-depth research, it has been found that solid-state batteries have extremely significant advantages, achieving intrinsic safety through non-flammable solid electrolytes; It can be compatible with electrode materials of higher energy density, thus having the potential to achieve higher energy density; And because of the more stable solid-solid interface and higher electrochemical stability, it is endowed with a longer cycle life. However, there are still many serious problems to be faced in realizing the industrialization of solid-state batteries. High impedance, side reactions and dendrite penetration at solid-solid interfaces remain the biggest technical barriers to moving from the laboratory to industrialization; All types of solid electrolytes face the challenge of balancing performance and cost; Moreover, the process consistency control of large-scale production, highcost equipment and blank supply chains further restrict the marketization process. Future development requires breakthroughs in some technologies such as multi-system composite electrolyte design and functional interface phase regulation, while relying on multi-disciplinary collaborative innovation (materials, chemistry, mechanical engineering) to improve large-scale production processes and supply chains. Despite numerous challenges, solid-state batteries are expected to become the core energy storage technology leading the development of the new energy industry after technological breakthroughs.

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