Research On the Application and The Interface Problem of Solid-State Batteries

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Abstract. Solid-state electrolytes (SSEs), the substitutes of liquid electrolytes which can create greater safety by preventing the penetration from lithium dendrites. However, there are still some defects, as the solid-solid contact may cause interface problems where gaps are formed between electrodes and SSEs. The interface issue can harshly affect the performance of batteries such as overpotential, electrical conductivity, and cycle life. By tackling such issues, traditional lithium-ion batteries can be completely replaced by solid-state batteries due to the outstanding performance of efficiency and capacity. So the solutions are listed by classifying SSEs into different types This essay provides new perspectives and ideas for the researchers by reviewing research on solid-state batteries.

Keywords: lithium-ion batteries, solid state electrolytes, interface problem.

1. Introduction

With the wide application of new energy technologies, the development trend of full electrification in modern transportation is becoming increasingly clear. This places higher demands on the safety, energy density and cycle life for secondary batteries. Lithium-ion battery, however, becomes the optimum choice for replacing fossil fuels where the latter energy can cause serious of dire consequences such as the formation of greenhouse gases like carbon dioxide, or toxic gases like sulfur dioxide and nitrogen oxides. At present, lithium-ion batteries (LIBs) boost and become a reliable and widely-used energy bank options because of the splendid energy density it contains as well as lightweight nature, which sets them apart from other conventional battery types. However, safety issues often lead by lithium-metal anodes, primarily because The formation of dendrites can penetrate the separator, resulting in internal short circuits within the cell and possibly causing fires[1]. Moreover, other safety concerns can be caused by the commonly employed organic liquid electrolytes in LIBs, which possess characteristics like flammability, corrosiveness, and thermal instability, hindering their broad adoption. Thus, solid stare batteries are developed in order to eliminate those safety concerns and further enhance the energy density.

Nevertheless, solid-state batteries (SSBs) still face numerous challenges before they can be widely applied in practical scenarios. Specifically, the issues at the interfaces between solid-state electrolytes (SSEs) and electrodes play a crucial role in determining the performance of SSBs [2]. Although significant progress has been made in recent years in developing high-conductivity SSEs for lithium-ion batteries, integrating these advanced materials into efficient battery systems has remained a complex task [3]. In solid-state batteries, the interface phenomena encompass the physical, chemical, and electrochemical interactions that take place at the boundaries between the SSEs and electrodes. Such interactions may result in several unfavorable outcomes, such as elevated interfacial resistance, reduced ionic and electronic conductivity, chemical instability, and mechanical deterioration.

Especially for the chemical instability, one of the factors that will cause serious consequences as this may trigger a series of exothermic reactions. When the chemical substances inside the battery undergo abnormal reactions, a large amount of heat will be generated. There are two classifications divided from the interface problem that can lead to chemical instability issues in batteries. One is before the electric cycle, the other is after the electric cycle. For the former one, which is the contact issue generally cause the effect of interface problem by insufficient contact area and insufficient contact pressure which is called physical contact problem. If there is a lack of touching surface between electrodes and electrolytes, this will narrow the charge transfer path and resulting in an increase in the interface resistance. For example, uneven coating or the presence of voids will reduce the contact area. For the pressure issue, for example, during the battery assembly process, if the pressure between the electrode and the electrolyte is insufficient, it will lead to poor contact. For instance, in pouch cells, the pressure between the electrode and the current collector needs to be guaranteed by an external pressure device. Insufficient pressure will increase the contact resistance.

For the latter one (after electric cycle) which is named as interface side reaction issues can cause severe chemical stability problem. The chemical reaction between solid electrolytes and electrode materials may lead to chemical stability problems at the interface by producing non-conductive by-products which will further increase the interface resistance and reduce the battery performance. What’s more is that chemical reactions may lead to the formation of interface layers, which may have a relatively low ionic conductivity, hindering ion transport. For example, the by-products produced between SSE and electrodes: Intense side reactions occur between the lithium metal anode and sulfide solid electrolytes (such as Li_6PS_5Cl), generating an unstable solid electrolyte interface (SEI) layer. Thus, a chemical stability issues can lead to a decline in battery performance after multiple charge and discharge cycles, shortening the battery's service life.

In general, the types of problems mentioned above about the interface problem can lead to severe safety issues such as the explosion or spontaneous combustion. This essay is planned to summarize the major methods of weakening the power of interface issues by introducing the consequences caused by lacking contact area basically, and then providing methods tackling on such issues.

2. The Effect Caused by Lack of Contact Area

2.1. Overpotential

Overpotential serves as a critical parameter in electrochemical reactions, indicating the kinetic resistance associated with electrode reactions. Its presence can result in various performance challenges, such as diminished energy efficiency in batteries, restricted charging and discharging rates, reduced battery lifespan, thermal management complications, and alterations in voltage platforms.

In contrast to conventional batteries where liquid electrolytes fully envelop both the cathode and anode, SSEs form interfaces with electrodes that influence their behavior during charge and discharge cycles. Figure 1a illustrates the specific scenario of how interface issues arise between electrodes and SSEs. In subsequent diagrams, the contact ratio (CR) represents the proportion of the contact area relative to the total surface area. A smaller CR generates a larger gap between the electrodes and SSEs. As shown in Figure 1b, a higher CR contributes to a reduction in overall discharge voltage and discharge duration. For instance, at a CR of 0.8, the discharge time at a cutoff voltage of 3.5 V decreases by approximately 22.1% compared to perfect contact conditions. In Figure 1c, a higher CR results in a lower increase in charge-transfer overpotential, thereby reducing interference with electron transfer at the cathode. Conversely, for the anode, the CR does not exhibit an increasing trend but rather remains constant, demonstrating that lower CR values correspond to greater overpotential. Additionally, a reduction in contact area leads to a higher concentration of intercalated lithium at the interface. This occurs because the same amount of lithium is generated but distributed across a smaller surface area, as depicted in Figure 1d. During discharge, the average lithium concentration at the SSE/cathode interface progressively increases from 16,100 to 32,200 mol m^{-3}. Meanwhile, the SSE/anode experiences a more consistent rise in intercalated lithium due to an increased accumulation rate caused by a reduced diffusion coefficient. Furthermore, the rate of accumulation of the average lithium concentration accelerates as the contact area diminishes. Based on this observation, a parameter termed the diffusion overpotential is introduced to quantitatively describe this phenomenon (as illustrated in Figure 1e). Notably, during the latter stages of discharge, it becomes apparent that the lower the CR, the faster the overpotential increases. Overall, a larger gap between the electrode and SSE results in reduced voltage, increased intercalated lithium, and heightened activation energy due to overpotential[4].

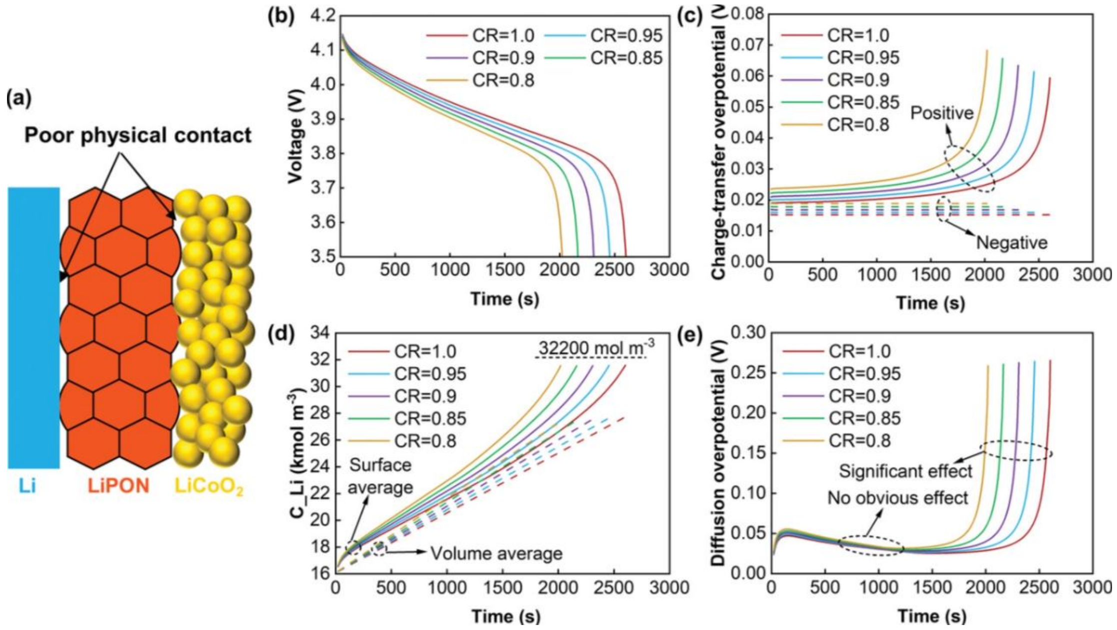

Figure. 1 The Influence of Contact Area Proportion on the Discharge Performance of All-Solid-State Batteries at a 1 C a) Poor contact at the interface between electrodes and the solid-state electrolyte; b) Discharge profiles; c) Charge-transfer voltage loss; d) The mean lithium concentration at the positive electrode interface; e) Diffusion-related voltage loss [4].

2.2. Ionic Conductivity

Interface problems in solid-state batteries can affect ionic conductivity through multiple mechanisms, thereby reducing the general capacity of them. Basically, for mechanisms of the ionic conductivity, the transport of ions in an electrolyte depends on the migration of ions. In solid electrolytes, ion migration usually occurs through vacancies or interstitial spaces in the lattice. For example, lithium ions (Li^+) migrate through vacancies in the lattice in inorganic solid electrolytes (such as Lithium lanthanum zirconium oxide). For the effects that cause by interface problems on ionic conductivity, it is the structure of one material that can affect the ionic conductivity. The microstructure of materials (such as grain size, grain boundary density, etc.) has a significant impact on ionic conductivity. Smaller grain sizes can increase the number of grain boundaries, thereby providing more ion transport paths. The inhomogeneity at the interface (such as pores and cracks) will interrupt the ion transport path and increase the resistance of ion transport. For example, interface cracks caused by changes in electrode volume will reduce the ion transport efficiency.

2.3. Cycle Life

The interface problem of solid-state batteries is one of the key factors affecting their cycle life. Interface issues can lead to various adverse phenomena in the battery during charging and discharging, thereby shortening the battery's usage. The major reason that cause the reduce in cycle life by interface problem is the mechanical contact problems. This sort of problem is led by volume changes in electrodes during charging and discharging, resulting in poor mechanical contact at the interface. For instance, lithium metal anodes expand and contract during charging and discharging, which may lead to cracks and voids at the interface.

3. Solutions Tackling the Problems of SSEs

3.1. Halogen SSEs

Halide electrolytes (such as chlorides, bromides, etc.) have unique performance advantages in solid-state batteries, such as high ionic conductivity and good electrochemical stability. However, halide electrolytes also have interface problems, such as poor interface contact, insufficient interface reactions and chemical stability, etc. Researchers proposed various of solutions tackling such issues.

First, for the problem of stability issue of halide in interface problem: When halide solid electrolytes meet electrode materials, they may decompose or undergo structural changes due to their unstable chemical properties. This can reduce the efficiency of charging and discharging of a battery as unstable interfaces will increase the internal resistance of the battery and reduce its efficiency. Solutions are carried out by chemical doping which regulate the electrochemical or chemical stability of halide solid electrolytes. For example, fluorine doping can promote the formation of a stable interface layer, thereby enhancing the interface stability [5].

Next comes the thermal stability issues of halide in interface problem: At high power or high current density, the interface between the halide solid electrolyte and the electrode may generate a large amount of heat, leading to thermal stability problems. Poor interfacial thermal stability may cause the internal temperature of the battery to rise, further increasing the internal resistance of the battery. Solutions such as using composite multilayer electrolytes is adopted to avoid the direct contact between halide electrolytes and the negative electrode. For example, the stratified design idea of halide -sulfide-anode can effectively improve the stability between solid electrolytes and other materials and reduce the interface impedance [6].

3.2. Polymer SSEs

Solid state polymer electrolytes have to face an obstacle which is weak ionic conductivity that act as a prevalent concern among researchers today. One widely adopted strategy involves lowering the glass transition temperature (Tg) of polymer electrolytes and enhancing the mobility of Li+ within the free segments of polymers. Among these materials, PEO-based solid electrolytes are the most extensively studied. They possess notable advantages such as strong lithium salt dissociation capabilities, excellent compatibility with lithium metal, favorable electrochemical stability, and low production costs. Nevertheless, their ionic conductivity in a room temperature condition remains too low, which restricts the practical application of PEO electrolytes [7]. As temperature exceeds 60 ℃, the ionic conductivity of PEO meet the operational requirements for batteries. At this temperature, however, PEO approaches a semi-molten state and exhibits weak mechanical strength. To achieve both high ionic conductivity and robust mechanical properties at room temperature, researchers have explored various strategies, including PEO grafting, copolymerization, blending, incorporation of plasticizers, and addition of inorganic fillers. Zhang developed a flexible polymer electrolyte based on PEO through an in-situ photopolymerization dual reaction [8]. By integrating tetrafluoroethylene glycol dimethyl ether and tetrafluoroethylene glycol dimethyl acrylate, cross-linked disordered structures were formed with PEO chains, significantly reducing the crystallinity of PEO. This resulted in an impressive ionic conductivity of 2.7×10^{-4} S cm^{-1} at 24 ℃, enabling stable performance of PEO-based solid-state batteries under normal temperature conditions.

3.3. Sulfide SSEs

Sulfide electrolytes are capable of attaining an ionic conductivity as elevated as 10^{-2} S·cm^{-1}, which is on par with the ionic conductivity of the liquid electrolytes presently utilized in lithium-ion batteries. However, when subjected to water and air, sulfide electrolytes display instability, are susceptible to decomposition, and exhibit poor interfacial compatibility with electrodes.

Studies have demonstrated that incorporating a [Li(triglyme)]+[TFSI]- (LiG3) solvent-salt complex can effectively stabilize Lithium germanium phosphorus sulfide electrolytes, and its application has been showcased in high-performance solid-state lithium-sulfur batteries. The addition of a small quantity of LiG3 to the cathode material markedly enhances the transfer rate of Li^+ and promotes the transition from solid-solid redox reactions involving sulfur species to solid-liquid two-phase redox reactions.

This implies that introducing a minor amount of ionic liquid additives into sulfide electrolytes not only elevates the ionic conductivity but also effectively alleviates issues such as decomposition and gas generation during battery charging and discharging, thereby enhancing safety and stability [9].

3.4. Oxide SSEs

Oxide electrolytes typically exhibit ionic conductivity around 10−4 S·cm−1. Their main drawbacks include inferior mechanical properties and challenges in film formation. During full battery preparation, uneven pressure on the electrolyte sheet may cause it to fracture, leading to short circuits and rendering the battery unusable. Both excessive and insufficient pressure can negatively impact the performance of the full battery. Additionally, unavoidable interface reactions result in increased interface impedance. The Goodenough team addressed the issue of poor interfacial compatibility of lithium lanthanum zirconium tantalum oxide (LLZTO) ceramic electrolytes through high-temperature carbon treatment (LLZTO-C) [10], Decreasing the amount of Li-Al-O glass phases, which have poor lithium-ion conductivity and are located at the grain boundaries on the garnet surface. The surfaces of carbon-treated garnet particles are free of Li_2CO_3 and display favorable wettability with metallic lithium anodes, organic electrolytes, and solid composite cathodes, leading to a significant reduction in interfacial resistance. Moreover, certain researchers have discovered that rapid acid treatment can also effectively address the issue of poor interfacial compatibility, thereby greatly enhancing battery performance [11, 12].

3.5. Two Technics for Weakening Interface Problem

Interface engineering: By optimizing the interface structure between the electrolyte and the electrode, the interface contact is improved, and the interface resistance is reduced. For example, Halide electrolytes are prepared into nanoparticles or nanofibers to increase their specific surface area, thereby enhancing the contact area with electrode materials. For example, the preparation of nanoscale halide electrolyte particles by sol-gel method or spray drying method can significantly improve the interface contact. This nanostructure design can optimize the ion transport path and reduce the interface impedance [13].

Design of composite electrolyte: By combining halide solid electrolytes with other solid electrolytes (such as polymers, oxides, and sulfide solid electrolytes), the solid electrolytes can complement each other's strengths and weaknesses, thereby integrating the advantages of different electrolytes and ultimately obtaining all-solid-state batteries with excellent performance. For example, by leveraging the strengths of halide and sulfide solid electrolytes, positioning the halide electrolyte near the high-voltage active cathode or utilizing it as a composite cathode material can avert the oxidation of the sulfide electrolyte. Meanwhile, placing the sulfide electrolyte adjacent to the lithium anode can inhibit the reduction of the halide electrolyte. These approaches can substantially bolster the battery's high-voltage resistance. [14].

4. Conclusion

To summarize, this essay primarily discusses the major challenges in solid-state batteries, such as interface issues that lead to a decline in charge and discharge properties as well as an increase in activation energy. To address these problems, techniques like coating and interface modification are employed to improve the wettability of the interface, thereby enhancing ion mobility. Additionally, research focuses on various types of SSEs, including polymers, sulfides, and oxides, with solutions aimed at modifying their fundamental structures. Furthermore, effectively combining electrolytes remains a key research direction, which involves balancing ionic conductivity and electrochemical stability. Low ionic conductivity can impair the rate and cycle performance of batteries, thus limiting the application scenarios of all-solid-state batteries. Therefore, it is essential to develop new types of electrolytes or improve existing ones.

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