Research Progress on Solid-state Electrolyte Interface Problems in Lithium-ion Batteries

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Abstract. Nowadays, compared with traditional liquid batteries, solid-state batteries have the superiorities of higher energy density, power density and safety due to their solid electrolytes. However, a series of interfacial problems at solid-solid interface have always hindered the further development of solid-state batteries. Based on these problems, this paper firstly introduces the types of solid-state batteries and interface, secondly describes the mechanical failure principles of cathode interface and anode interface, and finally elaborates the corresponding modification strategies for cathode interface and anode interface. By adopting various improved measures for these interfacial problems, the progress of wider commercialization of solid-state batteries can be facilitated.

Keywords: Solid-state electrolyte, interface problems, modified strategy.

1. Introduction

Currently, due to the overuse of fossil fuels, several serious effects have been caused, such as international energy crisis and environmental pollution. Hence, energetic markets must push the presence of new sustainable and environmentally friendly energy sources replacing fossil fuels. However, the dispersed geographical distribution of certain green energies, like solar energy, limits its application. Therefore, the efficient and feasible energy storage devices are designed as auxiliary [1]. In recent years, lithium-ion batteries with the advantage of high energy density are gradually being widely used in energy storage. While the bad performances in security are still under further research, which is largely due to the instability of liquid electrolytes. Subsequently, solid-state electrolytes, defined as SSE, served as an alternative of conventional liquid electrolytes, have the potential to solve these problems [2]. Also many advantages of solid-state lithium-ion batteries such as high safety, high energy density and great power density win a large amount of attention from the public [3], but there are serious application challenges, mainly owing to the interface problems between SSE and electrodes. As a result, this paper will focus on the interface problems of SSE, including the types, the mechanical failure models and relevant influencing factors, and improved strategies.

2. The types and interface of SSE

2.1. Types of SSE

Table 1. The comparison of the relevant properties of oxide SSE, sulfide SSE, and polymer SSE

Types of electrolytes	Polymer SSE	Sulfide SSE	Oxide SSE
Conductivity	Bad	Medium	Good
Manufacturability	Good	Bad	Medium preference
Thermal stability	Medium	Good	Medium preference
Lithium compatibility	Medium	Good	Medium preference
Water stability	Medium	Medium deviation	Bad

At present, SSE can be categorized into two main types: inorganic SSE and polymer SSE, where inorganic SSE are further classified as oxide-based and sulfide-based. There are huge differences in the material structure characteristics of the above, so they also differ in conductivity, lithium metal

compatibility and interface form, et al. Table 1 shows a comprehensive comparison of the relevant properties of oxide SSE, sulfide SSE, and polymer SSE.

2.1.1 Inorganic SSE

Since different structures lead to different performance, this article would interpret inorganic SSE from two different kinds: oxide SSE and sulfide SSE.

Oxide SSE have great potential for development owing to their excellent thermal stability, mechanical strength and ionic conductivity. However, the solid-solid interface between electrolytes and electrodes increase interfacial impedance, which hinders the diffusion of lithium ions [1]. Representatives of oxide SSE include garnet-type, NASICON-type and Perovskite-type electrolytes. Garnet-type electrolytes have the general formula of A3B2M3O12, NASICON-type electrolytes have the general formula of Li [A2B3O12], and Perovskite-type electrolytes have the general formula of Li3xLa2/3-xTiO3. It has been shown that these electrolytes can achieve higher ionic conductivity and better stability by adding or replacing certain elements [2-4].

Sulfide SSE typically exhibit high ionic conductivity, some even up to 10-2 S/cm. Typical sulfide SSE include lithium thiophosphate (100-x) Li2S·xP2S5 (L-P-S system), Li10GeP2S12, and sulfur silver germanium ore-type electrolytes (Li6PS5X). The studies on L-P-S system have represented that the ionic conductivity can be increased by adjusting the ratio of Li2S and P2S5 [5]. Li10GeP2S12 not only has high conductivity but also performs great stability over a wide temperature range, while high cost limits its wider application. Sulfur silver germanium ore-type electrolytes, such as Li6PS5Cl, have been widely studied for its optimized preparation process, showing high ionic conductivity [6].

2.1.2 Polymer SSE

The polymer SSE include polyethylene glycol, polymethyl methacrylate, and polyacrylonitrile, which are flexible and can be molded into different shapes. But they have low ionic conductivity and are unstable at electrolyte-electrode interface. Therefore, polymeric SSE are usually needed to be combined with inorganic fillers and lithium salts to form composite SSE [7]. This approach not only improves ionic conductivity and inter-interface compatibility, but also inhibits lithium dendrites' growth.

2.2. Types of SSE interface

Solid-state lithium-ion batteries are different from conventional liquid lithium-ion batteries, in that the electrolytes contact with electrodes as solid-solid interface. These contacts lead to poor interfacial compatibility and a series of interfacial problems. Although different electrolytes have different properties, the types of interface are roughly the same since they are still SSE. Therefore, the main types of interface are voids and interfacial membranes.

2.2.1 Voids

There are three different types of voids existing in solid-state lithium-ion batteries [8]. The first type of voids exist at solid-solid interface during encapsulation processes. Since solids cannot be fully infiltrated with each other like liquids, the voids' fraction is typically 10-40% [8]. Usually, a moderate amount of external pressure can be applied to shrink the size of voids. The second type of voids exist in SSE. The formational reasons are similar with the first type. The third type of voids are gradually penetrates and forms due to uneven deposition of lithium metal and the growth of lithium dendrites.

2.2.2 Interfacial membranes

There are two main types of interfacial membranes presenting in solid-state lithium-ion batteries generated by chemical or electrochemical reactions, respectively [8]. The first are the interfacial membranes generated by spontaneous chemical reactions during working periods of batteries. And these interfacial membranes refer to the CEI membranes which is thin films formed on the surface of the cathodes of lithium-ion batteries and the SEI membranes that formed on the surface of the anodes, which allow only ions to pass through, facilitating the transport of lithium ions. The second type of interfacial membranes emerge due to the electrochemical instability of the SSE [8], which may be

oxidized at high voltage or reduced at low voltage, leading to the decomposition of the contacting surfaces between electrolytes and electrodes. And that decomposition further promotes the false generations of SEI and CEI membranes and increases interface's resistance [8].

3. Mechanical failure principles of SSE interface

After clarifying the types of SSE interface of solid-state lithium-ion batteries, we will further studies the mechanical failure modeling and influencing factors of SSE, and moreover various interfacial problems and relevant solutions. By contrast, the interface problems between cathodes and electrolytes have less impact on batteries' performances, hence, current researches mainly focus on lithium dendrites and composite electrodes [9].

3.1. Cathode-electrolyte interface

During normal working periods of solid-state lithium-ion batteries, the volume of cathode materials would increase or decrease, which may produce interfacial tensile/compressive stresses on the interface between cathodes and SSE, leading to occurrence of cracks [9], that will shorten the effective life-span of batteries.

3.2. Modeling of growth of lithium dendrites

Due to unevenly lithium deposition on the interface between anodes and SSE, lithium dendrites form and continue to grow during charge operations, eventually penetrating SSE and leading to internal short circuits or even thermal runaway if lithium dendrites reach cathodes. It has been demonstrated that the influencing factors of mechanical interface failure vary in different electrolytes [10-16]. Owing to different relevant properties of polymer SSE and inorganic ceramic SSE, the factors influencing the interfacial failure will be described separately in the following. The exact modeling of lithium dendrites growth is still under the development.

3.2.1 Lithium metal-polymer SSE interface

Tikekar, et al showed that the deposition of lithium ions can be stabilized by pre-fixing right number of anions on diaphragms and applying polymer SSE with moderate modulus of rigidity [10]. Ganser, et al discovered that ions' transportation, related with interfacial phenomena, SSE' toughness and properties of ions' transportation, by the coupling modeling of electrochemical forces, would influence interfacial stability. Therefore, the growth of lithium dendrites can be addressed by modulating various types of force electrochemical properties of polymer SSE, rather than by single modulation of its toughness [11]. Stone, et al observed that a higher modulus of rigidity does not completely inhibit the growth of lithium dendrites, but it can be achieved by reducing the gap between lithium anodes and SSE [12]. Verma, et al found that by investigating the relationships between externally applied stacking pressure and the stability of lithium ions' deposition, external stacking pressure, higher temperatures and smoother surfaces all contribute to lithium ions' stable deposition [13]. Therefore, the interfacial properties between lithium anodes and polymer SSE play an important role in the growth of lithium dendrites.

3.2.2 Lithium metal-inorganic ceramic electrolytes interface

The researches show that lithium dendrites on inorganic ceramic electrolytes usually distribute at grain boundaries, cracks and voids. Tantration, et al further revealed that mechanical and electronic properties of grain boundaries would affect lithium dendrite growth through an electrochemical phase field model [14]. Yuan, et al found, through a force-electrochemical coupled phase field model and a multiphysics field coupled model [15], that long voids with sharp edges or sharp angles, high stacking pressures, and stresses driven by overpotential all stimulus cracks' extension and lithium dendrites' growth. In addition, the flowing properties of such electrolytes have gradually been proven to be one of the factors affecting the growth of lithium dendrites [16].

3.3. Modeling of rupture of layered composite electrodes

Rupture of layered composite electrodes refers to the phenomenon of delamination fracture of the active particles in SSE attributing to volume's expansion or contraction during lithium's insertion or departure. Bistri, et al demonstrated that the volume fraction of active particles synergistically affects the interfacial stresses between active particles and SSE, whereas the size and spatial distribution of active particles do not influence those interfacial stresses [17]. Fathiannasab, et al found that stresses can be relieved by adjusting the pore properties of active particles and by changing the volume of active particles, thus the occurrence of delamination fracture phenomenon will be reduced [18].

4. Improved solutions of SSE interfacial problems

4.1. Cathode-electrolyte interface

During the actual operations of solid-state lithium-ion batteries, the interfacial tensile/compressive stresses and cracks between cathodes and SSE may generate due to the expansion or contraction of cathode materials [1]. Therefore, several studies have shown that reinforcing the physical contacts between cathodes and SSE is an effective solution [19], which refers to coating treatments on the surface of cathodes. Meanwhile, this kind of surface coating must have following characterizes, such as the electrochemical stability of the coating, interfacial compatibility and high ionic conductivity with cathodes and SSE [20]. Currently, the most effective methods of coating on cathodes include atomic layer deposition, pulsed laser deposition and sol-gel methods. Nam, et al successfully developed the first bendable sulfide SSE membrane by modifying a polymer scaffold with a nonwoven polyaniline fabric, which made sure a close contact between cathodes and electrolytes, accordingly improving the energy density and multiplicity capability [21].

However, current studies are trying to make cathodes close to electrolytes as far as possible which ensures that external factors have been able to reduce most of the voids, but the voids still exist when viewed at atomic level. Accordingly, the relevant physical improvements are obviously not enough. It should be considered to introduce some of gel-state materials to the interface between cathodes and electrolytes, which will not participate in and affect the electrochemical reactions with the excellent conductivity and stability, therefore to improve the interfacial compatibility in chemical level by a closer contact.

4.2. Anode-electrolyte interface

The interface between anodes and SSE is solid-solid interface where voids are normally presenting, resulting in a reduction of effective contacting areas. And owing to the high likelihood of side reactions on the interface between lithium anodes and electrolytes, it is necessary to modify contacting interface to solve related interface problems by adopting appropriate processing techniques [22, 23].

4.2.1 Electrolyte modification

Alloying or surface coating of SSE can significantly improve the interfacial stability and compatibility between lithium anodes and SSE [22]. Shao, et al improved the interfacial stability of solid-state batteries by coating the interface of electrolyte with a graphite-based soft interfacial layer [24].

4.2.2 Composite anodes

The composite anodes formed by compositing lithium metals with carbon are aimed at improving the interface problems between lithium anodes and SSE to some extent [23]. Huang, et al relived the surface tension of lithium anodes and improved the compatibility with garnet SSE by incorporating g-C_3N_4 in lithium anodes [23].

4.2.3 Multi-dimensional structural design

The use of multi-dimensional structure can effectively minimizes the negative impact of lithium anodes' volume changes during working operations and inhibits the growth of lithium dendrites by reducing part current density at the same time. Liu, et al designed a composite material made of three-dimensional lithium and reduced graphene oxide, doping with a flexible interfacial layer, to ensure the continuous close contacts between anodes and electrolytes, significantly improving batteries' performances [25].

5. Conclusion

With increasing demands for greater safety, higher energy density, higher power and longer life-span lithium-ion batteries, solid-state lithium-ion batteries have been receiving much attention, but still face serious interfacial problems of SSE. Therefore, in this paper, after introducing the types of SSE and two types of existing interface: voids and interfacial membranes, the interfacial mechanical failure modelings would be argued in terms of the cathode-electrolyte interface, the growth of lithium dendrites and the rupture of layered composite electrodes, as well as relevant influencing factors, concluding that the factors affecting the growth of lithium dendrites at the interface between lithium anodes and polymer SSE are electrolytes' electrochemistry properties, modulus of rigidity and interfacial contacting properties, etc.; the factors affecting the growth of lithium dendrites at the interface between lithium anodes and inorganic ceramic electrolytes are the mechanical and electronic properties of grain boundaries, defects such as cracks and the mobility of electrolytes, etc.; and the factors affecting the rupture of layered composite electrodes are the volume fraction of active particles and the characteristics of the pores, etc. Besides, the improvements of interface problems are discussed respectively from cathode and anode, drawing conclusions that the improvement ideas of cathode-electrolyte's interface problems are to make cathodes and electrolytes maintaining a relatively close physical contacting; the improved thoughts of anode-electrolyte's interface problems are electrolyte modification, composite anodes and multi-dimensional structural design separately.

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