Interfacial Issues of All Solid State Lithium Batteries

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(Received 31 May 2018; revised 20 June 2018; accepted 5 July 2018)

Abstract: All solid state lithium battery is a promising next-generation battery system with improved cycle life, energy density, especially safety. However, its development is greatly hampered by a large impedance between the solid state electrolyte/electrode interface. How to build an ideal electrolyte/electrode interface to improve the interfacial stability and reduce the interfacial resistance is a huge challenge for improving battery performance. This paper reviews interfacial problems and introduces the formation mechanism of different interface layers between electrodes and electrolytes. In addition, the strategies for improving interfacial contact and reducing interfacial resistance are described in detail. Finally, the research directions for engineering interfaces in all solid state lithium batteries are proposed.

Key words: Lithium battery; all solid state; electrolyte; electrode; interfacial resistance

CLC number: O646 **Document code**: A **Article ID**: 1005-1120(2018)04-0578-12

0 Introduction

Lithium ion battery (LIB) market has been expanding from portable electronic devices to electric and hybrid vehicles field in the last decade because of the high energy density, excellent performance and no memory effect[1-2]. However, traditional organic electrolytes have many hidden dangers such as leakage, flammability, or gas production under high temperature, which hampered the rapid development of electric vehicles[3-5]. The emergence of all solid state batteries is expected to overcome these safety issues. As a key component of the all solid state batteries, the solid electrolyte plays as an ion conductor as well as a diaphragm, which greatly influences the performance of the batteries[6]. Compared with traditional liquid electrolytes, the main advantage of solid electrolytes is high safety[7], another feature is the possibility of internal series, which increases the energy density of the modules and systems.

Currently, the solid electrolytes generally fall into three categories according to the components: inorganic solid electrolytes, polymers and hybrid electrolytes[8-9]. Solid electrolytes are limited in lithium ion conduction and their ionic conductivity is far less than that of liquid electrolytes (about 10^{-2}). The development of inorganic solid electrolytes with high ion conductivity has increased in recent years, due to the rapid growth of research on solid state lithium batteries, such as NASICON[10-14], LISICON compounds[15-16], sulfides[17-21] and garnet-type materials[22-23]. Li et al[24] choose Ta as the dopant and prepared garnet-related oxides $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$ with a

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How to cite this article: Wang Leidanyang, Su Junming, Liu Siyang, et al. Interfacial issues of all solid state lithium batteries[J]. Trans. Nanjing Univ. Aero. Astro., 2018,35(4):578-589.
http://dx.doi.org/10.16356/j.1005-1120.2018.04.578

high ionic conductivity of 1×10^{-3} at room temperature by substituting Zr^{4+} sites with Ta^{4+} in the $Li_7La_3Zr_2O_{12}$ (LLZO). Among the inorganic electrolytes, the sulfides electrolytes possess the highest known ionic conductivity[21,25]. Solid polymer electrolytes (SPEs) offer good film formation and easy large-scale production, however, their extremely low conductivity at room temperature is the main limiting factor that prevents its application[26]. The integration of lithium salts[27-28] and ionic liquids[29-30] can compensate for their ionic conductivity defects while retaining flexibility. In addition, the introduction of inorganic fillers[31-32] or solid electrolytes[33-40] can lower the crystallinity of polymers, increase the free movement of segment, and promote the lithium ion conduction.

Although researchers have made unremitting efforts to increase ionic conductivity for decades, there has been no significant breakthrough in the development of all solid state batteries. This is primarily due to the large interfacial impedance[40-44]. Due to the fluidity, liquid electrolytes can infiltrate the electrode materials with relatively low ionic resistance. Unlike the conventional solid/liquid interface, the electrode and electrolyte are both solid in all solid state batteries. Therefore, a very large interfacial resistance will form between the solid/solid interfaces, which extremely limits the transmission of lithium ions in the battery and becomes a short board for solid state battery development. In this article, we mainly review the interfacial impedance problems between electrodes and electrolytes in all solid state batteries and discuss the relevant solutions.

1 Solid/Solid Interface Between Electrolyte and Electrode

High interfacial resistance between the electrodes and electrolytes is mainly caused by the following aspects: (1) Interfacial phases caused by elemental diffusion. The chemical/electrochemical compatibility between electrode and electrolyte materials greatly affects the interface composition and properties. (2) The space charge layer (SCL) that results from the shielding effects of the solid/solid interface on the electric field. (3) Interface contacts between solid and solid. Rigid contact of the solid material is far worse than the solid/liquid interfacial contact. (4) Mechanical stability of solid/solid interface. It is important to understand the variety of solid/solid interfacial contact caused by the changes in the volume of electrode materials during the cycles, and coordinate the stress matching between the electrodes and the electrolytes.

1.1 Interfacial phases caused by elemental diffusion

Kim et al.[45] found that an interfacial layer of thickness about 50 nm was developed between LLZO and $LiCoO_2$ (LCO) during the deposition of the positive electrode (Fig. 1). The energy dispersive X-ray spectroscopy (EDX) at the interface showed Co, La and Zr elements diffused into each other and formed an interface phase which was later confirmed to be the La_2CoO_4 composite with no Li^+ conductivity. This indicates that the reaction phase underlies the increase in interface resistance. To eliminate this interface phase, cathode materials are surface-modified by coating Al_2O_3[46], ZrO_2[47] and Li_3BO_3[48] or other oxides to inhibit direct contact between active materials and electrolytes, which effectively reduces the thickness of the boundary phase and the charge transfer resistance at the interface. Furthermore, introducing a buffer layer between the cathode and electrolyte can also effectively suppress elemental diffusion and reduce the interfacial resistance.

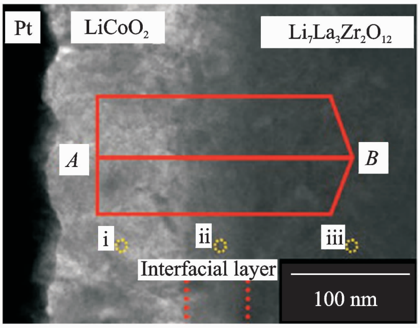
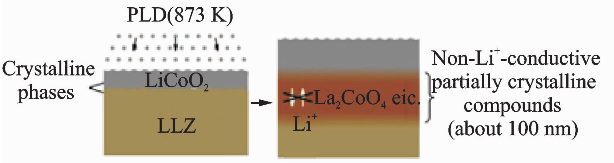
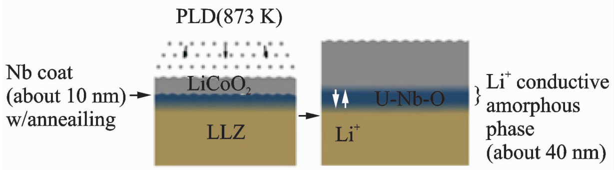


Fig. 1 Cross-sectional TEM image of LLZO/LCO interface[45]

Kato et al.[49] introduced an ultra-thin Nb buffer layer between LLZO and LCO via RF magnetron sputtering to suppress the inter-diffusion of elements and form an ionic insulation phase. During subsequent high temperature treatment, the Nb dissolved in LLZO and formed an amorphous ionic conductor Li-Nb-O film. Introducing the Nb layer significantly improved the capacity and rate capability of the battery (Fig. 2). The impedance of the LLZO/LCO was reduced from 2 600 Ω · cm^2 to 150 Ω · cm^2 via AC impedance test. When the Nb layer thickness was 10 nm, this results in a minimum charge transfer resistance at the interface. Replacing Nb with Ta layer also has the similar effect. Importantly, the thickness of the coating and the buffer layer can lead to the greater resistance due to their own insulating properties. Therefore, finding materials with high ionic conductivity can be a better choice.



(a) Non-modified interface



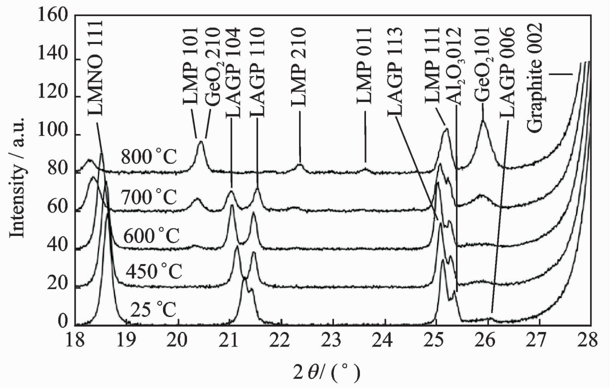
(b) Nb-modified interface

Fig. 2 Schematic of non-modified and Nb-modified LLZ/LCO interfaces[49]

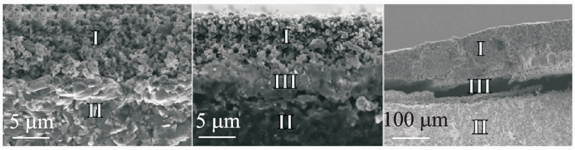
Composition and morphology determine the nature of the interface. Therefore, changing the composition of the electrolyte can also impact on the chemical stability of the interface. Kanno's group found a self-assembled respiratory interface between the electrolyte and the anode that increased the interface contact and improved the battery performance[17,50]. To explain this phenomenon, they compared thio-LISICON and glassy Li-Si-P-S-O systems as inorganic solid electrolytes. When the electrolyte composition is $Li_{3.25}Ge_{0.25}P_{0.75}S_4$, the interface formed between it and the Li-Al alloy anode can better support the rapid charge and discharge of the battery. However, a large impedance boundary layer emerged when it transformed into a glassy Li_3PO_4-Li_2S-SiS_2 electrolyte[51]. These proved that the formation of an interfacial phase depended on the composition of the electrolyte. Ohta et al.'s study of garnet-type oxides also confirmed this conclusion. All-solid-state cells with Nb substituted $Li_{6.75}La_3Zr_{1.75}Nb_{0.25}O_{12}$ (LLZNbO) electrolyte delivered a high capacity of 127 mA · h · g^{-1}. The cross-sectional FE-SEM image and EDX mapping demonstrated that no elemental diffusion occurred near the interface after 100 cycles of charge and discharge[52]. In addition, the interfacial resistance of LLZNbO/LCO remains constant throughout the cycle test, fully demonstrating the stability of the interface.

Robinson et al.[53] used in-situ XRD techniques to investigate the evolution of phases in $LiMn_{1.5}Ni_{0.5}O_4$ (LMNO)@$Li_{1+x}Al_xGe_{2-x}(PO_4)_3$ (LAGP) mixed systems at different calcination temperatures. New product peaks appeared along with gradually disappearing of initial peaks when the temperature exceeded 600 ℃. This further proved that reactions between LMNO and LAGP occurred at high temperatures and generated olivine $LiMnPO_4$ (LMP). LMP is considered to have a certain ionic conductivity, while it is disappointing that the discharge capacity of all solid state Li/LAGP/LMNO cells treated at 650 °C is only 2.5 mA · h · g^{-1}. They subsequently found that the interfacial phase did not appear between the cathode and the electrolyte until the processing temperature reached 750 ℃. If the temperature continues to rise, the interface will separate, and the gap will result in a larger interfacial resistance (Fig. 3).

Based on the above, enhancing the contact of the materials and increasing the ionic conductivity of the mixed system with the help of extra materials or controlling the internal reaction of active materials and electrolytes to form a uniform conductive interface phase are crucial for obtaining an all solid state battery with ideal electrochemical



(a) In situ XRD spectrum



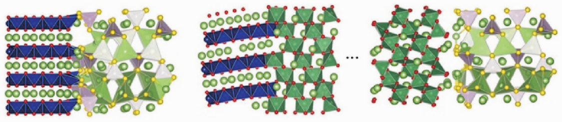
(b) 700 °C (c) 750 °C (d) 800 °C

Fig. 3 In situ XRD spectrum of mixed powder (LAGP and LMNO) and interface changes at different temperatures[53]

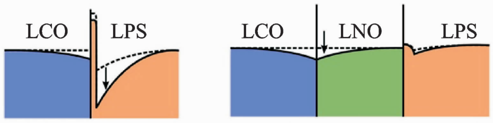
performance.

1.2 Space charge layer

The SCL effect is the redistribution of carriers in the space charge region near the interface when the two phases are in contact[54]. The all-solid-state batteries have electrodes and electrolytes in two distinct ionic conductors. When both are in contact, the Li^+ at the interface will migrate and generate holes to form a space charge layer due to the thermodynamic equilibrium. The conduction rate of Li^+ at the interface is significantly lower than that of the solid electrolyte due to the structure and composition of the interfacial layer deviate from the optimum state of the fast ion conductor, which leads to a large interfacial resistance. When the sulfide electrolyte is in direct contact with the oxide cathode, because the oxygen has the greater force on Li^+, the Li^+ will enrich on the side close to the oxide, and Li^+ concentration in the electrolyte is reduced. This concentration gradient causes a space charge layer on both sides of the sulfide and oxide[54-55]. When the oxide cathode is a mixed conductor, the electronic conductance will dilute the Li^+ concentration near the oxide so that the space charge layer on the oxide side disappears. At the same time, the Li^+ in the sulfide migrates to the oxide again, eventually increasing the space charge layer on the sulfide side, resulting in a larger interfacial resistance (Fig. 4)[56].



(a) Equilibrium (Atomic structure)



(b) Initial stage of charging (Li ion concentration)

Fig. 4 Interface structure and Li^+ concentration change at interface between oxide electrode and sulfide electrolytes[56]

In order to suppress the expansion of the space charge layer on the sulfide side and reduce the interfacial impedance, Ohta et al.[57] used $LiTiO_4$ to coat the cathode surface via spraying. This material can be considered to be a pure ionic conductor because it is electronically insulated in the operating voltage range of $LiCoO_2$. Inserting the $LiTiO_4$ film can build a double-layer interface that suppresses the expansion of the space charge layer. Electrochemical impedance spectroscopy (EIS) tests were performed on batteries with different coating thicknesses. As the thickness gradually increases, the space charge layer shrinks and the battery impedance gradually decreases. In contrast, the impedance increases again when the thickness exceeds 5 nm. This is attributed to the low conductivity of $LiTiO_4$ as the dominant factor in the interfacial impedance. In subsequent work, $LiTiO_4$ was replaced by $LiNbO_3$ with a higher ionic conductivity[58] and resulted in a smaller interfacial impedance and the enhanced rate performance.

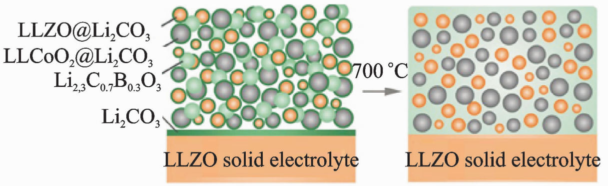
Similarly, an Al-rich layer will form in-situ on the surface when using the Al-substituted $LiAl_yCo_{1-y}O_2$ as a cathode to match a sulfide solid electrolyte. This buffer layer decreased the electron conductivity of the positive electrode and suppressed the formation of SCL[59]. Compared with other buffer layers and coatings mentioned above, this self-organized buffer layer can maintain good stability at high temperatures to avoid mutual diffusion between the coating layer and the active materials. Moreover, this method is simple and conducive to large-scale production.

Although the SCL effect between oxides and sulfides has been extensively studied, understanding the SCL effect at the interface of oxide/oxide or oxide/polymer is still in the initial stages and requires further exploration. In addition, the SCL effect inside the composite is another important factor affecting the ionic conductivity of the solid electrolytes.

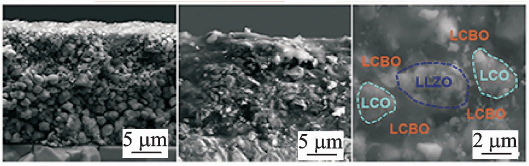
1.3 Interface contacts between solid and solid

Atomic layer deposition (ALD), pulse deposition, and magnetron sputtering are mainstream methods to guarantee a normal charge and discharge of all solid state lithium batteries. They introduced a buffer layer or coating to obtain good electrode/electrolyte contact. Recently, some new interface engineering and electrode assembly strategies have been proposed, including surface modification[60-61], porous interface[62], double porous electrolyte[63], organic metal skeleton based electrolyte[64], 3-D layer structure[65] and 3-D ordered microchannel structure composite electrolyte[66]. The electrode materials can be tightly embedded in the electrolyte particles due to the introduction of the porous interface. This open interface can increase the number of contact sites, enhance the interconnection between the electrolyte particles and the active materials, and provide more channels for the Li^+.

The composition of electrolytes and electrode materials greatly affects the contact characteristics between particles. LLZO is a promising solid Li ion electrolyte that reacts slightly with H_2O and CO_2 when exposed to air for a long time, and grows a layer of amorphous Li_2CO_3 on the surface. Due to its lower ionic conductivity, the rapid transmission of Li ions is suppressed and results in a large contact resistance. Although the entire operation is usually done in a glove box, this spontaneous reaction still puzzles the research of LLZO solid state electrolytes. Recently, Han et al. [67] used $Li_{2.3}C_{0.7}B_{0.3}O_3$ as a welding material to react with the Li_2CO_3 formed on LLZO surface at 700 ℃ to produce $Li_{2.3-x}C_{0.7+x}B_{0.3-x}O_3$ as a solid electrolyte intermediate phase, thus obtaining the electrode composition of all-ceramic structure (Fig. 5). The $Li_{2.3-x}C_{0.7+x}B_{0.3-x}O_3$ has superior wettability and offers a close connection between the LLZO and the LCO. The all solid state battery exhibited a capacity of 96 mA • h • g^{-1} at room temperature, and maintained good stability during charge and discharge even under large current. This report provides a novel method and idea to solve the problem of large contact resistance between active materials and electrolytes. They make full use of the spontaneous Li_2CO_3 film and convert them directly into "welding" materials at high temperature to integrate the active materials with the electrolyte particles. The all ceramic structure can reduce the overall impedance and facilitate the assembly of the batteries.



(a) Schematics of interphase-engineered all-ceramic cathode/electrolyte

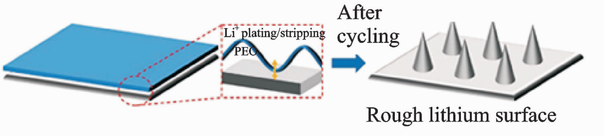


(b) Cross-section of cathode composite coated on LLZO pellet before (left) and after(middle and right) sintering

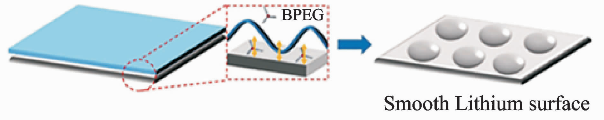
Fig. 5 Schematics of all-ceramic cathode/electrolyte and SEM images of cross-section and top surface of cathode composite before and after sintering[67]

Lithium is a perfect anode for rechargeable batteries because of its ultrahigh specific capacity[68-70]. However, the growth of lithium dendrites during the charging process in traditional liquid electrolyte systems will pierce the diaphragm and short circuit the battery. Although the solid electrolyte is a promising system to match the Li anode, the lithium dendrite problem still remains. For a single inorganic oxide electrolyte, during the charging process, Li^+ ions from the ceramic are preferentially plated on the ceramic grain boundary. Li ion flux is locally enhanced under the electric field, and the Li dendrite will grow continuously along the grain boundary, finally causes a short circuit. Introducing Ge[71], Si[72] or Au[73] to form alloys can make a better contact between electrolyte and Li anode to average the local flux of Li^+. Han et al.[74] used an ALD method to generate an ultra-thin Al_2O_3 film between the Li anode and a $Li_7La_{2.75}Ca_{0.25}Zr_{1.75}Nb_{0.25}O_{12}$ (LLCZN) electrolyte. This reduced the interfacial impedance from 1 710 $\Omega \cdot cm^2$ to 1 $\Omega \cdot cm^2$ at room temperature. The oxide coating wets the surface of the metallic lithium in contact with the garnet electrolyte and suppresses the formation of impurities such as Li_2CO_3. The TEM and EELS showed that the Li-Al-O transition layer first emerged close to the electrolyte during deposition of the Al_2O_3 film. This interface allows efficient lithium ion transport between the lithium metal anode and the garnet electrolyte, effectively eliminating the interfacial resistance. In addition, the stability of the interface was also calculated by first-principles calculations, confirming that the deposition of Al_2O_3 can improve the interfacial stability between both layers and prevent the decomposition reaction.

Hybrid electrolytes integrate the advantages of inorganic materials and polymers and compensate for their short board. The internal inorganic particles prevent the anion transport, reduce the double-layer electric field at the Li/polymer interface and prevent electrochemical/chemical degradation of polymers, which help to increase the coulomb efficiency of the battery. Furthermore, polymers can fill the gaps between inorganic particles and wet the surface of the Li metal. This decreases the Li^+ transfer resistance and produces a uniform Li^+ flux at the interface[75-77]. The combination demonstrates obvious dominants in inhibiting lithium dendrites growth (Figs. 6, 7). Goodenough's group[78] developed a three-dimensional network structure of cross-linked polymers (poly (ethylene glycol) methyl ether acrylate (CPMEA)). The main chain provided the framework, and the branches moved freely to accelerate the transmission rate of Li ions. In this polymer/LATP/polymer (PCPSE) sandwich electrolyte, the polymer adhered to the lithium metal surface has good wettability and contributes to uniform the Li^+ distribution at the interface, which suppresses the formation of dendrites and reduces the Li^+ transfer resistance. The assembled Li/CPMEA-LATP/LiFePO4 all solid state batteries exhibited a long life of 640 cycles with a coulomb efficiency as high as 99.8%—100%.

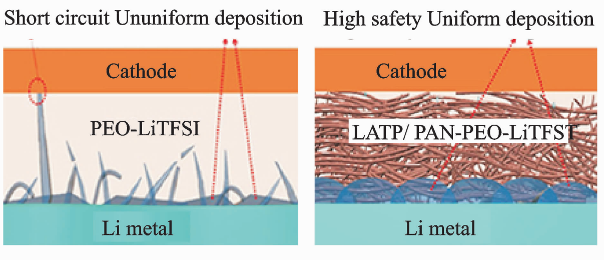


(a) CSE membrane without BPEG



(b) CSE membrane with BPEG

Fig. 6 Schematic of contact between lithium metal and different polymers[76]



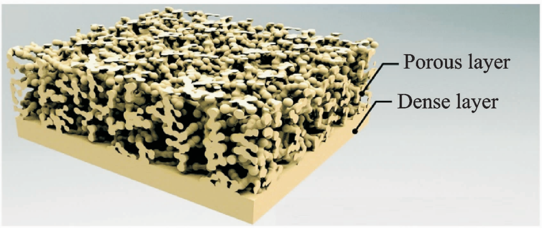
(a) Li|PEO-LiTFSI|$LiFePO_4$ (b) Li|LATP/PAN-[PEO-LiTFSI]|$LiFePO_4$

Fig. 7 Schematic of interfacial contact between lithium metal and composite electrolyte[77]

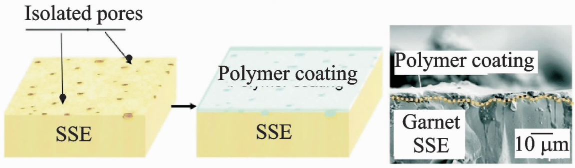
By using polymer/inorganic hybrid electrolytes, polymer/polymer coordinating electrolytes successfully reduced the contact impedance between electrodes and solid electrolytes. However, in order to meet the requirements of high voltage and high energy density, the search for comprehensive polymers with superior ionic conductivity at room temperature and stability is necessary, especially for the Li^+ transport mechanisms at the interface between the electrolytes and the electrodes after the modification, which is important for guiding the selection of electrolyte composition and structure design.

1.4 Mechanical stability of solid/solid interface

All-solid-state batteries have a large interfacial stress because of the special solid/solid interface, thus the solid electrolytes must ensure full contact with the active material particles in order to achieve lithium ion transport. However, any electrode material, whether graphite or ternary material, will have a volume change during charge and discharge[79-81]. The solid electrolytes have non-flow characteristics of solid electrolytes that inevitably lead to solid/solid separation once the volume of cathode materials changes. The conducting lithium ions will be blocked, resulting in a sharp decrease in the battery performance. Therefore, ensuring the mechanical stability of the interface between the electrode and electrolyte is another challenge for all solid state batteries. As for the selection of electrolytes, sulfides may be a better choice than oxides, because they are relatively soft. In addition, the development of effective interface construction technology also has a high application value for establishing a stable solid/solid interface.



(a) Solid-state bilayer framework



(b) Polymer coated dense garnet layer

Fig. 8 Schematic diagram of porous-dense double layer garnet electrolyte and polymer coating[65]

Hu and Wachsman's group[65] reported a hybrid solid electrolyte with a novel three-dimensional skeleton structure (Fig. 8). Among the double layer dense-porous garnet solid electrolyte skeleton structure, the porous layer provides more transport paths for lithium ion/electron conduction and suppresses the volume change of the active material, while the dense layer can inhibit polysulfide diffusion and lithium dendrite formation. Coating the structure with a polymer compensates for the interface roughness and allows Li ions to uniformly pass through the interface. Although the dense layer reduced to a thickness of several micrometers, it maintained good mechanical stability that ensured the safety of the lithium metal battery. The thick porous layer can support a variety of cathode materials and provide ion conductivity channels. This double-layered porous structure solves two major problems of chemical/physical short circuit and electrode volume change at the same time. To overcome the volume expansion of the cathode electrode during charge and discharge, Goodenough et al.[82] adopted a series structure with two electrolytes. The Ba-doped Li^+-glass electrolyte was attached to the Li anode, while the cathode side was contacted to succinonitrile (SN) plasticizer mixed with $LiClO_4$ salt. This mixed electrolyte guaranteed a completely contact with cathode particles, and it avoided the interface separation caused by the volume expansion of active particles because of the certain elasticity of plasticizers. Under a current density of 153 $mA \cdot g^{-1}$, the all solid cell demonstrated a long cycle life over 23 000 times, which is far beyond the ordinary lithium-ion battery. Filling the polymer between the electrolyte and the active material particles contributes to good physical contact between the electrolytes and the electrodes, reducing interfacial resistances and simultaneously alleviating the interfacial separation caused by the material expansion during the charge and discharge. The flexibility of the polymer ensures the transmission channel of Li^+. There is an urgent need to design more interface modification techniques to push the transition from traditional lithium batteries to all solid state batteries and enhance the safety and performance of lithium batteries simultaneously.

2 Conclusions

With the constant increase in the specific energy of the power battery, the traditional lithium-ion battery system has been unable to meet the design requirements of the high specific energy battery. However, there are various problems in solid electrolytes that limit its wide applications. The biggest limitation is the interfacial problems. Due to element diffusion and the presence of impurities, there is a large interfacial impedance between the electrolyte grain boundaries and the electrode/electrolyte interface. In addition, sufficient contact with the positive electrode particles cannot be ensured because of the non-flow property of solid electrolytes. In particular, the volume expansion of the positive electrode materials will exacerbate this problem during charge and discharge, resulting in a larger interfacial resistance. To solve these problems, researchers proposed various strategies, such as coating, buffer layer, ceramic-polymer composite electrolyte, double-layer interface and so on, and achieved a certain effect. It is inevitable to solve the interfacial issues to realize the application of all solid state lithium batteries. Some feasible suggestions for reducing the interfacial resistance could be concluded as:

(1) Adding elastic substance with ion conductivity to the active materials during the preparation to alleviate the volume expansion in charge and discharge process. Elastic substance acts as a bridging channel with the solid electrolyte to ensure the transport of lithium ions.

(2) Combined with polymers to build a soft contact interface between electrodes and electrolytes.

(3) Using multi-channel structures or polymer materials to uniform the local flux of Li ions and suppress the growth of lithium dendrites.

(4) Reasonably controlling and utilizing the chemical/electrochemical reaction between the electrode material and the electrolyte to obtain an excellent interfacial layer.

Acknowledgement

This work was supported by the Science & Technology Commission of Shanghai Municipality, China (No. 08DZ2270500).

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(Production Editor: Sun Jing)