

## Review article

## The interfacial behaviours of all-solid-state lithium ion batteries

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## ABSTRACT

All-solid-state lithium ion batteries (ASS-LB) will gradually replace traditional liquid lithium ion batteries owing to the inevitable volatility and explosion safety problems in traditional liquid lithium ion batteries. However, the development of all-solid-state batteries has been hindered because of the key role of interfacial behaviour, which can significantly influence battery properties, such as cycle life and specific energy. In this article, we reviewed the current knowledge regarding interfacial behaviour and modified methods in the ASS-LB and concluded that the contact area, pore distribution, phase structure and interfacial potential barrier directly affect interfacial ion transport performance. Therefore, we propose a novel design including microbial directed modification, freeze-drying method, and microwave technology in order to control the interface behaviours of ASS-LB. Finally, using the magnetron sputtering method, dense microcrystalline  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  was applied between the interfaces to verify that the reduction of the energy barrier and the control of the interfacial contact can effectively enhance the interfacial ion transmission.

## 1. Introduction

The relationship between energy utilization and environmental protection is interdependent on the further development of society. Efficient utilization of energy can indirectly reduce the environmental pollution issues. Energy conversion devices are a key factor in energy utilization owing to the need for the increased utilization efficiency. Lithium ion batteries play a crucial role in the fields of electronic equipment, automobiles and unmanned aerial vehicles due to their high specific energy, low self-discharge and good cycling performance [1–3]. However, the traditional liquid lithium-ion batteries show a gradual degradation of performance and cannot satisfy the demand of the existing electronic devices owing to the safety problems caused by the liquid electrolyte [4–6]. The organic liquid electrolytes with a narrow electrochemical window are easily decomposed and flammable, impeding the utilization of energy storage devices in the future [7–9]. Therefore, as a substitute for liquid electrolytes, a solid electrolyte can not only reduce the cost of raw materials and manufacturing but also dramatically raise the specific capacity, cycle and safety performance [10].

The fundamental difference between the ASS-LB and liquid lithium-ion batteries are the morphological characteristics of the ion transmission media in the electrolyte. The transmission media in liquid lithium-ion batteries is an organic electrolyte using which the transmission mode is solid-liquid-solid (flammable, labile, S-L-S), whereas the solid-solid-solid (stably, wide electrochemical window, S-S-S)

transmission mode is used in a solid battery. This change plays a great role in the enhancement of the capacity and energy density, and also shows a perfect safety improvement that is satisfactory for future battery development.

ASS-LB research began in 1950s. However, the development is restrained by the low ionic conductivity, which is caused by the interfacial issues. Based on the morphology of electrolyte, the ASS-LB can be classified as polymer batteries and inorganic batteries. To date, only the composite polymer solid electrolyte (1973–1990s) has been applied in solid batteries. However, the safety issues of this battery have not yet been completely solved because the polymer is also flammable. Fortunately, ASS-LB with a high ion conductivity ( $10^{-6} \text{ S cm}^{-1}$ ) is commercially feasible since the synthesis of the stable Lipon (Lithium phosphorous oxynitride) electrolytes using magnetron sputtering by researchers at the Oak Ridge National Laboratory in 1992 [11–15]. Between 1999 and 2005, the elementary structure of Lipon evolved from "one-chip" to "stacked" and then to "upright", thereby increasing the contact interfacial area and preserving the stable electrochemical properties in ASS-LB [16–18]. In recent decades, sulphide electrolytes and oxide solid electrolytes have been developed as promising inorganic crystal solid electrolyte, which has been the most popular research field. One of the advantages of sulphide electrolytes is their highest ion conductivity ( $> 10^{-3} \text{ S cm}^{-1}$ ) and wide electrochemical window (0–5 V) for the industrialization of ASS-LB. In 1980s, the ionic conductivity of the  $0.5\text{Li}_2\text{S}-0.5\text{GeS}_2$  electrolyte reached  $4.0 \times 10^{-5} \text{ S cm}^{-1}$  using the high-temperature synthesis method [19]. In addition,

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after a decade of research from 2001 to 2011, the Tokyo Institute of Technology had improved the ion conductivity of sulphide electrolytes from  $2.2 \times 10^{-3} \text{ S cm}^{-1}$  to  $1.2 \times 10^{-2} \text{ S cm}^{-1}$  [20]. The ion conductivity of solid oxide electrolyte LLZO ( $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ) reached  $3 \times 10^{-4} \text{ S cm}^{-1}$  with the 0.3 eV energy activity carried out by the transition element substitution reaction [21].

Despite the great progress made in ASS-LB research in recent decades, industrialization still has not been achieved. The main reason for this is the large interfacial impedance between the electrode and the solid electrolyte caused by the low ion conductivity and interfacial flux. Even though the gel-polymer electrolytes and sulphide electrolytes dramatically reduce the interfacial impedance, the ASS-LB cycle performance is still decreased owing to the impurity phases generated on the interface. Therefore, it can be concluded that the primary way to overcome the interfacial problems is to improve the interfacial performance of ASS-LB. Comprehensive research shows that both an excellent interface contact and high conductivity for the interface during charge-discharge can be the most important factors for improving the ASS-LB. Currently, only  $3.4 \text{ mAh g}^{-1}$  capacity (2.5% of theoretical capacity) can be achieved using  $\text{LiCoO}_2$ , metal Li and  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  as the cathode, anode and electrolyte, respectively. The strong interfacial impedance of ASS-LB results in the polarization phenomenon and the discordance between electrolytes and electrodes [22]. Interfacial impedance can be reduced 100 times from  $10^4 \Omega$  to  $90 \Omega$  by using an interfacial  $\text{LiBH}_4$  layer placed between the  $\text{Li}_3\text{PO}_4$  electrolyte (25 nm) and  $\text{LiCoO}_2$  cathode [23]. Radio frequency (RF) magnetron sputtering was explored to deposit Lipon between the  $\text{Li}_{1.3}\text{Al}_{0.3}\text{Ti}_{1.7}(\text{PO}_4)_3$  (LATP) solid electrolyte and the metal Li anode, and this modification method was found to be effective for reducing the interfacial reaction. Even though the battery capacity decreased from  $60 \mu\text{Ah cm}^{-2}$  to  $60 \mu\text{Ah cm}^{-2}$  after cycling 50 times, this approach was obviously effective for interfacial modification [24].

In this review, we provide a detailed summary of the research progress and novel interface modification methods of interface (microbial directed modification, freeze-drying method, microwave technology) for ASS-LB, and prove that the dense microcrystalline interface formed by magnetron sputtering can reduce the energy barrier and control the interfacial contact, which can effectively enhance the interfacial ion transmission. Interfacial classification, ion transport mechanism and modified method were derived, and future development of interfacial control is expected.

## 2. Interface classification and ion migration mechanism

### 2.1. Overview of Interface behaviour of ASS-LB

ASS-LB consists of the solid electrolyte, and the positive and negative electrodes [25,26]. Fig. 1 shows the structural diagram of ASS-LB. The organic electrolyte and diaphragm in the traditional liquid battery are replaced by a solid electrolyte. Thus, the lithium ion transport interface is changed from S-L-S to S-S-S. Therefore, ASS-LB has reliable safety, high specific energy and prolonged cycle performance due to its non-flammable and stable solid electrolyte. Thus, ASS-LB possess strategic superiority in the fields such as military applications, aerospace, unmanned aerial vehicles, and space exploration.

The electrolytes in ASS-LB can be divided into crystalline electrolytes and polymer electrolytes. Inorganic solid electrolytes are classified as either crystalline solid electrolytes ( $\text{Li}_3\text{N}$ ,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ,  $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ , etc.) or amorphous solid electrolytes ( $\text{Li}_2\text{S-P}_2\text{S}_5$  glass-ceramics, LISICON (lithium thiosulfate fast ion conductor), etc.) depending on the crystal type. On the basis of the colloid type, polymer electrolytes are divided into all-solid polymer electrolytes and gel polymer electrolytes (semi-solid). Therefore, complex interfaces are present in ASS-LB, as shown in Fig. 1(b), which can be mainly divided into the grain boundary interfaces (electrode, solid electrolyte and other internal grain boundaries) and the phase interfaces (electrode-solid electrolyte, electrode-pores,

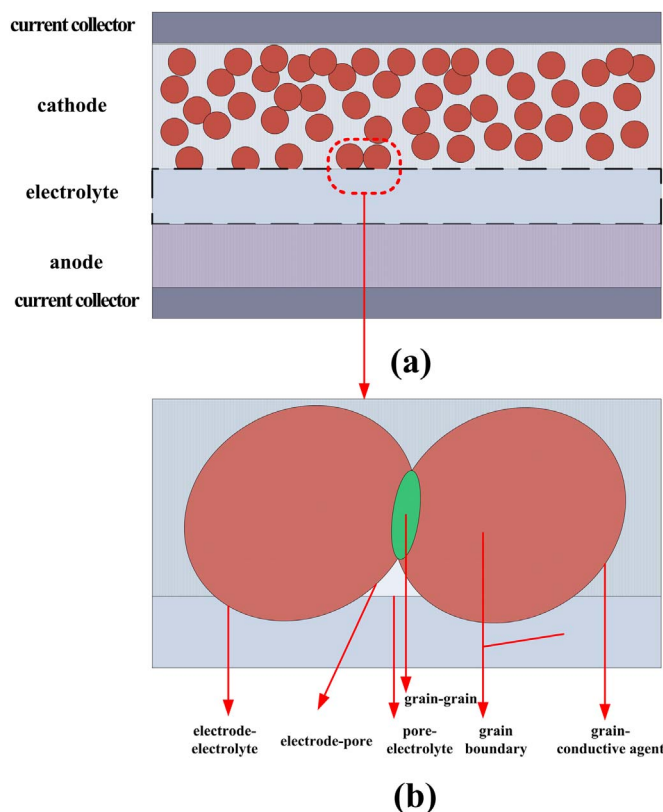


Fig. 1. Diagram of ASS-LB structure: (a) macro diagram; (b) interface in detail.

electrode-electrode, electrode-conductive agent, electrode-collector interface, etc.).

### 2.2. Transmission characteristics of interfacial ions

#### 2.2.1. Grain boundary

Grain boundary is an interface between the grains generated by a difference in crystal orientation during the sintering process. Fig. 2 shows two types of grain boundaries. The first is a dense grain boundary forming from different crystal directions which is present in the internal grains of both the electrolyte and electrode and which is relatively smooth and narrow; the second grain boundary is a small-size, porous issue from different grains during the treatment processes (temperature, pressure, atmosphere, etc.). Different crystal grains may belong to diverse crystal materials with stronger ion diffusion. The diffusion model at the interface is different from that of the inside of the grain owing to complicated internal structures that depend of defect concentration, crystal type and phase transformation. Therefore, we define "short circuit diffusion" as the diffusion model for the grain boundary. The interfacial charge-rich regions are formed by the aggregation of specific unsaturated bond structures, and these regions can control the surface work function and produce the interfacial field that can influence the interfacial ion transport model [27].

Ion hopping on the interface and inside the grain vary for the different structure. The grain boundary diffusion coefficient can be obtained using Fick's first law, Fick's second law, and the Arrhenius dependence of the hopping frequency [28], as shown in formulas (1)–(4):

$$J_i = -D_i \nabla C_i = -D_i \frac{\partial C}{\partial x} \quad (1)$$

$$\frac{\partial C_i}{\partial t} = \nabla(-D_i \nabla C_i) \quad (2)$$

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