

Performance Analysis of Different Types of Solid Electrolytes

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Abstract. The development and interest in environmentally friendly cars nowadays present new challenges to the lithium-ion batteries. With the safety problems caused by the liquid electrolyte in conventional batteries, the development of new electrolytes is becoming increasingly urgent. Based on the existing literature, this paper discusses the following: (1) the advantages and disadvantages of solid-state electrolytes; (2) Requirements for solid electrolytes; (3) Classification and characteristics of solid electrolytes; (4) Properties of different types of electrolytes; (5) Future application and research direction. Performance and possible applications of different solid-state electrolytes are presented in this paper. Specifically, it is found that inorganic solid electrolytes are the best in ion transference number, making them suitable for quick charging batteries. Polymer-based solid electrolytes perform better at electrochemical window, so they can be used to enhance the energy density of batteries. Polyethylene glycol (PEG) based composite solid electrolytes and sulfide solid electrolytes have the highest ionic conductivity, so they are optimum materials for high-rate performance batteries.

Keywords: Lithium-ion battery, Solid-state electrolyte, electrochemical property.

1. Introduction

At present, most of the commercial lithium-ion batteries use organic liquid electrolytes. Unfortunately, liquid lithium-ion batteries have worrying technical issues like cruising range anxiety as well as safety issues like flammability, explosion, and short-circuit. The mechanism of a conventional lithium-ion battery and all solid-state battery are shown in Figure 1(a) [1] and Figure 1(b) [2]. When charged, lithium ions are removed from the anode, transported through an electrolyte, and then embedded in the cathode. The external electronic conductor transfers electrons for charge balance from anode to cathode, thus ensuring that equal charges are received at both poles.

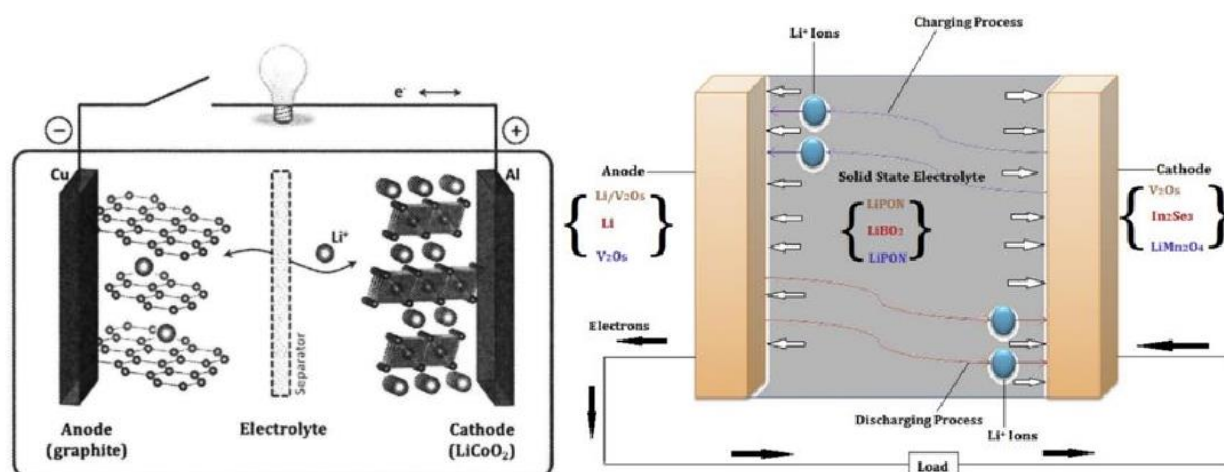


Figure 1. (a). Schematic diagram of typical lithium-ion battery [1]. (b) The working principle of all solid-state lithium-ion battery [2]

A critical requirement for industrial development is the creation of lithium-ion batteries with high energy density and outstanding safety performance. All-solid-state batteries have the advantages of safe operation and high theoretical specific capacity over conventional liquid lithium-ion batteries. As a result of their thorough research, they are recognized as the leading technology for next-

generation batteries. Solid-state electrolytes of different types have been presented by researchers. Wu et al. reported a Ga-doped lithium lanthanum zirconium oxide solid electrolyte with the conductivity reaching $2.06 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ [3]. Recently, Zhou successfully synthesized a Fe-doped lithium phosphorus oxynitride (LiPON) solid electrolyte thin film using radio frequency (RF) magnetron sputtering. It has a very high ionic conductivity ($1.08 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$) and a high ion transference number (0.974) [4]. Apart from that, much interest has been put into developing sulfide solid electrolytes too. This type of electrolyte possesses a very high ionic conductivity. According to Chen et al., the theoretical conductivity of $\text{Li}_{11}\text{AlP}_2\text{S}_{11}$ is $3.3 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ [5]. However, the electrochemical window is very low. It is estimated that the figure for $\text{Li}_6\text{PS}_5\text{Cl}$ is 1.71~2.01 V [6]. In recent works, sulfide solid electrolyte with acceptable electrochemical window is prepared. Ru et al. synthesized the electrolyte $\text{Li}_{10}\text{SiP}_2\text{S}_{12}$ by the ball milling-solid phase method and it has an electrochemical window of 5V [2]. A new polyvinylidene fluoride-hexafluoropropylene copolymer (PVDF-HFP) based gel solid polymer electrolyte with high ionic conductivity ($3.7 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$) and good thermal stability was prepared in situ by the thermal cross-linking method by Liu et al [7]. Despite much research in the respective field of solid-state electrolytes, there are not many papers focusing on the comparison on performance of different types of electrolytes. Hence, this paper aims at discussing and comparing comprehensive performance of different types of solid-state electrolytes. It presents the overview of solid-state electrolytes as well as characteristics of some novel solid electrolytes and is able to guide the direction of future research and application. In this paper, the comprehensive performance is mainly measured by ionic conductivity, ion transference number and electrochemical window using experimental data.

The rest of this paper is structured as follows. An overview of solid-state electrolytes is presented in section 2. Properties of different types of electrolytes are discussed in section 3 to 5. Finally, the conclusion and discussion are given in section 6.

2. Overview of Solid-State Electrolyte

The term 'solid-state electrolyte' refers to the ionic conductive substance existing in solid state at atmospheric temperature and pressure [8]. It is characterized by the migration of lithium ions while conducting electricity at solid state.

There are several advantages of solid-state electrolyte that makes it distinctive from its liquid counterpart and attracts much interest. The main advantages are listed as follows.

(1) No liquid components [9]. As a result, there will be no volatilization, flatulence and leakage problems, which makes it safer to use in batteries.

(2) Excellent mechanical properties [9]. The growth of lithium dendrites can be inhibited and the energy density would be enhanced.

(3) A wider electrochemical window to match high-voltage cathode materials [9]. Thus, the energy density can also be higher.

(4) The structure of batteries can be simplified [9]. If solid-state electrolyte is used, then the diagram in the battery is no longer needed.

Nonetheless, there are still certain issues with this type of novel electrolyte. The most common and most discussed ones are lower capacity and poorer cycling performance [3].

The disadvantages mentioned above are mainly due to the electrode/electrolyte interface problems, which are closely related to loosen physical contact, the existence of grain boundaries, side reactions, and other aspects [3].

Hence, as discussed before, solid-state electrolytes possess its own unique properties and drawbacks that are very different from liquid electrolytes. In order to get a wider application, its ideal physical and chemical properties must be specified so that further modification direction on solid-state electrolyte can be guided. For this kind of electrolyte, it should have an outstanding performance on ionic conductivity, lithium-ion transference number, chemical stability and electrochemistry

stability, wide electrochemical window, low electron conductivity and no side reaction with electrode materials [10].

To meet different performance requirements, three main types of solid electrolytes are currently under research or in use. Their definition and characteristics would be shown in the following part.

The first is inorganic solid-state electrolytes. This type of electrolyte can be further divided into two subcategories, which are oxide solid electrolyte and sulfide solid electrolyte. The main attributes of inorganic electrolytes include: high ionic conductivity, wide electrochemical window, good thermal stability, high energy density, brittleness, difficulties in preparation and poor compatibility with electrode interface. The second is composite solid-state electrolytes (CSEs). They are also known as ionic conducting polymers. They consist mainly of high molecular weight polymers as well as lithium salts and possess a relatively poor performance on ionic conductivity, but are more convenient to produce and have better performance on flexibility and interfacial compatibility. Finally, the Gel polymer electrolyte (GPE). When a certain amount of liquid component is added to the polymer electrolyte, the liquid component can be dispersed in the polymer space network as a filling medium [1]. Electrolyte systems which contain liquid components but are not fluid, are called gel electrolytes. Gel electrolyte is generally a complex consists of electron-donating polymers, alkali metal salts and one or more plasticizers. This type of electrolyte has shown better flexibility, better safety performance and better ionic conductivity compared to the composite ones mentioned above.

3. Properties of Inorganic Solid Electrolytes

3.1. Oxide Solid Electrolytes

Two different types of oxide solid electrolytes will be discussed in this section and there will be a brief comparison at the end. The first is the lithium lanthanum zirconium tantalum oxide (LLZTO) solid electrolytes and the second is the amorphous lithium silicon oxynitride (LiSiON) thin film electrolyte.

3.1.1. LLZTO solid electrolytes

LLZTO solid electrolyte was synthesized by high temperature solid state method [11]. The ionic conductivity was tested by electrochemical impedance spectroscopy (EIS) and the detailed data can be found in Figure 2. It could be calculated from the figure that the conductivity of this kind of garnet structure LLZTO electrolyte was $8.14 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ and it has an electrochemical window that is above 5 V [11].

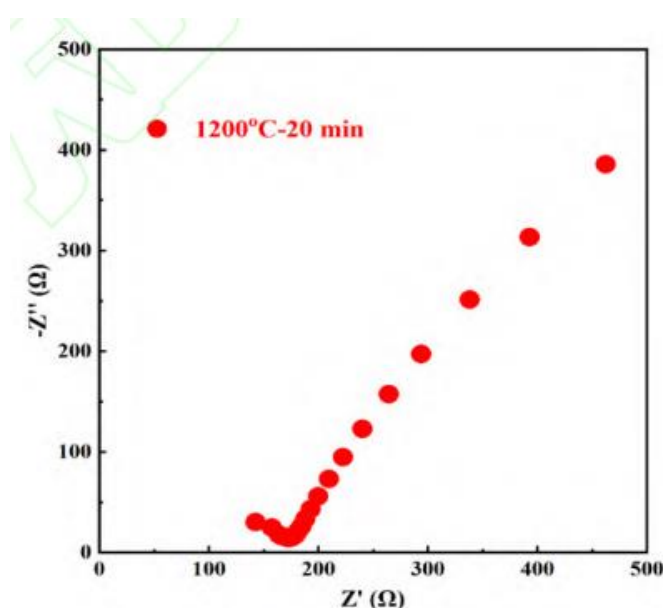


Figure 2. EIS of sample [11]

3.1.2. Amorphous LiSiON thin film electrolyte

The amorphous LiSiON thin films were prepared by RF magnetron sputtering at room temperature as solid-state electrolyte [12]. A sandwiched structure made of Pt, LiSiON, and Pt was used to test the ionic conductivity of the LiSiON thin film electrolyte and the electrochemical window was tested by cyclic voltammetry (CV) measurement. The results showed that it had high ion conductivity at room temperature ($6.3 \times 10^{-6} \text{ S} \cdot \text{cm}^{-1}$) and a very good performance on voltage window (5 V) [12]. Thus, it is a potential electrolyte material for developing all solid-state lithium battery. Its overall performance is better than any previously reported electrolyte with similar structure. The lithium-ion transference number was calculated to be 0.998 [12]. Hence it could be concluded that it was a very pure ionic conductor.

It is clear from the experimental data above that both electrolytes have a very wide electrochemical window. The ionic conductivity performance for LLZTO solid electrolyte is significantly better than LiSiON. The high conductivity makes LLZTO a material worth choosing and researching for solid-state electrolyte in high energy density battery with large capacity requirement.

3.2. Sulfide Solid Electrolytes

Sulfide solid electrolytes have been paid close attention by the industry and the academia for their high ionic conductivity at room temperature and good mechanical performance. In this section, the performance of Li₆PS₅Br electrolyte is analyzed.

Li₆PS₅Br solid electrolyte (LPSBr) was prepared via solid-state sintering method with Li₂S, P₂S₅ and LiBr as starting materials at 550 °C with 0.5 °C min⁻¹ [13]. The sample then went through a set of tests including EIS, direct current (DC) polarization measurements and CV measurements. The results showed that the ionic conductivity reached $1.22 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ and the ion transference number reached 0.994, indicating the electrolyte was almost a pure ionic conductor [13]. The DC curve is presented in Figure 3 [13]. The electrochemical window was around 5 V [13].

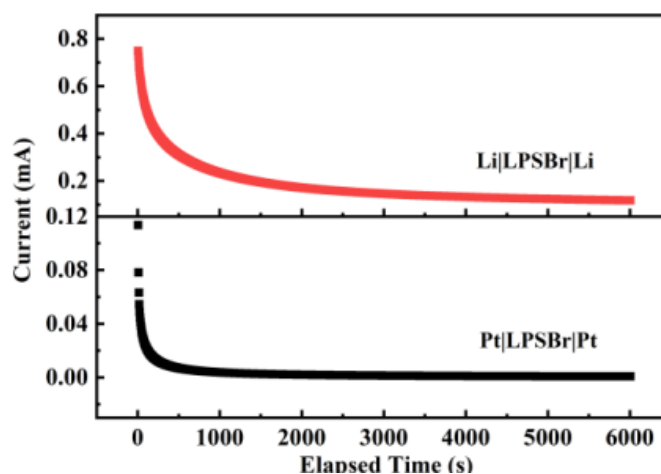


Figure 3. DC polarization curve of LPSBr electrolyte at a constant voltage of 0.1 V at 25°C [12]

It can be concluded that LPSBr is a sulfide electrolyte with significant lithium-ion transference number and a relatively high ionic conductivity at room temperature. It is a sulfide electrolyte with great application prospect.

4. Properties of Composite Solid-State Electrolytes

Currently, polymer electrolytes that have been widely studied include polyethylene oxide (PEO), polyacrylonitrile (PAN), PVDF and polymethyl methacrylate (PMMA). However, they all have certain defects, for example, PEO has a strong tendency to crystallize and a relatively low ionic conductivity; Interface compatibility for PMMA is poor; The contact between PAN and negative

electrode is unstable. In contrast, polypropylene oxide (PPO) polymer presents a special amorphous structure and possesses better physicochemical and electrochemical properties.

In this section, properties of two CSEs with different polymer bases will be discussed. The first is the PPO/ZrO₂ composite solid electrolyte thin films and the second is the PEO-SN₂₅-LiTFSI₁₀-Glass fiber (GF) thin films, where SN refers to as succinonitrile.

PPO/ZrO₂ composite solid electrolyte thin films were created by combining the thermal cross-linking method and the flow-delaying method, with polyetheramine-T403, adipic acid, and polyetheramine-D400 as precursors, a porous cellulose film as the backbone, and plasticizer peg400 and inorganic filler ZrO₂ as modifications [14]. Detailed preparation process is shown in Figure 4 [14].

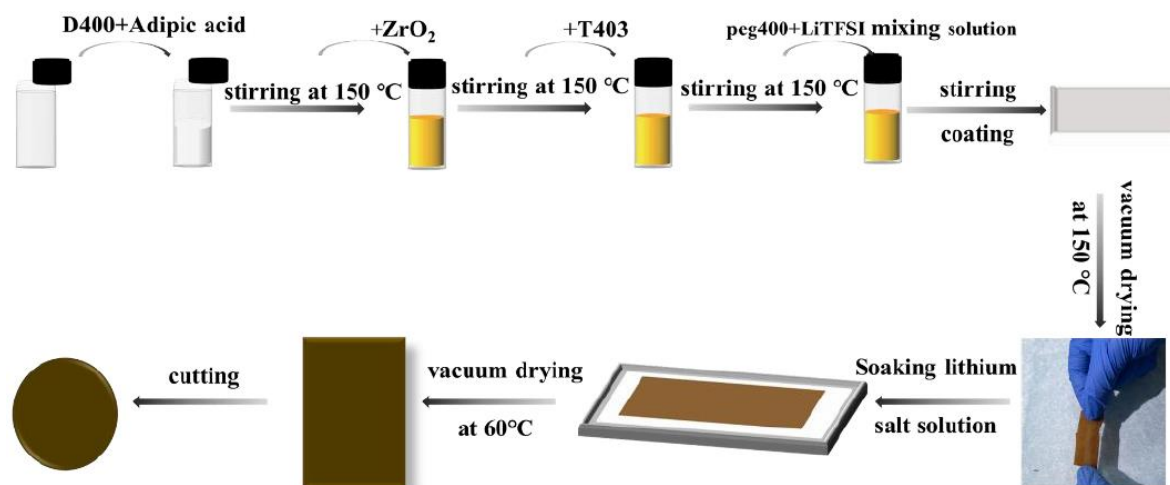


Figure 4. Preparation process of CSE thin films [14]

After the preparation, a series of tests (e.g., EIS, CV measurement, etc.) were carried out on the electrical properties of PPO based composite electrolyte films. The results showed that the ionic conductivity reached $6.67 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ at room temperature (25°C). The ion transference number reached 0.67, and the electrochemical window was 4.6 V [14].

PEO-SN₂₅-LiTFSI₁₀-GF composite solid electrolyte thin films were prepared in the following way. First, a certain proportion of PEO, SN and LiTFSI were mixed and dissolved in anhydrous acetonitrile, stirring for 12 hours. After the solution was fully mixed, it was poured onto the polytetrafluoroethylene (PTFE) plate, GF was then laid flat on the surface of the solution, and finally after the solvent evaporation, the CSE was prepared and ready to be tested [1]. After a similar set of tests, the results showed that the ionic conductivity of PEO based composite electrolyte reached $2.85 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$ and the electrochemical window was 5.5 V [1].

It can be concluded from the experimental data above that with the addition of ZrO₂ or SN and LiTFSI as the filler, the comprehensive performance of composite electrolyte can be improved effectively, which is beneficial to practical application. Although the ionic conductivity of PEO base composite is still lower than the PPO counterpart, the electrochemical window is significant higher. Hence, the stability of this kind of electrolyte is higher and makes it more suitable to use in some circumstances than the PPO base electrolyte.

5. Properties of Gel Polymer Electrolyte

In this section, one representative PEG base gel polymer electrolyte will be discussed and the preparation method will be given in detail.

The gel polymer electrolyte was prepared by in-situ thermal polymerization. Poly (ethylene glycol) methyl ether methacrylate (PEGMA) and polyethylene glycol diglycidyl ether (PEGDE) were mixed evenly and dissolved in 1 gram of liquid electrolyte and then azo-bis-isobutyronitrile (AIBN) was added into the mixture. The solution was heated at 80 °C for 60 minutes [15]. The GPE sample then

went through several tests and showed a very high ionic conductivity and electrochemical window. The ionic conductivity of this kind of electrolyte reached $3.1 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ (25°C), the ion transference number reached 0.68 and the electrochemical window was 5.2 V [15]. The detailed data of ion transference number can be found in Figure 5 [15].

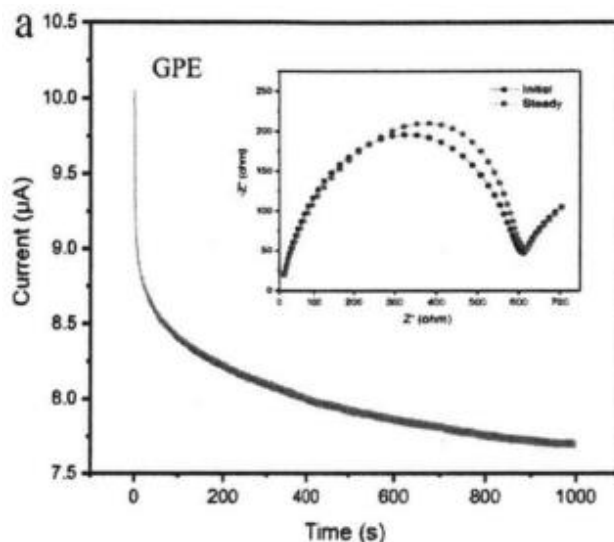


Figure 5. The ion transference number of Li/GPE/Li battery [15]

As the results have shown, at 25°C , this kind of PEG base electrolyte has excellent performance on ionic conductivity and possesses a significant electrochemical window. Thus, it can be matched with the lithium metal anode as well as high voltage cathode, which greatly improved the energy density of the battery. It even performs better than some inorganic solid electrolytes at ionic conductivity.

6. Conclusion

As this paper presented, it can be concluded that the ionic conductivity at room temperature for PEG based gel polymer electrolyte and sulfide solid electrolyte are significantly higher than any other types of solid-state electrolytes ($3.1 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$ and $1.22 \times 10^{-3} \text{ S}\cdot\text{cm}^{-1}$), indicating low inner resistant. Thus, they are the most suitable material for batteries that require excellent rate performance. The ion transference number for all inorganic solid electrolytes are high (0.994 and 0.998), indicating high power density. Hence, they are potential materials in quick charging batteries, but their electrochemical windows are low (all around 5 V) compared to some polymer-based electrolytes (5.5 V for PEO based CSE and 5.2 V for GPE). Thus, it can be concluded that despite some exceptions, polymer-based electrolytes as a whole perform better at stability, making them electrolytes suitable for high energy density batteries. Further researches and modification methods are also crucial to ease the problems of different types of electrolytes. Novel interfacial modification methods are needed to enhance the electrochemical window and ionic conductivity of some inorganic electrolytes and researches should be put into developing polymer-based electrolytes with good thermal stability and ion transference number.

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