Research Progress on Improvement Strategies of Polymer Electrolytes in Solid-State Batteries

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Abstract. The solid electrolyte material can replace the liquid electrolyte in the lithium-ion batteries, which ensures higher safety due to the flammable and corroded of liquid electrolyte. The polymer electrolytes demonstrated feasibility due to its suitable ductility. However, lithium ions in the polymer electrolytes are more difficult to ionize, resulting in worse ionic conductivity. At the same time, the mechanical strength of polymer electrolytes is not as good as that of inorganic electrolytes, which is not enough to inhibit the penetration of lithium dendrite. To solve these problems, researchers adopt two strategies: adding fillers or reactants and constructing artificial interface layers, focusing on improving ionic conductivity and mechanical strength. Based on the latest research, the problems faced by polymer electrolytes and improvement measures are reviewed, which provide references for the future development of polymer electrolytes.

Keywords: polymer electrolyte, ionic conductivity, mechanical strength.

1. Introduction

In the past few years, electric vehicles have extensively utilized Li^+ batteries. The technology of Li^+ batteries has been relatively mature. Traditional Li^+ batteries with liquid electrolytes face challenges in terms of safety and performance. For instance, lithium dendrites that form during the charge/discharge cycle can breach the electrolyte, resulting in electrolyte seepage, potential fire hazards, and corrosion. On the other hand, the energy density of lithium-ion batteries based on liquid electrolytes has approached the theoretical bottleneck. Therefore, researchers are exploring the safer and more efficient energy storage technology. As a follow-up technology of lithium-ion batteries, lot of researchs have been done on solid electrolyte batteries, because they can solve the safety risks, even providing higher energy density than liquid electrolyte batteries.

In lithium-ion batteries, the main function of electrolytes is to conduct lithium ions, which means the demand for high ionic conductivity, and mean while reduction of the conductivity of electron. In liquid electrolytes, lithium ions can dissociate easier and freely migrate. So generally, the liquid electrolytes conduct Li^+ better. In solid electrolytes, lithium ions are more difficult to dissociate and need to bind to electrolyte atoms, conducting through lattice defects or diffusion, therefore having a higher chemical energy barrier. So solid electrolytes generally have lower conductivity. It is crucial to enhance the ionic conductance of solid-state electrolytes.

Solid electrolytes can be categorized primarily as solid inorganic electrolytes (ISE) and polymer electrolytes (PE). ISE has better ability of conducting Li^+. However, its lack of flexibility results in suboptimal interface contacts and thermal stability, limiting its practical applicability. On the other hand, despite numerous obstacles such as insufficient mechanical durability, inability to effectively prevent the formation of lithium dendrites, and significant decrease in ionic conductivity at lower temperatures [1,2]. PE has more advantages in application due to its good interface properties, ductility, low cost and easy processing, environmental friendliness, and compatibility with mass production processes [2,3].

PE is formed by a high molecular weight polymer matrix, located between the positive and negative electrodes, which can conduct Li^+ [4]. PE is flexible, easily processed, and has wide electrochemical voltage windows. It also has high safety because it uses no corrosive solvent and produces no harmful gas [5]. Basically, there are two main types of PE: gel polymer electrolyte (GPE) and solid polymer electrolyte (SPE). GPE is more flexible but has poor mechanical strength [6], while SPE has better mechanical strength, indicating the bright application prospects of SPE [7].

However, the low ion conductivity of SPE at room temperature is the shortcomings, the improvement strategies mainly include three directions: ion conductivity, electrochemical stability window, and mechanical strength [8]. Researchers hope to improve its performance by combining various materials to form a composite polymer electrolyte (CPE). In recent years, many high-performance CPE materials and preparation methods have been studied and published. Compared to traditional SPE materials such as polyoxyethylene (PEO) and polyacrylonitrile, these CPE materials show better performance in terms of ionic conductivity, mechanical strength and temperature window. This paper aims to introduce the research progress of CPE materials and provide references for the follow-up research in electrolytes Li^+ battery technology.

2. Improvement Strategies of PE

2.1. Polymer Electrolyte (PE)

In a Li^+ battery, the electrolyte serves as a medium for transporting Li^+ between the anode and cathode. During discharge, Li^+ migrates from the anode material through the electrolyte and is then incorporated into the cathode. Conversely, during charging, Li^+ moves from the cathode through the electrolyte and is then absorbed into the anode. As the electrolyte serves as a bridge between the cathode and anode, the speed of Li^+ conduction in the electrolyte plays a crucial role in determining the charge and discharge rate of the battery. Therefore, ionic conductivity is a key factor in evaluating battery performance.

At present, solid electrolyte totally includes inorganic electrolytes and polymer electrolytes, and inorganic electrolytes are further divided into sulfide and oxide electrolytes [9]. The inorganic electrolytes demonstrate outstanding ionic conductivity and mechanical strength. The ionic conductivity of certain sulfide electrolytes approaches the performance level of liquid electrolytes. Unfortunately, its strong rigidity, which indicates the poor interface contact with electrodes, hinders its practical application. The polymer electrolyte has the characteristics of light weight, good flexibility, easy processing and low cost. So, it is suitable for large-scale production. Moreover, it can fit better with the electrode interface because of its stronger adhesion, so the interface stability is great, and the resistance is low [10]. Polymer electrolyte plays a crucial role in the advancement of Li^+ battery technology for the future.

However, PE still has problems. On the one hand, its ionic conductivity, especially at room temperature, is low; On the other hand, its mechanical strength is insufficient. These two issues of PE will be separately introduced later.

Polymers composed of single molecules are called homopolymers, and homopolymers commonly used as electrolytes are PEO, PVDF, PSS, and so on. In polymers, ion transport occurs mainly in the amorphous region. In detail, Li^+ is transferred mainly through a dynamic dissociation and binding process with the polymer carbon chain, so high crystallization of the electrolyte is averse to the migration of lithium ions. When the polymer is below its glass transition temperature, the crystalline region will greatly limit the hopping of lithium ions, causing decreased ionic conductivity in polymer electrolyte at room temperature [11]. Using multiple molecules to form copolymer electrolytes such as PVDF-HFP, can prevent crystallization to some degree [12]. Meanwhile, the fall of crystallization will cause a decreased mechanical strength and enhanced lithium dendrites problem, which will be discussed later.

The interface between electrolyte and electrode is an important research topic, which mainly includes two aspects: interface wetness and interface stability. When liquid contact a solid surface, they match well due to the liquidity. On the contrary, if the liquid is replaced by solid material, it cannot perfectly fit the interface of solid electrode. After a long-term of continued use, the physical and chemical deformation of solid electrolyte under high pressure and high heat will also affect their ions conductivity and safety performance. This fall of contact condition (interface wetness) will greatly affect the ion transport, causing interface impedance to rise.

Besides, the interface is where lithium dendrites grow, which requires high stability of the interface. Because the mechanical strength of polymer electrolytes is weaker than inorganic electrolytes, lithium dendrites can still grow and penetrate the electrolyte. Lithium dendrites mainly formed by electrochemical depositing on the interface between electrolyte and electrode when the Li^+ battery is charging or discharging [13]. Inorganic electrolytes have strong mechanical strength, which can stop the growth of lithium dendrites physically, while polymer electrolytes have poor mechanical strength and are easily penetrated by lithium dendrites. If lithium dendrites grow and penetrate the electrolyte, it may cause a short-circuit.

Take polyoxyethylene (PEO) as an example, which was first discovered by Wright in 1975. PEO forms a complex with alkali metal ions and can conduct alkali metal ions [14]. Since then, PEO has been the most popular polymer electrolyte matrix due to its strong dissociate ability to lithium salts, good compatibility with lithium, strong stability, and low cost [3]. The ionic conductivity of PEO is limited to approximately 10^{-7}S/cm due to its high level of crystallization, which typically ranges from 70% to 85% at room temperature [14,15]. When the temperature increases beyond the glass conversion temperature of PEO, the ionic conductivity will increase with the decrease of crystallinity, accompanied by a drop in mechanical strength [5].

Hence, it is crucial to enhance the ionic conductivity, as well as the mechanical strength and other characteristics of polymer electrolytes.

2.2. Improvement Strategies

The improvement strategies of polymer electrolyte include two types: electrolyte modification and artificial interface layer construction.

2.2.1. Addition of Fillers or Reactants

Adding fillers or reactants to the electrolyte can improve the performance, generally focusing on conductivity and mechanical strength.

To enhance the polymer's effectiveness at low temperature, it is necessary to reduce the crystallization degree. By introducing fillers, such as the metal-organic skeleton (MOF) which is formed by adding organic ligands to the metal, into the electrolyte, The solid polymer electrolyte's crystallinity may be decreased. Furthermore, Certain types of filters have the ability to not just decrease the polymer's crystallinity, but also improve its mechanical strength, improving the ionic conductivity and safety of the battery [16]. Commonly used fillers include metal oxides (such as TiO^2, SiO^2) and porous fillers (such as graphene oxide and montmorillonite) [17].

PEO is one of the most commonly used electrolyte substrates. Alternatively, it offers the benefits of being cost-effective, highly stable, and allowing easy dissociation of lithium salt. However, its application is significantly restricted by a high crystallization rate and low ionic conductivity at room temperature. Nevertheless, there is substantial potential for improvement. Cheng and Cai adopted one-dimensional zwitterionic nano cellulose (ZCNF) as the filler to prepare PL - ZCNF composite materials which contain polyethylene oxide (PEO) and double (three fluorine methanesulfonyl) lithium imide. This material shows significantly improved ionic conductivity, mechanical strength and lithium-ion migration [18]. Wang et al. used a bi-level structure of propylene carbonate (PPC) and polyethylene oxide (PEO) contacting with the cathode and anode, followed by the introduction of butanedionitrile (SN) to bind with lithium-ion, which aims to form a special structure to accelerate the conduction of lithium-ion in the electrolyte [19]. K. Khan et al. mixed the commonly used fillers $Li_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}$(LLZTO) with WO_3 to enhance the efficiency of PEO electrolyte. The results indicate an enhancement in the ionic conductivity and migration number of Li^+ near LLZTO, indicating outstanding overall performance [20].

Poly-ionic liquid (ILs) is a new polymer matrix. Solid electrolyte (PIL) prepared from ILS has been widely studied due to its advantages such as high ionic conductivity at room temperature, low flammability, excellent inter-facial wetness and high stability. Ma et al. developed a new way to prepare PIL-SPE in one step by in-situ polymerization in the presence of lithium ions [21], overcoming the problems of low ionic conductivity and high interface impedance during solid phase extraction.

2.2.2. Construction of Artificial Interface Layer

The artificial interface layer is mainly focused on improving the interface wetness, interface stability and mechanical strength concerning the boundary between the electrolyte and electrode. For example, salt fluoride is a common material used to build SEI, which has good Li^+ conductivity and stability. It has the ability to effectively prevent the formation of lithium dendrites, leading to a notable enhancement in both electrochemical performance and safety.

The interface performance can be improved by introducing artificial interface layer. Zhang et al. produced a polyether-based thin layer structure with the thickness of 10μm at the interface by in-situ polymerization, which shows stability under high voltage, high ionic conductivity, high mechanical strength, and suppression of the lithium dendrites growth [22]. Pei et al. proposed a polyether-ethyl carbamate-based structure, which uses the dynamic disulfide bond with low dissociation energy between ethyl carbamate groups to form a self-healing interface structure. It can be rearranged and repaired when the interface is deformed or defective, effectively improving mechanical strength and ionic conductivity [23].

The conventional polymer electrolyte might not have the capability to prevent the formation of lithium dendrites at the interface because of its decreased mechanical strength. It has been studied that the inorganic-rich electrolyte film can suppress the growth of lithium dendrites. The LiF membrane is an excellent choice. Zhang designed a single-phase polymer blend electrolyte called Li-polymer in F diluter (LPIFD), combining lithium polymer components and inert fluoride polymer components to form a LiF-rich solid electrolyte interface film. The formation of lithium dendrites can be effectively suppressed by this method [24].

3. Conclusion

In this article, we introduce polymer electrolyte (PE) properties and their advantages and disadvantages in detail. Based on the above, we discuss the possibility of enhancing the ionic conductivity and strength of polymers by incorporating fillers or reactants into the matrix, as well as improve electrochemical stability, safety, improving wetness of the interface, and inhibit the growth of lithium dendrites by introducing artificial interfacial layers.

These methods can be summarized as:

1. By preparing MOF structure by adding metal filler to the polymer matrix, the crystallization of the material can be decreased while the ionic conductivity and mechanical strength can be improved.
2. Introducing a reactant into the polymer to create a composite material or an artificial interface layer by in-situ polymerization, reduces interface impedance and enhances mechanical strength, inhibiting the growth of lithium dendrites.

Although these methods have made some progress in improving battery performance, there are still some problems and challenges. For example, many fillers need to be produced under specific conditions, which is costly and technically complex. Besides, the possibility of harmful side reactions of the introduced fillers in batteries needs to be considered. Also, stability of the artificial interface layer after long-term of use and its compatibility with the electrode material still need to be further studied.

To further improve battery performance, we summarize and propose the following strategies:

1. Develop new composite materials: A composite material can created by blending polymer electrolytes with inorganic nanoparticles, resulting in high ionic conductivity and mechanical strength. This aims to effectively prevent the growth of lithium dendrites while preserving strong interfacial stability.

2. Optimize the preparation process of the interface layer: By improving the synthesis method of polymer electrolyte and the coating technology of the interface layer, minimize the manufacturing expenses and enhance the reliability and security of the battery.

3. Research on self-healing coatings: Materials with dynamic covalent bonds and non-covalent interactions can perform self-healing and regulation of the interface layer, thereby improving the stability and safety of the battery.

4. Study the conduction mechanism of Li^+ in polymers: Further study the conduction behavior of Li^+ in polymer electrolytes and investigate potential new modes of Li^+ conduction, and offer a novel approach to addressing the issue of limited ionic conductivity in polymers under ambient conditions.

In summary, by implementing the aforementioned approaches, we can enhance the effectiveness of polymer electrolytes in terms of ionic conductivity, mechanical durability, stability and safety. This will contribute to the advancement of solid-state battery technology.

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