

Improvement of the Conductive Ability of Polymer Electrolytes

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Abstract. In current applied research, traditional electrolytes face significant challenges. The emergence and application of polymer electrolytes provide effective solutions to these problems. This paper will introduce the types and characteristics of polymer electrolytes based on three aspects. The star-shaped compound based on PEGMA, i.e., poly(ethylene glycol) methacrylate, can significantly enhance the mechanical and electrical properties of polymer electrolytes; the gel electrolyte prepared by compounding highly polar β -polyvinylidene fluoride (β -PVDF) with nylon 6 shows significant application potential in improving ion conduction efficiency and enhancing battery safety. Brush-shaped polymers have good performance in avoiding the crystallization of linear polymers and inhibiting the growth of lithium dendrites and improving mechanical strength. These three types of polymer electrolytes each have their characteristics and good application prospects. Still, they all face problems such as high cost and difficulties in industrialization at the present stage and need further development to better benefit human society. This paper aims to provide those who want to explore and do some decent research on this topic with some basic information as well as fundamental advice.

1 Introduction

Electrolytes are crucial in electrochemical energy storage. However, the safety issues of liquid electrolytes and the performance degradation caused by dendrite growth have seriously limited the practical application of lithium-ion batteries. Therefore, polymer electrolytes (PE) are expected to replace liquid electrolytes (LE). Although solid polymer electrolytes (SPE) have good safety and mechanical properties, they are limited by temperature, have low ionic conductivity, and have poor contact with electrodes and insufficient cycling performance. For example, the high crystallinity of linear polyethylene oxide (PEO) leads to a low ionic conductivity of SPE, and the strong complexation between PEO and lithium ions (Li^+) limits the conduction of Li^+ , resulting in a generally low lithium-ion transference number of the electrolyte. The scientific community is improving polymer electrolytes in various ways to achieve better performance.

This paper classifies and lists the main types and characteristics of polymer electrolytes, describes their preparation methods, and provides a preliminary overview of the research and

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application progress of polymer electrolytes. For the problems existing in the currently widely used electrolytes, polymer electrolytes are used in a targeted manner and their properties are precisely utilized to solve the problems. It is our hope to provide some inspiration in the direction of the further development of polymer electrolytes by subsequent researchers.

2 Star-shaped compounds

2.1 Structural optimization of star-shaped compounds

The structure of star-shaped compounds can be optimized by adjusting cross-linking agents in varieties of means and the relative molecular mass of PEGMA, i.e., poly(ethylene glycol) methacrylate. Incorporating star-shaped compounds into cross-linked solid polymer electrolytes significantly improves not only the mechanical but also electrochemical properties of the solid electrolyte. Studies have shown that adding poly(ethylene glycol) methacrylate (6 mmol), trimethylolpropane tris(3-mercaptopropionate) (2 mmol), and benzophenone (mass fraction 5%) into a solvent-free system and vigorously stirring for 4 hours to promote uniform mixing. Subsequently, the slurry was dropped into a polytetrafluoroethylene mold and irradiated with 365 nm UV light for 30 seconds to obtain a star-shaped compound (T475). Compared with the initial solid polymer electrolyte, after incorporating the star-shaped compound, the tensile toughness of the sample is significantly improved, indicating that incorporating star-shaped compounds into cross-linked polymer electrolytes in a solid state can significantly improve the mechanical properties of the solid electrolyte. [1]

2.2 Ionic conductivity and conductance performance

Ionic conductivity is one of the most effective indicators for measuring the applicability of SPEs. The mobility of polymer segments increases with increasing temperature, thereby accelerating the complexation and decomplexation processes between lithium ions and polymer segments and promoting the conduction of lithium ions.

The longer chain length of the PEGMA arm in the introduced T950 star-shaped plasticizer can further disrupt the regularity of polymer segments, increase the movement rate, and thus promote the conduction of lithium ions. Thanks to its better flexibility, it promotes the stable interface contact between the solid electrolyte film and the electrode, ensuring the smooth cross-interface transmission of lithium ions inside the battery [1].

The introduction of star-shaped compounds promotes the sufficient relaxation of polymer segments in the SPE - T950 structure, ensuring that it has both better ionic conductivity and better mechanical flexibility. In addition, the good flexibility of SPE - T950 promotes good interface stability between the SPE electrodes, providing a smooth channel for the cross-interface migration of Li^+ , which ensures that the Coulomb efficiency of the battery is maintained above 96% during the charge-discharge cycle[2].

3 Gel electrolytes

3.1 Improvement of battery safety performance

Highly polar β -polyvinylidene fluoride (β -PVDF) has all-trans conformations, with its Fluorine and Hydrogenium atoms located on opposite sides of the polymer backbone, and

has been proven to be a promising artificial solid electrolyte interface coating on copper and lithium metal anodes, enabling dendrite-free lithium deposition/stripping and enhanced cycling performance [3]. Molecules contain a large number of carbon - fluorine functional groups (-C—F), which can promote the movement of lithium ions in the electrolyte.

However, the polyvinylidene fluoride matrix has low mechanical strength and poor thermal stability and cannot be used alone as a polymer electrolyte, especially in a working environment that requires high-rate battery discharge [4]. The method of making a composite diaphragm from other polyvinylidene fluorides with good mechanical properties and thermal stability can effectively improve the performance of the polymer electrolyte matrix. Since nylon 6 (PA6) has a high melting point, is resistant to organic solvent corrosion, and is inexpensive, it has been widely used in various fields in the past few decades. Therefore, compounding nylon-6 - 6 with polyvinylidene fluoride to prepare a gel polymer electrolyte and applying it to lithium batteries has good prospects.

Dissolve polyvinylidene fluoride and nylon 6 in a formic acid - acetic acid mixed solution respectively, adjust the mass fraction, and then perform electrospinning for three layers. The first layer is a nylon layer, the second layer is polyvinylidene fluoride, and the third layer is again a nylon layer. Use the composite diaphragm to absorb a small amount of lithium hexafluorophosphate electrolyte (1 mol/L lithium hexafluorophosphate solution) to obtain a GPE as the battery electrolyte and lithium metal as the battery negative electrode. After that, prepare a positive electrode sheet by mixing commercial lithium iron phosphate, carbon black, and a binder in a mass ratio of 8:1:1. Finally, assemble a CR2025 type lithium-ion battery in an argon atmosphere-protected glove box, and then use a blue electricity tester to test the various properties of the battery in the end.

Tests show that if the battery experiences a thermal runaway due to an accidental local short circuit when the temperature rises above 160 °C, the polyvinylidene fluoride layer begins to melt, while the nylon layers on both sides remain stable at this time. The melted polyvinylidene fluoride will enter the pores of the nylon layer and block the pores, completely blocking the positive and negative electrodes of the battery. At this time, the circuit is interrupted at the power source, and the electrolyte is equivalent to an open circuit, with no current passing through. Therefore, the PA6/PVDF/PA6 composite diaphragm has good thermal stability, and when used as a gel polymer electrolyte, it can effectively improve battery safety [5].

4 Brush-shaped polymers

During the charging and discharging process of LMBs, the growth of lithium dendrites at the electrode/electrolyte interface can lead to a battery short circuit and even cause serious safety accidents [6]. The main strategies for inhibiting the growth of lithium dendrites include: constructing an artificial solid electrolyte interface (SEI) layer, constructing a nano-composite electrolyte [7], preparing a high-mechanical-strength 3D network polymer, and introducing new additives [8], etc. Polyacrylic acid (PAA) can react with lithium metal on the negative electrode surface in situ to form lithium polyacrylate (LiPAA), and the formed SEI layer can effectively inhibit the growth of lithium dendrites [9]. In addition, the brush-shaped polymer segments have strong mobility and can avoid the crystallization problem of linear polymers, making them an ideal solid polymer electrolyte matrix material. However, the grafting density of brush-shaped polymers currently used for SPE is low, and the synthesis steps are cumbersome. In addition, the irregular growth of dendrites on the lithium negative electrode surface is a major challenge for lithium metal batteries, and lithium dendrites may pierce the electrolyte membrane and cause a battery short circuit.

It has been reported that using poly2-((2-bromopropoxy) methyl) acrylate (PBMA) as a raw material, the PEG side chain is connected to the PBMA main chain by the "grafting-to"

strategy. This method obtains a PBMA - g - PEG brush-shaped polymer by dialysis and freeze-drying. Based on this, various brush-shaped polymers with different topological structures are constructed to inhibit the crystallization behavior of PEO, enhance the mobility of polymer segments, and improve the ion-conducting performance. At the same time, by designing a single-ion structure and introducing polyester or polycarbonate segments, the content of free Li^+ in the electrolyte is increased, and the lithium ion transference number is improved.

4.1 Inhibition of lithium dendrite growth

The interaction between the polymer matrix or lithium ions and the polymer can effectively inhibit the crystallization behavior of PEG, reducing the crystallinity of the electrolyte. The rigidity of the PS base combined with the flexibility of PEG reduces the brittleness of the material while avoiding the problem that PEG is difficult to form. The low crystallinity creates good conditions for ion movement. SPEs with high mechanical strength can migrate the growth of lithium dendrites on the lithium negative electrode surface as a way improve battery safety. The brush-shaped structure can promote the movement of polymer segments, enhance the ion-conducting ability of the electrolyte, and simultaneously improve the thermal and electrochemical stabilities of the electrolyte. When the main chain length of the brush-shaped polymer is the same, the lower the T_g (glass transition temperature) of the brush-shaped polymer electrolyte as the longer the side chain is, the more efficient the complexation - decomplexation process with lithium ions, and the higher the ionic conductivity. In addition, the single-ion structure can increase the content of free lithium ions moving through the electrolyte and improve the lithium-ion transference number [10].

4.2 Improvement of mechanical properties

Using a polycaprolactone (PCL)-based brush-shaped polymer electrolyte. A macromolecular initiator containing hydroxyl and carboxyl groups can initiate and catalyze the ring-opening process of the polymerization of ϵ -caprolactone monomers to obtain a brush-shaped polymer. Based on a series of PHMA macromolecular initiators with various polymerization degrees. Polyester-based brush-shaped polymers with the same PCL side chain length and different main chain lengths can be obtained by changing the consistency of reaction conditions, and how different main chain lengths affect the performance of SPEs can be studied. Mixing PH - PCL and PEO in a certain proportion and preparing SPEs with different brush-shaped polymer contents or different main chain lengths by solution casting method. That is, pouring the solution of the prepared PH - PCL and PEO mixture onto a clean and dry polytetrafluoroethylene mold, and then placing it in a refrigerator, repeatedly freezing and thawing to evaporate the water, thus obtaining a solid product with a coexistence of crystalline and amorphous states. Linear PCL is similar to PEO and is a semi-crystalline polymer, which is not conducive to the conduction of Li^+ . However, studies have shown that the brush-shaped structure helps to inhibit the crystallization of the polymer. This is because the PCL has a strong influence between itself and PEO can inhibit each other's behavior of crystallization. XRD results show that the brush-shaped structure can initially inhibit the crystallization behavior of linear PCL, and there are only a few crystalline regions in the polyester-based brush-shaped SPEs, which is obviously beneficial to improving its electrochemical performance. The strong complexation between the polyether matrix and Li^i limits the migration movement of Li significantly, so the t_{Li^+} of traditional PEO - based SPEs is low (0.20, 60 °C). In comparison, the t_{Li^+} of 0.6PCL is increased to 0.52 (60 °C), because the complexation between the carbonyl of the polyester matrix and Li^i is weak, allowing Li^i to migrate more efficiently in the electrolyte.

4.3 Improvement of interface stability

The interface stability between SPEs and the lithium metal anode significantly affects the cycling stability of LMBs. Studies have shown that the presence of an appropriate amount of carboxylic groups in the electrolyte helps to inhibit the growth of lithium dendrites on the lithium anode surface [11]. The carboxylic acid can react in situ with lithium metal to form a stable SEI layer as long as the amount is proper, which can have tremendous influence on the growth of lithium dendrites. Since the conduction of lithium ions in SPEs depends on the waving polymer chains, and general polymer chains lack sufficient movement ability at room temperature, LMBs are difficult to work at room temperature [7]. PCL has ideal chain flexibility and thanks to the brush-shaped structure, PCL can further enhance the movement ability of polymer chains by destroying the regularity of polymer chains.

4.4 Limitations and future development

The biggest problem with polymer electrolytes is that their manufacturing cost is relatively high, and the manufacturing process is complex, which is not conducive to large-scale industrial applications. Moreover, the volume of the electrolyte is too large, which goes against the current pursuit of smaller battery volumes. It is possible to further explore changes in polymerization methods such as emulsion polymerization to obtain higher molecular weight main chain polymers and increase the alcoholysis degree to obtain more grafts to enhance their electrochemical and mechanical properties.

5 Conclusion

This paper explores the incorporation of star-shaped compounds into polymer electrolytes to improve their ion passage performance and mechanical properties; it also explores and introduces that in gel electrolytes, the fluorine atoms in the main chain play an extremely important role in the transmission of lithium ions, and in addition, the gel electrolyte can protect the circuit well in case of a short circuit due to its characteristic of melting at high temperatures; furthermore, it introduces brush-shaped compounds for polymer electrolytes. Due to their unique characteristics of graft copolymers, they can create polymer electrolytes with multiple functional groups coexisting and thereby improve the ion transmission efficiency between the electrode and the electrolyte.

Whether it is star-shaped compounds, gel electrolytes, or brush-shaped polymers, the problems they all have lie in the low synthesis yield and high cost of high-molecular solid electrolytes at the present stage, and the unclear industrial application scenarios. However, they all demonstrate that high-molecular materials have a solid theoretical foundation and bright application prospects in reducing lithium salt crystallization and improving the migration ability of lithium ions in electrolytes in solid electrolytes. For example, the mechanical properties and the proportion of high-molecular amorphous states of solid electrolytes can be adjusted by regulating parameters such as polymerization degree and alcoholysis degree to achieve quantitative control of physical properties and improve SPEs.

In the future, polymer electrolytes will play a key role in human exploration of batteries.

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