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Application of triblock copolymers in lithium-ion batteries based on solid electrolyte

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Abstract. In the future, all-solid Li-ion batteries are expected to gain widespread acceptance in larger markets due to their high safety and excellent electrochemical performance. However, it is important to acknowledge their drawbacks, including the inadequate compatibility between the electrode and electrolyte interface and the low ionic conductivity at room temperature. This paper reviews the specific methods and the latest research progress of triblock copolymers to solve the above problems. Block copolymerization is an effective way to enhance the efficiency and performance of electrolyte. Its advantage is that two or more monomers with different properties can be polymerized into the same structure, which is conducive to the ionic conductivity of polymer electrolyte. In the latest research results, straight-chain block copolymers have been synthesized, which have better physical and chemical properties compared to traditional comb block copolymers. However, the electrochemical properties of the straight-chain block copolymer electrolyte and the stability of the interface between the electrode and the solid electrolyte are rarely reported. Therefore, it is particularly important to systematically study the electrochemical properties and interface properties of block copolymer electrolytes. In the future, more attention should be drawn to not only improving the properties of SPEs but also building a stable interface with low interface resistance.

Keywords: All-Solid-State Lithium Ion Battery, Triblock Copolymer, Polymer, Electrolyte, Electrochemistry.

1. Introduction

The pressing issues of climate change, pollution, and depleting fossil resources pose immence challenges for humanity. In order to achieve sustainable long-term development, it has become imperative to explore alternative transportation options, such as fully electric or hybrid vehicles [1]. However, a major hurdle in the immediate future is the need for a battery technology that is safe, affordable, and efficient, allowing electric vehicles to have an extended driving range of over 350 km. Lithium-ion batteries, as a novel energy storage solution, offer numerous advantages including high energy density, extended lifespan, high operating voltage, and no memory effect. Consequently, they have found widespread application in mobile phones, notebook computers, and various other consumer electronics sectors that are closely intertwined with people's daily lives.

However, the traditional organic liquid electrolyte has the risk of internal short circuits, leakage, inflating gas, flammability, and even explosion [2, 3]. In addition, the energy density of lithium-ion

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batteries using traditional organic liquid electrolytes is about to hit the ceiling, and it is difficult to match the development of future batteries [4]. In contrast, all-solid Li+ batteries have the advantages of high safety and excellent electrochemical performance [5]. Solid polymer electrolytes (SPEs) offer a solution to the safety concerns associated with liquid electrolytes by utilizing lithium salts within polar polymer matrices, eliminating the need for organic solvents. However, the development of SPEs has faced challenges due to the need for both high ionic conductivity and desirable mechanical properties [6]. Additionally, the limited power delivery caused by the concentration gradient resulting from the motion of lithium ions, which only contribute a small fraction of the overall ion current, can lead to detrimental effects such as dendritic growth [7]. Despite these obstacles, further research has shown promising advancements in the field of SPEs.

Block copolymer, a unique type of polymer formed by connecting multiple segments of polymer chains with distinct properties, offer a solution to enhance the ionic conductivity by reducing the crystallinity of PEO and increasing the proportion of its amorphous region. This paper takes triblock copolymers as the research object, reviews the research progress of these copolymers used in all kinds of solid Li+ batteries, and puts forward some suggestions and prospects for their development in future. In the preparation of copolymer electrolyte modification, the common structures are AB bi-block copolymer and BAB (or ABC) triblock copolymer. In this review, triblock copolymer is mainly discussed.

The investigation of triblock copolymers as solid-state electrolytes in Li+ batteries have practical significance and impact on the battery industry. Solid-state electrolytes provide numerous advantages compared to conventional liquid electrolytes, such as enhanced safety, increased energy density, and prolonged cycle life. The progress in solid-state electrolytes utilizing triblock copolymers can contribute to the advancement of solid-state Li+ batteries, which hold the potential to revolutionize energy storage technology.

2. Method

In this literature review, we focused on the application of triblock copolymers in solid electrolyte-based Li-ion batteries. The research methods mainly include literature collection and review analysis. First, the researcher selects the literature related to the topic by searching the relevant literature database. The databases Web of Science, Google Scholar, and CNKI Scholar were searched using the terms ‘triblock copolymer’, ‘lithium-ion battery’, ‘solid electrolyte, and ‘electrochemistry’. The selection criteria include publication years, research objects, experimental methods, and so on. Then, the researchers conduct a review analysis of the selected literature to sort out and summarize the research results, methods, and findings. The review analysis may include a discussion of the application areas of triblock copolymers in lithium-ion batteries, performance optimization strategies, and battery performance evaluation. Through these research methods, researchers can fully understand the application of triblock copolymers in solid electrolyte-based lithium-ion batteries and references for further research are given. Specifically, this review deals with the synthesis and structure of triblock copolymers and the application of triblock copolymers to solid electrolytes. In addition, the review also discusses the application prospects of triblock copolymers in lithium-ion batteries and possible optimization strategies, such as their potential application value in improving battery performance, extending battery life, and improving safety. Based on this, more than 20 related works were found.

3. Advancements and challenges in solid polymer electrolytes: the role of block copolymerization

Solid polymer electrolyte has drawn much attention due to its high flexibility, easy preparation and better interface connection between inorganic solid electrolyte and electrode. It is also a solid electrolyte that has been applied in commercial practice at this stage. However, the widespread use of solid polymer electrolytes is still hindered by inherent flaws within the electrolytes themselves. Therefore, there is a pressing need to improve the performance of solid polymer electrolytes. So far, PEO-based electrolyte is still regarded as the most promising solid polymer electrolyte, but problems such as low ionic

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conductivity under the circumstance of room temperature, and narrow electrochemical window need to be further improved. Block copolymerization is an effective modification method in enhancing the performance of electrolytes. Its advantage is that two or more monomers with different properties can be polymerized into the same structure. Figure 1 lists several block copolymer electrolytes with different molecular structures.

In 2005, Kanamura et al. prepared the pecked block copolymer by using the small-molecular weight short-chain polyethylene glycol methacrylate as the side chain (Figure. 1a). When $LiClO_4$ was treated as lithium salt at 30°C, the ionic conductivity was 10^{-4} S cm^{-1} and the electrochemical window reached 4.3V. In the $LiCoO_2$//Li battery, the discharge capacity reaches 100 mA h g^{-1} [8]. Bergfelt et al. prepared ester - and carbonate-based block copolymer electrolytes (Figure. 1b). When the test temperature reached 90°C, the ionic conductivity was 10^{-4} S cm^{-1} [9]. Kubo et al. prepared a PVC-based copolymer with a low glass transition temperature by copolymerizing VC with an ethoxy-oligomer with double bond closure (Figure. 1c). The incorporation of ethoxy-group into the polymer enhances the lithium-ion transport, while the accretion of PVC not only improves the thermal stability but also facilitates the lithium-ion transport. As a result, the thermal stability of the modified electrolyte is enhanced, reaching up to 300°C, while maintaining a high ionic conductivity of 1.2×10^{-4} S cm^{-1} at 30°C [10].

In the different block structures of block copolymers, usually one block can be an ion conductor, which plays a role in transporting Li+, while the other block can play a role in enhancing the mechanical strength of the material or participating in ion transport. At present, rigid blocks often contain a benzene ring structure [11, 12]. Karim et al. used the epoxy chain segment with the ability of transporting lithium ions to copolymerize with the polystyrene chain segment to prepare the combed-copolymer electrolyte (Figure. 1d). The ionic conductivity can reach 10^{-4} S cm^{-1} at room temperature, and the discharge capacity can reach 146 mAh g^{-1} at the rate of 0.04 C [13]. By comparing the properties of the straight-chain copolymer and the pecked copolymer, Devaux et al. found that the straight-chain block copolymer polystyrene-poly epoxy-polystyrene (PS-PEO-PS) had excellent physical and chemical properties [14]. However, research on its application as an electrolyte material in solid-state lithium batteries is rarely reported. As described above, whether the electrolyte can form a stable interface with the positive and negative electrodes of the battery plays a crucial role in the cycle performance of the battery during use.

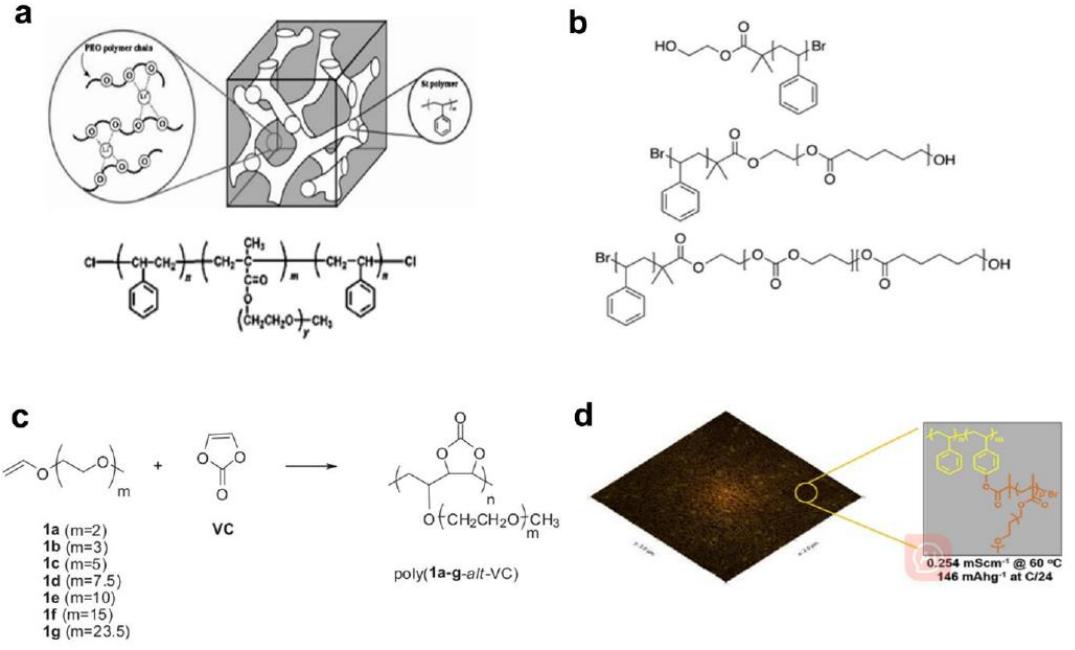

Figure 1. The pecked block copolymer(a) ester- and carbonate-based block copolymer electrolytes(b) a PVC-based copolymer with a low glass transition temperature(c) preparing the combed-copolymer electrolyte(d) [9-11, 15].

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4. A triblock copolymer PS-PEG-PS synthesized by ATRP & a new polyester-based triblock copolymer PCL-PPC-PCL

Bohao Chen et al. selected polyethylene glycol (PEG), which shares the identical structure as polyethylene oxide but has a lower relative molecular weight and stronger chain segment mobility, as the main structure of conducting lithium ions and introduced the copolymer polystyrene (PS) at both ends of PEG by means of atom transfer radical polymerization [15]. The triblock copolymer PS-PEG-PS was synthesized and mixed with lithium salt to prepare a polymer electrolyte. The crystallinity of the material was effectively reduced by copolymerization, and its ionic conductivity went up to 1.1×10^{-3} S cm−1 at 70°C. Through the investigating of interfacial compatibility between block copolymer electrolyte, it shows better interfacial properties than pure PEO. The introduction of PS can effectively improve the film formation of PEG and further reduce the crystallinity of the material, thereby facilitating the transport of Li-ions. The electrolyte exhibits excellent interface stability between the positive and negative electrodes of the battery, as demonstrated in batteries utilizing $LiFePO_4$ as the cathode material. After 120 cycles at a 0.2 C rate, the electrolyte maintains a capacity retention rate of 91% and a capacity of 143 m Ah g^{-1}. This indicates the electrolyte's favorable cycle stability in the battery system.

In addition, a PCL-PPC-PCL block copolymer was prepared by using polycaprolactone (PCL) as the main chain and introducing Poly carbonate (PPC) block by copolymerization, and used as solid polymer electrolyte. The results show that copolymerization effectively reduces the crystallinity of the material so that its ionic conductivity can reach 3×10^{-5} S cm−1 at 30°C, the electrochemical window is wide to 5 V, and it has a high ion migration number (0.4). The reason for the higher ion migration number than PEO was analyzed by DFT calculations. The transport of Li+ in PCL-PPC-PCL is facilitated by the looser coordination environment and lower binding energy of Li+. The lithium metal anode exhibits excellent compatibility with the newly developed electrolyte. During cycling, a stable and protective solid-electrolyte interphase (SEI) film forms between the electrolyte and the lithium metal anode, effectively preventing the growth of lithium dendrites. The battery performance of the electrolyte is promising, demonstrating satisfactory charge-discharge behavior at both high and room temperatures in the LFP//Li battery system. After 200 cycles at 70°C, the capacity retention rate remains at 90% with a discharge capacity of 161 m A h^{-1}. At room temperature, the discharge capacity reaches 141 m Ah g^{-1}. Furthermore, the NCM//Li battery system exhibits excellent reversibility, with a charge and discharge efficiency of 98% after ten cycles. This research provides a novel approach for the development of high-performance solid electrolytes based on polyesters.

5. An improved route to linear triblock copolymers

Daniel T. Krause et al. have achieved successful synthesis of linear triblock copolymers with well-ordered structures using an improved method [16]. These copolymers exhibit a narrow distribution of polymer chain lengths, allowing for long-range orientation within the membrane through controlled solution casting. These desirable morphological characteristics are crucial for an effective polymer electrolyte matrix, as they ensure optimal alignment of conductive channels and lithium-ion transport within the membrane. Furthermore, these copolymers can serve as structurally predetermined substrates in electrolytes, leading to significantly enhanced ionic conductivity.

6. A new PBnMA-POEGMA-PBnMA triblock copolymer using ATRP

Bergfelt et al. successfully synthesized a triblock copolymer composed of methyl methacrylate benzyl ester and oligo (ethylene glycol) methyl methacrylate ether through atom transfer radical polymerization [17]. This copolymer, labeled as PBnMA-POEGMA-PBnMA, was then mixed with lithium bis (trifluoro methanesulfonyl) imide (LiTFSI) to build a solid polymer electrolyte (SPE). Its ion conductivity was later studied using alternating current impedance spectroscopy in the temperature range of 30 to 90°C. To evaluate the performance of the electrolyte, a Li|SPE|LiFePO4 half-cell was assembled and cycled at 60°C. The discharge capacity of this half-cell under C/10 conditions was approximately 100 m Ah g^{-1}, and it successfully completed over 140 cycles. This method effectively alleviated the mass transport

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limitation of the cathode, thereby reducing the polarization and resistance of the battery. Consequently, the battery could be cycled at lower temperatures, minimizing undesired side reactions. These findings demonstrate that by synthesizing copolymers with specific structures and incorporating suitable salts, their ionic conductivity of SPEs can be improved, leading to excellent cycling performance in practical batteries. This progress is of great significance in the substitution of liquid electrolytes and the improvement of safety and efficiency in lithium batteries. Nevertheless, cyclic voltammetry analysis indicated that the electrolyte displayed electrochemical instability at 60 °C, potentially attributed to the creation of an interface between the electrolyte and lithium metal that is thermodynamically and/or kinetically unstable, leading to an inadequate passivating interphase.

7. Discussion

At present, as far as battery systems are concerned, though PEO-based electrolytes are still the most widely studied polymer electrolytes and are expected to be applied, with the development of electrolytes, more and more types of polymers can be used as matrix materials, and some amorphous polymers are gradually being found to be used as electrolytes and have excellent electrochemical properties. Besides, since every matrix material has some defects, it is still necessary to further find and develop polymer materials with better performance. Furthermore, in the context of battery systems, enhancing the efficiency of SPE alone is not sufficient. Equal attention should be given to the interface with low resistance is crucial for optimizing battery performance.

From another point of view, the internal structure of the new process was studied by means of solid-state nuclear magnetism, variable temperature XRD and small Angle X-ray diffraction, and the mechanism of lithium-ion transport was elucidated. It is also necessary to investigate the interface evolution between the SPE and the electrode during charge and discharge cycles. Understanding the factors causing incompatibility with the high-voltage cathode material is essential for developing the high-performance solid polymer electrolyte.

Future research should focus on solving these problems to promote the application of triblock copolymers in solid electrolyte Li+ batteries.

8. Conclusion

The solid-state electrolyte shows a crucial role in all-solid-state Li-ion batteries. Therefore, it is imperative to develop a solid-state electrolyte that possesses a broad electrochemical window, exhibits high ionic conductivity, minimizes the interface contact resistance between the electrode and the solid-state electrolyte, and facilitates efficient lithium-ion migration. Starting with the preparation of polymer electrolytes, the research progress of triblock copolymers used in Li-ion batteries and the problems solved are reviewed in this paper. However, it will take some time for solid polymer batteries to achieve large-scale industrialization, mainly due to the electrolyte material itself, and there are some outstanding problems between the electrolyte and the electrode. Therefore, there is still room for improvement in solid polymer electrolytes. In this literature review, certain deficiencies exist:

All relevant research literature cannot be covered, resulting in a lack of comprehensive understanding of the battery field. This is mainly because the scope of the literature search is limited or the screening criteria for some literatures are not clear enough. In the future, the search can be expanded to include more databases and academic resources. In addition, the screening criteria were clarified to ensure that all relevant literatures are included in the review. After the summary and introduction of the latest research, there might be still a lack of novelty in the idea of developing triblock copolymers. Therefore, more research gaps can be found in the future, and research directions and objectives can be proposed to increase the innovation and research value of the review.

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