

Solid-State Polymer Electrolytes for Lithium Batteries

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In all-solid-state rechargeable lithium batteries, the solid-state electrolyte is located between the cathode and the anode, acting as an electrolyte and a separator, so the performance of the solid-state electrolyte is crucial to the performance of the entire battery.

Keywords: solid-state ; rechargeable lithium batteries ; polymers ; Electrolytes

1. Solid-State Electrolytes

In all-solid-state rechargeable lithium batteries, the solid-state electrolyte is located between the cathode and the anode, acting as an electrolyte and a separator, so the performance of the solid-state electrolyte is crucial to the performance of the entire battery. As an all-solid-state polymer electrolyte for lithium batteries, it should meet the requirements of battery applications, such as high ionic conductivity, high lithium-ion migration number, excellent mechanical properties to resist the puncture of lithium dendrites, good chemical and thermal properties stability, etc. ^{[1][2][3][4]}.

In order to meet the performance requirements of the above-mentioned for solid-state lithium batteries, since polymers were formally proposed to use in lithium-ion batteries in 1970s ^[5], domestic and international researchers have been focusing on the application of polymers and polymer-based composite electrolytes in All-Solid-State lithium-ion batteries, including the exploration of ion transport mechanisms and the development of new polymer electrolyte systems ^{[6][7]}.

2. Polymer Matrix

The polymer matrix can be divided into polyethylene oxide (PEO) ^[8], polyacrylonitrile (PAN) ^[9], polyvinylidene fluoride (PVDF) ^[10], polymethyl methacrylate (PMMA) ^[11] and other polymers (PVC, PA, PCA) ^{[12][13][14]} according to the type of main chain.

2.1. PEO

Polyethylene oxide (PEO) is the polymer with the strongest complexing ability and the most widely used polymer electrolyte matrix ^{[1][4]}. The flexible polyether segment of PEO molecule can be complexed with alkali metal ions (Li⁺). Under the action of the electric field, Li⁺ continuously undergoes "coordination-dissociation" movement with the ether oxygen atom along with the thermal movement of the molecule, achieving directional and rapid migration. However, due to the high crystallinity of PEO, its ionic conductivity is poor ^[15]. Therefore, PEO is usually blended, copolymerized, and cross-linked with other polymers, or plasticized by adding low-molecular-weight solvents, adding nanoparticles, etc. to prepare a composite electrolyte to improve its performance.

2.2. PMMA

In addition to the above drawbacks, it is also worth noting that the low dielectric constant of PEO cannot completely separate the ions dissolved in it, and it is easy to cause ion aggregation to affect the migration of Li⁺ ^[4]. Introducing strong polar groups into the polymer molecular structure can improve the dielectric constant ^{[16][17]}, so polymers with strong polar carbonate groups have attracted extensive attention of researchers, and polymethyl methacrylate (PMMA) is the most widely used representative ^{[18][19]}.

The research on the application of PMMA polymer matrix in all-solid-state lithium batteries first started in 1985 ^[20]. Due to the abundant raw materials, easy synthesis and low cost of PMMA, it has aroused the strong interest of researchers in PMMA polymer electrolytes. The research on the mechanism and modification methods has also made good achievements in recent years.

2.3. PVDF

The PMMA-based polymer has a stable structure and is stable to metals, and the resistance of the passive film formed on the contact surface with the electrode is small. However, PMMA has the disadvantages of being hard and brittle after film formation, poor flexibility, and poor mechanical strength [6].

Poly (vinylidene fluoride) (PVDF) material has high melting point, good thermal stability, good electrochemical stability and good film-forming properties, and its high dielectric constant helps to promote the ionization of lithium salts, which can well make up for the shortcomings of PMMA and become a kind of Emerging polymer electrolyte matrices [21]. The ionic conduction mechanism of PEO can be expressed as: Li^+ is complexed with the coordinating groups on the polymer chain after the dissociation of the lithium salt, and transported in the system along with the molecular thermal motion [22]. Unlike PEO polymers, PVDF is a non-coordination polymer, Li^+ has not direct interaction with the polymer main chain, instead, after the dissociation of the lithium salt, countless anions line up on both sides to form a channel, and the coordination mode of the freely moving Li^+ and each anion is similar to that in the pure salt crystal structure. The coordination site jumps to the one that coordinates with the next anion, completing the migration [23].

However, the homopolymer structure of PVDF leads to a high intramolecular crystallinity (65–78%), which is not conducive to ionic conduction. Therefore, the modification methods for PVDF are usually to interact with other polymers or inorganic fillers to reduce the crystallinity and improve the electrolyte absorption rate, or to improve the ionic conductivity by cross-linking, blending, adding initiators [24][25][26][27][28].

2.4. PAN

Polyacrylonitrile (PAN) is a polymer containing nitrile group ($\text{C}\equiv\text{N}$) with strong electron withdrawing ability [29]. The ion migration mechanism of PAN is similar to that of PEO. Li^+ is complexed with the coordination group on the polymer chain after dissociation in the lithium salt, and the coordination site is migrated with the movement of the polymer matrix or jumps from a chain to another chain of the polymer [30]. But the difference is that the movement of Li^+ along the PAN segment chain at room temperature does not affect the ionic conductivity very much, and the Li^+ transfer number in PAN-based electrolyte is higher than that of PEO [31][32]. Its strong electrochemical stability, strong heat resistance, good flame retardancy and simple synthesis makes it become an ideal candidate for polymer electrolyte matrix materials [33].

However, the research applied to solid-state lithium batteries found that the poor wettability of PAN and electrodes leads to high interface impedance of lithium batteries, and the performance of batteries is not ideal. Therefore, it is usually necessary to add plasticizers or inorganic fillers to PAN to improve ionic conductivity and interfacial compatibility [32][34][35][36].

It can be seen that different polymer matrices have their own advantages, and they can complement their own defects through blending or copolymerization and improve the performance of solid-state lithium batteries from different aspects.

3. Solid-State Polymer Electrolytes

Based on the research background of polymer electrolytes and the defects of polymer electrolytes in the past, a series of new studies have been carried out in recent years to develop new polymer electrolytes to improve the performance of solid-state lithium rechargeable batteries, mainly including all-solid-state polymer electrolytes, polymer-inorganic composite electrolytes and porous polymer electrolytes.

3.1. All-Solid-State Polymer Electrolyte

All-solid polymer electrolytes consist of two parts: a polymer matrix and a lithium salt that can be dissolved in it. At present, all-solid polymer electrolytes generally suffer from low room temperature ionic conductivity or high electrolyte interface impedance, which greatly restricts all-solid-state polymer electrolytes [37]. For the practical application of polymer electrolytes, researchers have modified and optimized the polymer structure, including copolymerization (blending) [38], cross-linking [39] or grafting [40], to prepare new all-solid-state polymer electrolytes in recent years.

Subir et al. investigated the effect of blending host polymers on solid polymer electrolyte (SPE) membranes doped with ammonium iodide (NH_4I) salts. Experiments have shown that poly (ethylene oxide) (PEO)-poly (vinylidene fluoride) (PVDF) polymers mixed in suitable ratios can strengthen the amorphous part of the polymer matrix and facilitate fast ionic conduction through it. The addition of PVDF enhances the ion-polymer interaction in the system, resulting in more ion dissociation, while PEO provides a path for ion conduction. When the ratio of PEO and PVDF is 8:2, the ionic conductivity

of the solid polymer electrolyte is up to 1.01×10^{-3} S/cm [41]. PEO can also be blended with other polymers such as polyvinylpyrrolidone (PVP) [42], poly (methyl methacrylate) (PMMA) [43], polystyrene (PS) [44], 2,4-toluene diisocyanate/polyethylene glycol (TDI/PEG) [45], which can also significantly improve the conductivity of solid electrolytes. In addition to the most commonly used polymer matrix PEO, other emerging polymers can also be copolymerized or blended by the same method to prepare new solid polymer electrolytes. According to the different molecular structures of polymers, they can be divided into block copolymerization, graft copolymerization et al. [46][47][48]. The experimental results show that the performance of polymer solid electrolytes prepared by blending or copolymerization of single polymer electrolytes is significantly improved. It also significantly improves the cycle life and dendrite resistance of solid-state rechargeable lithium batteries.

Although the PEO polymer electrolyte can effectively improve the performance of the solid polymer electrolyte itself by means of blending, copolymerization, grafting, etc., the compatibility between the electrolyte and the electrode cannot be ignored in the application of solid lithium batteries. The unstable contacts of PEO and LiCoO₂ etc., cathode materials hinder its potential application in high-energy-density batteries. Fu et al. designed an ultrathin double-salt PEO-based polymer electrolyte (DPPE) with a cross-linked network to address these issues [49]. The formed cross-linked network greatly increases the amorphous region and room temperature ionic conductivity of PEO-based polymer electrolyte. The cross-linked network effectively inhibits the decomposition of PEO segments when contact with cathode and effectively maintains the chemical stability between the electrode and the electrolyte. The cycle performance and capacity retention rate of the battery are both satisfactory. This is undoubtedly good news for PEO-based solid-state electrolytes to be used in high-voltage solid-state rechargeable lithium batteries at ambient temperature and Many PEO-based polymers refer to this strategy to modify polymer electrolytes [50][51][52]. Recently, Tsai et al. conducted an in-depth study on the relationship between solute diffusion and crosslink density, demonstrating that polymer crosslinking has a significant effect on regulating solute diffusivity and polymer mechanical properties [53].

3.2. Polymer-Inorganic Composite Electrolytes

The low ionic conductivity and mechanical strength of polymer electrolytes seriously affect their practical application in solid-state rechargeable lithium batteries. As early as 1982, Weston and Steele found that adding 10% inorganic solid fillers to PEO-based polymer electrolytes, the mechanical properties of the electrolyte can be improved, but the effect on the ionic conductivity is small [54]. Since then, the research of a new electrolyte combining polymer electrolyte and inorganic solid electrolyte has started a new journey. The cations in the inorganic material Al₂O₃ can combine with the ether oxygen groups on the polymer segment as Lewis acid through Lewis acid-base interaction like Li⁺, inhibit the crystallization of the polymer, and form a physical cross-linked network system with the polymer segment, which can improve the mechanical properties and thermal stability of polymer electrolytes, but the problems of ionic conductivity and interfacial stability have not been solved. Such inorganic materials do not have ionic conductivity, so they are also called inert fillers. MgO, TiO₂, SiO₂ and ZnO also belong to such inert inorganic fillers.

Another inorganic filler is active inorganic filler. Unlike inert inorganic fillers, its conductivity is much higher than that of polymer matrix and lithium ions can migrate in fillers. Therefore, it can effectively improve the ionic conductivity of composite electrolytes to a certain extent. The garnet-type solid electrolyte is the active inorganic filler with the highest conductivity [55]. Recently, He et al. studied a garnet-type inorganic-polymer composite solid-state electrolyte Li_{6.4}La₃Zr_{1.4}Nb_{0.6}O₁₂-PEO, with a high conductivity of 1.4×10^{-3} S/cm at 60 °C and an electrochemical window of 5.2 V, the solid-state battery prepared with this electrolyte can be charged and discharged normally at room temperature and has a high-capacity retention rate after cycling. Other similar composite polymer electrolyte experimental data show that its conductivity is better than that of inert inorganic filler composite solid electrolyte, and the battery interface resistance is greatly reduced, and the stability and capacity retention rate are greatly improved [56][57][58][59][60][61]. The high stability of the battery is due to the close surface contact between the polymer matrix and the electrode, which reduces the volume and increase the interface contact. Polymers play an important role [62].

These active inorganic filler-polymer composite electrolytes can also choose perovskite [63][64][65], NASICON [66][67][68], sulfide [69][70][71], etc. as the active inorganic filler part, and PVDF as the polymer matrix. The experimental results show that, composite electrolyte can not only retain the high ionic conductivity and mechanical strength of inorganic solid electrolytes, but also exert the advantages of high flexibility and high interfacial compatibility of polymer solid electrolytes [72][73]. Polymer-inorganic composite electrolytes have good ionic conductivity, cycling performance, and thermal/mechanical properties, and will always be a research hotspot.

3.3. Porous Polymer Electrolyte

All-solid-state polymer electrolytes and polymer-inorganic composite electrolytes have achieved good results in improving ionic conductivity [74][75][76][77] and stabilizing the interfacial contact between electrodes and electrolytes [78][79][80] through various efforts in the past few decades. However, due to the increasing demand for high power, high voltage, long battery cycle life, etc. in practical applications, substantial improvements in their performance are still urgently needed.

In recent years, in order to explore solid electrolyte materials with better comprehensive properties, researchers have made many attempts. Among them, porous materials with natural internal pores have many excellent characteristics such as small specific gravity, large specific surface area, and strong adsorption performance. The inclusion of lithium-ion conductive materials or integrated functional groups in the pores is conducive to the transport of lithium ions in the pores, and the spatial network structure is mostly formed by covalent bonding, which has good thermal and chemical stability. This porous material with both function and structure can be widely used in electrochemical and energy storage devices, so it is considered as the best candidate for all-solid-state lithium battery electrolyte, and has received extensive attention and research in recent years. The most common porous polymer electrolytes are Metal Organic Frameworks (MOFs), Covalent Organic Framework (COFs), and the emerging Porous Aromatic Framework (PAFs).

MOFs are crystalline porous materials with periodic network structure formed by inorganic metal centers (metal ions or metal clusters) and bridged organic ligands connected to each other through self-assembly, also known as coordination polymers [81][82]. It has both the rigidity of inorganic materials and the flexibility of organic materials, and has the advantages of high porosity, low density, large specific surface area, regular pore channels, adjustable pore channels, and diverse and tailorable topology [83]. Its development potential in lithium battery electrolyte applications was first reported by Long et al. in 2011 [84]. Since then, in-depth research has been carried out on porous polymer electrolytes including MOF-incorporated polymer hybrids, lithium salt-supported MOF hybrids, and pure MOFs [85]. Continuous porous structure of MOFs providing unimpeded continuous channels for lithium-ion transport, overcoming the obstacles of traditional composite electrolytes and polymer electrolytes, and effectively improving the performance of solid-state electrolytes. Recently, it was found that the movement of larger anions in MOFs can be selectively restricted by modifying the pore size of the MOFs, which acts like an ion sieve to clear the barrier for the transport channel of Li^+ , thereby improving the ionic conductivity of the electrolyte and the performance of the battery [86]. Similarly, taking above advantage of the MOFs, adding them to conventional polymer electrolytes (PEO/LiTFSI) which significantly improves the ionic conductivity of electrolyte at room temperature [87]. The solid-state polymer electrolyte prepared by the addition of MOF not only improves the ionic conductivity, the stability of the electrochemical window and the lithium-ion migration number [88][89][90], but also effectively resists the piercing of lithium dendrites [91]. MOFs are considered as a promising new electrolyte for all-solid-state batteries.

The metal ions in the coordination center of MOFs materials and organic ligands are combined to form a three-dimensional network structure through coordination bonds, resulting in the disadvantage of poor thermal stability of most MOFs materials. Therefore, the ionic conduction of the electrolyte at high temperature is limited. UiO-66 and ZIF series MOFs materials have relatively good chemical stability and thermal stability, and UiO-66 and ZIF series MOFs materials have application prospects in mid-temperature ion conduction.

Covalent organic frameworks (COFs) are crystalline porous materials with two-dimensional or three-dimensional periodic structures formed by covalently linking organic molecular units. With the advantages of low frameworks density, high porosity, and open pore structure, it is beneficial to ion conduction. Their applications in solid-state lithium battery electrolytes are receiving increasing research interest [92]. Like metal-organic frameworks (MOFs), organic covalent frameworks (COFs) are porous crystalline materials that can precisely arrange organic building blocks to form an ordered structure, in which lithium ions are directionally transported in its ordered pores. But the porous polymer solid electrolyte remains structurally stable at high temperature (as high as 400 °C) [93], because the covalent network rigid structure of COFs endows them with better mechanical properties and thermal stability than MOFs. Recent research on COFs-based porous polymer electrolytes has made breakthroughs based on previous studies. The emergence of COFs-based porous polymer electrolytes opens a new chapter for the development of high-temperature solid-state lithium battery applications [94][95].

The regular and uniform pore structure of COFs is conducive to the transport of guest molecules in the pore, and the organic building units are connected by covalent bonds, which have high thermal stability and achieve rapid lithium-ion conduction above 100 °C. The pore size, crystallinity and other properties of COF materials depend on the building monomers, and the diversity of monomers endows COFs with diverse structures. If the pore size of COF is small enough, the more significant its ability to act as a solid electrolyte against lithium dendrites, because the solid-state electrolyte

layer is dense enough. Therefore, the emergence of COFs has opened a new chapter in the study of solid-state electrolytes. However, the research and development of new COFs materials requires the design of new functional monomers and the study of new connection methods, which are very challenging work and require more efforts in the future.

Porous Aromatic Framework (PAFs) are microporous network materials with open frameworks formed by linking aromatic units through covalent bonds. Its pores can be used as carriers for small molecular guests. The large specific surface area and excellent physical and chemical stability make such materials have broad application prospects in energy storage, adsorption, separation, and catalysis. In 2020, Ben's research group first disclosed a major breakthrough in the application of PAFs in all-solid-state Lithium Battery electrolytes. The research group found that PAF-1 has high adsorption characteristics for LiPF_6 due to the combination of the benzene ring in PAF-1 and the lithium ion in the lithium salt in the way of cation- π interaction. Lithium ion existed stably in the framework of PAF-1, while the continuous porous three-dimensional network and the large enough pore volume provided an unimpeded channel for the transmission of lithium ions and realizes the rapid operation of lithium ions. PAF-1 has high absorption rate and good stability of lithium salts, which meets the requirements of solid-state electrolyte lithium-ion batteries for high energy density, long cycle life and excellent rate performance. Compared with other solid-state electrolyte batteries with the same electrode materials, the battery can withstand higher current densities and longer cycle times in long-term cycling experiments ^[96].

The application research of PAFs in solid-state lithium battery electrolytes is still in its infancy, and there are still many challenges such as the mechanical strength of the electrolyte, the research cost, and the adsorption performance of other lithium-ion conductive materials that need to be solved urgently.

4. Summary

Traditional linear polymers have low preparation cost, good solubility of lithium salts, and are easy to synthesize, but their low ionic conductivity at room temperature often requires composite preparation with other types of electrolytes to reduce their crystallinity. There is no chemical bond between the molecules of linear polymers, and the molecules can move relative to each other after being heated or stressed, so they are flexible and suitable for the preparation of gel electrolytes, but the mechanical properties are not good and the stability needs to be improved.

Porous polymers are porous network materials composed of building units connected by covalent bonds. It has the characteristics of high surface area, high adsorption performance, low density, adjustable pores, designable composition and structure, and easy modification. Compared with conventional linear polymer electrolytes, porous polymer electrolytes exhibit better mechanical properties and faster Li-ion transport due to the high chemical stability conferred by the presence of covalent bonds, and the robust framework can withstand higher voltages and currents density. However, the preparation is cumbersome and the cost is high. If a simple and inexpensive preparation can be realized, the development of porous polymer electrolytes will be better promoted.

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