

Polymer-based Solid Electrolyte and Electrode/Electrolyte Interfacial Contact Characteristics Affecting Lithium-ion Battery Performance

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Abstract: Lithium-ion batteries (LIBs) are now embedded in people's daily life usage including portable electronic devices and electric vehicles. The demand for further developed LIBs with better energy storage, energy transport, safety, etc. However, the commercial and conventional LIBs use liquid electrolyte widely. Although it provides excellent ionic conductivity, its poor mechanical strength often induces the growth of dendrite, which is often considered as the primary factor that causes short circuits, undesired side reactions, and reductions in energy capacity. To address these issues, polymer-based solid-state electrolytes (SSEs) were developed. It exhibits comprehensive properties and can cooperate with other materials to resolve their defects, creating various novel materials in different scenarios. This paper covers four commonly used polymers in the fabrication of SSEs and key parameters indicating their energy density and stability. It provides a brief introduction to the reader about the characteristics of varying polymer-based electrolytes, and how these characteristics, combined with interface contact, affect the overall battery performance.

Keywords: Polymer-based electrolyte, interfacial contact, lithium-ion battery, ionic conductivity

1. Introduction

Lithium-ion batteries (LIBs) were first developed back in 1970. Since that time, LIBs have a long-persisted history in the energy area and are widely used in various electronic devices in both industry and daily usage circumstances. As global warming and environmental issues are more emphasized, electric vehicles have become one of the top choices to adapt to environmental issues. Therefore, the replacement from gasoline-combustion engines to battery-driven engines goes popular, where LIBs are mainly used as the energy source due to their rechargeability. At present, most of the conventional LIBs use liquid electrolytes, providing high ionic conductivity. However, as LIBs become mature in electric vehicles, the industry realizes that the operating safety has reached its boundary. The spontaneous formation of dendrites in lithium due to liquid electrolyte can cause serious reductions in energy efficiency and safety issues. These urge the industry to develop advanced substitutes to address these issues. Among all the options, solid-state electrolytes (SSEs) seem to be a promising candidate for their mechanical strength and stability. Serval families of SSEs are noticed, including oxide, sulfide, and polymer, etc. Among these families, polymer-based SSEs demonstrate

comprehensive properties, with high interfacial stability, and better mechanical strength, thermal stability compared to all-liquid electrolytes. They can also mix with other inorganic materials, like ceramic, to form composite polymer electrolytes (CPEs), further improve the ionic conductivity, or enhance its electrochemical stability window by modifying the polymer functional group [1]. Hence, this paper will mainly focus on polymer-based SSEs with their composite, and how their properties affect the electrolyte, battery performance. It is also worth noticing that most of the polymer-based SSEs do not meet practical requirements at this time and need further study to address issues like poor electrode wetting, poor ionic conductivity, etc. The research is aiming at offering a concise overview to the reader regarding the properties of different polymer-based electrolytes, and how these properties, in conjunction with interfacial contact, influence the overall performance of the battery.

2. Polymer-based SSEs

Although liquid electrolyte exhibits decent ionic conductivity and interfacial contact between electrolyte and electrode, it suffers from low electrochemical stability and formation of lithium dendrite due to weak mechanical strength. Hence, the demand for SSEs with high mechanical strength, high electrochemical stability and acceptable ionic conductivity rises. In general, polymer-based SSEs can be further classified depending on the choice of polymer family, including polyethylene (PEO), polyacrylonitrile (PAN), polyvinylidene difluoride (PVDF), polymethyl methacrylate (PMMA), etc. Furthermore, the polymer can cooperate with other family polymers with inorganic material to fabricate CPEs, or use as a scaffold to support liquid electrolytes, so-called gel polymer electrolytes (GPEs). The conduction of lithium-ion in polymer SSEs is mainly done in the amorphous region of the polymer. The loosely packed structure provides better flexibility, more free volume and lower energy barriers. All these properties allow ions to migrate through segmental motion along the polymer main chain and coordinate to binding sites.

2.1. PEO-based polymer electrolyte

PEO or polyethylene oxide was found to have the ability to conduct Li^+ back in 1973, and scientists realized its ability to conduct Li^+ ions. Due to the presence of an ether oxygen atom in the backbone, the Li^+ ion can coordinate strongly with the polymer, increasing the solubility of lithium salt, giving it a lower dielectric constant, ultimately generating more free Li^+ ions in the electrolyte system while other properties of the polymer remain the same. However, the ionic conductivity for PEO-based electrolyte is still much lower than application requirements, mainly due to its high crystallinity, ranging from 75% to 80% at room temperature [2]. Although the ionic conductivity of PEO-based electrolyte can be greatly enhanced by increasing the operating temperature above its melting point, the reduction in mechanical strength becomes noticeable, which raises more issues and is not suitable for practical application. Another aspect worth mentioning is that the addition of plasticizer cans with high dielectric constants can also enhance the ionic conductivity, by facilitating the dissociation of lithium salts, which increase the amount of free Li^+ ions. PEO can also cooperate with another polymer to form CPEs. For example, the PEO solvent can be injected into an LLZO/PVA nanofiber network formed by electrospinning to synthesize a PEO-based CPE. This CPE exhibits an ionic conductivity of $2.5 \times 10^{-4} \text{ S cm}^{-1}$, with an electrochemical stability window of 6V [3]. Adding a ceramic filler like LAGP is another approach to improving ionic conductivity and mechanical strength. This is done by reducing the crystallinity of CPE, which eventually accelerates segmental motion of Li^+ ions, and increases the ionic conductivity to $6.76 \times 10^{-4} \text{ S cm}^{-1}$, with an electrochemical stability window of 5.3V. A recent study indicates a design of PEO-HPMC@Ht CPEs and shows improving ionic conductivity of $1.1 \times 10^{-3} \text{ S cm}^{-1}$ at 30 °C, with an electrochemical stability window of 5.5V [4]. It also demonstrates relatively strong inhibition of lithium dendrite growth, which improves the long-

term performance of these CPEs. The hydroxyl and ether groups on HPMC have high polarity, which enhances the ionic conductivity. Ht itself possesses high mechanical strength and heat resistance, by introducing Ht nanoflakes into the PEO-based SSEs, the nanostructure of Ht can act as a scaffold to prevent failure of the PEO electrolyte film.

2.2. PAN-based polymer electrolyte

PAN or polyacrylonitrile was considered as a material for polymer electrolyte back in 1975. The presence of a nitrile group makes it possess higher ionic conductivity compared to PEO electrolyte. The nitrile bond is rigid and carries strong dipole-dipole interaction. It exhibits better mechanical strength with poor elasticity when compared to PEO, where it tends to fracture under pressure, rather than bending or stretching. Moreover, the interface between PAN and lithium anode often experiences strong passivation due to a reduction in the nitrile group, which results in the formation of a passivation layer which can greatly increase the interfacial resistance and affect the battery performance. Despite all these disadvantages mentioned above, PAN shows promising parameters with the addition of graphene oxide filler. The functional groups on the graphene oxide filler like -OH and -COOH weaken the polarity of the nitrile group, which improves the overall flexibility of the polymer and inhibits the formation of the passivation layer [5]. It can also cooperate with PEO to form a cross-linked network to further improve the mechanical strength and suppress the lithium dendrite growth. Meanwhile, PAN-based polymer also has great potential in quasi-solid-state polymer electrolyte as a separator. A quasi-solid-state polymer electrolyte based on PAN/Polysilsesquioxane nanofiber membrane was developed by Liu [6]. The electrospun PAN microporous diaphragm has a higher degree of porosity, high electrolyte wettability, and high ionic conductivity, but it is also limited by its poor mechanical strength due to its low molecular weight. Pure electrospun PAN membrane does not show strong interaction with electrolyte under pressure. To overcome the above problems, Liu coated a layer of polysilsesquioxane onto the surface of PAN nanofiber, improving the surface roughness and absorption rate of the electrolyte while keeping the 3D network structure unchanged. The PAN/Polysilsesquioxane composite membrane serves as a scaffold and can absorb liquid electrolyte to form a quasi-solid-state electrolyte. The ionic conductivity reaches $1.58 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature and inhibits lithium dendrite growth effectively.

2.3. PVDF-based polymer electrolyte

PVDF or polyvinylidene fluoride was studied together with PAN as the material for polymer electrolyte in 1975. It exhibits high electrochemical stability and relatively weak mechanical strength just like PAN. The -CF functional group is a good electron acceptor with a high electric constant, granting PVDF the ability to facilitate the dissolve of lithium salt by decreasing the electrostatic force and lowering the energy barrier for ion dissociation. Although the contact between PVDF and lithium anode is not stable, it often forms a LiF-rich solid electrolyte interface, which improves the interfacial ion conduction and mechanical strength. DMF or dimethylformamide is typically used as a solvent during the preparation of PVDF-based electrolytes. The residue of DMF can coordinate with the Li^+ ion to form a Li^+/DMF complex and can act as a plasticizer to turn down the crystallinity of electrolytes. PVDF also has great potential in CPE fabrication. Yao demonstrated a design introducing both DMF and palygorsike nanowires to overcome the poor mechanical strength of PVDF electrolyte. Drastic improvements on elastic modulus, yield stress and other mechanical parameters were observed, where ionic conductivity reaches $1.4 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C [7]. The cross-linking characteristic provided by palygorsike nanowires is responsible for this dramatic improvement. Another approach designed by Chai suggested an asymmetric CPR structure that contains a

PAN/PVDF-HFP bilayer with a metal organic framework embedded [8]. Within this design, the PAN layer provides high electrochemical stability and the PVDF-HFP layer offers a strong mechanical structure. The ionic conductivity is $1.13 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C , with an electrochemical stability window up to 4.85V.

2.4. PMMA-based polymer electrolyte

PMMA or polymethyl methacrylate was first applied to GPEs back in 1985. Compared to PEO, PMMA exhibits an amorphous characteristic which possesses higher ionic conductivity given other conditions the same. Moreover, PMMA has stunning interfacial stability compared to other polymers mentioned above. Although the amorphous nature brings PMMA electrolyte advantage over other materials, it also brings down the flexibility significantly and requires the addition of liquid electrolyte plasticizer, which makes PMMA more suitable for GPEs. Kang suggests a design that blends PEO, PMMA, and polystyrene together to form a tribasic GPE [9]. The blended PEO-PS-PMMA membranes have an optimized ratio of 3:1:1 and are immersed into liquid electrolyte to form GPE. The resulting GPE has an ionic conductivity of $1.2 \times 10^{-4} \text{ S cm}^{-1}$ at 25°C with excellent interfacial stability to the lithium electrode. Liang suggests another double layer polymer-inorganic composite electrolyte fabricated through UV curing [10].

3. Discussion

The growing demand for high-energy density LIBs has attracted scientists to develop polymer-based SSEs to adapt practical needs. Four polymer families were introduced and compared in this paper. Each of the polymers exhibits unique advantages but also exposes disadvantages that cannot be ignored. Polymer-based SSEs generally exhibit enough mechanical strength to suppress the growth of dendrite and a wider electrochemical stability window, allowing them to operate under higher voltage. The ionic conductivity of polymer-based SSEs compared to liquid electrolytes is nearly 10x lower. This can be improved by introducing composite materials but the huge gap in ionic conductivity still prevents the complete replacement of CPEs with liquid electrolytes. Other than that, the cost of these electrolytes limits the mass production for conventional usage. Further study on optimizing ionic conductivity, mechanical strength and interfacial stability is also needed. Each of the four polymer SSEs demonstrates a unique characteristic, with differences in their flaws. PEO polymer electrolyte has a relatively lower electrochemical stability window. This is mainly due to the terminal -OH group that will oxidize at voltage above 4.05V [11]. And the reactive -OH group can react with Li anode while in contact, bringing down the overall stability. PAN polymer electrolyte has the nitrile group which induces passivation reactions on Li metal anode. Although this issue has been addressed by introducing a solid electrolyte interface layer and the anode capacity retention reaches around 80%, it is still less competitive to liquid electrolyte at this specific parameter [12]. PVDF polymer electrolyte demonstrates satisfying characteristics but comes with a higher budget cost, which makes it challenging to mass production. PMMA polymer electrolyte is the cheapest among the other three, but the high glass transition temperature of PMMA makes it quite brittle under 100°C , and requires additional modification to solve its poor flexibility. Therefore, the polymer SSEs still need further improvement and strategy to bring their derivatives to the market at an affordable performance and price.

Another critical component that can significantly impact LIBs performance is the interfacial contact between electrolyte and electrode. The interfacial contact of polymer-based SSEs is generally poor compared to LEs due to their poor fluidity, leading to a severe reduction in Li^+ conduction and electrochemical stability. To further improve the contact and stability, several designs were studied to overcome issues like poor conduction, narrow electrochemical stability window, dendrite growth, etc.

In terms of cathode design, in-situ polymerization and integrated cathode-electrolyte are two classic approaches to improving interfacial contact. The in-situ polymerization was done by casting the liquid monomer directly onto the cathode, so that the precursor can fully permeate the cathode. UV curing is typically chosen as the initiator. However, UV curing is limited due to obstructed light penetration, restricting its use on complex structures like pre-assembled cells. Integrated electrolyte is done by injecting part of the polymer electrolyte component into the cathode, acting as an ion conductor and binding site at the same time. Then fill the pores of the cathode with polymer electrolyte solvent. The pre-injected polymer electrolyte component will form bonds with the solvent added later, and the stability of this structure heavily depends on this bonding strength.

When considering anode design, the choice of material is dominant over the structure design. Lithium metal is a typical choice for anode materials. It possesses excellent specific capacity and rarely undergoes reduction in routine conditions. Other materials like graphite or silicon suffer from issues like poor capacity, volume expansion after a long cycle, and dendritic formation. Hence, lithium metal is the top candidate for anode material. Two issues currently restricting the anode performance are undesired side reactions and uneven deposition of Li^+ ions. Interface layers or multi-layer strategies are mature to address these two issues, done by forming a LiF -rich layer which physically separates the anode from the electrolyte.

4. Conclusion

This paper summarizes four widely used and studied polymer-SSEs and interfacial contact between polymer SSEs and electrodes. As the demand for high-performance electric vehicles rises, the importance of LIBs has been realized with studies on improving battery cycle performance. The traditional LEs have reached their boundary on stability and the electric vehicle (EV) industry is urging for LIBs that have the same ionic conductivity as LEs with better stability. Polymer-SSEs is one of the most promising electrolytes that have the potential to create revolutionary change in the next generation of LIBs. Its diversity and ease of modification give them unlimited potential for new products.

However, this paper still lacks a comprehensive statistic and figure to explain the difference between different polymer-SSE families. The interfacial contact between electrode and electrolyte still needs further study to address the issue mentioned. It is another important component in LIBs and can be one of the approaches for improving battery performance. Among all the types of polymer-SSEs, gel and composite polymer SSEs have great potential for further study. Gel electrolyte has superior interfacial contact with electrodes and ionic conductivity. A Composite electrolyte combines multiple materials and draws their advantages into one single material. Besides that, the production of SSEs is still within the laboratory with high cost. A cost-effective, high-performance and stable LIB is the goal for researchers in this field and more efforts are still mandatory at the current time.

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