Modification Strategies and Applications of Poly (ethylene oxide)-Based Solid-State Electrolytes

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Abstract. The need for high-performance power batteries in the new energy vehicle sector is growing as a result of the global energy transition and the pursuit of carbon neutrality targets. Because organic electrolytes are inherently flammable and prone to leak, conventional lithium-ion batteries with liquid electrolytes have serious safety and energy density issues. All-solid-state lithium batteries are seen as a breakthrough for next-generation energy storage technologies because of their inherent safety and potentially high energy density. Solid polymer electrolytes (SPEs) have garnered a lot of interest as a crucial element among these. With its distinct molecular structure, remarkable ability to dissociate lithium salts, and outstanding processability, poly (ethylene oxide) (PEO) has become the most promising solid polymer electrolyte material for industrialization. However, the limited electrochemical stability window, low room-temperature ionic conductivity, and inadequate mechanical strength of PEO-based electrolytes prevent their widespread use. With a focus on three main areas—improving mechanical strength, expanding the electrochemical window, and enhancing ionic conductivity, this review highlights the state of research on PEO-based solid polymer electrolytes, evaluates their benefits and drawbacks, and suggest ways to modify them to overcome these obstacles. Lastly, the development tendencies of solid polymer electrolytes based on PEO are examined.

Keywords: All-solid-state batteries, solid polymer electrolytes, poly (ethylene oxide), modification strategies.

1. Introduction

In the context of rapidly increasing energy consumption, the urgency of carbon emission reduction and the development of new energy sources has become a focal point of global attention [1]. Energy storage technologies for renewable energy represent a critical pathway for transitioning from fossil fuels to sustainable energy systems. The widespread adoption of electric vehicles (EVs) not only reduces the combustion of non-renewable resources such as coal, petroleum, and sulfur-containing compounds but also enables more efficient energy conversion and utilization [2]. The rapidly evolving EV industry demands advanced battery systems with high energy density, long cycle life, and low cost. Although lithium battery technology continues to advance, current systems are approaching their theoretical energy density limit (300 Wh/kg) [3]. As lithium batteries are increasingly deployed in transportation applications, requirements for specific energy density have become even more stringent.

However, range anxiety remains a pervasive issue for EVs, posing a significant constraint on the sustainable development of the industry. Energy utilization efficiency is a key factor affecting driving range, making improvements in this area a major focus for commercial applications.

Solid-state electrolytes offer distinct advantages, including low cost, ease of processing, and high tolerance to vibration, impact, and mechanical deformation. The transition from liquid-electrolyte lithium batteries to all-solid-state lithium metal batteries has emerged as a promising development trend [4]. Compared to conventional liquid electrolytes, solid-state electrolytes exhibit superior mechanical strength, effectively suppressing lithium dendrite growth while offering enhanced safety through reduced flammability and elimination of leakage risks.

Nevertheless, inorganic solid-state electrolytes face challenges in pouch cell applications, driving extensive research efforts toward organic solid polymer electrolytes (OSPEs). OSPEs not only mitigate the polysulfide shuttle effect in lithium-sulfur batteries but also protect lithium metal anodes from atmospheric corrosion [5].

Because of its distinct molecular structure, poly (ethylene oxide) (PEO) has emerged as the most extensively researched OSPE material among several polymer matrices. Lithium salt dissociation is aided by the coordination of ether oxygen atoms with lithium ions in PEO chains. PEO also exhibits outstanding chemical stability and film-forming capabilities. Nevertheless, PEO-based electrolytes have three main drawbacks: (1) low ionic conductivity (usually less than 10-5 S/cm) due to high crystallinity at room temperature; (2) inadequate mechanical strength to stop lithium dendrite penetration; and (3) a limited electrochemical window (approximately 4V), which limits compatibility with high-voltage cathodes [6]. The practical use of PEO-based electrolytes is significantly hampered by these disadvantages.

Recent studies have demonstrated that nanofiller modification represents an effective strategy to enhance the performance of PEO-based electrolytes [7]. The incorporation of functional nanofillers can simultaneously address multiple challenges: nanoparticles disrupt PEO crystallinity, increasing amorphous phase content; certain fillers possess intrinsic ionic conductivity, creating additional lithium-ion transport pathways; rigid fillers significantly improve mechanical properties; and some functional fillers can widen the electrochemical window or stabilize electrode/electrolyte interfaces. This multifunctional synergistic effect makes nanofiller modification a hotspot in PEO-based electrolyte research.

This review systematically summarizes recent advances in PEO-based solid polymer electrolytes, critically analyzing their advantages and limitations. Focusing on three key modification strategies—enhancing ionic conductivity, broadening the electrochemical window, and improving mechanical strength—we provide an in-depth discussion of current optimization approaches. Finally, we offer perspectives on future development directions for PEO-based solid polymer electrolytes.

2. PEO-Based Solid Polymer Electrolytes: An Overview

2.1. Poly(ethylene oxide) (PEO)

Poly (ethylene oxide) (PEO) is a crystalline, thermoplastic, water-soluble polymer characterized by repeating ethylene oxide (−EO−) units in its molecular chain. Its glass transition temperature (Tg) and melting point vary with molecular weight. Conventionally, products with molecular weights below 20,000 are termed polyethylene glycol (PEG), which exist as viscous liquids, while those exceeding 20,000 are classified as poly (ethylene oxide), appearing as white powders. PEO with molecular weights ranging from 105 to 106 exhibits highly ordered structures, typically melting at approximately 65°C.

The ethylene oxide repeating units contain ether oxygen bonds, where oxygen atoms possess lone electron pairs. This structural feature enables PEO to demonstrate strong affinity for hydrogen atoms bonded to polar groups, facilitating complex formation with various small molecules, polymers, and inorganic nanoparticles. Among studied polymer electrolytes, PEO has attracted extensive research interest due to its high dielectric constant and exceptional lithium salt dissolution capability.

2.2. Lithium Ion Conduction Mechanism in PEO

Li^+ transport mechanism in PEO can be explained by the hopping conduction theory [8] (as shown in the Fig. 1.). The high electronegativity of oxygen atoms allows Li^+ to coordinate with 4-5 oxygen atoms in PEO, forming chelation complexes. When the environmental temperature exceeds PEO's Tg, the free molecular chains undergo segmental motion, disrupting the force equilibrium around Li^+ ions. This enables Li^+ to hop to adjacent oxygen atom clusters (4-5 oxygen atoms) and re-establish equilibrium. Under an electric field, this hopping process results in directional charge transport.

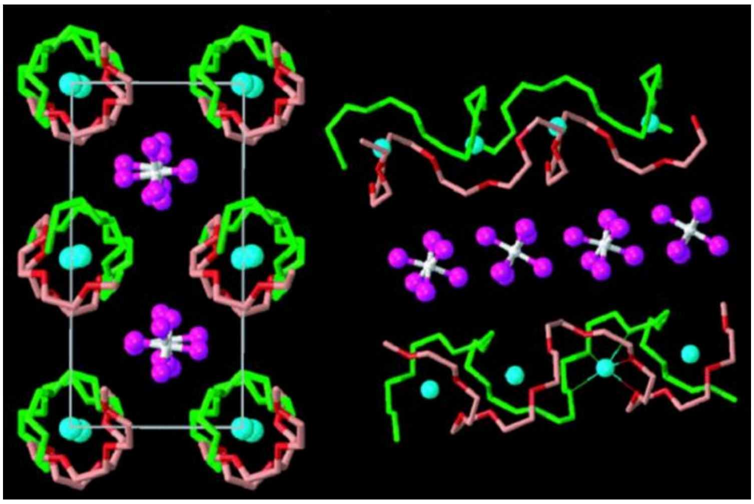

Figure 1. Structure of the polymer electrolyte poly (ethylene oxide) 6: LiAsF6 [8]

The most widely used solid polymer electrolyte material, PEO is typically employed with lithium salts. Upon dissolution of lithium salts in PEO, the resulting ions migrate with the polymer chain segments, thereby enhancing ionic conductivity. The lithium salt-polymer mixture reduces both Tg and melting point, promoting ion mobility and improving ionic conductivity. The lithium salt concentration directly determines charge carrier density in the electrolyte, significantly influencing conductivity. Within certain limits, increasing lithium salt concentration elevates charge carrier density and enhances ionic conductivity. The polymer and the added lithium salt form a mixture that reduces the glass transition temperature and melting point, and promotes ion migration and increasing the ionic conductivity. After the lithium salt dissolves, the solubility of the lithium salt in the polymer matrix is crucial as it might not be able to migrate in the form of free ions. The content of lithium salts directly determines the concentration of charge carriers in the electrolyte, and this concentration has a significant impact on conductivity. Within a certain range, increasing the concentration of lithium salts can enhance the concentration of charge carriers and the ionic conductivity. Mogurapett et al. [9] conducted a molecular dynamics simulation to study the effect of silica nanoparticles on the ion transport in the polyethylene oxide/lithium fluoroboride/ silica composite polymer electrolyte. They found that adding nanoparticles would slow down the movement of polymer chain segments and reduce the overall ionic conductivity of the electrolyte. Currently, the biggest challenge for PEO-based polymer electrolytes is the low room-temperature ionic conductivity, which is approximately 1.0×10^{-6} S cm^{-1}, much lower than the minimum requirement of 1.0×10^{-4} S cm^{-1} for lithium batteries in practical applications.

3. Modification Strategies for PEO-Based Solid Polymer Electrolytes

3.1. Ionic Conductivity Enhancement

GPrimary approaches for improving PEO's ionic conductivity include blending modification and plasticizer incorporation. Blending modification of PEO typically involves compounding with other polymers (e.g. PMMA, PVDF) or inorganic fillers (e.g. SiO_2, Al_2O_3) to suppress crystallization and enhance segmental mobility, thereby improving ionic conductivity. Plasticizer modification (using low-molecular-weight additives such as PEG or EC) reduces the glass transition temperature (Tg) of PEO, increases chain flexibility, and facilitates lithium-ion migration, significantly boosting conductivity. Both approaches optimize ion transport by tailoring the crystallinity and segmental dynamics of PEO. However, plasticizer modification may suffer from long-term stability issues due to the volatility or migration of small molecules, whereas blending modification offers superior structural stability.

Blending modification effectively disrupts the regular arrangement of poly (ethylene oxide) (PEO) molecular chains, significantly reducing crystallinity and thereby enhancing ionic conductivity. This method offers advantages of simple preparation and tunable physical properties. Rocco et al. [10] fabricated solid electrolytes by blending PEO with poly (methyl vinyl ether-maleic acid) (PMVE-Mac), demonstrating that hydrogen bonding between PEO and PMVE-Mac effectively suppresses PEO crystallization while increasing free volume and chain segment mobility. The PEO-PMVE-Mac-7.5% $LiClO_4$ system achieved room-temperature ionic conductivity of 10^{-5} S/cm. Tanaka et al. [11] reported a PEO/polyethyleneimine (PEI) blended system where the PEO/PEI (8:2)-$LiClO_4$ composition exhibited ionic conductivity of 10^{-4} S/cm at 30 °C, markedly higher than pure PEO-$LiClO_4$ electrolyte. This improvement stems from mutual crystallization inhibition between PEO and PEI, which enhances polymer chain mobility.

The introduction of plasticizers can significantly enhance the ionic conductivity of PEO-based electrolytes. Commonly used plasticizers include organic carbonate solvents, low-molecular-weight polyethylene glycol, and ionic liquids, etc. Cha et al. [12] prepared a composite electrolyte system based on PEO and poly (N, N-dimethylaminomethylacrylic acid ethyl ester) (PDMAEMA). The research results showed that when 4-ethyl-2-dimethyl ether glycol or the mixture of ethylene carbonate (EC) and propylene carbonate (PC) was added, the ionic conductivity of PDMAEMA/PEO/LiTFSI electrolyte at 25°C could reach 4.7×10^{-4} S/cm, which was two orders of magnitude higher than that of the system without plasticizers (10^{-6} S/cm).

Additional strategies involve introducing hyperbranched ethers or optimizing intermolecular interactions to further enhance PEO conductivity.

3.2. Electrochemical Window Modification

Significant progress has been made in improving the electrochemical stability of PEO-based polymer electrolytes through molecular structure design, interaction regulation, and multilayer architecture construction.

Molecular structure optimization via copolymerization effectively lowers the highest occupied molecular orbital (HOMO) energy level of polymer chains, dramatically enhancing oxidation resistance. Based on ethylene oxide (EO) segment positioning within the polymer backbone, copolymers can be categorized as main-chain block or side-chain graft types. Both architectures demonstrate wide electrochemical stability windows exceeding 4.5 V, attributable to chemically inert backbones and low-HOMO polar groups that inhibit oxidation of EO units.

Intermolecular interaction regulation, particularly ion-dipole and Lewis's acid-base interactions, critically determines PEO electrolyte stability (as shown in the Fig. 2.). Research confirms that ion-dipole interactions between lithium salts and polymer matrices not only govern Li+ conduction but also directly influence the electrochemical stability limits of "polymer-in-salt" and "salt-in-polymer" systems. Comparative studies by Hiller et al. [13] revealed that PEO electrolytes containing lithium difluoro (oxalato)borate (LiDFOB) exhibit higher decomposition voltage (4.7 V) than those with lithium bis (oxalato)borate (LiBOB) (4.5 V). Density functional theory calculations attribute this to LiDFOB's lower HOMO level (-8.94 eV) and induced electron redistribution effects. Furthermore, in high-concentration electrolytes, increased cation coordination strengthens lone pair electron stability on solvent molecules and anions. Yoshida et al. [14] demonstrated that optimized ether-based high-concentration electrolytes can achieve a 5 V electrochemical window, successfully applied in 4.2 V LiCoO2/Li cells.

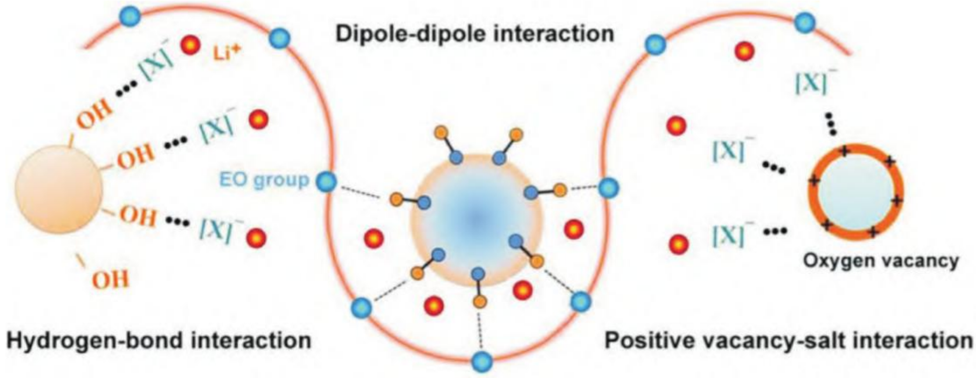

Figure 2. Schematic diagram of Lewis acid-base interactions enhancing oxidation stability [13]

Multilayer composite electrolytes exhibit unique advantages in interface engineering. The polymer/ceramic/polymer sandwich structure developed by Goodenough's group [15] enhances system stability by suppressing anion migration and weakening interfacial electric double layers. This design synergizes ceramic and polymer electrolyte advantages: ceramic layers block anion transport while polymer layers improve lithium metal wettability and homogenize Li^+ flux distribution. Building on this concept, Guo et al. [16] designed a Janus-interfaced PEO-LATP-PAN trilayer composite electrolyte that achieves exceptional cycling stability (89% capacity retention after 120 cycles at 0.5 C) in 4.3 V NMC622/Li cells. These studies provide crucial theoretical guidance and technical pathways for developing high-voltage stable polymer electrolyte systems

3.3. Mechanical Strength Modification

In recent years, significant progress has been made in the performance optimization of solid polymer electrolytes (SPE) through molecular structure design. In the design of copolymers, triblock copolymers have attracted much attention because they can inherit the advantages of each block. Bergfelt et al. [17] successfully synthesized poly (phenyl methyl acrylate)-poly (oligomeric ethylene glycol methyl ether methacrylate)-poly (phenyl methyl acrylate) triblock copolymer by atom transfers radical polymerization. The phenyl methyl acrylate block significantly enhanced the mechanical strength of the solid membrane. Electrochemical tests demonstrated that the $LiFePO_4$/SPE/Li battery based on this electrolyte exhibited excellent cycling stability at 60°C.

Constructing a network structure is an effective strategy to enhance the dimensional stability of polymer electrolytes. Daigle et al. [18] innovatively used ethylenediamine as a crosslinking agent to prepare a cross-linked copolymer of acrylic acid glycidyl ester and polyethylene glycol methoxy acrylate. The resulting solid-state membrane exhibited an elastic modulus as high as 1 GPa, and the assembled $LiFePO_4$/SPE/Li battery delivered a specific capacity of 151 mAh/g at 80°C and a C/6 rate. Khurana et al. [19] developed a crosslinked polyether electrolyte (PEO-PE-PEG) that achieved an ionic conductivity of 1.0×10^{-4} S/cm at 25 °C while demonstrating good lithium dendrite suppression capability.

Breakthroughs have also been made in composite electrolyte systems. Jacob et al. [20] introduced PEO into a PVDF-LiClO4 electrolyte, significantly enhanced the mechanical stability of the composite membrane, while increasing the ionic conductivity by two orders of magnitude. Guo et al. [21] designed a hierarchical "ceramic-in-polymer" and "polymer-in-ceramic" electrolyte, which precisely regulated mechanical strength, ionic conductivity, and interfacial compatibility, enabling its successful application in dendrite-free solid-state lithium metal batteries.

4. Conclusion

As the demand for electric vehicles, smart power grids, and flexible wearable electronic devices continues to grow, it is necessary to manufacture electrochemical energy storage devices with high energy density, long cycle life, and excellent safety. Traditional liquid lithium-ion batteries have almost reached their theoretical energy density limit, thus unable to provide long driving range for electric vehicles or be used in smart multi-functional electronic devices. Due to its excellent processability, safety, and superior interfacial compatibility, polyethylene oxide (PEO) has become an ideal material for solid-state batteries. The various modification methods introduced in this article can effectively overcome the defects of PEO itself, such as low ionic conductivity, limited mechanical strength, and narrow electrochemical stability window, enabling its wider application. From this perspective, based on modified PEO, solid electrolytes will undoubtedly continue to be the focus of research in the future.

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