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Progress in Preparation and Modification of Gel Polymer Electrolyte

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Abstract. Gel polymer electrolytes (GPEs) combine the safety of solid electrolytes with the high ionic conductivity of liquid electrolytes, making them an important research direction for high-performance lithium-ion batteries. This paper systematically reviews the composition, preparation methods, and performance optimization strategies of GPEs. To address the issues of low mechanical strength and poor interfacial stability, this review focuses on modification strategies including blending, copolymerization, cross-linking, and compositing. Studies show that multi-component blending (e.g., PEO-PS-PMMA system) and copolymerization cross-linking (e.g., crosslinked PDOL system) can significantly improve the ionic conductivity, mechanical stability, and electrochemical performance of GPEs.

Keywords: Gel polymer electrolytes, lithium-ion batteries, Polymer Matrix

1. Introduction

Due to the pressure for energy structure transformation caused by the oil crisis, the development of environmentally compatible renewable energy sources (such as photovoltaics, wind energy, and geothermal energy) has become a global consensus. In this context, the storage and transportation of energy have become key links in promoting the large-scale use of green energy. Traditional battery systems (such as lead-acid batteries and carbon-zinc batteries) have difficulty meeting the development needs of high-power power sources in terms of energy density. Alkali metals, due to their low density and low standard potential, have gradually become a research hotspot for high-performance electrode materials. Among them, metallic lithium, with its lowest standard potential, minimal atomic mass, and relatively small lithium-ion radius, possesses excellent solid-phase diffusion capability and intercalation reaction kinetics, demonstrating extremely high theoretical energy density, and is therefore regarded as one of the most promising anode materials.

Research on lithium-ion batteries can be traced back to 1962, when the American company Lockheed Missile and individuals such as Chilton Jr. and Cook first proposed the concept of a 'lithium non-aqueous electrolyte system,' marking the beginning of lithium battery research. In 1980, Professor John Goodenough's team reported a lithium-ion battery system using lithium iron phosphate ($LiFePO_4$) as the cathode material, significantly improving the battery's charge and discharge performance. In 1990, Japan's Sony Corporation took the lead in achieving industrial

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production of lithium-ion batteries, signaling the start of their commercialization. After more than thirty years of development, lithium-ion batteries, with advantages such as lightweight, high energy density, long cycle life, low self-discharge rate, and no memory effect, have been widely used in mobile phones, laptops, and other portable electronic products, and have gradually penetrated into the fields of hybrid and pure electric vehicles [1]. Although lithium-ion batteries have dominated the mobile device market, as device computing power increases, screen sizes grow, and the demand for thinner and lighter designs rises, the market is placing higher requirements on battery systems for greater efficiency, safety, and reliability, driving continuous optimization of battery components, especially electrode materials and electrolyte systems.

The performance of lithium-ion batteries highly depends on the synergy of their key components, among which the electrolyte serves as the core medium for ion transport and directly determines the battery's operating temperature range, capacity performance, safety, and cycling reversibility. Based on physical state, electrolytes can be divided into two major categories: liquid electrolytes and solid electrolytes. Liquid electrolytes have relatively high ionic conductivity, support high-rate charging and discharging, and perform well at low temperatures, making them the most widely used system in currently commercialized lithium-ion batteries. However, liquid electrolytes present safety risks in lithium metal anode systems, such as dendrite growth, solvent evaporation, internal side reactions, and leakage. Especially in systems containing flammable linear carbonate solvents, leakage can easily lead to fires or even explosions, severely limiting their application in high-energy-density batteries [2].

To overcome the aforementioned problems, researchers have gradually explored alternative systems. Among them, solid polymer electrolytes formed by dissolving lithium salts in a polymer matrix show significant advantages in terms of safety, but their ionic conductivity is generally low. Gel polymer electrolytes, on the other hand, combine the safety of solid electrolytes with the high ionic conductivity of liquid electrolytes. They form a stable gel structure by absorbing liquid electrolytes through the polymer matrix, effectively suppressing solvent evaporation and electrolyte leakage while maintaining good electrochemical performance. Therefore, they have become an important direction in current high-performance lithium-ion battery electrolyte research. This paper summarizes the composition, preparation, and optimization of lithium-ion battery gel electrolytes and can provide some guidance for the synthesis and application of gel electrolytes.

2. Composition of gel polymer electrolytes (GPEs)

GPEs are composed of polymer matrix materials, plasticizers, and alkali metal salts. The polymer matrix material primarily provides mechanical properties, Lithium salts mainly provide transportable and migratory lithium ions for the system. To obtain GPEs that combine the excellent properties of both liquid and solid electrolytes, battery designers must consider not only the selection of polymer matrix (including composition, morphological structure, and mechanical properties) when designing and preparing GPEs, but also the interactions between the matrix material and lithium salts as well as electrolytes (compatibility and phase separation aspects), the construction of ion transport channels. In addition, the interfacial stability between the polymer matrix and metallic Li electrode is also one of the factors to be considered [3].

3. Preparation method of gel polymer

There are various methods for preparing GPEs. In contrast, heterogeneous gels consist of three phases: a polymer matrix material, an electrolyte, and a liquid electrolyte absorbed and activated

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into a swollen GPE. The preparation of heterogeneous GPEs usually involves two stages: preparing a porous polymer membrane or a cross-linked network polymer, and activating it by swelling with a liquid organic electrolyte. When preparing electrolyte membranes, considerations include the thickness of the membrane, ionic conductivity, water absorption, and the extent of electrolyte absorption. The basic preparation methods mainly include the following two types.

3.1. Solution casting method

In the early stages, GPEs are typically prepared using the solution casting method, where the polymer matrix and a non-aqueous lithium salt electrolyte are co-dissolved in a low-boiling-point solvent (e.g., acetone-tetrahydrofuran, tetrahydrofuran, etc.)., and the resulting solution is cast onto molds and dried to obtain GPEs [4]. GPEs obtained by this method are usually viscous and have low mechanical strength. When used in actual batteries, they must be hardened through chemical or physical cross-linking. Besides the need for cross-linking, the main disadvantage is that the entire process must be carried out in an anhydrous environment because highly moisture-sensitive lithium salts are present at the initial stage. This critical environmental requirement increases costs and prevents its large-scale application.

3.2. In situ polymerization

In this method, a precursor composed of polymerizable monomers, liquid electrolyte, and initiator is directly placed into a lithium-ion battery and then cured under specific conditions to form a polymer network. Commonly used initiators are organic peroxides: dicarbonate peroxide, benzoyl peroxide (BPO), neopentyl glycol peroxide, and tert-pentyl ester of neopentanoic peroxide, as well as azo compounds like 2,2'-azobis(2-methylbutyronitrile) (AIBN).

3.3. Polymer-activation method

To facilitate industrial production, Bellcore was the first to propose this method. The polymer-activation process can be divided into four stages. Polymer matrix materials are prepared to form porous polymers or cross-linked prepolymers (after preparation, they need to be cross-linked with ultraviolet light to form cross-linked polymers), then cast into molds, and dried to form films. The required liquid electrolyte is prepared. In the third stage, the material is dried and immersed in liquid electrolyte to activate it into a GPE. In the final stage, it is assembled into an LIB. The electrolyte prepared by this method allows manufacturing in a fully open environment before being activated with an anhydrous liquid electrolyte.

3.4. Phase separation method

Phase separation methods prepare gel polymers by inducing a homogeneous solution to separate into polymer-rich and solvent-rich phases during gelation, forming a porous network. Key strategies include enhanced phase separation using two incompatible polymers to create large pores and high toughness; polymerization-induced microphase separation where spontaneous phase separation during polymerization forms nanoscale colloidal networks with high stability; and in situ phase separation employing mixed solvents to generate bicontinuous structures with ultra-high strength and shape memory. Classical aqueous methods like coacervation are also used. Final gel properties are controlled by parameters such as polymer concentration, solvent ratio, temperature, and pH.

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4. Methods for improving the performance of gel polymers

4.1. Blending

Blending mainly improves the performance of polymer electrolyte systems by modifying the properties of the polymer host materials. By utilizing the different polarities of the molecular chains of two polymers, which leads to different adsorption capacities for the electrolyte, it is possible to achieve good mechanical strength while maintaining good ionic conductivity. Among the two polymers used for blending, one polymer has a regularly arranged molecular chain that easily forms a crystalline structure, which is not conducive to lithium ion conduction but can provide mechanical backbone support. The other polymer, however, disrupts most of the regular molecular chain arrangements, making the entire polymer system an amorphous polymer. Compared with other methods, blending can control the material properties of the entire polymer system by adjusting the ratio of the two polymers and is a relatively economical method. However, this blended polymer electrolyte has a drawback: due to the different polarities between the two polymers, phase separation can occur in the entire electrolyte system, resulting in an inhomogeneous system, which affects the overall performance of the electrolyte.

A novel gel polymer electrolyte (GPE) was developed by blending polyethylene oxide (PEO), polystyrene (PS), and poly(methyl methacrylate) (PMMA) in a mass ratio of 3:1:1 using the solvent casting technique, followed by activation in a liquid electrolyte [5]. The ternary blending strategy combines the advantages of each polymer: PEO provides high Li^+ salt solubility and good interfacial stability with lithium metal, PMMA enhances electrolyte compatibility, and PS improves mechanical strength. The resulting PEO-PS-PMMA GPE exhibits a unique dense structure with low crystallinity, achieving an ionic conductivity of 0.12 mS/cm at 25 °C, a Li^+ transference number of 0.2, and an electrochemical stability window exceeding 4.3 V(Figure 1), demonstrating excellent interfacial compatibility and promising potential for safe batteries.

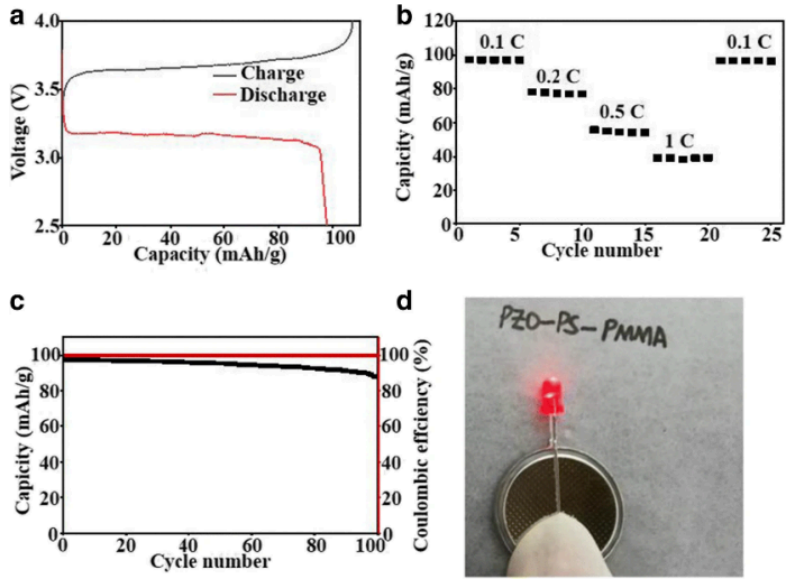


Figure 1. presents (a) charge/discharge profiles, (b) rate-dependent discharge capacities, (c) cycling stability, and (d) a photograph of quasi-solid-state lithium metal batteries incorporating a PEO-PS-PMMA GPE

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4.2. Copolymerization

Electrolyte membranes made from a single polymer have only one type of polymer monomer, making them uniformly polar. In fact, they can adsorb more electrolyte to form conductive channels. However, if too much electrolyte is adsorbed, the mechanical strength decreases, making it difficult to self-support into a membrane. Similar to blending, copolymerization aims to improve the polymer matrix material. One regular polymer serves as the monomer to provide a mechanical framework, while another monomer is added to disrupt its regularity. The difference is that the two polymer monomers are copolymerized together through chemical reactions, forming copolymers such as random copolymers, block copolymers, and comb copolymers. This is the most practical and widely used method for preparing GPE matrix materials. Compared with homopolymers, they have much lower crystallization tendencies, which may be due to the internal plasticization of the polymer matrix.

Lei et al. [6] developed a universal copolymerization strategy for crosslinked poly(1,3-dioxolane) (PDOL) solid polymer electrolytes by combining LiTFSI and LiDFOB. The key mechanism is that LiTFSI protects the boron active center and promotes chain growth via soft-soft interactions with cationic species, enabling homogeneous crosslinking with various epoxy monomers. As shown as Figure 2, the resulting benzene-centered crosslinked PDOL electrolyte exhibits high ionic conductivity (4.5×10^{-4} S cm^{-1}), excellent thermomechanical stability, complete suppression of crystallization, and significantly enhanced cycling stability in all-solid-state lithium metal batteries.

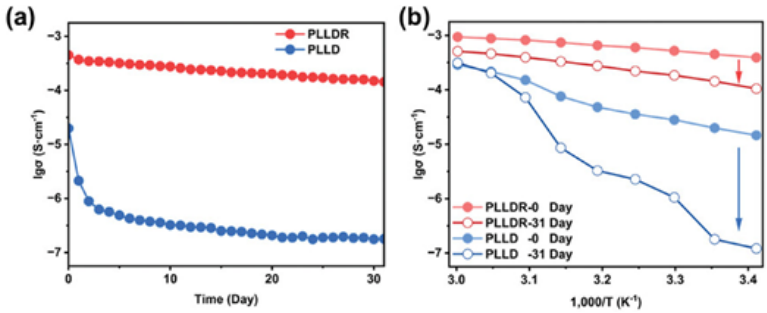


Figure 2. illustrates the electrochemical performance of the PLLDR solid-state electrolyte, including (a) time-dependent ionic conductivity curves for PLLDR and PLLD at 25 °C, and (b) temperature-dependent ionic conductivity curves for both electrolytes in different states

4.3. Crosslinking

Crosslinking can significantly improve the thermal stability and dimensional stability of GPEs. There are two roles of applying crosslinking to gel polymer electrolyte systems: one is to enhance their mechanical properties, and the other is to form a crosslinked network structure that helps encapsulate the swollen liquid electrolyte. After adding plasticizers to gel polymer electrolytes, the mechanical strength of the entire polymer system drops by one level. Only after physical or chemical crosslinking do their properties approach the requirements for industrial production. Crosslinking methods are considered simpler and more effective because they not only inhibit crystallization but also increase mechanical strength by constructing a three-dimensional network. Crosslinking is also very useful for ensuring the mechanical stability of gel electrolytes containing a large amount of plasticizer. Crosslinking methods include chemical crosslinking and radiation crosslinking. Chemical crosslinking refers to directly forming a GPE by initiating monomer polymerization using a photoinitiator under UV light. Radiation crosslinking refers to forming a

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crosslinked network polymer under the action of a crosslinking agent after the monomer has polymerized into a polymer, without initiators or chemical residues, achieving chain crosslinking and obtaining a gel polymer electrolyte with both abundant ion transport channels and good mechanical properties

The article of Katcharava reports the fabrication of pyrrolidinium-based poly(ionic liquid) dual-network gel electrolytes via thermal and photoinitiated polymerization. The synthesis combines covalent crosslinkers (up to 10 mol%) with a dynamic crosslinker containing quadruple hydrogen-bonding ureidopyrimidone (UPy) moieties.The resulting gel electrolytes exhibit exceptional electrochemical stability above 5 V, thermal stability up to 300 °C , non-flammability, and full reprocessability at 70 °C without compromising electrochemical performance, making them promising candidates for safe and sustainable next-generation battery applications.

4.4. Composites

Adding nano-inorganic fillers to GPEs to obtain NCPEs is also a very effective method to improve the ionic conductivity of electrolytes. After filling nano-inorganic particles into the GPE, the composition of some repeating units in the polymer is restricted or blocked, thereby reducing the volume of crystallization, which can effectively form ion transport channels and facilitate the transport and migration of Li. Ceramic fillers act as crosslinking centers and centers for Lewis acid-base interactions, thereby improving the conductivity of the composite system. Generally, fillers are divided into two categories: one type participates in the ion conduction process, such as LiAl2O3 and LiAlO2; the other type is electrochemically inert fillers, such as SiO_2, TiO_2, ZrO_2, Al_2O_3, and M90.

5. Conclusion

Gel polymer electrolytes show great potential for improving the safety and energy density of lithium-ion batteries. Their performance is highly dependent on the structural design of the polymer matrix, the construction of ion transport pathways, and the interfacial compatibility with electrodes. Current strategies such as blending, copolymerization, cross-linking, and the addition of inorganic fillers have achieved a certain balance between ionic conductivity and mechanical strength. However, challenges remain in practical applications, including interfacial side reactions, insufficient long-term cycling stability, and complex preparation processes. Future research should focus on the molecular design of multifunctional polymer matrices, optimization of in situ polymerization processes, and systematic regulation of electrode/electrolyte interfacial stability to promote the practical application of GPEs in next-generation high-safety and high-energy-density lithium metal batteries.

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