Classification Of Polymer Electrolytes and Their Applications in Batteries

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Abstract. The escalating demand for safer energy storage systems with enhanced energy density has positioned polymer electrolytes as a pivotal alternative to conventional liquid electrolytes, which suffer from fundamental drawbacks including flammability and electrolyte leakage. Owing to their intrinsic solid-state characteristics, mechanical flexibility, and tunable physicochemical properties, these electrolytes have emerged as essential constituents for developing next-generation high-safety, high-energy-density batteries with improved thermal stability. The article focuses on gel polymer electrolytes, all-solid-state polymer electrolytes, and composite polymer electrolytes. It analyzes their composition, ion-conduction mechanisms, and optimization strategies, with a particular emphasis on the interrelationships among key performance indicators such as ionic conductivity, mechanical strength, lithium-ion migration number, and chemical stability. Additionally, it reviews the practical application progress of polymer electrolytes in lithium-ion batteries (LIBs), zinc-ion batteries, and fuel cells, highlighting the current research challenges that need to be overcome, including low room-temperature conductivity, interface stability, and cost control. This study provides a theoretical basis for advancing multifunctional solid-state batteries and scalable electrolyte material applications.

Keywords: Classification of polymer electrolytes; New energy; State batteries.

1. Introduction

As energy technology advances towards higher energy density and greater safety, issues such as flammability, leakage, and lithium dendrite growth in traditional liquid electrolytes have become key bottlenecks limiting the performance of lithium-ion batteries (LIBs). The electrolytes used in LIBs are primarily composed of organic solvents, such as ethylene carbonate and propylene carbonate. However, these organic liquid electrolytes impose high requirements on battery packaging and pose a risk of leakage. Solid-state electrolytes for LIBs are safer and more reliable compared to liquid non-aqueous electrolytes. They adopt either all-solid or semi-solid structures, which overcome the problems of easy leakage, short circuits, and insufficient safety associated with liquid electrolyte batteries. Compared with inorganic solid electrolytes, polymer solid electrolytes have strong processability and good film-forming properties. They can use flexible packaging materials such as aluminum-plastic films to achieve bending and folding properties, making battery design more flexible and convenient. In addition, they can also reduce overall weight and significantly improve specific energy density. Solid polymer electrolytes are considered to be important materials to overcome the limitations of current liquid electrolytes and improve the performance of secondary LIBs.

In the 1970s, research on polymer electrolytes first came into being. *Wright* demonstrated that the composite system of polyethylene oxide (PEO) with alkali metal salts exhibited ionic conductivity. Later, Armand verified Wright's results and suggested using it as an electrolyte material for all - solid - state batteries [1]. From then on, research on polymer electrolytes has attracted wide-spread attention and is divided into three types according to the structure and composition of the electrolyte system: all-solid polymer electrolytes (SPEs) without liquid plasticizers, gel polymer electrolytes (GPEs) with liquid plasticizers, and composite polymer electrolytes (CPEs). Following Bellcore's introduction of gel polymer electrolytes for polymer LIBs in 1994, subsequent research has spurred substantial advancements in polymer electrolyte technology [2].

Today, electric vehicles represent the future direction of transportation development, making the research and iteration of high-performance batteries particularly urgent. Therefore, more attention is being directed towards polymer-based solid-state organic electrolytes. This article reviews the specific classification and related applications of polymer electrolytes based on existing literature and research, with a focus on their electrochemical performance.

2. Basic properties of polymer electrolyte

2.1. Definition and composition of polymer electrolyte

Research on polymer electrolytes originated in 1973, when Wright first measured the conductivity of polyoxyethylene (PEO) complexed with alkali metal salts in 1975, reporting that PEO-alkali metal salt composites exhibit high ionic conductivity. In 1979, Armand et al. reported that the ionic conductivity of PEO's alkali metal salts reached 10^{-5} S/cm at 40 to 60℃ and showed excellent film-forming properties. These composites can be used as electrolytes for LIBs, thus ushering in the era of polymer electrolyte research [3, 4].

Polymer electrolytes are composite systems formed by the coordination of high molecular weight polymers (such as PEO, polyacrylonitrile, etc.) with lithium salts (such as LiTFSI, $LiPF_6$, etc.), combining ionic conductivity and the flexibility of polymer materials. Their ion-conducting mechanism relies on the movement of polymer segments (for example, the dynamic coordination and dissociation of oxygen atoms with lithium ions (Li^+) in PEO) or the interfacial transport pathways of inorganic fillers.

Polymer electrolytes mainly consist of two parts: the matrix material and the conductive salt, with inorganic fillers or plasticizers often added as modifiers. The matrix material of a polymer electrolyte refers to the substance that dissolves lithium salts through the polar network structure of the polymer and provides ion transport channels, endowing the material with ionic conductivity. These materials must have a certain coordination ability to form dynamic coordination bonds with Li^+, such as the ether oxygen atoms (-O-) in PEO. They also need to exhibit segmental mobility and structural designability. The latter refers to the ability to adjust performance through copolymerization, cross-linking, or introducing inorganic fillers, for example, reducing crystallinity by copolymerizing polyvinylidene fluoride (PVDF) with hexafluoropropylene (HFP).

Inorganic fillers can form continuous ion channels, which is the core advantage of composite electrolytes. This advantage significantly enhances the conductivity of composite electrolytes. In 1982, Weston et al. applied inorganic ceramic materials to polymer electrolytes and studied the effects of inorganic fillers on the performance of polymer electrolytes. This marked the beginning of research on composite polymer electrolytes. By 1999, Boudin et al. used phase transformation methods to prepare porous PVDF-HFP copolymer electrolytes. The polymer membranes produced by this method have a sponge-like structure with a porosity as high as 70%. The room-temperature ionic conductivity of these polymer electrolytes reaches up to 3.7×10^{-3} S/cm [5-8].

Conductive salts are an indispensable component of polymer electrolytes, consisting of anions and Li^+. Their primary function is to generate Li^+ through dissociation as charge carriers, which participate in the construction of the electrode/electrolyte interface film, thereby endowing the electrolyte with ionic conductivity. For example, common salts such as LiTFSI (lithium bis-trifluoromethanesulfonate) and LiFSI (lithium bis-fluorosulfonate) both belong to this category, with their anion structures capable of modulating the physical and electrochemical properties of the electrolyte.

In polymer electrolytes, inorganic fillers are categorized into active fillers (such as LLZO, LATP) and inert fillers (such as SiO_2, Al_2O_3). Their function is to reduce crystallinity, enhance mechanical strength, and increase the Li^+ transport pathway. Plasticizers are used in gel polymer electrolytes (GPEs), where they improve ionic conductivity by introducing cyclic carbonates and other solvents. Both serve as electrolyte additives.

2.2. Key indicators of polymer electrolyte performance

2.2.1 Ionic conductivity

The size of the ionic conductivity of polymer separators determines the battery; impedance, rate discharge performance, and capacity, among other characteristics. Therefore, ionic conductivity is the most important indicator for evaluating the performance of polymer electrolytes. The room-temperature ionic conductivity of polymer electrolytes is influenced by factors such as the dissociation degree and concentration of lithium salts, the radius of anions, and the dielectric constant and viscosity of the polymer material. The ionic conductivity of polymer electrolytes is substantially influenced by temperature variations. At higher temperatures, the activation energy for ion transfer between chain segments decreases, leading to faster movement and thus higher ionic conductivity. Satisfying the operational demands of LIBs, characterized by a discharge current density of 10^{-3} A/cm^2, necessitates polymer electrolytes with room-temperature ionic conductivities approaching or attaining 10^{-3} S/cm [2, 9].

2.2.2 mechanical strength

The mechanical strength of polymer electrolytes is a core parameter that ensures the safety and performance of batteries. Processability and tensile strength are key factors in transitioning polymer electrolytes from the laboratory stage to practical applications. Many polymer electrolyte systems, in pursuit of high ionic conductivity, increase the fluidity of the electrolyte, leading to issues such as low mechanical strength and poor processability, thus failing to meet the requirements of actual production.

2.2.3 Chemical and electrochemical stability

The chemical stability of polymer electrolytes refers to their ability to resist chemical decomposition, oxidation, or side reactions with other components (such as electrode materials and solvents) during battery operation. This is primarily influenced by the molecular structure and environmental tolerance. Electrochemical stability, on the other hand, refers to the ability of polymer electrolytes to maintain structural and functional stability during electrochemical processes (such as charging and discharging, high voltage/high current conditions), including resistance to voltage and current density, as well as inhibition of redox side reactions.

The thermodynamic stability of polymer electrolyte is a necessary condition to ensure the safe charge and discharge of batteries. In the process of charge and discharge, heat will be generated inside the battery, which will increase the internal temperature, which may lead to the melting and decomposition of polymer electrolyte, resulting in a series of problems such as short circuit of batteries.

The electrochemical stability of the electrolyte in LIBs is also a critical parameter. An unstable electrolyte can lead to irreversible reactions and a decrease in battery capacity. The electrochemical stability of the electrolyte is typically characterized by an electrochemical stability window. To ensure normal charging of the battery, the electrochemical window of the polymer electrolyte generally needs to be above 4.5V.

2.3. Classification of polymer electrolytes

In order to meet the actual needs of modern social production and life, they can be classified into three categories according to the structure and composition of the electrolyte system: SPEs, GPEs and CPEs.

2.3.1 All solid polymer electrolyte

All-solid polymer electrolytes consist solely of polymers and salts. This type of polymer electrolyte was among the earliest to be studied, primarily through the direct dissolution of salts in polymers to form solid-solution systems. Research has shown that ion transport in polymer electrolytes is mainly achieved through chain segment motion in the amorphous regions. Therefore, key technical points for all-solid polymer electrolytes lie in suppressing polymer crystallization and lowering their glass transition temperature to achieve high ionic conductivity at room temperature, thereby enhancing battery performance. For instance, Tiqelaar. D.M prepared an electrolyte through cross - linking a chlorinated organic compound with PEO, attaining a maximum ionic conductivity of 3.9×10^{-8} S/cm at room temperature [10, 11]. LIBs using SPEs have significant advantages, such as improved safety; the elimination of internal short circuits, combustion explosions, and electrolyte leakage caused by corrosion of the battery's metal casing; and to some extent, reduced reactivity between the electrolyte and electrodes. They also offer better processability and flexibility, simplified battery construction, and improved packaging efficiency, while reducing manufacturing costs. All-solid-state polymer electrolytes, which contain no liquid plasticizers, can achieve very high mechanical strength. However, their ionic conductivity is low, failing to meet the actual requirements of LIBs. Currently, research on all-solid-state polymer electrolytes is still in the laboratory development stage and has not yet been widely applied.

2.3.2 Gel polymer electrolyte

In 1975, Fusillade and Perche first proposed girlified polymer electrolytes, which were later extensively studied by Abraham et al. Gel-type polymer electrolytes are a paste-like high molecular system formed by the combination of an electrolyte and a polymer. The electrolyte is fixed between the polymer molecular chains, and charges are transmitted through the movement of electrolyte and polymer chain segments. Their characteristics include: high liquid storage capacity; high ionic conductivity; good wetting of the electrolyte at the electrode interface; low battery impedance; and excellent cycling performance [12].

Polymer gel electrolytes consist of a ternary composition of high molecular compounds, metal salts, and polar organic compounds. They appear solid on the surface but differ significantly from solvent-free polymer solid electrolytes in structure and certain properties. Theoretically, the ionic conductivity of gel polymer electrolytes after adding plasticizers already meets the actual requirements of LIBs. As early as 1990, *Morita et al.* synthesized PEO-based gel electrolytes exhibiting a room-temperature ionic conductivity of 10^{-3} S/cm (25°C). However, their mechanical properties are poor, making them prone to deformation under external pressure changes. During use, issues like electrolyte leakage can easily take place, resulting in phase separation between the polymer matrix and the electrolyte solution. This can cause internal pore collapse, damage the structure, and even trigger short circuits within the battery. Therefore, improving the material rigidity of gel polymer electrolytes is one direction for enhancing battery material technology [13].

2.3.3 Composite polymer electrolyte

All-solid polymer electrolytes have strong mechanical strength but suffer from low ionic conductivity; gel polymer electrolytes exhibit excellent ionic conductivity but lack sufficient mechanical strength. Therefore, developing a new type of polymer electrolyte that combines the advantages of both all-solid and gel polymer electrolytes has become a goal of human exploration [14].

When Weston et al. initially introduced inorganic ceramic fillers into the PEO-$LiClO_4$ polymer - electrolyte system, people came to recognize the substantial influence of inorganic fillers in the polymer - electrolyte system. As a result, a new polymer-electrolyte system, namely CPE, was formed [5, 15].

Modern data indicate that inorganic fillers with large specific surface areas can restrain the crystallization behavior of polymer molecular chains [16], thus increasing the proportion of amorphous regions in polymers and decreasing their crystallinity and glass transition temperature. The conduction and migration of Li^+ within the polymer system are also promoted by the interaction between the surface groups of inorganic fillers and Li^+ [17-19].

3. Innovative applications of polymer electrolytes

3.1. Polymer zinc ion batteries (ZIBs)

Like Li^+, zinc ions can also be inserted into battery materials as alkali metal ions. PEO, one of the most appealing SPEs polymers, has a strong Li^+ solvation ability and good molecular chain flexibility, enabling Li^+ to transfer via segmental motion. In the same way, zinc ions can also transfer via segmental motion, and the application of PEO in ZIBs polymer electrolytes has drawn much attention. However, PEO is a semi - crystalline polymer. Its crystalline region has weak chain - segment dynamics. So pure PEO - based SPEs usually show low ionic conductivity at room temperature (about 10^{-6} S/cm), restricting their large - scale application in solid - state ZIBs. To enhance the electrochemical performance of solid - state ZIBs, researchers have put forward various strategies, such as adding zinc salts/fillers, developing multi - component/composite SPEs, and exploring ionic liquid - based polymer electrolytes to boost the ionic conductivity of SPEs. Besides rechargeable batteries, polymer electrolytes can also be used for fuel cell research.

3.2. Polymer fuel cells

Polymer electrolyte membrane fuel cell (PEMFC), also known as proton exchange membrane fuel cell, is an electrochemical device with the ability to directly transform the chemical energy of fuel and oxidant into electrical energy. It features high energy conversion efficiency, environmental friendliness, high specific energy (relative to batteries), low operating temperature, and fast start-up. The polymer electrolyte membrane is a core component of PEMFC, serving to separate fuel and oxidant, conduct ions, and insulate electrons. It is a hot topic in the field of fuel cell research.

But polymer fuel cells also have disadvantages that need further improvement, such as insufficient core material performance, high complexity in water-thermal management, poor start-up performance at low temperatures, low durability, and high catalyst costs. Meanwhile, the emerging high-temperature proton exchange membrane fuel cells, which promise to overcome technical barriers like low heat dissipation efficiency and poor environmental adaptability (carbon monoxide tolerance), have become one of the main directions for current fuel cell development.

4. Summary

Polymer electrolytes, as key materials for innovating battery technology, have demonstrated significant advantages in enhancing safety and energy density. SPEs improve ion mobility by suppressing crystallization, but their room-temperature conductivity remains insufficient; GPEs achieve high ion conductivity through liquid plasticizers, at the cost of mechanical strength; CPEs enhance both electrochemical performance and structural stability with the help of inorganic fillers, making them a current research hotspot. In terms of application, they have achieved flexible packaging and high-energy design in LIBs, need to overcome the low-temperature kinetic limitations of PEO matrices in zinc-ion batteries, and face challenges related to proton exchange membrane durability and catalytic costs in fuel cells. Future research should focus on: (1) developing new polymer matrices and salt systems to optimize Li^+ migration numbers and electrochemical windows; (2) designing multi-scale composite structures to synergistically improve ion conductivity and mechanical strength; (3) elucidating the reaction mechanisms at the electrode/electrolyte interface to suppress side reactions and lithium dendrite growth; (4) promoting low-cost preparation processes and large-scale production. With continuous breakthroughs in material design and interfacial engineering, polymer electrolytes are expected to accelerate the industrialization process of high-safety solid-state batteries and provide core support for next-generation energy storage and conversion technologies.

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