

Research Progress on Polymer Conductive Films

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Abstract. High-performance polymer materials, with their inherent high conductivity, excellent mechanical flexibility, environmental sustainability, and low processing costs, have demonstrated unparalleled advantages in the development of new conductive composite films and have become a research hotspot in the field of functional materials. This paper focuses on the application of conductive polymer membranes in advanced electronic devices and proton exchange membrane fuel cells. It provides a systematic review of charge transport mechanisms, preparation techniques, and functionalization approaches for conductive polymer materials. The discussion centers on preparation technologies such as electrochemical synthesis and chemical synthesis, detailing the application progress of these materials. Finally, the paper explores the future research prospects of conductive polymer composite films and their potential integration with artificial intelligence technology.

Keywords: conductive polymers, polymer membranes, conductive principles, proton exchange membranes

1. Introduction

As the global industrialization process accelerates, the excessive consumption of fossil fuels has triggered a severe environmental crisis, manifested primarily in global warming driven by the accumulation of greenhouse gases, the frequent occurrence of extreme weather disasters, and the threat posed by rising sea levels to coastal settlements. Meanwhile, the deep reliance on traditional fossil fuel materials has highlighted the urgency of energy security. Against this backdrop, promoting a green and low-carbon transition has become a global consensus. China has clearly outlined its strategic goals of “carbon peaking and carbon neutrality.” In recent years, polymer material technology has achieved a strategic transformation from traditional application areas to high-end manufacturing scenarios through the synergistic evolution of molecular design, structural regulation, and process innovation. This includes fiber-based lithium-ion battery technology in the new energy sector; the large-scale application of biodegradable bio-based materials in the field of environmentally friendly materials; and the innovative development of highly flexible energy storage components in the field of electronics and information technology. Among these, conductive polymer membranes (CPMs) serve as a critical foundational material for flexible electronic devices, new energy systems, and smart equipment, playing an indispensable role in supporting the achievement of carbon neutrality goals and enabling the development of a digital society, thereby

attracting widespread attention. However, the large-scale application of CPMs still faces significant technical challenges: during their preparation, there is often a difficulty in synergistically optimizing high conductivity with excellent mechanical properties, environmental stability, or specific functions (such as optical transparency and biocompatibility); some key raw materials are expensive; and the precise control of microstructures (such as chain arrangement, crystallinity, and phase separation) is complex. These factors severely limit their performance improvement and industrialization process. This paper primarily focuses on reviewing the preparation methods and principles of conductive polymer films, as well as their modification and applications, and offers insights and outlooks on the future development directions of conductive polymer films. It is hoped that this paper will provide researchers with a more comprehensive understanding of this field.

2. Classification of conductive polymers and conductive principles

Conductive polymers are generally categorized into intrinsic and composite types according to their conduction mechanisms. Intrinsic conductive polymers contain inherent conjugated structures that enable electrical conductivity via the delocalization of π -electrons, without requiring doping. Nevertheless, their intrinsic conductivity is generally limited, and doping is frequently employed to improve their conductive performance [1].

On the other hand, composite conductive polymers usually consist of conductive polymers blended with other functional materials. Typical conductive fillers include metal powders, carbon black, and carbon fibers. The properties of these composites are strongly affected by the filler type, concentration, and dispersion homogeneity. Despite this, their manufacturing processes are relatively straightforward and economical [2].

Research on the relationship between molecular and supramolecular structures and the physical and physicochemical properties of heterogeneous polymer systems indicates that structural formation is among the fundamental processes governing the performance of conductive polymer composites [3]. The conductivity of conjugated polymers (CPs) stems from conjugated π bonds along the polymer backbone, which features an alternating sequence of single and double bonds. While both bond types possess localized σ bonds, the double bonds also contain a π bond situated above the σ framework. Under an applied electric field, the localized π electrons become delocalized and move along the polymer chain. This occurs through continuous overlap of the unhybridized p orbitals from adjacent carbon atoms, facilitating charge transport [4].

3. Methods for preparing conductive polymer materials

Conductive polymer materials are composed of large conjugated structures, so research on conductive polymers revolves around how to construct these conjugated structures. The preparation of conductive polymer materials can generally be divided into two methods: chemical synthesis and electrochemical synthesis [5-6]. Chemical synthesis involves using an oxidizing agent to initiate the oxidation polymerization reaction of monomers, forming polymer chains with a conjugated π -bond backbone, followed by chemical doping (oxidation-reduction or proton acid treatment) to achieve conductivity. This method is suitable for large-scale production (solution/interface polymerization), has low costs, and is easy to scale up. Electrochemical synthesis refers to the process of directly polymerizing monomers on the electrode surface through anodic oxidation in an electrochemical system, while simultaneously achieving doping (ion embedding of the electrolyte).

3.1. Chemical synthesis method

The chemical synthesis method for conductive polymer materials involves polymerizing monomers through redox reactions in solution or at interfaces to form polymer chains with conjugated structures, followed by chemical doping to achieve conductivity. As shown in Figure 1, Li et al.[7] used acid-catalyzed condensation polymerization to synthesize a novel polymer from 4-acetylpyridine, p-terphenyl, and the comonomer 2,2, 2-trifluoroacetylbenzene to synthesize a novel polymer. Under anhydrous conditions, after doping with phosphoric acid (PA), the prepared membrane exhibited a proton conductivity as high as 0.142 S cm^{-1} . A single fuel cell based on this membrane achieved a peak power density of 395 mW cm^{-2} at 180°C using unhumidified H_2 and O_2 gases. Ain et al.[8] utilized a specially designed oxygen-containing Michael addition reaction to combine vinyl TFSI anions with alcohols, preparing trifluoromethane sulfonyl imide (TFSI)-functionalized cyclic pentene (PNB) polymers, as shown in Figure 1. The results showed that PNB-TFSI derivatives exhibited excellent thermal stability and mechanical strength, with propylene glycol carbonate-plasticized PNB-TFSI derivatives achieving lithium ion conductivity exceeding 10^{-5} S/cm at 30°C .

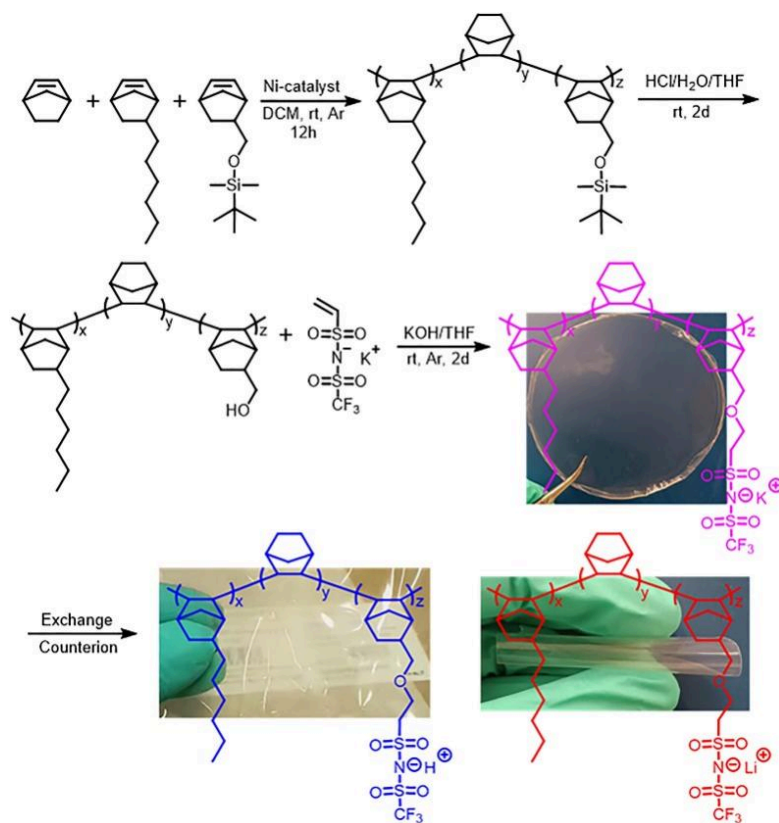


Figure 1. Preparation of polymers

3.2. Electrochemical synthesis method

The principle of electrochemical synthesis, also referred to as electro-polymerization or electro-deposition, entails the direct polymerization of monomers on an electrode surface via anodic oxidation within an electrochemical cell. This process simultaneously facilitates doping through the insertion of electrolyte ions into the polymer matrix. In comparison to conventional chemical synthesis routes, electrochemical synthesis offers distinct benefits such as highly controllable

deposition parameters, excellent reproducibility, and the ability to form uniform films in a single integrated step [9–10]. For instance, Zhou Weiqiang et al.[11] utilized a conventional three-electrode system to electrochemically polymerize 5-indoleboronic acid (InBA) within a mixed electrolyte composed of BFEE and acetonitrile (BFEE/ACN). Experimental results demonstrated that the resulting polymer film possessed a conductivity of $9 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$, along with notable redox activity and thermal stability.

Among conductive polymers, polyaniline (PANI) is regarded as one of the most promising materials for commercial applications. The electrochemical approach for synthesizing PANI presents multiple advantages: it employs commonly available laboratory equipment; the reaction occurs under mild and easily controllable conditions; there is no need for chemical oxidants, which helps maintain high product purity; and both polymerization and doping are accomplished simultaneously in one step. Nevertheless, this method is also associated with certain limitations, including relatively high operational costs due to energy consumption and electrode requirements, low production yields as the process is surface-limited, and challenges in scaling up for continuous industrial manufacturing [12]. These constraints have so far hindered its broad application beyond specialized high-value sectors.

3.3. Other preparation methods

Research on the preparation of high-performance conductive polymer films using other methods has also been abundant. To achieve both high dispersion quality and SWCNT concentration without affecting the conductivity of SWCNT films, Yuan et al. [13] developed a method for redispersing SWCNTs in an Nafion-ethanol system. Using this dispersion method, A4-sized films with a significant conductivity of 1.97 MS/m can be easily prepared. Zhang et al.[14] designed a continuous filler network in polyvinyl alcohol (PVA), using fluorinated graphene (FG) nanosheets and carboxylated carbon nanotubes (MWCNT-COOH) as fillers, and prepared a series of PVA/FG nanosheet/MWCNT-COOH (PFC) films using the solution casting method. When the contents of FG nanosheets and MWCNT-COOH were 2.82 wt.% and 0.18 wt.%, the in-plane and out-of-plane thermal conductivities of the composite films were 20.35 W/(m·K) and 0.88 W/(m·K), respectively, which are 72.7 times and 8.8 times that of PVA, and 8.7 times and 11 times that of PVA/FG films with the same FG nanoplate content. Mostafa et al.[15] used nanosecond pulsed laser liquid phase etching technology to synthesize a PVA structure embedded with nickel oxide nanoparticles (NiO NPs), and the optical and electrical properties of PVA were significantly influenced by the addition of NiO nanocomposites. Different methods have their own advantages when preparing polymer films for different applications. Selecting the appropriate preparation method under specific circumstances can achieve twice the result with half the effort. At the same time, we should continuously enhance our independent innovation capabilities and develop simpler, more environmentally friendly preparation methods.

4. Applications of conductive polymer films

4.1. Flexible electronic devices

Ultra-thin conductive polymer nanocomposite films have garnered significant research interest due to their remarkable mechanical strength, electrical conductivity, and optical clarity, positioning them as key materials for next-generation flexible electronics and sensing technologies. In one study, Gu et al.[16] fabricated nanocomposite films by exploiting electrostatic and hydrogen-bonding

interactions to co-assemble polystyrene (PS) with cellulose nanocrystals decorated with carbon nanotubes (CNC-CNT). The freestanding films produced through this process reach diameters up to 0.5 millimeters while maintaining ultrathin profiles, with thicknesses varying between 30 and 130 nanometers. Impressively, these lightweight structures demonstrate exceptional mechanical robustness, capable of supporting a mass of liquid over a thousand times greater than their own weight. This approach offers a straightforward and adaptable route for manufacturing large-area ultra-thin nanocomposites, thereby promoting the use of interfacial assembly techniques in designing tunable functional materials with tailored mechanical, electrical, and optical characteristics.

In a related advancement, as shown in Figure 2, Zhao et al.[17] developed a high-performance flexible humidity sensor by constructing a composite sensing layer of poly(diallyldimethylammonium chloride) (PDDA) and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets on a three-dimensional porous polyvinylidene fluoride (PVDF) hollow fiber membrane. The device was fabricated using a combination of pressure filtration and dip-coating deposition. The resulting PDDA/ $\text{Ti}_3\text{C}_2\text{T}_x$ /PVDF sensor exhibits outstanding sensing performance, including a wide impedance variation of three orders of magnitude across a broad relative humidity (RH) range (10%–90%), excellent linearity ($R^2 = 0.997$), minimal hysteresis ($\sim 5\%$ RH), high selectivity, and reliable operation under mechanical deformation. Moreover, the sensor demonstrates consistent long-term stability. Its high sensitivity is attributed to the synergistic contributions of each component: the $\text{Ti}_3\text{C}_2\text{T}_x$ MXene provides a large specific surface area and high electrical conductivity, the PDDA enhances humidity responsiveness, and the microporous and hollow-channel architecture of the PVDF substrate facilitates efficient vapor diffusion and absorption. This strategy presents a promising pathway for designing advanced flexible sensors, especially in wearable technology, where high sensitivity and environmental adaptability are critical.

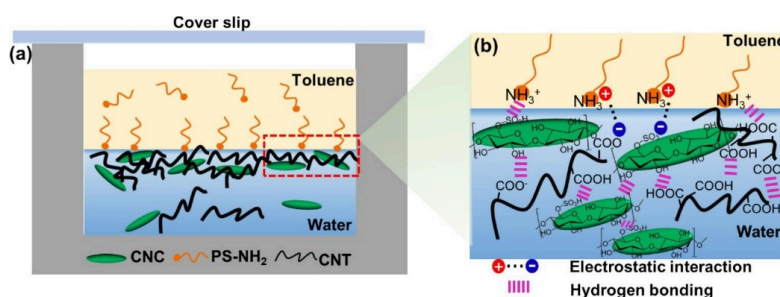


Figure 2. Preparation of nanocomposite membranes

4.2. Proton exchange membrane

Proton exchange membranes (PEMs) have attracted considerable research interest due to their designable proton transport channels, which are critical for applications in fuel cells and other electrochemical devices. Nevertheless, constructing efficient and stable proton-conducting pathways within composite membranes remains a major technical challenge. To address this, as shown in Figure 3, Li et al.[18] designed and fabricated a series of composite membranes reinforced with nanocomposites formed through electrostatic self-assembly of zirconium phosphate (ZrP) and poly(diallyldimethylammonium chloride) (PDDA)-modified sulfonated halloysite nanotubes (PSHNT). This strategy improved the dispersion of fillers and facilitated the formation of interconnected proton-conduction channels. Among the fabricated membranes, the SPI-ZrP/PSHNT-6 composite exhibited outstanding proton conductivity, reaching $288.2 \text{ mS} \cdot \text{cm}^{-1}$ at 80°C under fully

hydrated conditions. Owing to this exceptional conductivity, the membrane enabled an H₂–air fuel cell to achieve a peak power density as high as 230.2 mW·cm⁻², demonstrating significant potential for practical energy applications.

In a separate study aimed at enhancing the proton transport rate and hydrolytic stability of sulfonated polyimide (SPI)-based proton exchange membranes for fuel cells, Li Yuhuan et al.[19] adopted a gamma-ray radiation cross-linking approach. They conducted a systematic investigation by varying the irradiation time (as illustrated in Fig. 3) and evaluating its effects on membrane properties. The results indicated that the SPI membrane irradiated for 24 hours retained high proton conductivity while also exhibiting substantially improved resistance to water-oxidation, enhanced thermal stability, superior mechanical strength, reduced swelling, and increased tolerance to alcohols. These improvements are attributed to the radiation-induced cross-linking, which reinforces the polymer network and effectively suppresses membrane degradation under operational conditions. This method offers a promising pathway for developing durable and high-performance PEMs for use in advanced fuel cell systems.

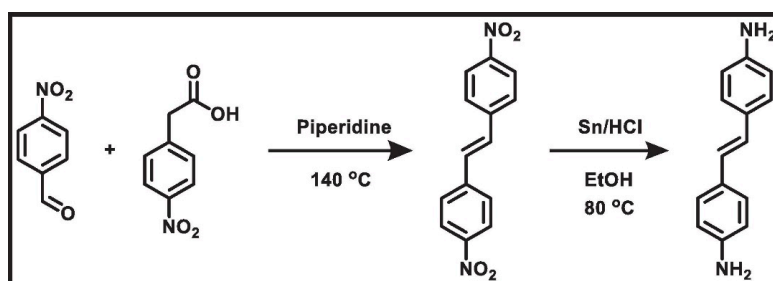


Figure 3. Polymer preparation diagram

4.3. Electromagnetic shielding composite film

With the relentless advancement of electronic information technology, the degree of integration and the operational frequency of electrical devices have seen exponential growth. While these sophisticated electronic devices have undeniably revolutionized and greatly facilitated modern life, the electromagnetic interference (EMI) and electromagnetic waves they incessantly generate have escalated into a severe form of environmental pollution, known as electromagnetic pollution. This phenomenon not only disrupts the normal function of nearby electronic equipment but also poses potential health risks to humans. Consequently, the development of high-performance electromagnetic shielding materials has become a critical research focus, with stringent requirements being placed on their effectiveness, durability, flexibility, and adaptability to next-generation applications [20].

In a significant contribution to the field in 2023, Tan Yanyan and her research team [21] pioneered a method to create a highly efficient composite film. They utilized polyvinylpyrrolidone (PVP K30) as an effective dispersant to ensure the homogeneous distribution of multi-walled carbon nanotubes (MWCNTs) within a polyvinylidene fluoride (PVDF) matrix. The fabrication process ingeniously combined solution mixing with a scraping technique applied onto a flexible PET non-woven fabric substrate. This approach resulted in the successful preparation of a composite film featuring a robust three-dimensional network structure of PVDF/MWCNTs. This unique architecture is crucial as it provides multiple pathways for the attenuation of electromagnetic waves. The composite film demonstrated a commendable maximum electromagnetic shielding effectiveness

(SE) of 20.1 dB, effectively blocking over 99% of incident radiation, thereby showcasing its potential for use in moderate shielding applications.

Building upon this foundation, a more recent breakthrough was achieved in 2024 by Jia Rufen and colleagues [22]. Their work involved the design of an advanced PTFE-based composite film with exceptional multifunctional properties. They selected polytetrafluoroethylene (PTFE) as the polymer matrix resin, renowned for its inherent chemical inertness and thermal stability. The conductive fillers incorporated were a sophisticated hybrid system consisting of multi-walled carbon nanotubes (MWCNTs), micro-sized silver flakes, and liquid metal (LM) particles that were pre-plated with a silver layer via a meticulous electrochemical process. After thorough ultrasonic dispersion to achieve a uniform mixture, the composite underwent drying and hot-pressing to form the final film. The resulting material exhibited outstanding properties, including remarkably high conductivity (with a surface resistance as low as $5.34 \Omega/\text{sq}$), excellent mechanical deformability, and an exceptionally high electromagnetic shielding effectiveness, reaching up to 60.5 dB. This SE value indicates the capability to block virtually all incident electromagnetic waves, making it suitable for even the most demanding environments. This study provides a novel and scalable methodology for the preparation of high-performance, flexible electromagnetic shielding composites, offering immense promise for future development in areas such as wearable electronics, flexible displays, and advanced aerospace communications.

5. Conclusion and outlook

Compared to traditional conductive materials, conductive polymer films, as a revolutionary material that combines conductivity and flexibility, are profoundly transforming the technological pathways and development models of human society. Their significance lies not only in the disruptive innovation they bring to traditional industries but also in providing critical support for technological breakthroughs in numerous future fields. This review aims to disseminate knowledge about conductive polymer membranes to those interested in the field, while also enabling professionals in the field to quickly grasp the general development trends of the past few years. This paper systematically reviews the research progress of conductive polymer membranes (CPMs) as a key functional material, with a focus on their classification, conductive mechanisms, preparation techniques, and cutting-edge applications. By elucidating the conductive mechanisms of intrinsic and composite conductive polymer materials, this paper lays the theoretical foundation for understanding the conductive essence of CPMs. In terms of preparation methods, it delves into the process principles, characteristics, and representative achievements of chemical synthesis and electrochemical synthesis in the synthesis of high-performance conductive polymers, while also briefly outlining the application of emerging technologies such as solution casting and laser etching composites in the preparation of multifunctional composite CPMs. In terms of applications, the paper highlights the outstanding value of CPMs in two key areas: flexible electronic devices and proton exchange membranes. In the future, with the rapid development of artificial intelligence (AI) technology, CPMs can be deeply integrated with AI. Through AI's scientific analysis and prediction, the trial-and-error phase in material R&D can be reduced, and an integrated, semi-automated mode of “R&D-synthesis-mass production” can be achieved.

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