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Graphene-reinforced Proton Exchange Membranes: A Comprehensive Review of Properties, Preparation, and Applications

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Abstract

This paper reviews the properties of graphene-reinforced proton exchange membranes (PEM), their preparation methods, and applications in fuel cells. Graphene is a crucial material for enhancing the performance of PEMs due to its excellent mechanical strength, electrical conductivity, and thermal stability. By combining graphene with conventional PEM materials such as Nafion, significant improvements have been made in proton conductivity, mechanical strength, and durability. The paper also discusses the current status, challenges, and future directions of graphene applications in PEM fuel cells (PEMFC). Although graphene composite PEMs show great potential for various applications, challenges related to large-scale production, graphene dispersion, cost control, and other issues still need to be addressed. With the advancement of technology, graphene composite PEMs are expected to play an increasingly significant role in fuel cells and other energy conversion systems.

Keywords

Graphene; Proton Exchange Membrane (PEM); Fuel Cell; Performance Enhancement; Membrane Material.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is a clean and efficient energy conversion technology widely evaluated in automobiles, portable electronic devices, and large-scale backup systems [1]. The core component of the PEMFC is the proton exchange membrane (PEM), which plays a crucial role in the energy conversion process of the cell [1,2]. The main function of the PEM is to excite protons and prevent the transfer of electrons and gases, thus directly affecting the efficiency, performance, and stability of the PEMFC [2]. However, conventional PEM materials (e.g., Nafion) still have some limitations in certain aspects, such as poor durability due to stability issues at high temperatures and high humidity conditions [3].

In recent years, with the continuous research of new materials, graphene has become an ideal choice to enhance the performance of PEM due to its excellent electrical conductivity, mechanical strength, thermal stability, and chemical stability [4]. Graphene, as a two-dimensional carbon material with very high specific properties and excellent electrical conductivity, can effectively enhance the proton conductivity, strength, and durability of PEM membranes [5]. Therefore, the graphene composite proton exchange membrane has gradually become a research hotspot in fuel cells.

Despite the great potential of graphene applications, introducing graphene into PEM still faces some challenges [4]. Firstly, graphene generally suffers from poor dispersion during the lamination process, which leads to difficulties in its uniform distribution in the film and thus affects its performance. Secondly, the production cost problem of graphene, especially in large-scale production, and how to reduce the cost while guaranteeing the quality remains an

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important issue. In addition, the compatibility problem of graphene with traditional PEM materials also limits its application in fuel cells.

Based on this, this paper will start from the perspective of graphene composite proton exchange membrane, systematically summarize the mechanism of graphene's role in the composite of proton exchange membrane, the composite technology and its impact on the membrane performance, and at the same time, discuss the current technical difficulties and the direction of the future development, to provide references and inspiration for the related research.

2. Principles of Proton Exchange Membranes

The PEMFC converts hydrogen and oxygen into electricity, heat, and water through an electrochemical reaction. The principle of operation is based on the decomposition of hydrogen into protons and electrons in the presence of a catalyst at the anode, where the protons are transferred to the cathode through a proton exchange membrane (PEM), while the electrons flow through an external circuit to generate an electric current [6]. At the cathode, oxygen combines with protons and electrons to form water. The role of the PEM is to provide a proton conduction channel while blocking the cross permeation of hydrogen and oxygen to ensure efficient operation of the cell [2].

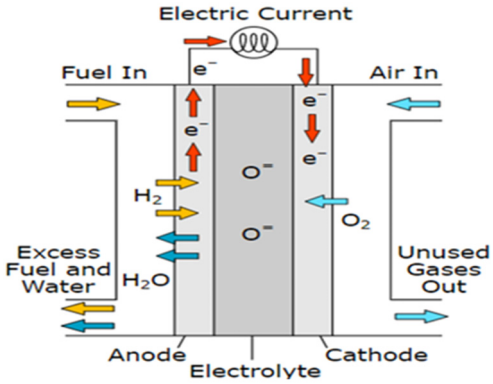

Fig 1. Schematic diagram of the working mechanism of SOFC [6]

Ideal PEMs need to be characterized by high proton conductivity, good dimensional stability, high-temperature resistance, and chemical resistance, thus ensuring the stability and high efficiency of fuel cells under various operating conditions [4]. To improve these surface properties, it is necessary to use graphene to enhance the performance of proton exchange membranes because there is a synergistic effect between the heteroatoms, and the co-doping of graphene, GO, and rGO with two or more different types of heteroatoms improves the electronic and electrochemical properties of both fuel cells and metal-air batteries [5]. In addition, Ozden et al. investigated the effect of graphene-based microporous layers on fuel cell performance, and fuel cells with graphene-based microporous layers increased the peak power density by almost 55% due to enhanced surface morphology properties by graphene deposition [7]. Therefore, it is particularly important to compound graphene with PEM to improve the overall performance.

3. Proton Exchange Membrane Preparation Methods

3.1. Preparation of Graphene

The preparation of graphene is usually carried out by both top-down and bottom-up methods [8].

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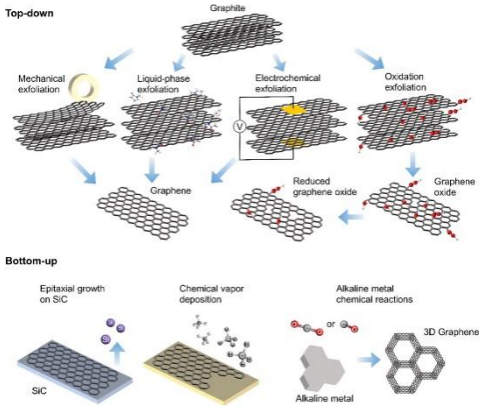

Fig 2. Graphene top-down and bottom-up preparation methods [8]

3.1.1. Top-down Preparation Methods

The top-down preparation method is a technique that starts from a larger material, such as graphite, and breaks it down into smaller graphene flakes by physical or chemical means [8]. This method is feasible because by applying an external force or chemical treatment to a material such as graphite, it is possible to exfoliate its layered structure and end up with single or fewer layers of graphene. Top-down methods are usually more scalable and suitable for large-scale production and are therefore widely used in the synthesis of graphene [8]

Mechanical or chemical exfoliation, is used to break the graphitic material into smaller layers [8]. Mechanical exfoliation methods include ultrasonic treatment, ball milling, etc., while chemical exfoliation involves the treatment of graphite by strong acids or oxidizing agents to separate the layers of graphite. Mohammedtur et al. pretreated graphite powder by using sulfuric acid (H_2SO_4), which ions effectively intercalated and facilitated the separation of graphite layers [9]. Then, the probe ultrasonic technique was employed to improve the exfoliation efficiency of graphene through a strong bubble cavitation effect, and it was more efficient than the traditional bath ultrasonic method. This method not only improves the yield and quality of graphene but also introduces functionalized groups during the exfoliation process, providing more possibilities for subsequent graphene applications.

In addition, Mei et al. employed an electrochemical exfoliation method to synthesize graphene from graphite powder [10]. They designed a graphite powder electrode with a sandwich structure and optimized the electrochemical exfoliation process by controlling the electrolyte concentration, exfoliation voltage, and the type of graphite powder (e.g., expanded graphite powder, natural flake graphite powder, and artificial graphite powder), which significantly improved the yield and quality of graphene. It was found that a high graphene yield of 42.5% with low defect density (ID/IG = 0.14-1.43) was obtained when sodium sulfate (Na2SO4) was used as the electrolyte and operated at a concentration of 0.1 M and a voltage of 10 V. The results of this study are summarized below.

3.1.2. Bottom-up Preparation Methods

The bottom-up approach starts with atoms, molecules, or small structural units and gradually builds them into larger material structures through chemical, physical, or biological methods [8]. At its core, it starts with simpler components and gradually builds complex structures through processes such as reactions or self-construction. Bottom-up synthesis methods are usually suitable for small-scale, high-precision electronic applications, such as nanotechnology, and high-performance materials for devices, and their corresponding applications are more specialized, focusing more on industries that require higher quality materials and are suitable for low-volume production.

Common bottom-up synthesis methods include chemical vapor deposition (CVD), epitaxial growth, pyrolysis laser ablation, etc [8]. The CVD method generates graphene at elevated

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temperatures from a carbon source gas (e.g., liquefaction), which allows precise control of the quality of the graphene and is particularly suited to the production of high-quality monolayer graphene. Extended growth methods generate graphene by pyrolyzing Silicon Carbide (SiC) materials and utilizing the rearrangement of atoms at high temperatures, and are suitable for applications where the number of graphene layers needs to be controlled. Pyrolysis and laser ablation techniques efficiently synthesize graphene in catalyst-free conditions through high temperatures and attenuation or laser light.

3.2. Preparation of PEM

The general process for synthesizing proton exchange membranes (PEMs) involves the selection of a suitable polymer substrate (e.g., fluorinated polymers or aromatic polymers), followed by sulfonation, which enhances the proton conductivity by introducing sulfonic acid groups into the polymer chain [11]. Commonly used sulfonation methods include sulfonation reactions using concentrated sulfuric acid or sulfonation reagents, or by nucleophilic aromatic substitution reactions (e.g., sulfonation of polyarylene ether nitrile). The sulfonated polymer is dissolved in a polar solvent to make a solution, which is prepared into a thin film by solution casting. The films usually need to be converted to the acid form by immersion in an acid solution to improve electrical conductivity. The prepared membranes are hydrated to remove residual solvents and the structural, thermal stability, and mechanical properties of the membranes are evaluated using characterization techniques such as FTIR, TGA, and DSC. Further performance tests include water adsorption, ion exchange capacity (IEC), and proton conductivity. Depending on the requirements, membrane materials can also be composited, filler-added, or cross-linked to improve their performance and stability.

3.3. Preparation of Graphene Composite PEMs

Composite methods of graphene with proton exchange membrane (PEM) include a variety of techniques, among which solution mixing, melt mixing, electrospinning, chemical vapor deposition (CVD), and layer-by-layer self-assembly (LBL) are common [12]. The solution mixing method involves dispersing graphene in a polar solvent, mixing it with a polymer substrate material (e.g. Nafion), and preparing a composite film by solution casting. This method is simple and applicable to different types of polymers and graphene. The melt blending method forms composites by mixing graphene and polymers at high temperatures and is suitable for thermoplastic polymers with good mechanical strength. The electrospinning method stretches the polymer and graphene solution into nanofibers through an electric field and is suitable for increasing the specific surface area and strength of membranes. The CVD method, on the other hand, deposits graphene onto polymer membranes through a chemical reaction, and is capable of precisely controlling the mass and number of layers of graphene, but at a higher cost. The layer-by-layer self-assembly method forms multilayer composite membranes by alternately adsorbing different materials, which can precisely adjust the thickness and functionality of the membrane. Different composite methods have their advantages and disadvantages, and the selection of suitable composite technology depends on application needs, production scale, and performance requirements.

4. Current Status of Applications

With the continuous development of technology, the practical application of PEMFC has gradually entered a more mature stage [13]. In an important study, researchers significantly improved the proton conductivity and stability of the film by compositing monolayer graphene with Nafion, a conventional PEM material [14]. Monolayers of graphene were synthesized on polycrystalline copper foils using chemical vapor deposition (CVD) and integrated with Nafion membranes by a hot pressing process. By optimizing the hot-pressing conditions (115°C, 45 s,

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200 psi), the hydrogen cross-transition of the composite membrane was reduced by about 50% from 0.33 mA/cm^2 to 0.17 mA/cm^2 compared to the pure Nafion membrane, showing better gas isolation. In addition, the proton conductivity of the composite membrane was maintained above 5 S-cm^2 in a high-humidity environment, which showed a significant improvement in conductivity compared to the conventional Nafion membrane. In another paper, it was mentioned that the incorporation of reduced graphene oxide (rGO) and few-layer graphene (FLG) in the composites significantly improved the electrical conductivity of the membranes [15]. In particular, the PTFE+FLG+CB composite membrane has an optimal electrical conductivity of 23.9 S/m and can maintain a low interfacial contact resistance (ICR) with a value of 12 mΩ-cm^2, which is in line with the requirements of PEMFC. In contrast, the conductivity of composite membranes containing more rGO is low, so the conductivity of the membranes can be significantly enhanced by optimizing the ratio and type of composite materials.

In the application of proton exchange membrane fuel cells, durability is an important factor affecting their long-term performance and commercialization. A study successfully enhanced the corrosion resistance of graphene oxide (GO) in the PEMFC operating environment by applying it to a copper-based current collector [16]. The results showed that the graphene oxide-coated current collector exhibited a significantly lower corrosion current density of about 40%, which effectively improved the lifetime of the copper current collector. In a 100-hour constant current discharge test, the hydrogen permeation rate of the ultra-thin PBI membrane containing SLG was significantly lower than that of the pure membrane, showing its significant advantage in preventing hydrogen cross-permeation [17]. In the hydroxide exposure test, the release of fluoride ions from the Nafion-TEG composite membrane was significantly lower than that of the pure Nafion membrane, indicating that the composite material is highly resistant to chemical degradation [18]. Meanwhile, the thermal stability of the composite membrane was also improved, and the degradation temperature of Nafion increased with the increase of graphene proportion.

5. Summary

This paper presents a comprehensive review of the properties of graphene-reinforced proton exchange membranes (PEMs), their preparation methods, and their applications in areas such as fuel cells. As a material with excellent electrical conductivity, mechanical strength, and thermal stability, the electrical conductivity, mechanical strength, and durability of PEMs have been significantly improved by the introduction of graphene, which further enhances the application prospects of PEMs in high-efficiency fuel cells and other energy systems.

Future research should focus on the optimization of the durability and long-term stability of graphene composite films under these conditions in high temperature and high humidity environments.

With the continuous development and breakthroughs in related technologies, graphene composite PEMs are expected to play a greater role in future energy conversion, energy storage systems, and other fields.

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