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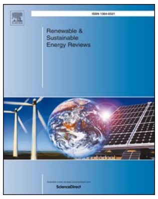

Graphene oxide: A promising membrane material for fuel cells

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ABSTRACT

Graphene has captured the attention of many researchers due to its wide potential in energy-related applications; it possess high thermal and electrical conductivity, great mechanical strength, optical transparency, inherent flexibility, huge surface area, and unique two-dimensional structure. Graphene oxide and polymer composites are commonly blended for various purposes, especially in energy devices. The fuel cell technology has discovered as one of the best alternative for future energy source; however, an extensive research is still required for the further improvement of key components such as proton exchange membranes, anode and cathode. This review has highlighted the influence of graphene in membrane modification for various fuel cells. There are many reviews on polymer exchange membranes but this is the only review that specifically deals with the graphene based membranes for fuel cells. Also, the review has covered the substantial types of fuel cells; however, focus is given to the polymer electrolyte fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). The discussion will provide a better understanding of graphene features, its compatibility with different polymers and solvents, its working principle in polymer matrices, and future prospects of graphene-based membranes in fuel cells.

1. Introduction

The global demand and consumption of energy are increasing at an alarming rate due to the rising of human population and industrial development; in the current scenario, there is an intense need to find alternative sources of renewable energy to prevent global energy exhaustion [1]. Energy storage and energy conversion systems are mostly attracted to use the renewable energy sources effectively. Currently, the development of environmentally friendly, low-cost, and high-performance energy storage and conversion systems is one of the most explored research areas around the world. In this regard, fuel cells have outstandingly been among the most promising energy storage and conversion electrochemical system. A typical fuel cell system comprises oxygen and hydrogen separated by proton exchange membrane. The proton exchange membrane must bond with water and be impermeable to gases in order to generate energy. The process is simple as chemical energy converts into electrical energy directly without any intermediate stages; hence, it is totally emission-free and an efficient way of energy generation. Therefore, fuel cell is a highly effective energy converter that produces energy without emitting harmful gases as per the safety concern of 21st century. The fuel cell technology can be employed in many applications and has the tendency to become a vital part of the future energy system. Fuel cell has drawn great attention as an upcoming alternative source of energy. The process of fuel cells involves the production of water, electricity, and heat without any toxic or pollutant byproduct [2]. Fuel cells have three major parts namely cathode, separation membrane, and anode. The two parts other than membrane are out of the scope of this review; however, it has been addressed to support the discussion wherever needed. Even though a significant progress has been made in membrane optimization over the last few years, but there is still a considerable gap and some major challenges associated with fuel cell membranes. Currently, the commercial fuel cell membrane faces some critical challenges such as high cost of production, methanol crossover, water balancing issues, safety problems (especially at high temperatures) etc. as discussed in detail in Section 2. Therefore, the optimization of fuel cell membranes requires extensive research in terms of material selection and their modifications, use of different methods and conditions and thorough structural and morphological studies of membranes.

Membrane performance is basically related to the material properties. For this reason, material technology is pivotal to develop the electrochemical energy storage and conversion systems. Carbon material, in this regard, has been determined to be excellent in these energy devices due to its stability, environmental friendliness, and abundance. In addition, it has outstanding thermal stability even across a wide range of temperatures, acidities, and media. Such properties of carbon material facilitate its application in electrochemical energy devices [3]. Previously, carbon nanotubes (CNTs) were of major concern as catalyst

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a material in fuel cells because it can improve the catalytic activities [4,5]. However, the research interest has shifted towards the most prominent 2D carbon material i.e. graphene in last few years [6–9]. Graphene has been used widely with serious attempts to rectify the recent problems in electrochemical applications. The excellent physical attributes of graphene have captured the attention of many researchers since its isolation in 2004 [10]. The implementation of graphene is regarded to be excellent in electrochemical applications, as it has large electrical conductivity, outstanding charge carrier rates, unique electron transfer, vast surface area, enhanced catalytic activity, and with much lower cost [11–15]. Therefore, graphene has found promising in several applications including fuel cells; it has enhanced the technical aspects and resolved some of the key challenges associated with the fuel cell membranes as mentioned in detail in Section 2. Currently, graphene has begun to use for its appraised outcomes to improve the current devices and become the heart of the research. Hence, graphene is viewed as the future of carbon material particularly to advance the energy-related fields. The researchers are optimistic that the remarkable features of graphene can surpass the already achieved performances, and it will be a major contributor in energy-efficient alternative in near future.

A host of other reviews have mentioned the application of graphene in sensors and supercapacitors; also, some other reviews have described the importance of graphene in fuel cells in general aspect [2,14,16–20]. Nonetheless, there is no review that specifically describes the role of graphene material in fuel cell membrane alteration; moreover, it gives an overview of compatibility of different polymers and solvents for graphene based fuel cell membranes. The review initially highlights the importance of membrane in fuel cells followed by an overview of extraordinary features of graphene and then investigate its role in fuel cell membrane modification. In this review, the polymer electrolyte membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) are of major concerns; however, a brief discussion on importance of graphene added membranes in other fuel cell will also be presented.

2. Importance of membrane in fuel cells: an overview

Since the development of fuel cell around 150 years ago by William Robert Grove in 1893, it is under microscopic research. The fuel cell came out as one of the best alternates for energy application in the late 1980s. Polymer electrolyte membrane (PEM) is the center of fuel cell, as the other components of fuel cell need to be designed according to the properties of PEM [21]. However, power density and efficiency of fuel cell also depend greatly on electrolyte conductance. The performance of Membrane Electrode Assembly (MEA) significantly affects the efficiency of PEMFC. Historically, the lifetime and efficiency of PEMFC have been determined to be dependent on proton conducting membranes (PEM) [22]. Presently, new polymeric proton conducting membranes are in focus to enhance the performance of fuel cells. However, Nafion is the center of research but scientists are still working on its modification and also on other polymers to fabricate the ideal membrane for fuel cells.

The proton conductor membrane in fuel cell must demonstrate the following properties:

1. High proton conductivity
2. Electrochemical and chemical stability
3. Hydrolytic and thermal stability
4. Excellent water uptakes
5. Good chemical properties
6. Low permeability to reactant species
7. Resistance to fuel transport
8. Good mechanical stability and strength
9. Highly durable and facilitates the quick electrode kinetics
10. Suitable with different fuels and low in cost

Additionally, the thickness and water management of a membrane have sound effect on the performance of fuel cells. Fundamentally, the membrane has two major functions in fuel cell: (1) it may work as an electrolyte between cathode and anode for ionic conduction; however, it is an electronic insulator, (2) it can act as a separator that separates the two reactant gases.

The progresses in the performance of fuel cell are thus far closely related to the progresses in membrane technology. At present, few membranes are commercially available and have found useful in fuel cell systems such as Nafion (DuPont de Nemours), Dow membranes (Dow Chemical), and perflourinated ionomer (PFI) membranes. The Nafion 117 is cheaper than Dow membranes, but Dow membrane shows remarkably better performances. However, the Dow membrane costs around 800USD and have a number of serious problems such as improper water balance and high methanol permeation. Moreover, more sets of equipment are required to address the safety problems during its preparation and use, and its limitations to temperature are the serious problems associated with the conventional membranes. The Nafion membrane degrades at high temperature, and the conductivity reduces by almost 10 times when the temperature changes from 60 °C to 80 °C. Subsequently, the corrosive gases and toxic intermediate evolutes at high temperature above 150 °C, and that raise the safety concerns. These problems in membranes can limit the recycling option of fuel cell and may lead to vehicle accidents [23]. Therefore, PFI membranes are not suitable to be commercialized in fuel cells due to their major drawbacks and high costs.

Consequently, there is a serious need to look for a cheaper polymer to obtain a good membrane for fuel cells. Currently, the properties of membrane need to be optimized in terms of proton conductivity, reduction of methanol crossover, and thermal stability. New polymeric low-cost membranes can be a solution to achieve the desired goals. Smitha et al. [23], reveals that there are 15 membranes out of 60 alternatives that can replace the conventional Nafion membranes. It is not easy to get the desired properties of membrane without its functionalization or some kind of modification. Hasani-Sadrabadi et al. [24], firstly modified the plain poly(ether ether ketone) by introducing sulfonated groups into the polymer that increases the negative functionalities, which leads to higher proton conductivity; further, they functionalized the SPEEK membrane with incorporation of modified montmorillonite (MMT) for the improved open circuit voltage (OCV) and reduced methanol uptake. The results have shown improved performances of functionalized SPEEK/MMT membrane compared to Nafion 117 and plain SPEEK membrane. Subsequently, Li et al. [25], has inserted phenylidane into polybenzimidazole (PBI) polymer matrix and achieved better proton conductivity when applied as an electrolyte membrane in high-temperature fuel cells. Similarly, Nafion has been modified in several other studies in different manner to enhance its performance. Makinouchi et al. [26], used sulfonated polyamide (SPI) to alter Nafion membrane, whereas, Hasanabadi et al. [27], prepared and applied γ-Fe_2O_3 nanoparticle to increase the performance of Nafion membrane. Additionally, palladium-silica (Pd-Si) nanofibers [28] and silica/silicotungstic acid (SiO_2/SiWA) inorganic composites [29] were incorporated into Nafion to minimize the methanol crossover problem without affecting its proton conductivity in fuel cell. Likewise, many other studies have shown the importance of membrane functionalization to improve their performance in fuel cells.

At this time, inorganic fillers are in huge demand for membrane modification for energy applications. Carbon nanotubes (CNT) has found so much effective in membrane alteration in fuel cells; however, the intention of the researchers has diverged after introduction of graphene. Graphene has contributed significantly well in optimizing the performance of fuel cells especially at cathode and in separation membranes. Recently, few studies have demonstrated the promising effect of the incorporation of graphene oxide (GO) in proton exchange membranes (PEMs). GO is basically a soft material with amphiphilic nature; it has excellent chemical and physical properties with large