Development of polybenzimidazole/graphene oxide composite membranes for high temperature PEM fuel cells

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ABSTRACT

In this study, phosphoric acid doped Polybenzimidazole/Graphene Oxide (PBI/GO) nano-composite membranes were prepared by dispersion of various amounts of GO in PBI polymer matrix followed by phosphoric acid doping for high temperature proton exchange membrane fuel cell (HT-PEMFC) application. The structure of the PBI/GO composite membranes was investigated by X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and by thermogravimetric analysis (TGA). The introduction of GO into the PBI polymer matrix helps to improve the acid doping, proton conductivity and acid leaching properties. The SEM analyses have proved the uniform and homogeneous distribution of GO in composite membranes. The composite membranes were tested in a single HT-PEMFC with a 5 cm^2 active area at 165 °C without humidification. HT- PEMFC tests show that PBI/GO composite membrane with 2 wt. % GO content performed better than bare PBI membrane at non humidified condition. At ambient pressure and 165 °C, the maximum power density of the PBI/GO-1 membrane can reach 0.38 W/cm^2, and the current density at 0.6 V is up to 0.252 A/cm^2, with H$_2$/air. The results indicate the PBI/GO composite membranes could be utilized as the proton exchange membranes for HT-PEMFC.

Introduction

Proton exchange membrane fuel cell (PEMFC) is considered as a promising clean energy conversion technology due to the high efficiency, high power density, low emissions and fast start-up [1]. Polyperfluorosulfonic acid (PFSA) membranes, such as Nafion are the most widely use polymer membranes electrolytes in PEMFC due to the high chemical stability and high proton conductivity. However, the major drawbacks of Nafion membrane for low temperature PEMFC application are low proton conductivity at temperatures above 100 °C and destruction of the polymer structure at higher temperature [2].

HT-PEMFCs are very promising alternative power generation systems because of their high carbon monoxide (CO) tolerance, low dependency on cooling systems, high amount of reusable heat energy, and high practicability in mixed

hydrogen feeding systems [3]. For HT-PEMFC water management and heat removal are not concerns. HT-PEMFC operates between 100 °C–200 °C. Therefore, water is in its gaseous phase at atmospheric pressure and can be easily removed from the system. Furthermore, the temperature gradient between the HT-PEMFC and the working environment is larger, which means that the heat removal from the system is easier and is an advantage over LT-PEMFC systems [4].

Among various types of alternative HT-PEMFC membranes developed so far, phosphoric acid doped poly (2,2-(m-phenylene)-5,5-bibenzimidazole (PBI)) was reported as a promising candidate for a low-cost and high performance membrane material for HT-PEMFC application [5]. PBI is a fully aromatic heterocyclic polymer and also has high chemical resistance and extremely high temperature. PBI membranes exhibited good proton conductivity when doped with phosphoric acid (PA), have good thermal and mechanical stability, low gas permeability, as well as requiring little to no humidification. However PBI membranes have some drawbacks, such as insufficient proton conductivity, acid leaching problem, and decreased mechanical property under HT-PEMFC operation condition, somewhat limit the performance PBI membranes for HT-PEMFC. In order to increase the proton conductivity, the PBI membrane acid doping needs to be enhanced, but this worsens the membrane mechanical properties. Significant efforts have been made to modify PBI membranes for the application at HT-PEMFC. To overcome the acid leaching problem of the PBI membrane, alternative polymeric membranes, such as nanocomposite membranes have been investigated. PBI and PBI composite membranes have been prepared containing inorganic oxides such as silica [6], clay [7], phosphotungstic acid [8] and sulfonated mesoporous organosilicate [9]. PBI nanocomposite membranes benefit from the advantages of inorganic materials such as high mechanical, thermal and chemical stability at high temperatures [10]. However, to date, PBI based composite membrane technology has not yet been put on the market, resulting from the low fuel cell performance caused by the transport limitation of the reactants due to the presence of phosphoric acid [11]. Therefore, one of the most critical challenges in developing new HT-PEMFC membrane is to enhance the fuel cell performance.

Graphene oxide (GO), which is oxidized from graphite, not only contains most good properties of graphite, but also improves some properties because of increased O and N atoms [12]. Pristine graphene, as a bulk material, has a strong tendency to agglomerate in composites because of its $\pi-\pi$ stacking between layers and incompatible surface characteristics with the polymer matrices. Therefore, the proper dispersion of graphene in a polymer matrix is still challenging [13,14]. To overcome this problem, several approaches such as surface modification *in-situ* polymerization, melt blending and solution mixing have been attempted. Among the various strategies employed, the use of graphene oxide (GO) as the precursor is the most reliable and effective approach for preparing graphene-based polymer composites [15,16]. Compared to pristine graphene, GO possesses rich oxygen-containing functional groups (such as epoxy, hydroxyl, and carbonyl groups) on the surface and edge. These functional groups allow the homogeneous dispersion of GO in an aqueous solution or water-soluble polymers and facilitate the interactions between the host polymer and GO through co-valent or non-covalent bond formation [17,18]. GO has plenty of oxygen-containing groups on the surface, these functional groups not only allow the good dispersion of GO in aqueous solution, but also facilitate the interaction between the host polymer and GO via covalent or non-covalent bonds [19]. The introduction of GO into the polymer electrolyte matrix increases proton conductivity of the polymer electrolyte and therefore it gained a lot of attention due to their excellent performance in various aspects. GO provide improving the improved the performance and thereby provide the better durability and increased lifetime of HT-PEMFC. Because of the oxygen-containing functional groups in graphene oxide (GO) nanosheets they generally have a better dispersibility in water or polar solvents than other nanoparticles. Feng et al. investigated GO sheets Nafion composite membranes for LT-PEMFC [20]. There was significant improvement as a result of Nafion membrane modification compared to the bare Nafion membrane. Zarrin and coworkers modified Nafion membrane with functionalized GO that led to the fabrication of composite F-GO/Nafion membrane shows better proton conductivity than unmodified Nafion membrane [21]. There are other studies on GO nanocomposites using different types of polymers aside from Nafion. Pandey et al. studied sulfonated polyimide (SPI) as matrix for sulfonated propyl silane graphene oxide (SPSGO). They have found that the proton conductivity of the membranes they have prepared were nearly equal to the Nafion 117 membrane. Also they have increased water retention capability of the membranes by adding SPSGO significantly, which is a key factor [22]. A review on nanocomposites with GO on different matrixes have been published recently by Chee et al. In this review, they discussed routes to produce graphene based materials, as well as methods and modifications used to get a better dispersion of graphene nanofillers within the polymer matrices [23]. In literature, there are a few studies on introduction of GO to PBI matrix. Xu et al. prepared both GO and sulfonated GO (SGO) particles and obtained enhanced performances compared to pristine PBI membrane. Xu and co-workers have increased proton conductivity of the membranes up to 0.027 S/cm and 0.052 S/cm with GO and sulfonated GO respectively. Membranes with sulfonated GO gave a maximum power density of 600 mW/cm^{-2} [24].

Since the publications in the field of PBI-based composite membranes concentrate mainly on ex-situ membrane properties, the important point of this materials' long term stability still remains open. The main goal of this work is to developed PBI/GO nanocomposite membrane and prove lifetime of the developed PBI/GO-membrane electrode assemblies (MEA) in long-term HT-PEMFC operation. We report the preparation and characterization of PBI/GO nanocomposite membranes to improve the HT-PEMFC performance. No works can be found related to the long term stability performance of PBI/GO membrane. This work contributes to the literature mainly because it elucidates the importance of development of PBI/GO membrane material. PBI/GO nanocomposite membranes were prepared by solvent casting procedure with GO nanoparticles. The membranes were characterized by using XRD, TGA, SEM analysis, and acid uptake and proton conductivity