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Polybenzimidazole-multiwall carbon nanotubes composite membranes for polymer electrolyte membrane fuel cells

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HIGHLIGHTS

- The highest proton conductivities were of 6.3×10^{-2} and 7.4×10^{-2} Scm^{-1}.
- The fuel cell performance improved for the cell using the composite membrane.
- Mechanical properties greatly improved with carbon nanotubes addition.
- Tensile strength increased by 32% and Young's Modulus by 147% in the composite.
- Thermal oxidative stability was also enhanced in the composite membrane.

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ABSTRACT

Polymer membranes are prepared as a composite of polybenzimidazole and non-functionalized multi-wall carbon nanotubes (PBI-CNT) and polybenzimidazole (PBI) only. Each is doped with H_3PO_4 (PA) and used as a proton exchange membrane (PEM) as the electrolyte in a fuel cell. The proton conductivities at 180 °C for the doped PBI membrane (PBIPA) and the doped PBI-CNT membrane (PBICNTPA) are 6.3×10^{-2} and 7.4×10^{-2} Scm^{-1} respectively. A single fuel cell having these membranes as electrolyte has a Pt catalyzed hydrogen gas fed anode and a similar oxygen cathode without humidification of feed gases; the cell with the PBICNTPA membrane has higher open circuit voltage (0.96 V) than that with a PBIPA membrane (0.8 V) at 180 °C. The mechanical stability of the membrane improves with CNTs addition. The tensile strength of the composite PBI-CNT membrane with 1 wt.% CNTs loading is 32% higher and the Young's Modulus is 147% higher than the values for a membrane of PBI alone. The improvement in conductivity and mechanical properties in the composite membrane due to the CNT addition indicates that a PBI-CNT membrane is a good alternative as a membrane electrolyte in a PEMFC.

1. Introduction

The proton exchange membranes fuel cell (PEMFC) is being commercialized and there are expectations for growth in the sustainable energy markets. The proton exchange membrane (PEM) is at the core of the most popular fuel cell, and this membrane along with the electrode catalysts determines the performance of the fuel cell's operation. The PEMFC based on Nafion family of electrolytes has been widely used for years. However, the generation of electrical power by fuel cells with Nafion membranes is strongly affected by water distribution and transport within the fuel cell, and limits the operation of the fuel cell with a Nafion membrane to lower temperatures (20–80 °C). Accordingly, there is little thermal energy for overcoming activation barriers, so effectiveness of the electrocatalyst is reduced and mass transport of reaction species is limited [1–5]. Due to these limitations, research has been focused on obtaining membranes which operate at higher temperatures. These efforts fall into the following groups: modified

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perfluorosulfonic acid (PFSA) membranes [6–12], non-fluorinated membranes or hydrocarbon membranes [13–16], acid–base complexes [17–19], and composite membranes [20–22]. Acid-doped polybenzimidazole-based membranes are one of the most promising alternatives to Nafion in PEMFCs. Acid doped PBI membranes have high ionic conductivities at high temperatures, excellent chemical and thermal stability within the fuel cell and low gas permeability [23–27]. Furthermore, the PBI polymer has been widely characterized, several synthetic routes have been explored [28,29] and it is also commercially available. However, PBI membranes still have limitations; the most remarkable are the leaching of phosphoric acid and poor membrane mechanical durability. These limitations have stimulated research on PBI composite membranes. Composites membranes show enhanced mechanical, thermal and conductive properties compared to traditional PBI-only membranes [30,31]. Carbon nanotubes (CNTs) are one of the fillers which can be used for making PBI composites membranes. CNTs have previously been used as reinforcement in different polymer membranes, mainly to improve mechanical and electrical properties. The use of CNTs as a filler in PBI composites membranes for a PEMFC is relatively new. Suryani et al. [32] prepared Nafion- and polybenzimidazole (PBI)-functionalized multiwalled carbon nanotubes (MWCNT–Nafion and MWCNT–PBI) membrane; they found that functionalized MWCNTs enhance the thermal and mechanical properties of the composite membranes. Moreover, the composites membranes had better proton conductivities and performance, under anhydrous conditions than the PBI membranes. Kannan et al. [33] blend phosphonated MWNTs (P-MWNTs) with PBI to develop composites membranes. The composite membranes had enhanced proton conductivity, stability and overall performance compared with PBI membranes. The addition of sulfonic groups to the carbon nanotubes contributed to an increase in the proton conductivity and a reduction of H_3PO_4 leaching. Wu et al. [34], prepared PBI-CNT nanocomposite membranes for alkaline direct methanol fuel cell (ADMFC) application. They added <1 wt.% of functionalized multiwall carbon nanotubes to the PBI, which promoted ionic conductivity of electrolytes and improved the fuel cell performance. Recently, Hasani-Sadrabadi et al. [35] developed Nafion-CNTs-PBI composites membranes doped with a superconductor: phosphotungstic acid (PWA). The hybrid membranes showed high proton conductivity at both low humidity and elevated temperatures. In the same way, they generated higher power density at low humidity compared with Nafion membranes. To avoid carbon nanotubes agglomeration, CNTs are usually functionalized. This process leads a better compatibility between the polymer matrix and the CNTs; however functionalization modifies the structure of CNTs for breaking of some C=C bonds, increasing the defects, which can decrease their mechanical and electrical properties [36–38]. In this study, multi-walled CNTs were incorporated into a PBI matrix, CNTs were not functionalized. PBI and PBI-CNT membranes were prepared and their chemical, thermal, mechanical, and electrochemical properties were evaluated.

2. Experimental

2.1. Materials

The polymer used in this study was a low molecular weight PBI (8000–10,000 g mol^{-1}) from PBI Performance Products (US), in the form of PBI matrix resin solution (PBI dissolved in DMAc at a 12% w/w concentration). The multi wall carbon nanotubes (MWNTs) with 20 nm inner diameter and 140 nm outside diameter, approximately 8 micron length, purity of >90 wt.% MWNT, with less than 0.1 wt.% metal (Fe) content, were received from Materials and Electrochemical Research Corporation (MER Corp from Tucson, Arizona, US). N–N Dimethylacetamide 99 wt.% from Aldrich was used and electrodes from E-TEK Inc., Somerset, NJ with 30% Platinum 0.25 mg cm^{-2}.

2.2. Membranes preparation

2.2.1. PBI membranes

PBI membranes were produced by spin coating; the PBI solution was spin-coated over a boro-aluminosilicate glass wafer (rate = 1000 rpm, t = 20 and 40 s), the thickness of each membrane was uniform, but from membrane to membrane, the thickness could be as low as 50 micron to as high as 180 micron. This mainly affects membrane performance result given. The results presented are for the 110 μm thick membranes.

Membranes were washed in deionized water for 2 days; subsequently they were immersed in concentrated H_3PO_4 85 wt.% (14.7 M) overnight at room temperature (22 °C). The acid doping level of the membranes was measured by drying the doped membranes at 100 °C to eliminate the effect of water uptake. The acid-doping level stated as moles of phosphoric acid per mole of PBI repeat unit was calculated using the equation:

$$Acid\ doping\ level = \frac{(W_2 - W_1)\left(M_{wPBI}\right)}{(W_1)\left(M_w H_3PO_4\right)} \tag{1}$$

Where W_2 is the weight of the doped dried membrane, W_1 is the weight of the non-doped dried membrane, M_{wPBI} is the molecular weight of PBI repeat unit, and $M_w H_3PO_4$ is the molecular weight of phosphoric acid (PA). According to this, PBI phosphoric acid doped membranes have a doping level of 5.6 mol PA/PBI.

2.2.2. PBI-CNT membranes

PBI in DMAc solution was heated at 150 °C, 1 wt.% of MWCNTs were added in the hot solution, while the mixture was kept stirring by a Teflon encapsulated magnetic stir bar at 400 rpm for 15 min. The viscous solution was poured onto a circular boro-aluminosilicate glass disk wafer on the vacuum chuck of a Headway spin coating device spinning at 1000 rpm, for a time of 20–40 s. The coated wafer was heated in a furnace at 150 °C to evaporate traces of DMAc. The film was lifted off from the wafer and gave a film with CNTs well dispersed and with uniform thickness. This composite membrane was washed in water and then doped with phosphoric acid in the same way as PBI only membrane. Since the percentage of CNTs in the membranes was only 1 wt.%, the acid doping level for composites membranes was estimated also using equation (1); PBICNTPA membranes have a doping level of 8 mol PA/PBI.

2.3. Characterization

PBI, non-functionalized CNTs, and PBI-CNT membranes were characterized by scanning electron microscopy (SEM) in a PHILIPS XL30 ESEM microscope. A cross section of PBI film was observed using an accelerating voltage of 7 kV. MWCNT were deposited in a silicon wafer, they were analyzed using an accelerating voltage of 5 kV. A piece of PBI-CNT membrane was immersed in liquid nitrogen during some minutes and after that, the sample was percolated as a cross section, a thin film of platinum was deposited using a Hummer 6 Sputtering Device. The sample was observed in a Hitachi S-4800 Type II Ultra-High Resolution Field Emission Scanning Electron Microscope with a Thermo NORAN System 6 X-Ray Microanalysis integrated at accelerating voltage of 15 kV. PBI, non-functionalized CNTs, PBI-CNT and PBI-CNT-PA (phosphoric acid doped) membranes were characterized by Fourier transform