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Fabrication of low-methanol-permeability sulfonated poly(phenylene oxide) membranes with hollow glass microspheres for direct methanol fuel cells

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HIGHLIGHTS

- Sulfonated poly(phenylene oxide) is used as matrix of proton exchange membrane.
- SPPO is introduced onto the surface of hollow glass microsphere via intermolecular interaction.
- Introduced SPPO onto the surface of HGM increase dispersion of HGM in the SPPO matrix.
- HGM is used as filler to reduce the methanol permeability.
- Reduced methanol permeability leads to improved selectivity of SPPO membrane.

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ABSTRACT

Organic/inorganic composite membranes, based on sulfonated poly(phenylene oxide) (SPPO) and hollow glass microspheres (HGMs), with various compositions are prepared for use as proton exchange membranes in direct methanol fuel cells (DMFCs). Reaction time between chlorosulfonic acid solution and PPO is controlled to improve proton conductivity of the SPPO membrane. As a result, SPPO at 38.2% sulfonation is selected as the optimum degree of sulfonation. Afterwards, SPPO is successfully introduced onto the surfaces of HGMs to increase their dispersion in the SPPO matrix. The ion exchange capacities (IEC) and proton conductivities of the membranes decrease with increasing amounts of the SPPO-HGMs, because of the decrease of ionic sites with increasing HGM content. The SPPO-HGM composite membranes exhibit proton conductivities ranging from 0.0350 to 0.0212 S cm^{-1} and low methanol permeability ranging from 1.02×10^{-6} to 3.41×10^{-7} cm^2 s^{-1} at 20 °C. Furthermore, the SPPO-HGM 9 wt%/SPPO membrane presents a maximum power density of 81.5 mW cm^{-2} and open circuit voltage of 0.70 V.

1. Introduction

Direct methanol fuel cells (DMFCs) have attracted considerable interest as power sources for portable and transport applications because of their stable operation, high efficiency, high power density, and low emissions [1–4]. In DMFCs, polymer electrolyte membranes (PEMs) are important components because they mediate the transfer of protons from the anode to the cathode while acting as a barrier to the permeability phenomenon of methanol. To achieve high fuel cell application efficiencies, PEMs must possess the following properties: negligible electronic conductivity, chemical and electrochemical stability under operating conditions, and adequate mechanical strength and stability [5]. Moreover, the proton conductivity and the methanol permeability are fundamental PEM properties and these are usually the first characteristics considered when evaluating membranes for potential fuel cell use. Therefore, recent studies have focused on developing PEMs with high selectivity.

There are two major methods to improve proton conductivity. The first is the sulfonation of the matrix. Sulfonation functionalizes the membranes with $-SO_3H$, allowing protonate water molecules and thereby improving proton conductivity [6]. T. Xu et al. reported sulfonated Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) membrane with improved proton conductivity (0.012 S cm^{-1}) at different sulfonation degrees [7], G. Zhang et al. synthesized sulfonated PEEKK with much higher proton conductivity

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(0.098 S cm^{-1}) than Nafion [8]. In addition, the proton conductivity of the membranes increases with the addition of inorganic fillers. Addition of conductive inorganic fillers improves not only proton conductivity but also mechanical and thermal stability. Therefore, the introduction of a filler is often used to improve DMFC efficiencies. S. Yun et al. employed sulfonated MWNT particles in a sulfonated PVA matrix which resulted in excellent proton conductivity ranging from 0.032 to 0.075 S cm^{-1} [9]. In another study, S.H. Yun et al. reported that nanofiber porous substrate/sulfonated PPO membrane showed improved proton conductivity from 0.03 to 0.08 S cm^{-1} [10].

Moreover, PEMs must exhibit low methanol permeability because penetrated methanol causes poisoning of the catalyst and reduction of the electrical performance and fuel efficiency. Therefore, in order to decrease the methanol permeability of PEMs, fillers are introduced to elongate the methanol permeability. Polymer membranes containing micrometer to nanometer size fillers have been used for the DMFC. A variety of fillers, including silica, zirconium phosphate, silane-based fillers, titanium oxide, graphene oxide, laponite, montmorillonite, zeolites, and palladium have been incorporated in a number of different polymer membranes. M.M. Hasani-Sadrabadi et al. introduced modified montmorillonite (MMT) in a sulfonated PPO matrix which resulted in lower methanol permeability (4.5×10^{-8} cm^2 s^{-1}) [11].

Generally, hollow glass microspheres (HGMs) have been used in the fabrication of polymer composite materials to decrease permeation. HGMs consist of a stiff glass shell containing an inert gas. This configuration gives them unique properties such as low thermal conductivities, low weight, and low dielectric constants. HGMs can be used to both significantly modify the properties and improve the technological conditions of polymer processing. H. Im et al. reported the improved swelling ratio of TPU/TPU-g-HGM composite for underwater applications [12]. H.S. Kim et al. synthesized HGM/epoxy resin composite to improve fracture toughness, flexural properties and impact force [13]. However, HGMs have not been studied as fillers for PEMs to decrease the methanol permeability.

In this study, composite membranes were prepared using sulfonated PPO as a matrix and HGM as filler. In the first stage, the degree of sulfonation of the PPO was increased to improve the proton conductivity. At 38.2% sulfonation, proton conductivity of sulfonated PPO is higher than that of Nafion 117. In the second stage, the HGMs were synthesized with SPPO to improve their dispersion within the SPPO matrix. There is an important consideration of affinity between SPPO and HGMs. Excellent interfacial adhesion between the SPPO and the HGMs and a high level of dispersion of the HGMs within the SPPO matrix are required to produce HGM/SPPO composites that have the desired mechanical and barrier properties. Finally, synthesized SPPO-HGM was introduced into the SPPO matrix with various weight percents. Introduction of the SPPO-HGMs into the SPPO matrix is expected to decrease methanol permeability and increase the selectivity of membrane.

2. Experimental methods

2.1. Materials

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with a molecular weight (MW) of 55,000 was obtained from Sigma–Aldrich Corp (Seoul, Korea). Hollow Glass Microspheres (HGMs, particle size = 10–25 μm) were obtained from 3 M Corp (Seoul, Korea). Chlorosulfonic Acid ($ClSO_3H$), chloroform ($CHCl_3$), sodium hydroxide (NaOH), phenolphthalein (pH indicator), and sodium chloride (NaCl) were purchased from Sigma Chemicals. Dimethyl acetamide (DMAc), methanol (CH_3OH), and deionized water (DI water) were purchased from Samchun Chemicals (Seoul, Korea). The Nafion 117 membranes were purchased from E.I. Dupont de Nemours & Co. Prior to testing, Nafion 117 membranes were pretreated in dilute solution of boiling H_2O_2, H_2SO_4 and deionized water, sequentially for 1 h each. The catalysts, Pt black for the cathode and Pt–Ru black for the anode, were purchased from Johnson–Matthey.

2.2. Synthesis of sulfonated poly phenylene oxide (SPPO)

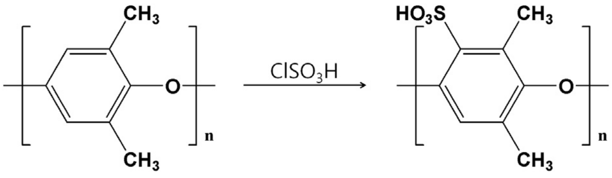
The fabrication procedure for the SPPO is shown in Scheme 1. The sulfonation of the PPOs was carried out in a chloroform solvent using chlorosulfonic acid as the sulfonating agent. Prior to the sulfonation step, the quantity of sulfonable material (ethanol and water) in chloroform (used as a solvent for PPO) was determined and neutralized with chlorosulfonic acid. PPO, 10 g, was added to 100 mL of neutralized chloroform in a three-neck reaction flask, and dissolved by stirring for about 30 min at room temperature. A 5% (v/v) solution of chlorosulfonic acid in 100 mL of chloroform was transferred into a dropper, and gradually added to the PPO solution. The mixture was vigorously stirred at room temperature for different durations to obtain different degrees of sulfonation [14]. The precipitated polymer SPPO was washed with distilled water repeatedly until the pH became neutral, and dried in air for 24 h at ambient temperature, followed by vacuum drying for about 48 h. The products were denoted as SPPO-0.5, SPPO-6, SPPO-12 and SPPO-24 for sulfonation times of 0.5, 6, 12 and 24 h, respectively.

2.3. Synthesis of functionalized HGM (SPPO-HGM)

The fabrication procedure for the SPPO-HGMs is shown in Scheme 2. All reactions were carried out under an inert nitrogen atmosphere. HGM, 10 g, was added to a NaOH (0.5 mol/L) aqueous solution (200 mL). The mixture was stirred for 2 h at 90 °C to create hydroxyl groups on the surface of the HGMs. The resulting solution was filtered through a 450 nm nylon membrane, and washed several times with water. Finally, the filtered powder was dried in a vacuum oven at 30 °C for 1 day [12]. Scheme 2 also shows the intermolecular bonds between the –OH group on an HGM and the –OH and $-SO_3H$ groups on the SPPO. Sulfonated PPO (10 g) was dissolved in 200 mL of dimethyl acetamide (DMAc) under mechanical stirring. HGM-OH was then added, at 140 °C, to the reaction mixture, which contained H_2SO_4 as a catalyst. The mixture was refluxed for 12 h, and then filtered through a 450 nm nylon membrane and washed several times with water. Finally, the product (SPPO-HGM) was dried at room temperature for 24 h.

2.4. Preparation of SPPO membranes and HGM treatment

The SPPO membrane was prepared using the solution casting method. The SPPO was dissolved in tetrahydrofuran (THF) to form a 10 wt% casting solution. The dissolved SPPO was stirred for 12 h to obtain a homogeneous solution. Then, HGMs and SPPO-HGMs were dispersed in a manufactured solution, and weight ratios of the blends were varied from 0% to 15%, respectively. The resulting



Scheme 1. Preparation of sulfonated PPO (SPPO).