

Low methanol permeable crosslinked sulfonated poly(phenylene oxide) membranes with hollow glass microspheres for direct methanol fuel cells



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ABSTRACT

Organic/inorganic composite membranes based on sulfonated poly(phenylene oxide) (SPPO) and hollow glass microspheres (HGMs) were prepared for use as proton exchange membranes in direct methanol fuel cells (DMFCs). First, SPPO was successfully introduced onto the surfaces of the HGMs (SPPO-HGMs) to increase dispersion of SPPO-HGMs in the SPPO matrix. The SPPO composite membranes were fabricated with varying amounts of SPPO-HGMs. Then the composite SPPO membranes were crosslinked to decrease the methanol permeability and increase the mechanical properties, and the crosslinking time was controlled to determine the optimal crosslinking time. As a result, a 12 h crosslinking time at 80 °C was selected as the optimum. The SPPO-HGM composite membranes exhibited proton conductivities ranging from 0.0294 to 0.0201 S cm⁻¹ and methanol permeability ranging from 5.20 × 10⁻⁷ to 1.99 × 10⁻⁷ cm² s⁻¹ at 20 °C.

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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) use a proton-conducting polymer membrane as an electrolyte, and they have attracted considerable interest as a reliable power source because of their ability to attain high power densities with high energy efficiency [1]. Among PEMFCs, direct methanol fuel cells (DMFCs) are attractive as promising power sources for portable electronics and electric vehicles applications owing to their advantageous properties such as high energy efficiency, high power density, low emission, and low operating temperature [2–4]. The proton exchange membrane (PEM) is one of the most important components for DMFCs because it serves as barrier for fuels and electrolytes for transporting protons from anode to cathode. For these reasons, PEMs require high proton conductivity, low fuel permeability, and thermal stability, as well as inexpensive operating cost [5]. Currently, DuPont's Nafion[®] is the most common polymer electrolyte membranes used in DMFC systems.

Up to now, Nafion[®] has been the reference membrane for DMFCs because of its good chemical resistance and mechanical

stability, as well as its high proton conductivity [6]. However, there are some specific limitations for Nafion[®], including high methanol permeability, high cost, and loss of desirable properties at high temperature [7]. Therefore, many kinds of sulfonated aromatic polymers have been studied as alternatives to Nafion[®]. Heo et al. synthesized composite sulfonated poly(ether imide) PEI/sulfonated multiwalled carbon nanotube (MWNT) membranes with much lower methanol permeability (1.17 × 10⁻⁸ cm² s⁻¹ at 5 wt% of sulfonated MWNT content) than Nafion[®] [8]. In another study, Yun et al. reported that nanofiber porous substrate/sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) membranes showed improved proton conductivity from 0.03 to 0.08 S cm⁻¹ [9]. These recent studies have focused on developing PEMs with low methanol permeability and high proton conductivity.

Generally, sulfonation has been considered one of the most attractive methods for obtaining high proton conductivity. Sulfonation functionalizes the membranes with –SO₃H, allowing proton hopping and thereby improving proton conductivity [10]. Xu et al. reported the fabrication of SPPO membranes with improved proton conductivity (0.012 S cm⁻¹) at different sulfonation degrees [11]. Zhang et al. synthesized sulfonated poly(ether ether ketone) (PEEK) with a much higher proton conductivity (0.098 S cm⁻¹) than Nafion[®] [12]. However, such high sulfonation polymers have notable weak points, such as high methanol permeability and high

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water uptake. The greater the number of $-\text{SO}_3\text{H}$ groups introduced into a polymer matrix, the greater the amount of water absorbed in the polymers, thus decreasing the dimensional stability due to the hydrophilicity of the acid groups. This phenomenon may lead to a loss in mechanical properties of the polymers, reducing their usefulness in a variety of applications [13].

Crosslinking could be a simple and powerful method to enhance such indispensable properties. Generally, a crosslinking reaction between polymer chains is considered to be an efficient means of limiting methanol permeability and enhancing the mechanical stability of the membranes. A crosslinked polymer matrix forms a network in which the macromolecular chains of the polyelectrolyte are immobilized and compacted. Many studies have been done on the use of the crosslinking method for PEMs to reduce methanol permeability. Wu et al. synthesized crosslinked sulfonated PPO membranes with low methanol permeability ($6.4 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) and good mechanical properties (tensile strength of 52.8 MPa) [14]. Wang et al. reported the fabrication of composite poly(butoxymethylenenorbornene-co-norbornenemethanol) (PNB/NOH) membranes with methanol permeabilities ranging from 4.2×10^{-7} to $2.5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, which is lower than that of Nafion[®] 115 [15]. With the crosslinking method, the introduction of a filler is a widely used method of decreasing the methanol permeability. Yun et al. reported the fabrication of a sulfonated polyethersulfone (PES) membrane with low methanol permeability ($9.1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$) by introducing sulfonated MWNTs as the filler [16]. Chhabra et al. synthesized sulfonated poly(ether ether ketone) (SPEEK) membranes containing trisilanol phenyl polyhedral oligomeric silsesquioxane (POSS) with a lower methanol permeability than that of an SPEEK/Nafion[®] membrane [17].

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 conductivity, low weight, and low dielectric constant. HGMs can be used to both significantly modify the properties and improve the technological conditions of polymer processing. Kim et al. synthesized an HGM/epoxy resin composite to improve fracture toughness, flexural properties, and impact force [18]. Im et al. reported the improved swelling ratio of a thermoplastic polyurethane (TPU)/TPU-g-HGM composite for underwater applications [19]. However, HGMs have not been studied as fillers for PEMs for the purpose of decreasing the methanol permeability.

In this study, composite membranes were prepared using sulfonated PPO (SPPO) as a matrix and HGMs as a filler. Further, synthesized membranes were crosslinked to decrease the methanol permeability. The properties of the membrane can be effectively controlled by controlling the extent of crosslinking of the polymers. First, the selectivity parameters of the crosslinked SPPO membrane were calculated for different reaction times in order to identify the optimum crosslinking time. Second, 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. Third, the synthesized SPPO-HGM was introduced into the SPPO matrix with various weight percents. Introduction of SPPO-HGM into the SPPO matrix is expected to decrease the methanol permeability and increase the selectivity of the membrane. Finally, the composite membranes were crosslinked using the optimized crosslinking time. The crosslinking process was expected to not only improve the mechanical properties but also reduce the methanol permeability of the membranes.

2. Experimental methods

2.1. Materials

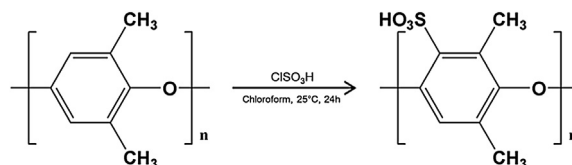
Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) with a weight-average molecular weight (M_w) of 55,000 was obtained from Sigma-Aldrich Corp (Seoul, Korea). Hollow glass microspheres (HGMs, particle size = 10–25 μm) were obtained from 3M Corp. (Seoul, Korea). Chlorosulfonic acid (ClSO_3H), sodium hydroxide (NaOH), chloroform (CHCl_3), phenolphthalein (pH indicator), and sodium chloride (NaCl) were purchased from Sigma Chemicals (Seoul, Korea). Dimethylacetamide (DMAc), methanol (CH_3OH), and deionized water (DI water) were purchased from Samchun Chemicals (Seoul, Korea).

2.2. Synthesis of sulfonated poly(phenylene oxide)

The fabrication procedure for the sulfonated PPO (SPPO) is shown in Scheme 1. The sulfonation of the PPO was carried out in a chloroform solvent system 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 removed by neutralization with additional chlorosulfonic acid. 10 g of PPO was added to 100 mL of neutralized chloroform in a three-neck reaction flask, and the mixture was stirred for approximately 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 over time lengths of 1 h–24 h to obtain a high degree of sulfonation [20]. 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 approximately 48 h.

2.3. Synthesis of functionalized HGMs (SPPO-HGM)

The fabrication procedure for SPPO-HGM is shown in Scheme 2. All reactions were carried out under an inert nitrogen atmosphere. 10 g of HGMs 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 [19]. Scheme 2 also shows the intermolecular bonds between the $-\text{OH}$ groups on an HGM and the $-\text{OH}$ and $-\text{SO}_3\text{H}$ groups on the SPPO. SPPO (10 g) was dissolved in 200 mL of DMAc under mechanical stirring. HGM-OH (10 g) 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.



Scheme 1. Preparation of sulfonated PPO (SPPO).

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