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Sulfonated mesoporous benzene-silica-embedded sulfonated poly(ether ether ketone) membranes for enhanced proton conduction and anti-dehydration

Junghwa Park, Dukjoon Kim*

School of Chemical Engineering, Sungkyunkwan University, Suwon, Kyunggi 440-746, Republic of Korea

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ABSTRACT

In polymer electrolyte fuel cell operation, a decrease in the proton conductivity of the membrane at reduced humidity is a main cause for poor cell performance at high temperature. To alleviate the dehydration of the membrane at high temperature, sulfonated mesoporous benzene-silica (sMBS) particles are embedded in sulfonated poly(ether ether ketone) (sPEEK) membranes. As the sMBS itself is highly sulfonated on both organic and inorganic moieties, the proton conductivity of composite membranes is much higher than that of the pristine sPEEK membrane, and it reaches that of Nafion 117 at a high relative humidity (RH) of 90%. The dehydration rate of the membrane is reduced significantly by the capillary condensation effect of sMBS particles with the nanometer-scale 2-D hexagonal cylindrical pores, and the proton conductivity of the composite membranes, $0.234 \times 10^{-1} \text{ S cm}^{-1}$, is much higher than that of pristine sPEEK membrane, $0.59 \times 10^{-3} \text{ S cm}^{-1}$, at a relatively low humidity of 40% RH. This maintenance of high conductivity at low humidity is attributed to the high water-holding capacity of the sMBS proton conductors. The sMBS-embedded sPEEK composite membranes show a much lower methanol permeability of $2 - 5 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ compared to that of Nafion 117, which is $1.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at room temperature.

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1. Introduction

Polymer electrolyte fuel cells (PEFC) have potential applications in diverse areas, including automobiles, spacecraft, mobile phones, and power plants. Proton exchange membrane, one of the core components of membrane electrode assemblies (MEA), plays an important role in the cell performance. It is well-known that commercial polymer membranes, which are typically Nafion series membranes from Du Pont, show good properties with regard to proton conductivity

and chemical and mechanical stability, and thus, their application fields are being expanded. Nafion series membranes, however, have also been reported to have some drawbacks associated with high fuel crossover, low conductivity at reduced humidity, and high cost [1–3]. In order to replace Nafion, researchers have studied a number of polymers, including poly (arylene ether ketone), polyimide, poly (vinyl alcohol), and poly (arylene ether sulfone) [4–17]. Poly(ether ether ketone) (PEEK) was one of the membranes potentially considered because of its cheap price, easy sulfonation process, and excellent chemical and mechanical resistance [18].

* Corresponding author. Tel.: +82 31 290 7250.

E-mail address: djkim@skku.edu (D. Kim).

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The weaknesses in fuel crossover and cost were possibly lessened by replacement with such hydrocarbon based polymer membranes, but low proton conductive property at high temperature was still a big hurdle to overcome regardless of the types of membranes as the dehydration of the membrane in association with water evaporation is irresistible at high temperatures.

Since periodic mesoporous organosilicas (PMOs) were discovered by Inagaki et al., they have been considered as remarkable porous materials with high surface area and pore volume, narrow pore size distribution, and adjustable mesopore sizes [19]. Recently, organo-bridged organoalkoxysilanes have frequently been used as precursors to synthesize PMOs [16,19–21]. By introducing such organo-bridged groups, PMOs possibly form organic–inorganic hybrid structures, where the organic moieties help to enhance the bulk properties. The well-defined and well-oriented mesopores in PMOs are expected to have advantages in the controllable transportation of small molecules and ions. Thus, we tried to sulfonate organic benzenes in PMOs to enhance the proton conductivity, and applied them to the preparation of fuel cell membrane [20]. This organo-sulfonated PMO had an advantage over non-sulfonated PMOs in the feasible diffusion and transportation of protons. Although the PMO/sPEEK composite membranes prepared exhibited low methanol permeability and an anti-dehydration effect under reduced humidity, the proton conductivity was not high enough for acceptable cell performance, especially at low RH. This low proton conductivity is thought to have been caused by the relatively low degree of sulfonation of PMOs compared with that of polymer electrolyte.

In this study, more highly sulfonated mesoporous benzene-silica was synthesized by sulfonating not only organic (benzene), but inorganic (silica) moieties in PMOs. This dual sulfonation may give rise to enhanced water imbibing and proton conductivity. The sPEEK-based composite membranes were prepared by embedding 2-D hexagonal mesoporous benzene-silica (MBS). Mesoporous structure in this MBS was expected to retain water at reduced humidity (high temperature) due to the capillary force. A variety of bulk and transport properties of the composite membrane prepared were investigated, including the water uptake, methanol permeability, ion conductivity, thermal stability, and mechanical stability, for comparison with Nafion membrane.

2. Experimental

2.1. Materials

Vitrex 450PF poly(ether ether ketone) (PEEK) with a molecular weight of $100,000 \text{ g mol}^{-1}$ was purchased from the ICI Company (Rotherham, UK). Methylsulfonic acid (MSA) (Acros Organics, Geel, Belgium) and PEEK were used to prepare sulfonated PEEK. Cetyltrimethylammonium chloride solution (CTAC) (25 wt%, Aldrich, St. Louis, Missouri, USA), 1,4-bis(triethoxysilyl)benzene (BTEB) (Aldrich, St. Louis, Missouri, USA), (3-mercaptopropyl)trimethoxysilane (MPTMS) (95 wt%, Aldrich, St. Louis, Missouri, USA), and sodium hydroxide (99 wt%, Duksan Reagents & Chemicals, Ansan, Korea) were used for the synthesis of mesoporous benzene-silicas.

Hydrogen peroxide (30 wt%, Duksan Reagents & Chemicals, Ansan, Korea) and sulfuric acid (Duksan Reagents & Chemicals, Ansan, Korea) were used as sulfonating agents. N,N-dimethyl acetamide (DMAC) (Fluka Chemie AG, Seelze, Germany) and hydrochloric acid (37 wt%, Aldrich St. Louis, Missouri, USA) were employed to prepare membranes.

2.2. Preparation of sulfonated mesoporous benzene-silica (sMBS)

Mesoporous benzene-silica (MBS) powder was synthesized using CTAC solution (25 wt%) as a template via the method reported by Inagaki et al. [21]. Typically, 7.63 g of CTAC was dissolved in a mixture containing 56.75 g of DI water and 0.66 g of sodium hydroxide at room temperature. After stirring for 2 h, 1.00 g BTEB and 0.73 g MPTMS were added. The mixture was stirred for another 12 h, followed by aging for 24 h at 90°C in an oil bath. A mixture containing 200 mL of ethanol and 3.00 g of HCl was employed to remove the surfactant and CTAC template at 65°C under stirring for 6 h. The next step was to extract the solids using a suction flask, and to wash them with DI water and acetone several times. The final product was dried at 120°C for 24 h.

For the sulfonation of mercaptopropyl group, 1 g of the prepared MBS was placed in 10 g of hydrogen peroxide (30 wt %) and kept under stirring for 12 h at room temperature. After stirring, a suction flask was used to filter the mixture, followed by washing with DI water and acetone several times. For the sulfonation of the benzene ring, 1 g of the partially sulfonated MBS was placed in 250 mL of sulfuric acid fuming SO_3 reagent. After stirring for 12 h at 105°C , the product was filtered and washed repeatedly with DI water and acetone. The final solid, sulfonated mesoporous benzene-silica (sMBS), was dried at 120°C for 24 h under vacuum.

2.3. Preparation of composite membrane

The commercial PEEK powder was sulfonated as reported elsewhere [15]. Typically, 10 g of PEEK powder was dissolved in 50 mL of MSA under stirring. After the powder was completely dissolved, the solution was mixed with 400 mL of sulfuric acid (98%). The mixture was kept in a three-neck flask with nitrogen flow at room temperature for 80 h. Then, the solution was dropped into DI water slowly, and then the precipitates were separated with a suction flask. The sulfonated PEEK (sPEEK) produced was washed with DI water several times and dried at 100°C for 24 h.

The composite membranes were prepared by a casting method. Typically, 0.3 g of sPEEK powder was dissolved in 9.7 g of DMAC with stirring at room temperature for 2 h. Then, sMBS powder was added to the polymer solution at different weight ratios of 0.05, 0.1, 0.15, and 0.2 relative to the sPEEK material. After stirring for 2 h at room temperature, each mixture was sonicated for 30 min and then cast onto glass dishes, followed by drying at 100°C for 12 h. Another 2 h of drying was employed at 120°C under vacuum to obtain the final composite membranes. The membranes prepared were immersed 100 mL DI water containing 0.1 g hydrochloric acid (HCl, 37 wt%) for 24 h for post-treatment before use.

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