



Silica-embedded hydrogel nanofiller for enhancing low humidity proton conduction of a hydrocarbon-based polymer electrolyte membrane



Keun-Hwan Oh^a, Insung Bae^a, Hongkyung Lee^b, Hyuk Kim^a, Hee-Tak Kim^{b,*}

^a Future Technology Center Corporate R & D, LG Chem Ltd., 188, Munji-ro, Yuseong-gu, Daejeon 305-380, Republic of Korea

^b Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291, Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea

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ABSTRACT

Poor proton conduction at low relative humidity (RH) remains a challenge for adopting hydrocarbon (HC) membranes for polymer electrolyte membrane fuel cells (PEMFCs). Here, we report a silica-embedded hydrogel (HG-silica) nanofiller as a water reservoir for improving the performance of the HC membrane under low RH conditions. The incorporation of HG-silica into a sulfonated poly(arylene ether ketone) (SPAEEK) membrane increases the proton conductivity at a low RH by an order of magnitude. The power performance under low RH conditions is also improved with the addition of HG-silica to the SPAEEK membrane. Therefore, a properly-structured hydrogel nanofiller can provide a way to improve the PEMFC performance under low RH conditions.

1. Introduction

For decades, perfluorosulfonic acid (PFSA) polymers have been widely used as electrolyte membrane materials for PEMFCs for their high proton conductivity and mechanical stability [1–3]. Despite their advantageous properties, most PFSA ionomers suffer from critical drawbacks including high production cost, a limited temperature window for operation, and high fuel crossover. As a solution to these problems, hydrocarbon (HC) ionomers have been intensively studied; sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(arylene ether sulfone) (SPAES), and sulfonated polyimide (SPI) are the typical examples in this regard [4–12]. While significant progress has been achieved with the molecular design of HC membranes, these HC ionomers have lower proton conductivities than that of the PFSA ionomers at low relative humidity (RH) conditions because their phase separation is not as effective as that of the PFSA ionomers in developing a proton conducting channel. The proton conductivity of the HC ionomers can be increased by conjugating a larger number of sulfonic acid groups to the backbones; however, it is accompanied by extensive swelling or even polymer dissolution, which significantly lowers the mechanical stability of the HC membrane [13].

One of the most widely employed strategies to address such an issue is the use of inorganic nanofillers such as silica, titania, zirconia, carbon materials, boron nitride, and heteropolyacids or other polymeric materials with a superior mechanical strength to create reinforced composite membranes [14–19]. However, the difficulties in exploiting those

conventional inorganic and polymeric additives are their segregation in the mother electrolyte matrix which diminishes the proton conductivity by blocking the ion conduction channel and diluting the sulfonic acid groups and the processing inconvenience arising from their poor dispersion in casting solutions [20–22]. For example, the SPAES composite membrane containing hygroscopic silica nanofillers showed an improved mechanical strength; however, it has an identical or lower proton conductivity than that of the unfilled SPAES membrane because the silica nanofillers decrease the water uptake and disrupt the proton conduction path [23,24]. To overcome these drawbacks, many previous works have focused on the surface modification of nanofillers with an acidic or basic polymer and functional groups capable of hydrogen bonding [25–31]. Despite these efforts, the issue of poor proton conductivity at low-RH has not been fully addressed.

Against this backdrop, we have explored the possibility of using hydrogel having hydrophilic three-dimensional polymer networks which can function as a water reservoir for low RH proton conduction. However, traditional synthetic hydrogels used in drug delivery, sensors, and smart valves are not mechanically robust for use in HC membranes due to their heterogeneous network structure and plasticization by water [32–35]. Thus, searching for an approach to improve the mechanical strength of hydrogels [36–38], we considered an organic-inorganic network structure. The outstanding mechanical robustness of an organic-inorganic network comes from the intimate mixing of the two materials on a molecular scale and the synergistic reinforcing effect of the two different networks. The chemical bonding between the

* Corresponding author.

E-mail address: heetak.kim@kaist.ac.kr (H.-T. Kim).

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organic and inorganic domain suppresses the aggregation of each material, and the simultaneous formation of organic-inorganic networks ensures a homogeneous dispersion of the inorganic particles [39]. Inspired by the organic-inorganic network structure, we designed silica-embedded hydrogel nanoparticles (HG-silica) which are highly dispersible, mechanically stable and properly function as a water reservoir. Interestingly, HG-silica, when introduced to a SPAEK membrane as a nanofiller, enhanced water retention, thus enhancing the proton conductivity at 32% RH by an order of magnitude. Because of the properties of the hydrogel nanofiller, the power performance of a HC membrane-based membrane electrode assembly (MEA) under low RH conditions was significantly improved. In this study, the synthesis and characterization of HG-silica, the properties and nano-morphology of a HG-silica containing SPAEK membrane, and the electrochemical performances of the MEA with the HG-silica are presented.

2. Experimental section

2.1. Materials

3-(Trimethoxysilyl) propyl methacrylate (MPS), *N*-isopropylacrylamide (NIPAm), potassium persulfate, 4,4-difluorobenzophenone (DFBP), hydroquinone sulfonic acid potassium salt (HQS), potassium carbonate, Dimethyl sulfoxide (DMSO), 9,9-bis(4-hydroxyphenyl)fluorene (BHF), benzene, and 0.1 mol L⁻¹ hydrochloric acid concentrate were purchased from Sigma-Aldrich and used without further purification. Methacryl polyhedral oligomeric silsesquioxane (mPOSS) was purchased from Hybrid Plastics Inc. in the U.S.A. Analytical grade acetic acid, 99.8%, was purchased from Acros Organics. Ethyl alcohol anhydrous, 99.9%, was purchased from Daejung Chemicals & Metals Co., LTD. Fumed silica (AEROSIL380) was purchased from Evonik Industries AG in Germany.

2.2. Synthesis and characterization of the silica-embedded hydrogel (HG-silica)

The introduction of a methacrylate group on the surface of the silica nanoparticles was accomplished through silanization with MPS coupling agent previously described elsewhere [40]. First, 6 mL of 1 vol% MPS aqueous solution and 1 g of fumed SiO₂ nanoparticles in a 95/5 vol % ethanol-water co-solvent were mixed, and the pH of the solution was controlled to be 4.5 with 1 mol L⁻¹ acetic acid. The pH controlled solution was stirred at room temperature for 20 h to carry out the silanization. Centrifuging and re-dispersion of the product were repeated several times to get rid of any unreacted MPS after the reaction, and the MPS modified silica was dried in a vacuum oven at 80 °C for 12 h. To synthesize a hydrogel covalently connected to the MPS modified SiO₂ nanoparticles, radical initiated precipitation polymerization was performed with the following procedures. The polymerization reaction was carried out in a 500 mL three-necked round bottomed flask fitted with a stirrer, heater, condenser, thermometer and N₂ purging. Additionally, a 2 wt% aqueous dispersion of the MPS modified SiO₂ was used as a seed. A 120 mL mixture of 4.4 g NIPAm and 0.5 g mPOSS, for which the pH was adjusted to 4.0 by 0.1 mol L⁻¹ HCl, was stirred for 30 min at 200 rpm under N₂ protection. Then, the HG-silica was washed through repetitive centrifugation and re-dispersion cycles; then, 30 mg of HG-silica was dispersed in ethanol with stirring for 12 h at 25 °C, and the dispersion was centrifuged at 15,000 rpm for 4 h. After repetitive purification, the sediments were collected and dried in vacuum oven for 24 h at 25 °C. The morphology of the HG-silica was investigated with field-emission transmission electron microscopy (FE-TEM, FEI corp. Titan G2 80–200). FT-IR spectra were recorded with a Jasco FT/IR-4100 type-A spectrometer with the ATM mode.

2.3. Preparation of the unfilled and composite membranes and their characterizations

SPAEK block copolymer was prepared by the one-pot condensation reaction. The hydrophilic block was synthesized by mixing DFBP (8.470 g, 38.82 mmol), HQS (8.221 g, 36.0 mmol), potassium carbonate (9.96 g, 72.0 mmol), DMSO (53.1 mL), and benzene (40.0 mL) in a 500 mL round bottom flask and then heating the mixture with a Dean Stark trap at 140 °C for 4 h and then at 180 °C for 20 h. The hydrophobic blocks were synthesized and attached to the hydrophilic blocks; DFBP (1.31 g, 6.0 mmol), BHF (3.58 g, 10.2 mmol), potassium carbonate (0.06 g, 0.4 mmol), benzene (20.0 mL), and DMSO (57.7 mL) were poured into the resulting solution of the hydrophilic block oligomers, and the mixture was heated at 140 °C for 4 h and then at 180 °C for another 20 h. After the polymerization, the product solution was diluted by adding 40 mL of DMSO. The diluted solution was poured into excess methanol to precipitate the resulting SPAEK, followed by washing with deionized water several times, and drying at 80 °C for 24 h in a vacuum oven. A predetermined amount of SPAEK was dissolved in the 1 wt% HG-silica dispersion in DMSO. The solution was cast onto a clean PET film, and the cast was dried at 40 °C for 3 h and further dried under vacuum at 100 °C for 12 h. The composite membranes were fully protonated in 1.0 mol L⁻¹ sulfuric acid solution at 80 °C for 24 h and then rinsed with deionized water. Water uptakes of the membranes were measured by the changes in weight after the soaking of the dry membranes, which had been dried under vacuum at 80 °C for 24 h, in deionized water at 80 °C for 1 h. Water uptake was calculated based on the following equation:

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

$$\Delta l (\text{or } \Delta t) = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} (\text{or } \frac{t_{\text{wet}} - t_{\text{dry}}}{t_{\text{dry}}}) \times 100 \quad (2)$$

where W_{wet} , l_{wet} , and t_{wet} are the weight, length, and thickness of the wet membrane, respectively. W_{dry} , l_{dry} , and t_{dry} are defined similarly for the dry membrane. Water retention ability was measured by recording the weight of the fully hydrated samples under storage at 24 °C and at 32% RH every 5 min. The proton conductivities of the unfilled and composite membranes were determined using a two point AC impedance spectroscopy measurements (Bio-Logics, HCP-803). The digital images of the measurement cell are shown in Fig. S1. The cell was equipped with a thermo-controlled humidifier and heater for measurement at RH lower than 100%. The resistance value related with the membrane conductance was determined from high frequency intercept of the impedance. Proton conductivity (σ) was calculated from the following equation.

$$\sigma = \frac{d}{t w R} \quad (3)$$

where, d is the distance between the two electrodes, t , w , and R are the thickness, width, and resistance of the membrane, respectively.

The surface morphology of the composite membrane was investigated with scanning electron microscopy (SEM, Hitachi S-4800). Stress-strain curves of the unfilled and composite membranes were attained with a universal testing machine (UTM, SHIMADZU AGS-X 100 N) at room temperature at a strain rate of 10 mm min⁻¹. The physical state of the water molecules in the membranes was investigated with differential scanning calorimetry (DSC, Mettler). Each sample was first cooled from 25 to -60 °C and then heated to 150 °C at a rate of 5 °C min⁻¹. For thermo-gravimetric analysis (TGA), the temperature was raised from 20 to 800 °C at a heating rate of 10 °C min⁻¹ under air by using a TGA 92-18 device (Setaram). The oxidative stability of membrane was investigated by immersing the membranes into Fenton's reagent (3 wt% H₂O₂ containing 2 ppm FeSO₄). Methanol permeability was measured at 23 °C by using a diffusion cell with a

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