



Improvement in characteristics of a Nafion membrane by proton conductive nanofibers for fuel cell applications



Takahito Makinouchi, Manabu Tanaka, Hiroyoshi Kawakami*

Department of Applied Chemistry, Tokyo Metropolitan University Hachioji, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan

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ABSTRACT

A novel proton conductive nanofiber composite membrane, which was composed of sulfonated polyimide (SPI) nanofibers and a typical polymer electrolyte, Nafion, was developed to improve electrolyte characteristics, especially proton conductivity at low relative humidity, for polymer electrolyte fuel cells. In addition to the contribution of the SPI nanofibers that were revealed to possess ultra-high proton conductivities in our previous study, the Nafion matrix indicated unique morphology in the composite membrane. The TEM observation suggested that the sulfonic acid groups in the Nafion matrix were attracted to the SPI nanofibers during the membrane formation process to construct acid-condensed layer near the nanofibers. Such acid-condensed layer at the interface of SPI nanofibers and Nafion matrix should have a positive impact on the proton conduction and water diffusion, especially under the low relative humidity conditions. Improved gas barrier property and membrane stability were also achieved by using the proton conductive SPI nanofibers as a framework for the polymer electrolyte membrane.

1. Introduction

Proton exchange membranes (PEMs) are key materials for polymer electrolyte fuel cells (PEFCs) and are desired various characteristics including proton conductivity, gas barrier property, membrane stability, and so on [1–4]. At the present moment, perfluorosulfonated polymers, such as Nafion® (Du Pont), has been most widely utilized for PEMs because of their outstanding proton conductive characteristics. However, many problems remain to be solved on the Nafion membranes for future PEFCs that will operate under more severe conditions to reduce system costs [5]. For example, insufficient proton conductivity at low humidity, relatively high gas permeability, and deficient membrane stabilities are major issues of the Nafion membranes for the long-term PEFC operation [6]. In order to overcome these problems, there are mainly two approaches, except for most recently reported special study [7–10]: One is the development of alternative PEMs based on non-fluorinated polymers. In past decades, sulfonated aromatic hydrocarbon polymers, such as sulfonated polyimides (SPIs) [11–13], sulfonated poly(arylene ether)s (SPAEs) [14–16], and sulfonated polyphenylenes (SPPs) [17,18], have been actively studied to exceed the conventional Nafion membranes. Nevertheless, to the best of our knowledge, there have been few commercial PEMs based on sulfonated aromatic hydrocarbon polymers due to their low proton conductivity at low relative humidity and insufficient membrane

durability for long-term PEFC operation. Another is a more realistic approach, in which characteristics of Nafion membranes are improved by functional additives. Various kinds of fillers, such as silica nanoparticles, titania nanotubes, and graphene oxide nanosheets, have been attempted for the improvement in membrane stability and gas barrier property of the Nafion membranes [19,20]. In the most cases, however, the proton conductivity of the Nafion composite membrane decreased compared to the pristine Nafion membrane without additives because the proton conductive pathway was inhibited and water uptake for better proton conduction was suppressed by the fillers. Although sulfonation of these additives is a possible alternative to maintaining proton conductivity of the composite membrane, these hydrophilic nanomaterials have risks to elute from the composite membranes by water diffusion during the PEFC operation.

Recently, much attention has been attracted to the development of composite PEMs containing polymer nanofibers, which were fabricated by an electrospinning method [21,22]. The electrospun polymer nanofibers with nanometer-scale diameters possess unique characteristics including extremely large surface areas, distinguished mechanical properties, and fast materials transport properties [23,24]. We have fabricated a series of nanofibers from various functional polymers by the electrospinning method. The obtained three-dimensional nanofiber network nanostructures have been attempted to wide variety of applications, such as catalysts [25], filters [26], flexible electrodes

* Corresponding author.

E-mail address: kawakami-hiroyoshi@tmu.ac.jp (H. Kawakami).

[27,28], and PEMs [29–32]. For instance, a nanofiber composite membrane consisted of proton conductive SPI nanofibers and SPI matrix showed better fuel cell performance compared with an SPI membrane without nanofibers [29]. In our recent study, it was revealed that the electrospun SPI nanofibers showed much higher proton conductivity along the nanofiber axis ($5.1 \times 10^0 \text{ S cm}^{-1}$ at 90°C , 95% RH) than the corresponding SPI membrane ($8.3 \times 10^{-2} \text{ S cm}^{-1}$) under the same conditions [33]. It is assumed that the SPI nanofibers formed an effective proton conduction pathway by molecular orientation in the nanofibers. Y. A. Elabd and coworkers also reported similar high proton conductivity ($1.5 \times 10^0 \text{ S cm}^{-1}$ at 30°C , 90%RH) on the electrospun Nafion nanofibers [34]. In addition to their outstanding proton conductive characteristics, the nanofibers are expected to improve other characteristics of polymer electrolyte composite membranes, such as gas barrier property and membrane stabilities.

In this study, in order to improve proton conductivity and other characteristics of a Nafion membrane, the proton conductive SPI nanofibers were utilized as a framework because the SPI nanofibers [33] possess better proton conductive characteristics than the Nafion nanofibers [34]. A series of PEM characteristics, such as proton conductivity, gas barrier property, and membrane stability, of the nanofiber composite membrane consisted of SPI nanofibers and Nafion matrix were investigated. In addition, morphological analyses including transmission electron microscopy (TEM) and small angle X-ray scattering (SAXS) were also attempted to the nanofiber composite membrane to discuss the effects of nanofibers on the Nafion membrane. Interestingly, the TEM observation first revealed the formation of acid-condensed layers at the interface of SPI nanofibers and the matrix Nafion. The acid-condensed layers have potential to construct efficient proton conductive pathways in the nanofiber composite membrane for future fuel cell applications.

2. Experimental

2.1. Materials

1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTDA) and Nafion dispersion (Nafion® perfluorinated resin solution, 5 wt% in lower aliphatic alcohols and water, contains 15–20% water) were purchased from Sigma-Aldrich Co. (St. Louis, MO, USA), and were used as received. 2,2-Bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (APPF) was purchased from the Wako Pure Chemical Industries Co. (Osaka, Japan), and was recrystallized twice from an ethanol solution prior to use. 4,4'-Diamino-biphenyl-2,2'-disulfonic acid (BDSA) was purchased from Tokyo Chemical Industry Co. (Tokyo, Japan). BDSA was purified by dissolution in an aqueous triethylamine solution, followed by precipitation in 1 M sulfuric acid. Finally, BDSA was dried in a vacuum oven at 80°C for 12 h. All other chemicals were purchased from Kanto Chemical Co. (Tokyo, Japan) and were used as received.

2.2. Synthesis and characterizations of SPI

Sulfonated polyimide (SPI: NTDA-BDSA-*r*-APPF) was synthesized according to our previous study [33]. The successful synthesis of the objective SPI with triethylammonium counter ions was confirmed by ^1H NMR spectroscopy (AVANCE III 500, Bruker BioSpin K.K.). The number-average molecular weight (M_n) and weight-average molecular weight (M_w) of the SPI were estimated to be 2.3×10^5 and 5.8×10^5 , respectively, by gel-permeation chromatography (detector: RI-2031, JASCO Co., Tokyo, Japan) using two Shodex SB-806HQ and SB-804HQ columns with a eluent of *N,N*-dimethylformamide containing 0.01 M lithium bromide at a flow rate of 1.0 mL min^{-1} .

2.3. Fabrication of SPI nanofibers

The SPI nanofibers were fabricated by an electrospinning apparatus (ES-1000, Fuence, Co., Ltd., Tokyo, Japan) based on our previous study [33]. A typical electrospinning procedure is as follows: First, SPI (triethylamine form) was dissolved in anhydrous DMF with a concentration of 10 wt%, and the polymer solution was loaded into a 1 mL syringe as the spinneret. A syringe pump was used to squeeze out the polymer solution at a constant speed ($20 \mu\text{L/min}$) through a needle with an inner diameter of 0.21 mm. The distance between the spinneret and a collector ($7.6 \text{ cm} \times 7.6 \text{ cm}$ aluminum foil) was 10 cm. The applied voltage between the spinneret and the collector was fixed to be 24 kV. Temperature and relative humidity inside the apparatus were maintained at $20\text{--}25^\circ \text{C}$ and 5–10%RH, respectively. The SPI nanofibrous membranes (nonwoven nanofiber mats) were collected on the aluminum foil, and their thickness was controlled by the electrospinning deposition time. The SPI nanofibrous membrane was dried under vacuum at 80°C for 12 h to remove the residual solvent from the fabricated nanofibers. Finally, the SPI nanofibrous membrane was acidified with a 1 M HCl solution for 3 h to obtain SPI (proton form) nanofibers. After washing the SPI nanofibrous membrane by water several times, it was dried under vacuum at 80°C for 12 h. The surface and cross-sectional images of the SPI nanofibrous membrane were obtained by scanning electron microscopy (SEM, JXP-6100P, JEOL, Tokyo, Japan). The average diameter of the SPI nanofibers was determined from the SEM images (at least five pictures and 25 nanofibers for each sample) by the Image-J software (Research Services Branch, NIH). The porosity of the SPI nanofibrous membrane was estimated by its apparent volume and weight.

2.4. Preparation of nanofiber composite membranes consisted of SPI nanofibers and Nafion matrix

The nanofiber composite membranes were prepared using a solvent-cast method based on our previous study [29]. First, porosity (P) of the SPI nanofibrous membrane was calculated from Eq. (1):

$$P(\%) = \left(1 - \frac{W(g)}{d \times l \times w \times t} \right) \times 100 \quad (1)$$

where d , W , l , w , and t are density of SPI, weight, length, width, and thickness of a piece of SPI nanofibrous membrane. The electrospun SPI (proton form) nanofibrous membrane, whose porosity was estimated to be 90%, was put in a petri dish. Then, a Nafion dispersion was slowly poured into the petri dish to fill in the void of the SPI nanofibrous membrane. The amount of Nafion dispersion was calculated from the volume of the SPI nanofiber, density of Nafion (not the Nafion dispersion but the Nafion solid after evaporating solvents), and the concentration of the Nafion dispersion to be the volume ratio of SPI nanofiber: Nafion matrix=10: 90 by considering the porosity of the SPI nanofibrous membrane. After pouring the Nafion dispersion, the petri dish covered with a clock glass was allowed to remain at room temperature for 12 h, to soak the Nafion matrix dispersion through the whole nanofibrous membrane. Then, the solvent was slowly evaporated in a vacuum oven at 60°C for 12 h. After drying, the nanofiber composite membrane containing the SPI nanofibers was peeled off from the petri dish and acidified three times with a 1 M HNO_3 solution at 80°C for 30 min each, and finally washed with deionized water. The resulting membrane was dried in a vacuum oven at 60°C for 24 h. For comparison, a recast-Nafion membrane without nanofibers was also prepared according to the similar procedure. Finally, both membranes were pre-treated by a typical annealing and acid immersion process reported elsewhere [35].

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