



Synthesis and characterization of multi-block poly(arylene ether sulfone) membranes with highly sulfonated blocks for use in polymer electrolyte membrane fuel cells

Jinok Yuk^{a,b}, Sojeong Lee^a, Adam F. Nugraha^{a,b}, Hyejin Lee^a, Seok-Hee Park^a,
Sung-Dae Yim^a, Byungchan Bae^{a,b,*}

^a Fuel Cell Laboratory, Korea Institute of Energy Research (KIER), 152, Gajeong, Yuseong, Daejeon 305-343, Korea

^b Renewable Energy Engineering, University of Science & Technology (UST), 217, Gajeong, Yuseong, Daejeon, Korea

ARTICLE INFO

Article history:

Received 4 May 2016

Received in revised form

24 June 2016

Accepted 25 June 2016

Available online 28 June 2016

Keywords:

Polymer electrolyte membrane fuel cell

Sulfonated(arylene ether sulfone)

Multi-block copolymer

Proton conductivity

ABSTRACT

We synthesized novel sulfonated poly(arylene ether sulfone)s (SPAESs) multi-block copolymer membranes containing highly sulfonated hydrophilic blocks. Two different kinds of multi-block SPAESs sharing the same structure of hydrophobic blocks were proposed to investigate the membrane properties based on the effects of the hydrophilic blocks bearing sulfonic acids. The higher local concentration and acidity of the sulfonic acid groups in the hydrophilic block induced higher proton conductivity. The block SPAESs showed comparable proton conductivities to those of the state-of-the-art perfluorinated sulfonic acid (PFSA) membranes, and their transmission electron microscopy (TEM) images revealed a well-developed phase separation. In particular, the SPAES 4 X10Y10 membrane showed excellent proton conductivity, which was higher than that of the PFSA over the entire relative humidity (RH) range at 80 °C. Moreover, the multi-block SPAES membranes showed a comparable fuel cell performance to the Nafion membranes, even at 50% and 30% RH.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) have been studied as possible devices to produce clean or renewable energy. The polymer electrolyte membranes in the PEMFCs are an essential material that provide the transport of protons from the anode to cathode [1]. Perfluorinated sulfonic acid (PFSA) membranes, such as Nafion (DuPont), have been adopted as a benchmark for use in PEMFCs due to their high proton conductivity and excellent chemical and physical stability. Nevertheless, several disadvantages have been reported for PFSA membranes, such as high manufacturing costs [2], a low glass-transition temperature [3], and a limited service temperature below 100 °C [4].

Sulfonated aromatic hydrocarbon polymer membranes have been investigated as alternatives to the PFSA membranes due to their thermomechanical properties, high glass-transition temperature, and low production costs. Most of these membranes are based on sulfonated poly(arylene ether sulfone)s (SPAESs) [4–7], sulfonated poly(arylene ether ketone)s (SPAEEKs) [8,9], sulfonated

poly(arylene sulfide sulfone)s (SPSSs) [10], sulfonated polyimides (SPIs) [11,12], and their derivatives. Most of these polymers are based on statistically random structures and require a high ion exchange capacity (IEC) to compete with the PFSA membranes.

Recently, Hey et al. reported that their arylene ketone random copolymers with intensively concentrated sulfonated moieties significantly improved the proton conductivity [13,14]. They showed comparable proton conductivity to the PFSA membranes, even with a low IEC. However, their proton conductivity was still lower than that of the PFSA membranes at low relative humidity (RH) and high temperature. Proton conductivity, especially at low RH and high temperature, is a critical issue for potential applications of PEMFC systems because they can significantly reduce the balance of plant and the cost of the system. Generally, random hydrocarbon membranes required high IECs (above 3.0 meq/g) to compete with PFSA membranes, which leads to considerable water uptake and a severe loss of chemical and mechanical stability [15].

One of the challenges for high-performance membranes is to develop multi-block copolymer membranes. These copolymers have shown better proton conductivities than the random copolymers. They can form a well-developed hydrophilic and hydrophobic phase separation, which enhances proton and water transport at all RH conditions [14,16]. McGrath et al. reported that

* Corresponding author at: Fuel Cell Laboratory, Korea Institute of Energy Research (KIER), 152, Gajeong, Yuseong, Daejeon 305-343, Korea.

E-mail address: bcbae@kier.re.kr (B. Bae).

the multi-block copolymers with a higher IEC hydrophilic block exhibited sharper phase separations and higher proton conductivities compared to the corresponding random copolymers, while maintaining mechanical properties [17].

Although highly sulfonated hydrophilic blocks have been successfully employed within these multi-block copolymers, most copolymers might experience poor solubility and defects owing to the perfluorinated chain-extendors that were used [7,18,19]. We previously reported densely sulfonated multi-block PAES membranes without any crosslinking by adopting an advanced polymerization technique. These polymers provided superior proton conductivity to the PFSA membranes and a comparable fuel cell performance, even at low hydration and high temperature [20].

We report an advanced version of our previous communications [20] by introducing different chemical structures into the hydrophilic block segment. We introduced a new sulfonated naphthalene moiety to increase the local IEC and the acidity of the hydrophilic block. Two kinds of multi-block copolymer membranes (SPAESs **4** and **5**) containing fully sulfonated benzene and naphthalene components (**1** and **2**) enabled us to compare the effect of the chemical structures and the local concentration of the hydrophilic blocks. Additionally, different block lengths were introduced to control the IEC of the SPAES membranes. The synthesized polymers were characterized by comparing the water uptake, dependence of proton conductivity on RH, proton diffusion behavior, morphologies, mechanical stabilities, and fuel cell performance.

2. Experimental

2.1. Materials

4,4'-dihydroxybiphenyl was obtained from Aldrich; 4,4'-difluorodiphenyl sulfone (FDPS) and 3,3'-disulfonated-4,4'-difluorodiphenyl sulfone (DSFDPS) were obtained from Yanjin (China). FDPS and DSFDPS were recrystallized before use. Potassium hydroquinone sulfonate (HQs) and sodium 3,6-dihydroxynaphthalene-2,7-disulfonate (NTs) was obtained from TCI. Potassium carbonate (K_2CO_3), N,N-dimethylacetamide (DMAc, anhydrous $\geq 99.9\%$), and dimethylsulfoxide (DMSO, anhydrous $\geq 99.9\%$) were obtained from Aldrich and dried over molecular sieves (3 Å) prior to their use. A Nafion NRE212 membrane and DE521 ionomer were purchased from DuPont. The gas diffusion layer (GDL), grade GDL 10BC and Pt/C, JM4000 were purchased from SGL group and Johnson Matthey catalysts, respectively.

2.2. Measurements

The 1H and ^{19}F NMR spectra were measured using a Bruker AVANCE III (600 MHz) spectrometer. Deuterated dimethyl sulfide ($DMSO-d_6$) was used as a solvent. Molecular weights were measured in dimethylformamide (DMF) or DMAc with 0.05 M LiBr using gel permeation chromatography (GPC) equipped with a Young Lin (Korea) YL 9120 UV-visible detector and YL 9112 isocratic pump. Shodex (Japan) SB-803HQ and KF-805L columns were used for the oligomers and polymers, respectively. The molecular weight was calibrated using standard polystyrene samples.

The Fourier transform infrared (FT-IR) spectra were measured using a Nicolet-5700 FT-IR spectrometer (Thermo Electron Corporation, USA) equipped with a diamond attenuated total reflection (ATR) accessory. All of the spectra were acquired as the average of 128 scans at 4.0 cm^{-1} resolution in the spectral range from 4000 to 650 cm^{-1} .

The IEC of the SPAES membranes was confirmed by back titration. A piece of the SPAES membrane was treated with a large excess of 5 M NaCl(aq) solution for at least 24 h. The HCl formed by ion exchange was titrated by a Metrohm 848 Titrimo Plus titrator with a standard 0.01 N NaOH aqueous solution. The IEC was calculated as follows

$$IEC\left(\frac{\text{mequiv.}}{\text{g}}\right) = \frac{\Delta V_{\text{NaOH}} C_{\text{NaOH}}}{W_d}$$

where W_d is the weight of the dry membrane, ΔV_{NaOH} is the consumed volume of the NaOH solution, and C_{NaOH} is the concentration of the NaOH solution.

The dependence of the water uptake on the RH was determined as a percentage of the absorbed water and that of the dry membrane. The membranes were dried at $120\text{ }^\circ\text{C}$ for 24 h and exposed to a given RH for at least 2 d in a temperature and humidity chamber (TH-ME-025, JEIOTECH, Korea). The water uptake was calculated as follows

$$\text{Wateruptake}(\%) = \frac{(W_w - W_d)}{W_d} \times 100$$

where W_d is the weight of the dry membrane and W_w is the weight of the fully hydrated membrane.

The proton conductivity of the SPAES membranes was determined using electrochemical impedance spectroscopy with a 4-probe conductivity cell. The measurements were performed using a BektTech (USA) conductivity cell (in-plane 4 probe method with controlled RH) [21] attached with a Solartron 1287 electrochemical interface and a Solartron 1260 impedance/gain-phase analyzer in the frequency range from 0.1 Hz to 10^5 Hz. The resistance values were chosen from the x-intercept of the Nyquist plot.

The humidity dependence of the proton conductivities was measured at $80\text{ }^\circ\text{C}$ as a function of RH. The proton conductivity was calculated as follows

$$\sigma = \frac{l}{A \times R}$$

where l is the membrane thickness, A is the conducting area, and R is the ion conducting resistance.

The densities of the dried SPAES and Nafion membranes were assumed to be $\sim 1.5\text{ g/cm}^3$ and 1.99 g/cm^3 , respectively, at $80\text{ }^\circ\text{C}$ according to a previous report [16]. The previous paper reported that the densities of the sulfonated block copolymers with similar structures were between 1.36 and 1.67 g/cm^3 , depending on the IEC.

From the density and water uptake data, the water volume fraction was calculated using the following equation

$$\Phi(H_2O) = \frac{\rho_{H_2O}}{\left(\frac{M_{H_2O}}{\rho_{H_2O}} + \frac{1}{\rho_{\text{polymer}}} \times \frac{100}{W(\%)}\right)}$$

where ρ is the density at $80\text{ }^\circ\text{C}$, M_{H_2O} is the molecular weight, and $W(\%)$ is the water uptake.

The transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100F with an accelerating voltage of 200 kV. The membranes were stained with Pb ions by cation exchange of the sulfonic acid groups in a 0.5 M lead acetate aqueous solution, rinsed with deionized water, and dried in a vacuum oven for 12 h. The stained membranes were embedded in an epoxy resin, sectioned to 90 nm thickness with an ultramicrotome, and placed on copper grids.

The tensile strength of the membranes was confirmed using a universal test machine (UTM) (TopTac 2000, Yeonjin Corp., Korea). The stress versus strain curves were obtained for samples that

Download English Version:

<https://daneshyari.com/en/article/632199>

Download Persian Version:

<https://daneshyari.com/article/632199>

[Daneshyari.com](https://daneshyari.com)