Journal of Membrane Science 542 (2017) 102–109

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

Modified sulfonated Poly(arylene ether) multiblock copolymers containing highly sulfonated blocks for polymer electrolyte membrane fuel cells

Taehyun Yoo, Md. Abdul Aziz, Kwangjin Oh, Sangaraju Shanmugam*

Department of Energy Systems Engineering, Daegu Gyeongbuk Institute of Science & Technology (DGIST), 333, Techno jungang-daero, Hyeonpung-Myeon, Dalseong-Gun, Daegu 42988, Republic of Korea

ARTICLE INFO

Keywords:
Polymer electrolyte fuel cells
Sulfonated Poly(arylene ether)
Block copolymers
Membrane
Proton conductivity

ABSTRACT

The sulfonated poly(arylene ether) (SPAE) multiblock copolymers composed of densely sulfonated hydrophilic blocks were designed and fabricated through aromatic nucleophilic substitution reaction. The modified SPAE (mSPAE) membrane showed a well phase separated morphology as revealed by transmission electron microscopy (TEM) studies. The dense sulfonic acid groups in mSPAE lead to higher ion exchange capacity and water uptake, resulting in well phase separated morphology and superior proton conductivity (247.18 mS cm^{-1}) compared with the pristine SPAE membrane (95.73 mS cm^{-1}) and a commercial Nafion (NRE-212) membrane (111.40 mS cm^{-1}) under fully humid condition at 80 °C. The mSPAE membrane showed improved fuel cell performance compared with pristine SPAE and NRE-212 membranes. The mSPAE membrane showed a current density of 1386 mA cm^{-2} at 0.6 V under 100% hydrated condition, whereas the pristine SPAE and NRE-212 membranes showed 766 and 1012 mA cm^{-2} current density under the same condition. A maximum power density of 928 mW cm^{-2} was achieved for mSPAE membrane, which was much higher compared with the pristine SPAE (518 mA cm^{-2}) and Nafion-212 (688 mA cm^{-2}) membranes indicating that mSPAE membrane would be a potential replacement of the Nafion-212 membrane.

1. Introduction

Recently, polymer electrolyte membrane fuel cells (PEMFCs) are considered as a source of clean energy because of their high energy density, environmentally friendly, and high efficiency. One of the key materials of PEMFCs is perfluorinated sulfonic acid (PFSA) ionomer, represented as Nafion (Du Pont). The state-of-the-art Nafion membranes exhibit high stability (physical and chemical) and high proton conductivity. However, several limitations, such as a high production cost, environmental incompatibility, and low glass-transition temperature using PFSA have been a great demand of alternative polymer electrolyte membranes to solve these arguments [1]. Hydrocarbon based polymers including acidic functional groups have been investigated as alternative membranes over Nafion membrane owing to their low production cost, good thermal stability and low gas permeability [2]. The flexible design and easy synthesis procedure of aromatic ionomers including sulfonated poly(arylene ether)s [3], polyimides [4], polybenzimidazoles [5] and their derivatives were well explored. However, hydrocarbon based polymer membranes exhibited poor durability and lower proton conductivity compared to the commercial Nafion membranes [3,6]. Recently, multiblock copolymers including sulfonated hydrophilic oligomers and hydrophobic oligomers exhibited the high proton conductivity and good durability at different humidity conditions [7]. Moreover, densely sulfonated block copolymers showed excellent proton conductivity with well hydrophilic/hydrophobic phase separation morphology [8]. Even though highly sulfonated hydrophilic segments showed improved proton conductivity but their fuel cell performance is still lower than commercial Nafion membranes. Therefore, polymer electrolyte membrane with tunable hydrophilic/hydrophobic phase separated morphology, high proton conductivity and significant fuel cell performances membrane should be developed for the next generation fuel cell technology.

In this article, we introduce a sulfonated poly(arylene ether) (SPAE) block copolymer membrane, where hydrophilic blocks represent a high concentration of sulfonic acid groups to increase the proton transfer across the modified SPAE (mSPAE) membrane. The modified aromatic structure of SPAE including well separated hydrophilic and hydrophobic phase morphology results in high ion exchange capacity (IEC) values correspond to higher proton conductivity compared with a pristine SPAE membrane. Moreover, the mSPAE membrane showed superior fuel cell performance at 80 °C under 100% relative humidity (RH). The synthesis, characterization, and fuel cell performance of the

---

* Corresponding author.
E-mail address: sangarajus@dgist.ac.kr (S. Shanmugam).

http://dx.doi.org/10.1016/j.memsci.2017.08.008
Received 14 June 2017; Received in revised form 26 July 2017; Accepted 3 August 2017

modified block copolymer membrane was discussed and compared with the commercial Nafion-212 membrane.

2. Experimental

2.1. Materials

Bis(4-fluorophenyl)sulfone (FPS), 9,9-bis(4-hydroxyphenyl)fluorene (BHF), and 4,4′-biphenol (BP) were obtained from TCI. Oleum 20%, H_2SO_4, Toluene, HCl, N, N- dimethyl sulfoxide (DMSO), Dimethylacetamide (DMAc) were obtained from Sigma-Aldrich. Methanol was purchased from OCI Company Ltd. Potassium carbonate, calcium carbonate were obtained from Daejung Chemicals. Nafion-212 (NRE-212) membrane and Nafion ionomer 5 wt% solution was obtained from Sigma-Aldrich. The gas diffusion layer (GDL, grade GDL 35 BC) was purchased from SGL group. Pt/C (40%), HiSPEC − 4000 was purchased from Alfa Aesar.

2.2. Synthesis of fluorine (F)-terminated oligomers 1

A 100 mL double-neck round-bottom flask was charged with BHF (4.4 g, 12.7 mmol), FPS (4.0 g, 15.7 mmol), potassium carbonate (4.3 g, 31.6 mmol) DMAc (20 mL), and toluene (10 mL). The reaction was carried out at 145 °C for 3 h equipped with a Dean-Stark trap for removal of water with toluene through an azeotropic condition in a nitrogen atmosphere. After the first step, the reaction temperature was increased to 170 °C and maintained for 12 h. Then, the temperature was cooled down to 25 °C, subsequently, viscous solution was precipitated by adding dropwise into 1 L of DI water. The white crude product was washed with hot DI water and methanol for several times. Then the product was filtered and dried overnight in the oven at 80 °C to give oligomer 1 in 89% yield.

2.3. Synthesis of sulfonated oligomer 1

A 100 mL round-bottomed flask was charged with oligomer 1 (Y = 4, 5 g) and oleum (30%). The mixture was stirred at room temperature for 72 h under a nitrogen atmosphere. After that, the purple mixture was added into the 1 L of DI water and was precipitated out through the addition of NaCl. The precipitate was filtered and dissolved in a 100 mL DI water, and basified with 1 M NaOH solution to transform sulfonic acid groups into sodium form. The brown mixture was filtered, again dissolved in DI water. After that, the solution was dialyzed with Spectra/Por Dialysis tube (cut-off molecular weight: 1000 kDa). Then, the mixture solution was evaporated in a vacuum oven at 110 °C for overnight.

2.4. Synthesis of hydroxy (OH)-terminated oligomer 3

The typical synthesis of oligomer 3 is as follows. A 100 mL double-neck round-bottom flask was charged with BP (3.1 g, 16.6 mmol), FPS (4.0 g, 15.6 mmol), potassium carbonate (4.6 g, 33.5 mmol), toluene (16 mL), and DMAc (32 mL). The mixture was heated at 145 °C for 2 h equipped with a Dean-Stark trap for removal of water with toluene through an azeotropic condition in a nitrogen atmosphere. After the first step, the reaction temperature was raised to 170 °C and maintained for 1.5 h. The temperature was cooled down to 25 °C. Then, the viscous solution was added into 1 L of DI water to precipitate a white powder. The crude product was washed with hot DI water and hot methanol several times. Drying in the oven at 80 °C during the night to give oligomer 3 in 85% yield.

2.5. Synthesis of block copolymer and membrane preparation

The oligomer 2 (0.34 g, 0.07 mmol), oligomer 3 (0.29 g, 0.07 mmol), potassium carbonate (0.029 g, 0.21 mmol), calcium carbonate (0.0701 g, 0.7 mmol), toluene (1 mL), and DMSO (4 mL) were added into a 100 mL double-neck round-bottom flask. The mixture was heated at 145 °C for 24 h equipped with a Dean-Stark trap. After completing the reaction, the mixture was cooled to room temperature. The block copolymer solution was added into 1 M HCl solution. Moreover, the dark brown fiber was washed with 1 M HCl, 3 M NaCl solution, and DI water to remove NaCl. Then the synthesized block copolymer was dried in a vacuum oven at 80 °C for 12 h. The block copolymer (0.3 g) was dissolved in 10 mL of DMAc solvent. The mixture was cast on a petri dish and allowed to dry in a vacuum oven at 55 °C for 4 h, 75 °C for 4 h. The membrane thickness was measured with a digital micrometer, and the average thickness was 45 ± 5 μm. Finally, the membrane was pre-treated by boiling in 5% H_2O_2, 1 M H_2SO_4, and DI water for 1 h in each step [11].

3. Measurements

3.1. ^{1}H NMR and gel permeation chromatography

The hydrophobic, hydrophilic oligomers, block copolymer chemical structure and repeat unit was identified by ^{1}H NMR. ^{1}H NMR spectra were obtained using a 400 MHz Bruker AV 400 spectrometer. Deuterated dimethyl sulfoxide (DMSO-d_6) was used as a solvent. Each oligomer molecular weight was measured by GPC. The hydrophilic oligomer molecular weight was measured by Breeze System using water containing $NaNO_3$ 0.02 N solution. The hydrophobic oligomer molecular weight was measured by Alliance e2695 using THF. A Waters Ultrahydrogel column was used for hydrophilic oligomer, and Waters Styragel column was utilized as the hydrophobic oligomer. The molecular weight of all samples was calibrated using standard polystyrene sample.

3.2. Water uptake and ion exchange capacity

The water uptake was measured by weight difference between wet and dry membranes. The membrane dried in an oven at 80 °C for 12 h. after that, the dry membrane weight was measured. Then, the dry membrane was immersed in DI water for 24 h and measured weight. Water uptake was measured as follows

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

W_{dry} is the dry membrane weight, and W_{wet} is the membrane weight which was immersed in water during 24 h.

Ion exchange capacity (IEC) of membranes was checked through back titration. A piece of the membrane was dried in the oven at 80 °C for 12 h, and dry membrane weight was measured. After that, dry membrane soaked in 3 M NaCl solution for 24 h to exchange H^+ to Na^+. Then, the dissolved HCl by the ion exchange was titrated with 0.01 M NaOH solution. IEC was measured as follows equation.

$$\text{IEC} = \frac{V_{NaOH}\times C_{NaOH}}{W_d}\ (\text{mequiv g}^{-1})$$

W_d is the dry membrane weight. C_{NaOH} is the NaOH concentration, and V_{NaOH} is the added NaOH solution volume.

3.3. Oxidative stability test

The oxidative stability was tested using the wet membrane in Fenton's reagent (3% H_2O_2 a solution containing 3 ppm $FeSO_4$) at 80 °C for 1 h. After that, the tested membrane was measured weight and compared with the pristine membrane. The oxidative stability of the membrane was calculated by the below equation.

$$\text{Oxidative stability}(\%) = \frac{W_{after}}{W_{before}}\times 100$$