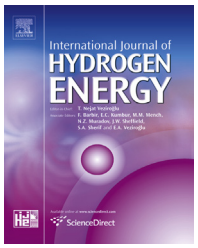
Available online at www.sciencedirect.com

ScienceDirect

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



Annealing effect of highly sulfonated polyphenylsulfone polymer

Je-Deok Kim [a,b,*], *Lee-Jin Ghil* [b]

[a] *Polymer Electrolyte Fuel Cell Group, Global Research Center for Environment and Energy Based on Nanomaterials Science (GREEN), National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*
[b] *Battery Materials Unit, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan*

ARTICLE INFO

Article history:
Received 29 September 2015
Received in revised form
10 February 2016
Accepted 15 February 2016
Available online 11 March 2016

Keywords:
Sulfonated polyphenylsulfone (SPPSU)
Crosslinked membrane
Annealing treatment
PEMFCs

ABSTRACT

Sulfonated polyphenylsulfone (SPPSU) membranes were prepared using alcohol solvents such as isopropanol and 1-propanol in combination with a highly sulfonated PPSU polymer. A covalently crosslinked membrane was obtained after annealing at 180 °C without a crosslinker. The membrane was stable in water, and the thermal stability was higher than that of a synthesized SPPSU polymer. This higher stability was because of the crosslinking effect through the sulfonyl and/or phenyl groups of SPPSU. A high conductivity of 0.1 S/cm and power density of 471 mW/cm^2 were obtained at 80 °C and relative humidity (RH) 100%.

Introduction

Proton Exchange Membrane Fuel Cells (PEMFCs) are among the most promising electrochemical devices for clean and efficient power generation. The performance of PEMFC is strongly affected by the electrode, the proton exchange membrane and their assembly [1,2]. Because the electrode of PEMFC requires platinum (Pt) as an active catalyst material, the reaction sites must be increased in the electrode layer. Recent studies display that low Pt and/or non-Pt catalysts have a high performance in fuel cells [3,4]. Another important factor is the proton exchange membrane. The most commonly used proton exchange membrane for both PEMFC and DMFC is perfluorinated copolymers, such as Nafion, which have high hydrolytic and oxidative stability and excellent proton conductivity [5]. However, the perfluorinated polymers have three major drawbacks hindering their application: high cost; loss of conductivity at relatively high temperatures (>90 °C) and low humidities; and high methanol permeability [6–8]. The drawbacks of perfluorinated membranes have prompted research into alternative membranes based on hydrocarbon polymers. For example, several aromatic polymer ionomer membranes, such as sulfonated polyimide, sulfonated polyethersulfone (SPES), polybenzimidazol (PBI), modified PBI monomers, sulfonated polyetheretherketone (SPEEK) and sulfonated

* *Corresponding author*. Battery Materials Unit, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan. Tel.: +81 29 860 4764; fax: +81 29 860 4984.
E-mail address: kim.jedeok@nims.go.jp (J.-D. Kim).
http://dx.doi.org/10.1016/j.ijhydene.2016.02.084
0360-3199/

polyphenylsulfone (SPPSU), are actively being investigated [9–13]. Among the various hydrocarbon polymers, polyetheretherketone (PEEK) based membranes [14–18] have a good thermal stability, appropriate mechanical strength, and high proton conductivity, which increases with their degree of sulfonation (DS). However, PPSU also has an excellent thermal stability and high chemical resistance and is not expensive; only a few reports investigate PPSU in electrolyte membranes [13,18–23]. This limited research is likely because of the high water solubility of SPPSU [21]. These aromatic polymer electrolytes with high ionic exchange capacity and a high proton conductivity also have weak mechanical properties because of the water solubility. These mechanical properties are a main obstacle in applying SPPSU in PEMFCs. Recently, a crosslinking process was investigated to increase the mechanical property and proton conductivity [18,24,25]. Various solvents (DMAc, NMP, water, water-alcohol, and water-acetone) and cross-linkers (glycerol, ethylene-glycol, and meso-erythritol)) were investigated [24]. Wu et al. [25] showed that a SPPO (sulfonated poly (2, 6-dimethyl-1, 4-phenylene oxide) membrane in the H^+ form could crosslink with itself during heating without other cross-linkers. After heat treatment, sulfonic acid groups are consumed; crosslinking occurs through the condensation of two sulfonic acid groups, and sulfone is formed to connect two rings. Although the crosslinking occurs through the sulfonic acid group, a major portion of acid functions is not involved in crosslinking and remains available for proton transfer. Therefore, high mechanical and proton conducting properties can be obtained by the crosslinking process with thermal treatment using highly sulfonated polymers.

In this study, we synthesized a polyphenylsulfone (SPPSU, IEC = 3.2 meq/g) polymer with a high ionic exchange capacity. The synthesized polymers are water soluble because of the high sulfonation. Isopropanol, 1-propanol, and water were used as solvents of SPPSU polymer to produce a membrane. Casting membranes occurred through annealing, and the study investigated the chemical, thermal, mechanical, proton conductivity, and single cell performance of the membrane.

Experimental

Direct sulfonation of PPSU

Polyphenylsulfone (Solvay, PPSU, Radel R-5000, 20 g, 50 meq) was dissolved in 1 L sulfuric acid (H_2SO_4; Wako 95%) and stirred at 50 °C for 6 days under nitrogen gas. The solution was poured into a large excess of ice-cold water under stirring; a white precipitate was obtained. After letting the reaction stand overnight, the precipitate was filtered and washed using a dialysis-tubing cellulose membrane until the pH = 7. SPPSU was obtained after evaporating the water. A piece of membrane was soaked in 20 mL of a 2 M NaCl solution and equilibrated for over 24 h to replace the protons with sodium ions. The solution was then titrated with a 0.02 M NaOH solution. The ion exchange capacity (IEC) was defined as milli-equivalents of sulfonic groups per gram of dried sample. The degree of sulfonation (DS), which was evaluated by titration, equaled 1.76, corresponding to an IEC of 3.25 meq/g.

Preparation of SPPSU membrane

SPPSU membranes were prepared using 1-propanol, isopropanol, and water. Five types of SPPSU membranes were prepared using different methods (Table 1). Sample 1 used SPPSU (1 g)/H_2O (10 mL); sample 2 used SPPSU (5 wt. %)/isopropanol (80 wt. %)/H_2O (15 wt. %); sample 3 used SPPSU (5 wt. %)/isopropanol (50 wt. %)/H_2O (45 wt. %); sample 4 used SPPSU (5 wt. %)/isopropanol (40 wt. %)/1-propanol (40 wt. %)/H_2O (15 wt. %); and sample 5 used SPPSU (5 wt. %)/isopropanol (25 wt. %)/1-propanol (25 wt. %)/H_2O (45 wt. %). The mixed SPPSU solutions were dissolved at room temperature. The solution was casted into a Petri dish and dried for 2 days at 60 °C. The membranes were peeled off and annealed in air at 120 °C (1 day), 160 °C (1 day), and 180 °C (1 day). The SPPSU membranes were flexible. The membrane color changed from transparent to dark brown after annealing at 180 °C. Even with the color, the membranes were a perfect electrical insulator.

Measurements

Structure characterization

Elemental analyses for C, H, and O, and S were performed by MT-3/MT-5 (Yanaco), EMGA-920 (Horiba), and DX-800 Ion Chromatography (Thermo Scientific).

The vibration properties of the molecular structure were characterized using attenuated total reflection (ATR) with an infrared (IR) spectrophotometer (Nicolet-6700, Thermo Scientific) in the frequency range of 4000–500 cm^{-1}.

^1H nuclear magnetic resonance (NMR) spectrum was recorded at room temperature with a JEOL JNM-ECA400 spectrometer operating at 400 MHz using deuterated dimethyl sulfoxide (d_6-DMSO) solutions. The chemical shift (ppm) is referenced to tetramethylsilane (TMS).

Water-uptake (W.U.), λ, and crosslink rate

The water-uptake of the samples was determined from the sample weight before and after hydration. Before the measurement, the membranes were cut into 10 mm × 10 mm in size and dried for 24 h at 100 °C in a dry oven. The weight of the dry membrane, W_{dry}, was measured. The membranes were then immersed in deionized water for 13 days at 80, 100, 120, and 140 °C in an autoclave. This treatment was performed to determine the equivalent state of the water in the membrane

Table 1 – Sample information of SPPSU membranes using different methods.

Sample no.	Solvent
Sample 1	H_2O
Sample 2	Isopropanol (80 wt. %)/H_2O (15 wt. %)
Sample 3	Isopropanol (50 wt. %)/H_2O (45 wt. %)
Sample 4	Isopropanol (40 wt. %)/1-propanol (40 wt. %)/H_2O (15 wt. %)
Sample 5	Isopropanol (25 wt. %)/1-propanol (25 wt. %)/H_2O (45 wt. %)