



Preparation and properties of cross-linked sulfonated poly(imide-siloxane) for polymer electrolyte fuel cell application

Chao-Chieh Lin, Chuan-Bi Chang, Yen-Zen Wang*

Department of Chemical Engineering and Materials Engineering, National Yunlin University of Science and Technology, 123 University Road, Section 3, Douliou, Yunlin 64002, Taiwan, ROC

HIGHLIGHTS

- ▶ The cSPI-SX is obtained by radical polymerization onto the silylmethyl group of PDMS.
- ▶ The unique phase separated morphology of cSPI-SX supports the hydrolytic stability.
- ▶ The PEFC assembled with cSPI-SX membrane has showed high power output.

ARTICLE INFO

Article history:

Received 14 May 2012

Received in revised form

14 September 2012

Accepted 15 September 2012

Available online 26 September 2012

Keywords:

Sulfonated polyimide

Poly(dimethylsiloxane)

Cross-linked networks

Polymer electrolyte membrane

Fuel cell

ABSTRACT

Cross-linked sulfonated poly(imide-siloxane) (cSPI-SX) is obtained by radical polymerization onto the silylmethyl group of poly(dimethylsiloxane) (PDMS). The chemical structure of the cSPI-SX thus formed is characterized by FT-IR and ^{13}C NMR. The properties required for a proton exchange membrane, such as ion exchange capacity, water uptake, dimensional change, hydrolytic stability, and proton conductivity, are measured and investigated in detail. A transmission electron microscopic (TEM) image shows the presence of large, well-connected hydrophilic domains that are responsible for the high proton conductivity of the cSPI-SX membrane. The unique phase separated morphology of the cSPI-SX membrane supports the outstanding hydrolytic stability. A PEFC assembled with the cSPI-SX membrane has showed high power output at a humidifier gas temperature of 30 °C, a cell operating temperature of 70 °C and a gas pressure of 0.3 MPa.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

As environmental concerns increase, polymer electrolyte fuel cells (PEFCs) have attracted considerable interest as sources of clean energy for transportable, stationary, and portable power applications, because they are highly efficient and cause little environmental pollution [1,2]. A polymer electrolyte is the key component of a PEFC system and it functions as a proton conductor and separates the fuel from the anode and cathode. Perfluorosulfonate ionomers (PFSI), such as DuPont's Nafion membranes, are commercially available and have the advantages of high proton conductivity, excellent chemical stability, and long-term stability. However, they have limited industrial applications due to their high cost, high gas permeability, low operating temperature below 80 °C, and the

environmental inadaptability of fluorinated materials [3,4]. Many researchers have sought to develop alternative polymer electrolyte membranes that are based on partially perfluorinated [5–8] and sulfonated hydrocarbon polymers [9–28].

Of various sulfonated polymers, sulfonated polyimide (SPI) with a six-member imide ring is recognized as one of the most promising materials for fuel cell applications due to their excellent properties of high thermal stability, excellent mechanical strength, superior chemical resistance, good film forming ability and very low methanol permeability [9–16]. However, the sulfonic group of SPI has lower acidity than that of perfluorosulfonated polymers [13]. Therefore, SPI must be increased by a high degree of sulfonation to promote its proton conductivity. At high sulfonation levels, most SPI membranes encounter problems that are associated with swelling, and hydrolytic stability. To solve these problems, SPI membranes are modified by chemically modified monomers [29–32], polymer blending [33,34], and cross-linking [35–37]. These have exhibited improved performance and have

* Corresponding author. Tel.: +886 5 534 2601x4617; fax: +886 5 531 2071.
E-mail address: wangzen@yuntech.edu.tw (Y.-Z. Wang).

attracted considerable attention. One of the simplest methods for improving hydrolytic stability involves cross-linking.

In our previous work, sulfonated poly(imide-siloxane) (SPI-SX) was synthesized from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), 4,4'-oxydianiline (ODA), 2,2'-benzidinedisulfonic acid (BDSA), and α,ω -diaminopropyl poly(dimethylsiloxane) (PDMS) [38]. The results show that the appending of highly flexible siloxane segments to the SPI backbone enhances proton conductivity; suppresses swelling, and influences membrane morphology. However, the ion exchange capacity (IEC) must be further increased to improve the proton conductivity of the SPI-SX. In this work, the mole proportion of BDSA in the SPI-SX is increased and radical polymerization is applied to the silylmethyl group of siloxane segments, initiated by benzoyl peroxide (BPO) [39,40]. Introducing a crosslink segment into the SPI-SX membrane not only maintained the degree of sulfonation but also improved the stability of the membrane.

In this work, an SPI-SX membrane was cross-linked by radical polymerization onto the silylmethyl group of poly(dimethylsiloxane). The properties of polymer electrolyte, such as ion exchange capacity, water uptake, dimensional change, hydrolytic stability, and proton conductivity, were investigated in detail. The performance of the SPI membrane, SPI-SX membrane, and cSPI-SX in a polymer electrolyte fuel cell (PEFC) was compared to that of Nafion 212 membrane.

2. Experimental

2.1. Materials

The 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA, 95% pure; Aldrich) was dried under vacuum before use. The 4,4'-oxydianiline (ODA, 98% pure; Aldrich) was used without further purification. The 2,2'-benzidinedisulfonic acid (BDSA, 70% pure; Tokyo Chemical Industry Co.) was dissolved in ethanol and was neutralized with triethylamine (TEA, 99.9% pure; Sigma–Aldrich) at 60 °C. The BDSA-TEA was purified by recrystallization from the ethanol solution and was dried under vacuum for 3 days. The α,ω -diaminopropyl poly(dimethylsiloxane) (PDMS) (Shin-Etsu Chemical; $M_w = 850 \text{ g mol}^{-1}$) was used without further purification. Benzoic acid (BA, 99.5% pure; Sigma–Aldrich) and benzoyl peroxide (BPO, 75%; Sigma–Aldrich) were used without further purification. *m*-Cresol (99% pure; Sigma–Aldrich) and Nafion-containing solution (Nafion® PFSA polymer dispersion, 5 wt%; DuPont Fuel Cells) were used without further purification.

2.2. Preparation of sulfonated polyimide membranes

Sulfonated polyimide (SPI) was prepared from NTDA, BDSA-TEA and ODA according to a method that has been described elsewhere [41], with an NTDA:BDSA-TEA:ODA molar ratio of 0.93:0.64:0.29. A randomly sulfonated poly(imide-siloxane) (SPI-SX) copolymer was prepared from NTDA, BDSA-TEA, ODA, and α,ω -diaminopropyl poly(dimethylsiloxane) (PDMS) according to a method that has been described elsewhere [38], with an NTDA:BDSA-TEA:ODA:PDMS molar ratio of 0.93:0.64:0.25:0.04. The SPI membrane and SPI-SX membrane were prepared by casting with 5 wt% *m*-cresol solutions (in TEA form) onto glass plates followed by drying in an oven at 80 °C for 12 h to remove residual solvent. The SPI-SX (TEA salt form) was dissolved in *m*-cresol, which was then stirred with BPO in an N₂ atmosphere at 30 °C for 12 h. The PDMS:BPO molar ratio was 1:3. The solution was cast onto a glass plate and dried in an oven at 80 °C for 12 h to remove residual solvent and at 130 °C for 12 h to initiate the radical polymerization onto the silylmethyl group of PDMS [39]. The prepared membranes, roughly

$50 \pm 10 \text{ }\mu\text{m}$ thick, were soaked in 1 M H₂SO₄ at room temperature for 24 h to transform the TEA salt into protonated form. These membranes were then thoroughly washed with de-ionized (DI) water. Scheme 1 shows the chemical structures of SPI-SX and cross-linked SPI-SX.

2.3. Polymer characterization

The prepared membranes were examined by Fourier transform infrared (FT-IR) spectroscopy with attenuated total reflection (ATR) (Spectrum One, Perkin Elmer). Signal-averaging was performed over a minimum of 8 scans with a resolution of 2 cm^{-1} in the $4000\text{--}650 \text{ cm}^{-1}$ range. ¹³C NMR spectra were recorded on solid state NMR (Avance 400, Bruker). Thermogravimetric analysis (TGA) (Q500, TA Instruments) was performed to estimate the thermal stability of membranes and the water weight loss of the hydrated membranes. The temperature was increased to 900 °C at a rate of $10^\circ \text{C min}^{-1}$ in a nitrogen atmosphere. The weight of the sample was about $7 \pm 2 \text{ mg}$.

2.4. Ion exchange capacity

The ion exchange capacity was measured using the titration method. Dried membranes were crushed using a cryogenic crusher and then soaked in 1 M NaCl solution for 48 h to release protons. Released protons were titrated using 0.01 M NaOH solution, using phenolphthalein indicator. The IEC value was recorded as an average value of each sample in milliequivalent NaOH per gram polymer (meq g^{-1}).

2.5. Water uptake and dimensional change

Water absorption of the membranes was determined at 30 °C. These membranes were dried in a vacuum at 100 °C for 24 h, weighed, and then immersed in de-ionized (DI) water at room temperature for 24 h. Wet membranes were dried by wiping and then weighed immediately. Water uptake (WU) of membranes was obtained from weight percentage, using the following equation:

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

Dimensional changes were derived as follows:

$$\Delta l_c = \frac{l_w - l_d}{l_d} \times 100\%$$

$$\Delta t_c = \frac{t_w - t_d}{t_d} \times 100\%$$

where t_d and l_d are the thickness and the length, respectively, of a membrane that is dried in a vacuum at 100 °C for 24 h, and t_w and l_w are the thickness and length of a membrane that is immersed in DI water at room temperature for 24 h.

2.6. Proton conductivity

Transverse proton conductivities of membranes were measured using an AC impedance analyzer (PGSTA30, Autolab) over a frequency range of 1–10,000 kHz. The hydrated membranes were sandwiched between two stainless steel electrodes, and placed in a temperature-controlled cell. The cell was sealed with water over the duration testing [26,28]. Conductivity, σ , in the transverse direction was calculated from impedance data using the following equation:

Download English Version:

<https://daneshyari.com/en/article/1287653>

Download Persian Version:

<https://daneshyari.com/article/1287653>

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