ELSEVIER

Effect of crosslinked chain length in sulfonated polyimide membranes on water sorption, proton conduction, and methanol permeation properties

Ho Bum Park [a,b], Chang Hyun Lee [a], Joon Yong Sohn [a], Young Moo Lee [a,*],
Benny D. Freeman [b], Hyoung Jun Kim [c]

[a] *School of Chemical Engineering, Hanyang University, Seoul 133-791, South Korea*
[b] *Department of Chemical Engineering, University of Texas at Austin, Burnet Road 10100, Austin, TX 78758, USA*
[c] *Fuel Cell Research Center, Korea Institute of Science and Technology, Seoul 136-791, South Korea*

Abstract

Crosslinked sulfonated polyimide (XSPI) membranes were synthesized using various crosslinkers (HO–$(CH_2)_n$–OH, $n = 2$–6, 10) with different chain lengths to investigate the effects of crosslinking on water uptake, proton conductivity, and methanol permeability for both polymer electrolyte membrane fuel cells (PEMFC) and direct methanol fuel cells (DMFC). Differing from a general expectation that crosslinking leads to the reduction of proton conductivity and methanol permeability, XSPI fabricated using longer crosslinkers showed higher proton conductivity ($\sigma = 9.3 \times 10^{-2}$ S cm^{-1}) and lower methanol permeability ($P_{MeOH} = 2.0 \times 10^{-7}$ cm^3 cm cm^{-2} s^{-1}) in comparison with non-crosslinked SPI membrane ($\sigma = 6.2 \times 10^{-2}$ S cm^{-1}, and $P_{MeOH} = 1.1 \times 10^{-6}$ cm^3 cm cm^{-2} s^{-1}). Crosslinking between polymer chains also resulted in improved membrane resistances to hydrolytic attack (40–50 days) in deionized water at 80 °C and free radical attack (33–42 h) in Fenton's solution as compared to non-crosslinked SPI having weak durability (1 day and 23 h, respectively). These properties and performances were found to be strongly related with the chain length of the crosslinker, but relationship between chain length and these properties was not linearly dependent. Interestingly, crosslinker with chain length of $n = 5$–6 was desirable considering overall membrane performances such as proton conductivity, methanol barrier property, and membrane durability. The electrochemical performances using a membrane electrode assembly (MEA) based on the XSPI with crosslinker size of $n = 5$ (900 mA cm^{-2} at 0.6 V in PEMFC, and 130 mA cm^{-2} at 0.4 V in DMFC) were similar or superior to those of Nafion 117 (800 mA cm^{-2} in PEMFC, and 125 mA cm^{-2} in DMFC) and non-crosslinked SPI membrane (488 mA cm^{-2} in PEMFC, and 25 mA cm^{-2} in DMFC) under the same measurement conditions.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Crosslinked sulfonated polyimide; Crosslinker size; Proton conductivity; Methanol permeability; Single cell performance

1. Introduction

Sulfonated polymers are often used in significant technological applications such as ion-exchange resins [1], electrodialysis [2], bipolar membranes [3], sensors [4], and dehydration [5]. More recently, sulfonated polymer membranes have been studied extensively, as can be seen from the increasing number of articles and patents, particularly for fuel cell applications [6–15]. Undoubtedly, PEMFC and DMFC are potential power sources for portable applications and transportation vehicles. This is mainly due to their high power density, simplicity, size flexibility and environmental benefits. Here, sulfonated polymer membranes are one of key elements of fuel cell systems and, accordingly, should be investigated with a high priority to realize early settlement of these promising technologies.

To date, perfluorinated sulfonated polymers such as Nafion®, Aciplex® and Flemion® have been perceived as the most suitable proton conductive membranes in their fully hydrated states because they meet many technical issues (i.e., high proton conduction, and excellent chemical and mechanical stability) occurring in fuel cell applications. However, these commercial membranes are very expensive (ca. $500 per m^2), which adds another burden to the ever-increasing total cost of fuel cell systems. Moreover, they also suffer from a decrease

in proton conductivity at temperatures above 80 °C, high methanol crossover, and high electro-osmotic drag among other drawbacks.

For these reasons, non-perfluorinated sulfonated polymer membranes are being highlighted in these fields. Among the promising fuel cell membrane materials, sulfonated polyimide membranes have gained much attention because of their high proton conductivity and excellent thermal, chemical, and mechanical stability. However, sulfonated polyimides with five-membered imide structures showed a very poor hydrolytic stability, and resultant brittleness or cracking due to chain scission after immersion into acidic water [16]. Fortunately, according to previous studies [16–19], this problem could be improved to some extent *via* a chemical modification of the polymer backbones using hydrolytically durable monomer such as six-membered naphthalenic dianhydrides, sulfonated and non-sulfonated diamines containing swivel group (–O– and –S–), and diamines which have sulfonic acid groups attached to their bridged phenyl rings.

To increase the efficiency of fuel cells, high proton conductivity through the sulfonated polymer membranes is essential. The sulfonated polymers with high degree of sulfonation typically exhibited much-improved proton-releasing capability owing to increasing content of fixed ions within the sulfonated polymers and, thereby, formation of concentrated proton carrier concentration in acidic water medium. However, high sulfonation also results in excessive water swelling (water-solubility), which consequently makes the membranes impractical in fuel cell applications. Accordingly, crosslinking could be a good solution to maintain a proper sulfonation level or water uptake content and, simultaneously, to enhance the mechanical properties. So far, many attempts have been made to crosslink various sulfonated polymer membranes such as polyimide [20–24], poly(vinyl alcohol) (PVA) [25,26], sulfonated polyphosphazene [27], sulfonated poly(aryl sulfinate)/poly(aryl sulfonate) [28], sulfonated poly(ether ether ketone) [29–31], and sulfonated polystyrene [32]. In most cases, crosslinking improved the mechanical properties and membrane stability, but also caused a significant loss in proton conductivity due to increased crosslinking density and reduced water uptake.

In the present study, the effect of crosslinkers in sulfonated polymer membranes on water uptake, proton conductivity, and methanol transport was systematically investigated to find an optimal condition of crosslinked sulfonated membranes which were expected to show high proton conductivity and sufficient membrane stability. Of course, crosslinking is a simple and well-known approach, but there are still not many studies exploiting broadly the role of crosslinking in sulfonated polymer membranes. In addition to crosslinking effect, the influence of crosslinked chain length will be discussed in detail in terms of water sorption, proton conductivity, and methanol permeability. Up to now, there is not any report to improve membrane performances by controlling crosslinker size. Furthermore, single fuel cell performances using the membrane electrode assembly (MEA) based on the crosslinked polymer membranes will be reported as compared to non-crosslinked membranes and Nafion 117.

2. Experimental

2.1. Materials

1,4,5,8-Naphthalene tetracarboxylic dianhydride (NTDA) as dianhydride, and 3,5-diaminobenzoic acid (DBA) and 4,4′-diaminodiphenyl ether (ODA) as diamines were purchased from Tokyo Kasei Co. (Tokyo, Japan) and used as received. ODA was converted into 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (SODA) using concentrated sulfuric acid (95%, Aldrich, WI, USA) and fuming sulfuric acid, SO_3 (30%, Aldrich, WI, USA) [18]. For fabrication of sulfonated polyimides, *m*-cresol (99%, Aldrich, WI, USA) was used as a solvent. 1,2-Ethanediol (EG, $n = 2$, 4.21 Å, end-to-end distance), 1,3-propanediol (PG, $n = 3$, 5.61 Å), 1,4-butanediol (BG, $n = 4$, 6.36 Å), 1,5-pentanediol (PtG, $n = 5$, 7.51 Å), 1,6-hexanediol (HG, $n = 6$, 8.84 Å), and 1,10-decanediol (DG, $n = 10$, 13.68 Å) were obtained from Aldrich (WI, USA) and used as thermally activated crosslinking agents.

2.2. Synthesis of carboxylic acid-containing sulfonated polyimides (SPI-Y)

SPI-III was fabricated using a solution-thermal imidization method as reported earlier [20]. Specifically, in a 250-mL three-necked round-bottomed flask equipped with a mechanical stirrer and nitrogen purge system, 0.576 g (1.6 mmol) of SODA, 0.68 g (5.6 mmol) of benzoic acid, 7 g (76.0 mmol) of toluene (used to remove water formed during imidization), and 0.96 g (9.5 mmol) of triethylamine (TEA) were added to 20 mL of *m*-cresol. After complete dissolution, 0.365 g (2.4 mmol) of DBA was added into the reaction vessel and stirred for 1 h minimum. Then, 1.072 g (4 mmol) of NTDA powder was slowly added, resulting in a brownish solution. The mixture was stirred at room temperature for 2 h, at 80 °C for 4 h, and then at 180 °C for 24 h. After cooling down to 110 °C, 40 mL of *m*-cresol was added to dilute the highly viscous polyimide solution. The SPI solution was slowly poured into 1000 mL of cold acetone to eliminate unreacted monomers or oligomers with low molecular weights. The precipitates were rinsed several times with cold acetone and then dried thoroughly in a vacuum oven at 120 °C. In the nomenclature of SPI-Y, the Roman numerals I–III correspond to SODA to DBA mole ratios of 6/4, 5/5, and 4/6, respectively. SPI-I and SPI-II, having different chemical compositions, were prepared by the same procedure mentioned above.

IR (KBr): 1680–1710 (C=O), 1390 (C–N–C), 700–740 (O=C–N), 1250 (S=O), 1080 (SO_3^-), 918 (S–OH).

2.3. Synthesis of crosslinked sulfonated polyimides (XSPI-Y-n)

Chemical crosslinking between sulfonated polyimides and various diols was carried out using a 15 wt.% SPI-Y solution in *m*-cresol. The diols in some mole ratios were added to the SPI-Y solutions. Then, the mixtures were stirred at 110 °C and 160 °C for 2 h and 8 h, respectively. After the solution temperature cooled down to 110 °C, additional *m*-cresol was added to