

Polymer Electrolyte Membranes from Novel Sulfonated Polyimides for Direct Methanol Fuel Cell

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A series of novel sulfonated polyimides (SPIs) were prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), sulfonated diamines such as bis(3-sulfopropoxy) benzidine (BSPB) and 4,4'-bis(4-amino-phenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS), and common nonsulfonated diamine monomers. Membranes were prepared by solution casting from *m*-cresol. Proton conductivity was measured as functions of relative humidity (RH) and water volume fraction. These SPIs showed high proton conductivities at high RHs (> 80%), which were comparable to or higher than those of Nafion 117. BSPB-based SPIs displayed percolation thresholds slightly higher than that of Nafion and lower than that of BAPBDS-based SPI. Methanol permeation behavior of these SPI membranes was investigated by liquid-liquid permeation method. Most of the SPI membranes displayed lower methanol permeabilities than those of Nafion membrane at 30 and 50°C. As a result, the ratio of proton conductivity (σ) to methanol permeability (P_M), Φ , for these SPI membranes was much larger than that of Nafion, indicating great potential for direct methanol fuel cell application.

Key words: polymer electrolyte membrane, sulfonated polyimide, proton conductivity, methanol permeability

1. INTRODUCTION

In the past decades, fuel cell has been developed as a promising alternative for energy conversion. The polymer electrolyte fuel cell (PEFC) is interesting for the power devices of computers and mobile phones [1-3]. Hydrogen would be a very convenient fuel for PEFC, due to its high electrochemical reactivity and practically zero pollution level. However, storage and delivery still provide complex problems. An alternative is the use of reformers to generate hydrogen from liquid fuels such as methanol. Direct methanol fuel cell (DMFC) technology needs suitable membranes with high proton conductivity and low methanol permeability. Nafion is a perfluorinated proton exchange membrane that is desirable for PEFCs because of their excellent chemical and mechanical stability, as well as high proton conductivity [4]. However, this membrane suffers from high cost, low operating temperature and high methanol permeability. Many nonfluorinated membrane materials based on sulfonated aromatic polymers such as polyether ketones [5], polysulfones [6], polybenzimidazoles [7], and polyimides [8-16] have been widely developed.

Sulfonated polyimides (SPIs) with sulfonic acid groups in the polymer main chains (noted as main-chain-type) have been studied as alternative polyelectrolytes for fuel cell applications [8-14]. These main-chain-type SPIs show relatively high proton conductivities comparable to those of Nafion 117 but suffer from limited membrane stability toward hot water [9,12,13]. Very recently, we reported novel homo-SPI membranes with sulfonic acid groups in the side chains (noted as side-chain-type) [15,16]. The side-chain-type SPIs is particularly interesting because of the structural difference and similarity between them and the widely

studied Nafion family materials. The difference lies in the composition of the backbone, aromatic hydrocarbon versus aliphatic fluorocarbon; the similarity is the nature of the sulfonate group, connected via flexible aliphatic side chain, although the length of side chain is a little different. In this paper, we report the proton conducting behavior for both main-chain-type and side-chain-type (co)-SPIs and their methanol permeation properties, compared with Nafion 117.

2. EXPERIMENTAL

The sulfonated (co)polyimides were prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), bis(3-sulfopropoxy) benzidine (BSPB), 4,4'-bis(4-amino-phenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS) and nonsulfonated diamine monomers. BSPB and BAPBDS monomers were prepared according to the method reported in previous papers [14,15]. The chemical structure of the sulfonated polyimides is shown in Fig. 1.

Membranes of the resulting SPIs were prepared by casting their *m*-cresol solutions (5 wt%) onto glass plates and dried at 110 °C for 10 h. The as-cast membranes were soaked in methanol at 60 °C for 1 h to remove the residual solvent, followed by the proton exchange treatment with 0.5 N sulfuric acid at 80°C for 1h and room temperature for 5 h. The proton-exchanged membranes were thoroughly washed with de-ionized water and then dried in vacuo at 150 °C for 10 h.

Proton conductivity was measured using an electrochemical impedance spectroscopy technique over the frequency range from 10 Hz to 100 KHz (Hioki 3552). A four-point-probe cell with two blackened platinum plate electrodes was mounted on a Teflon plate

at 0.5 cm distance. The cell was placed in either a thermo-controlled humidic chamber or de-ionized water to measure the humidity dependence of proton conductivity. The resistance value associated with the membrane conductance was determined from the high-frequency intercept of the impedance with the real axis. Proton conductivity, σ , was calculated from equation 1:

$$\sigma = d / (L_s w_s R) \quad (1)$$

where d is the distance between the two electrodes, L_s and w_s are the thickness and width of the membrane at a standard condition of 70% RH, respectively, and R is the resistance value measured. For the measurements in liquid water and under RHs above 85%, the swollen membrane thickness was used in the calculation of σ .

Water vapor sorption experiment was conducted at different water activities ($a_w < 1$) at 50 °C using a sorption apparatus (BEL-18SP) by means of a volumetric method. Water uptake in liquid water was also measured by immersing the SPI sample films (about 50mg) into water at a given temperature for 3-5 h. Then the films were taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake (WU) was calculated from equation 2:

$$WU = 100 \times (W_s - W_d) / W_d \quad (2)$$

where W_d and W_s are the weights of dry and corresponding water-swollen film sheets, respectively.

Methanol permeability of membranes was measured using a liquid permeation cell composed of two compartments that were separated by a vertical membrane. The membrane was first immersed in water for 2 h to get the well-swollen sample and then set into the measurement cell (effective permeation area: 16 cm²). One compartment (A) of the cell ($V_A = 350$ ml) was filled with a mixture solution of methanol (10wt%) and de-ionized water. Another compartment (B) was filled with de-ionized water ($V_B = 109$ ml). The compartments were stirred continuously during the whole permeability measurement. Methanol concentrations of the two compartments, C_A and C_B , were analyzed on a gas chromatograph (SHIMADZU, GC-8A) equipped with 3-m column packed with Polarpak Q (poly(ethylene glycol)-1000 supported on Shimalite F). The methanol permeability, P_M , was determined by equation 3:

$$q = A \cdot P_M \cdot \frac{\Delta C}{L} \cdot t$$

$$\Delta C = (C_{A0} + C_A - C_B) / 2 \quad (3)$$

where q is the methanol mol permeated into compartment B, t measuring time, ΔC the driving force between the two compartments during the permeation measurement, A and L are the effective area and thickness of the swollen membrane, respectively. C_{A0} is the initial methanol concentration in feed, C_A and C_B are the methanol concentrations in feed and in permeate, respectively, at time t .

3. RESULTS AND DISCUSSION

3.1 Water vapor sorption

The water vapor sorption isotherms of SPIs and Nafion 117 are shown in Fig. 2. With an increase in water vapor activity (a_w), the water vapor sorption

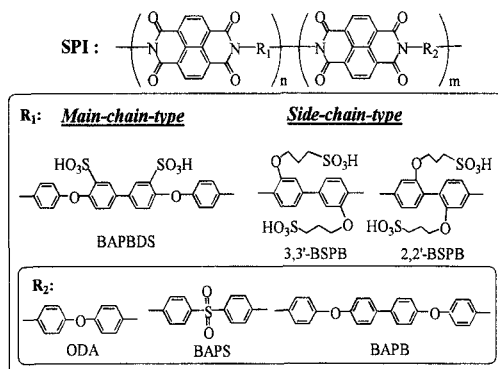


Fig. 1 Chemical structure of sulfonated polyimides.

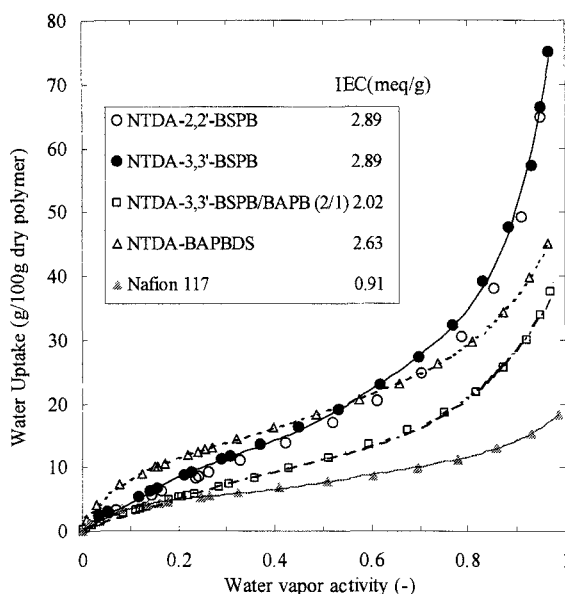


Fig. 2 Water vapor sorption isotherms of SPI membranes and Nafion 117 at 50°C.

increased sigmoidally. Polymers with higher ion exchange capacity (IEC) tend to show larger water uptakes. With similar IEC values, NTDA-BSPB polyimides showed a little different water sorption behavior from that of NTDA-BAPBDS. They showed slightly lower water uptakes at lower a_w (< 0.4), but much higher ones at higher a_w (> 0.8). BSPB-based co-SPI membrane showed clearly smaller water uptake than corresponding homo-SPI, due to the lower IEC. Their water vapor uptakes were larger than those of Nafion 117 in the whole a_w range.

3.2 Proton conductivity

Fig. 3 shows the RH dependence of proton conductivity for SPI membranes and Nafion 117 at 50 °C. The conductivity at 100%RH refers to the value measured in water. It can be seen that most of the SPI membranes displayed stronger RH dependence of proton conductivity than Nafion 117. NTDA-BSPB homo-SPIs displayed similar proton conductivities to those of NTDA-BAPBDS, with similar IECs. They showed higher σ values than Nafion at RHs higher than 80%. Both main-chain-type and side-chain-type copolyimides showed lower conductivity than corresponding homo-SPIs because of their lower IECs. However, the difference of proton conductivity between

main-chain-type homo- and co-SPIs was much smaller than that between side-chain-type homo- and co-SPIs.

The relationship between proton conductivity and water volume fraction is shown in Fig. 4. Based on the water uptake and density of dry membrane (ρ_p) under the assumption of the additive law of volume of water and polymer, the water volume fraction, C , was calculated from:

$$C = \frac{V_{\text{water}}}{V_{\text{total}}} = \frac{V_{\text{water}}}{V_{\text{water}} + V_{\text{dry}}} = \frac{WU}{WU + 100 / \rho_p} \quad (4)$$

The ρ_p values of SPIs were evaluated as 1.61, 1.57 and 1.55 g/cm³ for NTDA-2,2'-BSPB, NTDA-3,3'-BSPB and NTDA-BAPBDS, respectively, from the density values at a standard moisture condition of 70%RH. The ρ_p value of 2.3 g/cm³ was used for Nafion 117 [17]. The SPIs and Nafion 117 membrane showed the similar σ - C relationship that with increasing C , the σ increased first sharply, then slowly and finally leveled off. It is suggested that the proton conduction paths of water molecules are developed well enough to give high proton conductivities in these membranes equilibrated at high RHs (>90%). Compared with Nafion, the higher conductivities of the SPIs in fully hydrated state are due to their higher IECs. On the other hand, in the range of lower C , the SPIs especially NTDA-BAPBDS needed larger C values to display the same σ values as those of Nafion. This suggests the presence of a threshold water volume fraction C_0 , below which proton conduction is impossible, and the different threshold values for these membranes. Actually, the percolation behavior of these SPIs was investigated by percolation theory given by equation 5:

$$\sigma = \sigma_0 (C - C_0)^n \quad (5)$$

where C_0 is a threshold volume fraction required for protons to transport, n is referred to as a critical exponent that controls the scaling behavior, and σ_0 is a prefactor determined by carrier number and ion transport mobility. According to the percolation theory, the calculated σ values based on suitable C_0 values were best fit to those of the corresponding experimental data for SPI membranes. The percolation thresholds, C_0 , were evaluated to be 0.065, 0.075, 0.090, and 0.105 for Nafion, NTDA-2,2'-BSPB, NTDA-3,3'-BSPB and NTDA-BAPBDS, respectively. These results suggest that the proton percolation behavior of side-chain-type SPIs resembled that of Nafion 117 rather than that of main-chain-type ones.

3.3 Membrane stability toward water

Table I lists the water uptake and water stability of SPI membranes. Water stability was tested by immersing the membrane samples into boiling water to investigate whether and when the samples began to break by itself. Generally speaking, NTDA-BAPBDS showed good water stability due to its flexible structure and highly basic diamine moieties. In spite of very large water uptakes, side-chain-type homo-SPIs showed better water stability than BAPBDS-based main-chain-type one, due to the high basicity of BSPB and the microphase-separated structure of the membrane. In addition, side-chain-type co-SPIs exhibited much better water stability than corresponding homo-SPIs and main-chain-type SPI, due to the lower IEC and thus

smaller water uptakes.

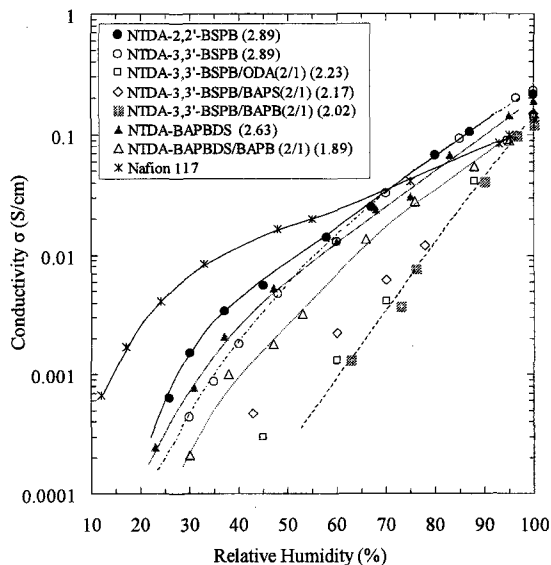


Fig. 3 Proton conductivity of SPI membranes as a function of RH at 50°C.

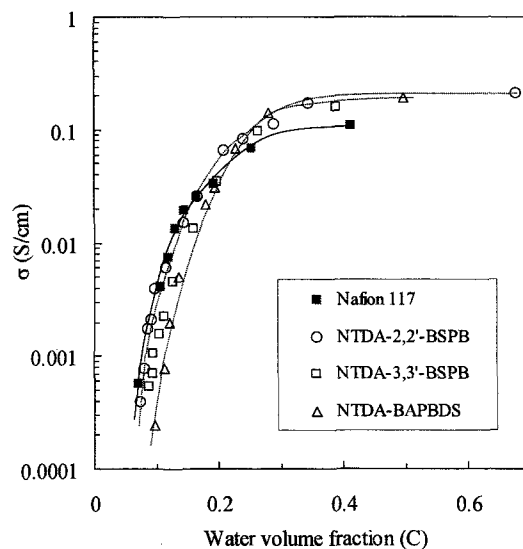


Fig. 4 Proton conductivity of SPI membranes and Nafion as a function of water volume fraction at 50°C.

Table I IEC, water uptake (WU) and water stability of various SPI membranes.

| SPIs | IEC (meq/g) | WU^a (%g/g) | Stability Time (h) ^b |
|---------------------------|-------------|---------------|---------------------------------|
| NTDA-BAPBDS | 2.63 | 103 | 1000 |
| NTDA-3,3'-BSPB | 2.89 | 250 | 700 |
| NTDA-2,2'-BSPB | 2.89 | 220 | 2500 |
| NTDA-3,3'-BSPB/ODA (2/1) | 2.23 | 73 | >3000 |
| NTDA-3,3'-BSPB/BAPB (2/1) | 2.02 | 47 | >3000 |
| NTDA-2,2'-BSPB/BAPB (2/1) | 2.02 | 44 | >3000 |

^aMeasured at 50°C. ^bMeasured at 100°C.

In order to check the stability of sulfonic acid group,

Table II Proton conductivity and methanol permeability of sulfonated polymer membranes

| Membranes | IEC (meq/g) | σ (S/cm) ^a | | P_M (10 ⁻⁶ cm ² /s) ^b | | $\phi = \sigma/P_M$ (10 ⁴ Scm ⁻³ s) | |
|---------------------------|----------------|------------------------------|-------|--|-------|---|-------|
| | | 30 °C | 50 °C | 30 °C | 50 °C | 30 °C | 50 °C |
| NTDA-2,2'-BSPB | 2.89 | 0.14 | 0.22 | 1.05 | 2.06 | 13 | 10.7 |
| NTDA-3,3'-BSPB | 2.89 | 0.17 | 0.20 | 1.96 | 3.85 | 8.7 | 5.2 |
| NTDA-3,3'-BSPB/ODA (2/1) | 2.23 | 0.13 | 0.14 | 1.21 | 1.62 | 11 | 8.6 |
| NTDA-3,3'-BSPB/BAPS (2/1) | 2.17 | 0.13 | 0.15 | 1.03 | 1.56 | 13 | 9.6 |
| NTDA-3,3'-BSPB/BAPB (2/1) | 2.02 | 0.08 | 0.11 | 0.69 | 1.23 | 12 | 9 |
| NTDA-BAPBDS | 2.63 | 0.14 | 0.19 | 1.14 | 2.58 | 12 | 7.4 |
| NTDA-BAPBDS/BAPB (2/1) | 1.89 | 0.13 | 0.15 | 0.86 | 1.19 | 15 | 13 |
| Nafion 117 | 0.91 | 0.105 | 0.11 | 2.2 | 3.3 | 4.8 | 3.3 |

^aMeasured in water. ^bMethanol concentration in feed: 10 wt%.

aging experiment was carried out by immersing the SPI membrane samples into 0.1mol/L sulfuric acid at 100 °C for 300h. It was found that for both main-chain-type and side-chain-type SPIs, the IEC values and proton conductivities didn't change after the aging test, suggesting the stability of sulfonic acid groups under this condition. For example, the IEC values were measured to be 2.58 (before) and 2.56 (after) for NTDA-BAPBDS, and 2.80 (before) and 2.80 (after) for NTDA-3,3'-BSPB, respectively.

3.4 Methanol permeation

Methanol permeability of SPI membranes is an important parameter to evaluate the membrane performance in direct methanol fuel cell (DMFC). Methanol permeability for both main-chain-type and side-chain-type SPIs was measured using a methanol concentration in feed of 10wt%, at 30°C and 50°C, respectively. The results are listed in Table II. The methanol permeability (P_M) of Nafion membrane was measured to be 2.2×10^{-6} cm²/s at 30°C, which was in agreement with the values of 2.3 and 2.6×10^{-6} cm²/s at room temperature reported in the literatures [18, 19]. As shown in Table II, most of the SPI membranes displayed smaller methanol permeabilities than Nafion 117. Both main-chain-type and side-chain-type homo-SPIs showed larger P_M values than the corresponding co-SPIs, probably due to their higher IECs and larger membrane swelling. The proton conductivities of various SPI membranes in water at 30 and 50°C are also shown in Table II. The ratio of proton conductivity to methanol permeability, ϕ ($=\sigma/P_M$), is an effective parameter to evaluate the methanol permeation hindrance ability. It can be seen that most of the SPI membranes displayed 2-3 times larger ϕ values than Nafion, suggesting potential for DMFC applications as good barriers toward methanol.

4. CONCLUSION

The sulfonated polyimides showed high proton conductivities comparable to or higher than those of Nafion 117 at high RHs (>80%). The percolation threshold values of side-chain-type SPIs were higher than that of Nafion and lower than that of main-chain-type one. Most of the SPI membranes displayed lower methanol permeabilities than Nafion. The ratios of proton conductivity to methanol

permeability, ϕ , for the SPIs were 2-3 times larger than those of Nafion, indicating potential application for direct methanol fuel cells at low temperature.

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