

Novel Sulfoalkoxylated Polyimide Membrane for Polymer Electrolyte Fuel Cells

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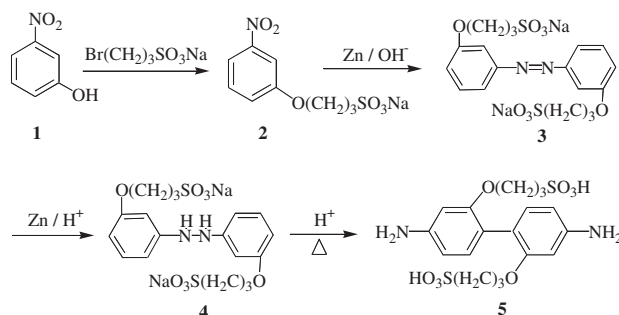
A novel sulfoalkoxylated diamine, 2,2'-bis(3-sulfopropoxy)benzidine (2,2'-BSPB) was successfully synthesized and the sulfonated polyimide was prepared from this diamine and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA). The resulting polyimide membrane displayed high proton conducting performance and excellent water stability, indicating potential application for polymer electrolyte fuel cells.

In the past decades, polymer electrolyte fuel cells (PEFCs) have been developed as promising power sources for mobile and stationary applications.¹ Polymer electrolytes well studied and practically used to date are perfluorosulfonate ionomers such as DuPont's Nafion, because of their high proton conductivity and good chemical stability.¹ However, some disadvantages such as high cost, low operation temperature and high methanol permeability limit their industrial applications. This promotes intense interests in developing alternative materials with high performance and low cost as well. Recently, sulfonated polyimides have been studied and expected as promising materials for PEFC because of their good mechanical and chemical properties and good film forming ability.²⁻⁶ Mercier et al. first prepared a series of sulfonated copolyimides from NTDA, 2,2'-benzidinedisulfonic acid (BDSA) and common nonsulfonated diamines such as 4,4'-diaminodiphenyl ether (ODA) and reported on a fairly high performance of H₂/O₂ fuel cell equipped with sulfonated copolyimide membrane of NTDA-BDSA/ODA(3/7 in molar ratio).² However, the BDSA-based copolyimide membranes have rather poor water stability and must be used in a low sulfonation level, resulting in low proton conductivities of 0.01 S/cm or less in liquid water at a room temperature.³ We developed novel sulfonated aromatic diamines such as 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (ODADS) and 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid (BAPBDS) and prepared a series of sulfonated (co)polyimides from NTDA and these sulfonated diamines, which displayed much higher proton conductivities and much better water stability compared with the BDSA-based copolyimides.^{4,5}

The sulfonated polyimides developed so far have the similar features that the sulfonic acid groups are bonded directly to the polymer backbone, namely, main-chain-type. Herein we report synthesis of a new kind of sulfonated diamine, 2,2'-BSPB, and the resulting sulfonated polyimide bearing sulfonic acid groups in the side chains (namely, side-chain-type). Its good proton conductivities at various moisture conditions and temperatures and excellent water stability are reported.

As shown in Scheme 1, 2,2'-BSPB was prepared using *m*-nitrophenol and 3-bromopropyl sulfonic acid sodium salt as the starting materials. Anal. Calcd for 2,2'-BSPB: C, 46.94; H, 5.25; N, 6.08; O, 27.79%. Found: C, 46.32; H, 5.17; N, 6.02; O, 28.22%. The resulting sulfonated polyimide, NTDA-2,2'-BSPB, was

synthesized in *m*-cresol in the presence of triethylamine using benzoic acid as a catalyst. The ion exchange capacity (IEC) obtained from classical titration (2.72 mequiv./g) was a little lower than the theoretical value (2.89 mequiv./g).



Scheme 1. Synthesis of 2,2'-bis(3-sulfopropoxy)benzidine.

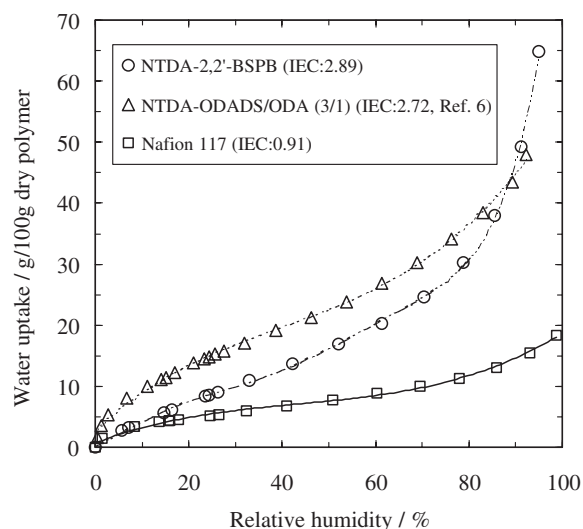


Figure 1. Water vapor sorption isotherms of sulfonated polymers at 50 °C.

The water vapor sorption isotherms of sulfonated polymers were measured by means of a volumetric method using a sorption apparatus (BEL-18SP) at 50 °C. The water uptake was also measured by immersing the membrane sheet (40-60 mg) into water at 50 °C for 5 h. Then the film was taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake of the films was calculated from:

$$W_U = (W_s - W_d) / W_d \times 100(\%) \quad (1)$$

where W_d and W_s are the weights of dry and corresponding water-swollen films, respectively. Proton conductivity was measured by

an ac impedance method with two pairs of blackened platinum electrodes using a Hioki 3552 Hitester instrument over the frequency range from 100 Hz to 100 kHz. The details of the measurement were reported in Ref. 5.

In this letter, Nafion 117 and NTDA-ODADS/ODA (3/1) membranes were used as typical examples of perfluorosulfonate and main-chain-type sulfonated polyimide, respectively, for comparison of water uptake and proton conductivity.

As shown in Figure 1, NTDA-ODADS/ODA(3/1) and NTDA-2,2'-BSPB showed higher water uptake than Nafion 117. It is interesting that NTDA-2,2'-BSPB displayed rather lower water uptake in the range of relative humidity (RH) of less than 85% compared with NTDA-ODADS/ODA (3/1), although they had quite similar IEC values.

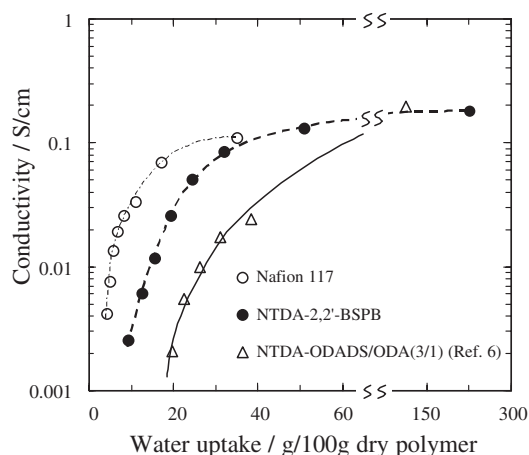


Figure 2. Proton conductivities of sulfonated polymers as a function of water uptake at 50 °C.

As shown in Figure 2, with an increase in water uptake, the proton conductivity increased first significantly, then gradually and finally leveled off. In spite of a low IEC of 0.91 mequiv./g, Nafion 117 showed high conductivities even with rather low water uptake. This is because Nafion 117 has high ion density clusters to form ion-rich channels being favorable for proton transport.⁷ On the other hand, NTDA-ODADS/ODA(3/1) with IEC of 2.72 mequiv/g needed much more water uptake to display proton conductivities similar to those of Nafion 117, probably because of the absence of such ion-rich domains. It is noted that the behavior of conductivity vs. water uptake for NTDA-2,2'-BSPB is close to that for Nafion 117 rather than for NTDA-ODADS/ODA(3/1). At the water uptake of 35 g/100 g dry polymer and 50 °C, the conductivity of NTDA-2,2'-BSPB was about 0.1 S/cm, which was comparable to that of Nafion 117 and 5 times larger than that of NTDA-ODADS/ODA(3/1). Thus, NTDA-2,2'-BSPB displayed higher proton conductivities even with lower water uptake compared with the main-chain-type sulfonated polyimides with the similar IECs including NTDA-ODADS/ODA(3/1). This suggests the presence of some kind of ion-rich domain in NTDA-2,2'-BSPB membrane.

As shown in Figure 3, with an increase in temperature, the proton conductivity of NTDA-2,2'-BSPB membrane increased gradually and then tended to level off. The conductivity at lower RHs displayed larger temperature dependence than that at 80%RH. The conductivities measured in liquid water were a

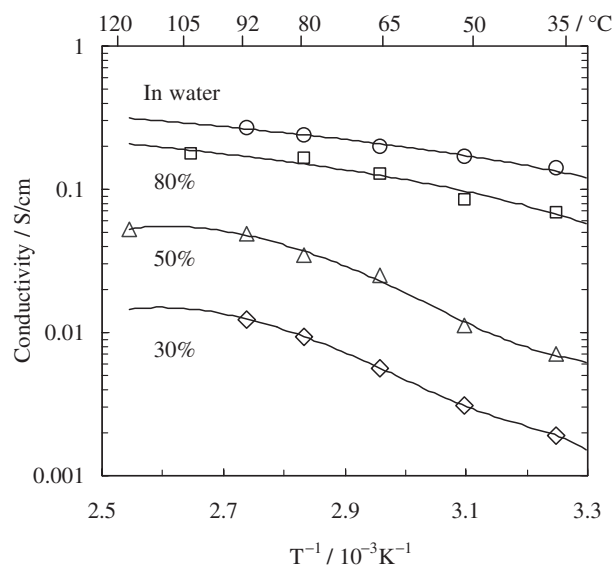


Figure 3. Proton conductivities of NTDA-2,2'-BSPB as a function of temperature under different moisture conditions.

little higher than those at 80%RH. It is noted that the membrane displayed fairly high conductivities of about 0.2 and 0.05 S/cm at 80%RH and 105 °C and at 50%RH and 120 °C, respectively, under 1 atm. This suggests that NTDA-2,2'-BSPB membrane is favorable for PEFC applications at temperatures higher than 100 °C and 80-50%RH.

It should be mentioned that besides its high proton conducting performance, NTDA-2,2'-BSPB also had excellent water stability. The polyimide membrane could bear the immersion in hot water (80 °C) for more than half a year without losing mechanical strength. This may be partly due to the higher basicity of 2,2'-BSPB moieties as a result of electron donating effect of the alkoxy groups.⁵ The more detailed research about relationship between polymer structure, proton conductivity and water stability is in progress.

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