

Synthesis and Proton Conductivity of Novel Sulfonated Polyimides

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Two types (main-chain type and side-chain type) of novel sulfonated diamines bearing sulfonic acid groups directly bonded to polyimide main chains (main-chain type) or in the side alkoxy chains (side-chain type), and the corresponding sulfonated polyimides were successfully synthesized. Water vapor sorption, proton conductivity, membrane stability toward hot water, size change with water uptake of the sulfonated polyimide membranes were investigated. The membranes, especially of the side-chain type sulfonated polyimides, exhibited much better water stability and higher proton conductivity compared with the conventional polyimides based on 2,2'-benzidinedisulfonic acid.

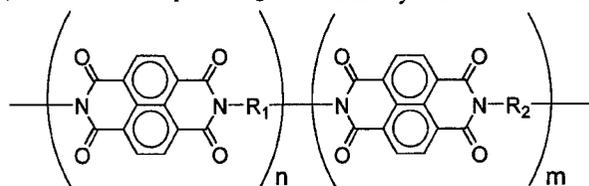
Key words: Sulfonated polyimide, Proton conductivity, Water vapor sorption, Polymer electrolyte fuel cell

1. INTRODUCTION

In recent years there has been intense research interest in the development of proton exchange membrane (PEM) fuel cells for transportation, distributed power, and portable power applications [1]. Perfluorosulfonic acid membranes such as Nafion have excellent chemical and mechanical stability, as well as high proton conductivity. However, there are some disadvantages that limit their industrial applications. These include high cost, low operation temperature, and high methanol permeability. This promotes research interests in developing alternative non-fluorinated materials with low cost and high performance. So far, many kinds of sulfonated aromatic hydrocarbon polymers have been developed for the application of fuel cells [1,2].

Sulfonated polyimides (SPIs) are one of the promising

materials among the PEM investigated [3-7]. Mercier and coworkers synthesized a series of SPIs with different ion exchange capacity (IEC) from 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA) and 2, 2'-benzidine-disulfonic acid (BDSA) [3,4]. The sulfonation degrees are controlled by copolymerization with non-sulfonated diamines. Their results showed low proton conductivities of 1×10^{-2} S/cm in water due to the low IEC, which was essential for maintaining water stability of the membranes. We synthesized a series of novel SPIs from NTDA and sulfonated diamines such as 4,4'-diaminodiphenylether-2,2'-disulfonic acid (ODADS) and 4,4'-bis(4-amino-phenoxy) biphenyl-3,3'-disulfonic acid (BAPBDS) and found that these SPIs had higher proton conductivities and better water stability than those of the BDSA-based copolyimides [5-7].



NTDA-based sulfonated polyimide

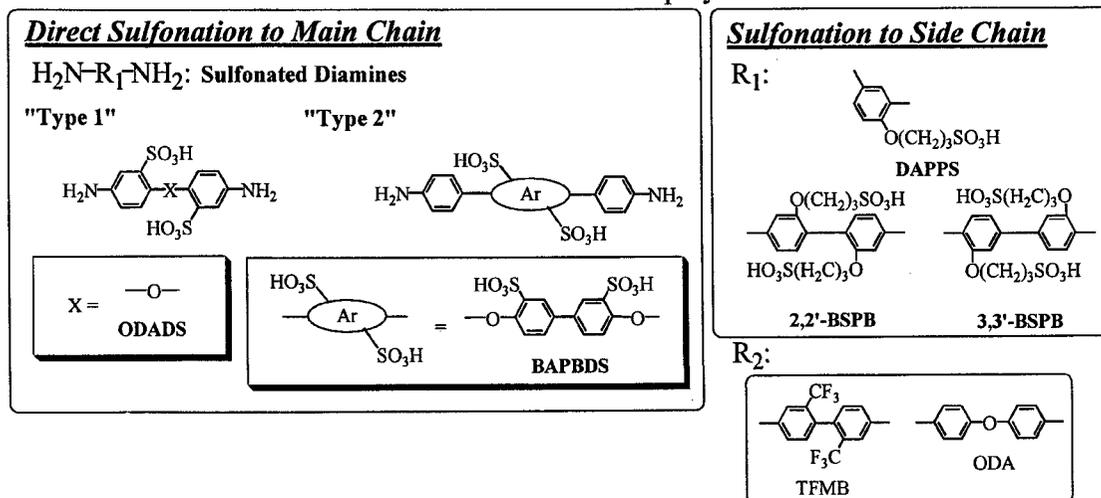


Fig. 1 Chemical structures of SPIs.

Up to date, most of the proton conductive polymers have similar structures that the sulfonic acid groups are directly attached to the polymer backbone. This generally results in rather homogenous morphology being different from that of Nafion. Nafion is known to have a microphase-separated structure and the ion-rich domains form channels being favorable for proton transport. Polymers having sulfonic acid groups attached to the side chains might have different properties from the main-chain type ones. Bae et al. synthesized alkylsulfonated polybenzimidazole (PBI) and reported proton conductivities for PBI-BS (butanesultone) in the order of 10^{-2} S/cm below 100 °C at 100% relative humidity (RH) [8]. We also synthesized alkoxysulfonated diamines such as 2,2'-bis(3-sulfo-propoxy)benzidine (2,2'-BSPB) and the corresponding SPIs bearing sulfonic acid groups in the side chains and reported their good proton conductivities and excellent water stability [9, 10].

In this article, water uptake, proton conductivity, water stability of the SPI membranes are comprehensively reported and discussed with relation to their chemical structures.

2. EXPERIMENT

The SPIs, of which the chemical structures are shown in Fig. 1, were prepared as described previously [5-7,9,10]. The SPIs (in triethylammonium salt form) were dissolved in DMSO, and the solutions (5 wt%) were cast onto glass plates at 80 °C for 10 h. The as-cast membranes were soaked in methanol at 60 °C for 1 h to remove the residue solvent, and then proton-exchanged by immersing the membranes into 1.0 N HCl solution for 10 h. After being washed with de-ionized water, the membranes were dried in vacuo at 150 °C for 10 h.

Proton conductivity was measured by an ac impedance method over the frequency range from 100 Hz to 100 KHz (Hioki 3552) and calculated from:

$$\sigma = L / (t_s w_s R) \quad (1)$$

where L is the distance between the two electrodes, t_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 [5,6].

Water vapor sorption isotherms were measured using a sorption apparatus (BEL-18SP) by means of a volumetric method. Water uptake of the membrane was also measured by immersing the sample sheets into de-ionized water at 80 °C for 5 h. Then the sheets were taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake (WU) was calculated from:

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

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

Density of the membranes (30-40 μm in thickness and 2.6 cm in diameter) was measured by the floating method using mixtures of carbon tetrachloride and xylene. The density was measured for a membrane at both a standard condition of 70% RH and fully hydrate state. Dimensional change of membrane was investigated by immersing the sample into de-ionized water at room temperature for a given time, the changes of thickness and diameter were calculated from:

$$\begin{aligned} \Delta t_c &= (t - t_s) / t_s \\ \Delta l_c &= (l - l_s) / l_s \end{aligned} \quad (3)$$

where t_s and l_s are the thickness and diameter of the membrane equilibrated at 70% RH, respectively; t and l refer to those of the membrane immersed in liquid water.

3. RESULTS AND DISCUSSION

3.1 Water vapor sorption

Figure 2 shows the water vapor sorption isotherms in a form of the number of sorbed water molecules per sulfonic acid group, λ , vs. water vapor activity a_w . The sorption isotherms are sigmoidal and similar to type II BET adsorption. The isotherms of the main-chain type SPIs (NTDA-ODADS/ODA, NTDA-BAPBDS and NTDA-BAPFDS/TFMB) were similar to that of Nafion 117, but different from those of the side-chain type SPIs (NTDA-2,2'-BSPB, NTDA-3,3'-BSPB and NTDA-DAPPS). The λ values at low water activities ($a_w < 0.6$) were lower for the latter apparently due to lower Langmuir-type sorption capacity.

The WU values measured in liquid water at 50 °C were much larger than the WU values in saturated water vapor ($a_w = 1$) estimated from Fig. 2, indicating the much larger membrane swelling in liquid water than in saturated water vapor resulting from larger relaxation of polymer chain packing in liquid water.

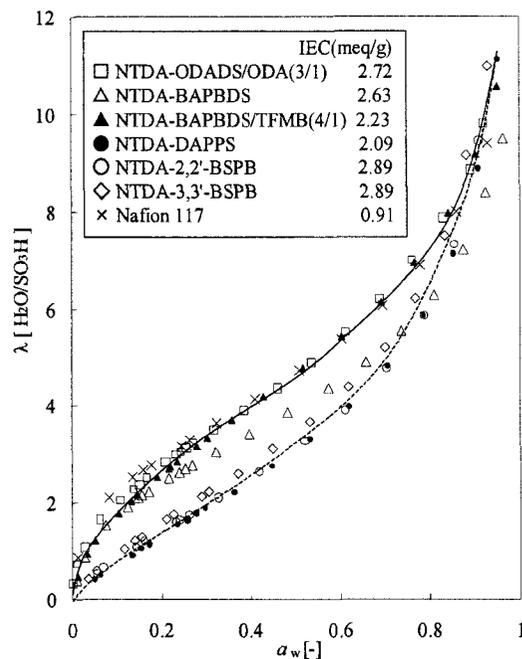


Fig. 2 Sorption isotherms of water vapor for SPI membranes at 50°C.

3.2 Proton conductivity

As shown in Fig. 3, with an increase in RH, the proton conductivities of SPIs and Nafion 117 increased significantly. The σ values of the membranes in liquid water were much larger than those for the membranes equilibrated with saturated water vapor, which were estimated by the extrapolation of the σ values in the range of high RH to 100%RH. This is because of much larger membrane swelling as mentioned above.

The relationship between σ and WU of SPIs is shown in Fig. 4. With an increase in WU , the proton conductivity increased first significantly and then gradually. Nafion 117 had the low WU s but the high σ values. Even with a very small increase in WU in the range of less than 10 g/100g dry polymer, the proton conductivity increased drastically. This is because Nafion 117 possesses high ion density clusters

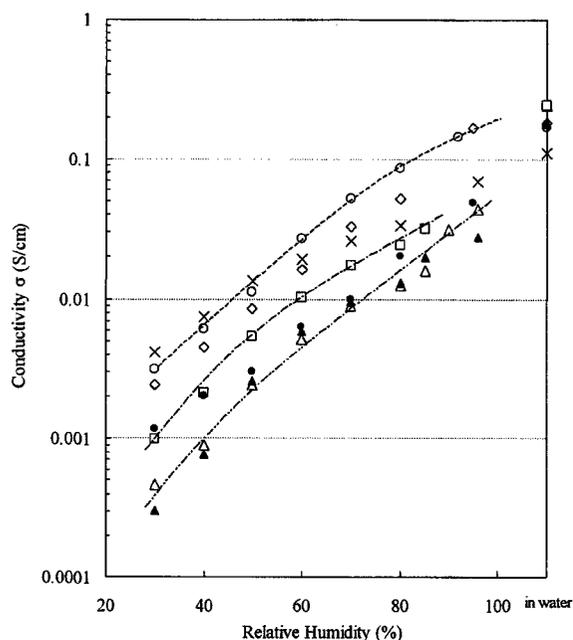


Fig.3 Relative Humidity dependence of proton conductivity for SPI membranes at 50 °C (The keys are the same as in Fig.2).

that have been proposed to form ion-rich channels being favorable for proton transport. On the other hand, the σ - WU relation lines for the SPIs shifted to the right side, that is the SPI membranes needed much more WUs to display the σ values similar to those of Nafion 117. The three main-chain-type SPIs with the similar IEC values roughly fall on the same σ - WU relation line. It is noted that the side-chain-type SPIs displayed the higher σ values than the main-chain-types ones in the similar WU level. Especially, NTDA-2,2'-BSPB displayed the highest proton-conducting performance among the SPIs investigated so far. In the intermediate WU level of 30-50 g/100g dry polymer, NTDA-2,2'-BSPB displayed the high proton conductivity of around 0.1 S/cm at 50 °C, which is comparable to that of Nafion 117. In the fully hydrated state (or in liquid water), most of the SPIs displayed larger proton conductivity (0.2 S/cm or more) than Nafion 117 (0.11 S/cm).

The temperature dependence of proton conductivity for NTDA-2,2'-BSPB membrane is shown in Fig. 5. With increasing temperature, the proton conductivity increased at a little more at lower RH, and then leveled off. At 80% RH, the proton conductivity was 0.2 S/cm at 105 °C, which is similar to that at 80 °C. the NTDA-2,2'-BSPB membrane is favorable for PEFC applications at temperatures higher than 100 °C.

The polyimides bearing sulfonic acid groups in the flexible side chains might make it possible to form a microphase-separated structure. The small angle X-ray scattering spectrum of NTDA-2,2'-BSPB showed a small peak at $2\theta = 2.4$ deg, suggesting the presence of domains of 4 nm in size, whereas NTDA-ODADS did not show such a peak. Although the presence of the ion-rich domains isolated from the hydrophobic polymer backbones is not clearly confirmed, it seems probable that the ion-rich domains lead to the high proton conductivity even in the low WU level.

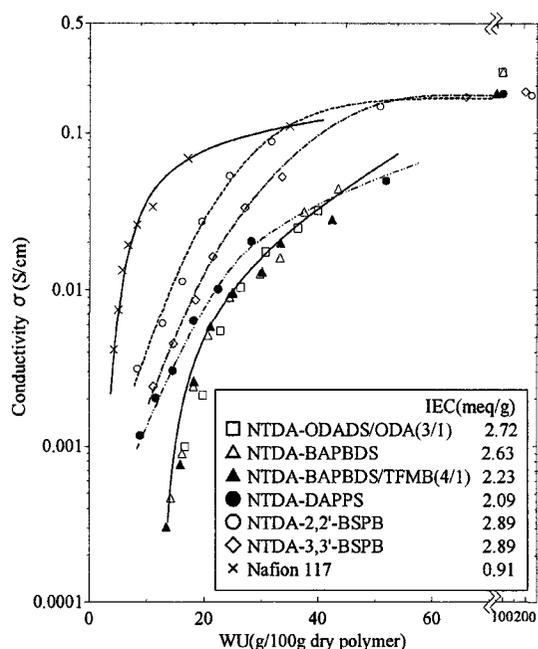


Fig.4 Proton conductivity of SPI membranes as a function of water uptake at 50 °C.

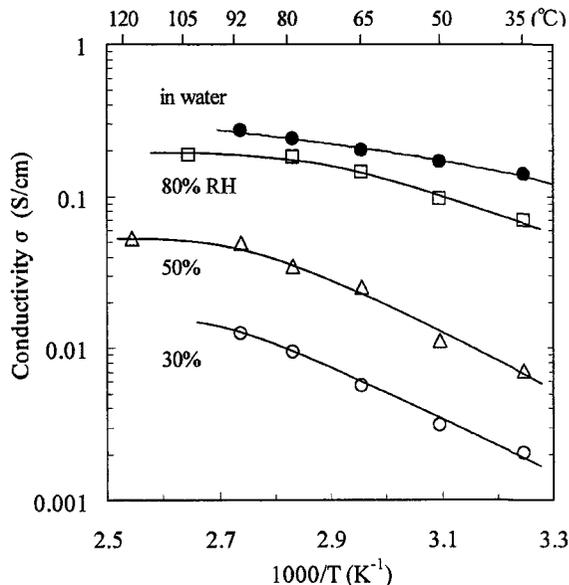


Fig.5 Temperature dependence of proton conductivity for NTDA-2,2'-BSPB.

3.3 Water stability and size change with water uptake

The test of membrane stability toward water was carried out by immersing the samples into de-ionized water at 80 °C and justified by the loss of mechanical strength of the hydrated membranes. The criterion for the judgment of the loss of mechanical strength is that the membrane is broken after being lightly bent. As listed in Table 1, the elapsed immersion time when the membranes began to lose the mechanical strength is in the order: NTDA-2,2'-BSPB \gg NTDA-3,3'-BSPB, NTDA-BAPBDS \gg NTDA-DAPPS $>$ NTDA-ODADS/ODA(1/1) \gg NTDA-BDSA/ODA (1/1).

Polyimides with flexible main chain and high basicity of

the sulfonated diamine moieties tend to have good water stability, because flexibility allows easy relaxation of polymer chain whereas high basicity of the sulfonated diamine moiety depresses the hydrolysis of imido ring. This is why BAPBDS-based polyimides had much better water stability than the corresponding ODADS- and BDSA-based polyimides with similar IEC. The extremely excellent water stability of NTDA-2,2'-BSPB might be explained by an additional reason, that is, the protons might be restricted in the ion-rich domains isolated from the polyimide main chain and thus the hydrolysis of imido rings of the SPI is depressed.

Table 1 Water stability of SPI membranes

SPI	Time [h]
NTDA-BDSA/ODA(1/1)	<5
NTDA-ODADS/ODA(1/1)	25
NTDA-BAPBDS	>1000
NTDA-DAPPS	200
NTDA-3,3'-BSPB	1000
NTDA-2,2'-BSPB	>4000

Table 2 Density, Water uptake and dimensional change of SPI membranes at room temperature

SPIs	IEC [meq g ⁻¹]	RH 70%		in water		Dimensional change	
		<i>d</i> (g/cm ³)	WU	<i>d</i> (g/cm ³)	WU	Δt_c [-]	Δl_c [-]
NTDA-BAPBDS	2.63	1.399	24	1.274	75	0.16	0.15
NTDA-BAPBDS/TFMB(4/1)	2.23	1.406	25	1.294	67	0.14	0.13
NTDA-DAPPS	2.09	1.405	22	1.305	53	0.10	0.11
NTDA-3,3'-BSPB	2.89	1.416	19	1.178	137	1.36	0

Table 2 lists the density *d* and *WU* of SPI membranes equilibrated at 70% RH and in liquid water at room temperature (around 20 °C), and the dimensional changes (Δt_c and Δl_c), determined using the 70% RH as the standard. After being immersed in water for 5 h, both the membrane thickness and diameter increased by 15% and 10% for NTDA-BAPBDS and NTDA-DAPPS, respectively, indicating an isotropic configuration of these SPIs. On the other hand, for NTDA-2,2'-BSPB and NTDA-3,3'-BSPB only the membrane thickness increased, but diameter hardly changed, indicating significant anisotropic change. The investigation of morphology of the SPIs membranes is in progress.

4. CONCLUSIONS

(1) Two types (main-chain type and side-chain type) of SPIs were successfully synthesized.

(2) NTDA-BAPBDS with more flexible main chain and more basic sulfonated diamine moieties displayed higher water stability. NTDA-2,2'-BSPB displayed the highest water stability probably because of an additional reason of presence of ion-rich domains.

(3) The side-chain type SPIs displayed the higher proton conductivities in lower RH range than the main-chain type ones, in spite of lower water uptakes. Especially, NTDA-2,2'-BSPB displayed high proton conductivities of 0.2 S/cm at 80%RH and temperature range of 80–105 °C.

5. ACKNOWLEDGEMENT

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