# Properties and Fuel Cell Performance of Sulfoalkoxylated Polyimide Membranes

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## ABSTRACT

A series of linear type and branched/crosslinked sulfonated polyimides (SPIs) containing pendant sulfoalkoxy groups were prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), sulfonated diamines such as 2,2'-BSPB and 3,3'-BSPB, nonsulfonated diamines such as 4,4'-bis(4-aminophenoxy)biphenyl-3,3'-disulfonic acid (BAPB), 4,4'-bis(3-aminophenoxy)phenyl sulfone (BAPPS) and a triamine monomer, 1,3,5-tris(4-aminophenoxy)benzene (TAPB). The resulting SPI membranes displayed water uptake values in the range of 39-250 wt% and the dimensional changes in water were rather anisotropic with much larger swelling in thickness than in plane. The SPI membrane of NTDA-3,3'-BSPB/TAPB(5/4) displayed high performance with a cell voltage of 0.69 V and a power output of 0.70 W/cm$^2$ at 1.0 A/cm$^2$ by the operation at 90°C and 0.3 MPa in a $H_2/O_2$ fuel cell system, which is comparable to that of Nafion 112.

**Key word:** sulfonated polyimide, polymer electrolyte membrane, water uptake, dimensional change, proton conductivity, fuel cell performance

## INTRODUCTION

Fuel cells have been attracting great attention as power sources in clean-energy fields because of their high efficiency and low pollution level. Proton conducting membrane materials are one of the key components in polymer electrolyte fuel cells (PEFCs). Highly conductive, chemically and mechanically stable, environmentally benign, and inexpensive polymeric materials are in great demand for improving the PEFC performance. Sulfonated polyimides (SPIs) are one of the most promising proton conductive polymers that have been receiving considerable attention for PEFC applications [1-3]. We have previously reported that the sulfonated polymers with acid groups attached to the pendant side groups (side-chain-type) were hydrolytically stable than those with acid groups directly bonded to the main chains (main-chain-type) [3]. Herein, we report on the physical properties and single $H_2/O_2$ fuel cell performance for a series of linear type and branched/crosslinked sulfoalkoxylated polyimide (SPI) membranes.

## EXPERIMENTAL

The chemical structures of linear type and branched/crosslinked SPIs are shown in Fig. 1. Linear type SPIs were synthesized from NTDA and sulfonated diamines such as 2,2'-BSPB and 3,3'-BSPB via random or sequenced polycondensation reaction. BAPB and BAPPS were used as nonsulfonated diamine comonomers. Branched/crosslinked SPIs were synthesized from NTDA, 2,2'-

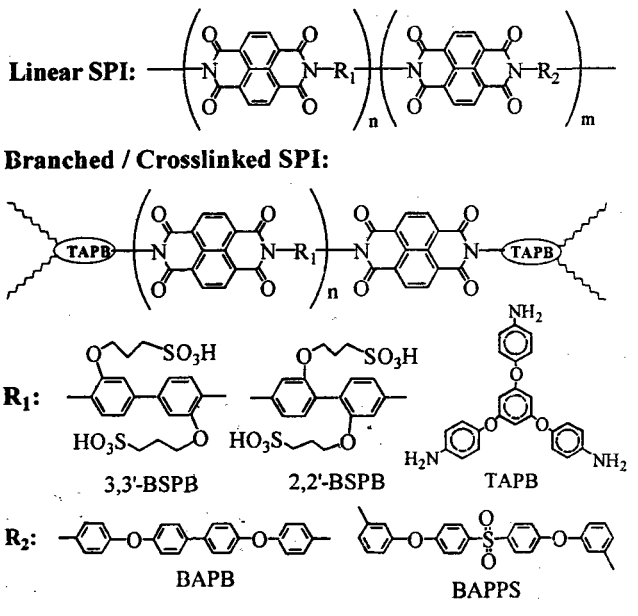


Fig. 1 Chemical structure of sulfoalkoxylated SPIs.

BSPB or 3,3'-BSPB and TAPB. The synthesis and membrane preparation of linear type SPIs was according to the method described in literature [5]. In the case of branched/crosslinked SPIs, sulfonated polyimide oligomers terminated by anhydride groups were first prepared, followed by addition of TAPB, the as-synthesized SPI solution was directly cast onto glass plate to get membranes. The proton-exchanged SPI membranes were characterized by water vapor sorption, dimensional change, proton conductivity and $H_2/O_2$ fuel cell performance.

## RESULTS AND DISCUSSION

The water vapor sorption isotherms of sulfoalkoxylated polyimide membranes were measured at 50°C. As shown in Fig. 2, with an increase in water vapor activity $a_w$, the sorbed water molecules per sulfonic acid group, $\lambda$ values increased sigmoidally. The side-chain-type SPI membranes generally the co-SPIs displayed smaller than those of homo-SPIs. Especially, at high relative humidities (RH > 90%), the difference of $\lambda$ values between co-SPIs and homo-SPIs became very large. This revealed that the polymer chain relaxation of co-SPIs was much more difficult than that of homo-SPIs.

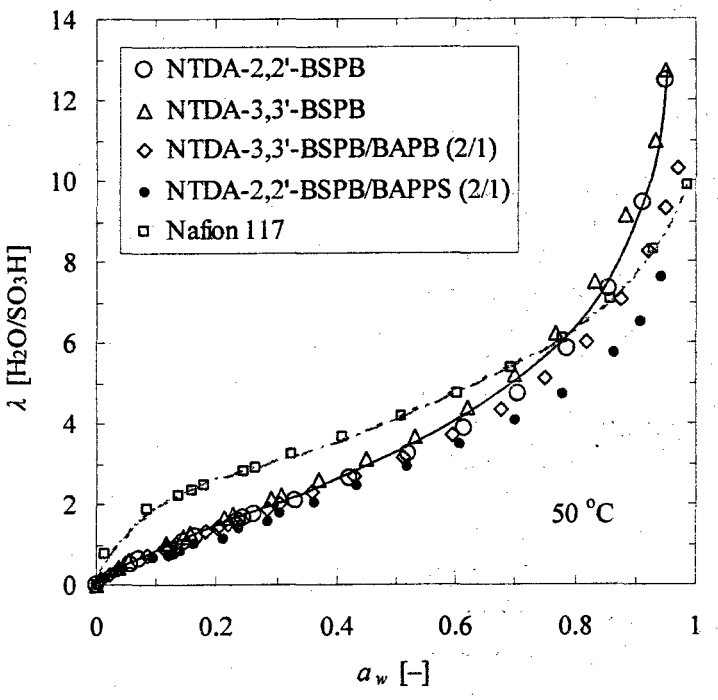

Fig. 2 Water vapor sorption isotherms of sulfoalkoxylated SPIs.

Table 1 lists the water uptake, dimensional change and proton conductivity of various sulfoalkoxylated SPI membranes. It was found that the co-SPIs generally showed much smaller water uptakes than those of corresponding homo-SPIs. As a result, the dimensional changes of co-SPIs were decreased to about 5%-30% as those of homo-SPIs. Most of the membranes displayed strong anisotropic dimensional change with much larger swelling in thickness direction than in plane. It is interesting that the co-SPIs with the same chemical composition but different batch, such as NTDA-2,2'-BSPB/BAPB(2/1)-No.0 to No.2, showed different water uptake (*WU*), dimensional change and proton conductivity ($\sigma$). This might be due to some kind of slight difference of the membrane morphology for these SPIs. It has been observed by TEM analysis that the co-SPI membrane displayed different membrane morphology from that of homo-SPIs. Although clear microphase-separated structure composed of hydrophilic domain and hydrophobic moiety was obtained, the ionic conducting channels in the co-SPIs were formed not so well. It is estimated that the membrane morphology for the same kind of co-SPI membranes might also be slightly different, which is responsible for their different physical properties as well as conducting behavior.

The membrane durability toward water was investigated by soaking the membranes into water at 100°C for 300 h, followed by measurements of proton conductivity and sulfur loss. It was found that the sulfur loss values for various co-SPI membranes were different from each other in the range from 5% to 21% (shown in Table 1). Correspondingly, the deviation of proton conductivity before and after soaking treatment for the co-SPIs was also different. This may also be attributed to the difference of membrane morphology. Note that the co-SPIs with sulfur losses of 5-6% displayed

hardly decreased conductivties at RHs of 70-100%. However, with sulfur losses of 11-21%, the proton conductivities of the corresponding co-SPIs decreased by about a half to one order of magnitude at 70%RH, although the $\sigma$ values at higher RHs (90-100%) were hardly decreased.

Table 1 WU, size change, sulfur loss and proton conductivity of alkoxylated SPI membranes.

| SPIs | IEC[b] | *WU* | Size change[c] | | [S] loss | Conductivity (S/cm)[d] | | |
|---|---|---|---|---|---|---|---|---|
| | (meq/g) | (wt%) | $\Delta t_c$ | $\Delta l_c$ | (mol%) | 100% | 90% | 70%RH |
| NTDA-2,2'-BSPB | 2.89 | 220 | 2.3 | 0.01 | — | 0.22 | 0.110 | 0.0350 |
| NTDA-2,2'-BSPB/BAPB (2/1)-No.0 | 2.02 | 44 | 0.14 | 0.03 | — | 0.06 | 0.018 | 0.0012 |
| NTDA-2,2'-BSPB/BAPB (2/1)-No.1 | 2.02 | 61 | 0.20 | 0.02 | — | 0.11 | 0.032 | 0.0038 |
| NTDA-2,2'-BSPB/BAPB (2/1)-No.2 | 2.02 | 76 | 0.49 | 0.05 | — | 0.14 | 0.078 | 0.0096 |
| after soaking in water[a] | | — | — | — | 21 | 0.11 | 0.080 | 0.0014 |
| NTDA-2,2'-BSPB/BAPB (2/1)-s | 2.02 | 87 | 0.55 | 0.05 | — | 0.11 | 0.101 | 0.0080 |
| after soaking in water | | — | — | — | 5 | 0.09 | 0.090 | 0.0110 |
| NTDA-2,2'-BSPB/BAPPS (2/1) | 1.95 | 39 | 0.11 | 0.02 | — | 0.05 | 0.018 | 0.0035 |
| after soaking in water | | — | — | — | 6 | 0.05 | 0.029 | 0.0026 |
| NTDA-3,3'-BSPB | 2.89 | 250 | 1.8 | 0.06 | — | 0.23 | 0.110 | 0.0300 |
| NTDA-3,3'-BSPB/BAPB (2/1)-No.0 | 2.02 | — | — | — | — | 0.12 | 0.116 | 0.0230 |
| after soaking in water | | — | — | — | 11 | 0.12 | 0.109 | 0.0091 |
| NTDA-3,3'-BSPB/BAPB (2/1)-No.1 | 2.02 | 62 | 0.48 | 0.03 | — | 0.11 | 0.031 | 0.0037 |
| NTDA-3,3'-BSPB/BAPB (2/1)-No.3 | 2.02 | 64 | 0.39 | 0.03 | — | 0.12 | 0.038 | 0.0068 |
| NTDA-3,3'-BSPB/BAPPS (2/1) | 1.95 | 49 | 0.11 | 0.02 | — | 0.09 | 0.066 | 0.0076 |

[a]Soaking condition: 100°C,300h. [b]Calculated values. [c]Measured at r.t. in water. [d]Measured at 50°C.

Despite the fact that the membranes had significant anisotropic membrane swelling, the proton conductivity in thickness direction estimated from the fuel cell performance was in roughly agreement with those measured in membrane plane direction by electrochemical impedance spectra. As shown in Fig. 3, the co-SPI of NTDA-3,3'-BSPB/BAPB (2/1) membrane showed lower fuel cell performance than Nafion 112 due to the relatively larger membrane resistance as a result of poor ionic conducting channel structure. However, the branched/crosslinked SPI membrane of NTDA-3,3'-BSPB/TAPB (5/4) displayed high fuel cell performance comparable to that of Nafion 112. This membrane displayed open circuit voltage (OCV) of 0.98 V, which is similar to that of Nafion membrane. On the other hand, a cell voltage of 0.69 V and a power output of about 0.7 W/cm$^2$ was obtained at 1.0 A/cm$^2$ by the operation at 90°C and 0.3 MPa in a $H_2/O_2$ fuel cell system.

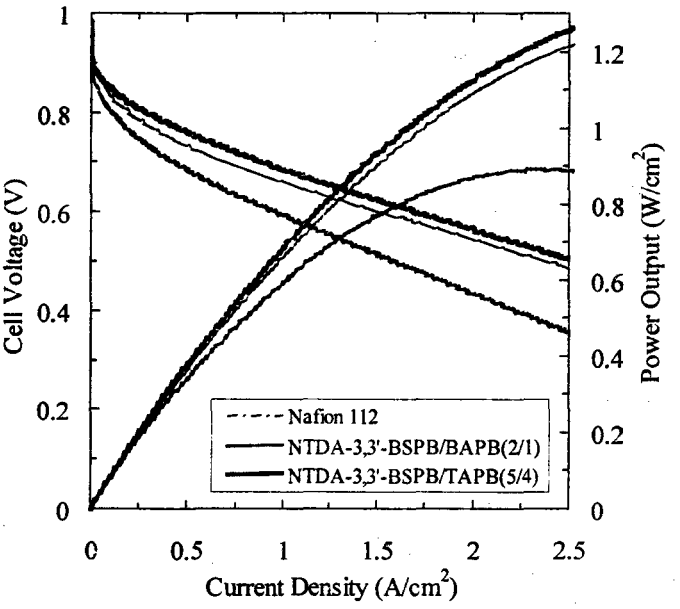


Fig. 3 $H_2/O_2$ fuel cell performance of side-chain-type SPI membranes at 90°C and 0.3 MPa.

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