

## Synthesis of Polyamidesulfamide Acid as a New Proton-Conductive Membrane

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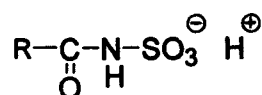
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### 1. Introduction

Sulfonamide moiety,  $\text{RNSO}_2$ , has been studied as biologically active compounds such as antibacterials.<sup>1</sup> Bissulfonylimide group,  $-\text{SO}_2\text{NHSO}_2-$ , has been introduced to the side chain of Nafion<sup>®</sup> to be the base moiety for an acid doping.<sup>2</sup> However, to the best of our knowledge, there has been no report on SULFAMIDE ACID (Scheme 1), one of the sulfonic acid derivatives. Sulfamide acid involves both an electron-drawing carbonyl group and a conjugated structure. We expect this compound shows a very high proton dissociation ability in a water-free state, with our computational study.



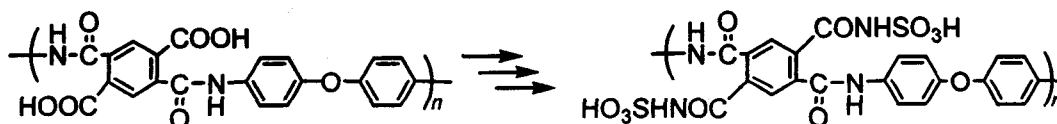
Scheme 1

In this paper, we focused on the sulfamide acid derivative as an effective proton donor under dry condition, which could be applicable for a high temperature PEM. We first studied the acid dissociation of benzenesulfamide acid (*N*-benzoylsulfamic

acid) among various sulfonic acids. Then we designed polyamidesulfamide acid, the backbone of polyimide precursor and side chains of sulfamide acids. Its synthesis and properties including proton conductivity were described.

### 2. Experimental

Poly(pyromellitic dianhydride-*co*-4,4'-oxydianiline) amic acid (polyamic acid) was prepared by the polycondensation of pyromellitic dianhydride and 4,4'-oxydianiline in *N,N'*-dimethylacetamide (DMAc). Two carboxylic acid groups (0.5 unit mmol) of the polyamic acid (0.21 g) were converted to the corresponding acid chlorides by 5 mmol (0.60 g) of thionyl chloride, reacted with 5 mmol (0.99 g) of triethylammomium amidosulfate, treated with a cation exchange resin (Amberlyst 15JWET) in the DMF solution, and then dried under vacuum at 60°C for a day. Poly(pyromellitic dianhydride-*co*-4,4'-oxydianiline) sulfamide acid was obtained as a yellowish powder with the yield of 0.22g (77%). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 500 MHz; ppm):



Scheme 2

**Table**  $pK_a$  of sulfonic acid derivatives (R-SO<sub>3</sub>H) in aqueous solution

R-	C <sub>6</sub> H <sub>5</sub> -CONH-	CH <sub>3</sub> NH-	<i>p</i> -CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -	CH <sub>3</sub> -	CF <sub>3</sub> -
$pK_a$	1.48	1.64	1.50	1.40	1.36

87.02–7.15 (m,4H,Ph), 7.50–7.70 (m,4H,Ph), 7.71–7.78 (m,1H,Ph), 7.95–8.23 (m,1H,Ph), 10.43–10.65 (m,2H,NH), IR (KBr; cm<sup>-1</sup>): 1051, 1116( $\nu_{S=O}$ ), 1656, 1685 ( $\nu_{C=O}$ ). GPC (DMAc solution of 0.05 M LiCl with polystyrene standard):  $M_w = 4.1 \times 10^4$ ,  $M_w/M_n = 1.8$ .

Membrane of polyamidesulfamide acid was prepared by casting the DMAc solution onto a gold electrode or a Teflon sheet and dried under vacuum at 60°C for a day. The ionic-exchange capacity (IEC) was measured by an acid-base titration in the DMSO solution. The IEC value was also estimated by the <sup>1</sup>H NMR spectra of the triethylammonium polyamidesulfamide acid. Swelling in water was determined by measuring uptake of water at room temperature using weight difference of the swollen to dry membrane, relative to the dry weight. Thermogravimetric data were obtained under nitrogen at a heating rate of 10°C min<sup>-1</sup>.

Proton conductivity of the membranes was measured by impedance spectroscopy over the frequency range from 1 Hz to 1 MHz, using a gold electrode cell, with Autolab PGSTAT30. The conductivity was also measured for the membranes of the starting polyamic acid and poly(styrenesulfonic acid) (PSS) as the control data.

### 3. Results and Discussion

Acid dissociation constant ( $pK_a$ ) was listed in Table. Benzenesulfamide acid showed relatively low acid dissociation constant or strong acidity among organic sulfonic acids such as *p*-toluenesulfonic acid. The carbonyl group in the sulfamide acid might accelerate the proton dissociation. The  $pK_a$  value in the absence of water will be also reported.

Polyamidesulfamide acid was soluble in DMAc, DMF, and DMSO and insoluble in water, methanol, and chloroform. Casting the polymer solution gave a brownish, tough, and mechanically strong membrane. Thermal degradation temperature ( $T_{d10\%}$ ) of the polyamidesulfamide acid was 230°C, and was 70°C higher than that of polyamic acid. The polymer was stable in the oxidative Fenton reagent solution.

The membrane of polyamidesulfamide acid absorbed 3 wt% of water when soaked in water, comparable to those of PSS (21 wt%) and polyamic acid (4 wt%). IEC of the polyamidesulfamide acid membrane was determined to be 3.2 meq g<sup>-1</sup> by the acid-base titration, which agreed with the value by the H NMR measurement.

Proton conductivity ( $\sigma$ ) of the hydrated polyamidesulfamide acid membrane at 30°C was in the order of 10<sup>-4</sup> S cm<sup>-1</sup> (Fig.), which was higher than that of the polyamic acid

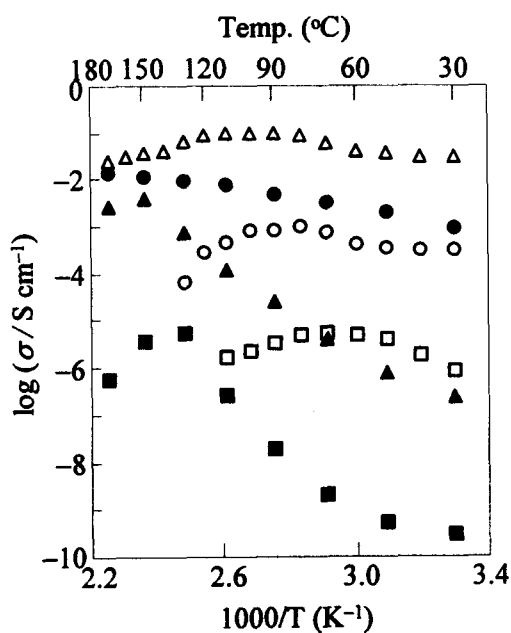


Fig. Temperature dependence of proton conductivity of the membranes, polyamidesulfamide acid (●: dry, ○: hydrated), polyamic acid (■: dry, □: hydrated), and PSS (▲: dry, △: hydrated).

membrane ( $10^{-6}$  S  $\text{cm}^{-1}$ ) but lower than that of the hydrated PSS membrane ( $10^{-2}$  S  $\text{cm}^{-1}$ ). The difference of the conductivity came from higher water uptake and IEC of PSS (5.4 meq  $\text{g}^{-1}$ ). The conductivity increased with temperature up to the order of  $10^{-3}$  S  $\text{cm}^{-1}$  at 80°C, above which the conductivity decreased due to loss of water.

Under non-humidified conditions, proton conductivity of the dry polyamidesulfamide acid membrane in the temperature range from 30 to 170°C was in the order of  $10^{-2}$ – $10^{-3}$  S  $\text{cm}^{-1}$ . This conductivity was surprisingly higher than that of the hydrated membrane. The conductivity reached to  $1.4 \times 10^{-2}$  S  $\text{cm}^{-1}$  at 170°C, which was much higher than those of the dry PSS membrane ( $3.0 \times 10^{-3}$  S  $\text{cm}^{-1}$ ) and the dry polyamic acid membrane ( $1.4 \times 10^{-5}$  S  $\text{cm}^{-1}$ ). The conductivity increase with

temperature obeyed an Arrhenius type, to give the activation energy of 22 kJ  $\text{mol}^{-1}$ . This activation energy of the proton conductivity for the polyamidesulfamide acid membrane was significantly small in comparison with those (84 and 99 kJ  $\text{mol}^{-1}$ ) for the PSS and polyamic acid membrane, respectively. High conductivity and low activation energy of the polyamidesulfamide acid membrane are considered to be realized by the high acid dissociation ability of the sulfamide acid under dry condition. The results indicated the polyamidesulfamide acid membrane is a potential candidate of a high temperature PEM.

#### Literature Cited

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