Available online at www.sciencedirect.com
SCIENCE DIRECT®

Polymer 44 (2003) 4509–4518

polymer

www.elsevier.com/locate/polymer

# Synthesis, proton conductivity and methanol permeability of a novel sulfonated polyimide from 3-(2′,4′-diaminophenoxy)propane sulfonic acid

Yan Yin[a], Jianhua Fang[a], Yongfang Cui[b], Kazuhiro Tanaka[a], Hidetoshi Kita[a], Ken-ichi Okamoto[a,*]

[a]*Department of Advanced Materials Science & Engineering, Faculty of Engineering, Yamaguchi University, Ube, Yamaguchi 755-8611, Japan*
[b]*Institute of Materials Science & Chemical Engineering, Tianjin Polytechnic University, 63, Chenglinzhuang road, Hedong district, Tianjin 300160, People's Republic of China*

Received 20 December 2002; received in revised form 11 April 2003; accepted 27 May 2003

---

## Abstract

A novel sulfonated diamine monomer, 3-(2′,4′-diaminophenoxy)propane sulfonic acid (DAPPS), was successfully synthesized and the sulfonated polyimide (SPI) was prepared from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and DAPPS. The resulting SPI, NTDA–DAPPS, was soluble in common organic solvents. The SPI membrane displayed proton conductivity $\sigma$ values of 0.12–0.35 S/cm at temperatures ranging from 35 to 90 °C in liquid water, which were similar to or higher than those of Nafion 117 and sulfonated hydrocarbon polymers. The $\sigma$ of the SPI membrane decreased significantly with decreasing relative humidity (RH) and became much lower than that of Nafion 117 at 30% RH. The SPI membrane displayed good water stability at 80 °C and was thermally stable up to 240 °C. It showed reasonable mechanical strength of a modulus of 1.3 GPa at 90 °C and 90% RH. Its methanol permeability $P_M$ was $0.57 \times 10^{-6}$ cm$^2$/s at 30 °C and 8.6 wt% methanol in feed, which was a fourth of that of Nafion 117. As a result, its ratio of $\sigma/P_M$ was $21 \times 10^4$ S cm$^{-3}$ s, which was about 4 times larger than that of Nafion 117, suggesting potential application of the SPI membrane for direct methanol fuel cell.

*Keywords:* Sulfonated polyimide; Proton conductivity; Methanol permeability

---

## 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 [1,2]. Hydrated perfluorosulfonic acid membranes, such as DuPont's Nafion membrane, are typically used as the polymer electrolytes in low-temperature hydrogen PEM fuel cells because of their excellent chemical and mechanical stability, as well as high proton conductivity [3]. However, they have some disadvantages that limit their industrial applications. These include high cost and low operating temperature and high methanol permeability [4]. In direct methanol fuel cells (DMFCs), which have many advantages over hydrogen PEM fuel cells, the methanol permeation through the membrane causes a serious problem of so called methanol crossover [5]. The membranes in DMFCs should be both good proton conductors and methanol barriers.

These promote research interests in developing alternative non-fluorinated materials with low cost and high performance. So far, many kinds of sulfonated polymers such as sulfonated polyether ether ketone [6], sulfonated polysulfone [7], sulfonated poly(arylene ether sulfone) [8], sulfonated polybenzimidazole [9], sulfonated poly(styrene) [10], and sulfonated poly(phenylene sulfide) [11] have been developed for the application of fuel cells. The introduction of sulfonic acid groups is realized either by direct sulfonation of the parent polymers or by polymerization of sulfonated monomers. Recently, sulfonated polyimides have been developed and are expected to be promising materials for polymer electrolyte fuel cells [12–19].

Because of their excellent thermal, chemical, and mechanical durability, polyimides have attracted much attention for their potential use in many industrial fields including microelectronic industries and separation membrane industries [20]. These advantages of polyimides are

---

* Corresponding author. Tel.: +81-836-85-9660; fax: +81-836-85-9601.
*E-mail address:* okamotok@po.cc.yamaguchi-u.ac.jp (K. Okamoto).

0032-3861/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0032-3861(03)00439-7

also favorable for PEM fuel cells. Mercier and co-workers synthesized a series of sulfonated copolyimides with different ion exchange capacity (IEC) from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and a commercialized sulfonated diamine monomer, 2,2′-benzidinedisulfonic acid (BDSA) [12–14]. The sulfonation degrees are controlled by copolymerization with non-sulfonated diamine monomers. Their results showed low proton conductivities less than 0.02 S/cm in water due to the low IEC, which is essential for maintaining water stability of the membrane. Litt's group also prepared a series of sulfonated copolyimides from NTDA, BDSA, and rigid and bulky or angled non-sulfonated diamines [15]. They reported that these sulfonated copolyimides having bulky comonomer units had high proton conductivity in the whole relative humidity (RH) range. The introduction of non-sulfonated diamines such as 2,2′-bis(trifluoromethyl)benzidine decreased the proton conductivity but the water stability was improved. Our group originally synthesized a series of novel sulfonated (co)polyimides from NTDA and sulfonated diamine of 4,4′-diaminodiphenyl ether-2,2′-disulfonic acid (ODADS) prepared by direct sulfonation of 4,4′-diaminodiphenyl ether (ODA) [16]. Successively, other sulfonated (co)polyimides were developed from NTDA and novel sulfonated diamines such as 9,9-bis(4-aminophenyl)fluorene-2,7-disulfonic acid (BAPFDS) [17] and 4,4′-bis(4-amino-phenoxy)biphenyl-3,3′-disulfonic acid (BAPBDS) [18,19], by the similar methods. It was found that these novel sulfonated diamine-based (co)polyimides had higher proton conductivities and better water stability than those of BDSA-based (co)polyimides.

To date, most of the proton conductive polymers have similar structures that the sulfonic acid groups are directly bonded 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 [8]. Polymers having sulfonic acid groups bonded to the side chains might have different properties from the main chain type ones. Bae et al. [21] synthesized a series of alkylsulfonated polybenzimidazole (PBI) from alkylsultone and PBI as polymer electrolytes. Their results showed quite different proton conducting performance of PBI with different length of side chains. The PBI–PS (propanesultone) membrane showed proton conductivities lower than $10^{-4}$ S/cm below 100 °C at 100% RH; while PBI–BS (butanesultone) displayed proton conductivities in the order of $10^{-2}$ S/cm under the same conditions [21]. Glipa et al. [22] reported the proton conductivities of methylbenzenesulfonated PBI prepared by grafting of sulfonated aryl groups on to polybenzimidazole. They reported a proton conductivity of $10^{-2}$ S/cm at 40 °C under 100% RH of this kind of polymer. Hay and co-workers [23] synthesized a series of sulfonated arylene ether/fluorinated alkane copolymers. They reported that the hydrated polymers showed proton conductivity of $3.4 \times 10^{-3}$ S/cm at temperatures up to 170 °C. Gieselman and Reynolds [24,25] also prepared a series of polybenzimidazole-based polyelectrolytes with sulfonic acid groups in the side chains but the proton conductivity was not mentioned. Rikukawa and co-workers [26,27] synthesized a series of sulfonated poly(4-phenoxybenzoyl-1,4-phenylene) (S-PPBP) and reported proton conductivities of $10^{-2}$ S/cm at room temperature and 100% RH.

In this article, a novel sulfonated diamine monomer, 3-(2′,4′-diaminophenoxy)propane sulfonic acid (DAPPS), is synthesized and the homopolyimide having sulfonic acid groups in the side chains is prepared from DAPPS and NTDA. Its physical properties, proton conductivity, methanol permeability and water stability are investigated.

## 2. Experimental

### 2.1. Materials

NTDA, 2,4-dinitrophenol and 3-bromopropane sulfonic acid sodium salt were purchased from Tokyo Kasei Co. NTDA was purified by vacuo sublimation prior to use. 2,4-Dinitrophenol and 3-bromopropane sulfonic acid sodium salt were used as received. Dimethylformamide (DMF) and triethylamine ($Et_3N$) were purified by distillation under reduced pressure and dehydrated with 4 Å molecular sieves prior to use. Other reagents were used as received.

### 2.2. Synthesis of 3-(2′,4′-dinitrophenoxy)propane sulfonic acid sodium salt (1)

To a completely dried 100 ml of 4-neck flask equipped with a Dean-Stark trap and a condenser were added 1.84 g (10.0 mmol) of 2,4-dinitrophenol and 10 ml of DMF with stirring under nitrogen flow. 0.40 g of NaOH (10.0 mmol) solution in 0.6 ml of water was added to the flask. The mixture was stirred at room temperature for 0.5 h and then 15 ml toluene was added. The reaction mixture was heated to reflux for 2 h, the produced water was evaporated as an azeotrope with toluene and collected in the Dean-Stark trap. When the reaction mixture was cooled to room temperature, 2.25 g (10.0 mmol) of 3-bromopropanesulfonic acid sodium salt was added in one portion. The reaction solution was then reheated up to 110 °C for 48 h. After cooling to room temperature, the solution mixture was filtered, the filtrate was distilled under reduced pressure and the solid was dried in vacuo. The obtained crude product was recrystallized from a mixture of ethanol/water (2:1 v/v) to give 1.60 g of slightly yellow solid product, which was dried in vacuo (Yield: 48%). mp (DSC): 171 °C. IR (KBr, $cm^{-1}$): 3598, 3086, 2979, 2948, 2882, 1616, 1523, 1367, 1285, 1209, 1174, 1061, 1020, 936, 915, 837, 796, 744, 629. $^1H$ NMR spectrum (DMSO-$d_6$, ppm): 8.85–8.70, 1H (phenyl ring), s; 8.65–8.45, 1H (phenyl ring), d; 7.69–7.50, 1H (phenyl

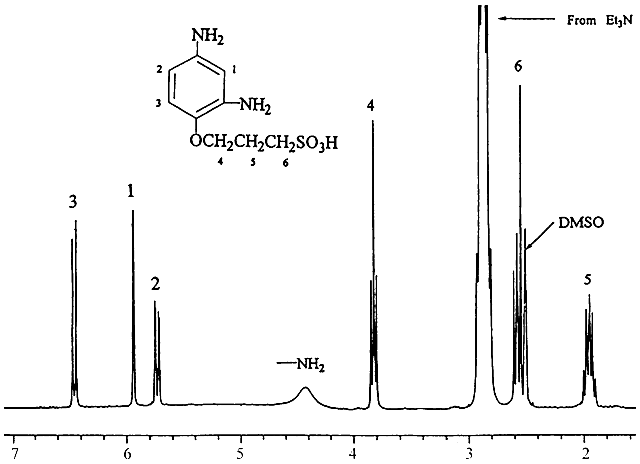


Fig. 1. $^1$H NMR spectrum of DAPPS.

ring), d; 4.55–4.35, 2H (–$OCH_2$–), t; 2.75–2.52, 2H (–$CH_2SO_3Na$–), t; 2.19–1.96, 2H (–$CH_2$–), m.

### 2.3. Synthesis of hydrochloric acid salt (2) of DAPPS

To a 100 ml of 4-neck flask were charged 1.64 g (5.0 mmol) of compound **1**, 6 ml of distilled water and 6 ml of ethanol, with stirring under nitrogen flow. Then 0.1 g of palladium/activated carbon was added. When the reaction temperature was raised to 90 °C, 4 ml of hydrazine monohydrate was added dropwise. After hydrazine monohydrate solution was completely added, the reaction was kept at this temperature for 20 h. After cooling to room temperature, the mixture was filtered into 6 ml of concentrated hydrochloric acid solution. Then the filtrate was poured into 100 ml acetone, and the precipitate was filtered off, washed with acetone and dried in vacuo at 60 °C for 20 h. 1.31 g of grey brown product was obtained (Yield: 92%). mp (DSC): 211.6 °C. IR (KBr, $cm^{-1}$): 3435, 2883, 2598, 1983, 1638, 1509, 1470, 1406, 1287, 1189, 1050, 1019, 873, 817, 787, 724, 614, 579. $^1$H NMR spectrum (DMSO-$d_6$, $Et_3N$ was added for dissolution in DMSO) of DAPPS is shown in Fig. 1.

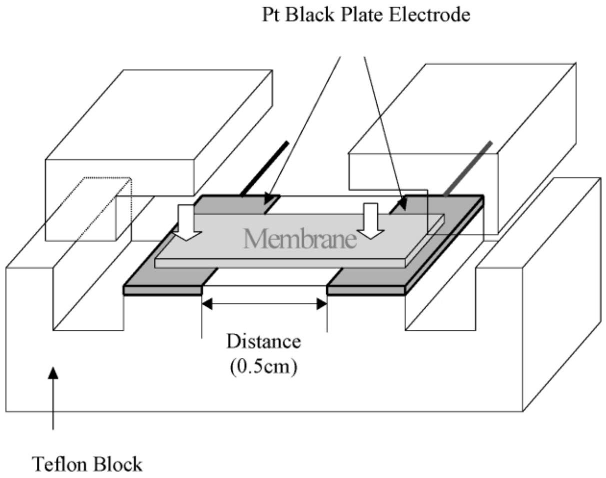


Fig. 2. Schematic diagram of proton conductivity measurement cell.

### 2.4. Polymer synthesis

To a 100 ml completely dried 4-neck flask were added 0.850 g (3 mmol) of DAPPS, 7 ml of *m*-cresol, and 0.92 ml of $Et_3N$, with stirring under nitrogen flow. After DAPPS was completely dissolved, 0.804 g (3 mmol) of NTDA and 0.52 g of benzoic acid were added to the flask. The mixture was heated to 80 °C for 4 h and then 180 °C for 20 h. After cooling to room temperature, additional 10 ml of *m*-cresol was added to dilute the highly viscous solution. The solution mixture was poured into acetone. The resulting fiber-like precipitate was collected by filtration, washed with acetone, and dried in vacuo.

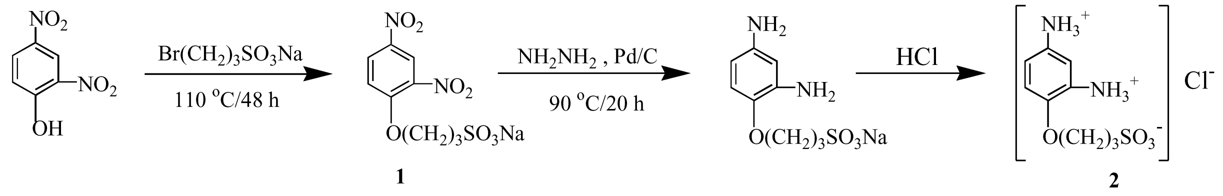
### 2.5. Membrane formation and proton exchange

The resulting sulfonated polyimide (SPI) in triethylammonium salt form was dissolved in DMSO, and the solution (5 wt%) was cast onto glass dish and dried at 80 °C for 10 h. The as-cast membrane was soaked in methanol at 60 °C for 1 h to remove the residual solvent, and then the proton exchange was performed by immersing the membrane into 1.0 N hydrochloric acid solution at room temperature for 10 h. The proton-exchanged membrane was thoroughly washed with de-ionized water and then dried in vacuo at 150 °C for 10 h.

### 2.6. Measurements

Infrared (IR) spectra were recorded on a Horiba FT-200 spectrometer as KBr pellets. $^1$H NMR spectra were recorded on a JEOL EX270 (270 MHz) instrument. Differential scanning calorimetry (DSC) was performed on a Seiko DSC-5200 at a heating rate of 5 °C/min. Thermogravimetry–Mass spectrometry (TG–MS) was performed on a JEOL MS–TG/DTA220 in helium (flow rate: 100 $cm^3$/min) at a heating rate of 5 °C/min. Dynamic mechanical analysis was performed on a (IT company) DVA-220/L2 spectrometer at temperatures below 100 °C and RH ranging from 0 to 90%. Gel permeation chromatography (GPC) was performed with an HLC-8020 apparatus (column: Shodex KD-80 M). NMP was used as the eluant at a flow rate of 1.0 ml/min. Polymer solution containing 0.05 M of LiCl and 0.05 M of phosphoric acid was filtered through a 0.5 μm PTFE filter prior to injecting into the column. Molecular weight was calculated against poly(ethylene oxide) standards.

Proton conductivity was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency ranging from 100 Hz to 100 KHz (Hioki 3552). The schematic diagram of the measurement cell is illustrated in Fig. 2. A four-point-probe cell with two blackened platinum plate electrodes was mounted on a



Scheme 1.

Teflon plate at 0.5 cm distance. The cell was placed in either a thermo-controlled humidic chamber to measure the temperature and humidity dependence of proton conductivity (for measurement at RH lower than 100%) or de-ionized water. The resistance value associated with the membrane conductance was determined from high-frequency intercept of the impedance with the real axis. Proton conductivity was calculated from the following equation:

$$\sigma = d/(L_s w_s R) \tag{1}$$

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 measurement in liquid water, the swollen membrane thickness was used in the calculation of $\sigma$.

Water vapor sorption at different water vapor activities ($a_w < 1$) was performed at 50 °C using a sorption apparatus (BEL-18SP) by means of a volumetric method. The weight of membrane samples used was 80–100 mg. Water uptake of the membrane was also measured by immersing two sheets of polyimide membranes (20–30 mg per sheet) into de-ionized water at a given temperature for 5 h. Then the films were taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake (WU) of the film was calculated from:

$$\mathrm{WU} = (W_s - W_d)/W_d \times 100\% \tag{2}$$

where $W_d$ and $W_s$ are the weights of dry and corresponding water-swollen film sheets, respectively. Water uptake of the polyimide was estimated from the average value of WU of each sheet.

The IEC of the polyimide was confirmed by classical titration. The dry membranes were soaked in a saturated NaCl solution. Released protons were titrated using 0.01 N NaOH solution.

Density of SPI membrane (40 μm in thickness and 2.6 cm in diameter) was measured by the floating method using mixtures of carbon tetrachloride and xylene at a room temperature. The density was measured for a membrane at both a standard condition of 70% RH and fully hydrated state. Dimensional change of the polyimide 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:

$$\Delta L_c = (L - L_s)/L_s$$

$$\Delta D_c = (D - D_s)/D_s \tag{3}$$

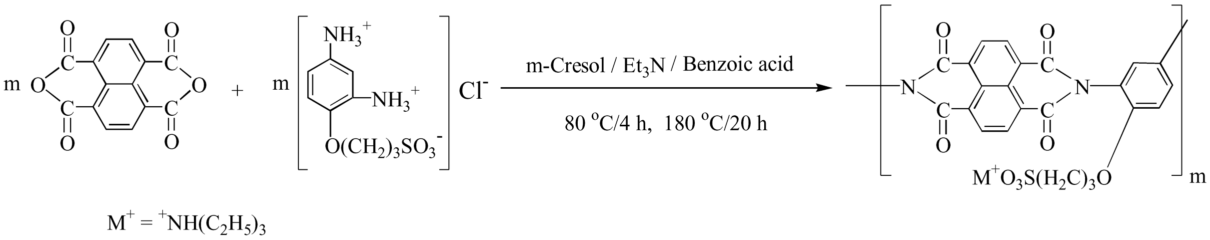
where $L_s$ and $D_s$ are the thickness and diameter of the membrane equilibrated at 70% RH, respectively; $L$ and $D$ refer to those of the membrane immersed in liquid water for 5 h. In this case, the dry films were difficult to be measured due to the shrink after being dried at 150 °C for 10 h. The shrunk films were first immersed in water to get smooth samples and then taken out and placed at ambient condition (70% RH) for 24 h, followed by the measurement of density and size as standards.

Methanol permeability of membranes was measured using a liquid permeation cell composed of two compartments, which were separated by a vertical membrane. The membrane was first immersed in water for 2–4 h to get the well-swollen sample and then set into the measurement cell (effective area: 16 $\mathrm{cm}^2$). One compartment of the cell ($V_A = 350$ ml) was filled with a mixture solution of methanol (8.6 wt%), 2,2-dimethyl-1-propanol (1 wt%) and de-ionized water. The other ($V_B = 109\ ml$) compartment was filled with 2,2-dimethyl-1-propanol (1 wt%) and de-ionized water. 2,2-dimethyl-1-propanol was used as an internal standard. The compartments were stirred continuously during the permeability measurement. The 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 Polarpack Q (poly(ethylene glycol)-1000 supported on Shimalite F). The methanol permeability, $P_M$, was determined by the following equation:

$$q = AP_M \cdot \frac{\Delta C_{av}}{L} t$$

$$\Delta C_{av} = (C_{A0} + C_A - C_B)/2 \tag{4}$$

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



Scheme 2.

## 3. Results and discussion

### 3.1. Synthesis and characterization of monomer and polyimide

As shown in Scheme 1, DAPPS was synthesized via two-step reactions. At first, 2,4-dinitrophenol reacted with 3-bromopropane sulfonic acid sodium salt in DMF to give the intermediate compound **1**. Then **1** was reduced in ethanol/water mixture using hydrazine monohydrate as the reducing agent and Pd/C as the catalyst to give the sulfonated diamine, which was treated with hydrochloric acid solution to get the hydrochloric acid salt **2** of DAPPS. The chemical structure of the obtained product was characterized by IR and $^1H$ NMR spectra. $^1H$ NMR spectrum of DAPPS is shown in Fig. 1. In this case, $Et_3N$ was employed to liberate the protons of amine group.

NTDA–DAPPS polyimide was synthesized by a one-step method in *m*-cresol in the presence of $Et_3N$ and benzoic acid (Scheme 2) [12]. The resulting SPI was in the triethylammonium salt form and was converted to the proton form by treating it with 1.0 N hydrochloric acid solution. The completion of proton exchange was confirmed from the disappearance of the peaks corresponding to the protons of $Et_3N$ in the $^1H$ NMR spectra of the SPI. Table 1 lists IEC and elementary analysis results of the SPI. The IEC value obtained from titration was 5% smaller than the theoretical value. The elementary analysis results were different from the calculated ones, but this was attributed to a small amount (4%) of sorbed water in the sample. The SPI in both triethylammonium salt form and proton form was soluble in common organic solvents such as *m*-cresol, DMSO and DMF. The molecular weight ($M_w$) of the SPI was about $5.5 \times 10^4$ ($M_w/M_n = 3.1$).

Fig. 3 shows the thermal stability of NTDA–DAPPS membrane by means of TG–MS analysis. The initial weight loss around 100 °C was due to the loss of sorbed water in the sample. The second stage weight loss starting from 240 °C was attributed to the decomposition of the aliphatic side chain ($-OCH_2CH_2CH_2-$) and the sulfonic acid group judging from the evolution of propene ($M = 42$), propadiene ($M = 40$), sulfur dioxide and water. The decomposition temperature of sulfonic acid group was slightly lower than that of wholly aromatic SPIs [12,16,17]. The evolution of sulfur dioxide reached maximum at around 290 °C. The third stage weight loss (450–700 °C) was attributed to the decomposition of the polymer backbone.

The dynamic mechanical properties of NTDA–DAPPS membrane under different RH are shown in Fig. 4. It can be seen that under a certain RH, there was no appreciable change in dynamic modulus $E'$ as temperature increased from room temperature to 90 °C. At completely dry state, the SPI membrane had a dynamic modulus $E'$ of 2.9 GPa. With an increase in RH, the dynamic modulus decreased down to 1.3 GPa at 90% RH. This is because at a higher RH the membrane had a higher water vapor sorption leading to a larger swelling degree. The SPI membrane was tough enough at high moisture conditions, which is favorable for practical application in PEMFC.

### 3.2. Water vapor sorption

The water vapor sorption isotherms of sulfonated polymers are shown in Fig. 5. With an increase in $a_w$, the WU increased sigmoidally. Polymers with higher IEC values showed higher WUs (Fig. 5(a)). Excluding the affect of IEC, the sorption isotherms in a form of the number of sorbed water molecules per sulfonic acid group, $\lambda$, vs. $a_w$ are shown in Fig. 5(b). The $\lambda - a_w$ isotherms of NTDA–ODADS/ODA(1/1) and NTDA–ODADS/ODA(3/1) were similar to that of Nafion 117. However, the $\lambda - a_w$ isotherm of NTDA–DAPPS was different from those of these polymers. NTDA–DAPPS showed lower $\lambda$ values at low water activities ($a_w < 0.6$), whereas higher $\lambda$ values at high water activities ($a_w > 0.8$).

From Fig. 5(a), the WU values in saturated water vapor

Table 1
IEC and elementary analysis of NTDA–DAPPS polyimide in proton form

| | IEC (meq/g) | C (%) | H (%) | N (%) | O (%) | N/C |
|---|---|---|---|---|---|---|
| Calcd | 2.09 | 57.74 (55.44) | 2.95 (3.26) | 5.86 (5.62) | 26.75 (29.26) | 0.1015 (0.1014) |
| Found | 1.98 | 55.65 | 3.53 | 5.71 | 31.53 | 0.1026 |

The values in parenthesis are the calculated values for the sample containing 4 wt% of water.

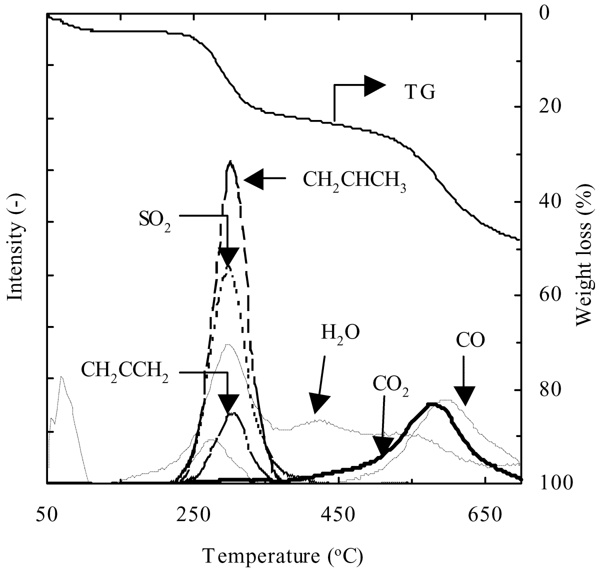


Fig. 3. Thermogravimetry–Mass spectrometry of NTDA–DAPPS membrane.

($a_w = 1$) were estimated to be about 20 and 70 g/100 g dry polymer (abbreviated as % here after) for Nafion 117 and NTDA–DAPPS, respectively. On the other hand, the WU values in liquid water at 50 °C were measured to be 35 and 105% for Nafion 117 and NTDA–DAPPS membranes, respectively. The membranes were much more swelled in liquid water than in saturated water vapor resulting from larger molecular relaxation of polymer chain in liquid water.

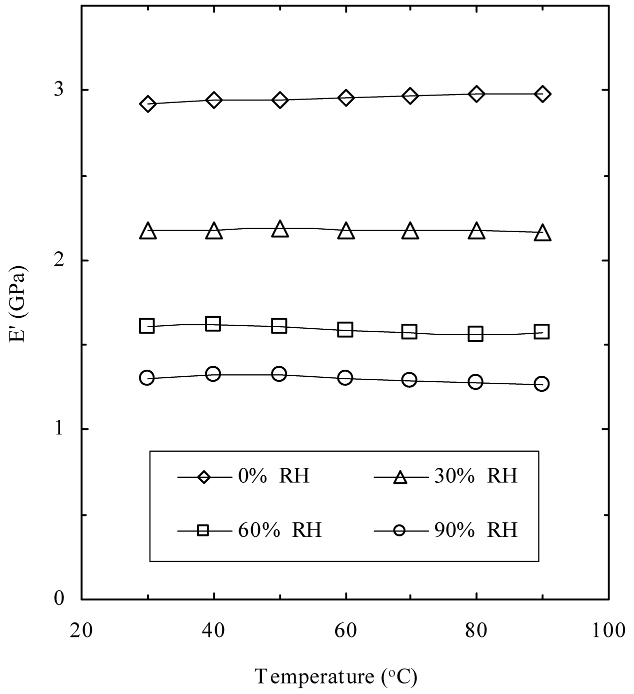


Fig. 4. Mechanical strength of NTDA–DAPPS polyimide membrane under various moisture conditions.

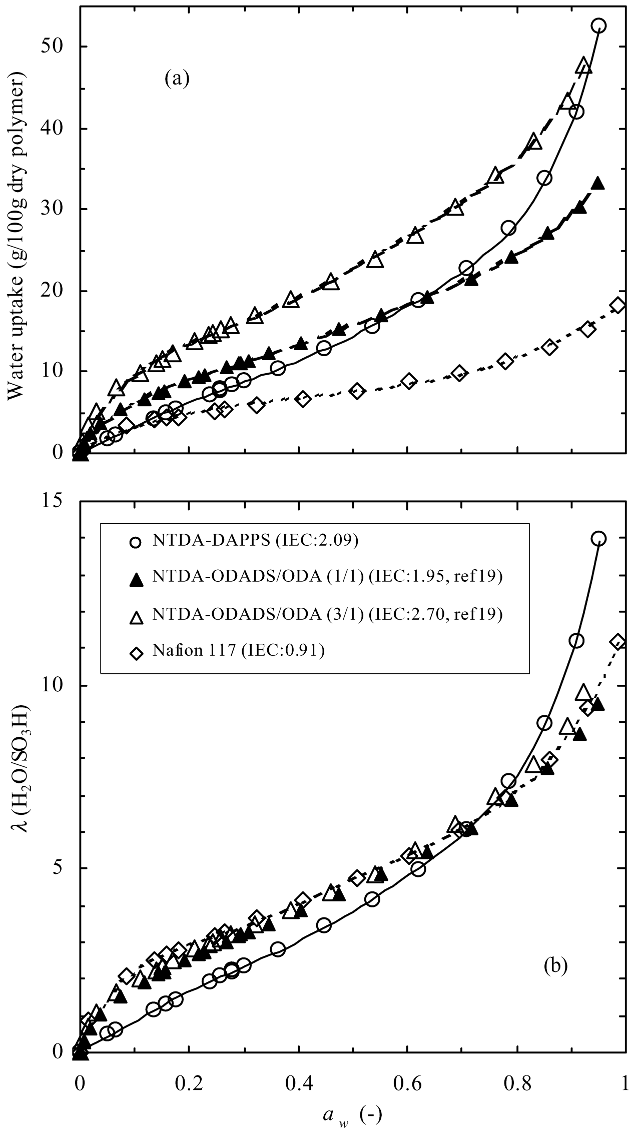


Fig. 5. Water vapor sorption isotherms of sulfonated polymer membranes at 50 °C.

### *3.3. Proton conductivity*

Fig. 6 shows the proton conductivities of sulfonated polymer membranes as a function of RH at 50 °C. With an increase in RH, the proton conductivities increased significantly. NTDA–DAPPS displayed proton conductivities similar to or slightly lower than that of NTDA–ODADS/ODA (3/1) [19] in the whole RH range. This is because the latter had a higher IEC as well as higher WU (see Fig. 5). The proton conductivity of Nafion 117 membrane has been widely investigated in several research groups but the deviation between the results is great. The data of Nafion 117 in Fig. 6, which were in consistent with those reported by Miyake et al. [4], were determined in our lab. NTDA–DAPPS and NTDA–ODADS/ODA (3/1) membranes displayed lower proton conductivities than Nafion 117 in the range of RH < 100%, whereas in fully

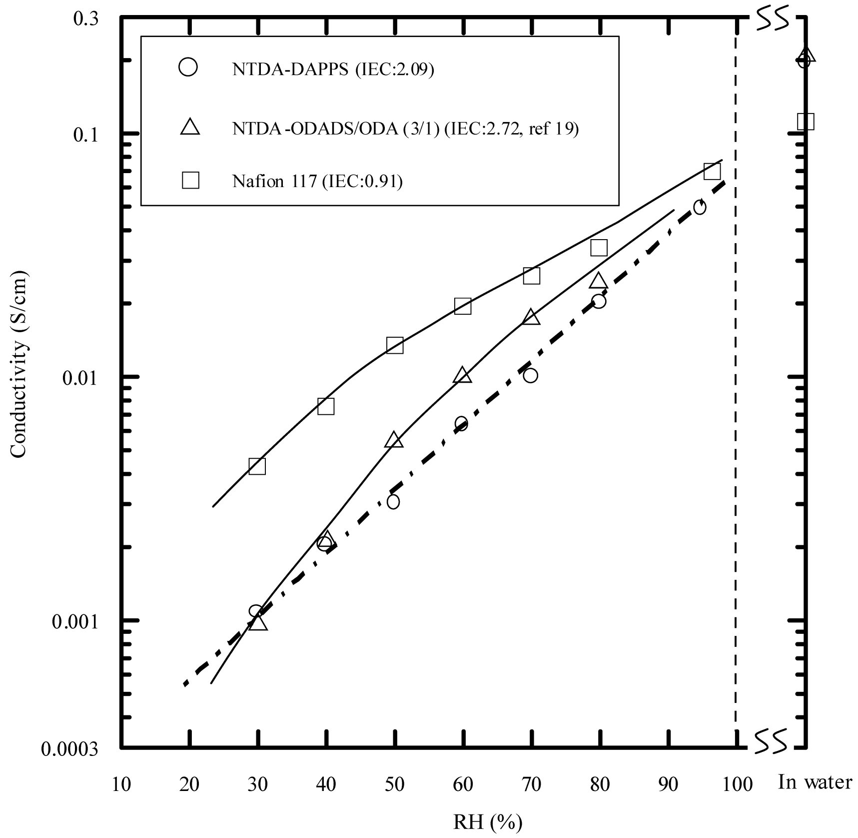


Fig. 6. Proton conductivity of sulfonated polymer membranes as a function of RH at 50 °C.

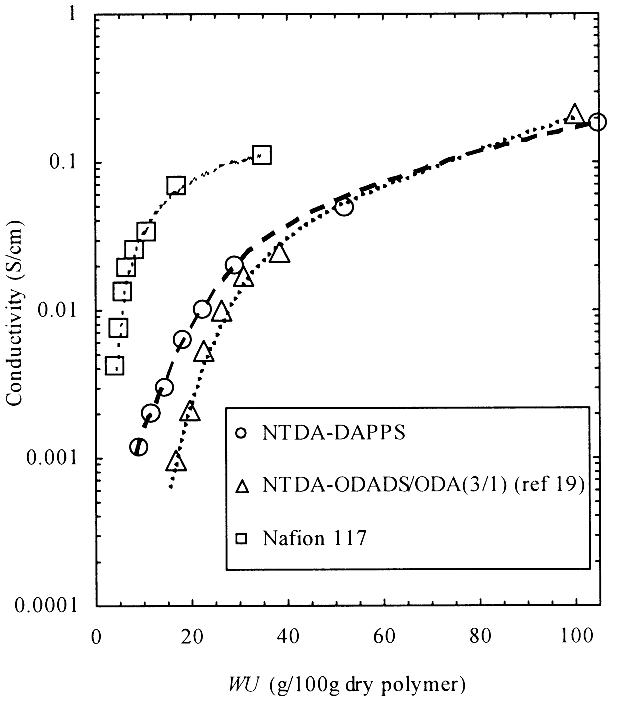


Fig. 7. Proton conductivity of sulfonated polymer membranes as a function of WU at 50 °C.

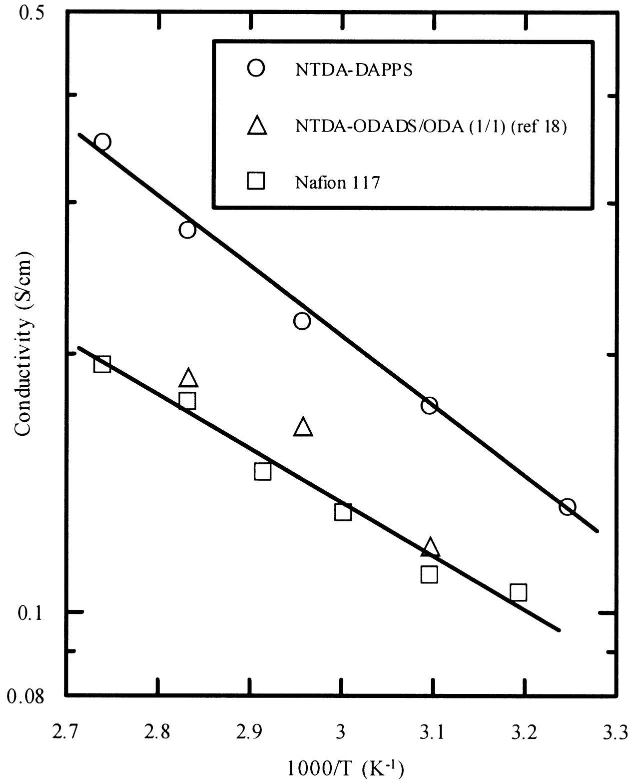


Fig. 8. Proton conductivity of sulfonated polymer membranes immersed in liquid water as a function of temperature.

Table 2
Water uptake and proton conductivity of polyelectrolytes under high moisture conditions

| Membranes | IEC[a] (meq/g) | $T$ (°C) | RH (%) | WU[b] (g/100 g dry polymer) | $\sigma$(S/cm) | Ref. |
|---|---|---|---|---|---|---|
| NTDA–DAPPS | 2.09 (1.98) | 50 | 90 | 40 | 0.035 | This study |
| | | 50 | In water | 105 | 0.18 | This study |
| PBI-BzS | 1.57 | 40 | 100 | 33 | 0.017 | [22] |
| S-PPBP | 1.85 | 50 | 100 | 29 | 0.01 | [27] |
| S-PPQ | 3.51 | 20 | – | 51 | 0.0098 | [29] |
| SPSU | (1.25) | 80 | – | – | 0.043 | [30] |
| PBI-BS | – | 50 | 90 | – | 0.17 | [31] |

[a] The data in parenthesis are experimental values and others are calculated values.
[b] Measured at 50 °C in this study and others at room temperature.

hydrated state (in water), these SPI membranes showed higher proton conductivities than Nafion 117.

The relationship between proton conductivity and water uptake of sulfonated polymer membranes is shown in Fig. 7. With an increase in WU, the $\sigma$ value increased first significantly and then gradually. It can be seen that Nafion 117 had low WU but high conductivities. Even with a very small increase in WU in the range of less than 10%, the proton conductivity increased drastically. This is because Nafion 117 possesses high ion density clusters that have been proposed to form ion-rich channels being favorable for proton transport [28]. On the other hand, the SPI membranes needed much more WUs to display the proton conductivities similar to those of Nafion 117, probably because of the absence of such clear ion-rich domains. It is interesting that NTDA–DAPPS displayed higher proton conductivities than NTDA–ODADS/ODA (3/1) in the similar WU level except for the fully hydrated state (WU of around 100%). In the fully hydrated state, these two SPI membranes displayed similar $\sigma$ values of around 0.2 S/cm, which were about two times larger than that of Nafion 117 (0.11 S/cm). This suggests that the proton conduction paths of sulfonic acid groups and sorbed water molecules are developed well enough to give high proton conductivity for these SPI membranes equilibrated in liquid water and that the higher conductivity of the SPIs compared with Nafion 117 is due to the larger number of proton carriers as a result of the higher IECs.

Fig. 8 shows the temperature dependence of proton conductivities of sulfonated polymer membranes in liquid water. With an increase in temperature, the proton conductivity of NTDA–DAPPS increased up to 0.35 S/cm at 90 °C with an apparent activation energy of about 16 KJ/mol, which was a little larger than that of Nafion 117 (12 KJ/mol).

Table 2 shows comparison of the proton conductivity between NTDA–DAPPS and other polyelectrolytes. Methylbenzene sulfonated polybenzimidazole (PBI-BzS) showed $\sigma$ of 0.017 S/cm at 40 °C and 100% RH [22], which was about a half of that of NTDA–DAPPS under the similar conditions. Linkous [29] reported on sulfonated aromatic polymers such as S-PEEK, S-PES and S-PPQ, among which the most conductive material, sulfonated polyphenylquinoxaline (S-PPQ), had a $\sigma$ of $9.8 \times 10^{-3}$ S/cm. Passalacqua and co-workers [30] synthesized a series of sulfonated polysulfone (SPSU) membranes and reported a best proton conductivity of $4.3 \times 10^{-2}$ S/cm at 80 °C and 100% RH. Recently, Manabe et al. [31] reported on PBI-BS with a higher IEC, which displayed high proton conductivity of 0.17 S/cm at 50 °C and 90% RH. Thus, the proton conductivity of NTDA–DAPPS was comparable to or higher than those of other sulfonated polymers.

### 3.4. Membrane stability

The membrane stability toward water for NTDA–DAPPS and other SPIs are listed in Table 3. The stability test of the polyimide membranes was carried out by immersing the samples into de-ionized water at a given temperature (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.

We have previously reported that besides IEC the structural flexibility as well as the basicity of the sulfonated diamine moieties also had great effects on water stability of SPI membranes [17]. Polyimides with high basicity of the sulfonated diamine moieties and flexible main chain tend to have good water stability because the high basicity depresses the hydrolysis of imido ring and the flexibility allows easy relaxation of polymer chain. This is why ODADS and BAPFDS-based polyimides had much better water stability than the corresponding BDSA-based ones with similar IEC [16,17]. Although the backbone of

Table 3
Water stability of SPI membranes at 80 °C

| Polyimide | IEC[a] (meq/g) | Time[b] (h) | Ref. |
|---|---|---|---|
| NTDA–DAPPS | 2.09 | 200 | This study |
| NTDA–BAPFDS/ODA(2/1) | 2.09 | <7 | [17] |
| NTDA–ODADS/ODA(1/1) | 1.95 | 25 | [16] |
| NTDA–BAPBDS | 2.63 | >1000 | [18] |

[a] Calculated value.
[b] Elapsed immersion time when the samples began to loose the mechanical strength.

Table 4
Results of Fenton's reagent test of SPI membranes at 30 °C

| Membranes | IEC (meq/g) | Thickness (μm) | $\tau_1$[a] (h) | $\tau_2$[a] (h) | Ref. |
|---|---|---|---|---|---|
| NTDA–DAPPS | 2.09 | 20 | 10 | 13 | This study |
| NTDA–ODADS/ODA (1/1) | 1.95 | 29 | 24 | – | [16] |
| NTDA–BAPFDS/ODA (2/1) | 2.09 | 30 | 16 | – | [17] |

Concentration of Fenton's reagent: 30 ppm $FeSO_4$ in 30% $H_2O_2$.

[a] $\tau_1$ and $\tau_2$ refer to the elapsed time that the membranes began to dissolve and dissolved completely.

NTDA–DAPPS is rather rigid, the basicity of DAPPS is clearly much higher than those of ODADS and BAPFDS due to the electron donating effect of the alkoxy group, resulting in better water stability. Nevertheless, NTDA–DAPPS membrane showed obviously lower water stability compared with NTDA–BAPBDS. This is probably because the latter has not only high basic moiety but also a flexible structure. The more detailed relationship between polymer structure and water stability is in progress.

The density of NTDA–DAPPS membrane equilibrated at 70% RH (with a WU of 23%) was measured to be 1.452 g/cm$^3$. The fully hydrated membrane with a WU of 91% showed a density of 1.305 g/cm$^3$. The dimensional changes of NTDA–DAPPS membrane were determined using the 70% RH as the standard, because at the dry state the membrane thickness and diameter could not be measured successfully because of the shrink of membrane. In water, the membrane thickness increased by 12% ($\Delta L_c$) and the diameter increased by 15% ($\Delta D_c$), indicating rather isotropic membrane swelling of this kind of SPI.

The oxidative stability of NTDA–DAPPS was also investigated by immersing the samples (the size of each sheet: 1.0 × 1.0 cm$^2$) into Fenton's reagent (30 ppm $FeSO_4$ in 30% $H_2O_2$; see Ref. [23]) at 30 °C. The oxidative stability of the samples was characterized by the elapsed time that the membranes started to dissolve and dissolved completely in the solution. As listed in Table 4, NTDA–DAPPS membrane showed poorer oxidative stability than ODADS and BAPFDS-based polyimide membranes. This is probably due to its alkoxy linkage in the side chains. However, the oxidative stability of NTDA–DAPPS is still higher than other sulfonated arylene ether/fluorinated alkane copolymers reported in literature [23] under the same conditions (dissolved in Fenton's reagent within 6 h at 25 °C).

### *3.5. Methanol permeability*

Table 5 lists the proton conductivity and methanol permeability and their ratio $\phi$ ($\phi = \sigma/P_M$) of NTDA–DAPPS and Nafion 117 membranes. The data of Nafion 117 and sulfonated poly(styrene) with 20% sulfonation degree (SPS$_{20}$) in Ref. [10] are also listed for comparison. The $P_M$ values of Nafion 117 were reported as 2.3 and $2.6 \times 10^{-6}$ cm$^2$/s at room temperature [32,33], which are in consistent to the present value of $2.2 \times 10^{-6}$ cm$^2$/s at 30 °C. The $P_M$ values of NTDA–DAPPS were about a fourth and a half of those of Nafion 117 at 30 and 50 °C, respectively. As a result, NTDA–DAPPS showed about 4 times larger $\phi$ values than Nafion 117. Compared with SPS$_{20}$, NTDA–DAPPS showed similar $P_M$ values and about 2 times larger $\sigma$ values and as a result about 2 times larger $\phi$ values. Thus, NTDA–DAPPS membrane had higher proton conductivity and lower methanol permeability. Judging from the water stability at 80 °C mentioned above, NTDA–DAPPS membrane is considered to have much longer water durability at temperatures below 50 °C, and therefore, it might be a potential polyelectrolyte for DMFC application at lower temperatures.

## 4. Conclusions

1. A novel sulfonated diamine, DAPPS, and the corresponding polyimide bearing sulfonic acid groups in the side chains were successfully synthesized.
2. NTDA–DAPPS membrane displayed higher proton conductivities at higher WU levels. In the fully hydrated state, it displayed higher proton conductivities than Nafion 117, whereas in the range of lower WU it displayed much lower conductivities than Nafion 117 but larger ones than NTDA–ODADS/ODA (3/1).

Table 5
Proton conductivity, methanol permeability and their ratio of sulfonated polymer membranes

| Membranes | IEC (meq/g) | $\sigma$ (S/cm)[a] | | $P_M$ ($10^{-6}$ cm$^2$/s)[b] | | $\phi = \sigma/P_M$ ($10^4$ S cm$^{-3}$ s) | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | 30 °C | 50 °C | 30 °C | 50 °C | 30 °C | 50 °C | |
| NTDA–DAPPS | 2.09 | 0.12 | 0.18 | 0.57 | 1.57 | 21 | 11.5 | This study |
| Nafion 117 | 0.91 | 0.105 | 0.11 | 2.2 | 3.3 | 4.8 | 3.3 | This study |
| Nafion 117 | 0.91 | – | – | – | – | 6.0[c] | 4.2[d] | [10] |
| SPS$_{20}$ | 1.41 | 0.05[c] | 0.086[d] | 0.52[c] | 1.19[d] | 9.6[c] | 7.2[d] | [10] |

[a] Measured in water.

[b] Methanol concentration in feed:8.6 wt%.

[c] Measured at 22 °C.

[d] Measured at 60 °C.

3. NTDA–DAPPS membrane exhibited much better water stability compared with ODADS and BAPFDS-based ones due to the high basicity of DAPPS resulting from the electron-donation effect of alkoxy group.
4. NTDA–DAPPS membrane showed much lower methanol permeability and as a result, much larger $\phi$ values compared with Nafion 117, suggesting potential as polyelectrolyte for DMFC applications. Further investigations are in progress as for its analogous SPIs [34].

## Acknowledgements

This work was supported partly by a Grant-in-aid for Exploratory Research (No 14655294) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

## References

[1] Savadogo O. J New Mater Electrochem Syst 1998;1:47.

[2] Acres GJK. J Power Sources 2001;100:60.

[3] Sone Y, Ekdunge P, Simonsson D. J Electrochem Soc 1996;143:1254.

[4] Miyake N, Wainright JS, Savinell RF. J Electrochem Soc 2001;148:A898.

[5] Miyake N, Wainright JS, Savinell RF. J Electrochem Soc 2001;148:A905.

[6] Alberti G, Casciola M, Massinelli L, Bauer B. J Membr Sci 2001;185:73.

[7] Genova-Dimitrova P, Baradie B, Foscallo D, Poinsignon C, Sanchez JY. J Membr Sci 2001;185:59.

[8] Wang F, Hickner M, Kim YS, Zawodzinski TA, McGrath JE. J Membr Sci 2002;197:231.

[9] Staiti P, Lufrano F, Arico AS, Passalacqua E, Antonucci V. J Membr Sci 2001;188:71.

[10] Carretta N, Tricoli V, Picchioni F. J Membr Sci 2000;166:189.

[11] Miyatake K, Shouji E, Yamamoto K, Tsuchida E. Macromolecules 1997;30:2941.

[12] Faure S, Cornet N, Gebel G, Mercier R, Pineri M, Sillion B. In: Savadogo O, Roberge PR, editors. Proceedings of Second International Symposium on New Materials for Fuel Cell and Modern Battery Systems.; 1997. p. 818. July 6–10.

[13] Vallejo E, Porucelly G, Gavach C, Mercier R, Pineri M. J Membr Sci 1999;160:127.

[14] Genies C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M. Polymer 2001;42:359.

[15] Kim HJ, Litt M. Polym Prepr 2001;42:486. American Chemical Society Division of Polymer Chemistry.

[16] Fang J, Guo X, Harada S, Watari T, Tanaka K, Kita H, Okamoto K. Macromolecules 2002;35:9022.

[17] Guo X, Fang J, Watari T, Tanaka K, Kita H, Okamoto K. Macromolecules 2002;35:6707.

[18] Watari T, Fang J, Tanaka K, Kita H, Okamoto K, Hirano T. Kagaku Kogaku Ronbunshu 2003;29:165.

[19] Watari T, Fang J, Guo X, Tanaka K, Kita H, Okamoto K. ACS symp ser Adv Mater Membr Sep 2003; in press.

[20] Ghosh MK, Mittal KL. Polyimides: fundamentals and applications. New York: Marcel Dekker; 1996. p. 7.

[21] Bae JM, Honma I, Murata M, Yamamoto T, Rikukawa M, Ogata M. Solid State Ionics 2002;147:189.

[22] Glipa X, Haddad MEI, Jones DJ, Roziere J. Solid State Ionics 1997;97:323.

[23] Miyatake K, Oyaizu K, Tsuchida E, Hay AS. Macromolecules 2001;34:2065.

[24] Gieselman MB, Reynolds JR. Macromolecules 1992;25:4832.

[25] Gieselman MB, Reynolds JR. Macromolecules 1993;26:5633.

[26] Rikukawa M, Sanui K. Prog Polym Sci 2000;25:1463.

[27] Kobayashi T, Rikukawa M, Sanui K, Ogata N. Solid State Ionics 1998;106:219.

[28] Gier TD, Munn GE, Wilson FC. J Polym Sci, Polym Phys Ed 1981;19:1687.

[29] Kopitzke RW, Linkous CA, Anderson HR, Nelson GL. J Electrochem Soc 2000;147:1677.

[30] Lufrano F, Gatto I, Staiti P, Antonucci V, Passalacqua E. Solid State Ionics 2001;145:47.

[31] Manabe H, Kawahara M, Rikukawa M, Sanui K. Polym Prepr, Japan 2000;49:3215.

[32] Pivovar BS, Wang Y, Cussler EL. J Membr Sci 1999;154:155.

[33] Kim J, Kim B, Jung B. J Membr Sci 2002;207:129.

[34] Yin Y, Fang J, Kita H, Okamoto K. Chem Lett 2003;32:328.