Preparation of Sulfonated Copolyimides Containing Aliphatic Linkages as Proton-Exchange Membranes for Fuel Cell Applications

Hüseyin Deligöz, Sibel Vantansever, S. Naci Koç, Faruk Öksüzömer, Saadet Özgümüş, M. Ali Gürkaynak

Chemical Engineering Department, Engineering Faculty, Istanbul University, 34320 Avcılar-Istanbul, Turkey

ABSTRACT: A series of random sulfonated copolyimides containing aliphatic linkages (co-SPIAs) with controlled degrees of sulfonic acid groups were synthesized via a conventional two-step polyimidization method. 2,4-Diaminobenzene sulfonic acid (2,4-DABS) and 1,6-diaminohexane (DAH) were used as sulfonated aromatic diamine and nonsulfonated aliphatic diamine compounds, respectively. Mixtures of diamine compounds were reacted with benzophenonetetracarboxylic dianhydride (BTDA) to obtain the co-SPIAs. The molar ratios of DAH/2,4-DABS were systematically varied to produce copolymers with controlled compositions that contained up to 70 mol % sulfonic acid moieties. The co-SPIAs were evaluated for thermal oxidative stability, ion-exchange capacity (IEC), water uptake, proton conductivity, solubility, and hydrolytic stability. The proton conductivity and hydrolytic stability of the co-SPIAs were compared with the fully aromatic polyimide, sulfonated homo-polyimide (homo-SPI) (BTDA/2,4-DABS). From thermogravimetric analysis, we observed desulfonation temperatures in the range 200–350°C, which suggested a high stability of the sulfonic acid groups. The co-SPIAs with 40–70 mol % 2,4-DABS showed higher proton conductivity than Nafion 117 in water. The proton conductivity values of the co-SPIAs were mainly a function of IEC and water uptake. Furthermore, the hydrolytic stability of the 2,4-DABS-based sulfonated polyimide membranes were improved by the introduction of the nonsulfonated diamine with aliphatic linkages. The optimum concentration of 2,4-DABS was found to be around 40 mol % from the viewpoint of proton conductivity, IEC, and hydrolytic stability. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1216–1224, 2008

Key words: copolymerization; ionomers; membranes; polyimides

INTRODUCTION

Polymer electrolyte membrane fuel cells (PEMFCs) have been developed as promising alternative energy supplies for mobile and stationary applications. The most important part of a fuel cell is the polymer electrolyte membrane (PEM).[1–3] To date, the commercially available PEMs for PEMFCs are perfluorosulfonic acid membranes, such as DuPont's Nafion membrane, which have high proton conductivities and excellent chemical stabilities. However, some drawbacks, including high cost, low conductivity at high temperatures, and high methanol permeability, seriously limit their further application.[3] Therefore, much effort has gone into the development of low-cost and high-performance nonfluorinated hydrocarbon membrane materials. The major approach has been the attachment of sulfonic acid groups onto highly stable aromatic polymers, such as polyaramide, poly(ether ether ketone), polysulfone, and poly(phenylene sulfide).[4–6]

Among many polymer materials, sulfonated polyimides (SPIs) with five- and six-membered imide rings have been studied as one of the promising candidates for fuel cell applications because of their low methanol permeability and excellent thermal and chemical stabilities.[7–16] Two different synthetic approaches for obtaining different types of SPIs have been described. Some SPIs have been prepared by direct sulfonation of the parent nonsulfonated polyimides with fuming sulfuric acid as the sulfonating reagent under proper conditions,[17] whereas other SPIs have been synthesized via a sulfonated diamine compound as a monomer.[7–16]

Recently, SPIs have been successfully developed in several laboratories. Mercier et al.[7] first synthesized various sulfonated copolyimides (co-SPIs) from naphthalene-1,4,5,8-tetracaboxylic dianhydride (NTDA), 2,2′-bendizine sulfonic acid (BDSA), and common nonsulfonated diamine monomers. These co-SPI membranes were practically tested in a fuel cell system and showed fairly good performance. Some co-SPIs showed both relatively high proton

conductivity and relatively high hydrolytic stability. The sulfonation degree was precisely controlled by regulation of the molar ratio between BDSA and common nonsulfonated diamines, such as 4,4′-oxydianiline, during the copolymerization process. In other studies, McGrath and coworkers[9,10] prepared a series of co-SPIs using different types of sulfonated diamine compounds in a one-pot polymerization. They reported that their 2,5-diaminobenzene sulfonic acid (2,5-DABS)/NTDA-based wholly aromatic six-membered ring sulfonated homo-polyimide (homo-SPI) exhibited poor hydrolytic stability, and they tried to synthesize novel types of sulfonated diamines to obtain SPI membranes with mechanical stability. On the other hand, Okamoto and coworkers[11–14] found that a sulfonated diamine monomer with a flexible structure, 4,4′-diaminodiphenylether-2,2′-disulfonic acid, displayed good protonic conductivity and hydrolytic stability.

There have been a few reports on SPI membranes with aliphatic linkages.[18–21] Watanabe and coworkers[18,19] tested an aliphatic linkages containing sulfonated homo-polyimide (homo-SPIA) for long term fuel cell conditions. Moreover, they reported that a SPI containing an aliphatic diamine exhibited a higher hydrolytic stability than that containing an aromatic diamine. Because an aliphatic diamine gave rise to a higher electron density on the imide nitrogen, despite the presence of an aliphatic chain, the polyimide had good thermal and oxidative stability.[20] Recently, Han et al.[21] investigated the effect of the chain length of aliphatic diamine compounds on the physical properties of sulfonated copolyimides containing aliphatic linkages (co-SPIAs), which were prepared from NTDA, BDSA, and aliphatic diamines. They concluded that the ion-exchange capacity (IEC) and proton conductivity of the co-SPIAs increased when the chain length of the aliphatic diamine decreased. The variation in the physical properties of 2,4-diaminobenzene sulfonic acid (2,4-DABS)-based co-SPIA membranes by the introduction of aliphatic linkages has not been yet reported.

In this study, we prepared a series of co-SPI membranes with aliphatic linkages, which were synthesized with benzophenonetetracarboxylic dianhydride (BTDA), 2,4-DABS, and 1,6-diaminohexane (DAH) as the nonsulfonated diamine compound. The goal was to identify the effect of aliphatic linkages in the polymer chain on the thermal oxidative and hydrolytic stabilities of the SPI membranes. In addition, a fully aromatic polyimide, homo-SPI (BTDA/2,4-DABS), was prepared to compare the proton conductivity and hydrolytic stability with the co-SPIAs. Furthermore, the relationships between the proton conductivity, water uptake, hydrolytic stability, and IEC values of the co-SPIAs were studied.

EXPERIMENTAL

BTDA, 2,4-DABS, and DAH were used as received from Merck Co. (Darmstadt, Germany). *N*-Methyl pyrrolidone (NMP), dimethyl acetamide (DMAc), and dimethyl sulfoxide (DMSO) were supplied from Merck Co. NMP was purified by distillation under reduced pressure and stored over a 5-Å molecular sieve. Methylene chloride (MeCl$_2$), tetrahydrofuran (THF), and toluene were used as received from Merck and Carlo Erba (Italy), respectively. The commercial product Nafion117 was purchased from Sigma-Aldrich Co. The water used in the protonic conductivity measurements was ultrapure Mili-Q water (18.2 MΩ).

Analysis

Attenuated total reflectance–Fourier transform infrared (FTIR) spectra of the co-SPIAs were recorded from a PerkinElmer Spectrum One spectrometer with a ZnSe prism with an incident angle of 45°. Each spectrum was collected by the accumulation of 64 scans at a resolution of 2 cm^{-1}. A Shimadzu (Japan) TGA 50-W thermogravimetric analyzer system was used to study the thermal stability of the co-SPIA membranes. All of the samples were heated from 25 to 750°C under an air atmosphere at a 5°C/min heating rate.

The proton conductivity of the co-SPIA membranes was measured at 25°C in water with a two-point probe alternating-current impedance analyzer with a Solartron (Hampshire, England) 1260 frequency response analyzer and a Solartron 1296 dielectric interface. An impedance spectrum was recorded from 20 MHz to 1 Hz at an amplitude of 10 mV. Conductivity measurements were performed with the homemade glass cell shown in Figure 1. The proton conductivity (σ) of the co-SPIAs was calculated with the following equation as given in a previous work:[21]

$$\sigma = \frac{L}{RAd} \tag{1}$$

where L is the distance between Pt electrodes, d is the thickness of the membrane, A is the cross-sectional area of the membrane, and R is the bulk resistance value measured. The distance between the two electrodes was 1 cm. The membrane size was 3×1 cm^2 for all of the conductivity measurements. The impedance analyzer result was computed by the Z-view 2 program (Scribner Associates, USA).

In the water uptake experiments, the membrane was dried in a vacuum oven at 110°C for 24 h until a constant weight was reached. The water uptake was determined by the immersion of a piece of SPI
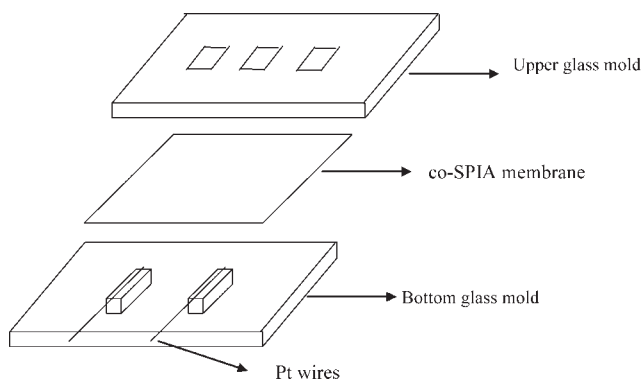
Figure 1 Schematic diagram of the proton conductivity measurement cell.

membrane (20–50 mg) in water at room temperature for 48, 120, and 240 h. Then, the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. The water uptake of the membrane was calculated by the following formula:

$$S = (W_w - W_d)/W_d \times 100\% \qquad (2)$$

where S is the water uptake and W_w and W_d are the weights of the wet and dry membranes, respectively.

The IEC of the homo-SPI and co-SPIAs were determined by a titration method. A sample membrane in proton form was soaked in a saturated NaCl solution for 48 h at room temperature to exchange H^+ ions with Na^+ ions. Then, the H ions released into the solution were titrated with a 0.01N NaOH solution with phenolphthalein as the indicator. The IEC values were calculated with following formula:

$$\text{IEC} = \frac{VM}{m_{\text{dry}}} \qquad (3)$$

where IEC is the ion-exchange capacity (mequiv/g), V is the added titrant volume at the equivalent point (mL), M is the molar concentration of the titrant, and m_{dry} is the dry mass of the sample (g).

Reactions

Preparation of the co-SPIAs

A series of random co-SPIAs were synthesized by thermal imidization with a two-pot method over a poly(amic acid) intermediate. We modified the method given in Woo's article[22] and used our procedure for the preparation of the co-SPIAs. The reactions are shown in Scheme 1. In the preparation of the poly(amic acid) solution, DMSO was used because 2,4-DABS was hardly soluble in NMP alone. co-SPIAs with different sulfonation levels were syn-

thesized with different molar ratios of 2,4-DABS/ DAH (from 20/80 to 70/30). For example, the synthesis of sulfonated poly(amic acid) (SPAA) with a BTDA: 2,4-DABS:DAH molar ratio of 2 : 1 : 1 was performed as follows: 0.66 g (3.5 mmol) of 2,4-DABS and 17.1 g of DMSO were added to a 50-mL, three-necked flask and stirred with magnetic stirrer under a nitrogen atmosphere at 70°C. When the 2,4-DABS solution was obtained, it was cooled down to room temperature. Then, 0.41 g (3.5 mmol) of DAH was added to this solution. Finally, 2.26 g (7.0 mmol) of BTDA was added, and the mixture was stirred at 30°C for 4 h. To obtain the co-SPIA membranes, the SPAA solution was diluted with a NMP/DMSO mixture (NMP/DMSO = 1/1 v/v). Subsequently, this homogeneous solution was used for the preparation of the co-SPIA membranes by casting onto well-cleaned Petri dishes. Thermal imidization of the co-SPIA membranes was carried out at 100°C for 1 h, 120°C for 1 h, 140°C for 1 h, and finally, 160°C for 5 h. For comparison, a fully aromatic SPI (2,4-DABS/BTDA) was also prepared in the same manner.

RESULTS AND DISCUSSION

A series of random co-SPIAs were synthesized by thermal imidization with a two-pot method over an SPAA intermediate. The SPAA intermediates with aliphatic linkages were transformed into co-SPIA form by thermal imidization, which was carried out below 200°C to prevent the decomposition of SO_3H groups in the polymer backbone. This procedure gave us an easier method for preparing the co-SPIA membranes.

The polymers were fabricated into membranes via a solution casting technique from DMSO or a mixture of NMP/DMSO (1/1) to study the film-forming properties. All of the SPI membranes fabricated with DMSO as a casting solvent exhibited low flexibility. This implied that DMSO was a poor casting solvent for PEM fabrication. After this result, the membranes were cast in a mold from an NMP/DMSO (1/1) mixture, and co-SPIA membranes with flexible and homogeneous appearances were obtained. The thickness of the prepared co-SPIAs was in the range 20–40 μm.

FTIR results

The chemical structure of the co-SPIAs was confirmed by FTIR spectroscopy. FTIR spectra of the homo-SPI and co-SPIAs are depicted in Figure 2. The asymmetric and symmetric absorpti̇ons of the imide carbonyl groups (C=O) were observed around 1705 and 1777 cm^{-1}, respectively. The
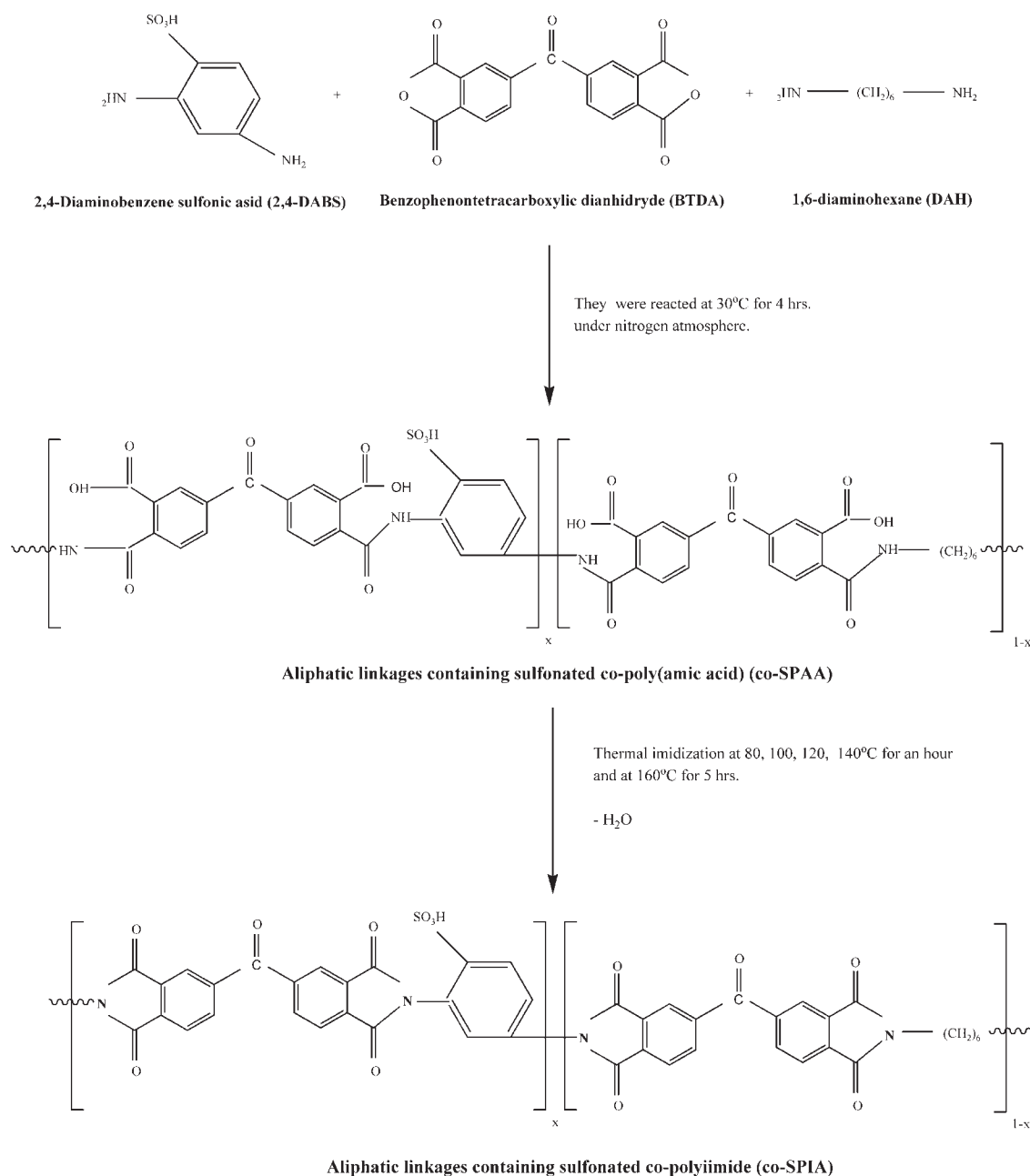
Scheme 1 Chemical structures of the monomers and co-SPIAs.

absorption of the SO_2 group of the sulfonic acid was observed as a broad peak around 1010–1030 cm^{-1} and as a peak around 1090 cm^{-1}. The out-of-phase bending of the imide ring was observed around 720 cm^{-1}. The C—N—C stretching vibration of the imide ring was observed around 1375 cm^{-1}. The aliphatic sp3 CH vibration of the diamine was observed around 2920–2940 cm^{-1}. This analysis confirmed that all of the co-SPIAs were successfully synthesized. Additionally, there was a wide and large water peak at 3300–3400 cm^{-1} in the IR spectra of the homo-SPI and co-SPIAs. This result showed us that membranes absorbed water very easily because of their hydrophilic natures.

Thermogravimetric analysis (TGA)

It was important to determine the thermal stability of the membranes because it is well known that fuel cells exhibit better performance when they are operated at high temperatures. The thermal stabilities of the co-SPIAs were investigated by TGA. The onset temperature was considered the degradation temperature. The onset temperatures for the degradation steps in an air atmosphere are given in Table I, and representative TGA patterns are given in Figure 3.

All of the prepared co-SPIAs exhibited similar TGA curves, and degradation took place in three steps. The first weight loss was observed around
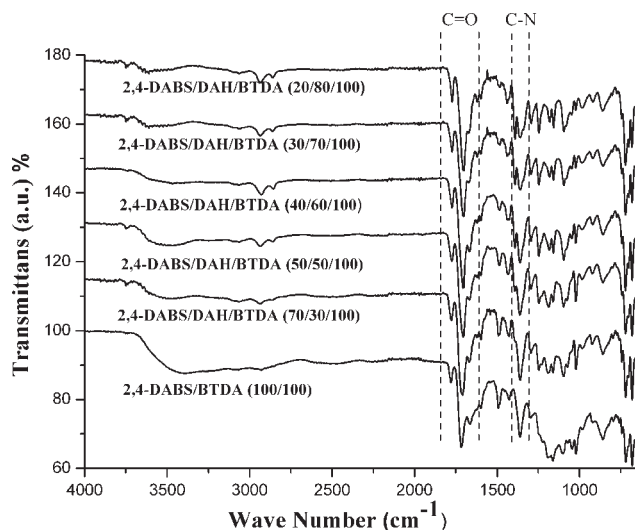
Figure 2 FTIR spectra of the prepared homo-SPI and co-SPIAs.

Figure 3 Thermal oxidative degradation curves of the homo-SPI and co-SPIAs.

100°C, which was due to the evaporation of absorbed moisture of the hygroscopic SPIs. The second degradation began around 200°C and was due to the decomposition of sulfonic acid groups; the third degradation step, which was attributed to the decomposition of imide groups in the polymer backbone, began around 500°C. As shown in Figure 3, the homo-SPI (2,4-DABS/BTDA) displayed a lower thermal stability than the co-SPIAs with various molar percentages of sulfonated diamine. The homo-SPI exhibited the second degradation step around 200°C, which induced the loss of —SO₃H groups, and the third degradation step around 510°C, which corresponded to the decomposition of the polymer main chain. Conclusively, we concluded that the incorporation of aliphatic linkages into the polyimide backbone slightly improved the thermal stability, and all of the co-SPIAs exhibited fairly good thermal stabilities.

Proton conductivity

Proton conductivity is one of the crucial properties for fuel cell membranes, and it directly depends on the water uptake and IEC values of the SPIs.[11] Generally, the proton conductivity of the polymer increases with increasing IEC and water uptake. This is because, with higher IEC and water uptake values, the formation of the hydrophilic domain increases and, hence, the proton conductivity increases. The proton conductivity of the prepared homo-SPI and co-SPIA membranes was measured, and the results are given in Table II. Furthermore, the variation in the impedance behavior (Nyquist plot) and proton conductivity of the co-SPIA membranes are given against the molar percentage of 2,4-DABS in the copolymer composition in Figures 4 and 5, respectively.

As shown in Table II, the homo-SPI membrane displayed the highest proton conductivity at 11 mS/cm among the prepared membranes because of its highest IEC. The proton conductivities of the co-SPIA membranes increased in the order 2,4-DABS/DAH (20/80) < 2,4-DABS/DAH (30/70) < 2,4-DABS/DAH (40/60) < 2,4-DABS/DAH (50/50) < 2,4-DABS/DAH (70/30) < 2,4-DABS/DAH (100/0). It was clear that the proton conductivity value tended to decrease with decreasing sulfonation degree (IEC). At a low sulfonation degree of 30 mol % 2,4-DABS, the membrane had a proton conductivity of only 1.22 mS/cm, which was lower than that of Nafion 117. Beyond 30 mol % 2,4-DABS/DAH (30/70), the co-SPIA membranes displayed higher conductivity values than that of Nafion 117. This suggested that the co-SPIA membranes had higher

TABLE I
Thermal Oxidative Properties of the homo-SPI and co-SPIA Membranes

Membrane	T_1 (°C)	T_2 (°C)
2,4-DABS/DAH/BTDA (20/80/100)	206	476
2,4-DABS/DAH/BTDA (30/70/100)	204	477
2,4-DABS/DAH/BTDA (40/60/100)	201	479
2,4-DABS/DAH/BTDA (50/50/100)	204	482
2,4-DABS/DAH/BTDA (70/30/100)	204	485
2,4-DABS/BTDA (100/100)	203	490

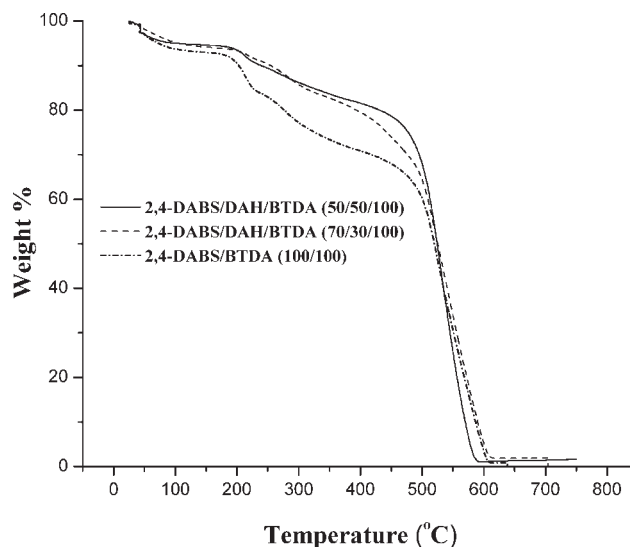T_1 = temperature at which the first-step degradation started; T_2 = temperature at which the second-step degradation started.

TABLE II
IEC and Proton Conductivity Values of the homo-SPI and co-SPIA Membranes

Membrane	Theoretical IEC (mequiv/g of sample)	Experimental IEC (mequiv/g of sample)	Proton conductivity (mS/cm)[a]
2,4-DABS/DAH/BTDA (20/80/100)	0.48	0.38	0.54
2,4-DABS/DAH/BTDA (30/70/100)	0.71	0.49	1.22
2,4-DABS/DAH/BTDA (40/60/100)	0.93	0.9	7.8
2,4-DABS/DAH/BTDA (50/50/100)	1.14	0.97	8.3
2,4-DABS/DAH/BTDA (70/30/100)	1.55	1.52	n.d.
2,4-DABS/BTDA (100/100)	2.11	2.07	11.0
Nafion 117	—	0.89	3.8

n.d. = not determined.
[a] This measurement was carried out at 25°C.

water contents in fully hydrated states than Nafion 117 because of their higher IEC values, which was helpful for the increased proton transport capability.[14] This result was in good agreement with those in a previous article.[23] Conclusively, as shown in Table II and Figure 5, the proton conductivity strongly depended on the IEC value of the membrane. (We could not determine the proton conductivity of SPI with 70 mol % 2,4-DABS because it was cracked in water during the measurement).

It was interesting to compare the proton conductivities of the SPIA membranes with that of Nafion 117 [Nafion is a copolymer of tetrafluoroethylene with 15 mol % of a CF2=CFR type monomer with a polar and ionic side group R = —O—CF2—CF(CF3)—O—CF2—CF2—SO3—]. The proton conductivity of Nafion 117 membranes as a function of relative humidity has been investigated in several laboratories.[11,24–26] However, the data are quite dif-

ferent from each other. The conductivity value belonging to Nafion 117 given in Table II was determined under our laboratory conditions and was found to be 3.8 mS/cm at 25°C.

Interestingly, as shown in Figure 5, the proton conductivity value significantly increased beyond 30 mol % 2,4-DABS in the copolymer composition. This result can be explained as follows. When the sulfonation part increased, the number of hydrophilic domains gradually increased, and finally, the water clusters began to be close and caused a rise in conductivity by the Grotthuss mechanism.[27] Similarly, this phenomenon was also observed for BDSA-based co-SPI systems by Okamoto et al.[11]

Iron Exchange Capacity (IEC)

The IEC of a polymer is an important property, and generally, the proton conductivity and water uptake of the final polymer directly depend on the IEC of the polymer. The variation in IEC with molar
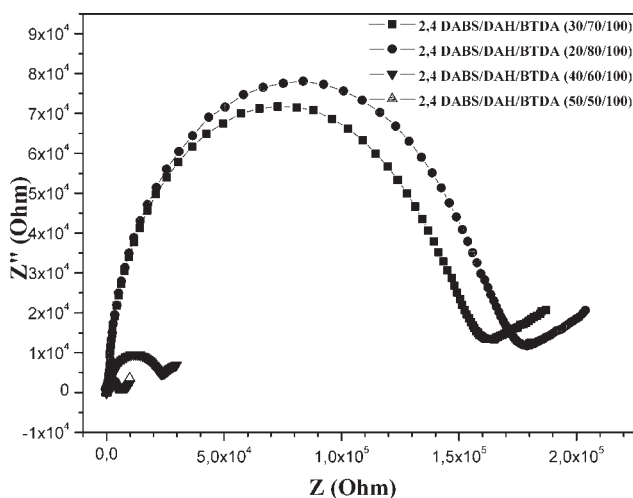

Figure 4 Variation in the impedance behavior of the co-SPIAs with copolymer composition (20 MHz–1 Hz) at room temperature. co-SPIA, aliphatic linkages containing sulfonated co-polyimide; co-SPAA, aliphatic linkages containing sulfonated co-poly(amic acid); Z, the real part of impedance; z″, the imaginary part of the impedance.
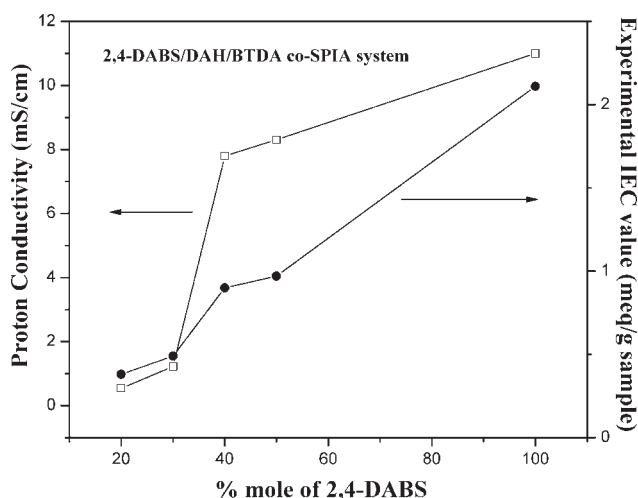

Figure 5 Variation in the proton conductivity and IEC of co-SPIAs with the molar percentage of 2,4-DABS.

Water Absorption and Hydrolytic Stability of the homo-SPI and co-SPIA Membranes

Membrane	Water Absorption (wt %)			Hydrolytic stability at 80°C
	48 h	120 h	240 h	
2,4-DABS/DAH/BTDA (20/80/100)	3.2	6.5	9.1	>100 h
2,4-DABS/DAH/BTDA (30/70/100)	9.7	13.2	15.1	>100 h
2,4-DABS/DAH/BTDA (40/60/100)	13.9	18.8	19.2	17 h
2,4-DABS/DAH/BTDA (50/50/100)	35.2	74.9	Cracked	3 h
2,4-DABS/DAH/BTDA (70/30/100)	54.3	Cracked	Cracked	3 h
2,4-DABS/BTDA (100/100)	Cracked	Cracked	Cracked	3 h
Nafion 117	15.1			>100 h[a]

[a] Shrinkage was observed.

percentage of 2,4-DABS in the co-SPIA structure is given in Table II and shown in Figure 5. The IEC of the homo-SPI and co-SPIAs increased in the following order: 2,4-DABS/DAH (20/80) < 2,4-DABS/DAH (30/70) < 2,4-DABS/DAH (40/60) < 2,4-DABS/DAH (50/50) < 2,4-DABS/DAH (70/30) < 2,4-DABS/DAH (100/0). As expected, the IEC values increased with increasing amount of sulfonated diamine compound in the polymer backbone. Furthermore, the experimental IEC values were compared with the theoretical ones. As shown in Table II, the theoretical IEC values were a little higher than the calculated ones.

Water uptake

The water uptake of PEMs is another important property for application in fuel cells. Generally, the proton conductivity of the polymer increases with increasing water uptake. It is more water uptake that improves the formation of the hydrophilic domain carrying the proton conductivity. The water uptake of a SPI membrane can be increased by increasing the ionic group content in the polymer chain. However, most often, a higher water uptake results in a higher swelling of the membrane, which leads to a loss of mechanical stability in the membrane. Moreover, higher swelling also leads to high methanol permeability. Hence, the optimization of water uptake and polymer swelling is required for successful operation in fuel cells.

The water uptakes of the co-SPIA membranes were evaluated at room temperature for different time intervals and are given in Table III. The water uptake increased in the order 2,4-DABS/DAH (20/80) < 2,4-DABS/DAH (30/70) < 2,4-DABS/DAH (40/60) < 2,4-DABS/DAH (50/50) < 2,4-DABS/DAH (70/30) < 2,4-DABS/DAH (100/0). As shown in Table III, the water uptake mainly depended on the sulfonic acid content of the copolymer. For example, the co-SPIA 2,4-DABS/DAH, 50/50 exhibited a 74.9% weight increase due to water uptake after 120 h. This result was consistent with the report

of Wang et al.[6] Another important parameter of the water uptake properties of co-SPIA membranes is the configuration of the nonsulfonated diamine compound. For this purpose, we used 4,4′-oxydianiline instead of DAH as a nonsulfonated diamine compound in another experiment and found that the membrane with aliphatic linkages exhibited a slightly higher water uptake than the wholly aromatic co-SPI membrane. On the other hand, the co-SPIA membranes absorbed slightly less water than Nafion117 for the same IEC values. This may be explained by the specific nature of the Nafion membrane.

Hydrolytic stability

It is essential for electrolyte membranes to retain their mechanical strength under humidified conditions in the light of the membrane electrode assembly to be used in fuel cells. To evaluate the mechanical properties of the membranes under wet conditions, the membranes were immersed in water at 80°C. In this study, the hydrolytic stability of the membranes was characterized by the time at which the membranes started to become a little brittle (a membrane was broken when it was lightly bent) after immersion in hot water at 80°C.[28,29] The water uptake and hydrolytic stability values of the homo-SPI and co-SPIAs are given in Table III.

It is known that the hydrolytic stability of SPI membranes is greatly affected by the structure of the sulfonated diamine moieties. 2,5-DABS-based SPI membranes generally show poor hydrolytic stability when the amounts of 2,5-DABS are increased in the copolymer composition. In addition, it was reported that sulfonated diamine moieties with a flexible structure, high basicity, and linear configuration resulted in a high hydrolytic stability of the SPI membranes.[9,14] In this study, we tried to investigate the effect of the aliphatic moiety on the hydrolytic stability of the prepared 2,4-DABS-based co-SPIAs. Interestingly, we found that SPIs containing aliphatic linkages with less than 30 mol % 2,4-DABS exhibited

TABLE IV
Solubility Properties of the homo-SPI and co-SPIA Membranes

Membrane	NMP	DMAc	DMSO	THF	DCM	Toluene
2,4-DABS/DAH/BTDA (20/80/100)	$\pm^h$	$\pm^h$	$\pm^h$	-, --	-, --	-, --
2,4-DABS/DAH/BTDA (30/70/100)	$\pm^h$	$\pm^h$	$\pm^h$	-, --	-, --	-, --
2,4-DABS/DAH/BTDA (40/60/100)	$\pm,^c \pm^h$	$\pm,^c \pm^h$	$\pm,^c \pm^h$	-, --	-, --	-, --
2,4-DABS/DAH/BTDA (50/50/100)	+	+	+	-, --	-, --	-, --
2,4-DABS/DAH/BTDA (70/30/100)	+	+	+	-, --	-, --	-, $\pm^h$
2,4-DABS/BTDA (100/100)	+	+	+	-, $\pm^h$	-, $\pm^h$	-, --
Nafion 117	-, --	-, --	-, --	-, --	-, --	-, --

- = insoluble at room temperature; -- = insoluble at 70°C; + = soluble at room temperature; $\pm^c$ = partly soluble at room temperature; $\pm^h$ = partly soluble at 70°C.

a similar hydrolytic stability to that of 1,4-bis (4-amino-2-sulfonic acid phenoxy)benzene based SPIs, with two flexible ether bonds, as reported by Xie et al.[30] This result shows that the hydrolytic stability of the 2,4-DABS-based SPI membranes was improved by the introduction of the nonsulfonated diamine with aliphatic linkages.

IEC is also an important factor that affects the hydrolytic stability of membranes. Generally, higher IEC values cause larger water uptakes and worse hydrolytic stabilities. In the light of these findings, SPIs with high IECs and hydrolytic stabilities can be developed by the choice of the proper molecular design of sulfonated diamine in the copolymer composition. For this purpose, the hydrolytic stability times of the co-SPIAs were compared with that of the homo-SPI, which had the highest IEC value (2.07 mequiv/g of sample). As one can see from Table III, the homo-SPI only maintained its mechanical strength for less than 3 h because of the high sulfonation degree. In contrast, the co-SPIA membranes with less than 40 mol % 2,4-DABS maintained their mechanical strength after they were soaked in water at 80°C for more than 100 h.

Another important result, as shown in Table III, was that the co-SPIAs started to lose their mechanical stability beyond 30 mol % 2,4-DABS in the copolymer composition. This mechanical instability was the result of a morphological change at the percolation threshold in which the hydrophilic domains became interconnected.[10]

Solubility

Polymer solubility is an important property that depends on several parameters, such as the type of polymer, configuration, and solvent type. The homo-SPI and co-SPIA membranes were tested for solubility in several common solvents, including DMAc, NMP, DMSO, THF, toluene, and dichloromethane (DCM). The solubility of the co-SPI membranes were typically examined at nearly 1% solid (w/w). The results are shown in Table IV.

The resulting co-SPIAs showed better solubility than Nafion 117. Although the co-SPIA membranes with more than 40 mol % 2,4-DABS in the copolymer composition were soluble in common polar solvents, such as NMP, DMAc, and DMSO, at room temperature, the co-SPIA membranes with less than 40 mol % 2,4-DABS were not dissolved in any of the solvents used. This result showed that the solubility of the SPI membranes was greatly improved by an increase in the sulfonation degree (higher IEC values). On the other hand, the co-SPIA membranes showed better solubility properties than Nafion 117 for the same IEC values.

CONCLUSIONS

A designed series of co-SPIAs was synthesized on the basis of 2,4-DABS/DAH and BTDA over a two-step procedure to evaluate the suitability for fuel cell application. Our conclusions can be summarized as follows:

- A sulfonated diamine monomer (2,4-DABS) and nonsulfonated diamine monomer with aliphatic linkages (DAH) were reacted with BTDA to yield co-SPIAs.
- All of the expected bands attributed to the imide ring were observed, as shown in Figure 1. The FTIR analyses of the co-SPIAs showed that all of the membranes were successfully synthesized. The intensity of the sulfonyl absorption band increased with increasing amount of 2,4-DABS.
- All of the prepared SPIAs exhibited similar TGA curves, and degradation took place in three places. The first weight loss was observed around 100°C, which was due to the removal of the absorbed moisture of the hygroscopic co-SPIAs. The second one, which began at about 200°C, was due to the decomposition of sulfonic acid groups, and the third degradation step began around 500°C, which was attributed to the presence of imide groups in the polymer backbone. Conclusively, the TGA patterns clearly indicated

that all of co-SPIAs had fairly good thermal stabilities.

- In water, the homo-SPI (2,4-DABS/BTDA) and co-SPIAs including more than 30 mol % 2,4-DABS in the copolymer composition displayed higher proton conductivities than Nafion 117, which were high enough for practical use (10^{-2}–10^{-3}S/cm). The proton conductivities of the co-SPIA membranes increased in the order 2,4-DABS/DAH (20/80) < 2,4-DABS/DAH (30/70) < 2,4-DABS/DAH (40/60) < 2,4-DABS/DAH (50/50) < 2,4-DABS/DAH (70/30) < 2,4-DABS/DAH (100/0). It was clear that the proton conductivities of the co-SPIA membranes strongly depended on the sulfonic acid group content, and the conductivity increased rapidly as IEC increased (Fig. 5).
- As shown in Table III, the homo-SPI only maintained its mechanical strength for less than 3 h because of its high sulfonation degree. In contrast, the co-SPIA membranes with less than 40 mol % 2,4-DABS maintained their mechanical strength after they were soaked in water at 80°C for more than 100 h.
- The optimum concentration of 2,4-DABS was found to be 40 mol % from the viewpoint of proton conductivity, IEC, and hydrolytic stability. To maintain a good compromise between the proton conductivity and hydrolytic stability, the IEC values of the co-SPIAs should be controlled in the range of 1.0 mequiv/g of sample.
- These results show that the co-SPIA membranes with less than 40 mol % 2,4-DABS in the copolymer composition may be considered an alternative membrane for PEMFC applications.

References

1. Hickner, M. Chem Rev 2004, 104, 4587.
2. Carrete, L.; Friedrich, K. A.; Stimming, U. Fuel Cells 2001, 1, 5.
3. Savadogo, O. J New Mater Electrochem Syst 1998, 1, 47.
4. Shermann, S. U.S. Pat. 4,595,708 (1986).
5. Wang, F.; Ji, Q.; Harrison, W.; Mecham, J.; Formato, R.; Kovar, R.; Osenar, P.; McGrath, J. E. Polym Prepr 2000, 41, 237.
6. Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. J Membr Sci 2002, 197, 231.
7. Genies, C.; Mercier, R.; Sillion, B.; Cornet, N.; Gebel, G.; Pineri, M. Polymer 2001, 42, 359.
8. Cornet, N.; Prat, O.; Gebel, G.; Jousse, F.; Marsacq, D.; Mercier, R.; Pineri, M. J New Mater Electrochem Syst 2000, 3, 33.
9. Gündüz, N.; McGrath, J. E. Polym Prepr 2000, 41, 182.
10. Einsla, B. R.; Hong, Y.-T.; Kim, Y. S.; Wang, F.; Gündüz, N.; McGrath, J. E. J Polym Sci Part A: Polym Chem 2004, 42, 862.
11. Guo, X.; Fang, J.; Tanaka, K.; Kita, H.; Okamato, K. J Polym Sci Part A: Polym Chem 2004, 42, 1432.
12. Woo, Y.; Oh, S. Y.; Kang, Y. S.; Jung, B. J Membr Sci 2003, 220, 31.
13. Watari, T.; Fang, J.; Tanaka, K.; Kita, H.; Okamoto, K.; Hirano, T. J Membr Sci 2004, 230, 111.
14. Fang, J.; Guo, X. S.; Harada, T.; Watari, K.; Kita, H.; Okamoto, K. Macromolecules 2002, 35, 9022.
15. Li, Y.; Jin, R.; Wang, Z.; Cui, Z.; Xing, W.; Goo, L. J Polym Sci Part A: Polym Chem 2007, 45, 221.
16. Meier-Haack, J.; Teager, A.; Vogel, C.; Schlenstedt, K.; Lenk, W.; Lehmann, D. Sep Technol 2005, 41, 207.
17. Wang, J. L.; Lee, M.-H.; Yang, J. Polym Bull 2005, 55, 357.
18. Aoki, M.; Asano, N.; Miyateke, K.; Hokida, H.; Watanabe, M. J Electrochem Soc 2006, 153, A1154.
19. Asano, N.; Aoki, M.; Suziki, S.; Miyateke, K.; Hokida, H.; Watanabe, M. J Am Chem Soc 2006, 128, 1762.
20. Asano, N.; Miyateke, K.; Watanabe, M. Chem Mater 2004, 16, 2841.
21. Jang, W.; Kim, D.; Choi, S.; Han, H. Polym Int 2006, 55, 1236.
22. Li, Y.; Jin, R.; Wang, Z.; Cui, Z.; Xing, W.; Gao, L. J Polym Sci Part A: Polym Chem 2007, 45, 222.
23. Miyake, N.; Wainright, J.; Savinell, R. J Electrochem Soc 2001, 148, A898.
24. Ye, X.; Bai, H.; Ho, W. J Membr Sci 2006, 279, 570.
25. Sone, Y.; Ekdunge, P.; Simonsson, D. J Electrochem Soc 1996, 143, 1254.
26. Morris, D. R.; Sun, X. J Appl Polym Sci 1993, 50, 1445.
27. Kreuer, K. Chem Mater 1996, 8, 610.
28. Yin, Y.; Yamada, O.; Hayashi, S.; Tanaka, K.; Kita, H.; Okamoto, K. J Polym Sci Part A: Polym Chem 2006, 44, 3751.
29. Rio, C. D.; Jurado, J. R.; Acosta, J. L. Polymer 2005, 46, 3975.
30. Shang, Y.; Xie, X.; Jin, H.; Guo, J.; Wang, Y.; Feng, S.; Wang, S.; Xu, J. Eur Polym J 2006, 42, 2987.