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Tuned Polymer Electrolyte Membranes Based on Aromatic Polyethers for Fuel Cell Applications

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Abstract: Poly(arylene ether sulfone)-based ionomers containing sulfofluorenyl groups have been synthesized for applications to polymer electrolyte membrane fuel cells (PEMFCs). In order to achieve high proton conductivity and chemical, mechanical, and dimensional stability, the molecular structure of the ionomers has been optimized. Tough, flexible, and transparent membranes were obtained from a series of modified ionomers containing methyl groups with the ion-exchange capacity (IEC) ranging from 1.32 to 3.26 meq/g. Isopropylidene tetramethylbiphenylene moieties were more effective than the methyl-substituted fluorenyl groups in giving a high-IEC ionomer membrane with substantial stability to hydrolysis and oxidation. Dimensional stability was significantly improved for the methyl-substituted ionomer membranes compared to that of the non-methylated ones. This new ionomer membrane showed comparable proton conductivity to that of the perfluorinated ionomer membrane (Nafion 112) under a wide range of conditions (80−120 °C and 20−93% relative humidity (RH)). The highest proton conductivity of 0.3 S/cm was obtained at 80 °C and 93% RH. Although there is a decline of proton conductivity with time, after 10 000 h the proton conductivities were still at acceptable levels for fuel cell operation. The membranes retained their strength, flexibility, and high molecular weight after 10 000 h. Microscopic analyses revealed well-connected ionic clusters for the high-IEC membrane. A fuel cell operated using the polyether ionomer membrane showed better performance than that of Nafion at a low humidity of 20% RH and high temperature of 90 °C. Unlike the other hydrocarbon ionomers, the present membrane showed a lower resistance than expected from its conductivity, indicating superior water-holding capability at high temperature and low humidity.

Introduction

Ion-conducting polymers are of interest for a variety of applications, such as sensors, actuators, batteries, and ion-exchange membranes or resins.[1] Particularly, recent progress in the area of polymer electrolyte membrane fuel cells (PEMFCs) has stimulated considerable interest in proton conductive polymer membranes.[2] Perfluorinated sulfonic acid ionomers such as Nafion have been the most studied as the electrolyte membrane for PEMFCs. Although almost a half-century has passed since DuPont developed Nafion membranes, they are still state-of-the-art because of their high proton conductivity and excellent stability. There is, however, a great demand for non-fluorinated alternative membranes in terms of production cost, environmental friendliness, and high-temperature stability.[3]

One possible approach for this purpose is acid functionalization of hydrocarbon polymers. Aromatic polymers have been extensively studied due to their excellent stability and high susceptibility to electrophilic sulfonation reactions. A number of aromatic polymers such as poly(ether ether ketone)s,[4] poly(arylene ether)s,[5] polyimides,[6] polyphosphazenes,[7] polybenzimidazoles,[8] polyphenylenes,[9] and others[10] have been sulfonated or doped with mineral acids. Recently, it has been reported by several research groups that the polymer electrolytes containing fluorenyl groups are highly proton conductive.[11,12]

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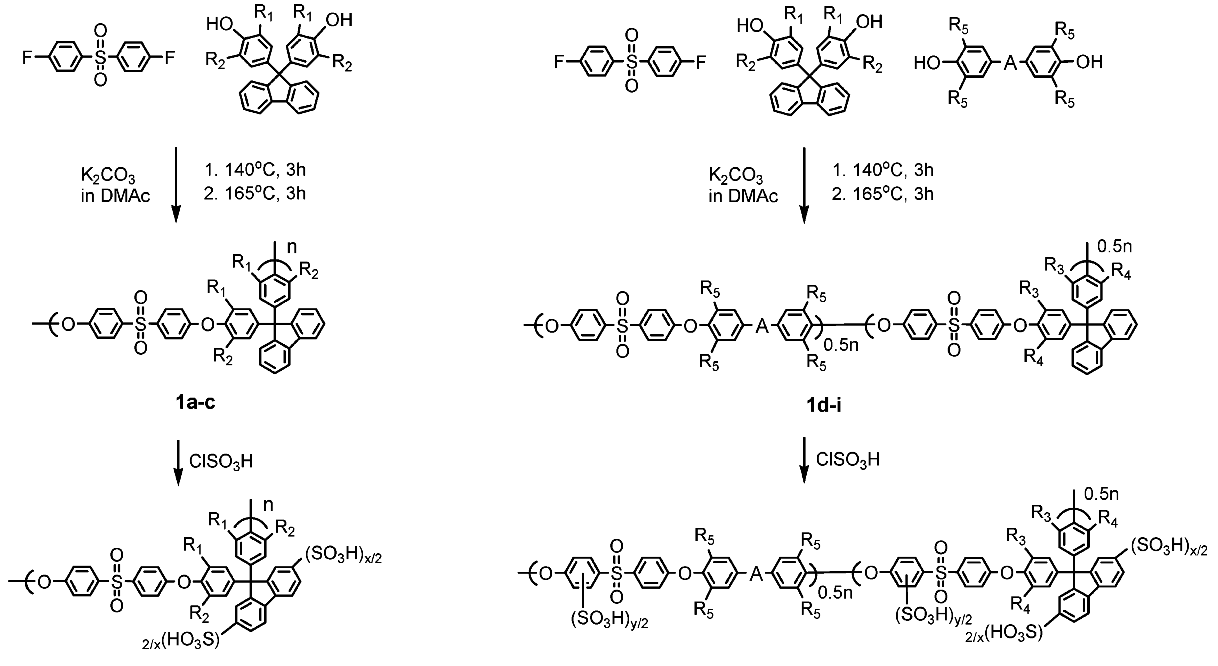
Scheme 1. Synthesis of a Series of Methyl-Substituted Poly(arylene ether sulfone)s Containing Fluorenyl Groups



2a-c

	a	b	c
R_1	H	H	CH_3
R_2	H	CH_3	CH_3

2d-i

	d	e	f	g	h	i
R_3	H	H	H	H	H	CH_3
R_4	H	H	H	H	CH_3	CH_3
R_5	H	CH_3	H	CH_3	CH_3	CH_3
A	$\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}$	$\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}$	—	—	—	—

Proton conductivity comparable to that of Nafion has been reported for some of these membrane materials; however, hydrolytic and oxidative stability are still issues to be addressed.

In previous reports, we proposed that pendent acidic groups (not attached to the main chain) keep the polymer chain in a hydrophobic environment and contribute to improved stability.[11] Novel sulfonated poly(arylene ether sulfone) ionomers containing fluorenyl groups (**2a** in Scheme 1) in which sulfonic acid groups were substituted only at specific (2,7)-positions on fluorenyl groups were synthesized. The ionomer membranes show high proton conductivity (0.2 S/cm) at 100% RH, low gas permeation, and high hydrolytic and oxidative stability. The **2a** membrane with an ion-exchange capacity (IEC) of 1.6 meq/g was durable for 5000 h in a H_2/air fuel cell operated at 80 °C and 90% RH.[13] This is, to the best of our knowledge, one of the greatest longevities reported for a non-fluorinated hydrocarbon ionomer membrane in an operating fuel cell.[14] There were only minor changes as confirmed by IEC, thickness, and molecular weight after the fuel cell operation indicating no practical degradation. Before the **2a** membrane is subjected for further evaluation, the heavy dependence of the proton conductivity on humidity has to be improved since fuel cells are often operated at low humidity. The challenge is how to increase the conductivity without sacrificing hydrolytic, oxidative, dimensional, and mechanical stability. In this paper, we describe our successful approaches to this purpose. Substituent effects have been studied in detail to tune the chemical structure for higher IEC ionomers. It turned out that the **2e** membrane in Scheme 1 shows considerably improved properties. Proton conductivity is comparable to that of Nafion at 20−93% RH and 80−120 °C and was at acceptable levels for fuel cell operation for 10 000 h. We have then demonstrated that the new membrane functions better than Nafion in a fuel cell operated at 90 °C and 20% RH.

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Experimental Section

Measurements. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR experiments were performed on a Bruker AVANCE 400S spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) or deuterated chloroform ($CDCl_3$) as the solvent and tetramethylsilane (TMS) as the internal reference. Molecular weight measurement was performed via gel permeation chromatography (Jasco 880-PU) equipped with two Shodex KF-805 columns and a Jasco 875 UV detector set at 300 nm. *N*,*N*-Dimethylformamide containing 0.01 M LiBr was used as the solvent at a flow rate of 1.0 mL/min. M_w and M_n were calibrated with standard polystyrene samples.

Materials. 9-Fluorenone (98%, TCI Co., Inc.), 2,6-xylenol (99%, TCI Co., Inc.), thioglycolic acid (80%, TCI Co., Inc.), 3,3′,5,5′-tetramethyl-(1,1′-biphenyl)-4,4′-diol (TMP) (98%, Aldrich Co., Inc.), propyl isocyanate (96%, TCI Co., Inc.), triethylamine (TEA) (98%, Aldrich Co., Inc.), tetrahydrofuran (THF) (99%, Kanto Chemical Co., Inc.), 9,9′-bis(4-hydroxyphenyl)fluorene (BHF) (98%, TCI Co., Inc.), 9,9′-bis(4-hydroxy-3-methylphenyl)fluorene (MBHF) (98%, TCI Co., Inc.), 4,4′-isopropylidenediphenol (BPA) (99%, Kanto Chemical Co., Inc.), 2,2′-bis(4-hydroxy-3,5-dimethylphenyl)propane (BDMPA) (98%, TCI Co., Inc.), 4,4′-dihydroxybiphenyl (DHP) (99%, TCI Co., Inc.), potassium carbonate (99.5%, Kanto Chemical Co., Inc.), toluene (99.5%, Kanto Chemical Co., Inc.), chlorosulfonic acid (99%, Kanto Chemical Co., Inc.), and dichloromethane (99.5%, dehydrated, Kanto Chemical Co., Inc.) were used as received. 4-Fluorophenyl sulfone (FPS) (99%, Acros Organics) was purified by crystallization from ethanol. *N*,*N*-Dimethyl acetamide (DMAc) (99%, Kanto Chemical Co., Inc.) was dried over 3A-molecular sieves prior to use. Other chemicals were of commercially available grade and used as received.

9,9′-Bis(4-hydroxy-3,5-dimethylphenyl)fluorene (DMBHF). DMBHF was synthesized according to the method described in the literature.[15] ^{1}H NMR (DMSO-d_6): δ (ppm) 2.01 (s, 6H), 6.63 (s, 4H), 7.28 (t, 2H), 7.34 (t, 2H), 7.39 (d, 2H), 7.85 (d, 2H), 8.09 (s, 2H). ^{13}C NMR (DMSO-d_6): δ (ppm) 16.8, 63.6, 120.2, 123.6, 126.0, 127.1, 127.4, 136.3, 139.2, 151.8.

3,3′,5,5′-Tetramethyl-4,4′bis(propylcarbamoyl)biphenol (TMPCB). TMPCB was synthesized according to a modified method in the literature.[16] A 100 mL, three-neck, round-bottomed flask equipped with a magnetic stirring bar, a gas inlet, and an addition funnel was charged with TMP (10.0 mmol, 2.423 g), propyl isocyanate (60 mmol, 5 mL), TEA (0.5 mL), and 50 mL of THF. The mixture was heated at 70 °C for 20 h under N_2 atmosphere. The mixture was evaporated to dryness to obtain a crude product. The product was purified twice by crystallization from chloroform/hexane. The resulting product was dried under vacuum at 50 °C for 15 h to obtain pure TMPCB in 64% yield. ^{1}H NMR (DMSO-d_6): δ (ppm) 0.90 (t, 6H), 1.49 (m, 4H), 2.16 (s, 12H), 3.05 (q, 4H), 7.33 (s, 4H), 7.79 (t, 2H). ^{13}C NMR (DMSO-d_6): δ (ppm) 11.1, 16.0, 22.6, 42.1, 126.4, 130.9, 136.6, 147.6, 153.9.

Homopolymers 1a−c. The polymerization procedure for **1a** has been described previously.[11] Polymers **1b** and **1c** were synthesized as follows. A 200 mL, three-neck, round-bottomed flask equipped with a magnetic stirring bar, a N_2 inlet, and an addition funnel was charged with MBHF (2.0 mmol, 0.757 g), FPS (2.0 mmol, 0.509 g), potassium carbonate (5.0 mmol, 0.691 g), toluene (2.0 mL), and 5 mL of DMAc. The mixture was stirred at room temperature for a few minutes and then heated at 140 °C for 3 h and at 165 °C for 3 h under N_2 atmosphere. Then, 60 mL of DMAc was added to the mixture to lower the viscosity. The solution was poured dropwise into 1 L of deionized water to precipitate a white flaked product. The product was washed with hot deionized water and methanol several times and purified by reprecipitation from chloroform/acetone. The resulting product was dried under vacuum at 60 °C for 15 h to give **1b** in 63% yield. Using DMBHF instead of MBHF gave polymer **1c** in 75% yield.

Copolymers 1d−i. The polymerization was carried out in the same manner as described for the homopolymers except that biphenol comonomer (BPA, BDMPA, DHP, or TMPCB) was also added. The molar ratio of BHF to the biphenol monomer was set at 1:1. White flaked pure copolymers **1d**−**i** were obtained in 66−85% yield.

Sulfonation. The sulfonation of polymers **1** using a flow reactor has been described previously.[11c] A typical procedure is as follows. A 200 mL syringe was charged with 100 mL of 0.01 M of polymers **1a**−**i** in dichloromethane, and a 100 mL syringe was charged with 30 mL of 1.0 M chlorosulfonic acid in dichloromethane. Both syringes were connected to the reactor via a Teflon tube. Each solution was supplied to the reactor simultaneously using a microfeeder. The flow rate of the polymer solution and the chlorosulfonic acid solution was set at 10 mL/min and 3 mL/min, respectively. The obtained mixture was poured dropwise into 500 mL of hexane. The resulting product was washed with hexane and water several times and dried under vacuum at 60 °C for 15 h to obtain a white powder of sulfonated polymers **2a**−**i**.

Membrane Preparation. Ionomers **2** (0.35 g) in 12 mL of DMAc were cast onto a clean, flat glass plate (9 cm × 6 cm). Drying the solution at 60 °C under atmospheric pressure for 15 h gave colorless and transparent membranes. The membranes were immersed in 1 N HNO_3(aq) for 12 h. The acidification process was repeated three times. The membranes were then washed with deionized water several times and dried under vacuum at 60 °C for 15 h.

Ion-Exchange Capacity (IEC). The IEC of the ionomer **2** membranes was determined by ^{1}H NMR spectroscopy and titration. In the ^{1}H NMR technique, changes in the integration ratio for the aromatic protons were taken. In the titration method, a piece of ionomer membrane was equilibrated in a large excess of 0.01 M NaCl(aq) for 15 h. The amount of HCl released from the membrane sample was determined by titration with 0.01 N NaOH(aq) using phenolphthalein as an indicator.

Oxidative Stability. A small piece of membrane sample with a thickness of 50 μm was soaked in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C for 1 h. The stability was evaluated by changes in molecular weight, IEC, weight, and appearance of the test samples.

Hydrolytic Stability. A small piece of membrane sample with a thickness of 50 μm was treated at 140 °C and 100% RH in a pressurized closed vial for 24 h. The stability was evaluated by changes in molecular weight, IEC, weight, and appearance of the test samples.

Mechanical Strength. Tensile testing was performed with a Shimadzu universal testing instrument Autograph AGS-J500N equipped with a chamber in which the temperature and the humidity were controlled by flowing humidified air with a Toshin Kogyo temperature control unit Bethel-3A. Stress versus strain curves were obtained at a speed of 10 mm/min for samples cut into a dumbbell shape (DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)).

Swelling Degree. The membrane samples were dried at 80 °C under vacuum for 3 h, and their sizes were quickly measured. Then the dried samples were immersed into deionized water at 25 or 50 °C for 3 h. The swelling degree was evaluated by the changes in thickness, area, and volume between dry and fully hydrated samples.

Water Uptake and Proton Conductivity. Water uptake and proton conductivity of ionomer **2** membranes were measured with a Bel Japan solid electrolyte analyzer system MSB-AD-V-FC equipped with a chamber, a magnetic suspension balance, and a four-point probe conductivity cell. For water uptake measurement, membrane samples (50−70 mg) were set in a chamber and dried at 80 °C under vacuum for 3 h until constant weight as dry material was obtained. The membrane was then equilibrated with N_2 gas at the given temperature and humidity for at least 1 h before the gravimetry was done. For the proton conductivity measurement, membrane samples (1.0 cm wide,

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3.0 cm long, and 50 μm thick) were set in the chamber where the temperature and the humidity were controlled by flowing humidified N_2. The membrane was then equilibrated with N_2 gas at the set temperature and humidity for at least 1 h before the measurement. The samples were contacted with two gold wire outer current-carrying electrodes and two gold wire inner potential-detecting electrodes. Impedance measurements were made using a Solartron 1255B frequency response analyzer and Solartron SI 1287 potentiostat. The instrument was used in potentiostatic mode with an ac amplitude of 300 mV with the frequency range from 1 to 100 000 Hz.

STEM Observation. The membranes were stained with silver by ion exchange of the sulfonic acid groups by immersing them overnight in a large excess of 0.5 M $AgNO_3$(aq), rinsed with water, and dried at room temperature for 12 h. The stained samples were embedded in epoxy resin and sectioned to yield 90 nm thick samples using a Leica microtome Ultracut UCT and placed on copper grids. Images were taken on a Hitachi HD-2300C scanning transmission electron microscope (STEM) using an accelerating voltage of 200 kV.

Membrane Electrode Assemblies (MEAs). Gas diffusion electrodes with three-layer structure were prepared by the following steps, i.e., wet-proofing treatment of a carbon paper (CP), coating of a gas diffusion layer (GDL) onto the CP, and coating of a catalyst layer (CL) onto the GDL. The GDL was fabricated by coating a slurry consisting of carbon black (Denki Kagaku Kogyo K. K. Denka black) and PTFE dispersions on CP (TGP-H-120, 360 μm, Toray Industries, Inc., wet-proofed with 15 wt % FEP).[17] The loading amount of the GDL (Denka black + PTFE) was 0.95 mg/cm^2. Pt-loaded carbon black (45.8 wt % Pt/CB; Tanaka Kikinzoku Kogyo TEC10E50E), 5 wt % Nafion ionomer solution, 2-propanol, and pure water were mixed in a planetary ball-mill. The weight ratio of Nafion to the CB was 0.7. The obtained catalyst ink was uniformly spread over the GDL. The electrode was cold-pressed followed by curing at 60 °C overnight and then hot-pressed at 130 °C for 3 min at 1.2 MPa. The loading amount of Pt was 0.41 mg/cm^2 for both the cathode and anode. The electrodes were treated with 1 N HNO_3 before assembling with the electrolyte membrane.

Membrane **2e** (IEC = 2.51 meq/g) or Nafion (DuPont NRE 212) was sandwiched between two gas diffusion electrodes (geometric active area = 3.1 cm^2) and hot-pressed at 130 °C for 3 min at 1.0 MPa. The membrane/electrode assembly (MEA) was mounted into a circular single test cell holder equipped with a reversible hydrogen reference electrode (RHE).

Fuel Cell Operation. All cells were operated at a cell temperature (T_{Cell}) of 90 °C under ambient pressure. Humidified H_2 was fed to the anode at 200 mL/min with the humidification temperature (T_{AH}) of 53 °C (20% RH) or 90 °C (100% RH). Humidified O_2 was fed to the cathode at 100 mL/min with the humidification temperature (T_{CH}) of 50 °C (18% RH), 53 °C (20% RH), or 80 °C (68% RH). Current−voltage ($I-V$) curves were measured under steady-state conditions. Ohmic potential drop (IR drop) was measured with a current interrupter (Nikko Keisoku NCPG 1010) by applying a current-off pulse for 100 μs to the cell and recording the resulting potential drop with a storage oscilloscope (Hitachi VC6023).

Results and Discussion

Synthesis and Characterization of Monomers, Polymers, and Ionomers. In order to prepare a series of poly(arylene ether sulfone)s having different numbers and/or positions of methyl groups, tetramethyl-substituted fluorenylidene biphenol (DMBHF) was synthesized from fluorenone and 2,6-xylenol by an acid-catalyzed reaction. Other methyl-substituted monomers were commercially available, while 3,3′,5,5′-tetramethylbiphenol was masked with propylcarbamoyl groups to improve its reactivity in the nucleophilic substitution polymerization.[16] These monomers were pure enough for polymerization as confirmed by NMR and LC−MS analyses. The parent homopolymers **1a−c** and copolymers **1d−i** were synthesized by a typical nucleophilic substitution polycondensation reaction starting from the corresponding biphenol and difluoride monomers (Scheme 1). Polymers **1d** and **1e** have isopropylidene units derived from bisphenol A monomers as main chain methylated derivatives, while the others have methyl groups on aromatic groups. Bisphenol A is an inexpensive and versatile material. All the polymers **1a−i** were soluble in DMAc, DMF, NMP, and CH_2Cl_2. As confirmed by GPC analyses, methyl-substituted polymers **1b−i** were of high molecular weight ($M_w > 2 \times 10^5$, $M_n > 3 \times 10^4$)[18] similar to that of the non-methylated **1a** and gave tough, flexible, and transparent membranes by solution casting. As a typical example, the ^{1}H NMR spectrum of **1e** is shown in Figure 1a in which all the protons are well-assigned to the supposed chemical structure. Integration ratios of the peaks correspond to the copolymer composition.

Polymers **1a−i** reacted with chlorosulfonic acid in CH_2Cl_2 to give the title sulfonated polymers **2a−i**. Since the ionomers are insoluble in CH_2Cl_2, they precipitated out of the solution soon after the polymer and chlorosulfonic acid solutions were mixed. In order to achieve efficient mixing, we have adopted a flow reactor for the sulfonation reactions as described in a previous paper.[11c] By changing the amount of chlorosulfonic acid used in the reaction, the IEC of the ionomers was easily controlled. Regardless of the number and the positions of methyl substituents, the ionomers are soluble in polar organic solvents such as DMSO, DMAc, DMF, and NMP. The ionomers gave flexible, ductile, and transparent membranes by casting from DMAc solution. In the cases of homopolymers **2a−c** (IEC < 2.5 meq/g) and copolymers **2d−i** (IEC < 1.5 meq/g), the ^{1}H NMR spectra suggested that the sulfonic acid groups were substituted only at 2,7-positions on the side fluorenyl groups. Attempts to obtain higher IEC ionomers under severe sulfonation reaction conditions (e.g., using more concentrated $ClSO_3H$ solution) resulted in main chain sulfonation as well. In the case of **2e** (IEC = 3.26 meq/g), the ^{1}H NMR spectrum (Figure 1b) indicated that most of the fluorenyl groups were sulfonated ($x = 1.76$ where x is the degree of sulfonation per fluorenyl group) and the arylene protons ortho to ether groups on the main chains were also sulfonated to some extent ($y + z = 2.92$ where y and z are the degree of sulfonation per copolymer repeating unit). The contribution of each sulfonation to the total IEC was determined to be $x = 1.46$ meq/g and $y + z = 1.80$ meq/g from a combination of titration and ^{1}H NMR spectroscopy. A series of sulfonated poly(arylene ether sulfone)s with different numbers of methyl substituents at different positions was obtained. The ionomers **2a−i** subjected to properties investigations are listed in Table 1 with their molecular weight and IEC values.

Mechanical, Oxidative, and Hydrolytic Stability. The mechanical properties of the ionomer membranes were studied at 85 °C and 93% RH simulating fuel cell operating conditions (Table 2). Ionomer **2** membranes showed a maximum stress of 5−23 MPa with the general trend of lower maximum stress for the higher IEC membranes. The **2a** membrane with an IEC = 2.76 meq/g was too weak to hold the weight of the sample clip even for a thick sample (100 μm) so that a reliable measurement

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(18) Some of the polymers show rather high polydispersity values (>6.0) due to the very high viscosity of the polymerization mixture.

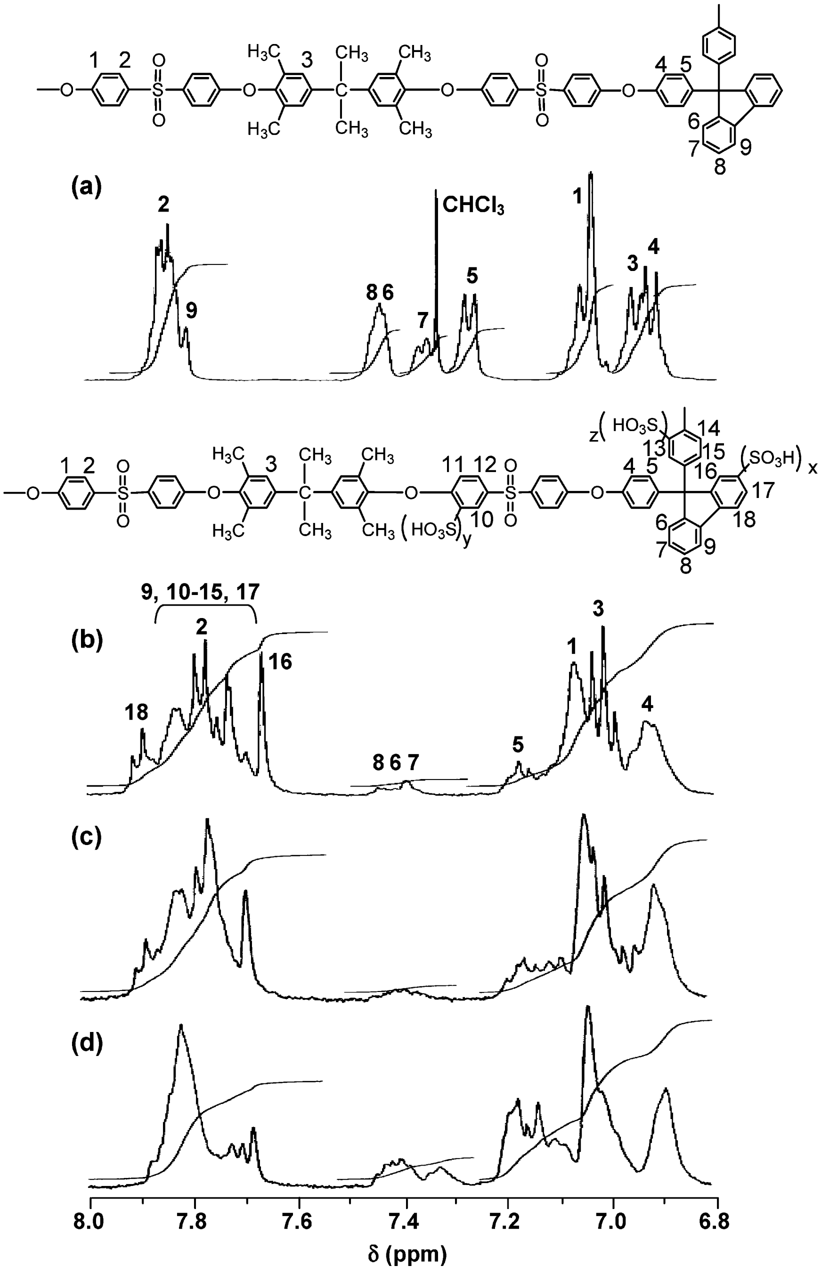

Figure 1. ^{1}H NMR spectra of (a) **1e**, (b) **2e** (IEC = 3.26 meq/g), (c) **2e-100** after a durability test at 100 °C and 80% RH for 10 000 h, and (d) **2e-120** after a durability test at 120 °C and 40% RH for 10 000 h.

could not be done. Comparison among the higher IEC (>2.5 meq/g) membranes revealed that ionomers **2e** and **2g** having methyl groups at the R_5 positions are mechanically stronger than the others. The maximum stress of **2e** with an IEC = 3.26 meq/g was 8.2 MPa and was comparable to that of the non-methylated **2a** with an IEC = 2.51 meq/g. The **2e** and **2g** membranes showed lower strain than the other membranes with similar IEC values. It is assumed that the methyl groups on the R_5 positions restrict the molecular motion of the polymer chains resulting in stronger membranes. In contrast, this effect was not distinct for the methyl substituents at the R_1-R_4 positions (compare **2a** with **2c** or **2i**) presumably because these methyl groups are placed on the bulky and robust fluorenyl groups as the larger building blocks. The methyl groups at the R_1-R_4 positions are in the vicinity of hydrophilic and amorphous sulfonated fluorenyl groups which could also account for their lesser effectiveness than that of the R_5 methyl groups.[19]

The oxidative stability of **2a**−**i** membranes was evaluated in hot Fenton's reagent for 1 h as an accelerated test. Losses of IEC, weight, and molecular weight of the membranes after the testing are shown in Table 2 and plotted as a function of IEC in Figure S1 in the Supporting Information. Membranes with an IEC lower than 1.8 meq/g showed relatively good resistance to oxidation and endured without dissolving for 1 h, while membranes with higher IEC dissolved to some extent and lost weight. It should be noted that the residual membranes after the test retained their IEC values as confirmed by titration. The results are indicative that the oxidative degradation of these ionomers occurs on the main chains rather than the pendent

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(19) The effect of methyl groups at R_5 positions was further investigated by thermal analyses. Since the sulfonated polymers decompose before the glass transition temperature, parent polymers were tested. As shown in Table S1 in the Supporting Information, substitution of methyl groups caused the T_g increase. This effect was observed for both the R_1-R_4 and R_5 positions.

Table 1. Molecular Weight and Ion-Exchange Capacity (IEC) of **2a**−**i** Membranes

ionomer	M_n (10^5)	M_w (10^5)	M_w/M_n	IEC (meq/g)^a
2a	2.86	10.24	3.6	1.59
2a	2.06	12.30	6.0	2.51
2a	1.24	11.57	9.3	2.76
2b	2.50	6.22	2.5	2.47
2c	3.53	8.20	2.5	2.27
2d	3.36	6.24	1.9	1.89
2d	3.84	9.70	2.5	2.09
2e	2.19	6.13	2.8	1.32
2e	1.36	5.17	3.8	2.51
2e	0.69	3.11	4.5	3.26
2f	3.50	13.26	3.8	1.84
2f	3.72	12.66	3.4	2.69
2g	2.03	7.90	3.9	2.36
2g	0.29	2.63	9.1	2.82
2h	1.87	5.53	3.0	2.01
2i	2.12	5.85	2.8	1.78

^{a} Determined by titration.

Table 2. Mechanical, Oxidative, and Hydrolytic Stability of **2a**−**i** Membranes

		mechanical strength		oxidative stability: decrease in			hydrolytic stability: decrease in		
ionomer	IEC (meq/g)	max stress (MPa)	strain (%)	weight (%)	IEC (%)	M_w (%)	weight (%)	IEC (%)	M_w (%)
2a	1.63	22.5	34	0	0	76	8	7	11
2a	2.51	8.4	179	100	^{a}	96	6	1	10
2a	2.76	^{a}	^{a}	100	^{a}	82	6	2	21
2b	2.47	13.1	25	100	^{a}	93	0	0	1
2c	2.27	5.9	88	5	0	78	0	0	0
2d	1.89	22.6	94	24	0	66	1	2	17
2d	2.09	10.0	291	100	^{a}	^{a}	1	2	47
2e	1.32	14.9	75	1	0	75	1	2	0
2e	2.51	7.0	190	100	^{a}	^{a}	3	2	0
2e	3.26	8.2	170	100	^{a}	98	2	12	19
2f	1.84	8.3	184	8	1	79	0	1	4
2f	2.69	4.5	317	98	^{a}	^{a}	0	0	26
2g	2.36	10.6	105	100	^{a}	^{a}	2	5	10
2h	2.01	8.1	122	3	0	60	2	0	0
2i	1.78	5.5	125	0	2	66	1	3	4
Nafion 117	0.89	23.4	332	2	0	^{a}	1	0	^{a}

^{a} Could not be measured.

sulfonic acid groups. It is reasonable to consider that the oxidative attacks by HO• and HOO• radicals are electrophilic and occur more likely on the main chain aromatic rings bound with electron-donating ether groups.[20] The oxidative stability of ionomer **2** membranes depends on the IEC but not on the number and positions of methyl substituents implying that these ionomers share the same oxidative degradation mechanisms with no participation of the methyl groups.

The **2a**−**i** membranes were also subjected to severe hydrolytic stability testing at 140 °C and 100% RH for 24 h. All the membranes maintained their transparency, flexibility, toughness, and original weight. Membranes with an IEC lower than 2.5 meq/g showed good stability to hydrolysis without any practical changes in the IEC and the ^{1}H NMR spectra. Among these, ionomer **2d** membranes showed greater M_w loss. A comparison of their chemical structures led to the assumption that the hydrolytic degradation of the ionomer membranes commenced on the main chain at the isopropylidene groups and/or at the vicinity of the hydrophilic sulfonic acid substituents. This hydrolytic susceptibility was significantly improved for ionomer **2e** membranes. Four methyl groups at the R_5 positions effectively protected the neighboring isopropylidene groups from attack by water. A similar but less effective effect was observed for ionomer **2b** and **2c** membranes compared with that of **2a**. From the mechanical, oxidative, and hydrolytic stability standpoint, the ionomer **2e** membrane containing tetramethyl bisphenol A components was the most appropriate chemical structure for a high-IEC membrane.

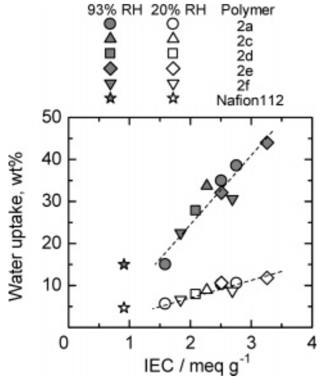

Figure 2. Water uptake of ionomer **2** membranes and Nafion 112 at 80 °C and at 20% and 93% RH.

Water Uptake and Swelling Properties. The humidity dependence of water uptake was measured for ionomer **2** membranes at 80 °C and at 20% and 93% RH (Figure 2). Two homopolymers (**2a** and **2c**) and three copolymers (**2d**, **2e**, and **2f**) were chosen as representative examples. As expected, higher IEC membranes absorbed more water at both humidity conditions. The tendency was more pronounced at 93% RH than at 20% RH. Membrane **2e** with the highest IEC = 3.26 meq/g showed the highest water uptake of 44 wt % at 93% RH, which corresponds to 7.5 water molecules per sulfonic acid group (λ). The λ value was similar to that of the lower IEC membranes (λ = 7.8 for **2a** with IEC = 2.76 meq/g). Extrapolation of the dashed lines in Figure 2 could give smaller λ values for ionomer **2** membranes with an IEC of 0.91 meq/g than that of Nafion 112. In typical hydrocarbon ionomer membranes,[21] λ increases with IEC due to excess swelling and therefore increased free volume. We then measured the swelling degree of ionomer **2** membranes in hot water and evaluated the effect of methyl groups.

Three membranes **2a**, **2b**, and **2e** were subjected to the swelling tests at 25 and 50 °C in water (Figure 3). All these membranes swelled more at higher temperature, and the differences were larger for higher IEC membranes. It should be noted that membrane **2e** (IEC = 3.26 meq/g) showed much lower swelling degree in both directions than membrane **2a** (IEC = 2.76 meq/g), despite the former's higher IEC value. Suppression of the swelling was remarkable at 50 °C compared to that at 25 °C. Similar to the mechanical and oxidative stability as discussed above, methyl substituents on the R_5 positions are effective for retaining the dimensional stability in water especially for higher IEC membranes.

Proton Conductivity. The humidity dependence of the proton conductivity was measured for membranes **2a**, **2c**, **2d**, and **2e** with different IEC values at 80, 100, and 120 °C (Figure 4). The proton conductivity of ionomer **2** membranes with IEC <

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(20) (a) Hübner, G.; Roduner, E. *J. Mater. Chem.* **1999**, *9*, 409. (b) Panchenko, A. *J. Membr. Sci.* **2006**, *278*, 269.

(21) Rozière, J.; Jones, D. J. *Annu. Rev. Mater. Res.* **2003**, *33*, 503.

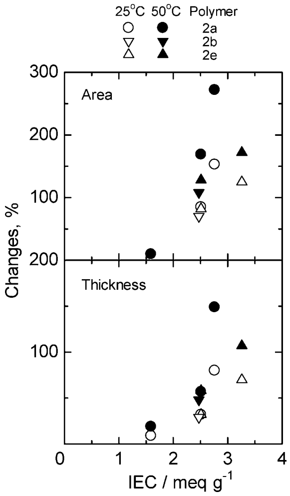

Figure 3. Swelling degree of **2a**, **2b**, and **2e** membranes in water at 25 and 50 °C.

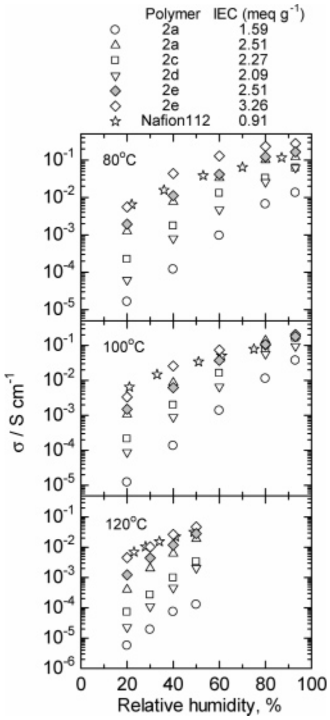

Figure 4. Humidity dependence of the proton conductivity of **2** membranes and Nafion 112 at 80, 100, and 120 °C.

2.5 meq/g showed great dependence on humidity. For example, the conductivity of **2d** (IEC = 2.09 meq/g) dropped from 6.3 × 10^{-2} S/cm (93% RH) to 6.2 × 10^{-5} S/cm (20% RH) at 80 °C. The conductivity at 20% RH was more than 2 orders of magnitude lower than that of Nafion 112. This is typical behavior for hydrocarbon ionomer membranes due to less developed microphase separation and lower acidity than those of the perfluorinated ionomers.[22] Increasing the IEC of ionomer **2** membranes could significantly increase the conductivity at low humidity. Ionomer **2e** (IEC = 3.26 meq/g) membrane showed 5.6 × 10^{-3} S/cm proton conductivity at 20% RH and 80 °C. The conductivity of the **2e** membrane was comparable to or even higher than that of Nafion 112 at 80−120 °C and 20−93% RH. All of the ionomer **2** membranes were durable in wet/dry cyclings during the measurement (several tens of hours) without detectable degradation.

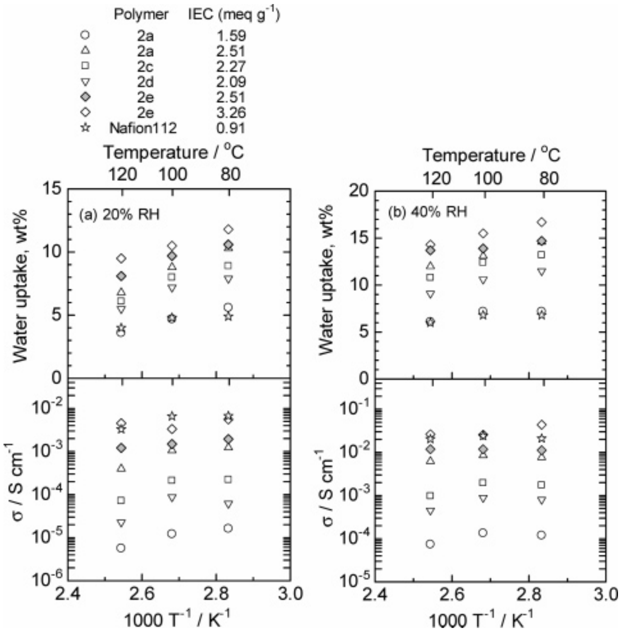

Figure 5. Temperature dependence of the proton conductivity and water uptake of **2** and Nafion 112 membranes at (a) 20% RH and (b) 40% RH.

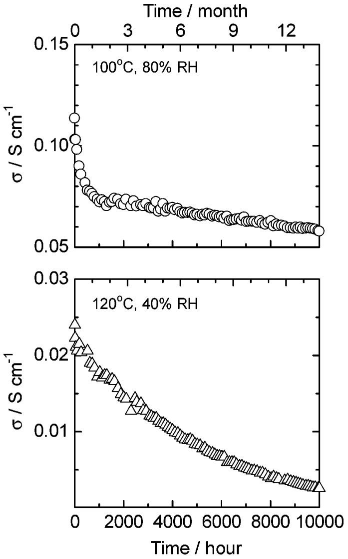

Figure 6. Durability of the proton conductivity of the **2e** (IEC = 3.26 meq/g) membrane at 100 °C and 80% RH and at 120 °C and 40% RH.

Proton conductivity and water uptake of the ionomer membranes at 20% and 40% RH are plotted as a function of temperature (Figure 5). Water uptake decreased with increasing temperature at both humidities for all the membranes. Due to the evaporation of water, the number of hydronium ions as the proton carrier decreases at high temperature resulting in a decrease in the proton conductivity for membranes **2a**, **2c**, and **2d**. In contrast, **2e** membranes showed proton conductivity less dependent on the temperature. It is considered that the lower concentration and the higher mobility of the carrier ions counteracted each other and resulted in a nearly constant value of the proton conductivity. This particular behavior, we believe, is because of well-connected proton transport channels in **2e** membranes (see the next section). Similar behavior was also observed for Nafion 112.

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[22] Kreuer, K. D. *J. Membr. Sci.* **2001**, *185*, 29.

Table 3. Property Changes of **2e** (IEC = 3.26 meq/g) Membrane after a 10 000 h Durability Test

							contribution to IEC (meq/g)		proton conductivity σ (S/cm)	
ionomer	test conditions	thickness (μm)	width (cm)	M_n (10^5)	M_w (10^5)	IEC (meq/g)	x (side chain)	$y + z$ (main chain)	100 °C 80% RH	120 °C 40% RH
2e	fresh	78	0.50	0.69	3.11	3.26	1.46	1.80	1.1×10^{-1}	2.4×10^{-2}
2e-100	100 °C 80% RH	78	0.50	0.59	2.91	2.16 (2.56)[a]	(1.45)[a]	(1.11)[a]	5.8×10^{-2} (1.1×10^{-1})[a]	
2e-120	120 °C 40% RH	62	0.46	0.78	3.19	1.82 (2.05)[a]	(0.91)[a]	(1.14)[a]		2.6×10^{-3} (1.3×10^{-3})[a]

[a] Numbers in parentheses are the values after acid treatment.

Since the **2e** (IEC = 3.26 meq/g) membrane showed the most preferable properties from the viewpoint of stability and proton conductivity, its longevity was evaluated at 100 °C and 80% RH (dew point = 93.8 °C) and 120 °C and 40% RH (dew point = 93.3 °C) (Figure 6). At 100 °C and 80% RH, the proton conductivity decreased from 1.1×10^{-1} to 7.2×10^{-2} S/cm during the first 1000 h of the test and then gradually decreased to 5.8×10^{-2} S/cm over 10 000 h. At 120 °C and 40% RH, the conductivity decreased from 2.4×10^{-2} to 2.6×10^{-3} S/cm over 10 000 h.

After 10 000 h of testing, **2e** membranes retained their strength and flexibility. Property changes of **2e** (IEC = 3.26 meq/g) membranes after the durability test are summarized in Table 3. It was found that the IECs of the recovered membranes were lower than that of the fresh **2e** membrane: 2.16 meq/g for **2e-100** and 1.82 meq/g for **2e-120** membranes. After treating **2e-100** and **2e-120** membranes with 1 N HNO_3(aq), the IEC and proton conductivity recovered to some extent but not to the original values. Therefore, we conclude that the conductivity decrease was attributed to two major reasons: loss of sulfonic acid groups and the cationic contamination. The latter has been derived from the stainless steel tubing used for flowing humidified nitrogen and/or from the environment. By analyzing the ^{1}H NMR spectra of the membranes (Figure 1, parts c and d), we could elucidate from which positions the sulfonic acid groups were removed. In both spectra, peaks around 7.3−7.5 ppm (nos. 6, 7, and 8) and 7.1−7.2 ppm (no. 5) ascribed to unsulfonated aromatic protons are larger than those of the fresh **2e** membrane (Figure 1b). In the **2e-100** membrane, loss of sulfonic acid groups was mainly from the main chains; the contribution of ($y + z$) to the total IEC decreased from 1.80 to 1.11 meq/g. This is reasonable when taking into account that hydrolytic loss of sulfonic acid groups is a nucleophilic substitution reaction with water and occurs more likely on the main chains (at the y position of the aromatic carbons ipso to the sulfonic acid groups) connected with electron-withdrawing sulfone groups. However, under more severe conditions, the loss of sulfonic acid groups was detected both from the main and the side chains (**2e-120**). The thickness and width of the membranes did not change for **2e-100** but slightly decreased for **2e-120**. Nevertheless, from GPC elution curves of the **2e**, **2e-100**, and **2e-120** membranes (Figure S2 in the Supporting Information), the molecular weight and its distribution remained almost the same after the durability test.

STEM Observation. In order to investigate hydrophilic/hydrophobic microphase separation and the proton transport pathway on the **2** membranes, scanning transmission electron microscopic (STEM) observations were carried out (Figure 7). The membranes were stained with silver ions; therefore, the dark areas represent hydrophilic (ionic) domains and the brighter areas represent hydrophobic domains. In Figure 7a, the **2a** (IEC = 1.63 meq/g) membrane exhibited spherical ionic clusters of relatively uniform size. These ionic clusters were not connected with each other but were rather isolated. More clusters were observed for the higher IEC **2a** membrane (Figure 7b); however, the situation seemed alike. The connectivity of these ionic clusters was significantly improved in the **2e** (IEC = 3.26 meq/g) membrane (Figure 7c) and was similar to that of the Nafion 112 membrane (Figure 7d). It has generally been considered that protons migrate as hydronium ions through hydrophilic ionic channels of ionomer membranes. The microscopic structure of the **2e** membrane is consistent with the above-mentioned proton conductivity behavior especially at low-humidity conditions.

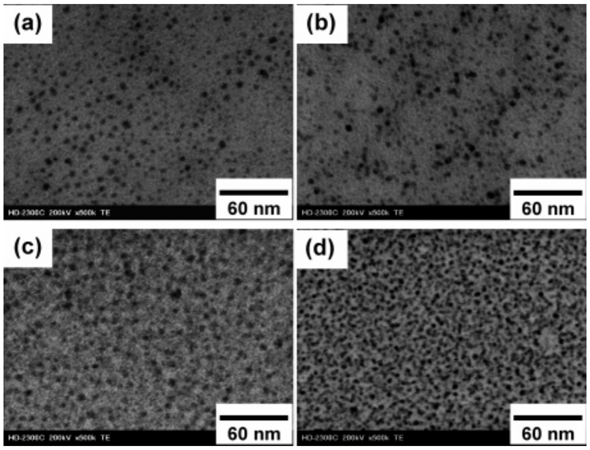

Figure 7. STEM images of (a) **2a** (IEC = 1.59 meq/g), (b) **2a** (IEC = 2.51 meq/g), (c) **2e** (IEC = 3.26 meq/g), and (d) Nafion112 membranes.

PEFC Performance. Fuel cell performance of the **2e** (IEC = 2.51 meq/g, 40 μm thick) membrane was tested and compared to that of Nafion NRE 212 (IEC = 0.92 meq/g, 50 μm thick). Proton conductivity and water uptake properties of the tested **2e** membrane are provided in Figure S3 in the Supporting Information and highlighted in gray color in Figures 4 and 5. Cells were operated at a rather high temperature of 90 °C and at three different humidity conditions. High humidity is 100% RH (anode) and 65% RH (cathode), medium humidity is 100% RH (anode) and 18% RH (cathode), and low humidity is 20% RH for both electrodes. As shown in Figure 8 (high- and medium-humidity conditions), the ohmic resistance of the **2e** cell was lower than that of Nafion (even taking the slight difference in thickness into account) so that the better $I-V$ performance was obtained at the current density from 0 to 1.0 A/cm^2. These data also indicate that the contact between the **2e** membrane and the Nafion-based electrodes was sufficiently good despite the different nature of each ionomer material.

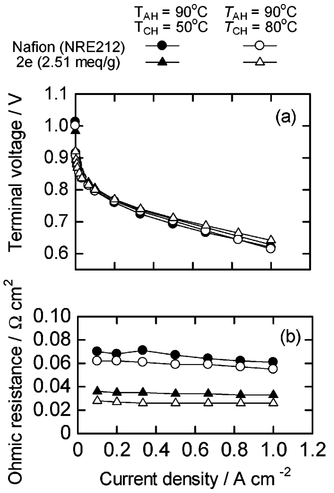

Figure 8. Steady-state terminal voltage (including IR loss) and ohmic resistance of fuel cells at high- and medium-humidity conditions for **2e** (▲, △) and Nafion (●, ○) membranes, respectively. All cells were operated at 90 °C.

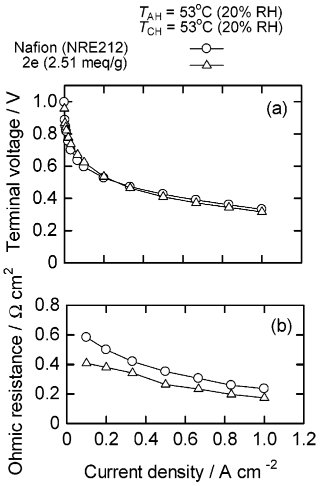

Figure 9. Steady-state terminal voltage (including IR loss) and ohmic resistance of fuel cells at low-humidity conditions for **2e** (△) and Nafion (○) membranes. All cells were operated at 90 °C.

The lower resistance of the **2e** cell than that of the Nafion cell was also true under low-humidity conditions (Figure 9). The inconsistency between cell resistance and proton conductivity (20% RH in Figure S3) is presumably due to the diffusion of water (produced at the cathode) into the membrane. The **2e** membrane is expected to have better water-holding capability at high temperature.[11] Unfortunately, the $I-V$ performance did not reflect much of the ohmic resistance because of inferior cathode performance of the **2e** cell as confirmed by the IR-free potential shown in Figure S4 in the Supporting Information.

Conclusions

The chemical structures of poly(arylene ether sulfone) ionomers containing fluorenyl groups (**2a**−**i**) have been tuned for fuel cell applications. The parent polyethers **1a**−**i** were sulfonated to give the ionomers with an ion-exchange capacity (IEC) up to 3.26 meq/g. Sulfonic acid groups were introduced only on the pendent fluorenyl groups with an IEC < 2.5 meq/g, while the main chains were also sulfonated for the higher IEC ionomers. The ionomers were high molecular weight ($M_w > 3 \times 10^5$, $M_n > 3 \times 10^4$) and formed tough and flexible membranes. Hydrolytic and oxidative stability was confirmed by accelerated tests. Isopropylidene groups in the bisphenol A copolymer units resulted in lower stabilities, which could be sufficiently improved by introducing tetramethyl groups on adjacent phenylene rings. The methylation was likewise effective in giving high mechanical strength and good dimensional stability. In contrast, methyl group substitution on fluorenylide biphenylene units was less effective. Sulfonic acid groups on the main chains were more susceptible to both hydrolysis and oxidation due to the concurrent electron-withdrawing sulfone and electron-donating ether groups.

The ionomer membranes were highly proton conductive. Increasing the IEC significantly increased the conductivity at low humidity. Ionomer **2e** membrane with the highest IEC of 3.26 meq/g showed a proton conductivity of 5.6×10^{-3} S/cm at 80 °C and 20% RH which is comparable to that of the perfluorinated Nafion membrane. Although there is a decline of proton conductivity with time, after 10 000 h the proton conductivities were still at acceptable levels for fuel cell operation. The membranes retained their strength, flexibility, and high molecular weight after 10 000 h. In the **2e-100** membrane, most of the sulfonic acid group loss was from the main chains, while the sulfonic acid groups were detached both from the main and the side chains in the **2e-120** membrane. Sulfonic acid groups on the fluorenyl groups were much less susceptible to the hydrolytic removal, corresponding to the results of the accelerated tests. Microscopic analyses revealed that the connectivity of ionic clusters was significantly improved in the **2e** (IEC = 3.26 meq/g) membrane compared to that of the lower IEC membranes and was similar to that of Nafion 112. The newly developed **2e** ionomer membrane has proved better ohmic performance than Nafion in H_2/O_2 fuel cells at a high temperature of 90 °C. The advantage of the **2e** membrane was confirmed under low- and high-humidity conditions and is possibly due to its good water-holding capability.

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Supporting Information Available: Detailed data on the ionomer's properties. This material is available free of charge via the Internet at http://pubs.acs.org.

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