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Poly(arylene ether) Ionomers Containing Sulfofluorenyl Groups for Fuel Cell Applications

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ABSTRACT: A new series of poly(arylene ether) ionomers containing sulfofluorenyl groups has been synthesized for the applications to polymer electrolyte fuel cells (PEFCs). The parent polyethers were regioselectively substituted with sulfonic acid groups to give the ionomers with the ion exchange capacity up to 2.0 mequiv/g. The ionomers **2a** (homopolymer) and **2b** (copolymer) gave a tough, flexible, ductile, and transparent membrane by casting from the solution. Thermal stability with decomposition temperature of ca. 250 °C and no glass transition temperature was confirmed for the ionomers. The membrane of **2a** (ion-exchange capacity (IEC) = 1.80 mequiv/g) showed outstanding stability to oxidation and hydrolysis as confirmed in the accelerated testing in hot Fenton's reagent or in the atmosphere at 140 °C and 100% relative humidity. The membrane of **2a** (IEC = 1.63 mequiv/g) exhibited better mechanical properties (lower elongation and higher strength) than those of Nafion 117. The fully hydrated membrane of **2a** (IEC = 1.14 meq/g) showed the highest proton conductivity (0.2 S cm^{-1}) at 140 °C. The proton conductivity was durable over 1300 h. Lower gas (H_2 and O_2) permeation was confirmed for **2a** rather than for Nafion. All those properties of the ionomers **2** are promising as an electrolyte membrane for high-temperature PEFCs.

Introduction

Ion-containing polymers, or ionomers, are among important classes of polymeric materials as cation-exchange resins, dopants for p-type electroconductors, matrixes for acid/base polymer complexes, and ion conductors.[1] Particularly, recent progress in the area of polymer electrolyte fuel cells (PEFCs) has stimulated considerable interest in the aromatic ionomers as proton conductive polymer membranes.[2] The requirements for a PEFC membrane are proton conductivity (>0.1 S cm^{-1}), thermal, chemical, and physical stability, and durability under the fuel cell operating conditions. The most used membrane materials for PEFCs are perfluorinated sulfonic acid ionomers such as Nafion (Du Pont), Flemion (Asahi Glass Co., Ltd), and Aciplex (Asahi Kasei Co., Ltd). The perfluorinated ionomers are highly proton conductive and substantially stable; however, their performance is lowered at higher temperatures than their glass transition temperatures, T_g (ca. 100 °C). High gas permeation and environmental inadaptability are other drawbacks for the commercial applications in fuel cells. Therefore, there is a great demand for alternative proton-conductive membranes. Considerable effort has been made to produce proton-conductive nonfluorinated aromatic ionomers with substantial stability for PEFCs.[3] For example, acid-functionalized poly(ether ether ketone)s,[4] polysulfones,[5] polyimides,[6] polyphosphazenes,[7] and polybenzimidazoles[8] fall into this category.

Poly(phenylene ether)s are one of the most important engineering plastics and have attracted much attention as a base skeleton for ionomers. Recently, a new series of poly(arylene ether) ionomers have been developed by several groups.[9,10] It has been proposed that pendant sulfonic acid groups could improve the hydrolytic stability of the ionomer membranes.[10] In our previous communication, we have synthesized a novel sulfonated poly(arylene ether) containing fluorenyl groups, in which the sulfonic acid groups were substituted only at specific (2 and 7) positions on fluorenyl groups.[11] The ionomer shows high proton conductivity (0.2 S cm^{-1}) and excellent hydrolytic stability under harsh hydrolytic conditions (140 °C and 100% relative humidity, RH). In this paper, we describe further investigation on the properties of the poly(arylene ether) ionomer containing sulfofluorenyl groups. The effect of the sulfonation degree on the proton conductivity, water uptake, hydrolytic and oxidative stability, mechanical strength, and gas permeation is discussed. Copolymers with bisphenol A (4,4′-isopropylidenediphenol) have been synthesized, of which properties are also included.

Experimental Section

Materials. 4-Fluorophenyl sulfone (FPS) (99%, Acros Organics) was purified by crystallization from ethanol. 9,9′-Bis(4-hydroxyphenyl)fluorene (BHF) (98%, TCI Co., Inc.), 4,4′-isopropylidenediphenol (BPA) (99%, Kanto Chemical 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. *N*,*N*-Dimethyl acetamide (DMAc) (99%, Kanto Chemical Co., Inc.) was dried over molecular sieves 3A prior to use. Other chemicals were of commercially available grade and used as received unless otherwise mentioned.

Synthesis of Homopolymer 1a. The typical procedure is as follows. A 100-mL four-neck round-bottomed flask equipped with a magnetic stirring bar, an N_2 inlet, and an addition funnel was charged with BHF (1.0 mmol, 0.350 g), FPS (1.0 mmol, 0.250 g), potassium carbonate (2.5 mmol, 0.346 g), toluene (7.5 mmol, 0.8 mL), and 3 mL of DMAc. The mixture was stirred at room temperature (RT) for a few minutes and then heated at 140 °C for 3 h and at 165 °C for 3 h under N_2 atmosphere. After the reaction, 15 mL of DMAc was added to the mixture to lower the viscosity. The solution was poured dropwise into 500 mL of deionized water to precipitate a white flake of the product. The product was washed with hot deionized water and methanol several times and treated in a

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Soxhlet extractor with acetone at reflux. The resulting product was dried under vacuum at 60 °C for 15 h. The pure homopolymer **1a** was obtained in 86% yield.

Synthesis of Copolymer 1b. The polymerization was carried out in the same manner as described for the homopolymer **1a** except that BPA was used as a comonomer. The molar ratio of BHF to BPA was set at 1:1. A white flake of pure copolymer **1b** was obtained in 95% yield.

Sulfonation. The typical procedure is as follows. To a solution of the polyether **1a** or **1b** (0.50 mmol) in 50 mL of dichloromethane, 10 mL of 1.0 M chlorosulfonic acid in dichloromethane was added dropwise at 30 °C. The mixture was stirred at 30 °C for 3 h and poured dropwise into 500 mL of hexane to precipitate a pale-purple powder. 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 the sulfonated polyether ionomer **2a** or **2b**.

Membrane Preparation. The ionomer **2a** or **2b** (0.30 g) in 10 mL of DMAc was cast onto a clean and flat glass plate. Drying the solution at 60 °C under atmospheric pressure for 15 h gave a clear and colorless transparent membrane. The membrane was immersed in 1 N HNO_3 aq for 12 h. The acidification process was repeated three times. The membrane was then washed with deionized water several times and dried under vacuum at 60 °C for 15 h.

Measurement. ^{1}H 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 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. Thermal analyses were performed on a Mac Science thermogravimetric differential thermal analysis (TG/DTA) 2000 instrument. For each run, the temperature was increased from RT to 400 °C at a heating rate of 20 °C/min under N_2.

Ion-Exchange Capacity (IEC). IECs of the ionomers **2** were determined by ^{1}H NMR spectra 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 membranes was equilibrated in large excess of 0.01 M NaCl aq for 15 h. The concentration of HCl released from the membrane sample was measured by titration with 0.01 N NaOH aq using phenolphthalein as an indicator.

Water Uptake. Water uptake of the ionomers was measured with a Bel Japan solid electrolyte analyzer system MSB-AD-V-FC equipped with a chamber and a magnetic suspension balance. 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 the gases at the given temperature and humidify at least for 1 h before the gravimetry was done.

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

Hydrolytic Stability. A small piece of membrane samples with a thickness of 50 μm was placed in a closed chamber and treated at 140 °C and 100% RH under a pressure of ca. 3.5 atm for 700 h as an accelerated testing. The stability was evaluated by changes in molecular weight, IEC and appearance of the test samples.

Mechanical Strength. Mechanical 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 vs 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)).

Proton Conductivity. A four-point-probe conductivity cell with two gold plate outer current-carrying electrodes and two platinum wire inner potential-detecting electrodes were fabricated. Membrane samples were cut into strips that were 0.5 cm wide, 4.5 cm long, and 50 μm thick prior to mounting in the cell. The cell was placed in a stainless steel chamber where the temperature and the humidity were controlled by flowing humidified N_2. Impedance measurements were made using Solartron 1255B gain phase analyzer and Solartron SI 1287 potentiostat. The instrument was used in galvanostatic mode with current amplitude of 0.005 mA with over a frequency range from 1 to 100 000 Hz.

Gas Permeability. Hydrogen and oxygen permeability through the ionomer membrane was measured with a GTR-Tech 20XFYC gas permeation measurement apparatus equipped with a Yanaco G2700T gas chromatography. The gas chromatography contained a Porapak-Q column and a TCD detector. Argon and helium were used as a carrier gas for the measurement of hydrogen and oxygen, respectively. A membrane sample (φ = 30 mm, thickness = ca. 50 μm) was set in a cell which has gas inlet and outlet on both sides of the membrane. The cell temperature was controlled by placing it in an oven. On one side of the membrane, a dry or humidified test gas (hydrogen or oxygen) was supplied at a flow rate of 30 mL/min, while on the other side of the membrane, the same gas as the carrier used in the gas chromatograph (flow gas) was supplied at a flow rate of 30 mL/min. The flow gas was humidified under the same conditions as the test gas so as to keep the membrane's wetting uniform. Before each measurement was done, the membrane was equilibrated with the gases at the given temperature and humidity for at least 3 h. Flow gas (3.7 mL) was sampled and subjected to the gas chromatography to quantify the test gas permeated through the membrane. The gas permeation rate, r (cm^3 (STD) cm^{-2} s^{-1}), and the gas permeation coefficient, Q (cm^3 (STD) cm cm^{-2} s^{-1} cm Hg^{-1}), were calculated according to the following equations

$$r = \frac{273}{T} \times \frac{1}{A} \times B \times \frac{1}{t}$$

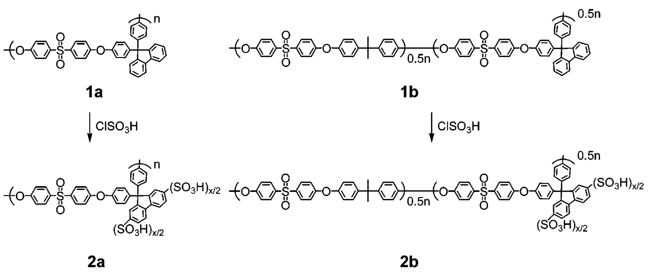
$$Q = \frac{273}{T} \times \frac{1}{A} \times B \times \frac{1}{t} \times l \times \frac{1}{76 - P_{H_2O}}$$

where T (K) is the absolute temperature of the cell, A (cm^2) is the permeation area, B (cm^3) is the volume of test gas permeated through the membrane, t (s) is the sampling time, l (cm) is the thickness of the membrane, and P_{H_2O} (cm Hg) is the water vapor pressure.

Results and Discussion

Synthesis and Characterization of Ionomers. The parent polymers **1a** and **1b** were synthesized by the typical nucleophilic substitution polycondensation reactions from the corresponding biphenol and difluoride monomers. For the copolymer **1b**, bisphenol A was chosen as a comonomer since it is one of the most commonly and the most inexpensive bisphenols available for the synthesis of poly(arylene ether)s. As confirmed by gas permeation chromatography (GPC) analysis, both polymers are high molecular weight ($M_w > 2 \times 10^5$, $M_n > 4 \times 10^4$) to give a tough, flexible, and transparent film by casting from CH_2Cl_2 solution. Polymers **1a** and **1b** were reacted with chlorosulfonic acid in CH_2Cl_2 to afford the sulfonated ionomers **2a** and **2b**, respectively (Scheme 1). The ionomers are soluble in polar organic solvents such as DMSO, DMF, and NMP and were well characterized by NMR analysis. As discussed in the previous communication,[11] ^{1}H NMR spectra have revealed that the sulfonic acid groups are substituted only at 2,7-positions on fluorenyl groups. Since the ionomers are not soluble in CH_2Cl_2, they

Scheme 1. Synthesis of Poly(arylene ether) Ionomers 2



precipitate out of the mixture sooner before the further sulfonation reactions take place on other positions when proper amount of chlorosulfonic acid was applied (see below). The ^{13}C NMR spectra also confirmed the ionomer structure. In Figure 1b is shown the ^{13}C NMR spectrum of **2a** in which the peaks 15–20 were assigned to carbons of sulfofluorenyl groups. All other peaks 1–14 in Figure 1b corresponds to those of **1a** (Figure 1a), supporting the suggested chemical structure of **2a**.

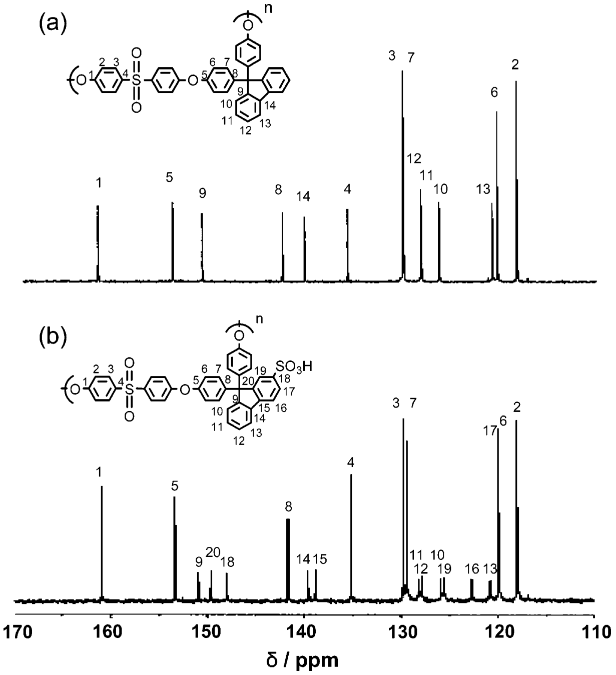


Figure 1. Aromatic region in ^{13}C NMR spectra of **1a** (a) in $CDCl_3$ and **2a** (b) in DMSO-d_6.

The degree of sulfonation (x) per repeating unit was determined from the integration ratio of the peaks of fluorenyl groups to those of the main chains in the ^{1}H NMR spectra. The degree of sulfonation could be easily controlled by changing the amount of chlorosulfonic acid used in the reaction (Figure 2). When three equimolar chlorosulfonic acid was reacted with **1a** or **1b**, ionomer **2a** with $x = 1.28$ (which corresponds to 1.92 mequiv/g of the IEC) or **2b** with $x = 2.10$ (1.79 mequiv/g of IEC) was obtained, respectively. More addition of chlorosulfonic acid was not effective since it caused unfavorable sulfonation on the main aromatic rings.

Ionomers give tough, flexible, ductile, and transparent membranes by casting from the solution. Unlike the conventional main chain sulfonated poly(arylene ether)s of which membranes are soft in wet but quiet brittle in the dry state,[12] membranes from **2a** and **2b** retain their strength and flexibility both under the wet and dry conditions. To confirm the IEC of the ionomer membranes, some of the membrane samples were subjected to titration with NaOH aq after equilibrated in an aqueous solution containing large excess of NaCl. As shown in Figure 3, the IECs obtained from the titration are in fair agreement with the values from ^{1}H NMR spectra. These results support the validity of the above NMR characterization and also indicate that the sulfonic acid groups of the ionomer membranes function adequately in aqueous medium.

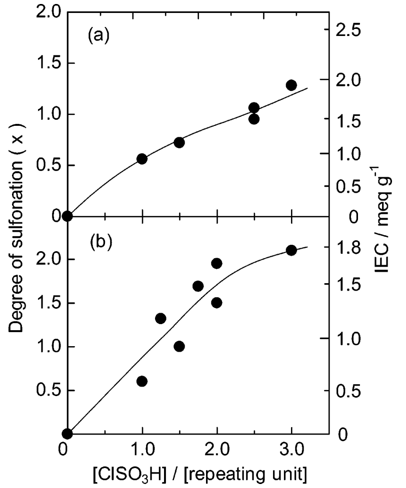


Figure 2. Effect of the concentration of chlorosulfonic acid on the degree of sulfonation for **2a** (a) and **2b** (b).

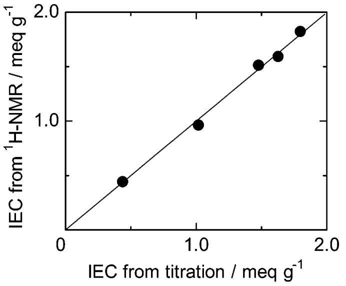


Figure 3. IEC of **2a** measured by titration and ^{1}H NMR spectra.

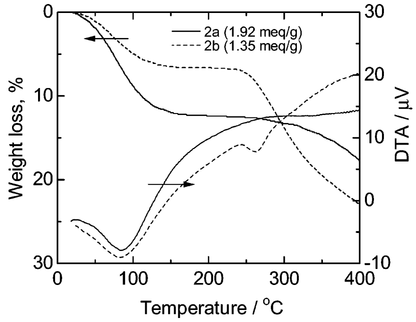


Figure 4. TG/DTA curves of **2a** (IEC = 1.92 mequiv/g) (solid line) and **2b** (IEC = 1.35 meq/g) (dotted line).

Thermal Properties. In TG analysis under a dry N_2 atmosphere, two-step weight loss was observed: desorption of hydrated water (<150 °C) and the polymer degradation. The ionomer **2a** (IEC = 1.92 mequiv/g) showed high thermal stability with the decomposition temperature of about 250 °C (Figure 4), which is comparable to that of the perfluorinated ionomer membrane (Nafion 112).[6e] Because of the whole aromatic rigid framework of **2a**, no distinct T_g value was detected in the DTA curve. The ionomer **2b** (IEC = 1.35 mequiv/

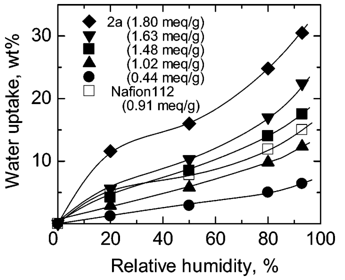


Figure 5. Humidity dependence of water uptake of **2a** membranes and Nafion 112 at 85 °C.

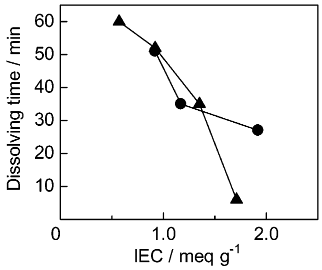


Figure 6. Dissolving time of **2a** (●) and **2b** (▲) membranes in hot Fenton's reagent as a function of IEC.

g) showed similar thermal properties except that the ash residue at 400 °C was a smaller amount. There were no significant differences observed in TG/DTA curves among the ionomers **2a** and **2b** regardless of their degree of sulfonation or IEC.

Water Uptake. The water uptake of **2a** membranes was measured at 85 °C under various humidity conditions (0−93% RH). The results are summarized in Figure 5, in comparison with those of Nafion 112. As expected, **2a** membranes with high IEC values showed considerably high water uptake; the membrane with IEC = 1.80 mequiv/g absorbed as much as 30.5 wt % of water at 93% RH, which corresponds to 9.4 water molecules per sulfonic acid group. The water uptake per sulfonic acid group is comparable to that of Nafion 112 (9.2 H_2O/SO_3H) under the same conditions, while the **2a** membranes with lower IEC values showed somewhat lower values; 6.6 H_2O/SO_3H (IEC = 1.48 mequiv/g) and 6.7 H_2O/SO_3H (IEC = 1.02 mequiv/g). Unlike the sulfonated polyimide ionomers containing fluorenyl groups which show maximum water uptake as decreasing the IEC,[6e] the poly(arylene ether) ionomers **2a** did not show such unusual behavior at any humidity conditions.

Oxidative and Hydrolytic Stability. The oxidative stability of **2a** and **2b** membranes was evaluated in hot Fenton's reagent as an accelerated testing to simulate the fuel cell operating conditions. The dissolving time of the membrane was plotted as a function of IEC in Figure 6. Although the membranes with lower IEC values than 0.7 mequiv/g showed relatively good resistance to the oxidative degradation without dissolving for almost 1 h, the membrane with a higher IEC value started to dissolve in the solution within 40 min. Nonetheless, the membrane of **2a** (IEC = 1.80 mequiv/g) still retained more than 90% of its original weight after 1 h of treatment. The molecular weight was lowered to about one-fourth of the original (from 853 × 10^3 to 170 × 10^3 in M_w); however, the IEC did not change at all as confirmed by their NMR spectra and the titration. The results are indicative that the oxidation degradation of the polyether ionomers is likely to take place on the main chain rather than the pendant sulfonic acid groups. As a reference, Nafion 112 lost ca. 3 wt % under the same oxidative conditions.

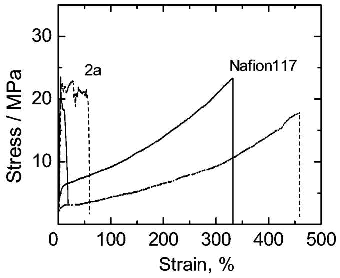


Figure 7. Stress vs strain curves of **2a** (IEC = 1.63 mequiv/g) and Nafion 117 at 85 °C (solid line) and 120 °C (dotted line) and 93% RH.

The membrane **2a** (IEC = 1.80 mequiv/g) was subjected to harsh hydrolytic testing at 140 °C and 100% RH and has revealed to endure for 700 h. After the testing, the membrane kept its flexibility and toughness without any practical changes in the GPC profile and NMR spectrum. There has been no standardized procedure to evaluate the oxidative and hydrolytic stability of fuel cell membranes. Yet, to the best of our knowledge, these above oxidative and hydrolytic stability of **2a** membranes are uppermost among the nonfluorinated hydrocarbon ionomers.

Mechanical Properties. Tensile strength of the ionomer membranes was measured under the heated (85 or 120 °C) and humidified (93% RH) conditions (Figure 7). Nafion 112 of 50 μm thick was not available for the measurement, because it was too weak to hold the weight of sample clip. Therefore, Nafion 117 of 180 μm thick was used. Nafion 117 membrane extended considerably with 334% of the strain and 24 MPa of the maximum stress at break at 85 °C. The mechanical properties were lowered by heating to 120 °C with 460% of the strain and 18 MPa of the maximum stress at break. While the maximum stress of **2a** (IEC = 1.63 mequiv/g) membrane in 50 μm thick was 24 MPa and comparable to that of Nafion 117, its elongation was as small as 19%. The **2a** membrane retained its good mechanical properties at 120 °C, only its elongation became somewhat larger (60%). Young's modulus estimated from the slope in the SS curves was as high as 0.5 GPa (85 °C) and 0.3 GPa (120 °C) for **2a** and merely 7.0 MPa (85 °C) and 3.9 MPa (120 °C) for Nafion 112, respectively. These mechanical properties would be of great advantage in the light of membrane electrode assembly in fuel cells, in which large stress is applied to membrane under heated and humidified conditions.

Proton Conductivity. Proton conductivity of the ionomer membranes was measured at 100% RH and depicted as an Arrenius plot in Figure 8. The ionomer **2a** (IEC = 1.14 mequiv/g) showed the most preferable proton-conducting properties with 0.2 S cm^{-1} of the highest conductivity at 120 and 140 °C. The apparent activation energy for the proton conduction estimated from the slope at 40−100 °C is 21 kJ/mol, which is similar to that of Nafion or other hydrated ionomer membranes.[6d,13] It is generally recognized that the proton conduction in ionomer membranes involves migration of protons as hydronium ions ($H^+(H_2O)_n$). The good water holding capability above 100 °C should be responsible for the high proton conductivity of **2a** (IEC = 1.14 mequiv/g) membrane. The same behavior has been also confirmed for the sulfonated polyimide ionomers containing fluorenyl groups.[6e] The proton conduc-

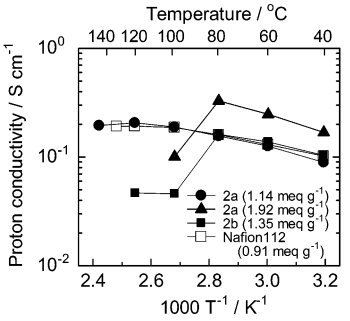


Figure 8. Temperature dependence of the proton conductivity of **2a** and **2b** membranes and Nafion 112.

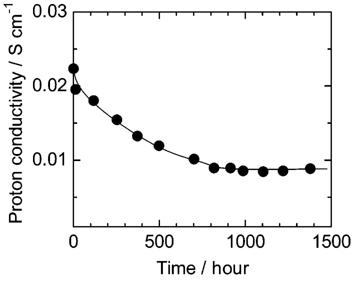


Figure 9. Durability of the proton conductivity of **2a** (IEC = 1.48 mequiv/g) at 100 °C and 80% RH.

tivity of **2a** (IEC = 1.14 mequiv/g) is comparable to that of Nafion 112 at 40−130 °C. Nafion 112, however, loses mechanical strength and does not show stable proton conductivity above 130 °C.[14] That is also the case for the higher IEC membranes of **2a** (1.92 mequiv/g) and **2b** (1.35 mequiv/g). Too many substitutions of sulfonic acid groups and the copolymerization with BPA probably result in lowering the molecular interactions among the ionomer main chains and losing structural stiffness under wet conditions.

The durability of the proton conductivity was evaluated for **2a** (IEC = 1.48 mequiv/g) at 100 °C and 80% RH (Figure 9). The conductivity gradually decreases from 2.2×10^{-2} to 0.8×10^{-2} S cm^{-1} over 1300 h; however, no degradation in chemical structure was confirmed in GPC, ^{1}H NMR spectra, and titration. Although we did not observe a T_g in dry state as discussed above (Figure 4), micro-Brownian segmental motion might take place during a long period of time under humidified conditions. This should cause morphological (hydrophilic/hydrophobic nanoseparation) changes to affect water affinity and the proton-transporting pathways.

The humidity dependence of the proton conductivity was measured for **2a** (IEC = 1.48 mequiv/g) and **2b** (IEC = 1.50 mequiv/g) at 80, 100, and 120 °C (Figure 10). When compared to Nafion 112, ionomers **2** showed much greater dependence of the conductivity on the humidity. The proton conductivity of **2a** membranes decreased several orders of magnitude down to the order of 10^{-5} S cm^{-1} at <40% RH. As discussed in the literature,[12] aromatic ionomers are unlikely to have well-developed hydrophilic domain (or cluster) and therefore lose much of the conductivity under low humidified conditions. The proton conductivity shows little dependence on the temperature, since the carrier (hydronium ions) concentration would be more crucial than its mobility.

Gas Permeation Properties. Hydrogen and oxygen permeability was investigated for **2a** (IEC = 1.63 mequiv/g) and Nafion 112 membranes both under dry and wet conditions. Both membranes are 50 μm thick. The gas permeation rate (r) and the gas permeability coefficient (Q) under dry conditions for the both membranes are summarized in Figure 11 as a function of temperature. Although the hydrogen and oxygen permeability is slightly higher for **2a** membranes than for Nafion 112 at 40 °C, elevating the temperature reverses the situation. This behavior is much more pronounced for oxygen than for hydrogen; $r(O_2)$ for **2a** (1.18×10^{-5} cm^3 (STD) cm^{-2} s^{-1}) is less than 10% of that for Nafion 112 (1.24×10^{-4} cm^3 (STD) cm^{-2} s^{-1}) at 120 °C. It would be of great advantage for a **2a** membrane targeting on higher temperature applications. Since the gas permeation shows Arrenius-type temperature dependence, the activation energy for the gas permeation was estimated by the least-squares calculation of the slope. The apparent activation energy of the gas permeation is much smaller for **2a** membrane ($E_a(H_2)$ = 15 and $E_a(O_2)$ = 17 kJ/mol) than for Nafion 112 ($E_a(H_2)$ = 39 and $E_a(O_2)$ = 53 kJ/mol). The E_a for Nafion 112 is larger than the values reported in the literatures (~20 kJ/mol),[15] probably because of the differences in the measurement technique.[16]

The gas-permeation properties under humidified conditions are depicted in Figures 12 and 13. At 80 °C, $r(H_2)$ and $Q(H_2)$ decrease for **2a** as increasing the humidity while those of Nafion 112 show little dependence on the humidity. At 120 °C, the situation has greatly changed; both $r(H_2)$ and $Q(H_2)$ decrease significantly for **2a** and

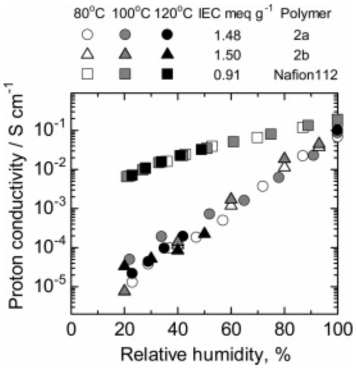


Figure 10. Humidity dependence of the proton conductivity of **2a, 2b**, and Nafion 112 at 80, 100, and 120 °C.

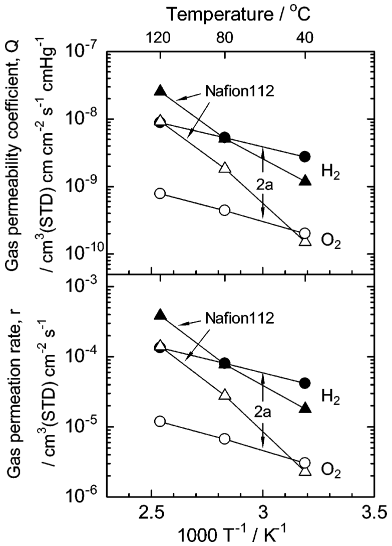


Figure 11. Temperature dependence of dry hydrogen and oxygen permeability for **2a** and Nafion 112.

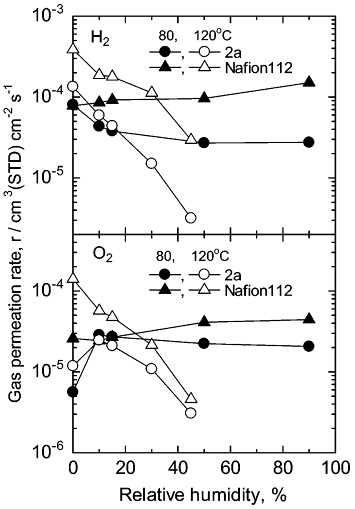


Figure 12. Humidity dependence of hydrogen (top) and oxygen (bottom) permeation rate for **2a** and Nafion 112 at 80 (●, ▲) and 120 (○, △) °C.

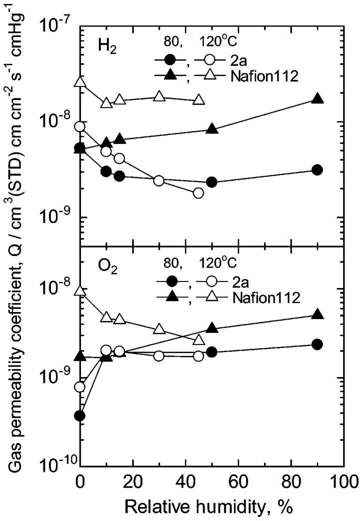


Figure 13. Humidity dependence of hydrogen (top) and oxygen (bottom) permeability coefficient for **2a** and Nafion 112 at 80 (●, ▲) and 120 (○, △) °C.

Nafion 112 as the humidity increases. These results are indicative that hydrogen permeates mainly though hydrophobic domains in the ionomer membranes at 120 °C. This tendency seems more pronounced for the polyether ionomers than the polyimide ionomers.[17] The oxygen permeation is much smaller amount for both membranes than the hydrogen permeation. Yet, the humidity dependence of oxygen permeation seems similar to that of hydrogen, suggesting the same permeation mode for both gases. In any cases, **2a** membrane shows much lower gas permeability than Nafion under fuel cell operating (heated and humidified) conditions.

Conclusions

Novel sulfonated poly(arylene ether) ionomers containing fluorenyl groups (**2a** and **2b**) have been successfully synthesized. Careful sulfonation reaction afforded the ionomers regioselectively substituted with sulfonic acid groups on 2,7-positions of pendant fluorenyl groups. The ionomers are of high molecular weight ($M_w > 2 \times 10^5$, $M_n > 4 \times 10^4$) to give tough and flexible membranes. Under dry conditions, the ionomers are stable up to 250 °C without any thermal transitions and decomposition. Under wet conditions at 140 °C and 100% RH, the ionomers do not show any hydrolytic degradation for 700 h. It is assumed that pendant sulfonic acid groups are effective to improve hydrolytic stability of the ionomers. The membrane **2a** (IEC = 1.14 mequiv/g) showed comparable proton-conducting properties to Nafion 112 and the highest proton conductivity (0.2 S cm^{-1}) was obtained at 140 °C and 100% RH. The ionomer membranes are highly mechanically stable at 85 °C and 93% RH and keep its strength even at 120 °C. Hydrogen and oxygen permeability of the **2a** ionomer membrane was much lower than that of Nafion 112 under a wide range of conditions (40−120 °C and 0−90% RH). These above properties of the poly(arylene ether) ionomers are uppermost among the hydrocarbon based ionomers for fuel cell applications.

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References and Notes

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