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Synthesis, Properties, and Fuel Cell Performance of Perfluorosulfonated Poly(arylene ether)s

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Poly(arylene ether)s containing superacid groups (FSPEs) were synthesized as proton conducting membranes for fuel cell applications. To obtain the title ionomers, a series of brominated poly(arylene ether)s were synthesized and perfluorosulfonated via Ullmann coupling. The chemical structure and the ion exchange capacity (IEC) of the FSPEs were characterized by ^{1}H and ^{19}F NMR spectra. Tough, flexible, and transparent membranes with the IEC ranging from 0.34 to 1.29 mequiv g^{-1} were obtained by solution casting. The FSPE membranes did not show obvious glass transition behavior up to the decomposition temperature (180 °C). Microscopic analyses revealed homogeneous and well-connected ionic clusters for the high IEC membrane. Compared to conventional sulfonated poly(arylene ether) membranes, the FSPE membranes showed much higher proton conductivity. The highest proton conductivity of 0.07 S cm^{-1} was achieved at 80 °C and 86% relative humidity (RH) with the IEC = 1.29 mequiv g^{-1} membrane. A fuel cell using the FSPE membrane showed comparable performance to that of a Nafion cell at 78% RH and 80 °C.

Fuel cells are clean and efficient energy devices that produce electric power via electrochemical reaction of fuels and oxidants. In a typical fuel cell, where hydrogen and oxygen (or air) are used as a fuel and an oxidant, the only by-product is water. Recent progress in the area of polymer electrolyte membrane fuel cells (PEMFCs) has stimulated considerable interest in proton conductive polymer membranes.[1] The state-of-the-art membranes are perfluorinated ionomers, such as Nafion, which consist of poly(tetrafluoroethylene) backbone and perfluoroether side chains containing sulfonic acid groups.[2,3] They are highly proton conductive and chemically stable under fuel cell operating conditions. However, these ionomer membranes face some issues such as high production cost and environmental incompatibility for practical applications. They show relatively low glass transition temperature ($<$100 °C) due to the flexible aliphatic framework, which limits the operation temperature of PEMFCs. It has been reported that copolymerization with a third comonomer[4] or shortening the side chains[5] are effective in improving the thermal properties. Incorporating hygroscopic inorganic compounds such as silica could also help the ionomer membranes retain their preferable properties.[6]

One possible candidate for alternative membranes is aromatic ionomers. Thermally and chemically stable, inexpensive aromatic polymers can be sulfonated to give proton conductive ionomer membranes.[7–10] A number of aromatic ionomers have been reported such as sulfonated poly(phenylene)s,[11,12] poly(ether ether ketone)s,[13,14] poly(ether sulfone)s,[15,16] and polyimides.[17,18] These ionomer membranes show high proton conductivity under hydrated conditions, however the conductivity drops by several orders of magnitude when membranes are dry or insufficiently hydrated. This is partly because of the weaker acidity of the aromatic sulfonic acid groups (e.g., the pK_a values of $ArSO_3H$ and perfluorosulfonic acid are ca. -1 and < -6, respectively).[19] Thus, the effective proton concentration and proton mobility are generally much lower in the aromatic ionomer membranes under low or nominally dry conditions. Less pronounced hydrophilic/hydrophobic separation would also be responsible for the low proton conductivity. The challenge is to produce highly proton conductive aromatic ionomer membranes at no expense of chemical, thermal, and mechanical stability. Recent research has revealed that block copolymer architecture[20–23] or introducing sulfonic acid group clusters[24–26] appear to be effective in constructing well-connected ionic domains to improve the proton mobility.

Our idea is to attach superacid groups onto aromatic polymers. In our previous papers, we reported that poly(arylene ether)s containing perfluorinated sulfonic acid groups showed similar thermal properties and higher proton conductivity compared to the conventional aromatic ionomers.[27,28] In this article, we report further investigation of the superacid-containing poly(arylene ether)s. A series of poly(arylene ether)s containing brominated fluorenyl groups were synthesized and perfluorosulfonated. Properties and fuel cell performance of the ionomers and membranes are described.

Experimental

Materials. 2,7-Dibromo-9-fluorenone (97%, TCI), phenol (99%, TCI), 3-mercaptopropionic acid (Kanto Chemical), sulfuric acid (96%, Kanto Chemical), 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonyl fluoride

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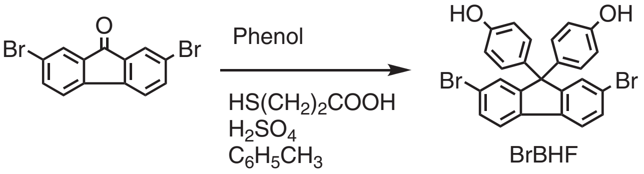
(PSA-F) (97%, Aldrich), 2,6-lutidine (TCI), tetrabutylammonium fluoride (1 M in tetrahydrofuran) (TCI), decafluorobiphenyl (98%, TCI), potassium carbonate (99.5%, Kanto Chemical), toluene (99.5%, Kanto Chemical), and dichloromethane (99.5%, dehydrated, Kanto Chemical) were used as received. Bis(4-fluorophenyl)sulfone (FPS) (99%, Acros Organics) was purified by recrystallization from ethanol. 4,4′-Difluorobenzophenone (FBP) (TCI) was purified by crystallization from toluene. Copper powders (99.5%, <45 µm, Kanto Chemical; 99.8%, <100 nm, Aldrich) were used as received. *N*,*N*-Dimethylacetamide (DMAc) (99%, Kanto Chemical) was dried over 3A-molecular sieves prior to use. Other chemicals were of commercially available grade and used as received.

Synthesis of 2,7-Dibromo-9,9-bis(4-hydroxyphenyl)fluorene (BrBHF). BrBHF was synthesized according to the literature (Scheme 1).[29] Briefly, a 100 mL three-neck round-bottomed flask equipped with a magnetic stirring bar and an N_2 inlet was charged with 2,7-dibromo-9-fluorenone (10 mmol, 3.38 g), phenol (40 mmol, 3.76 g), 3-mercaptopropionic acid (0.008 mL), sulfuric acid (0.32 mL), and toluene (2.4 mL). The mixture was stirred at 90 °C for 8 h under N_2 atmosphere. The mixture was poured dropwise into 1 L of deionized water to precipitate a brown flaky solid. The crude product was washed with hot deionized water several times and purified by recrystallization from acetone/hexane to obtain pure BrBHF in 80% yield.

Synthesis of Potassium 1,1,2,2-Tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonate (PSA-K). The PSA-K was synthesized according to the literature (Scheme 2).[30] Briefly, a 200 mL round-bottomed flask was charged with PSA-F (35.2 mmol, 15.0 g), dichloromethane (5.0 mL), deionized water (5.0 mL), 2,6-lutidine (44.8 mmol, 4.8 g), sulfuric acid (0.32 mL), and tetrabutylammonium fluoride (1 M in tetrahydrofuran) (0.1 mL). The mixture was stirred at room temperature for 4 d. The organic layer was extracted with three portions of 100 mL of dichloromethane and evaporated to dryness. To the obtained viscous product, potassium carbonate (20.4 mmol, 2.82 g) and tetrahydrofuran (THF) (30 mL) were added. The mixture was stirred at room temperature for 10 h and filtrated. The filtrate was evaporated to dryness and purified by recrystallization from THF/toluene to yield pure PSA-K in 85% yield.

Synthesis of Homopolymers. A typical procedure is as follows. A 200 mL three-neck round-bottomed flask equipped with a magnetic stirring bar, an N_2 inlet, and an addition funnel was charged with BrBHF (3.0 mmol, 1.52 g), FPS (3.0 mmol, 0.76 g), potassium carbonate (7.5 mmol, 1.04 g), toluene (2.0 mL), and DMAc (10 mL). The mixture was stirred at room temperature for a few minutes and heated at 140 °C for 6 h under N_2 atmosphere. Then, 30 mL of DMAc was added to the mixture to lower the viscosity. The mixture was poured dropwise into 1 L of deionized water to precipitate a white fibrous solid. The crude product was washed with hot deionized water and methanol several times and dried under vacuum at 60 °C for 15 h to obtain BrPE-1a in 92% yield.



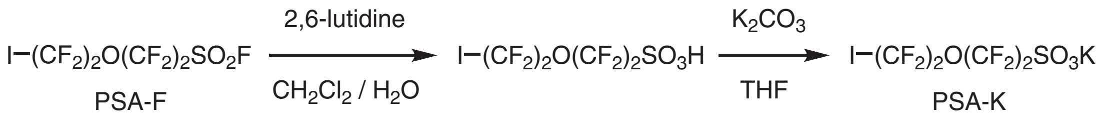
Scheme 1. Synthesis of 2,7-dibromo-9,9-bis(4-hydroxyphenyl)fluorene (BrBHF).

Synthesis of Copolymers. A typical procedure is as follows. A 200 mL three-neck round-bottomed flask equipped with a magnetic stirring bar, an N_2 inlet, and an addition funnel was charged with BrBHF (3.0 mmol, 1.52 g), FPS (1.5 mmol, 0.38 g), FBP (1.5 mmol, 0.33 g), potassium carbonate (7.5 mmol, 1.04 g), toluene (2.0 mL), and DMAc (10 mL). The mixture was stirred at room temperature for a few minutes and heated at 140 °C for 3 h and 160 °C for 20 h under N_2 atmosphere. Then, 10 mL of DMAc was added to the mixture to lower the viscosity. The mixture was poured dropwise into 1 L of deionized water to precipitate a white fibrous solid. The crude 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 obtain BrPE-1c in 68% yield.

Perfluorosulfonation. A typical procedure is as follows. A 100 mL three-neck round-bottomed flask equipped with a magnetic stirring bar, an N_2 inlet, and an addition funnel was charged with BrPE-1b (0.75 mmol, 0.60 g), copper powder (7.5 mmol, 0.48 g), and DMAc (10 mL). The mixture was stirred at 120 °C for 2 h under N_2 atmosphere. PSA-K (3.0 mmol, 1.3863 g) solution in DMAc (2 mL) was added to the mixture and heated at 160 °C for 40 h. The mixture was filtered and the filtrate was poured dropwise into 5 M HNO_3 aqueous solution to precipitate a fibrous solid. The crude product was washed with 5 M HNO_3 aqueous solution and deionized water. The resulting product was dried under vacuum at 80 °C for 15 h to give the perfluorosulfonated polymer (FSPE-1b).

Membrane Preparation. An FSPE-1 (0.4 g) solution in 10 mL of DMAc was cast onto a clean flat glass plate (9 cm × 6 cm). Drying the solution at 50 °C under atmospheric pressure for 15 h gave a brown and transparent membrane (50 µm thick). The membrane was immersed in 1 M HNO_3 for 12 h. The acidification was repeated three times. The membrane was then washed with deionized water several times and dried under vacuum at 80 °C for 15 h.

Measurements. ^1H (400 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 standard. Molecular weight measurements were per-



$$\underset{\text{PSA-F}}{I{-}(CF_2)_2O(CF_2)_2SO_2F} \xrightarrow[CH_2Cl_2\,/\,H_2O]{\text{2,6-lutidine}} I{-}(CF_2)_2O(CF_2)_2SO_3H \xrightarrow[\text{THF}]{K_2CO_3} \underset{\text{PSA-K}}{I{-}(CF_2)_2O(CF_2)_2SO_3K}$$

Scheme 2. Synthesis of potassium 1,1,2,2-tetrafluoro-2-(1,1,2,2-tetrafluoro-2-iodoethoxy)ethanesulfonate (PSA-K).

formed via gel permeation chromatography (Jasco PU-2080 Plus) equipped with two columns (Shodex K-805L and K-806L) and a Jasco MD-2010 Plus multi-wavelength UV detector. *N*,*N*-Dimethylformamide containing 0.01 M LiBr was used as the solvent at a flow rate of 1.0 mL min^{-1}. M_w and M_n were calibrated with standard polystyrene samples. TG/DTA was carried out with a Mac Science TG/DTA 2000 equipped with a Bruker MS 9600 mass spectrometer at a heating rate of 5 °C min^{-1} under dry argon atmosphere.

Ion Exchange Capacity (IEC). A piece of FSPE-1 membrane was equilibrated in a large excess of 0.01 M NaCl aqueous solution for 15 h. The amount of HCl released from the membrane samples was determined by titration with aqueous 0.01 M NaOH using KEM Automatic Potentiometric Titrator AT-510.

Oxidative Stability. A small piece of membrane sample 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 monitoring changes in molecular weight, IEC, and weight of the test samples.

Hydrolytic Stability. A small piece of membrane sample was treated at 140 °C and 100% RH in a closed, pressurized vial for 24 h. The stability was evaluated by monitoring changes in molecular weight, IEC, and weight 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–strain curves were obtained at a stretching rate of 10 mm min^{-1} for samples cut into a dumbbell shape (DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)).

STEM Observation. The membranes were stained with silver or lead ions by ion exchange of the sulfonic acid groups. The membranes were immersed overnight in 0.5 M $AgNO_3$ or 1 M $Pb(CH_3COO)_2$ aqueous solution, rinsed with water, and dried in vacuum at 80 °C for 15 h. The stained membrane was embedded in epoxy resin and sectioned to give a 90 nm thick membrane. The images were taken on a Hitachi HD-2300C scanning transmission electron microscope with an accelerating voltage of 200 kV.

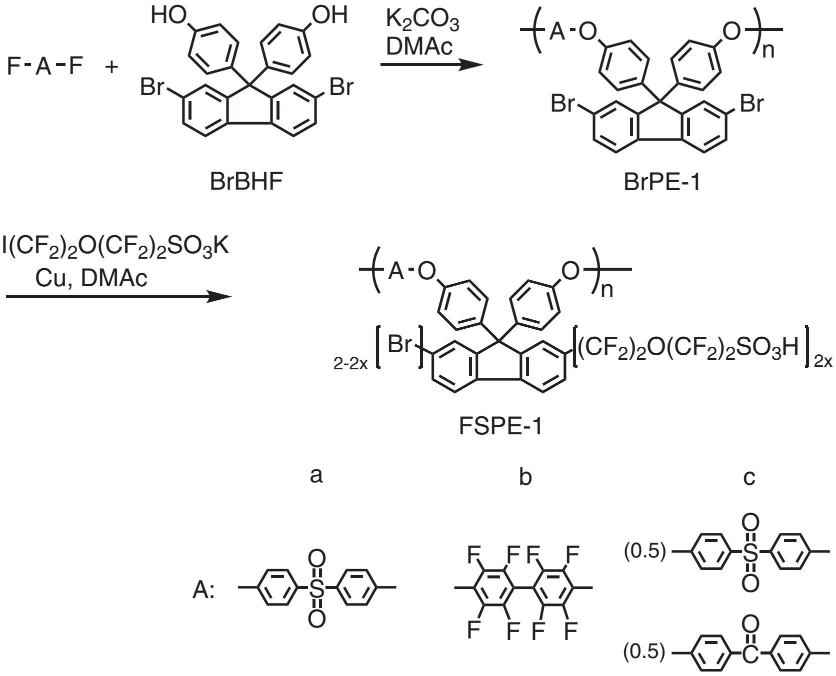
Water Uptake and Proton Conductivity. Water uptake and proton conductivity of the FSPE-1 membranes were measured with a Bel Japan solid electrolyte analyzer system MSB-AD-V-FC equipped with a chamber, a magnetic suspension balance, and a four-point probe conductivity cell. For water uptake measurements, membrane samples (50–70 mg) were placed in a chamber and dried at 80 °C under vacuum for 3 h until constant weight as a dry material was obtained. The membranes were then equilibrated with N_2 gas at given temperature and humidity for at least 1 h before the gravimetry was carried out. For the proton conductivity measurements, membrane samples (1.0 cm wide and 3.0 cm long) were placed in the same chamber. The samples were placed in contact with two gold wire outer current-carrying electrodes and two gold wire inner potential-detecting electrodes. Impedance measurements were carried out using a Solartron 1255B frequency response analyzer and Solartron SI 1287 potentiostat. The instrument was used in the potentiostatic mode with an ac amplitude of 300 mV and a frequency range from 1 to 100000 Hz.

Membrane Electrode Assembly (MEA). Gas diffusion electrodes with three-layer structure, and carbon paper/gas diffusion layer (microporous layer)/catalyst layer, were prepared according to a method previously reported.[31] Pt catalysts supported on carbon black (46.5%-Pt/CB, TEC10E50E, Tanaka Kikinzoku Kogyo), commercial Nafion solution (DE521, DuPont) and solvent (2-propanol + water) were mixed in a planetary ball mill for 30 min. The mass ratio of Nafion to CB was set at 0.7. The obtained slurry was sprayed over the commercial micro porous layer on carbon paper (25BCH, SGL Carbon). The gas diffusion electrodes thus prepared were dried and hot-pressed at 130 °C for 3 min in air with the pressure of 1.0 MPa. The geometric electrode area was 3.8 cm^2 and the Pt loading amount in the electrodes was 0.5 mg cm^{-2}. FSPE-1c (IEC = 1.29 mequiv g^{-1}) or Nafion (DuPont NRE 212) membrane was sandwiched by the two gas diffusion electrodes to give an MEA, which was mounted into a circular single test cell holder.

Fuel Cell Operation. Fuel cells were operated at 80 °C (T_{Cell}). Humidified H_2 was fed to the anode at 200 mL min^{-1} with the humidification temperature (T_{AH}) of 74 °C (78% RH) or 80 °C (100% RH). Humidified O_2 was fed to the cathode at 200 mL min^{-1} with the humidification temperature (T_{CH}) of 74 °C (78% RH) or 80 °C (100% RH). Current–voltage (*I*–*V*) curves were measured under steady-state conditions.

Results and Discussion

Synthesis and Characterization of Polymers. 2,7-Dibromo-9,9-bis(4-hydroxyphenyl)fluorene (BrBHF) was synthesized via electrophilic substitution reactions of dibromofluorenone with phenol (Scheme 1). BrBHF was obtained as a yellow cubic crystal in 80% yield. Three series of bromofluorenyl-containing poly(arylene ether)s, BrPE-1a–1c, were synthesized via nucleophilic substitution polycondensation reactions of BrBHF with aromatic difluorides (Scheme 3). BrPE-1a and -1b were homopolymers, while BrPE-1c was a 1:1 copolymer of diphenylene sulfone and benzophenone. The polycondensation reaction proceeded in DMAc with excess potassium carbonate. The progress of the polymerization was confirmed by an increase in the viscosity of the mixture. The polymerization results are summarized in Table 1. The polymerization of BrBHF and FPS was not very successful since the product (BrPE-1a) was low molecular weight ($M_n = 2$ kDa, $M_w = 5$ kDa) when the reaction temperature was 100 °C and insoluble when the reaction temperature was higher (140 °C). Decafluorobiphenyl being very reactive in the nucleophilic substitution reaction provided higher molecular weight ($M_n = 100$ kDa, $M_w = 220$ kDa) and soluble polymer BrPE-1b at 100 °C. The product was insoluble at higher polymerization temperature (140 °C) due to the possible crosslinking reaction. A 1:1 copolymerization of diphenylene sulfone and benzophenone with BrBHF proceeded rather smoothly to provide the copolymer BrPE-1c with $M_n > 19$ kDa, $M_w > 57$ kDa. BrPE-1b and -1c gave flexible and transparent membranes by solution casting while the membrane from BrPE-1a was brittle and broke into pieces due to its low



Scheme 3. Synthesis of perfluorosulfonated poly(arylene ether)s (FSPE-1a–1c).

Table 1. Synthesis of BrPE-1a, -1b, and -1c

Polymer	Reaction temp/°C	Reaction time/h	Solubility in DMAc	M_n /kDa	M_w /kDa
BrPE-1a	100	20	+	2	5
BrPE-1a	140	6	−	—	—
BrPE-1b	100	20	+	100	220
BrPE-1b	140	3	−	—	—
BrPE-1c	140	20	+	19	57
BrPE-1c	160	20	+	36	85

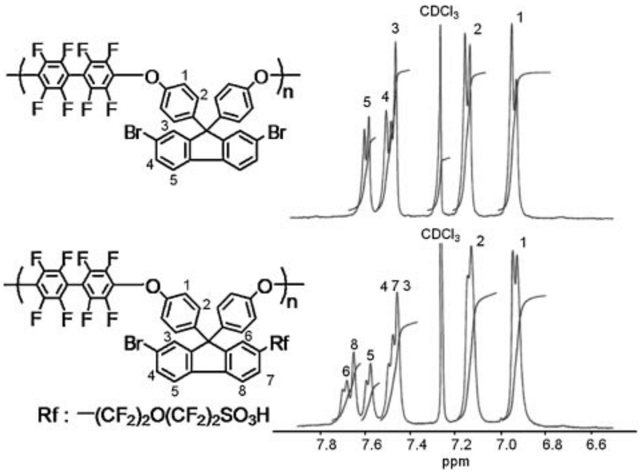


Figure 1. ^{1}H NMR spectra of BrPE-1b (top) and FSPE-1b (bottom) in $CDCl_3$.

molecular weight. NMR analyses confirmed the chemical structure of the polymers. The ^{1}H NMR spectrum of BrPE-1b is shown in Figure 1 as a typical example, in which all of the aromatic protons are well assigned to the supposed polymer structure. The integral ratios of the peaks are in fair agreement with the calculated values. The results suggest that the bromine groups were intact during the polycondensation reaction under the investigated conditions.

Polymers BrPE-1b and -1c were reacted with PSA-K in DMAc solution in the presence of copper powder via Ullmann coupling to provide perfluorosulfonated polymers FSPE-1b and -1c, respectively. PSA-K was prepared via hydrolysis of the corresponding sulfonyl fluoride prior to the coupling reaction (Scheme 2). The coupling reaction was conducted in two steps (Table 2). In the first step, precursor polymers (BrPE-1b and -1c) were reacted with copper powder. When the reaction temperature was lower than 140 °C, interpolymer crosslinking reaction did not occur. The diameter of the copper powder was crucial for the coupling reaction; degree of perfluorosulfonation was much higher with copper of smaller diameter (0.1 µm) than with that of the larger (45 µm). In the second step, a two-fold excess of PSA-K was added into the reaction mixture. The reaction was carried out at higher temperature and for longer time compared to the first step. The title polymers FSPE-1 were isolated as brown fibers, which were soluble in polar aprotic organic solvents such as DMF and DMAc but insoluble in less polar solvents such as chloroform and toluene. Casting from the solution provided pale brown, transparent, and ductile membranes. The degree of perfluorosulfonation was determined by titration to be <36% for FSPE-1b and <37% for FSPE-1c, respectively. The low conversion was due to rather low reactivity of the bromo groups in the Ullmann reaction.[27] Since the unreacted bromo groups were intact as suggested by ^{1}H NMR spectra (see below), the Ullmann reaction was repeated to achieve higher degree of perfluorosulfonation (63% for FSPE-1c). Accordingly, perfluorosulfonated FSPE-1 membranes with the ion exchange capacity (IEC) ranging from 0.34 to 1.29 mequiv g^{-1} were obtained.

Table 2. Perfluorosulfonation of BrPE-1b and -1c

Prepolymer	First step			Second step			IEC /mequiv g^{-1}
	Reaction temp/°C	Reaction time/h	Diameter of Cu/μm	Reaction temp/°C	Reaction time/h	Degree of perfluorosulfonation/%	
BrPE-1b	120	2	45	120	40	15	0.34
BrPE-1b	120	2	45	160	40	19	0.43
BrPE-1b	120	2	0.1	160	40	36	0.76
BrPE-1c	120	2	0.1	160	40	36	0.81
BrPE-1c	140	20	0.1	160	96	37	0.83
BrPE-1c[a)]	140	20	0.1	160	96	63	1.29

a) Ullmann coupling was carried out twice.

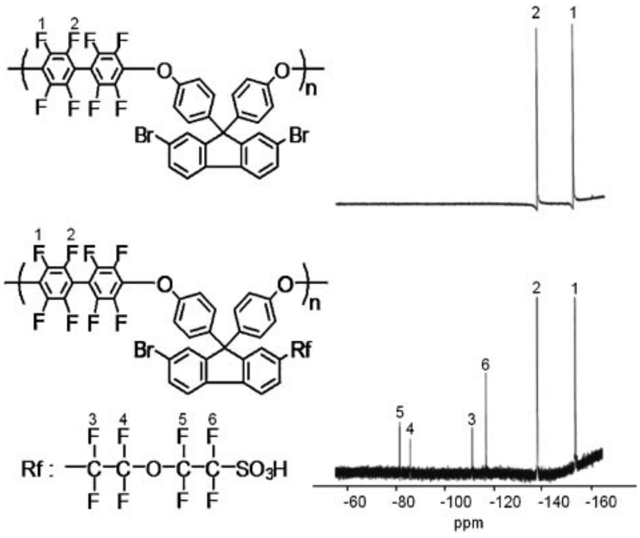


Figure 2. ^{19}F NMR spectra of BrPE-1b (top) and FSPE-1b (bottom) in $CDCl_3$.

The FSPE-1 polymers were characterized by ^1H and ^{19}F NMR analyses. Figure 1 compares the ^1H NMR spectra of BrPE-1b and FSPE-1b. While protons 1–5 of the unreacted brominated fluorenylidene units and the main chains showed only minor chemical shifts, the appearance of new peaks for protons 6–8 (Figure 1 bottom) suggested the introduction of the perfluorosulfonic acid groups. In the spectrum of FSPE-1b, peaks 3–5 of the brominated fluorenylidene units are smaller than those of BrPE-1b, and new peaks 6–8 at 7.4–7.7 ppm are assignable to the protons of the perfluorosulfonated fluorenylidene rings. Figure 2 compares the ^{19}F NMR spectra of BrPE-1b and FSPE-1b. In the spectrum of FSPE-1b, new peaks 3–6 between −120 and −80 ppm are well-assigned to the perfluorosulfonic acid groups in the side chains. The results indicate that the perfluorosulfonic acid groups were successfully introduced onto the fluorenylidene groups. In Figures 1 and 2, the integral ratio of the peaks gave comparable IEC values to those obtained by titration.

Thermal, Oxidative, Hydrolytic, and Mechanical Stability of FSPE Membranes. Thermal stability of the FSPE-1 membranes was evaluated by TG/DTA-MS analyses under dry Ar. As a typical example, TG/DTA-MS curves of FSPE-1c (IEC = 1.29 mequiv g^{-1}) are shown in Figure 3. FSPE-1c membrane did not show obvious glass transition behavior in the DTA curve. In the TG curve, weight loss was observed from 180 °C. The mass chromatograms confirmed that the weight loss was caused by the degradation of the perfluorosulfonic acid groups ($m/z = 47$ (CFO), $m/z = 50$ (CF_2), $m/z = 48$ (SO), $m/z = 64$ (SO_2)). The weight loss from 180 to 400 °C was 27%, which was in good agreement with the mass ratio of the side chains (28%). The onset decomposition temperature of FSPE-1c was comparable to that of our previous poly(arylene ether)s (SPE-1a, Figure 4) with sulfonic acid groups directly attached to the fluorenyl groups, and was lower than that of Nafion ionomers (ca. 250 °C).[32] Perfluorosulfonic acid groups were prone to thermal degradation when attached to aromatic rings compared to those attached to poly(tetrafluoroethylene) main chains.

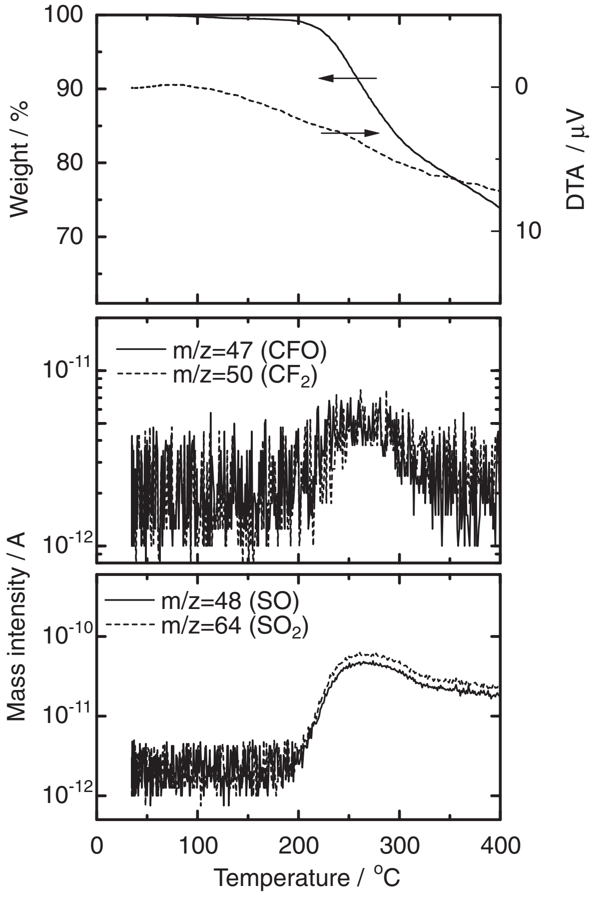


Figure 3. TG/DTA-MS curves of FSPE-1c (IEC = 1.29 mequiv g^{-1}) under dry argon.

Taking fuel cell applications into account, oxidative and hydrolytic stabilities are critical issues for proton conductive ionomer membranes. The stability of FSPE-1 membranes was investigated under accelerated testing conditions. The residue in weight, molecular weight (M_w) and IEC after the stability tests is plotted as a function of IEC in Figure 5. A general trend is that higher IEC membranes are less oxidatively stable due to the increased hydrophilicity. The FSPE-1b and -1c membranes with IEC of 0.76 and 0.81 mequiv g^{-1}, respectively, kept their form and weight after treatment with hot Fenton's reagent. The IEC values decreased by ca. 10% and the molecular weight (M_w) decreased more significantly (83% loss for FSPE-1b and 56% loss for FSPE-1c). This indicates that the major mechanism of the oxidative degradation is the main chain scission and the perfluorosulfonic acid groups are more robust than the main chains under the harsh oxidative conditions.

The membranes were more stable to hydrolysis than oxidation and no losses were observed in weight or molecular weight for either membrane. IEC values decreased by ca. 10%, similar to the oxidative stability. Since hydrolytic degradation should involve nucleophilic attack by water molecules, arylene ether polymers with high electron density are stable to hydrolysis. These oxidative and hydrolytic properties are similar to those of the SPE-1a with no superacid groups.[33] Therefore, it is concluded that the effect of the strong electron-withdrawing pendant perfluorosulfonic acid groups is minor on the thermal, oxidative, and hydrolytic stability of the poly(arylene ether) ionomers.

Stress–strain curves were measured for FSPE-1b (IEC = 0.76 mequiv g^{-1}) and -1c (IEC = 0.81 mequiv g^{-1}) membranes at 85 °C and 93% RH. The results are compared to that of Nafion membrane in Figure 6. Both FSPE-1 membranes showed ca. 17 MPa of the maximum stress at break, which was somewhat lower than that of Nafion membrane (23 MPa). The dimensional stability of the FSPE-1 membranes was much better than that of Nafion membrane, as confirmed by the formers' higher Young's modulus (0.31 GPa for FSPE-1b and 0.32 GPa for FSPE-1c). FSPE-1b membrane showed higher maximum strain (70%) than FSPE-1c (40%). The results seem reasonable taking into account the facts that the FSPE-1b is higher molecular weight and absorbs less water than the FSPE-1c membrane (see below).

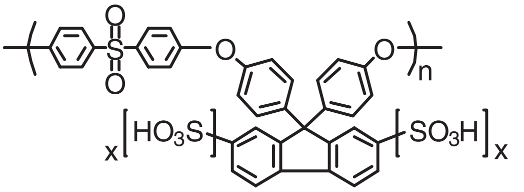


Figure 4. Chemical structure of sulfonated poly(arylene ether sulfone) (SPE-1a).

STEM Images of FSPE Membranes. STEM images of lead-ion-exchanged FSPE-1 membranes are shown in Figure 7 with Nafion NRE 212 membrane. The images were taken in transmission electron mode, in which the black domains were presumed to be ion-exchanged sulfonic acid groups (hydrophilic clusters). The FSPE-1b and -1c membranes with lower IEC (0.76 and 0.81 mequiv g^{-1}, respectively) did not

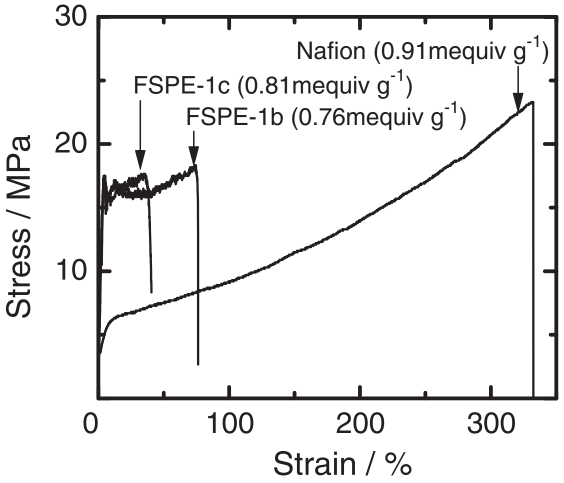


Figure 6. Stress versus strain curves of FSPE-1b, -1c, and Nafion NRE212 membranes at 85 °C and 93% RH with IEC in parenthesis.

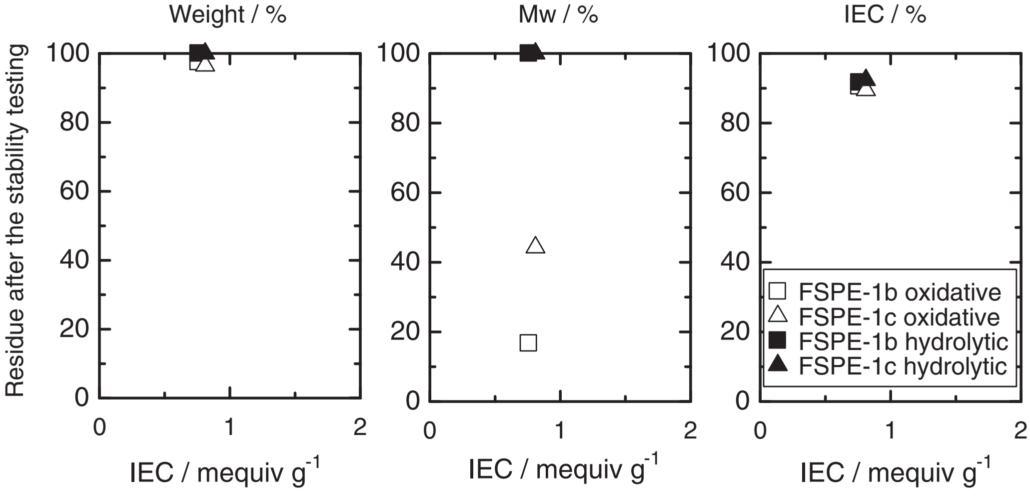


Figure 5. Oxidative and hydrolytic stability of FSPE membranes; losses in weight, M_w and IEC.

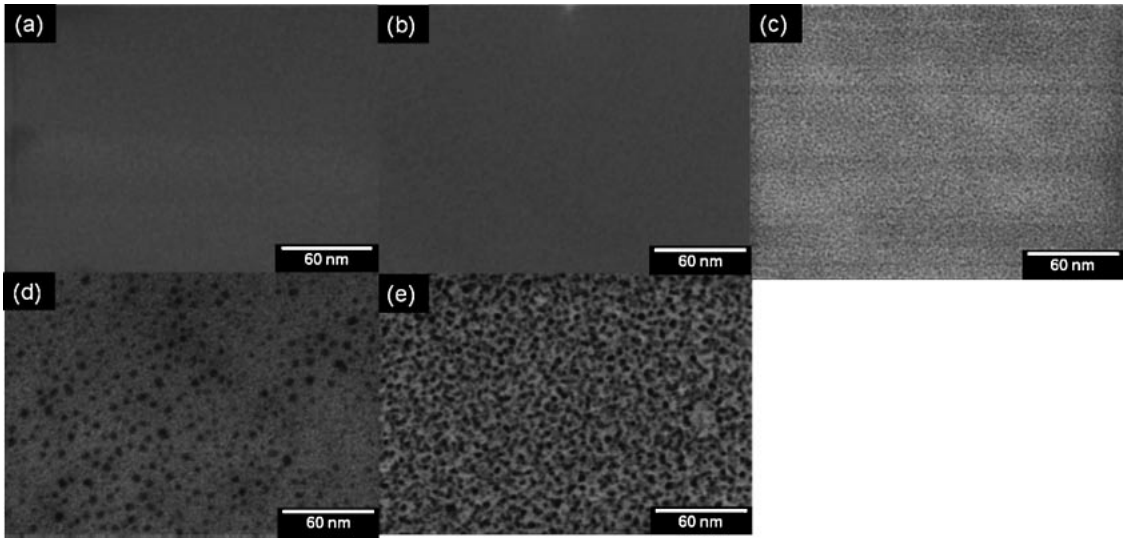


Figure 7. STEM images of (a) FSPE-1b (IEC = 0.76 mequiv g^{-1}), (b) FSPE-1c (IEC = 0.81 mequiv g^{-1}), (c) FSPE-1c (IEC = 1.29 mequiv g^{-1}), (d) SPE-1a (IEC = 2.51 mequiv g^{-1}), and (e) Nafion NRE212 (IEC = 0.91 mequiv g^{-1}) membranes.

show clear hydrophilic clusters. The main chain structures were unlikely to affect the morphology of these membranes with lower IEC. The FSPE-1c membrane with IEC = 1.29 mequiv g^{-1} showed small (ca. 2–3 nm in diameter) and uniformly-dispersed hydrophilic clusters. The morphology was distinct from that of the SPE-1a membrane. In the latter membrane, the hydrophilic clusters were isolated from each other. The morphology of FSPE-1c is more similar to that of Nafion membrane, which has homogeneous and well-connected hydrophilic clusters (ca. 5–6 nm in diameter). This indicates that the perfluorosulfonic acid groups are easier to aggregate than the aromatic sulfonic acid groups.

Water Uptake and Proton Conductivity of FSPE Membranes. Water uptake, λ (number of absorbed water molecules per sulfonic acid group), and proton conductivity of FSPE-1 membranes were measured at 80 °C. The data are plotted as a function of relative humidity in Figure 8. For comparison, data of Nafion and SPE-1a are also included. The water uptake of FSPE-1 membranes was in the order of their IEC value; the higher IEC membrane absorbed more water. The water uptake behavior of SPE membranes was significantly affected by the pendant superacid groups. Despite its lower IEC value, FSPE-1c (IEC = 1.29 mequiv g^{-1}) membrane showed higher water uptake than that of SPE-1a (IEC = 1.59 mequiv g^{-1}). The λ values of the three FSPE-1 membranes were higher than those of SPE-1a (IEC = 2.51 mequiv g^{-1}), and comparable to those of Nafion. The results indicate that the superacid groups have higher affinity to water than aromatic sulfonic acid groups.

Unlike the water uptake, proton conductivity of FSPE-1 membranes was not in the order of their IEC values. Comparison of FSPE-1b and -1c membranes revealed that the perfluorinated biphenylene groups in the main chains were effective in improving the proton conductivity; FSPE-1b (IEC = 0.76 mequiv g^{-1}) membrane showed slightly higher proton conductivity than that of FSPE-1c (IEC = 0.81 mequiv g^{-1}) at all humidity conditions, despite the former's lower IEC and water uptake. The pendant superacid groups affected more significantly the proton conductivity. FSPE-1c membrane (IEC = 1.29 mequiv g^{-1}) was much more proton conductive than the SPE-1a membrane (IEC = 1.59 mequiv g^{-1}). The effect was more significant at lower humidity and the difference in the proton conductivity at 20% RH was ca. one order of magnitude. As discussed above, better-connected hydrophilic clusters and higher water absorbability should be responsible for the higher proton conductivity of the FSPE-1 membranes. Since such effect has not been observed with the aromatic polymers with pendant aliphatic sulfonic acid (non-superacid) groups, side chain effect is considered to be minor.

Fuel Cell Performance. Fuel cell performance of the FSPE-1c membrane (IEC = 1.29 mequiv g^{-1}, 50 µm thick) was tested. The results are compared to that of Nafion (IEC = 0.91 mequiv g^{-1}, 50 µm thick) in Figure 9. Fuel cells were operated at 80 °C under two different humidity conditions (78% RH and 100% RH). The open-circuit voltages (OCV) of the FSPE-1c cell were 1.05 V at 78% RH and 1.03 V at 100% RH, which were comparable to those of the Nafion cell (1.03 V at 78% RH and 1.03 V at 100% RH). This indicates that the gas crossover (permeation) through the FSPE-1c membrane was low enough. The ohmic resistance of the FSPE-1c membrane was comparable to that of Nafion membrane at 100% RH. The results are in good accordance with the proton conductivity data. The ohmic resistances of Nafion membrane and FSPE-1c membrane calculated from their proton conductivity at 78% RH were 0.0599 and 0.0704 Ω cm^2, respectively. These values were somewhat lower than those measured in the operating fuel cells (0.0749 Ω cm^2 at 1 A cm^2 for Nafion cell and 0.137 Ω cm^2 at 1 A cm^2 for FSPE-1c cell). The minor differences in the ohmic resistance probably result from the contact resistance between the membranes and the gas diffusion electrodes. It should be noted however, that the *I*–*V* performance of the FSPE-1c cell was comparable to that of the Nafion cell. Durability of the FSPE-1c membrane was also confirmed for 200 h in the fuel cell operation, where no significant changes were confirmed in the cell voltage.

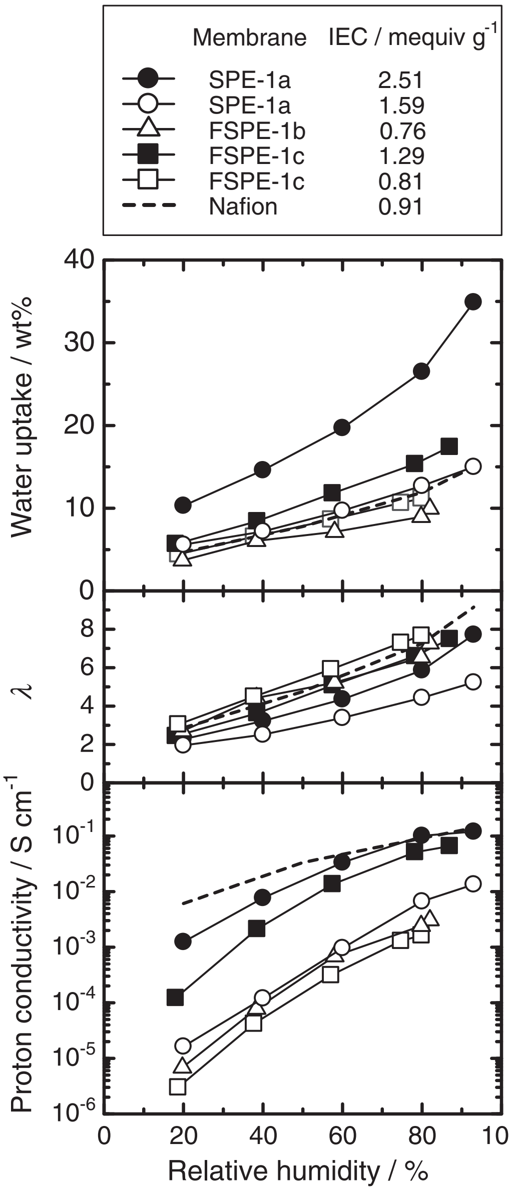


Figure 8. Humidity dependence of water uptake, λ, and proton conductivity of SPE-1a, FSPE-1b and -1c, and Nafion NRE 212 membranes at 80 °C.

Conclusion

Novel poly(arylene ether)s containing superacid groups (FSPE-1b and -1c) were synthesized. The precursor brominated poly(arylene ether)s (BrPE-1b and -1c) were perfluorosulfonated via Ullmann coupling to provide the ionomers with an ion-exchange capacity (IEC) up to 1.29 mequiv g^{-1}. The ionomers were soluble in polar organic solvents and formed tough and flexible membranes by solution casting. The ionomers did not show obvious glass transition behavior in the temperature range up to 180 °C, above which temperature the iomoners decomposed with the loss of pendant perfluorosulfonic acid groups. Hydrolytic and oxidative stabilities were confirmed by accelerated tests. The main chains were subject to degradation under harsh oxidative conditions while the perfluorosulfonic acid groups were more robust. The arylene ether main chains with high electron density were stable to hydrolysis because hydrolytic degradation should involve nucleophilic attack by water molecules. Stress–strain curves showed that these membranes have good mechanical and dimensional strength. The STEM images of the membranes with higher IEC showed uniformly dispersed and well-connected hydrophilic clusters. The superacid groups were effective in improving proton conductivity due to their high affinity to water. The FSPE-1c membrane (IEC = 1.29 mequiv g^{-1}) was much more proton conductive than the SPE-1a membrane (IEC = 1.59 mequiv g^{-1}). The effect was more significant at lower humidity and the difference in the conductivity at 20% RH was ca. one order of magnitude. The FSPE-1c (IEC = 1.29 mequiv g^{-1}) membrane showed comparable fuel cell performance to Nafion at 80 °C and 78% and 100% RH. The FSPE-1c membrane was durable for 200 h in operating fuel cells.

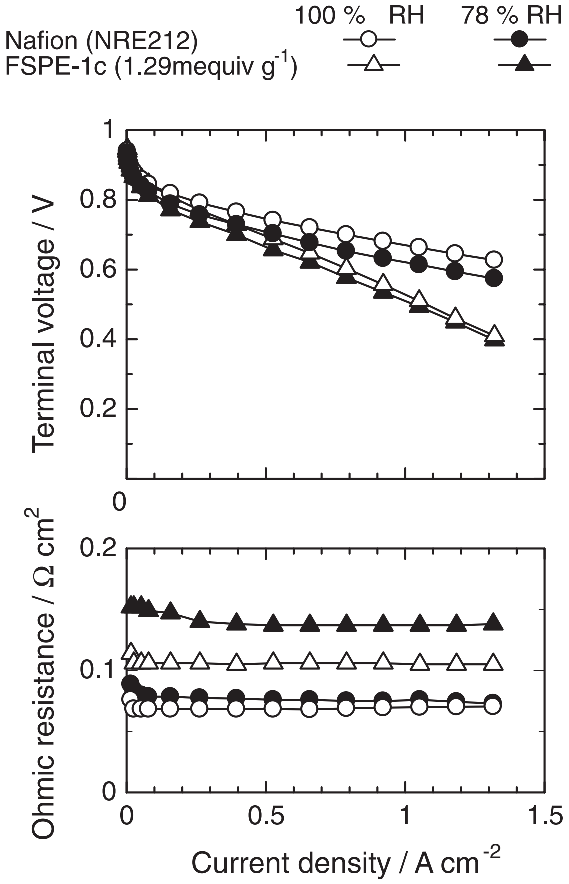


Figure 9. Steady-state terminal voltage (including IR loss) of fuel cell under high- and medium-humidity conditions for FSPE-1c (1.29 mequiv g^{-1}) and Nafion membranes. All cells were operated at 80 °C.

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