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Proton Conductive Polyimide Electrolytes Containing Trifluoromethyl Groups: Synthesis, Properties, and DMFC Performance

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ABSTRACT: A series of sulfonated polyimide copolymers (FSPIH-*X*; *X* refers to molar percentage of bis(trifluoromethyl)biphenylene content) with *X* from 0 to 60 mol % were synthesized, of which electrolyte properties were investigated and compared to those of the perfluorinated ionomer (Nafion 112). FSPIH-*X* membranes are thermally stable with no glass transition temperature observed below the decomposition temperature (280 °C). Oxidative stability of the membranes is improved with an increase in the content of trifluoromethyl substituents in the copolymer structure. FSPIH-60 endured for more than 9 h in Fenton's reagent at 80 °C. Bis(trifluoromethyl)biphenylene groups with the molecular size of 6.1 Å make each polymer chain separate and produce space to hold water molecules despite their hydrophobic property so that the maximum water uptake was observed for FSPIH-20. Unlike the fluorene groups containing polyimides (SPIH-*X*), a strong water confinement effect was not obtained for FSPIH-*X*. The optimum composition of bis(trifluoromethyl)biphenylene groups was 30 mol %, and the FSPIH-30 membrane showed higher proton conductivity than 0.2 S cm^{-1} at 30−140 °C. A direct methanol fuel cell (DMFC) using FSPIH-30 membrane has revealed that the methanol crossover through the membrane equivalent to the current density of methanol oxidation at cathode ($j(CH_3OH)$) is 64 mA/cm^2 and merely 30% of that of Nafion 112 at open-circuit potential. A terminal voltage of 0.38 V was obtained at 200 mA/cm^2 by the operation at 80 and 90 °C with supplying dry and humidified oxygen.

Introduction

Proton conductive polymers are one of the key materials in polymer electrolyte fuel cells (PEFCs) and direct methanol fuel cells (DMFCs).[1−3] Highly conductive, chemically and mechanically stable, environmentally benign, and inexpensive polymeric materials are in great demand for improving the performance and the real commercialization of the devices. Many researchers have focused on aromatic hydrocarbon polymers with acidic function in order to replace the perfluorinated ionomers (such as Nafion by Du Pont) as state-of-the-art materials.[4] Sulfonated polyimide electrolytes have recently been receiving considerable attention in the topical area because of their high proton conductivity at high temperatures (>100 °C).[5−7] They are readily available by the polycondensation method, and their chemical and physical properties are rather easy to control by simply changing the composition of hydrophobic diamine comonomers.

In the preceding paper,[8] we have reported the synthesis and properties of a new series of sulfonated polyimide copolymers containing fluorenyl groups (SPIHs). Their water uptake and proton conductivity depend greatly on the copolymer composition and the branching. The role of bulky fluorenyl groups was investigated, and their appropriate composition has been identified. Although these all-hydrocarbon-based (fluorine-free) materials are quite attractive and distinctive from the perfluorinated ionomers, we were interested in incorporating a small amount of fluorine containing groups into polyimides to elucidate whether we could combine both benefits of hydrocarbon and perfluorinated ionomers. Herein, we report another series of sulfonated polyimide electrolytes containing bis(trifluoromethyl)biphenylene groups (FSPIHs). The more hydrophobic but smaller architecture of bis(trifluoromethyl)biphenylene groups than fluorenyl biphenylene groups could potentially improve the hydrolytic and oxidative stability of polyimide electrolytes without losing their good proton-conducting properties. Their thermal, oxidative, mechanical, and conducting properties were investigated. DMFC was assembled and operated with the FSPIH membrane to evaluate methanol crossover (permeation) through the membrane.

Experimental Section

Materials. 4,4′-Diamino-2,2′-biphenyldisulfonic acid (DAPS) (80%, Acros Organics) was purified in the manner as previously reported.[7] Triethylamine (TEA) (99.5%, Aldrich Co., Inc.), 1,4,5,8-naphthalenetetracarboxylic dianhydride (TCND) (99.0%, Aldrich Co., Inc.), *m*-phenylenediamine (*m*-PDA) (>98.0%, TCI Co., Inc.), melamine (>98.0%, Kanto Chemical Co., Inc.), and benzoic acid (99.5%, Aldrich Co., Inc.) were used as received. 3,3′-Bis(trifluoromethyl)benzidine (FMB) (>98.0%, TCI Co., Inc.) was crystallized from ethanol. *m*-Cresol (>98.0%, 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.

Polymerization and Membrane Preparation. Sulfonated polyimide copolymers FSPIH-*X* (where *X* refers to the molar percentage of bis(trifluoromethyl)biphenylene content) with *X* from 0 to 60 mol % were synthesized (Table 1). A typical procedure is as follows. DAPS (2.6 mmol, 0.895 g), FMB (1.2 mmol, 0.384 g), and TEA (6.2 mmol, 0.86 mL) were dissolved in 18 mL of *m*-cresol in a 100 mL four-neck round-bottomed flask equipped with a magnetic stirring bar. The mixture was stirred at 160 °C for 5 min under a N_2 atmosphere. After a clear solution was obtained, TCND (4.0 mmol, 1.073 g), benzoic acid (16.0 mmol, 1.954 g), and 30 mL of *m*-cresol were added while stirring. Then, *m*-PDA (0.2 mmol, 0.022 g) was added to the mixture. The polymerization was carried out at 175 °C for 15 h and at 195 °C for 3 h to obtain a dark brown viscous

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Table 1. Composition, Equivalent Weight (EW), and Ion-Exchange Capacity (IEC) of FSPIH-*X*

polymer	*X* (mol %)	EW	IEC (mequiv/g)
FSPIH-0	0	288	3.47
FSPIH-10	10	331	3.02
FSPIH-20	20	378	2.65
FSPIH-27M[a]	27	418	2.39
FSPIH-30	30	429	2.33
FSPIH-40	40	505	1.98
FSPIH-50	50	614	1.63
FSPIH-60	60	786	1.27

[a] Branched polymer with 2 mol % of melamine.

solution. Membrane was prepared by casting from the solution and treated according to the procedure described in the preceding paper.[8]

Measurement. ^{1}H NMR experiments were performed on a Bruker AVANCE 400S spectrometer using deuterated dimethyl sulfoxide (DMSO-d_6) as the solvent and tetramethylsilane (TMS) as the internal reference. Infrared (IR) spectra were recorded on a Jasco FT/IR-500 spectrometer as KBr pellets in the range 400−4000 cm^{-1}. 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 TG-DTA 2000 instrument. For each run, the temperature was increased from room temperature (rt) to 400 °C at a heating rate of 20 °C/min under N_2.

Water Uptake. The membrane was dried at 80 °C under vacuum for 6 h until constant weight as dry material was obtained. It was placed in a humidor set at 93% relative humidity (RH) and 85 °C. After 2 h, the membrane was placed in a closed vial and quickly weighed.

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. The stability was evaluated by recording the time when membranes began to dissolve and dissolved completely.

Proton Conductivity. A four-point-probe conductivity cell with two gold plate outer current-carrying electrodes and two platinum wire inner potential-carrying electrodes were fabricated. Membrane samples were cut into strips that were 0.5 cm wide and 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 a Solartron SI1280 electrochemical impedance analyzer. The instrument was used in galvanostatic mode with current amplitude of 0.005 mA over a frequency range from 10 to 20 000 Hz.

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. 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)).

Electrodes and Membrane Electrode Assembly. Pt/Ru catalyst (30.4 wt % of Pt and 23.6 wt % of Ru particles supported on carbon black) was dispersed in butyl acetate, to which Nafion solution in 2-propanol was slowly added. The weight ratio of Nafion (dry based) to carbon black was 1.5. The mixture was coated on a wet-proofed carbon paper by filtration to obtain an anode containing 1.67 mg/cm^2 of Pt/Ru. A similar procedure was applied using Pt catalyst (46.3 wt % of Pt particle supported on carbon black) to prepare a cathode containing 1.00 mg/cm^2 of Pt. The electrodes were dried and then hot-pressed at 130 °C and 5 kgf/cm^2 for 3 s followed by treating with 3% H_2O_2 at 60 °C for 30 min and with 1 N HNO_3 at rt for 30 min. A membrane of FSPIH-30 with a thickness of 50 μm or Nafion 112 was sandwiched by the electrodes with an active area of 3 cm^2 and then hot-pressed at 120 °C and 5 kgf/cm^2 for 30 min. The resulting membrane electrode assembly (MEA) was mounted in a single cell holder constructed of two porous carbon plates with ribbed channels on one side for supplying methanol solution (anode) and oxygen gas (cathode), held in two carbon frames contacting with two copper plates for current collection.

Direct Methanol Fuel Cell (DMFC) Operation. The cell was operated at 80 or 90 °C under ambient pressure. 1 M methanol aqueous solution was pumped through the anode at a flow rate of 1 mL/min, corresponding to the methanol utilization of 6.22% at 0.2 A/cm^2. Oxygen gas was supplied to the cathode at a flow rate of 20 mL/min, corresponding to the oxygen utilization of 10.5% at 0.2 A/cm^2. Oxygen was supplied in dry state or humidified at 50 °C. Ohmic resistance (IR drop) was measured with a current interrupter (Nikko Keisoku NCPG 1010) by applying current-off pulses for 100 μs to the current-drawing cell and recording the resulting potential drop with a storage oscilloscope (Hitachi VC 6023). The drawing current was changed stepwise, and the potentials and the potential drops (IR) caused by ohmic resistance were logged at steady state. Methanol crossover (the amount of methanol reaching from anode to cathode) was determined by measuring the concentration of CO_2 in the cathode exhaust via gas chromatography after trapping water with an ice trap, since methanol could be oxidized completely at the cathode. The oxidation current density equivalent to the amount of the crossed over methanol, $j(CH_3OH)$, was calculated on the basis of the amount of formed CO_2.[9]

Results and Discussion

Synthesis of Sulfonated Polyimide Copolymers Containing Trifluoromethyl Groups. The sulfonated copolymers (FSPIH-*X*) were synthesized by the copolymerization of DAPS, FMB, and TCND as shown in Scheme 1. To give polymers enough solubility to grow high molecular weight, 5 mol % of *m*-PDA was added as a bent diamine comonomer. The composition, equivalent weight per sulfonic acid group (EW), and ion-exchange capacity (IEC) of FSPIH-*X* are summarized in Table 1. FSPIHs are soluble in polar organic solvents (DMAC, NMP, and DMSO) and form a flexible and tough film by casting from the solution. The FSPIH membranes are brown but somewhat lighter in color than the fluorenyl groups containing polyimide membranes (SPIHs). FSPIHs were analyzed by ^{1}H NMR and IR spectroscopies. The ^{1}H NMR spectra in DMSO-d_6 indicated that FSPIHs have the chemical structure and the composition as expected from the feed monomers and the mixing ratio. The IR spectra also confirmed their chemical structure, and the spectra were very similar to those of SPIHs since the absorption band of C−F stretching vibration (∼1180 cm^{-1}) overlaps with the stronger and broader peak at 1200 cm^{-1} ascribed to S═O asymmetric vibration of sulfonic acid groups.

The branched FSPIH-27M (Chart 1) was also synthesized by incorporating 2 mol % of trifunctional monomer (melamine) in the same polymerization procedure as for unbranched polymers. There were no differences observed in the appearances, IR and NMR spectra between the branched (FSPIH-27M) and the corresponding unbranched (FSPIH-30) copolymers. GPC analyses showed that both FSPIH-30 ($M_w = 287 \times 10^3$, $M_n = 90 \times 10^3$) and FSPIH-27M ($M_w = 220 \times 10^3$, $M_n = 65 \times 10^3$) are of high molecular weight.

Thermal Properties. FSPIH-*X* membranes were subjected to TG/DTA analyses to evaluate their thermal transition and decomposition properties. The TG and DTA curves were very similar (except for the amount

Scheme 1. Synthesis of Sulfonated Polyimide Copolymers FSPIH-*X*

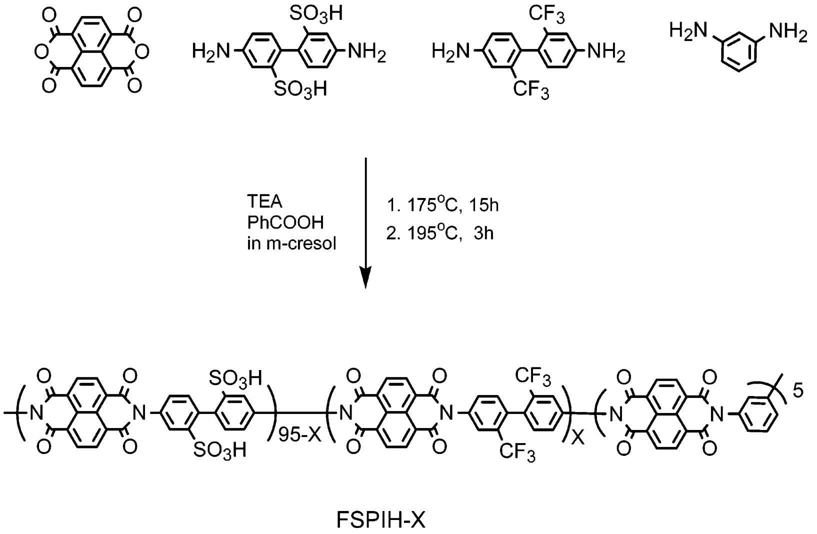
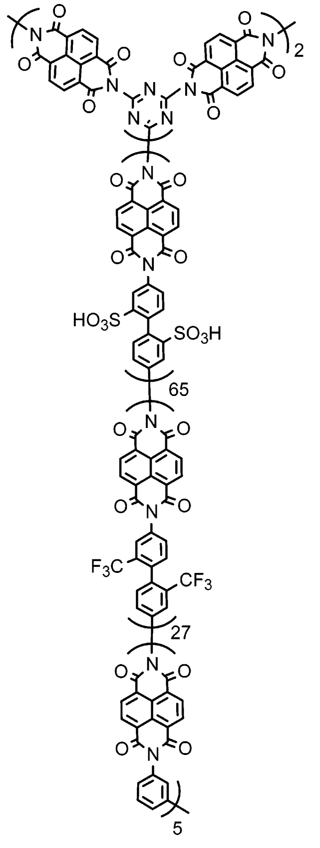


Chart 1. Molecular Structure of the Branched Sulfonated Polyimide Copolymer FSPIH-27M



of adsorbed water) among the FSPIHs with different composition and the other miscellaneous polyimide electrolytes; two-step weight loss with the first one from 20 to 170 °C and the second one from 280 °C and no glass transition and melting temperatures were observed. These and previous results[6-8] lead us to a general conclusion that the sulfonated aromatic polyimides start to decompose by the cleavage of $C_{Ar}-SO_3H$ bonds at 280 °C, which is lower temperature than that at which the glass transition of polymer chains would take place.

Water Uptake. The water uptake of FSPIH-*X*, FSPIH-27M, and Nafion 112 is plotted as a function of ion-exchange capacity (IEC) in Figure 1. The water uptake of FSPIH-*X* decreases from 102 wt % ($X = 0$, IEC = 3.47 mequiv/g) to 68 wt % ($X = 10$, IEC = 3.02 mequiv/g) with an increase in the bis(trifluoromethyl)biphenylene content. The water uptake shows its maximum of 73 wt % at $X = 20$ (IEC = 2.65 mequiv/g). The unique behavior was also observed for SPIH-*X* series containing fluorenyl groups as hydrophobic component,[8] but less pronounced for FSPIH-*X*. We explain the results by taking the molecular bulkiness of hydrophobic components into account (Figure 2). The molecular size of the bis(trifluoromethyl)biphenylene group estimated by semiempirical molecular orbital calculation (PM3) is 6.1 Å and smaller than that of the fluorenylbiphenylene group (9.0 Å) so that FSPIH-*X* should have smaller interchain spaces for having water molecules than SPIH-*X* does. The sulfonated polyimides containing naphthylene groups as a planar and smaller hydrophobic component do not show maximum water uptake behavior,[7] supporting our assumption that the water molecules could be confined in a space produced by bulky hydrophobic substituents. The water uptake of FSPIH-*X* decreases with further increase in bis(trifluoromethyl)biphenylene content and finally reaches down to 13 wt % for FSPIH-60 (IEC = 1.27 mequiv/g). As has been observed for SPIH, the branching with 2 mol % of melamine lowered the water uptake of FSPIH from 53 wt % (FSPIH-30) to 31 wt % (FSPIH-27M) due to the suppression of molecular motion.

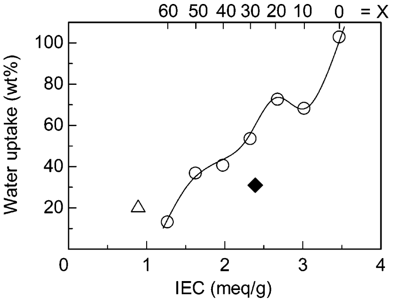


Figure 1. Water uptake of FSPIH-*X* (○), FSPIH-27M (◆), and Nafion 112 (△) at 85 °C and 93% RH.

Oxidative Stability. Oxidative stability of FSPIH-*X* membranes (50 μm) was examined by observing the dissolving behavior in Fenton's reagent at 80 °C (Figure 3). Both the dissolving and the dissolved time became longer by the increase in the hydrophobic group content.

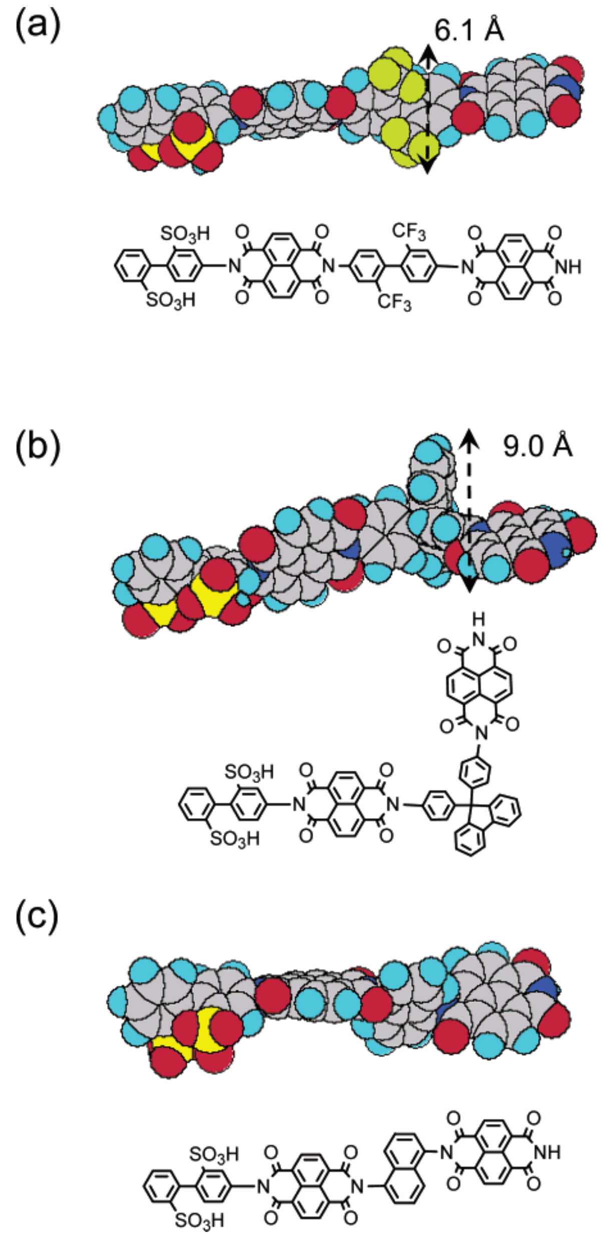


Figure 2. Space-filling molecular model of the model compounds for FSPIH (a), SPIH (b), and naphthylene groups containing SPI (c).

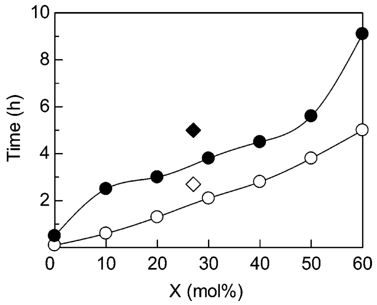


Figure 3. Oxidative stability of FSPIH-*X* (○, ●) and FSPIH-27M (◇, ◆) at 80 °C in Fenton's reagent. Open symbols represent the dissolving time, and the solid symbols represent the dissolved time.

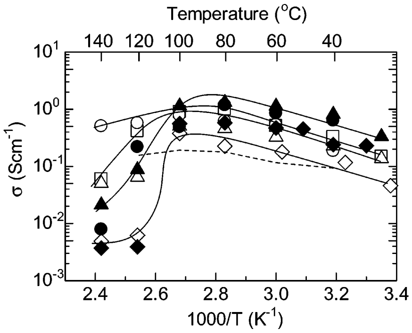


Figure 4. Temperature dependence of the proton conductivity of FSPIH-10 (●), -20 (▲), -30 (○), -40 (□), -50 (△), -60 (◇), -27 M (◆), and Nafion 112 (dashed line) at 100% RH.

FSPIH-60 membrane endured for 4 h before it started to dissolve. It was more than 9 h until the membrane had completely dissolved. The effect of hydrophobic groups on prolonging the dissolving time was more pronounced for bis(trifluoromethyl)biphenylene groups than fluorenyl or naphthyl groups. Introducing a small amount of fluorine containing groups (12.4 wt % of fluorine for FSPIH-60) was highly effective for improving the oxidative stability of the sulfonated polyimides because fluorine could protect the polymer main chains from being attacked by water molecules containing highly oxidizing radical species. The branched FSPIH-27M membrane showed even better oxidative stability than the corresponding unbranched FSPIH-30 membrane due to its lower water-absorbing capability as shown in Figure 1.

Proton Conductivity. The temperature dependence of the proton conductivity of FSPIH membranes and Nafion 112 at 100% RH is summarized in Figure 4. The logarithmic conductivities of FSPIHs showed a linear dependence on the reciprocal of the temperature below 80 °C. The conductivities are approximately in the order of the copolymer composition; i.e., the concentration of sulfonic acid groups or IEC determines the proton conductivity. At high temperatures than 100 °C, however, the conductivities decrease considerably, especially for FSPIH-27M and -60 membranes. The results imply that the absorbed water molecules evaporate out of the membranes above the boiling temperatures. The water confinement effect by the hydrophobic groups which was observed for SPIH series[6,8] was not obtained for FSPIH membranes probably because strongly hydrophobic trifluoromethyl groups lower the water-holding capability of the polyimide copolymers. Among the FSPIH-*X* membranes and Nafion 112, FSPIH-30 showed the most preferable proton-conducting properties with the conductivity higher than 0.2 S cm^{-1} at the temperatures ranging from 30 to 140 °C.

The FSPIH-30 membrane displayed good conducting performance also in the humidity dependence experiments (Figure 5). The conductivities were comparable to those of Nafion 112 under the given conditions (80−140 °C, 10−100% RH). FSPIH-50 and -60 membranes showed relatively high conductivity at <100 °C and >60% RH but low conductivity at >120 °C and <40% RH. The results are not contradictory to the above discussion for 100% RH conditions that the membranes lost water-holding capability and therefore proton conductivity as well at high temperatures.

Mechanical Properties. The tensile properties of FSPIH-30 and -27M membranes were measured at 85 °C and 93% RH and are depicted in Figure 6. Both membranes showed small strain with the elongation at break of 20% (FSPIH-30) and 8% (FSPIH-27M) compared to that of 334% (Nafion 112). The initial Young's modulus was the same value of 1.9 GPa for both FSPIH membranes. The maximum tensile stress at break was

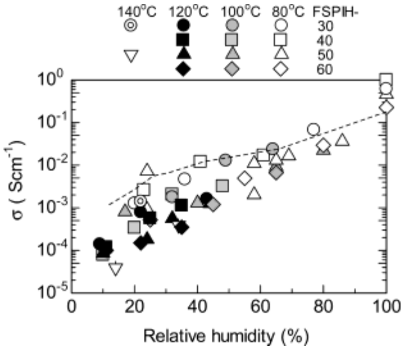


Figure 5. Humidity dependence of the proton conductivity of FSPIH-*X* at 80, 100, 120, and 140 °C and of Nafion 112 (dashed line) at 100 °C.

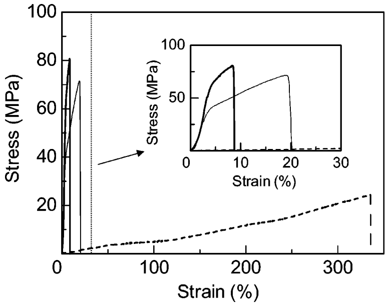


Figure 6. Stress vs strain curves for FSPIH-30 (thin), FSPIH-27M (thick), and Nafion 112 (dashed) at 85 °C and 93% RH. Inset is enlarged of the dotted region.

very large: 68 MPa (FSPIH-30) and 79 MPa (FSPIH-27M). These results suggest us the following two important findings, which are that the sulfonated polyimide electrolytes have smaller elongation and larger strength than the perfluorinated ionomer membranes under heated and humidified conditions and that a small amount of fluorine-containing groups and branching contribute to further improve the tensile properties.

DMFC Operation and Methanol Crossover through the Membrane. The FSPIH-30 membrane that was optimum in oxidative stability, proton conductivity, and mechanical properties was tested further in a direct methanol fuel cell (DMFC). Because the main objective of the DMFC experiments is to analyze the methanol crossover (permeation) through the FSPIH-30 membrane but not to obtain the best cell performance, we have used high loading amount of electrocatalysts (1.67 mg/cm^2 Pt/Ru for anode and 1.00 mg/cm^2 Pt for cathode). The proton conductive ionomer employed in the catalyst layers was the conventional Nafion so as to evaluate the effect of electrolyte membrane itself.

In Figure 7 is shown the DMFC performance using FSPIH-30 membrane or Nafion 112 at the cell temperature of 80 and 90 °C with dry oxygen fed to the cathode. It should be noted that the methanol crossover (j(CH$_3$OH)) of FSPIH-30 membrane is much lower than that of Nafion 112; about 30% at 80 °C and 40% at 90 °C, respectively. The lower methanol crossover of FSPIH-30 would be ascribed to the lower methanol affinity of (only partially fluorinated) hydrocarbon materials than that of perfluorinated materials.[10] The terminal voltage was higher at 90 °C than at 80 °C despite the increased methanol crossover because of the decreased overpotentials for oxygen reduction and methanol oxidation reactions at higher temperature. The ohmic resistance (ca. 0.1 Ω cm^2) was almost 10 times higher than the value (0.01 Ω cm^2) calculated for the fully humidified FSPIH-30 membrane from Figure 4, probably because the membrane was not well-humidified or the membrane/electrode contact was not sufficient. To investigate this issue in detail, the cell was operated with supplying oxygen gas humidified at 50 °C, of which performance is shown in Figure 8. As expected, the resistance of the membrane decreased considerably. However, j(CH$_3$OH) increased by humidifying oxygen because the methanol diffusion should be higher for the wetter membrane. A good DMFC performance with 0.38 V at 200 mA/cm^2 was obtained by the operation at 80 and 90 °C. These results have proved the potential availability of the

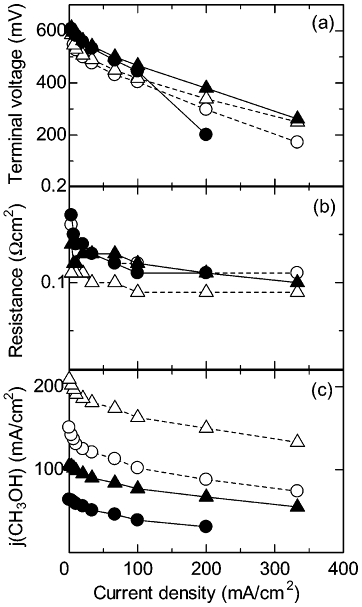


Figure 7. DMFC performance with FSPIH-30 (solid symbols) or Nafion 112 (open symbols) membrane at 80 (○, ●) and 90 °C (△, ▲): terminal voltage (a), ohmic resistance (b), and current density for the oxidation of crossed over methanol (c). Dry oxygen was supplied.

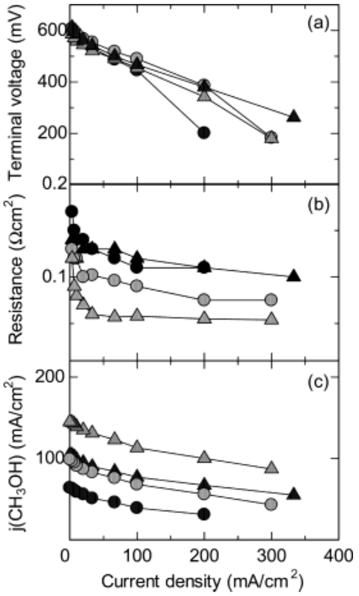


Figure 8. Effect of humidification of oxygen on the DMFC performance with FSPIH-30 at 80 (circle) and 90 °C (triangle): terminal voltage (a), ohmic resistance (b), and current density for the oxidation of crossed over methanol (c). Oxygen was supplied in dry state (solid symbols) or humidified at 50 °C (gray symbols).

sulfonated polyimide membranes as an electrolyte for DMFCs.

Conclusions

A series of sulfonated polyimide copolymers (FSPIH-*X*) having 0−60 mol % of bis(trifluoromethyl)biphenylene groups have been synthesized. The comparison of the properties with the other series of the sulfonated polyimides showed that the bis(trifluoromethyl)biphenylene groups with the molecular size of 6.1 Å could afford the polyimides interchain spaces to confine water molecules, although the effect is less pronounced than the more bulky fluorenyl groups with the molecular size of 9.0 Å. Regardless of the hydrophobic comonomer structure, the sulfonated polyimides do not display glass transition and melting temperatures. The thermal decomposition commences at 280 °C by the cleavage of $C-SO_3H$ bonding. The trifluoromethyl substituents are effective in improving the oxidative stability and the tensile properties of polyimide membranes. The maximum tensile stress at break of FSPIH is 79 MPa and almost 3 times higher than that of Nafion 112. FSPIH-30 membrane showed a higher proton conductivity than 0.2 S cm^{-1} at 30−140 °C and 100% RH. The optimum composition of bis(trifluoromethyl)biphenylene groups was found to be 30 mol % from the viewpoint of the oxidative stability, proton conductivity, mechanical properties, and their good balanced combination. DMFC experiments revealed that the methanol crossover through FSPIH-30 membrane was only 30% of that of Nafion 112. The lower methanol crossover would be ascribed to the lower methanol affinity of hydrocarbon polymers and be a great advantage over the perfluorinated ionomers when taking the efficiency of fuel cells into account.

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