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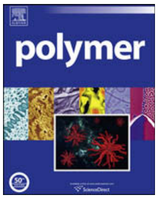

Fluorinated poly(arylenethioethersulfone) copolymers containing pendant sulfonic acid groups for proton exchange membrane materials

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ABSTRACT

Fluorinated sulfo-pendants poly(arylenethioethersulfone) copolymer, which contained 50 mol% sulfonate content per repeat unit (6F-SPTES-50), were synthesized by a nucleophilic polycondensation from 4,4-(hexafluoroisopropylidene)-diphenylthiol, 3,3′-disulfonate-4,4′-difluorodiphenylsulfone and 4,4′-difluorodiphenylsulfone. The 6F-SPTES-50 copolymer possessed high molecular weight, exhibited good film formability and thermal stability, and maintained adequate mechanical strength after immersion in water for 24 h. The proton conductivities of the 6F-SPTES-50 copolymer membrane increased with temperatures, reaching values above 120 mS/cm at 85 °C and 85% relative humidity. Preliminary MEA test shows acceptable performance, which indicated that these materials are promising proton exchange membranes (PEMs) for fuel cells operated at medium temperatures.

1. Introduction

The new polymer membranes in fuel cell applications are mostly based on hydrocarbon structure for the polymer backbone. The new membrane concepts include fluorinated, partially fluorinated, and aromatic polymer membranes as well as composite membranes [1]. DuPont's Nafion, a perfluorinated polymer membrane is the primary system and commercially available standard in the proton exchange membrane (PEM) fuel cell technology [2]. The hydrophobic polytetrafluoroethylene backbone of Nafion provides thermal and chemical stability, whereas, the perfluorinated side chains with terminating hydrophilic sulfonic acid (–SO_3H) provide a mechanism to conduct protons [3]. In spite of being the state-of-the-art material, Nafion has some drawbacks for fuel cell applications. The proton conduction is extremely sensitive to hydration limiting its performance at high temperatures (>80 °C) and low humidity levels [4,5]. Additionally, the cost of Nafion is extremely high due to the complex and extensive chemistry required for synthesis.

Hydrocarbon polymers containing polar groups that retain high amounts of water over a wide temperature range are particularly attractive and relatively much cheaper to synthesize than perfluorinated polymers. Sulfonated high performance polymer systems based on arylene ether, sulfone, and thioether linkages in the backbone have been synthesized and described in literature [6–8]. These polymer systems are potential candidates for fuel cell applications as they exhibit good thermal and chemical stability and high proton conductivity. In last decades, many researchers have been focused on the synthesis of various sulfonated aromatic polymers that have high thermal, chemical and oxidative stability, good mechanical properties and low cost. Usually they are prepared either by post-sulfonation of commercial polymers or by direct synthesis of sulfonated polymer via copolymerization of sulfonated monomers. The synthesis of sulfonated aromatic polymer materials by direct copolymerization of disulfonated monomers with other unsulfonated aromatic monomers may be a better approach to control the polymer homogeneity and the degree of sulfonation [9–11].

High molecular weight sulfonated poly(arylenethioethersulfone) (SPTES) polymers have been developed by our group [12,13]. The SPTES polymers all have an aromatic polymer backbone with a pendant acid functionality incorporated directly onto the backbone that will be an alternate, economical hydrocarbon polymer system to overcome the limitations of Nafion. Although the SPTES polymers showed very good potential usages in PEMs, they still have some drawbacks which require additional work. These drawbacks include inadequate mechanical stability with higher percentage of water uptake and swelling in high relative

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humidity; the low proton conductivity is especially notable when the polymer has a low amount of sulfonated groups. To improve the PEM performance and mechanical durability of the SPTES polymers, the aromatic fluorinated moiety or aliphatic fluorinated moiety was introduced to the SPTES polymer backbone by designing the composition to balance polymer hydrophilicity and hydrophobicity. The proper balance should enable good mechanical properties and reduce the swelling of the sulfonated polymers (which in turn weakens mechanical integrity), and produce greater proton transport channel in the microstructure, which will further enhance proton conductivity of the polymer membranes.

The present work reports a fluorinated sulfo-pendants poly(arylenethioethersulfone) copolymer, which contained 50 mol% sulfonate content per repeat unit (6F-SPTES-50) as proton exchange membrane materials synthesized by utilizing an hexafluoroisopropylidene diphenyl monomer, which is hydrophobic. The incorporation of the hexafluoroisopropylidene diphenyl moiety into the polymer not only enhances the polymer solubility without loss of thermal stability [14], but also promotes the hydrophobicity of unsulfonated backbone segments of the polymers [15]. The 6F-SPTES-50 copolymer membrane material showed high proton conductivity and thermal stability, and good mechanical strength in hot water.

2. Experimental

2.1. Materials

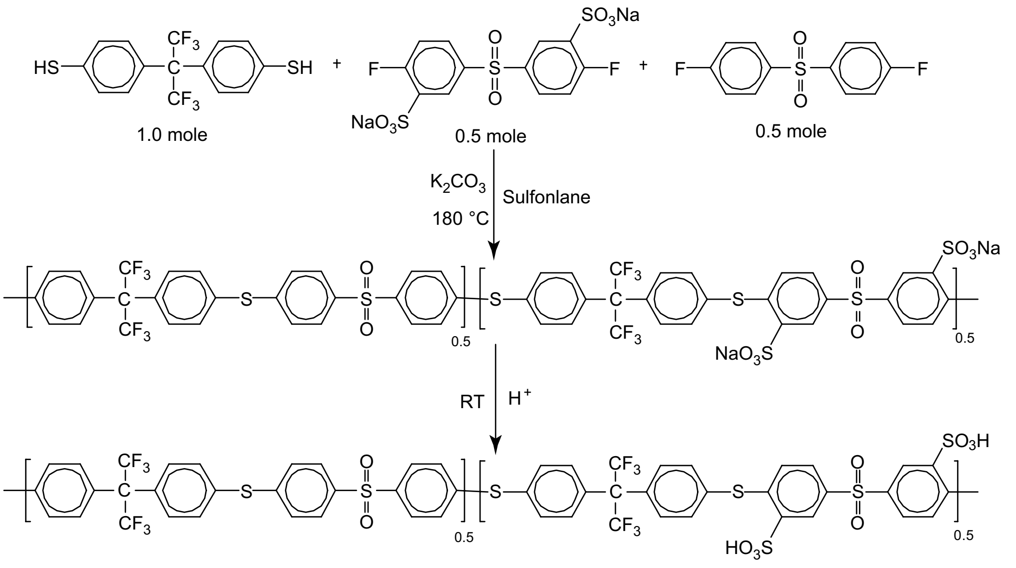
4,4′-Difluorodiphenylsulfone (4-Fluorophenylsulfone, 99%, Sigma–Aldrich Co.), 4,4-(hexafluoroisopropylidene) diphenol (Bisphenol AF, 6F-BPA, 97%, TCI America), *N*,*N*-dimethylthiocarbamyl chloride (97%, Sigma–Aldrich Co.), potassium carbonate (K_2CO_3, 99%, ACS reagent, Sigma–Aldrich Co.), sulfuric acid (Fuming, 30% SO_3, Sigma–Aldrich Co.), tetramethylene sulfone (Sulfolane, 99%, Sigma–Aldrich Co.), *N*,*N*-dimethylacetamide (DMAc, anhydrous, 99.8%, Sigma–Aldrich Co.) were used as-received. Other chemicals were of commercially available grade and used as-received unless otherwise mentioned. Sulfonated monomer, 3,3′-disulfonate-4,4′-difluorodiphenylsulfone, was prepared by following the procedures disclosed elsewhere [16]. 4,4′-(Hexafluoroisopropylidene)-diphenylthiol (Hexafluorobisphenylthiol A) was prepared in our laboratory according to literature procedure [17].

2.2. Polymer synthesis

The fluorinated sulfo-pendants poly(arylenethioethersulfone) (6F-SPTES-50) copolymer were prepared by a nucleophilic aromatic substitution polycondensation according to typical synthesis procedure in the literature [18,19]. The chemical reaction scheme is shown in Scheme 1. Hexafluorobisphenylthiol A (5.894 g, 16 mmol), 3,3′-disulfonate-4,4′-difluorodiphenylsulfone (3.667 g, 8.0 mmol), 4,4′-difluorodiphenylsulfone (2.034 g, 8.0 mmol) and potassium carbonate (5.750 g, 42 mmol) were charged into a 250 ml round-bottom flask maintained under a back pressure of nitrogen and equipped with a magnetic stirrer and an oil bath on a hot plate; sulfolane (100 ml) was added into the flask which is used as solvents. The reaction mixture was stirred for 45 min at room temperature and at 120 °C for overnight. The temperature of the reaction mixture was slowly raised to 180 °C and maintained for 8 h, then cooled down to room temperature, and precipitated in the mixed solvent of methanol and acetic acid (v/v: 10/1). The copolymer was filtered, Soxhlet-extracted with methanol for 48 h, and dried in vacuum at 80 °C overnight to afford a yield of 92%.

2.3. Membrane preparation

The salt form of the 6F-SPTES-50 copolymer was dissolved in DMAc to form ∼10 wt% clear solution, and filtered at room temperature. The membrane was directly cast onto a flat dish and dried at 80 °C in vacuum for 24 h. The membrane (in salt form) was converted to the corresponding sulfonic acids in the presence of diluted sulfuric acid (4.0 M) at room temperature for 48 h. The 6F-SPTES-50 copolymer membrane was washed by immersion in deionized water, and dried at room temperature followed by at 100 °C in vacuum for 24 h. This procedure yielded tough, clear, flexible membranes of the 6F-SPTES-50 copolymer. The thickness of all membrane samples was in the range of 75–100 μm.



Scheme 1. The reaction scheme of fluorinated sulfo-pentants poly(arylenethioethersulfone) (6F-SPTES-50) copolymer.

2.4. Characterization

Gel permeation chromatography (GPC) was used to determine molecular weights and molecular weight distributions, M_w/M_n, of synthesized polymer samples with respect to polystyrene standards. Molecular weight measurement was performed on TriSEC Version 3.00 in *N*-methyl-2-pyrrolidone (NMP) containing 0.5% LiBr at 70 °C.

Nuclear magnetic resonance (^{1}H NMR) analyses were conducted on a Bruker Avance 400 NMR spectrometer operating at a resonance frequency of 399.95 MHz for protons. All spectra were obtained from a 10% solution (w/v) in deuterated dimethylsulfoxide (DMSO-d_6) at room temperature.

2.5. Water uptake and ion exchange capacity (IEC) measurement

The 6F-SPTES-50 copolymer membrane was vacuum-dried at 100 °C for 24 h, weighed and immersed in deionized water at room temperature for 24 h. The wet membrane was wiped dry and then quickly weighed again. The water uptake of the polymer membrane is reported in weight percent as follows:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \qquad (1)$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively. This method provides an accurate measurement of water uptake and has been established in literature [2].

The ion exchange capacity (IEC) was measured by following procedure: The 6F-SPTES-50 polymer membrane was then immersed in a 2.0 M solution of NaCl for 4–5 h to replace the protons of sulfonic acid groups with sodium ions. The replaced protons were titrated using 0.1 M NaOH solution, with phenolphthalein as indicator. The moles of the proton are equal to the moles of sulfonic group and the IEC was calculated from the titration data.

2.6. Proton conductivity measurement

The proton conductivity of 6F-SPTES-50 copolymer membrane was measured using AC Impedance Spectroscopy with a standard 4-electrode measurement setup to eliminate electrode and interfacial effects. Proton conductivities in the longitudinal direction were measured at different temperatures over a period of 1 day for each PEM sample. A sample of membranes 5 × 1 cm^2 was clamped in a frame, providing electrical contact with two stainless steel electrodes, and placed in an environmental chamber open to air through a pinhole. The membrane in the frame was exposed to water vapor at different relative humidity (RH) during the experiments. The proton conductivity was calculated using

$$\sigma = \frac{l}{R \times (d \times w)} \qquad (2)$$

where l is the distance between the electrodes, d and w are the thickness and width of the films, respectively, and R was derived from the lower intersection of the high frequency semi-circle on a complex impedance plane with the axis of abscissas.

2.7. Thermal analysis

Thermogravimetry analysis was conducted using an Auto TGA 2950HR V5.4A thermogravimetric analyzer (TGA) in air at a heating rate of 10 °C/min to study the thermal stability of the 6F-SPTES-50 copolymer sample. The sample was preheated under air from room temperature to 150 °C at 10 °C/min to remove moisture, cooled to room temperature, and then reheated from that temperature to 900 °C at 10 °C/min.

A TA DSC 2920 differential scanning calorimeter (DSC) was employed to determine the glass transition temperature (T_g) of the 6F-SPTES-50 copolymer sample. The sample was preheated under nitrogen from room temperature to 150 °C at 10 °C/min to remove moisture, then cooled to −90 °C, and reheated from that temperature to 300 °C at 10 °C/min.

2.8. Dynamic mechanical analysis

Dynamic mechanical analysis (DMA) was performed to determine the influence of the polymer constitution on tensile modulus and mechanical relaxation behavior. A PerkinElmer DMA-7 was run in tensile mode at an oscillation frequency of 1 Hz with a static stress level of 5×10^5 Pa and a superposed oscillatory stress of 4×10^5 Pa. With this stress controlled instrument, the strain and phase difference between stress and strain are the measured outputs. Typically, the resulting strain levels ranged from 0.05 to 0.2% when the sample dimensions were 8 mm × 2 mm × 0.1 mm. A gaseous helium purge and a heating rate of 3 °C/min were employed. The temperature scale was calibrated with indium, and the force and compliance calibrations were performed according to conventional methods.

2.9. Fabrication of membrane electrode assembly (MEA)

MEA was fabricated using a painting technique to form electrodes on both sides of membranes with ink slurry. This slurry contained platinum black, water and Nafion solution (5 wt%) as binder, and a catalyst loading of 5 mg/cm^2 was used. The ink slurry was sonicated to break up the catalyst powder in order to obtain a homogenous mixture. Several layers of the ink were painted on both sides of the membranes. Samples were dried at 80 °C under vacuum for 10 h to remove residual solvents.

3. Results and discussion

3.1. Structures and properties of the 6F-SPTES-50 copolymer

The 6F-SPTES-50 copolymer was synthesized by copolymerization of a commercially available monomer: 4,4′-difluorodiphenylsulfone, a synthesized monomer: hexafluorobisphenylthiol A, and a synthesized disulfonated monomer: 3,3′-disulfonate-4,4′-difluorodiphenylsulfone in sulfolane as solvent at temperatures up to 180 °C. The chemical structures and reaction scheme for the 6F-SPTES-50 copolymer are shown in Scheme 1. The resulting copolymers have high molecular weight, relatively colorless or more lightly colored, and exhibit decreased water solubility. The high molecular weight of the 6F-SPTES-50 copolymer was evidenced by high intrinsic viscosity (η) value of 0.92 dL/g, measured in NMP at 30 °C, and confirmed by GPC results ($M_n = 25{,}800$), and also evidenced by the fact they could be cast into very tough films from DMAc. The high molecular weight 6F-SPTES-50 copolymer in the sulfonate form was soluble in dipolar aprotic solvents such as DMAc, NMP.

The composition of the 6F-SPTES-50 copolymer was analyzed by ^{1}H NMR in DMSO-d_6, and a typical NMR spectrum is shown in Fig. 1. Each signal in the spectra of the aromatic region of the 6F-SPTES-50 copolymer was assigned to a single or to a group of aromatic protons of sulfonated (A) or non-sulfonated (B) repeat unit. The NMR spectrum shows that the peaks at 7.90 and 7.40 ppm are in intensity as the amount of non-sulfonated (B) monomer; the ^{1}H NMR signal intensity value of sulfonated (A) proton peak at

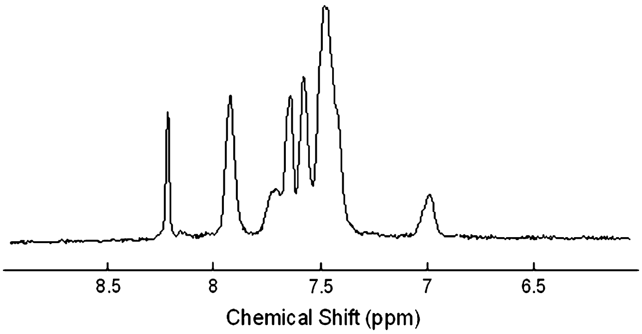


Fig. 1. ^{1}H NMR spectra of 6F-SPTES-50 copolymer in DMSO-d_6.

8.20 ppm is as the sulfonated (A) monomer. The composition of sulfonated (A) and non-sulfonated (B) monomers of 6F-SPTES-50 copolymer can be evaluated by integrating the aromatic region of NMR spectrum.

The analysis relies on the observation that the protons adjacent to the sulfonic acid at 8.20 ppm are resolved from all other protons, and the composition can be determined from the ratio of the peak at 8.20 ppm to the remaining aromatic protons. Since there are 12 aromatic protons in addition to the 2 protons at 8.20 ppm in the sulfonated monomer (A) and 16 protons in the non-sulfonated monomer (B), the ratio $\boldsymbol{r}$ is given by equation (3):

$$\boldsymbol{r} = \frac{2f_A}{12f_A + 16(1 - f_A)} \tag{3}$$

where f_A is the fraction of sulfonated monomer, which is called sulfonate content. Conversely, the value of f_A calculated from $\boldsymbol{r}$ is given by equation (4):

$$f_A = \frac{16\boldsymbol{r}}{2 + 4\boldsymbol{r}} \tag{4}$$

The calculated and measured sulfonate content of the 6F-SPTES-50 copolymer from the analysis of the aromatic peak intensities are listed in Table 1. The calculated sulfonate content of the 6F-SPTES-50 copolymer from NMR results was 46 mol%, which is in good agreement with the sulfonated monomer feed ratios (50 mol%), indicating that the polymerization was run to completion. We believe that the sulfonate content from the NMR experiments is more accurate than the titration results, which was 44 mol% for the 6F-SPTES-50 copolymer.

3.2. *Water uptake and ion exchange capacity*

The characteristics of the 6F-SPTES-50 copolymer membranes are listed in Table 1 including the SPTES-50 copolymer [13] and Nafion-117 as comparison. The ion exchange capacity (IEC) was obtained by calculation and experimental. The IEC numbers by experimental is 1.34 for 6F-SPTES-50 copolymer which has the proton conductivity in the value of 120 mS/cm. Based on the IEC values in Table 1, the sulfonate content was calculated, it is 44% for 6F-SPTES-50 copolymer.

The water uptake of the 6F-SPTES-50 copolymer at various temperatures is important factor for the evaluation of performance and dimensional stability of the membranes. Water uptake of the 6F-SPTES-copolymer membrane was measured by weighing films before and after immersed in deionized water at various temperatures for 24 h. Fig. 2 shows the water uptake comparison for the 6F-SPTES-50 copolymer, SPTES-50 copolymer, and Nafion-117. The 6F-SPTES-50 copolymer membrane showed water uptake in the range of 20–30 wt% over the whole temperature ranges while maintaining excellent mechanical integrity. This demonstrates that the 6F-SPTES-50 polymer has good dimensional stability, and is a good candidate for PEM materials in fuel cell applications. The Nafion-117 membrane showed adequate mechanical strength before and after immersion in water under the same conditions. Nafion-117 compared with 6F-SPTES-50 copolymer over the same temperature range exhibits similar trend results in water uptake. In the present study the 6F-SPTES-50 copolymer membrane can be compared with the previously studied SPTES-50 polymer [13], which exhibited greater water uptake for the polymers containing the same sulfonate content in polymer backbone. This difference may be attributed to the introduction of the –CF$_3$ group in the 6F-SPTES-50 copolymer backbone which affects the hydrophobicity, and result in a decrease in water uptake. And also it should be noticed that due to the structure difference, even at the same molar content of sulfonated monomer, the IEC values of the two polymers are different (6F-SPTES-50 is 1.34, SPTES-50 is 1.51). Therefore, it is possible that this water uptake difference comes partially from the IEC difference.

Table 1
Characteristics of 6F-SPTES-50 copolymer membrane.

Membranes	6F-SPTES-50 copolymer	SPTES-50 copolymer [13]	Nafion-117
Cal. IEC[a] (meq./g)	1.51	1.82	0.91
Exp. IEC[a] (meq./g)	1.34	1.64	N/A
Sulfonate content (mol%, IEC based)	44	45	N/A
Sulfonate content (mol%, NMR based)	46	47	N/A
Proton conductivity[b] (mS/cm)	120	135	100
Activation energy (kJ/mol)	19.0	18.2	9.79

[a] Defined as the number of milliequivalents of ions in 1 g of the dry polymer (meq./g). Titration was used to quantitatively determine sulfonic acid concentration in the polymer.

[b] Measured at 85 °C, 85% RH.

3.3. *Proton conductivity*

The proton conductivities (σ) of the 6F-SPTES-50 copolymer membranes in the longitudinal direction were measured by AC impedance spectroscopy. The membranes were initially hydrated

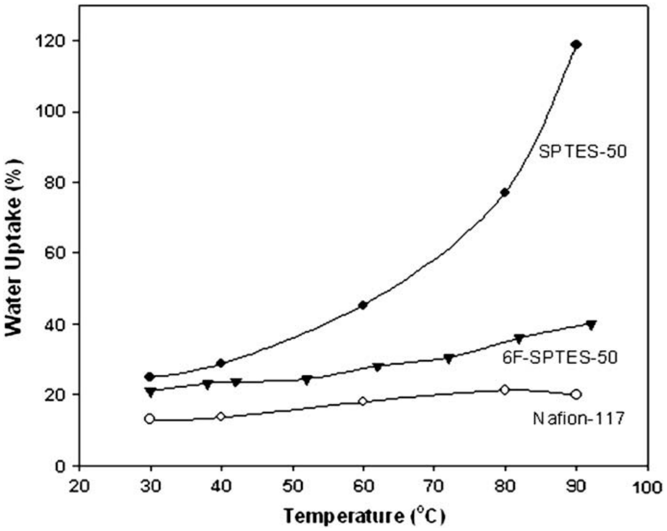


Fig. 2. Water uptake comparisons of the 6F-SPTES-50 copolymer, SPTES-50 copolymer, and Nafion-117 at different temperatures.

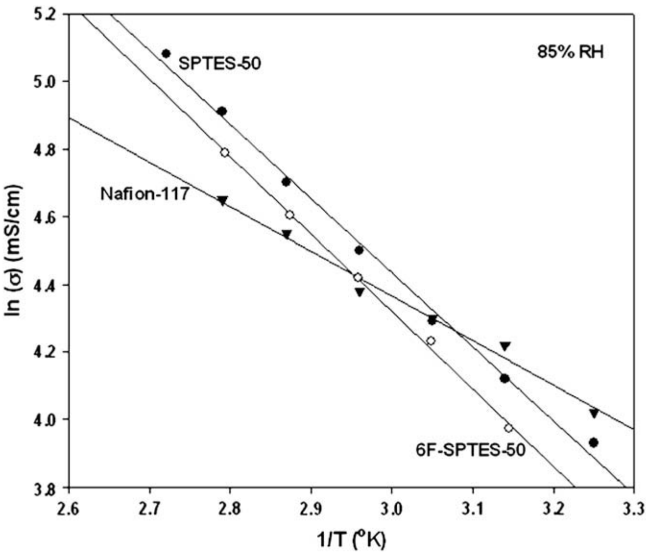


Fig. 3. Proton conductivity comparisons of the 6F-SPTES-50 copolymer, SPTES-50 copolymer, and Nafion-117 at different temperatures.

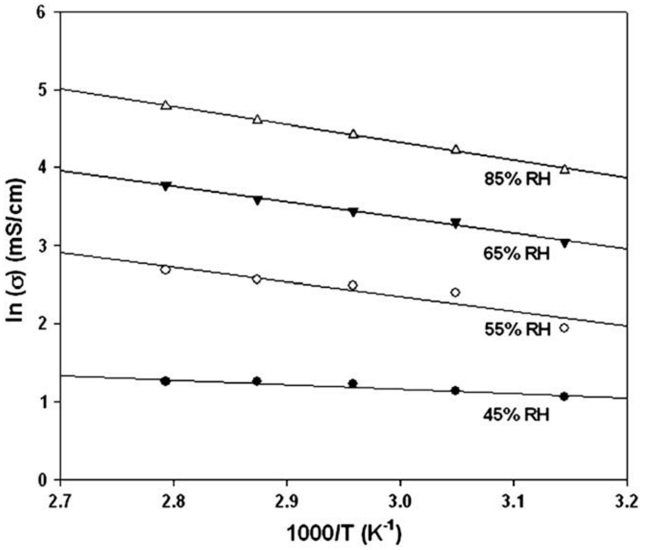


Fig. 4. The temperature dependence of proton conductivity of 6F-SPTES-50 copolymer at different relative humidity.

by immersion in deionized water for at least 24 h at room temperature. The general trend of proton conductivity at various temperatures for the 6F-SPTES-50 copolymer is shown in Fig. 3. These data show that the proton conductivities increased with increasing temperatures. The proton conductivities of the 6F-SPTES-50 copolymer membrane are in the range of 50–120 mS/cm at 4585 °C (85% relative humidity), which are high enough for the polymer to be considered promising PEM materials for fuel cell applications. We also note that the 6F-SPTES-50 copolymer has proton conductivity at 85 °C, superior to that of Nafion-117 (100 mS/cm, see Table 1).

From Fig. 3, we also found that the proton conductivity of the 6F-SPTES-50 copolymer has Arrhenius-type temperature dependent behavior. The activation energy (E_a) is calculated from a linear least square fit to the data presented in Fig. 3 according to Arrhenius equation (5) which is given by:

$$\sigma = Ae^{-E_a/RT} \tag{5}$$

where σ is the proton conductivity (mS/cm), A is the pre-exponential factor, E_a is the activation energy, R is the universal gas constant and T is the absolute temperature (K). The activation energies calculated for 6F-SPTES-50 copolymer, SPTES-50, and Nafion-117 are listed in Table 1. We noted that the activation energies we measured for the 6F-SPTES-50 copolymer and SPTES-50 copolymer are 19.0 kJ/mol and 18.2 kJ/mol, respectively, which indicated that the proton transfer mechanism is similar for the 6F-SPTES-50 copolymer and SPTES-50 copolymer. The activation energy of Nafion-117 is 9.79 kJ/mol, which is comparable with the reported values 9.53 kJ/mol [20]. The difference of the 6F-SPTES-50 copolymer and Nafion-117 in activation energy suggests that the proton conducting mechanism for the 6F-SPTES-50 copolymer is different from Nafion-117.

Fig. 4 shows the proton conductivity of the 6F-SPTES-50 copolymer under relative humidity conditions at different temperatures. The results show a significant dependence of the conductivity on the temperature and the relative humidity. As the relative humidity is increased, the conductivity increases in the whole temperature range. We believe that the increase in proton conductivity is related to the high degree of hydration in the membrane.

3.4. *Thermal properties of the 6F-SPTES-50 copolymer*

The thermal stabilities of the 6F-SPTES-50 copolymers and fluorinated poly(arylenethioethersulfone) (6F-PTES) polymer were studied by TGA in air, and the results are shown in Fig. 5. The 6F-PTES polymer has high thermal stability and an onset decomposition temperature (T_d) at ~450 °C and single step thermal degradation. The degradation of the salt form 6F-SPTES-50 copolymer is in the region 400–500 °C in TGA, and the salt form 6F-SPTES-50 copolymers showed higher thermal stability and single step thermal degradation; while the degradation of the 6F-SPTES-50 copolymer is in the region 270–430 °C, and the 6F-SPTES-50 copolymer exhibited two distinct thermal degradation steps: the first weight loss occurring at ~270 °C which is due to the decomposition of sulfonic acid groups by the desulfonation, and the second weight loss around 520 °C is assigned to the decomposition

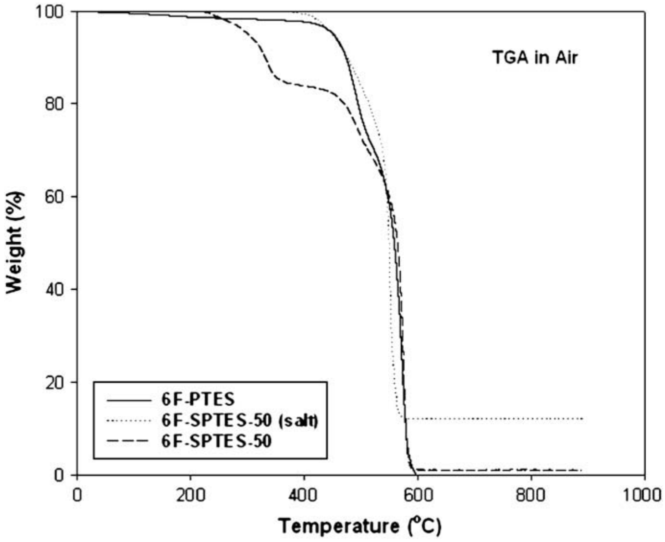


Fig. 5. TGA curves of the 6F-SPTES-50 copolymer, 6F-PTES polymer, and 6F-SPTES-50 copolymer salt.

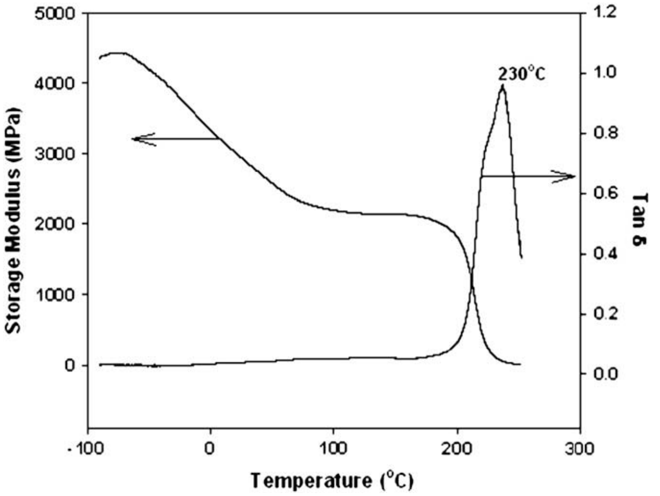


Fig. 6. DMA of the 6F-SPTES-50 copolymer.

of polymer main chain. The results of TGA indicate that the 6F-SPTES-50 copolymer is quite stable below 250 °C.

The dynamic mechanical properties of the 6F-SPTES-50 copolymer from DMA are depicted in Fig. 6. It shows that the 6F-SPTES-50 copolymer has an obvious glass transition temperature (T_g) at about 230 °C. Differential scanning calorimetry (DSC) analysis in nitrogen atmosphere at a heating rate of 10 °C/min was done to determine glass transition temperature. Three DSC thermograms of the 6F-SPTES-50 copolymer are shown in Fig. 7. The glass transition temperature is at 220 °C for all three runnings which were detected in DSC curves. It appears that the glass transition temperature of the 6F-SPTES-50 copolymer is above 220 °C which is sufficiently high for applications in polymer proton membrane for fuel cells at high temperature.

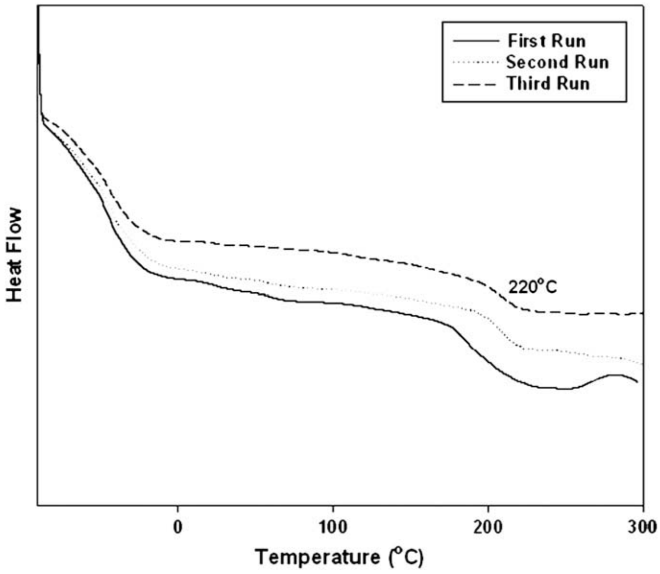


Fig. 7. DSC curve of the 6F-SPTES-50 copolymer.

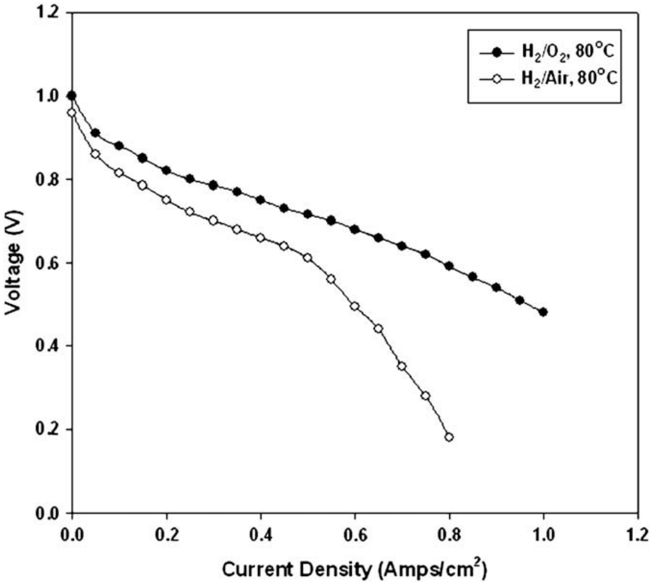


Fig. 8. Polarization plots of the 6F-SPTES-50 copolymer MEA at 80 °C in air and oxygen.

3.5. MEA performance of the 6F-SPTES-50 copolymer

The performance of a single cell was evaluated at test station (Fuel Cell Technologies, Inc.). Membranes with painted electrodes along with a gas diffusion layer (carbon cloth) were positioned in a single cell fixture and a serpentine flow-pattern with graphite blocks as current collectors. The gases (H_2, Air, and O_2) were humidified, with the gas humidity bottles set at 80 °C. 80% fuel utilization, along with a stoichiometry of 2 was used for the fuel gas and oxidant. Humidity was verified with an in-line high temperature humidity probe. Cell performance was obtained at 1 atmosphere with cell temperatures at 80 °C. MEAs using the 6F-SPTES-50 copolymer membrane with effective areas of 5 cm^2 were fabricated.

A typical polarization plot of the 6F-SPTES-50 copolymer MEA is shown in Fig. 8 at 80 °C using air and oxygen as a comparison of the performances under the conditions described above. The 6F-SPTES-50 copolymer MEA showed an overall lower performance in H_2/air than in H_2/O_2. A lower current density of 510 mA/cm^2 for the 6F-SPTES-50 copolymer membrane in H_2/air was obtained compared to 750 mA/cm^2 for the 6F-SPTES-50 copolymer membrane in H_2/O_2 at the same potential (0.6 V) under the same experimental conditions. As expected with oxygen the overall electrochemical performance is better.

Competing processes which include catalyst activity, interfacial resistance, and diffusion processes occur to different extents and contribute to losses observed in the polarization curve. The losses in the polarization curves are due to contribution from several competing processes, including catalyst activity, interfacial resistance, and diffusion processes. Table 2 shows the overall

Table 2
Comparison of cell performance of 6F-SPTES-50 membranes and SPTES-50 membranes *vs* Nafion.

Sample	ASR[a] (Ω cm^2) all voltage ranges	Rct[b] (Ω cm^2) @0.7 V	Open circuit voltage (OCV)
6F-SPTES-50 copolymer (100 μm)	0.35 ± 0.02	0.75	0.988
SPTES-50 copolymer (100 μm)	0.13 ± 0.01	0.34	0.975
Cast Nafion-117 (175 μm)	0.36 ± 0.02	0.83	0.990

[a] Area specific resistance (Ω cm^2).
[b] Charge-transfer resistance (Ω cm^2).

electrochemical performances of 6F-SPTES-50 copolymer MEA compared with Nafion-117 MEA and SPTES-50 copolymer MEA. The 6F-SPTES-50 copolymer MEA exhibited a higher OCV (open circuit voltage, 0.988 V) compared with MEAs from SPTES-50 copolymer (0.975 V), and showed similar OCV with Nafion-117 membrane (0.990 V). Presumably, this can be attributed to micro-porous defects in the 6F-SPTES-50 copolymer membrane that often occur during the membrane fabrication process. Calculated area specific resistance (ASR) is higher ($0.35 \pm 0.02\,\Omega\,\mathrm{cm}^2$) for 6F-SPTES-50 copolymer membrane compared to an area specific resistance of $0.13 \pm 0.02\,\Omega\,\mathrm{cm}^2$ for the SPTES-50 copolymer MEA and $0.30 \pm 0.03\,\Omega\,\mathrm{cm}^2$ for the Nafion-117 MEA. Estimates of hydrogen fuel permeability based on measured open circuit voltage indicate that 6F-SPTES-50 copolymer MEA exhibits similar rates of fuel crossover with Nafion-117.

4. Conclusion

Sulfonated, fluorinated poly(arylenethioethersulfone) (6F-SPTES-50) copolymer was successfully synthesized by an aromatic nucleophilic polycondensation. The 6F-SPTES-50 copolymer can be fabricated into tough, flexible films from DMAc; the 6F-SPTES-50 copolymer demonstrated good thermal stability and dimensional stability; and the cast 6F-SPTES-50 copolymer films have proton conductivity up to 120 mS/cm at 85 °C, 85% relative humidity. The proton conductivity is 1.2 times higher than that of the state-of-the-art Nafion-117 proton exchange membrane under comparable conditions. These results indicated that the 6F-SPTES-50 copolymer is promising candidates for PEM materials in fuel cells.

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