



Sulfonated poly(fluorenyl ether ketone nitrile) electrolyte membrane with high proton conductivity and low water uptake

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ABSTRACT

High molecular weight sulfonated poly(fluorenyl ether ketone nitrile)s with different equivalent weight (EW) from 681 to 369 g mequiv.⁻¹ are synthesized by the nucleophilic substitution polycondensation of various amounts of sulfonated difluorobenzophenone (SDFBP) and 2,6-difluorobenzonitrile (DFBN) with bisphenol fluorene (BPF). The synthesized copolymers are characterized by ¹H NMR, FT-IR, TGA, and DSC techniques. The membranes cast from the corresponding copolymers exhibit superior thermal stability, good oxidative stability and high proton conductivity, but low water uptake due to the strong nitrile dipole interchain interactions that combine to limit swelling. Among all the membranes, the membrane with EW of 441 g mequiv.⁻¹ shows optimum properties of both high proton conductivity of 41.9 mS cm⁻¹ and low water uptake of 42.6%. Accordingly, that membrane is fabricated into a membrane electrode assembly (MEA) and evaluated in a single proton exchange membrane fuel cell (PEMFC). The experimental results indicate its similar cell performance as that of Nafion[®] 117 at 70 °C, but much better cell performance at higher temperatures. At the potential of 0.6 V, the current density of fuel cell using the prepared membrane and Nafion[®] 117 is 0.46 and 0.25 A cm⁻², respectively. The highest current density of the former reaches as high as 1.25 A cm⁻².

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1. Introduction

The proton exchange membrane (PEM) is a critical component in proton exchange membrane fuel cells (PEMFCs) that acts as a separator for the reactants, a catalyst support, and provides ionic pathways for proton transport. Therefore, they require both good proton conductivity and mechanical strength. Up to now, perfluorinated polymer membranes, such as Dupont's Nafion, are the major membranes used in PEMFC due to their outstanding properties [1]. However, these membranes still have a number of drawbacks especially for large-scale applications, such as high cost, high methanol permeability and poor performance at temperatures above 80 °C, that calls for the development of new membrane materials [2,3].

Many achievements in the application of sulfonated aromatic polymers as alternative proton exchange membrane have been reported in literature [4]. Unfortunately, this kind of membranes has two bottle-necked problems to be overcome. Firstly, lower EW value in comparison with Nafion is crucial to obtain a conductivity comparable to that of Nafion [5]. For example, sulfonated poly(ether ether ketone) required an EW of 408 g mequiv.⁻¹ to afford con-

ductivity of 51 mS cm⁻¹ [6], and an EW of 651 g mequiv.⁻¹ for conductivity of 0.4 mS cm⁻¹ [7]. Generally, Low EW usually results in high water uptake for proton exchange membranes, leading to the loss of mechanical properties and deterioration under the operation condition in fuel cell. Secondly, the combination of hydrolytic and oxidative degradation makes many of them fail to be used as PEM due to the introduction of strong acidic sulfonated groups into the main chains [8,9].

The challenge therefore lies in keeping good proton conductivity but decreasing water uptake for high mechanical properties, and increasing the chemical stability for long lifetime. On one hand, many sulfonated block copolymers with phase separation like Nafion have been prepared in more complicated two-step polycondensation and the proton conductivity of the membranes with high EW was greatly increased with low water uptake [10–12]. Various crosslinked PEMs have been also reported to improve the poor dimensional stability and mechanical property of membranes with low EW value [13]. Moreover, to improve the chemical stability, the introduction of sulfonic acid groups onto the pendant chains via different reaction has been disclosed in literatures [14,15].

More recently, it has been reported that the introduction of nitrile groups into sulfonated poly(aryl ether sulfone) and poly(aryl ether ketone)s can reduce their water uptake and dimensional swelling [16–19]. In addition, the introduction of strongly polar

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Table 1
Feed amounts of copolymers a–f.

Copolymer	x	BPF		SDFBP		DFBN	
		Weight (g)	Mole (mmol)	Weight (g)	Mole (mmol)	Weight (g)	Mole (mmol)
a	0.4	0.7008	2	0.3378	0.8	0.1669	1.2
b	0.5	0.7008	2	0.4223	1.0	0.1391	1.0
c	0.6	0.7008	2	0.5068	1.2	0.1113	0.8
d	0.7	0.7008	2	0.5912	1.4	0.0835	0.6
e	0.8	0.7008	2	0.6757	1.6	0.0557	0.4
f	0.9	0.7008	2	0.7601	1.8	0.0278	0.2

nitrile groups most probably promotes the adhesion of polymers to other components via interaction with other polar chemical groups. The enhanced adhesive ability between poly(aryl ether nitrile)s with the catalyst is beneficial to the hot-pressing process of membrane electrode assemblies (MEAs) and therefore to the decrease of electrochemical impedance of fuel cell [17,20].

In the previous literatures, it was also found that the incorporation of fluorenyl groups into the main chain can greatly enhance the oxidative stability of the polymer [21,22]. These results shed a light on solving the bottle-necked problems of the state-art membranes.

In this work, we prepared a series of sulfonated copolymers with very low EW simply by one-step polycondensation from bisphenol fluorine, 2,6-difluorobenzonitrile and sulfonated 4,4'-difluorobenzophenone, and also reported the superior PEM properties of sulfonated poly(fluorenyl ether ketone nitrile) membrane, which are structurally new polymers. Membrane **d** even showed much better cell performance in PEMFC than Nafion® 117.

2. Experimental details

2.1. Materials

Bisphenol fluorene (BPF) [23] and sulfonated 4,4'-difluorobenzophenone (SDFBP) [24] were prepared according to the literature. 2,6-difluorobenzonitrile (DFBN), fuming sulfuric acid (50%), concentrate sulfuric acid (95–98%), N,N'-dimethylacetamide (DMAc), toluene, methanol, anhydrous potassium carbonate and other reagents were purchased from commercial sources and used without further purification.

2.2. Copolymerization

A 25 mL three-necked round-bottomed flask, fitted with a Dean-stark trap, a condenser, a nitrogen inlet/outlet and a magnetic stirrer, was charged BPF (0.7008 g, 2 mmol), SDFBP (0.3378 g, 0.8 mmol), DFBN (0.1669 g, 1.2 mmol), anhydrous potassium carbonate (0.3455 g, 2.5 mmol), DMAc (6 mL) and toluene (10 mL). Nitrogen was purged through the reaction mixture with stirring, and then the mixture was refluxed for 3 h at 140 °C. After the produced water was azeotroped off with toluene, the mixture was heated at 170 °C for 8 h. Then the reaction mixture was cooled to room temperature and precipitated in 100 mL of mixture of methanol and water. The precipitate was filtered and washed with water for three times to remove inorganic salts. The fibrous polymer was collected and dried at 110 °C under vacuum for 24 h. A total of 1.1211 g of copolymer **a** was obtained in high yield of 93%.

Proton-form polymer was obtained by soaking sodium-form polymer in 100 mL of 2N H₂SO₄ solution for 24 h and washed with water for three times, then dried at 110 °C for 24 h, and denoted as copolymer **a**. ¹H NMR (400 MHz, DMSO, ppm): 8.17 (s, 0.8H), 7.93

(d, 2H), 7.60 (m, 0.8H), 7.48 (d, 2.6H), 7.42 (d, 2H), 7.34 (d, 2H), 7.21 (d, 2.4H), 7.15 (d, 1.6H), 7.10 (d, 2.4H), 6.97 (d, 1.6H), 6.86 (d, 0.8H), 6.58 (d, 1.2H).

Copolymers **b**, **c**, **d**, **e**, and **f** were synthesized by the similar procedure to copolymer **a** except for the changed mole ratio of SDFBP and DFBN as shown in Table 1.

Copolymer **b**: yield: 89% (1.1234 g). ¹H NMR (400 MHz, DMSO, ppm): 8.17 (s, 1H), 7.93 (d, 2H), 7.61 (m, 1H), 7.48 (d, 2.5H), 7.42 (m, 2H), 7.35 (m, 2H), 7.21 (d, 2H), 7.16 (d, 2H), 7.09 (d, 2H), 6.97 (d, 2H), 6.86 (d, 1H), 6.58 (m, 1H).

Copolymer **c**: yield: 97% (1.2793 g). ¹H NMR (400 MHz, DMSO, ppm): 8.17 (s, 1.2H), 7.93 (d, 2H), 7.61 (m, 1.2H), 7.48 (d, 2.4H), 7.42 (m, 2H), 7.35 (m, 2H), 7.21 (d, 1.6H), 7.16 (d, 2.4H), 7.09 (d, 1.6H), 6.97 (d, 2.4H), 6.86 (m, 1.2H), 6.58 (m, 0.8H).

Copolymer **d**: yield: 95% (1.3067 g). ¹H NMR (400 MHz, DMSO, ppm): 8.17 (s, 1.4H), 7.93 (d, 2H), 7.61 (d, 1.4H), 7.48 (d, 2.3H), 7.42 (m, 2H), 7.35 (m, 2H), 7.21 (m, 1.2H), 7.16 (d, 2.8H), 7.09 (m, 1.2H), 6.97 (m, 2.8H), 6.86 (d, 1.4H), 6.58 (d, 0.6H).

Copolymer **e**: yield: 90% (1.2890 g). ¹H NMR (400 MHz, DMSO, ppm): 8.18 (s, 1.6H), 7.93 (d, 2H), 7.62 (d, 1.6H), 7.49 (d, 2.2H), 7.42 (m, 2H), 7.35 (m, 2H), 7.22 (m, 0.8H), 7.16 (d, 3.2H), 7.10 (m, 0.8H), 6.98 (d, 3.2H), 6.87 (d, 1.6H), 6.58 (d, 0.4H).

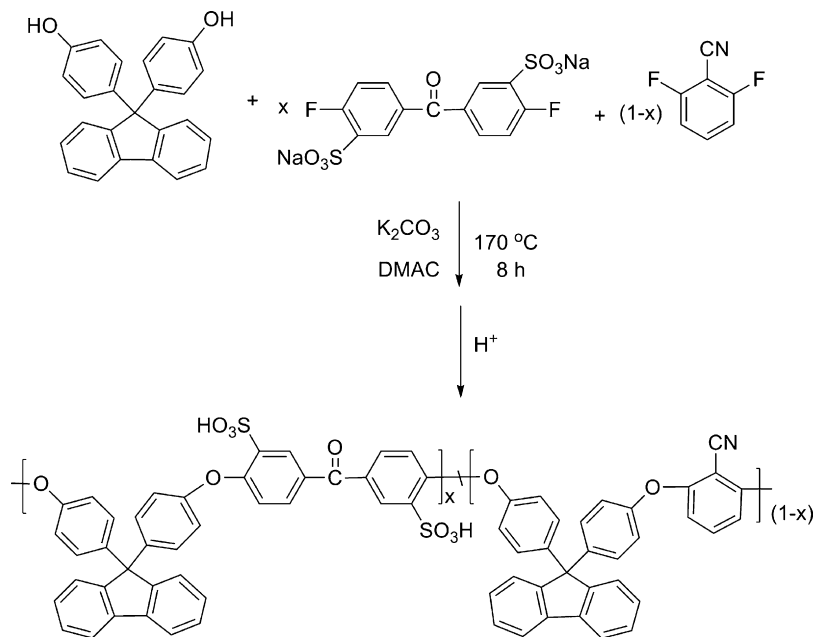
Copolymer **f**: yield: 91% (1.3547 g). ¹H NMR (400 MHz, DMSO, ppm): 8.18 (s, 1.8H), 7.93 (d, 2H), 7.62 (d, 1.8H), 7.49 (d, 2.1H), 7.42 (m, 2H), 7.34 (m, 2H), 7.22 (d, 0.4H), 7.17 (d, 3.6H), 7.12 (d, 0.4H), 6.96 (d, 3.6H), 6.86 (d, 1.8H), 6.58 (d, 0.2H).

2.3. Preparation of polymer membrane

The membranes **a–f** were prepared by casting from the corresponding 5% copolymers **a–f** solution in DMAc on a glass plate in the dust-free environment, then dried at 60 °C for 12 h and 110 °C under vacuum for 48 h. The thicknesses of all dry casted membranes are between 150 and 170 μm.

2.4. MEA preparation

MEAs were prepared from standard catalyst inks using a known procedure [25]. Carbon supported platinum catalyst (0.5 mg cm⁻² Pt) was used for the PEMFC anode and cathode (Johnson Matthey-Platinum 40% on Vulcan XC-72R carbon). TGP-H-120 carbon paper (Toray) with the thickness of 330 μm was used for gas diffusion media (GDM). In the catalyst layer, the same ionomer as the membrane host was used as binder to provide a more intimate contact between the polymer electrolyte membrane and platinum particles. The weight ratio of supported Pt catalyst to pure ionomer was maintained at 3:1. The GDL with catalyst layer was prepared by hot-pressed on double sides of prepared membranes for 60 s at 120 °C under a pressure of 60 atm to yield a membrane electrode assembly (MEA). At the hot-bonding temperature of 120 °C, the membrane with little water (the membrane was soaked in water before hot-pressing) became soft and can be bonded with the catalyst layer very tightly.



Scheme 1. Synthesis of copolymers **a–f**. (**a**) $x=0.4$; (**b**) $x=0.5$; (**c**) $x=0.6$; (**d**) $x=0.7$; (**e**) $x=0.8$; (**f**) $x=0.9$.

2.5. Measurement

The ^1H NMR spectra was recorded on a Bruker NMR instrument (Model: DRX 400 MHz) using dimethyl- d_6 sulfoxide ($\text{DMSO}-d_6$) as a solvent. For spectroscopy results, chemical shifts are given in ppm against tetramethylsilane as an internal standard.

The thermal stability of the polymers from 130 to 600 °C was determined by a PerkinElmer 6300 thermogravimetric analyzer [thermogravimetric analysis (TGA)/differential thermal analysis (DTA)] under a protective nitrogen atmosphere (200 mL min^{-1}) at the heating rate of $20\text{ }^\circ\text{C min}^{-1}$. The glass-transition temperature (T_g) was determined by using a Netzsch DSC 200PC instrument at the heating rate of $20\text{ }^\circ\text{C min}^{-1}$ under nitrogen protection. The second scan was immediately initiated after the sample was cooled to room temperature.

Inherent viscosity of polymer was determined in the 0.5 g dL^{-1} DMAc solution at $25\text{ }^\circ\text{C}$ with a calibrated Ubbelohde viscometer.

Oxidative stabilities were determined using Fenton's reagent (3% H_2O_2 containing 2 ppm FeSO_4) at $80\text{ }^\circ\text{C}$. The membranes were immersed in Erlenmeyer flask containing Fenton's reagent. The flask was shaken vigorously once every 10 min. The time of membrane breaking into pieces and the time of membrane disappearing were recorded to indicate the oxidative stability.

The water uptake of the membrane was evaluated by measuring the weight change between dried and humidified state at different temperatures. The membranes were first vacuum dried at $80\text{ }^\circ\text{C}$ for 24 h and then weighed. They were equilibrated in water at the tested temperature for 12 h, respectively, and quickly dry-wiped, weighed. The water absorption ($W\%$) was obtained via the following equation:

$$W(\%) = \frac{(W_1 - W_0) \times 100}{W_0}$$

where W_0 and W_1 are the mass of membranes before and after water absorption, respectively.

Proton conductivity measurement was performed on film samples by a Solartron 1255B frequency response analyzer functioning with an oscillating voltage of 10 mV using two probes with the frequency between 1 MHz and 5 KHz. The film samples were cut into a circle with the diameter of 1 cm and soaked in deionized

water for 24 h prior to each test. Each sample was clamped between the two gold electrodes and placed above liquid water in the temperature-controlled vessel, which was afforded by saturated water vapor environment. After the membrane equilibrated with saturated water vapor at the noted temperature, the proton conductivity (σ) of the specimen in the transverse direction (across the membrane) was calculated from the impedance data according to the following equation:

$$\sigma = \frac{l}{RS}$$

where l and S are the thickness and the face area of the specimen, respectively, and R is derived from the low intersect of the high frequency semicircle on a complex impedance plane with the $\text{Re}(Z')$ axis.

The active area of MEA used in the fuel cell tests was 4 cm^2 . A single PEMFC was operated at different temperature referred in the paper, 100% relative humidity and the back gas pressure of 0 MPa with pure hydrogen and oxygen as reactant gases. In order to provide the adequate oxidant to the fuel, the flow rates of the gases were fixed at 1.5 times the stoichiometry of hydrogen and twice the stoichiometric value of oxygen. The polarization curves were measured by applying a constant current for 3 min at each point using a fuel cell test station (Arbin Instruments, 160269).

3. Results and discussion

3.1. Synthesis and characterization of polymers

As shown in Scheme 1, copolymers **a–f** can be synthesized by the nucleophilic substitution polycondensation. The sulfonated copolymers **a–f** with different sulfonation degree can be easily controlled by varying the molar ratio of SDFBP and DFBN, meanwhile the provided amount of BPF is fixed. The polycondensation reaction was synthesized in DMAc solvent, toluene served as the azeotropic removal of water and potassium carbonate played as a weak base to form the required phenolate. The ^1H NMR spectra of the copolymer **a** was shown in Fig. 1, all the peaks in the spectra could be assigned to the synthesized molecule structure, so did the spectrum of the

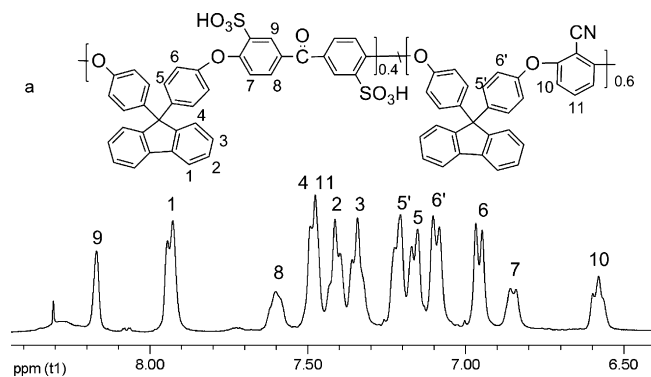


Fig. 1. ^1H NMR spectra of copolymer a.

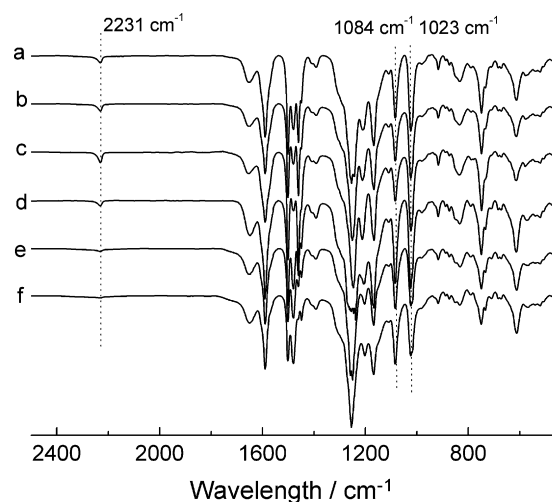


Fig. 3. FT-IR spectra of copolymers a–f.

other polymers in Fig. 2. The integration ratios of these peaks are well in accordance with the proposed molar ratios of each component of these copolymers. Fig. 3 is the FT-IR spectra of the sulfonated copolymers a–f. The symmetric and asymmetric stretching vibrations of sulfonate groups were observed at 1023 and 1084 cm^{-1} . The symmetric stretching band of nitrile groups was observed at 2231 cm^{-1} , whereas this band for copolymer e and f almost disappeared due to the very low content of nitrile groups. As shown in Table 2, the inherent viscosities (η_{inh}) of the sulfonated copoly-

mers a–f in DMAc at 25 °C ranged from 1.5 to 4.06 dL g^{-1} , indicating its very high molecular weights. Moreover these polymers showed good solubility in polar aprotic solvents, such as DMSO, DMAc and NMP, but were insoluble or only swollen in common solvent, such as H_2O , CH_3OH and toluene.

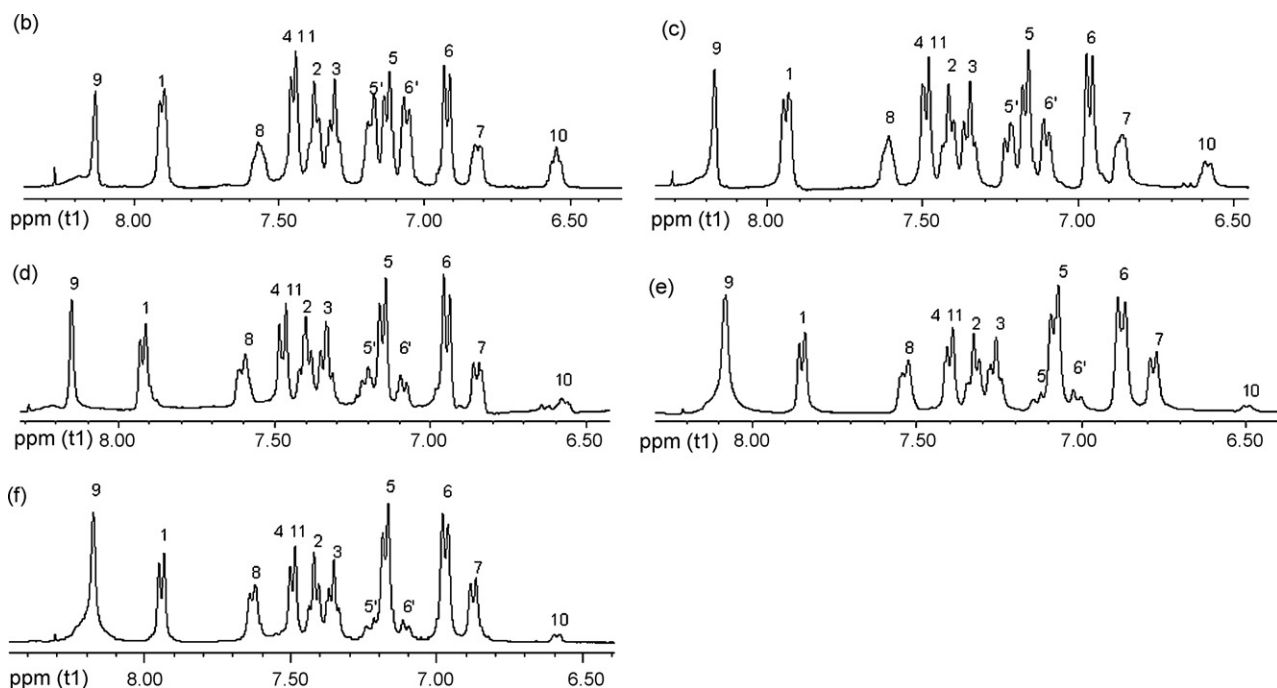


Fig. 2. ^1H NMR spectrum of copolymers b–f.

Table 2
Polymerization results and characterization of copolymers a–f.

Copolymer	EW ^a	Yield (%)	$\eta_{\text{inh}}^{\text{b}}$ (dL g^{-1})	Calculated degree of sulfonation ^c
a	681	93	2.66	0.80
b	569	89	2.84	1.00
c	494	97	3.06	1.20
d	441	95	1.69	1.40
e	401	90	1.50	1.60
f	369	91	4.06	1.80

^a Equivalent weight per sulfonic acid group.

^b Tested in 0.5 g dL^{-1} solution in DMAc at 25 °C.

^c Number of sulfonic acid groups per repeating unit.

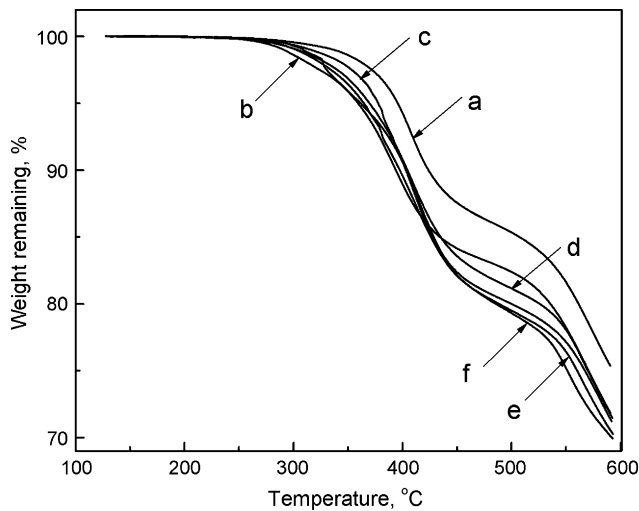


Fig. 4. TGA curves of copolymers a–f.

3.2. Thermal stability

Thermal stabilities of copolymers a–f were determined by TGA and DSC, respectively, and the TGA curves are shown in Fig. 4. A two-stepped degradation profile was observed from TGA curves. The first weight loss at about 300 °C was attributed to the elimination of sulfonic acid groups and the small amount of absorbed water, while the second weight loss peak at about 450 °C was due to the degradation of the main chain of sulfonated copolymers. The high degradation temperature implied the superior thermal stability of synthesized copolymers. Meanwhile, the DSC measurements indicated that no glass transition temperature (T_g) was present in the temperature range from 30 to 300 °C.

3.3. Oxidative stability

The current developed membranes failing miserably in Fenton tests perhaps outperformed Nafion in actual fuel cell conditions [26], however they have much shorter life time due to the oxidative degradation. The accelerating oxidation measurement was taken by soaking the membranes a–f in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 °C. As shown in Table 3, the oxidative stability decreases with increase of the sulfonation degree. In our present experiment, it took 175 min before membrane c started to break into small pieces and 198 min before it dissolved in the solution. Comparing to other researchers' report that a similar polymer synthesized using 4,4'-(hexafluoroisopropylidene) diphenol (6F-BPA) to substituting bisphenol fluorine was dissolved in Fenton's reagent after only 90 min [27], therefore, our results demonstrated that the incorporation of fluorenyl groups can enhance the oxidative stability of the polymer, which was also suggested in previous paper [25].

Table 3
Oxidative stability of membranes a–f.

	Membrane					
	a	b	c	d	e	f
t_1 (h:min)	10:38	4:39	3:33	2:16	0:40	0:9
t_2 (h:min)	–	–	5:25	2:48	0:55	0:12

t_1 time of membrane breaking into pieces; t_2 time of membrane disappearing; (–) undisappeared after 30 h.

Table 4

Water uptakes of membranes a–f at different temperatures.

Membrane	Water uptake, % (soaked in water for 12 h)			
	35 °C	55 °C	75 °C	95 °C
a	14.8	18.3	20.3	20.5
b	23.3	23.8	26.3	28.4
c	32.2	33.0	34.8	39.5
d	42.6	45.8	51.2	57.4
e	66.7	80.6	91.6	134.8
f	444.4	497.2	536.4	688.8

3.4. Water uptake and proton conductivity

Both high proton conductivity and superior mechanical strength are essential properties to the proton exchange membrane, which are closely related to EW of the polymer. Generally, the low EW of the polymer results in high water uptake and proton conductivity, but sacrifice of the mechanical strength [21]. Sulfonated poly(ether ketone)s have a morphology with narrower channels, but with highly branched channels and many dead-end channels. Generally, they require a much lower EW in comparison with Nafion1 to compensate for this and to obtain conductivities comparable to that of Nafion [5], whereas, low EW usually results in high water uptake for membranes, which further leads to the loss of mechanical properties and deterioration under the operation condition in fuel cell.

As can be seen from Tables 2 and 4, the EW of membranes a–f decreased from 681 to 369 g mequiv.⁻¹ with the increasing sulfonation degree from 0.8 to 1.8. Although with such low EW, the water uptake at 35 °C are limited from 14.8% to 66.7% for membranes a–e and 444.4% for copolymer f. Membranes a–e have much lower water uptake when compared with the polymers that did not contain nitrile at similar EW [16–19]. A plausible factor for this is the presence of strong nitrile dipole interchain interactions that combine to limit swelling water [28]. Nitrile is one of the most polar functional groups, having a high dipole moment of ~3.9 Debyes. According to Kim's model [19], strong interchain polar nitrile–nitrile interactions can lead to an ideal combination of high proton conductivity and low water swelling. As can be seen from Fig. 5, the proton conductivity of membranes a–f at 35 °C increased from 0.0161 to 0.143 S cm⁻¹, which are even much higher than that of Nafion. Meanwhile, both the water uptake and the proton conductivity of the polymer increase with the increasing temperature, especially for membrane f. The proton conductivity of membrane f with EW of 369 g mequiv.⁻¹ shows obviously high

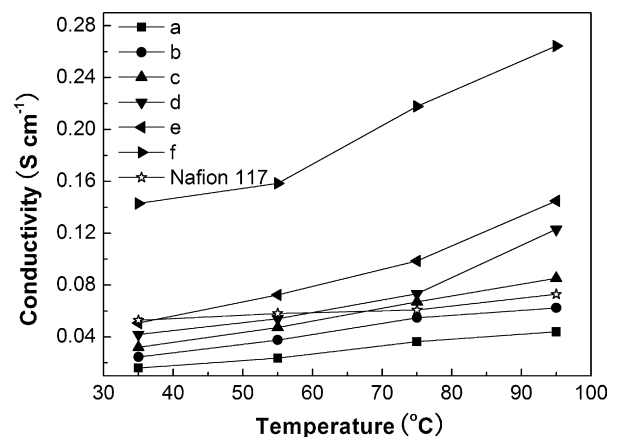


Fig. 5. Proton conductivities of membranes a–f and Nafion® 117 as a function of temperatures.

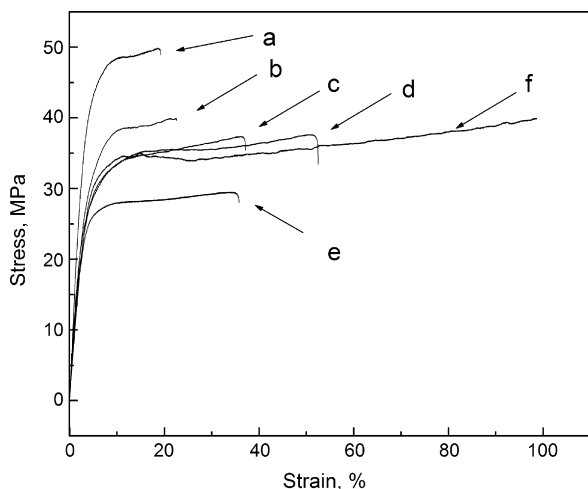


Fig. 6. Stress vs. strain curves for dry membranes a–f.

value, it reaches 0.2644 S cm^{-1} at 95°C . Although with such a high proton conductivity, membrane **f** is unsuitable to the application as the proton exchange membrane in PEMFC because its excessively high water uptake (688.8% at 95°C) can result in the deterioration of mechanical strength. Considering the balance of the mechanical strength with the proton conductivity, membranes **a–d** with EW of $681\text{--}441 \text{ g mequiv}^{-1}$ were regarded as promising candidate for proton exchange membrane in fuel cells, among which, membrane **d** with EW of $441 \text{ g mequiv}^{-1}$ has an ideal balance between high proton conductivity and reasonable water uptake in the range of the investigated temperature, such as proton conductivity of 41.9 mS cm^{-1} and water uptake of 42.6% at 35°C . It should show the best cell performance.

3.5. Mechanical strength of membranes a–f

The tensile properties of membranes **a–f** were measured at 23°C and 60% RH and are depicted in Fig. 6. All the membranes show high tensile strength of over 25 MPa. These data indicate these membranes are strong and tough enough to be applied as proton exchange membrane in the fuel cell.

3.6. Single cell performance of the MEA made from membrane d and Nafion® 117

Fig. 7 shows the polarization curves in H_2/O_2 single fuel cell using Nafion® 117 as PEM at the cell temperature of 75, 85, 95°C and 100% relative humidity, 0 MPa gas back pressure. At these referred temperatures, the cell using Nafion® 117 probably exhibits the best performance. As shown in Fig. 7, they have the same highest current density of 0.87 A cm^{-2} at the potential of 0.1 V. However, the cell gave the best power density at 75°C . Therefore, the performance of fuel cell using Nafion® 117 at 75°C is chosen to compare with that of fuel cell using membrane **d** in the following paragraphs.

As is shown in Fig. 8, membrane **d** has similar cell performance than Nafion® 117 at the cell temperature of 70°C . Above the polarization potential of 0.58 V, the current density of membrane **d** is slightly lower than that of Nafion® 117, whereas which is slightly higher than that of Nafion® 117 during 0.17–0.58 V. It was very encouraging that membrane **d** exhibited much better cell performance than that of Nafion® 117 in the whole range of current density at 80 and 90°C . At 0.6 V, the current density of cell using membrane **d** and Nafion® 117 was 0.46 and 0.25 A cm^{-2} , respectively. The highest current density of the former reaches as high as 1.25 A cm^{-2} . Membrane **d** had an open circuit voltage (OCV) of

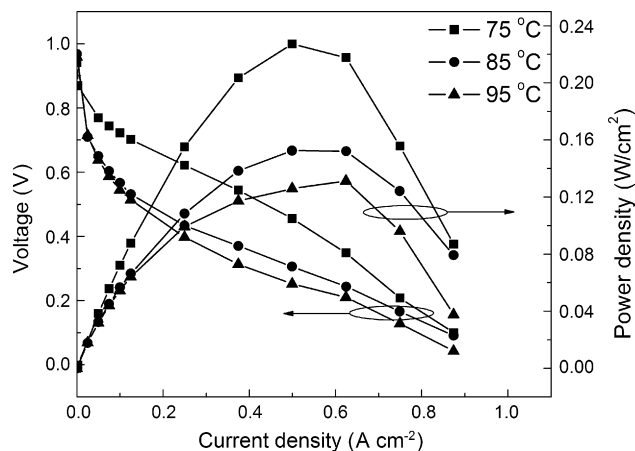


Fig. 7. Polarization curves and power density of PEMFC using Nafion® 117 as PEM operation conditions: 100% relative humidity, 0 MPa gas back pressure and cell temperature as referred in the figure.

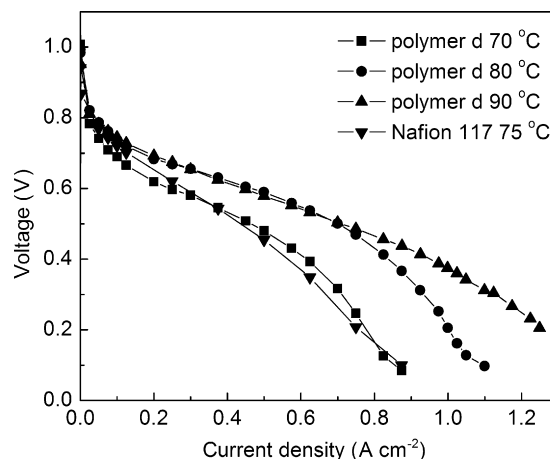


Fig. 8. Polarization curves of PEMFC using membrane **d** as PEM. Operation conditions: 100% relative humidity, 0 MPa gas back pressure and cell temperature as referred in the figure.

0.95 V , whereas that of Nafion 117 is 0.94 V . Since the OCV is a good measurement of H_2 or O_2 crossover through the PEMs to the cathode or anode, respectively [29], compared with Nafion® 117, Membrane **d** had stronger ability to suppress the gas crossover.

The performance of the fuel cell using membrane **d** greatly improved with the increasing temperature from 70 to 90°C . That is to say, the optimal cell operation temperature of membrane **d** is 90°C during the investigated temperature, which is 15°C higher than that of Nafion. This excellent cell performance encouraged us in developing new materials with low EW as proton exchange membrane applied in PEMFC which has an ideal balance between high proton conductivity and low water uptake.

We have carried out the life time assessment for membrane **d**. The single fuel cell could successfully operate at a constant voltage of 0.6 V for 20 h. During the life test, the power density was pretty stable and it did not decay even after 20 h. This is a clear evidence of no noticeable degradation of membrane **d** for such a long time operation. Detailed analyses are under investigation and will be reported elsewhere.

4. Conclusions

Copolymers **a–f** with the different low EW were simply synthesized from the nucleophilic substitution polycondensation of

SDFBP and DFBN with BPF. The EW of polymers could be easily controlled by varying the molar ratio of SDFBP to DFBN, meanwhile the provided amount of BPF is fixed. They have good thermal and chemical stability, also very high proton conductivity and low water uptake. Considering the balance of the mechanical strength with the proton conductivity, membranes **a–d** from the corresponding copolymers **a–f** with EW of 681–441 g mequiv.⁻¹ were regarded as promising candidate for proton exchange membrane in fuel cells, among which, membrane **d** with EW of 441 g mequiv.⁻¹ has an ideal balance between high proton conductivity and reasonable water uptake in the range of the investigated temperature. Therefore, membrane **d** was fabricated into a membrane electrode assembly (MEA) and evaluated in a single proton exchange membrane fuel cell (PEMFC), which showed similar cell performance as that of Nafion® 117 at 70 °C, but much better cell performance at 80 and 90 °C.

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