Properties and fuel cell performance of proton exchange membranes prepared from disulfonated poly(sulfide sulfone)

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ARTICLE INFO

ABSTRACT

A series of disulfonated poly(sulfide sulfone)s (SPSSF)s copolymers are synthesized via direct aromatic nucleophilic substitution polycondensation of 4,4′-dichlorodiphenylsulfone (DCDPS), 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (SDCDPS) and 4,4′-thiobisbenzenethiol at various molar ratios. Tough and flexible membranes with 30 mol% (SPSSF30) to 50 mol% (SPSSF50) SDCDPS monomers are obtained by casting from DMAc solution. Their physicochemical properties including thermal properties, mechanical properties, water uptake, swelling ratio and oxidative stability are fully investigated. And the fuel cell performance of SPSSF membranes at different temperature and relative humidity is evaluated comprehensively for the first time. It is found that the SPSSF40 membrane exhibited low dimensional change in the temperature range of 20–100 °C, good mechanical properties, high oxidative stability and comparable fuel cell performance to Nafion 212 membrane. Besides, the H_2 crossover density of the SPSSF40 membrane is only 50% of that of Nafion 212 membrane. Consequently, SPSSF40 membranes prove to be promising candidates as new polymeric electrolyte materials for proton exchange membrane (PEM) fuel cells operated at medium temperatures.

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1. Introduction

Proton exchange membrane fuel cells (PEMFC) are currently being explored widely for a wide range of applications in stationary, automotive, and portable power [1,2]. Proton exchange membrane (PEM), a key component of PEMFC, serves as a solid electrolyte separating the anode (hydrogen or methanol) from the cathode (oxygen/air) compartments. To date perfluorinated sulfonic acid ionomers, such as DuPont's Nafion, have been the most studied as PEM for PEMFC. The perfluorinated ionomer membranes are highly proton conductive and chemically and physically stable. However, several demerits of the perfluorinated ionomer membranes including high cost, limited operation temperature (<90 °C) and high fuel permeability strongly constrain their wide applications.

In the past decade, extensive efforts have been devoted to develop high performance and inexpensive PEM. Sulfonated aromatic polymers have been investigated widely as alternative non-fluorinated PEM materials [3,4]. Among the sulfonated aromatic polymers, sulfonated poly(arylene ethers), such as sulfonated poly(ether ketone) [5–8] and poly(ether sulfone) [9–12], possess excellent film forming behavior, favorable thermal stability and high proton conductivity, which make them promising as alternative material for PEMFC applications. In view of the similarities and differences of oxygen and sulfur, sulfonated poly(thioethers) have been synthesized to investigate thioether polymeric structures in recent several years. The thioether groups can be oxidized to sulfoxide groups by reacting with hydroxyl radicals that are brought about during the PEMFC operation. The transformation is thought to be an advantage to enhance the membrane oxidative stability and improve the membrane lifetime.

A few relevant studies have been reported [13–17]. McGrath and co-workers [13] have synthesized the sulfonated poly(sulfide sulfone)s (SPSSF) copolymers containing 20–50 mol% disulfonated monomers firstly by directly copolymerizing non-sulfonated chloro- or fluoro-activated dihalide monomers, the corresponding disulfonated dihalide monomers and 4,4′-thiobisbenzenethiol (TBBT). Compared with fluoro-activated dihalide monomers, they found chloro-activated dihalide monomers produced SPSSF copolymers with lower molecular weight due to its lower reactivity. The 40 mol% disulfonated copolymer membranes synthesized from the chloro-activated dihalide monomers have comparable proton conductivity to Nafion but its water uptake is beyond 200% at room temperature. Lee and Kerres [14] recently synthesized a series of arylene main-chain thioether copolymers using

fluoro-activated dihalide monomers in their own methods. The as-cast membranes with 40 or 50 mol% disulfonated monomers exhibit excellent oxidative stability. The water uptake and swelling ratio of the membranes is still somewhat high and the membranes split into pieces when heating at 90 °C. Bai et al. [15,16] have prepared the copolymers with high sulfonic acid content (50–80 mol% disulfonated monomers). The membranes exhibit proton conductivity greater than 0.1 S cm^{-1}. However, the excessive swelling ratio makes it difficult for their usage in PEMFC, especially at elevated temperatures. Moreover, the fuel cell performance of SPSSF membranes has not been reported in detail until now.

In our study, copolymerization of 30–80 mol% SDCDPS monomers with relatively cheap chloro-activated dihalide monomers and TBBT resulted in a series of SPSSF copolymers using a modified procedure recently reported by Fang and co-workers [18]. This paper focused on the copolymers with 30 mol% (SPSSF30) to 50 mol% (SPSSF50) disulfonated monomers. The as-cast membranes have acceptable physicochemical properties under the operating environment in PEMFC. The structure of copolymers was characterized. The SPSSF membranes were prepared by casting from DMAc solution. The objective of this work is to systematically investigate the properties of SPSSF membranes, especially its fuel cell performance. Their physicochemical properties including water uptake, swelling ratio, thermal stability, mechanical properties and oxidative stability were fully evaluated. Moreover, the single cell performance of SPSSF membranes at different temperatures and relative humidity was investigated comprehensively for the first time. Generally, the SPSSF membranes exhibited improved properties in comparison with the previous reports.

2. Experimental

2.1. Materials

4,4′-Thiobisbenzenethiol (TBBT) was purchased from TCI. 4,4′-Dichlorodiphenyl sulfone (DCDPS) was purchased from Acros and recrystallized before use. N,N-Dimethylacetamide (DMAc), anhydrous potassium carbonate, fuming sulfuric acid (50%), sulfuric acid and toluene were obtained commercially. Toluene was dried over 4 Å molecular sieve prior to use. DMAc was distilled under reduced pressure and dried with 4 Å molecular sieve before use. Anhydrous potassium carbonate was dried at 150 °C in vacuo for 10 h prior to use. Other chemicals were used as received. The synthesis of monomer 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (SDCDPS) according to a procedure described in literature [19].

2.2. Synthesis of disulfonated poly(sulfide sulfone) (SPSSF) copolymers

As shown in Scheme 1, all polymers are synthesized by polycondensation via typical high-temperature nucleophilic aromatic substitution reaction [18]. SPSSF with 40 mol% disulfonation (SPSSF40) was given as a representative example: DCDPS (1.3782 g, 4.8 mmol), SDCDPS (1.5720 g, 3.2 mmol), TBBT (2.0032 g, 8 mmol), anhydrous K$_2$CO$_3$ (1.22 g, 8.8 mmol) and DMAc (16 mL) were added into a 100 mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet and a Dean-Stark trap. Toluene (15 mL) was added dropwise through a dropping funnel and the system was heated at 140 °C for about 4 h to remove the water from the reaction system by the azeotropic distillation of toluene. The reaction temperature was then slowly increased to 160 °C for about 20 h. The resulting viscous polymer solution was then poured into 2-propanol. The resulting precipitate was thoroughly washed with 2-propanol and deionized
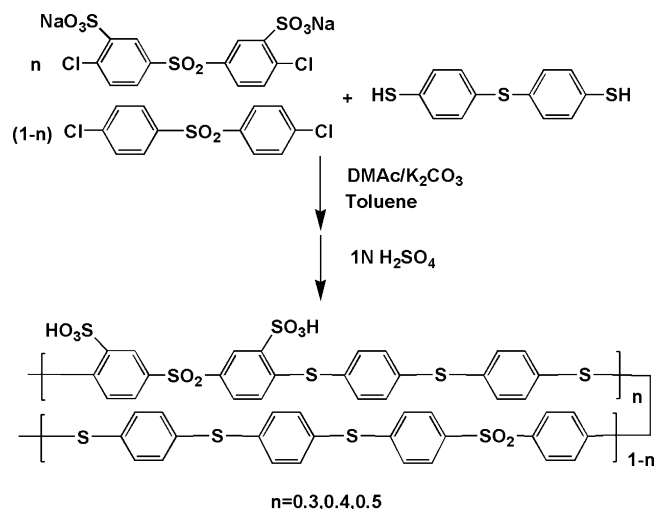
Scheme 1. Synthesis of sulfonated poly(sulfide sulfone) (SPSSF).

water to remove the salts and solvents, and dried at 120 °C for 48 h in vacuo.

2.3. Membrane preparation and proton exchange

The SPSSF membranes were prepared by casting their 6 wt% DMAc solutions onto the clean glass substrates and dried at 60 °C for 24 h. The as-cast membranes were soaked in water and peeled off from the substrates. Then, the proton exchange treatment was performed by immersing them in a 1 mol L^{-1} H$_2$SO$_4$ solution at room temperature for 48 h. The membranes were thoroughly washed with deionized water until the rinsed water became neutral. The SPSSF membranes in acid form were obtained with thickness of ~50 μm.

2.4. Measurements

2.4.1. FTIR and ^{1}H NMR

Infrared spectra were obtained as KBr pellets or membrane samples on a JASCO FT/IR-4100 spectrometer. ^{1}H NMR spectra were collected on an OXFORD 600 MHz instrument. d_6-Dimethylsulfoxide (d_6-DMSO) was used as NMR solvent and tetramethylsilane (TMS) was used as the internal standard chemical shift reference.

2.4.2. Viscosity and Ion exchange capacity (IEC)

Intrinsic viscosities (η_{inh}) were measured using an Ubbelohde viscometer in NMP solutions of polymers at 25 °C.

The ion exchange capacity (IEC) of SPSSF and Nafion 212 membranes was determined by titration. The membrane samples were soaked in saturated NaCl solution at least 48 h, and then the solution was titrated with 0.01 M NaOH solutions with phenolphthalein as indicator. The IEC was calculated as the ratio of the number of moles consumed NaOH to the weight of dried membrane sample.

2.4.3. Water uptake and swelling ratio

Water uptake and swelling ratio of SPSSF membranes were determined by measuring the weights and lengths variation before and after the hydration. The SPSSF membranes were dried under vacuum at 100 °C overnight and the weights and lengths were measured. Then the membranes were immersed in deionized water at predetermined temperature for 24 h. Before the weights and lengths of wet membranes were measured, the surface water

Table 1
IEC and inherent viscosities of SPSSF copolymers

Polymer	Feed ratio[a] (mol%)	IEC (mequiv g^{-1}) calculated	IEC (mequiv g^{-1}) experimental	η_{inh}[b] (dL g^{-1})
SPSSF30	30/70/100	1.17	1.16	0.91
SPSSF40	40/60/100	1.51	1.33	1.15
SPSSF50	50/50/100	1.83	1.63	1.23
Nafion 212	–	0.91	0.92	–

[a] Feed ratio of the monomer: DCDPS/SDCDPS/TBBT.
[b] 0.5 g dL^{-1} in NMP at 25 °C.

attached onto the membrane was removed and blotted with tissue paper.

The water uptake was calculated as

$$\text{water uptake (wt\%)} = \frac{w_{wet} - w_{dry}}{w_{dry}} \times 100\% \qquad (1)$$

where w_{dry} and w_{wet} are the weights of dried and wet membranes, respectively.

The swelling ratio was calculated as

$$\text{swelling ratio (wt\%)} = \frac{l_{wet} - l_{dry}}{l_{dry}} \times 100\% \qquad (2)$$

where l_{dry} and l_{wet} are the lengths of dried and wet membranes, respectively.

2.4.4. Tensile test, TGA and oxidative stability

Tensile test was performed with a tension tester AG-2000A (Shimadzu, AUTO graph) at a crosshead speed of 50 mm min^{-1} at room temperature. Stress versus strain curves were obtained for samples based on Chinese Standard QB-13022-91.

The thermal stability of SPSSF membranes in the salt form and in the acid form was performed using a TGA/DTA (Pyris Diamond TGA/DTA) system. Polymer membrane samples for TGA analysis were preheated at 150 °C for 30 min under nitrogen atmosphere to remove moisture. Samples were then heated from 100 to 800 °C at 10 °C min^{-1} under nitrogen atmosphere.

Oxidative stability was examined by immersing the membrane samples in Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 80 °C. Their weight loss in hot Fenton's reagent for 1 h and the time that the membrane started to dissolve were recorded.

2.5. Preparation of membrane electrode assembly and cell test

2.5.1. Membrane electrode assemblies (MEAs)

Gas diffusion electrodes with three-layer structure were prepared. Wet-proofing treatment of a carbon paper (SGL Carbon Group) was employed as backing layer. The gas diffusion layer (GDL) was fabricated by coating the slurry consisting of carbon black (Vulcan XC-72R, Cabot Co.) and PTFE dispersions on carbon paper. Catalyst layer was prepared by brushing the slurry consisting of Pt/C catalyst (46.6 wt% Pt/CB; TKK Corp.), PTFE suspension and 2-propanol dispersions onto the surface of the GDL homogeneously. The loading amount of Pt was 0.3 mg cm^{-2} for the anode and 0.7 mg cm^{-2} for the cathode, respectively. Then 5% Nafion solution (Du Pont) was sprayed onto the surface of catalyst layer of electrode before assembling with the electrolyte membrane. The loading amount of Nafion was 0.4 mg cm^{-2} for both the cathode and anode.

Membrane electrode assembly (MEA) was fabricated by a hot pressing process. A membrane with two gas diffusion electrodes (5 cm^2 of geometric area) was sandwiched and hot-pressed at 160 °C, 10 MPa for 2 min to form a MEA.

2.5.2. Fuel cell operation

The MEA was mounted in a single cell with stainless steel end plates and stainless steel mesh flow field as current collectors. The gases were passed through humidifiers before they were allowed to enter the fuel cell inlets. Humidified H_2 was fed to the anode at 300 mL min^{-1} and humidified O_2 was fed to the cathode at 300 mL min^{-1} with different humidification temperature to control the relative humidity (RH). Current voltage (I–V) curves were measured under steady-state conditions.

2.5.3. LSV

Linear sweep voltammetry (LSV) was performed to measure hydrogen crossover rate through the membranes [20]. H_2 was supplied to the MEA reference electrode (anode) with a flow of 300 mL min^{-1} and N_2 was fed to the opposite electrode (cathode) with a flow of 300 mL min^{-1}. The cell voltage was scanned potentiodynamically at 4 mV s^{-1} in the potential range of 0–550 mV under 0.2 MPa and 80 °C with 100% RH. An electrochemical working station (model Chi 600b) was used to control the potential.

3. Results and discussion

3.1. Synthesis and structure of polymers

SPSSFs with controlled sulfonated degrees were synthesized via the direct copolymerization of SDCDPS, DCDPS and TBBT in DMAc in the presence of K_2CO_3 at 160 °C for 20 h after removing the water from the reaction system by the azeotropic distillation of toluene, as shown in Scheme 1. The molecular feed ratio of monomers and the polymerization results were listed in Table 1. The inherent viscosities of the resulting polymers were in the range of 0.91–1.23 dL g^{-1} in NMP at 25 °C. The IECs of sulfonated polymers determined by titration agreed reasonably with their theoretical values.
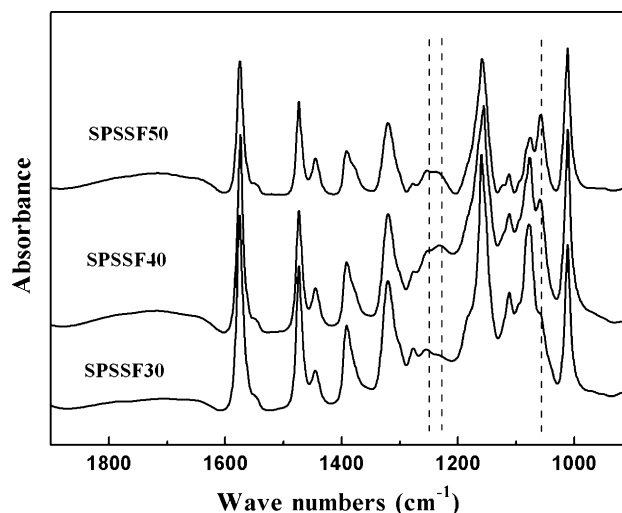

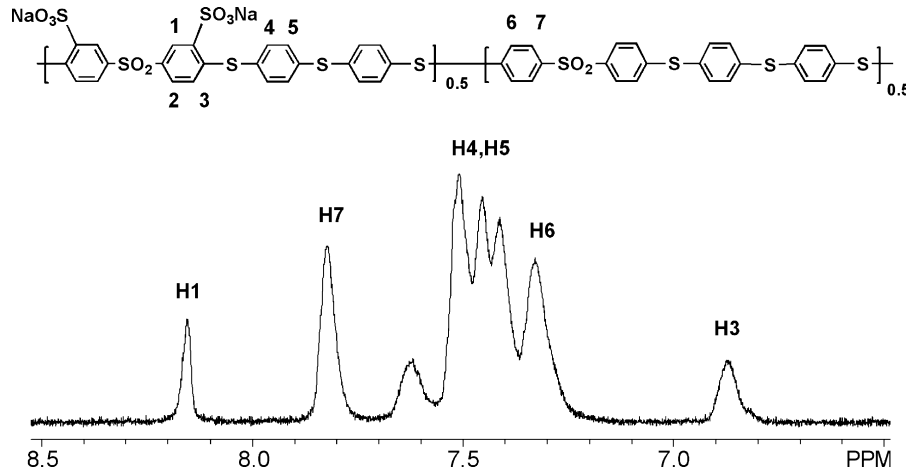**Fig. 1.** FTIR spectra of SPSSF30, SPSSF40 and SPSSF50 in their sodium forms.

Fig. 2. ^{1}H NMR spectra of SPSSF50 in sodium form in DMSO-d_6.

The structures of SPSSF copolymers were elucidated by FTIR and ^{1}H NMR. As shown in Fig. 1, the characteristic peaks at 1060, 1215 and 1250 cm^{-1} on the FTIR spectra, assigned to symmetric stretching and asymmetric of –SO$_3$ groups, respectively, were observed for all SPSSF copolymers. The intensity of these characteristic peaks ascended with an increase of the molar proportion of the disulfonated monomers. Fig. 2 displays the hydrogen signal assignment in the ^{1}H NMR spectra of SPSSF50 in the salt form, which showed the same characteristics as previous work [13]. These results indicated that the successful copolymerization was achieved.

3.2. Water uptake and swelling ratio

Water is the main vehicle by which protons are transported through the membrane, thus water uptake of PEM is closely related to the fuel cell performance. However, due to the humid environment and elevated temperature at which PEMFC were usually operated, excessive water uptake, leading to high-dimensional swelling ratio, is unacceptable. Therefore, appropriate water uptake and good dimensional stability are essential demands for PEM. The water uptake and dimensional swelling ratio of SPSSF membranes were measured at different temperatures and the results were displayed in Fig. 3. The swelling ratios of all the SPSSF membranes were below 9.1% and the water uptakes were less than 48% after immersion in water at room temperature (20 °C) for 24 h. Fig. 3 obviously shows that water uptake and swelling ratio ascended with the IEC and temperature increasing. Compared with the SPSSF40 and SPSSF30, SPSSF50 exhibited higher water uptake especially at higher temperatures. It have been reported that sulfonic-containing polymers have hydrophobic/hydrophilic nanophase separation, whereby the sulfonic acid groups form hydrophilic hydrated domains contributing to the water uptake and proton conductivity, and the polymer backbone forms hydrophobic domain providing dimensional and mechanical stabilities [21,22]. As IEC increased, the hydrophilic hydrated domains of SPSSF50 membranes became more continuous and formed large channels, which resulted in higher water uptake and lower mechanical strength. At 100 °C, though the SPSSF50 membranes exhibited excessive water uptake about 463.5% and swelling ratio of 61.7%, they still maintained their basic dimensional shapes after immersion for 24 h. The SPSSF30 membranes kept low water uptake and dimensional change in the whole temperature range and the SPSSF40 membranes had water uptake of 89.6% but swelling ratio less than 23.3% at 100 °C, suggesting they could be operated at elevated temperatures.

Significant differences in the water uptake of SPSSF membranes were presented in several different research groups. McGrath and co-workers reported that the 40 mol% disulfonated membranes synthesized using the same materials had water uptake above 200% at room temperature [13]. Lee and Kerres presented
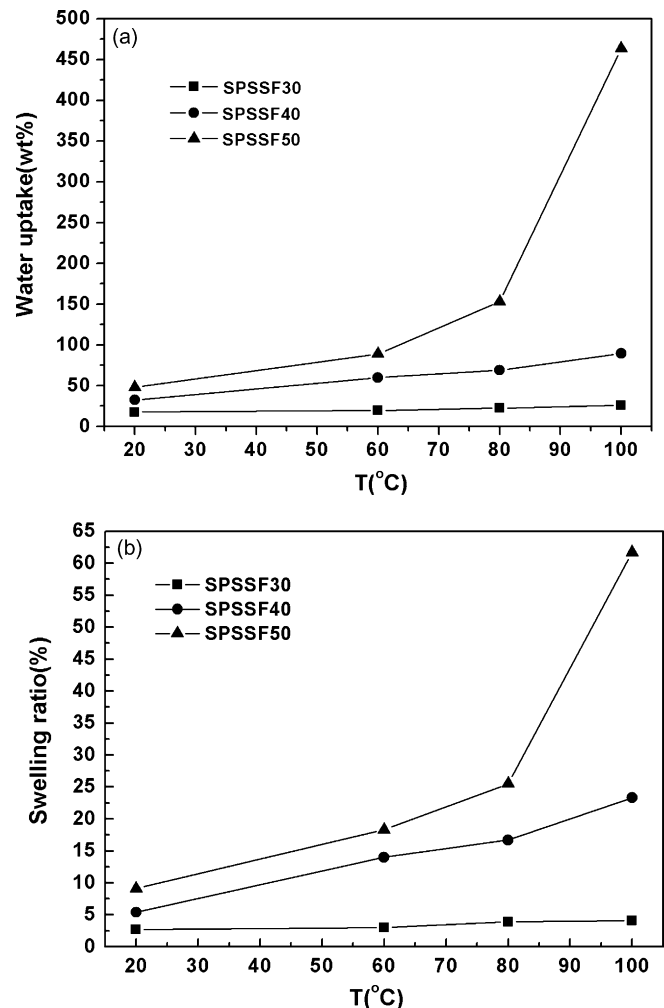

Fig. 3. Water uptake (a) and swelling ratio (b) of SPSSF membranes at different temperatures.

Table 2
Mechanical properties of sulfonated membranes

Membrane	Tensile strength (MPa)		Young's modulus (GPa)		Elongation at break (%)	
	Dry	Wet	Dry	Wet	Dry	Wet
SPSSF30	40.3	26.3	1.14	1.08	14.3	12.6
SPSSF40	38.9	21.5	1.07	1.04	11.8	10.0
SPSSF50	33.8	18.0	1.07	0.81	12.6	16.8
Nafion 212	23.9	19.4	0.27	0.20	136	119

that the membranes containing 50 mol% disulfonated monomer exhibited water uptake of 91% and swelling ratio of 25% at room temperature and the membranes split into pieces upon heating at 90 °C [14]. The excessive water uptakes make it difficult to use in PEMFC at elevated temperature. Dang reported the similar water uptake results of the membranes containing 50 mol% disulfonated monomers at room temperature to our study [15,16]. Generally, the reaction conditions for the polymerization have an important influence on the molecular weight of the polymers.

3.3. Mechanical and thermal properties

It is essential for PEM to keep good mechanical properties in either dry or wet states. The mechanical properties of SPSSF membranes were test at ambient conditions with RH ~50% and compared with Nafion 212 (Table 2). The SPSSF membranes in the dry state showed the maximum tensile strength of 33.8–40.3 MPa, Young's modulus of 1.07–1.14 GPa, and elongation at break of 11.8–14.3%. In the wet state, the absorbed water as a plasticizer resulted in the deterioration of mechanical strength and Young's modulus. However, as shown in Table 2, the SPSSF membranes showed higher tensile strength and Young's modulus than Nafion 212 in both states. It is enough for the SPSSF membranes to satisfy the PEMFC mechanical property requirement.

The thermal properties of SPSSF membranes in the acid form (–H) and sodium form (–Na) were preliminarily evaluated by TGA in N_2 heating at 10 °C min^{-1} (Fig. 4). The TGA curves of all of the SPSSF membranes in acid form (SPSSF–H) exhibits two distinct weight-loss processes. The first at around 300 °C was generally attributed to the loss of sulfonic groups, while the second at about 450 °C was related to fragmentation of the SPSSF main-chain. A summary of the thermal properties of SPSSF membranes was listed in Table 3. The data indicate that the SPSSF membranes are thermally stable within the temperature range for PEMFC applications. It could be observed

that as the IEC increasing, the decomposition temperature (T_d) and the 5% weight loss temperature (T_{d5}) decreased. Compared with the SPSSF–H membranes, the SPSSF–Na series showed markedly high thermal stabilities with T_d above 349 °C and T_{d5} above 416 °C.

3.4. Oxidative stability

The oxidative stability of SPSSF membranes was evaluated in hot Fenton's reagent (3 wt% H_2O_2 + 2 ppm $FeSO_4$) at 80 °C as an accelerated test. Their weight loss in hot Fenton's reagent for 1 h and the time that the membrane started to dissolve were shown in Table 3. The SPSSF membranes exhibited good oxidative stability. Because the oxidative attack by radical species (HO$^\bullet$ and HOO$^\bullet$) mainly occurs in the hydrophilic domains, a higher IEC leads to lower oxidative stability. The SPSSF50 membrane started to dissolve in about 70 min. The SPSSF30 had relatively good oxidative stability and they maintained dimensional shapes until they began to dissolve after 2 h. However, all of them showed a weight increase after treatment in Fenton's reagent at 80 °C for 1 h, which should be associated with the thioether groups [17]. The weight gain of the SPSSF membranes was resulted from the oxidation of thioether to sulfoxide, which could be confirmed in Fig. 5. The sulfide peak in the SPSSF membranes before Fenton's reagent was observed at the broad peak from 1025 to 1075 cm^{-1}. After the Fenton's reagent test, the asymmetric and symmetric strengths were observed apparently at 1040 and 1100 cm^{-1} and the intensity of the sulfide peak decreased to lower levels. The transformation of thioether groups into sulfoxide groups by reacting with hydroxyl radicals avoided the directly attack of hydroxyl radicals to polymer backbones. Thus, the SPSSF membranes may be expected to exhibit more durability in the PEMFC application.
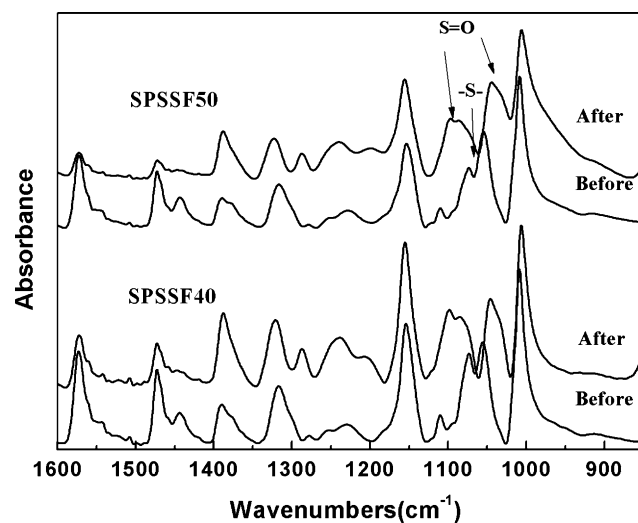

Fig. 4. TGA curves of SPSSF membranes under nitrogen.

Fig. 5. FTIR spectra of SPSSF membranes before and after soaking in Fenton test at 80 °C for 1 h.

Table 3
TGA and oxidative stability results of SPSSF membranes

Membrane	T_d (°C)[a]		T_{d5} (°C)[b]		Fenton test	
	–H	–Na	–H	–Na	RW (%)[c]	τ (h:min)[d]
SPSSF30	263/453	349/508	344	420	107	2:00
SPSSF40	252/450	350/511	335	427	104	1:30
SPSSF50	251/450	350/514	328	416	102	1:10

[a] Onset temperature of decomposition: the first stage/second stage.
[b] 5% weight loss temperature measured by TGA.
[c] Retained weights of membranes after treating in Fenton's reagent for 1 h.
[d] The time of polymer membranes start to dissolve.

3.5. Fuel cell performance

The fuel cell performance of SPSSF membranes (∼50 μm) were evaluated at different temperatures and relative humidity (RH). The fuel cell performance of the SPSSF membranes with different IEC at 80 °C and 100% RH were compared with that of Nafion 212 in Fig. 6. The cell performance boosted with increasing disulfonated monomer, due to the increasing proton conductivity. As the disulfonated monomer increasing from 30 to 40 and 50, the cell voltage at 1000 mA cm^{-2} increased from 0.608 to 0.695 and 0.724 V, and the peak power densities increased from 0.67 to 1.11 and 1.18 W cm^{-2}. The SPSSF40 membrane exhibited comparable cell performance to that of Nafion 212 under the test conditions. The SPSSF50 membrane showed better fuel cell performance than Nafion 212 membrane with the similar thickness, which was in agreement with the results that its proton conductivity was larger when compared with that of Nafion 112 [18].

Hydrogen crossover is the undesirable permeation of hydrogen across the electrolyte membranes. High rate of hydrogen crossover lowers the open circuit voltage (OCV), reduces the fuel efficiency and may lead to the pin-hole formation and result in the membrane deterioration, thus low hydrogen crossover is needed for fuel cell applications. The values of H$_2$ crossover density, together with thickness and open circuit voltage (OCV) of the SPSSF membranes and Nafion 212 were summarized in Table 4. The value of H$_2$ crossover density for Nafion 212 was 4.6 mA cm^{-2}, which was comparable to the result of Inaba at the similar test conditions [23]. It was clear that the H$_2$ crossover of the SPSSF membranes increased and the values of OCV decreased correspondingly with increasing IEC. The H$_2$ crossover density of the SPSSF40 membrane (2.3 mA cm^{-2}) was only 50% of that of Nafion 212 membrane and the value of OCV of the SPSSF40 membrane (1.008 V) was significantly

Table 4
Thickness, open circuit voltage (OCV), and H$_2$ crossover current density of SPSSF membranes and Nafion 212

Polymer	Thickness (μm)	OCV(V)	Hydrogen crossover (mA cm^{-2})
SPSSF30	53	1.028	1.7
SPSSF40	53	1.008	2.3
SPSSF50	55	0.986	4.2
Nafion 212	50	0.958	4.6

higher than that of Nafion 212 membrane (0.958 V). In view of the good mechanical properties, dimensional stability and oxidative stability, the SPSSF40 membranes showed more preferable properties for the PEMFC applications.

The effects of temperature and relative humidity (RH) on the fuel cell performance were also investigated. Fig. 7 shows the fuel cell performance of SPSSF40 and SPSSF50 membranes at 60 and 80 °C with 100% RH. As the cell temperature increased from 60 to 80 °C, because of the increase in the electrode activity [24], the cell voltage at 1000 mA cm^{-2} of SPSSF50 membranes increased from 0.713 to 0.724 V and SPSSF40 membranes increased from 0.671 to 0.695 V. Meanwhile, the peak power densities of the SPSSF50 and SPSSF40 membranes increased about 0.12 and 0.23 W cm^{-2}, respectively. Fig. 8 compares the cell performance of SPSSF50 and SPSSF40 membranes at different relative humidity. As can be seen in Fig. 8(a), when the relative humidity decreased from 100% to 50% RH and 25% RH at 80 °C, the cell voltage at 1000 mA cm^{-2} of SPSSF50 membranes decreased from 0.724 to 0.704 and 0.665 V, and the peak power densities decreased from 1.18 to 1.11 and 0.84 W cm^{-2}, respectively. The similar effects occurred for the SPSSF40 membranes with peak power densities diminishing about 0.2 W cm^{-2} when the relative humidity decreased from 100% to 50% RH (Fig. 8(b)). The relative humidity didn't have significant effects
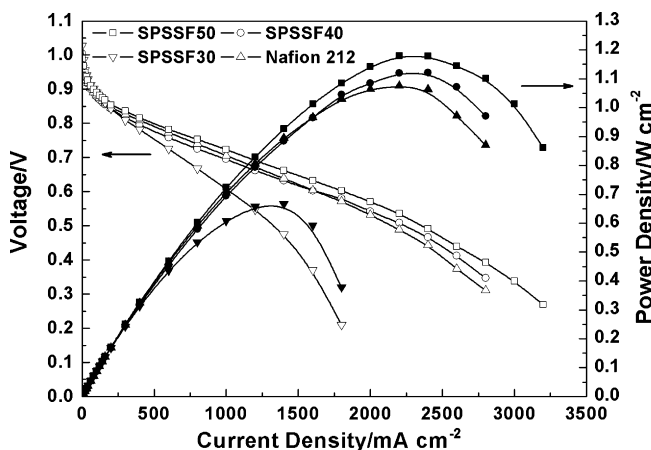

Fig. 6. PEM fuel cell performance of SPSSF membranes with different IEC at 80 °C and 100% relative humidity. $P_{H_2} = P_{O_2} = 0.2$ MPa.

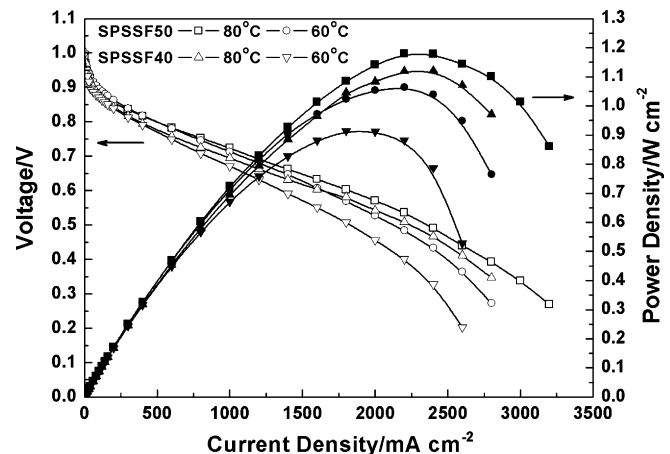**Fig. 7.** PEM fuel cell performance of SPSSF membranes at different cell temperatures and 100% relative humidity. $P_{H_2} = P_{O_2} = 0.2$ MPa.
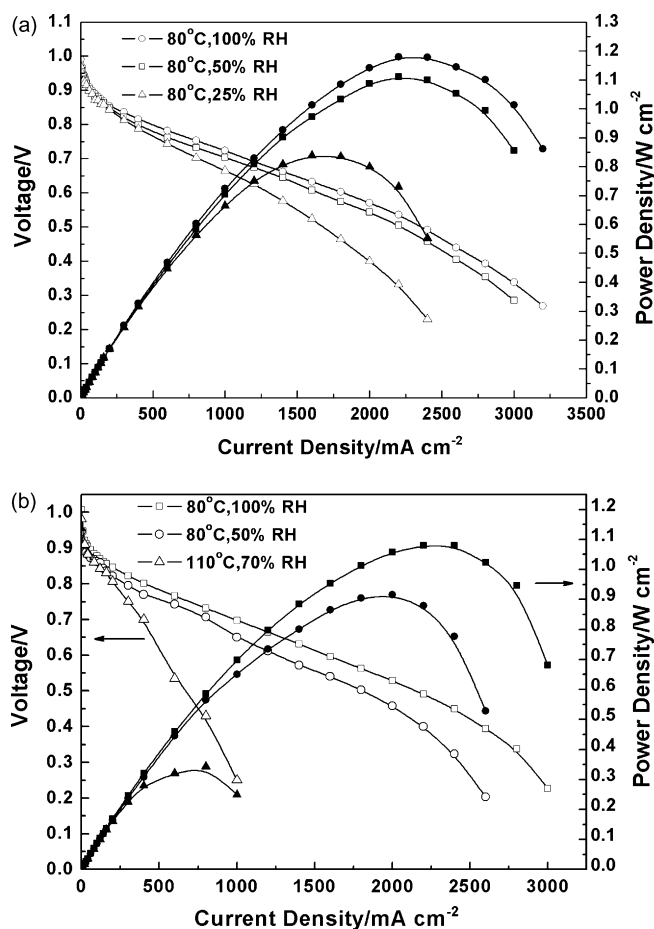
Fig. 8. PEM fuel cell performance of SPSSF50 (a) and SPSSF40 (b) membranes at different relative humidity. $P_{H_2} = P_{O_2} = 0.2$ MPa.

on the SPSSF membranes on the test conditions, which was somewhat different with the results of Jiang et al. [20]. Jiang et al. found the performance of the post-sulfonated poly(ether ketone) membranes suffered significantly at low relative humidity and ambient pressure at 80 °C. Compared with the SPSSF50 membranes, it can be found that the temperature and relative humidity had more pronounced influences on the cell performance of SPSSF40 membranes possibly due to its relative low proton conductivity.

The SPSSF40 membranes were tentatively operated at 110 °C and 70% RH. However, the cell performance fluctuated drastically and the data could not be recorded because of its serious loss of water at high temperature and low relative humidity. We had a try to enhance the water retention by incorporating 3 wt% SiO$_2$ particles into the SPSSF40 membranes. As was noted in Fig. 8(b), the stability of cell performance was improved to some extent but the non-conductive SiO$_2$ particles increased the cell resistance and led to poor cell performance. So improving the water-holding capacity of the SPSSF membranes at high temperature is the next step in the following research.

4. Conclusions

The SPSSF copolymers were successfully prepared with modified procedure and could be cast into tough and flexible membranes. The water uptake and swelling ratio of SPSSF membranes ascended with the IEC and temperature increase. The SPSSF30 and SPSSF40 membranes showed low dimensional change in the temperature range of 20–100 °C and SPSSF50 membrane exhibited large water uptake but still maintained its basic dimensional shapes after immersion in water at 100 °C for 24 h. All SPSSF membranes kept good mechanical properties in both dry and wet states. The SPSSF membranes showed a weight gain after soaking in Fenton's reagent at 80 °C for 1 h, which was resulted from the oxidation of thioether to sulfoxide and was confirmed by FTIR. With the similar thickness, the SPSSF40 membranes exhibited comparable cell performance with that of Nafion 212 membrane but significantly low H$_2$ crossover density at 80 °C and 100% RH. The SPSSF50 membranes showed superior fuel cell performance than Nafion 212 membranes. The SPSSF membranes at descending temperature and relative humidity showed degressive cell performance. The relative humidity did not have significant effects on the cell performance of SPSSF membranes at 80 °C, but the cell performance suffered significantly when temperature was beyond 100 °C because of the serious water loss. In conclusion, with excellent physical properties and fuel cell performance, the SPSSF40 membranes showed promising properties as new polymeric electrolyte materials for the applications in PEMFC at medium temperatures.

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