Novel sulfonated poly(phthalazinone ether ketone) ionomers containing benzonitrile moiety for PEM fuel cell applications

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Abstract

A series of benzonitrile-containing sulfonated poly(phthalazinone ether ketone) ionomers were successfully synthesized via the direct copolymerization of benzonitrile-containing bis(phthalazinone), 3,3′-sulfonated-4,4′-difluorodiphenyl ketone and 4,4′-difluoro-diphenyl ketone. The sulfonation degrees can been readily controlled by changing the feed ratio of monomers. The resulting sulfonated polymers with inherent viscosity ranging from 0.45 to 0.72 dL g^{-1} were characterized by ^{1}H NMR and other technologies. These sulfonated polymers had good solubility in polar aprotic solvents and afforded tough and ductile membranes by casting from DMAc solution at 60 °C. Due to the specially designed chemical structures, the membranes showed excellent thermal and oxidative stabilities. Thermogravimetric analysis (TGA) traces demonstrated that all the sulfonated polymers exhibited good thermal stability with initial weight loss > 220 °C. The membranes exhibited superior oxidative and hydrolytic stabilities as evidenced by Fenton's reagent. The membranes showed moderate water uptake in low sulfonation degree (≦1.2), and the proton conductivity of the membrane with sulfonation degree of 1.2 was 1.03×10^{-3} S cm^{-1} at 25 °C and 100% relative humidity. The proton conducting and other properties as a membrane can be tailorated by controlling the sulfonation degree.
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1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have attracted increasing attention as a potential candidate for automotive, stationary and portable power [1,2]. As one of the key components of PEMFC, proton exchange membrane (PEM) must suffer from harsh conditions during PEM fuel cell operation. Due to their outstanding properties such as good chemical stability, high proton conductivity, perfluorinated sulfonic acid membranes (especially for the Nafion of Dupont) have been almost the advanced membrane for use in practical fuel cell systems. But their high cost, low proton conductivity in high temperature and low relative humidity and high methanol permeation prevent applications in large scale. Therefore, it is significant to develop new kinds of proton exchange membranes with lower cost and considerable performances. By introducing proton conducting moieties into polymer chains through chemical modifications, high performance polymers can turn into proton conducting polymers without sacrificing their excellent thermal, mechanical properties and good oxidative stabilities. Sulfonated poly(ether ether ketones) [3–9], poly(arylene ether sulfones) [10–12], poly(phenylene sulfide) [13], polyimides [14–16] and polybenzimidazoles, etc. [17] fall into this category.

There are two strategies to prepare sulfonated polymers: postsulfonation by different sulfonation agents [18–24] and direct polymerization of sulfonated monomers [5–9,25–27]. Other than avoiding the main chain degradation and side chain cross-linking caused by postsulfonation, the latter has several advantages. First, the sulfonation degree can be precisely controlled by adjustment of the feed ratio of sulfonated monomers to unsulfonated monomers. Second, the copolymers synthesized by this method have higher acidity and better thermal stability due to the electron withdrawing effects of the withdraw groups such as carbonyl and sulfone groups. Third, the copolymers can possess more sulfonic acid groups up to 2 per repeat unit, which is an effective way to improve proton conductivity [28].

Harrison et al. [29] have reported that the incorporation of polar moieties such as phenyl phosphine oxide and phenyl nitrile

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into the molecular chains can to some extent improve the stability of the resultant polymers. Especially, the introduction of strongly polar nitrile group into polymers will promote the adhesion and import tightly of the polymer chains via interaction of polar chemical groups [30–33]. Additionally, nitrile functional groups can serve as potential sites for cross-linking. It is anticipated that the properties of polymers containing nitrile group can be improved through cross-linking of nitrile groups [34]. In previous works, we have synthesized a serial of sulfonated poly(phthalazinones) [5–9] and sulfonated poly(arylene ether) [21–24]. In this paper herein, we reported the synthesis and properties of the sulfonated poly(phthalazinone ether ketone) ionomers containing nitrile group as a candidate of proton exchange membrane for the applications in PEM fuel cell.

2. Experimental

2.1. Materials

2-(4-Hydroxylphenyl)benzoic acid **1** was prepared from phenolphthalein according to literature [35]. Sulfonated 4,4′-difuloro diphenyl ketone **5** was prepared by the sulfonation of 4,4′-difulorodiphenyl ketone **6** as depicted in literature [36]. Reagent-grade 2,6-difuloro benzonitrile, monohydrate hydrazine, N,N-dimethyl acetamide (DMAc), toluene, methanol and anhydrous potassium carbonate were obtained from commercial sources and used as received. 4,4′-Difulorodiphenyl ketone (DFDK) was recrystallized from ethanol and dried under vacuum before use.

2.2. Preparation of benzonitrile-containing dicarboxylic acid 3 [37,38]

To a three necked round bottom flask equipped with a nitrogen inlet/outlet, Dean-stark trap, condenser and magnetic stirrer was added 4.8446 g (20 mmol) 2-(4-hydroxyl-phenyl)benzoic acid **1**, 1.3910 g (10 mmol) 2,6-difuloro benzonitrile **2**, 4.85 g (35 mmol) anhydrous potassium carbonate, 40 mL DMAc, 20 mL toluene. Under the protection of nitrogen atmosphere, the reaction mixture was refluxed at 145 °C for 3 h to azeotrope off the formed water with toluene. After the removal of toluene, the temperature was slowly increased to 165 °C and maintained for another 12 h. After cooling to room temperature, the reaction solution was dissolved in 200 mL de-ionized water, then acidified by addition of diluted HCl to precipitate the product. The residue was filtered and washed with water for three times. The crude product was recrystallized from glacial acetic acid to give 4.95 g pale pink solid. Yield: 85%; M.P. 243–245 °C.

^{1}H NMR (DMSO-d_6) δ (ppm): 6.94 (d, 2H), 7.28 (d, 4H), 7.43 (d, 2H), 7.63–7.77 (m, 9H), 8.01 (d, 2H), 13.02 (s, 2H).

2.3. Preparation of benzonitrile-containing bis(phthalazinone) 4 [37,38]

To a flask equipped with a condenser were added 4.5836 g (7.85 mmol) dicarboxylic acid **3**, 2.00 g (40 mmol) hydrazine monohydrate and 180 mL methanol. The reaction mixture was heated to reflux at 80 °C for 12 h. As the reaction proceeded, the white emulsion became clear in half an hour and the product precipitated out from the solution about 2 h later. After cooling to room temperature, the precipitates were collected by filtration. A total of 3.93 g white solid was obtained. Yield: 87%; MP: 389–391 °C.

^{1}H NMR (DMSO-d_6) δ (ppm): 6.88 (d, 2H), 7.42 (d, 2H), 7.67 (t, 1H), 7.72 (d, 2H), 7.77 (d, 2H), 7.78–7.97 (m, 4H), 8.36 (d, 2H), 12.89 (s, 2H).

2.4. Preparation of benzonitrile-containing sulfonated poly(phthalazinone ether ketone) 7a–7f

Sulfonated poly(phthalazinone ether ketones) containing benzonitrile moiety with controlled sulfonated degrees were successfully synthesized via the direct copolymerization of bis(phthalazinone) **4**, sulfonated 4,4′-difluorodiphenyl ketone **5** and 4,4′-difluorodiphenyl ketone **6**. Sulfonated poly(phthalazinone ether ketone) ionomer **7a** was selected as a typical and the procedure was described as follows: to a three necked round bottom flask equipped with a nitrogen inlet/outlet, Dean-stark trap, condenser and magnetic stirrer were charged 0.5756 g (1 mmol) bis(phthalazinone) **4**, 0.0845 g (0.2 mmol) sulfonated 4,4′-difluorodiphenyl ketone **5**, 0.1746 g (0.8 mmol) 4,4′-difluorodiphenyl ketone **6**, 0.1935 g (1.4 mmol) anhydrous potassium carbonate, 6 mL DMAc and 6 mL toluene. Under the protection of nitrogen atmosphere, the reaction mixture was refluxed at 145 °C for 3 h with stirring to azeotroped off the water formed during the reaction with toluene. The temperature was raised slowly to 165 °C after the removal of toluene and maintained for another 20 h. After the solution became very viscous, the reaction mixture was cooled to 100 °C, diluted with the addition of 2 mL DMAc and poured into 200 mL rapidly stirred methanol/water solution (v/v, 1:1) to precipitate the product. The precipitant was filtered and washed with adequate water for three times. The product was collected and vacuum dried at 120 °C for 24 h. An amount of 0.774 g polymer was obtained in high yield of 97%.

Sulfonated poly(phthalazinone ether ketone) **7b**–**7f** were synthesized using the same procedure as described for the synthesis of polymer **7a**. The molecular feed ratio of monomers and the polymerization results were list in Table 1.

Table 1
Polymerization results and properties of sulfonated poly(phthalazinone ether ketones) **7a**–**7f**

Polymer	m/n	Yield (%)	η_{inh}[a] (dL g^{-1})	$T_{-5\%}$[b] (°C)	T_g	Solubility[d]
7a	2:8	97	0.69	373	ND[c]	
7b	4:6	98	0.72	361	ND[c]	DMAc
7c	5:5	95	0.66	358	ND[c]	DMSO
7d	6:4	91	0.49	345	ND[c]	NMP
7e	8:2	91	0.65	302	ND[c]	DMF
7f	10:0	89	0.45	292	ND[c]	

[a] Tested in 0.5 g dL^{-1} solution in DMAc at 25 °C.
[b] 5% weight loss temperature.
[c] Not detected.
[d] All polymers are soluble in DMAc, DMSO, NMP and DMF.

2.5. Membrane preparation

Approximately, 1 g of the sulfonated poly(phthalazinone ether ketone) ionomer in sodium salt form was dissolved in 20 mL of DMAc to afford 5–10% transparent solution. Then the solution was cast onto a leveled glass plate, and heated at 60 °C for about 12 h till most of the solvent was removed. The resulting transparent flexible membranes were acidified and converted into acid form by the refluxing of the as-made membranes in 0.5 M sulfuric acid for 2 h followed by 2 h of extraction in boiling de-ionized water.

2.6. Instrumentation

^{1}H NMR spectra were recorded on a Bruker NMR instrument (Model: DRX 400 MHz) using dimethyl-d$_6$ sulfoxide (DMSO-d$_6$) as solvent, chemical shifts were given in ppm against tetramethylsilane (TMS) as an internal standard. FTIR spectrum was measured on a Perkin Elmer Spectrum 100 Fourier transform spectrometer. Melting points were measured on a melting-point testing apparatus. The thermal stability of the polymers ranging from 70 to 600 °C was determined with a Seiko SSC-5200 thermogravimetric analyzer (thermogravimetric analysis (TGA)/differential thermal analysis (DTA)) under nitrogen atmosphere. The heating rate was 20 °C min^{-1}. The glass-transition temperatures (T_gs) were determined on a Seiko 220 DSC instrument at a heating rate of 20 °C min^{-1} under nitrogen protection. The second scan was immediately initiated after the sample was cooled to room temperature.

2.7. Inherent viscosity

Inherent viscosity was determined in 0.5 g dL^{-1} solutions in DMAc at 25 °C using a calibrated Ubbelohde viscometer.

2.8. Water uptake

The water uptake of the membrane was measured by weighting the weight change between dried and humidified forms at 80 °C. The membranes were first thoroughly dried at 150 °C in vacuum to a constant weight. The dried membranes were then immersed in water at 80 °C for 48 h until equilibrium of water absorption. The water uptake was reported as a percentage and was determined as follows:

$$\text{Water uptake} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

where W_{wet} and W_{dry} are the weights of the wet and dry membranes, respectively. W_{dry} is obtained after drying the wet membrane.

2.9. Ion-exchange capacity (IEC)

The ion-exchange capacity (IEC) was determined by titration. A piece of sulfonated membranes was immersed and equilibrated in large excess of 2 M NaCl aq for 48 h to exchange sodium ion with proton. The concentration of HCl released from the membrane sample was determined by titration with 0.1 M NaOH aqueous solution using phenolphthalein as an indicator. Ion-exchange capacity was calculated according to the following equation:

$$\text{IEC (meq g}^{-1}) = \frac{C_{\text{NaOH}} V_{\text{NaOH}}}{W}$$

where C_{NaOH} and V_{NaOH} refer to the concentration and volume of NaOH solution, and W is the weight of the sulfonated membrane.

2.10. Oxidative stability

A small piece of membrane sample (2 mm × 15 mm) was soaked in Fenton's reagent (2 ppm FeSO$_4$ in 3% H$_2$O$_2$) at 80 °C with continuous stirring. The oxidative stability measurement was carried out in our laboratory as follows: the membrane was immersed into a continuous stirring flask filled with Fenton's reagent (2 ppm FeSO$_4$ in 3% H$_2$O$_2$) at 80 °C. The oxidative stability was recorded as the expanded time that the membrane take to brake into pieces or fracture is observed. Every 10 min, the membrane was observed to make sure whether or not any change or fracture appears.

2.11. Hydrolytic stability

A small piece of membrane sample was treated in boiling water without stirring for more than 8 days. The hydrolytic stability was evaluated by the changes in shape and appearance.

2.12. Proton conductivity

Proton conductivity measurement was performed 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. Before the measurement, the membrane samples were full hydrated in de-ionized water for at least 24 h. The proton conductivity of the membrane was measured at 25 °C and 100% relative humidity. The conductivity (σ) of the samples was calculated from the impedance data, using the following equation $\sigma = d/RA$, where d and A are the thickness and face area of the sample, respectively, and R was derived from the low intersect of the high-frequency semicircle on a complex impedance plane with the Re(Z)' axis.

3. Results and discussion

3.1. Synthesis of sulfonated poly(phthalazinone ether ketone) ionomer 7

Bis(phthalazinone) monomer **4** was synthesized in a two-step sequence as depicted in Scheme 1. In the presence of potassium carbonate, the nucleophilic substitution reaction of 2-(4-hydroxylphenyl)benzoic acid **1** with 2,6-difluoro benzonitrile **2** afforded bicarboxylic acid **3**, which was converted to bis(phthalazinone) **4** by simply refluxing with hydrazine monohydrate in methanol via inner molecular ring-closure reaction.
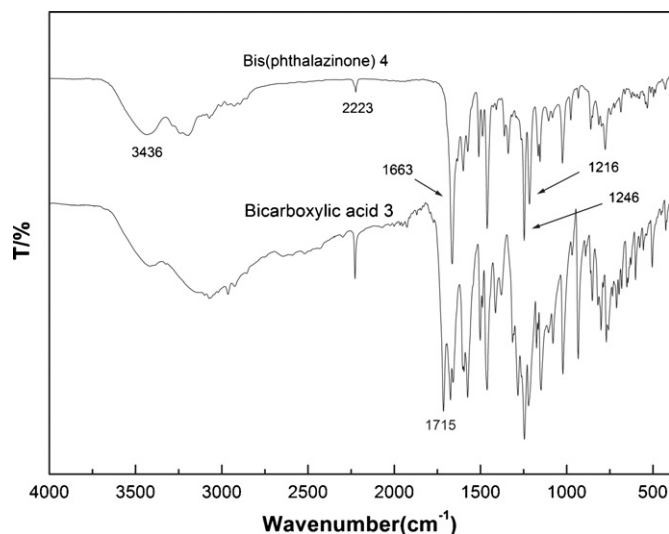
Scheme 1. Synthesis of benzonitrile-containing bisphathalazinone.

The desired bis(phthalazinone) containing benzonitrile moiety was confirmed using ^{1}H NMR spectrum (Fig. 1) and FTIR spectrum (Fig. 2). The characteristic peaks for the aromatic proton of phthalazinone can be clearly observed at 12.9, 8.3, 7.9 and 7.4 ppm, which was consistent with the previous results of phthalazinone-containing polymers by Wang and Yoshida et al. [37–39]. Fig. 2 showed the FTIR spectrum of bicarboxylic acid **3** and bisphthalazinone **4**. The absorption band at 3437 cm^{-1} can

Fig. 1. ^{1}H NMR spectrum of bis(phthalazinone) **4** containing benzonitrile moiety.

Fig. 2. IR spectrum of bicarboxylic acid **3** and bis(phthalazinone) **4**.

be assigned to N–H stretching vibration. The absorption band at 2223 cm^{-1} is attributed to CN stretching vibration of nitrile group. And the absorption bands at 1663 cm^{-1} can be assigned to C=O stretching vibration of (O=C–N–H) group. Additionally, the characteristic absorptions of the asymmetric C–O stretching vibrations of ether bands were observed at 1247 and 1216 cm^{-1}. By comparing the IR spectrums of bicarboxylic acid **3** to bisphthalazinone **4** in Fig. 2, it can be clearly seen that the absorption of C=O stretching vibration of carbonyl group at 1714 cm^{-1} in bicarboxylic acid **3** disappeared, which verified the complete loss of carbonyl group.

As depicted in Scheme 2, sulfonated poly(phthalazinone ether ketone) ionomers were synthesized by direct polymerization of bis(phthalazinone) with dihalide monomers in a dipolar aprotic solvent DMAc. The bis(phthalazinone) aza-nitrogen anions, which were formed via deprotonation by potassium carbonate, attacked the activated dihalides with the elimination of fluorides, resulting in high molecular weight polymers. By changing the feed ratios of disulfonated difluoro diphenyl ketone **5** to difluoro diphenyl ketone **6**. Accordingly, poly(phthalazinone ether ketones) with different sulfonation degrees were obtained. Conventionally, synthetic method of poly(arylene ether) was adopted to prepare sulfonated poly(phthalazinone ether ketone) ionomers. Because of the poor insolubility of monomers, the reaction temperature was controlled to be higher than 165 °C, ensuring to afford high molecular weight polymers. The polymerization results are summarized in Table 1. It can be seen that the inherent viscosity ranged 0.45–0.72 dL g^{-1} in DMAc at 25 °C for the synthesized polymers **7a**–**7f**. All polymers are soluble in dipolar aprotic solvents such as DMAc, DMF, DMSO and NMP.

Fig. 3 shows the ^{1}H NMR spectrum of sulfonated polymer **7c**. The protons of **7c** were assigned according to the chemical shifts of the protons of monomers. The peaks cannot be clearly clarified due to their overlap.

3.2. Thermal properties of sulfonated poly(phthalazinone ether ketone) 7

Thermal properties of sulfonated poly(phthalazinone ether ketones) **7a**–**7f** were characterized using thermogravimetric
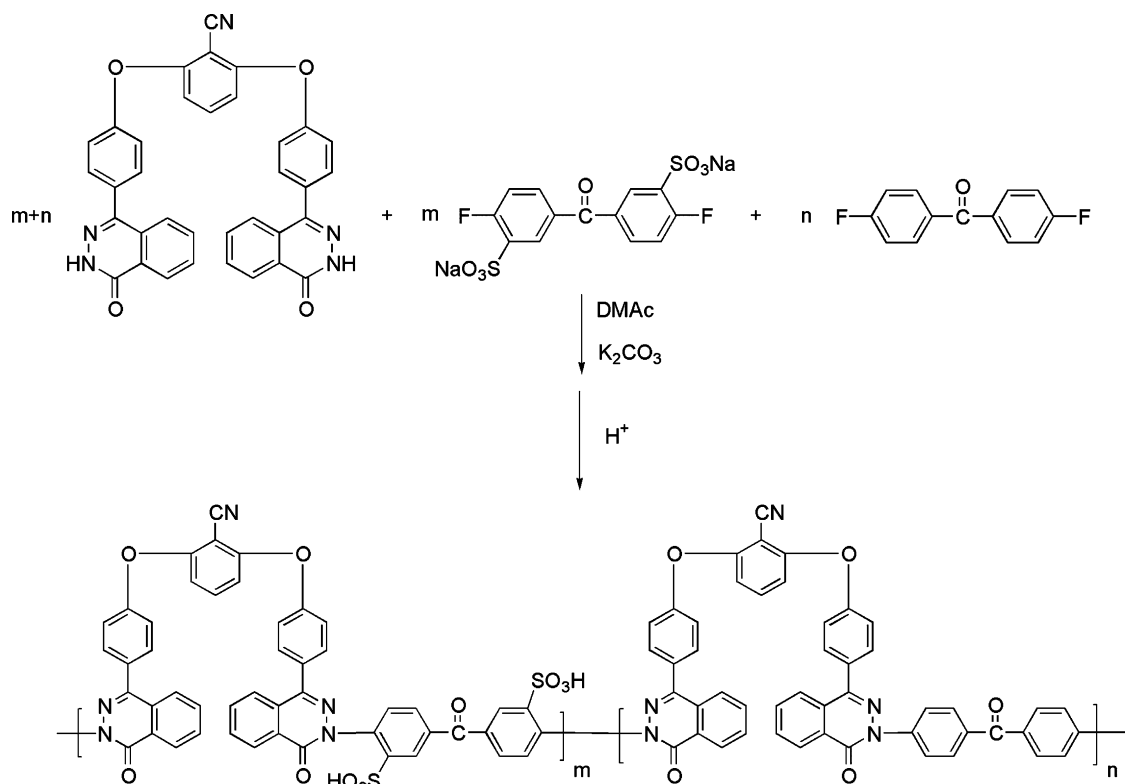
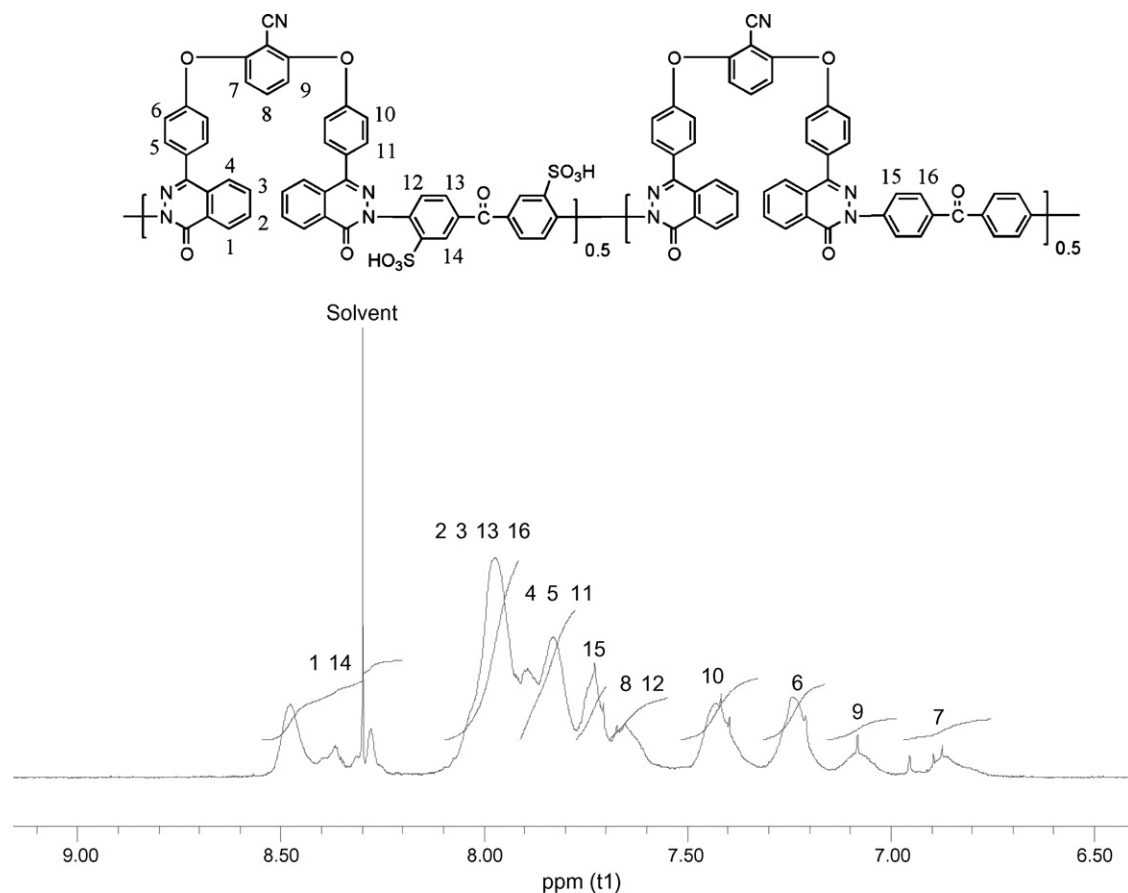Scheme 2. Synthesis of benzonitrile-containing sulfonated poly(phthalazinone ether ketones) **7a**–**7f**.

Fig. 3. ^{1}H NMR spectrum of sulfonated poly(phthalazinone ether ketone) **7c**.

analyser (TGA) and differential scanning calorimeter (DSC). Five percent of weight loss temperatures ($T_{-5\%}$) and glass-transition temperatures (T_g) are tabulated in Table 1. When subjected to TGA measurements, the samples were first heated to 150 °C and kept at this temperature for 10 min to remove the absorbed water followed by cooling to 70 °C, and the weight loss traces in the range of 70–600 °C were recorded at a heating rate of 20 °C min^{-1} in nitrogen. Fig. 4 shows the TGA traces of
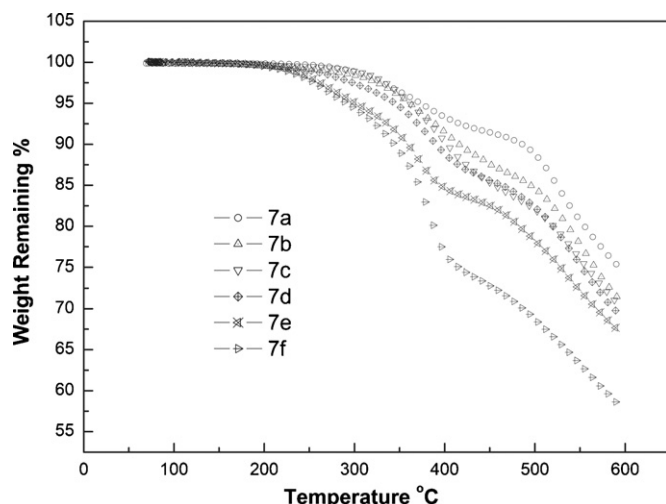
the synthesized polymers. A two-step degradation profile was observed, indicating the same decomposition mechanism for these polymers. The first weight loss at 220 °C was typically attributed to the desulfonation processes, whereas the second weight loss observed at about 400 °C was due to main chain degradation. It also can be clearly seen from Fig. 4 that the TGA curve became steeper with the increase of sulfonation degree of polymers.

No glass-transition temperatures were observed in the experimental temperature range for all synthesized polymers. This is the characteristic nature of ionomers.

3.3. Water uptake and IEC

Since the presence of water in proton exchange membrane is a prerequisite for reaching high proton conductivity, it is crucial that the membrane possesses a high water uptake capacity. The water uptakes of membranes were listed in Table 2. The water uptake increased significantly with increasing sulfonation degree (SD). Moreover, the membranes with SD values smaller than 1.2 showed moderate water uptake, while those with larger SD values were swollen and even soluble in hot water. Compared with Nafion 117 (IEC = 0.91 meq g^{-1}) with a water uptake of 28% at 80 °C, and sulfonated poly(phthalazinone ether ketone) membranes have higher IEC values in case they absorb an equivalent amount of water.

Fig. 4. TGA traces of sulfonated poly(phthalazinone ether ketones) **7a–7f**.

Table 2
Properties of sulfonated poly(phthalazinone ether ketones) **7a–7f**

Polymer	Water uptake[a] (%)	Resistance to oxidation[b] (h:min)	SD[c]	EW	IEC[d] (meq g^{-1})		Conductivity[e] (S cm^{-1})
					Calculated	Measured	
7a	14	5:10	0.4	1965	0.51	0.46	1.20×10^{-5}
7b	16	3:40	0.8	1022	0.98	0.95	6.37×10^{-4}
7c	23	2:30	1.0	834	1.20	1.13	7.83×10^{-4}
7d	25	2:10	1.2	708	1.41	1.37	1.03×10^{-3}
7e	83	1:20	1.6	551	1.82	1.73	[g]
7f	DS[f]	0:40	2.0	457	2.19	2.06	[g]
Nafion117	28	/	/	1100	0.91	0.88	2.01×10^{-2}

[a] Measured at 80 °C.
[b] Recorded as the expanded time that the membrane took to brake into pieces.
[c] Degree of sulfonation, number of sulfonic acid groups per repeating unit.
[d] Ion exchange capacity.
[e] Measured at 25 °C 100% relative humidity for hydrated membrane samples.
[f] Dissolved.
[g] Not obtained.

The ion exchange capacity values of the membranes were determined using titration method. The membranes were first immersed into 2 M NaCl for 48 h to exchange the sodium ions with protons. The resulting solution was titrated with 0.1 M NaOH using phenolphthalein as an indicator. From the results listed in Table 2, it can be seen that the obtained IEC values were consistent well with those calculated.

3.4. Oxidative and hydrolytic stabilities

The oxidative stability of proton exchange membrane is crucial for the lifetime of fuel cells. Membrane stability to oxidation was reported as the expanded time that the membranes were broken into pieces. As shown in Table 2, the oxidative stability of the membranes increased with the decrease of the IEC of the membranes. The synthesized polymers exhibited better oxidative resistance than other reported sulfonated polymers [40]. The hydrolytic stability was also investigated by treating the membrane samples in boiling water for more than 8 days. No obvious changes in both the shape and appearance were observed on all the membranes except **7f**, which was dissolved in water after 4 h. These results demonstrated that the synthesized polymers possessed good hydrolytic stability.

3.5. Proton conductivity

Proton conductivity of as-made membranes was measured as a function of sulfonation degree (or IEC) at 100% relative humidity. Since the conductivity is strongly related to the water absorbing and distribution of hydrophilic ionic domains. Prior to the measurements, the membrane samples were treated in refluxing sulfuric acid for 2 h, Subsequently, the membranes were hydrated to equilibrium at a specific temperature, and the data were collected after the proton conductivity reached a constant value. As a reference, the conductivity of Nafion 117 was also measured accordingly. The results were summarized in Table 2. As expected the proton conductivities increased with increasing SD. The proton conductivity of **7d** reached 1.03×10^{-3} S cm^{-1} at 25 °C and 100% relative humidity, which is close to that of

Nafion 117 (2.01×10^{-2} S cm^{-1}) under the same conditions. The proton conductivities of the polymers with high SD, such as **7e** and **7f**, were not reported due to their brittle nature.

4. Conclusions

Novel sulfonated poly(phthalazinone ether ketone) ionomers containing benzonitrile moieties with different sulfonation contents were successfully synthesized by direct polymerization from bis(phthalazinone), sulfonated diphenylketone and diphenylketone monomers. The resulted sulfonated polymers exhibited excellent thermal stability and resistance to oxidation. The proton conductivity of the sulfonated polymer with a sulfonation degree of 1.2 reached 1.03×10^{-3} S cm^{-1}. The introduction of nitrile groups onto the backbone could be potential sites for cross-linking and other reactions. These reactions are expected to improve the comprehensive properties of resulting polymeric membranes as proton exchange material.

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