Synthesis and characterization of novel sulfonated poly(arylene ether ketone) copolymers with pendant carboxylic acid groups for proton exchange membranes

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ABSTRACT

A series of novel side-chain-type sulfonated poly(arylene ether ketone)s with pendant carboxylic acid groups copolymers (C-SPAEKs) were synthesized by direct copolymerization of sodium 5,5′-carbonyl-bis(2-fluorobenzenesulfonate), 4,4′-difluorobenzophenone and 4,4′-bis(4-hydroxyphenyl) valeric acid (DPA). The expected structure of the sulfonated copolymers was confirmed by FT-IR and ^{1}H NMR. Membranes with good thermal and mechanical stability could be obtained by solvent cast process. It should be noted that the proton conductivity of these copolymers with high sulfonatation degree (DS > 0.6) was higher than 0.03 S cm^{-1} and increased with increasing temperature. At 80 °C, the conductivity of C-SPAEK-3 (DS = 0.6) and C-SPAEK-4 (DS = 0.8) reached up to 0.12 and 0.16 S cm^{-1}, respectively, which were higher than that of Nafion 117 (0.10 S cm^{-1}). Moreover, their methanol permeability was much lower than that of Nafion 117. These results showed that the synthesized materials might have potential applications as the proton exchange membranes for DMFCs.

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1. Introduction

Today, there is growing interest in developing highly conductive with low methanol crossover and low cost alternatives as proton exchange membranes (PEMs) for direct methanol fuel cells (DMFCs) in order to reduce Ohmic losses and enhance their efficiencies during operation [1–5]. Perfluorosulfonic acid membranes, such as Nafion®, are the current state-of-the-art PEM materials, because of their superior chemical and electrochemical stability, in addition to high proton conductivity with relatively low ion exchange capacity (IEC). However, their high cost, loss of proton conductivity at high temperature (>80 °C) and high methanol permeability hinder their applications in fuel cells [6,7]. Hence, great efforts have been devoted to the development of alternative PEMs.

In recent years, many kinds of sulfonated aromatic polymers have been widely investigated as candidates for PEM materials [8–16]. Among them are sulfonated poly(arylene ether ketone)s (SPAEKs) developed by several groups [17–19], due to their good thermal, mechanical stability and appropriate conductivity. Like

other sulfonated aromatic copolymers, SPAEKs require a high IEC to achieve sufficient proton conductivity. However, higher IEC usually leads to high water uptake which will result in the loss of the mechanical strength and high methanol permeability. This can be interpreted from their morphology. The model discussed by Kreuer on the basis of small angle X-ray scattering data for conventional SPAEK membranes shows a less pronounced phase separation than that of Nafion®, that is, a morphology with narrower channels than those in Nafion®, but with highly branched and many dead-end channels [7]. If novel SPAEK membranes are to be successful as PEMs, the morphology must be understood and controlled in such a way that will provide more distinct phase separation between hydrophilic and hydrophobic domains as well as connectivity between hydrophilic domains. Recently, incorporating proton conducting sites, such as sulfonic and carboxylic acid groups, onto the side chain of copolymers fell into this category to change the mirophase-separated structure [20,21]. Kim et al. have reported sulfonated poly(arylene ether sulfone) copolymers containing carboxylic acid groups on rigid backbone [22]. They observed that proton conductivity of these copolymers was not influenced by the pendant carboxylic acid groups obviously. Because of the space resistance, these carboxylic acid and sulfonic acid groups were isolated and unable to form defined hydrophilic domains efficiently. The rigidity of the hydrophobic backbone also

hindered ionic domains to connect with each other to form proton conducting pathways.

To overcome this drawback, in this communication, we synthesized novel SPAEK copolymers with carboxylic acid groups tethered to the flexible aliphatic chains by a direct copolymerization method. It is expected that the existence of the carboxylic acid groups on flexible aliphatic side chains is meaningful for the nanophase separation of hydrophilic and hydrophobic domains, and increasing proton conductivity. Carboxylic acid group as a proton donator can also contribute to the proton conductivity of the resulted membranes. The structure and properties of the membranes were studied in detail.

2. Experimental

2.1. Materials and reagents

4,4′-Difluorobenzophenone was purchased from Longjing Chemical plant, China. 4,4′-Bis(4-hydroxyphenyl) valeric acid (DPA) was purchased from Shanghai Chemical works, China. Potassium carbonate was dried at 180 °C for 10 h prior to be used. Dimethyl sulfoxide (DMSO) was dried with CaH_2 and distilled. Toluene was dried by azeotropic distillation. All other chemicals were obtained commercially and used as received.

2.2. Preparation of sulfonated poly(arylene ether ketone) copolymers with pendant carboxylic acid groups (C-SPAEKs)

To prepare the sulfonated poly(arylene ether ketone) copolymers, sodium 5,5′-carbony-bis(2-fluorobenzenesulfonate) (monomer m) was first prepared via sulfonated method [23]. The sulfonated monomer was further copolymerized with DPA and 4,4′-difluorobenzophenone (monomer k). C-SPAEK copolymers with different DS were prepared by varying the molar ratio of m to k. A typical synthetic procedure to prepare C-SPAEK-5 (DS = 1.0) was as follows: A 250 ml three-necked round-bottomed flask equipped with a mechanical stirrer, a N_2 inlet, and a Dean-Stark trap, was charged with DPA (0.025 mol, 7.15 g), monomer m (0.0125 mol, 5.275 g), monomer k (0.0125 mol, 2.725 g) and potassium carbonate (0.045 mol, 6.21 g). Then 35 ml DMSO and 15 ml toluene were added into the reaction flask under a nitrogen atmosphere. The reaction mixture was heated until the toluene began to reflux. After removal of toluene, the reaction temperature was increased to 180 °C. When the solution viscosity had increased obviously, the mixture was cooled to 100 °C and poured into 500 ml HCl (0.01 M) solution. The copolymers were washed with hot deionized water for several times, and then dried in vacuum at 80 °C for 24 h.

2.3. Membrane preparation

Membranes were prepared by dissolving C-SPAEK copolymers in dimethylformide (DMF) with 10% (w/v) composition under constant stirring. Resulting solution was casted onto the glass plate and dried at 60 °C for 24 h. The membranes were immersed into 1.0 M HCl solution for 1 day and washed with pure deionised water to get H^+ form membranes.

2.4. Characterization of C-SPAEK copolymers

FT-IR spectroscopy of dry membrane samples was recorded on the power samples dispersed in dry KBr in form of disks, using a BRUKER Vector 22 spectrometer at a resolution of 4 cm^{-1} min^{-1} from 4000 to 400 cm^{-1}. ^{1}H NMR spectrometer was measured on a 500 MHz Bruker Avance 510 spectrometer at 298 K with deuterated dimethyl sulfoxide (DMSO-d$_6$) as the solvent and tetramethylsilane (TMS) as the standard. A Pyris 1TGA (PerkinElmer) was employed to study the thermal stability behaviors of C-SPAEK copolymers. The TGA measurements were carried out under a nitrogen atmosphere using a heating rate of 10 °C min^{-1} from 50 to 720 °C.

2.5. Characterization of C-SPAEK membranes

2.5.1. DS

The low-field signals (6.5–8.5 ppm) were characteristic resonances of the aromatic hydrogen atoms. The signal at 8.18 ppm was assigned to the aromatic hydrogen atoms (H$_5$) at the ortho position to the electron-withdrawing –SO$_3$H groups. The DS of the copolymer was estimated by ^{1}H NMR [24,25] and calculated by the following equation:

$$\frac{DS}{16\text{-}2DS} = \frac{A_{H_5}}{\sum A_H} \tag{1}$$

where A_{H_5} was the peak area of H$_5$, $\sum A_H$ was the integral peak area of the signals corresponding to the other aromatic hydrogen.

2.5.2. Ionic exchange capacity (IEC) and water uptake

IEC and water uptake were measured as reported previously [26]. In this paper, the water uptake values of the membranes were measured at different temperatures for compare. The theoretical IEC can be calculated from DS with Eq. (2):

$$IEC = \frac{1000DS}{464 + 80DS} \tag{2}$$

2.5.3. Mechanical properties

The mechanical properties of the membranes were measured using SHIMADZU AG-I 1 KN at the speed of 2 mm min^{-1}. The size of the membrane was 15 mm × 4 mm. For each measurement, at least four samples were used and their average value was calculated.

2.5.4. Atomic force microscopy (AFM) analysis

AFM measurement was carried out with a commercial instrument (Digital Instrument, Nanoscope IIIa, Multimode) under ambient conditions at room temperature. The tapping mode image was measured at room temperature in air with the microfabricated rectangle glass cantilevers (Nanosensor).

2.5.5. Methanol permeability

Methanol permeability was measured using a liquid permeability cell described in the literature [27,28]. This cell consisted of two half reservoirs separated by the membrane. 1.0 M methanol was placed on one side (A cell) and distilled water was placed on the other side of the diffusion cell (B cell). The magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol in B cell was measured by using SHIMADZU GC-8A chromatograph. The methanol permeability was calculated by the following equation:

$$C_B(t) = \frac{A}{V_B}\frac{DK}{L}C_A(t - t_0) \tag{3}$$

where A (in cm^2), L (in cm) and V_B (in ml) were the effective area, the thickness of the membrane and the volume of permeated reservoirs, respectively. C_A and C_B (in mol m^{-3}) were the methanol concentration in feed and in permeate, respectively. DK (in cm^2 s^{-1}) denoted the methanol permeability.

2.5.6. Proton conductivity

Proton conductivity was measured by a four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzed (Solatron 1260) and an electrochemical interface (Solatron 1287,

Scheme 1. The synthesis of C-SPAEK copolymers.
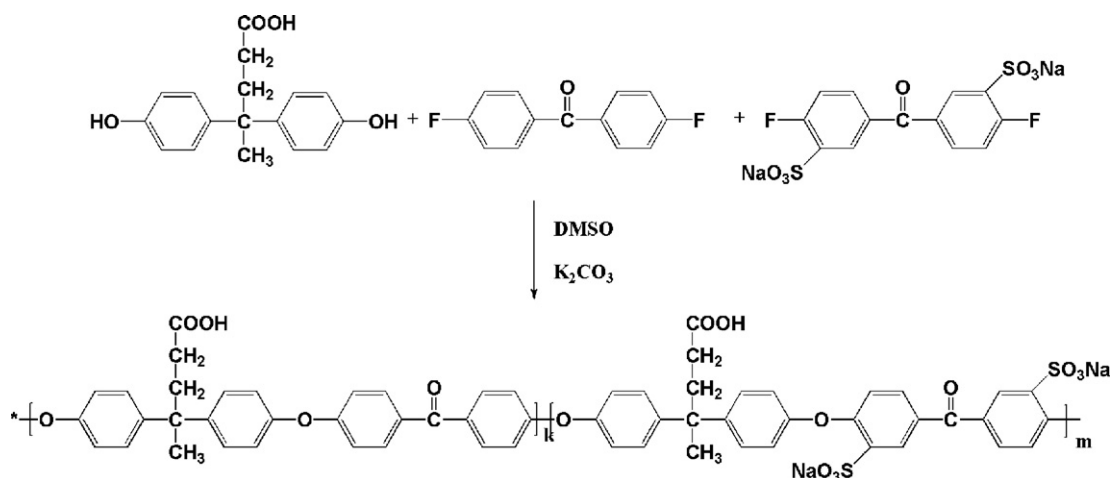
Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes and they were set in a Teflon cell. Conductivity measurement of fully hydrated membranes was carried out with the cell immersed in liquid water at desired temperature. The proton conductivity was calculated by the following equation:

$$\sigma = \frac{L}{RS} \tag{4}$$

where σ was the proton conductivity (in $S\,cm^{-1}$), L was the distant between the two electrodes ($L = 1\,cm$), R was the resistant of the membrane and S was the cross-sectional area of the membrane (in cm^2).

3. Results and discussion

3.1. Characterization of the C-SPAEK copolymers

The C-SPAEK copolymers were synthesized via nucleophilic substitution reactions (Scheme 1). FT-IR and ^1H NMR spectra were used to confirm the chemical structure of C-SPAEKs. Fig. 1 shows the comparative FT-IR spectra of C-SPAEKs with different DS. Observed bands at 1026 and 1084 cm^{-1} were assigned to symmetric and
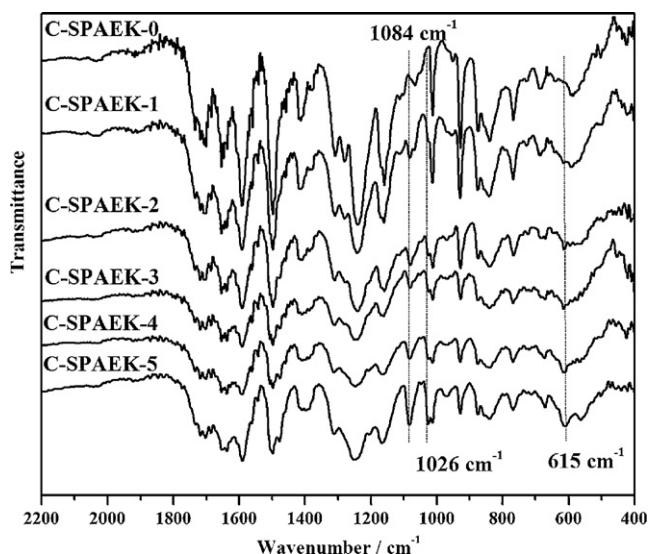

Fig. 1. Comparative FT-IR spectra of C-SPAEK copolymers.

asymmetric stretching vibrations of O=S=O. The absorption band at 615 and 1702 cm^{-1} could be assigned to the stretching of the C–S and C=O of carboxylic acid groups, respectively.

The molecular structure of C-SPAEKs was also confirmed with ^1H NMR spectra. The ^1H NMR spectrum of C-SPAEK-3 (DS = 0.6) and C-SPAEK-0 (DS = 0) are shown in Fig. 2. The peaks at 8.18 ppm were separated from the other aromatic groups, and were assigned to the hydrogen atoms adjacent to the sulfonic acid group. The peaks at 12.09, 2.36, 2.04 and 1.59 ppm were assigned to the hydrogen atoms of carboxylic acid group and aliphatic side chain, respectively. Therefore, both FT-IR and ^1H NMR spectrum showed that the sulfonated poly(arylene ether ketone) copolymers with pendant carboxylic acid groups were synthesized as desired.

As shown in Table 1, the calculated DS values from ^1H NMR spectra were in agreement with the expected DS derived from the monomer ratios. This result indicated that we could easily control the DS values by adjusting the molar ratio of monomer m to monomer k.

3.2. Thermal stability

The thermal stabilities of the copolymers were investigated by TGA measurement (Fig. 3). C-SPAEK-0 had only one weight loss step with an onset at around 370 °C, which showed better thermal stability than others. All the other C-SPAEKs in acid form exhibited three step degradation patterns. The first weight loss was observed around 100 °C. This weight loss was attributed to the loss of the absorbed moisture by the hygroscopic sulfonic acid and carboxylic acid groups in the membrane. The second weight loss occurred at around 220 °C, which was attributed to the splitting-off of sulfonic acid groups. The third degradation step around 430 °C corresponded to the main chain decomposition.

Table 1
Date on C-SPAEK copolymers.

Copolymers	m (mmol)	k (mmol)	m/k	DS[a]	DS[b]	Yield (%)
C-SPAEK-0	0	100	0:10	0	–	96
C-SPAEK-1	10	90	1:9	0.2	0.16	94
C-SPAEK-2	20	80	2:8	0.4	0.34	92
C-SPAEK-3	30	70	3:7	0.6	0.56	95
C-SPAEK-4	40	60	4:6	0.8	0.71	96
C-SPAEK-5	50	50	5:5	1.0	0.87	91

m: sodium 5,5′-carbony-bis(2-fluorobenzenesulfonate); k: 4,4′-difluorobenzophenone.

[a] DS: sulfonated degree obtained from monomer ratio.
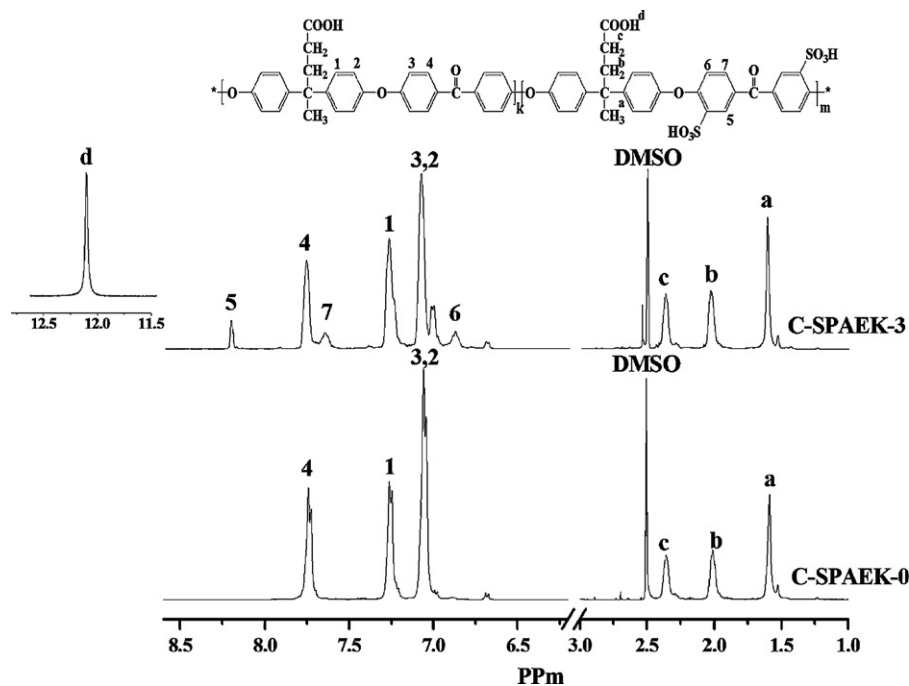
[b] DS: sulfonated degree obtained from ^1H NMR data.

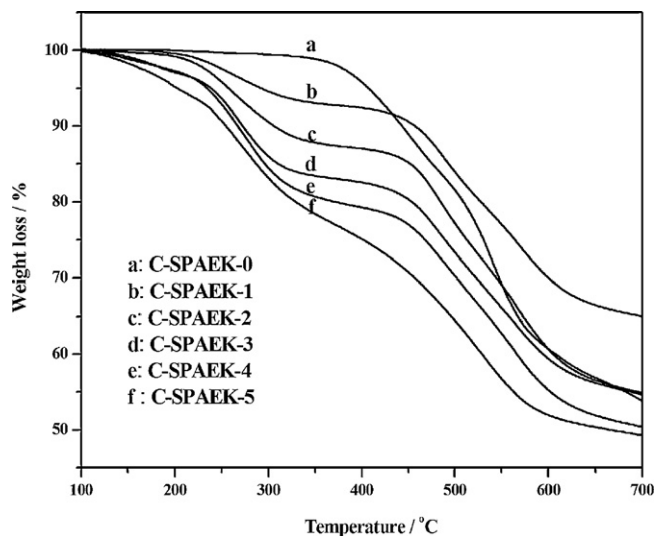**Fig. 2.** ^{1}H NMR spectrum of C-SPAEK-0 and C-SPAEK-3 copolymers in DMSO-d_6.

Fig. 3. TGA curves of C-SPAEK copolymers in acid form.

3.3. Mechanical properties

The mechanical properties of C-SPAEK membranes were evaluated and listed in Table 2. The membranes prepared from C-SPAEK-0 to C-SPAEK-5 had the tensile modules of 808.54–1598.31 MPa, elongations at break of 4.07–17.07, and tensile strength of

Table 2
The mechanical properties of C-SPAEK membranes.

Membranes	Tensile strength (MPa)	Elongation (%)	Tensile modulus (MPa)
C-SPAEK-0	41.36	6.80	934.22
C-SPAEK-1	41.14	4.07	1598.31
C-SPAEK-2	46.47	10.29	1293.74
C-SPAEK-3	41.76	4.38	1196.79
C-SPAEK-4	31.30	6.06	808.54
C-SPAEK-5	46.30	17.07	1162.60

31.30–46.47 Mpa. These results indicated that the C-SPAEK membranes were tough and ductile enough for potential use as PEM materials.

3.4. IEC and water uptake of the C-SPAEK membranes

IEC is usually defined as the moles of fixed SO_3 sites per gram of polymer, which plays a crucial role in deciding the water uptake and proton conductivity. The measured IEC values in $[(mmol–SO_3^- + mmol–COO^-)g^{-1}]$ and theoretical calculated IEC values by ^{1}H NMR in $[(mmol–SO_3^-)g^{-1}]$ are shown in Table 3. Due to the present of carboxylic acid groups, the measured values were higher than the calculated ones. The IEC values increased with DS, which would lead to an increase in both the proton conductivity and water uptake of the membranes.

It is well known that water serves the transport of protons in a proton exchange membrane and therefore influences the proton conductivity of the membrane. So the membrane must be able to absorb enough water. However, excess water uptake can lead to deteriorating mechanical properties of the membrane, which will limit the practical application of the membrane in fuel cells. Fig. 4 shows the water uptake values of C-SPAEK membranes at different temperature. As expected, the water uptake values of all C-SPAEK membranes increased with increasing temperature and IEC. For the membranes with low IEC (<1.13 mmol g^{-1}), the water uptake values increased moldly with increasing temperature. The membranes with high IEC (>1.13 mmol g^{-1}) exhibited a sharp increase in water sorption at high temperature (above 60 °C), which was partly attributed to the introduction of hydrophilic carboxylic acid groups on the polymer chains. The existence of carboxylic acid groups possibly lead to the formation of continuous ion network in sulfonated copolymers [10,29].

3.5. Morphology analysis

Tapping mode phase image of the acid-form C-SPAEK-4 was recorded under ambient condition on a 500×500 nm size scale to investigate the mirophase-separated structure (Fig. 5). The dark

Table 3
The analytic date of C-SPAEK membranes.

Sample	C-SPAEK membranes						Nafion 117[c]
	0	1	2	3	4	5	
IEC[a] (mmol g^{-1})	0.09	0.36	0.73	1.13	1.38	1.69	–
IEC[b] (mmol g^{-1})	–	0.33	0.69	1.10	1.35	1.63	0.92
Water uptake (%) (25 °C)	5.21	5.27	14.82	17.35	50.17	76.47	22
Water uptake (%) (80 °C)	9.43	9.81	17.91	61.60	169.28	506.90	38
Proton conductivity (S cm^{-1}) (25 °C)	1.51×10^{-3}	1.54×10^{-3}	7.40×10^{-3}	3.56×10^{-2}	7.33×10^{-2}	8.82×10^{-2}	0.08
Proton conductivity (S cm^{-1}) (80 °C)	3.63×10^{-2}	4.67×10^{-2}	0.06	0.12	0.16	0.13	0.10
Methanol permeability (cm^2 s^{-1})	1.10×10^{-8}	1.49×10^{-8}	9.28×10^{-8}	3.83×10^{-7}	8.62×10^{-7}	1.48×10^{-6}	2.38×10^{-6}

[a] IEC obtained by titration.

[b] IEC obtained by calculation from DS.

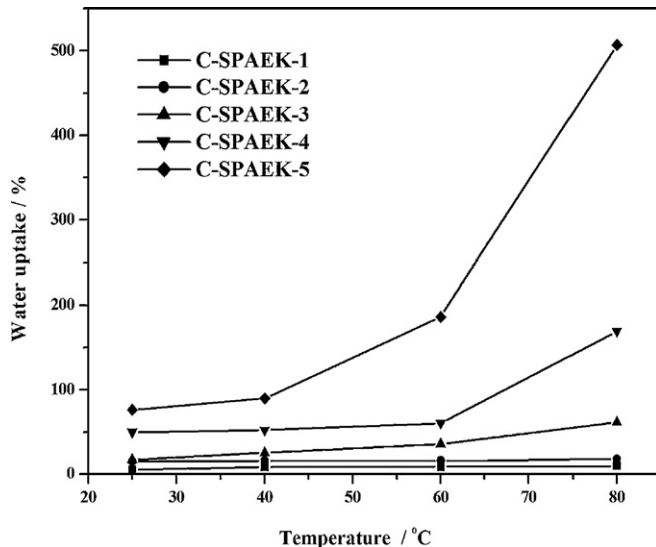[c] Date adapted from Ref. [30].

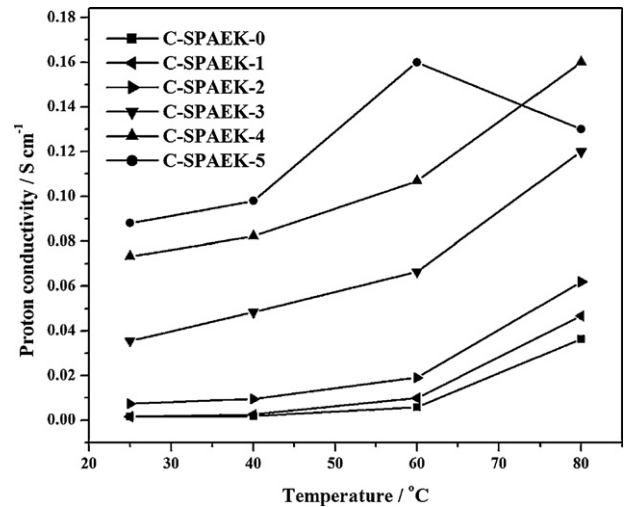**Fig. 4.** Temperature dependence of water uptake of various C-SPAEK membranes.

Fig. 6. Temperature dependence of proton conductivity of the C-SPAEK membranes.

Fig. 5. AFM tapping phase images for acid-form C-SPAEK-4 membrane. Scan boxes are 500 × 500 nm, and phase scale is 2.0°.

regions in the images were assigned to a soft structure, corresponding to the hydrophilic sulfonic and carboxylic acid groups containing water. The bright phases in the images were attributed to a hard structure, corresponding to hydrophobic polymer matrix. The ionic clusters with an average size 22 nm connected to each other to form proton conducting paths. This image provided a direct evidence of a biphasic-morphology for this type C-SPAEK membrane.

3.6. Proton conductivity

Proton conductivities of these C-SPAEK membranes were measured in water in the temperature range of 25–80 °C. As expected, proton conductivity depends significantly on IEC, water uptake and temperature (Table 3). Fig. 6 shows the temperature dependence of the proton conductivity. C-SPAEK copolymers with high DS showed high proton conductivity probably due to their higher water uptake and improved microphase separated structure. For example, the proton conductivity of C-SPAEK-4 membrane increased from 0.07 to 0.16 S cm^{-1} with temperature increasing from 25 to 80 °C, which was well agreement with its water uptake. The water uptake of C-SPAEK-4 membrane increased more obviously with temperature than that of Nafion 117 especially at high temperature (Table 3). With the temperature increasing, the molecular mobility increases and the water molecules can easily penetrate through the polymer backbone and hydrate a maximum number of sulfonic and carboxylic acid groups, which further leads to high proton conductivity at high temperature. However, excess water content dilutes the proton concentration in the membrane, thus resulting in a sharp decrease of the proton conductivity of C-SPAEK-5 membrane
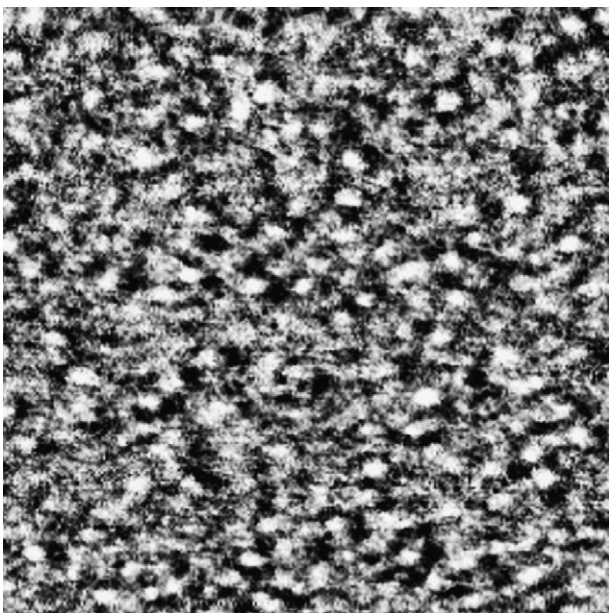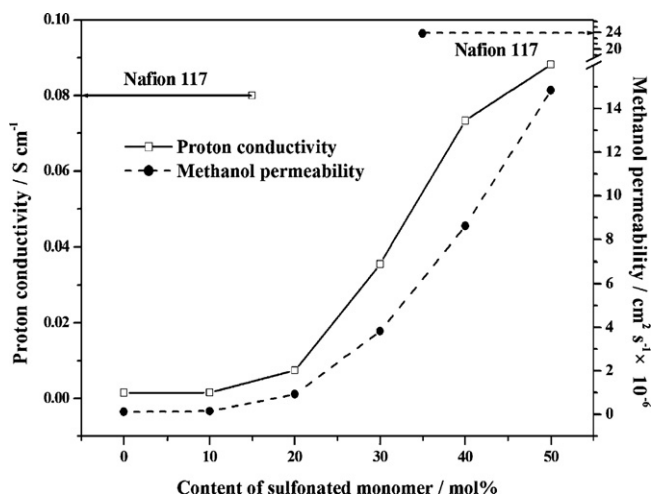
Fig. 7. Methanol permeability (at 25 °C) and proton conductivity (at RH 100%, 25 °C) as a function of the content of sulfonated monomer (m).

above 60 °C. On the other hand, microphase-separated structure is another important reason for their high proton conductivity. As mentioned above, the carboxylic acid groups are locked on the flexible aliphatic side chains of the copolymers, which can interact with sulfonic acid groups easily to form define hydrophilic domains. Especially at high temperature, the mobility of the flexible aliphatic side chains increases, consequently they form mirophase-separated structure where the ionic domains connect to each other to form proton conducting pathways [31]. As the result, the introduction of carboxylic acid groups in copolymers lead to a significant increase in proton conductivity and water uptake with increasing temperature.

3.7. Methanol permeability

The methanol permeability of the C-SPAEK membranes at room temperature are shown in Table 3. The membranes exhibited methanol permeability in the range of 1.10×10^{-8} to 1.48×10^{-6} cm² s⁻¹, which were all much lower than that of Nafion 117 (2.38×10^{-6} cm² s⁻¹). As reported previously [32,33], it appears that both proton conductivity and methanol permeation take place through the same pathway in the membranes as have the similar changing trend depending on DS. As shown in Fig. 7, both the methanol permeability and proton conductivity of the membranes increased linearly up to 20 mol% sulfonated monomer content, then a sudden increase was observed above 20 mol% sulfonated monomer content. This is referred to as the "percolation threshold" [22]. In general, the introduction of hydrophilic moieties on the polymer chains, such as carboxylic and sulfonic acid groups can increase the water content of the membranes, which will lead to enlarging the hydrophilic clusters, and also methanol molecules as well as proton can pass through these hydrophilic domains [34]. C-SPAEK-3 (IEC = 1.13 mmol g⁻¹) and C-SPAEK-4 (IEC = 1.38 mmol g⁻¹) membranes exhibited high proton conductivity and low methanol permeability and could be promising materials for DMFC application.

4. Conclusions

A series of novel sulfonated poly(arylene ether ketone)s containing pendant carboxylic acid groups with different DS were successfully synthesized by aromatic nucleophilic substitution polycondensation. ¹H NMR spectra was used to confirm the DS of

the copolymers. All C-SPAEK membranes in acid form possessed good thermal stabilities and mechanical properties. Carboxylic acid groups increased the hydrophilic ability of the copolymers, which resulted in the high water uptake values of the membranes. AFM observations suggested that the copolymer with high DS showed improved nanophase separation. High water uptake and improved micropahse separated morphology which was formed by the interactions of carboxylic and sulfonic acid groups were favorable for high proton conductivity. Take C-SPAEK-3 and C-SPAEK-4 membranes for example, their conductivity reached up to 0.12 and 0.16 S cm⁻¹ at 80 °C, respectively, which were all higher than that of Nafion 117 (0.10 S cm⁻¹) at the same measuring condition. This result demonstrated they probably were promising in DMFCs application. In addition, these kinds of C-SPAEK copolymers have reactive carboxylic acid groups which can react with crossing agent containing a hydroxyl or amide group to form a crossing membrane material, consequently increases their mechanical properties and decreases their water uptake as well as methanol permeability.

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