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Fluorenyl-containing sulfonated poly(aryl ether ether ketone)s (SPFEEKK) for fuel cell applications[☆]

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Abstract

A series of fluorenyl-containing sulfonated poly(aryl ether ether ketone)s (SPFEEKK) were synthesized via aromatic nucleophilic substitution polymerization. The sulfonation content (SC) was controlled by the feed ratios of sulfonated and nonsulfonated monomers. Flexible and strong membranes in the sulfonic acid form were obtained from cast membranes in the sodium salt forms by treatment with acid. The thermal properties, water uptake, swelling ratio, water state, oxidative stability, proton conductivity and methanol permeability were investigated. All the polymers had proton conductivities greater than 1×10^{-2} S/cm at room temperature, and the conductivity values of *m*-SPFEEKK-80 and *p*-SPFEEKK-80 were up to 1.86×10^{-1} and 1.78×10^{-1} S/cm at 100 °C. This series of polymers also possessed good dimensional stability in water and low methanol crossover.

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Keywords: Fuel cell; Proton exchange membrane; Sulfonation; Poly(ether ketone)s; Polymerization

1. Introduction

Proton exchange membrane fuel cells (PEMFC)s are promising clean power sources for automotive and portable applications [1,2]. Nafion[®], which is comprised of a perfluorosulfonic acid structure, is the principal material used as the polymeric electrolyte in PEMFC systems because of its excellent chemical and mechanical stabilities, and high proton conductivity. However, high cost, low operation temperature and high methanol crossover of Nafion and other similar perfluorinated membranes have limited their widespread commercial application in PEMFC. Currently, there is much research on developing non-perfluorinated polymers with better performance and lower cost as alternative proton exchange membrane (PEM) materials [3–6]. Aromatic polymers with sulfonic acid groups are regarded

as promising materials for PEMs because of their high thermal and chemical stability. Sulfonated derivatives of poly(ether ether ketone) (SPEEK) [7–11], poly(ether sulfone) (SPES) [12–14], polyimide (SPI) [15–17], poly(arylene ether) [18,19] and poly(phenylquinoxaline) [20] are among those being investigated as potential PEMs. However, further work is required in designing polymeric structures to obtain improvements in hot water dimensional stability and methanol resistance for materials with good proton conductivities.

Aromatic poly(ether ketone)s (PEKs) are well known as high performance thermoplastics for their overall combination of chemical, physical and mechanical properties [21,22]. As an important commercial polymer of the PEK family, aromatic poly(ether ether ketone ketone) (PEEKK) containing rigid ketone linkages show high glass transition temperature, excellent thermal stability and high strength modulus. For their relatively rigid backbones, PEEKK polymers even with bulky pendants showed improved solvent-resistant properties compared with their analogous PEEK polymers [23,24]. From the molecular design viewpoint, the incorporation of long and

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regular ether ether ketone ketone moieties should increase the relative length of nonsulfonated hydrophobic segments and make the hydrophilic segments well dispersed, thereby possibly improving the mechanical properties, and methanol and hot water stability. Most recently, Guiver and co-workers [25] and Na and co-workers [26,27] developed several series of sulfonated polymers comprising ether ether ketone ketone backbones, and several of them have exhibited attractive properties such as good mechanical properties and dimensional stability in water.

The introduction of fluorenyl groups into aromatic polymer chains would enhance the T_g and free volume, improve the solubility but maintain high thermal stability. Recently, sulfonated polyimides [28–30], sulfonated poly(ether sulfone)s [14] and sulfonated PEEKs [31] containing fluorenyl groups that exhibited good thermal and oxidative stability as well as high proton conductivity at elevated temperature were reported.

In order to investigate the effect of polymer structure on their properties and enhance the performance of PEEKK-type polymers, a new series of sulfonated aromatic polymers comprising rigid PEEKK backbones (associated with hot-water stability and low methanol permeability) and bulky pendant fluorenyl groups (associated with free volume, and thereby water uptake and proton conductivity) were prepared by the direct polymerization of sulfonated monomer. The properties relevant to fuel cells were investigated, including thermal and oxidative stability, water uptake, water state, swelling ratio and proton conductivity as well as methanol permeability.

2. Experimental

2.1. Materials

1,4-Bis(4-fluorobenzoyl)benzene (1,4-BFBB, Jilin University, China) and 1,3-bis(4-fluorobenzoyl)benzene (1,3-BFBB, Sigma–Aldrich Ltd.) were recrystallized from 1,2-dichlorobenzene and ethanol, respectively. *N,N*-Dimethylacetamide (DMAc), anhydrous potassium carbonate and toluene were obtained from Sigma–Aldrich Ltd., and used as received. 4,4'-(9-Fluorenylidene)diphenol (FDP) was obtained from Sigma–Aldrich Ltd., and recrystallized from toluene before use. All other solvents were used as received.

2.2. Synthesis of 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (S-BFBB)

The sulfonated monomer, 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene, was synthesized following a reported synthetic procedure [32,33].

FTIR (powder, cm^{-1}): 1659 (C=O), 1093, 1040 (S=O).

^1H NMR: (DMSO- d_6): 8.15 (dd, $J=6.8$ Hz, 2.0 Hz, 1 H), 7.89 (s, 2 H), 7.88–7.84 (m, 1 H), 7.39 (t, $J=8.4$ Hz, 1 H).

^{13}C NMR: (DMSO- d_6): 193.83, 161.40 ($J=257.9$ Hz), 140.07 ($J=17.6$ Hz), 133.19 ($J=9.1$ Hz), 131.90, 130.73, 130.08, 116.72 ($J=23.7$ Hz).

2.3. Synthesis of sulfonated poly(aryl ether ether ketone ketone)s in salt form (SPFEEKK-Na)

All the polymers were prepared by polycondensation via typical high-temperature nucleophilic substitution reaction conditions [34,35]. SPFEEKK from 1,4-bis(4-fluorobenzoyl)benzene with sulfonation content (SC) = 1.0 (*p*-SPFEEKK-50) is given as a representative example: 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (1.05 g, 2 mmol), 1,4-bis(4-fluorobenzoyl)benzene (0.65 g, 2 mmol), 4,4'-(9-fluorenylidene)diphenol (1.40 g, 4 mmol), anhydrous K_2CO_3 (0.72 g, 5.2 mmol), toluene (12 mL) and DMAc (12 mL) were added into a 100-mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet and a Dean-Stark trap. The system was allowed to reflux for 3–4 h to remove the water from the reaction system by the azeotropic distillation of toluene. The reaction mixture was then heated to 170–180 °C. Another 5 mL of DMAc were added into the viscous reaction mixture after 12 h at this temperature. The polymerization was complete after a further 3–4 h. The resulting viscous polymer solution was then poured into ethanol. The polymer was thoroughly washed with hot deionized water to remove the salts and solvents, and dried at 100 °C for 48 h.

2.4. Preparation of sulfonated poly(ether ether ketone ketone)s in acid form (SPFEEKK-H)

An amount of 1.0 g polymer in the sodium salt form was dissolved in 20 mL of DMAc and filtered. The filtered solution was poured onto a glass plate and dried at 50 °C under a constant purge of nitrogen for about one week. The film was removed from the plate by immersing it in water until it released. The resulting flexible membrane in sodium form was dried in a vacuum oven at 120 °C for 48 h.

SPFEEKK-H membranes were prepared by immersing SPFEEKK-Na membranes in 2N H_2SO_4 for 48 h at room temperature, and then in deionized water for 24 h, during which time the wash water was changed several times. The thickness of all membrane films was in the range of 60–80 μm .

2.5. Measurements

2.5.1. FTIR and NMR

FTIR spectra of SPFEEKK-Na samples were measured on a Nicolet 520 Fourier transform spectrometer, and a diamond cell was used as a support for the thin films of SPFEEKK-Na polymers and for S-BFBB monomer powder. The thin films for the FTIR measurements were cast from DMAc polymer solution. ^1H and ^{13}C NMR spectra of S-BFBB monomer and SPFEEKK-Na polymers were obtained on a Varian Unity Inova NMR spectrometer operating at frequencies of 399.95 MHz for ^1H and 100.575 MHz for ^{13}C . Deuterated dimethylsulfoxide (DMSO- d_6) was selected as the solvent and the DMSO signals at 2.50 ppm (^1H NMR) and 39.51 ppm (^{13}C NMR) were used as the chemical shift references.

2.5.2. Viscosity, DSC and TGA

Intrinsic viscosities (η_{inh}) were measured using an Ubbelohde viscometer in DMAc solutions of polymers at 30 °C.

A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for evaluating thermal stability of the polymers. Polymer samples for TGA analysis were preheated at 150 °C for 40 min under nitrogen atmosphere to remove moisture. Samples were then heated at 10 °C/min from 50 to 800 °C under nitrogen atmosphere. A TA Instruments differential scanning calorimeter (DSC) model 2920 was used for measuring T_g . Samples for DSC analysis were initially heated at a rate of 20 °C/min under nitrogen atmosphere to the temperature below their decomposition temperature, followed by quenching them to room temperature. Then the samples were heated at a rate of 10 °C/min from 50 to 400 °C under nitrogen atmosphere to evaluate T_g .

2.5.3. Water uptake and swelling ratio

The membrane films were dried at 100 °C overnight prior to the measurements. After measuring the lengths and weights of dry membranes, the sample films were soaked in deionized water for 24 h at predetermined temperatures. Before measuring the lengths and weights of hydrated membranes, the water was removed from the membrane surface by blotting with a paper towel.

The water uptake content was calculated by:

$$\text{Water uptake (\%)} = \frac{\omega_{\text{wet}} - \omega_{\text{dry}}}{\omega_{\text{dry}}} \times 100$$

where ω_{dry} and ω_{wet} are the weights of dried and wet samples, respectively.

The swelling ratio was calculated from films 5–10 cm long by:

$$\text{Swelling ratio (\%)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100$$

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

2.5.4. Oxidative stability and ion exchange capacity (IEC)

Oxidative stability of the SPFEEKK membranes was evaluated by immersing the films into Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C.

IEC of the SPFEEKK polymers was measured using a typical titration method. The films in acid form were equilibrated with 100 mL of 0.1 M NaCl for 24 h. The amount of the H⁺ released from the membranes was determined by titration of 0.01 M NaOH aqueous solution and phenolphthalein as an indicator.

2.5.5. Bound and free water

The study of water states of the SPFEEKK-H membranes was performed on a DSC 2920 thermal analyzer with a DSC module, purged with nitrogen and quenched with liquid nitrogen. The cell was calibrated using an indium standard. The bound (non-freezing) and freezing water of the SPFEEKK membranes in a fully hydrated state was determined by DSC.

A hydrated SPFEEKK membrane was hermetically sealed in a sample pan. The empty sample pan and the sealed pan were weighed, respectively. The sealed pan was quickly frozen inside the DSC chamber to -50 °C and several minutes were allowed for the system to come to equilibrium. Then, the sample holder assembly was heated up to 50 °C using a heating rate of 2 °C/min.

Calculation of the amount of free water in the membrane was done by integrating the peak area of the melt endotherm. The degree of crystallinity of the water, obtained from the heat of fusion of pure water, 334 J/g, was used as a standard [36,37].

2.5.6. Proton conductivity

The proton conductivities of SPFEEKK-H membranes were estimated from ac impedance spectroscopy data, obtained over a frequency range of 1–10⁷ Hz with oscillating voltage of 100 mV, using a Solartron 1260 gain phase analyzer. Specimens in the form of 20 mm × 7 mm strips were soaked in deionized water for at least 24 h prior to the test. Each specimen was placed in a temperature controlled cell open to the air by a pinhole, where it was equilibrated at 100% RH at ambient pressure. Each end of the membrane strip was clamped in a frame between two stainless steel electrodes. Measurements, in two-point mode, were carried out after sample conditioning in the closed cell overnight or longer. The conductivity (σ) of the samples in the longitudinal direction was calculated, using the relationship $\sigma = L/(R \times d \times W)$, where L is the distance between the electrodes, d and W are the thickness and width of the sample stripe, respectively. R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the $Re(Z)$ axis, as explained in Section 3.

2.5.7. Methanol permeability

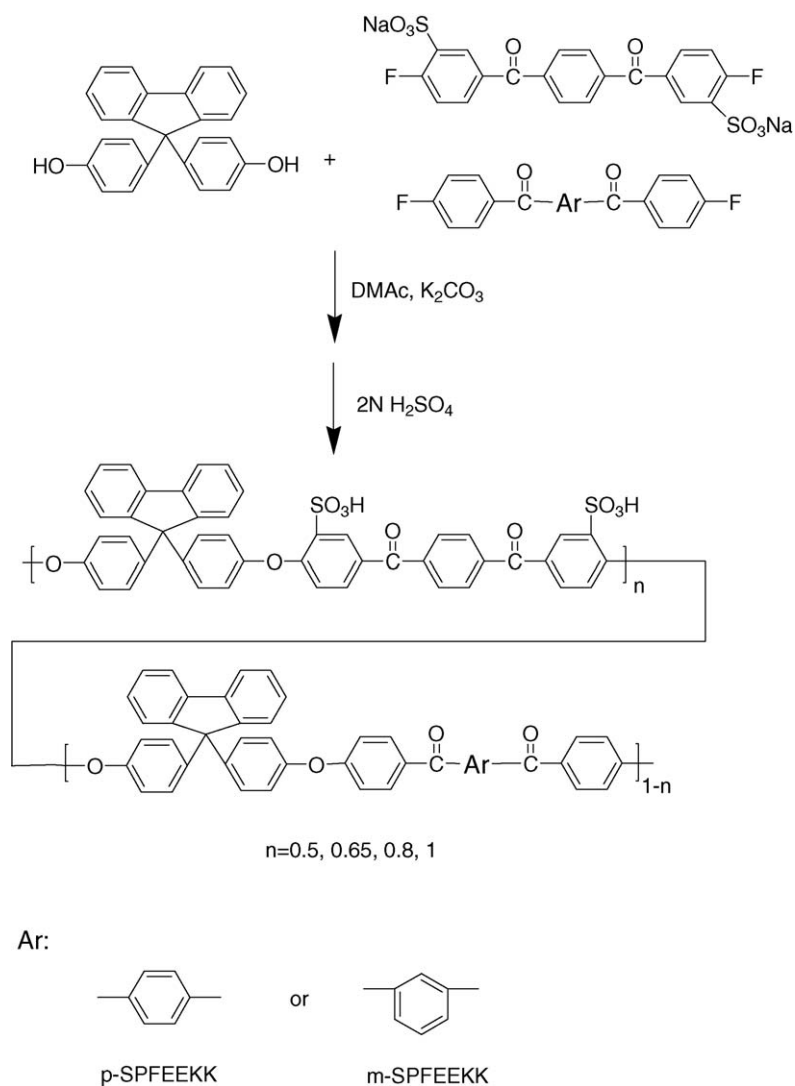
Methanol permeability was measured using a simple two compartment glass diffusion cell. A membrane (2 cm × 2 cm) was placed between two silicone rubber gaskets and with the two compartments clamped together around the gaskets. The active area of the membrane was 1.757 cm². Compartment A was filled with 100 mL of 10% (v/v) (2.47 M) methanol with an internal standard of 0.2% (v/v) (0.022 M) 1-butanol in aqueous solution. Compartment B was filled with 100 mL of 0.2% (v/v) 1-butanol solution.

The diffusion cell was placed in a water bath held at 30 °C and each compartment was stirred by a separate stir plate to ensure uniform stirring. Samples (4 μ L each) were removed from compartment B at intervals of approximately 15 min each. Methanol concentrations were determined by gas chromatography using an HP 6890 gas chromatograph with a mass selective detector (HP 5973).

3. Results and discussion

3.1. Synthesis and structure of polymers

A sulfonated monomer, 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene, was synthesized via an electrophilic reaction using fuming sulfuric acid (30%) as the sulfonation agent at 100 °C for 24 h [32,33]. ¹H and ¹³C NMR results showed



Scheme 1. Preparation of SPFEEKK polymers.

that the substitution reaction occurred exclusively on the position *ortho* to the fluorine atoms and that there was no evidence of sulfonation of the benzene ring connected with two carbonyl groups, even after an extended reaction time of 48 h at 100 °C.

Copolymerization of a bisphenol, 4,4'-(9-fluorenylidene)diphenol, with sulfonated difluoro-monomer, 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene, and activated nonsulfonated difluoro-monomer, 1,4-bis(4-fluorobenzoyl)benzene or 1,3-bis(4-fluorobenzoyl)benzene was carried out in the presence of K_2CO_3 in DMAc as the solvent at 170–180 °C after removing the water from the reaction system by the azeotropic distillation of toluene, as shown in Scheme 1. The SC of the polymers were controlled by the monomer feed ratios. Generally, the polymerization conditions for commercial PEEKTM (Victrex[®]) and PEEKKTM (Hostatec[®]) are extremely vigorous including high temperature (>300 °C), because of their tendency for crystallization that leads to precipitation at the initial stage of polymerization. In the present case of this polymerization, high molecular weight polymers were readily

obtained under relatively mild polymerization conditions due to the improved solubility brought about by the incorporation of bulky fluorenyl moieties into the polymer backbone. The inherent viscosities of the resulting polymers were in the range of 0.92–2.17 dL/g in DMAc at 30 °C (Table 1).

High-temperature polymerization reactions occasionally lead to a dissociation of sulfonated groups, and FTIR is a convenient way to confirm their presence. A typical FTIR spectral comparison of the polymers with different SC is given in Fig. 1. Absorption bands around 1028 and 1085 cm^{-1} arise from symmetric and asymmetric stretching vibrations of sodium sulfonate groups, that around 1478 cm^{-1} arises from trisubstitution of benzene rings caused by the introduction of sodium sulfonate groups, and a characteristic band at around 1656 cm^{-1} due to aryl carbonyl groups were observed. Absorptions at 1028, 1085 and 1478 cm^{-1} increased obviously with the increase of SC.

All the SPFEEKK polymers were soluble in common polar solvents such as *N,N*-dimethylformamide (DMF), DMAc, *N*-methyl-2-pyrrolidone (NMP) and dimethylsulfoxide (DMSO),

Table 1
Inherent viscosities and sulfonation contents of SPFEEKK copolymers

Polymer	Feed ratio ^a (mol%)	Theoretical SC	IEC (mmol/g (meq/g)) calculated	IEC (mmol/g (meq/g)) experimental	η_{inh} (dL/g)
<i>m</i> -SPFEEKK-50	50/50/100	1.0	1.40	1.39	1.17
<i>m</i> -SPFEEKK-65	65/35/100	1.3	1.76	1.72	0.92
<i>m</i> -SPFEEKK-80	80/20/100	1.6	2.10	2.08	0.95
<i>p</i> -SPFEEKK-50	50/50/100	1.0	1.40	1.38	2.17
<i>p</i> -SPFEEKK-65	65/35/100	1.3	1.76	1.74	1.30
<i>p</i> -SPFEEKK-80	80/20/100	1.6	2.10	2.06	0.95
SPFEEKK-100	100/0/100	2.0	2.52	2.43	2.10

^a Feed ratios of the monomer: S-BFBB/1,4-BFBB (or 1,3-BFBB)/FDP.

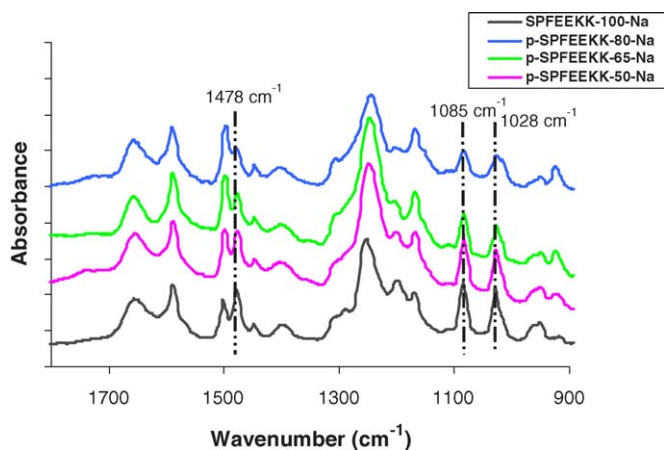


Fig. 1. FTIR spectra of *p*-SPFEEKK-50, -65, -80 and SPFEEKK-100 in their sodium forms.

and could be well characterized by NMR spectroscopy. Fig. 2 shows the ¹H NMR aromatic region for SPFEEKK-100-Na and *p*-SPFEEKK-65-Na. The proton signals for the homopolymer with 100% sulfonated monomer were easily assigned using homonuclear decoupling experiments on protons from the same spin systems. The spectrum of the 65% sulfonated copolymer shows the same signals arising from sulfonated repeat units and additional signals resulting from the un-sulfonated repeat units.

Table 2
TGA results of SPFEEKK copolymers

Polymer	T_{d5} (°C) ^a		T_{d10} (°C) ^b		T_d (°C) ^c		RW (%) ^d	
	-Na	-H	-Na	-H	-Na	-H ^e	-Na	-H
<i>m</i> -SPFEEKK-50	510	363	522	496	503	293/512	71.49	69.57
<i>m</i> -SPFEEKK-65	494	369	512	458	496	299/507	68.54	69.74
<i>m</i> -SPFEEKK-80	499	370	515	433	495	314/502	67.22	70.66
<i>p</i> -SPFEEKK-50	512	398	523	512	502	315/502	70.39	70.81
<i>p</i> -SPFEEKK-65	503	378	523	487	500	300/502	74.46	69.60
<i>p</i> -SPFEEKK-80	496	377	518	458	486	311/498	72.60	70.32
SPFEEKK-100	486	378	512	438	471	320/491	74.86	67.63

^a 5% weight loss temperature measured by TGA.

^b 10% weight loss temperature measured by TGA.

^c Onset temperature of decomposition.

^d Residue weight at 700 °C in N₂.

^e Decomposition temperature of polymers in acid form: the first stage/second stage.

3.2. DSC and TGA study

The thermal properties of the polymers in acid form (-H) and sodium form (-Na) were evaluated by DSC and TGA. No obvious glass transitions and melting endotherms were observed in the DSC traces of SPFEEKK polymers probably because of their aromatic rigid backbones and strong interaction between molecular chains caused by polar sulfonation groups.

A distinct two-stage decomposition was observed from the TGA curves of all of the sulfonated poly(ether ether ketone)s in acid form (SPFEEKK-H) (Fig. 3). The initial decomposition is generally associated with the loss of the sulfonic acid groups in the range of 293–320 °C, and the main loss is the result of polymer chain decomposition in the range of 491–512 °C. Compared with the SPFEEKK polymers in acid form, the SPFEEKK-Na series had high thermal stabilities with decomposition temperatures (T_d) above 471 °C and 10% weight loss temperatures (T_{d10}) above 512 °C in N₂ (Table 2).

3.3. Water uptake, swelling ratio and water states

Water uptake and swelling ratios of PEMs are closely related to SC, proton conductivity and mechanical strength. The water within the membrane provides a carrier for the proton, and maintains high proton conductivity. However, excessive water uptake in a PEM will lead to unacceptable dimensional change or loss of dimensional shape, which could lead to weakness or a

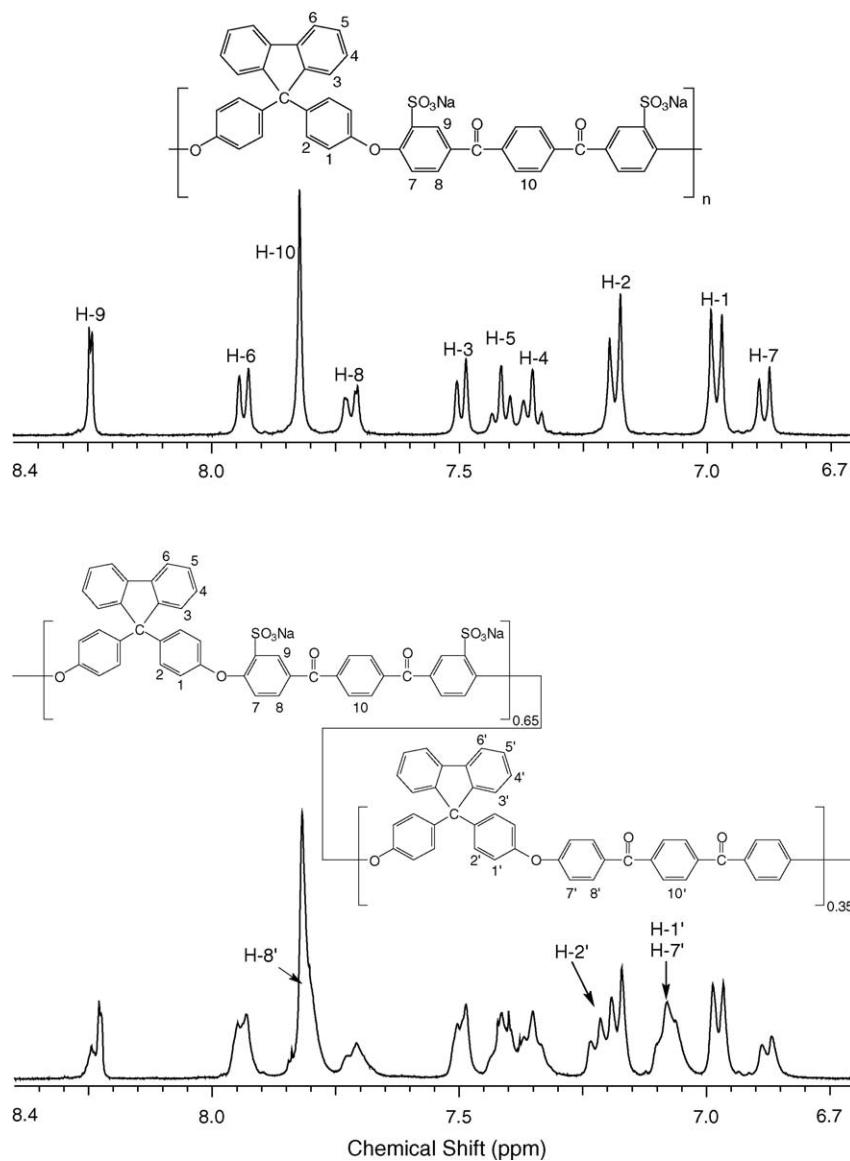


Fig. 2. ^1H NMR spectra of SPFEEKK-100-Na and *p*-SPFEEKK-65-Na in $\text{DMSO-}d_6$.

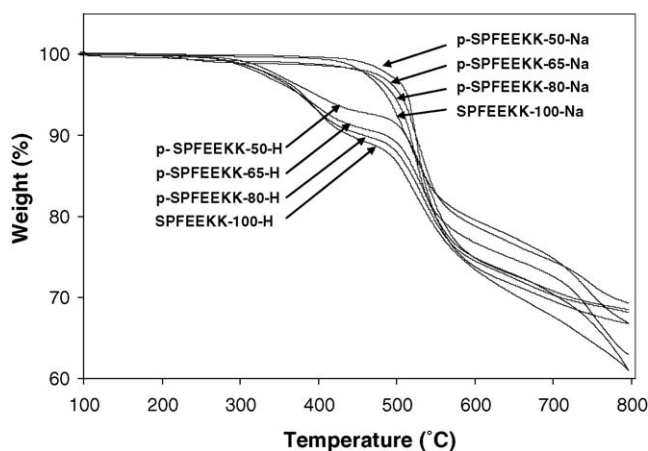


Fig. 3. TGA curves of SPFEEKK polymers under nitrogen.

dimensional mismatch when incorporated into a membrane electrode assembly (MEA). Therefore, the preparation of sulfonated polymers with ideal water uptakes and dimensional stability are one of the critical demands for their application as PEMs. The water uptake and swelling ratios of SPFEEKK copolymer membranes were measured at different temperatures, and the results are listed in Table 3 and shown in Fig. 4. The films were immersed in water at room temperature (21°C) for 24 h, after which time all the polymers had swelling ratios below 16.1%, and water uptakes less than 22.2%. At 80°C , *m*-SPFEEKK-50, -65, -80 and *p*-SPFEEKK-50, -65, -80 maintained their dimensional shapes, and SPFEEKK-100 was highly swollen. As expected, almost all the *p*-SPFEEKK membranes with more regular backbones had relatively lower water uptakes than *m*-SPFEEKK membranes especially at higher test temperatures. At 100°C , *m*-SPFEEKK-80 showed much higher water uptake and swelling ratio than the corresponding *para* copolymer. It is

Table 3
Water uptake, swelling ratio and proton conductivities of SPFEEKK copolymers at different temperatures

Polymer	Swelling ratio (%)			Water uptake (%)			σ (S/cm)		
	21 °C	80 °C	100 °C	21 °C	80 °C	100 °C	21 °C	80 °C	100 °C
<i>m</i> -SPFEEKK-50	7.3	7.9	8.0	5.4	9.5	10.3	0.010	0.038	0.064
<i>m</i> -SPFEEKK-65	12.1	15.9	18.0	7.8	16.2	17.5	0.033	0.100	0.139
<i>m</i> -SPFEEKK-80	14.1	16.9	48.5	15.5	26.5	97.6	0.043	0.127	0.186
<i>p</i> -SPFEEKK-50	6.9	8.6	8.7	6.1	7.0	8.2	0.011	0.036	0.051
<i>p</i> -SPFEEKK-65	12.1	14.5	16.1	13.4	15.6	16.7	0.030	0.094	0.145
<i>p</i> -SPFEEKK-80	13.4	22.2	27.2	19.1	23.5	37.1	0.041	0.119	0.178
SPFEEKK-100	16.1	–	–	22.2	–	–	0.095	0.220	–

noteworthy that *m*-SPFEEKK-50, -65 and *p*-SPFEEKK-50, -65 maintain their low water uptakes and dimensional shape even at 100 °C. This suggests they could be operated at elevated temperatures.

It is reported that an important reason for the higher methanol permeability for Nafion is its higher fraction of freezing bound and free water to total water [38]. Generally, a low fraction of free water in membranes leads to a low electro-osmotic drag under fuel cell operation, resulting in low methanol crossover

[39]. Therefore, the study of the state of water in the membranes might be informative.

Generally, the state of water in the polymer can be distinguished into free water, freezing bound water and non-freezing bound water [36,40]. Water molecules that are strongly associated with ionic and polar sites in the polymer chain are defined as non-freezing bound water, and cannot be detected by DSC. In addition, there are two types of freezing water, namely freezing bound water, which is defined as water that has a phase transition temperature less than 0 °C, and arises from a weaker interaction with the ionic and polar polymer sites and bulk water, and free water, which is seemingly unaffected by the polymer matrix.

Fig. 5 shows the typical DSC heating curves of membranes after being fully swollen. Quantification of each state of water by DSC is obviously of great interest but is difficult not only because of the two overlapping melting peaks but also because the heat of fusion of the absorbed water is not constant in these systems and varies with the strength of interaction between the water and copolymer [38]. It has been suggested that only non-freezing water exists in the polymer network up to a certain

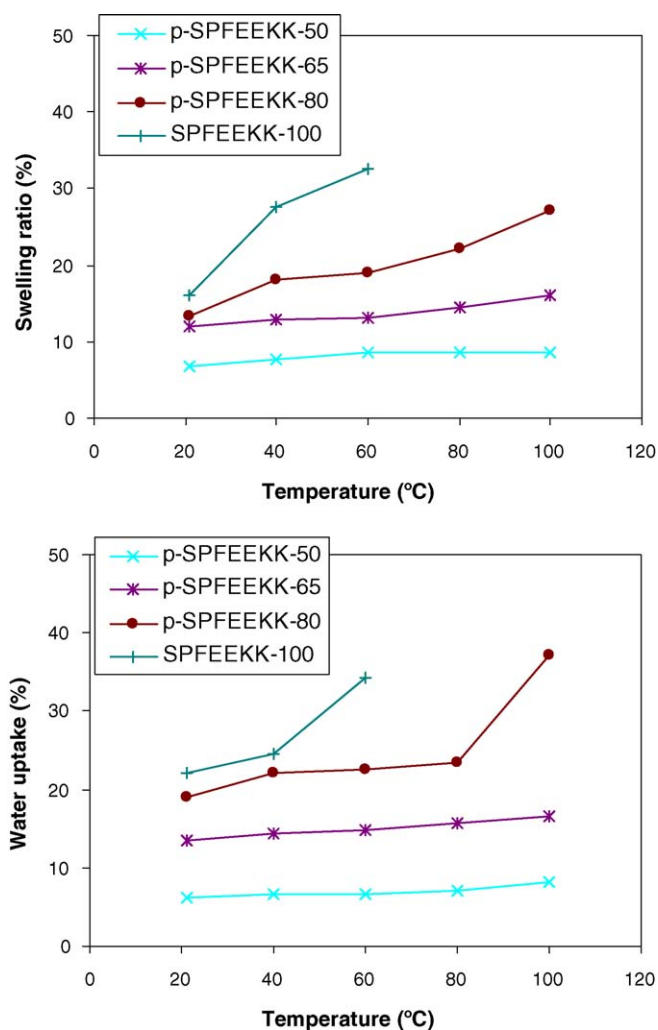


Fig. 4. Swelling ratio and water uptake of *p*-SPFEEKK copolymers and SPFEEKK-100.

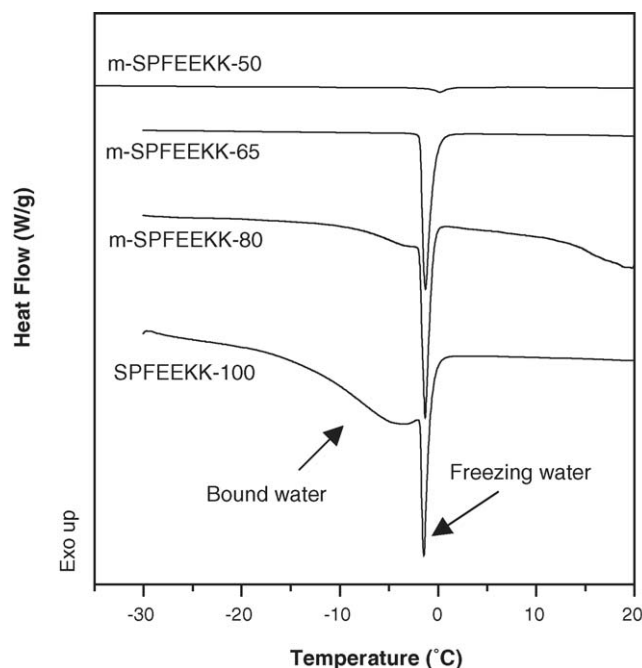


Fig. 5. DSC melting curves of swollen SPFEEKK membranes.

Table 4
Characterization of water content and fraction of each state of water in the membranes

Polymer	Water content (%)			λ [H ₂ O]/[SO ₃ H]		
	Total	Bound water	Freezing water	Total	Bound water	Freezing water
<i>m</i> -SPFEEKK-50	5.4	4.9	0.5	2.2 (1.00) ^a	2.0 (0.91) ^b	0.2 (0.09) ^c
<i>m</i> -SPFEEKK-65	7.8	5.9	1.9	2.5 (1.00)	1.9 (0.76)	0.6 (0.24)
<i>m</i> -SPFEEKK-80	15.5	9.9	5.6	4.1 (1.00)	2.6 (0.64)	1.5 (0.36)
<i>p</i> -SPFEEKK-50	6.1	5.6	0.5	2.5 (1.00)	2.3 (1.00)	0.2 (0.08)
<i>p</i> -SPFEEKK-65	13.4	11.0	2.4	4.3 (1.00)	3.5 (0.82)	0.8 (0.18)
<i>p</i> -SPFEEKK-80	19.1	12.2	6.9	5.2 (1.00)	3.3 (0.64)	1.9 (0.36)
SPFEEKK-100	22.2	12.5	9.7	5.1 (1.00)	2.9 (0.56)	2.2 (0.44)

Fraction of each state of water:

^a [λ of total water]/[λ of total water].

^b [λ of bound water]/[λ of total water].

^c [λ of freezing water]/[λ of total water].

percentage of water uptake before freezing water can be detected [37]. In the SPPFEKK system, the peak of freezing water (freezing bound or free water) at *m*- and *p*-SPFEEKK-50 is very small to be detected by DSC due to low water content. The *m*-SPFEEKK-80 and SPFEEKK-100 membranes exhibit two endothermic peaks, suggesting the existence of two states of freezing water. The peak below 0 °C in these membranes corresponds to the melting of freezing bound water, whereas the peak near 0 °C corresponds to the free water. Table 4 shows the water content corresponding to the freezing water and bound water as well as to the total water contents. Also, we calculated the number of water molecules per sulfonic acid group (λ , mol H₂O/mol SO₃H), and normalized the fraction of each state of water. In comparison with Nafion 117, the values of λ of the *m,p*-SPFEEKK membrane ($\lambda = 2.2$ – 5.2) were lower than that of Nafion 117 ($\lambda = 16$ – 20) [41,42]. Although the IECs of the *m,p*-SPFEEKK membranes were higher than that of Nafion 117 (IEC = 0.91), the water content of the *m,p*-SPFEEKK membranes were much lower than that of Nafion 117. Copolymers with high water content may be vulnerable to changes in the membrane morphology during drying and swelling [41]. It is a general tendency that a high content of sulfonated monomer induces a high level of bound water because bound water is derived from strong interactions between polar groups in the polymer chains and water molecules. As shown in Table 4, the bound water content increased with increasing sulfonated monomer. However, from the viewpoint of the fraction of bound water, the results were somewhat different. The fraction of bound water in the membranes decreased with increasing sulfonated monomer, whereas the fraction of freezing water ([λ of freezing water]/[λ of total water]) of the *m,p*-SPFEEKK membranes increased with increasing the sulfonated monomer. This suggests that with increasing sulfonated monomer, the free volume that can associate with the freezing water molecules increases more than the ionic sites that can hydrogen bond with bound water in the polymer structure. Here, we can expect that the methanol permeabilities of the SPFEEKK membranes would increase with increasing SC due to the high fraction of freezing water. However, in comparison with the fraction of freezing water content, the *m*, or *p*-SPFEEKK membranes showed a high the fraction of bound water content. Water molecules bind

strongly to ionic and polar sites on the polymer chains. A high bound water content would be an attractive membrane characteristic when employed in DMFCs [38,42]. Therefore, we expect that the SPFEEKK membranes may be desirable for use in DMFC applications.

3.4. Oxidative stability

The oxidative stability of the polymers was evaluated in Fenton's reagent at 80 °C. This method is regarded as one of the standard tests to gauge relative oxidative stability and to simulate accelerated fuel cell operating conditions [8].

In general with a polymer series, a higher SC leads to lower oxidative stability. As expected, SPFEEKK-100 membrane with high IEC value (2.43 mmol/g (2.43 meq/g)) was dissolved into the Fenton reagent in 10 min, and *m,p*-SPFEEKK-65 membranes were almost dissolved into reagent after 3 h of treatment. The membranes of *m*-PEEKK-50 (IEC = 1.39 mmol/g (1.39 meq/g)) and *p*-SPFEEKK-50 (IEC = 1.38 mmol/g (1.38 meq/g)) had relatively good oxidative stability and they maintained dimensional shapes until they broke into pieces by shaking after 3 h. They could not be dissolved in the reagent even after 10 h, which indicating their relatively higher oxidative stability [8,14].

3.5. Proton conductivity and methanol permeability

The proton conductivities of the membranes were estimated using impedance diagrams, acquired in the frequency range of 1– 10^7 Hz. In Fig. 6(a), an example of such a diagram, representative for all measured samples, is shown for samples *p*-SPFEEKK-80 and SPFEEKK-100. It can be seen from this figure that the response comprises a suppressed semicircle in the high frequency domain and a straight line at lower frequencies. This behavior is typical for an electrolyte, whose bulk resistance is responsible for the high frequency semicircle and the low frequency reaction is controlled by the diffusion of charged species with some impact of electrode polarization (slope angle of the line >45°). The diameter of the semicircle (its right side intersection with Z') corresponds to membrane bulk dc resistance, as the imaginary component Z'' at this point is negligible. The Z' values retrieved from these plots were then

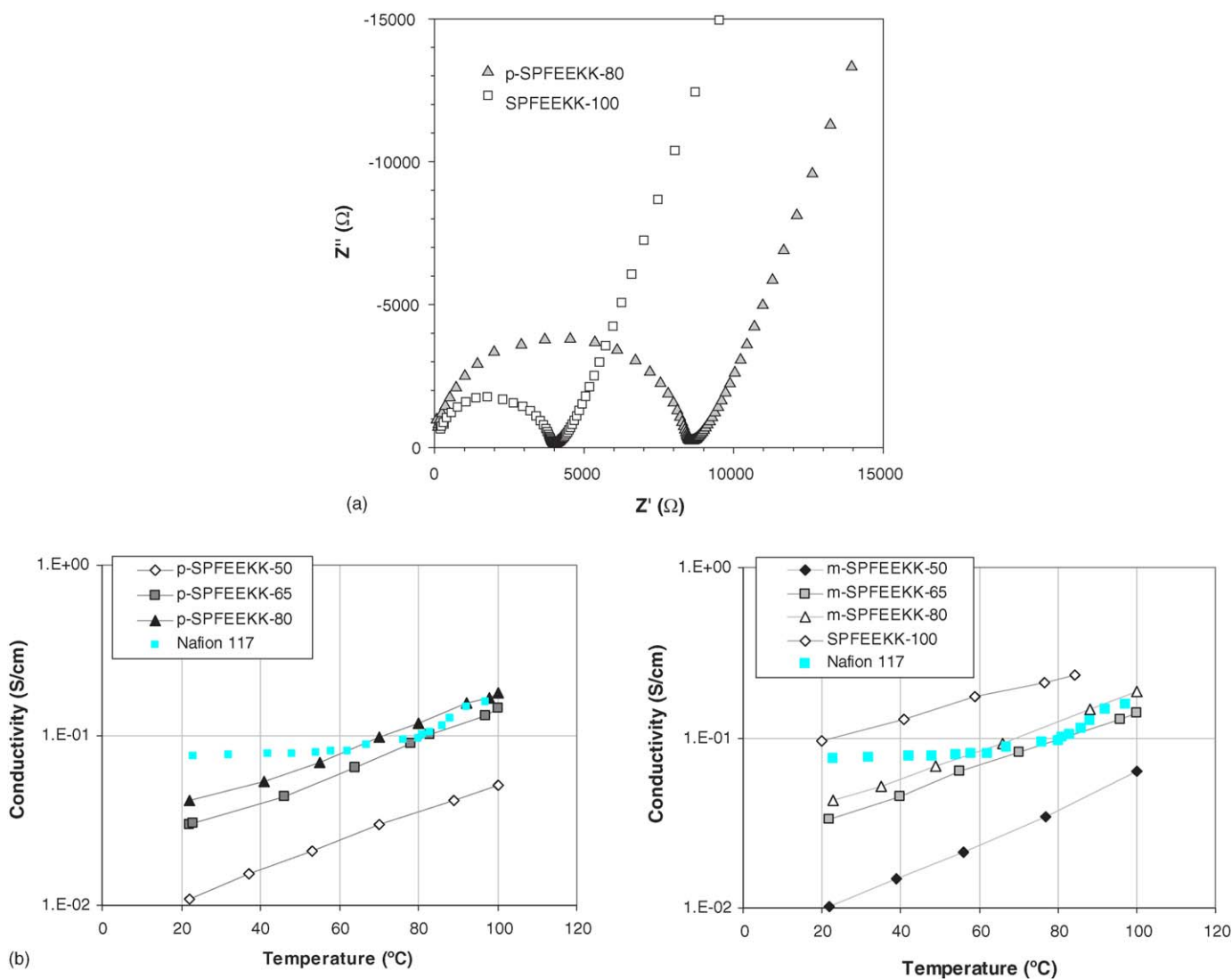


Fig. 6. (a) Complex impedance plots for the samples of p -SPFEEKK-80 and SPFEEKK-100. In the field of the plot the response is shown for frequency range of $1-10^7$ Hz. Conductivities, calculated according to the relation given in Section 2.5.6 are: σ (SPFEEKK-100) = $0.95 \text{ cm}/(4000 \text{ } \Omega \times 0.0045 \text{ cm} \times 0.55 \text{ cm}) = 0.096 \text{ S/cm}$. σ (p -SPFEEKK-80) = $0.95 \text{ cm}/(8480 \text{ } \Omega \times 0.0055 \text{ cm} \times 0.5 \text{ cm}) = 0.041 \text{ S/cm}$. (b) Proton conductivities of SPFEEKK polymers.

converted into conductivities using the membranes' geometrical dimensions. The results, obtained in such a manner for the membranes in SO_3H form are presented in Fig. 6(b) as a function of the temperature. It is seen from the figure that the conductivities of all the samples increase with temperature and if one traces the isotherms of the conductivity, they increase with SC. All the samples exhibited room temperature conductivities higher than 1×10^{-2} S/cm, which is conventionally regarded as the minimum value required for PEM practical application in FC. m -SPFEEKK-65, -80 and p -SPFEEKK-65, -80 membranes exhibited proton conductivities comparable to that of Nafion 117 above 60°C . At 100°C , proton conductivities of m -SPFEEKK-80 and p -SPFEEKK-80 were as high as 1.86×10^{-1} and 1.78×10^{-1} S/cm, surpassing that of Nafion 117. SPFEEKK-100 exhibited still higher proton conductivity, but its applicability in FC is limited by its poor dimensional stability in hot water.

Membranes intended for direct methanol FC (DMFC) must both possess high proton conductivity and to be an effective

barrier for methanol crossover from the anode to the cathode compartment [43]. Among the most significant of Nafion's drawbacks is its high methanol crossover in the DMFC application. This limitation is associated with Nafion microstructure, where interconnected ionic domains strongly contribute to its high proton conductivity, but at the same time contribute to fast methanol diffusion.

In order to compare the methanol permeability of the prepared membranes with that of Nafion 117, the latter was tested under the same conditions. The results of methanol permeability in relation to proton conductivity at room temperature are plotted in Fig. 7 in relation to Nafion. A tradeoff line is also included, which was previously introduced in ref. [43]. As can be seen, all the samples of the SPFEEKK series revealed methanol permeability in the range of 8.17×10^{-8} to $1.02 \times 10^{-6} \text{ cm}^2/\text{s}$ which constitutes a significant reduction compared with Nafion with value of $1.55 \times 10^{-6} \text{ cm}^2/\text{s}$. Both the m -SPFEEKK and p -SPFEEKK series demonstrated an increase in the methanol permeability

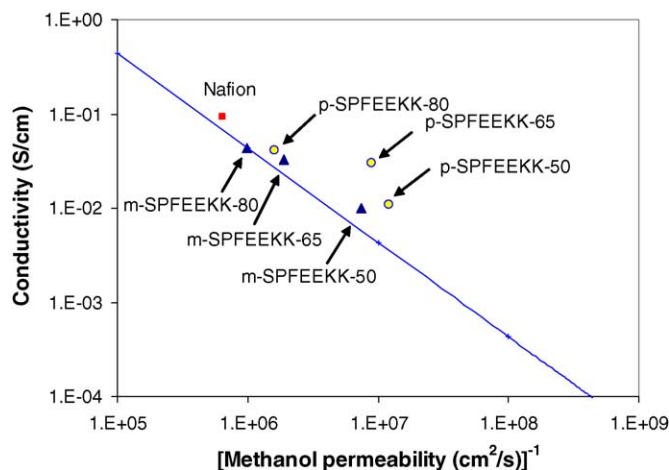


Fig. 7. Proton conductivity (room temperature) vs. the inverse of methanol permeability of SPFEEKK polymers at 30 °C.

with the SC. In comparison with each other, *p*-SPFEEKK series exhibited relatively lower methanol permeability than the corresponding *m*-SPFEEKK membranes. This observation could presumably be explained by the fact that the former have relatively more regular molecular chain structure.

The dimensional stability of *m,p*-SPFEEKK-50 and -65 were tested to further evaluate the potential of these polymers as DMFC materials. At room temperature, the swelling ratios of *m,p*-SPFEEKK-50 were less than 4% in 20% (v/v) methanol and 6% in 50% methanol after 24 h. At higher SC, films of *m,p*-SPFEEKK-65 also had good dimensional stability with swelling ratios of <15% both in 20% and 50% methanol. No obvious dimension deformation of *p*-SPFEEKK-50 (13% swelling ratio in 20% methanol, and 12% in 50% methanol) and *m*-SPFEEKK-50 (14% swelling ratio in 20% methanol, and 28% in 50% methanol) occurred in refluxing methanol for 24 h. The swelling ratios of *p*-SPFEEKK polymers were obviously lower than the corresponding *m*-SPFEEKK polymers either at room temperature or at refluxed temperature, which well supported the results of the methanol permeability.

4. Conclusions

Two series of aromatic poly(ether ether ketone)s containing fluorenyl groups and pendant sulfonic acid functions were prepared via nucleophilic substitution reaction from commercially available monomers. The sulfonic acid content (SC) of each copolymer series was controlled by adjusting the monomer feed ratios. The acid form SPFEEKK-H copolymer films showed good thermal stability, and good oxidative stability in Fenton's reagent at 80 °C. The proton conductivities of the SPFEEKK polymer series were higher than 1×10^{-2} S/cm at room temperature, and above 60 °C (conditions typical for any FC) for specimens with $SC \geq 1.6$, it was comparable to that of Nafion 117. The copolymer series shows a steady more linear increase in conductivity with increasing temperature, compared with Nafion.

SPFEEKK membranes revealed good dimensional stability under mild hydrothermal conditions. For example, *p*-

SPFEEKK-50 and -65 exhibited length-wise dimensional changes of 8.7% and 16.1% at 100 °C and water uptakes of 8.2% and 16.7%, respectively.

The SPFEEKK series are potential materials for DMFC and showed a significant reduction of methanol diffusion compared with Nafion-117. The *p*-SPFEEKK-50 film exhibited the lowest methanol permeability coefficient (10% methanol) of 8.17×10^{-8} cm²/s, and had relatively good proton conductivity when plotted against a performance tradeoff line of conductivity versus the inverse of methanol permeability. The films of *m,p*-SPFEEKK-50 and *p*-SPFEEKK-65 retained their dimensional shape in the presence of methanol solutions, even at elevated temperatures, suggesting their potential for application as PEM materials in DMFC.

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