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Direct synthesis of sulfonated poly(ether ether ketone ketone)s (SPEEKKs) proton exchange membranes for fuel cell application

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Abstract

A series of sulfonated poly(ether ether ketone ketone)s (SPEEKK)s based membranes have been prepared and evaluated for proton exchange membranes (PEM). The membranes show very good thermal and mechanical stabilities. The structures of membranes were studied with AFM. The membranes show very good proton conductive ability (25 °C: 0.007–0.04 s/cm) and methanol resistance (25 °C: 7.68×10^{-8} to 5.75×10^{-7} cm^2/s). The methanol diffusion coefficients of membranes are much lower than that of Nafion (2×10^{-6} cm^2/s). The SPEEKKs membranes show very good respective in direct methanol fuel cells (DMFC) usages.

Keywords: SPEEKK; PEM; Sulfonation

1. Introduction

Proton exchange membrane fuel cells (PEMFC) have received widely investigated as a promising new power source for vehicles and portable devices, due to their low emissions and high conversion efficiency [1–3]. Proton exchange membrane, as proton conductive material is a key component of the PEMFC for transferring protons from the anode to cathode as well as providing a barrier to the fuel gas cross-leaks between the electrodes. The membranes traditionally used in PEMFC are perfluorosulfonic polymers such as Dupont Nafion®. Although, they show superior performance in fuel cells operating at moderate temperatures (<90 °C) and high relative humidity with pure hydrogen as fuel, the high cost, low conductivity at low humidity or high temperature and high methanol permeability of Nafion® have limited their usages [4]. Hence alternative proton exchange membrane materials are being sought [5]. Poly(aryl ether ketone)s (PAEK) are high performance engineering thermoplastic. They have good mechanical properties and high-thermal oxidative stability. Attaching sulfonic acid groups onto PAEKs backbones are of interest for PEM. The hydrophobic domains formed by none sulfonated polymer segments provide the hydrated PEMs with mechanical strength, whereas the hydrophilic domains containing the sulfonic acid groups ensure the proton conductivity. The sulfonated PAEKs have been earlier prepared via modification of the polymer, in which sulfonated groups were achieved on the polymer chain by sulfonating agent such as concentrated sulfuric acid, complex sulfuric trioxide, chlorosulfuric acid and methanesulfuric acid [6]. An attractive alternative approach is the direct copolymerization of sulfonated monomers [7–9]. The direct synthesis of the S-PEEK from sulfonated monomer has been proven more advantageous than that of post-sulfonation [7–9]. Some of the advantages are listed below: (1) Compared with the post-sulfonated PEEK, the concentration as well as the positions of the sulfonate groups (e.g. *meta*-, *para*-, and *ortho*-) within the directly synthesized S-PEEKs can be readily controlled. This allows one to control the degree of sulfonation easily. (2) The direct-sulfonation method avoids the cross-linking and other side reactions [11], which may result in better thermal stability and mechanical properties. In our previous work, sulfonated PEEK polymeric membranes were prepared by direct synthesis of sulfonated monomer and evaluated for fuel cell applications [8]. Poly(ether ether ketone ketone)s (PEEKKs), members of PAEK family, also have excellent properties, including especially good thermal and

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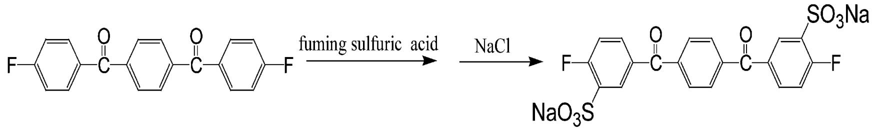


Scheme 1. Preparation of sulfonated monomer.

Table 1
The data of the sulfonated polymers

Polymer	m (mmol)[a]	k (mmol)[a]	m/k	Yield (%)	η_{sp}/c	D_s (t)[b]	D_s (c)[c]	$T_{10\%loss}$ (°C)[d]
SPEEKK-1	8	32	2:8	94	1.29	0.43	0.40	517
SPEEKK-2	16	24	4:6	93	2.04	0.83	0.80	476
SPEEKK-3	20	20	5:5	95	4.24	0.97	1.00	472
SPEEKK-4	24	16	6:4	93	1.12	1.34	1.20	455

[a] The amount of monomer m and monomer k in the reaction.
[b] Sulfonated degree obtained by titration.
[c] Sulfonated degree obtained by calculation.
[d] The 10% weight loss of temperatures.

mechanical properties in comparison with PEEK. In this study, sulfonated PEEKKs (SPEEKKs) membranes were prepared by the method of direct synthesis of sulfonated monomer and evaluated for fuel cell applications.

2. Experimental

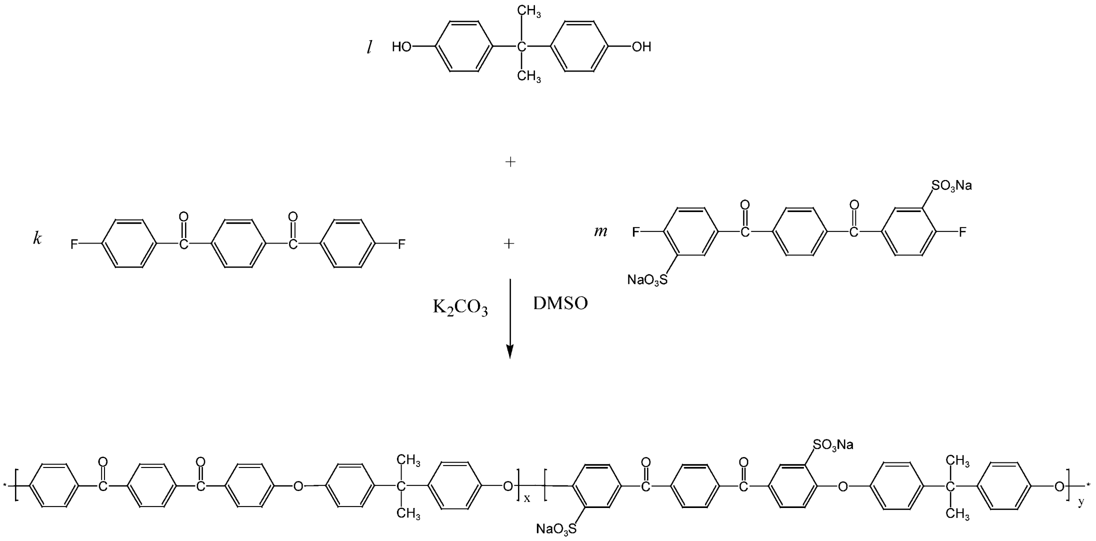
2.1. Membrane preparation

2.1.1. Monomer synthesis

The synthesis of sulfonated monomer (1,4-bi (3-sodium sulfonate-4-fluorobenzoyl) benzene) had accorded to a procedure described in our previous work [9,10]. As shown in Scheme 1, the 1,4-bi (4-fluorobenzoyl) benzene was first sulfonated with fuming sulfuric acid, followed by neutralizing with NaOH and precipitating with NaCl. The crude product was recrystallized with the mixture of methanol and water. The yield of this monomer was 81%. The chemical structure was confirmed by FT-IR and ^{1}H NMR. IR (KBr, cm^{-1}): 1656 (C=O), 1211, 1093, 621 (Ar–SO_3Na). ^{1}H NMR (500 MHz, DMSO, ppm): 8.12–8.15 (dd, 2.3 Hz, 4.5 Hz), 7.87 (s) 7.81–7.84 (m, 2.5 Hz, 2.0 Hz, 5.3 Hz), 7.34–7.38 (dd, 5.3 Hz, 5.3 Hz). ^{13}C NMR (500 Hz, DMSO, ppm): 194.74, 163.34, 161.29, 141.01, 133.98, 133.91, 132.81, 131.66, 130.29, 117.53.

2.1.2. Polymer synthesis

As shown in Scheme 2, sulfonated PEEKKs were synthesized via the nucleophilic aromatic substitution reactions of the following monomers: 1,4-bi (4-fluorobenzoyl) benzene (monomer k), 1,4-bi (3-sodium sulfonate-4-fluorobenzoyl) benzene (monomer m), and 4,4′-dihydroxydiphenyl propane (monomer l). The degree of sulfonation (D_s), which is the number of sulfonated groups per repeating unit was controlled by adjusting the ratio of monomer m to



Scheme 2. The synthesis of SPEEKKs polymers.

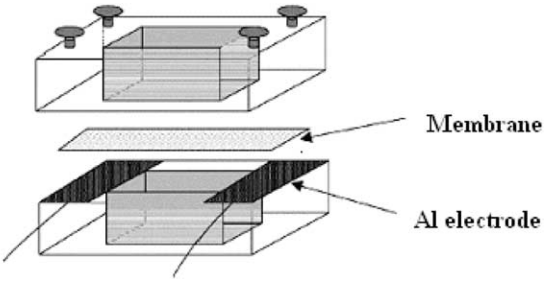


Fig. 1. Set up for conductivity measurement.

monomer *k*. In this reaction, the monomer *l* was fixed at 100 mmol, which is equal to the total amount of monomer *m* and monomer *k*, the ratio of *m* to *k* was listed in Table 1. After mixing the monomers in DMSO/tolune system, the mixture was stirred at 140 °C for 4 h and then raised to 170 °C for 6 h. The reaction mixture was cooled to room temperature and poured into acetone. The inorganic salts were removed by washing with boiling water. Analysis data of SPEEKK-3: IR (KBr, cm^{-1}) 1247, 1078, 699 (Ar–$\mathrm{SO_3Na}$), 1160 (–O–), 1656 (C=O), 2969 (–$\mathrm{CH_3}$).

2.1.3. Preparation of membranes

SPEEKK membranes were cast onto glass plate from their DMF solution (5–10%). The SPEEKK membranes (in sodium salt form) were transformed to their acid forms by soaking in 1.0 M HCl solution for 24 h. After that, the obtained membranes (in acid form) were immersed and washed with deionized water. The thickness of all membrane samples was in the range of 50 and 150 μm.

2.2. Characterization of membranes

2.2.1. Chemical and thermal properties

FT-IR was recorded on a Nicolet Impact 410 Fourier transform infrared spectrometer. TGA and DTA were performed on NETZSCH STA449C at the heat rate of 10 °C/min in air. The intrinsic viscosities of the polymers were measured in DMF at 25 °C with a polymer concentration of 5.0 g/l. D_s was determined by titration method [8]. Prior to the titration, the polymers were acidified by using an excess amount of HCl aqueous solution and rinsed several times by deionized water to remove the free acid. A standard NaOH of aqueous/DMF solution was used for titration. The ion exchange capacity (IEC) of SPEEKK membranes was determined by titration. The membranes in H^+ form (0.5–1.0 g) were immersed in 1 M NaCl solutions for 24 h to liberate the H^+ ions (the H^+ ions in the membrane were replaced by Na^+ ions). The H^+ ions in solution were then titrated with 0.05 M NaOH. The theoretical IEC values, which calculated from D_s were obtained from formula (1):

$$\mathrm{IEC} = \frac{1000D_\mathrm{s}}{510 + 80D_\mathrm{s}} \qquad (1)$$

Methanol and proton diffusion coefficients were determined by using a cell basically consist of two half cells separated by the membrane, which was fixed between two rubber rings. To methanol diffusion, methanol was placed on one side of the diffusion cell and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol was measured by using SHIMADU GC-8A chromatograph. Peaks areas were converted to methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated by the reference report [20]. And to proton diffusion, 0.5 M HCl was placed on one side of cell and water was placed on the other side. DDS-11C was used to record the conductivity changes vs time in solution B. $D_{\mathrm{H}+}$ of membranes was obtained by the slope of conductivity vs time liner [12,13].

2.2.2. Microstructure of membranes

Atomic force microscopy (AFM) was performed with SPA300HV/SPI3800N Probe Station, Seiko Instruments Inc., Japan in tapping mode. A silicon microcantilever (spring constant 2 N/m and resonance frequency ∼70 kHz Olympus Co., Japan) with an etched conical tip (radius of curvature ∼40 nm as characterized by scanning over very sharp needle array, NT-MDT, Russia) was used for scan. The scan rate was ranged from 1.0 to 2.0 Hz to optimize the image quality. Each scan line contains 256 pixels, and a whole image is composed of 256 scan lines.

2.2.3. Mechanical property and surface properties

The tensile strength of the membranes was measured using SHIMADIU AG-I 1KN at the test speed of 2 mm/min, the size of specimen was $15 \times 4\ \mathrm{mm}^2$. For each testing reported, at least three measurements were taken and average value was calculated. Contact angle of membranes on water (sodium sulfonate forms) was determined by FTA200 (First Ten Angstroms). The membranes were cast onto microscope slides for usages.

2.2.4. Physical properties of membrane

Measurement of swelling (S_w) was determined by the weight difference which sets between the fully hydrated membranes and dried membranes. The weight of drying membranes (W_drying) was weighed and then soaked in water until the weight remained constant. Then took them out and wiped out the surface water of membranes with blotting paper. The weight of the wet membranes (W_wet) was quickly weighed again. The S_w was calculated with formula (2):

$$S_\mathrm{w} = \frac{W_\mathrm{wet} - W_\mathrm{drying}}{W_\mathrm{drying}} \times 100\% \qquad (2)$$

The measurement of proton conductivity of the membranes were carried out by using Philips 1260 impedance/gain-phase analyzer over a frequency range of 10 Hz to 1 MHz. Conductivity measurements of fully hydrated membranes

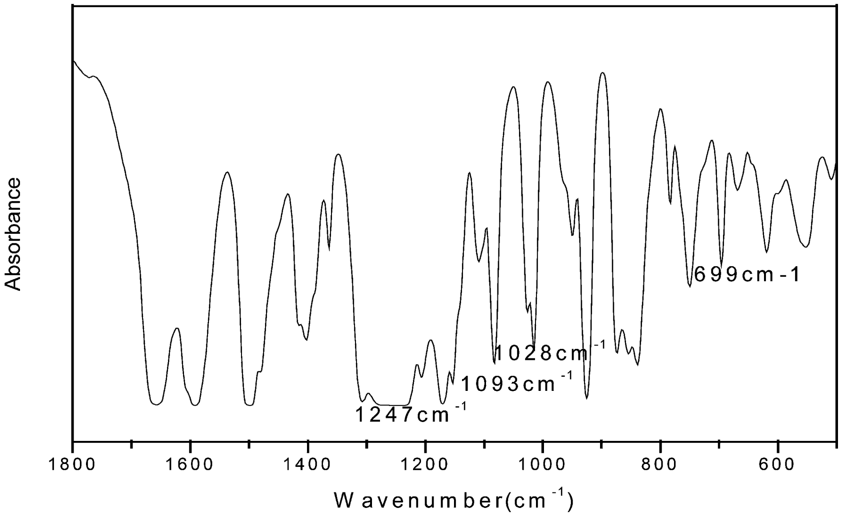


Fig. 2. The FT-IR of SPEEKK-3.

were carried out with the cell immersed in liquid water. The membrane conductivity was determined with the test cell shown in Fig. 1, similar to the one employed by Zawodzinski et al. [10]. The proton conductivity was calculated by formula (3):

$$\sigma = \frac{L}{RA} \tag{3}$$

where L is the distance between the two electrodes, R is the membrane resistance and A is the cross-sectional area of membrane.

3. Result and discussion

3.1. Polymer synthesis and characterization

3.1.1. Polymer preparation

A series of samples were prepared from aromatic nucleophilic substitution polycondensation of monomer *l* with different ratio of monomer *m* to monomer *k* (Scheme 2) in a DMSO/tolune solvent system. The polymerization results and analytical data were displayed in Table 1. The specific viscosities of all the polymers indicate that all the polymers have the high molecular weights. As shown in Table 1, the degrees of sulfonation determined by titration are consistent with the calculated values, which clearly suggests that degrees of sulfonation can be readily manipulated by controlling the amount of sulfonated monomer added.

The composition and structure of polymers were confirmed using FT-IR. Fig. 2 shows the IR spectrum of SPEEKK-3. The absorption bands at 1247, 1093 and 1028 cm^{-1} can be assigned to asymmetric and symmetric O=S=O stretching vibrations of sodium sulfonate groups. The absorption band at 699 cm^{-1} can be assigned to the S–O stretching of sodium sulfonate groups. No peaks attributed to aromatic sulfone group in arrange of 1140–1110 cm^{-1} indicates that no cross-linking occurred during copolymerization.

3.1.2. The properties of polymers

The thermal properties of polymers were examined by TGA and DTA under air atmosphere at heat rate of 10 °C/min. No glass transition temperatures were observed from SPEEKK-1 to SPEEKK-4 in a temperature range of 100–400 °C from DTA. This may be explained by the strong intermolecular interaction due to the introduction of $-SO_3Na$ [14]. No crystalline peaks were found in SPEEKKs. They show the amorphous structures of polymers. From the TGA result, we found that all the polymers have excellent thermal stability (the 10% loss weight temperatures in Table 1). The sulfonated polymers were stable at about 400 °C. And the 10% weight loss temperature of the polymers decreases as the content of sodium sulfonate groups increases. This may be caused by the thermal degradation of sodium sulfonate groups at relative low temperature compare with the backbones of polymers [14]. All the resulted polymers show excellent solubility in aprotic dipolar solvents such as DMF, DMSO and NMP. SPEEKKs show increased solubility in water with D_s increasing, SPEEKK-3 and SPEEKK-4 are swelling in water at high temperature and SPEEKK-1 and SPEEKK-2 are insoluble in water. This can be explained by the increased solvability between polymers and water due to the increasing the content of sulfonated groups in polymer backbone [14]. This also has testified the hydrophilicity property of the group of sodium sulfonate.

3.2. Membrane properties

3.2.1. Microstructure of membranes

The electrochemical behavior of SPEEKK membranes should be closely related to their internal structures,

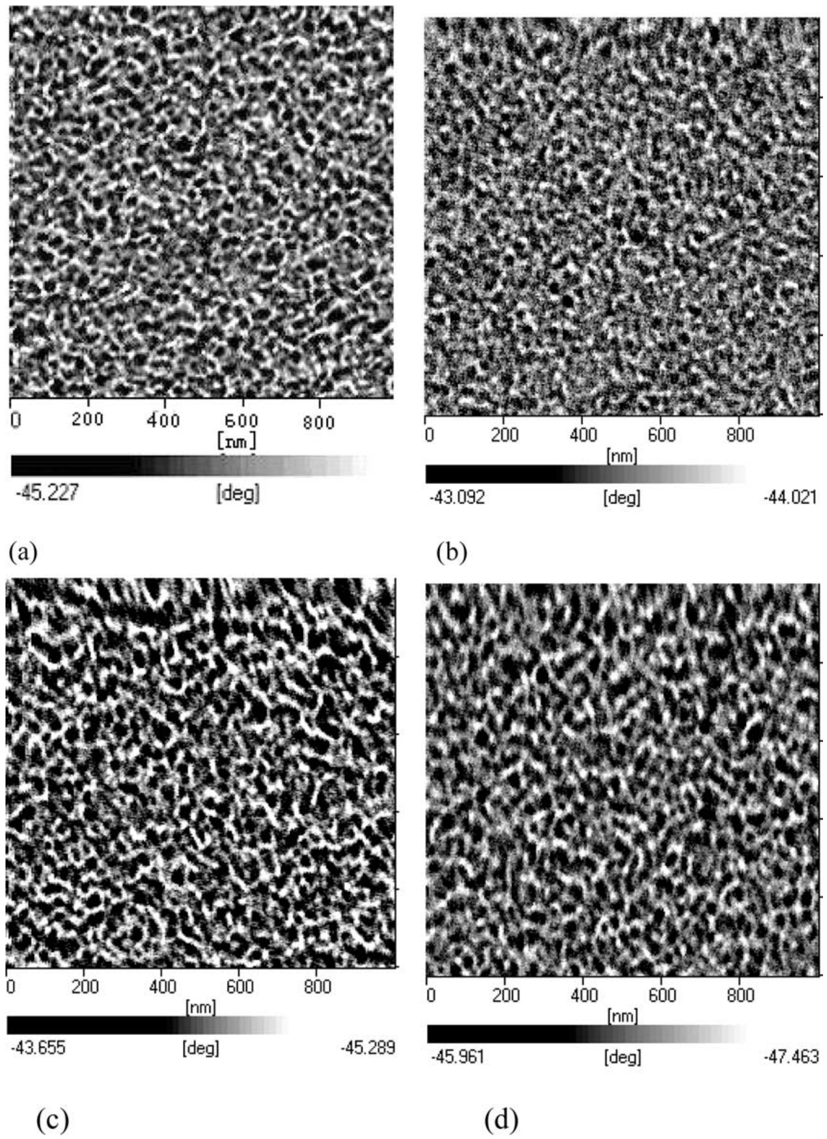


Fig. 3. AFM tapping phase image for SPEEKKs. (a): SPEEKK-1, (b): SPEEKK-2, (c): SPEEKK-3; (d): SPEEKK-4.

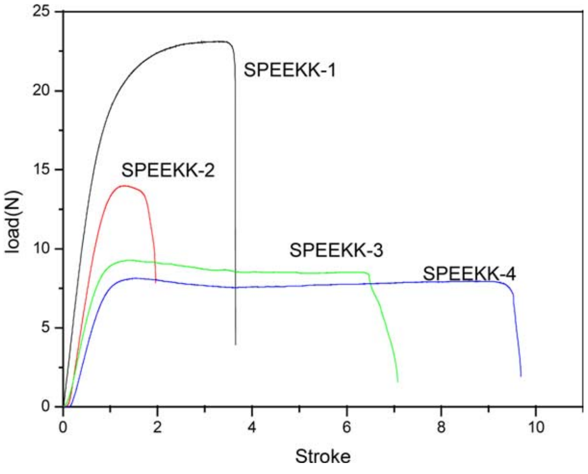


Fig. 4. Load-stroke behavior of SPEEKK membranes.

especially the spatial distribution of ionic site. To the state of aggregation of ions in ionic polymers, extensive studies have been carried out by SAXS, AFM, TEM etc. [21–24]. From the analysis of Eisenberg, sulfonated groups may aggregate into hydrophilic clusters, which can provide cation transport pathway or ionic transport channels [25]. Tapping-mode phase images of the SPEEKK membranes were recorded under ambient conditions on a 1×1 μm^2 size scale in order to investigate ionic clusters for SPEEKKs. Fig. 3 shows the phase images of SPEEKK-1 to SPEEKK-4, dark regions were assigned to a softer region which represents the hydrophilic sulfonic acid groups [7]. The domain size and continuous vary depend on the sulfonated degrees of SPEEKKs. The domain size and continuous of clusters increases with sulfonated degree increasing, which may provide more or larger proton transport channel. The

Table 2
The analytic data of SPEEKK membranes

Polymer	SPEEKK-1	SPEEKK-2	SPEEKK-3	SPEEKK-4	Nafion 117
Contact angle (°)	84	72	60	57	–
S_w (%) (25 °C)	6.02	9.29	11.48	15.62	–
S_w (%) (80 °C)	11.90	19.26	24.17	30.11	–
$\mathrm{IEC}_{(m)}$[a]	0.62	1.27	1.77	1.95	0.92
$\mathrm{IEC}_{(c)}$[b]	0.75	1.39	1.69	1.98	–
Methanol diffusion (× cm^2/s)	7.68×10^{-8}	3.23×10^{-7}	4.95×10^{-7}	5.75×10^{-7}	2×10^{-6}
Proton diffusion (m^2/s)	–	1.67×10^{-11}	3.68×10^{-11}	9.33×10^{-10}	–
Proton conductivity (S/cm) (25 °C)[c]	0.007	0.019	0.032	0.04	0.08
Proton conductivity (S/cm) (80 °C)[c]	0.016	0.064	0.08	0.10	0.10

[a] IEC obtained by titration.
[b] IEC obtained by calculation.
[c] The proton conductivity measured at the same condition.

result indicates the increased conductivity of SPEEKKs membranes with D_s increasing.

3.2.2. Mechanical and surface properties

The load-stroke behavior of SPEEKK membranes was shown in Fig. 4. The initial Young's modulus for the membranes of SPEEKK-1, SPEEKK-2, SPEEKK-3 and SPEEKK-4, are 1.17, 1.26, 1.14 and 1.03 GPa, which are higher than the ones of Nafion 117. All the four SPEEKK membranes show the elongation at break of 18, 27, 47 and 64%, and tensile strength ranging from 45 to 57 Mpa. These dates indicate that the SPEEKK membranes are strong and tough enough for the usages of PEM. Compared to the commercial proton exchange membranes (Nafion) SPEEKK membranes show relatively better mechanical properties, which shows the excellent properties derives from the none sulfonated PEEKK [15].

The values in contact angle of membranes in Table 2 decrease from 84 to 57° with sulfonated degrees increasing from 0.4 to 1.2, which implying the improved hydrophilic properties of membranes with increasing content of sulfonated groups [16]. The difference in hydrophilic properties of membranes may lead to difference in water content of membranes, which further influences the proton transport in membranes. All these results are consistent with the conclusion those from the solubility of polymers.

3.2.3. IEC and water uptake

Ion exchange capacity and water uptake were shown in Table 2. These SPEEKK membranes show increased IEC and water uptake with increased degrees of sulfonation. The experiment IEC values listed in Table 2 are in good agreement with the calculated IEC, assuming that all of the sulfonated monomers were incorporated into the polymer via sulfonated monomer copolymerization without any side reactions, which often be observed in post sulfonation method. SPEEKK membranes show increased water uptake with sulfonated degrees increasing due to the strong hydrophilicity of the sulfonate groups. From SPEEKK-1 to SPEEKK-4 the membrane show water uptake of 6.02, 9.29, 11.48 and 15.62%, respectively. Also the water uptake of membranes at 80 °C shows the similar tendency. Compared with Nafion, SPEEKK membranes show relatively lower water uptake, this may be due to the difference microstructures of the polymers. The extreme hydrophobicity of the polymer backbone and extreme hydrophilicity of the sulfonic acid groups lead to a spontaneous hydrophilic/hydrophobic nano-separation [17]. Therefore, only the hydrophilic domain of the nanostructure is hydrated in the presence of water. To SPEEKKs the sulfonated groups dispersed through acromatic matrix, which is less hydrophilic than Nafion. All these characteristics may lead to the lower water uptake of SPEEKK membranes than Nafion. To water uptake, there are two factors that influence the properties of PEM, one is the increasing proton conductivity with water uptake increasing, due to the reason that proton exchange reaction requires a significant amount of water to coordinate with proton as it moves through the membrane; the other is the decreasing mechanic properties of membranes. So selecting membranes with appropriate levels of water uptake is very important.

3.2.4. Methanol diffusion coefficient

SPEEKK membranes exhibit increased methanol diffusion coefficient at 25 °C depending on the sulfonated degrees. SPEEKK membranes show methanol diffusion at the range of 7.68×10^{-8} to 5.75×10^{-7} cm^2/s, which is much lower than Nafion (2×10^{-6} cm^2/s) at the same temperature. Such result suggests the influence of the position of sulfonate group in polymer on the hydrodynamic solvent transport (water and methanol) properties of membranes. In the SPEEKK membranes sulfonated groups dispersed throughout the polymer matrix and are not easily phase separated otherwise the sulfonate groups in Nafion is on the side chains of polymers which may easily lead to phase separated [19]. All these characteristics will lead to the methanol diffusion coefficient much lower for SPEEKK membranes than Nafion (2×10^{-6} cm^2/s), which may help

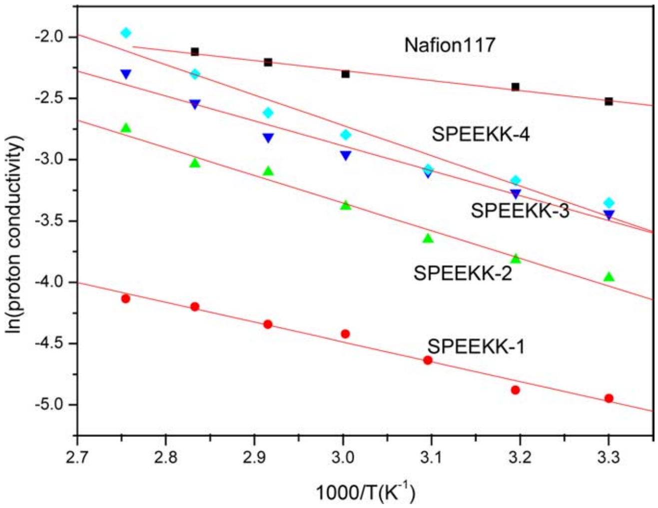


Fig. 5. The proton conductivity of SPEEKKs with different temperatures.

reduced the problem associated with water and methanol crossover for direct methanol fuel cells.

3.2.5. Proton diffusion and proton conductivity

The transport of H^+ has very great influence on the proton conductivity of membranes [26]. The diffusion coefficient of proton of the membranes with different D_s was shown in Table 2. The diffusion coefficient shows increase tendency with increasing sulfonated degrees. For example, SPEEKK membranes with D_s of 0.8, 1.0 and 1.2 exhibit diffusion coefficient of H^+ of 1.67×10^{-11}, 3.68×10^{-11} and 9.33×10^{-10} m^2/s, respectively. This might be due to the increasing size of clusters in membranes or large ion transport channel, which concluded from AFM [13]. Proton conductivity of the membranes at different temperatures was calculated from resistance measurement. The conductivity data was analyzed in terms of Arrhenius plot, as reported in Fig. 5. The proton conductivity increased both with D_s and temperature. Indeed high D_s resulted in high water uptake and higher proton conductivity. Expect for SPEEKK-1, other SPEEKK membranes show room-temperature proton conductivity higher than 10^{-2} S/cm, which is the lowest value of practical interest for use as PEMs in fuel cells. Compared to Nafion, SPEEKKs membranes show relatively lower proton conductivity. This is due to the different distribution of ion domains in membrane [17,18]. Nafion makes more ion-rich domains which allows the ions to migrate more easily than in the SPEEKKs. SPEEKK-3 and SPEEKK-4 show similar proton conductivity at 80 °C with Nafion, which may be an indication that percolation in the hydrophilic domain of these two polymers is possibly similar to that of Nafion 117 [27]. It is also noteworthy that the proton conductivities of the present membranes (e.g. SPEEKK-2, -3 and -4) show a more marked increase with temperature than the ones of Nafion 117 membranes. This is attributed to the lower hydrophobicity of SPEEKK polymer backbone compared with the perfluorinated backbone of Nafion as well as a relatively strong interactions between the water molecules and sulfonic acid groups [28], which would result in improved water retention and high proton conductivity at elevated temperature. In this study, SPEEKK-2 to SPEEKK-4 may have good prospective usages in PEM, in terms of water uptake, the mechanical stability, methanol permeability and proton conductivity.

4. Conclusion

SPEEKKs with different D_s were prepared by directly polymerization of sulfonated monomers. All the polymers were easily cast into tough membranes. SPEEKK membranes show good IEC (0.62–0.95), good proton conductivity (>0.01) and good thermal stability. SPEEKK membranes show much better mechanical properties and methanol resistance than Nafion. Especially methanol diffusion coefficients of the S-PEEKK membranes are about one order of magnitude lower than that of Nafion® making these S-PEEKK membranes are good alternative to reduce problems associated with high methanol crossover in direct methanol fuel cells.

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