Proton-Exchange Sulfonated Poly (ether ether ketone) (SPEEK)/SiO$_x$-S Composite Membranes in Direct Methanol Fuel Cells[*]

GAO Qijun (高启君)[1,2], **WANG Yuxin** (王宇新)[1,2], **XU Li** (许莉)[1,**], **WEI Guoqiang** (卫国强)[1,2] **and WANG Zhitao** (王志涛)[1,2]

[1] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China
[2] State Key Laboratory of Chemical Engineering, Tianjin 300072, China

Abstract   A sulfonated poly(ether ether ketone) (SPEEK) membrane with a fairly high degree of sulfonation (DS) can swell excessively and even dissolve at high temperature. To solve these problems, insolvable functionalized silica powder with sulfonic acid groups (SiO$_x$-S) was added into the SPEEK matrix (DS = 55.1%) to prepare SPEEK/SiO$_x$-S composite membranes. The decrease in both the swelling degree and the methanol permeability of the membranes was a dose-dependent result of addition of the SiO$_x$-S powder. Pure SPEEK membrane swelled 52.6% at 80°C, whereas the SPEEK/SiO$_x$-S (15%, by mass) membrane swelled only 27.3% at the same temperature. From room temperature to 80℃, all SPEEK/SPEEK/SiO$_x$-S composite membranes had methanol permeability of about one order of magnitude lower than that of Nafion®115. Compared with pure SPEEK membranes, the addition of the SiO$_x$-S powder not only leads to higher proton conductivity, but also increases the dimensional stability at higher temperatures, and greater proton conductivity can be achieved at higher temperature. The SPEEK/SiO$_x$-S (20%, by mass) membrane could withstand temperature up to 145°C, at which in 100% relative humidity (RH) its proton conductivity exceeded slightly that of Nafion®115 membrane and reached 0.17 S·cm^{-1}, while pure SPEEK membrane dissolved at 90°C. The SPEEK/SiO$_x$-S composite membranes are promising for use in direct methanol fuel cells because of their good dimensional stability, high proton conductivity, and low methanol permeability.
Keywords   sulfonated poly(ether ether ketone), functionalized silica, composite membrane, direct methanol fuel cell

1   INTRODUCTION

Development and research on direct methanol fuel cells (DMFCs) have been an area of active interest since the 1990s [1]. DMFC technology has made significant progress over the years, but two obstacles still need to be surmounted before DMFC commercialization [2, 3]. First, the anode catalyst is inactive and unstable enough causing a high overpotential loss of the anode. Second, severe methanol crossover of the commercially available perfluorosulfonic acid (PFSA) proton-exchange membranes (PEM) (*e.g.*, Nafion®) from anode to cathode reduces fuel efficiency and increases the mixed electrode potential of the cathode, resulting in low cell performance [2, 3]. Production of the commercially available PFSA polymer membranes is costly and time-consuming. Therefore, there is an urgent need to develop PEM with improved properties, including high proton conductivity, low methanol permeability, and low cost.

Much effort has been made in recent years to develop an alternative fluorine-free polymer membranes [4–8] and to modify PFSA polymer membranes [9]. It is widely recognized that sulfonated poly (ether ether ketone) (SPEEK) polymers are very promising materials for membranes in DMFCs [4]. SPEEK polymers can, in theory, have higher ion-exchange capacity (IEC) than PFSA polymers, which may compensate for the demerit of weaker acidity of their own sulfonic

groups (SO$_3$H). SPEEK membranes also exhibit lower methanol crossover and are less costly to produce than PFSA membranes [5]. The demand for high proton conductivity calls for SPEEK membranes to have a high degree of sulfonation (DS) and to function at high temperatures. However, highly sulfonated SPEEK membranes tend to swell excessively or even dissolve at high temperatures. There have been several attempts to overcome the excessive swelling while maintaining high proton conductivity, for example, by synthesizing SPEEK with various hydrophobic block: hydrophilic block ratios [10], by introducing cross-links between some of the sulfonic groups in the SPEEK membrane [11], and by blending the SPEEK polymer with non-conductive engineering thermoplastics (*e.g.*, SPEEK/PEI, SPEEK/PES, SPEEK/PBI) [12–14].

Addition of inorganic particles (*e.g.*, ZrO$_2$) into the SPEEK matrix is also an important approach in PEM research [15]. This approach has two objectives: one is to improve the mechanical properties of the composite membranes and the other is to physically counteract methanol crossover [16, 17]. It has also been suggested that the size of the particles (nano or micro), surface properties (acid or basic), and the functionalization determine whether the filler, besides acting as a reinforcing components as above mentioned, can impart a significant improvement in proton conductivity [16–22].

In this study, the functionalized silica with sulfonic acid groups (SiO$_x$-S) was added into the SPEEK

matrix (DS = 55.1%) to prepare SPEEK/SiO$_x$-S composite membranes. The molecular structure of the filler is shown in Fig. 1. The addition of SiO$_x$-S into SPEEK matrix is expected to lead to more dimensional stability membranes with high proton conductivity, low methanol permeability, and low swelling degree.
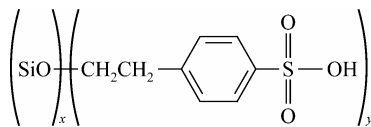

Figure 1 Molecular structure of the functionalized silica with sulfonic acid groups (SiO$_x$-S)

2 EXPERIMENTAL

2.1 Materials

Poly(ether ether ketone) (PEEK) pellets (Victrex®PEEK, grade 450P, $M_W = 38300$) were provided by Nanjing Yuanbang Engineering Plastics Co., Ltd. 4-ethyl benzenesulfonyl chloride-functionalized silica (SiO$_x$-Cl) was obtained from Sigma-Aldrich Chemistry Company. It has a density of 0.46 g·cm^{-3}, a loading of Cl groups equal to 1 mmol per gram of powder, a pore size of 6 nm, and a surface area of 500 m^2·g^{-1}. The nominal size of powder is 40−65 μm. Concentrated sulfuric acid (95%−98%), dimethylformadide (DMF), and absolute methanol were purchased from Kewei Chemistry Co., Ltd.

2.2 Preparation of SiO$_x$-S powder

The SiO$_x$-S gel can be prepared from SiO$_x$-Cl hydrolyzed for 6 h at 80°C as described in a previous study [17]. The gel was washed repeatedly with deionized water until pH of the rinse water was 7 and then dried at 70°C for 24 h to remove water. The resultant SiO$_x$-S was ground to fine powder by a QM-ISP04 ball mill and finally stored in an airtight bottle before being used.

The back-titration of sulfonic groups within the SiO$_x$-S powder was used to find whether the SiO$_x$-Cl hydrolyzed into the SiO$_x$-S completely.

2.3 Synthesis of SPEEK

PEEK (10g) was added gradually to 100 ml of concentrated sulfuric acid in a three-necked flask with vigorous stirring at 60°C. At a prescribed time point, the acid polymer solution was added to a large excessive ice-cold water with continuous agitation. The SPEEK precipitate was rinsed repeatedly with deionized water until the water reached pH 7. Then the SPEEK was dried at room temperature for 2 days followed by drying at 60°C for 24 h under vacuum. The IEC and DS of the sulfonated polymers were determined by a classical back-titration method as described in a previous study [23].

2.4 Membrane preparation

The membranes were prepared by solution casting. When the mass content of SiO$_x$-S powder is higher than 20%, the composite membrane becomes brittle in dry state at room temperature. Therefore, SPEEK/SiO$_x$-S (3%–20%) composite membranes (the degree of sulfonation for the SPEEK polymer is 55.1%, the mass content of SiO$_x$-S powder in the composite membranes is from 3% to 20%) were studied in this article.

SPEEK and SPES-C in prescribed amount were dissolved separately in DMF (10%, by mass) and then the two solutions were mixed and stirred for 6 h. The mixed solution was cast onto a glass plate and dried overnight at 60°C in a vacuum oven, followed by annealing at 100°C for 4 h. After cooling to room temperature, the membrane was peeled from the glass plate with deionized water.

SiO$_x$-S powder in prescribed amount was uniformly dispersed in DMF solvent with mechanical stirring. The desired amount of SPEEK was then added to the solvent to make a 10% (by mass) solution. After stirring for 6 h and degassing, the solution was cast onto a glass plate and dried overnight at 60°C in a vacuum oven, followed by annealing at 100°C for 4 h. After cooling to room temperature, the membrane was peeled from the glass plate with deionized water. Finally, the membrane was treated with 1 mol·L^{-1} sulfuric acid at room temperature for 24 h and subsequently rinsed with deionized water several times to remove acid completely. Membranes were kept in deionized water before testing. The thickness of the dried membranes was 80−95 μm.

2.5 Membrane characterization

Fourier transform infrared spectroscopy (FT-IR) were measured in absorbance mode by using an FT-IR spectrometer (Bio-RAD FTS 6000) in the range of wave numbers 600−4000 cm^{-1} to compare position of IR bands and to check the presence of functional groups and their interaction in composite membranes. Prior to FT-IR measurement, the samples were dried at 80°C for 24 h.

Thermogravimetric analysis (TGA) was used to estimate the thermal stability of the composite membranes. We used a TGA thermogravimetric analyzer (TA-50 Instrument Shimadzu TGA) at a heating rate of 10 K·min^{-1} in nitrogen gas in the temperature range 30−800°C. All specimens were dried overnight at 90°C under vacuum before measurements.

The morphology of the cross-section of samples was examined with an environment-scanning electron microscope (PHILIPS XL30 ESEM). The samples were cryo-fractured in liquid nitrogen to obtain fresh cross-sections, which were coated with gold before measurements.

The swelling degree (SD) of the specimens was obtained by measuring the area difference between the

dry and the wet states as described in Ref. [23]. The membranes were cut into 3 cm×4 cm rectangles and dried overnight at 90°C under vacuum before measuring the area (S_d). The dried membranes were immersed for 48 h in 1 mol·L^{-1} methanol to reach equilibrium at the desired temperature. The wet membranes were wiped dry with tissue paper and the area was measured again (S_w). SD was calculated (in area percent) as follows:

$$SD(\%) = \frac{S_w - S_d}{S_d} \times 100,$$

where S_d and S_w are the areas of dry and corresponding wet membrane sheets, respectively. Three sheets of each membrane composition were measured by the above method, and the average was calculated.

The methanol permeability was determined using a diaphragm diffusion cell [24]. A glass cell ($V = 16.8$ ml) containing solutions A and B in two identical compartments separated by the test membrane was used for the permeability tests. The membranes were held in place between the two compartments by a screw clamp. Solution A was 1 mol·L^{-1} methanol solution and solution B was deionized water. Both compartments were stirred by a magnetic follower during the experiment. The concentration of methanol in solution B was estimated using a differential refractometer (WINOPAL LCD 201). The refractometer is highly sensitive to methanol, which can be measured continuously during the test. The methanol permeability was calculated from the slope of the straight line plot of methanol concentration *versus* time. The measurement temperature was controlled from room temperature to 80°C.

The proton conductivity of samples in the lateral direction was measured with a measurement cell and a frequency response analyzer (FRA) (Autolab PG-STAT20). Two stainless steel electrodes connected to the FRA were pressed against the membrane to be tested. The measurement temperature was controlled from room temperature to 160°C. The conductivity, σ, was calculated from the impedance data, using the relation $\sigma = l/(R \cdot S)$, where l and S are the distance between the electrodes and the cross-section area of the membrane, respectively, and R was derived from the low intersection of the high-frequency semi circle on a complex impedance plane with the $Re(z)$ axis. For membranes that dissolved below 160°C, their dissolution was tested by measuring the weight before and after the proton conductivity measurement. Besides, the proton conductivity of SiO$_x$-S powder was obtained as described in a previous study [23]. The powder needs to be pressed into a slice before testing.

3 RESULTS AND DISCUSSION

3.1 Preparation of the SiO$_x$-S

The water suspension of the SiO$_x$-Cl (5%, by mass) needs to hydrolyze for 6 h at 80°C with me-

chanical stirring, otherwise the chemical groups of SiO$_x$-Cl could not transform into sulfonic acid groups completely. This can be confirmed from Table 1. It could be found that the back-titration results of the resultant SiO$_x$-S from SiO$_x$-Cl hydrolyzed for 6 h at 80°C, are in a good agreement with the loading of Cl groups of SiO$_x$-Cl powder and approaches 1 mmol·g^{-1}. In this study, the SiO$_x$-S (IEC = 1 mmol·g^{-1}, 1 mmol loading of SO$_3$H groups per gram of the SiO$_x$-S) was used as the filler to make composite membrane.

Table 1 The back-titration results of sulfonic groups within the SiO$_x$-S hydrolyzed at different time

Sample	Hydrolyzation time/h	The back-titration results/ mmol·g^{-1}
1	4	0.725
2	5	0.869
3	6	0.997
4	7	1.003
5	8	0.999

3.2 Sulfonation

SPEEK polymers with various DS values were obtained by adjusting the reaction time. The dissolvability and the swelling degree of SPEEK polymers were found to depend strongly on their DS. When DS was >38%, the SPEEK polymers were soluble at room temperature in strong polar aprotic solvents, including dimethylformadide (DMF), N,N-dimethylacetamide (DMAC), dimethyl sulfoxide (DMSO), and N-methyl-2-pyrrolidinone (NMP). The SPEEK polymers become soluble in methanol at >70% DS and are soluble in hot water at >90% DS. Polymers with >55% DS are greatly swollen and even dissolve in 1 mol·L^{-1} methanol at 90°C. The SPEEK polymers with <40% DS cannot be chosen because of their very low proton conductivity, although they have high temperature tolerance. Therefore, the SPEEK polymer with a relative high DS (DS = 55.1%, 0.551 SO$_3$H groups per repeat unit) and IEC (IEC = 1.70 mmol·g^{-1}, 1.70 mmol loading of SO$_3$H groups per gram of the polymer) was used as the basic material of the membrane. It was prepared by sulfonating PEEK at 60°C for 2.5 h.

3.3 FT-IR spectra

The FT-IR spectra of the SiO$_x$-S, SPEEK (DS = 55.1%) and SPEEK/SiO$_x$-S(20%) are shown in Fig. 2. The SiO$_x$-S sample shows characteristic bands at 467 cm^{-1} (characteristic of Si—O—Si bending), at 806 cm^{-1} (characteristic of symmetric Si—O—Si stretching), at 1099 cm^{-1} (characteristic of asymmetric Si—O—Si stretching), at 937 cm^{-1} (characteristic of Si—O—C—C stretching), at 1600 cm^{-1} (characteristic of aromatic C—CH quadrant stretching), at 1004 cm^{-1} (characteristic of S=O stretching), and at 694 cm^{-1} (charateristic
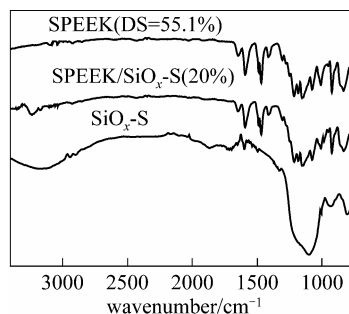
Figure 2 FT-IR spectra of SiO$_x$-S, SPEEK (DS = 55.1%) **and SPEEK/SiO$_x$-S** (20%) **composite membranes**

of symmetric S—O stretching). The SPEEK sample shows characteristic band at 1640 cm^{-1} (characteristic absorption band of —Ar—C(=O)—Ar—), at 1230 cm^{-1} (characteristic absorption band of —Ar—O—), at 1080 cm^{-1} (characteristic of symmetric O=S=O stretching), at 1080 cm^{-1} (characteristic of symmetric O=S=O stretching), at 1252 cm^{-1} (characteristic of asymmetric O=S=O stretching), at 1004 cm^{-1} (characteristic of S=O stretching), and at 709 cm^{-1} (characteristic of symmetric S—O stretching). Compared with the SiO$_x$-S and SPEEK membranes, the SPEEK/SiO$_x$-S (20%) composite membrane presents two new weak absorption bands at 3235 cm^{-1} and 986 cm^{-1}. The 3235 cm^{-1} band results from developing a intermolecular hydrogen bond between the hydroxyl of the SiO$_x$-S and the SO$_3$H groups of the SPEEK polymer. The intermolecular hydrogen bond also makes the absorption band at 1004 cm^{-1} (characteristic of S=O of stretching of the SiO$_x$-S) drift to 986 cm^{-1} in the composite membrane.

3.4 Thermal stability

The TGA curves for SiO$_x$-S powder, the SPEEK membrane, and the SPEEK/SiO$_x$-S (18%) composite membrane are shown in Fig. 3. Both SPEEK and SiO$_x$-S are thermally stable and hence their composites. The initial mass loss of all the membranes is about 2%−3% at 40−160°C, which is caused by the gradual desorption of residual water bonded to the hydrophilic sulfonic groups. The second stage of the

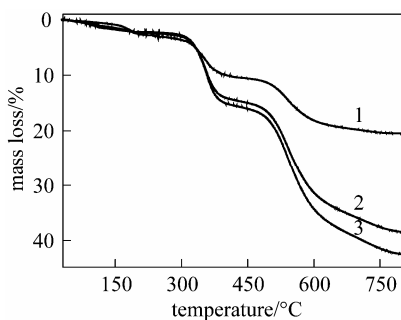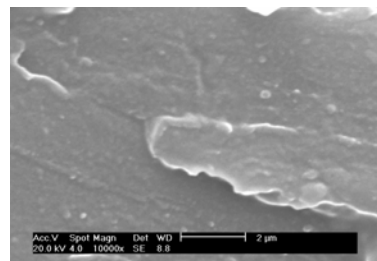**Figure 3 TGA curves of SiO$_x$-S powder, SPEEK/SiO$_x$-S** (18%) **composite membrane and pure SPEEK membrane**
1—SiO$_x$-S; 2—SPEEK/SiO$_x$-S (18%); 3—SPEEK (DS = 55.1%)
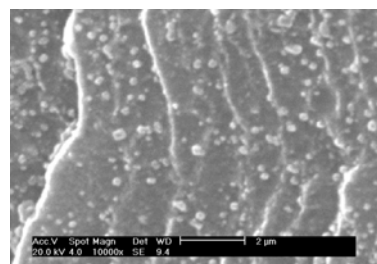
mass losses is at 300−400°C due to the decomposition of sulfonic groups [23, 25]. The last stage of the mass losses for all these samples is at 500−600°C, which can be attributed to the degradation of the polymer backbones of SPEEK and the organic segments of SiO$_x$-S [23, 25]. Compared with the pure SPEEK membrane, the amount of mass lost from the composite membranes at the second stage is less. Adding the SiO$_x$-S (IEC = 1 mmol·g^{-1}) to the SPEEK matrix (IEC=1.70 mmol·g^{-1}) decreased the composite membranes' IEC [*e.g.*, IEC = 1.56 mmol·g^{-1} for the SPEEK/SiO$_x$-S (20%) composite membrane], thus decreasing the content of sulfonic groups within the composite membranes. The mass losses for both the SPEEK and composite membranes are due to the decomposition of sulfonic groups at this stage [23, 25]. Therefore, the mass lost from the composite membranes at this stage are less than that of from pure SPEEK membrane.

3.5 Morphology

The basic homogeneous distribution of SiO$_x$-S powder within the SPEEK matrix and no sign of evident aggregation can be observed from the SEM images of the SPEEK/SiO$_x$-S composite membranes at magnification of up to 10000× (Fig. 4) although the SiO$_x$-S content reaches 20%. The nominal powder size is less than 500 nm as indicated by the SEM images.

(a) SPEEK/SiO$_x$-S (5%) composite membrane

(b) SPEEK/SiO$_x$-S (20%) composite membrane

Figure 4 Cross-section images of SPEEK/SiO$_x$-S (5%) **composite membrane and SPEEK/SiO$_x$-S** (20%) **composite membrane**

3.6 Swelling behavior

The membranes swelled to different extents in 1 mol·L^{-1} methanol as the temperature increased. The

swelling degree of the membranes, however, decreased markedly with the addition of SiO$_x$-S, especially at high temperatures (Fig. 5). The pure SPEEK membrane swelled 52.6% at 80°C, whereas the membrane with 20% SiO$_x$-S swelled only 27.3% at the same temperature. This helps to keep good dimensional stability of the membranes. Generally, there are two reasons for the decrease in swelling of the composite membranes. First, the hydrophilicity of the composite membrane was lower than the SPEEK membrane (IEC = 1.70 mmol·g^{-1}), which results from the lower IEC (IEC = 1 mmol·g^{-1}) of the SiO$_x$-S component. Second, the hydrogen bonds between sulfonic acid groups of SPEEK and SiO$_x$-S molecules will hinder the stretch of SPEEK molecular chains to some extent. Note that we give only the swelling degree of the membranes below 80°C here, which reflects the membranes' swelling in liquid feed DMFC. When the membranes are applied at temperatures above 100°C, methanol fuel is fed in the form of gas, thus the swelling degree of the membranes cannot use this above method to measure. The swelling degree at higher temperature is given in Section 3.9.
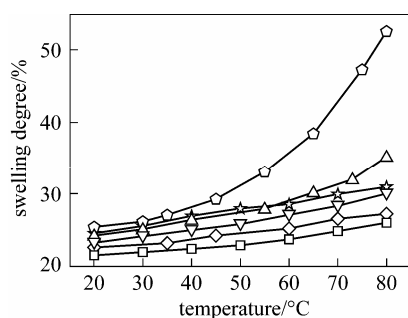

Figure 6 Arrehenius plots of methanol permeability for Nafion®115, pure SPEEK membrane, and SPEEK/SiO$_x$-S composite membranes
□ Nafion® 115; ○ SPEEK(DS = 55.1%); △ SPEEK/SiO$_x$-S(5%);
▽ SPEEK/SiO$_x$-S(10%); ◇ SPEEK/SiO$_x$-S(15%);
◁ SPEEK/SiO$_x$-S(20%)

Figure 5 Swelling degree of Nafion®115, SPEEK membrane and SPEEK/SiO$_x$-S composite membranes in 1 mol·L^{-1} methanol solution at different temperatures
◠ SPEEK(DS = 55.1%); △ SPEEK/SiO$_x$-S(5%);
▽ SPEEK/SiO$_x$-S(10%); ◇ SPEEK/SiO$_x$-S(15%);
□ SPEEK/SiO$_x$-S(20%); ☆ Nafion® 115

3.7　Methanol permeability

Methanol fuel is fed in the form of liquid below 80°C, thus the methanol crossover is more serious than in the form of gas at higher temperatures [2]. We analyze the methanol permeability of the membranes below 80°C here. Fig. 6 shows the methanol permeability as a function of temperature for Nafion®115, pure SPEEK and SPEEK/SiO$_x$-S composite membranes. The methanol permeability of Nafion®115 at room temperature is $1.02×10^{-6}$ cm^2·s^{-1}, which is very close to the value reported by Tricoli et al. [24, 26, 27], while that of SPEEK and SPEEK/ SiO$_x$-S membranes are approximately an order of magnitude lower than Nafion®115.

The difference in methanol permeability between Nafion®115 and the SPEEK membrane can be explained qualitatively by the differences in their microstructures and the acidity of their sulfonic acid func-
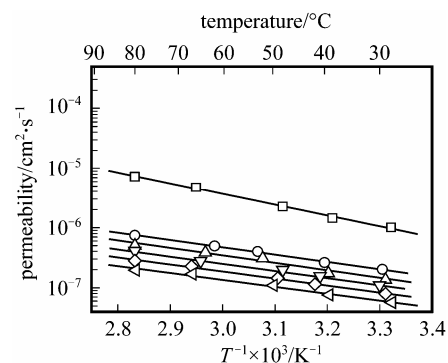
tional groups [4]. Nafion®115 macromolecules consist of very hydrophobic perfluorinated backbones and very hydrophilic side chains with sulfonic acid functional groups. The very different components lead to relatively large microphase separation in Nafion®115, which results in the low resistance to methanol permeation. The situation for SPEEK polymer is rather different. The carbon-hydrogen main chains with ether links, phenyl rings, and carbonyl groups in SPEEK make it less hydrophobic and more rigid compared with Nafion®115. Furthermore, the acidity of sulfonic acid functional groups of the SPEEK polymer is weaker than that of Nafion®115. Therefore, the microphase separation in the SPEEK membrane is not obvious and the hydrophilic ion channels are narrower, which results in low methanol permeability. This can also be proved by the results of schematic representation of the microstructure of Nafion®115 and SPEEK reported by Kreuer et al [4].

As can be seen in Fig. 6, the methanol permeability of the SPEEK/SiO$_x$-S composite membranes is even lower and decreases with the increased SiO$_x$-S content in the membrane. The addition of SiO$_x$-S inhibits effectively the swelling of SPEEK matrix (Fig. 5) and thus imposes higher resistance to methanol crossover. The higher resistance to methanol crossover of the SPEEK/SiO$_x$-S composite membranes is beneficial to improve open circuit voltage (OCV) of DMFCs [2].

3.8　Proton conductivity

The relation between the conductivity and the reciprocal of the temperature for all the SPEEK and SPEEK/SiO$_x$-S membranes, before they dissolve, can be described by the Arrhenius equation and exhibits straight lines in a semilogarithmic graph (Fig. 7). The apparent activation energy of proton transfer, which is equal to the slope of the corresponding lines of different membranes, is obtained from the Arrhenius plot.
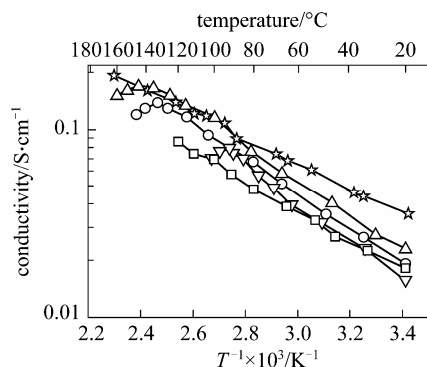
Figure 7 **Arrehenius plots of proton conductivity at 100%RH for Nafion®115, SiO$_x$-S powder, pure SPEEK membrane and SPEEK/SiO$_x$-S** (15%, 20%) **composite membranes under 100% RH**

☆ Nafion® 115; △ SPEEK/SiO$_x$-S(20%); ○ SPEEK/SiO$_x$-S(15%);
▽ SPEEK(DS = 55.1%); □ SiO$_x$-S

It is noteworthy that the apparent activation energy of the SPEEK membrane has approximately 38 kJ·mol^{-1}, in contrast to 9 kJ·mol^{-1} for Nafion®115. The very high apparent activation energy of the SPEEK membrane is believed to be a consequence of its low swelling degree and slow variation with temperature (as shown in Fig. 7). Narrow ion channels and rich branches with dead-end "pockets" in the membrane will contribute to the high barrier to proton transfer [4].

SPEEK and SiO$_x$-S materials are weakly acidic compared with Nafion®115. The dissociation of sulfonic acid functional groups in these materials increases at high temperatures [5, 23], whereas that of Nafion®115 approaches 100% at room temperature. Therefore, the elevation of temperature increases both the proton mobility and the proton content in the SPEEK and SPEEK/SiO$_x$-S membranes, which results in a much faster increase of proton conductivity with temperature.

The proton conductivity of SiO$_x$-S powder is 0.018 S·cm^{-1} at room temperature and 100% RH, and reaches 0.086 S·cm^{-1} at 120°C. The proton conductivity of composite membranes increases slightly as mass content of SiO$_x$-S powder increases, although SiO$_x$-S powder has lower proton conductivity than the pure SPEEK membrane. The increase in conductivity upon addition of SiO$_x$-S can be rationalized based on previous studies [16–22, 28]. This phenomenon has been observed by Kim *et al*. [29] in composite PEMs based on heteropolyacid in sulfonated polysulfones. The presence of the additive was found to enhance the proton conductivity, while at the same time decrease the water uptake. In this case, it is not completely understood whether the filler participates actively in the proton conduction by enhancing proton dissociation or by providing favorable pathways for the proton along polymer-particle interfaces [16–18, 22]. The conductivity results obtained in this study are very similar to that of previous studies above, and it is likely that a similar mechanism is in place. The lower apparent activation energy of proton transfer through the composite membranes than through the pure SPEEK

membrane also shows that the similar mechanism exists. The apparent activation energy of the SPEEK/SiO$_x$-S (20%) composite membrane is 33.09 kJ·mol^{-1}. The conductivity of SPEEK/SiO$_x$-S (20%) exceeds slightly that of Nafion®115 at 145°C and 100% RH and approaches 0.17S·cm^{-1}.

3.9   Working temperature

It has been reported that the proton conductivity of some polyaryl ether membranes does not increase monotonically with temperature but reaches a maximum value [27]. The apparent decrease of conductivity beyond a certain point is actually due to the dissolution and loss of mechanical stability of the membrane. The dissolution of the membranes was verified by measuring the mass change before and after the conductivity measurement. For instance, the SPEEK (DS = 55.1%) membrane at 90°C and 100% RH for 0.5 h in the measurement cell lost 26.79% of its mass. The temperature at which the conductivity reaches a maximum is denoted T^*, which is used to reflect approximately the highest working temperature of the membranes in DMFC.

Figure 8 shows T^* as a function of the mass content of SiO$_x$-S in the composite membranes. SPEEK membranes of 55.1% DS is useful only below 90°C. The T^* of the composite membranes is, however, markedly increased as the mass content of SiO$_x$-S powder increases. As discussed in Section 3.6, the addition of SiO$_x$-S to SPEEK matrix inhibits effectively the swelling and dissolution of the membranes below 80°C. The membranes' swelling at temperature above 100°C was quickly measured by measuring the area changes after their conductivity was tested at the temperature. It can be found that the content of SiO$_x$-S increased from 10% to 20%, the swelling degree of composite membranes decreased from 67.8% to 30.4% at 110°C and the content of SiO$_x$-S increased from 15% to 20%, the swelling degree of composite membranes decreased from 72.3% to 35.8% at 130°C. The increase of T^* with the increased content of SiO$_x$-S in the composite membrane should be attributed to the depressed swelling and dissolution of the composite membranes at high temperatures.
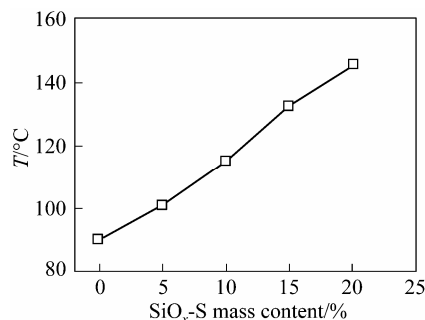

Figure 8 T^* **of the SPEEK/SiO$_x$-S composite membranes with different SiO$_x$-S mass contents**

The extension of the working temperature of the membrane is beneficial for DMFC in many aspects. Working at higher temperature, the membrane exhibits higher proton conductivity, which leads to lower ohmic losses in DMFC. The electrocatalysts are also more active and more tolerant to carbon monoxide poisoning [30] at high temperatures. When methanol fuel is fed in the form of gas at high temperature, the methanol crossover and its negative effects can be reduced markedly. Operating at high temperature also simplifies the management of water and heat in the DMFC systems [30].

4 CONCLUSIONS

The results of this study indicate a strong potential of these composite membranes for use in DMFCs. SPEEK/SiO$_x$-S composite membranes with high levels of dimensional stability were prepared. The methanol permeability of the membranes was shown to be about one order of magnitude lower than that of Nafion®115, and to decrease with the increase of SiO$_x$-S content. The addition of the SiO$_x$-S into the membranes not only increases slightly the proton conductivity of composite membranes but also effectively inhibits their swelling, which enables them to be used at higher temperature, thus presenting higher proton conductivity. The results of this study indicate a strong potential of these composite membranes for use in DMFCs.

REFERENCES

1 Kuver, A., Kamloth, K.P., "Comparative study of methanol crossover acrosselectropolymerized and commercial proton exchange membrane electrolytes for the acid direct methanol fuel cell", *Electrochim. Acta*, **43** (16), 2527−2535 (1998).

2 Ren, X., Zawadzinski, T.A., Uribe, F., Dai, H., "Methanol cross-over in direct methanol fuel cells", *Electrochem. Soc. Proc.*, **95** (23), 284−289 (1995).

3 Heinzel, A., Barragan, V.M., "A review of the state-of-the-art of the methanol crossover in direct methanol fuel cells", *J. Power Sources*, **84**, 70−74 (1999).

4 Kreuer, K.D., "On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells", *J. Membr. Sci.*, **185**, 29−39 (2001).

5 Yang, B., Manthiram, A., "Sulfonated poly(ether ether ketone) membranes for direct methanol fuel cells", *Electrochem. Solid-State Lett.*, **6**, A229−A231 (2003).

6 Wycisk, R., Lee, J.K., Pintauro, P.N., "Sulfonated polyphosphazene-polybenzimidazole membranes for DMFCs", *J. Electrochem. Soc.*, **152**, A892−A898 (2005).

7 Dai, H., Guan, R., Li, C.H., Liu, J.H., "Development and characterization of sulfonated poly(ether sulfone) for proton exchange membrane materials", *Solid State Ion.*, **178**, 339−345 (2007).

8 Shahi, V.K., "Highly charged proton-exchange membrane: Sulfonated poly(ether sulfone)-silica polyelectrolyte composite membranes for fuel cells", *Solid State Ion.*, **177**, 3395−3404 (2007).

9 Park, K.T., Jung, U.H., Choi, D.W., Chun, K., Lee, H.M., Kim, S.H., "ZrO$_2$-SiO$_2$/Nafion (R) composite membrane for polymer electrolyte membrane fuel cells operation at high temperature and low humidity", *J. Power Sources*, **177**, 247−253 (2008).

10 Zhao, C., Li, X., Na, H., "Synthesis of sulfonated poly(ether ether ketone) (S-PEEKs) material for proton exchange membrane", *J. Membr. Sci.*, **280**, 643−650 (2006).

11 Mikhailenko, S.U.D., Wang, K.P., Kaliaguine, S., Xing, P.X.,

Robertson, G.P., Guiver, M.D., "Proton conducting membranes based on cross-linked sulfonated poly(ether ether ketone) (SPEEK)", *J. Membr. Sci.*, **233**, 93−99 (2004).

12 Mikhailenko, S.D., Zaidi, S.M.J., Kaliaguine, S., "Electrical properties of sulfonated polyether ether ketone/polyetherimide blend membranes doped with inorganic acids", *J. Polym. Sci., B: Polym. Phys.*, **33**, 1386−1395 (2000).

13 Manea, C., Mulder, M., "Characterization of polymer blends of polyether sulfone/sulfonated polysulfone and polyether sulfone/sulfonated polyetherether ketone for direct methanol fuel cell applications", *J. Membr. Sci.*, **206**, 443−453 (2002).

14 Zhang, H.Q., Li, X.F., Zhao, C.J., Fu, T.Z., Shi, Y.H., Na, H., "Composite membranes based on highly sulfonated PEEK and PBI: Morphology characteristics and performance", *J. Membr. Sci.*, **308**, 67−74 (2008).

15 Silva, V.S., Ruffmann, B., Silva, H., Gallego, Y.A., Mends, A., Madeira, L.M., Nunes, S.P., "Proton electrolyte membrane properties and direct methanol fuel cell performance/I. Characterization of hybrid sulfonated poly (ether ether ketone)/zirconium oxide membranes", *J. Power Sources*, **140**, 34−40 (2005).

16 Uchida, H., Ueno,Y., Hagihara, H., Watanabe, M., "Self-humidifying electrolyte membranes for fuel cells—Preparation of highly dispersed TiO$_2$ particles in Nafion 112", *Electrochem. Soc.*, **150**, A57−A62 (2003).

17 Martinelli, A., Matic, A., Jacobsson, P., borjesson, L., Navarra, M.A., Fernicola, A., Panero, S., Scrosati, B., "Structural analysis of PVA-based proton conducting membranes", *Solid State Ion.*, **177**, 2431−2435 (2006).

18 Kim, D.S., Park, H.B., Rhim, J.W., Lee, Y.M., "Preparation and characterization of crosslinked PVA/SiO$_2$ hybrid membranes containing sulfonic acid groups for direct methanol fuel cell applications ", *J. Membr. Sci.*, **240**, 37−48 (2004).

19 Croce, F., Persi, L., Scrosati, B., Serraino-Fiory, F., Plichta, E., Hendrickson, M.A., "Role of the ceramic fillers in enhancing the transport properties of composite polymer electrolytes", *Electrochimi. Acta*, **46**, 2457−2461 (2001).

20 Shao, Z.G., Joghee, P., Hsing, I.M., "Preparation and characterization of hybrid Nafion-silica membrane doped with phosphotungstic acid for high temperature operation of proton exchange membrane fuel cells", *J. Membr Sci.*, **229**, 43−51 (2004).

21 Xu, W.L., Liu, C.P., Xue, X.Z., Su, Y., Lv, Y.Z., Xing, W., Lu, T.H., "New proton exchange membranes based on poly (vinyl alcohol) for DMFCs ", *Solid State Ion.*, **171**, 121−127 (2004).

22 Sambandam, S., Ramani, V., "SPEEK/functionalized silica composite membranes for polymer electrolyte fuel cells", *J. Power Sources*, **170**, 259−267 (2007).

23 Li, L., Wang, Y.X., "Sulfonated polyethersulfone Cardo membranes for direct methanol fuel cell", *J. Membr. Sci.*, **246**, 167−172 (2005).

24 Li, L., Wang, Y.X., "A hybrid membrane of poly(vinyl alcohol) and phosphotungstic acid for fuel cells", *Chin. J. Chem. Eng.*, **10** (5), 614−617 (2002).

25 Zaidi, S.M.J., Mikhailenko, S.D., Robertson, G.P., Guiver, M.D., Kaliaguine, S., "Proton conducting composite membranes from polyetherether ketone and heteropolyacids for fuel cell applications", *J. Membr. Sci.*, **173**, 17−34 (2000).

26 Tricoli, V., Carretta, N., Bartolozzi, M., "A comparative investgation of proton and methanol transport in fluorinated ionomeric membranes", *J. Electrochem. Soc.*, **147**, 1286−1290 (2000).

27 Huang, M.Y., Wang, Y.X., Cai, Y.Q., Xu, L., "Sulfonated poly(ether ether ketone)/zirconium tricarboxybutylphosphonate composite proton-exchange membranes for direct methanol fuel cells", *Acta Polymerica Sinica*, **4**, 337−342 (2007).

28 Gasa, J.V., Boob, S., Weiss, R.A., Shaw, M.T., "Proton-exchange membranes composed of slightly sulfonated poly(ether ketone ketone) and highly sulfonated crosslinked polystyrene particles", *J. Membr. Sci.*, **269**, 177−186 (2006).

29 Kim, Y.S., Wang, F., Hickner, M., Zawodzinski, T.A., McGrath, J.E., "Fabrication and characterization of heteropolyacid (H$_3$PW$_{12}$O$_{40}$)/ directly polymerized sulfonated poly(arylene ether sulfone) copolymer composite membranes for higher temperature fuel cell applications", *J. Membr. Sci.*, **212**, 263−282 (2003).

30 Li, Q.F., Huang, R.H., "Approaches and recent development of polymer electrolyte membranes for fuel cells operating above 100°C", *Chem. Mater.*, **15**, 4896−4915 (2003).