



Novel modification method to prepare crosslinked sulfonated poly(ether ether ketone)/silica hybrid membranes for fuel cells

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ABSTRACT

Crosslinked organic–inorganic hybrid membranes are prepared from hydroxyl-functionalized sulfonated poly(ether ether ketone) (SPEEK) and various amounts of silica with the aims to improve dimensional stability and methanol resistance. The partially hydroxyl-functionalized SPEEK is prepared by the reduction of some benzophenone moieties of SPEEK into the corresponding benzhydrol moieties which is then reacted with (3-isocyanatopropyl)triethoxysilane (ICPTES) to get a side chained polymer bearing triethoxysilyl groups. These groups are subsequently co-hydrolyzed with tetraethoxysilane (TEOS) and allow the membrane to form a crosslinked network via a sol–gel process. The obtained hybrid membranes with covalent bonds between organic and inorganic phases exhibit much lower methanol swelling ratio and water uptake. With the increase of silica content, the methanol permeability coefficient of the hybrid membranes decreases at first and then increased. At silica content of about 6 wt.%, the methanol permeability coefficient reaches a minimum of $7.15 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, a 5-fold decrease compared with that of the pristine SPEEK. Despite the fact that the proton conductivity is decreased to some extent as a result of introduction of the silica, the hybrid membranes with silica content of 4–8 wt.% shows higher selectivity than Nafion117.

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1. Introduction

Direct methanol fuel cells (DMFCs) have been considered as promising portable power source for their high efficiency, high power density, low noise and the simplicity of system [1–3]. Proton exchange membranes (PEM) are the key components of DMFC systems. Currently, the widely used PEMs are perfluorosulfonic acid membranes, such as DuPont's Nafion. These membranes have exceptional oxidative and chemical stability as well as high protonic conductivity [4]. However, several shortcomings such as the high cost, low conductivity at high temperature and low humidity and high methanol crossover have limited their applicability [5–8]. Therefore, the development of alternative PEMs that will overcome these problems is of great importance. Considerable efforts have been made to synthesize novel membranes, such as sulfonated poly(arylene ether ketone)s (SPAEK) [9–11], sulfonated poly(arylene ether sulfone)s (SPAES) [12–15], sulfonated

polyimide (SPI) [16–18], and acid-doped polybenzimidazole (PBI) [19–21], etc. Among the numerous alternative polymers, sulfonated poly(arylene ether ketone)s are good candidates on account of their low cost, high glass transition temperatures and high proton conductivity, which depend on their degree of sulfonation [22]. Compared to perfluorinated sulfonic acid membranes, sulfonated poly(arylene ether ketone)s are reported to have lower acidity and a smaller characteristic separation length and wider distribution of the proton-conducting channels with more dead-end “pockets” and a larger internal interface between the hydrophobic and hydrophilic domains [23]. Therefore, to achieve high proton conductivity, sulfonated poly(arylene ether ketone) membranes require a high sulfonation level. Unfortunately, such a high sulfonation level usually makes them swell excessively and even soluble in methanol/water solution which may lead to deterioration in mechanical properties and high methanol permeation making them unsuitable for DMFC applications [24]. Therefore, modification of PEMs to improve their dimensional stability and decrease the methanol swelling and crossover could be an effective approach to improve their performance.

Crosslinking could be a simple and powerful method to improve their dimensional stability and avoiding the irreversible swelling. By crosslinking, the synthesized polymers could satisfy the need for high degree of sulfonation and dimensional stability [25–27].

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Organic–inorganic hybrid membranes may be another alternative to provide controllable chemical and physical properties by combining the effects of organic polymers and inorganic compounds [28–30]. Several studies have showed that the presence of inorganic particles in the organic polymer matrix can reduce the methanol permeability of the hybrids due to the dispersed silica particles acting as methanol barriers [31–33]. Chang and Lin [33] synthesized a series of organic–inorganic composite materials based on polyethylene glycol (PEG)/SiO₂ through sol–gel processes. Due to the introduction of SiO₂, thermal stability of the hybrid membrane enhanced enormously. Some of the hybrid membranes exhibited low methanol permeability without sacrificing their conductivities significantly. Su et al. [34] developed a series of sulfonated poly(phthalazinone ether ketone) (sPPEK) and sulfonated silica nanoparticles (silica–SO₃H) nanocomposite membranes. The strong –SO₃H/–SO₃H interaction between sPPEK chains and silica–SO₃H particles led to ionic crosslinking in the membrane structure, which increased both the thermal stability and methanol resistance of the membranes. The membrane with 7.5 phr of silica–SO₃H (phr = g of silica–SO₃H/100 g of sPPEK in membranes) exhibited low methanol crossover, high bound water content, and a proton conductivity of 3.6-fold increase to that of the pristine sPPEK membrane. The properties of hybrid materials are in general influenced by particle sizes and interaction between the dispersed and continuous phases [35]. In order to obtain homogeneous and transparent organic–inorganic hybrid membranes, it is necessary to increase the compatibility between organic polymer and inorganic phase. The introduction of covalent bonds between organic polymer and inorganic phases would be effective in increasing the compatibility [35].

In this study, a novel modification method was used to prepare crosslinked organic–inorganic hybrid membranes based on sulfonated poly(ether ether ketone) (SPEEK) and silica with the aims to improve the dimensional stability and methanol resistance. The introduction of covalent bonds between organic polymer and inorganic component effectively avoided the phase separation. Firstly, the partially hydroxyl-functionalized SPEEK was performed by the reduction of some benzophenone moieties of SPEEK into the corresponding benzhydrol moieties. Then SPEEK/silica hybrid composite materials having covalent crosslinking bonds between two phases were prepared through the reaction of hydroxyl-functionalized SPEEK with (3-isocyanatopropyl)triethoxysilane (ICPTES) and tetraethoxysilane (TEOS). The molecular structure and morphology of the prepared SPEEK/silica hybrid membranes were characterized by FT-IR and scanning electron microscopy (SEM).

The water uptake, swelling ratio, proton conductivity and methanol permeability properties of the prepared hybrid membranes were studied and correlated with the molecular structure.

2. Experimental

2.1. Materials

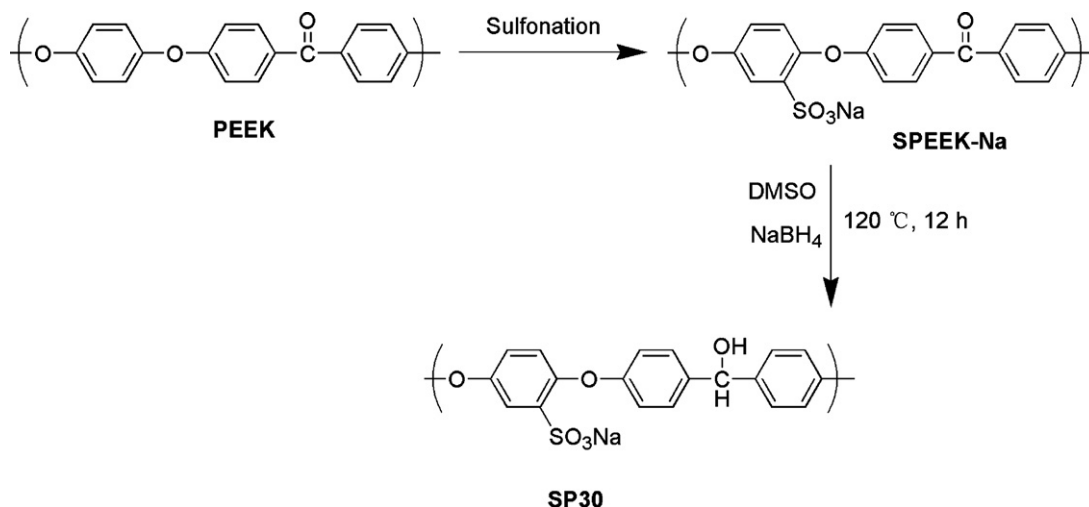
SPEEK was prepared as reported in the literature [36]. The sulfonation degree (SD) and ion exchange capacity (IEC) of SPEEK, used in this study, are 87.6% and 2.37 mequiv. g⁻¹, respectively. Sodium borohydride (NaBH₄), dimethylsulfoxide (DMSO), (3-isocyanatopropyl)triethoxysilane (ICPTES) and tetraethoxysilane (TEOS) were purchased from Beijing Chemical Co. China and used as received.

2.2. Hydroxylation of SPEEK

As shown in Scheme 1, hydroxyl-functionalized SPEEK containing 30 mol% hydroxyl group unit was synthesized as follows: DMSO (45 mL) and NaBH₄ (0.0363 g) were added to a 100 mL round bottomed flask equipped with a reflux condenser and a drying tube. The mixture was heated at 120 °C and 4.5 g SPEEK was then added. After stirring at 120 °C for 12 h, the polymer solution was cooled to room temperature and 3 mL methanol was added while stirring. The abbreviation used for membrane described in this article is as follows: SP30, where 30 refer to carbonyl reduction percentage of SPEEK.

2.3. Preparation of sol–gel precursor solution

The precursor solution was prepared by mixing two solutions, A and B. Solution A containing the triethoxysilyl-functionalized SPEEK was prepared as follows. ICPTES was added slowly into the above-prepared SP30 solution as a bonding agent (molar ratio of hydroxyl group/ICPTES = 1). The mixture was stirred and refluxed at 70 °C for 24 h to complete the reaction. The reaction was carried out under dry nitrogen atmosphere to prevent moisture in the reactor. The triethoxysilyl-functionalized SPEEK was obtained by an addition reaction between isocyanic groups in ICPTES and hydroxyl groups in SP30. Solution B contained TEOS/H₂O with a molar ratio of 1:4. Diluted HCl was used as a catalyst for hydrolysis (pH 4). The mixture of A and B was aged at room temperature for 1 h and then at 30 °C for 3 h.



Scheme 1. Synthesis of SP30.

2.4. Preparation of hybrid membrane

The mixed solution was cast onto a clean glass plate and dried at 40 °C for 48 h and then 120 °C for 24 h to complete the hydrolysis and condensation of silica. The hybrid membranes were converted to the required acid form by immersing in 2 mol L⁻¹ sulfuric acid solution at 30 °C for 24 h, and then washed with deionized water several times to remove excess acid. The prepared membranes were designated as SPEEK/SiO₂-X, where X refers to weight percentage of silica relative to SPEEK.

2.5. Characterization

¹H NMR spectra were obtained with a Bruker 600 MHz spectrometer with dimethyl sulfoxide-d₆ (DMSO-d₆) as a solvent.

FT-IR spectra were obtained with a Shimadzu-FTIR-8400 Fourier transform infrared spectrophotometer.

Ion exchange capacity (IEC) of the membranes was measured by titration. Firstly, the membrane in acid form was immersed in 50 mL of 1 mol L⁻¹ NaCl solution for 24 h to replace the protons of sulfonic acid groups with sodium ions, then the released protons in solution was titrated with 0.01 mol L⁻¹ NaOH using phenolphthalein as the indicator.

Scanning electron microscopy (SEM) measurements were performed on a HITACHI S-5500 microscope with energy dispersive X-ray spectrometry (EDX). The membrane samples were fractured by immersing in liquid nitrogen and coating with carbon. The cross-sectional morphology of membrane was observed by SEM.

Thermo-gravimetric analysis (TGA) was recorded on a PerkinElmer 7 series thermal analysis system at a heating rate of 10 °C min⁻¹ under N₂ atmosphere. Before testing, all the membranes were preheated to 150 °C and kept at this temperature for 30 min to remove any residual moisture and solvent.

The water uptake of the membranes was calculated by setting the weight difference between the dry and wet membranes. The dried membranes were weighed and then soaked in water. Then they were wiped with blotting paper and weighed on an analytical balance until the weight became constant. The water uptake of membranes was calculated by the following equation:

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

where W_{wet} and W_{dry} were the weight of the wet and dry membranes, respectively.

The swelling ratio of the membrane sample was determined by immersing it into 2 mol L⁻¹ methanol/water solution at 30 °C for 24 h and measuring the change in length before and after the swelling. The samples with thickness around 50 μm and size of 70 mm × 12 mm were used for testing. The swelling ratio was calculated by:

$$\text{swelling ratio} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100$$

where L_{wet} and L_{dry} were the length of the wet and dry membrane samples, respectively.

Proton conductivity measurement was performed on fully hydrated film samples with a ZAHNER IM6 at an oscillating voltage of 10 mV, using a two-point probe electrochemical impedance spectroscopy technique at frequency ranging from 100 Hz to 3 MHz. The cell assembly was similar to that used in the literatures [12]. The proton conductivity (σ) of the specimen in the in-plane direction (electric field parallel to the membrane surface) was calculated from the impedance data, using the relation $\sigma = l/R \cdot S$, where l and S are distance between two Pt electrodes and cross-sectional area of

the membrane perpendicular to the current flow and R was derived from the high frequency intercept with the Re(Z) axis on a complex impedance plane plot.

Methanol permeability measurement was carried out using a liquid diffusion cell composed of two compartments containing solutions A and B. One compartment A ($V_A = 150$ mL) was filled with 10 mol L⁻¹ methanol solution. The other compartment ($V_B = 150$ mL) was filled with deionized water only. The membrane under test was immersed in deionized water for hydration before measurements and then vertically placed between the two compartments by a screw clamp. Both compartments were slowly stirred during the permeation experiments. Amount of methanol diffused from compartment A to B across the membrane was measured over time by a gas chromatograph (Shimadzu, GC-14B). The methanol permeability, P was calculated by the following equation [18]:

$$P = \frac{k \cdot V_B \cdot L}{A \cdot C_A}$$

where k was the slope of the straight-line plot of methanol concentration in solution B versus permeation time; V_B , L and A were the volume of solution B, the thickness and the effective area of the membrane, respectively.

3. Results and discussion

3.1. Synthesis of hydroxyl-functionalized SPEEK

Functionalized polymers have attracted great attention for their improved properties and new applications. Noiset et al. [37] reported the carbonyl group of amorphous PEEK can be reduced to hydroxyl group by treatment with sodium borohydride (NaBH₄) in DMSO solution at 120 °C for 3 days. Jin et al. [38,39] synthesized hydroxyl-functionalized poly(phthalazinone ether ketone) (PPEK) by the reduction of some benzophenone moieties into the corresponding benzhydrol moieties to introduce the active hydroxyl group into the main chain. Because of their similar structures, the reduction of SPEEK was also carried out by reducing some benzophenone moieties into the corresponding benzhydrol moieties leading to SPEEK with well-defined hydroxyl groups, as shown in Scheme 1.

The composition and structure of resulting SP30 samples were confirmed by ¹H NMR spectroscopy and FT-IR. In the ¹H NMR spectrum, recorded in DMSO, the C-H benzhydrol proton gave a resonance line at around 5.7 ppm (Fig. 1) [38]. FT-IR spectra for SPEEK and SP30 membranes are showed in Fig. 2. The membranes exhibited typical sulfonate groups absorption bands in spectrum, including strong characteristic peaks at 1252 cm⁻¹,

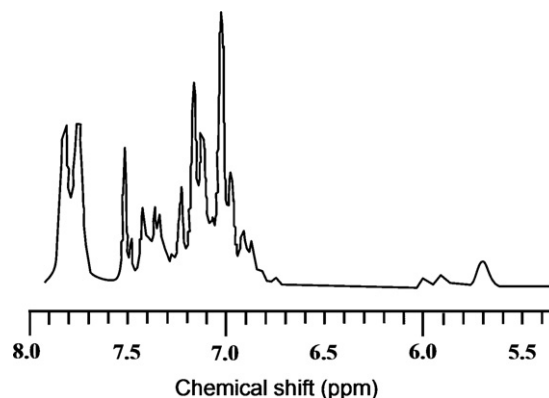


Fig. 1. ¹H NMR of SP30.

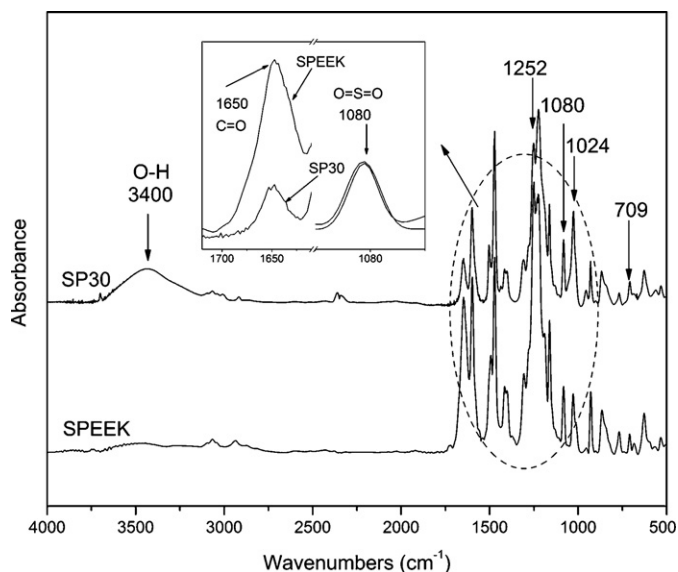


Fig. 2. FT-IR spectra for SPEEK and SP30.

1080 cm^{-1} , 1024 cm^{-1} and 709 cm^{-1} assigned to asymmetric O=S=O stretching, symmetric O=S=O stretching, S=O stretching and S–O stretching, respectively [10]. Compared to the SPEEK, the SP30 carbonyl band at 1650 cm^{-1} showed a significant decrease (1080 cm^{-1} as a internal standard) and a broad absorption band at 3400 cm^{-1} (O–H stretching) appeared [37].

3.2. Preparation of SPEEK/SiO₂ hybrid membranes

The reaction between SP30 and ICPTES is shown in Scheme 2. The covalent bonds between the organic and inorganic phases were introduced by reacting the hydroxyl group of SP30 with ICPTES to form a copolymer bearing a triethoxysilyl group, and the ICPTES played a bridge role between organic and inorganic phases. Fig. 3 demonstrates the FT-IR spectra of the reaction between SP30 and ICPTES. The figure displays the change of the characteristic peak of the NCO group of ICPTES at 2270 cm^{-1} and the carbonyl of HN–COO group in SP30 at 1694 cm^{-1} . The addition reaction of ICPTES caused the peak at 2270 cm^{-1} to disappear gradually and the formation of

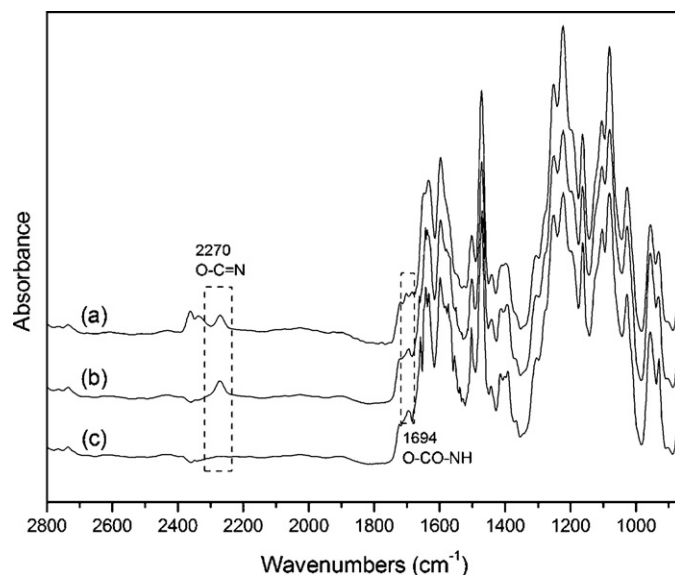


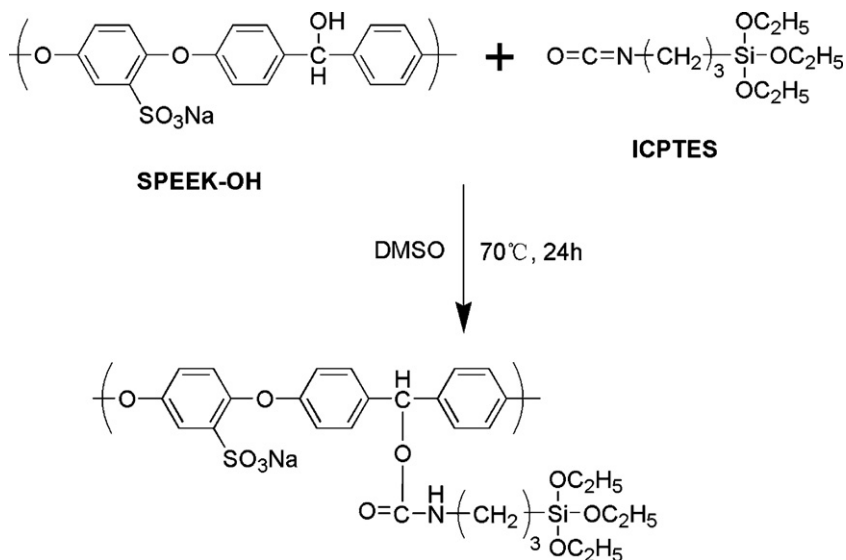
Fig. 3. FT-IR spectra of the reaction between SP30 and ICPTES. (a) Initial reaction, (b) 3 h, and (c) 24 h.

carbonyl group with SP30 caused the carbonyl group peak to appear significantly with time.

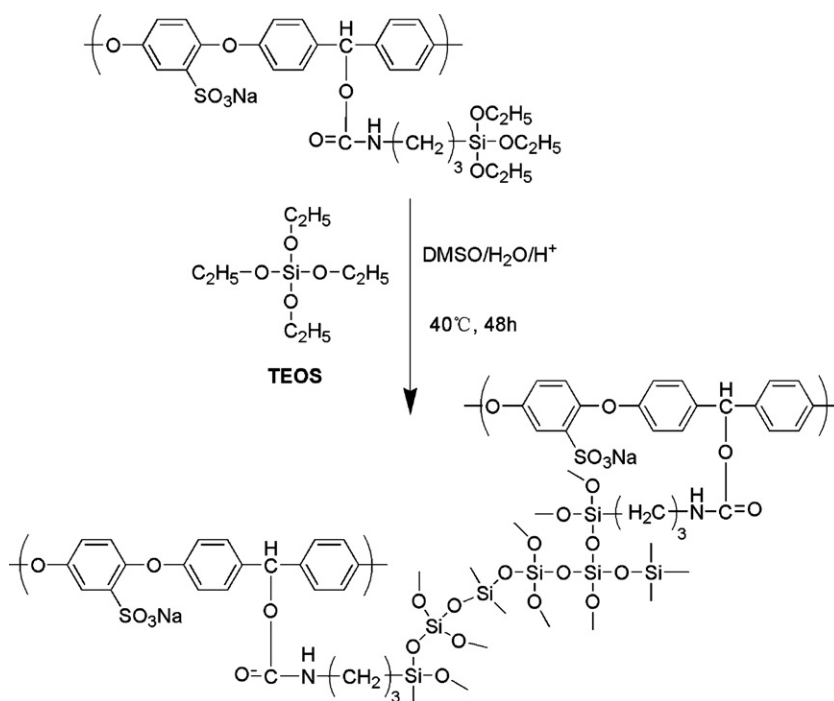
The chemical reactions for the preparation of the SPEEK/SiO₂ hybrid membranes are shown in Scheme 3. The ethoxysilyl groups contained in the polymer main chains were subjected to co-hydrolysis and co-condensation with TEOS in the sol–gel process. A large crosslinking network was formed of organic and inorganic phases that interpenetrated each other.

Fig. 4 shows the FT-IR spectra of the SPEEK and SPEEK/SiO₂–8 membranes. Compared to SPEEK, new broad bands appear at 955 cm^{-1} (characteristic of the Si–OH stretching), and at around 1129 cm^{-1} (characteristic of Si–O–Si asymmetric stretching) in sulfonated hybrid membrane, arising from the products of the sol–gel reaction. Furthermore, the broad absorption peak at around 3400 cm^{-1} (O–H stretching) in the hybrid membrane indicates that there were a significant number of –OH groups due to non-condensed $\equiv\text{SiOH}$.

Ion exchange capacity (IEC) of SPEEK and hybrid membranes is shown in Table 1. It can be noted that the IEC values of membranes



Scheme 2. The reaction between SP30 and ICPTES.



Scheme 3. Preparation of SPEEK/SiO₂ hybrid material.

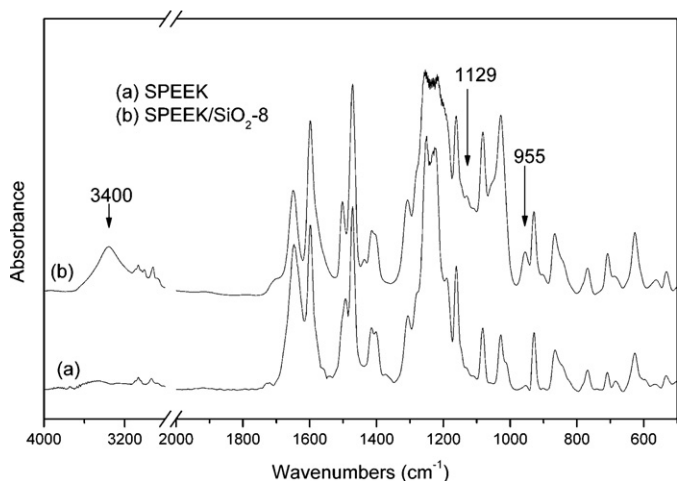


Fig. 4. FT-IR spectra of SPEEK and SPEEK/SiO₂-8 membranes.

decreased with the increasing of silica content, and were in the range of 1.91–2.37 mequiv. g⁻¹. The high IEC means that the hybrid membranes contained sufficient sulfonic acid sites for the intended proton transportation.

3.3. Morphology

The SPEEK/SiO₂ hybrid membranes with 4–20 wt.% silica content showed good transparent appearance (Fig. 5) indicating the formation of small silica nanoparticles from sol–gel process.

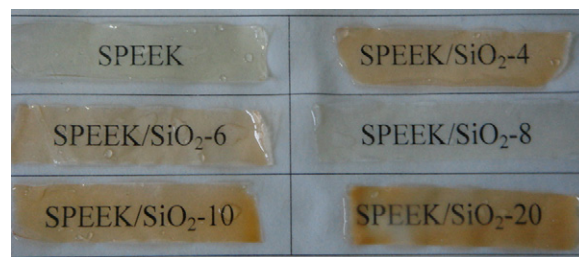


Fig. 5. Photograph of membranes.

Fig. 6 shows cross-sectional SEM images of hybrid membranes of SPEEK/SiO₂-6 (a) and SPEEK/SiO₂-20 (b). The presence of the silica particles were confirmed by using EDX spectrum shown in Fig. 7. It can be found from Fig. 6 that the silica particles were on the nanoscale in the hybrid membranes with no silica aggregation and phase separation occurred. The average size of the silica particles slightly increased with the increase of silica content. In SPEEK/SiO₂-6 membrane, the average diameter of inorganic particles was no more than 30 nm, and the size of the inorganic particles in SPEEK/SiO₂-20 was smaller than 55 nm. The figures presented a homogeneous distribution of the silica in the observation area indicated that the silica nanoparticles homogeneously distributed in the SPEEK matrix. Moreover, it was noted that the introduction of silica nanoparticles to the polymer matrix did not introduce porosity, allowing a good contact between the polymer matrix and the filler. We expect that the silica particles embedded in the membrane matrix act as a methanol barrier, and consequently methanol permeability will be reduced.

Table 1

Ion exchange capacity (IEC) of SPEEK and hybrid membranes.

Sample	SPEEK	SPEEK/SiO ₂ -4	SPEEK/SiO ₂ -6	SPEEK/SiO ₂ -8	SPEEK/SiO ₂ -10	SPEEK/SiO ₂ -20
SiO ₂ content (wt.%)	0	4	6	8	10	20
IEC ^a (mequiv. g ⁻¹)	2.37	2.21	2.17	2.08	2.01	1.91

^a Measured IEC of the membranes by titration.

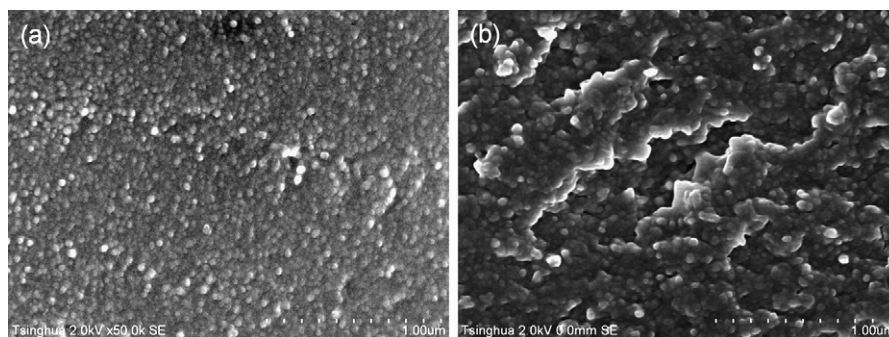


Fig. 6. Cross-sectional SEM images of membranes. (a) SPEEK/SiO₂-6, and (b) SPEEK/SiO₂-20.

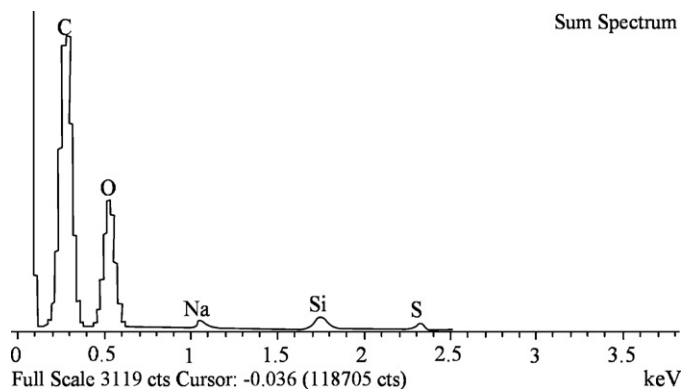


Fig. 7. EDX spectrum of SPEEK/SiO₂-6.

3.4. Thermal property

The thermal stability of pristine SPEEK and SPEEK/SiO₂ hybrid membranes were studied using TGA in N₂. The membrane samples for TGA analysis were preheated to 150 °C at 10 °C min⁻¹ under nitrogen atmosphere and held isothermally for 30 min for moisture removal. As shown in Fig. 8, a two-step degradation profile was observed for acidified form SPEEK. The first weight loss region around 350 °C was assigned to result from the desulfonation and possibly loss of tightly bound water. In the second weight loss region, the polymer residues were further degraded at $T=540^{\circ}\text{C}$, which corresponds to the decomposition of the SPEEK main chain.

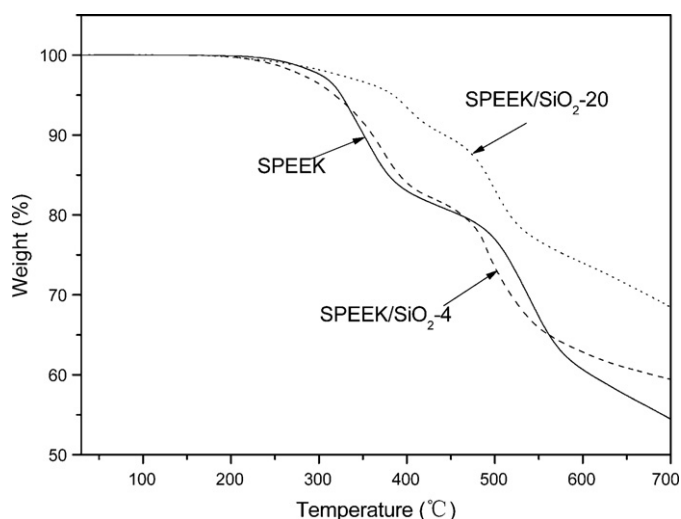


Fig. 8. TGA curves of SPEEK and hybrid membranes.

The weight remaining after the polymer decomposition depended on the content of the inorganic component. That is, the weight residues of the SPEEK/SiO₂-4 and SPEEK/SiO₂-20 hybrid membranes containing silica at $T=700^{\circ}\text{C}$ were higher than that of pristine SPEEK membrane. The TGA studies revealed that the hybrid membranes had good thermal stabilities below 200 °C, which could completely satisfy the requirement of PEMs in DMFCs.

3.5. Water uptake and methanol swelling

Fig. 9 shows the water uptake of the SPEEK/SiO₂ hybrid membranes as a function of SiO₂ content at 30 °C. It is noted that the hybrid membranes exhibited a lower water uptake compare to pristine SPEEK, but all hybrid membranes had similar water uptake. The water uptake of the hybrid membranes decreased to about 45% of that of pristine SPEEK. When the co-condensation reaction between the ethoxysilyl groups contained in the polymer chains and TEOS in the sol-gel process occurred, a crosslinked hybrid network might have been formed. It is known that the crosslinking increases the interaction of the polymers and hinders chains mobility which results in more compact membranes with a decrease in the free volume capable of holding water molecules. An increase in the content of silica moieties is associated with more crosslinking density, and further restrictions on the mobility of polymer chains will further decrease in the water uptake. However, sol-gel process performed at relatively low temperatures (<300 °C) might limit the gel reaction conversions to result in silica possessing high contents of silanol groups. These retained silanol groups contribute to the high hygroscopic character of the formed silica [40,41].

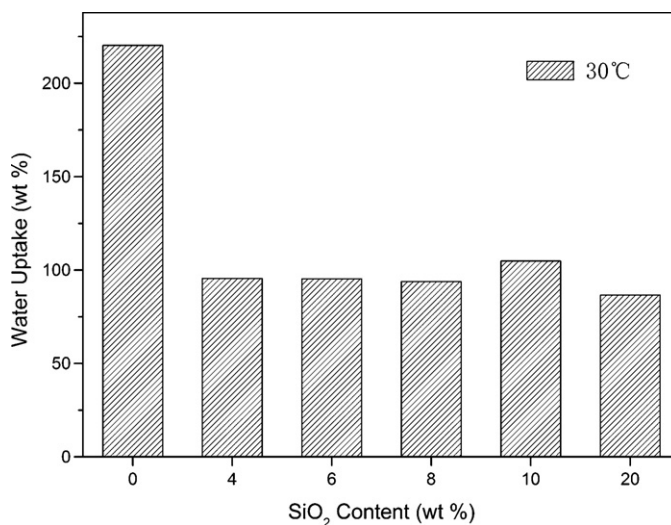


Fig. 9. Water uptake of SPEEK and hybrid membranes at 30 °C.

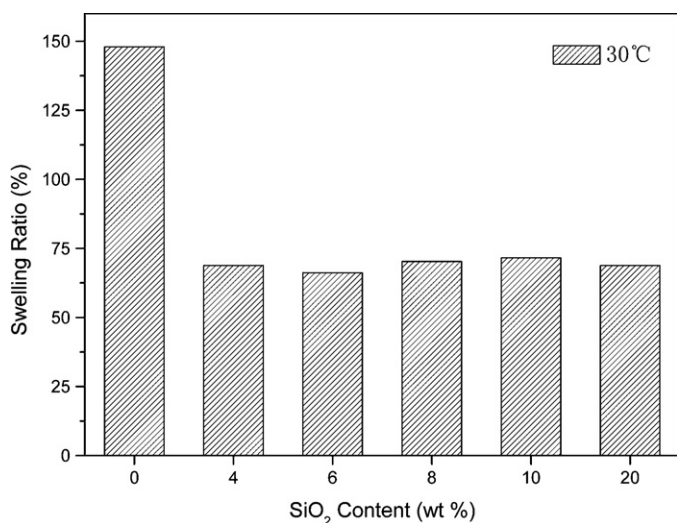


Fig. 10. Swelling ratio of SPEEK and hybrid membranes at 30°C.

Although the free volume that could associate with the water molecules in the polymer structure decreased with an increasing degree of crosslinking, the silica particles also could absorb water molecules. Both crosslinking and hygroscopic effect dominated the water uptake of hybrid membranes.

Membrane swelling is a more important parameter than water uptake for DMFC applications. A disadvantage of most sulfonated hydrocarbon polymer membranes is their high swelling behavior in methanol/water solution, especially at high temperature or high methanol concentration, which may cause excessive dimensional changes, uneven stresses between the membrane, electrodes and seal, even resulting in the breakage of membrane in fuel cells [26]. The swelling ratio of the SPEEK and hybrid membranes in 2 mol L⁻¹ methanol aqueous solution at 30°C as a function of SiO₂ content is shown in Fig. 10. It can be found from Fig. 10 that all hybrid membranes had similar swelling ratio and a significant reduction relative to those for the pristine SPEEK, and followed a similar trend as observed for the water uptakes. The change in swelling ratio could be because the crosslinking increased the interaction of the polymer molecules which restrained the movement of polymer chains, while hygroscopic effect might contribute to the increase in swelling ratio.

3.6. Proton conductivity

Fig. 11 shows the proton conductivities of the SPEEK and hybrid membranes at 30°C in liquid water. As the silica content is increased, the proton conductivity of hybrid membranes decreased. Specifically, it decreased from 0.121 S cm⁻¹ for pristine SPEEK membrane to 0.088 S cm⁻¹ for the SPEEK/SiO₂ hybrid membrane with 6 wt.% SiO₂ content, which resulted in 27% decrease compared to pristine polymer. In general, two principal mechanisms describe proton diffusion through the membranes [42,43]. One is the Grotthus mechanism (hopping mechanism) wherein a proton is passed down a chain of water molecules. The protons are transferred from one proton acceptor site to another by hydrogen bonds (proton hopping). The other is the vehicle mechanism whereby a proton combines with vehicles such as H₃O⁺ or CH₃OH₂⁺ and also with unprotonated vehicles (H₂O), thus allowing the net transport of protons. It is possible that the bound water participates by the Grotthus mechanism, and the free water takes part mostly by vehicle mechanism [34]. The decrease in proton conductivity could be resulting from the crosslinking effect of inorganic network restricting mobility of polymer chains and decreasing the

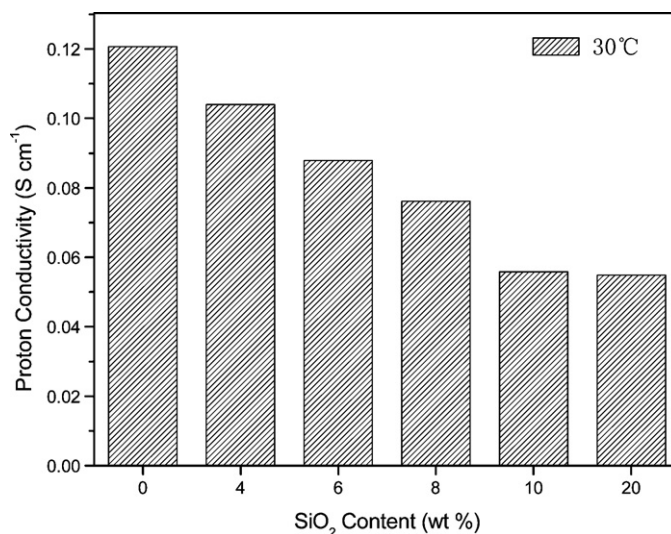


Fig. 11. Proton conductivity of SPEEK and hybrid membranes at 30°C.

free volume, which might result in less and smaller hydrophilic channels for hydrated proton transport. Further, addition of silica to SPEEK might cause the lower IEC and the reduced membrane hydration in the hybrid membranes so as to lower the membrane's proton conductivity.

3.7. Methanol permeability

To evaluate the suitability of hybrid membranes for DMFCs, methanol permeability coefficient was measured and is shown in Fig. 12. The methanol permeability coefficient of the hybrid membranes decreased at first and then increased. At silica content of about 6 wt.%, the methanol permeability coefficient was at its minimum of 7.15×10^{-7} cm² s⁻¹, a 5-fold decrease compared to that of the pristine SPEEK membrane. The reduction in methanol permeability coefficient might be explained as follows: crosslinking network could effectively hinder the polymer chain mobility and suppress the swelling of network in aqueous methanol solution, which could reduce the channels to pass methanol molecules increasing the resistance to methanol diffusion. In addition, the silica particles in the polymer matrix could

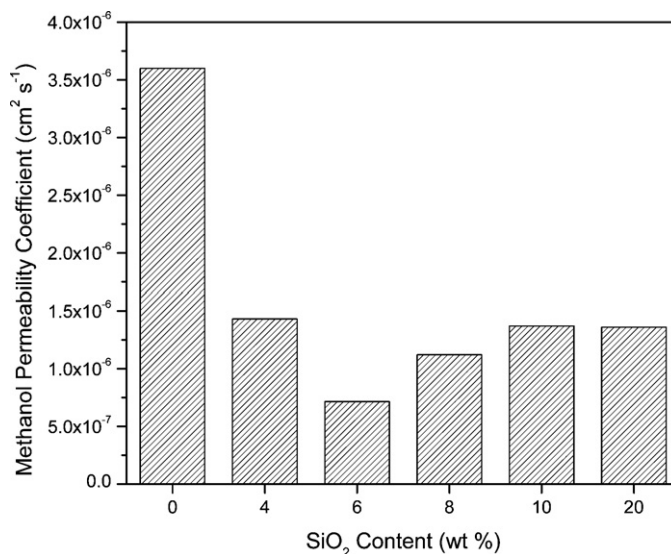


Fig. 12. Methanol permeability coefficient of SPEEK and hybrid membranes at 30°C.

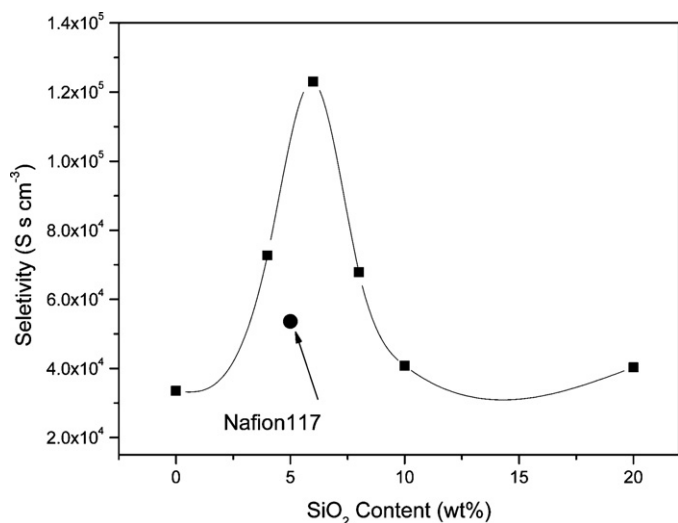


Fig. 13. Selectivity of the SPEEK and the hybrid membranes as a function of SiO₂ content.

be acting as methanol barriers, inhibiting the methanol crossover through the membranes. Increase in silica content would bring more blocking, resulting in the decrease of methanol crossover of the membranes. However, for a silica content of greater than 6 wt.%, the methanol permeability coefficient of the hybrid membranes increased gradually. This reversal might be a result from the average diameter of silica nanoparticles gradually increased with the increasing the content of silica. The bigger silica particles in hybrid membranes decreased the resistance opportunity for methanol transport, which resulted in more methanol crossover through membranes. Hence, small silica particle size and highly crosslinking degree were preferred for hybrid membranes with excellent methanol barrier property.

3.8. Selectivity

Both methanol permeability coefficient and proton conductivity are the two transport properties crucial for the fuel cell performance in DMFCs. Low methanol permeability coefficient and high proton conductivity are desired [44]. The potential performance of DMFC membranes is often evaluated in terms of the ratio of proton conductivity to methanol permeability coefficient defined as selectivity [45]. Higher selectivity is necessary for achieving better membrane performance. Selectivity of the SPEEK and the hybrid membranes as a function of SiO₂ content at 30 °C is shown in Fig. 13. It was found that selectivity of the hybrid membranes increased at first and then decreased with the increase in SiO₂ content. The membranes with 4–8 wt.% SiO₂ showed higher selectivity than Nafion117 because of their lower methanol permeability coefficient. At the silica content of about 6 wt.%, the selectivity was at its maximum, about 2.29-fold higher compared to that of Nafion117.

4. Conclusions

To improve the dimensional stability and methanol resistance, sulfonated poly(ether ether ketone) (SPEEK) was partially reduced to corresponding hydroxyl-functionalized SPEEK which was then reacted with ICPTES and TEOS to get a series of crosslinked organic–inorganic hybrid membranes. The introduction covalent crosslinkage between organic and inorganic phases reinforced the compatibility between SPEEK chains and the silica particles. Compared with pristine SPEEK, all hybrid membranes exhibited lower methanol swelling ratio and methanol permeability coefficient.

Although the conductivity slightly decreased by the addition of silica, the overall performance of the hybrid membranes was still superior and the hybrid membranes with silica content of 4–8 wt.% showed higher selectivity than Nafion117.

Although still suffered from relatively high methanol swelling ratio which attributed to the original high value of pristine SPEEK, the hybrid membranes get an obvious improvement in dimensional stability and methanol resistance at a large extent. On this point, the modification method provided in this paper is effective and it was expected that much better membranes could be prepared by this method using other polymers which possess of relatively lower swelling ratio (ex., sulfonated poly(ether ketone) or sulfonated poly(ether ketone sulfone) synthesized by direct copolymerization from sulfonated monomers) as matrix. Further study as mentioned above remains to be continued in our lab.

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