



Novel hybrid polymer electrolyte membranes with high proton conductivity prepared by a silane-crosslinking technique for direct methanol fuel cells

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ARTICLE INFO

Article history:

Received 20 August 2010

Received in revised form

30 September 2010

Accepted 1 October 2010

Available online 8 October 2010

Keywords:

Sulfonated poly(arylene ether ketone)

Proton exchange membrane

Polysiloxanes

Fuel cell

ABSTRACT

In order to prepare a hybrid proton exchange membrane with low methanol permeability and high proton conductivity, two silane monomers, namely 3-glycidoxypropyl-trimethoxysilane (GPTMS) and 3-mercaptopropyl-trimethoxysilane (MPTMS) are first blended with a sulfonated poly(arylene ether ketone) (SPAEK). Then the blended membrane is heated to induce the grafting of GPTMS onto SPAEK. Finally, a hydrolysis-condensation is performed on the grafted membrane to induce cross-linking. The –SH groups of MPTMS are oxidized to sulfonic acid groups, which are attributed to enhance the proton conductivity of hybrid membranes. Fourier transform infrared spectroscopy is used to characterize and confirm the structures of SPAEK and these cross-linked hybrid membranes. The proton conductivity of a cross-linked hybrid membrane G50M50 reaches up to 0.20 S cm^{-1} at 80°C , which is comparable to that of SPAEK and much higher than that of Nafion. Meanwhile, the methanol permeability is nearly three times lower than that of Nafion and two times lower than that of SPAEK. The ion-exchange capacity, water uptake, membrane swelling and thermal stability are also investigated to confirm their applicability in fuel cells.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs), especially direct methanol fuel cells (DMFCs) continue to receive extensive attention because of their utility as promising clean power sources for automotive, stationary, and portable applications [1–3]. In PEMFCs, a proton exchange membrane (PEM) plays an important role as a core material, which requires high proton conductivity, sufficient thermal stability, low permeability of fuel and oxidant as well as inexpensive operating cost [4]. Currently, the widely used membrane materials are perfluorinated sulfonic ionomers, such as Dupont Nafion[®]. Superior proton conductivity and excellent long-term durability in fuel cells have made them to be the mostly studied electrolytes. However, high methanol permeability, high cost and loss of the preferable properties at high temperatures limit their widespread commercial applications [5–8]. Therefore, considerable efforts have been carried out to search for alternative cost-effective proton exchange membrane materials.

Sulfonated aromatic polymers, including sulfonated poly(arylene ether ketone) (SPAEK) [9–12], fell into this category. They can offer the attribute of adjustable proton conductivity, excellent mechanical and thermal stabilities [13–15]. Generally,

membranes based on these polymers only reach high proton conductivity at high degree of sulfonation. However, the more sulfonated the polymers are, the more permeable they are to methanol, thus diminishing dimensional stability and eliminating any advantages with respect to Nafion when used in the solid state.

Cross-linking is a powerful and simple method to suppress the methanol crossover and water swelling of PEMs. After a cross-linking treatment, the polymer matrix forms a network where the macromolecular chain of polyelectrolyte is immobilized and compacted [16–19]. Plenty of work has been done to use the cross-linking method in the area of PEMs to reduce the methanol crossover successfully for DMFCs [20–22]. However, in most of these cases, proton conductivity decreased significantly due to diminishing the free protons of conductive materials or the addition of non-conductive materials. Thus it is significant to develop constituent materials which can be cross-linked with polymer backbone while preserving the free protons of the polymer.

The organic–inorganic hybrid PEM is becoming another important approach to improve their properties. They are generally prepared by *in situ* growth of constituent particles using sol–gel techniques [23–27]. Recently, many silane monomers have been introduced into PEMs by Kohl's and Ramani's groups, and the resulted hybrid membranes showed good proton conductivity and greatly decreased methanol permeability [28–30]. In this paper, we develop a novel procedure to obtain a covalently cross-linked

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Table 1
The cross-linked hybrid membranes sample description.

Membrane	SPAEK (g)	GPTMS (g)	MPTMS (g)	E_a (kJ mol ⁻¹)
SPAEK	2.0	0	0	22.0
G100	1.90	0.10	0	14.8
G75M25	1.90	0.075	0.025	14.9
G50M50	1.90	0.05	0.05	19.4
G25M75	1.90	0.025	0.075	15.0
Nafion 117	–	–	–	10.8

hybrid PEM for DMFC applications, combining the condensation of carboxyl groups/epoxide, the oxidation of –SH and the silane-crosslinking techniques. Firstly, we chose a SPAEK bearing carboxyl groups as the polymer backbone. Then we grafted a special silane monomer, 3-glycidoxypropyl-trimethoxysilane (GPTMS), onto the SPAEK backbone by a reaction between the epoxy groups and the carboxyl groups. 3-Mercaptopropyl-trimethoxysilane (MPTMS) containing –SH groups was also blended into the system to induce silane-crosslinking by a hydrolysis-condensation. The advantage of this system is that the sulfonic acid groups of SPAEK are not involved in the cross-linking reaction. Then, the –SH groups of MPTMS were oxidized to sulfonic acid groups, which could enhance the proton conductivity of hybrid membranes. Thus, the cross-linked membranes not only exhibited low water uptake and low methanol crossover, but also achieved high proton conductivity. The ion-exchange capacity (IEC), water uptake, methanol permeability and thermal properties of the cross-linked membranes have been investigated in detail.

2. Experimental

2.1. Materials

SPAEK was synthesized by the aromatic nucleophilic polycondensation of sodium 5, 5'-carbonyl-bis(2-fluorobenzene-sulfonate), 4,4'-difluorobenzophenone and phenolphthalin accord-

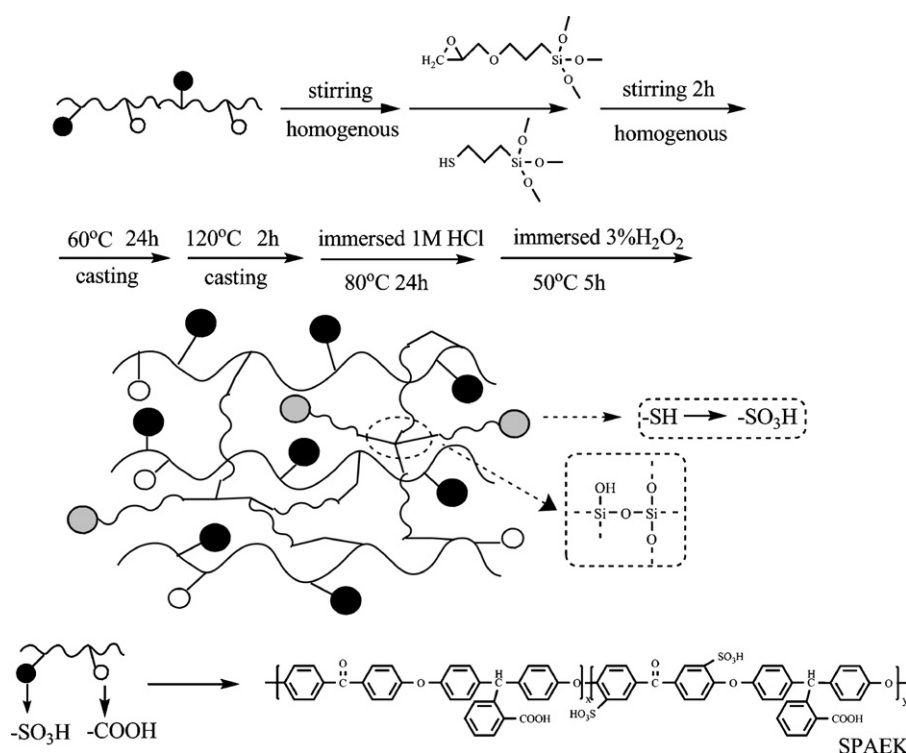
ing to a procedure described in our previous work [31]. The IEC and the inherent viscosity of SPAEK is 1.6 mequiv. g⁻¹ and 0.97 dL g⁻¹, respectively. MPTMS and GPTMS were obtained from Nanjing Lipai chemical company. All other reactants and solvents were obtained from Tianjin Tiantai chemical company and used as received without further purification.

2.2. Membrane preparation, cross-linking and oxidation treatment

The preparation of cross-linked hybrid membranes was performed by three steps. SPAEK solutions in NMP blending with different weight ratios of GPTMS and MPTMS were cast into films and thermally treated at 100 °C for 1 h and at 120 °C for 2 h to lead the epoxy groups of GPTMS to react with carboxyl groups of SPAEK. Dried membranes were peeled off from the substrate and immersed in a 1 M HCl solution at 80 °C for 24 h to complete the hydrolysis-condensation and cross-link the hybrid membranes. Then the cross-linked membranes were placed in a 3% H₂O₂ solution at 50 °C for 5 h to oxidize the –SH *in situ* into –SO₃H. The mechanism is shown in Scheme 1. The nomenclature used to describe the cross-linked hybrid membranes with different amounts of GPTMS and MPTMS is shown in Table 1. For example, G50M50 refers to the cross-linked hybrid membrane with SPAEK 1.90 g, GPTMS 0.05 g and MPTMS 0.05 g. Moreover, the thickness of all the membranes is 100 ± 10 μm. Before use, the membranes were kept in distilled water at room temperature.

2.3. Characterization

The inherent viscosity of the copolymer was measured in DMF at 25 °C with a polymer concentration of 5.0 g L⁻¹. Fourier transform infrared spectroscopy (FT-IR) spectra of powder samples were obtained between 4000 cm⁻¹ and 400 cm⁻¹ with a Bruker Vector 22 FT-IR spectrometer. Thermo-gravimetric analysis (TGA) and derivative thermogravimetry (DTG) was recorded on a Pyris-1



Scheme 1. Scheme for illustrating the preparation of cross-linked hybrid membranes.

(Perkin Elmer) series thermal analysis system at a heating rate of $10^{\circ}\text{C min}^{-1}$ under N_2 atmosphere. Before testing, all the membranes were preheated to 120°C and kept at this temperature for 20 min to remove any residual moisture and solvent.

2.4. Mechanical properties of membranes

The mechanical properties of membranes were investigated using a SHIMADZU AG-I 1KN stress-strain device at room temperature at a constant cross-head speed of 2 mm min^{-1} . The tensile measurements were conducted on membrane samples of 4 mm width and 15 mm length. Prior to the measurements, the membrane samples were stabilized at ambient temperature and humidity, which was around 30% relative humidity.

2.5. Water uptake, membrane swelling, ion-exchange capacity, methanol permeability and proton conductivity of membranes

The water uptake was determined by measuring the change in the weight between the dry and swollen membranes. A detailed procedure was reported previously [32]. The membrane swelling was defined as follows:

$$\text{Membrane swelling (\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100 \quad (1)$$

where L_{wet} and L_{dry} are the length of wet and dry membranes, respectively.

The IEC values of the cross-linked hybrid membranes were determined by classical titration. The membrane sample was immersed in a 1 M NaCl solution for at least 24 h to exchange the H^+ ions from Na^+ . The exchanged protons within the solutions were titrated with 0.05 N NaOH solutions using phenolphthalein as an indicator. Each sample must be measured three times until it had reached to a constant value. The IEC values were recorded in unit of millimole NaOH per gram of the membrane samples (mequiv. g^{-1}) as an average value for each sample.

Methanol permeability was measured using a home-made glass diffusion cell, which consisted of two compartments and divided by a membrane sample. 125 mL methanol–water solution (10 M) was placed on one side of the diffusion cell (cell A, donor reservoir) and 125 mL water was placed on the other side (cell B, receptor reservoir). Both compartments were continuously stirred using submersible magnetic stirrers. The concentration of the methanol in cell B was measured by using SHIMADZU GC-1020A chromatograph. Peak areas were converted to the methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated by Eq. (2), as stated elsewhere [33–35].

$$C_{\text{B}}(t) = \frac{A}{V_{\text{B}}} \frac{DK}{L} C_{\text{A}}(t - t_0) \quad (2)$$

where A , L and V_{B} are the effective area, the thickness of membrane and the volume of receptor reservoir, respectively. C_{A} and C_{B} are the methanol concentration in the donor and receptor reservoirs, respectively. D , K and t_0 are the methanol diffusivity, the partition coefficient and the time lag, respectively. The methanol permeability (P in $\text{cm}^2 \text{s}^{-1}$) is defined as the product of diffusivity and partition coefficient, i.e., $P = DK$, and the concentration change of C_{B} with time is obtained from a linear slope (α), using Eq. (3).

$$P = DK = \alpha \times \frac{V_{\text{B}}}{A} \times \frac{L}{C_{\text{A}}} \quad (3)$$

The proton conductivity was measured by a four-electrode ac impedance method from 0.1 Hz to 100 kHz, 10 mV ac perturbation and 0.0 V dc rest voltage using a Princeton Applied Research Model 2273 potentiostat/galvanostat/FRA. The membranes were cut into 1 cm wide, 4 cm long and were fixed in a measuring cell made of

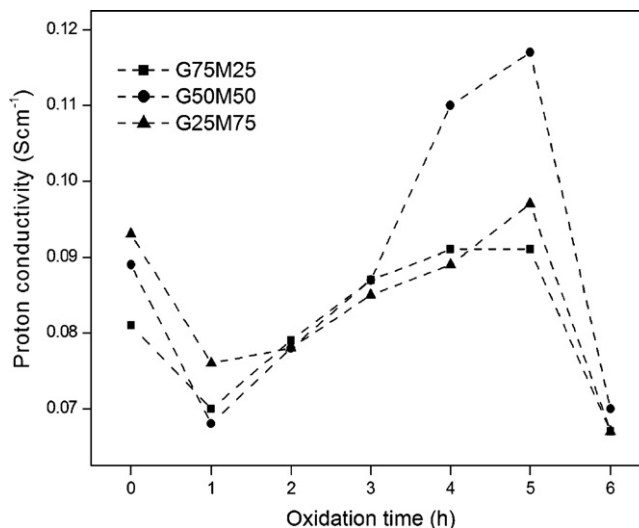


Fig. 1. The proton conductivity change of cross-linked hybrid membranes in 3% H_2O_2 aqueous solution at 50°C .

two outer gold wires (A, D) to feed current to the sample and two inner gold wires (B, C) to measure the voltage drops [36]. All the membranes were mounted between two polytetrafluoroethylene plates. The cell was immersed into water during measurement. Before measurement, the films were full hydrated in water for 24 h. The proton conductivity was calculated by following Eq. (4):

$$\sigma = \frac{L}{RA} \quad (4)$$

where σ is the proton conductivity in S cm^{-1} , L is the distance between the two electrodes (1 cm), R is the resistance of the membrane and A is the cross-sectional area of membrane (the product of width and thickness of the membrane, in cm^2).

3. Results and discussion

3.1. Preparation of cross-linked hybrid membranes

A SPAEK copolymer containing pendant carboxyl groups were synthesized by a nucleophilic aromatic substitution ($\text{S}_{\text{N}}\text{Ar}$) polycondensation of activated aromatic halides with phenolphthalein under standard conditions. The inherent viscosity of the SPAEK is 0.97 dL g^{-1} in DMF at 25°C , indicating that a high molecular weight was obtained. We expected here to obtain covalently cross-linked hybrid membranes without decreasing proton conductivity.

To find a proper oxidation condition which can oxidize $-\text{SH}$ to the greatest extent and avoid membrane degradation, all the cross-linked hybrid membranes were oxidized in 3% H_2O_2 at 50°C . The proton conductivities of them as a function of time are displayed in Fig. 1. It was observed that the proton conductivity of all the membranes began to decrease at the first hour due to the slight degradation. After 1 h, the proton conductivity increased with time, indicating that the $-\text{SH}$ was oxidized to $-\text{SO}_3\text{H}$. After 5 h, the proton conductivity began to decrease drastically due to the degradation. Thus, we chose 5 h as the best oxidation time. In this paper, all the cross-linked hybrid membranes containing $-\text{SH}$ were oxidized in 3% H_2O_2 solution at 50°C for 5 h.

FT-IR spectra were performed to confirm the structures of GPTMS (a), MPTMS (b), SPAEK(c) and G25M75 (d) membranes. As shown in Fig. 2, SPAEK shows the characteristic bands at 1080 cm^{-1} for $\text{O}=\text{S}=\text{O}$ stretching vibrations of sulfonic acid groups. The characteristic bands of sulfonic acid groups are also present in the spectrum of G25M75, indicating the preservation of sulfonic acid

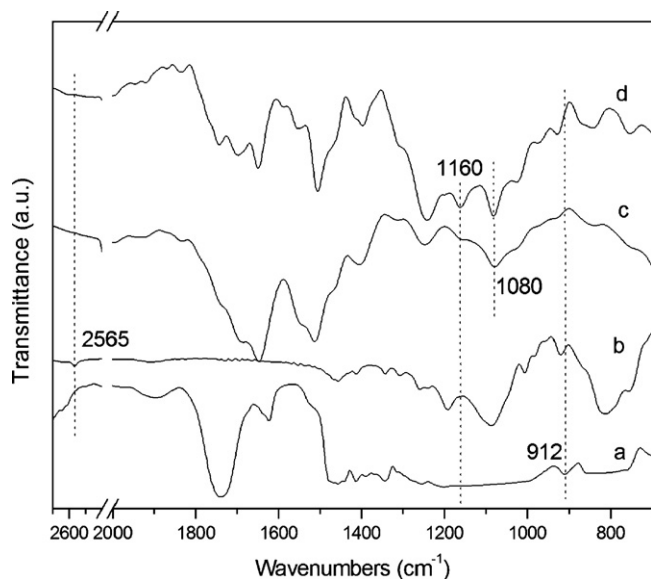


Fig. 2. FT-IR spectra of GPTMS (a), MPTMS (b), SPAEK (c) and G25M75 (d).

groups in the composite membranes. In the spectra of GPTMS and MPTMS, 912 cm^{-1} can be assigned to the epoxy characteristic bands, and 2565 cm^{-1} can be assigned to the sulfhydryl characteristic bands, respectively. After heating, hydrolysis–condensation and oxidation treatments, the epoxy and sulfhydryl peaks are no longer present in the spectrum (d). A similar behavior for FT-IR data was observed by Kim et al. [28]. They found that the thiol peak at 2570 cm^{-1} disappeared within 2 h of oxidation in peroxide, indicating that the thiol groups were converted to the sulfonic acid groups by adding the hydrogen peroxide. Furthermore, Si–O–Si peaks appearing at 1160 cm^{-1} became obvious in the spectrum (d), which confirmed the formation of Si–O–Si cross-linking structure.

3.2. Thermal stability

The thermal stability of membranes, which is critical for the durability during fuel cell operation at high temperature, was evaluated using the TGA experiments and the results are displayed in Figs. 3 and 4. It was shown that the thermal degradation profiles were similar to one another. They all decomposed in two stages.

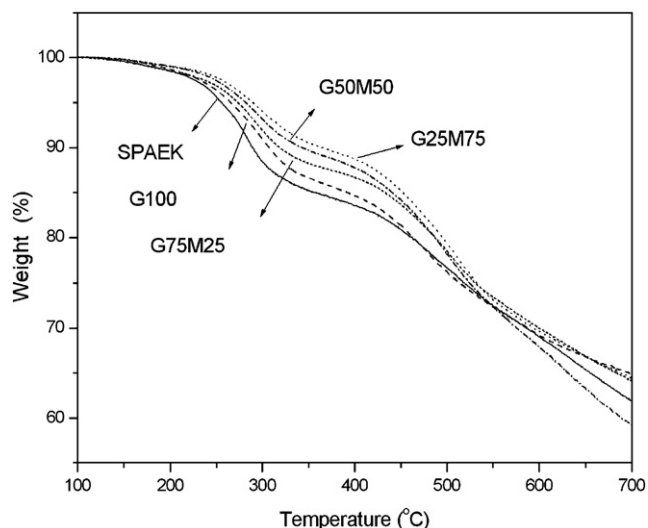


Fig. 3. TGA curve of SPAEK and cross-linked hybrid membranes in N_2 .

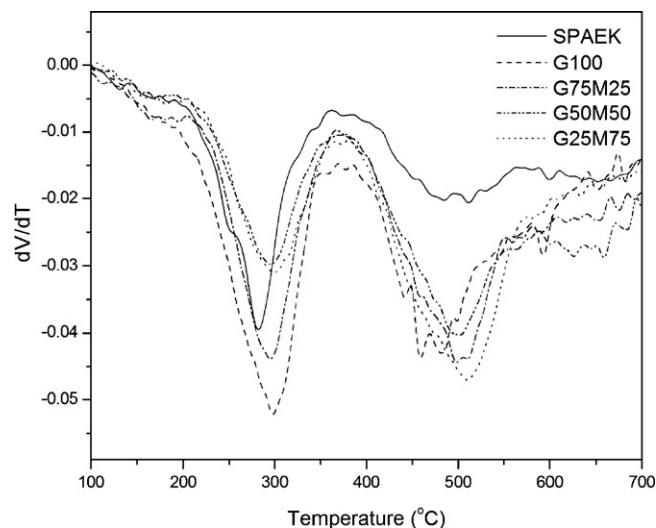


Fig. 4. DTG curve of SPAEK and cross-linked hybrid membranes in N_2 .

The first stage ($250\text{--}350\text{ }^\circ\text{C}$) was associated with a desulfonation process or the elimination of flexible chains of GPTMS and MPTMS, while the second stage starting at about $400\text{ }^\circ\text{C}$ was related to the mainchain's decomposition of the cross-linked membrane. The onset of thermal degradation (T_d) for the pristine SPAEK and hybrid membranes obtained from their derivative of their TG traces (DTG curves) are shown in Table 2. The desulfonation temperature of the hybrid membranes was observed at above $265\text{ }^\circ\text{C}$, higher than that of pristine SPAEK ($255\text{ }^\circ\text{C}$), indicating that the Si–O–Si cross-linked structure can enhance the desulfonation temperature and make these membranes more thermally stable within the temperature range for fuel cell application.

3.3. Mechanical properties

The mechanical properties of the SPAEK and hybrid membranes were measured using a tensile testing instrument at room temperature and 30% relative humidity. As listed in Table 2, the G100 membrane shows a maximum stress of 65.7 MPa and Young's modulus of 1088 MPa at a comparable yield point. However, after oxidation in 3% H_2O_2 at $50\text{ }^\circ\text{C}$ for 5 h, the hybrid membranes show deterioration in mechanical strength. The Young's moduli of them are still high, providing the membrane sufficient mechanical integrity for fuel cell applications.

3.4. Ion-exchange capacities, water uptake, and membrane swelling

Water uptake in PEMs is an important factor that can directly influence proton conduction. The water uptake is typically a function of the degree of sulfonation or IEC, a measure of the exchangeable proton in materials. It is well known that the incorporation of non-conductive inorganic or organic materials into SPAEKs could decrease the proton conductivity. So, it is necessary to use highly sulfonated copolymers or introduce inorganic or organic materials bearing sulfonic acid groups to obtain high proton conductivity. Thus, SPAEK with a measured IEC value of 1.6 by titrating was chosen as the polymer backbone and MPTMS with $-\text{SH}$ which can be oxidized to $-\text{SO}_3\text{H}$ was chosen to be incorporated into the polymer matrix. The IEC values are shown in Table 3. They decreased from 1.6 to about $1.2\text{ mequiv. g}^{-1}$ after incorporating GPTMS. The reduction of the measured IEC was mainly attributed to the dilution effect of silane monomer. Noting that the IEC of

Table 2
The thermal and mechanical properties of SPAEK and cross-linked hybrid membranes.

Membrane	T_d^c (°C)	Maximum stress (MPa)	Elongation at break (%)	Young's modulus (MPa)
SPAEK	255.05	47.4 ± 2	6.07 ± 2	1053 ± 53
G100	265.5	65.7 ± 3	15.3 ± 2	1088 ± 30
G75M25	273.4	16.4 ± 2	3.0 ± 1	906 ± 50
G50M50	281.7	29.7 ± 3	5.2 ± 2	1087 ± 60
G25M75	289.4	14.7 ± 3	3.6 ± 2	1087 ± 60
Nafion 117	–	30.3 [35]	270 [35]	357 [35]

Table 3
The IEC, water uptake, membrane swelling, proton conductivity and methanol permeability of the SPAEK and cross-linked hybrid membranes.

Membrane	IEC (mequiv. g ⁻¹)	Water uptake (%)		Membrane swelling (%)		Proton conductivity (10 ⁻² S cm ⁻¹)		Methanol permeability (×10 ⁻⁷ cm ² s ⁻¹)
		25 °C	80 °C	25 °C	80 °C	25 °C	80 °C	
SPAEK	1.6	51.3 ± 0.6	115.8 ± 0.8	13.0 ± 0.1	36.0 ± 0.3	5	20	6.65
G100	1.215	40.0 ± 0.9	104.0 ± 1.0	12.2 ± 0.2	32.0 ± 0.1	4.5	12	3.56
G75M25	1.22	56.2 ± 0.4	124.8 ± 1.0	12.9 ± 0.1	39.1 ± 0.1	5	14	3.8
G50M50	1.14	55.0 ± 0.8	126.3 ± 0.8	13.5 ± 0.2	40.7 ± 0.2	5.2	20	3.9
G25M75	2.0	52.8 ± 0.6	128.5 ± 1.0	16.7 ± 0.3	43.7 ± 0.4	6.3	17	3.64
Nafion® 117	0.92	18.3 ± 3	27.9 ± 7	11.0 ± 2	17.2 ± 3	7.6	14.6	10.05

G25M75 increases to 2.0. The incorporation of MPTMS could produce enough sulfonic acid groups.

In general, the hydrocarbon-based membranes require higher IECs to achieve comparable conductivity to Nafion [37]. However, increasing –SO₃H groups in the hydrocarbon-based polymers often accompanied by excessive water uptake and dimensional change of membranes, which leads to weakness or a dimensional mismatch when incorporated into a membrane electrode assembly. As listed in Table 3, the G100 membranes have a lower water uptake as compared with the pristine SPAEK membrane, indicating that the cross-linking bonds help to hold the polymer chains together to restrict the hydrophilic domains, and thus decrease the water uptake. With the content of MPTMS increasing, the content of –SO₃H groups is increasing. The water uptake of the hybrid membranes is 124.8%, 126.3% and 128.5% at 80 °C, respectively, which is comparable to that of the pristine SPAEK (115.8% at 80 °C). Moreover, the values of membrane swelling show a similar trend. These results revealed that the cross-linked structure successfully avoided the diminishing dimensional stability despite the higher IEC.

3.5. Proton conductivity and methanol permeability

The proton conductivity of the hybrid membranes as a function of temperature is displayed in Fig. 5. All samples showed room temperature proton conductivities higher than 10⁻² S cm⁻¹, which is the lowest value for practical use as PEMs in fuel cells. It is obviously observed that the proton conductivity of G100 decreased a lot when compared to the pristine SPAEK membrane. However, with the content of MPTMS increasing, the proton conductivity of the hybrid membranes increased from 0.045 to 0.063 S cm⁻¹ at 25 °C and from 0.12 to 0.20 S cm⁻¹ at 80 °C, which can be attributed to the increase of sulfonic acid groups. It should be noted that the conductivity of G25M75 did not improve at 80 °C as compared to G50M50 having a higher content of sulfonic acid groups. For example, the proton conductivity of G25M75 is 0.17 S cm⁻¹ at 80 °C, which is similar to that of G50M50 (0.20 S cm⁻¹). The excessive water uptake at 80 °C has the dilute effect on the concentration of sulfonic acid groups, which is believed to be responsible for the similar proton conductivity between G50M50 and G25M75. Furthermore, the activation energy was calculated from an Arrhenius relationship, using the following Eq. (5):

$$\ln(\sigma) = \frac{\ln(\sigma_0) - E_a}{RT} \quad (5)$$

where R is the gas constant (8.314 J mol⁻¹ K⁻¹), and T is the absolute temperature (K). The values of E_a were estimated from the slopes of the Arrhenius plots in Fig. 5 and are listed in Table 1. The values of the cross-linked hybrid membranes were clearly smaller than the activation energy of SPAEK, which was 22.0 kJ mol⁻¹. The smaller activation energy indicates the easier proton transfer. In addition, the E_a value of G100 hybrid membrane in this paper is 33% lower than that of SPAEK, and the ratio of decreasing E_a value is much lower than the hybrid SPAEK membrane with KH550/PWA (15%) [38] and the SPAEK membrane blended with polyaniline (15%) [39]. It can be concluded that silane-crosslinking is a useful method to decrease the activation energy.

The methanol permeability of the SPAEK and cross-linked hybrid membranes at room temperature is shown in Table 3. The cross-linked hybrid membranes exhibited low methanol permeability ranging from 3.56 × 10⁻⁷ to 3.9 × 10⁻⁷ cm² s⁻¹. They are all lower than that of pure SPAEK (6.65 × 10⁻⁷ cm² s⁻¹) and Nafion 117 (10.05 × 10⁻⁷ cm² s⁻¹), revealing that the methanol permeability can be drastically reduced by a silane-crosslinking

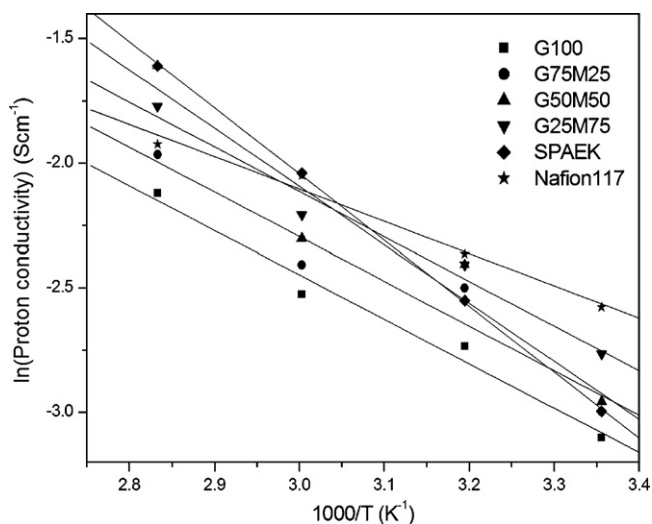


Fig. 5. The proton conductivity of SPAEK and cross-linked hybrid membranes as a function of temperature.

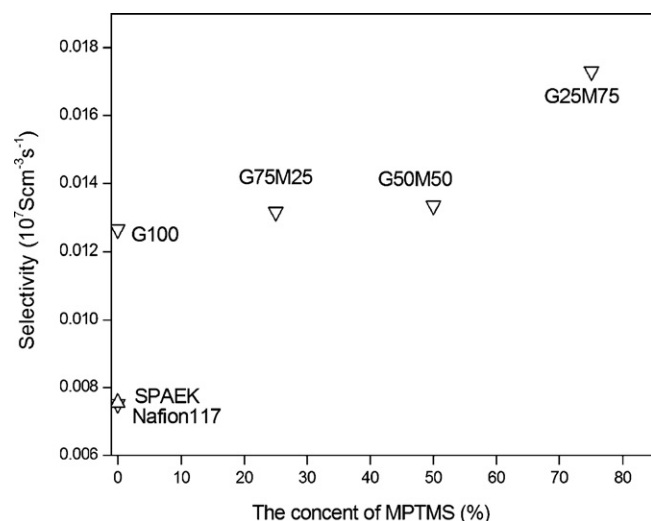


Fig. 6. The selectivity as a function of the content of MPTMS.

technique. In addition, the methanol permeability of the cross-linked hybrid membranes in this paper is lower than that of an ionically cross-linked SPAEK membrane with 15 wt.% polypyrrole ($5.31 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) [40], and also lower than that of a covalently cross-linked SPAEK membrane with 20 wt.% epoxy resin ($5.26 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) [41]. It can be concluded that silane-crosslinking is also a useful method to reduce the methanol cross-over.

Membranes for the practical usage of PEMs in DMFCs were required to possess high proton conductivity and low methanol permeability. The selectivity, which is defined as the ratio of proton conductivity to methanol permeability, is often used to evaluate the potential performance of DMFC membranes [42]. In this case, the selectivity can be used just as a barometer to develop the best proton conductivity with reducing methanol permeability. Fig. 6 shows the selectivity as a function of the content of MPTMS for the SPAEK and cross-linked hybrid membranes. With the content of MPTMS increasing, the proton conductivity increases while the selectivity increases, which are higher than those of SPAEK and Nafion 117. Especially, G25M75 possesses better selectivity and proton conductivity. The results suggest that the incorporation of MPTMS into the SPAEK membranes and the formation of cross-linked structure have both impact on the reduction of methanol permeability and the increase of proton conductivity, and the cross-linked membranes would have a potential application in DMFCs.

4. Conclusions

A cross-linked hybrid SPAEK membrane was obtained through a silane-crosslinking technique, and MPTMS was introduced into the system to decrease the diluting effect of cross-linker. The properties of the cross-linked hybrid membranes, such as thermal stability, methanol permeability and selectivity were significantly improved. The cross-linked hybrid membranes showed excellent proton conductivities varying from 0.045 to 0.063 S cm^{-1} at 25°C and 0.12 to 0.20 S cm^{-1} at 80°C , which are comparable to that of Nafion 117. Furthermore, the methanol permeability values were lower than those of pure SPAEK and Nafion 117.

Acknowledgements

The authors would like to thank the China High-Tech development 863 program (Grant no. 2007AA03Z218) for financial support of this work.

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