



Short communication

Novel hybrid polymer electrolyte membranes prepared by a silane-cross-linking technique for direct methanol fuel cells

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ABSTRACT

To prepare a cross-linked hybrid proton exchange membrane with high mechanical and oxidative stability, a silane monomer, namely 3-glycidoxypropyltrimethoxysilane (KH-560), is first grafted to sulfonated poly(arylene ether ether ketone)s bearing carboxyl groups (SPAEK-C) and hydrolysis–condensation is then performed on the grafted membranes to make them cross-link. ¹H NMR measurements and Fourier transform infrared spectroscopy are used to characterize and confirm the structures of SPAEK-Cs and hybrid polymer electrolyte membranes, respectively. The Si–O–Si cross-linking structure enhances the stability of the PEM greatly. The proton conductivities of the hybrid membranes with 5% KH-560 in weight reach 0.155 S cm^{−1} at 80 °C which is comparable to that of Nafion[®] membranes. The ion-exchange capacity, water uptake and swelling, methanol permeability, mechanical properties are 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 a promising clean power sources for automotive, stationary, and portable applications [1–3]. At the core of these devices is a proton exchange membrane (PEM) that serves as both electrolyte and separator. Currently, the widely used membrane materials are perfluorinated sulfonic ionomers, such as Dupont Nafion[®]. These membranes exhibit excellent chemical and electrochemical stability in oxidizing environments as well as high proton conductivity when hydrated. However, methanol readily migrates through Nafion[®] membrane between the electrodes and causes reduction of DMFCs voltage and poisoning at cathode. Furthermore, their high cost and loss of the preferable properties at high temperatures have also limited their widespread commercial applications [4]. Therefore, considerable efforts to search for alternative cost-effective proton exchange membrane materials have been carried out. Sulfonated aromatic polymers, including poly(arylene ether ketones) (SPAEEKs), fell into this category [5–8].

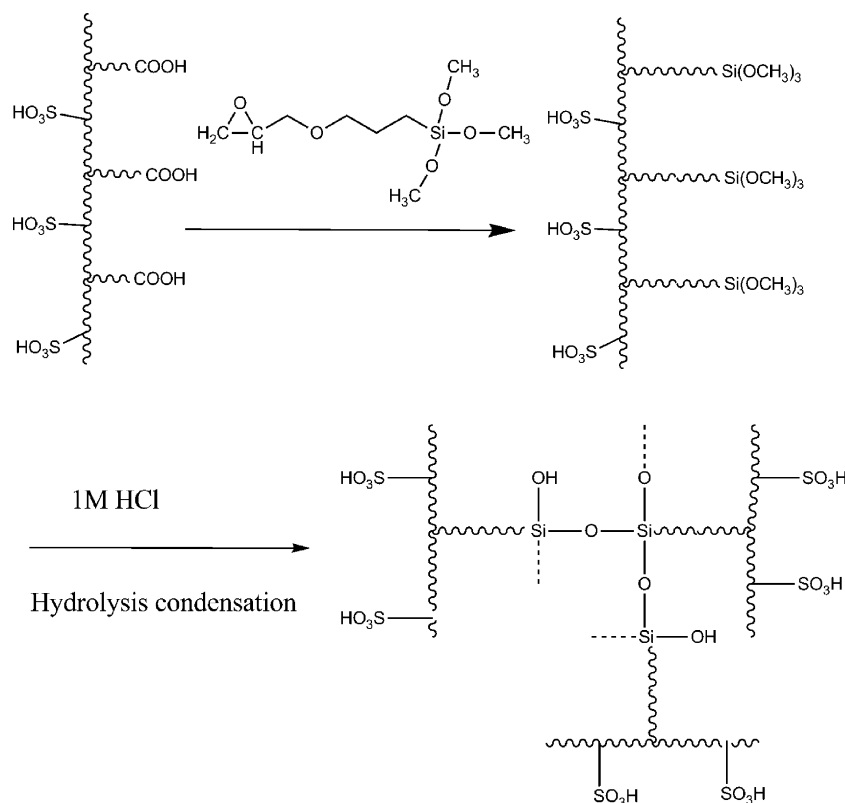
SPAEEK membranes as a series of well-known polymer electrolyte membranes have been widely studied for their application in intermediate temperature fuel cells due to their low cost, excellent mechanical, high conductivities and thermal properties [9–11]. However, the more –SO₃H groups introduced to the polymer

matrixes functional groups, the more water absorbed in the polymers with diminishing dimensional and chemical stability due to the hydrophilicity of the acid groups. Moreover, increasing loading of acidic groups leads to excessive methanol crossover.

Cross-linking is an efficient method to improve PEM properties, which could suppress the methanol crossover and water swelling, and improve dimensional and chemical stability [12–15]. Ionic cross-linking, such as acid–base composite membranes, is introduced by interactions between the acid and base functional groups. For example, Kerres et al. prepared several acid–base blend membranes mainly from sulfonated poly(ether sulfone) or poly(ether ether sulfone) and different kinds of basic polymers, such as polybenzimidazole, aminated polysulfone, and polyethylenimine [16–18]. They observed the ionic cross-linked membranes show high decomposition temperature, low swelling ratio and reduced methanol permeability as expected. However, ionic cross-linking loses its effect at elevated temperatures. Chemical cross-linking by covalent bonding not only provides membranes with excellent thermal and mechanical stability, but also retains the characteristics of being cross-linked even at high temperatures [19–22].

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]. For example, many kinds of inorganic materials have been successfully introduced into Nafion[®] membranes, such as heteropolyacid (HPA) [28], SiO₂, TiO₂, and montmorillonite (MMT) [29,30]. These inorganic compounds are expected to improve water retention and thermal stability of the hybrid PEMs. However, because of lacking covalent bonds between the inorganic

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

and organic interfaces, it is found that some hydrophilic inorganic particles are easily leached out after long immersion in water [27]. Thus, it is significant to develop constituent particles which can covalently cross-link with polymer backbone in order to enhance homogeneity, mechanical strength and morphology.

In this work, we developed a covalently cross-linked hybrid PEM combining the condensation of carboxyl groups/epoxide and silane-cross-linking techniques [20]. We chose sulfonated poly(arylene ether ether ketone)s bearing carboxyl groups (SPAEEK-C) as polymer backbones. Then we grafted a special silane monomer, which has an epoxy group to react with a carboxyl group and a trimethoxysilyl group amenable to silane-cross-linking to SPAEEK-C base film. After grafting, hydrolysis–condensation by HCl solution was performed to give the PEM cross-links (Scheme 1). The degree of cross-linking can be optimized by controlling the addition amount of silane monomer. The silane-cross-linked hybrid PEMs were expected to possess high proton conductivities and chemical stability. The ion-exchange capacity (IEC), water uptake, methanol permeability, mechanical and thermal properties of the hybrid PEMs were also investigated.

2. Experimental

2.1. Materials

SPAEEK-C was synthesized by the aromatic nucleophilic polycondensation of sodium 5,5'-carbonyl-bis(2-fluorobenzene-sulfonate) (SDFBP), 4,4'-difluorobenzophenone (DFBP) and phenolphthalin (PPL) according to a procedure described in our previous work [11]. The degree of sulfonation (the number of SO₃H groups per repeating unit), as obtained by ¹H NMR, is 0.9. ¹H NMR is shown in Fig. 1. The inherent viscosity of the SPAEEK-C is 2.62 dL g⁻¹. All other reactants and solvents were obtained from Tianjin Tiantai Chemical Company and used as received without further purification.

2.2. Membrane preparation and cross-linking treatment

SPAEEK-C (1.90 g) and 3-glycidoxypropyltrimethoxysilane (GPTMS, Trade name: KH-560) (0.10 g) were dissolved in 20 mL of DMF at room temperature and stirred for 6 h. Then the clear homogeneous solution was cast on a glass plate and placed in a vacuum oven at 60 °C for 24 h to remove the residual solvent completely and then at 100 °C for 1 h and at 120 °C for 2 h. Dry membranes were peeled off from the substrate and immersed in a 1 M HCl solution at 80 °C for 24 h to hydrolysis–condensation. The

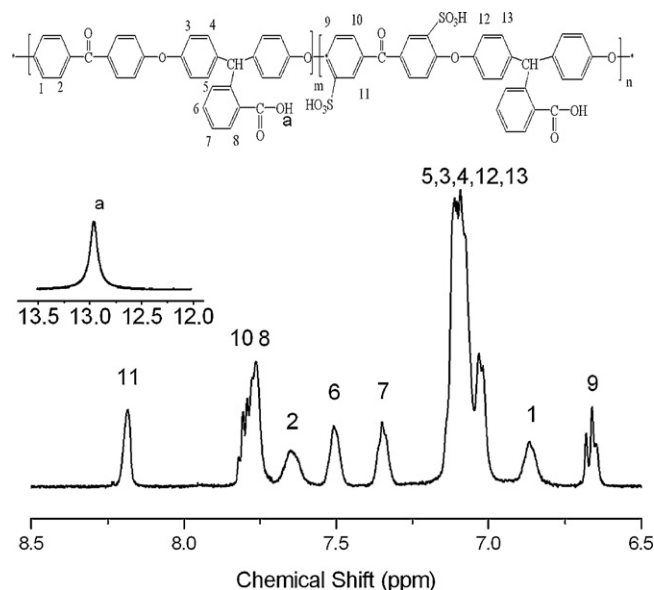


Fig. 1. ¹H NMR spectra of SPAEEK-C copolymers in DMSO-*d*₆.

cross-linked film, referred to as SPAEK-C/KH-560-5% (5% refers to weight percent of KH-560 for the cross-linked membranes). The cross-linked film prepared from SPAEK-C (1.80 g) with KH-560 (0.20 g), referred to as SPAEK-C/KH-560-10% were also prepared using the same procedure (Scheme 1). The thickness of the cross-linked and SPAEK-C membranes is 80–90 μm . Moreover, the Nafion® 117 with a thickness of $100 \pm 10 \mu\text{m}$ was used to compare the properties. The cross-linked membranes were kept in distilled water at room temperature before use.

2.3. Characterization

Inherent viscosities of the copolymers were measured in DMF at 25 °C with a polymer concentration of 5.0 g l^{-1} . FT-IR spectra of powder samples were obtained between 4000 and 400 cm^{-1} with a Bruker Vector 22 FT-IR spectrometer. ^1H NMR spectra (in d_6 -DMSO) were recorded on a 500 MHz Bruker Avance 510 spectrometer. The chemical shift of tetramethylsilane was used as the internal reference standard. Thermo-gravimetric analysis (TGA) and derivative thermo-gravimetry (DTG) was recorded on a Pyris-1 (PerkinElmer) 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 pre-heated to 120 °C and kept at this temperature for 20 min to remove any residual moisture and solvent. The chemical stability of cross-linking membranes was characterized by placing it in a 3% H_2O_2 aqueous solution at 60 °C and measuring the weight of cross-linking membranes and the 3% H_2O_2 solution was replenished every 24 h.

2.4. Mechanical properties of membranes

The mechanical properties of SPAEK-C/KH-560-5% and SPAEK-C/KH-560-10% membranes were investigated using a SHIMADZU AG-I 1KN instrument at room temperature at a constant crosshead speed of 2 mm min^{-1} . The uniaxial 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 25% relative humidity.

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

The water uptake (WU) was determined by measuring the change in the weight between the dry and swollen membranes. A detailed procedure was reported previously [11]. The membrane swelling (MS) 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 relative water uptake and relative membrane swelling is defined as following:

$$\text{relative water uptake} = \frac{\text{WU}_{\text{membrane}}}{\text{WU}_{\text{Nafion}^{\circledR} 117}} \quad (2)$$

$$\text{relative membrane swelling} = \frac{\text{MS}_{\text{membrane}}}{\text{MS}_{\text{Nafion}^{\circledR} 117}} \quad (3)$$

The IEC values of cross-linking membranes were determined by classical titration. The membrane sample was immersed in 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 0.05N 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. 100 ml methanol–water solution (10 M) was placed on one side of the diffusion cell (cell A, donor reservoir) and 100 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-8A chromatograph. Peaks areas were converted to the methanol concentration with a calibration curve. The methanol diffusion coefficient was calculated by Eq. (4), as stated elsewhere [31–33].

$$C_B(t) = \frac{A}{V_B} \frac{DK}{L} C_A(t - t_0) \quad (4)$$

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. (5).

$$P = DK = \alpha \times \frac{V_B}{A} \times \frac{L}{C_A} \quad (5)$$

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 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). The membranes were cut into 1 cm wide, 4 cm long and were fixed in a measuring cell made of two outer gold wires (A and D) to feed current to the sample and two inner gold wires (B and C) to measure the voltage drops [34]. All the membranes were mounted between two polytetrafluoroethylene (PTFE) 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. (6):

$$\sigma = \frac{L}{RA} \quad (6)$$

where σ is the proton conductivity in Scm^{-1} , L the distance between the two electrodes (1 cm), R 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).

The relative proton conductivity is defined as following:

$$\text{relative proton conductivity} = \frac{\sigma_{\text{polymer}}}{\sigma_{\text{Nafion}^{\circledR} 117}} \quad (7)$$

3. Results and discussion

3.1. Polymer synthesis and cross-linking treatment

As shown in Fig. 1, ^1H NMR characterization methods confirmed the structure of SPAEK-C. Fig. 2 presents the IR spectrum of SPAEK-C (a), KH-560 (b), SPAEK-C/KH-560-5% (c) and SPAEK-C/KH-560-10% (d) membranes. The IR spectra of SPAEK-C show two characteristic bands at 1080 and 1017 cm^{-1} for asymmetric and symmetric O=S=O stretching vibrations of sulfonic acid groups. All of these characteristic bands of sulfonic acid groups are also presented in the spectra of SPAEK-C/KH-560-5% and SPAEK-C/KH-560-10%, which indicates the preservation of sulfonic acid groups in SPAEK-C/KH-560-5% and SPAEK-C/KH-560-10%. Additionally, the intensity of

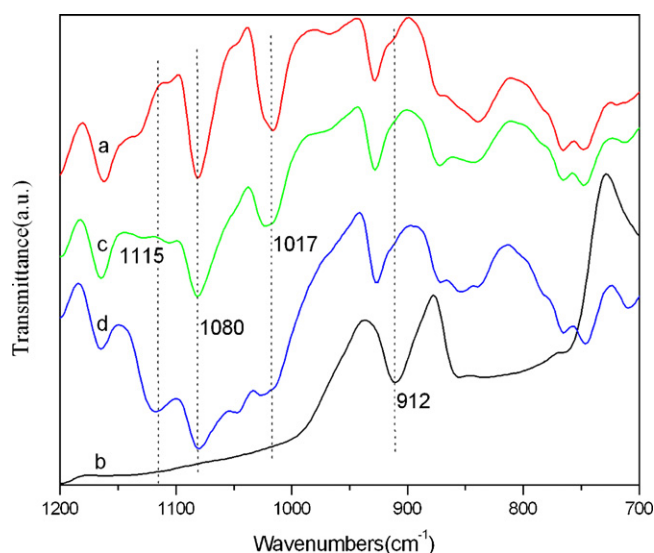


Fig. 2. FT-IR spectra of SPAEK-C (a), KH-560 (b), SPAEK-C/KH-560-5% (c) and SPAEK-C/KH-560-10% (d).

1080 and 1017 cm^{-1} decrease with increasing weight ratio of KH-560. It is attributed to the dilution effect of the KH-560 which was lack of the sulfonic acid groups. In the spectra of KH-560, the band at 912 cm^{-1} can be assigned to epoxy characteristic bands. After heating and hydrolysis–condensation, the epoxy peaks are no longer present, and Si–O–Si peaks appear at 1115 cm^{-1} become more obvious with increasing ratio of KH-560 as seen in spectrum (c) and (d), which confirms the formation of the Si–O–Si cross-linking structures.

3.2. Thermal stability

As shown in Fig. 3, all membranes exhibited a typical two-step degradation pattern. The first weight loss region (occurring between temperatures of 250–350 $^{\circ}\text{C}$) was believed to be associated with the elimination of sulfonic acid groups or flexible chains of KH-560 and the second weight loss step starting at about 450 $^{\circ}\text{C}$ corresponded to the main cross-linking polymer chain of decomposition. The onset weight loss temperatures (T_d) of SPAEK-C and SPAEK-C/KH-560 cross-linked membranes obtained from their derivative of their TG traces (DTG curves) are shown in Table 1. The desulfonation temperature of cross-linked membranes were observed at above 293 $^{\circ}\text{C}$, higher than that of the pristine SPAEK-C (278 $^{\circ}\text{C}$). From these results, it is concluded that the Si–O–Si cross-linking structure can enhance the desulfonation temperature and make the hybrid PEM be thermally stable within the temperature range for fuel cell applications. In addition, the high desulfonation temperature provides the ability to effectively hot press these membranes into membrane electrode assembly (MEA).

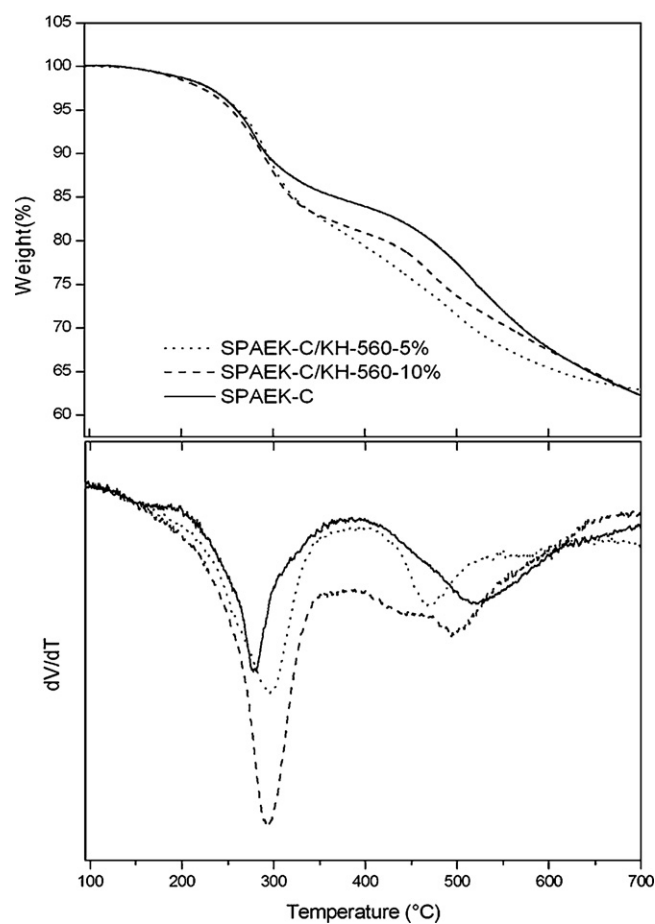


Fig. 3. TGA and DTG of SPAEK-C and SPAEK-C/KH-560 membranes in N_2 .

3.3. Mechanical properties

It is essential for PEMs to possess adequate mechanical integrity to withstand fabrication of the membrane electrode assembly. The mechanical properties of the SPAEK-C and cross-linked membranes were measured using a tensile testing instrument at room temperature and 25% relative humidity. As shown in Table 1, The membranes show a maximum stress and Young's modulus at a comparable yield point, with a tensile strength that varies from 45 to 49 MPa and Young's modulus that varies from 1200 to 1312 MPa, while that of Nafion[®] 117 is much lower. Table 1 also shows that Young's modulus increases to 1280 and 1312 MPa after cross-linking modification, indicating that cross-linking is an efficient mean to enhance the mechanical stability.

Table 1
The thermal and mechanical properties of the SPAEK-C and SPAEK-C/KH-560 membranes.

Membrane	IEC (mequiv. g^{-1})		T_d^c ($^{\circ}\text{C}$)	Maximum stress (MPa)	Elongation at break (%)	Young's modulus (MPa)
	IEC ^a	IEC ^b				
SPAEK-C	1.55 ± 0.1	1.58	278	49 ± 2	132 ± 22	1200 ± 83
SPAEK-C/KH-560-5%	1.22	–	295	48 ± 3	12 ± 2	1280 ± 70
SPAEK-C/KH-560-10%	0.84	–	293	45 ± 5	7 ± 2	1312 ± 110
Nafion [®] 117	–	0.92	–	30.3 [35]	270 [35]	357 [35]

^a IEC obtained from the titration.

^b IEC obtained from ^1H NMR.

^c Extrapolated onset for first weight loss.

Table 2

The water uptake, membrane swelling, proton conductivity and methanol diffusion coefficient of the SPAEK-C and SPAEK-C/KH-560 membranes.

Membrane	Water uptake (%)		Membrane swelling (%)		Proton conductivity ($10^{-2} \text{ S cm}^{-1}$)		Methanol permeability ($\times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) 25 °C
	20 °C	80 °C	20 °C	80 °C	25 °C	80 °C	
SPAEK-C	42.1 ± 0.6	68.1 ± 0.9	13.5 ± 0.1	22 ± 0.2	3.6 ± 0.1	16 ± 0.5	5.75
SPAEK-C/KH-560-5%	29.1 ± 0.4	40.4 ± 0.6	10.9 ± 0.1	15.0 ± 0.1	6.2 ± 0.2	15.5 ± 0.8	1.57
SPAEK-C/KH-560-10%	21.8 ± 0.5	23.7 ± 0.3	8.26 ± 0.1	9.8 ± 0.1	1.5 ± 0.1	5.4 ± 0.2	2.99
Nafion®117	18.3 ± 3	27.9 ± 7	11.0 ± 2	17.2 ± 3	7.6 ± 0.3	14.6 ± 0.4	10.05

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

It is well known that the incorporation of inorganic materials without proton conductivity into sulfonated poly(arylene ether ketone)s could lower the proton conductivity, so it is necessary to use a highly sulfonated copolymers with high IEC to obtain high proton conductivity in sulfonated membranes. Thus, SPAEK-C with measured IEC values of 1.55 by titrating and theoretical IEC values of 1.58 by ^1H NMR was chosen for polymer backbones. The measured IEC values by titrating in [(mmol- SO_3^- + mmol- COO^-) g^{-1}] or theoretical IEC values by ^1H NMR in [(mmol- SO_3^-) g^{-1}] are shown in Table 1. With increasing weight ratio of KH-560, the measured IEC values of cross-linking membranes decreased from 1.55 to 0.84 mequiv. g^{-1} . The reduction of measured IEC was mainly attributed to two factors: (i) the dilution effect of the KH-560 which was lack of the sulfonic acid groups. (ii) The decrease of carboxyl acid groups because of the formation of covalent bond between carboxyl acid groups and epoxy group.

In general, hydrocarbon-based electrolyte membranes need many more sulfonic acid groups to achieve proton conductivity comparable to Nafion® because the perfluorosulfonic acid in Nafion®117 is highly acidic. However, increasing $-\text{SO}_3\text{H}$ groups in the polymer often accompanied by excessive water uptake and dimensional change of the membranes, which leads to weakness or a dimensional mismatch when incorporated into a membrane electrode assembly. For example, the highly acidic moieties of SPAEK-C result in over 68.1% water uptake and a dimensional change of 22% after immersing in 80 °C water. It is obvious that cross-linking bonds help to hold the polymer chains together to restrict the hydrophilic domains and thus decrease the water uptake. As listed in Table 2, the SPAEK-C/KH-560 membranes have a lower water uptake as compared with the pristine membrane. As displayed in Table 2, the dimensional change that occurs in water at a high temperature was drastically reduced after cross-linking. For example, the water uptake and membrane swelling of SPAEK-C/KH-560-10% at 80 °C are reduced to 23.7% and 9.8%, respectively. These values are even slightly lower than Nafion®117. Fig. 4 shows the relative water uptake as a function of the relative membrane swelling of the SPAEK-C and SPAEK-C/KH-560 membranes. As compared to Nafion®117, high relative water uptake values were characterized for SPAEK-C and SPAEK-C/KH-560 membranes, but all of them showed low relative membrane swelling, especially at 80 °C. The targeted membranes should be located on the left-hand side of the figure, with modest water uptake values and low swelling ratios. These results revealed that the cross-linking membranes were more dimensional stable than SPAEK-C due to cross-linking structures.

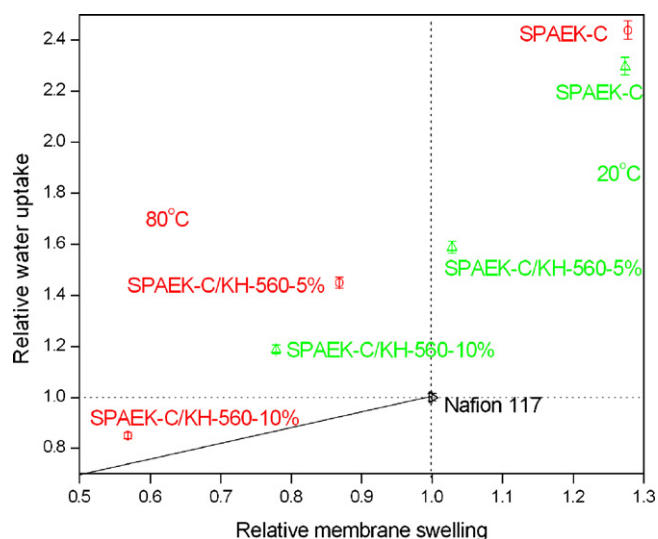
3.5. Oxidative stability

During the fuel cell operation, the H_2O_2 is originated from oxygen diffusion through the membrane and incomplete reduction at the fuel cell anode, bringing about a severe degradation of the polymer electrolyte membrane [36–38]. Testing polymer electrolyte membrane lifetimes in actual fuel cells is both time-consuming

and expensive. Thus, it is desirable to develop rapid and simple methods for evaluating the new candidate membranes. In general, the chemical stability of the polymer electrolyte membrane is tested by the Fenton reagent, where Fe^{2+} is added to the H_2O_2 solution. However, we found that all of the prepared polymer electrolyte membranes decomposed within several hours. Therefore, we chose a more moderately accelerated testing, such as testing in the H_2O_2 solutions without Fe^{2+} ions. In this study, the chemical stability of the cross-linking membranes was tested in a 3% H_2O_2 aqueous solution at 60 °C [39]. The weight change of the cross-linked and non-cross-linked membranes was determined as a function of time. As shown in Fig. 5, it was found that the degradation (determined as a weight loss) began after about 48 h for the cross-linked membranes, while the pristine SPAEK-C was completely dissolved after about 48 h. Here, the time elapsed before onset of degradation is a parameter of the chemical stability of the PEM. Thus, the cross-linked membranes possessed better oxidative stability than the pristine SPAEK-C membrane. It is believed that cross-linking is an important factor, strongly affecting chemical stability and the introduction of Si–O–Si cross-linking structures can significantly improve the chemical stability. Additional, it is interesting that the 10% KH-560 filled membrane shows higher weight loss compared to the 5% filled membrane. This may be because the formation of polysiloxanes cross-linking structure of the 5% KH-560 addition just consumes the carboxyl group of SPAEK-C to introduce Si–O–Si cross-linking structures, so the increased 5% KH-560 addition will be easily disengaged from the polymer backbones.

3.6. Proton conductivity and methanol permeability

Proton conductivities as a function of temperature are displayed in Fig. 6 for SPAEK-C and SPAEK-C/KH560 membranes. The proton conductivity of pristine SPAEK-C is 0.16 S cm^{-1} at 80 °C, which is

**Fig. 4.** The relative water uptake as a function of the relative membrane swelling.

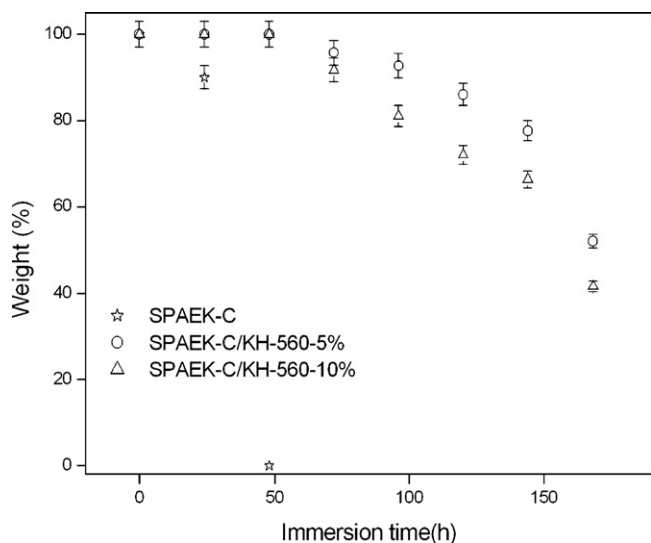


Fig. 5. Weight changes of SPAEK-C and SPAEK-C/KH560 membranes in 3% H₂O₂ aqueous solution at 60 °C.

higher than that of Nafion® 117 (0.146 S cm⁻¹ at 80 °C); however, the water uptake and water swelling values are so much high to decrease the fuel cell performance.

In general, the proton conductivities of the hybrid membranes decrease with an increasing KH-560 addition amount due to the lower water uptake and lower IEC caused by the dilution effect of the KH-560 and the increased hydrophobicity by the network structure. It is obviously that the proton conductivities of SPAEK-C/KH-560-10% decreased a lot compared to the pristine SPAEK-C membrane. However, it is interesting to find that the conductivity of SPAEK-C/KH-560-5% decreased slightly at 80 °C or even increased at temperatures ranging from 25 to 60 °C. For example, the proton conductivity of SPAEK-C/KH-560-5% is still 0.155 S cm⁻¹ at 80 °C, which is similar to that of SPAEK-C. The minimized polysiloxanes network structure formed by slightly cross-linking is believed to be responsible for the high conductivity of SPAEK-C/KH-560-5%. This indicates that the slight silane-cross-linking just consumes the carboxyl group of SPAEK-C, which has minimal effect on the conductivity. The quantity of sulfonic acid groups per unit volume

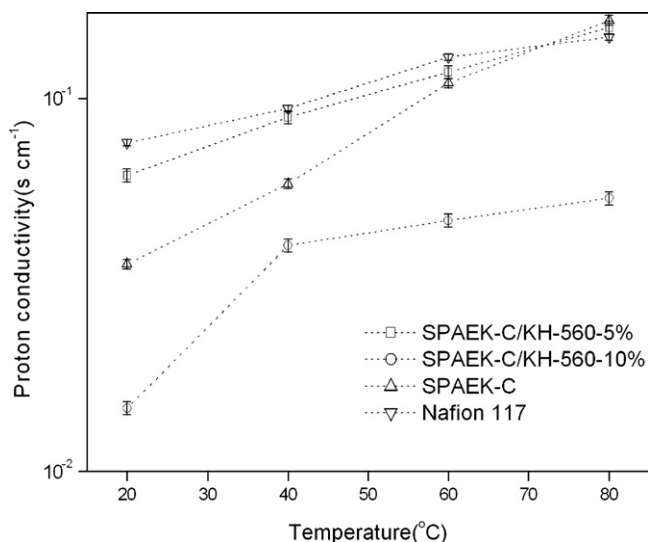


Fig. 6. Proton conductivity of SPAEK-C and SPAEK-C/KH-560.

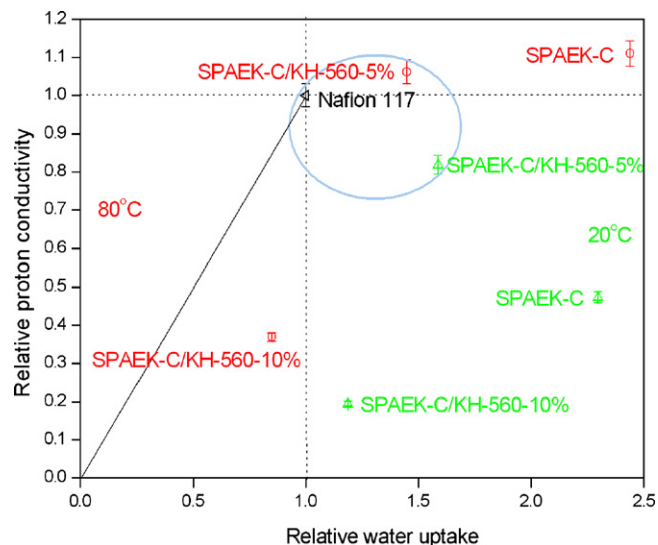


Fig. 7. The relative proton conductivity as a function of the relative water uptake.

is still high, which ensures the high proton conduction mobility. On the other hand, the backbone of polysiloxanes and the –CH₂CH₂O– linkages in the silica framework also provide bonding sites for hydrogen bonding with water and allow the formation of a bound-water layer that facilitates the hopping of protons [40]. Furthermore, compared to SPAEK-C/KH-560-10%, the smaller slope of SPAEK-C/KH-560-5% curve indicates that protons transfer with a low activation energy. The smaller activation energy indicates the easier proton transfer. So in this system, there are two factors that influence the proton conductivity of the hybrid membranes: (i) the existence of the bound-water layer facilitate the hopping of protons; (ii) the hydrophobicity of silica framework interrupts the proton transportation though the bound-water layer. The two factors determine the overall proton conductivity of the hybrid membranes.

As shown in Fig. 7, SPAEK-C/KH-560-5% membranes located within the target area which possessed high conductivities and a modest water uptake compared with Nafion® 117.

The methanol permeability of the SPAEK-C and SPAEK-C/KH-560 membranes at room temperature is shown in Table 2. They exhibited methanol permeability in the range of 1.57×10^{-7} to 5.75×10^{-7} cm² s⁻¹, which are all lower than that of Nafion® 117 (1.01×10^{-6} cm² s⁻¹) measured at the same condition. It is obvious that the methanol permeability can be drastically reduced through silane-cross-linking technique.

Membranes for the practical usage of PEMs in DMFCs were required to possess high-proton conductivity and low methanol permeability [11]. 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. In this case, the selectivity can be used just as a barometer to develop the best proton conductive polymer membranes with reducing methanol permeability. Fig. 8 shows the selectivity defined as the ratio of proton conductivity to methanol permeability of SPAEK-C and cross-linked membranes. The selectivity of SPAEK-C/KH-560-5% membranes was significantly improved after slight cross-linking. The result suggested that the incorporation of 5% KH-560 into the SPAEK-C membranes and the formation of cross-linking structure had more impact on reduction of methanol permeability than proton conductivity, and the cross-linked membranes have a potential application in DMFCs.

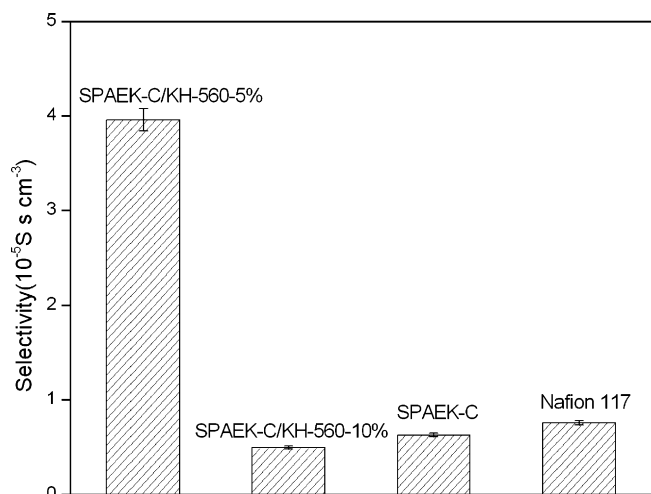


Fig. 8. Selectivity of SPAEK-C and SPAEK-C/KH-560.

4. Conclusion

A cross-linked SPAEK-C membrane with high mechanical and oxidative stability was successfully prepared by a silane-cross-linking technique. The cross-linked membranes show excellent mechanical properties with maximum stress varying from 45 to 49 MPa and Young's modulus varying from 1200 to 1312 MPa, much higher than those of Nafion[®] 117. The oxidative stability was proved by taking more than 168 h for SPAEK-C/KH-560 membranes start to break up into pieces (in 3% H₂O₂ at 60 °C). Furthermore, the WU, MS and methanol permeability were drastically reduced as compared to the pristine SPAEK-C membranes while the highest proton conductivities can reach 0.155 S cm⁻¹ obtained for SPAEK-C/KH-560-5% at 80 °C which is comparable to that of Nafion[®] 117. The present results indicate that the Si–O–Si cross-linked SPAEK-C membranes have a potential application in DMFCs.

Acknowledgements

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