



Chemically stable hybrid polymer electrolyte membranes prepared by silane-crosslinking and thiol-ene click chemistry

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HIGHLIGHTS

- ▶ A series of cross-linked hybrid membranes were prepared by a combination of silane-crosslinking and thiol-ene click chemistry.
- ▶ The cross-linked structure makes a great contribution to the improvement of dimensional and chemical stabilities.
- ▶ The cross-linked hybrid membranes showed lower swelling, lower methanol permeability and high selectivity for direct methanol fuel cells.

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ABSTRACT

A series of cross-linked hybrid membranes with low water uptake, high dimensional stabilities, as well as high oxidative stabilities are prepared by a combination of silane-crosslinking and thiol-ene click chemistry based on a sulfonated poly (arylene ether ketone) (SPAEEK) with propenyl groups. ¹H NMR measurement and Fourier transform infrared spectroscopy are used to characterize and confirm the chemical structure of SPAEEK and its cross-linked hybrid polymer exchange membranes. We also investigate the changes in methanol permeability, proton conductivity and mechanical properties. Our findings demonstrate that the Si–O–Si cross-linked structure makes a great contribution to the improvement of dimensional and chemical stabilities. Therefore, these cross-linked hybrid membranes could be considered as promising materials for direct methanol fuel cell applications.

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1. Introduction

Researches on direct methanol fuel cells (DMFCs) are very attractive due to their unique properties, such as high efficiency, low power-source emissions, as well as the simplicity of system [1]. 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. However, several drawbacks including expensive cost, high methanol permeability and poor properties at higher temperatures (>80 °C) [2,3] have limited their applicability. Therefore, considerable efforts have been made to search for alternative cost-effective PEMs.

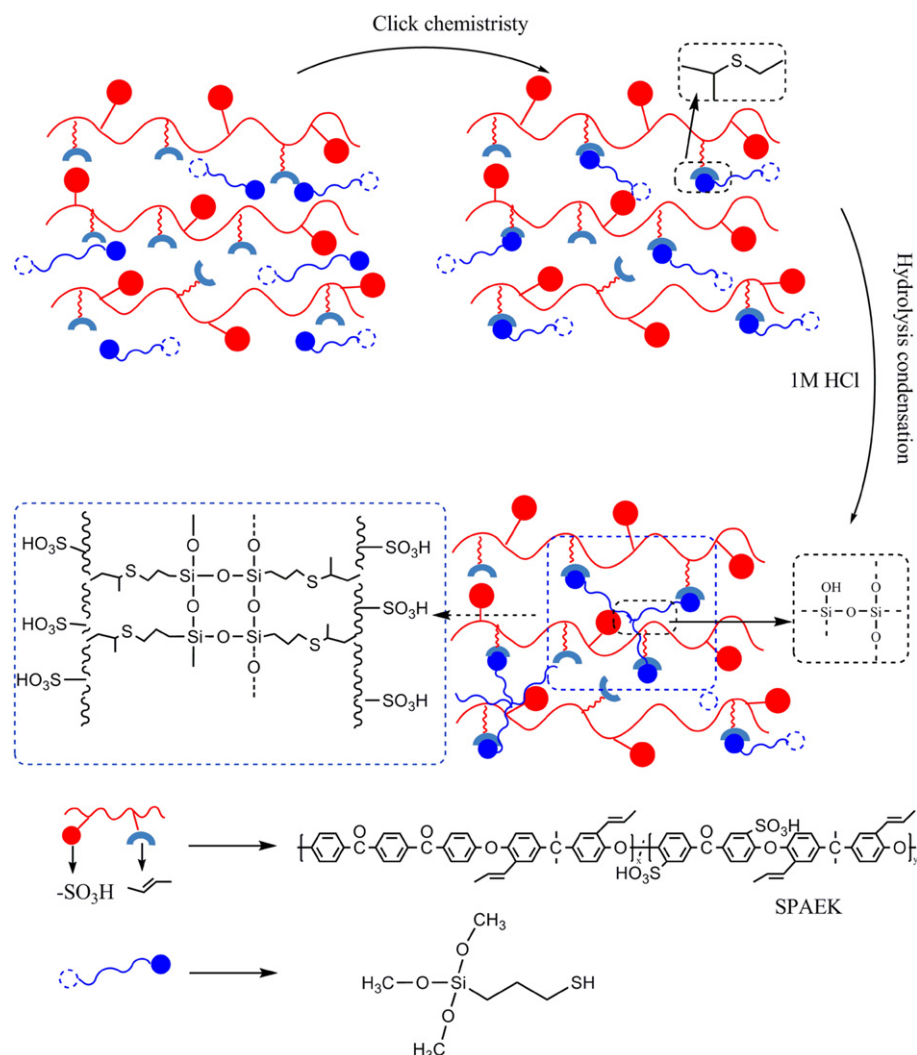
Recently, several fluorine-free ionomer membranes such as sulfonated polysulfones [4,5], sulfonated polyimides [6,7], and sulfonated poly(arylene ether ketone)s (SPAEEKs) [8–15] are attracting a great deal of attention. These materials possess

remarkable properties, such as good mechanical properties, excellent thermal stability, and high proton conductivity that can be controlled by the degree of sulfonation [16–19]. However, high methanol permeability and water swelling would be induced due to the increasing number of sulfonic acid groups. Organic–inorganic hybrid method can be considered as a way to improve the dimensional stabilities and the methanol resistance of membranes [20,21]. Chen et al. incorporated a hydrophilic polymer to prepare covalently cross-linked polysiloxanes through organic–inorganic hybrid method with aim to modify Nafion membranes [22]. It was found that the methanol permeability was decreased greatly. However, because of lacking covalent bonds between the inorganic and organic interfaces, it was also observed that some hydrophilic inorganic particles were easily leached out after long immersion in water [23]. Crosslinking of polymer membrane can be considered as another effective way to alleviate swelling and methanol permeability. Thermal and mechanical stabilities of the membranes can also be improved. Zhong et al. and Heo et al. have reported photochemically cross-linkable aromatic membranes containing a double bond in the side chain or the main

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Scheme 1. Scheme for illustrating the preparation of cross-linked hybrid membranes using silane-crosslinking and thiol-ene click chemistry.

chain of polymers [24,25]. Chikashige et al. prepared a tri-functional monomer for branching or crosslinking of the polymer main chain [26]. Both the ionic and covalently cross-linked membranes, accompanied with detailed comparison, were introduced by Kerres [27,28]. However, during the crosslinking reaction, the ion exchange capacity (IEC) decreased greatly due to the elimination of sulfonic acid groups, which brought the reduction of the proton conductivity. Thus, it is necessary to find or design a novel polymer backbone with other functional groups that can be cross-linked with a cross-linker without a dilution of sulfonic acid groups.

Side-chain-type propenyl based sulfonated poly(arylene ether ketone)s, combined with a suitable cross-linker, can be considered as promising materials to improve the properties of membranes. Propenyl, containing a double bond, is an excellent crosslinking agent, because it can initiate a radical reaction by heating or UV irradiation. It could be involved in thermally and photochemically initiated thiol-ene click reactions using thiol and allyl functionalized polymers. The thiol-ene click reaction has received a growing interest over the last years, which is mainly attributable to the recognition of its click characteristics [29,30].

In this paper, we chose 3-mercaptopropyltrimethoxysilane containing $-\text{SH}$ groups (Trademark: KH590) as a cross-linker for

propenyl-containing SPAEK membranes. As shown in Scheme 1, we grafted the special silane monomer, KH590, onto the SPAEK backbone by the thiol-ene click reaction. The silane-crosslinking was then induced by a hydrolysis–condensation. The hydrophilic SPAEK could be blocked in the Si–O–Si network, making a contribution to the decrease of swelling and methanol permeability. The advantage of this system is that the sulfonic acid groups of SPAEK are not involved in the crosslinking reaction. Moreover, other properties of the cross-linked hybrid membranes, such as water uptake, oxidative stability and mechanical properties were also investigated as compared with the pristine SPAEK membrane.

2. Experimental

2.1. Materials and reagent

Diallyl bisphenol A was purchased from the East China University of Science and Technology. Sodium 5,5'-carbonyl-bis(2-fluobenzenesulfonate) (SDFBP) was synthesized according to a procedure described in our previous work [31]. All the other solvents and reagent were purchased from Tianjin Tiantai chemical company. They were obtained commercially and used without further purification.

2.2. Synthesis of SPAEK containing propenyl groups

Sulfonated poly(arylene ether ketone) containing propenyl groups was synthesized according our previous work [32]. The detailed procedure is described as follows. Diallyl bisphenol A (9.24 g, 0.03 mol), K_2CO_3 (4.554 g, 0.033 mol), bis(4-fluorobenoayl) benzene (3.864 g, 0.012 mol), SDFB(7.596 g, 0.036 mol) were added to a three neck bottom flask equipped with a mechanical stirrer, a nitrogen inlet and a Dean–Stark trap. Sulfolane/toluene (34 ml/20 ml) solvent system was used in this reaction. The reaction bath was heated to 140 °C and kept at this temperature for 3 h to remove water. Then the temperature was raised to 180 °C for 7 h. The product was washed with boiling deionized water for several times. Then it was dried in a vacuum oven at 80 °C for 48 h to obtain a constant weight.

1H NMR (500 MHz, DMSO- d_6 , d, ppm): 1.55–1.8 (–CH₃ of propenyl groups and –CH₃ of bisphenol A), 6.33 (HC=C of propenyl groups ortho to methyl), 6.66 (HC=C of propenyl groups ortho to aromatic group), 8.2 (ArH ortho to –SO₃Na groups), 6.8–7.8 (other ArH). IR (KBr, thin film, cm^{-1}): 1650 (carbonyl groups), 1079 and 1027 (–SO₃Na), 965 (propenyl groups).

2.3. Preparation of the hybrid membranes

The hybrid membranes were prepared according to the following procedure. SPAEK was dissolved in 10 mL dimethylformamide (DMF) at room temperature to obtain a 10 wt.% homogeneous solution. Certain weights of KH590 and benzoyl peroxide were added to the SPAEK solution. The resulting solution was stirred for 0.5 h. The mixtures were then cast onto glass dishes and thermally treated at 100 °C for 2 h and at 120 °C for 6 h to lead the –SH groups of KH590 to react with propenyl 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 reaction for the hybrid membranes. The SPAEK/KH590 hybrid membranes were noted as SPAEK/KH590- $x\%$ ($x\%$ refers to weight percent of KH590 in the cross-linked membranes). All membranes were then sufficiently soaked in distilled and deionized water at room temperature for 24 h before use.

2.4. Characterization

2.4.1. Structural characterization

FT-IR spectra of powder samples and thin films were recorded on a Bruker Vector 22 spectrometer from 4000 to 400 cm^{-1} . 1H NMR spectra (in DMSO- d_6) were obtained on a 500 MHz Bruker Avance 510 spectrometer.

2.4.2. Thermogravimetric analysis (TGA)

Thermo-gravimetric analysis was recorded on a Perkin Elmer thermal analysis system at a heating rate of 10 °C min^{-1} under N₂ 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.

2.4.3. Ion exchange capacity and water uptake

IEC was determined by titration method. Membrane samples in acid form were immersed in 1 M NaCl solution for 48 h to liberate the H⁺ ions (the H⁺ ions in the membrane were replaced by Na⁺ ions). Then the H⁺ ions were titrated with 0.01 M NaOH solution using phenolphthalein as an indicator.

2.4.4. Water uptake and swelling ratio

The water uptake of the membranes was calculated by measuring the weight difference between the dry and wet

membranes. The membranes were vacuum-dried and then soaked in water for 24 h at different temperatures. Then they were wiped with blotting paper and immediately weighed on an analytical balance after wiping out the surface water. The water uptake was calculated by the following equation:

$$\text{water uptake (WU)(\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

where W_{dry} and W_{wet} are the weight of dry and corresponding water-swollen membranes, respectively.

The swelling ratio was calculated by the following equation:

$$\text{swelling ratio\%} = \frac{T_{\text{wet}} - T_{\text{dry}}}{T_{\text{dry}}} \times 100\% \quad (2)$$

where T_{dry} and T_{wet} are the thickness of dry and corresponding water-swollen membranes, respectively.

The number of water molecules per sulfonic acid group (λ) is determined by water uptake and IEC according to the following equation:

$$\lambda = n(H_2O)/n(SO_3^-) = WU/(18 \times IEC) \quad (3)$$

where 18 is the molecular weight of water.

The swelling degree in methanol solution of the membrane was determined by immersing the dried membranes into 10 M methanol solution for 1 day at different temperatures. The swelling degree was calculated by the change in weight between dry and wet samples.

2.4.5. Proton conductivity and methanol permeability

The in-plain proton conductivity (σ) was determined 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 cell was immersed into water at 25, 40, 60 and 80 °C during the measurement. The proton conductivity was calculated by the following equation:

$$\sigma = L/RA \quad (4)$$

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

Methanol permeability was measured using a diffusion cell at ambient temperature. The cell consisted of two reservoirs separated by the membrane. Methanol (1.0 M) was placed on one side (A cell) and distilled water was placed on the other side of the diffusion cell (B cell). The magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol in water reservoir was monitored by SHIMADZU GC-8A chromatograph. The methanol permeability was calculated by the following equation:

$$C_B(t) = \frac{A D K}{V_B L} C_A(t - t_0) \quad (5)$$

where A (cm^2) and L (cm) are the effective area and the thickness of the membrane, respectively, V_B (cm^3) is the volume of diffusion reservoir, C_A and C_B ($mol L^{-1}$) are the methanol concentration in methanol reservoir and water reservoir, respectively, DK is the methanol permeability ($cm^2 s^{-1}$).

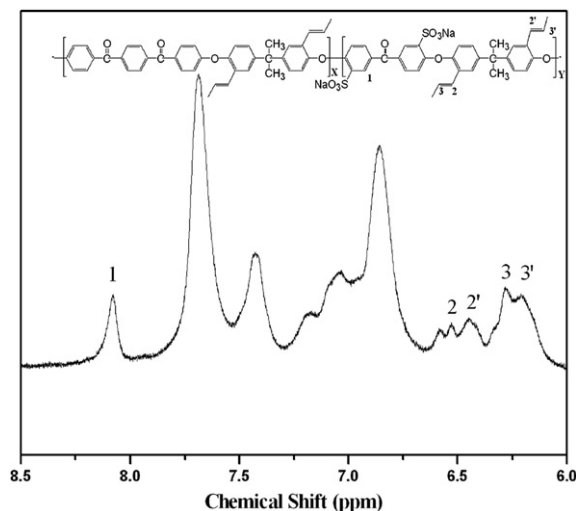


Fig. 1. ^1H NMR spectrum of propenyl-containing SPAEK.

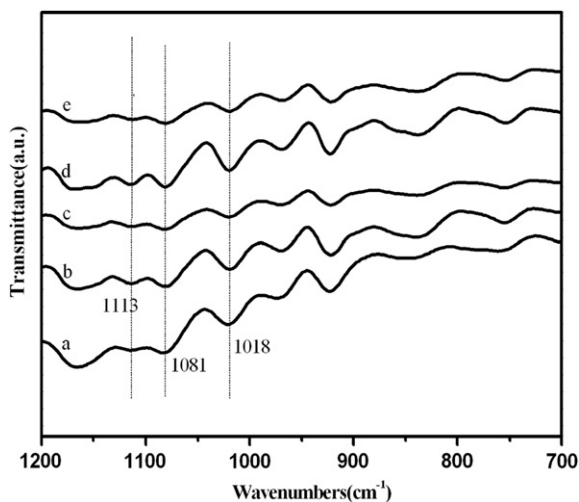


Fig. 2. FT-IR spectra of (a) SPAEK, (b) SPAEK/KH590-5, (c) SPAEK/KH590-10, (d) SPAEK/KH590-15, and (e) SPAEK/KH590-20.

2.4.6. Mechanical properties

The mechanical properties of the membranes were investigated by “stress–strain” tests using SHIMADZU AG-1 1KN at the test speed of 2 mm min^{-1} . The size of the films was $1\text{ mm} \times 4\text{ mm}$. Each sample was used at least 3 times and their average value was calculated.

2.4.7. The oxidative stabilities

The oxidative stabilities of the membranes were tested by immersing the films into Fenton reagent (3% H_2O_2 containing 2 ppm FeSO_4) at $80\text{ }^\circ\text{C}$. The stability was evaluated by recording the time when membranes break into pieces.

Table 1
Solubility of SPAEK/KH590- $x\%$ membranes in various common organic solvents.

Sample	Water		DMAc		DMF		NMP		DMSO		Methanol		Chloroform	
	25 $^\circ\text{C}$	60 $^\circ\text{C}$	25 $^\circ\text{C}$	60 $^\circ\text{C}$	25 $^\circ\text{C}$	60 $^\circ\text{C}$	25 $^\circ\text{C}$	60 $^\circ\text{C}$	25 $^\circ\text{C}$	60 $^\circ\text{C}$	25 $^\circ\text{C}$	60 $^\circ\text{C}$	25 $^\circ\text{C}$	60 $^\circ\text{C}$
SPAEEK	I	I	Sw	S	Sw	S	Sw	S	Sw	S	I	I	I	I
SPAEEK/KH590-5	I	I	I	I	Sw	Sw	Sw	Sw	Sw	Sw	I	I	I	I
SPAEEK/KH590-10	I	I	I	I	Sw	Sw	Sw	Sw	Sw	Sw	I	I	I	I
SPAEEK/KH590-15	I	I	I	I	Sw	Sw	Sw	Sw	Sw	Sw	I	I	I	I
SPAEEK/KH590-20	I	I	I	I	Sw	Sw	Sw	Sw	Sw	Sw	I	I	I	I

S: soluble; I: insoluble; and Sw: slightly swollen.

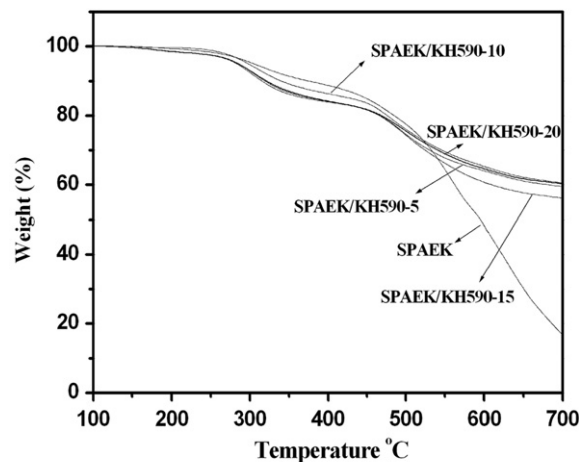


Fig. 3. TGA of SPAEK and SPAEK/KH590- $x\%$ membranes in N_2 .

3. Results and discussion

3.1. Structure characterization

The molecular structure of SPAEK was confirmed by its ^1H NMR spectrum (dimethyl sulfoxide- d_6 ($\text{DMSO}-d_6$), d , ppm). The ortho proton peak (1) to the sulfonate group on the aromatic ring appeared at the most downfield, which was due to the electron-withdrawing of $-\text{SO}_3\text{Na}$ groups. The peaks from 6.3 to 6.7 ppm confirmed the existence of the propenyl groups (Fig. 1). The ^1H NMR spectrum showed that the SPAEK containing propenyl groups was successfully synthesized.

The typical FT-IR spectra of SPAEK and SPAEK/KH590- $x\%$ membranes are shown in Fig. 2. The observed bands at 1081 cm^{-1} and 1018 cm^{-1} were assigned to the asymmetric and symmetric $\text{O}=\text{S}=\text{O}$ stretching vibrations of sulfonic acid groups. The preservation of sulfonic acid groups in the cross-linked hybrid membranes can be confirmed by the presence of the characteristic bands of sulfonic acid groups in their spectra. After the heating and hydrolysis–condensation, $\text{Si}-\text{O}-\text{Si}$ peaks appeared at 1113 cm^{-1} for the SPAEK/KH590- $x\%$ membranes, which demonstrated the formation of $\text{Si}-\text{O}-\text{Si}$ cross-linked structure in the hybrid membranes.

After hybridisation with KH590, the SPAEK/KH590- $x\%$ membranes cannot be dissolved in several organic solvents at $60\text{ }^\circ\text{C}$ (Table 1), indicating the successful incorporation of cross-linked network structure into SPAEK membranes.

3.2. Thermal stability

The thermal stabilities of the SPAEK and SPAEK-KH590- $x\%$ membranes were investigated by thermo-gravimetric analysis. Fig. 3 shows the TGA curves of the representative membranes. We can see that all the membranes in acid form exhibit two step

Table 2
The swelling properties in water and methanol solution of membranes.

Sample	IEC (mequiv g ⁻¹)	Swelling ratio (%)		Water uptake (%)		Methanol solution uptake (%)		λ	
		25 °C	80 °C	25 °C	80 °C	25 °C	80 °C	25 °C	80 °C
SPAEK	2.04	7.40	11.11	28.84	44.18	33.42	52.99	7.85	12.03
SPAEK/KH590-5	1.93	7.35	10.45	28.04	43.01	32.59	48.32	8.07	12.3
SPAEK/KH590-10	1.52	6.70	10.17	27.59	35.10	28.45	46.80	10.1	12.8
SPAEK/KH590-15	1.34	5.80	8.14	24.37	33.91	27.29	43.61	10	14.1
SPAEK/KH590-20	1.31	3.17	4.76	21.51	31.38	26.09	40.35	9.1	13.3
Nafion 117	0.92	11.0	17.2	18.3	27.9	–	–	11.1	16.8

degradation patterns. The first degradation step occurring between 280 and 350 °C was attributed to the splitting-off of sulfonic acid groups or flexible chains of KH590. The second weight loss step started at 460 °C was assigned to the decomposition of main polymer chain. The residual temperatures of hybrid membranes were much higher than SPAEK membrane. The 5% weight loss temperature and 10% weight loss temperature of all the membranes were higher than 280 °C, which indicated that all of the membranes had excellent thermal stabilities.

3.3. IEC, water uptake and swelling ratio

The ion exchange capacity indicates the number of protons per ionomer unit mass that can be replaced by other cations, which is responsible for their water uptake and proton conductivity. The water uptake of PEM is another factor that decides proton conductivity and mechanical properties of the membranes [33]. However, high water uptake always accompanied by dimensional change or even soluble of membranes. As shown in Table 2, IEC of SPAEK membrane is higher than those of SPAEK/KH590-*x*% membranes. The IEC values of these membranes decreased from 2.04 mequiv g⁻¹ to 1.31 mequiv g⁻¹, when the ratio of KH590 was increasing. The phenomenon was due to the dilution effect caused by adding KH590 that did not have sulfonic acid groups.

Fig. 4 presents the water uptake of the hybrid membranes at different temperatures.

According to the result of water uptake, it can be observed that the water uptake shows a decreasing tendency with the increasing weight fraction of KH590. For example, the water uptake of SPAEK/

KH590-20 decreased to 21.51% at 25 °C and 31.38% at 80 °C, as compared to the pristine SPAEK membrane (44.18% at 80 °C). The lambda value of the SPAEK/KH590 hybrid membranes depends on the temperature at which water uptake is measured. The SPAEK membranes with various KH590 contents have similar lambda values in the range 8–10 at 25 °C and in the range 12–14 at 80 °C. This result indicates that the main factor affecting the decrease in the percentage of water uptake is the decrease in the IEC values. Similarly, the swelling ratio of the hybrid membranes was also suppressed by the cross-linked network. As listed in Table 2, the dimensional change that occurs in water at a high temperature was drastically reduced after crosslinking.

The swelling degrees in 10 M methanol–water solution of the membranes were also measured and the results are listed in Table 2. In this experiment, the membrane is primarily hydrated by water and the methanol plays a small role in hydration of the polymer structure. Similar to the swelling degree in the pure water, both the swelling degrees at 25 °C and 80 °C decreased with the increasing proportion of KH590, which was caused by the formation of cross-linked structure. It is obvious that the formation of Si–O–Si network structure is helpful to restrict the mobility of chains and hold polymer chain together, thus causing the reduction of solution uptake and swelling ratio.

3.4. Mechanical properties

The mechanical properties of SPAEK membrane and hybrid membranes in dry state were evaluated and listed in Table 3. After a crosslinking process, Young's modulus of the hybrid membranes increased to 1634 and 1834 MPa. The result shows that crosslinking can help to enhance the mechanical stability effectively. The maximum stress of all the membranes ranges from 36.9 to 70.8 MPa, indicating that the hybrid membranes have adequate mechanical integrity to be used in fuel cell.

3.5. Oxidative stability

The oxidative stabilities of the pristine SPAEK and the cross-linked hybrid membranes were tested in Fenton's reagent at 80 °C. The results are displayed in Fig. 5. It was evaluated by the expended time that the membranes broke into pieces in Fenton's reagent. Compared to the pristine SPAEK membrane, the cross-

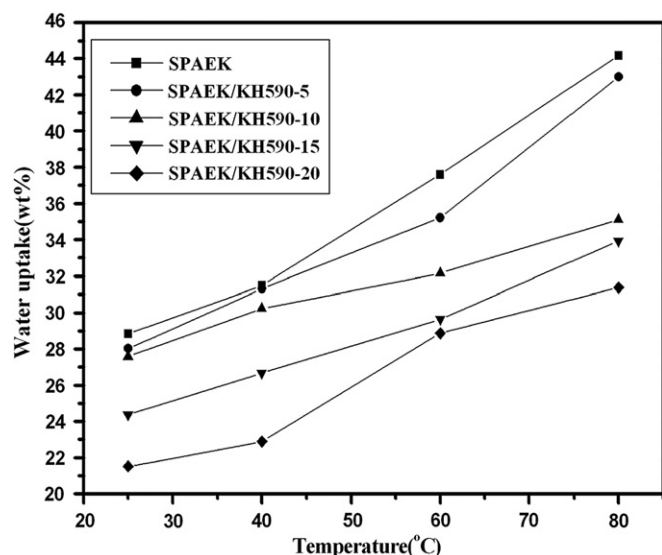


Fig. 4. Water uptakes of SPAEK and SPAEK/KH590-*x*% membranes.

Table 3
Mechanical properties of membranes.

Membranes	Maximum stress (MPa)	Young's modulus (MPa)	Elongation at break (%)
SPAEK	48.7	1192.3	6.9
SPAEK/KH590-5	36.9	1833.7	4.4
SPAEK/KH590-10	70.8	1661.9	7.9
SPAEK/KH590-15	54.2	1633.9	7.4
SPAEK/KH590-20	59.8	1686.3	15.3

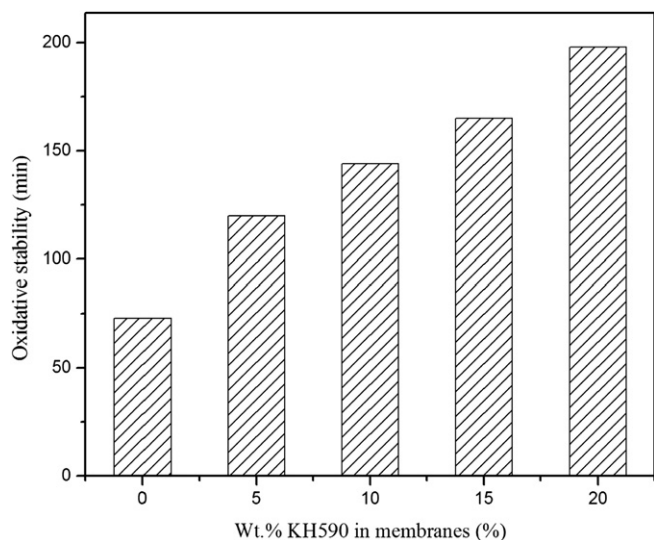


Fig. 5. The oxidative stability of the pristine SPAEK and the cross-linked hybrid membranes in Fenton's reagent.

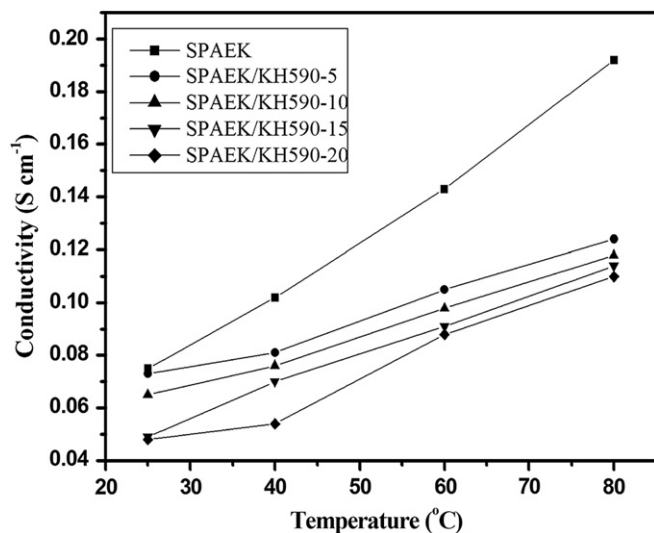


Fig. 6. Proton conductivities of SPAEK and SPAEK/KH590-*x*% membranes.

linked hybrid membranes exhibited a significant improvement in the oxidative stability. The pristine SPAEK membrane broke into pieces after immersing in Fenton's reagent for about 73 min. On the contrary, SPAEK/KH590-20 broke into pieces after 198 min. We can also observe that the oxidative stability of the hybrid membranes increased with the amount of KH590 increased. It can be explained by the formation of Si–O–Si structure. There are two reasons: (1)

the Si–O–Si structure shows good oxidation stability and (2) the cross-linked network restricts the swelling of the membrane, decreasing the attack opportunity of free radicals in absorbed water.

3.6. Proton conductivity and methanol permeability

Fig. 6 displays the proton conductivities of the cross-linked hybrid SPAEK membranes as a function of temperature. It was found that the proton conductivity of all the membranes increased with increasing temperature. Due to the formation of cross-linked structure, the hybrid membranes showed lower proton conductivities than those of SPAEK membrane. However, all the hybrid membranes still maintained high conductivity, which met the requirement of a PEM used in fuel cell.

The methanol permeability of SPAEK and cross-linked hybrid membranes at room temperature is shown in Table 4. The cross-linked hybrid membranes exhibited low methanol permeability ranging from 3.18×10^{-7} to 1.24×10^{-7} cm² s⁻¹. They are all lower than that of the pristine SPAEK (4.25×10^{-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 technique.

Membranes for the practical usage of PEMs in DMFCs were required to possess high proton conductivity (σ) and low methanol permeability (P). The selectivity (σ/P), which is defined as the ratio of proton conductivity to methanol permeability, is often used to evaluate the potential performance of DMFC membranes [34]. In this case, the selectivity can be used just as a barometer to develop the best proton conductive with reducing methanol permeability. With the content of KH590 increasing, the selectivity increases, which are all higher than those of SPAEK and Nafion 117, indicating that the cross-linked membranes would have a potential application in DMFCs.

4. Conclusions

A series of SPAEK/KH590-*x*% membranes with high oxidative stability and low water uptake and swelling ratio have been prepared successfully by a combination of silane-crosslinking and thiol-ene click chemistry for DMFCs. The method is simple and efficient, and could be widely used to enhance the performance of other ion exchange membranes. Compared to the pristine SPAEK membrane, it is found that the oxidative stability have been increased from 73 min to 198 min. The hybrid membranes also exhibit lower water uptake, methanol permeability and swelling due to the introduction of Si–O–Si network. The results suggest that these new copolymers possess great potential in DMFC applications.

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Table 4
Proton conductivity, methanol permeability and relative selectivity of membranes.

Sample	IEC (mequiv g ⁻¹)	σ (S cm ⁻¹)		P ($\times 10^{-7}$ cm ² s ⁻¹)	σ/P ($\times 10^5$ S cm ⁻³ s ⁻¹)
		25 °C	80 °C		
SPAEK	2.04	0.075	0.192	4.25	1.76
SPAEK/KH590-5	1.93	0.073	0.124	3.18	2.30
SPAEK/KH590-10	1.52	0.065	0.118	2.56	2.54
SPAEK/KH590-15	1.34	0.049	0.114	1.55	3.16
SPAEK/KH590-20	1.31	0.048	0.110	1.24	3.87
Nafion 117	0.92	0.076	0.146	10.05	0.76

References

- [1] B.C.H. Steele, A. Heinzel, *Nature* 414 (2001) 345–352.
- [2] K.D. Kreuer, *J. Membr. Sci.* 185 (2001) 29–39.
- [3] K. Goto, I. Rozhanskii, Y. Yamakawa, T. Otsuki, Y. Naito, *Polym. J.* 41 (2009) 95–104.
- [4] F. Lufrano, I. Gatto, P. Staiti, V. Antonucci, E. Passalacqua, *Solid State Ionics* 145 (2001) 47–51.
- [5] C. Manea, M. Mulder, *J. Membr. Sci.* 206 (2002) 443–453.
- [6] C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel, M. Pineri, *Polymer* 42 (2001) 359–373.
- [7] J.H. Fang, X.X. Guo, S. Harada, T. Watari, K. Tanaka, H. Kita, K. Okamoto, *Macromolecules* 35 (2002) 9022–9028.
- [8] Y. Zhang, Y. Wan, C.J. Zhao, K. Shao, G. Zhang, H.T. Li, H.D. Lin, H. Na, *Polymer* 50 (2009) 4471–4478.
- [9] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, *J. Membr. Sci.* 173 (2000) 17–34.
- [10] M. Rikukawa, K. Sanui, *Prog. Polym. Sci.* 25 (2000) 1463–1502.
- [11] C.J. Zhao, Z. Wang, D.W. Bi, H.D. Lin, K. Shao, T.Z. Fu, S.L. Zhong, H. Na, *Polymer* 48 (2007) 3090–3097.
- [12] B. Bauer, D.J. Jones, J. Roziere, L. Tchicaya, G. Alberti, M. Casciola, L. Massinelli, A. Peraio, S. Besse, E. Ramunni, *J. New Mater. Electrochem. Syst.* 3 (2000) 93–98.
- [13] S.P. Nunes, B. Ruffmann, E. Rikowski, S. Vetter, K. Richau, *J. Membr. Sci.* 203 (2002) 215–225.
- [14] B. Yang, A. Manthiram, *Electrochem. Solid-State Lett.* 6 (2003) A229–A231.
- [15] K.D. Kreuer, M. Ise, A. Fuchs, J. Maier, *J. Phys. IV* 10 (2000) 279–281.
- [16] F. Wang, M. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, *J. Membr. Sci.* 197 (2002) 231.
- [17] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, S. Kaliaguine, *Polymer* 46 (2005) 3257–3263.
- [18] J.H. Pang, H.B. Zhang, X.F. Li, D.F. Ren, Z.H. Jiang, *Macromol. Rapid. Commun.* 28 (2007) 2332–2338.
- [19] M.K. Rahman, G. Aiba, Md.A.H. Susan, M. Watanabe, *Electrochim. Acta* 50 (2004) 633–638.
- [20] K. Xu, C. Chanthad, M.R. Gadinski, M.A. Hicker, Q. Wang, *Appl. Mater. Interfaces* 11 (2009) 2573–2579.
- [21] L.J. Su, L. Li, H. Li, J.K. Tang, Y.M. Zhang, W. Yu, C.X. Zhou, *J. Power Sources* 194 (2009) 220–225.
- [22] W.F. Chen, P.L. Kuo, *Macromolecules* 40 (2007) 1987–1994.
- [23] J. Chen, M. Asano, Y. Maekawa, M. Yoshida, *J. Membr. Sci.* 296 (2007) 77–82.
- [24] S.L. Zhong, C.G. Liu, H. Na, *J. Membr. Sci.* 326 (2009) 400–407.
- [25] Y. Chikashige, Y. Chikyu, K. Miyatake, M. Watanabe, *Macromol. Chem. Phys.* 207 (2006) 1334–1343.
- [26] K.-B. Heo, H.-J. Lee, H.-J. Kim, B.-S. Kim, S.-Y. Lee, E. Cho, I.-H. Oh, S.-A. Hong, T.-H. Lim, *J. Power Sources* 172 (2007) 215–219.
- [27] J.A. Kerres, *J. Membr. Sci.* 185 (2001) 3–27.
- [28] J.A. Kerres, *Fuel Cells* 5 (2005) 230–247.
- [29] C.R. Becer, R. Hoogenboom, U.S. Schubert, *Angew. Chem. Int. Ed.* 48 (2009) 4900–4908.
- [30] J.W. Chan, C.E. Hoyle, A.B. Lowe, *J. Am. Chem. Soc.* 131 (2009) 5751–5753.
- [31] F. Wang, T.L. Chen, J.P. Xu, Sodium sulfonate-functionalized poly(ether ether ketone)s, *Macromol. Chem. Phys.* 199 (7) (1998) 1421–1426.
- [32] S.J. Zhong, T.Z. Fu, Z.Y. Dou, C.J. Zhao, H. Na, *J. Power Sources* 162 (2006) 51–57.
- [33] T.A. Zawodzinski, T.E. Springer, J. Davey, R. Jestel, C. Lopez, J. Valerio, S. Gottesfeld, *J. Electrochem. Soc.* 140 (1993) 1981–1985.
- [34] B.S. Pivovarov, Y.X. Wang, E.L. Cussler, *J. Membr. Sci.* 154 (1999) 155–162.