

Crosslinked sulfonated poly(ether ether ketone) proton exchange membranes for direct methanol fuel cell applications

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Abstract

In the present study, a series of the crosslinked sulfonated poly(ether ether ketone) (SPEEK) proton exchange membranes were prepared. The photochemical crosslinking of the SPEEK membranes was carried out by dissolving benzophenone and triethylamine photo-initiator system in the membrane casting solution and then exposing the resulting membranes after solvent evaporation to UV light. The physical and transport properties of crosslinked membranes were investigated. The membrane performance can be controlled by adjusting the photoirradiation time. The experimental results showed that the crosslinked SPEEK membranes with photoirradiation 10 min had the optimum performance for proton exchange membranes (PEMs). Compared with the non-crosslinked SPEEK membranes, the crosslinked SPEEK membranes with photoirradiation 10 min markedly improved thermal stabilities and mechanical properties as well as hydrolytic and oxidative stabilities, greatly reduced water uptake and methanol diffusion coefficients with only slight sacrifice in proton conductivities. Therefore, the crosslinked SPEEK membranes with photoirradiation 10 min were particularly promising as proton exchange membranes for direct methanol fuel cell (DMFC) applications. © 2006 Elsevier B.V. All rights reserved.

Keywords: Crosslinking; Sulfonated poly(ether ether ketone)s; UV irradiation; Proton exchange membrane; Direct methanol fuel cell

1. Introduction

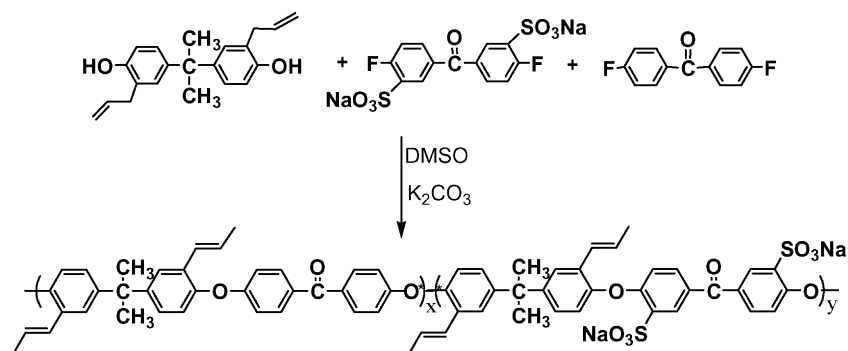
Recently, direct methanol fuel cell (DMFC) is considered a highly promising power source due to its several advantages: no fuel processing unit, low temperature and pressure operation, high energy efficiency and low emission, compact cell design, etc. [1–3]. Conventional DMFC consists of a proton exchange membrane with catalyzed electrodes bonded to both sides. The membrane materials commonly used in DMFC are perfluoro-sulfonic acid ionomers (e.g., Nafion[®]) because of their good chemical and physical stability as well as high proton conductivity. However, high cost and methanol diffusion have limited their extensive applications [4,5]. In particular, the high methanol diffusion leads to poisoning of the catalyst and reduction of the electrical performance and the fuel efficiency during the DMFC operation. Hence, the primary criterion for choosing DMFC membrane is not only high proton conductivity but also good

efficiency as methanol barrier. Besides, the water uptake is also a key consideration for proton exchange membranes. Too low water uptake induces the reduction of the proton conductivity due to the less water absorption, while extreme water uptake will cause the loss of the dimensional stability and mechanical strength [6,7].

Crosslinking is an efficient means to limit methanol diffusion and overfull water uptake, also enhance stabilities and mechanical properties of the membranes [8–10]. UV irradiation-induced crosslinking is thought to be one of the most effective methods to generate three-dimensional polymer networks owing to its easiness, relative safety and low cost as well as high initiation rate under intense illumination [11–13].

Therefore, in this paper, we prepared the crosslinked SPEEK membranes for DMFC usages by UV irradiation. The crosslinked membranes were expected to possess low methanol diffusion and water uptake but high stability and mechanical strength. For the comparison of the properties of the crosslinked and the non-crosslinked membranes, the thermal stability and the mechanical behavior, the ion exchange capacity and the water uptake, the hydrolytic and oxidative stability, the methanol

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Scheme 1. The synthesis of SPEEK polymers.

diffusion coefficient and the proton conductivity were fully investigated.

2. Experimental

2.1. Materials

Diallyl bisphenol A was supplied by East China University of Science and Technology. 4,4'-Difluorobenzophenone was got from Longjing Chemical plant. 5,5'-Carbonyl-bis(2-fluorobenzenesulfonate) was synthesized by sulfonation of 4,4'-difluorobenzophenone according to the procedure described by Wang et al. [14]. Potassium carbonate was dried at 180 °C under vacuum for 10 h before used. Other reagents and solvents were obtained commercially and used without further purification.

2.2. Synthesis of the sulfonated polymers

The preparation of the SPEEKs containing propenyl groups was reported by our previous work [15]. As shown in Scheme 1, the SPEEKs were synthesized via nucleophilic substitution reaction of diallyl bisphenol A (monomer l) with 4,4'-difluorobenzophenone (monomer k) and 5,5'-carbonyl-bis(2-fluorobenzenesulfonate) (monomer m) in DMSO/toluene solvent system. The mixture was first refluxed at 140 °C for about 3 h to remove the water produced in this system, and then was slowly raised up to 180 °C and kept that temperature for 16 h. The product was purified with boiling deionized water and dried in vacuum oven at 70 °C for 3 days. The polymerization results were summarized in Table 1.

Table 1
The data of the sulfonated polymers

Polymer	<i>m</i> (mmol)	<i>k</i> (mmol)	<i>m/k</i>	DS ^a	DS ^b	Yield (%)	η_{sp}/c (dL g ⁻¹)	<i>T_g</i> (°C)
SPEEK-0	0	100	0:10	0	–	96	0.90	146
SPEEK-28	20	80	2:8	0.4	0.36	94	1.06	163
SPEEK-46	40	60	4:6	0.8	0.81	95	1.11	219
SPEEK-55	50	50	5:5	1.0	0.97	96	1.28	–

m = 4,4'-difluorobenzophenone. *k* = 5,5'-carbonyl-bis(2-fluorobenzenesulfonate). η_{sp}/c = measured at a concentration of 5.00 g L⁻¹ in DMF at 25 ± 0.1 °C. – = not detected between 50 and 350 °C.

^a DS = sulfonated degree obtained from monomer ratio.

^b DS = sulfonated degree obtained from ¹H NMR data.

2.3. Preparation of non-crosslinked and crosslinked SPEEK membranes

The non-crosslinked SPEEK membranes were prepared by pouring the solution of 10–15% SPEEKs in DMF into a glass plate and dried at 70 °C for 3 days.

The crosslinked SPEEK membranes were formed according to the following procedure: the solution of 10–15% SPEEKs in DMF was prepared with benzophenone (BP) and triethylamine (TEA) as the photo-initiator system. The resulting mixture was continuous stirring until a transparent solution was obtained. Then the solution was cast onto a glass plate and dried at 70 °C for 3 days, followed the dried membranes were irradiated for different time in a 600 W UV light.

The non-crosslinked and the crosslinked SPEEK membranes were acidified by immersing the sodium salt membranes into 1.0 M HCl solutions for 24 h, and then the membranes were rinsed with deionized water to remove any excess acid.

2.4. Measurement

FTIR spectra were obtained on a Nicolet Impact 410 spectrometer. For all samples, KBr pellets were prepared and measured in the range from 4000 to 400 cm⁻¹.

Thermogravimetric analysis (TGA) measurements of the acid form membranes were performed on a Pyris 1TGA (Perkin-Elmer). Before testing, all the acid form membranes were preheated to 150 °C and kept at this temperature for 20 min to remove any residual moisture and solvent, followed the samples were cooled to 100 °C and then reheated to 700 °C at a heating rate of 10 °C min⁻¹ in N₂ flow.

The ion exchange capacity (IEC) of the membrane was determined by classical titration method. First, the membrane in acid form was immersed in 50 mL 1.0 M NaCl solution for 24 h to replace the protons of sulfonic acid groups with sodium ions. Then the released protons in solution were titrated with 0.01 M NaOH solution using phenolphthalein as indicator.

The titrated IEC was determined from formula:

$$\text{IEC} = \frac{C \times V}{M} \times 100$$

where C and V are the concentration and the volume of NaOH solution, respectively. M is the weight of dried membrane.

The membrane in acid form was vacuum-dried at 100 °C until constant weight was obtained. The dried membrane then was immersed into deionized water for 24 h at 25, 80 and 100 °C, respectively. Subsequently, the membrane was took out, wiped with tissue paper and quickly weighed on a microbalance.

The water uptake was calculated using the following formula:

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

where W_{wet} and W_{dry} are the masses of wet and dry membranes, respectively.

Methanol diffusion coefficient was measured using a glass diffusion cell described in the literatures [16,17]. The cell consists of two reservoirs, which were separated by a vertical membrane. 1.0 M methanol was placed on one side of the cell and water was placed on the other side. Magnetic stirrer was used in each reservoir to ensure uniformity during the diffusion experiment. Before testing, the acid form membranes were hydrated in deionized water for at least 24 h. The increases of the concentration of methanol in the water cell with time were determined using a SHTMADU GC-8A chromatograph. The methanol diffusion coefficient was calculated as follows:

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

where A (cm²) and L (cm) are the effective area and the thickness of membrane, respectively. V_B (cm³) is the volume of diffusion reservoir. C_A and C_B (mol L⁻¹) are the methanol concentration in feed and in diffusion reservoir, respectively. DK is the methanol diffusion coefficient (cm² s⁻¹).

To investigate the hydrolytic stability of the membrane, all the membranes were immersing in 85 °C water for 2 weeks. The hydrolytic stability was estimated by comparing the proton conductivities before and after immersing the membrane in 85 °C water for 2 weeks.

The oxidative stability was investigated by immersing the small pieces (5 mm × 5 mm) into Fenton's reagent (3% H₂O₂ containing 2 ppm FeSO₄) at 80 °C and evaluated by recording the time that membranes began to break into pieces.

The mechanical property of membrane was measured using SHIMADIU AG-I 1KN. The gauge length and width of dumb-bell tensile specimens were 15 and 4 mm, respectively. The specimens were placed between the grips of the testing machine, and the speed of testing was set at the rate of 2 mm min⁻¹. At

least five samples of each type of membrane were measured and their average value was calculated.

Proton conductivity (σ) of membrane was measured by SI 1260 + SI 1287 impedance analyzer over the frequency range from 10 to 10⁶ Hz. Before the measurement, the acid form membrane (2 cm × 1 cm) was equilibrated with distilled deionized water for at least 24 h. Then the membrane was clamped between two stainless steel electrodes and immersed into distilled deionized water to keep the relative humidity of 100% during the experiment. The proton conductivity was determined in equation:

$$\sigma = \frac{d}{Rtw}$$

where d is the distance between the electrodes, t and w are the thickness and width of membrane, respectively. R is the resistance value from the impedance data, which is determined from the low intersect of the high frequency semi-circle on a complex impedance plane with the real axis.

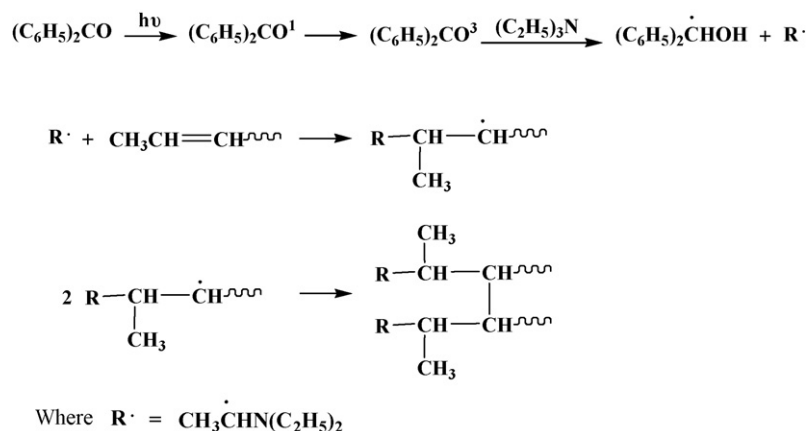
3. Results and discussion

3.1. The main UV crosslinking mechanism

The photo-initiator is a key factor for achieving a fast and extensive crosslinking by means of UV light. Therefore, it is important to select the efficient photo-initiator for the given SPEEK membranes. The benzophenone (BP), commonly used as photo-initiator to crosslink double bonds, was selected here because of its high hydrogen abstraction efficiency and long-lived excited states [11]. In addition, previous work by Cohen et al. [18], Davidson and Wilson [19] and Sandner et al. [20] had proven that excited benzophenone could undergo efficient interaction with triethylamine (TEA) and hence the combination of BP and TEA might provide an interesting synergism for UV-induced crosslinking. So, in this paper, we chose BP and TEA as the photo-initiator system. The main UV crosslinking mechanism was illustrated in Scheme 2. First, BP undergoes several photophysical processes, affording an n, π^* triplet state which proceeds to reduction of benzophenone and TEA radical formation. Then the TEA radical plays the role of photo-initiator, which further leads to the formation of the SPEEK radical. The UV crosslinking occurred mainly by a recombination reaction of two macroradicals to produce carbon-carbon bonds between the polymer chains [11,21].

3.2. FTIR spectra

The successful introduction of the sodium sulfonate groups was confirmed by comparing the FTIR spectra of SPEEK-0 and SPEEK-46 (Fig. 1). In SPEEK-46 spectrum, the characteristic peaks at 1027 and 1079 cm⁻¹ were assigned to the symmetric and asymmetric O=S=O stretching vibrations of sodium sulfonate groups, respectively. However, for the pure SPEEK-0, no related stretching vibrations of the SO₃Na were found. The absorption peak at 965 cm⁻¹ proved the presence of propenyl.



Scheme 2. The main UV crosslinking mechanism of SPEEKs.

It was attributed to that the allyl was isomerized to the propenyl under the alkaline situation [22,23].

After different UV irradiation time, the structural changes of SPEEK-0 were characterized by FTIR spectroscopy and were showed in Fig. 2. It was noticed that the intensity of the absorption peak at 965 cm^{-1} assigned to C=C double bonds became weaker and weaker with increasing UV irradiation time, which indicated the increment of crosslinking extent in the SPEEK membranes. At the same time, the crosslinked materials became gradually insoluble in DMF, DMSO and NMP solvents due to crosslinking.

3.3. Thermal properties

The thermal stabilities of the crosslinked membranes were evaluated through the TGA experiments. Prior to testing, all the acid form membranes were preheated to remove moisture and solvent, and then the samples were heated from 100 to $700\text{ }^\circ\text{C}$ in nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. The TGA curves of the crosslinked and the non-crosslinked membranes of

SPEEK-46 were used to exemplify the thermal stability (Fig. 3). It can be seen from Fig. 3 that both the crosslinked and the non-crosslinked membranes had a two step degradation pattern. The first weight loss reflected the splitting-off of the sulfonic acid groups. The second degradation step corresponded to the decomposition of the main chain. This may be caused by the thermal degradation of sulfonic acid groups at relative low temperature compared to the polymer backbone. It was also observed that the crosslinked membranes exhibited better thermal stability than the non-crosslinked membranes. For the non-crosslinked SPEEK-46, 5% weight loss was found at $305\text{ }^\circ\text{C}$, whereas in the case of the crosslinked SPEEK-46-20 min, it was at $345\text{ }^\circ\text{C}$. The shift in 5% weight loss temperatures from 305 to $345\text{ }^\circ\text{C}$ was attributed to the crosslinking of the double bonds in SPEEK, which increased the cohesion and ordering of the polymer and therefore enhanced the thermal stabilities of the SPEEK membranes [24]. Moreover, the crosslinked samples showed a lower amount of weight loss at $250\text{--}430\text{ }^\circ\text{C}$ compared to the non-crosslinked samples. Degradation of sulfonic acid groups was contributed to this temperature. For SPEEK-46, the decom-

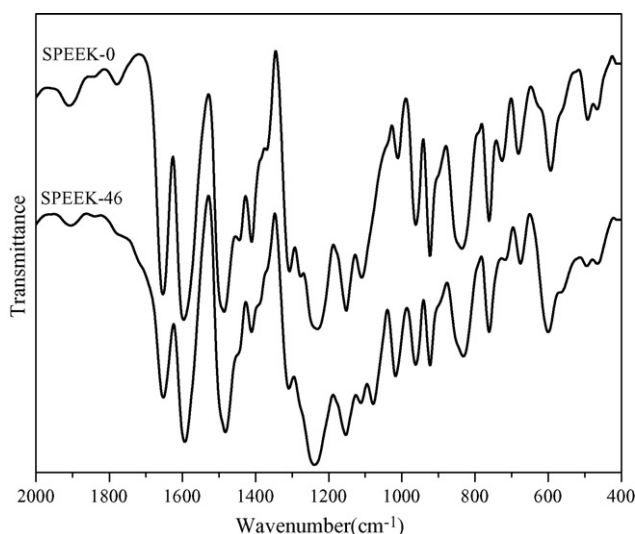


Fig. 1. Comparative FTIR spectra of SPEEK-0 and SPEEK-46.

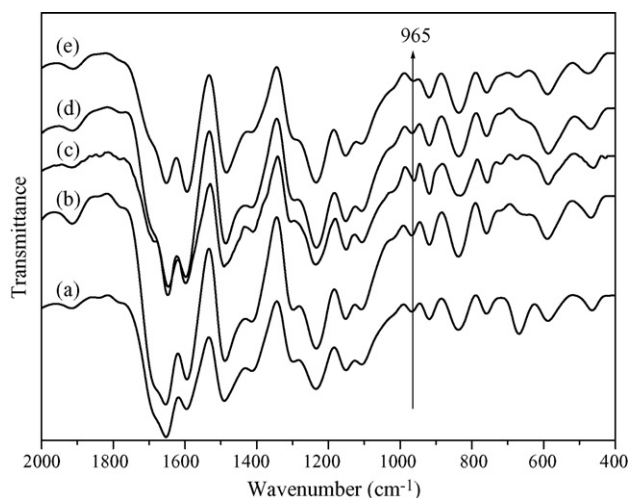


Fig. 2. FTIR spectra of SPEEK-0 membranes at different photoirradiation time: (a) 0 min, (b) 5 min, (c) 10 min, (d) 15 min, and (e) 20 min.

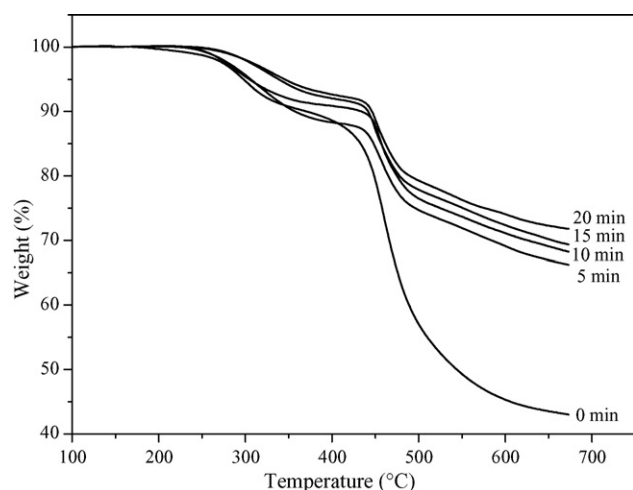


Fig. 3. TGA curves of SPEEK-46 at different photoirradiation time.

position of sulfonic acid groups ended at around 420 °C with the weight loss of 13.4%. Whereas for SPEEK-46-20 min, the decomposition of sulfonic acid groups ended at about 430 °C and only 9.1% weight loss was observed. It is mean that the formation of the network structure in the membranes restrained the degradation of sulfonic acid groups and hence increased the thermal stability of the membranes.

3.4. Ion exchange capacity (IEC)

Many important properties of proton exchange membrane, such as the water uptake and proton conductivity, depend on ion exchange capacity (IEC) [25]. IEC provides an indication of the ion exchangeable groups present in a membrane matrix [26]. The IEC values of the SPEEK membranes were showed as a function of the photoirradiation time in Table 2. Apparently, the IEC values of the crosslinked SPEEK membranes were very dependent upon the photoirradiation time. Take SPEEK-46 for example, the non-crosslinked membrane showed the IEC of 1.429 mmol g⁻¹, whereas the crosslinked membranes exhib-

ited the IEC of 1.365, 1.245, 1.173 and 1.065 mmol g⁻¹ with increase of photoirradiation time. Because the same SPEEK-46 were used here to prepare the crosslinked SPEEKs, the sulfonic acid contents were same in all the crosslinked SPEEKs. Hence the decrease in IEC despite the same sulfonic acid contents could be attributed to the increment of crosslinking extent with the increasing photoirradiation time. The increase in crosslinking extent could induce structural reorientation and decrease chain mobility. Thus, the crosslinked membranes have denser network structure than uncrosslinked one, which may result in less and smaller hydrophilic channels for proton mobility and water absorption, and hence not being available for the exchange of protons for Na⁺ ions in the titration, the IEC values therefore decreased. It is well known that the water uptake depended on the IEC value, so it was expected that the water uptake of the membranes could be restricted by crosslinking. This behavior will be discussed in the following section.

3.5. Water uptake and methanol diffusion

The water uptake of the crosslinked and the non-crosslinked membranes were summarized in Table 2. As expected, the water uptake of the membranes lowered due to the presence of polymer crosslinking. For example, the SPEEK-46 membrane absorbed 20.9% water at 25 °C, whereas the water uptake of the SPEEK-46-20 min membrane under the same temperature was only 9.9%. This result clearly indicated that the presence of double bands in the SPEEKs led to crosslinking of the SPEEKs, which eventually hindered their mobility and reduced the water uptake of membranes. In addition, the water uptake measurements provided an implication of the crosslinking extent in the polymer network. As the photoirradiation time increased, the crosslinking extent increased and further restriction was imposed on the mobility of SPEEK chains; thereby more decrease in the water uptake of the membranes occurred. That is, the lower water uptake corresponded to the higher crosslinking extent [27]. Hence, compared with non-crosslinked membranes, the water uptake of crosslinked membranes gradually decreased with increasing photoirradiation time.

In DMFC, the PEM is required to have low methanol diffusion coefficient because the diffusion of methanol from the anode to the cathode lead to power loss and other undesirable consequences. The membranes with lower methanol diffusion coefficient may allow for higher methanol feed concentration, thereby increasing the effective energy density of the fuel cell system. Fig. 4 illustrated the relationship between methanol diffusion coefficient and photoirradiation time. Similar to the water uptake behavior, the methanol diffusion coefficients of the crosslinked SPEEK membranes significantly decreased with increasing photoirradiation time. Take SPEEK-46 for example, the methanol diffusion coefficient reduced from 30.9×10^{-8} to 8.5×10^{-8} cm² s⁻¹ when photoirradiation time increased from 0 to 20 min. Similar trends in the water uptake and the methanol diffusion coefficient provided an indirect proof that the crosslinked membranes were denser and free volume reduced with the increment of photoirradiation time, which effectively

Table 2
The IEC and water uptake of crosslinked membranes

	IEC (mmol g ⁻¹)	Water uptake (%)		
		25 °C	80 °C	100 °C
SPEEK-28	0.624	13.6	17.3	26.2
SPEEK-28-5 min	0.600	10.9	13.5	22.2
SPEEK-28-10 min	0.586	9.1	12.2	20.3
SPEEK-28-15 min	0.571	8.3	11.7	18.5
SPEEK-28-20 min	0.522	6.9	9.2	14.9
SPEEK-46	1.429	20.9	42.7	76.8
SPEEK-46-5 min	1.365	16.2	37.4	50.3
SPEEK-46-10 min	1.245	14.8	34.6	46.2
SPEEK-46-15 min	1.173	11.7	32.7	42.8
SPEEK-46-20 min	1.065	9.9	27.0	37.6
SPEEK-55	1.700	33.6	69.2	107.3
SPEEK-55-5 min	1.609	25.7	52.1	79.3
SPEEK-55-10 min	1.497	22.1	46.8	70.9
SPEEK-55-15 min	1.313	18.9	40.0	62.1
SPEEK-55-20 min	1.292	14.2	34.2	54.1

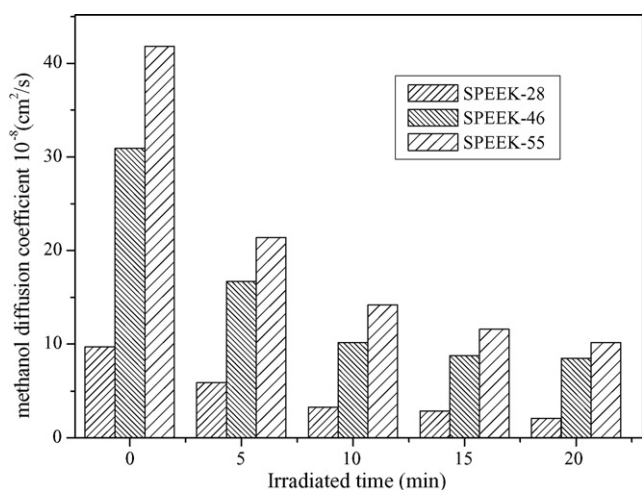


Fig. 4. The methanol diffusion coefficients of crosslinked SPEEK membranes at different photoirradiation time.

suppressed membrane water absorption and inhibited chain mobility and methanol passage, and hence resulted in the reduction of methanol diffusion coefficient.

For comparison, the methanol diffusion coefficient of Nafion117[®] was also measured in our laboratory under the same experimental conditions. The notable feature was that the methanol diffusion coefficients of all the crosslinked membranes were dramatically lower than that of Nafion 117[®] ($2.38 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$). This meant that methanol diffusion can be vitally reduced if these crosslinked SPEEK membranes are used in DMFC.

3.6. Hydrolytic stability, oxidative stability and mechanical property

The hydrolytic stability of the SPEEK membranes with and without crosslinking was investigated by treating the membrane

samples in 85 °C water for 2 weeks. It was found from Table 3 that the proton conductivity values of the non-crosslinked membranes slightly diminished after 2 weeks. This indicated that the sulfonic acid groups in the membranes were partially decomposed during 85 °C water test. However, it should be mentioned that the proton conductivities of the crosslinked membranes developed in this work nearly had no change after 2 weeks, which revealed that the crosslinked membranes possessed much better hydrolytic stability than the non-crosslinked ones. It is because that due to the formation of crosslinked network structure, the sulfonic acid groups were maintained and did not decompose in the crosslinked membranes.

Besides the excellent thermal and hydrolytic stability, the membranes applied in fuel cells should also possess good oxidative stability. To evaluate whether the crosslinked membrane can withstand a stronger oxidizing environment during the fuel cell operation, the oxidative stability of the crosslinked and non-crosslinked membranes was compared by the expended time that the samples started to break into pieces in Fenton's reagent at 80 °C. It was found that the crosslinked membranes with longer photoirradiation time (higher crosslinking extent) had better oxidative stability. For instance, the SPEEK-46 membranes started to break into pieces after 320 min, whereas the durability time was 11 h for the SPEEK-46-5 min membrane. In particular, the SPEEK-46-10 min, SPEEK-46-15 min and SPEEK-46-20 min kept intact after 24 h. Obviously, the chemical crosslinking modification plays an important role in mending the oxidative stability. The elevated oxidative stability may base on the fact that the crosslinking can reduce the water uptake to a greater extent, which leads to better mechanical properties of the membranes and lower degradation of the polymer chain. Hence the oxidative stability of the membranes enhances, which may considerably prolong their lifetime in fuel cells.

Based on the above discussion, we could conclude that crosslinking is very effective in improving the hydrolytic and oxidative stability of the membranes.

Table 3
The proton conductivities and mechanical properties of crosslinked SPEEK membranes

	Proton conductivity (S cm^{-1})			Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)
	25 °C	85 °C ^a	85 °C ^b			
SPEEK-28	0.0084	0.028	0.0261	809.69	43.96	10.13
SPEEK-28-5 min	0.0081	0.025	0.0246	1190.50	52.75	7.32
SPEEK-28-10 min	0.0070	0.024	0.024	1333.65	59.52	6.21
SPEEK-28-15 min	0.0056	0.018	0.0178	1351.81	63.01	6.37
SPEEK-28-20 min	0.0041	0.012	0.012	1405.32	63.25	4.03
SPEEK-46	0.012	0.046	0.0421	876.78	47.93	8.28
SPEEK-46-5 min	0.0106	0.043	0.042	1295.26	60.25	6.51
SPEEK-46-10 min	0.00908	0.039	0.0385	1321.32	65.89	6.37
SPEEK-46-15 min	0.0088	0.033	0.033	1451.49	69.93	5.74
SPEEK-46-20 min	0.0074	0.028	0.028	1454.50	73.57	4.22
SPEEK-55	0.025	0.072	0.0659	766.75	46.20	7.31
SPEEK-55-5 min	0.0235	0.067	0.0643	1202.34	53.55	6.45
SPEEK-55-10 min	0.0215	0.062	0.062	1385.35	58.87	5.56
SPEEK-55-15 min	0.017	0.053	0.053	1390.23	63.49	4.01
SPEEK-55-20 min	0.013	0.046	0.0458	1479.57	62.32	4.26

^a 85 °C = proton conductivity before 85 °C water test.

^b 85 °C = proton conductivity after 85 °C water test.

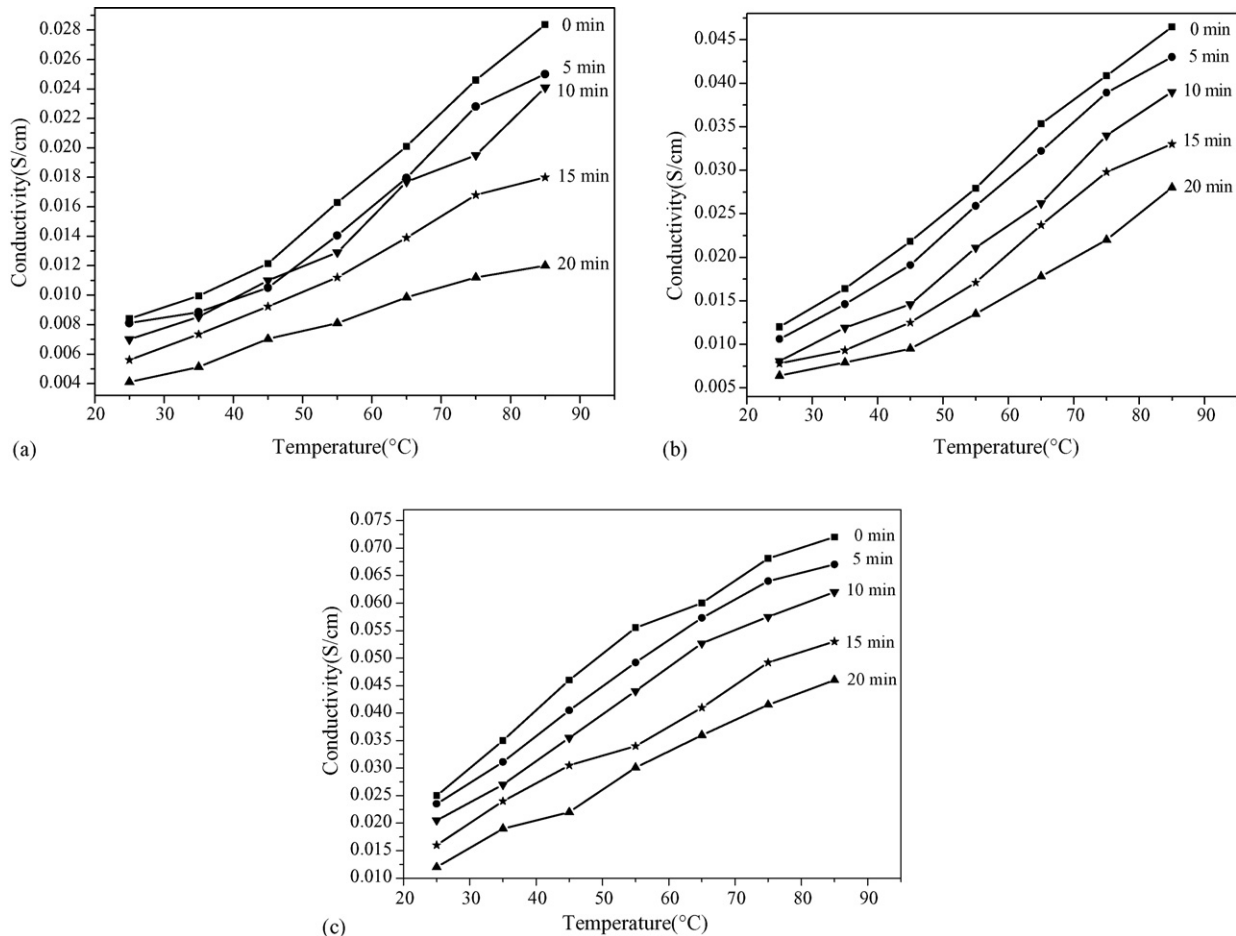


Fig. 5. The proton conductivities of crosslinked SPEEK membranes at different temperatures and photoirradiation time: (a) SPEEK-28, (b) SPEEK-46, and (c) SPEEK-55.

It is essential for PEM to possess adequate mechanical strength. The mechanical properties of the crosslinked and the non-crosslinked membranes were presented in Table 3. It can be seen that the tensile modulus and tensile strength of the crosslinked membranes enhanced with increase of photoirradiation time. They enhanced sharply before photo irradiating 5 min. After that, they enhanced slowly and even tended to level off. For example, from SPEEK-46 to SPEEK-46-5 min, the tensile modulus and the tensile strength fast enhanced from 876.78 and 47.93 MPa to 1295.26 and 60.25 MPa, respectively. However, they only enhanced to 1454.50 and 73.57 MPa until photo irradiated 20 min. The crosslinked membranes exhibited higher tensile modulus and tensile strength than the non-crosslinked membranes, which could be because that crosslinking can enhance the contact among molecules available and compactness of membranes, and thereby increase the mechanical strengths of the membranes. The elongation at break of the SPEEK-46 membrane decreased from 8.28 to 4.22 MPa with photoirradiation time increased from 0 to 20 min. This may be ascribed to that the enhancement of crosslinking extent reduced the chain flexibility, hence the membranes became fragile and the elongation at break fell off [28,29].

3.7. Proton conductivity

In order to explore the possibility of using the crosslinked SPEEK membranes in DMFC, the proton conductivities of crosslinked SPEEK membranes in liquid-water-equilibrated were measured at temperatures ranging from 25 to 85 °C and the results were showed in Table 3 and Fig. 5. It can be noticed that the proton conductivities of crosslinked SPEEK membranes had a decreasing trend with increasing photoirradiation time. This trend could be base on the fact that proton conductivity is a function of ion exchange capacity and water uptake, both of which are affected by the crosslinking extent. When photoirradiation time increases, the crosslinking extent improves, which induces structural reorientation and decrease chain mobility. Hence, the crosslinked membranes have denser network structure and lower cation-exchangeable sites than uncrosslinked one, which result in less and smaller hydrophilic channels for water absorption and water mobility and hinder the mobility of H^+ in the water phase, hence the proton conductivity is compromised. Besides, the crosslinked membranes have more rigid backbones than uncrosslinked one, which also resists water absorption and water percolation, and results in the decrease of the proton conductivity due to the reduction

of enough space to retain water around sulfonic acid groups [9,30,31].

Be contrary to the crosslinking, the rise of temperature improved proton conductivity levels. For example, the proton conductivity of SPEEK-46-5 min gradually increased from 0.0106 to 0.043 S cm⁻¹ with increasing temperature. It is due to the elevating of temperature increases mobility of water and polymer chain as well as enhances the mobility of H⁺. The proton conductivity of the membranes therefore goes up. So it can be concluded that the temperature is also very essential to achieve high conductivity levels.

The crosslinking extent here was controlled by adjusting the photoirradiation time. Therefore, it is possible to achieve a relative balance of the methanol diffusion and the proton conductivity by controlling the photoirradiation time. We found that the crosslinked SPEEK membranes with photoirradiation 10 min exhibited the optimum performance for DMFC applications. In the case of photoirradiation 10 min, for all the membranes, more than half of methanol diffusion coefficients were decreased, whereas only slight reduction in proton conductivities.

4. Conclusions

The crosslinked SPEEK proton exchange membranes were prepared by exposing the SPEEK membranes to UV light in the presence of benzophenone and triethylamine as photo-initiator system.

The studies showed that compared with the non-crosslinked membrane, the crosslinked membranes exhibited higher thermal stabilities, mechanical strength, hydrolytic and oxidative stabilities as well as lower water uptake and methanol diffusion coefficients with increasing photoirradiation time, which could enhance the durability of membranes in DMFC applications. However, the elongation at break and proton conductivities of the crosslinked membranes decreased with the increment of photoirradiation time, which were disadvantageous for PEM usage. To obtain excellent PEM with relatively good performance and durability, the photoirradiation time should be controlled and the unitary performance of membranes should be optimized. The experimental results revealed that the crosslinked SPEEK membranes with photoirradiation 10 min had the most appropriate performance for DMFC applications. That is, the crosslinked SPEEK membranes with photoirradiation 10 min markedly improved thermal stabilities and mechanical properties as well as hydrolytic and oxidative stabilities, greatly reduced water uptake and methanol diffusion coefficients with only slight reduction in elongation at break and proton conductivities, which made the crosslinked membranes very viable as PEMs for DMFC applications.

In conclusion, the experimental results indicated that crosslinking offered an effective route to improve the unitary performance of membranes and the crosslinked SPEEK membranes were particularly attractive as the proton exchange membranes for direct methanol fuel cell applications.

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