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Crosslinked sulfonated poly (bis-A)-sulfones as proton exchange membrane for PEM fuel cell application

Jianjia Yu · Chao Dong · Jianhong Liu ·
Cuihua Li · Jianhua Fang · Rong Guan

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Abstract The crosslinked sulfonated poly (bis-A)-sulfone (SPSF) proton exchange membranes were prepared by immersing the SPSF membrane into the presence of phosphorous pentoxide–methanesulfonic acid (PPMA) in the ratio of 1:10 by weight. The occurring of crosslinking reaction was proved and the membrane properties before and after crosslinking were evaluated. The results showed that the crosslinking treatment has reduced the water uptake, depressed the swelling, and enhanced the dimensional stability of SPSF membranes with just only slight sacrifice in proton conductivity. The ordered arrangement of molecular chain internal SPSF membrane was reduced and the efficiency of crosslinking reaction showed a random property along the depth direction of the membrane in the process of crosslinking.

Introduction

Perfluorosulfonate ionomers such as Nafion® are extensively evaluated for their applications in polymer electrolyte membrane fuel cells (PEMFC). Nafion® is currently the one of the best performing proton exchange membranes because of its excellent chemical and mechanical stability as well as its high proton conductivity at temperature less than 100 °C. However, high cost and low stability at high temperatures have limited their extensive applications [1–3]. For this reason, many efforts have been done to try to find the alternatives, such as synthesizing the new proton conductive materials derived from sulfonated aromatic structures [4, 5], nanostructure composites [6], or fluorine backbone [7–9], etc. The major challenge among these studies is how to balance the contradiction between high proton conductivity and low dimensional stability when the ion exchange capacities (IECs) are at high levels to reach the high proton conductivity.

Higher IEC values mean more sulfonic acid groups internal the polymer membranes, which may increase the proton conductivity. However, it may lead to undesirable large swelling and thus result in a dramatic loss of mechanical properties. Crosslinking is a simple and efficient method to retain indispensable properties such as swelling behavior, high proton conductivity, and dimensional stability [10–13]. It has been known that the water uptake is a very 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 [14, 15]. Water uptake can be controlled effectively by adjusting the crosslinking density of the prepared membrane. So far, there have been several studies on the crosslinking of polymer electrolyte membranes including ionic crosslinking of acid–base blend membranes [16, 17], covalent crosslinking [18, 19], and UV photo-crosslinking [20, 21].

Recently, Fang and his coworkers have reported a new crosslinking method that was based on the condensation reaction of the sulfonic acid groups and activated (electron-rich) aromatic hydrocarbons in phosphorous pentoxide–

J. Yu · C. Dong · R. Guan (✉)
College of Chemistry and Chemical Engineering,
Hubei University, 430062 Wuhan, China
e-mail: rongguan@hubu.edu.cn

J. Liu · C. Li
College of Chemistry and Chemical Engineering,
Shenzhen University, 518060 Shenzhen, China

J. Fang
School of Chemistry and Chemical Technology, Shanghai Jiao
Tong University, 200240 Shanghai, China

methanesulfonic acid (PPMA) [22]. This crosslinking method with PPMA as crosslinking regent is thought to be a new and facile approach showing greatly improved water stability while maintaining high proton conductivity [23]. But the details about the substance of crosslinking reaction and how the crosslinking reaction occurred were not known; the optimal crosslinking conditions that expected to use for proton conductive materials that derived from other sulfonated aromatic structures have also not been reported.

Therefore, in the present article, we prepared the crosslinked SPSF membranes via the condensation reaction between the sulfonic acid groups and the activated hydrogen atom of SPSF in the PPMA. The crosslinked membranes were expected to possess low water uptake but high stability and proton conductivity. Through the research of the effects of the crosslinking time on the IEC and the crosslinking density, the water uptake and the swelling ratio, the morphology and the proton conductivity, the substance of crosslinking reaction and the optimal crosslinking conditions were investigated.

Experimental

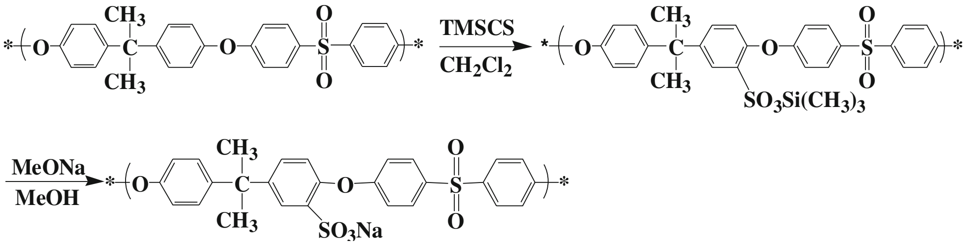
Sulfonation of PSF

The poly (bis-A)-sulfone (PSF) kindly supplied by Solvay (Udel® P3500NT), was dried at 110 °C under vacuum for 24 h before sulfonation. Trimethylsilyl chlorosulfonate (Aldrich) and Sodium methoxide (Aldrich) were used as received. The PSF polymer was dissolved in chloromethane at room temperature, and then treated with trimethylsilyl chlorosulfonate to produce a silyl sulfonate polysulfone intermediate product. The extent of sulfonation was controlled by varying the ratio of PSF and trimethylsilyl chlorosulfonate. Then a slight excess of sodium methoxide was added to the solution to cleave silyl sulfonate intermediate and the final sulfonated product was obtained. The sulfonated samples were vigorously washed with ethanol and rinsed several times with deionized water, until the pH value of the water bath reached 6–7. The completely rinsed samples were then dried in a 100 °C oven for 12 h. The detailed procedures for the sulfonation can be found in the patent [24]. The sulfonation process is shown in Scheme 1.

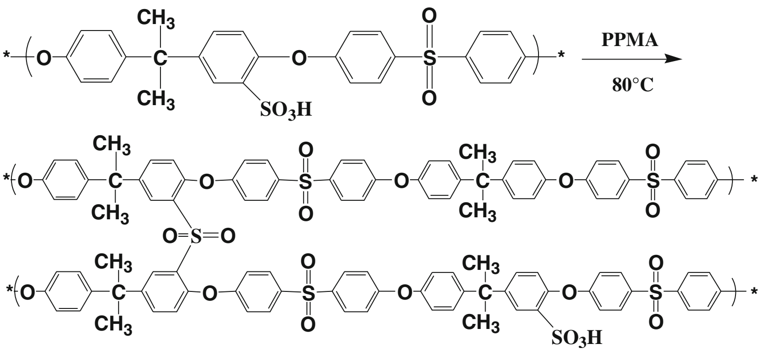
Membrane preparation and crosslinking treatment

The dried sulfonated polymer was first dissolved in DMAC to form a 6–10% solution, and then filtered. The filtrate was cast onto a glass plate and dried at 60 °C for 48 h in an air oven, and the residual solvent was completely removed under vacuum at 120 °C for another 48 h. The dry membranes were immersed into the medium of PPMA in the ratio of 1/10 by weight at 80 °C for different times to generate crosslinking [23]. The crosslinked SPSF membranes were washed by deionized water until the pH of washings reached 7, and then dried in vacuum for 24 h at 120 °C to remove the water remained in the membranes. The crosslinking process is shown in Scheme 2.

Scheme 1 Sulfonation of PSF



Scheme 2 Crosslinking of SPSF by PPMA



Membrane characterization

FTIR spectroscopy was used to certify the substitution of sulfonic acid with the hydrogen of aromatic rings and calculate the crosslinking density of the crosslinked membranes. The specimens were prepared as thin and homogenous membranes and then examined by a FTIR spectrometer (Perkin-Elmer Paragon 1000PC spectrometer) with a wave number resolution of 4 cm^{-1} in the range 400–4000 cm^{-1}.

Ion exchange capacity values of the SPSF membranes before and after crosslinking were measured by a titration method. The membrane in acid form was immersed in saturated NaCl solution for 24 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 using phenolphthalein as an indicator.

Both uncrosslinked and crosslinked SPS membranes were soaked in DMAC, DMSO, dichloromethane, and ethanol for 96 h at 50 °C to obtain their solubility data. If the crosslinked membranes show better solvent-resistance than the corresponding uncrosslinked membranes, the crosslink reaction could be testified initially.

The X-ray diffraction patterns of the SPSF membranes before and after crosslinking were obtained with a rotating anode Rigaku D/max-IIIc X-ray diffractometer using a Cu-Kα radiation source with a wavelength of 1.5418 À.

Water uptakes of the crosslinked and uncrosslinked SPSF membranes were determined by measuring the change of the weight before and after hydration. The water uptake measurement experiments were carried out by immersing the membrane samples into water at a given temperature for 5 h, taken out the membranes, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake of the membranes was calculated from the equation below:

$$\text{Water uptake \%} = \frac{W_{\mathrm{wet}} - W_{\mathrm{dry}}}{W_{\mathrm{dry}}} \times 100\% \qquad (1)$$

where W_{dry} and W_{wet} are the weight of the dry and the corresponding water-swollen membranes, respectively. Water uptake of the membrane was estimated from the average value of the membrane samples.

The swelling ratio was calculated as follows:

$$\text{Swelling ratio \%} = \frac{l_{\mathrm{wet}} - l_{\mathrm{dry}}}{l_{\mathrm{dry}}} \times 100\% \qquad (2)$$

where l_{dry} and l_{wet} are the length of the dry and the corresponding water-swollen membranes, respectively. Swelling ratio of the membrane was estimated from the average value of the membrane samples.

Proton conductivity in the longitudinal direction was measured by AC impedance spectroscopy over the frequency of 10–10^6 Hz with an oscillating voltage of 100 mV, using a system based on Solartron 1260 impedance/gain-phase analyzer. Membrane samples (1 cm × 4 cm) were sandwiched between four platinum plate electrodes set in a Teflon cell. All membrane samples were immersed in double-distilled water for 24 h before measurement and the cell was placed in double-distilled water at room temperature for measurement. The resistance value related to the membranes' proton conductivity was determined from the low intersect of the high frequency semi-circle on a complex impedance plane with the real axis. The proton conductivity was calculated by the formula:

$$\sigma = \frac{L}{RA} \qquad (3)$$

where σ is the proton conductivity (in S cm^{-1}), L is the distance between the electrodes used to measure the potential ($L = 1$ cm). R is the impedance of the membranes and A is the surface area required for a proton to penetrate the membranes (in cm^2).

Results and discussion

Certification of crosslinking reaction

There are three ways to prove the occurring of crosslinking and calculate the crosslinking density, and the first one is evaluating the changes of IEC values before and after crosslinking treatment, which implied the content of sulfonic acid groups. The crosslinking density is defined as the ratio of the decreased IEC values after crosslinking to the IEC values of uncrosslinked SPSF membranes, which described the consumption of sulfonic acid groups. The results are shown in Figs. 1 and 2, with the increasing of crosslinking time, the IEC values of crosslinked SPSF decreased and the crosslinking density is increased, which indicated that the crosslinking reaction was occurring during the process of PPMA crosslinking.

Moreover, the crosslinking evidence can be directly found from the FT-IR spectra. Figure 3 shows the FT-IR spectra of SPSF membrane before and after crosslinking treatment. No significant changes are observed between these two spectra except that the relative intensity of the absorption band at 1027 cm^{-1} which is assigned to the stretch vibration of the sulfonic acid group decreased after crosslinking. This is because some of the sulfonic acid groups were consumed during the crosslinking process. The consumption of sulfonic acid group due to the crosslinking reaction was also reflected in the reduction of IEC and the increasing of crosslinking density as before mentioned.

Solubility of SPSF membranes before and after crosslinking can also be used to prove the occurring of

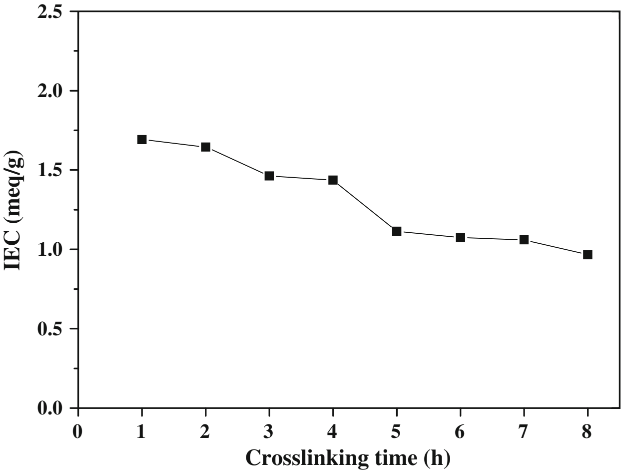


Fig. 1 The IEC of crosslinked SPSF membranes with different crosslinking time

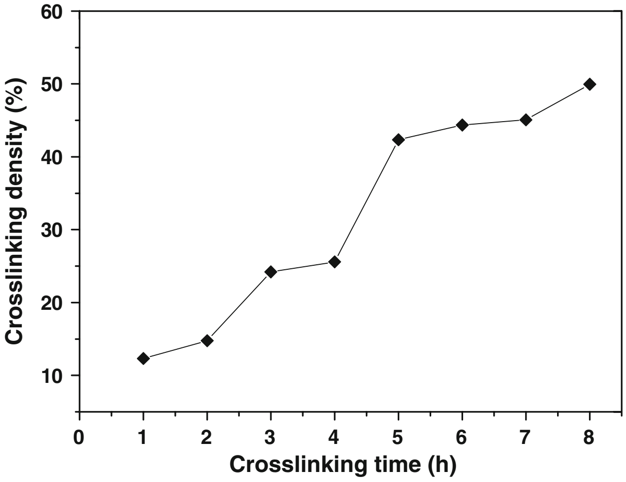


Fig. 2 The crosslinking density of crosslinked SPSF membranes with different crosslinking time

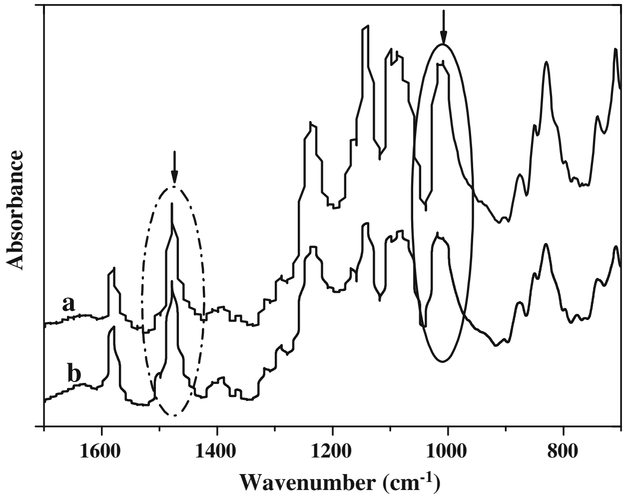


Fig. 3 FTIR spectra of SPSF membranes with IEC = 1.85: (*a*) uncrosslinked, (*b*) crosslinked

Table 1 Solubility of SPSF membranes before and after crosslinking

Sample	Solubility			
	DMSO	DMAC	Dichloromethane	Ethanol
SPSF-1.85-0 h	++	++	−	−
SPSF-1.85-1 h	++	++	−	−
SPSF-1.85-2 h	+−	+−	−	−
SPSF-1.85-3 h	+−	+−	−	−
SPSF-1.85-4 h	−	−	−	−
SPSF-1.85-5 h	−	−	−	−
SPSF-1.85-6 h	−	−	−	−
SPSF-1.85-7 h	−	−	−	−
SPSF-1.85-8 h	−	−	−	−
SPSF-1.85-9 h	−	−	−	−

++ soluble, +− partially soluble, − insoluble on heating

crosslinking. As Table 1 showed, the SPSF membranes with the IEC values of 1.85 meq/g easily dissolve in the solutions of DMSO and DMAC. The crosslinked membranes with 2-h crosslinking treatment can exist in the solutions only with a little amount of swelling at room temperature, which become extremely swelling as the temperature rose to 80 °C, but still maintained the membranes' shapes. While the crosslinking treatment was beyond 3 h, the crosslinked membranes were stable in the solutions even in the conditions of heating. The results not only proved the occurring of crosslinking but also showed that crosslinking treatment greatly improved the ability of anti-swelling.

Water uptake and swelling ratio

The aim of crosslinking is to improve the dimensional stability, which closely associates with the water uptake; a higher water uptake can lead to the membrane's swelling even soluble and then lost its dimensional stability. Figure 4 shows the effects of crosslinking time on the water uptake of crosslinked SPSF membranes with the IEC values of 1.85 meq/g in room temperature. It can be seen that the water uptake decreased from 183 to 60% after 1-h crosslinking treatment, and with the further increasing crosslinking time, the water uptake varied little. It can be explained that the crosslinking reaction consumed parts of sulfonic acid groups, which connected with the activated hydrogen atoms in the benzene ring to form a new sulfonate group, the content of sulfonate increased with increasing crosslinking time, limited the polymer chains' movement, lead to the decrease of space of water solubilization. Even though, crosslinked membrane not only greatly improved the water resistance, but also maintained a high level water uptake.

Figure 5 shows the water uptake variation of crosslinked SPSF membrane of a higher IEC value with different

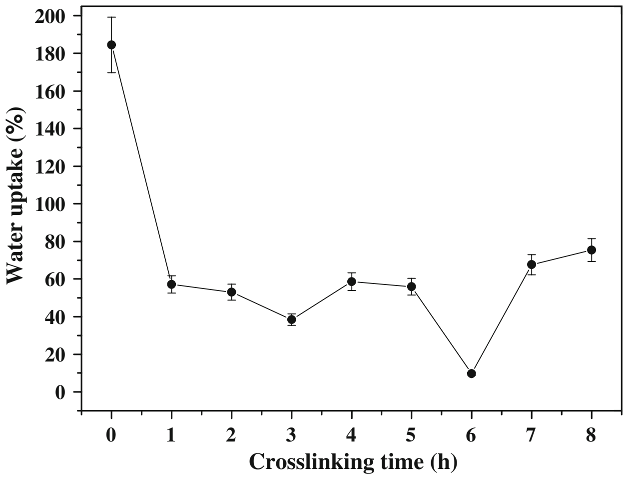


Fig. 4 Water uptakes of crosslinked SPSF (IEC = 1.85) membranes with different crosslinking time at room temperature

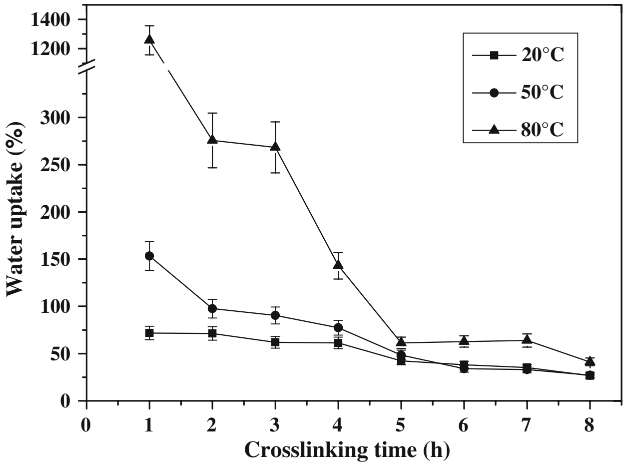


Fig. 5 Water uptakes of crosslinked SPSF (IEC = 2.10) membranes with different crosslinking time

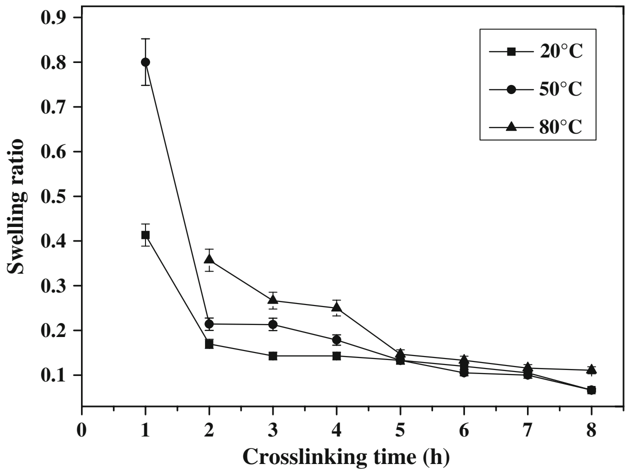


Fig. 6 Swelling ratios of crosslinked SPSF (IEC = 2.10) membranes with different crosslinking time

crosslinking times in different temperatures. The SPSF membrane before crosslinking was severely swelling in water and dissolved in water even at room temperature. Compared with non-crosslinking membranes, the crosslinked membranes' water uptake can be tested without dissolution. It can be seen that the tendency of curves in Fig. 5 is as same as that shown in Fig. 4. The SPSF membrane with 1-h crosslinking treatment did not dissolve in water even in 80 °C, and as the crosslinking time increased to 5 h, the water uptake can keep up to 67% at the condition of high temperature.

Figure 6 shows the relationship between swelling ratio and crosslinking time of the SPSF membrane with the IEC values of 2.10 meq/g. Although the membrane with 1-h crosslinking treatment can exist in the water at 80 °C, it swollen severely, the length, width, and thickness can not be measured, so the values of swelling in 1 h were not shown in Fig. 6. As shown in Fig. 6, the swelling ratio decreased with increasing crosslinking time. With crosslinking time increased from 1 to 2 h, the swelling ratio sharply decreased from 0.43 and 0.81 to 0.18 and 0.22 at 20 and 50 °C, respectively. When the temperature raised to 80 °C, the changes become especially evident, which from swelling dramatically to less than 0.40. The swelling ratio of crosslinked membrane decreased continually when crosslinking time increased from 2 to 5 h, and while crosslinking time was beyond 5 h, the membranes keep good shapes. So crosslinking treatment improved the water resistance and lead to the membranes keeps an excellent dimensional stability.

It can be found that the most significantly changes of water uptake and swelling ratio of crosslinked SPSF membranes were taken place when crosslinking time was 1 h. In order to explore the internal structure of crosslinked membrane and the reaction position of crosslinking, the dimensional changes at three different directions were also investigated. As shown in Fig. 7, changes in the length and width of crosslinked membranes decreased with increasing crosslinking time, but showed a random tendency in the depth direction, this result matches the conclusions in related reference [25]. It can be inferred that the crosslinking reaction may be taken place along the depth direction of membranes. Since the sulfonic acid groups distribute random internal the SPSF membrane, the efficiency of crosslinking reaction was also showed a random property along the depth direction in the process of crosslinking with PPMA as the crosslinking reagent.

XRD

To further confirm the internal structure change of crosslinked SPSF membranes, X-ray diffraction was used to

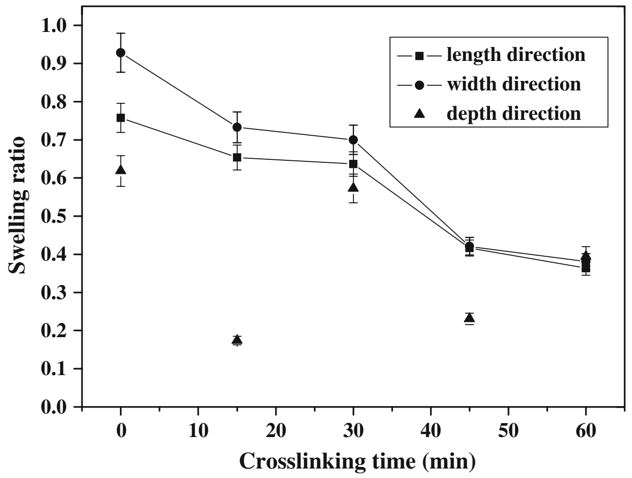


Fig. 7 Swelling ratios of crosslinked SPSF (IEC = 2.10) membranes with different crosslinking time in different directions

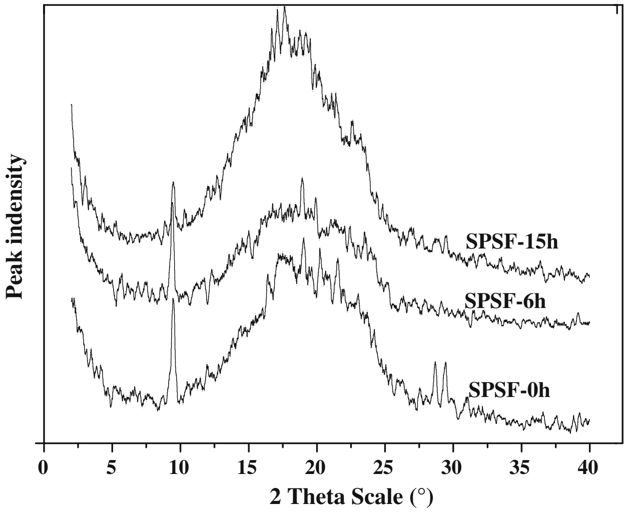


Fig. 8 XRD spectrum of SPSF (IEC = 1.78) membrane crosslinked at different time

evaluate the macromolecule state of aggregation, the results were shown in Fig. 8. Compared with the uncrosslinked SPSF membrane, the peak's position of crosslinked one was no shift, but the width values increased with increasing crosslinking time, which indicated the increase of the long-term disturbance between polymer chains. The results showed that crosslinking treatment has reduced the ordered arrangement of molecular chain inter SPSF membrane.

Morphology of crosslinked membrane

The photographs of crosslinked SPSF membranes are shown in Fig. 9. The morphology of membrane before crosslinking was uniform and transparent, however, it became milky white and opaque after crosslinking treatment, and the color is darker with increasing crosslinking time. It can be observed a slight fold on the surface of crosslinked membrane, which may be attributed to the crosslinking reaction that occurred along the surface to the internal membrane, and the crosslinking density in the surface is larger than that internal membrane with crosslinking time increasing. The results of phenomenon in the macro level are consistent with the swelling change in the three directions as discussed before.

Figure 10 shows the phase images of SPSF membrane before and after crosslinking with different time. As many literatures described about sulfonated aromatic hydrocarbon polymer membrane, there are microphase separation comprised of hydrophilic and hydrophobic regions. Polar sulfonic acid groups containing small amounts of water are aggregated to form ionic clusters. The domain size and continuous depends on the numbers of sulfonic acid groups, which may provide more or larger proton transport channels [26]. In Fig. 10, the bright spots depict softer hydrophilic regions and the dark spots correspond to rigid hydrophobic regions. The hydrophilic ionic clusters connected each other before crosslinking, and the content of connection deceased with increasing crosslinking time. After crosslinking time reached 15 h, the hydrophilic regions can hardly be seen. That is the water uptake, the proton conductivity of crosslinked SPSF membranes decreased with increasing crosslinking time.

Conductivity of crosslinked SPSF membrane

The mechanism of crosslinking is the dehydration condensation reaction between the sulfonic acid group and the activated hydrogen atom in the benzene ring of SPSF, which needs to consume some sulfonic acid groups and so leads to the decrease of proton conductivity. The proton conductivity of SPSF membrane before crosslinking was not given, because the membrane dissolved in the water at 25 °C and 100% relative humidity, but the crosslinked one can keep the membrane's shape in the water and the proton conductivity can be measured. As shown in Fig. 11, the proton conductivity decreased with increasing crosslinking time, which is a small decline compared with the water uptake and swelling ratio. Since the crosslinking time is not more than 5 h, the proton conductivity is higher than 0.09 S cm^{-1}, which is the reported value of Nafion® 112. That is the crosslinked SPSF membrane can be used for the PEM fuel cell materials.

Optimization of crosslinking conditions

In order to find an optimal condition to balance the relationship between dimensional stability and proton conductivity, the effect of crosslinking treatment on swelling

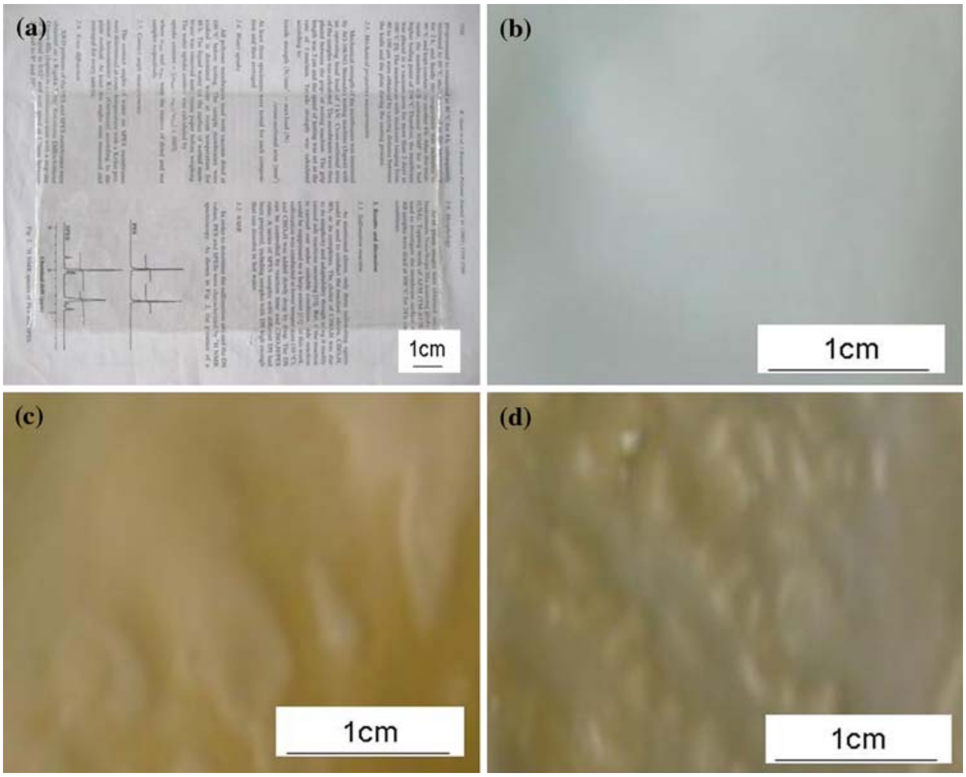


Fig. 9 Photographs of crosslinked SPSF (IEC = 2.10) membranes: **a** 0 h, **b** 2 h, **c** 6 h, **d** 15 h

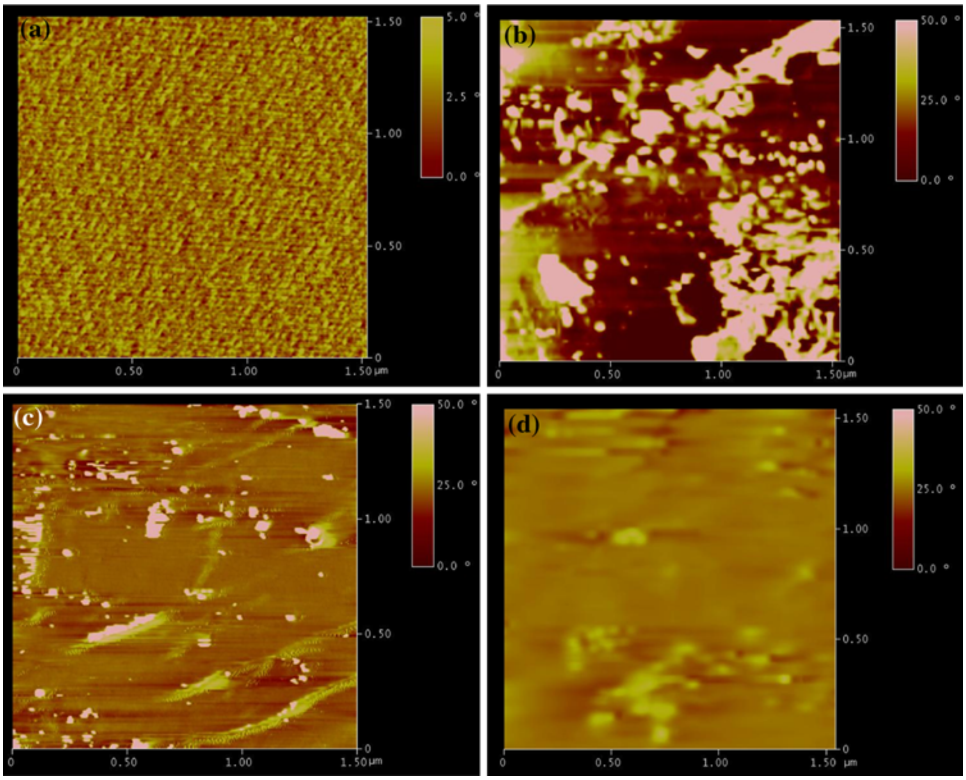


Fig. 10 AFM tapping phase images for crosslinked SPSF (IEC = 2.10) membranes at different crosslinking time: **a** 0 h, **b** 2 h, **c** 6 h, **d** 15 h

ratio and proton conductivity was studied, as shown in Fig. 12. It can be observed that both swelling ratio and proton conductivity decreased with increased crosslinking time, the proton conductivity decreased from 0.1087 to 0.08428 S cm^{-1} as the swelling ratio decreased from 0.14 to 0.10. The relative reduced range of proton conductivity

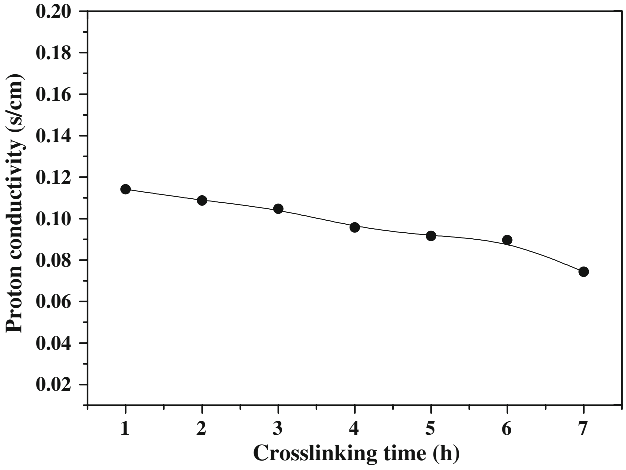


Fig. 11 Proton conductivity of crosslinked SPSF (IEC = 2.10) membranes with different crosslinking time

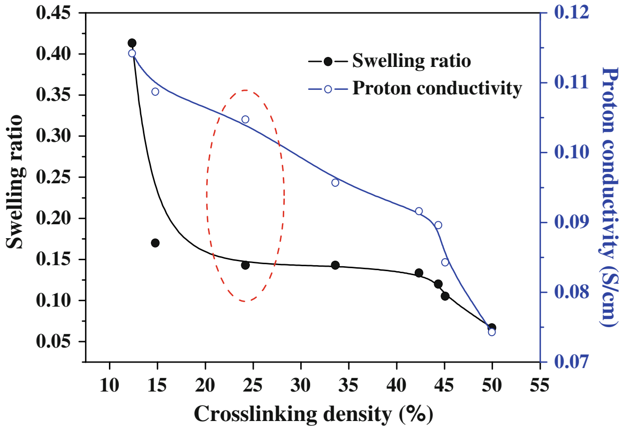


Fig. 12 Swelling ratios and proton conductivity of crosslinked SPSF (IEC = 2.10) membranes via the crosslinking density

is smaller than swelling ratio, and the dimensional stability can fit for the applications of PEM materials when the swelling ratio is lower than 0.14. Hence while considering the two factors that ensure cost savings and a high conductivity, the optimal crosslinking condition is identified as the crosslinking density of 24%.

Conclusion

The crosslinked SPSF proton exchange membranes were prepared by immersing the SPSF membranes into the PPMA. The investigation proved the occurring of crosslinking reaction, and the IEC, water uptake, swelling ratio, solubility, and proton conductivities were also investigated. The ordered arrangement of molecular chain internal SPSF membrane was reduced and the efficiency of crosslinking reaction showed a random property along the depth direction in the process of crosslinking with PPMA as crosslinking reagent. The crosslinking treatment depresses the swelling, reduces the water uptake and enhances the dimensional stability of SPSF membranes with just only slight sacrifice in proton conductivity. The proton conductivities of crosslinked SPSF membranes maintain in the same levels of Nafion® 112, it can be considered in the usage of PEM materials for PEM fuel cell applications.

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