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Crosslinked Tri-side-chain-type Sulfonated Poly(arylene ether ketone) with Enhanced Proton Conductivity by a Friedel-Craft Acylation Reaction

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Abstract

A series of cross-linked sulfonated poly (arylene ether ketone) containing tri-side-chain pendent sulfonic

groups (SQNPAEK) were prepared by the Friedel-Craft acylation reaction in order to solve the problem of

high methanol crossover and maintain high proton conductivity for direct methanol fuel cells. For this

10 purpose, sulfonated poly(arylene ether ketone) with pendent carboxylic acid groups was synthesized based

on phenolphthalein carboxylic monomers to be used as a macro-crosslinker. The cross-linked membranes

showed improved mechanical properties, chemical resistance and oxidative stability. The water uptake and

swelling ratio of cross-linked membranes decreased from 57.3% to 18.7%, and from 12.2% to 3.03%,

respectively. And the methanol permeability decreased from 0.94×10^{-7} cm^2 s^{-1} to 0.37×10^{-7} cm^2 s^{-1}.

15 Regarding the high proton conductivity, it showed enhanced performance than the pristine membrane, up

to 0.29 S cm^{-1}. Thus, the cross-linked membranes possessed the better performance implying its potential

for practical application in high-energy-density devices.

1. Introduction

Polymer electrolyte membrane fuel cells(PEMFCs) have attracted wide scientific interest because of their

20 high efficacy for direct conversion of chemical fuels to electricity for applications including low or zero-

emission electric vehicles, smart grids and portable electronics.[1,2] The proton exchange membrane (PEM)

is one of the key components of the PEMFC in terms of performance and production cost.[3-5] The long-term

performance and excellent high proton conductivity of Nafion produced by DuPont make it the most

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commonly used PEM.[6-7] However, some other notable drawbacks, such as high production cost, loss of proton conductivity at low humidity and fuel crossover still limit its widespread industrial applications. Hence, a number of non-fluorinated acid ionomers, especially the sulfonated aromatic hydrocarbon polymers, have been extensively studied as alternative PEMs.[8-39] These aromatic PEM materials include sulfonated derivatives of poly (arylene ether ketone)s,[19] poly (arylene ether sulfone)s[11] and polyimides.[13] Most of these sulfonated aromatic polymers are the main-chain-type ionomers, implying that the sulfonic acid groups are directly located on the main chains of these aromatic polymers. They have been proven to possess high thermal stability and low methanol permeability, and some of them exhibit desirable proton conductivities at a high degree of sulfonation (Ds). Unfortunately, these aromatic ionomers at a high Ds face the accompanying problem of poor dimensional stability, which potentially causes the delamination of catalyst layers on both sides of the electrode. Meanwhile, the methanol permeability remains at a high level that hinders their further applications in direct methanol fuel cells (DMFCs).

To enhance the dimensional stability in water while maintaining high proton conductivity, one approach is to control the morphology of the membranes by optimizing the chemical structure. Recent progress has proved that side-chain-type sulfonated aromatic polymers with pendent flexible sulfoalkyl groups showed improved dimensional stability and high conductivity.[22-25] In our previous work, we have prepared sulfonated poly(arylene ether ketone) with tri-side-chain pendent sulfonic groups (SQNPAEK), which displayed higher proton conductivity than the perfuorinated ionomer membranes.[40] Such high proton conductivity was based on unique long flexible side sulfonic acids groups that resulted into phase separation with interconnected ionic channels. Whereas, the problematic issues of the tri-side-chain-type SQNPAEK include relatively high methanol permeability and swelling ratio which might compromise it further applications.

On the other hand, cross-linking is an efficient method to enhance the mechanical properties, to suppress membrane swelling degree as well as significantly reduce the methanol permeability. There are numerous reports on the preparation of cross-linked sulfonated polymer membranes in the literature.[35-39] However, these cross-linked membranes suffer from decreasing of proton conductivity due to the loss of sulfonic acid

groups by the cross-linking reaction. Moreover, the extra addition of cross-linkers without ionic exchange

capacity also dilutes the concentration of sulfonic acid groups in the membrane, thus further decreasing the

proton conductivity. Recently, our groups synthesized a series of highly sulfonated poly (arylene ether

ketone)s bearing pendant carboxylic acid groups. In these copolymers, the carboxylic acid groups can

5 undergo Friedel-Craft acylation with the nucleophilic phenyl rings in the main chain to form cross-linked

bonds and the sulfonic acid group act as a benign solid catalyst. Since the sulfonic acid groups do not take

part in the cross-linking reaction and no extra cross-linkers are introduced into the system, the proton

conductivity of those cross-linked membrane is not compromised. Meanwhile, water uptake, swelling ratio

and methanol permeability of the cross-linked membranes decreased obviously.[40] In this paper, we applied

10 the Friedel-Craft acylation cross-linking technique to the SQNPAEK membrane with tri-side-chain pendent

sulfonic groups to solve the problem of high methanol crossover. Herein, we synthesized a macromolecular

cross-linker sulfonated poly(arylene ether ketone) (SPAEK-COOH-*x*) containing both carboxylic acid and

sulfonic acid group in the same unit. The carboxylic acid groups in SPAEK-COOH-*x* can undergo Friedel-

Craft acylation with the nucleophilic phenyl rings in the SQNPAEK main chain to form cross-linked bonds

15 at 160 $^{\circ}$C, while the sulfonic acid groups not only conducting protons, but also act as a catalyst for Friedel-

Craft reactions.[40-44] Additionally, the introduction of the sulfonated macromolecule offers more cross-

linking points which improve the dimensional stability. With adjustable Ds, the new macromolecular cross-

linker offers an alternative way to control the three-dimensional structure of the membrane. Results showed

that there were great improvements in both the dimensional and oxidant stability while the cross-linked

20 membranes still maintain higher proton conductivity.

2. Experimental section

2.1 Materials

1,5-Bis(4-fluorobenzoyl)-2,6-dimeth-oxynaphthalene (DMNF), (4-methoxy) phenyl hydroquinone (MHQ),

phenolphthalein (PPL), naphthalene-based poly(arylene ether ketone) (TMQNPAEK) and naphthalene-

25 based poly(arylene ether ketone) bearing tri-hydroxyl groups (QNPAEK-OH) were synthesized according

to our previous work.[41] 1,4-Butane-sultone and boron tribromide (BBr$_3$) was obtained from Beijing

Chemical Reagents. Bis(4-fluorophenyl)-methanone (DFBP) was purchased from Yanbian Longjing

Chemical Company. SDFBP which is the abbreviation of sodium 5,5`-carbonylbis(2-fluorobenzene-

sulfonate) was synthesized according to the procedure described.[45] Other reagents were commercially

available grade and used without further purified.

2.2 Synthesis of the macro-crosslinker SPAEK-COOH-*x* and SQNPAEK-*x*

2.2.1. Synthesis of SPAEK-COOH-*x*

A typical synthetic procedure to prepare SPAEK-COOH-*x* copolymers is shown in Scheme 1.[46] Taking

SPAEK-COOH-60 for example, PPL (16.01 g, 50 mmol), SDFBP (12.7 g, 30 mmol), DFBP (4.4 g, 20

mmol), and anhydrous potassium carbonate (10.4 g, 75 mmol) were placed in a three-neck round-bottomed

flask equipped with a mechanical stirrer, a Dean-Stark trap with a reflux condenser, and a nitrogen inlet

with thermometer. Dimethyl sulfoxide (DMSO) and toluene were subsequently introduced as solvents to

offer the solid concentration of 25 wt.%. The reaction mixture was then heated until the toluene began to

reflux and kept at this temperature for 3 h. Then gradually increased to 180 $^{\circ}$C after draining toluene, and

kept this for 6h. Then viscous reaction mixture was cooled to room temperature and poured into hydrogen

chloride (HCl) solution. The precipitated copolymer was then washed several times with ethanol, and dried

in a vacuum oven for 24 h. The "*x*" represents the molar fraction of SDFBP.

2.2.2. Synthesis of SQNPAEK-*x*

A typical synthetic procedure to prepare SQNPAEK-*x* copolymers is illustrated by preparation of

SQNPAEK-2 in Scheme 2.[41] QNPAEK-OH (1 g, 0.0053 mol hydroxyl groups), toluene (8 mL) and NaOH

(0.5 g, 0.0125 mol) were dissolved in DMSO (20 mL) under nitrogen atmosphere. The mixture was stirred

at room temperature for half an hour and then heated up to 140 $^{\circ}$C and kept at this temperature for 2 h.

Then 0.36 ml 1,4-butanesultone (0.00353 mol) was added into the reaction system and then slowly heated

to 150 $^{\circ}$C and kept for 12 h. The resulted sulfonated polymers were precipitated in 200 mL acetone. After

washed by deionized water, the obtained polymer was dried in a vacuum at 80 $^{\circ}$C. The "*x*" represents the

amounts of grafting 1,4-butanesultone in one unit.

2.3 Preparation of SQNPAEK/COOH-*x* cross-linked membrane

The cross-linked membranes were obtained by simply thermal curing reaction at 160 ^{o}C as shown in Scheme 3. SPAEK-COOH-60 of 0.0282 g, 0.0564 g, 0.113 g and 0.169 g was added to the solution of polymer SQNPAEK-1.8 (1 g) in DMSO (12 mL), respectively. Then, the mixtures were cast onto clean plate glass plates and heated at 60 ^{o}C for 24 h to get a thick, transparent, tough film. And then the membranes were cured at 160 ^{o}C for 10 h in a vacuum. Then, the samples were treated with 1 M H_2SO_4 for 24 h to obtain the acid form cross-linked membranes. The cross-linked membranes were described as SQNPAEK/COOH-*x*, where "*x*" represents the weight percent of macro-crosslinker. As a contrast, we have also prepared a blending membrane with 11.27 wt.% content of SPAEK-COOH-60 without a thermal curing procedure, which is marked with SQNPAEK+SPAEK-COOH-60(11.27 wt.%).

2.4. Characterization

^{1}H NMR spectrum was measured on a Bruker Avance 510 spectrometer using DMSO-d_6 as the solvent and tetramethylsilane (TMS) as the standard. Fourier transform infrared spectroscopy (FT-IR) spectra were obtained by a Bruker Vector 22 FT-IR spectrometer between 4000 cm^{-1} and 400 cm^{-1}.The degree of the sulfonation (Ds) is defined as the number of sulfonic groups in per unit. The calculation of the Ds is referenced as our previous work.[40]

2.4.1 Thermal and mechanical properties of membranes

The thermogravimetric analysis (TGA) measurements were carried out on a Perkin-Elmer TGA-1 thermogravimetric analyzer from 80 to 720 ^{o}C at a heating rate of 10 ^{o}C min^{-1}under N_2 atmosphere. The mechanical properties of membranes was measured by SHIMADZU AG-I 1KN at a speed of 2 mm min^{-1}. The size of the samples was 15 mm×4 mm.

2.4.2. Ion Exchange Capacity, Water Uptake and Swelling Ratio Measurements

The ion exchange capacity (IEC) of membranes was measured by titration, and calculated by the formula (1):

$$IEC = \frac{V_{NaOH} \times C_{NaOH}}{\text{Weight of the dried membrane}} \text{(mequiv.g}^{-1})$$

(1)

The water uptake was measured after dried the membranes which immersing in the water at individual temperature for 24 h quickly. Each sample has been measured four times and then calculated using the formula (2):

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

(2)

where W_{wet} and W_{dry} are the weights of the wet membrane and the dry membrane, respectively.

The dimensional change of membranes is measured both in the length (l) and thickness (d), and calculated with the following formula (3):

$$\text{Swelling ratio } (\triangle l, \%) = \frac{l_w - l_d}{l_d} \times 100$$

$$\text{Swelling ratio } (\triangle d, \%) = \frac{d_w - d_d}{d_d} \times 100$$

(3)

where l_w, d_w and l_d, d_d are the lengths and thickness of the wet membrane and dry membrane, respectively.

2.4.3. Proton conductivity and methanol permeability

The proton conductivity (σ, S cm^{-1}) of all the membranes was measured under fully hydrated condition. By a four-point probe AC impedance spectroscopy, the electrode system is connected with a Princeton Applied Research Model 2273 potentiostat/galvanostat/FRA. The resistance value (R) was measured over the frequency range from 10^{-1}Hz to 10^6Hz. The proton conductivity performed at desired temperature was calculated by the following formula (4):

$$\sigma = \frac{L}{RS}$$

(4)

where L (cm) is the distance between the electrodes, R (Ω) is the membrane resistance, and S (cm^2) is the cross-sectional area of membrane. Repeated measurements were then taken at that given temperature with 30 min interval until no more change in conductivity was observed.

The methanol permeability was determined with a diffusion cell described in the literatures.[43] The concentration of methanol was determined by using SHIMADZU GC-8A chromatograph. The methanol permeability is calculated by the following formula (5):

$$C_{B(t)} = \frac{A}{V_B} \frac{DK}{L} C_{A(t-t_0)}$$

(5)

where C_A and C_B (mol L^{-1}) are the methanol concentration in feed and in diffusion reservoir, respectively. A (cm^2), L (cm) V_B (mL) are the effective area, the thickness of the membrane and the volume of diffusion reservoir, respectively. DK is the methanol diffusion coefficient (cm^{2}s^{-1}). (t-t_o) is the testing time.

2.4.4. Oxidative stability of the cross-linked membrane

Small pieces of membrane samples were soaked in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 80 $^{\circ}$C. The oxidative stability was characterized by recording the time when the membranes began to break into pieces. The residual weight (RW) was calculated after immersion in Fenton's reagent for 4 hours.

3. Results and discussion

3.1. Synthesis and characterization of SPAEK-COOH-x

As shown in Scheme 1, a novel series of sulfonated poly(arylene ether ketone)s SPAEK-COOH-x containing carboxylic groups were synthesized by a nucleophilic aromatic substitution reaction. The Ds was controlled by adjusting the ratio of DFBP (monomer m) to SDFBP (monomer n). ^{1}H NMR spectroscopy in Figure 1 showed that the chemical shift 12.96 ppm is characteristic absorption peak of hydrogen carboxylic acid group and 8.2 ppm is attributed to hydrogen on the aromatic group next to sulfonic acids. This proved that the polymer was in good agreement with our expection.[46]

3.2. Preparation and characterization of the cross-linked membranes SQNAPEK/COOH-*x*

3.2.1. Option of the Ds of the macromolecular SPAEK-COOH-*x* and the original membrane SQNPAEK

We have synthesized three SPAEK-COOH-*x* copolymers with different degrees of sulfonation according to the molar ratios of monomers. And they were cast onto the glass to obtain membranes. Preliminary results are presented in Table 1. SPAEK-COOH-50 and SPAEK-COOH-60 possess higher IEC and suitable water uptake in hydration state. But for SPAEK-COOH-70, the water uptake is too high, resulting in poor dimensional stability. As for SPAEK-COOH-50, the proton conductivity is much lower than SPAEK-COOH-60. Overall, SPAEK-COOH-60 has relatively high proton conductivity, moderate water uptake and low methanol diffusion coefficient, which would be the best choice for the macro-crosslinker. On the other hand, we have synthesized SQNPAEK-*x* membranes with degree of sulfonation of 1.8. SQNPAEK-1.8 membranes possessed good dimensional stabilities and relatively higher fuel diffusion efficiency which was suitable for pristine membrane.[41] In this paper, it is short for SQNPAEK membrane**.**

3.2.2. The amount of the macro-crosslinker SPAEK-COOH-x in each cross-linked membrane

Based on the chemical structure of SQNPAEK, there were nine positions in the SQNPAEK polymer bone where the Friedel-Craft acylation reaction could happen to achieve cross-linked membranes with different cross-linking degrees, the weight percentage of macro-crosslinker SQNPAEK-COOH-60 in the cross-linked SQNPAEK membrane was set to 2.82%, 5.64%, 11.27% and 16.91%, respectively. Certain content of SQNPAEK-COOH-60 and SQNPAEK were dissolved and stirred to make a homogenous mixed solution and casted on clean glass plates. Then the cross-linked membranes were obtained by thermal curing reaction at 160 $^{\circ}$C for 6 hours (Scheme 3).[42]

3.2. 3 Solubility and FTIR of the membranes (Insoluble Fraction)

To confirm the formation of cross-linked structure in the SQNPAEK/COOH-*x* membrane, we cut one piece of the samples and then put them into organic solvents, such as NMP, DMSO and DMF. All of them

were not dissolve in any of the solvents, except turning out great swollen after being in an oven for 24 hours at 80 $^{\circ}$C, suggesting the cross-linked membranes were successfully prepared.

And also, we have tested the insoluble fraction of crosslinked membranes. Table 2 showed weight percent of each membrane after 24 hours immersed in the DMSO. Intuitively, all the crosslinked did not dissolve in the solvent. The insoluble fraction was calculated by the ratio of the weight of the cross-linked membranes after extraction from DMSO to the initial weight. All the cross-linked membranes displayed a high insoluble fraction, and it increased with higher amounts of crosslinker which indicated the crosslinking density is increased with the macro-crosslinker.

Figure 2 shows the FTIR spectra of SQNPAEK, the blended SQNPAEK/SPAEK-COOH-60 (11.27 wt.%) and cross-linked SQNPAEK/COOH-11.27. As we can see, most of the FTIR absorption did not show apparent change during the crosslinking process. 1226 cm^{-1} and 1033 cm^{-1} were assigned to the asymmetric and symmetric stretching vibration of sulfonic acid groups. The new absorption peak around 1403 cm^{-1} corresponding to the absorption band of carboxylic groups appeared in the cross-linked SQNPAEK/COOH-11.27 membrane. Moreover, the intensity of peak 1733 cm^{-1} which attributed to carbonyl group of crosslinked membrane has slightly increased after thermal treatment. These results implied the cross-linked reaction occurred between carboxylic group and hydrogen in the benzyl groups and the crosslinked membrane had been successfully prepared.

3.3. Thermal Properties, Mechanical Properties and Oxidative Stability of SQNPAEK/COOH-*x*

The thermal stability of the PEM is a key quality of the durability operating in fuel cell.[17] The thermal stability of the SQNPAEK/COOH-*x* series membranes was tested by TGA at a heating rate of 10 $^{\circ}$C min^{-1}under nitrogen atmosphere. As shown in Figure 3, the pristine tri-side-chain SQNPAEK showed three weight loss steps. The first weight loss around 100 $^{\circ}$C was due to the water loss in the membranes. The second step observed in the range of 230 $^{\circ}$C was due to the decomposition of pendent flexible sulfoalkyl groups. The last step around 480 $^{\circ}$C was attributed to the decomposition of the polymer chain. After cross-linking treatment, the desulfonation temperatures of SQNPAEK/COOH-*x* exceeded 250 $^{\circ}$C which was higher than that of SQNPAEK. For example, the desulfonation temperature of SQNPAEK/COOH-11.27

was higher than 350 ^{o}C, which shows very high thermal stability. Moreover, it should be noticed that all of the cross-linked membrane residual were higher that 45% at 720 ^{o}C. On the contrary, the residual of pristine SQNPAEK was 40%. This result indicated that the cross-linking of the membranes improved the thermal stability of the polymer main chain. The reaction between carboxylic group and hydrogen in the benzyl group formed a C-C single covalent bond. Therefore, the thermal curing cross-linked membrane showed better thermal stability than the original membrane. Excellent mechanical property would be benefit for the membrane electrode assembly (MEA) fabrication.[1,2] An investigation into the mechanical properties of the SQNPAEK/COOH-x membranes was performed. Table 2 shows the mechanical properties of all the membrane. No overall correlations could be seen for this series of cross-linked membranes other than mechanical properties ranged from 60.7 to 66.3 MP tensile stress and 9.2-11.6% elongation at break due to the introduction of cross-linked structure and naphthalene moiety in the main-chain. However, all of the crosslinked membranes showed higher tensile strength, Young's modulus, and the elongation at a break than those of pristine membrane. The result indicated that the introduction of macro-crosslinker and Friedel-Craft acylation cross-linking improved mechanical properties of the SQNPAEK. It also indicated that all the membranes met the requirement sufficiently for fuel cell applications.[48]

Excellent chemical stability is another necessary requirement for ideal PEMs because the chemical property affects the overall fuel cell performance.[4] We have mimicked the environment in the fuel cell by immersing the membrane in the 3% H_2O_2 and 2 ppm $FeSO_4$ solution at 80 ^{o}C. Then we recorded the time before the every sample membrane breaking down due to polymer chain degradation. The results are shown in Table 2. As we can see, the breaking time increased first and then decreased with the amount of macro-crosslinker. The original membrane possessed the shortest time before breaking which was only 32 minutes. For the cross-linked membrane, the breaking times were ranged from 96 to 240 minutes. Overall, SQNPAEK/COOH-5.64 showed the longest time before breaking down (240 minutes). However, the breaking time began to decrease from 240 to 96 minutes as increasing the amounts of macro-crosslinker from 5.64% to 16.91%. Due to the introduction of SPAEK-COOH-x, there are more phenolphthalein

groups in the membrane, which are vulnerable to attack of the radical group. Nevertheless, the breaking time of SQNPAEK/COOH-16.91 was still much higher than the pristine membrane. The residual weight (RW) after immersing in Fenton's reagent for 4 hours is also shown in Table 2. The RW decreased rapidly as the amounts of macro-crosslinker increased. The possible reason would be as the macro-crosslinker increased, the amounts of the benzyl benzoic acid group and the sulfonic acid group both increased which gave more chances for the free radical attacking the polymer bone more easily. The oxidative stability test showed that the oxidative stability of the membrane was indeed enhanced a lot by cross-linking, which was favorable for PEM.

3.4. IEC, Water Uptake and Swelling Ratio

Table 3 shows ion exchange capacity (IEC), water uptake and swelling ratio of cross-linked membranes. IEC is the one of the most important factors in the performance of the PEMs. Theoretically, IEC usually decreases with the macro-crosslinker fraction in the membrane.[5] In our case, the Ds of the macro-crosslinker was 1.8, which was relatively high. After crosslinking, the cross-linked membranes showed a slightly increment in IEC. For example, IEC of SQNPAKE/COOH-11.27 was 1.54 mmol g^{-1}, which was higher than SQNPAEK. It could be attributed to the high IEC macro-crosslinker bearing multi-acid groups which did not dilute the concentration of the sulfonic acid groups in the pristine membrane.

The water uptake and swelling ratio of the membranes are also very important properties for fuel cell operation due to their critical effects on the proton conductivity and the methanol permeability of the membranes.[5] Excess water absorption would lead to dimensional instability; but, a lack of water absorption results in lower proton conductivity. Furthermore, excessive water in the membrane promotes water flooding problem during fuel cell operation.[47] Figure 4 and Figure 5 show water uptake and swelling ratio of the cross-linked membranes as a function of temperature, respectively. Compared with high water uptake of the pristine SQNPAEK membrane (57.3% at 80 °C), all the cross-linked membranes showed a decrease in the water uptake, ranging from 18.7% to 36% at 80 °C. However, water uptakes did not reduce significantly as the hydrophilic sulfonic acid groups in the main polymer bone were strongly associated

with water molecules. Therefore, the additional macro-crosslinker also promoted the water uptake in a moderate range, and the water uptake increased with increasing of the addition of macro-crosslinker.

Regarding to the swelling ratio, all the cross-linked membranes have incredible dimensional stability. All the membranes have lower swelling ratio than Nafion 117 under each temperature. Taking SQNPAEK/COOH-16.91 for example, it had the largest dimensional change among these cross-linked membranes with only 7.3% in thickness and 11.6% in length change at 80 $^{\circ}$C, which were still lower to the values of Nafion 117 (13.8% in thickness and 17.2% in length change). There was no obviously relation between swelling ratio and the fraction of macro-crosslinker. As the amounts of macro-crosslinker increased, SQNPAEK/COOH-16.91 showed a little bit increase in the change of length and thickness. But compared to the original membrane and other sulfonated polymer, they were still in less than 10%. It can be concluded that cross-linking was a useful method for constraining dimensional change, since the network resulted in a compact structure, especially for the macro-crosslinker.

3.5 Proton Conductivity and Methanol permeability

The proton conductivity and methanol permeability of the cross-linked membranes was measured while the membranes were fully hydrated (Figure 6, Table 3). For comparison, the proton conductivity and methanol permeability of Nafion 117 were measured under the same experimental conditions. Nafion 117 has excellent proton conductivity, but it has been found that more than 40% of methanol can be lost in a DMFC across the membrane due to excessive swelling.[33] As we can see, the proton conductivity of the cross-linked membrane was maintained at a very high level, ranging from 0.20 S cm^{1} to 0.29 S cm^{-1}, while the original SQNPAEK was 0.21 S cm^{-1} at 80 $^{\circ}$C. The acid groups in the macro-crosslinker and the long chain side sulfonic acid groups of the pristine SQNPAEK membrane could form ionic channel which facilitated the proton conduction.

For the cross-linked membranes reported in the literature, the more cross-linkable moiety was introduced, the lower the proton conductivity was resulted.[38] However, it is interesting to find that the proton conductivity of the cross-linked membranes in this work was not reduced, but slightly increased compared to the pristine membrane at 80 $^{\circ}$C. It can be observed from Figure 6 that the proton conductivity of all the

cross-linked SQNPAEK/COOH-*x* membranes was comparable or even higher than that of pristine SQNPAEK and Nafion 117 at 80 ^{o}C. For example, SQNPAEK/COOH-11.27 showed the proton conductivity of 0.29 S cm^{-1}. At the same condition, Nafion 117 only had the proton conductivity of 0.15 S cm^{-1}. The higher conductivity was attributed to the introduction of highly conductive SPAEK-COOH-60.

5 Since the sulfonic acid groups were not involved in the Friedel-Craft acylation reaction, the cross-linked membranes maintained the sufficient ionic groups and still exhibited high proton conductivity even after heat treatment. Furthermore, among these cross-linked membranes, SQNPAEK/COOH-11.27 with the highest IEC value of 1.54 mmol g^{-1}has the best proton conductivity performance, and got higher conductivity at higher temperature than SQNPAEK/COOH-16.91. These results were consistent with the

10 IEC, water uptakes and swelling ratios (Figure 4, Figure 5). The reason for this abnormal trend would be explained in this way: As the amounts increased from 0 to 5.64%, the introduction of the macro-crosslinker diluted the ionic concentration in the membrane which decreased the conductivity, even with sulfonic group in the macro-crosslinker; ranging from 5.64% to11.27%, as the introduction of the macro-crosslinker compensated of the loss of the sulfonic acid groups, the proton conductivity increased even higher than

15 that of the pristine membrane; as the content of the macro-crosslinker increased from 11.27% to 16.91%, , the membranes became more compact, and the movability of the protons were reduced, turned out the decrement of proton conductivity, but still higher than pristine membrane.

Methanol permeability is one of the critical factors for DMFC applications because methanol crossover reduces the fuel cell performance.[38] The methanol permeability of the original, cross-linked and Nafion

20 117 membranes at a set of temperature listed in Table 3. The cross-linked membranes all showed much lower methanol permeability (0.75-0.94 cm^2 s^{-1}×10^{-7}) than the pristine membrane. It is obvious that the methanol permeability can be drastically decreased by introducing cross-linking structure. Compared with Nafion 117, these cross-linked membranes exhibited much lower methanol permeability and higher proton conductivity at 80°C, suggesting that they have a potential application in DMFCs.

25 **4. Conclusions**

New cross-linked membranes (SQNPAEK/COOH-*x*) were successfully obtained by introducing macro-

crosslinker of SPAEK-COOH-60 containing sulfonic acid group as the hydrophilic part and carboxylic group as a cross-linkable moiety for Friedel-Craft acylation reaction. The cross-linked membranes were prepared by simply thermal curing in which the polymer network structures were cross-linked with covalent bonds. Cross-linking method greatly reduced the water uptake and the swelling ratio of the membranes, while high proton conductivity (0.043-0.29 S cm^{-1}) and low methanol permeability (2.6×10^{-8}-9.51×10^{-8} cm^2 s^{-1}) were maintained. In this study, we have proved that introducing the macro-crosslinker was an effective method for changing the transport properties. These results indicated that the SQNPAEK/COOH-x cross-linked membranes are promising candidates for optimizing the polymer structure of PEMs for fuel cell applications.

Acknowledgment

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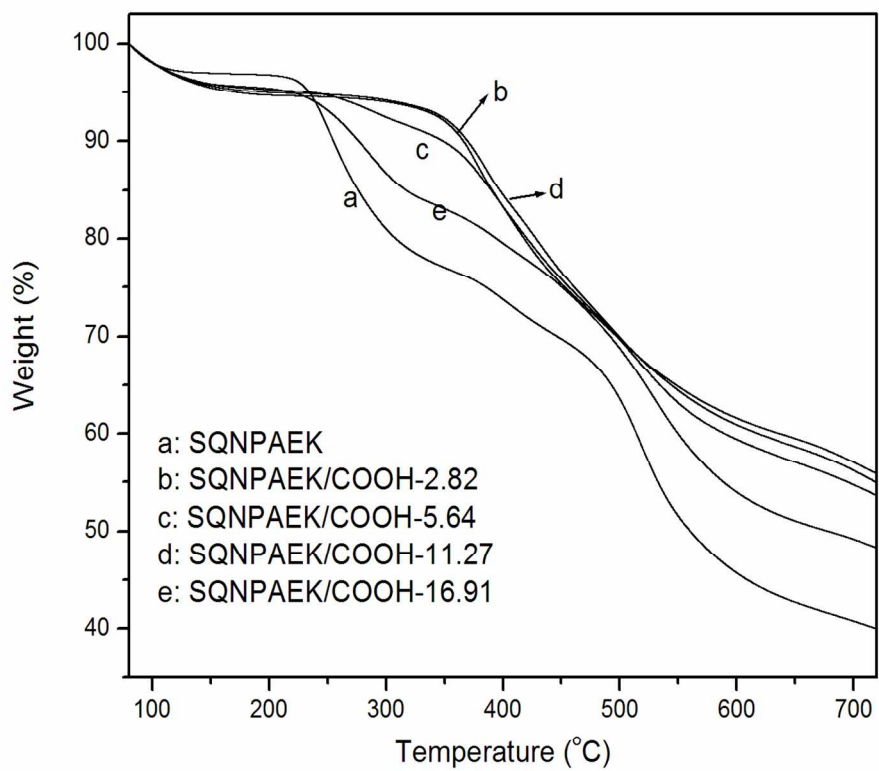
Caption

Figure 1 ^{1}H NMR of different Ds of SPAEK-COOH-*x*: (a) SPAEK- COOH-50, (b) SPAEK-COOH-60, (c) SPAEK-COOH-70.
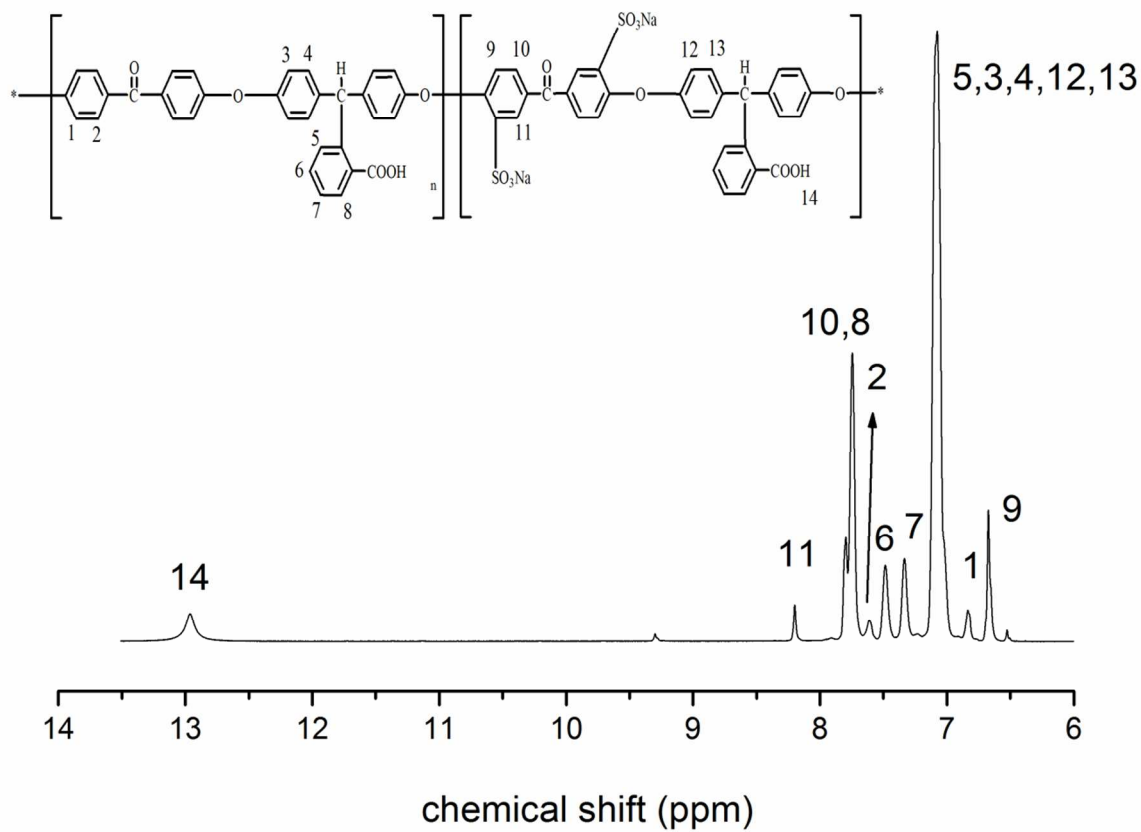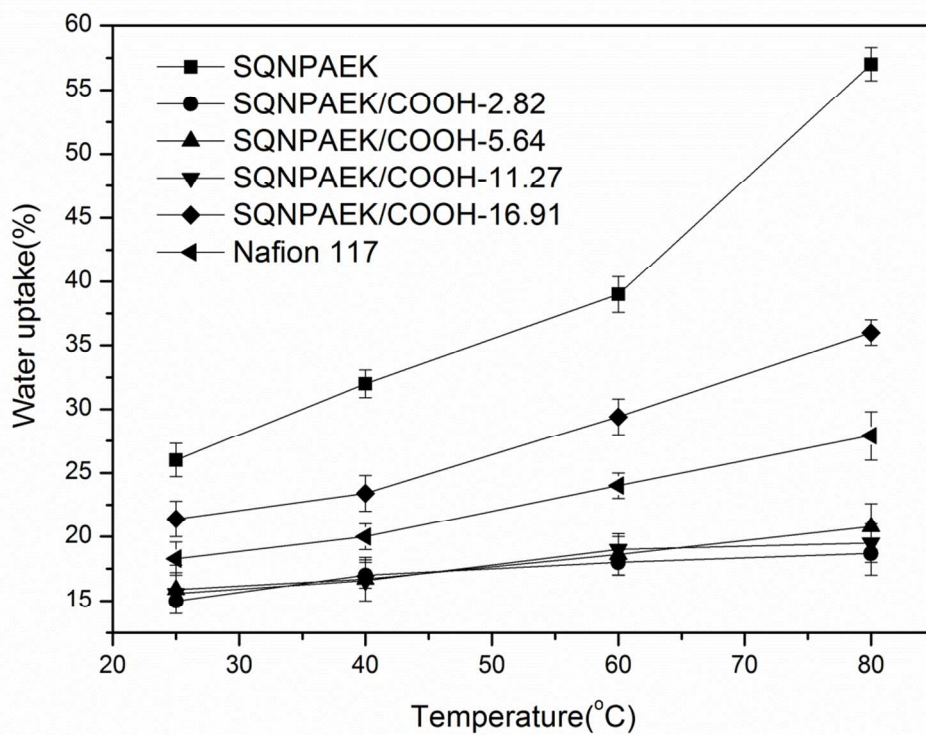
Figure 2 FTIR spectra for SQNPAEK, SQNPAEK+SPAEK-COOH-60(11.27wt.%),
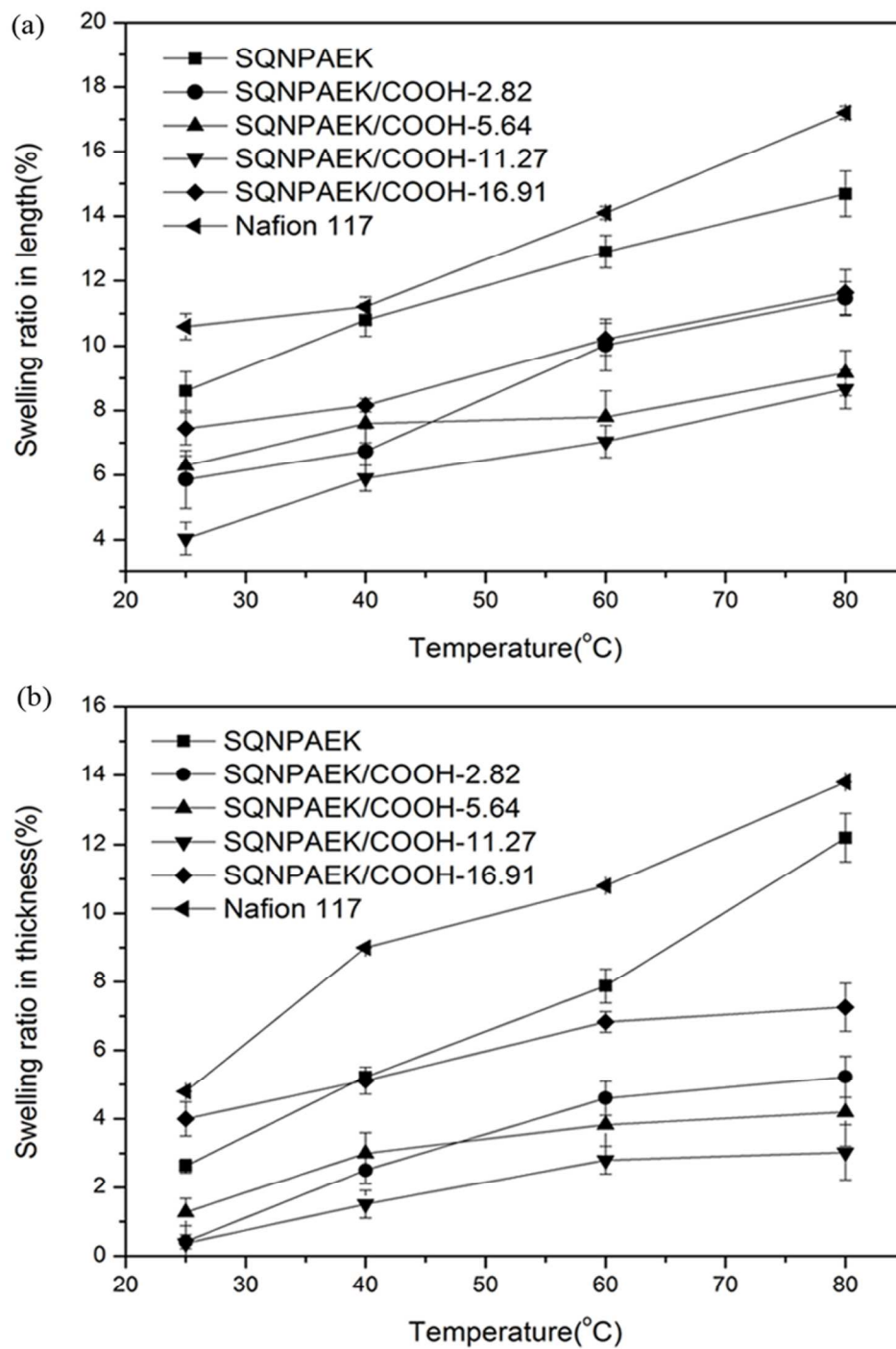
SQNPAEK/COOH-11.27.
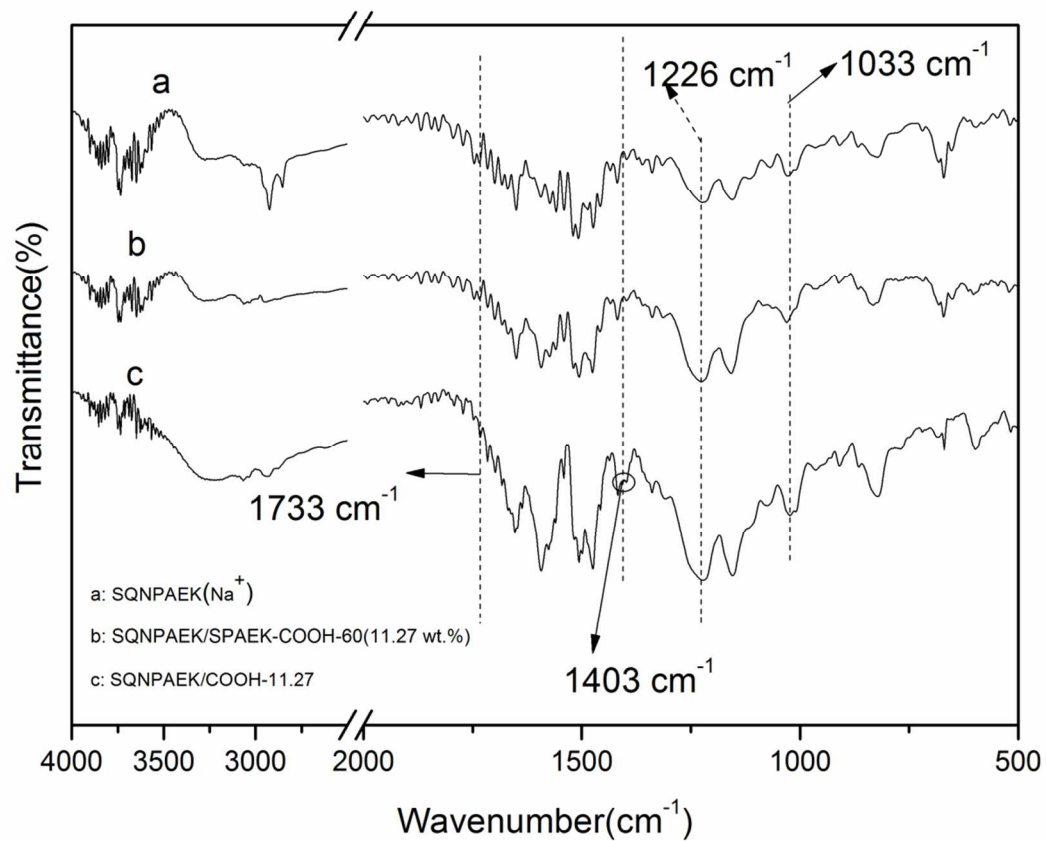
**Figure 3** TGA curves for crosslinked membranes SQNPAEK/COOH-*x* under N_2 at 10 ^{o}C min^{-1}.

Figure 4 Water uptake of SQNPAEK-*x* membrane under fully hydrated at a range of temperature.
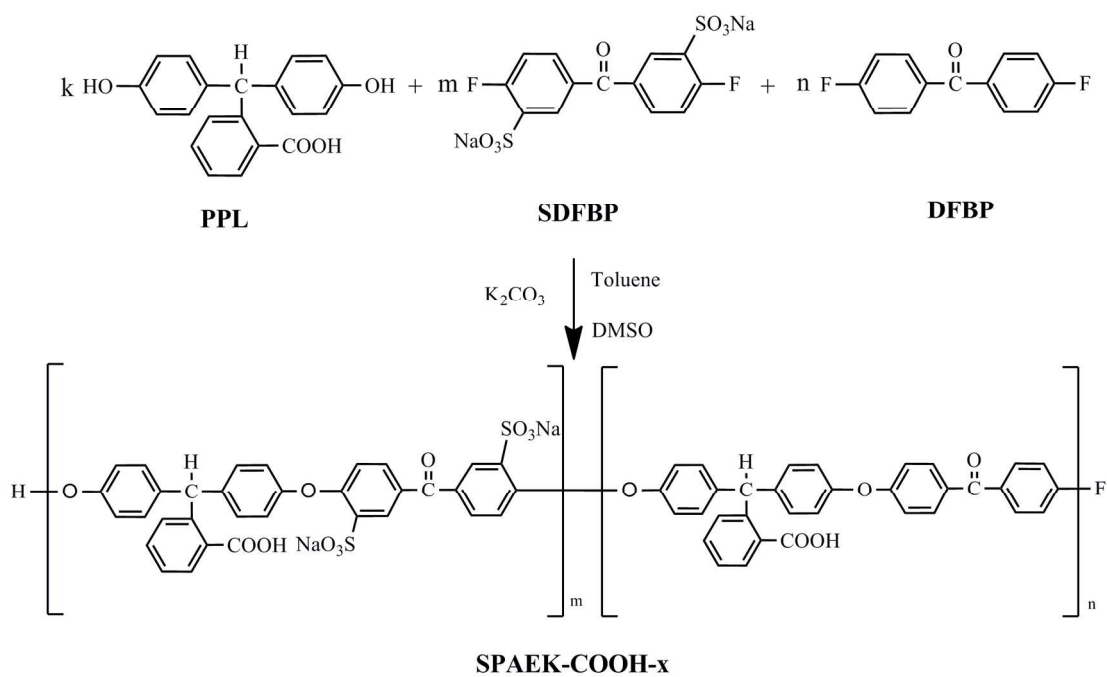
Figure 5 Dimension stability of SQNPAEK/COOH-x and Nafion 117 membranes (a) swelling ratio in length; (b) swelling ratio in thickness.
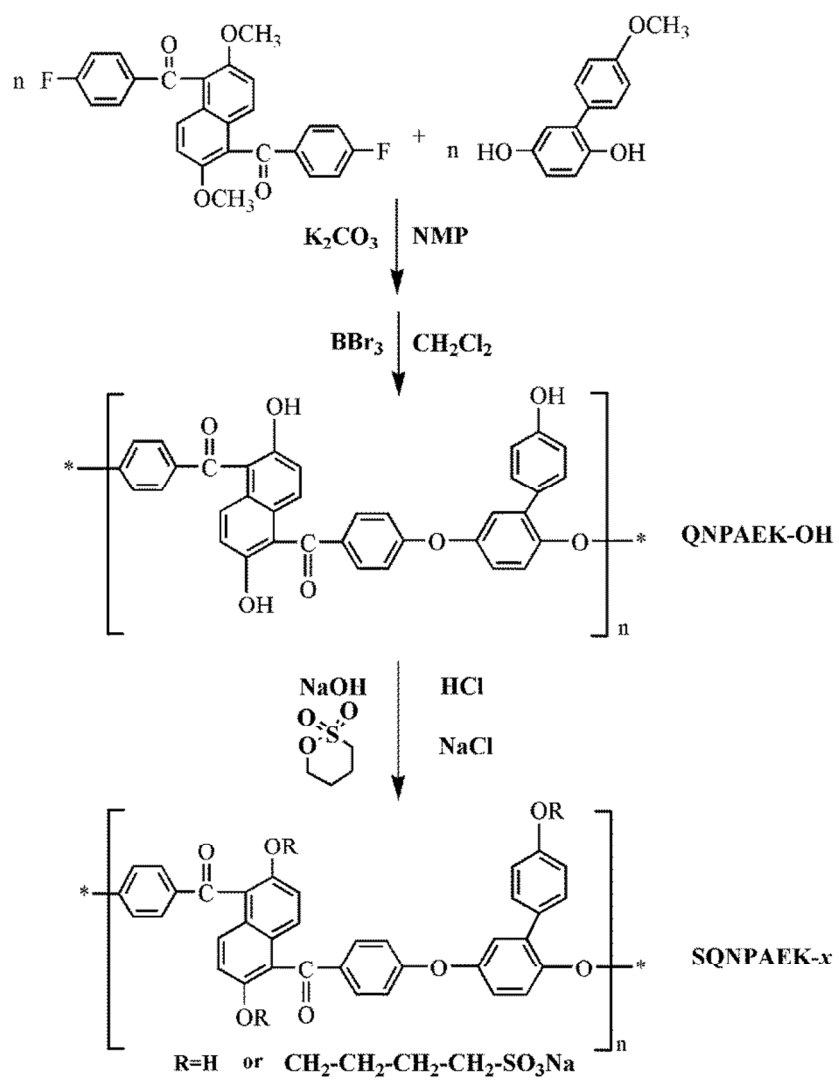
Figure 6 Temperature dependence of proton conductivity (measure in water) for SQNPAEK/COOH-x and

Nafion 117.

5
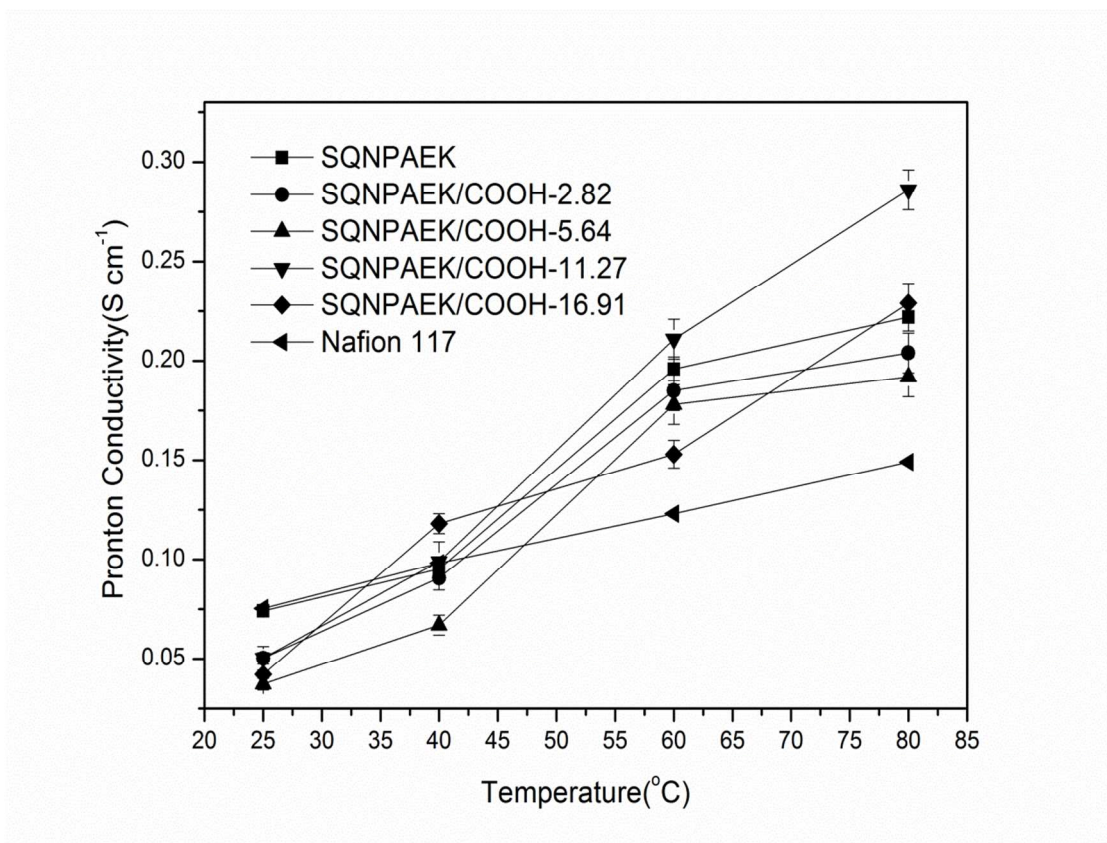
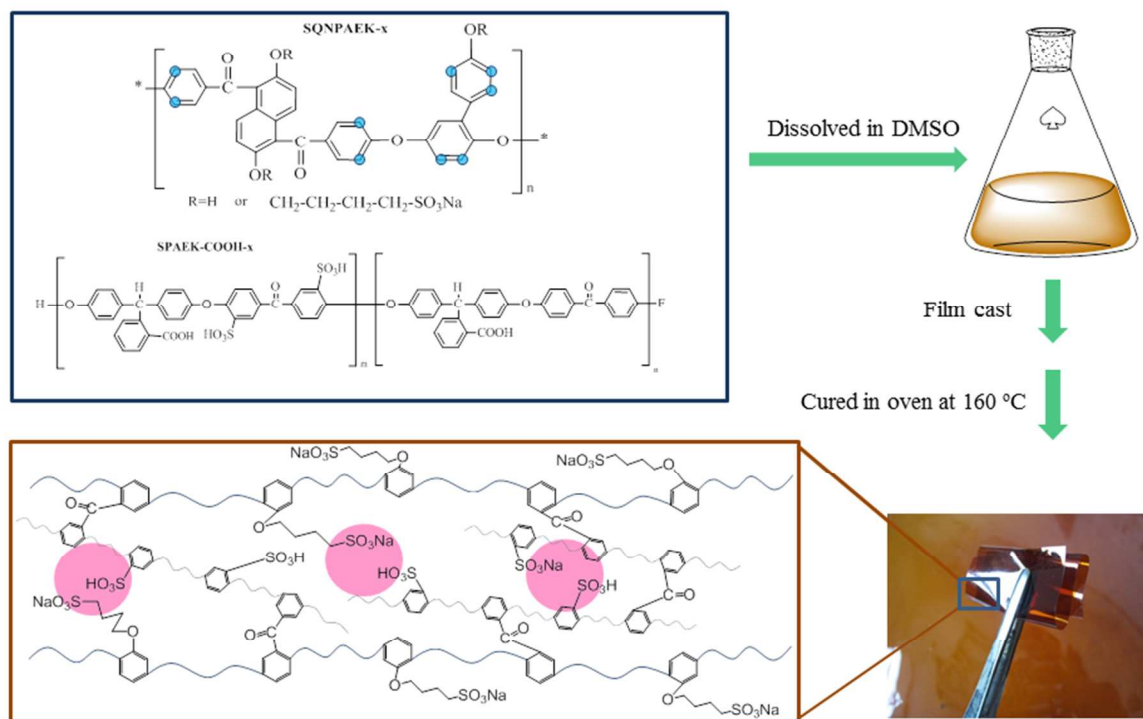**Scheme 1** The synthetic procedure to prepare SPAEK-COOH-*x* copolymers.

SPAEK-COOH-x

Scheme 2 Synthesis of SQNPAEK-x.

Scheme 3 Procedure of cross-linked membrane (Pink circles implie the cluster in the membrane).

• The possible crosslinking points

Table 1 The IEC, water uptake, swelling ratio and proton conductivity of the SPAEK-COOH-*x* membrane.

Macro-crosslinker	IEC (mequiv.g^{-1})	Water Uptake (%)	Swelling Ratio (%)	Methanol Permeability (cm^{2}s^{-1})×10^{-7}	Proton Conductivity (S cm^{-1}) 25 °C	80 °C
SPAEK-COOH-50	1.55	42.1	13.5	5.8	0.036	0.16
SPAEK-COOH-60	1.84	56.5	18.8	8.2	0.069	0.27
SPAEK-COOH-70	2.11	148.8	34.3	12.8	0.095	0.24

Table 2 Thermal and mechanical properties and oxidative stability of the membrane.

Samples	Tensile Strength (MPa)	Young`s Modulus (GPa)	Elongation at Break (%)	Oxidative Stability (minutes)	RW (after 4 hours, %)	Insoluble Fraction (%)
SQNPAEK	58.7±5.0	1.37±0.11	8.5±1.2	32	28.8	0
SQNPAEK/COOH-2.82	65.5±1.7	1.61±0.02	11.6±0.3	210	95.1	45.5
SQNPAEK/COOH-5.64	66.3±2.6	1.68±0.14	9.2±2.1	240	90.2	55.3
SQNPAEK/COOH-11.27	64.8±2.7	1.53±0.12	11.4±0.6	123	50.0	60.7
SQNPAEK/COOH-16.91	60.7±1.2	1.47±0.05	10.1±0.7	96	20.6	68.5
Nafion 117	29.4[a]	0.357[a]	270[a]	>300	99.8	-

a: Mechanical properties data from DuPont.

RW: residual weight calculated by the residual weight to original membrane weight.

Table 3 Properties of the SQNPAEK/COOH-*x* and Nafion 117 membranes.

Polymers Membranes	IEC[a] (mmol g^{-1})	Proton Conductivity (S cm^{-1}) 25 °C	80 °C	Methanol Permeability (cm^{2}s^{-1})×10^{-7}	Swelling Ratio (%) $\triangle l$ 25 °C	80 °C	$\triangle d$ 25 °C	80 °C
SQNPAEK	1.50	0.071±0.002	0.21±0.007	4.24±0.1	8.6±0.6	14.7±0.7	2.6±0.2	12.2±0.7
SQNPAEK/COOH-2.82	1.44	0.051±0.003	0.20±0.01	0.75±0.2	5.9±0.9	11.5±0.5	0.4±0.2	5.2±0.6
SQNPAEK/COOH-5.64	1.2	0.045±0.003	0.19±0.01	0.37±0.4	6.3±0.3	9.2±0.7	1.3±0.4	3.4±0.5
SQNPAEK/COOH-11.27	1.54	0.050±0.0006	0.29±0.01	0.43±0.1	4.0±0.5	8.7±0.6	0.4±0.5	3.0±0.8
SQNPAEK/COOH-16.91	1.44	0.043±0.002	0.23±0.01	0.94±0.1	7.4±0.5	11.6±0.7	4.3±0.5	7.3±0.7
Nafion 117	0.92	0.075	0.15	23.8	10.6±0.4	17.2±0.2	4.8±0.004	13.8±0.004

a: IEC values obtained by titration.