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Preparation and Proton Exchange Properties of GO Grafting modified Cross-linked Membranes

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The cross-linked membranes were prepared with DS 68% SPEEK and epoxy resin. Sulfonated graphite oxide was grafted into SPEEK main bonds to study the sulfonic acid groups on the impact of proton exchange properties. Using solartron electrochemical testing system to analysize the conducting proton properties of membranes. It is found that to achieve the same proton conductivity, the graft sulfonated graphene oxide content in the membrane need to be high. When the proton conductivity reaches a certain value and continue to increase the content of sulfonated graphene oxide, there will be a ‘blocking effect’ which due to the proton conductivity reduce instead. The cross-linked of epoxy resin has part of the effects on the proton conductivity of graft membrane. The highest value reached 5.2×10^{-2} $S\cdot cm^{-1}$. But it is still falling with the increase content of epoxy resin. Introduction of the sulfonic acid groups provide springboard for proton exchange membrane conduction protons. The interpenetrating network structures increases the chains winding and piling to increase the density of the membranes. And the water swelling resistance has a good improvement. The structure will not be loose at high temperature, and guide protons performance is not affected.

Keywords: Electrochemical properties, SPEEK, membranes, grafting

1. INTRODUCTION

The global energy shortage, urgent demand of environment protection and sustainable development have become increasingly prominent, the fuel cells are booming because of its outstanding advantages [1-3]. Direct methanol fuel cells have high energy conversion efficiency, fast start, non-polluting, renewable fuel, easy storage and transportation advantages, which is become a focus of new energy system [4-6]. Proton exchange membrane as an integral part of the fuel cell, its modified and study of the main properties got a lot of attention in recent days. Fuel cell is the power generation device to change the fuel chemical energy directly into electrical energy, which has the advantages of clean, efficient and without recharge. The conversion efficiency of fuel cell system in fuel-power was 45% ~ 60% [7].

In the early 1990s, the research of proton exchange membrane fuel cell (PEMFC) as the core of fuel cell has been significant progress, which is showing excellent actual using value [8-9]. In all kinds of fuel cell, PEMFC has many advantages, like startup speed is quick, simple and compact structure, high reliability and low cost advantages in the room temperature, which becomes the most widely application prospects of fuel cell.

SPEEK proton exchange membrane with its good chemical and mechanical stability and well proton conductivity in the proton exchange membrane fuel cell research has caught attention [10-12]. The high-temperature thermal performance is very outstanding which can generally be used under 250 $^{\circ}$C for a long time, and the instantaneous temperature is up to 300 $^{\circ}$C. It has great rigidity, dimensional stability, and the linear expansion coefficient is small, which close to the metal aluminum. At the same time, the microstructure of SPEEK membranes characteristic makes the alcohol resistance excellent performance than the Nafion membrane [13]. It is highlights the excellent applied prospects in DMFC. Only with the increase of sulfonation degree (DS), the swelling and mechanical performance of SPEEK membranes will be a significant reduction. But the proton conduction ability of low degree sulfonation of SPEEK is weak, which do not meet the basic requirements of the DMFC [14].

In the applications of DMFC, the main performances of SPEEK proton exchange membranes are proton conductivity, solvent resistance and alcohol resistance performance. The performances are affected by the factors of SPEEK membrane material, the kinds of solvents or membrane structure. However, the performances often appear the trend of containment. At present, the most important parts in direct methanol fuel cell proton exchange membrane have the weakness of poor alcohol resistance performance, high cost and polluting environment to restrict the large-scale commercial development prospects. Therefore, scientists are looking for a kind of high conductivity, low methanol permeability, good resistance to solute and more environmentally friendly materials to replace the commercial Nafion membrane. SPEEK proton exchange membrane is widely considered to be important candidate materials of DMFC proton exchange membrane, which has become one of focused research topics [15].

In this paper, SPEEK with DS of 68% were prepared by post-sulfonation. Using diethylenetriamine as the epoxy cross-linking agent, which uniformly distributed in the grafted SPEEK, to form SPEEK/epoxy membrane performances. Graphene oxide was synthesized according to Hummers method and organic in γ-chloropropyl triethoxysilane. Sulfonated graphite oxide was grafted into SPEEK main bonds. Finally a series of SPEEK-g-GO, SPEEK/epoxy-g-GO membranes were prepared and the properties were research and analyzed, like thermal properties, proton conductivity, methanol permeability and water swelling.

2. EXPERIMENTAL SECTION

2.1 The preparation of grafted membranes

SP60 was soluble in 10 ml DMAc according to the formula in table 1. The constant voltage funnel containing a moderate amount of graphene oxide uniform dissolved into droplets to the SP60 DMAc solution and stirring 20 h to obtain graphene oxide graft sulfonated polyether products (SP-G). SP60 and GO with quality are 1:0.1. 0.866 g aminobenzene sulfonic acid (SA) was directly added into SP-G solution, ultrasonic 4 hours and then mechanical stirring for 24 h at 65 ºC. Distillation to remove DMAc, and obtain the products of aminobenzene sulfonic acid oxidation graphene graft SPEEK resin (SP-E-G). The reaction process is shown in figure 1.

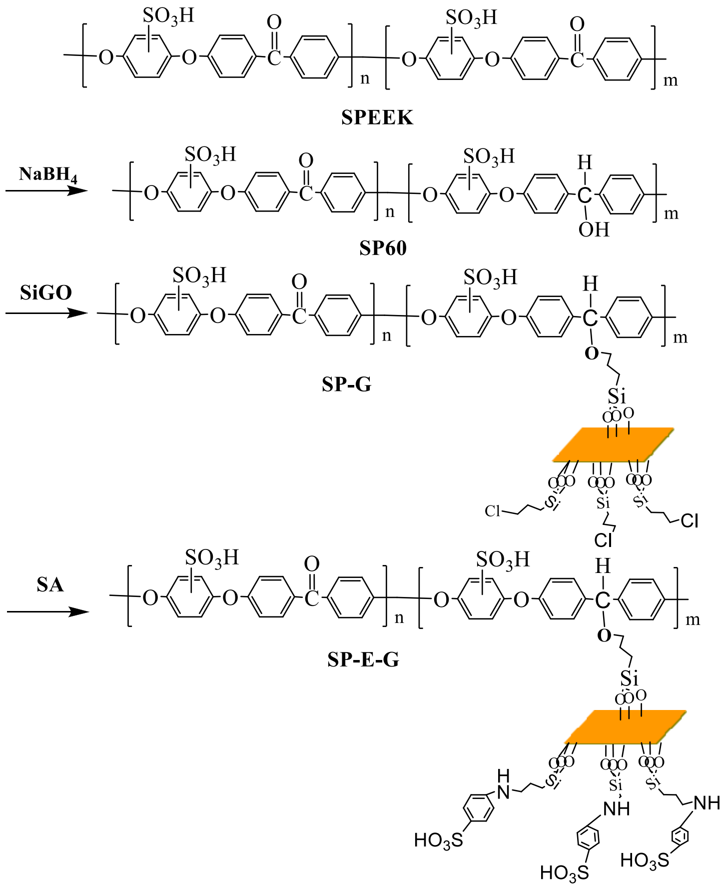


Figure 1. Synthesis of SP-E-G

Take grafting degree for 10 wt.% of sulfonated polyethylene oxide graphene grafted polyether ether ketone resin soluble in 10-channel DMAc in table 2, according to requirements of the film sample formula to join 10-channel DMAc soluble epoxy resin solution. Ultrasonic dispersion 4 h and join divinyl three amine under 150 ºC. Using magnetic blender mixing 30 min, and let stand after 10 wt.% of homogeneous liquid membrane.

Table 1. Recipe for grafting reactant

CODE	SPEEK (wt.%)	GO (wt.%)
SPEEK	100	0
SP-G02	98	2
SP-G05	95	5
SP-G08	92	8
SP-G10	90	10
SP-G15	85	15

Measuring 10 ml membrane casting solution in the cavity of the glass, and get dry film surface level off is smooth. The thickness of the films are about 100 microns. Grafting modified SPEEK/epoxy resin proton exchange membranes have half interpenetrating network structures as shown in figure 2. Effect of epoxy resin by divinyl three amine occurs crosslinking network structure formation with sulfonated polyether ether ketone structure. The long chain throughout the network formed half interpenetrating network structure and connected sulfonic acid groups on the package of graphene oxide dispersion.

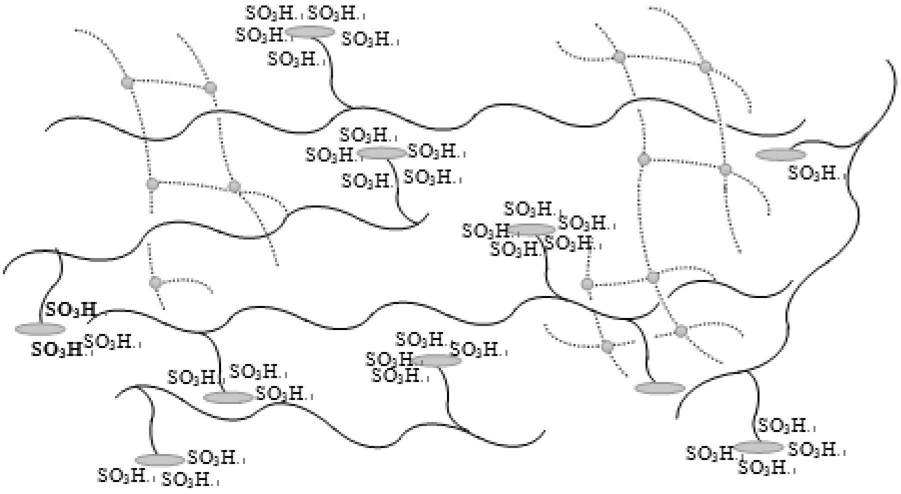


Figure 2. Schematic of GO grafted SPEEK/epoxy composite membranes

Table 2. Recipe for Graphene oxide derivative grafted membranes

CODE	SP-G10 (wt.%)	E-51 (wt.%)
SP-E10-G10	90	10
SP-E15-G10	85	15
SP-E20-G10	80	20

2.2 Characterization and testing

Fourier transform infrared (FTIR) spectra of proton exchange membrane structure characterization will first samples mixed with KBr powder through dry processing, on the basis of Beer-tablet of Lambert's law made thin enough. Then the Nicolet-type AVATAR380 Fourier transform infrared spectrometer (Thermo Nicolet Corporation, Madison, USA, FTIR) on synthesis of modified membrane samples of infrared testing, condition of room temperature (25 °C) wave number range of 500-4000 cm^{-1}, scanning of 16 times.

The microstructures of solid residues were recorded using a Cambridge S250MK3 scanning electron microscope. The solid residue of the samples degraded to various extents was also prepared using the TGA instrument under nitrogen atmosphere. The materials were heated from room temperature to 800 °C with a heating rate of 10 °C/min, and then rapidly cooling the residue to room temperature.

The EIS recorded over a frequency range of 1-10^{6} Hz. All the membrane specimens were soked in 1 mol/L hydrochloric acid solution for 24 h before tests, after then rinsed with de-ionized water several times. Then, the proton conductivity and resistance of membranes performance were calculated as described. Using a measurement cell way to measure the proton conductivity performance by AC Electrochemical Impedance Spectroscopy, the detailed mechanism was narrated in literature [16].

A self-made diaphragm diffusion cell was using to measure the methanol permeability of the membranes, which was closed to the one described in Ref [7]. Immersing the membranes into de-ionized water at 25 °C for 24 h, and then both of the thickness and areas were measured. Where after, the membranes were settled down at test temperature above 1h and then tested the methanol permeability. 70 mL 5 mol/L methanol was poured into the diffusion cell and equal volume de-ionized into the other. Magnetic stirrers were stirring in both compartments. The interrelationship of peak areas and methanol concentration were detailed in in Ref 7. The methanol permeability coefficient was calculated by the second law of Fick’s diffusion.

Through measuring the dry and hydrous weight to calculate the water uptake (S_w) of the membrane detailed in Ref 7. The mass$_{dry}$ weight was measured by membrane specimens dried at 90 °C for 24 h were. Then, put it into deionized water for 24 h. The mass$_{wet}$ weight was quickly measured by membranes specimens wiped by blotting paper to remove the surface water. The S_w was calculated using equation $Sw=(m_{wet}-m_{dry})/m_{dry}\times100\%$ [17].

3. RESULTS AND DISCUSSION

The SP-G10 structure characterization is shown in figure 3. The 3400-3450 cm^{-1} have a weak characteristic absorption peak which should be flake graphite oxide layer structure -O-H stretching vibration absorption peak. 929 cm^{-1} is due to Si-O stretching vibration absorption peaks. 1120 cm^{-1} is due to C-Si stretching vibration absorption peaks. 1191 cm^{-1} is due to C-O-C stretching vibration absorption peak. All above showed that silane coupling agent and SPEEK reduction group hydroxyl -

OH oxygen is linked together, and also prove that the sulfonated graphene oxide groups grafted onto SPEEK bones.

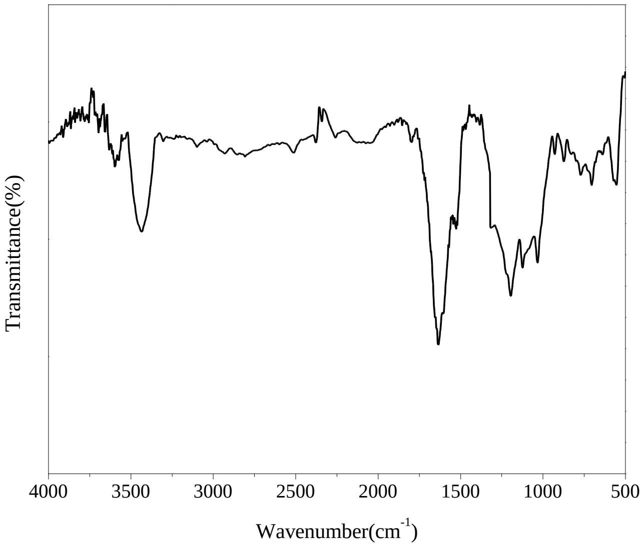


Figure 3. FT-IR spectrum of SP-G10

The FTIR spectra of SP-E10-G10 is shown in figure 4. 1360 cm^{-1} is accroding to C-N stretching vibration absorption peak, 3400-3450 cm^{-1} strong stretching vibration peak is due to the N-H. All above improved that silane coupling agent modified oxidation was sulfonated graphene [18].

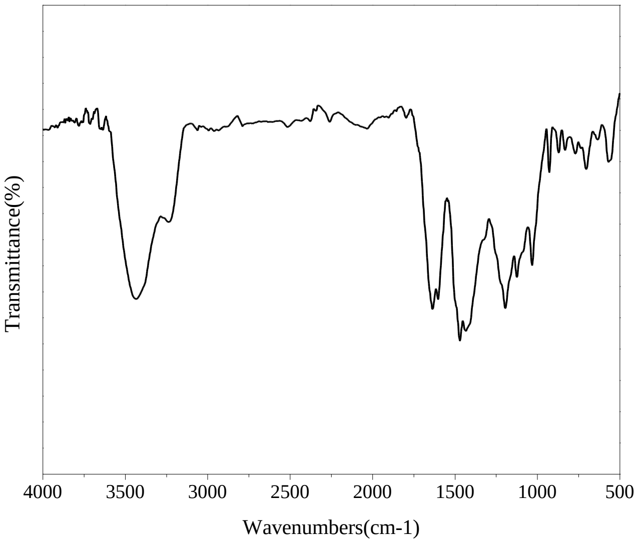
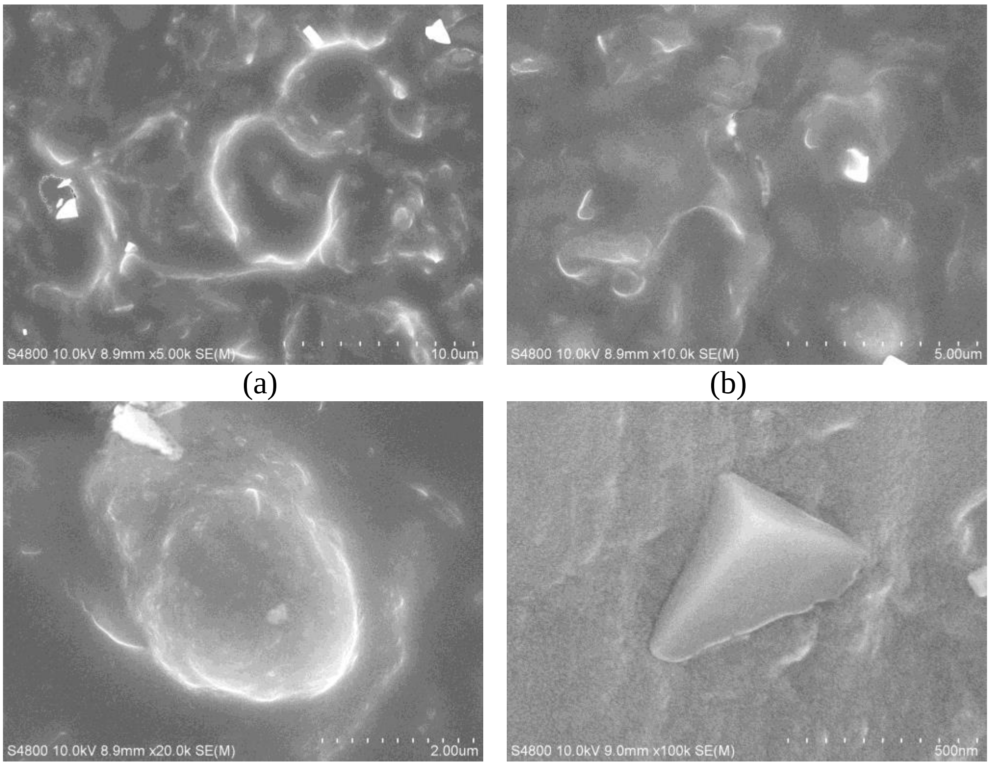


Figure 4. FT-IR spectrum of SP-E-G

The half interpenetrating network microstructures of SPEEK/Epoxy resin proton exchange membrane are shown in figure 5. The membrane samples are from 5000 to 30000 times magnification of SEM morphology.



(a) (b)

(c) (d)

Figure 5. Morphology of grafted SPEEK/epoxy membranes

The figure 5 shows that epoxy resin to form continuous phase after dealing with the cross-linked epoxy resin. The separation of two kinds of polymer interface is not obvious, which around the SPEEK particles surrounded by epoxy resin. It is formed through the network structure in the grain, and shall be the graft sulfonated graphene oxide. Compared with doping modification membranes, the sulfonated graphene oxide particle density is low than the long chain of SPEEK throughout the whole half interpenetrating network structure [19]. Sulfonated graphene oxide particles with epoxy resin and a half interpenetrating network structure has side. There is no clear separation of interface which shows graft sulfonated graphene oxide to SPEEK and exists a half interpenetrating network structure can be stable. But the GO is less easy to loss.

TG curves of the three type of epoxy resin grafted half interpenetrating network of SPEEK proton exchange membranes as shown in figure 6. The half interpenetrating network grafting SPEEK/epoxy resin membranes have several thermo-gravimetric process stages. The first stage for trace weightlessness occurred in 150-300 ºC due to the un-completely dry water or residual solvents. The second stage of the initial weightlessness occurred in 300-450 ºC is the weightlessness of sulfonic acid groups on the benzene ring and the sulfonic acid group on the sulfonated graphene oxide C-S decrease cracking. And the pyrolysis and decomposition caused by a small amount of cross-linked epoxy resin [20]. The third stage is mainly the body weight loss phase, which occurred in above 400 ºC and the weightlessness is mainly caused by thermal decomposition of the main chain rigidity group.

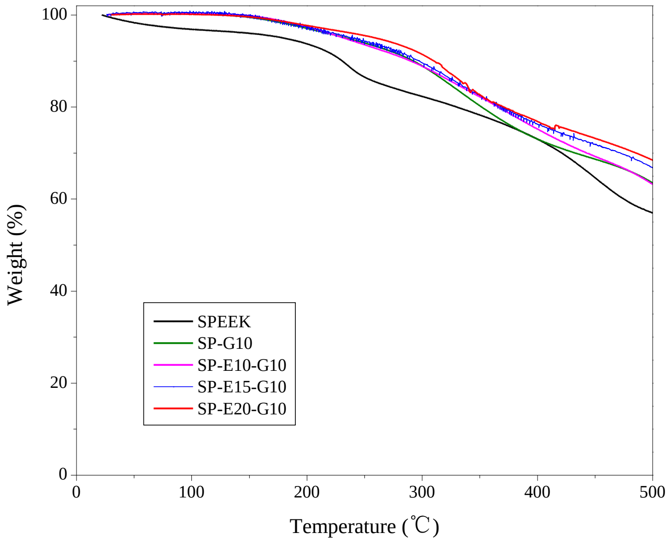


Figure 6. TG curves of grafted SPEEK/epoxy semi-IPN membranes with different epoxy contents

The pyrolysis experiment data analysis shows that the sulfonated graphene oxide grafting SPEEK membranes delayed the initial decomposition temperature. While grafting sulfonated graphene oxide, the interaction force between long chain is increased which infects the initial decomposition temperature of the membranes. To half interpenetrating network type of grafting SPEEK membranes, it is not difficult to find that the initial weight loss temperature increased with the increase of the epoxy resin content. Crosslinking network and grafted chemical bones have the synergy effects in the process of heating, and its solid residual rate is also high. Crosslinked network structures covered with the long chain of SPEEK and sulfonated graphene oxide particles. The more half interpenetrating network overall improved better thermal performance.

Figure 7 is the proton conductivity curves of pure SPEEK and sulfonated graphene oxide grafted SPEEK membranes changing with temperature. It is shows that the proton conductivity has significantly improved performance compared with the pure SPEEK membrane. it is worth mentioning that the proton conductivity were all higher than 10 $S\cdot cm^{-1}$ above 60 ºC. It is because the sulfonic acid groups in the pure SPEEK membranes are less to form a continuous ion cluster channels. The proton conduction relies mainly on the H_3O^+, $H_5O_2^+$ and $H_9O_4^+$ transmission in water medium. Along with the increase of grafting degree, the guide protons performance is also increase. When the grafted rise to 10 wt.%, the proton conductivity performance of membrane is stable. Continue to rise the grafting degree, the proton conduction didn't happen bigger effect. 10 wt.% of the grafting degrees have reached a maximum of water medium and molecular diffusion, continue to increase the degree of grafting does not increase the conduction carrier of the proton and conduction velocity.

Figure 8 is the curve of proton conductivity of pure SPEEK and half interpenetrating network sulfonated graphene oxide grafting SPEEK/epoxy resin membranes changing with temperature. With the increase of epoxy resin, SP-E10-G10 membrane proton conductivity performance declined. But the proton conductivity was much higher than pure SPEEK membrane. When the temperature higher than 70 ºC, the proton conductivity are more than 10 $S\cdot cm^{-1}$ [21]. SP-E10-G10 membrane has the excellent comprehensive properties.

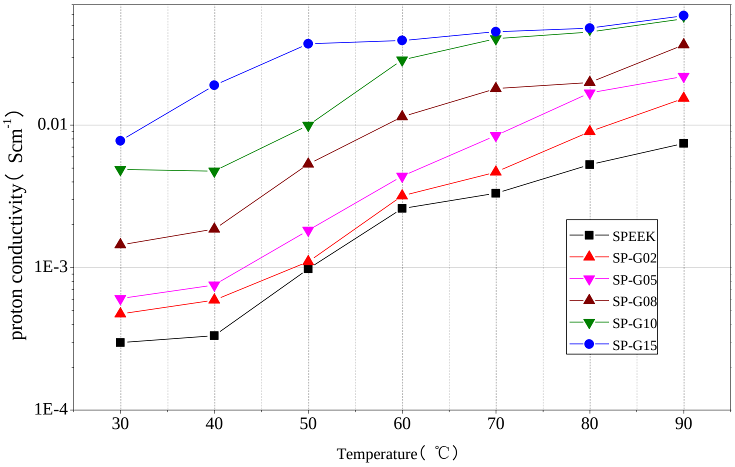


Figure 7. Proton conductivity of SPEEK membrane and SSiGOs grafted membranes vs temperature

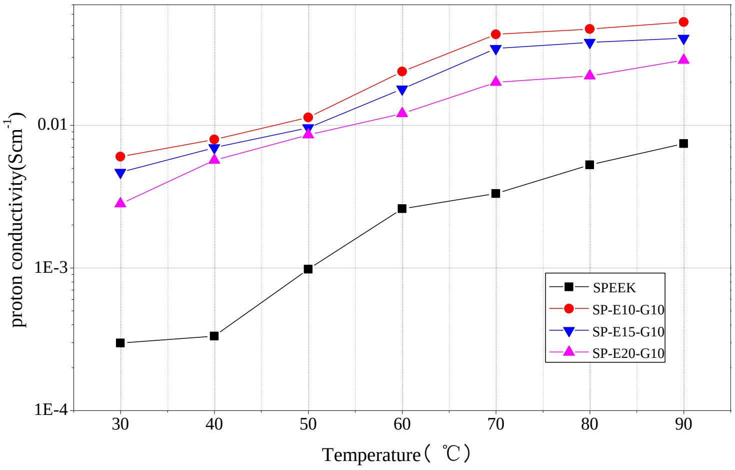


Figure 8. Proton conductivity of GO grafting SPEEK/epoxy membranes vs temperature

The proton conductivity of SP-E10-G10 and SP-E15-G10 are closed above 60 ºC. The proton conductivity of SP-E10-G10 and SP-E10-G10 membranes are 5.2×10^{-2} S·cm^{-1} and 4.3×10^{-2} S·cm^{-1} at 90 ºC, respectively. Amount of epoxy resin as cross-linking increases, the proton conductivity of membrane are gradually reduced under corresponding temperature. It may be that part epoxy crosslinking increased the density of proton exchange membrane, and reduce the part number of sulfonic acid groups involved in proton conduction. Thereby reducing the proton conductivity, but the water swelling resistance of the membranes had better improve and form ion clusters of sulfonic acid groups which did not cause bigger impact. To avoid the high temperature caused by pure SPEEK membrane structure loose, the conducting proton performance is not high [22]. The temperature rising increased the transfer activity of proton and improve the efficiency of the transition in the film, so the proton conductivity of membrane samples increases with temperature rise.

Using GC9800 type gas chromatograph in lab homemade diaphragm diffusion pool device of pure SPEEK and SPEEK/epoxy resin membranes modified alcohol resistance performance test under 30 ºC, which are shown in figure 9.

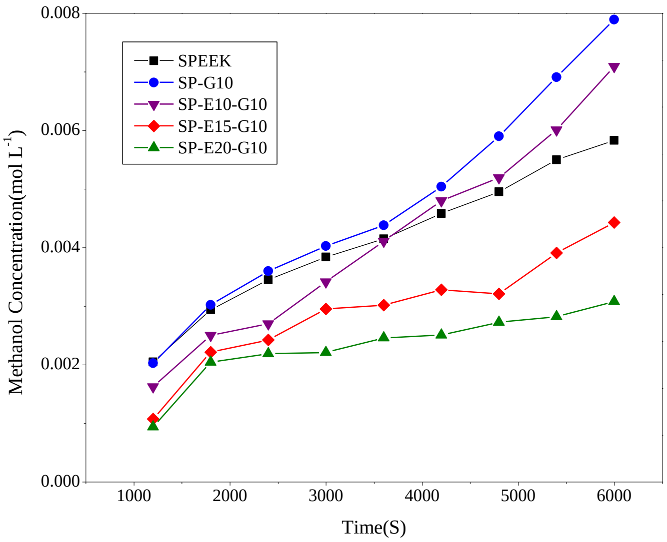


Figure 9. Methanol concentration of GO grafting SPEEK/epoxy membranes vs temperature

The figure 10 shows that the methanol penetration concentration is gradually increased with the increase of time. The alcohol resistance performance of SP-G10 and SP-E10-G10 proton exchange membranes are slightly lower than the pure SPEEK membrane. It may be due to the simple grafting result in proton exchange membrane skeleton loose. The methanol permeability concentration of SP-E15-G10 and SP-E20-G10 proton exchange membranes are higher than pure SPEEK membranes. And the methanol concentration permeability of SP-E10-G10 proton exchange membranes is relatively slow changing with time, and pure SPEEK is faster change over time. Contrast the resistance alcohol performance of SP-E-G10 type exchange membranes, the SP-E10-G10 methanol permeability concentration is relatively close with pure SPEEK proton exchange membrane. With the increase content of epoxy resin, the methanol permeability concentration decreases. The methanol concentration permeability of SP-E15-G10 and SP-E20-G10 proton exchange membranes are relatively close. It is most probably because SP-E15-G10 and SP-E20-G10 has stable hydrophobic skeleton and further increase content of epoxy resin. The hydrophobic skeleton activities will not cause a larger degree of stability. Considering the proton conductivity and methanol permeability coefficient, the SP-E10-G10 membrane is the best.

The preparation of epoxy resin and half interpenetrating network graft sulfonated graphene oxide grafting SPEEK proton exchange membrane, the results of water absorption and swelling degree are shown in figure 10 and 11. The water absorption and swelling degree of sulfonated graphene oxide grafted SPEEK/epoxy resin membranes are increased with temperatures rise. The higher the temperature, the more obvious increase trend. But with the increase of epoxy resin and half interpenetrating network, the water absorption and swelling degree reduced [23].

The figure 10 and 11 shows that the absorption water rate of SP-E10-G10 membrane is 60.77% and the swelling degree reached 20.84%, which is lower than SP-G10 membrane at 90 ºC, but still higher than that of pure SPEEK membranes. With the increasing of half interpenetrating network, the water absorption and swelling degree of SP-E20-G10 and SP-E15-G10 membranes are lower than the pure SPEEK membrane at 90 ºC. The bibulous rate of SP-E15-G10 and SP-E20-G10 membranes are 59.01% and 58.90% respectively, and the swelling degree reached 24.6% and 21.36%, which are all lower than pure SPEEK membrane. The composite membranes still keep well proton conductivity and resistance performance with epoxy resin. The more half interpenetrating network, the better performance of its resistance to water swelling.

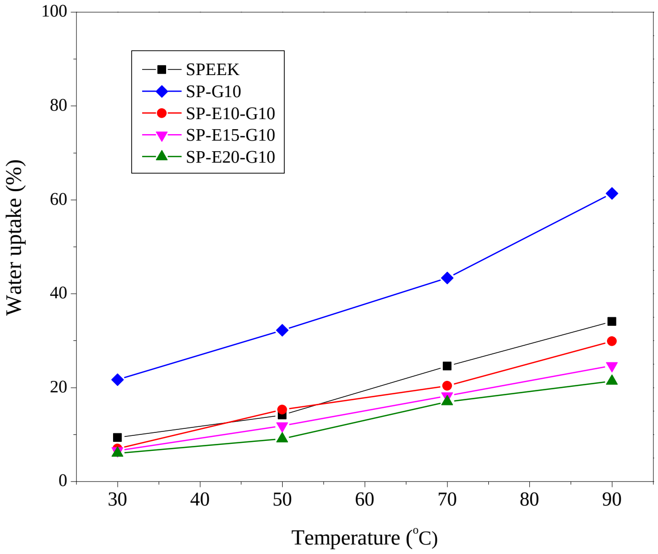


Figure 10. Water uptake of GO grafted SPEEK/epoxy membranes vs temperature

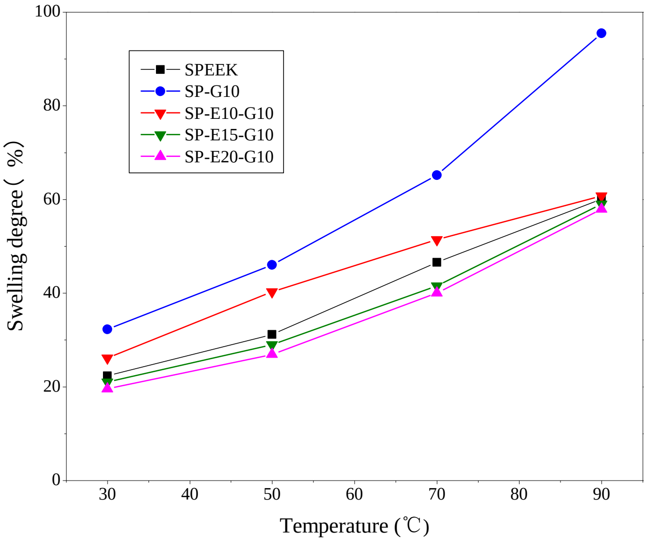


Figure 11. Swelling degree of GO grafted SPEEK/epoxy membranes vs temperature

After grafted sulfonated graphene oxide, a large number of sulfonic acid groups were introduced into the lateral links of SPEEK backbone. There are strong polarity and increases the proton conductivity. But the water swelling resistance performance was degradation. After half-interpenetrating network were built with epoxy resin and SPEEK hydrogen bonds to formed crosslinking network. Then the polymer chain movement is restricted, because that SPEEK and epoxy resin molecular inter-atomic forces enhancement effect and the stability of the membrane was improved.

4. CONCLUSIONS

The DS 68% SPEEK composite membranes were prepared by post-sulfonation. Using epoxy is as cross-linking agent to form SPEEK/epoxy interpenetrating network structures and explore half-interpenetrating networks on the impact of membrane performances. The sulfonated graphite oxide was grafted on the SPEEK backbones and optimized the formulation. Finally a series of SPEEK/epoxy proton exchange membranes were prepared. It is found that the graft sulfonated graphene oxide content in the membrane need to be high to achieve the same proton conductivity. When the proton conductivity reaches a certain value and continue to increase the content of sulfonated graphene oxide, there will be a ‘blocking effect’ which due to the proton conductivity reduce instead. The cross-linked of epoxy resin has part of the effects on the proton conductivity of graft membrane. The highest value reached 5.2×10^{-2} S·cm^{-1}. But it is still falling with the increase content of epoxy resin. Introduction of the sulfonic acid groups provide springboard for proton exchange membrane conduction protons. The part of epoxy crosslinking increased the density of proton exchange membrane. The water swelling resistance of the membrane has a good improvement. The structure will not be loose at high temperature, and guide protons performance is not affected. Alcohol by gas chromatography of the membrane resistance performance, found half interpenetrating network could effectively improve the proton exchange membrane resistance performance, with the increase of epoxy resin content in methanol permeability decreasing. When the epoxy resin content is above 15 wt. %, the decline is not obvious and the methanol permeability coefficient are less than 1.8×10^{-8} S·cm^{-1}. Epoxy cross-linking components significantly reduce SPEEK skeleton absorb moisture capacity, effective the control of membrane structure and increase the interaction between the polymer and sulfonated graphene oxide. In additional, the sulfonated graphene oxide and epoxy resin increase the mechanical stability and alcohol resistance performance of membranes.

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