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Electrochemical Properties of SPEEK/Epoxy/ Graphene Oxide Composites as Proton Exchange Membrane

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The DS 68% SPEEK composite membranes were prepared by post-sulfonation. Using diethylenetriamine as the epoxy cross-linking agent, which is uniformly distributed in the grafted SPEEK to form SPEEK/epoxy semi-interpenetrating network structure and explore the semi-interpenetrating network on the impact of membrane performances. Graphene oxide was synthesized according to Hummers method and organic in γ-chloropropyl triethoxysilane. Sulfonated graphite oxide doped SPEEK were prepared and optimized the formulation. Finally a series of SPEEK/epoxy/graphene oxide proton exchange membranes were prepared. With the increasing content of epoxy resin semi-interpenetrating network structure, the thermal properties of the proton exchange membrane are also increased. Covered with crosslinked network structure, the more long chain of SPEEK and graphene oxide particles, the more thermal performance improved. The methanol permeabile concentration is relatively close with pure SPEEK proton exchange membrane. The concentration of methanol permeability decreases with the increase of epoxy resin content. The semi-interpenetrating network structure increase the interaction with the matrix bonds and reduce the sulfonic acid groups on the excessive absorption of water molecules. But the membrane structure still exist problems such as density, which due to the loss of doped sulfonated graphene oxide. But there are only semi-interpenetrating network cannot be fully resolved.

Keywords: Electrochemical properties, proton exchange membrane, Graphene oxide, doping

1. INTRODUCTION

In order to promote the green, cyclic and low carbon development as the main task, improving energy utilization rate and developing clean energy have become an inevitable trend of scientific research. With environmental protection, energy saving, high efficiency and convenient using, direct methanol fuel cell has been developing application in many fields [1-3].

In the fuel cell, proton exchange membranes have gained a lot of attention. It is because of its relatively low and room temperature characteristics, combined without chemical hazards to human body, harmless to the environment and suitable for application in daily life [4]. Triad membranes are the core component of direct methanol fuel cell, which combinated by negative, positive electrode and proton exchange membrane with hot pressing [5-6]. In the long term exploration process of direct methanol fuel cell, the study of the proton exchange membrane has never been interrupted. The proton exchange membranes as the core element of direct methanol fuel cell are mainly from proton conducting property, chemical stability and mechanical properties of the aspects to retard their application. In the late 1960's, polystyrene sulfonic acid membrane had been used in direct methanol fuel cell [7]. But styrene sulfonic acid as the proton exchange membrane material has some fatal flaws, like easy degradation occurred in the using process. Which is not only lead to shorten the battery life and reduced the power density, but also cause the battery formation water is polluted without using. Along with the progress of science and technology, fuel cell technology is updated constantly. And the development of fuel cell is the durability of the proton exchange membrane. The most commonly used proton exchange membrane is still the perfluorinated sulfonic proton exchange membrane (Nafion) which was invented by E. I. Du Pont Company in 1962. Nafion membranes solve some pitfalls of the styrene sulfonic proton exchange membrane, and promote greatly growth in the fuel battery life. However, the research and development of fuel cell technology have not been able to large-scale promotion for decades. The problems such as stability, durability and high cost are also the bottleneck of commercialization. Actively development of new materials is the only way to solve the problem, which is also the research focus of proton exchange membrane [8-9].

At present, the materials which can be used as proton exchange membrane are mainly divided into perfluorinated sulfonic acid and non-fluorinated proton exchange membrane. Non-fluorine sulfonic acid membranes are low cost and little pollution to environmental, which is a trend of the development of proton exchange membrane [10]. Non-fluorine sulfonic acid membrane materials have many kinds, but the key is how to apply them to proton exchange membrane used in fuel cell after processing. In numerous materials of non-fluorine sulfonic acid membrane, sulfonated poly(ether ether ketone) (SPEEK) proton exchange membrane has widely attention for its excellent alcohol resistance performance, high mechanical strength, excellent thermal chemical stability and modest proton conductivity. The proton conductivity of SPEEK membranes with modest proton conductivity, high mechanical strength, thermal stability, relatively lower cost and the methanol permeability coefficient than commercial Nafion membrane, which is considered to be a potential material to replace the Nafion membranes. The research of sulfonated poly(ether ether ketone) has some preliminary results. From synthetic to modification are all the hot research topics. However, due to the limitations of proton conduction and methanol permeability, there inevitably cannot achieve ideal level and widely used. Thus, it still needs more effort [11-15].

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 semi-interpenetrating network structure and explore the semi-interpenetrating network on impact of membrane performances. Graphene oxide was synthesized according to Hummers method and organic in γ-chloropropyl triethoxysilane. Sulfonated graphite oxide doped SPEEK were prepared and optimized the formulation. Finally a series of SPEEK/epoxy/graphene oxide composite 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 binary doped membranes

The classic Hummers method was used to synthesize graphene oxide. Using γ-propyl chloride triethoxy silane connect on the graphene oxide to obtain good dispersibility, high dispersion in organic solvents and long chain polymer. The synthetic route is shown in figure 1. Before the synthetic reaction, all reagents and drugs must remove the moisture and impurity. 1 g graphene oxide and 20 ml γ-propyl chloride triethoxy silane were added into 100 ml dimethylacetamide at one-time, ultrasonic dispersion 6 h and reflux reaction for 24 h under 100 °C. Black turbid liquid were obtained. Product was cooled to room temperature and dissolved into a beaker of ethanol and deionized water, repeatedly washing to remove excess γ-propyl chloride triethoxy silane. Standing stratification, and then the water upper and tan organic phase lower were separated. Distillation to remove the solvent under vacuum at 0.1 MPa and 70 °C, and obtain silane coupling agent modified graphene oxide (Si-GO).

9.186 g aminobenzene sulfonic acid was dissolved in 250 ml toluene solution and put into 500 ml three flask. Then slowly drop 50 ml toluene dissolved 3 g Si-GO. Added 10 ml triethylamine as acid binding agent under nitrogen atmosphere at 50 °C with mechanical stirring 24 h. Cooling to room temperature, removing solvent and vacuum drying at 70 °C for 12 h to obtain sepia sulfonated graphene oxide (SSi-GO).

The trituration of pure SPEEK dissolved in 10 ml dimethylacetamide solvent to made 10 wt.% solution. According to table 1 to add sulfonated graphene oxide, ultrasonic dispersion 8 h to form 10 wt.% of uniform membrane solution. Take the membrane solution into the vitreous cavity under 60 °C for 12 h, then up the temperature to 100 °C for 4 h. Solvent was removed and respectively prepared 5 wt.%, 8 wt.% and 10 wt.% membrane samples and the thickness of membranes is about 100 microns.

According to the guide of graphene oxide doped SPEEK proton performance, 8 wt.% of SPEEK semi-interpenetrating network modified membrane was prepared for example. 8 wt.% sulfonated graphene oxide was triturated and dissolved in 10 ml dimethylacetamide. In accordance with table 2, a suitable amount of epoxy resin E-51 (51: epoxy group on the number of amount of substance in per 100 g resin) with 1:20 scale soluble in dimethylacetamide solution, then one-time added to SPEEK solution. Ultrasonic dispersion 6 h and join diethylenetriamine, stirring and curing at room temperature for 20 h and up to 150 °C for 30 min. Stopping the reaction and form a uniform fluid of the membrane. The quality percentages of epoxy resin are 10 wt. %, 15 wt. % and 20 wt. %, and the dry film thickness is about 100 microns. Epoxy resin occurs crosslinking with diethylenetriamine to form network structure. The long chain of sulfonated polyether ether ketone and crosslinked cured epoxy resin were formed semi-interpenetrating network structure by sulfonic acid group package of graphene oxide dispersion in the semi-interpenetrating network.

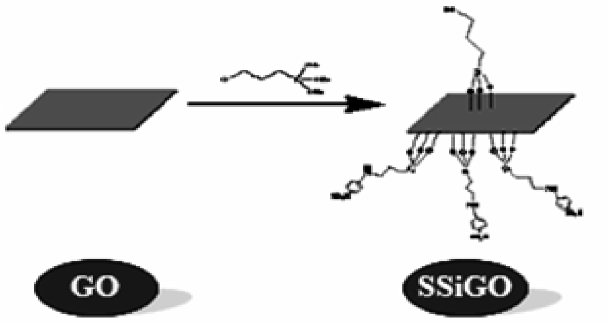


Figure 1. Synthesis of SSiGOs

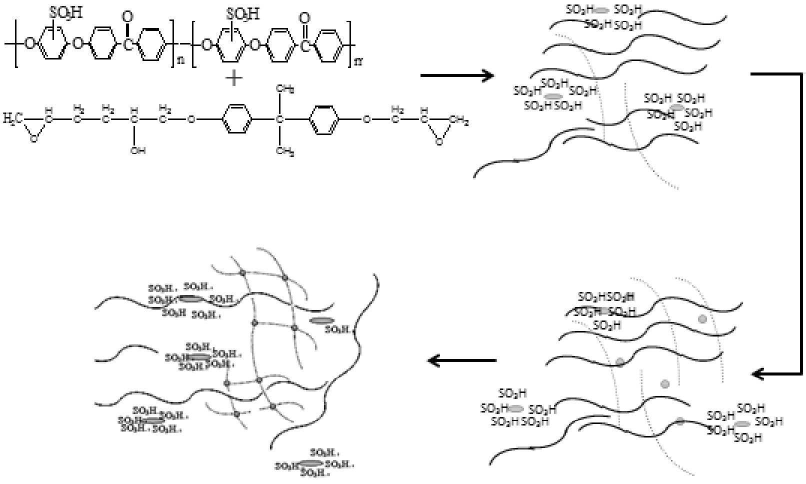


Figure 2. The formation diagram of semi-interpenetrating network structure

Table 1. Codes of composite membranes

CODE	SPEEK (wt.%)	SSiGO (wt.%)
SPEEK	100	0
SP-D05	95	5
SP-D08	92	8
SP-D10	90	10

Table 2. Codes of SPEEK/epoxy/graphene oxide proton exchange membranes

CODE	SPEEK (wt.%)	SSiGO (wt.%)	Epoxy (wt.%)
SP-E10-D08	92	8	10
SP-E15-D08	92	8	15
SP-E20-D08	92	8	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.

Using JMS-6700F Scanning electron microscopy (SEM) investigated the morphology of membranes. The membrane samples surface without any treatment and form to brittle fracture section under the liquid nitrogen. Spray a layer of platinum in section place again to observe the microstructure of the modified layer with different magnification.

The American Q-500 type thermo-gravimetric analyzer (TA, USA) thermo-gravimetric performance test was carried out on the preparation of membrane samples. Record the change of the sample quality with the temperature curves. Temperature and heat enthalpy with metal indium sample correction, record the corresponding thermal degradation curve and analyzed.

Spectrometer of AC impedance method to measure the vertical proton conductivity of membrane. The homemade laboratory simulation of steam medium measurement was used in the process. Before the test, the modified membrane samples for proton which are namely first soaked in 1 mol/L hydrochloric acid solution soak in deionized water to neutral. Cut into 1 cm diameter sample of the modified layer fixed between the diameter of 4.30 mm copper electrode, and placed in a water bath pot together above the steam medium test to simulate the actual working conditions of proton exchange membrane. The detailed mechanism was narrated in literature [16].

Using Solartron1287 intelligent potentiostat and Solartron1255B frequency response analyzer of Solartron electrochemical test system (British lose power company) for AC impedance diagram. Temperature range from room temperature to 90 °C, 1-10^6 Hz frequency range, and the applied voltage is 10 mV. Capacitance and inductance effect exist in the process of test, the corresponding phase advance and phase lag. The imaginary part of complex impedance Z" corresponding to zero real part number is membrane impedance values of Z'.

Using self-made diaphragm diffusion pool, simulate the selection of the proton exchange membrane permeability condition, and cooperate with GC9800 type gas chromatography device record retention time and peak area, methanol permeability coefficient per unit area, calculated rate of change over time. The methanol permeability coefficient with P said, which was closed to the one described in Ref [7].

The water swelling resistance of the modified layer with testing refers to measure quite a long time after soaking in solution sample rate and the quality of the modified membrane size rate of change. Using modified membrane width for 20*10 mm place into the oven, drying under 120 °C for 24 h, record M_{dry} (dry film quality) and according to its volume V_{dry}. Then modified membrane in deionized water, adjust the temperature at 30 °C, 50 °C, 70 °C and 90 °C respectively soaking out after 24 h to the surface moisture absorption record wet film quality as M_{wet}. And measuring the length, volume V_{wet} size calculation. Modified membrane sample test three times in each group averaged.

Water uptake is calculated by S_w as type $S_w = \frac{M_{wet} - M_{dry}}{M_{dry}} \times 100\%$, swelling degree by S_d as type $S_d = \frac{V_{wet} - V_{dry}}{V_{dry}} \times 100\%$ [17].

3. RESULTS AND DISCUSSION

The structure of SPEEK/epoxy/graphene oxide (SP-E10-D08) semi-interpenetrating network proton exchange membrane was analyzed by FTIR and the spectrum is shown in figure 3. The characteristic peaks of SPEEK are all in the figure, which is indicated that the crosslinking epoxy did not affect SPEEK internal structures. In addition, 929 cm^{-1} due to -Si-O- stretching vibration absorption peaks, 1120 cm^{-1} due to C-Si stretching vibration absorption peak. All above showed that silane coupling agent is connected with the graphene oxide. 950 cm^{-1} is epoxy characteristic absorption peak and 1750 cm^{-1} is ester base of characteristic absorption peak, which prove that the epoxy resin has crosslinking [18]. Therefore, SPEEK/epoxy/graphene oxide proton exchange membrane formed semi-interpenetrating network.

The microstructure of SPEEK/epoxy/graphene oxide (SP-E10-D08) semi-interpenetrating network proton exchange membrane is shown in figure 4. Figure 4(a-d) are the SEM photos of membrane samples from 5000 to 50000 magnification times. The figure shows that part of the phase separation areas were appeared in figure 4 (a), which should be the sulfonated graphene oxide dispersion in the system and the interference of crosslinking caused uneven of epoxy resin. It can observed homogeneous phase with increased magnification.

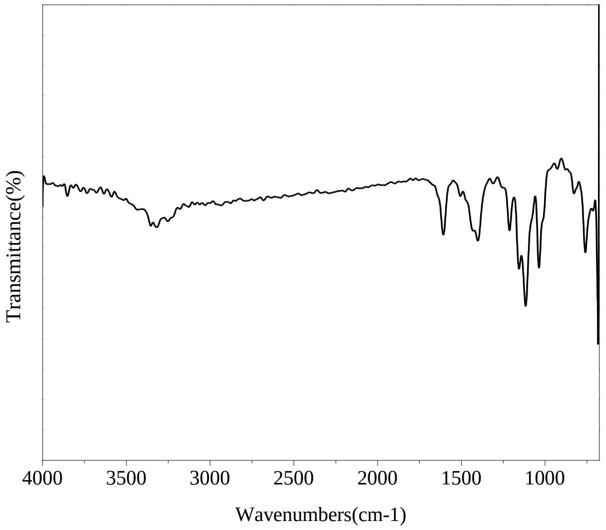
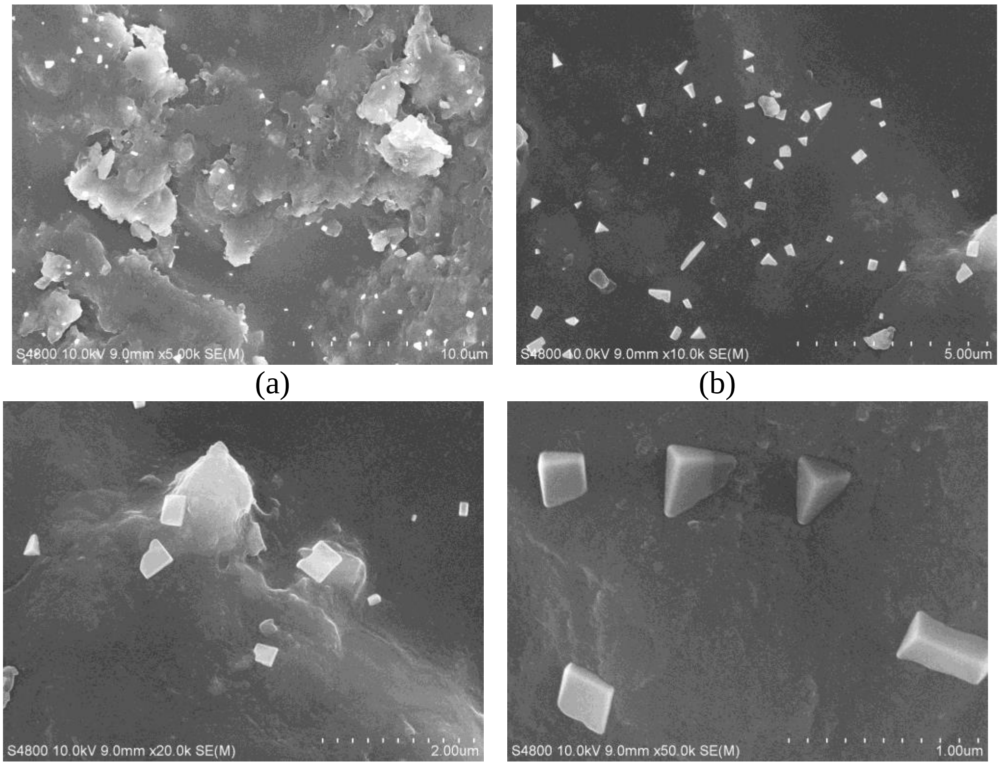


Figure 3. FTIR spectrum of SP-E10-D08 proton exchange membranes



(a) (b)

(c) (d)

Figure 4. Morphology of SPEEK/epoxy/graphene oxide (SP-E10-D08) membrane in different magnification: x5000, x10000, x20000 and x50000

A large number of polar groups closed contact with SPEEK in the process of membrane forming which cause adhesion between the two contact bodies. After dealing with the crosslinking, a continuous phase area was formed. Graphene oxide will only interfere with part of epoxy crosslinking, and most of the epoxy resin can still normal crosslinking to form a continuous phase [19]. After dealing with the crosslinking, epoxy resin formed continuous phase area. There are continuous particles, which should be doped sulfonated graphene oxide. Figure 4 (b) has uniformity graphene oxide particles and a clear separation of interface with epoxy resin semi-interpenetrating network structure, which proves that graphene oxide doped in semi-interpenetrating network structure is relatively easy to loss.

For the study the influence of semi-interpenetrating network structure on the thermal decomposition characteristics of SPEEK membrane, three kinds of SPEEK/epoxy/graphene oxide semi-interpenetrating network membranes and corresponding SPEEK/epoxy/sulfonated graphene oxide membranes were compared. TG curves analysis are shown in figure 5. Epoxy resin and a semi-interpenetrating network SPEEK membranes have several stages of thermal weightlessness. 150-300 °C weight loss is mainly the molecules bound water evaporate within the membrane. 300-450 °C of weightlessness is mainly cracking of C-S key for benzene sulfonic acid and sulfonated sulfonic acid groups on the graphene oxide. And a small amount of pyrolysis and decomposition caused by cross-linked epoxy resin. Above 400 °C weightlessness is mainly the thermal decomposition of rigid group.

Through the analysis of pyrolysis experiment data, it shows that the initial decomposition temperature of graphene oxide doped SPEEK membranes is about 100-150 °C, which is lower than the pure SPEEK membrane. The main reason could be that the space steric hindrance between long chain increases by introduction of the graphene oxide in sulfonated polyether ether ketone. The interaction force is abate and meantime hinder the formation of hydrogen bond, which caused the decrease of initial decomposition temperature. Therefore, SPEEK/epoxy/graphene oxide membranes has lower initial decomposition temperature. But the initial weight loss temperature of semi-interpenetrating network SPEEK membranes is relatively high and reached above 150 °C. The crosslinking network covered smaller sizes of solid particles in the process of heating, therefore the solid residue rate is higher. In addition, the comparison of figure curves shows that the thermal properties of the proton exchange membrane increasing with the increase of epoxy resin semi-interpenetrating network [20]. The more crosslinked network structure, the more SPEEK long chain and graphene oxide particles covered and overall improved the thermal performances of semi-interpenetrating network membranes.

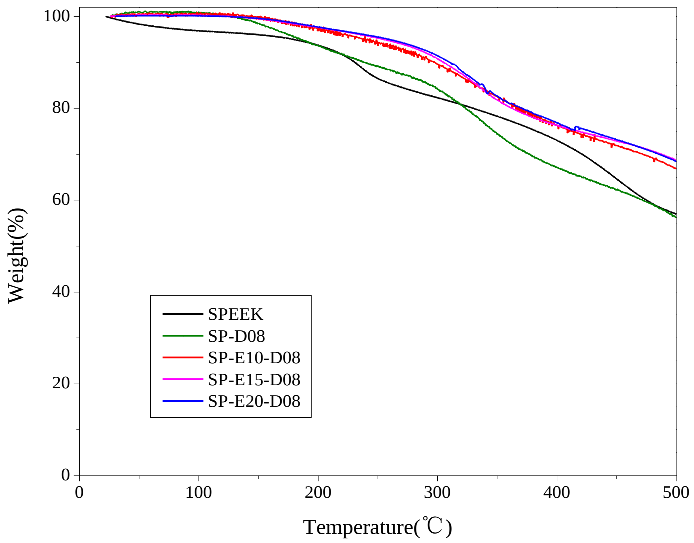


Figure 5. TG curves of SPEEK/epoxy/graphene oxide membranes

As a factor to measure of proton exchange membrane, proton conductivity has become a basic and necessary indicators to evaluate proton exchange membrane. Expected to exploit a membrane to replace the Nafion, which must study its proton conductivity and to be excellent. After soaking in deionized water for 24 h, using two electrode method simulate fuel cell which was made in the laboratory to obtain the relationship of conductivity with temperature relative humidity under 100%. Figure 6 is the curve of proton conductivity changing with temperature of pure SPEEK and SPEEK/graphene oxide membranes. The figure shows that compared with the pure SPEEK, SP-D05, SP-D08 and SP-D10 membranes guide protons performance fall later after rising first. It is worth mentioning that the proton conductivity of three membranes were higher than 10 S·cm^{-1} above 60 °C, specially SP-D08 membrane. It arrived 10 S·cm^{-1} at 40 °C. The proton conductivity reached maximum 5.85 x 10 S·cm^{-1} at 90 °C. This is because that little sulfonic acid groups in pure SPEEK, which are not form continuous ion cluster channels. So the proton conduction is mainly relies on the H_3O^+, $H_5O_2^+$ and $H_9O_4^+$ transmission in water medium. The introduced of sulfonic acid group by doping modified sulfonated graphene oxide to form a convenient transport channel and increase the proton conductivity. But the trend is not a linear growth with the increase of the doping amount. When the doping amount reaches 10 wt.%, a 'blocking effect' was appeared [21-22]. That too much sulfonated graphene oxide particles will hinder the movement in ion channels along polymer chain, thus the proton conductivity decreased. So SP-D08 membrane is considered as the most promising proton conduction membrane.

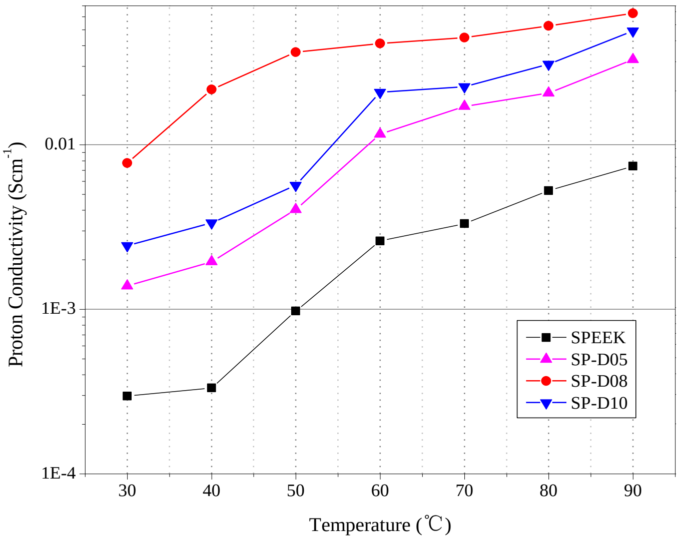


Figure 6. Proton conductivity of SPEEK/graphene oxide membranes vs temperature from 30 ºC to 90 ºC

According to the conducting proton performance of doping modification, 8 wt.% of semi-interpenetrating network SPEEK/epoxy/graphene oxide proton exchange membrane was synthesized. AC impedance method is used to further measured SP-E-D08 series guide protons performance of proton exchange membrane along with the change of temperature under the simulation environment of 100% relative humidity, the curves are shown in figure 7.

The figure 7 shows that the protons conductivity of SP-E-D08 proton exchange membrane was higher than pure SPEEK membranes. The proton conductivity increases with the rising of temperature. When the temperature rose to 70 °C, its proton conductivity are more than 10 S·cm^{-1}. In figure 7, the proton conductivity of SP-E-D08 series of proton exchange membrane has no significant decline compared to SP-D08. It is proves that the introduction of epoxy resin didn't destroy the ion channels formed by sulfonated graphene oxide. The protons conductivity is declined with the increase content of epoxy resin semi-interpenetrating network, but not obvious, especially at the temperature 90 °C. It is could be that epoxy increased the crosslinking density of proton exchange membrane, the water swelling resistance of the membrane is improved and the sulfonic acid groups formed by ion clusters had not bigger impact [23]. So as to avoid the lower of protons conductivity by structure loose at high temperature.

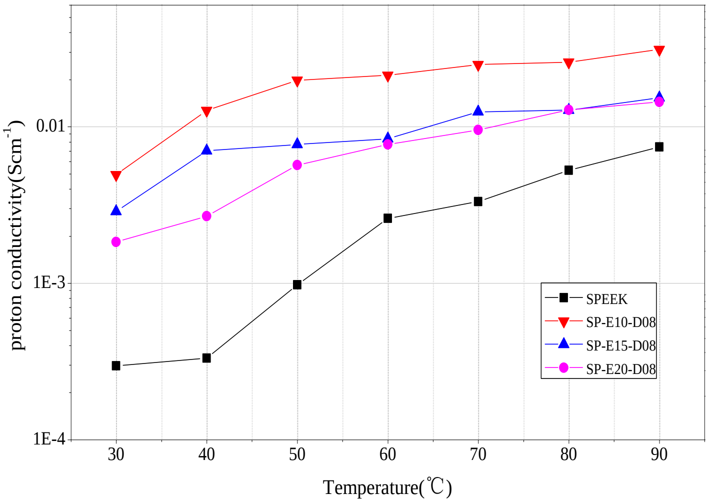


Figure 7. Proton conductivity of SPEEK/epoxy/graphene oxide membranes vs temperature from 30 °C to 90 °C

Using GC9800 gas chromatograph to test the methanol permeability of pure SPEEK and SPEEK/epoxy/graphene oxide semi-interpenetrating network membranes under homemade diaphragm diffusion device, the relationship of methanol permeability concentration changing with time is shown in figure 8 [24].

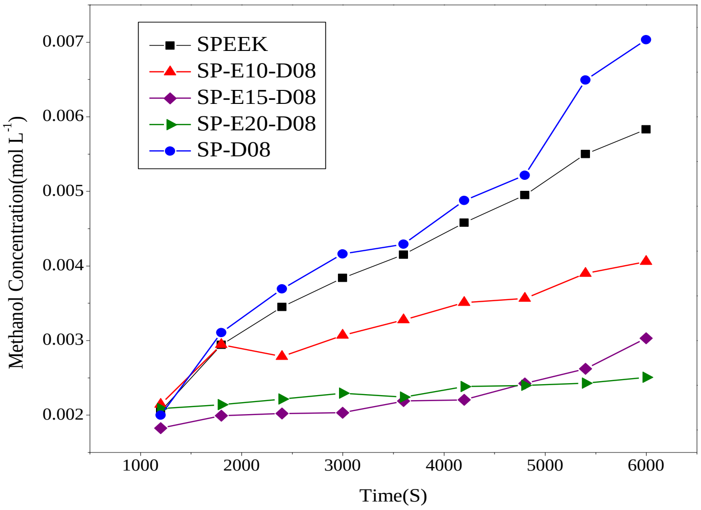


Figure 8. Methanol concentration of SPEEK/epoxy/graphene oxide membranes vs time

Figure 8 shows that the penetration of methanol concentration gradually increased with the increase of the time. The methanol permeability of SP-D08 proton exchange membrane is slightly lower than the pure SPEEK membrane. It may be due to the skeleton osteoporosis of proton exchange membrane by doping. The methanol permeability concentrations of SP-E-D08 series proton exchange membranes were lower than pure SPEEK and changed over time is relatively slow. But the pure SPEEK changes faster over time. Comparison with SP-E-D08, the methanol permeability concentration of SP-E10-D08 is relatively close to pure SPEEK proton exchange membrane. The concentration of methanol permeability decreases with the increase of epoxy resin, the methanol permeability concentration of SP-E15-D08 and SP-E20-D08 proton exchange membranes are relatively close. SP-E15-D08 has stable hydrophobic skeleton and not formulate a larger degree of stability of hydrophobic skeleton activities with the increase of epoxy resin content.

To SP-D08 semi-interpenetrating network proton exchange membrane, methanol permeability is decreased with the increase of epoxy resin crosslinking. The methanol permeability coefficient of SP-E15-D08 and SP-E20-D08 modified membranes achieved 10^{-8} cm^{-2}/S and increased two orders of magnitude compared to the Nafion membrane. SP-E-D08 series proton exchange membranes showed better performance of methanol permeability. Epoxy cross-linking components significantly reduce and SPEEK skeleton absorb moisture capacity effectively increase, the synergy of two kinds polymers to increase the mechanical stability performance, effectively improve the methanol permeability of membranes. The doped sulfonated graphene oxide played a "block" which decrease the diameter of the hydrophilic channel effectively [25].

Swelling degree of pure SPEEK membrane and doped SPEEK/epoxy/graphene oxide semi-interpenetrating network membranes vs temperature are shown in figure 9. Under the environment of 90 °C high temperature, the water absorption and swelling degree of sulfonated graphene oxide doping SPEEK membranes increased significantly and reached twice more than pure SPEEK membrane. High water absorption and swelling degree will lead to a weakened interaction between polymer chains, so as to make the structure of the membrane is loose and affected dimension stability. Combined with the proton conductivity analysis, the decline of proton conductivity rate may be due to excessive water and ion clusters disappeared by phase separation affected at the high temperature. More sulfonic acid groups provide a large number of springboard for proton conduction, but also there is no denying that the higher the hydrophilic is like a nest bursts to affect the use of the proton exchange membrane. Epoxy resin semi-interpenetrating network increase the interaction of two polymers and reduce the excessive absorption of water molecules by doping SPEEK sulfonic acid groups [26]. But the doped sulfonated graphene oxide outflow easily and the membrane structure still exists problems such as non-densification, which are not only semi-interpenetrating network can fully resolved.

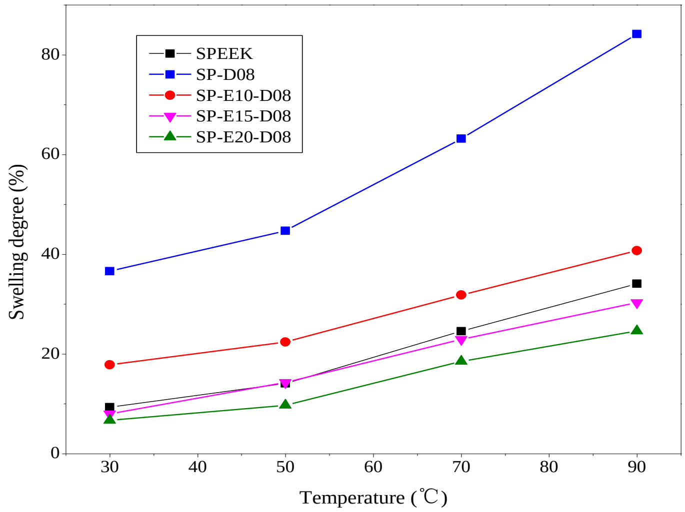


Figure 9. Swelling degree of SPEEK/epoxy/graphene oxide membranes vs temperature from 30 °C to 90 °C

4. CONCLUSIONS

The SPEEK composite membranes with 68% DS were prepared by post-sulfonation. Using diethylenetriamine as the epoxy cross-linking agent, which is uniformly distributed in the grafted SPEEK, to form SPEEK/epoxy semi-interpenetrating network structure and explore the impact of semi-interpenetrating network on the performances as proton exchange membrane. Graphene Oxide was synthesized according to Hummers method and organic in γ-chloropropyl triethoxysilane. Finally, kinds of SPEEK/epoxy/graphene oxide proton exchange membranes were prepared. Using FTIR, TG and SEM analysed the structures, thermal performences and morphology of the semi-interpenetrating network structure. The semi-interpenetrating network structure was proved by FTIR, SEM analysis. TG analysis shows that semi-interpenetrating network structure could effectively improve the initial decomposition temperature and strengthen the thermal stability of the membranes. Graphene oxide is introduced on the sulfonic acid groups and formed a convenient transport channels which caused the proton conductivity increased. But the trend is not a linear growth with the increase of the doping amount, when the doping amount reaches 10 wt.%. A 'blocking effect' was formed. Too many graphene oxide particles will interdicted the movement of ion channels in the long polymer chains, thus the proton conductivity decreased. SP-D08 membrane shows better performance of methanol permeability. The crosslinking of epoxy resin is significantly reduce SPEEK skeleton to absorb moisture capacity and increase the synergy of two kinds of polymers, thus increase the mechanical stability and improve the methanol permeability. Graphene oxide as the 'blocking effect' will effectively decrease the diameter of the hydrophilic channel. Epoxy resin and semi-interpenetrating network can effectively improve the water absorption and swelling degree of doping membranes.

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