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Electrochemical Properties of SPEEK/Epoxy Semi-interpenetrating Network Composites as Proton Exchange Membrane

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The DS 68% SPEEK composite membranes with were prepared by post-sulfonation. Using diethylenetriamine as the epoxy cross-linking agent, which is uniformly distributed in SPEEK, to form SPEEK/epoxy semi-interpenetrating network structure and explore the impact of semi-interpenetrating network on the performances as proton exchange membrane. The contents of epoxy resin are 10 wt.%, 15 wt.% and 20 wt.%, respectively. The thermal properties of the proton exchange membranes are increases with the increase of crosslinking structure of epoxy resin. But the conductivity proton performances are slightly declined with the increase of semi-interpenetrating network. Crosslinking increased the density of proton exchange membrane, improved the anti-water swelling property and avoided the proton conductivity rising slowly at high temperature. With the increases of epoxy resin, the methanol permeability coefficient decreases.

Keywords: Electrochemical properties, SPEEK, epoxy resin, semi-interpenetrating network

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 the inevitable trend of scientific research. With the 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, the 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 are many kinds of, but the key is how to apply them to proton exchange membrane after processing used in fuel cell. 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, DS 68% SPEEK composite membranes were prepared by post-sulfonation. Using diethylenetriamine as the epoxy cross-linking agent, which is uniformly distributed in SPEEK, to form SPEEK/epoxy semi-interpenetrating network structure and explore the impact of semi-interpenetrating network on the performances as proton exchange membrane..

2. EXPERIMENTAL SECTION

2.1 The preparation of SPEEK/epoxy semi-interpenetrating network membranes

The trituration of pure SPEEK is dissolved into dimethylacetamide solvent to made a 10 wt.% solution. According to Table 1, taking a suitable amount of epoxy resin dissolve in dimethylacetamide solution with 1:20 scale, and then one-time added to SPEEK solution. Ultrasonic dispersion for 6 h. Adding divinyl three amine curing agent and stirring for 20 h at room temperature, then heated the temperature to 150 °C and reacted 30 min to form a uniform membrane fluid. Using the film casting method, 10 ml solution was poured into a glass cavity and dry under 60 °C for 12 h, then heat up to 100 °C for 4 h. Removing the solvent and 10 wt.%, 15 wt.% and 20 wt.% quality percentage membrane samples were obtained. And there are marked as SP-E10, SP-E15 and SP-E20, accordingly. The thickness of dry film is about 100 microns.

Table 1. Codes of composite membranes specimens

CODE	SPEEK (wt.%)	Epoxy resin (wt.%)
SPEEK	100	0
SP-E10	90	10
SP-E15	85	15
SP-E20	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, FT - IR) 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. Nitrogen protection, traffic: 60 ml/min. Sample specifications: 5-10 mg. Heating rate: 10°C/min. Scope of temperature: room temperature to 600 °C.

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 Solartron 1287 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 GC 9800 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 chemical structural characterization of SPEEK/epoxy resin semi-interpenetrating network for proton exchange membrane (SP-E10) was detected by FTIR, and the spectra are shown in figure 1. It can be observed that SPEEK characteristic peaks appear in the cruve, which is indicated that SPEEK structure did not change with epoxy resin curing. In addition, two absorption peaks are notability. 950 cm^{-1} due to the characteristic absorption peak of epoxide group. 1750 cm^{-1} due to the characteristic absorption peak of ester group. It is prove that the epoxy resin has solidified and SPEEK/epoxy resin semi-interpenetrating network was formed.

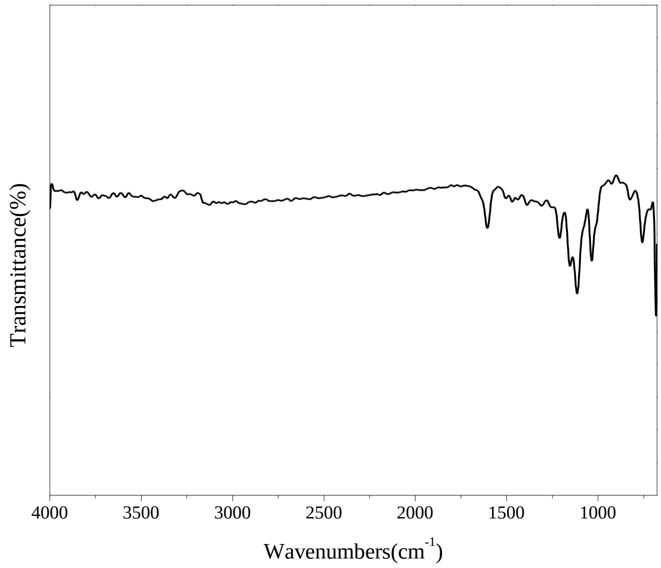

Figure 1. The FTIR spectrum of SPEEK/epoxy semi-interpenetrating network membrane

The surface microstructure of SPEEK/epoxy resin semi-interpenetrating network proton exchange membranes are shown in figure 2. Figure 2 (a)-(d) are 5000 to 30000 times magnification of SEM microscopic images of SP-E15 sample.

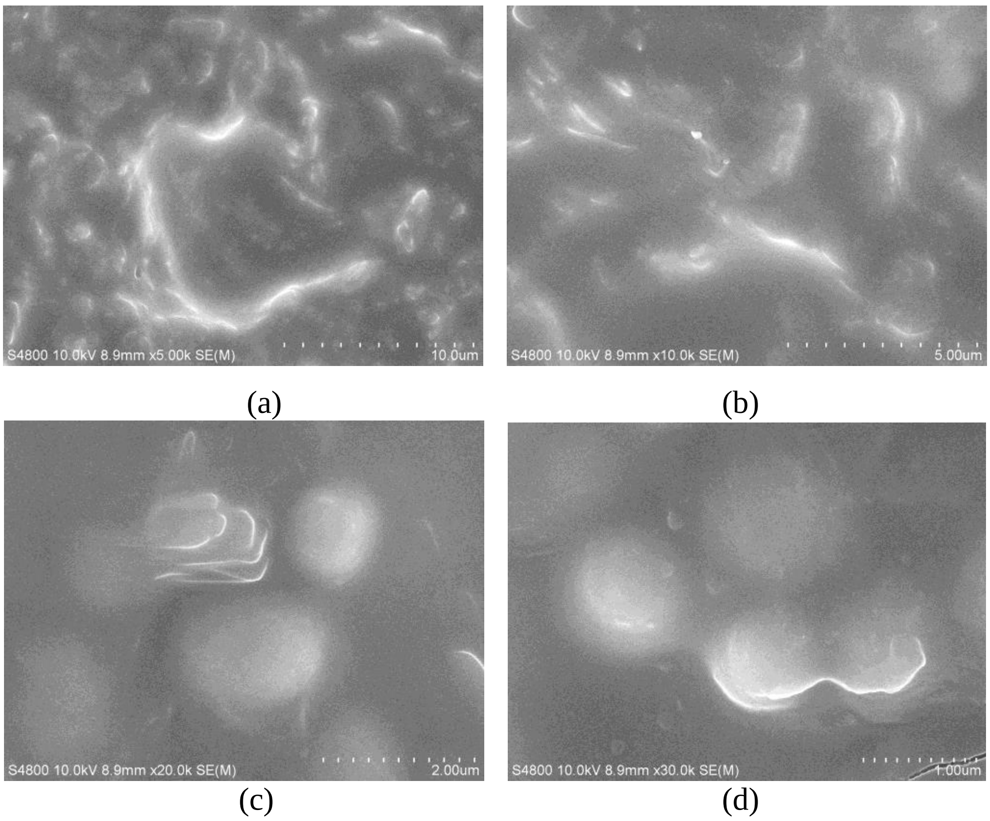

Figure 2. Morphology of SP-E15 SPEEK/epoxy semi-interpenetrating network membrane in different magnification: x5000, x10000, x20000 and x30000

The figure 2 shows that the surface of SP-E15 membrane is without apparent phase separation, and appear white composition which are two kinds of materials to produce different signals. Because of there are a large number of polar groups in epoxy resin close contact with SPEEK segments in the forming process, which are caused adhesion between two contact matrix. After dealing with crosslinking, a continuous phase area was formed. Figure 2 (c) and (d) can be observed that the separation of two kinds of polymer interface is not obvious, but the presence of granular material, and the grain boundaries are not very clear. It proves that SPEEK exist independently and surrounded by partially crosslinked epoxy resin to form semi-interpenetrating network structures. Because of the package, it is can effectively increase the thermal stability of membranes at the same time of saving some original properties of the SPEEK. These are consistent with the FTIR spectra of SPEEK still exists and crosslinking with epoxy resin [18].

As semi-interpenetrating network structure were synthesized to study the influence of the thermal decomposition characteristics of SPEEK membrane, and three kinds of SPEEK/epoxy resin semi-interpenetrating structure corresponding to pure SPEEK membrane by thermogravimetric analyzer. The analysis results of TG curves are shown in figure 3. The figure shows that pure SPEEK membrane exist thermal decomposition at room temperature to 150 °C. SPEEK has a trace of weightlessness, which are mainly the molecules bound water evaporate within the membrane. The range of 250-350 °C is initial thermal decomposition phase for pure SPEEK membrane. It is mainly containing the decrease of C-S bond energy of sulfonic acid groups on the benzene ring, taking faults and then break away from sulfonic acid group [19]. When the temperature exceeds 400 °C, the aggregation owner chain cracking.

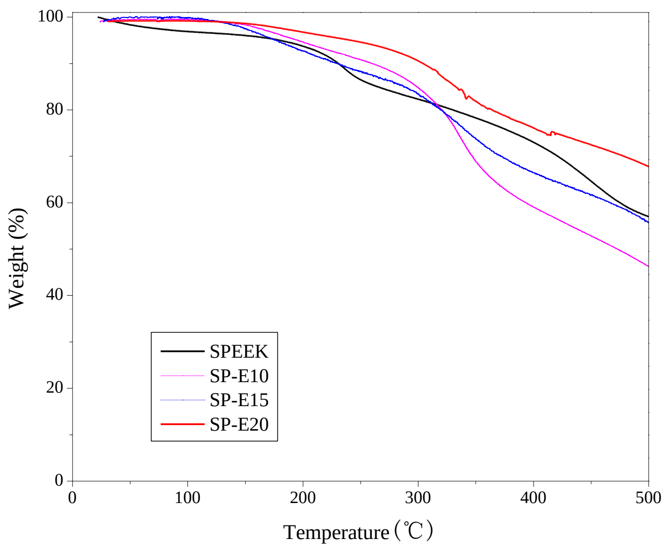

Figure 3. TG curves of SPEEK/epoxy semi-interpenetrating network membranes with different epoxy contents

The figure 3 shows that the weightlessness of semi-interpenetrating network SPEEK/epoxy resin membreans (SP-E10, SP-E15, SP-E20) are mainly the water molecules and solvent residue in

100-300 °C. Within the range of 300-400 °C, material weight loss is bigger. Its thermal decomposition is divided into the following stages: 100-200 °C weightlessness is mainly the undried water or volatilization of residues small molecules. The 300-400 °C weightlessness is mainly the decrease of C-S bond energy of sulfonic acid groups on the benzene ring, taking faults and then break away from sulfonic acid group. Above 400 °C, the thermal decomposition of is mainly the weightlessness of main chain rigidity groups. More curve in the figure, the thermal properties of the proton exchange membrane increases with the increase of content of epoxy resin crosslinking structure below 350 °C. That indicated that the more crosslinked network structure, the more covered SPEEK long chain, and improved the thermal performance of semi-interpenetrating network membrane [20]. The initial decomposition temperature of SPEEK/epoxy resin semi-interpenetrating network proton exchange membrane was increased up to 300 °C. Analysis of the causes may be at the beginning of the thermal decomposition, semi-interpenetrating network crosslinking polymer covered on the surface of the polymer that make a decompose shielding effect. Effectively prevent heat transfer between hydrophilic and hydrophobic phase, protect the substrate material and delay its continue to break down. The other semi-interpenetrating network makes the polymer structure more compact and lead to more neat and orderly. The initial decomposition temperature is higher, the potential energy to damage structure is the bigger. The using temperature of proton exchange membrane is around at 90 °C, priority should be given to less decomposition at 200-350 °C. The solid retention rate of semi-interpenetrating network proton exchange membrane were higher than excluding crosslinking system above 350 °C, which is expected to be used as proton exchange membrane materials.

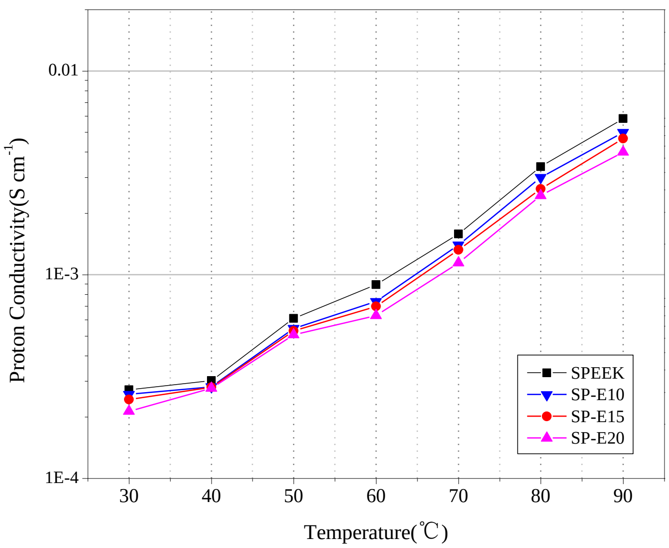

Figure 4. Proton conductivity of SPEEK/epoxy semi-interpenetrating network membranes vs temperature

Before testing, immersed SP-E membrane samples into a concentration of 1 mol/L HCl solution 6 h for protonation, and then repeatedly washed with deionized water to neutral. Using electrochemical workstation to test the impedance and generation and induced into the formula of relation with temperature, the electrical conductivities are shown in figure 4. The figure shows that all the proton conductivity of membrane increases with the rising of temperature, but the size of amplification are differences. The proton conductivity of all semi-interpenetrating network membranes guide protons are lower than that pure SPEEK membrane below 90 °C. When the temperature is up to 90 °C, the proton conductivity of SP-E10 membrane is 7.12×10^{-3} $S\cdot cm^{-1}$, which is close to the pure SPEEK but less than 10^{-2} $S\cdot cm^{-1}$. Along with the increase of the semi-interpenetrating crosslinked content, the proton conductivity performance of modified membrane is declined. SP-15 and SP-E20 have the same charts.

The semi-interpenetrating network by epoxy cross-linking has a hindering effect to protons conductivity performance of SPEEK/epoxy proton exchange membrane, but affects is small. The best conducting proton performance is SP-E10 membrane as similar to pure SPEEK. Crosslinking modification of epoxy resin on the proton conductivity performance is not obvious. Crosslinking increases the density of proton exchange membrane and has a good improvement to the water swelling resistance of the membrane in order to avoid conducting proton performance rising slowly by the structure loose of pure SPEEK membrane at high temperature [21].

The methanol concentration of SPEEK/epoxy semi-interpenetrating network membranes vs temperature are shown in figure 5. From figure 5, the methanol infiltration concentration of proton exchange membrane is gradually increased with the time increase. The methanol permeability concentrations of SP-E series of proton exchange membrane were lower than pure SPEEK membrane, and relatively slow over time. But pure SPEEK changes faster over time. Contrast the methanol-resistance performance of SP-E series of proton exchange membrane, the methanol osmotic concentration of SP-E10 is relatively close with pure SPEEK proton exchange membrane. With the increase of epoxy resin content, the methanol concentration permeability decreases. When the content of epoxy resin crosslinking is from 15 wt.% to 20 wt.%, the methanol osmotic concentration variation do not obvious increase with 10 wt.% to 15 wt.%.

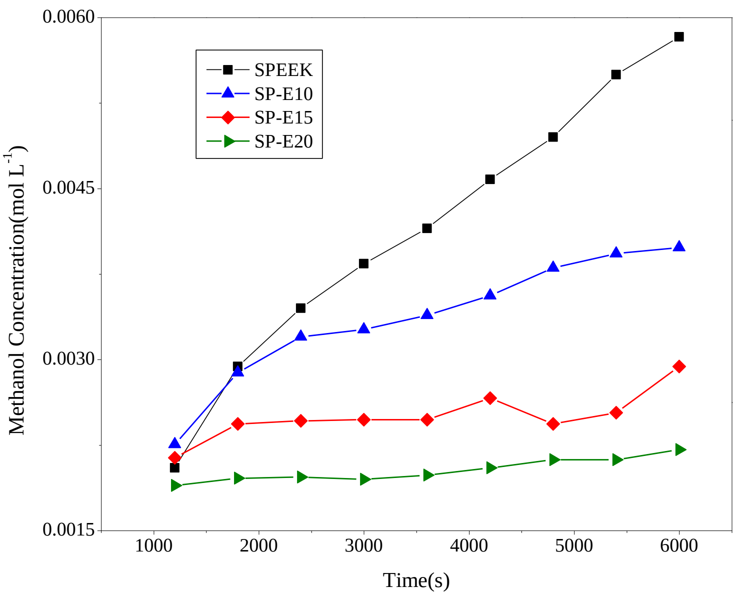

Figure 5. Methanol concentration of SPEEK/epoxy semi-interpenetrating network membranes vs temperature

The methanol permeability coefficient of DS 68% SPEEK is 1.295×10^{-7} $cm^2\cdot s^{-1}$. With the increase content of the crosslinking epoxy resin, the methanol permeability coefficient is less. The methanol permeability coefficient of SP-E15 and SP-E20 two modified membrane achieves 10^{-8} $cm^2\cdot s^{-1}$, and increase two orders of magnitude compared to the Nafion membrane [22]. SP-E series membranes show good resistance performance of methanol permeability for the epoxy resin crosslinking components significantly reduce SPEEK skeleton's ability to absorb water and effectively increase the synergy of two kinds of polymer. That are all increase the mechanical stability and methanol permeability of membrane performance.

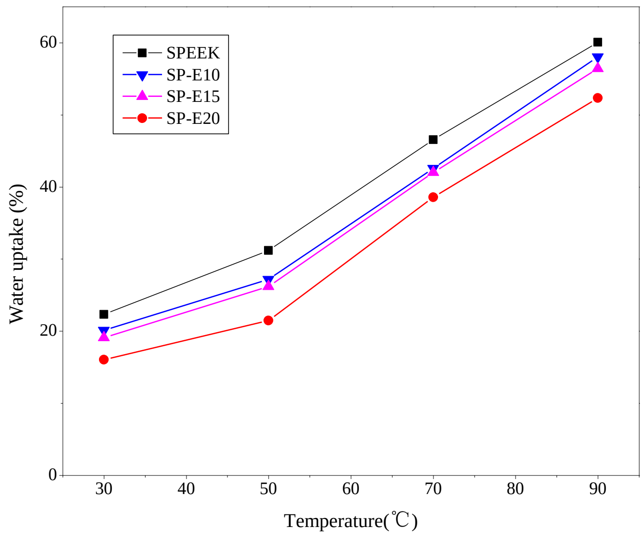

Figure 6. Water uptake of pure SPEEK membrane and SPEEK/epoxy semi-interpenetrating network membranes vs temperature

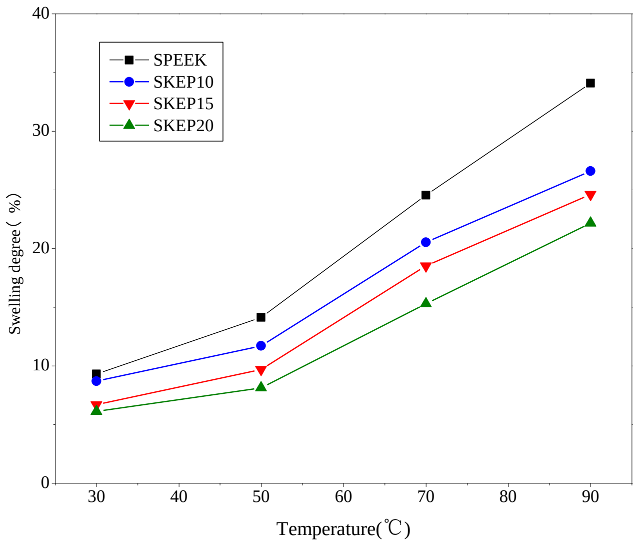

Figure 7. Swelling degree of SPEEK/epoxy semi-interpenetrating network membranes vs temperature

The Water uptake of pure SPEEK membrane and SPEEK/epoxy semi-interpenetrating network membranes vs temperature are shown in figure 6, 7. From figure 6 and 7, it is indicated that the water absorption and swelling degree were rised with temperature. Compared with the pure SPEEK membranes, the bibulous rate of SP-E series membranes show slightly change, especially epoxy resin content up to 20 wt.%. The figure shows that the water absorption and swelling degree of SP-E series membrane were closed to pure SPEEK membranes and the bibulous rate is 58.02% at 90 °C. The highest swelling degree of SP-E10 membrane was 27.6%. It should benefit from the network of divinyl three amine and epoxy resin through SPEEK. The structure increases the interaction between two kinds of polymers and reduces the excessive absorption of water molecules by sulfonic acid groups on the SPEEK segments. Effective control the water retention of proton exchange membrane [23].

The water absorption and swelling degree of proton exchange membrane were controlled by the number of sulfonic acid group and the crosslinking interaction between polymer segments. The sulfonic acid groups can increase the space steric hindrance which was leading loose areas in the membrane structure and excessive infiltration of water molecules. Semi-interpenetrating network can prevent excessive moisture penetration, control its content and crosslinking degree, and effectively restrain loose structure caused by excessive water absorption. There are significantly increase the service life and in addition to have no effect on the loss of proton conduction.

4. CONCLUSIONS

The 68% DS 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 impact of semi-interpenetrating network on the performances as proton exchange membrane. That covered with crosslinked network structure. The more semi-interpenetrating network improved the thermal performance of membranes. Along with the increase contents of semi-interpenetrating network crosslinked modified, the conductivity proton performance is slightly declined. Crosslinking modification by epoxy resin on the proton conductivity performance of membrane is not obvious. Crosslinking increased the membrane density and the water swelling resistance of the membrane has a significantly improvement. Crosslinking increases the density of proton exchange membrane and has a good improvement to the water swelling resistance of the membrane in order to avoid conducting proton performance rising slowly by the structure loose of pure SPEEK membrane at high temperature. The methanol permeability concentrations of SP-E series of proton exchange membrane were lower than pure SPEEK membrane, and relatively slow over time. Semi-interpenetrating network can prevent excessive moisture penetration, control its content and crosslinking degree. The structure increases the interaction between two kinds of polymers and reduces the excessive absorption of water molecules by sulfonic acid groups on the SPEEK segments, which can effectively improve structure to significantly higher service life.

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