

Preparation and Properties of SeO₂ and PWA Binary Compound Doped SPEEK Proton Exchange Membranes

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Herein, we prepared proton exchange membranes by adding SeO₂ and phospho-wolframic acid (PWA) into DS 85 wt% sulfonated polyether ether ketone (SPEEK). The result indicates that their proton conductivity is increasing without decrease of their methanol permeability. SeO₂ has a "V" type of lattice which provides favorable channels for proton transfer. The structures of composite membranes had changed in the chemical reactions. The characteristic peaks of Keggin in PWA appeared in infrared spectrum, but some peaks disappeared in X-ray diffraction pattern. Moreover, the result reveals that their proton conductivities is gradually increasing. After treated with an 8 T high magnetic field at 120°C for 10 h, the composite membranes showed anti-magnetic property. The thermal performance of composite membranes with SeO₂ and PWA molar ratio of 2:1 increased obviously.

Keywords: Electrochemical properties, SeO₂, PWA, Binary compound doped

1. INTRODUCTION

In order to promote the green development, cyclic development and low-carbon development deemed as the main task, which improves the energy utilization rate and promote the clean energy development, have become the inevitable trend of scientific research. Direct Methanol fuel cell (DMFC) is a high-efficiency power generation device that directly converts chemical energy into electrical energy with energy conversion efficiency of about 70%. The byproducts of energy transformation are mainly water and carbon dioxide (CO₂) without any pollution. It is obvious this strategy exhibits some advantages in environmental protection, energy saving and high efficiency in energy storage[1-3].

Proton exchange membrane fuel cells (PEMFCs) have attracted increasing attention because of their special properties, such as lower temperature characteristics. Considering its features of few chemical hazards to the human body and even harmless to the environment, it is suitable for wide applications in daily life. [4]. Triad membrane electrode (TME) is the core component of PEMFC, which combined by negative, positive electrode and proton exchange membrane with hot pressing [5-6]. Scientific researchers have never stopped the study of proton exchange membranes in the long-term exploration of PEMFC. From the point of materials applications, proton exchange membranes as the core element of TME are mainly from the aspects of conducting proton property, chemical stability and mechanical properties. In the late 1960's, polystyrene sulfonic acid membrane had been used in PEMFC [7]. However, styrene sulfonic acid as a proton exchange membrane material still has some serious drawbacks, for example, it is prone to degradation during use, which directly leads to shortened battery life and reduced power density, and causes the formation of water in the battery to be contaminated leading to limit application in astronauts. With the progress of science and technology, fuel cell technology is constantly updated, and the development of proton exchange membrane fuel cell is durability test of the proton exchange membrane. Until now, the most commonly used proton exchange membrane (PEM) is still the perfluorinated sulfonic proton exchange membrane (Nafion) produced by Du Pont Company in 1962. Although the Nafion membrane solves many problems with the styrene sulfonic acid proton exchange membrane, it still increases the service life of the fuel cell. Besides, the research and development of fuel cell technology have not been popularized for decades. In addition to the well-known stability, it has also been urged on such issues as durability and high cost, which are bottlenecks encountered in commercialization. To actively develop new materials is the only way to solve this big challenge, which is also the hotspot of proton exchange membrane fuel cell research [8-9].

At present, materials used as proton exchange membrane materials are mainly divided into perfluorinated sulfonic acid and the fluorine-free sulfonic acid. Fluorine-free sulfonic acid membrane not only low cost, but also the environmental pollution is relatively small, is the proton exchange membrane development trend [10]. Among many fluorine-free sulfonic acid membrane materials, SPEEK geomembrane has attracted much attention due to its excellent diamagnetic resistance, excellent mechanical properties, good thermal properties and high electrical conductivity. The proton conductivity of SPEEK membranes with moderate, high mechanical strength, thermal stability, relatively low cost and the methanol permeability coefficient is lower than that of current commercial Nafion membrane, which is considered to be a relatively potential candidates to replace nafion membrane materials. Currently, the study of sulfonated polyether ether ketone has preliminary results from synthetic to modification are the hot research topic. However, it is almost possible to achieve ideal level because of the guide protons and resistance performance of alcohol limit [11-15]. SeO_2 has the different lattice structures with PWA, which provides the different mechanism for the proton conduction.

In this paper, the SPEEK composite membranes with DS of 85% were prepared with binary doping SeO_2 improving its methanol resistance and anti-swelling property and and PWA increasing the proton conductivity. Through the treatment of an 8T high magnetic field for 10 h at 120°C to study the properties of proton exchange membrane of composite membranes.

2. EXPERIMENTAL SECTION

2.1 The preparation of binary doped membranes

The trituration SPEEK85 resin soluble in DMAc solvent to mixture 10 wt.% solution. Stir in size 100 nm SeO_2 and powder for 24 h to make SeO_2 dispersed evenly in the SPEEK solution. Then, a certain amount of acetone and PWA were added, stirring the membrane liquid for 2-4 h and ultrasonic treatment for 1-2 h, making SeO_2 and PWA dopant further evenly dispersed in the liquid system of SPEEK membranes. The molar ratio of SeO_2 and PWA are 1:1 and 2:1 respectively, and the total amount of doping respectively 5 wt.%, 10 wt.% and 15 wt.%. Using pipette measured 13 ml of liquid membrane and casting in a clean glass to cavity flow film, and drying under 50°C for 24 h. After drying for 4 h under 120°C and natural cooling to room temperature, a small amount of deionized water in the vitreous cavity was introduced to open the membrane with a dry film thickness of about 200 microns. The codes of membranes were described in Table 1.

Table 1. Codes of composite membranes specimens

Code	SPEEK (wt.%)	SeO_2 (wt.%)	PWA (wt.%)	Strong Magnetic Field (8T)
SP	100	0	0	-
SP- SeO_2	99	1	0	-
SP-S1P4	95	0.7	4.3	-
SP-S0P5	95	0.4	4.6	-
SP-S1P9	90	0.7	9.3	-
SP-S2P8	90	1.4	8.6	-
SP-S1P14	85	1.1	13.9	-
SP-S2P13	85	2.0	13.0	-
SP-S1P4-PE8	95	0.7	4.3	Perpendicular
SP-S0P5-PE8	95	0.4	4.6	Perpendicular
SP-S2P8-PE8	90	1.4	8.6	Perpendicular

2.2 Strong magnetic field treatment of the membrane sample

Using the superconducting Magnetic Field generator (Oxford Instruments, UK), SP composite membranes were put into an 8 T strong magnetic field sample storehouse and evenly distributed under 100°C for 1h. The direction processing field and membrane plane is 90° as vertical relationship as shown in figure 1. The arrows represent the magnetic field direction.

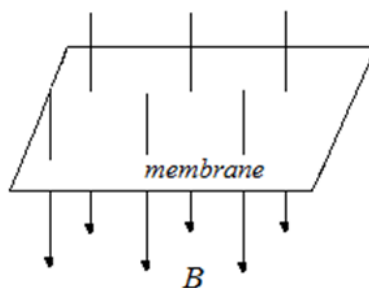


Figure 1. Directional processing field and film surface vector relationship

2.3 The mainly characterization and testing

Fourier transform infrared (FTIR) spectra of proton exchange membrane structure characterization will first mix the samples with KBr powder through dry processing, on the basis of Beer-tablet of Lambert's law to make it 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 $500\text{-}4000\text{ cm}^{-1}$.

Wide-angle X-ray scattering measurements (XRD) were performed on a Bruker AXS-D8 Avance X-ray diffractometer with a copper target (40 kV, 40mA).

Varying temperature system of low field Nuclear Magnetic Resonance (LF-NMR, Shanghai new McLaren electronic technology co., LTD.), water probe method was used to analyze the doping the water distribution within the membrane. Resonance frequency 21.800 MHz, 0.51 T magnet strength, probe coil diameter 10 mm. First immersed the membrane samples in distilled water for 24 h, remove surface moisture on filter paper, after the film sample into the bottom of 10 mm tube. The sealing tube mouth was tested in 35°C magnet box, using hard CPMG pulse sequence sampling. The index law and attenuation curves of sampling and multiple index model and wheat marquardt method and optimum algorithm of film sample CPMG on attenuation curve fitting and optimization calculation, get the transverse relaxed Time (the Relaxation Time 2, T_2) Relaxation spectrum. After the sampling tube first came out, tube mouth is uncovered on sealing membrane in the 105°C magnet heating drying for 3 minutes, open the heat pump and sealing tube mouth in 35°C magnet box testing. Using hard CPMG pulse sequence sampling and sampling according to the index law of attenuation curve. Peel off the film sample tube mouth sealing membrane, heat and dry the magnet at 105°C , open the heat pump and then repeat the above operation to repeat sampling every 3 minutes, until all the moisture in the sample has left.

The LakeShore companies in the United States of 7407 type Vibrating Sample Magnetometer (Vibrating Sample Magnetometer, VSM) film sample of magnetization M with magnetic field intensity H of relations, namely the characterization of membrane M - H curve is used to Sample the magnetization characteristic. At room temperature, VSM electromagnet used magnetic field intensity H is about 1.8 T, film sample put in vibration sample rod low-end sample tank, will receive the strong magnetic field processing of the film sample and be tested in the direction of the magnetic field. For

accurate characterization of the magnetic, all test results are minus the test device substrate diamagnetic semaphore.

Proton conductivity of membrane specimens in the traverse direction was measured in a measurement cell using an AC Electrochemical Impedance Spectroscopy, which consisting of a Solartron Instruments 1287 electrochemical interface and a Solartron Instruments 1255 B frequency response analyzer (UK) [16]. The EIS recorded over a frequency range is $1-10^6$ Hz. Before the tests, all membrane specimens were abundantly immersed in 1 mol/L hydrochloric acid solution for 24 h then rinsed with de-ionized water for several times. Consequently, resistance of membranes was measured and proton conductivity was calculated as described.

3. RESULTS AND DISCUSSION

A thermo Nicolet 6700 with ATR infrared spectrometer was employed to collect information. FTIR spectrum line of as-obtained samples are shown in Figure 2.

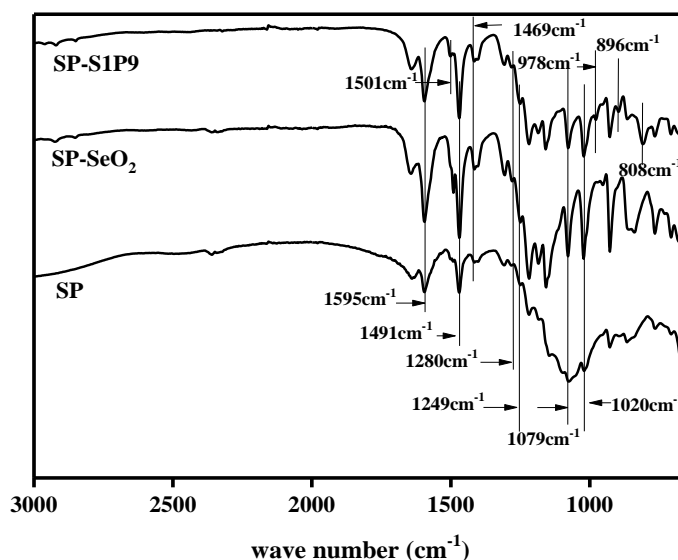


Figure 2. The IR spectra of SP, SP-SeO₂ and SP-L1P9

Three membrane specimens and 1280 cm^{-1} , 1079 cm^{-1} of punishment is O=S=O bond of symmetric and asymmetric stretching vibration peak, is 1249 cm^{-1} -Ar-O-Ar- groups of characteristic peak, is 1020 cm^{-1} S=O bond stretching absorption peak, show the same membrane matrix structure of the sample, it doesn't change due to the addition of dopant. In the SP-SeO₂ sample, the characteristic peak at 1252 cm^{-1} may be ascribed to the peak shift of -O- bond caused by rare earth oxide-doped SeO₂. The absorption peaks of SP and SP-S1P9 membrane samples in 1595 cm^{-1} , 1469 cm^{-1} and 1491 cm^{-1} is attributed to benzene ring, and SP-S1P9 film sample of characteristic peak at 1501 cm^{-1} , benzene ring may be sulfonic acid group and PWA caused by the interaction of SeO₂ [17]. The characteristic peaks at 978 cm^{-1} , 1079 cm^{-1} , 896 cm^{-1} and 808 cm^{-1} SP-S1P9 originated from keggin

characteristic peak belong to the PWA tetrahedron argument of oxygen (P-O) vibration, the argument of oxygen (W=Ot) vibration, bridge oxygen argument (W-Oc) and argument (W-Oe) vibration, respectively. And 1079 cm^{-1} is resulted from O=S=O bond symmetric stretching vibration peak, so it get relative spectral peak. Se-O spectral peak wave number was not within the scope of the testing, SeO_2 and the interaction is difficult to be observed[18].

SP film sample for typical amorphous diffraction peak, SP- SeO_2 , SP-S0P5-PE8 and SP-S1P4-PE8 membrane diffraction peaks of the sample (111), (200), (220), (311) and (222) are in accordance to the corresponding position of the diffraction peak SeO_2 . The doped film contains the crystal structure of SeO_2 . And it is not affected by the 8 T parallel magnetic field treatment, which is possible that SeO_2 and sulfonic acid groups form the coordination effect, and the crystal structure of the two-phase interface in the doped film has no influence. Besides, small changes in internal or membrane and is not reflected in the diffraction characteristic peak (Figure 3). When doped with membrane after vertical 8T magnetic field treatment, SP-S0P5-PE8 diffraction peak in the sample (211), (222), (400), (440) and (622), and SeO_2 database corresponding to the diffraction peak position of the perfectly. By 8T magnetic field vertical handle 4 h under 120°C , SP-S1P4-PE8 film sample of SeO_2 , according to the characteristics of diffraction peak again show that the molecular structure of the doped film inside change under strong magnetic field, form a range of SeO_2 small chip area [20].

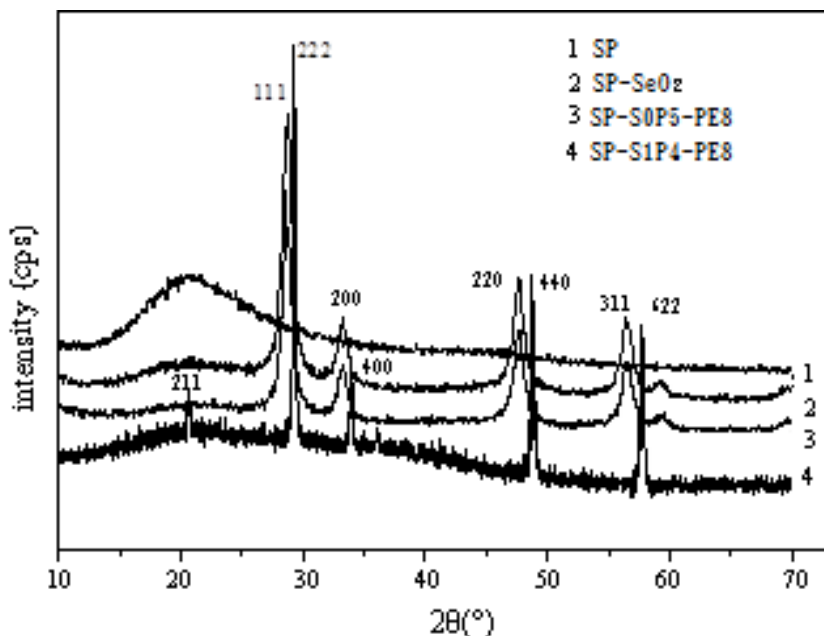


Figure 3. Diffraction characteristic peak of film sample

We use low field nuclear magnetic resonance (LF-NMR) device equipped with variable temperature system in variable temperature magnet box of binary mixed membrane samples to analyze samples. The obtained relaxation spectra of SP-S0P5 and SP-S1P4 film samples are shown in table 2. The relaxed time (time 2, T2) represents the size of the water molecules inside the film sample. Nuclear magnetic signal (amplitude, A) is a indicator of the unit mass binary mixed film sample moisture content.

Table 2. T₂ and A of membrane specimens

CODE	SP-S1P4	SP-S0P5
Relaxed time T ₂ (ms)	3.42	3.27
Nuclear magnetic signal A(p.u.)	22270.71	30786.78

The LF - NMR water probe method, and through the CPMG on attenuation curve fitting and optimization calculation, get dual doped film sample of T₂ relaxation time and nuclear magnetic signal of A curve as shown in figure 4, the abscissa is logarithmic, ordinate is numeric.

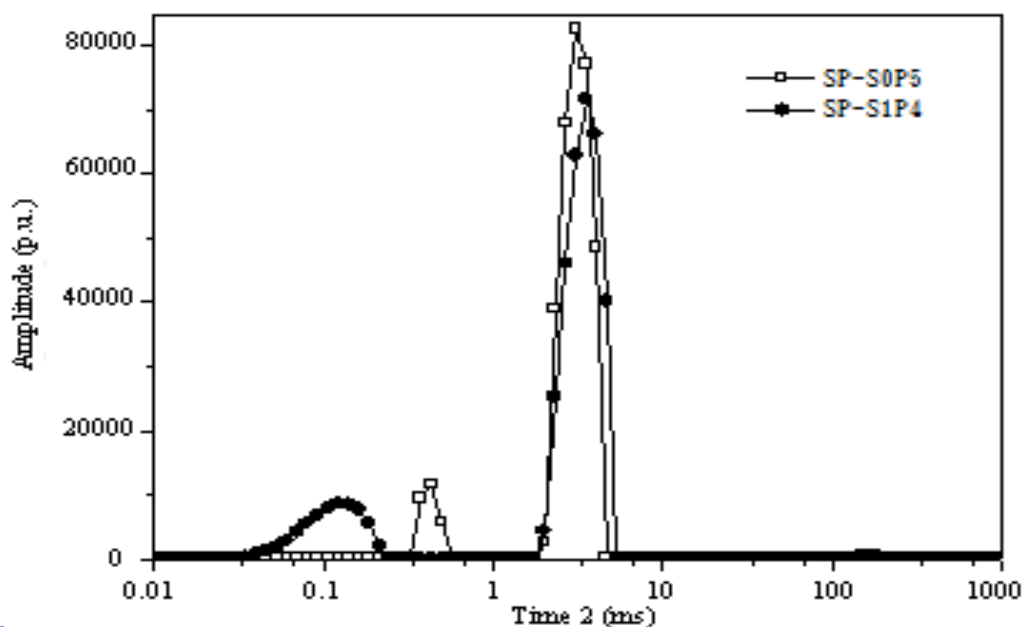
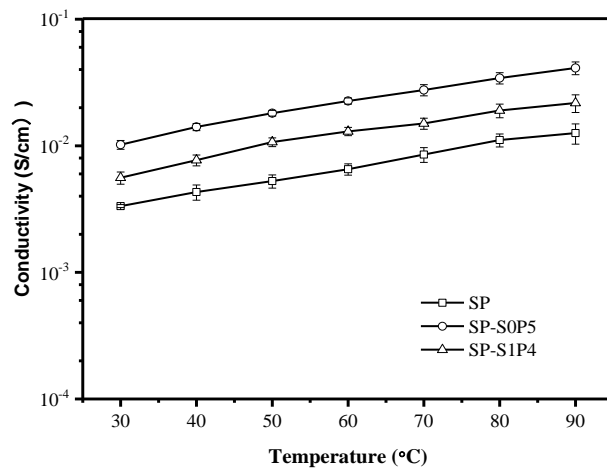
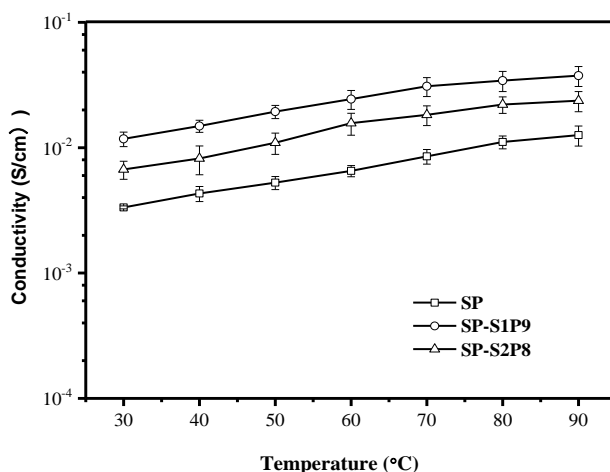


Figure 4. T₂ relaxation time of double-doped film samples and nuclear magnetic signals of A-curve

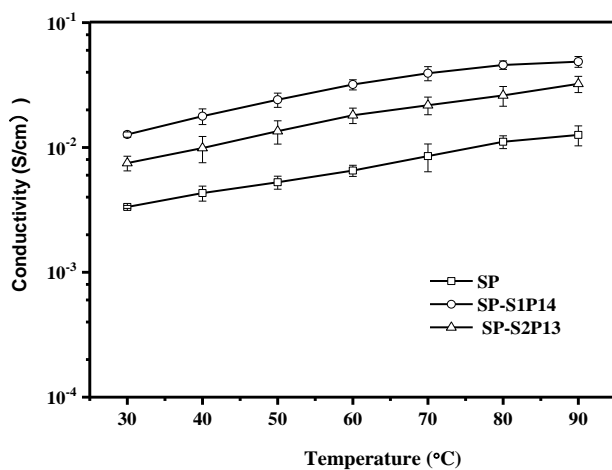
The SP-S0P5 sample has three T₂ distribution regions: 0.33-0.50, 2.01-4.04 and 132.19-200.92 ms. SP-S1P4 sample has two T₂ distribution regions: 0.01-0.22 and 2.01-4.64 ms. For the same SP85 matrix, the molar ratio of different levels of membranes is different for internal water molecules binding, and the membrane's water content and water storage capacity is different. The larger the T₂ distribution area, the smaller the value is, which indicates that the larger the storage capacity in the film sample. A numerical value, water content indicates higher water content in the membrane sample. Therefore, SP-S0P5 film sample have higher moisture content and storage capacity than SP-S1P4 sample. It is possible that the molar ratio of SeO₂ to PWA is 1:1 or the relative content of PWA is increased, and the intermolecular interaction of double doped films is increased, or the moisture absorption of PWA is enhanced, so that inner water molecules in the samples are attracted to be effective and stored [21].



(a)



(b)



(c)

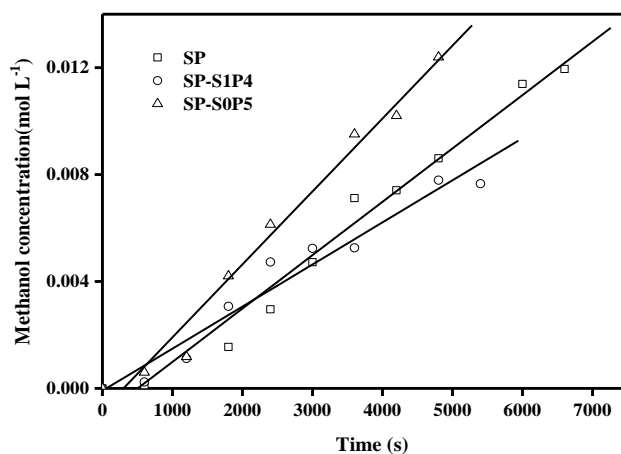
Figure 5. Conductivity of protonation membrane specimens vs. temperature: (a) 5wt.%, (b) 10wt.% and (c) 15wt.% content

The molar ratio between SeO₂ and PWA with the specific value of 2:1 or PWA content is relatively low. The dual doping within membrane molecular inter-atomic forces than 1:1 ratio of mixed within the film or the film sample PWA dominant relatively weak absorption, which makes water molecules relatively easy to lose. So that, the dual doped membrane samples exhibit weak ability towards internal water molecules storage.

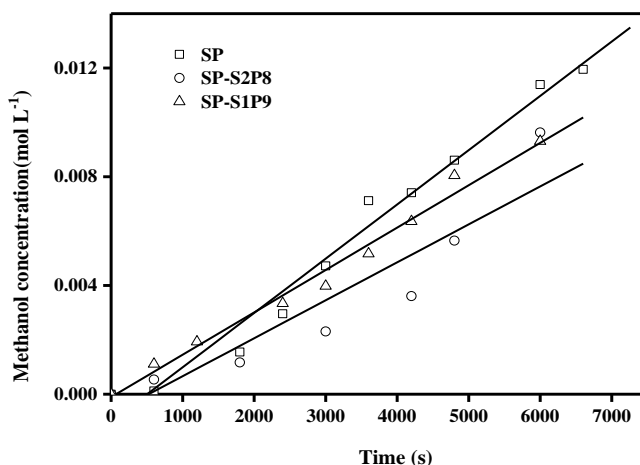
Testing the protonation of film sample get doped film in 30-90°C when the conductivity versus temperature is shown in Figure 5.

The conductivity of membrane is greater than that of the proton conductivity corresponding to the membrane. Compared with the increase slightly in conductivity of the SP membrane, the conductivity of the doping membrane increases obviously. It is well-known that film sample test to reduce the impact of protons on membrane samples, and to increase the number of protons, is conducive to the proton conduction in the film. The same doping amount of doping film doped with SeO₂ and PWA in a molar ratio of 1:1, the conductivity is higher than that of the 2:1 film sample, and the same as the film sample. The protonation indicates the performance of the film sample directed to the proton, more about the environment within the membrane for proton jumps, the large storage capacity of membrane samples (Figure 5), and higher proton conversion efficiency in the membrane. It can be seen that the conductivity of PWA doped SeO₂ doped membrane is expected to decrease [22-23]. However, doping molar ratios and the same amounts were 5 wt.%, 10 wt.% and 15 wt.% of dual doped membrane conductivity only slightly increase, may PWA doped quantity to increase, or nano rare earth oxide SeO₂ and PWA and caused by the interaction of sulfonic acid group.

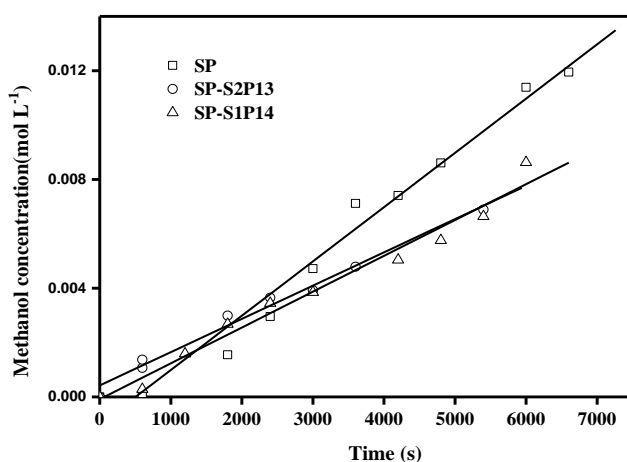
GC9800 type gas chromatograph was used to detect pure SP film sample and its dual doped film, and the relationship between the concentration of ionized water and the methanol concentration at room temperature of the film sample was obtained as shown in figure 6.



(a)



(b)



(c)

Figure 6. The relationship of methanol diffusion concentration of membrane specimens vs. time at room temperature: (a) 5wt.%, (b) 10wt.% and (c) 15wt.% content

In Figure 6(a), the line slope of SP sample is larger than SP-SOP5 membrane, but the sample of the SP-S1P4 membrane is slightly smaller than the SP membrane. Figure 6(b) and 6(c), SP-S2P8 and SP-S1P9, SP-S2P13 and the sample of the straight slope SP-S1P14 membrane are very similar, both lower than SP. It is no doubt that methanol diffusion in the membrane sample concentration and diffusion time, but also directly related to dual dopant. The double doped film samples were made more compact by the interaction of SeO₂ with PWA and sulfonic acid group to reduce methanol over time by diffusion the concentration sample. However, the concentration of methanol decreased with the increase of doping amount, and it was lower than that of SP film. This indicates that binary mixed filling as a placeholder and PWA within the membrane may be a content limitation. This is not only because of its rich in water molecules through the channel to form methanol molecules, but also through the interaction to improve the alcohol resistance of doped membrane.

Dual-doped test film sample of magnetic field treatment have good quality, in order to obtain the alcohol coefficient of the doped film at different dopant content, their relationship curve were shown in Figure 7. The doping membrane is lower in methanol permeability than the pure film. When the content of SeO_2 is the same, the higher the PWA content, the larger the alcohol coefficient through the membrane. The higher PWA content corresponds to the smaller alcohol coefficient when the same content of SeO_2 is same. SP, the penetration coefficient of methanol in the 8T vertical direction magnetic field decreased slightly. However, the alcohol coefficient decreases accordingly with SeO_2 content increasing, such as SP-S0P5-PE8 sample has a coefficient of reduction methanol about $1 \times 10^{-7} \text{ cm}^2/\text{s}$, and SP-S2P8-PE8 sample has a large coefficient of reduction methanol of $3.48 \times 10^{-7} \text{ cm}^2/\text{s}$. Doped with SeO_2 leads to the decrease of alcohol coefficient, while PWA doping increases the conductivity of the membrane sample. The vertical direction of the supermagnetic treatment can improve the performance of the doping film to guide proton and can improve the resistivity of the doping membrane, so the modified SPEEK membrane with SeO_2 and PWA is a good modified tactic [24].

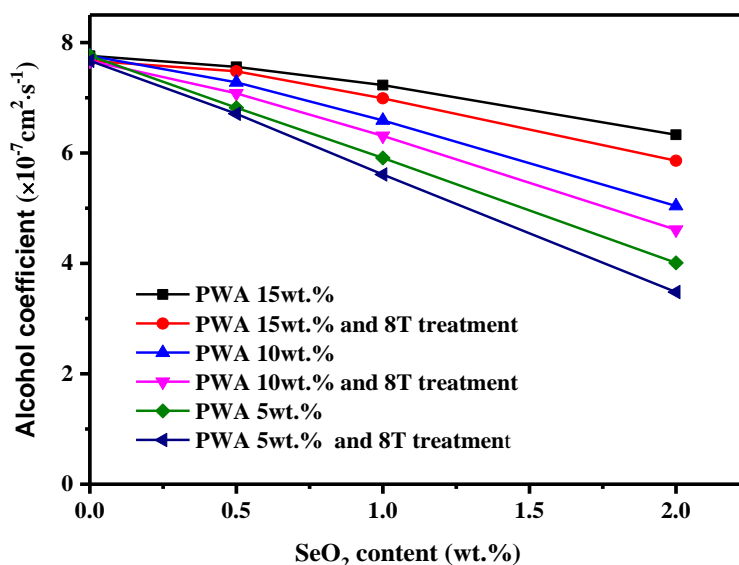


Figure 7. The relationship of methanol permeability vs. high magnetic field treatment and different dopant content

Within 90 h before the failure of PWA within 60 h, the quality of the doped film samples were basically stable (Figure 8). The wear rate of PWA doped films decreases with time, and the more the SeO_2 doping amount, the lower the wear rate of the film samples.

PWA doping can improve the proton conductivity of the doped proton membrane, but the drawback is that the temperature and humidity are more sensitive and easily weaken the ability in the water storage. The conductivity of the doping membrane gradually decreases during use process. Therefore, most of the researchers adopt pretreatment of organic matter to make it stable in proton exchange membrane. In this dissertation, we adopt doping modification of SeO_2 and PWA

coordination effect and hydrogen bonding effect. Under the action of strong magnetic field, the doping of thin films can not only reduce the PWA turnover rate, but also reduce the thin film samples through the alcohol coefficient to ensure high proton conductivity, indicating that the dual doping of SeO₂ and PWA can improve doping of doped films comprehensive performance [25].

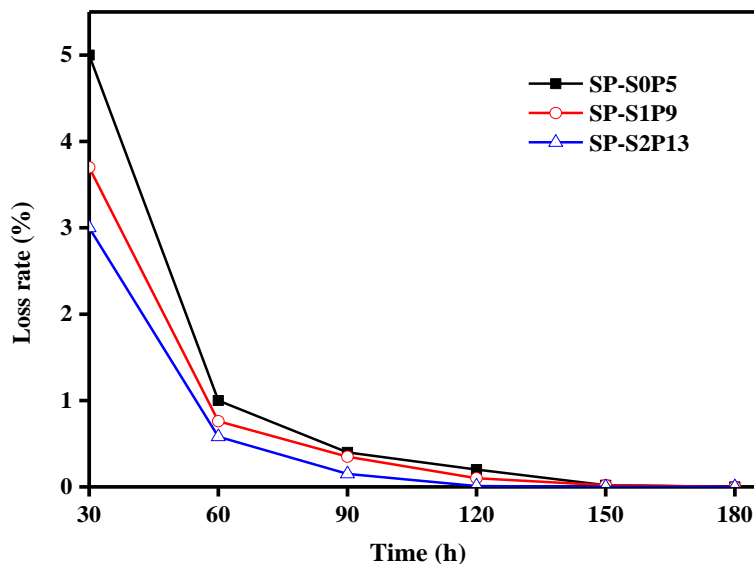


Figure 8. The dual doped film sample of PWA turnover rate with time

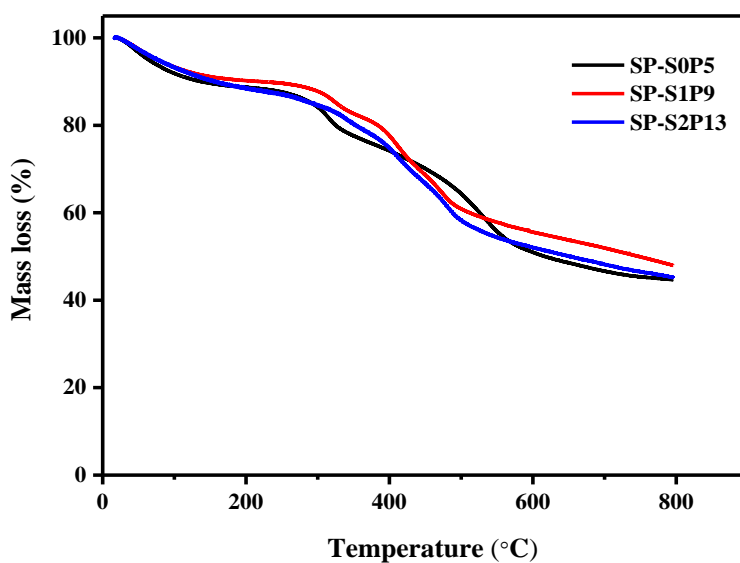


Figure 9. The TG curves of binary doped membrane samples

The three membrane samples are in the same heat temperature zone (Figure 9). In the first stage within the 150°C, main adsorption of water film inside the sample and the evaporation of solvents and other small molecules or volatile substances gives rise to the quality shift. The second stage between 300-350°C, is mainly resulted from sulfonic decomposition and PWA crystallization of water dissociation. The third stage above 350°C is mainly due to the thermal decomposition of SPEEK backbone. The above result indicates that film samples have good thermal stability. The dual membrane samples with same PWA doping amount and different SeO₂ doping amount has a good interaction between the molecules, leading to the fact that sulfonic acid group is not easy to disintegrate. Thereby increasing the thermal stability, not caused by changes in different SeO₂ doping amount.

4. CONCLUSIONS

SeO₂ and PWA modified 85 wt% DS SPEEK proton exchange membrane show that SeO₂ coordination with sulfonic acid groups and causes a change in chemical structure. When the SeO₂ content is related with the conductivity of membrane, the water absorption rate and the swelling degree increases with increasing PWA doping level through alcohol coefficient. When the content of PWA is constant, with the increase of doped SeO₂ content, the conductivity of membrane decreased slightly. Through alcohol coefficient, the lower water absorption and swelling degree, the lower the turnover shows an increase in the PWA storage capacity. On the doped membrane after 120°C, its electrical conductivity increases about 1.9 times and the alcohol coefficient decreased slightly, bibulous rate is basically no change by 8T strong magnetic field vertical processing 10 h.

The sulfonic acid groups within membrane are easy bibulous to form small watershed, reducing the adjacent effective distance and facilitating the proton transfer. The proton movement is active inside the film due to the temperature increase, but the volatilization and micro-drainage area are narrow. All two different factors affect the conductivity. For pure SPEEK membranes, district heating in low temperature has a great effect on the activity of proton. The conductivity increased significantly. The effect of high temperature on moisture is greater, as the temperature increases, the lower the conductivity. For rare earth oxides doped membrane, the interaction between rare earth ions and sulfonic acid groups increase the storage capacity, reducing the volatilization of water, strengthening the proton activity and improving the conductivity.

Compared with other researchers' research, this paper focus on doping of SeO₂ and PWA to prepare DS 85% SPEEK composite membrane. The methanol resistance, swelling resistance, and proton conductivity of the proton exchange membrane were improved, and the initial experimental scenario was successfully implemented. The performance of the proton exchange membrane was optimized, and it was hoped that it would promote the development of the fuel cell.

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