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Electrochemical Properties of Proton Exchange Membrane I: The Influence of Sulfonation Degree and Solvent

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The sulfonic acid groups in SPEEK proton exchange membranes are belonging to hydrophilic groups, which are generally affect the performance of the proton conductivity, methanol permeability and anti-swelling properties. That is, the sulfonation degree affects the level of the performance of the membrane. Different sulfonation degree of SPEEK membranes were prepared to compare the results to determine an appropriate degree of sulfonation. With the sulfonation degree increasing, the property of proton conductivity increased, methanol permeability and water swelling properties decrease, and the thermal stability performance improved. sulfonation degree lower, all the corresponding performance are opposite. DMAc solvent is more suitable as film-forming solvent, and the sulfonation degree of SPEEK resin from 40% to 70% are more suitable as base materials for the doped membranes.

Keywords: SPEEK, properties, sulfonation degree, solvent

1. INTRODUCTION

Aromatic polymer is a class of specialty excellent performance polymer materials with benzene ring structures as the backbone, high mechanical strength, good heat resistance, chemical and electrochemical stability, relatively low price and structurally diverse in favor of modified, etc. These are considered the most promising new future proton exchange membrane by sulfonated prepared for fuel cell membrane [1-3]. The behavior of the polyether ether ketone (PEEK) polymer is semi-crystalline and thermoplastic, and their melting point is 370 °C. Sulfonated polyether ether ketone (SPEEK) which sulfonated on the aromatic ring of PEEK, could make it crystalline decreased or even disappeared. In addition, diverse structures of SPEEK could provide excellent performance, which have been keen attention by researchers in the last decade [4,5].

Using post-sulfonation to sulfonate PEEK resin by homogeneous or heterogeneous, due to the higher electron density at benzene rings which simultaneously linkage connected on two ether bond, the sulfonation reaction is more likely to occur on the benzene ring. By electron-withdrawing effect of the adjacent carbonyl groups, the electron density of repeating structural units in addition two benzene rings is relatively low, which cause that the generally sulfonation substitution reaction does not occur. Therefore, each repeating unit is substantially only conjunction with one sulfonic acid group, that is the degree of sulfonation (DS) will not exceed 100%.

The selected sulfonating agent are mainly concentrated sulfuric acid, chlorosulfonic acid, fuming sulfuric acid and trimethylsilyl chloride, etc. The study founds that chlorosulfonic acid or oleum as sulfonating agent sulfonated PEEK polymer can cause a wide range of cross-linking or degradation, and milder trimethylsilyl chloride sulfonated lower efficiency sulfonating agent. Thus, using the concentrated sulfuric acid as sulfonating reaction reagent [6-8]. The reaction of concentrated sulfuric acid and sulfonated PEEK is a reversible reaction, with the reaction continued and concentration of sulfuric acid solution becoming less, the reaction dynamic equilibrium finally. By controlled the reaction conditions DS, such as at room temperature, by controlling the sulfonation reaction time to prepare different DS of SPEEK [9-13]. In the same Sulfonation time, the higher reaction temperature the greater DS. But the high temperature could cause other side reactions occur, such as intramolecular crosslinking or degradation. By heating and mechanical agitation to shorten the sulfonation reaction time, and get different DS of SPEEK [14-18]. Daoust has been proposed PEEK sulfonation reaction kinetics model which consider that the DS of PEEK is a function of time, sulfonated reaction of PEEK is first-order reaction kinetics with respect to the system of unreacted structural units and the initial establishment of sulfonated PEEK kinetic equation, but these conclusions are still need further validation [19].

The preparation and characterization document of PEEK are major research on the physical and chemical properties of SPEEK, study and discuss its thermal stability, kinetic theory and degradation mechanism of sulfonated, and using SPEEK as proton exchange membrane fuel cells until 2000 to be appeared. It is indicated that the adsorption of methanol SPEEK membranes which is less as Nafion® membrane at 2001, which confirmed the feasibility of SPEEK membrane applied to the DMFC [20]. Thereafter, SPEEK study as proton exchange membrane DMFC caused widespread concern.

The sulfonic acid groups in SPEEK proton exchange membrane are belonging to hydrophilic group, which generally affect methanol permeability, proton conductivity and anti-swelling properties, namely the DS of SPEEK will affect the level of the performance of the membrane. However, the impact of the difference between the larger, low DS of SPEEK proton exchange membrane can not be used because the conductivity is too low, too high of the DS SPEEK proton exchange membrane is also unusable due to excessive swelling. Using different organic solvents to prepared the same DS of SPEEK proton exchange membrane, its performance is often subject to different degrees of impact. In this paper, using different preparation process to obtain SPEEK resin membranes to study the effects of different solvents, and different DS, on the performance of SPEEK proton exchange membrane.

2. EXPERIMENTAL SECTION

2.1 The materials

The Poly(etheretherketone) (PEEK) polymer was obtained at School of Material Science of Tongji University (Shanghai, China). Different degree of shlonation SPEEK samples were prepared in reference [7]. It was dissolved in dimethylacetamide to make 10wt% solution. Then, casted the membrane samples on the glass plat and dry in the vacuum oven. Through control the weight of SPEEK to obtain the thickness of SPEEK membranes above 100 μm.

2.2 The testing and characterization

Using TG (Q500, TA Company, USA) to analysis the thermal performance of membranes at 10°C·min^{-1} heating rate and keep the temperature from 40-500°C. Using a Perkin-Elmer Pyris 2 DSC analyzer to analysis the glass transition temperature at10 ºC/min heating rate and under N_2 atmosphere. Using the FT-IR spectra to conformed the structure of membranes by AVATAR370 infrared spectrometer (ThermoNicolet Instrument Co., USA). SEM technology HITACHI S-4800 (Tokyo, Japan) is used to analysis the morphology of samples.

EIS analysis was carried out to test the proton conductivity and methanol permeability coefficient of the samples. Solartron Instruments 1255 B is used in the detection of the samples. The sample temperature from 30 to 90 degrees Celsius. RH was form 50% to 100%. Before testing, all samples need to be treated with dilute hydrochloric acid soaking and treated by deionized water for several times. The proton conduction coefficient calculated by the method of literature described in reference [21].

Methanol permeability coefficient by self-made instrument detection.Detection method for 6 described in the literature.Sample mould in deionized water soaked after 24 hours, measuring the thickness and area.Sample module level into the detection unit.Methanol solvent into the other side of the equipment.Through the Fick’s diffusion formula to calculate the coefficient of permeability of methanol, as follows (Equation 1) [22]

$$S_d = \frac{V_{wet} - V_{dry}}{V_{dry}} \times 100\% \qquad (1)$$

Water swelling (S_w) by drying of membrane materials and membrane weight after soaking [23]. Dry 24 hours under 90 degrees Celsius, according to dry film sample weight ($mass_{dry}$). In deionized water soak for 24 hours, call to soak film sample weight ($mass_{wet}$). Through the formula to calculate the water swelling coefficient $S_w=(mass_{wet}-mass_{dry})/mass_{dry}\times 100\%$..

3. RESULTS AND DISCUSSION

Using FT-IR technology to synthetic the chemical structure of SPEEK, and the cruve is shown in figure 1. It is indicated that, 1646 cm^{-1} peak is conform to -Ar-C(=O)-Ar- groups. 1188 cm^{-1} peak is conform to -Ar-O- groups, which indicate that the presence of SPEEK in ether ketone structure. 1224 cm^{-1} peak is conform to O=S=O groups. 1080 cm^{-1} peak is conform to O=S=O groups. 1022 cm^{-1} peak is conform to S=O groups, which indicate that a sulfonic acid group on the benzene ring of hydrogen generated electrophilic substitution [24]. All above prove that, the sulfonic acid groups are successfully introduced into the PEEK polymer.

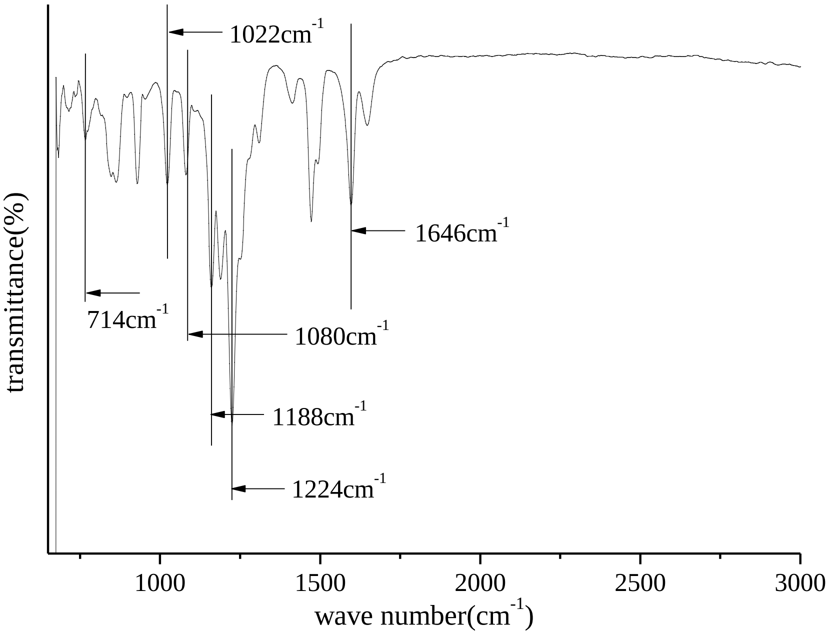
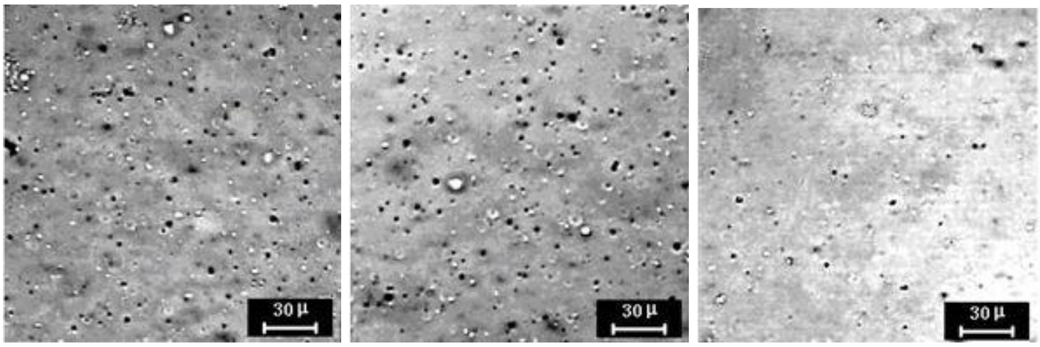


Figure 1. FT-IR spectrum of SPEEK

Using BX60 optical microscope, observated three film samples SP57, SP57/DMSo and SP57/DMF which are prepared by DMAc, DMSo and DMF solvents and the surface topography obtained. And the cruves are shown in figure 2.



(a) SP57 (b) SP57/DMSo (c) SP57/DMF

Figure 2. The surface of membranes by solvents

The film samples surface are smooth with pores which may due to the evaporation of the solvent during the preparation. As shown in Figure 3, due to hydrogen bonds between molecules DMF and sulfonic acid groups from the view of molecular structure, the evaporation reduction. So that the surfaces are densitythe of the samples prepared by DMF solvent, and the pore size on the surface of the microporous are smaller than the other two membrane samples prepared in the solvent and uniformly distributed. DMAc and DMSo may not exist hydrogen bond with hydrogen bonds, which between the sulfonic acid groups with SPEEK or is relatively weak. Therefore, large holes formed with the solvent evaporated, but the SPEEK film surfaces morphology are similar dense which preparated by these three solvents.

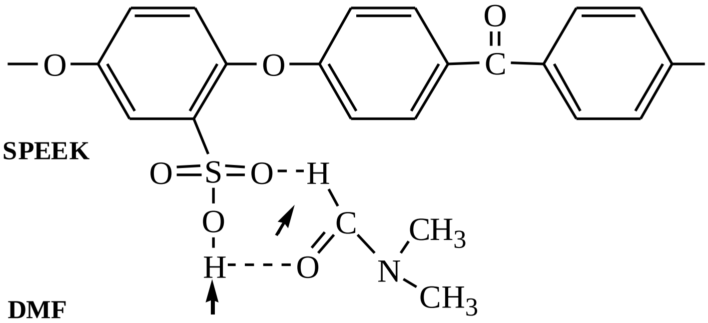
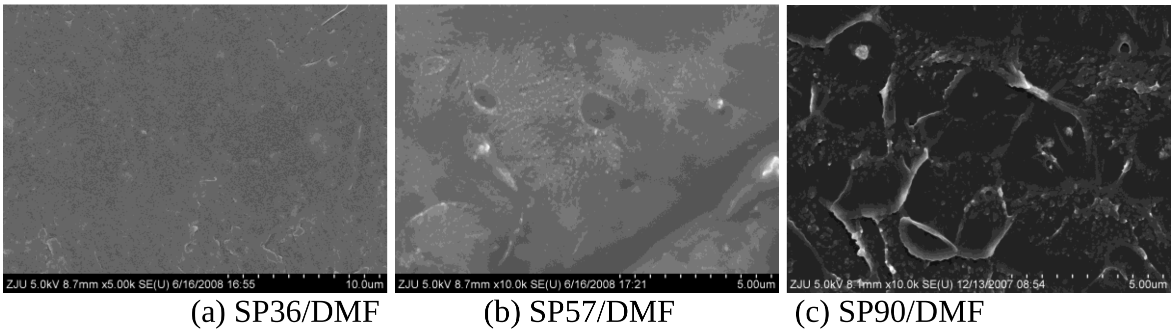


Figure 3. Interaction between-SO_3H groups and DMF solvent

36%, 57% and 90% DS of SPEEK films were observed by BX60 which prepared by DMF solvent to obtain cross-sectional shapes of SP36/DMF, SP57/DMF and SP90/DMF film samples. Its are shown in figure 4.



(a) SP36/DMF (b) SP57/DMF (c) SP90/DMF

Figure 4. Cross-section shapes of film samples

Using projected light to observe film samples, and therefore, the color brightness changes could be caused by two reasons: Firstly, because the formation cross-sectional fluctuations in the process of film samples. Secondly, the differences reflect visible light of different regions in the internal membrane material, which means differences anisotropic, caused by material density area or defect aggregation structure or other aspects. The section structures of different DS SPEEK film samples have dense, uniform and no obvious defects. The films can be divided into two outer surface layers and an intermediate layer. The surface layer are dark which could be possibly because the film and the glass mold contacting the cavity surface of the material by surface tension effect of the glass plate, the surface of the material density and aggregation structure is different from the interior of the intermediate layer [25].

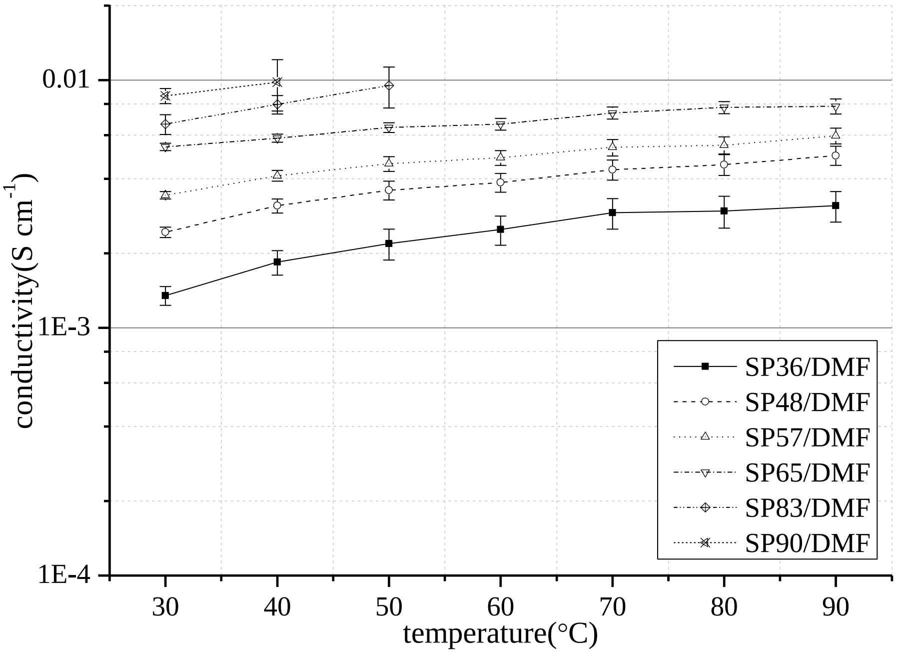


Figure 5. Conductivity of DMF solvent samples vs. temperature

A surface layer of the film may also be in the sample preparation process impurity film on a glass plate or expose Rally and introduce some defect during film. The middle layer is bright and presents alternating light and dark stripes fine, which could be due to a layered structure inside the membrane or presentation layer distributed on the material properties and the rules of more closely aligned between the layers. With the increase of DS, the layered structure of the intermediate layer is more obvious. Because of both hydrophilic sulfonic acid groups and hydrophobic carbon chain backbone in the main bone of SPEEK, layered phenomenon is indicated. With the increasing of DS, the proportion of hydrophilic phase increased and intensified layer phenomenon, which showed light and dark stripes under optical microscope.

The impedances of SP36/DMF, SP48/DMF, SP57/DMF and SP90/DMF four film samples are calculated the rate varies with temperature in the range of 30 to 90 °C. The rate varies with temperature curves are shown in figure 5.

The film samples proton conductivity are increased with temperature increasing, and the SP36/DMF membrane conductivity at 90 °C is 2.3 times than 30 °C. The conductivity of the film sample rises with DS increasing. The conductivity of SP90/DMF film sample is 1.7 times than SP65/DMF, 3.5 times of SP48/DMF and 6.4 times of SP36/DMF film sample at 30 °C, the increase was more apparent. SP90/DMF and SP83/DMF film samples could not be tested, due to the excessive swelling in the 40 and 50 °C. There may be more sulfonic acid groups in a high DS film, attracting large numbers of water molecules, which caused the membrane samples containing more water molecules and excessive swelling. In addition, the regular layered distribution of SPEEK film samples (figure 4) are favor to proton transitions, but the interactions of sulfonic acid groups and DMF effect proton transfer in the membrane. Therefore, there was no electrical conductivity within the test range of 10^{-2} S·cm^{-1}, which could be caused by the proton conductive depends on the transition region between the hydrophilic areas. Probably due to the different test methods or different resin structures, the obtained of SPEEK membrane conductivity values are described a larger gap with the literature [26].

Using self-made membrane diffusion cells and GC9800 gas chromatograph to evaluate the methanol permeability of different DS of SPEEK films prepared by DMAc solvent at 30 °C, and calculated the alcohol coefficient as shown in figure 6. With DS increasing, the corresponding number of sulfonic acid groups hydrophilicity increased in the membrane samples. So that the hydrophilic region increased and the permeability alcohol coefficient also increased, which indicated that the hydrophilic sulfonic acid groups number directly affect the methanol permeability SPEEK film samples. Pure SPEEK membranes do not like Nafion® membranes. Its dense structure can maintain good alcohol resistance performance even higher DS of SP90 films. Its permeability coefficient alcohol is 8.80×10^{-7} S·cm^{-1}, which lower than Nafion® 117 alcohol membrane in an order of magnitude, and the permeability coefficient is 2.38×10^{-6} S·cm^{-1} [27]. It is indicating that the alcohol resistance properties of film was mainly influenced by the molecular structure of the resin matrix, but the DS impact on the methanol permeability can not be ignored. The alcohol coefficient of SP90 film is 1.7 times than SP36.

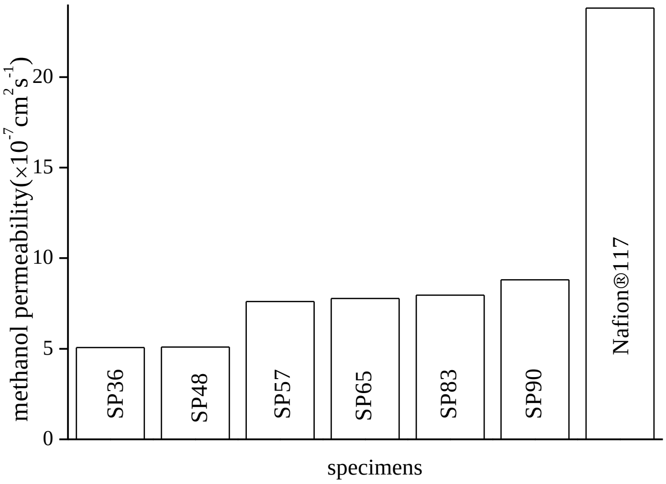


Figure 6. The methanol permeability of films at 30°C

36-90 DS of SPEEK proton exchange membranes were prepared by DMAc solvent and the water absorption is shown in figure 7.

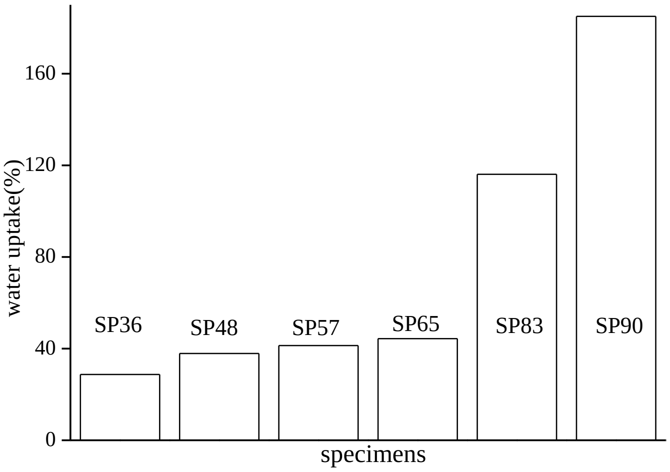


Figure 7. The water absorption of films at 30°C

Water absorption of the samples has a direct relationship with DS, and water absorption increased with the DS increasing. The water absorption of SP36 and SP48 films were 28.66% and 37.90%, which are all lower than the 40% value. The water absorption SP57 and SP65 films are slightly greater than 40%, while SP83 and SP90 are more than 100% even up to 185%. Excessive water absorption leads to excessive swelling, deformation and the decline of mechanical properties, affecting the normal use of the film. Therefore, excessive swelling phenomenon occurs when the measured at higher temperature, leading to the conductivity can not be tested. It can be seen that the water absorption of films are observably dependent on the hydrophilic acid groups.

The curves in figure 8 are indicated the thermal gravimetric analysis of PEEK resin and different DS SPEEK resin samples are detected by TGA Q500 thermal gravimetric analyzer.

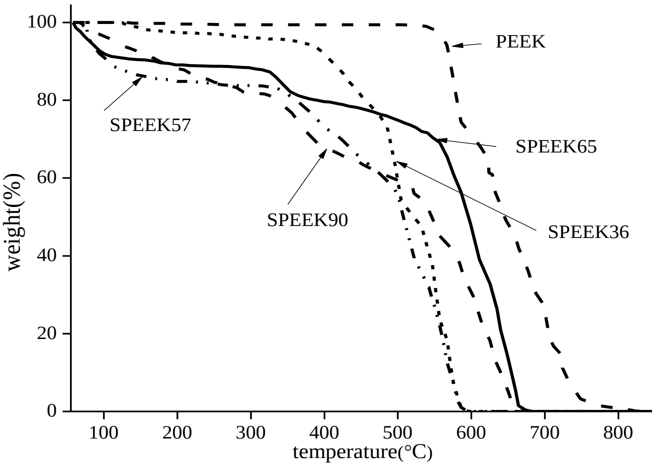


Figure 8. TGA curves of PEEK and SPEEK resin

PEEK resin has higher thermal stability, no significant degradation occurs before 550 °C and significant weight loss after. The weightlessness of SPEEK36 resin samples is not obvious about 100 °C which may be due to some water molecules or solvent evaporation. SPEEK65 resin has first significant weight loss in the vicinity of 90 °C, but SPEEK90 resin sample appears first weight loss at about 120 °C. The results are indicated that the first time weightlessness of SPEEK resin relates with the moisture content of the sample.

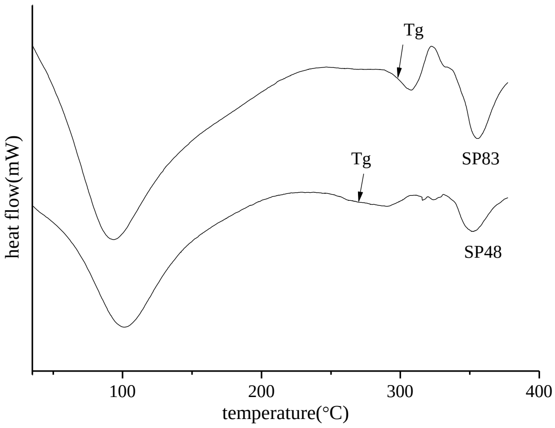


Figure 9. DSC curves of SP48 and SP83 films

High DS SPEEK resin contains more hydrophilic sulfonic acid groups, making the membranes are easier to absorb water molecules. The water evaporation process longer, and causing the first partial weightlessness hypothermia moved to lower temperature. The second significant weight loss happened at 300-400 °C. The sulfonic acid groups decomposited are caused this. Thus, the temperature range of weightlessness was due to the acid groups thermal degradation [28]. The third significant weight loss of SPEEK65 resin is substantially the same as PEEK which are indicated that the the higher DS SPEEK thermal performance are main chain stability better. And backbone thermal decomposition temperature of SPEEK36, SPEEK57 and SPEEK90 are in the range of 400-550 °C, high DS SPEEK resin maintain higher thermal stability.

Using Q2000-type DSC to analysize the thermal properties of 83 and 48 DS SPEEK film samples, and the DSC curves of SP83 and SP48 are shown in figure 9.

The endothermic peak shapes of the DSC curves are similar with the literature [29]. From the curves, we can see that the first endothermic peak is broad due to the small molecules and solvent molecules. The second endothermic peak is the Tg of the film sample, wherein SP83 is about 298 °C, and SP48 is 265 °C. With the DS increasing, the Tg of SPEEK film samples are also increased. The introduction of electron-withdrawing sulfonic acid groups by sulfonated PEEK, the interaction force between molecules are increased which caused the movement of segments not easier. Therefore, the Tg of PEEK is significantly higher than 143°C.

Three kind of membrane samples, SP57/DMF, SP57 and SP57/DMSo, which were prepared by DMF, DMAc and DMSo and tested at 57% DS in 1mol/L hydrochloric acid solution from 30 to 90 °C temperature. The figure 10 shows the conductivity compared temperature curves. The conductivity of films are increased as the temperature rises, and SP57 has the highest conductivity, the conductivity of SP57/DMF is minimum, SP57/DMSo in between. Because of the hydrogen bonding in the sulfonic acid groups in DMF solvent, the proton transfer is not easy to pass. All above are indicated that the proton conducting of SPEEK proton exchange membrane membrane related to the hydrophilic sulfonic acid groups, but also affects by the interaction between the molecular groups. DMSo has higher crystallinity which are a certain extent of impede proton transfer, the interaction between DMAc solvent and sulfonic acid group may not be stronger as DMF that there is more solvent evaporation, or there are low crystallinity in the film which is more favorable proton conductivity in the membrane.

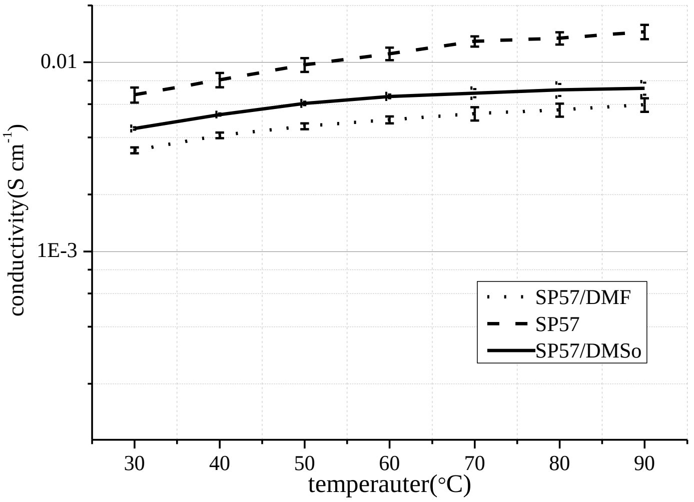
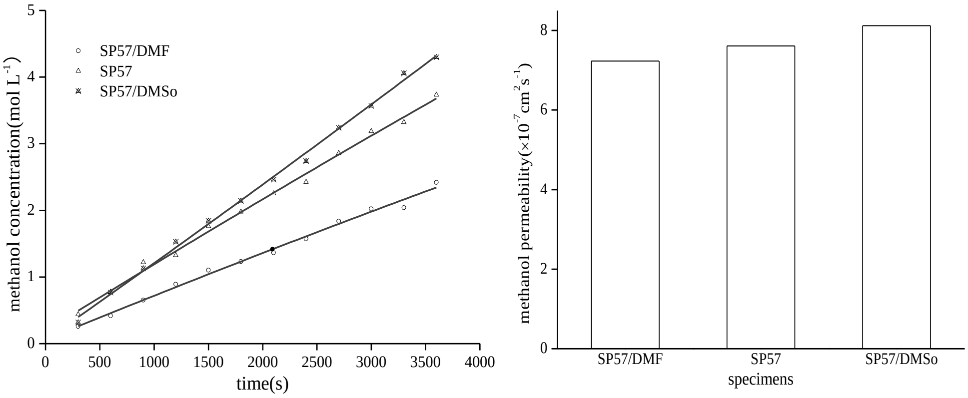


Figure 10. The proton conductivity of membrane samples

The conductivity values of film samples prepared by three solvents under the same test conditions are not significant, which are indicated that the proton conductivity of the same DS and different sample preparation solvent SPEEK film are mainly affected by the structure of the resin matrix, the membrane solvent interaction between SPEEK just an impact to a certain extent.

Using self-made membrane diffusion cells and GC9800 gas chromatograph to evaluated the methanol permeability of membranes prepared by DMF, DMAc and DMSo solvents with 57% DS at 30 °C. The figure 11 shows membrane alcohol permeability coefficient through a sample of the alcohol concentration of the water side of SP57/DMF, SP57 and SP57/DMSo, the changes over time. In figure 11(a), methanol concentration by deionized water side are increased with time. The slope of a linear fit to represent their relationship through alcohol level of performance between them, and through alcohol coefficient is proportional to the size of the film sample. The slope of SP57/DMSo is larger, the SP57/DMF film is small slope, whereas SP57 membrane followed in between. The hydrophilic sulfonic acid groups in SPEEK film were clustered. After absorption of water, the molecules surrounding the formation of micro aqueous phase which are contributing to the diffusion of methanol. The presence of hydrogen bonding interaction, between DMF and sulfonic acid groups, so that the surface of the microporous membrane sample aperture ratio SPEEK film DMSo and two solvents DMAc prepared sample is small, and uniform pore distribution. Thus, the alcohol permeability coefficient of SP57/DMF is minimum but hindered alcohol performance is highest. The presence of crystallinity in SP57/DMSo film increased hindered to methanol molecules, but the presence of methanol diffusion channels simultaneously, so that the methanol permeability membrane relative decline. SP57 film with the matrix due to the good solvent compatibility, ease of membrane proton transitions and while preventing the diffusion of small molecules of methanol.



(a) (b)

Figure 11. The membranes methanol permeability (a) the relationship of methanol concentration vs. time, (b) methanol permeability.

The solubility property of SPEEK57 resin in various solvents at 30 °C are shown in Table 1. SPEEK57 dissolved faster in DMSo, dissolved in DMF and DMAc, but the dissolution rate is relatively slow.

Table 1. The solution and swelling of SPEEK57 resin

Solvent	DMF	DMAc	DMSo
solubleness	Miscible	Miscible	Soluble
Water absorption(%)	39.88	38.29	33.97
Swelling degree(%)	18.19	14.42	8.45

DMF solvent SPEEK sulfonic acid groups in spite of the presence of hydrogen bonds, but the film preparation has the highest water absorption and swelling degree is the highest. The proton conductivity minimum film sample (figure 10). The solvent is prepared SPEEK membrane water absorption of sulfonic acid groups in addition to attract water molecules, the solvent molecules residing easily form hydrogen bonds, with little water molecules. And increasing water absorption and swelling of the film sample to some extent, but not to proton conductive play an effective role in promoting, DMSo lowest water absorption film prepared by the solvent, but the membrane proton conductivity is higher than the prepared film samples prepared in DMF solvent, the solvent may be the effect of the sulfonic acid groups is not obvious, it may be interesting to effect film having a high crystallinity affect the sulfonic acid group of water molecules, thus at the same DS and water absorption has a lower degree of swelling than other film samples. Similarly, DMAc with a sulfonic acid group effect is not obvious, but also has a low crystallinity, in which the film made of the solvent tends to evaporate. Thus weakening the absorption and swelling of the film, but they can maintain a high proton conductivity. The solvent for the influence of membrane water absorption and swelling of the same water absorption greater its degree of swelling of the membrane sample is large, but the effect is different. From SPEEK resin matrix structural analysis, which are still better compatibility between hydrophobic carbon chain backbone and hydrophilic sulfonic acid groups and did not form a clear phase separation. The other with a proton exchange membrane phase matrix material ratio, SPEEK57 proton resin and three organic solvents for the preparation of low water absorption and swelling of the exchange membrane are adopted in Table 1, that has a high resistance to water swelling properties [30].

After SPEEK film sample absorbent, hydrophilic groups attract water molecules around it to form a hydrophilic region so as to increase the hydrophilic region, a sulfonic acid group effective spacing" smaller, conducive proton hydrophilic sulfonic acid group transitions between groups, suggesting that proton transmission film may be mainly by protons in the membrane absorbing transition sulfo group transfer between the hydrophilic region is formed. As the temperature increases, the moisture content of the film sample decreased, in the form of hydrated protons decrease in the hydrophilic region, but the temperature also enhances the activity of the proton, the hydrophilic region by means of different sulfonamide transition speed between acid groups increases, so the electrical conductivity with increasing temperature continues to increase, but not a linear increase. However, as the DS increases, the sulfonic acid groups contained increases in the membrane, so that the methanol permeation of small molecules in the film also increases, methanol permeability decreased with the increase of DS (figure 6), with water absorption increase the DS increased (figure 7). However, the structure of the film showed that SPEEK, structure of the resin matrix more compact, and therefore, the conductivity and permeability coefficient of the film was an alcohol to maintain a relatively low value.

4. CONCLUSIONS

Using PEEK as raw material and sulfuric acid as the sulfonating agent, react at room temperature or 60 °C in 6-387 h to obtain different DS (36-90%) SPEEK resin. The longer sulfonation reaction time at the same temperature, the higher DS. The higher sulfonated temperature at same reaction time, the higher DS. By changing the reaction mode or reaction time, it can be obtained different DS SPEEK resin.

DS impacts the proton conduction performance, alcohol resistance properties, resistance to water swelling properties and thermal stability of SPEEK membrane. The proton conductivity performance of SPEEK membranes are increased with DS increasing. The methanol permeability decreased, water swelling properties decreased and thermal stability performance improvement. All the corresponding performance is the opposite with the DS lower.

Using 57% DS SPEEK resin as film material, choice of DMF, DMAc and DMSo as solvents to study the SPEEK resin film performances. DMF solvent membrane has the lowest conductivity and alcohol penetration coefficient. DMAc solvent membrane has the highest conductivity and the alcohol penetration coefficient be followed. DMSo solvent membrane has highest conductivity and the permeability coefficient.

DMAc solvent is more suitable as the SPEEK film-forming solvent, and the DS from 40% to 70% of SPEEK resin is more suitable as the base material of doped film.

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