

Sulfonation of Poly(phthalazinone ether sulfone ketone) by Heterogeneous Method and Its Potential Application on Proton Exchange Membrane (PEM)

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ABSTRACT: A series of sulfonated PPESK (SPPEKs) were synthesized through a heterogeneous sulfonation process with fuming sulfuric acid as sulfonating agent in a chloroform solvent. Membranes prepared from SPPEKs were investigated and proved to be candidates of proton exchange membrane in fuel cell operating at high temperature and low humidity. The heterogeneous sulfonation reaction is verified to first occur on the interface of the acid phase and the chloroform phase, then went on in the acid phase. SPPEKs with sulfonation degree (DS) up to 2.0 are obtained through a new reprecipitation method. Effects of reaction temperature, reaction time, acid/polymer ratio, and chloroform/polymer ratio on the sulfonation reaction are reported in details. An increase in sulfonation degree results in the increase of

hydrophilicity, bringing about a substantial gain in proton conductivity. SPPEK membranes exhibit high water uptake of about 105.4% with DS of 1.01, almost two times higher than that of Nafion[®] with similar dimensional variation. Conductivity values at 35°C, 60% R.H. ranging from 10^{-3} to 10^{-2} S/cm were measured, which are comparable to or higher than that of Nafion[®] 112 (1.635×10^{-2} S/cm) under the same test condition. Thermogravimetric analysis shows that SPPEK membranes are stable up to 290°C in N₂. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 1002–1009, 2007

Key words: sulfonation; poly(phthalazinone ether sulfone ketone); proton exchange membrane; fuel cell; heterogeneous reaction

INTRODUCTION

In recent years, proton exchange membrane fuel cell (PEMFC) has been identified as a promising power source for vehicle transportation and for other application requiring clean, quiet, and portable power.^{1–3} Perfluorinated polymer electrolytes, such as Nafion[®] membrane, have satisfactory properties for a successful application on PEMFC. However, high cost and low proton conductivity at high temperature or low humidity restrict their large-scale commercial use.⁴ Sulfonation of nonfluorinated polymers is a promising way to prepare high performance proton exchange membrane (PEM). There are various sulfonation processes,^{5–9} either homogeneous or heterogeneous, with different sulfonating agents such as sulfuric acid, chlorosulfonic acid, and SO₃–triethyl phosphate complex to synthesize sulfonated nonfluorination poly-

mers. Sulfonated nonfluorination polymers could even be prepared from sulfonated monomers.^{10,11} Membranes prepared from some sulfonated nonfluorination polymers,^{12–15} such as sulfonated poly(benzimidazole) (SPBI), sulfonated polyphosphazene (SPOP), sulfonated poly(ether ether ketone) (SPEEK), sulfonated poly(ether sulfone) (SPES), etc. have been reported to exceed Nafion[®] in water uptake, thermal stability or proton conductivity. Sometimes further modifications on sulfonated polymers such as cross-linking,^{15–17} surface grafting¹⁸ and blending^{12,19–21} with heteropolyacids or other polymers are reported in literature to improve their properties of conductivity, mechanical stability or methanol resistance.

A series of poly(phthalazinone ether sulfone ketone) copolymers, containing different ratios of diphenylsulfone and diphenylketone units, have high thermal stability (T_g from 284°C to 305°C) besides outstanding physical and chemical properties. Membranes prepared from PPESK and sulfonated PPESK (SPPEK) exhibit excellent properties in the previous research work, such as high temperature ultrafiltration and nanofiltration membranes.^{22–25} They are cheaper when compared with other high performance membranes such as Nafion[®]. In this paper we study their possible application as proton exchange membranes. In the report by Dai et al.,²⁶ PPESK was sulfonated by homogeneous method with concentrated or

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fuming sulfuric acid as both sulfonating agent and solvent. Unfortunately, too much acid (acid/PPESK ratio is about 33 (mL/g)) and very long reaction time (10–100 h) were necessary to reach the desired sulfonation degree, which seriously decreased the efficiency of sulfonation reaction. This is often the case in many other homogeneous sulfonation reactions with concentrated or fuming sulfuric acid.^{7,12}

In the present work, sulfonation was carried out in a heterogeneous media using fuming sulfuric acid only as sulfonating agent in a chloroform solvent. PPESK was dissolved in chloroform instead of sulfuric acid, so that the acid can access to and react with the polymer chains as soon as the reactants were mixed. As a result, the reaction time shortened and the consumption of acid decreased (almost sixfold reduction). Owing to the posttreatment process we developed, high sulfonation degree was obtained. It was reported²⁷ that the heterogeneous sulfonation reaction was performed only on the interface of the acid phase and the solvent phase. Whereas in our experiments, it was found that the reaction first occurred on the interface of the two phases, then went on in the acid phase. Furthermore, SPPEK membranes with different sulfonation degree were prepared and their properties of proton conductivity, water uptake, and thermal stability were studied systematically.

EXPERIMENTAL

Materials

The PPESK random copolymer²⁸ used in this study has a sulfone/ketone (S/K) ratio of 1 : 1. Chloroform, dimethylacetamide (DMAc), ethyl ether, acetone, fuming sulfuric acid (23–25% SO₃), and other chemicals were analytical grade and used without further purification.

PPESK sulfonation by heterogeneous method

PPESK was dried in vacuum at 120°C for 24 h. Thereafter 1 g PPESK was dissolved in chloroform at ambient temperature. Then a measured amount of fuming sulfuric acid was added into the solution dropwise under vigorously stirred within 15 min. Meanwhile the acid drops could disperse in the chloroform solution. The resulting heterogeneous system was slowly heated up to the desired temperature and stirred for several hours. Then the reaction mixture was cooled and the top chloroform layer was decanted. Afterwards the isolated acid layer was added dropwise to 80 mL ethyl ether under stirring. The obtained precipitate was filtered, then dissolved in 25 mL DMAc, and reprecipitated in 300 mL acetone. The resulting polymer was filtered, washed with acetone until neutral, while acetone could be reused after distillation.

Finally, the polymer was dried in vacuum at 120°C overnight.

Analysis of sulfonated product

As shown in Scheme 1, PPESK was a random copolymer with S and K in the ratio of 1 : 1. We defined every S or K with one —SO₃H substitution as DS = 1.0 to compare with other aromatic polymers such as PEEK, PES etc. Therefore the average molar weight of S and K was used to calculate DS. Subsequently, ion exchange capacity (IEC) was calculated from the value of DS.

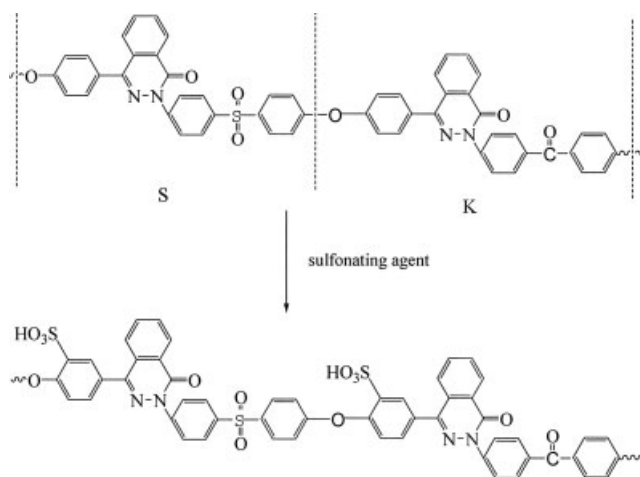
Sulfonation degree of the sulfonated polymer was measured by titration method following the procedure reported in literature.¹³ A known weight (approximately 0.1 g) of dry polymer was placed into 25 mL of 3.0M NaCl solution and shaken occasionally for 24 h. Then 5 mL solution sample was removed and the amount of H⁺ released by the polymer was determined by titration with 0.01M NaOH. Repeating the titration operation for three times, then averaging the consumed volume of NaOH and calculating DS by dividing the total number of moles of HCl formed by the dry weight of the polymer.

Preparation of membranes

A solution (about 20 wt %) of the sulfonated polymer in DMAc was prepared and cast on a glass plate. After evaporation of the solvent at ambient temperature, the flat-sheet membrane was carefully removed from the glass and dried in vacuum at 120°C to evaporate the residual solvent. All membranes were approximately 100 μm in thickness.

Characterization of SPPEK membranes

The swelling characteristics were determined by water uptake measurements. The dry rectangular



Scheme 1 Sulfonation reaction of PPESK with DS 1.0.

SPPEK membranes were weighted and measured of their dimensions (width and length), then immersed in distilled water at 25°C until no more weight gain was observed (about 30 h). Before weighting and measuring again, the excess water on the membranes surface was removed carefully with absorbent paper. The water uptake was calculated from the weight difference between the wet and the dry membrane, reference to the weight of the dry specimen: $(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}} \times 100\%$, while the dimensional variation was defined as the area variation of the membrane, reference to the area of the dry specimen: $(A_{\text{wet}} - A_{\text{dry}})/A_{\text{dry}} \times 100\%$.

The thermogravimetric analysis (TGA) was carried out with TGA/SDTA 851 to investigate the thermal stability of SPPEK membranes. Approximately 10 mg sample membranes were first dried in vacuum at absolute pressure less than 1 kPa under 160°C for 24 h to remove the moisture and solvent. Then placed the sample membranes in the sample chamber and programmed from 25°C to 600°C at a rate of 10°C/min under a nitrogen atmosphere.

The proton conductivity was determined using a complex impedance analyzer (Princeton Potentiostat/Galvanostat Model 283) over a frequency range of 1–10⁶ Hz. SPPEK membrane of about 100 μm thickness was sandwiched between two polished Cu electrodes (about 1 cm² area) and an AC perturbation of 5 mV was applied to the cell. The cell was placed in the upper space of a water bath, in which the temperature of water was controlled, so that the air in the upper space of the water bath was kept at about 60% R.H. and 35°C during the measurement. To provide a reference, Nafion[®] 112 was measured under the same condition.

RESULTS AND DISCUSSION

Reaction mechanism

Sulfonation of PPESK in chloroform is a heterogeneous reaction due to the poor solubility of fuming

sulfuric acid in chloroform. At the same time, chloroform is an excellent solvent for PPESK whereas a non-solvent for sulfonated PPESK. When the fuming sulfuric acid was added dropwise into the PPESK solution under vigorously stirred, the acid drops *i.e.*, the acid phase, dispersed in the chloroform solution. It was reported in literature²⁷ that this kind of heterogeneous reaction happened only on the interface of the two phases. While in our experiment, we find the reaction was first occurred on the interface, then went on in the acid phase. Table I summarizes the content and DS of the polymers in both the acid phase and the chloroform phase with different reaction time. To analyze the chloroform phase, chloroform was evaporated and the left polymer was washed with acetone until neutral, then dried and analyzed. As can be seen in Table I, a large amount of polymer was detected in the acid phase when the reaction time was about 15 min (15 min was the time when the addition of acid was finished and the analysis of the polymer could be done). While at that time in the chloroform phase, there was few polymer left. In the acid phase sulfonation degree of the polymers increased gradually with the reaction time went on. Therefore, the polymer underwent sulfonation on the interface of the acid and chloroform phases very quickly, then entered the acid phase because of the higher solubility of SPPEK in acid than in chloroform. In the acid phase the sulfonation reaction went on.

Reaction conditions

Influence of chloroform

The function of chloroform in the reaction is studied in the experiments. As shown in Figure 1, with increasing the volume of chloroform the sulfonation degree first increased to a maximum value and then went down. In the heterogeneous reaction where the acid phase dispersed in the chloroform phase, the volume of chloroform influenced not only the concentration of PPESK, but also the dispersing condition of the heterogeneous system, such as viscosity of the system

TABLE I
Polymers Gained in Both Acid Phase and Chloroform Phase^a

Reaction time (min)	Content of polymers ^b (%)		DS	
	Acid phase	Chloroform phase	Acid phase	Chloroform phase
15	90.4	9.6	0.50	0.092
30	100		0.58	
45	100	Little or no polymer detected	0.65	No measurement
75	100		0.72	
105	100		0.79	

^a Reaction performed at ambient temperature, acid/chloroform/PPESK ratio of 5/15/1 (mL/mL/g).

^b Content of polymers refers to the weight of polymer in acid phase or chloroform phase divided by the total weight of PPESK.

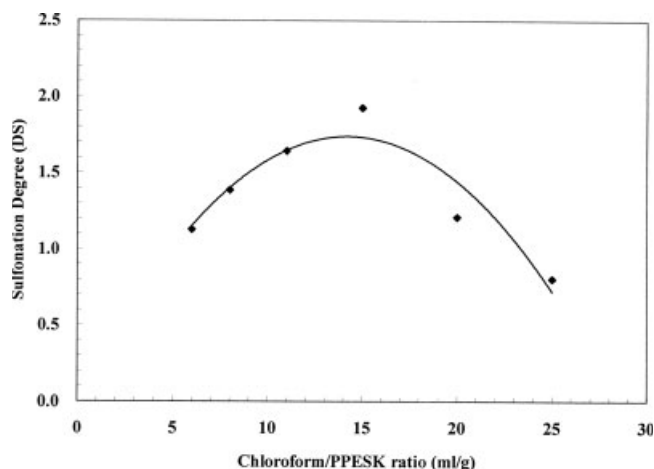


Figure 1 Sulfonation level of PPESK as a function of chloroform/PPESK ratio (60°C for 3 h, acid/PPESK ratio 5/1 (mL/g)).

and size of the acid droplets. When the ratio of chloroform/PPESK increased, viscosity of the heterogeneous system decreased and the size of the acid droplets became smaller, the better dispersing condition led to the expanding interface of the two phases, so that the higher sulfonation degree. On the other hand, with the increase of the ratio of chloroform/PPESK the concentration of PPESK in the chloroform phase decreased, which reduced the rate of the reaction and decreased the sulfonation degree. As the result of the two contrary effects of chloroform, the sulfonation degree appeared to be a maximum value when the chloroform/PPESK ratio was about 15 mL/g.

Influence of acid/polymer ratio

Figure 2 shows the variation of the sulfonation degree as a function of acid/PPESK ratio for a reaction performed at 60°C for 2 h. When the acid/PPESK ratio increased, the sulfonation degree first increased rapidly at low acid/PPESK ratio because of the increase of the concentration of sulfonating agent then reached the relatively stable high value as the ratio greater than 5 mL/g. It shows that the acid/PPESK ratio of 5 (mL/g) is enough in our heterogeneous method. Compared with the previous homogenous sulfonation of PPESK²⁶ in which the acid/PPESK ratio was about 33 (mL/g), the present heterogeneous process is an economical and environment-friendly method. This is because PPESK was dissolved in chloroform instead of sulfuric acid, so that the acid can improve its efficiency as sulfonating agent.

At very lower acid/PPESK ratio, for example the acid/PPESK ratio less than 1 mL/g, the obtained sulfonated polymer only partly dissolved in DMAc (an excellent solvent for both PPESK and SPPEK). It is thought that the polymer chains in the high viscous

acid phase would have the opportunity to go through crosslinking. Hence homogeneous sulfonation product could not be obtained because of the high viscosity of the acid phase.

Influence of precipitation method

In literature, water was often used as the precipitation agent in sulfonation reaction because of its low cost.^{5-7,12} The only disadvantage of water is that it is impossible to obtain water-soluble sulfonated products, which can prepare PEM by crosslinking or blending with other polymers. For this consideration we turn to organic precipitation agent. Ethyl ether is a nonsolvent for SPPEK and could wash out a large amount of acid by forming oxonium ion with H⁺. There is still some acid trapped in the polymer chains after precipitated by ethyl ether, which is difficult to be removed. That is often the case for some other organic precipitation agents and is a main disadvantage compared with water. To solve this problem, Nolte et al.¹⁵ used Soxhlet system to extract the polymer for a long time. Wycisk et al.¹³ first neutralized the sulfonated polymer solution with NaOH, then let the solution through ion exchange resin to convert it into acid form. We developed a reprecipitation process by pouring DMAc solution of the ether precipitant into another nonsolvent acetone, then it was easy to wash out the trapped acid in the polymer chains with acetone.

In the experiments we compared the two different precipitation agents of organic agent and water. As can be seen in Figure 2, precipitation with organic agent always resulted in higher sulfonation degree than did precipitation with water for the same reaction batches. For example, precipitation with organic agent gave a sulfonation degree of about 1.2 when the

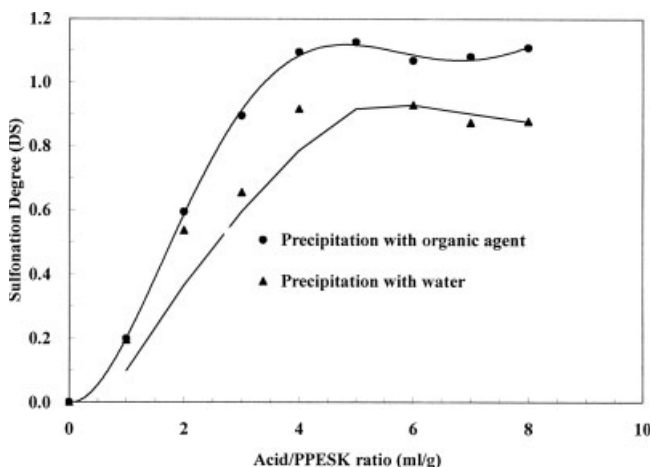


Figure 2 Influence of acid/polymer ratio on the sulfonation level of PPESK (60°C for 2 h, chloroform/PPESK ratio 15/1 (mL/g)).

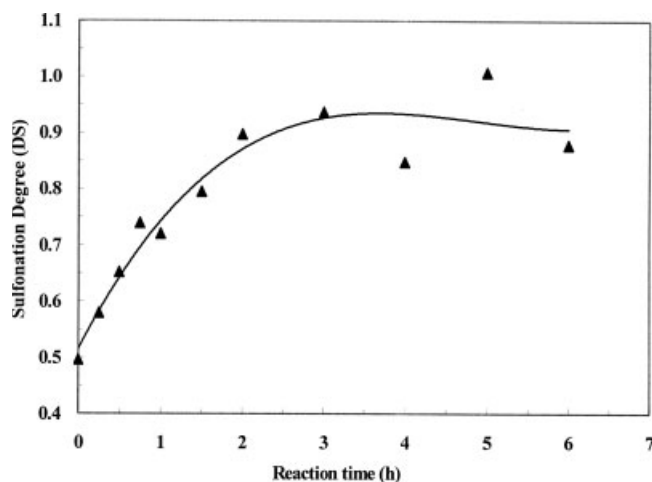


Figure 3 Sulfonation level of PPESK as a function of reaction time (25°C, chloroform/acid/PPESK ratio 15/5/1 (mL/mL/g)).

acid/PPESK ratio was about 4 mL/g. Whereas at that acid/PPESK ratio, precipitation with water only obtained a sulfonation degree of about 0.9 because SPPEK of high sulfonation degree was washed out by water. Therefore, SPPEK with high sulfonation degree can be prepared by this organic agent precipitation method. Owing to this posttreatment method both water soluble and insoluble SPPEK can be prepared in the present heterogeneous sulfonation.

Influence of reaction time and temperature

Figure 3 shows the influence of reaction time on the sulfonation degree. When the reaction time increased, the sulfonation degree increased first rapidly, then more slowly and reached a platform because of the decreased concentration of the sulfonating agent.

As expected, the sulfonation degree increased with reaction temperature when reaction time was about 3 h. If the reaction batches are kinetically controlled, sulfonation degree of the samples at different temperature represents the observed reaction rate constant.²⁹ When the Arrhenius relationship was used to correlate the sulfonation degree with the reaction temperature, a good correlation was obtained (linear Arrhenius plot, Fig. 4). The activation energy was found to be 14.3 kJ/mol. This value is slightly smaller than that obtained for sulfonated polyethersulfone cardo (21 kJ/mol),²⁹ which indicates that the reaction is easy to perform.

Water uptake

Water uptake of the sulfonated polymer is known to have profound effect on the proton conductivity and mechanical properties. Sulfonated aromatic polymers were reported to have high ability of water absorp-

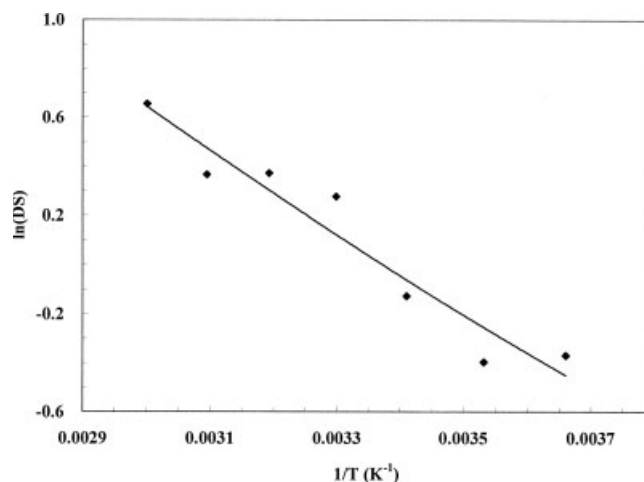


Figure 4 Arrhenius plot for sulfonation degree at different temperatures (chloroform/acid/PPESK ratio 15/5/1 (mL/mL/g) in 3 h).

tion.^{12,15,16} It is also the case for SPPEK. In Figure 5, the water uptake of SPPEK membranes is plotted against the sulfonation degree. It could be found in the curve that the water absorption of SPPEK membranes increased relatively slow up to DS of about 0.9 and thereafter very rapidly. The high ability of water uptake with high DS may involve in clustering of ionomers, which could accelerate the transfer of proton.

On the other hand, higher water uptake may produce mechanically less stable membranes. That is, with higher DS the membranes could be likely to swell too strong and lost their dimensional stability. Therefore dimensional variation of the membranes must be taken into account as we studied the water uptake. Table II indicates the relationship between water uptake (wt %) and their corresponding dimensional variation (area %) of SPPEK membranes and Nafion[®] at 25°C.^{12,30} SPPEK-1.01, whose dimensional

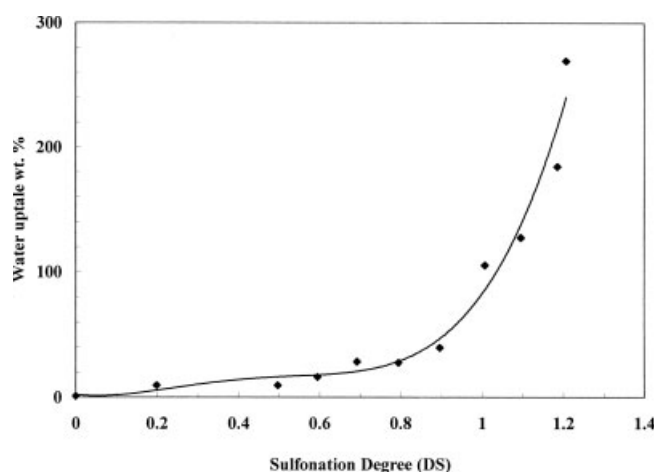


Figure 5 Water uptake of SPPEK membranes at 25°C for 30 h in distilled water.

TABLE II
Water Uptake and Dimensional Variation of SPPEsk Membranes and Nafion[®] at 25°C

Samples ^a	Water uptake (wt %)	Dimensional variation (area %)
SPPEsk-0.79	27.5	1.9
SPPEsk-0.90	39.7	4.4
SPPEsk-1.01	105.4	27.6
SPPEsk-1.10	127.5	37.7
SPPEsk-1.185	184.2	84.4
SPPEsk-1.21	269.6	93.1
Nafion ^{®b}	34.0	24.5

^a SPPEsk-*n*: *n* refers to DS of the samples.

^b The values of water uptake and dimensional variation for Nafion[®] derived from Refs. 12 and 30, respectively.

variation was slightly higher than that of Nafion[®], had high water uptake, reached a value of 105.4%, almost two times higher than that of Nafion[®]. Such a high water uptake makes it possible to operate the membranes on PEMFC without external humidification at ambient temperature. Therefore, this kind of membrane could have potential applications as portable power sources, such as power sources for notebook PC or mobile telephone etc. This work is on going in our group.

Thermal stability

Examples of TGA and DTG curves of PPESK and SPPEsk membranes with different sulfonation degree are shown in Figure 6 and Figure 7, respectively. Since PPESK is a thermal stable polymer, the weight loss of this polymer, obviously due to the main chain decomposition, started at about 502°C. While for SPPEsk there are three weight loss stages observed at three separate temperature ranges in the curves of TGA and DTG. Table III summarizes the percentage and tem-

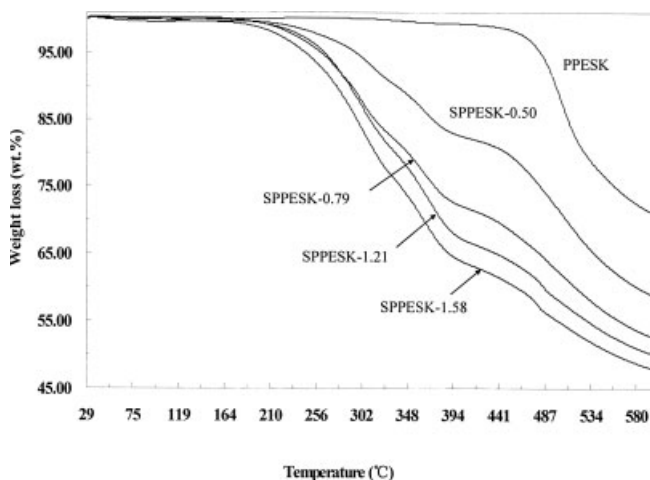


Figure 6 TGA curve of PPESK and SPPEsk membranes with different sulfonation degree under N₂ atmosphere.

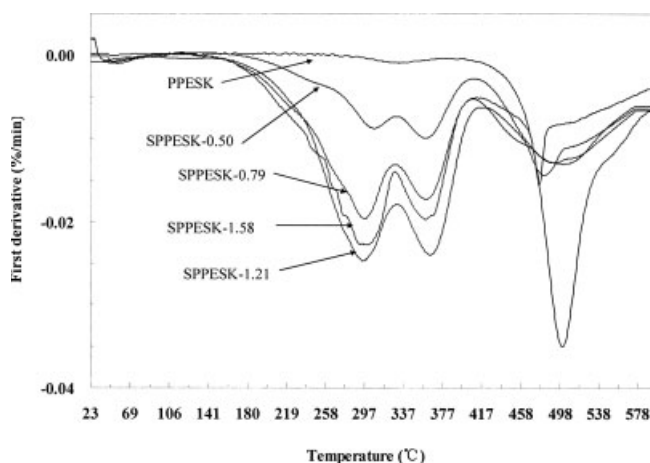


Figure 7 DTG curve of PPESK and SPPEsk membranes with different sulfonation degree under N₂ atmosphere.

perature range for the three weight losses. In the first stage, the weight loss was observed at the range of 292–306°C and had a trend of decrease with increasing DS. While the temperature of the second weight loss stage for all tested samples was almost the same around 360°C. The third stage involved in the decomposition of the SPPEsk main chains with the temperature range from 500°C to 476°C with DS increased. The percentage of weight loss in the first stage was consistent with what calculated from DS assuming that the decomposition of a sulfonic acid group releases one SO₃ molecule. This is an evidence that the first weight loss peak for SPPEsk is caused by the decomposition of the sulfonic acid group. It is thought that the second weight loss stage is related to the evaporation of the residual DMAc, similar to Kruczek's explanation.²⁷ In such a high temperature (around 360°C) of the second weight loss stage, SPPEsk is already in a rubbery state because the *T_g* of SPPEsk is in the range of 278–330°C.²⁶ An increase in temperature would increase the free volume and the activity of the polymer chains, which would enhance the evaporation of the residual solvent entrapped in the polymer chains at glassy state. It should be noticed that temperature of the second weight loss stage is much higher than the boiling point of DMAc at atmosphere pressure (about 160°C), which means the residual solvent strongly bound to the glassy state polymer and could not be removed from the SPPEsk membrane by the drying procedure (160°C in vacuum). We also noticed that the percentage of the weight loss in the second stage is in the range of 8–14%, which is much higher than some other sulfonated polymers, e.g., the percentage for SPPO is about 5%.²⁷ The possible explanation is that the aromatic rings in the SPPEsk chains are not coplanar, which would induce many cavities in the SPPEsk chains. As a result, small molecules such as solvent or water

TABLE III
Thermal Characterization by Thermogravimetric Analysis

Samples	1st peak			2nd peak		3rd peak
	T_{\max} (°C) ^a	Weight loss (wt %)		T_{\max}	Weight loss (wt %)	T_{\max} (°C)
		By TGA	By titration			
SPPEsk-0.50	306.76	8.38	9.47	359.83	8.29	500.36
SPPEsk-0.79	297.47	12.77	17.31	359.17	11.02	492.34
SPPEsk-1.21	294.81	18.18	19.61	363.15	14.19	478.23
SPPEsk-1.58	292.81	22.54	23.44	359.83	13.49	476.24

^a Maximum weight loss temperatures of the peaks by TGA at 10°C/min under N₂ atmosphere.

could be hold inside the polymer chains. It might be a reason for the excellent water uptake of SPPEsk membranes.

Conductivity study

Before conductivity measurements, all the membrane samples were soaked in distilled water to reach hydration equilibrium. Then the proton conductivity of the SPPEsk membranes was measured at about 35°C and 60% R.H. As reference, conductivity of Nafion[®] 112 was measured under the same condition. Figure 8 shows the effect of Ion Exchange Capacity (IEC) on the conductivity of SPPEsk membranes and Nafion[®] 112. The proton conductivity of all SPPEsk membranes measured were in the range of 1.062×10^{-3} to 3.177×10^{-2} S/cm, with IEC increased from 1.14 to 2.73 mmol/g (DS from 0.50 to 1.185). The values were higher or comparable to that of Nafion[®] 112 under the same condition, 1.635×10^{-2} S/cm. Therefore, the conductivity of SPPEsk membranes is sufficient for their application on PEMFC.

Although conductivity of SPPEsk membranes is comparable with that of Nafion[®] 112, the absolute conductivity value of Nafion[®] 112 measured in our experiment is lower than the typical value of 8×10^{-2} S/cm in literature. There are three possible reasons for the lower conductivity. Firstly, the film was measured transversely instead of longitudinally. Secondly, the film was measured at 60% R.H. instead of 100% R.H. Thirdly, although we polished the Cu electrodes before each test, the use of Cu electrodes is not optimal since they still have a chance to develop an oxide layer. Despite of this, the value of Nafion[®] proton conductivity measured in our experiment is still in the rational range because in literature, the value for Nafion[®] is in a broad range of about 1.1×10^{-1} S/cm to 3×10^{-3} S/cm at ambient temperature, 100% R.H.^{19,31}

There is a question for SPPEsk membranes that greater ion exchange capacities are needed to achieve the same conductivity as that of perfluorosulfonic acid Nafion[®] polymers (As shown in Fig. 8 the IEC of SPPEsk were up to 2.73 mmol/g). Similar conclu-

sions have been drawn from literature for some other aromatic sulfonated polymers. According to Kim et al.,¹⁹ it is because acidity of aromatic sulfonic acid in hydrocarbon polymers is much lower than that in a perfluorosulfonic acid polymer. As to SPPEsk, there are two possible reasons for the low acidity. One reason is that the sulfonic acid group is covalent bound to the aromatic ring instead of pendant to a fluoroalkyl group as Nafion[®] does. Another reason is the acid-base effect between the SPPEsk molecular chains, as shown in Scheme 1. PPEsk can be viewed as a base polymer because atom N in the PPEsk carries free electron pairs. When PPEsk was sulfonated, the base group can interact with the sulfonic acid group through hydrogen bridges and electrostatic force by proton transfer from the acidic to the basic group. As a result, it slightly reduces the proton transfer efficiency. More research work must be done via FTIR spectroscopy or nuclear magnetic resonance measurements to identify the mechanism of proton conduction.

CONCLUSIONS

SPPEsk has been prepared following a heterogeneous sulfonation method and their possible applications as PEMs are investigated. SPPEsk with high sulfona-

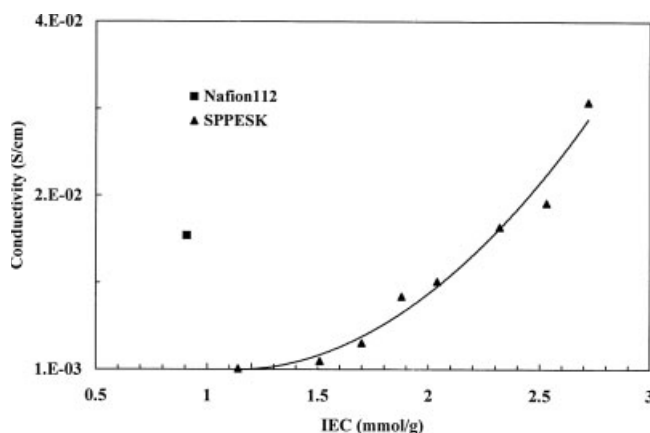


Figure 8 Proton conductivity of Nafion[®] 112 and SPPEsk membranes at 35°C, 60% R. H.

tion degree (up to 2.0) are prepared by the organic agent precipitation procedure. The chloroform solvent in the heterogeneous system contributes to the less acid consumption and the shorter reaction time usage when compared with the previous homogeneous sulfonation developed in reference.²⁶ The heterogeneous sulfonation reaction is verified to first occur on the interface of the acid phase and the chloroform phase, then went on in the acid phase. From the Arrhenius plot of the reaction, activation energy is calculated to be 14.3 kJ/mol, which indicates the reaction was easy to perform. Plate-sheet membranes of SPPEKs exhibit a rather high conductivity up to 10^{-2} S/cm at ambient temperature and 60% R.H., which is higher or comparable to Nafion[®] 112 under the same condition. SPPEK membranes could absorb water till much high level, nearly two times higher than that of Nafion[®] at the same dimensional variation. Three weight loss steps are measured from the first derivative of the TGA curves. The first weight loss is in the range of 292–303°C, which could safely fulfill the demand of high temperature fuel cell. As a conclusion, SPPEK membranes with various sulfonation degree are easy to be prepared. Their high proton conductivity combined with high water uptake and thermal stability qualify the SPPEK membranes to be considered as alternatives to Nafion[®]-based membranes used in PEMFC. Further studies on the behaviors of SPPEK membranes operating at high temperature or low humidity are in progress and will be reported in the near future.

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