

Research Article

Preparation and Application of Aromatic Polymer Proton Exchange Membrane with Low-Sulfonation Degree

Yushan Gao ¹, Zhidan Zhang ¹, Shuangling Zhong ¹ and Reza Daneshfar ²

¹College of Resources and Environment, Jilin Agricultural University, Changchun 130118, China

²Department of Petroleum Engineering, Petroleum University of Technology (PUT), Ahwaz, Iran

Correspondence should be addressed to Shuangling Zhong; zhongs1235@163.com and Reza Daneshfar; reza_daneshfar@ut.ac.ir

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4,4'-Dichlorodiphenylsulfone-3,3'-disulfonic acid (disodium) salt and 4,4'-difluorodiphenylsulfone were used as sulfonated monomer. 4,4'-Fluorophenyl sulfones were used as the nonsulfonated monomer. 4,4'-Dihydroxy diphenyl ether or 4,4'-thio-dibenzenethiol was used as the comonomer. The sulfonated poly (aryl ether sulfone) (SPES) and sulfonated poly (arylene thioether sulfone) (SPTES) with sulfonation degree of 30% and 50% were successfully prepared by nucleophilic polycondensation. Two kinds of aromatic polymer proton exchange membranes were prepared by using sulfonated poly phthalazinone ether ketone (SPPEK) material and fluidization method. The performance of the prepared aromatic polymer proton exchange membrane was researched by the micromorphology, ion exchange capacity, water absorption and swelling rate, oxidation stability, tensile properties, and proton conductivity. Experimental results show that there is no agglomeration in the prepared aromatic polymer proton exchange membrane. The ion exchange capacity is 0.76–1.15 mmol/g. The water absorption and swelling rate increase with the increase of sulfonation degree. The sulfonated poly (aryl ether sulfone) membrane shows better oxidation stability than sulfonated poly (aryl sulfide sulfone). They have good mechanical stability. The prepared aromatic polymer proton exchange membrane with low sulfonation degree has good performance, which can be widely used in portable power equipment, electric vehicles, fixed power stations, and other new energy fields.

1. Introduction

Energy is an important material basis for the survival and development of human society. With the development of society, the problems of environmental pollution, ecological damage, and climate change caused by the production, conversion, and use of fossil energy have posed a serious threat to human survival and development. In order to solve the contradiction between economic development, energy shortage, and environmental pollution, it is urgent to develop a clean, efficient, and sustainable new energy.

Fuel cell (FC) is considered as a new generation of power system with energy revolution significance after steam engine and internal combustion engine. It converts the chemical energy in fuel and oxidant directly into electric energy without combustion. Because it is not limited by Carnot cycle, its energy conversion efficiency reaches 40%~

60%, and the actual use efficiency is 2~3 times of that of ordinary internal combustion engine. Fuel cell is also a kind of environment-friendly power generation device [1]. It hardly emits pollutants such as SO_x and NO_x to the outside world during its working process. It is these outstanding advantages that arouse people's extensive interest in fuel cell. The development of fuel cell has experienced a rather tortuous and long historical process. As early as 1839, Grove successfully carried out the reverse reaction of electrolytic water, creating the world's first fuel cell model. Later, the slow progress of electrode reaction kinetics and the success of thermal engine process delayed the research of fuel cell for nearly a century, until the successful application of fuel cells in space flight has aroused people's research interest again [2], and the breakthrough progress of electrochemistry has also laid a solid theoretical foundation for the development of fuel cells. In the 90s of the 20th century, in the atmosphere

of energy shortage and serious environmental pollution, people gradually realized that fuel cell, as a kind of sustainable development clean energy, has incomparable advantages, thus setting off a new round of fuel cell research upsurge.

Fuel cells can be classified according to different standards. At present, the most common classification method is based on electrolyte, which can be roughly divided into five categories: alkaline fuel cell, phosphoric acid fuel cell, solid oxide fuel TV, molten carbonate fuel cell, and proton exchange membrane fuel cell. As the fifth generation fuel cell, proton exchange membrane fuel cell (PEMFC) has the advantages of high power density, high current density, low operating temperature, and fast start-up speed. In addition, due to the use of polymer as electrolyte, there are no electrolyte leakage and corrosion problems, less environmental pollution, and longer service life [3]. Proton exchange membrane fuel cell (PEMFC) can be used not only in the construction of decentralized power plants, but also as a mobile power source. Proton exchange membrane fuel cell research has become the mainstream of a variety of fuel cell research tide, and breakthroughs have been made in key materials and battery pack [4–7], which is expected to be commercialized as soon as possible.

Proton exchange membrane fuel cell (PEMFC) has a wide application prospect in the field of portable power equipment, electric vehicles, and fixed power stations due to its high energy density, high energy conversion efficiency, environmental friendliness, flexibility, and portability. In recent years, researchers have devoted themselves to developing PEM with high performance and low cost. Sulfonated aromatic polymers, such as sulfonated polyetherketones and sulfonated polyethersulfones, have excellent film-forming properties, good thermal stability, and high proton conductivity, which makes them promising as alternative materials for PEMFC applications. Similar to Nafion, sulfonated aromatic polymers also exhibit nano phase separation between hydrophobic main chain and hydrophilic side chain. However, compared with Nafion, sulfonated aromatic polymer membranes have narrower ion channel size, more “dead ends,” and phase discontinuities, resulting in lower proton conductivity [8]. However, in order to obtain a higher degree of sulfonation in hot water, a higher degree of sulfonation strategy will lead to higher proton conductivity. Bai et al. prepared sulfonated poly (aryl sulfide sulfone) copolymer with high sulfonation degree. When the sulfonation degree reached 70%, the water absorption rate of the polymer membrane in hot water at 80°C exceeded 800% and even dissolved in water at 90°C; the sulfonated polyether ether ketone with sulfonation degree of 62.7% prepared by Zhang et al. was also dissolved in hot water at 70°C. How to balance the proton conductivity and dimensional stability is the main bottleneck restricting the development of sulfonated aromatic polymer proton exchange membrane [9]. In order to overcome these problems, researchers have adopted a variety of strategies to adjust the performance of the membrane and have carried out a lot of research on side chain type, block type, and composite type

proton exchange membrane. Although the performance of the membrane has been improved by these methods, the preparation method is more cumbersome, especially difficult to meet the requirements of industrialization. In this paper, two kinds of sulfonated aromatic polymers with low sulfonation degree were prepared by simple nucleophilic polycondensation and changing the element composition of the main chain of the polymer. They were sulfonated poly (arylene thioether sulfone) (SPTES) and sulfonated poly (aryl ether sulfone) (SPES). The proton exchange membranes of the two kinds of low sulfonated aromatic polymers were compared, and the aromatic polymer protons with different properties were obtained. Exchange membranes can be used in applications with different requirements.

2. Materials and Methods

2.1. Main Raw Materials. Sulfonated poly phthalazinone ether ketone (SPPEK) and 4,4'-fluorophenyl sulfones (99% purity) were purchased from Dalian Baolimo New Materials Co., Ltd. Isopropanol recrystallization, 4,4'-thio-dibenzenethiol (98% purity), phenol, 4,4'-oxybis- (98% purity), and potassium carbonate anhydrous (99% purity) were purchased from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. N-Methyl pyrrolidone (high analytical grade) and isopropanol (high analytical grade) were purchased from Tianjin Fuchen Chemical Reagent Factory; Sulfolane (purity $\geq 99\%$) was purchased from Sinopharm Chemical Reagent, Co., Ltd., Beijing, China. Sodium chloride (high analytical grade) was purchased from Tianjin Fuchen Chemical Reagent Factory. Other reagents and solvents were of high analytical grade, which can be directly applied. The infrared spectrum characterization results of SPPEK of raw materials in this paper are shown in Figure 1. The number marked in the figure is the telescopic vibration peak.

2.2. Main Instruments. Nuclear magnetic resonance instrument, AVANCE 400, was purchased from Bruker Bio-Spin AG, Switzerland. Synchronous thermal analyzer, SDT/Q600, was purchased from TA Instruments, USA. Fourier transform infrared spectrometer, VECTOR 22, was purchased from Bruker, Germany. Field emission scanning electron microscope, Nova NanoSEM 450, was purchased FEI Company, USA. Electrochemical work station, CHI660D, was purchased from Shanghai Chenhua Instrument Co., Ltd. Microcomputer controlled electronic universal testing machine, CMT6104, was purchased from Shenzhen Century Tianyuan Instrument Co., Ltd.

2.3. Preparation of Proton Exchange Membrane. The transparent and strong proton exchange membranes of two polymers were prepared by tape casting method. The sulfonated poly (aryl ether sulfone) (SPES) and sulfonated poly (arylene thioether sulfone) (SPTES) with sulfonation degrees of 30% and 50% were prepared. SPES-50 and SPTES-50 were used as an example. Under the protection of

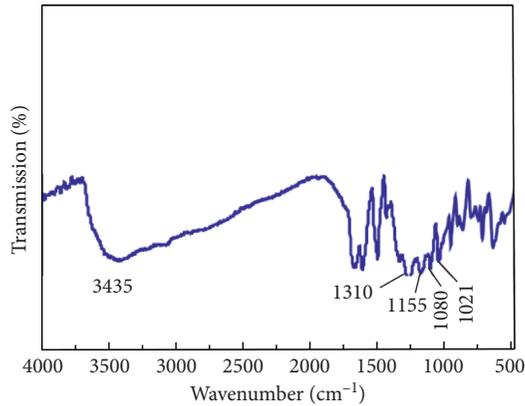


FIGURE 1: SPPEK Infrared characterization.

nitrogen, 2.29 g (5 mmol) of 3,3'-disulfonic acid salt-bis(4-chlorophenyl) sulfone, 1.259 g (5 mmol) of 4,4'-difluorodiphenyl sulfone, and 25 ml sulfolane (TMS) were successively added to the dry three-port flask equipped with magnetic stirrer, condenser, and water separator. When SPES-50 was synthesized, 2.02 g (10 mmol) of 4,4'-dihydroxydiphenyl ether was added. In the synthesis of SPTES-50, 2.504 g (10 mmol) of 4,4'-thiodibenzenethiol was added. They were stirred at room temperature for 30 min to make the monomer fully mixed. Two grams (3.312 g when SPTES-50 was synthesized) of anhydrous potassium carbonate and 10 ml of toluene were slowly heated to 160°C with water for three hours. The toluene was evaporated out of the reaction system and then it was heated to 180°C for twelve hours. After the reaction, the viscous reaction liquid was naturally cooled to room temperature [9] and poured into the mixed solution of methanol and glacial acetic acid (V (methanol): V (glacial acetic acid) = 8:2 precipitation). The polymers were shredded, filtered, and washed with hot deionized water for several times, and then they were extracted by Soxhlet extraction with methanol for 72 h and dried in a vacuum oven at 100°C for 24 h to obtain the dried polymer SPES-50 or SPTES-50. The yield of SPTES is 90% and the yield of SPES is 92%.

2.4. Sulfonation Reaction Process. SPPEK powder was dried in vacuum at 105°C for 24 hours to remove the water absorbed by the sample. In a completely dry four-port flask with a constant pressure drop funnel, SPPEK powder was dissolved in chloroform to produce a chloroform solution of 0.1 g/ml. After full dissolution, a certain proportion of concentrated sulfuric acid and fuming sulfuric acid were added to the solution with a constant pressure and low drop funnel for sulfonation [10]. The degree of sulfonation was controlled by controlling the reaction conditions. After the reaction, the mixture was poured into a large amount of ice and water mixture and precipitated to obtain fibrous precipitate. The residual acid was removed by repeated washing with water ions, and then it was filtered and dried to obtain sulfonated poly phthalazinone ether ketone (SPPEK). The sulfonation reaction was controlled by nucleophilic polycondensation.

2.5. Performance Test of Proton Exchange Membrane

2.5.1. Microscopic Appearance of Aromatic Polymer Proton Exchange Membrane. Before FEI sirion-200 scanning electron microscope was used to observe the micromorphology of the membrane, the samples were sputtered and sprayed with gold to prevent the discharge phenomenon.

2.5.2. Ion Exchange Capacity. Ion exchange capacity (IEC) is the amount of $-\text{SO}_3\text{H}$ group substance contained in a unit mass polymer, and its unit is mmol/g. The equivalent weight (EW) is the reciprocal of ion exchange capacity. There are many methods to measure IEC value. In this experiment, acid-base back titration is used to measure IEC value [11]. Firstly, it is necessary to prepare 0.01 mol/L NaOH standard solution and 0.01 mol/L hydrochloric acid standard solution according to GB/T-601-2002. After accurately weighing and taking SPPEK dry film with certain quality, we cut it up and put it into a certain volume of NaOH standard solution for soaking for 24 hours and then titrated the blank solution. By repeating the measurement for three times, we take the average value. The formula of calculating the IEC value is shown as follows:

$$\text{IEC} = V_{\text{NaOH}} \times C_{\text{NaOH}} - V_{\text{HCl}} \times C_{\text{HCl}} \quad (1)$$

In Formula 1, C_{NaOH} denotes the molar concentration of NaOH standard solution. C_{HCl} denotes the molar concentration of HCl standard solution. V_{NaOH} denotes the volume of NaOH standard solution. V_{HCl} denotes the volume of HCl standard solution.

The sulfonation degree is the percentage of $-\text{SO}_3\text{H}$ group in the total number of basic chain segments of polymer. One mol of molecular chain segment of SPPEK participates in the cyclization reaction (the molar mass of SPPEK is M_{PPEK}). The degree of sulfonation is represented by DS. When DS is less than 1, the chain segment of DS mol is sulfonated, and the mass of sulfonated polymer is $\text{DS} (M_{\text{PPEK}} + 80)$. Other $(1-\text{DS})$ mol chain segments do not contain $-\text{SO}_3\text{H}$ groups, and their mass is $(1-\text{DS}) M_{\text{PPEK}}$. Thus, the formula of ion exchange capacity of SPPEK is

$$\text{IES} = \frac{\text{DS}}{\text{DS} (M_{\text{PPEK}} + 80) + (1 - \text{DS}) M_{\text{PPEK}}} \quad (2)$$

If more than one sulfonation site is replaced by $-\text{SO}_3\text{H}$ group on the basic chain segment of each polymer, DS is more than 1. Formula (3) can be obtained by formula (2):

$$\text{IES} = \frac{\text{DS}}{M_{\text{PPEK}} + 80 \text{DS}} \quad (3)$$

The sulfonation degree can be obtained by ion exchange capacity.

The sulfonation degree of polymer is affected by the activity of sulfonating agent, concentration of polymer in sulfonating agent, reaction time, reaction temperature, and other factors [12], so different sulfonation degree products can be prepared by controlling sulfonation conditions.

2.5.3. Test of Water Absorption and Swelling. The water absorption and swelling rate of membrane are analyzed by the change of its mass and size. A 2 cm × 3 cm dry film is taken, and the mass of dry film is weighed. After soaking in deionized water at different temperatures for 24 h, it is necessary to make the film fully absorb water and swell, and then the mass and area of film are recorded at different temperatures, respectively [13]. The water absorption and swelling rate of membrane are calculated by

$$\begin{aligned} \text{Water absorption rate} &= \frac{W_{\text{wte}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%, \\ \text{Swelling rate} &= \frac{A_{\text{wet}} - A_{\text{dry}}}{A_{\text{dry}}} \times 100\%. \end{aligned} \quad (4)$$

In the previously mentioned formulas, W_{dry} and W_{wet} are, respectively, the mass of dry film and the mass of wet film after full water absorption and swelling, g . A_{dry} and A_{wet} are the area of dry film and the area of wet film after full water absorption and swelling, cm^2 , respectively.

2.5.4. Oxidation Stability Test. Firstly, we immersed the 2 cm × 2 cm membrane in Fenton reagent (H_2O_2 solution containing 2 mg/kg FeSO_4 3%) and kept it heated in water bath at 80°C [14]. After that, we recorded the remaining mass of membrane immersed in Fenton reagent for 1 h and the time of complete dissolution of membrane.

2.5.5. Tensile Property Test. According to GB-1040.3-2006 standard, the tensile properties of membrane samples were tested. The loading rate was 2 mm/min, and the formula to calculate the tensile strength was shown as follows:

$$\sigma_t = \frac{P}{b \cdot d} \quad (5)$$

In formula (1), σ_t denotes the tensile strength of membrane. P denotes the maximum load, the breaking load and the yield load. b denotes the width of sample. d denotes the thickness of sample.

The formula of the breaking elongation of specimen is as follows:

$$\varepsilon_t = \frac{L - L_0}{L_0} \times 100\%. \quad (6)$$

In formula (2), ε_t denotes the breaking elongation. L_0 denotes the original line marking distance of sample. L denotes the distance between line markings when the sample breaks.

The formula of elastic modulus is shown as follows:

$$E_t = \frac{\sigma_t}{\varepsilon_t} \quad (7)$$

In formula (7), E_t denotes the elastic model. σ_t denotes the tensile strength. ε_t denotes the elongation at break.

2.5.6. Proton Electroconductibility Test. The conductivity property of proton exchange membrane is generally characterized by conductivity. However, the measurement of conductivity is not as simple, convenient, and intuitive as liquid electrolyte. The carrier in proton exchange membrane is hydronium proton, and the carrier in conductor and electrode is electron. In the measurement process, the charge transfer may appear in the interface between electrode and proton exchange membrane [15], thus forming a double electric layer. In addition, the charge transfer impedance will be formed at the interface between the electrode and the proton exchange membrane, so the conductivity of proton exchange membrane cannot adopt the DC resistance method but should select the AC impedance method. The complex concentration polarization and ion accumulation at the electrode-proton exchange interface can be eliminated by AC impedance method, and the influence of charge transfer resistance on the electrode proton exchange interface can be avoided. We used EG&PARRC Potentiostat/Galvanostat Model 273 electrochemical workstation to test the conductivity of proton membrane. The test frequency ranged from 10 to 10^5 Hz, and the AC microdisturbance amplitude was 5 mV. During the test, two stainless steel inert electrodes were used to act on the cathode and anode, the test membrane was clamped between the cathode and the anode, and then the membrane and the electrode were fixed with polytetrafluoroethylene sleeve. After that, the stainless wire was connected to the instrument. The schematic diagram of test device and battery device is shown in Figure 2.

Before the test, the proton exchange membrane to be tested is immersed in deionized water for 24 hours, so that it is fully hydrated. And then, the proton is measured in deionized water.

The self-resistance R_b value of membrane is the abscissa value corresponding to the intersection of high-frequency semicircle and low-frequency straight line in Cole-Cole curve. If the test frequency is not too high or the system conductivity is high, the high-frequency semicircle does not appear, and the AC impedance curve is approximately a straight line in the high frequency [16]. Thus, R_b is the intersection of the straight line and the abscissa. The conductivity is calculated by formula (4):

$$\delta = \frac{L}{R_b \cdot S} \times 100\% \quad (8)$$

In formula (4), L denotes the membrane size between the two electrodes. R_b denotes the actual contact area of the two electrodes. S denotes the measured membrane resistance.

3. Results

3.1. Micromorphology of Aromatic Polymer Proton Exchange Membrane. The SEM photos of the surface direction and cross-section direction of proton exchange membrane of aromatic polymer are shown in Figure 3, where the graticule of electron microscope is 2 μm .

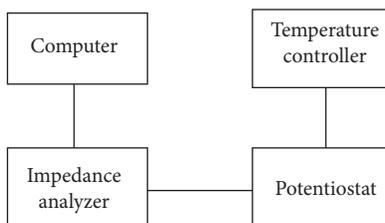


FIGURE 2: Schematic diagram of the proton conductivity test device.

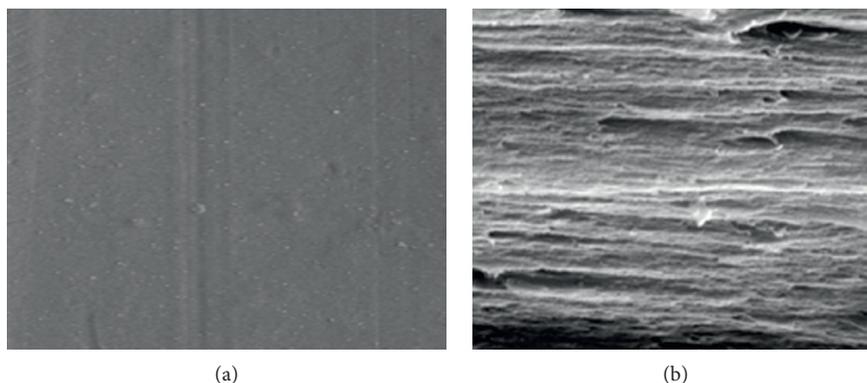


FIGURE 3: SEM photo of 20% aromatic polymer proton exchange membrane. (a) Surface orientation before sulfonation. (b) Surface orientation after sulfonation.

According to experimental results in Figure 2, we can see that the reaction of aromatic polymer proton exchange membrane after the low-sulfonation reaction is relatively uniform without agglomeration. The structure of aromatic polymer proton exchange membrane with low sulfonation degree is fine and close. Thus, the effectiveness of the sulfonation reaction can be proved.

3.2. Ion Exchange Capacity. The changes of sulfonation degree of aromatic polymer proton exchange membrane in different reaction conditions are shown in Table 1.

Table 1 shows that when concentrated sulfonic acid was only used as sulfonating agent to react at room temperature for 24 hours, SPPEK was basically not sulfonated. When the reaction temperature was raised to 50°C for 24 hours, only SPPEK products with low sulfonation degree were obtained. Therefore, it was difficult to obtain SPPEK products with high sulfonation degree only by concentrated sulfuric acid. In this experiment, the mixture of fuming sulfur and concentrated sulfuric acid was used for sulfonation.

The ion exchange capacity of four aromatic polymer proton exchange membranes obtained by acid-base titration was tested. The theoretical value of ion exchange capacity was calculated by formula (1), and then the value was compared with Nafion-117 membrane. The test value and theoretical value of ion exchange capacity were shown in Table 2.

Table 2 shows that the IEC test value of copolymers ranges between 0.76 and 1.15 mmol/g. Due to the exchange equilibrium in the process of proton exchange, the H⁺ in polymer cannot be completely replaced, and there are some

residues. Meanwhile, there are absolute errors in the measurement, so the determination result is slightly lower than the theoretical value, but it is basically consistent with the theoretical value. The reaction is relatively completed. With the increase of sulfonation degree, more and more -SO₃H groups are introduced into the main chain of polymer, and the IEC value of membrane is also increased.

3.3. Water Absorption and Swelling Rate of Membrane.

As the carrier of proton transport, water content will influence the proton transport process, so the water absorption of the membrane has an important impact on the proton transport performance of proton exchange membrane. In addition, the water absorption affects the swelling performance of membrane, so as to influence the mechanical properties and stability of the membrane. Table 3 shows the test results of water absorption and swelling rate of polymer membrane.

From the experimental results in Table 3, we can see that the water absorption of SPES-50 and SPTES-50 membranes is much higher than that of Nafion-117 membrane. With the increase of temperature, the water absorption of the membrane shows an increasing trend. Because the increase of temperature, the molecular movement is intensified, and the movement of macromolecular chain is more active. Finally, the water absorption is increased. Due to the low sulfonation degree of SPES-30 and SPTES-30, the water absorption has little change with the increase of temperature. The water absorption of SPES-50 and SPTES-50 increases rapidly after the temperature is higher than 58°C, reaching 137.5% and 104.7%, respectively, at 80°C. SPES has higher

TABLE 1: Effect of reaction conditions on the degree of sulfonation.

SPPEK quality (g)	Sulfuric acid (ml)	Time (h)	Oleum (ml)	Temperature (°C)	IEC (mmol/g)	DS (%)
6	55	24	0	RT	≈0	≈0
6	55	48	0	RT	0.75	7
6	55	4	0	60	0.71	12
6	30	4	30	RT	0.63	20
6	0	4	30	60	1.06	36
6	0	8	30	60	1.08	48
6	0	24	30	60	1.12	56
6	0	6	30	60	1.14	67
12	0	6	50	60	1.15	85
12	0	7	50	60	1.15	91

TABLE 2: Ion exchange capacity of the aromatic polymer proton exchange membrane.

Polymers	Measurements (mmol/g)	Theoretical value (mmol/g)
SPES-30	1.86	1.85
SPES-50	2.12	2.11
SPTES-30	2.28	2.27
SPTES-50	2.06	2.05
Nafion-117	2.31	2.30

TABLE 3: Water absorption and swelling ratio of different polymer films.

	Polymers (°C)	SPES-30	SPES-50	SPTES-30	SPTES-50	Nafion-117
Bibulous rate (%)	18	16.8	50.7	11.2	35.7	16.7
	38	17.5	59.5	12.5	41.3	
	58	18.7	76.5	13.5	55.8	
	78	23.9	137.5	16.3	104.7	27.5
Swelling rate (%)	18	15.9	40.2	3.9	7.4	12.6
	38	17.2	50.1	5.9	12.5	
	58	18.8	73.8	7.2	24.5	
	78	22.9	115.4	9.8	69.8	20.8

water absorption than SPTES. This may be due to the formation of conjugated structure of sulfur atom, benzene ring, and sulfone group in SPTES, but the structure hinders the free movement of macromolecular chain and limits the water absorption of sulfonic acid group. The size stability is also an important index of fuel cell performance. Table 3 shows the test results of water absorption and swelling ratio of SPES and SPTES membranes and the relevant data of Nafion-117. With the increase of temperature, the swelling rate of all membranes is increased. Due to the higher water absorption, the swelling ratio of SPES-50 and SPTES-50 is higher than that of Nafion-117. Compared with the results of water absorption, the swelling rate of sulfonated polymer is consistent with the increasing trend of water absorption of sulfonated polymer. SPES has higher swelling ratio than SPTES. At 78°C, the swelling ratios of SPES-50 and SPTES-50 are 115.4% and 69.8%, respectively. SPTES-50 has lower swelling rate than SPES-30 before 50°C. The reason is the conjugation effect of sulfur atom and benzene ring in SPTES. At low temperature, the lack of chain segment movement limits the swelling of SPTES. When the temperature rises, the swelling of polymer breaks through the limit of insufficient chain movement with the increase of water absorption. Thus, the amount of water absorption dominates the swelling rate of polymer, so the

swelling rate of SPTES-50 is more than SPES-30 when it rises to a certain temperature. Through the test of water absorption and swelling rate, it is found that there is a certain correlation between the swelling rate and water absorption, but there are many factors influencing the water absorption and swelling degree of sulfonated polymer. This experiment shows that the water absorption and swelling rate of polymer can be affected by increasing the intermolecular force.

3.4. Oxidation Stability of Membrane. It is unavoidable for proton exchange membrane to contact with air during the processing, storage, and use, and some free radicals such as $\text{HOO}\cdot$ and $\text{HO}\cdot$ will be formed in positive pole under the operating environment of fuel cell. It is easy to lead to the degradation of membrane materials, so the oxidation stability is another important performance index of proton exchange membrane.

Table 4 shows the residual mass ratio and the time of complete dissolution of polymer film in Fetion's solution at 80°C for 1 h.

After 1 h oxidation in Fetion's reagent, the residual mass of SPES-30 is 95.8% and the residual mass of SPES-50 is 93.2%, while the residual mass of SPTES-30 is 105.7% and

TABLE 4: Oxidation stability of the film.

Polymers	Remaining mass ratio (%)	Complete dissolution time (h)
SPES-30	95.8	>12
SPES-50	93.2	2.14
SPTES-30	105.7	>12
SPTES-50	99.8	2.68
Nafion-117	98.9	0

TABLE 5: Comparison of tensile properties of different aromatic polymer proton exchange membranes.

Polymers	Maximum stress (MPa)	Maximum strain (%)	Young's modulus
SPES-30	25.38	8.49	0.28
SPES-50	43.52	5.85	0.74
SPTES-30	43.52	3.45	2.42
SPTES-50	44.85	3.75	1.85
Nafion-117	28.46	3.85	0.08

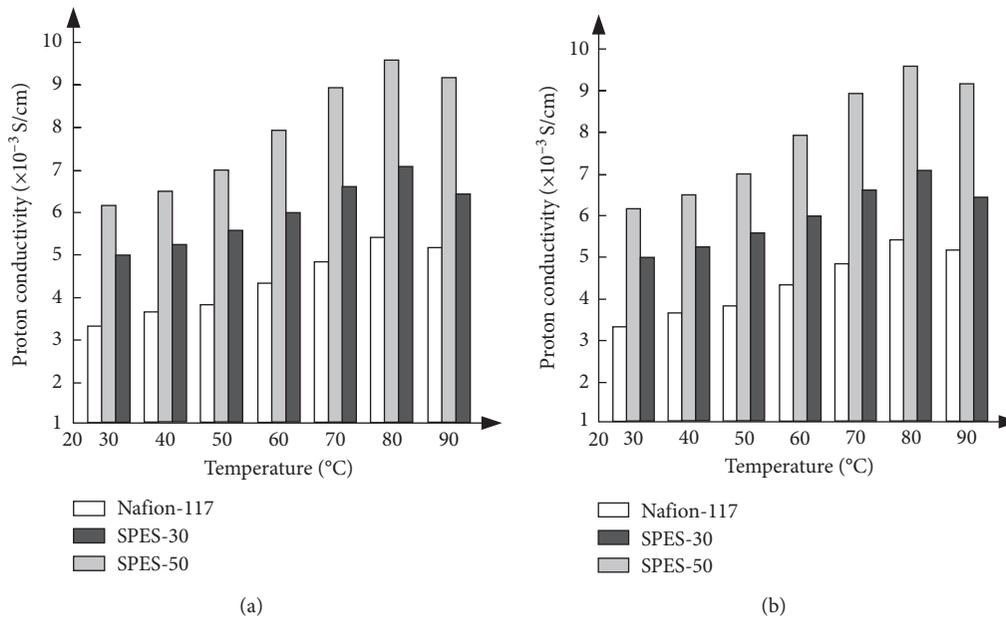


FIGURE 4: Effect of temperature on the proton conductivity of the aromatic polymer proton exchange membrane. (a) SPES membrane. (b) SPTES membrane.

the residual mass of SPTES-50 is 99.8%. These show an increasing trend in mass. SPES-50 and SPTES-50 are dissolved after 2.14 h and 2.68 h. SPES-30 and SPTES-30 membranes maintain complete after 12 h. The mass of SPTES membrane after 1 h oxidation is increased. This may be related to the C-S bond in polymer. The oxidation of thioether bond to sulfoxide bond results in the increase of membrane weight. The thioether group is converted into sulfoxide group by reaction with free radicals, so as to avoid the direct attack of hydroxyl radicals on the main chain of polymer. Therefore, SPTES membrane has better oxidation stability than that of SPTES. The increase of sulfonation degree of polymer leads to the decrease of oxidation stability of polymer. This is mainly because the oxidation attack of free radicals ($\text{HO}\cdot$ and $\text{HOO}\cdot$) appears in the hydrophilic region, and more sulfonic groups lead to the poor oxidation stability of polymer.

3.5. Tensile Properties. The tensile properties of aromatic polymer proton exchange membrane were tested, and the tensile properties of Nafion-117 membrane were compared with it. The comparison results are shown in Table 5.

The following conclusions can be drawn from the experimental results in Table 5. Compared with Nafion-117 membrane, SPES membrane and SPTES membrane have higher tensile strength and lower elongation at break, so that they have better mechanical stability.

3.6. Proton Conductivity. The proton conductivity is one of the main indexes to evaluate the proton exchange performance. The proton conductivity of SPI-X membrane is measured by AC impedance method. The change curves of conductivity of SPES membrane, SPTES membrane, and Nafion-117 membrane with temperature are shown in Figure 3. Before the test, the aromatic polymer proton

exchange membrane was processed with acid for 24 hours, and thus it changed from salt form to proton form, and then it was kept in water for 24 hours to make the membrane fully hydrated (Figure 4).

At room temperature, the conductivity increased with the increase of sulfonation degree, and the conductivity of the SPES-30 membrane reached 5.1×10^{-3} S/cm. The proton conductivity of Nafion-117 membrane was always lower than that of the SPES-30 membrane under similar conditions. With the increase of temperature, SPES-30 increases the conductivity of membrane, causes molecular motion to accelerate, and promotes $-SO_3H$ groups in the hydrated membrane and the formation of the ion clusters, whereas low temperature, relative to the high temperature, can provide more energy, on the side chain $-SO_3H$ groups can be wandering degree increases, eventually leading increase in the speed of the proton transfer, and thus the proton conductivity increases. When the test temperature was high, the electrical conductivity of SPES-30 film reached a maximum of 6.8×10^{-3} S/cm at 87°C due to the influence of high temperature dehydration. The conductivity of SPES-30 membrane began to decrease at 80°C, which was due to the decrease of the number of $-SO_3H$ groups and the decreased water retention capacity of the membrane. Proton conductivity was strongly dependent on the water content in the membrane, and the evaporation of water at high temperature had a more significant effect on the SPES membrane with a lower degree of sulfonation. The data viewing method of SPES-50 membrane, SPTES-30 membrane, SPTES-50 membrane, and Nafion-117 membrane is the same as that of SPES-30 membrane. According to the experimental data, the proton conductivity of the proton exchange membrane obtained in this paper is higher than that of the traditional proton exchange membrane, indicating that the research results in this paper have effective application results.

4. Conclusions

Through simple nucleophilic polycondensation, we have successfully prepared two kinds of sulfonated aromatic copolymers with low sulfonation degree: sulfonated poly (aryl ether sulfone) (SPES) and sulfonated poly (arylene thioether sulfone) (SPTES). Meanwhile, we can control the sulfonation degree of two kinds of polymers accurately. Both membranes are transparent and tough, and they have good mechanical properties. Their tensile strength is more than 40 MPa. Water absorption, swelling, and IEC are increased with the increase of sulfonation degree. The IEC of SPES-50 is 2.12 mequiv/g, while that of SPTES-50 is 2.06 mequiv/g. SPES and SPTES membranes show good comprehensive properties, so they have good future in application of proton exchange membrane fuel cell.

Data Availability

No datasets were generated or analyzed during the current study.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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