

PREPARATION AND PROPERTIES OF A CLASS OF LOW SWELLING RATE SULFONATED POLYARYLETHERSULFONE PROTON EXCHANGE MEMBRANE MATERIALS

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Abstract: Through a two-step organic reaction, a reactive difluorosulfone monomer with a 3,5-diphenylbenzene side group structure—3,3'-bis(3,5-diphenylbenzene) was designed and synthesized. -4,4'-Difluorodiphenylsulfone. Using this monomer, 4,4'-difluorodiphenylsulfone and 4,4'-dihydroxybenzophenone as starting materials, a series of Sulfonated polyarylsulfone proton exchange membrane (TS-PAS-xx). The structure of the prepared polymer was characterized and analyzed by infrared spectroscopy and hydrogen nuclear magnetic resonance spectroscopy, respectively. The results show that the prepared proton exchange membrane exhibits moderate water absorption and low swelling rate. At 80 °C, the swelling rate of the membrane does not exceed 15.7%. Atomic force microscopy tests showed that these proton exchange membranes formed an obvious "hydrophilic-hydrophobic" phase separation structure, which was conducive to the improvement of proton conductivity. The proton conductivity of TS-PAS-34 membrane reached 182 mS / cm, comparable to Nafion112, superior to other reported conductivities of some polyarylsulfone proton exchange membranes with the same ion exchange capacity (IEC). The film also has good thermal properties, mechanical properties and excellent stability against chemical oxidation.

Keywords: Proton exchange membrane; Sulfonated polyarylsulfone; Water absorption; Swelling rate; Chemical oxidation stability

1 EXPERIMENTAL PART

Proton exchange membrane fuel cell (PEMFC) is widely used in automobiles, electronics, aerospace and other fields have broad application prospects, and have become the focus of research in various countries [1]. As the key technical material of PEMFC, proton exchange membrane plays an important role in conducting ions, separating fuel and providing support for catalysts. Its performance determines the efficiency and service life of fuel cells. At present, PEMFC mostly uses perfluorosulfonic acid membrane (Nafion) produced by DuPont of the United States. This type of membrane has high proton conductivity, chemical stability and mechanical strength, but has high methanol permeability, low working temperature and high cost. This greatly limits its commercial application. After active research and development at home and abroad, a series of aromatic sulfonated polymers (such as sulfonated polyarylether ketone, sulfonated polyarylether sulfone and sulfonated polyimide, etc.) have been developed as substitute products [2]. Due to the rigid molecular chain characteristics of aromatic polymers, it is usually difficult for aromatic sulfonated polymers to form effective hydrophilic/hydrophobic phase separation morphology structures and ion transport channels. Therefore, this type of proton exchange membrane usually requires a higher ion exchange capacity ($IEC > 1.6$ mmol/g) to achieve a suitable ion conductivity, but when the IEC value exceeds 1.5 mmol/g, the aromatic sulfonate Excessive water swelling will appear in the polymeric proton exchange membrane material, which will lead to poor chemical oxidation resistance stability and mechanical properties [3~5].

It is found that the performance of aromatic sulfonated polymers at low IEC values can be effectively improved by introducing sulfonic acid groups into the molecular structure of polymers as side chain functional groups. However, the design and preparation of such side chain sulfonated polymers are usually challenging and require rational design

Polymer precursors with sulfonatable active sites, and selection of suitable post-Sulfonation reaction [6]. This research intends to design and synthesize a kind of active difluorosulfone monomer containing 3,5-diphenylbenzene side group structure and its polyarylsulfone copolymer through a relatively simple synthetic route, and further through a mild post-sulfonation reaction in the Multiple side chain sulfonation structures were introduced into the molecular structure of the polymer, and the corresponding side chain type sulfonated polyarylsulfone proton exchange membrane was prepared. Due to the introduction of multiple side-chain sulfonic acid groups in the sulfonated structure, the hydrophilic sulfonic acid and hydrophobic polymer main chains and non-sulfonated structural units can be further separated to promote the formation of polymer membranes. The material forms a clear phase-separated morphological structure, which can further improve the performance of the membrane material.

1.1 Main Reagents

(3,5-diphenylbenzene) boric acid (98%): Suzhou Sukailu Chemical Technology Co., Ltd.; Tetrakis(triphenylphosphine) palladium (98%): Shaanxi Kaida Chemical Co., Ltd.; 4,4'-Dihydroxybenzophenone (99%): TCI (Shanghai) Chemical Industry Development Co., Ltd.; N-Bromosuccinimide (NBS, 99%): Shanghai Runjie Chemical Reagent Co., Ltd.; 4, 4'-Difluorodiphenylsulfone (98%) : Jiangxi Renming Pharmaceutical Chemical Co., Ltd., recrystallized from ethanol; 3,3'-bis(3,5-diphenylbenzene)-4,4'-difluorobis Phenylsulfone: self-made in the laboratory; N-methylpyrrolidone (NMP, 99.5%): Aladdin Reagent Co., Ltd.; other commercial reagents were used directly.

1.2 Synthesis Of Monomers

1.2.1 Synthesis of 3,3'-dibromo-4,4'-difluorodiphenylsulfone intermediate

Add 50.85 g (0.2 mol) of 4,4'-difluorodiphenyl sulfone and 400 mL of concentrated sulfuric acid to a 1000 mL three-necked round-bottom flask, and stir at room temperature until 4,4'-difluorodiphenyl After the sulfone was completely dissolved, 78.33 g (0.44 mol) N-bromosuccinimide (NBS) was added in batches, stirred vigorously until the solution was in a homogeneous state, and the reaction was completed after 6 h. The reaction solution was slowly poured into 1500 mL of ice water while stirring, and after cooling, it was suction-filtered with a Buchner funnel to obtain a white powdery solid, which was washed repeatedly with water until neutral, dried and recrystallized with toluene. After hot filtration, cooling and standing, suction filtration, the product was further dried in a vacuum oven at 80 °C for 24 h to obtain 64.60 g of white crystal product—3,3'-dibromo-4,4'-difluorodi Phenylsulfone, yield 78%.

1.2.2 Synthesis of 3,3'-bis(3,5-diphenylbenzene)-4,4'-difluorodiphenylsulfone monomer

24.72 g (0.06 mol) of 3,3'-dibromo-4,4'-difluorodiphenylsulfone, 34.54 g (0.126 mol) of 3, 5-diphenylphenylboronic acid, 200 mL toluene, 100 mL ethylene glycol dimethyl ether and 2. 30 g tetrakis(triphenylphosphine) palladium. Stir at 60 °C until completely dissolved, add 200 mL of 20% sodium carbonate solution to the solution, raise the temperature to 105 °C, continue the reaction for 8 h, distill and separate the organic solvent, obtain the crude product after filtration, and wash with water several times. The obtained crude product was first dissolved with dimethylacetamide (DMAc), and then a sufficient amount of ethanol was added to precipitate it to obtain a powdery product. The product was recrystallized with DMAc after drying to obtain 30.31 g of white granular crystals—3,3'-bis(3,5-diphenylbenzene)-4,4'-difluorodiphenylsulfone, yield 71%.

1.3 Synthesis of Side Chain Polyarylsulfone

PAS-xx (PAS: Poly(arylene sulfone) s; xx: mole fraction of 3,3'-bis(3,5-diphenylbenzene)-4,4'-difluorodiphenylsulfone). Take PAS-18 as an example: 0.9565 g (1.35 mmol) of 3,3'-bis(3,5-diphenylbenzene)-4,4'-difluoro Diphenylsulfone, 1.5636 g (6.15 mmol) of 4,4'-difluorodiphenylsulfone, 1.6066 g (7.5 mmol) of 4,4'-dihydroxybenzophenone, 1. 2897 g (9.33 mmol) of anhydrous potassium carbonate, 11 mL of NMP (solvent) and 3 mL of toluene (water agent), first stirred at 150 °C for reaction after 2-3 hours, distill the toluene and the generated water through azeotropic distillation, then continue to heat up to 160 °C, and finish the reaction after 6-7 hours. Pour the solution into V (ethanol) while stirring: V (water) = 1: 1 solution, the product was washed several times with hot water, then placed in a vacuum oven, and dried in vacuum at 100 °C for 5 h to obtain a dry white filamentous product.

1.4 Sulfonation of Polyarylsulfone and Membrane Preparation

Add 1 g of polymer and 20 mL of concentrated sulfuric acid (98%) into a three-necked flask (protected under nitrogen), stir at 40 °C for 4 h, and then slowly settle the solution in an ice-water mixture prepared with deionized water to obtain The product was washed with deionized water for several times, filtered out by Buchner funnel, and dried in a vacuum oven at 80 °C for 5 h to obtain a granular dry sulfonated polymer.

Weigh 0.7 g of sulfonated and dried polymer, dissolve it in 13 mL of DMAc with heating and stirring, filter the solution through a sand core funnel, pour it into a rectangular glass container with a length of 15 cm and a width of 6.5 cm, and place it in Dry at 75 °C for 24 h, then cool down to room temperature, then soak the glass plate in deionized water, and peel off to obtain a flexible sulfonated polyarylsulfone proton exchange membrane.

Under the same conditions, PAS-xx was sulfonated with concentrated sulfuric acid to obtain TS-PAS-xx (TS: Tetrasulfonation).

1.5 Performance Testing and Characterization

1.5.1 ¹H-NMR test

With deuterated dimethyl sulfoxide as the solvent and tetramethylsiloxane as the internal standard, the chemical structures of the monomers, polymers and sulfonated polymers were characterized by ¹H NMR spectroscopy using a German Bruker DMX-400 nuclear magnetic resonance instrument.

1.5.2 Mechanical properties (GB-T13022) test

WDT II -5 electronic universal experiment produced by Shenzhen Kaiqiang Machinery Co., Ltd. Machine, take 10 cm × 1 cm film samples with different degrees of sulfonation, the tensile load is 5 kN, the tensile rate is 5 mm/min, and the average value of three tests is taken.

1.5.3 FT-IR test

The German Nicolet-8700 Fourier transform infrared spectrometer was used to test the sulfonated polymer membrane with a resolution of 4 cm⁻¹, the scanning range is 400 ~ 4000 cm⁻¹, and the number of scanning is 128 times. Swelling rate: SR = (L_{wet} W_{wet} - L_{dry} W_{dry}) / (L_{dry} W_{dry}).

1.5.4 Thermogravimetric (TGA) analysis

The thermal stability of the sulfonated polymers was tested with a thermal analyzer from Perkin-Elmer, USA. Before the test, the sample needs to be vacuum-dried at 60 °C for 10 min to remove the residual moisture and solvent in the sample. The heating rate is 20 °C / min, and the temperature range is 50 ~ 850 °C.

1.5.5 Determination of water absorption and dimensional stability of membranes

Obtained by the change of the polymer before and after drying and fully absorbing water.

1.5.6 Determination of membrane proton conductivity

The proton conductivity of the sulfonated polymer was tested by an electrochemical comprehensive analyzer (Solartron), and the frequency used was 0.1 ~ 100 kHz.

1.5.7 Morphology observation of sulfonated membrane

The NanoWizard 3 atomic force microscope produced by Germany JPK Company was used for analysis. First dry the TS-PAS-xx film in a vacuum oven at 100 °C to remove excess water and solvent, then take 0.05 g of TS-PAS-xx film and dissolve it in 10 mL DMAc (dissolved by heating with a magnetic stirrer), and use Filter the solution through a 0.45 μm type PTFE syringe filter, and then pour an appropriate amount of the solution was spread on a transparent glass slide of 2 cm × 2 cm, and dried in an oven at 80 °C for 12 h to obtain a processed AFM test sample.

1.5.8 Chemical Oxidation Stability Test

The membrane was tested after immersion in Fenton's reagent (3% H₂O₂, 2 × 10⁻⁶ g / L FeSO₄).

2 RESULTS AND DISCUSSION

First use NBS to carry out the bromination reaction of 4,4'-difluorodiphenyl sulfone to obtain the intermediate --- 3,3'-dibromo-4,4'-difluorodiphenyl sulfone (the previous literature of the laboratory has been reported [7,8]). On this basis, the intermediate is catalyzed by Pd (PPh₃)₄ and (3,5-diphenylbenzene) boronic acid via Suzuki coupling reaction to obtain a new type of monomer containing diphenylbenzene side group structure, and its structure was characterized by NMR. The ¹H-NMR spectrum of 3,3'-bis(3,5-diphenylbenzene)-4,4'-difluorodiphenylsulfone, in which the chemical shifts of all hydrogen protons are assigned. Since the sulfone group is a strong electron-withdrawing group, affected by its shielding effect, the adjacent H7 and H8 appear at the low field with a high chemical shift, and all the proton peak area ratios are close to the theoretical values, indicating that the monomer was successfully synthesized.

2.1 Synthesis and characterization of monomers

Afterwards, sulfonation reagents such as chlorosulfonic acid and concentrated sulfuric acid are used for direct sulfonation, and the post-sulfonation reaction using concentrated sulfuric acid as the sulfonation reagent is relatively mild.

2.2 Synthesis and characterization of polyarylsulfone and its sulfonated polymer

The preparation of side-chain sulfonated polymers mainly adopts two methods: polymer grafting reaction and polymer direct post-sulfonation reaction to introduce sulfonic acid. Among them, the introduction of sulfonic acid through grafting reaction requires the design and preparation of precursor polymers containing functional group-containing side chains that can be further reacted, such as hydroxyl-type polymers, amino-type polymers, etc., and then combined with small sulfonic acid-containing

Molecular compounds undergo grafting reactions to obtain corresponding sulfonated reagents. This preparation route usually requires multi-step reactions to complete, and the preparation process is relatively complicated [9].

The key to preparing side-chain sulfonated polymers through direct post-sulfonation of polymers is the need to design polymers that contain direct sulfonated side groups. However, in this paper, sulfonated polyarylsulfones are first prepared with 3,3'-bis(3,5-diphenylbenzene)-4,4'-difluorodiphenylsulfone, 4,4'-difluorodiphenylsulfone and 4,4'-dihydroxybenzophenone as starting materials, after aromatic A series of polyarylsulfones (PAS-xx) with

side chains containing benzene ring structures were prepared by nucleophilic co-condensation. The side chain benzene ring in this type of polyarylsulfone is in an electron-rich activation state, and the benzene ring in the main chain structure is in an electron-withdrawing passivation state of the sulfone group and the ketone group, so it can be directly post-sulfonated. into the sulfonic acid group. Since the prepared polymer PAS-xx has good solubility in concentrated sulfuric acid, concentrated sulfuric acid can be selected as the sulfonation reagent, and side chain sulfonic acid can be introduced under milder reaction conditions. The sulfonation process was carried out at room temperature, and the reaction time was 4 h. Fig. 1 is the appearance picture of the TS-PAS-18 membrane. It can be seen from the figure that the prepared membrane is uniform in thickness, light yellow and transparent, and has toughness. The intrinsic viscosity of the four functional polyarylsulfones ranges from 0.58 to 0.63 dL/g, and the relative molecular mass distribution coefficient is 1.7 to 1.9, which indicates that this series of polymers has a relatively high relative molecular mass and moderate molecular mass distribution.



Fig. 1 Photographs of the TS-PAS-18 films cast from DMAc

The exchange capacity (IEC) is measured to determine whether the sulfonation reaction is complete, and the results are shown in Table 1. The measurement range of the TS-PAS-xx membrane is 1.23 ~ 1.90 mmol/g, which is close to the theoretical value calculated by the initial molar ratio. The test results show that the sulfonation reaction is complete, and the initially designed side chains are successfully prepared. Sulfonic acid structure. The structures of polymers before and after sulfonation were analyzed by infrared spectroscopy and hydrogen nuclear magnetic resonance spectroscopy, taking PAS-18 and TS-PAS-18 as examples.

2.3 Water Absorption and Swelling Rate of Membrane

Generally, the water in the proton exchange membrane can be divided into free water and bound water. The two kinds of water are crucial for the dissociation of protons and the formation of nanochannels for the transfer of hydrogen protons. In this paper, the water absorption of TS-PAS-xx membranes under different temperature conditions was studied. The test results are shown in Table 2, and the corresponding water absorption curve. As the temperature increases, the water absorption rate continues to increase. The figure also shows the change curve of water absorption of Nafion112 with temperature. It can be seen that the rising trend of water absorption of Nafion112 is relatively slow, and there is an obvious slowing trend at 60 ~ 80 °C. However, the water absorption rate of TS-PAS-xx membrane increased relatively greatly, especially at 80 °C, the water absorption rate of membrane TS-PAS-34 reached 56.5%, which was due to the increase of the content of sulfonic acid groups in the membrane. The ability to bind water is also improved.

Table 1 Ion exchange capacity (IEC), water uptake and swelling ration of TS-PAS-xx mem-branes

Copolymers	IEC / (mmol·g ⁻¹)		Water uptake / %		Swelling ratio / %	
	Cal. a	Tit. b	20°C	80 °C	20°C	80°C
	TS-PAS-18	1.26	1.23	10.1	28.5	1.5
TS-PAS-22	1.46	1.41	12.4	35.4	2.4	5.8
TS-PAS-26	1.64	1.63	15.3	40.2	3.3	7.5
TS-PAS-30	1.81	1.79	18.5	45.9	4.6	11.1
TS-PAS-34	1.96	1.90	22.4	56.5	7.0	15.7
Nafion 112			17.5	30.6	10.1	17.8

The increase of water absorption will cause the swelling of the membrane, which will affect the mechanical properties and proton conductivity of the membrane. According to relevant literature reports [10], the nano-phase separation structure of the membrane will be affected during the swelling process, and proton dilution will occur. From the corresponding swelling rate change curve, it can be concluded that the swelling rate of TS-PAS-xx membrane increases linearly with the increase of IEC value and temperature. 7%, the ion exchange capacity of TS-PAS-34 is the highest (1.96 mmol/g), and its swelling rate is also the highest, and there is a relatively obvious

upward trend at 80 °C, but even in the case of high water absorption In both cases, the swelling rate is also significantly smaller than that of Nafion112. The low water absorption and good dimensional stability are attributed to the introduction of the side chain polysulfonic acid phenyl structure, which increases the free volume and combines the hydrophilic sulfonic acid with the hydrophobic polymer main chain and non-sulfonated structure. The separation of the units further improves the water-resistant stability of the non-sulfonated polymer backbone, thereby effectively inhibiting the swelling of the membrane. This similar situation was also observed in another type of side-chain proton exchange membranes containing multiple phenylsulfonic acid groups [11].

2.4 Proton Conductivity and Membrane Morphology

Proton conductivity is one of the most critical factors determining the performance of proton exchange membranes. The proton conductivity of TS-PAS-xx membrane at different temperatures was tested by electrochemical workstation, and compared with Nafion112. As the IEC value and temperature increased, the proton conductivity of the membrane also increased. At 80 °C, the membrane The conductivity of TS-PAS-34 reached 182 mS/cm. In the case of 80 °C and similar IEC values, it is compared with different structural protons reported in other literatures THE conductivity of the exchange membrane was compared. The 2F-SPAES-40 proton exchange membrane reported by Jiang et al. [12] had a main chain sulfonated structure. Although the proton conductivity reached a high level, the swelling rate was much higher than that of TS -PAS-30 membrane, because the sulfonic acid group is directly connected to the main chain, the main chain is easy to absorb water and swell at high temperature, and the mechanical properties of the membrane are reduced. The SPDCDBB-6 side chain type proton crossover reported by Jang et al.[13] the membrane was replaced, and a similar swelling rate was achieved but the conductivity was much lower than that of this paper. Reported that it reached 78.9 mS/cm, which may be due to the better connectivity of ionic domains in the TS-PAS-30 membrane. In addition, the swelling rate and conductivity of TS-PAS-xx membranes are superior to some block-type reports, such as SP-LA (60, 50) (sulfonated polyaryletherketone/ Polylactic acid) block type proton exchange membrane, its swelling at 80 °C. The conductivity reached 14%, but the conductivity only reached 116 mS/cm, which may be due to the rigidity of the aromatic group in the block polymer affecting the self-assembly effect of the PLA phase. This shows that the introduced polysulfonic acid benzene side group structure can effectively inhibit the swelling of the membrane and form a good phase separation morphology, thereby ensuring good proton conductivity.

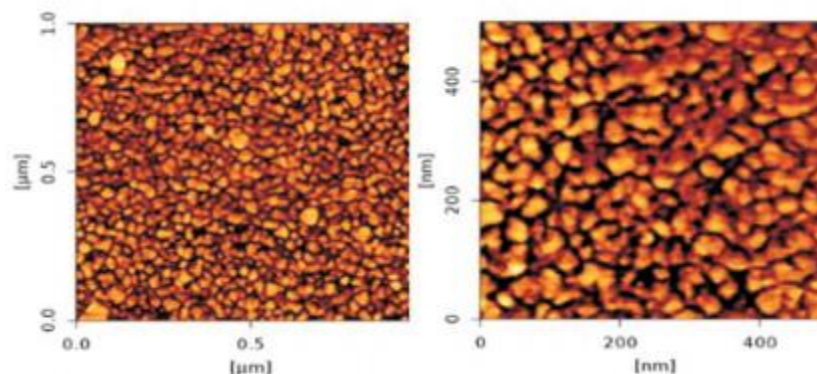


Fig. 2 AFM phase images of TS-PAS-34scale: 1 × 1 μm and 500 × 500 nm

The proton conductivity and dimensional stability of membranes are closely related to their internal morphology. In order to elucidate the structure-morphological correlation of the prepared membrane, the AFM was set in the tapping mode to study the microphase separation structure of the proton exchange membrane. Fig. 2 shows that the TS-PAS-34 membrane has a significant microphase separation structure, the resolution of the phase diagram is 1 μm × 1 μm and 500nm × 500 nm, and the darker regions generally correspond to softer sulfonic acid groups The formed hydrophilic domains, the brighter areas generally correspond to the harder hydrophobic main chains. It can be seen from the figure that the TS-PAS-34 membrane has a well-connected nanoscale ion transport network, due to the hydrophilic side chain sulfonic acid and The incompatibility of the hydrophobic backbone leads to this unique self-assembled morphology. In addition, due to the dense grafting of side chains on the main chain, the proportion of hydrophobic and hydrophilic segments can be increased at similar IEC values, which can further enhance the aggregation of ionic domains, which is beneficial to the improvement of proton conductivity.

2.5 Thermal Properties, Mechanical Properties and Oxidation Stability of the Film

Using TGA to test the thermal stability of the TS-PAS-XX polyarylsulfone membrane dried at 100 °C for 12 h in a vacuum oven (nitrogen atmosphere), the first downward trend appeared between 100 °C and 200 °C, which is

mainly Corresponds to the evaporation of bound water hydrated by residual solvent and sulfonic acid groups in the membrane. When a mass loss of 7% is reached, the temperature in the graph is close to 255 °C. Next, there are two obvious thermal degradation stages. The degradation of sulfonic acid group mainly corresponds to 225 ~ 350 °C in the figure, and the degradation of polyarylsulfone molecular main chain mainly occurs between 500 ~ 595 °C. Analyzing the thermal degradation trend in the graph, as the degree of sulfonation increases, the initial degradation temperature of TS-PAS-xx polyarylsulfone membranes also decreases, which is consistent with the remaining mass of thermal degradation of each polyaryl ether sulfone membrane at 800 °C. The fractions correspond, further evidence that it is the degradation of the sulfonic acid groups that initially occurs.

Generally, the application of the membrane in fuel cells is simulated by testing the mechanical properties of the proton exchange membrane in the hydrated state, which can better reflect the real mechanical properties of the membrane. Each membrane sample was completely soaked in deionized water for 24 h before the test. The test results of the TS-PAS-XX membrane are shown in Table 2. The tensile strength is 28.9 ~ 39.6 MPa, and the tensile modulus is 0.63 ~ 1.26 GPa, the elongation at break is 10% ~ 30%. And by Table 2 It can be seen that the tensile strength and tensile modulus of the membrane TS-PAS-XX decrease with the increase of the IEC value, because the water absorption of the proton exchange membrane increases with the increase of the IEC value, due to The plasticizing effect of water reduces the tensile strength and modulus. Compared with the previously reported sulfonated aromatic proton exchange membranes, the mechanical properties of TS-PAS-XX membranes have reached a considerable level, which can meet the application environment of fuel cells [15].

Table 2 Mechanical properties and oxidative stability of TS-PAS-xx membranes

Copolymers	Tensile strength / MPa	Tensile modulus / GPa	Elongation at break / %	t /h	RW / %
TS-PAS-18	39.6	1.26	10	15	100
TS-PAS-22	35.1	1.15	15	12	100
TS-PAS-26	32.8	0.98	20	10	99
TS-PAS-30	30.6	0.76	twenty four	9	99
TS-PAS-34	28.9	0.63	30	7.4	98

The oxidation resistance of TS-PAS-XX membranes is very important because the working environment of fuel cells is very harsh. Fenton's reagent (3% H₂O₂ and 2 × 10⁻⁶ g / L FeSO₄ aqueous solution) were used as the determination of the oxidation resistance of the proton exchange membrane. Oxidation resistance is usually recorded as the time required for the film to be completely dissolved when it is put in. The test results of TS-PAS-XX films with different degrees of sulfonation in Fenton reagent are shown in Table 2. The oxidation resistance time of all TS-PAS-XX films is between 7 and 15 h. The test result of TS-PAS-XX film completely dissolving at 80 °C is 15 h. After soaking the film in Fenton's reagent for 1 h, All membranes had a residual mass of over 98%. The degradation of sulfonated polymers was mainly due to the attack of HO·/HOO· in the region of hydrophilic groups, and with the increase of IEC value, the water absorption of the membrane increased, which facilitated the transport of free radicals. In this series of sulfonated polyarylsulfones, the sulfonic acid groups are connected to the side groups of diphenyl groups, which can better slow down the degradation of the polymer main chain and improve high film oxidation stability. Compared with the reported polyarylsulfone proton exchange membranes containing side chain sulfoalkyl groups, this series of sulfonated polyarylsulfone proton exchange membranes has better oxidation stability[15].

3 CONCLUSION

- (1) Through a two-step organic reaction, a new active difluorosulfone monomer containing 3,5-diphenylbenzene side group structure was designed and synthesized—3,3'-bis(3,5-diphenyl phenyl)-4,4'-difluorodiphenylsulfone. Using this monomer, 4,4'-difluorodiphenyl sulfone and 4,4'-dihydroxybenzophenone as raw materials, a series of sulfonated polymers were prepared by using aromatic nucleophilic substitution polycondensation and post-sulfonation reaction. Arylsulfone proton exchange membrane. The results of FT-IR and NMR analysis confirmed that the desired structure was obtained, and the intrinsic viscosity was between 0.58 and 0.63 dL/g.
- (2) The prepared polymer membrane has good heat resistance, moderate water absorption and low swelling rate. The swelling rate of TS-PAS-34 proton exchange membrane at 80 °C is 15.8%, which is the same as that of IEC value, phase it exhibits a lower swelling rate than other reported proton exchange membranes.
- (3) The highest conductivity reaches 182 mS/cm at 80 °C, which is attributed to the obvious "hydrophilic-hydrophobic" nanophase separation structure formed by the polyarylsulfone proton exchange membrane with side chain polysulfonic acid structure. The chemical oxidation resistance time of all films in the Fention test at 80 °C

exceeds 7 h, and their tensile strengths range from 28.9 to 39.6 MPa. Taking these properties together, this type of membrane has the prospect of long-term use in fuel cells.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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