

Short communication

A new and facile approach for the preparation of cross-linked sulfonated poly(sulfide sulfone) membranes for fuel cell application

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Abstract

A new and facile approach has been developed for the preparation of cross-linked sulfonated poly(sulfide sulfone) (SPSSF) membranes. The cross-linking reaction was performed by immersing the SPSSF membranes into polyphosphoric acid at 180 °C for 1.5 h and the cross-linking bond was the very stable sulfonyl group. Cross-linking significantly improved the membrane performance, i.e., the cross-linked membranes showed better mechanical properties, lower water uptake and lower methanol permeability than the corresponding uncross-linked ones, while reasonably high proton conductivity was maintained. For example, for the membrane containing 40 mol% sulfonated moiety, by cross-linking the tensile strength increased from 39 MPa (dry) or 21 MPa (wet) to 44 MPa (dry) or 30 MPa (wet) and the elongation at break from 17% (dry) or 18% (wet) to 65% (dry) or 21% (wet), while the water uptake was reduced from 74 to 38 wt% and the methanol permeability from 7.0×10^{-7} to 1.6×10^{-7} cm² s⁻¹ (30 °C). The proton conductivity, however, did not decrease too much (from 0.076 to 0.043 S cm⁻¹ in water at 30 °C). © 2007 Elsevier B.V. All rights reserved.

Keywords: Sulfonated poly(sulfide sulfone); Membrane; Cross-linking; Proton conductivity

1. Introduction

In the past decade sulfonated polymers have attracted much attention because of their important applications in polymer electrolyte membrane fuel cells (PEMFCs) which provide clean, quiet and portable power sources for vehicular transportation and electronic devices. Researches in this field mainly focus on the development of low cost and high performance (high proton conductivity, good mechanical properties, excellent chemical and electrochemical stability, low reactant crossover, etc.) sulfonated hydrocarbon polymers in order to replace currently used sulfonated perfluoropolymers, typically, DuPont's Nafion. Proton conductivity and membrane stability are the most important two properties which determine the fuel cell performance. Generally high proton conductivity can be readily achieved by controlling the ion exchange capacity (IEC)

at a relatively high level (e.g. >2.0 mequiv. g⁻¹). However, high IEC often causes poor water stability of the membranes, i.e., the membranes highly swell or even dissolve in water and thus lose mechanical properties. Cross-linking is a common method to enhance the mechanical properties, to suppress membrane swelling degree and to improve the membrane durability. Up to now, many cross-linking methods have been developed such as photo-cross-linking [1], ionic (acid–base) cross-linking [2–4] and covalent cross-linking (e.g. esterification) [5–11]. However, most of these methods suffer from either the weak cross-linking bonds or the complicated preparation process or other problems. Recently we have developed a facile approach for the preparation of cross-linked sulfonated polyimide (SPI) membranes and the cross-linking is based on the reaction between the sulfonic acid groups and activated phenyls in the presence of phosphorus pentoxide or phosphorus pentoxide/methanesulfonic acid (1:10 by weight) [12]. In this paper, we report on a new and facile approach for the preparation of cross-linked sulfonated poly(sulfide sulfone) (SPSSF) membranes.

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2. Experimental

2.1. Materials

4,4'-Dichlorodiphenyl sulfone (DCDPS) and 4,4'-thiobisbenzenethiol (TBBT) were purchased from Aldrich and TCI, respectively. *N,N*-Dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), anhydrous potassium carbonate, fuming sulfuric acid (50% SO₃), sulfuric acid, polyphosphoric acid (PPA), toluene and methanol were purchased from SCRC. Potassium carbonate was vacuum dried at 160 °C for 20 h. DMAc was distilled under reduced pressure and dried with molecular sieve 4 Å prior to use. Other materials were used as received. 4,4'-Dichlorodiphenylsulfone-3,3'-disulfonic acid disodium salt (DCDPSDS) was synthesized by sulfonation of DCDPS at 120 °C using fuming sulfuric acid as the sulfonating reagent.

2.2. Polymerization

The polymerization was performed according to a modified literature method [13]. The detailed experimental procedures are described as follows using SPSS-50 (here the figure '50' refers to the percentage molar fraction of DCDPSDS) as an example.

To a 100 mL dry 3-neck flask equipped with a Dean-Stark trap and a condenser were added 0.9820 g (2.0 mmol) of DCDPSDS, 0.5740 g (2.0 mmol) of DCDPS and 1.0016 g (4.0 mmol) of TBBT, 0.61 g (4.4 mmol) of anhydrous potassium carbonate and 8 mL of DMAc under nitrogen flow with stirring. Fifteen millilitres of toluene was added dropwise through a dropping funnel and the reaction mixture was heated to 140 °C. Water and toluene were evaporated as the azeotrope and collected in the Dean-Stark trap. After water was completely evaporated (the Dean-Stark trap became clear), the reaction temperature was raised to 160 °C and the polymerization was continued at this temperature overnight. The resulting highly viscous solution was diluted with additional 10 mL of DMAc and then slowly poured into methanol. The resulting fiber-like precipitate was thoroughly washed with methanol and water, respectively, and dried at 120 °C in vacuo.

2.3. Membrane formation and proton exchange

SPSSF membranes (in salt form) were prepared by casting their DMSO solutions (~5 wt%) onto glass dishes and dried at 80 °C for 10 h. The as-cast membranes were soaked in methanol at 60 °C for 1 h to remove the residual solvent, and then immersed into 1.0 M sulfuric acid at room temperature for 2 days for the proton exchange. The membranes were thoroughly washed with deionized water till the rinsed water became neutral followed by drying in vacuum at 120 °C for 20 h.

2.4. Cross-linking treatment

Dry SPSSF membranes in their proton form were immersed into PPA in a glass vessel at 180 °C for 1.5 h under nitrogen atmosphere. The membranes were taken out, thoroughly rinsed

with deionized water till the rinsed water became neutral and dried in vacuum at 120 °C for 20 h.

2.5. Measurements

FT-IR spectra were recorded on a Perkin-Elmer Paragon 1000PC spectrometer. Inherent viscosity (η) was measured in DMSO with an Ubbelohde viscometer at 30 °C. IEC was measured by titration method. About 0.2–0.3 g of dry membranes (proton form) were cut into small pieces and immersed into saturated sodium chloride salt solution with stirring for 2 days. The resulting solution was titrated with 0.01N sodium hydroxide solution using phenolphthalein as an indicator. Tensile measurement was performed with an Instron 4456 instrument at room temperature in ambient atmosphere (~60% relative humidity) at a crosshead speed of 1 mm min⁻¹.

Water uptake (WU) measurements were carried out by immersing the membranes (0.2–0.3 g per sheet) into deionized water at 30 °C for 24 h. Then the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. Water uptake S was calculated from

$$S (\%) = \frac{W_s - W_d}{W_d} \times 100 \quad (1)$$

where W_d and W_s refer to the weight of dry and wet membranes, respectively.

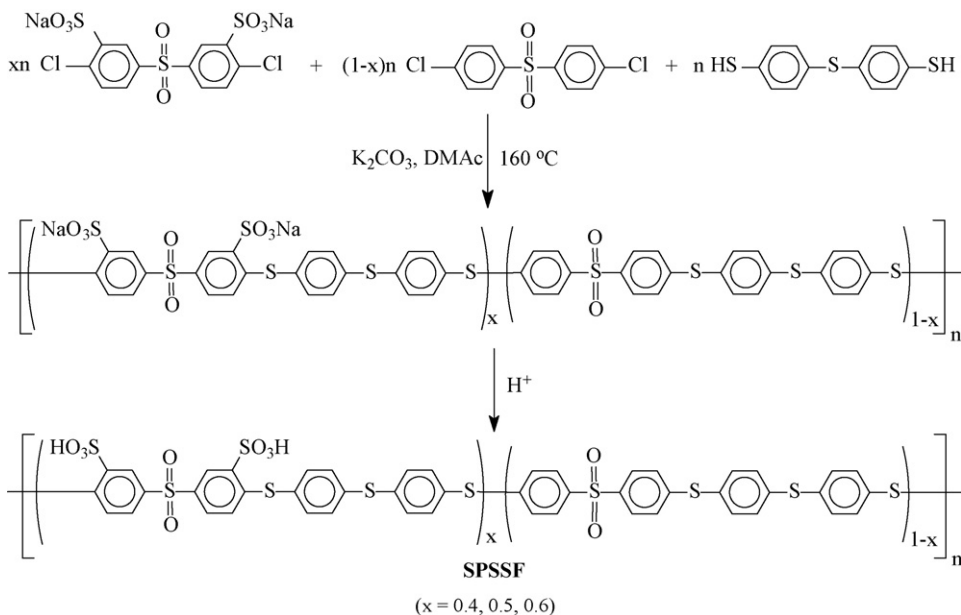
Proton conductivity (σ) was measured using a four-point-probe electrochemical impedance spectroscopy technique over the frequency range from 100 Hz to 100 KHz (Hioki 3552) [14,15]. Methanol permeability (P_M) was measured using a liquid permeation cell and measuring the methanol concentration in feed and in permeate with permeation time at 30 °C [16]. The initial methanol concentration in feed was 8.6 wt%, while pure water was used in the permeate side (the volume is exactly the same as that of the feed). The composition of solutions (feed and permeate) were analyzed with a GC9790II gas chromatography apparatus. Methanol permeability coefficient was calculated from the following equation:

$$P = \frac{C_b V_b L}{A C_a t} \quad (2)$$

where C_a and C_b refer to the methanol concentration in feed and permeate, respectively. V_b is the solution volume of permeate. L , A and t refer to membrane thickness, membrane effective area and time, respectively.

3. Results and discussion

SPSSFs with different IECs were synthesized by random copolymerization of DCDPSDS, DCDPS and TBBT in DMAc in the presence of anhydrous potassium carbonate at 160 °C for 20 h (Scheme 1). The molar ratio of DCDPSDS to DCDPS was regulated at 40:60, 50:50 and 60:40 to give the copolymers with different IECs. The resulting SPSSFs showed high inherent viscosity (Table 1), and tough and ductile membranes were prepared by solution cast method, indicating that high molecular weight polymers were obtained.



Scheme 1. Synthesis of sulfonated poly(sulfide sulfone).

Table 1
Inherent viscosity of the polymers and the maximum stress (MS), elongation at break (EB), IEC, water uptake (WU), proton conductivity (σ), methanol permeability (P_M) and the ratio of σ to P_M (Φ) of the cross-linked and uncross-linked SPSSF membranes

Polymer	η^a (dL g ⁻¹)	Cross-linking treatment	IEC ^b (mequiv. g ⁻¹)	MS (MPa)		EB (%)		WU ^c (wt%)	σ^d (S cm ⁻¹)	P_M^e (10 ⁻⁶ cm ² s ⁻¹)	Φ (10 ⁴ S cm ⁻³ s ⁻¹)
				Dry	Wet	Dry	Wet				
SPSSF-40	4.30	No	1.38	39	21	17	18	74	0.076	0.70	11
		Yes	1.20	44	30	65	21	38	0.043	0.16	27
SPSSF-50	3.74	No	1.66	40	22	18	16	161	0.12	1.0	12
		Yes	1.34	44	33	27	20	80	0.065	0.43	15
SPSSF-60	1.90	No	1.89	36	14	17	10	320	0.17	1.9	9
		Yes	1.60	46	19	28	12	171	0.13	1.0	13
Nafion112			0.91					30	0.10	2.4	4.2

^a 0.5 g dL⁻¹ in DMSO at 30 °C.

^b Measured by titration method.

^c At 80 °C.

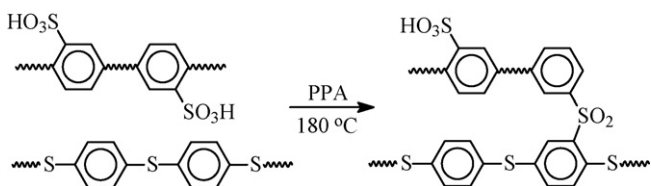
^d In water at 30 °C.

^e Methanol concentration in feed: 8.9 wt% at 30 °C. The data of Nafion 112 were cited from reference [16].

Cross-linked membranes were prepared by treating the proton form membranes with PPA at 180 °C for 1.5 h. PPA is the condensation reagent and the cross-linking is based on the chemical reaction between the sulfonic acid groups and the activated phenyl rings of TBBT moiety (Scheme 2). The formation of cross-linking was judged by the insolubility of the SPSSF

membranes in organic solvents (DMSO, DMAc) in which the membranes were well soluble before treating with PPA. Fig. 1 shows the FT-IR spectra of SPSSF-50 membrane before and after cross-linking treatment. The two spectra are quite similar but the relative intensity of the absorption band around 1039 cm⁻¹ (stretch vibration of sulfonic acid group) is smaller for the cross-linked membrane. This indicates that part of the sulfonic acid groups were consumed due to the cross-linking treatment. Similar phenomenon was observed with other SPSSF membranes. Cross-linking treatment also caused the reduction of IEC (determined by titration, Table 1) which is just consistent with the results of FT-IR analysis.

The effects of cross-linking on the mechanical properties, water uptake (WU), proton conductivity (σ) and methanol permeability (P_M) of SPSSF membranes were examined and the



Scheme 2. Diagram of cross-linking reaction.

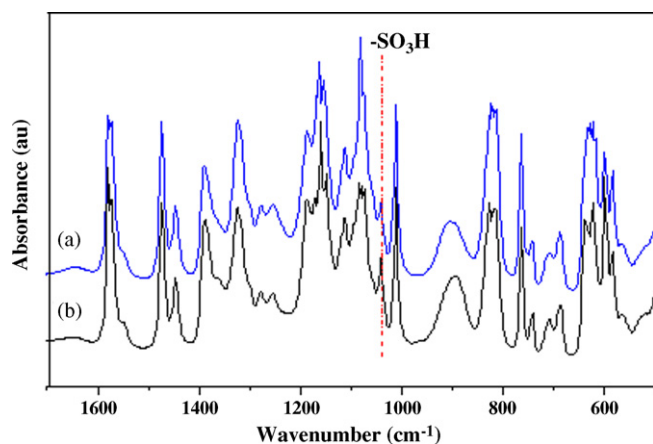


Fig. 1. FT-IR spectra of SPSSF-50: (a) cross-linked and (b) uncross-linked.

results are shown in Table 1. It can be seen that cross-linking led to significant improvement in the mechanical properties of the membranes. All the cross-linked membranes showed higher tensile strength (MS) than the corresponding uncross-linked ones especially in wet state. Elongation at break (EB) also increased due to cross-linking and the increase was more pronounced for the dry membranes than for the wet membranes. To further enhance the EB values of the wet membranes, higher cross-linking density might be needed and this can be achieved by longer cross-linking time. Cross-linking also caused significant depression of membrane swelling judging from the largely reduced water uptake (WU) of the cross-linked membranes, i.e., the water stability of the membranes was much improved due to cross-linking.

The cross-linked membranes displayed somewhat lower proton conductivities than the corresponding uncross-linked ones because of the reduced IECs of the former. Nevertheless, the proton conductivities of the cross-linked membranes were still at reasonably high level. Cross-linked SPSSF-50, for example, showed a proton conductivity of 0.065 S cm^{-1} at 30°C in water which is comparable to that of Nafion 112 under the same conditions.

Methanol permeability was significantly reduced by the cross-linking treatment. Cross-linked SPSSF-40, for example, showed the methanol permeability of $0.16 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ at 30°C which is about one-fourth of that of the uncross-linked membrane and one order lower than that of Nafion 112. The ratio of proton conductivity to methanol permeability (Φ) is often used to evaluate the overall performance of the membranes and the higher Φ , the better performance. All the cross-linked membranes exhibited larger Φ than the uncross-linked ones indicating better performance of the cross-linked membranes. The

effects of cross-linking density on methanol permeability and other properties are in progress.

4. Conclusions

A novel and facile cross-linking method has been developed for the preparation of cross-linked sulfonated poly(sulfide sulfone) (SPSSF) membranes by using PPA as the condensation reagent. The cross-linked membranes showed better mechanical properties, lower water uptake and lower methanol permeability than the corresponding uncross-linked ones, while reasonably high proton conductivity was maintained indicating better performance due to cross-linking.

Acknowledgments

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