Novel Preparation Method of Cross-linked Sulfonated Polyimide Membranes for Fuel Cell Application

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A facile cross-linking method has been successfully developed for sulfonated polyimide (SPI) membranes. The SPIs with electron-rich phenyl rings in the non-sulfonated diamine moiety were readily cross-linked by immersing the membranes into a solution of phosphorous pentoxide and methanesulfonic acid at 30–80 °C. The resulting SPI membranes cross-linked via sulfonyl groups showed greatly improved water stability compared with the uncross-linked ones, while high proton conductivity was maintained. They have potential for fuel cells at high temperatures above 80 °C.

Polymer electrolyte membrane (PEM) is the key component of polymer electrolyte fuel cell (PEFC) and direct methanol fuel cell (DMFC). Current state-of-the-art PEMs are sulfonated perfluoropolymers such as DuPont's Nafion. However, some drawbacks such as high cost, high fuel crossover, and low operation temperature seriously limit their industrial application. This promotes the development of alternative membrane materials with low cost and high performance. Many sulfonated hydrocarbon polymer membranes[1] such as sulfonated polysulfones, sulfonated poly(ether ketone)s, sulfonated polyphenylenes, and six-membered ring sulfonated polyimides (SPIs)[2–4] have been reported to have comparable or even higher proton conductivities than Nafion in fully hydrated state. However, a major problem associated with most of the sulfonated hydrocarbon polymer membranes is their poor water stability, i.e., the membranes highly swell or even dissolve in water especially at higher temperatures. Cross-linking is a common and effective method to enhance the mechanical properties, to suppress membrane swelling and to improve the membrane durability. There are many reports on preparation of ionically or covalently cross-linked PEMs.[5] However, some serious problems still remain, that is, brittleness of the cross-linked membranes especially in dry state, weakness of cross-linking bond in water at high temperatures above 70 °C, and complicated preparation process. We developed a series of branched/cross-linked SPI membranes which were prepared through the reaction of anhydride-end-capped SPI oligomers and a triamine monomer.[6] These SPI membranes showed good water stability as well as high proton conductivity. In this paper, we report on another facile method for preparation of cross-linked SPI membranes.

Random and sequenced co-SPIs (Figure 1) were synthesized by one-step condensation polymerization of 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) and sulfonated and non-sulfonated diamine monomers in *m*-cresol in the presence of triethylamine (Et_3N) and benzoic acid.[3] 4,4-Bis(4-aminophenoxy)biphenyl-3,3′-disulfonic acid (BAPBDS) and 2,2′-bis-(4-sulfophenoxy)benzidine (BSPOB) were used as sulfonated diamines. They were synthesized as previously reported.[3,7] 4,4-Bis(4-aminophenoxy)biphenyl (BAPB) and 1,3-bis(4-aminophenoxy)benzene (BAPBz) were used as non-sulfonated diamines. Membranes were prepared by casting SPI solutions in *m*-cresol onto glass plates and dried at 120 °C for 10 h. The as-cast membranes were soaked in methanol at room temperature for 48 h followed by the proton exchange treatment in 1 M sulfuric acid at 50 °C for 2–5 days. The dry SPI membranes in proton form were immersed into the medium of phosphorous pentoxide/methanesulfonic acid in the ratio of 1/10 by weight (PPMA) at a given temperature for a given time to generate cross-linking. The cross-linking reaction is based on the chemical reaction between sulfonic acid groups of sulfonated diamine moieties and the activated phenyl rings of non-sulfonated diamine moieties in the presence of PPMA, and the resulting cross-linking linkage is the very stable sulfonyl group (Scheme 1). This is based on Ueda's reports on synthesis of diaryl sulfones by condensation reaction of arenesulfonic acids and activated (electron-rich) aromatic hydrocarbons in PPMA.[8] We expect that SPI membranes might be readily cross-linked by treating them with PPMA without introducing additional cross-linkable functional groups.

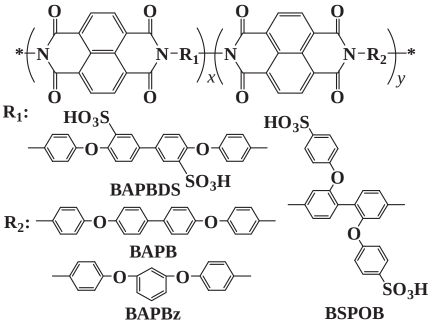
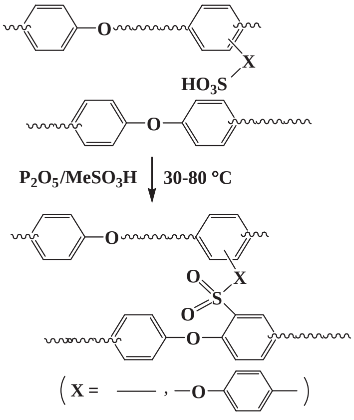


Figure 1. Chemical structure of SPIs.



Scheme 1. Cross-linking reaction of SPI membranes.

Table 1. Properties of cross-linked and uncross-linked SPI membranes

Membrane	Cross-linking condition	Solubility^{a}	IEC^{b} /meq g^{-1}	WU^{c} /%	σ^{d}/mS cm^{-1}			MS^{e} /MPa	EB^{e} /%
					50%	70%	in water		
NTDA-BAPBDS/BAPBz(2/1)-r	No	○	1.88 (1.96)	58 (70)	2.3	13	102	58	96
	80 °C, 8 h	×		64	2.6	12	96	45	55
	30 °C, 48 h	×						60	56
NTDA-BSPOB/BAPB(2/1)-r	No	○	1.94 (1.89)	78 (109)	7	30	170	120 (76)^{f}	50 (8)^{f}
	80 °C, 5 h	×	1.71	76 (90)	6.1	25	136	102 (79)^{f}	20 (16)^{f}
NTDA-BSPOB/BAPBz(1/1)-s	No	○	1.55 (1.56)	57 (73)	2.2	14	118	94 (64)^{g}	50 (11)^{g}
	80 °C, 8 h	×		55	1.8	9	95	90 (73)^{g}	18 (14)^{g}
	30 °C, 48 h	×	1.39	57	1.9	10	100	100 (77)^{h}	40 (15)^{h}

[a] In *m*-cresol + TEA. [b] By titration, data in parenthesis theoretical. [c] At rt, data in parenthesis at 100 °C. [d] At 60 °C. [e] Stress and elongation at break, data in parenthesis the membranes after aging in water at 130 °C. [f] For 192 h. [g] For 300 h. [h] For 500 h.

Table 1 lists the cross-linking treatment conditions and results for SPI membranes. The formation of cross-linking was judged from the insolubility of the membranes in *m*-cresol containing TEA in which the membranes were soluble before. Although all the SPI membranes were insoluble in PPMA, the cross-linking reaction could still occur by immersing them into PPMA at 30 °C for 48 h. At the higher temperature, the immersion time could be shortened, for example at 80 °C for 5 h. The optimum cross-linking condition may depend on the polymer structure and desired properties. With the cross-linking, the ion exchange capacity (IEC) decreased slightly by about 10% and the proton conductivity σ decreased slightly. The water uptake (WU) at room temperature hardly changed, but that at 100 °C decreased slightly with the cross-linking. The mechanical tensile strength was measured at 25 °C under 50% RH. With the cross-linking, the Young's modulus hardly changed and was in the range of 1.0 to 2.5 GPa. The maximum stress at break (MS) hardly changed or decreased by 20% and the elongation degree at break (EB) decreased by 20–60%. The decreases in MS and EB were slightly larger with the cross-linking at 80 than at 30 °C. However, the cross-linked membranes showed sufficiently high mechanical strength and toughness, indicating that polymer chain scission in the cross-linking treatment with PPMA occurred only to a small extent even at 80 °C.

For BSPOB-based SPI membranes, the water stability tests were performed by aging them in water at 130 °C for 192–500 h. The tensile strength data for the aged membranes are listed in parentheses in Table 1. The cross-linked membranes maintained higher mechanical strength than the uncross-linked ones, although the latter had fairly high mechanical strength after the aging. Especially, in the dry state, the uncross-linked membranes fairly lost the toughness, whereas the cross-linked ones maintained the toughness, that is, the aged membrane sheets could be folded to zero degree and then folded back. No appreciable change in proton conductivity with the aging was observed in the whole range of relative humidity for both the cross-linked and uncross-linked membranes.

The cross-linked SPI membranes showed reasonably high proton conductivity at high temperatures, for example, 0.22 S/cm in water and 0.03 S/cm under 50% RH at 120 °C for cross-linked (80 °C, 5 h) membrane of NTDA-BSPOB/BAPB (2/1). Using Pt/C and Pt–Ru/C fuel cell electrodes (Pt: 1.8 mg/cm^2, Pt–Ru: 2.2 mg/cm^2), a membrane–electrode assembly was prepared by hot-pressing an electrode/membrane/electrode sandwich at 150 °C for 3 min under 30 kg/cm^2. The cross-linked membrane displayed a high DMFC performance of open circuit voltage of 710 mV and power output of 160 mW/cm^2 at 500 mA/cm^2 with supply of 5 wt % methanol and air at 90 °C, which was comparable to that of the uncross-linked membrane. The performance was maintained stably for 350 h so far. The cross-linked SPI membranes have high potential for fuel cells at high temperatures above 80 °C.

It should be noted that the present cross-linking method is also applicable to other sulfonated hydrocarbon polymer membranes.

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