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Communications

Synthesis of New Sulfonated Polyimide and Its Photo-Crosslinking for Polymer Electrolyte Membrane Fuel Cells

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Introduction

In the field of polymer electrolyte membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC), perfluorosulfonated polymers such as Nafion®, Aciplex® and Flemion® have been widely used due to their high proton conductivity and excellent mechanical property.[1] However, they have some drawbacks such as limited operation temperature (<100 °C) and relative humidity (>80%RH), high fuel crossover (e.g. high methanol crossover in DMFC) and high cost,[2] which hold up the development of PEMFC for large-scale commercial applications.

Recently, considering the significant function of new PEMFC materials, crosslinking was introduced to sulfonated polymer systems to improve membrane properties in fuel cell systems. Crosslinking is an efficient and convenient method to generate the network polymer structure theoretically. As a result, improved membrane properties such as low methanol crossover, optimum water absorption, excellent mechanical property and decent dimensional stability can be achieved. Up to now, photo-crosslinking,[3] ionic (acid-base) crosslinking[4] and covalent crosslinking (e.g. esterification)[5] have been developed. However, most of these methods suffer from either weak bond strength of crosslinking due to the low chemical stability in acidic sulfonated polymer systems such as sulfonated polyimide (SPI) and sulfonated poly(ether ether ketone) (SPEEK) not to mention the complicated process.[6]

In this communication, we report the synthesis of new SPI containing double bonds in the main chain and novel photo-crosslinking method based on thiol-ene reaction between the new SPI and activated dithiols.

Results and Discussion

The new SPI was synthesized by copolymerization of naphthalenetetracarboxylic dianhydride (NTDA), 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid (SODA) and 3,3'-diaminochalcone (3DAC) in the presence of triethyl amine (TEA) and benzoic acid (BA) as illustrated in Scheme I. SODA and 3DAC were prepared according to the literature.[7] Detailed synthetic procedures are described in the reference.[8] In this communication, same mole ratio of SODA and 3DAC was used to prepare a copolyimide of 50 mol% 3DAC content. The resulting polymer was soluble in *N,N*-dimethylformamide (DMF) and dimethylsulfoxide (DMSO). The polymer shows high inherent viscosity (η_{inh}=1.79, 0.5 g/dL in DMF at 25 °C) indicating the relatively high molecular weight. The chemical structure of resulting SPI was confirmed by ^{1}H NMR and FTIR. The strong absorption peaks at around 1714 cm^{-1} and 1675 cm^{-1} were assigned as stretch vibration of asymmetric and symmetric carbonyl groups of imide rings, respectively. The peak at 1345 cm^{-1} was assigned as C-N-C structure in imide ring. Stretch vibration of S=O in sulfonic acid groups was observed as broad peaks at around 1025 cm^{-1}. Peaks at 1205 cm^{-1} and 982 cm^{-1} correspond to

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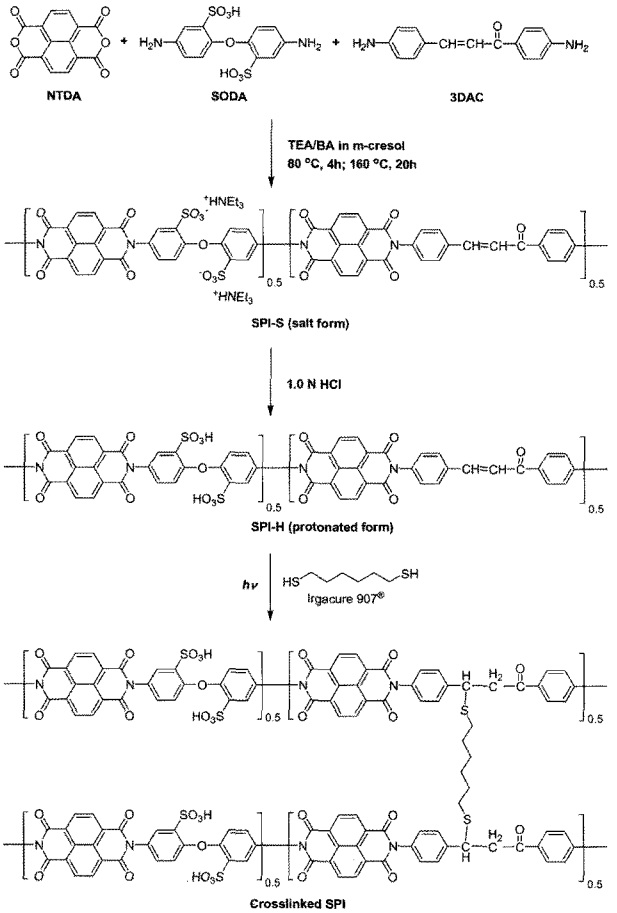

Scheme I. Synthetic diagram of SPI.

the chalcone structure in 3DAC. In the ^{1}H NMR spectra of SPI, peaks at 7.92, 7.46, and 7.24 ppm were attributed to the aromatic protons of SODA. Peak observed at 8.76 ppm belongs to NTDA whereas the peaks observed at 8.28, 8.05, 7.80, 7.67 and 7.60 ppm correspond to 3DAC, respectively.

Vinyl protons of C=C in chalcone unit were found at 7.03-6.56 ppm. Thermal stability of SPI was investigated by thermogravimetric analyses (TGA). The decomposition of SPI occurs in two steps. The initial decomposition (T_d^1) was observed at 304 °C, which was attributed to the thermal degradation of sulfonic acid group. The second decomposition (T_d^2) corresponding to the main-chain decomposition of SPI occurs at 542 °C.

The result of photo-crosslinking is illustrated in Scheme I. Compared to the conventional crosslinking methods such as thermal or chemical crosslinking, this novel photo-crosslinking method has many advantages. For example, various membrane fabrication techniques become possible such as solution coating or micro-patterning, and thermally unstable polymers can also be employed to improve mechanical stability.

In this work, 1,6-hexanedithiol (HDT) and IRGACURE 907® were chosen as a crosslinking agent and photo-initiator, respectively. After the film casting of membrane, subsequent UV irradiation was performed on a dry SPI film containing crosslinking agent (10 wt% to SPI) and photo-initiator (5 wt% to SPI) by using a conventional high pressure Hg arc light source (198 mW/cm^2) for 30 min. Firstly, IRGACURE 907® decomposes under UV irradiation to generate free radicals which subsequently abstract hydrogen radical from thiol groups producing thiyl radical (RS·). The thiyl radical reacts with double bond (ene group) of the chalcone moiety forming a S-C bond and a free radical centered at the adjacent carbon which abstracts hydrogen radical from other thiol groups propagating the radical reaction cycle. Therefore, thiol-ene crosslinking occurs between two polymer chains and HDT.[9] Due to the stable thiyl radicals towards oxygen radicals, the thiol-ene reaction does not require nitrogen purging during the photo-irradiation, consequently providing simplistic process.

While uncrosslinked membranes are soluble in DMSO and DMF, crosslinked membranes do not dissolve in any organic solvents, assuring the ample crosslinking.

Membrane properties of uncrosslinked (u-SPI) and crosslinked (c-SPI) membranes were also investigated as summarized in Table I. The hydrolytic stabilities of the u-SPI and c-SPI membranes were tested by immersing the membrane samples (3 cm × 3 cm) in deionized (DI) water at 25, 80 and 100 °C, respectively. The stability was estimated by recording the time when membranes began to break into pieces if they were folded for three times. The c-SPI membranes showed drastically improved hydrolytic stability of longer than 2000, 800 and 100 h at 25, 80 and 100 °C, respectively. To evaluate whether the crosslinked membrane can withstand a stronger oxidizing environment during the fuel cell operation, the oxidative stabilities of u-SPI and c-SPI membranes were compared for an extended time period in Fenton's reagent (3% H_2O_2 containing 2 ppm $FeSO_4$) at 25 and 80 °C, respectively (Table I). It was also found that the c-SPI membranes had better oxidative stability. For instance, the c-SPI membranes started to break into pieces after 2 h at 80 °C, whereas the u-SPI membrane broke in 1 h. After crosslink-

Table I. Membrane Properties of Uncrosslinked (u-SPI) and Crosslinked (c-SPI) SPI Membranes

Membrane	Hydrolytic Stability (h)			Oxidative Stability (h)		IEC (mmol/g)	Water Uptake at 80 °C (%)
	25 °C	80 °C	100 °C	25 °C	80 °C		
u-SPI	200	20	8	20	1	1.2293	40.21
c-SPI	>2,000	>800	100	24	2	0.7896	20.01

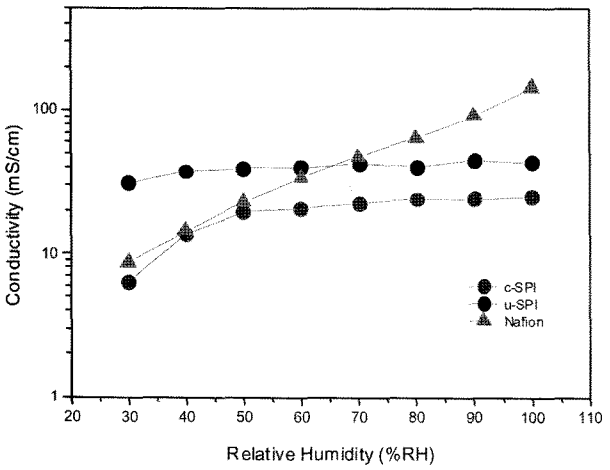

Figure 1. Proton conductivity at 80 °C under various relative humidity (%RH).

ing, water uptake (at 80 °C) decreased from 40.21% to 20.01%, and ion exchange capacity (IEC) was also decreased by 35.8%. The improved hydrolytic and oxidative stability of c-SPI can be ascribed to that the crosslinked structure decreases the water uptake by reducing a free volume leading to better mechanical properties and less degradation.

The proton conductivity of SPI membranes were measured at 80 °C under various relative humidity (%RH) as illustrated in Figure 1. Under 100%RH, both of u-SPI and c-SPI membranes showed lower conductivity (43.65 and 24.95 mS/cm, respectively) compared to that of Nafion® 112 (145.2 mS/cm). The proton conductivity of c-SPI membrane was lower than that of u-SPI membrane, implying that the c-SPI membrane has denser network structure and lower proton-exchangeable sites than u-SPI membrane, which results in less or smaller hydrophilic channels for water absorption and water mobility and hinder the mobility of H^+ in the water phase.[10] However, under the lower relative humidity (lower than 70%RH), conductivities of both SPI membranes were found to be moderately high. Especially, u-SPI membrane exhibited even higher conductivity (31.38 mS/cm) compared to that of Nafion® 112 (8.7 mS/cm) under 30%RH. This phenomenon probably attributes to the difference of chemical structure between perfluorosulfonated Nafion® and sulfonated aromatic polyimides.

In summary, we synthesized a new sulfonated polyimide containing photo-crosslinkable chalcone moiety in the main chain, and demonstrated thiol-ene based novel photo-crosslinking method using the sulfonated polyimide. Based on the above results, we could conclude that the thiol-ene crosslinking in sulfonated polyimide system is a simple but straightforward method to improve the hydrolytic stability, oxidative stability and mechanical properties of the membranes. Further results of membrane properties including the methanol crossover measurement with respect to the various polymer compositions and degree of crosslinking will be reported elsewhere.

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(8) *Synthesis of SPI*: Copolyimide of NTDA/SODA and NTDA/3DAC with 0.5:0.5 mol ratio was synthesized and used throughout the experiments. SODA (0.28 mol), TEA (0.67 mol) and 3DAC (0.28 mol) were added successively to 4,500 mL of *m*-cresol in a 3-neck flask with stirring. After SODA and 3DAC were completely dissolved, NTDA (0.56 mol) and benzoic acid (1.12 mol) were added. The mixture was stirred at 80 °C for 20 h and 180 °C for 24 h under nitrogen atmosphere and then the reaction mixture was precipitated into ethyl acetate. The fibrous precipitate was filtered and dried at 80 °C in vacuo. *Preparation of SPI membranes:* Firstly, uncrosslinked membranes were prepared by pouring the *m*-cresol solution of 10% SPI onto a glass plate (4 cm × 10 cm) and dried at room temperature for 3 d in air, 60 ° for 24 h and 140 °C for 24 h in

vacuo, respectively. The crosslinked membranes were obtained from SPI solution in *m*-cresol containing 10 wt% (to SPI) of 1,6-hexanedithiol (HDT) and 5 wt% (to SPI) of IRGACURE 907® as a crosslinking agent and photo-initiator, respectively, following the above process with subsequent UV light irradiation (198 mW/cm^2) for 30 min. The uncrosslinked and crosslinked membranes were acidified by immersing the membranes of TEA salt form into 1.0 M HCl solution at room temperature for 48 h, and then soaked in methanol and deionized water successively to remove excess acid and any impurity.

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