

Proton Conducting Membrane Based on Crosslinked Sulfonated Polyimide for Direct Methanol Fuel Cell

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Abstract : Crosslinked membrane based on sulfonated polyimide was prepared by the introduction of crosslinkable monomer in polymerization process and crosslinking during membrane casting. Crosslinked membranes showed different properties from non-crosslinked membranes. Crosslinking decreased methanol crossover and therefore unit cell using crosslinked membrane showed increased open circuit voltage, 0.81 V, in comparison with unit cell using non-crosslinked membrane, 0.71 V. In addition, water uptake of crosslinked membrane, 40.5%, was lower than that of non-crosslinked membrane, 57.0%, and this resulted in improved dimensional stability. However, proton conductivity of crosslinked membranes showed rather low relative to non-crosslinked membrane due to reduced water uptake.

Keywords : Sulfonated polyimide, Crosslinking, Water uptake, Methanol crossover

1. Introduction

Direct methanol fuel cells (DMFCs) have been developed as a power source for portable electronic devices such as notebook computers and cellular phones. The main part of DMFCs is the membrane/electrode assembly (MEA) that is composed of a solid polymer electrolyte membrane sandwiched between catalyzed anode and cathode. The conventional membrane is Nafion due to its high proton conductivity, good oxidative stability, and good chemical/electrochemical stability.¹⁾ However, it has several drawbacks including high cost, high methanol permeability, and limited operation temperature. To solve these problems, several alternative membranes based on polyaromatic type of engineering plastics have been investigated,²⁻⁴⁾ among which sulfonated polyimide (sPI) is thought to be one of the promising substitutes for Nafion because of its excellent thermal stability, high mechanical strength, and good film forming ability. Despite these advantages, much water uptake must be improved because it causes reduction of dimensional stability and

increases of methanol crossover. The dimensional stability is directly connected with long-term operation⁵⁾ and methanol crossover lowers open circuit voltage (OCV) and efficiency of fuel utilization.

The objective of this research is the development of crosslinked membrane using sulfonated polyimide. Crosslinking is expected to increase mechanical stability which is directly connected with dimensional stability. In addition, it can reduce water uptake and therefore lower methanol crossover. On the basis of these assumptions, crosslinked proton conducting membrane based on sulfonated polyimide (sPI) was prepared for DMFC operation.

2. Experimental

2.1. Materials

2,2'-benzidinedisulfonic acid (BDSA), hydrochloric acid, and triethylamine (TEA) were purchased from Tokyo Kasei Co., 4,4'-oxydianiline (ODA), 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), maleic anhydride, benzoic acid, m-cresol, and isoquinoline were from Aldrich Inc., and methanol was from Merck. BDSA, ODA, NTDA, maleic anhydride, and benzoic acid were dried under vacuum

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before use and TEA, *m*-cresol, isoquinoline, hydrochloric acid, and methanol were used without further purification. 5 wt.% Nafion solution (1100 E.W., sulfonic acid form) were purchased from E. I. Dupont.

2.2. Synthesis of non-crosslinked and crosslinkable sPI

Both sPIs were synthesized by the reaction of dianhydrides and diamines. For the synthesis of non-crosslinked sPI (nc-sPI), 2.0 mmol of BDSA and 4.8 mmol of TEA were introduced in a 100 ml three-necked flask with 18 g of *m*-cresol under nitrogen flow. This mixture was stirred until complete dissolution of BDSA. Then, 2.0 mmol of ODA, 4.0 mmol of NTDA, and 5.6 mmol of benzoic acid were added. The mixture was stirred at room temperature for a few minutes and then heated at 80°C for 4 hrs. In this process, the amic acid form, the precursor of imide, was made and then converted into imide form by heating at 180°C for 18 hrs. Isoquinoline was added for complete imidization. The reaction mixture was cooled to about 100°C and 5-10 g of *m*-cresol was added to dilute the viscous solution. The reaction mixture was poured into acetone and the fiber-like product was precipitated. The product was collected by vacuum-induced filtration and washed with acetone several times. The resulting polymer, nc-sPI, were dried under vacuum at 100°C for 1 day.

Crosslinkable sPI was prepared through rather different procedures from nc-sPI. The significant feature of crosslinkable sPI synthesis is that crosslinkable end-group such as maleic anhydride is used. Because maleic anhydride reacts with amine group, the amount of diamine should be more than that of dianhydride. For this reason, ODA was added more than NTDA and the ratio of diamine to dianhydride was shown in 20 to 19. After the imidization, the reaction mixture was cooled to 130°C and maleic anhydride was added to obtain end-capped sPI with maleimide having double-bond. The reaction maintained for 6 hrs. Subsequent processes including precipitation, filtering, and drying were the same as that of nc-sPI. Crosslinkable polymer was obtained as the resulting products.

2.3. Membrane Preparation

For nc-sPI membranes, nc-sPI of triethylammonium salt form was dissolved in *m*-cresol (5% w/v) and heated to obtain homogenous solution. The solution was directly cast onto clean glass plate and dried at

100°C for 5 hrs and at 150°C for 5 hrs. For crosslinked sPI (c-sPI) membranes, crosslinkable sPI of triethylammonium salt form were dissolved in *m*-cresol (10% w/v) at room temperature. After the same drying process as nc-sPI membrane, additional drying at 200°C for 2 hrs and at 250°C for 2 hrs was needed for crosslinking between maleimide groups of crosslinkable sPI.

Both nc-sPI and c-sPI membranes were peeled from glass plate by immersing them in deionized water and then soaked in methanol at 60 °C for 1 hr to remove residue. The membranes of triethylammonium salt form were completely converted to the acid form by immersing them in 1.0 M HCl solution at room temperature for 1 day. The membranes were thoroughly washed with deionized water several times.

2.4. Membrane Characterization

To confirm the structure of synthesized sPI, FT-IR spectroscopy was investigated using a Bomem 102 Fourier transform spectrometer. The thermal stability of sPI was measured by a Setsys 16/18 thermal analyzer. Before the thermal analysis, both nc-sPI and c-sPI membranes were dried under vacuum at 120°C for 1 day to remove absorbed water. And then, the samples were evaluated over the range of 30-800°C at a heating rate of 10°C·min⁻¹ in nitrogen.

The ion exchange capacity (IEC) of both sPI membranes was determined by titration. Both membranes were thoroughly washed with deionized water several times and immersed in 0.1 M NaCl aqueous solution for 1 day. The protons in sulfonic acid group of sPI were substituted by Na⁺ ions and released protons were titrated with 0.01 M NaOH aqueous solution using phenolphthalein as an indicator. The IEC was calculated with the following equation:

$$IEC(\text{mequiv/g}) = \frac{V_{NaOH} \times N_{NaOH}}{W_{sPI}}$$

Where V_{NaOH} is the volume of NaOH solution consumed for the titration, N_{NaOH} is the normality of NaOH solution, and W_{sPI} is the weight of dry sPI membrane, respectively.

The water uptake was determined by the weight difference between dry and wet membranes. The wet membrane in deionized water at room temperature was wiped and quickly weighed. After vacuum-drying at 100°C for 1 day, the weight of dry membrane was measured and the water uptake of membranes

was reported in weight percent as follows:

$$\text{water uptake (wt.\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100$$

where W_{wet} and W_{dry} is the weight of the wet and dry membrane, respectively. Dimensional change was obtained by the dimension difference between dry and wet membranes through the same procedures as water uptake.

Conductivity measurement of membranes was performed using AC impedance spectroscopy (1400 FRA and 1470E, Solartron).⁶⁾ The AC signal had the amplitude of 10 mA and an impedance spectrum was recorded over the frequency range from 10 MHz to 10 Hz. Proton conductivity of membranes was measured in fully hydrated state at 50°C.

2.5. MEA preparation for DMFC operation

For the preparation of MEA, the gas diffusion electrodes were prepared. To obtain Nafion-based electrodes, catalyst ink was prepared using Nafion dispersion (5 wt.%, 1100 E.W., sulfonic acid form). Pt/Ru black (E-TEK Inc.) and Pt (E-TEK Inc.) were used for the anode and the cathode, respectively. Each catalyst ink was applied to carbon paper (TGPH090, Toray) by brushing technique and the loading amount of catalyst was 5 mg cm⁻² for both the anode and the cathode. The membranes were sandwiched between the anode and the cathode by hot-pressing at 160~180°C for 10 minutes under the pressure of 800 psi.

2.6. Electrochemical Characterization of MEA

Both MEAs using nc-sPI and c-sPI membranes were installed in a test fixture and connected to a test station equipped with an electronic load (Won-A tech, Korea). 2.0 M of methanol solution was supplied to the anode at 1.0 cc·min⁻¹ and the oxygen gas was to the cathode at 200 cc·min⁻¹, respectively. The operation temperature was controlled at 50°C and monitored at the cathode compartment by thermocouples. The response of voltage according to the change of current density was measured and current-voltage behavior of both MEAs was obtained.

Limiting current density of both MEAs was investigated to evaluate methanol crossover. The operation condition was the same as above except for the cathode feed. Instead of oxygen gas, helium gas as an inert gas was supplied to the cathode at 30 cc·min⁻¹ and the current density was measured with applied voltage.

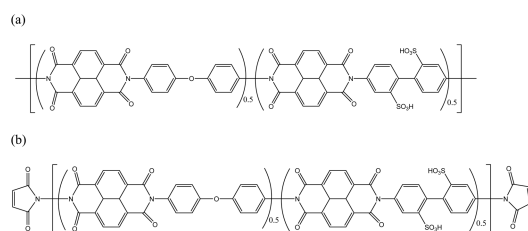


Fig. 1. Molecular structures of (a) nc-sPI and (b) cross-linkable sPI.

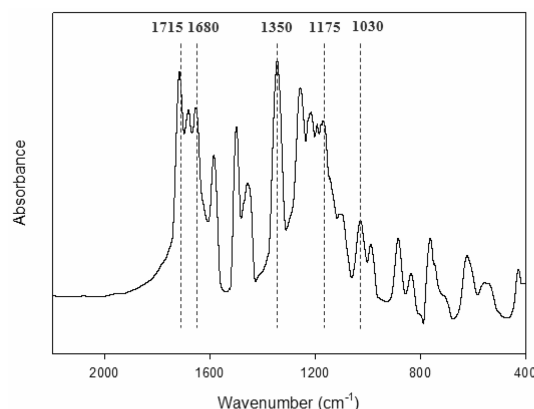


Fig. 2. FT-IR spectra of nc-sPI.

3. Results and Discussion

3.1. Structure analysis of nc-PI and c-PI

The sPI was synthesized by polycondensation reaction of dianhydrides and diamines, and Fig. 1 shows the chemical structure of nc-sPI and crosslinkable sPI. In Fig. 2, FT-IR spectra of nc-sPI displayed the naphthalimide adsorption bands at 1715, 1680, and 1350 cm⁻¹. The adsorption bands at 1175 and 1030 cm⁻¹ were associated with the sulfonic acid groups. The detailed assignment of the adsorption band is expressed in Table 1.⁷⁾

Table 1. Assignments of adsorption bands in FT-IR spectra of nc-sPI

wave number (cm ⁻¹)	assignment
1715	$\nu_s(\text{C}=\text{O})$ in naphthalimide
1680	$\nu_{as}(\text{C}=\text{O})$ in naphthalimide
1350	$\nu(\text{C}=\text{C})$ and $\nu(\text{C}-\text{N}-\text{C})$ in naphthalimide
1175	$\nu_s(\text{O}=\text{S}=\text{O})$ in SO_3H
1030	$\nu_{as}(\text{O}=\text{S}=\text{O})$ in SO_3H

The crosslinking between maleimide groups of crosslinkable sPI occurred during casting and drying process. According to several reports on maleimide,⁸⁻¹⁰ its double bond is broken and crosslinking is done at 200-250°C. In this experiment, cast solution of crosslinkable sPI was dried with a gradual increase of temperature up to 250°C while that of nc-sPI was at 150°C. The FT-IR spectra of c-sPI are very similar to those of crosslinkable sPI except for disappearance of the maleimide C=C band at 1150 cm⁻¹, as shown in Fig. 3. This is because maleimide double bonds were broken after crosslinking.¹¹ The crosslinking mechanism of maleimide was shown in Fig. 4. This mechanism involves the thermal initiation to form free radicals, which can react with maleimide double bonds to form a crosslinked network.

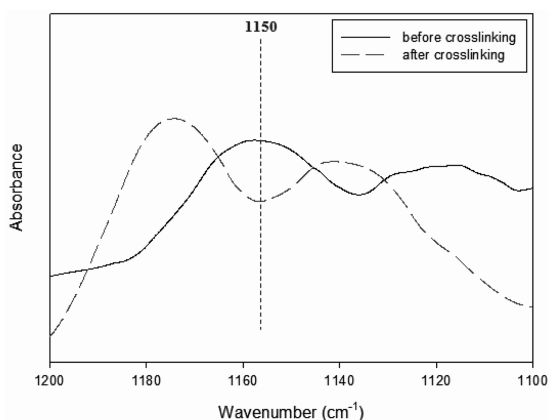


Fig. 3. FT-IR spectra of crosslinkable sPI and c-sPI (before crosslinking and after crosslinking).

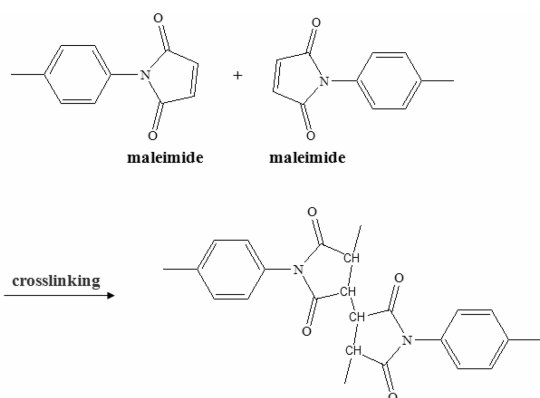


Fig. 4. Crosslinking mechanism of maleimide at the end of crosslinkable sPI.

3.2. Membrane properties

The thermal stability of nc-sPI and c-sPI membranes was investigated by thermogravimetric analysis (TGA). A two-step degradation profile was observed for both membranes. The initial weight loss around 300°C was assigned to degradation of aromatic sulfonic acid group, and this means that these sulfonated polyimides have thermal stability up to 300°C. The second weight loss at 550°C indicates main-chain decomposition of sulfonated polyimide.^{12,13} In Fig. 5, c-sPI shows a small increase of the second degradation temperature in comparison with nc-sPI. Crosslinking of polymer chains helps chain-interaction and chain-ordering, and therefore the thermal stability of c-sPI was increased.

The IEC was measured by titration and c-sPI, 1.49 mequiv·g⁻¹, exhibited a little low IEC relative to nc-sPI, 1.50 mequiv·g⁻¹. It is because the introduction of maleic anhydride for crosslinking increased molecular weight of repeating unit in c-sPI structure, and therefore the amount of sulfonic acid group in c-sPI membrane was decreased compared with nc-sPI membrane. Water uptake and dimensional change of nc-sPI and c-sPI membranes was measured and the results are given in Table 2. Water uptake depends primarily on IEC because water is absorbed mainly in hydrophilic region. However, c-sPI shows less water uptake than nc-sPI although both

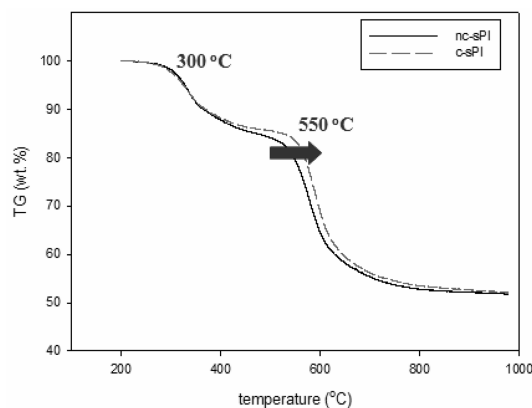


Fig. 5. TGA thermograms of nc-sPI and c-sPI.

Table 2. Water uptake and dimensional change of nc-sPI and c-sPI membranes.

	water uptake (wt.%)	dimensional change	
		ΔL	ΔT
nc-sPI	57.0	10	19
c-sPI	40.5	5	13

of them have very similar IEC values. The difference in water uptake seems to result from crosslinked structure of c-sPI. Crosslinking decreases polymer swelling and this may be the reason for the reduced water uptake of c-sPI. For the same reason, dimensional change of c-PI was less than that of nc-PI and this improved dimensional stability of c-sPI membrane is expected to have a good effect on membrane durability.

The effect of crosslinking on proton conductivity was also investigated. Both nc-PI and c-PI membranes have similar IEC and this means that they have similar amount of proton source. However, crosslinking of c-sPI led to reduction of water uptake and then the continuity of hydrophilic channel was decreased. For this reason, proton conductivity of c-sPI, $0.095 \text{ S}\cdot\text{cm}^{-1}$, was lower than that of nc-sPI, $0.107 \text{ S}\cdot\text{cm}^{-1}$.

3.3. MEA properties

Fig. 6 is the cell voltage versus current density plot, the polarization curve, of sulfonated polyimide at 50°C and OCV can be obtained as the voltage where current begin to flow. The OCV of c-sPI, 0.81 V, was higher than that of nc-sPI, 0.71 V, and this can be explained as the effect of crosslinking which decrease water uptake and limit methanol permeation with water. In the region of ohmic loss, voltage loss of c-sPI is rather large relative to nc-PI due to their difference in proton conductivity.

Fig. 7 shows limiting current density with applied voltage at 50°C and MEA using c-sPI membrane show low limiting current density in comparison with nc-sPI. Limiting current density is increased with methanol crossover through the membrane because the electron flow is generated by the oxidization of per-

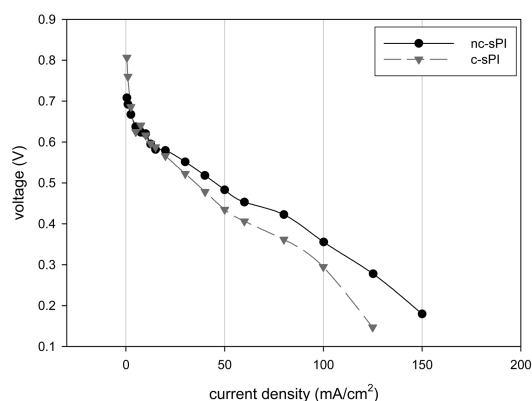


Fig. 6. Polarization curves of MEAs using nc-sPI and c-sPI membranes at 50°C .

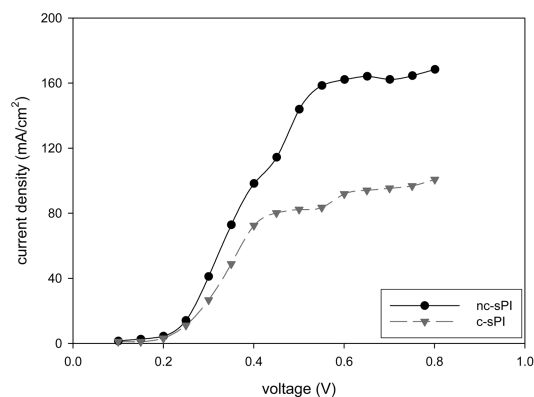


Fig. 7. Limiting current density of MEAs using nc-sPI and c-sPI membranes at 50°C .

meated methanol. In c-sPI membrane, crosslinking could reduce methanol crossover and therefore limiting current density was decreased. This result is in good agreement with OCV data of voltage-current behavior.

4. Conclusions

Two types of sPI membranes, nc-PI and c-PI, were synthesized using dianhydride and diamine containing sulfonic acid groups. Thermal stability of c-sPI was improved relative to nc-sPI. Also, crosslinking decreased water uptake of membranes and therefore caused reduction of dimensional change. Proton conductivity of c-sPI showed rather lower than that of nc-sPI because of decreased water uptake. Electrochemical characteristics of MEA using c-sPI membrane were also investigated. Although crosslinking lowered MEA performance due to increased ohmic resistance, reduced methanol crossover by crosslinking was proved by measurement of limiting current density and this resulted in increased OCV.

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