Modification of Nafion Membranes for Reduction of Methanol Transport Rate

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Introduction

Nafion is one of the most widely used commercial polymer electrolyte membranes for fuel cells. The Nafion molecule is composed of hydrophobic polytetrafluoroethylene (PTFE) backbones with ether containing pendant groups ended up with strong acid group imparting high ion exchanging capacity. PTFE back-bone provides mechanical strength in water swollen state, and sulfonic acid group ion conductivity. The major problem in the application of Nafion is the methanol crossover phenomenon through the membrane from anode side to cathode, by which the oxidation reaction occurs not only in anode but cathod, leading to considerable loss of electrical potential and fuel itself [1, 2].

In order to reduce the methanol crossover, the methanol permeable phenomenon is to be understood. The presence of anionic ions such sulfonic acid groups in Nafion make it possible to transport protons. When the water is absorbed, the anionic groups are aggregated to form hydrophilic domains, and when its content increases, it produces the water pools connected by water channels [3-5]. This hydrophilic/hydrophobic phase separation occurs more significantly when the polymer molecule has highly strong hydrophilic groups as well as hydrophobic groups such as Nafion. Percolation with wide water channel developed by this phase separation is reported to result in not only high proton conduction but high methanol crossover. It is expected that addition of small amount of base polymer to Nafion membranes reduce the methanol permeability caused by formation of smaller percolation associated with strong acid- base ion interaction.

In this research, acid/base complex membranes were prepared by addition of small amount of base polymers to Nafion solution. The proton conductivity and methanol crossover of the prepared membranes were characterized to compare its effect.

Experimental

Materials. 5 wt% Nafion solution (equivalent weight 1100, Dupont) was used for acid polymer, and polyethylenimine (PEI, Mn: 60000, 10000, 1800, 423, Aldrich Chemical Company, Milwaukee, WI), poly(4-vinylpyridine) (P4VP, Mn: 160000, 50000, Aldrich), and polyaniline (PAn, Mn: 10000, Aldrich) for base polymer materials. 1-methyl-2-pyrrolidinone (NMP, Aldrich), isopropyl alcohol (IPA, Aldrich), hydrosulfuric acid (H_2SO_4, J.T. Baker), 1M sodium hydroxide solution (NaOH solution, Daejung) were used as solvents.

Preparation of Nafion/base polymer membranes.
Na^+-Nafion solution was prepared by adding 1 M NaOH aqueous solution to 5 wt% Nafion solution. Na^+-Nafion solution was dried in oven at 70℃ and then was dissolved in NMP to produce 5 wt% Na^+-Nafion/NMP solution. The basic polymers were added to this solution to have the ion exchange capacity (IEC) of 0.85, 0.7, 0.55, and 0.4, respectively. The IEC values of Nafion/basic polymer membranes were determined using equation (1). The membranes were prepared by casting the polymer solution on the petri-dish and dried at 130℃ for 12 h and then in vacuum oven for 1 h.

$$IEC \ (meq \ / \ g) = \frac{\dfrac{w_1}{EW_{Nafion}} - \dfrac{w_2}{EW_{basicpolymer}}}{w_1 + w_2} \times 1000 \qquad (1)$$

Here, w_1 and w_2 indicate the weights of Nafion and basic polymer, respectively. The equivalent weight of Nafion in this experiment was 1100 and those of PEI, P4VP, PAn, 43, 105, and 91, respectively.
The membranes were easily detached from Petri-dish in distilled water for 30 min. The Na+ Nafion membrane was protonated by placing the membranes in 1 M H_2SO_4 aqueous solution at 80 ℃ for 4 h. The H_2SO_4 solution present on the surface of membrane was

removed in distilled water at 60 ℃ for 4 h. The thickness of the composite membranes prepared were 120~150 μm.

Characterization. Attenuated total reflection fourier transform infrared spectrometer(ATR-FTIR, Bruker IFS-66/S, Bruker) was used to identify the chemical structure and morphology of membranes. Scanning electron microscope (SEM, JSM7000F, JEOL) and energy dispersive spectroscopy (EDS) were used to analyze the morphology and atomic composition of membranes. Cross sectional surface was analyzed after the membrane was quenched in liquid nitrogen and then fractured. Thermogravimetric analyzer (TGA, TGA7, Perkin-Elmer, USA) was used to analyze the thermal stability of polymer membranes. The measurement range was from 25 to 800℃ at the scanning rate of 30℃/min in the nitrogen gas environment. Universal tensile machine (UTM, model 5565, Lloyd, GB) was used to measure the mechanical strength of polymer materials. the samples in the shape of 2 cm×5 cm were gripped and their tensile strength was measured at the pulling speed of 50 mm/min. 5 measurements were conducted for each sample, and the average value was calculated for its determination. Equilibrium water uptake was measured by gravimetric method. It was determined measuring the weights before and after water absorption. After the dry polymer samples were weighed, the samples swollen in the distilled water were weighed periodically until no weight change was observed. The equilibrium water uptake was determined by equation (2).

$$Water \ uptake(\%) = \frac{w_{wet} - w_{dry}}{w_{dry}} \times 100 \qquad (2)$$

Here, w_{wet} is the weight of sample at equilibrium water uptake, and w_{dry} the weight of dry sample.
Impedance spectroscopy with 2 probe method (Solartron 1260, frequency range 10Hz to 32MHz, Solartron, UK) was used to measure the ionic conductivity. Frequency range was from 10^2 to 10^6 Hz, and the response was measured at room temperature with 10 mV input. Methanol permeability was measured using a glass diffusion cell. The membrane was placed between two compartments, one filled with 50 ml 2M MeOH aqueous solution, and the other 50 ml pure water. The methanol concentration was continuously measured using a RI detector (RI750F, Younglin, Korea), and the methanol permeability was calculated by equation (3).

$$C_b(t) = \frac{A}{V_B} \frac{P}{L} C_A (t - t_0) \qquad (3)$$

Here, C_A is the concentration in methanol compartment. C_B concentration of water compartment, A cross sectional area of membrane, L thickness, V_B volume of compartment.

Results and discussion

Chemical structure and morphology. Figure 1 shows the ATR-FTIR spectra of Nafion/basic polymer composite membranes with IEC of 0.55.
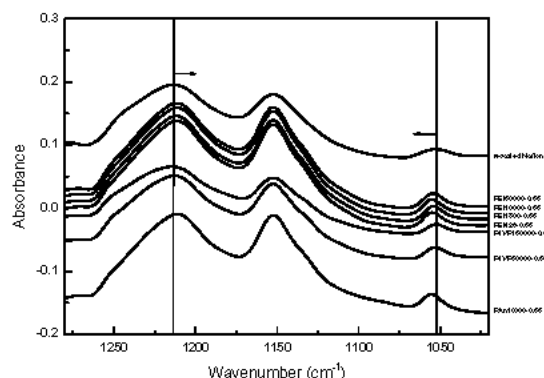

Figure 1. FTIR spectra of Nafion/basic polymer membranes.

The presence of sulfonic groups in the polymer membrane was detected at 1055 cm^{-1} (symmetric stretching) and 1220 cm^{-1} (anti-symmetric stretching) peaks. The formation of acid-base complex was detected by shifting of the 1055cm^{-1}and 1220cm^{-1} peaks associated with the dipole-dipole interaction between the sulfonic acid group of Nafion and basic polymer.

Atomic composition and distribution inside the membrane (IEC of 0.55) was measured by SEM-EDS. The atoms comprising Nafion and basic polymer, C, N, O, F, S were detected. Especially, the N atom in basic polymer molecule was well detected with uniform distribution over the entire composite cross section.

Thermal and mechanical properties. Thermal stability of the membranes, both pure Nafion and Nafion/basic polymer composite prepared was compared. The recast Nafion started to loose its weight from 300 ℃, but Nafion/basic polymer composite from 320 ℃ The composite membrane was thermally more stable than the two homo polymers, PEI and Nafion. The enhanced thermal stability was caused by ionic interaction between acid and base.

Figure 2 shows the mechanical properties of Nafion/PEI(Mn= 10000) composite membranes. The tensile strength of homo nafion was 15.5 MPa, but Nafion/PEI composite membranes were higher than that of Nafion. Those decraesed from 16.3 to 21.8 MPa with decreasing IEC values (with increasing PEI contents) from 0.85 to 0.4. This inclination was also caused by the same reason mentioned above-acid/base ionic interaction.
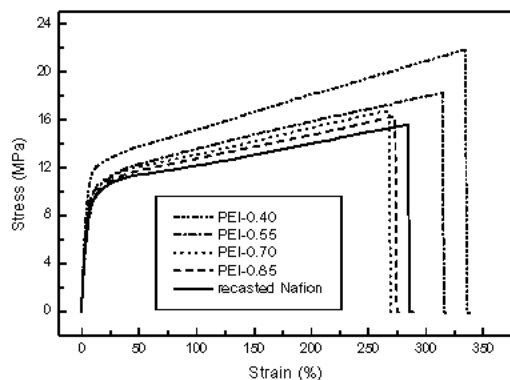

Figure 2. Tensile behavior of polymer membranes

Water uptake. Water uptake behavior for Nafion/basic polymer composite membranes according to IEC values is shown in Figure 3. The percentage water uptake of bare nafion membrane with IEC value of 0.91 was 27.9 %. The water uptake decreased with decreasing IEC values or increasing basic polymer contents. This behavior was caused by decrease of hydrophilicity via neutralization of sulfonic acid groups by basic group of polymers incorporated. The effect of the molecular weight of basic polymer on the water uptake was negligible in this experimental range. The content of sulfonic acid group in polymer electrolyte was possibly estimated from IEC values of corresponding polymers.

Proton conductivity and methanol permeability. The proton conductivity of Nafion/basic polymer composite membranes was measured. The proton conductivity decreased with decreasing IEC values or increasing basic polymer content. Higher basic polymer content in the membrane resulted in higher acid/basic interaction. The reduced hydrophilicity induced lower water uptake and thus lower proton conductivity. The molecular weight of basic polymers did not have significant effect on the proton conductivity.

Figure 4 shows the methanol permeability according to IEC valuesThe bare Nafion membrane show the methanol permeability of 1.65×10^{-6}cm^2/s. The methanol permeability also decreased with decreasing IEC values or increasing basic polymer contents. for the same reason as mentioned above for water uptake and proton conductivity behavior.
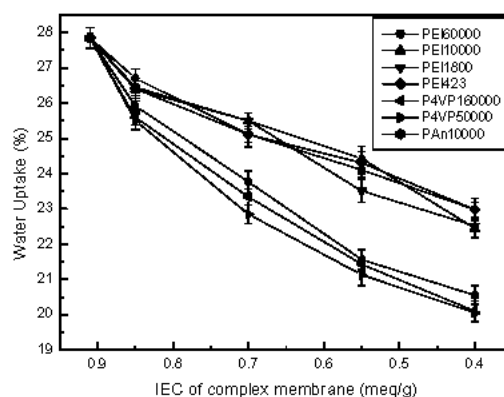

Figure 3. Water uptake behavior for Nafion/basic polymer composite membranes
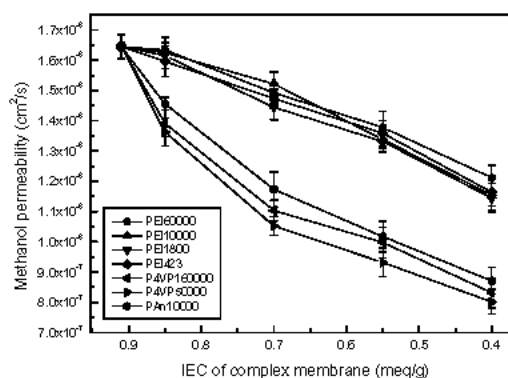

Figure 4. Methanol permeability for Nafion/basic polymer composite membranes

Conclusions

Nafion/basic polymer composite membranes were prepared to reduce the methanol crossover for the application of direct methanol fuel cell. The thermal and mechanical properties increased with increasing basic polymer contents due to the formation of complex via acid/basic interaction. The water uptake, proton conductivity, methanol permeability decreased with increasing basic polymer concentration by reduction of acidity associated with the formation of acid/base complex. The molecular effect on those properties was not considerable.

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