Modification of Nafion membranes by incorporation of cationic polymers for reduction of methanol permeability

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Abstract−A small amount of basic polymer was incorporated in the Nafion membrane. Compared with the re-cast Nafion membrane, the Nafion/basic polymer membrane reduced the methanol permeability considerably. The equilibrium water uptake and proton conductivity decreased, but the thermal and mechanical stability was enhanced with increasing concentration of basic polymer. These property changes were caused by formation of cation/anion complex between acidic Nafion and basic polymer molecules. The effects of the types and molecular weights of basic polymers on the methanol permeability and proton conductivity were not significant.

Key words: Nafion Membrane, Methanol Permeability, Proton Conductivity, Polymer Electrolyte

INTRODUCTION

The fuel cell is an environmentally adaptable power generation device with high efficiency [1,2]. As fuel cells are classified according to the types of electrolytes and fuels, they have many applications from stationary to mobile energy sources. [3] The polymer electrolyte membrane fuel cell (PEMFC) and direct methanol fuel cell (DMFC) use polymer membranes as electrolyte materials. DMFC has the advantage of using liquid state of fuel but the drawback of slower electro-oxidation reaction than PEMFC. For this reason, DMFC has been studied to seek its application for mobile power sources requiring relatively low power density than stationary ones [1,2]. In DMFC, the fuel, methanol is oxidized in an anode electrode usually composed of platinum (Pt)/ruthenium (Ru) catalyst to produce electrons and protons. The electrons produced are transported through the external electrical circuit, while the protons are through the polymer membrane to cathode where they are combined to react with oxygen to produce water.

Nafion is one of the most widely used commercial polymer electrolyte membranes for fuel cells. Its molecular structure is composed of hydrophobic polytetrafluoroethylene (PTFE) backbones and hydrophilic ether-containing pendants attached with strong acid group. While the PTFE backbone provides mechanical strength in water swollen state, the sulfonic acid group has high ion exchanging capacity. The major problem in the application of Nafion is the methanol crossover phenomenon from anode to cathode through the membrane, as it leads to the occurrence of an oxidation reaction not only in the anode but in cathode and considerable loss of electrical potential and fuel [4-6].

When water is in Nafion, the anionic groups are aggregated to form hydrophilic domains and eventually water pools connected by channels [7-10]. The percolation phenomenon developed by this phase separation is reported to cause not only high proton conduction but high methanol crossover [11-13].

Among many trials to reduce the methanol crossover in the DMFC membranes, one of the effective ways is to incorporate a small amount of basic molecules. Acid/basic interaction is expected to induce a reduction of ionic cluster size and thus free water, followed by reduction of methanol drag. A question regarding this rationale is how much different types of basic molecules have different influence on the membrane performance, especially ionic conductivity and methanol crossover. In the previous contribution [14], it was reported that the addition of small amount of poly(4-vinyl imidazole) to Nafion membranes considerably reduced the electro-osmotic drag due to the formation of smaller ion clusters. In this research, several acid/base complex membranes were prepared by addition of different types of base polymers, PEI (polyethylenimine), P4VP [poly(4-vinylpyridine)], and PAn (polyaniline) to Nafion. The effects of type and molecular weight on the water uptake, proton conductivity and methanol crossover of the prepared membranes were investigated.

EXPERIMENTAL

1. Materials

Nafion solution (equivalent weight 1100), 5 wt%, was purchased from Du Pont. Several types of basic polymers, polyethylenimine (PEI, Mn: 60,000, 10,000, 1,800 and 423 g/mol), poly(4-vinylpyridine) (P4VP, Mn: 16,0000 and 50,000 g/mol), and polyaniline (PAn, Mn: 10,000 g/mol) were from Aldrich Chemical Company (Milwaukee, WI, USA). 1-methyl-2-pyrrolidinone (NMP, Aldrich), isopropyl alcohol (IPA, Aldrich), hydrosulfuric acid (H_2SO_4, J. T. Baker), and sodium hydroxide solution (NaOH solution, Daejung, Korea) were used as solvents.

2. Preparation of Nafion/base Polymer Membranes

Na^{+}-Nafion solution was prepared by adding 1 M NaOH aqueous solution to Nafion solution. Na^{+}-Nafion solution was dried in an oven at 70 °C and the product was dissolved in NMP to prepare 5 wt% Na^{+}-Nafion/NMP solution. Each of PEI, P4VP, PAn, was added to this solution to have ion exchange capacities (IEC) of 0.85, 0.7, 0.55, and 0.4, respectively. The IEC value of Nafion-basic poly-

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Table 1. IEC values of complex membranes according to wt% of basic polymer

IEC	PEI (wt%)	P4VP (wt%)	PAn (wt%)
0.85	0.24	0.56	0.5
0.70	0.88	2.04	1.78
0.55	1.52	3.6	3.12
0.40	2.16	5.14	4.48

mer complex membrane was determined from Eq. (1), and the amount of basic polymer added to each solution is shown in Table 1. The membrane was prepared by casting the polymer solution in a petri-dish and dried at 130 °C for 12 h and then in a vacuum oven for 1 h.

$$IEC(meq/g) = \frac{\frac{w_1}{EW_1} - \frac{w_2}{EW_2}}{w_1 + w_2} \times 1000 \qquad (1)$$

Here, w_1 and w_2 indicate the weights of Nafion and basic polymer, respectively, and EW_1 and EW_2 the equivalent weights of Nafion and polymer, respectively. EW_2 of PEI, P4VP, and PAn are 43, 105, and 91, respectively.

The membrane was easily detached from a petri dish in distilled water. The Na^+-Nafion membrane was protonated when it was placed in the 1 M H_2SO_4 aqueous solution at 80 °C for 4 h. The H_2SO_4 solution present on the surface of membrane was removed in distilled water at 60 °C for 4 h. The thickness of the composite membranes prepared was 120-150 μm.

3. Characterization

The attenuated total reflection fourier transform infrared spectroscopy (ATR-FTIR, Bruker IFS-66/S, Bruker) was used to identify the chemical structure of membranes. A scanning electron microscope (SEM, JSM7000F, JEOL) and energy dispersive spectroscopy (EDS) were used to analyze the morphology and atomic composition of membranes. The morphology of the cross-sectional surface of the membrane was analyzed after the membrane was quenched in the liquid nitrogen and then fractured. A 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 °C at a scanning rate of 30/min in a nitrogen environment. A universal tensile machine (UTM, model 5565, Lloyd, GB) was used to measure the mechanical strength of polymer films. The samples in the dimension of 2 cm×5 cm (W×L) were gripped and the tensile strength was measured at a pulling speed of 50 mm/min. Five measurements were conducted for each sample, and the average value was calculated for its determination. The equilibrium water uptake was determined by gravimetric method. After the dry polymer sample was weighed, the sample was swollen in the distilled water. The wet sample was weighed periodically until no weight change was observed. The equilibrium water uptake was calculated by Eq. (2).

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

Here, w_{wet} and w_{dry} are the weight of sample at equilibrium water uptake and dry sample, respectively.

Impedance spectroscopy with the two probe method (Solartron

1260, Solartron, UK) was used to measure the ionic conductivity. The frequency range was from 10^2 to 10^6 Hz, and the response to 10 mV input was measured at room temperature. Methanol permeability was measured by using a glass diffusion cell. The membrane was placed between two compartments: one 50 ml 2 M MeOH aqueous solution, and the other 50 ml pure water. The methanol concentration was continuously measured by using an RI detector (RI750F, Younglin, Korea), and the methanol permeability, P was calculated by Eq. (3).

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

Here, C_A and C_B are the concentration of methanol and water compartments, respectively. A is the cross sectional area of membrane, L thickness, V_B volume of compartment B.

RESULTS AND DISCUSSION

1. Chemical Structure and Morphology of Composite Membrane

Fig. 1 shows the ATR-FTIR spectra of Nafion/basic polymer composite membranes with IEC value of 0.55. The presence of sulfonic groups in the polymer membrane was detected at 1,055 cm^{-1} (symmetric stretching) and 1,220 cm^{-1} (anti-symmetric stretching) peaks. The formation of acid-base complex was confirmed by shifting of the 1,055 cm^{-1} and 1,220 cm^{-1} peaks by a dipole-dipole interaction between the anionic sulfonic group of Nafion and cataionic group of basic polymer.

Fig. 2 shows the atomic composition and its distribution inside the membrane (IEC of 0.55) measured by SEM-EDS. All atoms comprising Nafion and basic polymer, C, N, O, F, and S were detected. Especially, the N atom of the basic polymer was well detected with uniform distribution over the entire composite cross section. It indicates the uniform blending of two polymer systems and the uniform interaction of two ionic groups through the whole membrane.

2. Thermal and Mechanical Properties

Thermal stability of the two membranes, pure Nafion and Nafion/basic polymer composite membranes, was compared. The recast Nafion started to lose weight from 300 °C, but Nafion/basic poly-
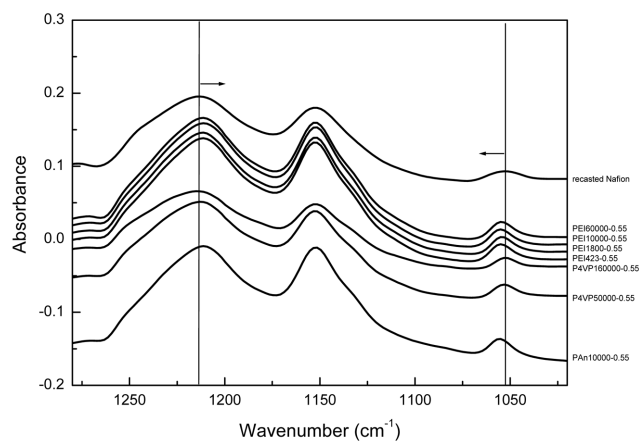
Fig. 1. ATR-FTIR spectra of Nafion/base complex membrane.
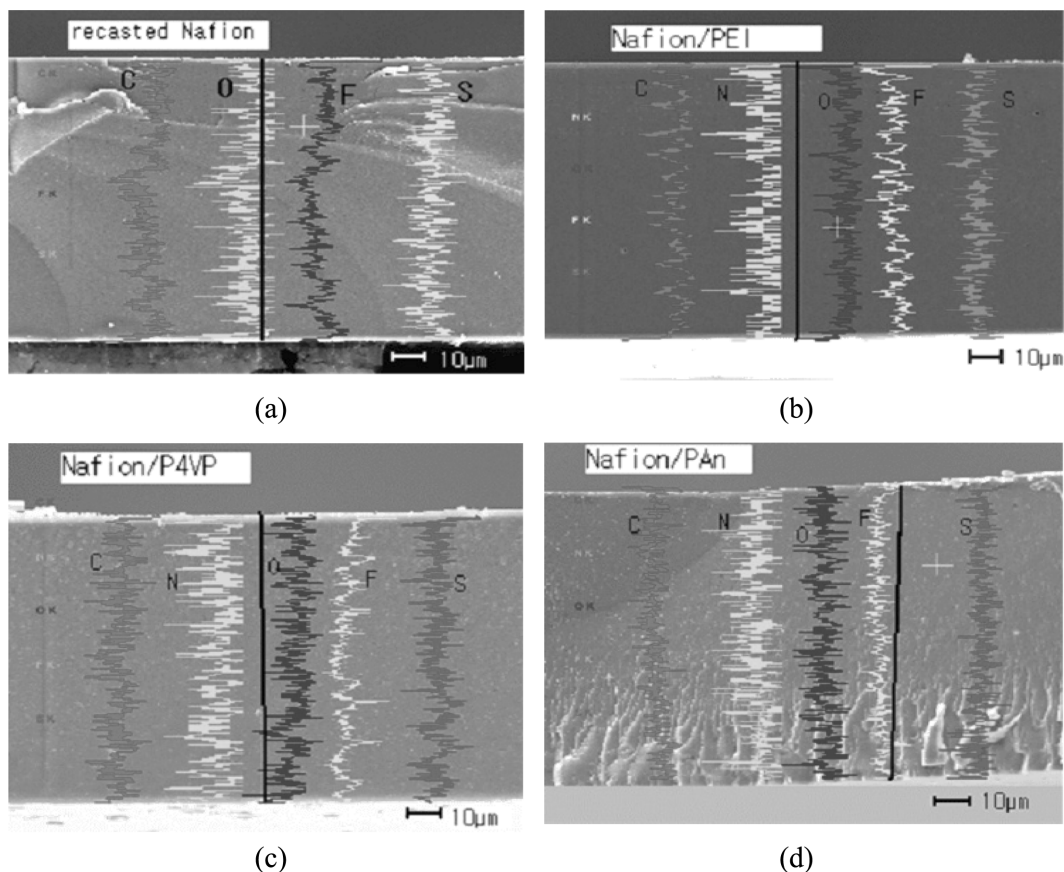
Fig. 2. EDS analysis of Nafion/base complex membrane. (a) recast Nafion, (b) Nafion/PEI, (c) Nafion/P4VP, and (d) Nafion/PAn, respectively.
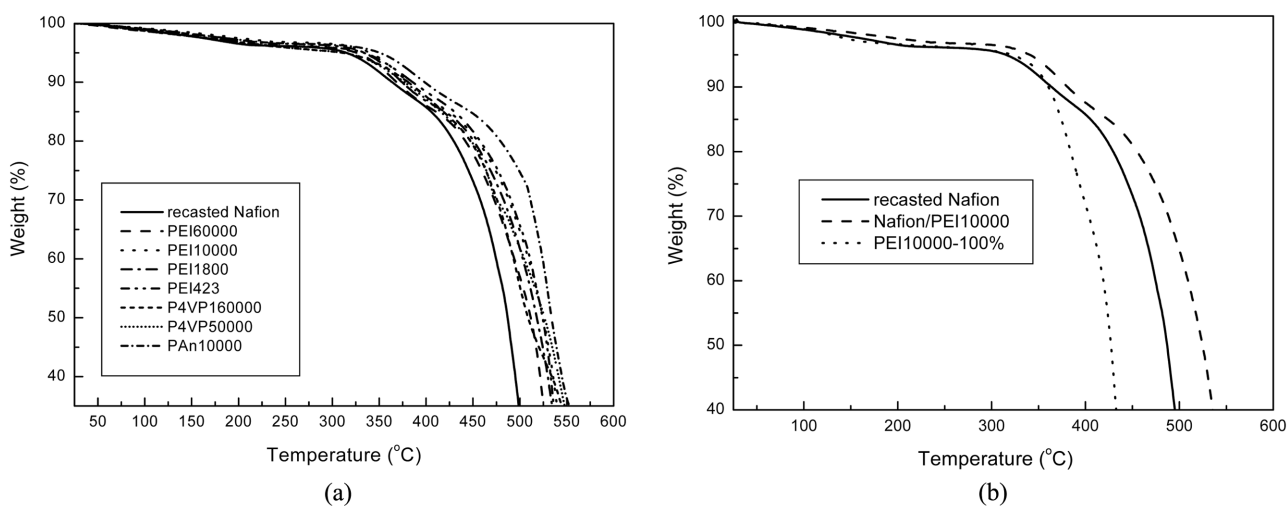

Fig. 3. TGA curves of (a) Nafion/base complex membrane and (b) recast Nafion, Nafion/PEI and pure PEI10000, respectively.

mer composite from 320 °C as shown in Fig. 3(a). In Fig. 3(b) 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.

Fig. 4 shows the mechanical properties of Nafion/PEI (Mn= 10,000) composite membranes. The tensile strength of homo Nafion was 15.5 MPa, but Nafion/PEI composite membranes were higher than that of Nafion. It increased from 16.3 to 21.8 MPa with de-

creasing IEC values (with increasing PEI contents) from 0.85 to 0.4. This inclination was also caused by the same reason mentioned above.

3. Water Uptake

Water uptake behavior for Nafion/basic polymer composite membranes according to basic polymer contents is shown in Fig. 5. The percentage water uptake of bare Nafion membrane with IEC value of 0.91 was 27.9%. The water uptake decreased with increasing
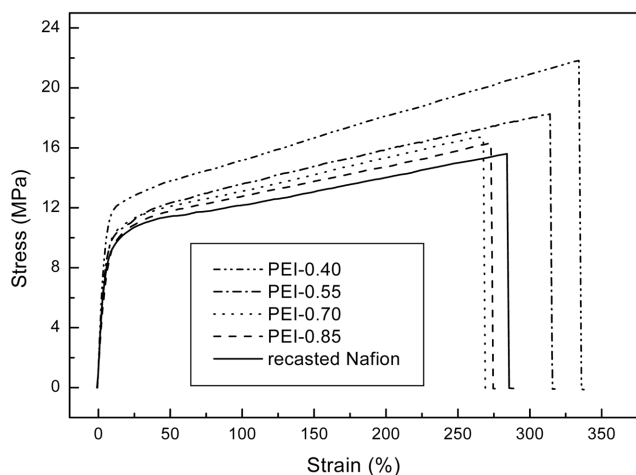
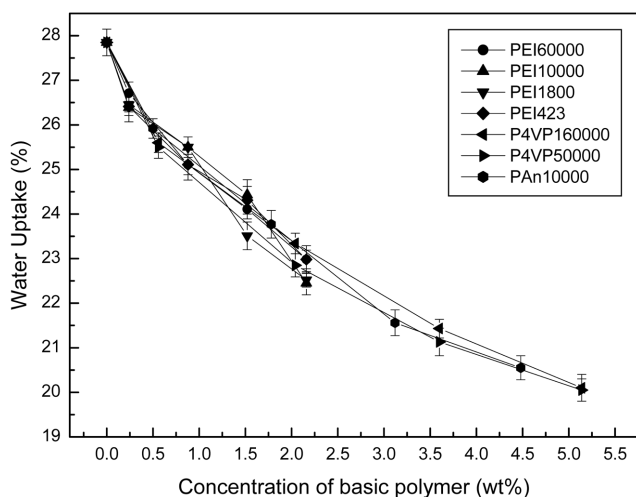**Fig. 4. Mechanical property of Nafion/PEI complex membranes.**

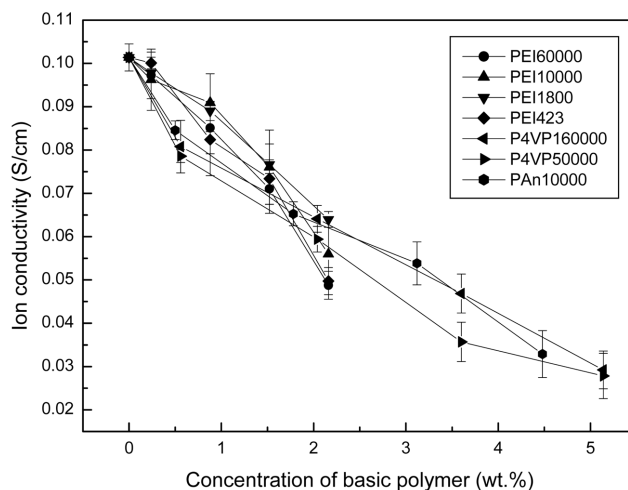**Fig. 5. Water uptake according to concentration of base polymer.**

Fig. 6. Ion conductivity according to concentration of base polymer.
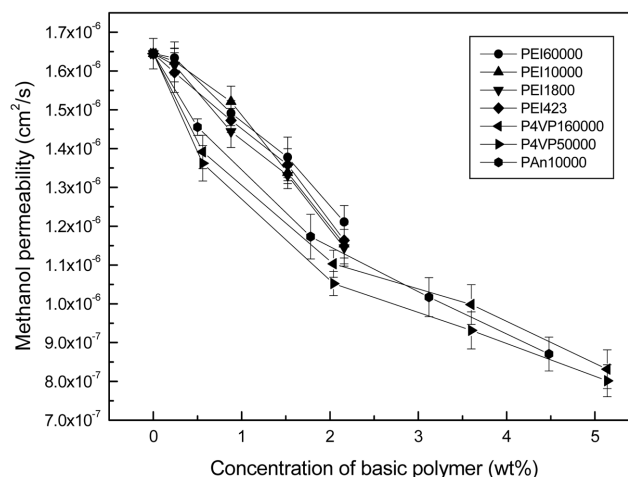
Fig. 7. Methanol permeability according to concentration of base polymer.

basic polymer content. This behavior was caused by decrease of hydrophilicity via neutralization of sulfonic acid groups by the basic group of the polymers incorporated. The effect of 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.

4. Proton Conductivity

The proton conductivity of Nafion/basic polymer composite membranes is shown in Fig. 6. The proton conductivity decreased with increasing basic polymer content, because the higher basic polymer content in membrane, the higher acid/basic interaction. The reduced hydrophiclicy induced lower water uptake and thus lower proton conductivity. The molecular weight of basic polymer did not have significant effect on the proton conductivity.

5. Methanol Permeability

Fig. 7 shows the methanol permeability as a function polymer composition. The bare Nafion membrane shows methanol permeability of 1.65×10^{-6} cm²/s. The methanol permeability also decreased with decreasing IEC values or increasing basic polymer content

for the same reason as mentioned above.

CONCLUSION

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, and 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.

ACKNOWLEDGMENT

REFERENCES

1. K. Kordesch and G. Simader, *Fuel cells and their applications*, VCH, Weinheim (1996).
2. J. Larminie and A. Dicks, *Fuel cell systems explained*, John Wiley & Sons Inc., England (2000).
3. M. L. Perry and T. F. Fuller, *J. Electrochem. Soc.*, **149**(7), S59 (2002).
4. A. S. Aricò, S. Srinivasan and V. Antonucci, *Fuel Cells*, **1**, 134 (2001).
5. A. Heinzel and V. M. Barragn, *J. Power Sources*, **84**, 70 (1999).
6. J. Sauk, J. Byun, Y. Kang and H. Kim, *Korean J. Chem. Eng.*, **22**, 605 (2005).
7. N. Carretta, V. Tricoli and F. Picchioni, *J. Membr. Sci.*, **166**, 189 (2000).
8. G. Gebel, *Polymer*, **41**, 5829 (2000).
9. P. Dimitrova, K. A. Friedrich, B. Vogt and U. Stimming, *J. Electroanal. Chem.*, **532**, 75 (2002).
10. J. Kim, B. Kim and B. Jung, *J. Membr. Sci.*, **207**, 129 (2002).
11. K. D. Kreuer, *J. Membr. Sci.*, **185**, 29 (2001).
12. W. Y. Hsu, J. R. Barkley and P. Meakin, *Macromolecules*, **13**, 198 (1980).
13. T. D. Gierke, G. E. Munn and F. C. Wilson, *J. Polym. Sci., Polym. Phys. Ed.*, **19**, 1687 (1981).
14. B. Bae, H. Y. Ha and D. Kim, *J. Electrochem. Soc.*, **152**(7), 1366 (2005).