

친수성 술폰화 주쇄를 가지는 수소이온 전도성막의 상분리 거동과 전달 특성

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Phase separation behavior and transport properties of proton exchange membrane with hydrophilic sulfonated backbone

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1. Introduction

Proton exchange membrane (PEM) is a polymer electrolyte with an ability to transport protons selectively in the fuel cell system. Among the many ways such as functional group introduction and acid doping to give that ability to polymer, sulfonation has been most widely used for PEM under the common operation condition, 70-90°C and 90-100%RH[1].

Sulfonated membranes are mainly divided into two types according to introduced site of sulfonic acid group. The first type of PEM has a branched side chain and sulfonic acid group is located at the end of side chain. Most perfluorinated PEMs are classified into the first type of PEM. In the second type of PEM, sulfonic acid group is introduced directly to polymer backbone, which is shown in the most hydrocarbon PEMs especially *via* condensation polymerization[2].

These sulfonated PEMs are supposed to have very complex structure due to micro phase separation between sulfonated hydrophilic and non-sulfonated

hydrophobic moieties. Despite of many efforts to disclose the exact structure of sulfonated PEMs, most of researches have been focussed on commercial Nafion. Resultantly, there is only a little information about phase separation behaviour in PEMs with sulfonated backbone.

In this study, for enhancement of our knowledge about complex structure of PEM, polyimide membranes having sulfonic acid group at their backbone were fabricated with different composition of hydrophilic and hydrophobic domains. Their proton conductivity and water uptake were investigated to clarify the relationship between phase separation and transport properties in PEMs, and comparative study will be conducted between molecular simulation of PEM structure and experimental results.

2. Experimental

Block sulfonated polyimides (SPIs) were fabricated by polycondensation with dianhydride and sulfonated and non-sulfonated diamines. SPI membranes were prepared by typical solution-casting method and those membranes were dried at 180 °C in vacuum oven. As mole ratio of sulfonated diamine was varied from 0.2 to 0.8, various hydrophilic block sizes could be introduced to resulting SPI membranes. Acidification of those membranes was carried out with 1M HCl solution at room temperature for 5 hr.

Water uptake was calculated from equation (1).

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \quad (1)$$

where W_{dry} is weight of dried membrane and W_{wet} is weight of fully hydrated membrane at room temperature for over 24hr.

Proton Conductivity was obtained from equation (2).

$$\sigma(S/cm) = \frac{l}{R \times S} \quad (2)$$

where R is the ohmic resistance measured by a four-probe AC impedance method, l is the distance between counter electrode and working electrode, and S is the cross-sectional area of the membrane.

Wide angle X-ray diffraction (WAXD) will be discussed in the presentation to investigate the structural change of SPI membranes resulting from increase of the composition of sulfonated diamine. Additionally, molecular simulation will be carried out based on Molecular dynamics (MD) and Monte carlo (MC) simulation.

3. Results and Discussion

Hydrophilic moiety of PEM plays a key roll in proton transport behavior. According to vehicle mechanism, proton is transported together with water molecules in the form of complex ion such as H_3O^+ , $H_5O_2^+$, $H_7O_3^+$ through water channel[3]. Therefore, morphology of hydrophilic channel as ion pathway affects proton conduction behavior significantly, which can be deduced from water uptake behavior.

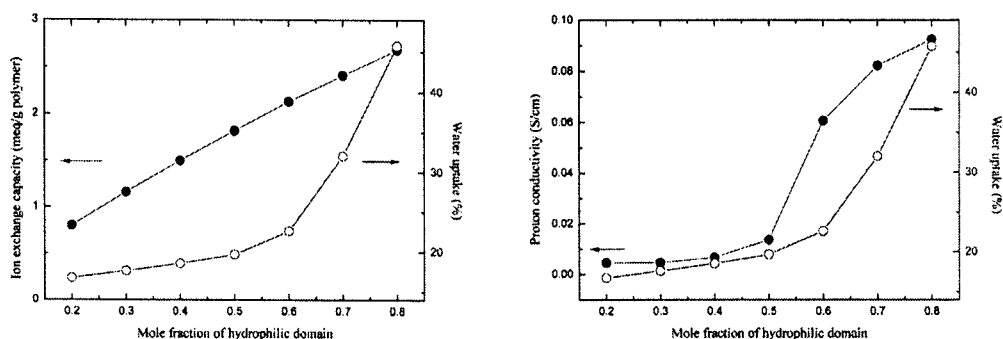


Figure 1. Ion exchange capacity, water uptake and proton conductivity with different mole ratio of hydrophilic domain.

Generally, ion exchange capacity (IEC) shows linear proportionality to the amount of sulfonic acid groups[4]. In the figure 1, such a tendency could be also observed. As increasing the mole fraction of hydrophilic moiety, IEC was also improved. Whereas, in case of water uptake and proton conductivity, there was no linear relationship to mole fraction of sulfonated hydrophilic domain. In the region of low mole fraction, those properties showed linear and slower increment than IEC. However, both of water uptake and proton conductivity increased very sharply over 0.5 of mole fraction, which was supposed to show percolation behavior.

Further discussion of these results will be carried out in the presentation with additional structural analysis and molecular simulation.

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5. Reference

- [1] J. Meier-Haack, A. Taeger, C. Vogel, K. Schlenstedt, W. Lenk, D. Lehmann, "Membranes from sulfonated block copolymers for use in fuel cells", *Separation and Purification Technology*, 41, pp. 207 (2005).
- [2] O. Savadogo, "Emerging Membranes for Electrochemical Systems: (I) Solid Polymer Electrolyte Membranes for Fuel Cell Systems", *Journal of New Materials for Electrochemical Systems*, 1, pp. 47 (1998).
- [3] T. J. F. Day, U. W. Schmitt, G. A. Voth, "The Mechanism of Hydrated Proton Transport in Water", *Journal of American Chemical Society*, 122, pp. 12027 (2000)
- [4] Y. Woo, S. Y. Oh, Y. S. Kang, B. Jung, "Synthesis and characterization of sulfonated polyimide membranes for direct methanol fuel cell", *Journal of Membrane Science*, 220 pp. 31 (2003)