

## 술폰화 폴리이미드 막의 수소이온 전도도에 대한 소수성영역의 효과

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### **Effect of hydrophobic domain on proton conductivity of sulfonated polyimide membranes**

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#### **1. Introduction**

The proton transport through proton exchange membranes is controlled by the distribution of hydrated structure connected with negative-charged fixed ions such as phosphonic acid, carboxylic acid and sulfonic acid, or water molecules within the membrane. The proton transport mechanism is very complex, and vehicle or hopping mechanism is well-accepted hypothesis for the transport. In complex proton transport mechanism, the distribution of hydrophobic and hydrophilic domains causes the micro-separation and the subsequent formation of ionic clusters. In other words, the increase of hydrophilic domains to hydrophobic domain resulted in the change of membrane morphology and influenced directly on the proton transport behavior.

In this study, the percolation concept [1] was applied to observe the relationship between the morphology in micro-phase and the proton transport behavior in sulfonated polyimide membranes having different distribution of hydrophilic-hydrophobic domains.

## 2. Experimental

### 2.1. Preparation of sulfonated polyimide membranes

To observe the effect of hydrophobic domain on proton transport behavior, the sulfonated polyimides were prepared by polycondensation of 1,4,5,8-naphthalenic dianhydride (NTDA) with various chemical composition of 4,4'-diaminodiphenyl ether (ODA) and disulfonated ODA (ODADS) [2]. The sulfonated polyimide membranes were prepared using sulfonated polyimides soluble in *m*-cresol by typical solution-casting method and then drying at 180 °C in vacuum oven for one day.

### 2.2. Characterization of sulfonated polyimide membranes

Well distribution of hydrophilic-hydrophobic domains in the sulfonated polyimide membranes was a key factor to determine the proton transport behavior through hydrophobic channel containing water molecules. To apply the percolation behavior in proton conduction, the proton conductivity of the sulfonated polyimide membranes having the different amount of hydrophobic block were investigated by AC impedance spectrometer at ambient temperature. In addition, water uptake, methanol permeability, and average *d*-spacing will be discussed.

## 3. Results and Discussion

The temperature dependance on the proton transport behavior measured by using four probe method at 95% RH for sulfonated polyimide membranes was shown in Figure 1. Although there were some difference in the increment of proton conductivity, proton conductivity of all polyimide membranes increased continuously with elevated temperature and molar ratio of the introduced hydrophilic monomer. Especially, the increment of proton conductivity decreased drastically at 40 % molar ratio of hydrophobic content, so called percolation threshold, showing flat curve in comparison with sigmoial curve of sulfonated polyimide containing high hydrophobic content.

Theta value in XRD study as shown in Figure 2 tends to increase as the amount of hydrophilic domain is more introduced. This means that the introduction of hydrophilic block in sulfonated polyimide membranes was

induced to a reduction of the chain distance between amorphous polymer chains with sulfonic acid groups and the subsequent segregation of hydrophilic and hydrophobic domains to make the microphase separation, due to increase of the hydrogen bonding between sulfonic acid groups.

The proton conduction was also affected by water content within the membrane. As shown in Figure 3, the equilibrium water content of the sulfonated polyimide membranes increased exponentially with the formation of dense hydrophilic-hydrophilic domains in relation to increase of sulfonic acid groups. This trend is in a good agreement with the proton conductivity results.

## References

- [1] H. B. Park, S. Y. Ha, Y. M. Lee, "Percolation behavior of gas permeability in rigid-flexible block copolymer membranes," *J. Membr. Sci.*, **177** (2000) 143-152
- [2] J. Fang, X. Guo, S. Harada, T. Wateri, K. Tanaka, H. Kita, K. Okamoto, "Novel sulfonated polyimides as polyelectrolytes for fuel cell application. 1. synthesis, proton conductivity, and water stability of polyimides from 4,4'-diaminodiphenyl ether-2,2'-disulfonic acid," *Macromolecules*, **35**, pp. 9022-9028 (2002).

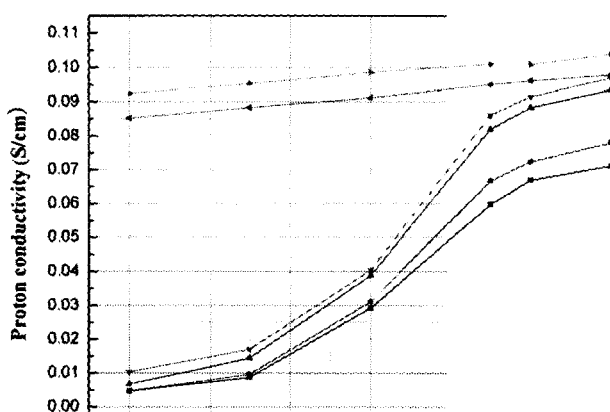


Figure 1. The temperature dependance on proton conductivity in sulfonated polyimide membranes having different hydrophobic molar ratio.

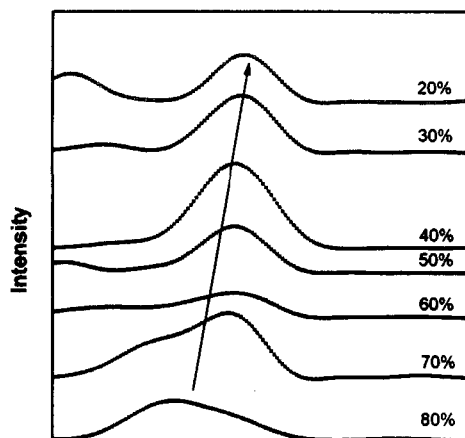


Figure 2. Wide angle X-ray diffraction patterns in the sulfonated polyimide membranes prepared in this study

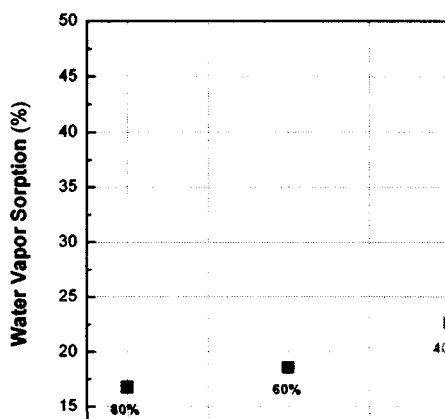


Figure 3. The water uptake content in the sulfonated polyimide membranes as a function of SO<sub>3</sub>H mol %