

## 수소이온전도성 산-염기 고분자 블렌드막의 제조 및 특성평가

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### Preparation and Characterization of Proton Conductive Acid-Base Blend Ionomer Membranes

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#### 1. Introduction

Recently many researches have been focused on the development of novel proton conductive membranes in a variety of methods such as grafting and cross-linking of polymer matrices, acid-base polymer blending, and organic-inorganic composite. Among them, acid doped complexation of basic polymers has been achieved well by dissolution of various inorganic mineral acids such as phosphoric, sulfuric acid, hydrochloric, perchloric, hydrobromic and nitric acid in PBI [1-4]. In addition, amphoteric composite membranes have been prepared by the formation of ionic bond between sulfonated polymers and low molecular weight basic materials such as pyrazole and imidazole. In spite of high proton conductivity even in high temperature and low humidity, these membranes suffered from leaching of doping agent or basic materials during fuel cell test. Accordingly, it is necessary to solve the fundamental problem and to maintain their high performances for fuel cell application.

In the present study, amphoteric membranes were prepared by some kinds of covalent bonds between sulfonated polyimides and low molecular weight basic materials in order to prevent them diffusing out of matrix and to stabilize the sulfonated polyimides chemically and hydrolytically. Eventually, the proton conductivity at high temperature and low humidity and the methanol permeability were also discussed in relation to the introduction of basic materials with low molecular weight.

## 2. Experimental

### 2.1. Preparation of sulfonated polyimide-based amphoteric membranes

The sulfonated polyimide (NOD) was prepared by thermal solution imidization of 1,4,5,8-naphthalenic dianhydride (NTDA) with a certain chemical composition of 4,4'-diaminodiphenyl ether disulfonic acid (ODADS) and diaminobenzoic acid (DBA). Then, various amphoteric polyimides were prepared using 2-(1H-pyrazole-3-yl) phenol (PPNOD), 1H-pyrazole-1-carboxamide hydrochloride (PCNOD), and 1,1'-carbonyldiimidazole (CNINOD) at 150 °C, respectively. Finally, the amphoteric membranes were obtained by solution casting method on glass plate and then drying at 180 °C in a vacuum oven for one day.

### 2.2. Characterization of amphoteric polyimide membranes

The formations of some kinds of covalent bonds were confirmed by FT-IR spectroscopy. The hydrophilicity of each membrane was measured in terms of water vapor sorption in constant relative humidity (RH) at the ambient condition. The proton conductivity under a constant RH and temperature was measured using a four point probe A.C impedance spectroscopic technique. The methanol permeability was measured using a two-chamber diffusion cell using a gas chromatography equipped with a thermal conductivity detector (TCD) at room temperature. The hydrolytic stability was measured after immersion of each membrane into deionized water at 80 °C

## 3. Results and Discussion

The temperature dependance on the proton transport behavior measured using four probe method at 95% RH for sulfonated polyimide membranes blended with base materials is shown in Figure 1. Although there were some difference in the increment, the proton conductivities of all the ionomeric membranes increased continuously with temperature.

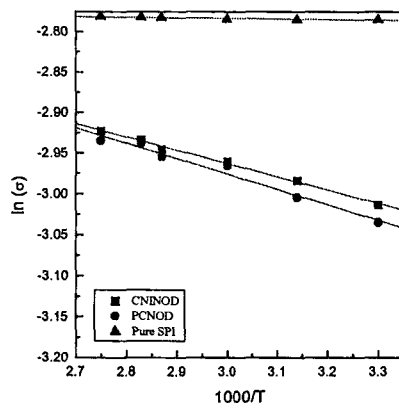


Figure 1. The temperature dependence on proton conductivity in sulfonated polyimide and amphoteric polyimide membranes having the same polymer matrix

The proton conductivity and the methanol permeability were significantly affected by the amount of water within the membrane. As shown in Table 1, the amphoteric polyimides showed lower water uptake than pure sulfonated polyimide membranes, which led to the reduction of the proton conductivity and the methanol permeability in each membrane. In addition, the incorporation of basic materials into sulfonated polyimide with high acidity resulted in the improvement of hydrolytic stability due to the stabilization of the acidic polymer.

Table 1. The relationship of water vapor sorption at 90 % RH and methanol permeability at room temperature

	Nominal thickness (μm)	Water vapor sorption (%)	Methanol permeability (cm <sup>2</sup> / sec)	Hydrolytic stability (day)
NOD	30	28.8	1.06E-6	3
PCNOD	20	29.7	2.78E-7	17.2
PPNOD	30	22.8	1.20E-7	15
CNINOD	20	25.8	2.68E-7	15.2
Nafion 117	170	25.3	1.43E-6	-

Figure 2 shows the selectivity ( $\Phi$ ) which is a standard factor to evaluate the membrane performances in terms of both the proton conductivity ( $\sigma$ ) and the methanol

permeability ( $P_{\text{MeOH}}$ ). Currently, the ideal values achievable in the proton conductivity and the methanol permeability are about 0.1 S/cm in water and  $10^{-8}$  cm/sec respectively for practical fuel cell application. In the comparative study, Nafion 117 and pure sulfonated polyimide membranes showed similar the proton conductivity and the methanol permeability. However, the present amphoteric polyimide membranes showed one order of magnitude larger  $\Phi$  values than Nafion 117 owing to their similar proton conductivities and reduced methanol permeabilities. Therefore, the preparation of amphoteric polymer having characteristics of both acid and base would be an effective method to prevent methanol transport without sacrificing proton conductivity.

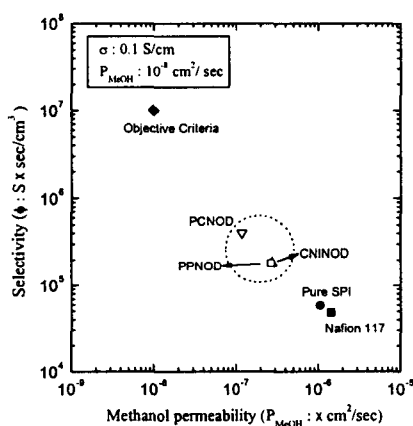


Figure 2. The selectivity ( $\Phi = \sigma / P_{\text{MeOH}}$ ) of Nafion, sulfonated polyimide (NOD), amphoteric polyimides (PCNOD, PPNOD, CNINOD) and objective criteria as the ratio of proton conductivity to methanol permeability

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