일반강연 A-7

가교 설폰화 폴리이미드막: 가교도에 따른 수소이온전도도 및 메탄올 투과도의 변화고찰

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Cross-linked Sulfonated Polyimide Membranes: Effect of Cross-linking Degree on Proton Conductivity and Methanol Permeability

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1. Introduction

Proton exchange membrane (PEM) should satisfy stringent demands with respect to proton conductivity, chemical, mechanical, and electrochemical properties. To fulfill many requirements in the fuel cell conditions, various sulfonated polymers have been prepared through the sulfonation of parent polymer or the monomer sulfonation-subsequent polymerization. However, the introduction of sulfonic acid groups leads to some limitations in membrane performance. That is, although high IEC is preferentially needed to achieve high proton conductivity, sulfonated polymers have a limited IEC as highly sulfonated polymers are soluble in water medium or swells excessively at elevated temperature, and lose their mechanical properties. For this purpose, cross-linking would be an effective method to restrict severe water swelling and to enhance membrane performance.

According to other researches, the cross-linking has been carried out through thermally activated cross-linking between polyatomic alcohols and sulfonic acid groups in PEEK [1-3], UV photo-cross-linking of methyl-phenoxy, ethyl-phenoxyl and isopropyl-phenoxy-substituted polyphosphazene by benzophenone photo-initiator [4-6], chemical-thermal cross-linking between hydroxyl group (-OH) in PVA and carboxylic acid group (-COOH) in SSA [7-8], and ionic cross-linking between acid-base membrane [9]. As expected, the introduction of cross-linking causes the significant improvement of the mechanical properties and subsequent long-term stability. Simultaneously, the proton conductivity is slightly reduced. In DMFC applications, in particular, considerable decrease was observed in water and methanol diffusivity owing to low water uptake.

In this study, two kinds of cross-linked sulfonated polyimides was prepared by using hydroxyl terminated chemcial cross-linkers with (HYU 3) and without sulfonic acid group (HYU 2) by the chemical-thermal cross-linking . The effect of the content of cross-linkers was observed in terms of proton conductivity, methanol permeability and hydrolytic stability.

2. Experimental

2.1. Preparation of cross-linked sulfonated polyimide membranes

A sulfonated polyimide (HYU-1) was prepared by polycondensation of 1,4,5,8-naphthalenic dianhydride (NTDA) with disulfonated ODA (ODADS) and 1,3-diamino benzoic acid (DBA) [10]. Cross-linked sulfonated polyimides were also prepared by the introduction of ethylene glycol (EG ; HYU 2) and a fixed charged ion containing chemical cross-linker (BES ; HYU 3) with three different kinds of chemical composition. Then, the crosslinked sulfonated polyimide membranes were prepared by typical solution-casting method and drying at 180 °C in vacuum oven.

2.2. Characterization of amphoteric polyimide membranes

To observe the effect of degree of cross-linking, each sulfonated polyimide membrane was investigated by X-ray diffraction (XRD) spectroscopy, water vapor sorption, proton conductivity, methanol permeability and hydrolytic stability. Finally, the effect of cross-linkers on their performances was also studied.

3. Results and Discussion

The hydroxy groups in two kinds of cross-linkers react competitively with carboxylic acid in DBA or sulfonic acid in ODADS. That is, there might be two types of ester (carboxylic acid ester and sulfonic acid ester) formed by introduction of cross-linkers [2]. As a result, there are a few probabilities in the formation of various cross-linking and grafting structures with types of ester. The more content of cross-linkers was expected to cause change of membrane performances by differences in the degree of cross-linking.

As shown in Table 1, the more addition of cross-linkers resulted in narrower average interchain distance by cross-linking and intrinsic hydrogen bonds by sulfonic acid and carboxylic acid groups, and grafted hydroxyl groups. The proton conduction and methanol permeability were affected by water content within the membrane. Highly cross-linked sulfonated polyimide membrane showed reduced water uptake. Consequently, it caused reduction of proton conductivity and methanol permeability in each membrane.

Figure 1 shows proton conductivity and methanol permeability of cross-linked sulfonated polyimide membranes as a function of degree of cross-linking. As expected, the introduction of cross-linking caused considerable decrease in methanol permeability owing to low water uptake. Simultaneously, proton conductivity was slightly reduced. In particular, this behavior was significantly observed in cross-linked polyimides with low content of cross-linkers.

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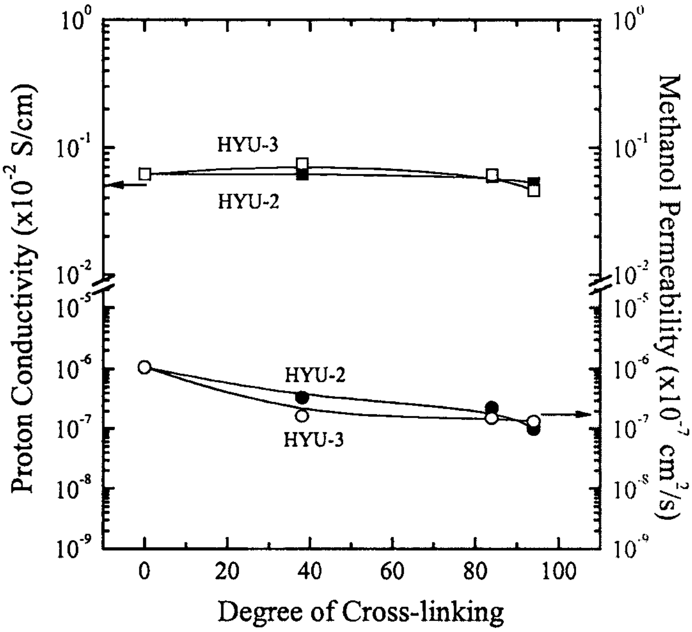

Figure 1. The proton conductivity and methanol permeability of cross-linked sulfonated polyimide membranes as a function of degree of cross-linking.

Table 1. The relationship between water uptake and average interchain distance in cross-linked sulfonated polyimide membranes with different degree of cross-linking.

	HYU-1	HYU-2			HYU-3		
		Degree of cross-linking			Degree of cross-linking		
		38 %	84 %	94 %	38 %	84 %	94 %
Water Vapor Sorption (%)	28.8	37.4	27.5	22.9	37.1	32.2	26.4
2 theta XRD	21.1	21.5	-	22.7	22.9	-	23.3
d-spacing value (Å)	4.21	4.14	-	3.92	3.88	-	3.82