일반강연 A-3

랜덤 및 블록 공중합에 따른 고분자 전해질막의 이온전도특성

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Ion transport characteristics through random or block polymer electrolyte membranes

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1. Introduction

Polymer electrolyte membranes have been studied widely in chloro-alkali electrolysis, cationic exchange resins, and fuel cell applications. Especially, sulfonated polyimide membranes have been suggested as a potential polymer electrolyte in PEMFC due to their excellent thermal stability and high proton conductivity.

Sulfonated polyimide can be prepared by a direct sulfonation of polyimide using sulfonating agents such as fuming sulfonic acid, chlorosulfuric acid or sulfuric acid. In addition, sulfonated polyimide can be prepared by sulfonation of diamine monomers and subsequent polymerization. The latter method is prefered to the former due to easy control of sulfonation degree and preventing further chemical degradation in the polymer chain by inappropriate sulfonation [1].

In this study, random and block sulfonated copolyimides containing carboxylic acid group were prepared *via* polycondensation using sulfonated diamine monomers in order to observe morphological effect in relation to the proton transport behavior and water vapor sorption for the different distribution in the hydrated structure connected with negative charged fixed ions. In addition, the effect of different chemical crosslinkers on methanol permeability through random and block copolyimide membranes will be also discussed.

2. Experimental

2.1. Preparation of sulfonated polyimide membranes

To observe the effect of random and block copolyimide on proton transport behavior, sulfonated polyimides (Class 1) were prepared by polycondensation of 1,4,5,8-naphthalenic dianhydride (NTDA) with various chemical composition of disulfonated ODA (ODADS) and 1,3-diamino benzoic acid (DBA) [2]. Crosslinked sulfonated polyimides (Class 2 and 3) were also prepared by introduction of different chemical crosslinkers such as ethylene glycol (EG) and fixed charged ion containing chemcial crosslinker (BES) into the pre-described random and block copolyimide. 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.

2.2. Characterization of sulfonated polyimide membranes

Distribution of hydrophilic segments in the random and block sulfonated polyimide membranes was a key factor to determine the proton transport behavior through water medium. To observe the morphological effect in relation to distribution of hydrophilic domain in random and block copolyimides, each sulfonated polyimide membrane was investigated by proton conductivity, water vapor sorption, methanol permeability, atomic force microscopy (AFM) and X-ray diffraction (XRD) spectroscopy. Additionally, the effect of crosslinkers on crosslinked sulfonated polyimides with different arrangement of hydrophilic segments was also studied.

3. Results and Discussion

The proton conduction behavior through the membrane on ambient temperature and humidity was shown in Figure 1. The proton conductivity of sulfonated polyimide membranes was higher than that of Nafion 117 at 90% RH. For non-crosslinked sulfonated polyimide membrane Class 1, the proton conductivity of block copolyimide was higher than that of random copolyimide with same chemical composition due to extensive distribution of homogeneous hydrophilic segments by inter- or intramolecular physical crosslinking between carboxylic acid groups. However, random copolyimide had higher conductivity than that of block copolyimide for crosslinked sulfonated polyimide membranes due to the reduction of carboxylic acid groups and the formation of hydrophobic segment by crosslinking reaction even though Class 2 had fixed charged sulfonic acid groups. In addition, random and block copolyimide Class 2-5 had improved proton conduction behavior through introduction of a chemical crosslinker with fixed charged sulfonic acid groups to compensate reduction of water uptake by thermal activated crosslinking reaction.

The water uptake behavior similar to proton transport behavior of sulfonated polyimide membranes was shown in Figure 2. The water content was lower due to crosslinking, as compared with non-crosslinked polyimides.

Reference

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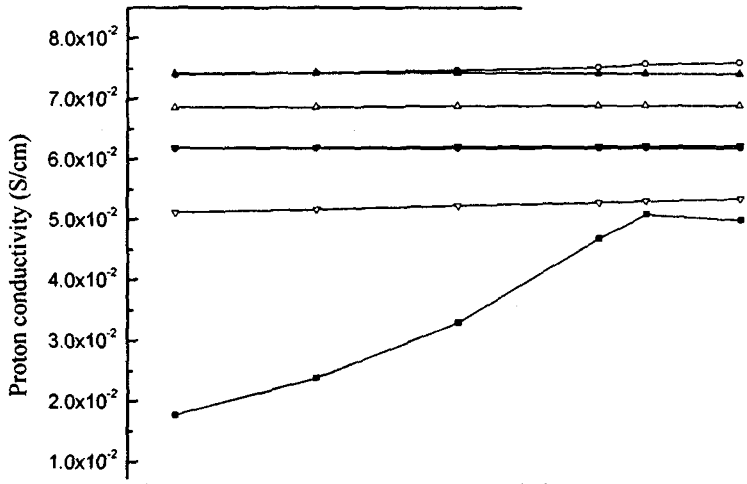

Figure 1. The temperature dependance on proton conductivity in random and block copolyimide membranes

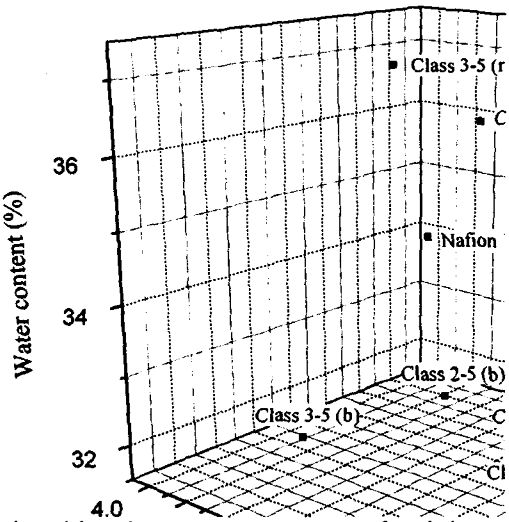

Figure 2. Mutual relationships between proton conductivity, methanol permeability and water content in sulfonated polyimide membranes