

연료전지용 가교 설폰화 폴리이미드막: 가교제에 따른 수소이온전도도 및 메탄올 투과도 특성변화

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Cross-linked Sulfonated Polyimide Membranes: Effect of Kinds of Cross-linkers on Proton Conductivity and Methanol Permeability

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1. Introduction

Sulfonated polyimide (SPI) has been recently investigated as a potential material to fulfill tough membrane criteria for fuel cell application due to its easy fabrication, excellent thermal, chemical and mechanical stability [1-7]. In the many literatures, sulfonated diamines were used with the combination of various dianhydrides for the fabrication of SPI membranes. However, there are some problems in SPI as reported. Most of all, the phthalic-SPI membrane with five membered imido structures shows poor hydrolytic stability on the harsh fuel cell test condition [3]. This can be considerably improved using six membered-naphthalenic dianhydride [8]. Moreover, highly sulfonated polyimide membranes may become water-soluble and also show poor mechanical properties, as other highly sulfonated aromatic polymers do [4]. Meanwhile, a sulfonated polyimide membrane with low sulfonation degree showed high mechanical properties but low proton conductivity owing to low water uptake. Therefore, proper sulfonation level is necessary to enhance both the proton conductivity and the mechanical properties. In a sense, cross-linking can be better solution to improve the proton conductivity and to reduce the methanol permeability.

Our ultimate goals of the present study are to investigate the effect of cross-linking on membrane performances and to study the effect of cross-linker size on important properties such as the proton conductivity and the methanol permeability.

2. Experimental

2.1. Synthesis of NTDA-ODADS-DBA copolyimides (HYU-1) and NTDA-ODADS-DBA copolyimides cross-linked with diols (HYU-2)

HYU-1 was prepared using a polycondensation of 1,4,5,8-naphthalenic dianhydride (NTDA) with the mole ratio (4/6) of sulfonated diamine(ODADS) to carboxylic acid-containing diamine(DBA), respectively. All HYU-2 membranes were prepared in the same method for the preparation of HYU-1, and it is distinguished from HYU-1 by the introduction of various hydroxy terminated chemical cross-linkers having the different number of alkyl chains ($\text{HO}-(\text{CH}_2)_n-\text{OH}$, $n=2\sim 6, 10$). HYU-1 and HYU-2 were prepared using sulfonated polyimides soluble in *m*-cresol by typical solution-casting method and then drying at 180 °C in a vacuum oven for 24 h.

2.2. Characterization of HYU-1 and HYU-2 membranes

The chemical structure of SPIs was analyzed using ^1H - and ^{13}C -NMR, and Fourier transform infrared (FT-IR) spectroscopy. The ion exchange capacity (IEC, meq/g) as the amount of hydrogen ions released from the fully protonated SPI membrane per each polymer weight was measured using a classical acid-base titration method (ASTM 2187). The solubility of SPI membrane samples was evaluated after vigorously stirring in common polar aprotic solvents at 25 °C for three days. After the test, insoluble residuals in a specific solvent were filtered, washed, and weighed. The hydrophilicity of SPI membranes was measured in terms of the water vapor sorption under 90% RH at 25 °C and the equilibrium water content of membranes from the ratio of the swollen weight to the dry weight of each membrane in deionized water at 25 °C. The proton conductivity was obtained from the impedance of membrane. The methanol permeability was measured using a two-chamber diffusion cell. The average *d*-spacing values of SPI membranes were obtained from X-ray diffraction (WAXD). Finally, the hydrolytic stability and the accelerated peroxide radical stability were measured after the immersion of each SPI membrane into deionized water at 80 °C of practical fuel cell operating temperature and in H_2O_2 and ferrous ammonium sulfate solution, respectively.

3. Results and Discussion

The ^1H NMR spectra of HYU-2-III-2, HYU-2-III-4, and HYU-2-III-10 samples,

which were cross-linked with diols ($\text{HO}-(\text{CH}_2)_n\text{-OH}$) containing the number of alkyl chains of $n=2, 4$ and 10 , respectively, are shown in Figure 1. In HYU-2, the hydroxy group in diols might react competitively with carboxylic acid in DBA or sulfonic acid in ODADS. That is, presently, there might be two types of ester (carboxylic acid ester and sulfonic acid ester) formed by introduction of diols. Although there are a lot of probabilities in the formation of various cross-linking and grafting structures with two types of ester, ^1H NMR (a) revealed that only three kinds of esters (1. cross-linked ester from only carboxylic acid, 2. grafted ester from carboxylic acid, 3. grafted ester from sulfonic acid)coexisted in the present HYU-2 membranes. As a result, fully cross-linking did not occur from the introduction of chemical cross-linkers.

Indeed, it was expected that a longer cross-linker would lead to higher content of grafted ester as compared with that of cross-linked ester owing to its lower reactivity by the broader average interchain-distance. In this ^1H NMR (b), the content of cross-linked ester from carboxylic acid decreased with the number of alkyl chain from $n=2$ to $n=4$, as expected. However, the content of cross-linked ester oppositely increased with longer cross-linker from $n=4$ to $n=10$. In addition, a peak derived from sulfonic acid ester was observed in all ^1H NMR, but it was weak enough to be negligible as compared with a peak from carboxylic acid ester due to low reactivity by resonance stabilization of sulfonic acid groups and the inductive effect of electron-donating ether groups [9,10].

For HYU-2-III- n membranes with different number of alkyl chain in Figure 2, their proton conductivities were almost constant or reduced a little from $n=2$ to $n=4$ due to the reduction of water content within the SPI membranes by the decrease of cross-linking content. However, the introduction of longer cross-linkers from $n=4$ to $n=10$ caused broader average interchain distance of SPI chains and higher water uptake, followed by the increase of proton conductivity. Interestingly, proton conductivity increased significantly up to 9.3×10^{-2} S/cm over $n=6$, in spite of similar water uptake of non-cross-linked SPI. In addition, all HYU-2-III- n showed similar or higher proton conductivities than Nafion 117, indicating the formation of effective channels for proton conduction in terms of morphology.

The effect of cross-linker size on methanol permeability for HYU-2-III- n membranes is conspicuously observed in Figure 3, indicating that their methanol permeation behavior is similar to their water uptake and proton transport behavior. The introduction of cross-linkers from $n=2$ to $n=4$ caused successive reduction up to 1.96×10^{-7} cm^2/sec in methanol permeability. The longer cross-linkers from $n=4$ to $n=10$ resulted in the increase of methanol permeability. In summarizing the result presented so far, it can be concluded that HYU-2-III-5 with $n=4$ to 5 might be the most suitable membrane in DMFC application with similar proton conductivity and much lower methanol

permeability as compared with Nafion 117.

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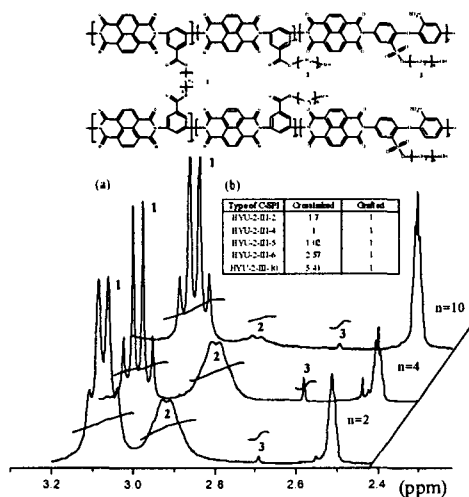


Figure 1. ¹H NMR spectra of HYU-2-III-2 (n=2), HYU-2-III-4 (n=4), and HYU-2-III-10 (n=10). (a) 1. crosslinked ester from carboxylic acid, 2. grafted ester from carboxylic acid, 3. grafted ester from sulfonic acid (b) the integration ratio of adjacent protons to oxygen element in crosslinked ester to grafted ester from carboxylic acid

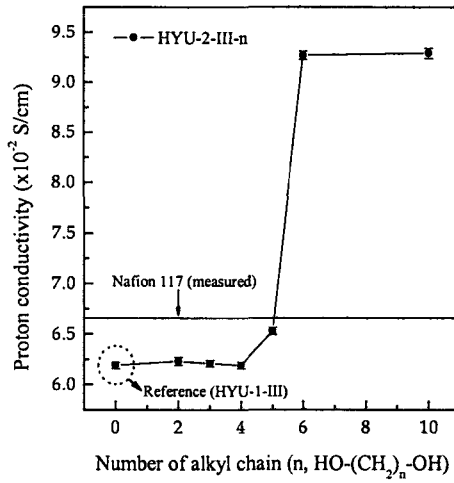


Figure 2. Variation of proton conductivity of HYU-2-III-n containing various diols with different number of alkyl chain ($\text{HO}-(\text{CH}_2)_n\text{-OH}$, $n=2\sim 6, 10$).

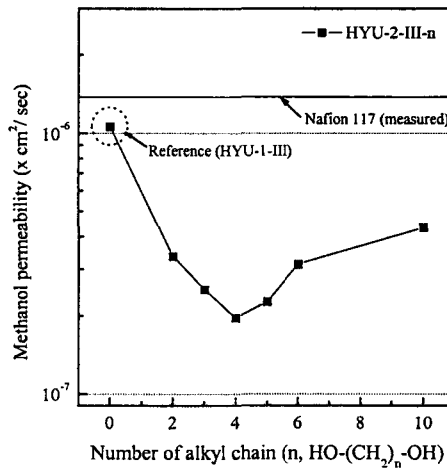


Figure 3. Variation of methanol permeability of HYU-2-III-n containing various diols with different number of alkyl chain ($\text{HO}-(\text{CH}_2)_n\text{-OH}$, $n=2\sim 6, 10$).