

# 높은 수화안정성을 갖는 연료전지용 유무기복합막의 제조 및 특성

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## Hydrolytically Durable Organic-Inorganic Composite Membranes for Fuel cell Application

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### 1. Introduction

Organic-inorganic composite membranes are fabricated by the incorporation of various inorganic materials into an organic polymer matrix to enhance membrane performances such as thermal stability, mechanical properties, and proton conductivity. Especially, organic-inorganic composite membranes have been utilized to maintain high water retention level, thereby leading high proton conductivity at high temperature. In many literature [1-5], hydrophilic micron size metal oxide particles such as silica, zirconium oxide, titanium oxide, TEOS and montmorillonite (MMT) were incorporated in the perfluorinated ionomer structure to maintain proton conductivity in high temperature through the reduction of water loss and to prevent excessive methanol permeation through the membrane. In addition, heteropolyacids such as phosphotungstic acid (PWA) and silicotungstic acid (SiWA) were

utilized with the main objective of increasing proton conductivity of polymeric materials [6–8].

In the present study, sulfonated polyimide (SPI) composite membranes containing hydrophilic and hydrophobic silica in a nanoscale, were prepared to reinforce mechanical and thermal properties of a sulfonated polyimide and to enhance membrane durability to hydrolysis and peroxide radical attack. Our ultimate goal of this study is to investigate the solvent–polymer interaction associated with proton conductivity and the effect of compatibilizer for uniform distribution of fumed silica, and to observe membrane performances in combination with hydrophilicity of silica nano-particles for development of suitable composite membrane materials for fuel cell application.

## 2. Experimental

### *2.1. Synthesis of NTDA ODADS DBA copolyimides (HYU 1) and NTDA ODADS-DBA copolyimides containing hydrophilic and hydrophobic fumed silica*

The SPI (HYU-1) 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 SPI-silica composite membranes were fabricated through the incorporation of hydrophilic fumed silica (aerosol 200, BET surface area = 200 m<sup>2</sup>/g) and hydrophobic silica (aerosol 812, BET surface area = 260 m<sup>2</sup>/g) in *m*-cresol and DMSO, after wetting of silica particles. Urethane acrylate non-ionomer (UAN) was used as compatibilizer for homogenization of silica particles. The nano-sized fumed silica was dispersed well into the polymer matrix with different silica contents. In the case of SPI-silica composite membrane without compatibilizer, dispersed silica was aggregated with the average diameter of 50–70 nm. On the contrary, the compatibilizer reduced average diameter of silica domain below 20 nm in the SPI-silica composite membrane.

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

The chemical structure of HYU-1 was confirmed by Fourier transform infrared (FT IR). 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 by the two-chamber cell method. The homogeneous dispersion was observed using SEM and TEM. Finally, the hydrolytic stability and the accelerated peroxide radical stability were measured by immersion of each SPI membrane into deionized water at 80 °C of practical fuel cell operating temperature and in  $\text{H}_2\text{O}_2$  and ferrous ammonium sulfate solution, respectively.

## 3. Results and Discussion

Figure 1 shows the dependence of proton conductivity on temperature of organic-inorganic composite membranes. The proton conductivity of all SPI membranes increased successively with elevated temperature. In Figure 1 (a), the increase of water retention level by hydrophilic fumed silica caused higher proton conductivity in composite membranes as compared with original SPI, HYU-1. The proton conductivity of composite membranes using DMSO as solvent was significantly higher than that of composite membranes using *m*-cresol with the same silica content. That is, inter- and intramolecular hydrogen bonding between six hydrogen atom of DMSO and two oxygen of S=O in  $\text{SO}_3\text{H}$ , and oxygen in S=O of DMSO and one hydrogen atom of  $\text{SO}_3\text{H}$  disturbed the dissociation of proton from  $\text{SO}_3\text{H}$  and obstruct the proton mobility. In Figure 1 (b), similar tendency in proton conductivity was observed with respect to the solvent-sulfonated polyimide interaction and hydrophilic silica content. Furthermore, hydrophobic silica made hydrophilicity of composite membrane lower and contributed the reduction of proton conductivity.

The incorporation of silica enhanced considerably the hydrolytic stability of SPI membrane over 5,000 hr as compared to 70 hr of HYU-1. Also, it made remarkable improvement in oxidative stability to free radical.

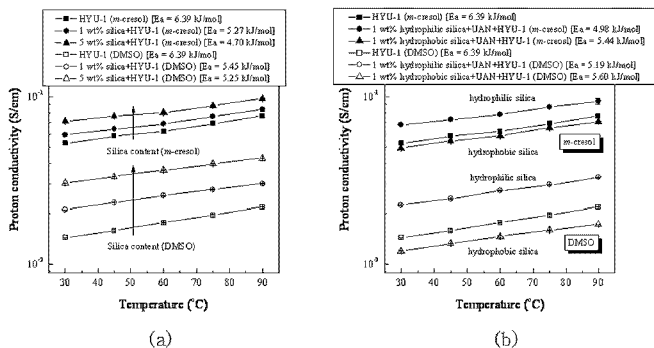


Figure 1. Proton conductivity (a) sulfonated polyimide-hydrophilic fumed silica with different silica content and solvents for preparation, (b) sulfonated polyimide-hydrophilic and hydrophobic silica composite containing a compatibilizer.

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