

연료전지용 유/무기 나노복합막의 제조 및 특성

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Preparation and Characterization of Organic-Inorganic Nanocomposite Membranes as Proton Exchange Membranes for Fuel Cell Application

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Introduction

Organic-inorganic composite membranes were prepared by the incorporation of inorganic nano-particles into an organic polymer that serves as the matrix component to enhance membrane performances such as thermal stability and mechanical property. The inorganic solid may present intrinsic proton conduction properties. Especially, organic-inorganic composite membranes have been utilized especially in high temperature fuel cell application. For perfluorinated ionomer membranes, inorganic oxide such as silica, zirconium oxide, TEOS and montmorillonite (MMT) were incorporated to keep the content of water-uptake constant even in high temperature and to improve membrane stability [1-4]. In addition, heteropolyacids such as phosphotungstic acid (PWA) and silicotungstic acid (SiWA) were utilized to compensate the reduction of proton conductivity by water vaporization in high temperature [5-8]. In this study, sulfonated polyimide (SPI)-silica composite membranes were prepared by the introduction of hydrophilic and hydrophobic silica in a nanoscale to improve mechanical, thermal

and hydrolytic stability of sulfonated polyimide. Commercial oligomers as compatibilizers were further added to induce the homogeneous dispersion of nano-sized silica into polymeric matrix. Eventually, the effect of hydrophilic and hydrophobic silica were discussed in the present study. Finally, the effect of compatibilizer was also investigated in relation to uniform distribution of fumed silica.

Experiments

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 prepared using hydrophilic fumed silica (aerosol[®] 200, BET surface area = 200 m²/g) and hydrophobic silica (aerosol[®] 812, BET surface area = 110 m²/g) in m-cresol. Oligomers with different molecular weight and hydrophilicity were used as compatibilizers.

Results and Discussion

The nano-sized fumed silica was dispersed well into the polymer matrix with different compatibilizers. In SPI-silica nanocomposite membrane without any compatibilizer, silica particles were aggregated with the average diameter of 50-70 nm. Meanwhile, the average diameter of silica domain was reduced below 20 nm through the introduction of compatibilizers. Figure 1 shows the dependence of proton conductivity on types of compatibilizer of organic-inorganic composite membranes. The proton conductivity of all SPI membrane increased successively with length of hydrophilic moieties in compatibilizer. In Figure 1 (a), the increase of length of hydrophilic moieties in compatibilizer caused higher proton conductivity of composite membranes than that of original SPI. Sulfonated polyimide-silica nanocomposite membranes were fabricated using fumed silica and non-ionic chemical modifier as a compatibilizer and crosslinker to improve membrane stability and to increase water retention level at the elevated temperature.

However, more addition of hydrophobic silica increase hydrophobicity of composite membrane and contributed the reduction of proton conductivity in Figure 1 (b). The incorporation of silica enhanced considerably the hydrolytic stability of SPI membrane over 5,000 hr compared to 70 hr of a pristine SPI. Also, it made remarkable improvement in oxidative stability to free radical. The crosslinked sulfonated polyimide nano-sized silica composite membranes showed high tensile strength up to 120 MPa. Thus, the introduction of compatibilizers along with silica nano-particles caused significant improvement in mechanical properties of the composite membranes owing to the effect of urethane groups in compatibilizer.

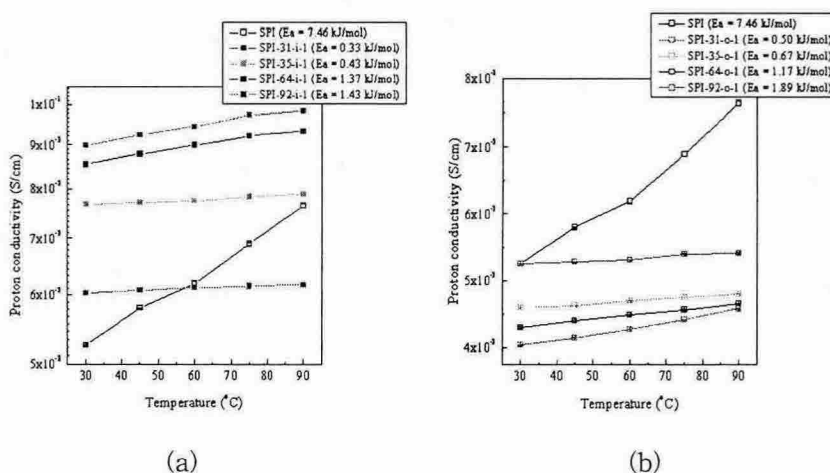


Figure 1. Proton conductivity of (a) Sulfonated polyimide-hydrophilic silica composite with different compatibilizer for membrane preparation. (b) Sulfonated polyimide-hydrophobic silica composite with different compatibilizer for membrane preparation.

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