수소이온 전도성, 메탄올 저투과성 폴리아릴렌계 실리카 나노복합막

민경아, 이창현, 이영무*
한양대학교, 응용화학공학부

High Proton Conductive and Low Methanol Permeable Polyarylene-fumed Silica Nanocomposite Membranes

Kyung A Min, Chang Hyun Lee, Young Moo Lee*
School of Chemical Engineering, Hanyang University, Seoul 133-791, Korea
Tel. 82-2-2220-0525, E-mail:ymlee@hanyang.ac.kr

1. Introduction

Poly(arylene ether) (PAEs) polymers are well-known engineering thermoplastics with excellent thermal, chemical, and hydrolytic stability, and mechanical properties. Incorporation of sulfonic acid groups in the PAEs led to highly proton conductive membranes. However, highly sulfonated PAEs can be soluble or excessively swellable in water medium at elevated temperature, and lose its mechanical properties.

2. Theory

In the present study, sulfonated poly(phthalazinone ether sulfone ketone) (SPPESK) was prepared *via* the post sulfonation process. Then, SPPESK-silica hydrid membranes and SPPESK-silica nanocomposite membranes were fabricated through sol-gel process from TEOS and dispersion of hydrophilic fumed silica using compatibilizers, respectively. Eventually, the effect of silica and the influence of compatibilizer were discussed in relation to performances in the organic- inorganic nanocomposite membranes. Furthermore, electrochemical characteristics including single cell performance and long term stability during DMFC operation were investigated using the organic-inorganic nano-composite membranes showing high proton conductivity (1.08^{-1} S/cm at 30 ℃) and lower methanol permeability (8.60×10^{-8} cm^2/sec).

3. Experimental

The PPESK was added to a mixture of H_2SO_4/fuming SO_3 (4:6 v/v) under an N_2 gas at temperature 60 ℃ for 4 hrs. After dissolution of SPPESK in NMP, organic-inorganic hybrids was fabricated *via* the sol-gel process. Moreover, direct mixing of fumed silica in SPPESK solution resulted in the sulfonated polyarylene-fumed silica nanocomposite.

4. Result and Discussion

The incorporation of compatibilizers was expected to significantly contributed homogeneous dispersion of nanosized fumed silica with an average particle size of about 7 nm. It was also anticipated that the different types of fumed silica such as Aerosil 200 and Aerosil 812 gave rise to completely different microstructure, because hydrophilic fumed silica would be located along with the hydrophilic moieties of polymer matrix, and prevent the formation of large hydrophilic cluster as a methanol barrier. There is a limitation to show the exact microstructure of the polyarylene-fumed silica nanocomposite membrane including uniform distribution of the silica particles. However, from the SEM image in Figure 1, no phase separation of the membrane surface can be observed, indicating the nanocomposite membranes have a homogeneous dense structure. Furthremore, the formation of uniform silica network in SPPESK-silica hydrid membrane was also observed.

The proton conductivities and methanol permeabilities were listed in Table 1. The proton conduction is associated with proton hopping between SiOH and water molecules as well as proton transport through the hydrophilic cluster. It is apparent that the existence of hydrophilic fumed silica helps the resultant composite and hydrbid membranes achieve a higher proton conductivity than SPPESK membranes. However, an excess hydrophilic silica phase inhibits proton conduction in the membrane. The methanol permeability of the silica composite membrane decreased with silica content.

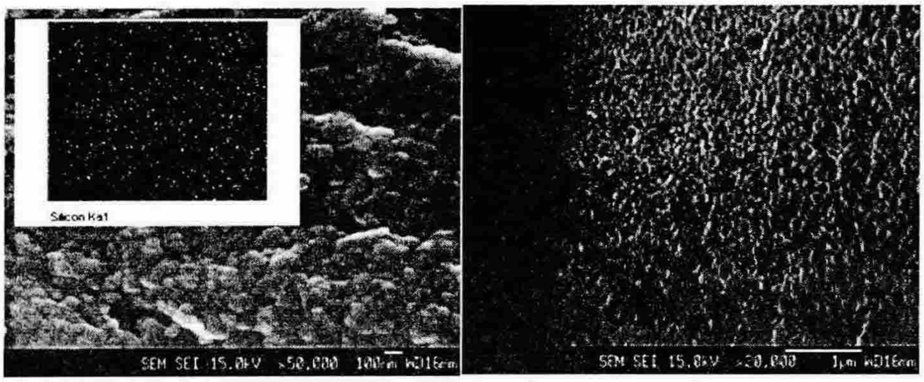

Fig. 1 SEM image of SPPESK-silica nanocomposite membrane (left), and SPPESK-silica hybrid membrane (right).

Table 1. Proton conductivities and Methanol permeabilities

	Proton conductivity (S/cm at 30 °C)	Mehtanol permeability (cm^2/sec at 10 M)
SPPESK-2h	1.78^{-1}	-
SPPESK-1h	3.62^{-2}	8.16^{-7}
SPPESK-1h-hybrid	9.68^{-2}	1.06^{-7}
SPPESK-1h-composite	1.08^{-1}	8.60^{-8}

5. Reference

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