

연료전지용 유무기복합 고분자 전해질막의 개발

김대식, 신광호, 박호범, 남상용¹ 이영무*
한양대학교 화학공학과
¹경상대학교 고분자공학과

Development of Organic/Inorganic Hybrid Electrolyte Membrane for Fuel Cell

Dae Sik Kim, Kwang Ho Shin, Ho Bum Park, Sang Yong Nam¹
Young Moo Lee*

School of Chemical Engineering, Hanyang University, Seoul 133-791, Korea

¹Department of Polymer Science and Engineering, Gyeongsang National University, Chinju 660-701, Korea

1. Introduction

A direct methanol fuel cells (DMFCs) using polymer electrolyte membranes are one of the most attractive power sources for a wide range of application from vehicles to portable utilities due to the stable operation at a rarely low temperature, the high energy generation yield and energy density, the simplicity of system.

Many efforts to synthesize cost-effective and thermally stable alternative membranes, including sulfonated poly(arylene ether sulfone) copolymer polybenzimidazoles, poly(ether ether ketone)s, and substituted polyphenylenes have been initiated, and several have continued to attract interest[1]. Poly(arylene ether sulfone)s are important, well-known engineering thermoplastics that display excellent thermal and mechanical properties, as well as resistance to oxidation and acid catalyzed hydrolysis[2].

The poly(phthalazinone ether sulfone ketone)(PPESK) family of polymers has high glass transition temperatures and excellent physical properties and thermostability. Membranes made from PPESK have shown good separation and permeation properties for gas and liquid separation. Sulfonated PPESKs (SPPEK) has been prepared from previously synthesized polymers to improve the polymers' hydrophilicity and thereby utilize this type of polymer for membranes for application in ion exchange membrane [3].

In this study, the proton exchange membranes were prepared using PPESK as the base materials. The introduction of sulfonic acid group into polymer matrix was achieved by the sulfonation with concentrated sulfuric acid and fuming sulfuric acid. The silica content from 0.5 to 5 wt% were introduced into the polymer matrix using fumed silica. Their water swelling, ion exchange capacity, proton conductivity were investigated in an attempt to characterize membranes for DMFC application.

2. Experimental

The PPESK was added to a mixture of H₂SO₄/fuming SO₃ (4:6 v/v) under an N₂ gas at temperature 60°C for 4h. Inorganic-organic hybrids were prepared by dissolving sulfonated PPESK (SPPEK) in NMP, and followed by the addition of fumed silica. This solution was mixed at room temperature. The amount of fumed silica was 0.5%, 1%, 3% and 5% by weight to SPPEK weight. This solution was poured into a glass plate and cast using the doctor blade process. Freshly cast films were initially heated at 80 °C for 24h, then 100 °C for 24h.

3. Results and discussion

The objective of this study is to evaluate of proton conductivity and methanol permeability of the SPPEK/silica hybrid membrane with hydrophilic / hydrophobic fumed silica. To do this, the introduction of sulfonic acid group into polymer matrix was achieved by the sulfonation with concentrated sulfuric acid and fuming sulfuric acid mixture, and fumed silica was introduced into the polymer matrix. Their water swelling, ion exchange capacity, proton conductivity and methanol permeability were investigated in an attempt to characterize membranes for DMFC application. The proton conductivities and methanol permeabilities were listed on Table 1. The proton conduction is associated with proton hopping between SiOH and water molecules. It is apparent that the existence of hydrophilic fumed silica as a proton conductor helps hybrid membrane achieve a higher proton conductivity than SPPEK membranes. However, an excess of the silica phase could result in a counter effect, and the hydrophobic silica phase inhibits proton conduction in the membrane. The methanol permeability of SP-B-x series hybrid membrane decreased with silica content.

Acknowledgments

The authors would like to thank Research Park/LG Chem, Ltd. and Ministry of Commerce, Industry and Energy for funding this research in the frame work of the Korean government/industry joint project for the development of 50W direct methanol fuel cell systems.

References

1. Brian R. Einsla, James E. Mcgrath. J Polym Sci Part A:Polym Chem 2004; 42;862-874
2. Feng Wang, James E. Mcgrath, J Mem Sci 2002; 197;231-242
3. Y.Dai, X. Jian, X. Liu, M.D.Guiver, J.Appl. Polym. Sci. 79 (2001) 1685-1692

Table 1. proton conductivities and methanol permeabilities of membranes

sample	Proton conductivity($\times 10^{-2}$ S/cm)				Methanol permeability ($\times 10^{-7}$ cm ² /s)
	30 °C	60 °C	80 °C	90 °C	
SPPEsk	6.76	6.89	7.03	7.03	8.16
SP-P-0.5	7.15	7.31	7.44	7.44	1.91
SP-P-1	6.85	7.00	7.15	7.15	2.24
SP-P-3	6.48	6.65	6.75	6.75	3.13
SP-P-5	6.19	6.35	6.51	6.51	4.5
SP-B-0.5	6.06	6.17	6.25	6.28	1.19
SP-B-1	5.92	6.07	6.16	6.23	0.99
SP-B-3	5.84	5.95	6.06	6.13	0.91
SP-B-5	5.50	5.61	5.75	5.85	0.82