# Sulfonated Poly(styrene-divinyl benzene)/PTFE Composite Membranes for DMFC

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### 직접메탄올 연료전지를 위한 술폰화 폴리스틸렌-디비닐벤젠/테플론 복합막의 특성연구

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#### 1. Introduction

Polymer-electrolyte membranes have attracted much attention in the past few decades due to their application in fuel cell systems. The mainly used proton-exchange membranes are perfluoro-polymers such as DuPont's Nafion<sup>®</sup>, and Asahi Chemical's Aciplex<sup>®</sup> because of high proton conductivity and excellent chemical stability. However, some weaknesses such as high preparation cost, low conductivity at high temperature, and expecially, high methanol permeability have limited severely their practical DMFC application. Many studies have been done for the development of polymer electrolyte membranes with low preparation cost and low methanol crossover. Composite membranes are prepared by impregnation of polymer electrolyte into chemically inert and mechanically strong porous thin films, which would be good candidates to

substitute for the perfluoro-polymer membranes. They can reduce cost and methanol permeability, and enhance mechanical and electrochemical properties. Accordingly, there have been many reports about this type of composite membranes. Gore-select<sup>®</sup> membranes, where Nafion solution is impregnated in porous polytetrafluoroethylene (PTFE), can be an excellent example of composite membranes. But, it was found not appropriate for DMFC application because of high methanol crossover. In polystyrene-divinyl prepared sulfonated this study. we benzene (PS-DVB)/PTFE composite membranes and report their performance for DMFC fuel cell application.

#### 2. Experimental

Porous PTFE membrane was used as a support material for sulfonated PS-DVB/PTFE composite membrane. Styrene, divinyl benzene (DVB) and AIBN were used as a monomer, a crosslinker and initiator, respectively. PTFE membrane was impregnated with different ratio of styrene-divinyl benzene monomer mixtures and polymerized with the aid of PET film and a specially designed reaction vessel. Then, sulfonation was conducted with mixture of chlorosulfonic acid and 1,2-dichloroethane to give the composite membranes. The chemical and physical structures of the composite membranes were characterized by FT-IR and SEM. Ion exchange capacity (IEC), ion conductivity and methanol permeability were studied as functions of weight ratio of styrene/DVB.

#### 3. Result & Discussion

Methanol permeability and ion conductivity of sulfonated PS-DVB/PTFE composite membranes were measured as a function of the ratio of styrene/DVB and were compared with Nafion<sup>®</sup>117. The methanol permeability decreased with decreasing the ratio of styrene/DVB because of higher crosslinking and lower sulfuric acid groups(-SO3<sup>-</sup>H<sup>+</sup>) formed in the pores of composite membranes. As shown in Fig. 1, the value of methanol permeability of the membranes

prepared were  $6.6\times10^{-7}$ ,  $3.7\times10^{-7}$ ,  $1.5\times10^{-7}$ , and  $1.3\times10^{-7}$  cm/s according to the ratio of styrene/DVB of 95/5, 93/7, 90/10, 85/15 wt.%, respectively. As Nafion<sup>®</sup>117 showed  $1.02\times10^{-6}$  cm/s, methanol permeability of all the composite membranes were much lower than that of Nafion<sup>®</sup>117, presumably due to the chemical structure difference. As shown in Fig. 2, ion conductivity decreased with decreasing the ratio of styrene/DVB, like the methanol permeability behavior. The value of ion conductivity of the membranes were  $0.11\text{S/cm}(25\,^{\circ}\text{C})$ ,  $0.09\text{S/cm}(25\,^{\circ}\text{C})$ ,  $0.09\text{S/cm}(25\,^{\circ}\text{C})$ , and  $0.08\text{S/cm}(25\,^{\circ}\text{C})$  according to the ratio of styrene/DVB of 95/5, 93/7, 90/10, 85/15 wt.%, respectively, which are higher than that of Nafion<sup>®</sup>117(0.0824S/cm).

#### 4. Conclusions

The sulfonated PS-DVB/PTFE composite membranes with different ratio of styrene/DVB were synthesized successfully. The composite membranes developed showed lower methanol permeability and higher ion conductivity than Nafion<sup>®</sup>117.

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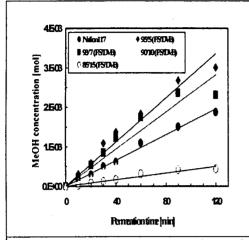


Fig. 1 Methanol concentration of SPS-DVB/PTFE composite membranes as a function of the permeation time.

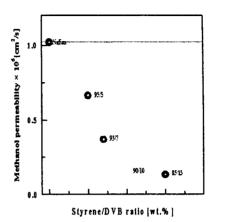


Fig. 2 Methanol permeability of SPS-DVB/PTFE composite membranes as a function of the ratio of styrene/DVB.

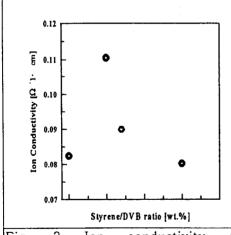


Fig. 3 Ion conductivity of SPS-DVB/PTFE composite membranes as a function of the ratio of styrene/DVB.

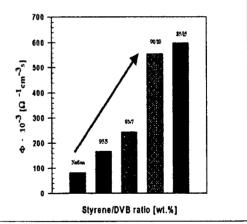


Fig. 4 Characteristic factor of SPS-DVB/PTFE composite membranes as a function of the ratio of styrene/DVB.

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