

## Preparation of Laminated Composite Membranes by Impregnation of Polypropylene with Styrene in Supercritical CO<sub>2</sub> for Direct Methanol Fuel Cells

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**Abstract**—Composite membranes were formed by grafting styrene using supercritical carbon dioxide (scCO<sub>2</sub>) impregnation and polymerization procedures. A polypropylene membrane, styrene monomer, divinylbenzene (DVB), and 2,2'-Azoisobutyronitrile (AIBN) were placed in a reactor, and CO<sub>2</sub> was injected into the reactor at 38 °C for the scCO<sub>2</sub> impregnation process. After impregnation, the polymerization process was carried out at 78 °C. The grafted membranes were sulfonated in concentrated sulfuric acid at 95 °C. These polypropylene grafted polystyrene sulfonic acid (PP-g-pssa) membranes were characterized by using various methods. The morphology and structure of the PP-g-pssa membranes were analyzed with scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FT-IR) and energy dispersive spectrometer (EDS). The ion conductivity and methanol permeability were also measured. The ion conductivity of the PP-g-pssa membranes was higher and the methanol permeability of the laminated membrane was lower than that of Nafion membranes. The performance of the PP-g-pssa/Nafion laminated membranes was evaluated in a DMFC unit cell at 90 °C.

**Key words:** Polypropylene Grafted Polystyrene Sulfonic Acid, Supercritical Carbon Dioxide, Impregnation, Direct Methanol Fuel Cell, Laminated Membrane

### INTRODUCTION

Direct Methanol Fuel Cells (DMFCs) have been the focus of attention in alternative energy research, because of their high efficiency, high energy power density, zero or low emission and so on [Li et al., 2003; Hongarth et al., 1996; Surempudi et al., 1994; Wang et al., 1995]. Nowadays, some portable product models applying DMFC systems are available, but there remain two major limitations to their practical use: the low activity of the catalysts and the crossover phenomenon of methanol with the latter being caused by the diffusion and electro-osmotic drag of methanol [Park et al., 2005]. The methanol crossover phenomenon leads to a serious decrease in the cathode performance, and to a loss in the overall fuel cell efficiency [Parsons et al., 1988; Goodenough et al., 1988; Otsuka et al., 1986]. Although commercial perfluorinated ion-exchange polymers, such as Nafion from DuPont are highly suitable for use as polymer electrolyte membrane (PEM) in hydrogen fuel cells, they are unsuitable for DMFCs due to the high methanol permeability of these polymers [Lee et al., 2004; Manea et al., 2002]. Hence, recent trends of research have been focused on the development of new polymer electrolyte membranes, in order to decrease the cost and mitigate the methanol crossover phenomenon.

Supercritical carbon dioxide (scCO<sub>2</sub>), which is by far the most widely used supercritical fluid (SCF), is relatively cheap, nontoxic, and nonflammable and has zero ozone-depletion potential. The interest in the supercritical fluid impregnation of polymeric materials stems from the opportunity to utilize the SCF properties (high diffusivity, low surface tension, ease of solvent recovery, etc.) of the

resulting polymeric material [Kazarian et al., 2000]. One of the most interesting applications of supercritical fluid impregnation is the modification of polymers via the infusion of a monomer and an initiator into a CO<sub>2</sub>-swollen polymer matrix, followed by the subsequent polymerization of the monomer within the polymer matrix [Beckman et al., 2004].

The work done by Muth et al. [2000] has shown that this approach can be extended to combine impregnation and in situ polymerization for systems including polycarbonate (PC), polyvinyl chloride (PVC), and polytetrafluoroethylene (PTFE) as the polymer matrices and styrene, methyl methacrylate (MMA) and methacrylic acid (MAA) as the monomer. PTFE has demonstrated the least ability to be modified by this technique, due to its limited swelling capability. Liu et al. [2002] reported that the grafted copolymer could be prepared by free radical polymerization in the swollen isotactic polypropylene (iPP) matrix with the aid of scCO<sub>2</sub> which acts as a solvent for methyl methacrylate, and a swelling agent for the iPP matrix.

In our previous study, we attempted to improve the conductivity of Nafion membranes and inhibit the permeation of methanol through the radical grafting of a styrene monomer onto Nafion 115 membranes using scCO<sub>2</sub> [Sauk et al., 2004]. In this work, we prepared grafted membranes using polypropylene (PP) membranes as the starting material by using similar methods, and then fabricated laminated membranes based on Nafion 112 to the direction of cathode in order to reduce the interfacial resistance of the cathode.

We focused on the effect of changing the concentration of the cross-linking agent DVB when preparing the grafted membranes. In all cases, the initiator was azoisobutyronitrile (AIBN). The morphology and structure of the prepared membranes were determined with scanning electron microscopy (SEM) and energy dispersive

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spectroscopy (EDS). Also, their DMFC performances were tested by using purpose-built equipment.

## EXPERIMENTAL

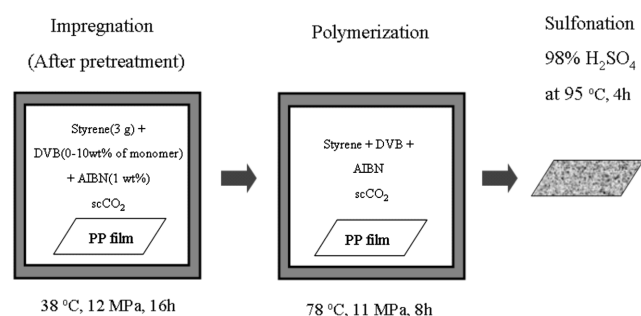
### 1. Materials

Polypropylene samples (PP, Celgard<sup>®</sup> 2500) in the form of microporous membrane were obtained from Celanese. The thickness of the PP membrane was 25.4  $\mu\text{m}$  and the porosity was 47%. We used these as the base membranes, because they were known to be thermally, mechanically and chemically stable [Bae et al., 2003]. The PP membranes were soaked in ethanol for one day, in order to remove the pollutant and dried at room temperature. The inhibitor present in the styrene monomer (99.5%, JUNSEI) was eliminated by means of an alumina column and the dissolved oxygen was removed by nitrogen purging. The initiator, 2,2'-Azobisisobutyronitrile (AIBN, Aldrich), was recrystallized twice from methanol. The cross-linking agent divinylbenzene (DVB, 80%, Aldrich) was used without any other treatment. Carbon dioxide with a purity of 99.99% was purchased from Korea industrial gas and used as received.

### 2. Preparation of Membrane

In this study, the experiments were carried out in a 30 ml SUS316 reactor that has one window located on the top-side, through which the inner phase change could be observed.  $\text{CO}_2$  was supplied with a gas booster pump (Maxpro Technologies Inc. Model DLE 75-1). To minimize the pressure fluctuations resulting from the pump and to maintain stable feeding, a 300 ml reservoir was installed between the pump and the reactor. Fig. 1 shows the experimental procedure that was used for the preparation of the PP-g-pssa membranes. The experiment was composed of two processes, the first being the impregnation process, in which the PP membranes were placed in the reactor along with the styrene monomer, AIBN and DVB. The amounts of styrene and AIBN used in this process were 3 g and 1 wt% of the monomer, respectively, while the amount of DVB was varied from 0 to 10 wt% of the monomer. In the second process,  $\text{CO}_2$  was injected into the reactor until a pressure of 12 MPa was attained at 38 °C for the  $\text{scCO}_2$  impregnation process. After 16 hours of impregnation, some of the  $\text{CO}_2$  was released and the polymerization process was started by raising the temperature to 78 °C and maintaining the reactor at this temperature for 8 h. During this time, the pressure was 11 MPa. Then the reactor was cooled to below 31 °C and the sample was dried in a vacuum oven at 70 °C.

Sulfuric acid (>98%, Aldrich) was used as the sulfonating agent.



**Fig. 1. Experimental procedure for preparation of polypropylene-grafted-polystyrene sulfonic acid (PP-g-pssa) membranes.**

After the grafting reaction, the grafted membranes were sulfonated at 95 °C for 4 h. Following their sulfonation, the membranes were washed with deionized water until their pH was neutral and then dried in a vacuum oven.

The PP-g-pssa/Nafion laminated membrane was made by hot pressing the PP-g-pssa membrane and Nafion 112.

### 3. Characterization of PP-g-pssa Membranes

The surface and cross-sectional morphological characteristics of the grafted membranes after impregnation and polymerization were observed by means of a field emission scanning electron microscope (FE-SEM, JSM-6700F). The surface was coated with platinum to prevent its becoming charged.

The infrared (IR) attenuated total reflection (ATR) spectra of the PP, PP-g-ps and PP-g-pssa membranes were measured with an FT-IR spectroscope (Jasco-200).

To confirm whether the polypropylene grafted polystyrene (PP-g-ps) membranes were sulfonated or not, the surface and cross-section of the polypropylene grafted polystyrene sulfonic acid (PP-g-pssa) membranes were analyzed by using an energy dispersive spectroscope (EDS). The EDS analysis enabled the presence of sulfur element in the PP-g-pssa membranes to be determined.

A four-probe AC electrochemical impedance spectroscopy (EIS, EG&G model 273A potentiostat/galvanostat) was used to measure the proton conductivity. The membrane resistance of each sample was measured at room temperature. The impedance analyzer was operated with an AC current amplitude of 10 mV by the Nyquist method. The membrane resistance was obtained by extrapolating the data to infinite frequency. The conductivity was calculated from the electrode area of the cell and the thickness of the membrane [Woo et al., 2003].

### 4. Measurement of Methanol Permeability

The methanol permeability of each membrane was measured by using the method proposed by Tricoli [Tricoli et al., 2000]. The permeability experiments were carried out utilizing a Teflon diffusion cell at room temperature. One compartment of the cell was filled with methanol and the other with de-ionized water. The membrane was clamped between the two compartments, both of which were kept under stirring during the experiment. The concentration of methanol in the permeate stream increased with time and it was measured with a refractive index detector (NAR-3T, ATAGO), in order to calculate the methanol permeability given by :

$$c_B = \frac{A P}{V_B L} c_A (t - t_0)$$

Where A, L and  $V_B$  are the membrane area and thickness and volume of the water compartment, respectively. P is the membrane permeability, and c is the methanol concentration of each part.

### 5. Fuel Cell Experiments

The membrane electrode assembly (MEA) was made by the hot pressing method, with Pt black as the cathode and Pt-Ru electrode as the anode. The hot pressing for compaction was done with a pressure of 13.8 MPa at 125 °C for 2 min. The electrode was supplied by E-TEK.

The PP-g-pssa/Nafion laminated membranes were tested as electrolytes under fuel cell conditions (methanol concentration: 2 M, cell temp.=90 °C and a pressure of 2 kgf/cm<sup>2</sup> of pressure between the cathode and anode). The flow rate of air was controlled by means

of a mass-flow controller (300 ml/min).

## RESULTS AND DISCUSSION

### 1. Characterization of PP-g-pssa Membranes

All of the impregnation and polymerization experiments were

conducted at  $38^\circ\text{C}$  and  $78^\circ\text{C}$ , respectively. As in the study conducted by Liu et al. [2002], the impregnation pressure was maintained at 12 MPa. To optimize the operational conditions, the effect of varying the amounts of DVB on the morphology was studied.

The morphology of the PP-g-pssa membranes is shown as a function of the DVB content in the range of 0 to 10 wt% in Fig. 2. The

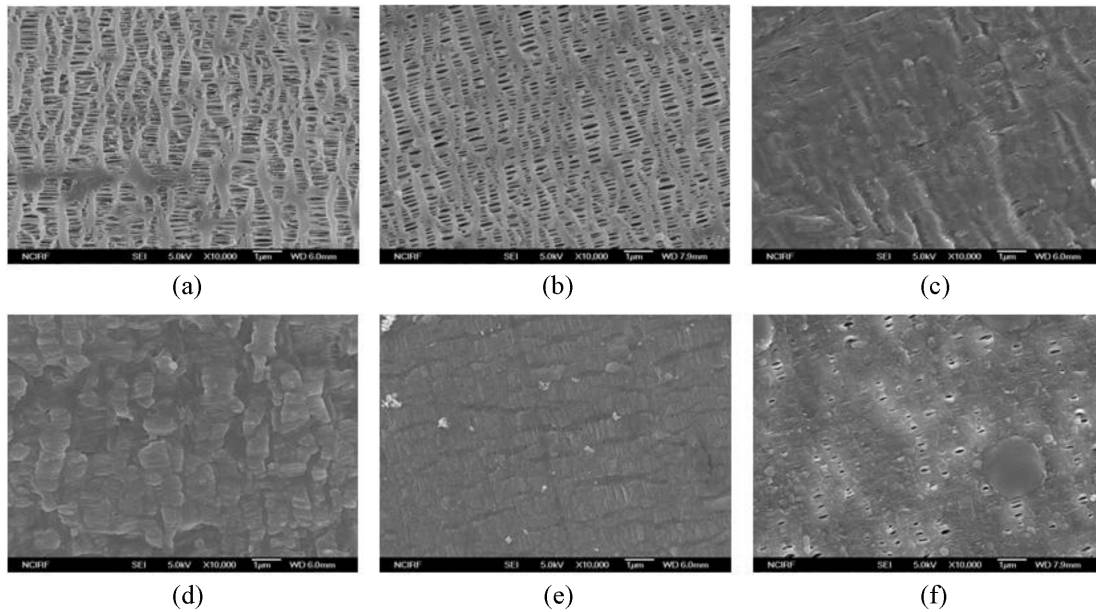


Fig. 2. The surface morphologies of (a) raw microporous PP membrane and PP-g-pssa membranes with (b) 0 wt%, (c) 2.5 wt%, (d) 5 wt%, (e) 7.5 wt%, (f) 10 wt% DVB.

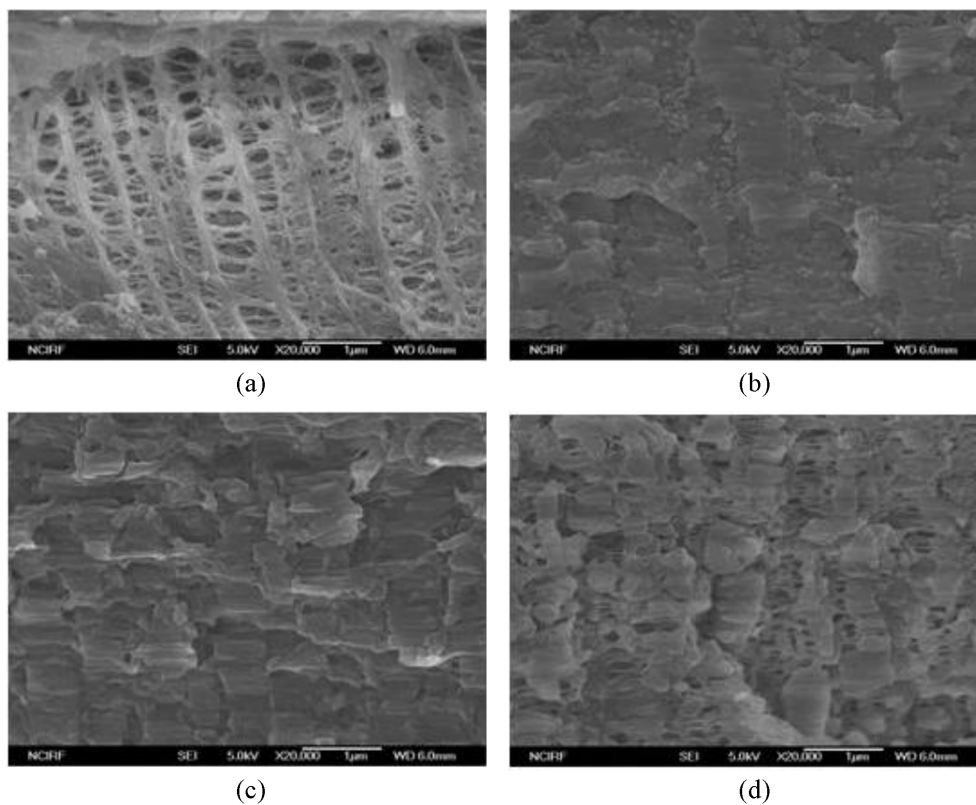


Fig. 3. The cross-sectional morphologies of PP-g-pssa membranes with (a) 2.5 wt%, (b) 5 wt%, (c) 7.5 wt%, (d) 10 wt% DVB.

surfaces of the PP-g-pssa membranes were completely covered with polystyrene sulfonic acid when the DVB concentration was more than 2.5 wt% of the styrene monomer (Fig. 2(c)). Fig. 3 shows that the cross-sectional morphology of the PP-g-pssa membranes was also filled with polystyrene sulfonic acid when the DVB concentration was more than 5 wt% (Fig. 3(b)). However, the membrane in which 10 wt% of DVB was used (Fig. 3(d)) had some pores in the center. When the concentration of DVB as cross-linking agent was too high, cross-linking occurred rapidly in the membranes during the polymerization, and it caused more limited mobility of the chain segments in the cross-linked polystyrene, so the cross-linked polystyrene in the PP membrane could not grow any more. Hence it could not be polymerized completely as well as the membranes with proper DVB.

The ATR spectra of the PP, PP-g-ps and PP-g-pssa membranes are given in Fig. 4. The characteristic peaks in the PP membrane are 2,956 and 2,932  $\text{cm}^{-1}$ , which represent the C-H stretching vibration, and 1,379 and 1,454  $\text{cm}^{-1}$ , which arise from the bending vibrations of  $\text{CH}_2$  and  $\text{CH}_3$ . The existence of polystyrene in the grafted membranes is confirmed by the decrease in the absorbance peaks ( $\text{CH}_2$ ,  $\text{CH}_3$ ) for the non-grafted PP. The absorption bands for polystyrene that appear in the regions of 745 and 699  $\text{cm}^{-1}$  are due to the aromatic C-H bonds and the out of plane benzene ring C-C bond, respectively. The sulfonated PP-g-ps membrane has strong absorbance peaks in the regions of 638 and 1,012  $\text{cm}^{-1}$ , which represent

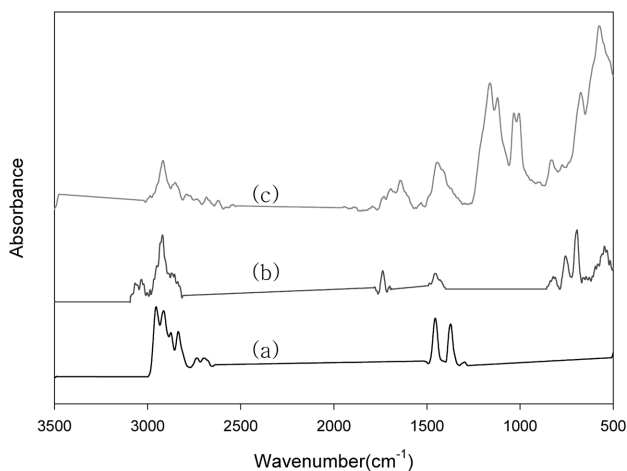


Fig. 4. FT-IR reflectance (ATR) of (a) PP, (b) PP-g-ps and (c) PP-g-pssa membranes.

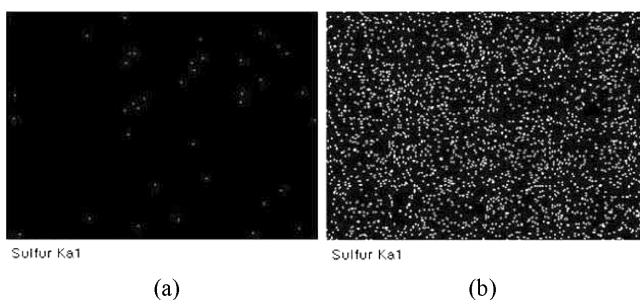
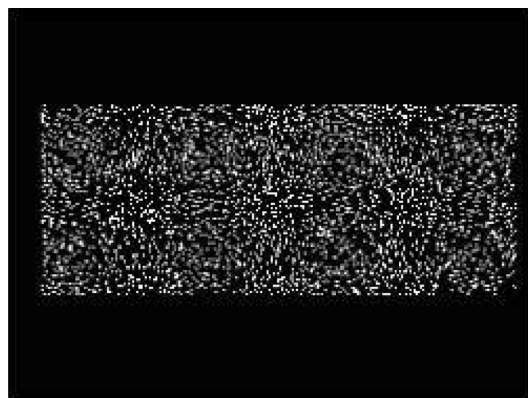


Fig. 5. Mapping of sulfur element at surface by EDS analysis; (a) raw PP membrane and (b) PP-g-pssa membrane.



Sulfur Ka1

Fig. 6. Mapping of sulfur element at cross-section of PP-g-pssa membrane with 5 wt% DVB by EDS analysis.

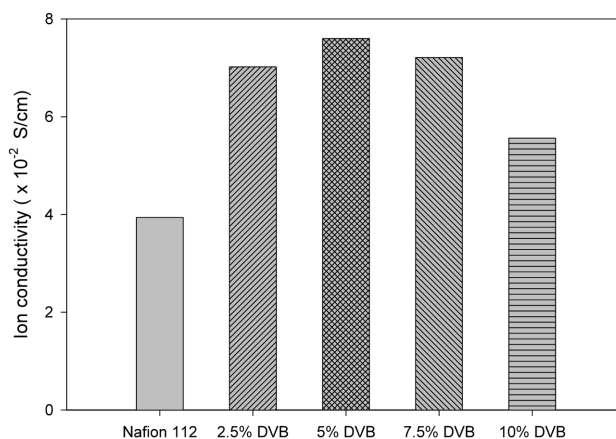


Fig. 7. Ion conductivities of Nafion 112 and PP-g-pssa membranes.

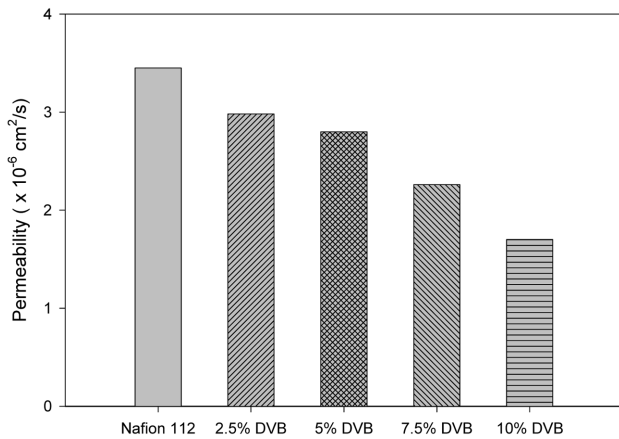
the S-O stretching vibrations, and 1,163 and 1,398  $\text{cm}^{-1}$ , indicating the presence of S=O stretching vibrations.

After the sulfonation treatment of the PP-g-ps membranes, we performed an EDS mapping analysis, to confirm the existence of  $\text{SO}_3^-$ . As shown in Fig. 5, we verified that the surface of the PP-g-pssa membrane was covered with a considerable amount of sulfur element. We also carried out an EDS mapping analysis of the cross-section of PP-g-pssa (5 wt% DVB) membranes. Fig. 6 shows that the membranes were sulfonated successfully.

The ion conductivity of the PP-g-pssa membrane itself was measured (see Fig. 7). All of the PP-g-pssa membranes had a higher ion conductivity than Nafion 112, and the highest ion conductivity was observed for the PP-g-pssa membrane with a DVB content of 5 wt%. These results can be explained by using Fig. 2 and Fig. 3. The grafting of polystyrene was insufficient in the case of the PP-g-pssa membrane with a DVB content of 2.5 wt% (see Fig. 3(a)), so that the resulting membrane that did not have good conductivity, while the PP-g-pssa membranes with a DVB content of more than 5 wt% had too much cross-linking at the surface, so that they had a higher membrane resistance.

## 2. Methanol Permeability of Laminated Membranes

The methanol permeability was measured for the PP-g-pssa/Nafion laminated membranes. The methanol permeability of these mem-



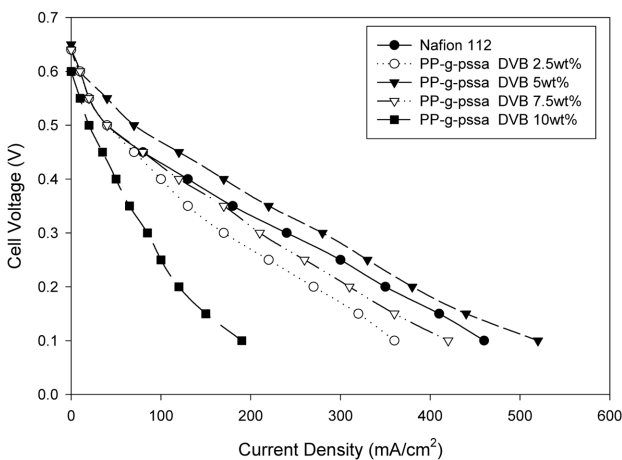
**Fig. 8. Methanol permeability of Nafion 112 and PP-g-sssa/Nafion 112 laminated membranes.**

branes is shown as a function of the concentration of DVB in Fig. 8. As the DVB concentration increased, the permeability was decreased. The permeability of Nafion 112 was  $3.45 \times 10^{-6} \text{ cm}^2/\text{s}$ , as calculated by the Tricoli equation, while that of the laminated membrane with a DVB content of 10 wt% DVB was  $1.7 \times 10^{-6} \text{ cm}^2/\text{s}$ . The methanol permeability of the laminated membrane was down to only 49% that of Nafion 112.

### 3. Cell Performance Test

To reduce the interfacial resistance of the cathode, a polymer electrolyte membrane with a laminated structure was obtained by hot pressing the PP-g-sssa membrane with Nafion 112 to the direction of cathode.

Fig. 9 shows the cell performance of the laminated membranes as function of the concentration of DVB. We performed the tests in a DMFC single cell at  $90^\circ\text{C}$  with air in the cathode. The best cell performance was observed for the PP-g-sssa/Nafion laminated membrane with a DVB concentration of 5 wt% DVB of the styrene monomer. At 0.35 V, the current density of the PP-g-sssa membrane with a DVB content of 5 wt% was 220 mA, while that of Nafion 112 was 180 mA. These results can be attributed to the degree of



**Fig. 9. Cell performance of PP-g-sssa/Nafion 112 laminated membranes according to changing concentration of DVB at  $90^\circ\text{C}$  DMFC system.**

grafting of the polystyrene. However, the performance of the PP-g-sssa/Nafion laminated membrane with a DVB content of 10 wt% was lower than that of the membrane with a DVB content of 2.5 wt%. This can be explained by the fact that the latter membrane had a higher membrane resistance, due to the greater amount of cross-linking that occurred at the surface. In laminated membranes, as the concentration of DVB became higher, the interfacial resistance was increased between PP-g-sssa membrane and Nafion 112. Hence, although the ion conductivity of PP-g-sssa membranes was higher than that of Nafion 112, the PP-g-sssa/Nafion 112 laminated membranes with 7.5 and 10 wt% DVB had poor cell performance.

### CONCLUSION

PP-g-ss membranes were prepared by grafting styrene into PP membranes in the presence of supercritical carbon dioxide ( $\text{scCO}_2$ ). Since the PP-g-ss membranes were sulfonated, they could be used as proton exchange membranes. The morphology and structure of these membranes were observed with SEM and ATR. We were able to verify the existence of  $\text{SO}_3^-$  in the membranes by using EDS analysis to map out the distribution of sulfur element. The ion conductivities of the PP-g-sssa membranes were higher than that of Nafion 112. The methanol permeability of these laminated membranes was studied as a function of the concentration of DVB. As the DVB concentration increased, the crossover phenomenon was decreased. The cell performance of the PP-g-sssa/Nafion laminated membranes was as much as 22% higher than that of Nafion 112 at 0.35 V.

### ACKNOWLEDGMENT

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