

## New Considerations on Nafion Membrane Modification for DMFC Application

직접 메탄올 연료전지용 나피온 막의 개질에 관한 새로운 고찰

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### 1. Introduction

Recently, the direct methanol fuel cell (DMFC) is considered to be one of the promising power sources. Methanol crossover is one of the main problems which should be resolved since it wastes fuel, and also causes performance losses at the cathode due to the consumption of oxygen and catalyst poisoning. There have been two approaches to reduce methanol crossover : One is the development of highly active anode catalysts coupled with a suitable anode structure for the direct methanol oxidation [1, 2]. The other is the prevention of methanol crossover from anode to cathode through the polymer electrolyte membrane [3]. Significant research efforts have focused on the improvement of proton conducting membranes [4-7]. In particular, various Nafion film modifications have been tried, however, they have still problems to be overcome for commercial applications.

In this study, we report the preparation and characterization of 1) the proton conducting semi-IPNs based on Nafion and crosslinked poly(AMPS) and 2) the coated Nafion with polymer blend. These films exhibit low methanol permeability and good compatibility between membrane and electrode while maintaining a good proton conductivity.

### 2. Experimental

The native Nafion 115 membrane and Nafion 117 membrane were pretreated and dried under vacuum before experiment.

## 2.1. semi-IPNs

2-acrylamido-2-methyl-1-propanesulphonic acid (AMPS), 1, 6-hexanediol propoxylate diacrylate (HPDA), and ethyl methacrylate (EMA) were dissolved in DMF (dimethylformamide). Benzophenone as a photoinitiator was added to the solutions. Curable monomer of AMPS, HPDA and EMA impregnated in the Nafion membranes were polymerized by exposing to ultraviolet radiation. To remove the nonreactive monomers, the film was washed and dried under vacuum.

## 2.2. Coated Nafion

Blend solutions were vigorously stirred and then poured into Petri dish. Nafion 117 membranes were immersed in the solution and the coated membranes were dried.

## 3. Results & discussion

### 3.1. semi-IPNs

The proton conductivity of the semi-IPNs at room temperature is shown in Table 1. The Nafion 117 membrane showed the proton conductivity of  $1.78 \times 10^{-2}$  S/cm. Proton conductivity in semi-IPNs was increased with increasing AMPS content. The proton conductivity of AMPS 60 ( $1.85 \times 10^{-2}$  S/cm) was similar to that of Nafion 117. As shown in Table 1, the methanol permeability of Nafion 117 was  $2.32 \times 10^{-6}$  cm<sup>2</sup>/s. The methanol permeabilities of semi-IPNs changed almost linearly from  $6.55 \times 10^{-8}$  cm<sup>2</sup>/s for AMPS30 to

Polymer	Proton conductivity (S/cm)	MeOH permeability (cm <sup>2</sup> /s)
AMPS30	$8.05 \times 10^{-3}$	$6.55 \times 10^{-8}$
AMPS40	$9.45 \times 10^{-2}$	$1.61 \times 10^{-7}$
AMPS50	$1.20 \times 10^{-2}$	$5.61 \times 10^{-7}$
AMPS60	$1.82 \times 10^{-2}$	$1.12 \times 10^{-6}$
Nafion117	$1.78 \times 10^{-2}$	$2.32 \times 10^{-6}$

Table 1. Proton conductivities and methanol permeabilities of the native Nafion and the semi-IPNs.

$1.12 \times 10^{-6} \text{ cm}^2/\text{s}$  for AMPS60. The semi-IPNs suppressed the methanol permeabilities while maintaining high proton conductivity.

The state of water in the Nafion and the semi-IPNs was investigated with thermal analysis. The total water uptake of AMPS60 was similar to that of Nafion. However, the Nafion contained more freezable water than AMPS60. An important reason for the lower methanol permeability of the semi-IPNs is its lower fraction of freezable water compared to that of Nafion membrane

From the polarization test of DMFC based on AMPS60 and Nafion shown in Fig. 1, it is found that AMPS60 shows a higher performance than the native Nafion. It might be due to lower methanol permeability and similar proton conductivity of AMPS60 compared to Nafion.

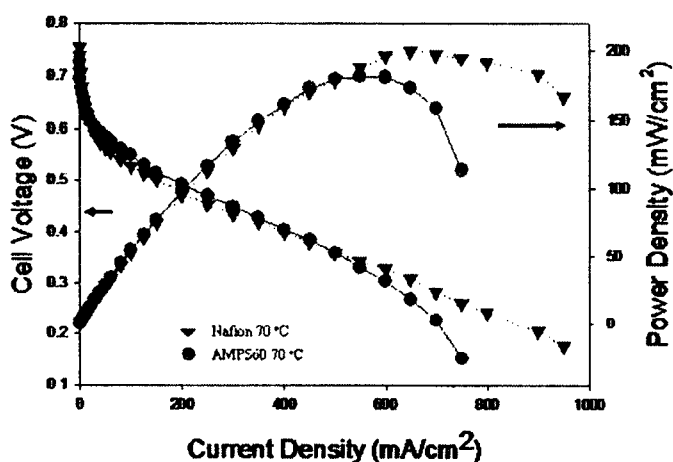


Figure 1. The cell performance of the native Nafion and AMPS60

### 3.2. Coated Nafion

To reduce the methanol crossover, we prepared the coated Nafion with polymer blends. As shown in Fig. 2, the methanol crossover of the coated Nafion was much suppressed, compared with that of the native Nafion.

In contrast, the proton conductivity was decreased from  $1.78 \times 10^{-2} \text{ S/cm}$  to  $8.92 \times 10^{-3} \text{ S/cm}$  because of the coating layers. However, the cell performance of the coated Nafion was enhanced by introduction of the blended coating layer. It is attributed to improved compatibility between electrode and membrane. The long-term stability was also found to be much enhanced.

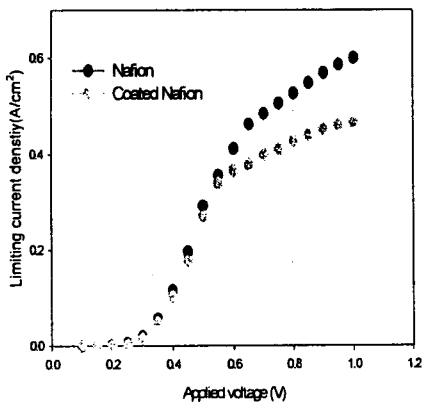


Figure 2. The methanol crossover of the Nafion 117 and the coated Nafion.

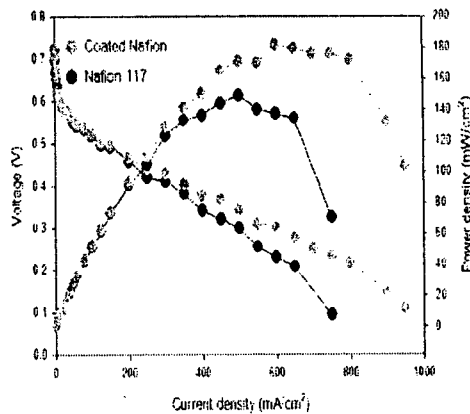


Figure 3. The cell performance of the native Nafion and the coated Nafion at 70°C

#### 4. Conclusion

Our modified Nafion could significantly reduce methanol crossover without sacrificing the proton conductivity. In addition, the enhanced compatibility between the membrane and electrode played a critical role in determining the cell performance.

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