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Characterization of Methanol Crossover through Nafion Membranes by Direct Cell Performance Measurement

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Abstract. Power densities produced by the permeation of methanol through membranes were directly measured by inserting the membrane in front of anode in a membrane-electrode-assembly of a direct methanol fuel cell (DMFC). The power density was closely related to the loss of power in the DMFC and was strongly affected by temperature. As the cell temperature was increased, the power density resulting from methanol crossover was increased. The increase in methanol crossover had be attributed to diffusion caused or affected by temperature. Methanol crossover a major effect on the performance of a DMFC at a relatively low temperature with 26% loss at 30°C. In order to reduce methanol crossover, a conventional Nafion membrane was modified by the incorporation of Pt or Pd. The reduction in methanol crossover was investigated in these modified membranes by our cell performance measurement. Pt and Pd particles incorporated in the Nafion membranes block methanol pathway and prevent methanol transport through the membranes, which was proved by combining with liquid chromatography.

Key words : Methanol crossover, Direct methanol fuel cell, Nafion membrane, Metal incorporation

1. Introduction

Solid polymer electrolytes (SPE) for use as proton conducting membranes have been used in direct methanol fuel cells (DMFCs)[1]. The protons produced from the anode pass through the electrolyte, a proton conducting membrane such as fluorinated sulfonic acid polymer electrolytes including Nafion membranes. They react with oxygen at the cathode to form water. In general, water transport in the polymer electrolyte membrane can occur in several ways, that is, diffusion by a gradient of water activity across the membrane, an electro-osmotic drag on proton migration when the cell is under current, and hydraulic permeation by differential pressure across the membrane[2,3]. On the other hand, similar to water transport, the permeability of methanol fuel from the anode to the cathode through the membrane is mainly controlled by diffusion as the result of a difference in the methanol gradient between both electrodes and dominated by the electro-osmotic drag of proton migration[4].

Accordingly, the permeability to methanol of perfluorosulfonic acid membranes cannot be avoided in DMFC[5]. Methanol crossover through SPE membranes reduces the efficiency of fuel utilization at the anode and causes a mixed potential as the result of methanol oxidation at the cathode. These lead to a degradation in performance by the poisoning effect of the Pt catalyst for oxygen reduction. Therefore, the crossover of methanol in DMFC has been studied in order to minimize the reduction of cell performance[6-8].

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Quantitative analyses of methanol crossover are typically performed by gas or liquid chromatography at the cathode in the DMFC[8,9], while other analyses have been rarely reported. In this paper, we report on a novel measurement of methanol crossover through the membrane in front of a membrane-electrode-assembly (MEA) of a DMFC. Besides, in order to reduce or prevent methanol crossover through the membrane, we modified the Nafion membrane by incorporating elemental Pt or Pd particles into the membrane called a *tested membranes*. So three kinds of tested membranes such as unmodified membrane, Pt- and Pd-modified membranes were studied by DMFC unit cell performance measurement.

2. Experimental

The MEA was a form of sandwich inserted into an unmodified Nafion 117 membrane between the anode and cathode of metal catalysts such as PtRu and Pt, respectively (Figure 1(a))[10-12]. The tested membrane was inserted into between carbon plate as a methanol flow path and stainless steal (s.s) gauze as a current collector in front of anode in the MEA as shown in Figure 1(b). Since the MEA was only linked with unit cell test station, connecting s.s gauze and carbon plate as current collector at cathode with electronic load, the tested membrane was electrically isolated in the whole circuit. Accordingly, the tested membrane plays a role as rather a crossover path for providing the MEA with the methanol as a fuel. The crossovered methanol leads to a fuel for methanol oxidation in the DMFC. That is, the increase of the methanol crossover through the tested membrane means

higher amount of a fuel for the MEA. Thus, the higher cell performance measured by the MEA would be responsible for higher rate or amount of methanol crossover through the tested membrane. The tested membranes for the methanol crossover were exchanged and inserted in every membrane measurement. Prior to inserting the tested membrane, MEA of DMFC was fully activated in order to achieve reproducibility in each measurement. In addition, all methanol crossover tests were performed using the same MEA with the same performance of the DMFC.

In order to investigate methanol crossover in a membrane, a conventional Nafion membrane was modified by incorporating Pt (Pt-Nafion) and Pd (Pd-Naifon) into Nafion membranes as described in the literature[8, 13-15]. The membranes, pretreated in 3 wt% H_2O_2, were dipped in metal salt solutions (H_2PtCl_6 or $PdCl_2$) stirring continuously during overnight. And then, metal salts were reduced in a solution containing a reducing agent ($NaBH_4$) for several hours. In this method, the Pt or Pd anions were penetrated into membrane and were then reduced to Pt or Pd nanoparticles in the pore of the membrane. Finally, the membranes were treated in 0.5 M H_2SO_4 for 1 hr in order to exchange Na^+ for H^+ and then rinsed in boiling deionized water for 1 hr.

The catalyst layer was pasted to teflonized carbon paper (Toray TGPH-090, 20% PTFE) using a 5 wt% Nafion ionomer solution (Aldrich Co.) as a binder. The anode (PtRu black, Johnson-Matthey Co.) and cathode (Pt black, Johnson-Matthey Co.) catalysts contained 15 and 7 wt% Nafion ionomer, respectively. PtRu and Pt black in catalyst layers loaded at a level of 5 mg/cm^2 were formed on the carbon paper. The MEA was fabricated by pressing anode/cathode layers and Nafion 117 membrane at 110°C and 800 psi for 3 min.

The MEA was installed in single cell within 2 cm^2 active area. The paths for fuel and oxidant flow were machined onto graphite plates. The polarization curve of MEA and current density *vs.* time by methanol crossover were measured using a potentiometer (WMPG-3000). A 2 M methanol solution was supplied to a Masterflex liquid micro-pump with 1 cc/min and dry O_2 was regulated by a flow meter with 500 cc/min.

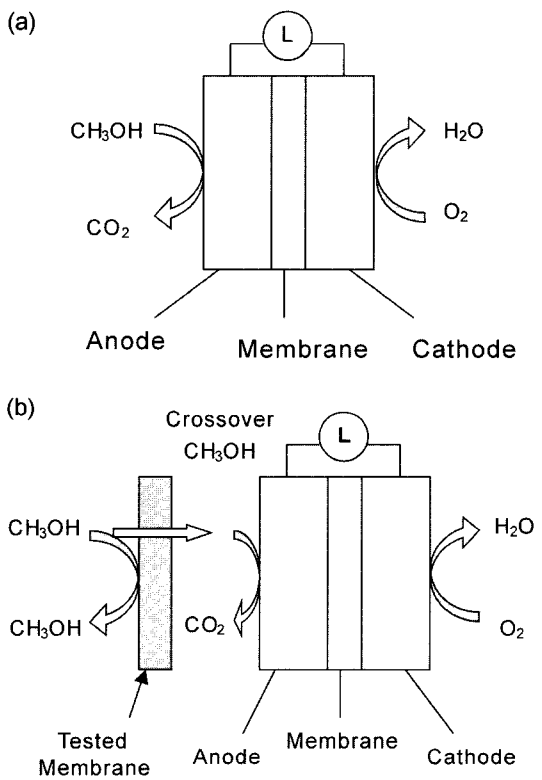

Fig. 1. (a) Schematic diagram of typical direct methanol fuel cell (DMFC) and (b) modified DMFC using methanol crossover provided through the tested membrane. The tested membrane is inserted and exchanged with the same MEA structure in every methanol crossover measurement. The "L" symbol in the (a) and (b) means electronic load system controlled by computer.

3. Results and Discussion

In order to investigate the effect of temperature on methanol crossover, polarization curves using unmodified Nafion membrane at several temperatures were obtained as shown in Figure 2(a). Figure 3(a) shows cell performance by methanol crossover through unmodified Nafion as a function of cell temperature, 30, 50, and 70°C. The maximum power densities at 30, 50, and 70°C were determined to be 14, 18, and 28 mW/cm^2, respectively. As the cell temperature was increased, methanol crossover was increased, as expected, indicating an increase in the loss of power density in the DMFC. In general, methanol permeability in a membrane is mainly controlled by diffusion caused by a difference in the methanol concentration gradient. The concentration gradient for the diffusion of methanol through the membrane is known to be proportional to tempearature[16]. Thus, it is evident that, since methanol crossover is increased with temperature, as shown in Figures 2(a) and 3(a), the power density produced by methanol crossover was increased with cell temperature. Figures 2(b) and 3(b) show a typical DMFC performance as a function of cell temperature. The maximum power densities at 30, 50, and 70°C were determined to be 53, 102, and 200 mW/cm^2, respectively. Compared with power densities by methanol crossover, shown in Figure 3(a) and a typical DMFC performance, shown in Figure 3(b), the effect of methanol crossover is strongly related to cell temperature.

Figure 4 shows plot of maximum power densities and loss of power (%) *vs.* cell temperature for methanol crossover and a typical DMFC. In Figure 4, the loss of power (%) is the ratio of maximum power densities measured at Figure 3(a) by methanol crossover and at the typical DMFC of Figure 3(b). The power density in both cases, as has already been seen in Figure 3, was increased with elevating temperature. In addition, in Figure 4, the loss of power density between methanol crossover and the typical DMFC was reduced with cell temperature, which was determined to be 26, 18 and 14% at 30, 50, and 70°C, respectively. This suggests that the performance of the DMFC at 70°C is relatively less affected by methanol crossover through the membrane than that at 30°C. Due to an improvement in the conductivity of Nafion

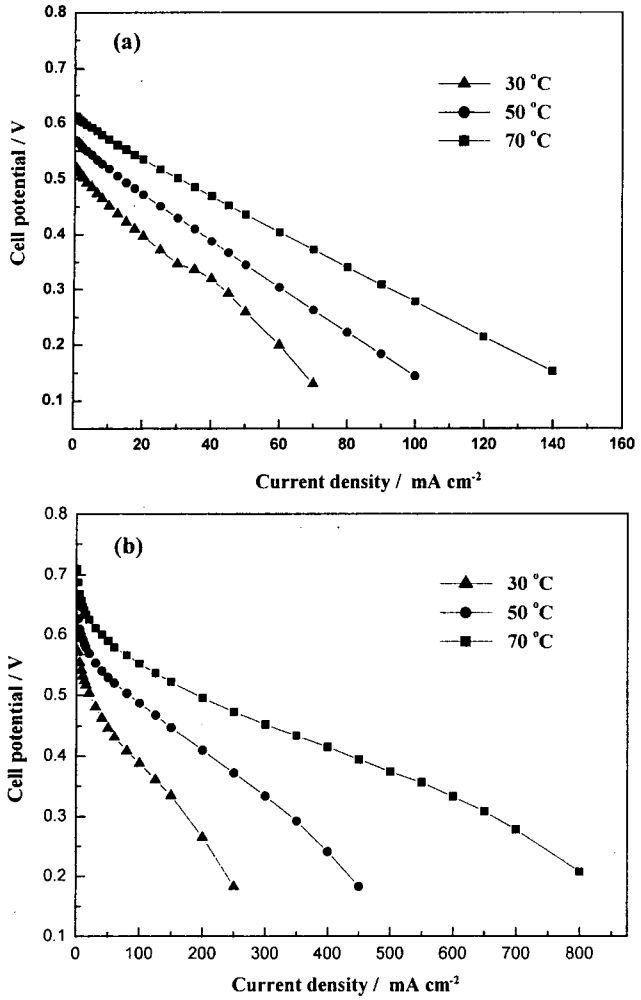

Fig. 2. Comparison of polarization curve as a function of cell temperature using an unmodified Nafion membrane (a) by methanol crossover and (b) in a typical DMFC.

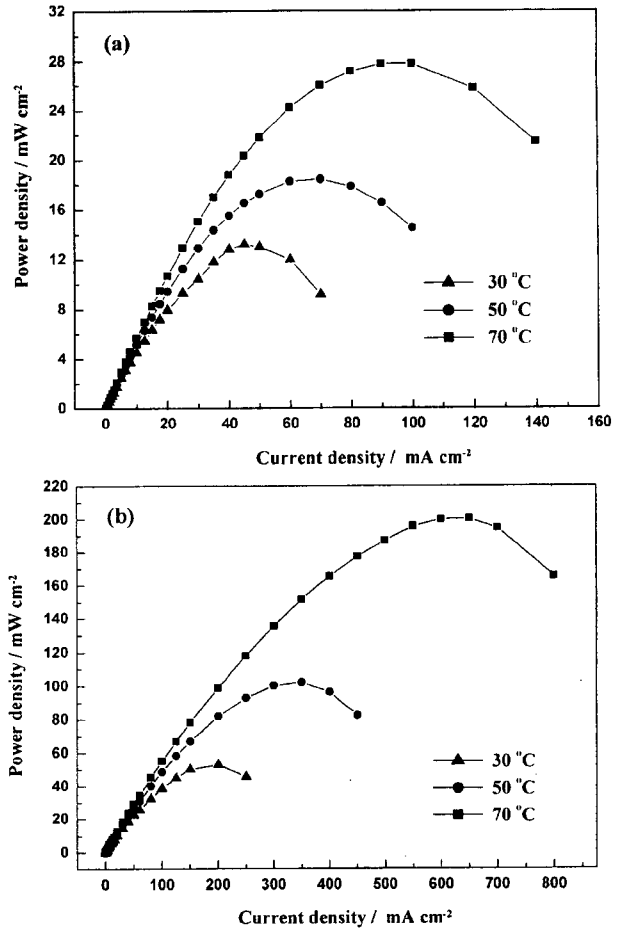

Fig. 3. Comparison of power density as a function of cell temperature using an unmodified Nafion membrane (a) by methanol crossover and (b) in a typical DMFC.

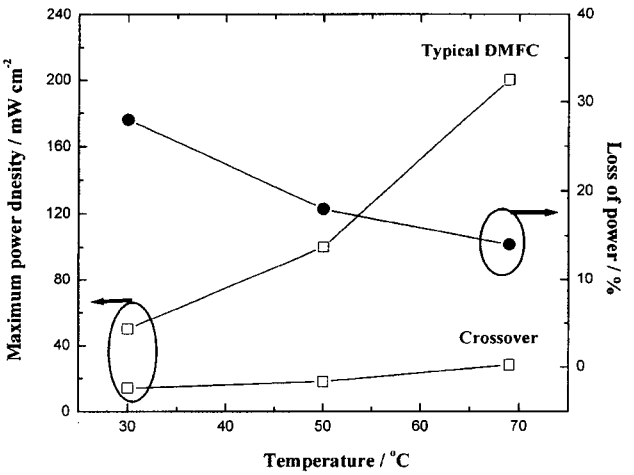

Fig. 4. Dependence of maximum power density on cell temperature by methanol crossover and in a typical DMFC and loss of power (%) calculated from the difference in maximum power densities between the two.

membranes and the catalytic activity of the anode/cathode at high temperature (>70°C), methanol crossover might be a minor effect on the performance of a DMFC. It is obvious that performance loss occurs at a relatively low temperature and cannot be ignored.

Accordingly, in order to investigate the effect of methanol crossover for a membrane at 30°C in more detail and the reduction in methanol crossover, the steady state current produced by methanol crossover *vs.* time was measured at a constant cell voltage, 0.5, 0.4 and 0.3 V using both unmodified and Pt and Pd modified Nafion membranes (Pt-Nafion and Pd-Nafion). Figure 5 shows a comparison of cell performance produced by the methanol permeated through the tested membranes at 30°C. As the cell voltage was decreased, the current density by the MEA, attached horizontally to the tested membrane, was increased. After an abrupt drop of current at 20 sec, all samples maintained a steady current at a constant cell voltage. However, the saturation current varied with the tested membrane. The current density using unmodified Nafion at 0.5, 0.4, and 0.3 V, respectively, was the highest, compared with the Pt and Pd modified Nafions. This suggests that Pt- and Pd-Nafion reduced methanol crossover by blocking methanol flow into the membrane (see below).

Figure 6 shows a comparison of steady state current at 30°C under constant cell voltage obtained using three kind of tested membranes. The unmodified Nafion in Figure 6(a) required a slightly longer time, 10-20 s, to approach steady state conditions and had a higher initial current and steady state current than Pd-Nafion and Pt-Nafion. Figure 6(b) shows that after a rapid drop of current for 10-15 s, the current of Pd-Nafion approaches a steady state. In Figure 6(c) after a decrease in current within 10 s, the current of Pt-Nafion approaches a steady state. The time required to approach a steady state current (t_s), depending upon tested membranes, is the duration for the saturation of methanol crossover under any potential. Accordingly, the membrane with the short t_s can prevent crossover and continue a steady state within a short time effectively. The Pd- and Pt-Nafion with the shorter t_s than unmodified Nafion could be better membrane for reducing methanol crossover.

Figure 7 shows the power density (loss of power) at the steady state for various tested membranes. Pd- and Pt-Nafion were superior to the unmodified Nafion in power density over the entire voltage range and even at 0.3 V. The cell performance and power density after inserting the tested membrane were produced by methanol crossover through the tested membrane. That is, a higher power density results

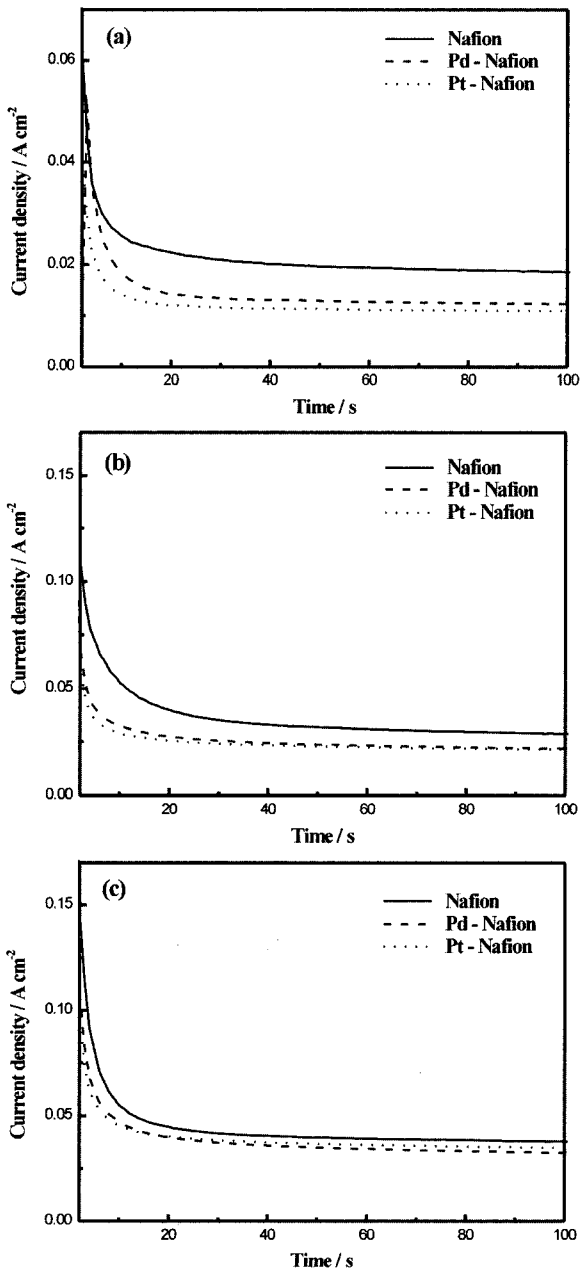

Fig. 5. Current density *vs.* time plot as a function of cell voltage of (a) 0.5 V, (b) 0.4 V, and (c) 0.3 V for 100 s at 30°C for methanol crossover through unmodified Nafion membrane (Nafion), Pd- and Pt- modified Nafion membranes (Pd-Nafion and Pt-Nafion).

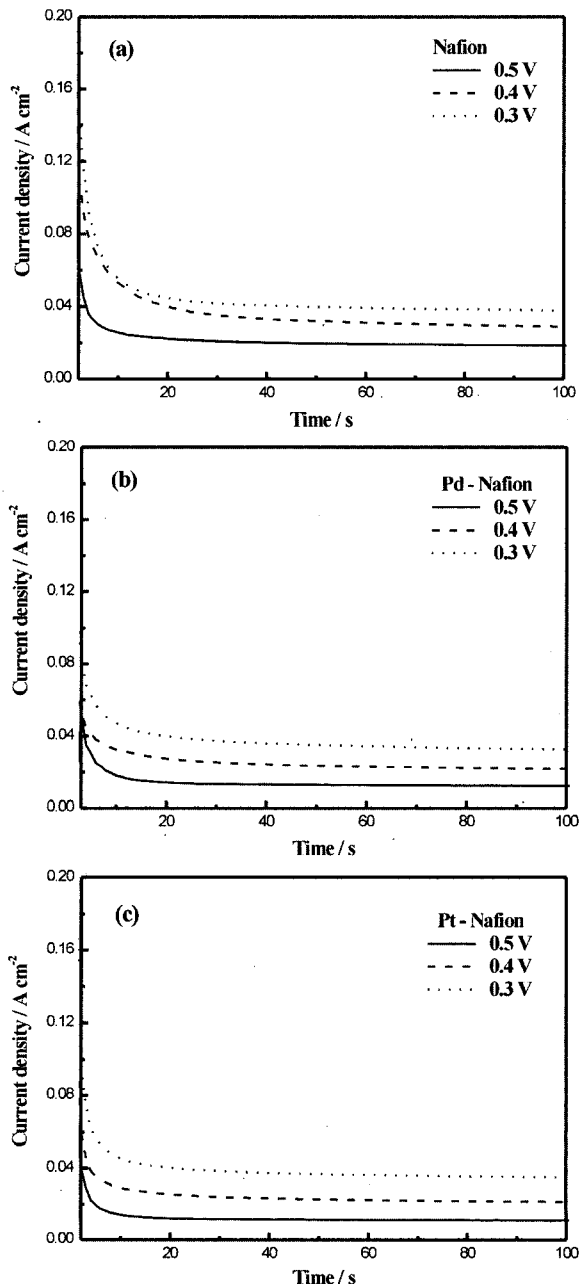

Fig. 6. Current density *vs.* time plot at various cell voltages for 100 s at 30°C for (a) Nafion, (b) Pd-Nafion, and (c) Pt-Nafion.

from more methanol crossover through the tested membrane. The polarization curve for the unmodified Nafion membrane showed a higher open circuit voltage (OCV) (not shown here) and higher current density with voltage, compared with the modified membranes. However, the membranes modified with Pt and Pd had a lower OCV and current density, indicating less methanol crossover than for the unmodified Nafion membrane. In Figure 7, the maximum power density of unmodified Nafion was determined to be 14 mW/cm^2, higher than the Pd and Pt modified membranes; Pd-Nafion (12 mW/cm^2) and Pt-Nafion (10 mW/cm^2) at 30°C. In Figure 3(b), the performance of a conventional DMFC supplied with a 2 M methanol solution at the anode and dry O_2 at the cathode was 53 mW/cm^2 at 30°C when 5 mg/cm^2 of PtRu and Pt black were used. The difference in power density loss between the unmodified and modified Nafion were approximately 40, 25 and 14% at 0.5, 0.4 and 0.3 V, respectively.

A membrane modified by the incorporation of Pt has been reported in the literature[8,13,17]. The Pt in the membrane is known to be able to oxidize methanol permeating into the membrane, thus reducing the methanol crossover effectively, shown by the equation below:

$$CH_3OH + 3/2O_2 \rightarrow CO_2 + 2H_2O$$

However, our tested Pt-Nafion membrane has little possibility to get the crossover O_2 from the far away cathode. So the incorporation of Pt in the Nafion membrane may block methanol pathway and prevent methanol transport through the membrane. The Pd modified membrane showed a reduced methanol crossover as well. It has been known that the selectivity of Pd to protons in the Pd-Nafion prevents the methanol from being transmitted, selectively passing protons in the membrane[18-20]. However, the tested Pd-Nafion membrane has low probability to produce proton and can hardly be explained by Pd selectivity. So the incorporation of Pd in the Nafion membrane would also block methanol pathway like Pt-Nafion membrane. This can be reasonable since the power densities produced by methanol crossover through Pt- and Pd-membranes represent similar values in Figure 7. Further, as shown in Table 1, quantitative analyses of methanol crossover were performed by liquid chromatography, which could mainly measure the amount of methanol permeating through the membrane per time. The Pt and Pd modified membranes showed the lower permeabilities of methanol, 5.0×10^{-7}~3.8×10^{-8} cm^2/sec, than unmodified membrane, 2.5×10^{-6} cm^2/sec, in relatively good agreement with that tested by our cell performance measurement. This suggests that our methanol crossover measurement is (and can be) comparable and reliable in characterizing methanol crossover properties in the modified or any new membranes.

4. Conclusions

The methanol crossover through polymer electrolyte membranes was directly measured by putting the membrane in front of anode in DMFC. The measured power density was linked to the loss of power in the DMFC. In addition, power loss was strongly affected by temperature of the DMFC. As the cell temperature was increased, the current by methanol crossover was increased. The reduction of cell performance by methanol crossover was serious at relatively lower temperature. To further confirm our measurement, we modified a conventional Nafion membrane by incorporating Pt and Pd nanoparticles. As a result, a Nafion membrane modified with Pd or Pt was superior to the unmodified Nafion membrane in our methanol crossover measurements. We confirmed that the Pt and Pd-Nafion reduced methanol crossover by blocking methanol in the membranes. Consequently, our crossover measurement represented an useful analytical method for characterizing the properties of methanol or other chemical crossover of membranes. More quantitative and comprehensive studies on the effect of Pt and Pd incorporation are necessary and are currently underway.

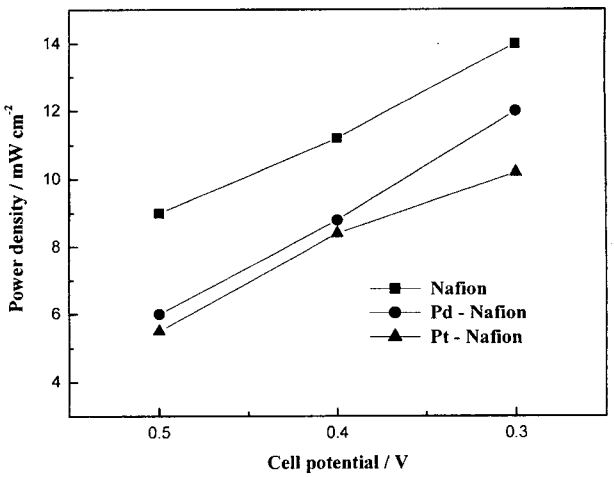

Fig. 7. Power density *vs.* cell potential plots using unmodified Nafion membrane, Pd- and Pt- modified Nafion membranes.

Table 1. Comparison of methanol permeability passing through the membranes measured by liquid chromatography.

	Nafion	Pt- and Pd-Nafion
Methanol permeability (cm^2 / sec)	2.5×10^{-6}	5.0×10^{-7} ~ 3.8×10^{-8}

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