



Reaction analysis of a direct methanol fuel cell employing a porous carbon plate operated at high methanol concentrations

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ARTICLE INFO

Article history:

Received 7 July 2008

Received in revised form

22 September 2008

Accepted 26 September 2008

Available online 17 October 2008

Keywords:

Passive DMFC

Reaction product

Porous carbon plate

Methanol crossover (MCO)

ABSTRACT

It is known that a small amount of intermediate products, i.e., formaldehyde, formic acid and so on, is exhausted from a direct methanol fuel cell (DMFC). The production rates of such intermediates are affected by the methanol and water concentrations at the anode, and also the distribution of these products is variable. We investigated the production of the intermediates from a passive DMFC containing a porous carbon plate (PCP), which allows the use of methanol at high concentrations up to 100% due to the high resistivity to the methanol transport through the PCP. The production rates of each intermediate and their distribution were measured not only for a DMFC employing various PCPs with different transportation resistivities, but also for a DMFC without PCP. The results were analyzed in terms of the rate of methanol crossover (MCO) and water flux through the membrane. The detected intermediates were formaldehyde, formic acid, and methylformate, in accordance with previous reports. The production rates of the intermediates were strongly dependent on the flux of the MCO rather than the apparent methanol concentration. When the DMFC was operated under the rate limiting conditions of the methanol transport by the PCP, the production rates of the intermediates were low. However, when it was operated outside of the rate limiting conditions, the production rate increased with the increasing rate of methanol crossover.

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1. Introduction

Direct methanol fuel cells (DMFCs) have recently attracted much interest as a promising candidate of mobile and portable power-units having a compact volume and a high energy density [1–5]. However, based on the current status of technology, the energy density of the DMFC is still far from what is expected from a theoretical consideration due to the methanol crossover (MCO) and sluggish electrode-reactions. As a result of the MCO, the low concentrations of methanol from 1 to 3 M [6,7] under active conditions and about 5 M [8–10] under passive conditions have generally been used in the DMFC operation. Only a few papers have reported a technique for the utilization of a high concentration of methanol in DMFCs [11–14].

In liquid feed DMFCs operated at low methanol concentrations, it is known that CO₂ is the main product at the anode [15], and a small amount of intermediates, such as formaldehyde (HCHO), methylformate (HCOOCH₃), formic acid (HCOOH) and CO, are also formed [16,17]. In the gas feed DMFC with a PBI membrane operated at a low water/methanol mole ratio and high temperatures like 150–190 °C, methylal (CH₂(OCH₃)₂) was found as the main prod-

uct [18]. The reaction products of the electrocatalytic oxidation of methanol have also been investigated in an aqueous electrolyte [19,20] and in a gas in contact with the electrolyte membrane [21–24]. The product distribution and the production rate were affected by the water/methanol mole ratio, temperature, current density and catalyst morphology [24]. When the water/methanol ratio is low, methylformate and methylal in the presence of an acid catalyst [18,24,25] were preferentially formed, and the percentage of these products was sometimes greater than 60% [24]. However, when excess water exists, these become negligible and formaldehyde and formic acid are the predominant products besides CO₂.

Recently, we have demonstrated that a DMFC with a novel electrode structure employing a porous carbon plate (PCP) as the anode could efficiently be operated using methanol at very high concentrations up to 100% [15]. The porous plate significantly controlled the methanol crossover through the MEA [11–13]. In this type of DMFC, liquid methanol is vaporized at the PCP surface and then supplied to the anode surface, and water is supplied from the cathode through the membrane [12,13]. Hence, the actual atmosphere of the anode must differ from that without the PCP. When using a high concentration of methanol, the water/methanol mole ratio at the anode would be low and then a relatively high amount of the intermediates may be produced. Since the production of intermediates reduces the energy conversion efficiency of the DMFC and also some of the products are harmful to human health [26], it is

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Table 1
Character of PCPs used in this experiment.

	Thickness [mm]	Average pore radius [μm]	Porosity [%]
PCPY1	1.0	1.88	11.6
PCPY2	2.0	17.3	50.1

important to evaluate the reaction products and the behavior of the novel DMFC.

In this study, we quantified the intermediate products from the DMFC with the PCP operated at high methanol concentrations including 100% methanol under atmospheric conditions. The results were compared to that of a conventional DMFC without PCP operated at low methanol concentrations. The production rate and distribution of the intermediates were discussed on the basis of the rate of the measured methanol crossover.

2. Experimental

2.1. MEA preparation

The MEA, in which Pt and Pt–Ru black were used as the catalyst for the cathode and anode, respectively, was prepared and fabricated in the same manner as described in our previous reports [12,13]. The catalyst loading was $10\text{--}12\text{ mg cm}^{-2}$ in each electrode. Nafion 112 was used as the membrane electrolyte.

2.2. Single cell DMFC with and without PCP

Passive DMFCs with and without a porous carbon plate (PCP), similar to our previous DMFC [12,13], were used in this experiment. Two porous carbon plates, PCPY1 and PCPY2, supplied from Mitsubishi Pencil Co., Ltd., with 1.0 and 2.0 mm thicknesses were used in this study. The pore structure of the PCP analyzed by a mercury porosimeter (Pascal 140+440, Thermo Finnigan, Inc.) is shown in Table 1. The PCPY1 had a higher resistivity for controlling the MCO than that of PCPY2 as will be described later. The PCP was placed at the anode and the single cell DMFC assembly with and without PCP has been described in our previous reports [12,13]. The conventional DMFC without PCP was also used in this experiment as a reference.

2.3. DMFC operation and the analysis of the reaction products

The experimental setup for the evaluation of the reaction products during the DMFC operation is shown in Fig. 1. The DMFC with and without PCP was operated by injecting a methanol solution into

the reservoir and by feeding oxygen to the cathode at 35 ml min^{-1} under ambient conditions. Power generation was conducted at a constant cell voltage for several hours. During the operation, the gas produced at the anode was collected in a gas bag that was connected to the methanol reservoir. The gas exhausted from the cathode was also collected using another gas bag that was connected through the two cold traps and a combustion column as shown in the figure. The combustion column was prepared in order to convert the gaseous methanol and other intermediates to CO_2 with the help of a PtRu catalyst dispersed on glass wool. The electrochemical performance of the cell during the operation was measured using an HZ3000 electrochemical measurement system (Hokuto Co., Ltd.) The cell temperature was measured at the surface of the cathode by a thermocouple.

After 2 h of power generation at a constant cell voltage, the amount and the composition of the solution in the reservoir as well as the cold traps, and the gaseous products collected in the bags were analyzed. When the PCP was used, the measurements were conducted after a 1 h pre-operation followed by replacement of the remaining solution in the reservoir with a fresh solution to ensure a steady state mass transport through the PCP. For the quantitative analysis of the products, gas chromatography with columns of Porapack-T/PEG6000 and the UV technique (Nash method [27] for formaldehyde) were used. The methanol crossover through the MEA was directly measured by totaling up the amounts of CO_2 and other C1 compounds collected by the traps and the gas bag at the cathode during the operation, and then, it was compared to that calculated from the changes in weight and composition of the solution remaining in the reservoir [12]. Water crossover was also obtained in a manner similar to that already reported [12].

3. Results and discussion

3.1. Current density performance during operation

The single cell DMFC was operated at different methanol concentrations depending on the PCP type and either using PCP or not. Fig. 2 shows the current density versus time for each DMFC at the different methanol concentrations, i.e., in the range from 16 M up to 100% methanol for the DMFC with PCPY1, in the range between 6 and 16 M for the DMFC with PCPY2, and in the range below 4 M for the DMFC without PCP. The relatively stable current densities with time, i.e., for all three concentrations for PCPY1 and 6 M, 9 M for PCPY2, resulted from the rate controlling step due to the methanol transport from the reservoir to the anode through the PCP [12,13]. The current density under these conditions was determined by the resistivity of the PCP for the methanol transport and the methanol

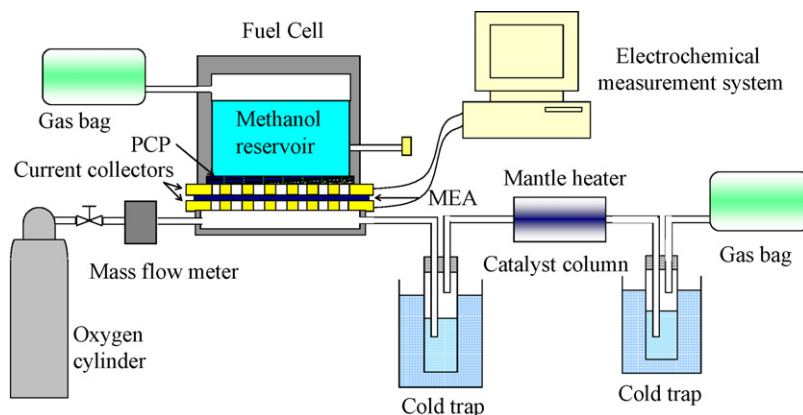


Fig. 1. Experimental setup for measuring the amount of reaction products during cell operation.

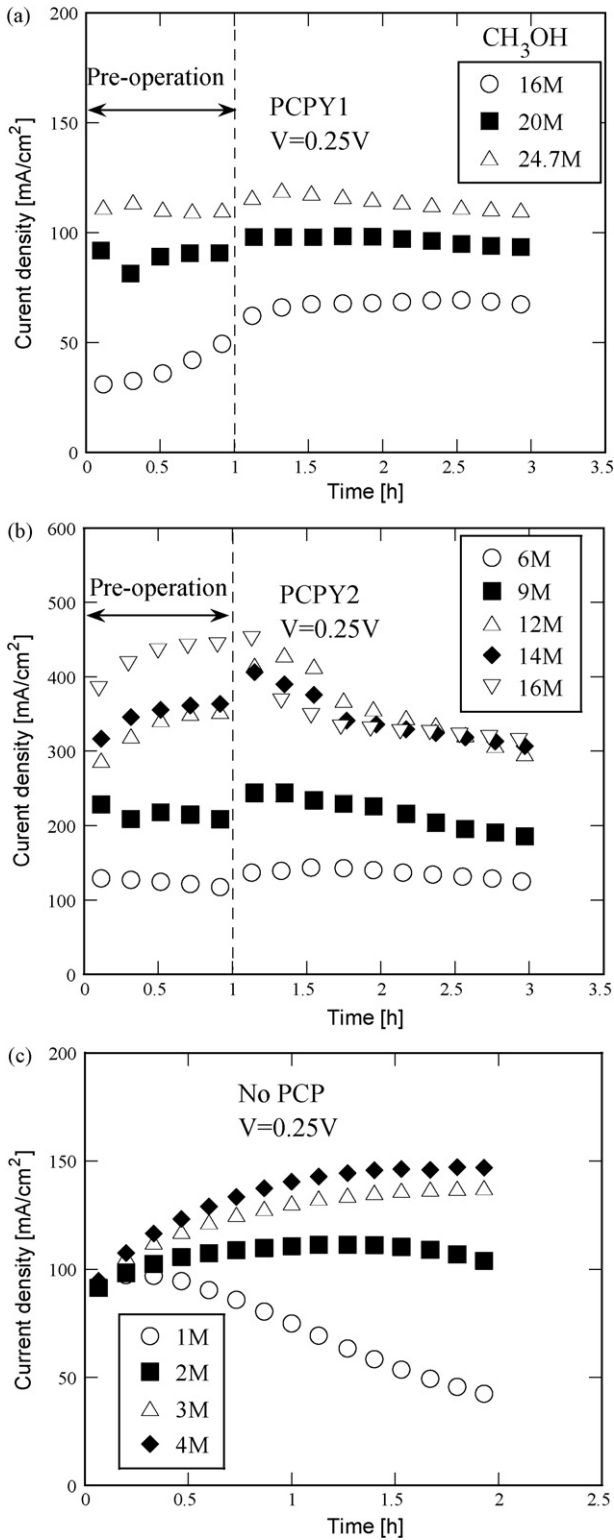


Fig. 2. Current density profile during cell operation at 0.25 V cell voltage (a) with PCPY1, (b) with PCPY2, and (c) without PCP.

concentration used for a certain cell structure. Because of the much higher resistivity of the PCP, the current densities for PCPY1 were limited by the resistivity and much lower than that of PCPY2.

Fig. 3 shows the current density measured after a 2 h operation at the different methanol concentrations. For the DMFC with PCPY1, a linear relationship was observed between the current density and

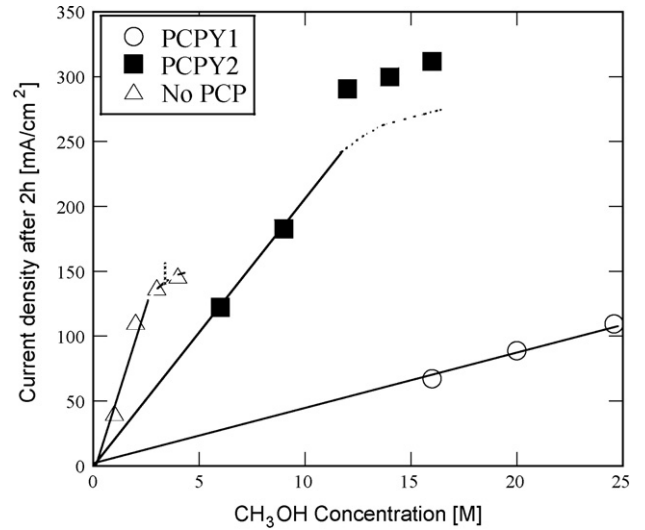


Fig. 3. Effect of methanol concentration on steady current density for MEA with and without PCP.

the concentration in the range up to 100% methanol. This linear dependency expresses the rate limiting rather due to the methanol transport, and the slope of the straight line corresponds to the reciprocal of the resistivity for the methanol transport through the PCP. It was shown that the resistivity for PCPY1 was low and the current density was controlled by the methanol transport even for the 100% methanol. This is the reason why the current densities for PCPY1 were relatively small. Similarly, the current densities below 12 M were also methanol transport rate limiting for the DMFC with PCPY2. The non-linear dependency above 12 M suggests a change in the rate limiting process from the methanol transport to another. The relatively high current densities at over 12 M, compared to that expected from the linear trend below 12 M were due to the much higher temperatures than that for the cases below 12 M caused by the large methanol crossover as will be shown in the next section. The methanol permeated through the membrane easily oxidized by oxygen in the air at the cathode and produces heat. When the methanol crossover increased by the change in the rate limiting process from the methanol transport to another, heat produced by the methanol oxidation increased and then the temperature increased. In this experiment, an increase in the temperature of almost 10 K was observed in the range of 9 and 12 M. The DMFC without PCP showed a linear dependence below 3 M. The relatively low peak current density in this case would be caused by flooding at the cathode due to the large crossovers of water and methanol through the membrane without PCP.

3.2. Methanol and water fluxes

It was confirmed that the methanol crossover obtained from the CO₂ and other C1 compounds collected at the cathode exit almost agreed with that calculated from the lost methanol at the anode during operation. The error in the molecular balance for each C, H, O in the experiments was within ±3%, suggesting that there was no major product other than the compounds, shown as will be later, detected in this experiment.

Fig. 4 shows the relationship between the methanol concentration and the flux of the measured MCO. As shown in this figure, the flux of MCO increased with the increasing methanol concentration. However, the MCO profile was different from each other depending on the PCP used. The MCO at 4 M for the DMFC without PCP was almost equivalent to that at 14 M for the DMFC with

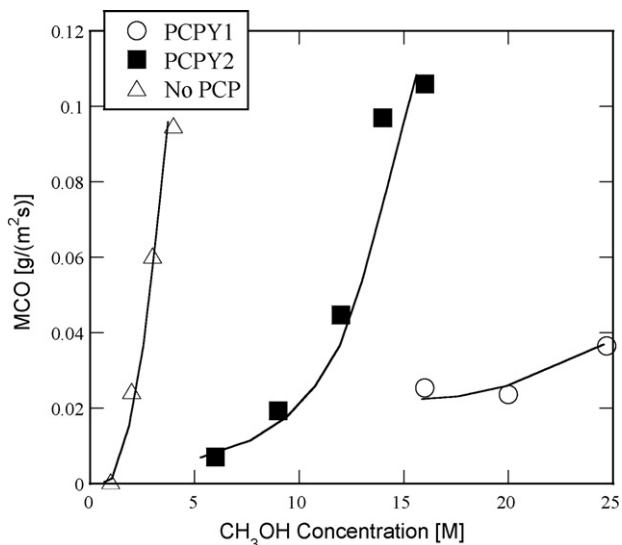


Fig. 4. Effect of methanol concentration on MCO for MEA with PCPY1, Y2 and without PCP.

PCPY2 having a value of $0.10 \text{ g m}^{-2} \text{ s}^{-1}$. By comparing the methanol concentration that corresponds to the same MCO level, it is clearly understood that the resistivity for controlling the MCO was high in the order of PCPY1, PCPY2, and without PCP. It was confirmed that the DMFC with PCPY1 controlled the MCO to a low level even for neat methanol, 24 M, as discussed in the previous section. When PCP is used, a CO_2 gas layer is formed between the PCP and the anode and it requires the methanol transporting as a vapor in it, and the vaporization flux would be controlled by the properties of the pore structure. Hence, it allows the DMFC operation at a high methanol concentration possible with a high efficiency and a high energy density [12].

By comparing the results of Figs. 3 and 4, the mass transport rate-limit for the power generation occurred in the range where the MCO was less than $0.04 \text{ g m}^{-2} \text{ s}^{-1}$ in this experiment.

The water flux during the DMFC operation was plotted in Fig. 5. For the DMFC without PCP, the water flux was positive, i.e., the direction of the water transport was from the anode to cathode through the membrane. In this case, the anode was in contact with

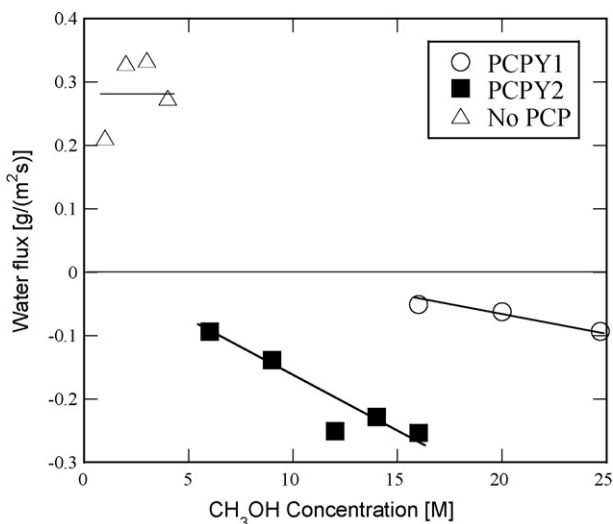


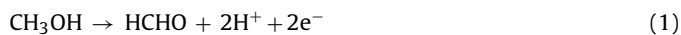
Fig. 5. Effect of methanol concentration on the water flux for MEA with PCPY1, Y2 and without PCP.

the liquid methanol solution at the low methanol concentrations, and the Nafion membrane absorbed sufficient water. On the other hand, the results of the DMFC with PCP showed negative water fluxes suggesting that the water back diffusion occurred from the cathode to the anode through the membrane [12]. The back diffusion of water was caused by the electrode structure with PCP where the CO_2 gas layer is formed between the anode and PCP. The concentration of water at the CO_2 gas layer should be lower than that at the cathode where water is produced by the oxidation of protons and the permeated methanol. The water flux in this case becomes negative, and negatively increased with the increasing methanol concentration. The magnitude of the negative water flux must be related to the magnitudes of both the current density and the methanol crossover, because these affect the rate of water formation at the cathode. It can then be understood that the water flux for the DMFC with PCPY2 was more negative than that of PCPY1.

3.3. Intermediate products and formation rates

As the anode reaction products, except for CO_2 , formaldehyde, formic acid and methylformate were detected similar to that reported by a previous study [16]. They were detected only from the solution in the reservoir and no products other than CO_2 were detected from the gas bag connected to the reservoir. The production rates in each DMFC measured at different methanol concentrations are shown in Fig. 6. The production rates and the distributions were different from each other among the DMFCs with and without PCP. However, in all cases, the production rate of each substance increased with the increasing methanol concentration. The methanol concentration in the reservoir is the apparent one and not the actual one for the anode surface, because there was a high resistance for the methanol transport through the PCP and also the methanol was diluted with CO_2 in the CO_2 gas layer as already mentioned. The apparent methanol concentration may then not be appropriate as a representative factor affecting the production rate of the intermediates. However, we did not have any technique to evaluate the water and methanol in the gas layer in this study. Hence, we used the flux of the methanol crossover as a factor for the production rate instead of the apparent methanol concentration. Figs. 7 and 8 show the relationship between the MCO flux and the production rate of the intermediates for the DMFC with and without PCP, respectively. When we see these figures, we can find some common features in these figures. At first, the production rate of formaldehyde (HCHO) was not strongly dependent on the MCO and almost similar to each other, i.e., between 10 and $50 \mu\text{g m}^{-2} \text{ s}^{-1}$ in both figures. Second, the production rate of formic acid (HCOOH) was negligibly small when the MCO was not greater than $0.08 \text{ g m}^{-2} \text{ s}^{-1}$. And third, the production rate of methylformate (HCOOCH_3) significantly increased when the MCO was over $0.04 \text{ g m}^{-2} \text{ s}^{-1}$, noting that the production rate of methylformate, that was plotted on the right vertical-axis in Fig. 7, was several times higher than that without PCP in Fig. 8. The difference in the formation rate of methylformate between with and without PCP would come from the difference in the concentration of water at the anode based on the difference in the water flux as shown in Fig. 5. The water concentration at the anode without PCP would be much greater, and the methanol/water ratio would be lower, then the production rate of methylformate would be lower than that with PCP.

For the methanol oxidation steps including formaldehyde, formic acid and methylformate as the intermediates, the following mechanism was considered on the basis of previous studies [18,21].



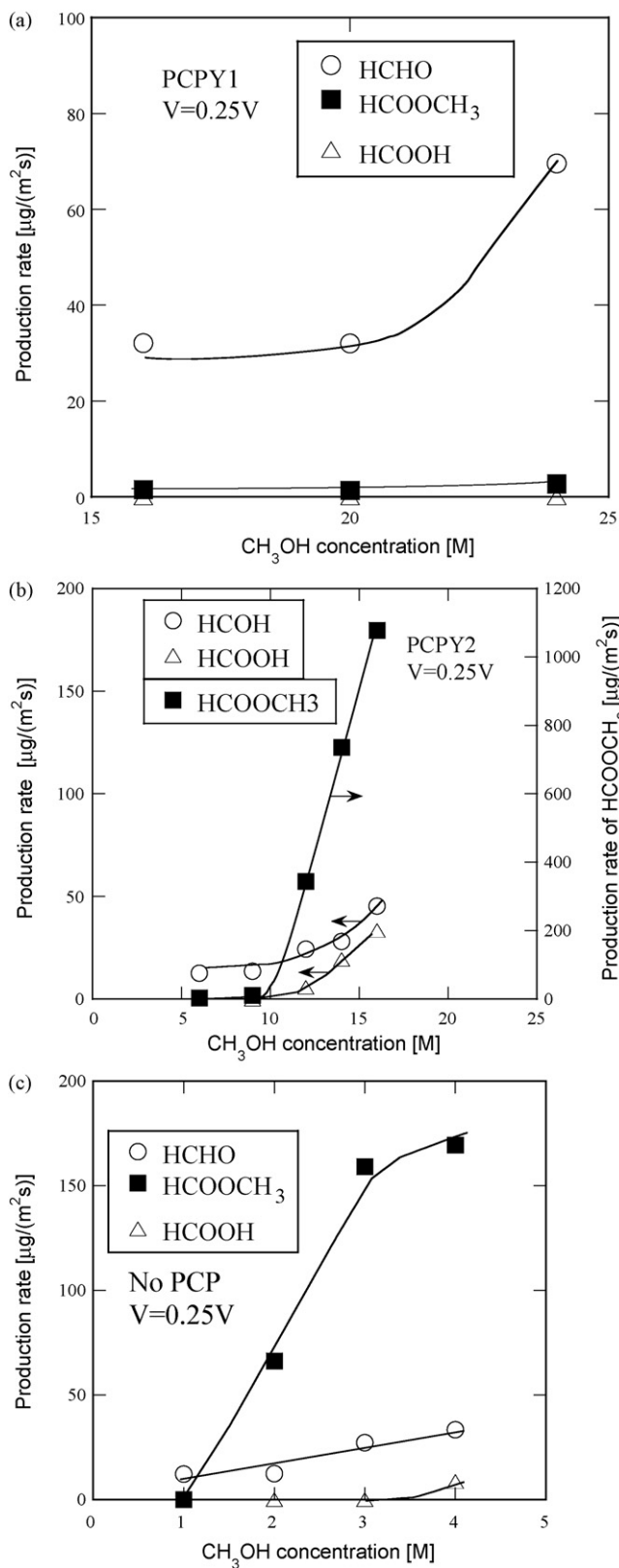


Fig. 6. Effect of methanol concentration on the production rate of the intermediate products (a) with PCPY1, (b) with PCPY2, and (c) without PCPY.

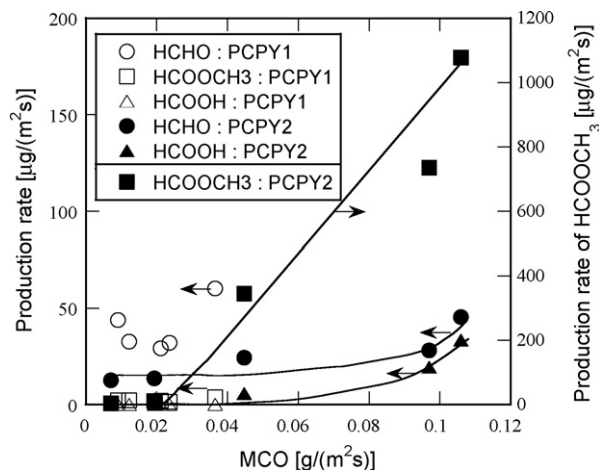
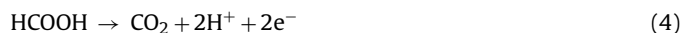
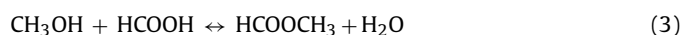
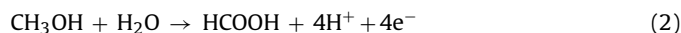
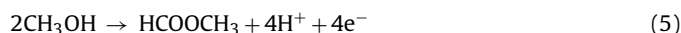


Fig. 7. The production rate of the intermediate products for the DMFC with PCP operated at high methanol concentrations.



When the anode reaction of a DMFC was rate limited by the methanol transport from the reservoir to the anode, i.e., the methanol concentration was as low as the linear dependence indicates versus the current density, the anode surface is deficient in methanol. In such a case, the productions of the intermediates were low. The formaldehyde based on Eq. (1) was predominant under this condition as shown in Fig. 7. When the methanol concentration was high enough to cause an MCO greater than $0.04 \text{ g m}^{-2} \text{ s}^{-1}$, the anode would be deficient in water and methylformate was predominantly produced from the methanol as follows:



The difference in the production rate of methylformate between the DMFC with and without PCP as shown in Figs. 7 and 8 would be related to the concentration of water at the anode. The concentration of water at the anode without PCP should be higher than that at the anode with PCP. In the case of the DMFC with PCP, the actual composition of the atmosphere at the anode is directly related to

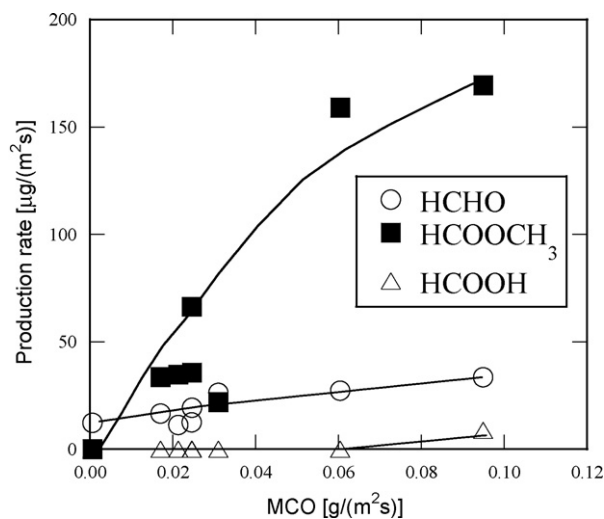


Fig. 8. The production rate of the intermediate products for the conventional DMFC without PCP operated at low methanol concentrations below 4 mol l^{-1} .

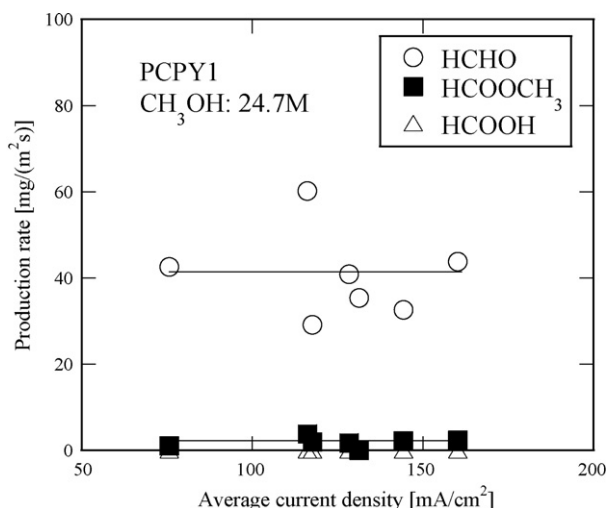


Fig. 9. The production rate of the intermediate products for the DMFC at different average current densities using MEA with PCPY1.

the production rate of the intermediates [18]. However, it was difficult to analyze the gas at the anode in this study because we did not have the proper setup. We are now going to evaluate the gas composition at the anode using the mass spectrometry technique which will be reported in the future.

3.4. Effect of current density

Figs. 9 and 10 show the effect of the average current density on the production rate of the intermediate products for the DMFCs with PCPY1 and without PCPY, respectively. The effect of the current density on it was low or not clear. This was not in accordance with the reports of studies using flowing methanol solutions [16] and vapors [24] that showed the production rate of each component increased with the increasing current density. The disagreement between these studies and the present study would be due to the difference in the type of methanol supply, i.e., actively flowing and not flowing. When the methanol solution was not flowing as in this experiment, the produced intermediates at the anode surface would be easily utilized in the following reaction as a reactant at

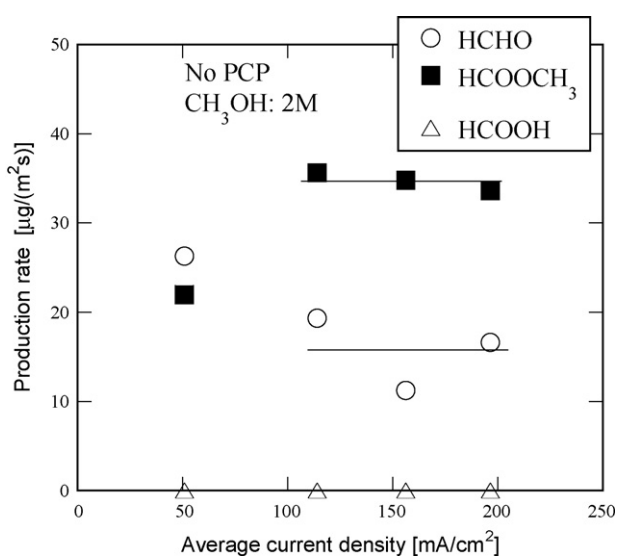


Fig. 10. The production rate of the intermediate products for the DMFC at different average current densities using MEA without PCPY.

the anode, resulting in a constant production rate irrespective of the current density by a balance between the rate of production and that of consumption.

3.5. Energy loss due to the intermediate products

The selectivity of the total intermediate products from the converted methanol was calculated to be at most 1.0% even when the production rate of the methylformate for the DMFC with PCPY was over $1000 \mu\text{g m}^{-2} \text{s}^{-1}$ in this experiment. Hence, we can say that the energy loss by the intermediate products for the DMFC with PCPY was negligibly small. We do not need to pay attention to the energy loss by the production of the intermediates as long as the MCO is controlled within a certain low level, like $0.1 \text{ g m}^{-2} \text{ s}^{-1}$, as shown in this experiment, because the production rate of the intermediates, especially for methylformate, could be controlled by controlling the MCO.

4. Conclusion

The reaction products, apart from CO_2 , at the anode of the DMFC that employs PCP and operated with a high methanol concentration was analyzed. Two PCPs with different resistivities for methanol transport through it was used and compared to each other and also with that from the DMFC without PCP. The detected products were formaldehyde, methylformate and a very small amount of formic acid under some conditions. The production rates were low and negligible based on the calculation of the energy efficiency. The production rate could be summarized by using the flux of the methanol crossover for the DMFC with and without PCP. The production rate of methylformate was significantly affected by the MCO and it significantly increased when the MCO was over $0.04 \text{ g m}^{-2} \text{ s}^{-1}$. The production rates of formaldehyde and formic acid weakly increased with the increasing rate of MCO, while the production rate of the latter was very low. It is suggested that the production rate of the intermediates was directly affected by the activities of the methanol and water at the surface.

Acknowledgements

A part of this study was supported by KAKENHI (1936057) and the Nippon Sheet Glass Foundation for Materials Science and Engineering.

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