



Short communication

Performance degradation of a direct methanol fuel cell by an eluted plasticizer

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ABSTRACT

The cause of the power degradation that occurred in a direct methanol fuel cell (DMFC) with a plastic tube for the connection was investigated. The DMFC had a unique electrode structure with a porous carbon plate in order to control the methanol crossover, and then operated with a 99.8 wt% methanol solution. A certain amount of di-(2-ethylhexyl) phthalate (DEHP), a plasticizer, was detected in the circulated methanol solution. The degradation in performance by DEHP was confirmed by comparing the performances with and without DEHP addition in the methanol. It was postulated that the methanol transport through the PCP was significantly affected by the addition of DEHP.

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1. Introduction

Direct methanol fuel cells (DMFCs) have been receiving much attention as an alternative portable power source because of the attractive properties of methanol, i.e., its high theoretical energy density, the easy handling of a liquid fuel, and a compact system. However, the power densities and the energy conversion efficiencies of the current DMFCs were still far from those of theoretical mainly due to methanol crossover (MCO) and slow electrochemical reaction kinetics. One of the authors has proposed a unique electrode structure that employs a porous carbon plate (PCP) for the anode [1] in order to control the methanol crossover. By using this electrode structure, the DMFC could use high concentration methanol solutions including 100% methanol [1]. In the novel electrode structure, liquid methanol was vaporized on the surface of the PCP and then it was supplied to the anode in a CO₂ gas layer formed between the anode surface and PCP [1–3]. At that time, water required for the anode reaction was supplied from the cathode to the anode through the membrane by diffusion [1].

Although previous studies of the DMFC with the PCP have been mainly conducted for the passive type system [1–5], the electrode structure has been extended to an active type DMFC in order to increase the power output. We then fabricated a single cell (30 cm²) DMFC with the novel electrode structure. During the operations

of the active DMFC with the PCP, an increasing degradation in the power output versus the operating time occurred only when a plastic tube was used as the connection between the methanol reservoir and the cell. Due to the high concentrations of methanol, some contaminants could elute from the plastic tube in the methanol solution, and then decrease the cell performance. It is important to determine the contaminant that decreased the performance and how it affects the DMFC performance. So far, there have been a few studies about the effect of contaminants, i.e., metal ions [6], by-products of the methanol oxidation [7,8] and impurities in methanol [6,9], on the DMFC performance.

In this paper, the contaminant that eluted into the methanol solution from the plastic tube and reduced the cell performance was determined, and how did the eluted material affected the power generation of the DMFC with the PCP was investigated.

2. Experimental

2.1. The cell structure and the experimental setup

Fig. 1 shows a schematic illustration of the single cell structure with the PCP and the experimental setup of the DMFC power generation used in this study. The cell was designed and fabricated in a cooperative study with Chemix Co., Ltd., Japan. The cell consisted of a carbon plate with air flow-field, a MEA, a spacer with 0.5 mm thickness, a porous carbon plate (PCP) with a 0.5 mm thickness, and another carbon plate with a methanol flow-field. In contrast to the conventional cell structure, the PCP with the spacer was installed between the anode and the plate with the methanol flow-field.

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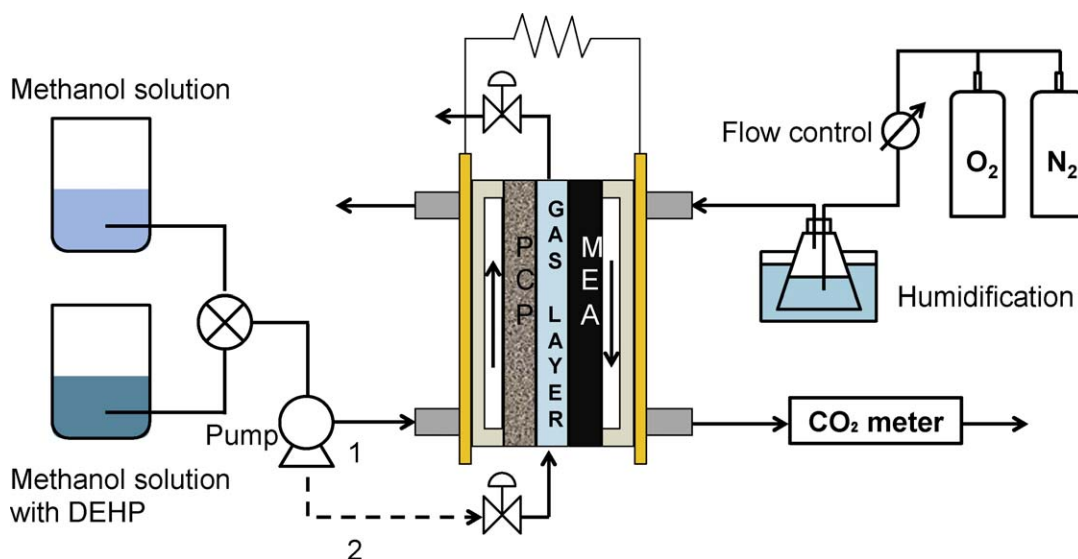


Fig. 1. Experimental setup.

The total thickness of the cell component was 6 mm. The PCP had pores with the average diameter of a few micrometers. In this cell structure, when the power generation started by a methanol solution being supplied to the methanol flow-field, CO_2 gas produced at the anode accumulated in the space and formed a gas layer between the anode and the PCP, resulting in the methanol being supplied as a vapor to the anode [1–3]. This electrode structure allows the direct feeding of 100% liquid methanol to the DMFC possible [1,4,5].

For the MEA, a hydrocarbon membrane, of which the proton conductivity and methanol permeability were equivalent to those of Nafion-115 [10,11], was used as the electrolyte, and PtRu black (5 mg cm^{-2}) and Pt/C ($3 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) were used as the catalyst for the anode and cathode, respectively. The active electrode area was 30 cm^2 .

The methanol in the reservoir was supplied to the cell by a pump through a tube with 4 mm i.d., and 0.7 m length. For this tube, either a plastic TYGON® R-3603 tube or a stainless tube was used. The TYGON tube was chosen as a plastic tube with a relatively high chemical resistance from the commercial ones.

The DMFC was operated by feeding liquid neat methanol (99.8 wt% purity), 2 mL min^{-1} , and humidified air (RH 95%), 0.30 or 0.60 mL min^{-1} , at 318 K under atmospheric pressure.

When the effect of adding a contaminant to the methanol solution was investigated, two fuel tanks for the methanol solutions with and without the contaminant were prepared and either fuel from the tanks was supplied to the cell by switching the valve. The changes in the DMFC performance after switching the fuel from the solution without contaminant to that with contaminant were then investigated.

The methanol and other chemical compounds used in this study were of chemical grade purchased from Wako Pure Chemical Industries.

2.2. Measurement of the DMFC performance

The electrochemical measurements were conducted using an electric load meter (PLZ-4W, Kikusui, Co., Ltd.). The ohmic resistance of the cell was measured using a digital AC impedance meter (FC-100R, CHINO, Co., Ltd.). The rate of methanol crossover (MCO) was calculated based on the CO_2 concentration in the effluent gas from the cathode outlet measured by an IR gas concentration meter (CGT-7000, Shimadzu, Co., Ltd.).

3. Results and discussion

Fig. 2 is a comparison of the power generation obtained using the stainless steel tube and that using the plastic tube for the connection between the reservoir and the cell. The DMFC was operated by circulating liquid neat methanol at 2 mL min^{-1} for 50 h. When the DMFC was operated with the plastic tube, the power output gradually decreased, from 0.90 W to 0.42 W, with the increasing operating time for 50 h. On the other hand, when the DMFC was operated with the stainless steel tube, the power density was almost constant, about 1.0 W, during the operation after the initial degradation related to the initial conditions. It was considered that in the DMFC system with the high concentration methanol and the plastic tube, a component of the plastic tube eluted into the methanol solution, and it would cause the power degradation during operation.

In order to specify the eluted component from the plastic tube, a liquid neat methanol (99.8 wt% purity, 70 mL) was circulated throughout the plastic tube for 50 h, and the solution was analyzed using a GC-Mass according to EN 14372. As a result, di-(2-ethylhexyl) phthalate (DEHP, 40.1 g L^{-1}) was detected in the solution. No other contaminants were detected. DEHP is generally used in plastic tubes as a plasticizer. It was clarified that a

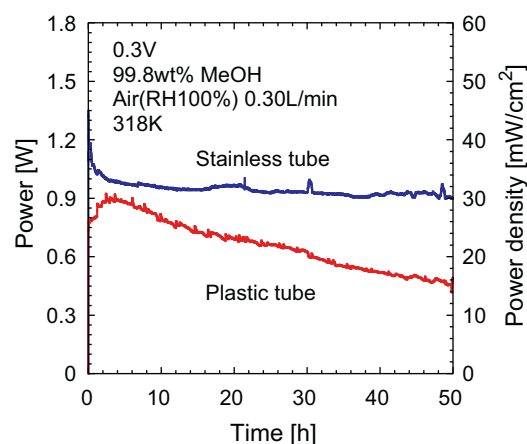


Fig. 2. Power generation characteristics of the DMFC that used a stainless steel tube or a plastic TYGON tube between the DMFC and the methanol reservoir.

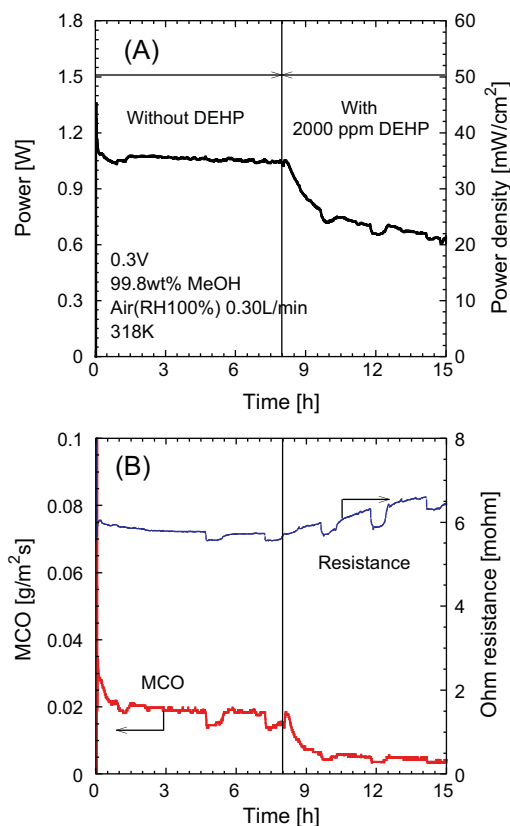


Fig. 3. Effect of 2000 ppm DEHP in the 99.8 wt% methanol solution on the DMFC performance. (A) Power and power density and (B) methanol crossover (MCO) and ohmic resistance.

certain amount of DEHP was eluted from the plastic tube into the methanol solution, and it would influence the electrode reaction and/or mass transport of the reactants. DEHP is a viscous liquid and it easily forms colloids in a water solution, thus it may affect the methanol transport through the PCP that had pores of a few microns in diameter.

The effect of DEHP as a contaminant in the methanol solution on the cell performance was investigated using the model methanol solution with a certain amount of DEHP. Fig. 3 shows the effect of 2000 ppm DEHP added to the liquid neat methanol on the power density (A), the MCO and the cell resistance (B). The concentration of 2000 ppm was used as a representative between 0 and 40,000 ppm that detected in the experiment. After switching of the methanol fuel to that with DEHP, at 7.5 h from the start, the power output suddenly decreased from 1.05 W to 0.79 W for 2 h, and then gradually decreased. It was noted that MCO also suddenly decreased from the switching similar to the degradation of the power. It was revealed that DEHP as a contaminant in the methanol decreases the power output of the DMFC. In the DMFC with the PCP, methanol was first sucked into the PCP and the methanol is vaporized on the surface of the PCP and the vapor diffused to the anode in the gas layer. Since the vapor pressure of DEHP is quite low, 3.04×10^{-5} Pa at 20 °C [12], it was considered that DEHP mainly affected the mass transport of methanol through the PCP. DEHP would be adsorbed on the surface of the pores of the PCP and then it would reduce the methanol transport rate through the PCP. Then MCO would suddenly decrease after the methanol with the DEHP was introduced into the cell.

Additionally, in order to check the effect of DEHP on the electrode reaction, the power generation using a 2 M methanol solution containing 2000 ppm DEHP was investigated by feeding the solution to the gas space, i.e., to the anode surface. Fig. 4 shows the

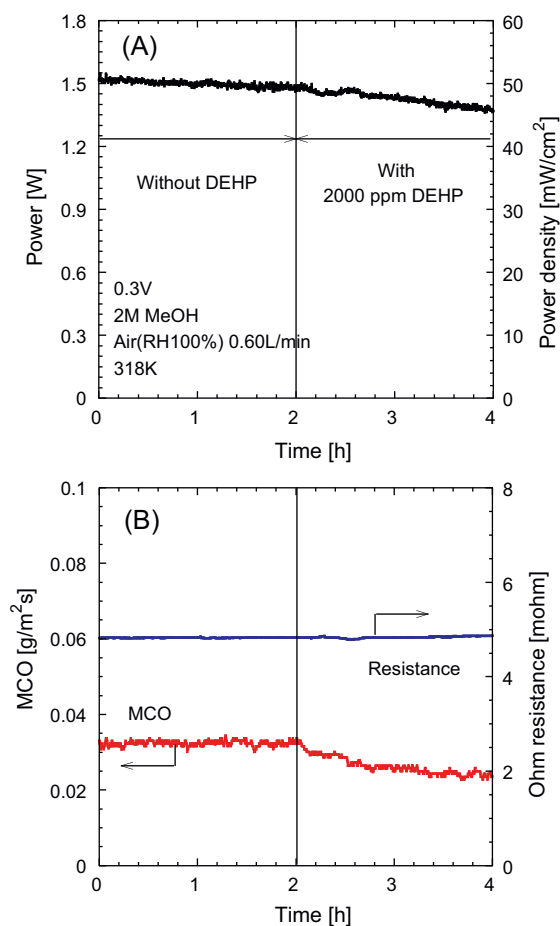


Fig. 4. Effect of 2000 ppm DEHP in 2 M methanol solution when the solution was fed to the gas space, i.e., the anode surface. (A) Power and power density and (B) methanol crossover (MCO) and ohmic resistance.

power output, MCO and the cell resistance before and after switching the fuel from the 2 M methanol to that with 2000 ppm DEHP when the solution was fed to the gas space using the feeding route 2 shown in Fig. 1. The power output was relatively high, 1.5 W, compared to that, of 1.10 W with the vapor feed shown in Fig. 3, due to the hydration of the membrane by the 2 M methanol solution. In this case, both the power density and MCO were weakly affected by the DEHP. Although the similar concentration, 2000 ppm, of DEHP was used, the degradation of the performance was not very significant compared to that when the liquid neat methanol with 2000 ppm DEHP was supplied to outside of the PCP, route 1 shown in Fig. 1, as shown in Fig. 2. This means that the DEHP strongly affected the methanol transport through the PCP and only weakly affected the electrode reaction and mass transport through the membrane. It is necessary to avoid the DMFC with PCP from such contamination not only for the electrode reaction but also for the mass transport.

4. Conclusions

A certain amount of DEHP eluted into the liquid neat methanol was detected in the methanol for the DMFC with the PCP and a plastic tube. The addition of 2000 ppm DEHP to the liquid neat methanol decreased the power output of the DMFC with the PCP. It was considered that DEHP strongly affected the methanol transport through the PCP and weakly affected the electrode reaction and the mass transport through the membrane.

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