# Formation Behaviors of Formaldehyde and Formic Acid in Various Operating Conditions of DMFC

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## Introduction

In DMFC the methanol electro-oxidation at the anode is believed to be complicated reactions through some intermediates such as formaldehyde, formic acid and/or carbon monoxide [1,2]. We have investigated the effluences from anode and cathode by a chemical analysis technique. As a result, it was found that some formaldehyde and formic acid are contained in the off gas from cathode in addition to the outflow fuel from anode under the open circuit and loading condition [3]. In this study, the influences of fuel concentration and operating temperature on the formation behavior of these species were investigated in order to understand the methanol electro-oxidation process in DMFC.

## Experiment

A quantitative analysis of formaldehyde and formic acid in the outflow fuel and off gas from a single cell operated with various conditions was curried out. The membrane electrode assembly had a Nafion117$^{TM}$ and two catalyzed electrodes of 25cm$^2$. The loading of anode Pt-Ru/C and cathode Pt/C catalyst were 0.5mg/cm$^2$ and 0.7mg/cm$^2$ respectively. The I-V characteristics were measured by Scribner$^{TM}$ model 980. In the measurement, the load was changed every 35 minutes. Fifteen minutes after the load change, each effluence from anode and cathode was taken for ten minutes by a glass trap and an impinger in the ice bath, respectively. The impinger filled with purified water (<0.1 $\mu$ S) of 40ml. In order to avoid the association of formaldehyde, some 2,4-dinitrophenylhydrazine (DNPH) was added to the effluence immediately. Then the formaldehyde and formic acid in these effluences were quantified by the liquid chromatograph (Shimadzu, LC10) and the ion chromatograph(DIONEX,IC20), respectively.

## Results and discussion

Formaldehyde of about 0.1 $\mu$ g/ml and no formic acid were detected in the flesh fuel, however, considerable amount of these species were contained in the outflow fuel. The formation of formaldehyde and formic acid as a function of current density with various fuel concentrations is shown in Figure 1. This indicates that the formation of these species increases with increasing the fuel concentration, and the formation of formic acid is about ten times that of formaldehyde. This result suggests that formaldehyde could be easy to electro-oxidize than formic acid in DMFC.

Figure2 shows a yield percentage of formaldehyde and formic acid as a function of current density with various fuel concentrations. The yield percentage of formaldehyde decreases with increasing the current density asymptotically regardless of the fuel concentration. This phenomenon would be caused by the acceleration of electro-oxidation since the anodic potential was polarized to noble potential with increasing the current density [4]. However, the yield percentage of formic acid doesn't indicate asymptotic decreases in the high fuel concentration. This result implies that the electro-oxidation activity of formic acid would be not enough in this case; therefore the surface of electrocatalysts might be occupied with much formic acid.

In conclusion, it was verified that the methanol electro-oxidation in DMFC should be complicated reactions through formaldehyde and formic acid. These formations depend on the electrode potential, fuel concentration and operating temperature. Furthermore we suppose that the enhancement of catalytic activity for formic acid would be necessary to achieve a high performance of DMFC.

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## References

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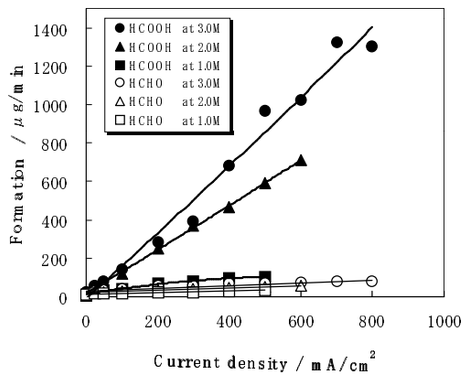


Figure 1. Formation of formaldehyde and formic acid in the anode outflow fuel at 80℃ 0.3MPa with 5ml/min

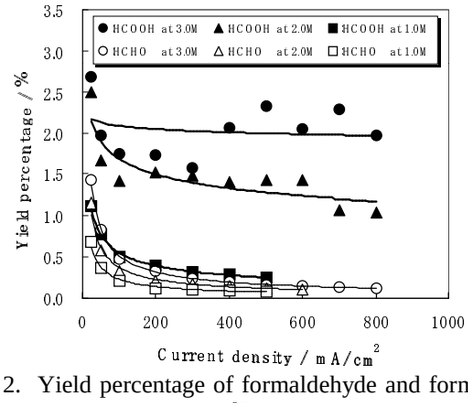


Figure 2. Yield percentage of formaldehyde and formic acid in the anode outflow fuel at 80℃ 0.3MPa with 5ml/min