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Effect of the Impurities in Methanol Fuel on the Performance of MEA for Direct Methanol Fuel Cell

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1 Introduction

The impurities in the methanol fuel that is used for direct methanol fuel cell (DMFC) could greatly affect the performance of membrane electrode assemblies (MEA). The most common impurities in the commercial methanol fuel are mainly ethanol, acetone, acetaldehyde, or ammonia. In this study, the effect of impurities in methanol fuel was investigated on the performance of MEA. We will propose the optimum compositions and limit concentration of impurities in methanol fuel for high performance of MEA for DMFC.

2 Experimental

The effect of impurities in the methanol fuel was evaluated using the 6 different kinds of commercial methanol fuels (methanol W, A, B, C, D, and E), as listed in Table 1.

The MEA was fabricated using commercial Nafion 115 as a membrane, PtRu/C (HISPEC 12100, Johnson Matthey Fuel Cells) as an anode catalyst, and Pt/C (HISPEC 13100, Johnson Matthey Fuel Cells) as a cathode catalyst. A single cell with active electrode area of 9.0 cm^2 was tested using an electrochemical test system (Won-A Tech., Korea). The changes of voltage/power density of the cells during the supply of methanol fuel with different commercial methanol were performed at 60^oC and constant operating current of 1.35 A (150 mW cm^{-2}) under ambient pressure. A solution of 1M methanol solution was fed into the anode at a flow rate of 2 cc min^{-1} and air was supplied into the cathode at a flow rate of 400 cc mim^{-1}. The anode polarization of the cells was also measured under the same conditions as those of a single cell test, except that hydrogen (H_2) gas was supplied to the cathode at a flow rate of 10 ml min^{-1} in order to make a dynamic hydrogen electrode (DHE).

Impedance spectra of the single cells during an electrochemical reaction at 60^oC and galvanostatic operation of 1.35 A (150 mW cm^{-2}) were observed using an electrochemical analysis instrument (Zahner, IM6&IM6eX, Germany). Cyclic voltammograms (CV) test was measured in the three electrodes, and the scan rate of the CV was 1 mV s^{-1}. A glassy carbon disk (1 cm^2) with electrocatalysts is used as working electrode, Pt mesh as counter-electrode, and Ag/AgCl electrode as reference. 0.5 M H_2SO_4 and 1 M methanol solution were served as electrolytes for the CV test and N_2 was bubbled into the electrolytes during the experiment.

Table 1: Property table of commercial methanol (methanol W, A, B, C, D, and E).

Matter \ Methanol	Methanol W	Methanol A	Methanol B	Methanol C	Methanol D	Methanol E
Water (%)	max. 0	max. 0.2	max. 0.01	max. 0.1	max. 0.2	max. 0.2
Non-volatile matters (%)	max. 0	max. 0.001	max. 0.001	max. 0.001	max. 0.001	max. 0.001
Acid (as CH_3COOH) (%)	max. 0	max. 0.003	max. 0	max. 0	max. 0.003	max. 0.003
Alkali (as NH_3) (%)	max. 0	max. 0.0003	max. 0	max. 0	max. 0.0003	max. 0.0003
Acetone, Aldehydes (as C_2H_5OH) (%)	max. 0	max. 0.003	max. 0.001	max. 0.001	max. 0.003	-
Assay (by G.C) (%)	min. 99.9	min. 99.8	min. 99.8	min. 99.8	min. 99.8	min. 99.5

3 Results

The changes of voltage/power density of the cells during the supply of methanol fuel with different commercial methanol are shown in Fig. 1. MEA 1 was constantly supplied with methanol W, whereas MEA 2 was supplied with different methanol listed in Table 1 for the period of 24 h. A solution of 1 M Methanol of MEA 2 was replaced as the following order; methanol W → methanol A (A sector) → methanol W → methanol B (B sector) → methanol W → methanol C (C sector) → methanol W → methanol D (D sector) → methanol W → methanol E (E sector) → methanol W. As shown in Fig. 1, when MEA 2 was supplied with methanol A, the performance of the cell was abruptly decreased as compared with the other methanol solution. The cell supplied with methanol A showed the performance loss of about 10 mW cm^{-2}. When MEA 2 Also was supplied with methanol E, the performance of the cell was slightly fluctuated. These results indicate that a methanol solution supplied into a DMFC cell could affect the performance and durability of the cell.

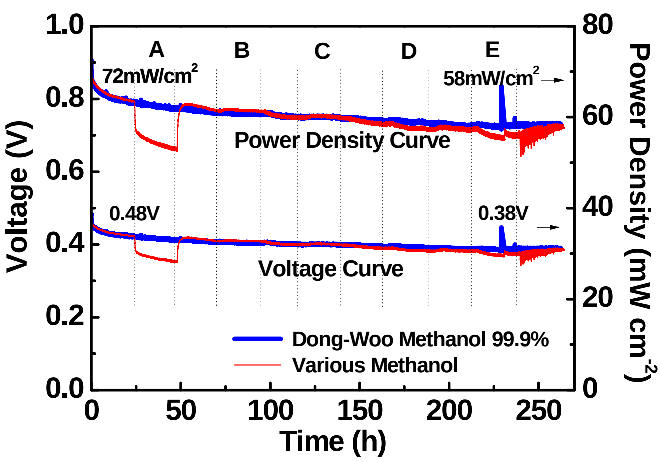


Figure 1: Changes of voltage/power density of the cells during the supply of methanol fuel with different commercial methanol (operating current: 1.35 A (150 mW cm^{-2})).

Such results appear to be proved from anode polarization curve of the cells (Fig. 2) and impedance analysis (Fig. 3). Fig. 2 shows anode polarization curves of the cell supplied with methanol W and methanol A. It was found that anode overpotential loss of the cell supplied with methanol A was higher than that of the cell supplied with methanol W (Fig. 2). In addition, as presented in Fig. 3, charge transport resistance of the cell supplied with methanol A was higher than that of the cell supplied with methanol W. These results indicate that methanol A supplied into a DMFC cell adversely affected electrochemical reactions on the anode electrode. Assumedly, it appears to be ascribed to impurities in commercial methanol A.

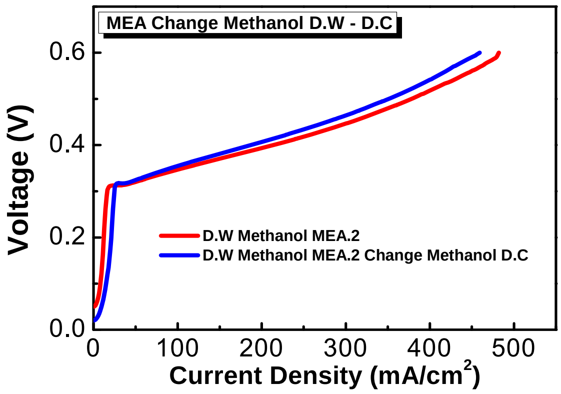


Figure 2: Anode polarization curves of the cell during the supply of methanol fuel with methanol W and methanol A.

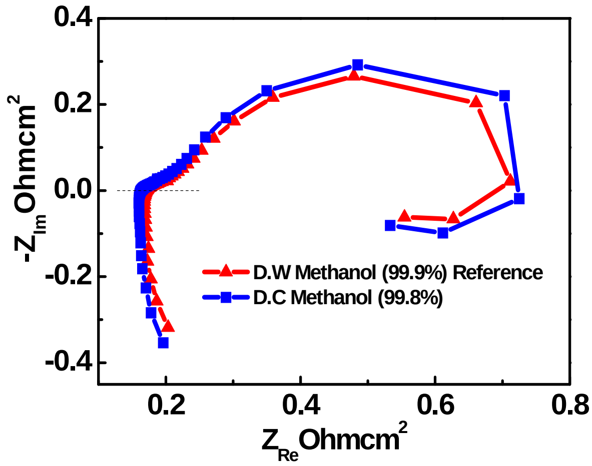
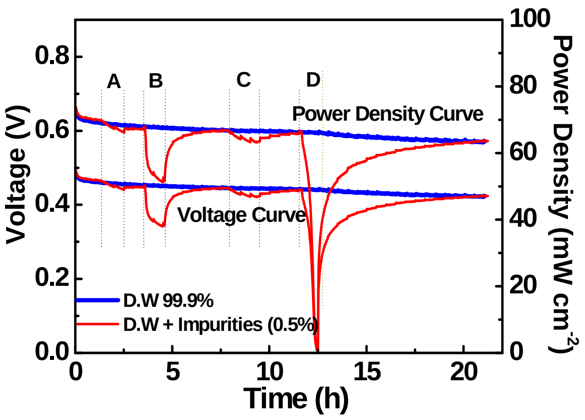


Figure 3: Anode impedance spectra of the cell during the supply of methanol fuel with methanol W and methanol A.

According to Table 1, commercial Methanol A, which showed higher performance loss than the other methanol, includes impurities such as ethanol, acetone, acetaldehydes and ammonia. Therefore, to examine effects on the performance of cells of these impurities in methanol fuel, the following study was performed with methanol fuel adding ethanol, acetone, acetaldehydes, and ammonia of 0.5 wt% to standard methanol W, as presented in Fig. 4. Methanol fuel including different impurities (0.5 wt%) was replaced as the following order; methanol W → methanol W + ethanol (A sector) → methanol W → methanol W + acetaldehyde(B sector) → methanol W → methanol W + acetone(C sector) → methanol W → methanol W + NH_3 solution(D sector) → methanol W.



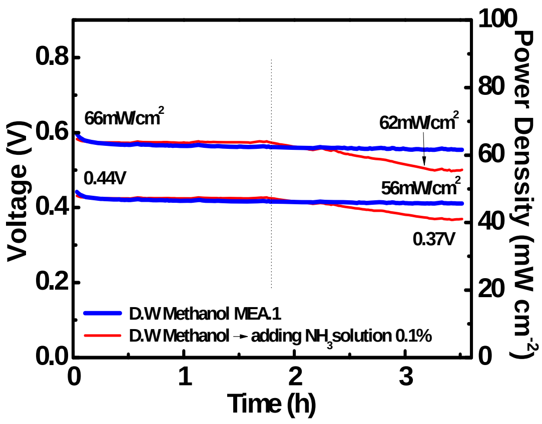


Figure 4: Changes of voltage/power density of the cell with impurity (0.5 wt%) in methanol fuel with methanol W.

Figure 5: Changes of voltage/power density of the cell with ammonia in methanol fuel with methanol W (impurities: 0.1 wt%).

As shown in Fig. 4, when methanol fuel including ethanol or acetone as an impurity was supplied into the cell, the cell voltage slightly dropped from 0.47 V to 0.45 V and 0.44 V, respectively. In contrast, when methanol fuel including acetaldehyde or ammonia was supplied into the cell, the cell voltage significantly dropped from 0.45 V to 0.35 V and 0.0015 V, respectively. Especially, ammonia as an impurity in methanol fuel made the cell severely damaged. However, it should be noted that these impurities did not bring about irreversible performance losses of the cell. Although voltage recovery rate of the cell varied with a kind of impurity, the cell was finally recovered to a normal voltage by supplying methanol W, which includes less impurity.

Fig. 5, Fig. 6 and Fig. 7 exhibit change of voltage/power density of the cells according to concentration of ammonia (Fig. 5: 0.1 wt%, Fig. 6: 0.05 wt%, Fig. 7: 0.01 wt%) in methanol fuel. When methanol fuel including ammonia of 0.1 and 0.05 wt% was supplied into the cell, the cell voltage dropped from 0.44 V to 0.37 V and 0.39 V, respectively (Fig. 5 and 6). On the other hand, when methanol fuel including ammonia of 0.01 wt% was supplied into the cell, the cell voltage did not drop, as shown in Fig. 7. This indicates that the performance of the cell was affected by concentration of ammonia in methanol fuel. These results present that concentration of ammonia in methanol fuel is below 0.01 wt% to avoid the performance degradation by supplied methanol fuel.

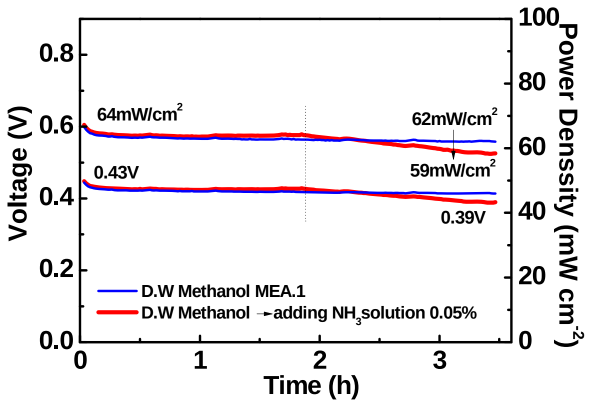


Figure 6: Changes of voltage/power density of the cell with ammonia in methanol fuel with methanol W (Impurities: 0.05 wt%).

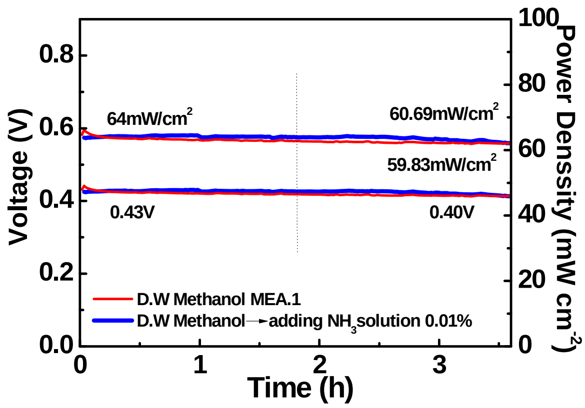


Figure 7: Changes of voltage/power density of the cell with ammonia in methanol fuel with methanol W (Impurities: 0.01 wt%).

To investigate change of electro-activity of the anode catalyst (PtRu/C, HISPEC 12100, Johnson Matthey Fuel Cells) according to the concentration of ammonia in methanol fuel, cyclic voltammetry of the anode catalyst was measured in 0.5 M H2SO4 and 1M methanol solution including ammonia of 0.5 and 0.05 wt%. From cyclic voltammetry of Fig. 8, it was found that as concentration of ammonia increased, oxidation current of methanol gradually decreased. This result indicates that as concentration of ammonia increased, electro-activity of the anode catalyst decreased.

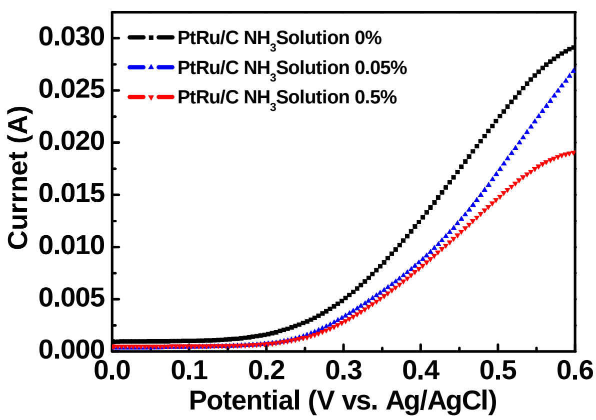


Figure 8: Cyclic voltammetry in methanol fuel with the concentration of ammonia (0.05 wt% and 0.5 wt%)

4 Conclusion

In this study, the effect of impurities in methanol fuel was investigated on the performance of MEA for DMFC. The methanol solution with commercial methanol A was supplied into the DMFC cell, the performance of the cell was decreased compared with the other methanol solution. When methanol E was supplied into the cell, the performance of the cell was slightly fluctuated. According to the anode polarization curves and impedance spectra, anode overpotential loss and charge transport resistance of the cell supplied with methanol A was higher than that of the cell supplied with methanol W.

The methanol fuel including acetaldehydes or ammonia as an impurity was supplied into the cell, the cell voltage significantly dropped from 0.45 V to 0.35 V and 0.0015 V, respectively. Especially, ammonia in methanol fuel made the cell severely damaged. The performance of the cell was directly affected by concentration of ammonia in methanol fuel. This study present that concentration of ammonia in methanol fuel is below 0.01 wt% in order to avoid the performance degradation by supplied methanol fuel. However, it should be noted that these impurities did not bring about irreversible performance losses of the cell. From the results of cyclic voltammetry, it was found that as concentration of ammonia impurity increased, electro-activity of the anode catalyst decreased.

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