Effect of the Impurities in Bioethanol on Current Density of a Direct Ethanol Fuel Cell

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The degradation of current density by impurities in bioethanol from lignocellulosic biomass for use in a direct ethanol fuel cell was evaluated. The degradation experiment of using a single cell was conducted by adding nine impurities, i.e., methanol, acetaldehyde, acetic acid, 1-propanol, allyl alcohol, ethyl acetate, 3-methyl-1-butanol, acetal (acetaldehyde diethyl acetal), and benzaldehyde, to a 2 M ethanol aqueous solution. The current density of the single cell was degraded by the quasi bioethanol including the nine impurities. To clarify the principal poisoning impurity, we performed the cell measurement by only adding each single impurity. As a result, allyl alcohol turned out to be the main catalyst poison under the estimated condition. The negative effects by the other impurities were almost negligible.

Key Words
Bioethanol, Direct fuel cell, Impurity, Catalyst poisoning

1. Introduction
Bioethanol is a renewable fuel produced from many types of biomasses and has been used in automotive engines. Direct ethanol fuel cells (DEFCs) have attracted attention because they are compact devices without a reformer and their energy conversion efficiency can be higher than engines by direct conversion from chemical energy to electricity. In recent years, significant effort in research and development has been devoted to direct alcohol fuel cells, like direct methanol fuel cells (DMFCs) and DEFCs, for the practical use. Although the development of DMFCs is currently more advanced than that of DEFCs, DEFCs have essentially attracted attention because ethanol is not harmful. The direct use of bioethanol in DEFCs is expected due to the importance of less external energy input for the purification of ethanol. The crude bioethanol generally contains some impurities depending on the raw materials and/or the fermentation process, and traces of the impurities in the bioethanol may suppress the current density of DEFCs by catalyst poisoning and/or obstructing the ionic path of the polymer electrolyte. For DMFCs, it has been reported that organic impurities such as acetic

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acid, ethanol, acetone, 1-propanol, 2-propanol, and 1-butanol are poisons for the catalyst. For this reason, the effect of the impurities on the current density of DEFCs needs to be understood. However, almost no information is available concerning the effect of impurities in the crude bioethanol on the current density of the DEFCs. Although the DEFCs are in the development phase, we believe this information is important for the development and commercialization of the DEFCs.

In the present study, the degradation of the current density for DEFCs by the impurities in the bioethanol was evaluated. Lignocellulosic bioethanol by fermentation was assumed to be used for the DEFCs. The relation between the impurity species at specific concentrations and the degradation of the current density was studied. The PtRu alloy catalyst on carbon black was used as the anode catalyst because PtRu/C is known as one of the active electrocatalysts for the ethanol oxidation reaction.

2. Experimental

2.1 Membrane electrode assembly

The Membrane electrode assembly (MEA) was prepared by a procedure similar to that in our previous study. The homemade PtRu/C electrode (catalyst: TEC61E54, Tanaka Kikinzoku Kogyo K.K.; catalyst loading: 1.4 mg-PtRu cm⁻²; backing layer: EC-TP1-060T, Toray Industries, Inc.) as the anode, the electrolyte membrane (NRE-212, DuPont), and the commercial Pt/C electrode (EC-E20-10-07, ElectroChem, Inc.) as the cathode were hot pressed at 130 °C and 5 MPa for 3 min. The projected area of the electrode was 4.84 cm². The MEA was fixed in a cell module containing serpentine flow channels (FC-05-02-H2RB, ElectroChem, Inc.). Three similar MEAs were prepared, and the MEA was replaced when the MEA was irreversibly poisoned.

2.2 Impurities and the quasi bioethanol solution

Nine impurities, i.e., methanol, acetaldehyde, acetic acid, 1-propanol, allyl alcohol, ethyl acetate, 3-methyl-1-butanol, acetal (acetaldehyde diethyl acetal), and benzaldehyde (Wako Pure Chemical Industries) were tested as typical impurities in the bioethanol based on the report of Habe et al. which showed compositions of the four different bioethanols made from hinoki (Japanese cypress), eucalyptus, pine, and straw by the fermentation method and dehydration (Table 1). A 2 M quasi bioethanol solution was prepared by adding these nine impurities at the highest concentrations in the four bioethanols (except allyl alcohol because of its toxicity) to a 2 M ethanol aqueous solution. The estimated weight concentrations of the impurities in the 2 M quasi bioethanol solution are shown in Table 1. The 2 M ethanol solution with a single impurity was also investigated in order to study the effect of each impurity. The concentration of each impurity was the same as that in the 2 M quasi bioethanol, and some higher concentrations were also tested to clarify the effect.

2.3 Fuel cell test

The effect of the impurity was measured by the change in the current density of the single cell at a constant voltage. A schematic diagram of the experimental system with the single cell is shown in Fig. 1. The constant voltage measurement at 0.2 V was carried out under flowing 2 M ethanol at the anode (1.5 mL min⁻¹) and dry air at the cathode (0.5 L min⁻¹). The cell temperature was controlled at 80 °C by a module heater. The voltage of the single cell was controlled and current from the single cell was measured by using a potentiostat (HZ-3000 or HZ-5000, Hokuto Denko).
Corp.). The 2 M ethanol aqueous solutions with/without the impurity were prepared. The power generation was initially started by flowing 2 M ethanol without the impurity. The 2 M ethanol with the impurity (or the 2 M quasi bioethanol) was then introduced into the single cell. The ohmic resistance of the single cell was measured during the measurement using an AC impedance meter (FC-100R, Chino, Co., Ltd.) to obtain information on the obstruction of the ionic path at the membrane. After the measurements, the cell was flushed by feeding distilled water for 1 h to remove the adsorbed compounds on the catalyst. The degradation fraction of the current was evaluated using the following equation similar to the previous study of the DMFC.

\[
\phi_{60} = \frac{1}{i_0} [\left(i_0 - i_{0b}\right) - 2(i_{-30} - i_b)]
\]

where \(\phi_{60}\) [-] is the degradation fraction of the current at 60 min (0 \(\leq \phi_{60} \leq 1\)), and \(i_0\) [mA cm\(^{-2}\)] is the current density at t min. In the present study, \(t = 0\) min is defined as the time when the fuel solution was switched from without impurities to with the impurity. The second term of the bracket denotes the baseline correction. The regression lines as the baselines were obtained with enough linearity by using 30 min-data before the addition of impurities (current density at \(-30\) min \(\leq t \leq 0\) min). A lower \(\phi_{60}\) value indicates a higher tolerance to the impurity.

### 3. Results and discussion

#### 3.1 Quasi bioethanol

The degradation of the current density by switching to the 2 M quasi bioethanol is shown in Fig. 2. The degradation of the current density using the bioethanol was observed. The degradation fraction, \(\phi_{60}\), of the single cell was 0.17. In contrast, the ohmic resistance was not changed after switching to the 2 M bioethanol. Hence, the degradation of the current density was due to the catalyst poisoning. The effect of each impurity is discussed in the next section.

#### 3.2 Effect of each single impurity

The current densities of the single cells were gradually decreased during repetitive use, thereby the initial current densities in the following figures were not the same. Similar to the result described in section 3.1, the
ohmic resistances were not changed by the addition of the impurities for all the single cells (around 55 mΩ).

The change of the current density due to the addition of acetaldehyde is shown in Fig. 3. The degradation of the current density was observed at the acetaldehyde concentrations of 10³ and 10⁴ ppm. Acetaldehyde is known to form poisoning adsorbates, i.e., CO₅ads and CHₓads, by C–C bond cleavage. These adsorbed compounds occupy the active sites, while Ru can supply OH₅ads to the active site. The reaction between OH₅ads and the adsorbed compounds should refresh the active sites. Also, the current density of the single cell was degraded by the incorporation of 1-propanol (data not shown). The partial oxidation of 1-propanol formed CO₅ads on the Pt. The current density of the single cell was suppressed by addition of 3-methyl-1-butanol (data not shown). This degradation of the current density is also considered to be caused by CHₓads and CO₅ads.

The effect of allyl alcohol at various concentrations is shown in Fig. 4. The current densities of the single cells were significantly degraded by the incorporation of allyl alcohol at the relatively low concentrations. The partial oxidations of allyl alcohol form intermediates with the C=C bond (Fig. 4), and these are believed to be strongly adsorbed on Pt. The degradation fraction of current density at addition of 1 ppm allyl alcohol was 0.40 suggesting that the degradation fraction of the quasi bioethanol shown in Fig. 2 was principally caused by the allyl alcohol. In addition, the current density of the single cell did not recover by flushing with distilled water. The current density of the single cell recovered by electrolysis at a higher overpotential at the anode. Strong adsorption by the intermediates is also suggested based on this result.

The effect of methanol at 9.5 × 10³ ppm is shown in Fig. 5. The addition of methanol to the 2 M ethanol solution did not cause any degradation of the current density. Generally, the current densities of direct methanol fuel cells are higher than that of DEFCs at same voltage because there is no C–C bond cleavages during the elementary reactions. Thus, methanol is not the poison. The current density of the cell also did not decrease by the addition of ethyl acetate (data not shown). The effect of acetic acid at 10³ and 10⁴ ppm is shown in Fig. 6. Acetic acid did not show the poisoning effect at the concentration of 10³ ppm. The acetate adsorption on the Pt model catalyst was studied by Heinen and coworkers, and acetate showed a Langmuir-type adsorption isotherm. The adsorbed acetate is believed to be low at 10³ ppm under this condition. Acetal and benzaldehyde (data not shown) weakly suppress the current density of the single cell at the tested concentrations. Their
toxicity is negligible at the concentrations in the 2 M quasi bioethanol as shown in Table 1.

A summary of the degradation fraction for the nine impurities is shown in Fig. 7. Only the degradation fraction of acetic acid (10^4 ppm) was calculated as \((i_i - i_0)/i_0\) to avoid overestimation of the baseline. Allyl alcohol showed a relatively strong toxicity, whereas the other impurities did not affect the current density of the single cell around the assumed concentrations of the 2 M quasi bioethanol in Table 1. We suggest an acceptable concentration of the impurity, which is defined as the concentration of \(\phi_{60} < 0.03\) (Table 1). Allyl alcohol concentration in the dehydrated bioethanol from hinoki and straw were less than 5 g m\(^{-3}\) (Table 1, data from Ref. 9). This corresponds to concentration less than 0.6 ppm in 2 M bioethanol, thus bioethanol from these materials is suitable for fuel cell applications. The research and development of separation technology for the allyl alcohol is also required.

4. Conclusion

The degradation of the current density of the DEFC by the impurities in the 2 M bioethanol was evaluated. The current density of the single cell was degraded using the quasi bioethanol. The degradation of the current density was considered to be caused by catalyst poisoning. Allyl alcohol, which has a double bond, showed a serious poisoning effect, while the poisoning by the other impurities was negligible at the estimated concentration in the bioethanol.
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