



# Effect of the impurities in crude bio-methanol on the performance of the direct methanol fuel cell

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## ARTICLE INFO

### Article history:

Received 10 February 2011  
Received in revised form 20 July 2011  
Accepted 5 August 2011  
Available online 11 August 2011

### Keywords:

DMFC  
Crude bio-methanol  
Impurity  
Performance degradation  
1-Butanol

## ABSTRACT

As an environmental friendly and economical methanol for the fuel of a DMFC, we focused on a crude bio-methanol from woody biomass without refining. The effects of the impurities, i.e., ethanol, 1-butanol, methyl formate and diisopropyl ether, contained in the crude bio-methanol on the DMFC performance were investigated. Methyl formate and diisopropyl ether hardly or only slightly affected the DMFC performance, while ethanol and 1-butanol caused a significant degradation in the performance. When multiple impurities are present in the fuel as well as the crude bio-methanol, the degradation was somewhat lower than that of the single impurity, 1-butanol, which was the most harmful component of the multiple impurities. When using the crude bio-methanol as a DMFC fuel, removal of the harmful impurities, such as ethanol and 1-butanol, is necessary, otherwise a novel catalyst, which is also active for the oxidation of these impurities, required.

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## 1. Introduction

Direct methanol fuel cells (DMFCs) have received considerable attention due to their high theoretical energy density,  $4800 \text{ Wh L}^{-1}$ , the easy handling of the liquid fuel and are a compact system. Therefore, the DMFC is expected to be an alternative power source of various portable electric devices, such as a notebook-PC and cell phone.

Methanol has been mainly produced from fossil fuels, like natural gas and coal, through the processes of syngas production, methanation and refining. However, it is necessary for our future society not to depend on fossil fuels, because they are exhaustible resources and the source of greenhouse gases [1]. Less dependence on fossil fuels requires another source for methanol, and hence, biomass is an alternative carbon-neutral and renewable energy resource. Bio-methanol is produced from woody biomass [2] via the syngas process. However, it has been pointed out that the bio-methanol production is still not economically viable [3]. As a solution of this issue, we focused on the direct use of the crude bio-methanol, which is produced from biomass without being refined, as a fuel for the DMFC. This methanol can reduce not only the cost but also the energy consumption which roughly accounts for 10% of the total energy required for the methanol production [4] in the refining process. Therefore, the crude bio-methanol must be one of the alternatives because of its ecological and economic advantages.

Table 1 shows the typical chemical compositions of the crude methanol produced from the woody biomasses, A and B, and from natural gas, C, via syngas [5]. The crude bio-methanol contains some organic impurities, such as ethanol, 1-butanol, methyl formate and diisopropyl ether, depending on the process conditions and type of biomass used, and the components and their concentrations were somewhat different from these of natural gas. Similar to the harmful effect of carbon monoxide, which is a common impurity in hydrogen produced from hydrocarbons through steam reforming and the shift conversion, on the proton exchange membrane fuel cell by poisoning the Pt catalyst [6], the impurities in the crude methanol may cause a performance degradation of the fuel cell. For the direct use of the crude bio-methanol in the DMFC, the effect of the impurities in the methanol on the power generation characteristics must be determined.

There have been a few studies about the effect of impurities in the methanol on the power generation characteristics of a DMFC. Chloride anion,  $\text{Cl}^-$ , caused a degradation of the DMFC performance [7] due to  $\text{Cl}^-$  being adsorbed on the active sites of the PtRu catalyst. The metal, i.e., Na [8,9], Al, Ni and Fe [9], ions also caused a voltage drop [9], and these degradations were attributed to the reduction in the proton conductivity of the membrane caused by the adsorption of the metal ion onto the sulfonic acid group of the electrolyte membrane [9]. In terms of an organic impurity, the effects of formic acid, ethanol, acetone, 1-propanol, 2-propanol, methyl formate and acetic acid on the DMFC performance have been investigated [9]. These organic impurities might be contained, more or less, in the fuel as a by-product of the methanol oxidation [10–12] and/or resulting from the corrosions of the components in the DMFC mate-

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**Table 1**

Typical composition of crude methanols as prepared with syngas from gasified woods, A and B, and from natural gas, C [5].

Component	Woody biomass (wt%)		Natural gas (wt%)
	A	B	C
Methanol	91.3	93–95	96.8
Ethanol	–	0.3–0.5	0.29
1-Butanol	1.5	0	–
Methyl formate	6.0	<0.001	0.92
Methyl acetate	–	–	0.09
Dimethyl carbonate	–	–	0.06
Dimethyl ether	–	–	0.19
Diisopropyl ether	0.7	–	–
Water	0.5	4–5	1.64
Other	–	<0.1	<0.03

rials by the by-product [9]. It was reported that the acetic acid, ethanol, acetone, 1-propanol and 2-propanol showed significant degradations in the cell voltage at 200 ppm, while methyl formate and formic acid hardly affected the cell performance [9]. They confirmed that these voltage drops can be regenerated by supplying the impurity-free methanol. Moreover, the 2-propanol, which changes to acetone during the oxidation process, and acetone showed very similar trends in the voltage drops, meanwhile, the 1-propanol, which changes to propionic acid during the oxidation process, showed a different trend in the voltage drop. Based on these results, they assumed that the oxidized products and/or the organic impurities themselves cause the voltage drops. Although these studies were quite beneficial regarding the fuel management of the DMFC, they were not sufficient for determining the crude bio-methanol. For instance, there is little information about 1-butanol and diisopropyl ether as an impurity. Moreover, the effect of the impurity was investigated as a single component in the methanol, although the crude bio-methanol contains multiple impurity components as shown in Table 1, and the effect of the presence of multiple impurities on the performance has not been clarified. The effect of these multiple impurities should be clarified, since these impurities may cause a negative influence on the DMFC performance.

In this study, in order to consider the use of the crude bio-methanol as an alternative fuel of a DMFC, the effects of the organic impurities in the methanol solution at various concentrations and temperatures on the DMFC performance were investigated. Referring to Table 1, ethanol, 1-butanol, methyl formate and diisopropyl ether were evaluated as impurities. They were investigated as a single component and also as multiple components in the methanol. The quasi crude-bio methanol containing the four types of impurities was also prepared, and the effects of the impurities on the DMFC performance were discussed.

## 2. Experimental

### 2.1. Fuel preparation

All the chemicals used in the experiment including methanol and the four compounds as the impurities were of ultrapure grade (purity >99.8%) purchased from Wako Pure Chemical Industries, Ltd. The water was distilled water (Kyoei Pharmaceutical Co., Ltd.), A4 grade of JIS K0557 [13]. As the fuel of the DMFC, a 2 M aqueous methanol solution was prepared from the above chemicals and was used as the standard methanol solution that does not contain the impurities. In all the experiments, the concentration of methanol was 2 M. The methanol with impurities was prepared by adding a certain amount of the impurity component to the standard methanol solution. The quasi-crude bio-methanol with the four impurity components was prepared as shown in Table 2, determined by referring to compositions A and B in Table 1.

**Table 2**

Composition of the quasi crude bio-methanol and the concentration of the impurities in the 2 M crude bio methanol–water solution.

Component	Composition of the quasi crude bio-methanol (wt%)	Concentration in the 2 M methanol (g g <sup>-1</sup> solution)
Methanol	91.3	65,100 ppm (2 mol L <sup>-1</sup> )
Ethanol	0.3	210 ppm
1-Butanol	1.5	1100 ppm
Methyl formate	6.0	4300 ppm
Diisopropyl ether	0.7	490 ppm

When the effect of the single impurity was investigated, the 2 M-methanol solutions with different concentrations of the impurities, i.e., 0.3–3000 ppm for ethanol, 0.1–10,000 ppm for 1-butanol, 5000 and 6500 ppm for methyl formate and 62–6200 ppm for diisopropyl ether, were prepared and used.

### 2.2. Membrane electrode assembly (MEA) preparation

NRE 212 (Dupont) was used as the polymer electrolyte membrane. In order to activate the proton conductivity, the membrane was pretreated by sequential immersion in boiling solutions of 3 vol.% H<sub>2</sub>O<sub>2</sub>, de-ionized water, 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub>, and de-ionized water, in that order for 1 h. Pt–Ru black (HiSPEC 6000, Johnson Matthey Fuel Cells Co., Ltd.) and Pt black (HiSPEC 1000, Johnson Matthey Fuel Cells Co., Ltd.) were used as the catalyst for the anode and the cathode, respectively. The catalyst ink was prepared by dispersing an appropriate amount of the catalyst in a solution of de-ionized water, isopropyl alcohol, and 5 wt% Nafion solution (Wako Inc.). The ink was then coated on the carbon cloths (35% Teflonized, ElectroChem, Inc.), which were painted with 3–4 mg cm<sup>-2</sup> of carbon black containing 10% Nafion on their surface, to form the electrodes. The catalyst loading was 12 mg cm<sup>-2</sup> and 9 mg cm<sup>-2</sup> for the anode and the cathode, respectively, and the ionomer loading on the catalyst layer as 15 wt% for the anode and 10 wt% on the cathode. The MEA was then fabricated by sandwiching the membrane between the anode and the cathode and hot pressing them at 408 K and 5 MPa for 3 min. The projected area of the MEA was 4.84 cm<sup>2</sup> (2.2 cm × 2.2 cm).

### 2.3. Experimental set-up and cell structure

Fig. 1 is a schematic diagram of the cell structure, a, and the experimental set-up of the DMFC operation, b, used in this study. The cell consisted of current collectors, separators, rubber sheets and the MEA. The MEA was sandwiched between the separators (FC005-01 SP, ElectroChem, Inc.) with the rubber sheets made of graphite blocks having serpentine flow channels. Two fuel tanks for the 2 M methanol solution with and without impurities were used, and either fuel from the tanks could be supplied to the cell by switching the valve. The cell was operated at temperatures between 303 and 353 K under atmospheric pressure. The fuel to the anode and the oxygen to the cathode were preheated to the cell temperature at the inlet of the cell. The supply flow rates of the fuel and the oxygen were fixed at 3.64 and 500 mL min<sup>-1</sup>, respectively.

### 2.4. Measurement of the DMFC performance

As a pretreatment, the DMFC was operated with the standard methanol solution at the constant cell voltage of 0.1 V until the current became stable. In order to investigate the effect of the impurities in the methanol solution, the current density vs. time at the constant cell voltage of 0.2 V was continuously measured before and after switching of the fuel from the standard methanol solu-

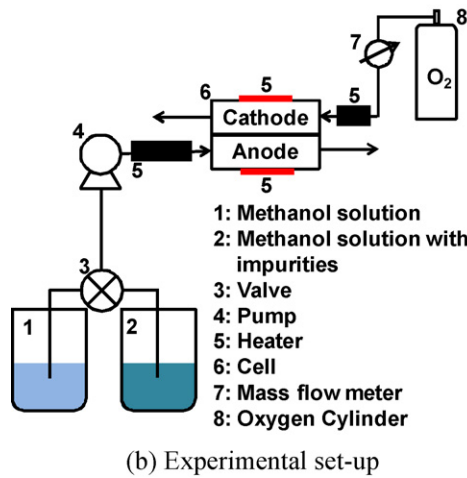
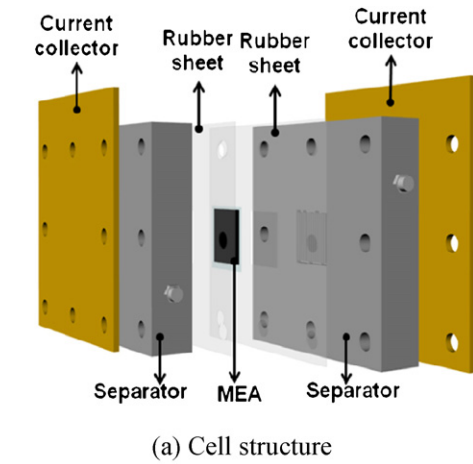


Fig. 1. Schematic diagram of the cell holder and the experimental set-up.

tion to that with the impurity compounds. After the experiments, the cell was flushed with distilled water for 1 h as a regeneration operation.

The measurements were conducted using an electrochemical measurement system (HAG-5010, Hokuto Denko, Co., Ltd.). The ohmic resistance of the cell was also measured using a digital fuel cell AC ohmic meter (FC-100R, CHINO). The current density and cell resistance were recorded at the interval of 1 min.

### 3. Results and discussion

#### 3.1. Effect of the single impurity

##### 3.1.1. Ethanol

Fig. 2 shows the effect of 300 ppm ethanol added to the standard methanol solution on the current density at different temperatures, i.e., 303 K, 323 K and 353 K. The fuel was changed from that without the impurity to that with 300 ppm ethanol at 0 min. It was clearly shown that, just after the switching to the fuel containing the impurity, the current density suddenly decreased at all temperatures.

In order to quantify the degradation caused by the impurity, we defined the degradation,  $\phi_{60}$  [-], in the current density at  $t = 60$  min as follows:

$$\phi_{60} = \frac{1}{i_0} \left\{ (i_0 - i_{60}) - (i_{-30} - i_0) \frac{60}{30} \right\} \quad (1)$$

where  $i_t$  is the current density at  $t$  min from the switching of the fuel, therefore,  $i_0$  denotes the initial current density just at the time

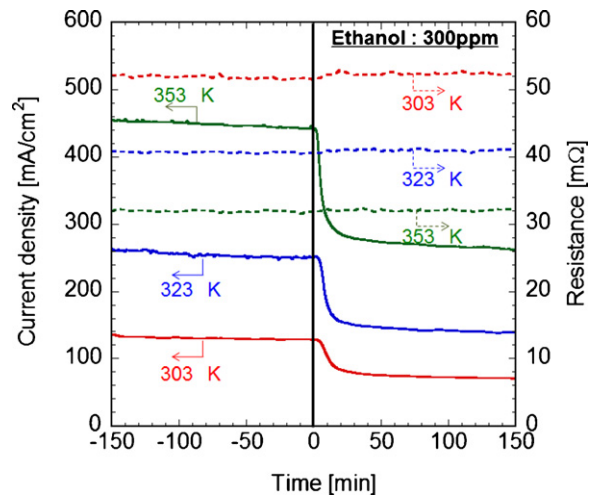


Fig. 2. Effect of 300 ppm ethanol addition to the standard 2 M methanol solution on the current density and the cell resistance at different temperatures.

when the fuel was switched to that with the impurities. To eliminate the influence of the current decrease caused by any other reason on the degradation, the gradient in the current density just before the fuel switching for 30 min,  $(i_{-30} - i_0)/30$ , was subtracted from the gradient for 60 min just after the switching,  $(i_0 - i_{60})/60$ . Hence, the total gradient provides the degradation in the current density at 60 min only occurring from the effect of the impurity based on Eq. (1). Using the degradation  $\phi_{60}$ , the current density reduced by the impurities after 60 min from the fuel switching,  $i_{60}$ , can be calculated and is related to the initial current density,  $i_0$ , as follows:

$$i_{60} = (1 - \phi_{60})i_0 \quad (2)$$

The degradation  $\phi_{60}$  for the 300 ppm ethanol in Fig. 2 was calculated to be 0.41 at 303 K, 0.42 at 323 K and 0.38 at 353 K, suggesting that the degradation was almost the same irrespective of the temperature. On the other hand, the cell resistance was hardly affected by the ethanol suggesting that the proton conductivity of the polymer electrolyte membrane was hardly affected by the ethanol. Such a large degradation for such a very small concentration of ethanol was in accordance with the results from a previous report [9].

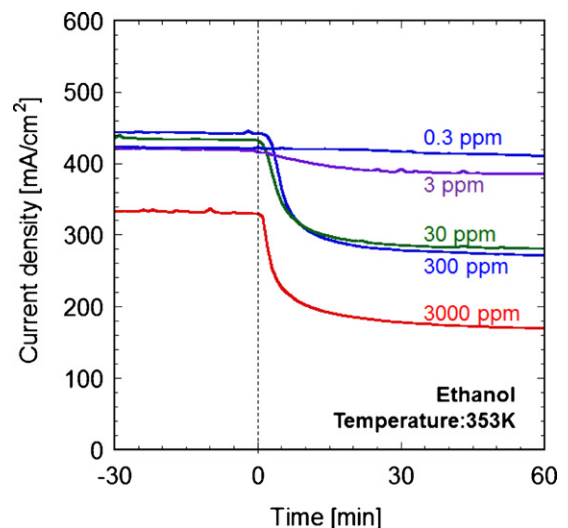


Fig. 3. Effect of ethanol concentration in 2 M methanol on the current density at 353 K.

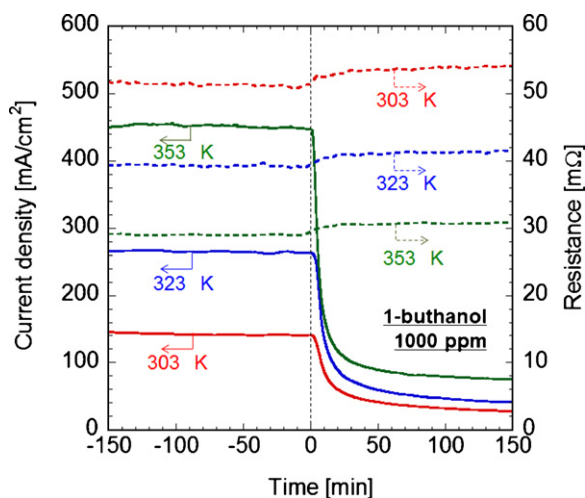


Fig. 4. Effect of 1000 ppm 1-butanol addition to the standard 2 M methanol solution on the current density and the cell resistance at different temperatures.

Fig. 3 shows the effect of the ethanol added to the methanol solution at various concentrations on the current density at 353 K. In this figure, only the initial current  $i_0$  at 3000 ppm was rather low compared to that at the other concentrations. This was due to a degradation caused by the measurements using 1-butanol which caused a degradation that could not completely be regenerated by the 1 h flushing operation as mentioned in the next section. However, for all cases in the figure except for the 3000 ppm case, the degraded current density by the ethanol was almost regenerated to the initial value  $i_0$  by flushing the anode with distilled water for 1 h, suggesting that the degradation may be caused by the weakly adsorbed species on the catalyst as will be discussed later. This means that the relative degradation based on  $i_0$  was not significantly affected by the initial current itself.

The degradation  $\phi_{60}$  increased with the increasing ethanol concentration. It was 0 and 0.05 at 0.3 ppm and 3 ppm, respectively, and then it significantly increased to 0.33 at 30 ppm, then 0.38 at 300 ppm and 0.47 at 3000 ppm. The dependence of  $\phi_{60}$  on the concentration of the ethanol suggested that the degradation might be caused by a blockage of the catalyst active sites by some species provided by the ethanol oxidation. This will be discussed in the last section. These results showed that the ethanol in the crude bio-methanol was harmful to the DMFC performance, and it must be practically removed to a level of 0.3 ppm or lower.

### 3.1.2. 1-Butanol

Fig. 4 shows the effect of 1000 ppm 1-butanol on the current density at different temperatures. The current density significantly decreased as soon as the fuel was changed to the methanol containing 1-butanol. The degradation was quite significant, and  $\phi_{60}$  was 0.72 at 303 K, 0.80 at 323 K and 0.80 at 353 K, and was similar at the different temperatures. It was noted that the cell resistance slightly increased by switching the fuel at these temperatures. The increase in the cell resistance would be due to the decreased proton conductivity of the catalyst layer and the electrolyte membrane, that may be caused by an obstruction of the ionic path [14] by 1-butanol and/or some species produced by the 1-butanol oxidation. Moreover, 1-butanol is known to cause a strong swelling of the Nafion membrane, since it has both hydrophobic and hydrophilic properties. Fig. 5 shows the effect of the concentration of 1-butanol in the methanol solution on the current density at 353 K. The current density suddenly decreased by switching the fuel to the 2 M methanol containing the 1-butanol even when the 1-butanol concentration

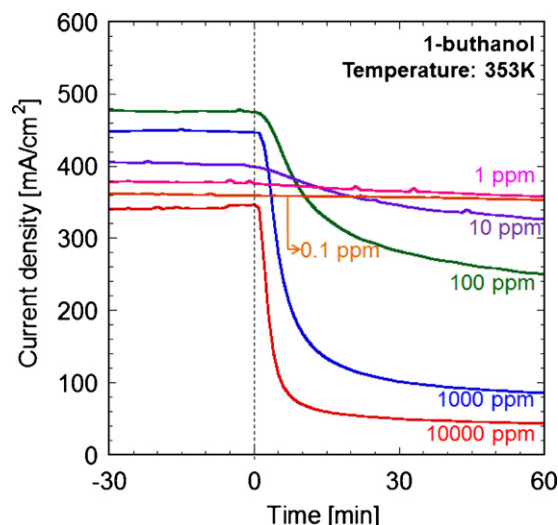


Fig. 5. Effect of 1-butanol concentration in 2 M methanol on the current density at 353 K.

was as low as 1 ppm. The degradation  $\phi_{60}$  was calculated to be 0.00, 0.03, 0.15, 0.46, 0.80 and 0.87 at 0.1 ppm, 1 ppm, 10 ppm, 100 ppm, 1000 ppm and 10000 ppm, respectively, and it increased with the increasing 1-butanol concentration. When the degradation by 1-butanol is compared to that by ethanol at a similar concentration, it is easily understood that the degradation by 1-butanol is greater, meaning that 1-butanol is more harmful than ethanol in the DMFC even when the difference in their molecular weight, 46 and 74, respectively, was taken into account.

When the anode of the cell was flushed with distilled water for 1 h after the current measurement, the performance was somewhat regenerated, but could not be completely regenerated. This reason will be discussed later based on the adsorption of the 1-butanol and/or some species from the 1-butanol oxidation.

### 3.1.3. Methyl formate

The effect of the methyl formate at different concentrations, i.e., 5000 ppm, and 6500 ppm, under different operating temperatures was investigated. These concentrations were much higher than that assumed when using the crude bio-methanol. Although we did not show the data, the current density was hardly affected by the methyl formate under these conditions in accordance with the previous study [9], and the degradation  $\phi_{60}$  was 0.00 and 0.00 at 5000 ppm and 6500 ppm, respectively. The cell resistance was also not affected by the methyl formate. Therefore, methyl formate at these concentrations was not harmful during the DMFC power generation.

### 3.1.4. Diisopropyl ether

Fig. 6 shows the effect of the 620 ppm diisopropyl ether added to the methanol solution on the current density at the different temperatures. When the diisopropyl ether entered the cell, current density was slightly affected, and it gradually decreased with time. The degradation  $\phi_{60}$  was calculated as 0.04 at 303 K, 0.05 at 323 K, and 0.03 at 353 K, and these were much lower than those of ethanol and 1-butanol. The resistances at 353 and 323 K were almost constant, on the other hand, at 303 K, it slightly increased due to the impurity. Diisopropyl ether may affect the electrolyte membrane similar to the 1-butanol. The effect of the diisopropyl ether concentration in the methanol solution on the current density is shown in Fig. 7. Even at a concentration as high as 6200 ppm, the degradation was similar to that at the lower concentrations. The degradation was calculated to be nearly zero, 0.02, and 0.03 at 62 ppm, 620 ppm

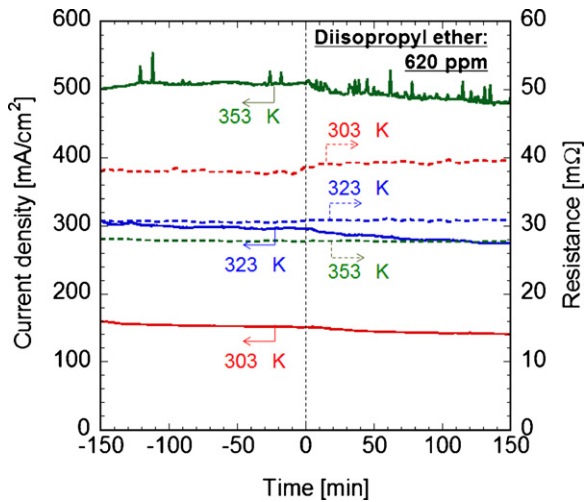


Fig. 6. Effect of the 620 ppm diisopropyl ether addition to the standard 2 M methanol on the current density and the cell resistance at different temperatures.

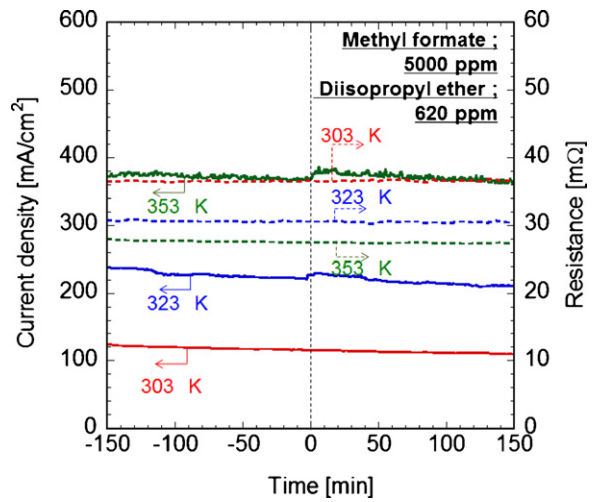


Fig. 8. Effect of the multiple impurities, 5000 ppm methyl formate and 620 ppm diisopropyl ether, added to the standard 2 M methanol on the current density and the cell resistance at different temperatures.

and 6200 ppm, respectively. Therefore, the diisopropyl ether in the 2 M methanol only slightly affected the cell performance in the concentration range from 62 ppm to 6200 ppm. The weak degradation caused by diisopropyl ether was completely regenerated by the water flushing for 1 h.

3.2. Effect of the presence of multiple impurities in the methanol solution

3.2.1. Methyl formate and diisopropyl ether

Methyl formate and diisopropyl ether, that only slightly affected the cell performance, were mixed in the 2 M methanol, and the effect of the presence of the two impurities on the cell performance was investigated. Fig. 8 shows the effect of the multiple impurities, i.e., 5000 ppm methyl formate and 620 ppm diisopropyl ether, added to the methanol solution on the current density and the cell resistance at the different temperatures. A slight increase in the current density was observed at 353 K and 323. At 303 K, no remarkable change in the current density was caused by the presence of the two impurities. Moreover, the cell resistance remained constant before and after switching to the methanol containing the impurities. The

degradation  $\phi_{60}$  was 0.00, 0.07 and 0.00 at 303 K, 323 K and 353 K, respectively, and was quite low or negligible as similar to the case of diisopropyl ether as shown in Fig. 6.

3.2.2. Methyl formate and 1-butanol

Methyl formate, which hardly affected the DMFC performance, and 1-butanol, which significantly affected the DMFC performance, were added to the methanol solution and the effect of the presence of these two impurities on the DMFC performance was investigated. The result was shown in Fig. 9. The current density suddenly decreased after the fuel was changed to the methanol containing these impurities. The trend in the current decrease was similar to that for the methanol solution containing 1-butanol as shown in Fig. 4. The degradation was calculated to be 0.54 at 303 K, 0.64 at 323 K and 0.68 at 353 K. Considering the fact that the 1000 ppm 1-butanol caused a significant degradation, 0.72 at 303 K, 0.80 at 323 K and 0.80 at 353 K, as shown in Fig. 4, the degradation between 0.54 and 0.68 for the binary impurities were somewhat lower than that of only 1-butanol, between 0.72 and 0.80, measured as a single impurity.

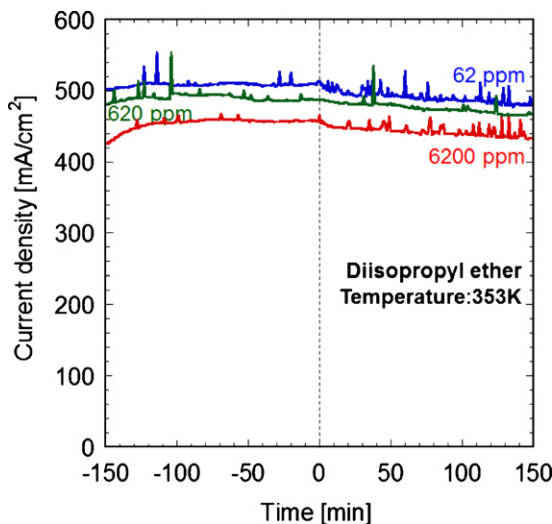


Fig. 7. Effect of the concentration of the diisopropyl ether in 2 M methanol on the current density at 353 K.

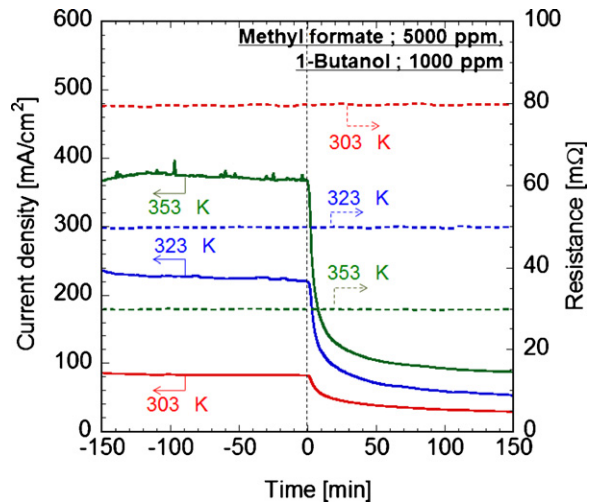


Fig. 9. Effect of multiple impurities, 5000 ppm methyl formate and 1000 ppm 1-butanol, added to the standard 2 M methanol on the current density and the cell resistance at different temperatures.

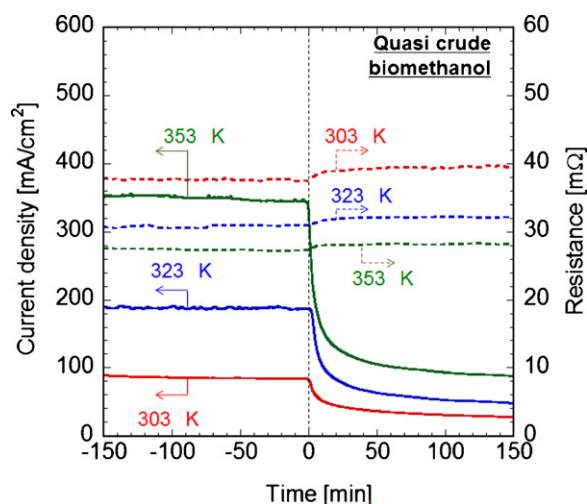


Fig. 10. Effect of introducing 2M crude bio-methanol using the quasi crude bio-methanol.

### 3.3. Effect of the quasi crude bio-methanol on the DMFC performance

Fig. 10 shows the current density measured for the methanol solution using the quasi crude bio-methanol described in Table 2. The current density decreased just after changing to the crude bio-methanol, and at the same time, the cell resistance slightly increased at all temperatures. The degradation was calculated to be 0.58, 0.67 and 0.69 at 303 K, 323 K and 353 K, respectively, and was similar to that for the two impurities, i.e., methyl formate and 1-butanol, as shown in Fig. 9, but was lower than that of the 1000 ppm 1-butanol of 0.80. As has already been mentioned, when multiple impurities were present, the degradation was lower than that of the single impurity which showed the strongest effect by the impurities. This may be due to the interaction between the different impurities on their adsorption characteristics on the catalyst.

### 3.4. Factors affecting the performance degradation in bio-methanol

The main reason for the performance degradation would be the strong adsorption of some species formed during the oxidation of the impurities on the PtRu anode catalyst and that they obstructed the smooth methanol oxidation on the catalyst. Methyl formate is known as an intermediate of the methanol oxidation [12–14], and its oxidation rate is very fast on a PtRu catalyst [15,16]. Referring to the ethanol oxidation using the PtRu catalyst, the main products are known to be acetaldehyde and acetic acid, and not CO<sub>2</sub> [17]. The rate determining step of the ethanol oxidation the lower potential is considered to be the dissociative adsorption of ethanol on Pt [18]. During the oxidation, most of the intermediates are strongly adsorbed on the Pt surface, while a part of the dissociated species like acetaldehyde may diffuse into the bulk. In the higher potential region, H<sub>2</sub>O could be activated and the resulting OH species could facilitate the incomplete ethanol oxidation to acetic acid.

By taking these previous results into account, it is considered that the dissociative adsorption of ethanol and/or intermediates would occur when ethanol was presented in the fuel as an impurity. The oxidation activities of the intermediates would be quite low, therefore, the adsorbed species occupied the active sites on the catalyst surface which caused the degradation. The oxidation of 1-butanol might occur via more complicated steps compared to that of ethanol thus providing more intermediate species with a greater molecular size, that includes some species strongly adsorbed on

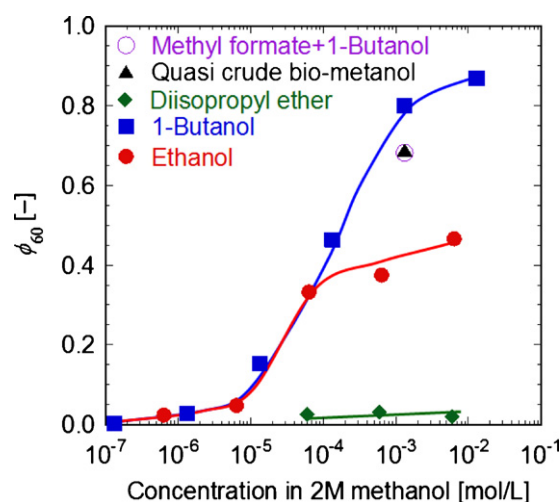


Fig. 11. Relationship between the concentration in the 2M methanol and degradation,  $\phi_{60}$ , measured at 353 K when using this compound as an impurity (methyl formate + 1-butanol and quasi crude bio-methanol were also plotted vs. the concentration of the 1-butanol).

the catalyst. Gootzen et al. reported that the adsorbate coverage obtained for 5 mM 1-butanol on platinum was 0.82, and this was considerably higher than that for the ethanol of 0.44 [19]. On the other hand, the adsorbate coverage for 1 M methanol on PtRu/C was around 0.35 [20]. These results suggest that the more strongly adsorbed species that occupied the active sites for 1-butanol and strongly adsorbed species for ethanol in the methanol solution. The degradation that could not be completely regenerated by the 1 h flushing with water would be caused by such strongly adsorbed species.

The effect of the presence of multiple impurities, shown in Figs. 8–10, would be explained by the adsorption theory that such the adsorption site is occupied based on the adsorptivity of the adsorption species in the multiple species near the surface. The stronger the adsorptivity, the higher occupied ratio of the total adsorption site. The reaction site for the methanol oxidation, in the case of multiple impurities, would be governed by the strongly adsorbed species from the 1-butanol, and it controlled the current density in the methanol solution containing the multiple impurities.

Fig. 11 shows the relationship between the impurity concentrations in the 2M methanol and the degradation  $\phi_{60}$  measured at 353 K. For the multiple impurities, i.e., methyl formate with 1-butanol (the case of Fig. 9) and the quasi crude bio-methanol (the case of Fig. 10), they were also plotted vs. the concentration of the 1-butanol in the figure. The degradation of the ethanol and 1-butanol gradually increased with the increasing impurity concentration up to  $10^{-5}$  mol L<sup>-1</sup>, and then they sharply increased followed by a gradual increase with the increasing impurity concentration. The S-shaped curve may be related to the adsorption isotherm that corresponds to the relationship between the amount of the adsorbed species and the concentration of the species. The somewhat smaller degradations observed in the multiple impurities compared to the case of the single impurity, which was strongly affected, may also be explained as a result of the competitive adsorption of the multiple adsorption species. Based on the above adsorption theory, the effect of the impurity on the degradation would be explained.

For use of the crude bio-methanol as a DMFC fuel, the removal of the harmful impurities, such as ethanol and 1-butanol, is necessary, otherwise novel catalysts, which are active for the oxidation of the impurities, are required.

#### 4. Conclusions

As an environmental friendly and economical methanol for use in a DMFC, we focused on the utilization of crude bio-methanol from woody biomass, and the effects of the impurities, i.e., ethanol, 1-butanol, methyl formate and diisopropyl ether, on the DMFC performance were investigated. The main results are as follows:

- (1) The degradation  $\phi_{60}$  showed different values depending on the impurity and its concentration. On the other hand, it was not affected by the operating temperature in the range of this study.
- (2) The  $\phi_{60}$  was low for the methyl formate, diisopropyl ether, ethanol and 1-butanol contained in the fuel as a single impurity in this order.
- (3) The  $\phi_{60}$  of the multiple impurities was slightly lower than that of the most effective impurity as a single impurity in the multiple impurity solutions.
- (4) Degradation could be regenerated by flushing the cell with water for 1 h except for the 1-butanol case.
- (5) Refining is necessary to use the crude bio-methanol as a DMFC fuel with the PtRu anode catalyst.

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