

Anode reaction mechanism and crossover in direct dimethyl ether fuel cell

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Abstract

The anode reaction mechanism and the crossover of a direct dimethyl ether fuel cell (DDMEFC) have been investigated. This was done by considering the anode products of the half-cell and DDMEFC experiments. It was found that the CO₂ current efficiency of the DDMEFC was almost 1 at 30–80 °C and that this value was higher than that of a DMFC. The main by-products of the DDMEFC were methyl formate and methanol whose amounts are negligibly small compared to CO₂. With respect to crossover, the influence of DME on the oxygen reduction reaction (ORR) was examined with a half-cell, and the amount of crossover of DME was measured while operating an actually constructed DDMEFC. From these experiments, it was found that DME does not influence the ORR as much as methanol under similar conditions. Furthermore, the amount of crossover of DME decreased with an increase in temperature and current density and it was one-half that of methanol on open circuit and at 80 °C.

The CO₂ current efficiency of the DDMEFC is higher than that of a DMFC, and the influence of crossover in the DDMEFC is less than that in the DMFC. Since the temperature dependence of the reactivity of DME is larger than that of methanol, the higher output is expected for the DDMEFC at the elevated temperature. Therefore, the DDMEFC has a promising potential as a portable power source in the future.
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1. Introduction

Recently, portable PCs and cellular telephones have been developed extensively for ubiquitous computing. Because their functions and capability are growing rapidly, it is necessary to increase the energy output of the power sources. Although the commercialized power sources (i.e., lithium and nickel metal hydride secondary batteries) have provided sufficient energy for these portable devices up to now, their output power will not catch up with such evolving devices in the near future.

Fuel cells can generate electricity as long as fuel is supplied. Their weight energy density and volume energy density

are about one order higher than those of these secondary batteries [1]. Being a liquid fuel and available as an industrial material, methanol has been considered as a candidate fuel for portable power sources. Based on these advantages, direct methanol fuel cells (DMFCs) have been studied by many researchers, and DMFCs have almost reached the practical stage [2–13]. Nevertheless, there are still serious problems remaining in commercialization of DMFCs, i.e., voltage and utility loss due to excessive fuel crossover, low activity of methanol electro-oxidation and the toxicity of methanol. Especially, the most important issue is to assure safe handling considering the toxicity of methanol for their commercialization. Thus, there might be room to consider other less toxic fuels.

Dimethyl ether (DME) that has a molecular structure similar to that of methanol has been made in mass production

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in recent years. It is easy to liquefy and has lower toxicity than methanol; also its explosion limit is narrower than that of methanol and hydrogen [14,15]. Because DME is a virtually non-toxic and environmentally friendly material, it is widely used as a compressed gas for aerosol propellants, solvents and coolants. Further, it is also expected to be a new alternative diesel fuel [14–16].

As the new fuel, considering the many advantages given above, DME would be another candidate replacing methanol for portable power sources. The fuel cell into which DME is fed directly is called a direct dimethyl ether fuel cell (DDMEFC). Because the molecular weight of DME is larger and its solubility in water is lower than those of methanol, energy loss due to fuel crossover in a DDMEFC is expected to be smaller than that in a DMFC. Although DME is less electrochemically active than methanol at 50 °C [17], the performance of the DDMEFC was almost the same as that of a DMFC under 5 atm at 130 °C [18]. Based on these facts, DME is a promising fuel for direct feeding of a fuel cell, and the DDMEFC would have potential as a portable power source.

As one of the anode by-products, traces of methanol were detected from the anode exhaust of the DDMEFC by Müller et al. [18]. On the other hand, formic acid was detected by Tsutsumi et al. under atmospheric pressure at 80 °C [19]. The amount of formic acid increased with an increase in the current density, but neither methanol nor formaldehyde was detected. Based on these results, they proposed different electro-oxidation mechanisms for DME. The former suggested that one methyl group of DME was oxidized and then hydrolyzed to form methanol by cleaving the C–O–C bond. The latter proposed that both methyl groups were oxidized simultaneously and that two COHs were formed resulting in cleavage of the C–O–C bond. However, from these reports, there has been neither a clear view of the anode products of the DDMEFC nor a clear mechanism concerning the current efficiency of converting DME into CO₂. To design catalysts for enhancing the anode reaction, it is important to analyze the anode products and clarify the anode reaction mechanism.

According to Müller et al., the crossover of DME to the cathode was typically equivalent to about 100 mA cm⁻² with Nafion®117 under 5 atm at 130 °C [18]. However, the DME concentration in the cathode outlet stream did not change when the cathode was switched from oxygen to hydrogen operation. This fact indicated that DME was not oxidized at the cathode. The amount of crossover of DME was about one-tenth that of methanol according to Tsutsumi et al. [20]. On applying a mixed gas, i.e., oxygen including 4% DME, to the cathode in a H₂/O₂ fuel cell, they examined the degradation of cell performance due to the contamination of DME under atmospheric pressure at 80 °C. They found that this amount of DME had little effect on the degradation of cell performance, and they suggested that DME was not oxidized at the cathode. On the contrary, Mench et al. indicated that both DME and intermediates from DME were oxidized at the cathode where substantial amount of DME crossed over to the cathode with Nafion®112, and the cell performance

was degraded tremendously [21]. The question of whether the DME is oxidized at the cathode remains.

In order to obtain some insight into the electro-oxidation mechanism at the DDMEFC anode, we analyzed the anode products qualitatively and quantitatively using a half-cell and operating an actually constructed DDMEFC. Furthermore, to obtain some insight into the influence of DME on the ORR, oxygen with DME or methanol was introduced to half-cells to examine the cathode behavior, and an actually constructed DDMEFC was operated to analyze the DME and CO₂ quantitatively.

2. Experimental

2.1. Half-cell experiments

2.1.1. Electro-oxidation of DME

The working electrode was made by the following method. Fifty weight percent Pt/C (N.E.CHEMCAT) was dispersed in ethylene glycol dimethyl ether (Junsei Kagaku: purity >99.0%). Five weight percent Nafion® solution (Aldrich) was added to this suspension and stirred to produce a catalyst ink (weight ratio Pt/C: Nafion® = 4:1). This ink was uniformly painted onto a gold mesh (1 cm × 1 cm, 80 mesh) to give a catalyst layer loading of 1 mg cm⁻² of Pt. Five weight percent Nafion® solution was additionally painted on the catalyst layer. After drying, the electrode was heat treated at 80 °C in N₂ atmosphere for 30 min, then at 135 °C in N₂ atmosphere for 60 min.

Half-cell experiments were conducted using a conventional three-electrode glass cell equipped with a working electrode (described above), a platinumized platinum counter electrode and a reversible hydrogen electrode (RHE) as a reference. All potentials given in this work refer to RHE. The electrolyte was 1 M (=mol dm⁻³) sulfuric acid (Junsei Kagaku analytical grade) with Milli-Q water. DME (Sumitomokasei: purity >99.0%) was saturated in the electrolyte under atmospheric pressure. To control the electrode potential, a HZ-3000 (Hokuto Denko) was used to operate the electrochemical system.

For electrochemical pretreatment, the working electrode was swept between 0.05 and 1.2 V at 1 V s⁻¹ until it reached a steady state in the DME-saturated electrolyte. Constant potential measurements were conducted at 600 mV for 600 min under bubbling DME. The temperatures were 30, 50 and 70 °C. Carbon dioxide in the anode exhaust gas was analyzed by a gas chromatograph (Shimadzu GC-8A) with a TCD detector. Porapak Q was used for its column and the carrier gas was He. The exhaust gas flow rates were measured by a film flow meter.

2.1.2. Influences of DME on ORR

The rate of ORR was compared under pure O₂ with DME and methanol added to O₂ at 30 °C in 1 M sulfuric acid. It was examined by the same apparatus described in Section

2.1.1 except for the working electrode. A bare Pt ($\text{Ø}1 \text{ mm}$; 0.89 cm^2) was used for the working electrode. To examine the effect of DME, the gas flow rates of DME and O_2 were set at 10 and $100 \text{ cm}^3 \text{ min}^{-1}$, respectively. The solubility of DME in 1 M sulfuric acid at 30°C is 0.66 M under atmospheric pressure [22] (See Table 1 in Section 3.1.1). Thus, DME would dissolve to about 0.06 M when the flowing mixture gas had the gas composition mentioned above. In order to compare the effect of DME, the methanol concentration was the same 0.06 M and $100 \text{ cm}^3 \text{ min}^{-1}$ of oxygen gas was bubbled into the solution.

For the electrochemical pretreatment, the working electrode was swept between 0.05 and 1.5 V at 1 V s^{-1} until it reached a steady state in each electrolyte. The slow scan voltammeteries (SSVs) were carried out from 1.2 to 0.5 V at a scan rate of 5 mV s^{-1} .

2.2. DDMEFC experiments

To prepare the gas diffusion electrodes (GDEs), a catalyst ink of the same composition as in Section 2.1.1 was painted uniformly onto waterproofed carbon paper (Toray TGP-H090, $5 \text{ cm} \times 5 \text{ cm}$). After drying, the electrode was heat treated at 80°C in N_2 atmosphere for 30 min, then at 135°C in N_2 atmosphere for 60 min. The catalyst loading of the anode and the cathode was 3 mg Pt cm^{-2} . Membrane-electrode assemblies (MEAs) consisting of two GDEs and Nafion[®] 112 were formed by hot-pressing (at 90°C , 0.2 MPa, for 30 s and then at 135°C , 5 MPa, for 90 s).

Fully humidified DME ($50 \text{ cm}^3 \text{ min}^{-1}$) and oxygen ($100 \text{ cm}^3 \text{ min}^{-1}$) were fed to the anode and cathode, respectively. The DDMEFC was operated under atmospheric pressure, and the cell temperature was 30, 50 and 80°C . The exhaust gases of the anode and cathode were analyzed by a GC, and the gas flow rates were measured by a film flow meter.

3. Results and discussion

3.1. Half-cell experiments

3.1.1. Anode products

In this section, CO_2 current efficiency was investigated with a half-cell at various temperatures. Fig. 1 shows the CO_2 current efficiency at 600 mV as a function of temperature. The data were taken after reaching a stable value during 400–600 min and were 0.93–0.98 and almost 1 at 30, 50 and 70°C , respectively. The CO_2 current efficiency increased with the increase in temperature. However, because the solubility of DME in 1 M sulfuric acid decreases with increased temperature as shown in Table 1, the efficiencies could not be directly compared. However, the tendency for the CO_2 current efficiency to increase with increased temperature was also seen in the methanol electro-oxidations [13,23]. Under experimental conditions similar to those of our half-

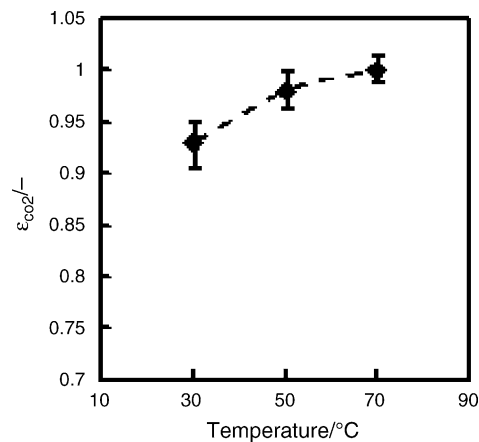


Fig. 1. Dependence of CO_2 current efficiency of DME on temperature at Pt/C in a half-cell at 600 mV in 1 M H_2SO_4 .

Table 1

DME solubility in water and 1 M sulfuric acid under atmospheric pressure

	Temperature ($^\circ\text{C}$)			
	30	40	50	60
Water	0.35	0.31	0.18	0.1
1 M H_2SO_4	0.66	0.45	0.29	0.12

cell experiments, the CO_2 current efficiency of methanol was at most 0.69 (at 25°C in 1 M methanol) after 50 min [24]. In comparing these values, the CO_2 current efficiency of DME is higher than that of methanol. Wasmus et al. showed the relative distribution of products in the DMFC at 160°C . The CO_2 relative distribution was ca. 98% [23].

3.1.2. Influence of DME on ORR

In this section, the influence of DME permeated through the membrane on the ORR was investigated with a half-cell to focus on the cathode reaction. Fig. 2 shows the polarization curves for the ORR in 1 M sulfuric acid with and without DME or methanol. The potential was swept from 1.2 to 0.5 V

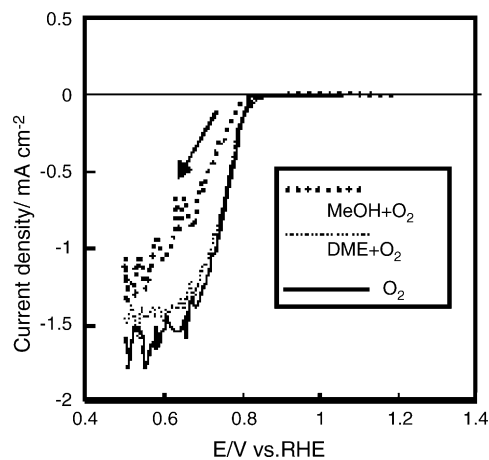


Fig. 2. Influence of DME and methanol on ORR at bare Pt in a half-cell at 30°C in 1 M H_2SO_4 .

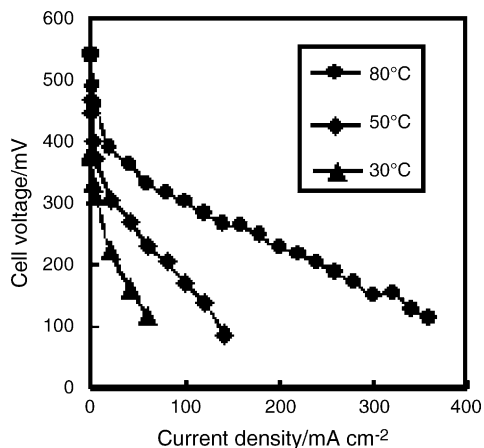


Fig. 3. Cell performance in DDMEFC under atmospheric pressure with DME/O₂ at 30, 50 and 80 °C.

at a sweep rate of 5 mV s⁻¹. The solid, the fine dotted and the dark dotted lines show the results obtained under O₂, DME + O₂ and methanol + O₂, respectively. The curve for pure oxygen was almost the same as that for DME + O₂ down to 0.75 V. In the case of MeOH + O₂, its current density was smaller than those for pure O₂ or DME + O₂. This would be caused by the methanol oxidation current that apparently reduced the oxygen reduction current; when only methanol was added to 1 M sulfuric acid, an oxidation current due to methanol oxidation appeared. Another reason supporting the above phenomenon would come from catalytic poisoning that inhibited the ORR in the presence of methanol. With respect to DME, due to its lower oxidation rate than that of methanol, only a small degradation in the oxygen reduction current was observed. As a result, this indicated that the influence of DME on the ORR was less than that of methanol.

3.2. DDMEFC experiments

3.2.1. Anode products of DDMEFC

Fig. 3 shows the cell performance of the DDMEFC, where the open circuit voltage was around 550 mV at 80 °C, and under load 200 mA cm⁻² to 230 mV was observed. The cell voltage increased when the temperature was raised. Fig. 4 shows the average CO₂ current efficiency, which increased with increased temperature. Thus, DME was dominantly oxidized to CO₂ at high temperature. This tendency corresponded with Fig. 1 for the half-cell experiments. However, the CO₂ efficiency in Fig. 4 was slightly lower than that in Fig. 1. The data in Fig. 1 were obtained by collecting the products with a half-cell, so that all the products of the anode reactions were analyzed. On the contrary, the data in Fig. 4 were obtained by collecting the products of the anode exhaust from an actually constructed DDMEFC, so that the materials that passed through the membrane to the cathode from the anode were not collected. The exhaust gas from the cathode was also analyzed to determine the mass balance of CO₂ (see Section of 3.2.2 for discussion). With respect

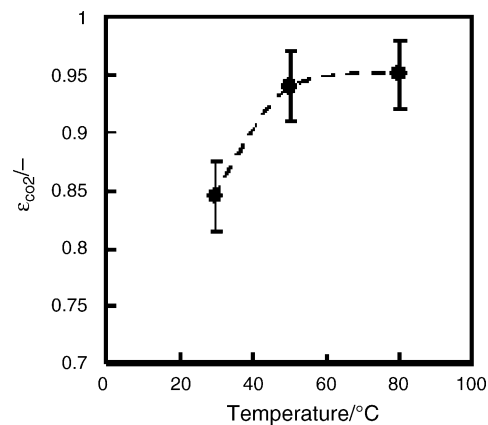


Fig. 4. Dependence of CO₂ current efficiency of DDMEFC on temperature determined by the anode exhaust.

to CO₂ crossover to the cathode in the DMFC, a certain amount of CO₂ permeated through the membrane, and that amount tended to increase with a decrease in temperature [7]. Therefore, the difference in CO₂ current efficiency between Figs. 1 and 4 might be attributed to CO₂ crossover to the cathode.

The main by-products of the DDMEFC were methanol and methyl formate. Fig. 5 shows dependence of the rate of methanol formation on the current density, and Fig. 6 shows the rate as a function of temperature. In Fig. 5, the rate did not depend on the current density and it was almost constant, while in Fig. 6, the rate increased with an increase in temperature. If methanol is produced by electrochemical reactions, the rate of formation would depend on the current density, unless the rate of formation and consumption of methanol are exactly equal. Therefore, methanol may be produced by non-electrochemical reactions. Furthermore, it may be produced by DME hydrolysis as shown in Eq. (1):

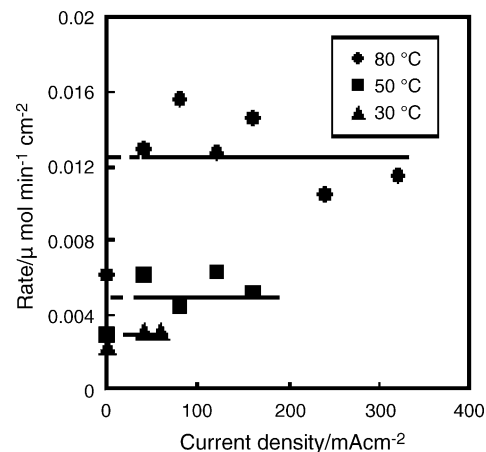
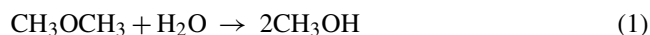


Fig. 5. Dependence of the rate of methanol formation in DDMEFC on current density determined by the anode exhaust.

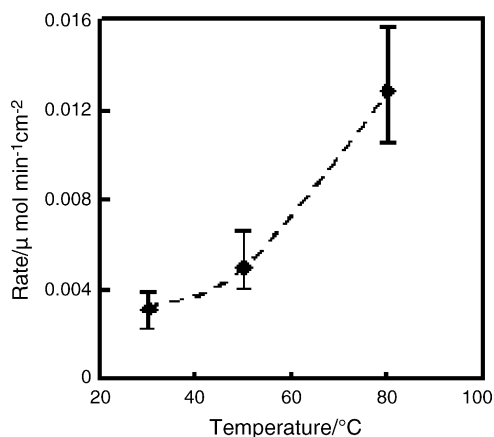


Fig. 6. Dependence of the rate of methanol formation in DDMEFC on temperature determined by the anode exhaust.

However, the amount of methanol was negligibly smaller than that of CO₂.

Fig. 7 shows the dependence of the rate of methyl formate formation on the current density, and this was nearly proportional to the current density. From this relation, it was expected that methyl formate was produced by an electrochemical reaction. Fig. 8 shows the rate as a function of temperature at 60 mA cm⁻², and the rate of its formation tended to decrease with an increase in temperature. This tendency corresponded with the rate of CO₂ generation. Namely, the rate of a by-product (i.e., methyl formate) formation decreased, while the rate of CO₂ formation increased with the increase in temperature. When the amount of the by-product was converted to current efficiency, these values were ca. 0.024, 0.017 and 0.012 at 30, 50, and 80 °C, respectively. This efficiency was far smaller than that of CO₂. As a whole, it was suggested that, at higher temperature, the rate of oxidation of methyl formate to CO₂ was more dominant than the rate of oxidation of DME to methyl formate.

The rate of formation of methanol and methyl formate had no correlation with either temperature or current density.

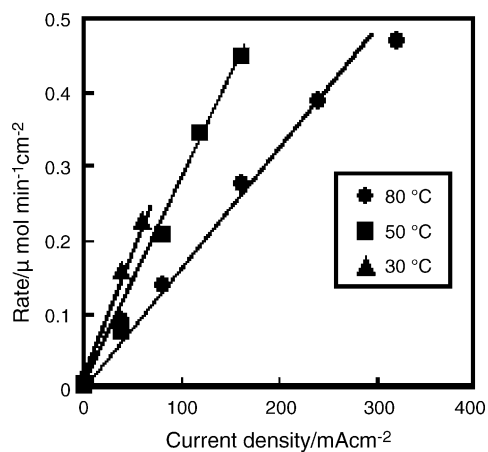


Fig. 7. Dependence of the rate of methyl formate formation in DDMEFC on current density determined by the anode exhaust.

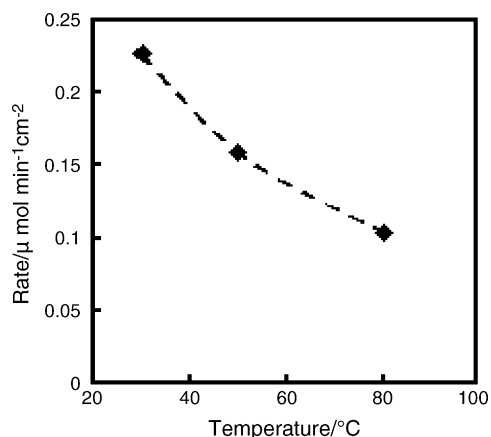


Fig. 8. Dependence of the rate of methyl formate formation in DDMEFC at 60 mA cm⁻² on temperature determined by the anode exhaust.

Therefore, the formation processes of methanol and methyl formate were expected to be independent. The formation of methanol would come from hydrolysis of DME as shown in Eq. (1). In contrast, because methyl formate was produced nearly in proportion to the current density, the formation of methyl formate was assumed to occur through the following reaction:



3.2.2. Crossover of DME in DDMEFC

In Section 3.1.2, it was indicated that DME had less effect on the ORR than methanol in the half-cell experiments. In this section, the quantity of DME on crossover is then determined under the operating conditions of the DDMEFC, and the characteristics of the crossover are explained.

To investigate the crossover, the gas stream from the cathode was analyzed by a GC as well as that from the anode. Fig. 9 shows the DME and CO₂ exhaust rates as a function of current density at 30, 50 and 80 °C. From this figure, on open circuit, the amount of CO₂ was almost 0; nevertheless, a

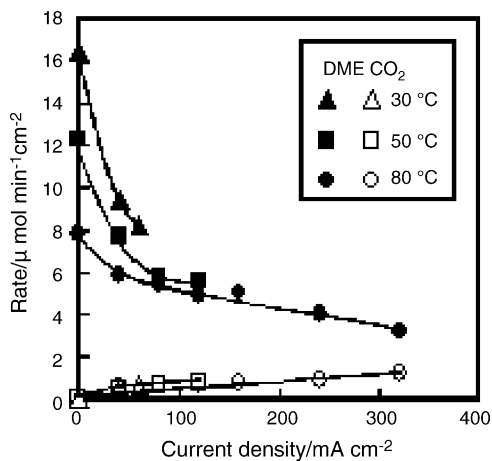


Fig. 9. Dependence of DME and CO₂ exhaust rates in DDMEFC on current density determined by the cathode exhaust.

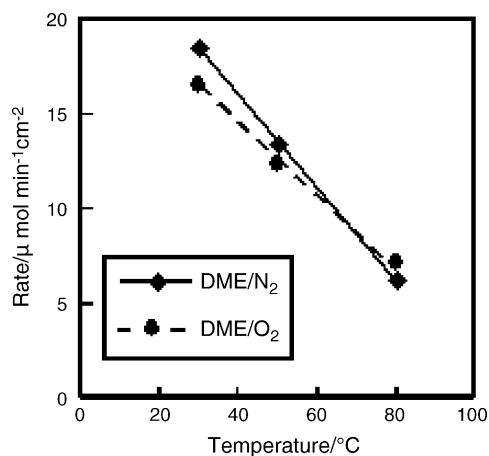


Fig. 10. Dependence of DME exhaust rates in DDMEFC on temperature determined by the cathode exhaust on feeding N₂ or O₂ into the anode.

significant amount of DME was detected at each temperature and the crossover of DME increased with a decrease in temperature. As shown in Table 1, the solubility of DME in water decreases with temperature. Therefore, based on the characteristics of crossover in the DDMEFC, the solubility of DME in a humid membrane was deduced to decrease with temperature in a similar way. In addition to this effect, the increase in water vapor pressure with temperature was assumed to decrease the ratio of DME gas in the anode stream. As shown in Fig. 10, when N₂ was introduced into the cathode chamber instead of O₂ to prevent the possibility of oxidation of DME, almost the same amount of DME was detected under N₂ and O₂ in the cathode exhaust.

On the contrary, in the DMFC, the amount of methanol crossover increases with an increase in temperature [7,8]. This was attributed to an increase in the diffusion coefficient of methanol with temperature. Comparing the amount of crossover in the DDMEFC with the DMFC, DME was estimated to be one-half that of methanol on open circuit and at 80 °C [8].

The amount of crossover decreased with an increase in the current density. DME on the surface of the anode would be consumed more with an increase in the current density, and the concentration of DME would then decrease. Furthermore, the water produced at the cathode also inhibits the gas (DME) permeation to reduce its crossover more with an increase in the current density.

The total CO₂ current efficiency from the anode and cathode exhausts was slightly higher than that in the half-cell experiments. The difference would be due to the oxidation of DME at the cathode. Based on this result, it was deduced that most of the CO₂ was produced at the anode and part of it permeated through the membrane to the cathode (Fig. 11).

Finally the performance of the DDMEFC and the DMFC is compared. At low temperature such as 30 °C, the anodic oxidation of DME takes place more slowly than methanol and the power density of the DDMEFC is lower than that of the DMFC. However, the dependence of the reactivity

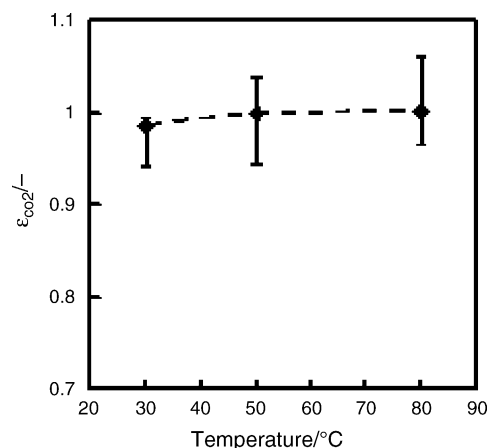


Fig. 11. Dependence of the total CO₂ current efficiency in DDMEFC determined by the anode and cathode exhausts.

of DME on temperature is larger with DME than methanol [25], therefore the cell performance and the power density will much increase with increase of temperature. Further, the higher cathode potential with the DDMEFC is preferable for the fuel cell operation than that with the DMFC.

Actually at 130 °C, the power density of the DDMEFC almost reached the data of the DMFC [18].

Considering the facts found in this paper, the DDMEFC would be one of the promising candidates for the energy conversion devices.

4. Conclusions

The electro-oxidation mechanism of the anode of a DDMEFC and the crossover were investigated. The CO₂ current efficiency of the anode was found to be nearly 1. As the main by-products, methyl formate and methanol were detected by GC. The amount of methyl formate was far smaller than that of CO₂, while the amount of methanol was negligibly smaller than that of CO₂. The CO₂ current efficiency of the DDMEFC is higher than that of a DMFC. The amount of DME crossover decreased with an increase in the temperature, and it was one-half that in the DMFC on open circuit and at 80 °C. Additionally, in the DDMEFC, permeated DME was less oxidized at the cathode than methanol was in the DMFC.

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