

# *I*–*V* characteristics of a direct type fuel cell using acetaldehyde as a fuel

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## Abstract

*I*–*V* characteristics were investigated for a direct type fuel cell with Pt–Ru catalyst, using acetaldehyde aqueous solution as a fuel. The cell voltage decreased from 0.26 to 0.19 V at 20 mA cm<sup>−2</sup> as the fuel concentration increased from 0.1 to 1 mol dm<sup>−3</sup>. This result was compared with the data obtained with ethanol aqueous solutions. The cell voltage increased from 0.19 to 0.24 V at 20 mA cm<sup>−2</sup> as the concentration of ethanol increased from 0.1 to 1.0 mol dm<sup>−3</sup>. The anode and cathode overvoltages were measured using a dynamic hydrogen electrode as a reference electrode to investigate the origin of the voltage drop observed with acetaldehyde solutions. It was found that the opposite relation between the cell voltage and the fuel concentration was originated in the anode polarization. It is confirmed that the oxidation process of acetaldehyde to carbon dioxide with Pt–Ru catalyst is different from that of ethanol to acetaldehyde.

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**Keywords:** DMFC; Ethanol; Acetaldehyde; DEFC; Carbon dioxide

## 1. Introduction

Direct type fuel cells working with liquid fuels are highly promising, particularly direct ethanol fuel cells (DEFCs) have attracted special interest recently, and several investigations have been reported [1–8].

Electrocatalytic oxidation of ethanol using platinum or platinum alloy catalyst has been investigated [9–13], and the products formed by the electrocatalytic oxidation of ethanol and the oxidation reactivity of ethanol were discussed from many aspects. Iwasita and Pastor studied the adsorb behavior of ethanol on a polycrystalline platinum using a differential electrochemical mass spectroscopy (DEMS) and FTIR [9]. They reported many adsorbed species formed by the oxidation of ethanol and observed the evolution of CO<sub>2</sub>. Souza et al. reported the performance of a co-electrodeposited PtRu catalyst for the oxidation of ethanol using in situ FTIR and concluded that CO<sub>2</sub> was the main product [10]. Fujiwara et al. also investigated the oxidation reactions of ethanol on a PtRu catalyst using DEMS, and concluded that ruthenium promotes the oxidation reactions of chemical species formed from the ethanol [11]. Camara et al.

reported that the oxidation reaction of ethanol was sensitive to the atomic ratio of platinum and ruthenium [12]. Spinacé et al. developed a deposition process of platinum on a Ru/C catalyst which was effective for the oxidation of ethanol [13].

Because of the main intermediate species, it is necessary to investigate the influence of acetaldehyde in a DEFC system. Electrocatalytic oxidation of acetaldehyde has been investigated using Pt alloy catalysts recently by Kokoh et al. [14]. They reported that the main products were acetic acid, formic acid and CO<sub>2</sub>. The measurement was not made by using a membrane electrode assembly (MEA) but perchloric acid solution.

Rodríguez et al. investigated the acetaldehyde on Pt (1 1 1) and Pt (1 0 0) surfaces using in situ FTIR [15]. They reported that the adsorbed species on the catalyst did not form acetic acid. Silva-Chong et al. compared platinum electrode with rhodium from the viewpoint of the reactivity of the oxidation of acetaldehyde using DEMS [16]. They showed that CO<sub>2</sub> was the main product for both catalysts in the acetaldehyde solution and observed that the yield of the products depended on the adsorption potential. Recently, we reported about the anode products in the DEFC working process with a circulating fuel system [8]. The used MEA consisted of PtRu anode catalyst and Nafion 117® membrane. The main anode products observed were acetaldehyde and CO<sub>2</sub>.

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In this report,  $I$ - $V$  characteristics of a direct type fuel cell using a PtRu anode catalyst and acetaldehyde aqueous solution as a fuel are investigated. Anode and cathode overvoltages are observed by using a dynamic hydrogen electrode (DHE) [17,18] to investigate the difference in  $I$ - $V$  characteristics between acetaldehyde and ethanol.

## 2. Experimental

The membrane electrode assembly (MEA) used for the measurement consists of a PtRu anode catalyst (Pt loading:  $2 \text{ mg cm}^{-2}$ , Ru loading:  $1 \text{ mg cm}^{-2}$ ), a Pt cathode catalyst (Pt loading:  $2 \text{ mg cm}^{-2}$ ) and a Nafion 117<sup>®</sup> membrane whose thickness is  $180 \mu\text{m}$  (Electrochem. Co.). The concentrations of acetaldehyde and ethanol aqueous solutions were  $1.0 \text{ mol dm}^{-3}$  (M), 0.5 and 0.1 M. The cell temperature and fuel flow rate were  $80^\circ\text{C}$  and  $5.0 \text{ ml min}^{-1}$ , respectively. Oxygen was humidified at  $80^\circ\text{C}$  and supplied at a rate of  $50 \text{ ml min}^{-1}$  as a cathode gas. No backpressure was applied to the fuel and oxygen feed systems. The fuel solution was circulated through the anode compartment and a fuel reservoir of 100 ml. The detail of the experimental set up is shown in our previous report [8].

Anode and cathode overvoltages were measured using a DHE as a reference electrode. AuPd alloy foil was used for the electrode material, considering the adsorption of hydrogen to palladium. The applied voltage and current density of the DHE were  $1.2 \text{ V}$  and  $4 \text{ mA cm}^{-2}$ , respectively. The electrodes of the DHE were placed on the membrane of the MEA. The size of the active area of the DHE was  $5 \text{ mm} \times 5 \text{ mm}$ . The distance from the edge of the electrode of the MEA to the electrode of the DHE was  $3 \text{ mm}$ .

## 3. Results and discussion

### 3.1. Relation between $I$ - $V$ characteristics and acetaldehyde concentrations

The  $I$ - $V$  and  $I$ - $P$  curves measured with acetaldehyde solution are shown in Fig. 1. It is clearly shown that the maximum power density decreases as the concentration increases. This relation has not been reported. The maximum power density marks high value at very low concentration of acetaldehyde. A power density of  $5.8 \text{ mW cm}^{-2}$  was observed at  $30 \text{ mA cm}^{-2}$  using a 0.1 M solution, while in the case of a 1.0 M solution, the maximum power density is  $4.0 \text{ mW cm}^{-2}$  at  $30 \text{ mA cm}^{-2}$ . The cell voltage drops from 0.26 to 0.19 V at  $20 \text{ mA cm}^{-2}$  as the concentration increased from 0.1 to 1.0 M. The cell voltage for 0.1 M solution drops sharply in the higher current density region over  $35 \text{ mA cm}^{-2}$ , because of the mass transport limitation.

The open circuit voltages are shown in Table 1. The open circuit voltage increased with the concentration of acetaldehyde.

### 3.2. Comparison with the ethanol data

The  $I$ - $V$  curves measured with ethanol fuel are shown in Fig. 2. The current is related to the oxidation of ethanol to acetaldehyde. Although the cell was operated in the same con-

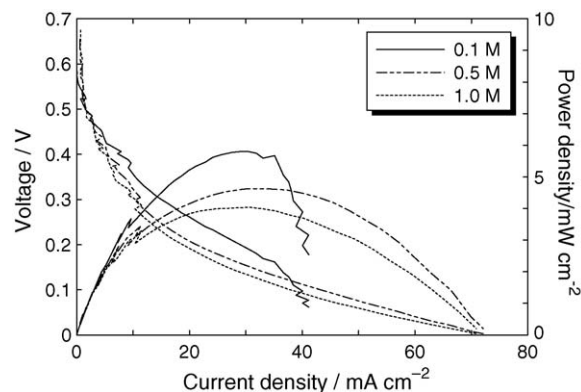


Fig. 1.  $I$ - $V$  and  $I$ - $P$  curves obtained with acetaldehyde solutions for different concentrations. Anode catalyst: PtRu (Pt loading:  $2 \text{ mg cm}^{-2}$ , Ru loading:  $1 \text{ mg cm}^{-2}$ ), cathode catalyst: Pt (Pt loading:  $2 \text{ mg cm}^{-2}$ ), temperature:  $80^\circ\text{C}$ , fuel flow rate:  $5.0 \text{ ml min}^{-1}$ , cathode gas:  $\text{O}_2$  (humidified),  $\text{O}_2$  flow rate:  $50 \text{ ml min}^{-1}$ .

Table 1  
Open circuit voltages measured as a function of concentrations

Concentration (M)	Open circuit voltage (V)	
	Ethanol	Acetaldehyde
0.1	0.626	0.638
0.5	0.612	0.655
1.0	0.563	0.675

dition as the case of acetaldehyde, the power increased as the ethanol concentration increased. The power density had the maximum value of  $4.6 \text{ mW cm}^{-2}$  at  $20 \text{ mA cm}^{-2}$  for 0.1 M solution, while with 1.0 M solution, the maximum value was  $5.4 \text{ mW cm}^{-2}$  at  $30 \text{ mA cm}^{-2}$ . This relation between the power density and fuel concentration obviously differs to the results with acetaldehyde solutions. This result suggests that the oxidation process from ethanol to acetaldehyde on PtRu catalyst differs to that of acetaldehyde to  $\text{CO}_2$ .

The open circuit voltages for ethanol solutions are compared in Table 1 with those for acetaldehyde solutions. The open circuit voltage with the ethanol solution decreases as the concentra-

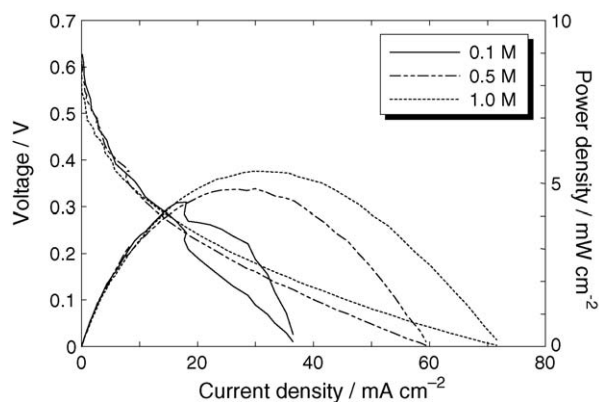


Fig. 2.  $I$ - $V$  and  $I$ - $P$  curves obtained with ethanol solutions for different concentrations. The MEA and the operating conditions are the same as the case of acetaldehyde.

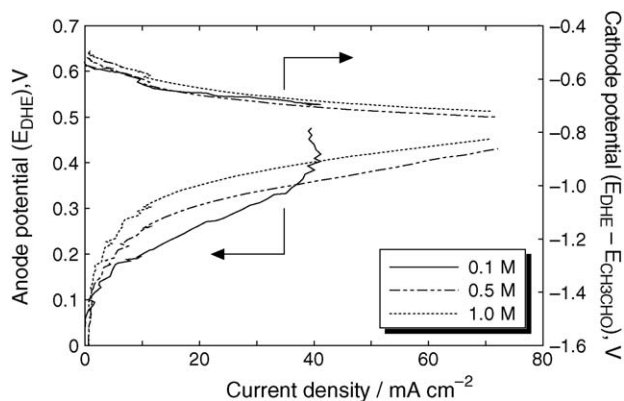


Fig. 3. Anode and cathode potentials measured for different concentrations of acetaldehyde. The vertical axis of cathode potential is scaled from the EMF of acetaldehyde ( $E_{\text{CH}_3\text{CHO}} = 1.176 \text{ V}$ ).

tion increases, which is expected to be the results of ethanol crossover. This reduction in open circuit voltage is not observed in the case of acetaldehyde, which suggests a small crossover.

### 3.3. Overvoltage measurement

Anode and cathode overvoltages for acetaldehyde and ethanol solutions are measured to investigate the origin of the voltage drop seen in Figs. 1 and 2. Fig. 3 shows the overvoltages obtained with acetaldehyde solutions for various concentrations. The anode overvoltages increase rapidly as the current density increases. It is clearly shown that the anode overvoltage for thicker solution is larger than that for thinner solution, i.e., 0.26 V for 0.1 M solution and 0.35 V for 1.0 M solution at  $20 \text{ mA cm}^{-2}$ . Adsorption of acetaldehyde at high concentration to the co-catalyst (Ru) is a possible mechanism to explain the increase in the anode overvoltage. The relation between anode overvoltage and concentration is also investigated for ethanol solution. Fig. 4 shows the overvoltages measured with ethanol solution. The anode overvoltage decreases as the concentration of ethanol increases, i.e., 0.31 V for 0.1 M solution and 0.27 V for 1.0 M solution at  $20 \text{ mA cm}^{-2}$ .

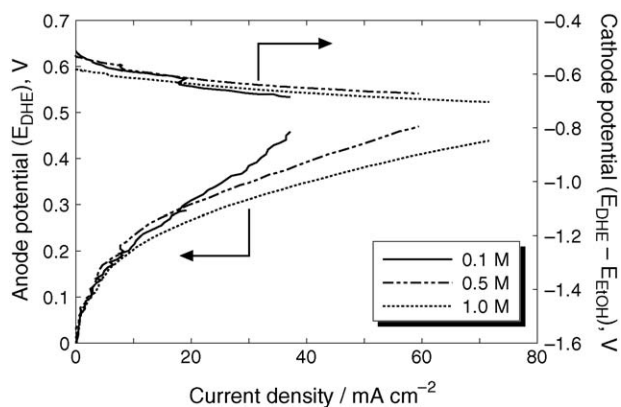


Fig. 4. Anode and cathode potentials measured for different concentrations of ethanol. The vertical axis of cathode potential is scaled from the EMF of ethanol ( $E_{\text{EtOH}} = 1.145 \text{ V}$ ).

The cathode overvoltages for acetaldehyde and ethanol solutions are also compared. It is shown by comparing Figs. 3 and 4, that the slope of the cathode overvoltage for acetaldehyde is slightly larger than that for ethanol solution. No apparent difference was observed in the cathode overvoltages between acetaldehyde and ethanol. The large cathode overvoltage for the thick ethanol solution indicates the crossover of ethanol. The anode overvoltage is obviously larger than the cathode overvoltage for both solutions. The anode overvoltage is the main factor of the difference in  $I$ - $V$  characteristics between acetaldehyde and ethanol solutions.

## 4. Conclusion

The  $I$ - $V$  characteristics and overvoltages are investigated for a direct type fuel cell with acetaldehyde solution and Pt–Ru catalyst. A similar measurement was made with ethanol solution as a reference. An opposite relation between the power density and the concentration of the fuel was observed in the case of acetaldehyde. This relation was found to be originated to the increase in anode overvoltage in the acetaldehyde cell. From the analysis of the experimental data, it is concluded that the anode reaction condition must be considered to avoid the considerable increase in the concentration of the resulting acetaldehyde, when we develop a high performance DEFC with Pt–Ru catalyst which converts the chemical energy to electric energy through the reaction from ethanol to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

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