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Electro-oxidation of mixed reactants of ethanol and formate on Pd/C in alkaline fuel cells

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ABSTRACT

Direct ethanol fuel cells have attracted attention as an alternative energy technology due to several advantages such as high theoretical energy density and abundant supply of ethanol. In spite of the advantages, commercialization of direct ethanol fuel cells is hampered by the relatively low performance caused by its slow oxidation kinetics and difficulty of complete oxidation. In this study, formate, which has relatively faster oxidation kinetics, was mixed with ethanol to compensate the latter's sluggish kinetics. Effects of pH, concentration, scan rate, and temperature on the mixed reactants oxidation on Pd were investigated by electrochemical experiments such as potential sweep and potentiostatic methods. Furthermore, the potential of the mixed reactants as fuel was evaluated by single cell experiments. As a result, we demonstrate that mixing formate with ethanol results in enhanced power performance in a single cell system.

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1. Introduction

Direct ethanol fuel cells (DEFCs) have attracted a lot of attention to replace direct methanol fuel cells, which is the most studied among direct liquid fuel cells [1,2]. Ethanol is less toxic than methanol and when ethanol is completely oxidized, it could produce 12 electrons per each mole of ethanol. It is really impressive number because of lower value from formate (2e⁻) and methanol (6e⁻). In addition to these advantages, the mass production of ethanol from lignocellulosic biomass, especially agricultural waste biomass, is highly possible [3].

Pd has been known as a less active electrocatalyst toward ethanol oxidation in acidic media, whereas shows distinct catalytic activity in alkaline media [4–7]. The outstanding ethanol oxidation of Pd is resulted from less strongly adsorbed intermediates formed on the Pd than Pt [8]. It is clearly presented based on the understanding of the small hysteresis in the forward and backward scans in cyclic voltammogram on Pd [6]. In spite of the excellent catalytic activity of Pd, DEFCs still have low power output due to the slow oxidation kinetics and difficulty of complete oxidation and thus, it is needed to improve the oxidation kinetics of ethanol for en-

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hancing performance in DEFCs. To this end, a number of scientists have focused on the development of better Pd-based electrocatalysts, applying various approaches of modification of catalyst morphology, alloying metals/metal oxides and the usage of alternative carbon supports [2–4,8–21]. However, the high onset potential is still challenged which should be solved for high power output of DEFCs. The kinetics of ethanol oxidation is strongly related to the surface OH or OH⁻, since it lowers the activation energy of each step in ethanol oxidation [22,23]. Since potential for surface OH adsorption is fixed, it is hard to expect that great improvement in DEFCs performance by previous approach developing electrocatalyst which reduces overpotential of OH adsorption. Thus, collaborating with another approach is needed to solve the challenges.

Of late, formate oxidation on Pd in alkaline fuel cells has been studied [24–29] and according to previous study reported by Haan et al., formate shows relatively fast oxidation kinetics. Therefore, we assume that formate could compensate slow kinetics of ethanol oxidation, resulting in relative high current density of fuel mixture at low overpotential and finally high power density.

In this paper, we tried to introduce novel approach of combination between ethanol and formate to overcome the limitation of ethanol oxidation. To support our hypothesis, electrochemical characteristics of fuel mixture on Pd with various experiment conditions were intensively investigated and its possible application in a single fuel cell system was carried out.

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Fig. 1. Cyclic voltammograms of 60 wt% Pd/C at scan rate of 50 mV/s (1000 rpm) in 0.5 M phosphate buffer solutions containing (a) 50 mM ethanol and (b) 50 mM HCOOK, respectively. The pH was controlled by proper combinations of KH₂PO₄, K₂HPO₄, and K₃PO₄.



Fig. 2. Comparison among cyclic voltammograms of 60 wt% Pd/C at scan rate of 50 mV/s in 1 M KOH containing various ratios of ethanol to HCOOK (1:0, 4:1, 3:2, 2:3, 1:4, and 0:1). The total mole concentration of mixture of ethanol and HCOOK was fixed to 50 mM.

Table 1. Apparent activation energy, calculated from Fig. 5, for 50 mM ethanol and 50 mM HCOOK, respectively, at various voltages of -0.5, -0.4 and -0.3 V.

	<i>E</i> _a (50 mM EtOH)	E _a (50 mM HCOOK)
-0.5 V	12.08 kJ/mol	5.75 kJ/mol
-0.4 V	5.82 kJ/mol	7.89 kJ/mol
-0.3 V	4.11 kJ/mol	9.67 kJ/mol

2. Experimental

All electrochemical measurements were performed using a three-electrode system connected to a potentiostat/galvanostat (Biologic, VSP). For the working electrode, catalyst ink was prepared by 10 mg catalyst (Premetek Co., 60 wt% Pd/Vulcan XC-72, 60 wt% Pt/ Vulcan XC-72) in a mixture of 10 μ L of nafion solution (Sigma-Aldrich, 10 wt%), 2.5 mL of distilled water (18.2 MΩ), and 2.5 mL dimethylformamide (Junsei). The catalyst ink was sufficiently sonicated until it was well dispersed. 20 μ L of the well-dispersed catalyst ink was dropped onto a rotating glassy carbon disk electrode (0.196 cm²) using a micro-pipet so that the amount of the catalysts on the electrode was about 204 μ g/cm². Pt wire and Hg/HgO were used as counter and reference electrodes, respectively. The potential for Hg/HgO reference electrode, which was measured in H₂ saturated 1 M KOH, was 0.097 V [30,31].

Table 2. Diffusion coefficients and the number of electrons, calculated from Fig. 6, for various ratios of ethanol to HCOOK (1:0, 4:1, 3:2, 2:3, 1:4 and 0:1). The total mole concentration of mixture of ethanol and HCOOK was fixed to 50 mM.

Electrolyte	Diffusion coefficient $(10^{-7} \text{ cm}^2/\text{s})$	# of electron
50 mM EtOH	2.20	4
40 mM : 10 mM	3.05	3.27
30 mM : 20 mM	3.90	2.81
20 mM : 30 mM	4.74	2.47
10 mM : 40 mM	5.59	2.31
50 mM HCOOK	6.44	2

To investigate effect of pH on the oxidation of ethanol and formate cyclic voltammograms (CVs) were recorded with a rotating speed of 1000 rpm in various electrolytes of which the pH values were 8.64, 10.66, and 12.22. The pH was controlled by a buffer solution using appropriate amounts of KH_2PO_4 , K_2HPO_4 , and K_3PO_4 (Sigma-Aldrich). The buffer solution and rotating the electrode were applied to minimize the pH difference between electrode surface region and bulk solution.

For oxidation behavior of mixed reactants of ethanol and formate, various ethanol to formate ratios of 1:0, 4:1, 3:2, 2:3, 1:4 and 0:1 were prepared with supporting electrolyte of 1 M KOH (Sigma-Aldrich). All solutions were saturated with N₂ to minimize the effect cathodic current by oxygen reduction reaction. The concentration for all the ratios of ethanol to formate was fixed at 50 mM. CVs were performed at various scan rates of 20, 30, 40, and 50 mV/s at 298 K to investigate the transport characteristics of the mixed reactants and were conducted at various temperatures of 298, 308, and 318 K to obtain the apparent activation energy. The temperature was controlled by circulation of ethylene glycol flowing into a water jacket of the electrochemical cell. In addition to CVs, chronoamperograms (CAs) at various voltages of -0.5, -0.4, -0.3, and -0.2 V (vs. Hg/HgO) were obtained at 298 K.

In order to minimize effect of impurities on the electrode surface, a cleaning process, which was performed by voltammetric cycling from -0.95 to 0.4 V (vs. Hg/HgO) at 100 mV/s for 50 cycles, was conducted before every electrochemical experiments [32].

For fuel cell experiments, the 4 cm^2 of membrane electrode assembly (MEA) was prepared as follows. Pd/C (Premetek Co., 60 wt% Pd/Vulcan XC-72) and Pt/C (Tanaka Co., 46.7 wt% Pt/Ketjen black) of $1 \text{ mg}_{metal}/\text{cm}^2$ were loaded on the plain carbon paper (Toray, TGPH-060) for anode and cathode, respectively, by conventional spraying method. Anion exchange resin (Tokuyama Co., AS-4) was also sprayed together with the catalysts. An anion exchange

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