

## Porous/Disk-dual Microelectrode: Preparation and Electrochemical Detection of Methanol Electrooxidation Product at Pt/C Powder Electrocatalyst

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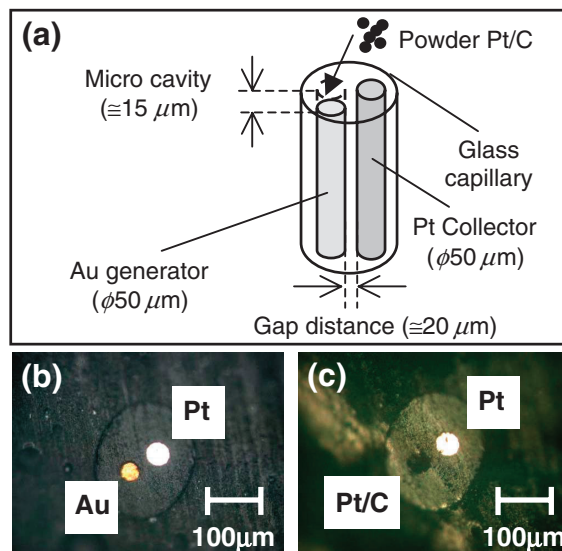
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In this study, we propose a novel porous/disk-dual microelectrode for the electrochemical detection of reaction products/intermediates that originate from methanol electrooxidation at a powder electrocatalyst. We have succeeded in detecting reaction products as a product of methanol electrooxidation generated at the Pt/C powder for the first time.

The methanol electrooxidation mechanism, i.e., the study of reaction products/intermediates, has been investigated using many techniques (e.g., mass spectroscopy,<sup>1,3</sup> infrared spectroscopy,<sup>4,5</sup> and fluorometry<sup>6</sup>). For electrochemical methods, only the detection of the reaction product using an interdigitated Pt microarray electrode has recently been reported.<sup>7</sup> However, with regard to the Pt/C powder electrocatalyst for practical uses in direct methanol fuel cells (DMFCs), no electrochemical technique for studying methanol oxidation products/intermediates has been developed. In this work, we have constructed a novel electrode of porous/disk-dual microelectrode (P/D-ME) that combines the features of a porous microelectrode (PME)<sup>8</sup> for powder materials and those of dual microelectrodes.<sup>9,11</sup> Using the P/D-ME, we have successfully detected protons as a product of methanol electrooxidation generated at the Pt/C powder electrocatalyst.

Figure 1 shows a schematic illustration and optical micrographs of the tip of P/D-ME. As illustrated in Figure 1a, Au wire ( $\phi 50 \mu\text{m}$ ) and Pt wire ( $\phi 50 \mu\text{m}$ ) were embedded in the P/D-ME tip as a generator electrode and a collector electrode, respectively. First, a theta glass capillary (Harvard Apparatus Ltd., TGC150-10) was pulled with a pipette puller (Model PN-30, Narishige) to obtain a thin septum thickness of theta glass so that the two electrodes can be settled closely. The theta glass, named for its resemblance to the Greek letter theta when viewed from the capillary end, performs as an electric insulator for the two wires. Au and Pt wires were separately inserted into the capillary and then heat-sealed by decompressing the glass inside. The tip of the glass capillary was reinforced with epoxy cement (Araldite<sup>®</sup>, Nichiban Co.). By using rapping films (Sumitomo 3M), the tip of the P/D-ME was polished to a mirror finish. Subsequently, the Au generator was etched in 1 M HCl aq solution with a current density of  $150 \text{ mA cm}^{-2}$  for 10 min,<sup>8</sup> resulting in a cavity as illustrated in Figure 1a. The depth of this formed microcavity was measured using a laser microscope (OLS-1200, Olympus). Unless otherwise stated, a P/D-ME with a cavity depth of  $15 \mu\text{m}$  was used. By packing Pt/C (Pt 20 wt %, elerochem Co.) or Pt/C (Ketjen) (Pt 46.8 wt %, Tanaka Kikinokoku) powder electrocatalyst in the microcavity of the generator, electrochemical measurements were carried out. Figure 1b and 1c

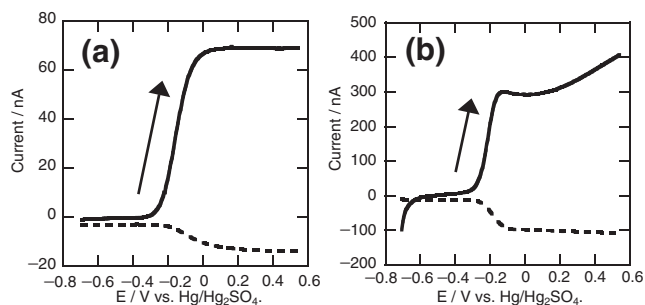


**Figure 1.** Schematic illustration (a) and optical micrographs of P/D-ME at the tip packed with (c) and without (b) Pt/C.

show the optical micrographs of P/D-ME before and after packing the Pt/C, respectively.

Current-potential ( $I-E$ ) curves were measured in a 5 M  $\text{CH}_3\text{OH} + 0.1 \text{ M H}_2\text{SO}_4$  or 10 mM  $\text{K}_4[\text{Fe}(\text{CN})_6] + 0.5 \text{ M KNO}_3$  solution by utilizing a bi-potentiostat (BS-1, BAS). A Pt wire and a  $\text{Hg}/\text{Hg}_2\text{SO}_4$  were used as a counter electrode and a reference electrode, respectively. The electrolytic solution was deaerated prior to the electrochemical measurements. All the measurements were conducted at room temperature.

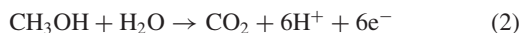
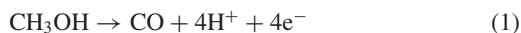
Figure 2a shows  $I-E$  curves at P/D-ME with an electrode gap distance of  $20 \mu\text{m}$  without Pt/C packing. Figure 2b shows  $I-E$  curves at the same P/D-ME packed with Pt/C (Pt 20 wt %) both in 10 mM  $\text{K}_4[\text{Fe}(\text{CN})_6] + 0.5 \text{ M KNO}_3$ . While the generator potential was swept toward the anodic direction (solid line), the collector potential was fixed at  $-0.7 \text{ V}$  (dotted line). The  $x$  axis represents the electrode potential of the generator. In Figure 2a, both the Au generator and Pt collector responses show limiting current, which is one characteristic behavior of the microelectrode.<sup>12</sup> On the basis of the ratio of the limiting current, the collection efficiencies of these P/D-MEs were estimated to be about 0.136 (without Pt/C) and 0.186 (Pt/C containing). This difference in collection efficiency is considered to be due to the difference in the geometric structure of the Au disk and the powder Pt/C. On the other hand, the collection efficiency becomes almost 0 at a P/D-ME with a gap distance of approxi-



**Figure 2.**  $I$ - $E$  curves at P/D-ME packed with (b) Pt/C (Pt 20 wt %) and without (a) Pt/C in 10 mM  $K_4[Fe(CN)_6]$  + 0.5 M  $KNO_3$ . Pt collector potential was fixed at  $-0.7$  V vs  $Hg/Hg_2SO_4$ . Solid line: Au (a) or Pt/C (b) generator. Dotted line: Pt collector. Scan rate:  $20$   $mVs^{-1}$ .

maturity  $80$   $\mu m$ . It is therefore deduced that the P/D-ME requires a minimum gap distance for the detection of reaction products. In the following measurement of methanol electrooxidation, P/D-ME with a gap distance of  $20$   $\mu m$  was employed.

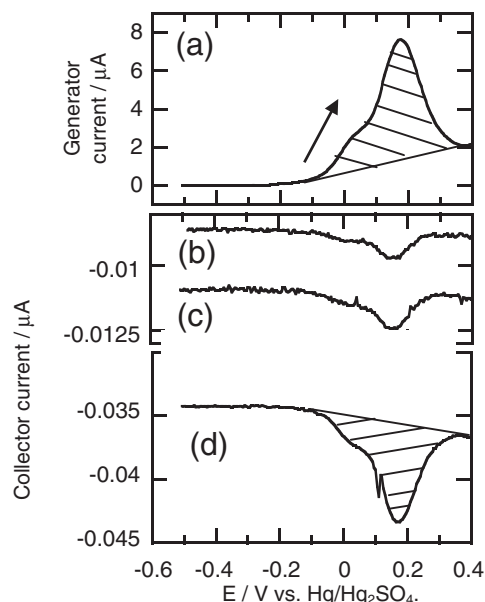
Figure 3 shows  $I$ - $E$  curves at the P/D-ME containing Pt/C (Pt 46.8 wt %) in  $5$  M  $CH_3OH$  +  $0.1$  M  $H_2SO_4$ . The Pt/C generator potential was swept toward the anodic direction, and the Pt collector potential was fixed at various potentials of  $-0.6$ ,  $-0.65$ ,  $-0.7$  V (vs  $Hg/Hg_2SO_4$ ). When the Pt collector potential is fixed at  $-0.6$  and  $-0.65$  V, the collector current shows a negative current response corresponding to the methanol-electrooxidation-based Pt/C generator current. However, these intensities of the collector response are small and noisy. In contrast, when the collector potential is fixed at  $-0.7$  V as negative as the hydrogen evolution region, the collector current shows an obvious mirror response of the generator current. In the previous report,<sup>7</sup> it is proven that the collector current response indicates a reduction current of proton produced by methanol electrooxidation at the Pt generator in addition to the hydrogen evolution background current. From the results shown in Figure 3, methanol electrooxidation takes place at the Pt/C generator according to Eqs 1 and 2.<sup>5</sup> Then, the proton generated at the Pt/C generator diffuses to the neighboring Pt collector over the gap distance of  $20$   $\mu m$ ; the generated protons are reduced at the Pt collector on the basis of Eq 3.



Next, we calculated the collection efficiency of the P/D-ME ( $N_{P/D-ME}$ ) as defined by

$$N_{P/D-ME} = (Q_{Collector}/Q_{Generator}) \times 100.(%) \quad (4)$$

Here,  $Q_{Collector}$  represents the charge passed by the reduction reaction at the Pt collector by subtracting the background.  $Q_{Generator}$  is the charge of the oxidation reaction at the Pt/C generator. Each  $Q$  is calculated by integrating the peak current (shaded area in Figure 3). As a result of the calculation, the magnitude of  $N_{P/D-ME}$  is known to be  $0.10\%$ . This value can be appropriate when we consider the  $N_{P/D-ME}$  of interdigitated microarray electrode (IDAE)<sup>7</sup> and the difference of geometric structure between IDAE and P/D-ME.



**Figure 3.**  $I$ - $E$  curves at the P/D-ME packed with Pt/C (Pt 46.8 wt %) in  $5$  M  $CH_3OH$  +  $0.1$  M  $H_2SO_4$ . (a) Pt/C generator. Collector potential was fixed at: (b)  $-0.6$  V, (c)  $-0.65$  V, and (d)  $-0.7$  V (vs  $Hg/Hg_2SO_4$ ). Scan rate:  $20$   $mVs^{-1}$ .

Consequently, we have developed a novel electrode of P/D-ME and observed a successful electrochemical detection of protons as a product generated at the Pt/C electrocatalyst for practical uses in DMFCs.

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