Electrochemical detection of methanol electrooxidation productgenerated at Pt/C micropowders by using a porous/disk-dual microelectrode

K. Kashima, M. Umeda, A. Yamada, I. Uchida[1]

Department of Chemistry, Faculty of Engineering, Nagaoka University of Technology, Kamitomioka, Nagaoka, 940-2188, Japan
[1]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Aoba-ku, Sendai 980-8579, Japan

Investigating a methanol electrooxidation mechanism, *i.e.*, study of reaction intermediates is indispensable to improve the direct methanol fuel cell (DMFC) performance. Electrochemical detection of the intermediates using an interdigitated Pt microarray electrode has been recently reported.[1)] However, there has been no report detecting the intermediates generated at powder Pt/C catalyst used in commercial DMFCs, based on electrochemical techniques. In the present study, we have constructed a new electrode of porous/disc-dual microelectrode (P/D-ME) that combines features of porous microelectrode (PME)[2)] and dual microelectrode. By using the P/D-ME, a reaction intermediate of methanol electrooxidation at the Pt/C and Pt-Ru/C catalysts was detected.

P/D-ME has Au generator (ϕ 50 μm) and Pt collector (ϕ 50 μm) electrodes at the tip. Au and Pt wires were separately inserted into a theta glass capillary, and heat-sealed by decompressing the glass inside. After polishing the tip of the electrode, Au electrode was etched in 1M HCl, resulting in a 20μm-depth cavity for the Pt/C powder catalyst. After packing the Pt/C Powder in the cavity (see Fig. 1), current-potential (I-V) curves were measured in 5M CH_3OH + 0.1M H_2SO_4 solution by utilizing a dual-potentiostat. For the electrochemical measurement, a Pt foil and an Hg/Hg_2SO_4 were used as a counter electrode and a reference electrode, respectively.

Figure 2 demonstrates I-V curves of methanol electrooxidation at the Pt/C-containing P/D-ME. The generator current response well reproduces that reported at the PME filled with Pt/C.[2)] Therefore, the current peak at the generator of Fig. 2 stands for a methanol electrooxidation. As seen in Fig. 2, when the collector potential is fixed at –700 mV vs. Hg/Hg_2SO_4, the most clear current response at the collector corresponding to the generator current is observed. When we take the result of Pt microarray electrode[1)] into account, the observed collector current will represent an electroreduction of protons produced by methanol oxidation at the Pt/C generator. We will also discuss the methanol electrooxidation mechanism from potential-dependent collection efficiency.

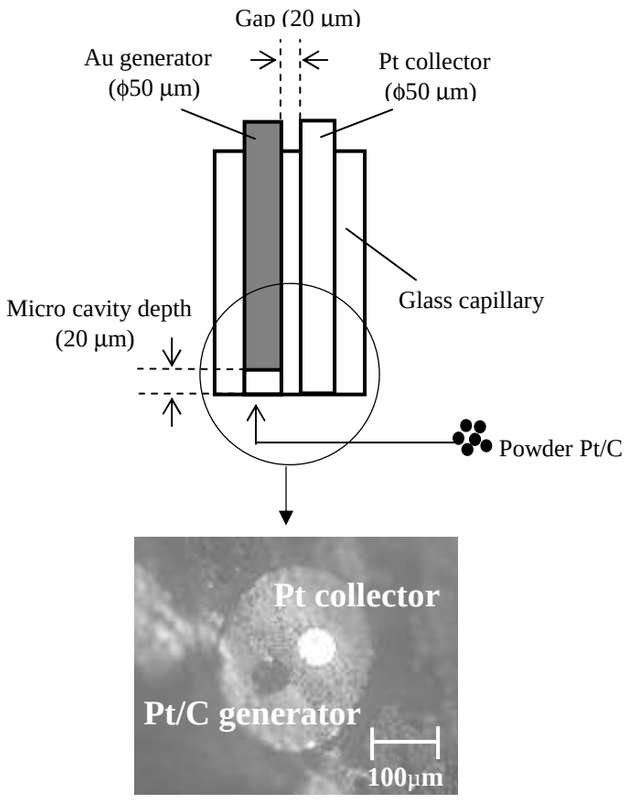

Fig. 1 Schematic side view and optical bottom view of the P/D-ME.

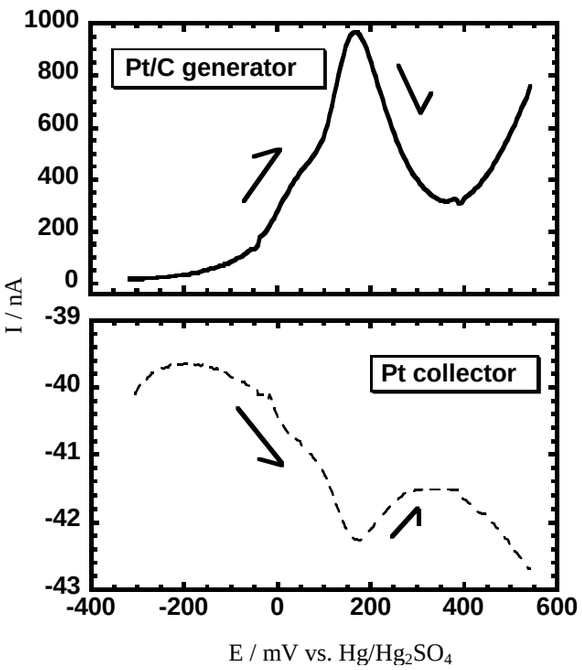

Fig. 2 I-V curves of methanol oxidation at P/D-ME in 5M CH_3OH + 0.1M H_2SO_4. Pt/C generator potential sweep rate: 20mV/s. Pt collector potential fixed at –700mV vs. Hg/Hg_2SO_4.

References

1) H. Ojima, et al., *Electroanalysis,* **15,** 1677 (2003).
2) M. Umeda, et al., *Electrochimica Acta,* **48,** 1367(2003).