

Methanol Oxidation of Ultra-fine Gold Deposited Catalysts

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Small-sized fuel cells, which are referred to as micro fuel cells, based on the principle of direct methanol fuel cells (DMFCs) are attracting much attention as power sources of portable electronic devices. One of the major problems, which impair the efficiency of chemical energy conversion of methanol fuel to electrical energy in DMFCs, is the slow methanol electro-oxidation reaction kinetics at anode. This is principally due to self-poisoning of the surface by reaction intermediates, which is strongly adsorbed on platinum catalyst during electro-oxidation of methanol. The addition of a second element to Pt is a well-known strategy for improving its electro-catalytic activity. In particular, Pt-Ru catalysts have been reported to be some of the most active catalysts for electro-oxidation of methanol. However, the activity of Pt-Ru catalysts was not enough high for electro-oxidation of methanol.

Recently, we reported electro-oxidation of methanol and ethylene glycol on ultra-fine gold catalysts deposited on Pt/ α -Fe₂O₃ in alkaline solution.^{1, 2)} And these catalysts showed higher activity than Pt-Ru and Pt-Pb in a lower potential region.

In the present work, ultra-fine gold particle was deposited on Pt-Ru catalysts and electro-oxidation of methanol was investigated in acidic solution.

Ultra-fine gold deposited on Pt-Ru/C (Au/Pt-Ru/C) was prepared by gas-phase grafting method.³⁾ The deposited gold was characterized by X-ray diffraction, X-ray photoelectron spectroscopy and atomic absorption spectroscopy. The size of deposited Au was about 5 nm in the present study.

Cyclic voltammetry and steady-state polarization were carried out in a three-electrode cell using a potentiostat. Pt-Ru/C (50 wt.% Pt-Ru, Tanaka Kikinzo K.K.) and Au/Pt-Ru/C with Nafion served as a working electrode, and electrolytes were 1 mol dm⁻³ (M) HClO₄ dissolved in ultra-pure water. Reversible hydrogen electrode (RHE) was used as a reference electrode. Unless otherwise mentioned all potential was referred to RHE. The temperature of the cell was maintained at 30°C in a temperature-controlled water bath. Before measurements, the potential of the working electrode was scanned repeatedly at 100 mV s⁻¹ under an argon atmosphere to confirm that there were no residual impurities. Then, 1 mol dm⁻³ methanol (Wako Pure Chemicals, 99.9%, infinitely pure) was added to the solution.

Figure 1 showed steady-state polarization curves of Pt-Ru/C and Au/Pt-Ru/C for electro-oxidation of methanol. Enhancement of current density was observed with ultra-fine gold deposited catalysts. In particular, ultra-fine gold deposited catalyst showed a higher activity at a lower potential region (than 450 mV). A current density of Au/Pt-Ru/C was about 2.2 times as large as that of Pt-Ru/C at 350 mV.

Figure 2 showed current density curves for potentiostatic oxidation of methanol at 350 mV. Initial current density of Pt-Ru/C and Au/Pt-Ru/C were almost

identical. However the current decay of Au/Pt-Ru/C was much smaller than that of Pt-Ru/C. These results indicated that ultra-fine gold catalyst suppressed CO poisoning at 350 mV.

In summary, electro-catalytic activity of Pt-Ru/C and ultra-fine gold deposited Pt-Ru/C catalyst toward methanol oxidation was studied and compared. Enhancement of electro-catalytic activity was observed at a lower potential region, when using ultra-fine gold deposited Pt-Ru/C catalyst.

References

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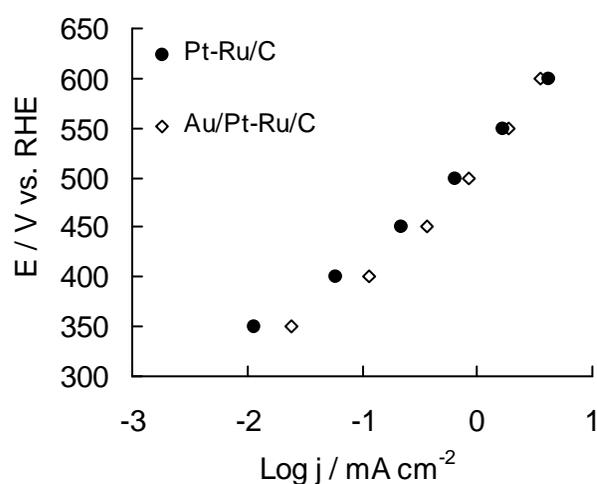


Fig.1 Steady-state polarization curves of Pt-Ru/C and gold deposited Pt-Ru/C in 1 M HClO₄ + 1 M methanol at 30 °C.

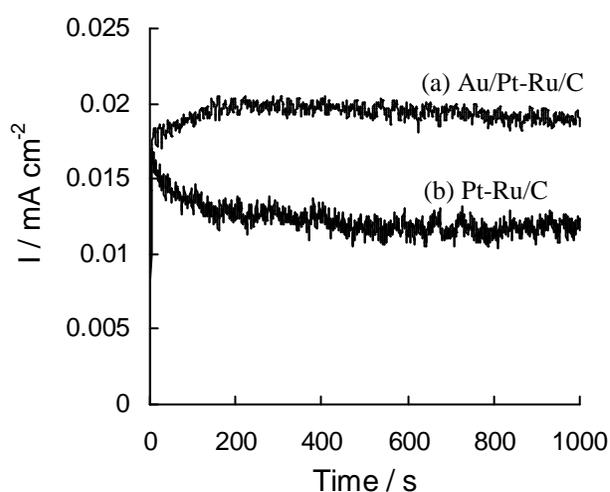


Fig. 2 Time vs. current density plots of (a) ultra-fine gold deposited on Pt-Ru/C (b) Pt-Ru/C for methanol oxidation at 350 mV. Temperature: 30 °C

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