Electrochemical Oxidation of Methanol on Platinum Electrodes with Ruthenium Ad-atoms in Hot Phosphoric Acid

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1 INTRODUCTION

Direct methanol fuel cell (DMFC) is an attractive system for a wide spectrum of applications where high efficiency and light weight are required. To date, the DMFC has not been considered a serious option for transportation applications such as a reformed methanol fuel cell (RMFC) due to its low power density, resulting from the lack of sufficiently active catalysts for the methanol anode, which needs at least a few mg/cm² of precious metals. The high temperature operation should enhance the methanol (MeOH) oxidation kinetics and also should depress the poisoning effects associated with strongly adsorbed intermediates, *e.g.*, CO. The attempt of higher temperature operation (>100 °C) has been demonstrated with a humidified Nafion® as the electrolyte under pressurized condition¹⁾ or with a polybenzimidazole doped with phosphoric acid²⁾. They have achieved current densities which are 1/3 to those achieved with RMFCs, but still used a large amount of precious metals. Therefore, it is essential to develop more active anode catalysts. We have reported an enhancement of Pt electrocatalytic activity by Ru ad-atoms for MeOH oxidation³⁾, and a preparation and the activity of highly dispersed Pt-Ru alloys supported on carbon black⁴⁾ in a conventional low temperature region.

Under the background mentioned above, this paper reports an enhancement of the electrocatalysis on Pt electrodes (symbolized in Pt(subs)) with Ru ad-atoms by the elevation of the operating temperature.

2 EXPERIMENTAL

A silica tube cell (40 mm in diameter) with a Teflon cap which mounted three electrodes was used for the measure-

ment of anodic oxidation of methanol at various elevated temperatures. A Pt working electrode ($d=0.3$ mm, $l=25$ mm, exposed from a Pyrex glass tube), a counter electrode of Pt mesh with Pt-black and a hydrogen reference electrode (RHE) were separated each other by covering with a silica tube in the silica cell. First of all, a reagent grade 100% H₃PO₄ was pre-electrolyzed at 120 °C by a Pt-gauze electrode with Pt-black kept at 0.2 V vs. RHE, followed by an anodic potential treatment for the electrode in the other cell containing 0.5 M H₃PO₄ solution and then washing the electrode with pure water. The treatment was repeated until hydrogen adsorption curves on a cyclic voltammogram on the working electrode before and after keeping the potential at 0.05 V for 10 min fell within 10% difference. Then, *ca.* 1 M reagent grade MeOH was added to the electrolyte. On the other hand, ad-electrodes, Ru-Pt(subs), were prepared by electrodepositing Ru ad-atoms on the working electrode in a conventional H-type cell containing purified 0.5 M H₂SO₄ dissolving *ca.* 10⁻⁶ M RuCl₃ in the same manner as reported previously³⁾. After determining the coverage³⁾ and washing well with pure water, the ad-electrode was transferred into the silica cell and the polarization curves for MeOH oxidation were measured by increasing the potential stepwise with 1 min interval.

3 RESULTS AND DISCUSSION

An oxidation current of MeOH on Pt(subs) at a constant potential increased with increasing the concentration of MeOH at 120 °C and showed a maximum at 1 M, where the MeOH was considered to be saturated in the electrolyte. By the elevation of operating temperature from 60 °C to 190 °C, the polarization was decreased by *ca.* 0.2 V and the limiting current increased by more than 50 times. The apparent activation energy at 0.6 V vs. RHE was calculated to be 10.2 kcal/mol at temperatures higher than 120 °C. However, this increased in the temperature region lower than 120 °C, presumably because the observed activation energy, *ca.* 18.0 kcal/mol, included that for the MeOH diffusion to Pt catalyst sites in viscous electrolyte.

The activity of Pt(subs) was enhanced dramatically with

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Fig. 1. The relationship between the current density for MeOH electrooxidation at 0.5 V and the Ru coverage on Pt(subs) anode in 100% hot H_3PO_4 .

Ru ad-atoms at every operating temperature, resulting in the reduction of the overpotential at each optimum Ru coverage, for example, 0.2 V at 120 °C, 0.12 V at 150 °C and 0.08 V at 190 °C, respectively. Figure 1 shows the relationship between the oxidation current density of MeOH at 0.5 V and the Ru coverage on Pt(subs), which is shown at typical operating temperatures. It is clear that a maximum activity is obtained at around $\theta_{\text{Ru}}^{\text{Pt}} = 0.5$ and the lower the operating temperature, the larger the enhancement ratio at Pt(subs) with the optimum Ru coverage. The lowest enhancement ratio of 2 was seen at 190 °C; the small effect could be attributed to the insufficient MeOH adsorption rate in comparison with the oxidation rate at the relatively large overpotential. The enhancement ratios in the Tafel region are 15 at 120 °C, 20 at 150 °C and 12 at 190 °C, respectively.

Figure 2 shows the change of the activation energies for MeOH oxidation at 150 °C together with that of the current densities at 0.5 V as a function of $\theta_{\text{Ru}}^{\text{Pt}}$. The activation energy for Pt(subs), 15 kcal/mol, decreases with increasing $\theta_{\text{Ru}}^{\text{Pt}}$ in the region less than ca. 0.5 and shows a minimum of 5 kcal/mol at $\theta_{\text{Ru}}^{\text{Pt}} > 0.5$. We have proposed "Bi-functional Enhancement Mechanism" for the MeOH oxidation on Ru-Pt(subs) at a low temperature in 0.5 M H_2SO_4 solution³, expressed by the following equations.

Fig. 2. The change of the activation energies for MeOH oxidation at 150 °C together with that of the current densities at 0.5 V as a function of the Ru coverage on Pt(subs) anode.

Although the adsorbed species was not specified previously, many recent studies using IR-spectroscopies claim the adsorbed species "R" to be CO. Regardless what is the real adsorbed species, the above theory is still valid for the present discussion, i.e., the surface reaction (3) may be the rate-determining step and oxygen species may be the limited reactant, where Pt and Ru sites on the ad-electrode act as adsorption sites for organic species and oxygen species, respectively. Consequently, the activation energy decreases with increasing Ru sites and the current density increases in proportion to the number of Ru sites. At the Ru coverage over 0.5, sufficient Pt sites for the dissociative adsorption of MeOH do not exist, resulting in the linear decrease with decreasing Pt sites in spite of the minimum activation energy for oxygen species to adsorb on Ru sites.

Based on the above results, it becomes clear that a higher temperature operation (>100 °C) of DMFCs is advantageous in the hot H_3PO_4 electrolyte and the enhancement of Pt(subs) by Ru ad-atoms predicts the optimum and highest activity for Ru-Pt alloys under the operating condition.

REFERENCES

- 1) J.S. Wainright, J.-T. Wang, D. Weng, R.F. Savinell and M. Litt, *J. Electrochem. Soc.*, **142**, L121 (1995).
- 2) X. Ren, M.S. Wilson and S. Gottesfeld, *Electrochem. Soc. Proceedings*, **95-23**, 252 (1995).
- 3) M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, **60**, 259 (1975).
- 4) M. Watanabe, M. Uchida and S. Motoo, *ibid.*, **229**, 395 (1987).