— Communication —

Temperature-Dependence of Direct Methanol Oxidation Rates at Various Platinum Alloy Electrodes

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The temperature dependence of the methanol oxidation reaction (MOR) rate at various Pt alloy electrodes was investigated by using a thin layer flow cell in a wide temperature range from 20 to 120 °C in 1 M CH₃OH + 0.1 M HClO₄ solution under pressurized operation. At 60 °C and 0.55 V vs. RHE, the MOR current densities at Pt-Sn and Pt-Ti were about 4 times higher than that at pure Pt, although it was still lower than Pt-Ru. Such enhanced MOR activities at Pt alloyed with non-precious metals were ascribed to the modified electronic structure of Pt skin layer formed on the alloy surface, facilitating the oxidation of weakly adsorbed CO. However, these alloys lost high MOR activities once heated at the high temperature (>80 °C) in the acid electrolyte solution, probably due to the thickening of Pt skin layer by a considerable dissolution of non-precious metal components from the alloys.

Key Words : Direct Methanol Fuel Cell, Methanol Oxidation, Anode Catalyst, Platinum Alloy

1 Introduction

Direct methanol fuel cells (DMFCs) have attracted a great interest as a primary power source for portable electronic devices, wheelchairs, vehicles and robots. The development of highly active anode catalysts for the methanol oxidation reaction (MOR) is one of the most important subjects to achieve a high efficiency at DMFCs. Platinum-based alloys such as Pt-Ru, Pt-Sn, and Pt-Mo have been examined as unsupported or supported anode catalysts.¹⁻³⁾ While DMFCs can work at a low temperature for portable electronic devices, they should be operated at higher temperature (above 100 °C) to achieve a higher conversion efficiency or a higher power density with a low noble metal catalyst loading. However, there have been a few systematic researches on the temperature-dependencies of the electrocatalytic activities for the MOR,⁴⁻⁷⁾ and their methods are not always adopted easily.

Recently, we developed an evaluation method of the “real” MOR activity in a wide temperature range from 20 to 120 °C in 1 M CH₃OH + 0.1 M HClO₄ solution by using a thin layer flow cell under pressurized operation.⁸⁾ Pt-Ru alloy was found to exhibit excellent activity in the whole temperature range examined. However, it is essential to develop alternative catalysts less expensive than Pt-Ru. Here, we report temperature dependencies of the MOR activities at various Pt alloy electrodes at 20 to 120 °C.

2 Experimental

Thin-film Pt-M (M = Ru, Sn, Ti, and Ni) alloys or pure Pt working electrodes were prepared on a gold disk (1 cm in diameter) by Ar-sputtering a Pt target with/without M target at room temperature (SH-33D, ULVAC Co.

Ltd.). The gold disk is inert to the MOR as well as hydrogen adsorption/desorption and acts just as a support for the sputtered catalysts. The thickness and projected surface area of each catalyst were *ca.* 90 nm and 0.071 cm², respectively. The resulting alloy compositions determined by fluorescent X-ray analysis (EDX-800, Shimadzu) were Pt₅₄Ru₄₆, Pt₅₈Sn₄₂, Pt₅₁Ti₄₉, and Pt₅₃Ni₄₇ (atomic ratio). To determine the crystallographic structure of each alloy, a grazing incidence ($\theta = 1^\circ$) X-ray diffraction (GIRD) was examined for the alloy film prepared on a glass substrate in the same manner.

The working electrode was mounted into a homemade, thin-layer flow cell.⁸⁾ An electrolyte flow channel between the working electrode and a Pt counter electrode was 0.1 mm in gap and 4 μ L in volume. All the electrode potentials in this paper are referenced to the reversible hydrogen electrode RHE(*t*) at the cell operating temperature *t* °C. By flowing 1 M CH₃OH + 0.1 M HClO₄ solution at appropriate rates (>200 μ L/s) with the back-pressure of N₂ gas up to 1.5 kg-G/cm², we obtained steady-state voltammograms and determined the MOR activities of these electrodes. During elevating the cell temperature for the Pt-Sn, Pt-Ti, and Pt-Ni, their potentials were kept at 0.3 V in the methanol-containing electrolyte solution. For the Pt-Ru alloy, however, the potential was not particularly controlled under contacting with the above solution during changing the cell temperature after the first stabilization by repetitive potential sweeps at 120 °C.

3 Results and Discussion

GIRD patterns of these Pt alloys indicated the formation of solid solutions with a face-centered cubic (fcc) crystal structure.

Fig. 1 Cyclic voltammograms at electrochemically stabilized Pt alloys in N_2 -purged 0.1 M $HClO_4$ at 20 °C. Sweep rates were 0.1 V/s for Pt-Sn, Pt-Ti, and Pt-Ni, and 0.2 V/s for Pt-Ru (to avoid the oxidation damage).

Fig. 2 Changes in roughness factors R_f at Pt-Sn, Pt-Ti, and Pt-Ni alloy electrodes with temperature.

Figure 1 shows typical cyclic voltammograms (CVs) at these alloy electrodes after electrochemical stabilization (typically 30 cycles from 0.05 to 0.8 V) in N_2 -purged 0.1 M $HClO_4$ at 20 °C. A precious (corrosion-resistant) metal Ru was remaining at Pt-Ru surface in the acidic solution at high temperature even at 120 °C.⁸⁾ In contrast, by using a X-ray photoelectron spectroscopy (XPS),^{9, 10)} *in situ* scanning tunneling microscopy (STM),¹¹⁾ and electrochemical quartz crystal microbalance (EQCM),¹²⁾ we found that the non-precious metal atoms in Pt alloys leached out into an acidic electrolyte solution and Pt skin layer was formed on the alloy surface with a modified electronic structure. The CVs at Pt-Sn, Pt-Ti, and Pt-Ni resembling to the CV of pure Pt strongly indicate that Pt skin layers were formed on them. Then, the active surface area of Pt (S_{Pt}) on these Pt-skin type alloys was determined from the hydrogen desorption charge ΔQ_H , supposing $\Delta Q_H = 0.21 \text{ mC/cm}^2$ for a smooth Pt polycrystal. Just after the MOR measurement, each S_{Pt} was measured again in the blank solution.

The values of roughness factor R_f (ratio of S_{Pt} to geometric surface area 0.071 cm^2) are shown in Fig. 2 as a function of temperature. The R_f of pure Pt was calculated to be 1.4. The R_f of Pt-Ru after stabilized at 120 °C was 2.9, assuming that Ru sites behaved as Pt sites for H adsorption/desorption and that contributions of OH for-

mation and H absorption^{13, 14)} to ΔQ_H at Ru sites could be ignored. The values of R_f at the Pt-Sn and Pt-Ti alloys are almost constant at 20 to 60 °C, but steeply decrease between 60 and 80 °C. The decrease in R_f is relatively small for Pt-Ni, which is similar to that observed for the oxygen reduction measurement at 20 to 90 °C.¹⁵⁾

Figure 3 shows the steady voltammograms for the MOR at various electrodes in the positive-going potential sweep with a flow of 1 M CH_3OH + 0.1 M $HClO_4$ solution at 60 °C. The current density j was expressed as the current per S_{Pt} of each electrode measured just after the MOR. While the onset potential E_{onset} for the MOR is *ca.* 0.55 V on pure Pt, the E_{onset} shifts to less positive potential at all the alloy electrodes. Besides Pt-Ru, Pt-Sn and Pt-Ti exhibit high activity with respect to the less positive E_{onset} and steep increase in the current density.

Figure 4 shows Arrhenius plots for the j at a constant overpotential, corresponding to 0.55 V vs. RHE(20 °C). Since both the standard potential E° for the MOR and $E[RHE(t)]$ shift to less positive values in a different manner, the corrected potential E is applied so as to keep a constant overpotential for the MOR at each temperature.⁸⁾ At 20 °C, the values of j at 0.55 V on pure Pt and Pt-skin type alloys were negligibly small, but only the $Pt_{54}Ru_{46}$ exhibited an appreciable activity. While linear relationship between $\log j$ and $1/T$ is observed at $Pt_{54}Ru_{46}$ with an activation energy of 16 kJ/mol,⁸⁾ somewhat strange temperature dependencies of j are seen for the other alloys. At 40 °C, the Pt-Ni exhibits the MOR activity almost comparable to that of pure Pt, but higher activities are seen at Pt-Sn and Pt-Ti. For the Pt-Sn and Pt-Ti, the j increases with elevating temperature and reaches the maximum at 60 °C. The value of j on Pt-Sn and Pt-Ti at 60 °C is about 4 times higher than pure Pt, although it is still lower than Pt-Ru. The MOR activity at Pt-Ni still increases up to 100 °C. However, the MOR activities at Pt-Sn and Pt-Ti degraded down to almost the same level of pure Pt once heated at 80 °C, and such “deactivated” electrodes could not recover the original activity observed at low temperature region.

Then, we discuss why these Pt alloys showed different

Fig. 3 Linear sweep voltammograms for MOR on various electrodes in 1 M CH_3OH + 0.1 M $HClO_4$ solution (flow rate $> 200 \mu\text{L/s}$) at 60 °C. Sweep rate = 20 mV/s.

Fig. 4 Arrhenius plots of MOR current densities at various electrodes at constant overpotential, corresponding to 0.55 V vs. RHE(20 °C), in 1 M CH₃OH + 0.1 M HClO₄.

temperature dependencies of the MOR activities. As seen in Fig. 3, the hydrogen-desorption charges (at 0.05 to 0.40 V) at all the electrodes are greatly reduced by strongly adsorbed intermediate(s) in the MOR. The dominant species is certainly adsorbed CO (CO_{ad}) as observed by *in situ* FTIR.¹⁶⁾ Recently, we found that the surface sites for the hydrogen oxidation reaction (HOR) at $E < 0.1$ V on Pt-Ru and Pt skin formed on Pt-Co were not so rigidly blocked by CO_{ad} due to its enhanced mobility.¹⁷⁾ It was also found that linearly adsorbed CO was dominant at the Pt skin on Pt-Co alloy electrode even at low CO coverage, whereas a large fraction of CO_{ad} at pure Pt was bridged form, by which the HOR active sites were blocked more seriously. Considering that CO_{ad} on Pt-Ru and Pt-Co was not oxidized at a low potential region $E < 0.1$ V, both interesting properties were ascribed to an electronic effect caused by the second element Ru in Pt-Ru and by underlying alloy of Pt-Co. Such properties could also accelerate the MOR, because water molecules might be easily accessible to the free sites. It was found by EQCM that the weakly adsorbed CO at Pt skin layer on Pt-Fe was oxidized even at 0.3 V and room temperature.¹²⁾

In addition to such an electronic effect, the CO_{ad} oxidation at Pt sites on Pt-Ru alloy can be facilitated further by oxygen species adsorbed at Ru sites (Ru-OH), so-called “bi-functional mechanism”.^{1,16)} Thus, the apparent activation energy for the MOR is much lower at Pt-Ru compared with Pt-skin type alloys.

The degradation of the MOR activity at the Pt-skin type alloys at high temperature (≥ 80 °C) is certainly ascribed to a dealloying of non-precious metal component in a hot acid solution, resulting in a thick Pt layer, the electronic state of which is no longer affected by the underlying alloy. It is noted, however, that the surface roughness of the alloys decreases sharply at the same temperature region as shown in Fig. 2. This is due to an increased migration rate of surface Pt atoms at elevated

temperature. Hence, the operating temperature for Pt-skin type alloys may be limited to $t \leq 60$ °C, except Pt-Ni showing relatively high corrosion resistance up to 100 °C. For the use of Pt-skin type alloys in the MOR at higher temperature, an addition of corrosion-resistive metal component⁷⁾ as well as stable oxides³⁾ may be effective to modify the electronic structure and to supply OH species.

4 Conclusion

By using a thin layer flow cell, it was found that the Pt-skin type alloys of Pt-Sn and Pt-Ti exhibited moderate MOR activities at 40 to 60 °C, *i.e.*, superior to pure Pt but inferior to Pt-Ru. Such an enhanced activity resulted from an electronic effect, which could weaken the Pt-CO interaction. These Pt-skin type alloys, however, degraded once heated at 80 °C, due to the thickening of Pt skin-layer, the electronic state of which is no longer affected by the underlying alloy.

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