Methanol Electrooxidation on Carbon-Supported Pt$_3$Ru$_2$Sn Ternary Catalyst

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The electrocatalytic methanol oxidation over Pt–Ru–Sn/C ternary alloy catalysts was investigated. The catalytic activity of Pt$_3$Ru$_2$Sn/C was significantly higher than that of PtRu/C. Sn in ternary alloy catalyst modified the Pt electronic structure without the large increase of Pt–Pt bond distance, which may enhance the catalytic activity for methanol oxidation by improving CO tolerance.

Direct methanol fuel cells (DMFCs) have been received much attention because of their characteristics such as high energy conversion efficiency, low pollutant emission, high energy density of methanol, and fuel availability. However, there are some obstacles inhibiting the application of DMFC; it is well known that the low catalytic activity of anode is major problem. Although Pt the best material for methanol activation, i.e., the C–H bond break followed by several reaction steps, chemisorbed CO and/or CHO intermediates poison the catalyst surface. To enhance the catalytic activity for methanol oxidation at lower potentials, there has been an intensive research on Pt alloy catalysts that minimize the catalyst poisoning. The Pt alloys with transition metals like Ru,[1] Sn,[2] Mo,[3] Ni,[4] and W[5] have been studied for methanol oxidation catalysts to minimize the poisonous effects.

In this work, we examined carbon supported Pt–Ru–Sn ternary alloy catalyst for methanol oxidation. It is reported that the promoting mechanism of Pt–Ru alloy is different from that of Pt–Sn alloy. Masel et al.[6] proposed that the main role of Ru is to dissociate water, and thereby Pt–Ru alloy exhibits the enhanced catalytic activity for both CO and methanol oxidations mainly by bifunctional mechanism. On the other hand, Sn affects the catalytic activity by the modification of Pt electronic state in Pt–Sn alloy. The CO oxidation activity of Pt–Sn alloy is higher than that of Pt–Ru alloy.[2] Most of the studies relating to Pt–Sn alloy, however, have reported little or no enhancements of methanol oxidation. Recently, some groups have studied Pt–Ru–Sn based alloy catalysts for methanol oxidation. Arico et al.[7] presented that Pt–Ru–Sn–W (3:1:1:1 molar ratio) quaternary catalyst was higher active than Pt–Ru catalyst. Götz et al.[8] reported that Pt–Ru–Sn (1:1:1) catalysts is less active than Pt–Ru catalyst. Until now, the promoting effect and mechanism of Sn in ternary catalysts toward methanol oxidation are uncertain.

The purpose of this work is to investigate the catalytic activity of Pt–Ru–Sn ternary catalyst with composition and to elucidate the alloying effects of Ru and Sn in ternary alloy for methanol oxidation.

Carbon supported Pt alloy catalysts were prepared by conventional NaBH$_4$ reduction method. The required amounts of metal chlorides(H$_2$PtCl$_6$·6H$_2$O, H$_2$RuCl$_6$ solution, and SnCl$_4$) in stoichiometric ratio were dissolved in ultrapure water. Then the appropriate amount of carbon powder (Ketjenblack, specific surface area of $1000\,\mathrm{m^2g^{-1}}$) was added into the metal precursor solution. After sufficient mixing, metal precursor was reduced by an ice-chilled NaBH$_4$ solution at room temperature under the vigorous stirring for 3 h. The resulting powder was filtrated and washed by pure water. The powder was dried at 60 °C for 12 h. The crystalline structures of samples were measured by X-ray diffractometer using Cu Kα radiation ($\lambda = 0.1542\,\mathrm{nm}$). From the broadening of (111) diffraction peak in XRD patterns, the average crystal size and lattice constant were calculated. The binding energies of each component were measured by XPS. Electrochemical characterization of catalysts was performed in an electrochemical cell with three electrodes using a rotating disk electrode at room temperature. A Pt disk and Ag/AgCl (in saturated KCl) were used as the counter and reference electrodes, respectively. The fabrication of working electrode and the electrochemical measurements of both CO/H$_2$ and methanol oxidations were performed as described by Ref. 9. The methanol oxidation current was expressed as a specific current density in terms of the surface area of catalyst which is determined from CO stripping measurement.

The XRD patterns of carbon-supported Pt alloy catalysts are shown in Figure 1. All XRD peaks of PtRu/C were shifted to higher 2θ values as compared to Pt/C. By contrast, those of Pt$_3$Sn/C were shifted to lower values. Such shifts represent the PtRu and Pt$_3$Sn alloy phases are formed in the prepared Pt alloy catalysts. The ternary alloy, Pt$_3$Ru$_2$Sn/C has an intermediate value between PtRu/C and Pt$_3$Sn/C, then it is expected that both Ru and Sn were partially alloyed with Pt. However, the observed shift is not sufficient to assess any change by Sn alloying. Figure 2 shows the binding energies at Pt 4f$_{7/2}$ peaks of catalysts. The order of binding energy was Pt/C > PtRu/C > Pt$_3$Ru$_2$Sn/C > Pt$_3$Sn/C. Arico et al.[10] reported that the Pt 4f binding energy of PtRu/C was akin to that of Pt/C, while a definite negative shift in the binding energy of Pt$_3$Sn/C was found in relation to both Pt/C and PtRu/C. These negative shifts mean that the electron transfer from Sn to Pt occurs more favorably than that from Ru to Pt. That is in agreement with the electronegativity differences between Sn (1.96), Ru (2.20), and Pt (2.28). Table 1 summarizes the results of XRD and XPS.

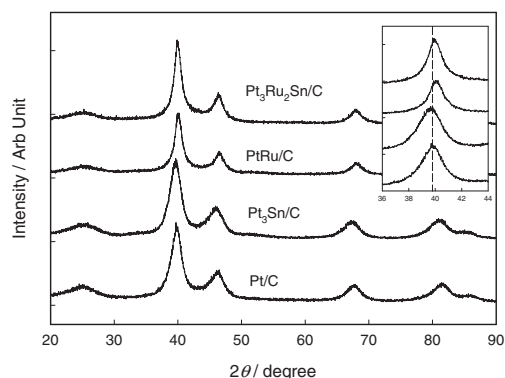To examine the CO tolerance properties of the Pt alloy cata-

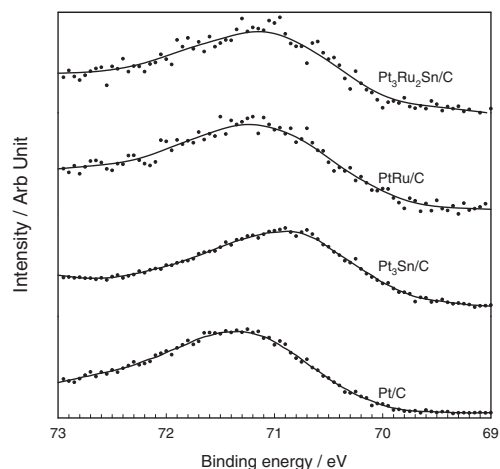**Figure 1.** XRD patterns of carbon-supported Pt alloy catalysts. The inset shows (111) peaks of catalysts.

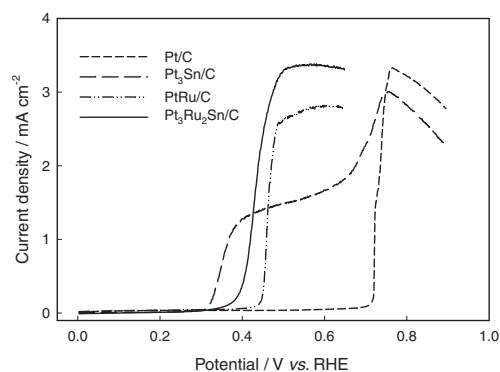**Figure 2.** Pt $4f_{7/2}$ peaks of carbon-supported Pt alloy catalysts.

Figure 3. The potentiodynamic oxidation of 2% CO/H_2 on the carbon-supported Pt alloy catalysts at room temperature (electrolyte: 0.1 M H_2SO_4, rotating speed: 2500 rpm, loading weight of catalyst: based on the same $21 \mu g_{Pt}/cm^2$).
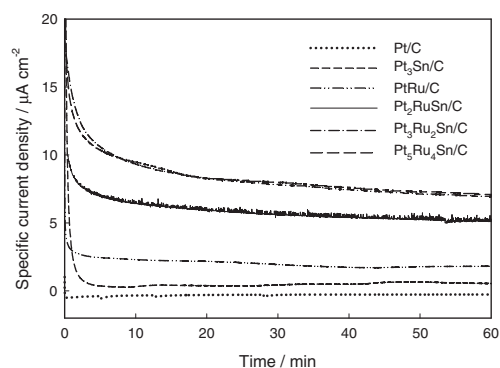

Figure 4. Methanol oxidation currents with time on the carbon-supported Pt alloy catalysts at room temperature (potential : 0.45 V vs. RHE, electrolyte: 0.1 M H_2SO_4, 0.5 M methanol, loading weight of catalyst: based on the same $21 \mu g_{Pt}/cm^2$).

lysts, the potentiodynamic oxidation of 2% CO/H_2 was performed at room temperature. For Pt/C, H_2 oxidation was completely suppressed until ca. 0.72 V by CO poisoning as shown in Figure 3. The onset potentials of catalysts in H_2 oxidation were ca. 0.43, 0.38, and 0.32 V for PtRu/C, Pt_3Ru_2Sn/C, and Pt_3Sn/C, respectively. These results suggest that Sn is more effective than Ru as an alloying component for CO tolerance, which agree well with the results of other investigation.[11] Sn in alloy catalysts modified the electronic environment around Pt-sites and hence promoted the CO oxidation.

Figure 4 shows the current-time curves for methanol oxidation. By contrast with the results of CO/H_2 oxidation, the catalytic activity of Pt_3Sn/C was improved a little as compared to Pt/C although the CO tolerance property was enhanced significantly. Mukerjee et al.[2] suggested that the increased Pt–Pt bond distance and the lower Pt d-band vacancies of Pt–Sn alloys result in an unfavorable environment for the initial adsorption and breaking the C–H bond for the first step in methanol oxidation. Our XRD and XPS results of Pt_3Sn/C are agreed well with their explanation. On the other hand, the activity of Pt–Ru–Sn/C catalyst was significantly improved for the methanol oxidation. As shown in Figure 4, the methanol oxidation currents for Pt_3Ru_2Sn/C and Pt_5Ru_4Sn/C at 0.45 V were almost 4 times higher than that for PtRu/C after 1 h. Based on the potentiostatic measurements of the alloy catalysts, the activity of methanol oxidation after 1 h increased in the sequence $Pt_5Ru_4Sn/C \approx Pt_3Ru_2Sn/C > Pt_2RuSn/C > PtRu/C > Pt_3Sn/C > PtSn/C \approx Pt/C$. The binding energy shift of Pt in Pt–Ru–Sn/C interpreted as the modification of electronic structure of Pt by electron transfer mainly from Sn to Pt. This may enhance the catalytic activity for methanol oxidation by increasing CO tolerance. From our results and the study of Mukerjee et al., the optimized electronic state of Pt exists for highly active catalyst. Furthermore the Pt–Pt bond distance of the ternary catalyst was shorter than that of Pt/C, which is highly active for methanol dehydrogenation.

In conclusion, the higher active Pt–Ru–Sn/C ternary alloy catalyst for methanol oxidation was prepared by conventional $NaBH_4$ reduction method. From the XRD, XPS, and electrochemical measurements, the Sn in Pt_3Ru_2Sn/C catalyst modified the electronic structure of Pt, which may enhance the catalytic activity for methanol oxidation by improving CO tolerance. Now, a detailed investigation is under progress to prepare the optimized catalysts.

Table 1. The particle size, lattice parameter (Pt–Pt bond distance), and binding energy of Pt $4f_{7/2}$(eV) of catalysts obtained by XRD and XPS, respectively

Catalyst	Particle Size/nm	Lattice Parameter, a_{fcc} (Pt–Pt bond distance) /Å	Binding Energy of Pt $4f_{7/2}$ /eV
Pt/C	4.4	3.925(2.775)	71.32
Pt_3Sn/C	4.0	3.939(2.785)	70.88
PtRu/C	5.8	3.902(2.759)	71.25
Pt_3Ru_2Sn/C	5.8	3.904(2.761)	71.11

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