Short communication

Preparation and evaluation of a multi-component catalyst by using a co-sputtering system for anodic oxidation of ethanol[☆]

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Abstract

In this study, a remarkable promotion of ethanol electrooxidation by a Pt–Ru–W alloy is reported for an improvement of the anodic reaction of a direct ethanol fuel cell (DEFC). Pt-based binary and ternary electrocatalysts including Pt–Ru–W deposited onto a Au substrate were prepared by co-sputtering process. By using this process, several metals can be arranged simultaneously and uniformly. The catalysts deposited onto Au were evaluated for anodic electrode in 1 mol dm^{-3} ethanol + 0.5 mol dm^{-3} sulfuric acid by electrochemical measurements. The performance of Pt–Ru–W was desirable in comparison to that of binary alloys, such as Pt–W, Pt–Sn and Pt–Ru, which exhibit higher catalytic activity than single Pt metal layer electrode. Ethanol electrooxidation on Pt–Ru–W alloy showed a cathodic shift in the onset potential and a higher current density than the binary alloy electrodes. It was found that Pt–Ru–W ternary catalyst effects to not only methanol oxidation reaction but also ethanol oxidation reaction and that the current density of ethanol oxidation with Pt–Ru–W is about 2/3 to that of methanol at 0.5 V versus Ag/AgCl. The onset potentials for the ethanol oxidation reaction matched well the anodic peak potentials of the background volutammograms, i.e., 0.15 V versus Ag/AgCl for Pt–Ru–W and 0.35 V versus Ag/AgCl for Pt–W and Pt–Ru electrodes. That is, it was postulated that the background peak current indicates the generation of oxide species like metal—OH necessary to complete the ethanol oxidation to CO_2.
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1. Introduction

Recently, a new-type fuel cell called the direct methanol fuel cell (DMFC) is drawing attention, wherein DMFC is a fuel cell that conducts power generation with a construction similar to that of a polymer electrolyte membrane fuel cell (PEMFC), except that methanol is supplied directly to the anode for oxidation reaction. Generally, DMFC system may become compact, because methanol whose state at a normal temperature and pressure is liquid has a high energy density and the system does not need the conversion from methanol to hydrogen. For the reason, DMFC has a potential to be a portable power source. Nevertheless, there exists also a problem in that the anodic oxidation reaction of methanol causes a large overvoltage. Moreover, wariness persists that the toxicity of methanol can harm the human health. From the foregoing viewpoint, there have been proposed various direct-type fuel cells that use ethanol, dimethylether and the like, in place of methanol. Ethanol is more safer than other hydrocarbons, and the energy density of ethanol is higher than that of methanol. For the reason, we paid attention to direct ethanol fuel cell (DEFC). The further improvements are needed because DEFC cannot provide the output

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performance superior to the one obtained in the case methanol is used. In this study, we concentrated on the development of an anodic electrocatalyst, which is one of a key point of DEFC.

Until now, various electrocatalysts have been investigated to promote methanol electrooxidation [1]. Pt-based binary and ternary alloys have been considered [2], and ruthenium element is known as one of the most contributory promoter. At the same time, little is known and investigated about the characteristics of ethanol electrooxidation and its reactions mechanism.

Here, we report a novel and remarkable performance of ethanol electrooxidation with some Pt-based multi-component systems, compared with the conventional catalysts.
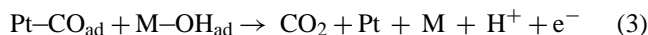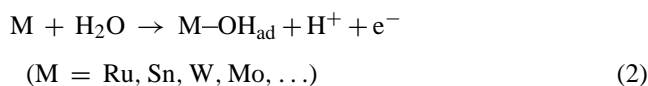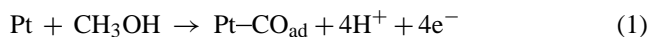
2. Experimental

The electrocatalysts were prepared by multi-target co-sputtering method onto single side of Au substrate of 5 mm diameter and 0.3 mm thickness. The catalyst layer on Au had thickness of about 0.3 μm. In addition, Pt, Si and glassy carbon (GC) were also used as substrates for comparison. The binary or ternary catalyst deposition was performed with a carousel type co-sputtering apparatus (Anelva, L-350-C). The catalyst alloy deposition was carried out at 150 and 300 °C in the vacuum chamber filled with pure Ar gas up to 10 Pa pressure under a substrate rotation speed of 20 rpm. Several varieties of multi-component alloy layers were obtained by heating a substrate and rotating a substrate simultaneously, applying various sputtering power to respective sputtering targets. Elemental analysis of the catalyst layer was conducted by using an X-ray fluorescence spectrometer (Seiko Instruments, SEA5120), an electron probe micro analyzer (Shimadzu, EPMA-V6) and the alloy phase structures were analyzed with an X-ray diffractmeter (Shimadzu, XD-D1) using Cu Kα radiation.

Then, a test solution was prepared by adding methanol or ethanol to a sulfuric acid solution obtaining a concentration of 1 mol dm^{-3} alcohol + 0.5 mol dm^{-3} H$_2$SO$_4$. After deaerating the test solution, an electrochemical measurement was conducted on this test solution by a potential control method (potentiostat, Hokuto Denko HA1010) by using the electrodes of the comparative sample as the working electrode and a platinum wire as the counter electrode, while using Ag/AgCl for the reference electrode. Before the measurement in the test solution containing ethanol, the surface of the working electrode was cleaned electrochemically by potential cycling in 0.5 mol dm^{-3} H$_2$SO$_4$. All the electrochemical measurements were carried out at 23 °C. The measurement was conducted with the potential scanning rate of 10 mV s^{-1}. Since it is impossible to determine the real surface area of alloys correctly, the current densities are thus referred to the geometric surface area of the electrodes.
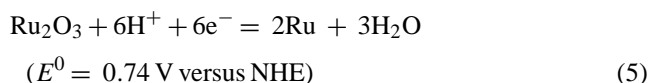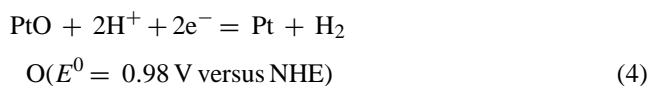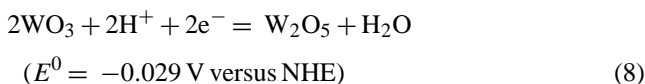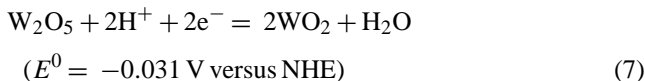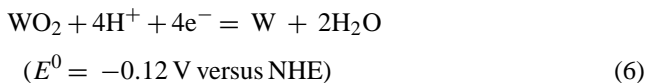
3. Results and discussion

3.1. The role of a second metal or a third metal for the anodic oxidation of an alcohol

Platinum is considered to be the only stable and active catalyst for the electrooxidation of alcohol in a strong acid environment as Nafion. Unfortunately, the dissociative chemisorption of an alcohol leads to the formation of poisoning species like CO, which adsorb on platinum surface strongly and block the electroactive sites of the catalyst. For such reason, modifications of the catalyst for an alcohol electrooxidation are required to reduce the formation of the strongly absorbed species or to remove the species by oxidation at lower potentials. Convenient way to modify the electrocatalytic properties is considered to make platinum-based binary or even ternary alloys. The favorite metal as a second metal of Pt-based binary electrocatalyst is ruthenium. Hence, platinum and ruthenium play roles to dissociate C−H bond (methanol or ethanol) or C−C bond (ethanol) by chemisorption (Eq. (1)) typically, and to provide preferential sites for OH-adsorption (Eq. (2)) at low potentials (0.35 V [3], 0.45 V [4], 0.55 V [5]/RHE), respectively. And finally, methanol (or ethanol) is completely oxidized to CO$_2$ by bi-functional mechanism indicated reaction (Eq. (3)).

$$Pt + CH_3OH \rightarrow Pt\text{−}CO_{ad} + 4H^+ + 4e^- \qquad (1)$$

$$M + H_2O \rightarrow M\text{−}OH_{ad} + H^+ + e^-$$
$$(M = Ru, Sn, W, Mo, \ldots) \qquad (2)$$

$$Pt\text{−}CO_{ad} + M\text{−}OH_{ad} \rightarrow CO_2 + Pt + M + H^+ + e^- \qquad (3)$$

The OH-adsorption potentials of references are seemed to be different because of different measurement conditions and various compositions of Pt:Ru. The OH-adsorption potentials are determined from the anodic peak current of background cyclic voltammograms in sulfuric solution [5], while on the surface of single platinum, OH adsorption by water dissociation occurs at the potential at least 0.6 V versus RHE above [6]. In other words, a complete oxidation of an alcohol does not occur below 0.6 V versus RHE. The other binary alloys, for example, Pt–Sn has OH adsorption potential of about 0.3 V versus RHE and Pt–W of 0.55 V versus RHE [5]. These OH-adsorption potentials match well the onset potentials for initial oxidation of an alcohol. It is considered the onset potentials relate to the individual metals' values of electrochemical equilibria in aqueous solutions by Marcel Pourbaix. For example, Eqs. (4)–(8);

$$PtO + 2H^+ + 2e^- = Pt + H_2$$
$$O(E^0 = 0.98\,\text{V versus NHE}) \qquad (4)$$

$$Ru_2O_3 + 6H^+ + 6e^- = 2Ru + 3H_2O$$
$$(E^0 = 0.74\,\text{V versus NHE}) \qquad (5)$$

$$WO_2 + 4H^+ + 4e^- = W + 2H_2O$$

$$(E^0 = -0.12 \text{ V versus NHE}) \tag{6}$$

$$W_2O_5 + 2H^+ + 2e^- = 2WO_2 + H_2O$$

$$(E^0 = -0.031 \text{ V versus NHE}) \tag{7}$$

$$2WO_3 + 2H^+ + 2e^- = W_2O_5 + H_2O$$

$$(E^0 = -0.029 \text{ V versus NHE}) \tag{8}$$

The Pt-based specific metal, which electrochemically has the lower standard redox potential and structurally be stable in a metallic state, would be desirable one.

Here, Pt-based binary alloys Pt–Ru, Pt–W, Pt–Sn and Pt–Mo deposited on Au or Si substrate by multi co-sputtering method at 150 or 300 °C were evaluated. Fig. 1 shows the results of linear sweep voltammograms of these binary alloy systems deposited on Si substrate at 150 °C in 0.5 mol dm^{-3} $H_2SO_4 + 1 \text{ mol dm}^{-3}$ ethanol solution compared to Pt and Pt–Ru alloy electrodes. This figure indicates electrochemical properties are sensitive to changing of the compositions of binary metals, and particular compositions of tungsten or molybdenum are equal to the property of ruthenium. Linear sweep voltammogram of Pt–Sn indicates that the onset potential is shifted to cathodic side; in other words, the overpotential decreases with about 0.2 V compared to Pt–Ru, Pt–W and Pt–Mo. This fact of Pt–Sn and ternary alloys of Pt–Ru–Sn whose electrochemical property decreases as mentioned later is in agreement with the result by Napporn et al. [7]. Nevertheless, according to the comparison with various temperatures showed by Fig. 2 of voltammograms in 0.5 mol dm^{-3} H_2SO_4 and Fig. 3 of voltammograms in 1.0 mol dm^{-3} $C_2H_5OH + 0.5 \text{ mol dm}^{-3}$ H_2SO_4, Pt–Sn has a large gap to the sputtering temperature, while Pt–Ru and Pt–W do not have. After all, properties of the alloys, which include tin metal, are seemed to be more dependent on particularly sputtering temperature, a type of an alcohol and substrates for supporting sputtered metal than other alloys.
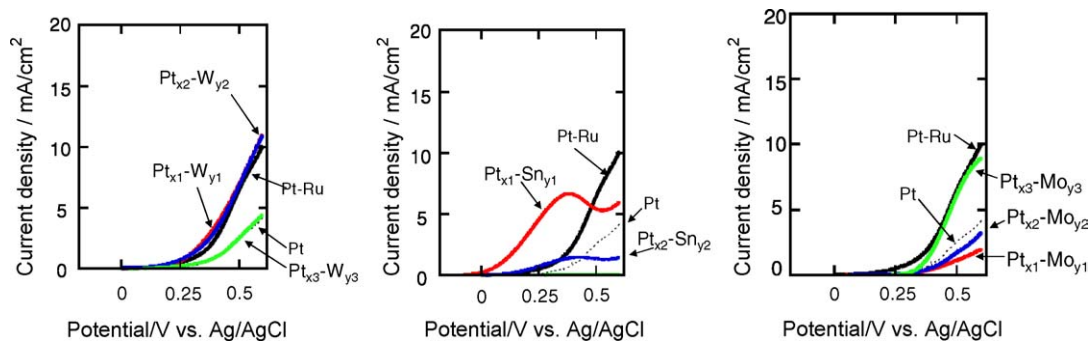

Fig. 2. Cyclic voltammograms of the Pt–metal alloy electrodes in 0.5 mol dm^{-3} H_2SO_4. Substrate, Si; heating temperature, 150 or 300 °C; scan rate, 10 mV s^{-1}. Elemental compositions (at%) are Pt–W = Pt85:W15; Pt–Sn = Pt80:Sn20.

Fig. 3. Voltammograms of Pt–metal alloy electrodes in 0.5 mol dm^{-3} $H_2SO_4 + 1 \text{ mol dm}^{-3}$ ethanol solution compared to Pt–Ru. Substrate, Si; heating temperature, 150 or 300 °C; scan rate, 10 mV s^{-1}. Elemental compositions (at%) are Pt–Ru = Pt80:Ru20; Pt–W = Pt85:W15, Pt–Sn = Pt80:Sn20.

Meanwhile, we introduce the results of ternary alloys here. Fig. 4 shows the results of linear sweep voltammograms of ternary alloy systems deposited onto Au substrate at 300 °C in a sulfuric acid solution and 0.5 mol dm^{-3} $H_2SO_4 + 1 \text{ mol dm}^{-3}$ methanol solution and in 0.5 mol dm^{-3} $H_2SO_4 + 1 \text{ mol dm}^{-3}$ ethanol solution compared to Pt–Ru alloy electrodes. It makes clear that the Pt–Ru–W ternary electrocatalyst provides superior performance of alcohol oxidation as compared with binary

Fig. 1. Voltammograms of Pt–metal binary alloy electrodes in 0.5 mol dm^{-3} $H_2SO_4 + 1 \text{ mol dm}^{-3}$ ethanol solution compared to Pt and Pt–Ru. Substrate, Si; heating temperature, 150 °C; scan rate, 10 mV s^{-1}. Elemental compositions (at%) are Pt–W: X1 = 85, Y1 = 15, X2 = 60, Y2 = 40; Pt–Sn: X1 = 95, Y1 = 5, X2 = 80, Y2 = 20; Pt–Mo: X1 = 70, Y1 = 30, X2 = 65, Y2 = 15, X3 = 35, Y3 = 65.
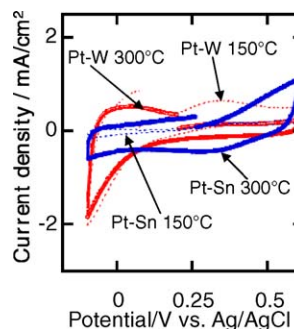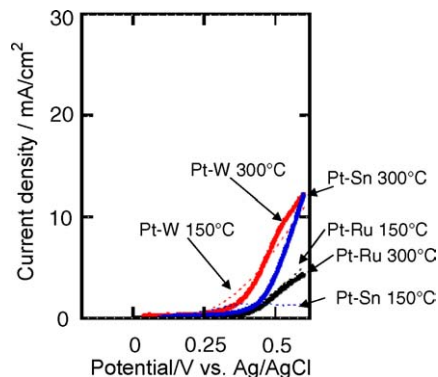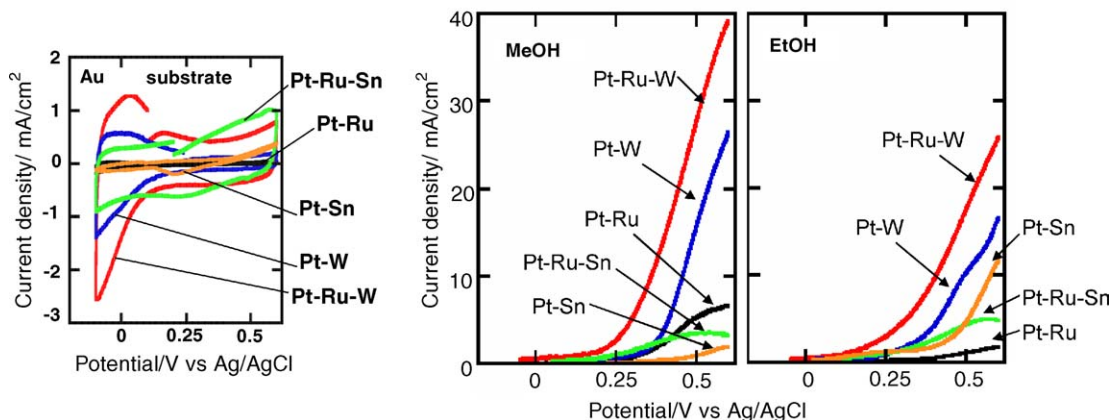
Fig. 4. Voltammograms of Pt–metal alloy electrodes in 0.5 mol dm^{-3} H$_2$SO$_4$, and voltammograms of Pt–metal alloy electrodes in 0.5 mol dm^{-3} H$_2$SO$_4$ + 1 mol dm^{-3} methanol or ethanol solution compared to Pt–Ru. Substrate, Au; heating temperature, 300 °C; scan rate, 10 mV s^{-1}. Elemental compositions (at%) are Pt–Ru = Pt80:Ru20; Pt–Sn = Pt80:Sn20; Pt–W = Pt85:W15; Pt–Ru–Sn = Pt60:Ru15:Sn25; Pt–Ru–W = Pt65:Ru20:W15.

alloy composition known conventionally. The onset potential of methanol and ethanol oxidation is around 0.15 V versus Ag/AgCl, which corresponds to the anodic peak potential of background cyclic voltammetry measurement in 0.5 mol dm^{-3} H$_2$SO$_4$. Besides, little improvement of the electrochemical property of Pt–Ru–Sn is observed for methanol and ethanol as compared with Pt–Ru–W.

3.2. Characterization of the sputter-deposited electrodes

According to Fig. 4, it becomes evident that the Pt–Ru–W ternary electrocatalyst provides superior performance of ethanol oxidation as compared with binary alloy composition known conventionally. As stated to bi-functional mechanism for alcohol oxidation on Pt-based binary alloys above, its mechanism is plausible for ternary alloys. Our view is derived form the structural analysis of binary and ternary alloys by XRD. Fig. 5 shows XRD patterns of Pt, Pt–Ru and Pt–Ru–W on Au substrate prepared by sputtering process, and Fig. 6 shows EPMA images of Pt–Ru–W on Au substrate. Platinum, ruthenium and tungsten are distributed uniformly. At Pt–Ru binary alloy, ruthenium and platinum which belongs to fcc crystal structure form a solid solution, and at Pt–Ru–W ternary alloy, ruthenium and Pt$_2$W which belongs to orthorhombic crystal structure form a solid solution. It is considered that ruthenium exists as the same formation at both Pt–Ru and Pt–Ru–W, and that electrochemical properties of Pt–W or Pt–Ru–W are more desirable than Pt or Pt–Ru because tungsten adjoins platinum for the crystal structure of Pt$_2$W and this arrangement is easy to occur bi-functional mechanism.

3.3. Effect of the material substrate

In this study of the binary and the ternary alloy electrodes, an effect of the substrate was investigated and can be noticed that the substrate affects the nature of the alloy. We examined various substrates, namely Au, Pt, Si and glassy carbon. Both
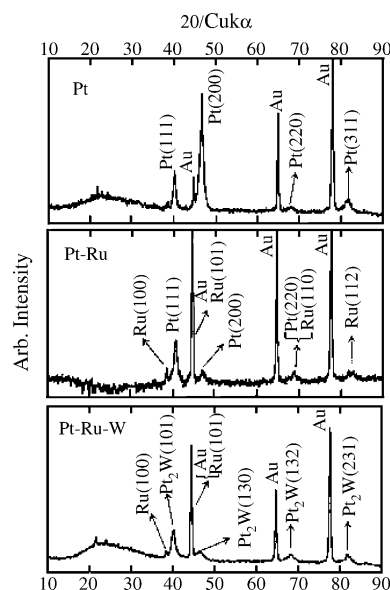

Fig. 5. XRD patterns of Pt, Pt–Ru and Pt–Ru–W on Au substrate prepared by sputtering process.

current densities in methanol and ethanol electrooxidation were decreased when the substrate was changed from Au to Pt, Si or GC. The catalysts deposited onto Au could be active for the oxidation of ethanol. The role of the gold substrate may
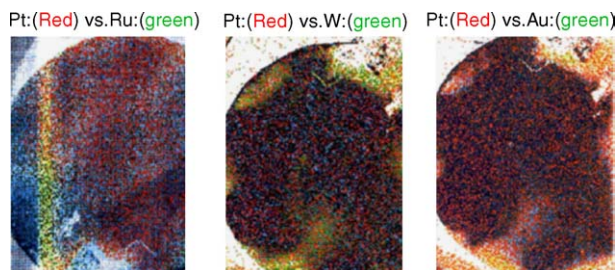

Fig. 6. EPMA images of Pt–Ru–W alloy on Au substrate prepared by sputtering process.
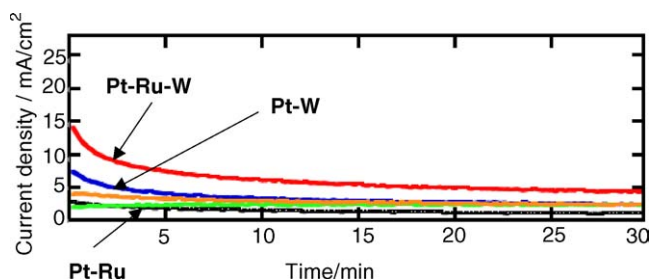
Fig. 7. Current density vs. time curve at Pt–metal alloy sputtered on Au substrate measured in 0.5 M H_2SO_4 + 1 M ethanol solution compared to Pt–Ru. The potential was stepped from each rest potential to 0.5 V vs. Ag/AgCl. Elemental compositions (at%) are Pt–Ru = Pt80:Ru20; Pt–W = Pt85:W15; Pt–Ru–W = Pt65:Ru20:W15.

be considered by looking at the following electrode reaction (Eq. (9)):

$$Au_2O_3 + 6H^+ + 6e^- = 2Au + 3H_2O$$

$$(E^0 = 1.46\ V\ versus\ NHE) \tag{9}$$
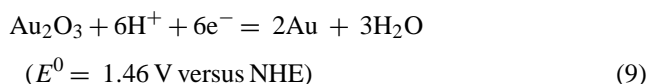
This reaction points out that a direct participation of Au to form $M–OH_{ad}$ is unlikely to occur. Therefore, the Au substrate is presumed to affect indirectly the number of $M–OH_{ad}$ formed on the Pt–Ru–W surface to complete the ethanol oxidation.

As shown in Fig. 6, a feature of W-included Pt–metal alloy supported onto Au substrate has been estimated that Au ultra fine particles or atomic clusters emerge to the surface of the alloy by sputtering the Au substrate surface during a sputtering deposition.

Sputter-depositing temperature of these alloy layers could probably promote the formation of adsorbed oxide species linked to enhance the bi-functional mechanism at ethanol electrooxidation [3].

At the same time, the details of characteristics and mechanism of ethanol electrooxidation remain still unknown by the reason that the anodic oxidation of ethanol is a complicated reaction in which various elementary reactions and intermediate reactions are tangled intricately.

We are focusing attention on PVD method of co-sputtering system equipped with multi-targets; the co-sputtering system can facilitate alloying process developments of catalytic layer in microscopic scale and its gas phase deposition is capable of controllability of alloy's elemental composition and its microstructures. At present, we are starting to search the optimal conditions of fabricating some quaternary alloy catalysts favoring for ethanol electrooxidation.

3.4. Stationary potential electrolysis

Several varieties of electrodes, such as Pt–Ru, Pt–W and Pt–Ru–W, were conducted under the stationary potential electrolysis for 30 min. The experimental results of I–t curves are shown in Fig. 7. The Pt–Ru–W electrode demonstrated the highest current density; nevertheless, it is gradually stabilized

at about 35% of its initial value after 30 min. It indicates that the anode oxidation reaction of ethanol is much more complicated than the reaction of methanol. Active species, such as –COH, CO, –COOH and –CH_3, adsorbed on the platinum surface cause the problem of poisoning, and are probably formed from various dissociation species or intermediate species, such as CH_3–CHO, CO–CH_3, CH_3–COOH and the like, formed during the anode electrochemical reactions [8].

To improve the characteristics of the alloy electrode, it is necessary to design the elemental composition and control the microstructure of the alloy thin film, and to analyze the reaction of ethanol electrooxidation by means of useful analytical method like differential electrochemical mass spectrometry (DEMS).

4. Conclusions

A promising promotion of ethanol electrooxidation by Pt–Ru–W alloy sputter-deposited onto Au substrate is reported. The performance of Pt–Ru–W was favorably compared with that of binary alloys, such as Pt–W, Pt–Sn, and Pt–Ru, which exhibit higher catalytic activity than single Pt metal layer electrode. Ethanol electrooxidation at Pt–Ru–W alloy system showed a cathodic shift in the onset potential and a higher current density than the binary alloy electrodes comparatively. According to EPMA analysis of the alloy layer, it is easily inferred that Pt_2W and Ru are distributed in the form of a solid solution. Moreover, the stationary potential electrolysis designated that the Pt–Ru–W system deposited onto Au substrate exhibits higher ethanol oxidation activity; nevertheless, it gradually stabilizes at about 35% of its initial value after 30 min. To improve the characteristics of the alloy electrode, it is necessary to design the elemental composition and to establish suitable fabrication conditions so as to control the microstructure of the multi-component alloy catalysts, and to analyze the reactions of ethanol electrooxidation.

Acknowledgement

References

[1] A. Kabbabi, R. Faure, R. Durand, B. Beden, F. Hahn, J.-M. Leger, C. Lamy, J. Electroanal. Chem. 444 (1998) 41.
[2] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J.-M. Leger, J. Power Sources 105 (2002) 283.

[3] M. Watanabe, S. Motoo, J. Electroanal. Chem. 60 (1975) 267.

[4] G. Samjeske, H. Wang, T. Loffler, H. Baltruschat, Electrochim. Acta 47 (2002) 3681.

[5] M. Umeda, H. Ojima, M. Mohamedi, I. Uchida, J. Power Sources 136 (2004) 10.

[6] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau, J. Leger, J. Power Sources 105 (2002) 283.

[7] W. Napporn, H. Laborde, J.-M. Leger, C. Lamy, J. Electroanal. Chem. 404 (1996) 153.

[8] C. Lamy, E.M. Belgsir, J.-M. Leger, J. Appl. Electrochem. 31 (2001) 799.