Ternary $Pt_{45}Ru_{45}M_{10}$/C (M=Mn, Mo and W) catalysts for methanol and ethanol electro-oxidation

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Abstract–Ternary $Pt_{45}Ru_{45}Mn_{10}$/C, $Pt_{45}Ru_{45}Mo_{10}$/C and $Pt_{45}Ru_{45}W_{10}$/C catalysts were synthesized and physical and electrochemical properties were characterized. Particle sizes of the catalysts were determined by X-ray diffraction to be 3.9, 4.8 and 4.6 nm for the Mn, Mo and W incorporated catalysts, respectively. Electrochemically active surface areas were calculated from CO stripping results, which were 17.7, 17.2 and 15.7 m^2/g_{catal} for the $Pt_{45}Ru_{45}Mn_{10}$/C, $Pt_{45}Ru_{45}Mo_{10}$/C and $Pt_{45}Ru_{45}W_{10}$/C catalysts, respectively. In methanol electro-oxidation, the $Pt_{45}Ru_{45}W_{10}$/C catalyst showed highest mass and specific activities of 2.78 $A/g_{cat.}$ and 177 mA/m^2, respectively, which were 22 and 100% higher than those of commercial PtRu/C. In the case of ethanol electro-oxidation, the $Pt_{45}Ru_{45}Mo_{10}$/C catalyst exhibited highest mass and specific activities of 4.8 A/g_{catal} and 280 mA/m^2, respectively. Specific activity of the $Pt_{45}Ru_{45}Mo_{10}$/C catalyst was 56% higher than that of the commercial PtRu/C.

Key words: Electrocatalyst, Direct Alcohol Fuel Cell, Methanol Electro-oxidation, Ethanol Electro-oxidation, CO Stripping

INTRODUCTION

Global warming and increasing price of fossil fuels are strongly driving a demand for clean energy generation sources. Fuel cells that convert the chemical potential into electricity are widely studied as new eco-friendly power sources because their by-products are water or carbon dioxide. There are various kinds of fuel cells such as polymer electrolyte membrane fuel cell, phosphoric acid fuel cell, alkaline fuel cell, and solid oxide fuel cell. Among these fuel cells, a direct alcohol fuel cell (DAFC), which uses alcohols such as methanol and ethanol as anode fuels and oxygen as a cathode fuel, provides a special advantage of ease of liquid fuel handling. This merit made DAFC the most promising candidate for portable power source applications, such as notebook computers and cellular phones [1-4].

Methanol is the most popular fuel for DAFC due to its simple structure, which means it can be fully oxidized easily. Pt was first introduced as a methanol electro-oxidation reaction (MOR) catalyst, but easy poisoning by CO reduces its activity rapidly. Incorporation of Ru could significantly improve CO tolerance of the Pt catalyst by producing Ru-OH to react with Pt-CO [5], the so-called "bi-functional mechanism." However, the PtRu catalyst still needs higher activity and cost down as both Pt and Ru are expensive novel metals.

To achieve these goals, various efforts were made such as surface modification of the PtRu catalyst [5] and incorporation of third or fourth metals. PtRuFe [7,8], PtRuNi [9-11], PtRuW [12-15], PtRuCo [8,12] and PtRuMoW [16] were reported to have higher activity than commercial PtRu catalyst. A review by Demirci suggested that addition of a third metal into PtRu would be the best way to improve

MOR activity [17], based on theoretical calculations for d-band shift and surface segregation [18,19]. In the review, promising promoters were suggested as an order of Mo>W>Co>Fe>Ni>Cu.

In the present study, we synthesized $Pt_{45}Ru_{45}Mn_{10}$/C (PtRuMn/C), $Pt_{45}Ru_{45}Mo_{10}$/C (PtRuMo/C), and $Pt_{45}Ru_{45}W_{10}$/C (PtRuW/C) catalysts to find the most promising candidate for methanol and ethanol electro-oxidation. With Mo and W, which Demirci [17] suggested as the most promising candidates, Mn was also investigated as a third metal because its surface segregation behavior is similar to that of Ru. In PtRu alloy, Pt is very strongly segregated on the surface while Ru exhibits strong anti-segregation [17-20], and Mn has the same surface segregation property with that of Ru. Physical and electrochemical properties were analyzed by using X-ray diffraction (XRD), transmission electron microscopy (TEM), CO stripping, and methanol electro-oxidation activity. In addition, ethanol electro-oxidation reaction (EOR) was also studied, as ethanol is a promising fuel to replace highly toxic methanol. Furthermore, ethanol can be easily obtained by fermenting abundant biomass such as corn [21].

EXPERIMENTAL

1. Synthesis of Catalysts

Conventional impregnation and $NaBH_4$ reduction method was used to synthesize the catalysts [22]. Carbon support (Vulcan XC72R) was dispersed in isopropyl alcohol and de-ionized (DI) water mixture. Appropriate amount of metal precursors was dissolved in the carbon-solvent mixture. H_2PtCl_6, $RuCl_3$, $MnCl_2 \cdot 4H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and $(NH_4)_6H_2W_{12}O_{40}$ were used as Pt, Ru, Mn, Mo and W precursors, respectively. The resulting mixture was heated to 80 °C and stirred for 1 h. To reduce metal precursors, 0.2 M $NaBH_4$ solution was added to the mixture with stirring, and further stirred for 3 h to confirm termination of the reduction reaction. The final

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product was filtered and washed with DI water, and then dried in an oven overnight.

2. XRD and TEM Measurement

XRD experiments were performed with a Rigaku D/MAX-IIIC machine. Cu Kα radiation was used with a continuous scan mode at a scan rate of 3°/min. For TEM (Hitachi, HF-2200) observation, catalyst samples were dispersed in ethanol and sonicated for homogeneous mixing, and then 5 μL of the dispersion was dropped on a carbon-coated Cu grid (300 mesh).

3. Electrochemical Characterization

Electrochemical properties were measured in a three electrode beaker cell equipped with a platinum wire counter electrode, an Ag/AgCl reference electrode (BAS Co., Ltd., MF-2052 RE-5B), and a glassy carbon working electrode (3 mm diameter, BAS Co., Ltd., MF-2012). The working electrodes of the catalysts for electrochem-
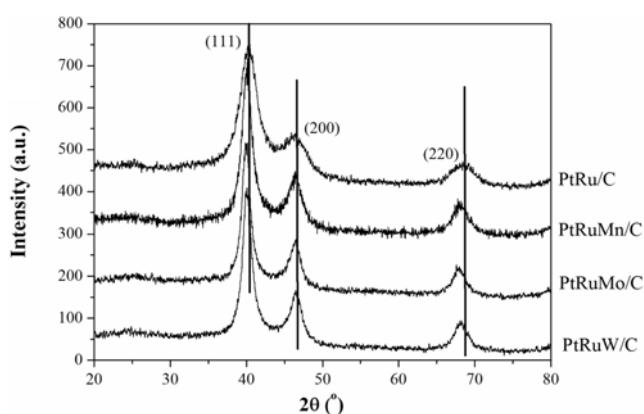

Fig. 1. XRD results of the PtRu/C, $Pt_{45}Ru_{45}Mn_{10}$/C, $Pt_{45}Ru_{45}Mo_{10}$/C and $Pt_{45}Ru_{45}W_{10}$/C catalysts.
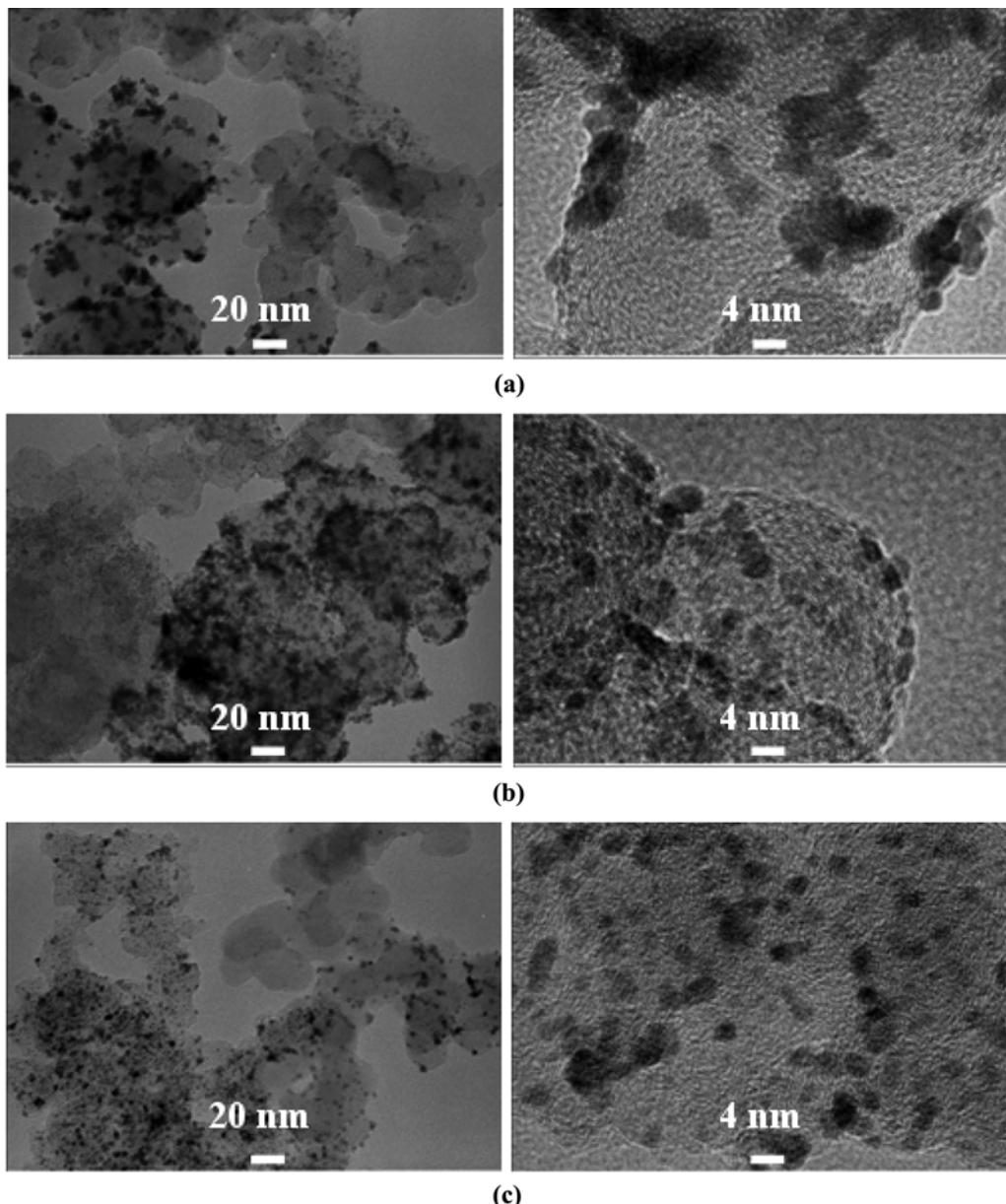
Fig. 2. TEM observation results of the (a) $Pt_{45}Ru_{45}Mn_{10}$/C, (b) $Pt_{45}Ru_{45}Mo_{10}$/C and (c) $Pt_{45}Ru_{45}W_{10}$/C catalysts.

ical analysis were prepared by the thin-film electrode method [23]. The catalysts were dispersed in DI water followed by sonication, and dropped on the glassy carbon working electrode. After drying in room temperature, 5 wt% Nafion ionomer solution was dropped on the glassy carbon electrode to stabilize the catalyst layer.

CO stripping experiments were performed in a 1 M $HClO_4$ solution as the electrolyte, which was N_2 purged before the test. CO was bubbled through the cell for 1 h, to adsorb CO on the catalyst surface. And then the electrolyte was purged with N_2 for 50 min to remove CO dissolved in the electrolyte. During the CO and N_2 bubbling, the working electrode was kept at 0.1 V. Electro-oxidation of CO was measured by cycling potential between 0 and 1.2 V (vs. reversible hydrogen electrode, RHE) at a scan rate of 15 mV/s.

Methanol and ethanol electro-oxidation was measured in a 1 M H_2SO_4+1 M methanol (or ethanol) solution by cycling voltage between 0 and 0.8 V (vs. RHE) at a scan rate of 15 mV/s. All electrochemical experiments were carried out at 25 °C, and all potentials used through this paper were converted to RHE scale.

RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction results of the synthesized and commercial catalysts. Particle sizes of the catalysts calculated by the Scherrer equation were 3.9, 4.8, 4.6, and 2.7 nm for the PtRuMn/C, PtRuMo/C, PtRuW/C and PtRu/C (E-tek) catalysts, respectively. The Pt (220) peaks at 68° were used for the particle size calculation. In the figure, peak shifts of the ternary catalysts to lower 2θ values than that of the PtRu/C catalyst were observed in the (111) and (220) peaks. Incorporation of Ru into Pt crystal structure causes shrinkage of lattice parameters as Ru (atomic No. 44) has much smaller radius than that of Pt (atomic No. 78). In other words, the higher degree of alloying of Pt with Ru results in a larger shift of the 2θ value to higher degrees. Therefore, the peak shifts of the ternary catalysts to lower 2θ values imply that alloying of Pt with Ru and third metals was achieved to a lower degree than that of the commercial PtRu/C catalyst. TEM results are shown in Fig. 2, where well dispersed catalyst particles on the carbon support were observed.

CO stripping results are displayed in Fig. 3. For comparison, enlarged image near 0.5 V is separately shown in Fig. 3(d). In the figure, it is shown that on-set potentials for CO electro-oxidation of the PtRuMn/C and PtRuW/C catalysts are lower than that of PtRu/C, indicating enhanced CO electro-oxidation activity by incorporation of Mn and W. In the case of PtRuMo/C, in Fig. 3(d) this catalyst appears to exhibit a high CO electro-oxidation activity; however, the current density at low potential originated from redox reactions of MoO_x [24], indicating that Mo was synthesized as its oxide forms.
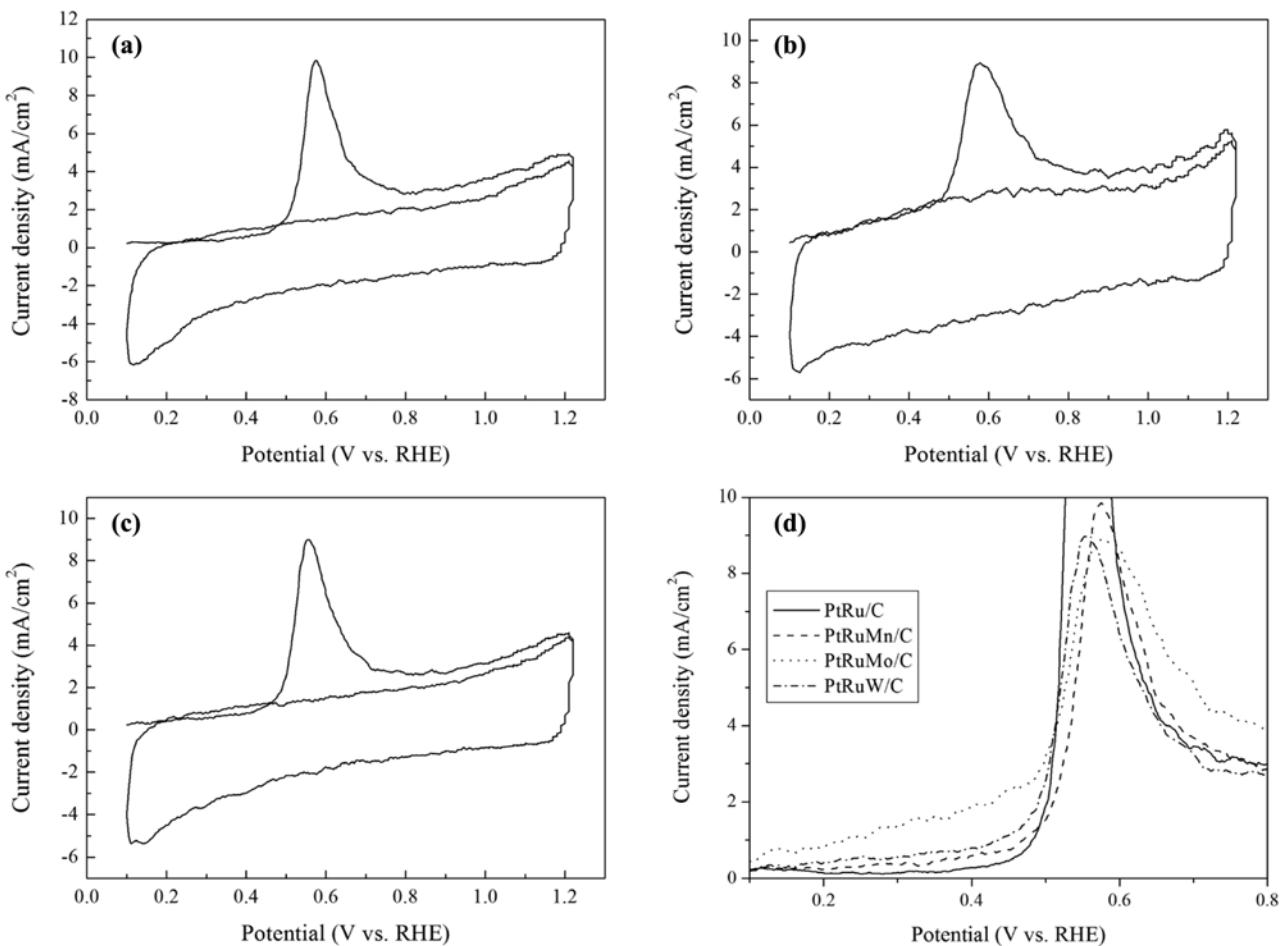

Fig. 3. CO stripping results of the (a) $Pt_{45}Ru_{45}Mn_{10}$/C, (b) $Pt_{45}Ru_{45}Mo_{10}$/C, and (c) $Pt_{45}Ru_{45}W_{10}$/C catalysts. (d) Enlarged image of the CO stripping results near 0.5 V.

Fig. 3(b) well explains this behavior where 1st and 2nd cycles are identical at low potentials. Electrochemically active surface area (EAS) was calculated from the CO oxidation area, with an assumption that the charge of CO monolayer adsorption is 420 $\mu C/cm^2$. EAS values were 17.7, 17.2, and 15.7 $m^2/g_{cat.}$ for the PtRuMn/C, PtRuMo/C and PtRuW/C catalysts, respectively. Though particle sizes of the catalysts were 3.9, 4.8 and 4.6 nm for the PtRuMn/C, PtRuMo/C and PtRuW/C, respectively, EAS did not show the same order. In the case of the PtRuMo/C catalyst, EAS was similar to that of PtRuMn/C though the PtRuMo/C catalyst had much larger particle size, indicating that Pt-rich surface was formed in PtRuMo/C.

MOR activity measurement results are shown in Fig. 4. At 0.5 V, PtRuW/C catalyst exhibited the highest current density, while PtRuMo/C showed the lowest current density. Mass activities for PtRuMn/C, PtRuMo/C, PtRuW/C, and PtRu/C were 2.11, 1.84, 2.78 and 2.28 $A/g_{cat.}$, respectively. Specific activities calculated by dividing mass activities by EAS values were 119, 107, 177 and 87.7 mA/m^2 for PtRuMn/C, PtRuMo/C, PtRuW/C and PtRu/C, respectively. A summary of the electrochemical properties is listed in Table 1. Among the four catalysts, the highest mass and specific activities were observed in the PtRuW/C catalyst. The mass and specific activities were 22 and 100% higher than those of the commercial PtRu/C catalyst, respectively, indicating that W is the most promising candidate as a third member of the PtRu/C catalyst among Mn, Mo and W. The PtRuMn/C and PtRuMo/C catalysts exhibited 36 and 22% higher specific activities than that of PtRu/C, respectively, indicating that there is still room for further development in these catalysts.

When considering our previous report on $Pt_{45}Ru_{45}M_{10}$/C (M=Fe, Ni and Co) [6], the order of high mass activity for MOR is W>Fe>Ni>Co≈Mn>Mo, while that of specific activity is W>Ni>Co≈Mn>Fe>Mo. In both cases, W showed the best activities, indicating PtRuW is the most promising catalyst among the synthesized catalysts. The order of MOR activities performed in the experiments is not much different from the order suggested by Demirci, except for Mo [17]. Though he suggested Mo as the most promising promoter, our results show that Mo is the worst promoter for MOR. The high activity of the PtRuW/C catalyst can be explained by the facile coordination of WO_2/WO_3 system with water to produce hydroxyl species [1] and d-band energy shift in Pt [17]. This shift is caused by alloying of Pt with other metals [25]. By lowering electron density of Pt, bond strength of Pt-CO is weakened, which results in easy removal of CO. In the case of Mo, similar behavior by MoO_3 was expected and much higher activity was previously reported by Lima et al. [26]; however, we could not find promotion effect. The poor performance of the PtRuMo/C catalyst in this study might come from the preparation method and composition used in this paper, as surface state of the catalysts is significantly affected by synthesis condition and composition [22]. Mn was not highlighted in the theoretical calculation [17], but the improvement of the MOR activity observed in our tests shows that further research is desirable as there were no reports on the contribution of Mn metal/oxides to the MOR activity.

EOR results are shown in Fig. 5. Mass activities of the PtRuMn/C, PtRuMo/C, PtRuW/C and PtRu/C catalysts were 1.8, 4.8, 2.1 and 4.6 $A/g_{cat.}$, respectively. Interestingly, the PtRuMo/C catalyst, which showed the lowest activity for MOR, exhibited the highest mass activity for EOR. Specific activities were 100, 280, 130 and 180 mA/m^2 for the PtRuMn/C, PtRuMo/C, PtRuW/C and PtRu/C
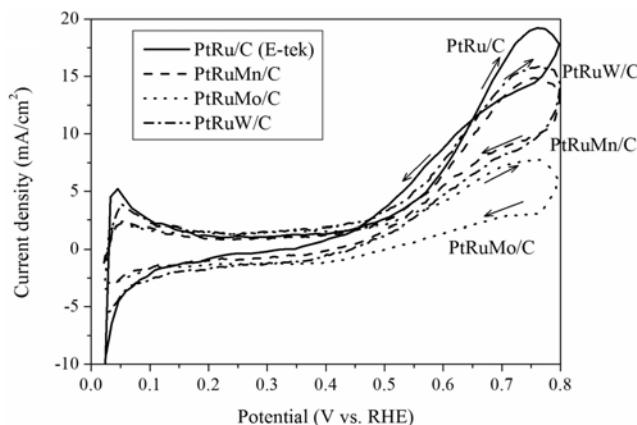

Fig. 4. MOR activity test results of the $Pt_{45}Ru_{45}Mn_{10}$/C, $Pt_{45}Ru_{45}Mo_{10}$/C, $Pt_{45}Ru_{45}W_{10}$/C and PtRu/C catalysts in 1 M methanol+1 M H_2SO_4 electrolyte solution.
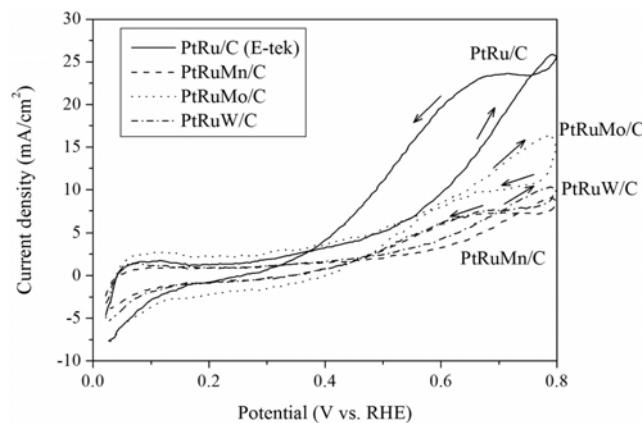
Fig. 5. EOR activity test results of the $Pt_{45}Ru_{45}Mn_{10}$/C, $Pt_{45}Ru_{45}Mo_{10}$/C, $Pt_{45}Ru_{45}W_{10}$/C and PtRu/C catalysts in 1 M ethanol+1 M H_2SO_4 electrolyte solution.

Table 1. Summary of electrochemical properties of the Pt45Ru45Mn10/C, Pt45Ru45Mo10/C, Pt45Ru45W10/C and PtRu/C catalysts

	EAS $(m^2/g_{cat.})$	Mass activity for MeOH $(A/g_{cat.})$	Specific activity for MeOH (mA/m^2)	Mass activity for EtOH $(A/g_{cat.})$	Specific activity for EtOH (mA/m^2)
$Pt_{45}Ru_{45}Mn_{10}$/C	17.7	2.11	119	1.8	100
$Pt_{45}Ru_{45}Mo_{10}$/C	17.2	1.84	107	4.8	280
$Pt_{45}Ru_{45}W_{10}$/C	15.7	2.78	177	2.1	130
PtRu/C (E-tek)	26.0	2.28	87.7	4.6	180

catalysts, respectively. The PtRuMo/C catalyst showed 56% higher specific activity than that of PtRu/C, indicating that incorporation of Mo could significantly improve EOR activity. The promotion of the catalytic activity for EOR by incorporation of Mo into PtRu/C was also reported in previous reports [27,28]. Opposite to the MOR results, Mn and W incorporated catalysts exhibited lower specific activities than that of PtRu/C. In EOR, it was reported that the main product was CH_3CHO (79%), while CH_3COOH was a minor product (20%) when Pt was used as a catalyst [29]. Ratio of CO_2 was only 1% indicating that only partial oxidation occurs during EOR with Pt. Based on our result that PtRuMo/C exhibited the worst and best activities for MOR and EOR, respectively, the role of MoO_x might be related to partial oxidation of ethanol, because the bi-functional mechanism and hydrogen spill-over which were also suggested as a promoting effect by Mo [24] should have improved methanol electro-oxidation, too. A summary of the EOR activity measurement results is listed in Table 1.

In recent reports, dissolution of Ru was observed during stability study of DMFC [30-32]. In the present study, we used Mn, Mo, and W as third metals, and dissolution of these metals should be discussed, as the dissolution of anode catalyst is one of the key parameters of DMFC performance degradation. In the case of Mn, it can be dissolved at high potentials according to the electrochemical reactions shown below:

$$Mn -> Mn^{2+} + 2e^- \qquad 1.18 \text{ V}$$
$$MnO_2 + 4H^+ + 2e^- -> Mn^{2+} + 2H_2O \qquad 1.28 \text{ V}$$
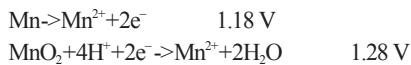
It was reported by Bonakdarpour et al. that Mn was leached from Pt-Mn alloy when soaked in 1 M H_2SO_4 solution at 80 °C for 10 days [33]. Therefore, the stability of Mn is questionable and needs further investigation. In the case of Mo, Lebedeva and Janssen observed dissolution of Mo from PtMo/C alloy catalysts during cyclic voltammetry in anodic potential region of 0-0.8 V [34]. D.M. dos Anjos et al. also reported dissolution of Mo in Pt-Mo alloy catalyst after cyclic voltammetry and chronoamperometry experiments [35]. On the other hand, Mukerjee et al. reported that a PtMo/C catalyst from E-tek was stable for 1,500 h in 0.6 V operation with H_2 and 100 ppm CO [36]. D.M. dos Anjos et al. suggested that the higher content of Mo can suppress dissolution of Mo by the formation of an alloy [35]. Thus, further investigation on composition dependence of Mo dissolution might be helpful in finding a highly active and stable EOR catalyst. When W was used as an anode catalyst with Pt and Ru, it was reported that corrosion occurred in W-rich catalysts, where W content was above 50% [12]. Thus, W dissolution from the $Pt_{45}Ru_{45}W_{10}$/C catalyst of this paper is not preferred during the anodic reactions.

CONCLUSION

The effect of third metal was investigated in the electro-oxidation of methanol and ethanol by incorporating one of Mn, Mo and W into the PtRu catalyst. In methanol electro-oxidation, the $Pt_{45}Ru_{45}W_{10}$/C catalyst showed the highest mass and specific activities, which were 22 and 100% higher than those of the commercial PtRu/C, respectively. The $Pt_{45}Ru_{45}Mo_{10}$/C catalyst exhibited the lowest mass and specific activities for methanol electro-oxidation, but 56% higher specific activity was obtained for ethanol electro-oxidation.

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