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The effect of PtRuW ternary electrocatalysts on methanol oxidation reaction in direct methanol fuel cells

Dae Kyu Kang*, Chang Soo Noh, Sang Tae Park***, Jung Min Sohn***,†, Seung Kon Kim***, and Young-Kwon Park******

*Petroleum Displacement Technology Research Center, Korea Research Institute of Chemical Technology (KRICT),
Sinseongno, Yuseong-gu, Daejeon 305-600, Korea
**Department of Hydrogen and Fuel Cells Engineering, Specialized Graduate School,
***Department of Mineral Resources & Energy Engineering,
Chonbuk National University, Jeonju 561-756, Korea
****Faculty of Environmental Engineering, University of Seoul, Seoul 130-743, Korea

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Abstract−PtRu and PtRuW ternary electrocatalysts were synthesized using an $NaBH_4$ reduction method. A uniform distribution of particles, with average particle size of 3-3.5 nm was indentified from X-ray diffraction (XRD) and transmission electron microscopy (TEM). The electrochemically active surface area was slightly decreased after the addition of W into PtRu. When W was added to PtRu, the specific and mass activity of methanol electro-oxidation was increased. The most active catalyst was Pt_5Ru_4W, of which specific and mass activities were 265.38 mA/m^2 and 6.21 A/g·catal, respectively. The specific and mass activity was 390 and 320% higher than that of PtRu.

Key words: Direct Methanol Fuel Cell, Methanol Oxidation Reaction (MOR), PtRuW, CO Stripping

INTRODUCTION

A direct methanol fuel cell (DMFC) has a lower power density than a hydrogen fuelled cell, but the high energy storage of methanol (5,019 A h Kg^{-1}) makes the DMFC an attractive electrochemical power source [1]. During the last decade, the direct methanol fuel cell has been widely studied for applications in transportable and portable electronic devices [2-4]. The use of fuel in a DMFC has several advantages compared to that of hydrogen: transport and storage, ease of handling and low operating temperature, and a high energy density [5-7].

Platinum was initially used as an electrocatalyst in the anode, as it was known to be the best electrocatalyst for the electro-oxidation of methanol. However, the use of platinum is limited due to the CO poisoning effect; therefore, the use of binary electrocatalysts, where a new metal is added onto the Pt-base, has been studied [8-10].

It is well known that the addition of Ru to Pt-based electrocatalysts lowers the overpotential for the methanol electro-oxidation reaction via a so-called bifunctional mechanism [11].

$$Pt+CH_3OH \rightarrow Pt\ CO_{ads}+4H^++4e^- \quad (1)$$

$$Ru+H_2O \rightarrow Ru\text{-}OH+H^++e^- \quad (2)$$

$$Pt\ CO_{ads}+Ru(OH)_{ads} \rightarrow CO_2+Pt+Ru+H^++e^- \quad (3)$$

With the PtRu catalyst the activity is increased due to a bifunctional effect, which involves the discharge of water onto Ru to produce Ru-OH [11]. From reaction (2), the main role of the Ru was the decomposition of water. Reaction (3), which produces carbon dioxide, is the only rate determining step with the PtRu catalyst. To increase the catalytic activity of the anode, the introduction of a PtRu binary catalyst was found to be the best electrocatalyst, because of its tolerance to CO, and has been widely used in DMFC for the electro-oxidation of methanol [12].

The platinum and ruthenium used with the precursors for electrode catalyst are very expensive, and noble metals as a resource are limited; therefore, new alternative materials for electrocatalysts are required. The use of a new material is essential to minimize the noble metal loading and optimum the catalytic performance. Many authors have intensively investigated Pt-based binary, ternary and even quaternary compounds to improve the performance of the electrocatalyst for the electro-oxidation of methanol [13-17]. Metal-metal oxide electrocatalysts are also being investigated with respect to electro-oxidation reactions [18].

In this paper, PtRuW ternary alloy electrocatalysts were prepared with Pt : Ru : W molar ratios of 5 : 4 : 1, 3 : 2 : 1 and 2 : 1 : 1 using a conventional $NaBH_4$ reduction method, and designated Pt_5Ru_4W, Pt_3Ru_2W and Pt_2RuW, respectively. A PtRu catalyst was prepared by the same method for a comparative study. The formation of nanoparticles was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD). The anodic electrochemical activity of the ternary alloy electrocatalysts was carried out by CO stripping and methanol electro-oxidation.

EXPERIMENTAL

The PtRuW ternary electrocatalysts were synthesized by using a conventional reduction method with $NaBH_4$. Pt ($H_2PtCl_6xH_20$), Ru ($RuCl_3$) and W (WCl_6) salts were used as the metal precursors for preparation of the electrocatalysts. The metal precursors were initially mixed in de-ionized water, with stirring at 80 °C for 1 h, until completely dissolved. A 0.2 M $NaBH_4$ solution was added to reduce

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†To whom correspondence should be addressed.
E-mail: jmsohn@jbnu.ac.kr

the solution mixtures. The resulting solutions were mixed thoroughly for 3 h, with stirring, followed by filtering and washing with hot de-ionized water. The resulting electrocatalysts were dried overnight in an oven.

The compositions of the prepared electrocatalysts were determined by energy dispersive X-ray (EDX) analysis using JSM-6400. X-ray diffraction (XRD) analyses of the electrocatalysts were performed by using a Rigaku DMAX-2500 with a Cu Kα radiation source. Transmission electron microscopy (TEM) was performed to measure the metal particle size with a JEM2010.

Electrochemical measurements were made at 25 °C by using a three-electrode cell, with a Pt-wire and Ag/AgCl electrode (BAS Co., Ltd., MF-2052 RE-5B) as the counter and reference electrodes, respectively. A glassy carbon working electrode (3 mm diameter and 0.07 cm^2 electrode area) was prepared by the thin-film method suggested by Schmidt et al. [19]. For the fabrication of the working electrode, the catalyst was dispersed in de-ionized water and subjected to sonication. The resulting catalyst suspension was pipetted onto the glassy carbon substrate. After air drying, the deposited catalyst was covered with a 5 wt% Nafion solution to stabilize the catalyst layer. The electrolyte solutions, 1 M $HClO_4$, 1 M H_2SO_4+ 1 M CH_3OH, were constantly stirred and purged with nitrogen gas prior to the experiment. All potential values are quoted versus the RHE (reversible hydrogen electrode). All the electrochemical experiments were measured at a scan rate of 15 mV/s.

In the CO stripping experiment, CO gas was bubbled through the working electrode for 1 h, while a constant voltage of 0.1 V (vs. RHE) was maintained. The dissolved CO in the electrolyte was purged by nitrogen gas bubbling for 50 min.

RESULTS AND DISCUSSION

The relative Pt : Ru : W ratios of the prepared electrocatalysts

Table 1. The atomic compositions of the prepared electrocatalysts by EDX analysis and particle size by TEM analysis

Electrocatalyst	Nominal content			Determined by EDX			Particle size by TEM (nm)
	Pt	Ru	W	Pt	Ru	W	
PtRu	1	1	-	51.67	48.33	-	-
Pt_5Ru_4W	5	4	1	51.58	39.35	9.07	3.0
Pt_3Ru_2W	3	2	1	52.18	31.27	16.55	3.5
Pt_2RuW	2	1	1	51.87	24.17	23.96	3.2

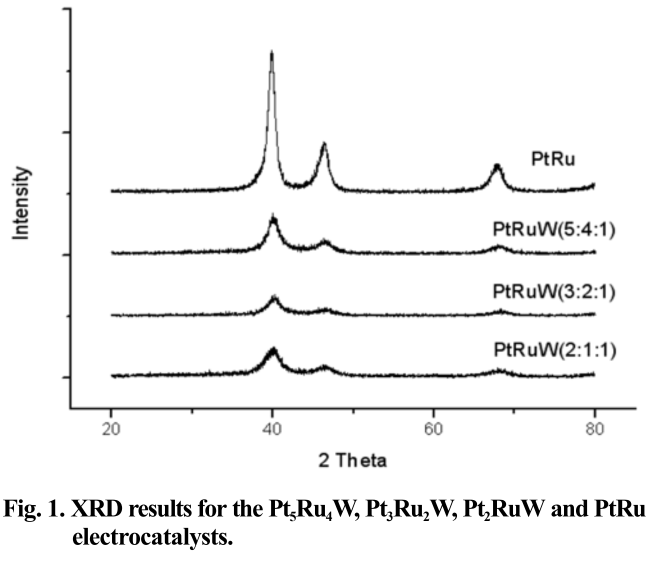

Fig. 1. XRD results for the Pt_5Ru_4W, Pt_3Ru_2W, Pt_2RuW and PtRu electrocatalysts.

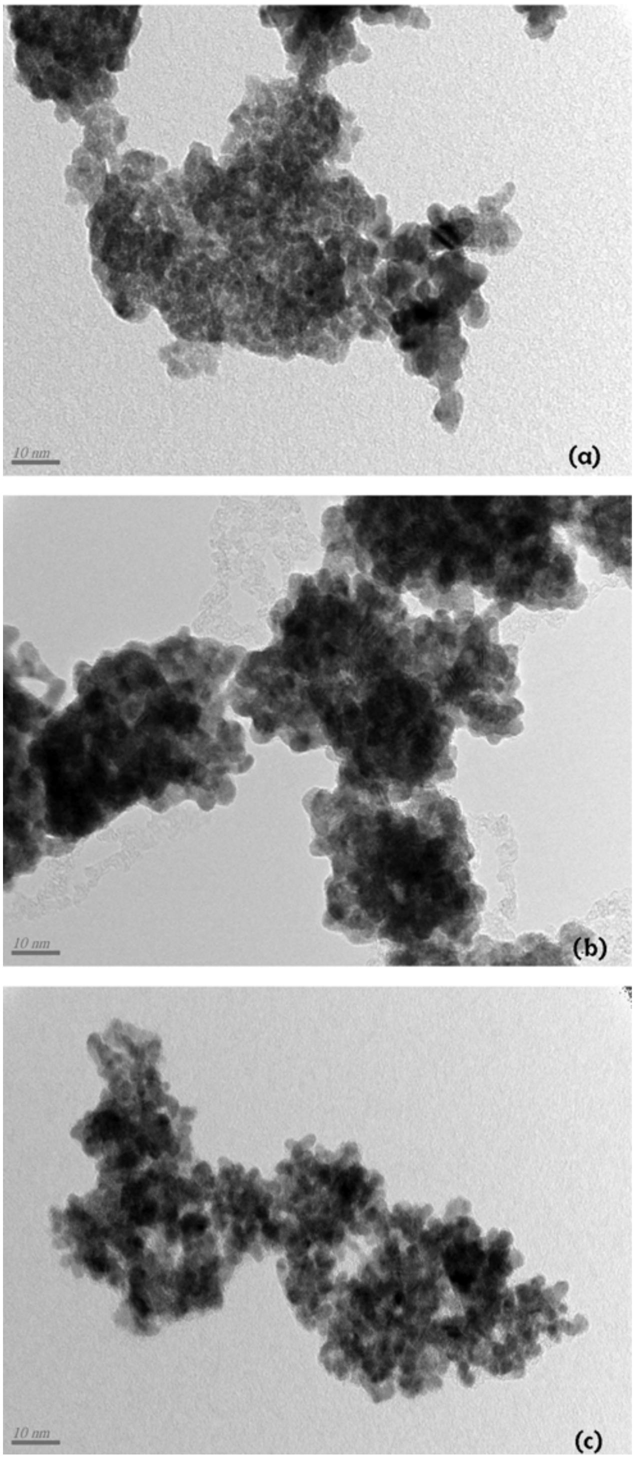

Fig. 2. TEM images of the: (a) Pt_5Ru_4W, (b) Pt_3Ru_2W and (c) Pt_2RuW electrocatalysts.

were determined by EDX analyses. As shown in Table 1, the EDX compositions of the prepared electrocatalysts were quite similar to the nominal ones, such as 51.58 (Pt) : 39.35 (Ru) : 9.07 (W) for Pt_5Ru_4W, 52.18 (Pt) : 31.27 (Ru) : 16.55 (W) for Pt_3Ru_2W, 51.87 (Pt) : 24.17 (Ru) : 23.96 (W) for Pt_2RuW, respectively.

Fig. 1 shows the X-ray diffraction patterns of the Pt_5Ru_4W, Pt_3Ru_2W, Pt_2RuW and PtRu electrocatalysts. The XRD patterns of the electrocatalysts showed peaks at approximately 2θ=39.82°, 46.4° and 68.04°, respectively. These peaks are characteristic of face-centered cubic (fcc) crystalline Pt, corresponding to (111), (200) and (220) planes, respectively, indicating that the electrocatalysts have good alloy formations.

The 2θ of the (111) peak for Pt_5Ru_4W, Pt_3Ru_2W, Pt_2RuW, which shows a higher angle shift than 39.82° of PtRu, were 39.97°, 40.04° and 40.08°, respectively. The diffraction peaks for the ternary electrocatalysts were very slightly shifted to higher 2θ values, indicating the formation of an alloy involving W substituted into the fcc structure of PtRu, suggesting the effect of a different atomic rate of W in the ternary catalyst.

The particle size distributions of the electrocatalysts were observed through transmission electron microscopy (TEM); the typical TEM images of the Pt_5Ru_4W, Pt_3Ru_2W and Pt_2RuW electrocatalysts are presented in Fig. 2(a), (b) and (c), respectively. From the TEM images, the average size of the uniform particles was found to be approximately 3-3.5 nm (Table 1).

Fig. 3 shows the results of CO stripping of the PtRu, Pt_5Ru_4W, Pt_3Ru_2W and Pt_2RuW electrocatalysts. CO stripping experiments were used to estimate the EAS (electrochemically active surface area). Due to the strong adsorption of CO onto the Pt surface, the hydrogen adsorption-desorption of the Pt was completely blocked in the hydrogen region; indicating the presence of a saturated CO adlayer [20]. The electrochemically active surface areas of the electrocatalysts were calculated by using Eq. (4) [21,22].

$$S_{EAS}=\frac{Q_{CO}}{G\times 420(\mu C/cm^2)} \tag{4}$$

Where Q_{co} is the charge for CO desorption electro-oxidation in microcoulomb (μC) and G the loading of the catalyst in the electrode, assuming an adsorption charge of 420 ($\mu C/Cm^2$) for a CO monolayer. The electrochemically active surface areas of the PtRu, Pt_5Ru_4W, Pt_3Ru_2W and Pt_2RuW electrocatalysts were 28.5, 23.4, 27.9 and 25.1 $m^2/g\cdot$catal, respectively. Peak separation was observed in Fig. 3(b), (c) and (d) when W was added into PtRu. Similar peak separation for PtRu alloy system was reported by Tong et al. [23]. They indicated that the peak separation was due to the formation of Ru-island-covered Pt surface (the low potential peaks) and pure

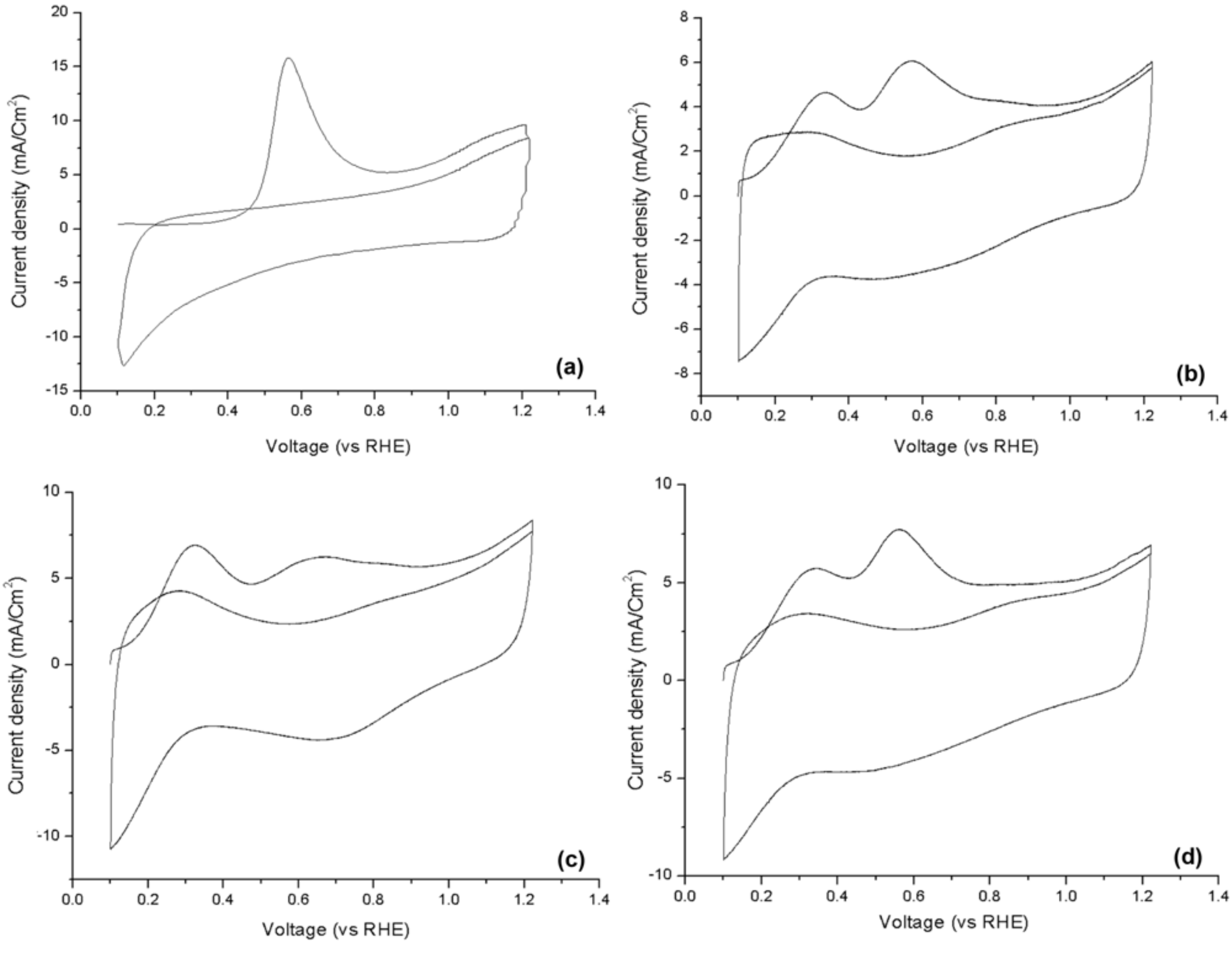

Fig. 3. CO stripping results for the: (a) PtRu, (b) Pt_5Ru_4W, (c) Pt_3Ru_2W and (d) Pt_2RuW electrocatalysts.

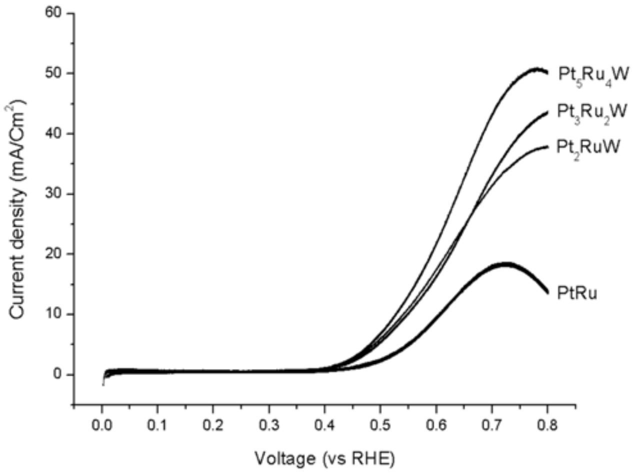

Fig. 4. Liner sweep voltammetry (LSV) curves of Pt_5Ru_4W, Pt_3Ru_2W, Pt_2RuW and PtRu for the oxidation of methanol in a solution of 1 M H_2SO_4+1 M CH_3OH at room temperature.

Pt surface (the high potential peaks). From our results, it could be assumed a heterogeneous surface structure with different surface composition. From the results of CO stripping, the onset potentials of the low potential peaks of the Pt_5Ru_4W, Pt_3Ru_2W and Pt_2RuW electrocatalysts were 0.26, 0.23 and 0.21 V, respectively, compared to the 0.45 V of the PtRu electrocatalyst. These results indicate that the lower CO electro-oxidation potential was due to the addition of tungsten into the PtRu electrocatalyst, suggesting that the homogeneous PtRuW different from PtRu was formed separately on the surface. The CO electro-oxidation potential is one of the key properties for determining the catalytic activity of the electro-oxidation of methanol as the CO oxidation reaction is a slow step during the methanol electro-oxidation reaction [2].

The cyclic voltammograms for the electro-oxidation methanol on the electrocatalysts in 1 mol/L CH_3OH and 1 mol/L H_2SO_4 solutions are shown in Fig. 4. The onset potential for the oxidation of methanol in a positive scan was a key factor for evaluating the catalyst activity [24]. The onset potentials for the oxidation of methanol on the Pt_5Ru_4W, Pt_3Ru_2W and Pt_2RuW electrocatalysts were slightly lower than that on the PtRu electrocatalyst.

Fig. 4 reveals that the current density for the methanol oxidation reactions (MOR) of the Pt_5Ru_4W, Pt_3Ru_2W and Pt_2RuW electrocatalysts were 7.06, 5.34 and 6.02 mA/Cm^2 at 0.5 V (vs. RHE), respectively, which were significantly higher than that of the PtRu electrocatalyst, which was 2.2 mA/Cm^2 at 0.5 V (vs. RHE). The electrocatalysts containing tungsten showed an advantage with respect to methanol oxidized. The maximum activity for the MOR was found with the Pt_5Ru_4W catalyst.

Similar results were reported by Kawaguchi et al. [25], who also investigated the performance of ternary electrocatalyst with various compositions of a third metal. They prepared PtRuRh/C catalysts with 13 different alloy compositions. Among these prepared catalysts, with increasing Rh content, an increase in activity was observed up to $PtRuRh_2/C$. However, an increase in Rh beyond this composition led to a decrease in activity. They said that this reason may be the difference in particle size and electrochemical active surface area since the metal loading was slightly higher for the composition of $PtRuRh_2/C$.

Actually, we could not indicate the reason why Pt_5Ru_4W showed the best activity in the series of PtRuW ternary alloys and will carry out further characterization to determine the more certain effect of promotion depending on tungsten amount.

Table 2 shows the electrochemical properties of the electrocatalysts. The specific and mass activities of the electrocatalysts were obtained to compare the catalyst activities. The Pt_5Ru_4W, Pt_3Ru_2W and Pt_2RuW electrocatalysts showed higher specific activities and mass activities than the PtRu electrocatalyst.

CONCLUSIONS

The PtRuW ternary electrocatalysts with different atomic ratios, prepared using the $NaBH_4$ reduction method, have shown enhanced electrocatalytic activities for the oxidation of methanol compared to a PtRu alloy catalyst. The maximum activity of the ternary electrocatalysts for the oxidation of methanol was found with the Pt_5Ru_4W electrocatalyst. The current density, mass activity and specific activity of the Pt_5Ru_4W electrocatalyst at 0.5 V (vs. RHE) were 7.06 mA/cm^2, 6.21 A/g·catal and 265.38 mA/m^2, respectively. The PtRuW ternary electrocatalyst exhibited a lower onset potential for CO electro-oxidation than that of the PtRu alloy electrocatalyst.

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Table 2. Electrochemical properties of the PtRu, Pt_5Ru_4W, Pt_3Ru_2W and Pt_2RuW electrocatalysts

Catalysts	EAS (m^2/g·catal)	Current density at 0.5 V (vs. RHE) (mA/cm^2)	Mass activity at 0.5 V (vs. RHE) (A/g·catal)	Specific activity at 0.5 V (vs. RHE) (mA/m^2)
PtRu	28.5	2.2	1.94	68.07
Pt_5Ru_4W	23.4	7.06	6.21	265.38
Pt_3Ru_2W	27.9	5.34	4.70	168.45
Pt_2RuW	25.1	6.02	5.30	211.15

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