Quaternary Pt$_2$Ru$_1$Fe$_1$M$_1$/C (M=Ni, Mo, or W) catalysts for methanol electro-oxidation reaction


*Nuclear Fuel Cycle Process Development Division, Korea Atomic Energy Research Institute, Daedeok-daero 989-111, Yuseong-gu, Daejeon 305-353, Korea
**Institute for Integrated Cell-Material Sciences (iCeMS), Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
***Department of Chemical and Biomolecular Engineering, University of Notre Dame, Notre Dame, IN 46556, USA

(Received 4 March 2014 • accepted 1 July 2014)

Abstract—Quaternary Pt$_2$Ru$_1$Fe$_1$M$_1$/C (M=Ni, Mo, or W) catalysts were investigated for the methanol electro-oxidation reaction (MOR). Electrocatalytic activities of the quaternary catalysts for CO electro-oxidation were studied via CO stripping experiments, and the Pt$_2$Ru$_1$Fe$_1$Ni$_1$/C and Pt$_2$Ru$_1$Fe$_1$W$_1$/C catalysts exhibited lowered on-set potential compared to that of a commercial PtRu/C catalyst. MOR activities of the quaternary catalysts were determined by linear sweep voltammetry (LSV) experiments, and the Pt$_2$Ru$_1$Fe$_1$W$_1$/C catalyst outperformed the commercial PtRu/C catalyst by 170 and 150% for the mass and specific activities, respectively. X-ray photoelectron spectroscopy (XPS) was employed to analyze surface oxidation states of constituent atoms, and it was identified that the structure of the synthesized catalysts are close to a nano-composite of Pt and constituent metal hydroxides and oxides. In addition, the XPS results suggested that the bi-functional mechanism accounts for the improved performance of the Pt$_2$Ru$_1$Fe$_1$Ni$_1$/C and Pt$_2$Ru$_1$Fe$_1$W$_1$/C catalysts.

Keywords: Methanol Electro-oxidation Reaction, Direct Methanol Fuel Cell, Electrocatalyst, X-ray Photoelectron Spectroscopy, CO Electro-oxidation

INTRODUCTION

Development of high performing methanol electro-oxidation reaction (MOR) electrocatalysts is desired due to their use in direct methanol fuel cells (DMFCs). DMFC has the attractive characteristic that it uses a liquid fuel, enabling design and fabrication of small cells. However, the use of methanol also has some drawbacks, such as low catalytic activity for the MOR and methanol cross-over from the anode to the cathode, resulting in suppressed cathode performance [1]. Pure platinum was first introduced for the MOR, but CO poisoning caused a rapid drop of catalytic activity. The poor CO tolerance of pure Pt catalyst was significantly improved by incorporating Ru, and a bi-functional mechanism was suggested to account for the improved CO tolerance [2-5]. According to the bi-functional mechanism, CO produced on the Pt surface reacts with OH generated on the surface of Ru to produce CO$_2$. The following reactions explain the bi-functional mechanism:

1. $\text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{Pt-CO} + 4\text{H}^+ + 4\text{e}^-$
2. $\text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru-OH} + \text{H}^+ + \text{e}^-$
3. $\text{Pt-CO} + \text{Ru-OH} \rightarrow \text{Pt} + \text{Ru+} + \text{CO}_2 + \text{H}^+ + \text{e}^-$

Although the PtRu catalyst achieved significantly improved MOR activity, research continues in the quest for catalysts with higher activity, lower cost, and enhanced stability. Among various efforts to develop highly active MOR electrocatalysts, transition metal doped PtRu catalysts such as PtRuNi [6-9], PtRuCo [10,11], PtRuMo [12], and PtRuW [10,11,13-15] exhibited promising results [16-18]. In addition to the bi-functional effect, electronic effect also accounts for the improved MOR activity of the transition metal doped PtRu catalysts [19-22]. Briefly, the electronic effect suggests that a modification of the Pt electronic structure is induced by neighboring transition metals, resulting in weakened Pt-CO bonding. Normally, the bi-functional mechanism can be identified through CO stripping experiments, because a lowered on-set potential for the CO$_2$ electro-oxidation reaction is observable when the bi-functional mechanism is operative. On the other hand, X-ray photoelectron spectroscopy (XPS) is widely employed to verify the electronic effect, because a change of Pt electronic state is caused by the transition elements.

Previously, Jeon et al. [23] reported that Pt$_2$Ru$_1$Fe$_1$/C catalyst (PtRuFe/C) significantly outperformed a binary PtRu/C catalyst. The high activity of the PtRuFe/C catalyst was also observed in a combinatorial study of various compositions of this ternary system [24]. The XPS analysis results revealed that electronic structure of Pt was significantly changed by the incorporation of Fe, meaning the electronic effect of Fe could weaken Pt-CO bonding to enhance the MOR and CO electro-oxidation activities of the PtRuFe/C catalyst. In the present study, a further investigation of the PtRuFe/C catalyst was performed by adding secondary transition metals of Ni, Mo, and W to produce quaternary compositions of Pt$_2$Ru$_1$Fe$_1$Ni$_1$/C (PtRuFeNi/C), Pt$_2$Ru$_1$Fe$_1$Mo$_1$/C (PtRuFeMo/C), and Pt$_2$Ru$_1$Fe$_1$W$_1$/
C (PtRuFeW/C). A review of Demirci [18] provided a rationale for selecting Mo and W as additional members of the PtRuFe/C catalyst. In the review, Demirci suggests Mo and W as promising candidates to promote the MOR activity of the PtRu catalyst according to surface segregation and d-band shift properties. Nickel was chosen according to previous results which reported promising MOR activities of ternary Pt-Ru-Ni catalysts [6-9]. The quaternary composition electrocatalysts were analyzed using various techniques including X-ray diffraction (XRD), CO stripping, linear sweep voltammetry (LSV), and X-ray photoelectron spectroscopy (XPS).

### EXPERIMENTAL

1. Synthesis of Catalysts

The quaternary catalysts were synthesized by a chemical reduction method using NaBH4 as a reducer. First, the carbon support (Vulcan XC72R) was dispersed in an isopropyl alcohol and de-ionized (DI) water mixture. An appropriate amount of metal precursors was dissolved to adjust the atomic ratio of Pt : Ru : Fe : M (M=Ni, Mo, or W) to 2 : 1 : 1 : 1. The total amount of metals was adjusted to achieve 60 wt% metal loading. H2PtCl6, RuCl3, (NH4)2Fe(SO4)2, NiCl2, NH3·H2O, (NH4)6Mo7O24·4H2O, and (NH4)6H2W12O40 were employed as metal precursors. The mixture solution was stirred at 80°C for 1 h, and then a 0.2 M NaBH4 solution was added to the mixture for reduction of the precursors, followed by further stirring for 3 h at 80°C to complete the reduction reaction. The reduced catalysts were filtered and washed with hot DI water and then dried at 120°C for 12 h.

2. Structural and Electrochemical Characterization of the Catalysts

The XRD (Rigaku D/Max-IIIc, 40 kV, 45 mA) patterns of the catalysts were measured at a scan rate of 3°/min in a θ-2θ scan mode. Electrochemical analysis was performed using a three-electrode-type beaker cell. Pt wire and Ag/AgCl electrodes (BAS Co., Ltd., MF-2052 RE-5B) were employed as the counter and reference electrodes, respectively. A glassy carbon electrode (3 mm dia., BAS Co. Ltd., MF-2012) was employed as a working electrode by depositing a catalyst layer on the electrode by the thin-film method [25]. A catalyst ink was prepared by sonicating a mixture of catalyst, DI-water, and 5 wt% Nafion ionomer solution to achieve homogeneous mixing. A quantity of the mixture was dripped onto the glassy carbon electrode and then solvent was removed at room temperature. After the solvent was evaporated, 5 wt% Nafion ionomer solution was dripped onto the catalyst layer to produce a Nafion thin-film on the catalyst layer to provide mechanical strength to the catalyst layer during electrochemical tests.

The CO stripping experiments were performed using 1 M HClO4 solution as an electrolyte in a three-electrode-type beaker cell. Carbon monoxide was bubbled through the cell for 1 h while keeping the working electrode at 0.1 V (vs. reversible hydrogen electrode (RHE)) to saturate the catalyst surface with CO. Residual CO in the electrolyte solution was removed by purging nitrogen gas through the cell for 50 minutes. Carbon monoxide electro-oxidation was performed by increasing the potential of the working electrode from 0.1 to 1.2 V (vs. RHE) at a rate of 15 mV/s. When the potential reached 1.2 V (vs. RHE), the potential was cycled between 0.1 and 1.2 V at a scan rate of 15 mV/s to confirm complete removal of CO. MOR activities of the catalysts were measured by increasing the potential of the working electrode from 0.0 to 0.5 V at a ramping rate of 1 mV/s, which is so-called the LSV technique. All potentials in this paper were converted to the RHE scale.

The XPS experiments were performed using a surface analysis system (LHS-10, SPECS GmbH) equipped with a multiplate channel detector using Mg Kα radiation (8.4 kV and 14 mA). To measure the XPS spectra, the catalyst samples were pressed at 1,000 psi to fabricate a pellet. The pelletized samples were loaded into the preparation chamber and then transferred into the main chamber where the pressure was maintained at 1×10⁻⁹ Torr by using a turbo molecular pump.

### RESULTS AND DISCUSSION

1. XRD Analysis Results

The XRD measurement results of the catalysts are shown in Fig. 1, with the peak positions of Pt for comparison purpose. Based on the (220) peak positions, signs of alloying were observed in the commercial PtRu/C (E-tek, 60 wt%, Pt : Ru=1 : 1 atomic ratio) and the quaternary catalysts. Lattice parameters of the samples could be calculated using an equation of

\[
a(220) = \frac{\lambda}{2\theta}\cos\theta
\]

where \(\lambda\) represents wavelength of X-ray (0.15406 nm), and \(\theta\) is

![Fig. 1. The XRD patterns of the quaternary PtRuFeNi/C, PtRuFeMo/C, and PtRuFeW/C catalysts along with that of a commercial PtRu/C catalyst. Peak positions of pure platinum are denoted with solid vertical lines.](image)

<table>
<thead>
<tr>
<th>Table 1. Summary of the XRD measurement results</th>
</tr>
</thead>
<tbody>
<tr>
<td>(220) Peak position (°)</td>
</tr>
<tr>
<td>-------------------------</td>
</tr>
<tr>
<td>PtRu/C</td>
</tr>
<tr>
<td>PtRuFeNi/C</td>
</tr>
<tr>
<td>PtRuFeMo/C</td>
</tr>
<tr>
<td>PtRuFeW/C</td>
</tr>
</tbody>
</table>

Korean J. Chem. Eng.(Vol. 32, No. 2)