Effect of Tungsten on PtRuW/C Catalysts for Promoting Methanol Electro-oxidation

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1. Introduction

Fuel cells have attracted much attention for various applications as a next generation power source[1,2]. There have been studies on various fuel cells as energy sources for mobile devices, such as laptops and mobile phones, including the direct methanol fuel cell (DMFC). It has a high energy density, easily handling as a liquid fuel, as well as low operating temperatures and volumetric energy density; about 10 times larger than those of lithium ion batteries[3,4]. However, this merit of DMFC also results in drawbacks of methanol cross-over and low catalytic activity of anode catalysts for methanol electro-oxidation. Platinum was initially used for methanol electro-oxidation, but is easily poisoned by intermediate CO. Therefore, the use of binary catalysts, with the introduction of a new metal into the Platinum-base, has been studied[5-9]. Although PtRu is known to be the best catalyst for methanol electro-oxidation, improvement is required for its commercial application to the DMFC.

It is well known that the addition of Ruthenium to Platinum-based catalysts lowers the overpotential of the methanol electro-oxidation reaction via a bifunctional mechanism[10]:

\[ \text{Pt} + \text{CH}_3\text{OH} \rightarrow \text{Pt-CO}_\text{ads} + 4\text{H}^+ + 4e^- \quad (1) \]
\[ \text{Ru} + \text{H}_2\text{O} \rightarrow \text{Ru-OH}_\text{ads} + \text{H}^+ + e^- \quad (2) \]
\[ \text{Pt(CO)}_\text{ads} + \text{Ru(OH)}_\text{ads} \rightarrow \text{CO}_\text{ads} + \text{Pt} + \text{Ru} + \text{H}^+ + e^- \quad (3) \]

The activity of the PtRu catalyst is increased by the bifunctional

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The platinum and ruthenium used with the precursors for electrode catalyst are very expensive. Also, noble metals as a resource are limited; therefore, new alternative materials for electrode catalysts are required. Thus, studies on more complicated systems, such as ternary and quaternary metals, have also been conducted[12]. These ternary and quaternary catalysts, such as PtRuW[13], PtRuRh[14], PtRuNi[15,17], PtRu[Ru[18], PtRuFe[19], PtRuSn[4], PtRuMoW[20], PtRuRhNi[21] and PtRuOsIr[22], were shown to have higher methanol oxidation than the PtRu catalyst.

In this work, PtRuW/C ternary catalysts, with the addition of different amounts of tungsten, were prepared using a conventional impregnation method employing NaBH₄ as a reducing agent and compared with commercial PtRu/C (60 wt%, E-tek). The catalysts were characterized by TEM, energy dispersive x-ray (EDX) and XRD, respectively. Further, their electrochemical properties were analyzed via CO stripping, linear sweep voltammetry and chronoamperometry, respectively, using a three-electrode half cell.

2. Experimental

A conventional impregnation method (reducing agent: sodium borohydride, NaBH₄) was used to synthesize the catalysts. Initially, Vulcan XC72R carbon black was dispersed in a mixture of de-ionized water and isopropyl alcohol and then sonicated. Metal precursors were dissolved in de-ionized water and stirred. H₂PtCl₆ ⋅ xH₂O (Kojima Chem. Co.), RuCl₃ (Aldrich Chem. Co.) and WCl₆ (Aldrich Chem. Co.) were used as the Pt, Ru and W precursors, respectively. The amounts of metal precursors were adjusted to give Pt : Ru : W of different molar ratios; namely 5 : 4 : 1, 2 : 1 : 1, 1 : 1 : 1, and 1 : 2 : 2, with a total metal content in the catalyst of 60 wt%. The mixture was heated to, and maintained at, 80 ℃ for 1 h with stirring. A 0.2 M NaBH₄ solution was added to reduce the mixture. The resulting solution was mixed thoroughly for 3 h, followed by filtering and washing with hot de-ionized water. The catalysts were then dried overnight in an oven at 80 ℃.

XRD patterns were recorded on a Rigaku DMAX-2500 using a Cu Kα radiation source, and TEM images of the in-house catalysts using a JEM2200FS. Moreover, the compositions of the in-house catalysts were determined by EDX analysis using JSM-6400.

Electrochemical measurements were carried out at 25 ℃ using a potentiostat (Bio-Logic, SP-150). A three-electrode half cell, with a Pt-wire, Ag/AgCl (BAS Co., Ltd., MF-2052 RE-5B) and glassy carbon electrode (3 mm diameter, BAS Co., Ltd., MF-2012) used as the counter, reference and working electrodes, respectively.

The glassy carbon working electrode was prepared by the thin-film method suggested by Schmidt et al.[23] For the fabrication of the working electrode, the catalyst was dispersed in de-ionized water with sonication, and the catalyst suspension then dropped onto the glassy carbon substrate. After drying at room temperature, a 5 wt% Nafion ionomer solution was dropped onto the surface to stabilize the catalyst layer. Further, working electrode of commercial PtRu/C (60 wt%, E-tek) was also prepared by same method compared to properties of our catalysts. The 1 M HClO₄ and 1 M CH₃OH in 1 M H₂SO₄ electrolyte solutions were purged with nitrogen gas (N₂) before the experiments.

3. Results and Discussion

Figure 1 shows the X-ray diffraction results of the catalysts prepared using the addition of different mounts of tungsten. In all diffraction results, a broad peak at about 25° marked with C was associated with the (002) plane of the hexagonal structure of carbon black support material.

As can be seen from Figure 1 there were no other distinct reflection peaks, which indicated the presence of Ru and W metals, except hexagonal structure of carbon black, in-house ternary alloy catalysts have approximately 39.5°, 46.1°, and 67.7° of face centered cubic (FCC) crystalline Pt phase, corresponding to Pt (111), (200), and (220) planes, respectively.

Significant changes were observed in spectrogram of PtRu₆W/C catalyst. Firstly, spectrogram of PtRu₆W/C was very smooth than that of other catalysts and was not observed significant Pt and Pt alloy peaks. The behavior of binary and/or ternary alloys with respect to electrocatalysis can be understood in terms of “dilution effects”. Many investigators[24-26] reported that when second and/or third metal of high concentration was added into Pt and Pt alloy catalysts, it could block on active sites of Pt. Judging from this, very smooth spectrogram of PtRu₆W/C is probably due to the amounts of ruthenium and tungsten were adjusted two times higher than of platinum.

Secondly, one additional peak was observed at approximately 2θ = 34°, and was identified as (200) phase of the tungsten oxide (WO₂). [27] Furthermore, the diffraction peaks of the in-house catalysts were slightly shifted to higher 2θ values than that of commercial PtRu/C,
due to the formation of an alloy involving the incorporation of Ru and W into the fcc structure of the Pt[28].

The crystalline sizes of in-house catalysts were calculated using the Debye-Scherrer equation[29] and listed in Table 1.

\[
d = \frac{k\lambda}{\beta_{1/2} \cos \theta}
\]

Where \(d\) is the particle size (nm), \(\lambda\) is the wavelength of X-ray, \(\theta\) is the angle of maximum peak, \(\beta_{1/2}\) is the width of the diffraction peak at half height, \(k\) is a coefficient of 0.89 to 1.39 (0.9 here).

Obviously, all catalysts had comparatively small crystalline sizes which were approximately 3.5 ∼ 5.5 nm and a good alloy formation as observed from the TEM analysis shown in Figure 2. Uniform dispersion of the in-house catalysts, except PtRu\(_2\)W\(_2\)/C, was observed for all catalysts without agglomeration. Moreover, the chemical compositions of the catalysts were determined by EDX analysis and were quite similar to the nominal value.

The CO stripping was measured in a 1 M HClO\(_4\) solution, with a scan rate of 15 mV \cdot s\(^{-1}\), as follows; CO was bubbled through the working electrode for 1 h, while maintaining a constant voltage of 0.1 V (vs. RHE). The dissolved CO in the electrolyte was purged by nitrogen gas bubbling for 50 min. The CO stripping results for the in-house and commercial (60 wt%, E-tek) catalysts are showed in Figure 3. Significant changes were observed at two points:

Firstly, the potential of the in-house catalysts became more negative...
saturated CO blocked in the hydrogen region; this indicates the presence of a surface. Hydrogen adsorption-desorption on the Pt was completely surface area (EAS). Due to the strong adsorption of CO onto the Pt, CO adsorption was performed to measure the electrochemically active diffusion to generate the well-resolved peak separations. Predictions, although the theoretical model assumes virtually no surface away from the Ru sites. Our CO stripping results support these theoretical peak was attributed to CO oxidation on the Pt atoms much further the Pt sites next to the ruthenium island edge, while a high potential A peak observed at a low potential was assigned to CO oxidation on the Pt atoms much further surfaces Pt-Ru bimetallic alloy predicted two CO stripping peak maxima. As shown in Figure 5, the current densities of the in-house catalysts were much larger than that of commercial catalyst, except that of PtRuW/C catalyst had the highest methanol oxidation activity. The electrochemical properties of the catalysts were much larger than that of commercial catalyst, except that of PtRuW/C catalyst had the highest methanol oxidation activity. The electrochemical properties of the catalysts were listed in Table 2.

Table 2. Electrochemical Properties of In-house and Commercial Catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>On-set voltage for CO oxidation [V]</th>
<th>SEAS [m²(g catal)⁻¹]</th>
<th>Current density at 0.5 V [mA cm⁻²]</th>
<th>Mass activity [A(g · Pt)⁻¹]</th>
<th>Specific activity [mA m⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtRuW/C</td>
<td>0.243</td>
<td>39.65</td>
<td>5.44</td>
<td>14.24</td>
<td>121.05</td>
</tr>
<tr>
<td>PtRuW/C</td>
<td>0.187</td>
<td>36.80</td>
<td>3.40</td>
<td>8.90</td>
<td>81.52</td>
</tr>
<tr>
<td>PtRuW/C</td>
<td>0.183</td>
<td>18.09</td>
<td>1.42</td>
<td>5.28</td>
<td>69.09</td>
</tr>
<tr>
<td>PtRuW/C</td>
<td>0.161</td>
<td>13.86</td>
<td>0.34</td>
<td>2.40</td>
<td>21.64</td>
</tr>
<tr>
<td>PtRuW/C (E-tek)</td>
<td>0.490</td>
<td>42.56</td>
<td>2.79</td>
<td>7.30</td>
<td>57.80</td>
</tr>
</tbody>
</table>

The in-house catalysts mainly showed reduced mass activities of 14.24 A(g · Pt)⁻¹ for PtRuW/C and PtRuW/C, which were higher than the 7.30 A(g · Pt)⁻¹ of the commercial PtRu/C catalyst, respectively. PtRuW/C catalyst had the highest methanol oxidation activity. The electrochemical properties of the catalysts are listed in Table 2.

Figure 4. On-set voltage for the CO oxidation of PtRuW/C (dash), PtRuW/C (dash dot), PtRuW/C (dash dot dot), PtRuW/C (dot), and commercial PtRu/C (solid).

Figure 5. Liner sweep voltammetry (LSV) curves for in-house and commercial catalysts for the methanol oxidation in a solution of 1 M H₂SO₄ + 1 M CH₃OH at room temperature.

as the amount of tungsten increased. The CO oxidation potential is one of the key properties in determining the catalytic activity for methanol oxidation, as the CO oxidation reaction is a slow step during the methanol oxidation reaction[30]. The on-set voltages of the in-house catalysts for CO oxidation are compared in Figure 4. The on-set voltages of the CO oxidation of PtRuW/C, PtRuW/C, PtRuW/C, and PtRuW/C, which were all lower than the 0.49 V of commercial PtRu/C, were 0.243, 0.187, 0.183, and 0.161 V, respectively, indicating incorporation of W could lower the CO oxidation potential, as expected; secondly, the appearance of a new peak at a more negative potential on the addition of W. Koper et al. investigated[31] island-covered heterogeneous surfaces Pt-Ru bimetallic alloy predicted two CO stripping peak maxima. A peak observed at a low potential was assigned to CO oxidation on the Pt sites next to the ruthenium island edge, while a high potential peak was attributed to CO oxidation on the Pt atoms much further away from the Ru sites. Our CO stripping results support these theoretical predictions, although the theoretical model assumes virtually no surface diffusion to generate the well-resolved peak separations.

Furthermore, a CO stripping experiment to evaluate the amounts of CO adsorbed was performed to measure the electrochemically active surface area (EAS). Due to the strong adsorption of CO onto the Pt surface, hydrogen adsorption-desorption on the Pt was completely blocked in the hydrogen region; this indicates the presence of a saturated COads layer[32]. The electrochemically active surface areas of the catalysts were calculated using Equation (2)[27,33].

\[ S_{EAS} = \frac{Q_{CO}}{G \times 420(\mu C m^{-2})} \]  

Equation (2)

where \( Q_{CO} \) is the charge for CO desorption-electro-oxidation in micro-coulomb (µC), \( G \) represents the summation of catalysts metal loading (µg) in the electrode, and 420 is the charge required to oxidize a monolayer of CO on the catalyst in µC cm⁻². The calculated S_EAS were 42.56, 39.65, 36.80, 18.09, and 13.86 m²(g catal)⁻¹ for commercial PtRu/C, PtRuW/C, PtRuW/C, PtRuW/C, and PtRuW/C, respectively. The in-house catalysts mainly showed reduced S_EAS with increasing tungsten content, such as the PtRuW/C and PtRuW/C catalysts. The results from this experiment confirmed that exposure of Pt to the surface of the catalyst particles was obstructed by W contents.

The methanol oxidation activity was measured in a solution of 1 M CH₃OH + 1 M H₂SO₄ at a scan rate of 15 mV · s⁻¹. As shown in Figure 5, the current densities of the in-house catalysts were much larger than that of commercial catalyst, except that of PtRuW/C catalyst had the highest methanol oxidation activity. The electrochemical properties of the catalysts are listed in Table 2.

The current densities were converted into mass and specific activities. The mass activities at 0.5 V were 14.24, 8.90, 5.28, 2.40, and 7.30 A(g · Pt)⁻¹ for PtRuW/C, PtRuW/C, PtRuW/C, PtRuW/C, and PtRuW/C, and the commercial PtRu/C catalyst, respectively. PtRuW/C and PtRuW/C exhibited mass activities of 14.24 A(g · Pt)⁻¹ and 8.90 A(g · Pt)⁻¹, which were higher than the 7.30 A(g · Pt)⁻¹ of the commercial PtRu/C catalyst.
catalyst. The PtRuW/C catalyst showed a mass activity especially higher; about twice that of the commercial PtRu/C catalyst. For the specific activity, the Pt5Ru4W/C catalyst was still approximately twice that of the PtRu/C catalyst, and both PtRuW/C and PtRu/C also showed higher specific activities than the PtRu/C catalyst.

To investigate the tolerance of the in-house catalysts during the methanol oxidation, chronoamperometry tests were performed for 2000 s in a solution of 1 M CH3OH + 1 M H2SO4. Figure 6 showed the chronoamperometry results for the in-house catalysts at a fixed potential of 0.5 V, which shows the incipient currents for methanol oxidation were higher than those found by linear sweep voltammetry at the same potential, due to the lower amounts of Pt oxides (PtOx) in the catalysts [34]. Furthermore, the potentiostatic current decreased rapidly within a short time; this may have been due to the formation of COads and other intermediate species, such as CH3OHads, CHOads, and OHads, during the methanol oxidation reaction[35], and the effect of diffusion limitation of reactants on the electrode. The in-house catalysts were gradually oxidized, similarly to that of the commercial catalyst; the poisoning rate (δ) of catalysts with use over a long time were calculated using Equation (3), [36,37] and are listed in Table 3.

\[
\delta = 100 \times \left( \frac{dI}{dt} \right)_{t=500s} (\% \cdot s^{-1})
\]  
Equation (3)

Where \( \frac{dI}{dt} \) is the slope of the linear portion of the current decay above 500 s and \( I_0 \) is the current at the start of polarization back extrapolated from the linear current decay.

In Table 3, the poisoning rate of the Pt5Ru4W/C catalyst (0.01 % ⋅ s⁻¹) was lower than that of the commercial catalyst (0.02 % ⋅ s⁻¹). Further, the Pt5RuW/C and PtRuW/C catalysts, except the PtRu2W2/C catalyst showed slightly high poisoning rate than the commercial catalyst, but were confirmed to have comparatively low poisoning rates; 0.03 % ⋅ s⁻¹.

As shown in Figures 3~7, the anodic efficiency decreased with increasing amount of tungsten. After a 10 mole% of tungsten composition, as in the standard, the poisoning rate (circle) and specific activity (square) was increased and decreased, respectively.

The above results indicated that by the addition of tungsten, the PtRuW ternary alloy structure was observed to have the resistance to CO poisoning and promote electrical performance to methanol electro-oxidation. Further investigation for understanding the detailed mechanism is carried out.

4. Conclusions

PtRuW/C catalysts were prepared with the addition of different amounts of tungsten using the impregnation method employing NaBH4 as a reducing agent. The catalytic activities of the in-house catalysts were measured via electrochemical experiments, including CO stripping, linear sweep voltammetry and chronoamperometry, and compared to commercial PtRu/C.

From the CO stripping, the catalysts were confirmed to move to more negative potentials as the amount of tungsten was increased. Furthermore, the maximum specific activity of the catalysts for methanol oxidation was found with Pt5Ru4W/C; 121.05 mA ⋅ m⁻². And poisoning rate of Pt5Ru4W/C catalyst (0.01 % ⋅ s⁻¹) was lower than that of commercial catalyst (0.02 % ⋅ s⁻¹). We realized in this experiment that Pt5RuW/C catalyst gave a higher performance than commercial PtRu catalyst.

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