Radiolytic Synthesis of Pt-Ru Catalysts Based on Functional Polymer- Grafted MWNT and Their Catalytic Efficiency for CO and MeOH

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Pt-Ru catalysts based on functional polymer-grafted MWNT (Pt-Ru@FP-MWNT) were prepared by radiolytic deposition of Pt-Ru nanoparticles on functional polymer-grafted multiwalled carbon nanotube (FP-MWNT). Three different types of functional polymers, poly(acrylic acid) (PAAc), poly(methacrylic acid) (PMAc), and poly(vinylphenyl boronic acid) (PVPBAc), were grafted on the MWNT surface by radiation-induced graft polymerization (RIGP). Then, Pt-Ru nanoparticles were deposited onto the FP-MWNT supports by the reduction of metal ions using $\gamma$-irradiation to obtain Pt-Ru@FP-MWNT catalysts. The Pt-Ru@FP-MWNT catalysts were then characterized by XRD, XPS, TEM, and elemental analysis. The catalytic efficiency of Pt-Ru@FP-MWNT catalyst was examined for CO stripping and MeOH oxidation for use in a direct methanol fuel cell (DMFC). The Pt-Ru@PVPBAc-MWNT catalyst shows enhanced activity for electro-oxidation of CO and MeOH oxidation over that of the commercial E-TEK catalyst.

1. Introduction

Although carbon-supported Pt-Ru nanoparticles (Pt-Ru/C) are known to be the best anode catalysts for direct methanol fuel cell (DMFC), they are still insufficient for the commercial application. Many researcher efforts have been devoted to improving the catalytic performance of Pt-Ru/C by catalyst dispersion [1–3]. In previous paper, we deposited Pt-Ru nanoparticles on the surface of various carbon supports, including Vulcan XC-71, Ketjen-300, Ketjen-600, SWNTs, and MWNTs for use as fuel cell catalysts [4]. However, the metallic alloy nanoparticles were aggregated on the surface of the carbon supports due to their hydrophobic nature. The metal (Ag or Pd) and alloy (Pt-Ru) nanoparticles were also deposited on the surface of single-walled carbon nanotubes (SWNTs) [5], and porous carbon supports using $\gamma$-irradiation without protecting agents [6]. Silva et al. [7] reported the preparation of Pt-Ru/C electrocatalysts using $\gamma$-irradiation in water/ethylene glycol. This paper showed the patterns of Pt-Ru nanoparticles on carbon supports; however, it did not indicate the catalytic efficiency of MeOH oxidation based on the aggregation degree. It is proposed that the catalytic efficiency is affected by the metallic nanoparticle aggregation degree on carbon supports.

To overcome the aggregation of the metallic nanoparticles, the carbon support surface was modified with hydrophobic properties to obtain hydrophilic properties by in-situ polymerization of $\beta$-caprolactone, methacrylate, and pyrrole using oxidizing agents as the initiator [8]. Pt-Ru nanoparticles were then deposited on the polymer-wrapped MWNT supports to produce a direct methanol fuel cell (DMFC) catalyst. Pt-Ru at poly(pyrrole)-MWNT catalysts obtained high catalytic efficiency for CO stripping and methanol oxidation. The surface of MWNTs was then coated using conductive polymers such as aniline, pyrrole, and thiophene to go from hydrophobic properties to hydrophilic properties [9]. Finally, the metallic nanoparticles were deposited on conducting polymer-wrapped MWNTs. However, the prepared Pt-Ru catalysts provided lower catalytic efficiency compared to that of commercial E-TEK catalyst.

Radiation-induced graft polymerization (RIGP) is a useful method for the introduction of functional groups onto different polymer materials using specially selected monomers. There have been several reports about RIGP...
of polar monomers onto polymer substrates to obtain hydrophilic properties for versatile applications [10–14]. The RIGP method can easily functionalize the surface of MWNTs to the desired properties. In a previous paper, we described the functionalization of MWNTs by RIGP of derivatives vinyl monomers and their application in enzyme-free biosensors [15]. However, little has been reported about the deposition of Pt-Ru nanoparticles on the functionalized MWNT supports by γ-irradiation for DMFC catalysts.

In this study, Pt-Ru nanoparticles were deposited on the functional polymer (FP)-grafted MWNT obtained from RIGP using γ-irradiation to produce an anode catalyst for DMFCs. The obtained Pt-RuatFP-MWNT catalysts were characterized by XRD, XPS, TEM, and elemental analysis. Furthermore, the catalytic efficiency of the Pt-RuatFP-MWNT catalyst was evaluated for CO stripping and MeOH oxidation for use in a DMFC and compared to the catalytic efficiency of the commercial E-TEK catalyst.

2. Experimental

2.1. Chemicals. H2PtCl6 × H2O (37.5% Pt), RuCl3 × H2O (41.0% Ru), acrylic acid (AAc), methacrylic acid (MAc), and 4-vinylphenylboronic acid (VPBAc) were of analytical reagent grade (Sigma-Aldrich, USA) and used without further purification. MWNTs (CM-95) were supplied by Hanwha Nanotech Co., Ltd (Korea). The commercial E-TEK catalyst (metallic content, 30 wt%-%) was purchased from E-TEK (BASF Fuel Cell Inc., NJ, USA). Nafion (perfluorinated ion-exchange resin, 5% (w/v) solution in a solution of 90% aliphatic alcohol/10% water mixture) was also purchased from Sigma-Aldrich (USA). Solutions for the experiments were prepared with water purified in a Milli-Q puls water purification system (Millipore Co. Ltd, USA). The final resistance of water was 18.2 MΩ cm⁻¹ and degassed prior to each measurement. Other chemicals were of reagent grade.

2.2. RIGP of Functional Monomers on the Surface of MWNTs. MWNTs were purified to remove the catalyst and noncrystallized carbon impurities with phosphoric acid solution. The purified MWNTs were used as the supporting materials for grafting of various vinyl monomers. The MWNTs (2.0 g) and AAc (2.0 g) were then mixed in aqueous solution following equation [16]:

\[
\text{H}_2\text{O} \rightarrow e_{aq}^- , \text{H}^+ , \text{H}^- , \text{OH}^- , \text{H}_2\text{O}_2, \text{H}_2
\]  

Among them, the solvated electrons, e_{aq}^− and H^− radicals can be used as strong reducing agents. The metal ions were reduced to the zero-valent state as shown in the following:

\[
\text{M}^+ + e_{aq}^- \rightarrow \text{M}^0
\]

Similarly, multivalent ions, such as Pt^{4+} and Ru^{3+}, are reduced by a multistep reaction. On the other hand, the hydroxyl radical (OH·) can be oxidized for the ions or zero-valence metal atom. In order to protect the oxidizing agent (OH·), 2-propanol was added to the reaction solution. The OH· radical was reacted with 2-propanol as shown in (3).

2.3. Preparation of Pt-RuatFP-MWNT Catalysts by γ- Irradiation. The Pt-RuatPVPBAc-MWNT catalysts were prepared as follows: H2PtCl6 × H2O (0.43 g) and RuCl3 × H2O (0.41 g) were dissolved in deionized water (188 mL) in 2-propanol (12.0 mL) as the radical scavenger. 1.0 g of PVPBAc-MWNT support was added to the above solution. Nitrogen was bubbled for 30 min through the solution to remove oxygen and then irradiated under atmospheric pressure and ambient temperature. A total irradiation dose of 30 kGy (a dose rate = 6.48 × 10^5/h) was applied. Pt-Ru nanoparticle-deposited PVPBAc-MWNT catalysts were precipitated after γ-irradiation. The Pt-RuatPVPBAc-MWNT and Pt-RuatPMAc-MWNT catalysts were prepared as described above.

2.4. Characteristics of Pt-RuatFP-MWNT Catalysts. Particle size and morphology of the Pt-RuatFP-MWNT catalysts were analyzed by HR-TEM (JEOL, JEM-2010, USA). The content of Pt and Ru in samples was analyzed by inductively coupled plasma-atomic emission spectrometer (ICP-AES) (Jobin-Yvon, Ultima-C, USA). X-ray diffraction (XRD) patterns for samples were obtained using a Japanese Rigaku D/max γA X-ray diffractometer equipped with graphite monochromatized Cu Ka radiation (l = 0.15414 nm). The scanning range was 5–80° with a scanning rate of 5°/min.

To evaluate the catalytic efficiency of Pt-RuatFP-MWNT catalysts for the electro-oxidation of CO and MeOH, the Pt-RuatFP-MWNT-coated electrode was prepared as follows. Firstly, the catalytic inks were prepared by mixing of Pt-RuatFP-MWNT catalysts (5.0 mg) and 5% Nafion solution (0.05 mL) and stirred for 24 hrs. Secondly, the catalytic inks were applied on a glass carbon (0.02 cm²) by wet coating and degassed prior to each measurement. Other chemicals were of reagent grade.

3. Results and Discussion

3.1. Radiolytic Preparation of Pt-RuatFP-MWNT Catalysts and Its Characterization. Pt-RuatFP-MWNT catalysts were prepared by radiolytic reduction of metallic ions in water/2-propanol solution in the presence of FP-MWNT supports at room temperature. When γ-ray irradiated in aqueous solutions, various species were generated, as shown in the following equation [16]:

\[
\text{H}_2\text{O} \rightarrow e_{aq}^- , \text{H}^+ , \text{H}^- , \text{OH}^- , \text{H}_2\text{O}_2, \text{H}_2
\]  

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results, the metal ion was then reduced to zero-valence metal atom by 2-propanol radical as shown in the following.

\[
\text{(CH}_3\text{)}_2\text{CHOH} + \cdot\text{OH} \rightarrow \text{(CH}_3\text{)}_2\text{C'}\text{OH} + \text{H}_2\text{O} \\
\text{M}^+ + \text{(CH}_3\text{)}_2\text{C'}\text{OH} \rightarrow \text{M}^0 + \text{(CH}_3\text{)}_2\text{C} = \text{O} + \text{H}^+ 
\]

(3)

Figure 1 shows the TEM images of the Pt-RuatMWNT (a), Pt-RuatPAAc-MWNT (b), Pt-RuatPMAc-MWNT (c), and Pt-RuatPVPBAc-MWNT (d) catalysts prepared by \( \gamma \)-irradiation. As shown in Figure 1(a), there are no Pt-Ru nanoparticles on the surface of MWNT, whereas large amounts of Pt-Ru nanoparticles are shown on the surface of FP-MWNT supports, Figures 1(b), 1(c), and 1(d). Large amounts of Pt-Ru nanoparticles were successfully loaded on the surface of FP-MWNT. The mean particle sizes of the Pt-Ru nanoparticle on the surface of PAAc-MWNT, PMAc-MWNT, and PVPBAc-MWNT supports were in the range of 2.5–4.0 nm, 5.0–7.5 nm, and 2.0–2.5 nm, respectively. On the other hand, the commercial E-TEK catalyst showed a mean particle size of 2.5 ± 0.7 nm [17]. As shown in the TEM image, the Pt-Ru nanoparticles were well dispersed on the surface of FP-MWNT supports because the surface of carbon is changed from hydrophobic property to hydrophilic property. The property of metallic nanoparticles was also possessed as hydrophilic property. Thus, these catalysts are expected to have good efficiency for methanol oxidation.

To clarify the chemical state of Pt-Ru nanoparticles deposited on FP-MWNTs, X-Ray photoelectron spectroscopy (XPS) measurements were taken. Figure 2 shows the regional Pt_{4f} and Ru_{3p} XPS spectra of Pt-RuatPAAc-MWNT (a), Pt-RuatPMAc-MWNT (b), and Pt-RuatPVPBAc-MWNT catalyst (c) prepared by \( \gamma \)-irradiation. The Pt_{4f} peaks of the catalysts appeared about 72 eV and 75 eV due to metallic Pt and Pt(IV)O\(_2\), respectively. Li and Hsing [18] reported that the Pt_{4f} XPS signal was appeared into three components with respective binding energies of 71.8, 72.9, and 74.6 eV. It was concluded that these signals were attributed to the metallic Pt, Pt(II)O, and Pt(IV)O\(_2\) species. On the other hand, the Ru_{3p1/2} and Ru_{3p3/2} peaks for the Pt-RuatPAAc-MWNT and Pt-RuatPMAc-MWNT were shown at 486 eV and 463 eV, respectively. The 463 eV signals are due to metallic Ru(0). Li and Hsing [18] interpreted 463 eV signal due to Ru(0) and RuO\(_2\). In Figure 2(c), the Ru_{3p} signals of Pt-RuatPVPBAc-MWNT catalysts were shifted onto the larger binding energy compared to that of Pt-RuatPAAc-MWNT and Pt-RuatPMAc-MWNT. It may be considered that the hydrous ruthenium oxide, RuO_xHy, was produced from the reaction of boronic acid group of the grafted PVPBAc onto MWNT during \( \gamma \)-irradiation. However, a further investigation is needed to clarify these signals.

Figure 3 shows the X-ray diffraction patterns of the Pt-RuatFP-MWNT catalysts prepared by \( \gamma \)-irradiation. All samples showed the peak at about 20°, which was associated
Figure 2: X-ray photoelectron spectroscopy (XPS) spectra of Pt and Ru on Pt-RuatPAc-MWNT (a), Pt-RuatPMAc-MWNT (b) and Pt-RuatPVBAc-MWNT catalyst (c) prepared by γ-irradiation.
Table 1: Contents of Pt-Ru on the prepared catalyst(a).

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Pt content (wt-%)</th>
<th>Ru content (wt-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt-Ru at MWNT</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Pt-Ru at PAAc-MWNT</td>
<td>8.77</td>
<td>10.8</td>
</tr>
<tr>
<td>Pt-Ru at PMAc-MWNT</td>
<td>8.20</td>
<td>9.98</td>
</tr>
<tr>
<td>Pt-Ru at PVPBAc-MWNT</td>
<td>11.2</td>
<td>6.01</td>
</tr>
<tr>
<td>E_TeK catalyst(30 wt-%)</td>
<td>21.6</td>
<td>10.5</td>
</tr>
</tbody>
</table>

(a) Metal content (wt-%) was determined by ICP-AES.

to the MWNT supporting material. The crystallinity of PtRu catalysts was confirmed by the presence of peaks around 39.9°, 46.2°, and 67.4°. These peaks are assigned as Pt(111), (200) planes, and (220), respectively, of the face-centered cubic (fcc) structure of platinum and platinum alloy particles [19]. The XRD peaks corresponding to metallic ruthenium with hexagonal structure were not detected for these samples. The average particle size of the Pt-Ru catalysts can be calculated via XRD patterns according to Scherrer’s formula [20, 21].

\[ d_{XRD} = \frac{0.9\lambda}{\beta_{1/2} \cos \theta} \] (4)

where \( d_{XRD} \) is the average particle size (nm), \( \lambda \) is the wavelength of the x-ray (0.15406 nm), \( \theta \) is the angle at the peak maximum, \( \beta_{1/2} \) is the width (radians) of the peak at half height. The calculated mean sizes from the diffraction peak of Pt(111) are as follows: 3.2 nm in Figure 3(a), 3.1 nm in Figure 3(b), and 2.9 nm in Figure 3(c). There are no size changes of Pt-Ru catalyst on various functionalized polymer-grafted MWNT. This behavior may show that the growth of nanoparticles is prevented via dimethylketone during \( \gamma \)-irradiation, as shown in (5).

Table 1 shows the content (wt-%) of Pt and Ru elements in the Pt-Ru at FP-MWNT catalysts. In ICP-AES results of the Pt-Ru at FP-MWNT catalyst, the Pt element content (wt-%) in the Pt-Ru at PAAc-MWNT, Pt-Ru at PMAc-MWNT, and Pt-Ru at PVPBAc-MWNT catalysts was determined as 8.77%, 8.20%, and 11.20% for all that addition of 16.125% in reaction mixture, respectively. While Ru element content in the Pt-Ru at PAAc-MWNT, Pt-Ru at PMAc-MWNT, and Pt-Ru at PVPBAc-MWNT catalysts was obtained as 10.8%, 9.98%, and 6.01%, for all that addition of 16.81% in reaction mixture, respectively. In the case of Pt-Ru at PVPBAc-MWNT catalyst, the Pt content is higher than that of the other catalysts. In commercial E-TEK catalyst, the Pt content is higher than Ru content, as shown in Table 1.

3.2. Catalytic Efficiency of Pt-Ru at FP-MWNT Catalyst for CO and MeOH. To find the catalytic efficiency of Pt-Ru at FP-MWNT catalysts, they were tested for the electrochemical oxidation of carbon monoxide (CO). Figure 4 shows the cyclic voltammograms (CVs) of electro-oxidation of CO for Pt-Ru at FP-MWNT catalyst prepared by \( \gamma \)-irradiation.

Figure 3: XRD spectra of Pt-Ru at PAAc-MWNT (a), Pt-Ru at PMAc-MWNT (b), and Pt-Ru at PVPBAc-MWNT (c) catalyst for DMFC.
in 0.5 M H₂SO₄: (a) RuatPAAc-MWNT, (b) Pt-RuatPMAc-MWNT, and (c) Pt-RuatPVPBAc-MWNT catalyst. To compare CO adsorption efficiency, it was measured and compared to the commercial E-TEK catalyst containing 30 wt% Pt on carbon. The higher CO stripping peak at the commercial E-TEK catalyst electrode is more apparent than that of the Pt-RuatPAAc-MWNT and Pt-RuatPMAc-MWNT catalyst electrodes, as shown in Figures 4(a) and 4(b). However, the measured CO stripping peak at Pt-RuatPVPBAc-MWNT catalyst electrode is significantly higher than that of the commercial E-TEK electrode in spite of the metal catalyst in high amount as shown in Figure 4(c). A significant current density is noticed at the Pt-RuatPVPBAc-MWNT catalyst electrodes for the CO oxidation starting from 0.72 V. The electrochemically active specific area (SEAS) of the catalysts was calculated using the charges deduced from the CV of CO adsorption and desorption electro-oxidation process and using (5) [22].

\[
\text{SEAS} = \frac{Q_{\text{CO}}}{G} \times 420, \quad (5)
\]

where \(Q_{\text{CO}}\) is the charge for CO desorption electro-oxidation in microcoulomb (\(\mu\text{C}\)); \(G\) represents the summation of Pt + Ru metals loading (\(\mu\text{g}\)) in the electrode, and 420 is the charge required to oxidize a monolayer of CO on the catalysts in \(\mu\text{C cm}^{-2}\). The electrochemical SEASs are 60 m² g⁻¹ for the commercial E-TEK catalysts. In the case of the prepared catalysts, the electrochemical SEASs are 34, 30, and 126 m² g⁻¹ for the Pt-RuatPAAc-MWNT, Pt-RuatPMAc-MWNT, and Pt-RuatPVPBAc-MWNT catalysts, respectively. The SEAS of Pt-RuatPVPBAc-MWNT catalysts prepared by \(\gamma\)-irradiation are higher than that of commercial E-TEK catalysts due to hydrous ruthenium oxide. It might be based on the promotion of CO oxidation on Pt atoms by the second metal (Ru) which provides OH-type species, the more oxidizable second metal, thus promotes catalytic activities.

Figure 5 shows the cyclic voltammograms of E-TEK catalyst and the prepared catalysts for 1.0 M MeOH oxidation in 0.5 M H₂SO₄ at room temperature. The higher current peak at about 0.6 V versus Ag/AgCl electrode appeared due to methanol oxidation on the commercial E-TEK catalyst, as shown in Figures 5(a), 5(b), and 5(c). However, the methanol oxidation peak for Pt-RuatPAAc-MWNT catalyst and Pt-RuatPMAc-MWNT catalyst were lower than that of the E-TEK catalyst, as shown in Figures 5(a) and 5(b). In the case of Pt-RuatPVPBAc-MWNT catalyst, the large catalytic efficiency at 0.8 V was observed. As a result, the prepared Pt-RuatPVPBAc-MWNT catalyst can be used on a direct methanol fuel cell electrode.

4. Conclusion

The functionalized MWNTs were prepared by radiation-induced graft polymerization of vinyl monomers with the desired functional group. Subsequently, Pt-Ru nanoparticles were deposited on the surface of the functionalized MWNT for using as a fuel cell electrode catalyst. The efficiency
of the prepared catalysts was investigated. The following conclusions are based on the results.

1. The catalytic efficiency of Pt-Ru@PVPBAc-MWNT catalyst for CO stripping was higher than that of the commercial E-TECK catalyst in spite of the low metallic content.

2. The stripping voltammograms for the adsorbed CO at Pt-Ru@PVPBAc-MWNT catalyst prepared by γ-irradiation reveal that the CO oxidation is energetically favorable at these electrodes.

3. The MeOH oxidation peak appeared at 0.8 V on Pt-Ru@PVPBAc-MWNT catalyst prepared by γ-irradiation which appears to be suitable for the electrode assembly in direct methanol fuel cells.

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References


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