PT-BASED ALLOY NANOPARTICLES/CNT COMPOSITE FOR HIGH PERFORMANCE DIRECT METHANOL FUEL CELL

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Abstract
Pt, Pt-Ru alloys and Pt-Ru-Mo alloys, decorated on multi-walled carbon nanotube(MWCNT) by using flash light irradiation as changing irradiation energy was investigated. Pt, Pt₅₀Ru₃₀ and Pt₄₇Ru₄₇Mo₈ alloys were coated on the MWCNT followed by flash light irradiation to form the nanoparticle alloy on MWCNT. The fabricated Pt based alloy nanoparticle/MWCNT were evaluated by X-ray diffraction(XRD), RAMAN spectroscopy and scanning electron microscope(SEM), respectively. From cyclic voltammetry(CV) study, it was found that Pt₄₇Ru₄₇Mo₈/MWCNT catalyst shows higher activity and stability for methanol electro oxidation compared to Pt/MWCNT and Pt₅₀Ru₃₀/MWCNT one.

1. Introduction
Recently, DMFC has attracted a lot of interests as the most suitable and promising option for portable devices due to its characteristics such as low working temperature, high energy conversion efficiency and low emission of pollutant. However, it still has the problem, slow reaction and short life time due to CO poisoning of the catalyst and high cost of the catalyst metal, platinum. Therefore, to overcome these problems, many researchers have conducted to develop Pt-based nanoparticle-alloy catalysts to increase its reactive surface area and reduce the cost and the CO poisoning phenomena. Various of metals(Ru, Mo, Ni, Co and W, etc.) were proposed as the partner of Pt-based catalysts in the forms of binary catalysts(Pt-Ru, Pt-Mo, Pt-Co, Pt-W, Pt-Ni, Pt-Fe, Pt-Rh, Pt-Au), ternary catalysts(Pt-Ru-Mo, Pt-Ru-Rh, Pt-Ru-Fe, Pt-Ru-Co, Pt-Ru-Ni) and quaternary catalysts (Pt-Ru-Mo-W, Pt-Ru-Ni-P)¹⁻⁵. Among these Pt-based catalysts, Pt-Ru/MWCNT as binary catalyst and Pt-Ru-Mo/MWCNT as ternary catalyst were considered to be the best catalyst until now⁶⁻⁹. However, the synthesis of these metal nanoparticle-alloys is much more difficult than that of pure metal nanoparticles because of the difficulty in uniform alloy formation and composition controlling. Here, we demonstrated novel method for the formation of nanoparticle-alloys on MWCNT by flash light irradiation.

2. Experiments
2.1 Material preparation
The Pt based alloy nanoparticles/MWCNT composite catalyst were prepared as following procedure. Firstly, 8mg of MWCNT(CM-95, >99% purity, diameter 10~15nm, length 200µm) and 45ml of N-dimethylformamide(DMF) (99.8%, Sigma-Aldrich Co.) mixed together in ultrasonic bath for 2 hours. The MWCNT/DMF solution was spread on the silicon wafer and dried at 120°C on a hot plate. By using the E-beam evaporator (MEP5000, SNTEK), metal layers were coated on MWCNT. 2mg of Pt was coated on MWCNT for Pt slurry. For the binary alloy catalyst, 1.317mg of Pt and 0.683mg of Ru were coated. 1.265mg of Pt, 0.655mg of Ru and 0.08mg of Mo were coated on MWCNT for the ternary alloy case. The purities of all of the metals were higher than 99.99% The atomic ratio of the metals above were determined based on the best composition for each binary and
ternary catalysts on commercialized anode catalysts in market\textsuperscript{10,11}. For formation of nanoparticle-alloys from the coated metal layers on MWCNT, the flash light was irradiated. The xenon lamp emits a spectrum of light that covers a wide range of wavelength from 160nm to 2.5\textmu m through arc plasma generation as shown in Fig. 1. In the present work, the pulse number, width and gap were fixed as 3, 5ms and 5ms, respectively and the total pulse energy was 40J/cm\textsuperscript{2}. After the flash light irradiation, the metal/MWCNT-composite was mixed with 3.5ml of Ethanol (>99.9% purity, Samchun. Co) and 0.7ml of 5wt% NaFion solution (EW=1100, perfluorinated ion exchange resin, 5wt% solution, Dupont Co.) and stirred using the ultrasonicator() for 30 min. 

\section{2.2 Characterization}

To characterize the particle size and phases of materials, crystal phase analysis was conducted using XRD(D/MAX RINT 2000, CuK\textalpha radiation). The morphologies of Pt/MWCNT catalyst, Pt-Ru/MWCNT catalyst and Pt-Ru-Mo/MWCNT catalyst were characterized by SEM(JSM-6330F). To quantify the quality of metal alloy nanoparticles/MWCNT material, Raman spectroscopy(NRS-3100) was employed. 

Cyclic voltammetry test was performed by using a potential stat(Ref600, Gamry) with a three-electrode cell in 0.5M H\textsubscript{2}SO\textsubscript{4} solution for characterizing electrochemical activities of absorption and desorption of hydrogen. And for characterizing electrochemical activities of methanol oxidation, CV test was performed in 0.5M H\textsubscript{2}SO\textsubscript{4} + 1M CH\textsubscript{2}OH solution. All of CV studies were conducted at 60\textdegree C and a scan rate 50mV/s from -0.3V~1.0V\textsuperscript{12,13}. Glassy Carbon electrode(GCE, I.D 3mm, O.D 6mm, CHI Co.) was polished with 0.05\textmu m alumina to a mirror finish. 10\mu L of the catalysts slurry was loaded with 10\mu L of 5wt% nafion solution onto the surface of the electrode. Then, GCE was dried at 70\textdegree C by heat gun for yielding a catalysts loading. Ag/AgCl electrode(CHI Co.), saturated in 3.3M KCl and Pt wire electrode were used as the reference electrode and counter electrode, respectively.

\section{3 Results and discussions}

The XRD patterns of Pt/MWCNT, Pt-Ru/MWCNT and Pt-Ru-Mo/MWCNT catalysts exhibited diffraction peaks of (111), (100), (004), (220), (110), and (311) at 2\theta value of 39.8\textdegree, 42.4\textdegree, 54.7\textdegree, 67.4\textdegree, 77.4\textdegree and 81.9\textdegree, respectively. The peaks of (111), (220) and (311) indicate the structure of the bonding with Pt,Ru,Mo metals. Compared to the diffraction peaks of pure platinum, those of Pt-Ru alloys and Pt-Ru-Mo alloys were shifted positively and there are no observable peaks corresponding to those of pure ruthenium and molybdenum\textsuperscript{14}. The shift of peaks in 20 values corresponds of a decrease in the lattice parameter compared to pure platinum fcc structure due to the incorporation of ruthenium and molybdenum atoms\textsuperscript{15}. The peaks of (100), (004) and (110) indicate the graphite of MWCNT\textsuperscript{16}. Based on the peaks (111) of Pt/MWCNT, Pt-Ru/MWCNT and Pt-Ru-Mo/MWCNT, the mean size of alloy particles can be calculated by Scherer’s formula as following\textsuperscript{16}.

\begin{equation}
L = \frac{0.9\lambda}{Bcos\theta}
\end{equation}

$L$ is the mean size of alloy particles, $\lambda$ is the X-ray wavelength(CuK\textalpha $\lambda$=0.1541nm) $\theta$ is the maximum angle of the (111) peaks, and B is the half-peak width for (111) in radians. Thus, the mean sizes of alloy are 10.42nm for Pt/MWCNT, 15.63nm for Pt-Ru/MWCNT, and 7.44 for Pt-Ru-Mo/MWCNT.

Fig. 2, and Fig. 3, show the SEM images of metal nanoparticle-alloys formation of Pt-Ru/MWCNT and Pt-Ru-Mo/MWCNT as function of the flash light energy, respectively. The sputtered Pt,Ru and Mo layers start to be melted and agglomerated when the light energy was higher than 20 Jcm\textsuperscript{-2} and 30 Jcm\textsuperscript{-2}, respectively. The metal nanoparticle-alloys were completely formed when the light energy was 40 Jcm\textsuperscript{-2}. We could observe that the metal nanoparticle-alloys with 15~20nm of the diameter were formed uniformly on MWCNT. Which are matched well with the mean diameter of the granulated nanoparticles calculated from the XRD results above.

RAMAN spectroscopy was employed to quantify the quality of metal nanoparticle-alloys. Fig. 4, shows the results of Raman spectra. It shows two obvious peaks. One is D-band which involves the first-order scattering of sp\textsuperscript{2} carbons by defects that break the basic symmetry of the graphite sheet. The other is G-band which is related to vibration in all sp\textsuperscript{2} carbon materials\textsuperscript{17}. The D-band and G-band are detected at
1334～1343 cm⁻¹ and 1567～1576 cm⁻¹, respectively. The defects on CNTs can be measured by using R-value (i.e. the ratio of intensity of D-band to intensity of G-band) due to the origin of the respective bands. The larger the R value, the larger the amount of the defects. As shown in Fig. 4, the R-value decreased from 1.02 to 0.978 as the flash light increased, which reveals that the flash light irradiation could purify MWCNT by removing the contaminants such as impurities, amorphous carbon and any metals on MWCNT. By nanogrulation of Pt-Ru alloy onto MWCNT, every peak has shifted from 1334cm⁻¹ and 1567cm⁻¹ to 1343 and 1576 cm⁻¹, respectively. This peak shift is attributed to the strong C-metal bonding. This strong adhesion between the nanoparticles and MWCNT might come from the complete melting the coated metal layers by flash light irradiation followed by firm welding of metal nanoparticle-alloys on MWCNT.

To investigate the electrocatalytic activities of the light induced fabricated Pt/MWCNT, Pt₅₀Ru₅₀/MWCNT and Pt₄₇Ru₄₇-Moₓ/MWCNT catalysts, Cyclic Voltammetry(CV) test was conducted. Fig. 5, and Fig. 6, show the image of CV test and the results of CV studies, respectively. Compared to Pt/MWCNT electrode, the well-defined hydrogen adsorption-desorption peaks (-0.2V ~ 0.1V) was decreased gradually as decreasing the amount of Pt (Fig. 6). Additionally, electrochemical surface area (ECSA), a standard of measuring the reaction of Pt adsorption and desorption was measured for accurate analysis. The results of ECSA indicated that the reaction ratio of Pt/MWCNT (518.14cm²/mg) was higher than those of Pt₅₀Ru₅₀/MWCNT (375.83cm²/mg), Pt₅₀Ru₅₀/MWCNT (227.35cm²/mg) and Pt₄₇Ru₄₇-Mo₆/MWCNT (207.54 cm²/mg). Another CV studies were tested for evaluating electrocatalytic activities for methanol oxidation in 0.5M H₂SO₄ solution containing with 1M CH₃OH. From the result, Onset potential, forward potential and the ratio of I/Iₒ values for Pt/MWCNT, Pt₅₀Ru₅₀/MWCNT and Pt₄₇Ru₄₇-Mo₆/MWCNT electrodes were determined as shown in Table 1. The lower onset potential indicates clear evidence for superior electrocatalytic activity for methanol oxidation. The high I/Iₒ values of the ternary and binary alloy catalysts implied the relatively complete oxidation of methanol to carbon dioxide compared to the pure Pt catalyst.

As shown in Table 1, the Pt₄₇Ru₄₇-Mo₆/MWCNT catalyst shows the lowest onset potential of 0.245V and the greatest I/Iₒ value of 7.24 after 30 cycles. These results highlight the high activities for methanol oxidation on Pt₄₇Ru₄₇-Mo₆/MWCNT prepared by flash light irradiation.

4. Conclusion

In this paper, We could fabricate the ternary and binary catalysts successfully by flash light irradiation in room temperature and ambient condition. From the study, it was found that Pt₄₇Ru₄₇-Mo₆/MWCNT catalysts made by flash light irradiation shows the best performance in electrochemical activities of methanol oxidation. It is expected that the developed flash light induced fabrication method of Pt based alloy/MWCNT nanocatalyst could reduce the manufacturing cost and time compared to other conventional chemical processes.

![Fig. 1. Process of making metal alloys by using flash light irradiation](image1)

![Fig. 2. SEM images of Pt₅₀Ru₅₀/MWCNT after flash irradiation with: a) 20Jcm⁻², b) 30Jcm⁻², c) 40Jcm⁻²](image2)
Fig. 3. SEM images of Pt$_{47}$-Ru$_{47}$-Mo$_6$/MWCNT after flash irradiation with: a) 20Jcm$^{-2}$, b) 30Jcm$^{-2}$, c) 40Jcm$^{-2}$.

Fig. 4. The image of RAMAN spectra as a function of the flash light energy.

Fig. 5. The image of the CV experiment.

Fig. 6. CV for each Pt-based alloy/MWCNT electrodes. Measurements were carried out in 0.5M H$_2$SO$_4$ at a scan rate of 50mV/s.

Table 1. Peak potential and I$_f$/I$_b$ ratios of each electrocatalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Onset Potential (V vs. Ag/AgCl)</th>
<th>Forward potential (V vs. Ag/AgCl)</th>
<th>I$_f$/I$_b$ after 30 Cycles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt$_{100}$</td>
<td>0.26</td>
<td>0.695</td>
<td>1.12</td>
</tr>
<tr>
<td>Pt$<em>{50}$Ru$</em>{50}$</td>
<td>0.245</td>
<td>0.705</td>
<td>3.04</td>
</tr>
<tr>
<td>Pt$<em>{47}$Ru$</em>{47}$Mo$_6$</td>
<td>0.24</td>
<td>0.70</td>
<td>5.24</td>
</tr>
</tbody>
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References


