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 flsh light irradiation as changing irradiation energy was investigated. Pt, Pt_{50}-Ru_{50} and Pt_{47}-Ru_{47}-Mo_6 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 Pt_{47}-Ru_{47}-Mo_6/MWCNT catalyst shows higher activity and stability for methanol electro oxidation compared to Pt/MWCNT and Pt_{50}-Ru_{50}/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 now[6~9]. 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℃ 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[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 2.5μm 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^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.

2.2 Characterization

To characterize the particle size and phases of materials, crystal phase analysis was conducted using XRD(D/MAX RINT 2000**,** CuKαradiation). 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_2SO_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_2SO_4 + 1M CH_3OH solution. All of CV studies were conducted at 60℃ and a scan rate 50mV/s from -0.3V~1.0V[12,13]. Glassy Carbon electrode(GCE, I.D 3mm, O.D 6mm, CHI Co.) was polished with 0.05μm alumina to a mirror finish. 10μL of the catalysts slurry was loaded with 10μL of 5wt% nafion solution onto the surface of the electrode. Then, GCE was dried at 70℃ 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.

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 2θ value of 39.8˚, 42.4˚, 54.7˚, 67.4˚, 77.4˚ and 81.9˚, 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[14]. The shift of peaks in 2θ values corresponds of a decrease in the lattice parameter compared to pure platinum fcc structure due to the incorporation of ruthenium and molybdenum atoms[15]. The peaks of (100), (004) and (110) indicate the graphite of MWCNT[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[16].

$$L = \frac{0.9\lambda}{B\cos\theta} \quad (1)$$

L is the mean size of alloy particles, λ is the X-ray wavelength(CuKα λ=0.1541nm) θ 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^{-2} and 30 Jcm^{-2}, respectively. The metal nanoparticle-alloys were completely formed when the light energy was 40 Jcm-^{2}. We could observe that the metal nano particle-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^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^2 carbon materials[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 nanogranulation 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[18]. 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, Pt_{50}-Ru_{50}/MWCNT and Pt_{47}-Ru_{47}-Mo_6/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 (518.14cm^2/mg) was higher than those of Pt_{75}-Ru_{25}/MWCNT(375.83cm^2/mg), Pt_{50}-Ru_{50}/MWCNT(227.35cm^2/mg) and Pt_{47}-Ru_{47}-Mo_6/MWCNT(207.54 cm^2/mg). Another CV studies were tested for evaluating electro-catalytic activities for methanol oxidation in 0.5M H_2SO_4 solution containing with 1M CH_3OH. From the result, Onset potential, forward potential and the ratio of I_f/I_b values for Pt/MWCNT, Pt_{50}-Ru_{50}/MWCNT and Pt_{47}-Ru_{47}-Mo_6/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_f/I_b values of the ternary and binary alloy catalysts implied the relatively complete oxidation of methanol to carbon dioxide compared to the pure Pt catalyst case[13]. From Table 1, the Pt_{47}-Ru_{47}-Mo_6 /MWCNT catalyst shows the lowest onset potential of 0.245V and the greatest I_f/I_b value of 7.24 after 30 cycles. These results highlight the high activities for methanol oxidation on Pt_{47}-Ru_{47}-Mo_6 /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 $Pt_{47}Ru_{47}Mo_6$ /MWCNT catalysts made by flash light irradiation shows the best performance in electrochemical activities of methanol oxidation [12,13]. 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.

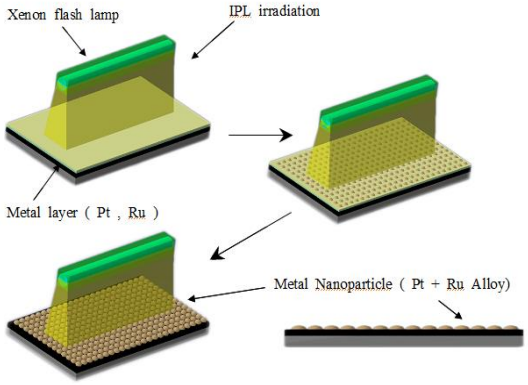

Fig. 1. Process of making metal alloys by using flash light irradiation

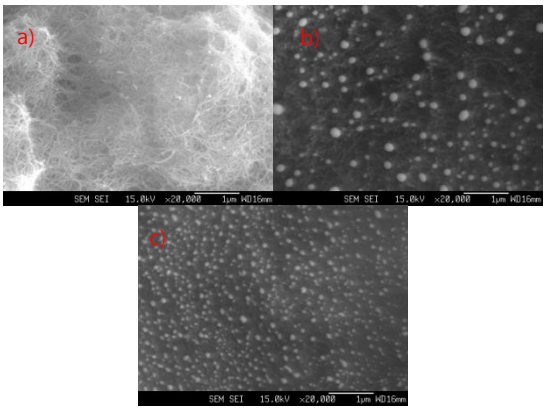

Fig. 2. SEM images of Pt_{50}-Ru_{50}/MWCNT after flash irradiation with : a) 20Jcm^{-2}, b) 30Jcm^{-2}, c) 40Jcm^{-2}

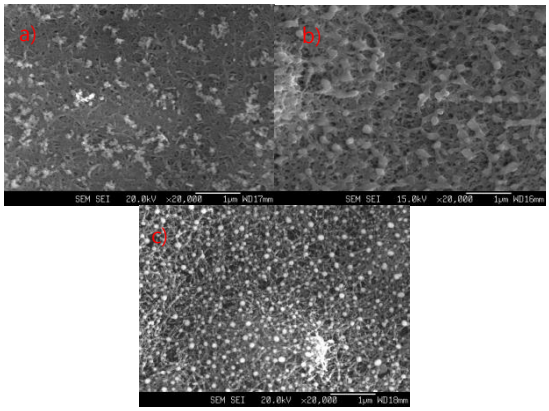

Fig. 3. SEM images of Pt_{47}-Ru_{47}-Mo_6/MWCNT after flash irradiation with : a) 20Jcm^{-2}, b) 30Jcm^{-2}, c) 40Jcm^{-2}

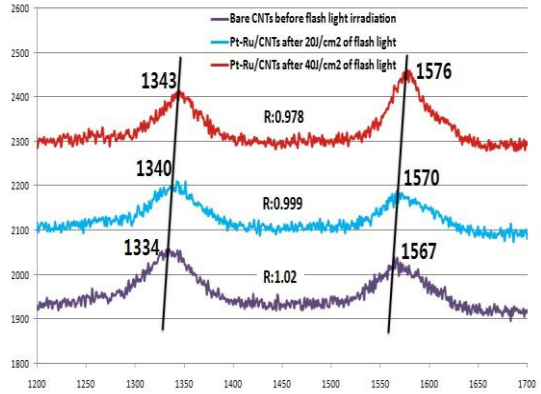

Fig. 4. The image of RAMAN spectra as a function of the flash light energy.

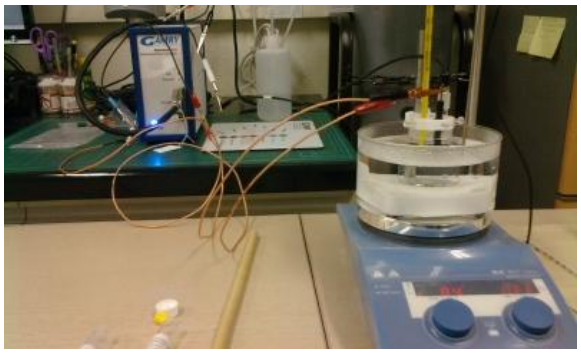

Fig. 5. The image of the CV experiment

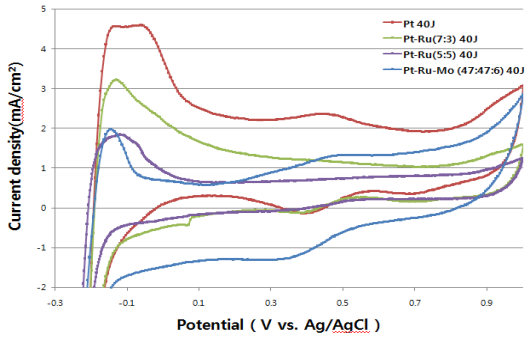

Fig. 6. CV for each Pt-based alloy/MWCNT electrodes. Measurements were carried out in 0.5M H_2SO_4 at a scan rate of 50mV/s.

Table 1. Peak potential and I_f/I_b ratios of each electrocatalysts

Catalyst	Onset Potential	Forward potential (V vs. Ag/AgCl)	If/Ib after 30Cycles
Pt_{100}	0.26	0.695	1.12
$Pt_{50}Ru_{50}$	0.245	0.705	3.04
$Pt_{47}Ru_{47}Mo_6$	0.24	0.70	5.24

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