

# Deposition and Electrochemical Activity of Bimetallic Pt-M (M= Fe, Co, and Ni) Nanocatalysts on Carbon Nanotube Electrodes

Chien-Te Hsieh\*, Chia-Yi Lin

Tel: 886-3-4638800 ext. 2577; Fax: 886-3-4559373; E-mail: [cthsieh@saturn.yzu.edu.tw](mailto:cthsieh@saturn.yzu.edu.tw)

Department of Chemical Engineering and Materials Science, Yuan Ze University, 135 Yuan-Tung Rd., Chung-Li, Taoyuan 320, Taiwan

This article reports an approach to prepare bimetallic Pt-M (M = Fe, Co, and Ni) nanoparticles as electrocatalysts and examines their electrochemical activities in 1 M sulfuric acid. The approach consists of chemical oxidation of carbon nanotubes (CNTs), two-step refluxing, and subsequent thermal reduction in hydrogen atmosphere. Three bimetallic pairs of Pt-M catalysts are found to deposit well onto CNT surface, forming Pt-M/CNT composites. The electrochemical behavior of Pt-M/CNT electrodes was investigated in 1 M H<sub>2</sub>SO<sub>4</sub> using cyclic voltammetry (CV) and ac electrochemical impedance spectroscopy. The active surface coverage (= electrochemical surface area/geometric surface area) of Pt-M catalysts is significantly enhanced, i.e., Pt-Co (85.1%) > Pt-Ni (80.4%) > Pt-Fe (76.2%) > Pt (26.3%). This enhancement of electrochemical activity can be attributed to the fact that the introduction of Co and Ni may reduce the required potential for water electrolysis and thus the associated carbon oxidation, thereby contributing to hydrogen adsorption. The results shed some light on how use of Pt-M/CNT composite would be a promising electrocatalyst for high-performance fuel cell applications.

## 1. Introduction

In recent years, a number of platinum-based metal (Pt-M) alloys have been demonstrated to possess greater activity than pure Pt for catalyzing the oxygen reduction reaction (ORR) in acidic electrolytes, which is one of the primary electrochemical reactions in low-temperature fuel cells. The bimetallic nanoparticle catalysts usually consist of a primary metal that has a high performance in catalytic activity and a secondary metal that can enhance the catalytic activity or prevent poisoning problems. Most of literature reports concerning bimetallic electrocatalysts are related to Pt-Ru, while combinations of Pt with other secondary metals such as Sn and Co have also been reported. To date, the performance of current fuel cells is still limited by high overpotential and slow kinetic for ORR at cathode. Typically, one of the 3d transition metals, iron (Fe), cobalt (Co) and nickel (Ni), can be used to modify the nature of Pt catalysts for increased activity. These transition metals are expected to be cheaper than ruthenium. However, the role that the attachment of bimetallic catalysts (Pt-transition metal) on carbon supports plays in enhancement of electrochemical activity in acidic electrolyte has not yet been clearly elucidated. The other aspect for improving the activity is to uniformly deposit bimetallic catalysts over carbon supports. Various catalyst supporting materials such as alumina, carbon black, mesoporous carbon, and carbon nanofibers have been investigated for the development of fuel cells. Our previous study has reported an efficient approach that combined with chemical-wet oxidation and reduction by refluxing. There has been increasing interest in multiwalled carbon

nanotubes (CNTs) as a heterogeneous catalyst support because of their high porosity and high electrical conductivity. It is believed that good dispersion of bimetallic electrocatalysts on CNTs would resolve the slow kinetic problem as CNTs have a unique one-dimensional structure. In this article, we present a surface modification approach to deposit bimetallic electrocatalysts (Pt–M, M = Fe, Co, and Ni) on sidewalls of CNTs. First, chemical-wet oxidation in nitric acid was employed to implant surface oxides on both ends and defects of nanotubes, creating a number of oxide groups such as carboxylic (–COOH), carbonyl (–CO), and hydroxylic (–COOH). Then, a two-step chemical reflux allowed deposition of nanosized bimetallic alloys on the oxidized CNTs. The first reflux aims to coat the primary electrocatalyst (Pt), followed by the second reflux that introduces the secondary catalyst (Fe, Co, and Ni) to form binary metallic catalysts. This work intends to investigate electrochemical activity of CNTs decorated with different bimetallic Pt–M electrochemical catalysts, including electrochemical surface area, surface coverage, and cycle stability in acidic electrolyte. These results would shed some light on replacement of novel metal catalysts using transition metals, and how introduction of transition metals in bimetallic catalysts enhances the electrochemical reactivity.

## 2. Experimental

In this study, multiwalled CNTs (purity: > 99 %; outer diameter: 30–50 nm; length: 5–10  $\mu\text{m}$ ) were prepared by a catalytic chemical vapor deposition technique, using ethylene and Ni particle as a carbon precursor and a catalyst, respectively. Chemical oxidation was applied to implant surface oxide groups on CNTs, in which the CNT samples were well impregnated in a 3 N nitric acid at 90°C for 2 hr. After that, the oxidized CNT samples were rinsed with distilled water several times until the pH value of the carbon slurry was higher than 5. Then the CNTs were heated at 150°C under an Ar atmosphere for 1 hr. The chemical-wet oxidation has been frequently used to maximize the number of surface carboxylic acid groups at the defect sites of CNTs.

The Pt-based bimetallic nanoparticles deposited on CNTs were synthesized using the two-step refluxing process. First, oxidized CNTs (1 g) were mixed with an aqueous 0.1 M  $\text{PtCl}_4 \cdot 5\text{H}_2\text{O}$  (Alfa Aesar) solution at an ambient temperature for 8 hr. The impregnation process led to the formation of Pt-adsorbed intermediates on CNT surface. Then, the first-step reflux was performed at 110°C for 6 hr, using 50 mL of ethylene glycol as the solvent. Next, Pt-coated CNT composites were separated from ethylene glycol solution using a filtration apparatus. A thermal reduction process was carried out in a tubular reactor at 500°C under 5 vol%  $\text{H}_2$  atmosphere to ensure reduction of Pt particles. After the deposition of platinum, the weight fraction of Pt to CNTs was measured to be *ca.* 30 wt%. The weight fraction of metal to CNTs was determined by weight gain before and after metal loading onto the oxidized CNTs. The second chemical refluxing was also conducted at 110°C for 8 hr, using ethylene glycol as solvent. The Pt-attached CNTs were placed into different ionic salts: 1 M  $\text{Fe}(\text{NO}_3)_2$ ,  $\text{Ni}(\text{NO}_3)_2$  and  $\text{Co}(\text{NO}_3)_2$ . The Pt-attached CNTs were impregnated in three types of metal nitrate solutions. The chemical impregnation was performed at room temperature for 24 hr. The reflux process allows the transition metals to coat on Pt surface. Again, hydrogen reduction was used to reduce Pt–M alloy, generating bimetallic nanocatalysts.

CNTs coated with different Pt–M alloys were used to fabricate electrodes. Prior to the formation of electrodes, each Pt–M/CNT sample was added into a solution of polyvinylidene fluoride (PVdF) in N-methyl pyrrolidinone (NMP), and then the mixture was mixed at an ambient temperature to form a carbon slurry. Electrodes were prepared by pressing the slurry on stainless steel foils with a doctor blade, followed by evaporating the solvent, NMP, with a blower dryer. The carbon layer, which consisted of 10 wt% PVdF and 20 wt% graphite powder (size: 20–30  $\mu\text{m}$ ) as binder and conducting material, respectively, was adjusted to have a thickness of 100  $\mu\text{m}$ . Electrochemical measurements were investigated at ambient temperature using 1 M  $\text{H}_2\text{SO}_4$  as the electrolyte solution. A Pt wire was used as the counter electrode and a Ag/AgCl electrode as the

reference. The working electrodes were constructed by coating the CNTs onto stainless steel foil (as current collector). Cyclic voltammetric (CV) measurements of the CNT electrodes were made in the potential range of 0 to 1.0 V vs. SCE with five sweep rates, i.e., 1, 5, 10, 20, and 30 mV/s.

### 3. Results and Discussion

Bright-field TEM images for each pair of the bimetallic nanoparticles deposited on oxidized CNTs are shown in Figs. 1(a)–1(d). From these observations, oxidized CNTs have an average outer diameter of 30–50 nm and a wall thickness of ~10 nm. The dark spots correspond to Pt-based nanoparticles, which were only deposited on the sidewalls of CNTs.

XRD patterns of the CNTs decorated with Pt and bimetallic Pt–M catalysts are collected in Fig. 2. First, an obvious diffraction peak at  $ca. 2\theta = 26^\circ$  indicates the crystalline nature of graphite, which is attributed here to the graphitic structure of CNTs. The interlayer distance,  $d_{002}$ , of CNT crystallines can be obtained by Bragg's equation. The interlayer space ( $d_{002}$ ) for all CNTs shows an average value of  $ca. 0.340$  nm, which is close to highly oriented graphite carbon (0.335 nm). Next, we observe that the peak at  $2\theta \approx 40^\circ$  corresponds to fcc structure of platinum (111). After the addition of transition metals, the diffraction peaks of bimetallic Pt–M alloys tend to shift to higher diffraction peaks ( $2\theta$ ), e.g., a comparison of the  $2\theta$  of (111) peak for Pt–M alloys ( $40.1^\circ$ – $40.4^\circ$ ) and pure Pt ( $39.95^\circ$ ). Additionally, other diffraction peaks are characterized to different types of transition metal oxides, which may be oxidized during sample preparation for XRD analysis.

According to Scherrer's formula, the average particle size of the bimetallic catalysts can be calculated through XRD patterns. The calculated mean sizes according to the diffraction peak of Pt (111) were listed in Table 1. The result shows that the introduction of transition metals leads to enlarge the average size of the bimetallic alloy. The larger size can be attributed to one possible reason that the two-step chemical reduction would generate core-shell (Pt–M) crystalline structures. It can be presumably due to that transition metal may cover over Pt particle, thus slightly increasing the bimetallic particle.

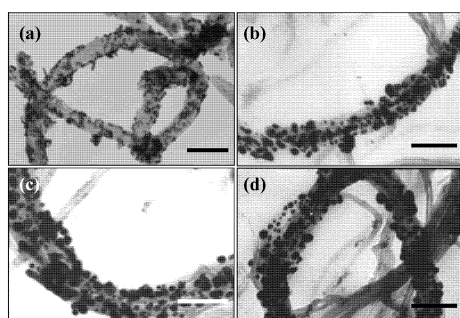


Fig. 1. TEM images of different types of Pt and Pt–M/CNT samples: (a) Pt, (b) Pt–Fe, (c) Pt–Co, and (d) Pt–Ni. The scale bar is 100 nm.

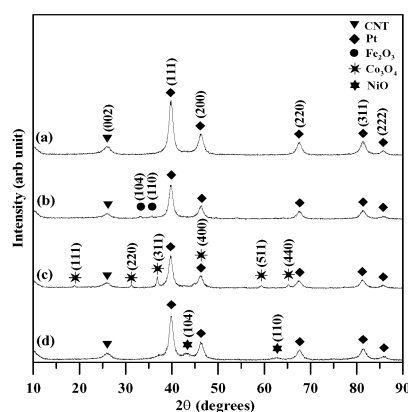


Fig. 2. X-ray diffraction pattern of different types of Pt and Pt–M/CNT samples: (a) Pt, (b) Pt–Fe, (c) Pt–Co, and (d) Pt–Ni, showing characteristics crystalline faces of Pt and transition metals. The peak of C was identified as graphite from CNTs.

Table 1. Crystalline size and active surface areas of different Pt–M catalysts determined from XRD patterns and CV measurements in 1 M H<sub>2</sub>SO<sub>4</sub>, respectively.

Catalyst	$d_{\text{XRD}}$ (nm)	$S_{\text{ESA}}$ (cm <sup>2</sup> /mg)	$S_{\text{CSA}}$ (cm <sup>2</sup> /mg)	$\Theta$ (%)
Pt/CNT	6.26	118	448	26.3
Pt–Fe/CNT	6.74	317	416	76.2
Pt–Co/CNT	6.74	354	416	85.1
Pt–Ni/CNT	6.78	333	414	80.4

Figs. 3(a)–3(d) shows cycle voltammograms for CNT electrodes decorated with Pt-based bimetallic nanoalloys in 1 M H<sub>2</sub>SO<sub>4</sub> at different sweep rates (1, 5, 10, 20 and 30 mV/sec). The CV scans start from an open circuit potential and sweep within the entire potential region between -0.2 V and 1.0 V vs. Ag/AgCl. In comparison, it can be seen that the CV features are similar, but the electrochemical activities are quite different. As a result of the CV transformation, this indicates that the addition of transition metals to Pt catalyst may play an important role in affecting the electrochemical activity of bimetallic nanocatalysts. The voltammetric features of all Pt bimetallic catalysts are similar to polycrystalline Pt. Essentially, hydrogen was adsorbed in the cathodic direction and then oxidized in the anodic direction, and the Pt/CNT electrode shows well-defined hydrogen adsorption–desorption peaks in potential region. All Pt–M bimetallic catalysts seem to keep the adsorption/desorption peaks of hydrogen but enhances the peak intensities. The alloying or coating effect due to these transition metals is shown in the CVs as an enhanced activity. However, Faradaic current in the potential region of 0.4–0.6 V vs. Ag/AgCl are apparent. The oxidation/reduction peaks is attributed to the presence of small amounts of metal oxides, such as ferric oxide, cobalt oxide, and nickel oxide.

Additionally, we find that an increase in the peak currents is nearly proportional to the sweeping rates for all bimetallic catalysts. This shows that the electrochemical redox kinetic on Pt–M/CNT electrodes dominates the overall reaction in 1 M H<sub>2</sub>SO<sub>4</sub>, which is similar to our previous study. The phenomenon can be inferred by the following: (i) good-dispersion of bimetallic catalysts over CNTs leads to fast redox kinetic, and (ii) the presence of CNTs not only acts as the catalyst support but also allows rapid electron transportation and provides available adsorptive sites for hydrogen storage and double-layer formation. Interestingly, Pt–M/CNT electrodes exhibit high double-layer capacitance, suggesting the improvement of surface hydrophilicity due to the presence of metal oxides and the adsorption of OH<sup>−</sup> onto the metal surface.

The electrochemical activity of Pt–M nanocatalysts was evaluated from the CV measurement. The specific charge transfer, contributed from bimetallic nanocatalysts ( $Q_{\text{cat}}$ ), can be obtained from

$$Q_{\text{cat}} = Q_t - Q_{\text{dl}} \quad (1)$$

where  $Q_t$  is the total specific charge transfer in the hydrogen adsorption/desorption potential region, and  $Q_{\text{dl}}$  is the double-layer capacitive charge transfer from the CNT electrode. The value of  $Q_t$  can be evaluated by integrating the CV curves in the relevant potential region:

$$Q_t = \frac{1}{2\nu} \int_{0.2}^{0.2} (I_d - I_a) \cdot dE \quad (2)$$

where  $\nu$  is the sweep rate;  $I_d$  and  $I_a$  are the specific current of desorption and adsorption, respectively; and  $E$  is the potential.

The electrochemical surface areas ( $S_{\text{ESA}}$ ) can be determined through the charge transfer due to hydrogen adsorption/desorption on Pt or Pt–M catalysts according to the following equation

$$S_{ESA} = \frac{Q_{cat}}{Q_{Pt}} \quad (3)$$

where  $Q_{Pt}$  is estimated to be  $0.21 \text{ mC/cm}^2$ , determined from electrical charge associated with monolayer adsorption of hydrogen on Pt. These  $S_{ESA}$  values for different types of bimetallic electrocatalysts according to CV results (as shown in Figs. 2) are calculated and listed in Table 1. This table clearly shows that the introduction of transition metals efficiently improves the  $S_{ESA}$  values, indicating enhancement of surface accessibility for hydrogen adsorption/desorption. Because these crystalline sizes of the bimetallic catalysts are different, a normalized active surface coverage of nanocatalysts should be given, and the estimation would clarify how much surface coverage is electrochemically active, i.e., the contribution to electrochemical hydrogen adsorption/desorption.

Assuming that the bimetallic catalysts have spherical shape, the chemical or geometric surface area ( $S_{CSA}$ ) of the catalysts can be obtained from the average particle size  $d_{XRD}$ ,

$$S_{CSA} = \frac{6}{\rho d_{XRD}} \quad (4)$$

where  $\rho$  is the density of Pt ( $\sim 21.4 \text{ g/cm}^3$ ). The  $S_{CSA}$  values determined from Eq. (4) are also collected in Table 1. It is generally recognized that the active surface coverage ( $\Theta = S_{ESA} / S_{CSA}$ ) is an important indication in determining electrochemical activity of a catalyst. The higher the surface coverage, the greater the electrochemical activity can be obtained. Based on data from Table 1, the calculated surface coverage has the following order: Pt-Co (85.1%) > Pt-Ni (80.4%) > Pt-Fe (76.2%) > Pt (26.3%). This result demonstrates again that bimetallic Pt-based electrocatalysts shows better electrochemical activity in acid electrolyte than pure Pt catalyst. This enhanced  $\Theta$  value ( $> 80\%$ ) can be attributed to the fact that (i) deposition of transition metals leads to lower overpotential of Pt/CNT electrode in acidic solution and (ii) good dispersibility of the bimetallic catalysts generates more available active sites for redox and double-layer formation.

It should be noted that the Pt-based catalysts, Pt-Co and Pt-Ni, appear to have a greater surface accessibility, i.e.,  $> 85\%$ , which is close to Pt-Ru catalyst of our previous study. This means that both Pt-Co and Pt-Ni serve as a promising candidate to replace Pt-Ru catalyst. One possible explanation is given to figure out this improvement of surface activity. In the presence of Pt-based catalysts, the oxidation of carbon support in aqueous solution can be expressed as:



Generally, this is a water-electrolyzed reaction that usually takes place at approximately 1.4 V in the presence of platinum. Here, the CNT support serves as a carbon source to convert to gaseous carbon dioxide. In the meanwhile, Pt particles are possibly separated from the carbon support, thus resulting in the loss of electrochemical activity, i.e., decrease of  $S_{ESA}$ . The introduction of Co and Ni metals in the bimetallic metals is expected to reduce the required potential for water electrolysis and thus the associated carbon oxidation. The reduced potential (as shown in Figs. 3(c) and 3(d)) provides one possible way to avoid the unwanted separation of bimetallic catalysts from the carbon support.

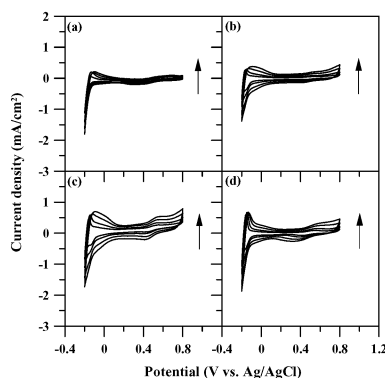


Fig. 3. Cyclic voltammograms for different types of Pt and Pt-M/CNT electrodes: (a) Pt, (b) Pt-Fe, (c) Pt-Co, and (d) Pt-Ni. Measurements were performed in 1 M  $H_2SO_4$  with different sweep rates of 1, 5, 10, 20, and 30 mV/sec, and each arrow in the figures indicates an increase of sweep rate.

#### 4. Conclusions

This study has investigated the electrochemical activity of CNTs coated with Pt and Pt-M (M = Fe, Co, and Ni) nanoparticles, prepared by chemical reduction approach. TEM images showed good dispersion of bimetallic catalysts over CNT surface (i.e., Pt-M/CNT composites), and XRD analysis indicated a slight change in the crystalline size of the bimetallic alloys, ranging between 6.26 nm and 6.78 nm. Nitrogen physisorption reflected that the specific surface areas and pore size distributions of Pt-M/CNT composites slightly altered after the Pt-M deposition. This demonstrated that the fabrication technique enables deposition of bimetallic alloy particles onto CNTs. CV measurements showed that the composition of Pt-M catalysts plays an important role in affecting the electrochemical activity of the bimetallic nanocatalysts. The Pt-Co and Pt-Ni catalysts were found to have better electrochemical activity, i.e., active surface coverage exceeds 85 %, which is much better than Pt and close to Pt-Ru catalyst in our previous study. This improvement of electrochemical activity on the catalysts was attributed to one possible reason that the introduction of Co and Ni metals in the bimetallic metals would reduce the required potential for water electrolysis and thus the associated carbon oxidation. The fact that the design of bimetallic Pt-M catalysts in preparing Pt-M/CNT composites facilitates the electrochemical storage of hydrogen in acidic electrolyte is a great improvement on the development of fuel cell systems.

#### References

- Hsieh C.T., Chou Y.W. and Lin J.Y., 2007, Fabrication and electrochemical activity of Ni-attached carbon nanotube electrodes for hydrogen storage in alkali electrolyte, *Intl. J. Hydrogen Energy* 32, 3457–3464.
- Hsieh C.T., Chou Y.W. and Chen W.Y., 2008, Fabrication and electrochemical activity of carbon nanotubes decorated with PtRu nanoparticles in acid solution, *J. Alloys Compd.* 446, 233–240.
- Wang M.Y., Chen J.H., Fan Z., Tang H., Deng G.H., He D.L. and Kuang Y.F., 2004, Synthesis of coiled/straight carbon nanofibers by catalytic chemical vapor deposition, *Carbon* 42, 3257–3260.
- Xu Y., Ruban A.V. and Mavrikakis M., 2004, Adsorption and dissociation of  $O_2$  on Pt-Co and Pt-Fe alloys, *J. Am. Chem. Soc.* 126, 4717–4725.