Synthesis and Characterization of Carbon Supported Nano-Structured Pt-Ni Catalyst for Alcohol Fuel Cell

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ABSTRACT

A series of Pt-Ni bimetallic nanoparticles supported on carbon with various Pt:Ni molar ratios (Pt_xNi_y/C) have been synthesized by the polyol reduction under ultrasonic irradiation. The reducing reagent was ethylene glycol (EG) and support materials were carbon Vulcan XC-72R and carbon nanotube (CNT). The morphology, structure and specific area of synthesized materials were characterized by transmission electron microscopy (TEM), nitrogen adsorption (BET). The electrocatalytic activity for alcohol oxidation of synthesized Pt_xNi_y/C materials and the commercial 10wt.% Pt/C catalyst (Aldrich Sigma, Pt/C_com) was investigated by cyclic voltammetry (CV) and chronoamperometry (CA). The major size of synthesized metallic particles was around 2 nm. The Pt_2Ni_1/C exhibited excellent catalytic properties for alcohol oxidation compared to other catalysts on the same support. The CNT was found to be more effective than carbon Vulcan for use as a support for alcohol oxidation catalysts.

Keywords: alcohol fuel cell, carbon, catalyst, nickel, platine.

1 INTRODUCTION

In last decades, fuel cell has been developed as a promising energy conversion device for the future due to high energy conversion efficiency and power density sufficient for a range of application [1, 2]. Platinum (Pt) metal is one of the most widely used catalysts for fuel cells. However, challenges for this catalyst are its scarcity and high cost, as well as the poisoning by the intermediates of the fuel oxidation, such as carbon monoxide (CO). In recent years, bimetallic PtNi and PtRu materials are have attracted much attention because of their active and stable electrocatalytic performance for alcohol oxidation at low temperatures in proton exchange membrane fuel cells (PEMFCs). While Pt is an effective catalyst for hydrogen oxidation and C-H, C-C bond cleavage in alcohol molecules, Ru and Ni activates H_2O creating oxides that convert carbon containing fragments, derived from alcohols or impurities such as CO in H_2 feed, to CO_2 [3].

A variety of techniques have been applied to synthesize electrocatalysts for fuel cell, one of these is sonochemical method [2, 4, 5]. The advantage of this method is generating nano alloy particles with comparatively unique size in short time. In liquids, the ultrasonic energy creates a cavitation, that is the formation, growth, and implosive collapse of bubbles. Cavitational collapse produces intense local heating (~5000 K), high pressures (~1000 atm), enormous heating and cooling rates (> 109 K/sec) and liquid jet streams (~400 km/h). These extreme conditions allow homogenization of the alloy phases and lead to the formation of uniformly distributed and nanosized bimetallic materials [4, 6].

In this work, nanoscale bimetallic PtNi catalysts with different molar ratios of Pt to Ni on carbon Vulcan XC-72 and carbon nanotube (CNT) as supports were synthesized by polyol reduction method under ultrasonic irradiation. The physical properties of catalysts were determined by transmission electron microscopy (TEM) and nitrogen adsorption (BET). The electrocatalytic performance was evaluated by cyclic voltammetry (CV) and chronoamperometry (CA) under simulated fuel cell working conditions.

2 EXPERIMENTALS

2.1 Treatment of Carbon Supports

Vulcan XC-72R carbon powder (Cabot, USA) was treated by soaking in 6.0 M HNO_3 (Merck) solution at room temperature for 10 h, followed by ultrasonic irradiation for 15 min. The suspension was then filtered, washed with deionized water (DI, 18.2 MΩ) dried at 105°C for 2 h. Following the procedures described in [7], raw carbon nanotubes (rCNT) were synthesized by thermal chemical vapor deposition (T-CVD) and purified to form the purified carbon nanotubes (pCNT)

2.2 Synthesis of Nano PtNi Catalyts

By polyol method, 2 mM solution of H_2PtCl_6 and $Ni(NO_3)_2$ (Sigma- Aldrich) in ethylene glycol (EG) was ultrasonically homogenized for 10 min and magnetically stirred at room temperature. The precursor solution was adjusted to pH $\geq$ 10 by adding dropwise 1.0 M solution of NaOH in EG (NaOH/EG). Then treated carbon Vulcan or CNT powder was dispersed in the solution by strirring 1 h. After that, the reaction mixture was transferred into a becher for ultrasonication with Heilscher-UP200Ht immersion sonicator, operated at 26 kHz frequency and 17 W/cm^2 acoustic power, with 100 W input power. The product of bimetallic nanoparticles on carbon supports was filtered with 0.45 µm-pore-diameter Whatman membrane, washed with DI water and dried in an oven at 100^{o}C for 2 h. The ratio of total metal loading to carbon support was 20 wt%. The synthesized materials were coded Pt_xNi_y (molar ratios of x to y were 3:1, 2:1, 1:1, 1:2, 1:3).

2.3 Characterization of PtNi Nanoparticles and Electrochemical Measurements

The morphology of catalysts was characterized by transmission electron microscopy (TEM) using a JEOL JEM 1400 microscope at 120 kV. Brunauer-Emmett-Teller specific surface area (S_{BET}) was determined by nitrogen adsorption measurement (QuantaChrome Autosorb 1C), remove gas at 200^{o}C in 2 h.

The catalytic behavior of synthesized nano Pt_xNi_y/C or Pt_xNi_y/CNT for alcolhol electrooxidation was studied by cyclic voltammetry (CV) and chronoamperometry (CA) using potentiostat/galvanostat PGSTAT320N (Autolab Metrohm). The electrochemical measurements were performed in a three electrode cell with the working electrodes (WE) being a glassy carbon foil covered by a Pt/C, Pt_xNi_y/C or Pt_xNi_y/CNT film. A Pt wire of a geometric area about 1.41 cm^2 was used as the counter electrode (CE) and an Ag/AgCl/3.0 M KCl used as the reference electrode (RE) (0.21 V *vs*. SHE). The electrolyte was 0.5 M KOH (Merck) in 1.0 M alcohol solution. The measurements were carried out at 25^{o}C in nitrogen (99.999%) atmosphere. The

The Pt/C, Pt_xNi_y/C or Pt_xNi_y/CNT film were prepared by using 2.50 mg of Pt_xNi_y/C (carbon Vulcan - supported) or Pt_xNi_y/CNT (CNT - supported) catalysts and 10 µl of 5 wt% Nafion (Sigma Aldrich, 65%) were added to 1.0 mL of ethanol solution. The formed ink was irradiated sonically in 1 h. 75 µl of the ink was dropped on a glassy carbon support (12.56 mm^2), and the prepared WE was dried at room temperature in 1 h. The electrochemical behavior of synthesized catalysts was compared with commercial Pt/C powder (Sigma Aldrich, loading 10%wt Pt on active carbon) (Pt/C_com).

3 RESULTS AND DISCUSSION

3.1 Physical Properties of PtNi Electrocatalysts

TEM images showed that Pt_xNi_y materials dispered as nano-particles on the carbon aggregates and the particle sizes of Pt_xNi_y/C and Pt_xNi_y/CNT distributed from 1 to 3 nm with major part of 2 nm, except Pt_1Ni_1/pCNT (figure 2g). Interestingly, the synthesized Pt_2Ni_1/C was almost mono-sized of 1 nm. Compared to Pt_xNi_y/C, the Pt/C particles were larger and multi-distributed in size though they were synthesized with the same method. Table 1 shows that the BET surface areas (S_{BET}) of synthesized catalysts on CNTs were higher than that of catalysts on carbon Vulcan, which is obviously correlated with particle size. Pt_1Ni_1/pCNT possessed highest S_{BET} and average particle size.

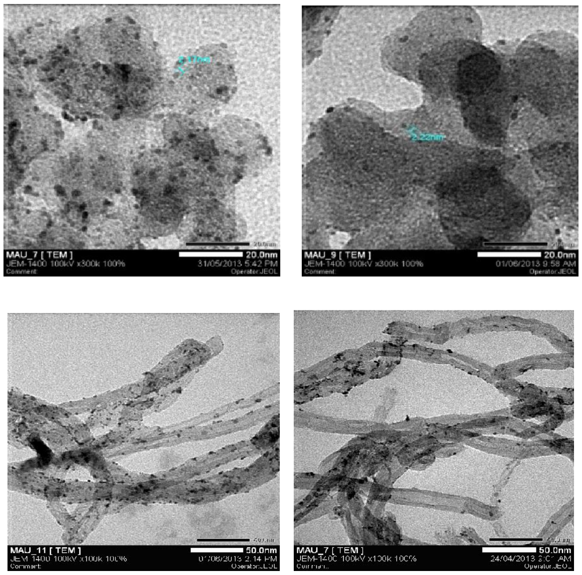

Figure 1: TEM images of Pt_1Ni_2/C (top left), Pt_1Ni_3/C (top right), Pt_1Ni_1/pCNT (left bottom) and Pt_1Ni_1/rCNT.

Table 1: Particle size distribution and specific area of electrocatalysts

Material	Main sizes (nm)	Average size (nm)	S_{BET} (m^2/g)
Pt/C	2-7	3.8	
Pt_3Ni_1/C	1-3	2.3	178.92
Pt_2Ni_1/C	1-2	1.1	192.53
Pt_1Ni_1/C	1-3	1.8	199.90
Pt_1Ni_2/C	1-3	1.5	187.60
Pt_1Ni_3/C	1-3	1.5	119.13
Pt_1Ni_1/pCNT	2-5	3.05	220.95
Pt_1Ni_1/rCNT	1-3	2.50	200.16
Pt/C_com	-	-	57.41

3.2 Electrochemical Behavior of Nanocatalyst for Alcohol Oxidation

The real electrochemical surface area (ECA) of a Pt-based catalytic electrode may be determined by the charge values of hydrogen adsorption-desorption on the electrode in 0.5 M $HClO_4$. ECA is calculated from the following formula [8]:

$$ECA = Q_H/Q_M$$

where Q_H (µC) is the charge associated with peak area in the hydrogen desorption region (-0.16 – 0V) on the cyclic voltammograms (CVs). Q_M is the charge density associated with monolayer adsorption of hydrogen (210 $\mu C.cm^{-2}$) [9,10]. Figure 3 shows the CVs of the studied electrodes in the potential range between -0.2 V and 1.0 V at 50 mV/s scan rate.

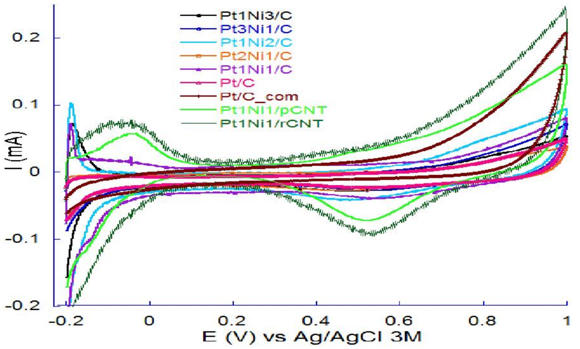

Figure 1: CVs of Pt and Pt_xNi_y electrodes in 0.5 M $HClO_4$, scan rate 50 mV/s, 25^0C

The real ECA was also determined by the coulombic charge corresponding to the oxide reduction peak at potiential of 0.57 V (figure 3). The calculated ECA of electrocatalysts was showed in table 2. From the studied ratios of Pt to Ni on carbon Vulcan, the ECA of Pt_1Ni_1/pCNT was the highest. Compared to Pt/C_com, the electrocatalysts of PtNi on carbon Vulcan and CNT had larger specific area. From the result of table 1, the BET area of the electrocatalyst on treated CNT was higher than that on carbon Vulcan, this maybe lead to the higher ECA of electrocatalyst on treated CNT. With the larger pore size of carbon nanotube, metallic particles can be easy to deposite on the support.

Synthesized Pt and Pt_xNi_y nanoparticles were used as anodes in the study of the electrocatalytic activity for methanol oxidation reaction (MeOR) and glycerol oxidation reaction (GOR) using CV, CA measurement.

In the cyclic voltammograms (CVs) of Pt and Pt_xNi_y electrodes on various supports, two peaks of MeOR were observed on CVs, the first one at about onset potential of -0.20 V in the forward scan and the other one in the backward scan at more negative potentials at about -0.30 V. The anodic peak in the forward scan may be explained by the oxidation of freshly chemisorbed methanol molecule while the one on reverse scan is primarily associated with removal of carbonaceous species which are not completely oxidized in the forward scan [11]. Thus the ratio of the forward anodic oxidation peak current density (i_f) to oxidation peak current on backward scan (i_b), i_f/i_b can be used as a criteria of the catalyst tolerance to carbonaceous species accumulation. A high ratio shows good methanol oxidation to carbon dioxide during the forward scan and the less accumulation of carbonaceous residues on the catalyst surface [12].

According to table 2, the ratios of i_f/i_b for the synthesized electrodes were higher than 1. Moreover, the i_f/i_b ratios were higher for PtNi than Pt catalyst. This result suggested that alloy PtNi catalyst behaved a better tolerance for MeOR and the presence of Ni can improve the catalytic activity. From table 2, we also can see that i_f/i_b ratio of Pt_2Ni_1/C was highest at 6.56 on carbon Vulcan compared with the other ratios. At the same ratio of Pt to Ni (1:1), the rate of MeOR and GOR on carbon Vulcan were lower than that on carbon nanotube.

Table 2 : Electrochemical parameters of MeOR and GOR on nano metallic electrodes

Materials	ECA (m^2/g)	MeOR			GOR		
		E_f(V)	i_f(mA/cm^2)	i_f/i_b	E_f(V)	i_f(mA/cm^2)	i_f/i_b
Pt/C	9.38	-0.17	0.18	1.73	-0.15	1.86	1.56
Pt_3Ni_1/C	11.73	-0.16	2.27	2.92	-0.14	4.71	2.91
Pt_2Ni_1/C	10.89	-0.19	2.20	6.56	-0.20	9.20	4.18
Pt_1Ni_1/C	17.93	-0.20	6.02	4.89	-0.11	5.65	2.53
Pt_1Ni_2/C	15.88	-0.15	2.22	4.96	-0.15	4.48	3.47
Pt_1Ni_3/C	11.85	-0.15	1.91	5.08	-0.17	2.61	3.48
Pt_1Ni_1/pCNT	22.63	-0.2	5.27	5.17	-0.05	5.47	2.82
Pt_1Ni_1/rCNT	10.32	-0.16	3.93	1.26	-0.17	1.90	2.40
Pt/C-com	11.67	-0.17	0.18	1.73	-0.16	0.51	2.32

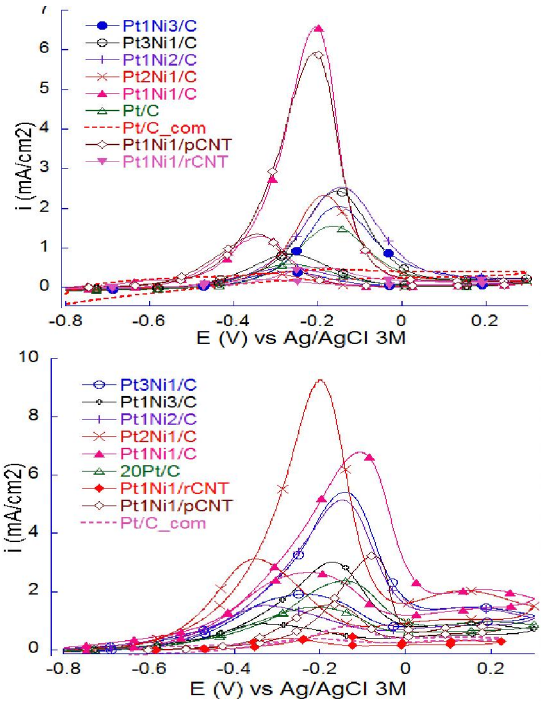

Figure 2: CVs of PtNi/C and Pt/C electrodes in 1.0M KOH solution containing 1.0M MeOH (top) and 1.0M glycerol (bottom), scan rate 50mV/s, 25^{o}C

Figure 3 shows the CVs of GOR obtained for Pt and Pt_xNi_y electrodes on various supports. Similarly to methanol oxidation reaction, the ratios of i_f/i_b for metallic electrocatalysts were also higher than 1. Compared to MeOR; however, i_f/i_b ratios of GOR on almost metallic electrocatalysts were lower. This can be explained that the glycerol oxidation to CO_2 is very complicated; compared to methanol, it requires the cleavage of C-C bonds and the efficient removal of C_1 and C_2-type intermediate species including CO [13,14].

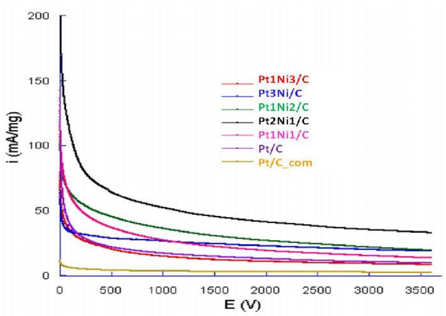

Figure 3: CA curves at -0.30 V of 1.0 M KOH + 1.0 M MeOH on Pt/C, Pt_xNi_y/C electrodes

Figure 4 shows the chronoamperograms (CA) of Pt/C, Pt_xNi_y/C in 1.0 M KOH containing 1.0 M MeOH at a set-up potential of -0.30 V in 3600 s. It can be seen that the current density decreased rapidly in about first 100 s. At following time, the current decayed slowly and stable in the next 500 s. From the figure 4, it can be seen that the Pt_2Ni_1/C showed the highest current at any time, while Pt/C_com showed the lowest oxidation current.

4 CONCLUSIONS

Synthesized bimetallic PtxNiy catalysts consist of spherical nanoparticles with 1 to 5 nm particle size. PtxNiy/C (carbon Vulcan supported) particles, mostly sized of 2 nm, were a little smaller than CNT-supported (~ 3 nm). Pt2Ni1/C material showed the best catalytic performance for MeOR compared to other catalysts synthesized on the same support. At the same Pt to Ni molar ratio of 1:1, bimetallic materials synthesized on carbon nanotube performed the better catalytic activity for alcohol oxidation reaction than that on carbon Vulcan.

5 ACKNOWLEDGMENTS

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