



ELECTROCHEMICAL ACTIVITY OF PtM (M=Co, Cu, Ni) CATALYSTS SUPPORTED ON CARBON VULCAN FOR OXYGEN REDUCTION REACTION (ORR) IN FUEL CELLS

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Received: 10 March 2018; accepted for publication: 14 May 2018

ABSTRACT

PEMFC - proton exchange membrane fuel cell is electrochemical devices producing electricity and heat from reaction between a fuel (often hydrogen) and oxygen. Therefore, energy production is generally clean and effective without burning the fuel like the tradition way in combustion engines. The obstacles encountered fuel cell commercialization are mainly due to expensive catalyst materials (Platinum) and long-term instability performance. For this reason, numerous investigations have been undertaken with the goal of developing low-cost, efficient electrocatalysts that can be used as alternatives to Pt. In this paper, a two-step procedure at room temperature was applied to prepare a bimetallic Pt-M(M = metal) supported carbon Vulcan. First, the chemical reduction of M metal ions by sodium borohydride in the presence of carbon powder is performed. Second, the partial galvanic replacement of M particle layers by Pt is achieved upon immersion in a chloroplatinate solution. The major size of synthesized metallic particles was around 2-3 nm. From the slope of Koutecky-Levich plot for ORR using PtM/C materials as catalysts it was found that the overall electron transfer number ranged from 3 to 4, leading to the suggestion of H₂O₂ formation as an intermediate of the ORR.

Keywords: catalyst, electrochemical, oxygen reduction reaction, fuel cell.

1. INTRODUCTION

Fuel cells are attractive power sources for both stationary and electric vehicle applications due to their high conversion efficiencies and low pollution [1]. The commonest electrocatalyst for fuel cells is Pt, which is highly effective for accelerating the slow kinetics of oxygen reduction reaction (ORR) where i_o is 2.8×10^{-7} mA/cm² at 30 °C. 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). For this reason, numerous investigations have been undertaken with the goal of developing low-cost, efficient electrocatalysts that can be used as

alternatives to Pt. In recent years, bimetallic PtM materials have attracted much attention because of their active and stable electrocatalytic performance for alcohol oxidation and oxygen reduction reaction at low temperatures in proton exchange membrane fuel cells (PEMFCs). A variety of techniques have been applied to synthesize electrocatalysts for fuel cell, one of these is chemical reduction method [2]. The advantage of this method is generating nano alloy particles with comparatively unique size in short time. These extreme conditions allow homogenization of the alloy phases and lead to the formation of uniformly distributed and nano sized bimetallic materials [3]. In this work, nanoscale bimetallic PtNi, PtCo, PtCu catalysts on carbon Vulcan XC72R as supports were synthesized by reduction method under ultrasonic irradiation. The morphology, structure and specific area of synthesized materials were characterized by X-Ray diffraction (XRD), transmission electron microscopy (TEM). The catalytic activity for oxygen reduction reaction (ORR) of PtM/C was investigated by CV and linear sweep voltammetry (LSV) under simulated fuel cell working conditions.

2. EXPERIMENTALS

2.1. Synthesis of nano PtM/C catalysts

Briefly, Ni(NO₃)₂(or Co(NO₃)₂.6H₂O; CuSO₄ -SigmaAldrich) was dissolved in ultrapure water. After 15 min of constant stirring carbon Vulcan and citric acid (CA) was added to the solution. M material nanoparticles supported on carbon were formed by reduction of the metal precursor with NaBH₄ which was added as a solid to the mixture in a weight ratio of 3:1 to metal. The resulting mixture was then left under constant stirring over night and the formed supported catalyst was collected via suction filtration, washed thoroughly with ultrapure water, ethanol, and acetone and finally dried over night at 80 °C. Afterwards, the synthesized M/C, CA and H₂PtCl₆ 0.05 M (Aldrich) were dissolved in ultrapure water. After 1 hour of constant stirring, the mixture was treated with NaBH₄ 0.15 M which was added and left under stirring over night and the formed Pt(M) supported on carbon was collected via suction filtration, washed thoroughly with ultrapure water, ethanol, and acetone and finally dried over night at 80 °C. The ratio of total metal loading to carbon support was 20 wt%.

2.2. Electrode preparation

2.50 mg of PtM/C (M = Co, Cu, Ni) (carbon Vulcan - 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 ultrasonically in 1 hour. A volume of 75 µl of the ink was dropped on a glassy carbon support (12.56 mm²), and the prepared working electrode was dried at room temperature in 1 hour.

2.3. Physical – chemical and electrochemical characterization

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 °C for 2 h.

The catalytic behavior of synthesized nano PtM/C was studied by cyclic voltammetry (CV) and chronoamperometry (CA) using potentiostat/galvanostat PGSTAT 320N (Metrohm Autolab). 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, PtNi/C, PtCo/C, PtCu/C film. A Pt wire of a geometric area about 1.41 cm² was used as the counter electrode (CE) and an Ag/AgCl/3.0 M KCl was used as the reference electrode (RE) (0.21 V vs. SHE). The measurements were carried out at 25 °C in nitrogen (99.999 %) atmosphere. The electrochemical behavior of synthesized catalysts was compared with commercial Pt/C powder (Sigma Aldrich, loading 10% wt Pt on active carbon) (coded as Pt/C com).

For ORR, a glassy carbon rotating disk electrode (GC-RDE) coated with PtM/C paste has been used as WE. The ORR kinetics was studied by linear sweep voltammetric (LSV) in the potential range from 0.8 V to -0.15 V with the scan rate of 10 mV/s. The rotating speed was set on different values and an oxygen-saturated 0.5 M H₂SO₄ was used. The saturated concentration of oxygen (25 °C) was 36.4 mg/L, measured by WTW Oximeter Oxi 538 with a WTW Cellox 325 electrode.

3. RESULTS AND DISCUSSION

3.1. Structure, composition and size of the PtNi/C, PtCo/C and PtCu/C synthesised materials

As shown in Fig. 1, TEM images can be clearly seen that the metal nanoparticles with a narrow particle size distribution are uniformly dispersed on the surface of carbon. It showed that the particle sizes of PtM/C distributed from 1 to 5 nm with major part of 2 nm. Interestingly, the morphologies of the PtNi nanoparticles are generally spherical, and the mean diameter is almost mono-sized of 1 nm (Fig. 1a). Compared to PtNi/C, the PtCo/C and PtCu/C particles were larger and multi-distributed in size though they were synthesized with the same method. The BET surface areas (SBET) of synthesized PtM/C catalysts showed that PtNi/C were higher than that of catalysts of PtCo/C and PtCu/C, which is obviously correlated with particle size. It results that PtNi/C possessed highest SBET and smallest particle size. Thus, it is inferred that, the size of PtM nanoparticles are influenced by the radius M metal atom. The calculated SBET of PtNi/C, PtCu/C and PtCo/C are 199.90, 177.60 and 115.13 m².g⁻¹, respectively.

The XRD pattern of Pt/C catalyst shows in Fig. 2. The wide diffraction peak located at a 2θ angles of about 25.0° is attributed to carbon (002) crystal face, which matches well with the standard C peak (JCPDS No.75-1621) [4]. The diffraction peaks of (111), (200) and (220) at 2θ values of 39.9°, 46.55° and 67.85° were characterized the face-centered cubic (fcc) structure of the synthesized Pt nano materials. Fig. 2 also shows the X-ray diffraction patterns of PtNi, PtCo, PtCu alloys catalysts deposited on Vulcan XC-72 carbon. However, the diffraction peaks at 40°, 46°, and 68° display primarily the characteristics of fcc Pt without any trace of fcc M metal. And XRD patterns of PtM/C catalysts are gradually shifted to higher 2θ angles with presenting M metal in Table 1. This indicated a contraction of the lattice and confirmed the formation of Pt–M alloys due to the incorporation of M metal into the fcc structure of Pt. No characteristic diffraction peaks of metallic or M oxides were detected, indicating that the oxidation of M can be effectively prevented by the use of flowing argon gas in the reduction process. The diffraction peaks of the PtM alloy catalysts were broader than those of Pt, which are due probably to Pt atom and M atom are only partially alloyed, and the residual M atom is oxidized.

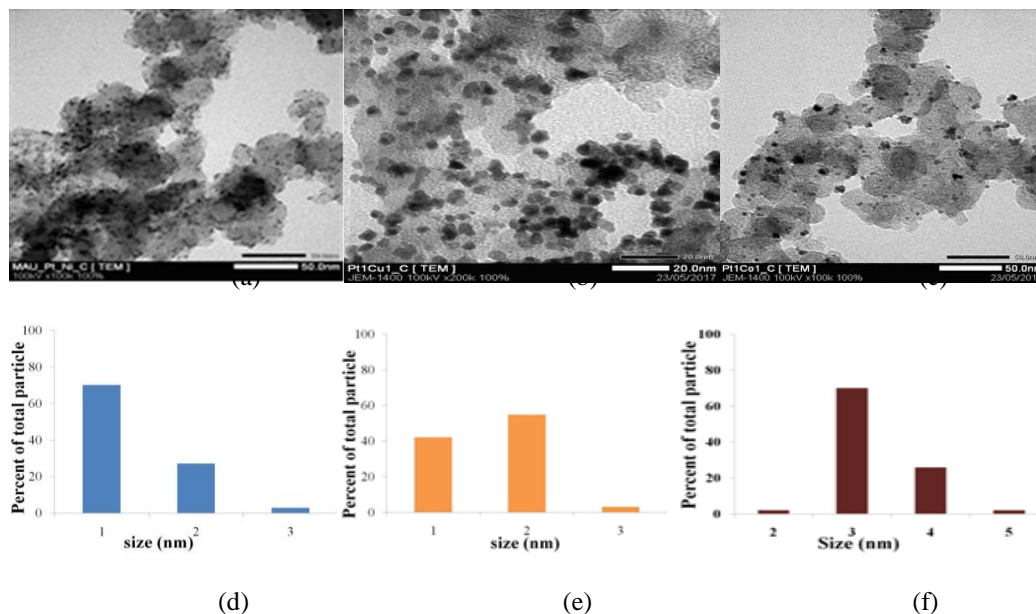


Figure 1. TEM images of (a) PtNi/C, (b) PtCu/C, (c) PtCo/C catalysts and the particle size distribution of (d) PtNi/C, (e) PtCu/C, (f) PtCo/C catalyst.

The diffraction peaks for Pt (111) and Pt (200) are used to estimate the particle size by the Scherrer's equation:

$$D = \frac{0.9\lambda}{B \cos \theta}$$

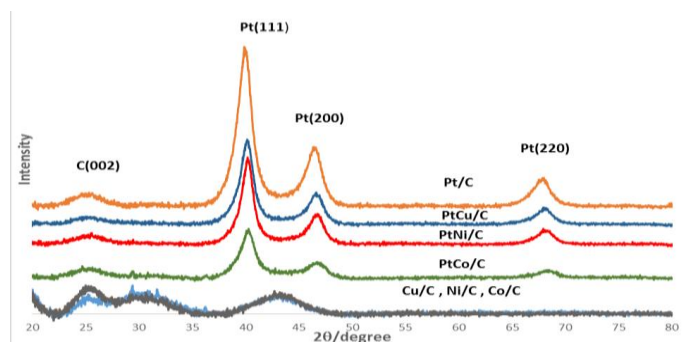


Figure 2. XRD pattern of 20Pt/C catalyst and PtNi/C, PtCo/C, PtCu/C catalysts.

Where D is average particle size (nm), λ is wavelength, is the angle of Pt (200) peak and B is the full width at half-maximum in radians [5, 6]. The calculated average particle size of PtNi, PtCu and PtCo nanoparticles dispersed on carbon are 1.306, 2.869 and 3.4216 nm, respectively; which are well consistent with the TEM results.

Table 1. The shifted diffraction peak of PtM catalysts.

Sample	2θ		
	110	200	220
Pt/C	39.46	46.41	67.46
PtNi/C	40.20	46.81	68.02
PtCu/C	40.02	46.71	67.85
PtCo/C	41.11	46.77	68.80

3.2. Electrochemical characterization

Electrochemically active surface area estimation

The real electrochemical active surface area (ECSA) of a Pt-based catalytic electrode may be determined by the charge values of hydrogen adsorption-desorption on the electrode in 0.5 M HClO₄. ECSA is calculated by $ECSA = Q_H/Q_M$ where Q_H (μC) is the charge associated with peak area in the hydrogen desorption region (-0.16 – 0 V). Q_M is the charge density associated with monolayer adsorption of hydrogen ($210 \mu\text{C}\cdot\text{cm}^{-2}$) [7, 8].

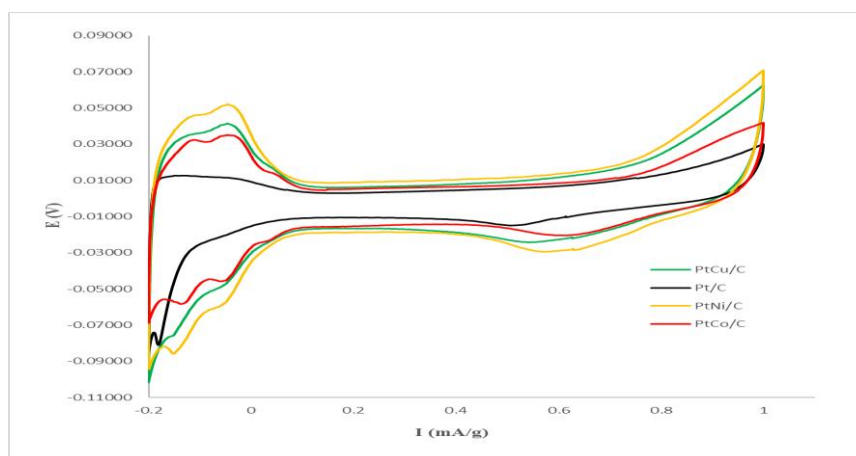


Figure 3. The CV curves of Pt/C, PtCu/C, PtNi/C and PtCo/C in 0.5 M H₂SO₄ solution from -0.1 V to 1.2 V at 25 mV.s⁻¹ scan rate.

Table 2. ECSA and if/ib of Pt/C, PtCo/C, PtCu/C and PtNi/C.

Electrode	ECSA (cm ² /mg)
Pt/C	0.18
PtCu/C	0.55
PtCo/C	0.45
PtNi/C	0.65

Figure 3 shows the cyclic voltammograms (CV) curves of the studied electrodes from -0.1V to 1.2 V at $25 \text{ mV}\cdot\text{s}^{-1}$ scan rate, high purity argon gas was used during the experiments. The results of calculation and the corresponding the different molar ratios of Pt to M are shown in Table 2. Among the electrocatalysts, PtNi/C has the highest ECSA at $0.65 \text{ cm}^2\cdot\text{g}^{-1}$, which is attributed to the smallest particle size of Pt nanoparticle loaded on the carbon [9].

Oxygen reduction reaction activity of PtM/C nanoparticle electrocatalysts

Linear sweep voltammetric (LSV) profiles of PtM/C alloy electrocatalysts for ORR obtained from the rotating disk electrode (RDE) experiments and compared with that for commercial Pt/C catalyst are showed in Fig. 4. Obviously, compared to Pt/C and PtM alloys performed as much better catalysts for the ORR. At potential of -0.15 V and the same 1398 rpm rotating speed, the current density of ORR on PtM/C was from -1.2 to -1.7 $\text{mA}\cdot\text{cm}^{-2}$, compared with -0.15, -0.17 and 0.12 $\text{mA}\cdot\text{cm}^{-2}$ on the Ni/C, Cu/C and Co/C. Clearly, the presence of M in the Pt-based catalysts improved significantly their electrocatalytic activity for ORR. Thus, the low catalytic activity of Pt/C may be attributed to the large size of particles.

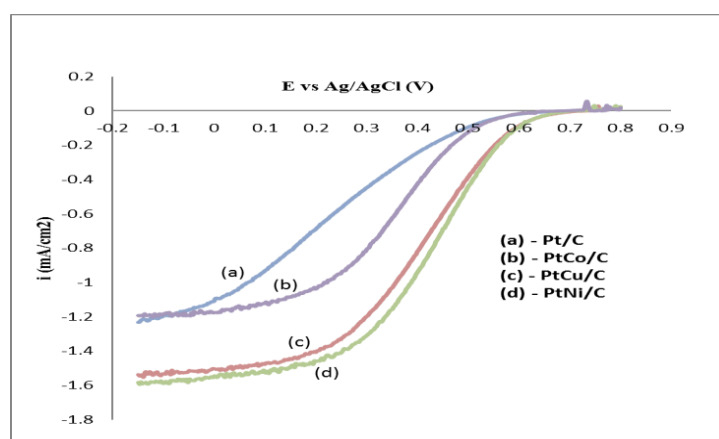


Figure 4. The LSV in O_2 - saturated $0.5 \text{ M H}_2\text{SO}_4$ of PtCo/C, PtCu/C, PtNi/C and Pt/C catalyst.

The onset potential (OP, V) as well as the mass activity (MA, $\text{mA}/\text{mg}_{\text{Pt}}$) and specific activity (SA, $\text{mA}/\text{cm}^2_{\text{Pt}}$) at 0.9 V vs RHE or at $0.7 \text{ V (vs. Ag/AgCl (NaCl 3M))}$ of PtM/C are showed in Table 4. According to Table 4, PtNi/C is the most active material for ORR with the high onset potential of 0.696 V (or with the low overpotential). Meanwhile, PtNi/C is the least active material since ORR which was catalysed by PtM/C has not begun yet at $0.9 \text{ V vs. Ag/AgCl (NaCl 3M)}$. The worst activity of PtCo/C can be explained by the low proportion of active sites which can be seen in XRD, TEM results. Due to the low solubility of oxygen in acid media, the ORR depends strongly on hydrodynamic conditions. The polarization curves of PtCu/M electrocatalyst in oxygen saturated $0.5 \text{ M H}_2\text{SO}_4$ electrolyte were obtained by correcting the total current density at different rotation rate in Fig. 5.

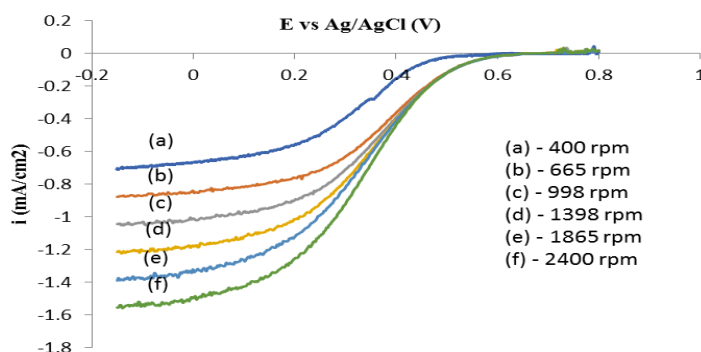


Figure 5. The polarization curve achieved by LSV method in O_2 -saturated 0.5 M H_2SO_4 of PtCu at different rotation rate.

Table 4. Onset potential, mass activity, specific activity at 0.7.

Sample	E_{op} vs Ag/AgCl (KCl 3M) (V)	MA ($mA \cdot mg^{-1} Pt$)	SA $E = 0.70$ V ($mA \cdot cm^{-1}$)
PtNi/C	0.696	0.901	0.057
PtCu/C	0,636	0.678	0.044
PtCo/C	0.612	0.572	0.034
Pt/C	0.507	0.500	0,035

ORR in aqueous solution occurs mainly by two pathways: (i) the direct four – electron reduction pathway from O_2 to H_2O ; (ii) the two-electron reduction pathway from O_2 to hydrogen peroxide H_2O_2 [10]. The ORR mechanism is deduced from Koutecky – Levich equation. We use the overall electron transfer number (n) which is calculated from the slope (a) of Koutecky – Levich plots ($1/i - 1/\omega^{1/2}$) [11].

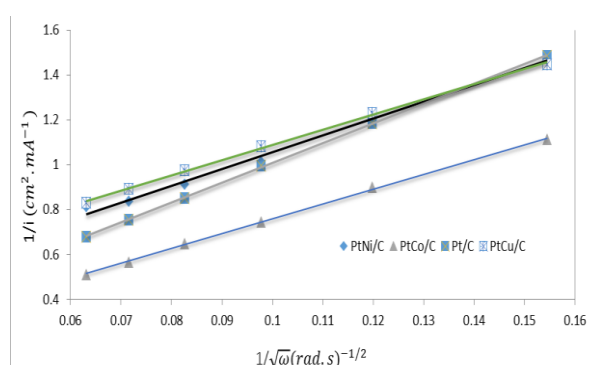


Figure 6. Koutecky – Levich plot PtM/C alloys. The theoretical line is calculated according to Levich theory for a 4-electron O_2 reduction process.

The Koutecky – Levich plots of PtM/C from Fig. 6. show that the overall electron transfer number of ORR at most of the studied catalyst was from 3 to 4. Thus, it clearly proved the formation of H_2O_2 as an intermediate in the reaction.

4. CONCLUSIONS

Different catalysts synthesized bimetallic PtM (M=Co, Cu, Ni) catalysts consist of spherical nanoparticles with 1 to 5 nm particle size. PtNi/C (carbon Vulcan supported) particles, mostly sized of 1 nm, were a little smaller than PtCo, PtCu (~3 nm). PtM/C material showed the best catalytic performance for ORR compared to other catalysts synthesized on the same support. It results that the electrocatalyst of PtM nanoparticles follow the order of PtNi/C > PtCu/C > PtCo/C.

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