

SYNTHESIS AND CHARACTERIZATION OF PALLADIUM-BASED NANO-CATALYST ON N-DOPED GRAPHENE FOR DIRECT ETHANOL FUEL CELLS

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Received: February 14, 2017

Abstract. Pd-containing catalyst becomes an alternative materials in the recent years since Pd has similar properties to Pt with high catalytic activity, has high abundance and is low cost material. Pd alloy is favorable applied as binary compound catalyst for cultivating activity of oxygen reduction reaction (ORR) for direct ethanol fuel cell (DEFC). This catalyst could inhibit the particle agglomeration after long time processing, require low production cost and exhibit good electrostatic force. In this study, new binary nano-catalysts (Pd-Ni) were prepared with various ratio of Pd:Ni (5:1, 4:1 and 3:1) via solution route method. Powder X-ray diffraction (XRD) was applied to confirm the formation of alloy of Pd-Ni phase. The solid-supported Pd-Ni catalysts were then prepared on N-doped graphene by solution route, microwave-assisted and polyol methods. Sodium borohydride (NaBH_4) was used as a reducing agent for solution route method whereas ethylene glycol was used as a reducing agent for microwave-assisted and polyol methods. The well-dispersion of Pd-Ni nanoparticles on N-doped graphene which prepared by polyol method was observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques. TEM micrograph showed that particle sizes of synthesized catalysts were in the range of 3-7 nm and the electrochemical performance was $0.39 \text{ A/cm}^2 \cdot \text{mol}$ at 600 mV.

1. INTRODUCTION

Nowadays, environmental pollution is a major problem in the world. The production of carbon dioxide (CO_2) and carbon monoxide (CO) from manufacturing processes and vehicles can cause air pollution which leads to increased health problems as well as contribute to global warming problem. The fuel cell is a device that can convert chemical to electrical energy throughout electrochemical reaction. In most simplistic case hydrogen (H_2) and oxygen (O_2) gas are converted to water (H_2O). Fuel cells, such as alkaline fuel cell (AFC), phosphoric-acid fuel cell (PAFC), and proton exchange membrane fuel cell (PEMFC), are subjected to be the future sources of green energy and benign environments which the

electricity can be produced by continuously feeding O_2 and H_2 gas into the cell [1]. Among the various types of fuel cells, direct ethanol fuel cells (DEFC) have attracted considerable attention as alternative energy resources [2]. Ethanol is a suitable choice for fuel due to its low toxicity and its elevated energy density. Moreover, ethanol can be produced from agricultural bioprocesses which is considered a renewable energy source [3-5]. Currently, platinum (Pt) is the most commonly used catalytic metal in anode and cathode catalyst for the fuel cells because of its excellent properties in high catalytic activity of oxidation and reduction of fuel cell. Moreover, the cost of Pt is a major impediment in the commercialization of fuel cell technology, because it alone accounts for approximately

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54% of the total fuel cell stack cost [4]. Moreover, pure Pt catalysts have been reported that it activates the 2e⁻ reaction [5]. By this reason, pure Pt is not suitable catalyst for ORR at the cathode. Moreover, Pt agglomeration is typical after long time operation. Thus, the development of the novel non-precious metal catalysts which can substitute for the Pt-based catalyst and operate efficiently in low temperature acidic electrolytes has been strongly required [6]. On the other hand, it has recently been demonstrated that some non-Pt catalysts such as Pd, Pd-M (M= Co, Fe, Cu, Ni) can be effectively used for the ethanol oxidation reactions and the oxygen reduction reactions (ORR) [2,7]. Pt and Pd have very similar properties (same group in the periodic table, same fcc crystal structure, similar atomic size). However, the cost of palladium is lower than that of platinum, so it could be a good substitute for Pt as the catalyst in fuel cells. Pd is an interesting as it is at least fifty times more abundant on the earth than Pt [5]. Therefore, instead of using Pt, Pd can be a promising-catalyst for fuel cells. In addition, Pd alone presents satisfactory activity for oxidation reactions when used as catalyst material. It is well known, chemical interactions between atoms/molecules happen at the surface of catalysts. Smaller size catalysts contribute to higher chemical activity. Bimetallic or multi-metal nanoparticles receive considerable attention as new catalysts because the combination of two or more metals within a nanoparticle generates a new species of nanoparticles with certain properties. Also, Pd-based catalyst is suitable catalyst for fuel cells, its catalytic activity outperformed Pd alone for use bimetallic catalysts materials in fuel cell [2,4,7]. Therefore, Pd-based catalyst was introduced to fix this problem [8,9]. Carbon black is commonly used as fuel cell catalysts supports, but its properties are not completely satisfactory [10]. Thus, carbon black alternative materials such as nanostructured carbons have been investigated [11]. Recently, graphene and other 2D atomic structures are of considerable interest for catalysis because of their unique structural and electronic properties. Over the past decade, these materials have been used in a variety of reactions [12]. In addition, graphene has been investigated as a supporter for low-temperature fuel cell catalysts because of its high surface area, excellent electrical conductivity, good chemical and environmental stabilities and strong coupling with catalyst nanoparticles. Furthermore, it has been demonstrated recently that via doping (e.g. N-doping) the physical and chemical properties of graphene can be tailored opening up new possibili-

ties. The N content of the non-noble metal catalysts on the oxygen reduction reaction (ORR) has been identified as the most important factor for electrocatalytic performance. It has been found that higher the density of the catalytic sites on their surface, the better is their performance as electrocatalyst [13]. Nitrogen-doped (N-doped) carbon nanomaterials have received increasing attention as effective metal-free electrocatalysts. Thus, catalysts formed from transition metals, nitrogen and carbon compounds are a promising potential catalysts material for ORR.

2. EXPERIMENTAL

2.1. Preparation of N-doped Graphene (NrGO)

Firstly, graphene oxide (GO) was synthesized by a modified Hummers method [14]. Graphite and sodium nitrate (NaNO₃) were mixed with sulfuric acid (H₂SO₄) (95%) and H₂SO₄ in a 500 ml round bottom flask with was placed in an ice bath. While maintaining vigorous stirring, potassium permanganate (KMnO₄) was added to the suspension in batches stirring at 5 °C for 2 hours. Then the reaction was kept stirring at room temperature for 1 hour and at 40 °C for 1 hour. After that, 660 ml of deionized water was slowly added into the pasty with vigorous agitation. Then the reaction was stirred at 98 °C for 1 hour, before 30 ml of hydrogen peroxide (H₂O₂) (30%) was added into the mixture. For purification of GO, the mixture was washed by rinsing and centrifugation with 5% hydrochloric acid (HCl) solution and then deionized water for several times. The graphene oxide suspension was collected after centrifugation. The gray GO powder was obtained from drying in an oven for overnight at 60 °C, and then it was annealed at 500 °C for 5 hour under nitrogen atmosphere. The GO powder were mixed with melamine as 1:5 weight ratios. Finally, it was annealed at 800 °C for 1 hour under nitrogen atmosphere.

2.2. Preparation of the Pd, Pd-Ni and Pd-Ni/NrGO catalysts

In preliminary experiment, Pd and Pd-Ni nanoparticles with different Pd:Ni atomic ratios (5:1, 4:1, and 3:1) were synthesized by the solution route method using ethylene glycol (EG) as a solvent. Firstly, the solution of palladium chloride (PdCl₂), nickel chloride-6-hydrate (NiCl₂·6H₂O) and sodium hydroxide (NaOH) in EG were partially prepared. The concentration of NaOH was twenty times as high as that of NiCl₂·6H₂O. After that, the solution

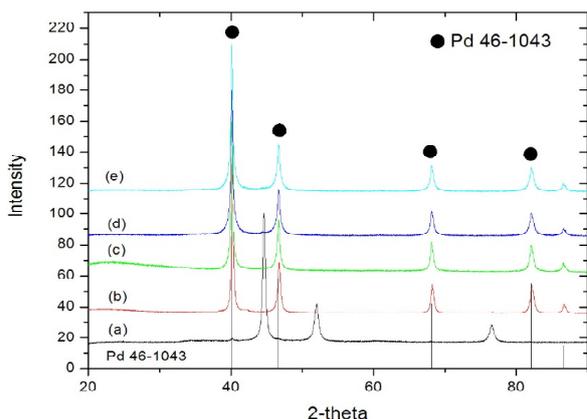


Fig. 1. XRD patterns of (a) Ni, (b) Pd, (c) Pd₇₅Ni₂₅ (3:1), (d) Pd₈₀Ni₂₀ (4:1), (e) Pd₈₃Ni₁₇ (5:1).

was heated at 170 °C for 1 hour. The catalyst powders were centrifuged, washed with ethanol and dried overnight in an oven. All the chemicals were of analytical grade. There were three methods employed to synthesize the Pd-Ni/NrGO catalysts. For the polyol process, the solution of PdCl₂, NiCl₂·6H₂O and NaOH in EG were partly prepared. The concentration of NaOH was twenty times over NiCl₂·6H₂O. For N-doped graphene, it was ultrasonicated in 25 ml of EG. After that, the solution mixed with N-doped graphene suspension was prepared. This was the mixture precursor for preparation of the catalysts. Then, the mixture was heated to 170 °C and continuously stirred. Finally, purification of catalysts, the mixture was washed by ethanol and centrifugation with deionized water for several times.

As for the NaBH₄ reduction method, it was realized as follows. First, N-doped graphene was added into EG at pH 9, which adjusted by adding potassium hydroxide. Then, stoichiometric amounts of metal precursors were added. After that, stoichiometric amount of NaBH₄ solution was added for a reduction process and the reaction was stirred for 1 hours. The final powders were centrifuged, washed with methanol and dried overnight in oven. For the microwave method, N-doped graphene was firstly

added into EG. Then, stoichiometric amounts of metal precursors were added. After that, the mixture was placed in a microwave oven. The reaction used microwave power at 1100 W. The reaction was conducted using microwave method, time to on microwave and off microwave was called 1 microwave cycle. The reaction used reduction time was on microwave for 50 second and off microwave 3 minutes repeated for 20 times. The received powders were centrifuged, washed with methanol and dried overnight in oven.

2.3. Material structure characterizations

The catalysts properties were characterized by using XRD (D500/D501, Siemen), SEM (JSM-5910LV, JEOL) EDS (INCA, The Microanalysis Suite Issue-16), TEM (JEM-2022FS, JEOL) and single cell testing (Department of Chemistry, Faculty of Science, Lampang Rajabhat University, Thailand) techniques.

Standard cell was prepared by using the commercial 20% Pt/C for both anode and cathode. The test cell was fabricated by using commercial catalysts for anode side and prepared catalyst for cathode side. Hydrogen gas was flowed to the anode side and oxygen gas at the cathode side. The gas pressure was 50 sccm for both sides. The single

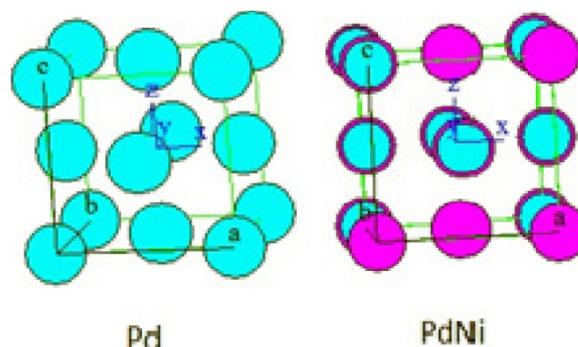


Fig. 2. Unit cell structure of Pd metal and Pd-Ni alloy.

Table 1. The relative intensities for planes of Pd-Ni alloys.

Sample	2-theta(111)	2-theta(200)	2-theta(220)
PdNi STD*	40.11(100)	46.65(60.0)	68.11(42.0)
Pd₇₅Ni₂₅ (3:1)	40.12(100)	46.67(36.6)	68.12(21.7)
Pd₈₀Ni₂₀ (4:1)	40.13(100)	46.67(36.5)	68.12(21.2)
Pd₈₃Ni₁₇ (5:1)	40.13(100)	46.68(35.47)	68.13(21.08)

Pd-Ni STD* simulated by CaRine3.1

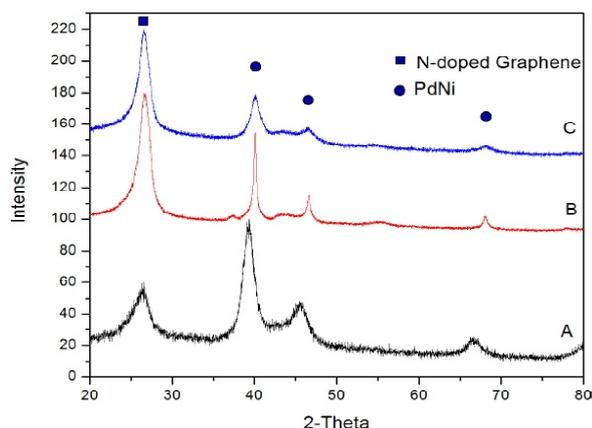


Fig. 3. XRD patterns of samples catalysts prepared by (A) Polyol method, (B) NaBH_4 reduction method, (C) Microwave method.

cell was operated at current density about 0 to 1.0 A at room temperature for four times.

3. RESULTS AND DISCUSSION

The prepared catalysts methods were coded in Table 1. The XRD patterns of Pd-Ni alloy with different Pd-Ni atomic ratios are shown in Fig. 1. The (a) and (b) patterns correspond to Ni and Pd, respectively. For diffraction patterns of (c), (d) and (e), the diffraction peaks at 2-theta about 40° , 46° , 68° , and 82° attributed to (111), (200), (220) and (311) planes of Pd (JCPDS no. 46-1043). It indicated that there is the alloy formation of Pd and Ni. Computer program (CaRine3.1) allows Pd-Ni alloy structure to be simulated based on Pd cubic structure; in which Pd and Ni atoms were randomly occupied all face centered cubic (fcc) coordinates. All the samples exhibit reflections characteristic of a fcc structure obtained from [15]. Fig. 2. shows simulated Pd-Ni alloy unit cell compared with Pd pristine structure.

Diffraction data was obtained, which calculated degree 2-theta and relative intensities for (111), (200), and (220) planes of Pd-Ni alloys with 5:1, 4:1, and 3:1 ratio was tabulated in Table 1 along with data from all experimental conditions. It was observed that 2-theta (degree) values from experiments approximate to Pd-Ni alloys in other ratios. The XRD patterns of Pd-Ni alloys catalyst were shown in Fig. 3. The catalysts were prepared by three methods (polyol method, NaBH_4 reduction method and microwave method) on N-doped graphene with weight ratio (3:1). The results of catalysts were separated into three method. The XRD patterns of catalysts, which synthesized by three methods at ratio of 3:1 contained peaks at about 40° , 47° , and 68° . These peaks corresponded to (111), (200) and (220) dif-

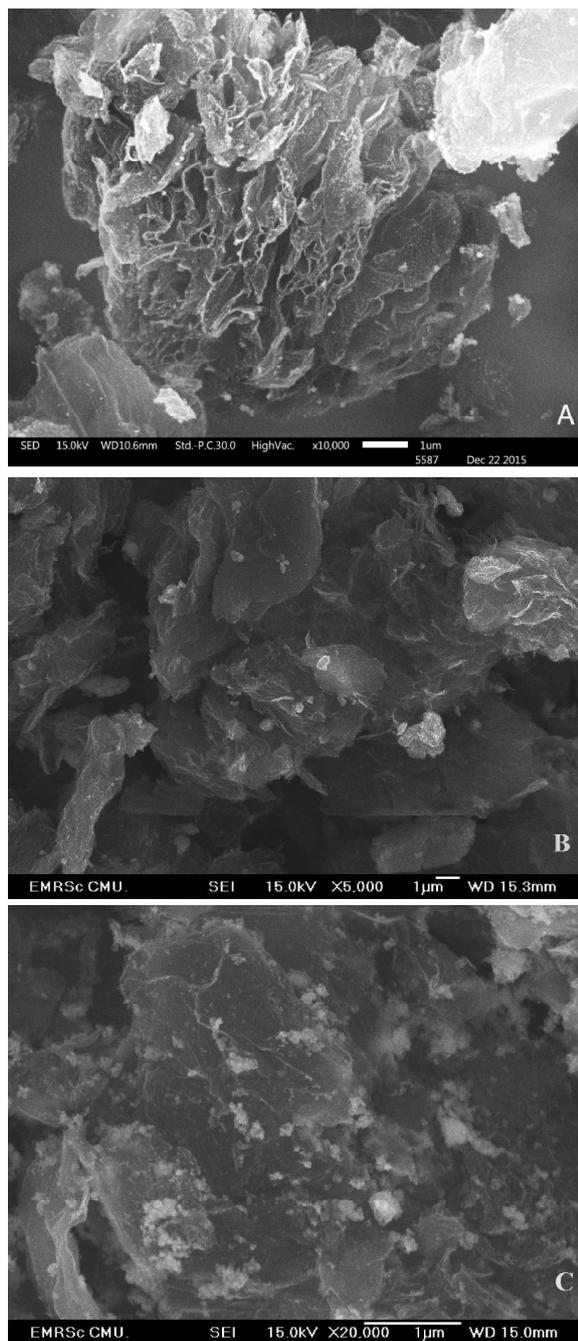


Fig. 4. SEM images of samples catalysts prepared by (A) Polyol method, (B) NaBH_4 reduction method, (C) Microwave method.

fraction plane of palladium. Referring to the simulated XRD patterns of fcc Pd-Ni phase, all of diffraction peaks can be indexed to fcc structure, refer to the simulated XRD of fcc Pd-Ni phase. In case of Pd-Ni can be indexed as mixed phases of fcc Pd and Ni. Previously, there are no standard XRD pattern of Pd-Ni alloy in JCPDS data base. For this reason, the XRD pattern simulation by CaRine3.1 is necessary to confirm the phase of Pd-Ni alloy in this experiment. The simulated structure (base on

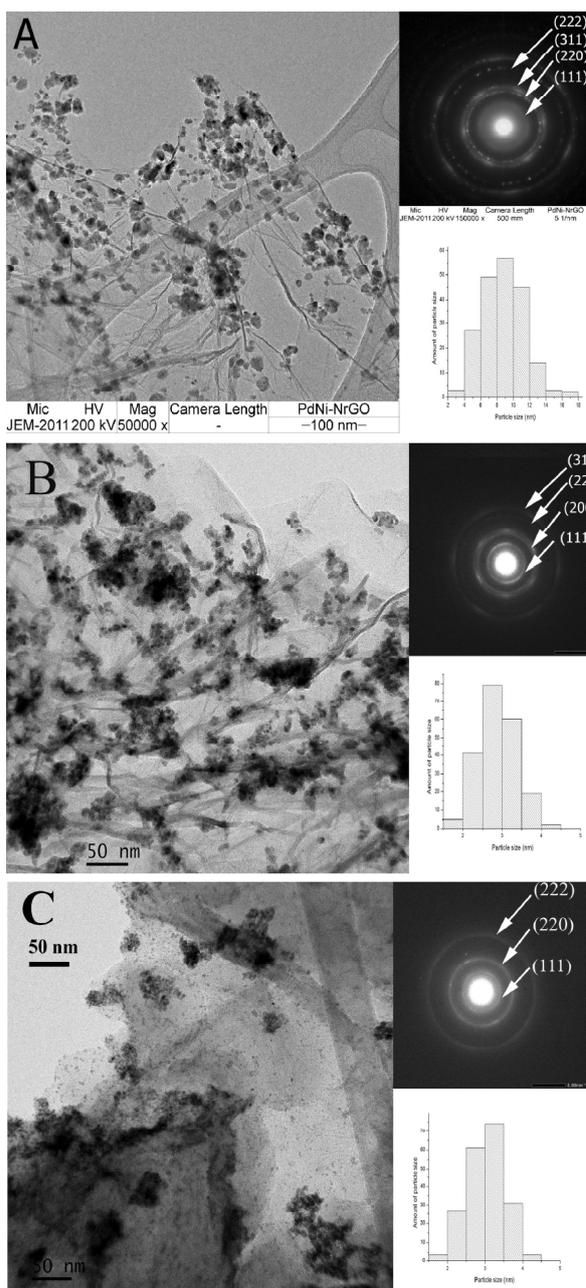


Fig. 5. TEM images of samples catalysts prepared by (A) Polyol method, (B) NaBH_4 reduction method, (C) Microwave method.

Table 2. Average particle size of all catalysts prepared from all methods.

Preparation method	Particle size (nm)
Polyol method	7.26 ± 0.61
NaBH_4 reduction method	2.86 ± 0.47
Microwave method	3.03 ± 0.52

the cubic Pd structure (JCPDs No. 46-1-43, space group $\text{Fm}\bar{3}\text{m}$) of Pd-Ni was showed in Fig. 2. Therefore, the diffraction patterns of Pd-Ni catalyst on NrGO in Fig. 3 contained the information of Pd-Ni alloy and NrGO.

SEM images (Fig. 4) display the overall morphology of the prepared catalysts Pd-Ni alloy particles dispersed thoroughly on NrGO. Among these products, the polyol method provided the better dispersion of Pd-Ni particles than the other methods.

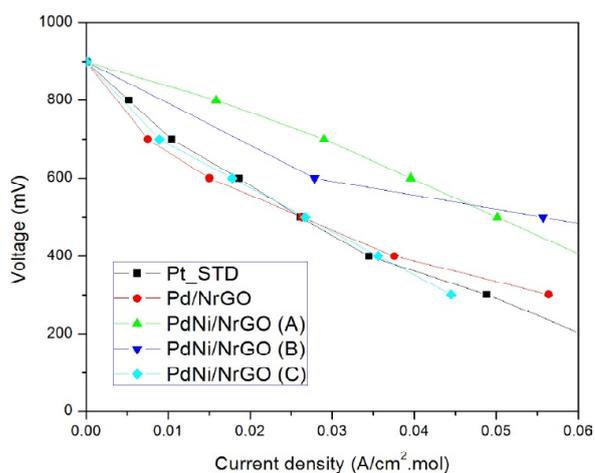


Fig. 6. Polarization curves of samples catalysts prepared by (A) Polyol method, (B) NaBH_4 reduction method, (C) Microwave method compared with standard Pt catalyst.

Table 3. Current density of catalysts at 600 mV and the content of Pd-Ni and NrGO calculated from XRD patents.

Preparation method	Current density ($\text{A}/\text{cm}^2 \cdot \text{mol}$)	Pd-Ni content (wt.%)	NrGO content (wt.%)
Pt/C (Fuel Cell)	0.017	-	-
Polyol method	0.039	28.17	71.83
NaBH_4 reduction method	0.027	14.26	85.74
Microwave method	0.018	9.02	90.98

The TEM images of catalyst on N-doped graphene for polyol method, NaBH₄ reduction method and microwave method were shown in Fig. 5. It was found that the catalysts were synthesized by the polyol method nanoparticles with a good dispersion on N-doped graphene surface more than the catalysts were synthesized by NaBH₄ reduction method and microwave method. TEM images taken from each sample were presented in Fig. 5. The selected area electron diffraction (SEAD) patterns in the insets of all images corresponded to Pd-Ni. Size of the particles was measured and the average values were presented in Table 2. The particle size histograms were shown in Fig. 5. The results showed that particle size of catalysts prepared by NaBH₄ reduction method was smaller than the catalyst particles prepared by polyol methods and microwave method. There was no significant difference in particles size among three samples. This result was confirmed by the Energy dispersive Spectrometry (EDS) analysis that Pd and Ni were detected.

Samples prepared from different types of methods showed no differences in chemical and physical properties as examined by XRD, SEM, and TEM techniques. Single cell testing then was applied to identify their electrochemical property compared with standard cell. Polarization curves obtained from standard and samples cells were shown in Fig. 6 indicating the better performance of sample catalysts over standard cell. Table 3 showed the current density and the content Pd-Ni and NrGO of all products. The content of Pd-Ni was calculated from volume fraction calculation of XRD. At the voltage of 600 mV, the catalyst prepared by polyol method provide the highest current density than the others due to it contained the highest content of Pd-Ni. Interestingly, at the lower voltage, the current of catalyst from NaBH₄ reduction method decreased slower than that of catalyst from polyol method. This could be implied that the NaBH₄ reduction method might provide high current density catalyst when the cata-

lyst from NaBH₄ reduction method would exhibit higher current density when it had higher content of Pd-Ni.

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