Effects of carbon supporter on oxygen reduction reaction catalytic activity in proton exchange membrane fuel cell of bimetallic Pt-Ni nanoparticles electrocatalysts

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Abstract. Platinum nanoparticles supported on carbon black (Pt/C) are widely used as the electrocatalysts for oxygen reduction reaction (ORR) in proton exchange membrane fuel cells (PEMFCs). Nevertheless, the kinetics of the ORR or rate of reaction is relatively slow. Recently, researchers theoretically report that, the bimetallic platinum-nickel supported on carbon black (Pt-Ni/C) have extremely high ORR activities. Therefore, this work aims to synthesize Pt-Ni/C nanoparticles electrocatalysts for ORR via solid-state chemistry method (gas phase synthesis), which involved impregnation of metal precursors on supported carbon and reducing them in an environment of carbon monoxide (CO) and hydrogen (H₂) gases mixture. The Pt-Ni nanoparticles were prepared with different carbon (i.e. Graphene, Vulcan XC-72R and Ketjen black). The ORR activities and durability of these electrocatalysts were examined by voltammetry technique, which consisted of cyclic voltammetry (CV) and linear sweep voltammetry (LSV) under acidic condition. The results demonstrated that different types of carbon supporter could affect the ORR catalytic activities. Pt-Ni nanoparticles supported on ketjen black (Pt-Ni/K) had the highest ORR activities for both specific activity (SA) and mass activity (MA). Furthermore, after 4,000 voltage cycles of the accelerated durability test (ADT), the Pt-Ni /Ketjen black still showed better ORR stability than Pt-Ni/Vulcan XC-72R and Pt-Ni/Graphene, respectively.

Keywords: Pt-Ni/C catalysts, Solid-state chemistry, Oxygen reduction reaction, PEM fuel cell

1. Introduction

Fuel cells are expected to become an alternative technology for generating electricity in the future because high-energy efficiency and low emissions. Fuel cells are a device that generates electricity by an electro-chemical reaction of Hydrogen (H₂) and Oxygen (O₂). Byproducts from the reaction are water (H₂O) and heat without pollutant emissions. Therefore, fuel cells are a technology of clean energy. There are several types of fuel cells but “Proton Exchange Membrane fuel cells (PEMFCs)” is the most popular type and will be used for the next generation of electric vehicles (EVs) in the near future [1]. PEMFCs have been widely educated in recent years [2]–[5]. The membrane electrode assembly (MEA) is the essential component, which generates electricity through electrochemical processes. At the anode of
MEAs, hydrogen oxidation reaction (HOR) will occur while oxygen reduction reaction (ORR) occur at the cathode. The MEA must have the catalysts on both sides of the membrane, which is particularly important to facilitate the electrochemical reaction [2], [3], [6]. Platinum (Pt) nanoparticles have been extensively used as the catalysts for PEMFCs because of their high activity for the ORR [4], [5], [7]. However, Platinum is a high cost and limited resource. In addition, the kinetics of the ORR or rate of reaction is relatively slow so it is essential to improve the Pt activity particularly for using as cathode catalysts [8], [9]. Many previous researches efforts have focused on decreasing Pt loading by added transition metal such as Ni, Co, Fe, etc. to Pt as a Pt-M bimetallic catalysts. Recently, researchers theoretically report that, the bimetallic platinum-nickel supported on carbon black (Pt-Ni/C) which synthesized by solvothermal method [8], [10]–[12] and solid-state chemistry method [13]–[15] have extremely high ORR activities. However, among several types of carbon black, just only Vulcan XC-72R have commonly used as a carbon supporter for Pt-Ni nanoparticles electrocatalyst. Therefore, this work aims to synthesize Pt-Ni/C nanoparticles electrocatalysts with different carbon supporters i.e. Graphene, Vulcan XC-72R and Ketjen black for used as a cathode catalyst for PEMFCs. Effects of different carbon supporters on electrochemical properties i.e. electrochemical surface area (ECSA), ORR catalytic activity and ORR stability were studied by voltammetry technique.

2. Experimental

2.1. Preliminary testing
The bimetallic Pt-Ni/C were synthesized with different synthesis methods include solvothermal method and solid-state chemistry method, which are liquid phase and gas phase synthesis, respectively. The solvothermal technique is a normal synthesis of Pt-Ni/C catalyst which involved simultaneous reduction of Pt and Ni precursors in liquid phase with reducing agent. The Pt(acac)2 (48.0% of Pt, Alfa Aesar), Ni(acac)2 (95%, Sigma-Aldrich), carbon black i.e. Vulcan XC-72R (Cabot) and benzoic acid (C6H5COOH, 95%, Sigma-Aldrich) were dispersed in dimethylformamide (DMF, (CH3)2NCOH, 99.8%, RCI Labscan) with using Teflon-lined stainless-steel autoclave, and then, the autoclave was heated to 150°C and maintaining at this temperature for 12 hours. After that, prepare the Pt-Ni nanoparticles without carbon supporter with same synthesis procedure. From preliminary testing, it was found that the nanoparticles of prepared Pt-Ni/C and Pt-Ni without carbon supporter were not well dispersed (see results and discussion section). So, in this work, the Pt-Ni/C electrocatalysts will be synthesized via solid-state chemistry method.

2.2. Synthesis of bimetallic Pt-Ni nanoparticles supported on carbon black
The Pt-Ni/C were synthesized with varying carbon supports i.e. Graphene (Cheap Tubes), Vulcan XC-72R (Cabot) and Ketjen black (Cabot) via solid-state chemistry method (gas phase synthesis), which involved wet impregnation of metal precursor on supported carbon and reduction of the dried mixture. The platinum (II) acetylacetonate (Pt(acac)2, 48.0% of Pt, Alfa Aesar) and nickel (II) acetylacetonate (Ni(acac)2, 95%, Sigma-Aldrich) were used as a metal precursors and acetone (C3H6O, 99.5%, RCI Labscan) was a solvent. First, Pt(acac)2 and Ni(acac)2 were dissolved in acetone. Carbon was added into Pt and Ni precursors solution in bottle with cap in order to mix them by shaking for 1 hour, and then, acetone was evaporated from the mixture. The dried mixture was reduced in an environment of carbon monoxide (CO, 99.9%, Labgaz) and hydrogen (H2, 99.9%, Linde) gases in CO:H2 ratio of 90:30 by volume at temperature 200°C for 1 hour.

2.3. Physical characterization
The metal loadings of Pt and Ni were evaluated by inductively coupled plasma-atomic emission spectrometry (ICP-OES), when metal precursors solution were taken out before and after wet impregnation process. The dispersion and morphologies of prepared nanoparticles were observed by transmission electron microscopy (TEM) and the crystalline structure was characterized using X-ray diffraction analysis (XRD).
2.4. Electrochemical measurement

The ORR activities and durability of Pt-Ni/C electrocatalysts were examined by voltammetry technique which using a bi-potentiostat (Pine Instrument Co.) with a standard three-electrode system. A platinum wire, Ag/AgCl in 3M KCl solution and glassy carbon rotating disk electrode (GC-RDE) were applied as a counter electrode, reference electrode and working electrode, respectively. In term of catalyst ink preparation for GC-RDE surface coating, 10 mg of synthesized Pt-Ni/C electrocatalysts were mixed in 5ml of stock nafion solution, which was prepared by mixing 79.6 ml of deionized water (RCI Labscan) with 20 ml of isopropanol (RCI Labscan) and 0.4 ml of 5wt% nafion solution (1000 EW, Dupont) [16]. This catalyst ink was sonicated to well-dispersed for 20 min. After that, the catalyst ink was coated to the GC-RDE surface (0.196 cm$^2$). Pt loading of catalyst on the GC-RDE surface were kept constant at 35 µg Pt cm$^{-2}$. The electrochemical surface areas (ECSA) of these Pt-Ni/C were measured using hydrogen under potential deposition (HUPD) method via cyclic voltammetry (CV) technique. Cyclic voltammetry was operated at a scan rate of 50 mV s$^{-1}$ in a He-saturated with 0.5M sulfuric acid (H$_2$SO$_4$, 96%, RCI Labscan) as the supporting electrolyte at room temperature. The ORR activities both specific activity (SA) and mass activity (MA) were measured from linear sweep voltammograms or ORR polarization curves via linear sweep voltammetry (LSV) technique at room temperature in an O$_2$-saturated with 0.5M H$_2$SO$_4$ electrolyte at a scan rate of 20 mV s$^{-1}$, where a GC-RDE rotation speed was 1600 rpm. The accelerated durability test (ADT) for examining the ORR stability of Pt-Ni/C was performed in an O$_2$-saturated 0.5M H$_2$SO$_4$electrolyte via cyclic voltammetry at a scan rate of 50 mV s$^{-1}$ between 0.4 and 1.2 V$_{SHE}$ (V versus standard hydrogen electrode). The cyclic voltammograms and ORR polarization curves were measured before and after 4000th voltage cycles.

3. Results and discussion

3.1. Bimetallic Pt-Ni nanoparticles on carbon supporters

From preliminary testing, the bimetallic Pt-Ni nanoparticles without carbon supporter and Pt-Ni/C were synthesized with different approaches named as solvothermal method (liquid phase synthesis) and solid-state chemistry method (gas phase synthesis). The preliminary results found that the nanoparticles of both Pt-Ni without supporter and Pt-Ni/C from solvothermal method did not disperse well, which the Pt-Ni nanoparticles were aggregated as shown in the TEM images figure 1(a) and (b). Furthermore, the Pt-Ni nanoparticles shown larger size when carbon was added as the support as shown in figure 1(b).

On the other hands, the Pt-Ni nanoparticles prepared by solid-state chemistry method (figure 1(c)) had better dispersion and the particle size were likely smaller than that from solvothermal technique (figure 1(b)). The particle size of catalysts could effect on catalytic activity, whereas the catalysts with smaller particles would have grater specific surface area. This infers to have the better reactive area [17], [18]. Consequently, the Pt-Ni/C was preferred to prepare via solid-state chemistry method.

![Figure 1](image1.png)

**Figure 1.** TEM images of Pt-Ni nanoparticles (a) Pt-Ni without C, (b) Pt-Ni/C that synthesized via solvothermal method and (c) Pt-Ni/C that synthesized via solid-state chemistry method.
The bimetallic Pt-Ni/C were prepared with different carbon supports i.e. Graphene, Vulcan XC-72R and Ketjen black. The Pt-Ni nanoparticles were well-dissipated on all of carbon supports with similar particles shape and size as shown in TEM images (figure 2(a) to (c)) and the mean particles size was approximately 3 nm as shown in figure 2(d).

**Figure 2.** TEM images of Pt-Ni/C nanoparticles that synthesized via solid-state method with different carbon supports (a) Pt-Ni/Graphene, (b) Pt-Ni/Vulcan XC-72R and (c) Pt-Ni/Ketjen black. (d) Particles size distribution (counted 1,000 particles).

The crystalline structure of Pt-Ni/C electrocatalysts was characterized by X-ray diffraction analysis. XRD patterns of the prepared Pt-Ni/C show that standard peaks are in accordance with many previous researches ([10]–[14], [19]) about bimetallic Pt-Ni catalysts. The diffraction peaks of Pt metal in all synthesized Pt-Ni/C have a significant shift toward the Ni metal pattern (figure 3) that suggests the creation of Pt-Ni alloy. The Pt and Ni compositions in mass basis for Pt-Ni/C catalysts are shown in table 1 which measured by ICP-OES analysis. The Pt mass loading was approximately from 17.62%wt. to 18.04%wt, where Ni mass loading was about 1.48%wt. to 1.74%wt. for all carbons.

**Figure 3.** XRD patterns of Pt-Ni/C that synthesized via solid-state chemistry method.

**Table 1.** Specifics surface area of carbon supports and metals loading in synthesized Pt-Ni/C.

| Catalysts             | Specifics surface area of carbon supports (m² g⁻¹) | Metals loading (wt.%):          |
|-----------------------|-----------------------------------------------------|---------------------------------|
|                       |                                                     | Pt     | Ni     |
| Pt-Ni /Graphene       | 887.37                                              | 18.04  | 1.52   |
| Pt-Ni /Vulcan XC-72R  | 259.08                                              | 17.95  | 1.74   |
| Pt-Ni /Ketjen black   | 1499.11                                             | 17.62  | 1.48   |
3.2. Electrochemical activities of synthesized Pt-Ni/C

The ORR activities and durability of Pt-Ni/C electrocatalysts were examined by voltammetry technique. The electrochemical surface areas (ECSA) of Pt-Ni/C electrocatalysts were measured using hydrogen under potential deposition (HUPD) method via cyclic voltammetry (CV) technique, cyclic voltammograms as shown in figure 4(a).

From the results in figure 4(a), it is found that, the current response from hydrogen desorption presents in the potential range between 0.05 and 0.35 V SHE. The ECSAs were calculated by integrating hydrogen desorption area. According to the calculation of ECSAs in figure 4(b), the Pt-Ni/Ketjen black showed an outstanding ECSA of 60.13 m² gPt⁻¹, while the Pt-Ni/Graphene and Pt-Ni/Vulcan XC-72R had ECSA of 25.25 and 10.97 m² gPt⁻¹, respectively. The ECSAs indicated the significant information about the number of available active sites in the electrocatalysts. This means that higher ECSAs lead to have more electrochemical active sites [8]. Moreover, it is found that the specific surface area of supporter is related to the ECSA in catalysts. The Ketjen black had a highest specific surface area of 1499.11 m² g⁻¹ (table 1) following by graphene (887.37 m² g⁻¹) and Vulcan XC-72R (259.08 m² g⁻¹), respectively. An analogously, the ECSA showed that Ketjen black had a highest electrochemical active area followed by graphene and Vulcan XC-72R, respectively.

The ORR activities of synthesized Pt-Ni/C were measured from ORR polarization curves via linear sweep voltammetry (LSV) technique. Figure 5(a) illustrates the 1st cycle linear sweep voltammograms of three Pt-Ni/C catalysts, while the specific activity (SA) and mass activity (MA) of ORR were calculated from current that measured at 0.9 V SHE. For the 1st cycle (fresh catalysts), the Pt-Ni/Ketjen black had a highest both SA and MA of 572.5 μA cm⁻² and 344.3 A gPt⁻¹, respectively, as shown in figure 5(b) and (c). The SA of Pt-Ni /Ketjen black (572.5 μA cm⁻²) which was 1.3 folds higher than Pt-Ni/Graphene (448.7 μA cm⁻²) and 3.9 folds higher than Pt-Ni/Vulcan XC-72R (147.7 μA cm⁻²) as presented in figure 5(b). The MA of Pt-Ni /Ketjen black (344.3 A gPt⁻¹) which was 3.0 times higher than Pt-Ni /Graphene (113.3 A gPt⁻¹) and 21.3 times higher than Pt-Ni /Vulcan XC-72R (16.2 A gPt⁻¹) as
shown in figure 5(c). Since Ketjen black had a highest electrochemical active surface, these could be directly influenced on ORR catalytic activities [20], [21]. Hence, Pt-Ni /Ketjen black yields the remarkable ORR activities both SA and MA more than Pt-Ni /Graphene and Pt-Ni /Vulcan XC-72R. Furthermore, the ORR stability of synthesized Pt-Ni/C were examined by the accelerated durability test (ADT) which performed via cyclic voltammetry between 0.4 and 1.2 V 

\[ \text{SHE} \] in saturated O



After that, ORR polarization curves were measured after 4000th voltage cycles and calculate ORR activities. After 4000th cycles of ADT, the SA and MA of ORR were calculated and indicated in a similar trend with before ADT. The Pt-Ni /Ketjen black still had a highest both SA of 481.5 \( \mu \text{A cm}^{-2} \) and MA of 289.5 A g\text{Pt}\(^{-1}\). These values decreased around 15.9% from the 1st cycle. Moreover, the SA and MA after ADT of Pt-Ni /Graphene (319.9 \( \mu \text{A cm}^{-2} \) and 80.8 A g\text{Pt}\(^{-1}\), respectively) decreased 28.7% from the 1st cycle. The Pt-Ni /Vulcan XC-72R had the SA and MA about 110.8 \( \mu \text{A cm}^{-2} \) and 12.2 A g\text{Pt}\(^{-1}\), which lower than 1st cycle activities around 25.0%. It is noted that the degradation of nanoparticles catalyst from Ketjen black was lowest after ADT.

From these results, the Pt-Ni supported on Ketjen black have the effective catalytic activity and stability for oxygen reduction reaction or ORR, in which occurs at the cathode side of PEMFCs. So, the Pt-Ni/Ketjen black could be applied as effective cathode electrocatalysts for PEM fuel cells. Consequently, this work technically shows that Pt-Ni bimetallic electrocatalysts prepared via the same method yielded different electro-active surface area. It is found that the specific surface area of carbon supporter had direct influence. This is probably due to the high specific surface area of supports making better Pt-Ni dispersion resulting to well expose of Pt-Ni active site. Moreover, this work proves that the durability of catalysts in oxygen reduction reaction depended primarily on specific surface area of supported carbon, also.

4. Conclusion

The bimetallic platinum-nickel supported on carbon black (Pt-Ni/C) were synthesized with different carbon supports i.e. Graphene, Vulcan XC-72R and Ketjen black via solid-state chemistry method. The results indicated that different types of carbon supporters could affect the electrochemical properties of catalysts i.e. ECSA, ORR catalytic activities (SA and MA) and ORR stability. The Pt-Ni/Ketjen black had a highest ECSA. SA and MA as a result of specifics surface area of Ketjen black. Moreover, the accelerated durability test (ADT) of these catalysts demonstrated that, Pt-Ni /Ketjen black still showed better ORR stability than Pt-Ni/Vulcan XC-72R and Pt-Ni/Graphene, respectively.

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