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# The Effect of NaOH in The Formation PtNi/C Nanocatalyst for Cathode of PEMFC

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**Abstract:** PtNi/C alloy nanocatalysts were successfully synthesized by refluxing a polyol solution with platinum (Pt) and nickel (Ni) salt with different NaOH volumes. The strategy of the enhancement of cathode performance in Proton Exchange Membrane Fuel Cell (PEMFC) is the use of custom nanocatalysts that could improve the macroscopic kinetics rate of the Oxygen Reduction Reaction (ORR). In this study, development of polyol reduction method of depositioning simultaneously Pt and Ni in carbon surface while hindering the agglomerations of alloy particles was carried out. The prepared catalyst was characterized by X-Ray Diffraction (XRD), Energy Dispersive X-ray (EDX) analysis and selective chemisorptions. The results show that the diffraction pattern of crystallites changes when the content of NaOH varies. XRD patterns show disorder structure of face cubic centre (fcc) with particle size around 5 nm. From EDS analyses, PtNi compositions on carbon from the sample are around 29% and hydrogen adsorption on Pt atom that is showed on the nanocatalyst surface is approximately also 29%. Activity of the carbon-supported PtNi catalyst for oxygen reduction reaction was tested by Cyclic Voltammetry (CV) at 900 mV vs. RHE in 1M $HClO_4$. The resulted ESA is around 37 $cm^2/mgPt$ and specific activity (SA) is 99 $\mu A\ cm^{-2}$. The result shows that PtNi/C of NaOH 5 mL sample provides SA that is three times as high in comparison to commercial Pt/C catalyst.

**Key words:** PEM fuel cell, cathode catalyst, Pt-alloy nanoparticle, polyol process

## INTRODUCTION

Fuel cell is an electrochemical device that directly converts chemical energy stored in the fuel to electrical energy without taking the loop of heat production, which is a highly efficient electrochemical power generation. The fuel (hydrogen; methanol; natural gas) is electrochemically oxidized water (Larminie and Dicks, 2000). However, there are some problems in the utilization of the electrocatalysts that can improve Oxygen Reduction Reaction (ORR) rates in the PEMFC cathodes, because of its complex kinetics and the need for better electro catalysts, for enhancing PEMFC performances.

The carbon supported platinum (Pt/C) is an electro catalyst that is still commercially used, although not only that is it easily eroded, but it is also expensive and has a limited availability. The investigation of alternative electro catalyst for reducing Pt loading is the focus of PEMFC researchers around the world. The metal alloy electro catalyst especially the alloy of Pt with 3d-transition metals is potential to be used as ORR (Stamenkovic et al., 2007; Chen et al., 2010). Beside the fact that it is cheaper and more durable, the Pt based transition metal alloys have the best prospect for use as a cathode catalyst and will

improve catalytic activity and voltage output. The cathode side ideally requires mainly the four electrons to break O-O strong bond quickly, forms water while avoiding Pt-OH production (Lyons et al., 2006; Zhang et al., 2005; Mitchell, 1963).

The electronic theory that supports the use of alloy for catalyst has been promoted since the 1990s, but it had only been developed in the 1990s due to the industrial need to push the technology of reformer. In bimetallic alloy electrocatalysts, atoms are not individually free, but form a combination of individual atoms. The bulk of the nanostructure for the ORR is closely related with particle sizes, crystallite structures and atomic arrangements in the surface.

Greeley et al. (2007) studied the modeling of ORR rate as a function of particle size with different crystal facets of various metals. Particle size effect, which is linked to the structure sensitivity of the ORR, can lead to significant changes in catalytic activity as a function of particle size. Geometric concept of atomic position will influence the characters of the catalyst adsorption. The surface composition of alloy will determine the surface energy that is caused by electronic effect (a vacancy in orbital 5d) including geometric effect (ensemble) and

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ligand effect. The interaction between particle size, electronic and morphological properties is not fully uncovered yet, so it needs more specific research to investigate catalytic activity.

A polyol process that has been used to prepare bimetallic nanoparticles on the size control mechanism with ethylene glycol (EG) as the reaction media, has been successfully prepared for the Ru nanoparticle via conventional refluxing (Yan *et al.*, 2001; Song *et al.*, 2007). Oh *et al.*, 2007), synthesized Pt/C nano particle sized 3 nm in pH around 11 by adding NaOH. The particle dimensions and alloy quality vary against prepared conditions.

In this present study, a polyol process with reduction agent of ethylene glycol additional different NaOH volumes is utilized to produce carbon-supported PtNi. The process and reaction condition were developed to obtain the crystalline structure of pure PtNi metal alloys. The objective of this study is to understand the relationship between particle size, crystalline quality, Pt loading and specific activity in the PEMFC cathode. Hence, this study is being approached toward interrelationships between the surface metal ability to provide sites for adsorption of $O_2$ and the macroscopic activity of the ORR. N.R., W.P.W., M.N., L.H., developed the concept and designed research experiments. N.R., M.N. and W.P.W. developed the polyol method and the electrochemical interpretation. N.R. and M.N. developed and performed the Chemisorptions Test of PtNi surface. N.R. and L.H. discussed the nanoparticle surface.

## MATERIALS AND METHODS

**Research experiment:** In the scheme below, the synthesis of PtNi nanosize particle will be described. Structural characterization of the carbon supported PtNi (PtNi/C) was performed by X-Ray Diffraction (XRD).

The element compositions were measured by using Energy Dispersive X-Ray analysis (SEM-EDX/LEO420), the adsorbed hydrogen by Pt was carried out by using Chemisorption Test (CT). The PtNi/C catalyst synthesis
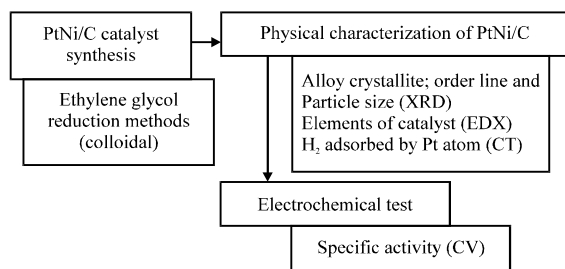


Scheme 1: Flow diagram of research experiment

and chemisorption test were conducted at Department of Chemical Engineering, University of Indonesia. The electro catalytic activity (Specific activity/SA) of the catalysts was measured by Cyclic Voltametry (CV).

**Materials and Preparation Method of PtNi/C nanocatalyst samples:** The used materials as precursors in the experimental research were: Hexachloroplatinic acid $(H_2PtCl_6)$ from Aldrich and Nickel Chloride $(NiCl_2. 6H_2O)$ from Merck. Activated Carbon Vulcan XC72R from Cabot was utilized as carbon support. The other chemical materials were Sodium Hydroxide (NaOH) from Merck and 95 vol. % Ethylene Glycol (EG) aqueous solution from Merck. For reference, the Pt/C commercial electrocatalyst used was from E-TEK's product. The PtNi nanocatalyst is generally obtained from complex salt of $H_2PtCl_6$ and $NiCl_2$. $6H_2O$ with carbon Vulcan XC72R as a supporting media.

The PtNi/C samples are prepared by polyol method with EG as reduction agent. One gram Vulcan XC72R was added to 100 mL EG and the solution were stirred. The $H_2PtCl_6$ solution in 10 mL EG and the $NiCl_2. 6H_2O$ solution in 10 mL EG were mixed well and added to Vulcan XC72R solution in ethylene glycol under constant stirring process in $N_2$ environment. 2.5 M NaOH was added to the resultant solution to adjust the pH of the solution. NaOH's variations were as follows; 1 mL NaOH as NaOH 1 mL sample, 5 mL NaOH as NaOH 5 mL sample, 10 mL NaOH as NaOH 10 mL sample and 25 mL NaOH as NaOH 25 mL sample. They are identical with pH 7, 10, 12 and 13.

The resultant solution was then refluxed by water at 190°C for 2 h. The system was cooled to room temperature, the obtained products were washed with distilled water and was filtered under vacuum. Finally, the solid residu was dried at 80°C overnight to yield PtNi/C powder. PtNi/C alloy has metal loading of 30 wt% and atomic ratio of Pt:Ni = 1:1.

**Characterization:** The prepared PtNi/C Nanocatalyst powder was characterized by XRD to determine the crystalline structure and particle size. The XRD was performed using Phillips PW1710 instrumentation at National Nuclear Energy Agency. The diffraction angles $2\theta$ (2 theta) were selected from 35 to 80° with scan step of 0.02°. The size of PtNi/C catalysts can be calculated using the Scherer's formula, based on PtNi (111) peak. The Scherer's formula is based on the width of XRD peak patterns. Large particles might contain several crystallites. However, it is common that the nanometer-sized particles contain only one crystallite. Smaller crystallite size produces wider diffraction peak due to a restricted number of reflection planes. The accuracy of this method is around 5 nm.

The CV measurement uses an Ag/AgCl electrode as the reference electrode and a platinum wire for the counter electrode. It was performed using Potensiostat eDAQ instrumentation. The electrolyte used is 1M $HClO_4$ solution (which is a weak anion adsorption acid and can be used to evaluate the mass activity). The scan rate is 50 mV $sec^{-2}$ and the ORR test is started after the oxygen bubbling for 20 min. The scan range is from 1.2V to -0.2 (Ag/AgCl). The ORR tests can be used to evaluate the catalytic activity i.e., Specific Activity (SA), the current per unit surface area of catalyst. The SA provides a measure of the electrocatalytic activity of platinum atoms over the particle surface, which can be obtained through Eq. 1 below:

$$SA = i_{0.9V} / w . ESA \qquad (1)$$

Where:
SA : Specific activity (mA $cm^{-2}$)
$i_{0.9V}$ : Current at the potential of 0.9V (μA)
w : Pt catalyst weight (mg)
ESA : Electrochemical surface area ($cm^2 mg^{-1}$)

## RESULTS

**The XRD characterization:** The XRD data obtained from the experiment shows alloy formation for PtNi nanoparticle (Fig. 1). The diffraction pattern shows that the peaks of Pt/C located at 2Θ of: 39,7°; 46,3° and 68°, those of which are corresponding to (111); (200) and (220) crystal plane, respectively (Table 1). The diffraction peaks of the NaOH 5 mL and NaOH 10 mL samples shift to higher angles as compared to that of Pt/C, indicating a lattice contraction arising from the substitution of the smaller Ni atoms to the larger Pt atoms. The XRD peaks are constrained to the face centered cubic (fcc) crystal system (Mitchell, 1963; Ross, 2008).

From the data in Table 1, the lattice parameter shows that the average Pt-Pt distance decreases when Ni atom gets in; it reflects the alloy characteristics. The NaOH 5 mL, NaOH 10 mL and Pt/C samples do not have additional peaks.

Since, the shoulder around 2Θ = 68° does not appear in the XRD results, the NaOH 5 mL and NaOH 10 mL sample have a disordered phase of face-centered cubic structure in which the Pt and Ni atoms are randomly distributed. This clearly indicates that the PtNi/C nanocrystalline is successfully prepared by ethylene glycol reduction method. The NaOH 5 mL sample is more ordered than that of the NaOH 10 mL crystalline, as shown by absence shoulder around 2Θ = 50.4°.

**The EDX characterization:** The element compositions were measured with EDX of which the comparison as shown in Table 2. The increasing pH of the solution decreases consequently with Pt loading. The data of NaOH 5 mL sample shows that the metal alloy loading is around 29% and the metal alloy has 23% Pt atoms.

**The chemisorption test:** Selective chemisorptions with hydrogen were utilized to determine specific area of the exposed platinum area as dispersion in carbon supported PtNi alloy catalyst. Following Richardson (1989), adsorption hydrogen in platinum exposed on the nanostructure surface can give monolayer coverage quickly. The surface area occupied was achieved by measuring the uptake of chemisorbed gas. The dispersion was calculated through Eq. 2 below:

$$D = \Sigma \ dn. \ Mr/ \ w. \ L \qquad (2)$$

Where:
D : Dispersion of Pt
Σdn : Adsorbed hydrogen concentration
Mr : Fraction of Pt atom mass
w : Catalyst weight
L : Pt loading

## DISCUSSION

**pH effect on formation and particles size of PtNi/C catalysts:** Figure 1 shows that NaOH 1 mL crystallite clusters do not display diffraction peak due to un-sufficient basic environment. The Adding of NaOH influences XRD pattern of the synthesized electrocatalysts. When NaOH was added to the solution from 1 to 5 mL, the pH changed from 7 to 10. XRD peak increased at 43.2° (111 crystal plane) and at 50.4° (200 crystal plane) caused by the formation of nucleation and was followed by a growth. At the time with the addition of NaOH up to 10 mL, the pH is change to become 12, then (200) crystal plane disappeared. At the time when NaOH increase from 10 mL to 25 mL, all of crystal plane was disappeared, as a consequence of the imperfect reduction condition. This phenomena was confirmed by Pourbaix (1974), that the Ni element has the domains of corrosion at pH higher that is than 12. The high loading Pt/C with a mean particle size of about 2.7 nm was successfully formed by Song *et al.* (2007) through pulse-microwave assisted polyol synthesis.

Particle size of NaOH 5 mL sample is 5.71 nm and NaOH 10 mL sample is 5.49 nm. Both have similar size with the size of commercial Pt/C nanoparticle (5.89 nm) and the result is shown in Fig. 2.
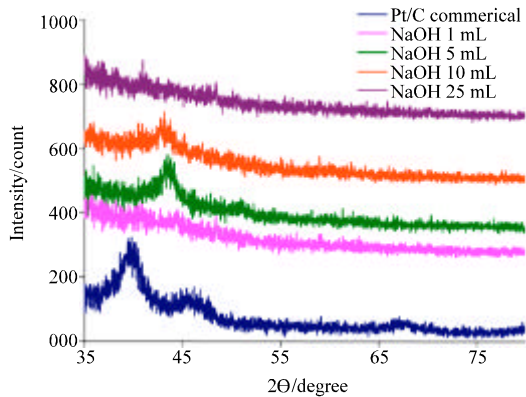
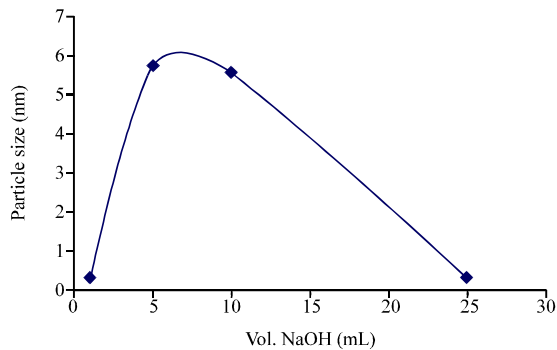Fig. 1: Variation of pH (NaOH content) effect in crystal structure electrocatalyst PtNi/C



Fig. 2: Dependence pH on particles size of prepared PtNi/C catalysts

As shown in Fig. 2, the major change in the improvement of particle size was observed within the pH range of 7-10. It was expected that at pH around 7, the glycolate anion concentration was low and then the formation of nucleation did not follow the growth step. A constant particle size occurred at the pH range of 10-12 and the nucleation and growth step were well developed. The particle size of metal in solution depended on pH as a function of glycolate anion concentration as elucidated by Oh *et al.* (2007) that glycolate anion concentration saturated at pH higher than 6. This condition supports the production of pure PtNi nano-metal alloy made at the pH range of 10-12. At pH around 13, the particle size was not detected, probably because the nucleation did not grow.

**Pt loading on carbon:** There are two interesting steps in this work, the first is the production of PtNi alloy and the second its is placement on the carbon surface. The presence of NaOH in the solution was able to control the particle size and the Pt loading. The carbon supported PtNi of NaOH 5 mL sample was measured to 29 wt%, indicating that the salt was reduced and loaded on carbon

Table 1: Plane spacing ($d_{hkl}$) and lattice parameter (a)

| Name of catalysts | Crystal parameter | | | |
|---|---|---|---|---|
| | $2\Theta$ | $d_{hkl}$ (°A) | a (°A) | Crystal plane |
| NaOH 10 mL | 43,2° | 2,10 | 3,64 | (111) |
| NaOH 5 mL | 43,2° | 2,10 | 3,64 | (111) |
| | 50,4° | 1,81 | | (200) |
| Commercial | 39,7° | 2,27 | 3,93 | (111) |
| Pt/C E-TEK | 46,3° | 1,96 | | (200) |
| | 68° | | | (220) |
| | 82° | | | (311) |

Table 2: Effect of NaOH volumes on resulting element compositions

| Name of catalysts | C : PtNi | Pt : Ni |
|---|---|---|
| NaOH 25 mL | 46 : 54 | 13 : 87 |
| NaOH 10 mL | 50 : 50 | 18 : 82 |
| NaOH 5 m L | 71 : 29 | 23 : 77 |
| NaOH 1 mL | 60 : 40 | 31 : 69 |

Table 3: Dispersion and $H_2$ adsorbtion of prepared PtNi/C and commercial Pt/C

| Name of catalysts | $H_2$ Chemisorbed (µmol/gram) | Dispersion (%) |
|---|---|---|
| NaOH 5 mL | 0.05049 | 15.2 |
| Commercial Pt/C E-TEK | 0.05384 | 52.5 |

completely due to adsorbsi or electrostatic force between metal alloy and carbon. As shown in Table 2, in the increasing pH range of 7-13 the PtNi alloy loading increases while the Pt loading decreases. From the EDX results, the Ni atom replaces Pt atom in the fcc structure, in relation to electron transfer mechanism. Referring the XRD data, when the Pt atoms are at the range of 23%, the PtNi has a cubic structure, in which Pt atoms occupy corner positions and the Ni atoms occupy the face centered positions. The PtNi system of the NaOH 5 mL sample exhibit a $PtNi_3$ type structures/$L1_2$ (Hultgren *et al.*, 1963). Further characterization like dispersion, electrochemical surface area and specific activity use NaOH 5 mL sample only.

**Hydrogen adsorption on Pt surface and catalytic activity of PtNi/C catalysts:** The chemisorbed hydrogen concentration by platinum surface was similar between NaOH 5 mL and commercial Pt/C catalyst (Table 3). This corresponds to adsorbed hydrogen per gram Pt's atoms. The dispersion from NaOH 5 mL is smaller than that of the commercial Pt/C E-TEK. It means that the surface of NaOH 5 mL sample which contains Pt element exposed was around of 29%, although particle size was not significantly different (5.71 nm for NaOH 5 mL and 5.89 nm for commercial Pt/C catalyst). Table 1 shows the lattice parameter of PtNi/C was reduced to 3.64° A, while the lattice parameter of commercial Pt/C is 3.93°. Somorjai (1994), has concluded that there was a connection between dispersion and number of atoms (particle size), i.e., for dispersion around 50% the number of atoms was around 1000.

Table 4: Comparison of electrochemical surface area (ESA) from prepared PtNi/C and commercial Pt/C

| Name of catalysts | ESA (cm$^2$/mg) |
|---|---|
| NaOH 5 mL | 36.56 |
| Commercial Pt/C E-TEK | 160.54 |

Table 5: Specific activity of prepared PtNi/C and commercial Pt/C

| Name of catalysts | SA ($\mu$A cm$^{-2}$) |
|---|---|
| NaOH 5 mL | 99 |
| Commercial Pt/C E-TEK | 30 |

Table 4, 5 and Fig. 4 show the comparison of voltametric behavior between the NaOH 5 mL and commercial Pt/C E-TEK sample. From hydrogen desorption peak areas in the CV curve and the Pt single crystalline activity surface area transition constant of $Q_m$ = 0.21 mC/cm$^2$Pt, the Electrochemical Surface Area (ESA) for these catalysts can be calculated. From Table 4, the NaOH 5 mL sample has Pt element exposed around 36.56 cm$^2$ mg$^{-1}$ Pt and has smaller ESA (around of 25%) than that of Pt/C commercial sample. When the transition metal is added, the surface area becomes smaller, because the platinum in the surface is replaced by nickel. The NaOH 5 mL sample surface contains Pt element exposed around 25%, which corresponds with the dispersion measurement or hydrogen adsorption. Therefore, the Pt atoms can be predicted of exposing particle surface around 25-29%.

From the crystal structure, composition and dispersion data the arrangement and composition of alloy elements on the particle surface can be predicted. The synthesized PtNi/C catalyst produce close-packed face cubic center microstructure forming cubo octahedral. Figure 3 shows the prediction of PtNi$_3$ surface construction. Radillo-Diaz *et al.* (2009) has investigated with the DFT framework that the structural and electronic properties of (PtNi$_3$)$_s$ with s = 4-6 are stable. For the (PtNi$_3$)$_s$ nanoalloys, the Pt atoms concentrate in the cluster core and the Ni atoms are segregated to the surface.

Takahashi *et al.* (2005) and Ross (2008) have studied the adsorption process in heterogeneous surface catalyst, where the surface properties have the different characters from cubo octahedral bulk. The experiment with CV measurement shows that the activity results are concerned with the formation Pt-OH effect. Inhibition of the formation of Pt-OH at potentials around 900 mV vs. RHE on Pt alloys, resulting in greater number of available Pt sites for dissociative adsorption of molecular oxygen has been shown by Stamenkovic *et al.* (2007) and Ross (2008). Attention will be focused on the region where the potential exceeds 0.9V vs RHE, is resulted in SA as can be in Fig. 4 and Table 5.
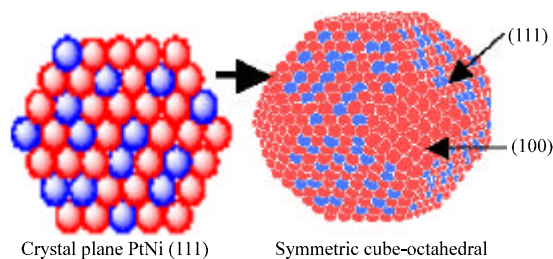


Fig. 3: Illustration of Symmetric cube-octahedral to predict of PtNi$_3$ surface on (100) and (111) crystal plane
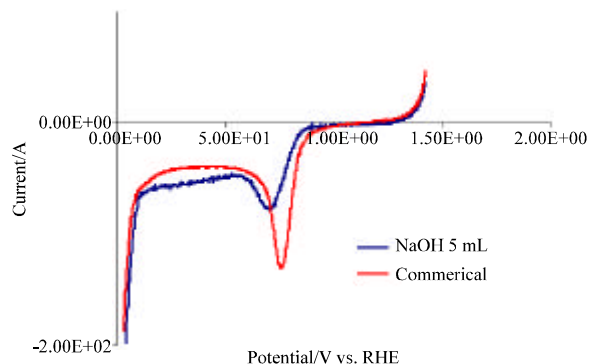


Fig. 4: The polarization curves for ORR on PtNi/C and Pt/C commercial. The potential scan speed is 5 mV sec$^{-2}$

The SA is a fundamental measure of intrinsic activity used in heterogeneous catalysis. It is shown that NaOH 5 mL Sample has SA of 99 $\mu$A cm$^{-2}$ and commercial Pt/C has SA 30 $\mu$A cm$^{-2}$.

Moreover, PtNi/C shows a higher ORR activity than that of commercial Pt/C E-TEK. This may be attributed to the addition of Ni to Pt/C catalyst. The more electropositive transition metal Ni that is pulled by oxygen provides electrochemical force which accelerates the four electron oxygen reduction pathways and then consequently improves the activity of the catalyst. The addition of Ni to Pt/C catalyst does not only reduce the Pt lattice parameter (the Pt-Pt nearest-neighbor distance plays an important role in determining the adsorption behavior), but also enhances the catalytic activity. Therefore the alloying effect is an important factor affecting the catalytic activity toward ORR. The most recent PEMFC studies showed threefold SA gains for PtCo/C catalyst compared to Pt/C as stated by Chen *et al.*, 2010. The above result was in close agreement with Stamenkovic *et al.* (2007) investigation that the pure single crystal of Pt$_3$Ni (111) configuration synthesized through a range of atomic lattice structures in an Ultra-High Vacuum (UHV) chamber has the ORR activity around 90 times better than that of Pt/C. The next step, to

increase the ORR activity, still required an additional process that could increase the greater number of available Pt sites on the surface.

## CONCLUSION

The characteristics of the prepared PtNi/C from this experiment are : Crystal structure with face-cubic centre (fcc), reflection plane in $2\Theta$ =39.7° (111) and $2\Theta$ = 46.3° (200) and disordered crystalline. The replacement of larger platinum atom by the smaller Ni atom indicates a lattice contraction. The particle size of synthesized nanoalloy has almost the same size as the size of the commercial Pt/C particle. The PtNi alloy loading on carbon support for NaOH 5 mL sample is around of 29% and %wt Pt atom measured by EDX in the particle surface is 23%. The exposed platinum atom shown by the dispersion for NaOH 10 mL sample is around 29%.

In this research, the prepared PtNi / C has three times enhancement in SA compared to commercial Pt/C, but has almost the same particle size. The fact revealed that PtNi/C has disordered structure while the Pt/C has ordered structure. Whereas the electrochemical surface area of the synthesized PtNi/C is 25% of the commercial Pt/C sample, but changes in Pt d-band vacancy and lattice parameter are some of the reasons attributed for the enhanced performance. The above conditions fulfill the requirement for PtNi/C to be used as a cathode PEMFC.

## ACKNOWLEDGMENTS

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