Synthesis and Characterization of 20% Pt-Fe/C Alloy as a Cathode Catalyst for Oxygen Reduction Reaction PEMFCs

Sukmin Kang[1,2,*], Sungyeol Yoo[1], Jina Lee[1], Bonghyun Boo[2], Bal Chandra Yadav[1] and Hojin Ryu[1]

[1]Energy Materials Research Center, Korea Research Institute of Chemical Technology, Yuseong, Daejeon 305-600, Republic of Korea
[2]Department of Chemistry, Chungnam National University, Yuseong, Daejeon 305-764, Republic of Korea

Abstract: *Proton exchange membrane fuel cells (PEMFCs) are highly efficient and non-polluting electrical power generators based on two electrochemical reactions. Therefore, PEMFCs are considered to be alternative electricity sources for electric vehicles, portable applications and stationary power systems due to their high power density and eco-friendly environment. However, PEMFCs are associated with many problems for their commercialization such as the high price of electrode catalyst and the slow rate of oxygen reduction reaction (ORR). In this study, two different reducing agents $NaBH_4$ and HCHO were used in the synthesis of carbon supported Pt-Fe catalysts (Pt-Fe/C-HCHO and Pt-Fe/C-NaBH$_4$). Both catalysts were characterized using x-ray diffraction (XRD), transmission electron microscopy (TEM) and cyclic voltametry in the range 0.05 -1.2 V vs. SHE. It was observed that reducing agent HCHO is more effective than $NaBH_4$. In order to reduce amount of platinum, the 20% Pt-Fe/C catalyst was prepared by using Fe. The catalysts were heat treated up to 600 °C for improve the activity and stability. It was found that a temperature of 500 °C yielded the best catalyst morphology and ORR activity at 0.9 V.*

1. INTRODUCTION

To solve the problem of energy and environment in the future, the research on renewable energy is being carried out in many fields such as solar, wind, water energy etc [1]. Among those, the fuel cell which uses hydrogen energy is very interesting. It has been studied actively as a future power device. Proton exchange membrane fuel cells (PEMFCs) are efficient and non-polluting electrical power generators based on two electrochemical reactions; one is the oxidation of hydrogen occurring at cathode and other is the reduction of oxygen at the anode. These have many benefits such as high current density and are available at low temperature (100°C) better than the other fuel cells. Consequently, PEMFCs are considered to be alternative electricity sources for electric vehicles, portable applications and stationary power systems [2-6]. But the expenditure on rare metals such as Pt in PEMFCs is one of the most important barriers to the commercialization of fuel cells. The state-of-art PEMFCs use an expensive carbon supported platinum catalyst which is very expensive. In addition, the slow reaction of the oxygen reduction reaction (ORR) leads to a higher potential at the cathode. Therefore, the study of the cathode catalyst with high catalytic activity for the ORR and decreased amount of Pt must be needed for the commercialization of PEMFCs [7-14]. To solve this problem, researchers proposed many methods such as Pt-alloy method, non-Pt catalyst and the crystallization structure of Pt controlled method [15-17]. In particular, according to the results of a recent study, it was found that transition metals such as Ni, Fe and Co are good candidates for forming an alloy with Pt. Also, the other metals such as Ta, W and Zr have investigated the capability of non-Pt catalyst. These metals have some catalytic activity for the ORR and are stable in acid state, although it is still not sufficient when compared to Pt. Additionally, Ti oxide catalyst were studied for their catalytic activity. Although the catalytic activity of Ti oxide catalyst was low, Ti oxide is value being studied as a non-Pt catalyst for the PEMFC because of plentiful natural resources and supports the electrochemical reaction [18,19].

This study was conducted to investigate the feasibility of producing a commercial PEMFC while reducing the use of the catalyst made of Pt, which is expensive, and Pt-Fe alloy cathode cata-

*To whom correspondence should be addressed: Email: fiafia@krict.re.kr
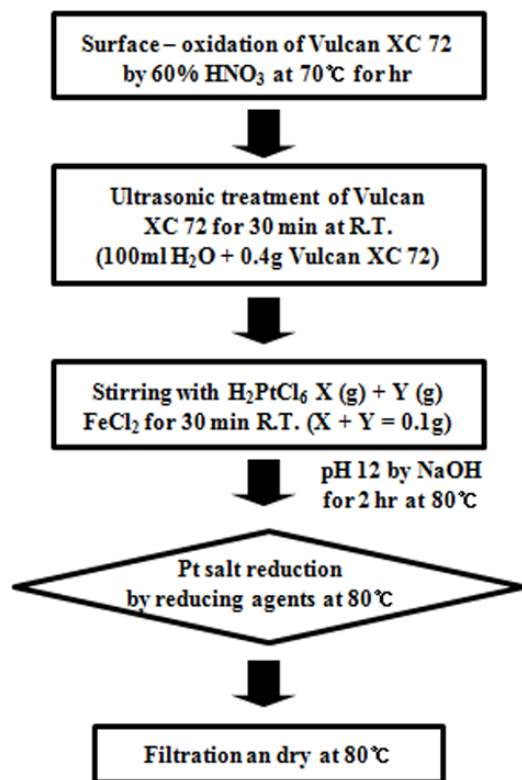Phone: +82-42-860-7376, Fax: +82-42-860-7237

Surface – oxidation of Vulcan XC 72
by 60% HNO₃ at 70℃ for hr

↓

Ultrasonic treatment of Vulcan
XC 72 for 30 min at R.T.
(100ml H₂O + 0.4g Vulcan XC 72)

↓

Stirring with H₂PtCl₆ X (g) + Y (g)
FeCl₂ for 30 min R.T. (X + Y = 0.1g)

pH 12 by NaOH
for 2 hr at 80℃

↓

Pt salt reduction
by reducing agents at 80℃

↓

Filtration an dry at 80℃

Figure 1. Schematic flow chart used for the prepared process of 20% Pt-Fe/C catalyst by chemical reduction method.

lyst was proposed as an alternative. In order to produce PEMFC catalyst with high catalytic activity, the most appropriate reducing agent for the study was selected through an experiment. Also, the amount of Pt used was reduced by substituting it with Fe. The catalytic activities for the ORR of 20% Pt-Fe/C alloy catalysts were evaluated using electrochemical measurements. Finally, the particle size and degree of crystallization of the Pt-Fe alloy catalyst were adjusted through heat treatment at a low temperature. The prepared catalysts were characterized by transmission electronic microscopy (TEM) and X-ray diffraction (XRD).

2. EXPERIMENTAL

2.1. Preparation of 20% Pt/C catalysts

The 20% Pt/C catalysts were synthesized by a chemical reduction method. Fig. 1 shows the schematic flow chart of preparation of catalyst using this method. First of all, we prepared pretreatment high surface area carbon (Vulcan XC-72R (Cobot. Co.)) as a Pt supporting material. Further it was stirred in 60% HNO₃ for 5 hrs at 70 °C and the obtained carbon was filtered, washed with distilled water and dried for overnight at 80 °C in an electrical oven. The 0.4 g of carbon which finished pre-treatment was dispersed in 100 ml of distilled water with ultrasonic treatment for 40 min with ultrasound treatment. Later for synthesis of 20% Pt/C particles metal salt H₂PtCl₆ (Kojima Co., 99%) was added to the pretreated carbon in the weight ratio of 1:4. And the above solution was added to 1g of NaOH. It stirred vigorously for 2hr at 80°C. To investigate the effects of different reducing agents, we used the

reducing agent NaBH₄ or HCHO. For this purpose 50 mL of each NaBH₄ or HCHO were added separately to above solutions and stirred for 1 hr at 80 °C. Finally, these were filtered, washed with distilled water and acetone. Thus prepared catalysts were dried for overnight at 80 °C in an electrical oven. To compare to commercial catalyst, we used 20wt% Pt/C catalyst which made by E-TECK. Co., Ltd.

2.2. The synthesis of Pt-Fe alloy catalyst by adding Fe in 20% Pt/C catalysts

During preparing 20% Pt/C catalyst, we added Fe to the prepared 20% Pt/C catalyst instead of decreasing amount of Pt. At this time, the amount of carbon was fixed. The source of Fe in this experiment was iron (II) chloride and the purity of the reagent was 99%. The compositions of the 20% Pt-Fe/C catalyst used are detailed below:

1) 20% Pt$_{0.8}$Fe$_{0.2}$/C

2) 20% Pt$_{0.6}$Fe$_{0.4}$/C

3) 20% Pt$_{0.4}$Fe$_{0.6}$/C

2.3. Electrochemical measurements

In order to evaluate electrochemical measurements, the three-electrode cell system was carried out under N_2 and O_2 at room temperature in a 1M H_2SO_4 electrolyte. The Ag/AgCl electrode and Pt wire used as the reference and counter electrodes. The working electrode was prepared. The 0.025 g of prepared 20% Pt-Fe/C catalyst was used. It was added into a nafion solution (DuPont Co., Type: SE-5012), which contained water and nafion in 9:1 mass ratio. After ultrasound treatment for 30 min, coating of the catalyst was done on a glassy carbon disk electrode. The catalyst coated glassy carbon disk electrode was then subjected for heat treatment at 120 °C for 1 hr. The electrochemical stability was evaluated by cyclic voltammetry under N_2. The summary of cyclic voltammetry ambiance is summarized in Table 1. It was measured in the range from 0.05 to 1.2V (versus SHE) and scan rate was 30mV/sec. The ORR current was obtained by the difference in the cathodic sweep current of the cyclic voltammograms in N_2 and O_2. And the steady potentials were measured in the range from 0.9 to 0.6V for 5 min, respectively.

2.4. Heat treatment of prepared 20% Pt-Fe/C catalyst

In attempt to control for the particle size and degree of crystallization of prepared 20% Pt-Fe/C catalyst, it were heat treated at 300, 400, 500 and 600°C for 1 hr in an electrical furnace under an inert atmosphere of Ar gas which was supplied at flow rate of 200mL/min. The temperature was raised at a rate of 4°C/min. After the heat treatment, we took out 20% Pt-Fe/C catalyst and preserved it at room temperature.

Table 1. The summary of cyclic voltammetry atmosphere

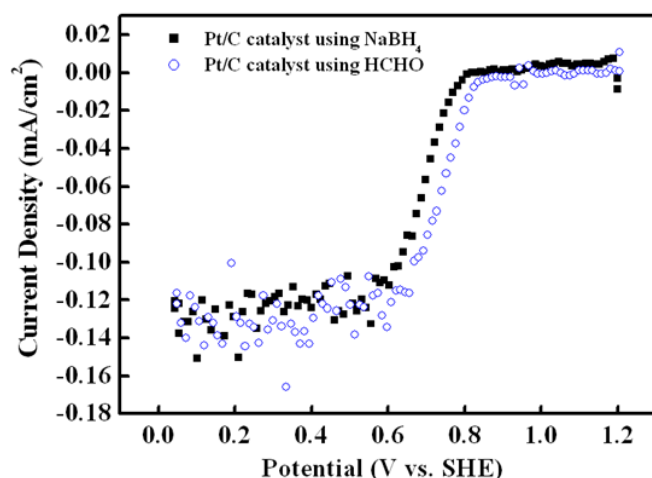|	
The range of electro potential	0.05-1.5 V vs. SHE
The rate of searching	30 mA / sec
At atmosphere	1 M, H_2SO_4

Figure 2. Current density of the oxygen reduction reaction (i_{ORR}) for the prepared 20% Pt/C using different reducing agents and commercial 20% Pt/C catalysts at room temperature with 1M sulfuric acid.
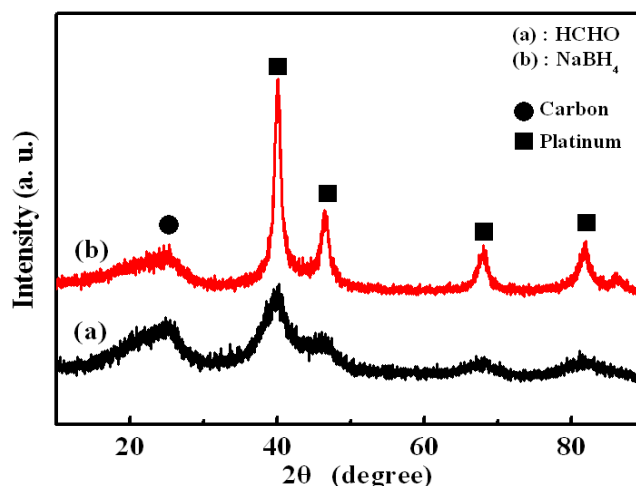

Figure 4. XRD patterns for the prepared 20% Pt-Fe/C using different reducing agents (a) reducing agent : $NaBH_4$, (b) reducing agent : HCHO.
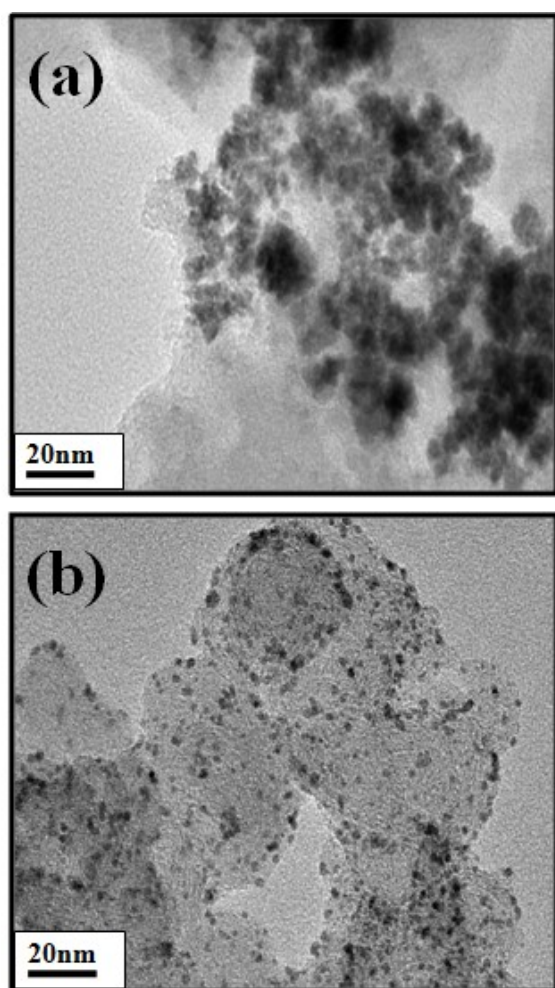

Figure 3. TEM images for (a) reducing agent: $NaBH_4$, (b) reducing agent: HCHO.

2.5. Physical characterization

The Physical properties of catalysts were characterized by TEM. The samples for the TEM analysis were prepared by dispersing in ethanol with ultrasound treatment for 10 min. To investigate degree of crystallization of 20% Pt-Fe/C catalysts, XRD analysis was also conducted at rate of 2°/min.

3. RESULT AND DISCUSSION

3.1. Analysis of prepared Pt/C depend on different reducing agents

We prepared 20% Pt/C catalyst by using different reducing agents e.g. $NaBH_4$ and HCHO. Fig. 2 shows the ORR current of prepared 20% Pt/C at room temperature using the difference reducing agents. On-set potential was measured at 0.8 - 0.1 V. The ORR current was irregularly appeared below 0.6 V because ORR can be affected catalytic activity as well as the movement of reactant by stirring in this part. Therefore, it was reasonable to evaluate the catalytic activity at high voltage. According to the graphs, we can see that prepared 20% Pt/C catalyst has highly ORR rate using HCHO. In particular, the current density of 20% Pt/C catalyst using HCHO was higher 0.04 than 20% Pt/C catalyst using $NaBH_4$ at 0.8V. The results were concluded on the basis of distribution rate of Pt particles. To confirm distribution rate, TEM and XRD were carried out. Figs. 3 (a) and (b) show the TEM images of as prepared 20% Pt/C catalyst using $NaBH_4$ and HCHO reducing agents. In case of using $NaBH_4$, Fig. 3 (a) reveals the surface morphology on which Pt particles were distributed heterogeneously and the average crystallite size was found as 10 nm. On the other hand, Fig. 3 (b) shows that Pt particles were almost distributed homogeneously on the substrate surface. The average crystallite size was found as 3 nm. The distribution rate was differenced as reducing agents. The most of the Pt particles are combined when using $NaBH_4$. And the activity sites were markedly reduced. In order to investigate degree of crystallization of 20% Pt/C catalysts, XRD was used at rate of 2°/min with Cu-Ka. Corresponding patterns are
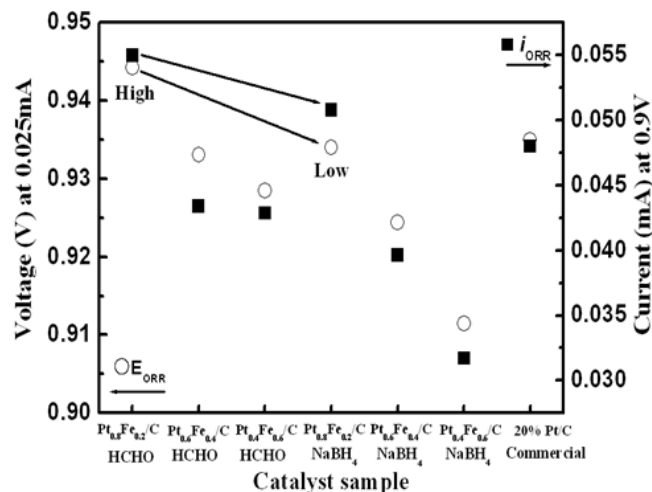
Figure 5. E_{ORR} at -0.025 mA and i_{ORR} at 0.9 V for the prepared 20% Pt-Fe/C catalysts with different reducing agents and Fe concentrations.
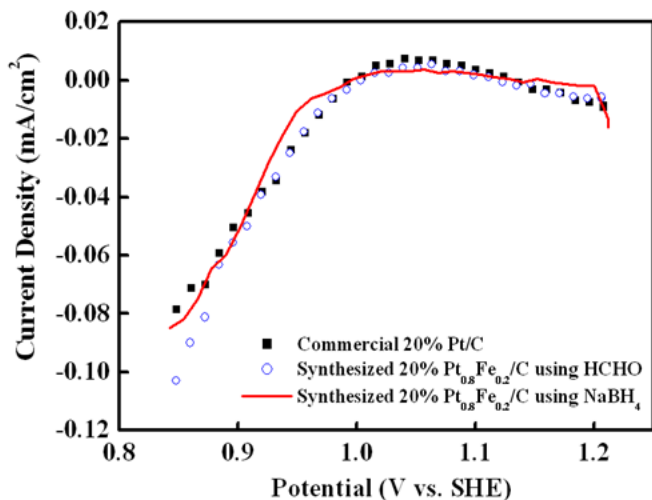

Figure 7. Cyclic voltammograms of the prepared 20% $Pt_{0.8}Fe_{0.2}$/C using different reducing agents and commercial 20% Pt/C catalysts at room temperature in the presence of N_2 with 1M sulfuric acid electrolyte.

Figure 6. Current density of the oxygen reduction reaction (i_{ORR}) for the prepared 20% $Pt_{0.8}Fe_{0.2}$/C using different reducing agents and commercial 20% Pt/C catalysts at room temperature with 1M sulfuric acid.

shown in Fig. 4. For pattern (a) near the peak at 25° the carbon is indicated as used substrate and the peaks at 39.7°, 46.2°, 67.4°, 81.2° are indicated as Pt. When using $NaBH_4$ (Fig. 4 (b)), the peak was sharper and containing larger intensity than using HCHO (Fig. 4 (a)). The sharp and large intensity peaks mean having a larger particle size and degree of crystallization. In conclusion, the HCHO as a reducing agent was a found to be most optimal.

3.2. The electrochemical activity of the prepared 20% Pt-Fe catalysts

Under the condition of using $NaBH_4$ or HCHO, we examined the effect of addition of Fe instead of decreasing the amount of Pt. We performed seven different cases. Fe was added in the range of
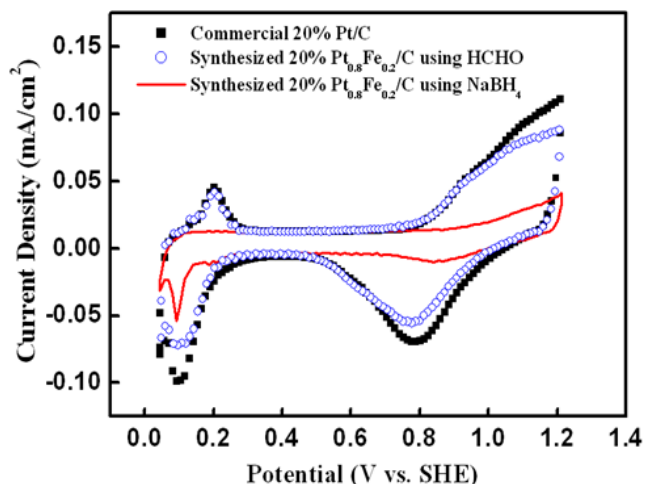
0.2~0.6% of the amount of Pt, respectively. Fig. 5 shows the catalytic activity of the 20% Pt-Fe/C catalyst produced in the experiment and the commercial Pt/C catalyst purchased from E-TECK. Co., Ltd. Fig. 5 summarizes the current measured at 0.9V and the voltage measured at 0.025mA. The black rectangle and the right axis represent the electric current at 0.9V and the white circle and the left axis represent the on set potential obtained at 0.025mA. The impact of Fe can be found by measuring the ORR (i_{ORR} at 0.9 V) and on-set potential (E_{ORR} at 0.025 mA). They demonstrate different effects depending on the amount Fe. The ORR of 20% $Pt_{0.8}Fe_{0.2}$/C catalyst shows best result among the entire composition ratio using HCHO. While for using HCHO maximum i_{ORR} at 0.9 V was found 0.0548 mA and E_{ORR} was the 0.9442 V at 0.025 mA. When using $NaBH_4$, maximum i_{ORR} of 20% $Pt_{0.8}Fe_{0.2}$/C catalyst was found as 0.0508 mA at 0.9 V and E_{ORR} was 0.9340 V at 0.025 mA. They were higher than catalytic activity of commercial catalyst despite of decreasing amount of Pt. Meanwhile, the activity of $Pt_{0.4}Fe_{0.6}$/C catalyst was lowest regardless of the reducing agents. Fig. 6 shows the actually ORR current of prepared 20% $Pt_{0.8}Fe_{0.2}$/C and commercial catalysts were evaluated at room temperature. As per nature of graphs, we can see that in spite of the reduction in amount of platinum of synthesized 20% $Pt_{0.8}Fe_{0.2}$/C using HCHO as reducing agent, ORR current in this case and the commercial 20% Pt/C catalysts are almost the same. When adding Fe in 20% Pt/C catalyst, some of the Pt particles were substituted by the Fe. The 20% Pt/C catalyst adding Fe has changed with a substitution solid solution of Pt-Fe alloy.

The cyclic voltammograms of commercial 20% Pt/C and prepared 20% Pt-Fe/C catalyst are shown in Fig. 7. In the beginning, the cathode current was appeared due to the adsorption of hydrogen. And anodic current was appeared due to the oxidation of adsorbed hydrogen in the range of 0.05 – 0.3 V successively. Since the activity site of Pt was decreased by assembling Pt particles, anodic current is not observed using $NaBH_4$. The anodic sweep (0.4 – 0.7 V) was an electrical double layer which was responsible for

Synthesis and Characterization of 20% Pt-Fe/C Alloy as a Cathode Catalyst for Oxygen Reduction Reaction PEMFCs / J. New Mat. Electrochem. Systems
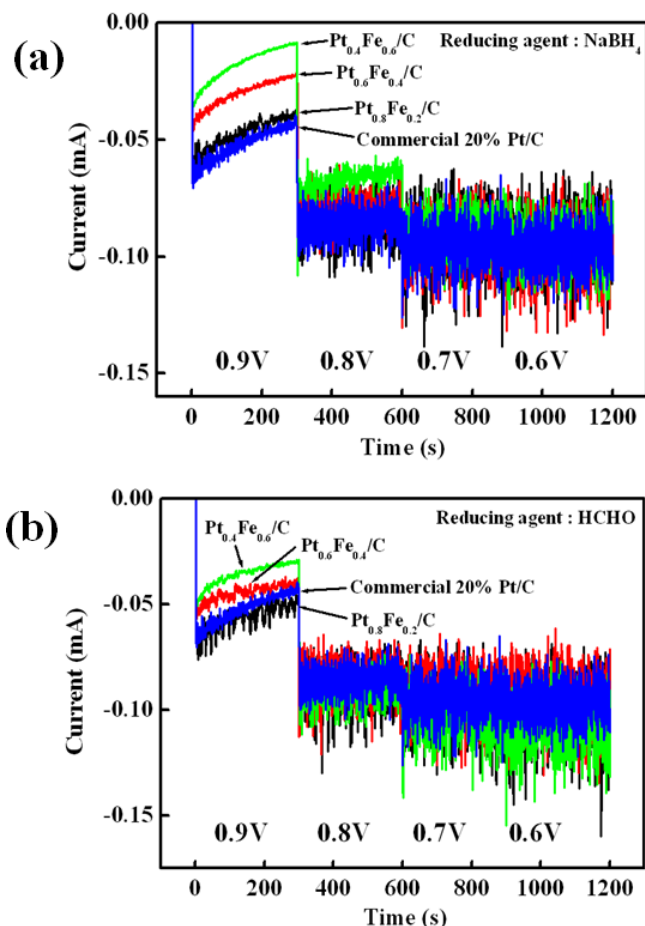
245

Figure 8. Variation of cathode current with variation in steady potentials (V vs. SHE) during 5 min for the prepared 20% Pt-Fe/C under 1 M sulfuric acid in O_2 using different reducing agents; (a) $NaBH_4$ and (b) HCHO.

the flow of charging current. Above 0.7 V, the reactions by the oxidation of H_2O on the Pt surface which gave an anodic current have been written as follows:
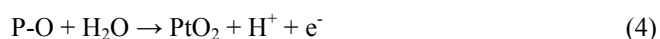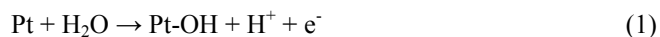
$$Pt + H_2O \rightarrow Pt\text{-}OH + H^+ + e^- \tag{1}$$

$$Pt\text{-}OH \rightarrow Pt\text{-}O + H^+ + e^- \tag{2}$$

$$Pt\text{-}O \rightarrow PtO \tag{3}$$

$$P\text{-}O + H_2O \rightarrow PtO_2 + H^+ + e^- \tag{4}$$

Also, Pt electrochemical active surface area (EAS) was measured during potential cycling test. The EAS results are shown in Table 2.

$$EAS = Q_H / [Pt] \times 0.21 \tag{5}$$

The columbic charge for hydrogen desorption (Q_H) was used to calculate from 0.05 to 0.4V at 30mV/sec. where [Pt] represents the platinum loading (mg/cm^2), Q_H the charge for hydrogen desorption (mC/cm^2), 0.21 represents the charge required to oxidize a monolayer of H_2 on bright Pt. An EAS level was related to catalytic activity because a high EAS level has many activity sites [20,21]. The EAS of prepared 20% $Pt_{0.8}Fe_{0.2}$/C catalyst with HCHO and commercial 20% Pt/C catalyst are 45.841 and 46.7855 cm^2/mg, respectively. They are almost the same. The activity of 20% Pt-Fe/C catalyst with $NaBH_4$ was lowest as a 27.6679 cm^2/mg.

Further, we also performed the experiment on steady potential in oxygen atmosphere at 0.9, 0.8, 0.7, 0.6 V, respectively for 5 min. The results obtained are shown by the Fig. 8 (a) and (b). Fig. 8 (a) exhibits variations in cathode current with time at different steady potentials when $NaBH_4$ was used as a reducing agent. All four catalysts gave results of similar nature. However, the prepared $Pt_{0.8}Fe_{0.2}$/C catalyst gave maximum cathode current (0.06555 mA) at steady potential 0.9 V. On the other hand, Fig. 8 (b) presents the variations in cathode current with time at different steady potentials with the use of HCHO. The prepared 20% $Pt_{0.8}Fe_{0.2}$/C catalyst gave maximum value of current (0.07617 mA). Also these results show consistency with previous results depicted. Therefore, it is noteworthy that the types of reducing agent and concentrations of Fe-ion had a lucid influence on the catalytic activity for ORR.

Jahn and Teller proposed [22-24] that the Pt-Pt nearest-neighbor distance and the particle size of Pt are the main factor affecting the catalytic activity for ORR. If the particle size of Pt was large by assembling Pt particle, ORR would become low because of decreasing a number of activity sites of Pt. On the contrary, if the particle size of Pt was too small, as well ORR would become low because of another reason that decreasing an EAS of Pt. In our experimental, when Fe-ion was added to the catalyst of Pt, it controlled the size of particle upholding properly the Pt-Pt nearest-neighbor distance which results the optimal particle size of Pt for highly ORR.

3.3. The effects of heat treatment on ORR

Experiments were carried out for investigating the effect of heat treatment on $Pt_{0.8}Fe_{0.2}$/C catalyst which has the best catalytic activity using HCHO. For this purpose, it was heat treated in an electrical furnace in the presence of oxygen at 400, 500 and 600 °C for 1 hr. After the heat treatment the catalyst was employed for cyclic

Table 2. . The EAS results of prepared and commercial catalysts

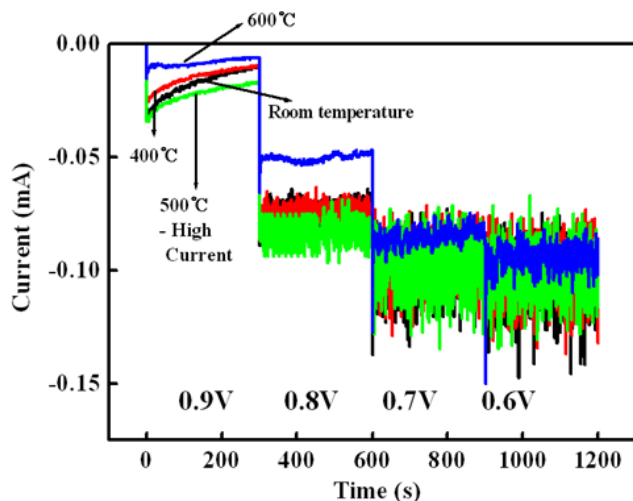| EAS=Q_H/ [Pt] x 0.21	EAS: (electrochemical active surface area) Q_H: charge for hydrogen desorption (mC/cm^2) [Pt]: represents the platinum loading (mg/cm^2) 0.21: represents the charge required to oxidize a monolayer of H_2 on bright Pt		
Catalyst	The prepared 20% $Pt_{0.8}F_{0.2}$/C	The prepared 20% $Pt_{0.8}F_{0.2}$/C	The commercial 20% Pt/C
Reducing agent	HCHO	$NaBH_4$	HCHO
EAS(cm^2/mg)	45.841	27.6679	46.7855

Figure 9. Variation of cathode current with variation in steady potentials (V vs. SHE) during 5 min for the 20% Pt-Fe/C as pre-pared and heat treated at different temperatures under 1M sulfuric acid in O_2.

voltametry at different steady potentials 0.9, 0.8, 0.7, 0.6 V respectively for 5 min and variations in cathode current with time were recorded. Corresponding data were plotted in Fig 9. These results show that the catalyst which was heat treated at 500 °C yielded average cathode current 0.09 mA and best suited for high ORR. This value is higher than the value obtained by the catalyst without heat treatment (0.085 mA). As a results, we infer that the heat treatment affects to the catalytic activity for ORR. Particle size and degree of crystallization by heat treatment can be considered as the factors affecting ORR of prepared Pt-Fe/C catalyst.

Fig. 10 shows a photograph of the TEM image as prepared without heat treatment (a) and heat treated catalysts at 400 (b), 500 (c), 600°C (d) for 1hr, respectively. All particles of the Pt-Fe/C catalyst were homogeneously distributed on the substrate surface. But Pt-Fe particles were formed clusters on heat treatment. The particle size was almost 1-5 nm before heat treatment of the catalyst (Fig. 10 (a); however the particle size was 2-7 nm after heat treatment at 400°C (Fig. 10 (b)). In case of heat treatment at 500°C, the particle size was 2-13 nm (Fig. 10 (c)). In addition, when heat treatment was done at 600°C, the larger particles were observed over 25 nm (Fig. 10(d)). The lowest activity was observed at 600°C because of decreasing activity site. The results are consistent with steady potential results. XRD was carried out and pattern is shown in Fig. 11. This pattern reveals that the degree of crystallization was increased by heat treatment. Generally, the EAS was larger in the catalyst that was crystallized than that in an amorphous state [25,26]. However, the Pt/C catalyst produced through the chemical reduction method is in nearly an amorphous state, where no crystallization has occurred. Because the particle size is 2-4nm, the EAS of Pt is small. Placing this type of Pt/C catalyst under heat treatment at a high temperature will increase the particle size and degree of crystallization of Pt, which in turn expands the EAS, yet reduces activity site number. This suggests that there is a negative correlation between the EAS and number of activity site, both of which
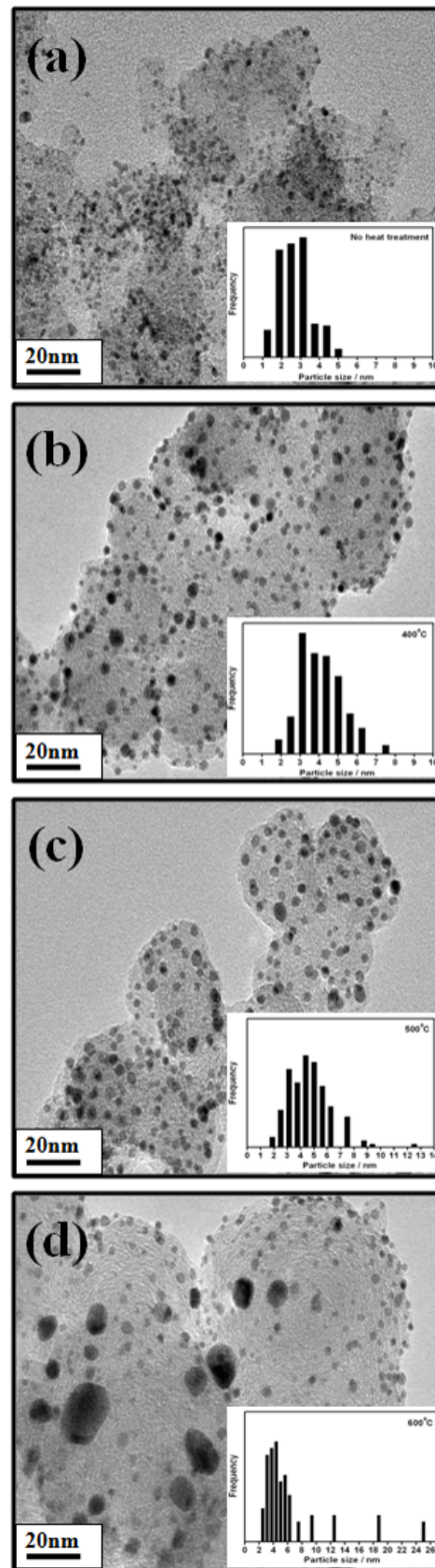

Figure 10. TEM images of 20% Pt-Fe/C (a) as prepared, (b) heat treatment at 400 °C, (c) 500 °C, and (d) 600 °C.
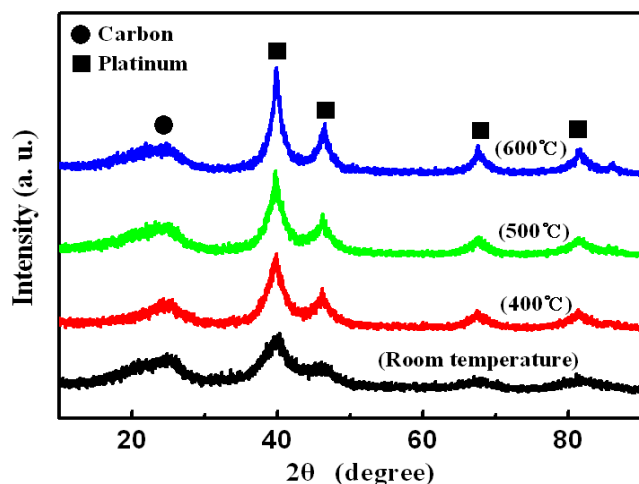
Figure 11. XRD patterns for the prepared 20% $Pt_{0.8}Fe_{0.2}$/C catalyst with various heat treatment temperatures at Room temperature, 400 °C, 500 °C, and 600 °C.

determine the activity of Pt catalysts. Thus, there is a need to produce a Pt-Fe/C with an appropriate particle size and degree of crystallization. In this study, the prepared 20% Pt-Fe/C catalyst was manufactured when heat treatment was performed at 500°C.

4. CONCLUSION

We prepared 20% Pt-Fe/C alloy catalyst for highly ORR. In the first step, the experiment was carried out using different reducing agents $NaBH_4$ or HCHO. The prepared Pt/C catalyst using a HCHO shows that Pt particle were almost distributed homogeneously on the substrate surface. On the other hand, the prepared catalyst using a $NaBH_4$ reveals the surface morphology on which Pt particles were distributed heterogeneously and the average crystallite size was found as 10 nm. The 20% Pt/C catalyst which used HCHO had highly ORR. In the next step, this analyzed the properties of prepared 20% Pt-Fe/C catalyst adding Fe-ion instead of decreasing amount of Pt. The prepared 20% $Pt_{0.8}Fe_{0.2}$/C catalyst obtained maximum value i_{ORR} at 0.9V as 0.0548mA and E_{ORR} at 0.025mA as the 0.9442V better than commercial 20% Pt/C catalyst. Thus EAS of Pt catalyst was measured during potential cycling test. The EAS of prepared 20% $Pt_{0.8}Fe_{0.2}$/C catalyst using HCHO as 45.841 cm^2/mg was almost same the commercial catalyst as 46.7855 cm^2/mg despite of reducing amount of Pt. The final step involved the control of the particle size and degree of crystallization of prepared 20% Pt-Fe/C catalyst by using heat treatment. When heat treated at 500 °C, it has the best catalytic activity all the prepared and commercial catalysts by optimizing the particle size and degree of crystallization.

5. ACKNOWLEDGEMENTS

REFERENCES

[1] J.W. Carl, Int. J. Hydrogen Energy, 34, 1 (2009).

[2] E. Antolini, Applied Catalysis B: Environmental, 74, 324 (2007).

[3] E. Antolini, Applied Catalysis B: Environmental, 74, 337 (2007).

[4] F. Barbir, T. Gomez, Int. J. Hydrtogen Energy, 10, 891 (1996).

[5] G. Sattler, J. of Power Sources, 86, 61 (2000).

[6] J.R.C. Salgado, E. Antolini, E.R. Gonzalez, J. of Power Sources, 138, 56 (2004).

[7] J.H. Kim, A. Ishihara, S. Mitsushima, N. Kamiya, K. Ota, Electrochimica Acta, 52, 2492 (2007).

[8] Y. Maekawa, A. Ishihara, J.H. Kim, S. Mitsushima, K. Ota, Electrochem. Solid-State Lett., 11, 109 (2008).

[9] K. Shirlaine, Y. Chengfei, M. Prasanna, S. Ratndeep, S. Peter, J. of Power Sources, 172, 50 (2007).

[10] W. Wenming, Z. Dan, D. Chong, Z. Zhiqing, Z. Xigui, X. Baojia, Y. Hui, L.A. Daniel, J. of Power Sources, 167, 243 (2007).

[11] C.S. Jose R., A. Ermete, R. G. Ernesto, J. of Power Sources, 141, 13 (2005).

[12] A.G. Hubert, S.K. Shyam, S. Bhaskar, T.W. Frederick, Applied Catalysis B: Environmental, 56, 9 (2005).

[13] Y. Ping, P. Marianne, P. Paul, J. of Power Sources, 144, 11 (2005).

[14] A. Ermete, Materials Chemistry and Physics, 101, 395 (2007).

[15] Y.H. Cho, B. Choi, Y.H. Cho, H.S. Park, Y.E. Sung, Electrochem. Comm., 9, 378 (2007).

[16] A.K. Shukla, R.K. Raman, N.A. Chaudhary, K.R. Priolkar, P.R. Sarode, S. Emura, R .Kumashiro, J. Electroanalytical Chemistry, 563, 181 (2004).

[17] L. Zhang, K. Lee, J. Electrochimica Acta, 72, 7964 (2007).

[18] H.J. Kim, S.M. Choi, S.N. Nam, M.H. Seo, W.B. Kim, Catal Today, 146, 9 (2009).

[19] M.A. Gracia-Contreras, S.M. Fernandez-Valverde, J.R. Vargas-Garcia, M.A. Cortes-Jacome, J.A. Toledo-Antonio, C. Angeles-Chavez, Int. J. Hydrogen Energy, 33, 6672 (2008).

[20] J. Wang, G. Yin, Y. Shao, S. Zhang, Z. Wang, Y. Gao, J. of Power Sources, 171, 331 (2007).

[21] G. Jerkiewicz, M.P. Soriaga, K. Uosaki, A. Wieckowski, J. of Electroanalytical Chemistry, 441, 295 (1998).

[22] A. R. Malherio, J. Perez, H.M. Villullas, J. Electrochem. Soc, 156, 51 (2009).

[23] S.C. Zignani, E. Antolini, E.R. Gonzalez, J. of Power Sources, 191, 344 (2009).

[24] H. Yang, C. Coutanceau, J.M. Leger, N.A. Vante, C. Lamy, J. of Electroanalytical Chemistry, 576, 305 (2005).

[25] M.K. Min, J. Cho, K. Cho, H. Kim, Electrochimica Acta, 45, 4211 (2000).

[26] Y.C. Wei, C.W. Liu, W.J. Chang, K.W. Wang, J. of Alloys and Compounds, 509, 535 (2011).