Using the palladium as core and platinum as shell for ORR

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Article Information

Abstract

In this work, electrocatalyst with core-shell structure (Pd as core and Pt as shell on VulcanXC-72R) was synthesis. Not only this structure can reduce the amount of platinum but it also can increase the gas diffusion electrode (GDE) performance in cathode reaction (Oxygen Reduction Reaction or ORR) of polymer electrolyte membrane fuel cell (PEMFC). To this meaning, one series of electrocatalyst with different molar ratio of metals (Pd @ Pt), was prepared and applied in electrode fabrication. The used synthesis method was impregnation with hydrothermal. The performance of the electrodes in ORR was studied by linear sweep voltametery (LSV), electrochemical impedance spectroscopy (EIS), chronoamperometery techniques and the MEA were also tested. Inductive coupled plasma (ICP), X-ray diffraction (XRD), transmission electron microscopy (TEM) techniques was used to characterize the electrocatalyst. The results indicated that the electrocatalyst with 3:1 molar ratio for Pd: Pt enhanced the cathode in MEA performance. This result can be attributed to the positive effect of Pd, particle size and catalyst distribution on substrate that consequently, provide the best three phase zone.

1. Introduction

Platinum has a wide range of catalysis applications due to its unique chemical and physical characteristic [1-4]. However, a critical problem for Pt catalysts is the high cost due to limited supply. [5]. The major challenge in this field at present is to reduce the fuel cell energy cost by developing low cost materials, processes and components [6]. Core–shell nanostructure is an effective way to increase the utilization efficiency of recious metal electro catalysts [7]. By producing Pt nanosphere shell with high surface to volume ratios, the high catalytic activity and utilization efficiency of Pt electro catalysts and low Pt loading and consequently reduced cost can be achieved [8-10]. Recently many researches focused on synthesized core-shell structure catalyst and applied in PEM fuel cells. In 2013 synthesis the Pt as shell on commercial Pd/C with different molar ratio and investigated ORR on catalyst were reported. The results indicated that activity of this catalyst was better than the commercial Pt/C and Pd/C [11]. H. Wang et al. [7] prepared the

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Pd @ Pt core-shell nanowire array using an anodized aluminum oxide template electro deposition and magnetron sputtering method. Their results indicated that this catalyst was highly active toward the electro oxidation of methanol in acid medium for DMFCs, in comparison with that of conventional Pt-Ru supported carbon (Pt-Ru/C) electrocatalysts. In 2012 [12] the Pt Pd core- shell structure was synthesized and mass activity of this catalyst compared with commercial Pt/C. L. Zhang et al. [13] were studied the anode of PEMFC and reported that the overall performance of (Ru @ Pt/Ti$_4$O$_7$) core- shell catalyst in the presence of CO at various concentrations was significantly higher than that of Pt Ru /C alloy catalysts. Pd-Au hollow were shown suitable core for Pt in ORR. This catalyst enhanced the performance of fuel cell [14]. M. Y. Duan et al [15] synthesized the Au@ Pt catalyst for methanol electro oxidation and results show that this catalyst has higher performance than 3 commercial Pt/C. The core- shell structure of Fe @ Pt/SWNT was prepared by K. Shimizu et al. [16]. This catalyst enhanced the ORR in comparison with commercial catalyst. The Ru @ Pt$_x$ Pd$_y$/C core-shell structure were synthesized and applied for formic acid oxidation. The higher electrocatalytic activity toward formic acid oxidation on core–shell structure Ru @ Pt$_x$ Pd$_y$/C catalyst than that on Pt$_x$ Pd$_y$/C suggests the high utilization of noble metals [17].

In this work, the core-shell of Pd @ Pt was synthesis by impregnation and hydrothermal method. The synthesized catalysts were investigated by ICP, TEM and XRD. The performance of catalyst for ORR was study by LSV, CV, Impedance techniques in conventional three electrode system and polarization and power density of MEA.

2. Experimental

2.1.Catalyst synthesis

Catalyst synthesized by a successive reduction route. First, Vulcan powders were pretreated by 10% HNO$_3$ and 30% H$_2$O$_2$ at 80 °C for 12 h followed by filtering,

washing and drying in 70 °C. The appropriate amounts of palladium chloride (PdCl$_2$) solution, and sodium citrate were dissolved in 15 ml ethylene glycol (EG) and then stirred for 1 h to entirely dissolve sodium citrate. Afterwards, as prepared C was added to the mixture, followed by pH adjustment to >10 by drop-wise addition of 5 wt% KOH/EG solution under vigorous stirring. The mixture was then transferred into a Teflon-lined autoclave and conditioned at 130 °C for 6 h, followed by filtering, washing and vacuum drying at 70 °C. The Pd/C was prepared.

Then, platinum chloride (H$_2$PtCl$_6$·6H$_2$O) solution was treated by a similar way as palladium, except that Pd/C was added instead of C. The atom ratio of Pd:Pt was 1:1, 2:1 and 3:1in each sample.

2.2. Electrode fabrication for three electrode cell and MEA

The three layer electrode including carbon paper (substrate), micro porous layer (MPL) and catalyst layer was fabricated. For MPL, a mixture consisting of 30 wt% PTFE and 70 wt% of VulcanXC72R and in 2-propanol (Merck), water, and glycerol (Merck) was sonicated for 20 min to prepare a homogeneous suspension. The suspension was then rolled onto the teflonized carbon paper TGPH-060T (Toray), and the electrode was dried in air at 120°C for 1 h and finally sintered in air at 340 °C for 30 min. To prepare the catalyst layer, a homogeneous suspension was produced from the desired amounts of a synthesized electrocatalyst, glycerol (Merck), 2- propanol (Merck), water, and Nafion solution(5% from Aldrich), by using a sonicator for 20 min. This suspension was rolled onto the diffusion layer; the electrode was dried at 70 °C for 30 min and then at 120 °C for 30 min. The catalyst loadings were 0.3 mg/cm^2 [18]. The same method used to prepare the cathode and anode of MEA. Of course, for anode fabrication the commercial Pt/C was used.

2.3. Material characterization

X-ray powder diffraction (XRD) patterns of the

catalysts were recorded by Philips pw 3710, using filtered Cu K_α radiation at 40 kV and 40 mA. The 2θ angles were scanned from 20° to 90°. The morphologies of the catalysts were analyzed via transmission electron microscope (CM Philips 30). Atomic ratio of metals was determined with ICP (ICP-AES, 314, Switz).

2.4. Electrochemical evaluation

An electrochemical potential state (EG&G 2273) was used for the electrochemical measurements. The performances of the porous GDEs (geometric exposed area 1 cm^2) in the reduction of oxygen were investigated in 0.5 M H_2SO_4. All measurements were performed at 25 °C in a conventional three-electrode cell, with O_2 flowing at 50 mL min^{-1}. The GDEs were 5 mounted into a Teflon holder that contains graphite disk as a current collector and oxygen feeding from the back of the working electrode. A large area platinum flat electrode was used as the counter electrode. An Ag/AgCl reference electrode was placed close to the working electrode surface (Fig. 1).The argon gas
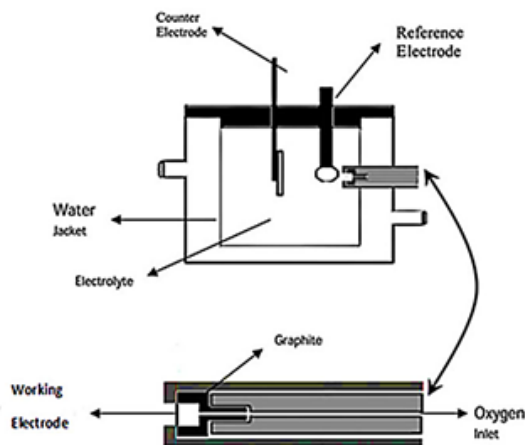

Fig. 1. Schematic diagram of the three electrode system.

flowing in 0.5 M H_2SO_4 was used to performance cyclic voltammetry test. All MEA experiments were conducted on a fuel cell test station (Scribner, 850e). Pure and fully humidified hydrogen was used in anode side. Pure and 50% humidified oxygen was used in cathode side (for reducing the flooding phenomenon). Cell temperature was 80°C. The cathode and anode gas flow were 200 ml min^{-1} conditions of MEA tested were reported in table 1.

3. Results and discussion

The use of Pd with Pt may help minimize the corrosion and loss of catalysts when they are used in an acidic environment such as the medium of a proton exchange membrane (PEM) fuel cell [19].

In 2011[20], effect of Pd: Pt molar ratio on ORR was studied, results indicated that among 2:1, 4:1, 5:1 and 8:1 for ORR, 2:1 of Pd: Pt molar ratio had the best performance, therefore in this work the 1:1, 2:1 and 3:1 of Pd: Pt molar ratio were synthesized and investigated.

In the presence of Pd seeds on Vulcan, since the crystalline structure of Pt and Pd was the same (fcc) and the lattice mismatch of Pt and Pd was very small, at 0.7%, and using a relevant mild reducing agent, Pt was prone to seed and grow to the Pd instead of on the Vulcan, therefore, the synthesized catalyst had a core-shell structure.

The XRD patterns of three catalysts are shown in Fig. 2. The peak centering where about 24° for all the catalysts can be ascribed to the carbon support. The peaks at 40, 47, 68 and 85 are attributed to the 111, 200, 220 and 311 of Pt crystalline plates respectively. The XRD patterns indicate that particle size of catalysts is nanometer (Table 2). Despite this, presence of

Table 1.The single cell experiment condition.

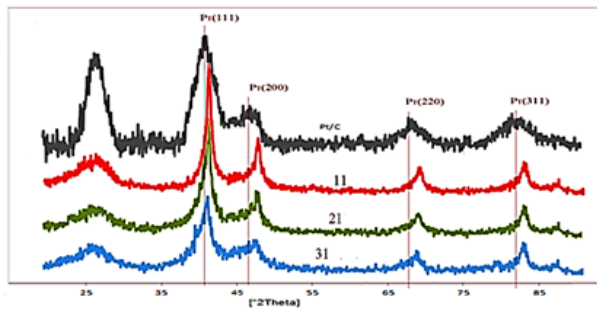| Activation procedure	T_{cell}	membrane	Anode Pt loading mg.cm^{-2}	Cathode catalyst loading mg.cm^{-2}	Electrode area cm^2
0.6 V for 10h	80 °C	N-112	0.3	0.3	5

Fig. 2. The XRD pattern of synthesized catalyst 3:1, 2:1, 1:1 (Pd: Pt molar ratio) and comercial Pt/C.

good dispersion of catalyst particle on carbon support in catalyst 31, but in catalyst 21 the particles were agglomerated and therefore, reduced three phase zone and consequently reduced the electrochemical performance for ORR. The electrochemical results (Fig.5 and Fig. 6) emphasis this idea.

The kinetic parameters of the ORR for a GDE can be obtained from the I-V curve (Fig 5). The analysis of the experimental polarization data was performed by using the Tafel equation [21]:

Table 2. The electrochemical parameter and particle size of synthesized catalysts (1:1, 1:2 and 1:3 Pd:Pt molar ratio)

catalyst	$i_0 \times 10^{-5}$ (A.cm^{-2})	b (mV.dec^{-1})	$i \times 10^{-4}$ at 0.9 (V) (A.cm^{-2})	i at 0.3 (V) (mA.cm^{-2})	EAS(m^2.g^{-1})	$D^{1/2} \times C^* \times 10^{-8}$ (mol. Cm^{-2}.s$^{-1/2}$)	d(nm)	R$_p$(ohm)
11	8.02	49.28	46.7	161.35	136.45	24.65	4.1	1.38
21	6.23	54.79	31.9	108.55	117.92	23.03	3.1	3.47
31	9.17	47.07	95.3	203.60	174.36	33.71	2.3	0.912

Pd in the core and molar ratio of it, affected on 2θ angles and these show the positive shift and dspacing of Pt in each catalyst decreased with respect to commercial Pt/C. These results is in agreement to the other reported researches in literatures [11, 12 and 14]. The small particle size (2.3– 4.1 nm) will increase three phase zone, if the dispersion of these is very well. The TEM images (Fig.3 and Fig. 4) indicate the
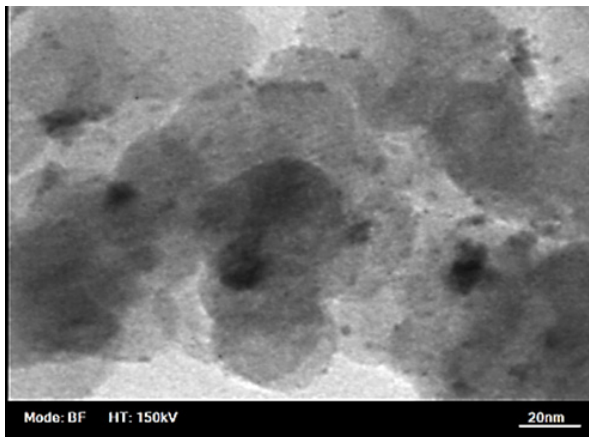

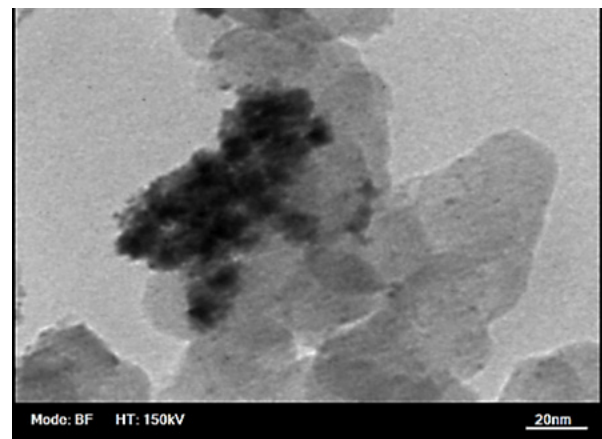**Fig.4. TEM image of catalyst include Pd and Pt with 2:1 molar ratio (GDE 21).**

Fig.3. TEM image of catalyst include Pd and Pt with 3:1 molar ratio (GDE 31).

$$\eta = E - E_{eq} = -b \, log \, \frac{i}{i_0} \qquad (1)$$

Where, η is the over-potential, E_{eq} is the open-circuit voltage, b is the Tafel slope, i is the current density, and i_0 is the exchange of current density for the ORR. The kinetic parameters of the ORR for the GDEs can be obtained from the I -V curves and these equations.
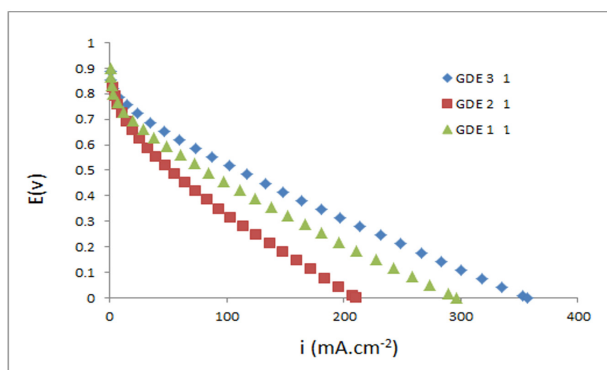
Fig. 5. LSV curve for synthesized catalyst ◊31, □21, Δ11 (Pd:Pt molar ratio) in H₂SO₄ 0.5 M (saturated O₂) with 5 mV.s⁻¹ scan rate at 25 °C.

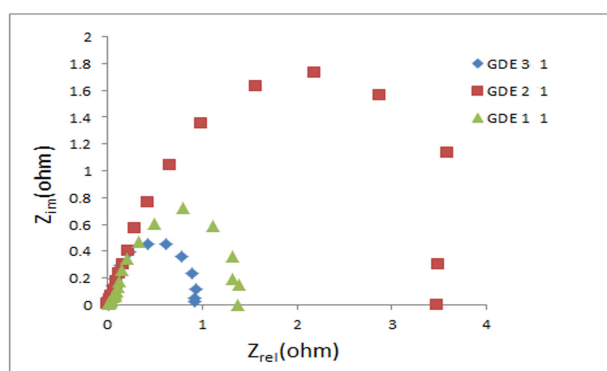**Fig. 6. Nycuist curve for synthesized catalyst ◊31, □21, Δ11 (Pd:Pt molar ratio) in 0.4 V and 100 kHz to 10 mHz.**

The exchange current density is the important kinetic parameter and indicated the rate of reaction on electrode surface. The small Tafel slope at high current density indicated the less activation loss in polarization curve, and then the electrode had better performance (Table 2). The cyclic voltammetry gave the electro active surface area. The columbic charge for hydrogen desorption was used to calculate the electro active surface area (EAS) of each electrode (Table 2) [22]:

$$EAS = \frac{Q_h}{0.21 \times [catalyst]} \qquad (2)$$

Where Q_h is the charge for hydrogen desorption (mC cm⁻²) and [catalyst] is the catalyst loading (mg cm⁻²) and 0.21 (mC cm⁻²) is the charge required to oxidize a monolayer of H₂ on bright catalyst. By using the chronoamperometery experiment and cottrell equation

can calculate the diffusion coefficient of oxygen at GDEs [23]:

$$i = nFA\left(D/\pi t\right)^{1/2} C^* \qquad (3)$$

Where i is the limiting current (mA), n the number of electrons, F is the Faraday constant (96485 Cmol⁻¹), A is the surface area of the electrode (cm²), D is the diffusion coefficient (cm² s⁻¹), t is the time (s), and C^* is the concentration of the reactant.

High diffusion coefficient resulted in to the good accessibility of reactant (Oxygen) and then the good performance for ORR.

It is because of the well dispersion of catalyst that electrochemical behavior of GDE 31 is better than GDE 21 (Fig. 3 and 4) and also, it may be because of the molar ratio effect and consequently the synergism effect in electrocatalyst 11 that electrochemical behavior of GDE 11 is better than GDE 21.

The electrochemical parameters (see Table 2) indicated that the GDE 31 had the best performance for ORR in this series. Paying more attention to the results we can conclude that the 3:1 molar ratio of Pd to Pt had the best particle size and catalyst dispersion and then prepared the better three phase zone than the other ratio for ORR.

The MEA was tested by using the best synthesized catalyst (31) as cathode and Pt/C as anode. As mentioned in table 1 the catalyst loading for MEA was 0.3 mg.cm⁻². The polarization curve obtained at 3 different gas pressures (5, 15 and 25 psi) and showed in Fig 7. The results showed that, increasing the gas pressure would increase the performance of MEA. This result could be attributed to the electro catalyst structure and composition that would supply the good diffusion coefficient of oxygen in cathode (Table 2). In presence work, the maximum power density (679 mw.cm⁻² at 0.41V) was remarkably higher than reported on literature (322 mw.cm⁻² at 0.4 V) for Pt-Pd/C [24].
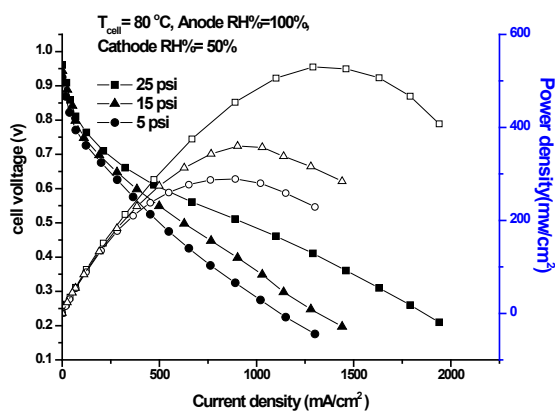
Fig. 7. Polarization curves and power density of catalyst 31 in cathode and Pt/C in anode at different gas pressure o5, Δ15 and □25 psi, cell temperature 80°C, anode RH=100% and cathode RH=50%.

4. Conclusion

In this work, the core-shell catalyst was synthesised by using the impregnation method and hydrothermal on Vulcan surface. The XRD patterns showed that the nano particle size of catalyst was synthesized.

The result of ICP indicates that this method is suitable for synthesis of catalyst. Observation of TEM images characterized the dispersion of catalyst on Vulcan substrate. The electrochemical results indicate performance of GDEs for ORR.

The results of physical and electrochemical investigate that the GDE with 3:1 ratio of Pt: Pd has the better dispersion, particle size and performance for ORR than the other catalyst. The MEA results show that this catalyst has the good performance on ORR. The maximum power density of this catalyst is 679 mw.cm^{-2} at 0.41 V.

5. Reference

[1] Li W., Sun K., Hu Z., Xu B.,” Characteristics of low platinum Pt-BaO catalysts for NOx storage and reduction.”Catal Today, 2010, 153: 103.

[2] Liu P., Wang J., Zhang X., Wei R., Ren X.,”Catalytic performances of dealuminatedHb zeolite supported Pt catalysts doped with Cr in hydroisomerization of n-heptane.” Chem. Eng. J. 2009, 148: 184.

[3] Ali J., Priscilla A., Sylvie L., Josette O. F., Jumas J. C., “Effect of indium in trimetallicPt/Al$_2$O$_3$SnIn-Cl naphtha-reforming catalysts.” J. Catal., 2010, 272: 275.

[4] Matsumoto T., Komatsu T., Arai K., Yamazaki T., et al. “Reduction of Pt usage in fuel cell electrocatalysts with carbon nanotube electrodes.” Chem. Commun., 2004, 7: 840.

[5] Liu Z., Ming Gan L., Hong L., et al. “Carbon-supported Pt nanoparticles as catalysts for proton exchange membrane fuel cells “ J. power sources, 2005, 139: 73.

[6] Moreira J., del Angel P., Ocampo A. L., et al.” Synthesis, characterization and application of a Pd/Vulcan and Pd/C catalyst in a PEM fuel cell.” Int. J. Hydrogen Energy, 2004, 29: 915.

[7] Wanga H., Xu C., Cheng F., et al.”Pd/Pt core–shell nanowire arrays as highly effective electrocatalysts for methanol electrooxidation in direct methanol fuel cells.” Electrochem.Communications, 2008, 10: 1575.

[8] Guo S.J., Fang Y. X., Dong S. J., Wang E. K.,” High-Efficiency and Low-Cost Hybrid Nanomaterial as Enhancing Electrocatalyst: Spongelike Au/Pt Core/Shell Nanomaterial with Hollow Cavity” J. Phys. Chem. C, 2007, 111: 17104.

[9] Zeng J. H., Yang J., Lee J. Y., Zhou W.J.,” Preparation of Carbon-Supported Core−Shell Au−Pt Nanoparticles for Methanol Oxidation Reaction: The Promotional Effect of the Au Core” J. Phys. Chem. B, 2006, 110: 24606.

[10] Tena-Zaera R., Katty A., Bastide S., Levy-Clement C.,” Annealing Effects on the Physical Properties of Electrodeposited ZnO/CdSe Core−Shell Nanowire Arrays.“ Chem. Mat., 2007, 19: 1626.

[11] Zhang G., Zhao Z. Lu G,W. et al. "Core–shell Pt modified Pd/C as an active and durable electrocatalyst for the oxygen reduction reaction in PEMFCs" Applied Catalysis B: Environmental, 2013, 132–133: 183.

[12] Humbert M. P., Smith B. H., Wang Q. et al. "Synthesis and Characterization of Pd –Pt Core –Shell Electrocatalysts for Oxygen Reduction" Electrocatal, 2012, 3: 298.

[13] Zhang L., Kim J., Zhang J. et al. "Ti_4O_7 supported Ru@Pt core–shell catalyst for CO-tolerance in PEM fuel cell hydrogen oxidation reaction" Applied Energy 103, 2013, 507.

[14] Y. Zhang, C. Ma, Y. Zhu et al." Hollow core supported Pt monolayer catalysts for oxygen reduction" Catalysis Today, 2013, 202: 50.

[15] Duan M.Y., Liang R., Tian N. et al. "Self-assembly of Au–Pt core–shell nanoparticles for effective enhancement of methanol electrooxidation." ElectrochimicaActa, 2013, 87: 432.

[16] Shimizu K., Cheng I. F., Wai C. M., "Aqueous treatment of single-walled carbon nanotubes for preparation of Pt–Fe core–shell alloy using galvanic exchange reaction: Selective catalytic activity towards oxygen reduction over methanol oxidation." Electrochem.Communications, 2009, 11: 691.

[17] Gao H., Liao S., Zeng J. et al. "Preparation and characterization of core–shell structured catalysts using PtxPdyas active shell and nano-sized Ru as core for potential direct formic acid fuel cellapplication." ElectrochimicaActa, 2011, 56: 2024.

[18] Gharibi H., javaheri M., Kheirmand M., Mirzaei R. A., "Optimization of the amount of Nafion in multi-walled carbon nanotube/Nafion composites as Pt supports in gas diffusion electrodes for proton exchange membrane fuel cells. " Int. J.Hydrogen Energy, 2011, 36: 13325.

[19] Stamenkovic V., Fowler B., Mun B., et al. "Improved Oxygen Reduction Activity on Pt 3 Ni(111) via Increased Surface Site Availability."Science, 2007, 315: 493.

[20] Thanasilp S., Hunsom M., "Effect of Pt: Pd atomic ratio in Pt-Pd/C electrocatalyst-coated membrane on the electrocatalytic activity of ORR in PEM fuel cells." Renewable Energy, 2011, 36: 1795.

[21] Bockris JO'M., "Modern electro chemistry."2nd ed. Plenum; 2000.p. 1054.

[22] Pozio A., Francesco M. D., Cemmi A., et al. "Comparison of high surface Pt/C catalysts by cyclic voltammetry."J. Power Sources, 2002,105: 13.

[23] Wang J., "Analytical electrochemistry." 2nd ed. Wiley; 2000.p 60.

[24] Limpattayanate S., Hunsom M.," Electrocatalytic activity of Pt- Pdelectrocatalysts for the oxygen reduction reaction in proton exchange membrane fuel cells: Effect ofsupports." Renewable Energy, 2014, 63: 205.