Preparation of Pt and PtRu Nanocatalysts Support on Carbon Black N115 for Proton Exchange Membrane Fuel Cell (PEMFC)

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ABSTRACT

In this work, carbon N115-supported Pt and Pt-Ru nanoparticles were prepared by a simple microwave-assisted solution method using ethylene glycol as both a reducing agent and solvent. By microwave radiation, Pt and Pt-Ru solution can be reduced by ethylene glycol and become Pt metal or Pt-Ru alloy support on carbon. Depending on these procedures Pt/C and Pt-Ru/C nanocatalysts were obtained. The particle size of Pt/C catalysts was measured to be about 2.50-3.00 nm and Pt-Ru/C catalysts was about 1.50-2.00 nm. Pt/C catalysts dispersed more homogeneously on carbon supporter than Pt-Ru/C catalysts. The catalyst products were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and transmission electron microscopy (TEM) techniques.

Key words: Pt and PtRu supported on carbon catalysts, Microwave-assisted solution method, Proton exchange membrane fuel cell (PEMFC)

INTRODUCTION

In these recent years, there has been a considerable interest in the development of renewable energy to solve the energy shortage problem. Pollution produced by the consumption of petroleum oil is a consequence that needs to be urgently considered. Because of the advantage of zero emission, a fuel cell, especially Proton Exchange Membrane Fuel Cell (PEMFC) was introduced in order to reduce the consumption of petroleum oil and the air pollution. PEMFC is an energy source that can operate whenever we supply the fuel to it. By feeding hydrogen gas at the anode and oxygen gas at the cathode with the assistance of appropriate catalysts, fuel cell can generate energy in the electric form without any air pollution. The reactions at anode, cathode and overall of PEMFC are

anode: $H_2 \rightarrow 2H^+ + 2e^-$ (1)

cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (2)

overall: $2H_2 + O_2 \rightarrow 2H_2O + \text{heat}$ (3)

The electrochemical performance of fuel cell depends on the properties of the catalysts. In general, the catalyst is prepared as nanometer size of noble metal

such as Pt on high surface area carbon supporter. Later on, due to the very high cost of Pt, the Pt alloy was introduced in order to reduce the amount of Pt and to enhance the performance of the catalysts (Jaffray et al., 2003). Carbon support materials also play an important role in the catalyst performance. Carbon supporter should have an excellent combination of electron conductivity, corrosion resistance, surface properties and low cost for fuel cell commercialization. Therefore, several research groups have been using various carbon support materials such as carbon nanotube (Wang et al., 2004), graphitic carbon nanofiber (Steigerwalt et al., 2001), carbon nanohorn (Yoshitake et al., 2002), carbon nanocoil (Hyeon et al., 2003), ordered uniform porous carbon networks (Yu et al., 2002), and so on, in order to replace commonly used Vulcan XC-72. However, the promising carbon support that could replace Vulcan XC-72 is not discovered yet. In this work, carbon black N115 was selected to be a supporter material due to its low cost, good conductivity and acceptable in high surface area and small particle. For the preparation of catalyst, it can be done by several methods. Impregnation method (Fujiwara et al., 2002; Che et al., 1998; Antolini et al., 2001; Steigerwalt et al., 2001; Hills et al., 2003) is done by adding the equivolume of Pt solution to carbon and basidified the solution by adding KOH solution for the uniform distribution and homogeneous dispersion on the carbon supporter. Then the solution was calcined and pyrolyzed with reducing gas at various temperature and time. Solution method (Sarakonsri et al., 2006) is always used with the basis of adding reducing agent in order to reduce Pt^{4+} to Pt nanoparticle support on carbon.

The microwave heated polyol (Yu et al., 1999; Baghurst et al., 1988; Komarneni et al., 2002; Chen et al., 2002; Liu et al., 2004) which is a simple and convenient technique that can provide the nanosize and good dispersion of Pt and PtRu alloy supported on carbon was selected in this experiment. Microwave radiator was used as the source of energy for initiating the redox reaction and inducing the solvent molecule (ethylene glycol) to reduce Pt^{4+} to Pt and Ru^{3+} to Ru nanoparticle supported on carbon. However, various synthesis parameters can affect the size and dispersion of the supported Pt metal and PtRu alloy on carbon involving the amount of water in the substrate solution, duration of sample in microwave radiator and the position of sample in microwave radiator. Furthermore, the good catalytic activity of catalysts depends on the small size (2-6 nm.) and good dispersion of metal or alloy on carbon supporter. Therefore it is important to prepare catalysts by controlling these parameters to obtain the high efficiency Pt/C fuel cell catalysts.

MATERIALS AND METHODS

Preparation of catalysts by microwave radiation method

Microwave radiation method was used to prepare nanoparticle 20%wtPt/C and 20%wtPtRu/C with well dispersion on the carbon surface. The description procedure is explained, as followed. Carbon black N115 (Thai carbon black public CO., LTD.) was pre-washed with 1 M H_2SO_4 (Lab scan, 98% purity) for 24 h to dematerialize the carbon impurities. Then it was washed in distilled water to

remove sulfuric acid and other impurities, followed by drying in an oven at 80°C overnight to obtain the cleaned carbon. After that 0.04 g of cleaned carbon was dispersed in 25 ml ethylene glycol (J.T. Baker, 99.9% purity). For Pt/C preparation, 5 ml. of 1 mM aqueous solution Pt was added and 0.75 ml. of 0.05 M Pt solution (H_2Cl_6Pt, Sigma) equivolume to 0.05 M Ru solution ($RuCl_3.XH_2O$, Aldrich) were added for the preparation of PtRu/C catalysts. Then the solution was basidified with 0.44 M KOH (BDH, 85.0% purity) 0.75 ml. An hour of high frequency sonication was applied to obtain a well dispersion of carbon in Pt ethylene glycol solution. Then the mixture was put into microwave radiator (SHARP Model: R-26 PS 800W.) for 50 s. and the resulting mixture was left to cool down to room temperature gradually. The product particle was collected by centrifugation which was then washed by methanol (J.T. Baker, 100.0% purity) and dried in an oven at 80°C for 24 hours.

Characterization of Pt/C catalysts

The phases and elemental composition of prepared catalysts were determined by X-ray powder diffraction (XRD, Siemen D500/501, Cu Kα (λ1.54) Ni filter, 2θ = 10-60°) and Energy Dispersive Spectroscopy (EDS) (JEOL JSM-6335F), respectively. The average sizes of Pt and PtRu particles were calculated by Debye-Scherrer equation using Pt (111), Pt (200), and Ru (100) peak. Pt and PtRu dispersion on carbon and their particle sizes were also checked using Transmission Electron Microscope (TEM) (JEOL JEM-2010) and Scanning Electron Microscopy (SEM) (JEOL JSM-5910LV) techniques.

RESULTS AND DISSCUSSION

The X-ray diffraction patterns of the prepared catalysts as shown in Figure 1 indicate a typical crystallographic structure of Pt ((111) 2θ = 39.673, (200) 2θ = 46.284) and Ru ((100) 2θ = 43.43) according to JCPDS number 04-0802 and 06-0663. The diffraction peak of carbon N115 ((002) 2θ = 25.20) has been shifted from the diffraction peak of carbon graphite ((002) 2θ = 26.43, JCPDS number 01-0640) by 1o because carbon N115 is partially amorphous and it is possible that its crystallographic structure has been distorted. The Pt particle size was calculated by using Scherrer's equation;

$$Br \cos \theta = k\lambda/L + \eta \sin \theta \quad (4)$$

Where η is strain, k is the numerical constant and λ is the wavelength of X-ray.

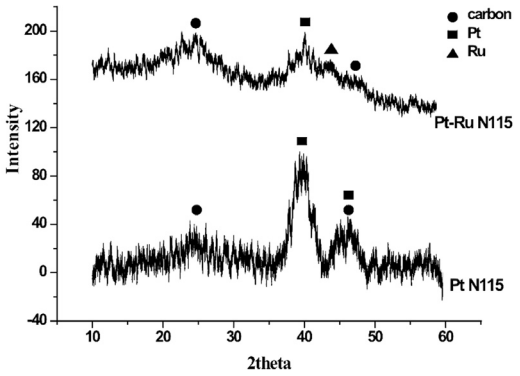


Figure 1. X-ray diffraction patterns of Pt and PtRu supported carbon N115.

The width at half maximum of each peak (Br) and 2θ was measured. Then a linear graph setting Brcosθ as x axis and sinθ as y axis was plotted. The slope which was equal to kλ/L was obtained. Therefore, the mean particle size (L) of Pt was calculated to be 5.93 nm. For the PtRu/C catalysts, the mean size of Pt particle was 6.09 nm and Ru was 5.55 nm. Moreover, the amounts of Pt and PtRu on carbon were obtained by the volume fraction calculation using direct comparison method. The detail of the calculation can be found in Element of X-ray Diffraction second edition (Cullity et al., 1978). The constant values are shown in Table 1, and the calculated volume fraction and calculated weight fraction are summarized in Table 2. The volume fraction and weight fraction of 53.75wt% Pt/C and 41.48wt% PtRu/C were obtained. It was noticed that calculated weight fraction values were higher than initial calculation from starting materials because of the partially amorphous of carbon N115 lowering the peak area of C(002).

Table 1. The constant values in X-ray diffraction of carbon and Pt for volume fraction calculation.

Phase(hkl)	Volume(CD) $\langle x10^{-30} \rangle$	Structure factor (F^2)	Multiplicity factor (P)	2θ	R
C(002)	35.93	286.47	2	25.20	0.795 x 10^{61}
Pt(111)	59.87	60552.96	8	39.67	102 x 10^{61}
Ru(100)	28.06	2855.87	12	43.43	27.0 x 10^{61}

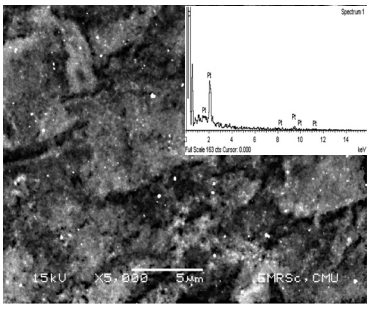
$$R = \left\{\frac{1}{V^2}\right\}\left[|F|^2 P\left\{\frac{1+\cos^2 2\theta \cos^2 2\alpha}{\sin^2\theta \cos\theta\left(1+\cos^2 2\alpha\right)}\right\}\right] \quad (5)$$

Where V: Volume of unit cell

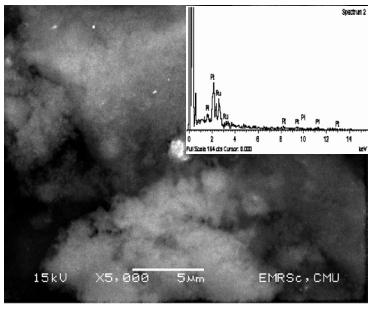
Table 2. Calculated volume fraction and weight fraction.

Catalysts	Element	2θ	Peak area	Volume fraction(%)	Density(kg/m^3)	Weight fraction (%)
Pt/C	Pt	39.67	87.80	1.80	21450	53.75
	C	25.20	206.33	98.20	338	46.25
PtRu/C	Pt	39.67	1022	0.39	21450	57.94
	Ru	43.43	488.3	0.99	12400	20
	C	25.20	1422	98.45	338	21.48

The back scattering SEM images (Figure 2 (a) and (b)) and EDS (Figure 2 (c) and (d)) of prepared catalysts shows that Pt and PtRu particles are well dispersed on the carbon surface. However, there are a few bright spots observe, which corresponded to particles agglomeration. Figure 3 (a) and (b) show TEM images of Pt and PtRu supported carbon N115, respectively. TEM images illustrate the homogeneously dispersed of Pt particles on carbon over PtRu particles. Ring diffraction pattern of Pt/C catalysts show in Figure 3 (c) indicates the crystallographic planes of carbon N115 (002), Pt (111) and (200). For PtRu/C catalysts, TEM images which illustrated in Figure 3 (d) shows the same crystallographic planes of carbon N115 and Pt as Pt/C catalysts. However, the missing ring pattern of Ru could be explained, as due to the d spacing of Ru (100) is located in between the planes of Pt (111) and (200). Therefore, the ring diffraction pattern of Ru (100) was very hard to observed. Moreover, the ring diffraction pattern of PtRu/C catalysts was observed as clouded area and obscured indicating the very small particle size of catalysts. Figure 4 shows histogram of Pt and PtRu size, measured from TEM images, the Pt particle size is about 2.50-3.00 nm. and the PtRu size is 1.50-2.00 nm. These measurements were in accordance with the broadening in XRD patterns. The smaller particle size, the higher peak broadening. It was noticed that the particle size calculated by Scherrer's equation from XRD spectrum is bigger than the measured value from TEM images because the calculation by Scherrer's equation is a mean particle size of whole prepared catalysts but TEM images measurement was the sampling from the whole catalysts.



(a)



(b)

Figure 2. Backscattered images and EDS spectrum of Pt/C and PtRu/C catalysts; (a) Pt/C and its EDS spectrum, (b) Backscattered image of Pt/C and its EDS spectrum.

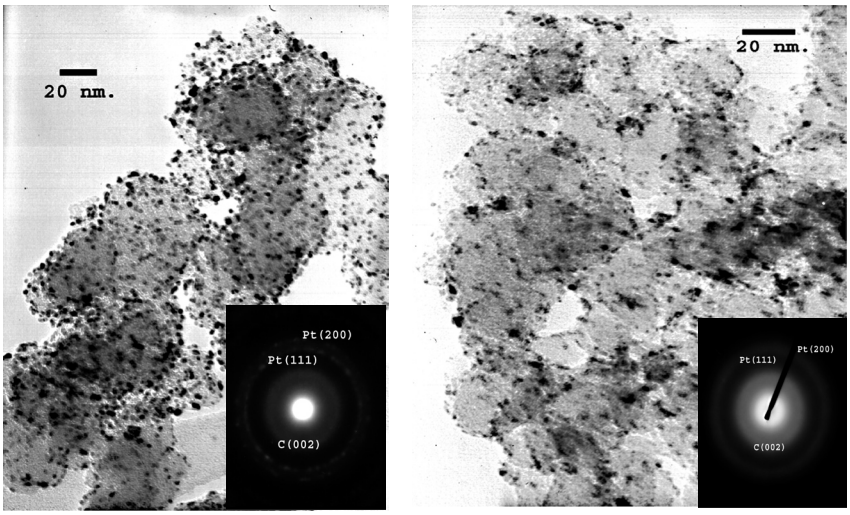


Figure 3. TEM images and diffraction patterns; (a) TEM image of Pt/C and its diffraction pattern, (b) TEM image of PtRu/C and its diffraction pattern.

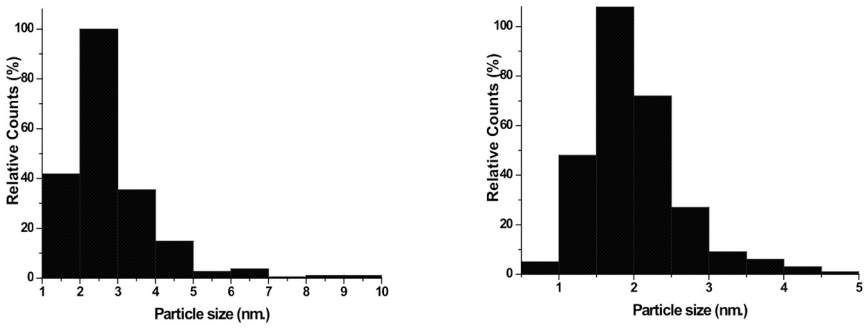


Figure 4. Histogram of particle sizes; (a) Pt/C, (b) PtRu/C on carbon supporter.

CONCLUSION

The well dispersed Pt and PtRu supported carbon N115 catalysts with 2.50-3.00 nm and 1.50-2.00 nm of Pt and PtRu particle size, respectively, can be obtained using an assisted microwave radiation method. The powder X-ray diffraction patterns, EDS spectrum, and Ring patterns of catalysts indicated Pt metal and PtRu alloy supported on carbon N115. TEM images showed the uniform dispersion of Pt particle on carbon. Moreover, the calculated particle size from XRD patterns and the measurement from TEM images ensured the nanosize of Pt and PtRu particles.

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