FABRICATION OF ELECTROCATALYST PLATINUM/CARBON XC72R FOR DIRECT METHANOL FUEL CELLS (DMFC) APPLICATION

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ABSTRACT

Platinum/Carbon XC72R (Pt/C) nanocomposite was synthesized *in-situ* by polyol method. Precursor of hexahydrated chloroplatinic acid $H_2PtCl_6.6H_2O$ was reduced by ethylene glycol (EG) so as to form Pt nanoparticles which were deposited on the surface of carbon. Pt/C composites (untreated or treated with 5% HNO_3 solution) were synthesized at pH = 6.5 and pH=11. The XRD pattern of Pt/C showed peaks assigned to the crystalline structure of Pt and carbon. TEM images showed that Pt nanoparticles dropped carbon are ultrafine spheres and the particles obtain sizes from 2 to 6 nm which are mostly concentrated on size of 3 nm. The electrocatalytic activity of Pt/C catalysts toward methanol oxidation was examined by cyclic voltammetry (CV). Pt/treated XC72R (pH=11) at potential (0.69V) exhibited better electroactivity (628mA/mgPt).

Keywords: platinum/carbon nanocomposite, electrocatalyst, direct methanol fuel cells (DMFC), cyclic voltammetry (CV).

1. INTRODUCTION

Among different types of fuel cells, direct methanol fuel cells (DMFC) are promising as highly efficient and clean energy source [1]. Methanol offers several advantages over hydrogen as including the ease the transportation and storage and high theoretical energy density. The methanol oxidation reaction (MOR) occurs at the anode in DMFC. Platinum is the most promising candidate among pure metals for application in DMFC. Platinum has the highest activity toward the dissociative adsorption of methanol. However, pure Pt surface is poisoned by CO, a by-product of MOR. Researchers have focused on dispersing nanocatalyst on high surface area supporting materials. Decreasing the amount of Pt used in fuel cell via increasing its utilization efficiency has been one of the interests during the past decade [2, 3]. The utilization

efficiency of catalysts is strongly related to their particle sizes, distributions, and types of support. According to Senthil S.M. et al. [6], activated carbon is considered to be used as one of the best catalyst supports. For the preparation of Pt/C nanocomposite, polyol method was reported as an attractive route since metal nanoparticles with narrow size distribution could be obtained and deposited on carbon support.

In this paper, Pt/C nanocomposites were synthesized *in-situ* by polyol method and characterized by XRD, TEM and electrochemical measurements.

2. EXPERIMENTAL

2.1. Chemicals

Chloroplatinic acid, $H_2PtCl_6.6H_2O$ (99 %), Prolabo; Ethylene glycol, $C_2H_6O_2$ (99 %), China; Vulcan XC72R carbon powder (99 %) Cabot; Acetone C_3H_6O (99.5 %), China; Nitric acid, HNO_3 (65 - 68 %), China; Sulfuric acid, H_2SO_4 (95 - 97 %), Merck; Methanol, CH_3OH (99.8 %), Merck; Nafion 117 solution (5 wt.% , Aldrich). Millipore water with 18 MΩ cm resistivity.

2.2. Methodogy

2.2.1. Treatment method of Carbon Vulcan XC72R: Carbon powder (0.5 g) was dispersed in a round bottom flask with 500 ml of the 5% HNO_3 solution. The mixture was refluxed for 16 h at 120 ^{0}C [6]. Treated carbons were centrifugated with 3000 rpm in 10 min, were washed several times with de-ionized water and acetone and then dried at 100 ^{0}C in an oven for 2 h.

2.2.2. Treated or untreated Vulcan XC72R carbon powder (0.1 g) was dispersed in 40 ml of EG, 20ml de-ionized water without NaOH (pH=6.5) or added NaOH 1 M solution (adjusted pH=11) in a three-neck flask. The mixture was stirred by using a magnetic bar under a nitrogen atmosphere. A 2×10^{-2} M H_2PtCl_6 solution was added drop wise to the mixture and then the mixture was refluxed at 110 ^{0}C for 3 h and stirred over night. The resultant Pt/C catalyst was centrifugated at 6000 rpm in 10 min, washed several times with de-ionized water and acetone then dried at 110 ^{0}C in a hot air oven for 2 h. All samples obtained 25 loading of Pt on carbon by weight.

2.2.3. TEM images were taken by JEM-1400, University of Technology-VNU HCM City. The histogram of the particle size distribution and the average diameter was obtained by measuring about 20-30 particles. XRD of Pt/C nanocomposite was characterized using D8 advanced Bragg X Ray powder diffraction with Cu Kα radiation (University of Technology-VNU HCM City).

2.2.4. Electrochemical measurements

à. Fabrication of electrode

Typically, 5 mg Pt/C nanocomposite was ultrasonically suspended in 2 ml of ethanol and 50 µl of Nafion 117 for 30 min to form a homogeneous ink. Then 2 µl of the ink was spread onto the surface of the glassy carbon electrode (GC, with a diameter of 4 mm) with the micropipette to form a thin film on the GC and to dry at room temperature (repeated 3 times) to obtain a uniform catalyst thin film.

b. Cyclic voltammetry

The electrochemical measurements were performed on an Autolab bipotentiostat instrument (PGSTAT 100N,Eco Chemie, the Nertherland) using NOVA 1.7 software in the three electrode glass cell with glassy carbon working electrode, Pt counter electrode, and a Ag/AgCl reference electrode. All potentials correspond to silver chloride electrode (0.21 V vs NHE).

The working electrode potential was scanned 10 cycles between 0.0 and 1.0 V in N_2-saturated 0.5 M sulfuric acid solution with scan rate of 100 mV/s to clean the electrode surface. Then it was measured between 0.0 and 1.0 V in N_2-saturated 0.5 M sulfuric acid solution with scan rate of 100 mV/s. After that, the CV curves for the Pt/C electrocatalyst in mixture of 1 M methanol solution and 0.5 M sulfuric acid (saturated with N_2) were recorded between 0.0 and 0.9 V with scan rate of 100 mV/s. All electrochemical experiments were carried out at room temperature and ambient pressure employing 0.5 M H_2SO_4 as the electrolyte solution.

3. RESULTS AND DISCUSSION

3.1. Physicochemical characterization

3.1.1. XRD

The XRD patterns of the treated and untreated Vulcan XC72R are shown in Fig.1. The peak around 25^0 corresponds to the (002) planes of graphitized carbon Fig.1. Figure 2 showed the XRD pattern for nanocomposite of Pt with the untreated Vulcan XC72R. The peak around 25^0 corresponds to the (002) planes of graphitized carbon and the diffraction peaks which located at 2θ value of 39.6; 46.3; 67.4; and 81.4^0 were assigned to (111), (200), (220) and (311) planes, respectively, characteristic of fcc crystal structure of platinum.

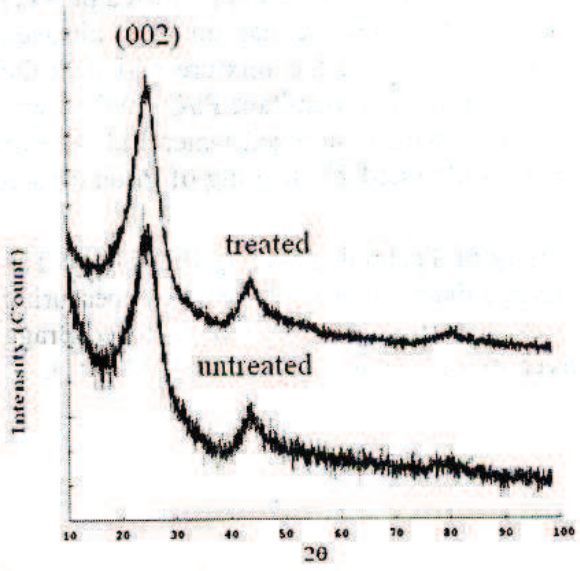

Fig. 1. XRD pattern of treated and untreated Vulcan XC72R

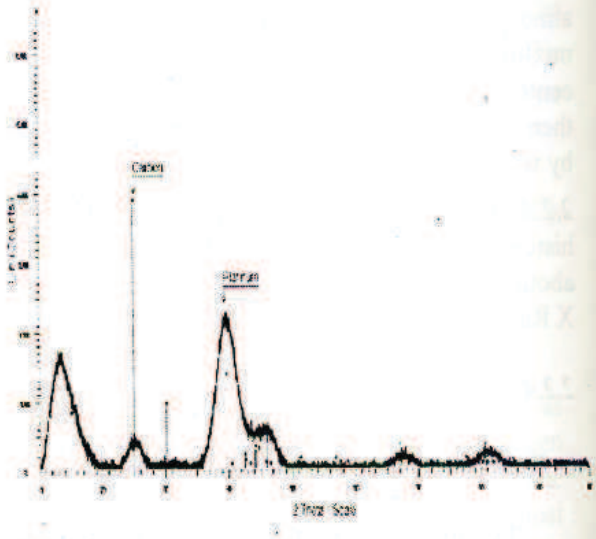

Fig. 2. XRD pattern of untreated Vulcan XC72R/platinum composite (pH = 11)

3.1.2. TEM Images

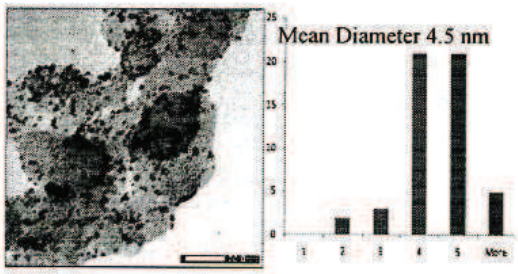

Fig. 3. TEM Image of untreated Vulcan XC72R/platinum nanocomposite (pH = 11)

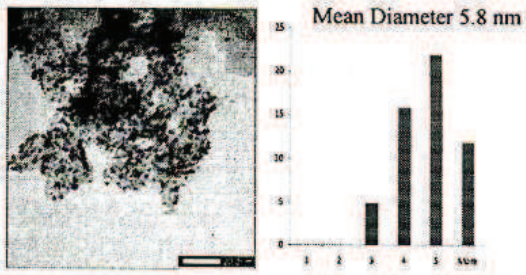

Fig. 4. TEM Image of untreated Vulcan XC72R/platinum nanocomposite (pH = 6.5)

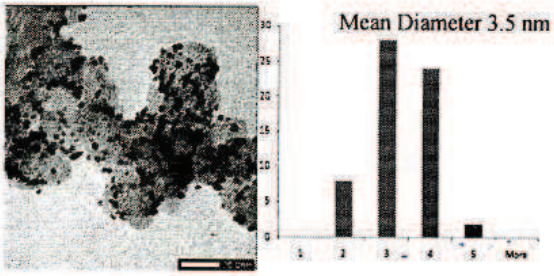

Fig.5. TEM Image of treated Vulcan XC-72R/platinum nanocomposite (pH=6.5)

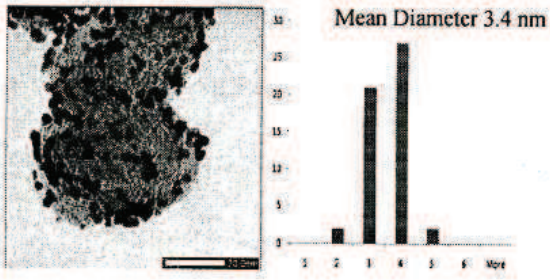

Fig. 6. TEM Image of treated Vulcan XC72R/platinum nanocomposite (pH = 11)

Figures 3, 4, 5, 6 showed the TEM images and distribution of the Pt/untreated and treated XC72R (pH = 6.5) the Pt/untreated and treated XC72R (pH = 11), respectively. The average diameters of Pt nanoparticles are showed in table 1. Increasing the solution pH from 6.5 (without NaOH) to 11 (with 270 µl 1 M NaOH solution), the Pt particle size is reduced down from 5.8 nm to 4.5 nm. This decrease in particle size is therefore attributed to the presence of glycolate ions in the solution resulting from the change in pH of solution from 6.5 to 11. To Hyung-suk Oh et al. [5], the stabilizing action of glycolate ions helps in controlling the particle size. Upon increasing the concentration of glycolate ions in the synthesis solution by increasing the solution pH, thus the particle size is decreased.

Table 1. Electrochemical activity parameters obtained for methanol oxidation reaction

Sample	Nature of carbon XC72R	pH	Pt particle size from TEM (nm)	Methanol oxidation				
				$I_{f(forward)}$ (mA/cm^2)	$I_{r(reverse)}$ (mA/cm^2)	I_f/I_r	I*(mA)	MA (mA/mgPt)
P1	Untreated	11	4.5	11.4	12.3	0.927	1.469	500
P2	Treated	11	3.4	14.6	16.8	0.869	1.837	628
P3	Treated	6.5	3.5	11.4	12.0	0.950	1.434	490

3.2. Electrochemical characterization

Figure 7 showed the cyclic voltammograms which were obtained for catalyst slurry of each Pt/C catalyst (untreated and treated at pH = 6.5 and pH = 11) deposited on a glassy carbon electrode. The voltammograms were recorded in 0.5 M sulfuric acid solution in the range of 0.0-1.0V with a sweep rate of 100 mVs^{-1}. In the oxidation scan, the CVs of treated XC72R (pH = 6.5 or pH = 11) showed a potential of around 0.37 V. This is explained by the carbonaceous species oxidizing to CO_2 on the carbon support surface. In the reduction scan, the CVs showed a peak around 0.55 V, which corresponded to the reduction of surface-oxide on Pt nanoparticles. The feature of the peak of treated XC72R (pH = 11) is that the position of peak at potential (0.69 V) compared with the peak of untreated XC72R (pH = 11) of 0.70 V and the peak of treated XC72R (pH = 6.5) of 0.65 V corresponding with a decrease in the particle size untreated XC72R (4.5 nm), treated pH = 11 (3.5 nm) and XC72R pH = 6.5 (3.4 nm). This tendency indicated that the oxygen species were more strongly adsorbed on smaller Pt particles, which were consistent with several reports [3, 4, 5].

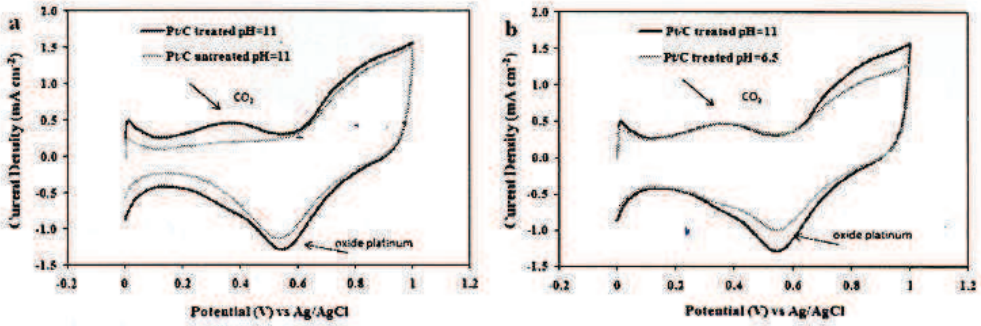

Figure 7. Cyclic voltammograms recorded at 100 mVs^{-1} in N_2 saturated 0.5 M sulfuric acid for a) P1 and P2. b) P2 and P3

The CV analyses for evaluating methanol oxidation efficiency of the electrodes were conducted at a scan rate 100 mVs^{-1} with potential ranging from 0.0 - 0.9 V for 5 cycles (Fig. 8). The electrode efficiency on methanol oxidation was compared in terms of items of forward current density, a ratio of the forward peak current density to the reverse peak current density and the mass activity (peak current density of methanol oxidation obtained from cyclic voltammogram per unit Pt loading mass). Among the forward peak current densities, Pt/ treated XC72R (pH = 11) exhibited a relatively higher value than those of others.

4. CONCLUSIONS

Pt/C nanocomposite was synthesized successfully *in-situ* by polyol method. The XRD pattern showed peaks assigned to the crystalline structure of Pt and Carbon. TEM images showed that Pt nanoparticles on carbon were ultrafine spheres and the particles obtain sizes from 2 to 6 nm which is mostly concentrated on size of 3nm. Through the electrochemical tests of methanol oxidation on catalyst electrode, the electrode with Pt/treated XC72R (pH = 11) at potential (0.69 V) exhibited better electro-activity (628 mA/mgPt).

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TÓM TẮT

CHẾ TẠO XÚC TÁC ĐIỆN HÓA PLATIN/CACBON XC72R ỨNG DỤNG CHO PIN NHIÊN LIỆU METANOL

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Nanocomposite Platin/cacbon(Pt/C) được điều chế *in-situ* bằng phương pháp polyol. Hạt nano Platin được chế tạo từ bằng cách khử axit cloroplatinic H_2PtCl_6 với chất khử là etilen glycol phủ lên bề mặt cacbon hoạt tính. Pt/C composite (cacbon được xử lí hoặc không xử lí với dung dịch HNO_3 5 %) được điều chế trong dung dịch có pH = 6.5 và pH = 11. Platin và cacbon của Pt/C được xác nhận qua giản đồ XRD xuất hiện tín hiệu đỉnh cấu trúc tinh thể của Pt và cacbon. Những hạt nano Pt phủ trên cacbon là những hình cầu đồng đều và kích thước phân bố từ 2 đến 6 nm tập trung nhiều nhất ở 3 nm được thể hiện qua ảnh TEM. Sử dụng phương pháp quét thế vòng tuần hoàn (CV) nhằm xác định hoạt tính xúc tác điện hóa của Pt/C trên phản ứng oxi hóa metanol. Với khảo sát CV, Pt/ cacbon được xử lí (pH = 11) có hoạt tính xúc tác điện hóa cao nhất (628 mA/mgPt) tại thế (0.69 V).

Từ khóa: nanocomposite Platin/cacbon, xúc tác điện hóa, pin nhiên liệu metanol (DMFC), quét thế vòng tuần hoàn (CV).