Journal of Applied Electrochemistry **34**: 461–467, 2004.

Effect of preparation conditions of Pt/C catalysts on oxygen electrode performance in proton exchange membrane fuel cells

J.H. TIAN*, F.B. WANG, ZH.Q. SHAN, R.J. WANG and J.Y. ZHANG
School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072 P.R. China
*(*author for correspondence, fax: +86 022 27403389, e-mail: jhtian@eyou.com)*

Received 31 January 2003; accepted in revised form 13 November 2003

Key words: heat-treated carbon black support, impregnation–reduction, proton exchange membrane fuel cell (PEMFC), Pt/C catalyst

Abstract

Supported Pt/C catalyst with 3.2 nm platinum crystallites was prepared by the impregnation–reduction method. The various preparation conditions, such as the reaction temperature, the concentration of precursor H_2PtCl_6 solution and the different reducing agents, and the relationship between the preparation conditions and the catalyst performance were studied. The carbon black support after heat treatment in N_2 showed improved platinum dispersion. The particle size and the degree of dispersion of Pt on the carbon black support were observed by transmission electron microscopy (TEM). The crystal phase composition of Pt in the catalyst was determined by X-ray diffraction (XRD). The surface characteristics of the carbon black support and the Pt/C catalyst were studied by X-ray photoelectron spectroscopy (XPS). The electrochemical characteristics of the Pt/C catalysts were evaluated from current–voltage curves of the membrane electrode assembly (MEA) in a proton exchange membrane fuel cell.

1. Introduction

The proton exchange membrane fuel cell (PEMFC) is a highly attractive power source for mobile and stationary applications due to its high power density at lower temperatures (55–95 °C) and its compact design. A large amount of work has been devoted to reduce the material costs of PEMFCs to achieve their widespread application, including the method of preparing a Pt catalyst with a large specific surface area to minimize the amount (and cost) of Pt required for a given level of activity.

Platinum remains the electrocatalyst of choice because of the poor reversibility of cathodic oxygen reduction ($i_0 \approx 10^{-10}$ A cm^{-2} at room temperature). To obtain the optimal utilization of Pt, it is generally dispersed as small particles on a conductive support, typically a high surface area carbon black. The highly dispersed nanometer-sized Pt catalysts can be prepared by the impregnation–reduction, colloid and inclusion method [1–3]. Although smaller Pt particles can be obtained by the last two methods, the first is of more practical importance because its preparation process is simple and easy to control.

This paper presents a study of the impregnation–reduction method for the preparation of Pt/C catalysts, including the optimization of preparation conditions and selection of a suitable carbon black support and reducers. The heat-treatment technology is used for the treatment of the carbon support. The size of the Pt particles can affect the surface structure and the electrocatalytic performance of catalysts, and is essentially controlled by the preparation conditions.

2. Experimental details

2.1. *Pretreatment of carbon black support*

Commercial carbon black Vulcan XC-72 with a specific surface area of 250 m^2 g^{-1} was used in the experiment. The carbon black was calcined at 873 K for 30 min in N_2 (99.99 wt %), and then used as a carrier to prepare Pt/C catalysts.

2.2. *Preparation of Pt/C catalysts*

Pt/C catalysts were prepared by means of the impregnation–reduction method. The preparation process was carried out in the following steps: (i) 5 ml water and 5 ml isopropanol were added to 200 mg carbon black, and then the suspension was ultrasonically stirred for 15 min; (ii) 5 ml H_2PtO_6 aqueous solution with a platinum concentration of 0.01 g ml^{-1} was added to the suspension, and then ultrasonically stirred for 30 min; (iii) the pH value of the suspension was adjusted to about 8 or 9 by adding 1 mol l^{-1} Na_2CO_3 aqueous solution; (iv) an excessive amount of reducing agents (e.g., the aqueous solution of formaldehyde) was added slowly into the suspension in one hour under stirring and then kept the agitation for 2 h; and, finally, (v) the suspension was filtered, washed with deionized water, and then dried in vacuum for 6 h at a temperature of 353 K.

2.3. *Relative physio-chemical characterization for Pt/C catalysts and carbon black supports*

The size and dispersion status of the Pt particles on the surface of carbon blacks were observed by TEM on Hitachi H-700 with a magnification of 1.9×10^5.

X-ray diffraction analysis (XRD) of the crystal phase composition of Pt/C catalysts and the carbon blacks was carried out on Rigaku D/max-2500 (graphite monochromater, CuK_α), with a working current of 100 mA and a working voltage of 40 kV.

X-ray photoelectron spectroscopy analysis (XPS) of Pt/C catalysts and carbon blacks was performed on PHI1600 (AlK_α) with a pass energy of 93.9 eV. A vacuum of about 10^{-8}–10^{-9} Pa was maintained during the whole operation. The combination energy of carbon 1s (284.6 eV) was chosen as a reference.

2.4. *Electrochemical measurement of Pt/C catalysts*

2.4.1. *Preparation of membrane electrode assembles (MEA)*

Pt/C catalyst, an appropriate amount of the deionized water and the isopropanol were mixed using an ultrasonic stirrer for 15 min, and then the 5 wt % Nafion® solution (Aldrich Chem.) was added to the mixture. The ratio of dry Nafion® to Pt/C was 1:3 by weight. Having been stirred for 30 min, the formed ‘ink’ was dried within the range 313–323 K in vacuum, until it became a porridge mixture. The ‘porridge’ was smeared on two pieces of 2 cm × 2 cm carbon papers (EC-TP1-060, Electrochem. Inc.) with the brushing technique, and then coated with the 5 wt % Nafion® solution. The two pieces of electrodes thus obtained were dried in air at room temperature, and then hot-pressed with a membrane Nafion®115 (Dupont Corp.) for 90 s under 0.35 MPa at 405 K. The treating method of a Nafion® membrane reported in the literature [4] was adopted. The loadings of Pt in MEA and the dry Nafion® were 0.4 mg cm^{-2} and 0.65 mg cm^{-2}, respectively.

2.4.2. *Electrochemical measurement of MEA*

The MEA obtained was mounted in a single cell with stainless steel end plates and graphite collector plates, which was designed with parallel ribbed channels for gas manifolding. The total geometric reaction area of the MEA was 4 cm^2. The reagent gas (hydrogen or oxygen) had a purity of 99.9%. A forced two-step activation process was carried out to make the cell run steadily. First, the pressures of hydrogen and oxygen were controlled at 0.10 and 0.12 MPa, respectively, and the two gases were separately humidified by passing through water at 333 and 323 K. The cell temperature was held at 323 K. The forced current density was gradually adjusted to 0.2 A cm^{-2} and the cell kept running for 12 h under these conditions. In the second activation process, the pressure of H_2 and O_2 were increased to 0.2 MPa and the humidification temperature of H_2 and O_2 were increased to 343 and 338 K, respectively. The cell temperature was held at 343 K and the current density was adjusted up to 0.5 A cm^{-2}, followed by running the cell for 8 h under above conditions. When the two-step activation process was finished, the *I*/*E* curves were measured with an electronic load.

3. Results and discussions

3.1. *Effects of preparation conditions of Pt/C catalysts*

3.1.1. *Effects of different kinds of reducing agents*

Three different kinds of reducing agents (i.e., aqueous solutions of formaldehyde, formic acid and KBH_4) were applied in the work. The mean particle sizes (d) of Pt in the prepared Pt/C catalysts were measured by TEM as shown in Table 1, where the related specific areas are also reported. The mean particle size of Pt was estimated according to Equation 1 [5]:

$$d = \frac{\sum f_i d_i^3}{\sum f_i d_i^2} \tag{1}$$

where d was the mean particle size and f_i was the occurrence frequency of the particles with a diameter of d_i in the sample. The specific surface area of Pt was calculated by the Equation 2 [6]:

Table 1. Properties of Pt/C catalysts prepared under different conditions

Catalyst	Reducing agent	Pt content in H_2PtCl_6 solution /g ml^{-1}	Reaction temp. /K	Particle size of Pt, d /nm	Specific surface area, s /m^{2}g^{-1}
1	0.05 mol l^{-1}KBH_4	0.01	313	6.3	44.5
2	0.15 mol l^{-1}HCOOH	0.01	313	4.6	60.0
3	0.15 mol l^{-1}HCHO	0.01	313	4.2	67.1
4	0.15 mol l^{-1}HCHO	0.005	313	5.2	53.9
5	0.15 mol l^{-1}HCHO	0.02	313	4.2	66.8
6	0.15 mol l^{-1}HCHO	0.033	313	4.3	65.2
7	0.15 mol l^{-1}HCHO	0.01	333	5.4	50.0
8	0.15 mol l^{-1}HCHO	0.01	353	5.8	46.6

$$s = \frac{6000}{\rho d} \quad (2)$$

where s was the specific surface area of Pt, ρ was the density of metal Pt (21.4 g cm^{-3}), and d was the diameter of the Pt particle, which was defined as the diameter of a volume equivalent spherical particle.

It can be seen from Table 1 that Pt/C catalysts (catalyst samples 1, 2 and 3) prepared by the three reducing agents exhibit apparently different physicochemical characteristics. A larger particle size of Pt was achieved for catalyst 1 because of the strongest reduction ability of KBH_4 solution among the three reducing agents, though a lower concentration of KBH_4 solution (0.05 mol l^{-1}) was used. Compared with KBH_4, the solutions of HCHO and HCOOH had a moderate reduction ability, which allowed $[PtCl_6]^{2-}$ anions to diffuse and adsorb more easily on the surface of the carbon black support. As a result, a Pt in Pt/C catalysts of a smaller particular size was obtained. When formic acid was chosen as a reducing reagent, the reaction time had to be appropriately prolonged because of its weaker reduction ability. In all preparation processes, the Pt content in H_2PtCl_6 aqueous solution was 0.01 g ml^{-1}, and the reaction temperature was 313 K. The reaction time was 2 h for catalyst samples 1 and 3, and 3 h for the catalyst sample 2.

3.1.2. *Effect of concentration of aqueous H_2PtCl_6 solution*

The formation and the subsequent growth of Pt crystal nuclei were carried out in a supersaturated solution, therefore, the effect of the concentration of $[PtCl_6]^{2-}$ anions must be considered in the experiment. As for the situation in a dilute solution, the size of the crystal formed is negatively affected by the degree of supersaturation provided the induced time is long enough. Thus, the smaller particle size can be obtained at a higher $[PtCl_6]^{2-}$ anion concentration. However, the Pt particles formed are likely to agglomerate in the solution with a higher concentration because of the poor mass transfer, and this may result in a broader size distribution and an inferior dispersion of the Pt particles. The influence of the concentration of the aqueous H_2PtCl_6 solution is listed in Table 1 (catalyst samples 3, 4, 5 and 6), where the Pt contents in H_2PtCl_6 solution were 0.005, 0.01, 0.02 and 0.033 g ml^{-1}, respectively. The reducing agent employed was 20 ml of 0.15 mol l^{-1} aqueous HCHO solution. The reaction temperature was 313 K and the reduction time was 2 h. As shown in Table 1, Pt/C catalyst with ideal Pt particle sizes were obtained when the content of H_2PtCl_6 solution was in the range 0.01–0.02 g ml^{-1}.

3.1.3. *Effect of reaction temperature*

Generally, the degree of supersaturation of a solution decreases with the increase in reaction temperature. At a lower temperature, the formation of crystal nuclei proceeds more rapidly than the growth. Therefore, smaller Pt particles were obtained at 313 K, compared with those obtained at 333 and 353 K (samples 3, 7 and 8). Temperatures below 313 K were not considered in order to ensure a sufficient rate of reaction.

3.2. *Effects of heat treatment of carbon black supports*

The platinum size and degree of dispersion of platinum crystallites in Pt/C catalysts are affected by the interaction between the metal platinum and the carbon black support. It is well known that heat-treatment of the carbonaceous materials significantly influences the number of surface functional groups, especially the oxygenated groups, such as carbonyl groups. The increase in the number of oxygenated functional groups on the surface is beneficial to the humidification of carbon black supports, but not to the adsorption of Pt precursors with negative charge, such as $[PtCl_6]^{2-}$ anions, on the surface of the supports. Therefore, it is important to carry out the heat-treatment process within a proper temperature range. It is known that a temperature above 773 K is needed to decompose the unstable complexes. Above 773 K, the number of functional groups on the surface of carbon black decreases with the increase in temperature of the heat treatment [6]. In this work, a temperature of 873 K was chosen to obtain a suitable amount of oxygen species on the surface, so as to benefit the dispersion of the Pt on the surface [7].

XPS spectra of carbon black are shown in Figure 1. After heat-treatment the oxygen content of the carbon black Vulcan XC-72 decreased from 4.68 at % to 2.81 at %; these values were deduced from the areas of the C1s peak and the O1s peak in Figure 1.

XRD patterns of the untreated and the heat-treated carbon black supports are shown in Figure 2. The crystalline structure and the degree of graphitization of the carbon black were evaluated by the structure parameters, such as L_a (the layer dimension in the plane of the layers in an *a*-axial direction, parallel to the basal plane of the graphite), L_c (the layer dimension in a *c*-axial direction, perpendicular to the basal plane of the graphite) and *d*-spacing (the distance between the layer planes). L_a and L_c were calculated according to Equations 3 and 4 [8]:

$$L_a = \frac{1.84\,\lambda}{(B_1 \cos\theta_1)} \quad (3)$$

$$L_c = \frac{0.89\,\lambda}{(B_2 \cos\theta_2)} \quad (4)$$

where λ was the wavelength of the X-ray beam (1.54 Å); θ_1 and θ_2 were the Bragg angles of the diffraction peaks for the C(100) and C(002) crystal faces, respectively; B_1 and B_2 were the angular widths of the diffraction peaks at the half-maximum intensity (corrected for instrumental line broadening) for the C(100) and C(002) crystal faces, respectively. Table 2 shows the calculated parameters. The value of *d*-spacing between two C(002) or two

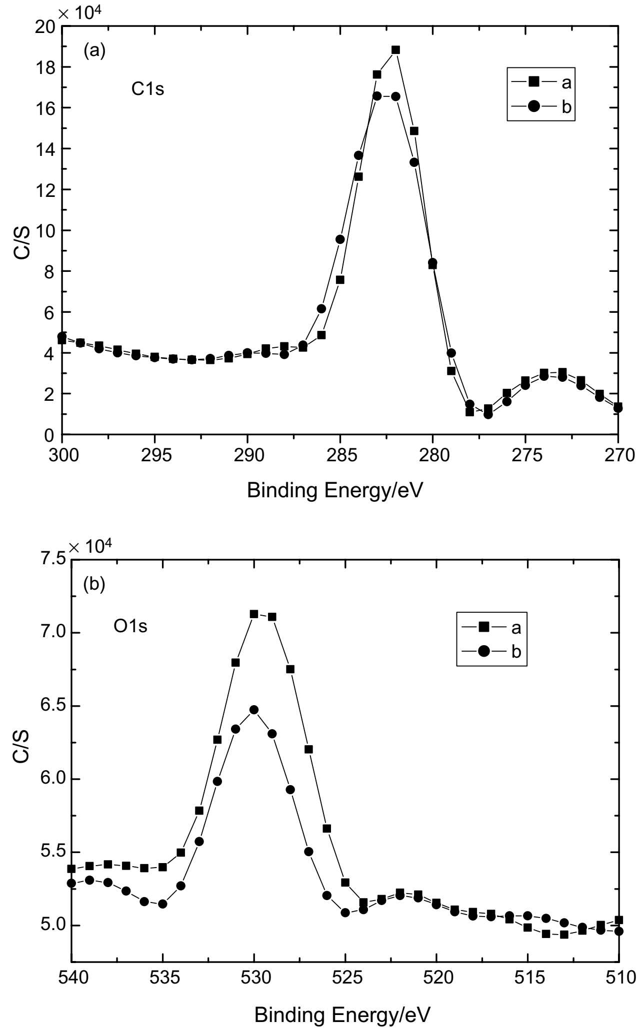

Fig. 1. XPS spectrum of C 1s and O 1s of carbon black Vulcan XC-72 (a) untreated and (b) heat-treated.

C (100) crystal faces and d_{002} and d_{100} are also listed in Table 2.

The crystal parameters presented in Table 2 show that no lattice difference can be seen for the carbon black with and without the heat treatment at 873 K. The heat treatment mainly results in the change of elemental compositions on the carbon black surface.

3.3. *Characterization of Pt/C catalysts*

3.3.1. *TEM results*

TEM photos of Pt/C catalysts prepared with the untreated and the heat-treated Vulcan XC-72 carbon black are shown in Figure 3. The TEM of a commercially available supported 20 wt % Pt/C catalyst (Johnson Matthey Comp.) is also presented in Figure 3 as a reference. The calculations of the mean particle sizes and the specific surface area are shown in Table 3. The preparation conditions of the catalyst 3 were applied because the Pt/C catalyst with the smallest Pt particle size could be obtained under these conditions as shown in Table 1. It is noted that the mean Pt particle size in the Pt/C catalyst prepared with heat-treated carbon black supports decreases by 1 nm comparing with that without heat treatment.

3.3.2. *XRD analysis*

XRD patterns of Pt/C catalysts 3, 9 and Johnson Matthey are shown in Figure 4. Some structural parameters obtained from the XRD measurement are presented in Table 4. Figure 4 indicates main diffraction peaks of Pt, which correspond to the crystal faces Pt (111), Pt (200) and Pt (220), respectively. From the peak intensities, using Equation 5:

$$I_{hkl}\% = \frac{I_{hkl}}{I_{111} + I_{200} + I_{220}} \times 100\% \tag{5}$$

where $I_{hkl} = I/I_0$, the relative intensity of the diffraction peak (I/I_0) (i.e., the surface-averaged distribution of Pt crystal faces was calculated). The results show that the values of $I_{111}\%$, $I_{200}\%$ and $I_{220}\%$ are 58.82%, 27.65% and 13.53% for catalyst 3, 61.35%, 25.77% and 14.42% for catalyst 9, and 59.88%, 26.35% and 13.77% for the Johnson Matthey catalyst, respectively. It is obvious that the relative content of the Pt (111) crystal face in catalyst 9 is higher than that in catalyst 3, and even higher than that in the Johnson Matthey catalyst. It has been reported that the oxygen reduction reaction (ORR) is sensitive to the Pt surface structure [9]. The Pt atoms at edges and corners are no more active than those on the crystal face Pt (111) or Pt (100) because of Lateral adsorption of oxygen atoms. In a polymeric electrolyte such as the Nafion® membrane, it is impossible for the anions to adsorb on the Pt (*hkl*) surfaces. The electrocatalytic activity of the catalyst entirely depends on the kinetic mechanism of the ORR on different crystal faces. Hence, the Pt (111) crystal face exhibits a higher activity due to the four-electron reduction process without the formation of H_2O_2 intermediate. The increase in the relative content of Pt (111) orientation indicates that the Pt/C catalyst prepared with the heat-treated carbon black support gives a higher electrocatalytic activity for the ORR in PEMFC.

The smaller *d* value benefits the dissociative adsorption of oxygen, and also the increase in catalytic activity of Pt/C catalysts. For catalyst 9, the *d* values of the three Pt crystal faces are close to that of Johnson Matthey catalyst.

3.3.3. *XPS surface analysis*

The electronic binding energy (E_b, refer to C1s at 284.6 eV as shown in Figure 1) and the surface compositions (at %) of Pt/C catalysts are presented in Table 5. The major scanning peaks are those for Pt 4f (7/2 and 5/2), O 1s and C 1s. The interaction of Pt with the support shifts the peak maxima (E_b of Pt $4f_{7/2}$) from the expected 70.9 eV value to the higher values of 71.25, 71.38 and 71.50 eV for catalysts 3, 9 and Johnson Matthey, respectively. This shift of E_b can be taken as a measurement of the presence of oxidized platinum

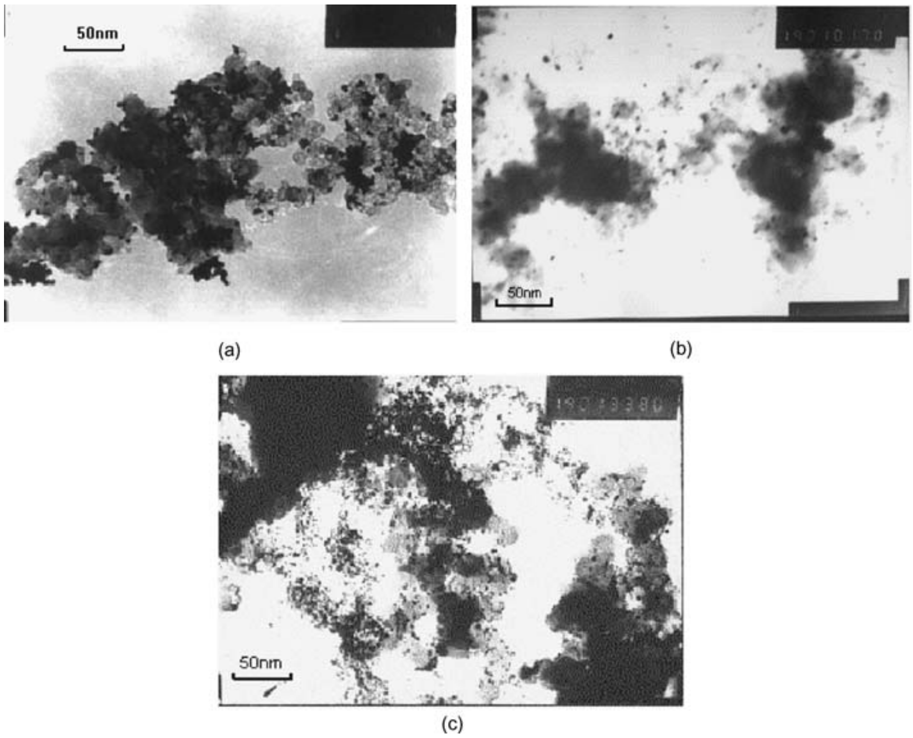

Fig. 2. TEM of (a) Pt/C with untreated carbon black, (b) Pt/C with heat-treated carbon black, and (c) Johnson Matthey Pt/C catalyst.

Table 2. Crystal parameters of the carbon black Vulcan XC-72

Carbon blacks	L_a /Å	L_c /Å	d_{002} /Å	d_{100} /Å
Common Vulcan XC-72	31.91	15.48	3.593	2.087
Heat-treated Vulcan XC-72	33.24	16.26	3.587	2.085

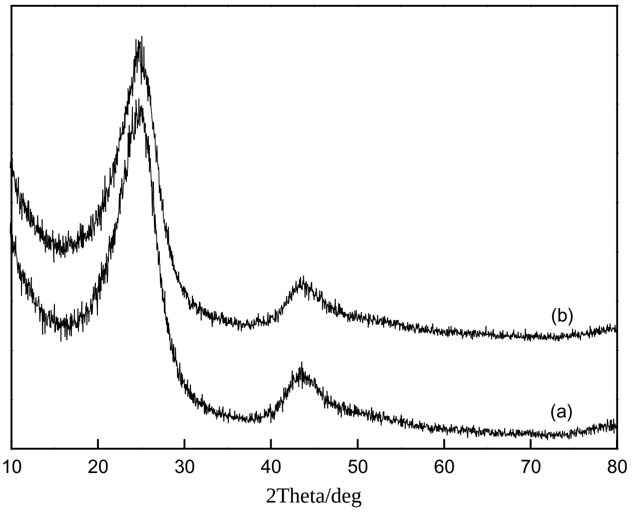

Fig. 3. XRD patterns of (a) untreated, and (b) heat-treated carbon black Vulcan XC-72.

species. For example, a variation of 0.9 to 2.5 eV for the Pt–O is reported [7, 10, 11]. The higher surface oxygen content and the lower Pt $4f_{7/2}$ peak maxima for catalyst 3 indicate an ineffective interaction between some of the oxygenated functional groups and the metal Pt.

Table 3. TEM results of Pt/C catalysts

Catalyst	Carbon black	Mean Pt particle size, D /nm	Specific surface area, s /m^2 g^{-1}
3	Common	4.2	67.1
9	Heattreated	3.2	88.1
Johnson Matthey	–	2.9	96.7

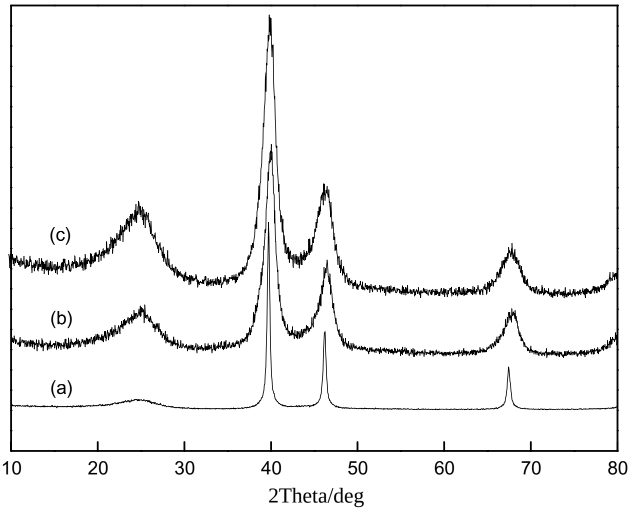

Fig. 4. XRD patterns of (a) Pt/C with untreated carbon black, (b) Pt/C with heat-treated carbon black, and (c) Johnson Matthey Pt/C catalyst.

The surface composition of the Pt/C catalyst is also presented in Table 5. It can be seen that the Pt surface content for catalyst 9 exhibits the same level as that for

Table 4. XRD results of Pt/C catalysts

Catalyst	Pt (111)			Pt (200)			Pt (220)		
	2θ /°	I/I_0	d /Å	2θ /°	I/I_0	d /Å	2θ /°	I/I_0	d /Å
3	39.72	100	2.2674	46.20	44	1.9633	67.44	23	1.3876
9	39.88	100	2.2587	46.48	42	1.9521	67.84	21	1.3803
Johnson Matthey	39.94	100	2.2554	46.16	44	1.9649	67.78	23	1.3814

Table 5. XPS data of Pt/C catalysts

Catalyst	Binding energy /eV				Surface elemental composition /at %		
	Pt $4f_{7/2}$	Pt $4f_{5/2}$	C1s	O1s	Pt	C	O
3	71.25	74.56	284.7	532.7	1.59	91.53	6.88
9	71.38	74.73	284.6	532.9	2.28	92.19	5.53
Johnson Matthey	71.50	74.85	284.6	532.8	2.29	92.03	5.68

Johnson Matthey catalyst, which suggests that the heat treatment of the carbon black plays an important role in the improvement of the adsorption of the precursor $[PtCl_6]^{2-}$ anion on the surface of the carbon black supports.

3.4. *Electrochemical measurement of Pt/C catalysts*

The current–voltage curves of a single PEMFC are shown in Figure 5, where the curve (a), (b) and (c) correspond to MEAs with catalysts 3, 9, and Johnson Matthey Pt/C catalysts, respectively. The curve (b) illustrates that the electrochemical performance of MEA with the catalyst 9 has clearly been improved, compared with that of MEA with catalyst 3, which indicates that the Pt/C catalyst based on the heat-treated carbon black support shows a higher electrocatalytic activity. The relation of the voltage with the current density is expressed in Equation 6:

$$E = E_0 - b \log i - Ri \tag{6}$$

where R is the internal resistance of the cell, b is Tafel slope for ORR and E_0 is the voltage, defined as $E_0 = E_r + b \log i_0$, where E_r is the reversible potential and i_0 is the exchange current density. SAS software was used to imitate the curve (b) and (c) in Figure 5. The result shows that the electrochemical performance of MEA with catalyst 9# is rather similar to that of Johnson Matthey catalyst at a low current density. Nevertheless, the MEA with Johnson Matthey catalyst exhibits better electrochemical performance at a higher current density because of its smaller R value.

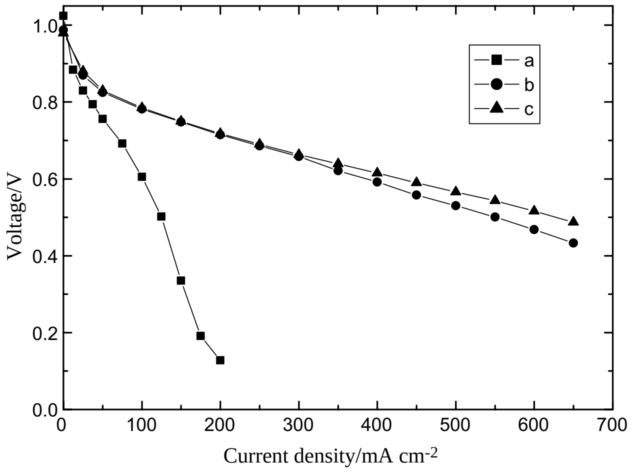

Fig. 5. Voltage–current curves of single PEMFC with catalyst of (a) Pt/C with untreated carbon black, (b) Pt/C with heat-treated carbon black, and (c) Johnson Matthey Pt/C catalyst. Test condition: $T(H_2) = 343$ K; $T(O_2) = 338$ K; $T(\text{Cell}) = 343$ K; $P(H_2) = P(O_2) = 0.2$ Mpa.

Table 6. Electrochemical performance parameters of MEA

Catalyst	E_0 /V	b /V dec^{-1}	R /Ω cm^{-2}
9	1.0094	0.0232	0.6170
Johnson Matthey	0.9808	0.0334	0.4182

4 Conclusion

The results obtained show that the heat treatment under suitable conditions for the commercial carbon black Vulcan XC-72 plays an important role in the improvement of the electrocatalytic activity of Pt/C catalysts. TEM measurement shows that Pt/C catalyst prepared with the heat-treatment carbon black support exhibits a narrow size distribution of the Pt particles. XRD phase analysis indicates that an increase in the relative content of Pt (111) orientation appears for the Pt/C catalysts prepared with the heat treatment carbon black support. This benefits the acceleration of the ORR in the PEMFC. The electrochemical performance of the Pt/C catalyst was evaluated by the I/E curves of a MEA in a single PEMFC. The result shows that the electrocatalytic activity of the Pt/C catalysts prepared in this work is similar to that of Johnson Matthey Pt/C catalyst.

References

1. J. Fournier, G. Faubert, J.Y. Tilquin, R. Cote, D. Guay and J.P. Dodelet, *J. Electrochem. Soc.* **144** (1997) 145.
2. Masahiro Watanabe, Makoto Uchida and Satoshi Motoo, *J. Electroanal. Chem.* **229** (1987) 395.
3. M. Götz and H. Wendt, *Electrochim. Acta* **43** (1998) 3637.
4. M.C. Dennis, G. Lalande and D. Guay, *J. Appl. Electrochem.* **29** (1999) 951.
5 A. Gamez, D. Richard, P. Gallezot, F. Gloaguen, R. Faure and R. Durand, *Electrochim. Acta* **41** (1996) 307.
6. K. Kinoshita, 'Carbon: Electrochemical and Physicochemical Properties' (J. Wiley & Sons, New York and Chichester, UK, 1983) p. 35.
7. P.L. Antonucci, V. Alderucci, N. Giordano, D.L. Cocke and H. Kim, *J. Appl. Electrochem.* **24** (1994) 58.
8. K. Kinoshita, *op. cit* [6], p. 32.
9. S. Srinivasan, O.A. Velev, A. Parthasarathy, D.J. Manko and A.J. Appleby, *J. Power Sources* **36** (1991) 299.
10. L. Kovr, Cs. Ujhelyi, D. Bernyi, D. Varga, I. Kadar, A. Kovr and J. Miller, *J. Electron Spectrosc. Related Phenomena* **14** (1979) 201.
11. K.S. Kim, N. Winograd and R.E. Davis, *J. Am. Chem. Soc.* **93** (1971) 6296.