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Hydrogen generation from catalytic hydrolysis of sodium borohydride for proton exchange membrane fuel cells

Chuan Wu*, Huaming Zhang, Baolian Yi

Fuel Cell R&D Center, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, PR China

Abstract

A novel hydrogen generation (HG) method for proton exchange membrane fuel cell (PEMFC) is developed. Carbon-supported platinum catalysts were synthesized by an impregnation method, and adopted to catalysis hydrolysis of $NaBH_4$ solution. These catalysts exhibit excellent hydrogen generation rates and approximate 100% efficiencies. A HG system with 100 mg 20% Pt/C catalyst has the ability to supply a 299 W PEMFC. Specific surface of the support is not a crucial factor affecting the HG performances of the catalysts, while Pt loading, Pt particle size and size distribution, and micropore structure play important roles in hydrogen generation reactions.

Keywords: PEMFC; Hydrogen generation; Sodium borohydride; Platinum; Carbon support

1. Introduction

As an environmental friendly electricity-generating method, proton exchange membrane fuel cell (PEMFC) has been widely studied in recent years. It is predicted as a promising alternative to internal combustion engines for its zero emission of environment pollutants. Pure hydrogen is adopted as the fuel in PEMFC. However, the currently used hydrogen is mostly produced from natural gas via catalytic reforming [1], which produces a mixture of H_2, H_2O, N_2, CO_2, and CO [2]. The performances of PEMFC are sensitive to the concentration of carbon monoxide in hydrogen [3–7]. Even a few parts per million carbon monoxides can cause the catalyst poisoning in PEMFC. The irreversible adsorption of carbon monoxide on active platinum catalyst may result in a continual decreasing of the performances of PEMFC. Therefore, a fast and clean hydrogen supply method is required, especially for a mobile PEMFC.

The hydrolysis of chemical hydrides is proved to provide pure hydrogen in a short time [8–14]. The slurry of sodium borohydride ($NaBH_4$) is stable at normal environmental temperatures and pressures on condition that the pH value of the slurry is high enough. Therefore, when small amount of NaOH is added to the $NaBH_4$ slurry, it can be stored stably in air for months. Only when selected catalysts are added, it can release hydrogen rapidly in the following way:

$$NaBH_4 + 2H_2O \rightarrow NaBO_2 + 4H_2,$$
$$\Delta H = -217\,\text{kJ/mol}. \qquad (1)$$

It is an exothermic reaction and can be initiated quickly even at 0 °C. The by-product $NaBO_2$ does no harm to the environment, and can be recycled as the raw material for producing $NaBH_4$. Thus, the above hydrolysis reaction is an environmental friendly and renewable process. So far, although the cost of $NaBH_4$ is not cheap, this hydrogen generation (HG) method can still be adopted where pure H_2 is needed in urgency, or the situations where cost is not a crucial factor.

Some metal ions or noble metals were adopted as the catalysts for hydrolysis of sodium borohydride [10–14]. According to the study of Brown and Brown [10], aqueous solutions of platinum, ruthenium and rhodium salts can be reduced by aqueous $NaBH_4$ solution. They found that black powder produced by treating chloroplatinic acid with $NaBH_4$ was pure platinum. Namely, $NaBH_4$ can reduce platinum metals to the element state, which exhibits high catalytic activity for the hydrolysis. Kojima et al. [11] reported that the HG reaction of $NaBH_4$ was accelerated by metal catalysts coated on metal oxides. According to Amendola et al. [12,13],

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* Corresponding author. Tel.: +86 10 68912508; fax: +86 10 68451429.
E-mail address: chuanwu@bit.edu.cn (C. Wu).

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resin-supported ruthenium has shown excellent activity for the hydrogen generation from sodium borohydride solution.

Since Pt/C catalysts have been widely used in PEMFC, it is attractive to adopt this kind of catalysts for $NaBH_4$ hydrolysis. Thus, $NaBH_4$ solution might be feed to PEMFC as fuel directly. Then, Pt/C catalysts may serve as two-effect catalysts. First, inducing the hydrolysis reaction to generate H_2; second, catalyzing the electrochemical reaction of H_2 with O_2.

In this study, carbon-supported platinum (Pt/C) catalysts were synthesized by an impregnation method. The HG activities of the catalysts were tested in a special HG reactor, and the effects of specific surface, Pt loading, Pt particle size and size distribution, and micropore structure on HG performances are discussed in detail.

2. Experimental

2.1. Catalyst preparation

Three kinds of carbon supports with different specific surfaces, Vulcan XC-72R, Acetylene black, and Pearly black were adopted. They were first impregnated in 0.04 mol/l chloroplatinic acid solution with the volume correspondent with the Pt loading for 24 h, and then calcined in a reductive gas atmosphere at 300 °C for 2 h. The samples were named as A–E. The components and the Pt loadings of all the as-prepared samples are listed in Table 1.

2.2. Catalyst characterization

Powder XRD patterns of all the as-prepared samples were recorded by a Rigaku X-3000 X-ray powder diffractometer with Cu Kα radiation. The scan range is from 5° to 85°, and the scan rate was 5°/min in step of 0.02°.

Nitrogen adsorption of the samples was measured at −196 °C with an ASAP 2010 surface area analyzer (Micromeritics Instrument). Prior to the measurements, the samples were vacuum-dried at 110 °C for 12 h. The specific surfaces of the samples were determined from the N_2 adsorption–desorption isotherms by the BET method.

For transmission electron microscopy (TEM) analysis, the samples were first ultrasonically suspended in ethanol. Then, a drop of the suspension was applied onto a copper grid and dried in air. The as-prepared specimens were examined using a JEOL JEM-2011 electron microscope operated at 100 kV.

Table 1
Components and Pt loadings of carbon-supported platinum catalysts

Sample	Pt loading (%)	Support	Impregnated time (h)
A	5	Vulcan XC-72R	24
B	10	Vulcan XC-72R	24
C	20	Vulcan XC-72R	24
D	20	Acetylene black	24
E	20	Pearly black	24

2.3. Hydrogen generation

Hydrogen generation tests were performed with a special HG system. The catalysts were placed in a reactor prior to the HG reaction. Then, the system was sealed, and pure nitrogen gas was feed into drive the air away from the system. After that, 10% $NaBH_4$–5% NaOH solution was pumped from a storage tank to the reactor, the catalysis hydrolysis reaction processed on the catalyst bed successively. The generated hydrogen was imported into a special bottle to wash out the residual alkali and water, then being stored or applied to a PEMFC.

3. Results and discussion

3.1. Structure characterization

The XRD patterns of samples B and C are weak and wide diffraction peaks, as shown in Fig. 1. It implies that they have amorphous-like platinum structures and good particle distributions. Additionally, a peak at about 25° is obvious, which belongs to the amorphous carbon support.

As for samples D and E, the diffraction peaks are much stronger and sharper than those of samples B and C, and the peaks of platinum are so strong, that the peaks of carbon supports cannot be identified distinctly. It indicates that these two catalysts have more integrated platinum crystal structures.

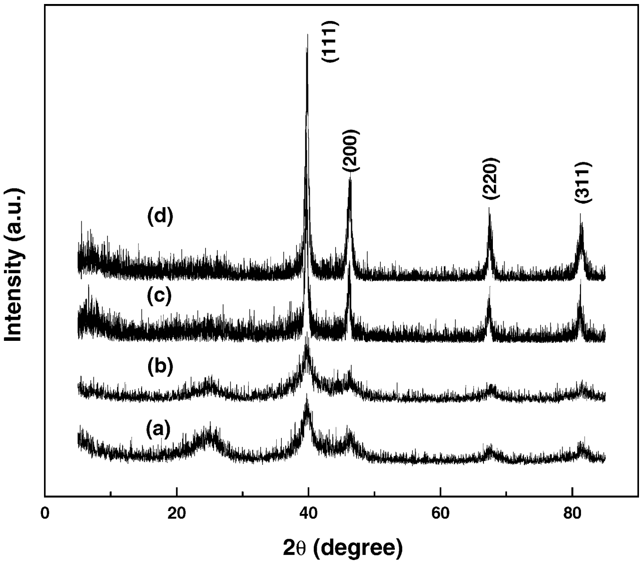

Fig. 1. Powder XRD patterns of various Pt/C catalysts: (a) 10% Pt/Vulcan XC-72R; (b) 20% Pt/Vulcan XC-72R; (c) 20% Pt/Acetylene black; (d) 20% Pt/Pearly black.

Table 2
The average Pt particle sizes evaluated from XRD patterns by Scherrer equation

Sample	$\theta_{\max}$ (°)	$B_{2\theta}$ (°)	Average Pt particle size (nm)
B	67.510	4.6265	4.5
C	67.491	5.0359	4.1
D	67.376	0.59388	34.7
E	67.521	0.66325	31.3

Scherrer equation was adopted to evaluate the average particle sizes of the catalysts, as described by Eq. (2):

$$L = \frac{0.9\lambda_{\mathrm{K}\alpha 1}}{B_{2\theta}\cos\theta_{\max}} \tag{2}$$

where $\lambda_{\mathrm{K}\alpha 1}$ presents the wavelength of Cu Kα1 radiation (1.54056 Å), $B_{2\theta}$ is the half-width of the diffraction peak. Another parameter $\theta_{\max}$ is the 2θ degree of the diffraction peak. The value of the average particle size L can be calculated through Eq. (2). Since the Pt (1 1 1), Pt (2 0 0) and Pt (3 3 1) diffraction peaks might overlap with those peaks

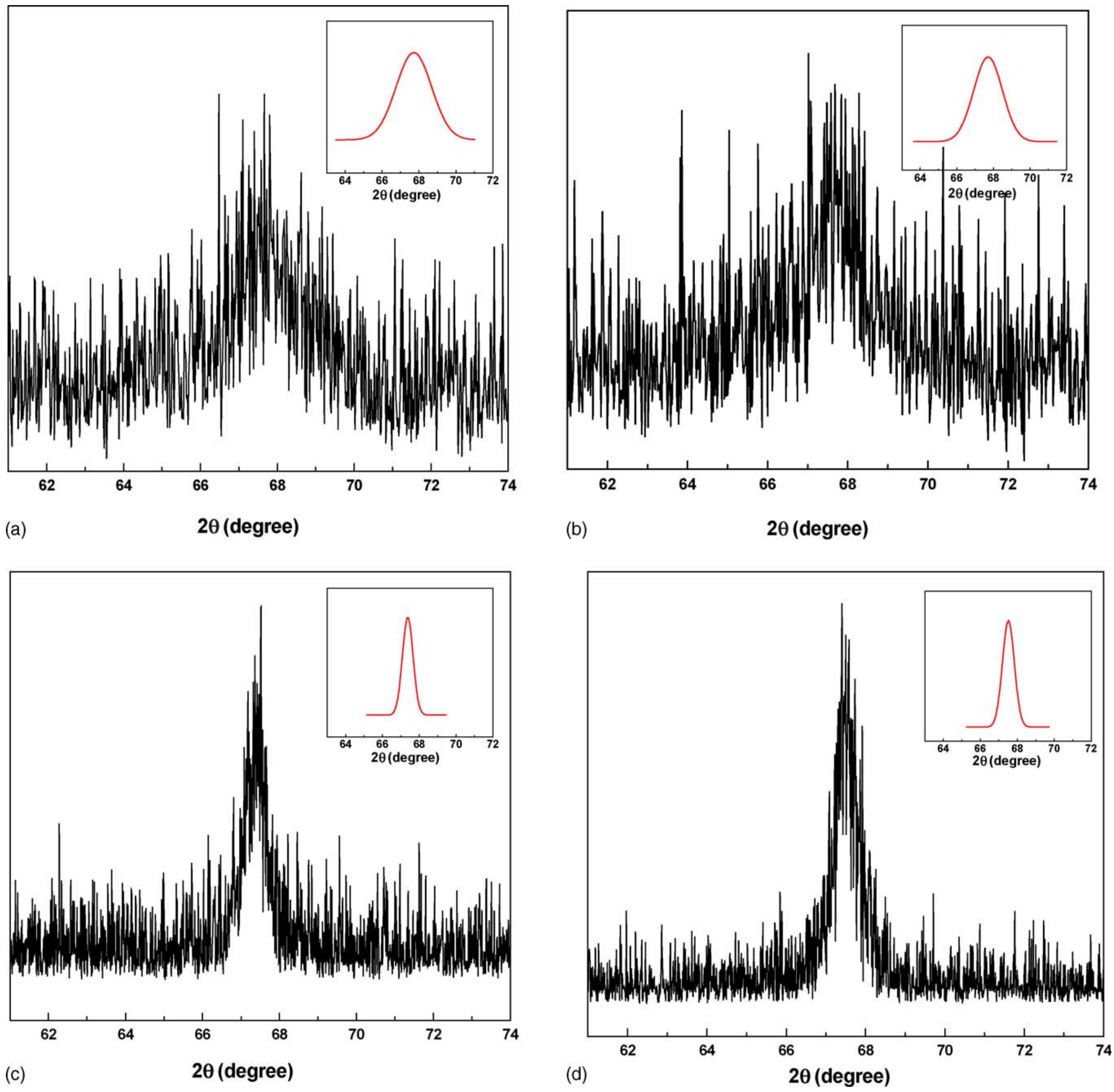

Fig. 2. Gaussian fits to the (2 2 0) facets of the Pt/C catalysts: (a) 10% Pt/Vulcan XC-72R; (b) 20% Pt/Vulcan XC-72R; (c) 20% Pt/Acetylene black; (d) 20% Pt/Pearly black. The inlets are the Gaussian fitted curves without the baselines.

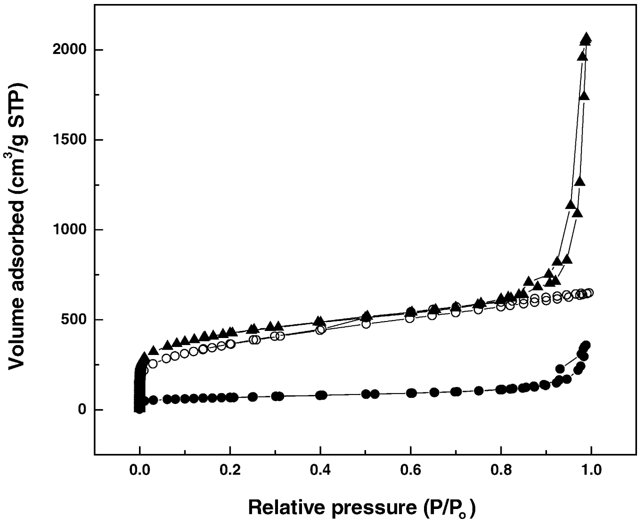

Fig. 3. Nitrogen adsorption–desorption isotherms for various carbon supports: (●) Vulcan XC-72R; (○) Acetylene black; (▲) Pearly black.

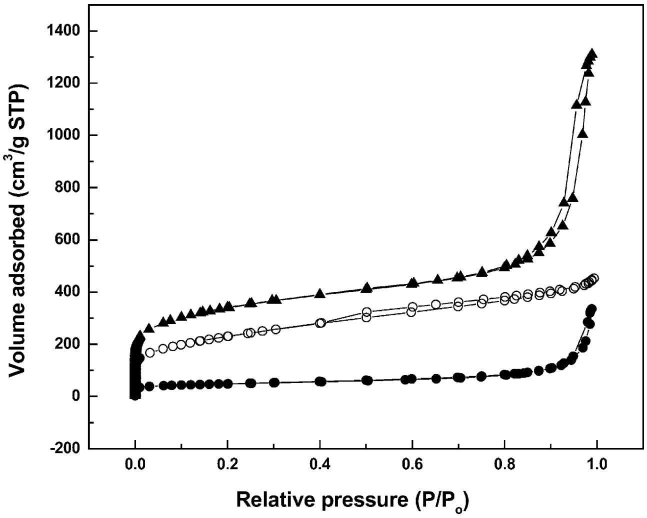

Fig. 5. Nitrogen adsorption–desorption isotherms for various 20% Pt/C catalysts. The carbon supports: (●) Vulcan XC-72R; (○) Acetylene black; (▲) Pearly black.

of the carbon supports, here we chose the parameters of Pt (2 2 0) peak to carry on the evaluation.

Fig. 2 shows the diffraction peaks of the Pt (2 2 0) facets. The inlets are the Gaussian fitted curves of the Pt (2 2 0) diffraction without baselines. The calculated results are listed in Table 2.

The average Pt particle size of Pt/Vulcan XC-72R catalysts are in the same order, even though the Pt loading increased from 10 to 20%. While with the same 20% Pt loading, the Pt particles grew on Vulcan XC-72R are much smaller than those grew on Acetylene black and Pearly black. This may be induced by the surface properties of these supports.

3.2. BET results

Figs. 3–5 are the nitrogen adsorption–desorption isotherms for the carbon supports and the catalysts samples. All the isotherms are in the similar shape. The specific surfaces of the carbon supports Vulcan XC-72R, Acetylene black, and Pearly black, are 235, 1304, 1487 m^2/g, respectively, as listed in Table 3. Acetylene black and Pearly

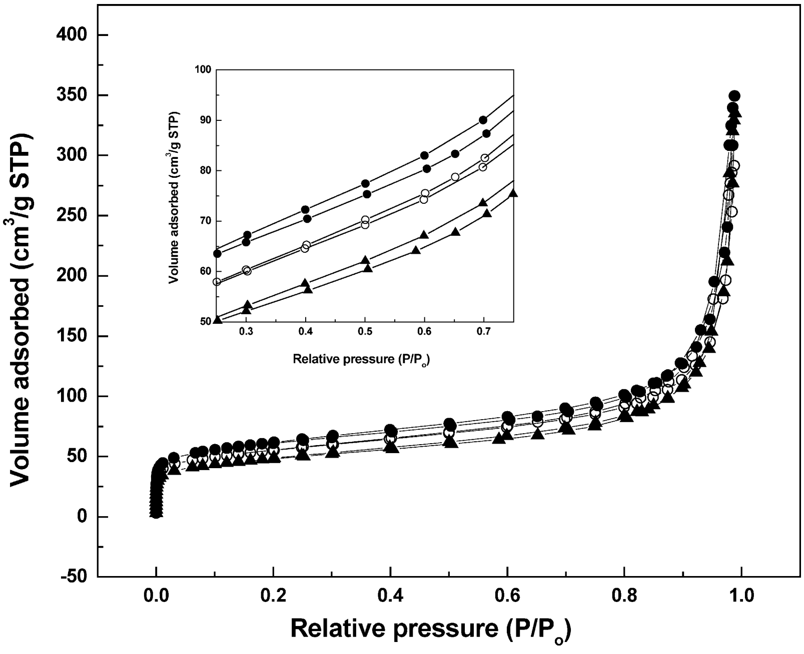

Fig. 4. Nitrogen adsorption–desorption isotherms Pt/C catalysts with Vulcan XC-72R carbon support: (●) 5% Pt loading; (○)10% Pt loading; (▲) 20% Pt loading. The inlet is the isotherms of the catalysts in the relative pressure range of 0.25–0.75.

Table 3
BET specific surfaces and pore structure parameters of the supports and the catalysts

Sample	S_{BET} (m^2/g)	Micropore area (m^2/g)	External surface area (m^2/g)	Average pore diameter (nm)
Vulcan XC-72R	235	82	153	9.4
Acetylene black	1304	184	1120	3.1
Pearly black	1487	486	1001	8.6
A	215	80	136	10
B	192	72	120	9.4
C	170	57	113	12
D	823	127	695	3.4
E	1196	409	787	6.8

black have close specific surfaces, but different micropore structures. The average pore diameter of the later is 6.8 nm, which is two-fold as that of the former.

When Pt particles grew on the supports, the specific surfaces decrease. As for Vulcan XC-72R support, higher Pt loadings result in smaller specific surfaces. The value of S_{BET} decreases from 212 to 170 m^2/g as the Pt loading increases from 5 to 20%.

3.3. Catalytic activity

To test the catalytic activities of the catalysts for HG reaction of $NaBH_4$ solution, a successive reaction mode is employed. In each experiment, 100 mg Pt/C catalyst was taken in the HG reactor. The solution of 10% $NaBH_4$–5% NaOH was pumped into the reactor with a speed of 10 ml/min; and 20 min later, the feeding was stopped. The cumulative volume of the generated H_2 was recorded by a flowmeter.

Fig. 6 shows the HG performances of Pt/Vulcan XC-72R catalysts with various Pt loading. The HG rates, HG efficiencies, and the corresponding power for PEMFC are listed in Table 4. It is clear that the HG rate is accelerated with increasing Pt loading, while the HG efficiency has the same tendency.

Table 4
Hydrogen generation performances of the Pt/C catalysts

Sample	H_2 generation rate (ml/min)	H_2 generation efficiency in 20 min (%)	Corresponding power for PEMFC[a] (W)
A	405	17.9	52
B	1689	73.9	219
C	2301	99.6	298
D	2309	100	299
E	1916	83.0	248

[a] The H_2 utilization is considered as 80%.

When the $NaBH_4$ feeding stopped at 20th minute, the HG efficiency of 5% Pt/Vulcan XC-72R is only 17.9%. It implies a delay of the HG reaction. Since the Pt loading is relatively low, the active sites for the HG reaction are not enough to drive the hydrolysis of $NaBH_4$ to finish in a short time, and result in a low HG rate. However, when the Pt loading is increased to 20%, a HG efficiency of 99.6% is achieved. Namely, the $NaBH_4$ solution is almost hydrolyzed out instantly. The HG rate of 20% Pt/Vulcan XC-72R is 2301 ml/min, which can give the H_2 supply for a 298W PEMFC, as shown in Table 4.

Fig. 7 compares the HG performances of Pt/C catalysts with different carbon supports. Sample D have similar HG performances to those of sample C. It achieves a HG efficiency of 100%, and a HG rate of 2309 ml/min, which can give the H_2 supply for a 299 W PEMFC. Generally, the catalyst with larger specific surface can result in better catalytic performance; for the active sits can fully touch with

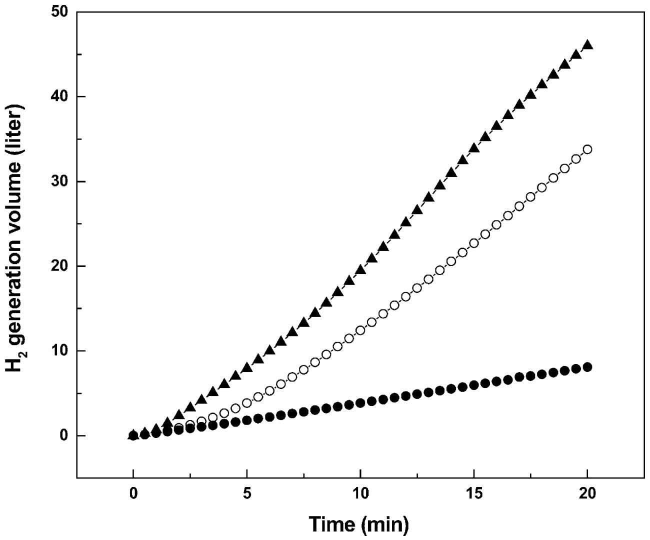

Fig. 6. H_2 volume generated as a function of time with 100 mg of Pt/Vulcan XC-72R catalysts. The reactant is the solution of 10 wt.% $NaBH_4$–5 wt.% NaOH. The Pt loadings: (●) 5%; (○) 10%; (▲) 20%.

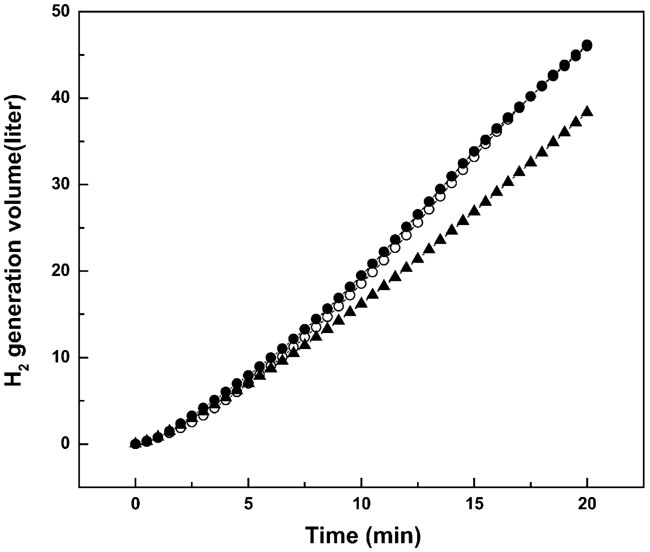

Fig. 7. H_2 volume generated as a function of time with 100 mg of 20% Pt/C. The reactant is the solution of 10 wt.% $NaBH_4$–5 wt.% NaOH. The carbon supports: (●) Vulcan XC-72R; (○) Acetylene black; (▲) Pearly black.

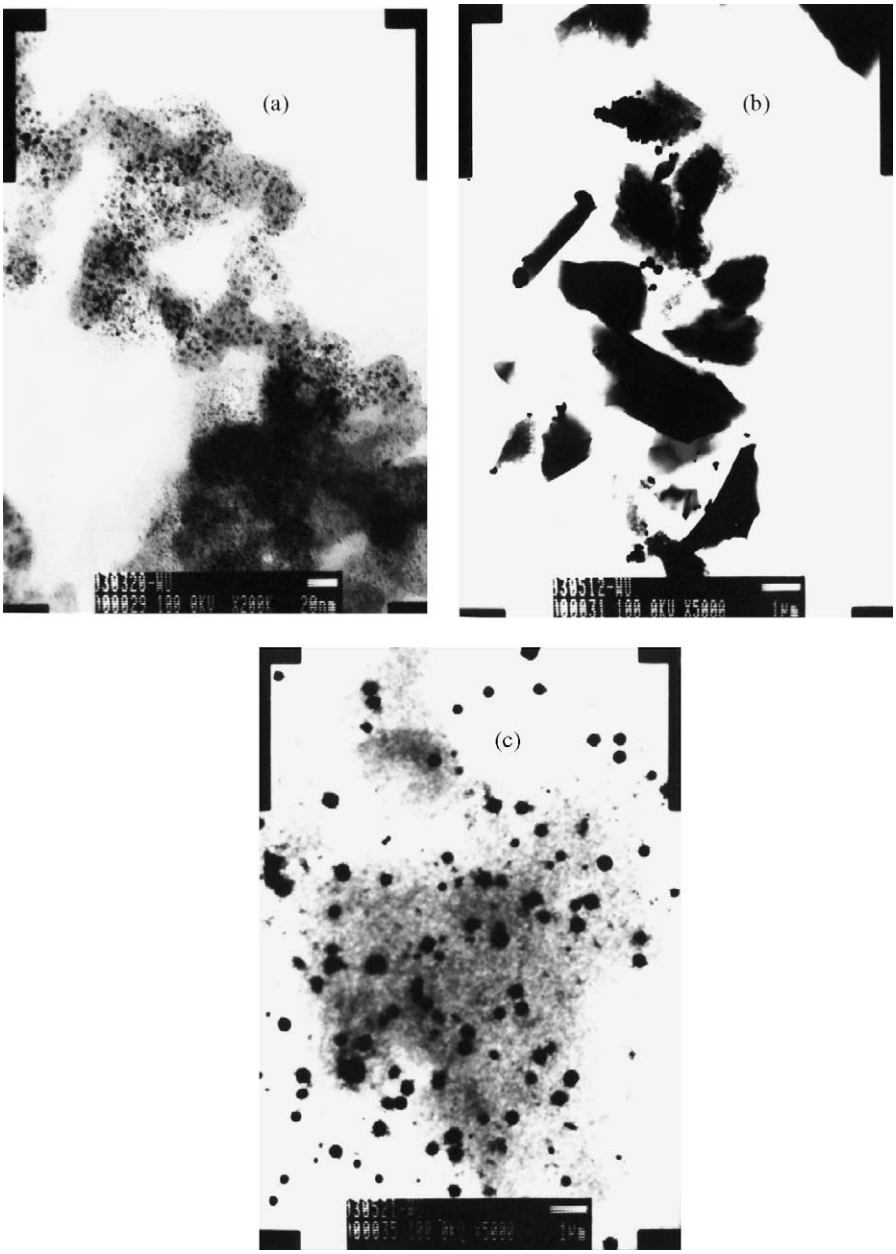

Fig. 8. TEM images of the 20% Pt/C catalysts: (a) 20% Pt/Vulcan XC-72R, the white bar presents 20 nm; (b) 20% Pt/Acetylene black, the white bar presents 1 μm; (c) 20% Pt/Pearly black, the white bar presents 1 μm.

the reactants. However, even though the Pt loading is the same as those of the former two, sample E, which has the largest specific surface, shows inferior results. The HG efficiency of sample E in 20 min is only 83%, and the HG rate is 1916 ml/min, which can supply a 248 W PEMFC. It seems that the specific surface is not the crucial factor for the HG performances of the Pt/C catalysts. The structures of the catalysts should have further analysis.

3.4. TEM analysis

According to TEM images, Pt particles are identified as small dark dots on the light carbon supports, as shown in Fig. 8. It is evident that the Pt particle size of 20% Pt/Vulcan XC-72R is 4–5 nm, which is correspondent with that evaluated from Scherrer equation. The small particle size and uniform size distribution result in a relative large surface of Pt active sites, leads to a high Pt utilization in the HG reaction. When $NaBH_4$ solution was pumped in the HG reactor, BH^- anions were contacting with enough catalyst instantly, the hydrolysis reaction was initiated immediately. Mass of hydrogen was released in a short time. Therefore, sample C exhibits high HG rate and efficiency.

As for 20% Pt/Acetylene black, the apparent Pt particle size is 200–500 nm, which is 10-fold as large as that evaluated from Scherrer equation. It implies that the Pt particles are agglomerated together to form large spheres during calcining. Some Pt particles are encircled in the spheres by the outer particles. In the HG reaction, the encircled Pt particles cannot act as hydrolysis catalyst, and the Pt utilization of the catalyst is depressed in this way. Thus, though the Pt loadings are the same, sample E shows a relative inferior HG rate and efficiency than sample C.

The Pt particles of 20% Pt/Acetylene black cannot be identified expressly in the TEM images, as shown in Fig. 8(c). Since the support Acetylene black is composed with large carbon particles, it is not suitable for TEM test. However, according to the BET results, sample D has the smallest average pore diameter (see Table 3). The large quantity of micropores can enhance the adsorbability of the catalyst and extend the active area, result in excellent HG performances.

4. Conclusion

Catalytic hydrolysis of $NaBH_4$ solution is a promising H_2 supply technique for PEMFC. A series of carbon-supported platinum catalysts were synthesized by an impregnation method, and adopted to catalytic hydrolysis of $NaBH_4$ solution. The Pt/C catalysts exhibit excellent hydrogen generation rates and approximate 100% efficiencies. A HG system, which employing 100 mg 20% Pt/C as the catalyst, 10 wt.% $NaBH_4$–5 wt.% NaOH as the reactant, and with a reactant feeding rate of 10 ml/min, has the ability to supply a 299 W PEMFC. Thus, $NaBH_4$ solution might be adopted as a direct fuel to PEMFC.

Specific surface of the support is not a crucial factor affecting the HG performances. Better hydrogen generation rates and efficiencies are revealed with increasing Pt loadings. Small particle size and uniform size distribution lead to high Pt utilizations, result in good performances. Additionally, large quantity of micropores can enhance the adsorbability of the catalyst and extend the active area, and affect the hydrogen output.

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