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Materials

Processes of depositing platinum on carbon nanotubes and their effect on performance of proton exchange membrane fuel cell

Yanhui Li[1], *Jun Ding*[1], *Junfeng Chen*[1], *Zongqiang Mao*[2], *Cailu Xu*[1], *and Dehai Wu*[1]

1) Department of Mechanical Engineering, Tsinghua University, Beijing 100084, China
2) Institute of Nuclear Energy Technology, Tsinghua University, Beijing 100084, China
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Abstract: The ultrafine platinum nanoparticles deposited on the surfaces of carbon nanotubes (Pt/CNTs) were prepared by a chemical precipitation method and used as the catalyst of proton exchange membrane fuel cell. The depositing process parameters such as the solution pH value, Pt content and treatment temperature were analyzed. The experimental results show that the optimum process parameters to prepare Pt/CNTs are the solution pH value of 7.0, the theoretical Pt content of 25% (mass fraction) and the heating temperature of 500°C, under the conditions the best performance of the proton exchange membrane fuel cell can be obtained and its voltage can reach 580 mV at a current density of 500 mA/cm^2.

Key words: carbon nanotubes; platinum; deposition; proton exchange membrane fuel cell

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1 Introduction

The proton exchange membrane fuel cell (PEMFC) is an apparatus that directly converts the chemical energy of hydrogen and oxygen into electrical energy through electrode reaction. It has many advantages such as the higher energy conversion efficiency which can reach 60%-80%, the lower working temperature, the diversification of fuel, the lower noise and environmental pollution [1]. So it is thought as a very ideal power source and becomes the worldwide focus of research and development.

In order to accelerate the electrochemical reaction of hydrogen and oxygen, platinum was usually used as electro-catalyst [2-5]. But the cost of platinum is very expensive due to its rare source, it was generally supported on the materials with large specific surface area such as activated carbon so as to improve the catalytic activity, decrease the dosage and particle size. The platinum particle size and their distribution on the surfaces of supporters mainly depend on the supporter's surface state, the specific surface area and depositing processes.

Carbon nanotubes (CNTs), a new member in carbon family, are a new type of carbon material, which are curled by multi-layer concentric graphite sheets and capped by hemisphere at the two ends. CNTs have high mechanical property and unique electrical property, so they show great potential applications in composite materials [6], field emission [7], energy storage [8], nanosized electro-devices [9] and wastewater treatment [10-12]. At the same time, CNTs have higher thermal and chemical stability, larger specific surface area, reasonable pore distribution and easily decorated surfaces to introduce large amount of functional groups, which make them an ideal catalytic supporter material [13, 14].

In this paper, nanosized platinum particles were deposited on the surfaces of CNTs (Pt/CNTs) through a chemical precipitation method, the process parameters such as the solution pH value, Pt content and treatment temperature were analyzed. The prepared Pt/CNTs were used as the catalysts of PEMFC and their catalytic property were measured.

2 Experimental

2.1 Preparation and treatment of CNTs

CNTs were fabricated by catalytic pyrolysis of the propylene-hydrogen (C_3H_6:H_2=2:1) mixture at about 750°C in a ceramic tube with Ni particles as the catalysts. Transmission electron microscopy (TEM) images show that the used CNTs have an average diameter of about 20 nm and a length ranging from hundreds of nanometers to micrometers.

Corresponding author: Yanhui Li, **E-mail:** liyanhui@tsinghua.org.cn

The prepared CNTs were ground into fine powders and soaked in HNO_3, subsequently, they were dispersed in H_2O_2 solution and stirred for 4 h, then CNTs were washed with distilled water, dried at 80°C and stored in a desiccator for further use.

2.2 Preparation and measurement of Pt/CNTs

The treated CNTs were mixed with distilled water and alcohol, then, different amount of H_2PtCl_6 solutions were slowly added into the CNTs solutions, respectively, and heated at 60°C for 30 min. The $Na_2S_2O_4$ solution was used as a reducer and slowly dropped into the mixed solutions, in this process, the pH value of the solutions were adjusted with KOH solution and stirred for another 24 h, then, the solutions were filtered and dried at 80°C. At last the powders were heated at different temperatures for 1 h under nitrogen atmosphere, and the Pt/CNTs were obtained.

The Pt/CNTs were analyzed by TEM and XRF (X-ray fluorescence spectrum).

2.3 Catalytic performance measurement of the Pt/CNTs on PEMFC

The Pt/CNTs was mixed with an aqueous Nafion solution in an ultrasonic oscillator. Then the mixture was sprayed on a carbon paper and dried at 150°C and the electrodes were obtained. The electrodes were installed in the measuring system of PEMFC, the voltage-current density curves of PEMFC were measured and used to evaluate the catalytic properties of Pt/CNTs.

3 Results and discussion

3.1 PH value effect on the Pt/CNTs and the performance of PEMFC

It is known that the solution pH value is an import factor that affects the degree of chemical reaction. During the process of the deposition of Pt on CNTs, the following chemical reactions take place:

$$S_2O_4^{2-} + PtCl_6^{2-} = PtCl_4^{2-} + 2Cl^- + 2SO_2\uparrow \qquad (1)$$

$$2S_2O_4^{2-} + PtCl_4^{2-} = 4Cl^- + SO_4^{2-} + 2SO_2 + Pt\downarrow + S\downarrow \qquad (2)$$

It can be seen that SO_2 is produced in the reaction. SO_2 was dissolved in water and produces sulfurous acid, which makes the solution pH value decrease and affects the deposition of Pt on CNTs, so the KOH solution was used to adjust the solution pH value to 5.0, 7.0, 9.0 and 11.0, respectively.

The effect of pH value on the Pt/CNTs was shown in **figure 1**. It can be seen that the Pt particles were about 3 nm and homogeneously deposited on the surfaces of CNTs at pH values of 5.0 and 7.0 (figures 1(a) and (b)). While the Pt particles became larger and occurred to aggregate at pH values of 9.0 and 11.0 (figures 1(c) and (d)). The result may be due to the slower chemical reaction rate at the lower pH value, so the finer Pt particles were prepared. The content of Pt in each sample (the theoretical Pt content is 25% (mass fraction, so as the follows)) was measured by XRF and listed in **table 1**. At the solution pH value of 5.0, the Pt content is only 14%, which is much lower than the theoretical Pt content. It increases with the pH value gradually and reaches 19.5% at a pH value of 11.0.

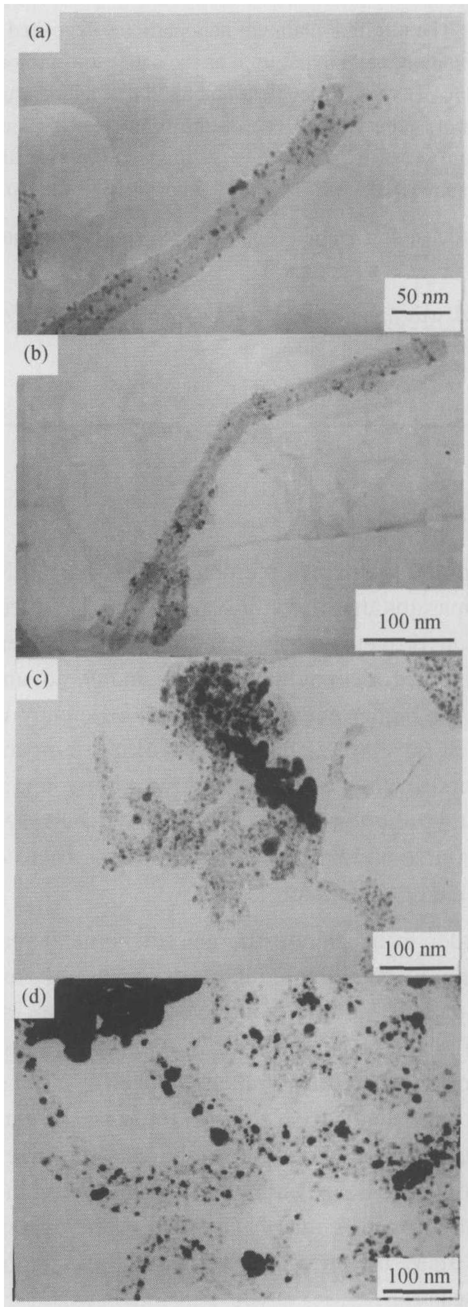

Figure 1 TEM images of Pt deposited on CNTs prepared at different pH values: (a) pH=5.0; (b) pH=7.0; (c) pH=9.0; (d) pH=11.0.

Figure 2 shows the performance of PEMFC using the catalysts of Pt/CNTs prepared at different pH values. It can be seen that the voltage of PEMFC decreases rapidly with the increase of current density for the sample with a pH value of 11.0 and only reaches 35 mV at a current density of 500 mA/cm^2. This may be attributed to the larger Pt particles deposited on the CNTs which decrease the specific surface area and then the catalytic activity although the sample has the largest Pt content. The voltage of the sample obtained at a pH value of 9.0 is 270 mV when the current density is 500 mA/cm^2 due to the decrease of the Pt size. Although the Pt content at a pH value of 5.0 is lower than that of the sample at a pH value of 9.0 (table 1), its Pt particles become smaller and have higher catalytic activity, its voltage increases accordingly and reaches 440 mV at a current density of 500 mA/cm^2. The Pt/CNTs prepared at a pH value of 7.0 has the best PEMFC performance, the voltage decreases slowly with the increase of current density and reaches 580 mV at the current density of 500 mA/cm^2. At the moment, the Pt particles have the smallest size and the highest catalytic efficiency.

Table 1 Pt content (mass fraction) in Pt/CNTs samples at different pH values %

pH value	5.0	7.0	9.0	11.0
Pt content	14	16.2	18.1	19.5

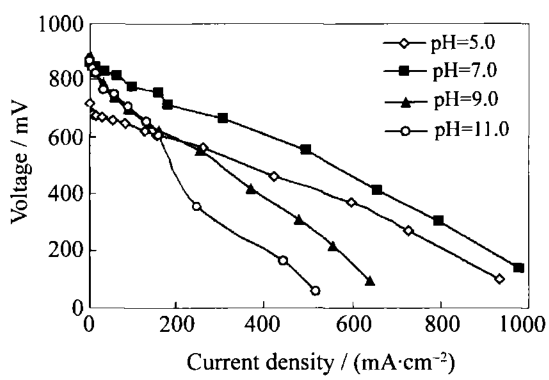

Figure 2 Effect of Pt/CNTs prepared at different pH values on the performance of PEMFC.

3.2 Pt content effect on the Pt/CNTs and the performance of PEMFC

The theoretical Pt contents of Pt/CNTs were 15%, 25% and 35%, respectively. The ultimate Pt contents of each sample were measured with XRF and were 10.5%, 16.2% and 20.5%, respectively. It can be seen that there is some loss of Pt in each sample of Pt/CNTs during the depositing process.

The TEM images show that there is a slightly increase in the size of Pt particles with the increase of theoretical Pt content from 15% to 25% (**figures 3**(a) and (b)), while the Pt particle size becomes larger obviously at a theoretical Pt content of 35% than those of the former two samples (figure 3(c)).

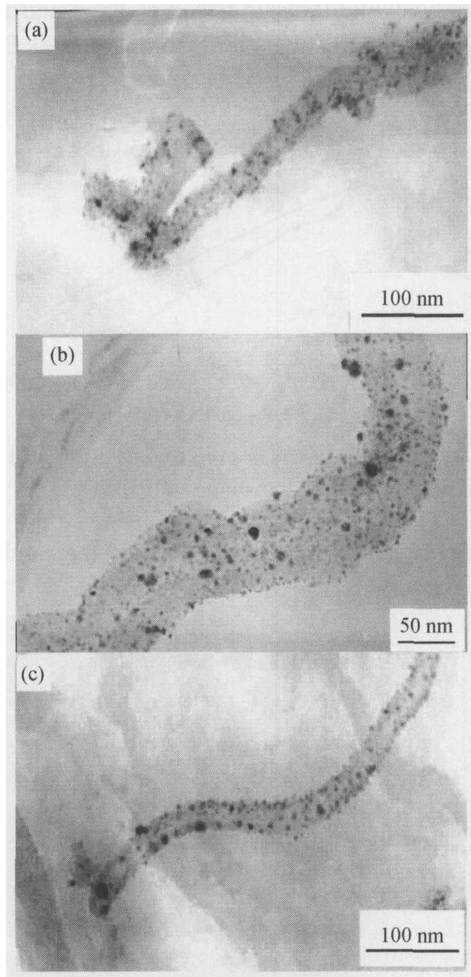

Figure 3 TEM images of Pt deposited on CNTs prepared at different theoretical Pt contents: (a) 15%; (b) 25%; (c) 35%.

The experimental results of the performance of PEMFC show that the sample of a theoretical Pt content of 15% has the poorest catalytic property and the voltage of PEMFC is only 350 mV at a current density of 500 mA/cm^2 (**figure 4**). This may be due to the lower actual Pt content (10.5%) which causes the worse catalytic ability of Pt/CNTs. The larger Pt particles of Pt/CNTs with a theoretical Pt content of 35% also cause the decrease of the performance of PEMFC. So the Pt/CNTs has the best performance of PEMFC at a theoretical Pt content of 25% and the voltage can reach 580 mV at a current density of 500 mA/cm^2.

3.3 Treatment temperature effect on the Pt/CNTs and the performance of PEMFC

The Pt particles in the sample of Pt/CNTs directly prepared through the chemical reaction of equations(1) and (2) are usually in the form of compounds, so their catalytic properties are not high. The heat treatment can make the compounds decompose into pure Pt and improve the catalyst activities. **Figure 5** shows that the ultrafine Pt particles with a size of 3 nm are obtained at Pt/CNTs treatment temperatures of 400, 500 and 600°C, while the size becomes large and reaches above 6 nm at a treatment temperature of 800°C.

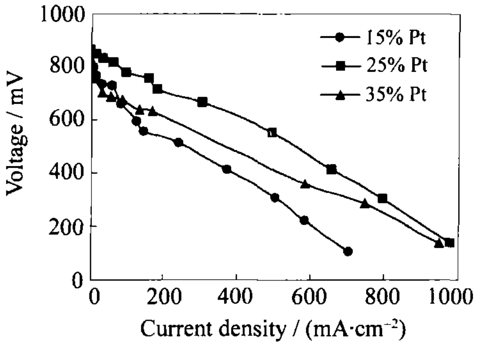

Figure 4 Effect of Pt/CNTs prepared at different theoretical Pt contents on the performance of PEMFC.

The performances of PEMFC using the catalysts of Pt/CNTs heated at different temperatures are indicated in **figure 6**. It can be seen that the voltage of the sample heated at 400°C decreases abruptly with the increase of current density and reaches 150 mV at a current density of 500 mA/cm^2 (figure 6). This means that 400°C is lower than the decomposition temperature of Pt compounds and thus pure Pt can not be obtained at this temperature. The voltage reaches the largest value of 580 mV at a current density of 500 mA/cm^2 as the heating temperature raised to 500°C and the Pt/CNTs have the highest catalytic activity. When the heating temperature increases further, the Pt particles will grow up increasingly and make the PEMFC performance decrease. So the heating temperature of 500°C is most suitable for preparing Pt/CNTs and the best PEMFC performance can be obtained.

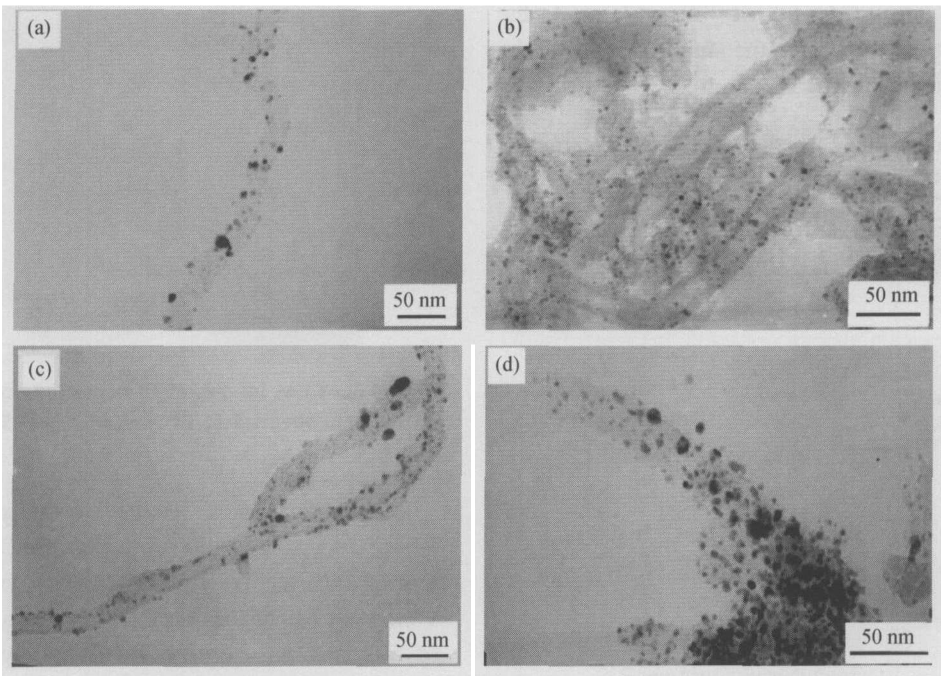

Figure 5 TEM images of Pt deposited on CNTs prepared at different temperatures: (a) 400°C; (b) 500°C; (c) 600°C; (d) 800°C.

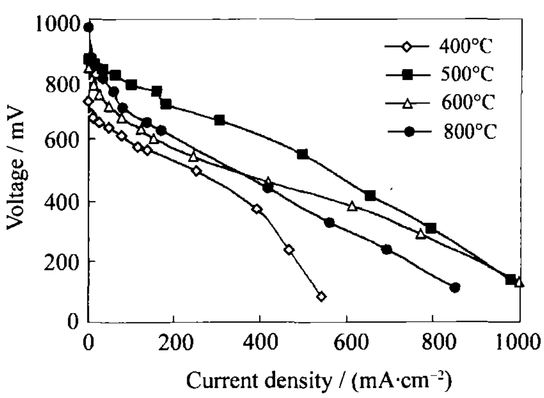

Figure 6 Effect of Pt/CNTs prepared at different temperatures on the performance of PEMFC.

4 Conclusions

CNTs were prepared by a catalytic pyrolysis method and oxidized with HNO_3 and H_2O_2, respectively. Platinum nanoparticles were deposited on the surfaces of CNTs that used as the supporters through a chemical precipitation method. The experimental results show that if the sample was prepared at a solution pH value of 7.0, a theoretical Pt content of 25% and a heating temperature of 500°C, the best PEMFC performance can be obtained and the voltage can reach 580 mV at a current density of 500 mA/cm^2.

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