High dispersion and electrocatalytic properties of platinum on well-aligned carbon nanotube arrays

H. Tang a, J.H. Chen a,*, Z.P. Huang b, D.Z. Wang b, Z.F. Ren b, L.H. Nie a, Y.F. Kuang a, S.Z. Yao a

a State Key Laboratory of Chemol/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Yuelu Southern Road, Changsha 410082, PR China

b Department of Physics, Boston College, Chestnut Hill, MA 02467, USA

Received 11 August 2003; accepted 15 October 2003

Abstract

Platinum (Pt) electrocatalyst was electrochemically dispersed on well-aligned carbon nanotube (CNT) arrays by a potential-step method. The structure and elemental composition of the resulting Pt/CNT electrode were characterized by scanning electron microscopy, transmission electron microscopy and energy dispersive X-ray spectroscopy. The electrocatalytic properties of the Pt/CNT electrode for oxygen reduction reaction have been investigated by linear sweep voltammetry. Compared with a Pt/graphite electrode, higher electrocatalytic activity of the Pt/CNT electrode can be observed. This may be attributed to the high dispersion of platinum catalysts and the particular properties of CNT supports. The results imply that the Pt/CNT has good potential applications in proton exchange membrane fuel cells.

Keywords: A. Carbon nanotubes, electrodes; B. Chemical vapor deposition; D. Electrochemical properties

1. Introduction

Proton exchange membrane fuel cells (PEMFC) are attractive electrical power sources without environmental pollution. However, one of the serious problems for PEMFC is the low rate of the oxygen reduction reaction (ORR) at cathode [1]. Platinum (Pt) seems to be the best choice of the catalysts for the electroreduction of oxygen in acidic media. The electrocatalytic activity of platinum catalyst is dependent on many factors [2,3]. Among them, the good properties of the catalyst supports, such as high surface area and good electronic property, are essential for Pt catalyst to produce high catalytic activity [4]. Carbon nanotubes (CNTs), as a new form of carbon, have received numerous theoretical and experimental studies [5]. Due to their nanometer size and interesting properties, CNTs are also of great interest for many applications, for example, batteries [6], flat panel displays [7], chemical sensor [8], etc. Furthermore, high accessible surface area, low resistance and high stability [9] suggest that CNTs are suitable materials for electrodes and catalyst supports in PEMFC. The metallic particles with electrocatalytic activity may decorate the external walls or be encapsulated in the interior of the nanotubes [10]. Several papers have focused on this area using tangled and substrate-free carbon nanotubes [11–16]. Pt has been deposited on activated single or multi-wall carbon nanotubes by chemical reduction method and the resultant electrodes show good electrocatalytic properties for hydrogenation [11] and oxygen reduction [12,13].

For the applications in electrode and catalyst support, two kinds of CNT electrodes have been developed: binder-free [17] and binder-enriched [18]. In the binder-free electrode, carbon nanotubes are mechanically and electrically loose. When a binder is used, it brings impurities into the electrode and degrades the electrochemical performance. Furthermore, both methods result in a high contact resistance between the active material (CNT) and current collectors (graphitic or metallic substrate). In this paper, the well-aligned carbon nanotubes are grown directly on the titanium
(Ti) substrate and used for the first time as catalyst support for fuel cell. This not only simplifies the preparation of CNT electrodes but also can greatly reduce the contact resistance of CNTs and Ti substrate. Additionally, compared with the tangled CNTs or flat electrode (such as graphite disk and carbon cloth), the well-aligned CNT arrays with a space between each of CNTs will be helpful to disperse Pt catalyst on each of CNTs.

On the other hand, for preparation of the platinum catalysts, chemical reduction method is commonly used [11–14]. However, the impurities are easily involved from the bath solutions, which may deteriorate the catalytic activity of platinum catalysts. At the same time, the electrodeposition of platinum particles has received more and more attention due to its advantages, such as high purity of deposits and simple procedure for deposition. Furthermore, electrodeposition method can control easily the loading mass of the metallic catalyst [19]. This paper reports the uniform deposition of platinum catalysts on each of well-aligned carbon nanotube arrays by potential-step electrodeposition method and their electrochemical characterizations. The main concern in this paper is to investigate the effect of the CNT electrode with three-dimensional structure on the dispersion and electrocatalytic properties of Pt catalyst. For comparison, a flat electrode, graphite disk, is also investigated in this paper. The morphology of the platinum catalysts is characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The electrocatalytic properties of Pt/CNT electrode for ORR are investigated by cyclic voltammetry (CV) and linear sweep voltammetry.

2. Experimental

2.1. Chemicals and instruments

The well-aligned CNT arrays (geometry area 1 cm²) were used as working electrode. The detailed description of the synthesis of well-aligned carbon nanotubes has been reported in a previous paper [20]. The SEM image of the well-aligned carbon nanotubes used in this paper is shown in Fig. 1. The diameter of each nanotube is 50–70 nm with a length of 3–4 μm. A platinum foil served as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. CHI660A electrochemical workstation (CH Instruments, Inc.) was employed for the synthesis and electrochemical studies of platinum catalysts. All chemicals are of analytical grade. Freshly double-distilled water was used throughout.

The morphology and elemental composition of Pt/CNT and Pt/graphite electrodes were investigated by SEM (JSM 5600 LV, operating at 20 kV), TEM (HITACHI H800, operating at 200 kV) and energy dispersive X-ray spectroscopy (EDS) (Vantage 4105, NORAN), respectively.

2.2. Platinum deposition and electrochemical studies

Using a standard three-electrode cell, platinum catalysts were electrodeposited on the CNT arrays by potential-step deposition method from N₂ saturated 7.7 mM H₂PtCl₆ + 0.5 M HCl aqueous solution. The potential jumped from 0.65 V (the open-circuit potential of the CNT/Ti electrode in N₂ saturated H₂PtCl₆ aqueous solution) to –0.15 V (SCE) with a pulse width 0.001 s and carried out successively until a predetermined Pt deposition charge (Qdep) had reached. The high open-circuit potential of CNT/Ti electrode (+0.65 V) may result from the TiOₓ passivation films formed on Ti substrate during the following pretreatment process. Before platinum deposition, the CNT electrode was pretreated in 30 wt.% HNO₃ aqueous solution for 40 min to remove the metallic nickel particles that served as catalyst for the growth of CNTs. To further increase the electrochemical activity of CNTs in water solution [21], the CNT electrode was then cycled in N₂ saturated 0.1 M H₂SO₄ for 10 cycles under the potential range of –0.15 to 1.3 V at a sweep rate of 50 mV s⁻¹. After platinum deposition, the samples were cleaned by double-distilled water. The electrochemical properties of the Pt/CNT electrode for oxygen reduction were then investigated by linear sweep voltammetry in 0.1 M H₂SO₄ aqueous solution. An air flow of 50 cm³ min⁻¹ was introduced into the cell throughout the experiment to supply oxygen (O₂). For comparison, platinum particles were also electrodeposited on the graphite disk electrode (geometry area 1.71 cm²). All experiments were carried out at ambient temperature. All the potentials were referred to SCE.
3. Results and discussion

3.1. The morphology and elemental composition of Pt/CNT electrode

Platinum was electrodeposited on the surface of well-aligned carbon nanotubes by potential-step deposition method. The morphology of the Pt/CNT electrode with different Pt $Q_{\text{dep}}$ has been shown in Fig. 2. For comparison, the SEM images of the surface and the cross-section of the Pt/graphite electrode are shown in Fig. 3. From Fig. 2(A), it is shown when $Q_{\text{dep}}$ is 9.744 μC cm$^{-2}$, a great deal of platinum nanoparticles with size of 30–70 nm (Fig. 2(B)) were uniformly deposited on the surface of CNT arrays. However, the diameter of the platinum particles on graphite electrode is about 100–150 nm (Fig. 3(A)) at $Q_{\text{dep}} = 11.69$ μC cm$^{-2}$. It is probably due to the nanoscale effect of the carbon nanotubes on the platinum deposition. It is also worth noting that the higher dispersion and real surface area of platinum nanoparticles were obtained at CNT electrode. The interesting three-dimensional structure of Pt/CNT, high dispersion and small Pt nanoparticles may result in good electrocatalytic activity.

The significant difference is obvious between Fig. 2(A) and (C). When the $Q_{\text{dep}}$ of platinum is small, the platinum nanoparticles disperse individually and the nanotubes form bundles due to the surface tension (Fig. 2(A)). With the increase of $Q_{\text{dep}}$, the surface of the bundles of carbon nanotubes are coated uniformly by a thin platinum film (Fig. 2(C)) and the thickness of the platinum film is about 65 nm at $Q_{\text{dep}} = 572.5$ μC cm$^{-2}$ (Fig. 2(D)). From Fig. 2(C) and (D), no obvious platinum particles can be observed. However, for graphite electrode, when $Q_{\text{dep}}$ increases, the platinum particles will accumulate and form large particles. At $Q_{\text{dep}} = 537.7$ μC cm$^{-2}$, as shown in Fig. 3(B), the Pt particle size is about 400 nm. From the corresponding SEM cross-section image (Fig. 3(C)), the thickness of the platinum film is about 1000 nm. Furthermore, some cracks can be observed in Fig. 3(B). This means that the adhesion of platinum catalysts on graphite electrode is weak and may be easily peeled off from the substrate. However, the good adhesion between CNT and the thin uniform platinum film prevents peeling off of Pt from CNTs even when $Q_{\text{dep}}$ is 572.5 μC cm$^{-2}$. This may imply that Pt/CNT electrodes possess long-term stability.

Fig. 4 is the energy dispersive X-ray spectroscopy (EDS) of Pt/CNT electrode. It indicates that Pt and Ti are the major elements plus C. The EDS results confirm that the nanoparticles on the CNTs are platinum.

![Fig. 2 SEM (A, C) and TEM (B, D) images of platinum catalysts on well-aligned carbon nanotube arrays. (A), (B): $Q_{\text{dep}} = 9.744$ μC cm$^{-2}$; (C), (D): $Q_{\text{dep}} = 572.5$ μC cm$^{-2}$.](image-url)
3.2. Electrocatalytic properties of Pt/CNT electrode

The electrochemical and electrocatalytic properties of CNT, graphite, Pt/CNT and Pt/graphite electrodes have been investigated in 0.1 M H₂SO₄ aqueous solution. The corresponding results are presented in Fig. 5. Typical cyclic voltammogram of CNT electrode is observed in Fig. 5(A) (line I). A similar result has also been obtained for single wall carbon nanotubes [22]. The background current, which is the nature of capacitive current, is larger than that of graphite electrode (Fig. 5(A), line II).

Fig. 3. SEM images of platinum nanoparticles on graphite electrode with different loading mass (Qdep). (A) 11.69 μC cm⁻², (B) 573.7 μC cm⁻² and (C) cross-section SEM image of B.

Fig. 4. The EDS spectra of Pt/CNT electrode (Qdep = 9.744 μC cm⁻²).

Fig. 5. The cyclic voltammograms of CNT and graphite electrodes in N₂ saturated 0.1 M H₂SO₄ aqueous solution (A), linear sweep voltammograms (B and C) of Pt/CNT and Pt/graphite electrodes in 50 cm³ min⁻¹ air flow bubbled H₂SO₄ aqueous solution. (A) Line I, CNT electrode; line II, graphite electrode (CV sweep rate 50 mV s⁻¹). (B) Line I, Pt/CNT electrode (Qdep = 9.744 μC cm⁻²); line II, Pt/graphite electrode (Qdep = 11.69 μC cm⁻²). Linear sweep rate 200 mV s⁻¹. (C) Line I, Pt/CNT electrode (Qdep = 572.5 μC cm⁻²); line II, Pt/graphite electrode (Qdep = 573.7 μC cm⁻²). Linear sweep rate 200 mV s⁻¹.
This is attributed to the high specific surface area of the CNTs. On the other hand, it is shown that no O₂ reduction current is observed at CNT and graphite electrodes over the study potential range (Fig. 5(A)). This means that the carbon nanotubes and graphite substrate have no obvious electrocatalytic activity for ORR. Fig. 5(B) and (C) are the linear sweep voltammograms of Pt/CNT and Pt/graphite electrodes at different Pt Q_{dep}. For Pt/CNT electrode, a large oxygen reduction current can be observed at 0.36 V (SCE), which is the typical potential for oxygen electroreduction on platinum catalysts in H₂SO₄ solution [23]. Specific current [24], defined by peak current density (mA cm⁻²) per unit of Q_{dep} (μC cm⁻²), is used to evaluate the electrocatalytic activity of Pt catalysts for ORR. When the Pt loading mass is low (Q_{dep} = 9.744 μC cm⁻²), the specific current of Pt/CNT electrode (Fig. 5(B), line I) is 0.41 mA μC⁻¹, which is 1.4 times as large as that of Pt/graphite electrode (Fig. 5(B), line II). At high Q_{dep} (572.5 μC cm⁻²), the specific current of Pt/CNT electrode (Fig. 5(C), line I) is almost twice as large as that of Pt/graphite electrode (Fig. 5(C), line II). These results imply that the Pt/CNT electrode possess high electrocatalytic activity for ORR. For Pt/CNT electrode, the increase in O₂ reduction activity may be attributed to the following factors: (i) High dispersion of Pt on the three-dimensional structure of CNT electrode can provide high acceptable surface area of Pt for oxygen reduction. (ii) The particular structure and electrical properties of CNTs may be beneficial to the electrocatalytic reduction of oxygen. Brito et al. [25] studied the dissociation of adsorptive oxygen on the surface of CNTs as well as the charge transfer process and suggested that CNTs have the ability to promote electron-transfer reactions. Additionally, the activity of the catalyst, which could be involved in the interaction between metallic catalyst and catalyst support, can be strongly affected by properties of the support materials [24]. These results may imply that well-aligned carbon nanotube arrays may be good candidate for the cathodic catalyst supports in PEMFC.

3.3. The kinetics of oxygen reduction reaction at Pt/CNT electrode

In order to investigate the kinetics of oxygen reduction reaction at Pt/CNT electrode, the relationship of peak current density (I_p) and peak potential (E_p) for ORR with linear sweep rate (ν) have been studied. The results are shown in Figs. 6 and 7. Fig. 6 shows a linear relationship between peak current density and ν¹/² for Pt/CNT and Pt/graphite electrodes. This may imply that the ORR is controlled by diffusion process of oxygen [26]. These results are thought to be due to the relatively low concentration of dissolved oxygen and consequent limitation of mass transport. However, the slope of line I (Fig. 6, Pt/CNT electrode) is 6.7296, which is twice as large as that of line II (Fig. 6, Pt/graphite electrode, the slope = 3.3886). This result can also be observed for other carbon materials with high surface area [27] and is related to A_t (the active surface area of Pt catalysts per unit geometric area of electrode) of Pt/CNT and Pt/graphite electrodes. According to the Nicholson’s results [28], the peak current density of ORR is proportional with A_t (i.e.: I_p ∝ A_t) when other parameters are identical. From the slopes of the lines I and II, it may be deduced that the A_t of Pt/CNTs is almost one fold larger than that of Pt/graphite electrode.

Fig. 7 is the dependence of peak potential (E_p) of oxygen reduction and log (ν) in 0.1 M H₂SO₄ aqueous solutions with air flow rate = 50 cm³ min⁻¹. Line I, Pt/CNT electrode (Q_{dep} = 572.5 μC cm⁻²); line II, Pt/graphite electrode (Q_{dep} = 573.7 μC cm⁻²).
smaller than that for Pt/graphite electrode. The \( E_p \) of the Pt/CNT electrode is lower than that of Pt/CNT electrode at the same \( v \). At \( v = 200 \text{ mV s}^{-1} \), \( E_p \) shifts negatively by 170 and 236 mV (relative to \( E_p \) at \( v = 1 \text{ mV s}^{-1} \)) for Pt/CNT and Pt/graphite electrodes, respectively. This may imply that larger cathodic polarization occurs and the electrocatalytic properties of the electrode are deteriorated for Pt/graphite electrode. On the other hand, for an electrochemical reduction reaction at high \( v \), the linear relationship between \( E_p \) and \( \log(v) \) can be represented by the following equation [29,30]:

\[
E_p = A - \frac{2.3RT}{anF} \log v
\]

where \( A \) is a constant, which is related with the formal electrode potential \( (E^0) \) and standard rate constant at \( E^0 \). The transfer coefficient \( (\alpha) \), which characterizes the effect of electrochemical potential on energy of activation of an electrochemical reaction [31], can be calculated according to the slope of \( E_p \sim \log(v) \) in linear range. From Fig. 7, the \( \alpha \) values are calculated and equal to 0.124 and 0.097 (giving \( n = 2 \) for Pt/CNT and Pt/graphite electrodes, respectively). These indicated that ORR at both Pt/CNT and Pt/graphite electrodes was irreversible and the energy of activation for Pt/CNT electrode was smaller than that for Pt/graphite electrode at the same cathodic over-potential [31]. The smaller energy of activation for Pt/CNT electrode suggests that CNTs have a beneficial effect on the kinetics of oxygen reduction.

4. Conclusion

Highly dispersed platinum catalysts are electrodeposited by potential-step method on well-aligned carbon nanotube arrays. The electrocatalytic properties of Pt/CNT electrode for ORR have been investigated and high electrocatalytic activity is observed. This may be attributed to the high dispersion of nanoscale platinum catalysts and the particular properties of carbon nanotubes (such as unique electrical property, three dimensional structure and nanometer size, etc.). It also implies that well-aligned carbon nanotube arrays have good potential application in proton exchange membrane fuel cell. Additionally, the kinetics of ORR at Pt/CNT electrode has also been investigated. The ORR may be controlled by the diffusion process of oxygen.

Acknowledgements

This work is supported by the Natural Science Foundation of China under a grant 50172014 and 20275009 and the Project Sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry under the grant 2001-498. The work performed at Boston College is partly supported by the US Department of Energy under a grant DE-FG02-00ER45805.

References


