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RESEARCH ARTICLE

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Investigation of electro-oxidation activity of Pt-CNTs/GC electrodes

Abstract The morphology and structure of Pt-CNTs/GC electrodes were characterized via Transmission Electron Microscopy (TEM) and selected area electron diffraction. The electro-oxidation behavior of CO and methanol on Pt-CNTs/GC electrodes were studied with cyclic voltommograms or chronoamperometry. Three oxidation peaks were observed for CO absorbed on Pt-CNTs/GC electrodes. Methanol was found to be dissociated spontaneously on the electrode to produce a strong absorbed intermediate CO. Among the three oxidation peaks, peak I was presumed to be due to the bridged CO absorption while peaks II and III were attributed to the split in the linear CO which is absorbed on the Pt-CNTs/GC nanocluster with different particle size and Pt film. The oxidation current of methanol on the Pt-CNTs/GC electrode did not always increase with the increase in the amount of Pt loading. The result indicates that there is an optimal Pt loading for methanol oxidation. It is necessary to select the catalyst with proper Pt loading when the anode of a direct-methanol fuel cell is prepared.

Keywords platinum, carbon nanotube, methanol, carbon monoxide

1 Introduction

Investigations into the preparation of catalytic materials and catalytic reactions using carbon nanotube-supported metal nanoparticles such as Pt, Ru, Pd, Au and Ni, have attracted great interest recently. This is due to the nanoparticles' superior properties of absorption, desorption and space stereo-selectivity to reactants and products [1–3]. Electrodes modified by carbon nanotube-supported Pt or Pt-Ru nanoparticles were prepared, and their electro-catalytic activities for methanol oxidation were investigated by Chen Weixiang [4], Du Bingchen [5], and Li [6] et al. In addition, the electro-catalytic activity of electrodes modified by carbon nanotube-supported Pt-Sn nanoparticles and used as anode for ethanol oxidation was investigated by Zhao Xinsheng et al. [7].

In this paper, carbon nanotube-supported Pt cluster nanoparticles (Pt-CNTs) with uniform size and good dispersal were successfully synthesized by microwave dielectric heating method, using ethylene glycol as the reductant for H_2PtCl_6 and carbon nanotubes activated in HNO_3 at a certain temperature in advance. In addition, the behaviors of absorption and oxidation of CO and methanol on Pt-CNTs-modified glass carbon electrodes (Pt-CNTs/GC) were investigated, in order to get some useful information for developing carbon nanotubes as anode material of fuel cells.

2 Experimental

TEM images and Selected Area Electron Diffraction (SAED), were obtained on JEM-200CX-II microscopy working at 100 kV. Cyclic Voltommograms (CV) and chronoamperometry experiments were performed at the electrochemical working station (CHI631a, manufactured in Shanghai Chenghua Instrumental Factory). The working electrodes were carbon nanotubes or Pt nanoparticles loaded on carbon nanotube-modified carbon electrodes (CNTs/GC or Pt-CNTs/GC), respectively. A Pt wire served as the counter electrode. The reference electrode was a saturated calomel electrode (SCE).

All the experiments were performed at room temperature ($25 \pm 1C^{\circ}$). All the chemical reagents were of AR

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grade. CO gas was of high purity. All the solutions were prepared using super purified water ($\rho \geqslant 18$ MΩ·cm).

3 Results and discussion

Figure 1 shows the images of TEM and SEAD of Pt-CNTs which was prepared as follows: 0.0080 g CNTs were activated in 14.0 mol/L HNO_3 for 2.5 h and then heated for 5 s by microwave method, using surplus ethylene glycol as the reductant for H_2PtCl_6. Afterwards, 0.1875 mmol/g Pt nanoparticles were loaded on the CNTs. It can be seen from Fig. 1 that Pt polynanoclusters with diameter of about 2 nm were well loaded on the surface of the CNTs.

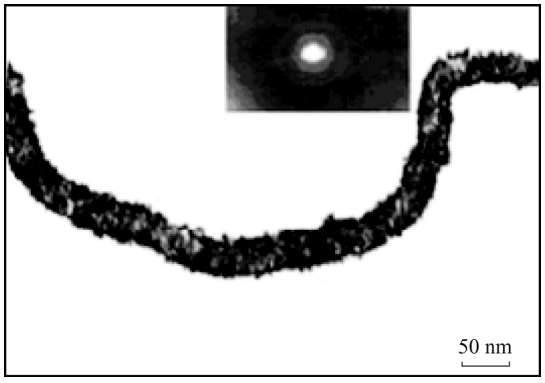

Fig. 1 TEM images and SAED of Pt-CNT
The ratio of Pt to CNT is 0.1875 mmol/g

Figure 2 shows the CV curves of CNTs/GC and Pt-CNTs/GC electrodes (with the Pt loading at 0.1875 mmol/g) in 0.5 mol/L H_2SO_4. From the curves in Fig. 2(a), a great double layer charge and discharge current curve can be seen in the case of the CNTs/GC electrode between the potential of −0.2–0.6 V, which was in agreement with Rajesh's result [8]. Because the CNTs were loaded with 0.1875 mmol/g Pt nanoparticles, the double layer charge and discharge current at the CNTs/GC was greatly suppressed, and the curve is very similar to the CV curve of the Pt electrode in H_2SO_4 [9] [see Fig. 2 (b)]. The experimental result in Fig. 2 further confirmed the experimental result in Fig. 1, in that it indicated that there was a very thick Pt nanoparticle layer loaded on the surface of the CNTs.

The Pt-CNTs/GC electrodes with Pt loading of 0.1250 mmol/g or 0.1875 mmol/g were immersed respectively in CO-saturated 0.1 mol/L H_2SO_4 for 30 min at the potential of −0.2 V. Then the electrodes were thoroughly rinsed with triple distilled water. Their CV curves were measured in 0.5 mol/L H_2SO_4. In Fig. 3(a), the current peaks (I, II, III) can be seen at the potentials of 0.27 V, 0.49 V and 0.61V respectively. Current peaks (I, II, III) can also be seen at the potentials of 0.19 V, 0.46 V and 0.51 V, respectively, when the Pt loading increased to 0.1875 mmol/g. The latter current peaks were shifted more negatively than the former, but peak II current intensity decreased by about a half, while peak III current intensity did not change significantly. So the current intensity ratio of peak III to peak II increased.

Peak I and peak II were attributed to the oxidation of the bridge and linear CO absorbed on platinum, respectively [10]. Oxidation peak III was presumed simply as the peak of CO oxidation on CNTs. Further experimental results indicated that there was no CO oxidation peak observed on CNTs without the modifying Pt nanoparticles. So it would be impossible for peak III to have come from CO oxidation on the surface of CNTs.

We also found that when the Pt loading increased to 0.3125 mmol/g, the CNTs were completely covered by Pt nanoparticles. Though the experiments were repeated many times, no obvious CO oxidation peak was detected except for the very weak shoulder peak at the counter

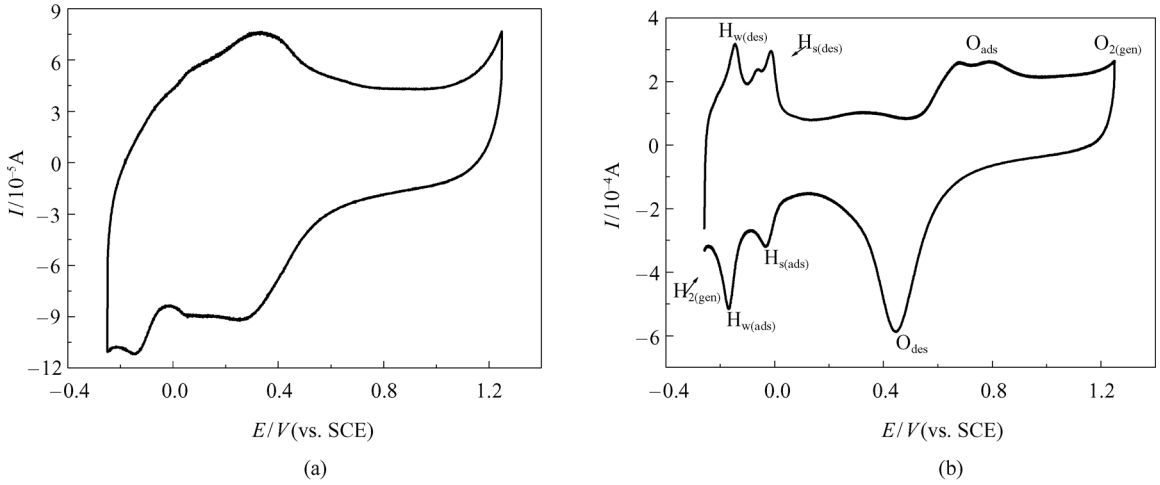

Fig. 2 CVs of CNTs/GC and Pt-CNTs/GC in 0.5 mol/L H_2SO_4
Scan rate: 50 mV/s^{-1}

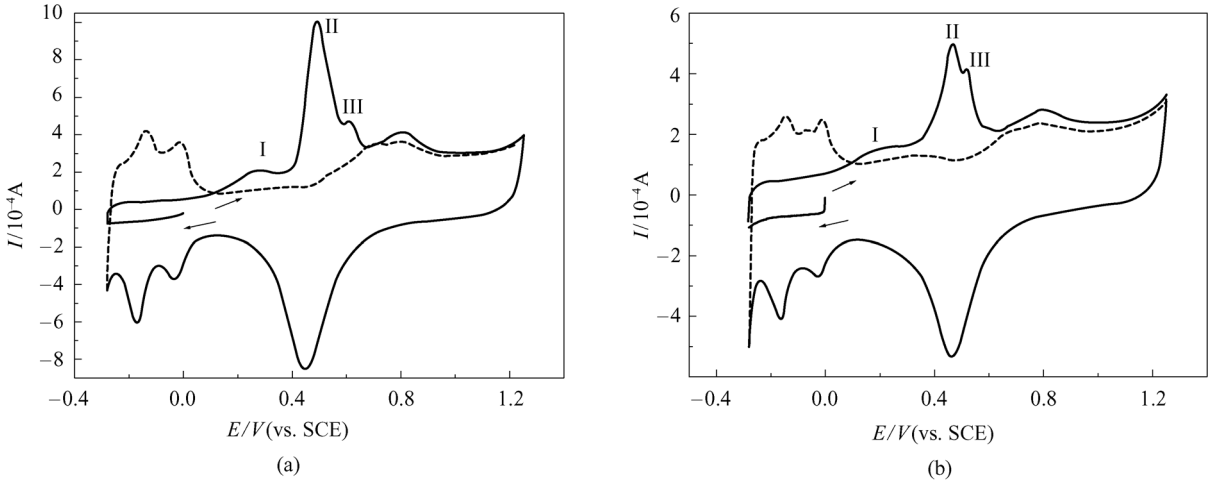

Fig. 3 CVs of different Pt-CNTs/GC with CO in 0.5 mol/L H_2SO_4
The ratio of Pt to CNTs: (a) 0.125 mmol/g (b) 0.1875 mmol/g

potential. The results indicate that the Pt nanoparticles loaded on CNTs by the Pt nanocluster form when the amount of Pt loading on the CNTs reaches 0.1250 mmol/g, so there is relatively strong electro-catalytic oxidation activity for the absorbed CO on the electrode [Fig. 3(a), peak II]. However, Pt film will form on the surface of the CNTs when Pt loading reaches 0.1875 mmol/g. This is possibly due to the increasing amount of Pt loading and because electro-catalytic oxidation of the CO absorbed on the Pt film is weaker than on the Pt nanocluster. The greater the amount of Pt loaded on the CNTs, the lesser the amount of Pt cluster formed and the thicker the Pt film formed. All of these gradually decrease the electro-catalytic oxidation activity of the Pt-CNTs/GC electrode, leading to a decrease in the current intensity of peak II in Fig. 3(b) and ultimately resulting in the electro-oxidation behavior of CO on the Pt electrode of polymorphic crystal structure. Therefore, we can conclude that peak II in Fig. 3(b) is due to the oxidation of the linear CO adsorbed on the Pt nanocluster, while peak III in Fig. 3 (b) is due to the oxidation of the linear CO adsorbed on Pt film [10]. It indicates that CO as the probe molecule can detect the change in the surface structure of electrode.

Figure 4 shows the CV curves of Pt-CNTs/GC electrode absorbed methanol in 0.5 mol/L H_2SO_4 solution. The surface of the electrode was washed by super purified water in advance, after being immersed in 0.1 mol/L CH_3OH + 0.1 mol/L H_2SO_4 solution for 5 min at open circuit potential. We can observe the CO peak at about + 0.47 V in Fig. 4, which suggests that CH_3OH can be dissociated spontaneously on the Pt-CNTs/GC electrode and produce strong absorption intermediate CO [11–13].

Figure 5 shows the CVs of Pt-CNTs/GC electrodes with different amounts of Pt loading immersed in 0.1 mol/L CH_3OH + 0.1 mol/L H_2SO_4 solution. The Pt-CNTs/GC electrode with a Pt loading of 0.1875 mmol/g has a stronger current density than those with Pt loading of 0.1250 and 0.2500 mmol/L, and has a higher electric potential than the latter two for CH_3OH oxidation. It shows that the oxidation peak current density of CH_3OH oxidation on a Pt-CNTs/GC electrode does not

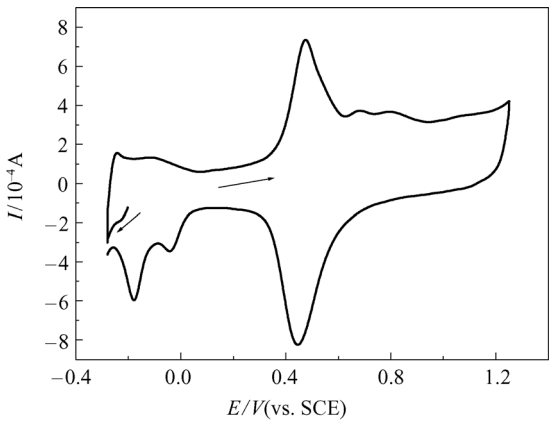

Fig. 4 CVs of Pt-CNTs/GC electrode with methanol in 0.5 mol/L H_2SO_4 solution

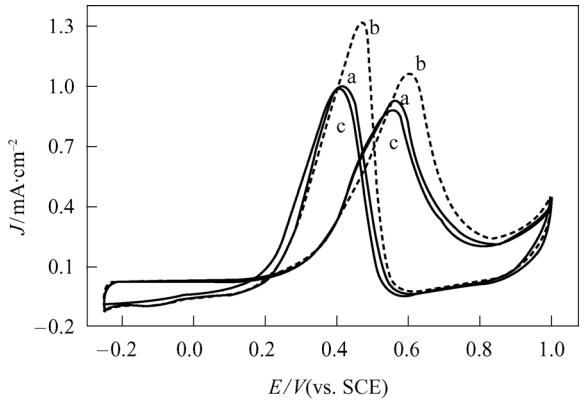

Fig. 5 CVs of different Pt-CNTs/GC electrodes in 0.1 mol/L CH_3OH + 0.1 mol/L H_2SO_4

always increase with an increasing amount of Pt loading when the Pt loading exceeds a certain quantity. Catalytic activity weakens (possibly because the particle size of Pt nanoparticles gradually gets larger with the increasing amount of Pt loading), the number of Pt nanoclusters declines, and Pt film gradually forms on CNTs, resulting in the loss of the nanostructure effect caused by Pt nanoparticles on CNTs. On the other hand, this experiment verifies the experimental result in Fig. 3. It is necessary to select the proper Pt loading when Pt-CNTs/GC electrode is prepared.

Figure 6 shows the *I-t* curves of Pt-CNTs/GC electrodes with different amount of Pt loading immersed in 0.1 mol/L CH_3OH + 0.1 mol/L H_2SO_4 solution (the insert shows the electric potential phase transition program during the chronoamperometry experiment.). When the working electrode potential shifted from −0.25 V to + 0.4 V in 2 s, the current of CH_3OH oxidation on Pt-CNTs/GC electrodes with three different Pt loading descended sharply, then became essentially stable at 5 s. The relationship between the stable current and Pt loading also supports the experimental result of Fig. 5.

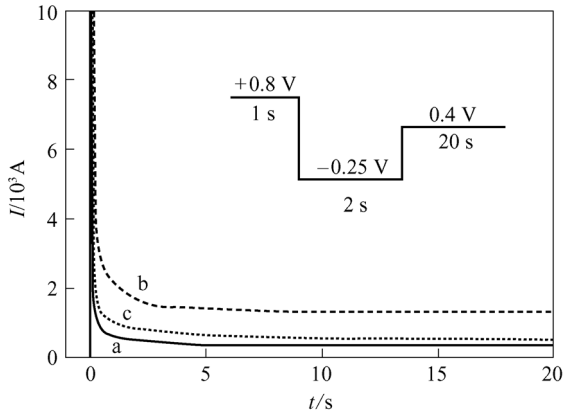

Fig. 6 *I-t* curves of different Pt-CNTs/GC electrodes in 0.1 mol/L CH_3OH + 0.1 mol/L H_2SO_4
(a) 0.1250 mmol/g; (b) 0.1875mmol/g; (c) 0.2500 mmol/g

4 Conclusions

Adsorption and electro-oxidation behaviors of CO and CH_3OH oxidation on Pt-CNTs/GC electrodes were investigated by traditional electrochemistry methods. Three peaks of CO oxidation on Pt-CNTs/GC electrodes were found at the initial time. CH_3OH could be dissociated spontaneously on Pt-CNTs/GC electrodes, and produce strong absorbed intermediate CO. However, the current of methanol oxidation on Pt-CNTs/GC electrode does not always increase with the increase in the amount of Pt loading on carbon nanotubes. So it is necessary to select the proper amount of Pt loading when the anode of direct-methanol fuel cell is prepared.

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