

Electrocatalytic oxidation of methanol on carbon-nanotubes/graphite electrode modified with platinum and molybdenum oxide nanoparticles

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Received 11 November 2005; accepted 28 September 2006

Abstract: Electrochemical codeposition and electrocatalytic properties of platinum and molybdenum oxide nanoparticles (Pt-MoO_x) on carbon-nanotubes/graphite electrode for methanol oxidation were investigated. The micrograph and elemental composition of the resulting Pt-MoO_x/CNTs/graphite electrode were characterized by scanning electron microscopy(SEM) and energy dispersive X-ray spectroscopy(EDS). The results show that the Pt-MoO_x particles with the average size of about 50 nm are highly dispersed on the CNTs surface. The Pt-MoO_x/CNTs/graphite electrode delivers excellent electrocatalytic properties for methanol oxidation. The highest mass activity(A_m) reaches 264.8 A/g at the loading mass of 159.3 μg/cm². This may be attributed to the small particle size and high dispersion of Pt-MoO_x catalysts deposited on the CNTs surface. The kinetic analysis from electrochemical impedance spectroscopy(EIS) reveals that the existed MoO_x phase can improve the chemisorptive and catalytic properties for methanol oxidation.

Key words: methanol oxidation; carbon nanotubes; molybdenum oxides; nanoparticles; fuel cells

1 Introduction

There is an increasing interest in the development of the direct methanol fuel cell(DMFC) due to its possible use in electric vehicles[1–2]. The performance of DMFC has improved markedly in the past years. Despite many efforts devoted to the DMFC development, there still remain problems to be overcome in terms of efficiency and power density. One of the reasons is the relatively slow kinetics of methanol oxidation reaction at the anode. Platinum has high activity for methanol oxidation and was used as anode catalysts for many years[3–4]. However, Pt catalyst will be poisoned by the adsorbed carboxyl species derived from methanol oxidation. In order to solve these problems, Pt-based binary and ternary metallic catalysts have been investigated extensively. The Pt-Ru binary catalyst is commonly accepted as the best catalyst for methanol oxidation[5–7]. However, there is a significant problem concerning the relatively sparsity of Ru. The fraction of Ru in Pt-group metal resources is less than 10%, which is much smaller than that of Pt. Therefore, it is important to develop a new anode catalyst without Ru species.

Recently, noble metal catalysts intermixed with inorganic oxides are of considerable interest for catalysis[8–10]. The oxide is used to physically separate the catalytic particles and decrease their agglomeration rate. Meanwhile, the oxide is believed to modify the electronic nature of the Pt particles, thus affecting their chemisorptive and catalytic properties. The improvement of CO-tolerance or catalytic activity for methanol oxidation on the Pt catalyst by the addition of certain kinds of oxides such as WO₃, MoO₃ and TiO₂ makes such system attractive for the application in DMFC[11–14]. On the other hand, to apply these catalyst systems in practical uses, the supporting materials with high surface area are necessary to disperse catalyst particle and reduce the Pt loading under the condition of keeping the high catalytic activity. Recently, carbon nanotubes(CNTs) are promising supporting materials because of their interesting properties, such as nanometer size and high surface area. Researchers have shown much interest in producing CNTs-supported Pt catalyst for oxygen reduction, hydrogen and methanol oxidation reactions[15–19]. However, to our knowledge, there is no work about Pt/oxides (especially for Pt-MoO_x) codeposited on CNTs

electro-catalyst for methanol oxidation.

In this paper, molybdenum oxide (MoO_x) was examined as a potential oxide phase to improve the electrocatalytic properties of Pt catalyst for methanol oxidation. We employed a simple electrochemical codeposition method to disperse the Pt- MoO_x nanoparticles on CNTs support. The advantage of this method is the mixing of metal and oxide on a microscopic level, simple procedure for deposition and easy control of the loading mass. The Pt- MoO_x /CNTs/graphite electrode is expected to improve electrocatalytic properties for methanol oxidation due to the metal-oxide interaction and high surface area of the catalyst particles with the low loading level.

2 Experimental

2.1 Preparation of CNTs/graphite electrode

The graphite electrode was sequentially polished with 1.0, 0.3 and 0.05 μm alumina emery paper, until a mirror-like surface was obtained. Then it was placed under ultrasonic conditions in double distilled water and ethanol. The CNTs used in this work were obtained from Chengdu Institute of Organic Chemistry and the purity was more than 95%. Further purification was accomplished by ultrasonically agitating the CNTs in concentrated nitric acid at 25 $^{\circ}\text{C}$ for 24 h. 2.5 mg of acid-treated CNTs was dispersed in 10 mL acetone with the aid of ultrasonic agitation to give 0.25 mg/L black suspension, and cast on the surface of graphite electrode. Finally, the solvent acetone was evaporated in air to form a CNTs/graphite electrode.

2.2 Co-deposition and electrochemical studies of Pt- MoO_x nanoparticles on CNTs/graphite electrode

Using a standard three-electrode cell, Pt- MoO_x nanoparticles were electrodeposited on a CNTs/graphite electrode from 2.2 mmol/L H_2PtCl_6 +0.2 mol/L Na_2MoO_4 +2.2 mol/L H_2SO_4 solutions by cyclic voltammetry(CV) under the condition of scan potential between 1.05 V and -0.25 V (vs SCE) and scan rate of 20 mV/s. An EG&G M273 potentiostat was employed for the deposition and electrochemical studies of Pt- MoO_x nanoparticles. The CNTs/graphite with a definite area of 1.0 cm^2 was used as the working electrode. A platinum foil served as the counter electrode and a saturated calomel electrode(SCE) was used as the reference electrode. The loading mass of Pt- MoO_x catalyst was determined from the mass gain of CNTs/graphite electrode after deposition. The micrograph and elemental composition of the Pt- MoO_x /CNTs/graphite electrode were investigated by transmission electron microscopy(TEM) (Philip 200 UT)

and scanning electron microscopy(SEM) (Hitachi S-4700) equipped with energy dispersive X-ray spectroscopy (EDS) (Vantage EST, NORAN).

The electrocatalytic performance of Pt- MoO_x /CNTs/graphite electrode for methanol oxidation was evaluated by CV in a solution of 1.0 mol/L CH_3OH in 0.5 mol/L H_2SO_4 . Electrochemical impedance spectroscopy(EIS) was measured using an EG&G PARC Model 5210 lock-in amplifier interfaced to Model 273 potentiostat. The impedance data were collected in the AC frequency range from 100 kHz to 0.1 Hz with an excitation signal of 10 mV. All experiments were carried out at ambient temperature. All the potentials were referred to the SCE.

3 Results and discussion

3.1 Electrochemical codeposition of Pt- MoO_x nanoparticles on CNTs/graphite electrode

The CV curves of Pt- MoO_x nanoparticles grown on the CNTs/graphite electrode are shown in Fig.1. The inner to outer curves correspond to the first and third CV done continuously at 20 mV/s. The peak currents increase with the increase in the number of cycles, which means that the particles are gradually grown on the surface of the CNTs/graphite electrode. In the potential range from 0.7 V to -0.10 V, there are one reduction peak at 0.062 V (peak *a*) and two corresponding oxidation peaks located at 0.225 V (peak *a'*), and 0.617 V (peak *a''*). These peaks may be ascribed to the redox reactions of molybdate species. Additionally, a pair of peaks (*b/b'*) at the potential of about -0.20 V are attributed to the deposition of Pt particles and hydrogen adsorption/desorption on the deposited Pt surface.

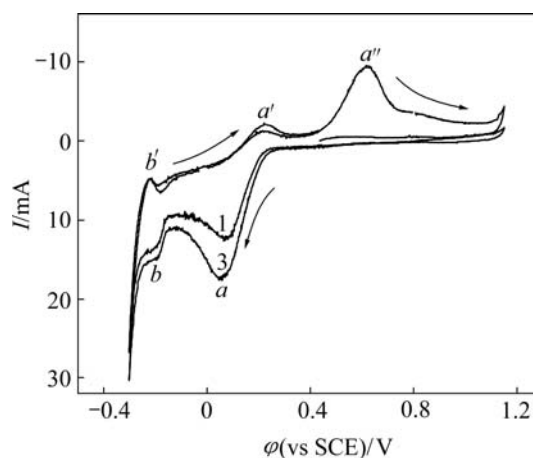


Fig.1 Cyclic voltammograms of Pt- MoO_x particles grown on CNTs/graphite electrode

The SEM image of the Pt- MoO_x /CNTs/graphite electrode in Fig.2(a) shows a three-dimensional web structure. The Pt- MoO_x nanoparticles are deposited

uniformly on the surface of the CNTs. The average particle size is about 50 nm. Also, the TEM image of Pt-MoO_x/CNTs particles is inserted in Fig.2(a). The Pt particles with size of about 20–40 nm are dispersed in the MoO_x. For comparison, the SEM image of Pt-MoO_x/graphite electrode under the same deposition condition is shown in Fig.2(b). The sizes of Pt-MoO_x particles deposited on the graphite electrode are much larger, with diameters typically in the range of 100–200 nm. The interesting three-dimension structure, small particle size and high dispersion of Pt-MoO_x/CNTs composite may result in large valuable surface area and good electrocatalytic properties for methanol oxidation.

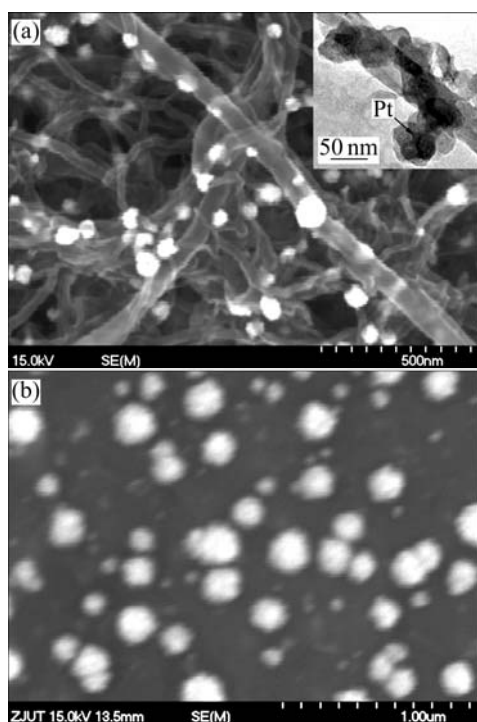


Fig.2 SEM images and TEM image (inserted) of Pt-MoO_x/CNTs/graphite electrode (Pt-MoO_x loading 62.7 μg/cm²) (a) and Pt-MoO_x/graphite electrode (Pt-MoO_x loading 57.4 μg/cm²) (b)

Fig.3 shows the EDS pattern of Pt-MoO_x/CNTs/graphite electrode. This indicates that Pt, Mo are the major elements plus C and O. The quantitative EDS analysis further shows that the Pt/Mo molar ratio is close to 3:2. In addition, we also tried to characterize the Pt-MoO_x/CNTs/graphite electrode by X-ray diffraction (XRD) analysis, however, the MoO_x phase was not identified probably due to the low crystallinity of the electrodeposited MoO_x.

3.2 Electrochemical properties of Pt-MoO_x/CNTs/graphite electrode

Fig.4 shows the CV curves of the CNTs/graphite

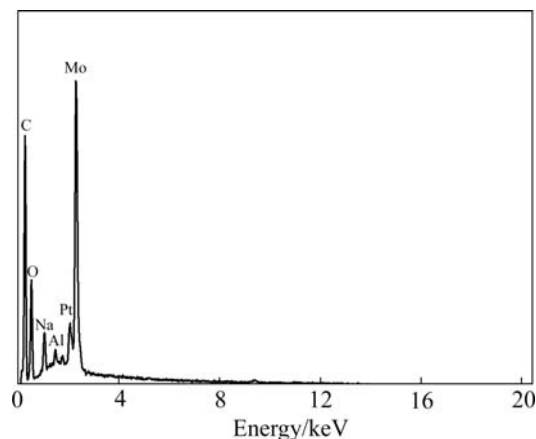


Fig.3 EDS pattern of Pt-MoO_x/CNTs/graphite electrode (Pt-MoO_x loading 62.7 μg/cm²)

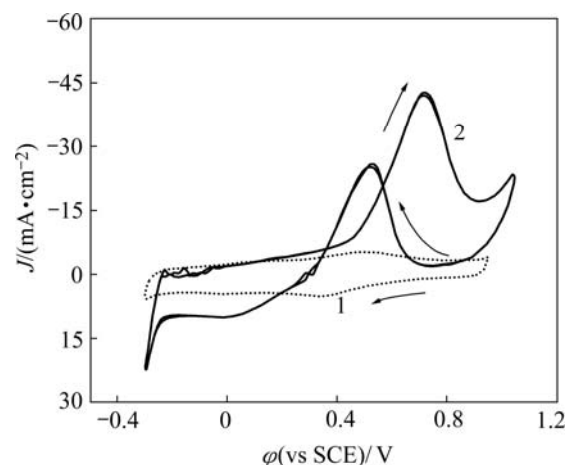


Fig.4 CV curves of CNTs/graphite 1 and Pt-MoO_x/CNTs/graphite 2 electrodes (Pt-MoO_x loading 159.3 μg/cm²) at 20 mV/s in 0.5 mol/L H₂SO₄+1.0 mol/L CH₃OH solutions

and Pt-MoO_x/CNTs/graphite electrodes in 0.5 mol/L H₂SO₄+1.0 mol/L CH₃OH solutions. From curve 1 in Fig.4, it can be seen that the background current of the CNTs/graphite electrode, which is the nature of the double-layer capacitance, is large due to the high surface area of CNTs. Additionally, a pair of broad redox peaks between 0.3 V and 0.5 V can be observed. This may correlate with the redox behavior of the carboxylic acid groups (such as —(COOH)_{ads} and —(OH)_{ads})[20]. No current peak of methanol oxidation is observed, indicating that the CNTs/graphite electrode has no obvious electrocatalytic activity for methanol oxidation. For the Pt-MoO_x/CNTs/graphite electrode, however, two current peaks of methanol oxidation are observed in curve 2 in Fig.4. The oxidation peak (E_p) obtained from the positive-going scan is due to methanol oxidation, as shown in Fig.5, its peak current density (J_p) is proportional to the square root of the scan rate ($\nu^{1/2}$), suggesting that the oxidation of methanol at the Pt-MoO_x/CNTs/graphite electrode may be controlled by diffusion process.

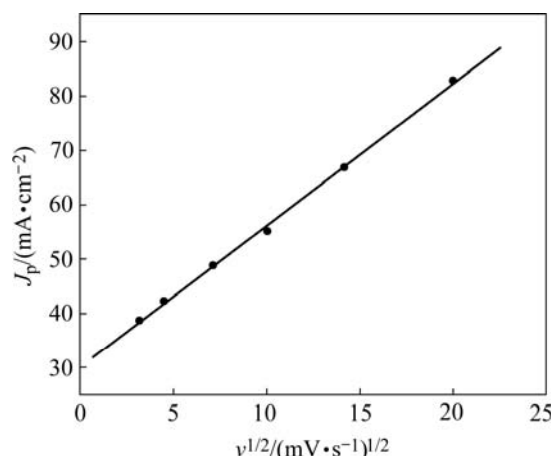


Fig.5 Dependence of peak current density (J_p) obtained from positive-going CV scan on $v^{1/2}$ (Pt-MoO_x loading 159.3 $\mu\text{g}/\text{cm}^2$)

3.3 Comparison of Pt-MoO_x/CNTs/graphite, Pt-MoO_x/graphite and Pt/CNTs/graphite electrodes

For comparison, the mass activity (A_m) of the catalysts is defined by peak current density per unit of loading mass and calculated by the following equation:

$$A_m = \frac{J_p}{m_d} \times 10^3 \quad (1)$$

where J_p (mA/cm^2) is obtained by the peak current obtained from the forward CV scan divided by exposed surface area of the electrode, and m_d ($\mu\text{g}/\text{cm}^2$) is loading mass of the Pt-MoO_x catalysts for Pt-MoO_x/CNTs/graphite, Pt-MoO_x/graphite electrode, or the Pt catalysts for Pt/CNTs/graphite electrode. Fig.6 shows the relationship between A_m and m_d for methanol oxidation. It is clear that the A_m of the Pt-MoO_x/CNTs/graphite electrode is much higher than that of the Pt-MoO_x/graphite electrode at both low and high m_d . The maximum of A_m (264.8 A/g) is obtained at $m_d=159.3 \mu\text{g}/\text{cm}^2$. As shown in Fig.2, the particle size of the Pt-MoO_x catalyst on the CNTs/graphite electrode is about 50 nm, which is much smaller than that on the graphite (about 100–200 nm). The smaller the particle size is, the bigger the specific surface area is, and so higher the catalytic activity is. The results show that the particle size of the Pt-MoO_x catalysts and nature of the supporting materials are very important factors on the catalytic activity. And also, the Pt-MoO_x/CNTs/graphite exhibits higher A_m compared with the Pt/CNTs/graphite electrodes at high m_d . This indicates that the codeposition of Pt-MoO_x oxide can improve the catalytic activity of Pt catalyst.

3.4 EIS of methanol oxidation on Pt-MoO_x/CNTs/

graphite electrode

In order to further investigate mechanism of

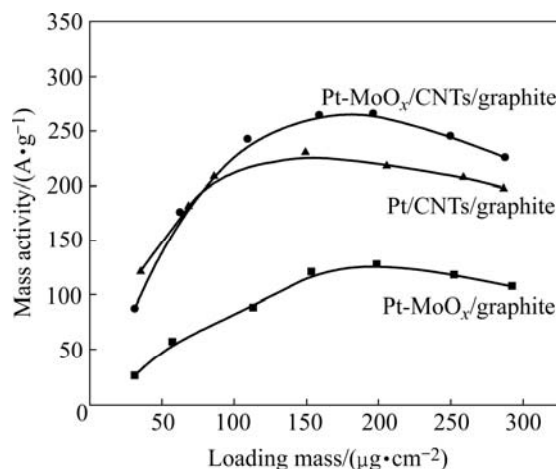


Fig.6 Relationship between mass activity and loading mass for methanol oxidation (Scan rate of CV is 20 mV/s)

methanol oxidation, electrochemical impedance spectroscopy(EIS) was carried out on the Pt-MoO_x/CNTs/graphite electrode at the potentials of 0.55 V and 0.70 V, respectively. For comparison, the EIS of the Pt/CNTs/graphite electrode is also presented in Fig.7. The EIS shape of both electrodes is similar, but the size of primary semicircle on the Pt-MoO_x/CNTs/graphite electrode is smaller than that of the Pt/CNTs/graphite electrode. This implies that the Pt-MoO_x/CNTs/graphite electrode provides fast reaction kinetics for methanol oxidation. At the potential of 0.55 V, the impedance plot of the Pt-MoO_x/CNTs/graphite electrode exhibits a clockwise capacitive-inductive loop (Fig.7(a)). The inductive behavior in low frequency range reveals that the CO_{ads} coverage decreases with increasing potential, and the decreasing CO_{ads} leads to an increase of Faradaic current[21]. According to bifunctional mechanism of methanol oxidation, a reasonable explanation is that with increasing potential, the large amounts of OH_{ads} are formed on MoO_x sites and react with CO_{ads} and decrease its coverage. The decreasing surface coverage of CO_{ads} will contribute to the adsorption of methanol on the Pt catalyst and enhance the Faradaic current. The similar inductive behavior in EIS at about 0.55 V is also observed recently at the PtRu/C anode catalyst of a DMFC[22–23]. Additionally, it is worth mentioning that the inductive response in low frequency at the Pt/CNTs/graphite electrode is not obvious. This means that molybdenum oxide contributes to the formation of chemisorbed hydroxyl, and may result in high electrocatalytic activity.

For methanol oxidation at high potential (0.70 V), the impedance plots of both electrodes are drastically changed. The impedance plots wrap around the origin anti-clockwise and the capacitive arcs flip to the second

quadrant with the real component of the impedance becoming negative (see Fig.7(b)), which is probably due

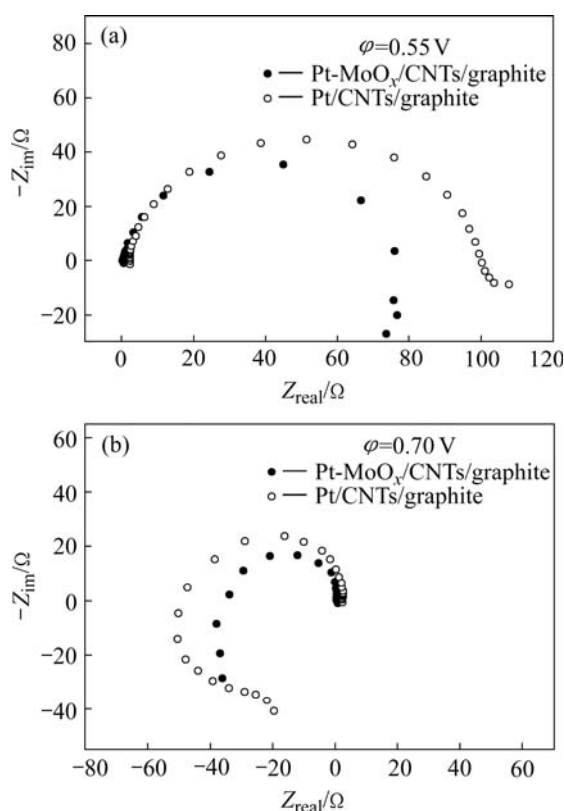
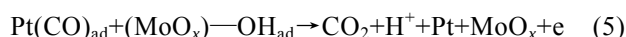
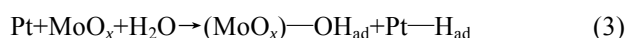
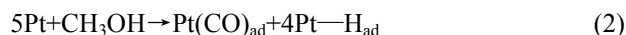


Fig.7 Nyquist plots of EIS for methanol oxidation on Pt-MoO_x/CNTs/graphite electrode and Pt/CNTs/graphite electrode at potentials of 0.55 V (a) and 0.70 V (b)

to the passivation of electrode surface[23]. The passivation at high potential can be explained by the formation of a large amount of CO_{ads} and OH on the surface of metal catalyst. Therefore, adsorption of methanol on Pt sites is inhibited due to the increase of coverage of CO_{ads} and OH on Pt sites and the electrooxidation rate decreases accordingly. The smaller negative resistance at the Pt-MoO_x/CNTs/graphite electrode indicates that the adsorption of poisonous CO_{ads} intermediates on Pt sites decreases in the presence of molybdenum oxide.

It has been reported that methanol oxidation undergoes dissociative adsorption and results in the formation of a series of adsorbed intermediates together with strongly bond-adsorbed CO species. For further oxidation of the intermediates to the final product, i.e., CO₂, the adsorbate must react with the adjacent adsorbed oxygen-containing species such as OH_{ad} or water in aqueous solutions. Hence, a good catalyst for methanol oxidation should easily adsorb methanol molecules and oxygen-containing species. In our case, the presence of MoO_x groups may induce the presence of the hydrous molybdenum oxides. The Pt-MoO_x/CNTs/graphite

electrode seems to possess the following bifunctional characteristic:



4 Conclusions

1) The Pt-MoO_x/CNTs/graphite electrode shows an excellent electrocatalytic activity for methanol oxidation. This may be attributed to the small particle size and high dispersion of Pt-MoO_x catalysts on the surface of CNTs.

2) The mixing of Pt and MoO_x nanoparticles on a microscopy level provides a modification of the chemisorptive and surface catalytic properties for methanol oxidation.

3) The Pt-MoO_x/CNTs/graphite electrode has good applications in DMFC because of the low loading mass of Pt-MoO_x catalysts and high catalytic activity for methanol oxidation.

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(Edited by LI Xiang-qun)