

# Catalytic oxidation of methanol on molybdate-modified platinum electrode in sulfuric acid solution

W.S. Li<sup>\*</sup>, L.P. Tian, Q.M. Huang, H. Li, H.Y. Chen, X.P. Lian

*Department of Chemistry, South China Normal University, Guangzhou 510631, PR China*

Received 8 May 2001; received in revised form 6 August 2001; accepted 25 September 2001

## Abstract

The catalysis of methanol oxidation on molybdate-modified platinum was studied by using linear sweep voltammetry (LSV), cyclic voltammetry (CV) and chronoamperometry in the solutions with H<sub>2</sub>SO<sub>4</sub> concentrations from 0.5 to 4.5 M. It was found that methanol oxidation was catalyzed on the modified platinum by lowering methanol oxidation potential and promoting methanol oxidation current. There was the strongest catalysis in 3.7 M H<sub>2</sub>SO<sub>4</sub> solution. In this solution, methanol oxidation took place on the modified platinum at the potential 0.2 V more negatively than on the non-modified platinum and the steady oxidation current of methanol on the modified platinum at 0.7 V versus SCE was 10 times that on the non-modified platinum. Molybdates were reduced to adsorbed hydrogen molybdenum(IV) bronzes on platinum in H<sub>2</sub>SO<sub>4</sub> solution at a very negative potential. The amount of reduced molybdates decreased with decreasing H<sub>2</sub>SO<sub>4</sub> concentrations. The reduced molybdates were oxidized to different forms of hydrogen molybdenum bronzes (H<sub>x</sub>MoO<sub>3</sub>, 0 < x < 2) depending on the H<sub>2</sub>SO<sub>4</sub> concentration. Platinum was modified by these hydrogen molybdenum bronzes, but under-modified in the solution with lower H<sub>2</sub>SO<sub>4</sub> concentration and over-modified in the solution with higher H<sub>2</sub>SO<sub>4</sub> concentration. The catalysis of methanol oxidation was weakened when the platinum was under- or over-modified. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Catalytic oxidation; Modification; Methanol; Platinum; Molybdate; Sulfuric acid

## 1. Introduction

It is urgent for the pollution from vehicles to be reduced in this modern society. Batteries and fuel cells are alternatives to internal combustion engine. Batteries offer the prospect of zero-emission vehicles. There are, however, environmental and engineering drawbacks to all the current types of batteries. Battery systems are thus only viewed as a short-term option. Fuel cell systems represent the best possible option in the long run [1–4], since they offer numerous benefits, including low or even zero emissions, higher efficiency and reliability.

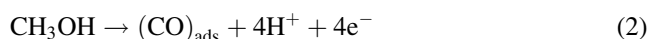
There are limitations in each type of fuel cells to be used in vehicles. Fuel cells based on molten carbonate and solid oxide electrolytes operate at temperatures in the range 650–1000 °C. Additional equipment and time are required to reach such high temperatures, which cannot meet the demands of vehicles. Fuel cells on vehicles need to generate sufficient power with the limited space. Proton exchange membrane fuel cells based on pure hydrogen as

fuel are unsuitable for small, privately owned cars, due to fuel distribution, handling and storage difficulties and on-vehicle space and weight constrains.

Methanol is an ideal fuel because of simple structure and easy storage and handling, especially because of its high energy density through a six-electron reaction



With the development of high performance catalysts, methanol is now readily available from oil, coal, natural gas and even wood. There are two options for methanol to be used as the fuel of fuel cells on vehicles. One involves an on-board reformer system which converts methanol into hydrogen. This system has similar problems with fuel cells based on pure hydrogen. The other is the best promising application, the direct methanol fuel cell (DMFC) where methanol fuel is supplied directly to the cell. However, the practical DMFC has not been obtained, mainly because no practical catalysts for methanol oxidation are available although much work has been done [2,5]. The main problem with methanol oxidation is the platinum anode poison from reaction intermediates such as (CO)<sub>ads</sub>.



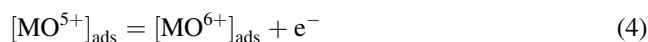
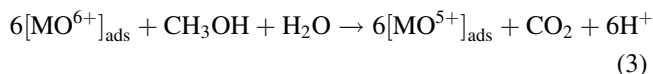
<sup>\*</sup> Corresponding author. Tel.: +86-20-8521-1368;

fax: +86-20-8521-0763.

E-mail address: liwsh@sclu.edu.cn (W.S. Li).

Much work has been done to enhance the activity of platinum by adding the second metal to platinum, such as Ru, Re, Os, Ir, Sn, Pb, W and Mo [6–12]. Several mechanisms for the activity improving have been proposed. Firstly, the secondary metal may modify the electronic properties of the platinum, weakening the chemical bond between platinum and the surface intermediates [11]. Secondly, the secondary metal may be unstable and leaches out of the alloy leaving a highly reticulated and active surface for the methanol electrosorption [12]. Thirdly, the secondary metal may oxidize and donate  $(\text{OH})_{\text{ads}}$  to adjacent platinum sites through a spillover process [12]. Conductive polymers such as PPy-Pt [13], PPn-Pt [14], and PTn-Pt [15] and metal oxides such as tungsten oxide [16] and nickel-modified manganese oxide [17] have also been used.

Several decades ago, molybdates were used as the catalyst for the methanol oxidation by adding molybdates into methanol solution [18]. It was thought that the catalysis was ascribed to the Mo(VI)/Mo(V) couple



The reaction (3) is so slow that the catalytic current of methanol oxidation is too small and the catalysis of methanol oxidation by molybdates has drawn few attentions since it was proposed. Recently, catalytic oxidation of methanol was proposed by using electrochemically codeposited platinum/molybdenum oxide [19,20]. A surface redox mechanism which involves the Mo(VI)/Mo(IV) couple in substoichiometric lower valence molybdenum oxides  $\text{MoO}_x$  ( $2 < x < 3$ ) and the proton spillover effect from hydrogen molybdenum bronze was proposed to explain the enhanced catalytic activity of this system [19].

Non-stoichiometric lower valence molybdenum oxide contains discontinued phases with compositions between  $\text{MoO}_2$  and  $\text{MoO}_3$  [21]. These mixed-valence oxides of molybdenum exhibit a wide range of optical and electrical properties and find their applications in electrochromism [22–24], lithium battery as cathode materials [25,26], catalysis for the electro-reduction of  $\text{ClO}_3^-$  and  $\text{BrO}_3^-$  [27], and so on. Molybdenum compound can catalyze methanol oxidation as mentioned above. Understanding more about electrochemical catalysis of methanol oxidation by molybdenum compound is required for the molybdenum catalysts to be applied in DMFCs. The purpose of this paper is to study the electrochemical catalysis of methanol oxidation on the modified platinum.

## 2. Experimental

Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were performed using a galvanostat/potentiostat (Model 553, ECO Instruments) with a programmer (Model

567, ECO Instruments), and an X–Y recorder (Type 3036, Hokushin Electronic Co.). Chronoamperometry was performed using a galvanostat/potentiostat (Model 273, EG&G Co.) with a computer. A conventional three-electrode cell was used in all the experiments. A platinum wire with an area of  $0.41 \text{ cm}^2$  was used as the working electrode. The electrolyte volume was 50 ml. A large platinum net was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. All the chemicals used were analytical grade reagents. Solutions were prepared with water de-ionized and distilled twice. All the experiments were carried out under room temperature.

## 3. Results and discussion

### 3.1. Catalytic oxidation of methanol

Reactions on platinum in sulfuric acid solutions involve the formation and oxidation of hydrogen atom and the formation and reduction of platinum oxide [28]. Fig. 1 shows the cyclic voltammogram of platinum electrode in 3.7 M  $\text{H}_2\text{SO}_4$  solution between  $-0.2$  and  $1.4$  V. The oxidation and reduction peak couples a'/a and b'/b in Fig. 1 correspond to the formation and oxidation of hydrogen atom and the formation and reduction of platinum oxide, respectively. The formation of hydrogen atom takes place at about  $0.18$  V and hydrogen evolution takes place at about  $-0.17$  V. The formation of platinum oxide takes place at about  $0.62$  V and its reduction peak potential is  $0.55$  V.

Fig. 2 shows linear sweep voltammograms of platinum electrode in four different solutions from  $-0.2$  to  $1.4$  V. The curve a in Fig. 2 was obtained in 3.7 M  $\text{H}_2\text{SO}_4$  solution. In this solution, the reduction current of proton can be observed from the beginning of the potential sweep ( $-0.2$  V) and the oxidation current of platinum from  $0.62$  V. The curve b was obtained in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing  $0.05$  M  $\text{Na}_2\text{MoO}_4$ . Compared with curve a, the curve b shows that molybdates are reduced at  $-0.2$  V and there appear three oxidation current peaks at  $0.26$ ,  $0.57$  and  $1.05$  V. These oxidation current peaks may be ascribed to the oxidation of the reduced molybdates.

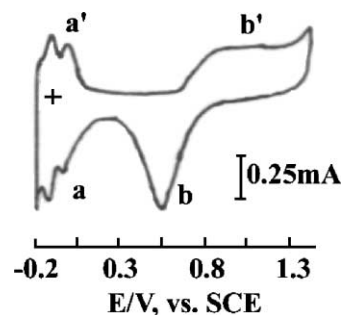


Fig. 1. Cyclic voltammogram of platinum electrode in 3.7 M  $\text{H}_2\text{SO}_4$  solution, sweep rate:  $100 \text{ mV/s}$ .

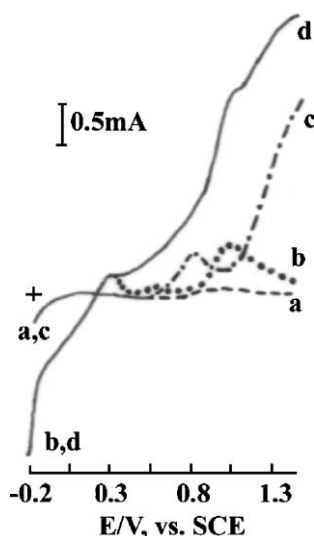
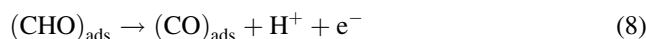
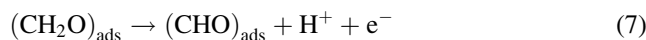
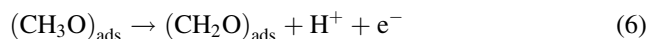
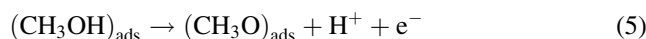


Fig. 2. Linear sweep voltammograms of platinum electrode in four different solutions. (a) 3.7 M  $\text{H}_2\text{SO}_4$ ; (b) (a) + 0.05 M  $\text{Na}_2\text{MoO}_4$ ; (c) (a) + 1 M  $\text{CH}_3\text{OH}$ ; (d) (b) + 1 M  $\text{CH}_3\text{OH}$ , sweep rate: 100 mV/s.

The curve c in Fig. 2 was obtained in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing 1 M  $\text{CH}_3\text{OH}$ . In this solution, the same reduction current of proton was recorded at  $-0.2$  V as in the solution without  $\text{CH}_3\text{OH}$ . As the potential increases anodically, oxidation current occurs at about 0.5 V, reach a peak at about 0.8 V, decreases to a valley at about 0.9 V, and then increases again. The curve d in Fig. 2 was obtained in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing 1 M  $\text{CH}_3\text{OH}$  and 0.05 M  $\text{Na}_2\text{MoO}_4$ . As in the solution without  $\text{CH}_3\text{OH}$ , the reduction current of molybdates occurs at the beginning of potential sweep and an oxidation current peak appears at 0.26 V. However, as the potential increases further the current, instead of decreasing as in the solution without  $\text{CH}_3\text{OH}$ , continues to increase up to the end of potential sweep.

To understand the oxidation mechanism of methanol, a cyclic voltammetric experiment was performed on platinum in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing 1 M  $\text{CH}_3\text{OH}$  from  $-0.2$  to 1.4 V and the result was shown in Fig. 3. There are four characteristic positions, A, B, C and D in the cyclic voltammogram of Fig. 3. A is the oxidation current peak of methanol. The oxidation current involves the formation of intermediates [29,30].



Reactions from (5) to (8) can be denoted by reaction (2).

It is certain that  $(\text{CO})_{\text{ads}}$  is the poison to platinum catalyst for further oxidation of methanol [5]. The oxidation current decrease due to the formation of platinum oxide and B appears [31]

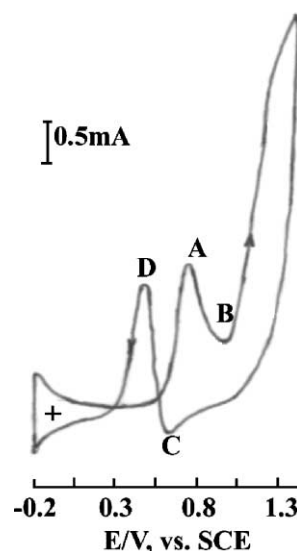
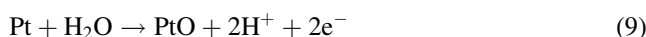
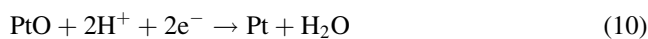


Fig. 3. Cyclic voltammogram of platinum electrode in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing 1 M  $\text{CH}_3\text{OH}$ , sweep rate: 100 mV/s.

As the potential increases further, the oxidation current increases again due to the direct oxidation of methanol to  $\text{CO}_2$  on the surface of platinum oxide as in reaction (1).

When the potential scans backward, there appears a reduction current peak C due to the reduction of platinum oxide



With the clean platinum available, the methanol oxidation takes place more easily and therefore the current peak D for methanol oxidation appears.

Far higher steady current of methanol oxidation can be obtained on the platinum with the reduced molybdates than without reduced molybdates at any potential higher than 0.3 V. Fig. 4 shows chronoamperometric curves obtained

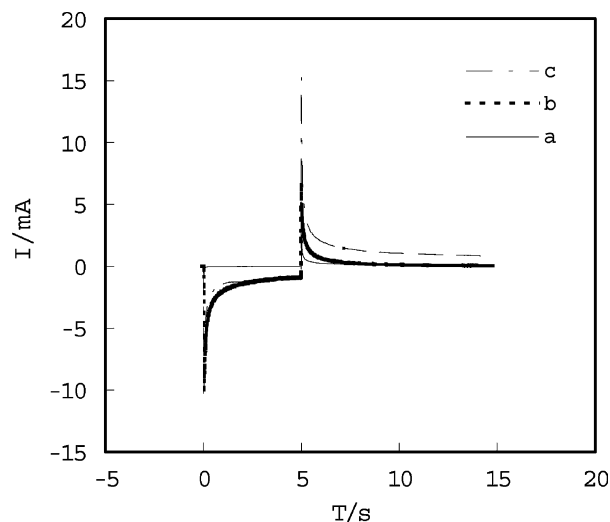


Fig. 4. Chronoamperometric curves of platinum electrode in three different solutions. (a) 3.7 M  $\text{H}_2\text{SO}_4$  + 1M  $\text{CH}_3\text{OH}$ ; (b) 3.7 M  $\text{H}_2\text{SO}_4$  + 0.05 M  $\text{Na}_2\text{MoO}_4$ ; (c) 3.7 M  $\text{H}_2\text{SO}_4$  + 1 M  $\text{CH}_3\text{OH}$  + 0.05 M  $\text{Na}_2\text{MoO}_4$ .

in three different solutions. The potential was set at  $-0.2$  V for 5 s at first and then at  $0.7$  V for 10 s. The curve a was obtained in  $3.7$  M  $\text{H}_2\text{SO}_4$  solution with  $1$  M  $\text{CH}_3\text{OH}$ . It shows that the currents for the proton reduction at  $-0.2$  V and for the methanol oxidation at  $0.7$  V are very low,  $-0.02$  and  $0.07$  mA, respectively. This indicates that it is difficult for methanol to be oxidized on platinum. The curve b was obtained in  $3.7$  M  $\text{H}_2\text{SO}_4$  solution with  $0.05$  M  $\text{Na}_2\text{MoO}_4$ . In this solution, there is a reduction current of molybdates at  $-0.2$  V, about  $-1.02$  mA, but the oxidation current at  $0.7$  V is almost the same as that of the curve a, which is far lower than the reduction current of molybdates. This indicates that only fraction of reduced molybdates is oxidized at  $0.7$  V. The curve c was obtained in  $3.7$  M  $\text{H}_2\text{SO}_4$  solution with  $1$  M  $\text{CH}_3\text{OH}$  and  $0.05$  M  $\text{Na}_2\text{MoO}_4$ . In this solution, the reduction current of molybdates is the same as that of the curve b. However, the oxidation current of methanol at  $0.7$  V is high, about  $0.8$  mA, which is more than 10 times that of the curve a or the curve b. It is apparent that methanol oxidation can be catalyzed on platinum with reduced molybdates by lowering the potential for methanol oxidation and improving the oxidation current of methanol. These two effects are useful in promoting the output power of DMFCs.

Fig. 5 shows linear sweep voltammograms of platinum electrode in  $3.7$  M  $\text{H}_2\text{SO}_4$  solution containing  $1$  M  $\text{CH}_3\text{OH}$  and  $0.05$  M  $\text{Na}_2\text{MoO}_4$  with different initial sweep potentials. The curve a is the same as the curve d in Fig. 2. The curve b was obtained with the initial potential  $0.2$  V. There also appears the reduction current of molybdates at  $0.2$  V, although it is far lower than that of curve a at  $-0.2$  V. As the potential increases, the curve b shows the catalytic currents of methanol oxidation at the potentials higher than  $0.3$  V. However, the catalytic currents of curve b in Fig. 5 are far lower than that of the curve a. The curve c in Fig. 5 was obtained with the initial potential  $0.5$  V. No reduction

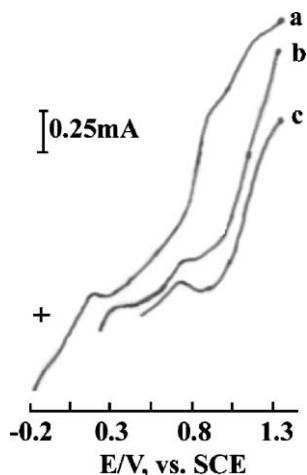


Fig. 5. Linear sweep voltammograms of platinum electrode in  $3.7$  M  $\text{H}_2\text{SO}_4$  solution containing  $1$  M  $\text{CH}_3\text{OH}$  and  $0.05$  M  $\text{Na}_2\text{MoO}_4$  with different initial sweep potentials. (a)  $-0.2$ ; (b)  $0.2$ ; (c)  $0.5$  V, sweep rate:  $100$  m V/s.

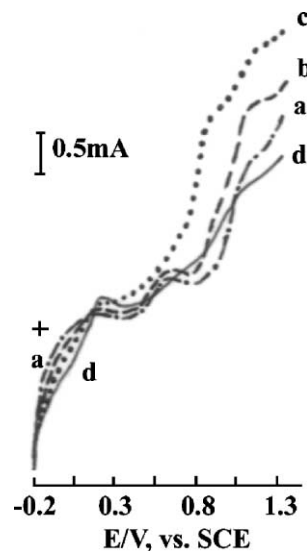


Fig. 6. Linear sweep voltammograms of platinum electrode in  $1$  M  $\text{CH}_3\text{OH}$  and  $0.05$  M  $\text{Na}_2\text{MoO}_4$  solutions with different  $\text{H}_2\text{SO}_4$  concentrations. (a)  $0.5$ ; (b)  $1.85$ ; (c)  $3.7$ ; (d)  $4.5$  M, sweep rate:  $100$  m V/s.

current of molybdates was observed at the initial potential and the oxidation behavior of methanol is almost the same as that of the curve c in Fig. 2 which was obtained in the solution without molybdates. This indicates that the catalytic mechanism of methanol oxidation on platinum in the solution containing molybdates is related to the reduced molybdates. There might be the mechanism related to the reactions (3) and (4), but the catalytic current from these reactions must be too low to be recorded.

Fig. 6 shows linear sweep voltammograms of platinum electrode in  $1$  M  $\text{CH}_3\text{OH}$  and  $0.05$  M  $\text{Na}_2\text{MoO}_4$  solutions with different  $\text{H}_2\text{SO}_4$  concentrations from  $-0.2$  to  $1.4$  V. Curves a–d were obtained in the solutions with  $\text{H}_2\text{SO}_4$  concentration of  $0.5$ ,  $1.85$ ,  $3.7$ , and  $4.5$  M, respectively. Compared with the curve c in Fig. 2, Fig. 6 shows that there is the catalysis of methanol oxidation in all these solutions. However, the catalysis is related to the  $\text{H}_2\text{SO}_4$  concentration. There is the strongest catalysis in  $3.7$  M  $\text{H}_2\text{SO}_4$  solution. As the  $\text{H}_2\text{SO}_4$  concentration increases or decreases from this concentration, the catalysis is weakened. In the solution with lower than  $3.7$  M  $\text{H}_2\text{SO}_4$ , catalytic current decreases with decreasing  $\text{H}_2\text{SO}_4$  concentration and the decrease of oxidation current appears with increasing potential due to the formation of platinum oxide. In the solution with  $4.5$  M  $\text{H}_2\text{SO}_4$ , the catalytic current is lower than that in  $3.7$  M  $\text{H}_2\text{SO}_4$  but there is no decrease of oxidation current with increasing potential due to the formation of platinum oxide.

### 3.2. Redox reactions of molybdate on platinum

To understand the catalytic mechanism of methanol oxidation by molybdates, reduction and oxidation behaviors of molybdates on platinum electrode in  $\text{H}_2\text{SO}_4$  solutions were

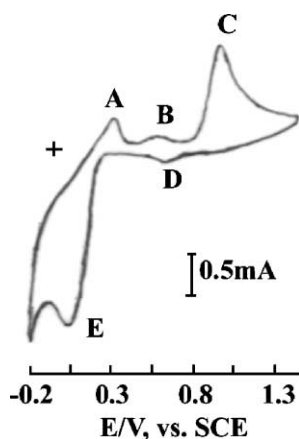


Fig. 7. Cyclic voltammogram of platinum electrode in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing 0.05 M  $\text{Na}_2\text{MoO}_4$ , sweep rate: 100 mV/s.

studied. Fig. 7 shows the cyclic voltammogram of platinum electrode in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing 0.05 M  $\text{Na}_2\text{MoO}_4$ . There appear oxidation current peaks, A, B, and C, and reduction current peaks, D and E. Compared with Fig. 1, the current of peak E is far higher than the hydrogen deposition current, so the peak E is ascribed to the reduction of molybdates. The reduction potential is about 0.22 V. The peak A and the peak B should be ascribed to the oxidation of the reduced molybdates because no such peaks can be observed in Fig. 1. The current of peak C is far higher than the corresponding formation current of the platinum oxide in Fig. 1, indicating that the oxidation peak C is mainly ascribed to the oxidation of the reduced molybdates. The current of peak D, which is ascribed to the reduction of platinum oxide, is lower than that in Fig. 1, indicating that the formation of platinum oxide is hindered by the reduced molybdates. There are three oxidation processes of reduced molybdates but there is only one reduction process of molybdates.

Hydrogen molybdenum bronze  $\text{H}_x\text{MoO}_3$  with  $0 < x \leq 2$  can be formed when molybdates are reduced in acid solution [32,33]. There are four hydrogen molybdenum bronze compounds with different colors, the first and the second are blue, for  $0.23 < x < 0.40$  and  $0.85 < x < 1.04$ , respectively, the third is red for  $1.55 < x < 1.72$ , and the fourth is green for  $x = 2$ .

When the platinum electrode was polarized in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing 0.05 M  $\text{Na}_2\text{MoO}_4$  at the potential of peak E for a moment, a green color on the surface of the electrode was observed. This indicates that the fourth hydrogen molybdenum bronze  $\text{H}_2\text{MoO}_3$  is formed and deposits on the electrode surface when molybdates in the solution are reduced. Therefore, the peak E corresponds to the reaction

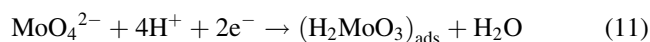


Fig. 8 shows cyclic voltammograms of platinum electrode in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing 0.05 M  $\text{Na}_2\text{MoO}_4$  with different sweep rates. The reduction current of molybdates

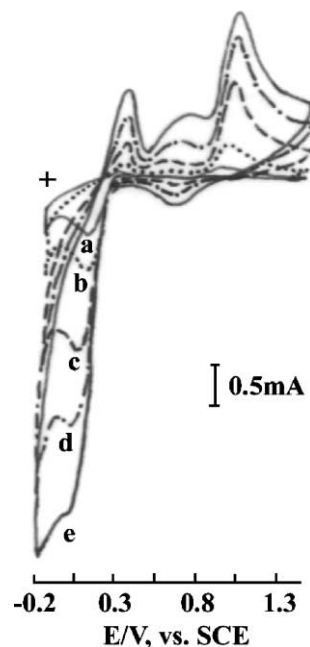


Fig. 8. Cyclic voltammograms of platinum electrode in 3.7 M  $\text{H}_2\text{SO}_4$  solution containing 0.05 M  $\text{Na}_2\text{MoO}_4$  with different sweep rates: (a) 9; (b) 25; (c) 100; (d) 225; (e) 400 mV/s.

increases with increasing sweep rates and there is almost linear relationship between the current of peak E in Fig. 7 and the square of sweep rate as shown in Fig. 9. This indicates that the reaction (11) is controlled by the diffusion of molybdates. The sum of the area of peaks A, B, and C is close to the area of peak E, indicating that almost all the

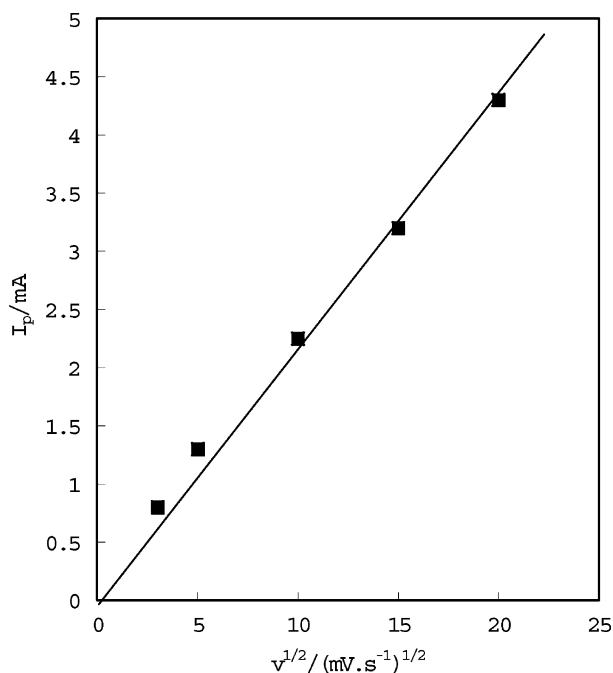


Fig. 9. Relationship of the peak current of molybdate reduction in Fig. 8 with the square of sweep rate.

reduced molybdates, i.e.  $(\text{H}_2\text{MoO}_3)_{\text{ads}}$ , is oxidized on the platinum electrode. Since the peak D corresponds to the reduction of platinum oxide, there are no reduction current peaks except peak E corresponding to the oxidation current peaks A, B, and C. This indicates that the  $(\text{H}_2\text{MoO}_3)_{\text{ads}}$  is oxidized to hexavalent molybdenum compound which dissolves in the solution and returns to molybdates ultimately.

Fig. 10 shows cyclic voltammograms of platinum electrode in 0.05 M  $\text{Na}_2\text{MoO}_4$  solutions with  $\text{H}_2\text{SO}_4$  concentrations other than 3.7 M. There are only current peaks A and C in the solutions with low  $\text{H}_2\text{SO}_4$  concentrations, as shown in Fig. 10a and b. The peak B disappears in the solutions with low  $\text{H}_2\text{SO}_4$  concentrations. Fig. 10c is obtained in the solution with 4.5 M  $\text{H}_2\text{SO}_4$ .

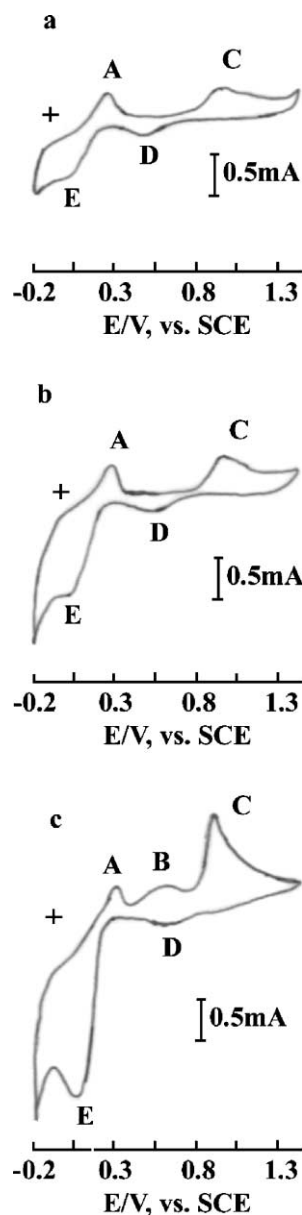
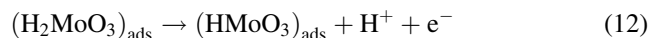


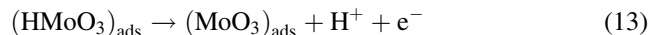
Fig. 10. Cyclic voltammograms of platinum electrode in 0.05 M  $\text{Na}_2\text{MoO}_4$  solutions with different  $\text{H}_2\text{SO}_4$  concentrations. (a) 0.5; (b) 1.85; (c) 4.5 M, sweep rate: 100 mV/s.

In this solution, there are three oxidation peaks A, B and C. The area of peak A is almost the same as that of peak B and the sum of area of peaks A and B is close to the area of peak C. In all the solution with different  $\text{H}_2\text{SO}_4$  concentration, the current of peak E increases with increasing  $\text{H}_2\text{SO}_4$  concentration. This indicates that higher  $\text{H}_2\text{SO}_4$  concentration favors the reduction of molybdates, because the reaction (11) shows that protons are needed for the reduction of molybdates.

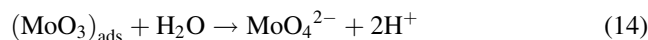
Considering the magnitude of area of oxidation peaks A, B, and C of reduced molybdates, and the four kinds of hydrogen molybdenum bronzes, different reaction mechanisms can be proposed to describe peaks A, B, and C. In the solution with low  $\text{H}_2\text{SO}_4$  concentrations, such as in 0.5 or 1.85 M  $\text{H}_2\text{SO}_4$  solution where there are two oxidation peaks of reduced molybdates, the reduced molybdate  $(\text{H}_2\text{MoO}_3)$  is oxidized through two steps. Firstly, the oxidation of the fourth hydrogen molybdenum bronzes  $((\text{H}_x\text{MoO}_3)_{\text{ads}}, x = 2)$  to the third hydrogen molybdenum bronzes  $((\text{H}_x\text{MoO}_3)_{\text{ads}}, 1.55 < x < 1.72)$  and the third to the second hydrogen molybdenum bronze  $((\text{H}_x\text{MoO}_3)_{\text{ads}}, 0.85 < x < 1.04)$  takes place simultaneously at the peak A, which is nearly an one-electron reaction and can be denoted by



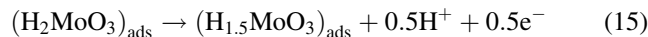
Secondly, the oxidation of the second to the first hydrogen molybdenum bronze  $((\text{H}_x\text{MoO}_3)_{\text{ads}}, 0.23 < x < 0.40)$  and the first to the adsorbed hexavalent molybdenum oxide  $(\text{MoO}_3)_{\text{ads}}$  also takes place simultaneously at the peak C, which is also nearly an one-electron reaction and can be denoted by



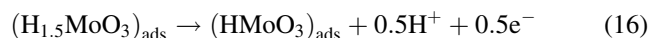
The  $(\text{MoO}_3)_{\text{ads}}$  dissolves in the solution and returns to molybdate



In the solutions with high  $\text{H}_2\text{SO}_4$  concentrations, such as in 3.7 or 4.5 M  $\text{H}_2\text{SO}_4$  solution where there are three oxidation peaks of molybdates, the reduced molybdate  $(\text{H}_2\text{MoO}_3)$  is oxidized through three steps. The oxidation of the fourth hydrogen molybdenum bronze to the third takes place at the peak A, which is nearly a half-of-one-electron reaction and can be denoted by



The oxidation of the third hydrogen molybdenum bronze to the second takes place at peak B, which is also nearly a half-of-one-electron reaction and can be denoted by



The difference of oxidation reactions of reduced molybdates in the solution with high  $\text{H}_2\text{SO}_4$  concentrations from low  $\text{H}_2\text{SO}_4$  concentrations may be ascribed to the proton concentration. Reactions (12), (15) and (16) release different number of protons. The lower proton concentration in the

solution with lower  $\text{H}_2\text{SO}_4$  concentration favors the reaction that release more protons.

The oxidation reaction taking place at peak C is an one-electron reaction which is the same as the reaction (13) and then the reaction (14) takes place.

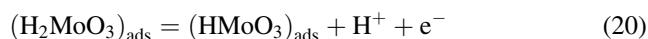
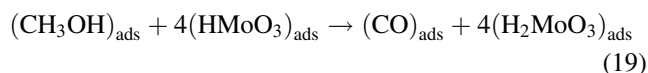
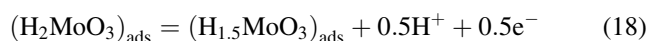
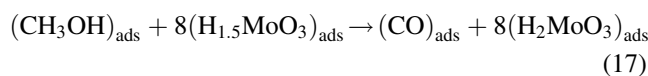
Whether in the solutions with lower or higher  $\text{H}_2\text{SO}_4$  concentrations, platinum electrode can be modified with different forms of hydrogen molybdenum bronzes, through the reduction of molybdates in the solution and the oxidation of the reduced molybdates on the platinum. Such a modified platinum electrode must show its different performances from non-modified platinum electrode.

### 3.3. Catalytic mechanism of methanol oxidation on molybdate-modified platinum

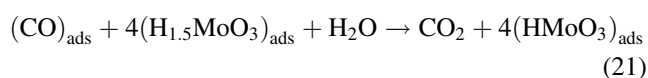
As discussed above, platinum is modified in  $\text{H}_2\text{SO}_4$  solution containing molybdates when molybdates are reduced on platinum, and methanol oxidation can be catalyzed on the modified platinum. It is difficult for methanol to be oxidized by the molybdates in the solution. Therefore, the catalysis of methanol oxidation must be ascribed to the modification of platinum by reduced molybdates.

The methanol oxidation takes place on the modified platinum at the potential about 0.2 V more negatively than on the non-modified platinum just after the potential of peak A of Fig. 7 and the oxidation currents are highly improved. At these potentials  $(\text{H}_{1.5}\text{MoO}_3)_{\text{ads}}$  or  $(\text{HMoO}_3)_{\text{ads}}$  is formed on platinum in the solutions with high or low  $\text{H}_2\text{SO}_4$  concentrations. Therefore,  $(\text{H}_{1.5}\text{MoO}_3)_{\text{ads}}$  or  $(\text{HMoO}_3)_{\text{ads}}$  is responsible for the catalytic oxidation of methanol in the solutions with different  $\text{H}_2\text{SO}_4$  concentrations. The catalytic mechanism can be interpreted as follows.

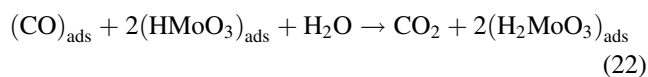
At the potential where methanol oxidation begins to take place,  $(\text{H}_{1.5}\text{MoO}_3)_{\text{ads}}$  or  $(\text{HMoO}_3)_{\text{ads}}$  combines hydrogen from  $(\text{CH}_3\text{OH})_{\text{ads}}$ ,  $(\text{CH}_2\text{OH})_{\text{ads}}$ , and  $(\text{CHOH})_{\text{ads}}$  on platinum, converting these intermediates to  $(\text{CO})_{\text{ads}}$



At higher potential,  $(\text{H}_{1.5}\text{MoO}_3)_{\text{ads}}$  or  $(\text{HMoO}_3)_{\text{ads}}$  combines hydrogen from water and converts the  $(\text{CO})_{\text{ads}}$  to  $\text{CO}_2$



and reaction (18) or



and reaction (20).

In this way,  $(\text{H}_{1.5}\text{MoO}_3)_{\text{ads}}$  or  $(\text{HMoO}_3)_{\text{ads}}$  keeps cleaning platinum surface and make it easier for methanol to be oxidized on the clean platinum.

The amount of reduced molybdates depends on the  $\text{H}_2\text{SO}_4$  concentration as shown in Fig. 10. When the  $\text{H}_2\text{SO}_4$  concentration is low, the amount of reduced molybdates is so small that platinum is under-modified. Less  $(\text{H}_{1.5}\text{MoO}_3)_{\text{ads}}$  or  $(\text{HMoO}_3)_{\text{ads}}$  is available for cleaning platinum which is active for the methanol oxidation, i.e. there are still platinum poisons by the intermediates. When the  $\text{H}_2\text{SO}_4$  concentration is high, the amount of reduced molybdates is so large that platinum is over-modified. There are fewer active platinum sites available for the methanol oxidation. This is why there is the highest catalytic current for methanol oxidation in 3.7 M  $\text{H}_2\text{SO}_4$  solution and the catalytic current decreases whether  $\text{H}_2\text{SO}_4$  concentration increases or decreases, as shown in Fig. 6. This modification of molybdates on platinum also holds after the potential at which platinum oxide is formed in the solution without molybdates. With the high hydrogen molybdenum bronzes  $(\text{H}_2\text{MoO}_3)_{\text{ads}}$  available when methanol is oxidized, the platinum oxide is not formed so easily on the modified platinum as on the non-modified platinum. The platinum oxide formed more on the under-modified platinum than well-modified or over-modified platinum. This is why current decrease of methanol oxidation due to formation of platinum oxide appears in the solution with low  $\text{H}_2\text{SO}_4$  concentration but does not appear in the solution with high  $\text{H}_2\text{SO}_4$  concentration. The methanol oxidation current decreases as the  $\text{H}_2\text{SO}_4$  concentration increases further, because of fewer active platinum sites available.

## 4. Conclusion

Molybdates are reduced to adsorbed hydrogen molybdenum(IV) bronzes on platinum in  $\text{H}_2\text{SO}_4$  solution at a very negative potential. The amount of reduced molybdates increases with increasing  $\text{H}_2\text{SO}_4$  concentration. The reduced molybdates are oxidized to different forms of hydrogen molybdenum bronzes  $(\text{H}_x\text{MoO}_3, 0 < x < 2)$ , depending on the  $\text{H}_2\text{SO}_4$  concentration in the solutions. Platinum is modified with these hydrogen molybdenum bronzes. Methanol oxidation can be catalyzed on the modified platinum by lowering methanol oxidation potential and promoting the methanol oxidation current. There is the strongest catalysis of methanol oxidation on the modified platinum in 3.7 M  $\text{H}_2\text{SO}_4$  solution. The catalysis is weakened with increasing or decreasing  $\text{H}_2\text{SO}_4$  concentrations, because platinum is under-modified in the solutions with lower  $\text{H}_2\text{SO}_4$  concentrations and over-modified in the solution with higher  $\text{H}_2\text{SO}_4$  concentrations. There is the couple  $(\text{H}_{1.5}\text{MoO}_3)_{\text{ads}}/(\text{H}_2\text{MoO}_3)_{\text{ads}}$  or the couple  $(\text{HMoO}_3)_{\text{ads}}/(\text{H}_2\text{MoO}_3)_{\text{ads}}$  available on the modified platinum in the solution with different  $\text{H}_2\text{SO}_4$  concentrations. These couples keep cleaning the platinum and make it easier for methanol to be

oxidized.  $(\text{H}_{1.5}\text{MoO}_3)_{\text{ads}}$  or  $(\text{HMoO}_3)_{\text{ads}}$  helps converting the adsorbed intermediates of methanol oxidation on platinum to  $\text{CO}_2$ .

### Acknowledgements

This work is supported by GDSF (970319), NSFC (50041004), SRF for ROCS, SEM, and Visiting Scholar Foundation of Key Laboratory in University.

### References

- [1] F. Panik, *J. Power Sources* 71 (1988) 36.
- [2] B.B. McNicol, R.A.J. Rand, M.R. Williams, *J. Power Sources* 83 (1999) 15.
- [3] M. Baldauf, W. Preidel, *J. Power Sources* 84 (1999) 161.
- [4] G. Sattler, *J. Power Sources* 86 (2000) 61.
- [5] R. Parsons, T. Vandernoot, *J. Electroanal. Chem.* 257 (1988) 9.
- [6] W. Lin, J. Wang, R. Savinell, *J. Electrochem. Soc.* 144 (1997) 1917.
- [7] B.N. Grgur, N.M. Markovic, P.N. Ross, *J. Electrochim. Acta* 43 (1998) 3631.
- [8] L. Kevin, R.X. Liu, C. Pu, Q. Fan, N. Leyarovska, C. Segre, E.S. Smotkin, *J. Electrochem. Soc.* 144 (1997) 1917.
- [9] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E.S. Smotkin, T.E. Mallouk, *Science* 282 (1998) 1735.
- [10] H. Gasteiger, N. Markovic, P. Ross, *J. Phys. Chem.* 99 (1995).
- [11] B. Grgur, N. Markovic, P. Ross, *J. Phys. Chem. B* 101 (1998) 3910.
- [12] M.P. Hogarth, G.A. Hards, *Platinum Metals Rev.* 40 (1996) 150.
- [13] H. Yang, T. Lu, K. Xue, S. Sun, G. Lu, S. Chen, *J. Electrochem. Soc.* 144 (1997) 2303.
- [14] W. Wu, Y. Wang, *Chin. J. Appl. Chem.* 13 (1996) 21.
- [15] H. Yang, C. Li, T. Lu, *Acta Phys. Chim. Sinica* 13 (1997) 542.
- [16] P.K. Shen, A.C.C. Tseung, *J. Electrochem. Soc.* 141 (1994) 3082.
- [17] P.V. Samant, J.B. Fernandes, *J. Power Sources* 79 (1999) 114.
- [18] J.A. Shropshire, *J. Electrochem. Soc.* 112 (1965) 465.
- [19] H. Zhang, Y. Wang, E.R. Fachini, C.R. Cabrera, *Electrochem. Solid State Lett.* 2 (1999) 437.
- [20] L.P. Tian, W.S. Li, H. Li, *Fine Chem.* 17 (2000) 107.
- [21] R.L. Moss, *Catalysis* 4 (1981) 31.
- [22] C.Z. Lampert, *Sol. Energy Mater.* 11 (1984).
- [23] G.C.S. Collins, D.J. Schiffrin, *J. Electroanal. Chem.* 132 (1982) 335.
- [24] A. Guerfi, R.W. Paynter, L.H. Dao, *J. Electrochem. Soc.* 142 (1995) 3457.
- [25] C.P. Li, D.M. Hercules, *J. Phys. Chem.* 88 (1984) 456.
- [26] N. Kumagai, K. Tanno, *J. Appl. Electrochem.* 18 (1988) 857.
- [27] B.X. Wang, S.J. Dong, *J. Electroanal. Chem.* 379 (1994) 207.
- [28] M.W. Breiter, *Electrochim. Acta* 8 (1963) 925.
- [29] V.E. Kazarinov, G.Y. Tsyachnava, V.N. Andreev, *J. Electroanal. Chem.* 65 (1975) 391.
- [30] G.R. Mundy, R.J. Potter, P.A. Christensen, A. Hammett, *J. Electroanal. Chem.* 27 (1990) 257.
- [31] G. Gilman, M.Q. Breiter, *J. Electrochem. Soc.* 109 (1962) 1099.
- [32] L. Campanella, G. Pistoia, *J. Electrochem. Soc.* 118 (1971) 1905.
- [33] C. Ritter, W. Muller-Warmuth, R. Schollhom, *J. Chem. Phys.* 83 (1985) 6130.