

## Co-deposition of Pt-H<sub>x</sub>MoO<sub>3</sub> and its catalysis on methanol oxidation in sulfuric acid solution

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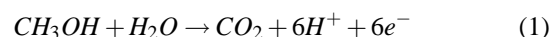
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**Abstract:** The deposition or co-deposition of Pt and/or Pt-H<sub>x</sub>MoO<sub>3</sub> (0 < y < x < 2) on a flat base platinum electrode from 0.5M H<sub>2</sub>SO<sub>4</sub> solutions with 0.005M H<sub>2</sub>PtCl<sub>6</sub> and/or 0.05M Na<sub>2</sub>MoO<sub>4</sub> and the catalytic oxidation of methanol on deposited and co-deposited electrodes in 0.1M CH<sub>3</sub>OH + 0.5M H<sub>2</sub>SO<sub>4</sub> solution were studied by cyclic voltammetry, chronoamperometry and alternative current impedance spectroscopy. A deposited platinum electrode obtained by cycling the base platinum from -0.2 to 0.8V (vs. SCE) in 0.005M H<sub>2</sub>PtCl<sub>6</sub> + 0.5M H<sub>2</sub>SO<sub>4</sub> solution had a larger surface area than the base platinum electrode. Hydrogen molybdenum bronze (H<sub>x</sub>MoO<sub>3</sub>) was deposited and could be oxidized in two steps to H<sub>y</sub>MoO<sub>3</sub> (y < x) when the base platinum electrode was cycled from -0.2 to 1.3V (vs. SCE) in 0.05M Na<sub>2</sub>MoO<sub>4</sub> + 0.5M H<sub>2</sub>SO<sub>4</sub> solution. A Pt-H<sub>x</sub>MoO<sub>3</sub> co-deposited electrode could be obtained by cycling the base platinum electrode from -0.2 to 0.8V (vs. SCE) in 0.05M Na<sub>2</sub>MoO<sub>4</sub> + 0.005M H<sub>2</sub>PtCl<sub>6</sub> + 0.5M H<sub>2</sub>SO<sub>4</sub> solution. There is a significant catalysis for methanol oxidation at the co-deposited electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> solution. The catalysis was ascribed to the interaction between platinum and the redox couple H<sub>x</sub>MoO<sub>3</sub>/H<sub>y</sub>MoO<sub>3</sub> (0 < y < x < 2). The hydrogen molybdenum bronzes with less hydrogen play a role as hydrogen acceptor, which help to free platinum from poison by the intermediates of methanol oxidation. The instability of the codeposited electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> solution was proposed.

**Key words :** Platinum, Hydrogen molybdenum bronze, Co-deposition, Methanol oxidation, Catalysis

### 1. INTRODUCTION

Direct methanol fuel cell (DMFC) technology is attractive in this modern society that more and more energy is required and environmentally friendly energy is desired. DMFCs are ideal power sources not only for large vehicle but also for portable electronics use, because methanol offers numerous benefits when it is used as a fuel. Methanol can be obtained from cost and reproducible sources such as wood, which can reduce the use of minerals such as oil. Methanol is an environmentally clean fuel due to only formation of carbon dioxide and water while methanol is burned. It can be handled and stored as easily as gas and more easily than hydrogen. Most of all, methanol has a high energy density through a six-electron reaction:



Theoretically, DMFCs have an energy density five times that of a Li ion battery which has been able to achieve 300-350 Wh/l.

Electrocatalytic oxidation of methanol plays an important role in the DMFC system. Much work has been reported on the development of electrocatalysts for the methanol oxidation and on the understanding of the electrocatalytic mechanisms [1-10]. Shropshire was the first to report the catalysis of molybdates on the methanol oxidation [11]. Since then the application of platinum-molybdenum electrode has been paid much attention [12-16]. However proposed mechanisms in the catalysis on the methanol oxidation are controversial. Some believed that the couple Mo(IV)/Mo(III) played an important role in the catalysis

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of methanol oxidation [12,13], but some believed that it was not the couple Mo(IV)/Mo(III) but the couple Mo(VI)/Mo(IV) [14]. The purpose of this work is to investigate the electrocatalytic mechanism by studying deposition of platinum and/or reduced molybdates and electrochemical behaviors of co-deposited platinum and hydrogen molybdenum bronzes ( $H_xMoO_3$ ,  $0 < y < x < 2$ ) in the sulfuric acid solution with and without methanol. The co-deposition method is used in order to prepare Pt- $H_xMoO_3$  with homogeneous compositions.

## 2. EXPERIMENTAL

All the experiments for the depositions of platinum and/or hydrogen molybdenum bronze and the determination of electrochemical behaviors were performed using a potentiostat/galvanostat (PGSTAT 30, Autolab) controlled by a computer with a GPES program. A conventional three-electrode cell was used in all the experiments. A platinum disk with an area of 0.196 cm<sup>2</sup> was used as the working electrode. A platinum wire was used as the counter electrode and a saturated calomel electrode (SCE) was used as the reference electrode. Potentials in this paper are referenced to SCE. The electrolyte volume in the cell was 100 cm<sup>3</sup>. All the chemicals used were analytical grade reagents. Solutions were prepared with water de-ionized and distilled twice. 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.005M H<sub>2</sub>PtCl<sub>6</sub> solutions with and without 0.05M Na<sub>2</sub>MoO<sub>4</sub> were used for the preparation of deposited platinum and co-deposited Pt- $H_xMoO_3$  electrodes. 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.1M CH<sub>3</sub>OH solution was used in the catalytic study. All the experiments were carried out at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1 Deposition and co-deposition of platinum and/or hydrogen molybdenum bronzes

#### 3.1.1 Deposition of hydrogen molybdenum bronzes

Fig. 1 shows the cyclic voltammograms of platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> solutions with and without 0.05M Na<sub>2</sub>MoO<sub>4</sub>. In the solution without molybdates, reversible formation and oxidation of adsorbed hydrogen atoms can be observed on the potentials between -0.2 and 0V, and the formation of platinum oxide beginning at about 0.45V and its reduction peak potential at about 0.45V can be identified. The reduction of molybdates and the oxidation of the reduced molybdates can be easily observed by comparing the voltammograms of platinum electrode in the solutions with and without molybdates. The reduction of molybdates begins at about 0.2V and reaches a peak current at about 0V before the hydrogen evolution takes place. The reduced molybdates deposits on the platinum surface, because colored deposition on the electrode surface can be observed when the potential scan ends at -0.2V. The reduction of molybdates in acid solution is accompanied by the inser-

tion of hydrogen ions into molybdenum oxides, forming hydrogen molybdenum bronzes,  $H_xMoO_3$  ( $x \leq 2$ ) [17,18]. The oxidation and reduction of hydrogen molybdenum bronze can be observed when transferring the platinum with colored deposition into 0.5M H<sub>2</sub>SO<sub>4</sub> solution without molybdates and cycling the electrode between -0.2 and 0.8V. This indicates that the colored deposition should be hydrogen molybdenum bronzes.

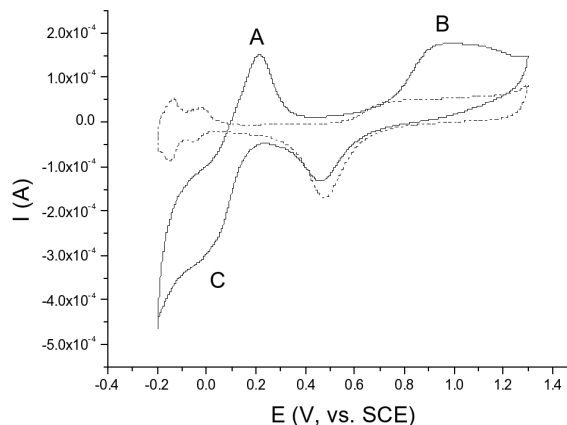


Figure 1: Voltammograms of platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> solutions with (solid line) and without (dash line) 0.05M Na<sub>2</sub>MoO<sub>4</sub>, scan rate: 50mV/s.

The formation and the oxidation currents of adsorbed hydrogen atoms on platinum in the solution without molybdates were not observed in the solution containing molybdates. This indicates that the platinum surface is covered with the deposited hydrogen molybdenum bronzes and no naked platinum is available for the formation of adsorbed hydrogen. Two oxidation current peaks can be observed from Fig. 1 at 0.24V (A) and 0.95V (B) on platinum in the solution containing molybdates. The currents near the second peak (B) is far higher than those observed on the electrode in the solution without molybdates, indicating that the second current peaks is mainly contributed by the oxidation of the reduced molybdates. Therefore, the oxidation of the reduced molybdates, hydrogen molybdenum bronzes ( $H_xMoO_3$ ), proceeds in two steps. No reduction currents correspond to the second oxidation of the hydrogen molybdenum bronzes and the reduction current peak of platinum oxide still can be observed on the electrode in the solution containing molybdates. This indicates that the deposited hydrogen molybdenum bronzes will dissolve in the solution after the second oxidation. The dissolution of hydrogen molybdenum bronze with higher oxidative state of molybdenum has been testified by several authors [19,20]. Naked platinum surface is available again and platinum oxide is formed due to the dissolution of hydrogen molybdenum bronzes.

To understand the reduction behavior of molybdates, the voltammograms of platinum electrode were measured in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.05M Na<sub>2</sub>MoO<sub>4</sub> solution with different potential scan rates. The results are shown in Fig. 2a. There is a proportional relationship between the reduction current at 0V and the square root of scan rate, as shown in Fig. 2b. This indicates that the reduction of molybdates is reversible and the equation (2) can be used [21].

$$i_p = (2.69 \times 10^5) n^{2/3} A D_o^{1/2} \nu^{1/2} C_o^* \quad (2)$$

$I_p$  is the reduction peak current of the reactant O,  $n$  the reaction electron number,  $A$  the electrode area,  $D_o$  the diffusion coefficient,  $\nu$  the potential scan rate and  $C_o^*$  the bulk concentration of the reactant.

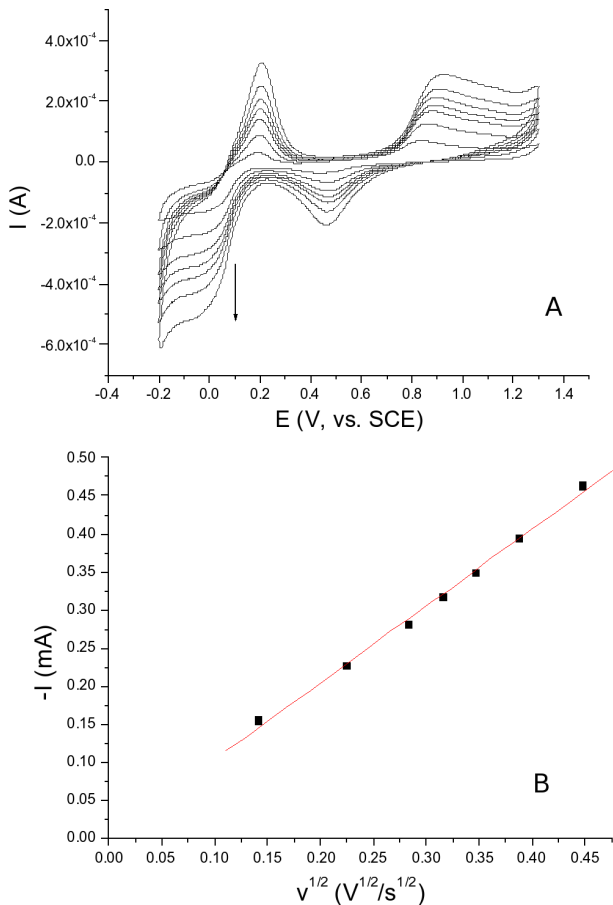


Figure 2: Voltammograms of platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.05M Na<sub>2</sub>MoO<sub>4</sub> solution with scan rates: 200, 150, 120, 100, 80, 50, and 20mV/s (a), the arrow shows the increase of the scan rate, and the variation of current at 0V with the square root of scan rate (b).

Fig. 3 is the chronocoulometric response of platinum electrode at 0V in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.05M Na<sub>2</sub>MoO<sub>4</sub> solution. There is a good linear relationship between the reduction coulomb of molybdates and the square root of reduction time and the equation (3) can be used [21].

$$Q = 2nFAD_o^{1/2}C_o^*\pi^{-1/2}t^{1/2} + Q_{dl} + nFA\Gamma_o \quad (3)$$

where  $Q_{dl}$  is the capacitive charge,  $\Gamma_o$  the surface concentration of adsorbed reactants,  $F$  the faradaic constant, other symbols have the same meaning as in equation (2). Although the diffusion coefficient is not available, the reaction electron number can be obtained by combining two slopes of the linear lines in Fig.2b and Fig. 3. As the slope is  $1.01 \times 10^{-3}$  V<sup>1/2</sup>/s<sup>1/2</sup> in Fig.2b and  $-1.88 \times 10^{-4}$  C/s<sup>1/2</sup> in Fig. 3, the reaction electron number obtained is 4.72.

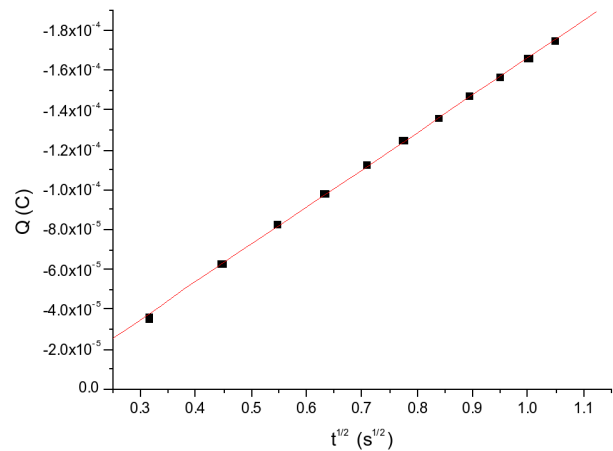
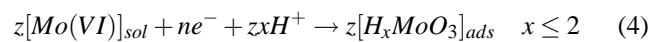


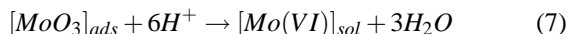
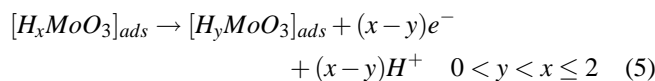
Figure 3: Chronocoulometric response of platinum electrode at 0V in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.05M Na<sub>2</sub>MoO<sub>4</sub> solution

In acid solution, molybdates exist in the form of polymolybdates [22]. The number of molybdenum atom in a polymolybdate molecule depends on the acid concentration. The reduction reaction of molybdates can be expressed as follows:



where  $z$  is the number of molybdenum atom in a polymolybdate molecule and  $x$  equals  $n/z$ . Since  $x \leq 2$  and  $n = 4.72$ ,  $z$  is larger than 2, i.e., a polymolybdate molecule in 0.5M H<sub>2</sub>SO<sub>4</sub> solution consists of more than two molybdate molecules.

Cycling the platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.05M Na<sub>2</sub>MoO<sub>4</sub> solution between -0.2 and +1.3V, the voltammograms in various cycles remains almost the same with the solid line in Fig. 1. This indicates that the amount of the deposited hydrogen molybdenum bronzes on platinum will not build up with cycles but dissolve into the solution again after two-step oxidation. The oxidation of hydrogen molybdenum bronze and the dissolution of the oxidized product can be expressed as follows:



### 3.1.2 Deposition of platinum

Fig. 4 shows the voltammograms of platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.005M H<sub>2</sub>PtCl<sub>6</sub> solution. The reduction of PtCl<sub>6</sub><sup>2-</sup> begins at about 0.3V, just after reduction of platinum oxide. The oxidation of adsorbed hydrogen atoms can be observed at negative potentials. Based on the variation of the oxidation charge of adsorbed hydrogen atoms with cycling from Fig.4, it can be found that the surface area of platinum increases with cycling. This means that the deposited platinum was dispersed on the base platinum surface. The deposited platinum was prepared in this paper by cycling the base platinum electrode for 30 cycles between -0.2 and 0.8V in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.005M H<sub>2</sub>PtCl<sub>6</sub> solution at a potential scan rate of 50 mV/s. Fig. 5 is SEM of different electrodes. Fig. 5b is the SEM of the prepared deposited platinum electrode, which shows the dispersion of the deposited platinum.

The surface area of platinum electrode can be evaluated by measuring the oxidation coulomb of adsorbed hydrogen atoms [23]. Fig. 6 shows the voltammograms of the base platinum and the deposited platinum electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The coulomb is 4.43 × 10<sup>-5</sup> C for the base platinum electrode and 1.06 × 10<sup>-3</sup> C for the deposited platinum electrode. The area of the deposited platinum electrode is about 24 times that of the base platinum electrode.

### 3.1.3 Co-deposition of platinum and hydrogen molybdenum bronze

Fig. 7 shows the voltammograms of platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.005M H<sub>2</sub>PtCl<sub>6</sub> + 0.05M Na<sub>2</sub>MoO<sub>4</sub> solution. The current peaks corresponding to the oxidation of adsorbed hydrogen atoms between -0.2 and 0V and the oxidation of hy-

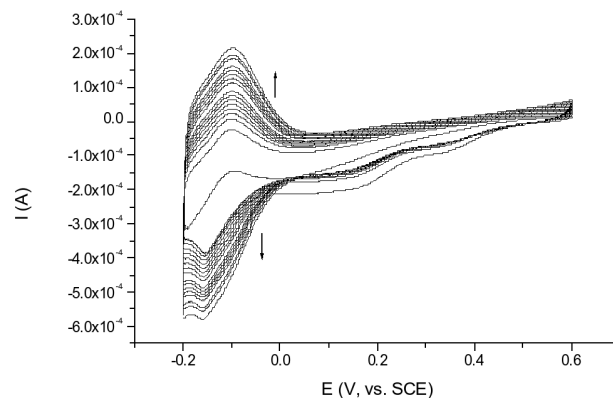


Figure 4: Voltammograms of platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.005M H<sub>2</sub>PtCl<sub>6</sub> solution, the arrows show the increase of cycle number, scan rate: 50mV/s.

drogen molybdenum bronzes between 0.1 and 0.3V can be observed. This indicates that co-deposition of platinum and hydrogen molybdenum bronze takes place. The naked platinum surface is always available during the co-deposition, which is different from the deposition of hydrogen molybdenum bronze on platinum as shown in Fig. 1. The co-deposited electrode was prepared in this paper by cycling the base electrode for 30 cycles between -0.2 and 0.8V in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.005M H<sub>2</sub>PtCl<sub>6</sub> + 0.05M Na<sub>2</sub>MoO<sub>4</sub> solution at a potential scan rate of 50 mV/s. Fig. 5c is the SEM of the prepared co-deposited electrode.

Fig. 8 shows the voltammograms of the deposited platinum and the co-deposited electrodes in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. It can be found that there is little difference between the deposited platinum electrode and the co-deposited electrode, except that the oxidation peak A at 0.22V and the reduction peak A' at 0.17V of hydrogen molybdenum bronzes can be observed and a little larger naked platinum surface is available on the co-deposited electrode. The naked platinum surface available on the co-deposited platinum electrode is about 1.2 times that on the deposited electrode. The peak A and peak A' in Fig. 8 correspond to the oxidation and reduction of a redox couple of hydrogen molybdenum bronzes. The difference of two peak potentials is 50mV, indicating that the redox reaction is considerably reversible. The redox potential of this couple can be estimated from their peak potentials. It is 0.2V, close to the potential (0.4V vs. SHE) for the conversion of H<sub>x</sub>MoO<sub>3</sub> phase I (0.23 < x < 0.40)/phase II (0.85 < x < 1.04) [24]. Therefore, the redox reaction can be expressed as:

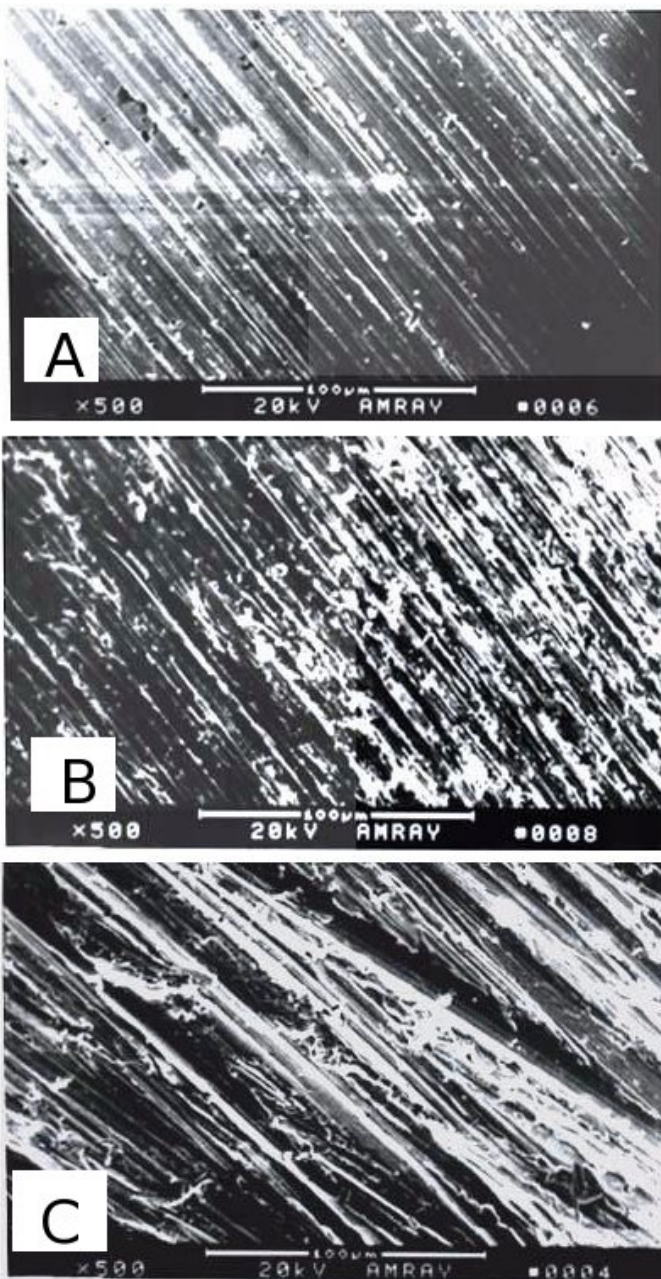


Figure 5: SEM of base platinum electrode (a), deposited platinum electrode (b), and co-deposited electrode (c).

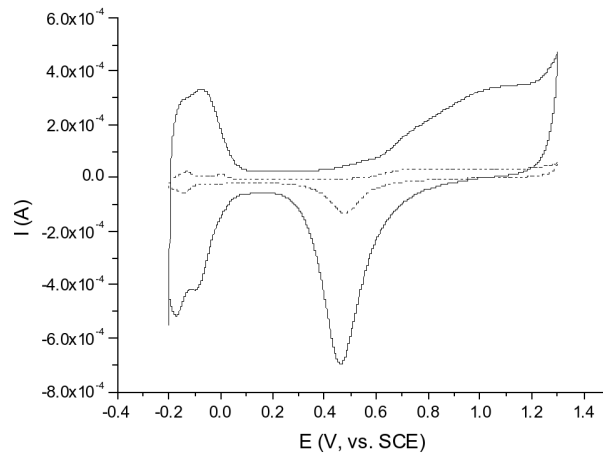


Figure 6: Voltammograms of base platinum electrode (dash line) and deposited platinum electrode (solid line) in 0.5M H<sub>2</sub>SO<sub>4</sub> solution, scan rate: 50mV/s.

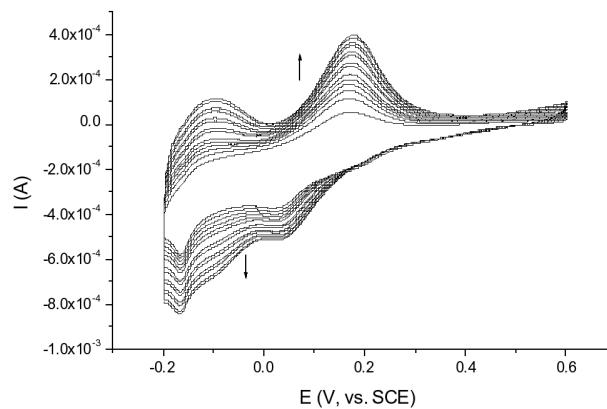


Figure 7: Voltammograms of platinum electrode in 0.5M H<sub>2</sub>SO<sub>4</sub> + 0.005M H<sub>2</sub>PtCl<sub>6</sub> + 0.05M Na<sub>2</sub>MoO<sub>4</sub> solution, the arrows show the increase of cycle number, scan rate: 50mV/s.

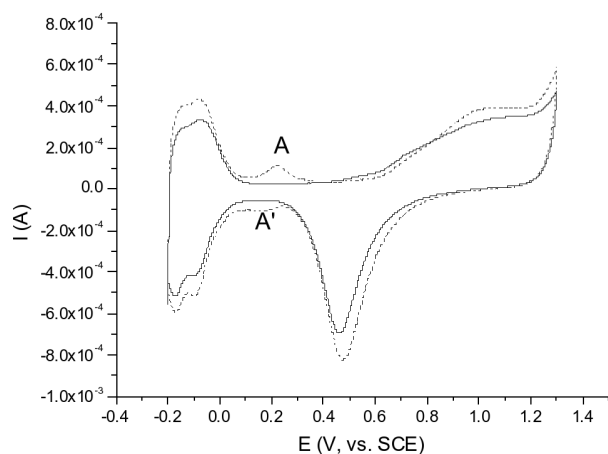
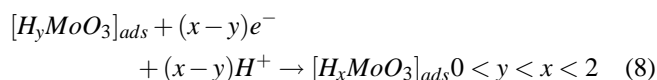


Figure 8: Voltammograms of co-deposited electrode (dash line) and deposited platinum electrode (solid line) in 0.5M H<sub>2</sub>SO<sub>4</sub> solution, scan rate: 50mV/s.



### 3.2 Catalytic oxidation of methanol on the co-deposited electrode

Fig. 9 shows the first cyclic voltammograms of the base platinum, the deposited platinum and the co-deposited electrodes in 0.1M CH<sub>3</sub>OH + 0.5M H<sub>2</sub>SO<sub>4</sub> solution. The potential scan began at -0.2V, reversed at 0.8V and ended at -0.2V. The electrode was kept at -0.2V for 3s before the scan started. It can be observed from Fig. 9a that the oxidation current of methanol increases with increasing potential slowly before 0.4V but quickly after 0.4V. The slow current increase is ascribed to the formation of reaction intermediates and the quick increase to the formation of partial platinum oxide which favors the conversion of intermediates to carbon dioxide [16]. The current magnitudes of methanol oxidation on these three electrodes are different: the highest on the co-deposited electrode and the lowest on the base electrode. Compared with the base platinum electrode, the deposited electrode and the co-deposited electrode apparently catalyze the methanol oxidation. For example, the current at 0.37V, where current increases slowly with increasing potential, on forward scan is  $2.26 \times 10^{-5}$  A for the base electrode, but the currents at the same potential are  $3.66 \times 10^{-4}$  A for the deposited electrode and  $6.85 \times 10^{-4}$  A for the co-deposited electrode, 16.2 and 26.4 times that for the base electrode, respectively.

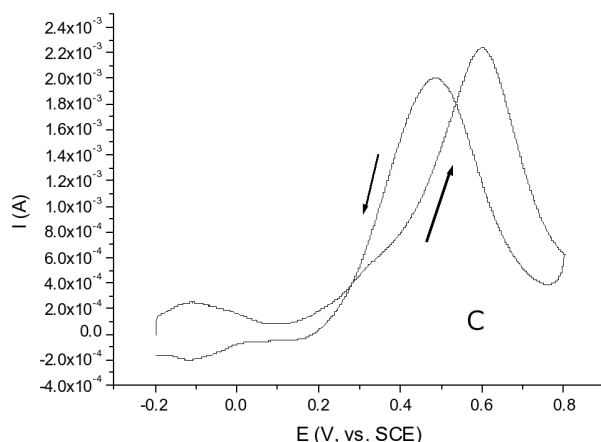
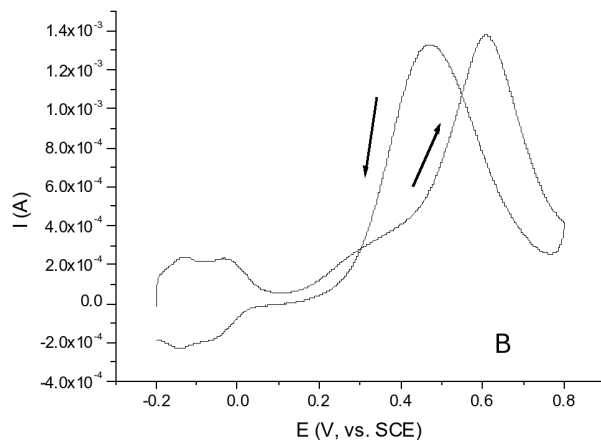
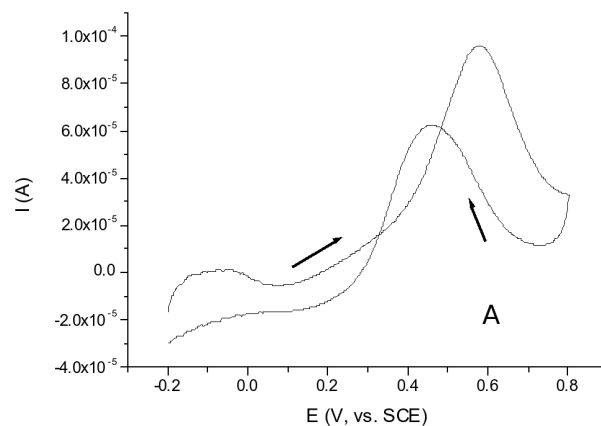


Figure 9: Voltammograms of the base platinum (a), deposited platinum (b) and co-deposited (c) electrodes in 0.1M CH<sub>3</sub>OH + 0.5M H<sub>2</sub>SO<sub>4</sub> solution, scan rate: 50mV/s.

The oxidation of methanol on polycrystalline and single crystal platinum has been well studied [25-28]. The reaction involves the formation of adsorbed intermediates such as CO [29] and COH [30], which will retard the further oxidation of methanol. The pathways for the methanol oxidation are similar on the base platinum electrode, the deposited platinum electrode and the co-deposited electrode. On the forward scan, the adsorbed methanol on platinum is directly oxidized to different forms of intermediates or even to CO<sub>2</sub>. The current increases with increasing potential, so the reaction is controlled by the charge transfer step. The current reaches a peak at about 0.6V and then decreases with increasing potential, indicating that the methanol oxidation becomes difficult on the surface covered completely with platinum oxide. On the backward scan, the current peak of methanol oxidation occurs at about 0.45V, 0.15V less negative than the current peak potential on the forward potential scan. This can be ascribed to the fresh naked platinum available due to the reduction of platinum oxide. The current for hydrogen adsorption is not so apparent for the base platinum electrode as for the deposited electrode and the co-deposited electrode. This indicates that the dispersed platinum favors the desorption of the reaction intermediates of methanol oxidation.

The catalysis for the methanol oxidation on the deposited electrode should be ascribed to the increase of real surface area and the geometric effect of the dispersed platinum on the deposited electrode. The real surface area of the deposited platinum electrode is 24 times that of the base platinum electrode. There are two types of adsorbed CO on platinum surface [31,32]. The distribution of different adsorbed CO depends strongly on the crystalline characteristics of the surface and the methanol oxidation depends greatly on surface structure [33]. The deposited platinum has a structure with dispersed platinum particles, which will favor the methanol oxidation.

There is a stronger catalysis for the methanol oxidation on the co-deposited electrode than on the deposited electrode. Based on the oxidation charge of adsorption hydrogen, it has been known that there is no significant difference in real platinum surface area between the co-deposited electrode and the deposited electrode. Therefore, the catalysis for the methanol oxidation on the co-deposited electrode must be ascribed to the existence of hydrogen molybdenum bronze. The current at 0.37V for the methanol oxidation increases by 16.2 times from the base electrode to the deposited electrode whose platinum surface area is 24 times that of the base platinum electrode. However, the current at the same potential for the methanol oxidation increases by 1.87 times from the deposited electrode to the co-deposited electrode whose platinum surface area is only 1.2 times that of the deposited electrode.

Some reports ascribed this catalysis to the direct methanol oxidation by Mo(IV) [15]. This mechanism seems unreasonable, because the formation potential for any other forms of molyb-

denum with lower valence than Mo(VI) is more negative than the potential for the methanol oxidation (as shown in Fig. 1). The catalysis for the methanol oxidation on co-deposited platinum/molybdenum oxide has also been reported [14]. A surface redox mechanism which involves the Mo(VI)/Mo(IV) couple in substoichiometric lower valence molybdenum oxide MoO<sub>x</sub> (2 < x < 3) was proposed to explain this catalysis. Based on our results obtained in this paper, not the Mo(VI)/Mo(IV) but the couple H<sub>x</sub>MoO<sub>3</sub>/H<sub>y</sub>MoO<sub>3</sub> (corresponding to the redox A/A' in Fig. 8, 0 < y < x < 2) is responsible for the catalysis of methanol oxidation.

We have reported that the catalysis for methanol oxidation on the platinum modified with reduced molybdates depends on the amount of the reduced molybdates [16]. The catalysis was reduced when platinum was under-modified or over-modified with hydrogen molybdenum bronze. Therefore, the catalysis for methanol oxidation on the co-deposited platinum and hydrogen molybdenum bronzes should be related to the interaction between platinum and hydrogen molybdenum bronze. Since the catalysis takes place after the oxidation peak A in Fig. 8, the catalysis is not ascribed to the direct methanol oxidation by H<sub>y</sub>MoO<sub>3</sub> (0 < y < 2). The catalytic mechanism can be explained as the proton spillover effect between platinum and hydrogen molybdenum bronzes. The redox couple H<sub>x</sub>MoO<sub>3</sub>/H<sub>y</sub>MoO<sub>3</sub> (0 < y < x < 2) is reversible. The hydrogen molybdenum bronze with high amount of hydrogen (H<sub>x</sub>MoO<sub>3</sub>) is easily oxidized on the platinum to form the hydrogen molybdenum bronzes with less hydrogen (H<sub>y</sub>MoO<sub>3</sub>). The latter plays a role as proton acceptors, which help the oxidation of adsorption intermediates, CH<sub>z</sub>O<sub>ads</sub> (0 ≤ z ≤ 4), on platinum. The electrocatalytic process can be formulated as:

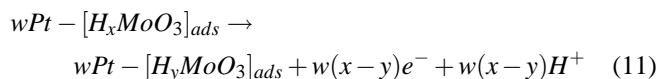
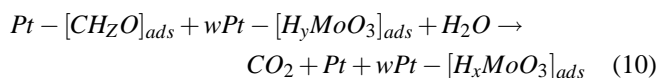


Fig. 10 shows the Nyquist plots of the base platinum electrode, the deposited electrode and the co-deposited electrode at 0.37V in 0.1M CH<sub>3</sub>OH + 0.5M H<sub>2</sub>SO<sub>4</sub> solution. It can be found from Fig. 10 that the Nyquist behaviors of these three electrodes at high frequency are similar: a flat semicircle, which represents a process controlled by the charge transfer step. This indicates that the methanol oxidation on these three electrodes is controlled by the charge transfer step. Charge transfer resistance can be obtained by fitting the Nyquist plots of Fig. 10 at high frequency (from 10<sup>5</sup>Hz to 1Hz) with a parallel equivalent circuit of

capacitance and resistance. It is  $11.4\text{k}\Omega$  for the base platinum electrode,  $1.4\text{k}\Omega$  for the deposited electrode and  $0.77\text{k}\Omega$  for the co-deposited electrode. The charge transfer resistance for the co-deposited electrode is almost half of the charge transfer resistance for the deposited electrode, although the naked platinum surface of the co-deposited electrode is almost the same as that of the deposited electrode. Therefore, the higher catalysis of methanol oxidation on the co-deposited electrode than the deposited electrode can be ascribed to the decreasing charge transfer resistance due to the interaction between platinum and hydrogen molybdenum bronze. This strengthens the proposed catalytic mechanism for methanol oxidation: hydrogen molybdenum bronzes help to clean platinum to make the methanol oxidation easier.

To determine the stability of the co-deposited platinum and hydrogen molybdenum bronze electrode, potential step experiment was carried out. Fig. 11 is the chronoamperometric responses of deposited electrode and co-deposited electrode at  $0.6\text{V}$  in  $0.1\text{M CH}_3\text{OH} + 0.5\text{M H}_2\text{SO}_4$  solution. At the beginning of the potential step, the current for the methanol oxidation at the deposited platinum electrode decreases significantly. The current on the co-deposited electrode is far higher than that on the deposited platinum electrode, for example, after the potential was maintained for 600s the current is  $7.513 \times 10^{-4}\text{A}$  for the co-deposited electrode, five times the current ( $1.492 \times 10^{-4}\text{A}$ ) for the deposited electrode. This verifies the catalysis of the co-deposited platinum and hydrogen molybdenum bronze on the methanol oxidation. However, after the potential was maintained for 1500s the current on the co-deposited electrode decreases and reaches almost to the current on the deposited electrode. This indicates that the catalysis of co-deposited electrode on the methanol oxidation is reduced. It was found that the redox couple peaks A/A' in Fig. 8 disappeared when measuring the voltammogram of the co-deposited electrode after potential step experiments, as shown in Fig. 12. This indicates that the deposited hydrogen molybdenum bronze can dissolve into sulfuric solution. The reduction of the catalysis of the co-deposited electrode is ascribed to the dissolution of the deposited hydrogen molybdenum bronze. In order for the catalytic system to be used in the fuel cell, efforts should be made to find out the methods for stabilizing hydrogen molybdenum bronze.

#### 4. CONCLUSIONS

Hydrogen molybdenum bronzes can be co-deposited with platinum. There is an interaction between the co-deposited platinum and hydrogen molybdenum bronzes, which catalyze the oxidation of methanol in the sulfuric acid solution. The catalysis can be ascribed to cleaning of poison adsorption intermediates formed from the methanol oxidation on platinum by the redox couple  $\text{H}_x\text{MoO}_3/\text{H}_y\text{MoO}_3$  ( $0 < y < x < 2$ ). However, the co-deposited platinum and hydrogen molybdenum bronze elec-

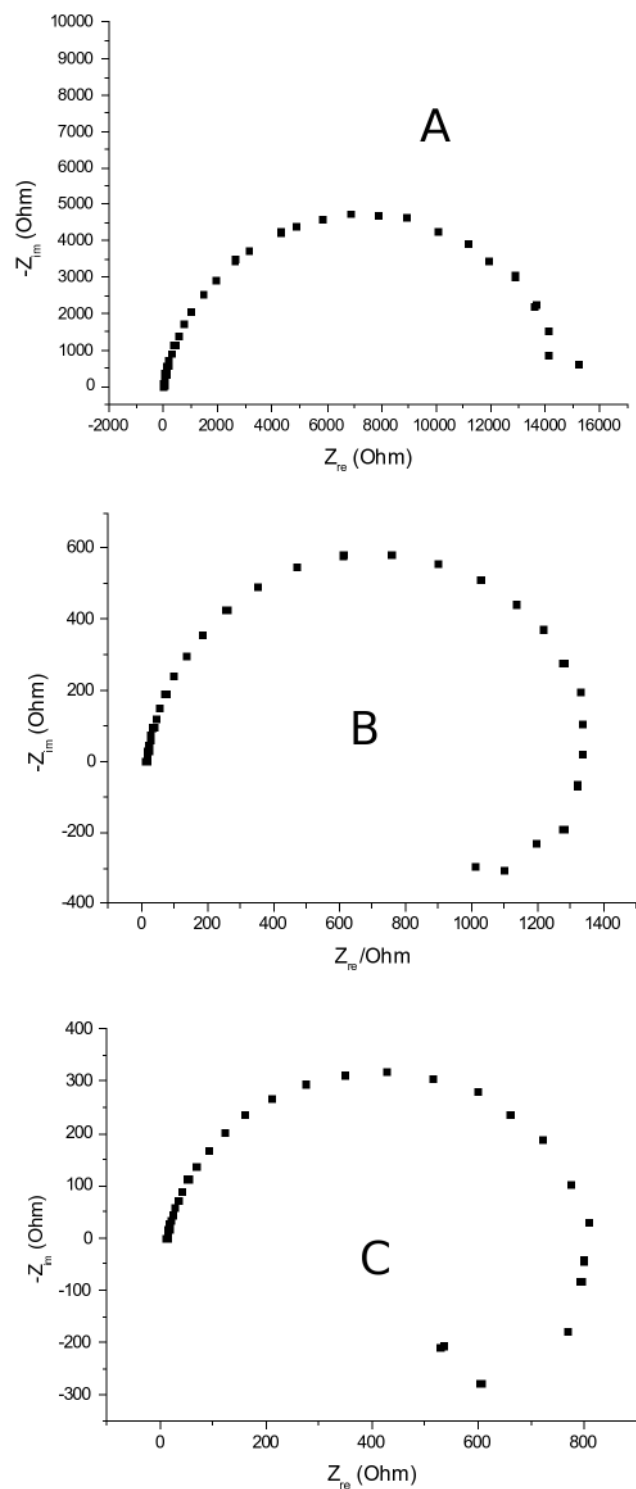


Figure 10: Nyquist plots of base platinum (a), deposited platinum (b) and co-deposited (c) electrodes at  $0.37\text{V}$  in  $0.1\text{M CH}_3\text{OH} + 0.5\text{M H}_2\text{SO}_4$  solution, frequency from  $100\text{kHz}$  to  $10\text{mHz}$ .



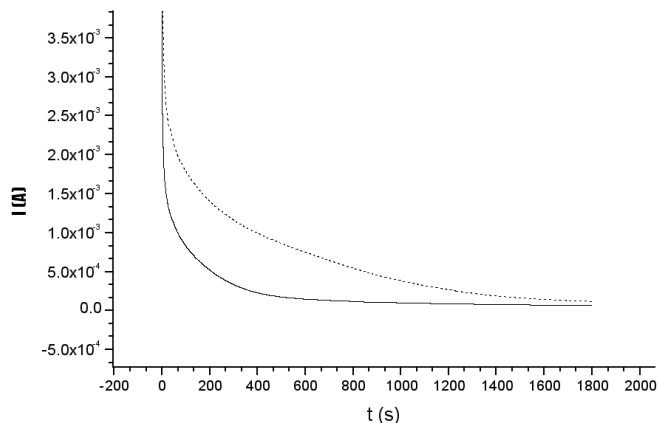


Figure 11: Chronoamperometric plots of deposited platinum (solid line) and co-deposited (dash line) electrodes at 0.6V in 0.1M CH<sub>3</sub>OH + 0.5M H<sub>2</sub>SO<sub>4</sub> solution.

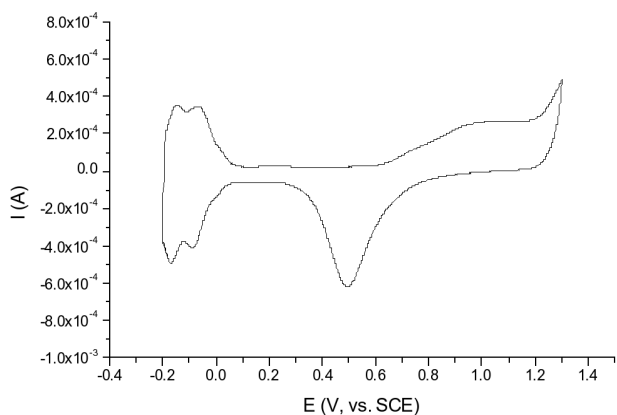


Figure 12: Voltammogram of the co-deposited electrode after potential step experiment of Fig. 11.

trode is not stable in sulfuric solution. Hydrogen molybdenum bronzes can dissolve in the solution.

## 5. ACKNOWLEDGMENTS

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