

Short communication

Electrocatalytic oxidation of small organic molecules on polyaniline-Pt-H_xMoO₃

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Abstract

Deposited platinum and co-deposited platinum and hydrogen molybdenum bronze were prepared on platinum or polyaniline. The electrocatalytic activity of these electrodes for the oxidation of methanol, formaldehyde and formic acid in 0.5 M H₂SO₄ solution was studied by using cyclic voltammetry between –0.2 and 0.8 V (versus saturated calomel electrode (SCE)). Results show that polyaniline and hydrogen molybdenum bronze can improve the electrocatalytic activity of platinum toward the oxidation of these small organic molecules. The polyaniline enhances the oxidation currents of these molecules on platinum at the higher potentials on forward sweep (from –0.2 to 0.8 V) and at all potentials on the backward sweep but hardly affects the oxidation at the lower potentials on the forward sweep. It accelerates the direct oxidation of the molecules to carbon dioxide but does not change the nature of adsorbed intermediates on platinum. Different from polyaniline, hydrogen molybdenum bronze enhances the oxidation currents of these molecules on platinum at the lower potentials on forward sweep. It accelerates the transformation of adsorbed intermediates on platinum to carbon dioxide.

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1. Introduction

Platinum is an active catalyst for the oxidation of small organic molecules, such as methanol, formaldehyde and formic acid. However, the reaction intermediates of these molecules, such as CO_{ad}, are poison to platinum catalyst [1]. This is one of the main issues that hinders the application of direct small organic molecule fuel cell and attracts a great deal of research interests [2–9]. Molybdenum can improve the activity of platinum toward the oxidation of these small organic molecules when it is added into platinum as an alloy element or a compound [10–13]. It has been shown by some authors of this paper that hydrogen molybdenum bronze (H_xMoO₃, 0 < x < 1) can be deposited on platinum electrochemically in sulfuric acid solution containing molybdates and the electrocatalytic activity of platinum toward the oxidation of

methanol, formaldehyde and formic acid can be improved by the modification with hydrogen molybdenum bronze [14–18]. The purpose of this paper is to understand the electrocatalytic activity of platinum modified with polyaniline as well as hydrogen molybdenum bronze toward the oxidation of methanol, formaldehyde and formic acid. To reach this purpose, three electrodes, deposited platinum, polyaniline-platinum and polyaniline-platinum-hydrogen molybdenum bronze were prepared and the voltammetric behavior of methanol, formaldehyde and formic acid on these electrodes were studied by using cyclic voltammetry.

2. Experimental

2.1. Electrochemical method

All the electrochemical experiments in the preparation of electrodes and the investigation of electrocatalytic oxidation

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of methanol, formaldehyde and formic acid on the prepared electrodes were performed using a potentiostat/galvanostat (PGSTAT 30; Autolab, Eco Chemie B.V. Company) controlled by a computer with a GPES program. A conventional three-electrode cell was used. A rotating platinum disk with an area of 0.196 cm^2 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 reported with respect to SCE expect for special remark. 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.

2.2. Electrode preparation

Deposited platinum (denoted as deposited Pt), polyaniline-platinum (denoted as Pan-Pt) and polyaniline-platinum-hydrogen molybdenum bronze (denoted as Pan-Pt- H_xMoO_3) electrodes were prepared on the working electrode (base platinum electrode) in $0.5 \text{ M H}_2\text{SO}_4$ solution. Fig. 1 shows the cyclic voltammogram of the base platinum electrode in $0.5 \text{ M H}_2\text{SO}_4$ solution. It can be found that only currents for the formation and oxidation of adsorbed hydrogen atoms and the formation and reduction of platinum oxides occur during cycling the electrode at the potentials between -0.2 and 1.3 V . This indicates that the electrode is pure platinum.

Deposited Pt was prepared by cycling the base platinum in $0.5 \text{ M H}_2\text{SO}_4 + 0.005 \text{ M H}_2\text{PtCl}_6$ solution at the potentials between -0.2 and 0.6 V for 30 cycles with a scanning rate of 50 mV s^{-1} . In the preparation of Pan-Pt and Pan-Pt- H_xMoO_3 electrodes, polyaniline electrode was first prepared on the base platinum electrode. Fig. 2 shows the current correspondence of the base platinum electrode in $0.1 \text{ M aniline} + 0.5 \text{ M H}_2\text{SO}_4$ solution to a potential step. At the beginning of the potential step, a rapid current decrease appears, which corresponds to the charging current for double layer capacitance, and then the current increases with time, which is ascribed

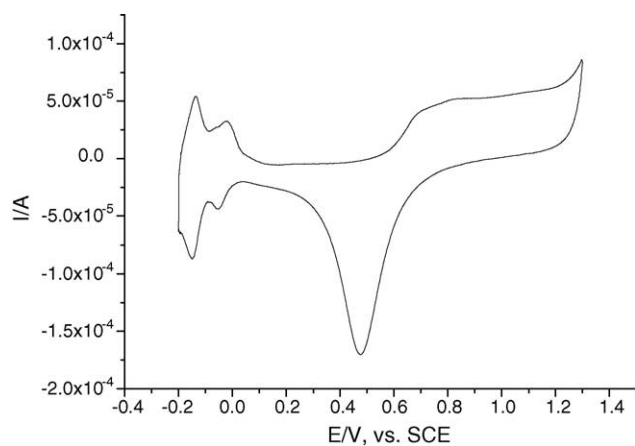


Fig. 1. Cyclic voltammogram of base platinum electrode in $0.5 \text{ M H}_2\text{SO}_4$ solution, 100 mV s^{-1} .

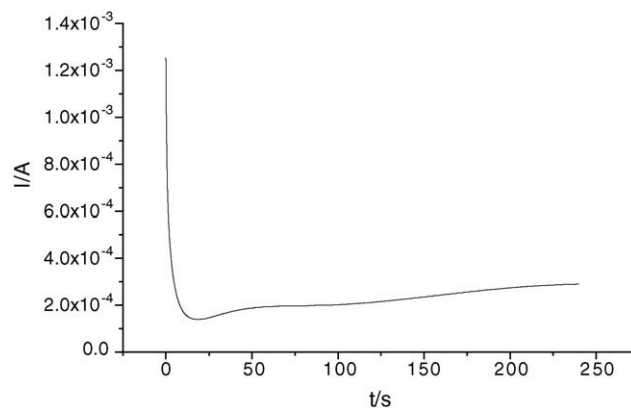


Fig. 2. Current correspondence of base platinum electrode to a constant potential of 0.9 V in $0.1 \text{ M aniline} + 0.5 \text{ M H}_2\text{SO}_4$ solution.

to the formation of polyaniline on the base platinum electrode. In this paper, the polyaniline electrode was prepared on the base platinum electrode by electrolyzing at a constant potential of 0.9 V for 240 s in $0.1 \text{ M aniline} + 0.5 \text{ M H}_2\text{SO}_4$ solution. Fig. 3 shows the voltammogram of the prepared polyaniline electrode. It can be found that multiple redox processes appear in the cycling voltammogram. These processes are ascribed to the structural transformations of polyaniline by the doping and undoping of protons or anions [19]. The redox current peaks at the potentials between 0 and 0.2 V are ascribed to the polyaniline transformation between the leucoemeraldine state (LM) and the emeraldine state (EM), and those at the potentials between 0.6 and 0.8 V to the transformation between the EM and the penigraniline state (PE).

Pan-Pt electrode was prepared by cycling the polyaniline electrode in $0.5 \text{ M H}_2\text{SO}_4 + 0.005 \text{ M H}_2\text{PtCl}_6$ solution at the potentials between -0.2 and 0.6 V for 30 cycles with a scanning rate of 50 mV s^{-1} . Pan-Pt- H_xMoO_3 electrode was prepared by cycling the polyaniline electrode in $0.5 \text{ M H}_2\text{SO}_4 + 0.005 \text{ M H}_2\text{PtCl}_6 + 0.005 \text{ M Na}_2\text{MoO}_4$ solution under the same conditions as the preparation of Pan-Pt electrode. Fig. 4 shows the cyclic voltammograms of deposited Pt, Pan-Pt and Pan-Pt- H_xMoO_3 electrodes in $0.5 \text{ M H}_2\text{SO}_4$

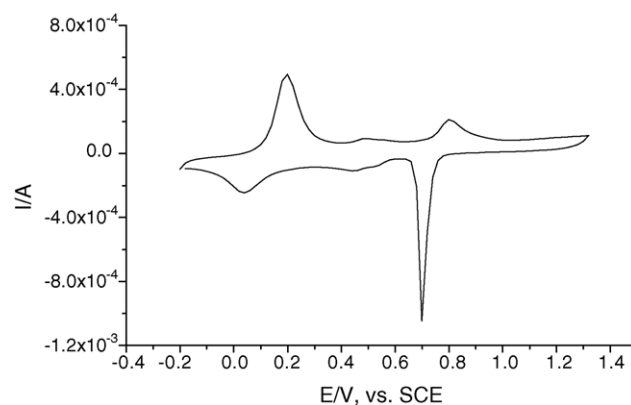


Fig. 3. Voltammogram of polyaniline electrode in $0.5 \text{ M H}_2\text{SO}_4$ solution, 100 mV s^{-1} .

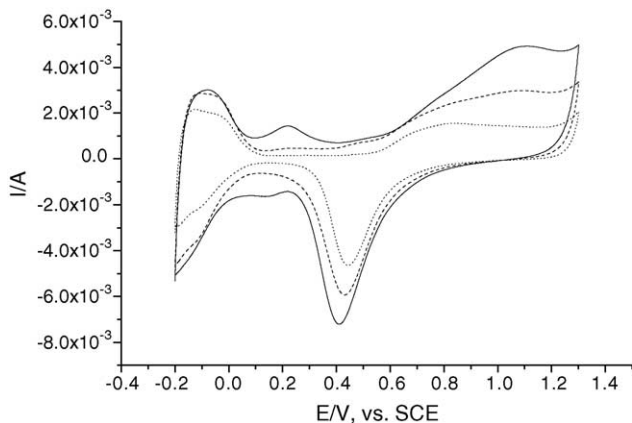


Fig. 4. Voltammograms of deposited Pt (dotted line), Pan-Pt (dash line) and Pan-Pt-H_xMoO₃ (solid line) electrodes in 0.5 M H₂SO₄ solution, 100 mV s⁻¹.

solution. Comparing Fig. 4 with Fig. 1, it can be found that the currents at the potentials for the formation and oxidation of adsorbed hydrogen atoms on these three electrodes are larger than those on the base platinum electrode. This indicates that the deposited platinum on these three electrodes is dispersed on the base platinum electrode or on the polyaniline electrode and larger platinum surface area can be obtained by electrodepositing platinum. Polyaniline can improve the dispersion of the deposited platinum because the currents on the Pan-Pt electrode (dash line in Fig. 4) for the formation and oxidation of adsorbed hydrogen atoms are larger than those on the deposited Pt electrode (dotted line in Fig. 4). Different from deposited Pt and Pan-Pt electrodes, the voltammogram of Pan-Pt-H_xMoO₃ electrode has a couple for the redox hydrogen molybdenum bronzes at the potentials between -0.1 and 0.3 V [14]. This indicates that hydrogen molybdenum bronze has been co-deposited with platinum. The currents for the formation and oxidation of adsorbed hydrogen atoms on Pan-Pt-H_xMoO₃ electrode are almost the same as those on Pan-Pt electrode, indicating that the co-deposited hydrogen molybdenum bronze does not change the real platinum surface area of deposited platinum.

3. Results and discussion

3.1. Oxidation of methanol, formaldehyde and formic acid on platinum

Among many small organic molecules, the oxidation of methanol, formaldehyde and formic acid on noble metal such as platinum has been most investigated due to their simple structures. It has been well accepted that the oxidation of these small organic molecules follows dual path mechanism:

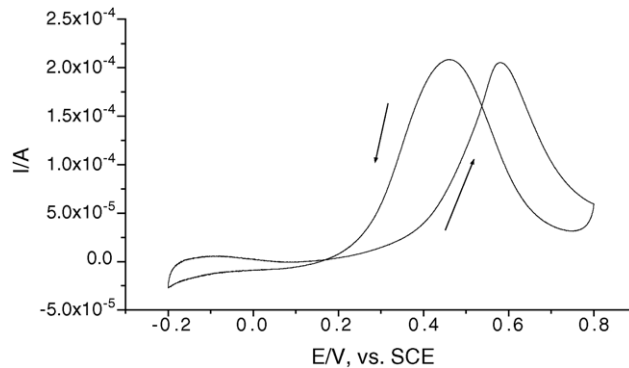
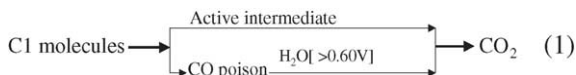


Fig. 5. Voltammogram of base platinum electrode in 0.5 M H₂SO₄ solution containing 0.1 M methanol, 100 mV s⁻¹.

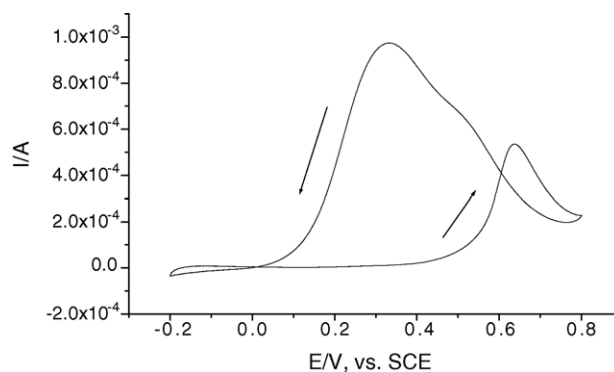


Fig. 6. Voltammogram of base platinum electrode in 0.5 M H₂SO₄ solution containing 0.1 M formaldehyde, 100 mV s⁻¹.

In the first path, small organic molecules are oxidized on noble metal to carbon dioxide at lower potentials than 0.6 V. In the second path, however, reaction intermediates poisonous to platinum are formed on platinum, which can be only oxidized to carbon dioxide at higher potentials.

The voltammograms of methanol, formaldehyde and formic acid on the base platinum electrode in 0.5 M H₂SO₄ solution are shown in Figs. 5–7. These voltammograms have such characteristics: on the forward potential sweep, the cur-

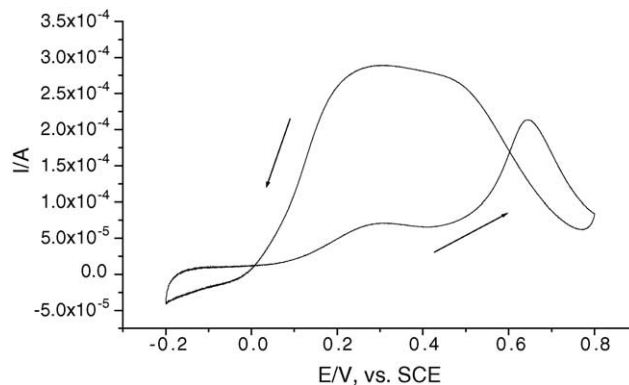
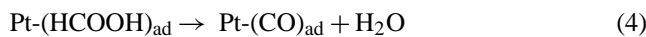
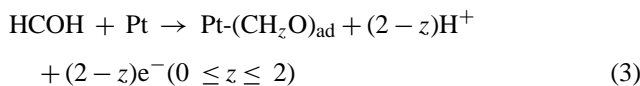
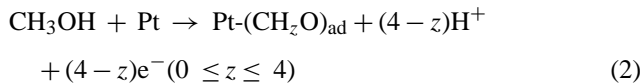


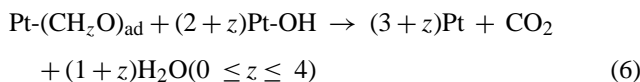
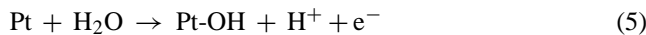
Fig. 7. Voltammogram of base platinum electrode in 0.5 M H₂SO₄ solution containing 0.1 M formic acid, 100 mV s⁻¹.

rent increases slowly at the potentials lower than and quickly increases at the potentials higher than 0.4 V with increasing potentials but a current peak appears at about 0.6 V, and on the backward potential sweep, larger current for the oxidation of these small organic molecules can be observed. These results are in agreement with those reported in literatures [20–22].

The slow increase in currents of Figs. 5–7 at lower potential on the forward sweep results from the poison of reaction intermediates to platinum from the oxidation of the small organic molecules. The reactions involved can be expressed as:



The quick increase in currents of Figs. 5–7 at higher potential on the forward sweep results from the partial oxidation of surface platinum, which help the transformation of intermediates to carbon dioxide. The reactions involved can be expressed as:



The current peaks of Figs. 5–7 at about 0.6 V are ascribed to the diffusion limit of the small organic molecules from solution to the platinum surface.

3.2. Behavior of methanol, formaldehyde and formic acid on polyaniline

The voltammograms of polyaniline electrode in 0.5 M H_2SO_4 solutions with and without methanol, formaldehyde and or formic acid are shown in Figs. 8 and 9. It can be found that there is no significant difference in the voltammetric behavior for the polyaniline electrode in sulfuric acid solutions with and without these small organic molecules. The redox processes for the structural transformations of polyaniline by the doping and undoping of protons or anions can be also observed in the solutions containing the small organic molecules. If there is any difference between the voltammetric behavior of polyaniline electrode in the solutions with and without the small organic molecules, it is that the reduction currents in the solution with the small organic molecules are a little lower than those in the solutions without the small organic molecules. This may result from the adsorption of the small organic molecules on polyaniline.

It is obvious that methanol, formaldehyde and formic acid cannot be oxidized on polyaniline in 0.5 M H_2SO_4 solution.

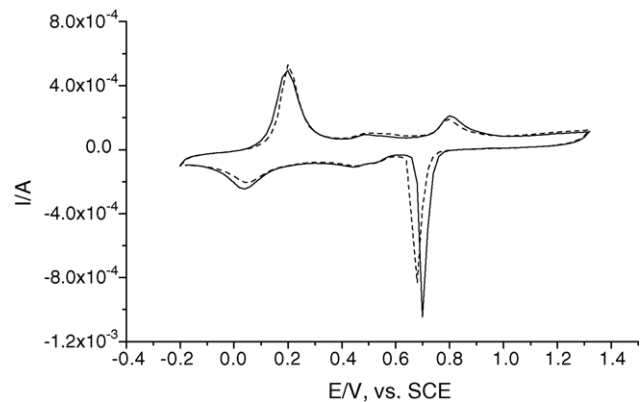


Fig. 8. Voltammograms of polyaniline electrode in 0.5 M H_2SO_4 (solid line) and 0.5 M H_2SO_4 + 0.1 M CH_3OH (dash line) solutions, 100 mV s^{-1} .

It has been well accepted that small organic molecules cannot be oxidized on polyaniline [23,24]. However, It was reported that the oxidation of methanol could happen on polyaniline in sulfuric acid solution when the methanol concentrations were higher than 1 M [25]. The mechanism was not given but this is not the subject of this paper. All the concentrations of methanol, formaldehyde and formic acid used in this paper are 0.1 M, the oxidation reaction of these molecules should not take place on polyaniline.

3.3. Electrocatalytic oxidation of methanol, formaldehyde and formic acid solution on Pan-Pt- H_xMoO_3

Fig. 10 shows the voltammograms of deposited Pt, Pan-Pt, and Pan-Pt- H_xMoO_3 electrodes in 0.5 M H_2SO_4 solution containing methanol. Comparing Fig. 10 with Fig. 5, it can be found that voltammetric characteristics of methanol are independent of the electrodes. However, the magnitude of the current change for the methanol oxidation on these electrodes

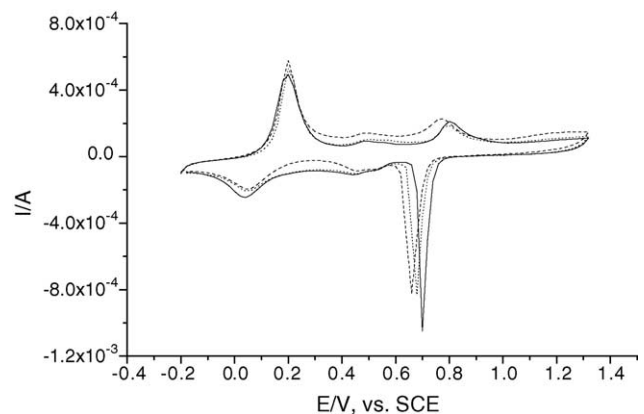


Fig. 9. Voltammograms of polyaniline electrode in 0.5 M H_2SO_4 (solid line), 0.5 M H_2SO_4 + 0.1 M HCHO (dotted line) and 0.5 M H_2SO_4 + 0.1 M HCOOH (dash line) solutions, 100 mV s^{-1} .

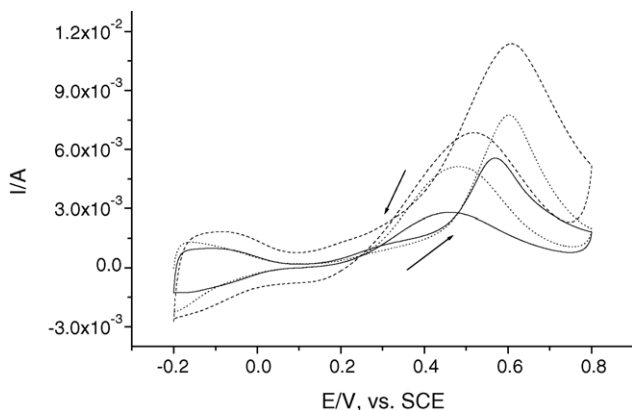


Fig. 10. Voltammograms of deposited Pt (solid line), Pan-Pt (dotted line) and Pan-Pt- H_xMoO_3 (dash line) electrodes in 0.5 M H_2SO_4 solutions containing 0.1 M methanol, 100 mV s^{-1} .

is different from each other. It is obvious that the current for the methanol oxidation on the deposited Pt electrode (solid line in Fig. 10) is far larger than that on the base platinum electrode (Fig. 5). For example, the current at 0.4 V on the forward sweep is 1.6×10^{-3} A for the deposited Pt electrode but only 4.0×10^{-5} A. This apparently results from the larger platinum surface available on the deposited Pt electrode than the base platinum electrode [26,27].

Comparing the solid line with the dotted line of Fig. 10, it can be seen that the currents of the Pan-Pt electrode at the potentials higher than 0.5 V on the forward potential sweep and at the potentials from 0.8 to 0.3 V on the backward sweep are larger than the deposited Pt electrode. For example, the current at 0.6 V on the forward sweep is 5.1×10^{-3} A for the deposited Pt electrode and 7.8×10^{-3} A for the Pan-Pt electrode and that at 0.4 V on the backward sweep is 2.5×10^{-3} A for the deposited Pt electrode and 4.1×10^{-3} A for the Pan-Pt electrode. However, the currents of the Pan-Pt electrode at the potentials lower than 0.5 V on the forward potential sweep is almost the same as that of the deposited Pt electrode. For example, the current at 0.4 V on the forward sweep is 1.6×10^{-3} A for the deposited Pt electrode and 1.5×10^{-3} A for the Pan-Pt electrode. This suggests that the existence of polyaniline accelerates the direct oxidation of methanol on platinum but does not change the nature of adsorbed intermediates on platinum.

Comparing the dash line with the dotted line of Fig. 10, it can be seen that all the currents of Pan-Pt- H_xMoO_3 electrode on forward potential sweep are far larger than those of Pan-Pt electrode. For example, the currents at 0.4 and 0.6 V on the forward sweep are 3.9×10^{-3} and 1.5×10^{-2} A, respectively, for the Pan-Pt- H_xMoO_3 electrode, but only 1.5×10^{-3} and 7.8×10^{-3} A, respectively, for the Pan-Pt electrode. There is also an increase in current on the backward sweep from the Pan-Pt electrode to the Pan-Pt- H_xMoO_3 electrode, but the magnitude of the current increase at the same potentials on the backward sweep is not so significant as that on forward sweep. For example, the current at 0.4 V on the back-

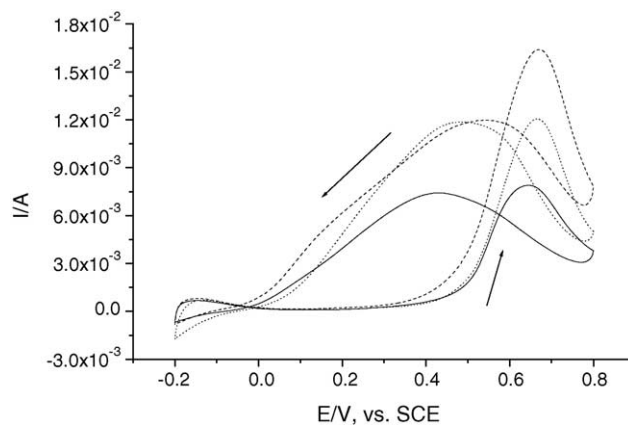


Fig. 11. Voltammograms of deposited Pt (solid line), Pan-Pt (dotted line) and Pan-Pt- H_xMoO_3 (dash line) electrodes in 0.5 M H_2SO_4 solutions containing 0.1 M formaldehyde, 100 mV s^{-1} .

ward sweep is 4.7×10^{-3} A for the Pan-Pt- H_xMoO_3 electrode and 4.1×10^{-3} A for the Pan-Pt electrode. It is obvious that the role the hydrogen molybdenum bronze plays in the oxidation of methanol is different from that polyaniline does. The existence of hydrogen molybdenum bronze accelerates significantly the transformation of adsorbed intermediates to carbon dioxide.

Similar to the voltammetric behavior of methanol, the deposited Pt, the Pan-Pt and the Pan-Pt- H_xMoO_3 electrodes do not alter voltammetric characteristics of formaldehyde and formic acid on platinum but alter the current magnitude in different extents. Figs. 11 and 12 show the voltammograms of the deposited Pt, the Pan-Pt and the Pan-Pt- H_xMoO_3 electrodes in the solutions containing formaldehyde and formic acid, respectively. The current for the oxidation of formaldehyde or formic acid is also improved to a great extent from the base platinum electrode (Fig. 6 or Fig. 7) to the deposited Pt electrode (solid line in Fig. 11 or Fig. 12) For example, the current at 0.4 V on the forward sweep is 1.8×10^{-5} and 6.6×10^{-5} A, respectively, for formaldehyde and formic acid on the base platinum

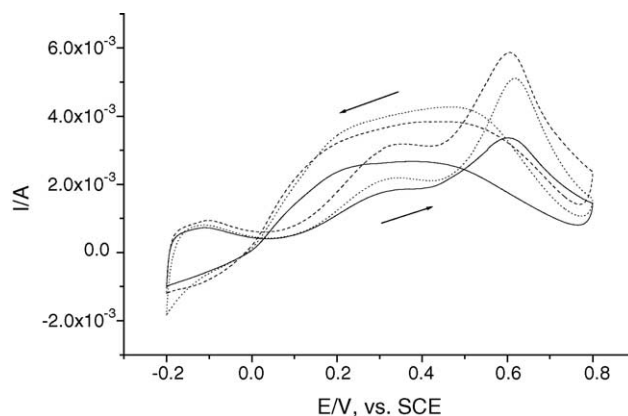


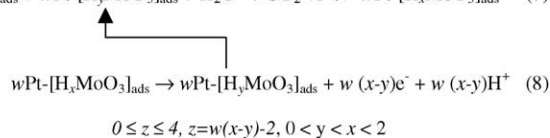
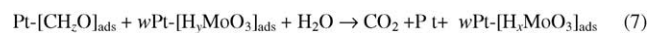
Fig. 12. Voltammograms of deposited Pt (solid line), Pan-Pt (dotted line) and Pan-Pt- H_xMoO_3 (dash line) electrodes in 0.5 M H_2SO_4 solutions containing 0.1 M formic acid, 100 mV s^{-1} .

electrode but 6.0×10^{-4} and 1.9×10^{-3} A, respectively, for formaldehyde and formic acid on the deposited Pt electrode.

In the same way as the influence of polyaniline on the methanol oxidation, polyaniline can improve the currents for the oxidation of formaldehyde or formic acid at the potentials higher than 0.5 V on the forward sweep and at the potentials between 0 and 0.8 V on the backward sweep but does not alter the currents at the potentials lower than 0.5 V on the forward potential sweep, as shown in Figs. 11 and 12. Therefore, the existence of polyaniline also accelerates the direct oxidation of formaldehyde and formic acid on platinum but does not change the nature of adsorbed intermediates on platinum.

The influence of hydrogen molybdenum bronze on the oxidation of formaldehyde or formic on the forward sweep is also similar to that of methanol, as shown in Figs. 11 and 12. However, the currents for the oxidation of formaldehyde or formic acid on the backward sweep are almost the same for both Pan-Pt and Pan-Pt- H_xMoO_3 electrodes. Therefore, hydrogen molybdenum bronze does not influence the direct oxidation of formaldehyde on platinum but accelerates the transformation of the adsorbed intermediates on platinum to carbon dioxide.

With the results available, it can be concluded that the electrocatalytic activity of platinum toward the oxidation of methanol, formaldehyde and formic acid can be improved by the modification of hydrogen molybdenum bronze. Considering the redox process of hydrogen molybdenum bronzes, as shown in Fig. 4, the mechanism for the improvement of the electrocatalytic activity of platinum toward the small organic molecules by hydrogen molybdenum bronze can be expressed as:



4. Conclusion

The oxidation reactions of methanol, formaldehyde and formic acid on platinum take dual path mechanism. One path is the direction oxidation of these molecules on platinum to carbon dioxide, which happens hardly at lower potentials on the forward potential sweep (from negative to positive potentials) but at higher potentials or on clean platinum. The other is the formation of reaction intermediates, which is poison to platinum and hinders the further oxidation of these molecules. The electrocatalytic activity of platinum toward the oxidation of these molecules can be improved significantly by the modification of polyaniline and hydrogen molybdenum bronze. The former accelerates the direction

oxidation of these molecules on platinum to carbon dioxide and the latter favors the transformation of the reaction intermediates to carbon dioxide.

Acknowledgements

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