Formation and Oxidation of Hydrogen Molybdenum Bronze on Platinum Electrode in Sulfuric Acid Solution

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Abstract: Hydrogen molybdenum bronze (H_xMoO_3) can be electrodeposited on platinum and oxidized in two steps to the hydrogen molybdenum bronze with less amount of hydrogen H_yMoO_3 (y<x) and MoO_3 when platinum electrode is cycled from –0.2 to 1.3V (*vs.* SCE) in 0.05 mol/L Na_2MoO_4 + 0.5 mol/L H_2SO_4 solution. During the formation of H_xMoO_3, the electrochemical reduction of molybdate existing in the form of polymolydate is reversible and is about a five-electron transfer reaction.

Keywords: Hydrogen molybdenum bronze, formation and oxidation, platinum, sulfuric acid solution.

Non-stoichiometric lower valence molybdenum oxide contains discontinued phases with compositions between MoO_2 and MoO_3[1]. These mixed-valence oxides of molybdenum exhibit a wide range of optical and electrical properties and have found their applications in electro-chromism[2], lithium battery as cathode materials[3], and catalysts for the electro-reduction of ClO_3^- and BrO_3^- ions[4]. Recently, it has been found that platinum can be modified through the reduction of molybdate and the oxidation of small organic molecules such as methanol and formic acid can be improved on the modified platinum[5,6]. Knowledge about the electrochemical behavior of molybdenum compounds is necessary for understanding the mechanism of their applications. This paper reports the formation and oxidation of hydrogen molybdenum bronze from the reduction of molybdate on platinum in 0.5 mol/L H_2SO_4 solution.

Experimental

All the experiments were performed using a potentiostat/galvanostat (PGSTAT 30, Autolab) controlled by a computer with a GPES program. A conventional three-electrode cell was used. A 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 referenced to SCE. All the chemicals used were analytical grade reagents. Solutions

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were prepared with water deionized and distilled twice.

Results and Discussion

Figure 1a shows the cyclic voltammograms of platinum electrode in 0.5 mol/L H_2SO_4 solutions, containing 0.05 mol/L Na_2MoO_4. The reduction of molybdates and the oxidation of the reduced molybdates can be 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 (point A) before the hydrogen evolution takes place. The reduced molybdates is deposited on the platinum surface, because colored deposition on the electrode surface can be observed when the potential is kept at –0.2V. The reduction of molybdates in acid solution is accompanied by the insertion of hydrogen ions into molybdenum oxides, forming hydrogen molybdenum bronzes, H_xMoO_3 ($x \leq 2$)[7]. So the colored deposition should be hydrogen molybdenum bronzes.

Two oxidation current peaks can be observed from **Figure 1a** at 0.24V (point B) and 0.95V (point C). The currents near the second peak (point C) are far higher than those observed on the electrode in the solution without molybdates, indicating that the second current peaks are mainly contributed by the oxidation of the hydrogen molybdenum bronzes. Therefore, the oxidation of hydrogen molybdenum bronzes 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 (point D) still appears 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. Naked platinum surface is available again and platinum oxide is formed due to the dissolution of hydrogen molybdenum bronzes.

There is a linear relationship between the current at 0V and the square root of scan rate, as shown in **Figure 1b**. This indicates that the reduction of molybdates is reversible and equation (1) can be used[8].

$$i_p = \left(2.69 \times 10^5\right) n^{3/2} A D_o^{1/2} v^{1/2} C_o^* \tag{1}$$

Where 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, v the potential scan rate and C_o^* the bulk concentration of the reactant.

Figure 2 is the chronocoulometric response of platinum electrode at 0V in 0.5 mol/L H_2SO_4 + 0.05 mol/L Na_2MoO_4 solution. There is a good linear relationship between the reduction charge of molybdates and the square root of reduction time and equation (2) can be used[8].

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

where Q_{dl} is the capacitive charge and Γ_o is the surface concentration of adsorbed reactants, other symbols have the same meaning as in equation (1). The reaction electron number can be obtained by combining two slopes of the linear lines in **Figure 1b** and **Figure 2**.

As the slope is 1.01×10^{-3} $V^{1/2}/s^{1/2}$ in **Figure 1b** and 1.88×10^{-4} $C/s^{1/2}$ in **Figure 2**, the reaction electron number obtained is 4.72.

Figure1 Voltammograms of platinum electrode
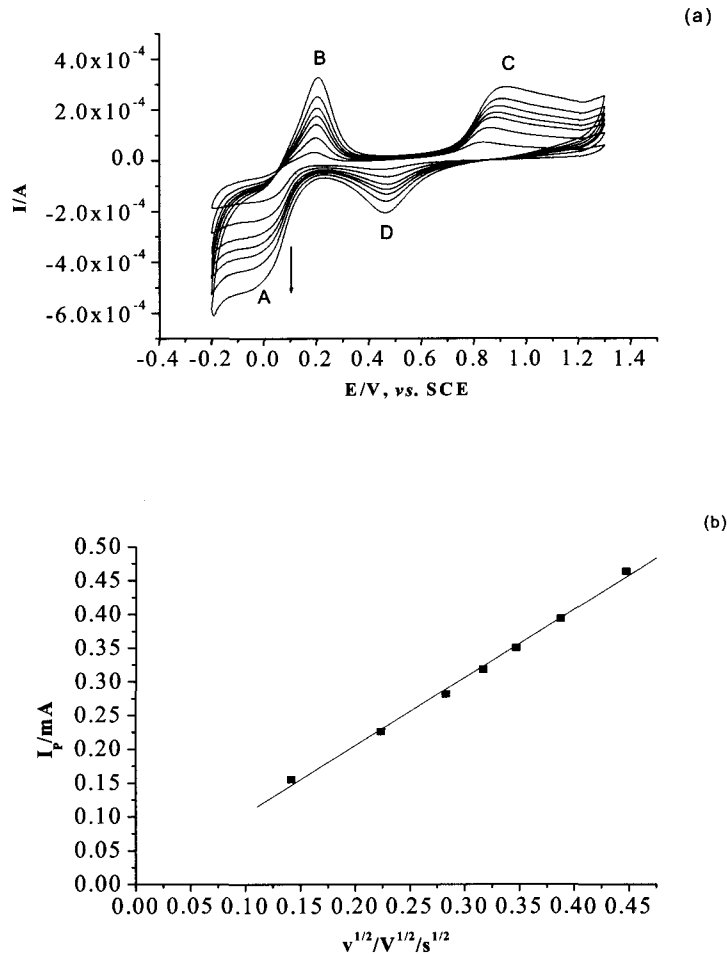
(a) in 0.5 mol/L H_2SO_4 + 0.05 mol/L Na_2MoO_4 solution with scan rates: 200, 150, 120, 100, 80, 50, and 20mV/s, the arrow shows the increase of the scan rate, (b) the variation of current at 0V with the square root of scan rate

In acid solution, molybdates exist in the form of polymolybdates[9]. The number of molybdenum atom in a polymolybdate molecule depends on the acid concentration. The reduction reaction of molybdates can be expressed as follows:

$$z\text{Mo(VI)} + n\ e^- + zx\text{H}^+ \rightarrow z\text{H}_x\text{MoO}_3 \qquad x \leq 2 \qquad (3)$$

where z is the average number of molybdenum atom in polymolybdate molecules and x

equals n/z. Since $n = 4.72$, z is 2.36 when taking $x = 2$, *i.e.*, a polymlybdate molecule in 0.5 mol/L H_2SO_4 solution consists of more than two molybdate molecules.

The oxidation of hydrogen molybdenum bronze and the dissolution of the oxidized product can be expressed as follows:
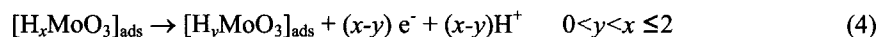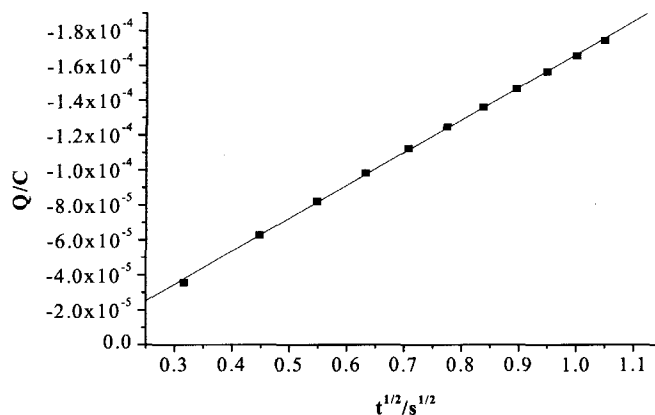
$$[H_xMoO_3]_{ads} \rightarrow [H_yMoO_3]_{ads} + (x\text{-}y)\ e^- + (x\text{-}y)H^+ \qquad 0<y<x \leq 2 \qquad (4)$$

$$[H_yMoO_3]_{ads} \rightarrow [MoO_3]_{ads} + y\ e^- + yH^+ \qquad (5)$$

$$[MoO_3]_{ads} \rightarrow [Mo(VI)]_{sol} \qquad (6)$$

Figure 3   Chronocoulometric response of platinum electrode at 0V

In 0.5 mol/L H_2SO_4 + 0.05 mol/L Na_2MoO_4 solution

Acknowledgments

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