Study on Lead Dioxide Modified Electrode and Its Application in Detection of Phenols

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The conditions for the preparation of PbO_2 modified Pt rotation disc electrode in solutions containing $HClO_4$ and Pb(II) were studied, and the morphology and composition of the obtained PbO_2 film were characterized by SEM and XRD techniques, respectively. The results show that the modification process of PbO_2 is dependent on the rotation velocity of the electrode and the concentrations of $HClO_4$ and Pb(II). And it was observed that the obtained PbO_2 film was rutile β-PbO_2 structure. At a certain positive potential, HO· and HO_2· radicals can be generated on the surface of the modified PbO_2/Pt electrode and then oxidize phenols. According to the change of the responding anodic current, the determination of phenols was realizable and good results were obtained.

Keywords PbO_2, modified electrode, phenol, determination

Introduction

Of late, there is a great interest in the improvement of lead dioxide as an anode material for electrosynthesis, ozone generation and wastewater treatment owing to its high electrical conductivity, large oxygen overpotential and chemical inertness.[1-5] PbO_2 can be obtained as anodic deposits from solutions of the low-valence ions, basic studies on these electrodes are mainly confined to the nucleation growth process of lead dioxide crystallites, or modified by other cations in order to improve its properties.[6] However, its electrocatalytic activity depends upon its structure, morphology and phase composition, which are highly relied on deposition methods. Meanwhile, we have noted that, to PbO_2 electrodes, very few results concerning electroanalytical applications have been reported. In this paper, a lead dioxide film modified electrode was prepared at platinum substrate and its deposition conditions were optimized. The obtained film was characterized through X-ray diffractometer (XRD) and scanning electron microscope (SEM) techniques. The electrochemical behaviour and formative mechanism of the lead dioxide film were studied. The application of this modified electrode as an analytical sensor to determine phenols was preliminarily studied with satisfactory results.

Experimental

Reagents and apparatus

$Pb(NO_3)_2$, $HClO_4$, 2,4-dichlorophenol and other chemical reagents were purchased from Shanghai Chemical Reagent Company. All reagents were of analytical grade. All solutions were prepared with doubly distilled water.

A rotating platinum disc electrode (RDE, 0.025 cm^2), platinum wire and saturated Ag/AgCl electrode were employed as the working electrode, counter electrode and reference electrode, respectively. All electrochemical experiments were performed on a CHI832 Electrochemical system (CHI, USA) and the rotation velocity of the working electrode was controlled by a rotator (Shanghai Dianguang Instrument Factory).

X-Ray data were collected using a D8ADVANCE X-ray power diffractometer (Bruker axs Com. Ger.) based on Cu Kα radiation. The 2θ (two-theta) angle of the diffractometer was stepped from 10° to 70° by 0.03° increments. Scanning electron micrograph (SEM) were obtained by a JSM-5610LV (JEOL) instrument.

Electrode preparation

All experiments were performed at ambient temperature [(25 ± 1) ℃]. The electrode was mechanically polished with 0.05 μm alumina paste before each experiment. Then it was treated in a 1:1 mixture of acetic acid and H_2O_2 (30%) for 2 min. The electrode potential was cycled within the range of −0.2 — 2.0 V at 100 mV/s in 0.5 mol/L $HClO_4$ solution until a reproducible background resulted. The PbO_2 film was electrochemically modified in 0.5 mol/L $HClO_4$ containing 0.02 mol/L $Pb(NO_3)_2$ by cycling the potential between 1.4 and 1.8 V at 100 mV/s for 10 min. After modification, the electrode was removed from the modifying solution and rinsed with doubly distilled water.

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Received June 14, 2002; revised August 28; accepted September 23, 2002.

Project supported by the Key Technology Research and Development Program of China's Tenth Five-Year Plan (No. 2001BA210A04).

Amperometric measurement of phenols

Amperometric responses of the PbO_2 modified electrode to phenols were measured as a steady state anodic current with a three-electrode system in a stirred 0.01 mol/L Na_2SO_4 solution by applying a potential of 1.35 V to the PbO_2 film electrode. The background current was allowed to decay to a steady value before phenol solutions were added, and then the net increase of phenols oxidation current was measured as the response current. Unless stated specially, the temperature was kept at (25 ± 1) ℃ during the measurements.

Results and discussion

Preparation of the modified PbO_2/Pt *film electrode*

Cyclic voltammetry experiments

Cyclic voltammetry (CV) curves obtained at the Pt-RDE electrode in the 0.5 mol/L $HClO_4$ solution in the absence or presence of Pb(II) are shown in Fig. 1. In Fig. 1a, the anodic branch of the curve, at potentials higher than 1.7 V, features an exponential current growth corresponding to the oxygen evolution. When Pb(II)-ion was added to the solution, the anodic current at the exponential area increases largely for the formation process of PbO_2. Current maximum is observed at the cathodic branch of the curve at potentials 1.35—1.5 V (Fig. 1b). This peak is due to the reduction reaction of PbO_2.

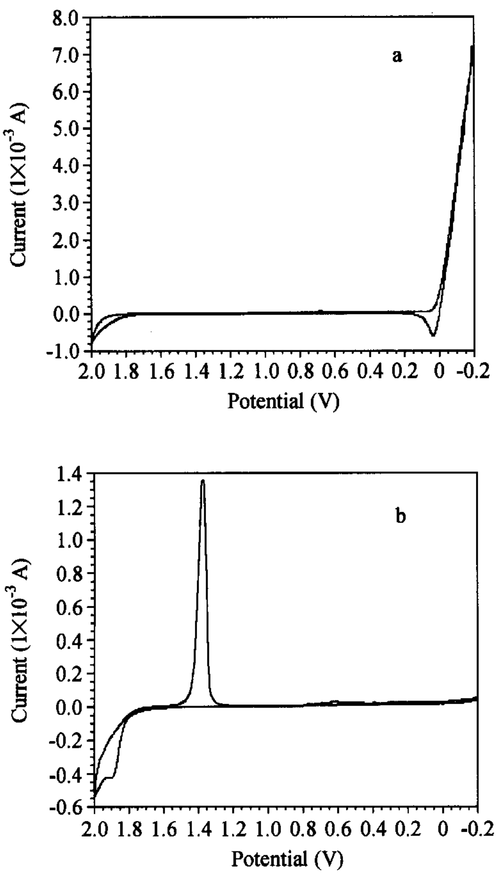

Fig. 1 CV curves of the Pt disk electrode in 0.5 mol/L $HClO_4$ solution without or with Pb(II). Conditions: scan rate, 100 $mV \cdot s^{-1}$; rotation velocity, 1800 $r \cdot min^{-1}$. Curves: (a) blank, (b) 0.02 mol/L Pb(II).

By comparing the CV curves obtained at the Pt-RDE electrode in the 0.5 mol/L $HClO_4$ solution without or with Pb(II) (Fig. 1), it should be noticed that the dominant process at the Pt electrode at the exponential area of the CV curve is Pb(II)-ion oxidation reaction with the addition of Pb(II)-ion. From gravimetric measurements, the quantity of the PbO_2 surface was characterized by the cathodic peak magnitude (I_p). Therefore I_p value can be used to estimate the effect of other conditions on the Pb(II)-ion oxidation reaction.

Effect of electrode rotation velocity on PbO_2 *modified process*

The effect of Pt disc electrode rotation velocity on PbO_2 formation process in the solution of 0.5 mol/L $HClO_4$ and 0.02 mol/L Pb(II) is shown in Fig. 2.

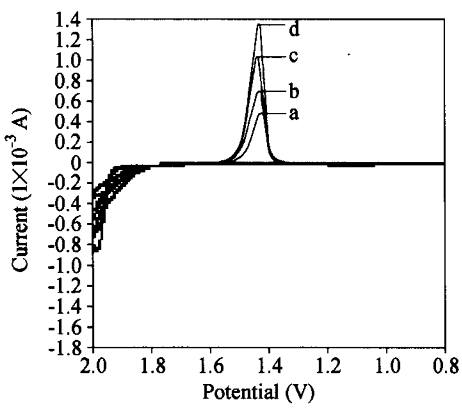

Fig. 2 CV curves of the Pt disk electrode at different rotation rates in solution containing 0.5 mol/L $HClO_4$ + 0.02 mol/L Pb(II). Conditions: scan rate: 100 $mV \cdot s^{-1}$; rotation velocity ($r \cdot min^{-1}$): (a) 0, (b) 560, (c) 1800, (d) 3200.

In Fig. 2, it is noted that the anodic current at the exponential area increases as the electrode rotation accelerates. Meanwhile, the reduction current peak also increases. This is due to the enhancement of the convective diffusion process of Pb(II) as the electrode rotation rate increases, which in turn accelerates the formation of lead dioxide. Furthermore, the removal quantity of PbO_2 has increased with the increase of the lead dioxide film thickness.

Effect of Pb(II) *concentration on* PbO_2 *modified process*

The CV curves of PbO_2 modification processes in solutions containing different concentration of Pb(II) are shown in Fig. 3.

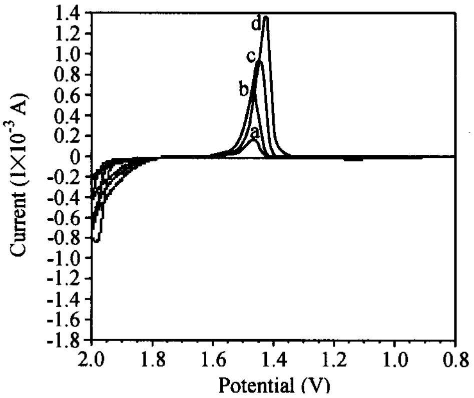

Fig. 3 CV curves of the Pt disk electrode in 0.5 mol/L $HClO_4$ solution with different concentrations of Pb(II). Conditions: scan rate, 100 $mV\cdot s^{-1}$; rotation velocity, 1800 $r\cdot min^{-1}$. Curves: (a) 0.005 mol/L $Pb(NO_3)_2$, (b) 0.01 mol/L $Pb(NO_3)_2$, (c) 0.02 mol/L $Pb(NO_3)_2$, (d) 0.03 mol/L $Pb(NO_3)_2$.

It shows that the reduction current peak increases with the increase of the concentration of Pb(II). This indicates that the rate of PbO_2 formation is larger at higher Pb(II) concentrations. Meanwhile, it is also observed that as the Pb(II) concentration increases, the cathodic peak increases and the peak potential shifts towards the negative direction. The possible explanation is that the higher the Pb(II) concentration is, the thicker the PbO_2 layer is formed at the same interval time of modification which leads to the larger internal resistance. Although more PbO_2 has been reduced making the peak increase, the increase of the internal resistance requires more PbO_2 reduction energy, and therefore, it makes the peak potential shift towards the negative direction.

Effect of pH *on* PbO_2 *modified process*

The CV curves obtained at the Pt-RDE electrode in solutions with different $HClO_4$ concentration are shown in Fig. 4.

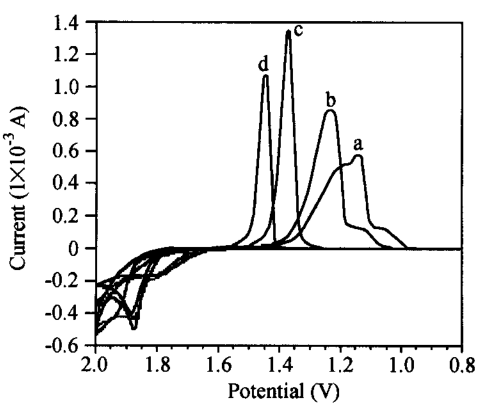

Fig. 4 CV curves of the Pt disk electrode in Pb(II) solution with different concentrations of $HClO_4$. Conditions: scan rate, 100 $mV\cdot s^{-1}$; rotation velocity, 1800 $r\cdot min^{-1}$. Curves: (a) 0.05 mol/L $HClO_4$, (b) 0.1 mol/L $HClO_4$, (c) 0.5 mol/L $HClO_4$, (d) 1.0 mol/L $HClO_4$.

It is found that as the pH value increases, the reduction peak becomes lower, the peak potential shifts to negative direction, while the reduction peak area increases. It is due to the increase of the lead dioxide formation rate and the modified quantity. However, with the further decrease of pH value, that is to say, with the further increase of the $HClO_4$ concentration, the reduction current peak (I_p) decreases (comparing the CV curves in 1 mol/L $HClO_4$ solution with those in 0.5 mol/L $HClO_4$ solution). It is possibly that the excessive $HClO_4$ restrains the reaction of the oxygen lead containing compounds, leading to the decrease of the reduction peak current.

Discussion of PbO_2 *modification mechanism*

The process of PbO_2 formation includes several stages described as the following.

$$H_2O \longrightarrow OH_{ads} + H^+ + e^- \quad (1)$$

$$Pb^{2+} + OH_{ads} \longrightarrow Pb(OH)^{2+} \quad (2)$$

$$Pb(OH)^{2+} + H_2O \longrightarrow PbO_2 + 3H^+ + e^- \quad (3)$$

The first stage is the formation of an oxygen containing species such as OH_{ads} chemisorbed on the electrode. At the following chemical stage these particles interact with lead compounds to form a soluble intermediate product Pb(III), which is oxidized electrochemically to form PbO_2.[6,7]

According to the mechanism proposed above, the reaction (1) could be under kinetic control, which is a fast reaction. However, the rate of PbO_2 growth is dependent upon the surface concentration of the intermediate product $Pb(OH)^{2+}$ formed during the reaction (2) on the electrode surface. That is to say, the rate of PbO_2 growth could be under transport control. Hence both the change of Pb(II) concentration and the increase of electrode rotation velocity affect the process of Pb(II) diffusion, which is in favour of the growing process of the modified PbO_2 layer, while an excessive concentration of $HClO_4$ will affect the reaction (1) and reaction (3).

Characterization of the modified PbO_2 *film*

Fig. 5 shows the XRD pattern and the SEM photograph for the PbO_2 modified electrode obtained by inserting a Pt electrode into the solution of 0.5 mol/L $HClO_4$ and 0.02 mol/L Pb(II) and cycle scanning between potential 1.4 and 1.8 V at 100 mV/s for 10 min. Comparing Fig. 5a with the standard pattern, it can be noticed that the obtained film is β-PbO_2. Fig. 5b suggests that the structure and size of the crystal grains are uniform and tetragonal rutile structure. Using the SEM photographs as guide, the PbO_2/Pt electrode was produced with good reproducibility.

Application of PbO_2/Pt *electrode in the determination of organic compounds*

Comparing the linear polarization curves of pure Pt elec-

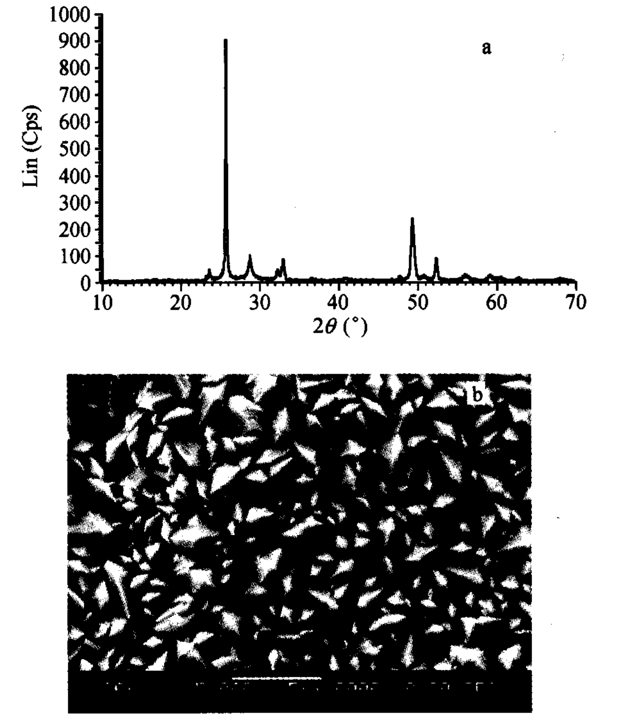

Fig. 5 (a) X-Ray diffraction patterns and (b) SEM photographs for PbO_2 film.

trode and PbO_2/Pt electrode in 0.1 mol/L H_2SO_4, it is shown that the oxygen overpotential of PbO_2/Pt electrode increased by an average value of 100—150 mV at the same current density. Therefore, more HO· and HO_2· radicals were generated on the surface of the PbO_2/Pt electrode than those on the surface of Pt electrode under positive potential.[8,9]

$$2H_2O - 2e^- \longrightarrow 2OH\cdot + 2H^+ \quad (4)$$
$$2OH\cdot \longrightarrow H_2O_2 \quad (5)$$
$$H_2O_2 - e^- \longrightarrow HO_2\cdot + H^+ \quad (6)$$
$$H_2O_2 + OH\cdot \longrightarrow HO_2\cdot + H_2O \quad (7)$$

The obtained HO· and HO_2· radicals are absorbed on the crystal sites of the modified PbO_2 film. According to the mechanism of anodic decomposition of organics,[3] the complete oxidation of organics to CO_2 and H_2O by electrogenerated HO · and HO_2· radicals on high oxygen overvoltage electrode materials could take place. Hence, the electrochemical methods can be used to obtain the organic substance values by the oxidation of the organic compounds on the surface of the electrode. The electrons released during the oxidation can be measured as electrical current, which is proportional to the organic substance values of the solution analyzed. The modified PbO_2/Pt electrode was dipped into electrolyte containing 0.01 mol/L Na_2SO_4 and 2,4-dichlorophenol with an increasing concentration by 5×10^{-4} mol/L stepped, and the current-time recordings obtained at 1.35 V are shown in Fig. 6.

By similar methods, the change of the currents corresponding to the oxidation of phenol, 4-chlorophenol, 2,4-dinitrophenol, 2-bromophenol, and 2-naphthol was measured and good linearity was obtained in the range of 5×10^{-4}—1×10^{-2} mol/L. Therefore it can be concluded that the modified PbO_2/Pt electrode can be applied as an analytical sensor in the determination of organic compounds such as phenols. More detailed work on these as well as a number of other redox system which can be analysed using this electrode is in process in this laboratory.

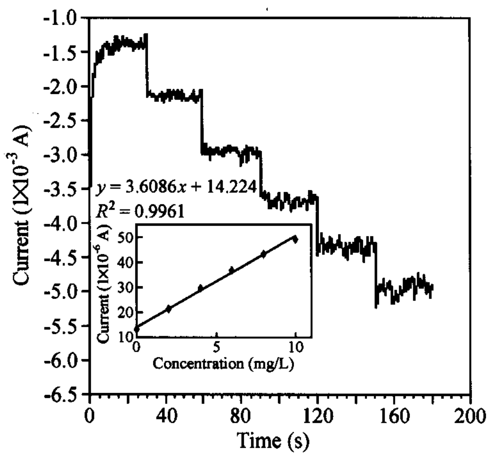

Fig. 6 Current-time recordings for 2,4-dichlorophenol with an increasing concentration by 5×10^{-4} mol/L stepped at the PbO_2 modified electrode. Conditions: electrolyte, 0.01 mol/L Na_2SO_4; applied potential, + 1.35 V; rotation velocity, 1800 $r \cdot min^{-1}$.

Conclusions

It can be concluded from the results that the modifying process of the modified PbO_2/Pt electrode is relied on the electrode rotation velocity, the concentration of Pb(II) and the pH value of the modifying solution. As the electrode rotation velocity and the concentration of Pb(II) increase, the formation of PbO_2 film is accelerated because the intermediate products depend on the convectional diffusion process. Likewise, the change of the concentration of $HClO_4$ will influence the reactions at the electrode surface in which H_2O discharges to oxygen containing compounds, and then will exert influence on the modifying process. The characterization of the morphology and composition of the modified PbO_2/Pt electrode by XRD and SEM techniques shows that the obtained PbO_2 is rutile β-PbO_2 structure. The modified PbO_2/Pt electrode was utilized to determine phenols in solution via measuring the change of current corresponding to the oxidation of phenols by HO· and HO_2· radicals. The data obtained show that the modified PbO_2/Pt electrode can well indicate the concentration of organic compounds with low concentration and could be effectively used in the electrochemical determination of organic compounds. Hence it could be said that the wide application of the modified PbO_2/Pt electrode as a chemical sensor in determination of organic compounds is promising.

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(E0206143 LI, L. T.; ZHENG, G. C.)