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Preparation and properties of $Ti/SnO_2–Sb_2O_5$ electrodes by electrodeposition

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Abstract

Sb and Sn coatings were deposited on Ti substrate by the method of cathode deposition, and the $Ti/SnO_2–Sb_2O_5$ electrodes were obtained by annealing at different temperatures for 3 h. $Ti/SnO_2–Sb_2O_5$ coating was characterized using technique such as X-ray diffraction (XRD), and scanning electron microscopy (SEM). $Ti/SnO_2–Sb_2O_5$ electrode calcined at 550 °C exhibits the best catalytic capacity. $Ti/SnO_2–Sb_2O_5$ electrode obtained by electrodeposition had longer service life and faster degradation capacity compared with that obtained by dip-coating. Accelerated service life tests were carried out in 0.5 mol L^{-1} H_2SO_4 solution with the current density of 100 mA cm^{-2}. Service life of $Ti/SnO_2–Sb_2O_5$ electrode prepared in present study was 15 h, and it was only 0.14 h for $Ti/SnO_2–Sb_2O_5$ electrode obtained by dip-coating.

Keywords: X-ray techniques; Deposition; Thin films; SnO_2; Phenol

1. Introduction

Electrochemical process for refractory organic wastewater has gained extensive attention in the past two decades [1–5]. Development of high-efficiency catalytic electrodes is always a hotspot in this field. Pt [6,7], Ti/IrO_2 [8],Ti/RuO_2 [9], Ti/PbO_2 [10], BDD [11–13] and Ti/SnO_2 [14–17] electrodes have been used to investigate electrocatalytic oxidation of organic pollutant.

The electrodes used for oxidation of organic pollutant should be steady in solution. The electrodes require high oxygen evolution reaction (OER) to produce high concentration OH radicals, which is favorable for the oxidation of organic pollutant on the electrodes surface [18,19]. The electrodes, such as Ti/PbO_2, BDD and Ti/SnO_2 electrodes possess relatively high OER potential.

Sb doped SnO_2 electrodes provide with good properties for disposal of organic pollutant. At present, the methods used for preparing electrodes include spray pyrolysis [20], sol–gel process [21], sputtering [22], chemical vapor deposition [23], electron beam evaporation [24] and thermal oxidation [25]. Thermal oxidation is one of the methods which is the most easy to operate. Sn and Sb layers were electrodeposited respectively, and then Ti/SnO_2 was prepared by the method of thermal oxidation. The properties of the as prepared Ti/SnO_2 electrode were compared with that of Ti/SnO_2 electrode prepared by dip-coating and thermal oxidation method [2,14]. In this paper, we fabricated $Ti/SnO_2–Sb_2O_5$ electrodes with compact coatings by a new and simple method of electrodeposition. In comparison

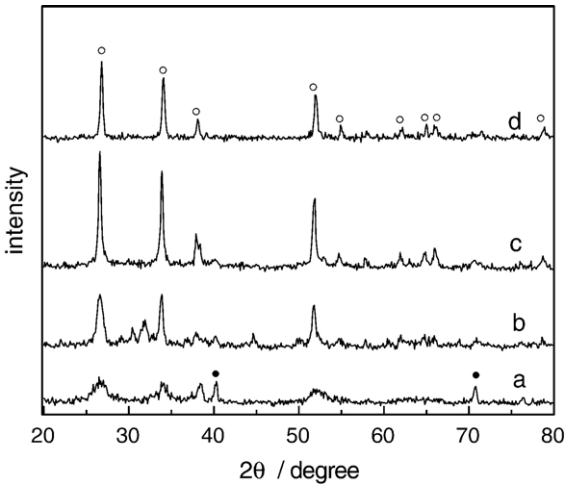

Fig. 1. XRD patterns of $Ti/SnO_2–Sb_2O_5$ electrodes prepared by dip-coating (a) and electrodeposition calcined at different temperatures of 450 °C (b), 550 °C (c) and 650 °C (d). (○:SnO_2; ●:Ti).

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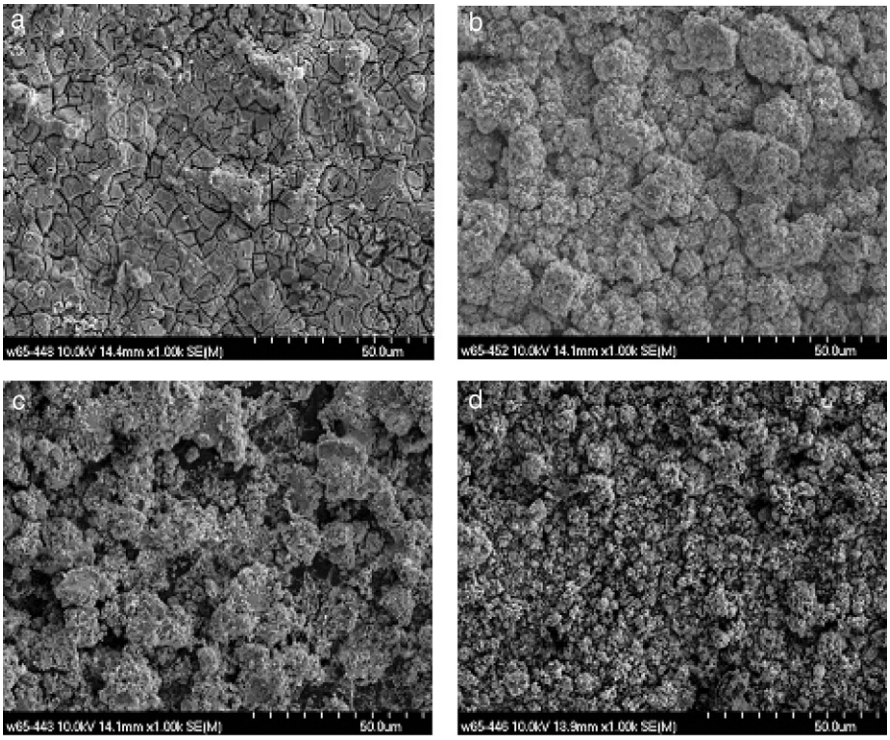

Fig. 2. SEM images (Electrodes prepared by dip-coating calcined at 550 °C (a); Electrodes prepared by electrodeposition calcined at 450 °C (b); 550 °C (c); and 650 °C (d)).

with electrodes prepared using dip-coating method, these electrodes possessed longer service life and higher catalytic activity for oxidation of organic pollutant.

2. Experimental

2.1. Electrode preparation

The Ti plates were rectangular in shape with the dimension of 2×3 cm^2 or 1×1 cm^2. They were polished with 320-grit sandpaper, degreased in 40 wt.% NaOH at 80 °C for 2 h, etched in 15 wt.% oxalic acid at 98 °C for 2 h, and last washed with deionized water.

$Ti/SnO_2–Sb_2O_5$ electrodes were prepared by dip-coating, and the procedures were as follows: the pretreated Ti substrates were impregnated into *n*-butanol solution containing of $SnCl_4$ and $SbCl_3$ (the molar ratio is $SnCl_4$:$SbCl_3$=94:6) and calcined at 80 °C for 5 min, then such procedures were repeated for 15–20 times, finally the electrodes were calcined at 550 °C for 3 h [14,16].

Procedures for the preparation of $Ti/SnO_2–Sb_2O_5$ electrodes by electrodeposition method were as follows: the pretreated Ti substrates were first cathodic electrodeposited in sulfuric acid solution including Sn^{2+} and followed in the citric acid solution including Sb^{3+} with the same current density of 10 mA cm^{-2} at 35 °C. The Sn^{2+} and Sb^{3+} irons were deposited on the Ti electrode with formation of Sn and Sb separately, due to electrochemical redox process. Deposition time was adjusted to control the mole ratio of Sn to Sb of 94:6. Such procedures were repeated for 5 times, finally the electrodes were calcined at 550 °C for 3 h to obtain the $Ti/SnO_2–Sb_2O_5$ electrode.

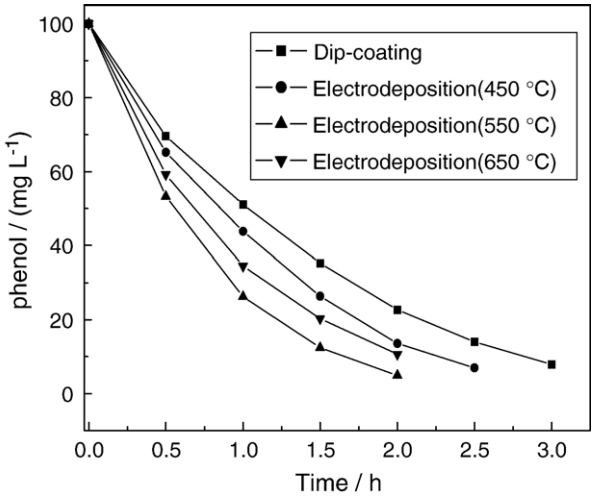

Fig. 3. Degradation curves of different electrodes.

2.2. Structure tests

X-ray diffraction (XRD) patterns of $Ti/SnO_2–Sb_2O_5$ electrodes were obtained by means of a Rigaku X-ray generator. The morphologies of $Ti/SnO_2–Sb_2O_5$ coatings were examined by a scanning electron microscope (HITACHI S-4700). All solutions used in this work were prepared with 18.2 MΩ cm water produced by reagent water system (MILLI-Q SP, Japan).

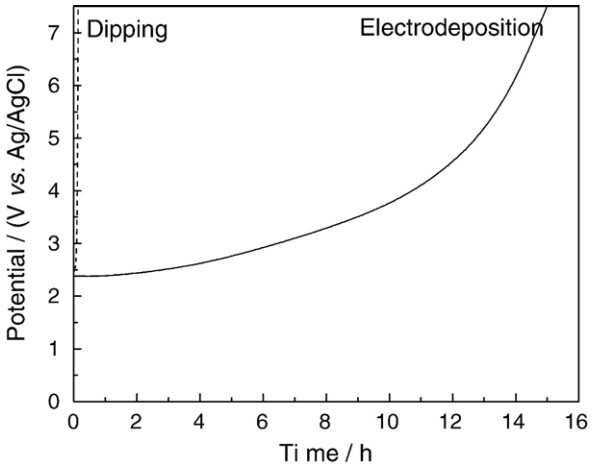

Fig. 4. Potential variation with time in accelerated life tests performed in 0.5 M H_2SO_4 solution under 100 mA m^{-2}.

2.3. Pollutant oxidation and accelerated life tests

Pollutant oxidation experiment: We used the as prepared Ti/SnO_2–Sb_2O_5 electrode with a dimension of 2×3 cm^2 as anode, and stainless steel as cathode. The experiment was carried out to dispose 100 mL 100 mg L^{-1} phenol with a current density of 10 mA cm^{-2}. Phenol concentration was examined by standard (GB 7490-87, China).

Accelerated service life tests: The tests were performed using a conventional three-electrode arrangement including a Ti/SnO_2–Sb_2O_5 working electrode (1×1 cm^2), a saturated Ag/AgCl reference electrode and a platinum (1.5×1.5 cm^2) counter electrode. The working electrode was characterized electrochemically in 0.5 mol L^{-1} H_2SO_4 solution with a current density of 100 mA cm^{-2}. All the electrochemical tests were measured by potentiostat/galvanostat (EG&G PAR263A). The test software is powersuite2.44 provided by PRAC company (USA).

3. Results and discussion

3.1. XRD analysis

Fig. 1 shows XRD patterns of Ti/SnO_2–Sb_2O_5 electrode prepared by dip-coating (a) and electrodeposition calcined at 450 °C (b), 550 °C (c) and 650 °C (d), respectively. The patterns prove the crystalline structure of SnO_2 coating on the surface of the electrode. All these diffraction peaks indicate tetragonal crystalline structure of the SnO_2 and the d-lines match well with the normal value reported by (JCPDS: 72-1147). The calculated lattice parameters by least square fit are $a=b=4.72$, $c=3.178$. Compared with SnO_2 prepared by dip-coating, the reflection intensities of SnO_2 synthesized by electrodeposition increase and the half-widths of the reflection peaks decrease, as shown in Fig. 1, which suggests better crystallinity of SnO_2 obtained from electrodeposition. The intensity of the crystal SnO_2 increases when the temperature increases from 450 °C to 550 °C, indicating formation of more crystal cores and growth of the integrate SnO_2 crystal on the coating. However, when the temperature increases up to 650 °C, the intensity of SnO_2 crystal decreases, which suggests coarsening of the SnO_2 crystal and reduce of the number of SnO_2 crystals at the same crystal axis. Thus, Ti/SnO_2–Sb_2O_5 electrode with the strongest intensity calcined at 550 °C has the best catalytic activity, which is described in Section 3.3.

3.2. SEM analysis

Fig. 2 shows scanning electron microscope images of Ti/SnO_2–Sb_2O_5 electrodes prepared by dip-coating and electrodeposition methods calcined at various temperatures, respectively. The surface morphology of Ti/SnO_2–Sb_2O_5 electrode prepared by dip-coating method is cracked, which will facilitate the formation of TiO_2 with poor conductivity and the falling of SnO_2–Sb_2O_5 film. Thus, it will result in the increase of the resistance of the electrode surface during the service life tests, and the activity of the electrode would be also reduced due to the formation of TiO_2 [26,27]. However, Ti/SnO_2–Sb_2O_5 electrodes obtained by electrodeposition method were more compact, and electrode layers adhered to the Ti substrate more tightly.

3.3. Activity

The degradation curves of several kinds of electrodes in 100 mL 100 mg L^{-1} phenol solution are shown in Fig. 3. Compared with other electrodes, higher catalytic activity was observed for the electrodes obtained by electrodeposition. The electrodes calcined at 550 °C showed the best catalytic activity, and the period of disposing phenol from 100 mg L^{-1} to 10 mg L^{-1} was only 1.7 h, which was much faster than that using electrodes prepared with dip-coating method.

3.4. Electrochemical stability

Fig. 4 compares the potential changing with time in the accelerated life tests for two different electrodes. It is observed that service life of SnO_2 electrodes obtained from electrodeposition reached 15 h, but it is only 10 min for the electrodes obtained from dip-coating method. This is perhaps because that the electrode prepared using electrodeposition method was more compact, and no crack was observed for the SnO_2 coating. Therefore, the formation of TiO_2 was suppressed, and the service life of electrode was greatly improved.

4. Conclusions

In this paper, Ti/SnO_2–Sb_2O_5 electrodes were fabricated by a simple method of electrodeposition process. The electrodes surface showed more compact examined by scanning electron microscope. The electrodes calcined at 550 °C exhibit the best degradation performance through degradation property tests, and service life of the electrodes at a high current density was superior to that of electrodes obtained from dip-coating.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2007.03.073.

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