Electrochimica Acta 56 (2011) 1576–1580

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Improved SnO_2–Sb_2O_4 based anode modified with Cr_3C_2 and CNT for phenol oxidation

Fengping Hu, Ziqiang Dong, Xinwei Cui, Weixing Chen*

Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta, Canada T6G 2G6

ARTICLE INFO

Article history:
Received 15 September 2010
Received in revised form 13 October 2010
Accepted 13 October 2010
Available online 19 October 2010

Keywords:
Chromium carbide
Tin based anode
Pulse electro-codeposition
Phenol oxidation
Chemical oxygen demand

ABSTRACT

Chromium carbide (Cr_3C_2) and carbon nanotubes (CNTs) improved Ti/SnO_2–Sb_2O_4 electrodes were successfully fabricated using pulse electro-co-deposition technique. The morphologies and phase constituents of these electrodes were characterized using scanning electron microscope (SEM) and X-ray diffraction (XRD). The service lifetime of anode was significantly increased by adding Cr_3C_2. The service lifetime of Ti/SnO_2–Sb_2O_4–Cr_3C_2 and Ti/SnO_2–Sb_2O_4–CNT–Cr_3C_2 electrode was 7.4 times and 5.6 times longer than that of the Ti/SnO_2–Sb_2O_4 electrode, respectively. The catalytic activity of phenol oxidation on these electrodes was systematically investigated by the cyclic voltammetry and the chemical oxygen demand (COD) test. The Ti/SnO_2–Sb_2O_4–CNT–Cr_3C_2 electrode shows the highest evolution oxygen potential, COD removal and current efficiency (CE).

1. Introduction

Electrochemical oxidation has been widely investigated for wastewater treatment because of its high oxidation efficiency, fast reaction rate and easy operation. Especially, electrochemical combustion method completely oxidizes some organic pollutants to CO_2 by hydroxyl radicals. In this case, the electrode material must have high electrocatalytic activity towards the electrochemical oxidation of organics to CO_2 and H_2O [1]. In addition, this process heavily depends on the activity of coating materials on the electrodes. Comninellis [2] reviewed the current advances and future trends in water treatment. It was suggested that the priority should be given to developing new materials to promote the efficiency of treatment. In recent years, the anodes made of SnO_2 or containing minor component of SnO_2 are quite interesting for their high oxygen evolution potential and attractive electrocatalytic properties for removal of organic [3,4]. High oxygen evolution potential is helpful for the enhanced electrochemical oxidation of pollutants [5]. Pollutants such as phenol and bisphenol can be readily oxidized at SnO_2 electrode compared with Pt and other dimensionally stable anodes (DSA). Meanwhile, the intermediate products including benzoquinone and some small molecular organic acids will be degraded quickly on the surface of SnO_2 electrode [6,7]. The applied potential of SnO_2 electrode is rather low due to the good conductivity of antimony doped SnO_2. Moreover, the SnO_2 electrode is easier and cheaper to prepare than the boron doped diamond (BDD) [8–10]. Nevertheless, the main problem for commercial applications of SnO_2 electrode is its short service lifetime because of the poor bonding between Ti substrate and SnO_2 coating [11]. Some noble or transition metals such as Ir, Au, Fe, Ni, and Gd [12–14] were chosen to overcome this disadvantage. However, there still exist some obvious and inevitable limitations. For example, although the incorporation of Ir [15] in the SnO_2 electrode could greatly enhance its service lifetime, the existence of IrO_2 would result in the electrode having a lower oxygen evolution potential [16]. The introduction of Au could increase the stability and electrocatalytic ability of SnO_2 electrode to some degree [17]. The improvement on service lifetime, however, was found to be limited. Therefore, some new methods must be developed to effectively increase the stability of SnO_2 electrodes without losing their excellent electrocatalytic performance and high oxygen evolution potential. Herein, we propose a novel approach to improve the electrochemical performance and stability of SnO_2 electrode fabricated through pulse electro-co-deposition of SnO_2 and Sb_2O_4 coating on Ti substrate in precursor solution containing porous Cr_3C_2 and CNT. It is known that there are two methods used for electrodeposition, the direct current (d.c.) method where the cathode potential is biased by a direct potential, and the pulse-plating one where the cathode potential is modulated in the pulse potential. The d.c. deposition is restricted by the fact that only one variable (current or potential) can be adjusted for the growth of film. The pulse-plating electrodeposition allows independent variation of three parameters: potential or current, period and duty cycle. It has some advantages over the d.c. electrodeposition, which may lead to an improve-

---

* Corresponding author. Tel.: +1 780 492 7706; fax: +1 780 492 2881.
E-mail address: weixing.chen@ualberta.ca (W. Chen).

0013-4686/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2010.10.037

ment of deposited coating's distribution and adhesion [18,19]. It can generate smoother, more compact and more chemically homogeneous surface and a more expedient composition control of the deposited film [20,21]. On the other hand, the addition of porous Cr_3C_2 and CNT would be helpful to increase the Sb-doped SnO_2 loading amount which may yield larger specific surface and space utilization of the Sb-doped SnO_2 coating. It is an effective way to increase the electrochemical activity of SnO_2 electrode by loading more electrocatalyst per unit area under the restriction of the finite geometrical area [22]. This paper focused on whether the novel fabricated Ti/SnO_2–Sb_2O_4–CNT–Cr_3C_2 electrode has better stability and electrocatalytic performance for the degradation of refractory organic pollutants. To evaluate the electrochemical degradation capability of these electrodes for the degradation of refractory organic pollutants, phenol was chosen as the model organic pollutant. Phenol is a typical pollutant that can be found in various industrial wastewaters including pulp and paper mill industries, petrochemical refineries, plastics and glue manufacturing as well as coke plants [23].

2. Experimental

2.1. Precursor solution and electrode preparation

The precursor solution was prepared by firstly dissolving citric acid (CA) in ethylene glycol (EG) at 60 °C and then raising the solution temperature to 90 °C for dissolving $SnCl_4{\cdot}5H_2O$, Sb_2O_5, porous Cr_3C_2 (as-prepared by heating Cr_2O_3 at 1100 °C with 10% methane in argon, 10 h) and CNT (Shenzhen Nanotech Port Co. Ltd.). The molar ratio of CA/EG/Me/Cr_3C_2/CNT was controlled to be 1/4.5/0.33/x/y, where Me is molar concentration of tin and antimony ions (the molar ratio of Sn/Sb is 9/1).

Titanium plates with a dimension of 10 mm × 20 mm × 2 mm and 20 mm × 30 mm × 2 mm were used as substrates to prepare the working electrodes for electrochemical behavior test and phenol electrolysis, respectively. Prior to the preparation process, the titanium plate was polished by sand paper. This was followed by a chemical treatment in hot 5% (w/w) NaOH solution for 1.0 h. The plate was then treated in hot oxalic acid 10% (w/w) for 2.0 h. Finally, the support was washed with purified water and stored in 1% (w/w) oxalic acid solution.

Electro-co-deposition scheme is the same as our previous work [24]. SnO_2 was co-deposited first at a current density of $-15\,mA\,cm^{-2}$ for 90 s with or without Cr_3C_2 and CNT; then Sb_2O_4 was co-deposited with them at $-4\,mAcm^{-2}$ for 10 s. These two sequential processes were repeated for 15 times. After electro-co-deposition, the working electrodes were rinsed with deionised water and dried in air. Finally, the electrodes were annealed at 500 °C for an hour. The total oxide loading of electrode was $8.5\,mg\,cm^{-2}$ (only oxide), $9.3\,mg\,cm^{-2}$ (with CNT), $10.4\,mg\,cm^{-2}$ (with Cr_3C_2), and $10.9\,mg\,cm^{-2}$ (with Cr_3C_2 and CNT), respectively.

2.2. Characterization

Surface morphology of different anodes was characterized using a Hitachi H2700 scanning electron microscope (SEM). The deposited samples were examined using thin film X-ray diffraction (XRD) with a Rigaku rotating Cu anode system (40 kV, 110 mA) in the step scanning mode.

Electrochemical voltammetric behaviour was investigated on Gamry Reference 600 (Camry Instruments. USA) system in 1 M H_2SO_4 + 500 mg L^{-1} phenol solution. A three-electrode cell was used and it consisted of a tin-based anode working electrode, a platinum foil counter electrode and a SCE reference electrode. Cyclic voltammograms were recorded between different potential ranges vs. SCE at 50 mV s^{-1}.

Table 1
Comparison of the service time and the evolution oxygen potential of phenol oxidation on Ti/SnO_2–Sb_2O_4–CNT electrodes.

x (CA/EG/Me/Cr_3C_2/CNT molar ratio:1/4.5/0.33/0.1/x)	0	0.01	0.02	0.05	0.1	0.2
Service time (min)	68.1	160.7	258.4	48.8	43.4	37.4
Evolution oxygen potential (V)	1.95	2.09	2.23	1.95	1.91	1.83

Me means Sn/Sb molar ratio was 9/1.

2.3. Accelerated life test

The accelerated lifetime test was carried out in a three electrode cell under galvanostatic conditions at 100 mA cm^{-2} using a Pt foil as a cathode and SCE as reference electrode in 1 M H_2SO_4 at 25 °C. The service life of the anode is defined as the duration from the beginning of the test to the time at which the cell potential reaches 10 V. The reaction on the electrode is H_2O electrolyzation but not phenol oxidation when the anode potential reaches 10 V vs SCE, indicating the inactiveness of the electrode for phenol oxidation.

2.4. Pollutant oxidation

Phenol was selected as the sample of the aromatic contamination for studying the Cr_3C_2 and CNT modified electrodes. SnO_2 based electrodes were used as anode and the stainless steel electrodes with the same dimension were used as cathode and the distance between them was 20 mm. A DC potentiostat was employed as the power supply with a voltage output up to 30 V. The volume of phenol solution was 80 mL with an initial concentration of 100 mg L^{-1}. 0.25 mol L^{-1} sodium sulphate (Na_2SO_4) was used as the supporting electrolyte. The electrolysis was performed under galvanostatic control at 60 mA so as to keep the current density 10 mA cm^{-2} at 25 °C.

2.5. COD measurement and CE calculation

COD was measured using a COD reactor and a spectrophotometer (AQ 2040, Orion, USA). CE is calculated based on the result of COD test and the following equation [25]:

$$\mathrm{CE} = \frac{\mathrm{COD}_t - \mathrm{COD}_{t+\Delta t}}{I \times \Delta t \times 8000} FV \times 100\% \qquad (1)$$

where COD_t and $\mathrm{COD}_{t+\Delta t}$ are the COD values at time t and $t + \Delta t$ (mg L^{-1}), I is the electrolysis current (A), Δt is the electrolysis time (s), F is the Faraday's constant 96,480 (C mol^{-1} electrons) and V is the volume of solution (L). The instantaneous current efficiency of phenol oxidation reaction was calculated at different electrolysis time.

3. Results and discussion

3.1. The optimization of Cr_3C_2 and CNT modified Ti/SnO_2–Sb_2O_4 electrode

Various CNTs or Cr_3C_2 modified tin based electrodes were characterized and the results obtained are summarized in Fig. 1. The 0.1 Cr_3C_2 sample showed the longest life time and the highest evolution potential compared with other ratio CNT or Cr_3C_2 samples. The service time of Ti/SnO_2–Sb_2O_4–Cr_3C_2 and Ti/SnO_2–Sb_2O_4–CNT–Cr_3C_2 electrode was calculated based the results in Fig. 1 and Table 1 to be 7.4 times and 5.6 times longer than that of the Ti/SnO_2–Sb_2O_4 electrode, respectively. To further