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Preparation and characterization of PbO_2–ZrO_2 nanocomposite electrodes

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ABSTRACT

PbO_2–ZrO_2 nanocomposite electrodes were prepared by the anodic codeposition in the lead nitrate plating bath containing ZrO_2 nanoparticles. The influences of the ZrO_2 nanoparticles concentration, current density, temperature and stirring rate of the plating bath on the composition of the nanocomposite electrodes were investigated. The surface morphology and the structure of the nanocomposite electrodes were characterized by scanning electronic microscopy (SEM) and X-ray diffraction (XRD), respectively. The experimental results show that the addition of ZrO_2 nanoparticles in the electrodeposition process of lead dioxide significantly increases the lifetime of nanocomposite electrodes. The PbO_2–ZrO_2 nanocomposite electrodes have a service life of 141 h which is almost four times longer than that of the pure PbO_2 electrodes. The morphology of PbO_2–ZrO_2 nanocomposite electrodes is more compact and finer than that of PbO_2 electrodes. The relative surface area of the composite electrodes is approximately 2 times that of the pure PbO_2 electrodes. The structure test shows that the addition of ZrO_2 nanoparticles into the plating bath decreases the grain size of the PbO_2–ZrO_2 nanocomposite electrodes. The anodic polarization curves show that the oxygen evolution overpotential of PbO_2–ZrO_2 nanocomposite electrodes is higher than PbO_2 electrodes. The pollutant anodic oxidation experiment show that the PbO_2–ZrO_2 nanocomposite electrode exhibited the better performance for the degradation of 4-chlorophenol than PbO_2 electrode, the removal ratio of COD reached 96.2%.

1. Introduction

Lead dioxide electrodes possess high electrical conductivity, good stability in acid media and are easily obtained at a low cost. In addition, they are characterized by a relatively high electrocatalytic activity in processes taking place at high positive overpotential such as the formation of ozone [1], the incineration of toxic organic compounds [2] and electrosynthesis [3]. The main disadvantage of pure lead dioxide electrodes is the relatively low service life, particularly when they are employed at high potentials [4]. Therefore, it is essential to find a way to enhance the electrochemical stability of lead dioxide electrodes.

In order to further improve the electrochemical stability of lead dioxide electrodes, incorporating some particles into lead dioxide matrix has been investigated, and several literature works report on the preparation of composite electrodes materials containing particles of different metal oxides including Co_3O_4, RuO_2 and La_2O_3 [5–8]. Valve metal oxides such as TiO_2 and ZrO_2 are particularly interesting as they are electrochemically and chemically stable oxides [9–13]. The lifetime of the electrodes containing the inert TiO_2 particles was found to be twice as long as that of traditional PbO_2 electrodes [9]. These research works indicated that the properties of the lead dioxide electrodes are influenced by their composition and microstructure, which are controlled by the plating process.

The aim of this study is to explore the effect of ZrO_2 nanoparticles on the electrochemical stability of lead dioxide electrodes. So we prepared PbO_2–ZrO_2 nanocomposite electrodes by composite plating technique in the lead nitrate plating bath containing ZrO_2 nanoparticles, the influences of ZrO_2 nanoparticles concentration, current density, temperature and stirring rate of the plating bath on the composition of the PbO_2–ZrO_2 nanocomposite electrodes were investigated. The physical properties of the nanocomposite electrodes were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The anodic oxidation of 4-chlorophenol (4-CP) using PbO_2–ZrO_2 electrodes was examined by bulk electrolysis to characterize the electrocatalytic activity of the nanocomposite electrodes. The stability of PbO_2–ZrO_2 nanocomposite electrodes was evaluated by accelerated life tests.

2. Experimental

2.1. Electrodes preparation

2.1.1. Ti plates pretreatment

Ti plates (99.5%, 20 mm × 50 mm) were degreased in absolute ethanol for 20 min, and then polished by 320-grit paper strips with

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water as lubricant. The plates were cleaned using ultrasound for 10 min to remove sand particles lodged in the metal. Next, Ti plates were treated by etching in boiling aqueous 20% oxalic acid for 2 h until TiO_2 was thoroughly dissolved, followed by thorough washing with de-ionized, doubly distilled water. Now, Ti plates were gray, and had lost the metallic sheen.

2.1.2. SnO_2–Sb_2O_3 interlayer preparation

The SnO_2–Sb_2O_3 interlayer deposited onto the pretreated Ti plates was prepared by thermal decomposition. In this step, 20.0 g $SnCl_2$, 2.0 g $SbCl_3$ and 13.2 mL of concentrated HCl were dissolved in 100 mL isopropanol. The Ti plates were dipped in this solution for 5 min, and then dried at 100 °C for 15 min, and the same procedure was repeated four times. Then, the Ti plates were thermally treated in a muffle furnace at 500 °C for 2 h.

2.1.3. Nanocomposite electrodes preparation

The PbO_2 electrodes and PbO_2–ZrO_2 nanocomposite electrodes were prepared by electrodeposition method. PbO_2–ZrO_2 nanocomposite electrodes were electrodeposited from the lead nitrate plating bath containing ZrO_2 nanoparticles. The composition of the plating bath was: 0.2 mol L^{-1} $Pb(NO_3)_2$, 0.1 mol L^{-1} HNO_3, 0.15 mol L^{-1} NaF, as our previous work [14]. The ZrO_2 nanoparticles (VK-R50, Wanjing Int. China, purity > 99.9%) were added to the solution from 2 to 10 g L^{-1}. The average size of the ZrO_2 nanoparticles was estimated to be 50 nm. All other chemicals were of analytical grade and were used without purification, purchased from Yuda Int. All solutions were prepared with deionized, doubly distilled water. The Pb electrode was used as the cathode, the anode was Ti coated with a SnO_2–Sb_2O_3 interlayer. Prior to plating, ultrasonic agitation was applied to mix the ZrO_2 nanoparticles and the electrolyte for 3 h. The operating conditions for plating were current density ranging from 1 to 5 A dm^{-2}, stirring rate from 60 to 300 rpm and bath temperature from 10 to 50 °C. The PbO_2 electrodes were also obtained under the same condition from an electrolyte without ZrO_2 nanoparticles. The electrodes were weighed before and after plating, and from the mass gain in each case the current-efficiency (CE) was calculated. The composition of the nanocomposite electrodes was analyzed by the procedures suggested by Velichenko et al. [10]. The PbO_2–ZrO_2 nanocomposite electrodes were dissolved in a mixture of 5 mol L^{-1} HNO_3 and H_2O_2 solution (1:1). The amount of PbO_2 in the composite electrodes was calculated by the content of Pb^{2+} in the solution, which was measured using the amperometric titration with diethyl dithiocarbominate.

2.2. Morphology and structure tests

Surface morphology of PbO_2 electrodes and PbO_2–ZrO_2 nanocomposite electrodes was examined by a scanning electron microscope (SEM, S4800). The phase structure of the PbO_2 electrodes and PbO_2–ZrO_2 nanocomposite electrodes was analyzed by BRUKER X-ray diffraction (XRD). The grain size of lead dioxide was determined using the Scherrer equation.

2.3. Electrochemical experiments

A conventional three-electrode cell was used to do the electrochemical experiments. The counter electrode was platinum electrode and the reference electrode was a saturated calomel electrode (SCE). The working electrodes were PbO_2 electrodes or PbO_2–ZrO_2 nanocomposite electrodes. Electrochemical measurements were conducted at 25 °C using CHI 604D electrochemical workstation. The anodic polarization curves in 2 mol L^{-1} H_2SO_4 solution were measured through linear potential scan by scanning the potential at 1 mV s^{-1}.

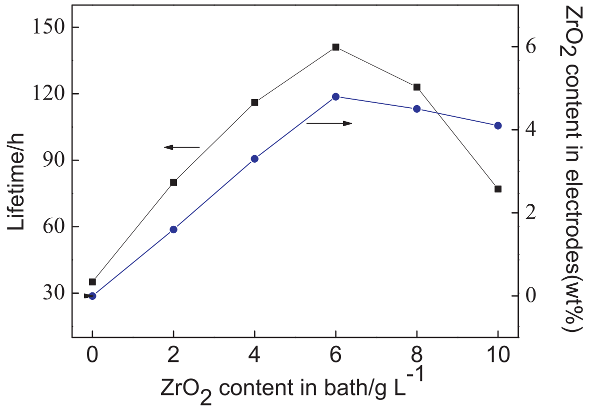

Fig. 1. Effect of the ZrO_2 nanoparticles concentration on the lifetime (left) and the weight percentage of the particles in the PbO_2–ZrO_2 nanocomposite electrodes (right).

2.4. Pollutant oxidation and accelerated life tests

The oxidation of 4-CP was carried out in an electrochemical reactor using PbO_2–ZrO_2 nanocomposite electrodes as anode, stainless steel as cathode and 0.1 mol L^{-1} Na_2SO_4 as supporting electrolyte. The electrolysis conditions were current density at 200 mA cm^{-2}, temperature at 25 °C and the electrodes distance with 1 cm. During the experiments, samples were drawn from the reactor at certain intervals and then analyzed. The chemical oxygen demands (CODs) of the samples were measured by the titrimetric method. The samples were oxidized by dichromate in acidic solution in a heater apparatus (Hachi, USA) at 150 °C for 2 h [15].

The service lifetime tests of PbO_2–ZrO_2 nanocomposite electrodes were investigated in 2 mol L^{-1} H_2SO_4 solution with the current density of 4 A cm^{-2} whose temperature was kept at 60 °C. During the lifetime tests, the cell potential was measured periodically, the stable cell potential is about 5.2 V. The lifetime of electrodes could be determined when the cell potential steeply increased until being higher than 10.0 V.

3. Results and discussion

3.1. Effect of preparation parameters on the lifetime and composition of PbO_2–ZrO_2 nanocomposite electrodes

Fig. 1 shows the influence of ZrO_2 nanoparticles content in the electrolyte on the PbO_2–ZrO_2 nanocomposite electrodes lifetime (left) and the weight percentage of the particles in the PbO_2–ZrO_2 nanocomposite electrodes (right) at current density 3 A dm^{-2}, temperature 30 °C and stirring rate 180 rpm. It was found that the lifetime increases sharply with the increase of ZrO_2 nanoparticles concentration in the plating bath up to 6 g L^{-1}. The increase of lifetime may be attributed to the increase of the weight percentage of the ZrO_2 nanoparticles in the composite electrodes. When the concentration of ZrO_2 nanoparticles reached 6 g L^{-1}, the lifetime of the PbO_2–ZrO_2 nanocomposite electrodes was about 4 times longer than the common PbO_2 electrodes without being modified by ZrO_2 nanoparticles. But as the ZrO_2 nanoparticles concentration in the electrolyte surpasses 6 g L^{-1}, the lifetime of PbO_2–ZrO_2 nanocomposite electrodes decreased. This can be attributed to the decrease of the weight percentage and the agglomeration of the ZrO_2 nanoparticles in the composite electrodes [16].

Fig. 2 shows that the current efficiency (CE) of PbO_2 during electrodeposition process without ZrO_2 nanoparticles was 98%. When ZrO_2 nanoparticles were introduced into the plating bath, the current efficiency decreased with the increase of ZrO_2