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Electrosynthesis and characterization of lead oxide thin films

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Abstract

Lead dioxide (PbO_2) is an important oxide material used extensively as anode material in batteries and fuel cells and its study has now taken new strides beyond the wide field of battery research. In the present study, lead dioxide films were electrodeposited onto precleaned copper substrate from nitrate baths. The film composition, morphology and structure were investigated using Energy Dispersive X-ray Analysis (EDX), scanning electron microscopy and X-ray diffraction techniques. The oxidation and reduction potential regions and the mechanism of lead dioxide film formation are discussed using cyclic voltammetry studies. X-ray diffraction results revealed tetragonal [α-PbO_2+β-PbO_2] structures of the films which are influenced by bath temperature and solution pH value. EDAX studies show that the films deposited at higher bath temperatures and low solution pH values are rich in lead content and low in oxygen content. The effects of bath temperature and solution pH on the morphological features of lead dioxide films are also described.

Keywords: Lead dioxide; Electrodeposition; Thin films; Structural studies

1. Introduction

During the past decade, lead dioxide (PbO_2) anodes have sparked a worldwide interest because of their structural, morphological, optical, and mechanical properties and their potential applications in waste water treatment [1,2], ozone generation[3], analytical sensors [4], electro-winning of metals [5] and battery electrodes [6]. The substantial growth in new avenues such as telecommunication networks, electronics, computers etc., has raised new challenges for PbO_2 batteries. PbO_2 electrodes are also applied in industrial processes such as an energy conversion process, recycling and environmental treatment [7]. It is well known that PbO_2 exhibits excellent chemical stability, high conductivity, large over potential and chemical inertness for electrolysis in an acid medium. Recently, the deposition behavior of lead oxide thin films prepared by metal organic chemical vapor deposition was reported by Zhao et al. [8]. Eftekhari reported the

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fabrication of a pH sensor based on a lead oxide thin film prepared by chemical deposition [9]. The influence of ultrasonic frequency on the electro-crystallization of lead oxide was reported by Saez et al. [10]. Devilliers et al. [11] have studied the selective electrodeposition of PbO_2 on anodized titanium substrates. Shen and Wei [12] studied the morphological behavior of electrochemically grown PbO_2 thin films. In the present study, PbO_2 films have been prepared by electrodeposition techniques because of the following reasons: easy control of thickness and morphology of films, low cost, easily maintainable equipment, and relatively uniform film which can be formed on substrates of complex shapes, and the method is more environmentally friendly. Even though several reports are available in the literature of PbO_2 films, systematic studies of deposition parameters on the film properties are scarcely reported. In the present study, a systematic investigation of cyclic voltammetry and the effects of solution pH and bath temperature on the structural and morphological properties of PbO_2 thin films are given.

2. Experimental details

Lead dioxide thin films were prepared by potentiostatic electrodeposition using an aqueous electrolyte bath. The experiments were performed in a conventional three-compartment electrochemical cell and a potentiostat [EG&G, model 362, USA] with a Saturated Calomel Electrode (SCE) as the reference electrode, a graphite electrode as the counter electrode and copper substrate as the working electrode. We have used copper substrates for the preparation of lead dioxide films because of their low cost and high electrical conductivity suitable for electrodeposition of thin films. Prior to the deposition, the substrates were polished mechanically with silicon carbide emery paper and then chemically treated in 10% sulfuric acid for 1 min. After each of these pretreatment steps, the substrates were subjected to acetone cleaning in an ultrasonic bath to remove the chemical contaminants on the surface before subsequently rinsing in double distilled water. The substrates were immediately transferred to the deposition bath. Analytical grade chemicals and reagents (Merck) were used for all the experiments. PbO_2 films were prepared from a 0.1 M $Pb(NO_3)_2$ solution with triple distilled water and 1 M HNO_3 was used as the supporting electrolyte. The deposition cell consisted of a 100 ml beaker containing the deposition solution. The pH values of the electrolyte bath were adjusted from 2.0 ± 0.1 to 5.0 ± 0.1. The deposition potential and bath temperature during the depositions were maintained as −1100 mV vs. SCE and 32 °C to 80 °C±2 °C, respectively. During the depositions, the electrolyte was not agitated. The deposition time and scan rate were 20 min and 50 mV/s, respectively. In the present study, other methods to prepare lead dioxide thin films were not attempted.

Cyclic–Voltammetry (CV) studies were carried out on well cleaned copper substrates in an aqueous bath potentiostatically in a conventional three compartment electrochemical cell. The deposited films were analyzed using an X-ray diffractometer (Philips Model PW 1710) using Cuk_α radiation with $\lambda=0.1542$ nm. Surface morphological and compositional analyses were carried out using a scanning electron microscope and an energy dispersive X-ray analysis (EDAX) set up attached to an SEM (Philips, Model XL 30).

3. Results and discussion

3.1. Cyclic–Voltammetry studies

A typical cyclic voltammogram of electrodeposition of PbO_2 from 0.1 M $Pb(NO_3)_2$ solution onto copper substrate is shown in Fig. 1. During the CV studies, the scan rate was kept as 50 mV/s. Different cathodic and anodic peaks are observed on this cyclic voltammogram. The elucidation of the PbO_2 electrodeposition mechanism is very important for electrocatalytic activity applications. Cyclic voltammetric studies of PbO_2 material have been reported earlier on tin oxide (SnO_2) [13] and gold (Au) [14] electrodes.

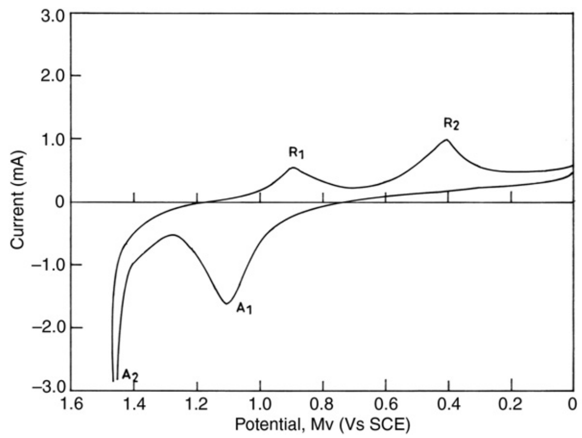

Fig. 1. A typical cyclic voltammogram of electrodeposition of PbO_2 from 0.1 M $Pb(NO_3)_2$ solution onto a copper substrate.