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The deposition of nanostructured β-PbO_2 coatings from aqueous methanesulfonic acid for the electrochemical oxidation of organic pollutants

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ABSTRACT

Highly crystalline, nanostructured, three-dimensional β-PbO_2 coatings were successfully obtained by galvanostatic deposition from baths containing aqueous lead(II) and methanesulfonic acid (CH_3SO_3H). This constitutes a much more environmentally friendly methodology compared to plating of β-PbO_2 in HNO_3. The deposits exhibited high quality and good adherence. The crystallite size was in the range 20–30 nm and AFM imaging revealed very uniform, rough deposits (i.e., 255–275 nm rms). The oxidative destruction of Methyl Orange azo dye was studied by electrochemical advanced oxidation processes (EAOPs). An electro-Fenton process with a high surface area carbon-felt cathode performed better than the single anodic oxidation. Rapid and complete decolorisation was achieved following pseudo first-order kinetics. The stability of the β-PbO_2 electrodes during the electrolyses was also demonstrated.

1. Introduction

The electrochemical advanced oxidation processes (EAOPs), which are aimed at eco-friendly water decontamination, require the use of high oxidation power anodes with a large O_2-overpotential [1]. PbO_2 coatings are inexpensive, easy to prepare, and stable in a wide range of electrolytes [2]. Many authors have reported the preparation of PbO_2 electrodes by anodic deposition, which traditionally employs very oxidising and toxic acidic media such as $HClO_4$ and HNO_3 [2,3]. In contrast, the use of more environmentally friendly electrolytes such as methanesulfonic acid (CH_3SO_3H) has been seldom reported. This acid is chemically stable, biodegradable, has low toxicity [4] and is capable of providing thicker PbO_2 coatings with enhanced mechanical properties [5] as well as an unusual high optical reflectance [6]; recently, it has been shown to be very promising for flow battery applications [5,7,8].

This work formed part of a programme which seeks to develop cleaner electrochemical water treatment technologies. A greener methodology to obtain suitable PbO_2 electrodes based on the use of CH_3SO_3H is proposed before their application to the $\cdot OH$-mediated oxidative destruction of organic pollutants in aqueous medium. The β-PbO_2 coatings exhibit an open, porous structure that provides large surface area, enhancing the adsorption of organics and $\cdot OH$ generation to favour the decontamination process [9]. Surface analysis confirmed that suitable β-PbO_2 electrodes could be achieved. The oxidation ability of the electrodes was assessed with Methyl Orange dye as a model pollutant.

2. Experimental details

2.1. Chemicals

Lead(II) methanesulfonate ($Pb(CH_3SO_3)_2$), CH_3SO_3H, and Methyl Orange (4-[4-(dimethylamino)phenylazo] benzenesulfonic acid sodium salt) were reagent grade from Aldrich and Fisher. Heptahydrated ferrous sulphate and anhydrous sodium sulphate were analytical grade. All solutions were prepared with ultra-pure water.

2.2. Electrodeposition

The deposition baths contained 1.0 mol dm^{-3} $Pb(CH_3SO_3)_2$ and 0.2 mol dm^{-3} CH_3SO_3H. Galvanostatic deposition was carried out at 20 mA cm^{-2} at 60 °C for 60 min in a small thermostated, cylindrical, undivided glass cell containing 80 cm^3 of electrolyte. Carbon/polyvinyl-ester composite (4.0 × 6.0 cm, 6 mm thickness) from Entegris GmbH was used as anode and cathode in a parallel plate cell with an inter-electrode gap of 2.0 cm. The back and sides

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of the electrodes were insulated. All electrodes were mechanically roughened using SiC paper of grades 800 and 1200. The cell was magnetically stirred at 300 rpm with a PTFE-coated bar to ensure reproducible stirring conditions. The mean thickness of the PbO_2 coatings was 45 μm.

2.3. Electrochemical advanced oxidation processes

Bulk electrolyses were carried out in a small, open, undivided glass cell containing 275 cm^3 of 0.25 mmol dm^{-3} Methyl Orange and 0.05 mol dm^{-3} Na_2SO_4, at pH 3.0 and at 22.5 °C, with vigorous stirring by a magnetic follower to enhance mass transport. The solution pH was very stable and was selected because it is the optimum value for Fenton's reaction [1,10]. The anodic oxidation process was carried out at 60 and 300 mA (i.e., 10 and 50 mA cm^{-2}, respectively) using a 6 cm^2 Ni plate cathode and an exposed PbO_2 anode area of 6 cm^2. Electro-Fenton (EF) studies involved electrolysis at 60 mA with 0.2 or 1.0 mmol dm^{-3} Fe^{2+}, using 6 or 60 cm^2 geometric surface area (yielding a cathodic current density of 10 and 1 mA cm^{-2}, respectively) carbon-felt cathode (Alfa Aesar, 9.86 g/10 × 10 cm). Hydrogen peroxide was produced from the two-electron reduction of pure O_2 dissolved into the solution. The oxygen was released into the solution through a microporous glass frit at ca. 1 dm^3 min^{-1}. In all cases, the inter-electrode gap was 2.0 cm in parallel configuration.

2.4. Apparatus and analysis procedures

Constant current deposition was performed with a PGSTAT30 potentiostat/galvanostat from Autolab computer controlled by GPES 4.9 software. The phase composition was analysed by X-ray diffraction (XRD) using a Bruker HiStar general area detector diffraction system with Ni-filtered CuK_α radiation. The morphology was examined using a thermal field emission scanning electron microscope (SEM, model JSM 6500F). Surface roughness was measured by atomic force microscopy (AFM) using an MFP-3D-standalone Asylum Research microscope. It was measured as a root mean square (rms) value by scanning an area of 80 × 80 μm, with an image resolution of 2048 × 2048 pixels. For the electrochemical characterisation, steady state cyclic voltammetry was carried out by using a purpose-built, three-electrode, undivided glass cell containing 50 cm^3 of solution at pH 3.0 and 22.5 °C, with a platinum gauze and a saturated calomel electrode (SCE) as the counter and reference electrodes, respectively. The exposed area of the working electrode was 1.8 cm^2.

Methyl Orange solutions treated by the EAOPs were analysed at regular intervals. The decolorisation decay was followed from the absorbance at the maximum visible wavelength (λ_{max}) of 503 nm, measured on a Scinco Co. Ltd. UV/Vis spectrophotometer controlled by LabPro Duo software. The anode, cathode, and cell potentials were continuously monitored.

3. Results and discussion

3.1. Characterisation of the electrodeposits

PbO_2 was deposited from solutions containing 1.0 mol dm^{-3} $Pb(CH_3SO_3)_2$ and 0.2 mol dm^{-3} CH_3SO_3H as high quality, adherent, matte coatings. The identification of the crystallographic structure was performed by comparison with the reference diffraction patterns. Clear and distinctive diffraction peaks at 25.5° and 32.1° were attributed to the (1 1 0) and (1 0 1) planes of β-PbO_2, respectively [2]. The predominance of pure β-phase at high temperature has also been reported in a HNO_3 medium [3]. The diffractograms exhibited well defined peaks in the whole 2θ range 20–90°, which is due to the high degree of crystallinity caused by effective nucleation and growth rates during the electrocrystallisation process. The mean crystallite size (L_{hkl}) estimated according to the Debye–Scherrer equation was in the range 20–30 nm. The formation of highly crystalline, nanostructured β-PbO_2 was thus ascertained. Fig. 1a shows the AFM image of such coatings. A perfect surface coverage with varied topography (i.e., peaks and valleys) is observed for the entire area analysed. A survey on different zones showed that the surface roughness was in the range 255–275 nm rms.

Electrochemical characterisation was conducted in 0.05 mol dm^{-3} Na_2SO_4 at pH 3.0 to assess the electrocatalytic activity. Fig. 1b shows the voltammograms obtained in the absence (i.e., blank solution) and presence of 0.25 mmol dm^{-3} Methyl Orange, as well as its azo structure. The potential sweeps started at +1.4 V *vs.* SCE, to ensure the stability of PbO_2 against reduction, towards positive potentials up to +2.0 V *vs.* SCE. In the absence of the dye, the 5th cycle is shown (dotted line) which corresponds to the behaviour of the stabilised hydrated polycrystalline surface. No current at potentials less positive than +1.65 V *vs.* SCE was observed, but at more positive potentials, a steep rise in anodic current appeared due to the oxygen evolution reaction. Therefore, the O_2-overpotential for the manufactured β-PbO_2 anodes was +0.66 V compared to the thermodynamic potential for O_2 evolution (= 1.23 V *vs.* SHE in acid media), which is similar to the values reported in Na_2SO_4 at 25 °C for electrodes prepared in HNO_3 [11].

In the presence of the dye the cyclic voltammogram shown in Fig. 1b corresponds to the 5th cycle (full line) and was identical to that of the 1st cycle (not shown). This indicates that the adsorption or possible polymerisation phenomena do not cause anode fouling. Two major features can be observed: a higher current at a given potential, and the absence of an oxidation peak. They can be explained by the mediated oxidation of Methyl Orange by very oxidising $PbO_2(\cdot OH)$ species adsorbed on the anode surface from water oxidation. At increasing potential, this mechanism competes with the plausible direct oxidation by electron transfer from the substrate, which was undetectable due to the corresponding low limiting current density. At the same time, these radicals prevented electrode fouling. In conclusion, the high surface-to-area ratio related to such rough β-PbO_2 coatings and the very small particle size provide a large area that favours the increased adsorption ability of reagent and ·OH.

3.2. Application in EAOPs

The β-PbO_2-coated carbon electrodes were used as the anodes in the treatment of aqueous solutions of 0.25 mmol dm^{-3} Methyl Orange. The oxidation ability of the anodic oxidation and EF processes was compared. Fig. 2a shows the percentage of color removal under different conditions. The decay of the absorption band is associated to the cleavage of the chromophore group. Anodic oxidation with a Ni plate cathode yielded 50% decolorisation in 120 min and total color destruction in 360 min at 10 mA cm^{-2} with β-PbO_2 prepared from either CH_3SO_3H or HNO_3. This confirms the ability of the electrodes proposed in this work to generate very active $PbO_2(\cdot OH)$ onto active centres in the gel layer of the coating. The high density of active sites provided by the rough surface [12], along with the open crystallographic β-PbO_2 phase structure [2], favours interaction between organic molecules and ·OH. A higher current density of 50 mA cm^{-2} allowed a much quicker decolorisation, with 50% and 100% color removal at 60 and 240 min, respectively, due to the larger amount of electrogenerated $PbO_2(\cdot OH)$. Then, a new combination of β-PbO_2 anode and carbon-felt cathode was tested under EF conditions at 60 mA, with cathodic H_2O_2 electrogeneration, aiming at profiting anode and cathode reactions. The use of a 6 cm^2 cathode with addition of either 0.2 or 1.0 mmol dm^{-3} Fe^{2+} as the catalyst facilitated a