



Electrodeposited nanometer-size IrO₂/Ti electrodes with 0.3 mg IrO₂ cm⁻² for sludge dewatering electrolyzers

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ABSTRACT

Dewatering electrolyzers are useful devices for efficiently reducing the water content of sewage sludge to <60%. High noble metal loadings of the dimensionally stable anodes, e.g. IrO₂-coated titanium electrodes, cause a main cost of such devices. In this paper, iridium oxide (IrO₂) coatings are electrodeposited on titanium to prepare the anodes. The loading amounts and morphologies of these IrO₂ deposits are varied by tuning parameters such as the electrodeposition potential, concentration of Iridium salts, and deposition time. An amorphous iridium oxide was obtained after electrodeposition, which was successively calcined at 500 °C. In the sludge electro-dewatering test, the electrodeposited IrO₂/Ti electrodes with an ultra small IrO₂ loading level (0.3 mg cm⁻²) shows acceptable performance, i.e. the water content of sludges in the electro-dewatering system can be reduced to about 60 wt% at 25 V and 55% at 35 V.

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1. Introduction

In China, deep dewatering of sewage sludges are required (water content <60 wt%) before they are allowed for delivery out of waste water plants [1]. Dewatering electrolyzers (also called electro-osmotic filter) may reduce the water content of the sludge cakes to 40–50 wt% in 20 min without adding chemicals [1,2]. However, only corrosion resistant anodes, such as the IrO₂ coated Ti anodes (dimensionally stable anodes, DSAs) are acceptable for these dewatering electrolyzers, of which the applied voltage is up to 20–80 V [2]. The DSAs usually employ about 0.5–1.5 mg cm⁻² noble metal oxides like RuO₂ and IrO₂ [3,4]. The conventional brush paste procedure, that requires a thick coating layer to achieve acceptable coverage, is believed to be responsible for such high catalyst loading level. In recent years, IrO₂ thin dense films can be prepared by several alternative new techniques, e.g. sputtering [5], thermal oxidation of evaporated iridium [6], and electrodeposition [7–10]. IrO₂ films prepared with electrodeposition may exhibit more uniform coverage because the coatings are formed wherever current is distributed [7]. Therefore, the loading level of IrO₂

electrodes may be reduced when they are prepared by electrodeposition [8]. Yamanaka's early report [7] in 1989 published extensive efforts on developing the anodic electrodeposition bath of IrO₂, from an aqueous oxalate solution (pH 10.5) containing IrCl₄, hydrogen peroxide, and K₂CO₃. Later, Petit [8] improved this technique by using K₃IrCl₆ instead of IrCl₄ to provide a more transparent IrO₂ film on ITO. Zhao and coworkers reported a method for the anodic deposition of stable IrO_x·nH₂O nanoparticle thin films on a variety of electrode surfaces, including platinum and gold [16]. However, to the best of our knowledge, there are very few reports, except for above mentioned, on successful preparation of such electrodeposited IrO₂/Ti, with Petit's method. In most cases these films have been grown on glassy carbon (GC) or fluorinedoped tin oxide (FTO) electrodes [8,12–15] and it has been difficult to obtain stable films on titanium electrodes. In these works, the preparation mechanism of the IrO₂ electrodeposition bath were ambiguous and conflict to each other, for example the choice about trivalent or tetravalent Ir salts. Therefore, it is of great importance to study the preparation method of IrO₂ electrodeposition bath and investigate IrO₂/Ti electrodes prepared by electrodeposition method in

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environmental applications.

2. Experimental

2.1. Materials

Iridium (III) chloride hydrate (IrCl_3) was purchased from Shanxi Kaida Chemical Engineering Co. Ltd, and other chemicals were purchased from the Sinopharm Chemical Reagent Co. Ltd. All chemicals were reagent grade and all solutions were prepared by deionized (DI) water. All sludge samples used in this study were taken from Jiading Sewage Treatment Plant located in Shanghai, China.

2.2. Fabrication of IrO_2/Ti electrodes by anodic electrodeposition

Prior to electrodeposition, the titanium plate was etched by a solution of 10 wt% oxalic acid at 80°C for 2 h until a dark brown solution appeared [4]. The method reported by Petit and Plichon [8] was adopted with modifications to prepare IrO_2 electrodeposition bath. Oxalic acid dihydrate (1 mmol) was added to an aqueous solution (30 ml) containing 0.2 mmol IrCl_3 , and the resulting solution was mixed for 10 min, and then K_2CO_3 (5 mmol) was added to adjust pH to 10–10.5. Then the solution was diluted to 50 ml and the final iridium ion concentration was 4 mmol L^{-1} . Three different sample solutions with 2, 6, and 8 mmol L^{-1} iridium ion concentrations were prepared with similar process. This solution was kept at 40°C for ca. 5 days to allow stabilization and then it was stored as a stock solution at 4°C . A three electrode system was equipped with Ti plate working electrodes (effective area: 1.0 cm^2), a saturated calomel (SCE) reference electrode, and a platinum plate counter electrode. IrO_2 was anodically electrodeposited on Ti electrodes from the stock solution (20 ml) at a potential of 0.6–0.8 V with total deposition charge 2–3 C. Linear sweep voltammetry (LSV) was performed using an electrochemical workstation (Ivium Stat) in the deposition solution from 0.5 V to 1.6 V with various scan rates. The IrO_2 electrodeposition was also conducted by applying constant potentials (0.5 V–0.9 V) for various deposition times (5–30 min). Finally, the samples were heat-treated for 1 h at 500°C under air. Coulombic efficiency of IrO_2 electrodeposition was obtained with a quartz crystal microbalance (CHI 440C). The loading amounts of IrO_2 on Ti were calculated by coulombic efficiency.

2.3. Characterizations

UV–visible absorption spectra were measured by a photodiode

array spectrophotometer (UV5800H). X-ray diffraction (XRD) measurements were carried out using a X-ray diffractometer (DX-27mini), and scanning electron microscope (SEM) images were recorded using Hitachi tabletop microscope TM3030. The electrochemical measurements were carried out in a single compartment cell, using Pt plate as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. Cyclic voltammograms of the modified electrode were measured in an aqueous solution of 0.5 M K_2CO_3 at different scan rates using the same electrochemical cell as the electrodeposition. Steady state polarization curves of the sample electrodes were measured at 0.5 mV s^{-1} . All the electrochemical data were recorded at $25 \pm 1^\circ\text{C}$.

2.4. The sludge electro-dewatering test

The sludge electro-dewatering tests were done by an experimental apparatus of the electro-dewatering system (Fig. 1). It consists of a cylinder cell fitted with an electrochemical workstation (Ivium Stat) and a bluetooth balance. The spherical sludge cakes loaded in test cell is 10 mm thick with diameter 76 mm. The IrO_2/Ti electrodes are adopted as anodes and the cathodes are stainless steel mesh. The voltages applied to the dewatering electrolyser were 25 V or 35 V. During electro-dewatering, the current densities and weight variations of sludge cakes were recorded. A commercial IrO_2/Ti anode, fabricated by manual brush paste and thermal oxidation method with an IrO_2 loading of 1.0 mg cm^{-2} (Changli Company, China), was tested for comparing.

3. Results and discussion

Fig. 2 a–d are the absorption spectrum of solutions containing different amounts of IrCl_3 and oxalic acid at 40°C . The fresh solutions often exhibited two absorption peaks at about 300–360 and 400–450 nm [14]. Such two peaks can be attributed to the formation of $[\text{IrCl}_6]^{3-}$ complexes, as reported by Ref. [18] and many references therein [18]. However, the two characteristic peaks of $[\text{IrCl}_6]^{3-}$ complexes can be hardly observed in 0 h curves in Fig. 2. This difference is perhaps due to different Ir salts adopted: K_2IrCl_6 in Ref. [14] and IrCl_3 in this study. As aging time went on, after 24 h absorbance bands at about 310–320 nm and 570–580 nm grew up while the solutions became light blue, which phenomenon has also been observed by literature studies [14,19,21]. The absorption band at about 310–320 nm and 570–580 nm in the present solution suggests the formation of Ir complex by aging the solution [14]. Zhao et al. suggested that absorbance peaks along with the blue color could be an indication of hydrolysis of $[\text{IrCl}_6]^{3-}$ complexes

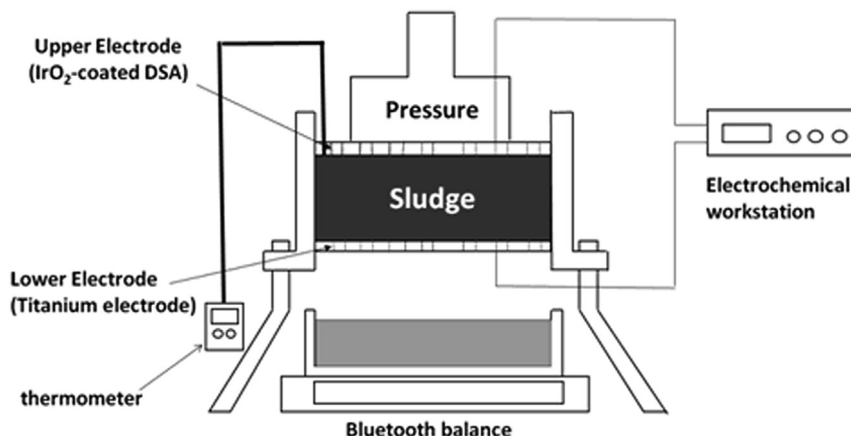


Fig. 1. Configuration of a laboratory-scale sludge dewatering electrolyser.

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