Research Article

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Preparation of Ti/IrO_2 Anode with Low Iridium Content by Thermal Decomposition Process: Electrochemical removal of organic pollutants in water

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Abstract: In this study IrO_2 (Iridium oxide) was coated onto a titanium plate anode from a dilute (50 mg/10 ml) $IrCl_3 \times H_2O$ salt solution. Coating was done at high temperature (550°C) using thermal decomposition. Surface morphology and characteristics of coated surface of Ti/IrO_2 anode were examined by FESEM and XRD. The coated anode was applied for electrochemical removal of organic pollutants from synthetic water samples in 100 mL compartment of batch electrochemical cell. About 50% COD removal was obtained at anode prepared with low Ir content solution while 72% COD removal was obtained with anode prepared at high Ir content. Maximum COD removal was obtained at 10 mA/cm^2 current density.

Keywords: Ti/IrO_2, thermal decomposition, COD removal

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1 Introduction

Iridium oxide (IrO_2) is a transition metal dioxide compound with rutile type structure and has very remarkable electrical and electrochemical properties [1]. IrO_2-based dimensionally stable anodes (DSA) are widely used for electrochemical O_2 and Cl_2 evolution [2, 3]. It was used with other transition metal oxides on titanium metal plates for Cl_2 evolution from sea water and for organic pollutants removal [4, 5]. In our previous study Ti/IrO_2 anode was used for electrochemical removal of PAHs by oxidative degradation from synthetic solutions [6]. Tran *et al.* [7] also used Ti/IrO_2 anode for electrolytic oxidation of polynuclear aromatic hydrocarbons (PAHs) from creosote solution. Various IrO_2-based electrodes with their applications are mentioned in the following Table 1.

Electrochemical processes effectively remove toxic materials from industrial effluents [19–22]. It is well known that the anode material plays a key role in advanced electrochemical oxidation systems, its performance depends upon the nature of coating materials on the electrodes [23, 24]. Coating materials must have high electrocatalytic activity for the electrochemical conversion of organics into CO_2 in water [25]. Electrical conductivity of the electrodes varies with amount of coating material (metal oxides) in precursors [2].

However, researchers are focusing on the active coating materials for electrochemical degradation of organic pollutants in wastewater. The active coating enables the electrical charge transport between the base metal and the electrode/electrolyte interface. Ti/IrO_2 anodes considered as active anodes due to their good catalytic activity towards oxygen evolution only permit the partial oxidation of organic compounds [26].

Objective of this study is to show the surface characteristics of Ti/IrO_2 anode prepared from low Ir-content solution. Electrocatalytic activity of Ti/IrO_2 anodes prepared

Table 1: Applications of Ti/IrO_2 electrode in electrochemical sciences.

Electrodes	Applications	Ref.
Ti/IrO_2	Oxygen evolution	[8]
Ti/IrO_2	Nitrate removal	[9]
Ti/IrO_2	Ammonia removal	[10]
Ti/RuO_2-IrO_2-SnO_2-Sb_2O_5	Cl_2 evolution from seawater	[5]
Ti/IrO_2–Ta_2O_5	Oxidation of sulfide ion	[11]
IrO_2–Ta_2O_5	Oxygen evolution	[12, 13]
Ti/IrO_2	PAHs removal	[6, 7]
Ti/IrO_2	Electrochemical incineration of chloranilic acid	[14]
Ti/IrO_2-Pt	Reduction of nitrate to nitrogen	[15]
Ti/IrO_2-Pt	Degradation of phenol	[16]
Ti/SnO_2-Sb_2O_5-IrO_2	Degradation of PAHs	[4]
IrO_2@RuO_2	Water splitting	[17]
IrO_2-Ta_2O_5|Ti	Treatment of contaminated soil	[18]

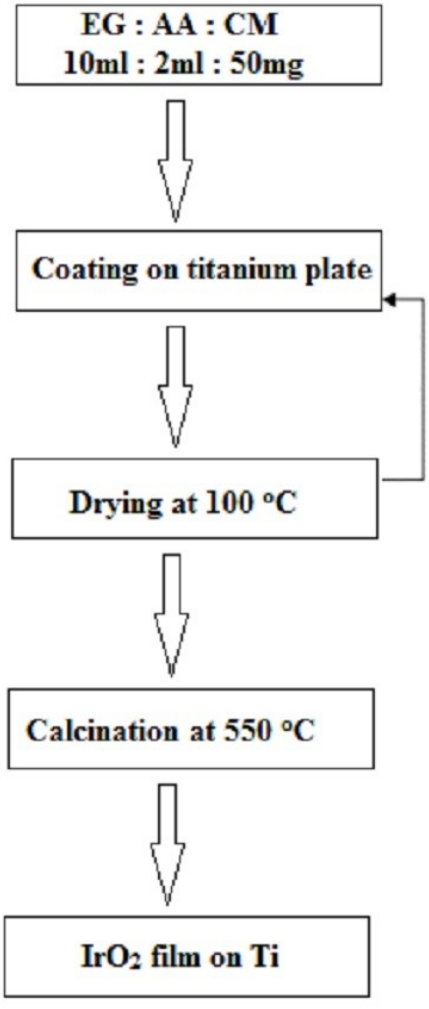

Figure 1: Procedure for IrO_2 coating on titanium.

from low and high Ir-content solution towards COD removal was also studied in this paper.

2 Materials and Methods

2.1 Coating Procedure

Pretreated titanium plates were coated with IrO_2 by thermal decomposition, complete procedure was given in previous study [6]. In this study we used 50 mg of $IrCl_3xH_2O$ in precursor 10 mL solution of ethylene glycol (EG) and acetic acid (AA). Pretreated Ti plate was coated with low Ir-content precursor solution at room temperature and dried at 100°C for 10 min after each application. After 10 applications Ti plate was heated at 450°C for 10 min and finally baked at 550°C for 2 h [6]. Flow diagram of coating procedure is given in Figure 1.

2.2 Analytical study of anode surface

Variable pressure field emission scanning electron microscopy (VP-FESEM) (CarlZeiss AG, Germany Model SUPRA 55VP) was used to study the surface morphology of the coated anode.

2.3 Electrochemical Cell

A laboratory scale electrochemical batch reactor with volume of 100 mL was used for electrochemical oxidation experiments for determination COD [4]. NaCl (1g/L) was used

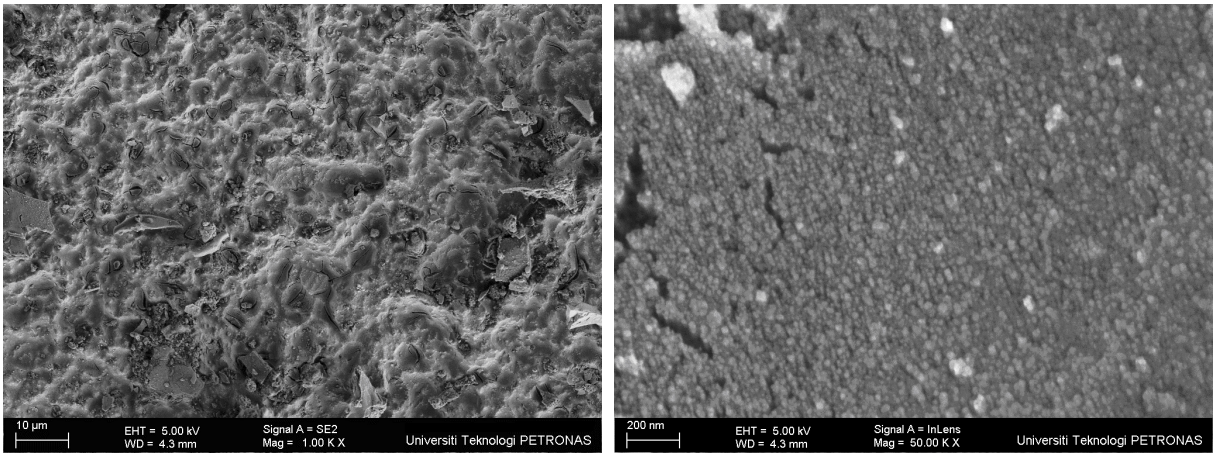

Figure 2: FESEM image (a) low and (b) magnification and (c) EDAX of Ti/IrO_2.

as the electrolyte. Three current densities (3.33, 6.66, 10 mA/cm^2) were applied for COD removal and electrolysis time was 4 h.

2.4 Sample preparation

Synthetic samples for COD were prepared from stock solution of polycyclic aromatic hydrocarbons (PAHs 100 µg/L in dichloromethane).

3 Results and Discussions

3.1 Properties of Ti/IrO_2 anode

Figure 2a and 2b shows the morphology and microstructure of Ti/IrO_2 surface at low and high magnifications prepared with low Ir-content solution. In previous study high Ir-content solution was used for IrO_2 coating [6]. Figure 2a and 2b do not show any particular surface structure and most of the surface remains uncoated. In Figure 2c higher Ti-peaks in EDAX spectrum confirmed that major part of surface is uncovered. In previous study surface is covered by a thin film of IrO_2 which appeared to have a rough morphology and does not exhibit cracked mud structure [6]. In Figure 3 XRD pattern at low Ir-content showed some small peaks of IrO_2 and sharp and wide peak of TiO_2. TiO_2 was formed during heating process. Structure of coated surface depends upon quantity of coating material in coating solution and drying and calcination temperature. IrO_2 precursor solution was easily dried at 100°C. Cracked mud surface usually formed when amount of coated material is high or high temperature is used for calcination.

3.2 COD removal

Electrocatalytic capability of Ti/IrO_2 anode was assessed by doing electrochemical oxidation experiments for COD removal. Anodes prepared with high and low Ir-content

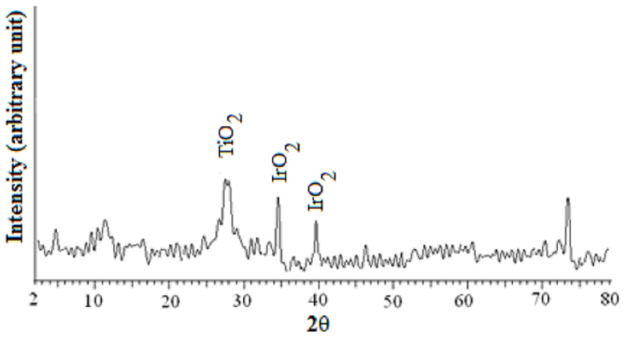

Figure 3: XRD of Ti/IrO_2 anode prepared with low content Ir-content.

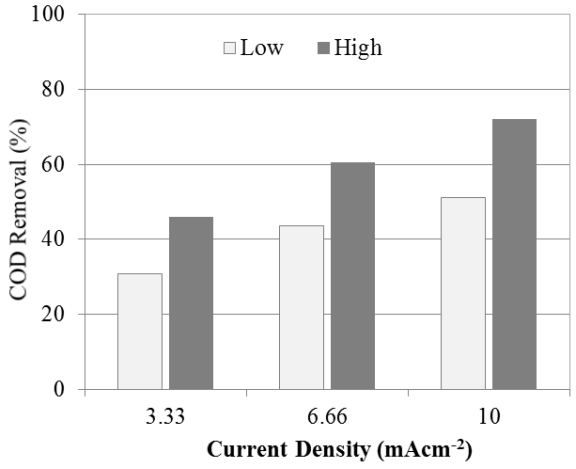

Figure 4: Comparison of low and high Ir-content Ti/IrO_2 anodes for COD removal at different current densities.

were applied for electrochemical removal of COD. Initial COD of synthetic solution was 750 mg/L. Figure 4 shows that removal of COD increased by increasing current density.

Ti/IrO_2 anode prepared with low Ir-content precursor solution showed COD removal of 31, 42 and 50% at 3.33, 6.66 and 10 mA/cm^2, respectively. While anode prepared with high Ir-content showed 48, 60 and 72% COD removal at 3.33, 6.66 and 10 mA/cm^2, respectively. Poor efficiency of low Ir-content anode was because of the formation of an insulating TiO_2 layer grown between Ti substrate and IrO_2 layer by oxidation of Ti substrate with oxidants [5]. Awad and Ghany [27] added ferrous ions (1 g/L Fe^{2+}) into a cosmetic wastewater for the generation of hydroxyl radicals which increases the COD removal efficiency upto 98% using modified Ti/IrO_2 anode. Similarly, Yang *et al.* [28] introduce ultrasound to get 94% COD removal. Coupling of advanced oxidation process can enhance the efficiency of anodes prepared from low Ir-content precursor.

4 Conclusions

Surface morphology of the anode showed that limited portion of Ti plate only was covered with IrO_2 using low Ir-content solution. Maximum COD removal was obtained at 10 mA/cm^2 current density. Performance of Ti/IrO_2 anode can be enhanced by increasing number of coating applications of low Ir-content precursor solution. It will also give more complete coverage of titanium plate.

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