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CATHODIC ELECTRODEPOSITION OF TITANIUM DIOXIDE FILMS

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ABSTRACT. A galvanostatic technique for deposition of nanocrystalline titanium dioxide thin films on titanium sheet was developed. This techniques is a two-stage process: 1) cathodic electrodeposition of titanium oxyhydroxide gel film from aqueous solution containing a Ti precursor and 2) subsequent heat-treatment of this gel film results in the formation of titanium dioxide film. The deposition current density and the pH of the electrolyte have a considerable effect on the formation of nanocrystalline film.

1. Introduction

Semiconductor photocatalytic reaction has been investigated extensively, with applications focussing on solar energy conversion and storage [1,2], reductive fixation of CO_2 [3-5], organic synthesis [6,7] or mineralization and/or detoxification of organic compounds [8-10]. Among semiconductors, titanium dioxide is one of the most popular and promising materials as a photocatalyst because it is stable in various solvents under photoirradiation, nontoxic, available commercially, and easy to prepare in the laboratory and has potent ability to induce various types of redox reactions.

In a series of studies on TiO_2 photocatalytic reactions [11-14] it has shown that the overall kinetics depend on both amount of substrate adsorbed on the surface to be reduced or oxidized by photoexcited electron (e^-) or positive hole (h^+), respectively, and rate of geminate recombination of e^- or h^+. To obtain highly active TiO_2 photocatalyst, therefore, it is necessary to give it, simultaneously, a couple of properties: large surface area to adsorb substrates and high crystallinity to diminish the e^- - h^+ recombination. When the semiconductor is a powder suspended in the wastewater, many pollutants, even at low concentrations (ppm), can be completely mineralized [15]. This method, however, cannot work continuously because, after the degradation process, the photocatalyst must be removed from the suspension, either by filtering or sedimentation, which can leave traces of particulate in the treated fluid. In this context, fixed bed photoreactors are more practical because they can work continuously. Moreover, when the support is a conducting one, the process efficiency can be improved by applying a suitable potential [16].

A TiO_2 photoanod can be obtained by sol-gel method (SGM) [17-22], chemical vapor deposition (CVD) [23], cathodic electrodeposition (CE) [24], electrochemical oxidation of titanium metal [25], anodic dissolution of titanium metal followed by cathodic photodeposition [26] or anodic oxidation of hydrolyzed $TiCl_3$ [27].

Our research focused on preparation of TiO_2 films by cathodic electrodeposition in galvanostatic conditions and study of its electrochemical behavior.

2. Experimental Section

Materials. Powder titanium (>98,5%) and plate titanium (99,99%) were supplied from Fluka AG. Ammonia (25%) was purchased from Reactivul - Romania and hydrogen peroxide (30%) from Chimopar- Romania. Sulfuric acid (97-98%) and potassium nitrate were supplied from Primexchim-Romania and Reactivul- Romania, respectively. Doubly distilled water was used to make the aqueous solutions throughout this study.

Preparation of titanium (IV) oxide precursor. In order to prepare the aqueous titanium oxysulfate solution, titanium powder was dissolved in H_2O_2 and ammonia (1:2 v/v) mixture.

$$H_2O_2 + HO^- \rightarrow HO_2^- + H_2O \tag{1}$$

$$Ti + 2HO_2^- + H_2O \rightarrow TiO^{2+} + 4HO^- \tag{2}$$

The excess H_2O_2 and ammonia was decomposed by heating the solution on a hot plate until a yellow colored gel was obtained. This yellow gel may be in monomeric or oligomeric form [28]. But, for simplicity, it was considered that this Ti (IV) species exists in monomeric form as mentioned in reaction 3.

$$TiO^{2+} + 2HO^- + xH_2O \rightarrow TiO(OH)_2 \cdot xH_2O \tag{3}$$

By dissolving the yellow gel in 2 M H_2SO_4 a red colored solution was obtained.

$$TiO(OH)_2 \cdot xH_2O + H_2SO_4 \rightarrow TiOSO_4 + (2+x)H_2O \tag{4}$$

This red solution was used as the stock solution for further deposition. The concentration of titanium oxysulfate solution was determinate by spectrophotometric method [29].

Cathodic electrodeposition of TiO_2 thin films. For electrochemical experiments a potentiostat/galvanostat (PS3 Meinsberg, Germany) and a three electrodes cell were used. A Pt-foil as the counterelectrode and a saturated calomel electrode (SCE) as reference electrode were used. The substrate for

TiO_2 thin film was a 10x10-mm titanium sheet. Before electrodeposition, the titanium plates were introduced in HCl (37%) : H_2O (1:1 v/v) solution, for 30 min. and then, washed by water and ethanol. The deposition electrolyte contained both Ti precursor and KNO_3. The concentration of nitrate ions was at least equal with TiO^{2+} concentration. Due to the reduction of nitrate ions at potentials more negative than – 0,9 V, the hydroxyl ions were generated as shown in reaction (5):

$$NO_3^- + 6H_2O + 8e^- \rightarrow NH_3 + 9OH^- \tag{5}$$

The generation of OH^- ions increased the local pH at the electrode surface resulting in the $TiO(OH)_2 \cdot xH_2O$ gel film formation on the electrode, reaction 3 [24]. The gel films were prepared in galvanostatic conditions, at 10, 15, 20 and 25 mA/cm^2 and different pH values (0,5; 2).

Thermal treatment of the obtained gel film. The gel films obtained in the preceding step was heat-treated at 400º C, for 30 min, to form TiO_2 film (reaction 6):

$$TiO(OH)_2 \cdot xH_2O \xrightarrow{\Delta} TiO_2 \tag{6}$$

Measurement techniques. Cyclovoltammetric measurements were performed with a PGSTAT 10 AUTOLAB computer-controlled potentiostat driven by Model GPES 4.4 electrochemical analysis software. A single – compartment cell with a working electrode, consisting of approximately 19 mm^2 of a TiO_2/Ti and a Pt-plate as counter-electrode was used. A Pt-wire served as a quasi-reference electrode. The measurements were carried out in the 1M $LiClO_4$ / acetonitrile.

X-ray diffraction measurements were made using a DRON 3M X-ray diffractometer using a Co (Co K_α λ = 1,7902Å) anode.

The morphology and thickness of TiO_2 films were observed using scanning electron microscopy (type Leica Cambridge Instruments S 360) with an accelerating voltage of 5 kV.

3. Results and Discussion

In the figure 1, cyclic voltammograms on the TiO_2/Ti electrode in $LiClO_4$/ acetonitrile solution with different lithium ion concentrations are shown. The potential scan was carried out in the potential range 0 to –3 V with scan rate of 10 mV/s. On the cathodic scan, when the potential was scanned till –3V, two broad peaks are seen and on the anodic scan two humps are seen. This shows that two redox reactions are involved. One must be reaction 7 and the other is probably lithium reduction/oxidation (reaction 8).

a) $Ti^{4+} + e^- \rightarrow Ti^{3+}$ (7)

b) $Li^+ + e^- \rightarrow Li$ (8)

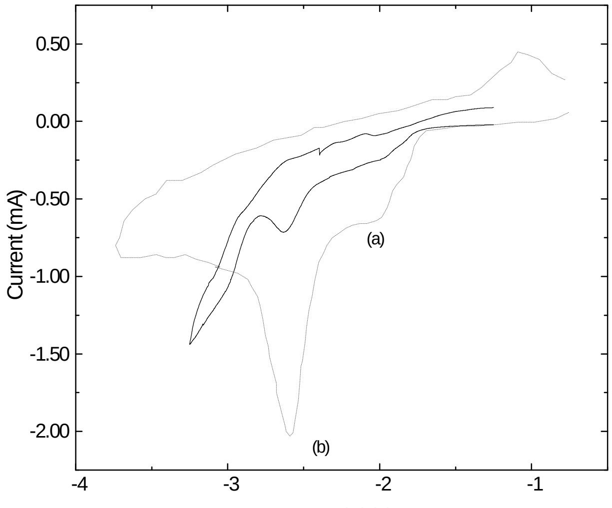

Figure 1. Voltammograms of TiO_2 films (deposited at 20 mA/cm^2, pH =0,5 and 25^{0}C) in $LiClO_4$/acetonitrile at different lithium ion concentrations

Using an electrolyte solution with 0.5M lithium ion concentration, a twice decreasing of the cathodic peak intensity to –1.9V was observed; this confirm that this peak (b) corresponds to Li reduction.

Table 1 shows that the optimal current intensity for the electrodeposition of the TiO_2 films is 15 mA/cm^2, the cathodic peak being at least twice higher than of those deposited at others current densities.

Table 1.

Ti^{4+} reduction peak intensities measured in 1M $LiClO_4$ (sweep rate 10 mV/s) of TiO_2 electrodes obtained at different current densities, in 1.25 M $TiO(SO_4)$ solution, pH =0,5 at 25^{0}C

Current density [mA/cm^2]	Cathodic peak intensity [mA]
10	0.38
15	3.56
20	0.64
25	1.25

The voltammograms of TiO_2 films obtained at two different pH values of $TiO(SO_4)$ solution (fig. 2) show that the cathodic peak of titanium ions (IV) deposited in aqueous titanium oxysulfate solution with pH=0,5 is three times higher than that obtained in electrolyte with pH=1,95. It means that the more acidic solution favours the preparation of a thicker film.

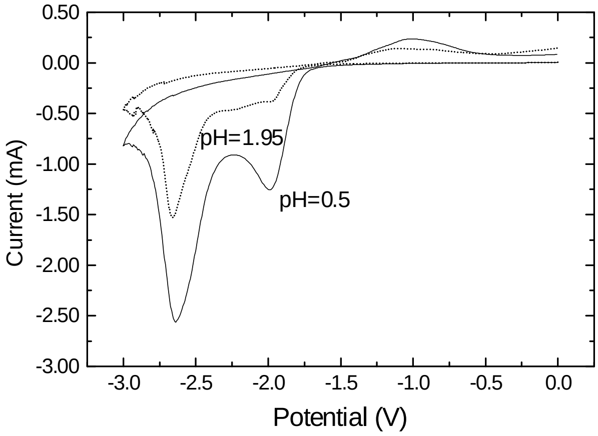

Figure 2. Voltammograms of TiO_2 films (obtained at two pH values of $TiO(SO_4)$ solution, 25mA), in 1M $LiClO_4$ / acetonitrile, at 25° C (v=10 mV/s)

Fig. 3 shows a linear relationship between the TiO_2 film thickness and the number of coating cycles. The line does not go through the origin due to the fact that the films from the second and subsequent coatings formed on previously formed material, while the first coating formed on the titanium substrate. The thickness of the first coating is about 0.15μm, while the average film thickness per coating cycle from the second coating onward is estimated to be about 0.08μm. The thickness was measured using scanning electron microscopy and the weight method.

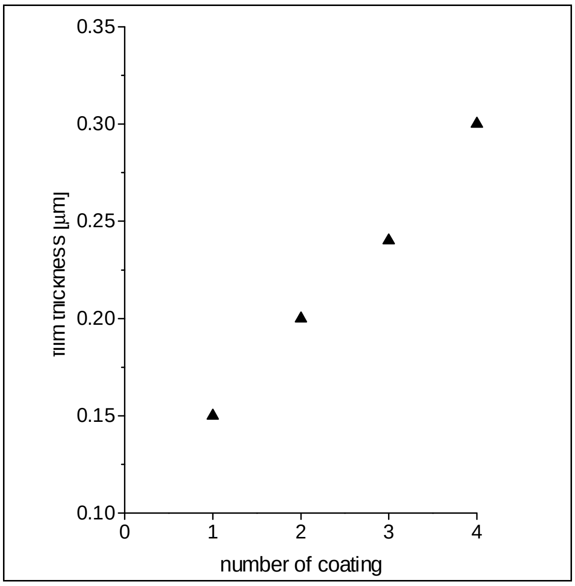

Figure 3. Relationship between film thickness and number of coating cycles (pH=0.5; i =15mA/cm^2; 25° C)

X-ray diffraction of the films deposited at 15 mA/cm^2 showed the formation of TiO_2 - anatase films (fig.4).

Fig. 5 presents the scanning electron microscopy of the surface of TiO_2 film deposited on titanium by 4 coating cycles. It is observed that the TiO_2 film has a nanocrystalline structure.

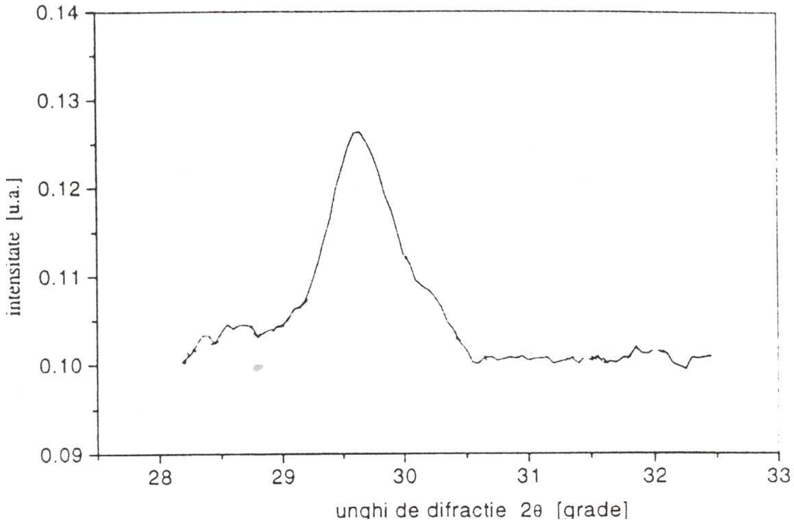

Figure 4. X-ray diffraction of the films deposited at 15 mA/cm^2 (pH=0.5; i =15mA/cm^2; 25^o C)

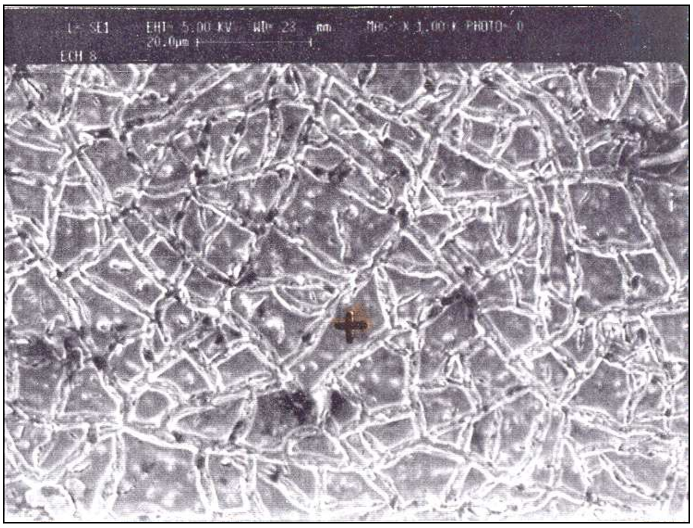

Figure 5. Scanning electron microscopy of the surface of TiO_2 film deposited on titanium by 4 coating cycles (pH=0.5; i =15mA/cm^2; 25^o C)

Conclusions

The results showed that by cathodic electrodeposition of titanium oxyhydroxide gel film from aqueous solution containing a Ti precursor, followed by heat-treatment of the gel film, nanocrystalline titanium dioxide-anatase thin films are obtained.

The optimal current density for electrodeposition of TiO2 films is 15 mA/cm^2.

The better pH value of aqueous titanium oxysulfate solution used to electrodeposition of TiO_2 films is 0,5.

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