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Novel Ti/Ta₂O₅-SnO₂ electrodes for water electrolysis and electrocatalytic oxidation of organics

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Abstract

Mixed metal oxide (MMO) electrodes have been applied to different technologies including chlorine production, organic compounds oxidation, water electrolysis, electroplating, etc. due to their catalytic, optical and electronic properties. Most of the existing MMO electrodes contain either toxic metals or precious metals of the platinum group. The aim of this study was to develop environmentally friendly and cost-effective MMO electrodes for water and organic compounds oxidation. Ti/Ta₂O₅-SnO₂ electrodes of different nominal composition were prepared, and electrochemically and physically characterized. For water oxidation, Ti/SnO₂ electrode with 5 at.% of Ta produced the highest electroactivity. Ti/SnO₂ electrode with 7.5 at.% of Ta showed the best performance for the oxidation of methylene blue (MB). The electrocatalytic activity of the Ti/Ta₂O₅-SnO₂ electrodes increased with the number of active layers. The maximum current of water oxidation reached 3.5 mA at 2.5 V when the electrode

was covered with ten layers of Ta₂O₅. In case of the oxidation of 0.1 mM MB, eight and ten active layers of Ta₂O₅ significantly increased the electrode activity. The prepared electrodes have been found applicable for both water electrolysis and organic compounds oxidation.

Keywords: Electrocatalytic oxidation; mixed metal oxide (MMO) electrodes; water electrolysis

1. Introduction

Mixed metal oxide (MMO) electrodes occupy an important place in many technological processes. They are widely used for the production of chlorine and oxygen and find extensive applications in electroplating, solar cells and supercapacitors [1-8]. For example, they are efficient electrodes for sustaining the oxygen evolution reaction (OER), which is of great importance in water electrolyzers, rechargeable batteries, and zinc, copper, cobalt and nickel electrowinning processes. MMO electrodes have also been applied for electrochemical and, in particular, electrocatalytic oxidation of refractory organic compounds in wastewaters [9-13]. The conventional composition of MMO electrodes consist of a base metal substrate, a protective passivating layer and the actual electrocatalyst [14]. The most common electrodes for water and organic compounds oxidation are Ti/Ta₂O₅-IrO₂, Ti/SnO₂-IrO₂, Ti/IrO₂-SnO₂-Sb₂O₃, Ti/RuO₂-IrO₂, Ti/Sb₂O₅-SnO₂, Ti/SnO₂-Sb₂O₅-RuO₂, and Ti/TiO₂-IrO₂ [15-20]. All these electrodes have a Ti substrate, because of its mechanical stability and uniform current distribution. In addition, they contain either a significant amount of platinum-group metal oxide electrocatalysts, such as IrO₂ and RuO₂, which are expensive or the Sb₂O₅ electrocatalyst, which is toxic to the environment. Refractory metal oxides such as Ta₂O₅ and TiO₂ are often used as passivating layers. Thus, the development of cost-effective and environmentally friendly metal oxide electrodes for water and organic compounds oxidation is desirable. To the best of our knowledge, there are no reports on the electrochemical oxidation of water and organic

compounds on Ti/Ta₂O₅-SnO₂ electrodes. Therefore, in this study, several Ti/Ta₂O₅-SnO₂ electrodes were prepared and structurally characterized. Water electro-oxidation was investigated in sodium sulfate solutions. In the same way, the electro-oxidation of methylene blue (MB) was studied as an example of organic compounds oxidation. Na₂SO₄ was chosen as the supporting electrolyte because of its neutral and non-corrosive properties in aqueous medium. MB was selected for the investigation of the catalytic oxidation activity of Ti-supported Ta₂O₅-SnO₂ electrodes because it is a typical representative of complex organic compounds with aromatic structure, which in addition is extensively used as a food and paper colorant, textile dye and bacteriology stain in human and veterinary medicine [21, 22].

2. Experimental

2.1. Electrode preparation

Several Ti/Ta₂O₅-SnO₂ electrodes were prepared by thermal decomposition of precursor solutions on titanium substrates [23]. The nominal composition Ta(*x*) - Sn(100 - *x*) of electrodes was modified by changing the *x* value from 0 atom (at.)% till 50 at.% Ta. The total concentration of metal ions was kept constant and was equal to 0.04 M.

In the preparation of the precursor solutions, stoichiometric amounts of tantalum (V) chloride (99.99% trace metal basis, Sigma-Aldrich) and tin (II) chloride 2-hydrate (pro analysis, Panreac) were dissolved in 10 ml of absolute ethanol (pro analysis, Panreac), stirred and refluxed for one hour at 80 °C. Titanium plates (99.7% trace metals basis, Sigma-Aldrich) were pretreated by degreasing in 10 wt% NaOH for 15 s, etching in boiled 18 wt% hydrochloric acid (pro analysis, Fluka) for 10 min, and rinsing with ultrapure water (18.2 MΩ ·cm, Millipore). The precursor solution was applied on the pretreated dry substrates by drop casting. A volume of 80 µL of the precursor solution was dropped on the titanium surface, dried at 80 °C for 5 min, allowing for the

complete solvent evaporation, and finally annealed at 550 °C for 5 min. This procedure was repeated for both electrode sides. In the following, the term layer will be employed to refer to the ultrathin film deposited on the titanium substrate upon the application and thermal decomposition of 80 µL drop of the precursor solution. This procedure was repeated until the desired number of layer was reached. After the last layer formation, each electrode was additionally annealed at the same temperature for 10 hours in order to generate Ta₂O₅-SnO₂ composite oxide structures on the electrode surface.

2.2. Physicochemical and Electrochemical Characterization of the Electrodes

The crystal structure of the electrodes was analyzed by X-Ray diffraction (XRD) spectroscopy. Scanning electron microscopy (SEM Hitachi S-3000N) coupled to X-ray detector (Bruker XFlash 3001) for energy-dispersive X-Ray (EDX) microanalysis and mapping was used to study the surface texture and bulk composition of the electrodes.

The electrochemical characterization of Ti/Ta₂O₅-SnO₂ composite electrodes was conducted by using cyclic voltammetry (CV) measurements. All the experiments were performed in a three electrode cell (200 ml) with computer-controlled Autolab PGSTAT30 and PGSTAT12 potentiostats. Both potentiostats were controlled by GPES EcoChimie software. A coiled platinum wire was used as a counter electrode and an Ag/AgCl/KCl (sat) electrode as a reference electrode. Unless otherwise stated, all the potentials are quoted versus this reference electrode. CV measurements were performed between 0.2 and 2.5 V potential limits at a scan rate of 50 mVs⁻¹. Before each measurement, working electrodes were electrochemically pretreated by conditioning them at potentials of 0.2 V for 15 s and 1.2 V for 5 s. All the working electrodes had the same surface area of 2.4 cm², which was controlled with Teflon ribbon.

CV was carried out at room temperature in supporting electrolyte solutions (blank solution) of 0.1 M Na_2SO_4 (anhydrous ACS reagent, Sigma-Aldrich) and in aqueous solutions of 0.1 M Na_2SO_4 and 0.1 mM MB (Certistain, Merck) hereafter referred to as the working solution. Solutions were deoxygenated by argon bubbling before every CV measurement.

3. Results and discussion

3.1. SEM and EDX analyses

SEM images of $\text{Ti}/\text{Ta}_2\text{O}_5$, Ti/SnO_2 and $\text{Ti}/\text{Ta}_2\text{O}_5\text{-SnO}_2$ electrodes and EDX element mapping of the electrode with a nominal composition $x = 7.5$ at.% Ta are shown in Fig. 1. As can be seen from Fig. 1k, in the case of 7.5 at.% Ta electrode, Sn uniformly covers the Ti substrate (Fig. 1l), while Ta deposition (Fig. 1j, 1i) is less homogeneous. The size of the resulting Ta_2O_5 particles varied from a few nanometers (particles regularly distributed on the SnO_2 films) to a few micrometers forming islands (bright white spots) on the electrodes surface. The surface of the electrodes had a slightly cracked structure as is the case for many MMO electrodes [24-26]. In the absence of Sn (Fig. 1a), the surface of the electrode was porous and rough, whereas in the absence of Ta (Fig. 1b), the surface was flattened and pores were clogged. As expected, when the number of active layers of Ta additive increases, the density of Ta_2O_5 crystals on the surface also increases, resulting in partial roughness recovery (Fig. 1c – 1e, g). The porosity of the electrodes was influenced by the number of deposited active oxide layers, although a tendency was not clearly observed (Fig. 1f – h).

The bulk composition of $\text{Ta}_2\text{O}_5\text{-SnO}_2$ thin films was determined by EDX microanalysis. Table 1 represents the data comparing atomic ratios obtained by EDX analysis with the nominal atomic ratios. Most of the analyzed electrodes consist of eight $\text{Ta}_2\text{O}_5\text{-SnO}_2$ oxide layers. These electrodes show a reasonably good agreement between EDX and nominal Sn/Ta atomic ratios.

When increasing the amount of Ta in thin films, Sn/Ta ratio decreased. It seems that films became enriched with Sn when the electrode had ten oxide layers while a significant enrichment in Ta was observed for the 4-layer electrode.

Table 1

Comparison of nominal and experimental atomic ratios of Ti /Ta₂O₅-SnO₂ electrodes

Ta at. %	Number of active layers	Sn/Ta atomic ratio	
		EDX	Nominal
50.00	8	0.68	1
25.00	8	2.14	3
12.50	8	5.55	7
7.50	4	6.41	12.33
7.50	8	12.05	12.33
7.50	10	15.78	12.33

3.2. XRD analysis

XRD analysis was used to study the crystal structure of obtained thin films electrodes. XRD patterns of Ti/Ta₂O₅-SnO₂ thin films are shown in Fig. 2. All patterns contained intense peaks corresponding to the hexagonal Ti substrate appearing at $2\theta = 38.422, 40.171, 53.005, 62.951, 70.663, 76.221, 77.370, 82.292$ and 92.732° associated to the (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), (2 0 1), (0 0 4) and (1 0 4) crystal orientations of titanium. TiO₂ was evidenced through the presence of (1 1 0), (0 0 4), (-1 -1 2), (-1 -1 4), (3 0 0) and (3 0 4) reflections. It was formed due to the oxygen solubility in the metal lattice of the substrate [27]. All the electrodes except those with $x = 50.0$ and 7.5 at.% (8 layers) revealed the presence of tetragonal rutile with

peaks corresponding to (1 1 0), (1 0 1), (1 1 1) and (2 1 1). The low intensity of the TiO_2 peaks can be attributed to a low crystallinity of the formed TiO_2 . The absence of TiO_2 in the electrodes of nominal composition $x = 50.0$ and 7.50 at.% could be explained by the dense Ta_2O_5 - SnO_2 coating obtained (see Fig. 1c, 1f), which prevented extensive Ti oxidation and as a result improved electrocatalytic activity of $\text{Ti}/\text{Ta}_2\text{O}_5$ - SnO_2 electrodes (see below).

XRD patterns also showed the reflections corresponding to the (1 1 0), (1 0 1) and (2 1 1) atomic planes typical of the tetragonal rutile SnO_2 structure [28]. Tantalum was mostly represented by orthorhombic Ta_2O_5 with main peaks corresponding to the (0 0 1), (1 11 0), (2 8 0), (1 11 1), (0 0 2) and (3 10 1) planes. However, the electrode of nominal composition $x = 7.5$ at.% (8 layers) contained only hexagonal β - Ta_2O_5 with peaks corresponding to the (0 0 1), (1 0 0) and (1 0 1) planes. The absence of Ta_2O_5 peaks in the XRD diffractograms of the $\text{Ti}/\text{Ta}_2\text{O}_5$ and $\text{Ti}/\text{Ta}_2\text{O}_5$ - SnO_2 ($x = 7.5$ at.%, 4 layers) electrodes and that of SnO_2 peaks in the diffractograms of $\text{Ti}/\text{Ta}_2\text{O}_5$ - SnO_2 ($x = 50.0$ at.%) is probably attributed to the low crystallinity of the formed oxides.

3.3. Cyclic voltammetry

Fig. 3a shows the CV results of prepared $\text{Ti}/\text{Ta}_2\text{O}_5$ - SnO_2 , Ti/SnO_2 and $\text{Ti}/\text{Ta}_2\text{O}_5$ electrodes in a 0.1 M Na_2SO_4 solution. It is found that both $\text{Ti}/\text{Ta}_2\text{O}_5$ and Ti/SnO_2 electrodes do not have enough conductivity to generate significant currents associated to the OERs in the potential range of 0.2 to 2.5 V. This is because both Ta_2O_5 and SnO_2 are wide band gap n-type semiconductors, i.e. no anodic reactions occur up to several volts versus SHE [29, 30].

When the amount of Ta (V) ions was increased to 2.5 at.% in the precursor solution, the OER current increased by a factor of 3.5 (from 0.08 mA to 0.27 mA at 2.5 V). A rise of Ta content till a nominal composition of $x = 5$ at.% increased the OER current by a factor of 75 , and thereby

showed the highest electroactivity toward water oxidation. As it is seen in the inset of Fig 3a, 7.5 Ta at.% apparently yielded a very low current of 2 mA after 5 at.%. At about 25 at.%, the current decreases to half the maximum value. At 50 at.%, no significant OER current is observed. This behavior suggests that Ta addition to a limited extent improves the carrier density and decreases the resistivity of SnO₂ films [31, 32].

Fig. 3b presents CVs (third cycles) recorded on Ti/Ta₂O₅-SnO₂, Ti/SnO₂ and Ti/Ta₂O₅ electrodes in 0.1M Na₂SO₄ + 0.1mM MB aqueous solutions. All voltammograms show anodic current peaks or shoulders which were absent in the blank voltammograms (Fig. 3a). At the same time, Ti/SnO₂ and Ti/Ta₂O₅ electrodes did not produce anodic currents except for those corresponding to the OER (see inset in Fig. 3b). However, the inclusion of Ta in SnO₂ films with Ta in an amount of 5 at.% enhanced the electrode activity towards MB oxidation. Anodic currents at potentials more positive than 1 V were observed due to the oxidation of MB. The oxidative activity of the electrodes reached a maximum at a Ta content of 7.5 at.%. The corresponding film was constituted only by β -Ta₂O₅ as deduced from the appearance of the (0,0,1), (1,0,0) and (1,0,1) diffraction peaks (Fig. 2). Therefore, it can be speculated that the presence of hexagonal β -Ta₂O₅ enhances the electrocatalytic activity of the Ta₂O₅-SnO₂ electrode film.

The increase of the oxidative activity coincides with a split of the MB oxidation peak. The first peak at 1.15 V is considered to display the electrocatalytic properties of the prepared electrodes and to correspond to the initial MB oxidation. At this potential electro-oxidation of MB perhaps occurred by the generation of nascent oxygen on the oxide surface, which would cause the formation of oxidation products [33]. These initial oxidation products would be further oxidized at potentials around 1.6 V. Electrochemical reactions taking place at potentials more positive than 1.6 V vs. Ag/AgCl were probably assisted by OER.

The relatively reversible currents at potentials 0.3 - 0.5 V are assigned to pseudo-capacitive processes. Comparing Figs. 3a and 3b, it may be concluded that the appearance of these currents is connected to the MB adsorption/desorption process on the electrodes surface. Further increase of Ta dopant in the thin films of SnO₂ over 7.5 at.% gradually decreased the electrocatalytic oxidation activity of the electrodes and shifted the onset potential for the OER to higher values. In this regard, we speculate that Ta₂O₅ could be responsible for both the electrocatalytic activity of the electrodes (anodic peaks at potentials more positive than 1 V) and the adsorption of MB (voltammetric signals at potentials in the range 0.3 – 0.5 V). The strong adsorption of MB on Ta₂O₅ active centers induced by a high Ta content in the surface films would block the catalytic activity of the electrodes with nominal composition $x > 7.5$ at.%. Moreover, the XRD analysis of the electrodes with nominal composition $x > 7.5$ at.% (Fig. 2) showed a low content of hexagonal β -Ta₂O₅, which may be related to their low electrocatalytic activity.

Several electrodes with a nominal composition of 7.5 Ta at.% were prepared with different number of oxide layers to assess the impact of the coating thickness on the electrocatalytic activity of the electrodes. Fig. 4 shows CVs for electrodes with different numbers of oxide layers in the absence and in the presence of MB. As the number of layers increases, the onset potential for the OER shifts to more negative values, and the currents generated by OER increase (see inset Fig. 4a). The inset of Figure 4a shows that for one active layer the potential needed to generate a 0.25 mA current is the most positive one (2.6 V) while increasing the number of active layers reduces the required potential from 2.6 V to less than 2 V. For currents equal to 0.5 and 0.8 mA the overpotential of OER decreased by 110 mV for ten-layer electrodes compared to the one layer electrode. Obviously at constant potential, the activity of the electrodes also increased with the number of layers.

The maximum current reached 3.5 mA for 10 active layers of Ta-doped SnO₂ electrode at 2.5 V. On the other hand, its electrocatalytic activity for MB oxidation (Fig. 4b) was similar to that of the 8-layer electrode. However, the peak profiles of the MB oxidation process are different for the 8 and 10-layer electrodes, indicating slight differences in their electrocatalytic activity. The current generated at potentials more positive than 1.6 V was mainly used for water oxidation. While running CVs with this electrode in the working solution, the height of the anodic peaks decreased with each scan (see inset in Fig. 4b). It can be explained by poor mass transfer at the surface of the electrode derived from the low concentration of the dye. During the first scan the MB coverage on the electrode surface was high, and thus the oxidation current was also high. However, with each subsequent scan, the coverage of MB decreased together with the anodic oxidation peaks. Moreover, the CV profiles corresponding to the OER recorded in the working solution were shifted towards positive potentials with respect to those of the blank solution. Therefore, poor mass transfer was also aggravated by fouling the electrode with degradation products of MB leading to the formation of organic films on the electrode surface, as is frequently the case for MMO [34, 35].

To check the reproducibility of these results and the ability of electrodes to recover their electrocatalytic activity some post treatment procedures were applied to the Ta-doped SnO₂ electrodes of nominal composition $x = 25$ at% and 37.5 at%. The chosen electrodes were: i) submitted to 10 voltammetric cycles between 0.2 and 2.5 V in the blank solution, ii) annealed at 550 °C for 1 hour, iii) cleaned in a ultrasonic bath (FinnSonic M08, 200 W, 40 kHz) for 30 minutes. CV measurements were recorded after each treatment both in the blank solution and in the working solution. Since both electrodes showed a similar trend of the recovery of electrocatalytic activity, the post-treatment measurements are shown only for Ta 37.5 at%.

Figure 5 shows the effect of different treatment methods on the electroactivity recovery. All the treatment applied to the electrodes demonstrated either a partial or a complete recovery of the electrocatalytic activity towards MB oxidation. As can be seen on Fig. 5a, in the blank solution, the onset potential for water oxidation shifted by 10 mV to less positive values after cleaning in the blank solution or applying the ultrasonic treatment and by 130 mV after the thermal annealing procedure. The Fig. 5b shows that onset potentials of anodic oxidation process shifted to more negative values by up to 400 mV, showing a significant activation of the MB oxidation process and hence improvement of the electrocatalytic properties of the electrode. Insets in Figure 5 show that electrode annealing at 550 °C is the most effective way to recover the electrode. The electro-activity towards water electrolysis (Fig. 5a) of the electrode increased five times from 0.7 mA to 3.5 mA and more than two times towards MB oxidation (Fig. 5b). Electrochemical cleaning in the blank solution slightly increased OER currents. However, it did not recover the electrocatalytic activity towards MB oxidation and cannot be recommended as a treatment procedure. Ultrasonic treatment appears to be a good way to clean the electrode due to increase of electro-activity towards both water oxidation and MB oxidation.

4. Conclusions

New Ti/Ta₂O₅-SnO₂ electrodes were developed and the electrocatalytic activity of Ta₂O₅ in synergy with SnO₂ was revealed. It is interesting to notice that changes in both metal concentration in the precursor solutions and number of active electrocatalytic layers strongly affects the electrochemical properties of the MMO electrodes, demonstrating the effect of doping on metal oxides. Hexagonal β -Ta₂O₅ was suggested as the phase responsible for the enhanced electrocatalytic activity towards the organic compounds oxidation process, whereas Sn is a cost-effective replacement of Ir in Ti/Ta₂O₅-IrO₂ electrodes. Moreover, the amount of Ta used in the

electrodes is relatively small. The electrodes showed good regeneration of their activity after thermal, ultrasonic and electrochemical treatment procedures. Besides, thermal treatment improved the electrochemical properties of the electrodes towards water oxidation by shifting potential of OER to more negative values. Therefore, Ti/Ta₂O₅-SnO₂ electrodes have been found applicable for both OERs and electrocatalytic oxidation of organic compounds and may further find application in the environmental protection and energy sectors.

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Fig. 1. SEM images of (a) Ti/Ta₂O₅, (b) Ti/SnO₂, and Ti/Ta₂O₅-SnO₂ electrodes of different nominal composition: (c) 50.0 at.%, (d) 25.0 at.%, (e) 12.5 at.% and (f) – (l) 7.5 at.% with different number of active deposited layers: (f) 4 layers, (g) 8 layers and (h) 10 layers; element-mapping for the electrode with x = 7.5 at.%: (i) total mapping, (j) Ta mapping, (k) Sn mapping and (l) Ti mapping.

Fig. 2. X-Ray diffractograms for Ti/Ta₂O₅, Ti/SnO₂, and Ti/Ta₂O₅-SnO₂ thin film electrodes

Fig. 3. Cyclic voltammograms of Ti/SnO₂, Ti/Ta₂O₅ and Ti/Ta₂O₅-SnO₂ electrodes in (a) 0.1 M Na₂SO₄ and (b) 0.1 M Na₂SO₄ and 0.1 mM MB; $\nu = 50 \text{ mVs}^{-1}$. The amount of active oxide layers is eight. Inset Fig. 3a: Cyclic voltammetry current at 2.5 V vs. atomic Ta content for Ti/Ta₂O₅-SnO₂ electrodes. Inset Fig. 3b: Cyclic voltammograms of Ti/SnO₂, Ti/Ta₂O₅ and Ti/Ta₂O₅-SnO₂ electrodes of nominal composition x = 2.5 at% in 0.1 M Na₂SO₄.

Fig. 4. Cyclic voltammograms of Ti/Ta₂O₅-SnO₂ electrodes of nominal composition x = 7.5 at.% and different number of active layers in (a) 0.1 M Na₂SO₄ and (b) 0.1 M Na₂SO₄ and 0.1 mM MB; $\nu = 50 \text{ mVs}^{-1}$. Inset Fig. 4a: Cyclic voltammetry potential required for attaining different currents by Ti/Ta₂O₅-SnO₂ electrodes with different number of active layers in 0.1 M Na₂SO₄; $\nu = 50 \text{ mVs}^{-1}$. Inset Fig. 4b: Different voltammetric cycles for Ti/Ta₂O₅-SnO₂ electrodes with eight active layers in 0.1 M Na₂SO₄ and 0.1 mM MB (scan 1-3) and third scan in 0.1 M Na₂SO₄ (blank); $\nu = 50 \text{ mVs}^{-1}$.

Fig 5. Cyclic voltammograms of Ti/Ta₂O₅-SnO₂ electrodes of the nominal composition x = 37.5 at.% in (a) 0.1 M Na₂SO₄ and (b) 0.1 M Na₂SO₄ and 0.1 mM MB (1) before and after cleaning by (2) cycling in the blank solution, (3) ultrasonic irradiation or, (4) annealing, $\nu = 50 \text{ mVs}^{-1}$. Insets: Cyclic voltammetry current produced by Ti/Ta₂O₅-SnO₂ electrode of nominal composition x = 37.5 at% in (a) 0.1 M Na₂SO₄ at 2.5 V and (b) 0.1 M Na₂SO₄ and 0.1 mM MB at 1.2 V after different treatment.

Figure 3a

Figure 3b

Figure 4a

Figure 4b

Figure 5a

Figure 5b

Figure 3a black and white

Figure 3b black and white

Figure 4a black and white

Figure 4b black and white

Figure 5a black and white

Figure 5b black and white