

## Electrochemical Characteristics of the Anodized Titanium Oxide Films in Sulfuric Acid

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### ABSTRACT

This article presents some research into titanium electrode anodizing in H<sub>2</sub>SO<sub>4</sub> solutions in the potential range -1 to 5 V at different scan rates (10, 50, 100 mV s<sup>-1</sup>) using cyclic voltammetry measurements. Linear potentiodynamic measurements had used before and after the oxide layer formed on the titanium surface. The characterization and the exact determination of the titanium oxides species on the Ti substrate surface had performed by XRD and SEM-EDS analyses. Three characteristic oxide peaks appeared in the electrochemical measurements. These had observed at 0.2 V, 2.3 V, and 3.5 V on cyclic voltammetry curves at all scan rates for all H<sub>2</sub>SO<sub>4</sub> concentrations. Even more, cyclic voltammetry measurements showed that all peaks observed were evident even at higher scan rates. That suggested that robust oxidation of the Ti surface had occurred. Voltammetric tests showed that the passivation of the titanium surface was effective. XRD and SEM-EDS measurements confirmed the existence of TiO<sub>2</sub> species in a crystalline form on the titanium surface after anodizing in 3M H<sub>2</sub>SO<sub>4</sub> and annealing the anodized Ti electrode at 400 °C in the airflow. A significant increase in the loading of TiO<sub>2</sub> film annealed at 400 °C of the previous anodized Ti anode in H<sub>2</sub>SO<sub>4</sub> was registered.

## 1. INTRODUCTION

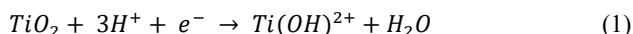
The exact nature of formed protective oxide films on the titanium surface during the anodization process is still not well known, even though, in the study of surface modifications, many of the latest techniques for the investigating of properties of such films have been used.<sup>1-9</sup> For oxide films formed at high voltages (>50 V), the existence of both crystal phases rutile, and anatase is evidence. For the formed films on the lower-voltage (<10 V) there are more uncertainties in interpretations of one or more of three natural crystal modifications of oxides (rutile, anatase, and brucite). Therefore, a series of different oxides of low-valent titanium is present in the oxide film.<sup>10-14</sup> The thin anode films on titanium surfaces, predominantly amorphous structure have been found in previous studies.<sup>15</sup> In the oxide film: TiO, Ti<sub>2</sub>O<sub>3</sub>, and Ti<sub>3</sub>O<sub>5</sub> oxides can be present depending on whether the oxidation process is carried out chemically (in the airflow in H<sub>2</sub>SO<sub>4</sub>, HCl, HNO<sub>3</sub>, or NaCl solutions) or electrochemically (anode polarization at low or high potentials). Energy-dispersive X-ray spectroscopy (EDX) or transmission electron microscopy (TEM) of the anodized oxide films has shown that the nature of TiO<sub>2</sub> film is also amorphous.

Therefore, the presence of the anatase crystals depends on the anode potential.<sup>16, 17</sup> The disagreements related to the morphology, increase in thickness, and crystallographic structure of the surface titanium oxides can result from differences in the surface preparation, type of solvent, methods of preparation, and conditions of growth of crystals.<sup>18-22</sup>

Literature data show the dependence of oxide film structure on the rate of film thickness growth. It has also suggested that the degree of solubility of films increases significantly with a

slight increase in the oxide film thickness.<sup>23</sup> It has also been shown that the films formed at a scan rate of 1 mV s<sup>-1</sup> dissolve almost ten times more slowly than those at 1 V s<sup>-1</sup>. The most likely explanation for this effect is that the aging of slowly growing films leads to a denser crystalline structure with an accompanying increase in a barrier height for ions migration.

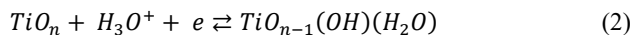
Electrochemical dissolution of the passive film occurs at the boundary of the oxide-solution phase, according to equation (1), where the dissolution is not localized.<sup>24</sup>



The electrochemical parameters significantly influence the behavior and characteristics of titanium oxide growth. The growth of the oxide film thickness results in systematic changes in surface topography, especially in the pore surface configuration. Anionic incorporation into the oxide film will not change the chemical composition, crystals type, or the titanium oxide structure such as anatase, rutile, and even rare brucite.<sup>25, 26</sup> According to many researchers, a constant increase in the anode film thickness is a variable value because it changes over time.<sup>27, 28</sup> It significantly affects the surface properties of anodic oxide films and the forming of an intermediate layer of the TiO<sub>2-x</sub> suboxide between a deep TiO layer of titanium substrate and a higher surface TiO<sub>2</sub> layer.<sup>29</sup> The structure of anode film changes from the amorphous to the crystalline phase, which forms above the "critical" thickness of oxide film. Changes in the electrochemical parameters have quantitative and qualitative effects on electrochemical behavior. These changes also increase the current efficiency and the growth rate of the formed titanium oxide films. Of

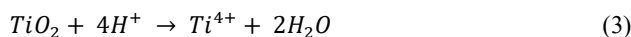
course, this behavior is significantly dependent on the nature of working electrolytes, as has been demonstrated by the experimental investigation.<sup>29, 11</sup>

The quantities of non-stoichiometric oxides obtained within the electrochemically formed oxide film depend on the potential and pH solution. This anodization can be represented according to the reaction (2):<sup>30</sup>



for  $1.5 \leq n \leq 2$

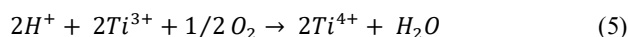
In sulphuric acid solutions at potentials above 3 V (vs. SCE), Kudelka et al. found quite different degrees of oxide growth on a variety of single grains of titanium oxide polycrystalline substrate.<sup>31</sup> Marino et al.<sup>32</sup> have published evidence that the anode current increases in passive titanium to 2.3 V (vs. SCE). That is probably due to a phase transformation of oxides in the older potentiodynamic formed oxide films, at potentials more positive than 2.3 V (vs. SCE). The X-ray diffraction obtained data indicate the presence of  $Ti_3O_5$  in a dominant  $TiO_2$  matrix. The following reactions of  $TiO_2$  film dissolution in sulphuric acid solutions occur:<sup>33</sup>



Different soluble Ti(IV) ions thus formed.  $TiO_2$ , which had formed as a protective layer, has been completely removed from some parts of the electrode surface by the formation of the  $Ti^{3+}$  ions. Hydrogen evolution occurs according to the following reaction:<sup>33</sup>



In the aerated solutions,  $Ti^{3+}$  is oxidized according to the following equation:<sup>33</sup>



The amorphous  $TiO_2$  oxide or a chemically and mechanically intense anatase-type  $TiO_2$  stable base permanently covers the titanium surface. On the other hand, the stability of the oxide film at a pH range from neutral to a low alkaline environment in the deaerated aqueous solution, could not be confirmed with certainty. So the stability of the titanium oxide film and changes in its properties should study in more detail.<sup>34</sup>

In many areas of the titanium application, as the production of dimensionally stable titanium anodes (DSAs), the presence of a small amount of  $TiO_2$  in the surface oxide layers for better adhesion of mixed metal oxide films (MMOs) on the Ti surface is necessary. On the other hand, the annealing at temperatures above 400 °C uses for preparing most MMO coatings on titanium DSAs, and for that should therefore be studied the formation of such titanium oxide films that can passivate the titanium surface and disable the operation of DSAs.

The main goal of this study is the electrochemical formation of titanium oxides films on the titanium metal substrate. That means using anodic oxidation treatments and an investigation of structural and electrochemical characteristics of obtained oxide films. We did experimental

work with great care, and we have performed the chemical and electrochemical procedures so that the results obtained could interpret with a full guarantee. Linear potentiodynamic measurements of the Ti-electrode and (Ti+ $TiO_2$ )-electrode were performed in sulfuric acid solutions with the scan rate of  $1 \text{ mV s}^{-1}$ . The kinetic parameters of electrochemical processes of (Ti+ $TiO_2$ )-electrode in the investigated  $H_2SO_4$  solutions were determined. The coverage degree by the oxide films on the titanium surface at the potentials 0.5 V, 1.0 V, and 1.5 V was calculated. XRD and EDS analyses of anodized and then annealed Ti samples showed an increase in the loading of oxide anodic film on the titanium electrode.

## 2. EXPERIMENTAL

We performed the experimental tests of electrochemical parameters for the formation and characterization of the titanium oxide layers in sulphuric acid solutions. The following concentrations of 1.5 M, 1 M, 0.5 M, 0.1 M, and 0.05 M  $H_2SO_4$  were used. The investigation included the following measurements into the electrochemical behavior of an anodized titanium electrode in the above-mentioned  $H_2SO_4$  solutions:

- Scanning of the titanium electrode cyclic voltammograms in sulphuric acid solutions at different scan rates ( $10 \text{ mV s}^{-1}$ ,  $50 \text{ mV s}^{-1}$ , and  $100 \text{ mV s}^{-1}$ );
- Scans were carried out per five cycles for any pre-indicated acid concentration and all of the above-speed recording, in the potential range of  $-1$  to  $5 \text{ V}$ ;
- Linear potentiodynamic measurements had taken after measuring the open circuit potential in various concentrations of  $H_2SO_4$  solutions;
- By using a cyclic voltammetry method, a passivating  $TiO_2$  oxide layer is applied to the surface of titanium electrode in sulphuric acid solutions at a scan rate of  $50 \text{ mV s}^{-1}$ ;
- Linear potentiodynamic measurements were performed with a titanium electrode on which a passive  $TiO_2$  film has previously applied according to the procedure described, at a scan rate of  $1 \text{ mV s}^{-1}$ .
- Anodic oxidation of a titanium electrode has performed in a 3 M  $H_2SO_4$  solution before XRD and SEM-EDS measurements in a cyclic voltammetry range ( $-1$  to  $5 \text{ V}$ ) at a scan rate of  $100 \text{ mV s}^{-1}$  during five cycles.

All experimental recordings had performed at room temperature in a three-electrode cell. The working electrode has made of titanium, the reference electrode was a saturated calomel electrode (vs. SCE), and the auxiliary electrode was a platinum electrode. After each recording batch, the working electrode was polished with grinding paper from 280 to 2000 grit and washed with distilled water. The IVIUMSTAT.xRe instrument provided hardware and software support.

X-ray analysis had performed on the instrument "Rigaku MiniFlex 600" with a "D/teX Ultra 250" high-speed detector and a copper anode X-ray tube. Recording conditions were: a range of angles  $3-90^\circ$ , step  $0.02^\circ$ , recording speed  $10^\circ/\text{min}$ . The X-ray tube voltage was 40 kV, and the current intensity was 15 mA. The identification of the minerals had made by the PDXL 2 Version 2.4.2.0. of software, and the resulting diffractograms compared with the data from the ICDD database (PDF-2 Release 2015 RDB). The detection limit of the XRD analysis is about 1 %.

The surface appearance and mineralogical composition investigation of the samples SEM (JEOL, JSM IT 300LV) and EDS (OXFORD Instruments) analyses were applied.

## 2.1 Materials and solutions

The working electrode was made of a titanium plate, like a spatula shape in the lower part, and dimensions of  $1.5 \times 1.5 \times 2.0$  cm, with a handle-length of 15.0 cm. Grade II indicates the degree of titanium purity with a chemical composition shown in Table 1.

**Table 1.** The degree of Grade II titanium commercial purity.

Content	Purity degree Grade II (wt. %)
N (max.)	0.03
C (max.)	0.10
H (max.)	0.0125
Fe (max.)	0.30
O (max.)	0.25
Ti	The rest

The working solution was sulphuric acid, 96 %  $H_2SO_4$  p.a. quality, manufactured at the “Zorka Factory” in Šabac, Serbia.

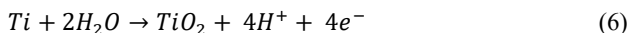
## 3. RESULTS & DISCUSSION

### 3.1 Cyclic Voltammetry

Figure 1. shows, respectively, the CV curves recorded in sulphuric acid solutions of different concentrations at different scan rates in the potentials range of  $-1.0$  to  $5.0$  V. All processes essential for the investigation of this system are in the selected potential range.

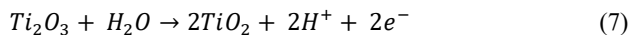
The way that section titles and other headings are displayed in these instructions, is meant to be followed in your paper.<sup>36</sup> An important parameter is the change in the scan rate because it influences the surface oxidation of the Ti-anode. The occurrence of the characteristic peaks that define the specific oxides assigned for the given test parameters was also supervised. The three apparent peaks at potentials 0.2, 2.2, and 3.5 V vs. SCE had detected at all scan rates. These current peaks formation are limited by the diffusion-controlled process.

Based on the CV curves shown, it is evident that after the titanium region presented in the active state, titanium oxidation took place, and the growth of the oxide film was usually in the form of  $TiO_2$  structure. It is suggested in recent data in literature that the first peak in the cycle may occur due to the formation of the titanium oxides with the lower Ti-valence. These would probably be  $Ti^{2+}$  and  $Ti^{3+}$  in the form of  $TiO$  and  $Ti_2O_3$  oxides, while the second and the third peaks correspond to the forming of  $TiO_2$  films.<sup>25</sup> Moreover, the layer that is formed mostly of  $TiO_2$  oxide was seen to have protective characteristics. The oxidation of a titanium substrate is shown by the following equation:<sup>37, 38</sup>

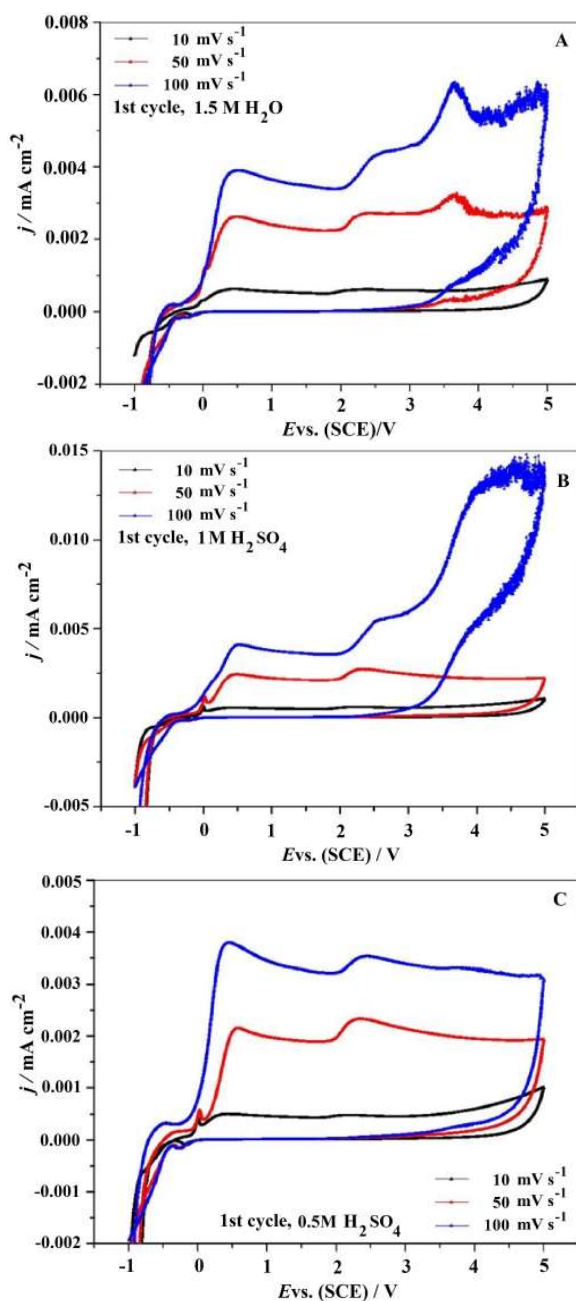


In addition to  $TiO_2$ ,  $Ti_2O_3$  also can be formed as an unstable compound. Therefore  $Ti_2O_3$  oxide was rapidly

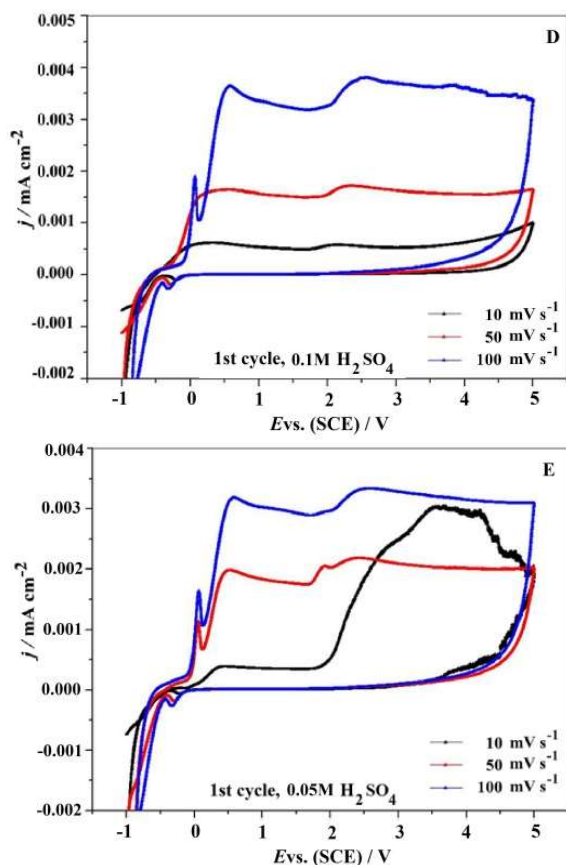
oxidized to  $TiO_2$  in contact with water according to the reaction:<sup>32,39</sup>



In all concentrations of sulphuric acid solutions tested at higher scan rates, the intensity of current peaks increases and indicates forceful titanium oxidation, which causes difficulty of a stable and compact film formation on the titanium surface. Blackwood et al. also showed that the stability of a potentiodynamic formed oxide film depends on the scan rate.<sup>33</sup>



**Figure 1.** Titanium cyclic voltammograms in: A) 1.5 M, B) 1.0 M, C) 0.5 M of  $H_2SO_4$  solution, respectively. The scan rate: 10, 50 and  $100 \text{ mV s}^{-1}$ .



**Figure 1.** Titanium cyclic voltammograms in: D) 0.1 M, E) 0.05 M of  $\text{H}_2\text{SO}_4$  solution, respectively. The scan rate: 10, 50 and  $100 \text{ mV s}^{-1}$ .

Moreover, an increase in the intensity of current peaks in the concentration range examined indicates the diffusion-controlled process.<sup>40</sup>

The so-called “low-voltage oxide films” characteristic of voltages below 20 V (usually up to 5 V) can have an amorphous structure and defective stoichiometry, while crystalline  $\text{TiO}_2$  occurs at higher potentials.<sup>38,42</sup> The intermediate  $\text{TiO}_x$  and  $\text{TiO}_{2-x}$  layers are inserted between the  $\text{TiO}$  layer on the titanium surface and the outer  $\text{TiO}_2$  oxide layer, which is why the composition of such films is not uniform.<sup>29, 11</sup> Besides, the composition of electrolytes also has a strong influence on the crystallinity of formed  $\text{TiO}_2$ .<sup>43</sup> Furthermore, the crystalline  $\text{TiO}_2$  with a compact structure arises in the electrolyte with a higher water amount.<sup>42</sup> Nevertheless, the mechanism of the formation of the crystalline oxide form is still unclear. Probably solution impurities affect the conversion of formed amorphous film to the crystalline type in the coating.<sup>44</sup> The most common type of crystalline  $\text{TiO}_2$  is in the form of anatase in the anodization. The anatase type of  $\text{TiO}_2$  oxide gives a characteristic yellow color to the oxide film,<sup>27</sup> obtained in our experiments. The disagreement in the literature data may be due to the different surface preparation and the conditions in which the growth of the oxide occurred, shown by the instant current density, chemical composition (solution concentration), and electrolyte temperature.<sup>4</sup>

Furthermore, according to curves presented in Figure 1. the current density increases at all recording speeds at the

potentials above 2 V, probably due to the start of intense oxygen evolution and the formation of unstable titanium peroxide  $\text{TiO}_3$ .

Moreover, the sharp decrease in the current density in the reverse scan is because of the passivation with an oxide film, consisting of oxides formed on the titanium surface. The stoichiometry of these oxides had not entirely determined in experimental studies, but the following oxides:  $\text{TiO}$ ,  $\text{TiO}_x$ ,  $\text{Ti}_2\text{O}_3$ ,<sup>30, 45, 46, 47</sup> and the most stable  $\text{TiO}_2$  oxide most probably formed. The current peak at a potential around  $-0.23 \text{ V vs. SCE}$  indicates, as well, a reduction of the unstable species on the metal surface.<sup>32</sup> Nevertheless, in the sulphuric acid solutions,  $\text{Ti}^{4+}$  ions are relatively facily reduced to  $\text{Ti}^{3+}$  and  $\text{Ti}^{2+}$  species.

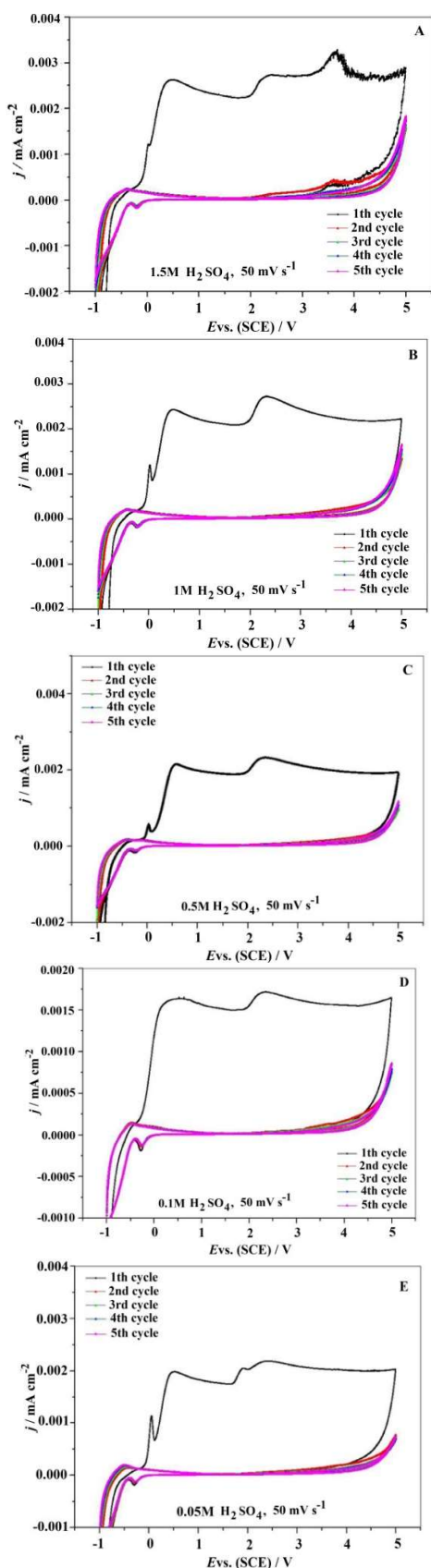
Figure 2. shows the CV curves obtained in sulphuric acid solutions. It can seem that an increase in the number of cycles leads to a significant decrease in the current density and the disappearance of the current peaks. That was easy to spot in the first cycle when the titanium oxide layers covered the surface. These layers had a significant variation in their stoichiometry and morphology, indicating oxidation of the unstable  $\text{Ti}^{2+}$  and  $\text{Ti}^{3+}$  type oxide species, like  $\text{TiO}$ , and  $\text{Ti}_2\text{O}_3$ , on the metal surface. It is also noticeable that after the first cycle at all concentrations of  $\text{H}_2\text{SO}_4$ , complete passivation of the titanium surface with stable  $\text{TiO}_2$  occurred.

### 3.2 Open circuit potential

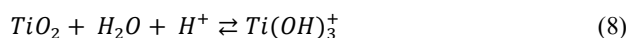
Open circuit measurements of Ti and (Ti+ $\text{TiO}_2$ )-electrodes had performed for 60 min in different concentrations of sulphuric acid solutions and the results obtained are presented in Figure 3., and Table 2. Based on the curves shown in Figure 3. it can see that in the sulphuric acid solutions, immediately after the electrode immersion, there is a sudden drop in the value of the open circuit potential, which most likely indicates titanium oxide dissolution on the electrode surface. Blackwood et al. found that the oxide film dissolution rate was the first-order reaction, given the proton concentration, and proposed the following dissolution reaction in an acidic solution.<sup>33</sup>

On the OCP values of the potential for the (Ti+ $\text{TiO}_2$ )-electrode at  $t=3600 \text{ s}$  in 1.5 M and 1 M  $\text{H}_2\text{SO}_4$ , the formation of the oxide film occurs at more positive potentials in comparison to other  $\text{H}_2\text{SO}_4$  concentrations. On the OCP potential for the Ti-electrode at  $t=3600 \text{ s}$  in the same  $\text{H}_2\text{SO}_4$  concentrations, the oxide film formation occurs at more negative potentials in comparison to 0.1 M and 0,05 M  $\text{H}_2\text{SO}_4$  concentrations.

A deviation in the OCP potential value in 0.5 M  $\text{H}_2\text{SO}_4$  at  $t=3600 \text{ s}$  is observed. The oxide film formation on Ti-electrode occurs at a more positive potential, and on the (Ti+ $\text{TiO}_2$ )-electrode occurs at a more negative potential value in comparison to all other  $\text{H}_2\text{SO}_4$  concentrations.



**Figure 2.** Titanium cyclic voltammograms in different  $\text{H}_2\text{SO}_4$  concentrations: A) 1.5 M, B) 1.0 M, C) 0.5 M, D) 0.1 M, E) 0.05 M. The scan rate is  $50 \text{ mV s}^{-1}$ .

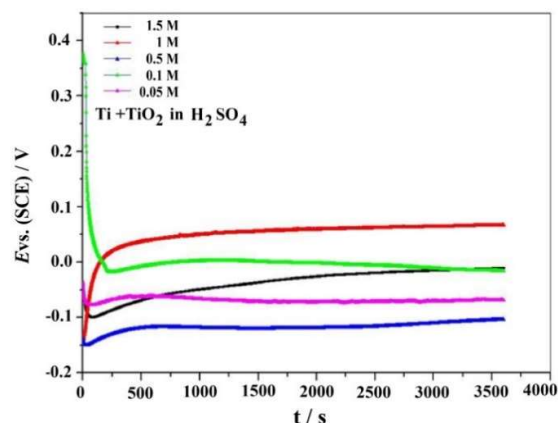


However, the value of the open circuit potential (OCP) increases by the further increase in anodization time that is a consequence of the thicker layer formation of oxide films on the titanium surface.<sup>19, 35</sup>

**Table 2.** The potential values for a Ti-electrode on OCP in different  $\text{H}_2\text{SO}_4$  concentrations.

Potential on $t = 3600 \text{ s}$	$\text{H}_2\text{SO}_4$ concentration				
	1.5 M	1 M	0.5 M	0.1 M	0.05 M
$E / \text{V}_{\text{SCE}}$	-0.0636	-0.0926	0.0166	-0.0205	-0.0363

Based on data in Table 2., and Figure 3. it can conclude that because of the change in the  $\text{H}_2\text{SO}_4$  concentration, in general, no significant deviation occurs in the oxidation process and formation of the oxide film on the electrode surface, both for bare Ti-electrode, as well as for (Ti+TiO<sub>2</sub>)-electrode.



**Figure 3.** The plot of the open circuit potential of (Ti+TiO<sub>2</sub>)-electrode in different concentrations of  $\text{H}_2\text{SO}_4$  solutions.

### 3.3 Linear potentiodynamic measurements

Figure 4. shows polarization curves in the various concentrations of sulphuric acid solutions of the titanium electrode and (Ti+TiO<sub>2</sub>)-electrode. A rapid formation of the oxide film observes from the polarization curves of the anode process at the beginning of the polarization process. By the further anodization process the passivation of the titanium surface causes increases in the potential because of the growth and the alignment of the oxide layers surface.<sup>48</sup>

In the furthest course of the oxidation process, on potentials higher than 1.5 V, there is an increase in the current density that undoubtedly indicates further oxidation of titanium. The passivation in the whole range of concentration observes. In the concentration range from 0.05 M to 0.5 M, a passivation plateau starts at the potential of 0.4 V vs. SCE. With a further increase in the concentration, the beginning of the passivation plateau moves to lower potential values: 0.345 V vs. SCE in 1 M  $\text{H}_2\text{SO}_4$  and 0.3 V vs. SCE in 1.5 M  $\text{H}_2\text{SO}_4$ . Moreover, the current density is constant in a wide range of potentials and increases at 1.54 V vs. SCE in 0.05 M  $\text{H}_2\text{SO}_4$  up to 1.65 V vs. SCE in 1 M  $\text{H}_2\text{SO}_4$  and 1.5 M  $\text{H}_2\text{SO}_4$ , suggesting that titanium

oxides formed are more stable in a solution of a higher sulphuric acid concentration.

However, the current density increases at those potentials are due to the film dissolution on the titanium surface.<sup>19</sup> The polarization curves of treated titanium electrodes indicate a lesser metals dissolution. In the pretreatment processes of titanium in H<sub>2</sub>SO<sub>4</sub> solutions, the formation of a thicker oxide film on the titanium surface causes the lower current density anodization values. Furthermore, cathodic polarization curves detect a reduction of unstable titanium oxides with low-valence titanium, which has a good agreement with cyclic polarization measurements.

Based on the polarization curves presented in Figure 4, have determined kinetic parameters of electrochemical processes in the mediums investigated: the corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $i_{\text{corr}}$ ), anodic ( $b_a$ ), and cathodic ( $b_c$ ) Tafel's slopes, which have presented in Table 3.

**Table 3.** Electrochemical parameters of (Ti+TiO<sub>2</sub>)-electrode

H <sub>2</sub> SO <sub>4</sub>	$E_{\text{corr}}/\text{mV}$	$i_{\text{corr}}/\text{mA cm}^{-2}$	$b_a$	$b_c$
1.5 M	$-0.44 \cdot 10^{-2}$	$1.74 \cdot 10^{-4}$	545.26	-283.53
1 M	$7.84 \cdot 10^{-2}$	$1.57 \cdot 10^{-4}$	359.59	-106.90
0.5 M	$-8.86 \cdot 10^{-2}$	$1.18 \cdot 10^{-4}$	597.20	-332.40
0.1 M	$-1.44 \cdot 10^{-2}$	$3.29 \cdot 10^{-5}$	111.98	-671.43
0.05 M	$-7.32 \cdot 10^{-2}$	$2.70 \cdot 10^{-5}$	357.21	-428.33

Table 4, also shows the coverage degree of the titanium surface at different concentrations of H<sub>2</sub>SO<sub>4</sub> at the potentials 0.5 V, 1.0 V, and 1.5 V, to obtain an image as complete as possible of the influence of the H<sub>2</sub>SO<sub>4</sub> concentration on the coverage degree of the titanium surface with Ti-oxide.

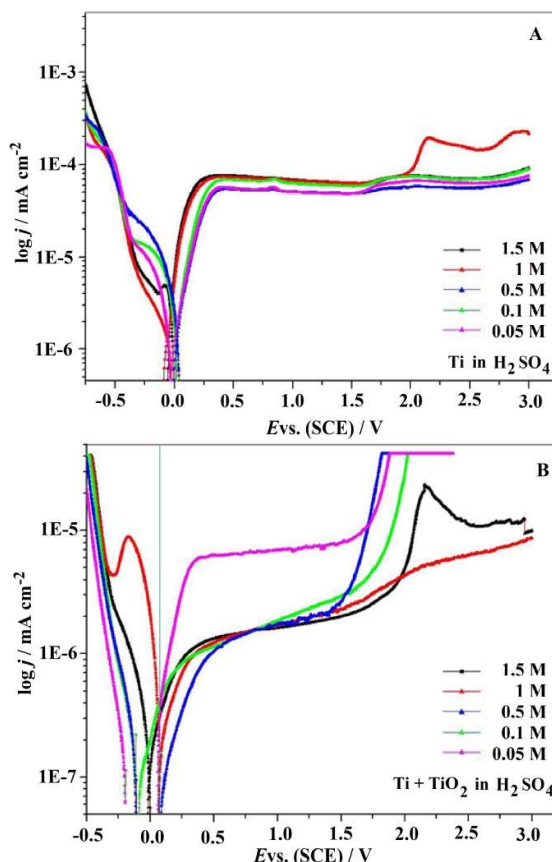
**Table 4.** Coverage degree of titanium electrode surfaces with oxide in various concentrations of H<sub>2</sub>SO<sub>4</sub> solutions on constant potentials.

H <sub>2</sub> SO <sub>4</sub> concentration	Coverage degree, $\theta$ (%)		
	$E=0.5 \text{ V}$	$E=1.0 \text{ V}$	$E=1.5 \text{ V}$
1.5 M	98.24	97.62	96.78
1 M	98.32	97.43	96.32
0.5 M	98.32	97.04	94.95
0.1 M	98.04	96.54	94.58
0.05 M	88.60	86.11	83.44

Based on these results, it can see that as the potential increases, there is a decrease in the surface coverage degree, indicating the occurrence of the dissolution of the titanium oxide films. It can also see that with the lowering of acid concentration, the degree of oxide surface coverage falls, which indicates the fact that with the increase of H<sub>2</sub>SO<sub>4</sub> concentration, the oxide formation on titanium surface unfolds faster.

#### 4. XRD and EDS analyses of anodized and annealed Ti substrates in H<sub>2</sub>SO<sub>4</sub>

XRD and SEM-EDS recordings show the indisputable presence of Ti-oxides in the anodized oxide layer. This oxide layer forms on the surface of the titanium electrode in 3M H<sub>2</sub>SO<sub>4</sub>.



**Figure 4.** The potentiodynamic polarization curves in H<sub>2</sub>SO<sub>4</sub> solutions: A) Ti electrodes, and B) (Ti+TiO<sub>2</sub>)-electrode. The scan rate is 1 mV s<sup>-1</sup>

The light yellow color of anodizing anatase crystals TiO<sub>2</sub>, from acidic solutions, is the most common crystalline TiO<sub>2</sub>, as said before.<sup>16, 17, 27, 40</sup> The anodization of Ti and getting of thick TiO<sub>2</sub> films before modification of titanium surface with mixed platinum metal oxides is not a good recommendation because of possible anode passivation. For some titanium applications, such as DSAs (Dimensionally Stable Anodes) preparation, thick layers lead to electrode passivation. However, the presence of TiO<sub>2</sub> on the surface is necessary for better adhesion and stabilization of the electrocatalytic oxides layer. The TiO<sub>2</sub> protecting films are permanently rebuilding when the electrodes are polarized anodically. The different deactivation mechanisms of DSAs can be the passivation of titanium substrate, coating detachment, and mechanical damages, which should consider in the production and application of these anodes.<sup>41, 42</sup>

Different ways of making DSAs with mixed metal oxide (MMOs) layers often involve using a thermal treatment, and it is the electrode annealing at different temperatures. For this reason, it has been necessary to study the behavior of the anodized Ti substrate, followed by annealing at 400 °C (characteristic annealing temperature for TiO<sub>2</sub> crystals of the anatase type).<sup>43</sup>

Figure 5. shows the XRD image of the Ti substrate after anodization in 3 M H<sub>2</sub>SO<sub>4</sub> and after annealing sample at 400 °C in the airflow, previously prepared in the same way.

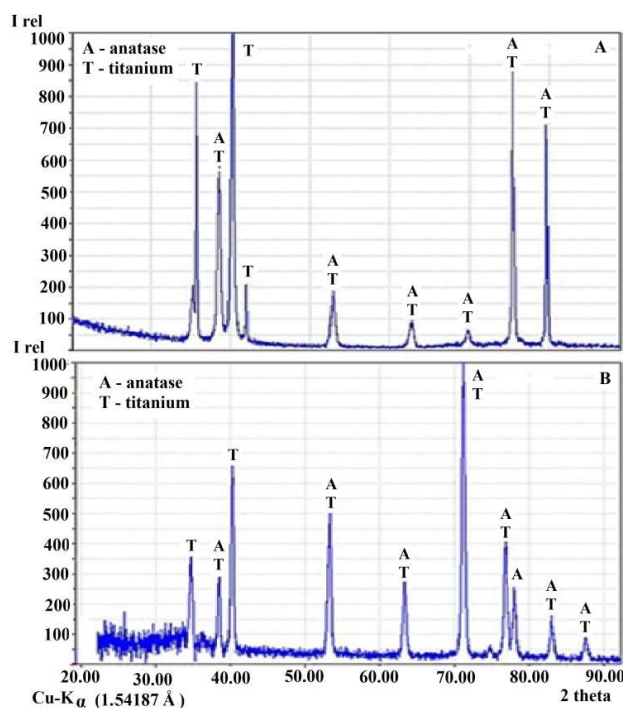
According to the results present in Figure 5, crystalline TiO<sub>2</sub> has formed by anodization of titanium in various

concentrations of  $\text{H}_2\text{SO}_4$ . The intensity of peaks for the anatase type of crystals also suggests a thin  $\text{TiO}_2$  film formation. The height of the same peaks increases after the annealing titanium electrode at  $400^\circ\text{C}$ , which indicates that the oxide film of anatase becomes thicker after heat treatment.

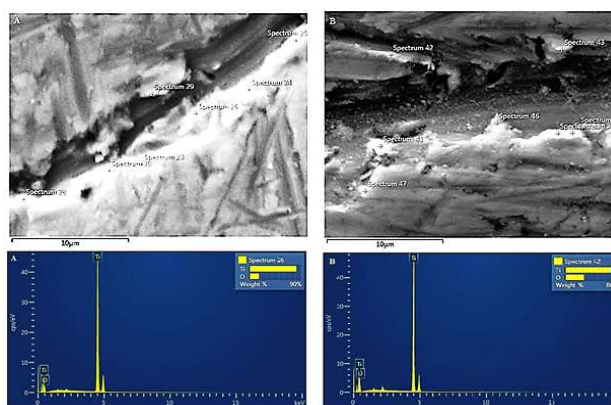
SEM-EDS analyses (Figure 6.) confirm the results obtained by XRD measurements. It can also observe that after anodization on the titanium surface Ti and  $\text{O}_2$  species exist. This suggests the formation of an oxide layer on the electrode surface. According to chemical analysis, after annealing of titanium, the content of  $\text{O}_2$  species increase indicates thicker  $\text{TiO}_2$  oxide films (Table 5.).

**Table 5.** Chemical composition of titanium surface after anodization in 3 M  $\text{H}_2\text{SO}_4$  and after annealing at  $400^\circ\text{C}$  at a time of 1 h.

Atomic species	O %	Ti %	Total %
after anodization	17.30	82.70	100.00
after thermal treat.	28.40	71.60	100.00



**Figure 5.** XRD patterns of Ti electrode: A) after anodizing in 3M  $\text{H}_2\text{SO}_4$ , B) after annealing the anodized Ti electrode, at  $400^\circ\text{C}$  in the airflow.



**Figure 6.** SEM-EDS images of A) Ti electrode after anodizing in 3M  $\text{H}_2\text{SO}_4$ , B) annealed Ti electrode at  $400^\circ\text{C}$  1 h after anodizing in 3M  $\text{H}_2\text{SO}_4$ .

## 5. CONCLUSIONS

The formation of oxides on the surface of titanium in  $\text{H}_2\text{SO}_4$  solutions carried out over a wide range of potentials. According to the results obtained, and characterization of formed oxide films observed several conclusions.  $\text{TiO}_2$  is the most stable formed oxide, but  $\text{TiO}$  and  $\text{Ti}_2\text{O}_3$  oxides are also formed by anodization from solutions investigated. The results obtained during CV measurements also indicate the rapid formation of an oxide layer with variations of the stoichiometry and morphology on the titanium surface.

Open circuit potential and potentiodynamic measurements indicate that there is generally no significant deviation in the oxidation process and the forming of the oxide film on the Ti and (Ti+ $\text{TiO}_2$ )-electrode surface. Based on the results of the potentiodynamic measurements, it can be seen that the formation of the oxide films is initiated at the very beginning of the polarization process. Furthermore, passivation of the titanium surface occurs because of the growth of the surface oxide layer and surface leveling.

XRD and SEM-EDS analyses confirmed the presence of titanium oxide films on the titanium anode. After thermal treatment of the electrode, XRD recordings showed a higher intensity of anatase peaks in the anodized oxide films. SEM-EDS recordings also confirmed the higher presence of oxides on the thermally treated titanium electrode. The appearance of the anatase structure of crystals in the oxide film was also certified.

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