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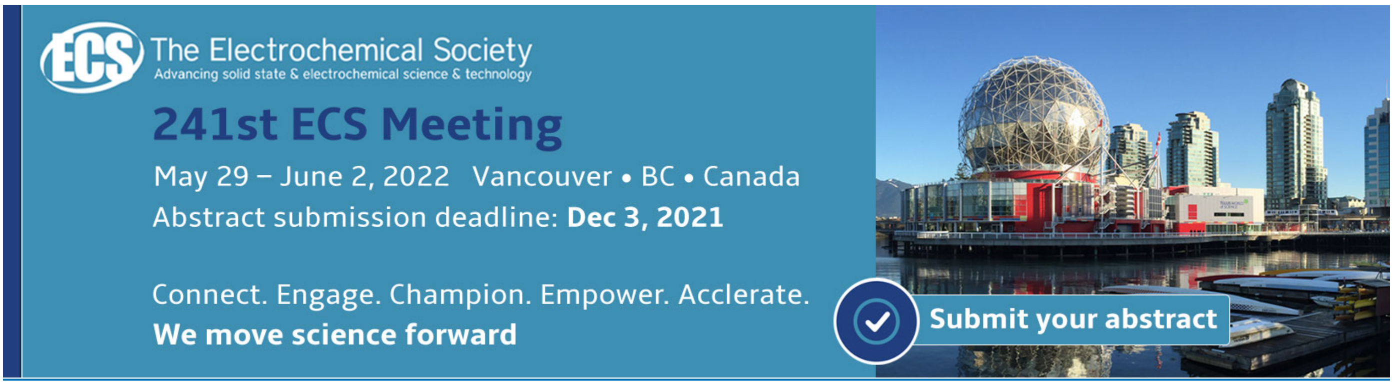

Influence of the H_2O content and the time on the formation of nanostructures in a chemical solution of $H_2O/HF/NH_4F/EG$

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Abstract. The influence of anodizing time on the length, morphology and photoelectrochemical properties of TiO_2 Nanotubes has been investigated. An optimum anodizing time of 20 min at 20V leads to 220nm long of the nanotubes. By having a detailed control of the electric current one can know exactly the time in which the nanotubes grew and the time in which the process stopped. The FEG-SEM measures show the morphology of the nanotubes and how they come to separate and fall after a certain time. However, the growth of these, is uniform with little remaining material on the surface. For the solution of the anodizing process it is very important to control the amount of water, ethylene glycol and hydrofluoric acid. Small modifications in the solution change the growth time and size of the nanotubes.

1. Introduction

Titanium (Ti) and its alloys are widely used to manufacture dental implants and orthopedic prostheses [1–6]. Titanate is also one of the materials used in the literature for the degradation of some materials [7]. The unique and exceptional mechanical and electronic properties of Ti nanotubes have provided a new impetus in their potential application in semiconductor nanocomposites as photocatalysts for the degradation of organic pollutants and bacteria. However, despite being a preferable candidate for a number of applications. The lack of mass production at low cost continues to be a limiting factor in all the practical uses of nanotubes [8,9]. The most common form is rutile, which is also the most stable form anatase and brookite both can be converted to rutile upon heating [10]. Increasing the applied voltage increases the pores diameter and significantly increases the thickness of Titania layer [11].

The importance of the production of the nanotubes of TiO_2 [12] at low cost has led us to give it an importance in the production of these by anodization. In this work there are several tests with variation of water, voltage and time to optimize the production of them, since it is an easy and cheap method.

2. Theoretical formalism

Several methods have been implemented to obtain nanostructured TiO_2 tubes [12]. Due to its simplicity simplicity, the following methods stand out: chemical, electrochemical and sol-gel [13].

There are other more complex methods among which can be presented: vapor deposition, sputtering and arc discharge. With respect to the simple methods that allow the synthesis of nanotubes, there are three processes: - 1 Hydrothermal route, bulk TiO_2 is reacted with $NaOH$ at temperatures not higher than 200^0C in a solution with constant agitation. -2 Electrochemical Route, a titanium plate is anodized at a specific voltage, in immersion of an electrolyte composed of controlled amounts of water and a source of fluorides. -3 Deposition, in a mold (porous alumina or other similar structure) material is deposited neatly, the mold allows the formation of the fields [14]. The first route creates an ordered array of nanotubes where the final geometry is defined by variables such as temperature, reagent quantities and flow velocity within the solution. The second route creates an orderly order that grows in a preferential direction. From the third route to using preformed molds to create nanotubular structures of TiO_2 specimens by means of porous alumina as a mold [15]. This investigation used method 2. Figure 1 shows the anodization process for obtaining the different samples in different condition of the electrolyte.

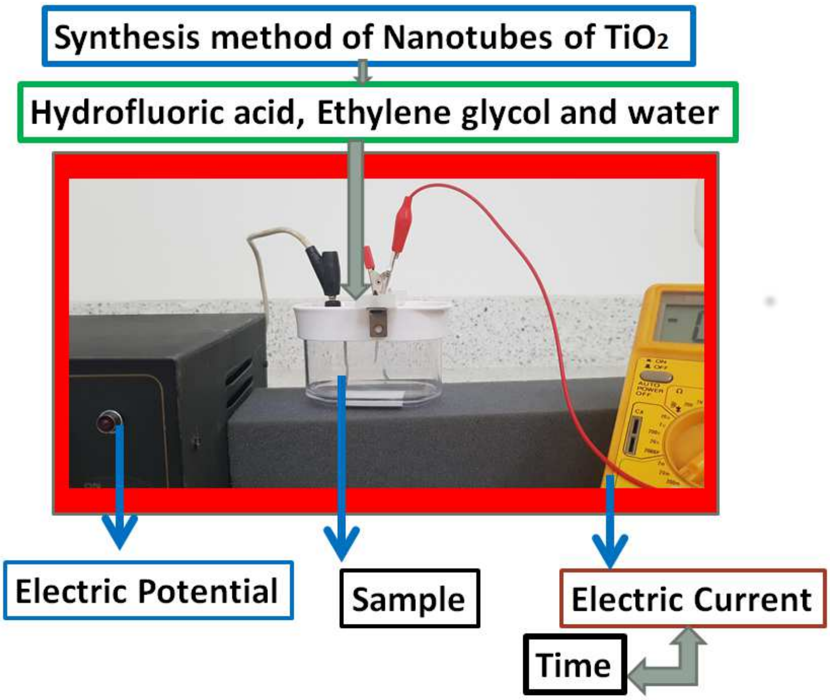

Figure 1. Experimental procedure for obtaining nanotubes from the titanium sheet.

Anodic oxidation is the process in which two metal plates are in contact through an electrolyte and are exposed to certain voltages and times. This process creates a rapid oxidation at the anode, generating an oxide layer that adheres to the "anodized" material. Titanium anodization is a technique commonly used in jewelry and has ornamental purposes by coloring the parts submitted to the process. It is possible to obtain a compact layer of oxide in a variety of colors by means of anodizing voltage control. The colored effect is produced by the superposition of the waves reflected in the metal/oxide interface as a function of the oxide/air interface [16].

3. Results and discussion

Figure 2(b) shows the electric current in milliamperes as a function of time, in this case in second. The titanium sheet was $0.3mm$ and the electrolyte concentration was $0.3g$ of NH_4F, $2ml$ of H_2O and $3ml$ of HF, for a time of 40 minutes.The inserted Figure 2(a) is a magnification of Figure 2(b), where it is observed when the nanotubes begin to grow in the anodizing process. That small inverted peak indicates that at that moment the nanotubes begin their process. The electrical current a time later reaches its maximum, then begins to diminish, this is an indicative that the nanotubes stopped growing. Then, the current practically is constant, indicating that they will not longer grow and possibly the nanostructures begin to fall.This is a very simple way to control the growth of nanotubes. Anodization is an electrolytic passivation technique used to increase the thickness of the natural oxide layer on metal surfaces. This technique has attracted great attention in recent years due to its simplicity as well as the reproducibility of the results obtained. The thickness and structure of the oxide layers formed (amorphous or crystalline) depend on the applied potential between the electrodes and duration of anodization process [11].

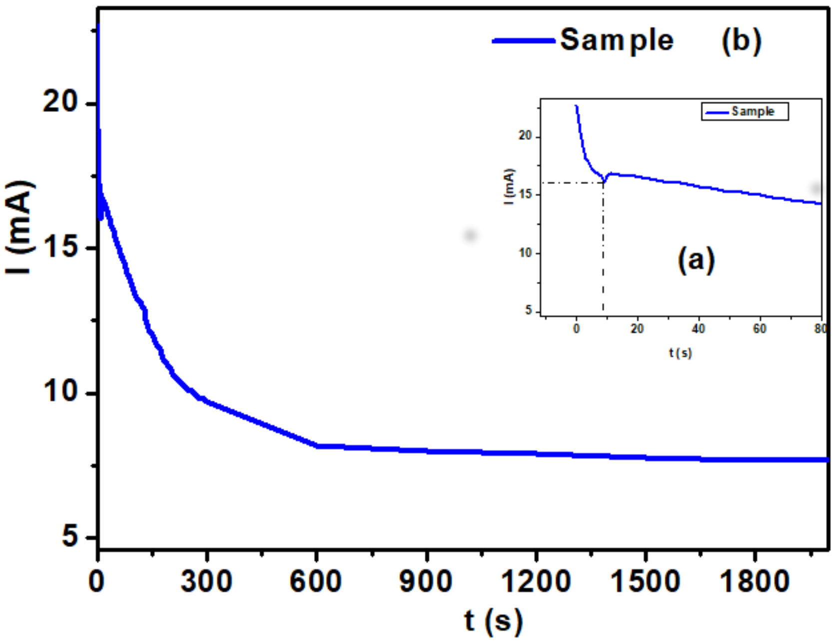

Figure 2. Electric current in (mA) as a function of the anodized time (s). For a sample subjected to 40 min in the electrolyte. Figure (a) inserted magnification of the discontinuity region in the graph.

In Figure 3 the sample is observed at 40 minutes of anodization; it is the same sample of the result of Figure 2. As shown in the FEG-SEM measurement, the nanotubes grew approximately 220nm. A self-organized and homogeneous layer of the nanotubes was obtained in all evaluated conditions. For samples anodized at 20 V. Figure 3 shows the uniform growth of the nanostructures and with the mouth of the open nanotubes. In spite of not submitting the samples at any time for calcination, the remaining layer of the material used in the solution is practically not observed.As we will see in a future work published by extensive, the diameter of the tube is linearly dependent on the applied potential during the growth of nanotubes.

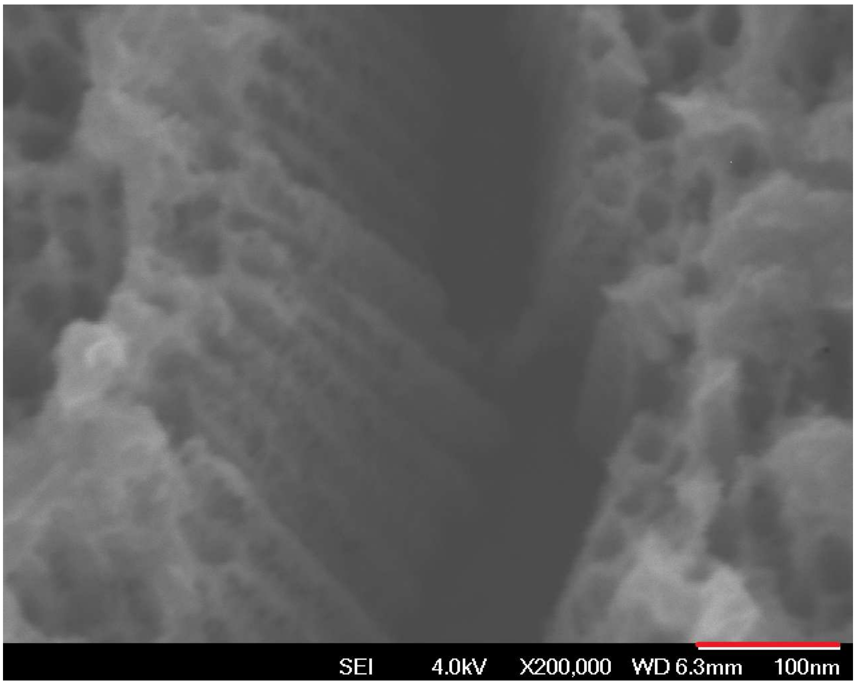

Figure 3. Field Emission gun scanning electron microscopy (FEG-SEM), for one sample at 20V to 40 minutes.

4. Conclusion

The anodization method is a way to obtain nanoestructures in a fast and cheap way. In addition, it is possible to know if the nanoestructures grew, only controlling the time and the current.

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