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# FABRICATION OF $TiO_2$ NANOTUBULAR MEMBRANES OPENED FROM BOTH ENDS BY ELECTROCHEMICAL ANODIZATION TECHNIQUE

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Titanium dioxide is one of the most studied materials nowadays. $TiO_2$ nanotubular membranes find their applications in solar energy conversion, hydrogen sensing, catalysis for decomposition of organic materials, in biomedical applications, etc. In this paper we propose an electrochemical cost-effective method for obtaining both-ends opened nanotubular membranes. The method implies several stages: the first anodization step for a short period of time followed by removal of the formed oxide, the second anodization for growing the membrane, and a final stage of detaching the membrane from the metal surface. By choosing the appropriate parameters for each stage we can fabricate nanotubular membrane with large specific surface and identical nanotube sizes.

Keywords: titanium dioxide, free-standing nanotubular membrane, electrochemical anodization.

Bioxid de titan este unul dintre cele mai studiate materiale în prezent. Membranele nanotubulare de $TiO_2$ îşi găsesc aplicabilitate în conversia energiei solare, senzori de hidrogen, cataliză pentru descompunerea materialelor organice, biomedicină, etc. În această lucrare noi propunem o metodă electrochimică rentabilă pentru obținerea membranelor nanotubulare cu ambele capete deschise. Metoda presupune mai multe etape: prima etapă de anodizare pentru o perioadă scurtă de timp, urmată de îndepărtarea oxidului format, a doua etapă de anodizare pentru creşterea membranei și o etapă finală de desprindere a membranei de pe suprafața metalului. Prin alegerea parametrilor corespunzătoare pentru fiecare etapă se poate fabrica membrane nanotubulare cu suprafaţă specifică mare şi dimensiuni identice nanotuburilor.

Cuvinte-cheie: bioxid de titan, membrană nanotubulară separată, anodizare electrochimică.

## I. INTRODUCTION

Titanium dioxide is a wide band gap semiconductor, with high chemical stability and unique functional properties.

In recent years, more and more attention has been paid to $TiO_2$ nanotubes due to their advantages over $TiO_2$ thin films, like larger surface-to-volume ratio and unidirectional electrical channel with fewer grain boundaries. Today, anodic oxidation appears to be the distinguishing alternative due to its simplicity, low cost, self-ordering process and easily controllable nanotube morphology. Without special treatment, the $TiO_2$ nanotubes prepared by anodization are generally attached to the Ti substrate and their bottom ends are closed. One end opened membranes are quite limited in applications, and an eventual opening process for the bottom end is absolutely necessary.

In order to open the bottom end of the membranes many attempts have been performed, like ultrasonic splitting [1], selective dissolution of the metallic Ti substrate, and selective dissolution of the amorphous layer between nanotube array and Ti substrate [2].

In spite of considerable research efforts, the bottom ends of the nanotubes remain partially closed, or the membrane is being destroyed. Chemical etching of the nanotube bottoms in acid vapors is an often used method for this goal. In this paper, we propose a simple way of obtaining both ends opened membranes using a single anodization step. By this way, bottom end opening process in hazardous acid vapors will be avoided, the second end of the membrane being opened during the fabrication process, detaching already both ends opened membrane.

The used electrolyte consists of a mixture of etilenglycol, ethanol and $NH_4F$, with a ratio of 50:2:1. The nanotube`s growing process is initiated under anodic voltage increase from 0 to 120 V at a rate of 1 V/s and then maintained for 2 h [3]. At the end, a higher voltage is applied to detach the membrane from the Ti substrate.

## II. EXPERIMENTAL PART

For nanotubular $TiO_2$ membranes fabrication Ti foils with a thickness of 250 µm and purity of 99.7 % were subjected to anodic oxidation. At the first step, the Ti foil was degreased in acetone and isopropanol in ultrasound bath and then rinsed in distilled water followed by drying in nitrogen atmosphere.

The electrochemical anodization process occurs by interaction of electrolyte with the surface of the Ti foil (99.7 % purity) under the influence of electrical field.

The electrolytic cell consists of a system with two electrodes. As electrolyte we used a mixture of ethanol, $NH_4F$ and etilenglycol. The Ti foil is connected in the circuit as anode, and a platinum mesh electrode is used as cathode. During the anodization process, the electrolyte is mechanically mixed by a magnetic stirrer. Temperature control is secured by using a cryostat.

The schematic representation of the set-up for $TiO_2$ membrane fabrication is illustrated in fig. 1.

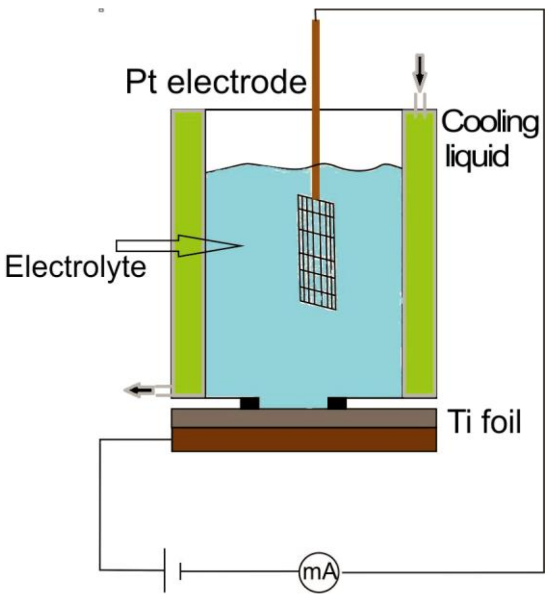


Fig. 1. Schematic view of the set-up used for $TiO_2$ tubular membrane fabrication

From the electrical source we apply a growing potential with a rate of 1V/s from 0 to 120 V and maintained for 2 h. In order to detach the membrane from the Ti substrate, a voltage as high as 100 V was applied for 20 s.

## III. RESULTS

Nanotubular structure formation under anodic oxidation process results after Ti ions migrates from the regions between pores to the surface. At high voltage of oxidation, electrical field value is high enough to be able to mobilize the ions, and as a result ions migration leads to voids formation between pores, which contribute to the tubular structure formation [4].

$TiO_2$ nanotubes formation process (fig. 2) is influenced by many factors as electrolyte composition and concentration, electrolyte temperature, oxidation time, electrical voltage applied during the growing process. Nanotubes formation process by anodic oxidation technique occurs in several stages. First, the Ti foil was degreased in acetone and isopropanol in ultrasound bath, rinsed in distilled water followed by drying in nitrogen atmosphere. After this process, a first anodization step for 15 min at 120 V was applied and then etching of this oxide was realized to obtain a textural surface. The second anodization step took place for 2 h in the same conditions. The final stage, consisting of detaching the membrane from the metal surface, occurs when a 220 V potential is applied for 20 s.

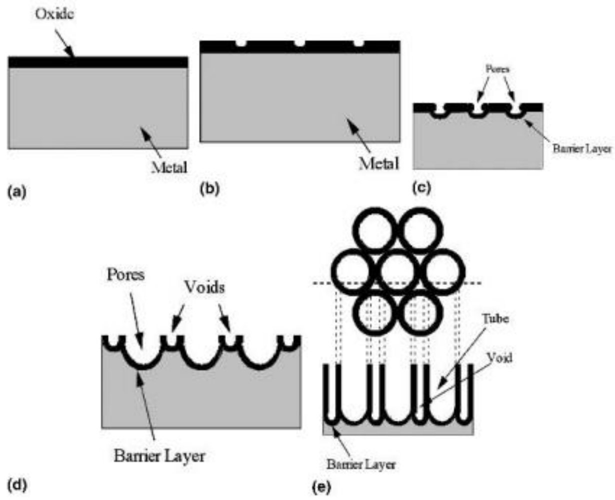


Fig 2. Schematic ilustration of $TiO_2$ nanotubes formation process: (a) oxide continuous layer formation on top of the Ti foil surface; (b) voids formation in the oxide layer after the voltage is applied; (c) voids growing in pores; (d) oxidation and dissolution of the metallic area between pores in the presence of external electrical field; (e) nanotubes formation [5]

Fig. 3 illustrates SEM images of nanotubular membranes obtained as a result of electrochemical anodic etching. Electrolyte concentration plays an important role in the membrane detaching from the substrate. For instance, fig. 3a shows that barrier layer is still present on the bottom end of nanotubular membrane. By increasing the oxidation time, it is possible to reach thickness of membranes as high as 50 µm and even more without any modifications in the nanotube walls thickness or diameter. Also, the process temperature has an important role. In particular, we observed that at temperatures of about 30 °C the growth process of $TiO_2$ nanotubular membranes occurs well, but increasing the temperature to 40 $^0$C, the surface of the membranes becomes not homogeneous, the nanotubes being separated, and nanotube etching occurs (fig. 3c). In the fig. 3d one can observe the membrane surface which was in contact with the electrolyte, and in the fig. 3e it is shown the opposite side of the membrane after optimizing process parameters, which had the barrier layer oxide. The membrane was detached from the barrier layer oxide by applying a high voltage after the growth process finished. Increasing the voltage, the nanotube walls become thinner and, at a certain time point, the membrane has no connections with the metal substrate, being released in the electrolyte solution.

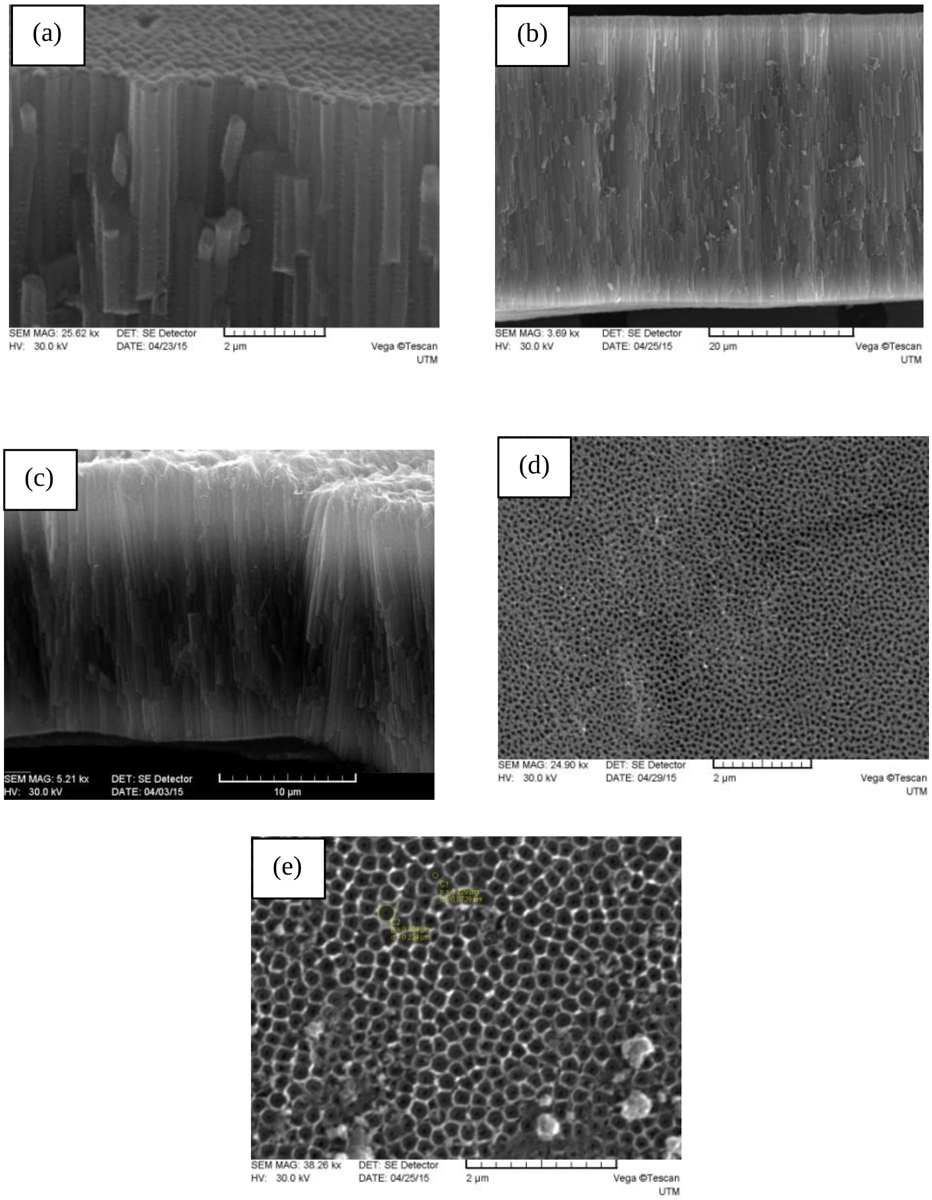


Fig. 3. SEM images of nanotubular membranes obtained without using ethanol in electrolyte composition (a); setting the electrolyte temperature at 30 $^0$C (b) and 40 $^0$C (c); top (d) and bottom (e) surfaces of a membrane after optimizing parameters

From the fig. 3d and 3e it is possible to see that the nanotubes diameter at the bottom side of the membrane is about 70 nm for the interior diameter and around 200 nm for the exterior one. We suggest that this is due to the gradient concentration of $F^-$ ions inside the nanotube. To avoid this phenomenon it is proposed for the future experiments to increase the stirring rate during the growth process.

## CONCLUSIONS

In this work, we demonstrated a cost effective method for obtaining both ends opened $TiO_2$ nanotubular membranes. An important advantage of the method is that an organic electrolyte is used for Ti foil oxidation instead of using hard acids. Opening the bottom end of the nanotubular $TiO_2$ membranes in the same technological process is both time- and cost- effective, making $TiO_2$ nanotubular membranes more accessible for future applications as templates.

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