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ELECTROCHEMICAL STUDIES ON TiO_2 NANOTUBES MODIFIED Ti ELECTRODES

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Lucrarea prezintă un studiu cu privire la modificarea suprafeței titanului cu nanotuburi de TiO_2 obținute în electrolit organic vâscos, PEG 600, cu o cantitate mică de apă şi NH_4F, şi de asemenea cu privire la posibilitatea eliminării stratului de ecranare TiO_2 – PEG, prin tratament cu ultrasunete.

Nanostructurile auto-organizate de tip nanotuburi de TiO_2 au fost caracterizate în funcție de timpul tratamentului cu ultrasunete prin tehnici electrochimice, respectiv curbe de polarizare Tafel, spectroscopie de impedanță electrochimică dar şi prin alte tehnici complementare precum microscopia electronică de baleiaj, măsuratori ale unghiului de contact şi spectroscopie FTIR.

The paper is a study about titanium surface modification with TiO_2 nanotubes elaborated in viscous organic electrolyte, PEG 600, with small water amount and NH_4F, also about possibility to remove of created shielding layer TiO_2 – PEG, with ultrasound treatment.

The self-organized nanostructures were characterized during ultrasound treatment by electrochemical techniques such as Tafel plots and electrochemical impedance spectroscopy, as well as other complementary techniques such as scanning electron microscopy; contact angle measurements and Fourier transform spectroscopy.

Keywords: Titania nanotubes, Anodizing, Polyethylene glycol, Ultrasonication

1. Introduction

Titanium and its alloys represent known materials in implantology, and the recent porous titanium and titanium alloys nanostructures show features which make them more suitable as surgical implant materials.

Their stability in biological environments is due to the fact that Ti spontaneously forms an oxide layer with a thickness of approximately 2–5 nm that provides corrosion resistance. TiO_2 films are naturally deposited on titanium, but in order to improve various properties of the surface, these films are produced through a wide range of technological approaches on titanium and its alloys.

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In the last decades, many approaches have been made to improve the surface activity of Ti and Ti alloys, by modifying TiO_2 properties in self organised nanostructure such as TiO_2 nanotubes using different chemical and physical procedures [1-3]. One of them is anodizing. This method allows easy, cheep and fast fabrication and offers superior control on nanotube dimensions [4-6].

Anodizing can be carried in inorganic or organic electrolytes. Some studies indicate that if organic electrolytes with F^- ions additions are used, the chemical dissolution of nanotubes layer is lower, mobility of F^- ions could be lower and also the current efficiency for TiO_2 nanostructures formation is significantly higher than compared to inorganic electrolytes. So, in the case of organic electrolytes with F^- ions, the formation mechanism and architecture of nanotubes are different, due especially to the change of viscosity [7, 8].

In many studies ethylene glycol (EG) [4, 8] and glycerol [7, 9, 10] are used as organic solvents. There are also few studies using polyethylene glycol for TiO_2 nanotube formation [11, 12].

The various nanotubes structures indicated that electrochemical stability and ion release are favourably modulated and significantly different, depending on the conditions of nanotubes formation, in particular for the nanotubes obtained in hybrid electrolyte with an organic component [7].

The TiO_2 nanotubes layer obtained in organic electrolytes with increased viscosity is homogenous, but partially covered with a "hazy" layer [7].

For some applications, like those implicating bicompatibility, the presence of PEG 600 in anodised electrolyte may be beneficial because PEG is known as the most widely used biocompatible polymer [13]. It is worth to mention that for other applications, like those in the dye-sensitized solar cells, for example, if TiO_2 nanotube layers are covered with a PEG film, a supplementary treatment for removing this shielding is necessary [14].

In this study, TiO_2 nanotubes, were obtained by Ti anodizing in electrolyte based on polyethylene glycol (PEG) 600 with a viscosity of 131 cSt at 25°C [15].

To control the formation and subsequent elimination of TiO_2-PEG layer that covered the TiO_2 nanotubes, the ultrasonication (US) procedure was applied for different US time.

2. Experimental section

2.1. Sample preparation using electrochemical technique

Experimental tests were performed on samples cut from commercially available titanium foil (2 mm thick, 99,7% Ti) from Sigma-Aldrich. Prior to anodizing, samples were thoroughly cleaned mechanically using silicon-carbide paper of increasing granularity of 600, 1000, 1200, 2400 and 4000 until a glossy surface was achieved, followed by ultrasonication in water (for 15 min), ethanol (15 min) and acetone (for 15 min). Cleaned and degreased samples were dried in air and were used immediately.

Electrochemical anodizing was carried out in a two-electrode arrangement with a platinum foil as a counter electrode. Synthesis of TiO_2 nanostructures was achieved by raising the voltage from 0 to 50 V using a MATRIX MPS-7163 electrochemical source. The voltage step used was 2 V/10 s and finally the voltage was maintained at 50V. The total anodizing time was 2 hours. The current variation during the anodizing process was recorded. The anodizing electrolyte was prepared using polyethylene glycol (PEG) 600 with additions of NH_4F (0.5 wt. %) and 4% ultrapure water. After the electrochemical treatment, the samples were rinsed with ultrapure water, one of them was chemically analyzed (sample A) and the other four were ultrasonicated in ethanol for 1 min. (sample B), 5 min. (sample C), 10 min. (sample D) and 20 min. (sample E) and there were analyzed, too. All the experiments were carried out at room temperature.

2.2. Samples analysis

The surface of the nanotube arrays synthesized *via* anodic oxidation was studied using a scanning electron microscope (SEM) FEI/Phillips XL30 ESEM.

The wettability of samples has been assessed by static contact angle measurements, recorded and analyzed at room temperature with a 100 Optical Contact Angle Meter – CAM 100. Reported contact angles are the average of at least three measurements. The ultrapure water was used for determinations.

To verify if any electrolyte remained on the surface of the samples, infrared spectra were recorded with a Spectrum 100 Series FT-IR Spectrometer from PerkinElmer USA.

The cell for evaluation of electrochemical stability of the samples consisted of a three-electrode configuration with platinum and Ag/AgCl electrode as a counter and a reference electrode, respectively. The electrolyte was a Hank solution with the following composition (g/L): 8 NaCl, 0.4 KCl, 0.35 $NaHCO_3$, 0.25 $NaH_2PO_4 \cdot H_2O$, 0.06 $Na_2HPO_4 \cdot 2H_2O$, 0.19 $CaCl_2 \cdot 2H_2O$, 0.19 $MgCl_2$, 0.06 $MgSO_4 \cdot 7H_2O$, 1 glucose [7]. Linear voltammetry and also electrochemical impedance spectroscopy (EIS) measurements were conducted with Autolab PGSTAT 302N using Nova software.

3. Results and discussion

The growth of the nanotube layer on the surface of the samples was evidenced by recording the current–time characteristics (Fig. 1). From point A to point B the voltage is increased from 0 to 50 V, with a 2 V/10 sec rate and between point B and F the voltage was kept constant at 50 V. In stage I, from point A to B, when the voltage is increased, the current also increases and a compact oxide layer is formed on the Ti surface. Between point B to C, in good agreement with literature [7, 16, 17], the compact TiO_2 barrier layer is consolidated, so a rapid decrease of the current density occurs. In the stage II, a rapid increase of the current density occurs between points C and D. The magnitude of the current density is higher compared to first stage. Due to the fluoride ions presence, an active electrochemical corrosion induces irregular nanoscale indents formed at the surface of oxide layer/solution [7, 16-19]. In this stage, the reduced water content in the viscous organic electrolyte reduces the rate of chemical dissolution of the oxide layer [5]. After the stage of pore initiation is overpassed, between points D and E the density of pores increase under steady-current conditions [16, 17]. When the density of the pores reaches saturation point (point E), the current density begins to decrease step by step and the nanotubes length is increasing [5] in stage III.

By integrating the area under the current density vs. time curve, the charge density calculated was 4.85 C/cm^2.

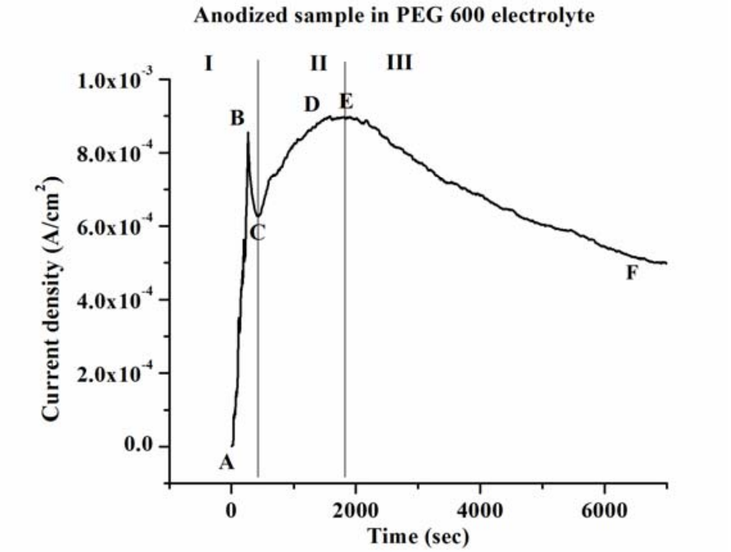


Fig. 1 The measured current density versus time curve during anodized of Ti sample in PEG 600 electrolyte at room temperature.

The SEM images presented in Fig. 2 show that the nanotubes are formed on the Ti surface but they are covered with an oxide PEG layer.

A layer on the top of the nanotubes was reported also in the case of anodizing of Ti samples in ethylene glycol with 0,2M HF.

The film obtained in such electrolyte with increased viscosity is homogenous, but partially covered with a “hazy” layer, which according to the literature data [7] for nanotubes obtained in ethylene glycol consists in conglomerates of partially dissolved nanotubes. Ti–PEG complex existing in environments may be a part of such layer as well.

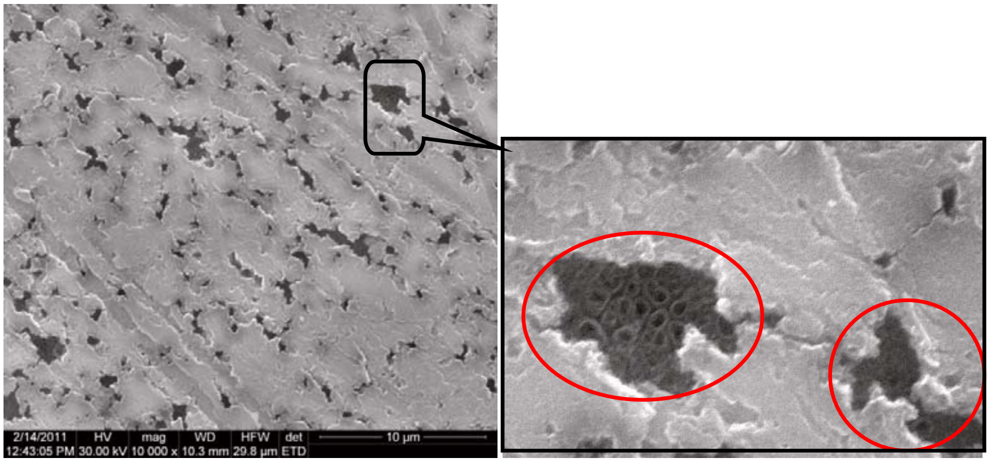
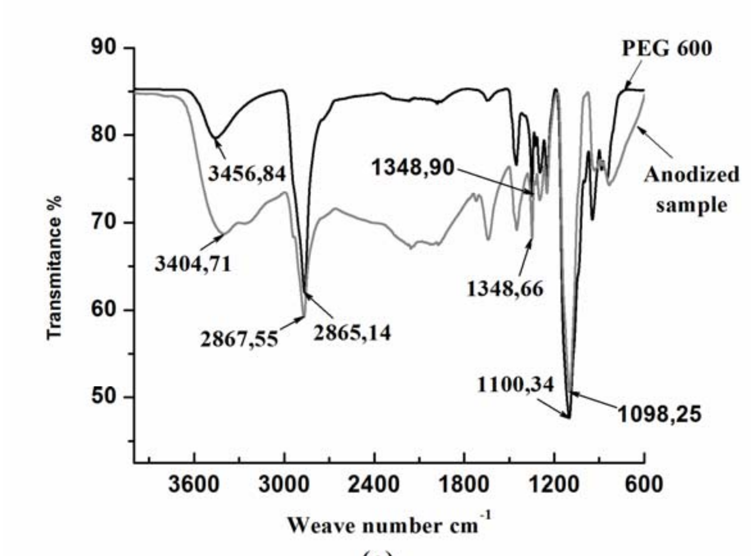


Fig. 2 Top view SEM images of anodized sample in PEG 600 with detail to show nanotubes shielded

To see if this layer contained remaining electrolyte, FTIR spectra were recorded. The samples were carefully rinsed with purified water and let to dry in the air before FTIR recordings. The spectra of PEG 600 and anodized sample are presented in Fig. 3 (a). The peaks for PEG 600 were attributed as follows: in the region of 3400 cm^{-1} is due to the stretching vibration of OH group, stretching vibration of CH_2 gives an intense peak in region 2860 cm^{-1}, in the region of 1348 cm^{-1} stretching vibration of - C-O-C- bond gives a peak and the most intense and sharp peak in the region of 1100 – 1980 cm^{-1} is caused by the C-C stretching. The same peaks appear in the case of anodized sample (A) more or less intense or shifted, evidenced that the electrolyte is still present meaning that the rinsing is



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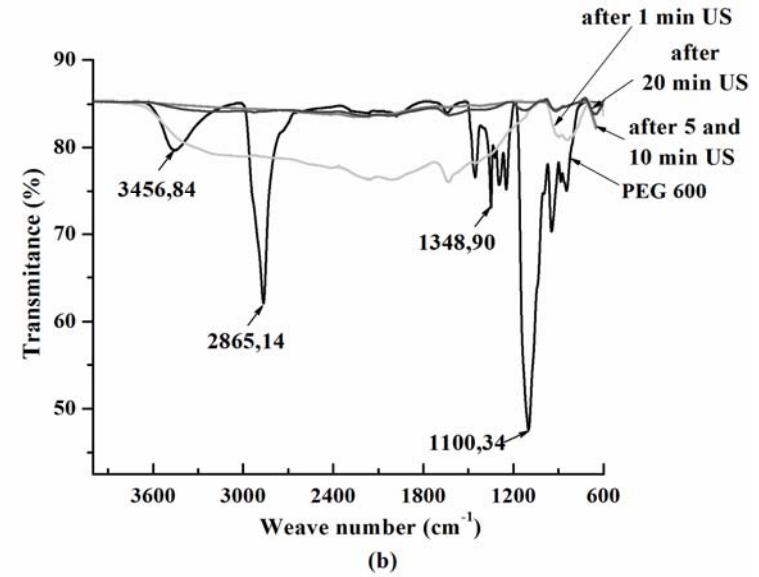


Fig. 3. The FTIR spectra of PEG 600 and anodized sample (a) and PEG 600 and anodized samples after ultrasonication (b)

In the Fig. 3 (b) the spectra show that after 1 min. at ultrasound, some of the electrolyte is still present, but it completly desapeared after 5, 10 and 20 min. US treatment.

The data presented in Fig. 4 show that after anodizing, water droplets exhibit contact angles of 12° so the sample surface is highly hydrophilic. After 1 min of ultrasonication treatment, the sample surface becomes hydrophobic. If ultrasonication time increases, the contact angle is decreasing, reaching the value around 88° after 20 min US, close to the value obtained for Ti untreated (Ti blank) 81°.

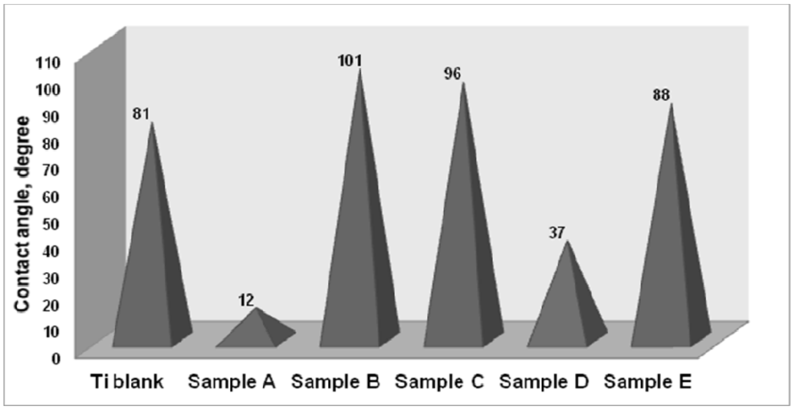


Fig. 4 Contact angle values for Ti blank, anodized sample and anodized samples after different ultrasonication times

Applications, like those in the dye-sensitized solar cells for example, those covered nanotubes are not beneficial and an treatment for removing this shielding is necessary [14]. In this case the ultrasonication treatment was applied and for understanding how this US treatment affect the anodized sample, the electrochemical characterization of the samples is presented.

Fig. 5 shows comparatively the Tafel plots for Ti, anodized sample and anodized samples after different US treatment times, obtained in a Hank solution. From Tafel diagrams we can observe that all anodized samples after US treatment treatment increase their corrosion resistance of Ti. Data from Tafel plots obtained with the Nova software were summarized in Table 1, that contains the values of corrosion potential (Ecorr), corrosion current (jcorr), corrosion rate and polarization resistance.

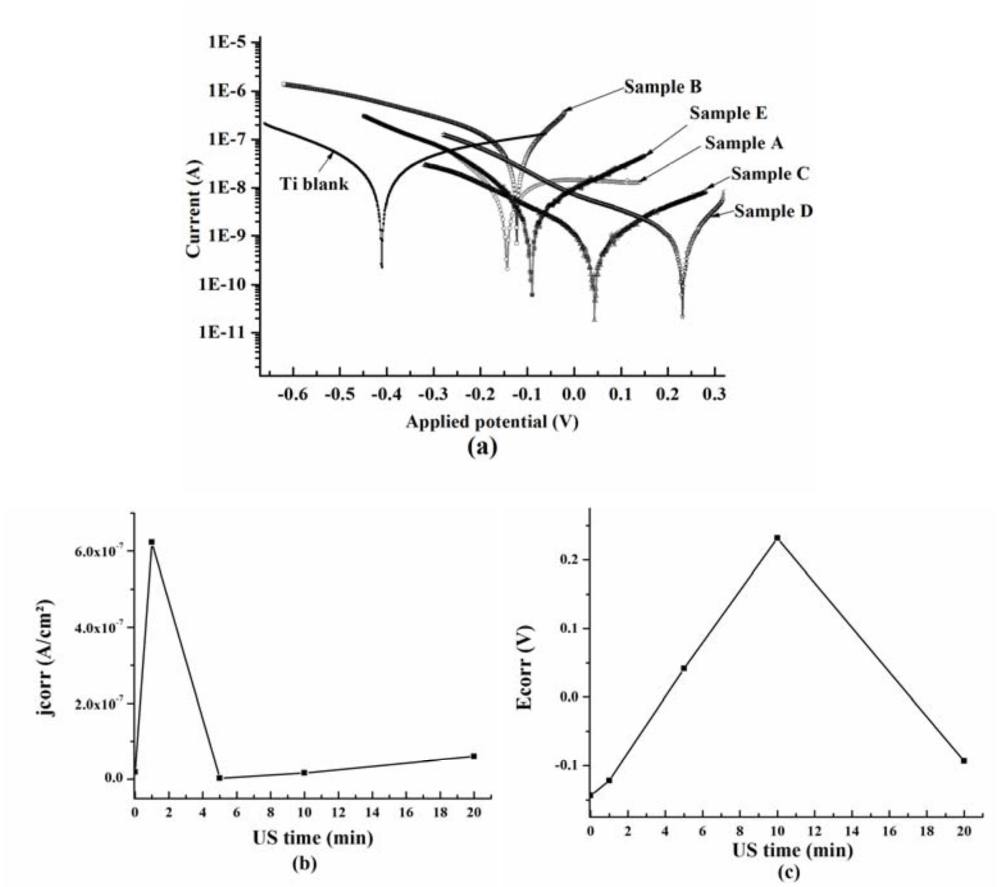


Fig. 5 (a) The Tafel plots in Hank solution for simply anodized sample (A), anodized sample after 1 min US (B), 5 min. ultr. (C), 10 min. US (D), 20 min. US (E) and untreated Ti sample; (b) the corrosion current *versus* US time plot; (c) the corrosion potential versus time plot

Table 1

The corrosion data obtained from Tafel plots

Sample	Ecorr (V) vs. Ag/AgCl	**jcorr x 10^8 (A/cm²)**	**Corrosion rate x10^4 (mm/year)**	**Polarization resistance x10^{-5} (Ω.cm^2)**
Ti blank	-0.41	19.24	16.75	28.27
Sample A	-0.14	1.94	1.69	58.2
Sample B	-0.12	62.28	54.20	5.30
Sample C	0.04	0.27	0.24	620.2
Sample D	0.23	1.66	1.45	281.6
Sample E	-0.09	6.01	5.23	87.89

In the graph from Fig. 5 (b), the corrosion current is increasing from 0 to 1 min US due to some cracks apparition in the oxide layer and partial removing of the PEG 600/oxide shielding layer from the TiO_2 surface. From 1 to 5 min US, the corrosion current is decreasing because the repasivation probably occurs, and a new barrier oxide layer is formed.

With increasing of US time, the corrosion current is increasing again, but with a slower rate, because of the continuum ruptures in the barrier and nanotubes layers.

In the graph from Fig. 5 (c), until 10 min US, the corrosion potential is shifted almost linearly towards more positive values, proving the passivation due to new protective layers; at 20 min US may be explained because of the removing of those protective layers.

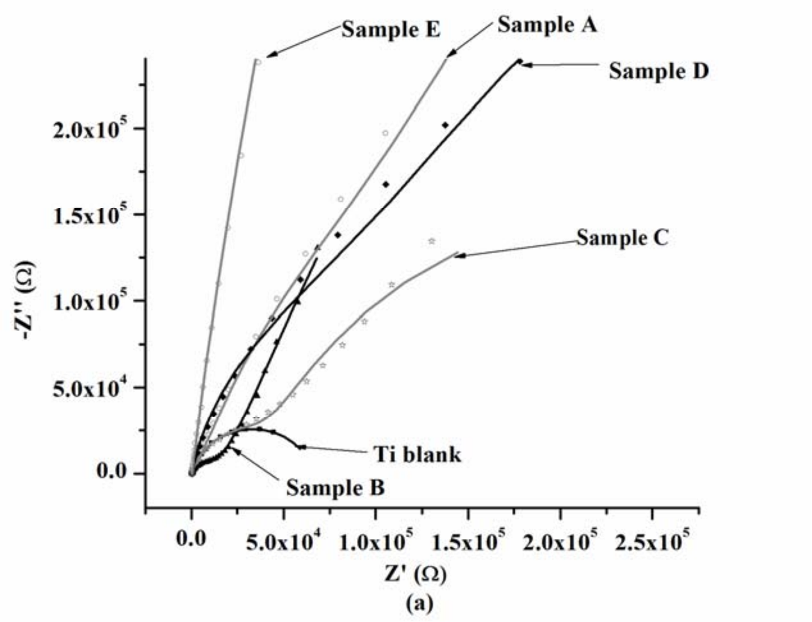


Fig. 6. (a) Nyquist diagrams for Ti blank and A-E samples in Hank solution

The processes at interface of Ti/TiO_2 nanotube layer/electrolyte are also illustrated in terms of EIS measurements data obtained in a Hank solution according to Nyquist diagrams presented in Fig. 6 (a).

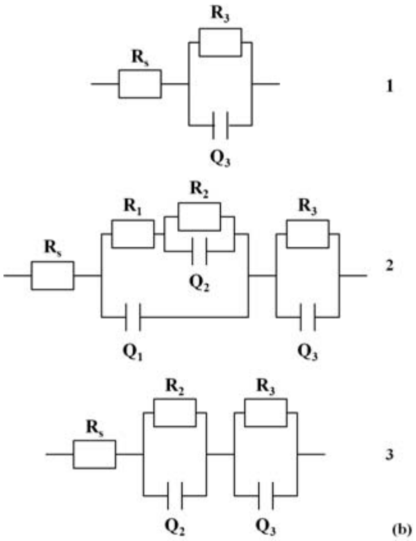


Fig. 6

Fig. 6 (b) Used circuits for fitting the data. In the three electrical schemes R is an ohmic resistances and Q is a constant phase element (CPE): Rs – solution resistance; R- resistance and Q constant phase element (CPE); R1, Q1 – for the titanium oxide/PEG 600 shielding layer, R2, Q2 – for the nanotubes layer and R3, Q3 - for the titanium oxide barrier layer

The data were fitted using the equivalent circuits drawn in Fig. 6 (b). For the untreated Ti sample and the anodized sample after 20 min US (E sample), the first circuit was used. In this case the circuit has only the solution resistance connected in series with a second circuit consisting of resistor (attributed to the polarization resistance) in parallel with a constant phase element (CPE) corresponding to an oxide layer. For the anodized sample and anodized sample after 1 min US the second circuit was used. In this case the circuit is more complex. Rs is the resistance of Hank solution, R_1 and Q_1 correspond to the PEG 600/oxide layer covering the nanotubes, shown also in the SEM images, R_2 and Q_2 are for the nanotube layer and R_3, Q_3 for the titanium oxide barrier layer associated with high impedance. For the anodized sample after 5 and 10 min US the third circuit is proposed having three modules connected in series. In this case the resistance and CPE for the PEG 600/oxide layer were eliminated indicating that this layer is removed.

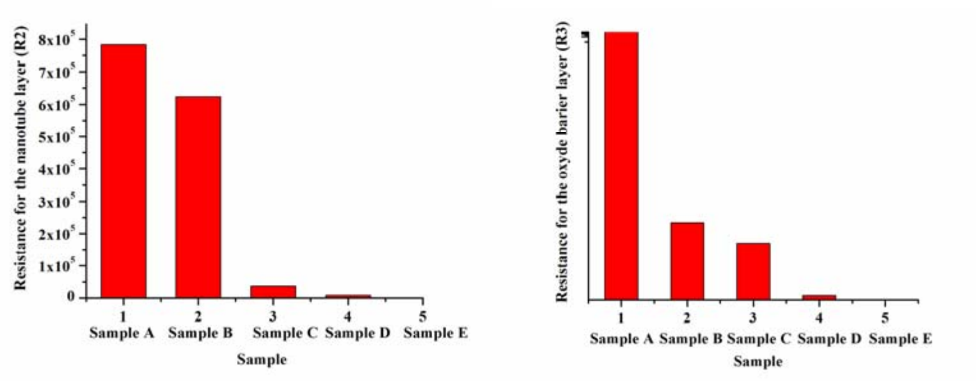
Table 2 presents the results of the fitting process.

Table 2

Parameters from EIS fitting data

Parameter		Sample A	Sample B	Sample C	Sample D	Sample E	Ti blank
R_S ($\Omega\cdot cm^2$)		289	453	402	375	379	242
R_1 ($\Omega\cdot cm^2$)		19855	10789				
Q_1	Y_0 ($\Omega^{-1}\cdot s^n$)	$2.4\cdot10^{-6}$	$5.2\cdot10^{-6}$				
	n_1	0.70	0.87				
R_2 ($\Omega\cdot cm^2$)		$7.83\cdot10^5$	$6.23\cdot10^5$	37507	8576		
Q_2	Y_0 ($\Omega^{-1}\cdot s^n$)	$5.49\cdot10^{-6}$	$8.56\cdot10^{-5}$	$5.57\cdot10^{-6}$	$6.56\cdot10^{-6}$		
	n_2	0.92	0.41	0.88	0.89		
R_3 ($\Omega\cdot cm^2$)		$3.3\cdot10^8$	$1.4\cdot10^6$	$1.3\cdot10^6$	$1\cdot10^6$	$6.9\cdot10^5$	$6.6\cdot10^4$
Q_3	Y_0 ($\Omega^{-1}\cdot s^n$)	$2.78\cdot10^{-6}$	$1.03\cdot10^{-4}$	$2.65\cdot10^{-5}$	$8.63\cdot10^{-6}$	$1.35\cdot10^{-6}$	$6.04\cdot10^{-6}$
	n_3	0.71	0.87	0.80	0.89	0.91	0.84

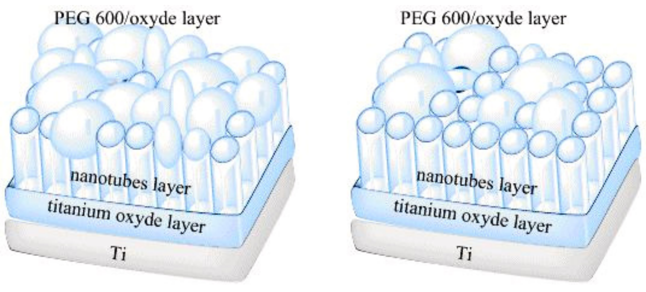
From the Table 2 the resistance for the nanotube and oxide barrier layer were extracted for each sample and compared in Figs. 7 (a) and (b). All results show a diminishing influence of the resistive oxide layers, and damage also in the nanotubes layer with the increasing of US time.



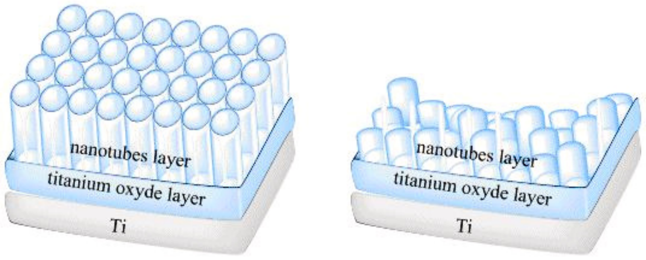
A B

Fig. 7 Comparison of the ohmic resistances assigned to the nanotube and oxyde layer (R_3) for simply anodized sample and anodized sample after different US times

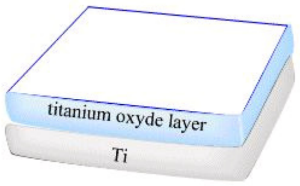
The obtained results offer an overall perspective evolution of ultrasonication action in time, illustrated also by Figures 8 (a)-(e).



a) Anodized sample in PEG 600 b) Anodized sample after 1 min. US



c) Anodized sample after 5 min US d) Anodized sample after 10 min. US



e) Anodized sample after 20 min. US

Fig. 8 The initial anodized sample surface and surface evolution during US treatment

6. Concluding Remarks

Self-organized TiO_2 nanotubes obtained in the presence of PEG 600 electrolyte with a small amount of water and NH_4F are obtained by forming a TiO_2 –PEG layer over TiO_2 nanotubes.

It is demonstrated and this is the new finding of the paper that the ultrasound treatment of anidized Ti samples is useful to control the shielding layer removing. The formation and damage of shielding PEG 600/oxide layer is an original part of the paper. This layer acts as a protective against corrosion layer, but is cracked after 1 minutes of US treatment and can be completly removed after 5 min. US time. When the time of US treatment is increased to 20 min, the TiO_2 nanaotubes barier layer is damaged.

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REFERENCES

[1] *I. Demetrescu, C. Pirvu, V. Mitran*, "Effect of nano-topographical features of Ti/TiO_2 electrode surface on cell response and electrochemical stability in artificial saliva", in Bioelectrochemistry, **vol. 79,** no. 1, 2010, pp. 122-129

[2] *D. V. Bavykin, A.N. Kulak and F.C.Walsh*, "Metastable nature of titanate nanotubes in an alkaline environment", in Crystal Growth & Design, **vol . 10**, no. 10, 2010, pp. 4421-4427

[3] *S. P. Albu, P.Roy, S. Virtanen and P. Schmuki*, "Self-organized TiO_2 nanotube arrays: critical effects on morphology and growth",in Israel Journal of Chemistry, **vol. 50**, no. 4, 2010, pp. 453–467

[4] *L. Yin, S. Ji, G. Liu, G. Xu and C. Ye*, "Understanding the growth behavior of titania nanotubes", in Electrochemistry Communications, **vol. 13**, 2011, pp. 454-457

[5] *S. Rani, S. C. Roy, M. Paulose, O. K. Varghese, G. K. Mor, S. Kim, S. Yoriya, T. J. LaTempa and C. A. Grimes*, "Synthesis and applications of electrochemically self-assembled titania nanotube arrays", in Phys. Chem. Chem. Phys., **vol. 12**, 2010, pp. 2780-2800

[6] *I. Man, C. Pîrvu and I. Demetrescu*, "Enhancing titanium stability in Fusayama saliva using electrochemical elaboration of TiO_2 nanotubes", in Revista de Chimie, **vol. 59**, no. 6, 2008, pp. 615-617

[7] *M. Mîndroiu, C. Pîrvu, R. Ion and I. Demetrescu*, "Comparing performance of nanoarchitectures fabricated by Ti_6Al_7Nb anodizing in two kinds of electrolytes", in Electrochimica Acta, **vol. 56**, 2010, pp. 193-202

[8] *J. M. Macak and P. Schmuki*, "Anodic growth of self-organized anodic TiO_2 nanotubes in viscous electrolytes", in Electrochimica Acta, **vol. 52**, 2006, pp. 1258-1264

[9] *C. C. Manole and C. Pîrvu*, "Surface and electrochemical analysis for the understanding of TiO_2 nanopores/nanotubes changes in post-elaboration treatment", in Surface and Interface Analysis, **vol. 43**, no. 7, 2010, pp. 1022-1029

[10] *C. C. Manole, C. Pîrvu and I. Demetrescu*, "Evaluation of TiO_2 nanotubes changes after ultrasonication treatment", in Molecular Crystals and Liquid Crystals, **vol. 521**, 2010, pp. 84-92

[11] *M. S. Akhtar, J. G. Park, H. Lee, S.-K. Lee and O-Bong Yang*, "A novel composite electrolyte of titania nanotubes as fillers and polyethylene gycol for dye-sensitized solar cells", in 34th IEEE Photovoltaic Specialists Conference, **vol. 1-3**, 2009, pp. 2398-2401

[12] *M. S. Akhtar, Ji-Min Chun and O-Bong Yang*, "Advanced composite gel electrolytes prepared with titania nanotube fillers in polyethylene glycol for the solid-state dye-sensitized solar cell", in Electrochemistry Communications, **vol. 9**, no. 12, 2007, pp. 2833-2837

[13] *J. M. Harris*, Poly(ethylene glycol) chemistry: biotechnical and biomedical application, Plenum Press, New York, 1992

[14] *D. Kim, A. Ghicov and P. Schmuki*, “TiO_2 Nanotube arrays: elimination of disordered top layers („nanograss”) for improved photoconversion efficiency in dye-sensitized solar cells”, in Electrochemistry Communications, **vol. 10**, 2008, pp. 1835-1838

[15] *R. C. Rowe, P. J. Sheskey and M. E. Quinn*, Handbook of pharmaceutical excipients, 6th ed., Pharmaceutical Press. xxvii, London, 2009

[16] *P. Roy, S. Berger and P. Schmuki*, “TiO_2 nanotubes: synthesis and applications”, in Angew. Chem. Int. Ed., **vol. 50**, 2011, pp. 2904 - 2939

[17] *J. Wan, X. Yan, J. Ding, M. Wang and K. Hu*, “Self-organized highly ordered TiO_2 nanotubes in organic aqueous system”, in Materials Characterization, **vol. 60**, 2009, pp. 1534 - 1540.

[18] *Y. LiXia, L. ShengLian, C. QingYun and Y. ShouZhuo*, “A review on TiO_2 nanotube arrays: fabrication, properties, and sensing applications”, in Chinese Sci. Bull., **vol. 55**, no. 4 - 5, 2010, pp. 331 - 338

[19] *J. Kunze, A. Seyeux and P. Schmuki*, “Anodic TiO_2 layer conversion: fluoride-induced rutile formation at room temperature”, in Electrochemical and Solid-State Letters, **vol. 11**, no. 2, 2008, pp. K11-K13