



Wettability of micro and nanostructured surface of titanium based electrodes: influence of chemical and electrochemical etching

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The present work investigates the effects of different surface micro- and nanostructures on electrode morphology, wettability, and electrochemical performance.

In their preparation, different etching agents have been used and compared. The nanostructures have been obtained by anodizing titanium foils in a glycerol medium.

The morphology of the so-prepared electrodes was analyzed by scanning electron microscopy. The electrochemical performance was evaluated by potentiodynamic polarization and impedance spectroscopy.

The wettability of the substrates was investigated by sessile-drop goniometry by the measure of the contact angle using both water and an organic solvent.

The preliminary results show that the surface treatments produced a substantial variation in the wettability of the treated substrates compared to that of untreated titanium. Contrary to the alkaline etching, the acid etching resulted in increased hydrophilicity. The nanotubular structures increased the materials hydrophobicity of air aged samples.

1. Introduction

Due to their mechanical and chemical properties, such as the high strength to weight ratio, the non-magnetic character, and the excellent corrosion resistance, titanium, and titanium-based materials have recently aroused growing interest. The technological applications range from aerospace both for structural design and propulsion to the automotive, for the construction of engine parts, exhaust-systems valves, and turbochargers. (Veiga et al., 2012). But Titanium is nowadays especially known for its biotechnological applications. The remarkable chemical inertness of this material, mainly due to its passivating ability, together with the notable capacity for osseointegration, high fatigue limit, and Young's modulus similar to that of the cortical bone, determine its outstanding biocompatibility (Kaur and Singh, 2019). Besides, due to the possibility of growing nanotubes on the surface, it is also possible to exploit titanium for a prolonged drug release directly in situ (Fathi et al., 2019). Being electrically conductive and resistant under even harsh conditions, titanium has been long used as an electrode material and for sensing. However, the immediate formation of the passivation film under oxidizing conditions prevents any reaction to proceed (Bewer et al, 1982) thus making necessary the activation of the surface via deposition of electrocatalytic conductive films. In particular, the titanium surface can be coated by inorganic oxide films, as in the dimensionally stable electrodes (DSA®) (Trasatti, 2000) or by covalent anchoring of organic films to develop, for example, bio-sensors (Battocchio et al., 2019). Mixed metal oxides films can also be deposited on noble metals such as Platinum (Sotgiu et al., 2017) but clearly, Titanium provides the double advantage of reducing costs and also allowing micro and nanostructuring of its surface. The adhesion of the

titanium-supported films can be ensured with an interlayer (Sotgiu et al., 2014) or through modification of the electrode surface (Sotgiu et al., 2015) and by anodization (Petrucci et al., 2018) to favor the growth of ordered Titania nanotubes.

To promote the adhesion as well as the formation of even coatings, the solvent must show an adequate ability to wet the substrate. To this aim, before the deposition of the precursor solution, the surface of these materials is degreased or chemically cleaned (Becke et al., 2016). Etching treatments present the advantage of increasing the specific surface, favoring load, and adhesion of the film (Huynh et al., 2019) and therefore electrocatalytic activity (Burleigh, 2000) and stability (Molitor et al., 2001) of the materials.

Recently, a new approach based on the possibility of producing structures at the nanoscale has been proposed with the significant advantage of tailoring the nanostructures by tuning the operative conditions while enhancing the interaction between the electrode and the electrolyte (Indira et al., 2015).

This work investigates the effect of different surface treatments on the morphological properties, wettability, and electrochemical response of titanium samples, to improve their applicability and performance with particular reference to the biomedical field. The proposed treatments include chemical etching with acids (hydrogen chloride, HCl, hydrogen fluoride, HF, and oxalic acid, C₂H₂O₄) or concentrated alkalis (Sodium hydroxide, NaOH) as well as combinations of oxidants such as the piranha solution (consisting of a solution of hydrogen peroxide, H₂O₂, and sulfuric acid, H₂SO₄). Some titanium samples were subjected to anodization treatments in a glycerol-based medium for the formation of self-organized titania nanotubes.

The morphological characteristics of the materials were analyzed with scanning electron spectroscopy (SEM) while the electrochemical properties through potentiodynamic polarization curves and impedance spectroscopy. The surface-wetting characterization has been conducted by sessile-drop goniometry.

2. Experimental

2.1 Materials

All reagents were supplied by Sigma Aldrich and used as received.

2.2 Electrode preparation

All the electrodes reported in Table 1 were obtained from titanium foils (99.6%, 2.0 cm x 1.5 cm) and, before each treatment, were subjected to ultrasonic cleaning with water/acetone solution (v/v, 50/50) for 10 min, then other 10 min in ethanol, and finally dried under a nitrogen stream at ambient temperature.

Each of the reported treatments was performed in duplicate to ensure the reproducibility of the method and for greater accuracy in data collection.

NC-02 (etch in HF): the samples were immersed in a 2% solution of HF (v/v) for 45 seconds and immediately washed with distilled water to neutral pH.

NC-03 (nanotubes): the procedure adopted is a modification of that previously proposed by other authors (Park et al., 2017). The anodization process was performed in glycerol solution (C₂H₈O₃, 60% v/v) containing NH₄F (0.25 % by weight) at room temperature. After an initial potentiodynamic ramp from 0 V to the final potential at a rate $v = 0.1 \text{ V}\cdot\text{s}^{-1}$, a potentiostatic electrolysis at the potential $E = 15 \text{ V}$ was conducted for 45 minutes.

NC-04 (etch in HCl): The samples were treated in an 18% solution of HCl at 80° C, for 10 minutes.

NC-05 (etch with NaOH): The samples were immersed in a solution of NaOH 5 M at 80° C, for 2 hours.

NC-06 (etch with piranha): The samples were treated in a solution 1:1 (v/v) of H₂O₂ (30 % in volume) and sulfuric acid at 80° C, for 30 minutes.

NC-07 (etch with oxalic acid): The samples were treated in a solution of oxalic acid (18 % by weight) at boiling temperature, for 10 minutes.

At the end of each treatment, all the samples were washed with distilled water, acetone and dried in air.

2.3 Surface Characterization

Morphological observation of the samples was obtained by Scanning Electron Microscopy using a Zeiss Gemini SIGMA 300 FEG SEM (Jena, Germany)

2.4 Surface wettability

Surface wettability was investigated through water contact angle (WCA) measurements carried out using a homemade contact angle meter equipment realized respecting the relative normative (UNI EN 828, UNI 9752, ASTM D-5725-99). Three samples were observed for each condition, depositing four drops (3 µl) on each; the corresponding image was captured with an Olympus Software Imaging System after 20s stabilization. The contact angle was measured using ImageJ software. All measurements were made on-air aged samples. The aging period was at least three weeks after the preparation at room temperature.

2.5 Electrochemical measurements

Corrosion characteristics of the samples were investigated by potentiodynamic polarization test using an AMEL System 5000 workstation, CorrWare software version 3.5c (Scribner) for the acquisition and CorrView software version 3.5c (Scribner) for the elaboration. Measurements were performed on 1 cm² samples areas at 22±2 °C in a three-electrode electrochemical cell with the sample as the working electrode (WE), a platinum wire as a counter electrode (CE) and Ag/AgCl as the reference electrode in a solution of Na₂SO₄ 0.1 M. The polarization tests were conducted at a scan rate of 1.0 mV/s in the potential range from -500 mV to 500 mV vs open circuit potential (OCP).

Electrochemical impedance spectroscopy (EIS) was recorded using a Solartron 1255B Frequency Response Analyzer. The frequency ranged from 60 kHz to 100 mHz, with an ac amplitude of ±10 mV. Before measurement, samples were immersed in the solution until the open circuit reached a steady-state value.

3. Results

The samples prepared with different etching and their principal data are reported in Table 1.

Table 1: Surface treatments and chemical-physical data.

Id	Surface Treatment	% Δm ¹	I_0 ($\mu A cm^{-2}$) ²	E_0 (V) ²	θ (in water) ³	θ (in CH ₂ l ₂) ³
NC-01	Ti	–	0.102	–0.125	66.28 °	50.21 °
NC-02	Ti etch HF	3.88	0.060	–0.091	111.40 °	62.40 °
NC-03	Ti - NT	≈ 0	0.013	–0.303	115.30 °	14.95 °
NC-04	Ti etch HCl	2.65	0.045	–0.151	116.99 °	53.33 °
NC-05	Ti etch NaOH	≈ 0	0.038	–0.296	43.71 °	49.40 °
NC-06	Ti etch piranha	3.23	0.095	–0.197	114.02 °	34.13 °
NC-07	Ti etch oxalic acid	0.17	0.049	–0.101	119.68 °	56.86 °

¹Weight loss percentage, calculated as % $\Delta m = [(initial\ mass - final\ mass)/initial\ mass] \cdot 100$

²Corrosion current and potential extracted from the potentiodynamic curves

³Contact angles

The effect on the Titanium surface morphology is highlighted by the SEM images shown in Figure 1. In general, a different result was observed under acid and alkaline etching conditions. The action of HCl produced a significant increase in roughness, and therefore in the exposed surface, without generating sharp edges. Oxalic acid generated extensive and deep holes along the entire surface. Finally, the action of HF caused considerable removals of material (as evidenced by the weight loss Table 1) but according to preferential directions that followed the crystallographic planes of the starting substrate.

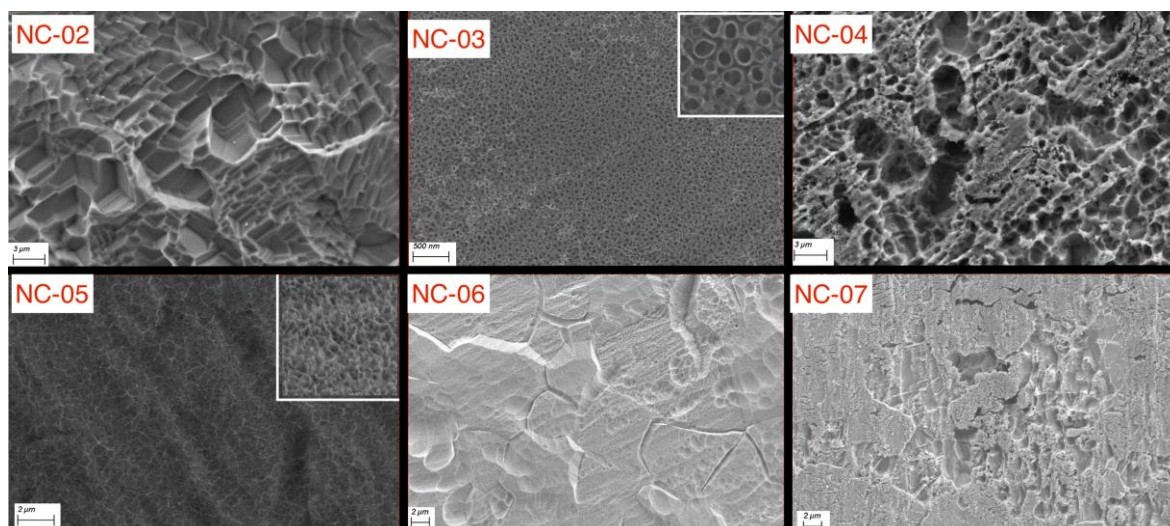


Figure 1: SEM images of E 8 (a) E 11 (b) and E 14 (c). Magnification: 500x

The treatment with hot NaOH gave rise to a sort of nanometric pitting on a scale with the formation of a particular honeycomb structure (Figure 1, NC-05 inset)

The combination of acid-alkali treatments represents a possible route to obtain a highly developed surface and an effective nanostructure for anchoring subsequent functionalizations. The micrographs show a "hybrid" morphology characterized by the presence of grooves and cracks (similar to those observed for HF, although with larger "islands"), and a dense and homogeneous nanostructure. Finally, through the electrochemical anodization treatment, the characteristic ordered array of nano-pores was observed, with an average diameter of less than 100 nm (Figure 1, NC-03 inset).

All prepared samples were then electrochemically tested. In detail, the analysis of the open circuit potential and the polarization curves were reported (Figure 2) to test their responses to any corrosive processes.

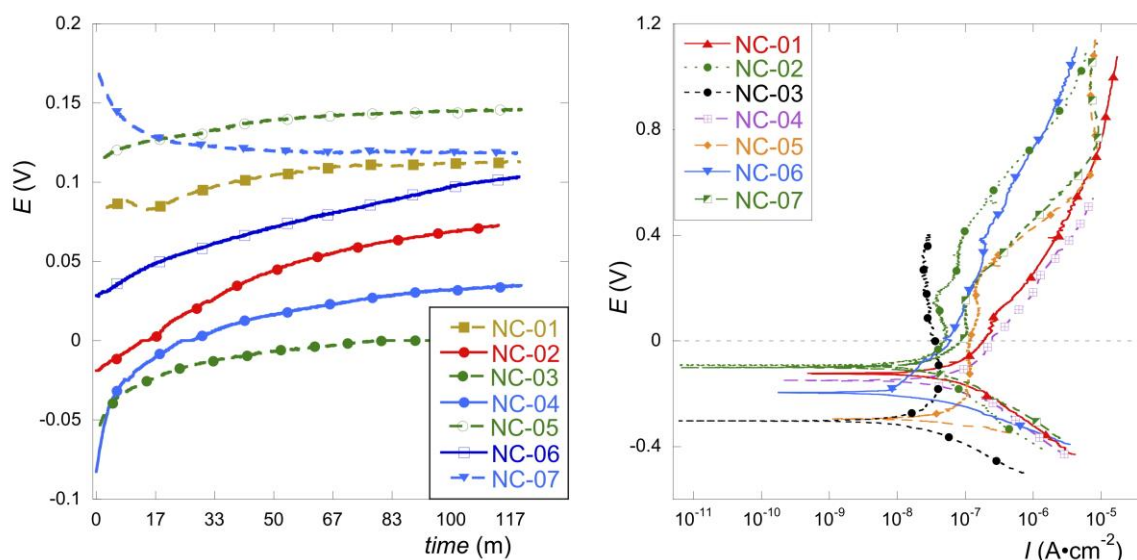


Figure 2: (a) Open circuit potential (OCP) curves; (b) Potentiodynamic polarization curves. Conditions: $\text{Na}_2\text{SO}_4=0.1 \text{ M}$, $v=0.1 \text{ mV}\cdot\text{s}^{-1}$

Acid etchings did not change significantly the active potential, based on the comparable value of the corresponding E_{corr} . Both the anodization process and the etching with NaOH caused a drop of about 170 mV in the corrosion potential, which can be related to the higher exposed surface as a consequence of the nanostructured morphology generated by these treatments (Figure 1). NC-06, obtained by the combined use of both strong acid and base, showed an intermediate behavior.

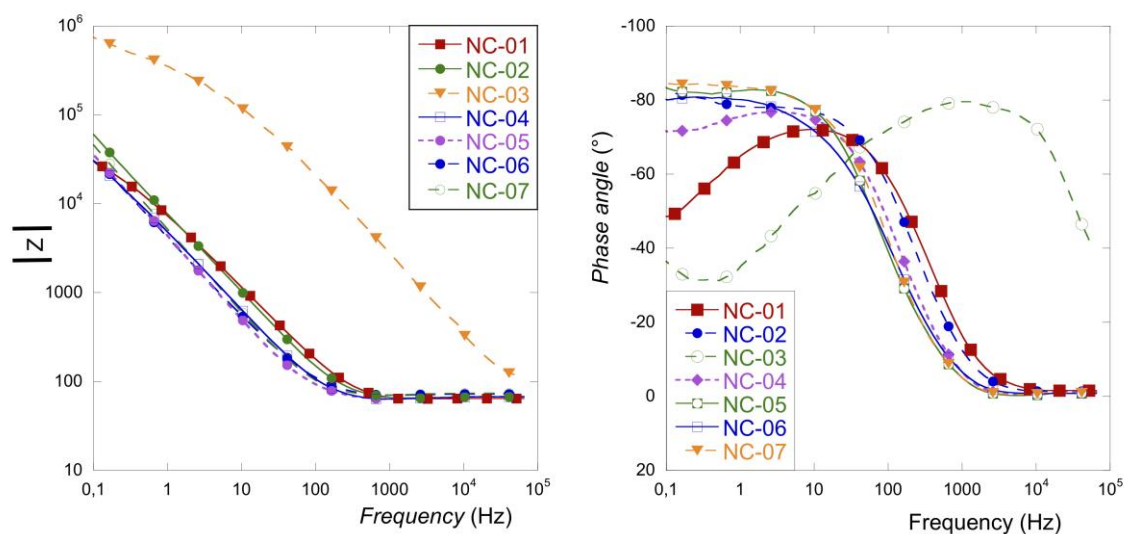


Figure 3: Electrochemical impedance Bode plots for (a) impedance magnitude ($|Z|$); (b) phase angle (θ) vs. frequency (f). Conditions: $\text{Na}_2\text{SO}_4=0.1 \text{ M}$.

All the surface pretreatments, except HCl etching and Piranha treatment, were able to induce a passivating behavior which was more pronounced for NaOH and nanotubes, with the latter showing the lowest I_0 value. All samples presented a comparable impedance modulus at the lowest frequency, indicating that corrosion resistance of the metal surface remained substantially unaltered. Considering the phase shift at the same frequency range, it was possible to further appreciate an increase in the oxide layer stability, as a higher phase shift in this region can be interpreted as a strong indicator of a good passive film. The anodized samples showed a significantly different impedance spectrum, evidencing the presence of diffusional phenomenon, which may be due to ionic species accessing the open nanotubular structure of the oxide film. The different ionic and electronic transport kinetics of this system requires further investigation. The wettability study was conducted using double distilled water as a polar solvent. For comparison, similar measurements were also carried out in diiodomethane (CH_2I_2), which is an apolar solvent that showed a complementary behavior. Only the results obtained with the polar solvent are here reported.

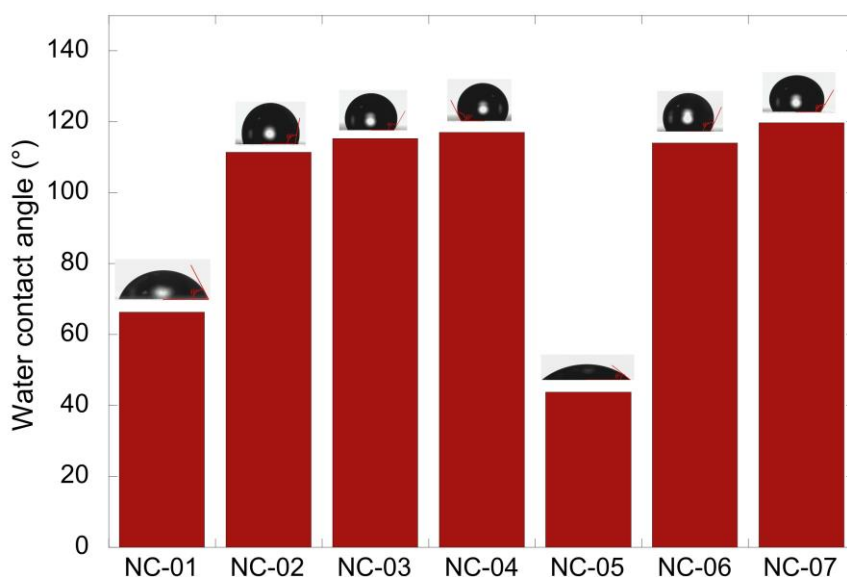


Figure 4: Effect of the surface treatment on the contact angle with water.

It is worth noting, that unlike the other materials, those subjected to anodization exhibited a remarkably different behavior depending on surface aging. Freshly prepared samples were highly hydrophilic while air aged samples showed significant hydrophobicity (NC-07). This behavior has already been found in previous work (Shin et al., 2011) and attributed to the growth and consolidation of the surface oxide layer. Mild chemical cleaning treatments conducted at room temperature with water, acetone, or ethyl alcohol, even in prolonged times, did not cause substantial changes in the behavior of the surface. In this study, to work with stabilized surfaces, all the samples were subjected to three-week preliminary aging.

Figure 4 shows that acid treatments made the surface more hydrophobic than untreated titanium presumably to the depletion of -OH groups. Therefore, the contact angle underwent a sharp increase from the value of 66.3° to values between 109.2° and 117° . In fact, while the passivating oxide, as mentioned, self-heals and reforms very quickly, the formation of -OH groups on the surface is a relatively slow process. It should be noted that despite the considerable differences in the morphological structures of the surfaces treated with acids, the effect on wettability was comparable.

The etching with hot NaOH, on the other hand, caused an increase in wettability as demonstrated by the decrease in the value of the contact angle from 66.3° to 43.7° . This behavior was probably due to the increase in the number of -OH groups; in fact, the hydroxyl group is polar with a strong affinity for H_2O and a great tendency to form hydrogen bonds. The treatment with piranha solution induced a net increase in the hydrophobic character of the surface, with an angle of 114° , comparable to that of acid etching. Finally, with the nanotube treatment, the effect on wettability was probably related more to a morphological component than to the chemical properties of the surface. In this case, the marked roughness probably influenced the ability of the drop to adhere to the surface.

4. Conclusions

Samples of commercially pure titanium were subjected to various surface treatments including chemical etching and anodization.

The results obtained show that, through the selection of an appropriate method, it is possible to control the surface properties of titanium, both in terms of structure and interaction with the solvent.

In particular, with acid treatments, the surface is eroded with an increase in surface development but mainly following the crystallographic structure of the bulk. Also, a markedly hydrophobic surface is obtained. On the other hand, alkali treatment with NaOH produced a typical honeycomb nanostructure potentially suitable for anchoring organic molecules with a hydrophilic surface. As fresh anodized samples exhibited highly hydrophilic surfaces. The nanotubes aging increased the hydrophobicity of the surface due to the conversion of titanium hydroxide into titanium oxide. The complexity of the interaction between the nanotubular surface was strongly affected by the possibility of solvent diffusion inside the pores. This was highlighted in particular by the impedance measurements in which the phase and modulus response of Z were very different, especially at low frequencies, compared to the other treated surfaces.

References

- Battocchio, C., Concolato, S., De Santis, S. Fahlman, M., Iucci, G., Santi, M., Sotgiu, G., Orsini, M., 2019, Chitosan functionalization of titanium and Ti6Al4V alloy with chloroacetic T acid as linker agent, *Materials Science & Engineering C*, 99, 1133-1140
- Becke, S., Merz R., Hasse H., Kopnarski, M., 2016, Solvent cleaning and wettability of technical steel and titanium surfaces, *Adsorption Science and Technology*, 34, 261-274.
- Bewer G., Debrod H., Herbst H., 1982, Titanium for Electrochemical Processes, *Journal of Metals*, 34, 37-41.
- Burleigh T.D. 2000, Oxides formed on titanium by polishing, etching, anodizing, or thermal oxidizing, *Corrosion*, 56, 1233-1241.
- Fathi M., Akbari B., Taheriazam A., 2019. Antibiotics drug release controlling and osteoblast adhesion from Titania nanotubes arrays using silk fibroin coating. *Materials Science and engineering C*, 103, 109743.
- Huynh V., Ngo, N.K. Golden, T.D., 2019, Surface Activation and Pretreatments for Biocompatible Metals and Alloys Used in Biomedical Applications, *International Journal of Biomaterials*, 3806504.
- Indira K., Mudali U.K., Nishimura T., Rajendran, N., 2015, A Review on TiO₂ Nanotubes: Influence of Anodization Parameters, Formation Mechanism, Properties, Corrosion Behavior, and Biomedical Applications, *Journal of Bio- and Tribo-Corrosion*, 1, 28.
- Kaur M., Singh K., 2019, Review on titanium and titanium based alloys as biomaterials for orthopaedic applications, *Materials Science and Engineering C*, 102, 844-862.
- Molitor P., Barron V., Young T., 2001, Surface treatment of titanium for adhesive bonding to polymer composites: A review, *International Journal of Adhesion and Adhesives*, 21, 129-136.
- Park J., Lee G., Choi J., 2017, Key anodization factors for determining the formation of TiO₂ microcones vs nanotubes, *J. Electrochem. Soc.* 164, D640-644.
- Petrucci E., Montanaro D., Orsini M., Sotgiu G., 2018, Micro- and nanostructured TiO₂ substrate: Influence on the electrocatalytic properties of manganese oxide-based electrodes, *Journal of Electroanalytical Chemistry*, 808, 380-386.
- Shin, D.H., Shokuhfar T., Choi C.K., Lee S.-H., Friedrich C, 2011, Wettability changes of TiO₂, *Nanotechnology*, 22, 31570.
- Sotgiu G., Foderà M., Marra F., Petrucci E., 2014, Production and characterization of manganese oxide-based electrodes for anodic oxidation of organic compounds, *Chemical Engineering Transactions*, 41, 115-120.
- Sotgiu G., Tortora L., Petrucci E., 2015, Influence of surface roughening of Titanium substrate in the electrochemical activity of Manganese oxide thin film electrode in anodic oxidation of dye-containing solutions, *Journal of Applied Electrochemistry*, 45 (7), 787-797.
- Sotgiu G., Montanaro D., Orsini M., Petrucci E., 2017, Manganese-containing mixed oxide electrodes as anode materials for degradation of model organic pollutants, *Chemical Engineering Transactions*, 57, 1639-1644.
- Trasatti S., 2000, Electrocatalysis: understanding the success of DSA®, *Electrochimica Acta*, 45, 2377-2385.
- Veiga C., Davim J.P., Loureiro A.J.R., 2012, Properties and applications of titanium alloys: A brief review, *Reviews on Advanced Materials Science*, 32, 133-148.