

Electrochemical evaluation of Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys for biomedical application by long-term immersion tests

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In this investigation the electrochemical behaviour of the Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys, for application as implant materials was evaluated in Hanks' solution by electrochemical techniques. The alloys were immersed in this solution for 410 days and periodically they were tested by electrochemical impedance spectroscopy. At the end of this period, polarization curves of the three titanium alloys were obtained. The electrochemical impedance experimental results were interpreted using an equivalent

electrical circuit that simulates a duplex structure oxide composed of an inner compact layer, here called barrier layer, and an outer and porous layer. The results indicated that all the alloys present a very high corrosion resistance in the electrolyte used, typical of passive alloys, and that the corrosion resistance is mainly due to the barrier layer. The passive like behaviour was maintained during the whole period of test.

1 Introduction

The biocompatibility of metallic materials used as implants must be guaranteed and this property is directly associated to the corrosion resistance of these materials. Corrosion products leached into the physiological fluids might cause allergenic or toxic reactions [1]. The physiological fluids are complex environments containing corrosive elements such as chlorides and other components and, consequently, act as good electrolytes. Dissolved gases in the body fluids such as nitrogen, oxygen and carbon dioxide, may also affect the corrosion performance of the implants leading to differential aeration cells [2]. Consequently, the electrochemical behaviour of implant materials, such as titanium alloys, in physiological environments, has been extensively investigated [3–8]. A great number of these studies, used electrochemical tests associated to surface analytical techniques to investigate the passive oxide film composition on the implant materials surface. Most of the reported literature, however, present results related to short-term tests, even though permanent implants should remain in the patient for rather long periods. Differences have been reported in literature between *in vitro* and *in vivo* tests of biomaterials [9, 10] and the length of their contact with the physiological medium could possibly be one of the reasons for the reported differences.

Among the techniques largely used in the corrosion studies of implant materials, electrochemical impedance spectroscopy (EIS) is a very appropriate one to evaluate the electrochemical behaviour evolution of the metallic material-electrolyte interface with time. Fitting of the experimental results to equivalent electrical circuits is a usual practice that can be very useful to monitor this evolution once a proper model is chosen. Since different equivalent circuits can fit very

well the same experimental data, leading to erroneous interpretation, previous to the proposal of a particular equivalent circuit to represent the electrochemical interface under investigation, its physical properties must be known.

Various equivalent electrical circuits have been proposed in literature to simulate the electrochemical behaviour of titanium and its alloys [3–12]. Most of these circuits are based on the model of a duplex structure oxide composed of an inner compact layer, called barrier layer, and an outer porous layer. According to literature [5–9], the barrier layer is mainly accountable for the high corrosion resistance due to the passive oxide layer on the titanium alloys, whereas the porous layer, of lower resistance, has been associated to these alloys biocompatibility [11]. This seems to be associated to the incorporation of components from the physiological fluids into the pores of this layer, favouring osteointegration [11, 12].

Most of the investigations on materials for use as biomaterials reported in literature has been carried out for relatively short contact periods between the electrolyte and the metallic material, and the electrochemical behaviour of such materials during long-term exposure to physiological environments has not been largely studied. Alternatively, the aim of the present study was to evaluate the electrochemical behaviour of the Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys, for use as implant materials, by long-term immersion tests (410 days) in Hanks' solution using EIS and polarization methods.

2 Materials and methods

The composition of Ti alloys used in this investigation is shown in Table 1.

The near- β Ti-13Nb-13Zr alloy was obtained by arc melting pure (99.9 %) Ti and Nb, along with Zr containing 4.5 % Hf, under argon, using a non-consumable electrode. The material was then heat-treated at 1000 °C for 1 h for homogenization and water-cooled. The alloy was subsequently cold forged to 6.5 mm in diameter. In this stage, the alloy was heat-treated again [13]. The Ti-6Al-4V alloy (Supra Alloy Inc.) was heat-treated by the manufacturer at 712 °C for 30 min, and the Ti-

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Table 1. Chemical composition (wt.%) of Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys

Element	Ti-13Nb-13Zr	Ti-6Al-4V	Ti-6Al-7Nb
C	0.0350	0.024	0.08
H	0.0109	0.005	0.009
N	0.0039	0.006	0.05
O	0.0775	0.18	0.20
Fe	0.085	0.17	0.25
Al	–	6.0	6.5
S	< 0.001	–	–
Hf	0.0550	–	–
V	–	4.1	–
Ta	–	–	0.50
Nb	13.179	–	7.50
Zr	13.489	–	–
Ti	Bal.	Bal.	Bal.

Table 2. Chemical composition of Hanks' solution

Component	Concentration (Mol/L)
NaCl	0.1369
KCl	0.0054
MgSO ₄ ·7H ₂ O	0.0008
CaCl ₂ ·2H ₂ O	0.0013
Na ₂ HPO ₄ ·2H ₂ O	0.0003
KH ₂ PO ₄	0.0004
C ₆ H ₁₂ O ₆ ·H ₂ O	0.0050
Red phenol 1%	0.0071
pH	6.8

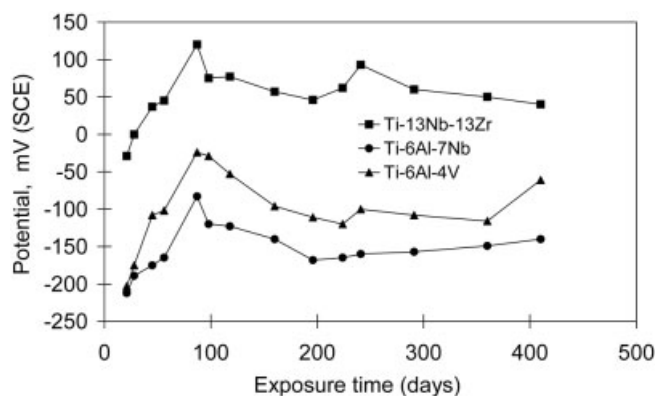
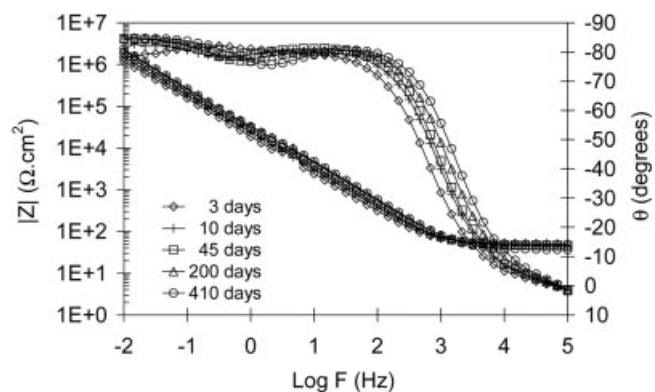
6Al-7Nb was acquired from IMI Titanium Limited England. The electrodes were prepared by epoxy cold resin mounting of alloys leaving areas for exposure to the electrolyte of 0.33 cm², 0.22 cm² and 0.25 cm², for the Ti-13Nb-13Zr alloy, Ti-6Al-4V and Ti-6Al-7Nb, respectively. The surfaces exposed to the electrolyte were prepared by sequential grinding with silicon carbide paper up to #2000 finishing, followed by mechanical polishing with diamond paste of 1 μ m. The samples remained immersed for 410 days in Hanks' solution naturally aerated at 25 °C, and at certain periods the corrosion potential was measured and electrochemical impedance spectroscopy (EIS) was performed. The potentiodynamic polarization tests were performed 410 days after immersion. The testing medium was a naturally aerated Hanks' solution, whose composition is given in Table 2. This solution was prepared by Instituto Adolpho Lutz, São Paulo SP, Brazil.

A three-electrode cell arrangement was used for the electrochemical measurements, with a saturated calomel electrode (SCE) as reference electrode and a platinum wire as the auxiliary electrode. All electrode potentials are referred to the SCE electrode. The polarization and EIS tests were carried out in duplicate to evaluate results reproducibility. Potentiodynamic polarization curves were obtained with a scan rate of 1 mV/s in the range from – 800 mV (SCE) to 3000 mV (SCE) using an EG&G273A potentiostat. The EIS tests were accomplished by means of a Solartron Model SI 1255 Frequency Response Analyzer coupled to a Princeton Applied Research (PAR) Model 273A Potentiostat/Galvanostat and controlled by an Electrochemical Impedance Software PAR model 398. The EIS measurements were obtained in potentiostatic mode and at the corrosion potential, E_{corr} with voltage perturbation amplitude of 10 mV in the frequency range from 100 kHz to 10 mHz, with 6 points per decade. All experiments were performed in naturally aerated conditions and at 25 °C.

3 Results

Fig. 1 shows the corrosion potential variation as a function of time for the three Ti alloys studied. The electrode potentials of the three alloys increased during approximately 90 days of immersion indicating oxide film thickening during that period. Subsequently it decreased until nearly 200 days, suggesting some oxide film deterioration or, followed but slight increase and fairly stabilization from 300 days onwards. The oscillations in potential observed suggest that the oxide film is not completely stable in the electrolyte (Hanks' solution). Despite the oscillations found in potential, the results suggest oxide film growth in the test solution used.

The evolution of the EIS diagrams with time of immersion in Hanks' solution is shown in Fig. 2 to Fig. 4 for the Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys, respectively. Highly capacitive results and high impedance values (order of 10⁶ $\Omega \cdot \text{cm}^2$) were obtained for all three alloys, during the whole test period. Phase angles close to – 90° were obtained at medium and low frequencies, suggesting a passive behaviour for all three alloys. Two time constants were easily distinguished in these diagrams, associated to the duplex oxide layer. In the range from 10 kHz to 0.1 kHz the phase angle increased with time of immersion for all alloys studied likely due to porous layer thickening. This porous oxide growth apparently had no significant effect on the alloy corrosion resistance, once it is mainly associated to the barrier layer.

**Fig. 1.** Corrosion potential variation with time of immersion for Ti-13Nb-13Zr, Ti-6Al-7Nb and Ti-6Al-4V alloys immersed in Hanks' solution at 25 °C**Fig. 2.** Bode diagrams for Ti-13Nb-13Zr alloy as a function of time of immersion in Hanks' solution, at 25 °C

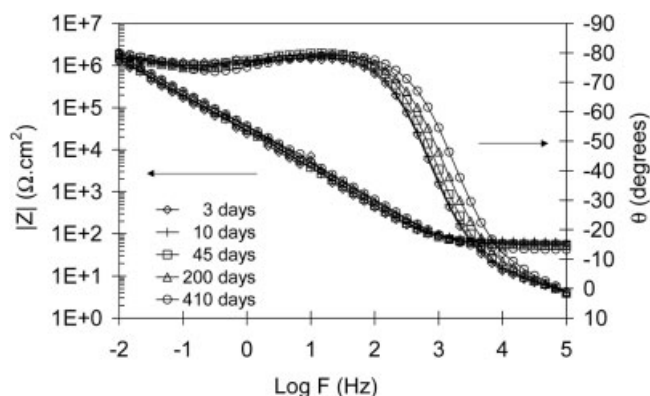


Fig. 3. Bode diagrams for Ti-6Al-4V alloy as a function of time of immersion in Hanks' solution, at 25 °C

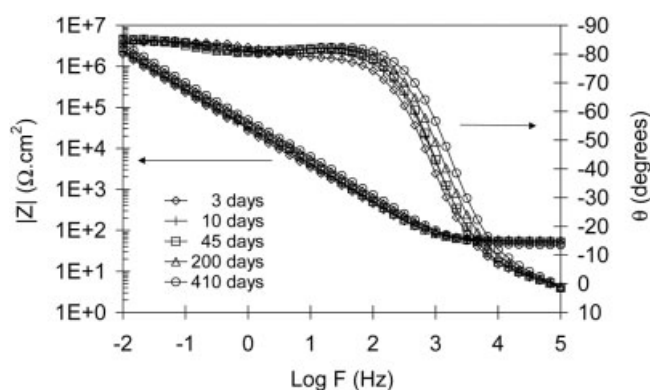


Fig. 4. Bode diagrams for Ti-6Al-7Nb alloy as a function of time of immersion in Hanks' solution, at 25 °C

The equivalent electrical circuit shown in Fig. 5 was proposed to fit the experimental data obtained for the three alloys. The Zview software was also used in this procedure. This equivalent circuit was adopted by Kolman et al. [14,15] and Yu et al. [16] to characterize oxide films formed on titanium and its alloys in aqueous environments.

The resistive components in the equivalent electrical circuit proposed R_s , R_p and R_b are associated to the solution resistance, the porous layer resistance and the barrier layer resistance, respectively. The constant phase elements, CPE_b and CPE_p are related to the capacitive behaviour of the barrier and porous layer, respectively. The porous layer contains microporosities where species from the environment are incorporated, resulting in its resistance increase with time of immersion. According to literature [11,12] this layer is related to the biocompatibility found in titanium alloys. The component R_p has been associated to the charge transfer resistance through the porosities of the porous layer. Eventually, the por-

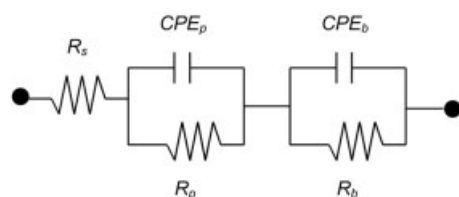


Fig. 5. Equivalent electrical circuit used to fit the EIS experimental results obtained in Hanks' solution, at 25 °C

osities might become sealed with compounds from the environment. According to the model proposed the barrier layer, represented by the parallel arrangement R_b and CPE_b , is the main responsible for the very high corrosion resistance of the titanium alloys. The component CPE_b , associated to the barrier layer oxide is responsible for the very high phase angles obtained at low frequencies. On the other hand, R_p is associated to the barrier layer resistance to charge transfer or species transport through it.

The variation of the resistance and capacitance values with time of immersion obtained from fitting to the equivalent electrical circuit proposed in Fig. 5 is shown in Figs. 6 and 7, respectively.

The main variations occurred in the porous layer during the first 50 days of test. For longer periods the values of resistance and capacitance showed a propensity to stabilization.

The oxide layer thickness was estimated assuming that the oxide layer behaves as parallel plates capacitor, using the equation $C = \epsilon \epsilon_0 A/d$, where C is the capacitance obtained from fitting the experimental results to the model proposed, ϵ is the dielectric constant of the oxide, ϵ_0 the dielectric permittivity of vacuum (8.85×10^{-12} F/m) and A and d represent the effective area and thickness of the oxide layer, respectively. The value of the dielectric constant, ϵ , for thin films depends on the experimental conditions, sample preparation

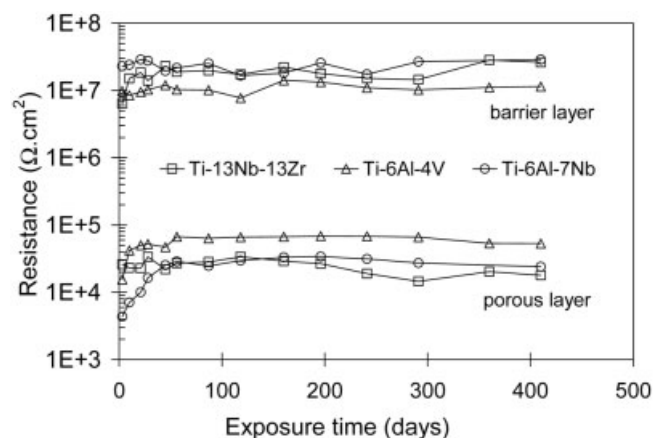


Fig. 6. Variation of barrier layer and porous layer resistance for the Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb as a function of time of immersion in Hanks' solution

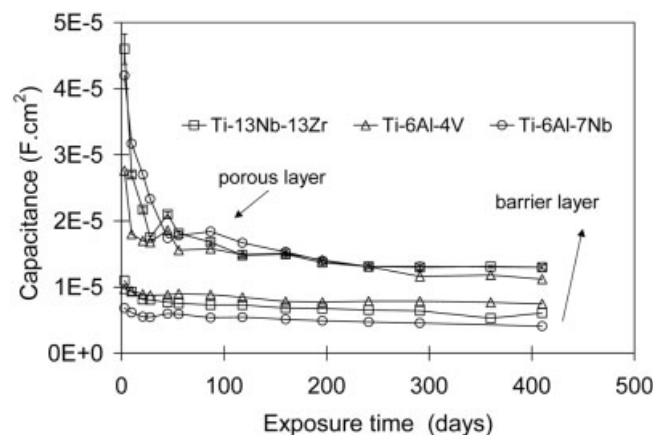


Fig. 7. Variation of barrier layer and porous layer capacitance of Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys with time of immersion in Hanks' solution

and oxide film growth rate, and this explains the variety of values found in the literature. Pan et al. [17], using a value of 65 for the dielectric constant of titanium oxide, and assuming a roughness factor of 1 for the barrier layer, and between 1 and 2 for the porous layer, obtained values of 6 nm for the barrier layer and between 2.5 and 5.0 nm for the porous layer, in a phosphate buffer solution (PBS).

The barrier layer thickness in the oxide on Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys after 410 days immersion in Hanks' solution was estimated using the capacitance values obtained from the EIS fitting to the proposed model and $\epsilon = 65$ for the dielectric constant of the oxide. The thickness values obtained for the three alloys as a function of time of immersion are shown in Fig. 8. The results showed the tendency to increase the barrier layer thickness with time, mainly for the Ti-6Al-7Nb alloy that presented the thicker barrier layer during the whole test period. For the two other titanium alloys, the thickness was fairly stable after approximately 150 days of immersion.

At the end of the 410 days of immersion, the samples of the titanium alloys were polarized and the polarization curves obtained are shown in Fig. 9. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were estimated from the polarization curves and these are -355 mV, -351 mV, -360 mV and 4.5 nA/cm², 8.3 nA/cm², 6.1 nA/cm² for Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb, respectively. For

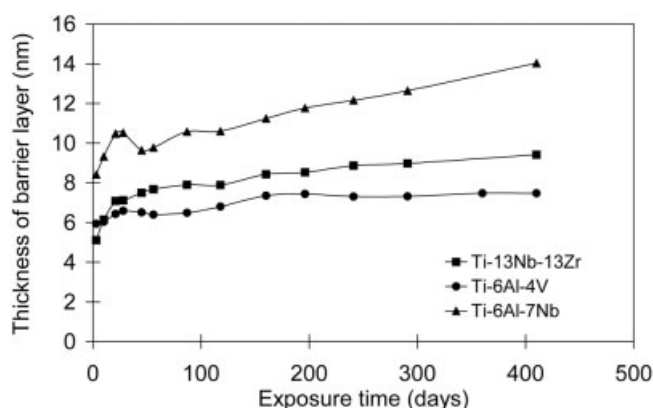


Fig. 8. Variation of the barrier layer thickness of Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys as a function of immersion time in Hanks' solution

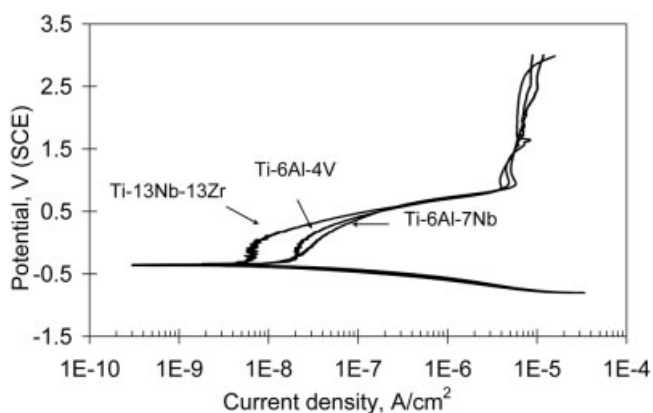


Fig. 9. Polarization curves for Ti-13Nb-13Zr, Ti-6Al-7Nb and Ti-6Al-4V alloys after 410 days in Hanks' solution at 25 °C. Scan rate: 1 mV/s

such a long-term immersion the values of E_{corr} are similar for the three alloys. From E_{corr} to approximately 900 mV the values of current density continuously increase with the overpotential for the Ti-6Al-7Nb alloy. However, for the Ti-13Nb-13Zr and Ti-6Al-4V alloys, from E_{corr} until approximately 50 mV there is a range behaviour typical of passive materials where the passive current density was 7 nA/cm² and 22 nA/cm², respectively. From 900 mV until 3000 mV, the polarization curves of Ti-13Nb-13Zr and Ti-6Al-7Nb alloys showed a typical passive behaviour, with current density values (i_{pp}) around 8 μ A/cm². At potentials close to 1500 mV, the Ti-6Al-4V alloy presented a slight different behaviour showing increase in current density, followed by a decrease to values close to that of the other two alloys. At potentials near to 2800 mV the current density increased again for the Ti-6Al-4V alloy reaching 15 μ A/cm² at approximately 3000 mV.

4 Discussion

The long-term electrochemical evaluation of the Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys in Hanks' solution showed that all three alloys presented similar electrochemical behaviour, typical of passive materials. The evolution of the impedance diagrams showed that the main variation occurred between 3 and 10 days of immersion and the two time constants found, associated to the duplex nature of the oxide (porous and barrier layers), became increasingly differentiated with time. From 10 days of immersion until the end of test (410 days), the impedance diagrams showed small variations, indicating a high stability of the surface under the test conditions applied. The values of the electrical parameters obtained from experimental data simulation showed that the resistance associated to the barrier layer is much larger than that of the porous one. The barrier layer resistance corresponded to tenths of M Ω · cm² whereas that of the porous layer was of the order of tenths of K Ω · cm², that is, superior by a factor of approximately 10³ times. Also the capacitance of the porous layer is superior to the barrier one by a factor of 1.5 to 3 times. These results support the hypothesis that the corrosion resistance of the titanium alloys is mainly due to the barrier layer. The Bode phase angles results at low frequencies for the three alloys corresponding to 410 days (Fig. 10) showed that the Ti-13Nb-13Zr and Ti-6Al-7Nb alloys presented higher phase angles associated to the barrier layer, than the Ti-

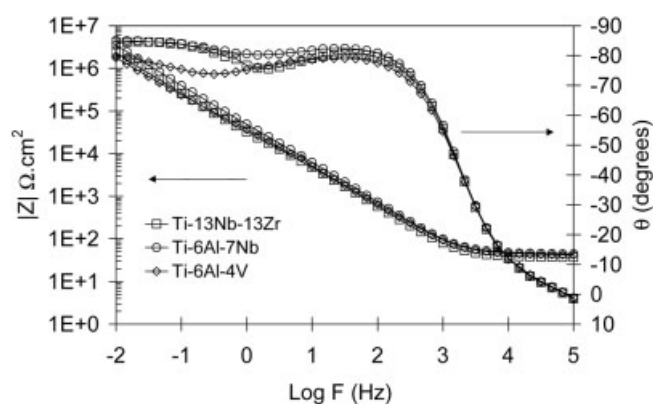


Fig. 10. Impedance diagrams for the Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys after 410 days of immersion in Hanks' solution, at 25 °C

6Al-4V alloy. This result suggest that this last alloy has a slightly inferior corrosion resistance than the other two in the physiological solution used as electrolyte, and this could be due to the thinner barrier layer formed on this last alloy comparatively to the other two.

The electrical parameters obtained from data simulation in fact showed increased resistance of the barrier layer for the Ti-13Nb-13Zr and Ti-6Al-7Nb alloys comparatively to Ti-6Al-4V alloy, despite of the fact that the E_{corr} and i_{corr} values obtained from polarization curves were very close for all the studied titanium alloys. The parameter values associated to the barrier layer showed only small variations with time of immersion although the thickness of this layer slightly increased with time. For the porous layer the capacitance decreased with time and stabilised after approximately 50 days, likely due to thickening.

5 Conclusions

The electrochemical evaluation of the Ti-13Nb-13Zr, Ti-6Al-4V and Ti-6Al-7Nb alloys in Hanks' solution during 410 days showed similar behaviour and high corrosion resistance for all the alloys, typical of passive metals. Electrochemical impedance spectroscopy was a very useful technique in the evaluation and monitoring of the electrochemical behaviour evolution of the titanium alloys allowing detecting small variations in the behaviour and corrosion resistance of the passive titanium alloys. A slightly improved corrosion resistance was associated to the Ti-13Nb-13Zr and Ti-6Al-7Nb alloys comparatively to the Ti-6Al-4V alloy.

6 References

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