

The Effect of Hydrogen Peroxide on the Electrochemical Behaviour of Ti-13Nb-13Zr Alloy in Hanks' Solution

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Titanium alloys are largely used for biomedical applications mainly due to their high corrosion resistance resulting from the protective oxide film formed on their surface. The literature, however, has pointed out discrepancies between in vitro tests and in vivo tests. These discrepancies have been ascribed to hydrogen peroxide (H_2O_2) generated by inflammatory reactions. In this investigation the electrochemical behaviour of a Ti-13Nb-13Zr alloy, which was developed as material for implants, has been evaluated in Hanks' solution, with and without H_2O_2 . The evolution of the electrochemical behavior was monitored by electrochemical impedance spectroscopy (EIS) and the results were fitted to an equivalent circuit that simulates an oxide film as a duplex layer structure composed of an inner barrier layer and an outer porous layer. In the solution without H_2O_2 , the oxide film was very stable during the whole test period. On the other hand, in the solution with H_2O_2 , the EIS results varied significantly, indicating a progressive decrease in the barrier layer resistance until 35 days which was followed by the restoration of the barrier layer protective characteristics against corrosion, either due to its growth or to its self-healing after partial consumption of the oxidant agent. The oxide film formed on the Ti alloy samples after 125 days of immersion in Hanks' solution, either with or without H_2O_2 was analyzed by XPS. The XPS results revealed the presence of TiO and TiO_2 on the samples immersed in the two electrolytes, however, Ti_2O_3 was only found on the samples exposed to the H_2O_2 containing solution.

Keywords: electrochemical impedance spectroscopy, Ti-13Nb-13Zr alloy, biomaterials

1. Introduction

Ti-13Nb-13Zr alloy is an important material for medical applications due to its good biocompatibility and corrosion resistance. It is a near-beta phase alloy containing excellent biocompatible elements. Besides, niobium is a beta phase stabilizer. This alloy was developed and patented by Smith and Nephew Richard Inc.¹⁻³ being standardized by ASTM F 1713-96 as a material for surgical implants. The main advantages of the Ti-13Nb-13Zr alloys compared to other titanium alloys like Ti-6Al-4V and Ti-6Al-7Nb, which are widely used as biomaterials, are its low elastic modulus, closer to that of bone, and the absence of aluminum and vanadium, which has been reported to cause short and long-term adverse effects. The combination of Nb and Zr in this alloy allowed to obtain a near-beta phase structure supposedly with improved corrosion resistance in comparison to the alpha-beta ones³. The Ti-13Nb-13Zr alloy contains three of the five elements (Ti, Nb, Zr, Ta and Pt) which are known for not being associated to any adverse reaction with the biological system^{4,5}. It has also been proposed that this alloy has better biocompatibility than the Ti-6Al-4V one due to the lower solubility of niobium and zirconium corrosion products comparatively to that of aluminum and vanadium³.

The corrosion resistance of titanium alloys has been largely investigated and many of the publications report the use of electrochemical techniques in their studies⁶. Most of these studies support the excellent corrosion resistance of these alloys in physiological media, such as Hanks or Ringer's solutions. The high corrosion resistance of the titanium alloys is mainly due to the characteristics of the thin oxide film (few nanometers), which forms spontaneously and is mainly composed of TiO_2 ⁷. Some significant differences are however reported between the corrosion resistance obtained by in vitro and in vivo tests. It has been reported that the oxide film thick-

ness on Ti implants, after some years in the body, may reach larger values than those attained by in vitro tests. Metallic ions have been found in tissues in the neighborhood of implants; also, the accumulation of these types of ions in organs such as liver, lungs and kidneys has been detected. The technique used for ions identification in the vicinity of implants was PIXE (Proton Induced x ray Emission)^{8,9}. Some researchers propose that these metallic ions are caused by electrochemical reactions rather than by wear processes⁷. Auger spectroscopy studies have revealed that the thickness and nature of the oxide on titanium implants vary with time of implantation and incorporation of mineral ions, such as phosphate and calcium ions in the film⁷. These observations led to the conclusion that passivity on these materials occurs under different conditions depending on either saline solutions (in vitro test) or physiological fluids (in vivo test) are the corrosive environments. Moreover, lower corrosion resistance is usually obtained by in vivo tests¹⁰.

According to Tengvall^{11,12} one of the possible causes of the lower corrosion resistance is the production of hydrogen peroxide by inflammatory reactions resulting from surgical procedures. The H_2O_2 is a strong oxidant that increases the oxidation reaction rate and consequently produces a thicker oxide layer. Pan et al.¹⁰ investigated the oxide films formed on Ti exposed to phosphate buffered saline solutions (PBS), either without or with 100 mM H_2O_2 . They found that H_2O_2 addition resulted in significant corrosion resistance decrease of titanium and also to oxide film thickening. Fonseca and Barbosa¹³ studied the electrochemical behaviour of Ti in PBS without e with 50 or 150 mM of H_2O_2 using EIS and concluded that corrosion resistance of Ti is strongly affected by the presence of H_2O_2 and when the peroxide is removed, the metal displays a resistance increase.

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The pH of the in vivo electrolytes could also have important effect on the corrosion resistance of implant materials. This effect has been reported in the literature^{14,15}. Usually the pH value is homeostatically regulated to a value 7.4, but in certain circumstances it may significantly vary. After implants surgery the pH of the affected area usually decreases to 5.2 due to implantation and recovers to 7.4 within two weeks¹⁶. According to literature¹⁷ in case of infection the pH decreases even further, reaching values around 3. Changes in the pH however are usually small once the body fluids are buffered solutions and the pH commonly remains between 7 and 7.4¹⁶.

In this study, the electrochemical behavior of a laboratory made Ti-13Nb-13Zr alloy was investigated by electrochemical impedance spectroscopy (EIS) in Hanks' solution, with and without H₂O₂ and the oxide film formed on its surface was analyzed by x ray photoelectron spectroscopy (XPS). The results of EIS were fitted to an equivalent electric circuit that simulates a double oxide film formed on titanium and its alloys and is composed of an inner barrier layer and an external porous layer.

2. Experimental

The alloy used in this study was a *near-beta* Ti-13Nb-13Zr alloy, laboratory made and heat-treated by Schneider¹⁸. The chemical composition of the alloy investigated is shown in Table 1. Samples of this alloy were prepared by cold resin molding, leaving an area corresponding to 0.33 cm² for exposure to the electrolyte. The metallic surface was mechanically polished with SiC paper up to #2000 and then degreased in an ultrasonic bath. A three-electrode cell set-up was used with a saturated calomel electrode (SCE) and a platinum wire as reference and counter electrodes, respectively. All the potentials are referred to this reference electrode. The electrolyte used in this study was the Hanks' solution, whose composition is shown in Table 2, with and without the addition of 100 mM of H₂O₂. This concentration was used based on literature results that reported the effect of this concentration on the corrosion resistance of Ti alloys^{7,10}. The electrolytes used (with or without H₂O₂) were naturally aerated and its temperature was controlled at 37 °C. The pH of the solution with H₂O₂ was 4, whereas of that without it was 6.4. The pH of the both electrolytes did not vary throughout the test period. Following surface preparation, the samples were immersed in the test solution and at certain regular periods, EIS tests were carried out. All EIS experiments were performed in the potentiostatic mode at the open circuit potential (OCP), and the first EIS was performed after 72 h of immersion. The frequency range studied was from 100 kHz to 10 mHz, using 10 mV (rms) as the amplitude of the perturbation signal and an acquisition rate of 6 points per decade.

EIS measurements were accomplished with a 1255 Solartron frequency response analyser coupled to a 273A EG&G PAR potentiostat, both controlled by the software Z_{plot}.

3. Results and Discussion

Figure 1 shows the variation of the open circuit potential with time of immersion in Hanks' solution for two test solutions, Hanks' solution with 100 mM of H₂O₂ and without H₂O₂. These measurements were taken previous to the EIS tests and the EIS diagrams were only obtained after the potential was fairly steady. The steady potential measured in the solution without peroxide was around 120 mV, during the whole test period. On the other hand, in the

solution with peroxide the potential varied with time. It was initially nearly 60 mV, but after 10 days of immersion it was around -40 mV and was fairly stable until 35 days of test. At the end of this period it increased again and at 54 days, the potential measured was 55 mV. The peroxide consumption in the test solution with time was likely the reason for the recovery of the OCP to its initial value.

EIS results for the Ti alloy at increasing immersion time in the Hanks' solution, without and with 100 mM of H₂O₂, are shown in Figures 2 and 3, respectively. Figure 2 shows that the general shape of the diagrams for the Ti alloy in the solution without H₂O₂ is very similar throughout the entire test period, indicating no change in corrosion mechanism. Bode phase angle diagrams in this solution are constituted by two time constants, probably related to the double layer nature of the oxide. It has been previously proposed¹⁹ that the broad capacitive phase angle in the medium frequency (MF) region is due to the outer porous layer whereas the one at lower frequencies, to the inner barrier layer. The phase angles close to -90° from medium to low frequencies indicate that the oxide film formed is highly protective. The impedance slightly increased in the first days but the main changes occurred between 3 and 7 days. Both time constants were affected, likely due to thickening of the oxide film with time. The results suggest that in the solution without hydrogen peroxide the effect was on both layers and indicate the improvement of the protective characteristics of the oxide layer.

The effect of immersion time on the porous layer must result from the incorporation of electrolyte compounds into the porosities, such as phosphates (calcium or magnesium), or to their deposition on the pores, resulting in the partial sealing of this layer. This also

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

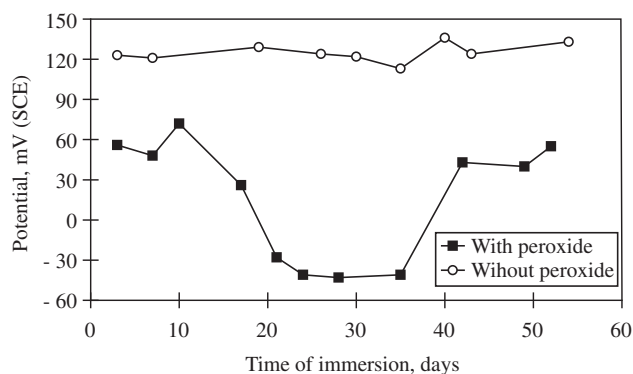


Figure 1. Open circuit potential as a function of time of immersion of Ti-13Nb-13Zr alloy in Hanks' solutions, without and with 100 mM of H₂O₂.

Table 1. Chemical composition of Ti-13Nb-13Zr alloy.

Element	C	H	N	O	S	Hf	Fe	Nb	Zr	Ti
wt. (%)	0.035	0.011	0.004	0.078	<0.001	0.055	0.085	13.18	13.49	Bal.

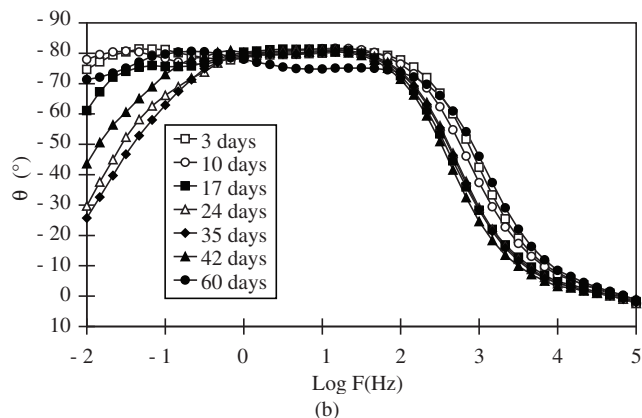
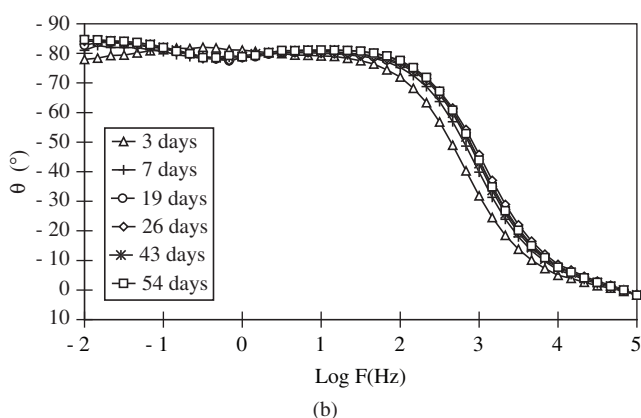
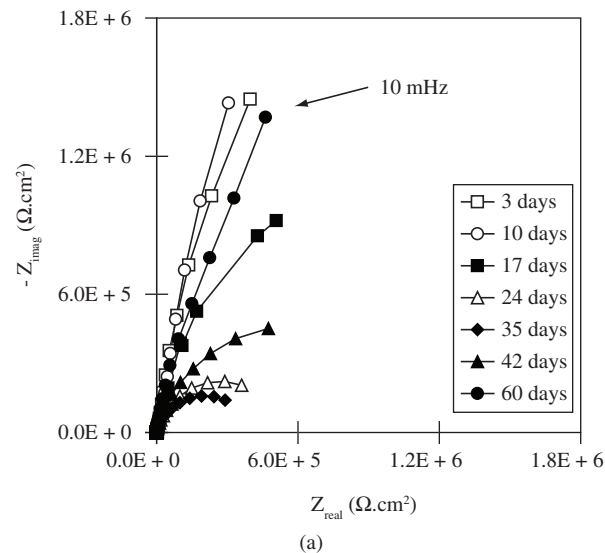
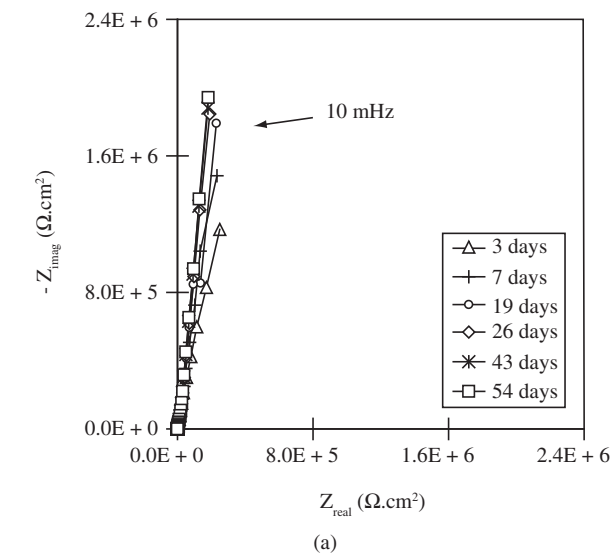


Figure 2. EIS results for Ti-13Nb-13Zr alloy at various periods of immersion in naturally aerated Hanks' solution without H_2O_2 , at 37 °C. a) Nyquist; and b) Bode diagrams.

Figure 3. EIS results for Ti-13Nb-13Zr alloy as function of immersion time in naturally aerated Hanks' solution with 100 mM of H_2O_2 , at 37 °C. a) Nyquist; and b) Bode diagrams.

affects the barrier layer electrochemical response, once it might block the area of this layer exposed to the electrolyte. The EIS diagrams showed no significant changes from 26 days onwards, suggesting that the film was very stable.

The electrochemical behaviour of the Ti alloy exposed to the solution with 100 mM of hydrogen peroxide (H_2O_2) shows a very distinct behaviour comparatively to the H_2O_2 free solution. The Nyquist diagrams of Figure 3 show cyclical changes. The impedance significantly increases between 3 and 10 days, likely due to film thickening, decreases between 10 and 35 days, likely caused by oxide film deterioration, and then increases again between 35 and 60 days, likely due to reform of film protective properties. The Bode diagrams showed that the main changes occurred at lower frequencies, indicating that the barrier layer was the mainly affected by oxide deterioration, likely caused by H_2O_2 attack. The effect of the corrosive attack of H_2O_2 on the oxide film was mainly noticed between 10 and 35 days, resulting in decrease of the barrier layer impedance. This observation is supported by the open circuit potential variation from 10 to 35 days as shown in Figure 1.

The following mechanism is proposed: initially the oxidant causes oxide thickening and, consequently, produces increase in the impedance. After this period, the oxide continues to grow, but at a lower rate, due to the requirement of higher fields for oxide growth

through a thicker film. At the same time, the oxide film is attacked by H_2O_2 , and with time this results in a defective layer of lower impedance explaining the results obtained between 10 and 35 days. For longer immersion periods, the H_2O_2 concentration diminishes due to consumption, and in the H_2O_2 depleted solution; the oxide film recovers its protective characteristics that could occur by incorporation of precipitates or ions into the film, resulting in the increase in impedance. This must be favored in the thicker porous layer formed in the first days of immersion in the solution with H_2O_2 .

The equivalent electric circuit showed in Figure 4 was proposed to adjust the experimental impedance results obtained in Hanks' solution, with or without H_2O_2 . This circuit was previously proposed by Kolman and Scully^{20,21} and Yu et al.²² to simulate the results of oxide films on titanium and titanium alloys in aqueous solutions, and has also been used to investigate the electrochemical behavior of titanium alloys in solutions that simulate the body fluids²³. This equivalent circuit is composed by resistance and constant phase elements (CPE). The resistive components R_s , R_p e R_b are related to the solution resistance, porous layer resistance and barrier layer resistance, respectively. The CPE_b and CPE_p , on the other hand, are related to the capacity of the barrier and the porous layer, respectively.

The porous layer formed on titanium alloys contains microscopic pores through which incorporation of components present in the elec-

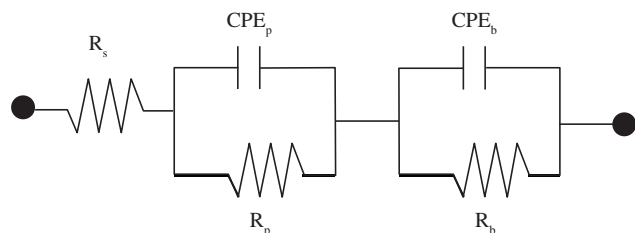


Figure 4. Equivalent electric circuit used for fitting experimental results.

trolyte can occur. This might lead to the increase in the layer resistance with time. According to literature^{7,24} this layer has been associated to the bioactivity of the titanium alloys. The R_p component is related to the pores resistance to current transfer. The association of R_b and CPE_b , in parallel represents the processes linked to the barrier layer. According to the model of a duplex structure oxide layer on titanium alloy, the barrier layer is mainly responsible for the corrosion resistance of this type of alloys. The CPE_b component is associated to the capacity of the barrier layer, and it is the cause of the high phase angles obtained at low frequencies. The R_b component is related to the resistance of the barrier layer to species transport and charge transfer.

Figures 5 and 6 show the results of experimental data fitting to the proposed equivalent electric circuit shown in Figure 4 for the Ti-13Nb-13Zr alloy in Hanks' solution without and with 100 mM of H_2O_2 . It is easily seen that in the H_2O_2 free solution, the values of the circuit components were rather invariable during the test period. On the other hand, in the solution with peroxide, the results show that the barrier layer was more affected by immersion than the porous one. It also shows that until 10 days, the barrier layer is the main responsible for corrosion resistance. During that period, the values of barrier layer resistance were two orders of magnitude larger than that of the porous one in the peroxide containing solution. The barrier layer resistance decreased with time from 10 until 28 days, and increased for longer periods. This increase in resistance occurred at the same time as the porous layer showed deterioration, suggesting that the increase in barrier layer resistance was not caused by blocking of the porous one. This last layer showed fairly stable values from the first days of test until 28 days and this could have been caused by the counteracting effects of film thickening and defects nucleation caused by the oxidant (H_2O_2). Steady capacitance values were also associated to the both layers formed in the solution without peroxide during the whole test period, as Figure 6 shows.

Figures 5 and 6 also show that variations in resistance and capacitance values always occurred in opposite directions. The decrease in the barrier layer resistance, which was accompanied by the increase in capacitance, was most likely due to the generation of defects in the oxide. This is supported by the results presented in these last two figures that show similar resistance and capacitance values for the barrier and the porous layer between 20 and 35 days, suggesting that the barrier layer becomes increasingly defective, approaching a porous type. The hypothesis of barrier oxide repair after 28 days is supported by the values of resistance and capacitance obtained for 60 days (see Figures 5 and 6), which were close to those obtained at the first days of test.

The deterioration of the porous layer, occurring at the same time as the increase in the barrier layer resistance, from 35 days onwards, could be explained by the consumption of the H_2O_2 from Hanks' solution. The reduced supply of this oxidant would inhibit oxide thickening but also, would avoid film attack. The repair of the defects in the barrier layer during that period might have occurred by incorporation of mineral ions from the solution into the defects/pores, or to film thickening. The resistance and capacitance values for 3 days and 60 days of immersion are very similar supporting the hypothesis of

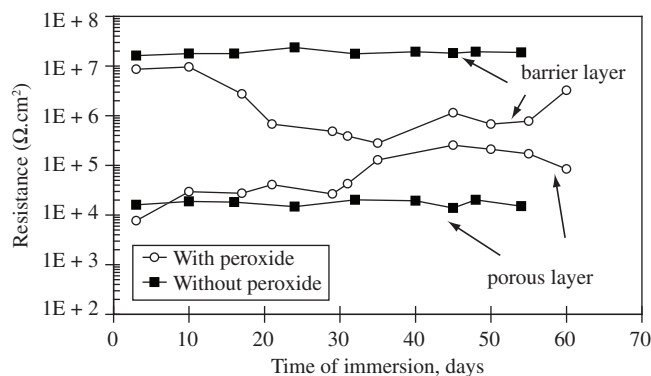


Figure 5. Variation of porous layer resistance (R_p) and barrier layer resistance (R_b) with immersion time in Hanks' solution without and with 100 mM of H_2O_2 . Values of R_p and R_b obtained from experimental data fitting to equivalent circuit of Figure 4.

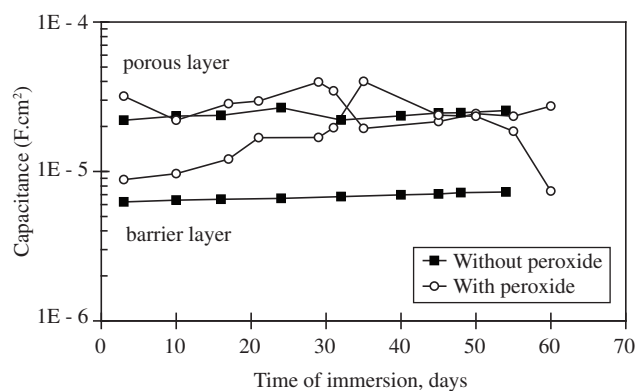


Figure 6. Variation of porous layer capacitance (CPE_p) and barrier layer capacitance (CPE_b) with immersion time in Hanks' solution without and with 100 mM of H_2O_2 . Values of CPE_p and CPE_b obtained from experimental data fitting to equivalent circuit of Figure 4.

film restoration. The decrease in capacitance for periods longer than 35 days, on the other hand, favors the hypothesis of film thickening. It is believed that oxide thickening and the incorporation of mineral ions into this layer favours implant osseointegration¹⁹. Experimental data fitting to a proposed electric equivalent circuit allowed the observation that the barrier layer was more sensitive to the presence of oxidant (H_2O_2) than the porous layer.

The samples of Ti-13Nb-13Zr alloy after 125 days immersion in Hanks' solution either without or with 100 mM H_2O_2 were analyzed by XPS. The survey XPS spectra exhibited peaks from titanium, zirconium, niobium, oxygen, carbon, nitrogen and sodium. The Ti2p peak was deconvoluted and the spectra are shown in Figure 7a and 7b for the samples exposed to the Hanks' solution without and with 100 mM H_2O_2 , respectively.

For both samples the main doublet peaks is attributed to Ti^{4+} showing that TiO_2 is the main constituent of the oxide films formed in both solutions. Besides, peaks corresponding to Ti and TiO were also detected on both types of samples. On the other hand, Ti_2O_3 was only detected on the samples immersed in the H_2O_2 containing solution, showing that the solution affected the type of oxide formed on the Ti alloy investigated.

4. Conclusions

The results showed that the oxide layer formed on Ti-13Nb-13Zr alloy by immersion in Hanks' solution without H_2O_2 is highly stable

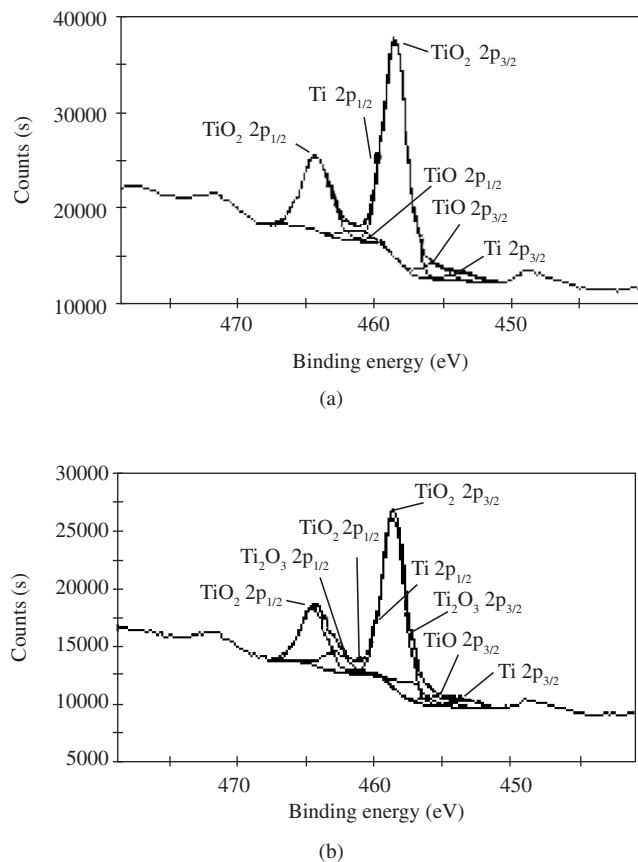


Figure 7. Deconvoluted Ti 2p XPS spectra recorded after 125 days immersion of Ti-13Nb-13Zr alloy in Hanks' solution a) without H_2O_2 ; and b) with 100 mM of H_2O_2 .

and protective. Addition of hydrogen peroxide into Hanks' solution increases the oxide film instability. At first, the impedance increases, likely due to film thickening but, subsequently, it is followed by a significant decrease in the protective properties of the oxide layer. The main effect of the oxidant occurs on the barrier layer and it is attributed to the generation of defects in this layer. At longer immersion periods, H_2O_2 is consumed in the solution and the barrier layer recovers its protective properties.

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