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Influence of different concentration of hydrogen peroxide on the corrosion behavior of Ti-6Al-4V alloy immersed in physiological solution

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Abstract. The materials used as implants are expected to be highly non toxic and should not cause any inflammatory or allergic reactions in the human body. The success of the biomaterials is mainly dependent on the reaction of the human body to the implant. Titanium and some of its alloys are used as biomaterials for dental and orthopedic applications. The most common grades used are commercially pure titanium and the Ti-6Al-4V alloy. Frequent utilization of titanium and titanium alloys as biomaterials due to their superior biocompatibility, and high corrosion resistance as to form a thin surface oxide layer, and good mechanical properties, as a certain elastic modulus and low density that make that these metals present a mechanical behavior close to those of bones. Strong and totally biocompatible, titanium is one of the few materials that naturally match the requirements for implantation in the human body. Hydrogen peroxide appears in the human body when an inflammation occurs. This research work aims to assess the influence of different concentrations of hydrogen peroxide on the corrosion behavior of Ti-6Al-4V alloy submerged in Hank's physiological solution. Electrochemical methods as Open Circuit Potential and Electrochemical Impedance Spectroscopy were applied for corrosion investigations. The results provide evidence that Ti-6Al-4V corrosion resistance is affected by inflammatory conditions presence in Hank solution.

1. Introduction

Metals have been used successfully for decades in fracture fixation and joint replacement. Mechanisms of implant failure were recently the target of intensive research as longevity and expectations from such implants are increasing.

Today's scientists and engineers are finding a wide variety of ways to negotiate materials making at the nanoscale seeking the advantage of their enhanced properties such as higher strength, lighter weight, increased control of light spectrum, and greater chemical reactivity than their larger-scale counterparts [1].

Biocompatibility is the property of a biomaterial, prosthesis or medical device to perform with a suitable host response in a specific application and a biocompatibility assessment. Assessing biological responses is a measure of the magnitude and duration of adverse changes in homeostasis mechanisms that determine the response of the host.



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Basically, the biological response of prosthesis is important because it has to be assessed whether the medical device works at the place of implantation and has no adverse effects on the person using it. Thus, the purpose of assessing the biological response is to see whether a biomaterial, medical device or prosthesis can be toxic to the patient and do not present adverse effects into the body [2].

According to Bath and Santos, biomaterials can be classified into four classes, according to the compatibility they have with the surrounding tissues:

Biotolerant: Implant separated from the surrounding bone by a layer of soft tissue over the interface. No contact in the osteogenesis. The layer is induced by the implant release of monomers, ions, and/or corrosion products. Almost all synthetic polymers and most metals are this category.

Bioinert: Implants in direct contact with bone tissue, occurring involvement in the osteogenesis.

However, there is no chemical reaction between the tissue and the implant. There is not, at least in amounts detectable by cells, the release of any component. Examples of bioinert biomaterials are: alumina, zirconium, titanium, tantalum, niobium, and carbon.

Bioactive: there is the interaction between the implant and the bone tissue, interfering directly in the osteogenesis. By chemical similarity, the mineral part of bone tissue binds to the implant, promoting osteoconduction. The main materials of this class are: Ca-phosphate, vitro-ceramic, and hydroxyapatite.

Bioresorbable: Materials that, after a certain period of time in contact with the tissues, end up by being degraded, solubilized, or phagocytosed by the body. They are of interest in clinical applications where it is inadvisable the reoperation to remove the implant. Representative of this class are tricalcium phosphate (TCP) and PLLA (poly-Lactic acid) [3].

Bone and its several associated elements—cartilage, connective tissue, vascular elements, and nervous components—act as a functional organ. They provide support and protection for soft tissues and act together with skeletal muscles to make body movements possible. Bones are relatively rigid structures and their shapes are closely related to their functions. Bone metabolism is mainly controlled by the endocrine, immune, and neurovascular systems, and its metabolism and response to internal and external stimulations are still under assessment [4].

Human joints such as those of the knee are delicate but complex structures that are capable of operating under critical conditions. They have such results because they function as a complex system consisting of articular cartilage, connective tissue with the role of protecting the bones that form the joint and the synovial fluid [5]. Some affections of the joints that occur over the life of some patients cause pain in time. According to a study, about 90% of the subjects analyzed, aged over 40, were diagnosed with joint diseases.

Ti and titanium alloys are among the most used materials for biomedical applications, such as joint prostheses, as they have increased corrosion resistance, high specific resistance and good biocompatibility. They can be classified as either α , near- α , $\alpha + \beta$, metastable β or stable β depending upon their room temperature microstructure. Thus, alloying elements for titanium fall into three categories: α -stabilizers (Al, O, N, C), β -stabilizers (Mo, V, Nb, Ta, Fe, W, Cr, Si, Ni) and neutral (Zr). α and near- α titanium alloys have increased corrosion resistance but in medicine they are used less because they have a low temperature resistance. In addition to these, $\alpha + \beta$ alloys have a higher corrosion resistance due to the presence of α and β phases. The properties of alloys vary depending on the composition, the relative proportions of the phases α / β and the heat treatment to which the alloy has been subjected [6].

Hydrogen peroxide (H_2O_2) is the component found in inflammatory conditions to a very patirents being used in our research work to simulate these inflammatory effects to corrosion resistance of tested alloy.

This research work aims to assess the influence of different concentrations of hydrogen peroxide on the corrosion behavior of Ti-6Al-4V alloy submerged in Hank's physiological solution. Electrochemical methods such as Open Circuit Potential and Electrochemical Impedance Spectroscopy were applied for corrosion investigations.

2. Materials and methods

A VoltaLab PGZ 301 potentiostat / galvanostat controlled by VoltaMaster4 software was used for electrochemical measurements. Electrochemical measurements were conducted in a three electrode cell with an Ag/AgCl as the reference electrode and a Pt-Rh grid as the counter electrode. The test sample was served as a working electrode and its chemical composition and mechanical properties are shown in Table 1. Before each corrosion experiment the working electrode was cleaned with ethyl alcohol and dried. The surface area of samples exposed to the electrolyte was 3 cm² with a measured roughness of 1.15 μm , as shown in Figure 1.

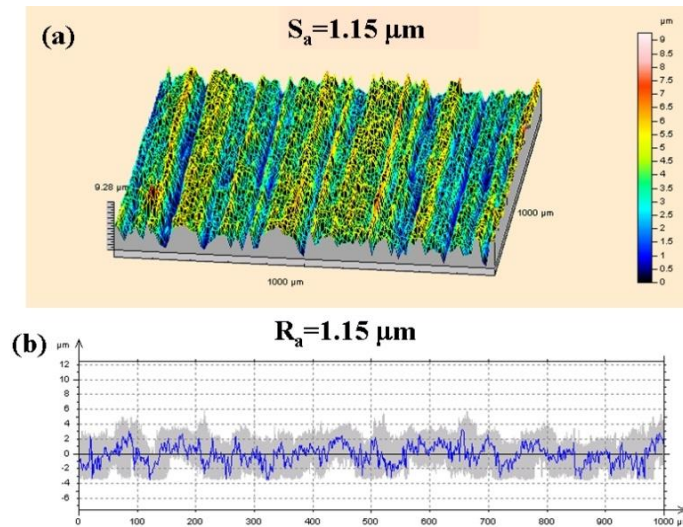


Figure 1. Measured roughness of Ti-6Al-4V: (a): 3D surface profile; (b) 2D surface profile.

The roughness of Ti-6Al-4V alloy samples was measured before electrochemical measurements using a high resolution microtopograph, STIL, equipped with optical fiber for light signal capture and intensity analysis with a side resolution of 1 μm and a vertical resolution of 30 nm. The captured images are transformed into a 2D profile surface and 3D surface with Surface Map software.

Table 1. Chemical composition and mechanical properties of Ti-6Al-4V alloy.

Specification	8-12-05832-1	N	Al	C	V	H	Fe	O	Ti
Ti-6Al-4V Grade 5	Max %]	0.003	6.01	0.008	3.83	0.002	0.083	0.088	89.976
	Min %]	0.003	5.86	0.008	3.73	0.002	0.068	0.084	90.245
Mechanical properties									
Resistance to flow [MPa]			Tensile strength [MPa]				Elongation [%]		
865			937				11		

To simulate the physiological conditions of the human body, the SBF solution (simulated body fluid) was used for in vitro corrosion studies. Its chemical composition is shown in Table 2.

The corrosion resistance of the Ti-6Al-4V alloy was determined in Hank solution; Hank solution doped with 1 mL / L H₂O₂, Hank solution doped with 4mL/ L H₂O₂ and Hank solution doped with mixed 10 mL / L H₂O₂. Hydrogen peroxide is of analytical grade with 30 % concentration. The volume of solution used for each experiment was 270 mL. All the experiments were conducted at room temperature 25°C.

Table 2. Composition of biological Hank solution.

Crt. nr	Compound	Concentration g/L
1	NaCl	8
2	KCL	0.4
3	CaCl ₂ *2H ₂ O	0.35
4	Na ₂ HPO ₄ *H ₂ O	0.25
5	MgCl ₂	0.19
6	MgSO ₄ *7H ₂ O	0.06
7	C ₆ H ₁₂ O ₆	1

3. Results and discussions

3.1. Open circuit potential

The open circuit (OCP) potential is the potential of the working electrode (metal sample) relative to the reference electrode when no potential or current is being applied to the corrosion system. In general, OCP of an electrode is a thermodynamic parameter which shows the thermodynamic tendency of those metallic materials to participate in the electrochemical corrosion reactions with the surrounding medium. The open circuit potentials were monitored during the exposure time of 1h until it has been reached a stable state value vs. Ag/AgCl reference electrode used. The potential time measurements of Ti-6Al-4V alloy determined in Hank solution doped with 1 mL / L H₂O₂, 4 mL / L H₂O₂ and 10 mL / L H₂O₂ are presented in Figure 2.

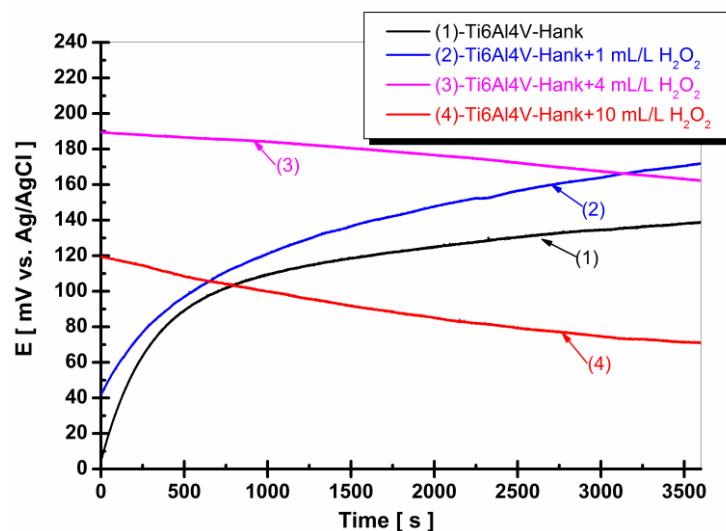


Figure 2. Evolution of open circuit potential of (OCP₁) during immersion time of 1h for: **(1) Hank solution;** **(2) Hank +1 mL/L H₂O₂;** **(3) Hank +4 mL/L H₂O₂;** **(4) Hank+10 mL/L H₂O₂.**

From Figure 2 it can be observed that Ti-6Al-4V immersed in Hank solution, shifted value of open circuit potential in the more positive direction, having at the end of 60 min. the value +121.38 mV vs. Ag/AgCl, compared with the initial immersion time value of +7.18 mV vs. Ag/AgCl.

For Ti-6Al-4V immersed in Hank solution with addition of 1mL / L H₂O₂ the open circuit potential show the same shifted trend to a more positive values from 42.5 mV vs. Ag/AgCl measured at initial immersion time to +171.57 mV vs. Ag/AgCl at the end of monitoring time.

The OCP values of Ti-6Al-4V immersed in Hank solution with addition of 4 mL / L H_2O_2 showed also very slow shifted value in the more negative (active) direction, having at the end of 60 min. the value +162.25 mV vs. Ag/AgCl, compared with the initial immersion time value of +189.94 mV vs. Ag/AgCl. For Ti-6Al-4V immersed in Hank solution with addition of 10 mL / L H_2O_2 the open circuit potential show the same shifted trend to a more negative (active) values from 119.57 mV vs. Ag/AgCl measured at initial immersion time to +70.79 mV vs. Ag/AgCl at the end of monitoring time.

The potential shift in the negative direction is smaller in the case of 4 mL / L H_2O_2 addition to the Hank solution, having only -27.69 mV, as compared with the potential shift in the Hank solution with 10 mL / L H_2O_2 addition, which value is -48.78 mV.

The lower value of potential found for the Hank solution without addition of H_2O_2 after 1h of immersion in comparison with Hank solution with addition of 1 mL / L H_2O_2 or 4 mL / L H_2O_2 may be due to a higher dissolution rate of the oxide in Hank solution due to chloride ions content. The H_2O_2 addition help Ti-6Al-4V surface to grow faster the oxide film formation.

Similar trends were obtained by other researchers [7] when evaluated the corrosion behaviour of titanium in biofluids containing H_2O_2 .

In Figure 3 the open circuit potentials (OCP_2) were monitored after 3h of immersion time during 1h.

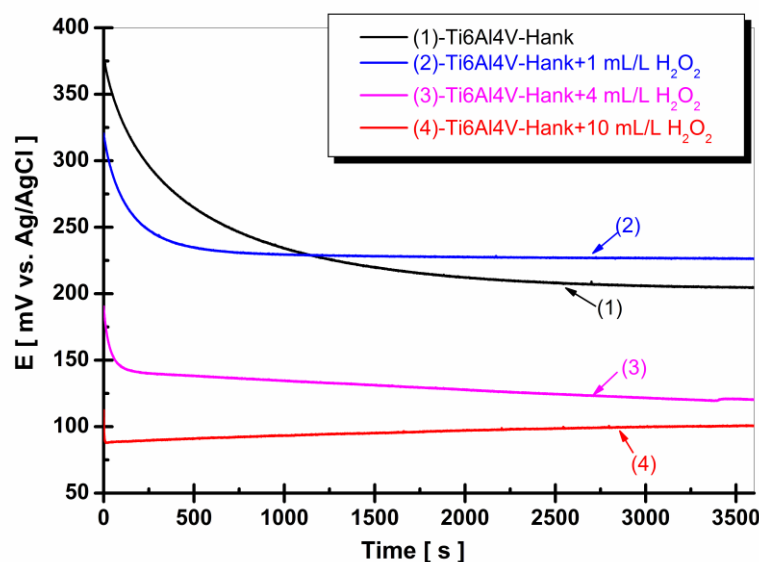


Figure 3. Evolution of open circuit potential of (OCP_2) after 3h of immersion time during 1h for: **(1) Hank solution; (2) Hank +1 mL/L H_2O_2 ; (3) Hank +4 mL/L H_2O_2 ; (4) Hank+10 mL/L H_2O_2 .**

From Figure 3 it can be seen even though hydrogen peroxide is a powerful oxidant that increases the rate of the oxidation reaction and consequently produces a thicker oxide layer after 1h of immersion time, after 3h addition of hydrogen peroxide into Hanks' solution increases the oxide film instability. Even at higher concentration of H_2O_2 of 4 and 10 mL / L the open circuit values reach the stable steady state after 3 hours from immersion time (during OCP_2 measurement), Figure 3. These behaviors are supported by the results obtained from electrochemical impedance spectroscopy.

3.2. Electrochemical impedance spectroscopy

The results obtained from impedance measurements in the form of Nyquist and Bode plots are presented in Figure 4, Figures 6 and 7. For each choice of the experimental conditions, measurements were performed 3 times.

EIS measurements performed in the frequency range between 100 kHz and 25 mHz, with an AC sine wave amplitude of 10 mV, 10 Hz frequency per decade.

These results were analyzed using ZView 3.4e software and the quality of the fitted results was evaluated with the chi-square value that was lower than 10^{-3} .

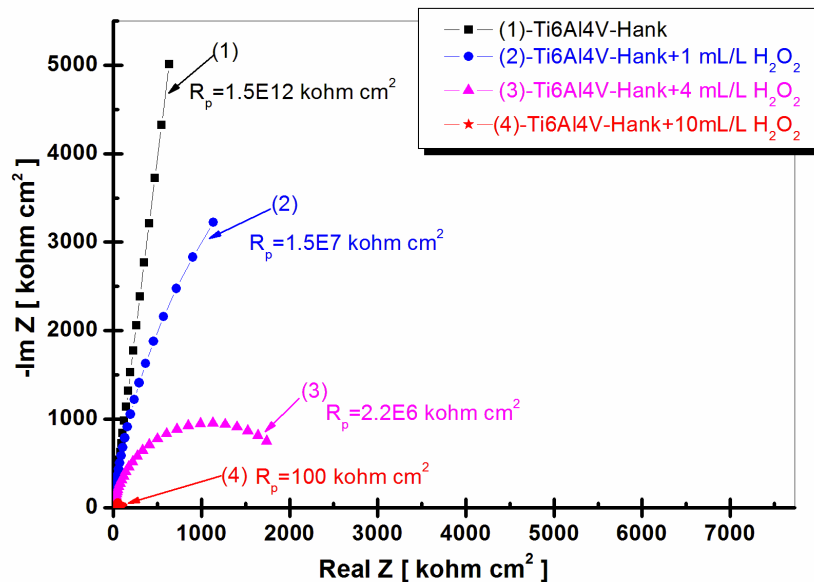


Figure 4. Nyquist electrochemical impedance spectroscopy of Ti-6Al-4V alloy immersed in: **(1) Hank solution**; **(2) Hank +1 mL/L H_2O_2** ; **(3) Hank +4 mL/L H_2O_2** ; **(4) Hank+10 mL/L H_2O_2** .

To analyze the experimental data, a simple Randles equivalent circuit showed in Figure 5 was used.

The equivalent circuit consists of R_1 as the electrolyte resistance, CPE1 and R_2 as the constant phase element and the specific polarization resistance.

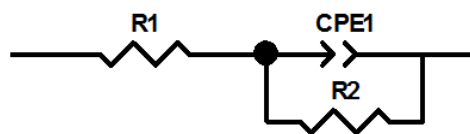


Figure 5. Schematic representation of Randles equivalent circuit.

The constant phase element (CPE) was used instead of a pure capacitor to explain the deviation of impedance data from a semicircle to a depressed semicircle due to inhomogeneous surfaces, which could have different adsorbed compounds connected with tested solutions.

The impedance expression with a constant phase element instead of capacitance can be written with the equation [8]:

$$Z_{CPE} = \frac{1}{Q(j\omega)^n} \quad (1)$$

Where: Q is a constant measured in $F \cdot cm^{-2} \cdot s^{(n-1)}$, n is a value representing the deviation from purely capacitive behavior, $j = \sqrt{-1}$ is an imaginary number, ω represent the angular frequency.

When the n value is 1 pure capacitive behavior is observed and Q is the layer capacitance.

The specific polarization resistance resulting from fitted results using the proposed equivalent circuits is higher for Ti-6Al-4V alloy immersed in Hank solution in comparison with Hank with addition of H_2O_2 .

The addition of H_2O_2 into Hank solution increases the rate of anodic and cathodic reactions and the specific polarization resistance decreases as the H_2O_2 concentration increases.

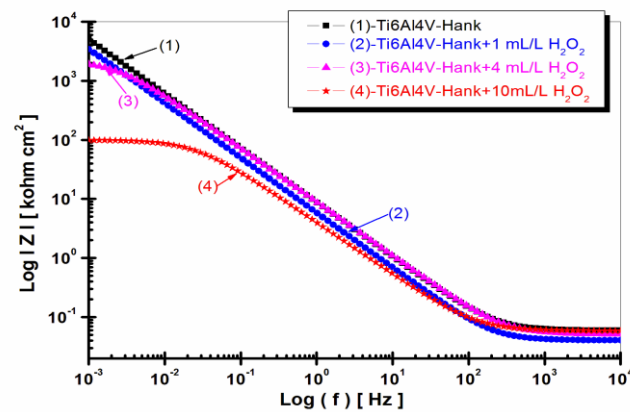


Figure 6. Electrochemical impedance spectroscopy diagrams in Bode representation as Modul Z vs. log frequency for: (1) Hank solution; (2) Hank +1 mL/L H_2O_2 ; (3) Hank +4 mL/L H_2O_2 ; (4) Hank+10 mL/L H_2O_2 .

From Figure 6 the higher impedance modulus reveals a higher corrosion resistance of Ti-6Al-4V alloy in Hank solution and a good stability during EIS measurements steps.

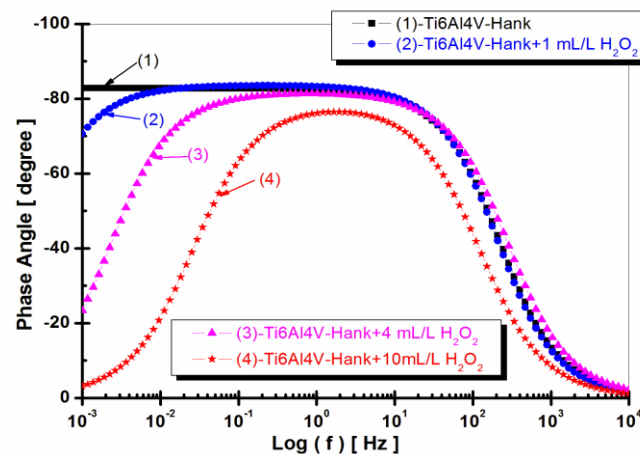


Figure 7. Electrochemical impedance spectroscopy diagrams in Bode representation as Phase angle vs. log frequency for: (1) Hank solution; (2) Hank +1 mL/L H_2O_2 ; (3) Hank +4 mL/L H_2O_2 ; (4) Hank+10 mL/L H_2O_2 .

From Figure 7 it can be observed that Ti-6Al-4V immersed in Hank solution exhibit a near capacitive response, illustrated by a phase angle close to 82° over a wide range of frequency this behavior indicates a thin passive and protective film.

4. Conclusions

The principal aim of this research work is to investigate the corrosion behavior of Ti-6Al-4V alloy immersed in Hank solution doped with different concentration of hydrogen peroxide (1 mL/L, 4mL/L and 10 mL/L) simulating the inflammatory state condition.

From the Open circuit potential it can be concluded that even though hydrogen peroxide is a powerful oxidant that increases the rate of the oxidation reaction and consequently produces a thicker oxide layer the addition of hydrogen peroxide into Hanks' solution increases the oxide film instability. After 3 h from immersion time the Open circuit potential reaches a stable value.

The EIS results reveal that the addition of H_2O_2 into Hank solution increases the rate of anodic and cathodic reactions and the specific polarization resistance of Ti-6Al-4V alloy decreases.

The electrochemical results conclude that the addition of hydrogen peroxide into Hank solution, simulating the inflammatory process, decreases even more the corrosion resistance of Ti-6Al-4V alloy, confirming the higher damage of Ti-6Al-4V alloy in the presence of inflammatory body processes.

5. References

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Acknowledgments

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