

Impact of Hydrogen Peroxide and Albumin on the Corrosion Behavior of Titanium Alloy (Ti6Al4V) in Saline Solution

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In this study our goal was to monitoring the corrosion behavior of titanium alloy (Ti6Al4V) in four solution: saline solution, saline solution with addition of 1% H₂O₂, saline solution with 1% albumin and saline solution with mixed 1% albumin + 1% H₂O₂ in order to see the synergistic effects of this two compound in combination. It is known that H₂O₂ is a ROS (reactive oxygen species) which appear in human body when inflammatory reactions occur and albumin it is used because is a protein (the most abundant) from the human body. In vitro studies for corrosion behavior of titanium alloy (Ti6Al4V) in a presence of saline solution, H₂O₂ and albumin in this study were investigated by different electrochemical measurements: OCP (open circuit potential), PD (potentiodynamic polarization curves) and EIS (electrochemical impedance spectroscopy). From the electrochemical results we can say that the presence of H₂O₂ in the saline solution decreases the corrosion resistance of the Ti6Al4V alloy, while the presence of albumin in the saline solution acts as an inhibitor and the corrosion resistance of Ti6Al4V alloy increases as compared to the solution in which it was added H₂O₂.

Keywords: Corrosion resistance; Titanium alloy; Reactive oxygen species; Albumin.

1. INTRODUCTION

The term "biomaterial" was defined first time in 1976 at ESB conference. This term can be found in the field of materials science and clinical medicine and can be defined as a synthetic material used to replace a part of a living system or to work closely with living tissue [1]. This minor change in the definition indicates that the biomaterial field has evolved. Currently, biomaterials are no longer used only to interact with the human body, but are also used to restore and regenerate degraded tissues. At present, the field of biomaterials has evolved, so are used about fifty different types of materials in over forty model of prostheses in different areas of the human body [2-5]. Science studying materials used in medicine is called bioengineering. It involves fundamental research and the development of technology

to achieve medical safety standards in the use of materials. Biomaterials are used to enhance the feature of existence of human and to increase the lifetime. A biomaterial may have all the mechanical, physical and chemical characteristics required by a medical application, but upon contact with biological media, including the human body, it finds particular physiological conditions with which it interacts through specific processes such as ion and fluid diffusion, lymphatic drainage, blood circulation, but also by physiological mechanisms (local and systematic) less predictable [6].

These specific reactions make the material to be or not tolerated by the environment. Moreover, in the same human organism, these mechanical, physicochemical and physiological conditions vary in a rather broad field. For example, the pH is 1.2-3 in the gastric juice up to 7.15-7.4 in the blood and 6-8 in the intracellular environment, or the body temperature that has a normal value of 37 ° C in a healthy person but may be 20°C - 42.5°C in certain diseases. The success of the medical act is ensured only by the interaction between the biomaterial and the human body, more precisely the biocompatibility between the material and the biological environment [7]. A material that initially meets all biocompatibility requirements can lose these qualities not only through wear, tiredness, degradation, but also because the original healthy tissues become ill or simply aged [8]. Irrespective of medical application, a biocompatible material must meet the following conditions: not to be toxic and to include filter compounds:

- it also does not have to induce allergic reactions, rejection by the body, change in blood composition, be hemocompatible, do not change the biological pH, do not cause sedimentation in tissues and biodegradation; not include hydrophilic or hydrophobic centers to stimulate the infiltration of cell and cell adhesion. Many implant materials are subject not only to aggressive body environments (saliva, blood), but also to specific conditions like inflammatory aspects [8]. In the inflammatory conditions there is found as principal component hydrogen peroxide (reactive oxygen species) [9-11]. The interaction of body proteins like albumin and hydrogen peroxide like inflammatory component becomes a very usefully research objective [12-17]. Therefore, the purpose of this study is to explore and evaluate the impact of hydrogen peroxide (reactive specie) in the presence of body protein (human albumin) on the corrosion resistance of Ti6Al4V in buffered saline electrolyte simulating body fluid environment at room temperature. The saline solution is buffered in order to keep constant the pH.

2. EXPERIMENTAL METHODS

For this experimental research work Ti6Al4V alloy (purchased from the Goodfellow Company) was used. The chemical composition of Ti6Al4V, surface roughness, the procedure for preparing the samples before each experiment, the surface active area, electrochemical cell used, volume of solution used and the number of samples made to determine the repeatability of the experiment can be consulted in a previous publication [17]. To establish in vitro corrosion resistance of Ti6Al4V by electrochemical methods, an electrochemical workstation was used (VoltaLab PGZ 301) with dedicate program software VoltaMaster4. To simulate the real conditions in the human body, for corrosion investigation was prepared a saline solution with pH 7.4, saline solution with addition of 1% Albumin (pharmaceutical grade), saline solution with 1% H₂O₂ (30 % p.a. grade) and saline solution with addition of mixed 1%

Albumin and 1% H_2O_2 . All of these compounds added in saline solution give us information of the inflammatory conditions from human body with and without presence of a protein such as Albumin, which is common protein from the human body. The amount of substance needed to prepare the electrolyte is indicate in Table 1.

Table 1. Chemical composition of the saline solution.

Nr. Crt.	Used reagents	Saline solution [g / L]
1	NaCl	0.8
2	KCl	0.2
3	KH_2PO_4	0.27
4	Na_2HPO_4	1.14
5	Albumin	1%
6	H_2O_2	1%
7	Albumin + H_2O_2	1% + 1%
8	pH	7.4

The pH of the electrolyte was determined with a portable pH meter Sension⁺. The electrochemical investigations applied for corrosion measurements are presented schematically in Fig. 1.

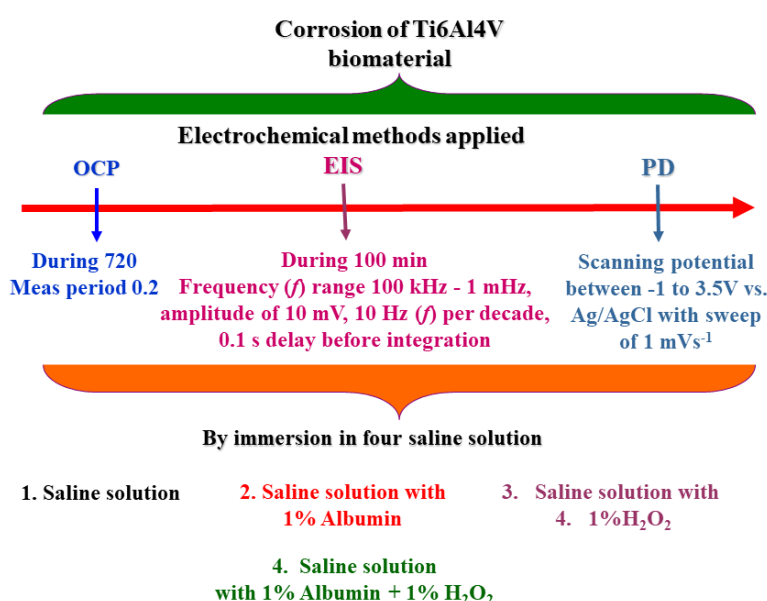


Figure 1. Schematic down of electrochemical measurements protocol for in-vitro corrosion investigations of Ti6Al4V alloy in saline solutions

3. RESULTS AND DISCUSSION

3.1. Open Circuit Potential evolution (OCP)

Most metals and alloys when they interact with liquids from the human body, are subject to corrosion, because these liquids are highly chlorinated (they are very aggressive) due to the presence of chloride ions and proteins. Electrochemical methods such as OCP show the thermodynamic trend of electrochemical oxidation of a material immersed in a corrosive medium. Generally after a certain period of immersion this value stabilizes around a stationary value, reaching the equilibrium state. As a result of the changes that may occur on the surface of the investigated material, the value of the potential may vary due to: formation of the passive layer, dissolution, oxidation etc. OCP is a method used to compare the oxidation tendency behavior of different materials in a corrosive environment. Measurements of the time function potential of the Ti6Al4V alloy immersed in the saline biological solution with addition of albumin, hydrogen peroxide or a mixture of this two compounds can be seen in Figure 2.

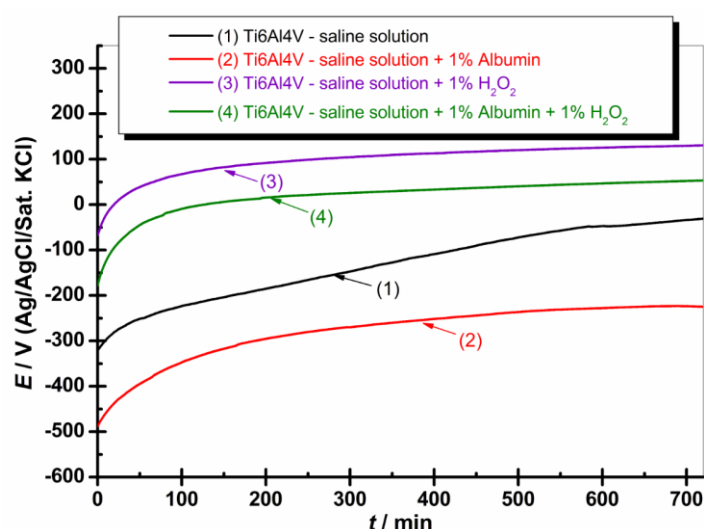


Figure 2. Open circuit potential (OCP) of Ti6Al4V alloy over 12 h of immersion period for: (1) saline solution, (2) saline solution with addition of 1% Albumin; (3) saline solution with addition of 1% H₂O₂; (4) saline solution with addition of 1% Albumin and 1% H₂O₂

Fig. 2 describes the evolution curves of the free potential as a function of immersion time in the saline electrolyte and the saline solution mixed with albumin, H₂O₂ or both albumin + H₂O₂.

In all four curves, it can be observed that the potential changes slowly from the initial value from immersion. The change is towards nobler (more positive) values with a slow growth for the titanium alloy immersed in all three saline solutions. For the saline solution, the displacement of the potential towards more positive amounts is more obvious, confirming the ability of the Ti6Al4V to develop on its surface a passive layer that slows down the corrosion process produced by the saline solution. The most positive potential, even from the immersion of the surface of the titanium alloy in the solutions was registered for the saline solution with addition of hydrogen peroxide, where the steady state value is reached quickly at the more positive value as compared with all other solutions, Figure 2, curve (3). The addition of H₂O₂ in saline solution help titanium alloy surface to grow faster the oxide film formation.

The same trend was reported in the literature by C. Fonseca and his colleague [13] when evaluating the corrosion behavior of titanium in biofluids containing reactive oxygen species (H_2O_2). The most negative potential from immersion time to stationary or steady state value is shown by the titanium alloy immersed in saline with addition of albumin, being even more negative than the potential values of the alloy immersed in the saline solution, Figure 2, curve (2). Therefore, the presence of albumin acts as an inhibitor on the surface of the alloy Ti6Al4V alloy, resulting in a lower OCP value [14]. The open circuit potential of titanium alloy immersed in saline solution mixed with albumin and hydrogen peroxide shown in Figure 2, curve (4) reveals values more positive as compared with the values of open circuit potential revealed for Ti6Al4V tested in saline solution, saline solution with addition of albumin, but more negative values as compared with the values of open circuit potential of titanium alloy immersed in saline solution with addition of hydrogen peroxide.

3.2. Electrochemical Impedance Spectroscopy

Nyquist plots of the impedance experimental results (symbols) for Ti6Al4V alloy immersed in all four solutions are shown in Figure 3.

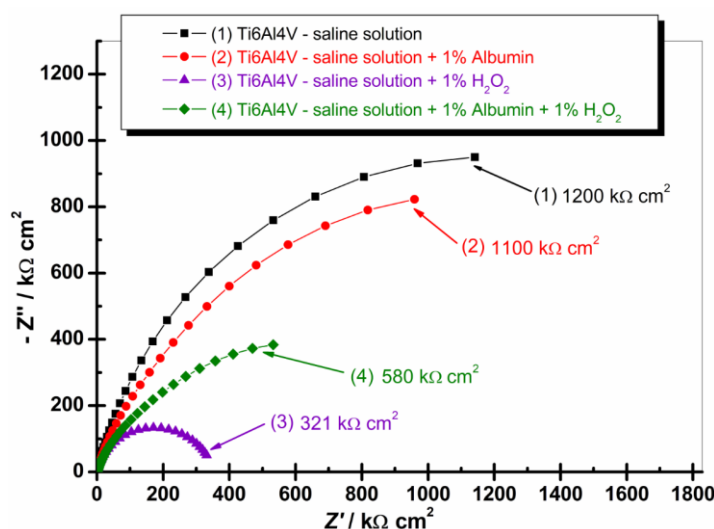


Figure 3. Nyquist plots of electrochemical impedance spectroscopy results (symbols) and fitted results (plain lines) of Ti6Al4V alloy for: (1) saline solution, (2) saline solution with addition of 1% Albumin; (3) saline solution with addition of 1% H_2O_2 ; (4) saline solution with addition of 1% Albumin and 1% H_2O_2

To evaluate the corrosion rate in the case of simple corrosion systems, the dissolving of metal in contact with the solution, is considered to be uniform on the whole surface. Then through the interface (I) the total current is [18]:

$$I = I_a + I_c \quad (1)$$

Where:

I_a and I_c are the anodic current and the cathodic current, respectively.

The measurable net current in case of spontaneous corrosion is $I=0$. If I_a and I_c are potentially

dependent, by differentiating equation (1), we obtain:

$$\frac{\Delta I}{\Delta E} = \frac{1}{Z_F} = \frac{\Delta I_a}{\Delta I_c} = \frac{1}{R_p} \quad (2)$$

Where E is the electrode potential rectified by the ohmic influence and R_p is the polarization resistance.

If I_a and I_c obeys the Tafel law, with the slopes b_a and b_c

$$I_a = I_a^0 \cdot \exp \frac{2.303}{b_a} \cdot E \quad (3)$$

$$I_c = I_c^0 \cdot \exp \left(-\frac{2.303}{b_c} \cdot E \right) \quad (4)$$

Likewise, for an balance potential ($I = 0$) the impedance is:

$$\frac{1}{Z_F} = \frac{1}{R_p} = 2.303 \cdot \left[\frac{I_a}{b_a} - \frac{I_c}{b_c} \right] \quad (5)$$

Z_F is the Faradaic impedance and at $I_a = -I_c = I_{cor}$, the relationship between impedance and corrosion current is:

$$\frac{1}{R_p} = 2.303 \cdot I_{cor} \frac{(b_a + b_c)}{b_a \cdot b_c} \quad (6)$$

Equation (6) is valid if the (R_p) is the same to the charge transfer resistance (R_{ct}), and the Faradaic impedance is autonom of frequency.

Simple corrosion systems (Randles circuit) can be described as simple corrosion systems. [18-19]. This equivalent circuit establishes a correlation between the electrochemical parameters of the system and the characteristics of the impedance elements [18] with R_s as ohmic solution resistance, R_p as polarization resistance and C as the double layer capacitance.

Current density corrosion, i_{cor} . Is related with the polarization resistance (R_p) by the equation [18]:

$$i_{cor} = \frac{B}{R_p} \quad (7)$$

where:

$$B = \frac{b_a \cdot |b_c|}{2.303 \cdot (b_a + |b_c|)} \quad (8)$$

In the equation (8) b_a and b_c are the Tafel slopes for anodic and cathodic corrosion reactions. Equation (7) is the Stern-Geary formula for evaluating corrosion resistance. In a simple situation C , corresponds to the capacitance of the electrical double layer, $C = C_{dl}$.

Then the impedance of the simple circuit is given by the equation:

$$Z(j\omega) = R_\Omega + \frac{R_p}{1 + j \cdot \omega \cdot C \cdot R_p} \quad (9)$$

with:

$$\text{Re} Z = R_\Omega + \frac{R_p}{1 + (\omega \cdot C \cdot R_p)^2}; \quad \text{Im} Z = -\frac{\omega \cdot C \cdot R_p^2}{1 + (\omega \cdot C \cdot R_p)^2} \quad (10)$$

By removing the frequency, we obtain:

$$\left(\text{Re } Z - R_{\Omega} - \frac{R_p}{2} \right)^2 + (\text{Im } Z)^2 = \left(\frac{R_p}{2} \right)^2 \quad (11)$$

Which is the equation of a semicircle in the Nyquist diagram with R_p as diameter [15].

C (capacitance) can be established from the resonant frequency, ω_m , at the utmost value of $\text{Im } Z$

$$C = \frac{1}{\omega_m \cdot R_p} \quad (12)$$

A linear representation is also possible to determine the elements of the equivalent electrical circuit.

Representing $\text{Re } Z$ versus $\omega \cdot \text{Im } Z$ according to:

$$\text{Re } Z = R_s + R_p - R_p \cdot \omega \cdot C \cdot |\text{Im } Z| \quad (13)$$

A straight line is obtained with a slope $-R_p \cdot C$ and an intersection of $R_{\Omega} + R_p$ for $\omega \rightarrow 0$.

If $\text{Re } Z$ is represented versus $-\text{Im } Z / \omega$ according to:

$$\text{Re } Z = R_s + \frac{|\text{Im } Z|}{\omega \cdot R_p \cdot C} \quad (14)$$

R_s can be determined from the intersection at $-\text{Im } Z / \omega = 0$.

Capacitance C can be established from the slope of the straight line according to equations (13) and (14).

Very often the impedance diagrams, measured at the corrosion potential, (E_{corr}), have the shape of a depressed semicircle. Kendig and Mansfeld [18, 20-21] expressed this comportment by insert an alpha (α) element as exponent in the equation (9):

$$Z(j\omega) = R_s + \frac{R_p}{1 + (j \cdot \omega \cdot C \cdot R_p)^{\alpha}} \quad (15)$$

In the equation (15) α is only a formal depiction of the experimental data and has no clear physical explanations. It is an expression of the inhomogeneity, roughness or others defects of the investigated surface.

The impedance of the system described according to the equation (15) corresponds to the electrical circuit equivalent shown in Figure 4, where the resistance of the solution (R_s) is in series with a sub circuit compose of a constant phase element (CPE or Q) that renders the capacitive characterization of the electrical double layer at the interface sample - electrolyte, which is in parallel with a polarization resistance (R_p).

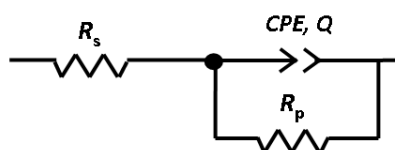


Figure 4. Randles equivalent circuit with constant phase element, noted CPE or Q

Taking into account that in this research work we have a complex interface given by the native oxide layer formed instantaneously on the titan alloys formed predominantly from titanium oxide (TiO_2) interface with saline solution and bulk titanium alloy interface with titanium oxide and electrolyte. Titanium oxide film will passivate the alloy slowing down the corrosion process. The dissolution of bulk alloy is much slower in the passive oxide film. Practically the passive film is removed slowly by corrosive environment and immediately rebuilt from bulk alloy.

Therefore, for better fitting of the resulted impedance data the proposed circuit contains two resistances and two constant phase elements corresponding with the two interfaces described as it is shown in Fig. 5.

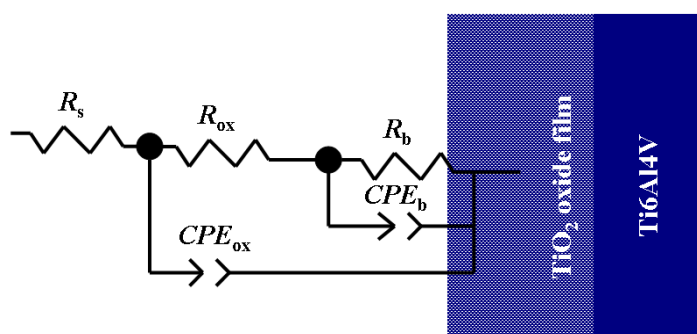


Figure 5. Equivalent electrical circuit to express the interface of Ti6Al4V immersed in saline solution, saline solution with addition of albumin, saline solution with addition of hydrogen peroxide and saline solution with addition of albumin + hydrogen peroxide

In Figure 5, R_s are the saline solution resistances with or without addition of compounds as albumin, H_2O_2 or a mix of two. R_{ox} represent the resistance and CPE_{ox} constant phase element of the oxide film - electrolyte interface, while the R_b and CPE_b represent the resistance and the constant phase element of bulk titanium alloy. The values obtained for these elements used in the construction of the equivalent electrical circuit necessary to express the interface of Ti6Al4V alloy immersed in all four solution used for this study are shown in Table 2. With the aid of the equivalent circuit from Figure 4, were determined the specific polarization resistances written in Figure 3 on each impedance diagram in the Nyquist representation for each type of saline solution as a sum of $R_{ox} + R_b$. From these diagrams it is shown that the higher specific resistance results for Ti6Al4V alloy immersed in saline solution, $1200 \text{ kohm} \cdot \text{cm}^2$. By adding albumin in the saline solution, the specific polarization resistance result has a value in the same order of magnitude as the amount of specific polarization resistance obtained in saline solution, being $1100 \text{ kohm} \cdot \text{cm}^2$.

The inflammatory compound of hydrogen peroxide specie affects drastically the specific polarization resistance of titanium alloy by decreasing it to the value of $321 \text{ kohm} \cdot \text{cm}^2$. This behavior could be explained by the strong oxidative effect, which forms an unstable oxide film that does not provide the same protection to the bulk alloy.

Table 2. The EIS parameters value obtained using the proposed equivalent circuits necessary to describe the interface of Ti6Al4V alloy immersed in four saline solution.

Elements of the electric equivalent circuits	Saline solution	Saline solution +1% Albumin	Saline solution + 1% H ₂ O ₂	Saline solution +1% Albumin + 1% H ₂ O ₂
$R_s (\Omega \text{ cm}^2)$	38	45	198	95
$CPE_b (\text{F cm}^2)$	3.8×10^{-5}	3.5×10^{-5}	1.9×10^{-5}	3.1×10^{-5}
α_b	0.86	0.88	0.96	0.80
$R_b (\text{k}\Omega \text{ cm}^2)$	1085	935	289	523
$CPE_{ox} (\text{F cm}^2)$	3.36×10^{-5}	3.3×10^{-5}	1.0×10^{-5}	2.8×10^{-5}
α_{ox}	0.87	0.84	0.93	0.78
$R_{ox} (\text{k}\Omega \text{ cm}^2)$	115	165	32	57

The saline solution with addition of albumin and hydrogen peroxide reveals a specific polarization resistance of titanium alloy which slightly increasing compared to the resulting specific polarization resistance for the saline solution with addition of only hydrogen peroxide. The albumin seems to protect the titanium surface against inflammatory effect the specific polarization value is $580 \text{ kohm} \cdot \text{cm}^2$, but the value is still much lower than for the solution with addition of albumin or saline solution. Similar behavior was obtained by F. Yu and his team [14] when evaluated the synergetic effect of (BSA) bovine serum albumin and hydrogen peroxide mixed in physiological solution on corrosion behavior of Ti6Al4V. In Figures 6 and 7 there are shown the Bode plots of impedance results as impedance modulus versus frequency in logarithmic scale, Figure 6 and Phase angle versus logarithm of frequency, Figure 7.

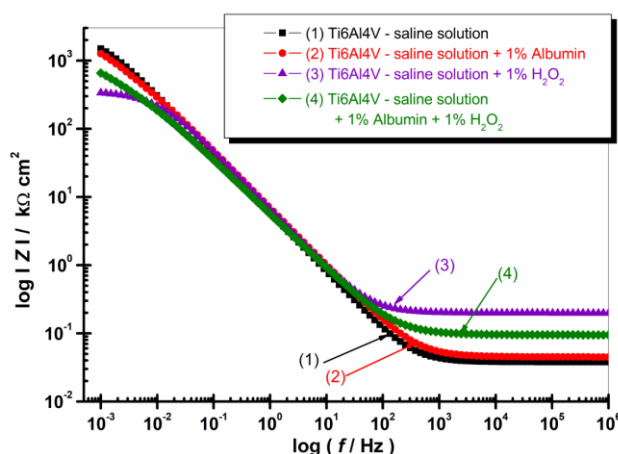
**Figure 6.** Bode plots as impedance modulus vs. frequency of electrochemical impedance spectroscopy results (symbols) and fitted results (plain lines) of Ti6Al4V alloy for: (1) saline solution, (2) saline solution with addition of 1% Albumin; (3) saline solution d with addition of 1% H₂O₂; (4) saline solution with addition of with 1% Albumin and 1% H₂O₂

Figure 6 reveal that the slopes of each diagram are very similar and close to 0.9 values. The smaller impedance modulus is revealed by titanium alloy surface immersed in saline solution with addition of inflammatory compound (H_2O_2). The impedance modulus of Ti6Al4V surface immersed in saline solution and with addition of albumin in saline solution are values close to each other, while the impedance modulus of the titanium alloy surface immersed in saline solution with addition of mixed albumin + hydrogen peroxide reveals a value slightly higher as compared with those resulted from saline solution doped with inflammatory compound, but still lower than the values resulted from saline solution or saline solution with addition of albumin.

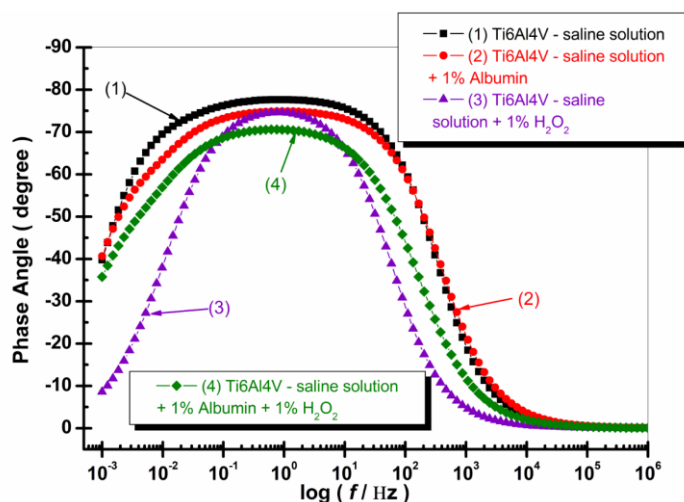


Figure 7. Bode plots as phase angle vs. frequency of electrochemical impedance spectroscopy results (symbols) and fitted results (plain lines) of Ti6Al4V alloy for: (1) saline solution, (2) saline solution with addition of 1% Albumin; (3) saline solution with addition of 1% H_2O_2 ; (4) saline solution mixed with 1% Albumin and 1% H_2O_2

The phase angle close to 80 degree on a larger frequency domain is shown for Ti6Al4V surface immersed in saline solution or saline solution with addition of albumin, confirming a good corrosion resistance in both solutions. The phase angle revealed of Ti6Al4V alloy surface immersed in saline solution with inflammatory compound or albumin mixed with hydrogen peroxide decrease to 70 degree and the frequency domain of this high value becomes narrower, the narrowest being for inflammatory conditions. This behavior confirms the negative effect of inflammatory compound, H_2O_2 , on the corrosion resistance of titanium alloy in saline solution.

3.3. Potentiodynamic polarization

From the potentiodynamic polarization diagrams, Figure 8, it is shown the beneficial effect of albumin addition to saline body fluid solution. The passivation domain is even larger that for Ti6Al4V alloy submerged in saline solution without any other addition. Thus the passive potential domain for Ti6Al4V immersed in saline solution with addition of albumin is between -0.81 V and +2.64 V having approximately a width of 3.45 V which is larger as compared with the passive potential domain of

Ti6Al4V immersed in saline solution with a width of 3.06 V (from -0.32 V and +2.74 V vs. Ag/AgCl, being approximately 3.06 V). Even the mean value of the passive current density, $5.7 \mu\text{A} \cdot \text{cm}^{-2}$, is smaller for Ti6Al4V immersed in saline solution with albumin as compared with the mean value of passive current density revealed for titanium alloy immersed in saline solution, which is $16.95 \mu\text{A} \cdot \text{cm}^{-2}$.

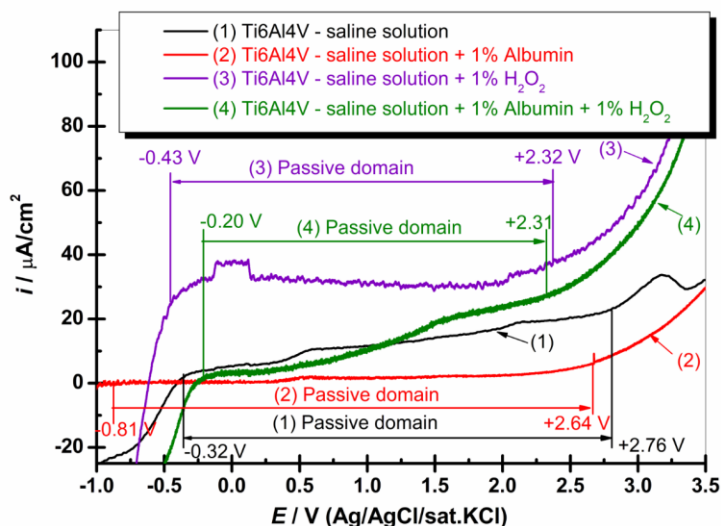


Figure 8. Potentiodynamic polarization diagrams of Ti6Al4V alloy for: (1) saline solution, (2) saline solution with addition of 1% Albumin; (3) saline solution with addition of 1% H_2O_2 ; (4) saline solution with addition of 1% Albumin and 1% H_2O_2

When inflammatory compound of hydrogen peroxide is added to saline solution the surface of titanium alloy is much more damaged. The passive potential domain becomes narrower having about 2.75 V with a higher passive current density of $37.51 \mu\text{A} \cdot \text{cm}^{-2}$ as mean value. The transpassivation current density is much higher as compared with the transpassivation current density revealed by titanium alloy submerged in saline solution and saline solution with addition of albumin. The beneficial effect of albumin is observed on the potentiodynamic polarization diagram of the Ti6Al4V immersed in the saline with addition of a mixture of albumin and H_2O_2 . The range of passivation potential remains narrower, Figure 8, curve (4) but the passivation current density becomes lower, although it has a small increase but continues until transpassivation. The mean value of passivation current density is $2.7 \mu\text{A} \cdot \text{cm}^{-2}$ at the beginning of passivation plateau increasing after to another plateau at $26.94 \mu\text{A} \cdot \text{cm}^{-2}$. The transpassivation current density becomes also higher being similar as for transpassivation current density of titanium alloy submerged in saline solution with addition of hydrogen peroxide. Even if albumin is probably adsorbed on titanium alloy surface it cannot completely eliminate the destructive impact on the surface of the Ti6Al4V of the hydrogen peroxide.

4. CONCLUSIONS

This study examine the impact of inflammatory conditions in the presence of albumin to corrosion behavior of titanium alloy in buffered solution, simulating the aggressive corrosive body

fluids. From the OCP evolution over 12 hours from the initial immersion time the most positive values are registered for registered for the saline solution with addition of hydrogen peroxide. The most negative potential from immersion time to steady state value is shown by the Ti6Al4V immersed in saline solution with addition of albumin, being even more negative than the potential values of the alloy immersed in simple saline solution.

The experimental data results disclose that the H₂O₂ addition into saline solution reduce the corrosion resistance of Ti6Al4V, whilst the albumin present in the saline solution is absorbed on the surface of the titanium alloy having a protective role.

In the case of saline solution mixed with hydrogen peroxide and albumin, the electrochemical results show that the polarization resistance of Ti6Al4V alloy, decrease also but less than in the case of saline solution with inflammatory compound, demonstrate the prevailing impact of ROS (reactive oxygen species) and also the protective effect of albumin. The inflammatory compound of hydrogen peroxide added to saline solution affect also the passivation state of titanium alloy, the passive potential domain becomes narrower having with a higher passive current density.

Overall conclusion it must be paid more attention on the implant materials in the case of inflammatory conditions.

CREDIT AUTHORSHIP CONTRIBUTION STATEMENT

Lidia Benea: Conceptualization, Methodology, Writing- Reviewing and Editing. Nicoleta Simionescu : Investigation, Writing- Original draft preparation, Software, Validation.

DECLARATION OF COMPETING INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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