

## Galvanic Corrosion Behaviour of Ti and Ti6Al4V Coupled to Noble Dental Alloys

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This study aims to evaluate the electrochemical corrosion behaviour of titanium and Ti6Al4V alloy coupled to the following noble dental alloys: Pontor® 2, Cerapall® 2, V-Gnathos® Plus and Pagalin® 2. The study was conducted in artificial saliva, pH 7.1, at 37°C, by linear sweep voltammetry, electrochemical impedance spectroscopy and chronoamperometry. The  $R_p$  values of the noble dental alloys varied from  $10^4$  to  $10^5 \Omega \text{ cm}^2$ . Data from  $E_{ocp}$  curves, linear polarization resistance, Tafel plots and electrochemical impedance spectroscopy lead to the same order for the resistance against corrosion of the four noble alloys in artificial saliva. The order from the less to the more reactive alloy is: Cerapall® 2 → Pontor® 2 → V-Gnathos® Plus → Pagalin® 2. Values of the  $i_{couple}$ , varying between 0.2 and  $0.7 \mu\text{A cm}^{-2}$ , were obtained for the four noble alloys when coupled to pure titanium or to the titanium alloy, respectively. Among the couples studied the Pontor® 2 | Ti was found to be the more resistant galvanic couple, while the Cerapall® 2 | Ti6Al4V presents the lowest corrosion resistance.

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**Keywords:** Titanium, Ti6Al4V alloy, noble dental alloys, corrosion resistance, electrochemical techniques, galvanic couples.

### 1. INTRODUCTION

Commercially pure titanium (CP Ti) and titanium based alloys have been widely used in restorative surgery, such as dental and orthopedic prostheses, due to their excellent mechanical

properties, good corrosion resistance, biocompatibility and biofunctionality in biological fluids, as it has been well reported in the literature [1-28]. Ti6Al4V alloy can coexist with different metallic dental superstructures and other dental restorations in a patient mouth. Under these conditions, galvanic corrosion phenomena can occur and that possibility cannot be discarded when determining the appropriate treatment for a specific patient [4, 6-8, 14, 17, 23, 27]. The Ti6Al4V alloy became popular due its chemical resistance, mechanical strength, low toxicity, lightness and excellent biocompatibility. It was the first Ti alloy to be registered as implant material [29].

Accordingly to Hsu et al. [13] until 2004 only a few articles on the corrosion behaviour of Ti6Al4V implant alloy in human body fluid could be found in the literature [20-23], but the number has increased in the last years [14-19, 24-28]. When producing a crown over a Ti or Ti6Al4V dental implant, it is very common to use high noble alloys as intermediate layer between the implant and the external porcelain layer. High noble alloys have a minimum of 60% content on noble metals (any combination of gold, palladium and silver) have been tested [30-31 and references therein] They usually contain a small amount of tin, indium and/or iron, which promote the formation of an oxide layer, facilitating a chemical bond for the porcelain. They have relatively high strength, durability, hardness and ductility. The presence of palladium imparts a white colour, even in small amounts, and this element also imparts a high melting temperature and contributes to reducing the price of the alloy.

As mentioned in the literature many studies have proven the biocompatibility and suitability of titanium, however it is also important to evaluate the galvanic corrosion process that may occur particularly in vivo (see the review by Adya et al. [6]. As stated by Adya et al. [6], under certain circumstances, the oral cavity can simulate an electrochemical cell with the less noble metal alloy acting as anode and the more noble as cathode. A potential difference of a few or various mV may be established as well as galvanic currents flowing through the saliva and the metallic contacts.

It is therefore very important to consider the possible galvanic couples and its electrochemical behaviour. Ti like many others non-noble metallic materials is covered by a protective oxide layer, [10-11, 14, 27, 32] although, thermodynamically stable, however ions may be released through the passive layer. Cortada et al. [7-8] have determined the metallic ions released in oral implants with superstructures of different metals and alloys used in clinical dentistry.

The aim of this study was to evaluate and compare the electrochemical corrosion behaviour of commercially pure titanium (CP Ti) and Ti6Al4V when coupled to the following commercially available noble dental alloys: V-Gnathos<sup>®</sup> Plus, Pontor<sup>®</sup>, Pagalin<sup>®</sup> and Cerapall<sup>®</sup> 2.

## 2. MATERIAL AND METHODS

### 2.1. Specimens

#### 2.1.1. Composition of alloys

The composition of the four alloys is listed in Table 1. They are commonly used in prosthetic dentistry, with V-Gnathos<sup>®</sup> Plus and Cerapall<sup>®</sup> 2 being used as bonding alloys and Pontor<sup>®</sup> 2 and Pagalin<sup>®</sup> 2 as casting alloys.

**Table 1** Composition of dental alloys (wt %).

Noble dental alloys	Code	Au	Pt	Pd	Ag	Cu	In
Cerapall <sup>®</sup> 2	(C)	2.0	-	78.5	-	6.9	4.5
Pontor <sup>®</sup> 2	(PO)	72.0	3.6	-	13.7	9.8	-
V-Gnathos <sup>®</sup> Plus	(VG)	85.9	11.7	-	-	-	-
Pagalin <sup>®</sup> 2	(PG)	3.0	-	23.0	65.0	6.5	2.0

### 2.1.2. Preparation of specimens

Coupons of the alloys with an area of about 0.9 cm<sup>2</sup> were soldered to a copper wire and inserted into a mould of epoxy resin and then glued into a glass tube. The electric contacts were insulated with Araldite<sup>®</sup>. The electrodes were successively polished with alumina pastes (ALPHA Micropolish II, agglomerated, Buehler) of different grain sizes, 1.0, 0.3 and 0.05 µm. A platinum grid counter electrode and a commercial Ag|AgCl, 3M KCl, reference electrode completed the configuration of a three-electrode electrochemical cell.

### 2.2. Test solution

The test solution used was artificial saliva with the composition given in Table 2, according to Duffó et al. [33]. The test solution was prepared with reagent grade compounds and ultrapure water (Milli-Q from Millipore<sup>®</sup>). The pH was measured with a pH meter from Metrohm, model 620. A value of 7.1 was obtained. All the experiments were conducted with the electrochemical cell in a thermostatic bath at 37°C.

**Table 2.** Composition of the artificial saliva [33]

Compounds	NaCl	KCl	CaCl <sub>2</sub> . 2H <sub>2</sub> O	KH <sub>2</sub> PO <sub>4</sub>	Na <sub>2</sub> HPO <sub>4</sub> . 12H <sub>2</sub> O	KCN	citric acid
(g L <sup>-1</sup> )	0.600	0.720	0.220	0.680	0.856	0.060	0.030

### 2.3. Electrochemical methods

For each alloy, the open circuit potential (OCP) was acquired and recorded, over a period of 24 h, using a computer-controlled digital HP / Agilent multimeter, *via* the IntuiLink software.

Linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS) were performed *via* a potentiostat/galvanostat Autolab PGSTAT12 equipped with a Frequency Response Analyzer (FRA2) from Metrohm Autolab B.V. Polarization curves recorded at 0.5 mV s<sup>-1</sup> were used to obtain the electrochemical parameters, relevant for the evaluation of the resistance against corrosion,

namely:  $E_{(i=0)}$ ,  $R_p$ , corrosion current density,  $i_{\text{corr}}$ , and corrosion potential,  $E_{\text{corr}}$ . Polarization curves covering a wider potential range were recorded at  $1 \text{ mV s}^{-1}$ .

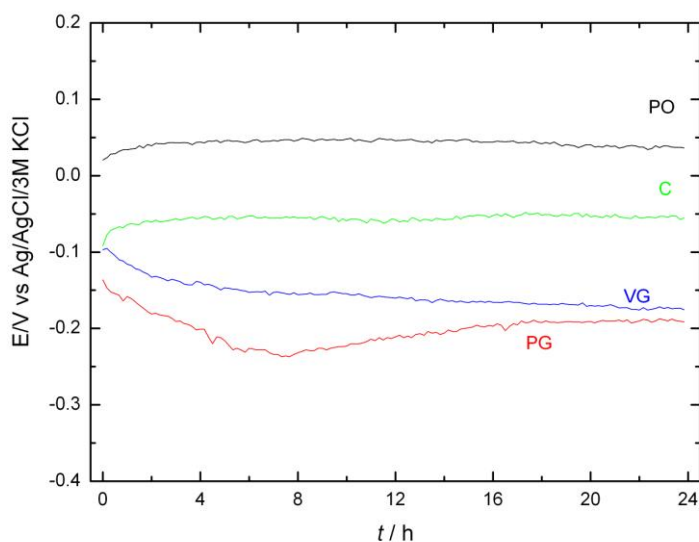
Electrochemical impedance spectra were obtained by applying a 10 mV rms sinusoidal potential wave around the open circuit potential, after keeping the electrode in the solution, at  $37 \text{ }^\circ\text{C}$ , during a period of 10 minutes, at OCP. Frequencies ranging from  $10^4$  to 0.1 Hz were used.

The galvanic voltage and the galvanic current density of the various galvanic pairs were measured in a two-compartment cell, at open and short circuit, respectively. The galvanic voltage was measured over a period of 10 minutes by using a high-impedance digital multimeter, while the current time transients were recorded during a period of 24 h. The chronoamperometric experiment was performed using a potentiostat/galvanostat (Autolab PGSTAT12). For the various pairs under study the charges under the current time transients were integrated over the studied time period ( $Q_{\text{couple}}$  from 0 to 24 h).

### 3. RESULTS AND DISCUSSION

#### 3.1. Open circuit potential curves

$E_{\text{ocp}}$  curves for the four alloys in the test solution, at  $37 \text{ }^\circ\text{C}$ , recorded over a period of 24 h of immersion, are given in Fig.1.



**Figure 1.**  $E_{\text{OCP}}$  curves of the four noble dental alloys in non-deoxygenated artificial saliva, at  $37 \text{ }^\circ\text{C}$ , during 24 hours.

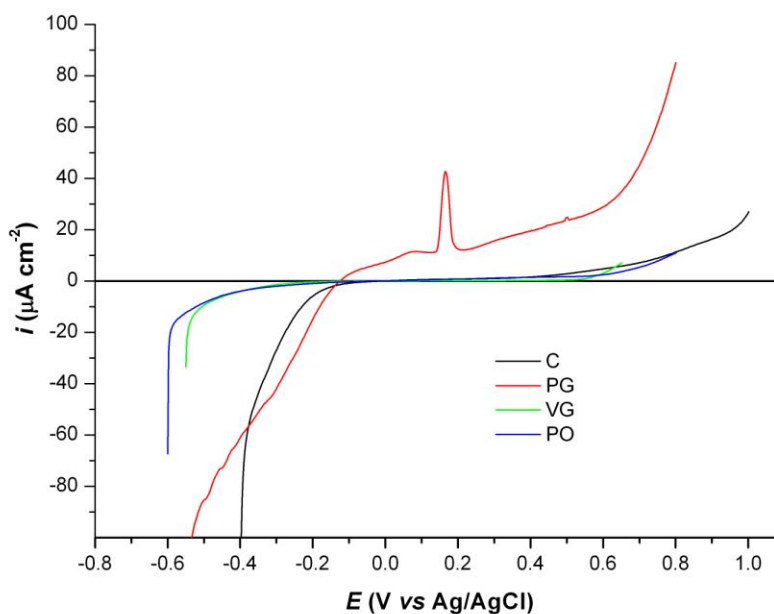
During the first hours of immersion the V-Gnathos<sup>®</sup> Plus and the Pagalin<sup>®</sup> alloys show a displacement of the potential in the negative direction, with the Pagalin<sup>®</sup> presenting a minimum value of  $-0.24 \text{ V}$ , after *ca* 6 h of immersion. The shift of the  $E_{\text{ocp}}$  in the negative direction suggests

dissolution of the air formed oxide film till the formation of a new oxide layer, which gives a quite stable potential during the last 8 h of immersion. A similar behaviour has been reported by Bhola et al. [6] for Ti immersed in normal saliva. The Pontor<sup>®</sup> 2 and the Cerapall<sup>®</sup> 2 alloys have shown only a very slightly displacement of the  $E_{\text{OCP}}$  in the positive direction during the 1<sup>st</sup> hour of immersion. Then a very stable and more positive potential was maintained for both alloys during the next 22 hours.

The average values of the  $E_{\text{OCP}}$  corresponding to the last 6 hours of immersion were:  $+0.038 \pm 0.002$  V;  $-0.054 \pm 0.002$  V;  $-0.170 \pm 0.002$  V and  $-0.190 \pm 0.002$  V (vs Ag|AgCl), for the Pontor<sup>®</sup> 2, Cerapall<sup>®</sup> 2, V-Gnathos<sup>®</sup> Plus and Pagalin<sup>®</sup> 2, respectively. Since the more negative potentials values mean less resistance against corrosion, then the order of resistance from the more to the less resistant is the following: Pontor<sup>®</sup> 2 > Cerapall<sup>®</sup> 2 > V-Gnathos<sup>®</sup> Plus > Pagalin<sup>®</sup> 2. Accordingly to the thermodynamics, the high percentages of the high noble metals on the Pontor<sup>®</sup> 2' composition may justify its behaviour, however the V-Gnathos<sup>®</sup> Plus contains also Au and Pt (high noble metals) even in higher percentages and its resistance is lower than that of the Cerapall<sup>®</sup> 2 which contains mainly Pd. This behaviour is most probably due not only to the percentages of Au and Pt on the alloy composition (high noble alloys) but also to the presence of Cu, even when present in a small percentage. The lower corrosion resistance of Pagalin<sup>®</sup> 2 is certainly explained by the high percentage of Ag in the alloy's composition. According to the Pourbaix's diagrams [32] the stability region of Au, Pt and Pd occurs at more positive potentials than that of Ag. As reported by Sastri et al. [34] on a study of silver-palladium alloys the Ag rich composition shows little resistance.

### 3.2. Linear Polarization Curves

Fig. 2 presents a set of polarization curves recorded at  $1 \text{ mV s}^{-1}$  for the four noble alloys immersed in artificial saliva, pH 7.1, at  $37 \text{ }^\circ\text{C}$ .

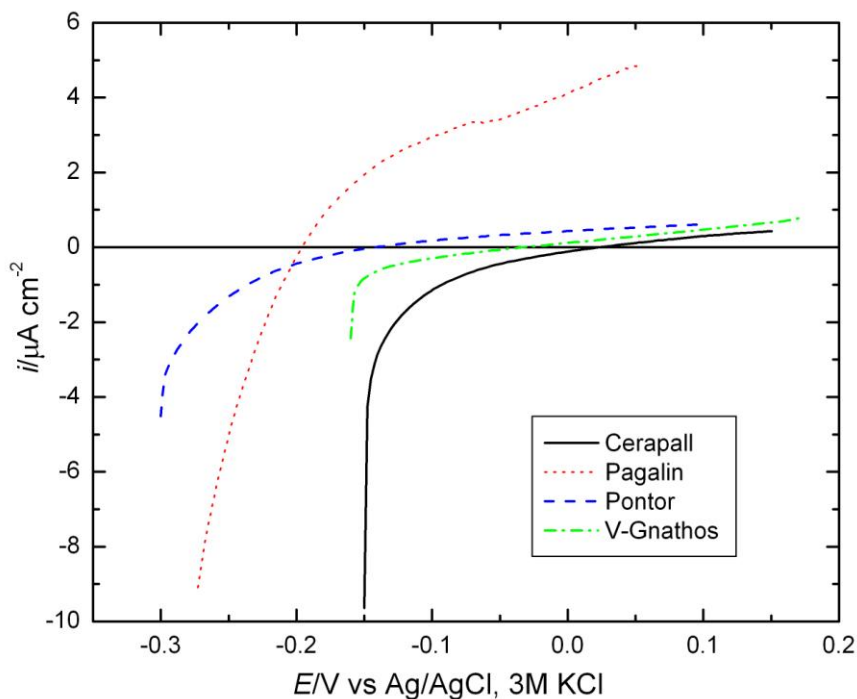


**Figure 2.** Linear polarization curves for the four noble dental alloys in non-deoxygenated artificial saliva, at  $37 \text{ }^\circ\text{C}$ , recorded at  $1 \text{ mV s}^{-1}$ , after 20 minutes of immersion.

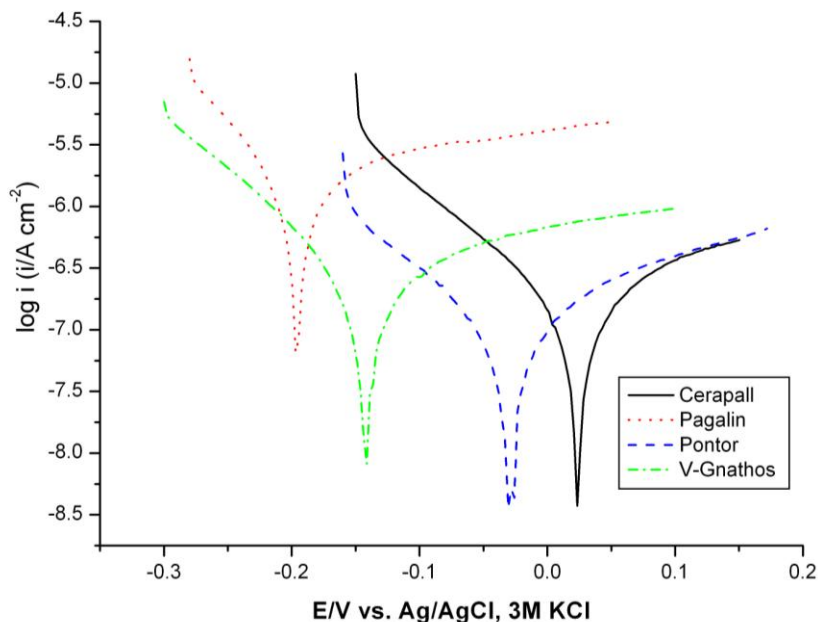
Data shows clearly, that under anodic potentiodynamic polarization, the Pontor<sup>®</sup> 2, V-Gnathos<sup>®</sup> Plus and Cerapall<sup>®</sup> 2 all present current plateaus, without any peak, and the current starting to rise steeply at values ranging between +0.55 and +0.65 V. On the other hand, the LSV of the Pagalin<sup>®</sup> 2 shows a very well defined anodic peak at +0.24 V. This anodic peak is most probably related with the high percentage of Ag in the respective alloy composition (65% Ag). During the anodic polarization the formation of AgCl may occur, leading to the observed anodic peak. A similar peak has been found by Sastri et al.[34] during the polarization of the one Ag-Pd alloy in chloride medium and, also, by Hassan et al. [35] during the polarization of pure silver in chloride aqueous solutions.

The breakdown potentials,  $E_b$ , calculated from the polarization curves, are the followings: +0.50, +0.55, +0.63 and +0.70 V, for the PG, VG, PO and C alloys, respectively. When comparing the current densities, at the same polarization potential, for example at + 0.50 V, the kinetics of the corrosion process are faster for the PG ( $24.5 \mu\text{A cm}^{-2}$ ), followed by C ( $2.9 \mu\text{A cm}^{-2}$ ), then PO ( $1.7 \mu\text{A cm}^{-2}$ ) and finally the VG ( $0.44 \mu\text{A cm}^{-2}$ ).

Linear polarization curves, recorded at  $0.5 \text{ mV s}^{-1}$ , for the four alloys immersed in the artificial saliva, pH 7.1, at  $37 \text{ }^\circ\text{C}$ , in the non-logarithmic and logarithmic forms, are given in Fig. 3. Data shows clearly that, among the four noble alloys, the Pagalin<sup>®</sup> 2 is the more active alloy: its corrosion starts at much more negative potentials and for the same potential it presents much higher current densities than the others. Pagalin<sup>®</sup> 2 and V-Gnathos<sup>®</sup> Plus are the most reactive followed by Pontor<sup>®</sup> 2 and Cerapall<sup>®</sup> 2.



**A**



**B**

**Figure 3.** Polarization curves for the four noble dental alloys in non -deoxygenated artificial saliva, at 37 °C, recorded at 0.5 mV s<sup>-1</sup>, after 20 minutes of immersion: (a) *i* vs. *E*; ( b) log *i* vs. *E*.

The polarization resistance ( $R_p = \Delta E/\Delta i$ ) at  $E_{(i=0)}$  as well as the  $E_{(i=0)}$  values obtained from the analysis of the linear sweep polarization curves of Fig. 3a are summarized in Table 3.

Data shows clearly that the corrosion resistance decreases from the Pontor<sup>®</sup> 2 to the Pagalin<sup>®</sup> 2. The higher resistance of the PO alloy is most probably due to the high percentage of gold in the alloy’s composition, while the lower resistance of PG can be attributed to its high contents of silver. The corrosion parameters obtained from the Tafel analysis of the curves presented in Fig. 3b are given in Table 4.

**Table 3.** Electrochemical data from the analysis of the  $E_{OCP}$  versus time curves and from the linear polarization curves recorded at 0.5 mV s<sup>-1</sup>

Noble dental alloys	$E_{(OCP, 24h)}$ (V vs. Ag AgCl)	$E_{(i=0)}$ (V vs. Ag AgCl)	$R_p$ (kΩ cm <sup>2</sup> )
Pontor <sup>®</sup> 2	+0.038 ( 0.002)	-0.010 (0.009)	520 (50)
Cerapall <sup>®</sup> 2	-0.054 (0.002)	+0.020 (0.006)	190 (10)
V-Gnathos <sup>®</sup> Plus	-0.170 (0.002)	-0.170 (0.007)	67 (4)
Pagalin <sup>®</sup> 2	-0.190 ( 0.002)	-0.190 (0.004)	18 (2)

The high corrosion resistance obtained for the Pontor<sup>®</sup> 2 is in agreement with data by Cortada et al. [8] who have concluded about the excellent corrosion resistance of alloys with high contents of gold.

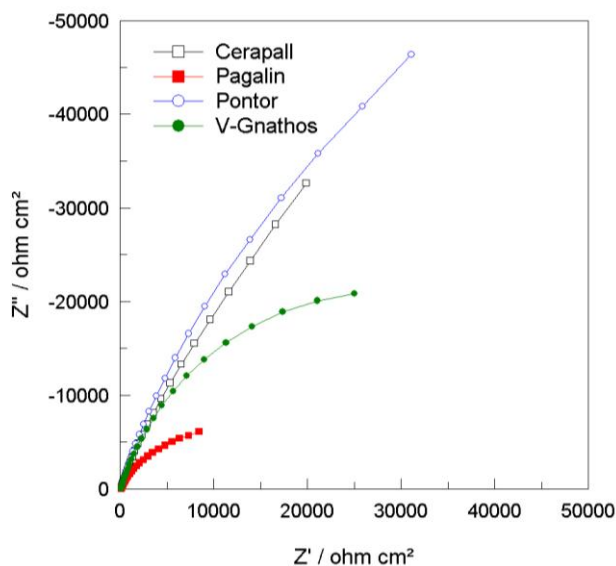
**Table 4.** Data from Tafel analysis of the curves of Fig. 3b.

Noble dental alloys	Cerapall <sup>®</sup> 2	Pontor <sup>®</sup> 2	V-Gnathos <sup>®</sup>	Pagalin <sup>®</sup> 2
$E_{corr}$ (V vs. Ag AgCl)	+0.020	-0.040	-0.150	-0.200
$i_{corr}$ ( $\mu\text{A cm}^{-2}$ )	0.35	0.75	1.1	2.4

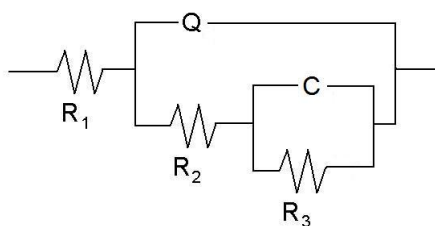
Values of  $i_{corr}$  varying from 0.35 to 2.40  $\mu\text{A cm}^{-2}$  were obtained. Corrosion current densities and corrosion potentials are in agreement for the classification of the reactivity of the four noble alloys. They can be ordered from the less to the more reactive as: C  $\rightarrow$  PO  $\rightarrow$  V-G  $\rightarrow$  PG. In general all the results are in full agreement leading to the conclusion that Pagalin<sup>®</sup> 2 presents the higher reactivity, due to its high contents of silver.

3.4. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy has been widely used to evaluate the corrosion resistance of dental alloys [36, 11, 14, 16, 18, 25 ]



A



B

**Figure 4.** (a) Nyquist diagrams for the four noble dental alloys in non-deoxygenated artificial saliva, at 37 °C (pH=7.1;  $\Delta E = 10$  mV;  $f = 0.1$  to  $10^4$  Hz.  $E_{(i=0)}$  (C) = +0.020;  $E_{(i=0)}$  (PG) = -0.190;  $E_{(i=0)}$  (VG) = -0.170;  $E_{(i=0)}$  (PO) = -0.010 V vs. Ag|AgCl); (b) Equivalent circuit used in the electrochemical impedance data simulation.



Nyquist plots, obtained from the EIS data, for the four noble alloys in non-deoxygenated artificial saliva, at 37 °C, are given Fig. 4.

The electrochemical impedance data was fitted to the equivalent circuit of Fig. 4b by the use of ZView software. This equivalent circuit accounts for the presence of a duplex oxide layer, with an inner barrier film represented by film resistance  $R_3$  and film capacitance  $C$ , whereas the porous outer layer accounts for the presence of a wall capacitance, represented by the constant phase element  $Q$  (where the element impedance is related with its characteristic parameters,  $Y_0$  and  $n$ , by  $Z_Q = 1 / [Y_0(j\omega)^n]$ ) and an additional solution resistance inside the pores,  $R_2$ . The overall solution resistance is represented by  $R_1$ . This circuit is normally associated to duplex oxide films where the outer porous region is much thicker than the inner barrier layer. Thus, the resistance of the pore wall has not been included, as it would be so high that its contribution to the circuit may be discarded. All the data sets were successfully fitted to this circuit, as documented by the low  $\chi^2$  values, in the range of  $10^{-4}$ , and the fitted parameters for the different electrical components of equivalent circuit are shown in Table 5.

**Table 5.** Values of the electrical components of the equivalent circuit of Fig. 4a.

Noble dental alloy	Cerapall <sup>®</sup> 2	Pontor <sup>®</sup> 2	V-Gnathos <sup>®</sup> Plus	Pagalin <sup>®</sup> 2
$R_1/(\Omega \text{ cm}^2)$	119	129	121	140
$R_2/(\text{k}\Omega \text{ cm}^2)$	58.6	81.2	45.0	10.7
$Y_0/(\text{S cm}^{-2} \text{ s}^n)$	$2.76 \times 10^{-5}$	$1.87 \times 10^{-5}$	$2.96 \times 10^{-5}$	$6.91 \times 10^{-5}$
$n$	0.83	0.85	0.83	0.78
$R_3/(\text{k}\Omega \text{ cm}^2)$	88.0	83.7	8.5	6.1
$C/(\mu\text{F cm}^{-2})$	20.2	15.0	23.3	152
$\chi^2$	$2.6 \times 10^{-4}$	$2.9 \times 10^{-4}$	$1.2 \times 10^{-4}$	$1.5 \times 10^{-4}$

The Cerapall<sup>®</sup> 2 and the Pontor<sup>®</sup> 2 alloys present quite high values for the inner barrier film resistance  $R_3$  (ca. 80  $\text{k}\Omega \text{ cm}^2$ ), while the V-Gnathos<sup>®</sup> Plus and the Pagalin<sup>®</sup> 2 present values one order magnitude lower (6-8  $\text{k}\Omega \text{ cm}^2$ ). For the corresponding film capacitance, the Pagalin<sup>®</sup> 2 shows the highest value (152  $\mu\text{F cm}^{-2}$ ), while all the others present much lower values, ranging between 15 and 20  $\mu\text{F cm}^{-2}$ . Assuming the model of a parallel plate capacitor, the capacitance of an insulating oxide film is given by  $C = \epsilon\epsilon_0/d$ , where  $\epsilon_0$  is the vacuum permittivity (8.85 pF/m),  $\epsilon$  the dielectric constant of the oxide film and  $d$  its thickness. Thus, the higher capacitance obtained for Pagalin<sup>®</sup> 2 may indicate a thinner film, which is in agreement with its lower resistance.

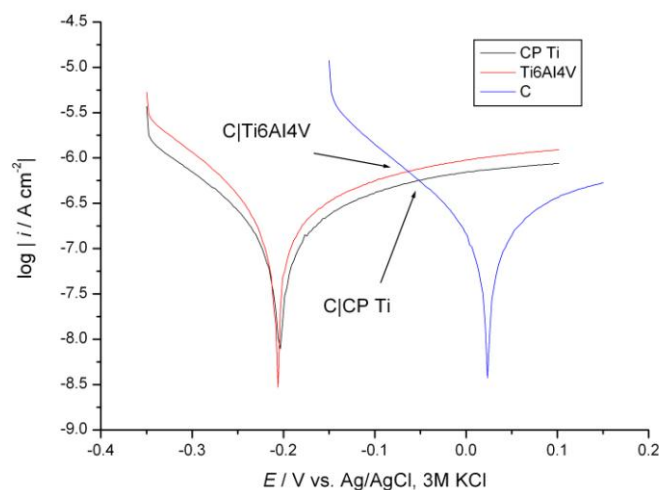
As mentioned above, the pores wall capacitance is represented in the circuit by a constant phase element,  $Q$ . It is normally assumed that a CPE showing  $n$  values above 0.75 represents a distributed capacitance and in that case the value of  $Y_0$  may be taken as an estimate of the capacitance value. Thus, again taking into account the  $C = \epsilon\epsilon_0/d$  relationship, the higher  $Y_0$  values obtained for the Pagalin<sup>®</sup> 2 pores wall (in comparison with the other alloys) may indicate the presence of a thinner and, in principle, less protective porous oxide film. This is also confirmed by the lower value obtained in this case for the additional solution resistance  $R_2$ , which might be due to a lower thickness of the pores.

Thus, from both the inner barrier oxide and porous oxide parameters, the Pagalin® 2 may be considered the alloy that shows the lowest resistance to corrosion.

Assuming that the  $R_p$  value corresponds to the real component of the impedance at very low frequencies ( $R_p=R_1+R_2+R_3$ ), then the behaviour of the four alloys according to the analysis of the EIS data is in agreement with the order given by the analysis of the polarization curves, where the alloys may be ranked according to their increased reactivity as Cerapall® (C) → Pontor® 2 (PO) → V-Gnathos® Plus (VG) → Pagalin® 2 (PG).”

### 3.5. Galvanic corrosion analysis

Figure 5 gives the  $\log i$  versus  $E$  plots of the polarization curves ( $v=0.5 \text{ mV s}^{-1}$ ) of the commercially pure titanium, Ti6Al4V alloy and V-Gnathos® Plus alloy. From the intersection point of the anodic sides of the pure Ti (CP Ti) and Ti6Al4V alloy and the cathodic branch of the V-Gnathos® Plus alloy, all recorded under the same experimental conditions, it was possible to obtain an estimated value of the galvanic current density ( $i_{\text{couple}}$ ) and the galvanic corrosion potential ( $E_{\text{couple}}$ ) of the corresponding galvanic couples.



**Figure 5.**  $\log i$  ( $i/ \text{A cm}^{-2}$ ) vs.  $E$  plots for the galvanic couples: Cerapall® 2 | Ti6Al4V and Cerapall® 2 | CP Ti.

The same analysis procedure was carried out for the others noble dental alloy | CP Ti and noble dental alloy | Ti6Al4V couples being the correspondent data displayed in Table 6.

Values of the  $i_{\text{couple}}$ , varying between  $0.2$  and  $0.7 \mu\text{A cm}^{-2}$ , were obtained for the four noble alloys coupled to pure titanium or to the titanium alloy. For all the couples slight lower values were obtained when the alloy was coupled to the pure titanium.

Arslan [14] has found for the Ti6Al4V/Au couple in Ringer's solution at  $37 \text{ }^\circ\text{C}$ , values of  $E_{\text{couple}}$  and  $i_{\text{couple}}$  the order of  $-0.020 \text{ V vs Ag/AgCl}$  and  $5.6 \mu\text{A cm}^{-2}$ , respectively. Then one may conclude

that the materials under study, alloys containing high noble (Au and Pt) and noble metals (Ag and Pd) when coupled to the titanium alloy give values only slightly lower than those reported by Arlsan et al. [14] for the Au | Ti6Al4V couple.

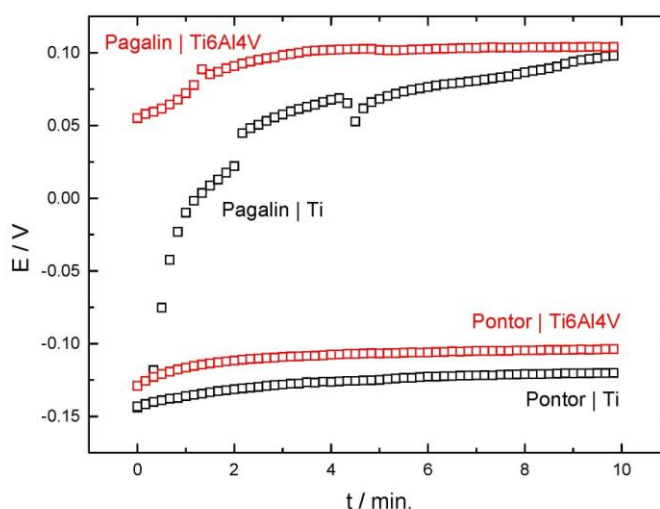
**Table 6.** Electrochemical parameters, obtained from the mixed potential theory, for the galvanic couples: noble dental alloy | Ti6Al4V and noble dental alloy | CP Ti.

Galvanic couples	$E_{\text{couple}}$ (V vs. Ag AgCl)	$i_{\text{couple}}$ ( $\mu\text{A cm}^{-2}$ )
Cerapall <sup>®</sup> 2   CP Ti	-0.051	0.6
Cerapall <sup>®</sup> 2   Ti6Al4V	-0.064	0.7
Pontor <sup>®</sup> 2   CP Ti	-0.104	0.4
Pontor <sup>®</sup> 2   Ti6Al4V	-0.116	0.5
V-Gnathos <sup>®</sup> Plus   CP Ti	-0.166	0.2
V-Gnathos <sup>®</sup> Plus   Ti6Al4V	-0.173	0.2
Pagalin <sup>®</sup> 2   CP Ti	*	*
Pagalin <sup>®</sup> 2   Ti6Al4V	*	*

\* it is not possible to apply the method

### 3.6. Galvanic cell voltage

Under certain circumstances, the oral cavity can simulate an electrochemical cell with the less noble metal alloy acting as anode and the more noble as cathode. Therefore a potential difference of a few or various mV may be established as well as galvanic currents flowing through the saliva and the metallic contacts.



**Figure 6.** Cell potential vs. time for the galvanic couples: Pontor<sup>®</sup> 2 | Ti6Al4V; Pontor<sup>®</sup> 2 | CP Ti; Pagalin<sup>®</sup> 2 | Ti6Al4V and Pagalin<sup>®</sup> 2 | CP Ti.

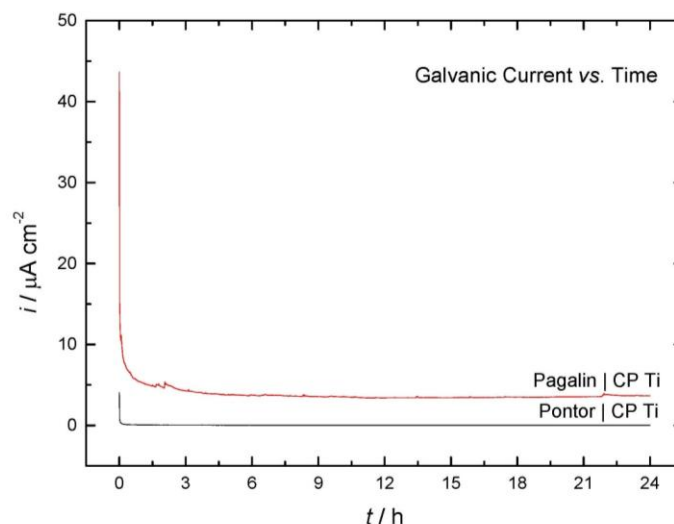
The galvanic cell voltage (potential difference) of the noble dental alloys when coupled to CP Ti and Ti6Al4V alloy was recorded, over a 10 minute period. Figure 6 gives the variation of the galvanic cell potential for the Pagalin<sup>®</sup> 2 and Pontor<sup>®</sup> 2 alloys coupled to CP Ti and Ti6Al4V. The data obtained for all galvanic cells represented by noble dental alloy | CP Ti and noble dental alloy Ti6Al4V couples is displayed in Table 7.

The Pontor<sup>®</sup> 2 | Ti and Pontor<sup>®</sup> 2 | Ti6Al4V couples present the more negative galvanic voltages, starting with values of -0.143 and -0.129 V and then keeping an almost constant value, over a period of 10 minutes, -0.120 and -0.104 V, respectively. The galvanic voltage for the of Pagalin | Ti couple starts with a value of -0.175 V and changes abruptly to +0.050 V, during the first 5 min, then varies less abruptly reaching +0.100 V, after the 10 minutes. The higher and more positive values of the galvanic cell potential for the Pagalin | Ti couple is in agreement with previous data. Effectively, the Pagalin corrodes easily due to the high percentage of Ag.

### 3.7. Galvanic current vs. time

Ti like many others non-noble metallic materials is covered by a protective oxide layer, although termodinamically stable, however ions may be released through the passive layer. Cortada et al. [8] have obtained for the titanium oral implant coupled with chromium-nickel alloy a high quantity of ions released, while for the implant coupled with titanium superstructure a very low value of ions released have been obtained. This behaviour is indicative of high corrosion resistance.

Fig. 7 presents the galvanic current vs. time curves, recorded at OCP for the Pagalin<sup>®</sup> 2 | Ti and Pontor<sup>®</sup> 2 | Ti couples immersed in the artificial saliva solution, at 37 °C. The galvanic current density of the various galvanic pairs was also evaluated and integrated over a 24 h time period.



**Figure 7.** Current vs. time curves over an immersion period of 24 h for the galvanic couples Pontor<sup>®</sup> 2 | CP Ti and Pagalin<sup>®</sup> 2 | CP Ti.

Table 7 gives the electrochemical parameters obtained from the analysis of the data of Figs. 6 and 7, for all the studied galvanic couples. The transients show a steep decrease during the first instants

leading to very low and steady currents, over periods of 24 h. The steady values are of the order of 5  $\mu\text{A cm}^{-2}$  for the Pagalin<sup>®</sup> 2 | Ti couple and almost zero for the Pontor<sup>®</sup> 2 | Ti couple.

**Table 7.** Cell potential ( $E$ ), integrated galvanic current density ( $Q_{\text{couple}}$ ) over 24 h and maximum galvanic current density ( $i_{\text{max}}$ ) for the galvanic couples: noble dental alloy | Ti6Al4V and noble dental alloy | CP Ti couples.

Galvanic couples	$E_{(0 \text{ min})}$ (mV)	$E_{(10 \text{ min})}$ (mV)	$Q_{\text{couple}}$ (mC cm <sup>-2</sup> )	$i_{\text{max}}$ ( $\mu\text{A cm}^{-2}$ )
Pontor <sup>®</sup> 2   Ti6Al4V	-129	-104	2	7
Pontor <sup>®</sup> 2   CP Ti	-143	-120	2	4
V-Gnathos <sup>®</sup> Plus   Ti6Al4V	-13	27	135	29
V-Gnathos <sup>®</sup> Plus   CP Ti	42	72	126	22
Cerapall <sup>®</sup> 2   Ti6Al4V	79	-29	90	36
Cerapall <sup>®</sup> 2   CP Ti	31	-10	113	28
Pagalin <sup>®</sup> 2   Ti6Al4V	55	104	*	*
Pagalin <sup>®</sup> 2   CP Ti	-144	98	367	44

The analysis of the data in Table 7, considering the maximum currents gives the following order for the reactivity of the dental alloys coupled to pure titanium from the less to the more reactive: PO (4  $\mu\text{A cm}^{-2}$ )  $\rightarrow$  VG (22  $\mu\text{A cm}^{-2}$ )  $\rightarrow$  C (28  $\mu\text{A cm}^{-2}$ )  $\rightarrow$  PG (44  $\mu\text{A cm}^{-2}$ ). When coupled to the titanium alloy the order is the same, but the values of the  $i_{\text{couple}}$  are slightly higher: PO (7  $\mu\text{A cm}^{-2}$ )  $\rightarrow$  VG (29  $\mu\text{A cm}^{-2}$ )  $\rightarrow$  C (36  $\mu\text{A cm}^{-2}$ ). Considering the charges,  $Q_{\text{couple}}$ , the couple Pagalin<sup>®</sup> 2 | CP Ti shows the most high values: 367 mC cm<sup>-2</sup> against 2 mC cm<sup>-2</sup> for the Pontor<sup>®</sup> 2 | CP Ti couple.

It should be stated that among the commercially high noble alloys studied in this work, V-Gnathos<sup>®</sup> Plus (VG) contains the highest percentage of gold (*ca* 86%) and a relative small percentage of platinum (*ca* 10%); Pontor<sup>®</sup> (PO) is a gold-platinum-silver-copper alloy, with 72% of gold; Cerapall<sup>®</sup> 2 (C) is a palladium (78%) based alloy with a small percentage of gold, copper and indium and, finally, Pagalin<sup>®</sup> (PG) is a silver- palladium-copper-gold alloy with a quite high percentage of silver (65 %).

#### 4. CONCLUSIONS

Concerning to the corrosion resistance of the four noble dental alloys studied, when immersed in artificial saliva, pH 7.1, at 37 °C, the order from the less to the more reactive is: Cerapall<sup>®</sup> 2  $\rightarrow$  Pontor<sup>®</sup> 2  $\rightarrow$  V-Gnathos<sup>®</sup> Plus  $\rightarrow$  Pagalin<sup>®</sup> 2. The electrochemical corrosion behaviour exhibited when coupling the different noble dental alloys with pure titanium or Ti6Al4V alloy depends not only from the noble dental alloy composition but also on the nature of the used Ti-based dental material. Among the alloys studied and according to the electrochemical data obtained the Pontor<sup>®</sup> 2 | CP Ti was the

couple that delivers the lowest galvanic currents ( $4 \mu\text{A cm}^{-2}$ ), while the Pagalin<sup>®</sup> 2 | CP Ti galvanic couple delivers currents ten times higher ( $44 \mu\text{A cm}^{-2}$ ).

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