

Article

Unraveling the Corrosion of the Ti-6Al-4V Orthopedic Alloy in Phosphate-Buffered Saline (PBS) Solution: Influence of Frequency and Potential

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Abstract: This paper addresses the interplay between electrical fields in the human body and the corrosion behavior of Ti-6Al-4V alloy, a prevalent orthopedic material. The study investigates the impact of alternative electrical signals at different frequencies on the alloy's electrochemical behavior in a simulated body environment. The human body always has natural sinusoidal potential due to, e.g., heart palpitations and brain/nervous system activities. Ignoring such natural activities may lead to underestimating the corrosion performance of the Ti-6Al-4V alloy in the body. By analyzing anodic and cathodic responses and the net faradaic current induced by alternating current potential, the research sheds light on the influence of electrical fields on corrosion rates. Understanding these dynamics could lead to improved implant materials, mitigating corrosion-related challenges and enhancing implant performance over the long term. Results of this work indicated that frequent oxidation and reduction at certain frequencies may induce corrosion and hinder biomimetic apatite formation, impacting osseointegration. Natural alternative currents in the body affect the corrosion performance of Ti-based implant alloys, highlighting the need for consideration in biomedical applications.

Keywords: titanium; implant; non-linear EIS; alternative voltage; corrosion



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1. Introduction

Biocompatibility, mechanical performance, tribological features, and corrosion resistance are the main criteria in metallic material selection for biological applications [1]. Ti-based alloys are one of the best candidates for implant alloys. These alloys have been successfully implemented in orthopedic applications owing to excellent corrosion resistance, appropriate mechanical properties, and exceptional osseointegration rates [2–4]. Ti-6Al-4V alloy has high strength-to-weight ratios and is characterized by its high corrosion resistance. It is a two-phase $\alpha + \beta$ alloy and is characterized by the lamellar structure of the α phase separated by β -phase interlayers inside the β -grain [5,6]. $\alpha + \beta$ are stabilized by Al and V, respectively [7–9]. The nature of the passive film on the surface of these alloys is the key factor when considering the corrosion resistance and osseointegration performance of such an alloy [8,10–14]. This intrinsic passive film primarily consists of different crystallographic forms of TiO_2 [15–17]. Reliable performance is the key factor in orthopedic alloy selection and evolution [18,19]. Despite the desirable chemical, physical, and biological properties of developed orthopedic alloys, numerous premature failures or incompatibility cases have been reported due to corrosion [20–23]. The corrosion behavior of metallic implants is influenced by numerous factors such as the chemical compound and microstructure of the material itself; the working conditions, including temperature; the

physiological compound; construction, such as the formation of galvanic cells, crevices, and external factors, for instance; mechanical loading; wear; and thermal shocks [24].

The degradation of implant alloys may contribute to the late loosening of the prosthetic components and impact metabolism and immunity. In addition, corrosion and the release of ions such as Ti^{4+} , Cr^{2+} , V^{4+} , and Al^{3+} from the dissolution of the multi-phasic alloys [25–27] promote inflammation, infection, and bone resorption [28,29]. For instance, trace elements incorporated in implantable alloys were detected in the blood, liver, and lung [30]. Decreases in DNA synthesis and the mineralization of alkaline phosphates [31] and cytotoxicity in osteoblasts [32] are other detrimental effects of alloying element release in the human body. Vanadium may also accumulate in some organs, such as the liver, and, in lower concentrations, in the kidneys, bones, and spleen [33].

Bioelectrochemical reactions in a physiological environment might affect the corrosion resistance properties of the Ti-6Al-4V evaluated in an under-controlled laboratory environment [20]. The corrosive environment of the human body, along with cyclic loads, wear, fretting, and temperature alternation, can significantly accelerate the degradation due to corrosion [2,8,34–37].

In addition, electrical currents in the body can influence the corrosion performance of an implant [20]. The electrical field induced in the human body can be classified into two main groups:

1. External sources: Everyone is exposed inadvertently to alternative electrical currents and potential. Electric transmission lines with operating voltages higher than 765 kV raise serious questions about the impact of high-strength electric fields or shock on living organisms [38,39]. Many studies have investigated the harmful effects of power frequency (50/60 Hz) on the human body [38]. Depending on the size of the organ [40], the electric and magnetic fields (EMFs) induce biological effects, since electric and magnetic fields induce weak current flows in a body due to alternative current (AC), which may lead to brain malfunction and adverse effects on health [41–43]. Additionally, direct current (DC) and AC external sources (at a frequency range of 1 Hz to 1 MHz) such as electrical field inducers are used to stimulate injured tissue healing [44–46].
2. Internal sources: Biopotentials are the internal and natural sources of electrical field in the human body. These potentials may originate from body motion [47], the growth and development of cells and tissues [48], and the heartbeat or brain [49,50]. In addition, injuries or any abnormal changes create a flux of various ions towards or outwards from the injured organ, which causes a stream of electrical current [51]. Considering the resistivity of tissues, these currents can produce voltage differences of between 10 and 100 mV/cm in the human body [20]. Strains in hard tissues like bones and teeth can also induce potential alternation due to the piezoelectric stimulation of dipolar collagens [20,52].

All the mentioned points highlight that tissues and organs in individuals are exposed to various alternative electrical signals. On the other hand, imposing an alternating electrical field can influence the corrosion activity of alloys [53–55]. For example, in a study on Ti-6Al-4V dental implants, Chen et al. showed that while the α phase portion of an alloy can promote the formation of insoluble Ti-Al passive film, under applied anodic potential conditions, the dissolution of β phase is favored, and the vanadium is released to the environment transpassively [56]. However, there is always a certain threshold for perturbation potential or frequency to observe tangible corrosion due to alternating electrical fields. Anodic or cathodic polarizing surfaces beyond the equilibrium potential range cause an extra faradaic reaction, providing a concentration of reactants and products on the surface. In the case of the alternative excitation of the surface, when the overvoltage reverses, the reverse reaction may not happen at the same rate due to the asymmetric kinetics of cathodic and anodic activation. As a result, repetitive forward and reversing overvoltage rectifies the net faradaic current, and corrosion ensues at an increasing rate [53,55,57,58]. However,

the charge transfer at the interface is not significantly fast and may be slowed even more with mass transport barriers like passive film.

The current produced by the anodic half wave of alternating potential is not equal to the cathodic counterpart; as a result, the net current induced by an AC is greater than the free-corrosion current [54,59,60].

It is imperative to study the influence of the electrical field in the human body on the corrosion behavior of orthopedic alloys, which is the objective of this paper. This study aimed to analyze the electrochemical behavior of Ti-6Al-4V alloy, one of the most common orthopedic alloys, under different alternative electrical signals with different frequencies in a simulated body environment.

2. Experimental Section

As the working electrodes, 40 mm × 20 mm specimens were cut from a 2 mm thick Ti-6Al-4V sheet, which complied with the ASTM F1472-014 specified for surgical implant applications [61]. For each experiment, three specimens were prepared and tested. Specimens were ground using SiC paper up to #1200 grit and then polished with 0.5 and 0.05 µm alumina suspension. Then, they were rinsed with ethanol in an ultrasonic bath for 1 min and dried immediately by blowing cool air onto them. Specimens were epoxy-coated to provide insulation and a circular surface area of 1.0 cm² was left in contact with the electrolyte. A 1X phosphate-buffered saline (PBS) solution of pH 7.4 [62], with the composition shown in Table 1, at a constant temperature of 37 °C with a stationary condition, was used in this study.

Table 1. The composition of 1 L 1X-PBS solution used in this study.

Reagent	Weight/Volume
Sodium chloride	8.00 g
Potassium chloride	0.20 g
Disodium phosphate (Na ₂ HPO ₄)	1.44 g
Monopotassium phosphate (KH ₂ PO ₄)	0.24 g
Water	Up to 1 L

It should be mentioned that no specific standard (e.g., ASTM) was followed for the electrochemical experiments since the application of an alternative potential is new. To evaluate the general polarization response of specimens exposed to PBS for 24 h at open circuit potential (OCP), potentiodynamic cyclic polarization tests were carried out by scanning potential from −200 mV vs. OCP to +700 mV vs. SCE and reversed to −100 mV vs. SCE with a scan rate of 1 mV/s.

Electrochemical measurements were carried out using a classical three-electrode arrangement consisting of a saturated calomel reference electrode (SCE), platinized platinum counter electrode, and the Ti-6Al-4V specimens as the working electrode. To ensure the reproducibility of the data, all measurements were repeated on three identical specimens. All electrochemical treatments and measurements were initiated after 24 h of exposure to a 37 °C PBS solution at OCP to reach a stable condition of the oxide film on working electrodes.

Electrochemical impedance spectroscopy (EIS) is a powerful technique to characterize surface conditions on metals and alloys. Conventional EIS can be employed only under small signal conditions, i.e., when the system response is linear. However, the kinetic information in the nonlinear part of the response would be missing under small signal conditions. In addition, small amplitude perturbation often leads to poor signal-to-noise ratio. The nonlinear electrochemical impedance spectroscopy (NLEIS) method can be considered an extended version of the EIS technique, wherein a large amplitude perturbation is applied to the system, and the response is recorded at the fundamental and higher harmonics [63].

In order to find the minimum adequate perturbation potential amplitude for the nonlinear distortion of current response, NLEIS measurements in the range of 100 kHz

to 10 mHz with different sinusoidal perturbation amplitudes of 5, 10, 20, 50, 100, and 200 mV were carried out sequentially. For each exciting frequency with a particular perturbation potential, the nonlinearity response of the current was calculated using the total harmonic distortion (THD) of the current signal, as written in Equation (1), expressed as follows [64,65]:

$$THD_i = \frac{\sqrt{\sum_{k=2}^{10} |\hat{I}_k|^2}}{\hat{I}_1} \quad (1)$$

where $\hat{I}_k$ denotes the k th component from the Fourier transform of the current response. Thus, $\hat{I}_1$ is the fundamental component of the current, while $k \geq 2$ is associated with non-fundamental harmonics. The first to 10th harmonics are used to calculate THD in this study. The stimulus potential where THD exceeds the value of 5% was considered to be the potential that causes nonlinear behavior [66]. This value was 100 mV for this study. After specimens were immersed in the PBS solution for 24 h at their OCP, a 100 mV sinusoidal alternating voltage with various frequencies of 500, 50, 5, 0.5, and 0.05 Hz was superimposed on the specimens.

The chemical composition of the Ti oxide film formed on the specimens is expected to be transformed or indiscernible when using the ex situ examination methods [4,67]. Thus, in situ Raman spectroscopy was used to study and compare the formation and transformation of the oxide crystal modifications as a function of electrochemical parameters [10,68]. The films formed on the surface of the specimens after 24 h of immersion in the PBS solution at 37 °C at their OCP, and were investigated when they were perturbed with 100 mV sinusoidal potential vs. OCP with different frequencies. The Raman spectra obtained were corrected for the electrolyte background. The necessity of this correction was discussed elsewhere [68].

3. Results and Discussion

A cyclic potentiodynamic polarization curve of the specimens tested in PBS solution at 37 °C and immersed for 24 h is shown in Figure 1. The whole curve depicts characteristics of passive behavior in the test environment. Up to +0.7 V vs. SCE potential excursion, there is no evidence of an active–passive transition related to the initiation of localized corrosion processes. Negative hysteresis at reverse potential scan confirms the stability and resistance to passive film breakdown [69–71].

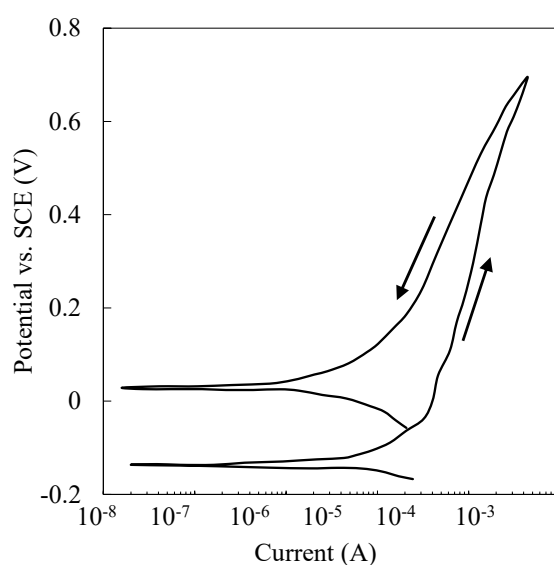


Figure 1. Cyclic potentiodynamic polarization curve of a Ti-6Al-4V specimen tested in 1X-PBS at 37 °C and immersed for 24 h.

It was found that the ratio of anodic to cathodic Tafel slope ($r = \beta_a / \beta_c$) determines a material's susceptibility to AC-induced corrosion [68–70]. In this experiment, where $r = 1.45$ ($\beta_a = 0.725$ V/decay, and $\beta_c = 0.500$ V/decay), it is plausible that the asymmetry of cathodic and anodic activation polarization rectifies the net faradaic current [55,72]. The current produced by the anodic half-wave of alternating voltage is not equal to its cathodic counterpart; as a result, the net current induced by AC is greater than the free-corrosion current [54,60].

Figure 2a shows the Nyquist plots obtained from the different EIS measurements with different stimulus potentials on the specimens immersed at their OCP for 24 h in the PBS solution at 37 °C.

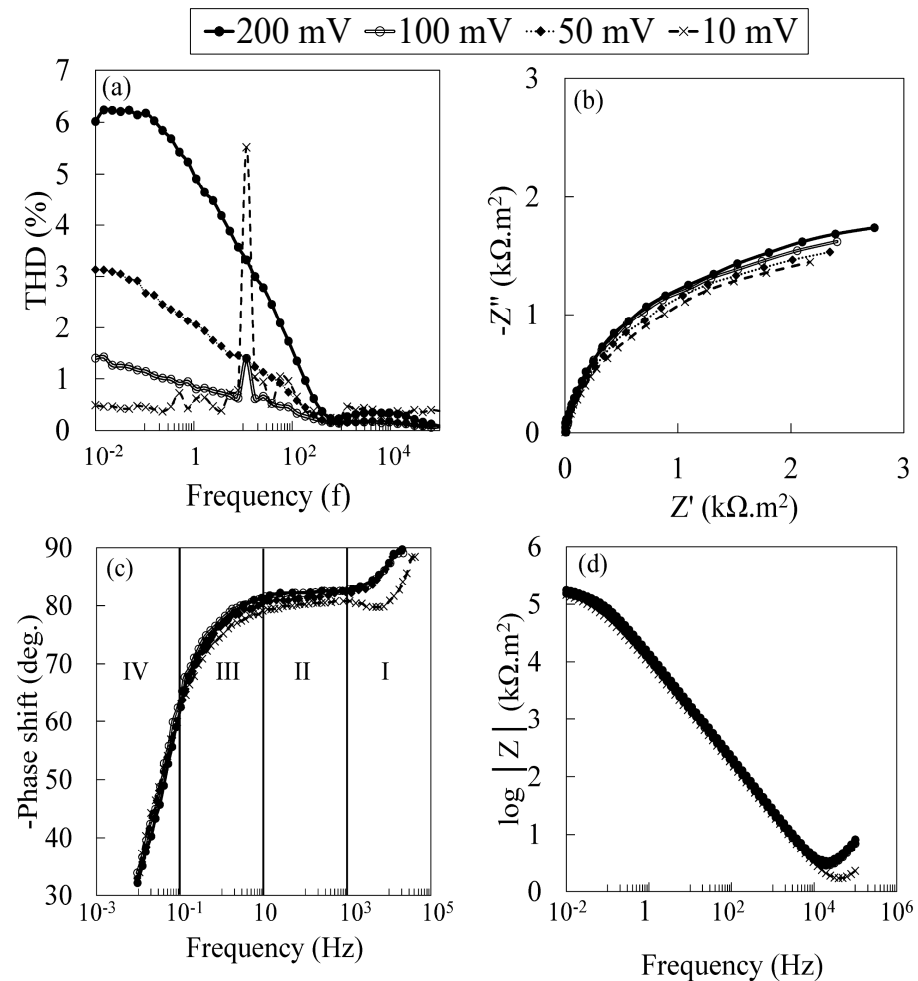


Figure 2. (a) Total harmonic distortion, (b) Nyquist plots and (c) corrected Bode phase angle, and (d) Bode plot obtained from the NLEIS measured on the specimens immersed at their OCP for 24 h in 1X-PBS solution at 37 °C.

Looking at total harmonic distortions obtained with different perturbation potentials, it is evident that increasing stimulus potential results in a nonlinear polarization response from the surface, especially at lower frequencies. In Figure 2b, it appears that increasing the stimulus potential decreased all the impedances of the system. In the high order of the harmonic potential, the interface layer capacitance (C_{dl}) and charge transfer (R_{ct}) response of the surface may yield nonlinear behavior to AC perturbation, and as a result, AC can potentially induce further dissolution [55,57,73]. As demonstrated in Figure 2b, a decrease in system impedances is observed by increasing potential perturbation in the whole spectrum. At high frequencies, the current is absorbed mainly by the interface capacitance, and the contribution of the nonlinear resistance of the charge transfer was

negligible. However, by decreasing the frequency, the current flowed progressively through the nonlinear charge transfer resistor, increasing the nonlinearity at low frequencies [66]. In addition to the nonlinear behavior of the charge transfer resistance against high-order potential perturbations, as shown in Figure 2a, faradaic distortion can affect the capacitive behavior at the electrolyte/oxide film/substrate [74–76].

Figure 2c shows the corrected phase angle Bode plot obtained from the current response of the EIS measurements. Phase angle correction by subtracting the solution resistance $\Phi_{adj} = -\tan^{-1}\left(\frac{Z_j}{Z_r - R_s}\right)$, yields valuable information concerning high and intermediate frequencies [77]. As shown in Figure 2c, the obtained phase angle spectra can be divided into four sections. At the highest frequencies of section I, the electrode geometry induced an inhomogeneous distribution of potential and current; as a result, phases were not steady [78,79]. This behavior was also attributed to the conductivity of the titanium oxide film formed on the surface of the specimens [76,80,81]. Increasing the excitation potential changed the behavior of the specimens, particularly at high frequencies. In section II, the phase angles showed constant values below 90° at intermediate frequencies, ascribing the constant phase element (CPE) behavior of the adsorptive layer at the electrolyte/oxide film [75,76,82]. In terms of CPE, the impedance associated with faradaic reaction without diffusion can be written as

$$Z(\omega) = R_s + \frac{R_{ct}}{1 + (j\omega)^\alpha Q R_{ct}} \quad (2)$$

where α is the CPE exponent, which can be obtained as follows:

$$\alpha = \left| \frac{d(\log|Z_j|)}{d(\log f)} \right| \quad (3)$$

Phase angle instability indicates inhomogeneous ohmic and kinetic distribution at the electrolyte/film/substrate. When $\alpha = 1$, the dielectric characteristic of the surface can be assumed as ideal capacitance, while deviation from ideal values shows instability and/or inhomogeneous ohmic and kinetic distribution at the electrolyte/film/substrate [83]. As shown in Table 2, the graphically obtained values for α decrease when increasing the excitation potential's amplitude. Increasing the excitation potential's amplitude, even in the very low range of activation polarization, can change the specimens' dielectric properties and charge transfer resistance. Decreasing values of α and instabilities in phase angles are indications of inhomogeneous ohmic and kinetic distribution at the electrolyte/film/substrate [83]. As a result, the surface can become vulnerable to film-dissolution-localized reactions after long-term exposure due to the detrimental effect of a high order of superimposed alternating potential [84–86]. Section III, known as the integration interval, mainly describes the relaxation time of the distributed capacitances [87,88]. In section IV, the Z approached the maximum value, and the frequency was sufficiently low to fully charge the capacitances [77].

Table 2. The composition of 1 L 1X-PBS solution used in this study.

Perturbation Amplitude (mV)	α
10	0.905
50	0.902
100	0.889
200	0.872

The effect of low potential excitation with different frequencies was investigated on the specimens after 24 h of immersion in the 1X-PBS electrolyte. The amplitude of 100 mV was chosen as the potential excitation, as it typically exists in the human body, tissue, and implant material [89]. For each condition, after preparation, the specimens were exposed

to the 1X-PBS solution for 1 h at their OCP. Then, 100 mV sinusoidal potential vs. their OCP was applied to the specimens with constant frequency for 24 h. Here, 500, 50, 0.5, and 0.05 Hz were chosen as the frequencies. These frequencies were selected to represent one frequency in each section in Figure 2c. The application of the alternating potential was stopped for approximately 10 min, and standard/linear EIS (± 10 mV perturbation at corresponding OCP, with a frequency range of 100 kHz to 1 mHz) was conducted on the specimens. Figure 3 shows the typical Nyquist and Bode phase (φ_{adj}) obtained from EIS measurements during 24 h exposure under different sinusoidal frequency perturbations.

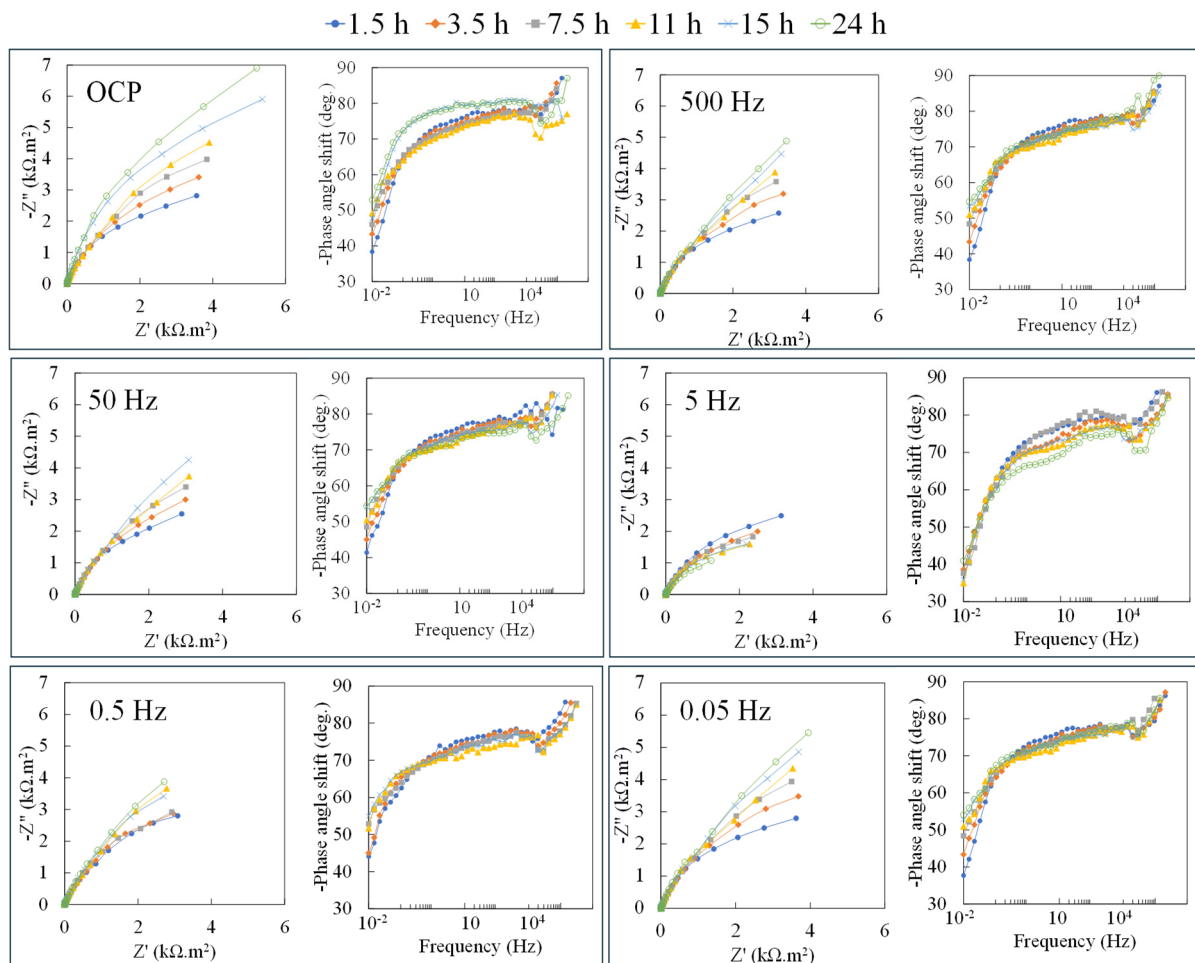


Figure 3. Typical Nyquist and Bode phases obtained from EIS measurements during 24 h exposure of Ti-6Al-4V in the 1X-PBS solution at 37 °C superimposed by applying a constant 100 mV at OCP and different frequencies.

In all measurements, a single depressed arc can be observed in the Nyquist plot, indicating that electrochemical reactions in all examined conditions were governed by charge transfer control. This characteristic is also evident in Bode phase plots, where no distinct local minima in the medium to low frequency were observed. The non-steady phase angles at frequencies above 10^3 Hz mainly arise from surface geometry inducing an even potential. In the specimen at OCP, the impedance consistently rises upon immersion time, with the phase angles stabilizing at higher angles. However, this trend cannot be observed in other specimens exposed to frequent oxidation and reduction at different frequencies. To better understand the change and trend of the electrochemical behavior of the examined specimens, the specimens' charge transfer resistances, i.e., R_t , were then obtained from the results of the EIS tests using the Brug method [90], presented in Figure 4.

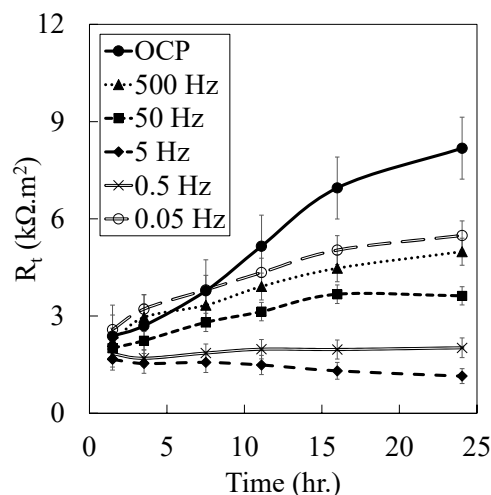


Figure 4. The evolution of charge transfer during 24 h exposure in the 1X-PBS solution at 37 °C was superimposed by applying a constant 100 mV vs. OCP amplitude with different sinusoidal frequencies.

It is noteworthy that regressed physicochemical quantities should be taken carefully. The specimens indicated nonlinear behavior due to the activation polarization and mass transport phenomena in low frequencies [66,91,92]. Thus, any mechanism proposed with an equivalent circuit may become more complex or degenerate by giving it the same impedance [76,93]. As time passes, charge transfer resistance increases for the OCP condition due to the stabilizing of the interface capacitance and the aging of the oxide film [94]. However, applying the potential truncated this trend. Applying 100 mV with 500 and 50 Hz frequencies reduced the charge transfer resistance compared to the OCP condition; however, their trends were positive. As shown in Figure 4, in this range of frequencies (section II), the responses of the specimens were mainly due to the non-faradaic current of the double-layer capacitance. As a result, the double layer's charge–discharge process consumed most of the current generated by the potential perturbation.

Additionally, further passivation and surface reduction could happen at slow rates. Decreasing the frequency to 5 Hz decreased the charge transfer with a negative slope vs. exposure time. Around this frequency, the dielectric capacitance of the double layer began to shift the phase and charge. Consequently, the involvement of the faradaic reactions increased. As a result, the oxide film formed during anodic activation reduced readily in the cathodic part, and the number of ions released from the surface increased [59]. Nevertheless, a further decrease in imposed frequency to 0.5 and 0.05 Hz again increased the charge transfer.

It is hypothesized that reducing the frequency provided sufficient time for the distribution of the dielectrics and relaxation. Consequently, the faradaic reaction consumed a larger portion of the current. As Huang and Blackwood proposed [67], a slow anodic scan rate (i.e., low frequencies) formed a thicker and more stable oxide film in each cycle.

Although, in this study, EIS measurements reflect the nonlinearities in relaxations due to high-amplitude perturbations, when the growth condition no longer applies, the electrochemical impedance of the electrode is mainly dominated by a space-charge layer at the solution–oxide film interface and thus not merely by the properties of oxide film [94,95]. As a result, the corrosion rate cannot readily be determined from impedance measurements. So, techniques such as Raman spectroscopy are required to qualitatively assess the oxide layer offered. Figure 5 shows the Raman spectra obtained from the in situ test on the specimens. Three strong emission bands at 145, 257, and 511 cm^{-1} and one weak band at 273 were detectable in all spectra. These Raman shifts correspond to typical Ti–O bending vibrations of very thin (around a few nanometers) Ti oxide film crystalline structures at the specimens' surface, presumably TiO_2 and Ti_2O_3 [10,68]. Due to the new structure formation, no apparent band was detected by applying potential perturbation on the surface

of the specimens during 24 h of immersion in the PBS solution. However, increasing the immersion time from 1 h to 24 h at the OCP increased the intensity of the peaks, implying an increase in the crystallinity of the Ti oxide formed on the surface [68]. Specimens treated with 100 mV at 500 Hz for 24 h yielded relatively analogous results, although with shorter spikes of Ti_2O_3 . Twenty-four hours of superposition of 100 mV at 5 Hz weakened and truncated the Raman bands. Peak broadening in the Raman bands ascribes the transformation of oxide film from crystalline structure to more disordered and defective crystals or an amorphous state [10,11].

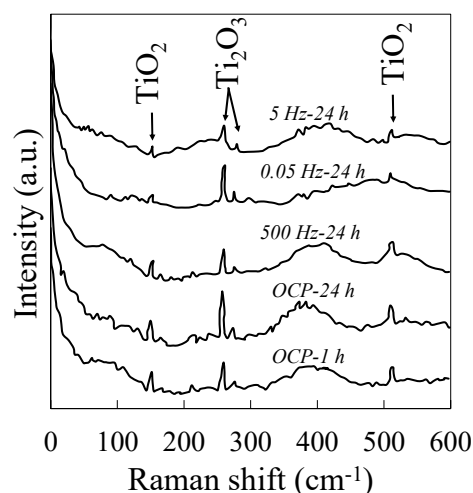


Figure 5. Raman spectra obtained after 24 h of exposure in the PBS solution at 37 °C superimposed with a constant potential of ± 100 mV amplitude vs. OCP and various frequencies.

Combined with the results from EIS tests, it was postulated that applying potential at certain intermediate frequencies did not allow the formation of a protective, stable, and integrated layer of oxide film on the surface of the specimens. As a result, the charge transfer decreased, and the interface dissolution increased. Potential perturbation applied with a frequency of 0.05 Hz was low enough to form a stable film that was not readily reducible in the cathodic part of each scan. Similar to the 24 h OCP condition, Ti_2O_3 peaks were more prominent than the TiO_2 for this frequency condition.

The n-type semiconductive behavior of the Ti oxide film can explain this behavior. During the growth of the Ti oxide film, the Ti (II) and Ti (III) act as donors and migrate through the oxide toward the electrolyte [16]. However, the Ti species are gradually oxidized [17,67,94]. At low frequencies when all the dielectrics were charged, the applied potential did not allow the Ti(II) to migrate further from the substrate, and consequently, these species oxidized more in the form of Ti(III)/ Ti_2O_3 rather than Ti(IV)/ TiO_2 . With a higher growth rate, for example at 5 Hz, when dielectric charge–discharge behavior was partly involved, high Ti(II) concentrations were trapped and partially reduced during the cathodic scan. The high donor densities were previously observed in a Ti film [96,97].

4. Conclusions

This study delved into the intricate electrochemical behavior of immersed specimens under various stimulus potentials and frequencies. The Nyquist plots demonstrated that higher potentials reduced impedance, implying a potential-dependent behavior. Different sections were identified through phase angle spectra analysis, each corresponding to distinct electrochemical processes. Applying 100 mV alternating potentials at different frequencies revealed complex charge transfer behaviors. While 500 and 50 Hz frequencies reduced charge transfer resistance due to dominant non-faradaic currents, lower frequencies (0.5 and 0.05 Hz) increased resistance through intensified faradaic reactions and relaxation effects.

Raman spectroscopy results aligned with EIS observations, providing insight into oxide film crystallinity and stability. The semiconductive behavior of the Ti oxide film and the migration of Ti species contributed to the observed effects. Moreover, it was revealed that frequent oxidation and reduction at a certain range of frequencies can induce corrosion and hinder the formation of biomimetic apatite, potentially affecting the osseointegration process.

There is always a natural alternative current or potential in the human body due to, e.g., heart palpitations and brain/nervous system activities. Ignoring such natural activities may lead to an underestimation of the corrosion performance of Ti-based implant alloys in the body. The study's implications extend to the design and optimization of implant materials for biomedical applications. However, further investigation is warranted to uncover underlying mechanisms and validate findings through complementary techniques and in vivo studies. Overall, this research contributes to our understanding of electrochemical interactions, offering insights that can drive advancements in biomaterials and their successful integration within biological systems.

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