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Chapter

An Insight on Corrosion Resistance Ability of Biocompatible Dental Implants through Electrochemical Impedance Spectroscopy

Duduzile Nkomo and Nomsombuluko Masia

Abstract

Corrosion resistance is an important requirement in the study of biomedical implants. Implant surface can be modified to provide good adherence and/or optimum biocompatibility with the human body at the bone-implant interface. Titanium alloys are typically used because of their excellent corrosion resistance and biocompatibility. However, to improve these properties, the alloy surface is roughened using alumina (Al_2O_3). More details on the corrosion resistance of these alloys can be obtained by using electrochemical impedance spectroscopy (EIS) method. EIS is the most suitable method for monitoring corrosion rate values due to its reproducibility, it is non-destructive and has reliable determination of small corrosion rates, much lower than those measured by other techniques. It can also study high-impedance systems, such as coatings and linings, high-purity water, and organic coating/metal systems or corrosion in a low-conductive solution. This method has been used to evaluate electrochemical properties of modified surfaces. This chapter will explore the effectiveness of EIS in studying the corrosion behaviour of machined and surface-modified Pure Ti grade 4 for dental implant applications. The basic EIS concepts are discussed and their derivation thereof to provide information about the corrosion resistance of biomedical implants is explored.

Keywords: Biomedical, EIS, Surface modification, Implants

1. Introduction

There are multiple ways to study the corrosion resistance of biomedical implants. The common laboratory procedures include open circuit potential test (OCP), potentiodynamic polarisation test (PDP) and EIS. The commonly used electrochemical methods present measurements of currents, electrical charges or electrode potentials as a function of time. In the previous years, the use of EIS method was seldom because contrary to other electrochemical methods, EIS presents the signal as a function of frequency at a constant potential. This limits the fundamental understanding of the method because electrochemists think in terms of time and not frequency. Moreover, issues associated with understanding the EIS

method are that it requires the knowledge of mathematics, Laplace and Fourier transforms, and complex numbers. However the evolution of this method has developed from using rather simple calculations and has rendered it useful in different applications such as solid materials, corrosion, passivity and batteries [1].

EIS has been used to investigate the corrosion resistance of biomedical implants. Currently we focus on the study of corrosion resistance of biomedical implants for dental applications. Different materials have been used for dental implants. Commercially pure titanium and titanium-aluminium-vanadium alloy (Ti-6Al-4 V) are most widely used biomaterials. They became popular because of their chemical resistance, mechanical strength, low toxicity, lightness and excellent biocompatibility. Ti and its alloys have the tendency to react with oxygen to form a stable oxide layer called titanium dioxide (TiO_2). This oxide layer is responsible for chemical stability and corrosion resistance of titanium [2].

The types of corrosive reactions that occur in the oral cavity are electrochemical, where the saliva plays the role. There are various types of corrosion that occurs in the oral cavity such as galvanic, fretting, pitting and uniform corrosion. Titanium implants coexist with different metallic dental superstructures and dental restorations in a patient mouth. This complexity can be linked to the occurrence of galvanic corrosion creating galvanic current, which passes through the surrounding tissue causing sharp pain. Extensive release of metal ions from a prosthetic device can result in adverse biological reactions and can lead to mechanical failure of a device itself. It is therefore important to conduct sufficient corrosion tests in order to avoid such failures and evaluate the efficiency of each corrosion test method used [2].

The advantages of using the EIS method are numerous. It provides a substantial information that can be further analysed in electrochemical properties investigations. Methods such as OCP, PDP and EIS have been used in the current study to determine the corrosion resistance of titanium pure Ti grade 4 in machined (TiGr4M) and roughened (TiGr4R) conditions in different Ringer's lactate solutions.

2. OCP

To compare the results obtained from each electrochemical testing method, we start with OCP investigations. The OCP test results shown in **Figure 1** for TiGr4 in the machined (TiGr4M) and roughened with alumina (TiGr4R) conditions are explained. OCP is the most common and simplest method used to study the film

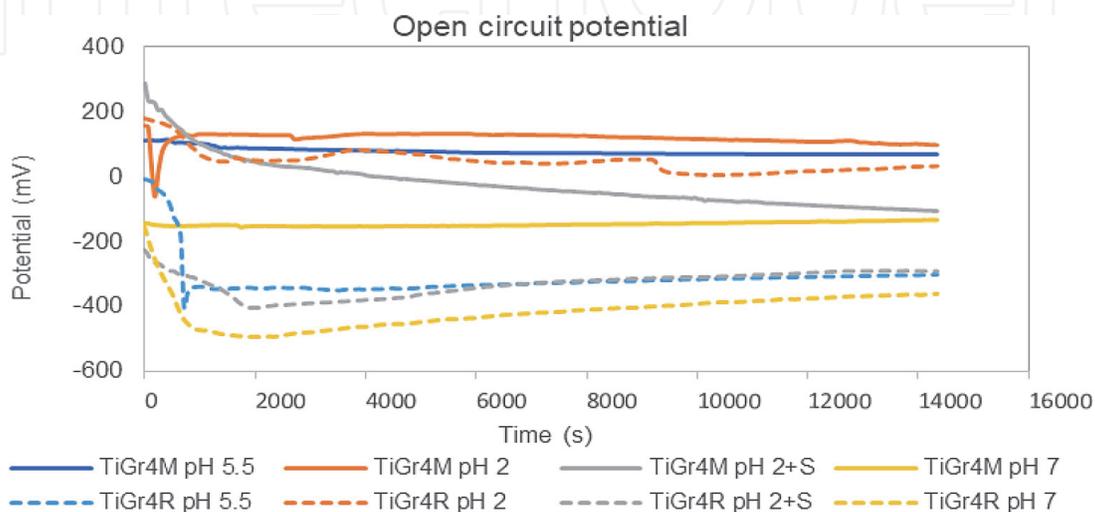


Figure 1.
OCP plots of TiGr4M and TiGr4R in different Ringer's lactate solutions.

formation and passivation of metallic structures. The potentials are measured against time and the results obtained reflect whether or not the passive film is stable in the particular environment. Thus, to mimic the nature of human mouth environment, the TiGr4M and TiGr4R samples were tested in four different pH solutions namely, the base Ringer's lactate solution-pH 5.5, Ringer's lactate-pH 2, Ringer's lactate-pH 2 with addition of sulphur and Ringer's lactate-pH 7. Each sample alloy was immersed in a solution for four hours in order to ensure stable formation of a passive oxide film. The onset of passive oxide layer stabilisation can be indicated by constant potential over a period of time.

The OCP plots for TiGr4M in all solutions was observed in the positive potential region compared to TiGr4R. In the case where no external potential applied or external disturbance such as surface defects on the test material, the formed passive oxide film remains attached to the bulk material and thus no further corrosion will be observed. A higher/more positive corrosion potential/OCP is an indication of more stable oxide film in a particular environment. Thus due to surface roughening with alumina on TiGr4R, an unstable passive oxide film formation is observed. This was observed for three different Ringer's lactate solutions except for pH 7 solution. The corrosion potential was measured at negative/more active potentials, indicating the unstable nature of the formed oxide layer. It can be deduced that the OCP test is an important step in electrochemical tests as a method studying the formation of a passive film. However, further information about the stability of the passive film is required in order to qualify new materials for use in corrosive environments such as the human mouth. This information can be obtained by applying external voltage stepwise and recording the resulting current due to anodic reaction taking place at the surface of the test material/working electrode. This has been done by use of PDP tests.

3. PDP

The PDP tests are ran such that the potential of the test sample is increased stepwise, which triggers the occurrence of either the oxidation or reduction reactions on the test material surface, and as a results the current is generated. The presentation of the potential in the function of current density (or log current density) for each measured point results in obtaining the polarisation curve. In the current presented work each scan was started from -250 mV to $+1500$ mV versus the corrosion potential/OCP at a scanning speed of 10 mV/min. The polarisation curve was used to determine the corrosion behaviour of the TiGr4 by Tafel slope extrapolation. The PDP plots for TiGr4M and TiGr4R in different Ringers' lactate solutions are shown in **Figure 2**.

The current density measured by Tafel slope extrapolation (cathodic and anodic reaction slope) was determined and subsequently the corrosion rates were calculated. The corrosion rates obtained were very low, less than 0.02 mm/year indicating that the material tested was in the fully passive condition. The passive behaviour of a test material can be studied by observing the increased current density as it is an indication of corrosion. Thus a material with high passive current is more prone to corrosion compared to the one with lower passive currents. Using the PDP plots, it can be observed that TiGr4R (dotted lines) showed higher passive currents than TiGr4M (solid lines) in all solutions, meaning with further exposure into Ringer's lactate solutions, the passive oxide film formed in TiGr4R has a tendency to move from passive-active as was indicated with OCP test results.

The PDP and OCP measurement are more dependent on time and thus limits these methods because with further exposure to corrosive environment, the

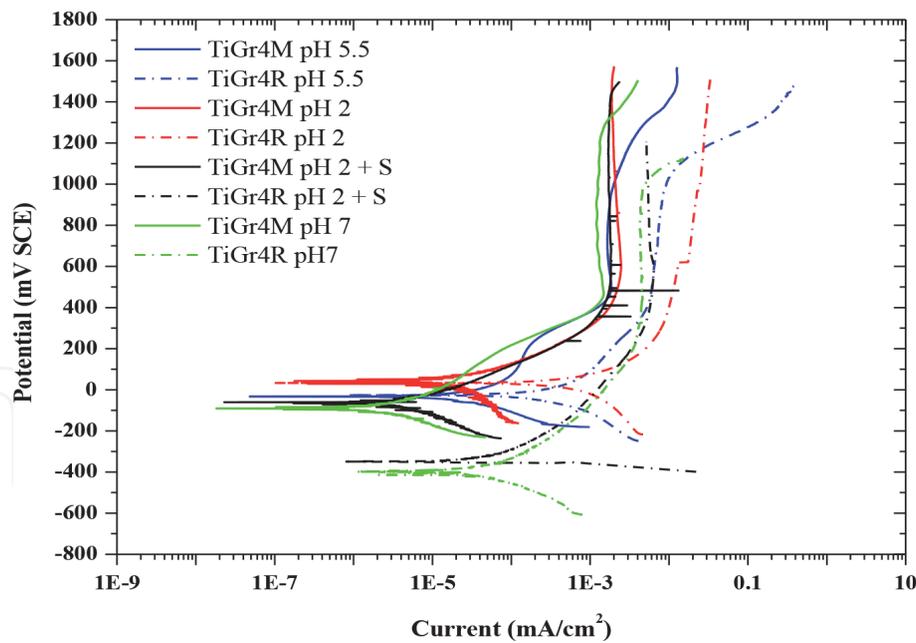


Figure 2.
Potentiodynamic polarisation plots of TiGr4M and TiGr4R in different Ringer's solutions.

exposed material can move from passive to active. Furthermore, using Tafel slope calculations for determination of corrosion rate requires that one uses data further away from the corrosion potential for accurate extrapolation and thus incorporating other reactions, which may bring significant errors in the obtained results, especially in this case where an additional phase of alumina has been introduced in TiGr4R. The EIS method can therefore be useful to obtain more accurate results in the study of electrochemical properties of this surface-modified and machined TiGr4 used for dental implant materials.

The use of EIS is highly recommended because it contains information that can be analysed at each frequency. That is, taking impedance at each potential produces series of data at different frequencies. The difference between the commonly used methods and EIS is that, although the polarisation resistance can be obtained from steady-state measurements by a potential-current plot slope, impedance plots provides more information at every point and not just at one value of polarisation potential. That is, it can be used for fine-tuning mechanisms and determining the kinetics of processes, resistances and capacitances, and it allows for the determination of real surface areas in situ. Particularly, EIS has been used for the following studies:

- Interfacial processes: redox reactions at electrodes, absorption and electroadsorption, kinetics of homogeneous reactions in solution combined with redox processes, forced mass transfer
- Geometric effects: linear, spherical, cylindrical mass transfer, limited-volume electrodes, determination of solution resistance, porous electrodes
- Application in power sources: (batteries, fuel cells, supercapacitors, membranes), corrosion, coatings and paints, electrocatalytic reactions, conductive polymers, sensors and semi-conductors

EIS calculations are carried out using mathematical formulations that provide meaningful models and therefore physically relevant. The extraction of information is carried out by determination of model parameters, which directly corresponds to

physical phenomena. The model parameters provides information about the measured quantity and shows a physical expected behaviour [3].

For materials, impedance spectroscopy provides possibilities to characterise the complex electrical behaviour such as resistivity, capacitive and inductive behaviour. Therefore, it is sensitive to both surface phenomena and changes of bulk properties including conduction mechanisms. It allows quantitative characterisation of corrosion processes as well as the evaluation of the anti-corrosion performance of protective coatings on corrosive metals. The use of EIS in corrosion includes detection of surface and material changes due to exposure, prediction of the lifetime of the protective passive film, evaluation of coating systems, identifying corrosion processes that lead to failures and measurement of water uptake by coatings. The EIS method follow the evolution of surface modified materials as they undergo either artificial or natural exposure to conditions that cause corrosion failure to provide information about the corrosion kinetics, which other methods do not offer [3].

Therefore, this study focuses on the use of EIS as the better method to further evaluate the corrosion resistance of TiGr4 in the machined and roughed condition. We look at the information that is obtained from EIS in comparison to that obtained from the OCP and PDP methods.

4. Nyquist plots

The first concept of EIS to tackle is the Nyquist plot. It has been established that EIS is applied to the characterisation of electrode processes and complex interfaces. Moreover, it studies the system response to the application of a periodic small amplitude of alternating current (AC) signal. Analysis of the system response contains information about the interface, its structure and reactions taking place there. The system response is generated from an electrical circuit, i.e. application of an electrical perturbation (current, potential) causes the appearance of a response. An application of a known potential $E(t)$ to a resistance R gives a current $i(t) = E(t)/R$. When the same potential is applied to the series connection of resistance R and capacitance C , the total potential difference is a sum of potential drops of each element. Taking into account that of capacitance, $E(t) = Q(t)/C$, where Q is the charge stored in a capacitor, Eq. (1) is obtained [4].

$$E(t) = i(t)R + \frac{Q(t)}{C} = i(t)R + \frac{1}{C} \int_0^t i(t)dt \quad (1)$$

Eq. (1) can be solved by using what is known as Laplace transform technique. This technique is an integral transform in which a function of time $f(t)$ is transformed into new function of a parameter s called frequency, $F(s)$ according to Eq. (2) [4].

$$\mathcal{L}[f(t)] = F(s) = \int_0^{\infty} f(t) \exp(-st)dt \quad (2)$$

The direct application of Laplace transform to Eq. (1), given that $\mathcal{L}(\int_0^t i(t)dt) = i(s)/s$, gives Eq. (3)

$$E(s) = i(s)R + \frac{i(s)}{sC} \quad (3)$$

Thus:

$$i(s) = \frac{E(s)}{\left(R + \frac{1}{sC}\right)} \quad (4)$$

The ratio of the Laplace transforms of potential and current, i.e. $E(s)/i(s)$ is expressed in units of resistance, Ω , referred to as impedance, $Z(s)$ [4]:

$$Z(s) = E(s)/i(s) = R + \frac{1}{sC} \quad (5)$$

The polarisation resistance R or R_p value is inversely proportional to the corrosion rate. This means, the decrease in the values of R_p with increasing concentration of corrosive ions indicate the increase in corrosion rate. This interpretation can be used to support results obtained from the OCP and PDP tests in terms of the stability of the passive layer [5].

EIS has been used to explain kinetic parameters for electron transfer at the implant/saliva interface and to understand mechanism of corrosion and passivation for metallic materials in various media conditions. We use the study conducted by AlOtaibi *et al.* [2] to simplify the interpretation of Nyquist plots and the information obtained. The typical Nyquist plots obtained after immersion in artificial saliva for different exposure times is shown in **Figure 3**. The plots shown in **Figure 3** can be best fitted to the equivalent circuit model shown in **Figure 4**. The impedance results are best analysed and interpreted in terms of equivalent electrical circuit models

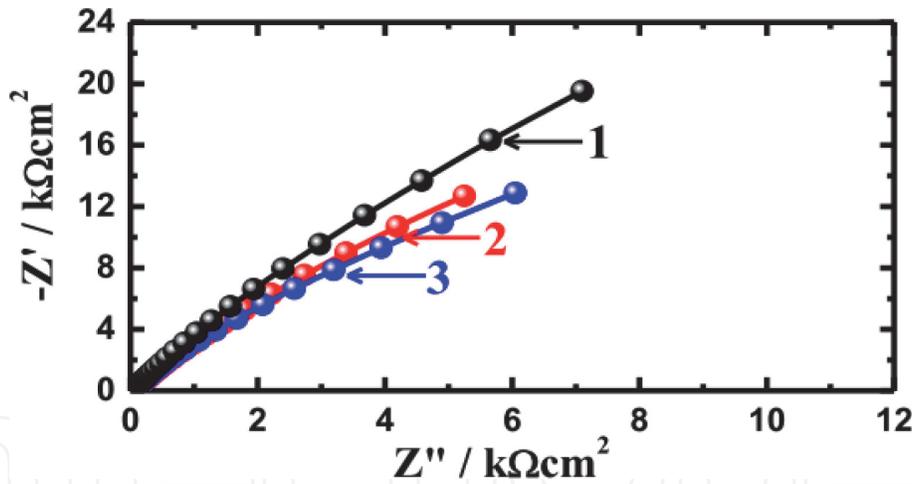


Figure 3.
Typical Nyquist plots of dental implants in an artificial saliva [2].

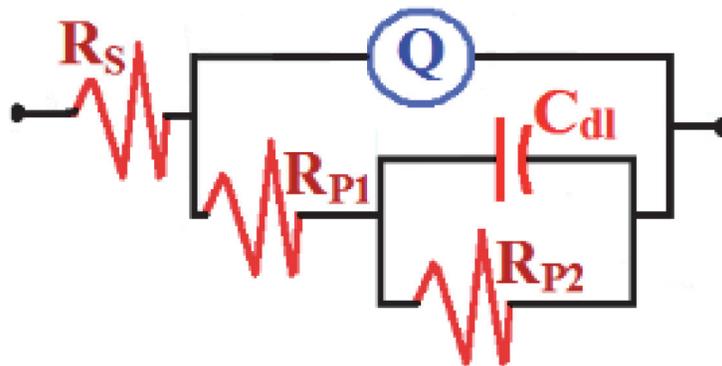


Figure 4.
The equivalent circuit model used to fit the EIS experimental data [2].

obtained by simulating the electrochemical behaviour of alloy-medium interface. The equivalent circuit refers to the presence of an oxide film layer where the inner barrier film is represented by R_{p2} and C_{d1} , but the outer layer is due to the presence of a wall capacitance, presented by Q and polarisation resistance R_{p1} of the oxide film. The overall solution resistance is presented by R_s . The electrical impedance parameters are therefore measured from this perspective.

Nyquist plots typically consists of capacitive loops at different frequencies. The loop can be at higher frequencies, medium frequencies and inductive loops at lower frequencies. The higher region frequency semicircle corresponds to the charge transfer of the corrosion process and oxide film effects. The medium frequencies semicircle corresponds to the mass transport associated with the diffusion of metallic species through the corrosion product layer. The relaxation of the surface adsorbed species is considered to be the beginning of lower frequency inductive loop. Thus, the diameter of the capacitive loops will decrease with increased concentration of corrosive species such as addition of sulphur in the Ringers solutions or decreasing of pH of the solution from 5.5 to 2 using sulphuric acid in the testing of Pure Ti dental implants [5].

We have established that Nyquist plots are often used in electrochemical literature because they allow for an easy prediction of the circuit elements. However, they do not show all details. Different types of Nyquist plots may be obtained from different values of capacitance. The only difference may be that the point on the semicircle would correspond to different frequencies. It is also possible to observe an incomplete semicircle over all the frequency range indicating a highly resistive surface [6]. This method can be used to determine the electrochemical parameters, which is AC impedance of the material. In the case of a series connection of the resistance and capacitance the impedance is given by Eq. (6). The result may be presented graphically using two plots namely Nyquist plots and Bode plots. The Nyquist plot is a plot of Z'' (y axis) versus Z' (x axis), that is real versus imaginary components plotted for various frequencies.

$$Z(j\omega) = 1 + \frac{1}{j\omega C} = R - \frac{j}{\omega C} \quad (6)$$

Where: $Z(j\omega)$ stands for faradaic impedance of the circuit and ω stands for angular frequency.

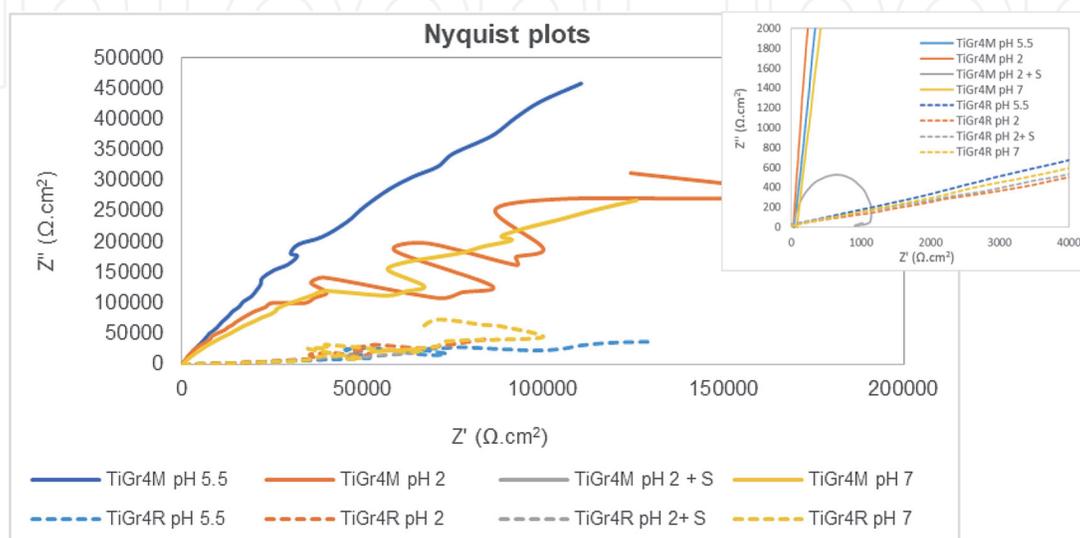


Figure 5.
 Nyquist plots for TiGr4M and TiGr4R in different ringers solutions.

In our study, the EIS measurements were performed for each surface treatment of TiGr4. The frequency sweep was applied from 0.01 to 100000 Hz with an AC amplitude of 10 mA. Frequency sweep change according to material characteristics. The Nyquist plot was used to determine the capacitive behaviour, simply indicated by the size of the diameter of semicircle. **Figure 5** shows the Nyquist plots for TiGr4M and TiGr4R in different Ringer's solutions. The plots observed showed a capacitive behaviour, which is an indication of high corrosion resistance associated with incomplete semicircle observed. The increase of the diameter of the semicircle gives an indication of a high passivation of the surface against corrosion. TiGr4M showed the highest corrosion resistance indicated by the largest diameter/open incomplete semicircle. The R for TiGr4M is always higher than that of TiGr4R, which is in accordance with the results obtained from PDP tests where higher corrosion resistance for TiGr4M were observed.

5. Bode plots

The Bode plots have some advantages over the Nyquist plots since frequency appears as one of the axes, this shows that impedance depends on the frequency. The plots uses the logarithm of frequency to allow a very wide frequency range to be plotted on one graph, but with each decade given equal weight. The Bode plots also show the magnitude ($|Z|$) on a log axis so that you can easily plot wide impedance ranges on the same set of axes.

The phase angle plots are used to determine whether or not the film formed on the metal surface is intact and behaving like a capacitor. The representation shows the phase angle versus frequency (f). Frequency is generally presented on a logarithmic scale [7]. The presence of time-constant (or frequency) distribution is frequently modelled by use of a constant-phase-element (CPE). The impedance response typically reflects a distribution of reactivity that is commonly represented in equivalent electrical circuits as a CPE. Different expressions for a CPE have been presented in the literature [8], e.g.:

$$Z(\omega) = Re - \frac{j}{(j\omega T_0)^\alpha} \quad (7)$$

If the phase is greater than 0° it exhibits a CPE behaviour. The magnitude of the complex capacitance would also then vary with the frequency. The phase angle expressed in degrees, is related to the CPE exponent n by the Eq. (8): [9].

$$\theta = 90(1 - n) \quad (8)$$

For $n = 1$, the CPE behaves as a capacitor; for $n = 0$, the CPE behaves as a resistor; and for $n = -1$ the CPE behaves as an inductor [8]. CPE behaviour was called frequency dispersion of capacitance because it appears as if the double-layer is behaving as a capacitor whose capacitance depends on the frequency [8, 10, 11]. Generally, the appearance of a CPE is due to the presence of inhomogeneity in the electrode material system and it can be described in terms of a distribution of relaxation times, or it may arise from non-uniform diffusion whose electrical analog is an inhomogeneous distributed RC transmission line [9].

The increased value of the phase angle at its maximum, particularly at low frequency values reveals the increased corrosion resistance [7]. **Figure 6** shows the phase angle plots for TiGr4M and TiGr4R in different Ringers solutions. Phase angles close to 80° were obtained at medium and low frequencies, suggesting a

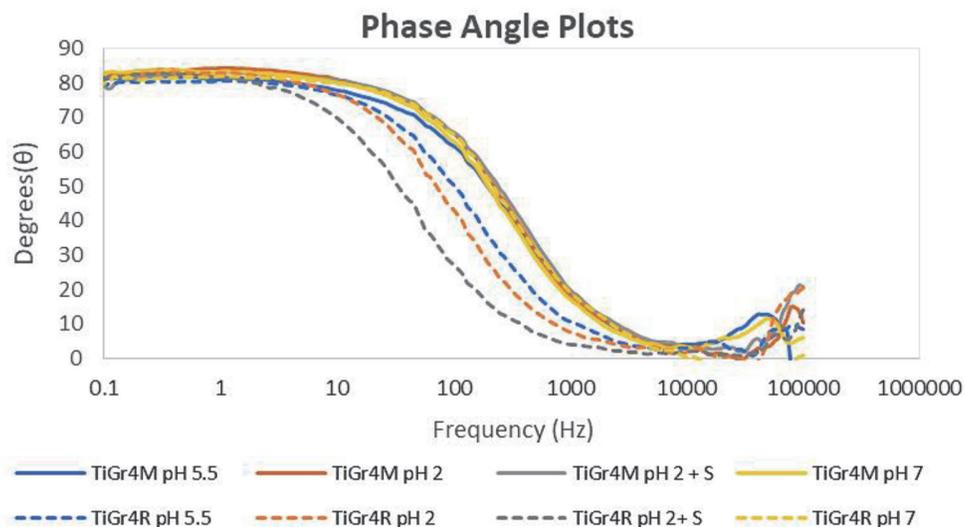


Figure 6.
 Phase angle plots for TiGr4M and TiGr4R in different ringers solutions.

passive behaviour for both TiGr4M and TiGr4R. TiGr4M behaved similar in all solutions. TiGr4R showed an increased value of the phase angle at low frequencies in high pH solutions. Meaning that reducing the pH and addition of sulphide ions decreased the corrosion resistance of the TiGr4R. High values of phase angle at low frequencies for TiGr4M is always higher than that of TiGr4R, which is in accordance with the results obtained from OCP, PDP and Nyquist plots where higher corrosion resistance for TiGR4M were observed.

The modulus plot determine the dissolution kinetics of metallic surface which is represented by the magnitude of charge transfer resistance $|Z|/Z'$. The magnitude is usually presented on a logarithmic scale as a function of frequency on a logarithmic scale. The slope of the line at low frequencies, therefore, has a value of -1 for the blocking electrode considered [8]. The $\log |Z|$ vs. $\log \omega$ curve can yield values of R_p and R_Ω . At the highest frequencies, the ohmic resistance dominates the impedance and $\log (R_\Omega)$ can be read from the high frequency horizontal plateau. At the lowest frequencies, polarisation resistance also contributes, and $\log (R_\Omega + R_p)$ can be read from the low frequency horizontal plateau. At intermediate frequencies, this curve should be straight line with a slope of -1 , as shown on **Figure 7**. Extrapolating this

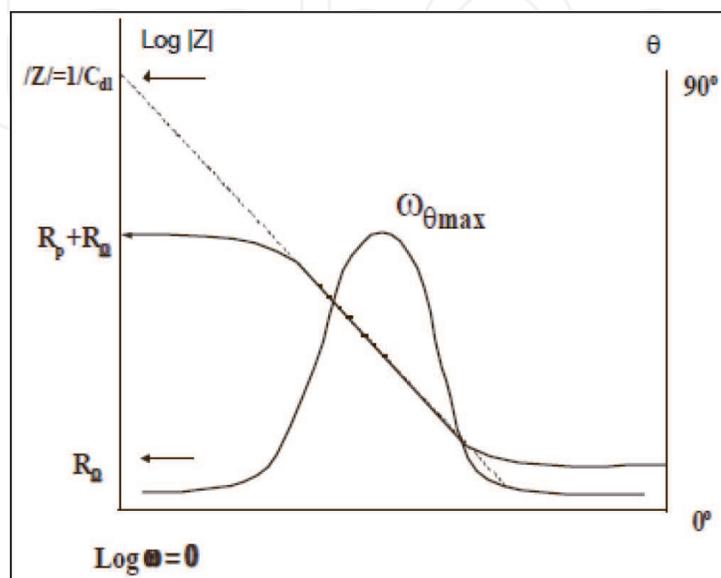


Figure 7.
 Bode plot for a simple electrochemical system [12].

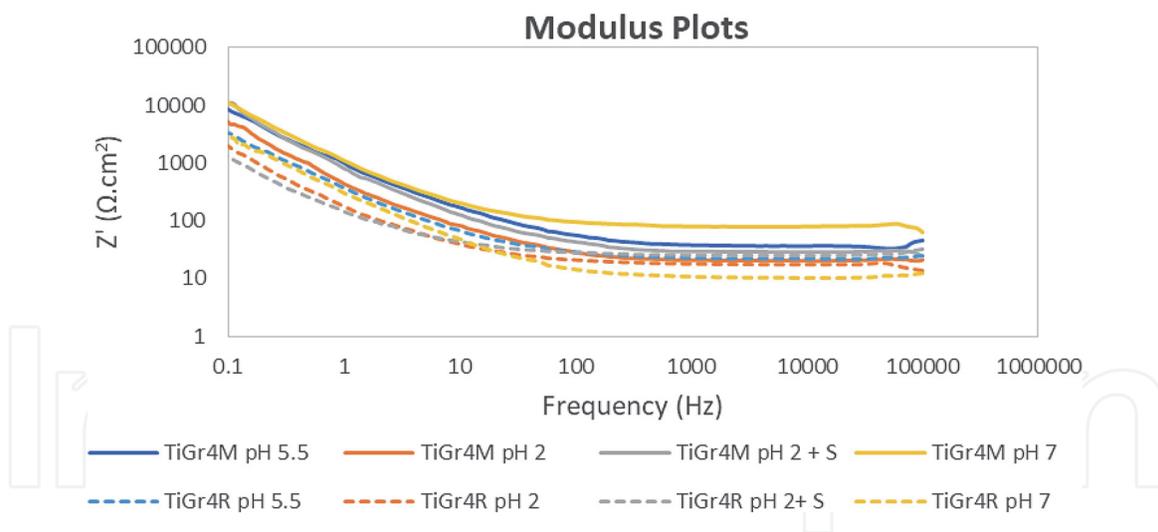


Figure 8.
Bode impedance of the interface, $|Z|$, plots for TiGr4M and TiGr4R in different ringer solutions.

line to the $\log |Z|$ axis at $\omega = 1$ yields the value of C_{DL} from the relationship, where $\omega = 2\pi F$ [12]:

$$|Z| = 1/C_{DL} \quad (9)$$

The higher the values of $|Z|$, especially at lower frequency range represents a higher corrosion resistance of the material [7]. The change of the Bode impedance of the interface ($|Z|$) with frequency for TiGr4M and TiGr4R is shown in **Figure 8**. The highest values of $|Z|$, particularly at the low frequency were recorded on both TiGr4M and TiGr4R in Ringer's pH 5.5 and Ringer's pH 7. The highest values of $|Z|$, at low frequencies for TiGr4M is always higher than that of TiGr4R, which is in accordance with the results obtained from PDP, Nyquist and Phase angle plots. Thus Bode impedance plots further proved higher corrosion resistance for TiGr4M compared to TiGr4R.

6. Conclusion

Corrosion testing of TiGr4 in roughened and machined conditions has been conducted. OCP tests were conducted for determination of corrosion potential of TiGr4. The passivity behaviour was studied using the PDP method. It was noted that both samples were capable of forming a passive oxide layer. From these tests it was observed that both samples were corrosion resistant, with TiGr4M demonstrating a slightly higher resistance.

A biomaterial used for dental implant application is subject to different corrosion reactions in the oral cavity and these reactions are electrochemical. Thus, we used the EIS models with a prominent parameter of frequency to forecast the lifetime of the passive layer of the proposed biomaterial. The requirement is that the implant should last a patient's lifetime once installed. Using EIS, we confirmed that indeed there is more information that could be obtained regarding the stability of the passive oxide layer formed/corrosion resistance during the exposure to artificial saliva. We used Nyquist plots, Bode plots and phase angle plots to generate information about the resistivity and capacitive behaviour of TiGr4 for both surface conditions in different pH artificial saliva solutions.

It was deduced that with regards to the passive nature of TiGr4M and TiGr4R: All the EIS plots showed that TiGr4M has the highest corrosion resistance in all the

pH conditions while TiGr4R has the lowest. This was demonstrated by an increase of the diameter of the semicircle which indicated high passivation of the surface against corrosion. TiGr4M showed the highest corrosion resistance indicated by the largest diameter/open incomplete semicircle. The increased value of the phase angle at its maximum, particularly at low frequency values revealed the increased corrosion resistance. The higher the values of $|Z|$, especially at lower frequency range represents a higher corrosion resistance of a material.

The analysis of these EIS plots indicated that TiGr4 is a suitable material for dental implant application. Surface-modification with alumina does decrease the corrosion resistance but, insignificantly as the TiGr4R also persistently showed a comparative capacitive behaviour as with TiGr4M. Thus, it is beneficial to modify the surface with alumina as it increases the bone-implant adherence and the corrosion resistance is not utterly compromised. This offers a biocompatible material.

Acknowledgements

Authors would like to acknowledge Mintek and Southern Implants (PTY) LTD for financial assistance, sample preparation and approval to publish this work. The authors also wishes to appreciate the assistance from the Mintek colleagues especially Ms. Melanie Smit and Dr. Alain Mwamba.

Conflict of interest

The authors declare no conflict of interest.

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