Bioceramics Development and Applications
ISSN: 2090-5025

Hilal et al., Bioceram Dev Appl 2019, 8:2

Research Article

Open Access

Impedance Study of Ni-Cr Alloy in Contact with Biologics and Organic Solution using Constant Phase Element

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Abstract

The electrochemical characterization and the physical parameters of the Ni-Cr dental implant alloy were studied in contact with two biological (artificial saliva and milk) and organic (vinegar) solutions at Open Circuit Potential (OCP) and at 37°C for one-hour time immersion. In this work we are focused to model the response function of this biomaterial using an Electrical Equivalent Circuit (EEC) to analyze data obtained by the Electrochemical Impedance Spectroscopy (EIS). The experimental results showed that the Ni-Cr alloy is a passive biomaterial which presents a quiet good resistance to corrosion. A model of electric circuit was proposed to describe the electrochemical behavior of this biomaterial on the frequency range (0,100 KHz). The Bode diagram indicated the presence of at least one time constant during the kinetic process. The nature of the film and the study of the morphology of the surface of the material are achieved with the present investigation. Other chemical measurements namely the SEM and EDX can be undertaken to confirm our results. The theoretical form of the proposed response function involved Constant Phase Elements (CPE) to explain the apparent heterogeneity on the interface Metal/film/Electrolyte. Theoretical model predictions are in good agreement with the experimental data with a best-fit corresponding to a minimum standard deviation (The Chi-square values χ^2 is of 10^{-4}).

Keywords: Ni-Cr; Impedance; Equivalent circuit; Phase element; Circuit potential

Abbreviations: EIS: Electrochemical Impedance Spectroscopy; EEC: Electrical Equivalent Circuit; CPE: Constant Phase Element; OCP: Open Circuit Potential

Introduction

Ni-Cr based alloys are part of materials used for dental purposes, especially as dental prostheses. The study on these biomaterials had been possible for two reasons first by their lower cost and second by their biocompatibility allowing a high resistance to corrosion in physiological solution. They are also referred as biomaterials having excellent mechanical properties [1]. One of their properties is the spontaneous formation of thin passive oxide film on the interface metal/electrolyte. The reactivity of the oxide superficial layer formation which is based especially on Cr_2O_3 will be investigated by EIS in presence with solutions ranging from neutral to moderate acid solutions namely (Milk, artificial saliva and vinegar). Moreover we check the reactivity of the formed film in Ni-Cr alloy by studying the contribution of the PH of these three different solutions; comparing it to Co-Cr-Mo based alloys in which it was found that the protective film formed depend highly on the acidity of the solution [2-4].

We are focused to study by impedance spectroscopy the reactivity of the formed passive oxide film. Ni-Cr alloy implant by analyzing the response function with an equivalent circuit based on simple electronic element which characterizes the kinetic behaviour of charge and matter elements subject of the corrosion phenomena.

Methods

Electrochemical characterization

Impedance spectroscopy measurements: The Electrochemical impedance spectroscopy or also AC impedance is a non-destructive technique and useful tool for studying corrosion and making possible the ability to distinguish the dielectric and electric properties of individual contributions of components [5]. It consists in measuring the response of an electrode to a weak potential modulation at different frequencies around the function point. The sinusoidal perturbation of potential E(t) induces a sinusoidal current I(t); their representations in the polar coordinates (1) and (2) is:

$$E(t) = |E_0|_{\exp}(j\omega t) \tag{1}$$

$$I(t) = |I_0|_{\exp}(j\omega t - J\phi) \tag{2}$$

And the impedance can be written as follow:

$$Z(w) = |Z_0|_{\exp}(J\phi) = |Z_0|(\cos\phi + j\sin\phi) \tag{3}$$

From (3) In the absolute impedance (4) and the phase angle (5) can be given by the following:

$$|Z(\omega)| = \sqrt{Zr^2 + Zim^2} \tag{4}$$

$$\tan\phi = \frac{Zim}{Zr} \tag{5}$$

Where Zr and Zim represent respectively the real and imaginary part of the impedance in (3).

Nowadays, many programs are manufactured to fit the data impedance and one among these programs used in the present work is ZSimpwin version 3.10. Reducing physical phenomena on simple or complex equivalent circuits, this helped researchers to use intensively this tool but with more accuracy especially when more than circuits are able to simulate data impedance.

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Received August 09, 2019; **Accepted** September 11, 2019; **Published** September 20, 2019

Citation: Hilal N, Leguedani N, Hafid MM (2019) Impedance Study of Ni-Cr Alloy in Contact with Biologics and Organic Solution using Constant Phase Element. Bioceram Dev Appl 8: 113.

Studying the response function Z(ω) and modeling its physical parameters using the base concept of electronic treatment passed away by interpreting two famous diagrams or representation namely the diagram of Bode and Nyquist. The literature which talked about the basic of EIS is in progress [6-11] and the field of its application covers many domains from biologic, medicine to industry.

The electrochemical impedance analysis has been performed on the commercial Ni-Cr alloys for the frequency range (0,100 KHz) and at OCP after the alloy had been immersed for 1 hour in three solutions (Milk, Artificial saliva and Vinegar).

Results

The Bode diagram Figures 1 and 2 of the Ni-Cr dental alloy recorded in the three different solution shows that at least one-time constant phase element can be distinguished for Milk; while for artificial saliva and vinegar, the shape of the curves is similar. At high frequencies the absolute impedance curve is almost independent of the frequency with a phase angle 0°, and the impedance of the system is reduced to the electrolyte resistance.

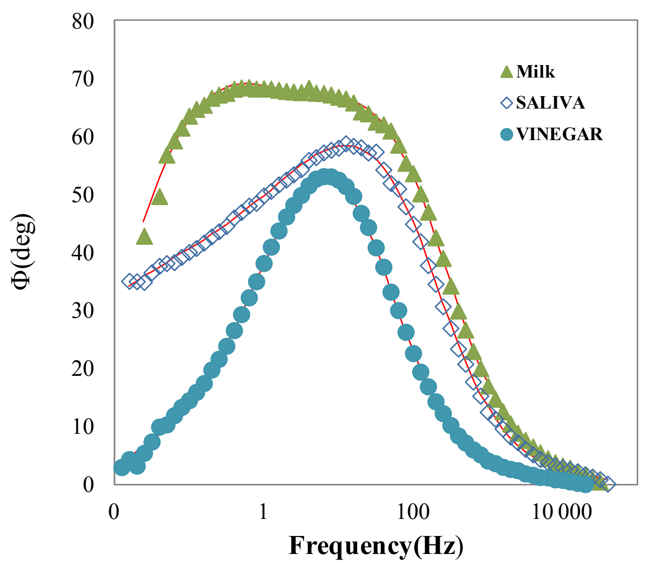

Figure 1: Phase angle plot for Ni-Cr dental alloys respectively for Milk, Saliva and Vinegar; maintained for 1 hour immersion time at open circuit potential and at 37°C.

For medium frequencies (1,100Hz) a linear frequency dependence of absolute complex impedance with a maximum angle (Which is characteristic for passive alloys) is reaching 70°, 65° and 55° for Milk, artificial saliva and vinegar respectively. This range of frequency is marked by stable film formation.

At low frequencies, the absolute impedance exhibits high values with the same order of magnitude for Milk and artificial saliva, these values are ten times higher than for Vinegar.

This difference in the order of magnitude between Milk, artificial saliva and vinegar make an idea of the film formation in these three solutions. This can be explained by the fact that the film formation exhibits a porous character in origin when compared to the other solutions.

Figure 3 presents the Nyquist plot for Ni-Cr dental alloys in three solutions (Milk, Artificial saliva and Vinegar) at potential corrosion Ecorr and 37°C. It can be seen from the ac impedance data that the Ni-Cr implant alloy/solution interface system exhibits capacitive behavior over a relatively wide frequency region, which is a typical passive alloy system.

The parameters for the solution bulk resistance Rs (experimentally determined by the intersection at the high frequency of the Nyquist plot with the real axis) are about the same order of magnitude in the three solutions (about 12.63 $\Omega.cm^2$ for Milk 19.88 $\Omega.cm^2$ for artificial saliva and 30,9 $\Omega.cm^2$ for vinegar).

The resistance of polarization Rp (experimentally determined by the diameter of the semi-circles on arc in the Nyquist plot) which is naturally related to the corrosion resistance is measured in the three solutions and found to have a high value which increased significantly when changing solutions from Milk, artificial saliva to vinegar.

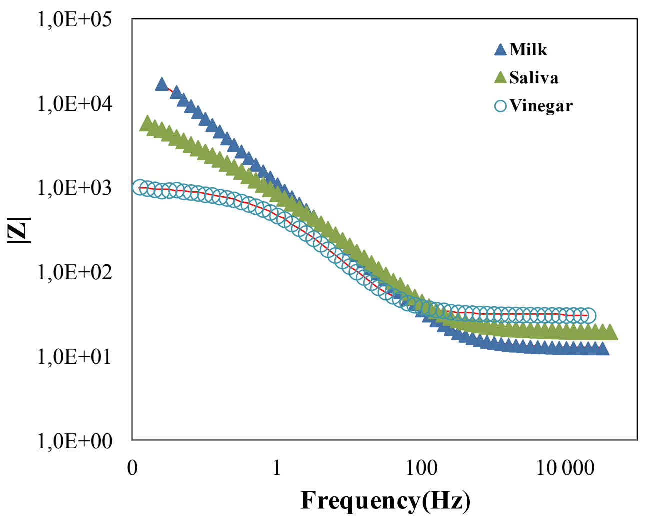

Figure 2: Measured (discrete points) and fitted (solid lines) of Z modulus for Ni-Cr dental alloys respectively for Milk, Saliva and Vinegar for 1 hour immersion at 37°C.

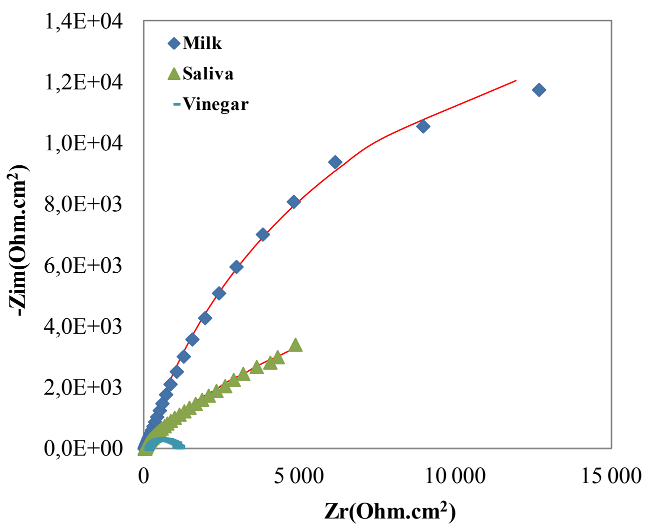

Figure 3: Nyquist diagram of Ni-Cr dental alloys in different solutions (Milk, artificial Saliva and vinegar) at OCP and 37°C.

This high values in Rp imply higher corrosion resistance of implant alloys clearly noticed in Milk and artificial saliva and their value of polarization resistance Rp are (about 25000 Ω.cm² for Milk; 1600 Ω.cm² for artificial saliva and 1000 Ω.cm² for vinegar). The weak values of Rp in vinegar showed that the Ni-Cr dental alloy has a weak corrosion resistance compared with Milk and artificial saliva which means that a high rate of released metallic ions into the oral environment.

Figure 4 shows the Cole-Cole plotting of the complex admittance show the same geometry aspect and its form depend clearly with the nature of the environment used. The diameter of the arc grows as we used vinegar, artificial saliva and milk respectively.

Modeling the impedance data

The proposed equivalent circuit based on CPE is described in Figure 5. Where Rs corresponds to the electrolyte resistance mounted in series with Q_{ext} in parallel with R_{ext} which is in turn in series with Q_{int} in parallel with R_{int}, Q_{ext} denote the pseudo-capacitance (CPE_{ext}) and the R_{ext} resistance of the Ni-Cr/protection film system whereas Q_{int} and R_{int} denote the double layer pseudo-capacitance (CPE_{int}) and the transfer resistance of the corrosion of the Ni-Cr/solution interface.

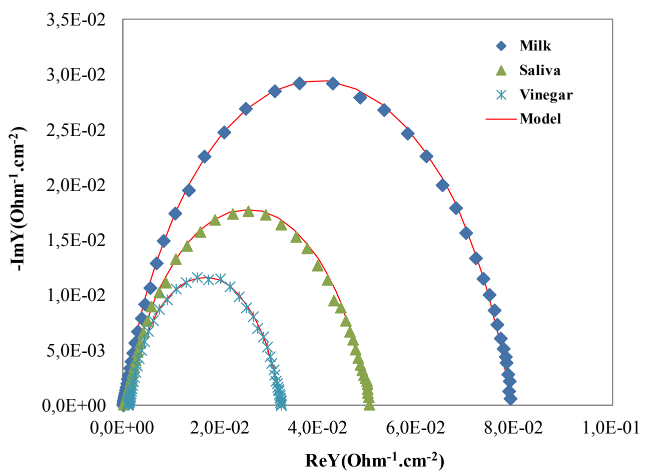

Figure 4: Admittance diagram of Ni-Cr dental alloys in different solutions (Milk, artificial Saliva and vinegar) at OCP and 37°C.

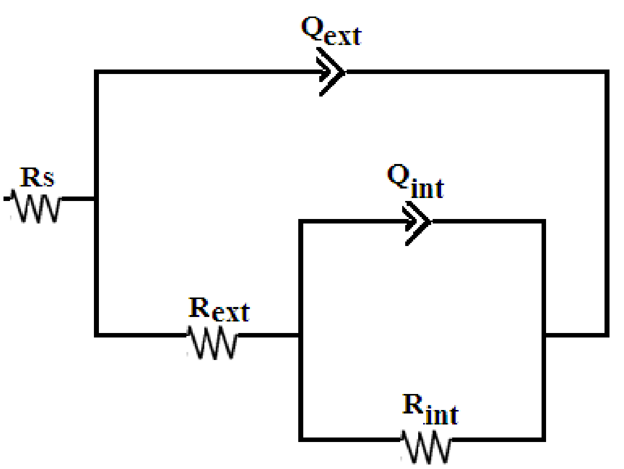

Figure 5: Equivalent Electric Circuit (EEC) used in the generation of simulated data.

Constant Phase Element (CPE) [6] was mathematically used in CEE to solve an electrochemical phenomenon with a non-ideal capacitor which assumed that the surface under investigation is non-homogeneous. The main reason for adding CPE in a matrix of CEE was especially attributed to distributed surface reactivity, surface inhomogeneity, roughness, electrode porosity [6]. This lack of homogeneity is modeled with a Q element, used to represent the CPE:

$$ZCPE = \frac{1}{Y_0 (J\omega)^n} \quad (6)$$

Where, Y_0 is the admittance of an ideal capacitance and n is an empirical constant, ranging from 0 to 1. The exponent n is related to a non-uniform current distribution due to the surface roughness [7,8]. It is noteworthy that when n=1, the CPE behaves as a pure capacitor, while when n=0, the CPE behaves a pure resistor and n=0.5, the CPE is the equivalent of the so-called Warburg element.

The impedance of ZCPE is defined by $ZCPE_{ext}=1/(j\omega)^{n1}Q_1$ and $ZCPE_{int}=1/(j\omega)^{n2}Q_2$, where $j^2=-1$, ω is the angular frequency ω=2µf, and the exponent n_1 et n_2 of the CPE_{ext} and CPE_{int} are related to a non-uniform current distribution due to the surface roughness. The Chi-square values (χ^2) for all data impedance are of magnitude 10^{-4} indicating an excellent agreement between the experimental data and the model using CPE in the fitting program.

Simulation criterion and optimal configuration

Taking into account that several circuits can fit the same response function of the biomaterial even though the values of the components are different; we are focused to determine which circuits are more suitable to describe best the corrosion phenomena on the Ni-Cr dental alloy. We used two criterions to decide which circuits numerically fitted the impedance data in search of an optimal configuration. First, only the simple elements introduced into the CEE must have a physical meaning and second the Chi-square value (χ^2) must be less than ~ 10^{-4}. Monitoring numerically the evolution of parameters one can determine which model can be kept, among others which have the same calculated impedance. Systematically, the standard deviation in the present work is found to be: 1.732e-04, 3.895e-04, 1.693e-04 for Milk, artificial Saliva and vinegar respectively.

From this model, it was possible to calculate the polarization resistance, the resistance Rs of the solution, the relaxation frequency of the system, the CPE parameters (the resistance and the capacity of the

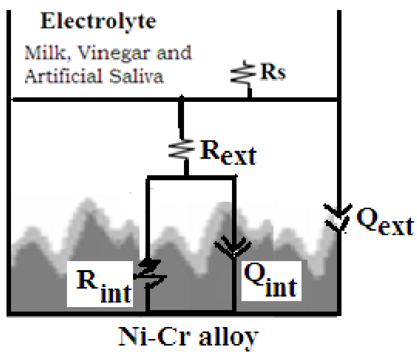

Figure 6: interface electrode/film/electrolyte of Ni-Cr dental alloys using the model.

Solution	Rs (Ω.cm²)	Q_{ext} (µ.Fcm^{-2})	n1	R_{ext} (Ω.cm²)	Q_{int} (µ.Fcm^{-2})	n2	R_{int} (Ω.cm²)	Chχ²
Milk	12,63	171,9	0,8177	2848	355E+01	0,8924	3,07E+04	3.895e-04
Saliva	20,06	163,5	0,8029	699	380,4	0,4631	2,79E+04	1.693e-04
Vinegar	31,06	313,6	0,8213	715,5	373,4	0,7151	275,7	1.732e-04

Table 1: Simulated values of circuit element parameters for Ni-Cr implant alloy in (Milk, artificial Saliva and vinegar) at 37°C.

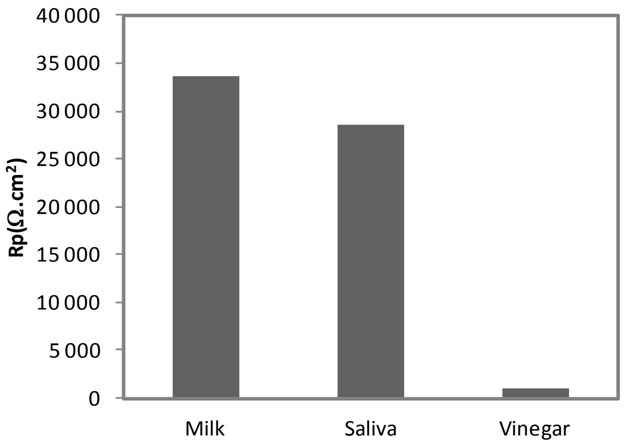

Figure 7: Resistance of polarization in Ni-Cr alloy with the solutions used.

oxide layer). Thus a simple schematization of the interface can be given in Figure 6.

Discussion

All simulated values of circuit element parameters for Ni-Cr implant alloy in (Milk, artificial Saliva and vinegar) at 37°C and one hour immersion time are listed in Table 1.

The Numerical calculation using the theoretical model in Figure 5 is represented in the Nyquist and the Bode plots by solid lines.

It was found that the Rs values for the Ni-Cr implant alloy is 12,63 Ω.cm² for Milk, 20,06 Ω.cm² for Saliva and 31,06 Ω.cm² for Vinegar.

The Resistance of polarization Figure 7, which is calculated in this model by the sum of R_{int} and R_{ext} is of 33,588 KΩ.cm² for Milk, 28,579 KΩ.cm² for saliva and 991,2 Ω.cm² for Vinegar. The theoretical model predictions are in good agreement with the experimental data.

Thus, the Q_{ext} capacitance values in all solutions were within a range of 172-314 µF cm^{-2} having n within a range of 0.8029-0.8213 which indicate a non-ideal capacitance interface (oxide passive layer exists).

Moreover, the Q_{int} capacitance values highly dependent of the Milk, saliva and especially on Vinegar; the values of n in have the same order (0,8924 for Milk) and (0,7151 for vinegar) except for saliva which has a value of 0,4361.

Conclusion

The corrosion interface of Ni-Cr alloy in biological (Milk and artificial saliva) and organic solution (Vinegar) were studied by Electrochemical Impedance Spectroscopy (EIS) based on a model using Constant Phase Element (CPE). Results had shown that this biomaterial exhibits good resistance corrosion for Milk, artificial saliva respectively and a weak value of this parameter for Vinegar. All the values of n in three solutions were found to be within a range of 0.7151-0.8924, indicating that the corrosion interface deviated from a pure ideal capacitor. The phase angle maximum (θ_{max}) in this biomaterial is measured at approximately -53° to -70°. Theoretical model predictions are in good agreement with the experimental data.

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