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INFLUENCE OF CAFFEINE ON THE PASSIVITY OF COBALT-CHROMIUM-MOLYBDENUM ALLOY IN ARTIFICIAL SALIVA

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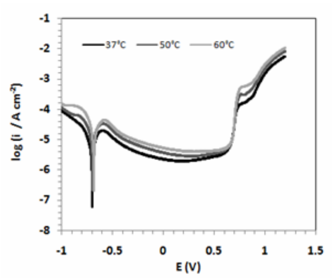
The influence of caffeine on electrochemical behavior and corrosion resistance of CoCrMo alloy has been evaluated in artificial saliva, at different temperatures. The inhibitory activity of caffeine was evaluated using several electrochemical methods: open circuit potential (OCP), potentiodynamic measurements and electrochemical impedance spectroscopy (EIS). The obtained data show that caffeine produces an inhibitory effect on the anodic currents due to its adsorption on the surface of the alloy.
Temperature has also an influence on corrosion processes. The increase of temperature leads to higher values of corrosion parameters.
A neural network based modeling was applied to evaluate by simulation the influence of caffeine and temperature on electrochemical behavior of CoCrMo.



INTRODUCTION

Various metallic materials are used in medicine as implants. Most commonly metals used in dentistry are those alloys which contain Co, Cr, Mo due to high biocompatibility which is correlated to an oxide film formed on alloy surface.[1,2] Cobalt based alloys posses good mechanical properties, therefore the resistance is proper in corrosive media. In oral cavity the implant is exposed to aggressive conditions due to food and beverage intake which bring the pH of artificial saliva to low values.[3] Several studies were carried out in order to describe the electrochemical behavior of dental alloys in artificial saliva[4,5] and in presence of different media such as beverages.[6,7]

Nowadays, caffeine is consumed by billions of people around the world from drinks and food. It is known that this organic compound is a stimulant for the central nervous system[8] and a good antioxidant for human body.

Caffeine, 1,3,7-trimethylxanthine, contains in it structure nitrogen, oxygen and multiple bounds (Fig. 1) and according to literature[9-12] belongs to organic compounds recognized as inhibitors of corrosion of alloys. The inhibitory activity is associated to adsorption of caffeine molecules on alloy surface.[10] The advantage of this organic compound is related to its non-toxic properties and because it is not an expensive reagent.

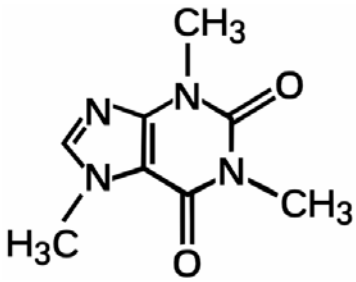


Fig. 1 – Structural formulae of caffeine (1,3,7-trimethylxanthine).

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Table 1

The electrochemical parameters of CoCrMo alloy in presence of caffeine at different temperatures

Temperature (°C)	OCP (mV)	i_{corr} (10^{-6}A/cm^2)	E_{corr} (mV)	i_p (10^{-6}A/cm^2)	E_{bd} (mV)
Artificial saliva + 0.7 mg/ml caffeine					
37	-243	6.8	-700.4	1.9	627
50	-250	10.3	-700.6	2.7	650
60	-256	11.6	-685	3.7	666
Artificial saliva + 1.5 mg/ml caffeine					
37	-246	4.7	-707	2.	620
50	-305	11.6	-683	3.	651
60	-244	14.9	-686	3.8	655
Artificial saliva + 2 mg/ml caffeine					
37	-278	4.6	-701	2.1	637
50	-264	12.9	-685	2.7	650
60	-263	14.9	-663	3.4	660
Artificial saliva + 3 mg/ml caffeine					
37	-248	3.7	-692	1.9	649
50	-282	7.5	-675	2.3	654
60	-251	11.8	-664	3.7	659

Temperature has an important role in the electrochemical processes[13-17] which accelerates the cathodic and anodic reactions of the CoCrMo alloy, thus the corrosion resistance is deacreasing.

However, no literature has been found on the study of the behavior of caffeine adsorption on CoCrMo alloys under the influence of temperature.

Some electrochemical studies were carried out in order to observe the influence of caffeine on CoCrMo alloy in artificial saliva. The inhibitory effect on corrosion process was confirmed by experimental data obtained from open circuit potential (OCP), potentiodynamic curves and electrochemical impedance spectroscopy (EIS).

RESULTS AND DISCUSSION

Open circuit potential (OCP)

The CoCrMo alloy was immersed in different solutions which contain artificial saliva with various caffeine concentrations under non-polarized conditions. The variation of OCP with time is influenced by the caffeine concentration and the temperature, according to Table 1 in which are presented the experimental data.

OCP shifts towards higher values due to the passivation of the CoCrMo alloy. The increase of potential is correlated with the growth of protective film, thus the corrosion rate decreases.

The increase of temperature influences the corrosion process by increasing the corrosion rate, in case of the lowest concentration (0.7 mg/ml) for which the potential does not depend on caffeine concentration.

Potentiodynamic curves

In Fig. 2 (a-d) are shown the potentiodynamic curves for CoCrMo alloy in presence of caffeine at different concentrations and in Table 1 are summarized the corrosion parameters extracted from potentiodynamic curves. The increase of temperature favors the corrosion process by increasing the values of corrosion current density

(i_{corr}) and passive current density (i_p). The corrosion potential (E_{corr}) is shifted to more anodic values with higher values of temperature. It is observed that the presence of caffeine in higher concentrations in artificial saliva leads to inhibitive effect on corrosion. The breakdown potential (E_{bd}) presents high values with the respect of caffeine presence, above 620 mV. In all the cases the CoCrMo alloy shows a large passive zone, this indicates a stable passivity of sample.

It is observed that all the potentiodynamic curves for the CoCrMo alloy immersed in artificial saliva with caffeine content at different temperatures exhibit active-passive behavior. The polarization curves can be divided in four potential domains. Thus, the cathodic domain includes potentials below -1100 mV where the current is determined by the reduction of water and, partially, of dissolved oxygen. The potential domain, between -1100 mV and -400 mV, is characterized by the transition from cathodic to anodic current at the corrosion potential. The third domain corresponds to the passive plateau and is comprised between -400 mV and around 600 mV. The last one, the transpassive domain, is characterized by the increase in current due to transpassive dissolution of the chromium oxide as well as water oxidation.

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy was carried out under OCP conditions. Impedance spectroscopy results are presented as Bode plots and shown in Fig. 3 (a-d). The phase angle maximum was reached between -70° and -80°, for all media.

One peak observed in phase angle plots indicates the involvement of single-time constant at open circuit potential for alloy. This behavior usually indicated that a thin passive oxide layer was formed on the surface.

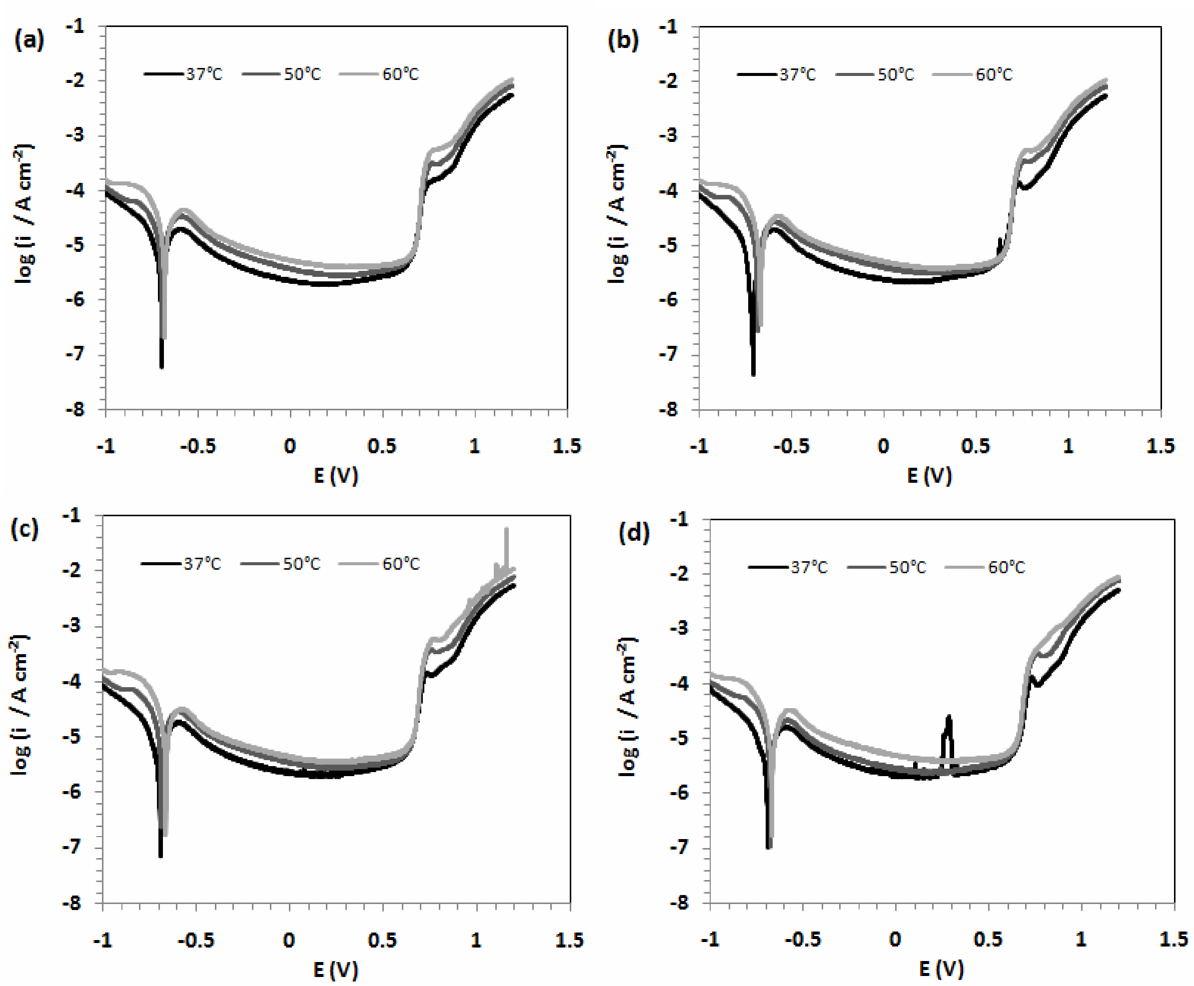

Fig. 2 – Potentiodynamic curves of CoCrMo alloy in artificial saliva with caffeine content:
(a) 0.7 mg/ml, (b) 1.5 mg/ml, (c) 2 mg/ml and (c) 3 mg/ml at different temperatures: 37, 50, 60 °C.

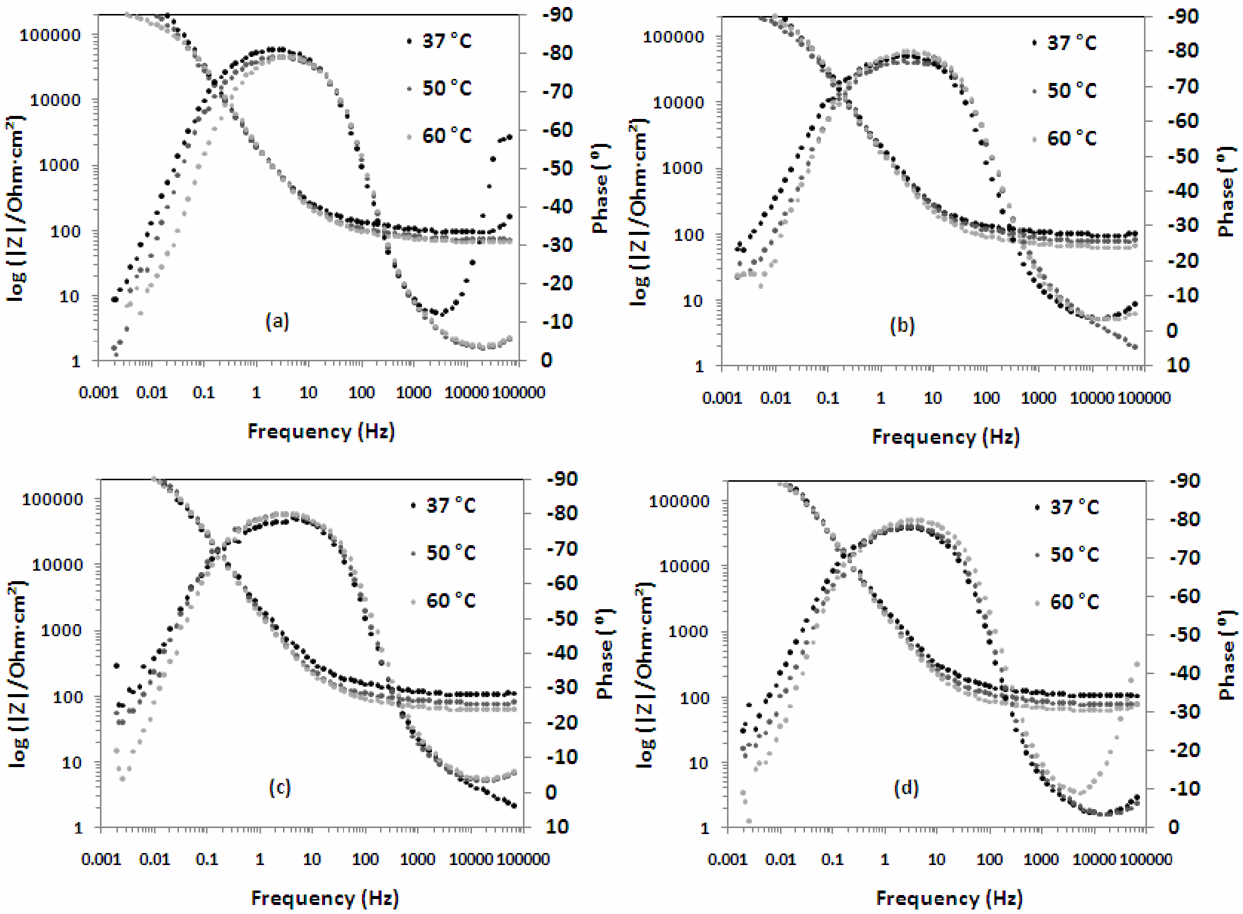

Fig. 3 – Bode plots of CoCrMo alloy in artificial saliva with different caffeine concentrations: (a) 0.7 mg/ml, (b) 1.5 mg/ml, (c) 2 mg/ml and (d) 3 mg/ml, at different values of temperature: 37, 50 and 60 °C.

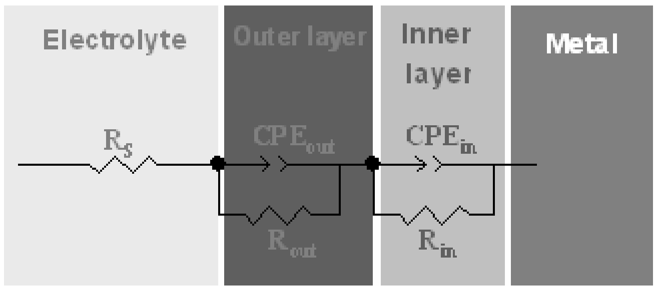

Fig. 4 – The equivalent electrical circuit.

Although from examination of the spectra in Fig. 3 it appears that the equivalent electrical circuit requires only one constant phase element, CPE, the quality of the fit is improved (associated errors are reduced), if the second CPE is introduced.

Therefore, two overlapped time constants can be considered in the impedance spectra. The first corresponding to outer layer (attributed to the presence of inhomogeneous passive film and to the passive dissolution of the passive layer) and the second related to the oxide film formed on CoCrMo alloy. According with this behavior the equivalent electrical circuit (EEC) used to model the experimental EIS data is selected (Fig. 4).[18,19]

The EEC presents the following elements: R_s, the solution resistance, R_{out}, the outer layer resistance, CPE_{out}, the constant phase element of outer layer, R_{in}, the inner layer resistance and CPE_{in}, the constant phase element of inner layer.

The CPE impedance is related to surface reactivity, surface roughness, electrode porosity and diffusion process.[10] Therefore, it can be obtained a good relation between the simulation and experimental data, the impedance of the CPE is given by relation:

$$Z_{CPE} = \frac{1}{C(j\omega)^n} \quad (1)$$

where for n = 1, the CPE represents an ideal capacitor, for n = 0, a simple resistor, C is the capacitance, ω is the angular frequency and j is imaginary number ($j^2 = -1$).[20]

The values of fitted parameters according to EEC chosen are presented in Table 2. The corrosion process is inhibiting by the addition of caffeine, while higher values of temperature decrease the corrosion resistance.

From the impedance results, the charge transfer resistance of the process (R_{ct}) was calculated as the sum of R_{out} and R_{in} and has been used for describing the influence of temperature on the corrosion mechanisms[18] of CoCrMo alloy in caffeine containing solutions. The higher value of R_{ct} is reached for the maximum concentration of caffeine (3 mg/ml) in solution, 841 kΩ·cm^2. The outer and inner capacitance values decrease with the caffeine adding which confirms that the caffeine molecules interact with the alloy surface through adsorption mechanism.[13]

Neural network modeling

Neural networks are alternative modeling tools for processes or systems where the phenomenology is not completely known. They possess the ability to derive meaning from complicated or imprecise data, being useful to extract patterns and detect trends that are too complex to be noticed by other computer techniques. The main characteristic of a neural model is the generalization capability, as a network which learned the behavior of a process (trained network) can be used to provide predictions for new situations (new set of data).

Depending on their structure and information flow, there are many types of neural networks, but the most common type is a layered feed-forward neural network, which generally represents good models, accurate and appropriate for optimal control procedures.

Table 2

The electrical parameter values of CoCrMo alloy

Temperature (°C)	R_s (Ω·cm^2)	R_{out} (kΩ·cm^2)	CPE_{out} (μF·cm^{-2})	n_{out}	R_{in} (kΩ·cm^2)	CPE_{in} (μF·cm^{-2})	n_{in}	R_{ct} (kΩ·cm^2)
Artificial saliva + 0.7 mg/ml caffeine								
37	99±0.5	100±0.9	39±0.3	0.98	677	27±0.9	0.88	777±0.9
50	74±0.8	83±0.6	45±0.5	0.97	248±0.6	39±0.1	0.85	332±0.2
60	68±0.2	36±0.8	43±0.3	0.97	154±0.64	41±0.6	0.86	191±0.4
Artificial saliva + 1.5 mg/ml caffeine								
37	100±0.5	488±0.8	87±0.5	0.99	200±0.23	22±0.2	0.91	689±0.1
50	77±0.07	59±0.3	56±0.9	0.9	201±0.21	49±0.01	0.81	260±0.5
60	64±0.7	60±0.8	43±0.8	0.99	187±0.26	40±0.6	0.85	248±0.1
Artificial saliva + 2 mg/ml caffeine								
37	108±0.6	51±0.06	41±0.1	0.9	641±0.95	33±0.9	0.87	693±0.01
50	79±0.4	88±0.3	40±0.1	0.99	454±0.24	37±0.4	0.85	542±0.5
60	63±0.1	78±0.3	43±0.1	0.96	217±0.6	41±0.3	0.86	295±0.9
Artificial saliva + 3 mg/ml caffeine								
37	105±0.7	78±0.4	48±0.6	0.98	762±0.52	32±0.3	0.84	841±0.01
50	79±0.03	66±0.04	46±0.5	0.94	397±0.01	42±0.6	0.86	463±0.05
60	64±0.7	63±0.2	43±0.6	0.97	204±0.6	41±0.8	0.86	267±0.8

The influence of caffeine concentration and temperature on the passive behavior of CoCrMo alloy in artificial saliva was considered. Therefore, temperature and caffeine concentrations were the two inputs for the neural model and the following four variables were chosen as outputs to characterize the behavior of the alloy: OCP, i_{corr}, E_{corr}, E_{bd}.

One of the most important characteristics of a perceptron network is the number of hidden layers and the number of neurons in the hidden layers, which determines the architecture of the model as input layer contains a number of input neurons corresponding to input variables (2 in the present case) and the output layer is related to the output variables (4 for the approached process). If an inadequate number of intermediate neurons are used, the network will be unable to model complex data, and the resulting fit will be poor. Consequently, the development of an adequate neural model from the point of view of its topology is an important requirement for the accuracy of the results.

The most basic method of developing a neural network, trial and error, accompanied, for training, by back-propagation algorithm was used in this approach. Different topologies of neural networks, including one or two hidden layers and different number of neurons, were tested based on mean squared error (MSE) criterion. The best performance in the training phase was registered by MLP(2:12:4:4), that means a multi-layer perceptron network, with 2 inputs, 2 hidden layers with 12 and 4 neurons and 4 output variables. For this model, MSE = 0.0001 and r = 0.9998 (correlation between experimental training data and simulation results).

The very good correlation between experimental data and neural network predictions proves that the network learned well the behavior of the system and, also, an adequate model was obtained.

The most important stage in a modeling methodology based on neural networks is the validation phase when the accuracy of the model is tested against new data, not included in the training set. Table 3 contains several validation data: experimental output variables compared with neural network predictions and relative errors for each simulation values. Errors below 10% represent satisfactory results and conclude that the multi-layer perceptron model render well the process.

EXPERIMENTAL

Materials

The working electrode under study is a CoCrMo alloy, Heraenium P (Heraeus Kulzer GmbH, Germany), with 8 mm diameter. Its nominal composition is (%wt): 59%Co, 25%Cr, 10%W, 4%Mo, 1%Si and 0.8%Mn. The alloy was polished with SiC papers of 1000, 2000 and 4000 grit and then it was degreased with ethyl alcohol and cleaned with distilled water. After, the sample was dried with compressed air, a PTFE tap was used for protecting the unexposed parts of the alloy to the electrolyte.

Test electrochemical media

The electrochemical tests were carried out in artificial saliva, which has the following composition: 0.4 g NaCl, 0.4 g KCl, 0.6 g $CaCl_2$, 0.58 g Na_2HPO_4, 1 g urea and distilled water until 1 liter. Due to the high pH value of the saliva, it was added HCl until was obtained a pH of 5.6. Caffeine concentration of 0.7, 1.5, 2, and 3 mg/ml was added to the artificial saliva. The solutions were kept at temperatures of 37, 50 and 60ºC. All electrochemical tests were performed in aerated conditions.

Electrochemical measurements

The electrochemical measurements were carried out in an electrochemical cell with double wall for temperature control and three electrode configuration: the CoCrMo alloy as working electrode, an Ag/AgCl (3M KCl) reference electrode and a platinum counter electrode. The potentiostat was a Solartron 1286 coupled to a Frequency Response Analyser Solartron 1250 connected to a personal computer. All potentials are referred to the Ag/AgCl electrode in the paper (205 mV versus SHE).

Table 3

Predictions of MLP(2:12:4:4) compared with experimental data in the validation phase

T (°C)	Concentration (mg/ml)	OCP (mV)	OCP net (mV)	error OCP (%)	i_{corr} (10^{-6} A/cm^2)	i_{corr} net (10^{-6} A/cm^2)	error i_{corr} (%)	e_{corr} (mV)	e_{corr} net (mV)	error e_{corr} (%)	E_{bd} (mV)	E_{bd} net (mV)	error E_{bd} (%)
37	1.5	-246	-228	7.3171	4.7	5.1	8.5106	-707	-693	1.9802	620	629	1.4516
50	2	-264	-290	9.8485	12.9	12.1	6.2016	-685	-682	0.438	650	643	1.0769
60	1.5	-244	-267	9.4262	14.9	13.7	8.0537	-686	-667	2.7697	655	656	0.1527

Before the electrochemical tests a cathodic cleaning at -1000 mV was applied. Open circuit potential, OCP, was measured for 1 hour. The potentiodynamic polarization tests were performed using an applied potential from -1000 mV to 1200 mV at a scan rate of 0.5 mV·s^{-1}. The corrosion potential (E_{corr}) and the corrosion current density (i_{corr}) were automatically extracted from the potentiodynamic curves through the Tafel slope extrapolation. Passive current density (i_p) and breakdown potential (E_{bd}) were also obtained from the potentiodynamic curves.

EIS measurements were performed under OCP conditions. The EIS spectra were recorded between 65535 Hz up to 2 mHz frequency range with a potential amplitude of ± 10 mV and 10 steps per decade. The impedance data was analyzed with Zview 2.70 software and fitted to the corresponding equivalent electrical circuits (EEC).

CONCLUSIONS

The electrochemical methods in this study were carried out in order to confirm the inhibitory activity of caffeine on corrosion process. The experimental data demonstrate and give important information about inhibitor role of caffeine.

The OCP was shifted towards to more anodic values with the increase of caffeine in electrolyte. During polarization curves the corrosion current density reached a minimum value for the highest caffeine concentration at 37 ºC and during EIS tests the maximum value of charge transfer resistance of alloy was obtained for 3 mg/ml caffeine in artificial saliva at the same temperature.

The temperature plays an important role decreasing corrosion resistance of CoCrMo alloy in artificial saliva with caffeine content. For all electrolytes the increase of temperature leads to high values of corrosion parameters.

The adsorption of caffeine on CoCrMo alloy surface enhances the protection of passive film by increasing the stability of it. Therefore caffeine can be considered a good corrosion inhibitor in corrosive media.

The experimental information was also checked experimentally; in addition, the developed neural model is able to make predictions for different initial conditions of the process.

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