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EVALUATION OF PROTECTIVE PROPERTIES OF POLY (VINYL) ALCOHOL THIN FILM FORMED ON STAINLESS STEEL FOR ORTHOPEDIC IMPLANT APPLICATIONS

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The surface characterization of 304L stainless steel for orthopedic implant applications, unmodified and modified with poly (vinyl) alcohol (PVA) in physiological serum (PS) is discussed according to electrochemical measurements, Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM / EDS) and X-ray Photoelectron Spectroscopy (XPS) techniques. The results obtained through polarization curves indicate that PVA reduces anodic dissolution and also decrease of the corrosion current (i_{corr}); decrease of the corrosion current (i_{corr}) was associated with a shift of corrosion potential (E_{corr}) to a less negative values; the polarization resistance(R_p) increases for the surfaces which were treated in physiological serum in the presence of PVA. SEM / EDS and XPS analysis showed that the surface layer which was formed on 304L stainless steel consists of PVA containing of small amount of other elements, such as: Na and Cl.

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1. Introduction

The metal materials used as implants must be biocompatible.Biocompatibility means absence of corrosion or alergic reactions. Corrosion is one of the most important processes that affects the physical properties, functionality and the duration of medical devices made of metals and their aloys used as implants [1-4]. The failures of the implants made of stainless steel were due to significant phenomena of localised corrosion. Corrosion as a test of biocompatibility is a very important factor, which produces metal ions in the biological medium and leads to the degradation of implants [1-11]. Reactions between the surface of metallic materials and living tissues are the initial events when the materials are implanted in human body.

The 304L steel with high chromium (18-20 % in weight) and nickel (8-15 % in weight) contents is usually used for making an implant such as femur prostheses. This steel is well tolerated by the human body but after a long contact of the metallic prosthesis with the body fluids some leaching of the alloy ions into the human fluids occurs. It has been proved that chromium hexavalent ions are even carcinogenic [12, 13].

PVA and its composites may be applied to tissue engineering as a long-term or permanent scaffold due to their good biocompatibility, elasticity and hydrophilicity [14].

PVA are eliminated exclusively by the mechanisms that do not involve saturable transport processes [15]. Furthermore, it was found that PVA are very stable in the body because no degradation product was detected in the urine and feces [15]. In this regard, the surface properties of materials modified using PVA are important. By surface modification of the implant made of 304L stainless steel, we followed two objectives: to increase the corrosion resistance, knowing the fact that implants manufactured from such steel present a certain degree of leaching which leads to

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expelling extremely toxic chromium ions into the organism and to prepare the surface such as to be proper for stabilizing tissue-implant interface.

This study discusses the results of characterization techniques like Tafel polarization, electrochemical impedance spectroscopy (EIS), SEM/EDS and XPS analysis for behavior of unmodified and modified surfaces with PVA of 304 L stainless steel in physiological serum (PS) solution simulating the tissue fluid conditions.

2. Experimental

Electrochemical measurements

For electrochemical measurements a standard cell has been used with a plate working electrode (surface 1 cm^2) made of stainless steel, a platinum auxiliary electrode (surface 1 cm^2) and a Ag/AgCl reference electrode. The electrode made of 304L stainless steel was polished with metalographic paper, washed in distilled water, degreased in acetone and dried in warm air. Chemical composition of stainless steel employed in this study is: (wt%): Cr 18-20; Ni 8-15; Mn 1-2 ; P 0,04; C 0,035; Si 0,03; S 0,03; Fe in balance. For each determination the samples were introduced time of 30 minutes, at room temperature in following solutions: physiological serum (PS; wt% - 0.9% NaCl; pH=5.5) and PS / 0.6 mM PVA (molecular weight of PVA was 49000 g·mol^{-1}).All reagents were obtained from Fluka. A potentiostat VoltaLab 40 connected to a PC with VoltaMaster 4 software was used in the measurements. Tafel polarization and EIS data were analyzed by means of *Excel* and *Zview*, respectively.

Surface characterization

SEM/EDS were accomplished using a Scanning Electron Microscope Jeol JSM 35-CF, resolution 60 Angstroms, magnification range: 10 X - 180 000 X and Energy Dispersive Spectrometer Edax 9100/40.

The measurements in XPS were accomplished using a VG ESCA MkII Spectrometer with SDP 32 software.XPS spectra were recorded in a VG ESCA 3 Mk II- EUROSCAN spectrometer with a Mg Kα X-ray source (1253.6 eV photons energy) operated at 300 W (accelerating voltage 12.5 kV, emission current 24 mA).

The pressure in the analysis chamber has not exceed the value of 5 x 10^{-9} torr during the all period of spectra acquisition. In order to perform the surface charge compensation , has been used a FG40 flood gun device (Specs Gmbh – Germany), with an 0.2mA electronic current at 2eV energy.The samples have been measured in an ”as received” condition with no other surface cleanning treatement (chemical etching or Ar$^+$ ion beam bombardment) [16, 17].Extended spectra were recorded with a window of 1250 eV and 100 eV pass energy.High resolution spectra for C1s and O1s lines were recorded with a window of 15eV and 20 eV pass energy; corresponding to an experimental resolution of 1.2eV.All spectra have been deconvoluted with SDP 2.3 XPS-International software, using Gaussian profile lines for peaks fitting.

3. Results and discussion

3.1 Electrochemical measurements

Tafel polarization

Tafel polarizations were recorded with a 304L stainless steel electrode (surface area was 1 cm^2) immersed in PS and PS containing 0.6 mM PVA. Fig. 1a shows the Tafel diagram, in the potential range of -400 to -100 mV vs.Ag/AgCl reference electrode, at a scan rate of 10 mV s^{-1}. The presence of PVA in the corrosive medium increases the anodic and cathodic overpotentials and decreases the corrosion current ($i_{corr.}$) from 1.88 μA/cm^2 in absence of PVA to 0.38 μA/cm^2 in presence of PVA. Decrease of the corrosion current was associated with an appreciable shift of corrosion potential *(E_{corr})* to a less negative value (see Fig.1a). The inhibition of 304L stainless steel in PS, in the presence of PVA is due to the adsorption of the PVA on the metal surface. The percentage inhibition efficiency *(IE)* of PVA inhibitor was also determined from the polarization measurements according to the following equation:

$$IE = \frac{i'_{corr} - i_{corr}}{i'_{corr}} \times 100 \tag{1}$$

i'_{corr} and i_{corr} are the corrosion current densities in solution without and with PVA, respectively, determined by extrapolation of Tafel lines to corrosion potential. The value of inhibition efficiency reached a value of 79.8 %.

Electrochemical impedance spectroscopy (EIS)

The impedance measurements of a stainless steel electrode in PS solution and in PS solution containing 0.6 mM PVA vs. Ag/AgCl reference electrode, were carried out at the corrosion potential in the frequency range from 10^5 to 10^{-1} Hz, with a value of 10 mV for the amplitude. Figures 1b and 1c show the Nyquist and Bode plots for 304L stainless steel in PS solution without and with PVA. It can be seen that the impedance response of stainless steel in NaCl solution shows a change after addition of PVA. This indicates that the impedance of stainless steel increases in presence of PVA (Fig.1c) and consequently the inhibition efficiency increases. It is also apparent from these plots that the Nyquist diagram is consisted of semicircles with the large diameters (Fig.1b) and extended domain for phase angle maximum in Bode diagram (Fig.1c).

For the description of EIS measurements an equivalent circuit is suggested in Fig.1, where *(R_s)* is the solution resistance of the bulk electrolyte and *(C_{coat})* is the capacitance of the coating. C_{coat} is implemented as a Constant Phase Element (CPE). If C_{coat}-P equals 1, the C_{coat}-T is simple capacitance value. *(R_{coat})* is the resistance of the coating. Coatings often have very small pores which contain electrolyte, providing a conduction path through the coating. *(C_{dl})* represents the double layer capacitance of the electrolyte at the metal surface. Because of inhomogeneities in the coating and metal surface, this capacitance is implemented as a CPE. *(R_{corr})* is the corrosion resistance of the metal. This model is based on the electrochemical system for organic coatings described in: "An Introduction to Electrochemical Corrosion Testing for Practicing Engineers and Scientists"; W. Stephen Tait, 1994; PairODocs Publications; 2048 St. Clair, Racine, WI 53402.

The impedance parameters derived from EIS measurements and respective fitting results are given in Table 1 and Figures 1b and 1c, respectively.

The fitting results show that R_s, C_{coat}-T and C_{dl} –T decrease, R_{coat} and R_{corr} increase suggesting that the amount of inhibitor molecules adsorbed increases. This decrease in C_{coat}-T and C_{dl} –T could be attributed to the decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, signifying that the PVA acts by adsorption at the interface of metal/solution. P values of 0.95 and 0.99 for the C_{coat}-P indicate a behavior closely related to a pure capacitor, reflecting the appropriate simulation of the electric double layer capacity. In the same manner, value approaching to 1 (0.97) of the exponent P of C_{dl}–P for the stainless steel / PS / 0.6 mM PVA system also indicate an important pseudo-capacity for the external layer, which certainly is less porous than stainless steel / PS blank solution system, where P value of C_{dl}–P is more deviated from 1 (0.93).

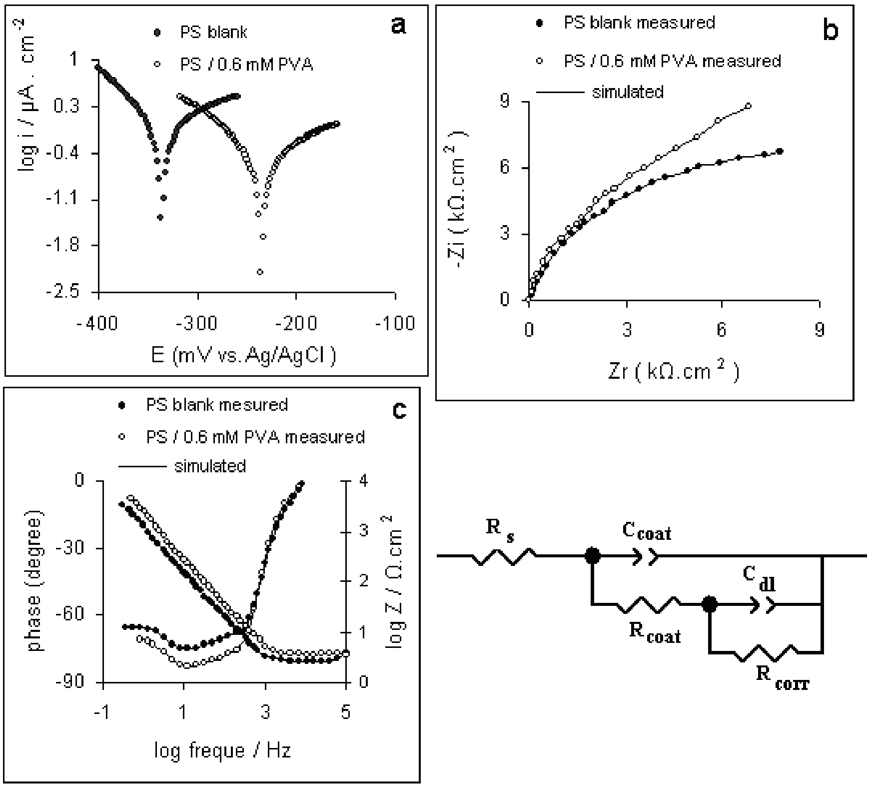


Fig. 1. Electrochemical results for 304 L stainless steel corroded in PS solution in absence and in presence of PVA at room temperature: a – Tafel diagram; b – Niquist plots; c – Bode plots; • PS blank measured; ◦ PS/ 0.6 mM PVA measured; — simulated

The change in R_s, R_{coat}, R_{corr}, C_{coat} and C_{dl} values was caused by the gradual replacement of water molecules by adsorption of the PVA molecules on the metal surface. The R_{corr} was used to calculate the inhibition efficiency from equation 2.

$$IE = \left(1 - \frac{R_{corr}{}^{0}}{R_{corr}}\right) \times 100 \tag{2}$$

where R^0_{corr} is corrosion resistance in absence of PVA and R_{corr} is the corrosion resistance in presence of PVA. The values of inhibition efficiency reached a value of 75.8 %.The numerical values of R_s, R_{coat}, R_{corr}, C_{coat} and C_{dl} were calculated using VoltaMaster 4 software with an error of ±1 %, and are presented in Table 1. The values of inhibition efficiency obtained from Tafel polarization and EIS measurements are in good agreement.

Table 1. Electrochemical parameters obtained from impedance measurements for 304 L stainless steel PS solution in absence and in presence of PVA.

C-PVA /%	Without PVA	With PVA
R_s /Ω cm^2	2.897	2.498
C_{coat}-T / µF cm^{-2}	490	298
C_{coat}-P / µF cm^{-2}	0.95	0.99
R_{coat} /Ω cm^2	258.4	659.7
C_{dl}–T /µF cm^{-2}	108	85
C_{dl}–P /µF cm^{-2}	0.93	0.97
R_{corr} / Ω cm^2	1645	6823
IE / %	0	75.8

3.2 Surface characterization

The electrochemically corroded stainless steel samples by Tafel polarization in both a PS solution without PVA and PS with 0.6 mM PVA were tested by SEM / EDS and XPS surface analysis; these indicate formation of superficial layer providing a very good protection on the corroded electrode, in the presence of PVA.

SEM observation

The SEM images of 304L stainless steel surface before corrosion (Fig.2a) and after occurrence of the corrosive processes in PS (Fig.2b) and in PS containing 0.6 mM PVA (Fig.2c) are presented.

In case of corroded 304L stainless steel in PS without PVA a non-uniform layer can be observed (Fig.2b). When PVA was used the texture is modified and the layer which was formed on the surface is more uniform. It can be seen that the surface morphology shown in the case of PS containing 0.6 mM PVA (Fig. 2c) is significantly different and more regular than that obtained in PS without PVA (Fig. 2b).

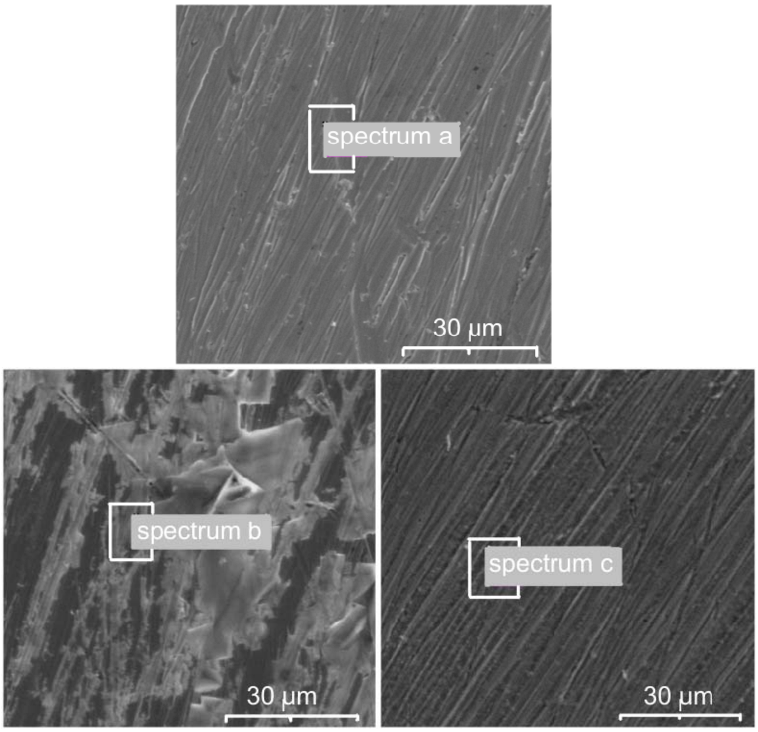


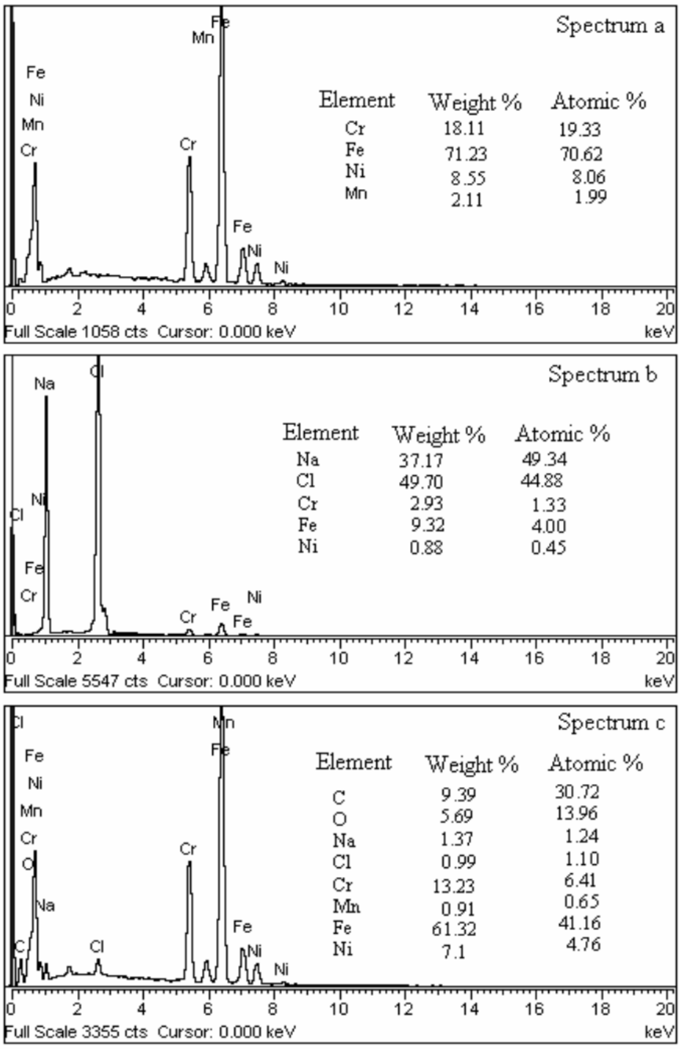
Fig. 2. SEM images of 304L stainless steel: a- before corrosion; after corrosion in: b - in PS without PVA; c – in PS containing 0.6 mM PVA

EDS surface composition

The 304L stainless steel spectrum before corrosion process (uncorroded sample) is presented in figure 3 (spectrum a).

The main difference between of the corroded sample in PS without PVA (spectrum b) and the uncorroded sample (spectrum a) consists in a considerable decrease of Fe, Cr and Ni peak heights. Moreover, after corrosion in PS blank (spectrum b) the presence of a considerable amount of Cl and Na elements on the surfaces of stainless steel can be noticed. This demonstrates the formation of a thick, non-uniform and porous layer on the corroded sample surface, consisting of NaCl ; the surface layer on stainless steel is not stable and the composition changes by incorporation of ions and molecules.

For the sample corroded in PS containing 0.6 mM PVA (spectrum c) a superficial layer on stainless steel was formed. From estimation of the EDS peaks of Fe, Cr, Ni and Mn (spectrum c), this layer has a smaller thickness than the one formed in the corrosion process without PVA, indicating that a thin film on the stainless steel surface was formed.



Element	Weight %	Atomic %
Cr	18.11	19.33
Fe	71.23	70.62
Ni	8.55	8.06
Mn	2.11	1.99

Element	Weight %	Atomic %
Na	37.17	49.34
Cl	49.70	44.88
Cr	2.93	1.33
Fe	9.32	4.00
Ni	0.88	0.45

Element	Weight %	Atomic %
C	9.39	30.72
O	5.69	13.96
Na	1.37	1.24
Cl	0.99	1.10
Cr	13.23	6.41
Mn	0.91	0.65
Fe	61.32	41.16
Ni	7.1	4.76

Fig. 3. EDS spectra of 304L stainless steel: a- before corrosion; after corrosion in: b - in PS without PVA; c – in PS containing 0.6 mM PVA.

The EDS peaks of oxygen and carbon (elements which are found in the chemical structure of PVA macromolecule) are also observed in the „spectrum c".This indicates that the substrate is covered with an oranic thin film which containing small amount of Na and Cl, in good aggrement with previous considerations. The ratio between carbon atoms and oxygen atoms is 2/1 (see spectrum c), indicating that this film consists in PVA; then, it can be considered that the composition of layer measured by EDS consists in PVA thin film containing of small amount of other elements, such as: Na, Cl.

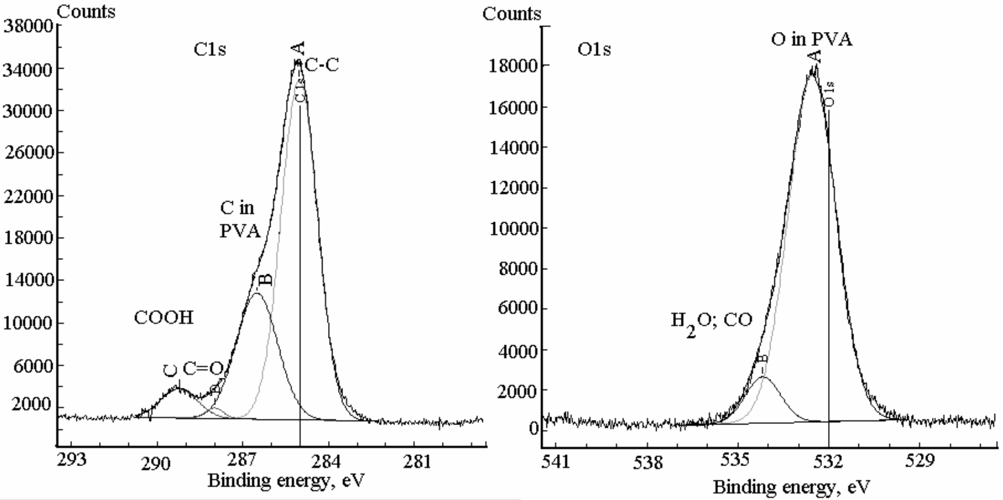
XPS analysis

The composition of surface layer on modified stainless steel with PVA was determined using XPS analysis (Fig. 4).

Figure 4 presents the high resolution XPS spectra for the C1s and O1s regions and the composition (measured by XPS) of thin layers deposited on the surface of stainless steel after corrosion in PS / 0.6 mM PVA solution.

Extended spectrum (recorded in a 1250eV window) shows two large peaks at 285eV and 532eV bending energy corresponding to C1s and O1s lines.The peaks at 195.5 eV and 1072.3 eV correspond to Na1s and Cl 2p lines, respectively; quantitative evalluation from XPS extended spectrum indicates atomic concentrations for Na and Cl, less than 0.5% (see Fig. 4) .The XPS peaks of Fe, Cr, Ni or Mn (chemical composition of stainless steel substrate) are not observable in the extended spectrum.

Sample/Element	C	O	Na	Cl
SS/PS/0.6 mM PVA atomic	74.2	25	0.5	0.3



Sample/Spectral line	BE(eV)	Bond	Atomic (%)
SS/PS/0.6 mM PVA / C1s	285	C-C	65.8
	286.51	C-O from PVA	27.6
	287.99	C=O	1
	289.24	COOH	5.7

Sample/Spectral line	BE(eV)	Bond	Atomic (%)
SS/PS/0.6 mM PVA / O1s	532	O ads	32.2
	532.75	O in PVA	54.2
	533.99	OH, OH2	13.6

Fig. 4. XPS spectra for the C1s and O1s regions of stainless steel corroded in PS containing 0.6 mM PVA, at room temperature.

This fact indicates that the substrate is completely covered.The binding energies for the peaks have been referenced to C-C bond at 285eV.The binding energies of 286.51 of peak B from C1s spectra and of 532.75 eV of peak B from O1s spectra respectively, confirm the presence of PVA layer on the surface sample and are in good accordance with the results presented in literature [18-20]; then, they are in good agreement with the data obtained by EDS measurements. The deconvolutions of spectra show the presence of -OH bonds and also of various contaminants at the surface. This confirm that PVA form a layer grown from solution and the significant feature is the adsorption of the –OH groups with a specific affinity to the substrate.

4. Conclusions

The results of corrosion data of 304L stainless steel in PS showed that the corrosion current density decreased and polarization resistance increased in presence of PVA, which indicates that this compound acts as inhibitor. The value of inhibition efficiency reached an approximate value of 79 %.

According to the data obtained from EIS measurements it can observe that R_{coat} and R_{corr} increase, suggesting that the amount of inhibitor molecules absorbed increases. A maximum value for inhibition efficiency of 76 % concentration was obtained. The value of inhibition efficiency obtained from Tafel polarization and EIS measurements are in good agreement.

These results are consistent with those obtained by SEM/EDS and XPS analysis, which confirms that PVA form a stable and uniform thin film and the significant feature is the adsorption. It can be considered that the composition of layer measured by EDS consists in PVA thin film containing of small amount of other elements, such as: Na, Cl. The XPS peaks of Fe, Cr, Mn or Ni are not observable in the extended spectrum. This fact indicates that the substrate is completely covered.

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