Lactic Acid Influence on the Electrochemical Behaviour of Stainless Steel and CoCrMo Alloy in Human Serum

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The aim of this study is to evaluate the influence of lactic acid on the electrochemical behavior of three alloys used as prosthetic joints, in simulated physiological conditions. The used alloys were: SS316 and SS316L and CoCrMo. We used open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization, as electrolyte being chosen the human serum with different concentrations of lactic acid The inhibitor efficiency of lactic acid has been established being greater for CoCrMo alloy and for greater lactic acid concentration.

Keywords: biomaterial, electrochemical behaviour, lactic acid, EIS

Nowadays, when is a significant trend in increasing the average age of the population at global level, a parallel increase in the number of implantation procedures is expected. After more than a hundred years when various metals such as aluminum, copper, zinc, iron and carbon steels, silver, nickel, magnesium have been tested for such procedures leading to the conclusion that all of them are too reactive in the body for long term, metallic alloys used in our century [1] are typically derived from three materials systems: stainless steels, which include 316 and 316 L [2], cobalt-chromium based alloys [3,4] and titanium alloys [5-7]. In all cases the stability of alloy is due to a passive oxide stratum formed spontaneously on the surface of alloy. Taking into account that due to the lower price of stainless steel and CoCrMo alloy compared to titanium, such alloys are the choice in many implant cases, the present paper is focused on electrochemical investigation on stainless steel and CoCrMo alloys.

When stainless steel was introduced in surgical applications its intergranular corrosion due to high carbon content(0.08%) and its significant susceptibility to pitting due to low molybdenum content were observed [8,9]. Only the austenitic molybdenum-bearing 316 was found to be better and 316 L alloy with lower carbon (0.03%) and reduced risk of intergranular attack. Cobalt-chromium-molybdenum alloys are used in implants due to their biocompatibility, hardness, strength and resistance to corrosion and wear. Depending on the carbon content there are three varieties of Co-Cr-Mo alloys with different microstructure as following: cast with low carbon, wrought, and wrought high carbon alloys. Each of them has applications according to their structure and properties. The cast CoCrMo alloy biomaterials is utilized for the stem of a total hip replacement whereas the femoral head can be machined from the high carbon CoCrMo alloy. Both of them have been studied to determine the effect of carbide inclusions on the electrochemical stability of the alloy. Results indicate that inclusions despite the fact that there were significant on the alloy surface, did not affect the stability and dissolution mechanism.

Such effect is due to the presence of proteins caused ligand-induced dissolution with increasing Cr concentration in the surrounding extracellular fluid.[10]. The implant is not completely isolated, but permanently in contact with physiological fluids and their compounds. One interesting blood compound is lactic acid which is produced from glucose by muscles, brain cells, red blood cells in anaerobic conditions. The glucose is transformed in lactic acid after ten enzymatic chemical reactions, the last one being:

$$\text{Pyruvate} + \text{NADH} + \text{H}^+ \xrightarrow{\text{LDH}} \text{Lactate} + \text{NAD}^+ \quad [11]$$

Normal values of lactate in venous blood are: 4.5-19.8mg/dL (0.5-2.2 mmol/L).

Lactate is used for medical purposes as well, being artificially introduced in the human body, as a major compound in intra-venous solutions: Hartman and Ringer-lactate, used in case of burn injury, trauma, surgery.

Until 1970 lactate was considered the dead-end waste, or the ultimate metabolite produced in anaerobic conditions and a major cause of muscle fatigue [12]. More recently researches try to prove that lactic acid has different role in the human body and is considered a new mobile fuel, its production being important for regenerating NAD^+ as well. In such way, lactic acid has a role in tissue regeneration and wound repair, and its newest function seems to be a cell-to-cell shuttle [13].

The present paper aims on the influence of lactic acid of various concentrations on the corrosion behaviour of Stainless steel 316, 316 L and CoCr Mo alloy.

Experimental part

The investigated materials were commercially alloys: SS316, SS316L and CoCrMo, produced by Beznoska S.R.O.-Czech Republic, having the composition showed in table 1.

We used as electrolyte human female serum from a group of female patients having the age between 54-56 years, and very similar biochemical compounds concentrations. The serum was obtained using disposable needles and vacuum tubes, the whole blood being drawn

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Table1
CHEMICAL COMPOSITION OF ALLOYS

	C	Si	Mn	Cr	Fe	Mo	N	P	Co	Ni
OL316	0.039	0.22	4.07	21.47	60.57	2.30	0.38	0.024		10.92
OL316L	0.023	0.36	1.9	17.05	62.86	2.82	0.09	0.018	-	14.87
CoCrMo	0.030	0.42	0.7	27.74	0.29	5.64	-	-	64.78	0.1

Table 2
EVOLUTION OF OCP IN TIME

samples	E_{corr} (mV) in SF		E_{corr} (mV) in SF +0.6045g/L lactic acid		E_{corr} (mV) in SF+1.209g/L lactic acid	
	beginning	after 30min	beginning	after 30min	beginning	after 30min
OL 316	-290	-250	-260	-236	-190.49	-144.95
OL 316L	-210.9	-195	-277.43	-222.15	-220.80	-164.40
CoCrMo	-370	-270	-296.65	-245.77	-307.18	-250

by venipuncture. It was separated by centrifugation and was tested for HCV antibodies, HBs- antigen, HIV1,2 and Syphilis , and the results were negative.

The concentrations of biochemical parameters of the serum (SF) were : total bilirubin : 0.45mg/dL, direct bilirubin: 0.1 mg/dL, cholesterol: 245 mg/dL, glucoza:78 mg/dL, creatinina:1.17 mg/dL, acid uric: 4.94,Uree:44.5 mg/dL, trigiceride:144 mg/dL, TGP:49U/L, TGO: 51U/L, LDH: 593U/L, GGT: 26 U/L, Mg:2 mg/dL, Ca: 8.3 mg/dL, Fe: 125 mg/dL. For these determinations we used an automatic biochemistry analyzer Prestige 24i, Tokyo Boeki Ltd.

The lactic acid that we used is from Fluka: L-(+)-lactic acid, and we prepared two sets of concentrations: 0.6045g/L (conc.1) and 1.209 g/L(conc.2).

The electrochemical behaviour of chosen alloys was studied in a classical electrolytic cell with three electrodes using a VoltaLab 40 electrochemical combine. The electrodes were: a platinum plate electrode of 128 mm^2 as a counter electrode, a saturated calomel electrode (SCE) as reference electrode and a cylinder made from the chosen material having 0.25 cm^2 as working electrode. The working electrodes were polished with SiC emery paper from 800 down to 3000, then with diamond pasta and alumina, degreased in acetone for 15 min, then washed with distilled water, and cleaned for 30 min in an ultrasonic bath-Bandelin. All three electrodes were immersed in solution and the cell was installed in a water bath (Falc FA90) to maintain the temperature from the cell near the value of 37°C.

The OCP (open circuit potential) was carried out for 30 minutes, EIS measurements were performed on the frequency range between 100kHz and 5mHz with an AC wave of 5 mV, for the potentiodynamic polarization the working electrode potential was scanned from -1000mV/SCE to 1000 mV/SCE with a scan rate of 1 mV/s, because potential value of a metallic biomaterial in the human body may vary from -1.0 V/SCE to 1.2V/SCE.

The impedance data were analyzed with the Zwiew 2.70 software package and fitted to the appropriate equivalent circuit.

Results and discussions

One simple approach to examine the corrosion behaviour of a metallic material is to monitor the OCP in time [14].

Table 2 shows the average values of E_{corr} observed for each material immersed for 30 min in aerated SF with/without lactic acid at 37^0 C.

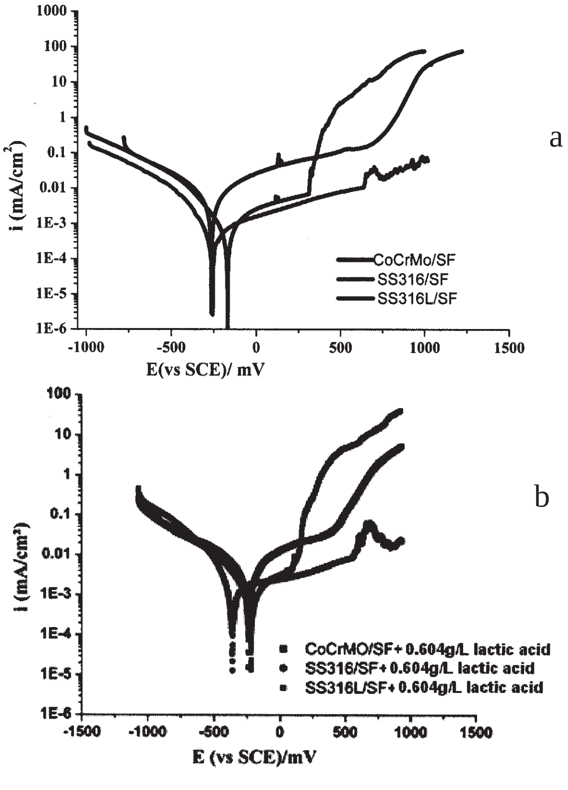
Following the immersion, an abrupt OCP displacement towards positive potentials was noticed a period of few min. Afterwards, the OCP remained slowly increasing, suggesting the growth of a film onto the metallic surface.

It can be seen that the stainless steel has corrosion potentials significantly more noble than CoCrMo which present more negative values.

The metallic materials which are typically used in biomedical applications, such as surgical stainless steel, Co-Cr and titanium alloys are self-protected by the spontaneous formation of a thin oxide film. The passive films formed on surgical stainless steel and Co-based alloys are strongly enriched in Cr_2O_3 oxide [15, 16].

From the corrosion point of view, the prevailing redox conditions are important. The oxygen content in the surroundings can vary depending on the specific application. In the case of alloys, the passivity of which is based on the presence of Cr_2O_3–rich passive film on the surface, highly oxidizing conditions can lead to dissolution of the passive film by formation of soluble Cr(VI) species. The stability of the passive film is dependent on the availability of oxygen. The adsorption of proteins, organic compounds and cells onto the surface of materials could limit the diffusion of oxygen to certain region of the surface causing preferential corrosion of the oxygen- deficient regions and lead to the breakdown of the passive layer. However, it has not yet been clarified unambiguously whether organic compounds accelerate or inhibit electrochemical reactions [17-19] most probably the effect is specific for a particular metal/organic compound.

Figure 1 shows the Tafel curves for stainless steel and CoCrMo immersed in SF with and without lactic acid; and table 3 presents the electrochemical parameters obtained from Tafel curves.



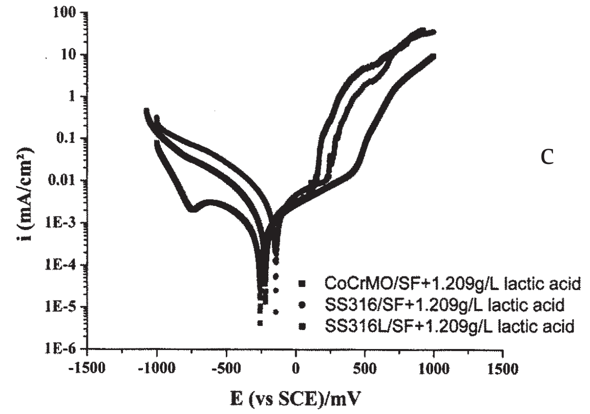


Fig 1 (a-c) Tafel plots for all samples in SF with and without lactic acid

In the cathode domain of Tafel curves the current is determined by the reduction of water and partially of dissolved oxygen [20], according with the following reaction:

$$2H_2O + 2e \rightarrow H_2 + 2HO^- \quad (E^0 = -1.033\ V_{Ag/AgCl})$$

$$O_2 + 2H_2O + 4e \rightarrow 4HO^- \quad (E^0 = 0.196\ V_{Ag/AgCl})$$

An alloy that prone to passivity will have the value of b_a greater than b_c, while an alloy that corrodes will have b_a less than b_c [21]. Comparing the b_a value with b_c value for all sample †can be said the corrosion processes occurring at the interface are under anodic control . This control implies the existence of a passive layer on the material surface. The exception is CoCrMo in solutions containing lactic acid, in which case the corrosions process is under mixed control.

As was observed from Tafel curves results, lactic acid acts as an inhibitor of the corrosion process. The inhibition efficiency (IE%) was calculated from the following equation:

$$IE\% = 1 - \frac{i_{corr/lactic}}{i_{corr}} \times 100$$

where $i_{corr/lactic}$ and i_{corr} are the corrosion current densities respectively and the results are presented in table 4.

Electrochemical impedance spectroscopy was employed to investigate the change in the passive film formed at the interface CoCrMo or stainless steels alloys with the solution . EIS was measured at OCP. Impedance spectra are shown in figure 2. The Nyquist plots are all semicircles arcs with center depressed below the x-axis. The EIS diagrams exhibit a typical behavior for passive state [22].

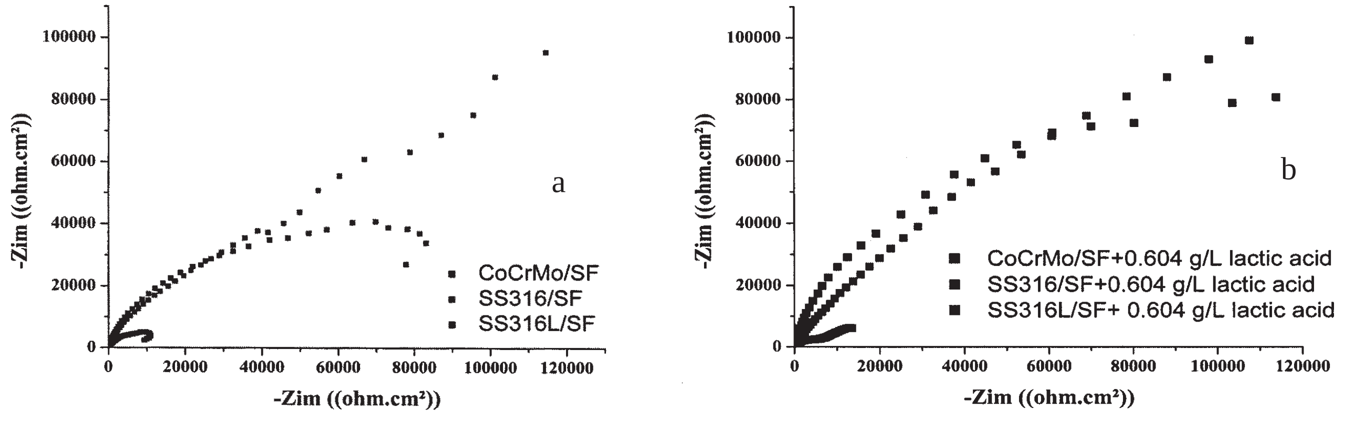
Two overlapped times constants can be considered. In the impedance spectra shown in figure 2, the first corresponding to outer layer, and the second to the oxide film formed on metallic substratum. The equivalent circuits

Table 3
ELECTROCHEMICAL PARAMETERS

No. Crt.	Electrode	Electrolyte	Ecorr, mV/SCE	icorr, µA/cm2	b_a, mV/dec	b_c, mV/dec	Corrosion, µm/year
1.	OL 316	SF	-260.4	2.9642	116	-75	34.4
2.	OL 316L	SF	-171.7	1.790	171	-151	20.77
3.	CoCrMo	SF	-266.8	5.5086	96.1	-95.3	62.55
4.	OL 316	SF+0.6045g/L lactic acid	-362.7	2.605	221.9	-107.6	30.23
5.	OL 316L	SF+0.6045g/L lactic acid	-222.3	1.21	186.2	-144.3	24.14
6.	CoCrMo	SF+0.6045g/L lactic acid	-242	2.720	87.8	-87.8	30.87
7.	OL 316	SF+1.209g/L lactic acid	-148.9	1.6409	165	-136.2	20.25
8.	OL 316L	SF +1.209g/L lactic acid	-253.0	0.8932	103.9	-76.0	10.36
9.	CoCrMo	SF +1.209g/L lactic acid	-260	0.9043	134.2	-136.7	10.26

Table 4
THE INHIBITION EFFICIENCY (IE %)

solution samples	SF	SF+0.6045 g/L lactic acid	SF+1.209g/L lactic acid
OL316	0	12.11	44.22
OL316L	0	32.40	49.89
CoCrMo	0	50	83.58



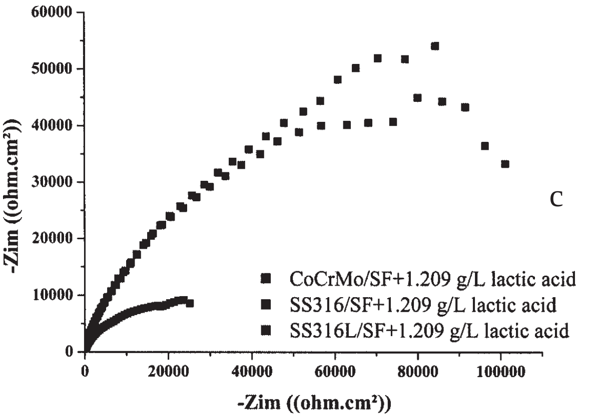


Fig 2. (a-c) Nyquist diagrams for of all samples in SF with and without lactic acid

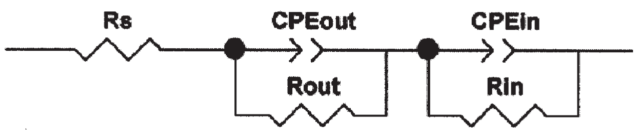


Fig. 3 Equivalent circuit for analysis of impedance of alloys

Table 5

EQUIVALENT CIRCUIT PARAMETERS FOR ALL SAMPLES IN SF SOLUTION AT 37°C

	R_s[Ω cm^2]	R_{out} [Ω cm^2]	CPE_{out} [μF/cm^2]	n_{in}	R_{in} [Ω cm^2]	CPE_{in} [μF/cm^2]	n_{out}
316	18.1	13.34	43	0.76	6692.35	36	0.97
316L	18.5	38.9	59	0.82	19413.09	39	0.98
CoCrMo	19	7.54	36	0.74	3764.16	34	0.98

Table 6

EQUIVALENT CIRCUIT PARAMETERS FOR ALL SAMPLES IN SF WITH 0.6045g/L LACTIC ACID AT 37°C

	R_s[Ω cm^2]	R_{out} [Ω cm^2]	CPE_{out} [μF/cm^2]	n_{in}	R_{in} [Ω cm^2]	CPE_{in} [μF/cm^2]	n_{out}
316	14.8	24.15	50	0.71	12054.32	28	0.92
316L	14.8	50.98	32	0.85	20153.97	31	0.96
CoCrMo	14.1	14	45	0.77	6986.12	26	0.90

Table 7

EQUIVALENT CIRCUIT PARAMETERS FOR ALL SAMPLES IN SF WITH 1.209g/L LACTIC ACID AT 37°C

	R_s[Ω cm^2]	R_{out} [Ω cm^2]	CPE_{out} [μF/cm^2]	n_{in}	R_{in} [Ω cm^2]	CPE_{in} [μF/cm^2]	n_{out}
316	11.6	65.03	28	0.74	32451.59	20	0.92
316L	10.8	63.77	39	0.72	21195.82	26	0.87
CoCrMo	11.3	59.23	46	0.8	19684.52	25	0.90

used to model the EIS data obtained for all alloys is presents in figure 3 and theoretical simulated impedance parameters for each solution are summarized in table 5-7. This simulation gave a reasonable fit with an average error of about 5%.

In this circuit R_s is the solution resistance , R_{out} and C_{out} can be attributed to a charge transfer process taking place in an outer layer, in which R_{out} is the charge transfer resistance resulting and C_{out} represents the capacitance of the double layer. The elements R_{in} and C_{in} are used to describe the passive layer on the metal surface. This circuit was already used by different authors [23-25].

Figure 2a shows the impedance results in SF solution. The polarization resistance decreased in following order: 316>316L>CoCrMo according to the lower diameter of Nyquist diagram. In the case of adding 0.6045g/L of lactic acid in SF solution the polarization resistance decreases in the following order: 316L>316>CoCrMo (fig 2b). Figure 2c shows the impedance results in SF with 1.209g/L of lactic acid. In this case, lactic acid generates an increase in the passive dissolution resistance of samples.

R_{in} increase with the concentration of lactic added in SF for all samples; while CPE_{in} reduced which means an increase in the thickness of passive layer.

Conclusions

The electrochemical behaviour of stainless steel and CoCrMo alloys was investigated by electrochemical techniques (OCP, Tafel curve, EIS) in human serum and in the presence of lactic acid with 2 different concentrations. EIS was used in order to characterize the interface metallic biomaterials/electrolyte and the corresponding surface processes were successfully modeled by applying an Equivalent Electric circuit.

Based on experimental data, the influence of lactic acid in terms of inhibition efficiency was established. This inhibition effect was increasing for CoCrMo alloy and for higher concentrations of lactic acid.

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