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### **Electrochemical behavior of a CoCrMo biomedical alloy in simulated body fluids**

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#### ***Abstract***

Cobalt-Chromium-Molybdenum (CoCrMo) alloys are commonly used in biomedical applications due to their high strength and excellent wear resistance combined with outstanding corrosion resistance and biocompatibility. The corrosion resistance and biocompatibility of this material is determined by physical-chemical behaviour of passive oxide layer that forms spontaneously on the metal surface. The CoCrMo alloys are traditionally produced via casting and/or forging route, however recently additive manufacturing (AM) techniques are employed in the fabrication. In this research, electrochemical behaviour of a biomedical CoCrMo alloy produced by direct metal laser sintering AM technique in two simulated body fluids was evaluated. The simulated body fluids included 0.14M NaCl and Phosphate Buffered Solution (PBS) both with and without addition of albumin. The influence of solution chemistry on the electrochemical behavior was evaluated using electrochemical impedance spectroscopy in addition to potentiodynamic tests conducted under controlled conditions of temperature and pH, 37 °C and 7.4, respectively, simulating human serum. The results show that the addition of albumin impair the corrosion resistance of the alloy in both simulated body fluids, decreasing the corrosion potential and increasing the current density. When comparing the two solutions, corrosion is less pronounced in the PBS solution.

**Keywords:** CoCrMo alloy, Corrosion resistance, Simulated body fluids.

#### **Introduction**

One of the main requirements of the metallic implants is to have high corrosion resistance in the human body environment. The presence of a passive layer on the surface of

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bio-implant alloys significantly increases their corrosion resistance; however, they are not completely inert in the body. Interactions between body fluids and the surface oxide layer may cause adverse biological reactions and ion release which could eventually lead to the failure of metallic bio-implants [1]. Implants are covered with a layer of adsorbed protein immediately after insertion into the body [2]. Proteins are negatively and metal ions are positively charged in the body fluids at pH 7.4. The interactions of metal ions with proteins generate colloidal organometallic complexes. These complexes change the pH of albumin solutions and may enhance the rate of metal dissolution and the corrosion rate [3,4].

Cobalt-based alloys have also been widely employed in orthopedic implants due to their high corrosion resistance, wear properties and hardness [5]. The mechanism of the resistance corrosion is explained by the spontaneous formation of a protective film with dielectrics properties [6]. The composition of this is predominantly  $\text{Cr}_2\text{O}_3$  oxide with some minor contribution of other oxides (Co- and Mo-oxides, especially if the film is air formed) [7].

The aim of this research is to evaluate the influence of solution chemistry on the electrochemical behavior of biomedical alloys (CoCrMo) in two simulated body fluids. Corrosion tests were carried out using a rod contact configuration with CoCrMo alloy immersed in simulated body fluids, NaCl and phosphate buffered solutions (PBS) with or without addition of bovine serum albumin (BSA) i.e. albumin, as model protein. This comparison is focused on the influence of solution chemistry and immersion time on the passive behavior using electrochemical techniques, potentiodynamic curves and electrochemical impedance spectroscopy (EIS).

## **Experimental**

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The experiments were carried out using four different simulated body solutions: 0.14 M NaCl, 0.14 M NaCl with 0.5 g/L of albumin (Sigma–Aldrich Inc.), PBS solution (0.14 M NaCl, 1 mM  $\text{KH}_2\text{PO}_4$ , 3 mM KCl,  $\text{Na}_2\text{HPO}_4$ ) and finally PBS with 0.5 g/L of albumin, in order to analyse the influence of phosphates and albumin on the electrochemical behaviour of the biomaterial. Temperature of the solutions was kept out 37 °C and pH 7.4 (human body conditions). The non-buffered solutions were adjusted to pH 7.4 with the addition of concentrated HCl and concentrated NaOH before each experiment.

The CoCrMo alloy (EOS CobaltChrome MP1) [8] was tested in the form of cube of 100 mm<sup>2</sup> in area. The nominal composition of this wrought alloy corresponding to ISO 5832-

12 is shown in table 1. The rods were embedded into non-conductive resin in order to obtain active area of  $A = 0.30 \text{ cm}^2$ .

Before each experiment, the samples were polished (1200 grit SiC paper), degreased with ethanol, washed with pure water and dried with compressed air before use.

**Table 1. Chemical composition of CoCrMo alloy**

ISO 5832-12	Elements (wt-%)							
	Co	Cr	Mo	Si	Mn	Fe	C	Ni
<b>Standard</b>	60 - 65	26 - 30	5 - 7	$\leq 1.0$	$\leq 1.0$	$\leq 0.75$	$\leq 0.16$	$\leq 0.10$

### ***Electrochemical Tests***

Open Circuit-Potential (OCP) was measured for 5 hours. The potentiodynamic polarization tests were performed by scanning the applied potential from  $-700 \text{ mV}_{\text{Ag/AgCl}}$  and moved in the anodic direction to  $1500 \text{ mV}_{\text{Ag/AgCl}}$  to the (OCP) at a rate of  $1 \text{ mV}\cdot\text{s}^{-1}$ . The test was terminated automatically when the current exceeds the value of  $1.0 \text{ mA}$ . EIS measurements were carried out under potentiostatic conditions. Impedance measurements were performed for 10 frequency decades from  $40 \text{ KHz}$  to  $6\text{mHz}$  with an amplitude of  $\pm 10 \text{ mV}$ . A double-wall three-electrode cell (volume  $100 \text{ ml}$ ) in aerated conditions and under agitation was used for all the electrochemical measurements. An  $\text{Ag/AgCl}$   $3 \text{ M KCl}$  reference electrode and a platinum wire was used as counter electrode. The potentiostats used were Autolab PGSTAT30.

## **Results and discussion**

### ***Open circuit potential (OCP)***

Fig. 1 shows that evolution with time of the OCP follows the same trend in all solutions, consisting in a continuous shifting towards more positive values with time. The positive potential evolution indicates probably formation of a protecting passivation layer on the CoCrMo alloy. This behaviour is more pronounced in the non-containing albumin solutions. Table 2 shows the mean values and standard deviation of the OCP measurements for material in the simulated body fluids.

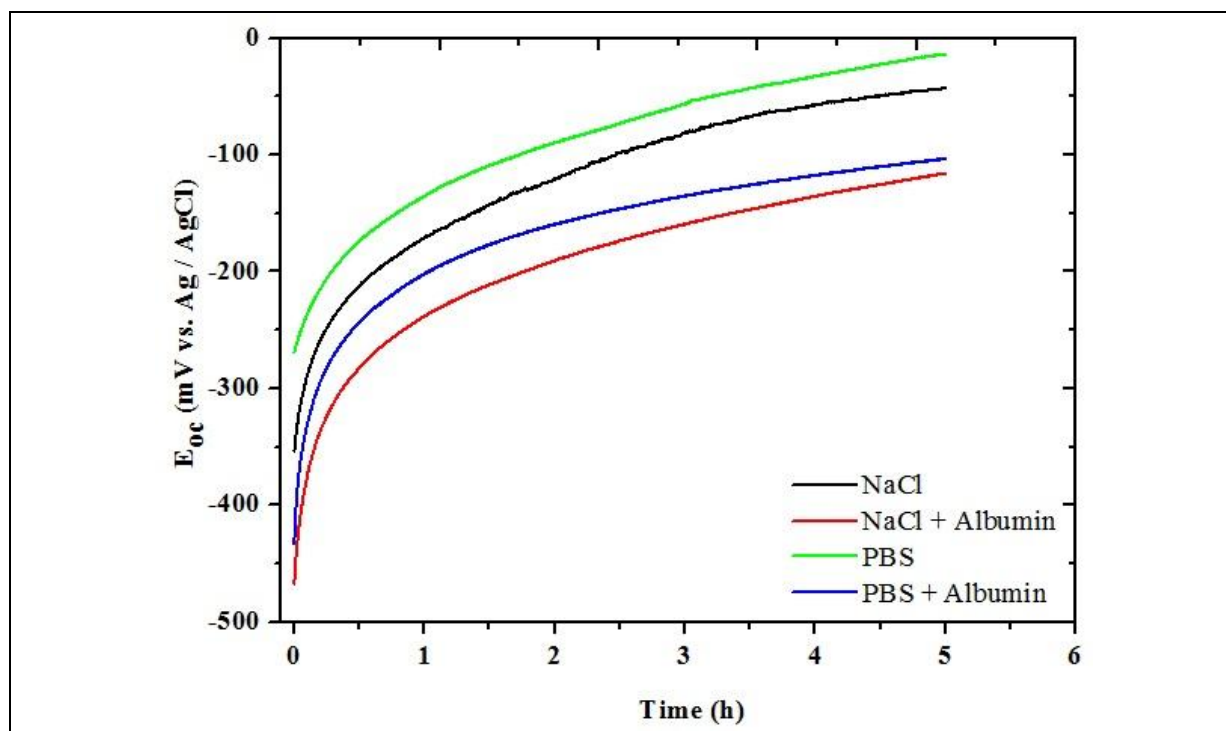


Fig. 1. Open circuit potential measurements for CoCrMo in simulated body solutions at 37 °C and pH 7.4 after 5 hours of immersion

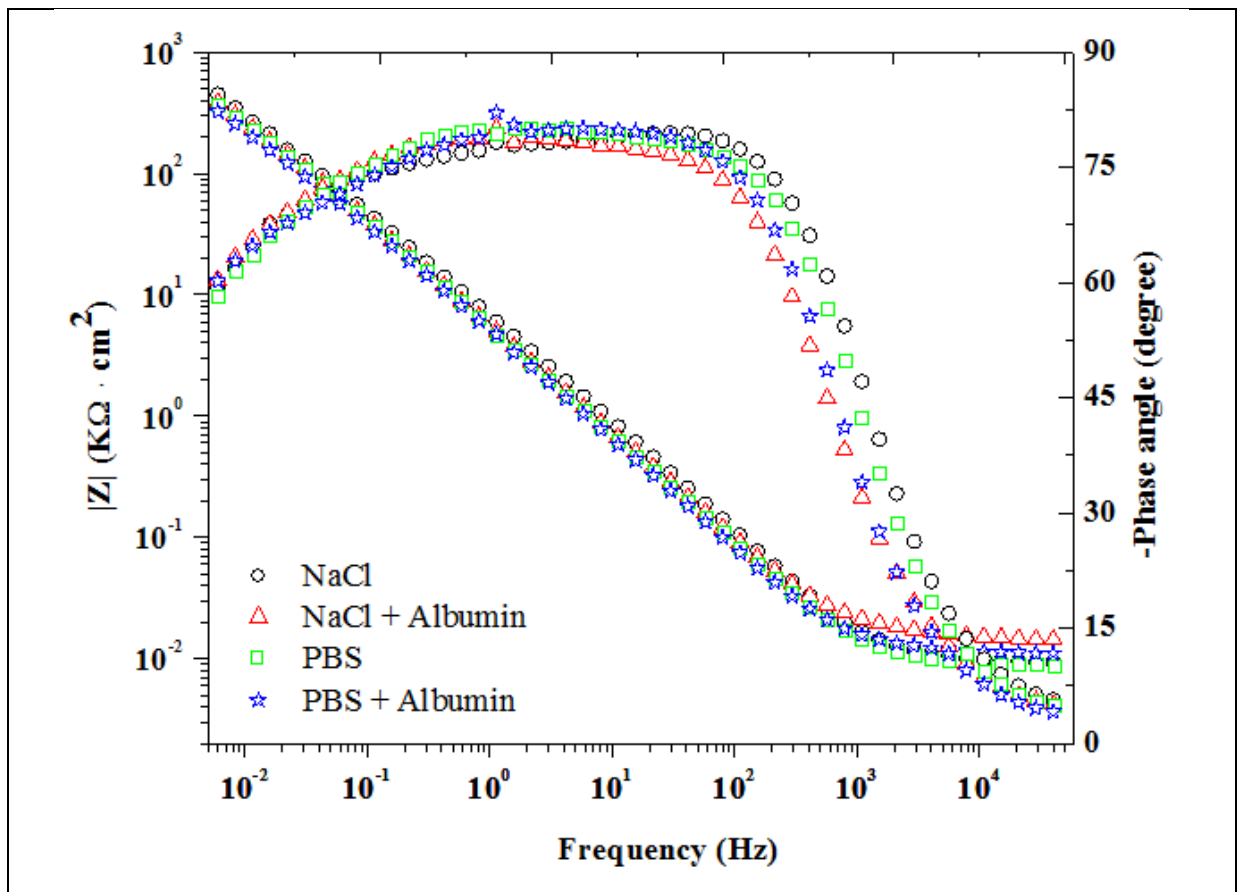
Solution chemistry significantly affects OCP of CoCrMo alloy. Main differences on the corrosion potential between both solutions are found in the albumin-containing solutions. Albumin notably shifts towards more negative values the OCP when added in two solutions. It is known that albumin may act as a cathodic inhibitor on CoCrMo alloys [9], thus shifting their OCP towards lower values while phosphates in PBS solution act as anodic inhibitor [10]. When both compounds are present in PBS solution, albumin action predominates on the electrochemical behaviour of this alloy. Comparing the two solutions, the OCP values are higher for the PBS solutions than NaCl solutions.

Table 2. Open circuit potential values for CoCrMo in simulated body solutions at 37 °C and pH 7.4 after 5 hours of immersion

OCP (mV)			
NaCl	NaCl + albumin	PBS	PBS + albumin
-42.80 ± 14.38	-115.75 ± 13.77	-13.61 ± 0.88	-103.45 ± 8.01

### *Electrochemical impedance spectroscopy (EIS)*

In Fig. 2, the Bode diagrams for CoCrMo alloy in NaCl and PBS solutions whether or not containing albumin at 37 °C and pH 7.4 are provided. The absolute impedance data was independent of frequency from  $10^4$  down to  $10^3$  Hz. This frequency range showed a resistive behaviour corresponding to the solution resistance between the working and the reference electrode. The phase values reached their maximum values ( $\sim 80^\circ$ ) at frequency range of 60–10 Hz. In these frequency ranges, the metallic samples showed capacitive behaviours. In addition, the passive behaviour of the metallic samples was observed at these frequency ranges because the phase angle values were independent of frequency while the absolute impedance values were increasing. The absolute impedance increased and the phase angle shifted to the lower values by decreasing the frequency from 10 to 0.006 Hz.



**Fig. 2. Bode and Bode phase plots of the CoCrMo alloy after 5 h immersion at OCP in aerated NaCl and PBS solutions at 37 °C and pH 7.4 with or without addition of albumin**

It is known that in CoCrMo alloy, albumin increases the  $R_{ct}$  (charge transfer resistance) due to the blocking effect of the organic molecule. However, this effect is reduced with time. By other hand, capacitance increases when albumin is present in the solution, this fact is due to the adsorption effect [11].

Previous study [12] measured at a fixed potential the impedance spectra of a CoCrMo alloy as a function of polarization time and was observed strong time-dependent changes specially in the phase shift response indicating that the properties of the passive film are strongly changing in the time range studied (from 15 min to 24 h). In NaCl + albumin solutions, properties of the passive film at an applied potential changes with time in the sense that charge transfer resistance decreases and the capacitance increases. On the contrary, phosphate effect improves the passive behaviour of the passive film, by both, increasing the charge transfer resistance and decreasing the capacitance. It is known that phosphates act as anodic inhibitor by adsorbing on the CoCrMo surface [10].

However, in this work the effect of solution chemistry in  $R_{ct}$  it was not very clear in 5 h of immersion. It is known that in the NaCl + albumin solution, charge transfer resistance decreases with time, while in the PBS + albumin solution resistance increases with time. This difference may be explained by the effect of the adsorbed proteins on the CoCrMo surfaces, being necessary to evaluate the behavior of the impedance and to characterize the formation of the passive film on the metal substrate in different immersion times.

### ***Polarization curves***

Typical polarization curves of CoCrMo alloy in NaCl and PBS solutions with and without albumin are shown in Fig. 4. To facilitate comparison, the following data were extracted forms the polarization curves and listed in Table 3: corrosion potential  $E_{corr}$  (potential at which the current changes sign), the corrosion current density  $i_{corr}$  (extracted through extrapolation of Tafel slopes at the corrosion potential), and breakdown potential (transpassive region)  $E_{bp}$ .

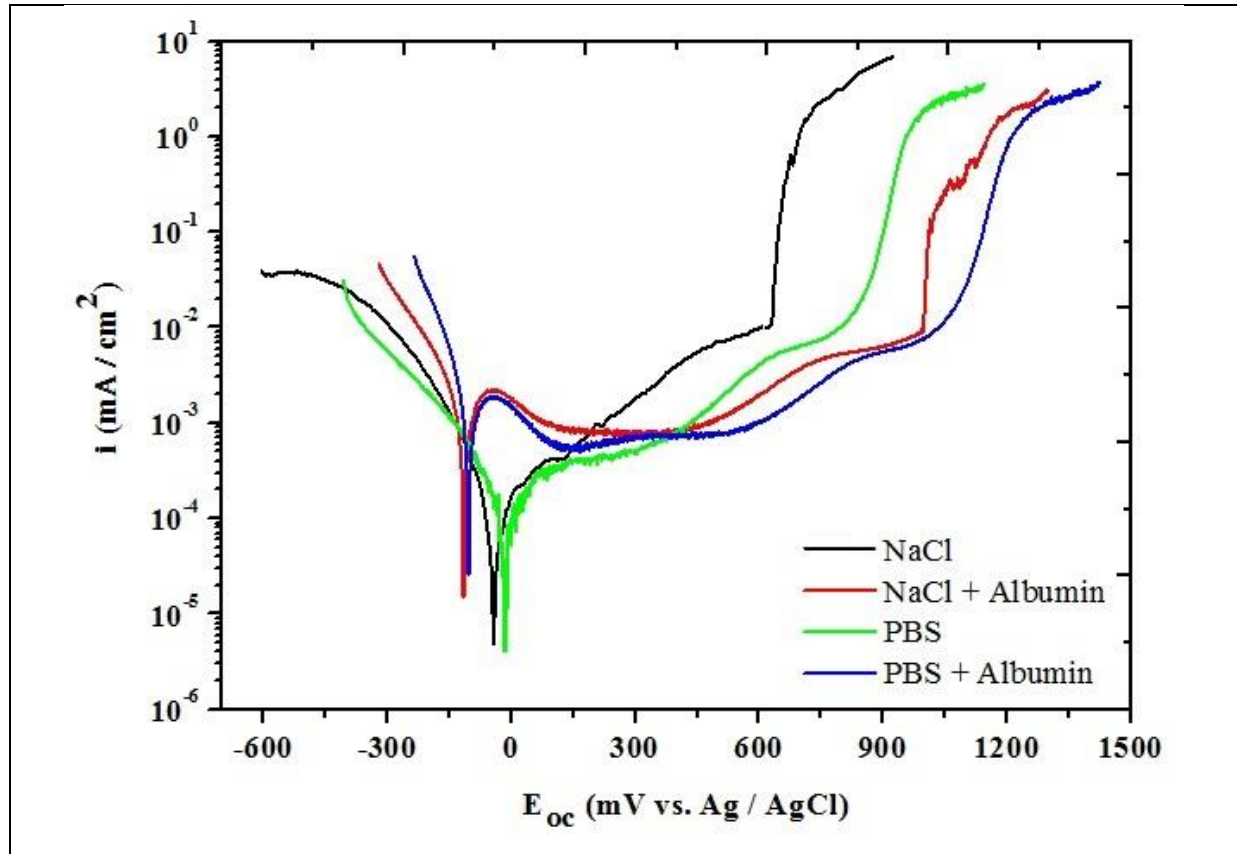


Fig. 4. Potentiodynamic curves for CoCrMo alloy in a 0.14 NaCl and b PBS with and without albumin (pH 7.4, 37 °C)

Table 3. Results of the electrochemical parameters for CoCrMo alloy in the studied solutions at 37 °C and pH 7.4

Parameters	NaCl	NaCl + albumin	PBS	PBS + albumin
$E_{\text{corr}}$ (mV)	$-42.80 \pm 14.38$	$-115.75 \pm 13.77$	$-13.61 \text{ mV} \pm 0.8$	$-103.45 \pm 8.01$
$i_{\text{corr}}$ (mA/cm <sup>2</sup> )	$(1.18 \pm 0.46) \times 10^{-4}$	$(6.44 \pm 0.37) \times 10^{-4}$	$(8.64 \pm 0.17) \times 10^{-5}$	$(9.68 \pm 0.28) \times 10^{-4}$
$E_{\text{bp}}$ (mV)	$631.21 \pm 6.78$	$997.74 \pm 14.08$	$807.4 \pm 9.62$	$1056.49 \pm 18.35$

Polarization curves can be divided in four potential domains. The cathodic domain includes potentials below  $-100 \text{ mV}_{\text{Ag/AgCl}}$  where the current is determined by the reduction of water and, partially, of dissolved oxygen. In this domain, albumin slightly increases the current density. This is in disagreement with the literature, which reports that albumin acts as a cathodic inhibitor. Such discrepancy may have been caused due to the agitation of the

electrolyte. Agitation can conduct a more efficient transport of oxygen which contributes to the formation of a passive layer, but can also be related other deleterious effects than mechanical, as to increase cathodic reaction at active sites increasing the overall reaction rate and facilitating the transportation of metal ions away from the surface compared with stagnant condition.

All corrosion reactions aggressive ions should be reach the metal surface and the corrosion products carried away from the surface. Ions and molecules can reach the metal surface by molecular diffusion because of a concentration gradient. In stagnant solution, the metal surface atoms go into solution as ions by the dissolution process. With agitation creating a turbulent flow on the surface of the sample, the amount of material reaching the surface increases by the action of the flow transport of oxygen to the surface improves. Nevertheless, the metal ions necessary for the formation of the passive layer will although easily due to increase of mass transfer through the diffusion layer, which is thinner. Therefore, the formation of the passive layer becomes more difficult. Even if formed, as indicated by a horizontal range of polarization curves of the albumin-containing solutions, the passive layer is thinner, and possibly discontinuous and less resistant than that formed in stagnant conditions. On the other hand, the presence of flow, besides promoting transportation of metal ions away from the surface, increases the intensity of the anodic and cathodic reactions further the increase in corrosion rate and shifting the curves for higher current densities [13].

The potential domain comprised between  $-100 \text{ mV}_{\text{Ag}/\text{AgCl}}$  and  $1.0 \text{ mV}_{\text{Ag}/\text{AgCl}}$  is characterised by the transition from cathodic to anodic current at the corrosion potential followed by some fluctuations of the anodic current. The presence of albumin shifts the corrosion potential towards more negative values. Phosphate ions have an opposite effect except in presence of albumin that determines the electrochemical behaviour in this domain. The third domain corresponds to the passive plateau and ranges from  $1.0$  up to  $900 \text{ mV}_{\text{Ag}/\text{AgCl}}$ . Here phosphate ions decrease the passive current density while albumin increases it. Finally, the transpassive domain is characterised by the increase in current due to transpassive dissolution of the chromium oxide as well as water oxidation. Phosphate containing solutions with or without albumin show a shoulder at approximately  $600$  and  $900 \text{ mV}_{\text{Ag}/\text{AgCl}}$ , respectively. Similar effect observed in presence of complexing agents (phosphate) and can possibly be attributed to the formation of phosphate–chromium ions complexes that activates transpassive dissolution [7].



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At the pH of the test solutions (7.4) albumin is negatively charged since its isoelectric point is 4.9 [14]. The polarization in the anodic direction, create electron depletion. This favours the adsorption of negatively charged species, and albumin would thus tend to form an adsorbed film. Since chemical and structural heterogeneities on the metal originate variations in the surface charge, albumin would be more easily attracted towards the most positively charged regions, namely those where metal cations are being released.

Albumin modifies the cathodic–anodic transition by decreasing the corrosion potential ( $E_{\text{corr}}$ ) and increases the current density in the cathodic domain. It can be conclude that phosphates act as anodic inhibitor on CoCrMo (the slope of anodic branch diminishes in relationship with the NaCl solution) while albumin acts as cathodic inhibitor or accelerating the metallic dissolution depending on solution chemistry. In CoCrMo experiments, the albumin always acts as cathodic inhibitor and it accelerates the anodic reaction in solution with and without phosphates. A competition between protein and chloride in NaCl solution and phosphate in PBS solution for adsorption would retard the film breakdown caused by the latter ion, thus explaining the more positive potentials and longer times for breakdown in albumin containing solutions.

### ***Conclusions***

According to the equilibrium potential (OCP) reached by the CoCrMo alloy, it spontaneously passivate in simulated body fluids.

Solution chemistry modifies the corrosion mechanisms of alloy. Phosphates act as anodic inhibitor while albumin acts accelerating the metallic dissolution depending on solution chemistry.

The EIS Bode-phase plots show one maxima in the high-mid frequencies. By plots it was not very clear the effect of solution chemistry in  $R_{\text{ct}}$  after 5 h of immersion being necessary to evaluate the behavior of the impedance and to characterize the formation of the passive film on the metal substrate in different immersion times.

Comparing the same solution NaCl or PBS, the addition of albumin modifies the cathodic–anodic transition by decreasing the corrosion potential ( $E_{\text{corr}}$ ) and increasing the corrosion current density. Between solutions chemistry, PBS presents less aggressive to the biomaterial probably due to the effect of the phosphate ions adsorbed on the surface of CoCrMo alloy acting as an anodic inhibitor.

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