

## **Influence of hydrogen peroxide in the tribocorrosion behaviour of a CoCrMo biomedical alloy**

**R. Catalán<sup>1</sup>, J. Navarro Laboulais<sup>1</sup>, A. Igual Muñoz<sup>1(\*)</sup>**

<sup>1</sup> Institute for Industrial, Radiophysical and Environmental Safety, Universitat Politècnica de València, P.O. BOX 22012, E-46071, Valencia, Spain

### **ABSTRACT**

This paper studies the influence of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) in simulated body fluids on the wear and corrosion behaviour of a CoCrMo biomedical alloy. CoCrMo are passive materials commonly used in prosthesis and implants because of its high corrosion resistance and mechanical properties. Hydrogen peroxide is produced by bacteria and leukocytes as a consequence of an inflammatory reaction which may modify the tribo-electrochemical response of metals implanted in the human body. Indeed, the oxidizing environment generated by the presence of the peroxide increases the metal dissolution rate. Electrochemical and tribocorrosion tests were carried out in a PBS solution with different addition of H<sub>2</sub>O<sub>2</sub> (0.5, 2, 4 and 12%).

**KEY WORDS:** tribocorrosion, wear, biomedical alloys, hydrogen peroxide.

### **1.- INTRODUCTION**

Metallic materials are widely used to restore or improve the functionality of different parts of the human body. Among the typical metallic alloys employed in the design of those implants one can find CoCrMo alloys, because of their high corrosion resistance and appropriate mechanical properties (high strength and wear resistance). They are also considered as biocompatible materials. CoCrMo are passive materials thus subjected to a passive dissolution mechanism [1][2] when immersed in typical simulated body fluids. However, it has been demonstrated [3] that degradation mechanisms of implants are a combination of wear and corrosion, thus constituting to a tribocorrosion system. A recent review on the tribocorrosion behaviour of CoCrMo alloys have been published [4] and it was concluded that degradation of CoCrMo alloys in water lubricated contacts are critically affected by the prevailing electrochemical conditions. Indeed, a wear transition between low and high wear values of more than one order of magnitude as a function of the electrochemical potential was observed.

Cell/tissue interaction with implanted metals is not well understood yet, although macrophages cells are often detected near the implants and in tissues with high amount of metal ions [5]. These cells are known to release reactive chemical species such as nitric oxide (NO) or hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>). These compounds may modify the surface chemistry of the metallic alloys (composition and thickness of the passive film), thus altering the tribocorrosion behaviour in their presence.

The aim of this work is to study the effect of the hydrogen peroxide on the corrosion and tribocorrosion behaviour of a CoCrMo biomedical alloy by tribo-electrochemical techniques.

## 2.- EXPERIMENTAL SET-UP

### 2.1.- Material and electrolyte

The studied biomedical alloy is a low Carbon CoCrMo alloy (%wt: C 0.253%, Cr 27.99%, Mo 5.35%, Si 0.78%, Mn 0.4%, Fe 0.16%, Ni 0.41% and Co 64.62%). The samples were ground with SiC emery paper up to 4000 grit and polished with diamond paste (1 $\mu$ m) until reaching a mirror-like surface finishing before each experiment. The exposed area to the electrolyte was 2.56 cm<sup>2</sup>.

The support electrolyte used in order to investigate the effect of hydrogen peroxide on the tribo-electrochemical behavior of CoCrMo biomedical alloys was a phosphate buffered solution (PBS) with the composition of 8 g/L NaCl, 0.2 g/L KCl, 1.44 g/L Na<sub>2</sub>HPO<sub>4</sub> and 0.25 g/L KH<sub>2</sub>PO<sub>4</sub>. Several amounts of H<sub>2</sub>O<sub>2</sub> (0.5, 2, 4, and 12 %wt) were added to the PBS solution in order to have different solutions PBS+xH<sub>2</sub>O<sub>2</sub> (where x is 0.15, 0.59, 1.18, 3.6 M). The buffered solutions were adjusted to pH 7.4. Temperature of the solution was room temperature.

### 2.2.- Electrochemical tests

Conventional electrochemical measurements were performed employing a three-electrode configuration using a Solartron 1286 potentiostat. Potentiodynamic curves were obtained for the CoCrMo alloy with a platinum wire as counter electrode and a silver-silver chloride as reference electrode (Ag/AgCl, 3M KCl). All potentials in this paper are given with respect to this reference electrode (-0.205V vs. SHE). The potential was swept with a scan rate of 2 mVs<sup>-1</sup>, starting at the OCP towards -1.1 V and ending at 1 V. All experiments were carried out under aerated conditions.

### 2.3.- Tribocorrosion tests

The investigated tribosystem involved a contact between a rotating CoCrMo disc and a counterpart made of alumina ball of 6 mm diameter with a surface finish of 0.02  $\mu$ m R<sub>a</sub> (according to the manufacturer). All experiments were carried out on a ball on disk tribometer connected to a potentiostat. The tribometer operated with an integrated electrochemical cell (3-electrode cell) including the specimen as working electrode, a Pt wire counter electrode and a reference electrode of Ag/AgCl 3M. The motor providing motion rotated at 60 r.p.m. and generated a circular stroke of 6 mm diameter (sliding velocity of 19 mm/s). Normal loads of 5 N was applied which correspond to average contact pressures of 886 MPa.

The test procedure was carried out using the following steps:

- Immersion of the CoCrMo alloy disc in the electrolyte under open circuit conditions (OCP) during two minutes.
- Cathodic polarization at -1.1 V<sub>Ag/AgCl</sub> during 5 minutes.
- Return to OCP conditions, measurement of the corrosion potential during 1 hour.
- Rubbing during 1 hour while registering the OCP.
- Rubbing is stopped, the OCP is measured for 20 minutes.

Wear was quantified using a confocal microscopy. For this, three profiles were measured across the wear track for each sample. The wear track volume was determined by multiplying the area of the profiles situated at heights below 0 (reference level corresponded to the non rubbed area) and multiplying it by the length of the wear track. Optical microscope and scanning electron microscope, SEM, (JEOL6300) were used to analyze wear tracks on the metal's disks and on the alumina counterparts.

### 3.- RESULTS AND DISCUSSION

#### 3.1.- Electrochemical behaviour

Cathodic polarization behaviour of the CoCrMo in PBS with different  $H_2O_2$  concentrations is shown in Figure 1. Cathodic current density increases with the presence of the peroxide.

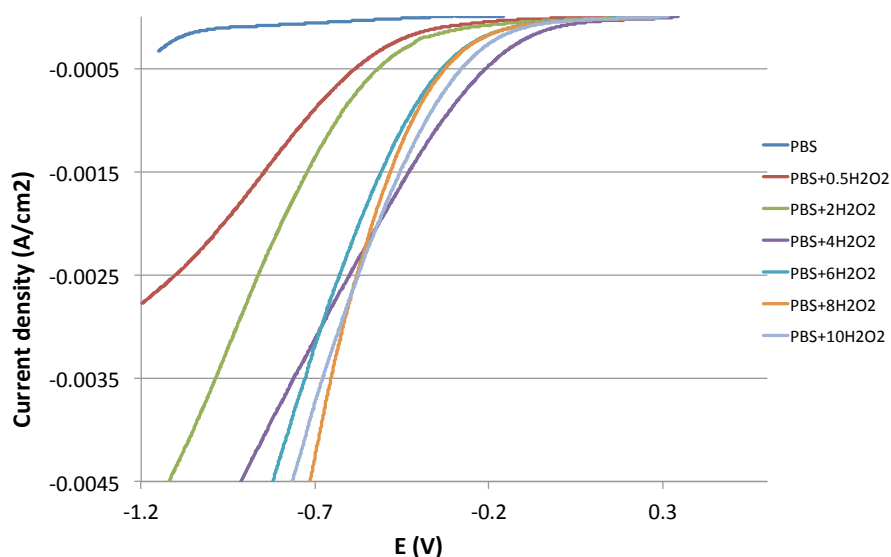


Figure 1. Cathodic potentiodynamic curves of the CoCrMo biomedical alloy in different PBS solutions.

Figure 2 shows the anodic polarization behaviour of the CoCrMo alloy in the PBS and in the peroxide containing solutions. Typical passive behaviour can be observed in the PBS solution, in which four clear potential domains can be distinguished. Between -1V and the corrosion potential the current density is given by the water reduction and partially of dissolved oxygen; at the corrosion potential a cathodic-anodic transition takes place and from the corrosion potential, -0.3V, to 0.6V the CoCrMo forms an oxide film mainly composed by chromium oxide [6][7], thus defining its passive domain, and finally at higher anodic potential the increase in current is due to a transpassive dissolution. The corrosion potential is shifted towards high anodic values in presence of  $H_2O_2$ . The oxidizing power of the peroxide hinders the passive domain of the CoCrMo, thus showing a transition from cathodic to transpassive dissolution. In all cases, above 0.8V the anodic current contribution is mainly due to the water oxidation.

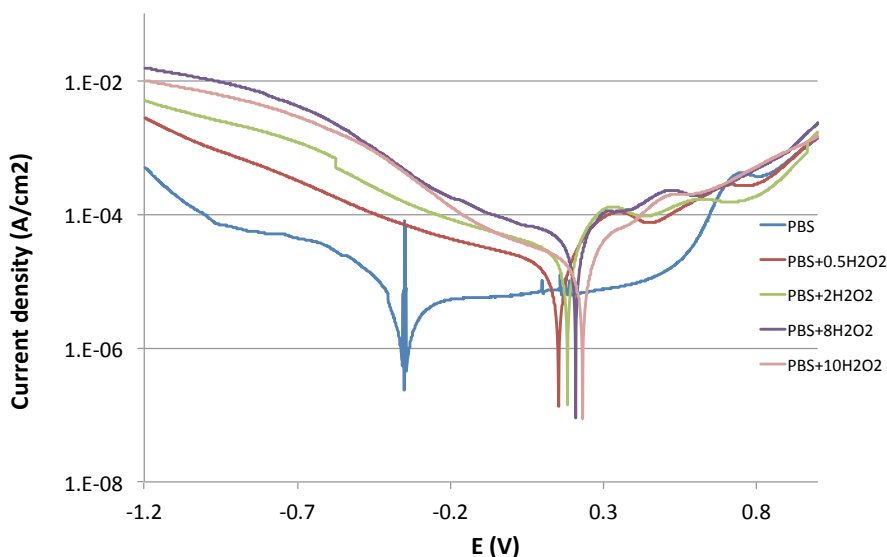


Figure 2. Potentiodynamic curves of the CoCrMo biomedical alloy in different PBS solutions.

### 3.2.- Tribocorrosion behaviour

Figure 7 shows the evolution of the open circuit potential with time before, during and after the sliding on the CoCrMo alloy in the PBS solutions.

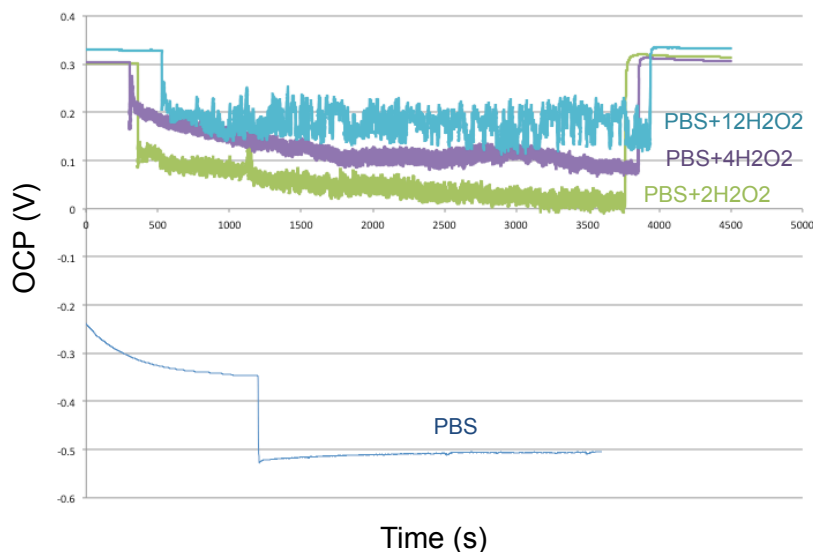


Figure 3. OCP evolution during sliding an alumina ball against CoCrMo alloy in different PBS solutions at 37°C. Normal load 5N.

In the PBS solution, a potential decay (from -0.3 to -0.4 V) is observed at the onset of the sliding due to the mechanical detachment of the passive film which causes a depassivation of the wear track, thus generating a galvanic coupling between the wear track (anode) and the passive sample (cathode). The OCP of the CoCrMo before sliding is much higher in the peroxide containing solutions than in the PBS solution, around 0.3 V. When sliding starts, there is also a potential drop due to the mechanical action which depends on the H<sub>2</sub>O<sub>2</sub> concentration. The potential during sliding shifts towards higher values with the H<sub>2</sub>O<sub>2</sub> concentration.

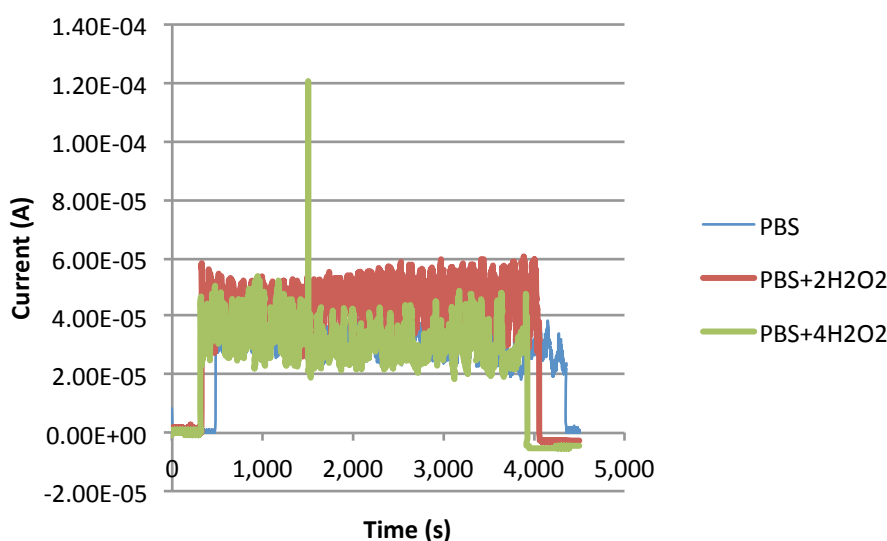


Figure 4. Current evolution during sliding an alumina ball against CoCrMo alloy at  $0.3 V_{Ag/AgCl}$  in different PBS solutions at  $37^{\circ}\text{C}$ . Normal load 5N.

As described elsewhere [8], total wear volume  $V_{\text{tot}}$  can be described as the sum of the wear accelerated corrosion  $V_{\text{wac}}$  and the mechanical wear  $V_{\text{mech}}$ .  $V_{\text{tot}}$  was determined as it is explained previously in 2.3 with confocal microscopy. On the other hand,  $V_{\text{wac}}$  was determined by integrating the current versus time during the potentiostatic tests at  $0.3 \text{ V}$  and applying the model proposed by Viera et al [9] and applied by Papageorgiou and Mischler [10] when the tribocorrosion tests were carried out at OCP.  $V_{\text{mech}}$  is obtained by the difference between  $V_{\text{tot}}$  and  $V_{\text{wac}}$ . The obtained  $V_{\text{wac}}$  values are listed in Table 1 together with the mechanical wear volume ( $V_{\text{mech}}$ ) and total wear volume ( $V_{\text{tot}}$ ). At OCP mechanical wear volume increases with the  $\text{H}_2\text{O}_2$  concentration while wear accelerated corrosion decreases as a function of the  $\text{H}_2\text{O}_2$  concentration in the peroxide containing solutions. On the other hand, the data measured in the PBS solution with or without  $\text{H}_2\text{O}_2$  (for  $\text{H}_2\text{O}_2$  concentration below 12 %wt) correspond well with the results obtained under electrochemically applied potential. This indicates the equivalence between chemical and electrochemical passivation of CoCrMo in the PBS solution.

The present triboelectrochemical results clearly show that the oxidizing effect of the environment directly affects the mechanical degradation of the CoCrMo alloy. Indeed, with the increase in the  $\text{H}_2\text{O}_2$  concentration in the electrolyte the contribution of the mechanical damage to the overall tribocorrosion degradation also increases.

Table 1. Average wear volumes ( $\cdot 10^{-3} \text{ mm}^3$ ) of the CoCrMo alloy in the studied solutions at  $37^{\circ}\text{C}$

Solution	Potential (V)	Vt	Vwac	Vmech
PBS	OCP (-0.3)	1.0	0.1	0.9
	0.3	5.8	3.6	2.2
PBS+0.5H <sub>2</sub> O <sub>2</sub>	OCP (-0.12)	5.8	4.8	1
PBS+2H <sub>2</sub> O <sub>2</sub>	OCP (0.05)	4.8	3.0	1.8
	0.3	6.5	5.5	1
PBS+4H <sub>2</sub> O <sub>2</sub>	OCP (0.1)	4.9	2.8	2.1
	0.3	16.6	3.3	13.3
PBS+12H <sub>2</sub> O <sub>2</sub>	OCP (0.2)	24.9	1.7	23.2

Wear morphology was analysed by SEM and Figure 5 shows the typical image taken in the centre of the wear track after the tribocorrosion test of the CoCrMo sliding against an alumina ball in the PBS solution. Scratches in the sliding direction causing an abrasive damage and small wear particles are observed.

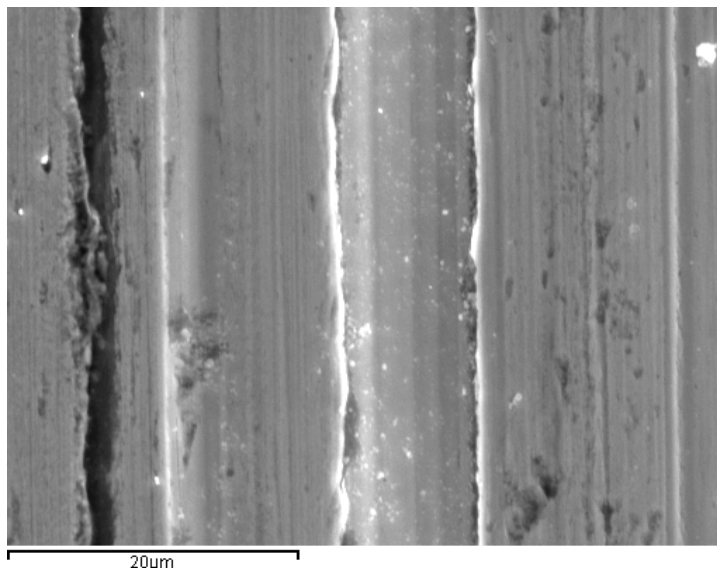


Figure 5. SEM images of the CoCrMo alloy in the middle of the wear track at the end of the tribocorrosion tests sliding against an alumina ball at OCP in PBS at 37°C. Normal load 5N.

Figure 6 shows two images of the centre of the wear track in the CoCrMo after being tested in PBS+4H<sub>2</sub>O<sub>2</sub> at OCP and 0.3 V respectively. In both cases, smooth surfaces with individual scratches are observed without the presence of wear debris.

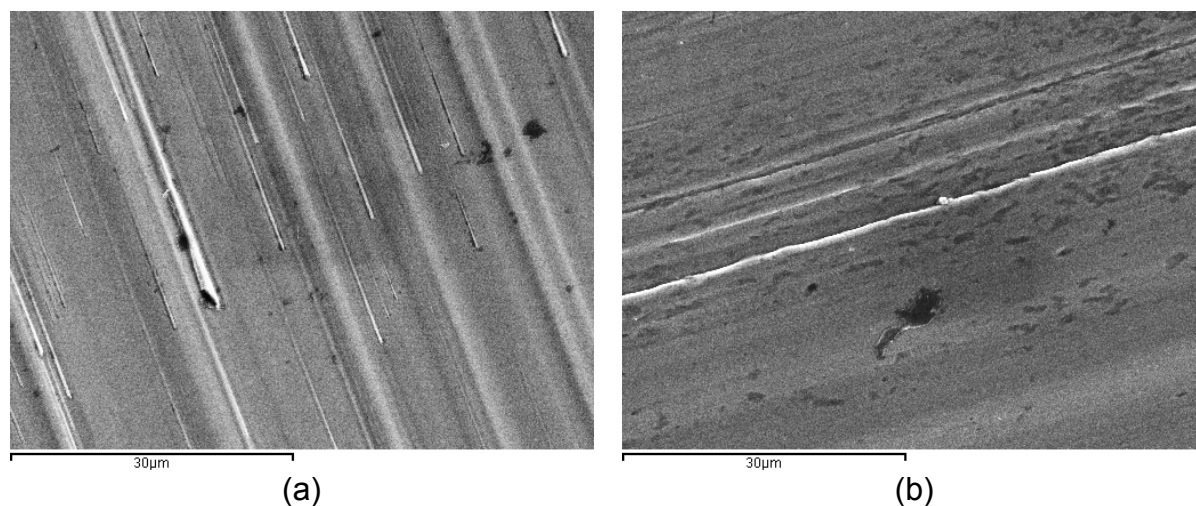


Figure 6. SEM images of the CoCrMo alloy in the middle of the wear track at the end of the tribocorrosion tests sliding against an alumina ball (a) at OCP and (b) at 0.3 V in PBS+4H<sub>2</sub>O<sub>2</sub> at 37°C. Normal load 5N.

#### **4- CONCLUSIONS**

Corrosion and tribocorrosion behaviour of a CoCrMo biomedical alloy was studied in a PBS solution with and without different concentrations of H<sub>2</sub>O<sub>2</sub>. The oxidizing power of the peroxide enhances the cathodic reaction and suppresses passive domain of the CoCrMo. Electrochemical conditions within the contact (OCP variations during sliding) modify the tribological behaviour of the biomedical alloy by increasing the mechanical damage when the H<sub>2</sub>O<sub>2</sub> concentration increases. At an applied constant potential, wear damage is very similar independently on the H<sub>2</sub>O<sub>2</sub> concentration. Therefore, the presence of hydrogen peroxide produced as a consequence of an inflammation process, causes and acceleration of the wear damage mainly due to the increase of the mechanical wear.

#### **5.- REFERENCES**

- [1] A.W.E. Hodgson, S. Kurz, S. Virtanen, V. Fervel, C.-O.A. Olsson, S. Mischler, Passive and transpassive behaviour of CoCrMo in simulated biological solutions, *Electrochim. Acta.* 49 (2004) 2167–2178. doi:10.1016/j.electacta.2003.12.043.
- [2] C. Valero Vidal, A. Igual Muñoz, C.-O.A. Olsson, S. Mischler, Passivation of a CoCrMo PVD Alloy with Biomedical Composition under Simulated Physiological Conditions Studied by EQCM and XPS, *J. Electrochem. Soc.* 159 (2012) C233–C243.
- [3] M.T. Mathew, S.P. P., R. Pourzal, A. Fischer, M.A. Wimmer, Significance of Tribocorrosion in Biomedical Applications: Overview and Current Status, *Adv. Tribol.* (2009) 1–12.
- [4] S. Mischler, A.I. Muñoz, Wear of CoCrMo alloys used in metal-on-metal hip joints: A tribocorrosion appraisal, *Wear.* 297 (2013) 1081–1094. doi:10.1016/j.wear.2012.11.061.
- [5] T. Rae, The action of cobalt, nickel and chromium on phagocytosis and bacterial killing by human polymorphonuclear leucocytes; its relevance to infection after total joint arthroplasty, *Biomaterials.* 4 (1983) 175–180. doi:10.1016/0142-9612(83)90006-6.
- [6] I. Milošev, H.-H. Strehblow, The composition of the surface passive film formed on CoCrMo alloy in simulated physiological solution, *Electrochim. Acta.* 48 (2003) 2767–2774. doi:10.1016/S0013-4686(03)00396-7.
- [7] I. Milošev, The effect of biomolecules on the behaviour of CoCrMo alloy in various simulated physiological solutions, *Electrochim. Acta.* 78 (2012) 259–273. doi:10.1016/j.electacta.2012.05.146.
- [8] S. Mischler, Sliding Tribo-Corrosion of Passive Metals: Mechanisms and Modeling, in: B. Peter, C. Jean-Pierre, D. Dirk, F. Friedrich (Eds.), *Tribo-*

Corrosion Res. Testing, Appl., ASTM international, 2013: pp. 1–18.  
doi:10.1520/STP1563-EB.

- [9] A.C. Vieira, L.A. Rocha, N. Papageorgiou, S. Mischler, Mechanical and electrochemical deterioration mechanisms in the tribocorrosion of Al alloys in NaCl and in NaNO<sub>3</sub> solutions, *Corros. Sci.* 54 (2012) 26–35.  
doi:10.1016/j.corsci.2011.08.041.
- [10] N. Papageorgiou, S. Mischler, Electrochemical simulation of the current and potential response in sliding tribocorrosion, *Tribol. Lett.* 48 (2012) 271–283.

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