Study of electrochemical properties of bio-inspired coating based ErGO

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Abstract

The useful life of a prosthesis is expected to be greater than 15 years, but in many cases traumatologists are forced to remove and replace them prematurely (between 7-10 years), mainly due to problems of loosening and osteolysis. It is estimated that 75% of failures in the prosthesis is due to loosening compared to 7% that occurs due to infection, 6% due to recurrent dislocations and 5% due to fractures.

Wimmer et al. studied 42 implants recovered with 11.7 years in average of use where it was detected carbon-rich layers caused by denaturation of pseudo-synovial fluid components, and that this film acts as a solid lubricant, decreasing wear on the pair, and as a protective layer against the release of metallic traces. In this research work it is tried to emulate said natural layers by means of the formation of layers Electrochemically Reduced Graphene Oxide (ErGO) and functionalized, on the substrates of CoCrMo and Ti6Al4V (main metals used for the manufacture of joint implants) formed by cyclic voltammetry.

In the one step reduction by cyclic voltammetry of CoCrMo in Graphene Oxide (GO) the signal of reduction of the Graphene Oxide can be observed between the It can be distinguished a signal of reduction of the OG between the -0.6 and -1.05 V / $E_{Ag/AgCl}$. These potentials correspond to the reduction of carboxylic groups (-0.85 V / $E_{Ag/AgCl}$), OH and C-O-C ((-1.05 V / $E_{Ag/AgCl}$). Electrochemical impedance tests show that the resistance of ErGO film is stable for 8 days and provides corrosion protection to the substrate.

In this work was used too a "2-step reduction" methodology, that consists in deposition a thin film of GO on the surface of an electrode, is dried out, and then is reduced. Film formations of ErGO coating by FTIR is not detected.

Keywords

Biomaterial, coatings, ErGO.

Introduction

The World Health Organization attributes the high incidence of problems associated with the musculoskeletal system with the aging of the population [1]. 40% of the population older than 70 years suffer osteoarthritis of the knee, presenting some limitation in mobility and 25% can not perform routine daily activities. On the other hand, the number of fractures related to osteoporosis has doubled in the last decade. It is estimated that 40% of women with more than 50 years of age will suffer some osteoporotic fracture and it is estimated that the number of hip fractures will increase considerably (from 1.7 million in the year 1990 to 6.3 million in the year 2050).

The useful life of a prosthesis is expected to be greater than 15 years, but in many cases traumatologists are forced to remove and replace them prematurely (between 7-10 years) mainly due to loosening and osteolysis problems. It is estimated that 75% of failures in the prosthesis is due to loosening due to osteolysis, compared to 7% due to infection, 6% due to recurrent dislocations and 5% due to fractures [3,4].

However, in addition to the release of particles and metal ions, the continuous sliding on the surface of the joint replacements is able to stimulate mechanochemical reactions on the surface, and as a consequence, generate thin layers known as tribological or tribochemical films, essential for Reduce the wear of Metal / Metal pairs. Wimmer et al. [5] Detected a solid carbonaceous deposit, firmly adhered on the surface and accumulated especially in areas adjacent to the wear areas, on the surfaces of hip implants removed from patients. These deposits appeared to act as a solid lubricant, and were composed of what was supposed to be similar to denatured proteins of the pseudo-synovial fluid.

Therefore, the objective of this research work is to determine the voltages and polarization times, as well as functionalization conditions that generate carbonaceous deposits with greater resistance to wear and corrosion on the Ti6Al4V alloys, in addition to evaluating their composition, morphology , roughness; as well as the electrochemical behavior of the films formed in the presence of simulated physiological media with and without cells by means of electrochemical and cell proliferation techniques to determine their viability as surface modification for their application in bone tissue replacement implants.

Experimental Methodology

The methodology consists of surfaces preparation, and deposition films of ErGO on the substrate CoCrMo by cyclic voltammetry. After each of these steps, the samples were analyzed in order to confirm the presence of desired coatings and study its electrochemical behavior.

Surface modification

The obtaining of the carbon base layers on CoCrMo and Ti6Al4V alloys was carried out by means of electrochemical techniques, specifically cyclic voltammetry. The tests will be carried out in the electrochemical cell used as reference electrode Ag / AgCl and, a graphite counter electrode.

Graphene oxide deposits will be obtained electrochemically reduced the optimum processing conditions by varying the concentration, number of cycles and voltage and will select the coatings with better performance as anticorrosive coating.

Characterization

The samples corrosion rate were analyzed using by electrochemical impedance and the polarization curves, which was performed to obtain information about the corrosion mechanism and protective properties of the coating, The Electrochemical techniques were measured in a 1650 of AC Gill galvanostat potentiostat a reference relectrode of Ag/AgCl and graphite as an auxiliary electrode, while the working electrode was the sample CrCrMo, using as an electrolyte the PBS physiological media pH 6.8.

Results and Discussion

Figure 1 shows the voltammograms of CoCrMo in GO at 2 and 10 minutes after contacting the electrolyte, in which a reduction in the reduction signal is observed to the point of not perceiving the redox potentials at the 10 minutes of immersion. This reduction signal is between -0.6 and -1.05 V / $E_{Ag / AgCl}$. These potentials correspond to the reduction of carboxylic groups (≈-0.85 V / $E_{Ag / AgCl}$), OH and COC (≈-1.05 V / $E_{Ag / AgCl}$) [5], not observing any oxidation signal, it is inferred that said reactions of reduction are irreversible under these conditions.

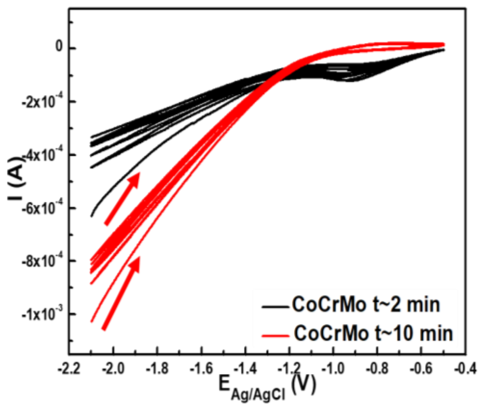

Figure 28. CoCrMo voltammogram immersed in GO at different immersion times.

Impedance spectra were shown in Figure 2 of samples with ErGO deposits deposited by cyclic voltammetry of -2.1 to -.05V for 10 cycles varying the scanning speed from 60 to 600 mV / min. Both spectra were simulated with a circuit [Rs (CPE1 (R1 Ws1))] (inside the figure) where Rs is the electrolyte resistance, R1 and CPE1 are associated with the charge transfer of the oxide reduction reactions and Ws1 is a Probably oxygen diffusive process between the agglomerates of ErGO whose values we see represented in Table 6 where we see a clear tendency of the resistance to increase as the scanning speed decreases, which would indicate that at a lower speed of sweep the coating has better performance against corrosion.

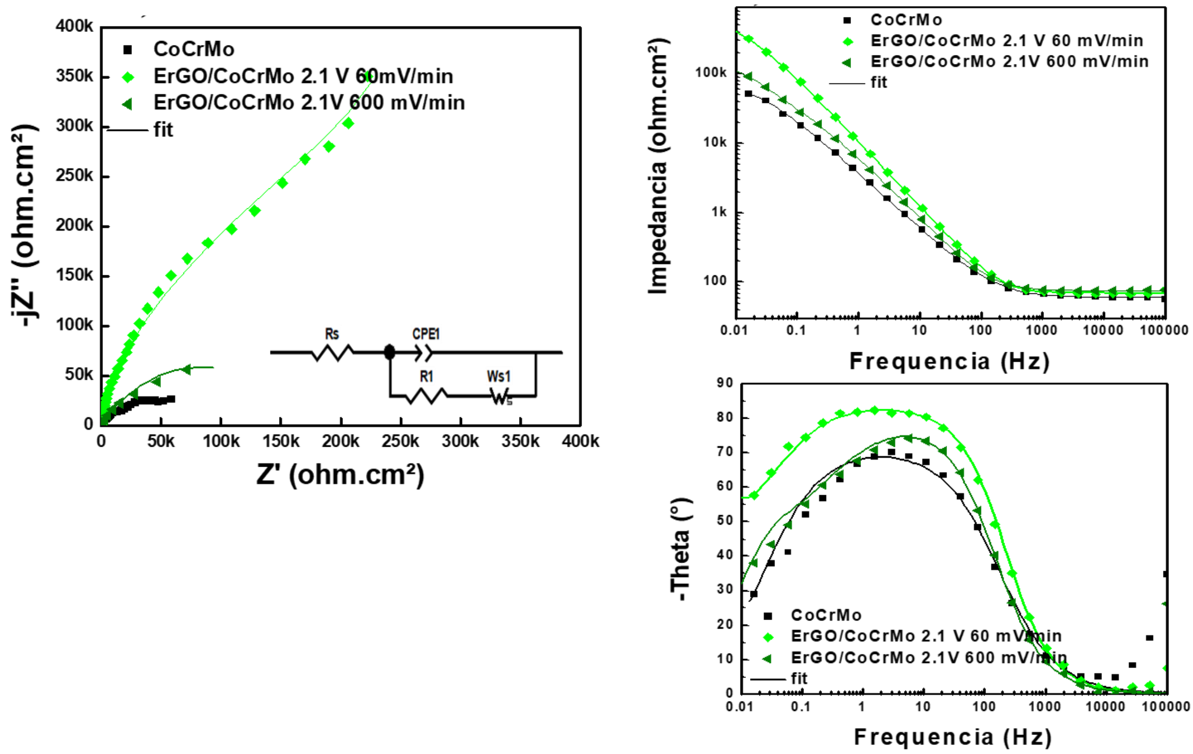

Figure 2. Impedance spectra measured in PBS of CoCrMo bare and with ErGO coating by cyclic voltammetry at different rate of polarization.

In Figure 3 Electrochemical Impedance Spectra of CoCrMo samples coated by cyclic voltammetry at different potentials during 10 cycles with a sweep speed of 0.01V / s are shown, samples polarized at -1, -1.5 and 2V were simulated by the equivalent circuit [Rs (CPE1 (R1))] (figure 44.I) which corresponds to a metal immersed in an electrolyte, in which the tendency to obtain greater impedances is observed, the lower the polarization voltages, Probably due to the formation of more compact and homogeneous graphitic layers.

In Figure 4 the deposited impedance spectra of -2.1 to -0.5 V are presented at 60mV / min varying the number of cycles, which were simulated with a circuit [Rs (CPE1 (R1 Ws1))] (within the figure), again there is a tendency to increase the resistance to load transfer as the number of cycles increases.

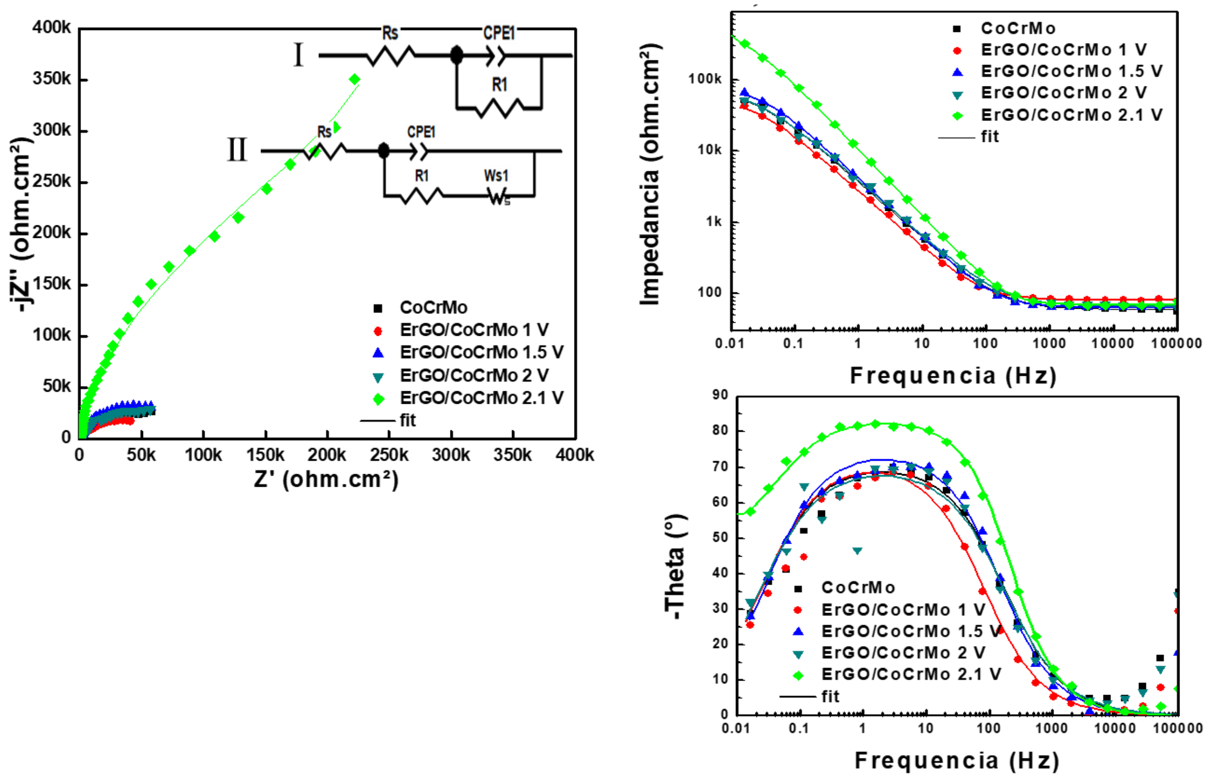

Figure 3. Impedance spectra measured in PBS of CoCrMo bare and with ErGO coating by cyclic voltammetry at different voltage of polarization.

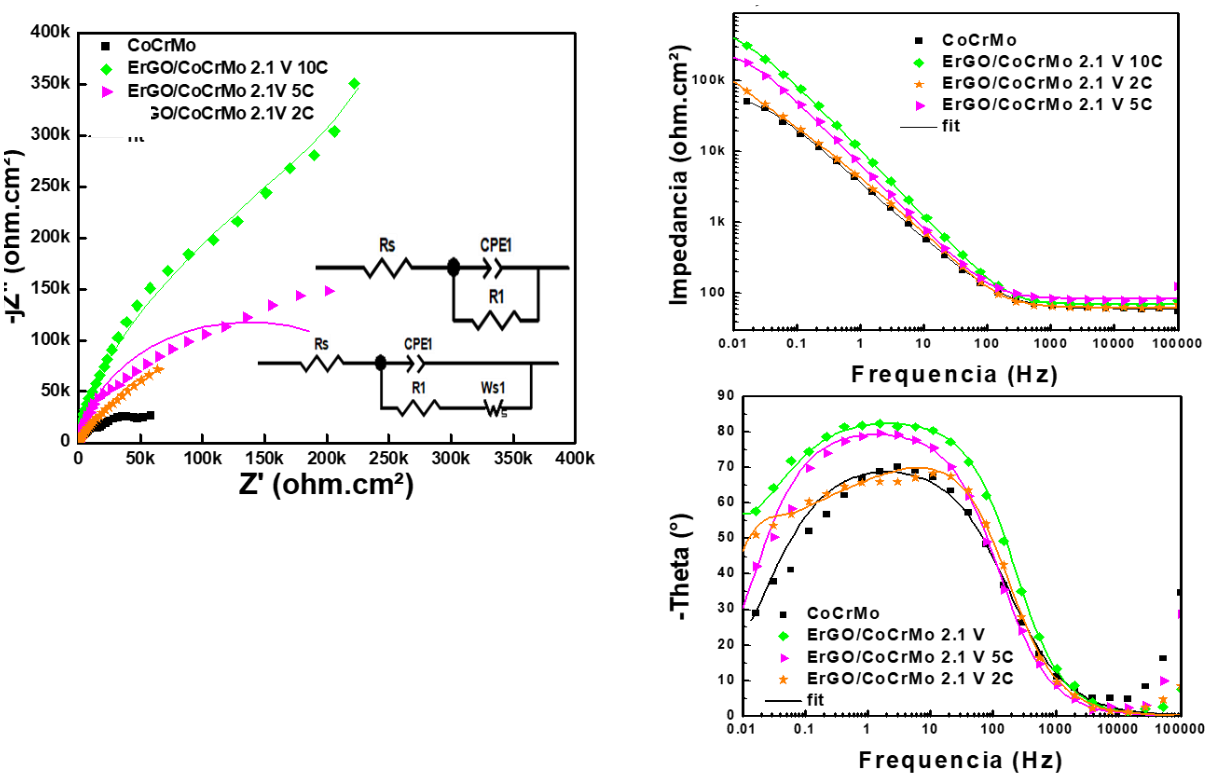

Figure 4. Impedance spectra measured in PBS of CoCrMo bare and with ErGO coating by cyclic voltammetry at different voltage of polarization.

Conclusions

The cyclic voltammetry of the Ti6Al4V alloy in graphene oxide reveals reduction signals of carboxylic groups, OH and C-O-C, in the range of potentials studied.

There is a clear trend in obtaining higher impedance layers at lower polarization rates, higher voltages and number of cycles, besides they seem to provide the CoCrMo alloy of corrosion resistance due to the effect of ErGO deposits.

References

1. S.M. Kurtz, K.L. Ong, E. Lau, M. Widmer, M. Maravic, E. Gómez-Barrena, M.F.de Pina, V. Manno, M. Torre, W.L. Walter, R. Steiger, R.G.T. Geesink, M. Peltola, C. Röder. Int Orthop. 35 (2011) 1783.
2. G. Gajski, z. Jelčić, V. Oreščanin, M. Gerić, V. Garaj-Vrhovac. Biochim Biophys Acta Bioenerg. 1 (2014) 565-576.
3. D. Granchi, E. Cenni, G. Trisolino, A. Giunti, N. Baldini. J Biomed Mater Res B Appl Biomater. 77 (2005) 257–264.
4. MA Wimmer, A. Fischer, R. Büscher, R. Pourzal, C. Sprecher, R. Hauert, JJ. Jacobs. Wear mechanisms in metal-on-metal bearings: The importance of tribochemical reaction layers. Journal of Orthopaedic Research 28 (2010) 436-443
5. S. Y. Toh, K. S. Loh, S. K. Kamarudin, W. R. Daud, *Chem Eng J.*, 251 (2014) 407.