Monitoring by Electrochemical Noise of TiO_2 Thin Films Immersed in Synthetic Physiological Media

José Fernando Flores-Álvarez[1], Francisco J. Rodríguez Gómez[1], Atahualpa O. Garcia-Delgado[1], Dwight Acosta-Najarro[2], Carlos R. Magaña-Zavala[2]

[1]*Depto. Ing. Metalúrgica, Fac. Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, México*

[2]*Depto. Materia Condensada, Instituto de Física, Universidad Nacional Autónoma de México, Ciudad Universitaria, México*

fxavier@unam.mx

Introduction

Electrochemical techniques have been used to assess corrosion since many years ago. Linear polarization resistance (LPR) and electrochemical impedance spectroscopy have been widely used. The relationship between input potential and output current results in the possibility of calculate corrosion rate [1]. However, a small input signal is necessary in those techniques.
On the other hand, electrochemical noise (EN) is an electrochemical technique, which does not disturb the system, recording the spontaneous oscillations in current and voltage, both produced by the formation of micropile on the metal surface.

EN has been used to determine the corrosion rate, by calculating the noise resistance, Rn, and it has been compared to the linear polarization resistance, Rp [2]. It has also been proved that electrochemical noise in corrosion process is bigger than the noise observed in redox systems [3], which has allowed using this technique in the characterization and prediction of localized corrosion. In spite of all advantages and applications of electrochemical noise technique, standardized method neither total consent don't still exist in the theoretical base for the interpretation of the data. EN is still validated with the results of another electrochemical technique used as a standard for comparison; this is especially possible when general corrosion occurs [4].

There is evidence in the literature [2, 5] that noise resistance is equivalent to the polarization resistance, allowing obtaining information about the reaction kinetics, and corrosion rate. The identification of the type of corrosion that is presented uniform, mixed or located is also an advantage of using this technique.

Since passive films are susceptible to suffer pitting corrosion, the use of stainless steel in human prosthesis has been limited, even if mechanical properties are suitable. Titanium dioxide is a good film from biological compatibility point of view, so if a thin film of TiO_2 could be applied on stainless steel, anticorrosive protection as well as compatibility should be assured. The aim of this work is to deposit TiO_2 thin films on stainless steel 316L and evaluate them in synthetic physiological media by electrochemical noise.

Experimental

Electrochemical noise tests were carried out by using an arrangement of three electrodes, including a working electrode (stainless steel 316L, 316L stainless steel coated with TiO_2 and TiO_2-Ce; these coatings were applied by spray pyrolysis), a reference (Saturated Calomel Electrode) and a counter-electrode (platinum wire). EN was carried out by means of a BioLogic SP-300 Science Instruments taking readings each 0.5s until obtaining 2048 points for statistical analysis. A Faraday cage was used in order to avoid interferences.
The experimental results were analyzed using ENAnalyse software for their handling and interpretation.

Results and Discussion

In figure 1a, potential time series are presented for AISI 316L, showing small variations during the first part of the experiment. This series were registered after 0.5 hour of exposure of the metal base in Hartmann solution, since the tested materials are supposed to be used as prosthesis. These variations in potential could be attributed to the passive film formation process and typical local breakup of that film. Figure 1b present the current time series for AISI 316L, showing variations of about 0.1 mA, a very high level in current associated with the formation of pits.

a **b**

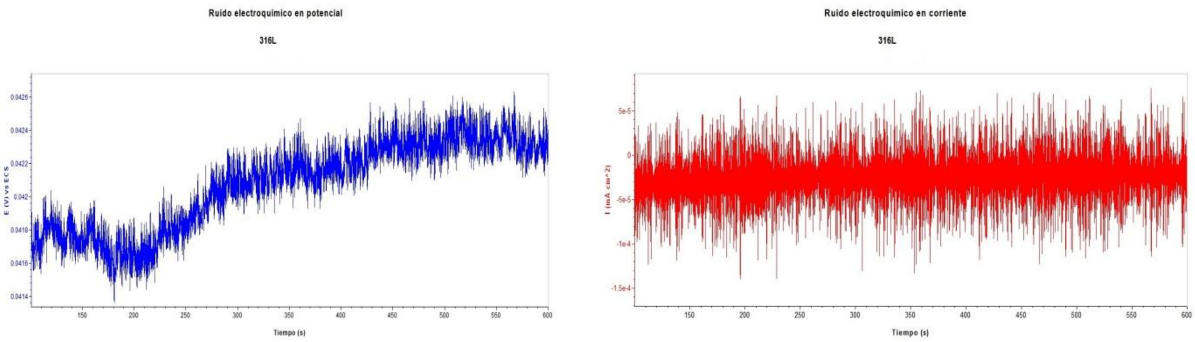

Figure 1 a) electrochemical noise in potential, b) electrochemical noise in current for AISI 316L stainless steel in Hartmann solution.

Potential time series for TiO_2 films are presented in figure 2a, showing variations in potential, which are attributed to the formation and dissolution of a passive layer in the pores of the TiO_2 film, since this layer is a thin coating, and localized corrosion is expected. The use of cerium salts during the formation of the film it is expected to improve the corrosion resistance and the morphology of the attack. It is observed clearly that at 500s there is a very pronounced rupture of the film which means that the material suffered a pit, and then there is a re-formation of corrosion products having protective nature. Figure 2b presents the current time series for TiO_2 films, where variations could be related with the formation and dissolution of products of corrosion, as previously discussed.

In time series for TiO_2 films containing cerium salts, EN was not very different to TiO_2 films. It is supposed from previous experiments that cerium could act as corrosion inhibitor in non-protected pores of the TiO_2 films. Previous experiments using LPR, EIS and Tafel plots showed an improvement in anticorrosion protection, almost an order of magnitude in corrosion rate.

The results from statistical analysis are shown in Table 1. Even if localized corrosion is present in all samples, corrosion rate was calculated; and it is clear that the presence of the TiO_2 thin film is positive even if the film is defective, because of a poor barrier effect due to the low thickness of it.

a b

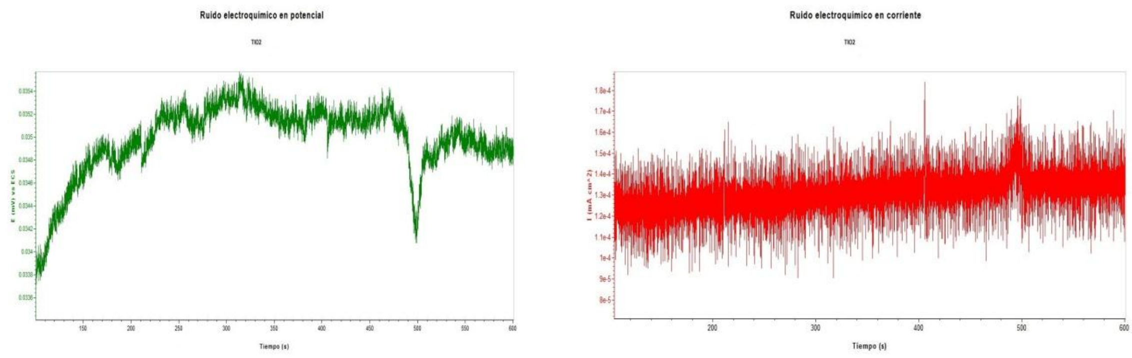

Figure 2 a) Electrochemical noise in potential, b) Electrochemical noise in current for a film of TiO_2 evaluated in solution Hartmann.

Table 1. Statistical results from EN experiments

Sample	$\sigma_{potential}$	$\sigma_{current}$	***Rn*** **(Ω)**	I_{rms}	***1/Rn***	***IL***	***Corrosion***
Hartmann Solution							
AISI 316 L	1.55E-4	2.30E-5	6.75	3.20E-5	0.1479	0.71	Localized
TiO_2 film	4.43E-3	8.20E-5	54.05	5.32E-4	0.0185	0.15	Localized
TiO_2-Ce Film	1.17E-3	8.41E-5	13.93	3.18E-4	0.0717	0.26	Localized

Conclusions

Localized corrosion was determined from EN experiments in all cases, showing an improvement in corrosion protection associated with the presence of the TiO_2 thin films. However, those films are defective and no effect of cerium salts as corrosion inhibitor was detected by using EN.

Acknowledgements

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