Characterization of Organic-inorganic Hybrid Coatings for Corrosion Protection of Galvanized Steel and Electroplated ZnFe Steel

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The development of hybrids materials has been extensively investigated in recent years. The combination of a wide variety of compositions and production processes had permitted the use of these materials in different applications like coatings for corrosion protection of metals. In this work organic-inorganic hybrid materials have been prepared from the hydrolysis of tetraethylorthosilicate and silanol-terminated polidymetilmetoxysilane using a sol-gel process. These materials have been applied on galvanized steel and on steel electroplated with a ZnFe. In order to evaluate the degradation behavior of these coatings, electrochemical techniques (Electrochemical Impedance Spectroscopy and Potentiodynamic Polarization) were used. EIS data was fitted to an equivalent circuit from which the electrochemical parameters were obtained. Results show a good protective character of the hybrid films, when compared with uncovered specimens. The overall performance of the coating systems appears to be highly dependent on the kind of metallic coating applied to the steel.

Keywords: *organic-inorganic hybrids, coatings and corrosion*

1. Introduction

Painted films have been widely used to provide protection and corrosive prevention for metallic surfaces; furthermore, these protective coatings permit the introduction of some properties, such as mechanical strength and hydrofobicity[1]. An industrial coating system may consist of several layers each one having different functions. A chemical-conversion coating of chromate or phosphate is often applied initially to provide a substrate of superior adherence. A primer coating of good surface adherence and inhibitive properties may be required; these improve the durability of the final topcoats, which have maximum resistance to weather conditions[2].

Nowadays, because of toxicity of chromate ions, environmental legislation has pressured for to prohibit the pre-treatment with chromates. As a consequence alternatives pre-treatments have been researched. Thus, organic-inorganic hybrid films made by sol-gel reaction can be developed as a viable alternative. The low temperature processing conditions of the sol-gel hybrids, and their fast curing behavior enables one to perform coil coating processes and to apply thin film on metal sheets[1,3].

The development of a hybrid material is based on the incorporation of oligomers and polymers species into the inorganic matrix. Silanol-terminated polymers or oligomers can be incorporated into an oxide network derived from tetraethylorthosilicate[4]. One kind of polymer species utilised like organic component are the polysiloxanes; they are polymers that contain silicon and oxygen atoms at the principal chain and are characterized for three-dimensional siloxanes net with organic substitutes constituting the units that form the net. Polysiloxanes have been developed for use as industrial raw materials such as resins, oils and rubbers, because of their excellent chemical, physical and electrical properties[5].

The present paper focuses on the corrosion resistance of a sol-gel derived organic-inorganic hybrid coating on steel galvanized and ZnFe electrocoated steel without chromate pre-treatment. The hybrid film coatings were made from tetraethylorthosilicate (TEOS) and Polidymetilmetoxysilane (PDMS) using a sol-gel process. Electrochemical techniques, such as EIS and potentiodynamic polarization, were used to monitor the corrosion behavior of the coating system in a corrosive electrolytic medium. Results were confronted with samples without resin coating to verify the effectiveness of this material. It was demonstrated that the hybrid coating could significantly enhance the corrosion behavior of the studied substrates and the differences between the uncoated surfaces appears to be an important influence upon the results.

2. Experimental Procedure

The experimental procedure was divided in three parts: Preparation of hybrids films, application of the coating upon the substrates and electrochemical characterization. The utilised substrates were: galvanized steel and electroplated ZnFe steel and their characteristics are presented in Table 1. None post plating passivation treatments was made on the substrates.

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2.1. Preparation of hybrids films

Sol-gel process was used in the hybrid films preparation. A proportion of 50% in weight of each component, TEOS and PDMS-OH, was mixed with Dibutylthin diacetate, catalytic, in the proportion of 0.2% weight. This blend was mixed during 15 minutes approximately, until getting an ideal viscosity to application on the substrates.

2.2. Application of the coating

Before coat application, the substrates were cleaned in order to remove any kind of grease. The hybrid film was applied with a baton that spread the covering upon the plates. A box specially designed and dimensioned was used to obtain a resin coating with 25 μm of thickness. The curing process was carried out during 12 hours at a temperature of 95 °C. Samples are referred as Zn and ZnFe, corresponding to the galvanized and electroplated ZnFe specimens and as Zn/C and ZnFe/C when they are coated with hybrid film.

2.3. Electrochemical characterisation

The electrochemical tests were performed at room temperature in a solution of 3% in weight of NaCl. A potentiostat-galvanostat PGZ 100 Voltalab (Radiometer, Denmark), controlled by the VoltaMaster-4 software, was used in the open circuit potential (E_{corr}), Electrochemical Impedance Spectroscopy (EIS), and potentiodynamic polarisation measurements. A three-electrode cell arrangement was used in all experiments. The exposed area of working electrode was 1.86 cm^2. The reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a wire of Platinum. The E_{corr} was monitored during 60 minutes, after which samples were anodically polarised in the range - 1700 to 1000 mV at a scan rate of 2 mV.s^{-1}.

EIS measurements were made at increasing exposure times, until 3 days of exposure. The impedance spectra were ranged from 10^5 to 10^{-2} Hz, using an a.c. signal imposed with amplitude of 10 mV.

The impedance spectra were analysed using ZView software and an electrochemical equivalent circuit model was used to adjust the EIS experimental data and to evaluate the behavior of coatings in the corrosive environment. The chi-squared and sum of squares were used to judge the quality of the fit.

Scanning Electron Microscopy (SEM) was used to study the morphology of coatings. Additionally, the chemical composition was evaluated in an energy dispersive spectrometer (EDS). Surfaces of resin coatings were analysed at the initial conditions and after EIS tests.

3. Results and Discussion

3.1. Electrochemical impedance spectroscopy test

Some characteristics of coatings, such as corrosion behavior, porosity, solution absorption and/or film delamination, can be predict by Electrochemical Impedance Spectroscopy[6,7]. The monitoring of the time dependence of the electrochemical impedance of the coated samples, exposed to the electrolytic solution, allowed the study of the protective character of each coating system to be compared. It is well known that equivalent electrical circuits can be used to explain the electrochemical impedance data obtained by the EIS tests. These

models use a combination of resistance, capacitance and other electrical elements, which have a clear physical meaning, related with the response of the electrochemical system[7]. In this work two equivalent electrical circuit models were used and were presented in Figure 1. Circuit 1, Figure 1a, is a simple circuit where the coating capacitance (C_c) and the polarization resistance (R_p) are represented; this circuit was used to adjust all results from sample Zn/C, and those regarding the first eight hours of immersion in sample ZnFe/C. On the other hand, circuit 2, Figure 1b, was used to fit the results of sample ZnFe/C, after eight hours of immersion, and the uncoated samples (Zn and ZnFe). In this last circuit R_{po} is the pore resistance of coating, C_c is the coating capacitance, R_{ct} is the charge-transfer resistance, C_{DL} is the double-layer capacitance at the coating/solution interface. In both circuits R_e is the electrolytic resistance. All the capacitances shown in the equivalent electrical circuit are mathematically modelled using a constant phase element (cpe); this element represents all the frequency dependent electrochemical phenomena[8]. The EIS experimental data were successful adjusted to these circuits.

In Figure 2 the open circuit potential (E_{corr}) obtained for all samples is presented. As it can be observed, after one hour of immersion, the ZnFe - coated steel sample exhibits a E_{corr} slightly higher than that of the galvanized steel (Zn). However, during immersion the behavior of the ZnFe sample appears to approach that of the Zn, this being an indication of a similar corrosion tendency for both samples. The hybrid film coated samples (Zn/C and ZnFe/C) reveal a corrosion potential substantially higher than their respective substrates, showing that these coating behave like a barrier, decreasing the tendency to corrosion of the substrates.

Figures 3 and 4 present the Bode plots resulted from the EIS tests, in which a comparison between uncoated and coated samples is made.
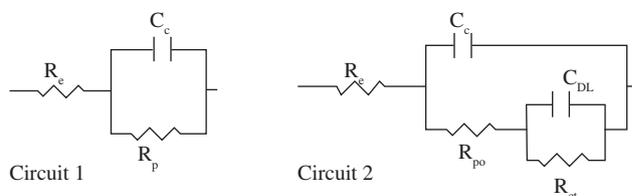

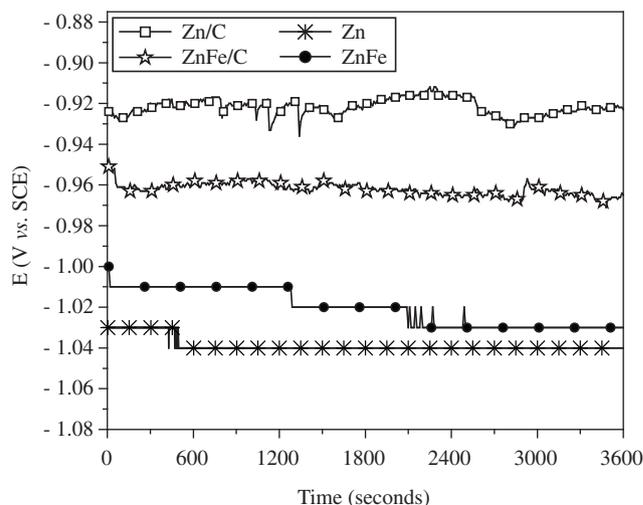**Figure 1.** Equivalent electrical circuits utilised to fit EIS data.

Figure 2. Evolution of open circuit potential with the time. in Zn, ZnFe, Zn/C and ZnFe/C systems.

Table 1. Substrates used and their characteristics.

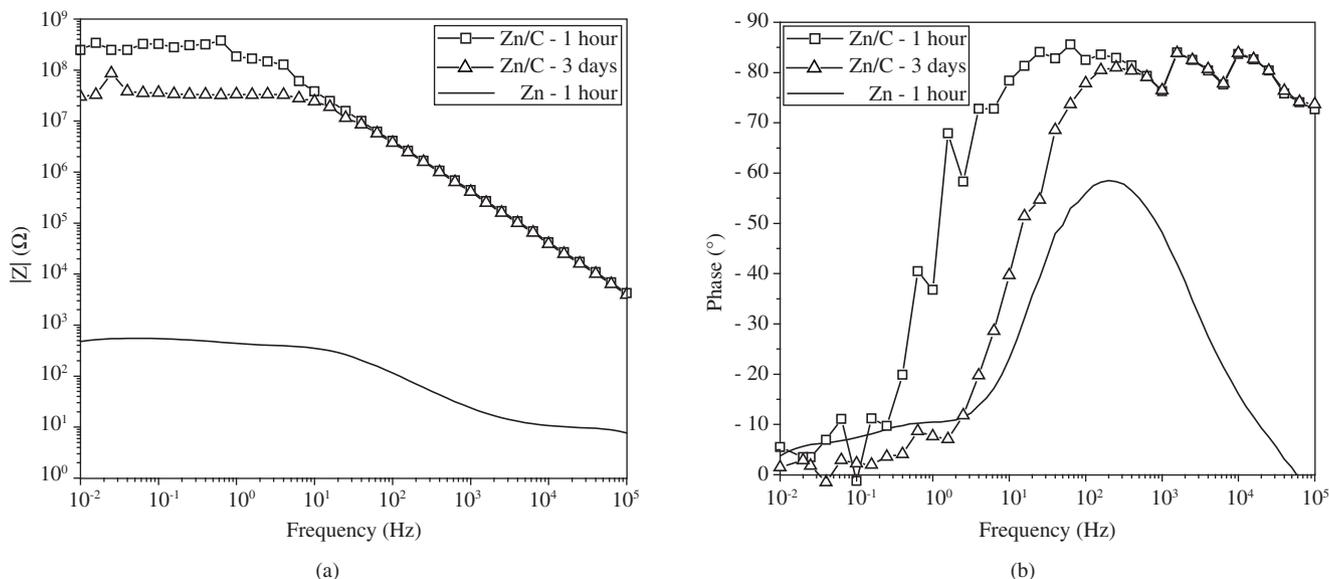| Substrate	Metallic coating thickness (μm)
Galvanized steel	5
Electroplated ZnFe steel	5

Figure 3. Representative Bode plots obtained in substrate Zn and coated Zn/C samples, after 1 hour and 3 days of immersion in 3% NaCl solution: a) Bode Z; and b) Bode Phase.
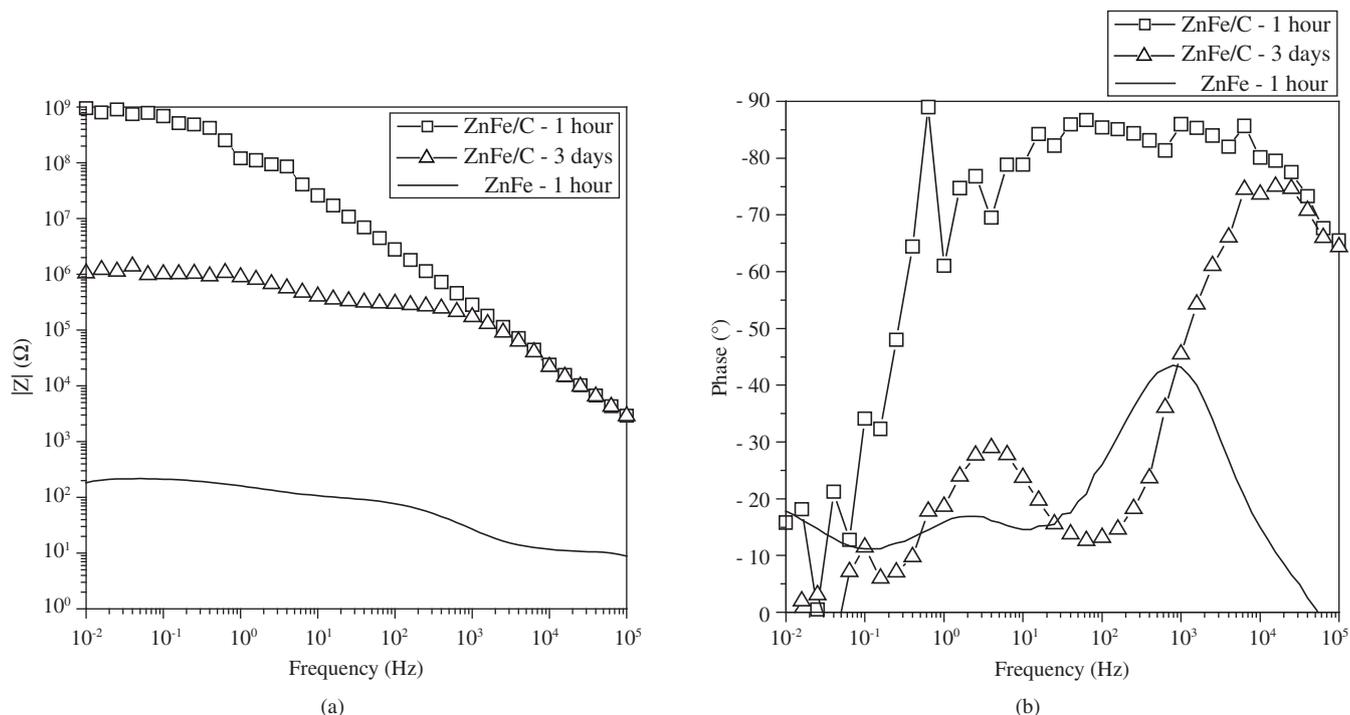

Figure 4. Representative Bode plots obtained in substrate ZnFe and coated ZnFe/C samples, after 1 hour and 3 days of immersion in 3% NaCl solution: a) Bode Z; and b) Bode Phase.

The first remark to be done refers to the barrier against corrosion provided by hybrid films. As it can be observed in Figure 3a and 4a, after one hour of immersion coated samples present impedance modulus (|Z|) values, at low frequencies ranges, several decades higher ($10^{-8}\Omega$ for Zn/C sample and $10^{-9}\Omega$ for ZnFe/C sample) than that found at the same immersion time in the uncoated samples (approximately $10^{-2}\Omega$ for both, Zn and ZnFe samples). Besides, phase angles approaching 90°, at high frequencies, are indicative of a capacitive behavior of the coatings (see Figure 3b and 4b).

Also, as it can be seen in Figure 3a and 4a, after the third day of immersion the |Z| values of the resin coated samples remains high

($10^{-7}\Omega$ for Zn/C sample and $10^{-6}\Omega$ for ZnFe/C sample), indicating that the hybrid film continues offering a good corrosion protection. Nevertheless, in the Zn/C sample a slight decrease in the |Z| values is observed, while in the ZnFe/C sample the |Z| values diminishes ca. three decades, suggesting a degradation of the protective properties of the hybrid film upon ZnFe substrate. This fact can be confirmed by a second relaxation time observed at the low frequencies region, as it can be seen in Figure 4b.

According to some authors, the evaluation of coating capacitance (C_c) can be associated to water uptake or the entry of electrolyte into the coating[6,9,10]. In Figure 5 the dependence of the C_c with the immer-

sion time is presented. Firstly, the C_c values for the Zn/C and ZnFe/C are always lower than the values calculated for the samples without resin (Zn and ZnFe), indicating a good protective character of the resin over the substrate. Also, as it can be observed in the figure, C_c for the Zn/C samples maintains very stable, throughout the immersion time, this being an indication of the maintenance of good protective properties of the hybrid film coating. Regarding the ZnFe/C sample, C_c values show a decline after eight hours of immersion, which can be attributed to the transition from one to two relaxation time; in other words, the surface of samples presents, from this moment on, two capacitances, one related to film hybrid coating (at high frequency ranges) and another (C_{DL}) associated a process that occur in the interface coating/ZnFe (at low frequency ranges). This double-layer capacitance (C_{DL}) is related to the area where the delamination or corrosion occurs[6], what means that hybrid film upon ZnFe substrate presents the lowest corrosion protection, due to the electrolyte that penetrate through the coating more easily.

In Figure 6 the evolution of polarisation resistance (R_p) as function of immersion time is presented. These values were extracted from the fitting of EIS experimental data and correspond to sum of R_{po} and R_{ct}. The protective ch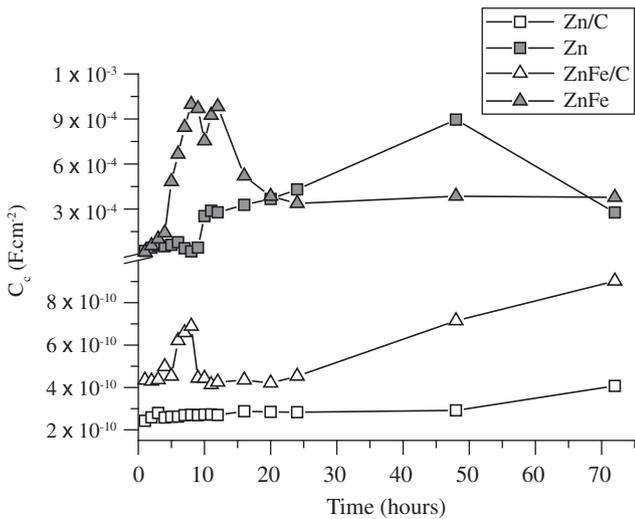aracteristics of hybrid films can be confirmed by the high values of R_p exhibited by samples Zn/C and ZnFe/C. However, the polarisation resistance decreases for both samples during the immersion time, indicating an increasing ionic conductivity for the coating and a low protective capacity[11]. In the first moments of immersion, R_p for the ZnFe/C sample has higher values ($10^9\,\Omega.cm^2$) than that calculated for the Zn/C sample and remains nearly constant with the increasing time. However, after twelve hours of immersion an abrupt decrease was observed and at the end of three days of immersion the R_p values for ZnFe/C coating comes to a value near $10^6\,\Omega.cm^2$, almost two decades lower than that of the Zn/C sample. These results shows that the hybrid films applied on galvanized substrate have a better protective behavior and a greater stability, since the R_p values of sample Zn/C remain in the range of 10^9 - $10^8\,\Omega.cm^2$ and almost constant after sixteen hours of immersion. In comparison, in uncoated systems (Zn and ZnFe) R_p values ranging between 10^2 and $10^3\,\Omega.cm^2$ were found.
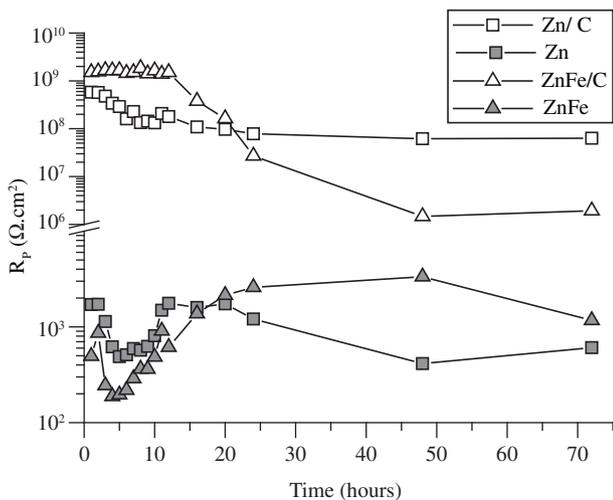
3.2. Potentiodynamic polarisation test

Representative potentiodynamic polarisation curves expressing the corrosion behavior of the samples are presented in Figure 7. A first remark to be made refers to the anodic polarisation curves for Zn/C and ZnFe/C samples. Both curves display a passive plateau with passive current densities smaller than their respective substrates. The calculated corrosion current densities are plotted in Figure 8. The smallest corrosion current density value found, corresponds to the Zn/C sample, confirming the better protective behavior to hybrid film upon galvanized steel, indicated by the EIS experiments (high R_p values and low C_c values). As it can be seen in Figure 7, the passive current density for the hybrid film coated samples (Zn/C and ZnFe/C) are ca. 2 decades lower than that of the Zn and ZnFe samples, respectively, this being a strong indication of the protective character of the hybrid film.

Table 2 shows a comparison between R_p and i_{corr} for the different samples. As expected a high R_p corresponds to a lower corrosion current density. The protection efficiency, P, of the hybrid film coating on the galvanized and ZnFe electroplated steel substrates can be calculated by using equation 1[1]. Where i^0_{corr} and i_{corr} denote corrosion current density of the substrate and coated samples, respectively.

$$P\% = 100(1 - i_{corr} / i^0_{corr}) \qquad (1)$$

The corrosion protection efficiency of hybrid film upon galvanized was found to be 99% and to hybrid film on ZnFe was 91%.

Figure 5. Time dependence of Coating capacitance for all samples.

Figure 6. Evolution of polarisation resistance with time for all systems (coated and uncoated samples).
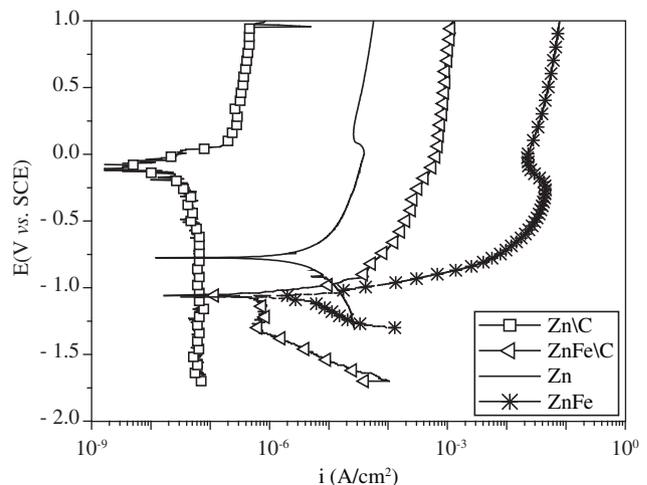

Figure 7. Potentiodynamic polarization curves of coated and uncoated samples.

The surfaces of samples after the three days of immersion in the saline solution did not show significant modifications on the surface after. The coatings appear to be very smooth and by EDS analysis it was not possible to identify the presence of any corrosion products at the surfaces of samples.

In fact, both EIS and potentiodynamic polarization results indicate that the behavior of the hybrid-coated samples is a consequence of the events happening at the hybrid film/substrate interface. Thus, as referred above, the ZnFe/C sample, although presenting a superior corrosion resistance in the beginning of the tests, during immersion these values have a tendency to decrease. The difference between the two substrates can be used to explain these results. Galvanized substrate presents a better behavior in terms of corrosion, what can be associated the better performance of hybrid film coating on this substrate.

In Figure 8 cross-sections representative of both hybrid-coated systems are presented. As it can be seen, in both systems the hybrid film coating appears to be very compact, and no open pores can be detected. However, the observation of the hybrid film/substrate interface reveals a defective adhesion of the coating to the ZnFe sample, Figure 8b, which might lead to accumulation of electrolyte, in case of its penetration through the coating. In another hand, the interface hybrid film/substrate to sample Zn/C, Figure 8a, presents very homogeneous, without any points indicative of a lost in an adhesion. These images reinforce the results obtained by electrochemical tests;

the behavior of hybrid film upon galvanized steel is better than upon ZnFe electroplated steel.

Figure 6 shows that R_p values to galvanized are higher than the values to ZnFe electroplated steel, this characteristic can exert influence upon samples with film hybrid coating in terms of maintenance of the properties. Another important factor could be the structure of coatings and the kind of interactions between the substrate surface and coating hybrid. However, the evaluation between the structure and the properties of coatings films has not established yet and are part of future researches.

4. Conclusions

The corrosion resistance of a sol-gel derived organic-inorganic hybrid coating on galvanized steel and ZnFe electrocoated steel, immersed in a 3% NaCl solution was studied by electrochemical spectroscopy impedance (EIS) and potentiodynamic polarisation techniques. It was well demonstrated that the EIS combined with the electrochemical standard technique are powerful methods to characterize the corrosion behavior and the efficiency of hybrid coatings.

These hybrid coatings, prepared by sol-gel processes, applied upon galvanized steel and ZnFe electrocoated steel substrates demonstrated ability of providing supplemental corrosion protection by forming a physical barrier. However the galvanized steel coated samples have shown to possess better corrosion resistance than ZnFe coated samples. It was found that differences on the response at the substrate/hybrid film interface might be responsible for this different behavior.

Acknowledgments

Table 2. Values of R_p and i_{corr} for all samples.

Sample	R_p ($\Omega.cm^2$) 1 hour	R_p ($\Omega.cm^2$) 3 days	i_{CORR} ($\mu A/cm^2$)
Zn	1710.5	630.6	1.5
ZnFe	314.5	1232.0	2.9
Zn/C	5.8×10^8	6.3×10^7	2.6×10^{-3}
ZnFe/C	1.5×10^9	1.4×10^6	2.5×10^{-1}
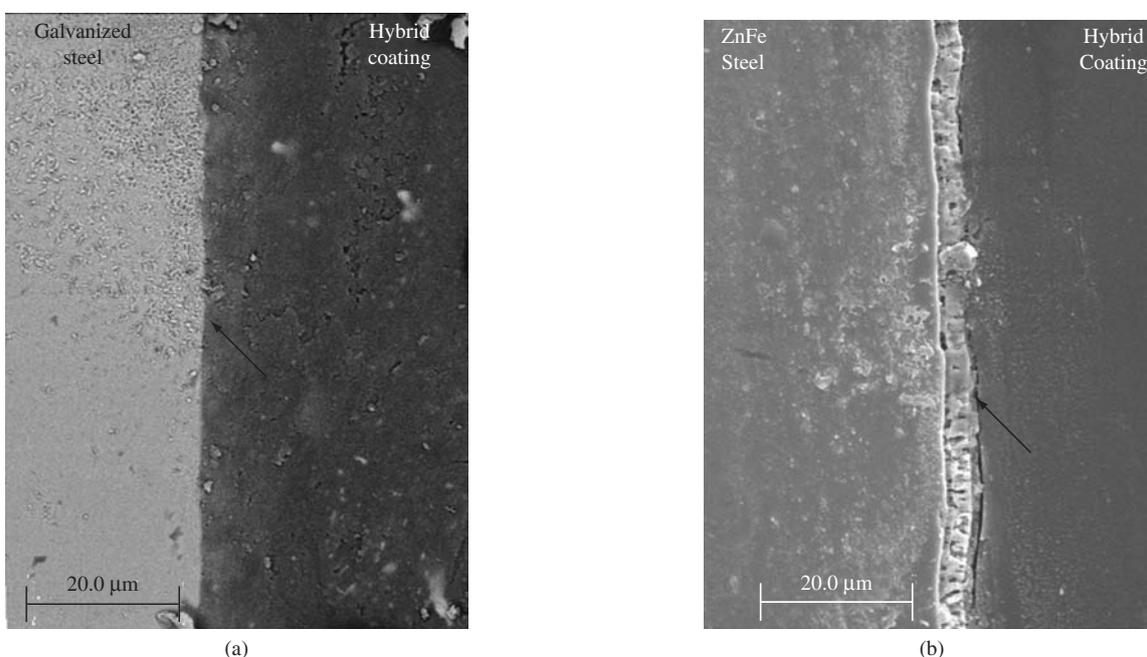
Figure 8. a) SEM micrographs of the cross section of Zn/C; and b) ZnFe/C.

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