

# ORGANIC-INORGANIC HYBRID COATINGS FOR CORROSION PROTECTION OF GALVANIZED STEEL AND ELECTROPLATED ZnFe STEEL

*M.E.P.Souza<sup>1,2\*</sup>, E.Ariza<sup>2</sup>, M.Ballester<sup>3</sup>, I.V.P.Yoshida<sup>4</sup>, L.A. Rocha<sup>2,5</sup>, C.M.A.Freire<sup>1</sup>*

<sup>1</sup>*Faculty Mechanical Engineering, UNICAMP, C.P. 6122, CEP 13083-970, Campinas, S.P, Brasil - eliziane@fem.unicamp.br*

<sup>2</sup>*Research Centre on Interfaces and Surfaces Performance, University of Minho, Guimarães, Portugal.*

<sup>3</sup>*Applied Physics Department, Physics Institute, UNICAMP, Campinas, S.P, Brasil.*

<sup>4</sup>*Chemistry Institute, UNICAMP, Campinas, S.P, Brasil.*

<sup>5</sup>*Department of Mechanical Engineering, University of Minho, Guimarães, Portugal.*

## ABSTRACT

*The development of hybrids materials by the sol-gel process has been extensively investigated in recent years. The combination a wide variety of compositions and production processes had permit the use of these materials in different applications like coatings for corrosion protection of metals and abrasion resistant coatings. In this work organic-inorganic hybrid materials have been prepared from the hydrolysis of tetraethylorthosilicate (TEOS) and silanol-terminated polydimethylmetoxysilane (PDMS) using a sol-gel process. The composition evaluated was 50% TEOS-50% PDMS. These materials have been applied on galvanized steel and on steel electroplated with a ZnFe alloy. In order to evaluate the degradation behaviour of these coatings, electrochemical techniques were used. They consisting in the monitoring of the open-circuit potential ( $E_{corr}$ ), and in the realization of potentiodynamic polarization measurements of the samples, which was performed in a 3% NaCl aqueous solution. Additionally, electrochemical impedance spectroscopy (EIS) was used as a complementary technique for the evaluation of the corrosion mechanisms of the coating system. The surface of the samples, before and after the electrochemical tests, have been inspected by SEM and EDS. 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 capacitance of the films increased with the immersion time, in accordance to the behaviour expected for an organic film. The overall performance of the coating systems appears to be highly dependent on the kind of metallic coating applied to the steel. Coatings applied upon galvanized steel showed larger  $|Z|$  values when compared with those applied to the electroplated steel, indicating a superior corrosion resistance of the former and a better stability throughout the immersion time.*

**Keywords:** *organic-inorganic hybrids, coatings, EIS, corrosion.*

## 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 (Chou, 2001). 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 (Jones, 1996).

Nowadays, because of toxicity of chromate ions, environmental legislation has pressured for to prohibit the pre-treatment with chromates. As a consequence alternative pretreatments 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 behaviour enables one to perform coil coating processes and to apply thin film on metal sheets (Schottner, 2001; Chou, 2001).

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 (Télez, 2003). 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 (Abe, 2000).

The present paper focus on the corrosion resistance of a sol-gel derived organic-inorganic hybrid coating on steel galvanized and ZnFe electrocoated steel without chromate pretreatments. The hybrid film coatings were made from tetraethylorthosilicate (TEOS) and Poldymetilmetoxysilane (PDMS) using a sol-gel process. Electrochemical techniques, such as EIS and potentiodynamic polarization, were used to monitor the corrosion behaviour 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 behaviour of the studied substrates and the differences between the uncoated surfaces appears to be an important influence upon the results.

## 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 postplating passivation treatments was made on the substrates.

**Table1:** Substrates used and their characteristics.

Substrate	Metallic coating thickness ( $\mu\text{m}$ )
Galvanized steel	5
Electroplated ZnFe steel	5

### 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.

#### 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 $\mu$ m 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.

#### 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<sup>2</sup>. 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 min, after which samples were anodically polarised in the range -1700 to 1000 mV at a scan rate of 2mV.s<sup>-1</sup>

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

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 behaviour of coatings in the corrosive environment.

The morphology of coatings was studied by Scanning Electron Microscopy (SEM). 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.

## **RESULTS AND DISCUSSION**

#### Electrochemical Impedance Spectroscopy test

Some characteristics of coatings, such as corrosion behaviour, porosity, solution absorption and/or film delamination, can be predict by Electrochemical Impedance Spectroscopy (McIntyre, 1996; Bonora, 1996). 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 (Bonora, 1996). In this work two equivalent electrical circuit models were used. Fig. 1., shows the circuit 1, which 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 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 (Macdonald, 1986). The EIS experimental data were successfully adjusted to these circuits.

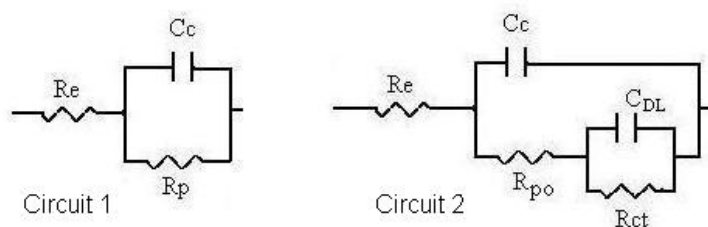


Figure 1: Equivalent electrical circuits utilised to fit EIS data.

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 behaviour 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.

Figure 3 presents the Bode plots resulted from the EIS tests, in which a comparison between uncoated and coated samples is made. The first remark to be done refers to the barrier against corrosion provided by hybrid films. As it can be observed in Fig. 3a and 3c, 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  $90^{\circ}$ , at high frequencies, are indicative of a capacitive behaviour of the coatings (see Fig. 3b and 3d).

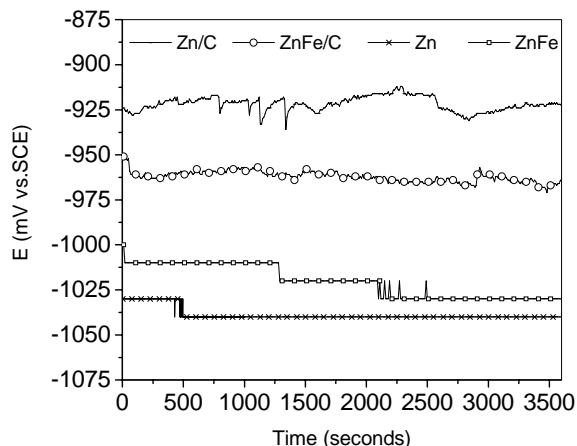


Figure 2: Evolution of open circuit potential with the time. in Zn, ZnFe, Zn/C and ZnFe/C systems

Also, as it can be seen in Fig. 3a and 3c, 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 3d.

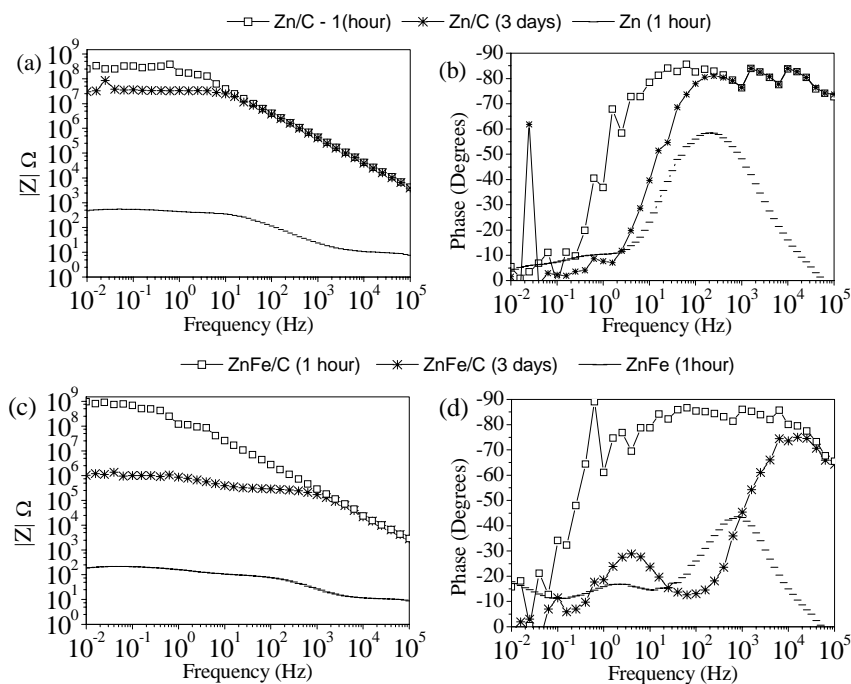


Figure 3: Representative Bode plots obtained in substrates (Zn and ZnFe) and coated (Zn/C and ZnFe/C) samples, after 1 hour and 3 days of immersion in 3% NaCl solution.

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 (Bajat, 2003; McIntyre, 1996 and Tsai, 1993). In fig. 4 the dependence of the  $C_c$  with the immersion 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 (McIntyre, 1996), what means that hybrid film upon ZnFe substrate presents the lowest corrosion protection, due to the electrolyte that penetrate through the coating more easily.

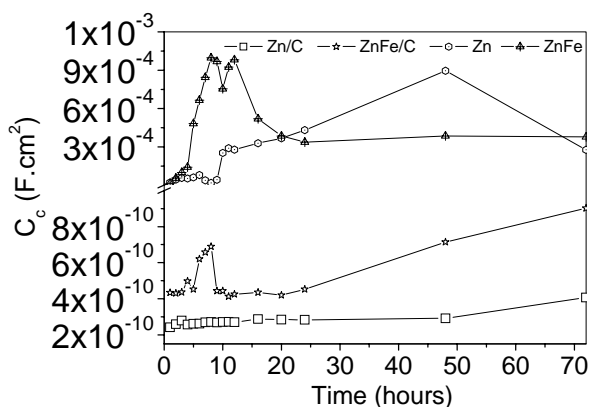


Figure 4: Time dependence of Coating capacitance for all samples.

In figure 5 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 corresponds to sum of  $R_{po}$  and  $R_{ct}$ . The protective characteristics 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 (Makasimovic, 1992). In the first moments of immersion,  $R_p$  for the ZnFe/C sample has higher values ( $10^9 \Omega \cdot cm^2$ ) 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  $10^6 \Omega \cdot cm^2$ , 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 behaviour and a greater stability, since the  $R_p$  values of sample Zn/C remain in the range of  $10^9 - 10^8 \Omega \cdot cm^2$  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.

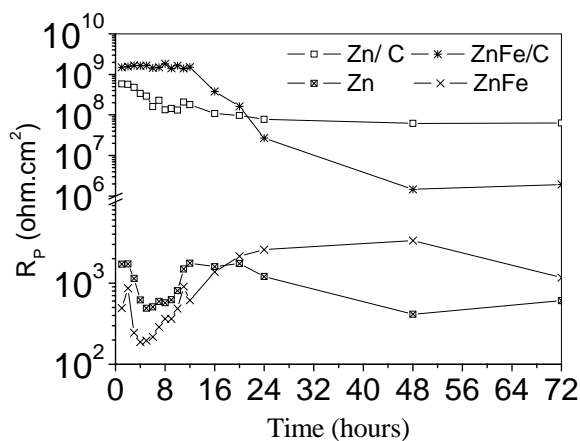


Figure 5: Evolution of polarisation resistance with time for all systems (coated and uncoated samples)

#### Potentiodynamic polarisation test

Representative potentiodynamic polarisation curves expressing the corrosion behaviour of the samples are presented in figure 6. 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 7. The smallest corrosion current density value found, corresponds to the Zn/C sample, confirming the better protective behaviour 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 Fig. 6, 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.

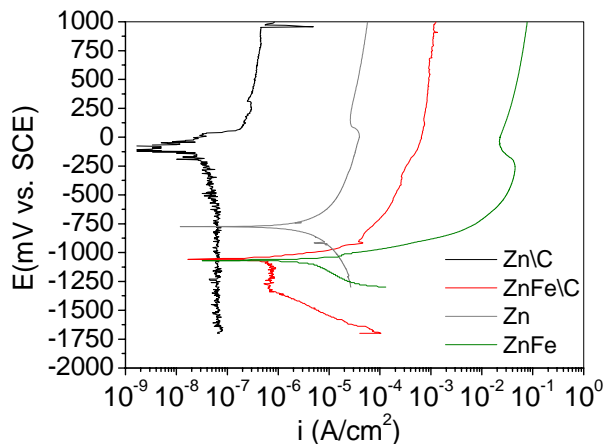


Figure 6: Potentiodynamic polarization curves of coated and uncoated samples.

Figure 7 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 (Chou, 2001) using equation 1.

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

where  $i_{corr}^0$  and  $i_{corr}$  denote corrosion current density of the substrate and coated samples, respectively. The corrosion protection efficiency of hybrid film upon galvanized was found to be 99% and to hybrid film on ZnFe was 91%.

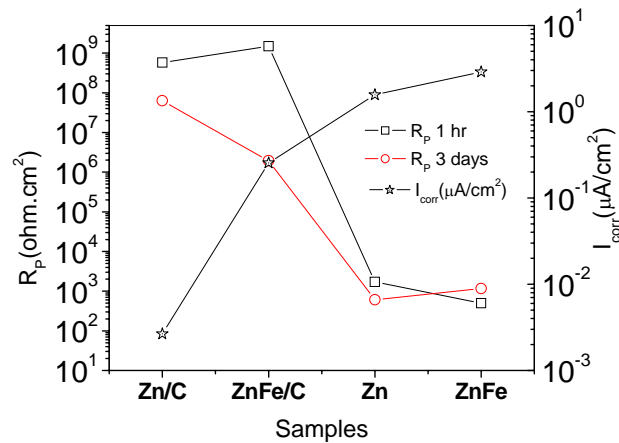


Figure 7: Evaluation of  $R_p$  and  $i_{corr}$  for all samples.

As it can be observed in figure 8, SEM micrographs of samples showed no significant modifications on the surface before the three days of immersion in the saline solution. 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.

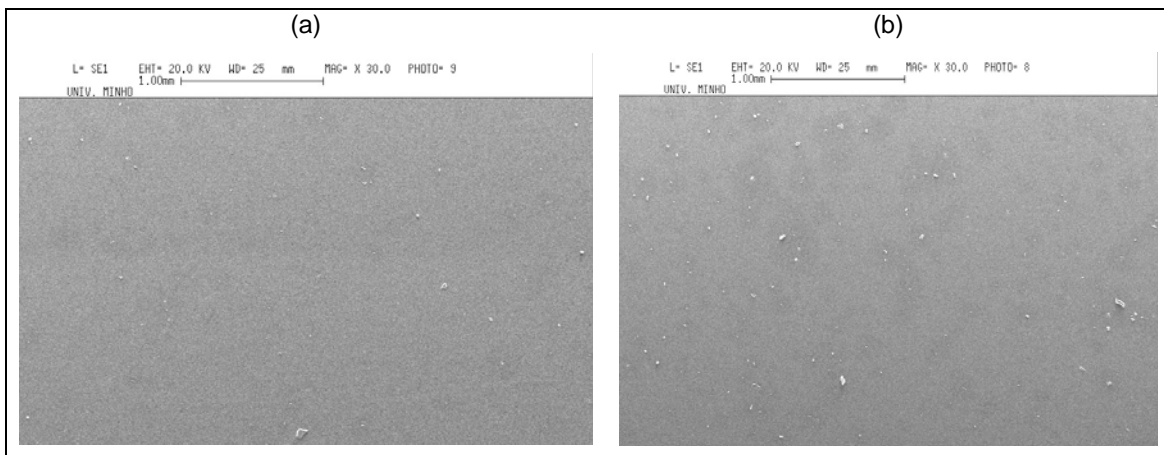


Figure 8: SEM micrographs of surface of sample ZnFe/C before EIS test (a) and after the EIS test (b).



In fact, both EIS and potentiodynamic polarization results indicate that the behaviour 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 behaviour in terms of corrosion, what can be associated the better performance of hybrid film coating on this substrate. Figure 5 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.

## 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 behaviour 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 behaviour.

## ACKNOWLEDGEMENTS

The authors gratefully acknowledgements to Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (**CAPE**S), to Conselho Nacional de desenvolvimento científico e Tecnológico (CNPq) of Brasil, and to Fundação para a Ciência e a Tecnologia (FCT), Portugal – project - SFRH/BPD/5518/2001 by the financier support.

## References

- 1- Abe, Y.; Kagayama, K.; Takamura, N.; Gunji, T.; Yoshihara, T.; Takahashi, N. Preparation and properties of polysilsesquioxanes. Function and characterization of coating agents and films. **Journal of Non-Crystalline Solids**, v. 261, p. 39-51, 2000.

- 2- Bajat, J.B.; Miskovic-Stankovic, V.B.; Kacarevic-Popovic, Z. The influence of steel surface modification by electrodeposited Zn-Fe alloys on the protective behaviour of epoxy coating. **Progress in Organic Coatings**, v. 47, p. 49-54, 2003.
- 3- Bonora, P.; Deflorian F.; Fedrizzi L. Electrochemical impedance spectroscopy as a tool for investigation underpaint corrosion. **Electrochimica ACTA**, v. 41, p. 1073-1082, 1996.
- 4- Chou, T.P.; Chandrasekaran, C.; Limmer, S.J.; Seraji, S.; Wu, Y.; Forbess, M.J.; Nguyen, C.; Cao, G.Z. Organic-inorganic hybrid coatings for corrosion protection. **Journal of Non-Crystalline Solids**, v.290, p. 153-162, 2001.
- 5- Jones, D.A. **Principles and prevention of corrosion**. USA: Prentice-Hall, Inc, 1996.
- 6- Maksimovic, M.D.; Miskovic-Stankovic, V.B. The corrosion behaviour of epoxy-resin electrocoated steel. *Corrosion Science*, v.33, n. 2, p. 271-279, 1992.
- 7- McIntyre, J.M.; Pham, H. Q. Electrochemical impedance spectroscopy; a tool for organic coatings optimizations. **Progress in Organic coatings**, v. 27, p. 201-207, 1996.
- 8- Schottner, G. Hybrid sol-gel derived polymers: applications of multifunctional materials. **Chem. Mater.**, v. 13, p. 3422-3435, 2001.
- 9- Téllez, L.; Rubio, J.; Rubio, F.; Morales, E.; Oteo, J.L. Synthesis of inorganic-organic hybrid materials from TEOS, TBT and PDMS. **Journal of Materials Science**, v. 38, p. 1773-1780, 2003.
- 10- Tsai, C.H.; Mansfeld, F. Determination of coating deterioration with EIS. 2. Development of a method for field testing of protective coatings. **Corrosion**, v. 49, n. 9, p. 726-737 1993.