

## Influence of Silane Films in the Zinc Coating post- treatment

Marlla Vallerius da Costa <sup>1, a</sup>, Cláudia Trindade Oliveira <sup>2, b, \*</sup>, Jean-Pierre Bonino <sup>3</sup>, Tiago Lemos Menezes <sup>1, c</sup>, Célia de Fraga Malfatti <sup>1, d</sup>, Iduvirges Lourdes Muller <sup>1, e</sup>

<sup>1</sup>Universidade Federal do Rio Grande do Sul (UFRGS) – PPGEM – Brazil

<sup>2</sup>Centro Universitário Feevale – ICET – Brazil

<sup>3</sup>Université Paul Sabatier – Institut Carnot CIRIMAT – France

<sup>a</sup>marlla.vallerius@gmail.com, <sup>b</sup>cto11973@gmail.com, <sup>c</sup>tiagolm@gmail.com,

<sup>d</sup>malfattimc@gmail.com and <sup>e</sup>ilmuller@ufrgs.br

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**Abstract.** The sol-gel process based on silanes precursors appeared in recent years as a strong alternative for post-treatment to provide an optimization of the protective efficacy of zinc. Moreover, this process has been used to replace chemical chromating conversion based on hexavalent chromium. The silane films are hybrid compounds that provide characteristics of both polymeric materials, such as flexibility and functional compatibility, and ceramic materials, such as high strength and durability. The present work aimed to evaluate the influence of silane films obtained by dip-coating, on the characteristics of electrodeposited zinc coatings. The xerogel films showed a homogeneous surface and a better performance on the corrosion resistance than zinc coating without post-treatment, what can be confirmed by the electrochemical impedance results. These tests showed that application of the silane film promotes the occurrence of one more time constant compared to pure zinc system, hindering the corrosion process.

### Introduction

Zinc is one of the most used protective coatings of steels, because of its role as sacrificial anode, its low cost and easy application. However, in high temperatures and wet atmospheres, zinc does not present a satisfactory performance [1]. In order to reduce the corrosion rate of zinc coatings, a post-treatment is necessary and generally consists in a chemical conversion layer. A very common zinc coating surface post-treatment is the passivation in chromates bath, which is very efficient both in reducing the zinc corrosion rate and increasing adhesion with organic films. Unfortunately the cancer-producing and toxic activity of Cr<sup>6+</sup> (important component of the post-treatment bath and chemical conversion layer) are well known. Many different treatments have been studied in the last decade in order to avoid the use of Cr<sup>6+</sup> [2].

Sol-gel coatings are presented as a promising alternative to chromate surface treatments. These films provide an excellent adhesion to the substrate and a suitable protection against corrosion by creating a chemically inert barrier between the metal and the aggressive environment [3]. A variety of metal alkoxides can be used as precursors, but to improve the protection against corrosion, alkoxides based on silane are the most employed. The silane films obtained by sol-gel process are hybrid compounds that provide characteristics of polymeric materials, such as flexibility and functional compatibility, and ceramic materials, such as high strength and durability. Literature reports that modification of silane films with inorganic inhibitors based on rare earth salts were tested and this inhibitor effectively

protected the substrate against corrosion [4]. The objective of this work was to study the influence of silane films in the post-treatment of zinc coatings. Silane-cerium coatings were obtained by dip-coating from a sol constituted by MAP and TEOS silanes precursors with the addition of cerium salts as corrosion inhibitor.

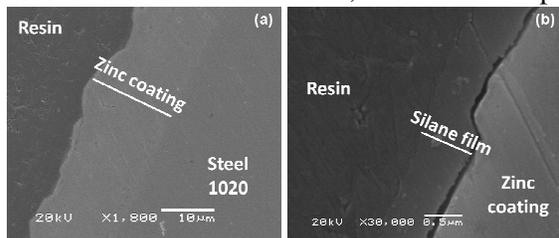
## Experimental

Zinc coatings were prepared on carbon steel substrates by electrodeposition from a plating bath containing:  $\text{ZnCl}_2$   $85\text{g.L}^{-1}$ ;  $\text{KCl}$   $210\text{g.L}^{-1}$ ,  $\text{H}_3\text{BO}_3$   $25\text{g.L}^{-1}$ . The electrolyte temperature was  $20^\circ\text{C}$  -  $35^\circ\text{C}$  and pH 4,8 - 5,2. The electrodeposition process of these coatings was carried out with a  $2\text{ A.dm}^{-2}$  current density. The zinc coating thickness was about  $20\mu\text{m}$ . The silane films were obtained on zinc coating by a dip-coating process in a sol constituted with silane precursors:  $\gamma$ -methacryloxypropyl-trimethoxysilane (MAP -  $\text{C}_{10}\text{H}_{20}\text{O}_5\text{Si}$ ), tetraethoxysilane (TEOS -  $\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$ ) and  $0.01\text{ mol.L}^{-1}$  of cerium nitrate ( $\text{Ce}(\text{NO}_3)_3$ ). Ethanol and water were used as solvent. The withdrawal speed of substrates from the sol was  $20\text{ cm.min}^{-1}$ . Scanning electron microscopy (SEM) was used to evaluate the thickness, by cross section, and the morphology of silane film/Zn coatings. The average roughness of the zinc and silane/zinc samples was obtained by optical profilometry (profilometer AMBIOS XP-2). The corrosion performance of the silane/Zn system has been evaluated by open circuit potentials (OCP) monitoring and electrochemical impedance spectroscopy (EIS) measurements in a 5% NaCl solution. The experimental apparatus used for the electrochemical investigation was a potentiostat (AUTOLAB PGSTAT 30) coupled to a frequency response analyzer (FRA) system. The EIS measurements were performed in potentiostatic mode at the OCP. The amplitude of the EIS perturbation signal was 10mV, and the frequency studied ranged from 10 kHz to 10 mHz.

## Results and Discussion

### Morphological Characterization

The results on Fig. 1 showed that the silane film prepared on the zinc coatings was homogeneous and presented a leveling off effect on the zinc coating. The silane thickness was about  $0.6\mu\text{m} \pm 0.06$ . Besides, the roughness of the Silane/Zn system, **Erro! Fonte de referência não encontrada.**, decreased compared to these coatings without post-treatment.



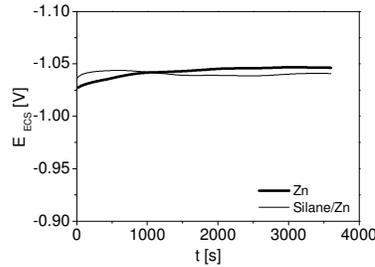
**Fig. 1:** SEM micrographs of (a) zinc coating and (b) silane film obtained from withdrawal speed of substrate from the sol of  $20\text{cm.min}^{-1}$  (cross-section).

**Table 1:** Average roughness of the samples of zinc and silane/zinc

Sample	Roughness
Zn	$0.5\mu\text{m}$
Silane/Zn	$0.3\mu\text{m}$

**Electrochemical Characterization**

Fig. 2 shows the open circuit potential values for Zn and Silane/Zn coatings for 1hour of immersion in a 5% NaCl solution. It seems that the OCP values are not influenced by the presence of silane film, indicating a high permeable coating and/or the existence of discontinuities in the silane film.



**Fig. 2:** OCP measurements in 5% NaCl solution for: Zn and Silane/Zn coatings.

Models of equivalent electrical circuits were used to explain the electrochemical behavior obtained by the tests of electrochemical impedance. These models are based on the combination of resistances, capacitances and other elements that have a physical meaning probably related to the electrochemical response of the system. Tables 2 and 3 present the values of electrical parameters obtained by fitting the equivalent electrical circuit diagrams to the experimental EIS data obtained for the zinc coatings with and without post-treatment with silane film during 168 hours of immersion in 5 % NaCl solution.

**Table 2:** Values of electrical parameters obtained from the adjustment of the equivalent electrical circuit to experimental impedance diagrams for zinc coatings without post-treatment with silane film along 168 hours of immersion in 5% NaCl solution.

	<b>1h</b>	<b>24h</b>	<b>48h</b>	<b>72h</b>	<b>168h</b>
$R_s[\Omega.cm^2]$	1.9	2.7	2.4	2.7	3.4
$R_{po}[\Omega.cm^2]$		15.2	15.6	17.7	20.4
$CPE_{po}[Fcm^{-2}s^{(n-1)}]$		6.83E-04	5.83E-04	6.42E-04	3.78E-03
n		0.81	0.78	0.75	0.48
$R_{ct}[\Omega.cm^2]$	158.1	92.7	111.1	120.4	132.7
$CPE_{ct}[Fcm^{-2}s^{(n-1)}]$	9.99E-05	1.13E-03	1.74E-03	1.65E-03	3.36E-03
n	0.81	0.73	0.67	0.72	0.72
$R_{cp}[\Omega.cm^2]$	90	110	43.8	53.60	----- *
$CPE_{cp}[Fcm^{-2}s^{(n-1)}]$	4.12E-01	1.10E-01	2.36E-01	4.31E-01	----- *
n	1	0.55	1	1	----- *

\* Time constant was not simulated because of the insufficient number of experimental data.

**Table 3:** Values of electrical parameters obtained from the adjustment of the equivalent electrical circuit to experimental impedance diagrams for zinc coatings with post-treatment with silane film, along 168 hours of immersion in 5% NaCl solution.

	<b>1h</b>	<b>24h</b>	<b>48h</b>	<b>72h</b>	<b>168h</b>
$R_s[\Omega.cm^2]$	13.0	5.5	4.6	7.7	5.3
$R_{spo}[\Omega.cm^2]$		2.7	55.4	3.6	2.6
$CPE_{spo}[Fcm^{-2}s^{(n-1)}]$		4.53E-06	2.94E-04	1.62E-07	2.35E-06
n		1	0.50	1	1
$R_{co}[\Omega.cm^2]$		313		94.6	
$CPE_{co}[Fcm^{-2}s^{(n-1)}]$		2.61E-04		3.41E-04	
n		0.52		0.43	
$R_{ct}[\Omega.cm^2]$	345	288.8	518	426.3	74
$CPE_{ct}[Fcm^{-2}s^{(n-1)}]$	1.10E-04	1.42E-04	2.32E-04	1.54E-04	5.82E-04
n	0.60	0.99	0.80	0.78	0.48
$R_{si}[\Omega.cm^2]$	1021	474	318	299	442
$CPE_{si}[Fcm^{-2}s^{(n-1)}]$	2.04E-03	2.21E-02	4.30E-02	1.77E-02	1.55E-03
n	0.83	0.82	0.94	0.90	0.66

The diagrams of experimental impedance measurements for zinc sample without post-treatment indicated the presence of two capacitive loops for 1 hour of immersion and the presence of three capacitive loops after 1 hour of immersion. For the first hour of immersion, the capacitive loop at low frequency is probably related to the diffusion through the corrosion product formed on the zinc coating, while the middle frequency loop is associated with the phenomenon of charge transfer on the interface of the zinc coating-electrolyte interface. For the following immersion times (between 24 and 168 hours), there is a new capacitive loop at high frequency associated to the increasing thickness of corrosion product due to the possible obstruction of the pores in corrosion product, what is in agreement with results obtained by other authors [4], while the capacitive loop at low frequency remains associated to the diffusion through the corrosion product and the middle frequency loop remains associated to the phenomenon of charge transfer on the interface of the zinc coating. The equivalent circuit of

Fig. 3(a) is proposed to explain the phenomenon of zinc corrosion from 24 hours of immersion, where  $R_s$  represents the electrolyte resistance,  $R_{po}$  and  $CPE_{po}$  represent the resistance and a constant phase element associated to the porous layer capacitance of the corrosion product formed on the zinc surface.  $R_{ct}$  and  $CPE_{ct}$  represent the resistance of charge transfer and a constant phase element associated with the double layer capacitance and  $R_{cp}$  and  $CPE_{cp}$  represent a resistance element and a constant phase element associated with the capacitance of the corrosion product, respectively.

For the zinc sample post-treated with silane film, Figure 4, it was observed the existence of two capacitive loops for the first hour of immersion, the first loop at medium frequency and the second loop at low frequency. The capacitive loop at low frequency is associated with the silane film, presenting a resistance value higher than the resistance of zinc charge transfer, Tables 2 and 3, represented by the capacitive loop at middle frequency. After 24 hours of immersion, it was possible to verify the presence of four time constants. The capacitive loop at the highest frequencies is associated with the effect of pores or discontinuities in the silane film, and the capacitive loop at high frequency is associated with

the formation of a cerium oxide or hydroxide film on the zinc surface. The capacitive loop at middle frequency is associated with the phenomenon of charge transfer at the zinc coating interface and the capacitive loop at low frequency is possibly associated with the silane film. The time constant concerning to a cerium oxide or hydroxide film disappears after 48 hours of immersion possibly indicating the dissolution of these products formed by the inhibitory action of cerium. At this time there remain only three time constants, related to the discontinuities of the silane film (high frequency), charge transfer of zinc (middle frequency) and the silane film (low frequency). However, after 72 hours of immersion, there is the reappearance of the time constant associated, possibly, with the formation of an oxide or hydroxide of cerium. This behavior indicates that cerium continues to react with the environment to form a product capable of hindering the corrosive process. The protective action of cerium was not observed in the subsequent times of immersion, and after 72 hours the system presents three time constants so as after 48 hours of immersion, indicating that the corrosive attack became more intense through the silane film pores, hindering the efficient action of the inhibitor. Some authors concluded that cerium ions have mobility within the film of silane. Thus, when there is a disruption of this film, these ions move to react with the electrolyte forming oxides or hydroxides of Ce III and IV, which precipitate in the defects [4]. With the continuous corrosive attack, the dissolution of the product formed by cerium occurs, because cerium will act to protect the zinc coating. This behavior can explain the disappearance of the time constant related to the product of cerium (oxide or hydroxide film). The equivalent circuit of

Fig. 3(b) is proposed to explain the phenomenon of corrosion of zinc post-treated with the silane film (for 24 hours of immersion) where  $R_s$  represents the electrolyte resistance,  $R_{spo}$  and  $CPE_{spo}$  represent resistance and a constant phase element associated with the capacitance of discontinuities in the silane film, and  $R_{ct}$  and  $CPE_{ct}$  represent the charge transfer resistance and a constant phase element associated with the double layer capacitance.  $R_{co}$  and  $CPE_{co}$  represent the resistance and a constant phase element associated with the capacitance of a cerium oxide or hydroxide film formed during the corrosion process, and  $R_{si}$  and  $CPE_{si}$  represent the resistance and a constant phase element associated with the capacitance of the silane film, respectively. The sample post-treated with silane showed zinc charge transfer resistance values greater than those of the sample without post-treatment up to 72 hours of immersion, due to the presence of the silane film on the zinc and the protective action of corrosion inhibitor. In addition, smaller capacitance values for the phenomenon of charge transfer in zinc were associated with post-treated samples, which represents the existence of a more effective barrier to permeation of moisture and species that favor the electrochemical processes [5]. However, the samples post-treated with silanes show a decrease of the  $R_{si}$  (resistance of the silane film) with the evolution of the immersion time. This decrease can be associated with the degradation of this film by the formation of cracks, which facilitated the permeation of the electrolyte and then the attack on the zinc coating [6]. Fig. 4 shows the experimental impedance diagrams obtained after 24 and 72 hours of immersion in 5% NaCl solution for zinc coatings with and without post-treatment with silane.

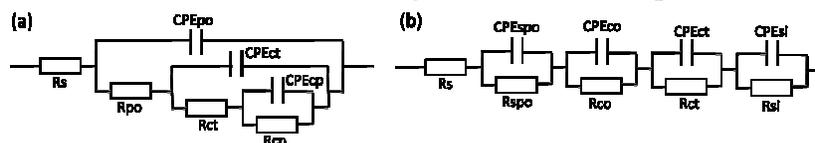


Fig. 3: Equivalent electrical circuit used to adjust the experimental impedance diagrams obtained with the zinc coating for 24 hours of immersion in 5% NaCl solution: (a) without post-treatment and (b) treated with silane.

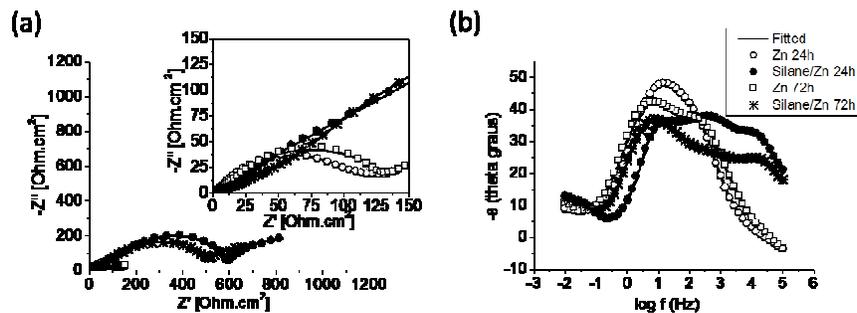


Fig. 4: Impedance diagrams for zinc coatings with and without post-treatment with silane film for 24 and 72 hours of immersion in 5% NaCl solution: (a) Nyquist diagrams and (b) phase angle plots.

## Conclusions

The morphological results indicated that it was possible to constitute a silane film on the surface of zinc by dip-coating, and this film presents a leveling off reducing the zinc coating roughness. The values of OCP indicated that the silane film formed is not an effective barrier between the environment and the zinc coating because the OCP values are not influenced by the presence of silane film. The EIS results showed that silane films with cerium salts post-treatment improve the characteristics of the protective zinc coating, thus being an effective alternative for the replacement of chemical chromating conversion.

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