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Compatibility between cathodoretic electro-coating and silane surface layer for the corrosion protection of galvanized steel

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ABSTRACT

The compatibility between a cathodoretic electro-coating and a silane layer applied on galvanized steel was evaluated by performing electrochemical impedance measurements on coated and uncoated samples. During electro-deposition, the water electrolysis induces hydrogen production. This process can induce degradation or destruction of the silane layer. This process was simulated by reproducing the application conditions of electro-coating in an aqueous solution of same pH (6) and conductivity (1600 μS) than the electro-coating bath, but without any pigments and binder. A current of 2 mA/cm² was applied between the sample and the counter-electrode during 10 and 20 s. These conditions are representative of the mean real application conditions just before the coating formation. The loss of the barrier effect offered by the silane layer was evaluated by EIS before and after simulation. This simulation shows whether it is possible to conveniently design the properties of the silane layer to maintain its protection and adhesion promotion properties after polarization. The barrier properties and the water uptake of the electro-coated samples were evaluated by EIS as a function of immersion time in a sodium chloride solution (0.1 M). The coated silane pre-treated samples show a good behaviour compared to the samples coated without pre-treatment. By properly managing the deposition conditions of sol–gel films it is possible to obtain cathodoretic coating with improved corrosion resistance. Silane sol–gel films of different thicknesses and curing temperature were produced. It was demonstrated that a 120 nm thick silane sol gel film cured at 180 °C ensures a very good compatibility with the electro-coat. In fact, this system shows a very high corrosion resistance even after 50 days of immersion in a sodium chloride solution. Also the resistance in the salt spray chamber of the electro-coated thin silane layer cured at 180 °C is remarkable. The results confirm that, if conveniently designed, silane sol–gel film properties, the silane layer is a good adhesion promoter of the cathodoretic coating on galvanized steel and this property is maintained for long exposure times.

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1. Introduction

Nowadays, cathodic electro-coating is a widely used technique for the application of primer layers for the protection against corrosion [1]. The cathodoretic electro-deposition is a widespread technique used in many fields, in particular in the automotive industry, for the protection of the automobile bodywork [2,3]. This deposition method has numerous advantages, such as high protection against corrosion of the coating and high material utilization, but it is also an environmentally friendly technique, owing to the absence of organic solvents (it is an aqueous system) [4]. This last statement is growing of importance, in the light of the recent legislation restriction in the

use of organic solvents containing VOCs (volatile organic carbon) [5].

In order to enhance the adhesion and the corrosion protection properties of the cathodoretic coating, the metal substrate is usually subjected to a surface conversion pre-treatment [6]. The automobile bodywork is composed of different metallic substrates such as hot dip galvanized steel (HDG), electrogalvanized steel (EZ), steel and aluminium alloys. These metallic parts are assembled before surface treatment. The conversion treatment widely used is the trication phosphatization which is after activation compatible with all these substrates. Nevertheless, this treatment presents some environmental and economical drawbacks. The bath contains heavy metals and the process forms slurries which obliges the baths treatment and their regeneration. Moreover, the phosphates are known to be responsible for the river eutrophication. From an economical point of view, the phosphates are widely used in the agriculture as fertilizers and their price is directly linked to this market. In the

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Table 1
Thickness of the studied samples.

	Silane sol–gel films	
	Curing temperature (°C)	Thickness (nm)
A 120	120	~120 nm
A 180	180	
B 120	120	~300 nm
B 180	180	

last 15 years silanes sol–gel films have been the subject of extensive development [7] solving, partially, the problems related to the environmental limitation to the use of hexavalent chromium compounds [8].

Silanes are hybrid organofunctional molecules and can be used as adhesion promoters between metallic substrates and organic coatings used for protection against corrosion. These molecules applied by using a sol–gel process can act as coupling agent between inorganic substrates and organic coatings. The chemical properties, surface chemistry tailoring and film formation mechanism have been widely studied and are reported elsewhere [9–12] in literature. It has to be underlined that besides being one of the most interesting way to replace phosphate conversion treatments, silane sol–gel pre-treatments are also environmentally friendly and ease of handling [13,14].

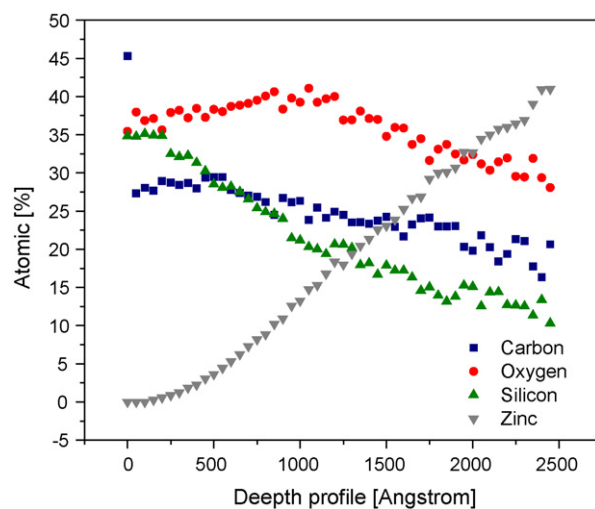
In this context, this paper aims at investigating the potential of silane sol–gel films as pre-treatment for galvanized steel which, nowadays, constitutes the biggest metallic part of the automobile bodywork. The final goal is to promote the adhesion and to improve the corrosion resistance of a cathoporetic coating.

The silane film studied in the present work is a water-based experimental mixture of three different silanes molecules. In particular they are: γ -glycidoxypropyltrimethoxysilane (γ GPS), tetraethoxysilane (TEOS) and methyltriethoxysilane (MTES). The cathoporetic coating is a commercial epoxy polymer, properly selected in order to ensure a chemical affinity to the silane film (every γ GPS molecule contains one epoxy functionality). Modifying conveniently the deposition and curing conditions it is possible to obtain silane film with different thicknesses and, consequently, different electrochemical properties. In particular, four different silane pre-treatments obtained by modifying the sol–gel deposition conditions and the curing temperature were tested.

First of all, a simulation of the deposition conditions of the cathoporetic coating on the silane pre-treated galvanized steel samples was carried out. The aim is to determine if the electro-coat conditions destroy or not the silane pre-treatment. Indeed, the electro-coat is accompanied by a hydrogen release on the surface of the galvanized steel samples (the cathode) [15]. This release can generate degradation or destruction of the pre-treatment. The estimation of the produced damage was investigated by means of electrochemical impedance spectroscopy (EIS), comparing the impedance spectra before and after the simulation. In the second part of the work, the performances of the cathoporetic coating applied on the different silane films were compared. The characterization of the corrosion protection cycles was accomplished by EIS measurements and exposures in salt spray chamber.

2. Experimental

Hot dip galvanized steel sheets (Zn–Al alloy, 0.25 wt% Al) obtained by a continuous process were supplied by ArcelorMittal (Liège), Belgium. The steel width was about 0.8 mm and the thickness of the zinc coating was in the range of 7–10 μ m. The sheets were cut to a size of 100 mm \times 60 mm and then degreased with acetone and ultrasounds for 15 min. The alkaline degreaser used

**Fig. 1.** Atomic percentage vs. depth profile obtained by XPS for sample A120.

for the samples is a solution containing KOH (Gardoclean[®], supplied by Chemetall). The samples were dipped into the degreasing solution for 5 min maintaining the temperature at 50 °C. The aim of this treatment is to provide an alkaline etching and a chemical activation of the surface. After the alkaline treatment, the samples were dipped into a silane containing solution in order to obtain a thin hybrid film for 2 min. The silane solution is an experimental water-based mixture of three different molecules, γ -glycidoxypropyltrimethoxysilane (99% pure), tetraethoxysilane (99% pure) and methyltriethoxysilane (99% pure), all purchased by Degussa and used as received without further purification. The silane solution was prepared by diluting 10 wt% of the mixture in deionised water. The pH of the solution was properly modified adding hydrochloric acid. The mixture consists of an equal weight percentage of each one of the three organosilane molecules. By managing the pH value and the hydrolysis time it was possible to prepare two different series of silane sol–gel films with different thicknesses. In particular, a few samples (named “A” series) were produced modifying the solution pH to 4 and carrying out the hydrolysis of the TEOS separately from the other molecules. Before mixing, the TEOS molecules hydrolyzed separately for about 120 min, while the other two silanes molecules (GPS and MTES) were hydrolyzed together for 90 min in order to achieve different degrees of hydrolysis. The other series of samples (named “B”) was produced modifying the solution pH to 3.5 and carrying out the hydrolysis of the TEOS, GPS and MTES all together in the same glass flask. The molecules were hydrolyzed for about 900 min. The HDG samples were dipped in vertical position into the silane diluted solutions and maintained in immersion for about 2 min. After the immersion the samples were withdrawn from the solutions at a constant speed, 25 cm/min. A heat treatment in oven followed after the drawing of the samples. The specimens treated with the experimental silane mixtures were cured at two different temperatures, 120 °C and 180 °C, for 15 min. The different curing temperature influences the condensation reactions (which are thermally activated) among different silane molecules.

In the industrial process, the electrocoating is deposited at constant voltage (potentiostatic method) by application of a high voltage between the body car and the counter electrode. Due to the formation of the film, the current density decreases very quickly. In order to study the building layer mechanisms, the galvanostatic deposition is generally preferred. The application of a high voltage between the two electrodes without building organic layer would

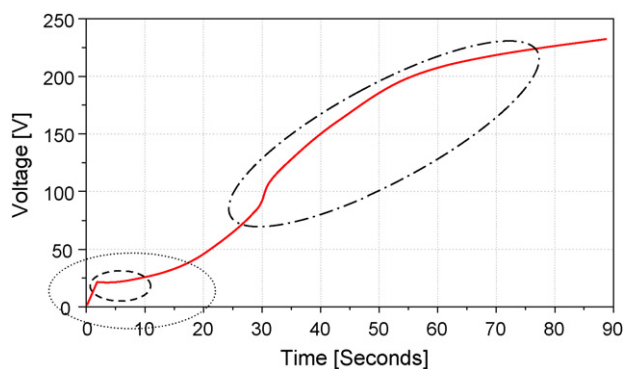


Fig. 2. Schematic representation of voltage as a function of time during an electro-coating formation obtained at constant current (about 1 mA/cm²).

induce a too high current density which is not representative of the real application conditions.

In this study before the application of the cathodic coating by potentiostatic method, the effect of a simulation of the electro-coat conditions on silane layer properties was investigated at constant current density. The main goal of this simulation was to determine if the electro-coat conditions destroy or not the silane pre-treatment. The simulation of the electro-coat was performed in a Na₂SO₄ aqueous solution, modifying its pH to 6 and the conductivity to 1600 μS. This solution simulates the most important parameters of the cathodic paint bath during electrocoating process. A stainless steel panel was used as anode, while the sol-gel coated samples were used as cathode. The distance between the anode and the cathode was maintained constant for all the simulations.

A VG Escalab 220iXL X-rays photoelectron spectrometer (monochromatic Al Kα radiation at 1486.6 eV) was used to measure the thickness of the silane sol-gel film. The samples were eroded using a 3 keV Argon beam operated at a target current of 1 μA, and rastered over an area of 3 mm × 3 mm. The calibration was performed by using SiO_x layers of known thickness and eroded in the same conditions.

Table 1 reports the different silane sol-gel film applied onto galvanized steel and their respective thickness, measured by means of XPS. These thickness values are very low compared to a classical trication phosphatization layer which has a thickness of about 1 μm.

In addition, the atomic percentage as a function of the depth profile for sample A120 is reported in Fig. 1 for example. The zinc can already be detected at 20 nm and this is due to the high roughness of the galvanized substrate. The samples named "A" are thinner than the samples "named" B. Moreover, the two different curing temperatures lead to a different degree of densification of the silane sol-gel network.

The evolution of silane properties before and after simulation was evaluated by means of electrochemical impedance spectroscopy. Electrochemical tests were performed using a Princeton Applied Research Potentiostat 273A and Schlumberger HF Frequency Response Analyser SI 1255. A classical three electrodes arrangement was used. An Ag/AgCl (+0.207 V vs. SHE) electrode and a platinum plate were used as reference and counter electrode, respectively. Electrochemical impedance measurements were performed using signal amplitude of 5 mV and frequency range from 10⁵ to 10⁻² Hz. The immersed area was 4.5 cm². The solution was 0.1 M sodium chloride. The impedance measurements were performed before and after the simulation of the electrocoat process.

A cathodic paint was applied on the galvanized steel samples pre-treated with the silane sol-gel layer. The cathodic paint consists of a lead free epoxy cathodic polymer (supplied

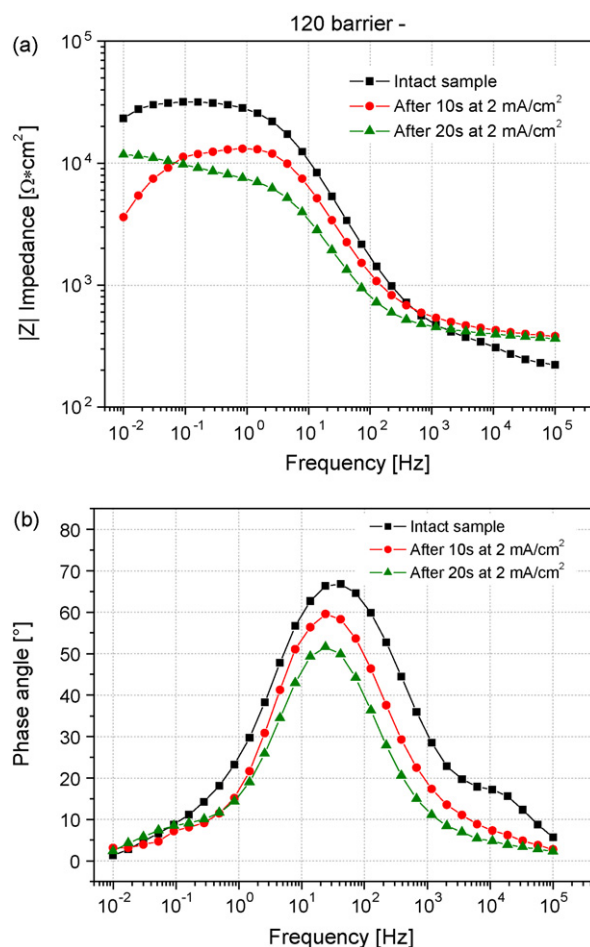


Fig. 3. Bode modulus (a) and phase (b) for samples A120 before and after the simulation of the electro-coat conditions.

by PPG France). To obtain an electro-coat thickness of 20 μm, 180 V were applied for 3 min between the electrodes at a bath temperature of 30 °C. The electro-coated samples were cured for 25 min at 175 °C, in order to achieve a proper reticulation of the polymer and to induce a chemical interaction between the polymer itself and the silane sol-gel layer. The quality of the cathodic deposition was investigated by means of electrochemical impedance spectroscopy. The measurements were carried out on intact samples, with the same equipment and arrangement previously described. The amplitude of the AC signal was 20 mV, the immersed area was 7.07 cm² while the testing solution was 0.5 M NaCl. The evolution of the electrochemical properties of the organic coatings was collected for a convenient lapse of time, up to 50 days. The resistance in the salt spray chamber (in accordance with ASTM B117 standard: 35 °C, 100% r.h., 5 wt% NaCl) was carried out on scratched samples. For comparison, these tests were also performed on electro-coated galvanized steel without the deposition of the intermediate silane sol-gel layer.

3. Results and discussion

3.1. Simulation of electro-coat conditions

The effect of the electro-coat conditions were investigated prior the deposition of the electro-coating. The highly alkaline environment and the consequent hydrogen release on the cathode can affect the properties of silane sol-gel film and can lead, eventually, to the complete degradation of the layer. The destruction of the

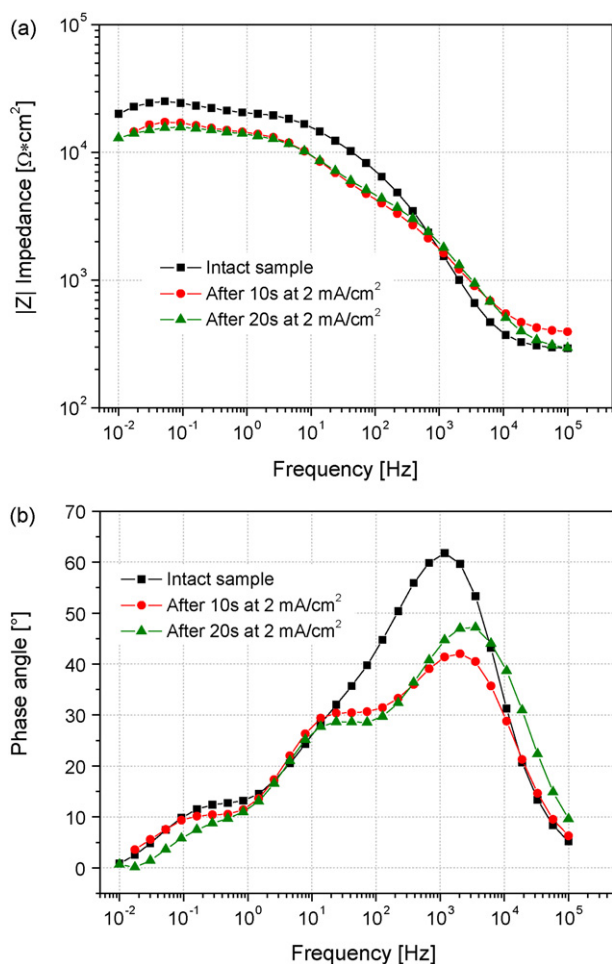


Fig. 4. Bode modulus (a) and phase (b) for samples A180 before and after the simulation of the electro-coat conditions.

silane sol-gel film not only affects the adhesion with the polymer, but it also leads to the formation of a heterogeneous deposition of the organic coating.

Following the Ohm law, at constant current the film resistance is directly proportional to the applied voltage. Fig. 2 shows a schematic evolution of voltage as a function of time at constant current (less than 1 mA/cm^2). This graph illustrates the kinetics of film formation: the resistance increases with the thickness of the film.

Considering the graph depicted in Fig. 2, three parts can be distinguished:

- highlighted by the dashed circle: a first part corresponding to water electrolysis at the cathode. This part represents the time to reach the pH corresponding to electrocoagulation. Film resistance is practically zero.
- highlighted by the dots circle: electro-deposition begins. The film resistance slightly increases.
- highlighted by the dot-line circle: the increase of the resistance corresponding to film formation. The rate of the film formation progressively decreases as the coating thickness increases due to the high resistance of electro-coating.

In this study, a current of 2 mA/cm^2 was applied on the sample during 10 s and 20 s. These conditions are slightly more drastic than the conditions used to study the building layer mechanisms (around 1 mA/cm^2). A time between 10 s and 20 s is representative of induction time before organic coating formation at constant cur-

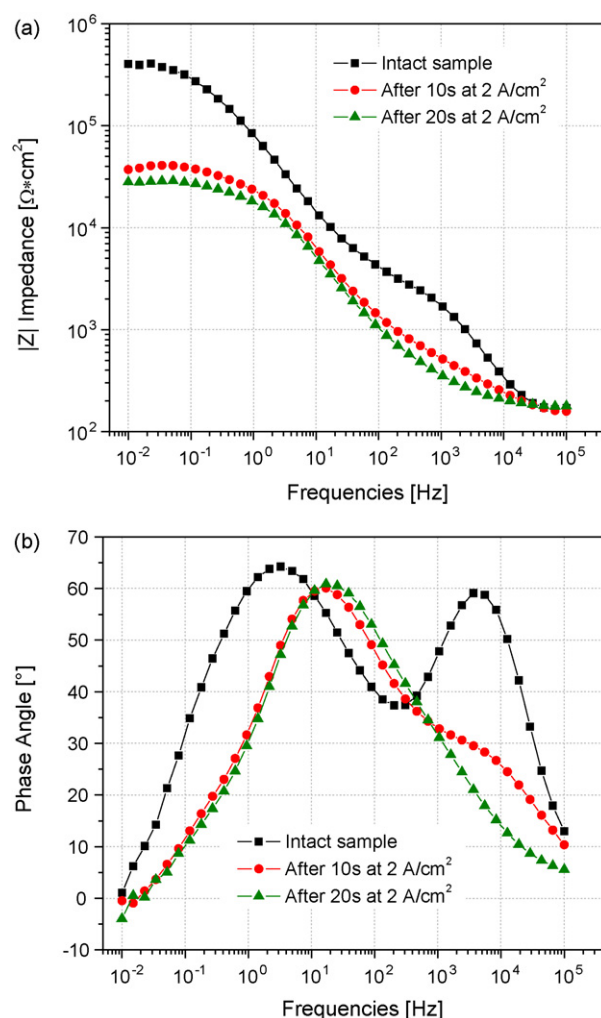


Fig. 5. Bode modulus (a) and phase (b) for samples B120 before and after the simulation of the electro-coat conditions.

rent. After this induction period, the film forms and the risk of pre-treatment degradation becomes limited.

The effect of the simulation on the properties of the sol-gel layer are reported in Figs. 3 and 4 for the samples A120 and A180, and in Figs. 5 and 6 for the thicker samples, B120 and B180. First of all, notice the great differences between the impedance at low frequencies of the two different kinds of samples. The samples with the thinner sol-gel film are characterized by values of the low frequencies impedance in the order of $10^4 \Omega \text{ cm}^2$, while in the order of $10^6 \Omega \text{ cm}^2$ for the other samples. This difference is directly related to the different thickness of the samples. A higher thickness leads to higher barrier properties of the silane sol-gel film but also to an increasing electrical resistance during the electrodeposition. By considering the Bode modulus in Figs. 3–6, it seems that the simulation leads to a considerable degradation of the properties of the thicker films. On the other hand, the thinner silane sol-gel layers show little decrease of the low frequencies impedance. In particular, sample A180 has very comparable values of the low frequencies impedance before and after the simulation. It is likely that the highest conductivity and lowest impedance of the low barrier samples lead to a lower extent of deterioration. This could be explained by a more uniform distribution of the current and hydrogen evolution on the entire surface. Indeed, the samples with high initial impedance does not allow the hydrogen evolution and the forced bubbling could be responsible of the decrease of the properties.

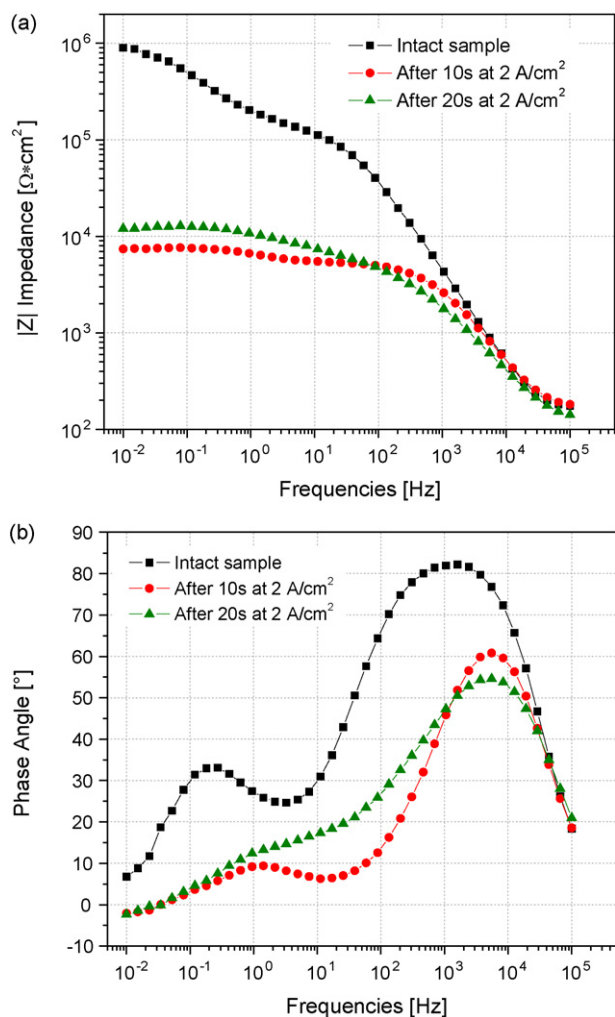


Fig. 6. Bode modulus (a) and phase (b) for samples B180 before and after the simulation of the electro-coat conditions.

It is possible to evaluate the influence of the simulated deposition conditions by considering the phase diagrams of Figs. 3–6. The high frequencies time constant (around 10^3 – 10^4 Hz) is commonly related to the silane sol–gel film [16]. Thus, by monitoring the evolution of the maximum value of the phase angle of the first time constant, it is possible to detect the degradation of the silane sol–gel layer. For the sample A120 the first time constant shows a very low phase angle even before the simulation. After the 20 s of simulation, the high frequency time constant is no more noticeable. The B120 silane behaves similarly. In fact, even if it shows an easily detectable high frequency time constant, the application of the 2 mA/cm² leads to a quick decrease of the silane sol–gel properties. The maximum value of the phase angle of the time constant at around 10^3 – 10^4 Hz shows a great decrease after 10 s of simulation, and eventually, it disappears completely after 20 s. The silane sol–gel films designed with high thickness show a huge decrease of the low frequencies impedance, up to two orders of magnitude. It is likely that this kind of pre-treatment have too high barrier properties, they are thick and, maybe, brittle. In spite of the correct reason, it is evident that the synergic effect of the hydrogen evolution and the local increase of the pH affect strongly the properties of this kind of films.

After the different simulations the low frequencies impedance are approximately the same for all the samples, in the order of 10^4 Ω cm². Regarding the different conditioning time, there is a slightly different behaviour after 10 or 20 s of simulation. In gen-

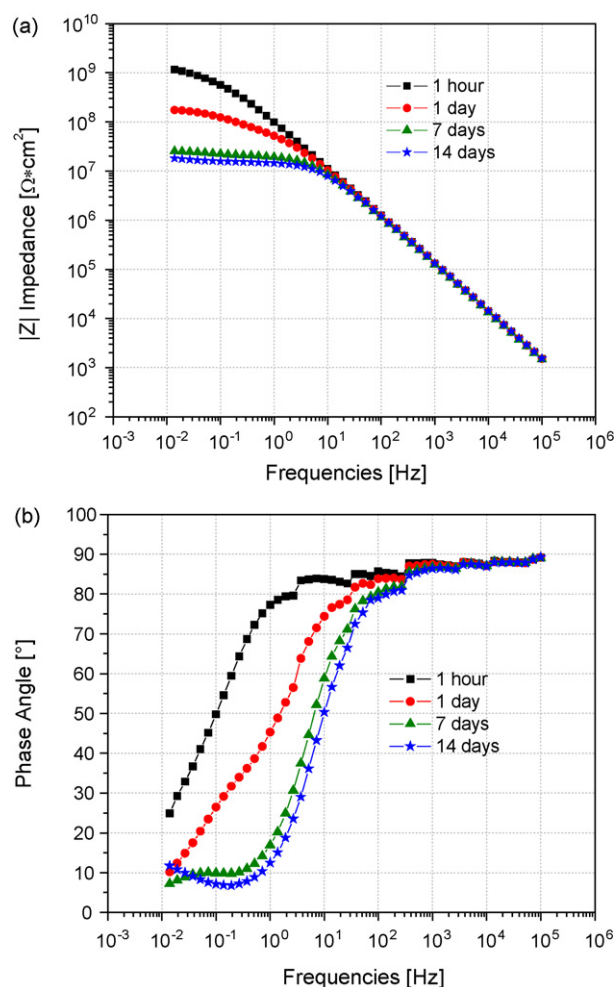


Fig. 7. Bode modulus (a) and phase (b) for the electro-coated galvanized steel sample.

eral, the longest the application of the current, the highest is the damage of the silane sol–gel film.

Coating the silane pre-treated samples with the electro-coat paint will allow at verifying if the degradation induced by the deposition conditions affects the final properties of the complete protection system.

3.2. Characterization of the electro-coated samples

According to the previously explained parameters, the electro-coat was applied on the different silane sol–gel treated samples and, for comparison, on bare galvanized steel. The mean thickness of the coatings after curing is reported in Table 2. All the samples have a thickness around 20 μm, except for the bare galvanized steel sample, whose value is lower (about 15 μm). This fact is probably related to the high hydrogen activation overvolt-

Table 2
Thickness of the electro-coat on the different samples.

	Thickness (μm)	
	Mean value	Standard deviation
A 120	19.9	1.4
A 180	21.6	2.2
B 120	19.9	1.5
B 180	18.8	1.7
Bare substrate	15.8	1.2

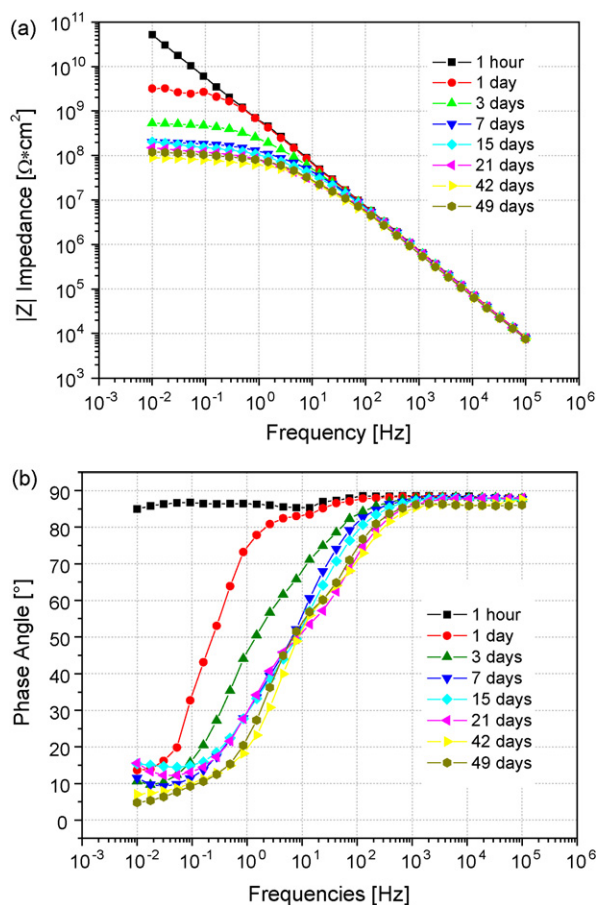


Fig. 8. Bode modulus (a) and phase (b) for the electro-coated A120 sample as a function of the time of immersion in the aggressive solution.

age on zinc which requires a higher applied voltage or a longer time to obtain the alkaline pH inducing the coating electrocoagulation.

Electrochemical impedance spectroscopy measurements were carried out on the intact samples, in order to assay the properties of the applied coating. This test aims at investigating the presence of macroscopic defects in the electro-coat and to analyse the electrochemical properties of the organic coatings. Impedance highlights the presence of macroscopic defects by means of a drop of the value of the low frequencies impedance in the first hours of immersion. By means of impedance spectroscopy it is possible to check if the presence of the silane sol-gel layer promotes the deposition of a uniform and homogeneous polymer film. In fact, the degradation induced by the previously discussed deposition conditions can affect the film formation and thus, the quality of the electro-coating and this can lead to the formation of a defective coating lacking in corrosion protection.

Fig. 7 shows the Bode modulus and phase for the electro-coated galvanized steel. Notice that since the first hours of immersion the coating shows a relatively low value of the impedance and of the phase angle in the low frequencies domain. It is commonly accepted that the total impedance in the low frequencies domain is an indicator of the protection properties of an organic coating. In this case, the electro-coating on the galvanized steel substrate is likely to be defected. Probably, one or more macroscopic defects are present in the coating and the electrolyte can easily reach the surface of the metal. In the light of the variables of the electro-coating process, the non-uniform hydrogen activation overvoltage on zinc substrate can induce a non-uniform hydrogen production and locally, more

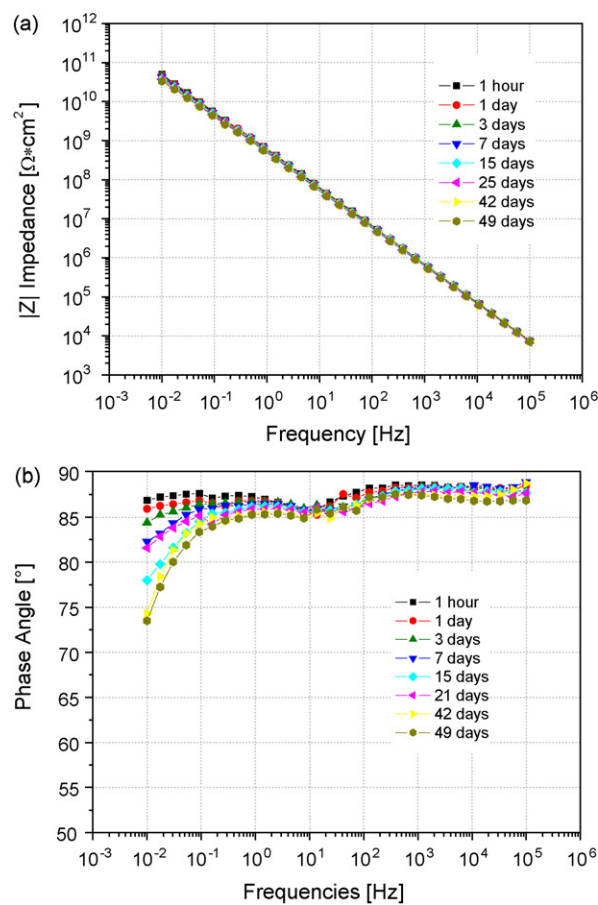


Fig. 9. Bode modulus (a) and phase (b) for the electro-coated A180 sample as a function of the time of immersion in the aggressive solution.

intensive bubbling can be responsible of the presence of defects in the applied coating.

Figs. 8 and 9 show the Bode modulus and phase for the electro-coated A120 and A180 samples, respectively. The cathoretic polymer applied onto the A120 pre-treated substrate shows a quick decrease of the low frequencies impedance. After 24 h of immersion the total impedance drops to $2 \times 10^9 \Omega \cdot \text{cm}^2$, starting from the value of $1 \times 10^{11} \Omega \cdot \text{cm}^2$ obtained after 1 h of immersion. This fact indicates that, probably, also this electro-coating is defected. Indeed, considering Fig. 8, it is possible to appreciate that the electro-coat applied onto A180 silane sol-gel film does not show evidence of the presence of macro-defect. In fact the impedance in the low frequencies domain is stable around the value of about $5 \times 10^{11} \Omega \cdot \text{cm}^2$ during the 50 days of immersion. This coating seems to be free of macro-defects generated during the electro-deposition.

To better understand the behaviour of this last sample compared to the electro-coat A120, the electrochemical impedance spectra were modelled using the convenient electrical equivalent circuits [17]. For the electro-coated A180 sample a R(QR) equivalent circuit was used, where the first resistance is the electrolyte resistance (R_{el}), the second is the coating resistance (R_c) and the constant phase element (Q_c) is related to the coating capacitance. This equivalent circuit was also used for the very first hours of immersion of electro-coat A120 sample. After the initial immersion period, the spectra of this sample were fitted using a R(Q(R(QR))) equivalent circuit, adding another time constant representative of both the Faradic resistance of the metal interface ($R_{charge\ transfer}$) and the double layer capacitance ($Q_{double\ layer}$). The results of the fitting procedure are reported in Fig. 10, which shows the values of the coating resistance (Fig. 10a) and capacitance (Fig. 10b) extrapolated from

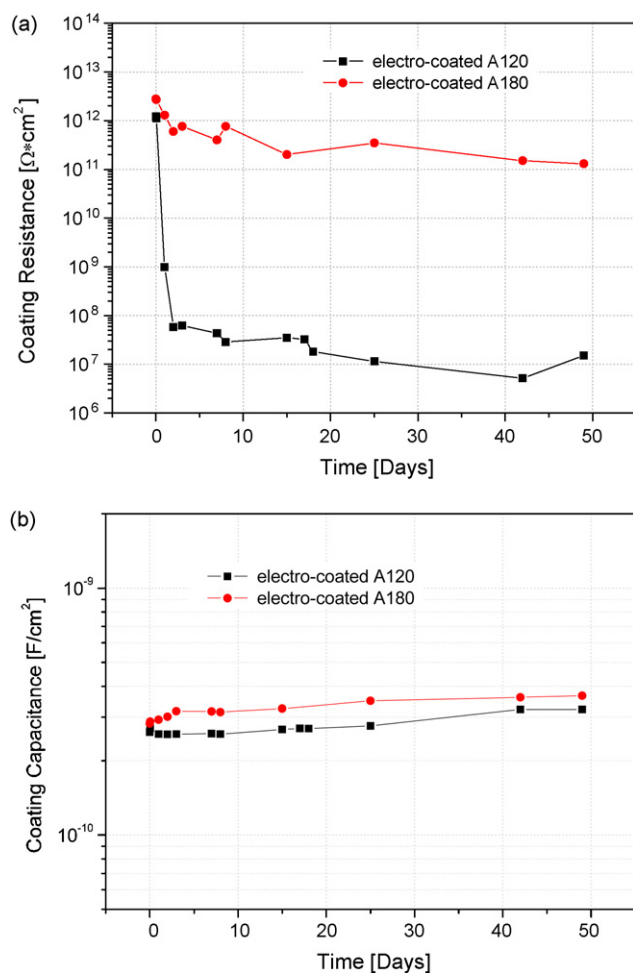


Fig. 10. Sol-gel resistance (a) and coating capacitance (b) as a function of the time of immersion in the aggressive solution.

the acquired impedance spectra. The presence of macro-defects in the coating applied on the A120 sample is evidenced by the drop of the corresponding coating resistance after about 1 h of immersion (see Fig. 10a). It was demonstrated [18] that the coating resistance R_c is related to the total number and the dimension of pores or capillary channels perpendicular to the substrate surface through which the aggressive solution reaches the interface. On the contrary, the electro-coating on sample A180 maintains high values of the coating resistance for all the time of immersion meaning that this coating is probably defect-free. Concerning the coating capacitance (see Fig. 10b), the values of the two different samples are very similar. It is well known that the capacitance is inversely proportional to the coating thickness. In the light of this statement, the capacitance values can be considered essentially the same, considering that the electro-coated A180 sample has a slightly higher average thickness. The experimental results summarized in Fig. 10 suggest that there are probably a few macro-defects on the coated A120 sample, big enough to allow the electrolyte to go through very quickly and to reach easily the surface of the metal, but not so many to influence dramatically the water absorption.

The Bode modulus and phase of the electro-coated B120 and B180 samples are reported in Figs. 11 and 12, respectively. Notice that for both samples the low frequencies impedance decreases very quickly. In particular, the drop of the total impedance occurs after a few hours of immersion for the electro-coated B180 sample, while the other sample maintains high values of the total impedance for about 1 week. After this lapse of time a second

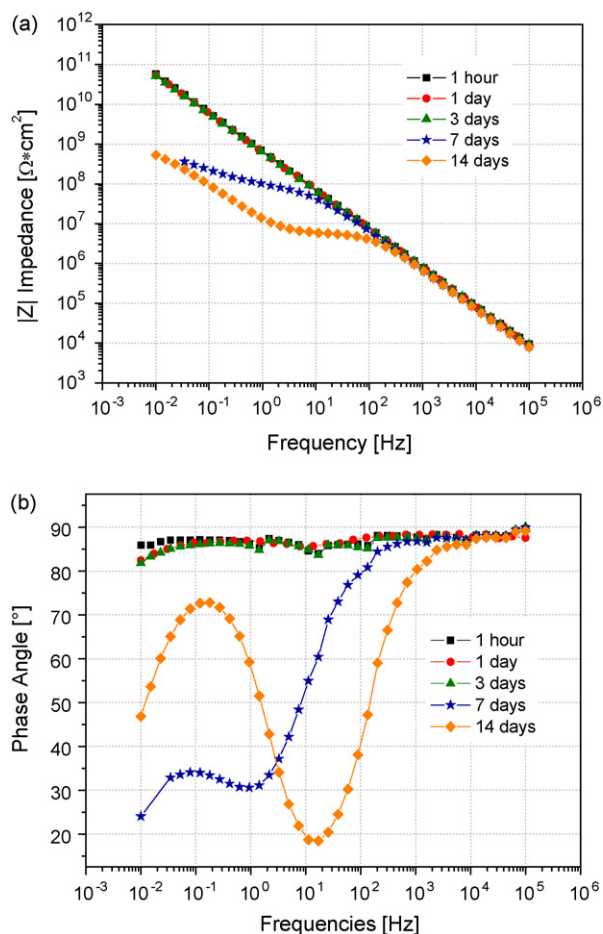


Fig. 11. Bode modulus (a) and phase (b) for the electro-coated B120 sample as a function of the time of immersion in the aggressive solution.

time constant is also noticeable in the Bode phase graph of sample B120 (see Fig. 11a). It is an evidence of the occurring of under-paint corrosion. Owing to the low protection properties of the electro-coat coating on samples B120 and B180 and the beginning of the corrosion processes on sample B120, the immersion in the aggressive solution was stopped after 2 weeks. It is likely that the electro-coatings applied on the thicker sol-gel films have a few macro-defects due to hydrogen release during the electro-coating process. It was previously highlighted that the deposition conditions have a remarkable effect on the properties of the B120 and B180 sol-gel gel layer. The results of the experimental measurements performed on the electro-coated samples confirm that the degradation of the sol-gel film caused by the chemical reactions on the cathode is more pronounced for the high resistance sol-gel layers.

The wet adhesion and the resistance to the under-paint propagation of the cathodic front were roughly estimated by means of salt spray test. Scratched samples were exposed in the salt spray chamber for about 500 h. The comparison between the experimental results is reported in Table 3. The samples pre-treated with the thicker silane sol-gel film show an extensive delamination starting from the artificial defect. Notice that the extent of delamination is higher than for the electro-coated galvanized steel. On the other hand, the samples pre-treated with the low resistance silane sol-gel film show a smaller delaminated area, related to the limited extent of the delamination process. It is likely that the A180 pre-treatment not only ensures the application of a defect free cathoporetic coating, but it also improves the resistance against the progress of the

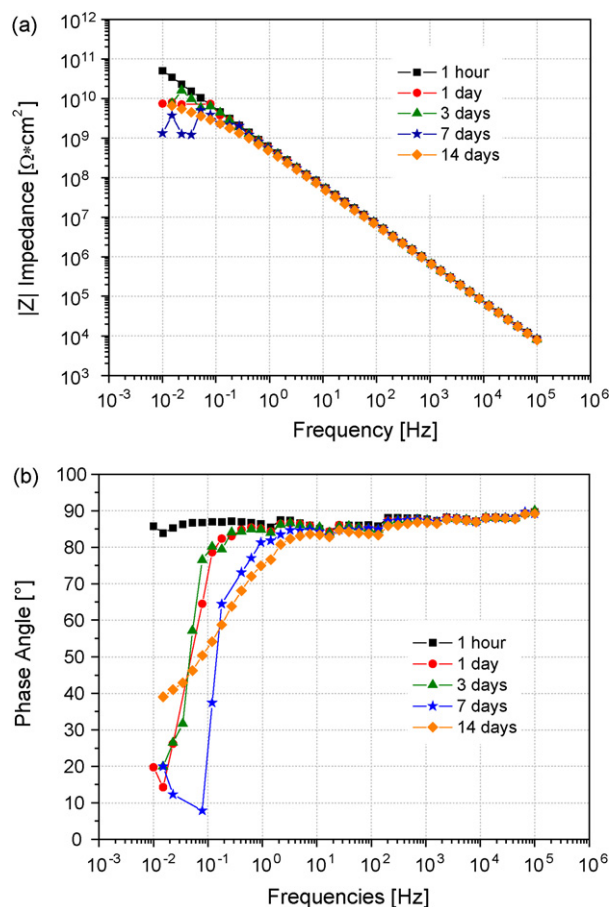


Fig. 12. Bode modulus (a) and phase (b) for the electro-coated B180 sample as a function of the time of immersion in the aggressive solution.

Table 3

Linear extent of delamination for the different samples after 500 h of exposure in the salt spray chamber.

	Linear extent of delamination (mm)
A 120	1.5
A 180	1.9
B 120	4.4
B 180	5.0
Untreated Al	3.6

delamination front. This test also confirms the degradation of the high resistance silane pre-treatment. The resistance of these samples to the salt spray test is the worst among the different samples, and it is even worse than the electro-coated galvanized steel. This fact is probably due to the deterioration of the silane sol–gel films, which leads to the formation of an inhomogeneous and defected cathodic film, characterized by poor adhesion to the substrate.

4. Conclusions

The effect of the electro-coating deposition conditions on different silane sol–gel pre-treated galvanized steel plates was investigated. In particular it was demonstrated that the properties of thin 120 nm silane sol–gel films are slightly affected by the electro-deposition conditions. Instead, thicker sol–gel films undergo noticeable degradation, likely due to the hydrogen production and bubbling. The thinner silane sol–gel film cured at 180 °C provides an electro-coating with a homogeneous cathodic paint film free of macro-defects. Moreover, the salt spray test evidenced that it also enhances the corrosion resistance of the organic coating by improving the stability of the polymer/metal interface. A thin silane sol–gel layer maintains the roughness of the zinc substrate which is a favourable parameter to the anchoring of the electrocoating, is not affected by the electro-deposition conditions and continues to play its adhesion promoter role. So, for an optimal compromise, a balance between the thickness, the barrier properties, the curing temperature of the silane sol–gel layer and the susceptibility to the degradation due to hydrogen production is to be struck.

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