The use of pre-treatments based on doped silane solutions for improved corrosion resistance of galvanised steel substrates

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Abstract

The present work aims at evaluating the corrosion resistance of galvanised steel substrates pre-treated with bis-[triethoxysilylpropyl] tetrasulfide silane doped with cerium nitrate or zirconium nitrate. The corrosion resistance of the pre-treated substrates was evaluated by electrochemical impedance spectroscopy, during immersion in NaCl solutions. The chemical composition of the surface was assessed by X-ray photoelectron spectroscopy and the surface morphology was studied by atomic force microscopy. The electrochemical results show that pre-treatments based on doped silane solutions provide good corrosion protection of the galvanised steel substrates. The work also aims at discussing the role of the dopants on the protective properties of the silane coatings formed on galvanised steel substrates.

Keywords: Silanes; Corrosion; Cerium; Zirconium; Dopant; Galvanised steel

1. Introduction

Silane-based pre-treatments are emerging as technologies for surface functionalisation of several metallic and non-metallic substrates. The procedure is easy to apply, being achieved by immersion of the substrate in alcohol or water-based silane solutions for a short period. The final result is a stable thin organic film, possessing good coupling properties with organic polymers.

Current knowledge of the coupling agent/substrate interface and of the coupling agent/polymer interface shows that the maximum coupling efficiency depends on the number of mineral O–Si (oxane) bonds formed with the substrate and on the nature of the organofunctional groups that interact with the polymers. Both bonds are stable, resisting to water uptake. These attributes attracted the attention of the corrosion researchers and literature \cite{1-20} shows that organosilicon-based coatings present promising potentials to be used as pre-treatments for corrosion protection of several metallic substrates such as aluminium alloys, copper, steel and galvanised steel.

Silane coatings are a “passive” organic coating \cite{21}, since they act essentially as a physical barrier that hinders the penetration of aggressive species towards the metallic substrate. However, this behaviour can be modified through the inclusion of small amounts of chemicals possessing corrosion inhibiting properties. This procedure was already successfully tested for hybrid sol–gel coatings \cite{22-24}, which revealed improved corrosion protection of aluminium and zinc substrates.

The procedure adopted in the present work aims at modifying the “passive” barrier properties of the silane coatings through doping with cerium nitrate or with zirconium nitrate.

Cerium is known to act as corrosion inhibitor and has been tested for corrosion protection of galvanised steel in aggressive aqueous medium \cite{25,26}. Aramaki \cite{27-30} also tested the corrosion behaviour of zinc substrates pre-treated...
with cerium nitrate and sodium silicate and coated with a silane film. The improved protection of the substrates was attributed to the formation of a passive film containing zinc hydroxide, zinc silicate and cerium/silicate complexes.

Pre-treatments based on the use of zirconium are also reported in the literature. Montemor et al. [31] showed that zirconium conversion films combined with silanes provide corrosion protection of painted hot dip galvanised steel substrates. Modification of sol–gel coatings with zirconium nanoparticles was also successfully tested for corrosion protection of aluminium alloys [32].

Following previous results [8–11,19,31,33], the present work aims at investigating the anti-corrosion behaviour of a novel pre-treatment for galvanised steel substrates based on bis-[triethoxysilyl]propyl] tetrasulfide silane (BTESPT) solutions doped with Ce(NO₃)₃ or Zr(NO₃)₃. The electrochemical measurements show that the corrosion resistance of galvanised steel substrates pre-treated with the doped silane solutions increases by more than two orders of magnitude when compared with the untreated substrates. Additionally, the presence of the dopant seems to increase the coating lifetime. The results show that pre-treatments based on doped silane solutions present improved anticorrosion performance. Furthermore, the methodology proposed in this work is simple to apply and it is compatible with the actual environmental concerns.

2. Experimental

2.1. Pre-treatments

The bis-[triethoxysilyl]propyl] tetrasulfide silane (BTESPT) (Sigma/Aldrich product) solution was prepared by dissolving 4% (vol/vol) of silane in methanol (90.5% vol/vol) and 5.5% (vol/vol) of an aqueous solution of 1×10⁻³ M of nitrate salt: Ce(NO₃)₃ or Zr(NO₃)₃. The final concentration of the nitrate salt in the doped silane solution was 5.5×10⁻⁵ M. The doped silane solution was stirred during 1 h and kept for 3 days before use.

The metallic substrate consisted of galvanised steel specimens having a zinc coating weight of approximately 140 g/m² and a thickness of approximately 10 μm. No post-annealing was performed on these substrates. The galvanised steel specimens were degreased using an alkaline cleaner. Following cleaning the panels were washed with distilled water, dried in air and immersed in the silane solution for 10 s. The excess of solution was removed by using air stream and then the panels were cured in a Memmert oven at 120 °C for 40 min.

2.2. Electrochemical techniques

The electrochemical impedance spectroscopy (EIS) measurements were performed at room temperature in a Faraday cage using a frequency response analyser and an electrochemical interface connected to a computer. A three-electrode electrochemical cell was used, consisting of the working electrode (3.15 cm² of exposed area), saturated calomel electrode (SCE) as reference and platinum as counter electrode. The measuring frequency ranged from 10⁵ Hz down to 10⁻² Hz.

Electrochemical experiments were performed during immersion in sodium chloride solutions with different concentrations: 0.005 M and 0.5 M, at least in duplicate samples.

2.3. Analytical techniques

X-ray photoelectron spectroscopy (XPS) analyses were carried out using a 310 F Microlab (VG Scientific). XPS spectra were taken in CAE mode (30 eV), using an Mg (non-monochromated) anode. The spot of the X-ray beam was around 3×3 mm.

Atomic force microscopy (AFM) measurements were performed using a Nanoscope Digital Instruments (NanoScope III) operated in tapping mode.

3. Results

3.1. Corrosion evaluation

The corrosion behaviour of the pre-treated substrates was assessed by EIS. Figs. 1 and 2 depict the EIS spectra obtained for galvanised steel substrates pre-treated with silane solutions doped with Ce(NO₃)₃ or with Zr(NO₃)₃, respectively, and immersed in sodium chloride solutions of different concentrations. Fig. 3 depicts the EIS Bode plots obtained on untreated galvanised steel and on galvanised steel samples pre-treated with different systems: silane without dopants, doped silane solutions and Cr(VI)-containing solutions. The spectra depicted in Fig. 3 were obtained after 24 h of immersion in 0.005 M NaCl and evidence the protection provided by the doped coatings comparatively to the other pre-treatments.

During the first 12 h of immersion, the EIS spectra obtained for the doped systems are characterised by the presence of a capacitive response over all the frequency range. The phase angle is close −90°, revealing that the coating behaves like a capacitor. Such response confirms the presence of an insulating and protective coating on the galvanised steel surface. With increasing immersion time, the behaviour of the EIS spectra starts to change and a resistive response develops at low frequencies. Such changes indicate that the electrolyte reached the metallic substrate. However, the low frequency resistance values are dependent on the dopant and on the NaCl concentration. For the Ce-doped coating immersed in the most dilute solution (0.005 M), the low frequency impedance values are above 10⁷ Ω cm² and are nearly constant with time—Fig. 1A. For the highest concentration (0.5 M) of
NaCl, the initial impedance values are above $10^7$ Ω cm$^2$, but later on they start to decrease attaining values around $10^6$ Ω cm$^2$ after 1 week of immersion—Fig. 1B. For the most aggressive chloride solution, the increase of the phase angle in the low frequency range after 2 days of immersion accounts for corrosion development. However, at the end of the tests only few signs of corrosion activity could be observed on the pre-treated surface—Fig. 4A. This means that the corrosion process could not proceed, contrasting with the behaviour observed for the untreated zinc surfaces and for the substrates pre-treated with silane only—Fig. 4B and C.

The EIS results obtained on the substrates pre-treated with the silane solution doped with zirconium nitrate during immersion also evidence very high resistance values—Fig. 2. During the first hours of immersion, the EIS spectra show a capacitive response identical to that observed for Ce-doped coatings. For the substrates pre-treated with the Zr-doped silane and immersed in the most dilute solution, the first signs of corrosion were observed after 1 week of immersion—Fig. 5A. However, for the substrates immersed in the most aggressive solution (Fig. 5B), corrosion activity was detected earlier. After 1 week of immersion, the corrosion signs were more evident than those observed on the substrates pre-treated with the Ce-doped coating.

The evolution of the EIS spectra during immersion in NaCl solutions can be associated with the equivalent circuits depicted in Fig. 6. During the first hours of immersion, the system shows a capacitive response, which corresponds to the capacitance of the doped coating ($C_c$)—Fig. 6A. As the immersion time elapses, the EIS response starts to change. After few hours of immersion (~12 h), the EIS spectra (Figs. 1 and 2) reveal a resistive contribution ($R_c$ in Fig. 6B) in the low frequency range. This change shows that the coating developed conductive pathways whereby electrolyte could reach the substrate. At this stage the electrochemical behaviour of the pre-treated substrate can be associated with the equivalent circuit depicted in Fig. 6B. For the pre-treated substrates immersed in the most aggressive NaCl solution, the accumulation of chloride ions at the interface coating/substrate leads to corrosion onset and build up of corrosion products. This process is characterised by the presence of a time constant ($R_{ct} - C_{dl}$), accounting the charge transfer resistance and the double layer capacitance, respectively—Fig. 6C.
The evolution of the different electrochemical parameters proposed in Fig. 6 during the immersion period is depicted in Figs. 7 and 8. These values were obtained by numerical fitting of the experimental EIS results.

During the first 12 h of immersion, the substrates pre-treated with the Ce-doped silane solutions present identical capacitance values, which are around $2 \times 10^{-9}$ F/cm$^2$, independent of the NaCl solution. After approximately 12 h of immersion, the system starts to reveal a resistive response, however the coating capacitance still remains in the $10^{-9}$ F/cm$^2$ range. Identical trend is observed for the Zr-doped coatings immersed in 0.005 M NaCl—Fig. 7A. However, the Zr-doped system immersed in 0.5 M NaCl shows a sharp increase of the coating capacitance after approximately 12 h of immersion, suggesting rapid deterioration of the coating due to electrolyte uptake.

The values of the coating resistance are dependent on the dopant and on the NaCl concentration—Fig. 7B. The

Fig. 2. EIS Bode plots obtained on galvanised steel substrates pre-treated with silane solutions doped with Zr(NO$_3$)$_3$ during immersion in (A) 0.005 M NaCl and (B) 0.5 M NaCl.

Fig. 3. EIS Bode plots obtained for untreated galvanised steel substrates and for galvanised steel substrates pre-treated with: Cr(VI) based solution, non-doped silane solution and silane solutions doped with Ce or doped with Zr. All the spectra were obtained after 1 day of immersion in 0.005 M NaCl.
highest coating resistances are observed for the Ce-doped system immersed in 0.005 M NaCl. The Zr-doped system immersed in the most dilute NaCl solution also presents very high resistances. However, the drop on the values of the coating resistance is more pronounced for the Zr-doped coatings then for the Ce-doped coatings. This result suggests that the Zr-doped coating is more prone to electrolyte uptake. Nevertheless, at the end of the immersion period in 0.005 M NaCl, the signs of corrosion activity on the surface of the Zr-doped coating were scarce—Fig. 5A.

Fig. 4. Picture of the galvanised steel substrates pre-treated with: (A) BTESPT doped with cerium nitrate after 7 days of immersion in 0.5 M NaCl; (B) untreated surface after 24 h of immersion in 0.005 M NaCl; and (C) substrate pre-treated with non-doped BTESPT after 24 h of immersion in 0.005 M NaCl.

For the highest concentration of NaCl, the resistances of the coatings show a sharper drop. After 7 days of immersion, the resistances of the Ce-doped coating are around $2 \times 10^5 \, \Omega \, \text{cm}^2$, whereas those of the Zr-doped coating are about one order of magnitude lower—Fig. 7B. This trend is in good agreement with the evolution of the coating capacitances and the results show that the Zr-doped coatings are more prone to the development of conductive pathways.

Corrosion activity was only detected on the doped coatings immersed in the most aggressive solution. For

Fig. 5. Picture of the galvanised steel substrates pre-treated with: (A) BTESPT doped with zirconium nitrate after 7 days of immersion in 0.005 M NaCl and (B) BTESPT doped with zirconium nitrate after 7 days of immersion in 0.5 M NaCl.
these substrates the evolution of the double layer capacitance and the evolution of the charge transfer resistance are depicted in Fig. 8A and B, respectively. The capacitance of the double layer for the Ce-doped system increases by three times, from $\frac{2}{10^7}$ to $\frac{6}{10^7}$ F/cm², whereas that of the Zr-doped coating increases by more than one order of magnitude: from $\frac{6}{10^7}$ to $\frac{2}{10^5}$ F/cm². The charge transfer resistances for the Ce-doped coatings are above $10^6$ V cm², whereas for the Zr-doped coatings the resistance decreases from $10^5$ to $3\times10^4$ V cm². The values of the charge transfer resistance show that the corrosion rate of the substrates pre-treated with the Zr-doped coatings is more than one order of magnitude higher than that of the Ce-doped coatings.

Comparison of the EIS results obtained on the doped coatings with the results obtained with substrates pre-treated with non-doped silane evidences the protection of the doped pre-treatment. Fig. 9 depicts the evolution of the different electrochemical parameters associated with the behaviour of galvanised steel substrates pre-treated with non-doped BTESPT immersed in 0.005 M NaCl. For these substrates, the stages presented in Fig. 6A could not be observed. This behaviour suggests that the coatings formed with non-doped BTESPT present more defects and preferential pathways for electrolyte uptake.

The capacitance ($Q_c$) of the doped coatings is about three orders of magnitude lower than that of the non-doped coatings for the same electrolyte concentration (0.005 M NaCl). An identical factor was found for the ratio between the coating resistance ($R_c$) of the doped and the non-doped coatings.

Although the differences in the concentration of aggressive species, the charge transfer resistance for the Zr-doped coating during immersion in 0.5 M NaCl is identical to the values measured for BTESPT. This trend reveals that the presence of Zr mainly affects the parameters associated with the coating.

For the Ce-doped coating immersed in the most aggressive solutions, the charge transfer resistance is more than one order of magnitude higher than that measured for the non-doped coating. This reveals that the presence of Ce decreases the corrosion rate of the substrate. Furthermore, the charge transfer resistance remains approximately constant, suggesting that the corrosion process is not able to proceed.

3.2. Analytical results

The chemical composition of the surface was assessed by X-ray photoelectron spectroscopy (XPS). However, neither...
Ce nor Zr could be detected in the surface film prior to immersion, suggesting that the amount of dopant in the outer layers of the film was too low to be detected by XPS. This result was also confirmed by secondary ion mass spectroscopy (SIMS). The XPS analysis revealed the presence of carbon, oxygen, silicon and sulphur, which are due to the silane coating.

In previous works [8,9,19], it was suggested that the silane coatings formed on galvanised steel substrates seem to be composed by two different layers: one outer layer rich in carbon, silicon, oxygen and sulphur and an inner layer richer in silicon and oxygen. The outer layer seems to delaminate during immersion, whereas the inner layer, rich in silicon and oxygen, is very stable and protective. After approximately 5 days of immersion, the XPS analysis could detect the presence of Ce for the substrates immersed in the most diluted NaCl solution. The photoelectron spectrum for the Ce3d ionisation is depicted in Fig. 10. The main ionisation (Ce 3d_{5/2}) reveals the presence of Ce(III) and Ce(IV), suggesting that both cations are present on the inner layers of the surface film. The existence of Ce(IV) is confirmed by the presence of a satellite in the high binding energy side of the spectra. Since the concentration of Ce is identical to that of Zr, the detection of the former element accounts for its accumulation at the coating/substrate interface. The accumulation of Ce in the inner layers of

![Fig. 8. Evolution of (A) double layer capacitance (Q_{dl}) and (B) charge transfer resistance (R_{ct}) during immersion in NaCl solutions of different concentration.](image)

![Fig. 9. Evolution of (A) coating capacitance (Q_{c}) and double layer capacitance (C_{dl}) and (B) coating resistance (R_{c}) and charge transfer resistance (R_{ct}) for substrates pre-treated with non-doped silane solution during immersion in 0.005 M NaCl.](image)

![Fig. 10. Ce 3d photoelectron spectra obtained on the substrates pre-treated with the Ce-doped silane solution after 5 days of immersion in 0.005 M NaCl.](image)
protective surface film may explain the improved corrosion resistance of the substrates due to the self-healing effects of cerium ions. In the case of the Zr-doped coating, it seems that the dopant is distributed over the coating in a concentration below the detection limit of the XPS technique. Moreover, the release of the outer layers of the coating during immersion also contributes to reduce the Zr content in the coating.

The changes on the surface morphology of the pre-treated substrates were assessed by atomic force microscopy (AFM). Fig. 11 shows the surface of the Ce and of the Zr-doped coatings before immersion in the aggressive solution. The AFM scans reveal a very uniform coating. However, the outer surface layers of the Ce-doped coating are slightly less uniform and contain some particles and few pores with dimensions in the range of some hundred of nanometers.

After 24 h of immersion in the most dilute NaCl solution, the morphology of the coatings changes and the AFM scans starts to reveal an “oxide-type” structure—Fig. 12. These changes are more pronounced for the Zr-doped coating. At this stage, both coatings reveal very high resistances (Fig. 7B), suggesting that the surface is still protected from corrosion. The changes observed in the AFM scans reveal that the outer layers of the coating (previously observed in Fig. 11) are released during immersion. Such release changes the morphology of the outer surface, which becomes closer to that of an oxide film. After about 1 week of immersion (Fig. 13), the doped coatings still present an oxide-type structure, however, the Zr-doped coating shows some signs of corrosion activity.

Fig. 14 presents the AFM scans obtained on the substrate pre-treated with non-doped BTESPT solution prior immersion. The scans clearly show that this coating is more heterogeneous than the doped ones.

4. Discussion

Cerium salts have been successfully tested as corrosion inhibitors in aggressive aqueous environments. Literature [25–30,34–36] reports that the use of cerium salts inhibits the corrosion process in aluminium alloys, steel and galvanised steel.

The improved corrosion protection of galvanised steel and zinc substrates in the presence of cerium ions has been widely discussed in literature. Hinton et al. [34,36] reports that the precipitation of protective cerium oxides on the cathodic sites hinders the cathodic reactions and decreases the corrosion rate. Montemor et al. [25,26] investigated the corrosion behaviour of galvanised steel substrates pre-
treated with Ce(NO₃)₃ conversion films and found the presence of both Ce³⁺ and Ce⁴⁺ in the surface film. Aramaki [27–30] reports that cerium may be involved in the formation on a hydrated or hydroxylated Ce-rich layer. This layer leads to the formation of a Ce₂O₃ framework on the zinc surface, hindering the cathodic reactions. This author also proposes that cerium cations lead to the formation of a protective “self-healing” film. Cerium ions have also been used to improve the corrosion protection of different aluminium alloys and several studies can be found in the literature [35,37,38]. The different mechanisms proposed in literature [27–30,34–38] show that the role of cerium in preventing corrosion development is not fully understood. Several models are proposed but none of them is fully proved. However, it is generally accepted that the presence of cerium either as corrosion inhibitor in aqueous solution or as conversion coating increases the corrosion protection of metallic substrates. Recently, the anti-corrosion behaviour of cerium was also studied for sol–gel coatings containing cerium ions. Literature [23,24] reports that hybrid silica sol–gel films modified with cerium revealed improved corrosion resistance because they behave as a conversion coatings on the zinc substrates. The anticorrosive effect of the cerium ions entrapped in the hybrid silica sol–gel is attributed to the self-repairing properties of the cerium ions (probably with Ce(OH)₃ precipitation) [23].

The addition of zirconium nanoparticles in sol–gel coatings is also reported in the literature [32]. The results evidence that the presence of zirconium nanoparticles improves the corrosion resistance of aluminium alloys. The doping of organosilane films is not reported in the literature. Thus the present work, which follows a previous one [33], presents a novel procedure in which the silane solutions are doped with cerium nitrate or zirconium nitrate. The pre-treatments with the doped silane solutions were tested on galvanised steel substrates. The beneficial effect of the dopants is reflected both in the improved barrier effects and longer durability of the coatings formed on the galvanised steel substrates. The evolution of the impedance plots demonstrates that the doped silane pre-treatments lead to the formation of effective barrier coatings, preventing electrolyte uptake. Moreover, during the first hours of immersion, the doped coatings behave like an insulating coating.

For the substrates pre-treated with the Ce-doped coating and immersed in the most dilute electrolyte, the corrosion process could not be detected in the EIS spectra. Such trend reveals that although electrolyte uptake (the EIS spectra show a resistive behaviour after 12 h of immersion) corrosion could not develop. For the Ce-doped systems exposed to the highest concentration of NaCl, the resistance drop is sharper and corrosion onset was detected in the EIS spectra. Nevertheless, the corrosion activity could not proceed as confirmed by the visual inspection of the surface after 1 week of immersion (Fig. 4A) and by the stable values of the charge transfer resistance, which remain approximately constant and around 2.5×10⁶ Ω cm²—Fig. 8B. This behaviour suggests that the Ce-doped film possesses corrosion inhibition properties. These are due to the presence of cerium ions, which can be released from the inner siloxane matrix, precipitating as cerium oxides and/or hydroxides and self-healing the anodic and/or the cathodic
areas. These assumptions are supported by the AFM and XPS analysis. The AFM scans reveal that the outer carbon layers of the coatings are released during immersion, leaving an “oxide-type” film on the surface, which contains traces of cerium as demonstrated by XPS. This layer constitutes a protective silicon oxide rich-barrier where cerium ions are entrapped. As soon as the corrosion process is initiated, the cerium ions, either Ce⁴⁺ or Ce³⁺, can precipitate on the anodic and/or cathodic places, hindering the corrosion process. The presence of Ce⁴⁺ has also been reported in the literature [39,40] and it is suggested that this ion results from oxidation of Ce³⁺ in the presence of H₂O₂ that is formed in an intermediate step of the reduction of oxygen.

The behaviour of the Zr-doped coatings is significantly different. Corrosion could be observed by naked eye for the substrates immersed in the 0.1 M NaCl solution—Fig. 5. During immersion in the most aggressive solution, the values of the charge transfer resistance were in the same range of the values observed for the non-doped coatings. This is consequence of the fact that zirconium ions do not possess self-healing properties.

The role of the dopants is strongly reflected in the coating parameters, i.e. coating resistance and coating capacitance. The capacitance of the doped coatings is more than two orders of magnitude lower than that of the non-doped coatings, revealing a much more effective barrier effect. The capacitance showed a slight increase during the first 12 h of immersion from values around 2 × 10⁻⁹ F/cm² to values around 6 × 10⁻⁹ F/cm². The resistance shows only a slight decrease. The decreased capacitance values in the presence of the dopants can be due to different factors: increased coating thickness and/or decreased conductivity and porosity. The former effect was already observed for sol–gel coatings doped with cerium nitrate [23]. It was found that the thickness of the coating was dependent on the Ce content in the coating. In the present work, the AFM results account for an identical result. The AFM scans obtained on the non-doped silane coatings prior immersion (Fig. 14) reveal the presence of the substrate features, contrasting with the scans obtained on the doped coatings where only a homogeneous and flat surface could be observed. Thus, the doped coating hinders the native surface roughness, indicating the presence of a thicker coating.

The decreased capacitance values also reflect a strong decrease on the coating conductivity and porosity. In fact, the EIS spectra obtained during the first hours of immersion reveal only a capacitive response, contrasting with the results obtained with the non-doped coatings that showed a resistive behaviour immediately after immersion in the NaCl solution. Literature [23] proposes that cerium ions may replace H⁺ ions in silanol groups. During coating polymerisation, the cerium ions may coordinate with oxygen to satisfy the electroneutrality of the glassy network, reducing the coating porosity and conductivity. However, the results obtained in the present work reveal the presence of Ce³⁺ and Ce⁴⁺ in the inner layers of the coating. These ions may lead to the precipitation of cerium oxides, such as Ce₂O₃ and CeO₂, helping to decreased coating conductivity and porosity. Nevertheless, the possible participation of cerium in the siloxane network cannot be excluded.

Concerning the Zr-doped coatings, it was not possible to detect the dopant in the XPS analysis. However, the evolution of the coating capacitances and resistances also evidences a reduced porosity for the Zr-doped coatings. Precipitation of ZrO₂ inside the structure of the siloxane film and/or bonding of the zirconium ions with the siloxane network during condensation and polymerisation is a possible explanation for the reduced coating porosity and/or conductivity. However, during immersion and due to release of the outer coating layers, the beneficial effects of the zirconium vanish, probably due to dissolution of zirconium ions in the aggressive solution.

The present work clearly evidences the beneficial properties of the pre-treatments based on organofunctional silane solutions doped with cerium nitrate or zirconium nitrate in what concerns corrosion protection of galvanised steel substrates. The role of the dopant is dependent on the cation; cerium being more effective than zirconium. Cerium affects both the coating properties and the corrosion process, whereas zirconium affects mainly the coating resistance and capacitance. Cerium ions may precipitate as insoluble oxides at the interface silane coating/substrate, self-healing the corrosion damages. Concerning the Zr-doped system, as soon as corrosion is initiated, zirconium ions have no effect on decreasing the corrosion rate of the substrate.

The presence of the dopant in very low concentrations can induce important changes in the silane coating, improving its protective barrier effect.

The pre-treatments investigated in this work present powerful potentiality in the field of the alternative and environmentally friend pre-treatments for galvanised steel substrates. Moreover, the addition of cerium to the silane solution modifies the “passive” barrier effect of the silane coating, conferring “self-healing” properties to the inner layers of the silane coating.

5. Conclusions

Pre-treatments for galvanised steel substrates based on bis-[triethoxysilyl]propyl] tetrasulfide doped with small amounts of cerium nitrate or zirconium nitrate are much more protective than the pre-treatments based on non-modified silane solutions.

The presence of the dopant reduces the capacitance and increases the resistance of the coatings. These effects are due to reduced porosity, lower conductivity and increased thickness of the coatings.

The beneficial effects of cerium are more important than those of zirconium. The former dopant accumulates mainly in the stable and protective inner layers of the surface film,
providing corrosion protection, whereas zirconium seems to be released during immersion.

The accumulation of Ce (III) and Ce (IV) ions in the inner layers of the film improves the lifetime of the coating and decreases the corrosion rate of the substrates due to the “self-healing” properties of the cerium ions.

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