Electrochemical assessment of the self-healing properties of Ce-doped silane solutions for the pre-treatment of galvanised steel substrates

W. Trabelsi a, P. Cecilio b, M.G.S. Ferreira b,c, M.F. Montemor b,*

a ENIT, Unité de Recherche de Corrosion, Tunis, Tunisie
b Instituto Superior Técnico, ICEMS, DEQ, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
c University of Aveiro, Department of Ceramic and Glass Engineering, 3810-193 Aveiro, Portugal

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Abstract

The present work aims at assessing the electrochemical behaviour of galvanised steel (GS) substrates pre-treated with bis-[triethoxysilylpropyl]tetrasulfide silane (BTESPT) doped with cerium nitrate. Furthermore, the work aims at evaluating the self-healing properties of the dopant and discussing the possible mechanisms involved in this process. The study was performed by electrochemical impedance spectroscopy (EIS) and by the scanning vibrating electrode technique (SVET), during immersion in NaCl solutions. X-ray photoelectron spectroscopy (XPS) was also used to complement the electrochemical results. The results show that the protective behaviour of the pre-treatments based on Ce-doped silane solutions is dependent on the concentration of the dopant. The results also show that the dopant improves the anti-corrosion performance of the silane coatings formed on galvanised steel substrates.

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1. Introduction

Silane-based pre-treatments have proved to be a technical solution to improve the corrosion resistance of several metals and alloys such as steel, galvanised steel (GS), aluminium alloys and copper [1–20]. Pre-treatments based on silanes present some important advantages such as competitive price, low environmental impact and compatibility with a wide range of inorganic and organic interfaces.

Silanes are hybrid molecules, possessing inorganic and organic functionalities. The hydrolysable inorganic groups can establish stable covalent bonds with the native oxide film existing on the metallic substrates, whereas the organic functionality is compatible with the painting systems. Silanes lead to the formation of a multifunctional self-assembled coating on the metallic substrate that resists to water uptake. Thus, the silane coating provides corrosion protection because it forms a physical barrier, which hinders the penetration of electrolyte towards the metallic substrate. Although the protection provided by the silane barrier, electrolyte reaches the metallic substrate through small cracks and defects, leading to corrosion onset. Thus, corrosion protection is dependent on the resistance of the silane coating against electrolyte uptake, i.e. its protective barrier effect. This barrier effect can be enhanced in order to make the silane coatings even more effective. Such goal can be achieved by the addition of small amounts of chemicals possessing corrosion inhibition properties, preferentially self-healing properties. One example of these chemicals is cerium nitrate, which is known to act as corrosion inhibitor in aqueous aggressive medium. Cerium nitrate has been successfully tested for corrosion protection of galvanised steel substrates [21–26] either as aqueous corrosion inhibitor or as conversion coating. The modification of the "passive" or inert role of thin organic coatings through the addition of cerium nitrate was tested for hybrid sol-gel coatings [27–29], which revealed improved corrosion protection of aluminium and zinc substrates.

The modification of silane coatings through doping with cerium nitrate is a procedure that combines the good barrier
properties of the silane coating with the corrosion inhibition properties of the cerium ions. It is expected that the cerium ions present in the silane coating can protect the damaged zones hindering the corrosion process.

The corrosion inhibition properties of cerium nitrate have been widely discussed in literature [21–34], however, very little is known on the mechanisms involved in such process. It is generally accepted that cerium ions lead to the precipitation of cerium oxides and/or hydroxides that hinder the corrosion reactions.

Following previous studies [21,22,35,36], the present work investigates the electrochemical behaviour of galvanised steel substrates pre-treated with bis-[triethoxysilylpropyl] tetrasulfide silane (BTESPT) solutions doped with cerium nitrate. The electrochemical impedance spectroscopy (EIS) measurements show that corrosion behaviour is dependent on the concentration of the dopant, revealing that there is an optimum amount of dopant. The scanning vibrating electrode technique (SVET) measurements evidence that the doped pre-treatments present improved corrosion resistance.

2. Experimental procedure

2.1. Pre-treatments

The bis-[triethoxysilylpropyl] tetrasulfide silane (Sigma-Aldrich product) solution was prepared by dissolving 4% (v/v) of silane in methanol (90.5%, v/v) and 5.5% (v/v) of aqueous solutions of cerium nitrate with different concentrations: 1 × 10⁻⁴, 1 × 10⁻³, 1 × 10⁻² and 1 × 10⁻¹ M. The final concentrations of cerium nitrate in the pre-treatment solution were: 5.5 × 10⁻⁶, 5.5 × 10⁻⁵, 5.5 × 10⁻⁴ and 5.5 × 10⁻³ M, respectively. However, in the text and pictures, the concentrations are always referred to the initial concentration of the cerium nitrate solution.

The doped silane solution was stirred during 1 h and kept for 3 days before use.

The metallic substrate consisted of galvanised steel coupons 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 using air stream and the panels were cured in a Memmert oven at 120 °C for 40 min.

2.2. Electrochemical techniques

The electrochemical impedance spectroscopy 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 down to 10⁻² Hz.

Electrochemical experiments were performed during immersion in 0.005 M NaCl at least in duplicate samples.

The scanning vibrational electrode technique measurements were performed using an applicable electronics apparatus. The scanned area was 1 mm × 1 mm.

2.3. Analytical techniques

X-ray photoelectron spectroscopy (XPS) analyses were carried out using a 310F 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 mm × 3 mm.

3. Results

Figs. 1 and 2 depict the EIS spectra obtained on galvanised steel samples pre-treated with silane solutions doped with different concentrations of cerium nitrate. After 1 day of immersion in 0.005 M NaCl (Fig. 1), the total impedance
The total impedance of the system is around $1 \times 10^7 \ \Omega \ cm^2$, being independent on the concentration of dopant. However, after 1 week of immersion, it can be observed that the total impedance depends on the amount of cerium (Fig. 2). The highest impedance values were obtained for the pre-treatment system prepared using $1 \times 10^{-3} \ M \ Ce(NO_3)_3$, whereas the lowest values were obtained for the pre-treatment prepared with the most concentrated Ce(NO$_3$)$_3$ solutions.

The EIS results show that the total impedance of the system, which is an indicator of the corrosion resistance, is dependent on the concentration of cerium nitrate in the silane coating; the effect being more marked for long immersion times.

The interpretation of the EIS results obtained during immersion in NaCl solutions can be made by numerical fitting, using the equivalent circuits depicted in Fig. 3. This equivalent circuit was proposed and described elsewhere [35]. In this equivalent circuit, constant phase elements were used instead of pure capacitors. During the first hours of immersion (6–12 h, depending on the coating), some of the pre-treated systems reveal only a capacitive response, which corresponds to the capacitance of the doped coating ($Q_c$) (Fig. 3A). Later on, all the systems start to reveal a resistive contribution ($R_c$ in Fig. 3B) in the low frequency range. These changes show that the coatings developed conductive pathways whereby electrolyte could reach the substrate. After few days of immersion, some of the EIS spectra show the formation of a time constant ($R_c \cdot Q_c$), in the low frequency range, which reveals corrosion activity and build up of corrosion products (Fig. 3C).

The evolution of the different electrochemical parameters defined by the equivalent circuits proposed in Fig. 3, is depicted in Figs. 4 and 5.

![Fig. 2. EIS results obtained on the substrates pre-treated with the silane solutions doped with different amounts of cerium nitrate after 7 days of immersion in 0.005 M NaCl.](image)

The capacitance and the resistance of the coating are indicators of the protective performance, i.e. the barrier properties of the coating. High resistances and low capacitances reveal a more protective coating. These parameters depend on the number of conductive pathways that develop on the coating. The coating doped with $1 \times 10^{-4} \ M \ Ce(NO_3)_3$ shows the lowest resistance and the highest capacitances at the end of the test period, suggesting that the increase of the cerium concentration promotes the formation of more defective coatings. After 7 days of immersion, the coating resistance is around $2 \times 10^5 \ \Omega \ cm^2$ and the coating capacitance ($Q_c$) is around $2 \times 10^{-8} \ F/cm^2$. This capacitance is about one order of magnitude higher than that of the coating containing $1 \times 10^{-5} \ M$.
Fig. 4. Evolution of the coating resistance and coating capacitance during immersion in NaCl solutions. Values were obtained by numerical fitting using the equivalent circuit depicted in Fig. 3.

Ce(NO₃)₃, whereas the resistance is two orders of magnitude below. Nevertheless, the resistances of the doped coatings are more than one order of magnitude higher than those of the non-doped coatings that are in the range 5 × 10⁴ to 1 × 10⁶ Ω/cm² [35]. Furthermore, the capacitances of the non-doped coatings are around 2 × 10⁻⁶ F/cm², two orders of magnitude above those of the Ce-doped coatings. This behaviour indicates that the presence of the dopant leads to an important decrease of the coating capacitance. Such drop can be due to an increase of the coating thickness and/or lower porosity and decreased conductivity. The evolution of the coating resistance and coating capacitance suggests that there is an optimum concentration of cerium nitrate for doping of the silane solutions.

The amount of cerium nitrate also affects the parameters characteristic of the corrosion process that is associated with the development of a time constant in the low frequency range of the EIS spectra. The charge transfer resistance, which is inversely proportional to the corrosion rate, decreases with increasing cerium content (Fig. 5). For the substrates pre-treated with the silane solutions doped with 1 × 10⁻³ M Ce(NO₃)₃, it was not possible to determine the charge transfer resistance. This behaviour is the consequence of the high resistance of the doped coating against corrosion onset. However, for the other coatings, it was possible to observe the presence of a low frequency time constant in the EIS spectra. For these coatings, the EIS results were fitted using the equivalent circuit depicted in Fig. 3C. The lowest resistances (below 1 × 10⁶ Ω/cm²) are observed for the coating doped with 1 × 10⁻¹ M Ce(NO₃)₃. The double layer capacitance is identical for all the coatings and increases by more than one order of magnitude during immersion. The EIS results also show that the coating doped with the highest concentration of cerium nitrate develops corrosion activity earlier than the other coatings. The first signs of corrosion activity in the substrate pre-treated with 1 × 10⁻¹ M Ce(NO₃)₃ were detected after 24 h of immersion, whereas for the others coatings (except the one containing 1 × 10⁻³ M Ce(NO₃)₃) it started after 4 days of immersion. These results are in good agreement with the evolution of the coating resistance and indicate that there is an optimum concentration of cerium in the silane solution. For the highest concentration of cerium nitrate, there is a negative effect on the barrier properties of the coating, facilitating corrosion activity.

Attending to the results depicted in Figs. 1 and 2, it was decided to study the self-healing effects of the cerium ions.
using the dopant concentration that led to the highest coating resistance, i.e. $1 \times 10^{-3} \text{M}$ Ce(NO$_3$)$_3$. Thus, the pre-treated substrate was immersed in 0.005 M NaCl during 24 h and then an artificial defect was created on its surface. This defect was made using a needle, which was strongly pressed against the surface. Identical procedure was performed for galvanised steel substrates pre-treated with silane only. For the bare material (galvanised steel), an artificial defect was also formed in order to ensure that the defect did not reach the iron substrate.

Fig. 6 shows the EIS results obtained on the systems pre-treated with silane and cerium nitrate, prior and after defect formation. Results for the bare material (also containing an identical defect) were also included for comparison. During the first day of immersion, before the formation of the defect, the EIS results show a small decrease of the total impedance of the system due to electrolyte uptake. At this stage, the electrochemical behaviour of the system can be described by the equivalent circuit shown in Fig. 3B. After the formation of the defect on the substrate pre-treated with the doped silane solution, there is a decrease of the impedance values by about one order of magnitude. However, after this initial decrease, the impedance values remain approximately constant, independently of the immersion time. These results show that although the presence of a defect, the corrosion process could not proceed, being hindered by the presence of cerium ions.

The EIS results obtained on the untreated galvanised steel show the presence of a time constant in the low frequency range, which is associated with corrosion activity. This time constant is not evident on the pre-treated substrates. Furthermore, the total impedance of the pre-treated substrates with an artificial defect is more than two orders of magnitude higher than the values measured for the untreated galvanised steel. These results clearly show that the cerium ions present in the silane coating reduce the corrosion rate of the substrate.

The corrosion inhibition properties of the cerium ions were also investigated using the SVET technique. Fig. 7A depicts the SVET results obtained on the galvanised steel substrates pre-treated with non-doped BTESPT solutions after 1 day of immersion in 0.005 M NaCl. During the first hours of immersion, the anodic activity is nearly zero, as expected due to the presence of the protective silane coating, but slightly increased with time. After 1 day of immersion, an artificial defect was created on the substrate pre-treated with non-doped BTESPT solution. This procedure aims at evaluating the behaviour of the damaged area during immersion. After
For the substrate pre-treated with BTESPT doped with $1 \times 10^{-3} \text{M} \text{Ce(NO}_3\text{)}_3$, no anodic activity could be observed during the first 24 h of immersion (Fig. 8A) in good agreement with the EIS measurements (Fig. 6). After this period, an artificial defect was also created on the surface. After few minutes of immersion, anodic activity is clearly observed in the defect and during the first hours of immersion there were some important changes on the behaviour of the areas surrounding the defect. During the first minutes after defect formation, there is development of anodic activity, and simultaneously, there is formation of a cathodic area close to the anode (Fig. 8B). The SVET results show that the location of the cathodic areas change with time, moving around the anodic spot and leaving the region where they were previously located without activity (Figs. 8B and 9A). This, for example, the first cathodic areas observed in Fig. 8B become inactive and a new cathode develops in a new region around the anodic spot (Fig. 9A). Later on, all the anodic and cathodic activity stops (Fig. 9B), suggesting that the corrosion reactions are strongly hindered. This trend was observed during the further 48 h after defect formation. These results contrast with those observed on the substrate pre-treated with silane only, where the anodic activity increased after defect formation. The SVET results clearly show that the presence of cerium ions contributes to hinder the corrosion process.

The surface of the galvanised steel substrate pre-treated with BTESPT solutions doped with cerium nitrate was investigated by XPS analysis. During the first stages of immersion cerium could not be detected in the surface of the coating. This result was confirmed by ToF-SIMS, which has a much better detection limit. The analytical results show that cerium is not present in the outer layers of the coating, being probably located deeper in the coating. After 3 days of immersion, a very weak signal for the Ce 3d XPS ionisation could be detected, revealing the presence of both Ce$^{3+}$ and Ce$^{4+}$ (Fig. 10). The presence of Ce$^{3+}$ is identified by the satellite peak on the high binding energy side of the spectrum that arises only from Ce$^{3+}$. The XPS results suggest that the pro-
The formation of a Ce$_2$O$_3$ framework over the zinc surface and the cathodic reaction, which leads to the production of H$_2$O$_2$. Ions in an intermediate step of the oxygen reduction during Ce$^{3+}$ and Ce$^{4+}$ oxides and/or hydroxides. A protective film formed on the surface incorporates a mixture of Ce$^{3+}$ and Ce$^{4+}$ oxides and/or hydroxides.

4. Discussion

Cerium nitrate is considered a good aqueous corrosion inhibitor for different metals and alloys, such as steel, aluminium, magnesium, tin and galvanised steel. Hinton [30] published the first works reporting the use of cerium chloride for corrosion protection of galvanised steel. The works report that the release of hydroxyl ions in the cathodic areas led to the precipitation of cerium hydroxides and oxides. Such species block the cathodic areas, hindering the transfer of electrons and consequently, the corrosion rate. Other works [37] reveal the presence of small amounts of Ce$^{4+}$. The presence of this ion was attributed to oxidation of Ce$^{3+}$ ions in an intermediate step of the oxygen reduction during the cathodic reaction, which leads to the production of H$_2$O$_2$. This fact is also reported by other authors [38].

The effect of Ce$^{4+}$ on the corrosion protection of organic coatings was investigated and the role of the cerium ions was attributed to the precipitation of Ce$^{4+}$ hydroxides/oxides in several steps, involving hydrolysed Ce$^{3+}$ ions and Zn(OH)$_2$. Furthermore, it is reported that prolonged exposure of the coatings to chloride ions leads to the formation of small amounts of Ce$^{3+}$. Once more, the presence of this ion is attributed to the formation of H$_2$O$_2$ as an intermediate product of the cathodic reaction [39].

Aldykeiwicz et al. [31] reports the presence of CeO$_2$ and explains its formation by oxidation, in solution of Ce$^{3+}$ ions to tetravalent CeO$_2$ and further precipitation to CeO$_2$. Other works [40] report a process in which Ce(OH)$_3$ is converted in CeO$_2$ in a dismutation solid state reaction. The electrooxidation of Ce$^{3+}$ to Ce$^{4+}$ inside the film is also postulated to explain the presence of the tetravalent cation.

The self-healing mechanism of cerium nitrate mixed with silica in a silane polymer is discussed by Aramaki [26] and it is shown that a passive film composed by Zn(OH)$_2$, ZnSi$_2$O$_5$ and Ce$_{3+}$/Si$_2$O$_5$ salt or complex may repair the damaged areas. The work concludes that the precipitation of silicate compounds in the defects of the coating prevents pitting corrosion.

In previous works, Montemor et al. [21,22] investigated the chemical composition of cerium conversion films formed on galvanised steel. It was shown that the presence of Ce$^{4+}$ seems to be associated with the thickening of cerium conversion layers and formation of corrosion spots. It is important to remark that this behaviour was observed on conversion films formed by immersion in Ce(NO$_3$)$_3$ solutions, without exposure to chloride-containing solutions. The same work also reports that the ratio Ce$^{3+}$/Ce$^{4+}$ increases with increasing film thickness. The experimental results also show that the increase of this ratio seems to be associated with the formation of defects on the conversion film. These previous results suggest that the formation of Ce$^{4+}$ does not depend on the presence of chloride ions, but seems to be related with film thickening and formation of anodic areas on the zinc substrate. The presence of Ce$^{4+}$ was attributed to the oxidation of Ce(OH)$_3$ to Ce$^{4+}$ according to the reaction [21]:

$$2\text{Ce(OH)}_3 + 2(\text{OH}^-) \rightarrow 2\text{CeO}_2 + 4\text{H}_2\text{O} + 2\text{e}^- \quad (1)$$

$$\text{H}_2\text{O}_2 + 2\text{OH}^- + 2\text{e}^- \rightarrow 2\text{OH}^- \quad (2)$$

These reactions account for the precipitation of CeO$_2$ at the cathodic places due to the release of OH$^-$ from oxygen reduction.

The SVET results depicted in Figs. 8 and 9 show that after formation of the defect, there is development of cathodic activity in the vicinity of the anodic area. Moreover, the results show that the cathodic places seem to move around the defect. Assuming that the cerium ions present in the silane coating can be released in the vicinity of the defect, they may precipitate as cerium hydroxides and/or oxides at the cathodic places as consequence of the pH raise. Taking into account reactions (1) and (2), Ce(OH)$_3$ may lead to the precipitation of CeO$_2$, identified in the XPS analysis (Fig. 10).

As soon as the cathodic places are covered with the mixture of cerium oxides and hydroxides, new cathodes are formed in order to counterbalance the anodic activity in the defect. Again, the process of cerium oxides and hydroxides precipitation may be repeated, and once more the cathodic places become inactive. The process seems to be repeated around the defect, and finally, all the areas surrounding the anodic place become covered with cerium precipitates. Since these precipitates hinder the flux of electrons from the anodic areas to new developing cathodic places, the cathodic reactions are hindered and consequently the anodic activity vanishes.

The above mechanism can be used to explain the improved corrosion resistance of galvanised steel substrates pre-treated
with silane solutions doped with cerium nitrate during immersion in NaCl solutions. The protection mechanism seems to be closely associated with the presence of cerium oxides/hydroxides at the interface silane-coating and blocking of the cathodic areas, hindering the corrosion processes. The addition of cerium to the pre-treatment solution strongly improves the barrier properties of the coating. The EIS results show that the coating resistance increases by more than two orders of magnitude comparatively to the non-doped coatings, whereas the capacitance strongly decreases. Such behaviour indicates that the number of conductive pathways is much more reduced in the presence of the dopant. Moreover, this behaviour is dependent on the amount of dopant. The presence of cerium nitrate reduces the coating porosity over, this behaviour is dependent on the amount of dopant. Literature [28] reports that cerium ions may replace H⁺ ions and/or conductivity and may increase the coating thickness. The presence of cerium nitrate reduces the coating porosity over, this behaviour is dependent on the amount of dopant. Literature [28] reports that cerium ions may replace H⁺ ions in silanol groups. During coating polymerisation, the cerium ions coordinate with oxygen to satisfy the electron neutrality of the glassy network that reduces the porosity of the coating, helping to decrease capacitance and increase resistance. The same work also reports that there is a critical concentration of Ce³⁺ in the range 0.2-0.6 wt%]. Higher concentrations of cerium could yield networking defects. An increase of the film thickness with increasing Ce³⁺ was also observed [28]. However, the results obtained in the present work reveal that Ce³⁺ and Ce⁴⁺ seems to be located in the inner layers of the coating. These ions may lead to the precipitation of cerium species, decreasing the porosity and the conductivity of the inner layers of the coating. Nevertheless, the possible participation of cerium in the siloxane network during the polymerisation of the silane chains cannot be excluded.

The increase of dopant in the silane coating promotes the formation of more defective coatings and thus, the barrier properties are negatively affected.

The results obtained in this work evidence that the doping of the silane solutions with small amounts of cerium nitrate leads to improved corrosion protection of galvanised steel substrates. This behaviour results from a combination of enhanced barrier properties of the silane coating and corrosion inhibition by cerium ions, in a process that overcomes the usual "passive" role of the silane coatings, making them "smarter" coatings.

5. Conclusions

Pre-treatments for galvanised steel based on the use of bis-[triethoxysilylpropyl] tetrasulfide silane doped with cerium nitrate show very good anti-corrosion properties; the corrosion rate decreases by more than one order of magnitude comparatively to the use of non-doped silane solutions. The addition of cerium nitrate, as dopant, improves the barrier properties of the silane coating by increasing the coating resistance and decreasing the coating capacitance. The results suggest that there is an optimum concentration of cerium nitrate around 1 × 10⁻³ M. Higher or lower concentrations of cerium nitrate decrease the coating resistance and increase coating capacitance, leading to a negative effect in the barrier properties of the coating.

The presence of cerium nitrate in the silane coating reduces the corrosion rate of the substrate. The mechanism involved in such process may be related with precipitation of cerium oxides and hydroxides in the vicinity of the anodic areas. These precipitates reduce cathodic activity and hinder the transfer of electrons from the anodic to the cathodic places.

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