Silanes and rare earth salts as chromate replacers for pre-treatments on galvanised steel

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Abstract

Cr(VI)-based pre-treatments have been in use for long time on several materials, however, they are target of great criticism and in the near future they could be definitely banned. The actual alternatives to Cr(VI) show pros and cons when sets of key properties are considered such as: corrosion resistance, adhesion of organic coatings, fatigue resistance, reliability and quality control. However, some of the possible alternatives show high potential, if some improvements are carried out and the if mechanisms involved are more deeply understood.

The present work focus on the use of rare earth (Ce, La) salts and bis-sulphur silane (BTESPT) as chromate substitutes for galvanised steel. These compounds when applied by immersion and subsequent curing originate films that improve corrosion resistance and paint adherence. The films were characterised by Auger and XPS spectroscopy. The corrosion resistance was assessed by electrochemical impedance spectroscopy and dc polarisation. Comparison with the chromate conversion pre-treatment is also carried out simultaneously with discussion of the possible mechanisms involved in the different processes.
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1. Introduction

Among the possible alternatives to the use of Cr(VI)-based pre-treatments the use of rare earth salts and silanes have been an envisaged solution. Rare earth (RE) salts have been successfully used in many metals and alloys for corrosion protection in aqueous environments. References to the use of $LaCl_3$ and $CeCl_3$ for corrosion inhibition in aluminium alloys [1,2], steel [3,4] and galvanised steel [5,6] are found in literature reporting good results. The use of RE salts to form conversion coatings is another way of achieving corrosion protection. These conversion coatings can be formed either by immersion [7,8] or by electrodeposition [9].

In spite of the increasing number of references found in literature in the recent years there is, however, some discussion on the mechanism by which the RE-based pre-treatments (namely with cerium) lead to increased corrosion protection. The first attempts on the field were made by Hinton [5,10]. These works propose that the cathodic reactions (oxygen reduction and hydrogen evolution) generate an alkaline environment that leads to precipitation of RE oxides and thus to the formation of a protective surface film. Davenport and co-workers [1,2] also investigated cerium deposition on aluminium alloys and showed that cerium is oxidised from Ce^{3+} to Ce^{4+} in solution by dissolved oxygen and in a final step it precipitates as insoluble CeO_2 on the cathodic sites. Montemor et al. [7,8] investigated the effect of the treatment time in the chemical composition and corrosion behaviour of $Ce(NO_3)_3$ conversion coatings on galvanised steel and found that the film composition and thickness changes with time. The thickening of Ce conversion films was accompanied by an enrichment in Ce^{4+} and by the development of defects, which decrease the corrosion resistance of both painted and unpainted galvanised steel substrates. The same authors also report that pre-treatments based on $La(NO_3)_3$ seem to be slightly more effective than those based on $Ce(NO_3)_3$ or $Y(NO_3)_3$ [8]. The mechanism

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of corrosion inhibition on zinc pre-treated with cerium salts was also investigated by Aramaki [6,11–13], who reports the formation of a hydrated or hydroxylated Ce-rich layer that is constructed by adsorption on the hydroxylated zinc surface. This process leads to the formation of a Ce_2O_3 framework on the zinc surface, which suppresses the cathodic reactions.

The different mechanisms proposed in literature show that the role of RE is not fully understood. However, it is generally accepted that they lead to increased corrosion protection and that they are a promising alternative as environmentally friendly pre-treatments.

The use of silanes has become another alternative to the conventional Cr(VI)-based pre-treatments. Its use is attracting the attention of many industries, because silanes are known as good coupling agents, conferring in addition corrosion protection [14–18]. Moreover, the pre-treatments processes are simple and comply with environmental issues.

Organofunctional silanes have a $X_3Si(CH_2)_nY$ type of structure, where X represents an alkyl hydrolysable group and Y is an organofunctional group. When the silane is symmetrical relatively to the functional groups, Y, i.e., if there are two hydrolysable SiX_3 groups at the ends, these molecules are termed bis-functional silanes. These bis-functional silanes have a $X_3Si(CH_2)_nY(CH_2)_nSiX_3$ type of structure.

The corrosion performance of a variety of silanes such as UPS (ureidopropyltrialkoxysilane), VS (vinyl-tri(m)ethoxysilane), BTSE (bis-1,2-[triethoxysily]ethane) and $(C_2H_5O)_3Si–CH_2CH_2–Si(OC_2H_5)_3$, has also been studied [15,18–22] and the main conclusions are that they could be used as effective anticorrosion agents if applied under proper process conditions. These include the control of parameters such as concentration and pH of the silane solution and curing procedure as reported by Franquet et al. [20].

Recently, references to the use of BTESPT (bis-[triethoxysilylpropyl]tetrasulphide) $(C_2H_5O)_3Si–(CH_2)_3–S_x–(CH_2)_3–Si(OC_2H_5)_3$ that has an average x value of 3.8, and bis-amino silanes were found [17,18]. BTESPT was tested with good results on Al alloys, Zn–Ni-coated steel, and galvanised steel [17]. Recently [18], the efficiency of BTESPT on the corrosion protection of Al 2024 was related with the presence of a highly crosslinked interfacial layer with small porosity and strong adhesion, hindering pit growth and cathodic activity.

The present work is a step towards the new field of environmentally friendly pre-treatments. The work aims mainly to understand the corrosion behaviour of Cr(VI)-free pre-treatments for galvanised steel. These pre-treatments use rare earth (Ce or La) nitrates to form a conversion film on the surface aiming mainly enhanced corrosion protection and the bis-functional silane (BTESPT), aiming to improve both corrosion protection and adhesion of the organic coatings. The investigation was preformed on uncoated and coated pre-treated hot dip galvanised (HDG) steel substrates.

2. Experimental

2.1. Preparation of the metallic substrates

The hot dip galvanised steel substrates (zinc coating $275\,g\,m^{-2}$ with 5% Al) degreased using an alkaline cleaner (NOVOMAX® 187 U supplied by Henkel). The cleaner was prepared as a 3% (v/v) solution, maintained at 60 °C. Following cleaning the panels were washed with distilled water and dried at air.

2.2. Solutions

Solutions of $Ce(NO_3)_3$ and $La(NO_3)_3$ (salts supplied by Sigma-Aldrich) were used, corresponding to salt concentrations of 0.01 M. A 4% BTESPT solution was prepared by dissolving the correct volume of silane in a mixture of methanol and deionised water: silane/DI water/methanol = 4/5.5/90.5% (v/v). The solution was kept for stabilisation at least 4 days before use.

2.3. Pre-treatments

The HDG samples were pre-treated according to the following alternative procedures:

(i) Immersion in the BTESPT solution during 10 s and cure at 120 °C during 40 min.
(ii) Immersion in the rare earth solution during 10 s, cure at 120 °C during 40 min.
(iii) Immersion in the rare earth solution during 10 s, cure at 120 °C during 40 min. Following this pre-treatment samples were immersed in BTESPT solution during 10 s and a new cure at 120 °C during 40 min was performed. This procedure is referred as the two-step pre-treatment.

A standard commercial Cr pre-treatment was also used as reference.

Electrochemical experiments for the uncoated samples were performed in 0.05 N NaCl, at room temperature with natural aeration. All the tests were made, at least in duplicate panels.

A set of samples pre-treated in the different ways was painted using a commercial epoxy primer (supplied by Hempel, Portugal) and tested in 0.5 N NaCl. The coating thickness was around 20–30 μm. Since the corrosion process is much slower in coated samples, a higher concentration of aggressive solution (0.5 N) was used, comparatively to that used for the uncoated substrates (0.05 N).

2.4. Techniques

2.4.1. Electrochemical techniques

The EIS measurements were carried out using a Gamry FAS1 Femtostat + PC4 Controller Board and all the measurements were performed at room temperature in a Faraday

cage. A three-electrode electrochemical cell arrangement was used, consisting on the working electrode ($3.15\,cm^2$ of exposed area), saturated calomel electrode as reference and Pt as counter electrode. The measuring frequency ranged from 10^5 down to 10^{-3} Hz. All the experiments were performed at the corrosion potential after stabilisation (~10 min).

The potentiodynamic polarisation experiments were performed starting at the open circuit potential (after ~10 min stabilisation), using a scan rate of 1 mV/s, in the anodic or cathodic direction, depending on the branch under study.

2.4.2. Analytical techniques

AES depth profiles, and XPS analyses were carried using a 310 F Microlab (VG Scientific) equipped with a field emission type electron gun, a concentric hemispherical analyser and a differentially pumped ion gun. Auger spectra were taken using a 10 keV and ~40 nA primary electron beam. The Auger depth profiles were obtained using a differential pumped ion gun with an ion beam accelerated at 2 keV. The etching current was around $0.75\,\mu m/cm^2$. These parameters were chosen in order to avoid damage of the surface and to reduce preferential sputtering. The electron beam was aligned with the centre of the sputtered region. Although the roughness of the surface increases with depth, the very high spatial resolution of the electron beam (100 nm) limits the deleterious effects of long sputtering on the final profiles.

XPS analyses were performed using an Mg (non-monochromated) anode. The spectra were taken in CAE mode (30 eV).

3. Results and discussion

3.1. Uncoated hot dip galvanised steel

3.1.1. Electrochemical results

The electrochemical behaviour of the pre-treated substrates was investigated by potentiodynamic polarisation. Figs. 1 and 2 depict the cathodic and the anodic curves, respectively, obtained on the pre-treated substrates and on the untreated metal. At the end of the tests all the samples showed signs of corrosion activity with some black deposits on the surface.

The cathodic currents (Fig. 1) show a decrease when the substrate is pre-treated. The current decreases following the order: HDG > Silane only > Ce only > La only > Cr > Ce + silane > La + silane. Relatively to the untreated HDG the treatment with silane only provides a slight reduction of the cathodic currents, however, the two-step pre-treatment leads to the strongest reduction. Comparatively to the Cr reference only the two-step pre-treatments are more effective in terms of cathodic polarisation.

Concerning the anodic curve (Fig. 2) all the pre-treatments lead to a slight reduction of the anodic currents,
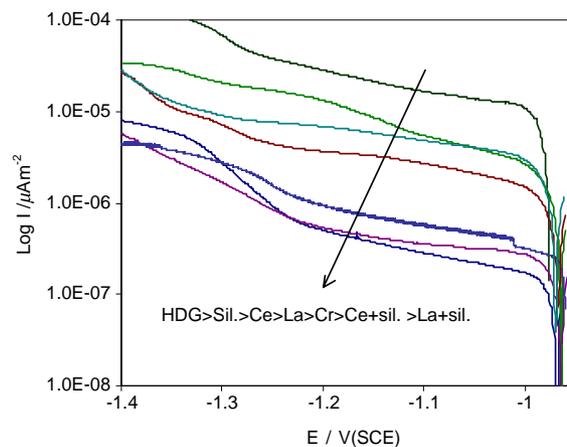

Fig. 1. Cathodic curves obtained for pre-treated HDG immersed in 0.05 N NaCl.

according to the following order: HDG > Ce only > La only > Cr > Ce + silane ~Silane only > La + silane. The pre-treatment with RE only slightly reduces the anodic current comparatively to the untreated substrate, but they are not so effective as the Cr reference. However, the two-step pre-treatments ($Ce(NO_3)_3$ plus silane and $La(NO_3)_3$ plus silane) tends to show the lowest anodic currents. For potentials between the corrosion potential and -0.85 V these pre-treatments reduce the anodic currents by about one order of magnitude, relatively to the untreated substrate.

The results clearly show that the pre-treatments affect both the cathodic and the anodic behaviour of the system. The main reactions occurring in the galvanised steel substrate are the anodic dissolution of zinc, with formation of Zn^{2+}, and the oxygen reduction that releases OH^- ions. These ions lead to the formation of zinc hydroxides and oxides that may complex with chlorides present in solution allowing corrosion onset. The trends observed both on the anodic and cathodic branches after pre-treatment could be explained attending to the role of the rare earth conversion coating and to the role of silane.
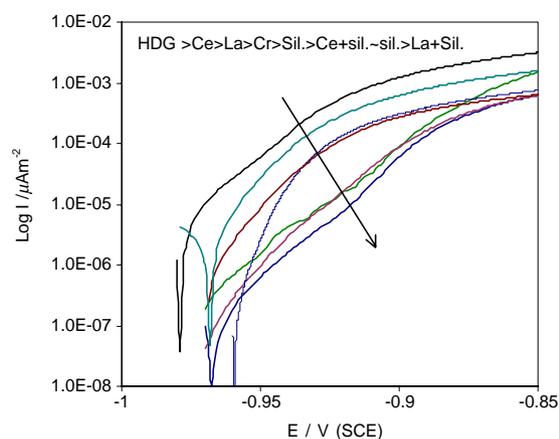

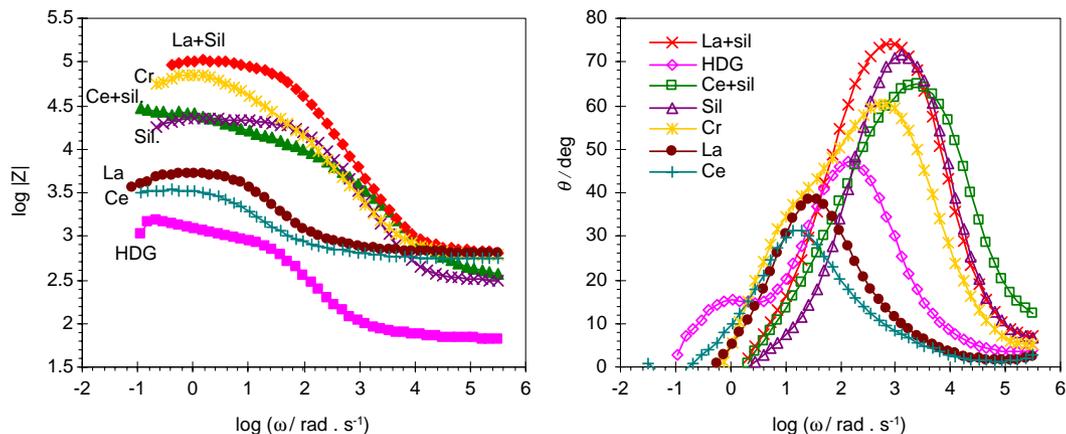Fig. 2. Anodic curves obtained for pre-treated HDG immersed in 0.05 N NaCl.

Fig. 3. EIS Bode plots obtained for pre-treated HDG immersed in 0.05 N NaCl during 1 h.

The reduction of the cathodic currents in the presence of RE salts is one of the most widely accepted mechanisms for improved corrosion protection [1,2,5]. Hinton [5] suggests that the development of the RE oxide film on the cathodic sites creates a barrier to the supply of oxygen or electrons to the oxygen reduction reaction. However, there are also references [3,7,8] to inhibition of the anodic reactions. The results obtained in the present work suggest that pre-treatments based on rare earth salts may act as mixed inhibitors reducing both anodic and cathodic activity.

The presence of the silane layer on the top of the conversion coating enhances these trends, especially the cathodic one, where the current decreases by more than one order of magnitude. Here, the silane acts mainly as a physical barrier covering the remaining active areas. The reduction of the total surface area, thus result in a decrease in the total cathodic current density. Identical results were observed for aluminium alloys pre-treated with the same silane [18].

The electrochemical behaviour of the pre-treated substrates was also investigated by electrochemical impedance spectroscopy (EIS). Figs. 3 and 4 depict the impedance plots

obtained after different periods of immersion in the aggressive solution (0.05 N NaCl). The spectra obtained after 1 h of immersion (Fig. 3) show that all the pre-treatments lead to increased protection comparatively to the untreated substrate. The total impedance of the system measured in the low frequency range (10^{-2} Hz) increases by more than one order of magnitude when the system is pre-treated with silane or with RE plus silane. There are no significant differences between the silane only and the Ce + silane pre-treatments and their impedance is slightly lower than that of the Cr reference. However, the pre-treatment with La plus silane leads to the highest impedance values, performing better than the Cr reference.

Results obtained after 24 h of immersion are depicted in Fig. 4. At this stage all the samples show some signs of corrosion activity in the form of small pits with colours ranging from white to dark grey. The pre-treatment with La only, shows impedance values very close to those of untreated HDG. The pre-treatment with silane only shows impedance values about one order of magnitude above that of HDG. However, the better results correspond to the two-step pre-treatments and among these, the highest impedances
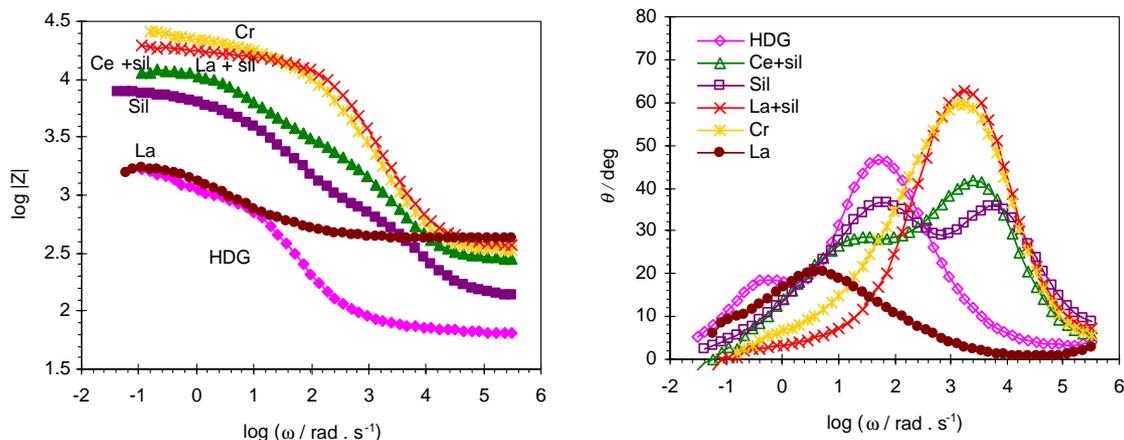

Fig. 4. EIS Bode plots obtained for pre-treated HDG immersed in 0.05 N NaCl during 24 h.

are observed for La plus silane, which is still very close to the Cr reference.

The behaviour of the impedance plots shows important changes with immersion time, which help to understand the role of the different pre-treatments. Initially, the pre-treatments involving the silane show the presence of a time constant in the high frequency range ($>10^3$ Hz). This time constant is characterised by capacitances around $0.5\,\mu F/cm^2$ and suggests the presence of a thin surface film, resulting from the presence of the silane layer, since it is not observed on the pre-treatments made with RE only, which show only one time constant (an inorganic oxide film) at lower frequencies.

After 24 h the time constant associated with the presence of the silane layer is still well defined, however, the substrates treated with Ce plus silane and with silane present a new time constant in an intermediate frequency range. Since this time constant appears at the same frequency of that of untreated HDG it suggests the presence of an oxide type surface film. The presence of a time constant, developing with time is referred in literature [15,18], being related with an intermediate phase between the external silane layer and the native oxide substrate. This phase involves the silane groups that form covalent bonds with the metallic substrate (Si–O–M). Since BTESPT has four sulphur atoms, which have good affinity for zinc, it is suggested that some sulphides may also be present in this interface. At frequencies below 10^{-2} Hz all the systems present a strong decrease of the phase angle, thus revealing corrosion onset.

The corrosion behaviour can be correlated with the evolution of the resistance of the system calculated at low frequencies (10^{-2} Hz) (Fig. 5). The addition of La only leads to a slight increase of the resistance comparatively to the untreated HDG. The addition of silane on HDG leads to an increase of about one order of magnitude on the resistance values. When the silane is added to the previous La-treated samples the effects on the resistance become much more pronounced. During the first stages the resistance increases by about two orders of magnitude, relatively to the untreated and to the La only treated substrates. This strong increase,
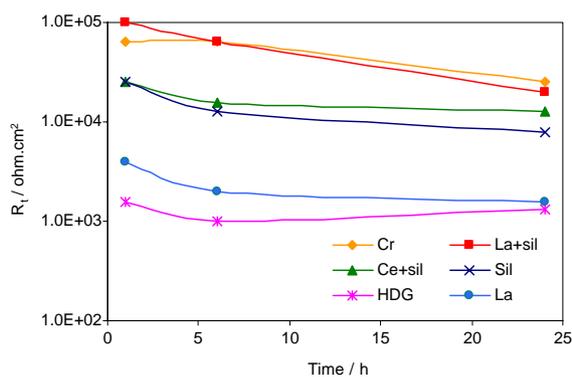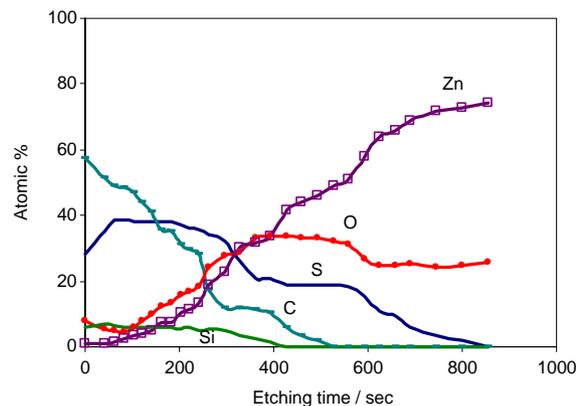

Fig. 6. Auger depth profiles obtained on HDG pre-treated with the silane.

when compared with silane only or La only suggests that the silane film seems to reinforce the protective behaviour of the La conversion coating. This may happens at expenses of an internal phase probably composed by sulphides and oxides/hydroxides of silicon and metal.

The electrochemical results clearly show that within the time range studied the more effective pre-treatments are those involving the silane. Among these, the two-step pre-treatments are slightly better. The best one, which approaches the Cr reference, involves deposition of La and silane. This behaviour is explained at the end of the next sections together with the further results.

3.1.2. Analytical results

The Auger depth profiles obtained on the substrates pre-treated with silane only and with the two-step pre-treatments are depicted in Figs. 6–8. The profiles were built from the main Auger ionisations for each element detected on the surface after background subtraction using the Shirley algorithm. The areas of each ionisation were corrected using sensitivity factors and converted into atomic percent.

For the substrate treated with silane only (Fig. 6) two distinct layers are clearly observed. The most external one
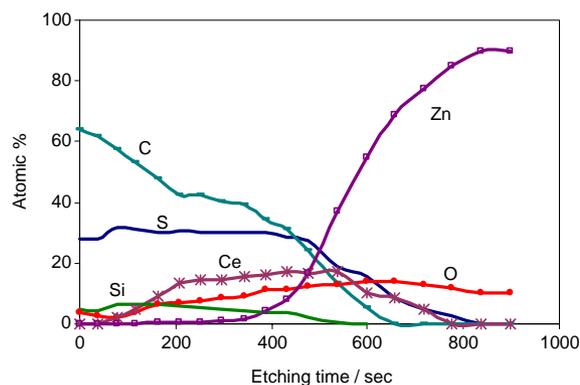

Fig. 5. Evolution of the resistance for pre-treated HDG immersed in 0.05 N NaCl during 24 h.

Fig. 7. Auger depth profiles obtained on HDG pre-treated with Ce(NO$_3$)$_3$ and silane.
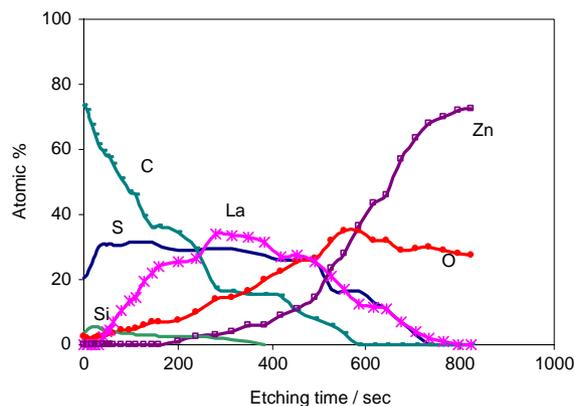
Fig. 8. Auger depth profiles obtained on HDG pre-treated with La(NO$_3$)$_3$ and silane.

Table 1
Composition of the HDG surface determined by XPS

Element	Silane	Ce + silane	La + silane
Zn–OH	2.9	0	0.13
Zn–O	0.9	0	0.6
O–Si	10.2	12.2	9.1
O–H	12.7	7.6	9
C–O/S	12.1	6.3	8.2
C–Hn	28.6	35.6	23.6
S–C	17.9	25	37.7
Si–O	14.6	13.4	11.7
Ce	–	0	
La	–	–	0

is essentially composed by carbon, sulphur and silicon and corresponds to the presence of the silane film. The more internal one, which is detected after 400 sec of sputtering, is rich in oxygen, sulphur and zinc and depleted in silicon and carbon. There is a stable plateau for sulphur, which closely accompanies the oxygen profile. This trend suggests some kind of interaction between the zinc oxides/hydroxides and the sulphur atoms of the silane molecule.

The Auger depth profiles obtained on the two-step pre-treated surfaces (Figs. 7 and 8) show that the outermost layers are very rich in carbon, silicon and sulphur. The signal from RE and from zinc was not detected, revealing that the silane layer formed on the surface is very homogeneous. The silicon signal vanishes after 500 s and the sulphur signal takes more time to be extinguished, closely following the RE and oxygen profiles. This behaviour once again suggests some interaction of sulphur with the RE oxides and hydroxides present on the surface. Although preferential sputtering cannot be excluded, the differences in the etching time for Si removal (400–500 s) and S removal (~800 s) are sufficiently high to overcome those effects.

Identification of chemical bonds for the elements present on the surface was assessed by XPS. Previous results obtained on HDG treated with RE only [7,8] showed that the RE film was essentially composed by a mixture of oxides and hydroxides. For the substrates treated with silane or with RE plus silane the identification of the different bonds is depicted in Table 1. This table was built attending to the following procedure: high-resolution energy windows were measured for each element. Then, after background subtraction, the different ionisations were deconvoluted into the peaks identified in Table 1. The analysis shows the presence of silicon, carbon and sulphur from the silane film, however, there are no traces of either zinc and RE, suggesting that the silane film binds well in the surface covering the metallic substrate (both RE film and zinc). Moreover, the contents of silicon are identical in the three cases, whereas the major differences are observed on the sulphur content, which is about twice for the sample pre-treated with La plus comparatively to that treated with silane only.

3.2. Coated hot dip galvanised steel

3.2.1. Electrochemical results

Following the previous characterisation of the uncoated substrates is very important to understand the behaviour of fully coated systems, since the final product is usually painted. Moreover, this is the main interest in industrial applications. The characterisation of these systems is very important since two aspects can be analysed: the barrier effect of the paint and the role of pre-treatment on the corrosion behaviour of the coated substrate. It is known that in the absence of defects the coating essentially behaves as a physical barrier between the aggressive electrolyte and the metal. Usually a very good coating (uniform and thick) behaves as an insulator showing very high resistances (GΩ m^2). Moreover, very low capacitances are usually obtained and the phase angle of the impedance plots is around $-90°$ over the measured frequency range. In this situation, a long time of exposure is necessary to allow corrosion onset. In the present work only a primer was used in order to reduce the experiment time and to facilitate the access of aggressive species to the metallic substrate and thus to understand the role of the different pre-treatments in the presence of the paint coating. Figs. 9 and 10 depict the EIS Bode plots obtained after 1 day of immersion and after 20 days of immersion in 0.5 N NaCl. For 1 day of immersion (Fig. 9) the log|Z| plot is characterised by two distinct parts. At high frequencies the response is purely capacitive and is due to the presence of the organic coating. However, at low frequencies the phase angle starts to decrease as a consequence of the ingress of electrolyte in the paint film. This means that the paint already presents conductive pathways whereby water and active species penetrate. This process leads to the presence of a resistive response, which at this stage can be assigned to the coating resistance. The value of this resistance is approximately the same for all the pre-treatments, being about one order of magnitude above the painted Cr pre-treated substrate. Moreover, for this last substrate the plot shows a distinct behaviour, where a time constant can be observed at low frequencies. The presence of this time constant is indicative of an interfacial process occurring at the metal substrate. Thus, the metal shows some corrosion
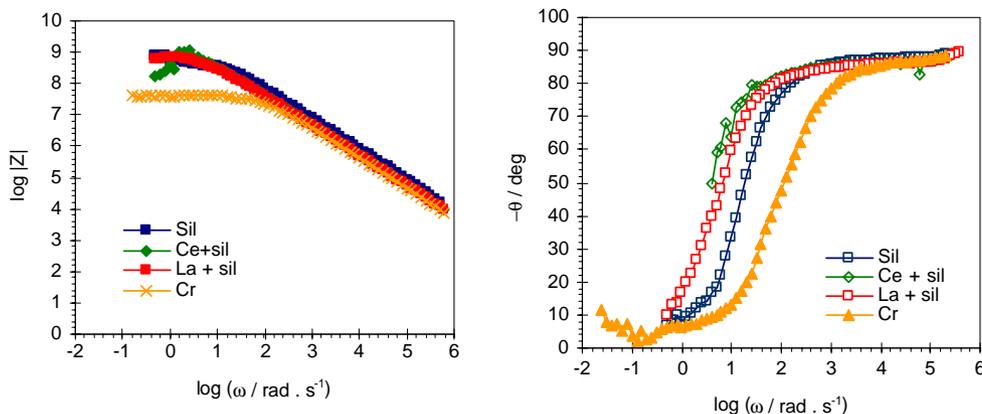
Fig. 9. EIS Bode plots obtained on coated HDG after 1 day of immersion in 0.5 N NaCl.

activity, which means that the paint coating does not provide the same degree of protection observed for the other three systems (silane and RE plus silane). This behaviour probably results from the fact that the silane film helps in the adhesion of the coating, difficulting the access of water and aggressive species to the metallic interface. After 20 days of immersion (Fig. 10) the shape of all the plots is slightly different. In the low frequency region a time constant is now present for all the samples, revealing corrosion activity.

The evolution of the resistance obtained in the low frequency range and the evolution of the capacitance (from the high frequency range) are depicted in Figs. 11 and 12. Initially, all the systems present identical resistance values, however, with time the resistance starts to decrease. After about 1 week the sample treated with silane only shows the most intense decrease, showing resistances about one order of magnitude below those of the two-step pre-treated substrates. The sample treated with Ce plus silane, follows the same trend but the resistance drop occurs slightly latter. The highest values of resistance were measured on the La plus silane sample. This behaviour reveals that this pre-treatment seems to result in increased corrosion protection of the coated samples. After 2 weeks, this system reveals

resistance values about one order of magnitude above the painted Cr reference.

The capacitance of all the systems sharply increases during the first stages of immersion, but becomes practically constant with time. The initial increase is due to water absorption through the coating. As soon as the coating saturates the capacitance becomes stable.

In what concerns the electrochemical results obtained in this work, the best performance (above Cr reference) was obtained for the La plus silane sample (Figs. 3 and 4). The Ce plus silane and silane are slightly below the Cr standard. The coated samples perform all above the coated Cr reference during approximately the first 2 weeks of immersion. The electrochemical results show that the silane under study, by itself presents good corrosion behaviour as pretreatment. However, its deposition on RE conversion films improves the corrosion performance of the systems (coated and uncoated). The silane deposits well over zinc and RE since the analytical data clearly shows the presence of a homogeneous film. Literature reports that this silane has a wide range of application, being classified as "universal silane" [15]. In this work good binding was observed on different metal oxides/hydroxides (Zn, Ce, La). The presence of the
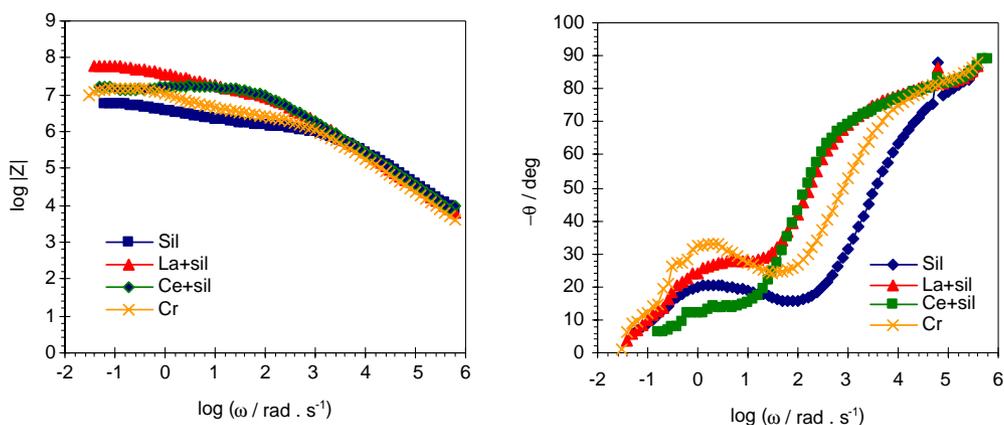

Fig. 10. EIS Bode plots obtained on coated HDG after 20 days of immersion.
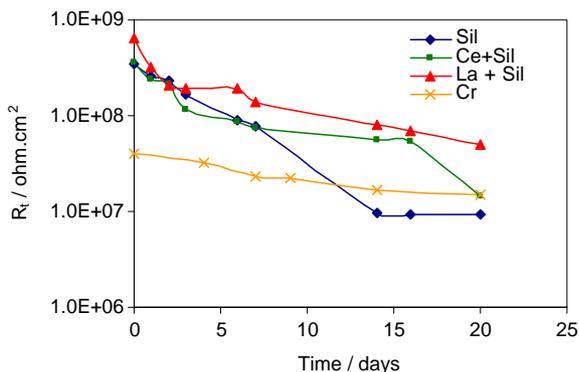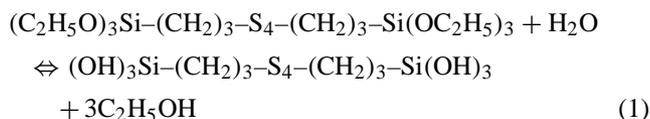
Fig. 11. Evolution of resistance at low frequency.

silane layer was clearly observed by Auger analysis and by EIS where a time constant develops in the high frequency part of the spectra.

The silane tested in the present work hydrolyses according to the reaction:

$$(C_2H_5O)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si(OC_2H_5)_3 + H_2O$$
$$\Leftrightarrow (OH)_3Si-(CH_2)_3-S_4-(CH_2)_3-Si(OH)_3$$
$$+ 3C_2H_5OH \qquad (1)$$

Initially, the $Si(OH)_3$ groups absorb through hydrogen bonds on the surface of the metal and later they react with the metallic hydroxides leading to the formation of a covalent bond with the native metal oxide (Si–O–M type bond). The excess of hydrolysed silicon groups $Si(OH)_3$ may react together, in solution, leading to the formation of a siloxane (Si–O–Si) network that forms the more external part of the film. The sulphur present in the BTESPT molecule may also react with the metallic substrate. Thus, it is expected that it could be present in the first layers mixed with the native oxides and hydroxides.

It is clear from the Auger depth profiles that a sulphur-rich layer is formed underneath the external silicon-rich layer. Literature [15] suggests that sulphur has good affinity for some metals such as Ni, Cu and Zn, leading to the formation of a thin sulphide film under the silane layer, which be-
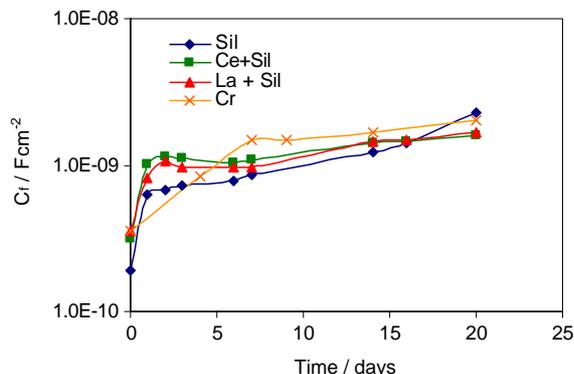
comes mixed with the native oxides existing on the surface. The results obtained in the present work account for a similar mechanism. For HDG there are two distinct plateaux for the sulphur profile, the more internal one containing about one-half of the amount of the most external one. For RE pretreated HDG the content of sulphur remains constant with depth and is very close to the RE profile, suggesting a mix between RE oxides/hydroxides and sulphides. The presence of this layer may help to increased resistance without affecting the barrier and coupling properties of the outermost silane layer. This effect seems to be more pronounced for the La conversion films, since a significant increase of the resistance was noticed during EIS measurements on uncoated substrates. Also important decreases of the cathodic currents were noticed evidencing the cathodic protection provided by these pre-treatments. The composition of the conversion layer is a mixture of La oxides and hydroxides [8]. This layer is homogeneous and no significant zinc areas are expected after the rare earth step. However, the silane step seems to reinforce the protection provided by the conversion coating. This may result form the join effect of the Si–O–M bonds and sulphides that form a very stable interface where the external silane network (Si–O–Si type of bonds) can grow.

4. Conclusions

Pre-treatments using the bis-functional silane (BTESPT) seem to have promising future as chromate replacers for pre-treatments on hot dip galvanised steel.

The two-step pre-treatments result in good corrosion protection, however, the best performance was obtained with the lanthanum conversion coating. This was observed either on uncoated and coated substrates. The silane (BTESPT) by itself also shows some improved corrosion protection.

The presence of the sulphur atoms on the silane molecule seems to play an important role on the deposition process. Thus, it can be suggested the presence of an internal layer rich in sulphur and RE or zinc hydroxides/oxides, which together with Si helps to improved corrosion resistance.

Fig. 12. Evolution of capacitance at high frequency.

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