Cerium salt activated nanoparticles as fillers for silane films: Evaluation of the corrosion inhibition performance on galvanised steel substrates

M.F. Montemor a,*, M.G.S. Ferreira a, b

a ICEMS/DEQB, Instituto Superior Técnico, Technical University of Lisbon, Av. Rovisco Pais, 1049-001 Lisboa, Portugal
b Universidade de Aveiro, CICECO, 3810-193 Aveiro, Portugal

Received 9 April 2007; accepted 6 May 2007
Available online 18 May 2007

Abstract
The present work investigates the electrochemical behaviour of galvanised steel substrates pre-treated with bis-[triethoxysilylpropyl] tetrasulfide silane (BTESPT) solutions modified with SiO2 or CeO2 nanoparticles activated with cerium ions. The electrochemical behaviour of the pre-treated substrates was evaluated via electrochemical impedance spectroscopy in order to assess the role of the nanoparticles in the silane film resistance and capacitance. The ability of the Ce-activated nanoparticles to mitigate corrosion activity at the microscale level in artificial induced defects was studied via scanning vibrating electrode technique (SVET). Complementary studies were performed using potentiodynamic polarisation. The results show that the presence of nanoparticles reinforces the barrier properties of the silane films and that a synergy seems to be created between the activated nanoparticles and the cerium ions, reducing the corrosion activity. The addition of CeO2 nanoparticles was more effective than the addition of SiO2 nanoparticles.

Keywords: Silanes; Corrosion; SVET; SiO2; CeO2; Nanoparticles

© 2007 Published by Elsevier Ltd.

1. Introduction
The use of silane formulations for the pre-treatment of metallic substrates prior to painting has been increasing during the recent years and some commercial formulations are available in the market of pre-painted galvanised steel. These formulations are very attractive because they present environmental friendliness, enhance adhesion to different paint systems due to the possibility of surface chemistry tailoring and provide a barrier layer that delays the corrosion processes. Furthermore, these formulations are easy to apply since the pre-treatment is achieved by dipping the substrate in the silane solution for short times. The silane-based pre-treatments for temporary corrosion protection of galvanised steel or for applications in coil coating processes are nowadays technical alternatives to replace the traditional formulations based on the use of Cr(VI). However, there are several differences between silane and chromate-based pre-treatments. Among them, the most important one is that chromate ions, due to their chemistry, are very effective as corrosion inhibitors, either applied as conversion coatings or used as inhibitors in solutions or in paint systems. Silanes do not show corrosion inhibition properties and corrosion protection arises from the fact that silanes lead to the formation of a hybrid compact and homogeneous surface film, which delays the initiation of corrosion activity. However, when the aggressive species reach the metallic substrate, silanes do not provide any additional protection and cannot contribute to the inhibition of the corrosion processes. As soon as the corrosion process starts, the accumulation of corrosion products and the pH changes at the metal/silane interface promote silane film deterioration and delamination. Since the silane pre-treatment also works as adhesion promoter, its delamination accelerates the failure of the painted system. Therefore, the modification of the “inert” behaviour of the silane films face to the corrosion process is an important contribu-
tion to enhance the lifetime of painted systems. In this way, the introduction of species with corrosion inhibition ability in the bulk of the pre-treatment layer provides an additional counter measure, contributing for the improved corrosion protection and durability of the painted material.

The modification of hybrid silane films or hybrid sol–gel coatings with different additives in order to introduce corrosion inhibition properties in their bulk has been reported in recent literature [1–9]. The modification of sol–gel coatings with organic inhibitors demonstrated positive effects on their protective performance [1]. Environmentally compliant inhibitors like Ce(NO)₃, NaVO₃ and Na₂MoO₄ were incorporated into a Zr-epoxy sol–gel [2]. Some of these inhibitors, like cerium nitrate did not damage the barrier properties, whereas others like sodium molibdate and sodium metavanadate did not reveal good barrier properties and coating delamination was observed. The corrosion behaviour of aluminium substrates treated with sol–gel systems containing cerium ions demonstrates that cerium could inhibit the corrosion processes [3]. Literature [4] also reports that hybrid silica sol–gel coatings containing Ce³⁺ ions behave as conversion coatings on metallic zinc substrates. The anticorrosive performance of the Ce³⁺ ions entrapped in the hybrid silica sol–gel network occurs by means of the inhibitor effect and the self-repairing mechanism (probably associated with Ce(OH)₃ precipitation) [4].

A new approach for the formation of ’smart’ self-healing anticorrosion coatings based on silica nanoparticles layer by layer-coated with polyelectrolyte molecules, acting as nanoreservoirs for corrosion inhibitors, incorporated in the hybrid sol–gel protective coatings is proposed in literature [5]. These nanoreservoirs improve corrosion protection of coated aluminium substrates and provide effective storage of the inhibitor and prolonged release, ’on demand,’ to the damaged areas, conferring active corrosion protection with self-healing ability.

Modification of silane films with organic and inorganic inhibitors like tolyltriazole, benzotriazole and inorganic cerium salts was tested. All these inhibitors effectively protected AA2024-T3 alloy against corrosion when immersed in a 0.5 M NaCl solution containing these inhibitors [6].

Another approach that has been proposed to improve the barrier properties of sol–gel or silane pre-treatments and therefore their corrosion protection performance is based on the addition of small particles. The corrosion resistance of Mg alloys pre-treated with sol–gel coatings containing ZrO₂ and CeO₂ nanoparticles was investigated and it was reported that the CeO₂ component provides enhanced corrosion protection, while ZrO₂ improves wear resistance [7]. W. van Ooij and co-workers [8] report that bis-sulfur silane films can be thickened and strengthened by loading them with silica particles. However, when the bis-sulphur silane film is heavily loaded with silica it tends to form a porous film, which promotes electrolyte intrusion and premature film delamination. The addition of SiO₂ nanoparticles to silane films electrodeposited on aluminium also revealed beneficial effects and a “critical content” was proposed [9]. The results obtained in these works were mainly focussed on the role of the nanoparticles in the barrier properties of the film and little has been discussed concerning the role of the nanoparticles in the electrochemical processes involved in the corrosion processes of metallic substrates.

The actual research work follows previous ones [10–17], which demonstrated that additives like cerium ions, zirconium ions and silica particles improved the corrosion protection performance of silane films formed on different metallic substrates. Following these results a new approach is proposed in this work: SiO₂ nanoparticles (average diameter 30–40 nm) and CeO₂ nanoparticles (average diameter 10–20 nm) were activated with cerium ions and then used as fillers in the silane films. The addition of nanoparticles aims at improving the barrier properties of the silane film and the presence of cerium ions aims at introducing corrosion inhibition properties in the bulk of the silane film. The activation of the nanoparticles with cerium ions also aims at reducing agglomeration of the nanoparticles due to stabilisation of the surface charge as demonstrated elsewhere [16]. It is also expected that the nanoparticles fix the cerium ions on their surface, distributing them homogeneously in the bulk of the film and releasing them on demand, i.e., the cerium ions can be leached out when the electrolyte reaches the particles as proposed in previous works [16,17]. The adsorption of cerium ions on the surface of the nanoparticles investigated in this work is very likely to occur due to the following reasons: the SiO₂ particles develop silanol groups (O=Si–OH) on their surface that can be ionised as SiO⁻³ above pH 2 [18], creating a negative charge over the silica surface and inducing a favourable electrostatic force for the adsorption of metallic cations; the CeO₂ nanoparticles present a positive surface charge and adsorption of cerium cations under near neutral conditions as suggested for the SiO₂ is more unlikely. However, CeO₂ particles easily form oxygen vacancies, producing reactive sites. Therefore, they easily incorporate dopants, metallic ions or even other oxide nanoparticles by forming charge-compensating defects on the oxygen sub-lattice [18,19].

The results obtained in the present work show that cerium-activated nanoparticles strongly improve the barrier properties of the silane films and that the corrosion activity is dependent on the nature of the nanoparticles. The CeO₂-filled films present better anti-corrosion performance when compared with the SiO₂-filled systems. Important anodic inhibition effects were observed for the silane films containing CeO₂.

2. Experimental procedure

2.1. Pre-treatment

The silica nanoparticles, with a purity ≥99.8% and an average diameter of 30–40 nm, were obtained from Degussa (Aerosil®) and the ceria nanoparticles with an average diameter of 10–20 nm were obtained from Sigma–Aldrich. The nanoparticles were ultrasonically dispersed in an aqueous solution of cerium nitrate in order to obtain a concentration of 250 ppm of nanoparticles and 250 ppm of cerium nitrate. This aqueous dispersion was then used for the preparation of the silane solution. Dispersions of the same nanoparticles but without cerium ions were also prepared.
The bis-[triethoxysilylpropyl] tetrasulfide silane (Sigma–Aldrich product) solution was prepared by dissolving 5% (v/v) of silane in a mixture of methanol (90%, v/v) and aqueous dispersion of nanoparticles. The silane solution was stirred for 1 h and was kept for few days before use.

The substrate was galvanised steel, 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 substrates were degreased using an alkaline cleaner (Novomax®) for 4–5 min at 50 °C, washed with distilled water, dried in air and immersed in the modified silane solution for 10 s. The panels were cured in the oven at 120 °C for 40 min.

2.2. Electrochemical techniques

The EIS measurements were carried out using a Gamry FAS1 Femtostat with a PC4 Controller Board. The experiments were performed at room temperature, in a Faraday cage, at the open circuit potential, using a three-electrode electrochemical cell, 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. The rms voltage was 10 mV. The EIS experiments were performed during immersion of the pre-treated substrates in solutions of 0.005 M NaCl for 1 week. Spectra were treated using the Z-view Software.

The SVET measurements were performed using Applicable Electronics equipment, controlled by the ASET program (Scientewares). The vibrating electrode was made of platinum–iridium covered with polymer, leaving only an uncovered tip with a diameter of 40–50 μm. The distance of the tip to the surface was kept at 200 μm, as previously optimised. The scanned area was 2 mm × 2 mm. To evaluate the corrosion inhibition performance of the modified silane film, a scratch was made on the surface using an edge knife. The dimensions of the scratch were approximately 10 mm length by 0.1 mm wide. The zinc surface was exposed in the scratch. The silane treated galvanised steel coupons were immersed in the aggressive solution (0.005 M NaCl) and measurements were taken periodically.

The potentiodynamic polarization curves were performed using a RADIOMETER-VOLTALAB PGZ 100 apparatus. The scan rate was 1 mV/s in the anodic or in the cathodic direction, starting from the open circuit potential after different stabilisation times. An electrochemical cell consisting of three electrodes as the one described for the EIS measurements was used. Tests were carried in 0.005 M NaCl. At least two identical samples were tested in each electrochemical experiment.

3. Results and discussion

Two approaches are reported in this work. The first one investigates the electrochemical behaviour of intact silane films, whereas the second approach investigates scratched films. The intact films were studied by electrochemical impedance spectroscopy (EIS) in order to assess the role of the activated nanoparticles on the barrier properties (capacitance and resistance) of the silane film and to investigate the behaviour of the metal/film interface. The studies carried out with the scratched films aimed at obtaining more detailed information on the role of the nanoparticles in the inhibition of the corrosion processes at the microscale level.

3.1. Intact silane films

Figs. 1 and 2 depict the electrochemical impedance spectra obtained on the galvanised steel substrates pre-treated with the silane film filled with SiO₂ nanoparticles and SiO₂ nanoparticles activated with cerium ions, respectively. The results showed that the impedance values were higher for the film containing the cerium ions. Furthermore, in the presence of cerium ions, the values of the total impedance were kept approximately constant during the experiment (one week of immersion in 0.005 M NaCl).

The EIS Bode plots obtained for the silane coatings filled with CeO₂ nanoparticles are presented in Figs. 3 and 4. The total impedance of the system was lower for the system contain-
ing CeO₂ only. The addition of cerium ions led to an important increase of the impedance. For example, after 1 day of immersion, the total impedance of the CeO₂ plus cerium system was more than one order of magnitude higher than that of the system filled with CeO₂ only.

The shape of the phase angle plot indicated the presence of two partially overlapped time constants (Figs. 1–4), which can be attributed to the response of the silane film (high frequency process) and to the response of processes occurring at the silane film/substrate interface (low frequency time constant).

A more detailed interpretation of the EIS measurements was performed by fitting the experimental plots using the equivalent circuit depicted in Fig. 5. This equivalent circuit included constant phase elements (CPEs) to simulate the capacitive responses observed in the EIS spectra. The presence of the CPE is due to distributed surface reactivity, surface heterogeneity, roughness of fractal geometry, electrode porosity and to current and potential distributions related with electrode geometry as reported elsewhere [20].

Figs. 6 and 7 depict the evolution of the fitting parameters used for the numerical simulation of the experimental results.

Generally, the high frequency resistance values showed a decrease during the first hours of immersion due to the development of conductive pathways inside the silane film (Fig. 6).

For the system filled with SiO₂ only (curve 4) there was a sharp drop after immersion, followed by a recovery after few hours. For this film, the high frequency resistance pass through a maximum and then started to decrease again. The initial drop was attributed to fast electrolyte uptake through the pores/defects present in the film. The access of aggressive species induces localised corrosion activity followed by precipitation of insoluble products, which block the pores/defects at the silane/film interface leading to a small recovery of the coating resistance.

The evolution of the high frequency resistance for the system filled with SiO₂ and cerium (curve 3) showed a more gradual decrease, from 5 MΩ cm² down to 200 kΩ cm². The CPE values were around 10 nF cm⁻² and showed a slight increase with time.
The films filled with CeO$_2$ nanoparticles only (curve 2) showed CPE values around 50 nF cm$^{-2}$ and film resistances that gradually decreased with time. The addition of cerium ions strongly modified the behaviour of the CeO$_2$-filled films. The capacitance decreased by about one order of magnitude, being around 5 nF cm$^{-2}$. After about 144 h (6 days) of immersion the CPE value increased, approaching the values observed for the other filled systems. The improved barrier properties of the CeO$_2$ plus cerium systems (curve 1) are well-reflected in the resistance values. During the first hours of immersion, the EIS response was nearly capacitive over the entire frequency range and the resistance values were above 100 M$\Omega$ cm$^2$. The resistance slowly decreased during the experiment period and after 144 h (6 days) the resistance suffered an important drop and approached the values measured for the other films.

Compared with the blank silane film, all the fillers led to an important improvement of the barrier properties. The evolution of the high frequency fitting parameters indicated that the addition of nanoparticles reinforces the barrier properties of the film. The results showed that either CeO$_2$ or SiO$_2$ nanoparticles (without cerium ions) led to identical resistances and CPE results. The addition of cerium to the nanoparticles changed this trend and
then the CeO₂–Ce filled systems became more protective than the other systems.

Based on the EIS results the effect of the nanoparticles in the barrier properties of the silane films immersed in NaCl solutions can be ranked as follows: CeO₂ + Ce ions > SiO₂ + Ce ions ~ SiO₂ ~ CeO₂ > blank film.

The use of small silica particles to improve the barrier properties of silane films has been reported in literature [7,8,21] and generally improved corrosion protection has been observed despite some recommendations related to critical contents. In a previous work [15] it was shown that the addition of 50 ppm of SiO₂ particles to silane films improved the corrosion protection due to the formation of thicker films with enhanced barrier properties. It was proposed that the SiO₂ particles accumulated in the inner layers of the silane film, stabilising them. Therefore, the improved barrier properties observed in the EIS parameters can be related with decreased porosity and conductivity because the nanoparticles can fill defects and voids inside the silane film. These effects were improved in the films containing particles activated with cerium ions and are in good agreement with results published elsewhere [12–14]. The formation of thicker films is also likely to occur since the addition of nanoparticles and cerium ions can induce some changes in the viscosity of the solutions and in the cross linking processes in the silane film.

The evolution of the fitting parameters associated with the low frequency behaviour of the EIS spectra (Fig. 7) gives information on the electrochemical activity at the interface silane/zinc. The SiO₂-containing films (curves 3 and 4) showed some fluctuations both in the CPE values and low frequency resistance. The initial CPE values were in the range of few μF cm⁻² and during the first day of immersion the CPE values decreased for about one order of magnitude and stabilised around 0.1 μF cm⁻². This drop occurred earlier for the film containing SiO₂ and cerium ions. These values are lower than those expected for corrosion processes controlled by charge transfer and are probably related with the growth of a protective oxide layer beneath the silane film. This agrees with the evolution of the low frequency resistance of the SiO₂-filled films that showed a fast drop during the first hours of immersion from 5 MΩ cm² to 0.5 MΩ cm² and then a gradual recovery and stabilisation around 1 MΩ cm². The addition of cerium ions to the SiO₂ nanoparticles led to more stable low frequency resistances (around 5 MΩ cm²). This trend revealed that the cerium-activated SiO₂ nanoparticles increased the low frequency resistance and therefore decreased the corrosion activity at the metallic substrate.

Concerning the systems modified with CeO₂ a distinct behaviour was observed. In the absence of cerium ions, the CeO₂-filled systems (curve 2) showed CPE values around 0.5 μF cm⁻² and resistances decreasing from 6 MΩ cm² to values around 0.5 MΩ cm². The activation with cerium ions had an important beneficial impact both in the low frequency CPE and resistance. During the first hours of immersion the EIS spectra were nearly capacitive and the low frequency parameters could not be estimated with accuracy. Later on, a resistive response started to appear at low frequencies (Fig. 4). The CPE values were below 0.1 μF cm⁻² and the resistances increased to values above 50 MΩ cm². As the immersion time elapsed, there was a gradual drop of the resistance and, at the end, the resistance and the CPE values approached the values observed for the other systems. In a previous work [14] it was demonstrated that the low frequency resistance and capacitance depend upon the cerium content. For concentrations of cerium ions identical to the ones used in this work, and after 4–5 days of immersion, the resistance values were approximately 1 MΩ cm² [14]. These values are identical to the values observed in this work for the films filled with CeO₂, but lower than those observed for the cerium-activated CeO₂ (>5 MΩ cm²), suggesting that a positive synergy seems to be created between the nanoparticles and the cerium ions.

The evolution of the low frequency resistance showed, in some cases, an increase after few hours, accompanied by a decrease of the CPE. Since the corrosion activity occurs in localised areas, it is likely to expect the precipitation of insoluble...
and passive corrosion products at those locations, decreasing the corrosion activity at the interface. In fact, the most pronounced changes were observed for the blank film and for the film filled with SiO₂, which are the ones presenting the poorest barrier properties and therefore more prone to early corrosion attack. This subject will be discussed in more detail below.

The behaviour of the EIS Bode plots at the low frequency suggested a decrease of the corrosion protective behaviour according the following order: CeO₂ + Ce ions > SiO₂ + Ce ions > SiO₂ ~ CeO₂ > blank film.

3.2. Scratched films

In the silane pre-treated substrates, corrosion activity starts at small defects, pores or scratches of the film and the presence of inhibiting species is essential to decrease or to hinder corrosion activity at these locations. However, the inhibitor activity depends upon the local chemical and electrochemical environment. The scanning vibrating electrode technique (SVET) is an electrochemical mapping technique that is able to resolve and quantify localized corrosion activity occurring on metallic substrates. SVET measurements are carried out in aqueous electrolyte and employ a vibrating microtip electrode that is mechanically scanned at a fixed distance from the corroding surface. An important assumption is that under correct experimental setup the SVET probe does not perturb the corrosion reactions under study [22]. The scanning vibrating electrode technique (SVET) has been used in a number of studies to elucidate the mechanisms of corrosion, like cut-edge corrosion in galvanised steel materials [23] or galvanised steel corrosion [24]. SVET is one of the most suitable techniques to investigate and to understand localised corrosion phenomena and inhibitors activity at those locations. Therefore, in this work the ability of the nanoparticles to mitigate corrosion activity at scratches was evaluated by the SVET.

Fig. 8 shows the SVET maps obtained on the systems filled with SiO₂ only and SiO₂ + Ce after 6 h of immersion. The maps show development of anodic activity over the scratch. The remaining surface behaved as cathodic. The anodic currents increased faster and were higher for the system filled with SiO₂ only. The addition of cerium ions to the SiO₂ nanoparticles led to a decrease of the anodic current densities for about one half and no significant changes in the dimensions of the anodic area were observed during a 6 h immersion period. For both samples, the values of the anodic currents measured over the defect were kept approximately constant during 24 h of immersion. However, after this period the dimensions of the scratched area increased due to silane film delamination and the film filled with

---

Fig. 8. SVET maps obtained in the scratched SiO₂ filled films during immersion in NaCl 0.005 M. Left column: maps of ionic currents; right column: surface image. Scan size: 2 mm × 2 mm. Current units: μA cm⁻².
SiO$_2$ nanoparticles without cerium was completely damaged (figures not shown). After 24 h of immersion, the SVET maps obtained on the films containing SiO$_2$ activated with cerium ions (Fig. 9) revealed an increase of the anodic activity and delamination around the scratch but the current densities were still lower than those measured in the SiO$_2$ films without cerium (Fig. 8).

The CeO$_2$-filled films revealed a distinct behaviour (Figs. 10 and 11). For the system filled with CeO$_2$ only the initial currents were very low (Fig. 10), but increased with time and after 72 h delamination could be observed around the initial scratch and more anodic spots were detected (Fig. 11).
For the cerium-activated CeO₂ film the current densities were very low (Fig. 10) since the early beginning and were kept constant for several hours. Measurements taken after 72 h revealed negligible anodic activity and negligible delamination around the scratched area (Fig. 11).

The SVET maps show that although the presence of a defect in the film, the anodic and the cathodic currents were very low for the films containing CeO₂ activated with cerium ions. The results suggest that the anodic activity at the scratch is stronger in the SiO₂ containing systems and hindered in the systems containing CeO₂. In order to assess more information on the mechanisms associated with the electrochemical behaviour of these systems, d.c. measurements were also performed.

The anodic potentiodynamic polarisation curves obtained on the scratched samples after 1 h and 6 h of immersion are depicted in Fig. 12.

After 1 h of immersion the blank silane film (curve 5) revealed the most negative corrosion potential (≈−0.92 V), close to the value observed for the metallic substrate (curve 6). The films filled with nanoparticles plus cerium (curves 1, 3) the most positive corrosion potential values (≈−0.8 V).

After 6 h of immersion the corrosion potential of the blank silane film was identical to that of HDG and the most positive value was that of the film filled with CeO₂ and cerium (≈−0.76 V).

The anodic current densities and the kinetics of the anodic processes were strongly affected by the presence of the fillers. After 1 h of immersion the highest anodic currents were measured for the blank silane film (curve 5) and for the SiO₂ filled film (curve 4) and the lowest ones for the CeO₂ and cerium film (curve 1), in good agreement with the SVET data. The films containing CeO₂ revealed a short passivation range of approximately 50–100 mV above the corrosion potential.

All the samples revealed a critical current density around \(1 \times 10^{-4} \text{ A cm}^{-2}\), which is in the range expected for zinc dissolution and that develops at nobler potentials for the films containing CeO₂ (curves 1 and 2). After 6 h of immersion the current densities and the shape of the curves for the blank film, the HDG substrate and the SiO₂-filled films were similar.

The trends observed in the anodic curves show that the presence of CeO₂ nanoparticles promotes the formation of a more stable and more protective surface film. This behaviour agrees with literature, where it is reported that CeO₂ and Ce₂O₃ improve the anodic passivation behaviour of stainless steels [25,26], causing a strong shift of the potential towards the anodic direction.

The cathodic polarisation curves are depicted in Fig. 13. The limiting current densities for oxygen reduction were very close for all the samples but a small reduction was observed in the
systems containing the nanoparticles activated with cerium ions (curves 1 and 3). This reaction can be due to the precipitation of insoluble cerium oxides/hydroxides at the cathodic sites as reported in literature [14,27,28].

The d.c. polarisation results showed that the presence of nanoparticles shifts the corrosion potential towards nobler values, decreases the anodic currents and changes the kinetics of the anodic processes. These effects were much more marked for the CeO2 nanoparticles when compared with SiO2 and agree with the SVET and EIS measurements. The electrochemical results also showed that the addition of cerium ions enhanced the protective role of the nanoparticles. In order to understand the role of the nanoparticles the following considerations can be drawn.

The zinc cations formed during anodic dissolution of zinc (reaction (1)) react with the hydroxyl ions (reaction (2)) in a sequence of reactions, which involve the formation of several intermediate species [29]. These lead to the formation of zinc hydroxides – Zn(OH)2, ZnO or a mixture of both, forming a passive layer.

\[
\text{Zn} \rightarrow \text{Zn}^{2+} + 2e \quad (1)
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e \rightarrow 4\text{OH}^- \quad (2)
\]

In the presence of NaCl, the chloride ion can react with Zn\(^{2+}\) or Zn\(^{2+}\) to form various species such as soluble ZnCl\(_2\), ZnCl\(_2\) and \(\beta\)-ZnOHCl that leads to the formation zinc hydroxychloride Zn\(_5\)(OH)\(_8\)Cl\(_2\) one of the main insoluble corrosion products [29].

Under current experimental conditions, different species like Zn\(^{2+}\), ZnCl\(^{2-}\), Zn(OH)\(^+\), ZnO and Zn\(_5\)(OH)\(_8\)Cl\(_2\) can co-exist contributing to the stability of the protective layer [30]. However, due to the presence of excess of chloride ions localized breakdown of the film occurs and corrosion activity proceeds via successive steps that involve anion adsorption, penetration in the passive film and nucleation and growth of localised cor-
corrosion spots [29]. Generally the increase of the free chloride content led to an overall potential shifted negatively.

In this work it was found that both the corrosion potential and critical potential were shifted to nobler values and that the anodic activity was strongly hindered in the presence of CeO2 or cerium-activated nanoparticles. This can be explained assuming a more stable surface film and/or lower amount of free chlorides available for adsorption/penetrating in the passive film. It is known that the CeO2 nanoparticles are very stable because the Ce4+ ions form a stable cubic coordination [CeO8] in the fluorite structure and present very low solubility in water. The CeO2 particles easily incorporate other species, like ions, by forming charge-compensating defects in the oxygen sub-lattice [18,19]. Generally, the species formed are ceria-based oxides, which are very stable. Therefore, the CeO2 nanoparticles can complex the species that promote the loss of passivation, contributing to stabilise the passive film. Furthermore, the CeO2-based species are very stable in a wide pH range from weak acidic to highly alkaline.

The SVET results obtained in this work showed that the anodic inhibition effects were much more pronounced for the films containing CeO2 nanoparticles in comparison with the films containing SiO2.

The behaviour of the films containing SiO2 can be explained attending that the cathodic activity that appears around the defects (as observed in the SVET maps (Figs. 8 and 9)) generates an alkaline environment that induces the SiO2 nanoparticles to enter the following reaction (3) as proposed in literature [8]:

$$\text{SiO}_2 + 2\text{OH}^- \rightarrow \text{SiO}_3^{2-} + \text{H}_2\text{O}$$

(3)

In low alkaline environments the silicates formed in reaction (3) can react with the zinc ions, forming a stable zinc silicate. This compound precipitates on the surface and may contribute to the stability of the protective film, delaying corrosion activity as proposed in literature [31,32]. These processes may explain the trends observed in the EIS spectra. The impedance results revealed that after few hours of immersion the low frequency CPE values decreased from the $\mu$F cm$^{-2}$ range to values around 0.1 $\mu$F cm$^{-2}$, which are values typical of a protective oxide film (Fig. 7). This indicates that the corrosion products formed in the presence of SiO2 enhance the protective properties of the interface metal/silane. The anodic polarisation curves revealed a shift of the corrosion potential towards more positive values and a decrease of the anodic currents compared with the blank silane film, suggesting that the surface layer formed on damaged areas is more protective in the presence of SiO2.

However, reaction (3) is pH dependent and in very alkaline environments (pH $>$ 9–10) silica becomes susceptible to alkaline decomposition with formation of an expansive silicate-based gel, which promotes both silane film delamination and particles degradation. Therefore, if the pH raises enough the protective behaviour of the SiO2 particles, as described above can be lost. This was the result observed in the SVET measurements conducted in the scratched SiO2-containing films. In the SiO2 filled systems the corrosion activity measured over the scratch was high and important delamination was observed. These effects were attenuated in the presence of cerium ions, probably due to the formation of a more stable passivation film (Fig. 9). In fact, literature [31,32] reports that cerium ions may react with silicates, leading to a cerium–silicate salt or complex, which helps to reduce corrosion activity. It is proposed that a passive film composed of Zn(OH)$_2$, ZnSi$_2$O$_5$ and Ce$^{3+}$–Si$_2$O$_3^{2-}$ salt or complex forms on the scratched surface and that preferential precipitation of zinc silicate occurred on the defects of the passive film, delaying corrosion [31,32].

The addition of cerium ions to the nanoparticles dispersions seems to create an important synergy with the nanoparticles, reinforcing the protective behaviour of the silane films. The new results obtained in this work demonstrated that CeO2 or SiO2 nanoparticles activated with cerium ions can be an effective methodology to improve the corrosion protection performance of galvanised steel pre-treated with modified silane films.

4. Conclusions

Silane films formed using bis-[triethoxysilyl]propyl]-tetrasulfide silane filled with 250 ppm of SiO2 and CeO2 nanoparticles revealed improved barrier properties compared with the blank silane films. The activation of the nanoparticles with cerium ions enhanced this behaviour.

In scratched surfaces, the SiO2 nanoparticles by themselves have no marked effects in the corrosion activity. The CeO2 nanoparticles have good corrosion inhibition properties in scratched surfaces probably due to their stability over a wide pH range and ability to complex other species, therefore contributing for the stabilisation of the passive film. In this way, these particles have an anodic inhibition mechanism.

The corrosion inhibition performance of the modified silane films is enhanced when the nanoparticles are activated with cerium ions. The CeO2 particles activated with cerium ions provide the best corrosion protection either in intact films or in the presence of scratches.

Acknowledgements

POCTI/CTM/59234/2004. The authors are grateful to P. Cecilio by the work carried with the SVET technique.

References


