Electrochemical and chemical characterization of electrodeposited zinc surface exposed to new surface treatments

J.M. Ferreira Jr. [a,*], K.P. Souza [a], F.M. Queiroz [a], I. Costa [a], C.R. Tomachuk [b]

[a] Instituto de Pesquisas Energéticas e Nucleares, IPEN/CNEN-SP, CCTM, Av. Prof. Lineu Prestes, 2242, CEP 05508-000, São Paulo, SP, Brazil
[b] Escola de Engenharia de Lorena da Universidade de São Paulo (EEL-USP), Departamento de Ciências Básicas e Ambientais, CEP 12602-810, Lorena, SP, Brazil

ARTICLE INFO

ABSTRACT

A new environmentally friendly passivation treatment for electrogalvanized steel has been investigated in this study. The passivation treatments consisted of immersion in solutions containing hexahydrated cerium nitrate and organic additive. The effect of citric acid as an additive into the treatment solution has also been evaluated. For comparison reasons, the electrogalvanized steel was passivated in a commercial chromating and the corrosion performance of the new treatments compared to this last one. The effect of the proposed treatments on the corrosion resistance of the surface was investigated by electrochemical impedance spectroscopy (EIS) in sodium chloride solution. The morphology of the treated surface was investigated by field emission gun scanning electron microscopy (SEM-FEG). The treated surfaces were chemically characterized by X-ray Photoelectron Spectroscopy (XPS). The electrochemical results showed higher impedances along the time of exposure to the electrolyte for one of the new proposed treatments compared to the surface passivated in the chromating solution. XPS results suggested that the new treatments resulted in the formation of an organic film on the electrogalvanized steel surface. The cerium ions showed a synergistic effect with the organic film formed resulting in long-term protection of the metallic substrate in the corrosive electrolyte. The layer formed apparently acted as anchoring sites for inhibiting corrosion products leading to prolonged protection of the surface film formed.

1. Introduction

Conversion coatings prepared by immersion in solutions containing salts of rare earths such as Ce, La, Pr, Nb and Y have been shown as one of the promising alternatives to toxic chromate conversion coating on various metals and alloys for provide exceptional resistance to localized corrosion through the formation of insoluble hydroxide/oxide layers [1–4]. One of the most investigated rare-earth (RE) for corrosion protection has been cerium and it has been applied on zinc and galvanized steels [5]. Rare-earth-based conversion coatings present some important advantages such as competitive price, low environmental impact, excellent corrosion resistance and compatibility with a wide range of inorganic and organic interfaces [6–8].

The pioneering studies in the field are those of Hinton [1]. Those works report the use of cerium chloride for corrosion inhibition on zinc and propose a cathodic mechanism to explain the formation of the RE oxide coating. According to that mechanism, the cathodic reactions generate an alkaline environment that leads to localized precipitation of RE oxides and thus to the formation of the surface coating.

Montemor et al. [8] complemented the mechanism with the view of a two-stage growth process with the formation of the conversion layer involving an oxidation process of Ce(III) to Ce(IV).

Recent studies have shown that layers with organometallic bonds obtained by treatments in solutions of carboxylic acids present significant corrosion resistance [6,9–14]. The inhibition of corrosion by carboxylic acid is due to the formation of a chemisorbed film on the steel surface, reveled by presence of a protective surface layer over the metal exposed to organics acid or when it is associated with the rare-earth salts [6,9].

Among the most investigated compounds used as potential replacements for hexavalent chromium conversion there are the oxyanions such as tungstates [15], molybdates [16], silicates [17–19], silanes [20, 21], and trivalent chromium [22–25]. However, the methods of preparation and the corrosion resistance associated to these coatings are not clear and their practical usage is still uncertain.

Surface films containing cerium might be produced by immersion in cerium salts solutions [26–31], electrodeposition from solutions with cerium ions [11,32–34], or by sol-gel processes [26,27].

Since the first studies carried out by Hinton [1,35] to investigate the effect of surface treatments with cerium compounds until now, the protection mechanisms propose the oxidation of trivalent cerium to tetravalent cerium [5,8,28].

According to Aldykiewicz Jr [36], oxygen acts as the oxidant agent that is consumed at the electrode vicinity. The cathodic reactions result

* Corresponding author at: Instituto de Pesquisas Energéticas e Nucleares, Centro de Ciência e Tecnologia de Materiais, Av. Prof. Lineu Prestes, 2242, CEP 05508-000, São Paulo, SP, Brazil.
E-mail address: jmfj111@hotmail.com (J.M. Ferreira).

in local pH increase leading to rare earth oxide/hydroxide precipitation and formation of a protective layer on the surface.

Aramaki [37] proposed a modification in the Ce_2O_3 film by introducing H_2O_2 as oxidant agent. The surface treatment was carried out in two steps. The first step consisted of immersion in a 10^{-3} mol/L $Ce(NO_3)_3$ solution at 30 °C for 30 min, and the second comprised exposure to a 10^{-2} mol/L H_2O_2 solution. The results showed that the surface layer formed was highly resistant to 0.5 mol/L NaCl solution. XPS analysis of the surface showed a thin film (thickness inferior to 50 nm) with few quantities of Ce^{4+} due to the oxidation of Ce^{3+} supported by H_2O_2. The presence of Ce^{4+} together with Ce^{3+} in the film was further investigated by Aramaki [38].

Scholes [39] investigated the role of H_2O_2 in the surface treatments with cerium and showed that complexes such as $Ce(H_2O_2)^{3+}$ are initially formed and this is followed by deprotonation, oxidation and precipitation processes, leading to $Ce(IV)(O_2)(OH)_2$ formation. They found a dependence on the peroxide content and the $Ce(IV)(O_2)(OH)_2$ crystal size. The crystal size decreased as the peroxide concentration increased.

Hamlaoui and Pedraza [12] investigated the effect of polyethylene glycol (PEG) on the composition and morphology of the cerium oxide film deposited on electrogalvanized steel. They found that the addition of PEG in the cerium nitrate solution decreased the cracks in the film and consequently hindered the hydrogen evolution reaction and the dissolution of the metallic substrate. The addition of organic compounds to cerium containing solutions has been investigated and it has been associated to an even surface where the defects in the conversion film were shielded.

In the present study, the effect of new surface treatments in solutions containing cerium nitrate and an organic compound, specifically 2 butyne-1,4 diol propoxylate, on the corrosion resistance of eletrogalvanized steel has been investigated. The influence of citric acid as additive in the treatment solution has also been evaluated. The corrosion resistance of the surfaces after the treatments was compared with that of a surface passivated in hexavalent chromium containing solution.

2. Experimental

2.1. Samples preparation

AISI 1010 steel sheets (100 mm × 65 mm × 1 mm) were eletrogalvanised using a cyanide-free alkaline bath containing Zn^{2+} (12.5 g/L), KOH (170 g/L), K_2CO_3 (50 g/L), additive (10 mL/L), brightening agents (1 mL/L), conditioner (10 mL/L). The following conditions were used: temperature (22 ± 2) °C and current density of 2 A/dm^2 for 45 min.

Prior to zinc eletrodeposition, all the steel plates were degreased in a sodium silicate-based alkaline solution, at room temperature applying a current density of 2 A/dm^2 for 2 min for improving the surface wettability. The samples were rinsed in deionized water, activated in ammonia bifluoride 5% solution for 30 s, and rinsed again with deionized water.

Immediately after electrogalvanizing, the samples surface was activated in HNO_3 1% solution (pH 1), for 10 s, and then, rinsed with deionized water. Subsequently, some of the electrogalvanized samples were passivated of the following conversion treatments: (i) immersion for 1,3, 5, 7, and 9 min in the solution with cerium nitrate and 2-butyne 1,4 diol propoxylate. The solution composed of 0.04 mol·L^{-1} NaNO$_3$, 0.04 mol·L^{-1} Na$_2$SO$_4$, 0.04 mol·L^{-1} of 2-butyne 1,4 diol propoxylate (organic additive) and 0.04 mol·L^{-1} of $Ce(NO_3)_3$·6H$_2$O, (pH = 2.85); (ii) immersion for 1,3, 5, 7, and 9 min in the previous solution modified by the addition of 0.05 mol·L^{-1} of citric acid (pH = 1.73); (iii) immersion for 30 s in a commercial chromating solution with 2 g/L of Na$_2$CrO$_7$, sodium chloride as a conductive salt and diluted HCl solution for pH adjustment = 1.8. After the treatments, the treated surfaces were rinsed in distilled water and dried in on oven at 80 °C for 15 min (Table 1).

These treatments were exposed to the salt spray test for selection of the best results for electrochemical evaluation.

Table 1
Description of the surfaces evaluated in the present investigation.

Surfaces	Description
Zn	Eletrogalvanized steel sheet without passivation
CeG5	Eletrogalvanized steel passivated in solution containing cerium ions and organic additive (pH = 2.85) during 5 min with mechanical stirring.
CeG7	Eletrogalvanized steel passivated in solution containing cerium ions and organic additive (pH = 2.85) during 7 min with mechanical stirring.
CeCiG5	Eletrogalvanized steel passivated in solution containing cerium ions, organic additive and citric acid (pH = 1.73) during 5 min with mechanical stirring.
CeCiG7	Eletrogalvanized steel passivated in solution containing cerium ions, organic additive and citric acid (pH = 1.73) during 7 min with mechanical stirring.
Cr VI	Zinc layer passivated in chromating solution with hexavalent chromium (pH 1.8) during 30 s with mechanical stirring.

Eletrogalvanized samples without passivation treatment were also tested for comparison reasons.

2.2. Chemical and morphology analysis

Morphology evaluation of the surfaces after the passivation treatments investigated was carried out by Scanning Electron Microscope (LEO 1450VP SEM) using scattered electron detector and Scanning Electron Microscopy-Field Emission Gun (JEOL JSM-6330F FEG-SEM) with a Si detector and 20 keV energy.

The chemical composition of the surface after treatments was evaluated by X-ray Photoelectron Spectroscopy (XPS) carried out using a spectrometer Thermofisher Scientific Theta Probe. The XPS spectra acquired used X-ray source with monochromator Al Kα (hν = 1486.6 eV). The analysis with X-ray spot radius of 300 μm and high-resolution spectra were acquired at 50 eV for passage of the species of interest, such as carbon and cerium. The other spectra were acquired with steps of 30 eV, the case of carbon, zinc and oxygen. The values used for adjustments of C 1s elements, O 1s, Ce 3d and Zn 2p will be shown for comparison.

XPS analyses were performed at three different points (spots) per sample and the spectra are representative of surface discarding local variations. Quantitative surface chemical analyses were calculated from the high resolution core level spectra following the removal of a non-linear Shirley background.

2.3. Electrochemical behavior

The experimental set up used consisted of a three electrodes cell arrangement with an Ag/AgCl, KCl saturated electrode and a platinum wire used as reference and counter electrodes respectively. The working electrode was the samples with the various surface treatments tested exposing an area of 1 cm^2 to the electrolyte. The electrolyte used in the electrochemical tests was a 0.1 mol·L^{-1} NaCl solution, quiescent and naturally aerated at (22 ± 3) °C. The evolution of the electrochemical behavior of the surfaces tested was monitored by electrochemical impedance spectroscopy (EIS) tests carried out in the frequency range from 100 kHz to 10 mHz, with a signal amplitude perturbation of 10 mV (rms), and data acquisition rate of 10 points per decade. EIS data was acquired in the potentiostatic mode at the open circuit potential (OCP), using a Gamry potentiostat controlled by Gamry Instruments software.

To evaluate the reproducibility and the reliability of the results, at least three tests were carried out for each condition tested.

The identification symbol and description of the investigated samples are summarized in Table 1.

3. Results and discussions

The researchers used 1,3, 5, 7, and 9 min and selected the treatments that passed ASTM B117 salt spray test (168 h in the salt spray test) and selected the treatment times corresponding to 5 min and 7 min for electrochemical evaluation.

3.1. Chemical characterization of electrogalvanized steel passivated in solution containing cerium ions and organic additive

The chemical composition of the surface after the CeG5 and CeG7 treatments and the chemical state of the elements in the film were characterized by XPS. Fig. 1 shows the XPS survey spectra of these surfaces. Note that the intensities of the peaks do not directly represent relative concentrations, as the elemental sensitivity factors and the analyzer transmission function must be taken into account.

It was observed, in Fig. 1, that the spectra corresponding to these two treatments are very similar showing the same peaks, C 1s, O 1s, Ce 3d and Zn 2p. The atomic percentage of the elements in the surface film formed was estimated and the results are shown in Table 2, indicating that the two surfaces have similar chemical composition.

The presence of carbon, oxygen, zinc, cerium were observed in XPS analysis. Zinc was found in the surface film in similar amounts to that of cerium for both periods of treatment showing that zinc from the surface is incorporated into the film and also cerium. The main differences between the films formed at 5 min or 7 min of treatment are in the amount of carbon and oxygen in it. High-resolution spectra for C 1s with chemical states are shown in Fig. 2, with the peak position used for fitting to C 1s. Chemical speciation led to surface compounds identification, as it will be shown.

The $C1s$ peaks can be decomposed into different components such as C–C/C–H, C–COO$_X$, C–O and C=O species [40,41]. Fitting was carried out using the following binding energies: C–C/C–H (284.7 ± 0.74 eV), C–COO$_X$ (285.3 ± 0.80 eV) and C=O (288.9 ± 0.74 eV). The carbon species and oxygen species detected by XPS and their respective amounts for the CeG5 and CeG7 surfaces are shown in Table 3.

High-resolution spectra for O 1s and the fitting peak position are shown in Fig. 3 whereas for Zn 2p$_{3/2}$ and the fitting peak position are shown in Fig. 4 for the CeG5, and CeG7 surfaces.

The results of peak deconvolution for Zn 2p$_{3/2}$ lines corresponding to Zn^0 (1019.6 ± 2.1 eV), ZnO (1021.7 ± 1.74 eV) and ZnO·OH (1022.7 ± 1.48 eV) are shown in Table 3.

High-resolution spectra for Ce 3d$_2$ and the fitting peak position are shown in Fig. 5 for the CeG5, and CeG7 surfaces.

It is possible to differentiate Ce^{3+} and Ce^{4+} species with distinct line shapes corresponding to various final states by XPS: Ce(III) = v$_0$ + v′ + u$_0$ + u′ and Ce(IV) = v + v″ + v‴ + u + u″ + u‴. The u‴ component is a fingerprint of Ce^{4+}. It is absence in the Ce^{3+} spectrum is characteristic of no 4f^0 state in these compounds [40].

The highest binding energy peaks u‴ and v‴ respectively are located at about 915.1 and 890 ± 0.1 eV. The satellite peak u‴ associated to the

Table 2
XPS determined elemental concentrations for CeG5 and CeG7 surfaces.

Surfaces	C (at.%)	O (at.%)	Zn (at.%)	Ce (at.%)
CeG5	44.87	41.96	6.84	6.32
CeG7	49.67	38.84	5.63	5.86

Ce 3d$_{3/2}$ is characteristic of the presence of Ce^{4+} ions, according with the literature [13,40,41].

The lowest binding energy states u, v, u″, v″ respectively located at 901, 883, 907 and 888 ± 0.1 eV are the result of Ce 3d^{9}4f^2 O 2p^4 and Ce 3d^{9}4f^1 O 2p^5 final states, according with the literature [40].

Therefore, based on the spectral literature [13,40,41], Ce^{4+} dopant was observed for CeG5 and CeG7 surfaces, a strong satellite near 915.14 eV, typical of +4 oxidation state showing that the surface film contains Ce^{3+} and Ce^{4+}.

Table 3 shows the results of XPS settings for CeG5 and CeG5 surface and the values of FWHM peaks and the atomic concentrations of species fitting.

The results in Table 3 confirm that the main components in the surface films formed are the same as it should be expected but their composition varied significantly. The film on the CeG7 surface is mainly composed of C–C/C–H whereas the film on the CeG5 surface consists mainly of C–COOX. These results show that the treatment time has a significant effect on the film composition with increasing amounts of C–C/C–H and decreasing of C–COO$_X$ and C=O with treatment time.

Fig. 2. XPS spectra of C 1s with chemical states; C 1s peak fitting with chemical states for (a) CeG5 and (b) CeG7 samples.
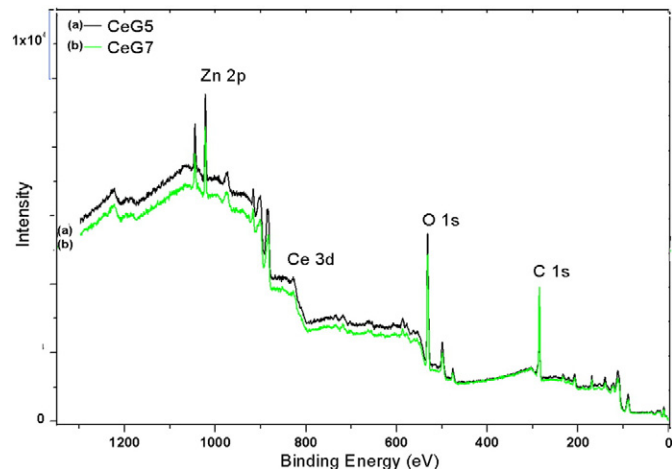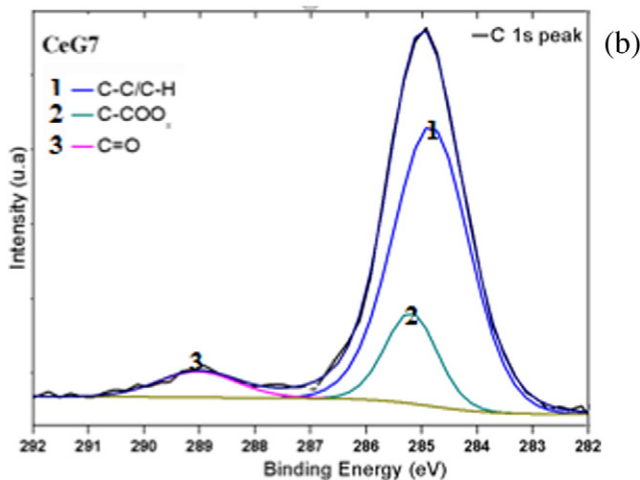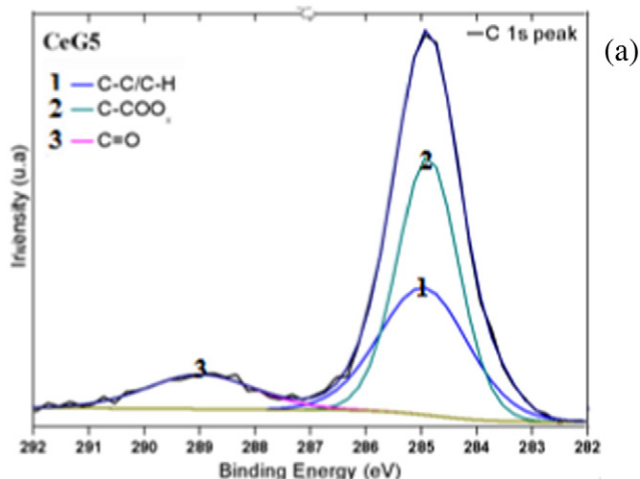

Fig. 1. XPS survey spectra of samples after surface treatments by immersion in solution with cerium nitrate and 2-butyne 1,4 diol propoxylate for 5 min (CeG5) and 7 min (CeG7).

Table 3
XPS results for CeG5 and CeG7 surfaces, signal for C 1s, O 1s, Zn 2p, Ce 3d, fitting species, binding energy values, FWHM and the atomic concentrations.

Surfaces	Signal	Fitting	BE (eV)	F.W.H.(eV)	at.%
CeG5	C 1s	C–C/C–H	284.7	0.74	50.31
		C–COOX	285.3	0.74	35.99
		C=O	288.9	0.74	11.96
	Zn 2p	ZnO	1019.6	2.1	3.93
		ZnO	1021.7	1.74	86.68
		ZnO·OH	1022.7	1.48	9.39
	O 1s	O^{2-}	529.5	2.1	34.3
		OH^-	532.3	2.1	65.7
	Ce 3d	Ce_2O_3	$v_0 + v' + u_0 + u'$		61.9
		CeO_2	$v + v'' + v''' + u'' + u' + u$		38.1
CeG7	C 1s	C–C/C–H	284.7	0.74	70.43
		C–COOX	285.3	0.74	14.77
		C=O	288.9	0.74	5.13
	Zn 2p	ZnO	1019.6	2.1	4.98
		ZnO	1021.7	1.74	87.57
		ZnOOH	1022.7	1.48	7.45
	O 1s	O^{2-}	529.5	2.1	38.9
		OH^-	532.3	2.1	61.1
	Ce 3d	Ce_2O_3	$v_0 + v' + u_0 + u'$		67.3
		CeO_2	$v + v'' + v''' + u'' + u' + u$		32.7

A time might be investigated in order to obtain the most effective ratio between the C–C/C–H and C–COO$_X$ and C=O for corrosion protection.
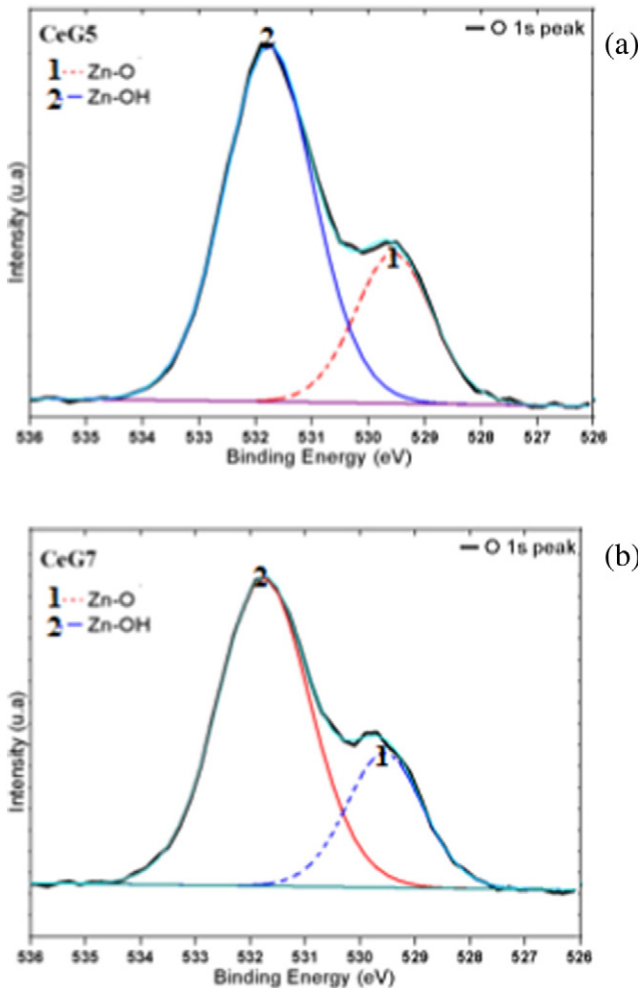

Fig. 3. XPS spectra of O 1s with chemical states; O 1s peak fitting with chemical states for (a) CeG5 and (b) CeG7 surfaces.
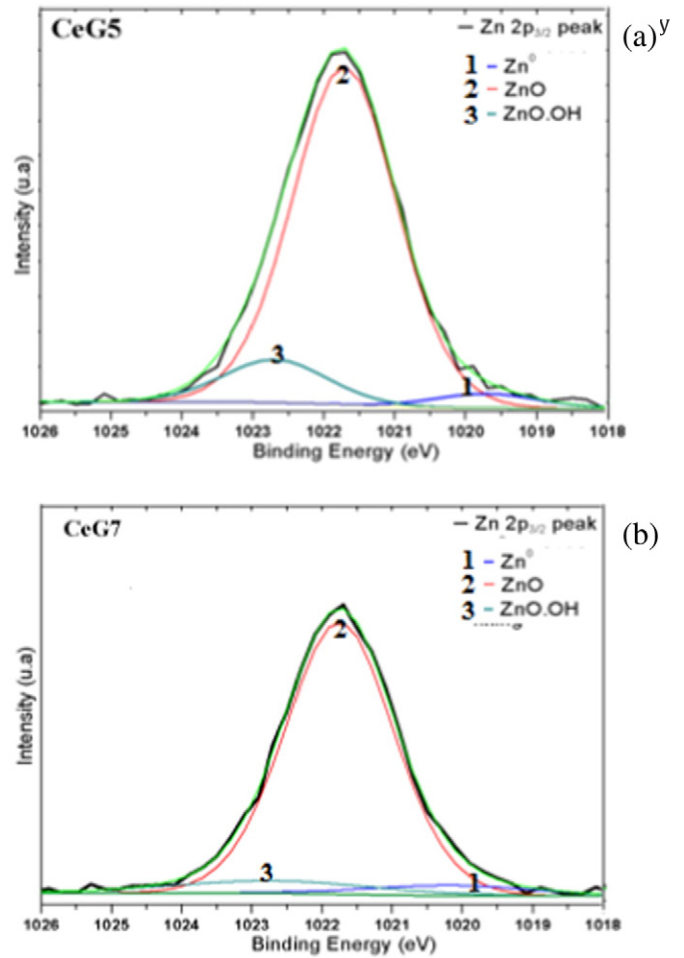

Fig. 4. XPS spectra of Zn 2p$_{3/2}$ with chemical states; Zn 2p$_{3/2}$ peak fitting with chemical states for (a) CeG5 and (b) CeG7 surfaces.

low (Table 2) and the Zn composition for the CeG5 and CeG7 surfaces are very similar. Zinc in the film is mainly found as oxide and hydrated oxide.

Based on the values in Table 3 and equations 1 and 2 the amounts of cerium oxide were estimated. The concentrations of Ce_2O_3 in the CeG5 and CeG7 surfaces were approximately 62% and 67%, and that of CeO_2 corresponded to 38% and 33%, respectively. These results indicated that for both surfaces the ratio between Ce_2O_3 and CeO_2 was similar and was in the 1.6 to 2.0 range.

The ratio CeO_2/Ce_2O_3 in the surface film obtained for a treatment time of 5 min was superior to that of a 7 min treatment. The corrosion resistance of the first film was also superior to that associated to the last treatment. Besides, the film obtained for a 7 min treatment was mainly composed of C–C/C–H whereas the film for 5 min treatment consists mainly of C-COOX. These results show that the treatment time has a significant effect on the film composition with increasing amounts of C–C/C–H and decreasing of C–COO$_X$ and C=O with treatment time, Table 3.

It is important to notice that for both surfaces, Ce^{3+} largely predominates. The first studies reporting the use of cerium treatments for metallic surface protection suggested that Ce^{3+} in the form of its oxide could be a source of cerium ions and these could be associated to self-healing effects [29,42,43].

Although the results show that treatment with solutions of cerium ions and organic additive shown potential for use as a treatment for passivation, the great number of surface defects prevents its use. In order to improve the surface morphology citric acid was added to the treatment and the surface was more homogeneous.
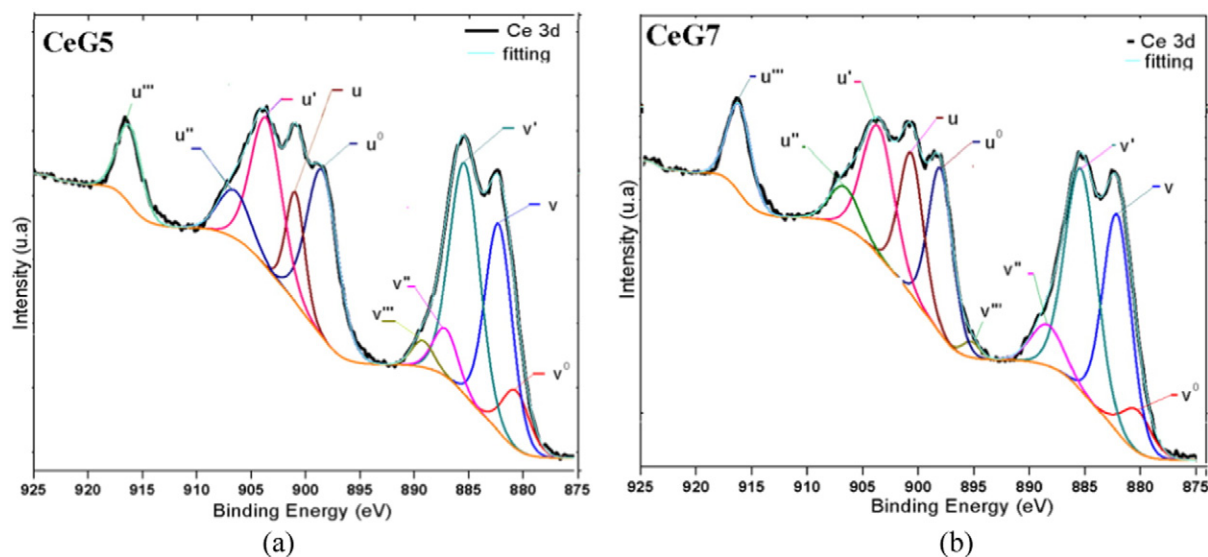
Fig. 5. XPS spectra of Ce $3d_{3/2}$ and Ce $3d_{5/2}$ with chemical states corresponding to (a) CeG5 and (b) CeG7 treatments.

3.2. Chemical characterization of electrogalvanized steel treated in solution containing cerium ions, organic additive and citric acid

The chemical composition of the surface film formed and chemical state of the elements in the surfaces after immersion in the solution presented in the previous sections modified by the addition of citric acid during either 5 min (CeCiG5) or 7 min (CeCiG7) were characterized by XPS. Fig. 6 shows the XPS survey spectra of the respective surfaces. Note that the intensities of the peaks do not directly represent relative concentrations, as the elemental sensitivity factors and the analyzer transmission function must be taken into account.

The spectra corresponding to CeCiG5 and CeCiG7 surfaces are similar showing the same peaks, C 1s, O 1s, Ce 3d and Zn 2p. The atomic percentage of the elements in the surface film formed was estimated and the results are shown in Table 4.

The surfaces treated in the solution without citric acid showed lower amounts of carbon (see Table 2) comparatively to that with it. The addition of citric acid allowed the formation of thicker layers due to the decreased pH. This is supported by the increased carbon amount and decreased zinc content at the treated surfaces as presented in Table 4.

The interaction of the treatment solution with the substrate resulted in a large number of carboxylic groups bonded.

Whereas the zinc oxide was predominantly found for the treatment in both solutions with or without citric acid, but in the modified solution with the addition of citric acid, larger amounts of ZnOOH were detected indicating a more prominent attack of the zinc surface.

Cerium was found in higher amounts at the surfaces treated in the solution without citric acid. The differences between the amount of cerium at the surfaces treated in the solutions with or without citric acid must be attributed to their thickness differences as thicker layers were obtained in the modified solution. It was also found that in the surfaces treated in the modified solution (CeCiG5 and CeCiG7). Cerium was mainly found as CeO_2 comparatively to Ce_2O_3. It must be mentioned that CeO_2 is more stable than the Ce_2O_3 [20,43].

The literature has reported that treatments of zinc in solutions with citric acid of pH above 3 favored the formation of thick layers with large quantities of carboxylic groups linked to the metal substrate [6].
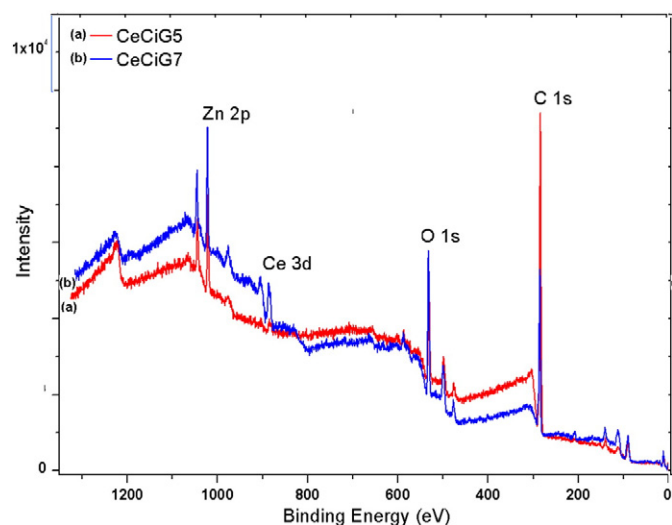

Fig. 6. XPS survey spectra of samples with surface treatments by immersion in cerium nitrate, additive organic and citric acid solution during 5 min (CeCiG5) and 7 min (CeCiG7).

Table 4
XPS results for CeCiG5 and CeCiG7 surfaces, signal for C 1s, O 1s, Zn 2p, Ce 3d, fitting species, binding energy values, FWHM and the atomic concentrations.

| Surfaces	Signal	Fitting	BE (eV)	F.W.H.M (eV)	at%
CeCiG5	**C** 1s	C–C/C–H	284.7	0.74	52.7
		C–COOX	285.3	0.74	33.72
		C=O	288.9	0.74	13.56
	Zn 2p	ZnO	1019.6	2.1	–
		ZnO	1021.7	1.74	69.32
		ZnO·OH	1022.7	1.48	30.68
	O 1s	O^2	529.5	2.1	46.23
		OH^-	532.3	2.1	53.77
	Ce 3d	Ce_2O_3	$v_0 + v' + u_0 + u'$		35.69
		CeO_2	$v + v'' + v''' + u'' + u' + u$		64.31
CeCiG7	**C** 1s	C–C/C–H	284.7	0.74	65.5
		C–COOX	285.3	0.74	24.72
		C=O	288.9	0.74	11.48
	Zn 2p	ZnO	1019.6	2.1	0.91
		ZnO	1021.7	1.74	61.22
		ZnO·OH	1022.7	1.48	37.87
	O 1s	O^{2-}	529.5	2.1	41.21
		OH^-	532.3	2.1	59.79
	Ce 3d	Ce_2O_3	$v_0 + v' + u_0 + u'$		47.98
		CeO_2	$v + v'' + v''' + u'' + u' + u$		52.32
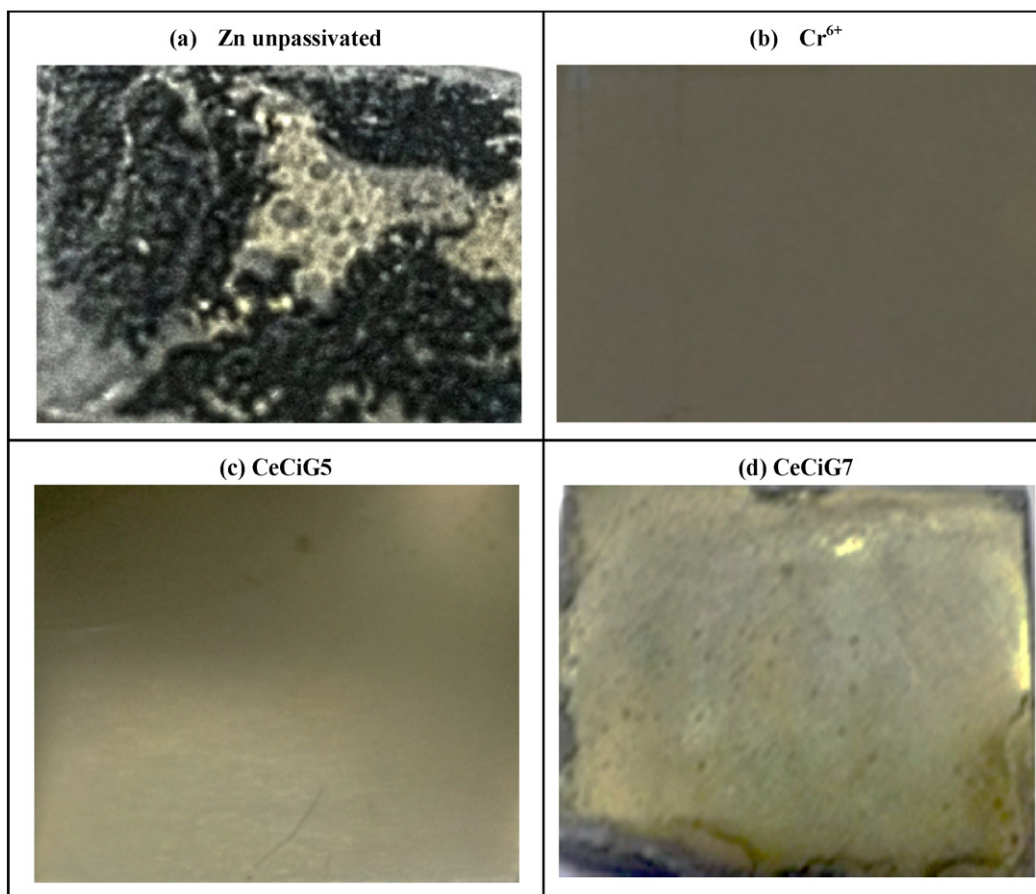
Fig. 7. Macrographs of surface of eletrogalvanized steel obtained after 15 days exposure to 0.1 mol·L^{-1} NaCl solution in the following condition: (a) unpassivated; (b) passivated in a solution containing Cr^{6+} salts; passivated in solution modified with citric acid for (c) 5 min and (d) 7 min, respectively. Magnification: 10×.

A comparison of the chemical composition of the CeCiG5 and CeCiG7 surfaces (Table 4) indicates larger amounts of C–COOX and C=O species for the CeCiG5 surface comparatively to the CeCiG7 one besides lower quantities of ZnO associated to this last treatment as compared to the first. This could be indicative of larger number of adsorbates associated to the first treatment on the ZnO substrate increasing the interfacial bonding properties associated to the layer of the CeCiG5 treatment on the Zn surface. The higher amounts of ZnOOH species on the CeCiG7 surface suggests that part of the zinc oxide surface interacted with hydroxyl ions from the environment impeding a highly effective interaction of the surface with the carboxyl groups in the treatment solution and consequently a lower fraction of surface coverage.

3.3. Morphology of surfaces passivated in solution modified with citric acid

#### 3.3.1. Macroscopic observation of treated surfaces

Macrographs of eletrogalvanized surfaces are shown in Fig. 7 for untreated samples (a) or treated in the modified solution with citric acid for (b) 5 min and (c) 7 min after exposure to the 0.1 mol·L^{-1} NaCl electrolyte for 15 days to the electrolyte. The results showed a bright and even surface after treatment for the various periods in the modified solution. The passivating effect of the treatment proposed in this investigation was clearly seen by surface observation of samples exposed to the 0.1 mol·L^{-1} NaCl solution during 15 days (Fig. 7). Corrosion products were seen all over the surface of the unpassivated electrogalvanized steel after 15 days of test (Fig. 7a). On the other hand, the passivated surfaces were still bright and only few spots of corrosion were found on their exposed surfaces. From macroscopic observation, the results suggested that a period of 5 min was related to the best corrosion performance among the tested ones.

3.3.2. Microscopic observation of treated surfaces

Microscopic surface observation was also carried out by SEM-FEG of the untreated (Zn) and treated samples, prior to exposure to the electrolyte, Fig. 8, and after 15 days of exposure to 0.1 mol·L^{-1} NaCl solution, Fig. 9.

As it can be seen in Fig. 8, the electrodeposited surface presents irregularities as some nodules due to incorporation of specimens from the bath solution into the surface. This represents defects on the surface and sites with higher susceptibility for corrosion nucleation due to an incomplete coverage of these particles. Small white particles were seen on the surfaces with the various periods of treatment but these increased in size with treatment time. For the surface treated for 5 min (CeCiG5), some of the white particles were apparently incorporated in the surface layer formed, whereas for that with 7 min treatment (CeCiG7), they presented a regular and round morphology, were large in sizes and were found on top of the treated surfaces. EDX analysis on the white particles showed that these were Ce rich precipitates.

Figs. 8 and 9 show that after 15 days of immersion, the treated surfaces showed significant differences depending on the time of treatment. For untreated surfaces, the corrosion products covered most of the surface and the morphology of the corrosion products show heterogeneous features but with predominance of round particles. The CeCiG5 surfaces did not show visible signs of corrosion after 15 days of exposure to the chloride test solution suggesting a high resistance of the layer formed to electrolyte penetration. This was confirmed by microscopic observation. For the surface treated for 7 min (CeCiG7) however, slight corrosion was indicated by macroscopic observation and the microscopic observation showed the formation of corrosion products with a very regular morphology and sizes consisting of round particles
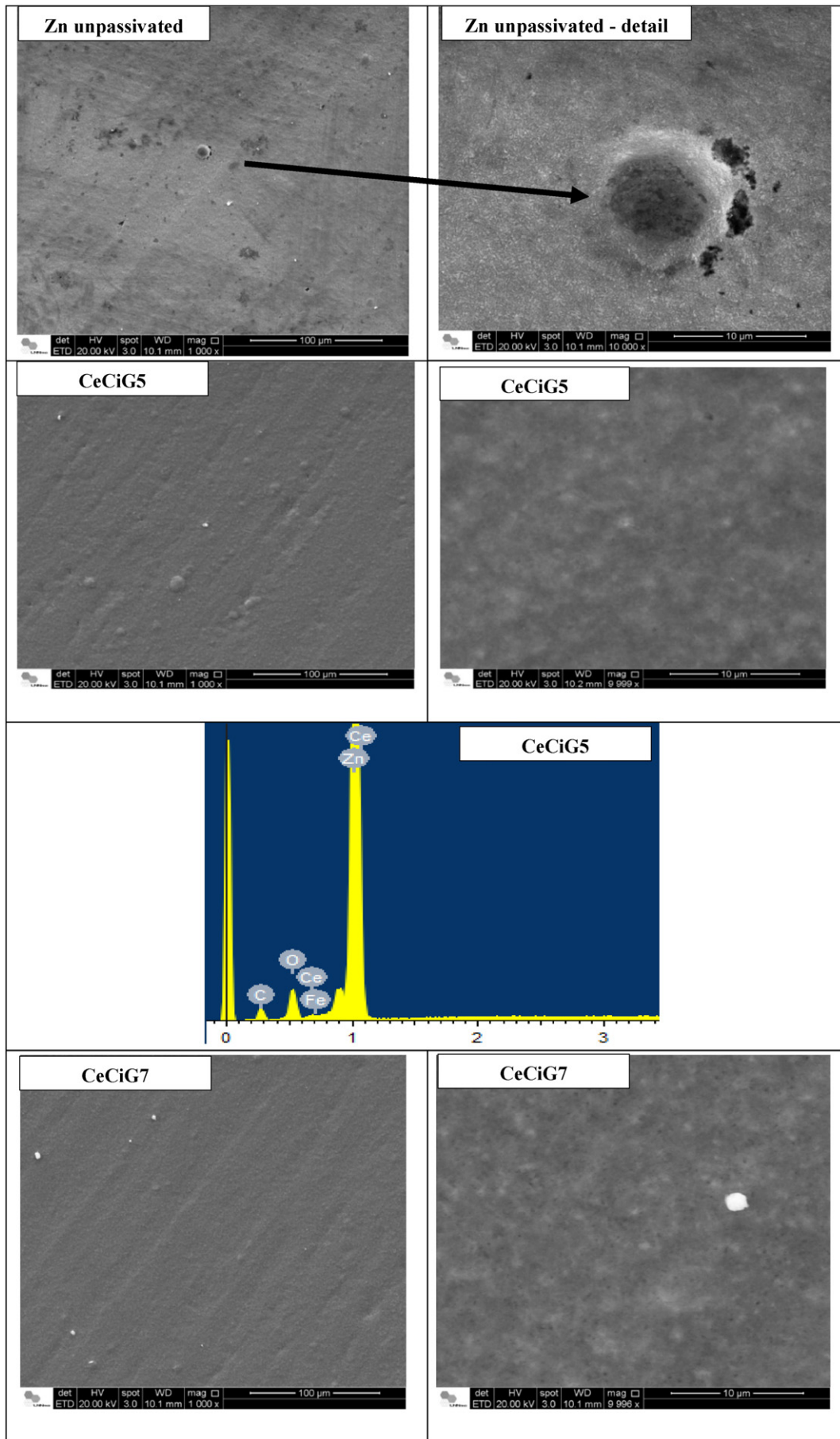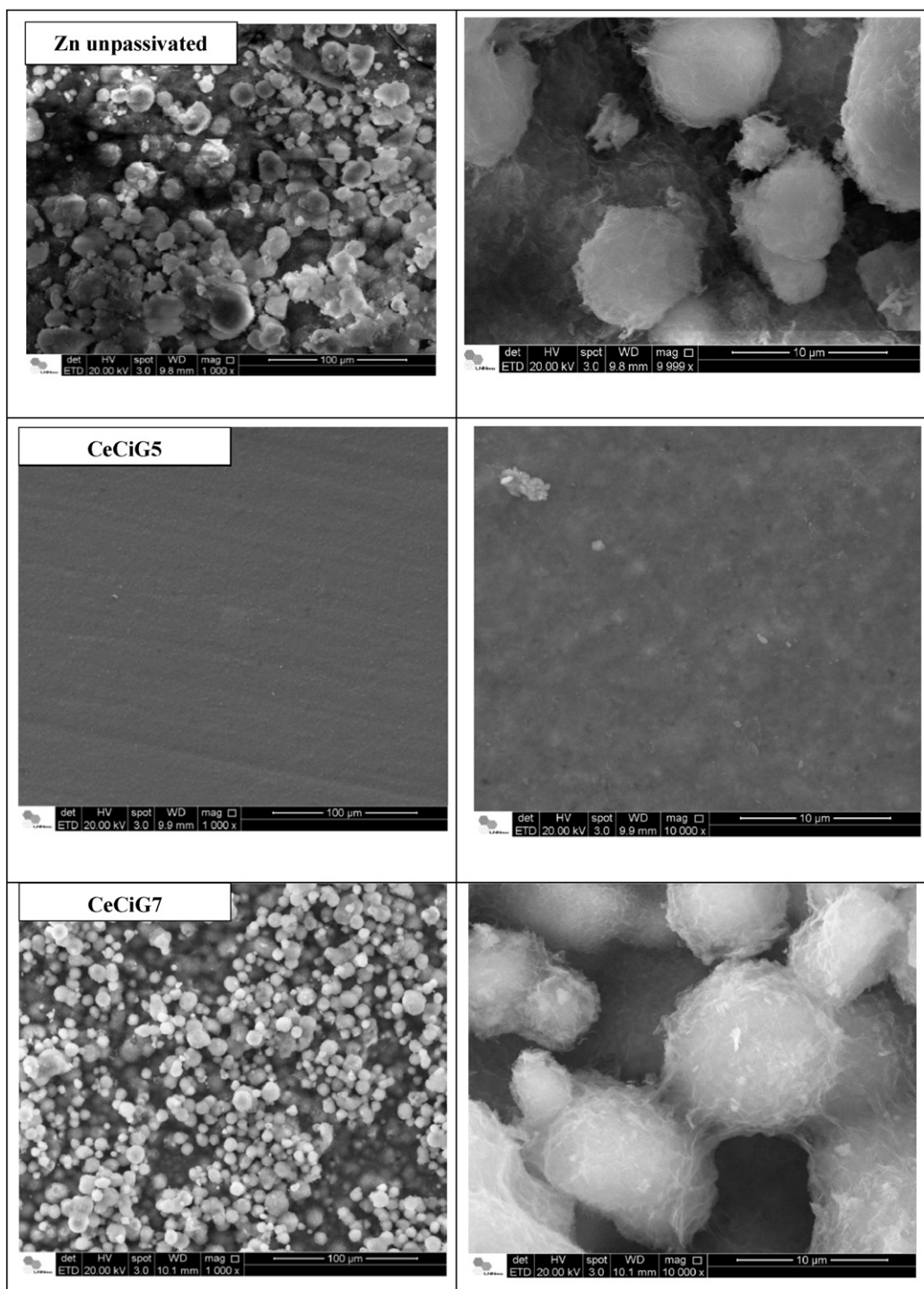
Fig. 9. SEM micrographs of electrogalvanized steel unpassivated (Zn) and passivated in the citric acid modified solution during 5 min (CeCiG5) and 7 min (CeCiG7) after 15 days of exposure to 0.1 mol·L^{-1} NaCl solution.

that were also seen on the unpassivated surfaces, indicating that these are zinc corrosion products. The differences between the unpassivated surface and the CeCiG7 one after 15 days of exposure is that for this last one, the corrosion products are connected by a viscous layer that helps keeping them attached to the metallic surface.

3.4. Electrochemical evaluation of untreated and treated surfaces in solution containing cerium ions, organic additive and citric acid

EIS results of surfaces treated in the modified solution with citric acid as a function of exposure time to 0.1 mol·L^{-1} NaCl solution are shown in Fig. 10. For comparison, EIS results for untreated electrogalvanized steel

Fig. 8. SEM micrographs of electrogalvanized steel unpassivated (Zn) and passivated in the citric acid modified solution during 5 min (CeCiG5) and 7 min (CeCiG7) prior to exposure to the electrolyte. EDS spectrum for CeCiG5 is presented indicating cerium on the surface.
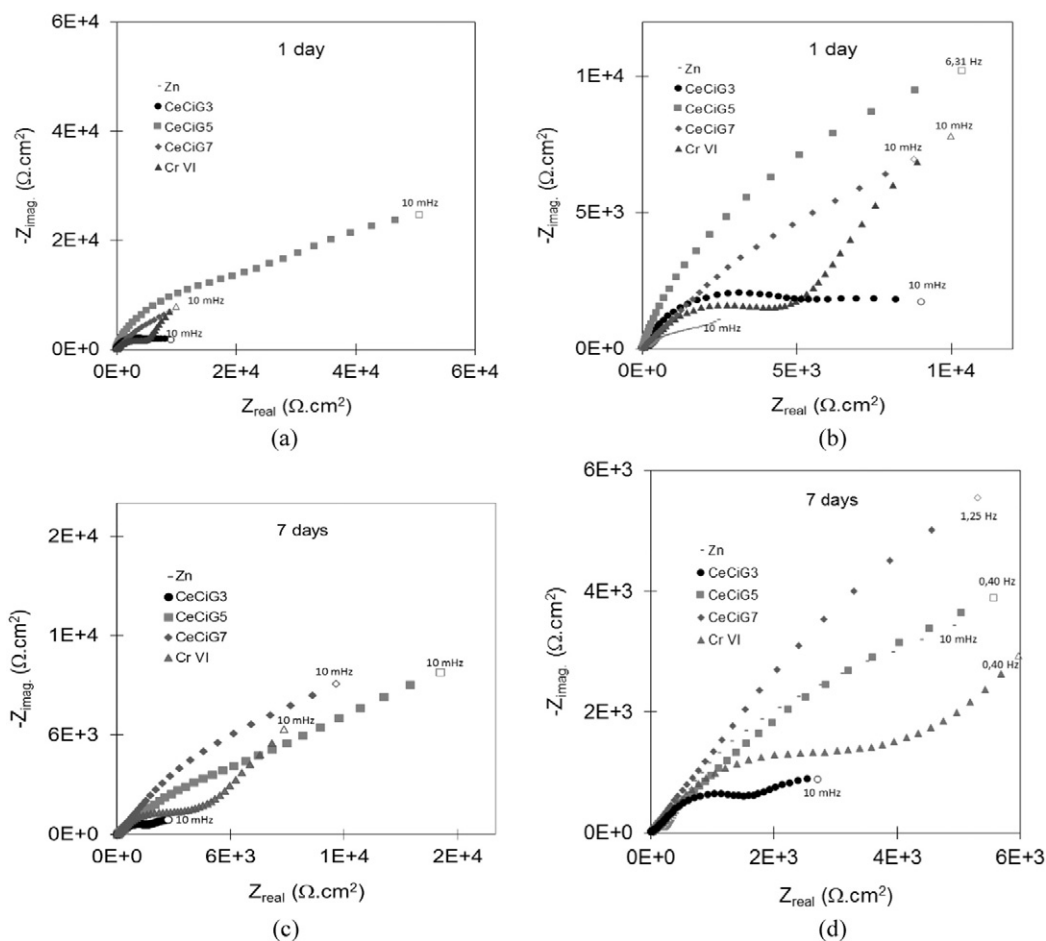
Fig. 10. EIS results for electrogalvanized steel untreated (Zn) or treated treatments corresponding to immersion in citrate containing solution for 3 min, 5 min, and 7 min for 1 day (a) and (b) and 7 days (c) and (d) of exposure to 0.1 mol·L^{-1} NaCl solution.

surface and treated in hexavalent chromium ions containing solution are also presented in Fig. 10. The comparison with this last treatment was only carried out until 7 days of immersion. For longer periods of test, the results are presented in Fig. 11.

The results showed that since the first days of immersion the surfaces presenting the higher impedances were those corresponding to CeCiG5 and CeCiG7 with this last surface presenting impedances of the same order of magnitude of the chromated one. Despite the degradation of the corrosion resistance of the CeCiG5 and CeCiG7 surfaces between 1 and 7 days of test, their impedances after 7 days of test were superior to that of the chromated one. The CeCiG3 surface however showed much lower impedances since the first days of test indicating that 3 min of treatment was not adequate for appropriate protection of the substrate. This was also found for longer periods of immersion as Fig. 11 shows. The CeCiG7 surface degraded rapidly and after 15 days of exposure to the electrolyte its impedance was inferior to that of the CeCiG5 surface, supporting the results of macroscopic and microscopic surface observation. Degradation of both surfaces, CeCi5 and CeCi7 occurred continuously but at a slow rate between 15 days and 49 days of exposure, Fig. 11.

Fig. 12 compares the two treatments that resulted in the best corrosion performance in the electrolyte used for periods of immersion corresponding to 28 days, 35 days and 49 days.

From 15 to 28 days of immersion, the impedances of both treatments, CeCiG5 and CeCiG7 diminished but the decrease was more pronounced for this last treatment. From 28 days of immersion until the end of test, after 49 days of exposure, the surface corresponding to the CeCiG5 treatment was fairly stable showing only slight decrease in impedance between 28 days and 49 days of test. These results indicated

that the two treatments, CeCiG5 and CeCiG7 could be good alternatives for surface treatments that generate toxic residues with advantage of the first one as corrosion resistance is concerned.

As Fig. 9 showed, the surface of the untreated electrogalvanized steel and the CeCiG3 surface presented a large amount of corrosion product particles after 15 days of exposure to the chloride electrolyte. At this period of test, the CeCiG7 surface was partially covered by zinc corrosion products, but these were apparently interconnected and were maintained attached to the surface due to a gel like film involving the corrosion product particles. This might be the reason for the large impedance increase observed between 1 day and 7 days of immersion and the slow degradation of the surface for longer periods of exposure due to the ingress of the electrolyte through the film. For the CeCiG5 surface it is seen that the film is continuous and more resistant to permeation of aggressive species and after 15 days of exposure to the 0.1 mol·L^{-1} NaCl electrolyte, the surface was still bright and showed no visible signs of corrosion. These results indicated that a very effective interaction between the treatment solution and the zinc surface requires an optimum time.

4. Conclusions

A new treatment in a solution containing cerium ions and organic additive, either with or without citric acid, has been accomplished. The results showed that the surface film formed contained CeO_2 and Ce_2O_3 but their ratios vary depending on the solution and time of treatment used. The citric acid had a beneficial effect on surface uniformity and on the formation of a film where CeO_2 predominates over Ce_2O_3.
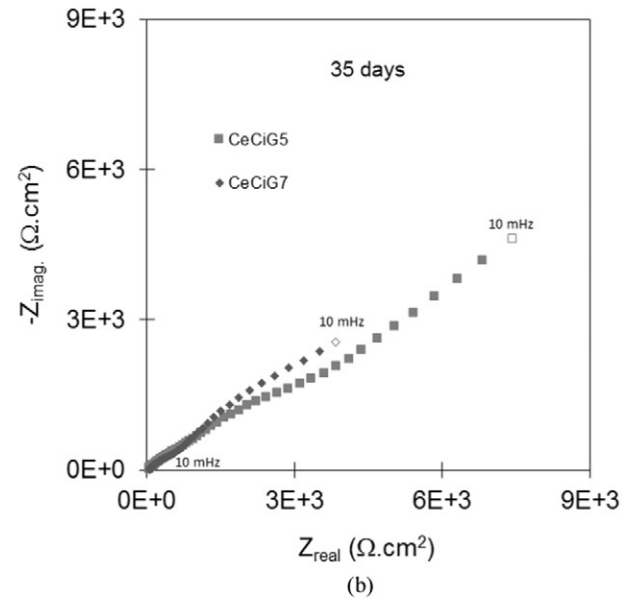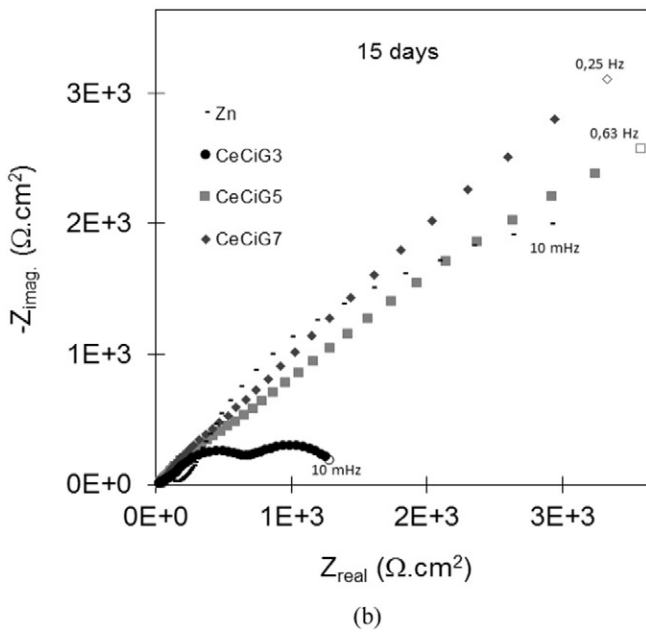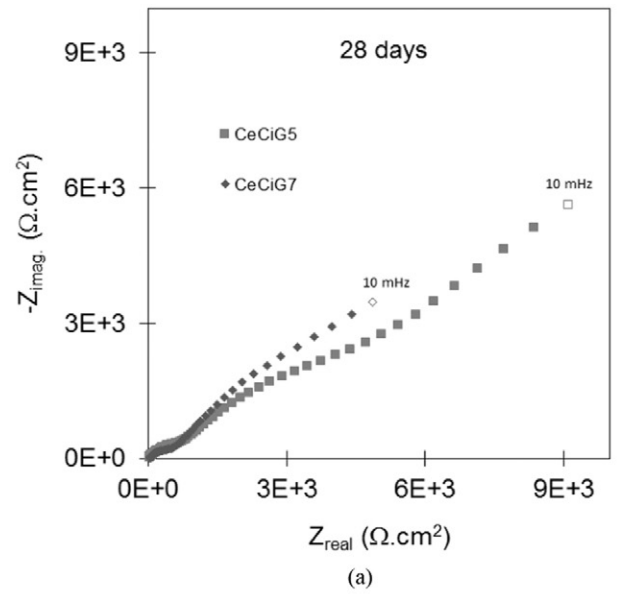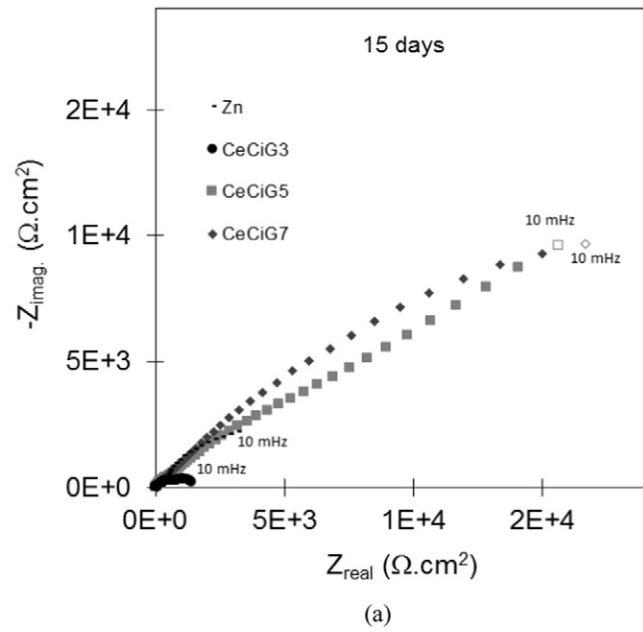
Fig. 11. EIS results for unpassivated and passivated electrogalvanized steel (Zn) in the modified solution with citric acid for 3, 5, and 7 min after (a) and (b) 15 days of exposure to 0.1 mol·L^{-1} NaCl solution.

The treatment time had a significant effect on the film composition with increased amounts of C–C/C–H and decreased of C–COO$_X$ and C=O as the treatment time increased.

The electrochemical characterization of the treated surfaces showed that 5 min of immersion treatment resulted in a surface of outstanding corrosion resistance of the substrate. The treatment investigated in this study resulted in outstanding corrosion resistance of the substrate. Surface observation after immersion test in a chloride solution supported the results indicating that this treatment could be an alternative to chromating treatments.
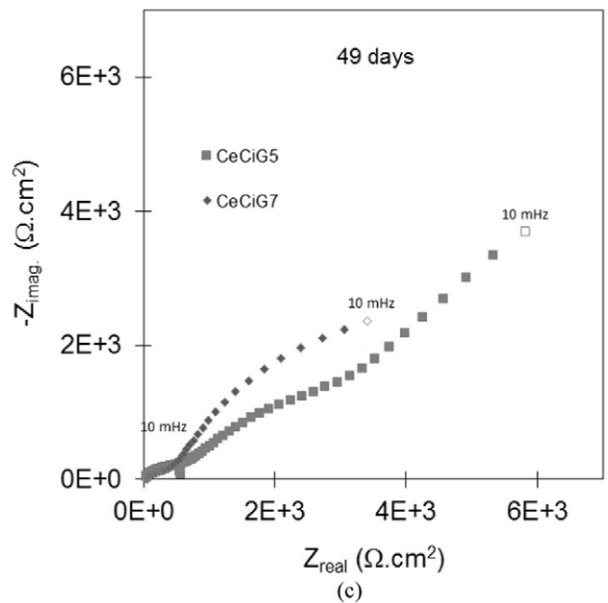
Fig. 12. EIS results for electrogalvanized steel passivated in the modified solution with citric acid for 5 and 7 min after (a) 28 days, (b) 35 days and (c) 49 days of exposure to 0.1 mol·L^{-1} NaCl solution.

Acknowledgements

References

[1] B.R.W. Hinton, The corrosion inhibition of zinc with cerous chloride, Corros. Sci. 29 (8) (1989) 967–975.

[2] W.G. Fahrenholtz, M.J. O'Keefe, H. Zhou, J.T. Grant, Characterization of cerium-based conversion coatings for corrosion protection of aluminum alloys, Surf. Coat. Technol. 155 (2002) 208–213.

[3] A. Amadeh, B. Pahlevani, S. Heshmati-Manesh, Effects of rare earth metal addition on surface morphology and corrosion resistance of hot-dipped zinc coatings, Corros. Sci. 44 (10) (2002) 2321–2331.

[4] D.R. Arnott, B.R.W. Hinton, N.E. Ryan, Cationic-film-forming inhibitors for the protection of the AA7075 aluminum alloy against corrosion in aqueous chloride solution, Corrosion 45 (1) (1989) 12–18.

[5] C. Motte, N. Maury, M.-G. Olivier, J.-P. Petitjean, J.-F. Willem, Cerium treatments for temporary protection of electroplated steel, Surf. Coat. Technol. 200 (2005) 2366–2375.

[6] G. Kong, L. Liu, L. Lu, C. Chen, Z. Zhong, Study on lanthanum salt conversion coating modified with citric acid on hot dip galvanized steel, J. Rare Earths 28 (3) (2010) 461–465.

[7] G. Kong, J. Lu, H. Wu, Post treatment of silane and cerium salt as chromate replacers on galvanized steel, J. Rare Earths 27 (1) (2009) 164–168.

[8] M.F. Montemor, A.M. Simões, M.G.S. Ferreira, Composition and corrosion behaviour of galvanised steel treated with rare-earth salts: the effect of the cation, Prog. Org. Coat. 44 (2) (2002) 111–120.

[9] G. Kong, L. Lingyan, J. Lu, C. Che, Z. Zhong, Corrosion behavior of lanthanum-based conversion coating modified with citric acid on hot dip galvanized steel in aerated 1 M NaCl solution, Corros. Sci. 53 (4) (2011) 1621–1626.

[10] G. Grundmeier, W. Schimidt, M. Stratmann, Corrosion protection by organic coatings: electrochemical mechanism and novel methods of investigation, Electrochim. Acta 45 (15) (2000) 2515–2533.

[11] Y. Hamlaoui, Cathodic electrodeposition of cerium-based oxides on carbon steel from concentrated cerium nitrate solutions: part I. Electrochemical and analytical characterisation, Mater. Chem. Phys. 113 (2) (2009) 650–657.

[12] Y. Hamlaoui, L. Tifouti, F. Pedraza, Corrosion protection of electro-galvanized steel by ceria-based coatings: effect of polyethylene glycol (PEG) addition, J. Mater. Eng. Perform. 22 (9) (2013) 2706–2715.

[13] E. Johansson, L. Nyborg, XPS study of carboxylic acid layers on oxidized metals with reference to particulate materials, Surf. Interface Anal. 35 (4) (2003) 375–381.

[14] M. Stratmann, R. Feser, A. Leng, Corrosion protection by organic films, Electrochim. Acta 39 (8) (1994) 1207–1214.

[15] C.-Y. Tsai, J.-S. Liu, P.-L. Chen, C.-S. Lin, A roll coating tungstate passivation treatment for hot-dip galvanized sheet steel, Surf. Coat. Technol. 205 (2011) 5124–5129.

[16] D.-L. Liu, Z.-G. Yang, Z.-Q. Wang, C. Zhang, Synthesis and evaluation of corrosion resistance of molybdate-based conversion coatings on electroplated zinc, Surf. Coat. Technol. 206 (2010) 2328–2334.

[17] L. Jiang, M. Wolpers, P. Volovitch, K. Ocle, An atomic emission spectroelectrochemical study of passive film formation and dissolution on galvanized steel treated with silicate conversion coatings, Surf. Coat. Technol. 206 (2012) 3151–3157.

[18] M.F. Montemor, M.G.S. Ferreira, Analytical characterization of silane films modified with cerium activated nanoparticles and its relation with the corrosion protection of galvanized steel substrates, Prog. Org. Coat. 63 (2008) 330–337.

[19] M.F. Montemor, R. Pinto, M.G.S. Ferreira, The corrosion behaviour of with CeO$_2$ nanoparticles, Electrochim. Acta 54 (2009) 5179–5189.

[20] W. Trabelsi, P. Cecilio, M.G.S. Ferreira, M.F. Montemor, Electrochemical assessment of the self-healing properties of Ce-doped silane solutions for the pre-treatment of galvanised steel substrates, Prog. Org. Coat. 54 (2005) 276–284.

[21] L. Wang, C.-S. Liu, H.-Y. Yu, C.-Q. An, Structure and corrosion resistance of a composite γ-glicidoxy propyl trimethoxy silane conversion coating on galvanized steel, J. Iron Steel Res. Int. 19 (911) (2013) 46–51.

[22] C.R. Tomachuk, C.I. Elsner, A.R. Di Sarli, O.B. Ferraz, Corrosion resistance of Cr(III) conversion treatments applied on electrogalvanised steel and subjected to chloride containing media, Mater. Chem. Phys. 119 (1–2) (2010) 19–29.

[23] C.R. Tomachuk, C.I. Elsner, A.R. Di Sarli, Anti-corrosion performance of Cr^{+6}-free passivating layers applied on electrogalvanized, Mater. Sci. Appl. 1 (2010) 32–45.

[24] C.R. Tomachuk, C.I. Elsner, A.R. Di Sarli, Behavior of electrogalvanized steel pretreated with Cr(III)-based baths and exposed to 0.5 M Na$_2$SO$_4$ solution, Port. Electrochim. Acta 30 (3) (2012) 145–162.

[25] A.R. Di Sarli, J.D. Culcasi, C.R. Tomachuk, C.I. Elsner, J.M. Ferreira Jr., I. Costa, A conversion layer based on trivalent chromium and cobalt for the corrosion protection of electrogalvanized steel, Surf. Coat. Technol. 258 (2014) 426–436.

[26] Y. Castro, B. Ferrari, R. Moreno, A. Durán, Protection and surface modification of metals with sol–gel coatings, Int. Mater. Rev. 52 (2007) 175–192.

[27] G.R. Salazar-Banda, S.R. Moraes, A.J. Motheo, S.A.S. Machado, Anticorrosive cerium-based coatings prepared by the sol–gel method, J. Sol-Gel Sci. Technol. 52 (2009) 415–423.

[28] J.M. Ferreira Jr., J.L. Rossi, M.A. Baker, S.J. Hinder, I. Costa, Deposition and characterization of a new mixed organic/inorganic cerium containing coating for the protection of electrogalvanized steel, Int. J. Electrochem. Sci. 9 (2014) 1827–1839.

[29] M.F. Montemor, D.V. Snihirova, M.G. Taryba, S.V. Lamaka, I.A. Kartsonakis, A.C. Balaskas, G.C. Kordas, J. Tedim, A. Kuznetsov, M.L. Zheludkevich, M.G.S. Ferreira, Evaluation of self- healing ability in protective coatings modified with combination of nanocontainers filled with corrosion inhibitors, Electrochim. Acta 60 (2012) 31–40.

[30] S.M.A. Shibli, F. Chacko, Development of nano CeO$_2$-incorporated high performance hot-dip zinc coating, Surf. Coat. Technol. 202 (2008) 4971–4975.

[31] M.A. Arenas, J.J. Damborenea, Surface characterisation of cerium layers on galvanised steel, Surf. Coat. Technol. 187 (2–3) (2004) 320–325.

[32] J. Creus, F. Brezault, C. Rebere, M. Gadouleau, Synthesis and characterisation of thin cerium oxide coatings elaborated by cathodic electrolytic deposition on steel substrate, Surf. Coat. Technol. 200 (2006) 4636–4645.

[33] Y. Hamlaoui, C. Remazeilles, M. Bordes, L. Tifouti, F. Pedraza, Electrodeposition of ceria-based layers on zinc electroplated steel, Corros. Sci. 52 (3) (2010) 1020–1025.

[34] X. Huang, N. Li, H.H. Wang, H. Dun, S. Sun, J. Zheng, Electrodeposited cerium film as chromate replacement for tinplate, Thin Solid Films 516 (6) (2008) 1037–1043.

[35] B.R.W. Hinton, Corrosion inhibition with rare earth metal salts, J. Alloys Compd. 180 (1–2) (1992) 15–25.

[36] A.J. Aldykiewicz Jr., A.J. Davenport, H.S. Isaacs, Studies of the formation of cerium-rich protective films using X-ray absorption near-edge spectroscopy and rotating disk electrode methods, J. Electrochem. Soc. 143 (1) (1996) 147–154.

[37] K. Aramaki, The effect of modification with hydrogen peroxide on a hydrated cerium(III) oxide layer for protection of zinc against corrosion in 0.5 M NaCl, Corros. Sci. 48 (3) (2006) 766–782.

[38] K. Aramaki, Protection of zinc from corrosion by coverage with a hydrated cerium (III) oxide layer and ultrathin polymer films of a carboxylate selfassembled monolayer modified with alkyltriethoxysilanes, Corros. Sci. 49 (4) (2007) 1963–1980.

[39] F.H. Scholes, C. Soste, A.E. Hughes, S.G. Hardin, P.R. Curtis, The role of hydrogen peroxide in the deposition of cerium-based conversion coatings, Appl. Surf. Sci. 253 (4) (2006) 1770–1780.

[40] E. Bêche, Ce 3d XPS investigation of cerium oxides and mixed cerium oxide (CexTiyOz), Surf. Interface Anal. 40 (34) (2008) 264–267.

[41] D.R. Mullins, S.H. Overbury, D.R. Huntley, Electron spectroscopy of single crystal and polycrystalline cerium oxide surfaces, Surf. Sci. 409 (2) (1998) 307–319.

[42] K. Aramaki, A self-healing protective film prepared on zinc by treatment in a Ce (NO$_3$)$_3$ solution and modification with Ce (NO$_3$)$_3$, Corros. Sci. 47 (5) (2005) 1285–1298.

[43] K. Aramaki, Preparation of chromate-free, self-healing polymer films containing sodium silicate on zinc pretreated in a cerium (III) nitrate solution for preventing zinc corrosion at scratches in 0.5 M NaCl, Corros. Sci. 44 (6) (2002) 1375–1389.