



Effect of cerium nitrate concentration on corrosion protection of hybrid organic/inorganic Si/Zr sol-gel coating applied on hot-dip galvanized steel

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ABSTRACT

This present work investigates the corrosion performance of hybrid organic/inorganic Si/Zr sol-gel doped with various cerium nitrate concentrations applied on hot-dip galvanized steel. The Si/Zr sol-gel solution was prepared from tetraethyl orthosilicate (TEOS), 3-(trimethoxysilyl)propyl methacrylate (MAPTMS), and zirconium (IV) propoxide (ZTP). The effect of the addition of cerium nitrate was evaluated by electrochemical impedance spectroscopy (EIS) versus immersion in 0.1 M NaCl solution and salt spray test. The results indicated that cerium nitrate contents affected the protective behavior of sol-gel coating in long term. Additionally, the sol-gel doped with 650 ppm Ce (III) presented the optimal corrosion protection of the sol-gel coating formed on hot-dip galvanized steel substrate.

1. Introduction

Zinc coatings are recognized for protecting steel from corrosion through the physical barrier and galvanic protection. These coatings are widely used in automotive, constructive, or household industries [1–3]. However, corrosion products originated from zinc coating formed in humid environments cannot provide sufficient protection for steel substrate in the long term and required a supplementary protection [4].

To enhance the corrosion resistance of zinc coating, a chromate conversion coating has been widely employed as the most effective conversion coating for zinc and zinc coating [4–7]. Nonetheless, due to its carcinogenic effects and environmental toxicity, the use of chromate has been restricted [7]. Therefore, many scientific efforts have been devoted to find new environmentally friendly and nontoxic conversion coatings that provide efficient protection and can replace chromate conversion coatings.

The hybrid sol-gel coating, which has both organic and inorganic parts, provides a promising potential to replace chromate conversion coating [8,9]. The crucial role of sol-gel film is the formation of a homogenous and dense self-assembled siloxane (Si-O-Si) network that prevents the ingress of water, or aggressive species toward the metallic surface. Thus, sol-gel coatings show good barrier properties, resulting in improvement of the anticorrosion behavior of the metallic substrates.

Besides, the introduction of zirconium alkoxides into the hybrid sol-gel contributes to mechanical properties such as adhesion with the substrate and film hardness [10,11]. In addition, zirconium improves the fracture of the hybrid coating and reduces crack formation thanks to its high expansion coefficient, leading to enhancing corrosion protection [12]. However, zirconium alkoxides are reactive thus they are usually chelated with organic acids such as methacrylic acid (MMA), acetylacetone (AcAc), and 2,2-bipyridine and consequently slow down the hydrolysis and condensation reactions. Among them, the chelation of zirconium(IV) tetrapropoxide (ZTP) and MMA presented the good effectiveness [13].

Rodič et al. [14] studied the protective properties of sol-gel hybrid (Si/Zr) based on tetraethyl orthosilicate (TEOS), 3-(trimethoxysilyl)propyl methacrylate (MAPTMS), and ZTP (denoted by TMZ) as a function of ZTP concentration to protect AA7075-T6 aluminum alloy. The presence of Zr in the sol-gel matrix improved the barrier property of AA7075-T6 in Harrison solution ((NH₄)₂SO₄ 3.5 g/L + NaCl 0.5 g/L) with a pronounced impedance modulus value superior to 8.10⁶ Ω.cm². Besides, the authors also studied and determined the different conditions and bath composition to find out the optimal conditions for obtaining protective sol-gel coating. The results indicated the optimal conditions for the sol-gel film with a molar ratio of Zr/Si 0.41, long ageing time (48 h hydrolysis), and curing at 100 °C for both

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electrochemical behavior and long-term immersion conditions [15]

However, the sol-gel coatings primarily provide barrier properties. When cracks or defects appeared on the sol-gel film, aggressive corrosive ions could easily attack the metallic substrates, producing their degradation after immersion in a corrosive medium for a long time [16]. To improve the corrosion resistance of the sol-gel coatings, environmental-friendly corrosion inhibitors, such as cerium salts, have been directly introduced [17–19] into the sol-gel matrix or indirectly [20–29] incorporated in nano-containers. Indirect incorporation of corrosion inhibitors using nano-containers or nano-carriers not only prevents direct interaction between inhibitors and the coating matrix but also enables controlled release of inhibitors and potentially responds to various stimuli such as pH value, temperature changes [16,30,31]. This is achieved through the slow release of the inhibitor into the defect sites. Although this method offers advantages over direct incorporation, it also presents some drawbacks, such as difficulty in controlling the quantity of inhibitors within the matrix and their dispersion. Conversely, direct incorporation of inhibitors into a sol-gel matrix provides distinct advantages compared to indirect methods involving nano-containers. This approach consists in an easy operation, controlling over loading concentrations, and ensuring homogeneous distribution [30]. Moreover, it also offers cost-effectiveness and scalability, making it a preferred choice for various applications

Numerous studies have reported that sol-gel coatings doped with cerium ions improved both the barrier properties and the film resistance in the protection of HDG steel [18,19,32–34]. The protective mechanism is explained that the cerium ions provided the self-healing effect for the sol-gel film by the formation of insoluble Ce (hydr)oxide at the defects and the damaged sites, thus hindering the cathodic reactions and thereby enhancing anti-corrosion properties of the coating for HDG steel [18,19]. Moreover, cerium ions could reduce the porosity of the film by blocking the defects and cracks in the coating on HDG steel substrates [19]. These results were in agreement with the result for zinc substrates given by Garcia-Heras et al. [32]. However, it is noticed that the concentration of cerium inhibitors plays a critical role in their effectiveness, with optimal concentrations typically falling in the range of 0.2 %–0.6 % (w/w) [32]. Excessive cerium salts may lead to defects, lattice deformation, and a reduced barrier performance in sol-gel layers as evidence by some authors [32,35,36]. It is important to note that the optimal cerium salt concentration can vary based on difference factors like the nature of the sol-gel matrix and the type of substrates [32,35–38]. Therefore, it could be impossible to obtain a general optimal cerium content

The objective of this work is to investigate the effect of cerium nitrate amount on the protective properties of a Si/Zr coating formulated with TEOS, MAPTMS, and ZTP precursors. The evolution of the sol-gel matrix in the presence of different cerium salt contents were monitored by rheological measurements and Fourier transform infrared (FTIR) spectroscopy. Subsequently, the corrosion protection performance of the undoped sol-gel film and the cerium salt-containing coatings were evaluated through electrochemical impedance spectroscopy and salt spray tests

2. Experimental method

2.1. Materials

2.1.1. Hot-dip galvanized steel substrate preparation

Hot-dip galvanized steel sheets (HDG steel) supplied by ArcelorMittal, Belgium were manufactured using a continuous process with a low content in aluminum. The sheets were submitted to immersion in the zinc melted bath and cooling to a skin passed treatment. The final roughness and thickness were of around 0.87 μm and 11 μm , respectively. Before applying the sol-gel film, the substrate with dimensions of 25 $\times$ 50 $\times$ 2.5 mm was firstly degreased with acetone, and then dipped in alkaline commercial solution (Gardoclean $\text{\textcircled{R}}$) at 50 $^{\circ}\text{C}$ for 30 s to

remove residual traces of oxide before experiments. After rinsing in deionized water, ethanol, the HDG steel sheets were quickly dried by compressed air.

2.1.2. Hybrid Zr/Si sol-gel-coating: formulation and deposition conditions

The employed sol precursors were tetraethyl orthosilicate (TEOS, VWR chemical, 100 %), 3-(trimethoxysilyl)propyl methacrylate (MAPTMS, Alfa Aesar, ≥ 97 %), zirconium(IV) propoxide, (ZTP: Zr (OPr)₄, 70 wt%, in 1-propanol, Aldrich), methacrylic acid (MAA, Merk, ≥ 99 %), isopropanol (IPA, Merk ≥ 99.7 %), and hydrochloric acid (HCl, 37 %, AppliChem). Cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O) was purchased from Aldrich (> 99 %). A hybrid sol-gel based on Zr/Si with the ratio of the main compositions and the experimental procedure proposed by Rodić et al. [14,17] was used and shown in Table 1 and Fig. 1, respectively. In this work, isopropanol (IPA) was added to the sol matrix as a solvent (added in the sol 2) to dilute the sol. Moreover, the final sol was fabricated by adding sol 1 to sol 2, which is the opposite of the reference procedure. For the specific experimental protocol, the sol 1 was prepared from a mixture of two different precursors: TEOS and MAPTMS in the acid medium by using HCl and stirred at 400 rpm for 2.5 h. The second one (sol 2) was composed of ZTP, MAA, and IPA and stirred for 30 min. After that, sol 1 was added drop by drop in sol 2 and then stirred at 400 rpm for 48 h to enhance the condensation process. The final sol is denoted as TMZ sol.

Different Ce(NO₃)₃ concentrations were then added into this TMZ sol to obtain the solutions containing 500, 650, 1000, 2000 and 5000 ppm Ce (III), which were stirred at 600 rpm for 10 min. Then, the speed was reduced to 400 rpm, and the solution was aged for 1 h [17]. Although we conducted testing and collected data for TMZ doped with 1000 ppm Ce, the results did not show a clear trend or significant change. Therefore, to focus on the most important and meaningful results, we decided not to include the results of the 1000 ppm Ce-doped sol-gel in this paper.

The doped and un-doped sol-gel films were applied on the HDG sheets by dip-coating with an immersion time of 2 min and a withdrawal speed of 500 mm/min. After deposition, the coated plates were dried in air for 5 min, then cured directly at 120 $^{\circ}\text{C}$ in the preheated oven for 1 h in order to achieve a faster curing process and efficient precursor cross-linking, ensuring effective film formation. The good cross-cut adhesion was checked on the various sol-gel coatings before ageing using the ASTM D3359–02 standard.

2.2. Fourier transform infrared spectroscopy (FTIR)

To better understand the chemical structure of the sol-gel coatings, the final solution droplets were dried in an oven at 120 $^{\circ}\text{C}$ and subsequently ground into a powdered form for FT-IR testing using an IRTracer-100 instrument (Shimadzu Co.), within the 600 to 4000 cm^{-1} wavenumber range.

2.3. Rheological measurement

The rheological behavior of sol-gel solutions with or without cerium salts was determined at room temperature (25 ± 0.1 $^{\circ}\text{C}$) using Anton Paar MCR 302 rheometer equipped with double-gap cylinders (ISO/WD 3219–2 standard). The flow curves of final sols were recorded in the controlled shear rate range of 0–200 s^{-1} . Subsequently, these final sols were left to age without stirring over time, and changes in viscosity were monitored as a function of ageing time. Each measurement was repeated twice for accuracy.

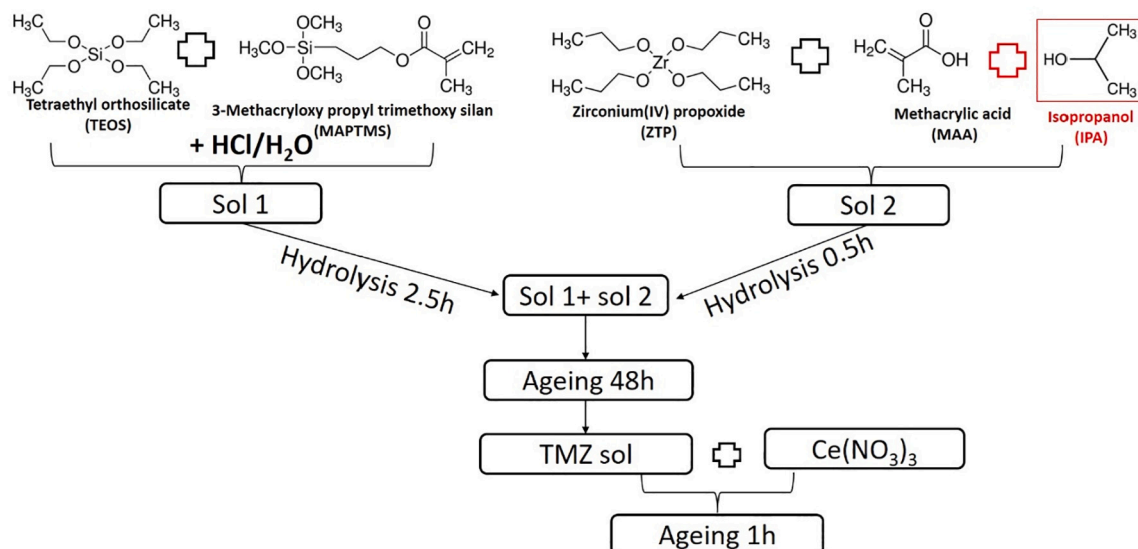
2.4. Field Emission scanning electron microscopy (FE-SEM/EDS)

The thickness of different sol-gel layers was analyzed by the FE-SEM technique, using Hitachi SU8020 coupled to an energy dispersive X-ray spectrometer analyzer (EDS). To prepare the samples for capturing cross-sectional SEM images, substrates coated with a Si/Zr sol-gel layer

Table 1

Chemical composition of the studied Si/Zr based sol-gel solutions.

Coating/molar ratio	TEOS	MAPTMS	H ₂ O	HCl	ZTP	MAA	IPA	Zr/Si	Ce(NO ₃) ₃
TMZ undoped [14]	0.18	1.0	2.075	0.001	0.12	0.12	0.4	0.1	–
TMZ + 500 ppm Ce (III)	0.18	1.0	2.075	0.001	0.12	0.12	0.4	0.1	500 ppm
TMZ + 650 ppm Ce (III)	0.18	1.0	2.075	0.001	0.12	0.12	0.4	0.1	650 ppm
TMZ + 2000 ppm Ce (III)	0.18	1.0	2.075	0.001	0.12	0.12	0.4	0.1	2000 ppm
TMZ + 5000 ppm Ce (III)	0.18	1.0	2.075	0.001	0.12	0.12	0.4	0.1	5000 ppm

**Fig. 1.** Experimental procedure for the preparation of Si/Zr-based sol-gel [14,17].

were initially cut into 1.5×2.5 cm dimensions using compressed air shears. The cross-sections of all samples were embedded in epoxy resin (Mecaprex) and polished with SiC abrasive paper ranging from grades 100 to 4000. Subsequently, they underwent further polishing using diamond paste (grade 3 and $1 \mu\text{m}$), were rinsed with distilled water and ethanol, and finally dried rapidly with compressed air. The chemical composition of corrosion product on the tested surface after two weeks of EIS measurement was detected by EDS analysis (using a SDD ThermoScientific detector). A 20 kV acceleration beam tension was applied.

2.5. Electrochemical measurements

The barrier property of sol-gel based on Zr/Si precursors and modified sol-gel films deposited on HDG steel were conducted by employing a Solartron Analytical ModuLab potentiostat. The electrolyte solution and the test area were 0.1 M NaCl and 1 cm^2 , respectively. A classical three electrodes system was used, with the different studied pretreated and coated HDG steel substrate (1 cm^2) as the working electrode, a Saturated Calomel Electrode (SCE) as the reference electrode, a platinum as the counter-electrode. For EIS tests, the experiments were measured at open circuit potential (OCP) and room temperature. A frequency range of 100 kHz to 10 mHz was scanned with a perturbation amplitude of 20 mV for un-doped and doped sol-gel Zr/Si films and 10 mV for HDG steel bare substrate. Each test was measured at least twice to confirm the reproducibility.

2.6. Salt spray test

The self-healing property and corrosion performance of hybrid sol-gel film coated on HDG steel were evaluated in a neutral salt spray test followed by ASTM B117 standard, using a 5 % NaCl solution. Before exposure, the back and the edges of the substrates were covered by adhesive tape. A scratch shape “x” of 1 cm long that reached the metallic

substrate was made on the sol-gel coating.

3. Results and discussion

3.1. FTIR spectroscopy

Fig. 2 presented the IR spectra of both un-doped TMZ as well as the Ce (III)-modified TMZ coatings. Moreover, the spectrum of TMZ + 5000 ppm Ce (III) was also depicted in the Fig. 2 (on the right side) to enhance the visualization and clarify the chemical structure of sol-gel network. The characteristic bands were listed in the Table 2. It is important to note that identical bands were observed in the spectra of both neat TMZ and TMZ doped with varying Ce (III) contents, suggesting that the incorporation of Ce (III) in the matrix sol solution did not alter the structure of the sol-gel network. However, some difference could be detected.

Upon examining the spectra, a broad band at the range $3600\text{--}3200 \text{ cm}^{-1}$ is attributed to the OH stretching vibration of silanols and adsorbed water molecules [14,37,39]. Additionally, C – H asymmetric and symmetric stretching bands at 2954 and 2893 cm^{-1} correspond to the C – H bonds of MAPTMS and MAA [37,39,40]. The prominent absorption band at $1200\text{--}1000 \text{ cm}^{-1}$ corresponds to the siloxane Si – O – Si group. Interestingly, distinct siloxane structures were identified in this wave number range. The band at 1010 cm^{-1} and a shoulder at 1075 cm^{-1} suggest the existence of both ladder-like and cage-like structure of Si – O – Si network, respectively [37,39,40]. As demonstrated in the literature [41,42], the ladder-like type is a result of the bonding between various cyclic species, while the cage-like structure probably generated by cross-condensation with siloxane bonds or organic linkers, thus creating a denser network [37,40,41,43], indicative of the high barrier properties of TMZ coating. Furthermore, bands are observed at around 1160 and 814 cm^{-1} corresponding to Si – O – Zr due to the hetero-condensation [14,40,44], demonstrating the reaction between sol 1 and sol 2. These

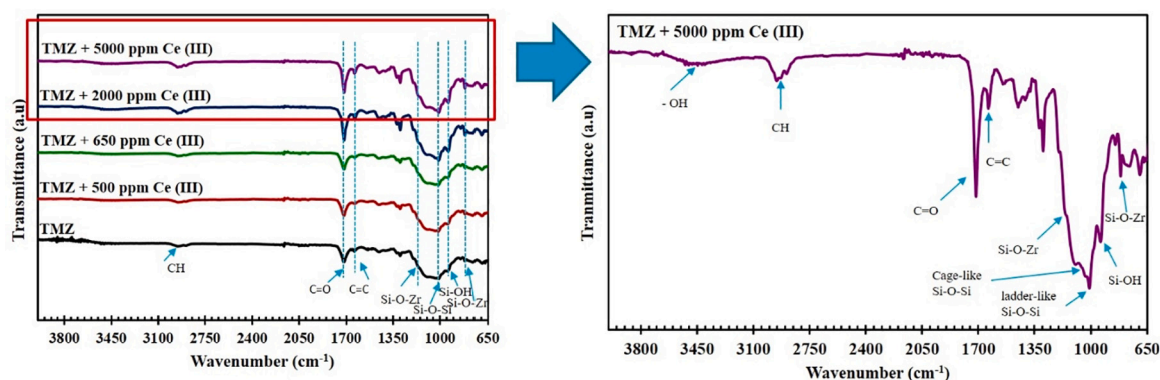


Fig. 2. FTIR spectra of un-doped TMZ and TMZ doped with various Ce (III) contents.

Table 2

The list of collected bands from the FTIR spectra.

Signal	Wavenumber (cm ⁻¹)
Si - O - Si (ladder-like)	1010
Si - O - Si (cage-like)	1075
Si - O - Zr	1160, 814
Si - OH	950
C=C	1633
C=O	1716
OH	3600–3200
C - H	2954, 2893

observations indicate that the zirconium precursor has been integrated into the silicate network, thereby establishing a uniform co-hybrid system.

It is highlighted that the intensity of this siloxane band (1200–1000 cm⁻¹) varies with the Ce (III) contents. For the sol-gel doped with lower Ce (III) concentrations (500 and 650 ppm), the intensity of this absorption band is comparable to the blank sol-gel. In contrast, at high Ce (III) concentration (above 650 ppm), the bands become more pronounced, reflecting improved reticulation due to accelerated hydrolysis and condensation reactions [35,36,39], as already mentioned in the literature [37,39]. This increase in intensity is associated with higher signals at 1633 cm⁻¹ (C=C group) and 1716 cm⁻¹ (C=O group), originating from the presence of MAA and MAPTMS.

3.2. Rheological behavior of un-doped and doped sol-gel

Fig. 3 illustrates the flow curves of both un-doped sol-gel and sol-gel doped with different concentrations of Ce (III) after 49 h of ageing, as well as the viscosity changes of sol-gel solutions overtime. The analysis of the flow curves indicates that these sol solutions exhibit Newtonian behavior, characterized by constant viscosity values at different shear rates (Fig. 3 (a)). Additionally, the non-doped sol-gel and sol-gel doped with 500 and 650 ppm Ce (III) exhibited the comparable viscosity (around 11.5–11.7 mPa.s) after 49 h of ageing. The incorporation of Ce (III) into the sol-gel solution resulted in slight changes in viscosity, with higher Ce (III) concentrations corresponding to greater viscosity (ranging from 11.7 to 12.3 mPa.s), indicating the catalytic effect of Ce (III) [35,36,39,45], consisting with the FTIR observation. Regarding the Fig. 3 (b), the viscosity slightly increased with longer ageing times. After 72 h of ageing, the viscosity of the neat sol-gel and sol-gel doped with <2000 ppm Ce (III) was quite identical, while the sol-gel containing the highest Ce (III) level showed the most pronounced increase. After 168 h, the reference sol-gel solution displayed a negligible increase in viscosity, whereas the sol-gel doped with Ce (III) solutions exhibited a higher increase in viscosity, particularly in the presence of the highest Ce (III) amount. This increase overtime can be attributed to the transition from the sol state to the gel state and the progressive formation of a siloxane network (Si - O - Si and Si - O - Zr) due to condensation reactions [46].

This slight increase in viscosity corresponded to a minor increase in the thickness of the coatings [23,32,39,47,48]. As depicted in Fig. 4, SEM images of the cross-sections of non-doped and sol-gel layers doped with low cerium content on HDG steel revealed the comparable thicknesses (12.2 and 12.4 μm). However, higher Ce (III) content (2000 ppm

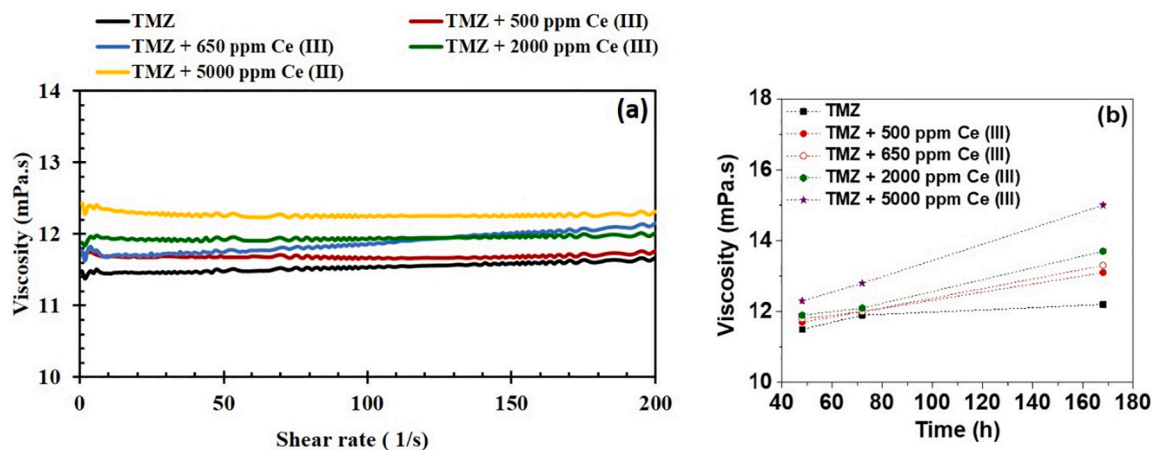


Fig. 3. Flow curves of un-doped sol-gel and sol-gel doped with various Ce (III) contents after 49 h of ageing (a) and Viscosity of un-doped sol-gel and sol-gel doped with various Ce (III) contents versus ageing time (b).

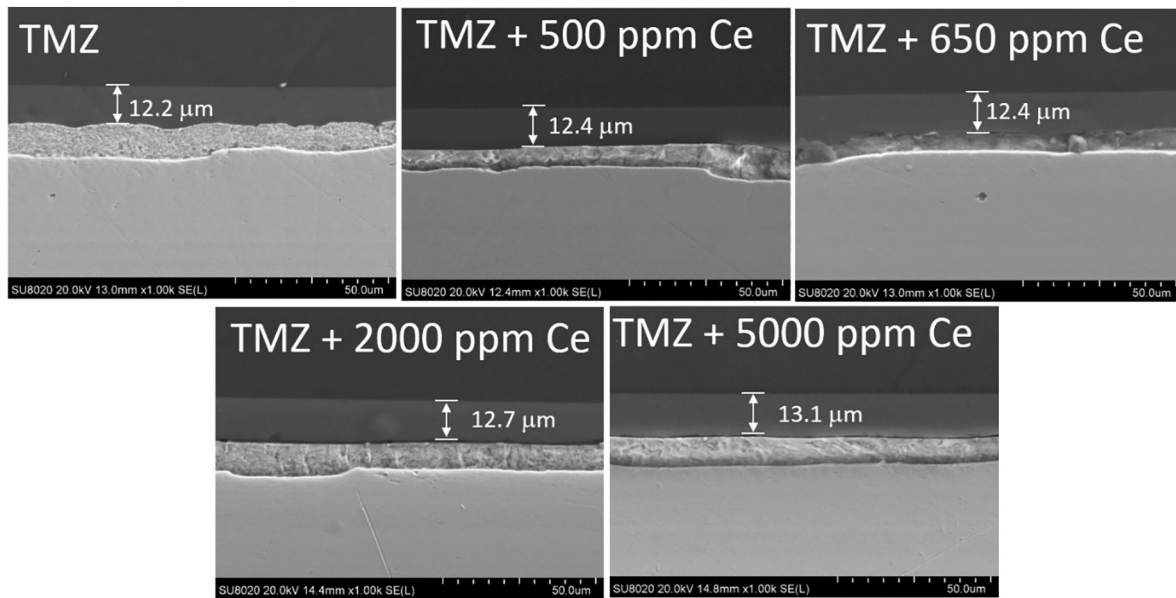


Fig. 4. SEM cross-section images of un-doped sol-gel and sol-gel doped with various Ce (III) contents.

and 5000 ppm) results in an insignificantly raise of film thickness, measuring 12.7 μm and 13.1 μm , respectively. This slight thickness increase was mentioned in the literature [23,32,39,47,48].

The slight difference in viscosity and coating thickness of the sol-gel layer suggests that cerium salt catalyzes the hydrolysis and condensation reactions in the solution [17,19,32,35,36,39,47]. Garcia-Heras et al. [32] proposed the replacement of hydrogen ions by cerium ions in the silanol groups ($\equiv\text{Si-OH}$). These modified groups ($\equiv\text{Si-O-Ce}$) react among them, and Ce (III) participated in the formation of the surface film. It was also assumed that these Ce (III) ions improve xerogel densification, leading to thicker coatings. Meanwhile, Montemor et al. [47] indicated that the presence of Ce (III) ions promoted the hydrolysis reactions, setting to increase the number of reactive silanol groups. As a result, more siloxane bonds are formed, which explains the slight increase in the thickness of cerium-doped coating. Moreover, the authors presented that these cerium ions could contribute to the reduced porosity and more organized structures thanks to the fill of defects generated during film assembly. The accelerated effect of Ce (IV) in the formation of silanol group and the polymerization was also revealed by Suegama et al. [39].

3.3. Electrochemical behavior of modified sol-gel Si/Zr coating

The Bode diagrams of HDG steel coated with TMZ coating versus immersion time in 0.1 M NaCl was showed in Fig. 5. The Bode diagrams

of bare HDG steel after 6 h immersion in 0.1 M NaCl are illustrated as the reference. For bare HDG steel, a time constant was observed at medium frequency domain which is related to the charge transfer [49,50]. The impedance modulus value at low frequency ($|Z|_{10\text{ mHz}}$) is around $8 \times 10^2 \Omega\cdot\text{cm}^2$. However, the corrosion behavior of HDG steel significantly changed when the bare substrate was covered by the TMZ layer, due to the barrier properties of the film. In phase diagram, the time constant in the high-frequency region could be attributed to the presence of a homogenous and dense sol-gel film with a high phase angle close to -85° , indicating the high capacity behavior of the coatings [15,19,20]. In the low-frequency area, a new time-constant starts to develop in a semi-loop form with a gradual increase in the phase angle over extended immersion times. This development may be related to the beginning of the corrosion process at the coating/metal interface [15,19]. Furthermore, the impedance modulus value at low frequency was remarkable and kept stable after 24 h of immersion, measuring around $10^7 \Omega\cdot\text{cm}^2$. It experienced a slight decrease to $5 \times 10^6 \Omega\cdot\text{cm}^2$ after 72 h of exposure but remained consistent up to 168 h (1 weeks) of immersion. Then, the impedance modulus value decreased by one order of magnitude after 336 h of testing, aligning with a gradual decrease in the capacity of the sol-gel coating. This decrease was characterized by the shift of the phase angle toward higher frequencies with increasing immersion time, suggesting a regular evolution of the corrosion process through the coating's pores [15,51].

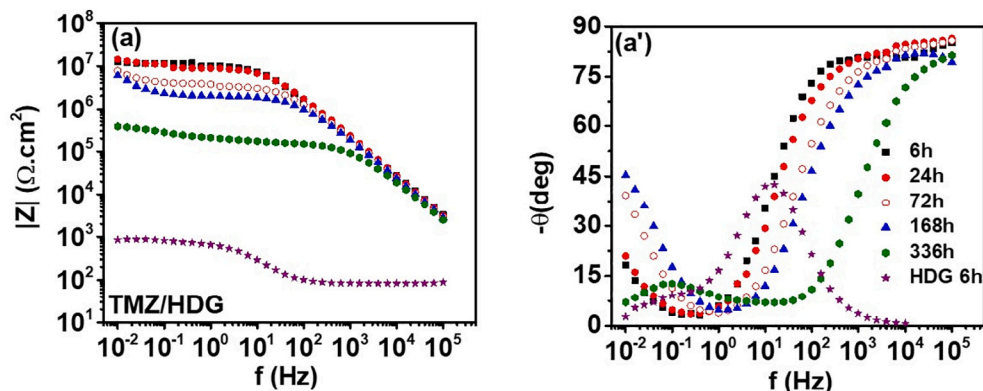


Fig. 5. Bode diagrams of HDG coated with un-doped sol-gel film versus immersion time in 0.1 M NaCl solution.

Fig. 6 presented the Bode diagrams for HDG-coated by sol-gel films doped with varying concentrations of Ce (III) during immersion in 0.1 M NaCl. The doped films are labeled as TMZ + 500 ppm Ce (III) (Fig. 6 (a, a')), TMZ + 650 ppm Ce (III) (Fig. 6 (b, b')), TMZ + 2000 ppm Ce (III) (Fig. 6 (c, c')), and TMZ + 5000 ppm Ce (III) (Fig. 6 (d, d')). Doping the film with cerium salt induced changes in the electrochemical behavior of the modified sol-gel film compared to the reference TMZ film and the

HDG steel substrate. Notably, the Bode diagrams reveal that the barrier properties of the sol-gel coatings are influenced by the concentration of Ce (III), and this effect becomes more pronounced with extended immersion times.

Initially, all four coatings exhibited a single time constant with a high phase angle (approaching -85°) extending from 10^5 Hz to 1 Hz, signifying exceptional capacitance properties. Additionally, the total

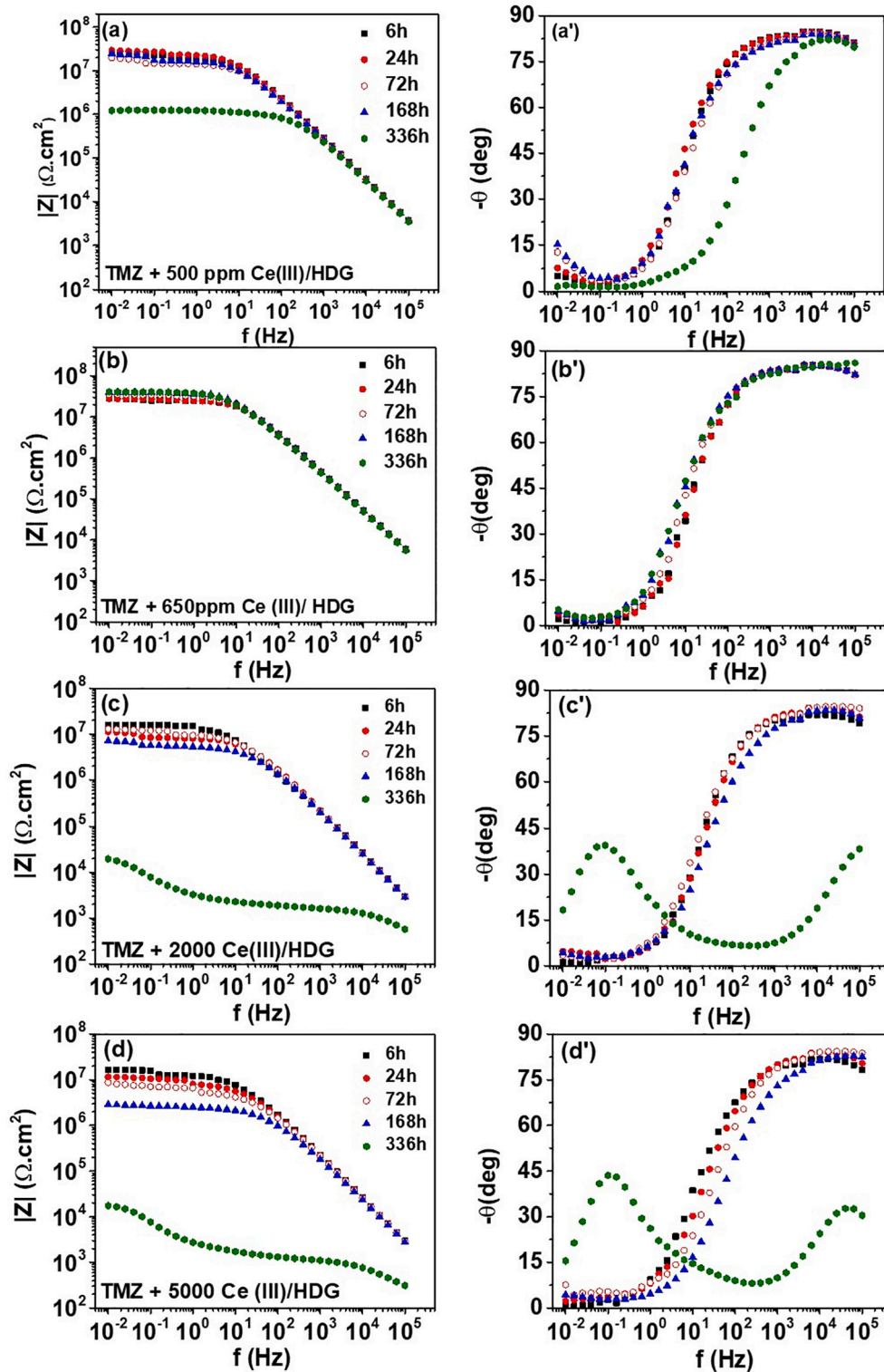


Fig. 6. Bode diagrams of HDG coated by sol-gel layers doped with 500 ppm Ce (III) (a, a'), 650 ppm Ce(III) (b, b'), 2000 ppm Ce (III) (c, c'), and 5000 ppm Ce (III) (d, d') versus immersion time in 0.1 M NaCl solution.

impedance values of these coatings were consistently 2 to 3 times higher than that of the neat TMZ layer, at about 2 or $3 \times 10^7 \Omega \cdot \text{cm}^2$. These properties remained stable up to 168 h of exposure (except TMZ + 5000 ppm Ce (III), which kept stable up to 72 h), particularly for the TMZ coatings doped with the two lowest Ce (III) concentrations.

The evolution of the phase angle in all samples, except TMZ + 650 ppm Ce (III), displayed a similar tendency after 336 h of immersion (Fig. 6 (a, a'), (c, c'), (d, d')). In the case of TMZ + 500 ppm Ce (III), although the phase angle shifted to a lower frequency range, it retained only one time constant, with an impedance modulus value around $10^6 \Omega \cdot \text{cm}^2$, still showing effective barrier properties. However, for the TMZ + 2000 ppm Ce (III) and TMZ + 5000 ppm Ce (III) films, the phase angle at high frequencies substantially decreased (lower than -40°), accompanied by a significant reduction in impedance modulus at low frequencies, demonstrating a strong deterioration in the corrosion protection of the sol-gel films. Furthermore, a second-time constant appeared in the low-frequency region, likely associated with different processes: a surface oxide or/and the corrosion process at the HDG/TMZ coating interface [19], which was supported by images obtained (Fig. 9) under EIS experiment after 336 h. While the TMZ + 650 ppm Ce (III) coating demonstrated remarkable characteristics throughout the immersion period. It consistently presented a single time constant at high frequencies with an unaltered phase angle, indicating its persistent capacitance and the enduring integrity of the Si/Zr coating. At medium-low frequencies (ranging from 10 Hz to 10 mHz), a stable plateau formed, which remained constant during the immersion period. This plateau was attributed to the corrosion protection provided by the coated HDG steel substrate when exposed to the corrosive medium [17]. Furthermore, the shape of the Bode diagram does not change after two weeks of immersion, and the impedance tended to progressively increase during the experiment (from 2.6×10^7 to $4 \times 10^7 \Omega \cdot \text{cm}^2$) and persisted in this high value up to two weeks of exposure. These results showed that the sol-gel doped with 650 ppm Ce (III) provided a high protective film. Therefore, the corrosion could not develop during immersion time.

Based on the Bode diagrams, the electrochemical behavior of sol-gel systems (doped and un-doped cerium) was fitted by two different Equivalent electric circuit (EEC) by using ZSim Win 3.50 (Fig. 7 (a, b)). In this simulation the constant phase element Q was used instead of ideal capacitance of the coating. Fig. 7 (a) modeled for TMZ, and for TMZ + 2000 ppm Ce(III) and TMZ +5000 ppm Ce (III) (after 336 h of immersion), which consisted of film Q_{coat} , film resistance R_{coat} , and the corrosion process ($Q_{\text{oxide}} - R_{\text{oxide}}$). It is important to highlight that the second time constant part is not distinctly identified for the sol-gel coating doped Ce(III), resulting in a high standard deviation. Consequently, our approach was focus on the first time constant, operational within the frequency domain of 10^5 to 1 Hz. After 336 h of exposure, TMZ + 2000 ppm and TMZ + 5000 ppm Ce(III) exhibited diminished barrier protection with significantly reduced phase angles at the first-time constant, resulting in a low R_{coat} . Consequently, we did not fit these films in the 336 h of test. Meanwhile, for the TMZ + 500 ppm Ce (III), TMZ + 650 ppm Ce (III) and the TMZ doped with two highest Ce (III) contents (within 168 h of immersion) (Fig. 7 (b)), only one time

constant observed at high frequency was fitted for the $Q_{\text{coat}} - R_{\text{coat}}$. From the fitting data, n values are >0.8 and the total impedance is much higher than the resistance of electrolyte solution (R_s). Hence, the capacitance of a film (C_{coat}) was calculated from Q_{coat} and n values by Brug's relationship as Eq. (1) [52]. The fitting results are given in Table 3. The quality of the impedance fit was characterized with errors in each EEC parameter values of 1–5 % [52].

$$C = Q^{1/n} \cdot R_s^{(1-n)/n} \quad (1)$$

In which C is the capacitance of a film, Q is the values of Q_{coat} , R_s is resistance of electrolyte solution and n is exponent values.

Fig. 8 demonstrated the evolution of electrochemical elements of the films versus immersion time in 0.1 M NaCl. As can be seen, the R_{coat} and C_{coat} of all system depended on the cerium salt contents and the immersion time. The sol-gel TMZ + 650 ppm Ce (III) showed the highest R_{coat} and the lowest C_{coat} values, followed by TMZ + 500 ppm Ce (III), TMZ and TMZ doped with the highest Ce (III) contents.

Regarding the Fig. 8 (a), for the non-doped coating and TMZ doped with 2000 and 5000 ppm Ce (III), the R_{coat} tended to decrease nearly one order magnitude, from $10^7 \Omega \cdot \text{cm}^2$ to $10^6 \Omega \cdot \text{cm}^2$ during 168 h of immersion time, indicating the formation of defects or pinholes in the layer, thus developing the corrosion process [17,51]. These results aligned to the stable C_{coat} presented in Fig. 8 (b).

Concerning the TMZ + 500 ppm Ce (III) and TMZ + 650 ppm Ce (III) film, incorporating low Ce (III) contents improved the barrier properties of the coatings. At the initial 72 h of immersion, all of two coatings presented the comparable R_{coat} value. However, in prolong time, the R_{coat} behavior changes. For the TMZ + 500 ppm Ce (III), the R_{coat} decreased over time up to 336 h of exposure but was still higher than

Table 3

Electrical parameters of the non-doped and doped with Ce (III) sol-gel films coated on HDG steel.

		6 h	24 h	72 h	168 h	336 h
TMZ un-doped	R_{coat} (M Ω , cm^2)	28.40	8.57	3.34	1.93	0.16
	C (nF/ cm^2)	0.37	0.35	0.34	0.34	0.33
	n_{coat}	0.94	0.92	0.91	0.89	0.86
TMZ + 500 ppm Ce (III)	R_{coat} (M Ω , cm^2)	31.0	32.27	20.90	15.05	1.09
	C (nF/ cm^2)	0.29	0.29	0.31	0.31	0.29
	n_{coat}	0.94	0.93	0.93	0.93	0.92
TMZ + 650 ppm Ce (III)	R_{coat} (M Ω , cm^2)	25.90	25.30	33.30	36.45	36.90
	C (nF/ cm^2)	0.19	0.20	0.20	0.2	0.20
	n_{coat}	0.93	0.93	0.93	0.93	0.93
TMZ + 2000 ppm Ce (III)	R_{coat} (M Ω , cm^2)	13.60	7.70	8.0	4.95	–
	C (nF/ cm^2)	0.39	0.39	0.36	0.37	–
	n_{coat}	0.93	0.93	0.91	0.88	–
TMZ + 5000 ppm Ce (III)	R_{coat} (M Ω , cm^2)	11.84	6.29	3.90	2.10	–
	C (nF/ cm^2)	0.35	0.37	0.37	0.38	–
	n_{coat}	0.92	0.92	0.91	0.88	–

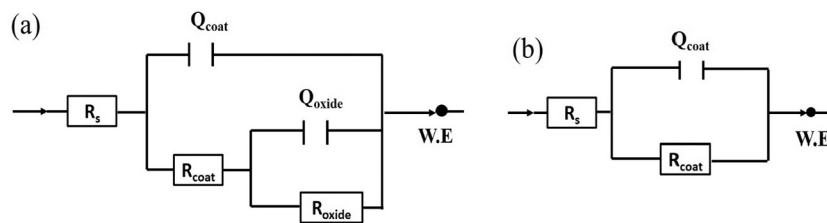


Fig. 7. Equivalent electrical circuit (EEC) used to fit the EIS experimental data. (a) model a for TMZ layer and TMZ doped with 2000 and 5000 ppm Ce (III) (after 336 h), and (b) model b for TMZ + 500 ppm Ce(III), TMZ + 650 ppm Ce (III) and TMZ doped with 2000, 5000 ppm Ce (III) (within 168 h): electrolyte resistance (R_s), coating capacitance (Q_{coat}), sol-gel film resistance (R_{coat}), oxide film capacitance (Q_{oxide}) and oxide film resistance (R_{oxide}).

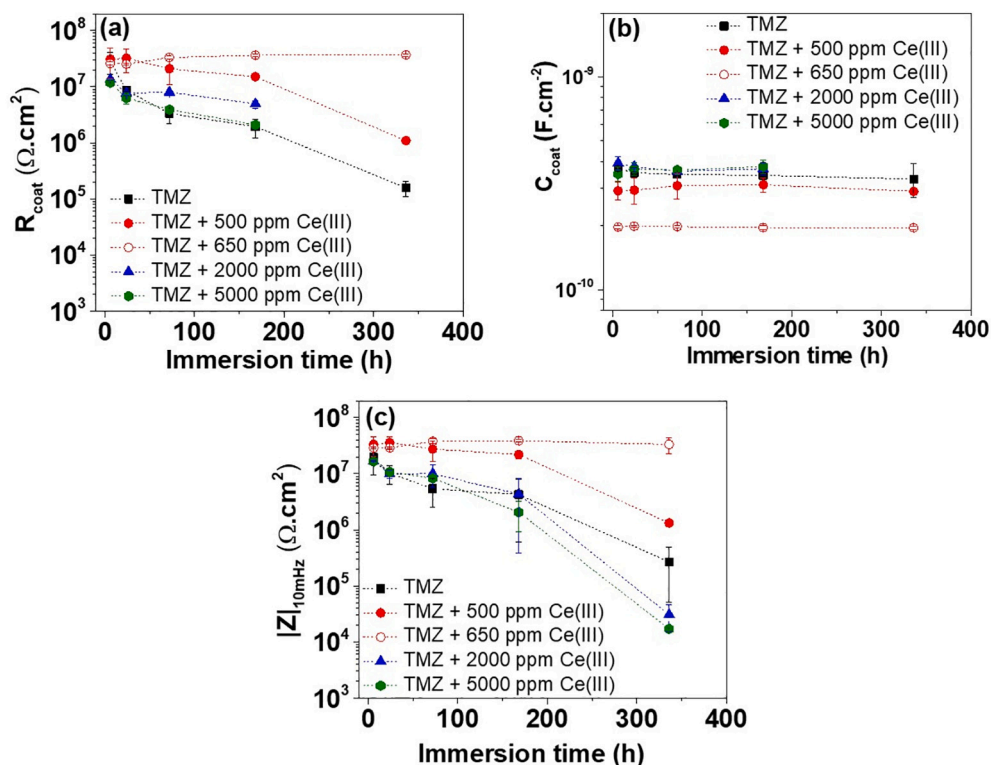


Fig. 8. Evolution of electrochemical parameters of un-doped sol-gel and sol-gel doped with different Ce (III) contents versus immersion time in 0.1 M NaCl solution: (a) R_{coat} , (b) C_{coat} , (c) Z 10mHz.

that of blank TMZ. Additionally, the film capacitance (Fig. 8 (b)) slightly increased during experiment test, probably indicating to the ingress of water or aggressive species into the film [20,38]. Meanwhile, TMZ + 650 ppm Ce (III) displayed remarkable stability and the most prominent R_{coat} values (Fig. 8 (a)) compared to four other films for prolonged immersion time, indicating a superior corrosion protection. It remained relatively high and unchanged throughout the testing period, suggesting a film without defects and preventing the penetration of water or corrosive species into the layer. Moreover, Fig. 8 (b) revealed that the incorporation of 650 ppm cerium nitrate in the sol-gel film leads to lowest film capacitance at around 2×10^{-10} F/cm² accompanied by a high value of n_{coat} (around 0.92–0.93) (Table 3), suggesting the presence of a compact and dense layer [17]. The observed evolution of film capacitance and resistance suggested good barrier property and enhanced the coating durability up to two weeks of immersion in aggressive environment. This observation can be related to higher Zn-O-Si/Zr bond density across the film [17], and a better reticulation of the sol-gel layer [39], leading to the formation a denser coating.

Regarding the $|Z|_{10mHz}$ evolution diagram (Fig. 8 (c)), it is evident that the presence of cerium in the coatings initially did not affect the maximum value of the impedance (at around 10^7 $\Omega \cdot cm^2$) at 10 mHz of the protective systems. However, it significantly influenced the stability

in a longer immersion time in the aggressive medium. The module $|Z|_{10mHz}$ of non-doped and doped with high Ce (III) levels (2000 and 5000 ppm) TMZ film was identical and gradually decreased after 168 h of immersion, from 10^7 $\Omega \cdot cm^2$ to 4×10^6 $\Omega \cdot cm^2$. However, after 336 h of immersion, the TMZ doped with high Ce (III) amounts dropped to approximately 4.5×10^4 $\Omega \cdot cm^2$, performing a poorer corrosion protection than neat TMZ (1.5×10^5 $\Omega \cdot cm^2$). Moreover, this value may primarily be attributed by the oxide layer formed in the sol-gel/metal interface. Indeed, after 336 h of EIS measurement, the tested surface of TMZ + 2000 ppm Ce (III) and TMZ + 5000 ppm Ce (III) presented some white and yellowish products, respectively (Fig. 9).

The TMZ doped with low Ce (III) concentrations (500 ppm and 650 ppm) showed the improvement of $|Z|_{10mHz}$ values compared to the reference TMZ coating. Concerning the TMZ + 500 ppm Ce (III), the $|Z|_{10mHz}$ slowly decreased within 168 h of immersion, then this value decreased one order of magnitude from 2×10^7 $\Omega \cdot cm^2$ to 1.3×10^6 $\Omega \cdot cm^2$ after 336 h of the test. Meanwhile, the sol-gel doped with 650 ppm Ce (III) presented the most significant impedance modulus at 10 mHz, which increased slightly up to the end of the measurement (about 4×10^7 $\Omega \cdot cm^2$), confirming a stable and long-lasting protective film without defects.

The EIS results reveal that the protective properties of the sol-gel film

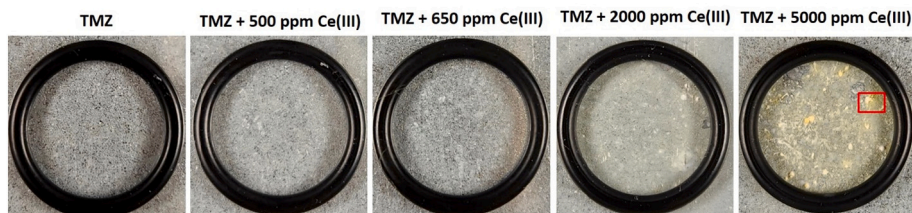


Fig. 9. HDG-coated with sol-gel coatings after 2 weeks under 0.1 M NaCl solution analyzed by EIS measurements. The red rectangle indicated in the photo of TMZ + 5000 ppm Ce (III) correspond to the area analyzed SEM/EDS (Fig. 10).

depend on the amount of Ce (III) doping. The incorporation of 650 ppm Ce (III) provides the best effectiveness, resulting in a denser and more compact film. The coatings containing 500 ppm Ce (III) offer superior and more stable protection over 336 h of immersion compared to TMZ. Meanwhile, the coatings with the two highest cerium concentrations deteriorated more rapidly and exhibited poorer corrosion protection efficiency in the advanced test compared to the other layers. These findings align with the images obtained after 336 h of EIS measurement, as depicted in Fig. 9. As evident, no sign of corrosion appeared on the tested surface of TMZ and TMZ doped with 500 and with 650 ppm of Ce (III) layers after 336 h of EIS measurement, indicating less evidence of sol-gel coating degradation. Conversely, the surface of TMZ doped with 2000 and 5000 ppm Ce (III) displayed the presence of white and yellow precipitation products, respectively. The sample containing TMZ with 5000 ppm of Ce(III) exhibited the highest level of corrosion products on the surface. This sample was chosen for SEM/EDS analysis, focusing on the area enclosed by the red rectangle, and is presented in Fig. 10. As can be observed, SEM image (Fig. 10 (a)) showed that the sol-gel layer was peeled off from the bare substrate, assigning to the fast degradation under EIS measure after two weeks. Furthermore, EDS analysis (Fig. 10 (b)) detected 1 wt% cerium in the precipitation products (in the entire red rectangle area), confirming the presence of cerium within the sol-gel matrix, along with the release of cerium from the sol-gel layer during the immersion time. Moreover, this yellow precipitation product may be associated with the mixture of the Ce^{3+}/Ce^{4+} [53–55].

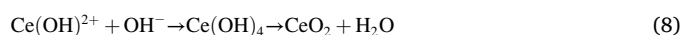
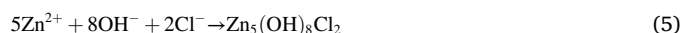
3.4. Performance in salt spray test

Fig. 11 presents the performance of sol-gel coatings versus exposure time to the salt spray test and HDG steel bare substrate using as a reference. The dashed black rectangles indicate the delamination areas. At the initial 24 h of exposure, the scratch was not observed on the surface of the HDG steel bare substrate due to the appearance of white rust, which covered the entire surface of the HDG steel. This white corrosion product is a result of the sacrificial dissolution of zinc [22,56]. Over time, the amount of this product increased, and after 72 h of the experiment, no red rust was observed, indicating that the corrosion process had not reached the steel.

Meanwhile, all coatings presented a protective property after 24 h of exposure by appearing with white/yellow corrosion products (due to the zinc coating sacrificial dissolution and the subsequent formation of zinc hydr(oxide)/simonkolleite ($Zn_5(OH)_8Cl_2$) (for TMZ) and also cerium hydr(oxide) (for TMZ containing Ce (III)) [22,56] along the scratch site. Notably, some differences were observed in the coatings containing the highest cerium levels, presenting the yellow product (more noticeable yellow colour and the broader yellow region over time) around the scratch sites in contrast to the other coatings. These yellowish products

were also observed after two weeks of EIS measurement, as mentioned in Section 3.3, indicating the mixture of Ce^{3+}/Ce^{4+} [18,53–55]. This observation confirmed the presence of cerium species in the sol-gel layer and the release of cerium from sol-gel layer into the defects, leading to the formation of cerium hydroxide on the scratch areas. Indeed, this result is in agreement with the research by Su et al. [18]. The authors reported the presence of cerium hydr(oxide) on the scratch, showing a mix-valance state that included Ce (III) and Ce (IV) in the sol-gel layer. However, within the scratches, Ce (III) was predominantly observed.

The formation of the corrosion products on the scratch areas could be described as following reactions:



where Ce^{3+} in reaction (6) originated from the Ce^{3+} within the sol-gel coating.

After 72 h of exposure, delamination was observed in all coatings. However, the beneficial effects of incorporating Ce (III) into the sol-gel matrix became evident. Firstly, no differences were observed in the non-scratch areas of all four coatings doped with various cerium concentrations, indicating an admirable barrier property. Notably, The TMZ doped with varying Ce (III) contents displayed less delamination compared to unmodified TMZ layer. Specifically, the coatings with highest Ce (III) concentrations and those with 500 ppm Ce (III) displayed clear delamination around the scratch area, highlighted in the dashed black rectangle. In contrast, TMZ + 650 ppm Ce (III) showed minor delamination along the scratch site upon careful visual inspection. This coating demonstrated the most effective resistance to delamination, being consistent with the findings from the EIS analysis.

4. Discussion

The addition of various Ce (III) concentrations in the sol-gel aimed to enhance overall corrosion protection and provide active protection to the sol-gel TMZ coating. In the sol-gel layer, Ce (III) can act as a corrosion inhibitor. Upon the defects appear, Ce (III) is released in those

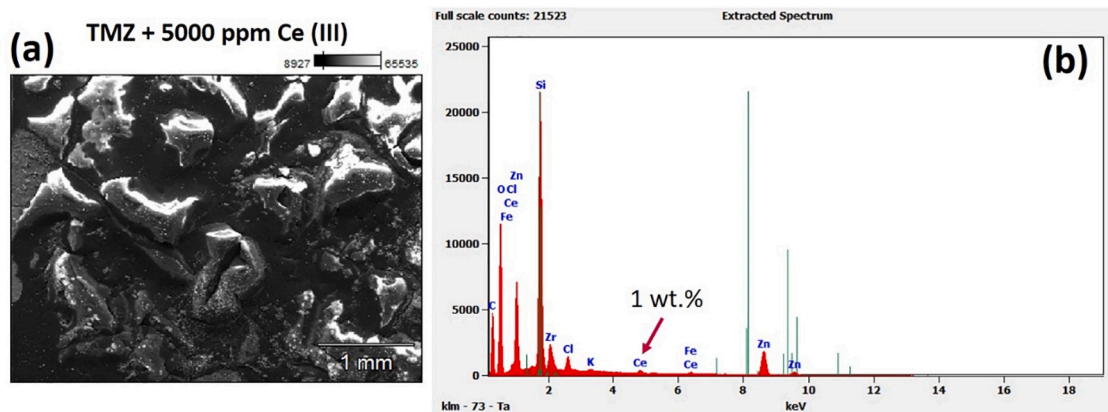


Fig. 10. SEM image and EDS pattern of TMZ + 5000 ppm Ce (III) of the red rectangle indicated in Fig. 9 after 2 weeks under 0.1 NaCl solution analyzed by EIS measurement.

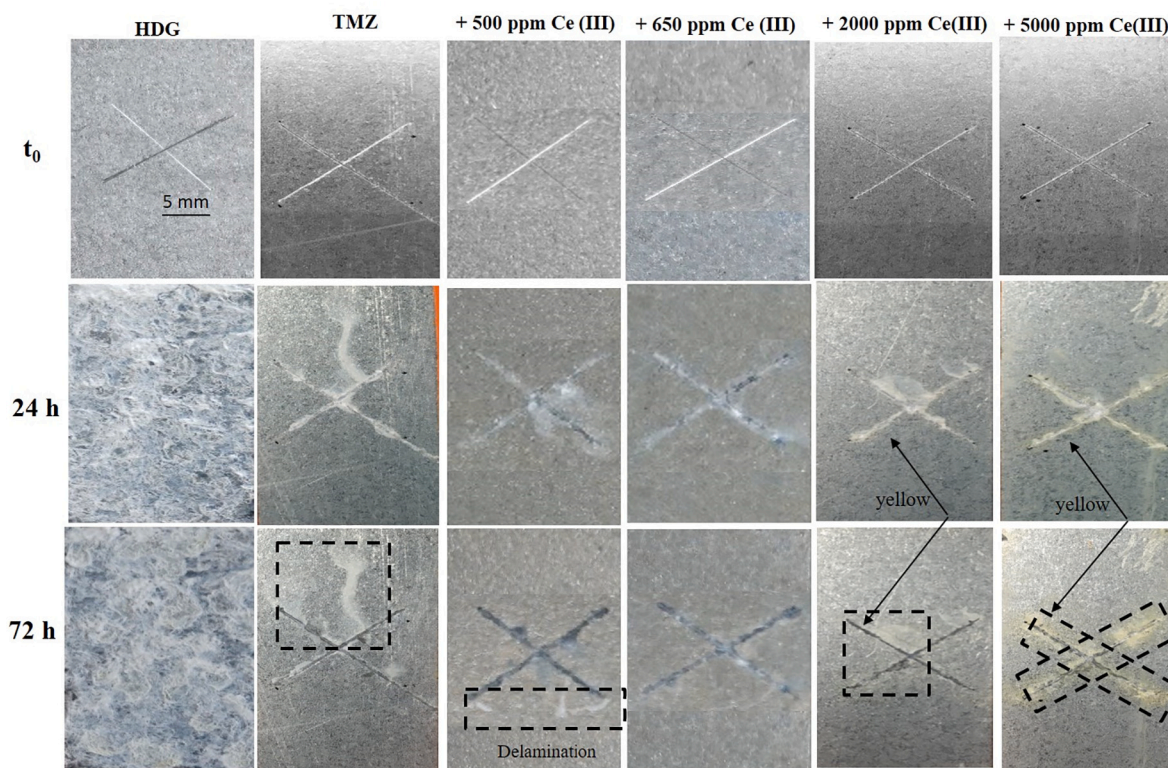


Fig. 11. Photographs of HDG steel bare substrate, un-doped sol-gel film and sol-gel films doped with various Ce (III) contents versus salt spray exposure time. The dashed black rectangles indicate the delamination areas.

areas, forming an insoluble cerium hydr(oxide) product that blocks cathodic sites and reduces the corrosion rate, offering active protective properties [17–19]. However, in some cases, Ce (III) ions may play an indirect role as a catalyst [17,35,36,39,45,46].

In our study, EIS results indicated an improvement in the barrier properties when low concentrations of Ce (III) (500 and 650 ppm) were added. Conversely, at higher Ce (III) contents (2000 ppm and 5000 ppm), the TMZ layers showed a reduction in barrier effect in the long term. Besides, salt spray results showed that the incorporation of 650 ppm Ce (III) exhibited the best protective performance. With lower or higher Ce (III) contents, the sol-gel coatings displayed extensive delamination areas.

In fact, due to the formulation of this sol-gel coating provides a dense film and good barrier properties, thus at low Ce (III) concentrations, Ce^{3+} could not be released from the layer when defects appear. This insufficient concentration of free Ce^{3+} prevented the effective initiation of a self-healing process. The development of this excellent barrier coating is a critical initial step in preparing for the growth of the multilayer on top.

Regarding the high Ce (III) contents, the release of Ce^{3+} within the coating was noticeable due to the appearance of the yellow precipitation products both after 336 h of EIS measurements (Fig. 9) and during the accelerated test with the presence of an artificial defect (Fig. 11) after 72 h of exposure. However, these precipitation products did not offer additional protection in long-term. The substantial deterioration of the sol-gel film, as evidenced by the EIS test during prolonged immersion time, can be suppressed by two main factors:

- Firstly, Ce (III) promotes hydrolysis and condensation reactions (as supported by a higher viscosity (Fig. 3) and a more intense siloxane band (Fig. 2) as detailed in Sections 3.1 and 3.2, respectively) [17,35,39]. However, the larger atomic radius of Ce (0.1978 nm) compared to Si (0.1068 nm) may destabilize the Si-O-Si network, potentially leading to nanopore formation that could facilitate

greater electrolyte penetration. Consequently, water uptake accelerates, reaching the surface of HDG steel and initiating corrosion, which increase the corrosion rate of the HDG steel substrate [17,35,45,46]. Additionally, the accumulation of water at the interface between the HDG steel and the sol-gel film promotes the hydration of the corrosion product (zinc oxide) at the water-enriched interface [57]. These corrosion products build up at the coating/metal interface and can have an impact on adhesion [57–59], potentially leading to the detachment of the sol-gel film from the HDG steel substrate, as observed in the SEM image. On the other hand, some authors [59] suggested that hydroxyl ions produced at the metal/coating interface cannot readily diffuse out, resulting in their diffusion along the interface and weakening the adhesion between the metal and the coating. While the release and transport of Ce^{3+} ions into the defects sites to react with the hydroxyl groups is a slow process. As a result, the corrosion rate and the loss adhesion are faster than the inhibition reaction (involving the Ce^{3+} ions released within the sol-gel layer and hydroxyl ions). This delay could explain why, although the release of Ce^{3+} ions was observed, they did not offer active protection.

- Secondly, high Ce (III) contents can result in excessive or agglomerated precipitation products. The agglomeration of these products causes the sol-gel layer to detach from the HDG steel bare substrate, leading to the degradation of barrier properties, as observed after 336 h under EIS measurement (Fig. 10 (a)). This significant degradation of sol-gel barrier due to the incorporation of high quantity of cerium salt, is a phenomenon that has been reported by some authors [35,39].

The results clearly indicate that it is essential to dope the proper cerium salt concentration into the sol-gel network so as not to affect the coating protective properties. Furthermore, the presence of cerium salt mainly reinforces the barrier effect of the coating, but a superior barrier might impede cerium release. To avoid the excess of cerium in the layer

and manage its release, alternative methods are necessary. These could include novel approaches like the incorporation of cerium salts into nano-containers, optimizing the use of cerium's corrosion-inhibiting properties within sol-gel systems.

5. Conclusion

In this study, a dense sol-gel coating based on tetraethyl orthosilicate (TEOS), methyltriethoxysilane (MAPTMS), and zirconium tetrapropoxide (ZTP) formulation was synthesized to protect the HDG steel substrate from corrosion in a 0.1 M NaCl solution. The investigation focused on the impact of varying Ce (III) concentrations within the sol-gel coating. The Ce (III) contents is a critical factor in the corrosion performance of the coatings. Low cerium concentrations improved the barrier effect, with 650 ppm Ce (III) showing the most substantial enhancement in corrosion resistance and providing long-lasting protection for HDG steel. In contrast, higher Ce (III) concentrations (2000 ppm and 5000 ppm) led to a sharp decrease in the overall corrosion protection of the coating in prolonged time, showing less effective in corrosion protection compared to the neat TMZ layer in the long-term. Besides, the rheology and FTIR results proved the catalytic effect of Ce (III) content on the reticulation of the sol-gel coatings. However, this excessive Ce (III) amount leads to the destabilization of the Si–O–Si (due to bigger size of Ce ion than Si atom), resulting in the drop of coating performance in long-lasting.

CRediT authorship contribution statement

Thi Thao Nguyen: Writing – original draft, Methodology, Investigation, Formal analysis, Data curation. **Thu Thuy Thai:** Writing – review & editing, Validation, Methodology. **Yoann Paint:** Investigation. **Anh Truc Trinh:** Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition. **Marie-Georges Olivier:** Writing – review & editing, Validation, Supervision, Project administration, Methodology, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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