Nanostructured sol–gel coatings doped with cerium nitrate as pre-treatments for AA2024-T3
Corrosion protection performance

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Abstract
Nanostructured hybrid sol–gel coatings doped with cerium ions were investigated in the present work as pre-treatments for the AA2024-T3 alloy. The sol–gel films have been synthesized from tetraethylorthosilicate (TEOS) and 3-glycidoxypropyltrimethoxysilane (GPTMS) precursors. Additionally the hybrid sol was doped with zirconia nanoparticles prepared from hydrolyzed tetra-n-propoxidezirconium (TPOZ). Cerium nitrate, as corrosion inhibitor, was added into the hybrid matrix or into the oxide nanoparticles. The chemical composition and the structure of the hybrid sol–gel films were studied by XPS (X-ray photoelectron spectroscopy) and AFM (atomic force microscopy), respectively. The evolution of the corrosion protection properties of the sol–gel films was studied by EIS (electrochemical impedance spectroscopy), which can provide quantitative information on the role of the different pre-treatments. Different equivalent circuits, for different stages of the corrosion processes, were used in order to model the coating degradation. The models were supported by SEM (scanning electron microscopy) measurements. The results show that the sol–gel films containing zirconia nanoparticles present improved barrier properties. Doping the hybrid nanostructured sol–gel coatings with cerium nitrate leads to additional improvement of the corrosion protection. The zirconia particles present in the sol–gel matrix seem to act as nanoreservoirs providing a prolonged release of cerium ions. The nanostructured sol–gel films doped with cerium nitrate can be proposed as a potential candidate for substitution of the chromate pre-treatments for AA2024-T3.

Keywords: AA2024; EIS; Corrosion; Nanostructured coating; Sol–gel; Inhibitor; Cerium

1. Introduction
The development of environmentally friendly pre-treatments for metallic substrates is a filed of growing interest due to banning the use of chromates as protective pre-treatments [1]. Among the possible candidates for environmentally friendly pre-treatments for aluminium alloys are the silica-based sol–gel ones [2]. Such pre-treatments are able to form a Si–O–Al conversion layer providing a stable alumina/sol–gel film interface, which impairs the onset of corrosion [3]. Schmidt et al. [4] reports that the alumina–silica mixed compounds present Gibs energy lower than the boehmite (AlO(OH)), which is the product of the first stage of aluminium oxidation in the presence of moisture. The lower value of the Gibs energy leads to thermodynamical stability of the silica/aluminium interface in corrosive environments. The chemical bonding of the sol–gel films to the aluminium substrate also contributes to improved adhesion. Moreover sol–gel coatings, especially the hybrid films, provide a dense barrier against electrolyte uptake [2]. However, the coating,

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by itself, is not sufficient to effectively protect for long term the metal substrate against corrosion. The sol–gel coatings contain micro-pores, cracks and areas of low cross-link density that provides pathways for diffusion of corrosive species to the coating/metal interface [2]. The corrosion processes start in these zones. The crack ability and porosity of the sol–gel films can be decreased by incorporation of oxide nanoparticles into the hybrid matrix [5]. However, even such films cannot offer an adequate protection when the coating is damaged due to the lack of self-healing properties.

Incorporation of corrosion inhibitors into the sol–gel films can improve the protective ability of the coatings, suppressing the corrosion process in the defects. Phosphates, vanadates, borates, cerium and molybdenum compounds were found to have inhibiting action on the corrosion processes [6–8]. It has been reported [6,9–11] that some of the most effective and environmentally friendly corrosion inhibitors for aluminium alloys are derived from cerium salts. This seems to result from deposition of hydrated cerium oxide on the cathodic intermetallic particles, existing in the aluminium alloy, thus suppressing the cathodic reaction [12]. Voevodin et al. [13] investigated the corrosion protection properties of the epoxy-zirconia sol–gel coatings containing inhibitor ions salts such as Ce(NO3)3, NaVO3, and Na2MoO4. The sol–gel films with NaVO3 and Na2MoO4 did not provide adequate corrosion protection due to the decrease of the sol–gel network stability. However, the sol–gel coatings with cerium dopants performed at least as good as the undoped epoxy-zirconia films [13]. Additional improvement of the corrosion protection was also revealed in the case of silane pretreatments when cerium nitrate was introduced in the coating [14].

Organic inhibitors can be also incorporated in the sol–gel matrix in order to improve the corrosion protection of metallic substrates. Khramov et al. [15] studied the protection properties of SNAP (Self-assembled Nanophase Particles) films with incorporated mercaptobenzothiazole and mercaptobenzimidazole as corrosion inhibitors. The β-cyclodextrin was also included in some of these coatings. The corrosion protection of sol–gel derived coatings was sufficiently improved when the encapsulation of the organic inhibitors in the presence or absence of β-cyclodextrin took place. However, the SNAP films with β-cyclodextrin exhibited superior corrosion protection due to the prolonged release of the inhibitor from the cyclodextrin–inhibitor complexes. As a result the incorporation of corrosion inhibitors absorbed in nanoparticles could be a good way to enhance the protection properties of these films. This procedure can provide an additional reinforcement of the hybrid matrix by the nanoparticles [5] and a prolonged release of inhibitor.

The present work aims at producing and assessing the corrosion protection conferred to the aluminium alloy AA2024-T3 by hybrid sol–gel films with incorporated zirconia nanoparticles and doped with cerium nitrate as corrosion inhibitor. The cerium inhibitor was added to the hybrid matrix or to the oxide nanoparticles at the respective hydrolysis steps. The hybrid film and the oxide nanoparticles were prepared by the controllable hydrolysis of 3-glycidoxypropyltrimethoxysilane (GPTMS) and tetra-etylorthosilicate (TEOS), respectively. Electrochemical impedance spectroscopy (EIS) was used to assess the corrosion performance of the developed pre-treatments. The surface morphology and the evolution of the coatings structure were investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM) techniques. The chemical composition of the pre-treated surfaces was assessed by X-ray photoelectron spectroscopy (XPS) and energy dispersive spectroscopy (EDS).

### 2. Experimental

#### 2.1. Sol–gel pre-treatments

The aluminium alloy 2024-T3 was used as substrate. The nominal composition of the used alloy is given in Table 1. The metallic samples were immersed in an alkaline aqueous solution containing 60 g/l of TURCO™ 4215 for 15 min at 60 °C followed by immersion for 15 min at room temperature in a 20 wt. % solution of nitric acid before coating application.

The nanostructured hybrid films were synthesized using the controllable sol–gel route. An organosiloxane acylsol with another acylsol containing the zirconia precursor were combined in order to provide the hybrid sol–gel solution.

The first organosiloxane sol was prepared by combining GPTMS, TEOS and 2-propanol in a 1:1:2 volume ratios and then stirring for 30 min at room temperature; 5 vol. % of the acidified water or the solution of Ce(NO3)3·6H2O (in the case of the hybrid matrix doped with inhibitor) was added to the mixture at the beginning of the stirring.

The second sol containing the zirconia nanoparticles was obtained by hydrolyzing TPOZ precursor. The sol was prepared by adding the acylation of acetic acid to the TPOZ, 70% in n-propanol, in a 1:1 volume ratio. This solution was stirred with the synchronous ultrasonic agitation at room temperature for 80 min. Acidified water (pH ~ 1) or solution of Ce(NO3)3·6H2O was added to the sol 20 min after the beginning of the solution stirring. The amount of acidified water was about 10 vol. %.

### Table 1

<table>
<thead>
<tr>
<th>Composition of aluminium alloy 2024-T3</th>
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<tbody>
<tr>
<td>Element</td>
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<tr>
<td>---</td>
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<tr>
<td>Concentration</td>
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</table>
Table 2

<table>
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<tr>
<th>Coating reference</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO₂ nanoparticles</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>−</td>
</tr>
<tr>
<td>Cerium in the hybrid matrix</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Cerium in the nanoparticles</td>
<td>+</td>
<td>−</td>
<td>+</td>
<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Concentration of cerium in the final coating (wt.%</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

water was varied in order to achieve 0.5 wt.% or 1 wt.% of cerium ions in final sol–gel coating.

The two prepared sol–gel solutions were mixed in 2:1 volume ratio, respectively. The final sol–gel system was stirred and ultrasonically agitated for 60 min and then aged for 1 h at room temperature before the pre-treatment of the substrates.

A reference coating using only the first sol stirred for 90 min was prepared in order to compare its performance with that of the doped coatings. The different types of coatings used in this work are shown in Table 2.

The sol–gel films were produced by a dip-coating procedure conducted by immersion of the clean substrate in the final sol–gel solution for 100 s, followed by controlled withdrawal with a speed of 18 cm/min. After coating application, the samples were cured at 130 °C for 1 h in an oven.

2.2. Experimental techniques

Electrochemical impedance spectroscopy (EIS) was used to estimate the electrochemical parameters associated with the corrosion process occurring on the AA2024-T3 pre-treated with the different hybrid sol–gel coatings during immersion in 0.005 M NaCl solution. Low concentration of the chloride ions was used in order to decrease rate of the corrosion processes since the sol–gel film is not a complete coatings and they are working only as a pre-treatment. The decreased rate of the corrosion allows more correct estimation of the processes on the early stages. However, as shown below, such concentration of chlorides is perfectly enough to cause drastic corrosion impact to the untreated AA2024-T3 substrate or the alloy coated with less protective pre-treatments. Use of such corrosive environments to study early stages of pre-treated metallic substrates is described elsewhere [16,17]. All the measurements were carried out at room temperature in a Faraday cage. A three-electrode arrangement was used, consisting of a saturated calomel reference electrode, a platinum foil as counter electrode and the exposed sample as a working electrode. The working area was 3.4 cm². The EIS measurements were performed using a Gamry FAS2 Femtostat with a PCH4 Controller. The impedance measurements were carried out in a 100 kHz down to 10 mHz frequency range with 10 steps per decade. All the spectra were recorded at open circuit potential with applied 10 mV sinusoidal perturbation. At least two samples prepared for the same conditions were tested in order to ensure reproducibility of the results. The impedance plots were fitted using different equivalent circuits in order to simulate the different stages of the pre-treated system during immersion.

The structure of the sol–gel coatings before and after immersion was studied by SEM (Hitachi S-4100 system with electron beam energy of 25 keV) and EDS (energy dispersive spectroscopy). The chemical composition of the sol–gel films was determined by XPS using a Microlab 310 (VG Scientific) equipped with a Mg (non-monochromated) anode and a concentric hemispherical analyzer. The spectra were taken at constant analyzer mode (CAE=30 eV).

The morphology of the sol–gel films was assessed by atomic force microscopy using a nanoscope digital instruments fitted with a NanoScope III controller and a silicon tip covered with PtIr in tapping mode to prevent scratching of the pre-treated surface.

3. Results and discussion

3.1. Structure and composition of the films

The SEM and AFM techniques were used in order to assess porosity and structure of the different coatings. Fig. 1 presents the SEM micrograph of the AA2024-T3 treated with the sol–gel film A. The surface of the sol–gel film seems to
be crack-free, containing few pinhole-like defects (Fig. 1a). The thickness of the film was estimated by the cross section analysis (Fig. 1b) and is about 400–500 nm.

The AFM scan presented in Fig. 2 demonstrates the surface morphology of the sol–gel coated substrate. The nano-sized particles incorporated into the film matrix are clearly defined in this scan. The distribution of the nanoparticles is relatively uniform and the particles have an average diameter around 50 nm. Several particles in the hybrid matrix have a bigger diameter and seem to result from agglomerates of smaller ones.

The composition of the hybrid films was investigated using the XPS technique. Fig. 3 depicts the XPS photoelectron spectra for Zr 3d and Ce 3d obtained on different coatings. The spectra were corrected for the C 1s at 285.0 eV. The results evidence that the binding energy of the Zr 3d5/2 peaks depends on the concentration of cerium ions. For the coatings without cerium nitrate addition the binding energy of the Zr 3d5/2 photoelectron spectra is around 182.8 eV, being characteristics of the presence of ZrO2. However, the Zr 3d5/2 ionization shifts towards lower binding energy (182.1 eV) for the coatings containing 1% of cerium nitrate. This result may be due to adsorption and/or absorption of cerium ions on zirconia nanoparticles. Simultaneously the Ce 3d5/2 photoelectron spectrum becomes evident. The well-defined cerium peak appears on the XPS spectrum only in the case of the sample with higher concentration of inhibitor ions. This result may be due to adsorption and/or absorption of cerium ions on zirconia nanoparticles. Simultaneously the Ce 3d5/2 photoelectron spectrum becomes evident. The well-defined cerium peak appears on the XPS spectrum only in the case of the sample with higher concentration of inhibitor ions. This result may be due to adsorption and/or absorption of cerium ions on zirconia nanoparticles.

3.2. EIS measurements

3.2.1. Equivalent circuit models

The impedance spectra can be used to provide adequate modeling of the physicochemical processes on the coated substrate during corrosion tests. Fig. 4 presents the evolution of the impedance spectrum of coating D (without cerium) after different periods of immersion in the NaCl solution. After 7 h of immersion the impedance spectra reveal the presence of two time constants at $4 \times 10^3$ and 0.1 Hz, which can be ascribed to the sol–gel film capacitance, $C_{\text{coat}}$, and the pore resistance of the sol–gel film, $R_{\text{pore}}$, respectively. The equivalent circuit used for numerical fitting of the exper-
double layer capacitance \( C_{dl} \) and polarization resistance \( R_{\infty} \) of the corroded areas. The main corrosion process at this stage. The mass transfer limitations during pit growth can provide an adequate model for the impedance spectrum at low frequency become visible (Fig. 4, 214 h). Addition of a Warburg element \( W \) to the equivalent circuit (Fig. 5D) can provide an adequate model for the impedance spectrum at this stage. All the coatings showed identical impedance values. However the impedance decreases with time. The smallest changes were revealed for the coating with Ce-doped nanoparticles. Fig. 8 presents EIS spectra of these coatings after 250 h of continuous immersion in 0.005 M NaCl solution. Impedance spectra in Fig. 8 were fitted using the equivalent circuits 5B and 5D for coatings A and D, respectively. Constant phase elements (CPE) instead of capacitances were used in all fittings presented in the work. Such modification is obligatory when the phase angle of capacitor is different from \(-90^\circ\). The impedance of the CPE depends on frequency according to the following equation:

\[
\frac{1}{Z} = Q(\omega \nu)^\beta \tag{1}
\]

where \( Z \) is the impedance, \( Q \) a parameter numerically equal to the admittance \((1/|Z|)\) at \( \omega = 1 \text{ rad s}^{-1} \), \( \omega \) the frequency, and \( \beta \leq 1 \) a power coefficient calculated as ratio of phase angle at maximum of corresponding time constant to \(-90^\circ\). The capacitance values for the different elements in the equivalent circuit were calculated using the following equation:

\[
C = Q(\nu_{\text{max}})^{-1} \tag{2}
\]

where \( \nu_{\text{max}} \) is the frequency at which the imaginary impedance reaches a maximum for the respective time constant [22]. The equivalent circuits were chosen for fittings basing on number of time constants and analyzing the goodness of fits. Table 3 presents parameters of the coatings A and D after 5 and 250 h of continuous immersion. The used equivalent circuits provide the adequate fitting of the experimental results and the good estimation of parameters. Fitting the experimental results with an incompatible equivalent circuit gives very high value of deviation (last column of
Table 3) and cannot be used for adequate estimation of sol–gel films.

The impedance of the aluminium alloy coated with the hybrid film containing Ce-doped zirconia nanoparticles (coating A) still shows high impedance value (above $10^6 \Omega \text{cm}^2$) at low frequencies. Two maxima (two time constants), one at $5 \times 10^4 \text{Hz}$ and another at 1 Hz can be seen in the phase angle plot, which can be ascribed to the sol–gel film and an intermediate mixed oxide layer formed on the alloy/film interface (as described above), respectively. Contrasting to this behaviour the coating without cerium (coating D) shows impedance values at a frequency of $10^{-2} \text{Hz}$ about five times...
lower. The impedance of the film with the Ce-doped matrix (not shown) reveals, at the same frequency, intermediate values of impedance. Additionally in the case of the last two films, the low-frequency (0.1 Hz) time constant appears due to starting of the corrosion activity as described above.

These results show that the hybrid sol–gel films prepared with cerium-containing zirconia nanoparticles confer higher corrosion protection than the undoped ones and those with the doped hybrid matrix.

The evolution of parameters of the coated systems was analyzed in order to assess the corrosion protection properties of the different pre-treatments. The parameters of the electrolyte/sol–gel film/substrate system were obtained using the fits of experimental spectra with equivalent circuits.

### Table 3

| Parameters of the sol–gel film/substrate systems obtained from fitting of the experimental impedance spectra with different equivalent circuits |
|---|---|---|---|---|
| Coating | A | | B | | C |
| --- | --- | --- | --- | --- |
| Immersion time (h) | 10 | 250 | 10 | 250 | 10 |
| Equivalent circuit | SB | SB | SB | SB | SC |
| $R_{solut}$ (kΩ cm$^2$) | 1412 ± 64 | 1248 ± 120 | 1412 ± 64 | 1248 ± 120 | 1412 ± 64 |
| $R_{coat}$ (kΩ cm$^2$) | 1249 ± 256 | 421 ± 120 | 1249 ± 256 | 421 ± 120 | 1249 ± 256 |
| $Q_{coat}$ (nS cm$^{-2}$) | 1249 ± 256 | 421 ± 120 | 1249 ± 256 | 421 ± 120 | 1249 ± 256 |
| $n_{coat}$ | 0.755 ± 0.009 | 0.745 ± 0.009 | 0.743 ± 0.009 | 0.744 ± 0.009 | 0.903 ± 0.009 |
| $R_{oxide}$ (kΩ cm$^2$) | 2392 ± 66 | 1170 ± 60 | 2870 ± 480 | 128 ± 10 | 258 ± 4 |
| $Q_{oxide}$ (μF cm$^{-2}$) | 3.95 ± 0.05 | 4.30 ± 0.15 | 4.30 ± 0.15 | 5.01 ± 0.24 | 7.76 ± 0.09 |
| $n_{oxide}$ | 0.938 ± 0.005 | 0.958 ± 0.006 | 0.913 ± 0.008 | 0.913 ± 0.008 | 0.829 ± 0.003 |
| $R_{polar}$ (kΩ cm$^2$) | – | – | – | 92 ± 6 | – |
| $Q_{dl}$ (μF cm$^{-2}$) | – | – | – | 18.6 ± 2.9 | – |
| $n_{dl}$ | – | – | – | 1.00 ± 0.30 | – |
| $W$ (μS cm$^{-2}$) | – | – | – | 1.00 ± 1.50 | – |
| Goodness | 1.59e–3 | 9492e–6 | 2.40e–3 | 3274e–6 | 12.46e–3 |
Fig. 9. Evolution of the capacitance for the sol–gel film for the different coatings during immersion.

presented in Fig. 5. Only models obtained highest goodness were used to fit experimental results and to extract parameters of the investigated systems.

3.2.2.1. Sol–gel film. The change of the sol–gel film capacitance during immersion in the chloride solution is presented in Fig. 9. Generally the capacitance of the dielectric film depends on the amount of absorbed water. Coating D prepared without addition of cerium inhibitor shows very stable capacitance for 350 h. The sol–gel film A with Ce-doped nanoparticles is also relatively stable; however the capacitance increases after around 200 h probably due to water absorption. The capacitance of the coating B (with Ce-doped matrix) exhibits significantly faster growth. Increase of the sol–gel film water uptake can be due to higher concentration of the cerium inhibitor in the sol–gel matrix, since cerium nitrate was introduced directly into the organosiloxane sol in contrast to the film A, where the inhibitor was added to the sol with zirconia nanoparticles. Probably the cerium ions can decrease stability of the hybrid film leading to faster hydrolytic destruction in the aqueous solutions.

Another important parameter is the pore resistance \( (R_{coat}) \) of the sol–gel layer that characterizes the crack ability and porosity of the hybrid film. The pore resistance consists of the resistance of electrolyte in pores, cracks and pits connected in parallel to each other. Fig. 10 shows the evolution of the pore resistance of sol–gel films. The undoped film D has the highest pore resistance for the beginning of immersion; however the resistance decreases during the first 25 h two orders of magnitude showing formation of cracks in the sol–gel layer. The initial pore resistance of the cerium-doped coatings A, B and C is lower in comparison to coating D especially in the case of the film C with higher concentration of inhibitor ions. However, short after immersion the pore resistances show fast increase of about one order of magnitude probably due to blocking of the pores as described in previous works [5,23]. Coatings A and B after the initial increase achieve pore resistance values close to the ones for undoped coating and keep similar values during further weathering.

3.2.2.2. Intermediate oxide layer. The compactness of the intermediate oxide layer formed between the sol–gel film and the metallic substrate is also very important from the point of view of corrosion protection, since breakdown of this film provide direct ingress of the corrosive agents to the metallic surface. Fig. 11 presents the evolution with time of the resistance of the intermediate oxide layer \( (R_{oxide}) \). The reference coating E prepared using only the hybrid organosiloxane sol without addition of \( \text{ZrO}_2 \) nanoparticles and cerium-based inhibitor shows very fast decrease of the resistance of the intermediate oxide layer from \( 4 \times 10^6 \) to \( 5 \times 10^3 \) \( \Omega \cdot \text{cm}^2 \) only after 150 h the pore resistance of the coating B (with doped matrix) is decreasing faster than coatings A and D, that is in a good accordance with the evolution of the capacitance for film B. The pore resistance of the sol–gel film C is dropping very fast showing that high concentration of cerium nitrate leads to formation of a fragile film with poor barrier properties. Therefore the addition of the cerium nitrate seems to negatively affect the barrier properties of the sol–gel layer. However incorporation of cerium into zirconia nanoparticles can reduce this negative effect.

Only after 150 h the pore resistance of the coating B (with doped matrix) is decreasing faster than coatings A and D, that is in a good accordance with the evolution of the capacitance for film B. The pore resistance of the sol–gel film C is dropping very fast showing that high concentration of cerium nitrate leads to formation of a fragile film with poor barrier properties. Therefore the addition of the cerium nitrate seems to negatively affect the barrier properties of the sol–gel layer. However incorporation of cerium into zirconia nanoparticles can reduce this negative effect.
after only 24 h of immersion. The AA2024 samples pre-
treated with the sol–gel system C with high concentration of
ceium show slower decrease of the resistance. The maximum
initial resistance of the intermediate layer was found for the
Ce-free coating D. However the resistance is dropping rela-
tively fast and achieves $10^7 \Omega \cdot \text{cm}^2$ after 330 h of immersion.
The coating B (with cerium-doped organosiloxane matrix)
shows a stable value for the intermediate layer impedance
during the first 100 h of weathering tests. After the initial
stable period the resistance of the oxide conversion layer is
decreasing relatively fast from $10^7$ to $10^5 \Omega \cdot \text{cm}^2$ that is close
to the value of the undoped D coating. The stable resistance
of the intermediate layer for 100 h can be obtained due to
the inhibiting and self-healing action of the cerium ions. The
cerium can suppress the cathodic reaction [12] preventing
the propagation of cracks in the intermediate layer. When the
cerium ions are completely released from the sol–gel matrix
the resistance value decreases rapidly.

The resistance of the oxide layer for coating A (with
cerium-doped nanoparticles) is about three times lower at the
beginning of immersion than for film B and behaves differ-
ently with immersion. The resistance slowly decreases dur-
ing 350 h of immersion from $5 \times 10^5$ to $5 \times 10^3 \Omega \cdot \text{cm}^2$ and
finally reaches a five times higher value than coatings B and
D. This behaviour can be explained in terms of prolonged
release of the cerium ions from the zirconia nanoparticles.
As a result the coating A prepared with zirconia nanoparti-
cles doped with cerium inhibitor shows higher stability of the
oxide intermediate layer and confers better corrosion protec-
tion properties from the point of view of long term corrosion
protection.

3.2.2.3. Corrosion process. The rate of the corrosion pro-
cesses can be estimated measuring the polarization resis-
tance ($R_p$). Fig. 12 shows the evolution of the polariza-
tion resistance during the immersion tests for the different
hybrid sol–gel coatings. The impedance spectra of AA2024-
T3 coated with coating A shows the first signs of third time
constant ascribed to the corrosion processes only at the final
stage of the immersion tests. Thus, the polarization resistance
in this case can be measured only after 275 h of immersion.
The value of the polarization resistance is at least one order
of magnitude higher than in the case of the other coatings.
The impedance spectra of coating B (cerium in matrix) show a
measurable response of the corrosion processes after 150 h of
immersion, which is in a good agreement with the evolution
of the resistance of both the intermediate layer and the sol–gel
film. The polarization resistance for the alloy coated with film
B is around $10^6 \Omega \cdot \text{cm}^2$ at this stage and fast decreases with
immersion. Decrease of the polarization resistance can start
when the most part of the cerium ions is already released from
the coating and the inhibition of the corrosion processes is
discontinued. In the case of the cerium-free coating D the
corrosion processes appear twice faster after 75 h. The coat-
ing C shows the first signs of corrosion after only 24 h of
immersion. The polarization resistance in this case is suffi-
ciently lower due to the poor barrier properties of this film.
The reference coating E has higher corrosion activity and
consequently low polarization resistance immediately after
the beginning of the immersion tests.

The above results demonstrate significant improvement of
the corrosion protection due to incorporation of the cerium-
inhibitor ions into the zirconia nanoparticles.

4. Conclusions

The EIS method can be used to model the metal/coating
interface of the sol–gel pre-treatments on aluminium alloys.
The corrosion resistance of the coating and the kinetics of the
corrosion process in chloride solution were evaluated for the
AA2024-T3 coated with hybrid sol–gel films.

Incorporation of zirconia nanoparticles leads to improve-
ment of the barrier properties of the organosiloxane hybrid
sol–gel coatings. Additional corrosion protection is conferred
by doping the sol–gel film with cerium-based inhibitor. How-
ever the too high concentration of cerium nitrate leads to
degradation of the barrier properties of the sol–gel matrix.

The hybrid sol–gel coatings with incorporated zirconium
oxide nanoparticles doped with cerium inhibitor provide
long term corrosion protection and can be prospective candi-
dates for development of new environmentally friendly pre-
treatments.
The nanostructured zirconia particles play the role of
nanoreservoirs for storage and controllable release of the in-
hibitor.

References

233.