Inhibitor-doped sol–gel coatings for corrosion protection of magnesium alloy AZ31

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This work presents new anticorrosive coatings for the AZ31 magnesium alloy, based on hybrid sol–gel films doped with a corrosion inhibitor. The sol–gel coatings were prepared by copolymerization of 3-glycidoxypropyltrimethoxysilane and zirconium (IV) tetrapropoxide. 8-Hydroxyquinoline (8-HQ) was chosen as a corrosion inhibitor to be incorporated into the sol–gel films at two different stages of synthesis, either before or after hydrolysis of the sol–gel precursors. The effectiveness of 8-HQ for corrosion suppression on AZ31 was verified by Scanning Vibrating Electrode Technique. Electrochemical Impedance Spectroscopy was used to monitor the evolution of the substrate/film systems in the course of immersion in 0.005 M NaCl. The morphology and the structure of the sol–gel films were characterized with SEM/EDS and TEM techniques. The sol–gel films exhibit good adhesion to the metal substrate and prevent the corrosive attack during 2 weeks under immersion test. Results showed that addition of inhibitor into the sol–gel films enhances the corrosion protection of the magnesium alloy and does not lead to deterioration of the barrier properties of the sol–gel matrix.

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1. Introduction

Magnesium is one of the lightest metals and its alloys have attractive properties for different industrial applications. In particular, their high strength-to-weight ratio makes Mg alloys appropriate for applications requiring light weight [1–3]. The Mg–3Al–1Zn alloys (AZ31) are of industrial interest because they show better ductility and strength in comparison with pure magnesium besides a homogeneous microstructure. However they are too reactive and exhibit high corrosion susceptibility. Therefore the use of Mg alloys is limited only to some components in mild environments [4–7]. Hence, improving their corrosion protection by depositing thin organic, inorganic or hybrid films on the metallic surface may expand the areas of Mg alloys applications [8].

The corrosion performance of Mg alloys results from the high intrinsic dissolution tendency of Mg which can be described by the following equations:

Anodic reaction:

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

Cathodic reactions:

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad (2) \]
\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad (3) \]

Overall reaction:

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

The corrosion mechanism includes all physical features and chemical reactions when metallic Mg is exposed to an environment. The dissolution is only partially blocked by the formed corrosion products, as MgO has a smaller molar volume compared to pure Mg, as characterized by a Pilling–Bedworth ratio lower than one. Thus, the formed Mg-oxide film is always porous and the resulting low pitting potential, more negative than the that of the hydrogen evolution reaction, will allow pits to grow with a fairly constant fraction of the dissolution current compensated by hydrogen evolution reaction (HER) inside the pit [9]. On the other hand, intermetallic phases act as local cathodes of microgalvanic cells with acceleration of corrosion. Song et al. [1–5] have indicated that corrosion mechanism of Mg has the following key points. In the general case, a partially protective film covers the surface and Mg dissolution occurs at defects in this film. Hydrogen evolution is associated with Mg dissolution in two different ways: electrochemical cathodic reactions, that balance Mg dissolution.

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reaction; \( H_2 \) is also produced directly by the reaction of \( Mg^+ \) ion with water.

**Cathodic partial reaction:**

\[
2H^+ + 2e^- \rightarrow H_2
\]

**Anodic partial reaction:**

\[
Mg \rightarrow Mg^+ + e^-
\]

**Chemical reaction:**

\[
2Mg^+ + 2H_2O \rightarrow 2Mg^{2+} + 2OH^- + H_2
\]

However the anodic reaction (1) can also take place by direct two-electron oxidation of magnesium to \( Mg^{2+} \). Therefore both anodic processes may occur at the same time.

The corrosion process in any case produces pH increase, what favours the formation of a magnesium hydroxide (\( Mg(OH)_2 \)) film. The dissolution is only weakly inhibited by the film of formed corrosion product. On the other hand, intermetallic phases act as local cathodes of microgalvanic cells causing acceleration of corrosion. In solutions of practical importance like 3% NaCl, Mg exhibits a highly negative corrosion potential, with a slightly more negative pitting potential [2].

The sol–gel process is effective for preparing adherent, chemically inert oxide or hybrid films at low temperatures (< 200°C) as it is required for Mg alloys, as was shown for Al and steel substrates [10–15]. The process is economic, environmentally friendly and films can be easily deposited at all kinds of surfaces, irregular shapes and larger integral structures.

Sol–gel films that contain either inorganic (e.g. Ce\(^{3+}\), molibdate, vanadate) or organic inhibitors (e.g. phenylphosphonic acid, benzotriazole) were reported [16–18]. Silanics compounds with long aliphatic chain [19] as well as functional silanes [20] have been successfully tested as pre-treatments for magnesium alloys. These pre-treatments provide corrosion protection in addition to surface functionality, improving the compatibility of the metallic substrate with the painting systems [21].

Various procedures of sol–gel coatings fabrication for magnesium alloys were reported in the literature [22]. The anticorrosive performance of mixed ZrO\(_2\) and tris(trimethylsilyl) phosphate sol–gel coatings on a magnesium alloy was studied by Lamaka et al. [23]. It was found that sol–gel film confers good corrosion protection due to its chemical interaction with the magnesium substrate which, most probably, leads to the formation of a graded film.

Tan et al. [20] studied sol–gel film based on 3-methacryloxypropyltrimethoxysilane or 3-mercaptopropyltrimethoxysilane and colloidal silica for sealing the porous of anodized layers on magnesium. It was found that the sol–gel layers provide corrosion protection by physical sealing of pores in the anodised layer and act as a barrier. Since defects and porosity in the coatings are the main causes of degradation, applying multilayers eliminates diffusion paths for corrosive species to reach the metal surface, thereby limiting the incidence of localised attack.

The development of new film systems with active corrosion protection implies not only mechanical covering of the protected surface with a dense barrier coating but also providing self-healing properties which allow corrosion protection even after partial damage of the film. These properties can be achieved impregnating specific corrosion inhibitors into the film system. Inhibitors can provide local anticorrosion protection in places where the main film is damaged [10].

It was shown in our previous works [24,29], that 8-HQ suppresses initiation of corrosion attack on 2024 aluminium alloy. The inhibiting action of 8-HQ is based on the polarization of active intermetallic zones (so called S-phases that cover around 3% of alloy surface) due to prevention of dissolution of Mg and Al as well as dissolution and redeposition of Cu. Dissolution of intermetallic inclusions is suppressed due to formation of insoluble chelate compounds on the entire surface of the alloy and atop the intermetallic inclusions. Moreover, adsorbed inhibitor impedes an access of aggressive chloride ions to the surface of the alloy. 8-HQ is known to form stable and hydrophobic metal/ligand complexes with magnesium. The formation of these complexes is instantaneous and reversible, but because of their high stability constants, the equilibrium is shifted to the side of the complex formation [25,26]. Apart from that, if corrosion process started, 8-HQ can also form highly insoluble complexes with Mg in pH range 9.4–12.7 and with Al at pH 4.2–9.8 [24]. Thus, studied mechanism of inhibition of AA2024 allowed us to assume that 8-HQ can also inhibit corrosion of magnesium-based alloys.

The main goal of this work was to develop a sol–gel process for enhancing the corrosion resistance of AZ31 alloy through the addition of 8-HQ into the sol–gel formulation.

The influence of the inhibitor was evaluated by using EIS and SVET methods. Based on our previous results [23,24,27–29], zirconia hybrid organic–inorganic sol–gel films were used as a matrix material providing barrier protection with the addition of 8-HQ as inhibitor aiming to impart active corrosion protection. 8-HQ was added at two different stages of the sol–gel formation: either before or after hydrolysis of the sol–gel components. The sol–gel films were prepared by dip-coating followed by curing. Results indicate that the hybrid sol–gel films doped with 8-HQ adhere well to the substrate and are corrosion-resistant. However, the overall corrosion protection can be affected depending on the stage of the sol–gel synthesis where inhibitor was added.

## 2. Experimental

### 2.1. Material and specimen preparation

The plates of cast AZ31B magnesium alloy used in this study as the metallic substrate were obtained from Alubin (Israel). Apart from Mg, AZ31 magnesium alloy employed in this study, contains about 3 wt.% Al and 1 wt.% Zn. The detailed composition of this alloy is given in Table 1.

The alloy samples with dimensions 22 mm × 40 mm × 4 mm without any surface finishing were cleaned by immersion in an acid pickling solution (concentrated H\(_2\)PO\(_4\), HNO\(_3\), CH\(_3\)COOH acids and water with a volume ratio of 3:2:4:1) during 3 s, washed in distilled water and dried in air.

### 2.2. Preparation of sol–gel film

The reference sol–gel films without inhibitor were synthesized by sol–gel route mixing two different solutions. Solution A was composed of zirconium (IV) propoxide (70% solution in 2-propanol) and ethylacetoacetate with volume ratio 1:1, hydrolysed by acidified water (pH – 0.5), sonicated at frequency 20 kHz and stirred electromagnetically for 1 h. Solution B composed of (3-glycidyloxypropyl)trimethoxysilane and 2-propanol with 1:1 volume ratio was hydrolysed by acidified water (pH – 0.5) and electromagnetically stirred for 1 h.

The final solution was synthesized by mixing two solutions (A + B) with a volume ratio of 1:1. This solution was sonicated and stirred electromagnetically for 1 h.

Inhibitor-doped sol–gel films were prepared adding 0.26 wt.% of 8-HQ at different stages of the synthesis. One sol–gel solution was produced by the addition of the 8-HQ in solution A, before the hydrolysis. Another sol–gel solution was prepared adding 8-HQ after the hydrolysis of solution B.

### Table 1

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Zn</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Ni</th>
<th>Mg</th>
<th>Balance</th>
</tr>
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<tr>
<td></td>
<td>3.00</td>
<td>0.83</td>
<td>0.31</td>
<td>0.01</td>
<td>0.003</td>
<td>0.001</td>
<td>0.001</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
All sol–gel formulations were left for 3 h of aging. Afterwards the dip-coating was performed at 18 cm/min to obtain a single-layer film on the AZ31 substrates. The coatings were subjected to drying/curing procedure at 130 ºC for 1 h.

2.3. Characterization of sol–gel films on AZ31

The SEM samples were cut, rinsed in distillate water and dried in cold air. The samples for evaluation of cross-section of the hybrid film were prepared by brittle rupture of the film. The morphology of the films was observed by scanning electron microscopy (semi-in-lens Hitachi SU-70 UHR Schottky (Analytical) FE-SEM microscope), EDS analysis was performed using a BRUKER AXS QUANTAX detector and ESPIRIT 1.8 software. TEM images and selected area diffraction SAD patterns of the cross-section of the film were obtained with a 200 kV TEM — JEOL 2200FS. The samples were prepared by thinning of the cross-section zone with an ion beam milling.

EIS technique was employed on this work to evaluate the corrosion protection performance of the developed hybrid sol–gel films on AZ31B during 2 weeks immersion in 0.005 M NaCl solution. EIS measurements were carried out using a Gamry FAS2 Femtostat coupled with a PCI4 Controller at open circuit potential applying 10 mV sinusoidal amplitude in the 100 kHz to 10 mHz frequency range. A conventional three-electrode cell was used, consisting of a saturated calomel reference electrode, a platinum foil as a counter electrode and sol–gel coated AZ31B substrate as working electrode with a surface area of 3.3 cm². All measurements were performed in a Faraday cage in order to avoid any electromagnetic interference. At least two samples were measured for each coating to check the reproducibility of results. A simplex method was employed to fit the impedance plots using Gamry Echem Analyst software, Version 1.35.

Low concentration of chloride-containing electrolyte, 0.005 M NaCl, was chosen to EIS measurements in order to decrease the corrosion rate of the electrochemically active magnesium alloy. This allows better differentiation between the systems under study. However such concentration of NaCl is enough to cause the high corrosion rate in the case of bare magnesium alloy. Meanwhile this concentration is too low to be used in the case of SVET (Scanning Vibrating Electrode Technique) measurements. The low concentration of electrolyte introduces higher experimental errors in the case of active substrate because of local change of conductivity. Therefore the SVET measurements were carried out in 0.05 M NaCl solution on bare AZ31 magnesium alloy samples. An Applicable Electronics (USA) commercial SVET system controlled by the

![Fig. 1. Optical microphotos and corresponding current density distribution over AZ31 samples in the course of immersion in 0.05 M NaCl: a) 1 min after beginning of immersion, sample was not treated with inhibitor; b) the same sample after 17 h of immersion. c) 1 min after immersion, sample was preliminary treated with alcohol 0.05% solution of 8-HQ; d) the same sample after 3 days of immersion. The black spots in optical microphotos a and c correspond to hydrogen bubbles. Scale unit in SVET maps is μA/cm².](image1)

![Fig. 2. Topography (a) and cross-section (b) of sol–gel film applied on AZ31. The SEM images were taken before the sample was exposed to NaCl solution.](image2)
Fig. 3. SAD of mixed (crystalline and amorphous) (a), and amorphous (b) regions of the TEM image of the cross-section of the sol–gel film (c).

Fig. 4. Topography of AZ31 coated by undoped sol–gel film (a), and by hybrid coating doped with 8-HQ (b); the amplified view of sample with inhibitor (c) and the EDS elemental map of corresponding region (d). SEM/EDS images were taken after 14 days of immersion in 0.005 M NaCl.
ASET program (Sciencewares) was used. The vibrating electrode was an insulated Pt–Ir wire with a Pt black deposited on the spherical tip of around 10 µm diameter. The probe was located 100 µm above the surface and vibrated in the perpendicular direction to the surface (Z) with a 20 µm amplitude. The frequency of probe vibration was 123 Hz. The scanned area was around 13 mm². The measured voltage difference was converted to ionic currents by using a prior calibration performed with a point current source.

3. Results and discussion

3.1. Evaluation of corrosion inhibitor

8-HQ is known as good complexant for number of metal cations including magnesium. In our previous works the high efficiency of this compound toward the corrosion inhibition of aluminum alloys was demonstrated [24, 29]. The mechanism of corrosion inhibition on AA2024 leads to the suggestion that 8-HQ can also inhibit corrosion of magnesium-based alloys. In presented work the inhibiting potential of 8-HQ was studied to prove its suitability to be used as active anticorrosion agent for hybrid coatings.

No inhibitor was added to the aqueous 0.05 M NaCl solution. SVET tests were carried out in the absence of inhibitor in NaCl solution. Instead, before SVET measurements, the sample presented in Fig. 1c and d was exposed to 0.05% alcohol solution of 8-HQ for 12 h. Fig. 1 of the manuscript presents optical micrographs and SVET maps of blank AZ31B specimen (a,b) and sample immersed in alcohol solution of 8-HQ before SVET tests (c,d). In the case of clean alloy surface without immersion to the 8-HQ very high corrosion activity is observed. The anodic currents in some cases achieve almost 1 mA/cm². Extensive hydrogen evolution is observed even in anodic zones showing that anodic process probably goes through one electron process (reactions 6 and 7) The immersion in inhibiting solution reduces significantly the corrosion activity on AZ31 magnesium alloy in 0.05 M NaCl electrolyte. Effective inhibiting effect observed after preliminary treatment of AZ31 by 0.05% alcohol solution of 8-HQ

![Graph 1](image1.png)

![Graph 2](image2.png)

Fig. 5. Bode results of AZ31 blank, with standard sol–gel film and sol–gel films with 0.26 wt.% 8-HQ after 14 days immersed in NaCl 5 mM solution.
indicates that the inhibitor most probably forms a thin adsorptive layer of chelate complexes on the surface of magnesium and prevents access of chloride ions to the surface of alloy when aggressive solution of sodium chloride is used. Thus 8-HQ is a potential candidate to be used as an inhibitor dopant in the hybrid sol–gel film.

3.2. Structure of hybrid sol–gel films

Fig. 2a shows the typical topography of the sol–gel films doped with 8-HQ (before corrosion tests and Fig. 2b shows a top view of the sol–gel film. The coating is homogeneous, compact and without visible de-adhesion or blistering zones. The thickness of the sol–gel film is around 3 μm.

The TEM image in Fig. 3c shows the cross-section of the sol–gel film before immersion in a corrosive media. Three different regions are aligned parallel to the substrate surface: (from right to left): a layer of magnesium substrate; an internal compact semicrystalline layer of native magnesium oxide; an amorphous silica–zirconia representing sol–gel film (b). It can be seen that the synthesized sol–gel film is uniform and free of visible defects.

Fig. 4a shows a topography of the undoped sol–gel film after 2 weeks immersion in 0.005 M NaCl solution. The film is sufficiently degraded demonstrating many cracks. The surface of inhibitor-doped hybrid film appears different after the immersion test, Fig. 4b. There are no cracks observed. However film-form deposits are formed in the coating. Detailed analysis of one of the deposits demonstrates that it is enriched with magnesium (Fig. 4c and d). Since there are no such deposits found in the case of undoped film, one can conclude that their formation is directly related to presence of 8-HQ in the film. Most probably this effect is caused by formation of insoluble complexes in the defects which appear during the immersion tests.

3.3. Electrochemical tests

The Electrochemical Impedance Spectroscopy was used in presented work as main technique to characterize the corrosion protection performance of the developed coatings.

The Bode plots obtained on bare AZ31, and magnesium substrates coated with different sol–gel films, after 14 days of immersion are shown in Fig. 5. The impedance modulus is generally higher in the case of the doped sol–gel coating in comparison to the undoped one.

The difference is even higher when compared to the bare alloy. Two well-defined time constants can be observed on the impedance spectra of coated alloy, as shown in Fig. 6. The high frequency time constant is associated with capacitance and resistance of hybrid sol–gel film. The low frequency relaxation process can be associated to capacitance of the electrochemical double layer on the metal/electrolyte interface. The resistance at the lowest frequencies is related to the polarization resistance of the corrosion reaction [29,30]. During the tests from the second day until the tenth day of immersion an additional time constant eventually appears at intermediate frequencies (not shown). This unstable time constant can be related to the response from the native metal oxide which exists between the metal and sol–gel layer. The addition of 8-HQ improves the corrosion resistance of the hybrid sol–gel films, as can be seen from the impedance modulus. The highest impedance values are observed in the case when inhibitor is added in solution B after the hydrolysis in the course of preparation of the of sol–gel formulation.

Detailed interpretation of the EIS plots was performed by numerical simulation, using an equivalent circuit composed of two-time constants. Fig. 6 shows the equivalent circuit used for numerical fitting of the impedance spectra obtained for sol–gel coated AZ31 alloy exposed to NaCl solution. This equivalent circuit reasonably fits the experimental results as can be confirmed in Fig. 6. Rs is the solution resistance of bulk electrolyte between reference and working electrodes. Rp is not influenced by electrode processes and its value depends on the conductivity of testing medium and the cell geometry. Rs is resistance of the sol–gel film and ROX is resistance of the metal oxide. Rs is polarization resistance which characterizes the electrochemical kinetics of the corrosion process. Constant phase elements were used in this equivalent circuit instead of pure capacitances due to the certain degree of nonuniformity of the sol–gel film and the electrochemical double layer [30].

In Fig. 6, CPE_sc is constant phase element related to the capacitance of sol–gel film and CPE_ox is constant phase element related to the capacitance of metal oxide. CPE_dl is another component of the model that expresses the capacitance of interface electric double layer in film-vulnerable regions exposed at the bottom of electrolyte penetration paths.

All the impedance spectra after different immersion times were fitted using the equivalent circuit shown in Fig. 6. The Table 2 presents the final results of the fittings of the plots obtained after 14 days of immersion in sodium chloride solution.

![Fig. 6](image-url) The experimental spectra (dots) for sol–gel doped with inhibitor before hydrolysis after 14 days of immersion in 5 mM NaCl solution together with fitting results (solid line). Insert: equivalent circuit used for numerical simulations of the EIS spectra.
Fig. 7a presents evolution of sol–gel film resistance which reflects the barrier properties of tested sol–gel films during immersion tests. The sol–gel film resistance of both inhibitor-doped hybrid coatings is more than one order of magnitude larger than the pore resistance of undoped sol–gel film at the beginning of immersion. During corrosion tests new defects appear in all the coatings leading to formation of conductive pathways and decreasing pore resistance of coatings. However even after a long immersion the pore resistance of inhibitor-

### Table 2

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Before hydrolysis</th>
<th>Error (+/-)</th>
<th>After hydrolysis</th>
<th>Error (+/-)</th>
<th>Undoped</th>
<th>Error (+/-)</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_s$</td>
<td>334.3</td>
<td>12.12</td>
<td>210.9</td>
<td>20.85</td>
<td>334.0</td>
<td>12.78</td>
<td>$\Omega$ cm$^2$</td>
</tr>
<tr>
<td>$R_{p}$</td>
<td>5.79E+05</td>
<td>9.72E+03</td>
<td>1.649E+06</td>
<td>78.98E+03</td>
<td>6.870E+05</td>
<td>12.09E+03</td>
<td>$\Omega$ cm$^2$</td>
</tr>
<tr>
<td>$R_{SG}$</td>
<td>7.231E+03</td>
<td>17.5</td>
<td>20.13E+03</td>
<td>586.4</td>
<td>4.701E+03</td>
<td>75.11</td>
<td>$\Omega$ cm$^2$</td>
</tr>
<tr>
<td>CPE$_{dl}$</td>
<td>3.493E-06</td>
<td>49.63E-09</td>
<td>2.949E-06</td>
<td>6.283E-03</td>
<td>4.139E-06</td>
<td>53.22E-09</td>
<td>S s cm$^{-2}$</td>
</tr>
<tr>
<td>CPE$_{dl}$</td>
<td>851.1E-03</td>
<td>5.159E-03</td>
<td>5.876E-03</td>
<td>6.283E-03</td>
<td>886.6E-03</td>
<td>4.567E-03</td>
<td>S s cm$^{-2}$</td>
</tr>
<tr>
<td>CPE$_{dl}$</td>
<td>112.9E-09</td>
<td>11.08E-09</td>
<td>53.01E-09</td>
<td>4.976E-09</td>
<td>145.1E-09</td>
<td>17.04E-09</td>
<td>S s cm$^{-2}$</td>
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<tr>
<td>CPE$_{dl}$</td>
<td>791.2E-03</td>
<td>9.314E-03</td>
<td>818.3E-03</td>
<td>8.893E-03</td>
<td>774.6E-03</td>
<td>11.09E-03</td>
<td>S s cm$^{-2}$</td>
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</tbody>
</table>

**Fig. 7.** Evolution of sol–gel film resistance ($R_{SG}$) (a) and polarization resistance ($R_p$) (b) during immersion in 0.005 M NaCl.
containing films is sufficiently higher confirming superior stability and barrier properties. The best performance is revealed in the case of the sol–gel system doped with 8-HQ after the hydrolysis process. The evolution of polarization resistance of different samples is demonstrated in Fig. 7b. Again the highest value is obtained in the case of hybrid coating with 8-HQ added after the hydrolysis.

The higher corrosion protection in the case of inhibitor-doped sol–gel coatings is most probably related to blocking of pores and defects by insoluble complex of 8HQ with magnesium as shown in Fig. 4. The difference in behaviour of the sol–gel films doped by 8-HQ to solution A before hydrolysis and to Solution B after hydrolysis cannot be fully explained. However, one can speculate that it is related to different interaction of 8-HQ with the components of the sol–gel formulation (GPTMS, TPOZ and ethylacetoacetate). Such interaction can partly deactivate the inhibitor. This explanation is in line with the fact that addition of 8-HQ to the Solution B after hydrolysis, when silane-based net was already formed, caused less interaction of sol–gel components with 8-HQ and leads to better anticorrosion performance of this sol–gel formulation.

4. Conclusions

Inhibitor-doped hybrid sol–gel coatings were synthesized and applied to magnesium-based alloy AZ31. Addition of corrosion inhibitor 8-HQ to the sol–gel films does not lead to deterioration of barrier properties of the film. Significant difference was found in protective properties of the sol–gel films doped with 0.26 wt.% of 8-HQ in comparison with the undoped films. A more stable film was obtained when 8-HQ was added to solution of GPTMS (Sol B) after acid catalyzed hydrolysis of the precursors. Positive effect of 8-HQ on corrosion performance of AZ31 coated with inhibitor-doped sol–gel films can be explained by formation of insoluble and stable complexes Mg(8-HQ)2 that block the propagation of corrosion closing the microporous and microdefects in the sol–gel film.

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References