

Article

Silica-Based Sol-Gel Coating on Magnesium Alloy with Green Inhibitors

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Abstract: In this work, the performances of several natural organic inhibitors were investigated in a sol-gel system (applied on the magnesium alloy Mg AZ31B substrate). The inhibitors were quinaldic acid (QDA), betaine (BET), dopamine hydrochloride (DOP), and diazolidinyl urea (DZU). Thin, uniform, and defect-free sol-gel coatings were prepared with and without organic inhibitors, and applied on the Mg AZ31B substrate. SEM and EDX were performed to analyze the coating surface properties, the adhesion to the substrate, and the thickness. Electrochemical measurements, including electrochemical impedance spectroscopy (EIS) and anodic potentiodynamic polarization scan (PDS), were performed on the coated samples to characterize the coatings' protective properties. Also, hydrogen evolution measurement—an easy method to measure magnesium corrosion—was performed in order to characterize the efficiency of coating protection on the magnesium substrate. Moreover, scanning vibrating electrode technique (SVET) measurements were performed to examine the efficiency of the coatings loaded with inhibitors in preventing and containing corrosion events in defect areas. From the testing results it was observed that the formulated sol-gel coatings provided a good barrier to the substrate, affording some protection even without the presence of inhibitors. Finally, when the inhibitors' performances were compared, the QDA-doped sol-gel was able to contain the corrosion event at the defect.

Keywords: sol-gel coating; magnesium; magnesium protection; organic inhibitors; corrosion inhibitors

1. Introduction

Sol-gel coatings have been widely used as a surface treatment method, due to their ability to provide unique advantages (both with processing and film properties) over many other conventional coating systems. Their low processing temperature, ease of handling, control of molecular structure and coating properties, and ability to coat complex shapes, etc., makes them an ideal treatment/coating method [1,2]. In the past, organic (as well as organic-inorganic (hybrid)) coatings have been designed with synergistic properties [3]. Numerous functional properties, such as corrosion protection, controlled porosity, anti-reflection, electrochromic, self-cleaning, anti-fogging, superhydrophobicity, and superhydrophilicity have been achieved using sol-gel routes, with applications including coatings for architectural, automotive, electronics, controlled drug release, orthopedic implant, and protection of cultural heritage [4–8].

The main limitation of sol-gel coatings is their inherent low thickness. Sol-gel coatings are typically in the nano to few microns thickness range. Thick coatings are susceptible to cracking, due to the stress generated during drying and thermal treatment [9]. Stresses can be generated due to shrinkage and thermal expansion mismatch [10]. Multiple layers have increased thickness as well as enhanced corrosion protection [11–14]. In addition, coatings can also be loaded with inhibitors, in order to enhance their performance [15]. For example, TiO₂ nanocontainers loaded with

8-hydroxyquinoline in sol-gel coatings were reported to improve corrosion protection properties of aluminum alloy AA 2024T3 [12]. Use of Cerium (Ce^{3+}), lanthanum (La^{3+}) cations, salicylaldehyde, and 8-hydroxyquinoline via hydroxyapatite reservoir, or the use of layered double hydroxides loaded with 2-mercaptobenzothiazole, phosphate, and vanadate to protect AA 2024-T3 have also been reported [16,17].

Limited literature exists on the use of organic corrosion inhibitors for magnesium (Mg) protection. Mg-based alloys have gained significant attention for their potential role in areas requiring light-weight applications [18–20]. Drive for low emission and improved gas mileage have challenged future usage of aluminum and steel alloys. However, high reactivity of Mg has still impeded complete substitution for aluminum and steel, and any future replacement will strongly depend upon its surface control from excess reactivity [21]. Corrosion inhibitors, due to their nature, have huge significance in reducing the reactivity of Mg surfaces. Organic corrosion inhibitors (OCR) are less toxic, with better biodegradability compared to their inorganic counterpart, and little research has been performed on their identification and testing for protection of magnesium substrates. Karavai et al. [22] demonstrated the ability of 1,2,4-triazole to inhibit and confine the corrosion at the defects in a sol-gel system for Mg AZ31. Galio observed that 8-hydroxyquinoline helps in maintaining the barrier properties of a sol-gel coated AZ31 [23]. Diethylenediamine at low concentrations were also demonstrated to inhibit corrosion of AZ31 alloys [24]. Similar observations were made for Mg ZE41 alloys [25]. Kartsonakis et al. [26–28] observed that 2-mercaptobenzothiazole/5-amino-1,3,4-thiadiazole-2-thiol, entrapped in TiO_2 /cerium molybdate, could improve corrosion protection of the Mg ZK10 alloy. The self-repairing properties of polyaniline (in a sol-gel coated Mg AZ31) have also been reported [29]. To contribute to the existing literature (in search for better corrosion protection of Mg), four organic inhibitors were loaded in a sol-gel system and tested for their corrosion inhibiting capabilities. Tests such as electrochemical impedance spectroscopy (EIS), anodic potentiodynamic polarization scan (PDS), hydrogen evolution measurement, and SVET were performed to characterize coating performances.

2. Experimental

2.1. Sol-Gel Formulation

The precursor sol-gel molecules (as shown in Figure 1) were 3-Glycidoxypropyltrimethoxysilane (GCPTS) and N-[3-(Trimethoxysilyl) propyl] ethylenediamine (TMSPED), both purchased from Sigma-Aldrich® (St. Louis, MO, USA). The epoxy and amine groups in the two molecules could also possibly react to form an epoxy-amine system in addition to sol-gel formation. 4.72 g of GCPTS and 2.22 g of TMSPED were initially added to 5 mL of solvent. The solvent (purchased from VWR international®, Batavia, IL, USA, Cat No. BDH1156-4LP) consisted of a mixture of methanol, ethanol, and isopropanol in the weight ratio of ~5:90:5. The precursors and solvent mixture were sonicated for 30 min in a water bath (this mixture is labeled as SG). After, ultrasonication 10 ml of ultra-pure 18 MΩ water was added slowly to 4 mL of SG; to this, 1 mL 1M acetic acid was added to facilitate sol-gel hydrolysis and condensation. For sol-gel with inhibitors, 4 mL of the SG, 9.5 mL water, 1 mL of 1 M acetic acid, and 0.5 mL of 0.1 M inhibitor were used. The total volume of mixture in all the systems was, therefore, the same. Inhibitors used were: quinaldic acid (QDA), betaine (BET), dopamine hydrochloride (DOP), and diazolidinyl urea (DZU). The choice of inhibitors was based on previous research and current laboratory trials (Figure 2). Potentiodynamic scans (PDS) on Mg AZ31 were performed in 3.5 wt % NaCl electrolyte, containing 0.01 M and 0.1 M inhibitor. Quinaldic acid (QDA) have been shown to inhibit corrosion of mild steel [30] and aluminum alloy AA 2024 T3 [31,32]. A porous poly(ether imides) coating on magnesium alloy AZ31 (loaded with QDA) was able to inhibit Mg corrosion, in contrast to a dense layer [33]. Both dopamine (DOP) and betaine (BET) displayed cathodic inhibition at two different concentrations, as seen in Figure 2. Dopamine is known to self polymerize [34,35], possibly resulting in the observed inhibition, whereas betaine has also been reported to be inhibitive [36]. Diazolidinyl urea (DZU) did not display any inhibition during the trials.

However, based on its structure it was chosen to be loaded in the sol-gel system. Coatings were smooth, with no observed aggregate/precipitate of the inhibitors.

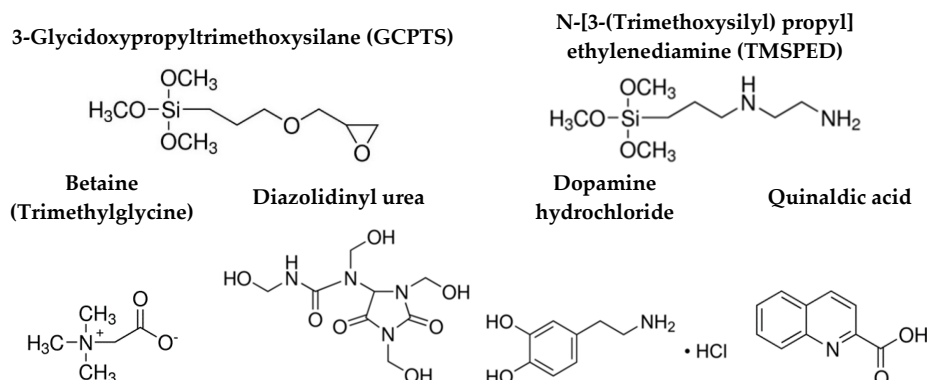


Figure 1. Precursor molecules; and, inhibitors for the sol-gel formulation.

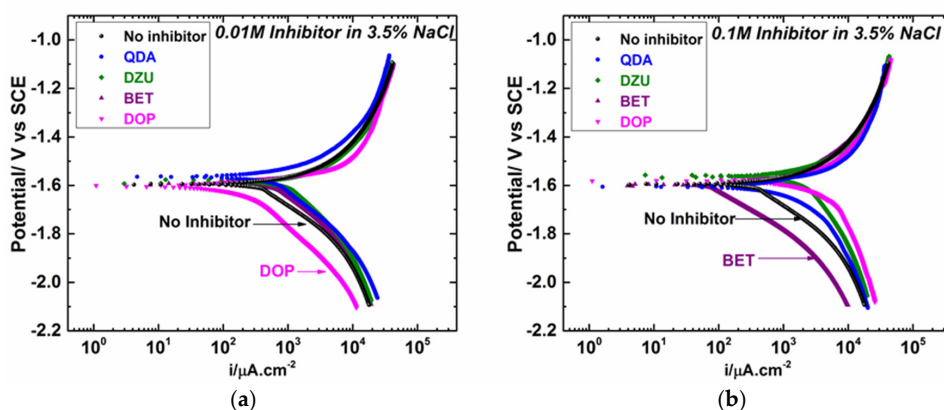


Figure 2. PDS plots of Mg AZ31 in 3.5 wt % electrolyte, containing (a) 0.01 M inhibitor and (b) 0.1 M inhibitor.

2.2. Coatings Preparation

Coatings were applied on the Mg alloy substrate Mg AZ31B (purchased from Magnesium Elektron®, Madison, WI, USA, with the specification AZ31B-F ASTM B107 HT-13021563). The Mg alloy was received in the form of a cylindrical rod with a 3.8 cm diameter. The cylindrical Mg alloy was sliced and cold mounted using an epoxy resin. The mount was such that only one face of the alloy was exposed, whereas the reverse side was protected (but connected with a copper wire) to facilitate electrical connection during electrochemical measurements. Figure 3a displays the Mg sample in the final form before coating. The exposed alloy surface was then polished up to 800 grit SiC paper. After polishing, the samples were washed in 18 MΩ ultra-pure water, followed by acetone, and then dried using an air drier and treated for 60 s in 5% HF solution. The sol-gel coatings were then applied on the treated surfaces, using the drop casting method. The samples were tilted at 45°, and the sol-gel liquid mixture was dropped on the surface using a micro pipette until the sample was covered completely and uniformly by the liquid. Any excess liquid oozed down under gravity. After 5 min, one more layer was added on top of this layer. Thus, two layers were applied. After an hour of room temperature exposure, the coated samples were dried in an oven at 60 °C for 20 min. Coatings were then rested overnight before any tests were performed. Coating without inhibitor was labeled as SG-No inhibitor, whereas coatings loaded with quinaldic acid, betaine, dopamine hydrochloride, and diazolidinyl urea were labeled as SG-QDA, SG-BET, SG-DOP, and SG-DZU, respectively. Surface morphology,

composition, adhesion, and coating thickness were analyzed using SEM and EDX. The sample cross section was polished, and the surface was gold sputtered prior to SEM. All the sol-gel coatings, both without inhibitor (SG-no inhibitor) as well as inhibitor-loaded (SG-inhibitors), were tested for their ability to protect magnesium, both electrochemically and via hydrogen evolution measurement.

2.3. Coating Characterization

Electrochemical measurements performed on coatings were anodic potentiodynamic polarization scan (PDS), electrochemical impedance spectroscopy (EIS), and SVET. The first two techniques were used to characterize coatings as-prepared, whereas SVET measurements were performed to test the ability of the inhibitors to suppress or confine corrosion at defects. For PDS and EIS, measurements were performed using the conventional 3-electrode electrochemical set-up (with the coated substrate as the working electrode (WE)), a platinum mesh as the counter electrode (CE), and a saturated calomel electrode (SCE) as the reference electrode (as is seen in Figure 3b). Measurements were performed with 3.5% NaCl exposed to 7.07 cm² of the working electrode. A Gamry™ potentiostat (IFC 1000) was used for the measurements. Data were acquired using Gamry Framework version 6.21. For EIS experiments a potential perturbation of 10 mV (rms) was applied and the impedance response from 10⁵ to 10^{−2} Hz was measured with an acquisition rate of 10 points per decade. EIS perturbs the sample/coated substrate using a small AC potential. Typically, a sine wave of amplitude ±10 mV (rms) is applied on a system with respect to its open circuit potential over a wide range of frequency, and the response of the current is measured at each frequency. Barrier properties, water uptake, and diffusion rate of organic coating (or the various processes involved during corrosion) can be measured. Anodic PDS was performed by scanning the potential of the working electrode from OCP to 0.5 V, at a scan rate of 1 mV/s. In polarization experiments such as PDS, the potential of the substrate under interest is scanned at a selected rate over a potential range of interest, and the current response is monitored (which can provide corrosion-related information such as corrosion current, corrosion potential, and corrosion rate, etc.).

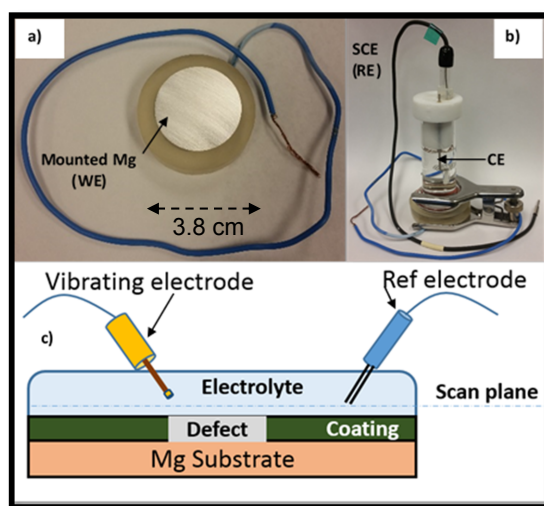


Figure 3. (a) Mounted magnesium AZ31 sample; (b) three electrode electrochemical configurations for EIS and PDS measurements; and, (c) schematic of SVET measurement.

SVET experiments were performed at OCP to measure the current density distribution in and around a defect in coating. SVET is a widely used technique for studying local corrosion [37–39]. A schematic of the SVET is shown in Figure 3c. The instrument was purchased from Applicable Electronics, New Haven, CT, USA. An artificial defect was created to study the effect of inhibitors on coating performance. SVET probe vibrates and scans the area of interest immersed in an electrolyte,

and measures current density distributions above the substrate. The substrate is generally at OCP, though measurements can also be made at an applied external potential. The current density distribution/mapping provides precise information on the location of local cathodes and anodes. Negative current density indicates cathodic regions, whereas positive current density indicates anodic regions (and, hence, corrosive and passive regions can be identified and located). Details of the experiment and measurement procedure are provided in reference [40]. The electrolyte used during SVET measurements was 0.5% NaCl.

Hydrogen evolution measurement (HEM) was other technique used for studying the performance of the coated magnesium alloy. HEM is a simple technique for studying and quantifying Mg corrosion [41,42]. Since 1 mole of hydrogen is generated for each mole of Mg reacted, higher hydrogen evolution indicates higher Mg corrosion and vice versa [43]. Any form of surface protection or reduced Mg surface reactivity would, therefore, decrease the amount of hydrogen evolved from Mg that is in direct contact with an aqueous electrolyte. The efficiency of coating on magnesium can therefore be studied using this technique [44].

3. Results and Discussion

3.1. SEM and EDX Results

Figure 4a–d displays SEM and EDX images of the sol-gel coating. The coating appeared to be intact without any discontinuity, implying good adhesion (Figure 4a,b). The surface displays some roughness (Figure 4c), but on visual inspection it appeared smooth. Thickness of the dry coating varied ranging from ~ 1 to ~ 3 μm . The metal surface was fully covered by the coated layer, implying no coating defect (also seen from the absence of Mg peak in EDX spectrum (Figure 4d) of the coated surface (Figure 4c)).

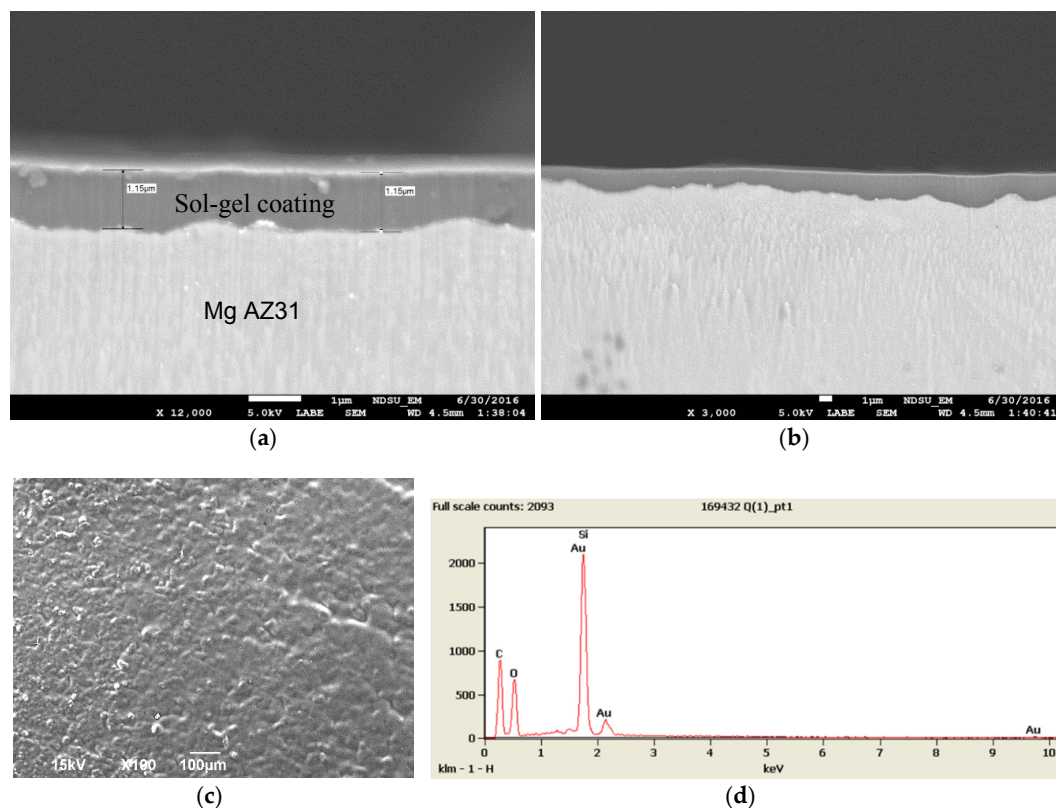


Figure 4. SEM images (a) of the side view at higher magnification ($\times 12,000$); (b) at lower magnification ($\times 3000$); (c) the top view; and, (d) the EDX elemental graph (of sol-gel coating).

3.2. Electrochemical Polarization and EIS Results

It was important to demonstrate that the sol-gel coating offers protective properties to the Mg alloy, and at the same time addition of inhibitors did not adversely affect the coating's protective properties. Therefore, EIS was performed on all systems (i.e., coatings with and without inhibitors), as well as on the bare Mg alloy (results are shown in Figure 5a). Compared to the bare Mg alloy, the coatings displayed almost 3 orders of magnitude higher impedance, clearly suggesting that the coating protected the Mg surface. In addition, no significant changes in the impedance behavior of inhibitor-loaded coating is observed when compared with blank sol-gel coating, implying that the addition of inhibitors did not affect the coating barrier properties. Similar impedance curves are observed for all the coatings; the anodic polarization curves, however, slightly distinguished between coatings. As can be observed from Figure 5b, the coatings loaded with dopamine (SG-DOP) and quinaldic acid (SG-QDA) displayed slightly reduced anodic current during polarization compared to blank sol-gel (SG-no inhibitor), suggesting higher resistance to polarization compared to blank sol-gel, betaine (SG-BET), and diazolidinyl urea (SG-DZU) loaded sol-gel.

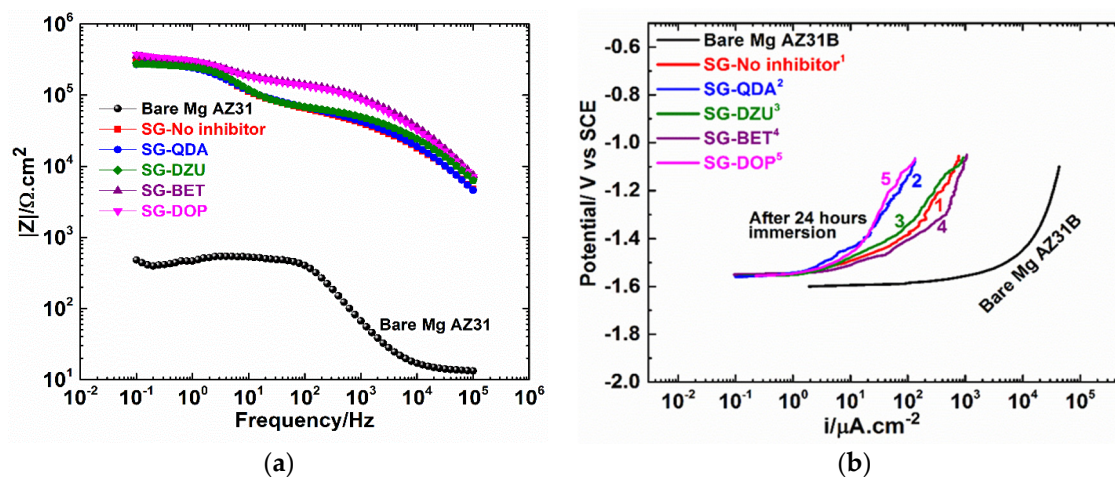


Figure 5. (a) EIS Bode modulus plots and (b) anodic polarization curves, of coatings with and without inhibitors.

3.3. Hydrogen Evolution Measurement (HEM)

The efficiency of sol-gel coating on magnesium was also measured using the HEM technique [44]. Figure 6a is a simple set-up, designed for hydrogen entrapment and measurement, and consisting of an inverted funnel and burette assembly above the experimental sample [43,45]. As seen from Figure 5b, SG-No inhibitors (as well as SG-inhibitor systems) display very low hydrogen evolution compared to bare alloys, indicating that the SG systems were effective at providing resistance to Mg corrosion. Up to 24 h, all the coating systems displayed no hydrogen evolution. After 48 h, some hydrogen evolution was measured for all the systems, implying some Mg exposure. Defects were observed at a few sites; most of the areas, however, were intact. On comparing all the SG systems, only SG-betaine displayed higher hydrogen evolution, compared to SG. The rest of all the SG-inhibitor systems displayed slightly reduced hydrogen evolution, compared to SG.

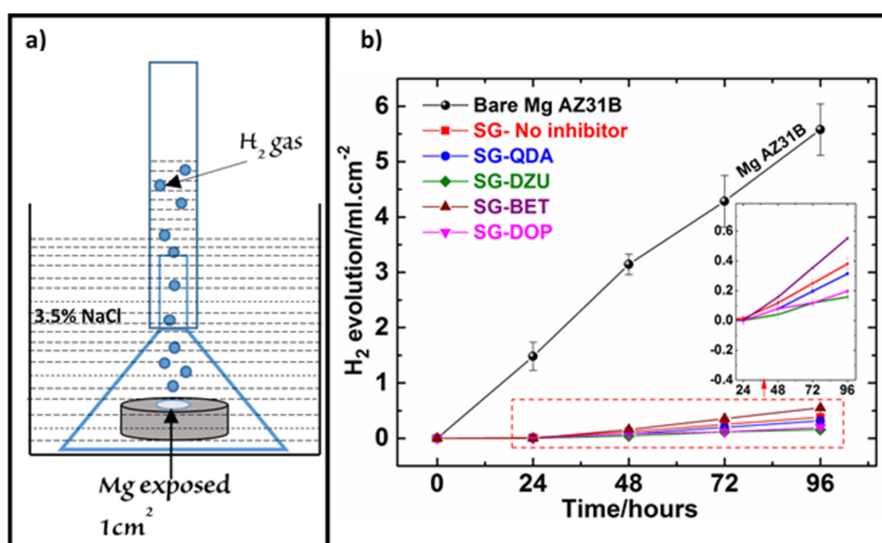


Figure 6. (a) Hydrogen evolution measurement set-up and (b) hydrogen evolution as a function of time for the inhibitors loaded in the sol-gel system.

3.4. Scanning Vibrating Electrode Technique (SVET) Measurements

It was seen in the previous sections that a defect-free coating displayed encouraging barrier results. It was of interest to investigate the effect of inhibitors on defects in coating. Therefore, a small defect was created at the center of the scanning region, to study the effect of inhibitors in containing or inhibiting the defect (created artificially). Figure 7 displays (both in 3D and 2D) the SVET mapping for all the systems studied under defect conditions. For convenience of comparison, the scales (as well as color codes) for all the figures are same. Moreover, the defects are circled in 2D maps. As seen from the mappings, the SG coating without inhibitor (SG-No inhibitor in Figure 7a,b) displays cathodic behavior at the defect and its periphery, as well as an anodic behavior outside the defect after 24 h of constant immersion in 0.5% NaCl. Depending upon the inhibitor incorporation, the coating displayed either improved performance or further deteriorated the protective and inhibitive nature of the coatings. For SG-dopamine (SG-DOP) coating, the corrosion activity is located throughout the coating (including the defect, such that the defect itself cannot be identified from the mapping). Both anodic and cathodic activities are seen throughout the mapping area, implying inability of the inhibitor at containing the defect. SG-betaine (SG-BET) coating displayed concentrated regions of cathodic and anodic activity just outside the defect, as seen from Figure 7e,f. Clear concentrated anodic and cathodic regions were seen with reduction in their activity (with increasing distance from their respective centers). For the SG-urea system (SG-DZU), higher cathodic activities are seen at and near the defect, whereas both anodic and cathodic activities are seen throughout the other areas. Intense anodic activities are also seen at certain random areas from the surface mapping. The abilities of SG-DOP, SG-BET, and SG-DZU of containing corrosion at the defects were therefore poor. In contrast, the sol-gel coating containing quinaldic acid (SG-QDA in Figure 6i,j) displayed anodic activity at the defect, whereas all other regions displayed cathodic activity (implying that the SG-QLDA coating behaved passively during the exposure period and no any anodic activity were observed outside the defect). From the 3D plot and 2D current values (associated to the color codes), it is observed that the anodic reaction at the defect is concentrated mostly at the center of the defect, whereas the defect edges are mostly cathodic, with increasing cathodic activity further away towards the coating. This suggests that quinaldic acid (QDA) was clearly more efficient in containing defects and enhancing coating passivity compared to the other inhibitor tested. It has been proposed that quinaldic acid can form a complex coordination with metal [33]. The complex coordination possibly prevented a lateral attack at the defect, in contrast to other inhibitors.

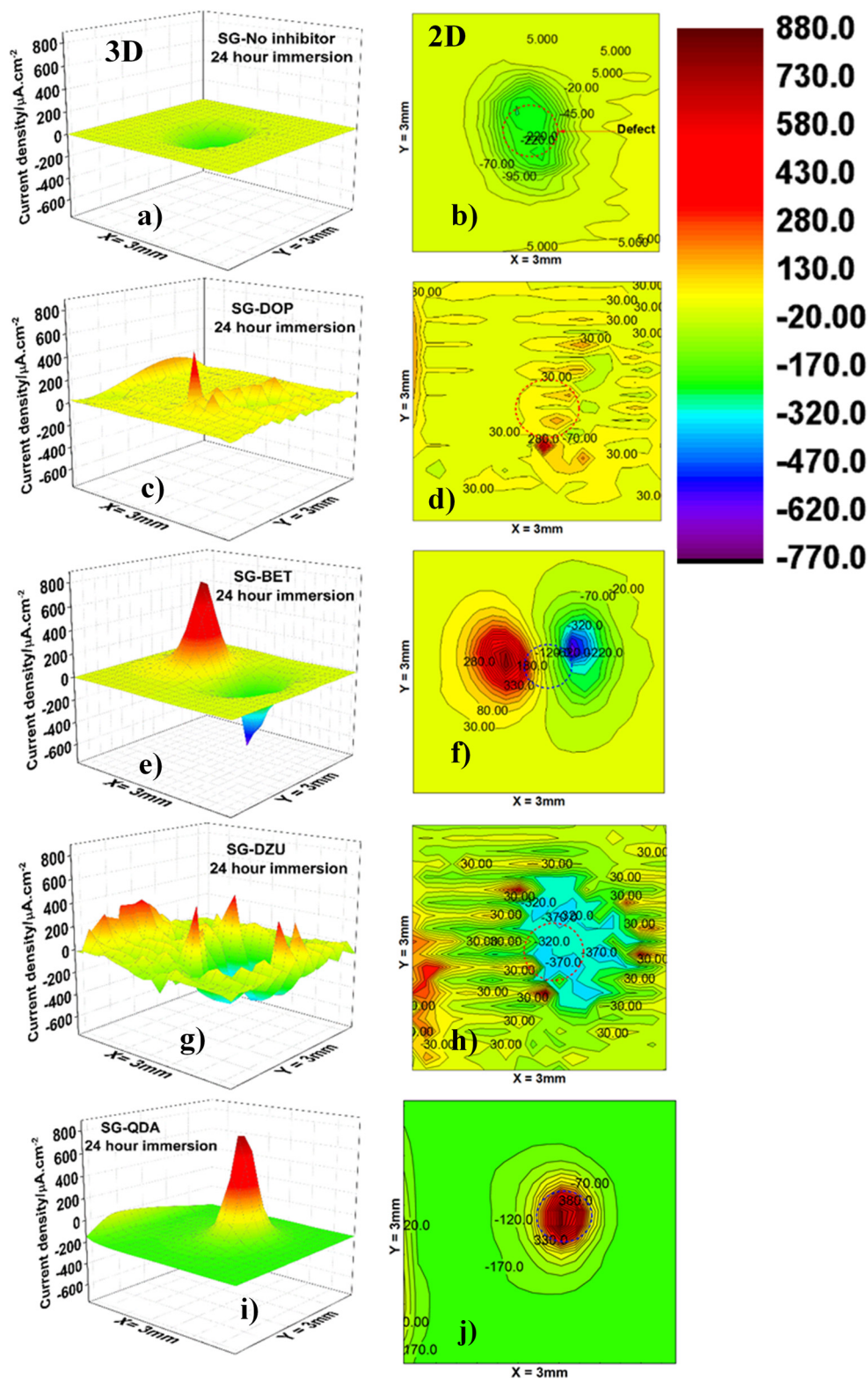


Figure 7. SVET 3D and 2D mapping of sol-gel coated Mg AZ31B, with and without inhibitors.

4. Conclusions

In search of a viable strategy for magnesium corrosion protection, a silica based sol-gel system was formulated, and the corrosion inhibiting performance of a few organic inhibitors loaded in

the sol-gel system was studied on Mg AZ31 substrate. Coatings were defect-free and provided enhanced protection, as observed from the PDS and EIS results (hydrogen evolution measurements also complemented findings from the electrochemical measurements). Of the four inhibitors tested using SVET under defect condition, only quinaldic acid (QDA) displayed improvement compared to the control (SG-No inhibitor) and maintained coating passivity during the 24-hour exposure period, with no measured anodic activity outside the defect.

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Author Contributions: Vinod Upadhyay and Dante Battocchi conceived and designed the experiments; Zachary Bergseth and Brett Kelly performed global electrochemical, and hydrogen evolution experiments. Vinod Upadhyay performed SVET experiments. Vinod Upadhyay and Dante Battocchi analyzed the data and wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wang, D.; Bierwagen, G.P. Sol-gel coatings on metals for corrosion protection. *Prog. Org. Coat.* **2009**, *64*, 327–338. [[CrossRef](#)]
2. Figueira, R.B.; Silva, C.J.R.; Pereira, E.V. Organic-inorganic hybrid sol-gel coatings for metal corrosion protection: A review of recent progress. *J. Coat. Technol. Res.* **2015**, *12*, 1–35. [[CrossRef](#)]
3. Dislich, H. Sol-gel: Science, processes and products. *J. Non. Cryst. Solids* **1986**, *80*, 115–121. [[CrossRef](#)]
4. Aegerter, M.A.; Almeida, R.; Soutar, A.; Tadanaga, K.; Yang, H.; Watanabe, T. Coatings made by sol-gel and chemical nanotechnology. *J. Sol.-Gel Sci. Technol.* **2008**, *47*, 203–236. [[CrossRef](#)]
5. Faustini, M.; Nicole, L.; Boissière, C.; Innocenzi, P.; Sanchez, C.; Grosso, D. Hydrophobic, antireflective, self-cleaning, and antifogging sol-gel coatings: An example of multifunctional nanostructured materials for photovoltaic cells. *Chem. Mater.* **2010**, *22*, 4406–4413. [[CrossRef](#)]
6. Mahadik, S.A.; Pedraza, F.; Vhatkar, R.S. Silica based superhydrophobic coating for long-term industrial and domestic applications. *J. Alloys Compd.* **2016**, *663*, 487–493. [[CrossRef](#)]
7. Liu, S.; Liu, X.; Latthe, S.S.; Gao, L.; An, S.; Yoon, S.S.; Liu, B.; Xing, R. Self-cleaning transparent superhydrophobic coatings through simple sol-gel processing of fluoroalkylsilane. *Appl. Surf. Sci.* **2015**, *351*, 897–903. [[CrossRef](#)]
8. Dislich, H.; Non, J. Sol-Gel 1984–2004 (?). *Cryst. Solids* **1985**, *73*, 599–612. [[CrossRef](#)]
9. Damborenea, J.; Pellegrini, N.; Sanctis, O.; Durán, A. Electrochemical behaviour of SiO₂ sol-gel coatings on stainless steel. *J. Sol-Gel Sci. Technol.* **1995**, *4*, 239–244. [[CrossRef](#)]
10. Hu, R.-G.; Zhang, S.; Bu, J.-F.; Lin, C.-J.; Song, G.-L. Recent progress in corrosion protection of magnesium alloys by organic coatings. *Prog. Org. Coat.* **2012**, *73*, 129–141. [[CrossRef](#)]
11. Tan, A.L.K.; Soutar, A.M.; Annergren, I.F.; Liu, Y.N. Multilayer sol-gel coatings for corrosion protection of magnesium. *Surf. Coat. Technol.* **2005**, *198*, 478–482. [[CrossRef](#)]
12. Mekeridis, E.D.; Kartsonakis, I.A.; Kordas, G.C. Multilayer organic-inorganic coating incorporating TiO₂ nanocontainers loaded with inhibitors for corrosion protection of AA2024-T3. *Prog. Org. Coat.* **2012**, *73*, 142–148. [[CrossRef](#)]
13. López, D.A.; Rosero-Navarro, N.C.; Ballarre, J.; Durán, A.; Aparicio, M.; Ceré, S. Multilayer silica-methacrylate hybrid coatings prepared by sol-gel on stainless steel 316L: Electrochemical evaluation. *Surf. Coat. Technol.* **2008**, *202*, 2194–2201. [[CrossRef](#)]
14. López, A.J.; Rams, J.; Ureña, A. Sol-gel coatings of low sintering temperature for corrosion protection of ZE41 magnesium alloy. *Surf. Coat. Technol.* **2011**, *205*, 4183–4191. [[CrossRef](#)]
15. Wittmar, A.; Wittmar, M.; Caparrotti, H.; Veith, M. The influence of the inhibitor particle sizes to the corrosion properties of hybrid sol-gel coatings. *J. Sol-Gel Sci. Technol.* **2011**, *59*, 621–628. [[CrossRef](#)]
16. Snihirova, D.; Lamaka, S.V.; Taryba, M.; Salak, A.N.; Kallip, S.; Zheludkevich, M.L.; Ferreira, M.G.S.; Montemor, M.F. Hydroxyapatite microparticles as feedback-active reservoirs of corrosion inhibitors. *ACS Appl. Mater. Interfaces* **2010**, *2*, 3011–3022. [[CrossRef](#)] [[PubMed](#)]

17. Tedim, J.; Poznyak, S.K.; Kuznetsova, A.; Raps, D.; Hack, T.; Zheludkevich, M.L.; Ferreira, M.G.S. Enhancement of active corrosion protection via combination of inhibitor-loaded nanocontainers. *ACS Appl. Mater. Interfaces* **2010**, *2*, 1528–1535. [[CrossRef](#)] [[PubMed](#)]
18. Mordike, B.L.; Ebert, T. Magnesium properties—application—potential. *Mater. Sci. Eng.* **2001**, *302*, 37–45. [[CrossRef](#)]
19. Friedrich, H.; Schumann, S. Research for a “new age of magnesium” in the automotive industry. *J. Mater. Chem.* **2001**, *117*, 276–281. [[CrossRef](#)]
20. Aghion, E.; Bronfin, B. Magnesium alloys development towards the 21st century. *Mater. Sci. Forum* **2000**, *350*, 19–30. [[CrossRef](#)]
21. Song, G.L.; Atrons, A. Corrosion mechanisms of magnesium alloys. *Adv. Eng. Mater.* **1999**, *1*, 11–33. [[CrossRef](#)]
22. Karavai, O.V.; Bastos, A.C.; Zheludkevich, M.L.; Taryba, M.G.; Lamaka, S.V.; Ferreira, M.G.S. Localized electrochemical study of corrosion inhibition in microdefects on coated AZ31 magnesium alloy. *Electrochim. Acta* **2010**, *55*, 5401–5406. [[CrossRef](#)]
23. Galio, A.F.; Lamaka, S.V.; Zheludkevich, M.L.; Dick, L.F.P.; Müller, I.L.; Ferreira, M.G.S. Inhibitor-doped sol-gel coatings for corrosion protection of magnesium alloy AZ31. *Surf. Coat. Technol.* **2010**, *204*, 1479–1486. [[CrossRef](#)]
24. Lamaka, S.V.; Xue, H.B.; Meis, N.N.A.H.; Esteves, A.C.C.; Ferreira, M.G.S. Fault-tolerant hybrid epoxy-silane coating for corrosion protection of magnesium alloy AZ31. *Prog. Org. Coat.* **2015**, *80*, 98–105. [[CrossRef](#)]
25. Ivanou, D.K.; Yasakau, K.A.; Kallip, S.; Lisenkov, A.D.; Sarykevich, M.; Lamaka, S.V.; Ferreira, M.G.S.; Zheludkevich, M.L. Active corrosion protection coating for a ZE41 magnesium alloy created by combining PEO and sol-gel techniques. *RSC Adv.* **2016**, *6*, 12553–12560. [[CrossRef](#)]
26. Kartsonakis, I.A.; Balaskas, A.C.; Koumoulos, E.P.; Charitidis, C.A.; Kordas, G. ORMOSIL-epoxy coatings with ceramic containers for corrosion protection of magnesium alloys ZK10. *Prog. Org. Coat.* **2013**, *76*, 459–470. [[CrossRef](#)]
27. Kartsonakis, I.A.; Koumoulos, E.P.; Charitidis, C.A.; Kordas, G. Hybrid organic-inorganic coatings including nanocontainers for corrosion protection of magnesium alloy ZK30. *J. Nanopart. Res.* **2013**, *15*, 1871. [[CrossRef](#)]
28. Kartsonakis, I.A.; Balaskas, A.C.; Kordas, G.C. Influence of TiO₂ nanocontainers on hybrid organic-inorganic coatings for corrosion protection of magnesium alloy. *Int. J. Struct. Integr.* **2013**, *4*, 127–142. [[CrossRef](#)]
29. Wang, H.; Akid, R.; Gobara, M. Scratch-resistant anticorrosion sol-gel coating for the protection of AZ31 magnesium alloy via a low temperature sol-gel route. *Corros. Sci.* **2010**, *52*, 2565–2570. [[CrossRef](#)]
30. Ebenso, E.E.; Obot, I.B.; Murulana, L.C. Quinoline and its derivatives as effective corrosion inhibitors for mild steel in acidic medium. *Int. J. Electrochem. Sci.* **2010**, *5*, 1574–1586.
31. Poznyak, S.K.; Tedim, J.; Rodrigues, L.M.; Salak, A.N.; Zheludkevich, M.L.; Dick, L.F.P.; Ferreira, M.G.S. Novel inorganic host layered double hydroxides intercalated with guest organic inhibitors for anticorrosion applications. *ACS Appl. Mater. Interfaces* **2009**, *1*, 2353–2362. [[CrossRef](#)] [[PubMed](#)]
32. Lamaka, S.V.; Zheludkevich, M.L.; Yasakau, K.A.; Montemor, M.F.; Ferreira, M.G.S. High effective organic corrosion inhibitors for 2024 aluminium alloy. *Electrochim. Acta* **2007**, *52*, 7231–7247. [[CrossRef](#)]
33. Scharnagl, N.; Blawert, C.; Dietzel, W. Corrosion protection of magnesium alloy AZ31 by coating with poly(ether imides) (PEI). *Surf. Coat. Technol.* **2009**, *203*, 1423–1428. [[CrossRef](#)]
34. Zheng, W.; Fan, H.; Wang, L.; Jin, Z. Oxidative self-polymerization of dopamine in an acidic environment. *Langmuir* **2015**, *31*, 11671–11677. [[CrossRef](#)] [[PubMed](#)]
35. Lee, H.; Dellatore, S.M.; Miller, W.M.; Messersmith, P.B. Mussel-inspired surface chemistry for multifunctional coatings. *Science* **2007**, *318*, 426–430. [[CrossRef](#)] [[PubMed](#)]
36. Howson, M.R. Removal of Sulfides using Chlorite and an Amphoteric Ammonium Betaine. U.S. Patent 5,082,576, 21 January 1992.
37. Isaacs, H.S.; Kendig, M.W. Determination of surface inhomogeneties using a scanning probe impedance technique. *Corrosion* **1980**, *36*, 269–274. [[CrossRef](#)]
38. Jadhav, N.; Vetter, C.A.; Gelling, V.J. Characterization and electrochemical investigations of polypyrrole/aluminum flake composite pigments on AA 2024-T3 substrate. *ECS Trans.* **2012**, *41*, 75–89.
39. Jadhav, N.; Vetter, C.A.; Gelling, V.J. The effect of polymer morphology on the performance of a corrosion inhibiting polypyrrole/aluminum flake composite pigment. *Electrochim. Acta* **2013**, *102*, 28–43. [[CrossRef](#)]

40. Upadhyay, V.; Qi, X.; Wilson, N.; Battocchi, D.; Bierwagen, G.; Forsmark, J. Electrochemical characterization of coated self-piercing rivets for magnesium applications. *SAE Int. J. Mater. Manuf.* **2016**, *9*, 187–199. [[CrossRef](#)]
41. Frankel, G.S.; Samaniego, A.; Birbilis, N. Evolution of hydrogen at dissolving magnesium surfaces. *Corros. Sci.* **2013**, *70*, 104–111. [[CrossRef](#)]
42. Song, G.; Atrens, A.; StJohn, D. An hydrogen evolution method for the estimation of the corrosion rate of magnesium alloys. *Magnes. Technol.* **2001**, *2001*, 254–262. [[CrossRef](#)]
43. Song, G.; Atrens, A. Understanding magnesium corrosion—A framework for improved alloy performance. *Adv. Eng. Mater.* **2003**, *5*, 837–858. [[CrossRef](#)]
44. Birbilis, N.; Williams, G.; Gusieva, K.; Samaniego, A.; Gibson, M.A.; McMurray, H.N. Poisoning the corrosion of magnesium. *Electrochem. Commun.* **2013**, *34*, 295–298. [[CrossRef](#)]
45. Lin, J.; Upadhyay, V.; Qi, X.; Battocchi, D.; Bierwagen, G.P. Hydrogen evolution and early blistering from magnesium-rich primers on AA2024-T3. *Corrosion* **2016**, *72*, 377–383. [[CrossRef](#)]



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