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# **Corrosion inhibition of pure Mg containing a high level of iron impurity in pH neutral NaCl solution**

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## **Abstract**

Three sodium salts of 2,5-pyridinedicarboxylate, 3-methylsalicylate and fumarate were studied as corrosion inhibitors for pure magnesium containing a high level (342 ppm) of Fe impurity. The inhibition effect of the three inhibitors was evaluated by means of hydrogen evolution, electrochemical and surface analysis techniques. Significant reduction in corrosion rate was revealed for of all the tested inhibitors in neutral pH NaCl electrolyte. 2,5-pyridinedicarboxylate and fumarate showed characters for mixed-type inhibitors, while 3-methylsalicylate performed more as a cathodic inhibitor, complying with the iron re-deposition model, where the electrochemical activity of iron-rich particles was effectively suppressed.

**Key words:** Magnesium; Iron Impurity; Iron Re-deposition; Corrosion Inhibitor;

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## 1. Introduction

Magnesium (Mg) and its alloys are characterized by several intrinsic properties (*e.g.* low density, high specific strength, electromagnetic shielding, biodegradability and recyclability, *etc.*), which make them materials of choice in transportation, electronics, bio-medical and battery applications [1-4]. However, relatively poor corrosion performance restricts the broader implementation of Mg alloys in those fields.

One of the critical factors that influence the corrosion behavior of Mg is the impurities that become incorporated into Mg alloys during the production processes [5-8]. The detrimental impurities for pure Mg and their tolerance limits were firstly addressed decades ago by Hanawalt *et al.*: Ni<5 ppm, Cu<1000-1300 ppm, Fe<170 ppm (ppm is denoted as mass percentage here and after) [9-11]. Among known impurities, iron (Fe) is definitely the most prevalent one due to its low solubility and presence at virtually every production step, *e.g.* tools and casting pots [8, 10]. As the content of Fe exceeds its solubility, the melted Fe precipitates as individual particles and gets embed in the Mg matrix because of the narrow solidification interval manifested in the Mg-Fe phase diagram [12, 13]. The standard reduction potential of Fe is by far more positive than that of Mg (Fe:  $-0.78 V_{\text{nhe}}$ ; Mg:  $-2.37 V_{\text{nhe}}$ [1]), thus micron or sub-micron Fe inclusions would serve as active cathodes in the micro galvanic corrosion cell. As a consequence, the corrosion of Mg tends to be initialized from individual spots and spreads towards the uncontaminated region in the Mg matrix [14-16].

In recent reports, Williams *et al.* investigated the influence of Fe concentration on the corrosion behavior of magnesium in aqueous NaCl solution, using scanning vibrating electrode technique (SVET) [14]. They confirmed that the Fe impurity acts as a persistent cathode during Mg corrosion, and claimed that the formation and propagation of the dark regions are intimately related with the content of Fe. Filiform corrosion (FFC) occurred on the sample with lower amount of Fe impurity ( $\leq 80$  ppm Fe), while such type of corrosion is replaced by disc-form corrosion as the Fe impurity increases to more than 280 ppm. Taheri *et al.* found Fe-rich particles in the outer columnar mixed magnesium oxide-hydroxide layer and asserted the corroded surface containing the sank Fe particles acting as the cathode with respect to the intact region. Hence, they concluded that the corrosion process of Mg is catalyzed by the nominal Fe impurity (50ppm) [17]. An iron-redeposition mechanism was proposed by Höche

*et al.*. They explained that the Fe inclusion could be detached from Mg substrate due to the undermining of Mg, followed by an electrochemical self-corrosion process (forming  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  or  $\alpha\text{-Fe}_2\text{O}_3$ ). Chemical and electrochemical reduction of oxidized Fe species would result in replating pure Fe “*in statu nascendi*” on Mg surface with even higher electrochemical activity than initial Fe-rich inclusion, enlarging the cathode area and accelerating the hydrogen evolution reaction (HER) via Heyrovsky mechanism [18]. Similar conclusion on influence of Fe-rich intermetallic particles has been recently made by Marcus’ group [19].

Application of corrosion inhibitors for slowing down the corrosion process of metallic-based materials is a straightforward and effective method. In the past decades, numerous chemicals have already been identified as excellent corrosion inhibitors for aluminum, steel, copper and their alloys [20-22]. However, only a limited number of chemicals have been reported until recently to be effective for Mg alloys, since Mg is chemically active with respect to most engineering metallic materials and even carbon fiber reinforced polymer/plastic (CFRP). The fully occupied outermost orbital (2p) restricts Mg accepting electrons from donative molecules forming stable chemical bonds [23]. In terms of the substance category, the reported Mg corrosion inhibitors can generally be divided into inorganic and organic. Fluorides (*e.g.*  $\text{CaF}_2$  and  $\text{NaF}$  [24]), nitrates ( $\text{Zn}(\text{NO}_3)_2$  [24-26]), phosphates (*e.g.*  $(\text{NH}_4)_2\text{HPO}_4$  [24]) and silicate (*e.g.*  $\text{Na}_2\text{SiO}_3$  [27]) have been proved advantageous inorganic inhibitors for Mg alloys. As explained by Kartsonakis and Chen *et al.*, the inhibition by most inorganic substances can be correlated with the formation of chemical conversion films that seal the intrinsic defects in magnesium hydroxide or oxide layers [24, 28]. Moreover, controversial results about the inhibition effect of rare earth elements have been reported in the recent literature. Corrosion promotion was revealed for  $\text{CeCl}_3$  and  $\text{LaCl}_3$  on most Mg alloys [29, 30], which is completely opposite to the results obtained from  $\text{Ce}(\text{NO}_3)_3$  and  $\text{La}(\text{NO}_3)_3$  on AZ63 and AM60 [28, 31]. Hence, the corrosion inhibition effects of  $\text{Ce}(\text{NO}_3)_3$  and  $\text{La}(\text{NO}_3)_3$  were resorted to the presence of nitrate rather than the rare earth elements. Inhibiting effect of a number of organic inhibitors has also been investigated [23-25, 32-40]. The inhibition mechanism of some mentioned organic molecules is ascribed to physical (electrostatic interaction) adsorption between functional groups (*e.g.* hydroxyl [41], carbonyl [32, 34] and carboxylate [33] *etc.*) of inhibitor molecule and  $\text{Mg}^{2+}$ , whereas formation of insoluble complex between  $\text{Mg}^{2+}$  or

metallic ions of the second/tertiary phase and electron donator(s) (*e.g.* O [35], N [23] and S [37] atom *etc.*) has been suggested for the other inhibitor compounds. Most recently, a new inhibition concept is proposed by Lamaka *et al.*, in which re-deposition of iron is significantly suppressed by iron complex agents [42]. That work was followed by a comprehensive screening of more than one hundred substances (all possessing the capability to bind  $\text{Fe}^{3+}/\text{Fe}^{2+}$ ) towards their ability to suppress Mg dissolution [29]. Sodium salts of 2,5-pyridinedicarboxylate, 3-methylsalicylate and fumarate were found to be highly efficient corrosion inhibitors for three grades of pure Mg. Remarkable, that inhibiting effect of 2,5-pyridinedicarboxylate, 3-methylsalicylate and fumarate is rather universal, *i.e.* it extended not only to pure Mg but also to six industrially relevant Mg alloys (WE43, ZE41, Electron 21, AZ31, AZ91 and AM50).

In this paper, the inhibition mechanisms of these three environmentally friendly compounds are studied upon commercially pure Mg (99.98 wt.%) containing high amount of Fe impurities (342ppm). Hydrogen evolution and various electrochemical techniques were applied to study the inhibition efficiencies of the selected inhibitors. The status of Fe impurity in Mg substrate, the corroded surface morphologies without and with inhibitor protection and the corrosion product layers were characterized with scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), SKPFM and UV-Vis-NIR spectroscopy. Based on the obtained results, different inhibition mechanisms considering the Fe impurities were proposed.

## **2. Experimental**

### **2.1. Materials and reagents**

As-cast pure magnesium (Mg) was studied in present study. The chemical composition determined by Spark OES (Spark analyser M9, Spectro Ametek, Germany) is 0.00402 wt.% Al, 0.00037 wt.% Cu, 0.0342 wt.% Fe, 0.00237 wt.% Mn, <0.0002 wt.% Ni, 0.0207 wt.% Si and Mg balance. In order to obtain an efficient feedback from hydrogen evolution experiment, Mg chips (with area-to-mass ratio of  $211 \pm 31 \text{ cm}^2/\text{g}$ ) were sliced from the bulk material by a turning lathe. Note that a diamond cutting tool was utilized for avoiding the contamination by additional critical elements, and the cutting parameters including feed rate, engagement and cutting speed were fixed to guarantee uniform Mg ribbons. Rectangular specimens ( $15 \times 15 \times 4 \text{ mm}^3$ ) were used in the electrochemical measurements. Prior to electrochemical measurements,

specimens were ground with emery papers up to 1200 grit, rinsed with deionized water and ethanol, and eventually dried in pressured air flow at room temperature.

The inhibitor reagents used in current work are: 2,5-pyridinedicarboxylic acid ( $C_7H_5NO_4$ , ACS reagent >98%, Sigma-Aldrich Chemie GmbH, Germany), 3-methylsalicylic acid ( $CH_3C_3H_6(OH)CO_2H$ , Reagent Plus, 99%, Sigma-Aldrich Chemie GmbH, Germany), fumaric acid ( $HOOCCH=CHCOOH$ , 98%, Alfa Aesar, Germany). The structural formulae of selected inhibitors are shown in Fig. 1. All the inhibitors were dissolved in 0.5 wt.% NaCl solution (denoted as blank solution here and after), and standard NaOH (1 M) was used to adjust the pH value of the solution until the neutral level (pH: 6.8-7.2). The pH value of prepared solutions was monitored by Metrohm 691 pH meter throughout the whole preparation process.

## 2.2. Hydrogen evolution

Hydrogen evolution tests were carried out upon 0.5 g Mg chips using eudiometers (NS45/27, Neubert-Glas, Germany). Unlike typical burette-funnel setup, eudiometers are an enclosed system that prevents the interference (*e.g.*  $CO_2$  and  $O_2$  *etc.*) from ambient environment, which guarantees the correctness of the measured results. In order to investigate the influence of the inhibitor concentration on inhibition efficiency, 5 mM, 10 mM, 50 mM and 100 mM of each inhibitor was added into the blank 0.5 wt.% NaCl electrolyte respectively. All tests performed for 24 hours without break, and the volume of released hydrogen was recorded manually. All experiments are conducted at room temperature (between 22-24 °C), and the volume of  $H_2$  resided in the eudiometer and dissolved in the aqueous medium were not considered, since the solubility of  $H_2$  in water is about 0.0016 g/kg at room temperature with 1 atm pressure (*i.e.* max. 16 ml for current condition). The values of inhibiting efficiency ( $IE_H$ ) were calculated using the following equation:

$$IE_H(\%) = \frac{V_{H_2}^0 - V_{H_2}^{Inh}}{V_{H_2}^0} \times 100\%$$

in which  $V_{H_2}^0$  and  $V_{H_2}^{Inh}$  are the released  $H_2$  volume with immersion in NaCl solution without and with addition of the various concentrations of inhibitors.

## 2.3. Electrochemical measurements

All the electrochemical characterizations were performed in blank NaCl solution (0.5 wt.%) without and with adding 50 mM inhibitors. A conventional three-electrode system with Gamry

Interface 1000 potentiostat was used. In this system, Mg coupons with 1 cm<sup>2</sup> exposed surface area were employed as the working electrode, along with a platinum wire counter electrode and a saturated Ag/AgCl reference electrode.

After 10min OCP stabilization, potentiodynamic polarization tests were performed applying a potential from OCP to -300 mV and 300 mV at a scan rate of 0.5 mV/s, respectively. Cathodic extrapolation was applied for calculating the corrosion current, and the inhibiting efficiency (IE<sub>P</sub>) can be obtained according to the following equation:

$$IE_P(\%) = \frac{I_{Corr}^0 - I_{Corr}^{Inh}}{I_{Corr}^0} \times 100\%$$

where  $I_{Corr}^0$  and  $I_{Corr}^{Inh}$  represent the corrosion current density of Mg substrate in blank NaCl solution and inhibitor containing solutions, respectively.

AC impedance measurements were carried out at OCP with applying an amplitude of 10 mV RMS sinusoidal perturbation over the frequency range from 10<sup>5</sup> Hz to 10<sup>-2</sup> Hz. Commercial software Zview was utilized for analyzing the obtained impedance spectra, and the inhibiting efficiency (IE<sub>I</sub>) was calculated as the given equation:

$$IE_I(\%) = \frac{R_{all}^{Inh} - R_{all}^0}{R_{all}^{Inh}} \times 100\%$$

where  $R_{all}^0$  and  $R_{all}^{Inh}$  ( $R_{all}=R_f+R_{ct}$ ) indicate the overall corrosion impedance of Mg immersed in blank NaCl solution and inhibitor containing solutions, respectively.

#### 2.4. AFM/SKPFM analysis

A commercial Atomic Force Microscope (AFM) Digital Instruments NanoScope III system equipped with Extender™ Electronic Module was used for acquiring topography and Volta potential on the polished Mg surface. The AFM images were acquired in tapping mode with highly doped Si probes coated with Pt purchased from BudgetSensors. The 40 × 40 micron maps with 256 × 256 points were obtained. At least three different places on samples have been scanned in order to ensure reproducibility. The principle of Scanning Kelvin Probe Force Microscopy (SKPFM) analysis is based upon the theory according to which a contact potential difference or Volta potential difference (VPD) arises between two metals having different work functions if they are electronically connected [43]. With some limitations, one can correlate this quantity with electrochemical activity of metals and study properties of the oxide films

[44-46]. During SKPFM measurements the tip was lifted off the surface to a distance of 100 nm, and an AC voltage of 5000 mV at the resonance frequency of the cantilever had been applied between the tip and the sample to cause electrostatically induced oscillations. Using the nulling technique the Volta potential difference between the alloy surface and the tip was measured. Volta potential values were referenced versus a standard surface of pure Ni.

Sample's preparation for AFM measurements has been as follows. At first, all metallic substrates were grinded on SiC sand papers and polished via SiO<sub>2</sub> suspension (100 nm). Afterwards, the polished samples were cleaned on a soft tissue soaked in 2-propanol, rinsed with plenty of 2-propanol, dried and stored in a desiccator before conducting the measurements.

## **2.5. Morphology and composition characterization**

A scanning electron microscope (Tescan Vega3) equipped with an energy dispersive X-ray spectrometer (EDS) was used for examining the raw well-polished Mg surface and the surface morphologies after exposure to blank NaCl (0.5 wt.%) solution in absence and presence of inhibitors after varied immersion periods. The adsorption of inhibitors on Mg surface was verified using UV-Vis-NIR spectrometer (Cary 5000, Agilent, USA) at room temperature. Prior to measuring the surfaces of the bulk Mg specimens, the reference spectra of the inhibitor chemicals were recorded. Diffuse reflectance accessory (DRA) and praying mantis accessory were applied for detecting the surface and chemical powders specimens, respectively. The spectra for both types were recorded over the wavelength of 200-800 nm. All the measurements were corrected by subtracting the background noise. A crossbeam workstation AURIGA 40 (Zeiss, Germany) equipped with a focused ion beam (FIB) column and electron microscopy (SEM) was used for the cutting and observation for the characteristic regions on the corroded surface. EDAX (Ametek GmbH, Wiesbaden, Germany) was used for the element detection afterwards.

## **3. Results**

### **3.1. Hydrogen evolution test**

In general, the corrosion of Mg can be interpreted as an electrochemical redox process of Mg oxidation accompanied by reduction and formation of H<sub>2</sub> from both hydrogen ions in electrolyte and/or hydrogen atom in H<sub>2</sub>O molecule [47]. The overall reaction of the process can be expressed in Equation 1.



Theoretically, without considering the minor dissolution in electrolyte, the hydrogen volume can directly be employed for calculating the consumption of Mg (*i.e.* 1 M H<sub>2</sub> production consumes 1 M Mg). It is known that as cast materials are often characterized by relatively low homogeneity in terms of distribution of impurities and morphology features. In order to improve homogeneity of as cast Mg material and to shorten the experiments, Mg chips (Fig. 2(a)) rather than bulks are used in this work for H<sub>2</sub> evolution measurements. The recorded H<sub>2</sub> volume-time curves for 0.5 g, 1 g, 2 g and 3 g Mg chips in blank NaCl solution are presented in Fig. 2(b). It can be seen that increasing the amount of Mg barely changes the consuming trend, and all weight-levels reveal as-linear increase within the initial 5 h followed by a deceleration in the increasing rate as indicated by a transition arc between 5 to 10 h. After that, the volume of evolved H<sub>2</sub> remains steady implying the complete consumption of Mg chips. Indeed, according to Equation 1, 0.5 g of pure Mg generates 463 ml H<sub>2</sub>. Thereby, for studying the inhibitive effect of different inhibitors, 0.5 g Mg chips are added in blank NaCl solution without or with addition of various concentrations of inhibitors, and the respective H<sub>2</sub> volume-time response is shown in Fig. 3. The inhibition efficiencies (IE<sub>H</sub>) of studied compounds are determined from corresponding plots after 5 h immersion and the values are listed in Table 1. With addition of selected inhibitors, the corrosion rate is significantly decreased even at the lowest concentration (5 mM). Moreover, the inhibition efficiency shows a proportional increase with increasing the concentration of inhibitors, and more than 90% is achieved by addition of 0.1 M of respective current inhibitors (Table 1). Although a higher concentration of inhibitors benefits the increase of inhibition rate, a moderate concentration (50 mM) is applied for the following corrosion characterizations in present work considering cost-efficiency for industrial applications.

## 3.2. Electrochemical results

### 3.2.1 Open circuit potential (OCP)

The open circuit potentials (OCP) of Mg substrates immersed in 0.5 wt.% NaCl solution in absence and presence of 50 mM inhibitors are presented in Fig. 4(a). Similar to the trend of some reported Mg alloys [31, 33, 38, 48], the OCP for Mg in the blank NaCl solution shifts the initial value of -1.82 V towards more noble potential, which can be one of indications of

surface enrichment with more noble metal, probably Fe [49], although similar effect for Cu has also been demonstrated recently [50]. With addition of 2,5-pyridinedicarboxylate and fumarate, the OCP curves are positively shifted and stabilized around -1.57 V throughout 10 min experiment. In contrast, the incorporation of the same molar concentration of 3-methylsalicylate reveals an initial OCP value quite close to the reference, but much slower shift towards the noble value is observed. As proposed in literature [31, 37], positive shift of OCP reveals the inhibition of the anodic dissolution reaction, while the limitation of the cathodic reduction reaction ( $H_2$  evolution) can be correlated to the negative shift of OCP. Thus, 2,5-pyridinedicarboxylate reveals some characteristics of anodic inhibitors that preferentially inhibits the dissolution of Mg, while 3-methylsalicylate behaves as cathodic inhibitor that retards the hydrogen evolution process. Since Fe-rich particles are expected to be the main active cathodic components in present case, the inhibitive action exerted by 3-methylsalicylate should be closely correlated with the evolution of Fe-rich particles.

In order to study the influence of inhibitors on adsorption kinetics, pre-dissolved inhibitors are added into the blank NaCl solutions at 300 s achieving the concentration of 50 mM in the neutral pH range (6.9-7.1) (Fig. 4(b)). During the free corrosion period (within 300 s without inhibitors), the OCP of all specimens shifts towards noble potential following the same trend. However, the OCP curves show completely different behaviors after adding inhibitors into NaCl electrolyte. The addition of fumarate and 3-methylsalicylate results in positive and negative shift of OCP respectively, which can be ascribed to the anodic and cathodic inhibition mechanism as illustrated in Fig. 4(a). However, with addition of 2,5-pyridinedicarboxylate, the OCP exhibits a sudden increase to -1.57V followed by a gradual decrease to around -1.75V. Such a variation in OCP indicates that 2,5-pyridinedicarboxylate requires relatively longer time to interact with the surface in comparison with 3-methylsalicylate and fumarate. Ultimately, OCP of 2,5-pyridinedicarboxylate reduces even lower than its value at 10 min, which suggests 2,5-pyridinedicarboxylate may also affect the corrosion process on the Fe-rich particles revealing the mixed type (anodic and cathodic) inhibition.

### **3.2.2 Potentiodynamic polarization**

DC potentiodynamic polarization measurements were performed scanning from OCP to 300 mV and -300 mV (vs. Ag/AgCl) respectively for characterizing the current response from Mg

substrate in NaCl solution in absence and presence of 50 mM inhibitors. Fig. 5 compares the polarization curves obtained in different electrolytes with 10 min stabilization. Similar to OCP changes in Fig. 4, addition of 2,5-pyridinedicarboxylate and fumarate reveals a positive shift of corrosion potential  $E_{\text{corr}}$  and 3-methylsalicylate registers a negative shift, which indicate their preferential influences on the respective corrosion reactions in anodic and cathodic domains. In order to understand the evolution of the corrosion process and surface condition for the specimens without and with inhibitors addition, polarization curves were recorded after consecutive immersion periods individually (10 min, 3 h, 6 h and 24 h), as illustrated in Fig. 6. Cathodic Tafel extrapolation is applied for analyzing the experimental polarization curves, and the derived parameters, including corrosion potential ( $E_{\text{corr}}$ ), corrosion current density ( $I_{\text{corr}}$ ) and inhibition efficiency ( $IE_p$ ), are listed in Table 2. It should be mentioned that ohmic potential drop caused by the electrolyte resistance was compensated during the calculation of these parameters. For the reference specimen (tested in blank NaCl solution), the polarization curve shifts to a nobler  $E_{\text{corr}}$  after 3 h of immersion and remains stable afterwards. The stabilized  $I_{\text{corr}}$  is more than one order of magnitude higher than the initial value. In addition to the shift of the polarization curves towards noble potential but lower current density, the addition of inhibitors also results in the visible pattern changes of both branches. Note that no obvious passivation transition region can be distinguished in the anodic zones, which suggests the weak corrosion resistance property of the hydr(oxide) is not completely changed by the added inhibitors. To be specific, with addition of 2,5-pyridinedicarboxylate, the anodic branch shows a continuous decrease in the slope while the cathodic branch remains almost stable within 24 h measurement. Such a potential evolution pattern indicates slight enhancement of barrier properties of formed products by the inhibitor, which fits well with the inhibition model proposed in reference [37]. In this model, organic inhibitor (sodium dodecylbenzenesulfonate, SDBS) is preferentially adsorbed on  $\alpha$ -Mg phase through S or O atoms of the  $-\text{SO}_3^-$  increasing the anodic polarization resistance through formation of inhibitor layer on Mg surface. Continuous shift of  $E_{\text{corr}}$  towards noble potential but lower current is found for 3-methylsalicylate. At 24 h, the lowest corrosion current density is  $12.5 \mu\text{A}/\text{cm}^2$  for 3-methylsalicylate, which implies the efficient corrosion inhibition. Compared to 2,5-pyridinedicarboxylate and 3-methylsalicylate, fumarate shows stable protection since the beginning (10 min) of immersion, because both the  $E_{\text{corr}}$  values and

anodic/cathodic branches of the polarization curves reveal negligible changes during the rest time. These results suggest a mixed type of corrosion inhibition mechanism, in which both of the anodic and cathodic sites are covered by the deposited corrosion products that insulate the contact between the corrosive electrolyte and Mg substrate.

As follows from Table 2, the corrosion current density for the specimens with inhibitor is about two orders of magnitude lower than that of the blank specimen after 3 h, and also an increasing trend in inhibition efficiency is revealed with just a few exceptions. Both of the results agree well with the hydrogen evolution measurements, and validate hydrogen evolution test using small pieces with high surface area Mg chips.

### 3.2.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance measurements were conducted in the frequency range from  $10^6$  Hz to  $10^{-2}$  Hz to study the corrosion process and interface condition in absence and presence of 50 mM inhibitors in the blank solution. EIS (Nyquist and Bode plots) spectra recorded after consecutive immersion periods (10 min, 1 h, 3 h, 6 h, 12 h and 24 h) are given in Fig. 7. For assisting the visual comparison between different samples, the Nyquist and Bode spectra for different electrolytes are plotted in the same scale. From a general view of the Nyquist plots in Fig. 7, the enhancement of the corrosion resistance by addition of inhibitors is obvious, as indicated by the larger semi-circles in comparison with the reference specimen. Bare Mg in blank 0.5 wt.% NaCl solution shows minor corrosion resistance (approx.  $300 \text{ ohm}\cdot\text{cm}^2$ ) since the beginning (10min) of the measurement, but consecutive decrease in impedance occurs after 1 h exposure in the blank NaCl electrolyte. Such a fast degradation process of Mg can be explained by the active thermodynamic properties of Mg and less protective capability of the formed hydr(oxide) layers [47], and more importantly in current case, the micro galvanic coupling with Fe impurities.

With addition of 2,5-pyridinedicarboxylate into NaCl electrolyte, two visible semi-circles appear in the Nyquist figure (Fig. 7(c)), which implies different electrochemical responses in the corrosion cell. The first high frequency (HF) arc ( $10^0$ - $5\times 10^4$  Hz) represents the barrier properties of the formed film, while the response from the electrochemical double layer is reflected by the second semi-circle located in the lower frequency (LF) range ( $10^{-2}$ - $10^0$  Hz). The diameters of both semi-circles keep increasing until 6 h, followed by a slight decrease

after 12 h, especially for the high frequency semi-circle. Up to 24 h, only one single depressed semi-circle can be observed in the Nyquist plot, which indicates the drastic decrease of charge transfer resistance. Correspondingly, the decreasing trend in film impedance is also revealed in the Bode plots, in which a continuous suppression of characteristic phase peak (at approx. 100 Hz) towards lower values and decrease in impedance occur after 3 h. When compared with the other inhibitors, 3-methylsalicylate shows the most effective corrosion inhibitive action as demonstrated by the continuous growth impedance and larger diameters of both semi-circles at any measuring points. However, similar to 2,5-pyridinedicarboxylate, slight decrease in both semi-circles occurs at 12 h and only one combined large semi-circle can be determined by the end of the EIS measurement (24 h). The continuous widening of phase peak from  $10^0$  Hz to  $10^3$  Hz together with increasing impedance indicates the gradual enhancement of the barrier film on Mg surface, which could be resulted from the increase in thickness/compactness of hydroxide layer and/or adsorption of inhibitor on Mg surface blocking the micro galvanic corrosion between Fe impurities and Mg substrate. The Nyquist plot obtained in the basic electrolyte with 50 mM fumarate addition is also characterized with double semi-circle pattern. However, the disappearance of the charge transfer response (second semi-circle) happens shortly after 3 h immersion, but the overall resistance of the whole system is kept increasing until achieving the peak value of  $2000 \text{ ohm}\cdot\text{cm}^2$  at 12 h. By the end of 24 h, the impedance decreases to the 3 h's level ( $2000 \text{ ohm}\cdot\text{cm}^2$ ). All the obtained EIS results confirm the contribution of inhibitors in construction of the deposited layer on Mg surface, which agree well with polarization and hydrogen evolution results.

In order to quantify the physical-chemical parameters of the corroding system, the impedance spectra were fitted with equivalent electrical circuits which mechanistically describe the corroding system. Regarding to the general degradation process reflected in EIS spectra, two different equivalent circuits (Fig. 8) were used for the fitting. Firstly, the two time-constant spectra were modeled by a cascade circuit which includes two relaxation processes described by two groups of combination of resistor ( $R_f$  and  $R_{ct}$ ) and constant phase element ( $CPE_f$  and  $CPE_{dl}$ ) (Fig. 8(a)). In this circuit,  $R_s$  represents the solution resistance,  $CPE_f$  and  $R_f$  are the constant phase element and resistance related to the capacitance and barrier properties of the film on the surface, while  $CPE_{dl}$  and  $R_{ct}$  are correlated with the double layer capacitance and

charge transfer resistance at corroding interface. The application of constant phase element, rather than pure capacitor, is on account of the non-uniform distribution of sample surface [33, 37]. As soon as the disappearance of the second time-constant, only one time-constant corresponding to the corrosion products layer was remained in the circuit, see Fig. 8(b).

The evolution of the parameters of circuit components and evaluation of corrosion efficiency ( $IE_I$ ) are given in Fig. 9. In terms of film resistance ( $R_f$ ), 2,5-pyridinedicarboxylate registers a low and constant value (approx.  $500 \text{ ohm}\cdot\text{cm}^2$ ) throughout the whole characterization period, whilst higher but fluctuated trends are found for 3-methylsalicylate and fumarate. After peaking at around  $2500 \text{ ohm}\cdot\text{cm}^2$  at 6 h, fumarate shows gradual decrease in  $R_f$  with achieving at  $1300 \text{ ohm}\cdot\text{cm}^2$  at 24 h. Even though some slight fluctuations in  $R_f$  are revealed during the whole period, 3-methylsalicylate attains its peak value at 24 h. Considering the variation trend of  $R_f$ , one can realize much fewer corrosion products (*i.e.*  $\text{Mg}(\text{OH})_2$ ) are formed upon Mg with addition of 2,5-pyridinedicarboxylate comparing with the other two inhibitors. This phenomenon could result from the formation of a layer of adsorbed inhibitor all over the surface exposed to the electrolyte, including Fe impurities. This layer prevents the direct contact between Mg substrate and corrosive medium. As for the charge transfer resistance  $R_{ct}$  (Fig. 9(b)), fumarate demonstrates the lowest values ( $300 \text{ ohm}\cdot\text{cm}^2$ ). After 1 h immersion, the second semi-circle in Nyquist plot for fumaric acid is almost undetectable, which means negligible charge transfer on Mg surface. A gradual decrease in  $R_{ct}$  is observed for 2,5-pyridinedicarboxylate and this feature disappears again by the end of EIS test. Moreover, obvious higher  $R_{ct}$  values are manifested for 3-methylsalicylate, which suggest more resistance in impeding the charge transfer reaction. Eventually, the inhibition efficiency ( $IE_I$ ) calculated using  $R_{all}$  values is presented in Fig. 9(c). As shown, the inhibition efficiency is stabilized by 3 h immersion for all the examined inhibitors, and a high and constant corrosion inhibition action (more than 90%) is maintained until the end of test.

### 3.3 Surface morphology

After 24 h immersion in blank 0.5 wt.% NaCl solution for EIS measurement, optical microscopy and SEM are applied to study the surface morphologies of Mg in absence and presence of inhibitors, as shown in Fig. 10. For the blank sample without inhibitor addition (Fig. 10(a)), the surface loses its integrity completely and an extremely rough morphology

characterized by deposited corrosion products is visible. This kind of morphology agrees well with the impedance results, which suggests the fast decrease in the corrosion resistance with time. The corrosion process is significantly impeded when 0.05 M inhibitors are added into the electrolyte. Single large corrosion spots (Area A) are detected upon the surfaces with 2,5-pyridinedicarboxylate (Fig. 10(b)) and fumarate (Fig. 10(d)) addition, while 3-methylsalicylate (Fig. 10(c)) reveals filiform corrosion defect on the corroded surface. At higher magnification, most of exposed areas (Area B) are filled with micro cracks, which are resulted from the dehydrated  $\text{Mg}(\text{OH})_2$ . However, the surface of specimen protected with 3-methylsalicylate possesses rougher morphology compared to other two inhibitors, and also characterized by numerous “saucer-like” spots.

### 3.4 AFM/SKPFM analysis

AFM and SKPFM analysis of Mg surface has been conducted in order to investigate how corrosive environment and inhibitors affect topography and electronic properties of Mg surface. Fig. 11 presents AFM and VPD maps acquired before and after corrosion in NaCl solution only and in 3-methylsalicylate based electrolyte. The maps were acquired on the same place after immersion. As-polished metal surface represents the Mg matrix which envelops a few Fe-rich intermetallics. These intermetallics have a higher topography level (Fig. 11 (a) and (e)) and more positive VPD with brighter color which can be easily recognized on maps presented in Fig. 11 (b) and (f). The higher VPD level observed in these places confirms existence of intermetallic inclusions enriched with Fe and Si as these were the main types of intermetallics found in this magnesium matrix. In general, a short term immersion in a corrosive electrolyte causes some corrosion products to deposit on the Fe rich particles forming some sort of precipitate domes atop (Fig.11 (c) and (g)). The VPD maps show well defined contrast between intermetallics and matrix before immersion. Such fingerprint attributed to intermetallics changes after immersion *i.e.* VPD contrast of intermetallics becomes less defined and diffuse (Fig.11 (d) and (h)). The other two inhibitors also produce some precipitates on the intermetallics and VPD contrast between intermetallics and Mg matrix decreases (not shown). In case of 2,5-pyridinedicarboxylate inhibitor solid precipitates deposit on Mg matrix as well.

The measurements performed by SKPFM on metals covered with passive oxide films are

somewhat more complicated than on pure metallic surface. In the latter case the difference in work function between the metal and the probe is directly related with the measured VPD difference [43]. However, in the former case there might be a significant contribution from the oxide film covering the metal surface. The Galvani potential difference including an oxide covered metal will be related to a sum of potential difference at the metal-oxide, across the oxide and oxide air interface (surface potential term) [49, 51]. Thus the semiconducting properties of the passive oxide film and surface potential terms will effectively contribute to the measured VPD. Moreover, as was presented by Hausbrand *et al.*, adsorption of gas molecules on passive films may change the work function and as a consequence the measured VPD [46]. Also adsorption of layers of polar or charged organic molecules on metal may contribute to the surface potential term thus affecting the work function [52].

Quantitative analysis of VPD changes of Mg surface is presented in Fig. 12. It shows the VPD potential measured before immersion (0 min) and after immersion (30 min) in different electrolytes. The VPD values were obtained as an average of three measurements of Mg surface with indication of the standard deviation expressed as the vertical margins on each of the black symbols. There are two types of trends which can be immediately noticed. The first one is that the VPD increases after immersion in NaCl and 3-methylsalicylate solutions (Fig. 12). The second trend is that the VPD decreases after immersion which is a characteristics of 2,5-pyridinedicarboxylate and fumarate systems.

Previous results indicate that the VPD increase on Mg (with 220 ppm of Fe) after immersion can be related to higher corrosion activity of the Mg (220 ppm of Fe) compared with the pure Mg (with about 50 ppm of Fe) as it was shown by Yasakau *et al.* [49]. During corrosion the passive oxide film may become thicker including more MgO with more defects which would largely affect its electronic properties. However, since the SKPFM measurements were conducted in air the influence of surface potential and band bending [46] on measured VPD is not excluded. Most plausibly the VPD increase, as observed in (Fig. 12) for NaCl and 3-methylsalicylate, can be attributed to changes in the passive oxide due to corrosion, with changes being higher upon immersion in 3-methylsalicylate solution which could be associated with the formation of mixed corrosion products of 3-methylsalicylate and Mg in the passive film.

Contrary to above results, VPD on Mg surface shifts to more negative values upon immersion in 2,5-pyridinedicarboxylate and fumarate electrolytes (Fig. 12). A more negative VPD on Mg surface after immersion may indicate a weaker and thinner passive film formed. Moreover the relative input of space charge layer and oxygen adsorption on VPD measurements in air should be much smaller. It may be speculated that the reason for that could be effective adsorption of the two organic compounds on the Mg matrix. The input of the surface dipole formation on the surface to the measured VPD does not seem to explain VPD changes because the chemical structure of the three inhibitors is quite similar. All of them have carboxyl groups and both 3-methylsalicylate and 2,5-pyridinedicarboxylate molecules have aromatic and heterocyclic groups. In spite of that the properties measured by SKPFM on Mg after immersion were substantially different between 3-methylsalicylate and the other two inhibiting molecules. Therefore the most rational conclusion which could be made is that the mechanism of inhibiting action towards Mg corrosion is different between 3-methylsalicylate and 2,5-pyridinedicarboxylate/fumarate inhibitors.

### **3.5 UV-Vis-NIR spectrometric analysis**

The original inhibitor powders and corrosion film deposited on Mg surface were further examined by UV-Vis-NIR absorption spectroscopy, and the results are presented in Fig. 13. With respect to the intrinsic variation in molecule structure, the spectrometric features of selected inhibitors are clearly reflected over the wavelength from 200 to 500 nm. In the spectrum of 2,5-PDCA chemical (Fig. 13(a)), two strong peaks are found at wavelengths of 255 nm (K band) and 293 nm (B band), respectively [53]. The formation of these two bands results from the  $\pi \rightarrow \pi^*$  charge transition of unsaturated N atom and conjugated double bonds in the pyridine ring. Similarly, three characteristic B bands are revealed in the wavelengths of 241, 275 and 303 nm respectively for 3-MSA, which can be assigned to the  $\pi \rightarrow \pi^*$  charge transition in the aromatic compounds. As for fumaric acid, a single broad K band can be revealed around 271 nm, and this character can be resorted to the existence of conjugated molecule structure.

In order to verify the adsorption of inhibitors on the Mg surface, the polished Mg substrates are immersed in solutions in absence and presence of inhibitors for 5 min, and the deposited films are dried and further examined using UV-Vis-NIR absorption spectroscopy in the same

wavelength range as the inhibitor powders. It can be seen from the obtained spectra that the curve of the blank sample (without inhibitor) is relatively featureless, and a weak peak exist at 220 nm and 320 nm for the blank sample (without inhibitor), which can be correlated with the formation of MgO and Mg(OH)<sub>2</sub> on the corroded surface [54]. In contrast, the films obtained from the electrolyte with inhibitor addition demonstrate a decent fit to the pattern of corresponding spectra of inhibitor chemicals. Moreover, red shifts are revealed on the characteristic peaks of the films with 2,5-pyridinedicarboxylate and 3-methylsalicylate addition. This might be attributed to the coordination ligands and Mg<sup>2+</sup> ions, which decreases the energy gap between  $\pi$  and  $\pi^*$  orbital of the ligand.

## 4. Discussions

### 4.1. Evaluation of inhibition efficiency obtained from different characterization methods

In current study, three typical methods have been involved for calculating the inhibition efficiency for the selected inhibitors, and the results are compared in Fig. 14. It can be seen that the efficiency derived from hydrogen evolution (IE<sub>H</sub>) is slightly lower than that obtained from electrochemical measurements (polarization (IE<sub>P</sub>) and EIS (IE<sub>I</sub>)). This difference in efficiency is mainly attributed to increasing the exposed area of Mg chips, which accelerates the corrosion process in blank NaCl solution resulting in complete consumption of Mg chips during the initial hours. The efficiencies calculated from the polarization and EIS are consistent with each other, especially after 3 h immersion. However, significant difference can be observed after 10 min immersion. As described above, cathodic polarization (from OCP to -300 mV vs. OCP) is conducted for revealing the potentiodynamic behaviors in different electrolyte systems, and the cathodic extrapolation is applied for determining the current density. Correspondingly, an excess release of H<sub>2</sub> gas enforced by cathodic reaction can affect the adsorption of inhibitor molecule and formation of protective layer on Mg surface. Afterwards, with formation of stabilized hydr(oxide) layers after longer immersion in inhibitor-containing electrolyte (e.g. 3-methylsalicylate and fumarate), the efficiency results obtained from the polarization and EIS fit well with each other.

### 4.2. Corrosion protection mechanism of selected inhibitors

It has been widely accepted that the tolerance limit of Fe in Mg substrate is about 100 ppm, above which the corrosion rate becomes several folds higher [55]. In general, owing to the low

solubility of Fe in Mg, Fe-rich impurities tend to precipitate during the normal solidification forming cuboid shape crystals [55]. To clarify the role of Fe particles the additional investigations were performed. The Mg substrate was well-polished and observed by SEM (Fig. 15(a)). It is not hard to distinguish Fe (light particles) from Mg substrate in back scattered electron (BSE) mode, and typical cubic and bar shape of Fe-rich particles are revealed in higher magnification (inset of Fig. 15(a)). Moreover, seven random Fe impurities are analyzed by point EDS analysis and the elemental compositions are listed in Table 3. The presence of intensive Mg in the Fe-rich particles suggests the penetration of electron beam with reaching surrounded Mg substrate. As mentioned, Fe-rich particles are the critical cathodes with respect to Mg substrate forming micro-galvanic cell, which is illustrated in Fig. 15(b-c). As shown by SEM micrograph before and after FIB cross-section cut of a typical saucer-like spot on the surface of sample with 3-methylsalicylate protection, Fe-rich particle locates at the center of the corrosion site and buried under the layer of corrosion products. It is also surrounded by the additional circle of corrosion products formed on the periphery. Cathodic reaction on Fe-rich particle is accompanied by dissolution of Mg around it and radial precipitation of corrosion products governed by local pH distribution (alkalinization over Fe-rich particle due to oxygen reduction reaction) and precipitation of  $Mg(OH)_2$ . This also correlates well with previously reported data [26, 28, 56]. Oxygen consumption over corroding Mg has been demonstrated recently [57, 58].

Described saucer-like corrosion sites were observed after immersion in NaCl electrolyte for short time, up to 30 minutes but as corrosion propagated rapidly, these sites became invisible with longer immersion times. Surface roughness increased dramatically, Fig. 10(a). Similar saucer-like corrosion features are observable on the surface after immersion in NaCl modified by adding 50 mM 3-methylsalicylate. In the latter case these features are still visible on the surface even after 24 hours of immersion (Fig. 10 (c)). At the very beginning of immersion in 3-methylsalicylate solution very rapid corrosion process can be noticed on Mg surface. SKPFM results demonstrate substantial changes in the VPD of the passive oxide film (Fig. 12) on Mg which is most probably correlated with the initial rapid corrosion. Besides, almost all the intermetallics become covered with corrosion products by the end of 30 min of immersion which has not been observed on other Mg samples after immersion in 2,5-

pyridinedicarboxylate and fumarate solutions. However, as follows from OCP evolution upon inhibitor addition, Fig. 4, the cathodic process is most likely inhibited. This means that although corrosion process started, it was passivated, probably by deactivating cathodic reaction on Fe-rich particles. Fig. 7 confirms the continuous increase of resistance of protective film which may incorporate 3-methylsalicylate as follows from UV-visible absorption spectra, Fig. 13.

Mechanistically, at least two possible scenarios might lead to passivation inhibition of cathodic reaction: 1) Blocking oxygen and water reduction reaction on Fe-rich particles due to adsorption of 3-methylsalicylate or due to precipitation of protective film including  $\text{Mg}(\text{OH})_2$  characterized by higher protective properties compared to that formed in blank NaCl (Fig. 16(II)); 2) Dissolution of Fe-rich particle due to undermining followed by detachment and self-corrosion (Fig. 16(III)). This process has been shown to end up either by re-plating dissolved Fe on Mg promoting its corrosion [18, 19] or by particle dissolution promoted by corrosion inhibitor that forms soluble complexes with  $\text{Fe}^{2+}/\text{Fe}^{3+}$  [42, 59]. 3-methylsalicylate and salicylate derivatives in general are known for the property to chelate iron cation [59]. The stability constants ( $\log K$  at 25 °C) of the complex constituted by 3-methylsalicylate and  $\text{Fe}^{3+}$  is 18.13 [60]. This value indicates that the dissolved  $\text{Fe}^{3+}$  is likely to be bounded into the complex. However, up to now, no direct experimental data could be collected that confirms increase of  $\text{Fe}^{n+}$  concentration in electrolyte modified by 3-methylsalicylate due to very low concentration of Fe-methylsalicylate complex that is formed locally, but rapidly diffuses to bulk electrolyte. Combination of scenarios 1) and 2) implying that the corrosion products form on Fe-rich particle which later is dissolved with participation of 3-methylsalicylate is also possible.

Although exhibiting equally high inhibiting efficiency, corrosion inhibition mechanism of 3-methylsalicylate differs from that provided by 2,5-pyridinedicarboxylate and fumarate. This is evident from different surface appearance (Fig. 10), OCP trends (Fig. 4), polarization curves (Fig. 5-6), EIS (Fig. 7) and SKPFM data (Fig. 11-12). 2,5-pyridinedicarboxylate and fumarate function as anodic corrosion inhibitors forming adsorptive layers all over Mg matrix and possibly over Fe-rich particles (Fig. 16(II')). SKPFM results clearly show that the measured VPD decreases on Mg matrix after immersion in these two inhibitors (Fig. 12). Cathodic

reaction is inhibited on the sample exposed to either 2,5-pyridinedicarboxylate or fumarate as follows from polarization curves provided in Fig. 5. Cathodic activity on Fe-rich particles is much less evident and the formation of saucer-like corrosion sites is not typical for the surfaces exposed to 2,5-pyridinedicarboxylate and fumarate containing NaCl electrolyte (Fig. 10 (b) and (d)). In the event of Fe dissolution from Fe-rich particle, it is also possible that 2,5-pyridinedicarboxylate and fumarate complex formed  $\text{Fe}^{n+}$  since both possess iron complexing ability.

Impedance associated with the protective layer  $R_f$  increases during immersion only in fumarate based electrolyte unlike for 2,5-pyridinedicarboxylate which exhibits the resistance drop (Fig. 7). Although the properties of the passive film on Mg surface are similar on the samples corroded in both these inhibitive solutions (Fig. 12), the films are much more defective in case of 2,5-pyridinedicarboxylate. Remarkable, that even defect breakdown evidenced by optical/SEM observations (Fig. 10), does not lead to dramatic decrease of low frequency impedance, indicating that newly exposed Mg or rapidly formed  $\text{MgO/Mg(OH)}_2$  get passivated by fumarate more efficiently. Besides, fumarate also reveals faster response in reaching stable OCP than 2,5-pyridinedicarboxylate, see Fig. 4(b). The superior protective ability of fumarate are possibly due to the size of molecule and its mobility in the aqueous electrolyte when the same molar amount of inhibitor is added in the blank NaCl solution. Therefore, it is presumable to have a homogeneous or even thicker inhibitor layer on the surface in a short term for fumaric acid providing enhanced protection to the substrate in comparison with 2,5-pyridinedicarboxylate.

In conclusion, both anodic and cathodic corrosion inhibitors significantly improve the corrosion performance of Mg containing high content of Fe impurities. Inhibiting efficiency of sodium salts of 2,5-pyridinedicarboxylate, 3-methylsalicylate and fumarate measured by three independent methods varied between 93 to 99%. Given limited number of effective anodic inhibitors and those able to suppress cathodic reaction on Fe impurities, the corrosion inhibitors discussed in this work might become new additives of choice for protective coatings applied on Mg alloys.

## 5 Conclusions

1. High corrosion inhibition efficiency is achieved by adding sodium salts of 2,5-

pyridinedicarbolxylate, 3-methylsalicylate and fumarate into 0.5 wt.% neutral NaCl solution, and the corrosion efficiency increases with increasing the concentration of inhibitors. After achieving stabilization, the inhibition efficiency of the given inhibitors is higher than 93%;

2. Formation and evolution of protective inhibitor layer on Mg surfaces is revealed by electrochemical methods (potentiodynamic polarization and EIS), UV-Vis spectroscopy and SKPFM. 2,5-pyridinedicarbolxylate and fumarate demonstrate anodic inhibitive effects with the elements of mixed inhibiting behavior, whereas 3-methylsalicylate performs more as cathodic inhibitor specifically deactivating Fe-rich particles. SKPFM measurements revealed that VPD decreases on Mg surface after immersion in 2,5-pyridinedicarbolxylate and fumarate solutions. On the contrary VPD increases on Mg after immersion in 3-methylsalicylate.

3. The inhibition mechanism of 3-methylsalicylate fits well with the iron re-deposition model, stipulating that  $\text{Fe}^{2+}/\text{Fe}^{3+}$  from chemical dissolution of detached iron-rich particles is consumed by inhibitor molecule forming Fe-Inh complex. Thus, strong iron complexing agents are effective corrosion inhibitors impeding the micro galvanic corrosion of Mg with high amount of Fe impurities.

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## **Data availability**

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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## 7. Figure captions

Fig.1 Structural formulas of selected inhibitors (a) 2,5-PDCA, (b) 3-MSA and (c) Fumaric acid

Fig.2 (a) Optical image of Mg chips and (b) H<sub>2</sub> volume-time curves for different weights of Mg chips in blank NaCl solution

Fig.3 Hydrogen evolution results of Mg chips in pH neutral NaCl solution (pH  $\approx$  7) without and with addition of various concentrations of inhibitors (a) 2,5-pyridinedicarboxylate, (b) 3-methylsalicylate and (c) Fumarate

Fig.4 The stabilization of open circuit potential (OCP) in basic NaCl solution in absence and presence of 50 mM inhibitors

(a) Incorporation of inhibitor before test (t=0 s); (b) Addition of inhibitors at t=300 s

Fig.5 Potentiodynamic polarization curves for Mg-342Fe immersed in 0.5.wt% NaCl solution in absence and presence of 50 mM different inhibitors with 10min stabilization

Fig.6 Potentiodynamic polarization curves for Mg-342Fe immersed in 0.5 wt% NaCl solution in absence and presence of 50mM different inhibitors after varied immersion periods (a) Blank NaCl solution, (b) 2,5-pyridinedicarboxylate, (c) 3-methylsalicylate and (d) Fumarate

Fig.7 EIS curves of Mg substrate immersed in blank NaCl solution without and with 50 mM inhibitors at varied times

(a)(b) Blank NaCl solution, (c)(d) 2,5-pyridinedicarboxylate, (e)(f) 3-methylsalicylate and (g)(h) Fumarate

Fig.8 Equivalent circuits for simulating different corrosion situations

(a) Mg substrate protected by adsorbed inhibitor layer and (b) After breakdown of the inhibitor layer

Fig.9 R<sub>f</sub>, R<sub>ct</sub> and IE<sub>I</sub> obtained from fitted EIS results by equivalent circuit

(a) R<sub>f</sub>, (b) R<sub>ct</sub> and (c) IE<sub>I</sub>

Fig.10 Optical and SEM images of characteristic surface morphology after 24 h EIS measurement in blank NaCl electrolyte (a) and with addition of 50 mM (b) 2,5-pyridinedicarboxylate, (c) 3-methylsalicylate and (d) Fumarate

Fig.11 Topography (a, c, e, g) and VPD (b, d, f, h) maps acquired on Mg before (a, b, e, f) and after (c, d, g, h) immersion in NaCl (c, d) or 3-methylsalicylate (g, h) solutions. Profiles were drawn across the images to emphasize exactly the same place before and after immersion.

Fig.12 Average VPD values measured on Mg samples before (0 min) and after immersion (30 min) in different solutions.

Fig.13 UV-visible absorption spectra of Mg immersed in NaCl solution in absence and presence of 50 mM inhibitors

(a) 2,5-pyridinedicarboxylate, (b) 3-methylsalicylate and (c) Fumarate

Fig.14 Comparison of inhibition efficiencies calculated from  $IE_H$ ,  $IE_P$  and  $IE_E$

Fig.15 SEM micrograph of intact Fe-rich particles and characteristic saucer-like corrosion feature after 24h immersion in 0.5 wt.% NaCl electrolyte containing 50 mM 3-MSA. (a) Selected Fe-rich particles for point EDS analysis, (b) top view and (c) cross-section view of the same site after FIB milling with Fe-rich particle in the middle.

Fig.16 Schematic illustration of corrosion inhibition mechanisms of selected inhibitors (II-III) Cathodic inhibitor, (II') Anodic inhibitor

Table 1 Inhibiting efficiencies ( $IE_H$ , %) of inhibitors tested in varied concentrations at 5 h by hydrogen evolution

Concentration (M)	2,5-pyridinedicarboxylate	3-methylsalicylate	Fumarate
0.005	84	80	68
0.01	91	85	87
0.05	94	93	94
0.1	97	91	97

Table 2 Critical parameters calculated from polarization curves and inhibiting efficiencies ( $IE_P$ , %) tested in blank solution with absence and presence of 50 mM inhibitors

	$E_{corr}$ (V vs Ag/AgCl)	$I_{corr}$ ( $\mu A/cm^2$ )	$IE_P$ (%)
NaCl-10min	-1.56±0.01	62±9	-
NaCl-3h	-1.55±0.03	794±257	-
NaCl-6h	-1.55±0.04	1143±720	-
NaCl-24h	-1.53±0.03	2155±483	-
2,5-pyridinedicarboxylate-10min	-1.58±0.02	13±4	79
2,5-pyridinedicarboxylate -3h	-1.56±0.05	18±5	98
2,5-pyridinedicarboxylate -6h	-1.52±0.08	11±2	99
2,5-pyridinedicarboxylate -24h	-1.49±0.04	79±25	96
3-methylsalicylate-10min	-1.65±0.05	31±24	50.
3-methylsalicylate -3h	-1.59±0.04	9±1	99
3-methylsalicylate -6h	-1.55±0.03	16±9	99
3-methylsalicylate -24h	-1.40±0.04	13±5	99
Fumarte-10min	-1.51±0.03	36±6	42
Fumarte -3h	-1.48±0.03	24±7	97
Fumarte -6h	-1.48±0.02	19±12	98
Fumarte -24h	-1.49±0.03	21±9	99

Table 3 EDS analysis of seven Fe-rich particles on polished Mg surface (at. %)

	1	2	3	4	5	6	7
Fe	12.9	1.9	0.3	6.4	5.8	7.0	1.8
Si	1.5	0.7	0.1	0.4	0.4	0.7	0.3
O	7.0	5.4	0.8	0.4	3.7	5.8	8.7
Al	0.4	0.1	0.2	0.1	0.4	0.4	0.2
Mg	78.2	92.0	98.5	92.8	89.7	86.1	89.1
Fe/Si	8.6	2.7	3.0	16	14.5	10.0	6.0