



## Local flux of hydrogen from magnesium alloy corrosion investigated by scanning electrochemical microscopy



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### ABSTRACT

Herein, we report the successful electrochemical detection and quantification of H<sub>2</sub> fluxes produced from a corroding magnesium alloy using the substrate-generation/tip-collection mode of scanning electrochemical microscopy (SECM). Using a platinum microelectrode, the variation in H<sub>2</sub> fluxes was imaged revealing the time-dependent corrosion reaction. Our results demonstrate that through careful control of the corroding media and immersion time, quantitative SECM approach curves, devoid of convective effects, were acquired. Comparison to an idealized numerical model enabled the quantification of the local H<sub>2</sub> flux for a given corroding area. These data demonstrated that the active site size increases throughout the reaction, whereas the flux of H<sub>2</sub> generated at an active site increased for the first hour of immersion followed by decrease in the flux of H<sub>2</sub> for times greater than 1 h.

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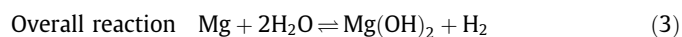
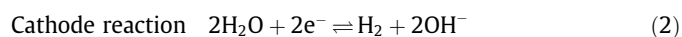
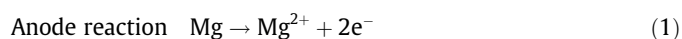
### 1. Introduction

Despite the high corrosion rates exhibited by magnesium alloys in aqueous solutions, the automotive industry is currently implementing magnesium alloy components into high-end vehicles to reduce the overall weight of the vehicle, thus reducing fuel consumption [1,2]. In trying to expand the use of magnesium alloy components across all vehicles, automotive industries need to remove expensive separators currently used to limit galvanic corrosion occurring between the Mg alloys and other nobler metal car parts (bolts, sheets). Unavoidably, the improvement in the corrosion resistance of the targeted Mg alloys and choice of protective layers will require detailed *a priori* understanding and careful control over the Mg alloy microstructure and distribution, which can be achieved through the use of a robust high-resolution analytical methodology to investigate the corrosion reaction *in situ*.

Microscopic real time investigations involving scanning electrochemical microscopy (SECM) will provide a much needed understanding of how heterogeneities within the Mg alloy or coating influences the local and overall corrosion reaction. Already several fundamental studies, monitoring macroscopic corrosion properties of new Mg alloys [2–4], pointed to an ill-defined time-dependent change of the surface topography and rate of corrosion.

There is evidence to suggest that Mg alloy corrosion is initiated at heterogeneous sites in the microstructure, e.g. at grain boundaries [5]. The heterogeneities are mainly due to localized variations in the chemical composition of the alloy formed during the casting process (e.g. die-cast, sand-cast or graphite-cast) [6]. The die-casting process is commonly used in Mg alloy component manufacturing because it allows high production rate, reproducibility of the cast component and lower cost compared to sand-cast or graphite-cast production [7]. In this work, the industrial AM50 die-cast alloy has been used since it represents one of the most corrosion resistant Mg alloys and is thus of great interest to the automotive industry. The AM50 alloy has a microstructure typically consisting of primary  $\alpha$ -Mg grains along with a network of partially or fully divorced mixture of intermetallic  $\beta$ -Mg<sub>17</sub>Al<sub>12</sub> and eutectic Mg. Various intermetallic phases of the Al–Mn system are also present in the microstructure [8,9].

The galvanic corrosion of Mg in aqueous solutions produce magnesium hydroxide, Mg(OH)<sub>2</sub>, and molecular hydrogen, H<sub>2</sub>, as summarized by the following reactions [2].

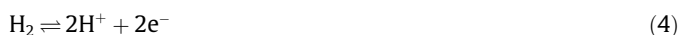


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where  $\text{Mg}^{2+}/\text{Mg}$  has a standard electrode potential of  $-2.37\text{ V}$  [10]. In dilute chloride solutions, which accelerate the corrosion reaction rate of Mg alloys, the observed corrosion potential of Mg is ca.  $-1.7\text{ V}$  vs. SCE [2]. Therefore, Mg is readily oxidized when galvanically coupled with other metals, e.g. Aluminum. Alloy AM50 undergoes spontaneous corrosion when immersed in aqueous solution due to the formation of microgalvanic couples between the bulk Mg (noted  $\alpha$  in Fig. 1) and the network of eutectic mixture of the intermetallic  $\beta$ - $\text{Mg}_{17}\text{Al}_{12}$  and Mg, Al–Mn intermetallic phases or Fe-containing inclusions that we simplistically refer to as  $\beta$  in Fig. 1. Within these couples and during the initial stages of corrosion, the  $\alpha$ -Mg matrix typically acts as the anodic sites (Eq. (1)) thereby releasing  $\text{Mg}^{2+}$ , while  $\text{H}_2$  is produced at the  $\beta$  cathodic sites (Eq. (2)) [11,12].

To monitor and quantify the *in situ* release of  $\text{H}_2$  produced at the  $\beta$  region and intermetallic cathodic sites of AM50, a platinum microelectrode (ME) was used (Eq. (4)).



SECM is a well-established scanning probe technique, where a ME [13] is positioned close to a substrate surface for localized detection of electrochemically active species (e.g.  $\text{H}_2$ ) [14–16] and its interaction with the substrate surface [17–21]. Typically, the current signal recorded at the ME relies on the diffusional mass transport of the redox-active species and the local surface reactivity of the substrate. Although a handful of SECM corrosion studies mapped the generation of specific metal cations at the anodic sites of the corroding surfaces [22–26] or amperometrically monitored the dissolved oxygen evolution in the electrolyte solution at the cathodic areas of the corroding sample [27–29], direct monitoring of  $\text{H}_2$  or  $\text{H}^+$  fluxes are limited [15,30,31]. The ability to perform quantitative approach curves is particularly challenging during Mg alloy corrosion because there is a limited experimental window in terms of corroding media and time that is devoid of significant convection effects originating from gas evolution and severe topographical deviations. Herein, we have successfully identified experimental conditions (0.6 M NaCl aqueous solution and immersion times smaller than 60 min) where substrate-generation/tip-collection mode of SECM can be used to monitor the local flux of  $\text{H}_2$  production from a Mg alloy surface. Eq. (3) shows that one mole of corroding Mg is accompanied by the production of one mole of  $\text{H}_2$ , hence a direct comparison of the detected  $\text{H}_2$  at the ME to the rate of corrosion can be made. SECM mapping and multiple SECM approach curves were performed to observe the time-dependent change of the die-cast AM50 Mg alloy surface. Quantitative approach curves were compared to a numerical model to evaluate the magnitude of the  $\text{H}_2$  flux as the active size of  $\text{H}_2$  producing features increased.

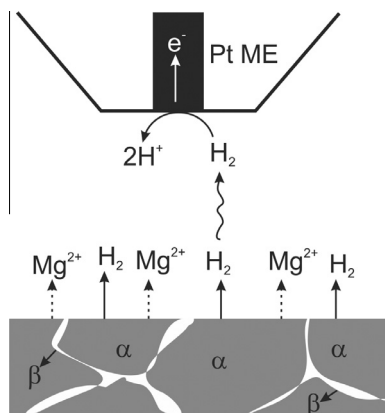


Fig. 1. Schematic representation of the process considered in SECM investigation of the aqueous  $\text{H}_2$  detection during Mg alloy corrosion for an active surface.

## 2. Experimental section

### 2.1. Materials and sample preparation

The aqueous NaCl (ACP, Montreal, QC) solution was made with analytical grade reagents and deionized water (Millipore MilliQ water 18.2 M $\Omega$ ). The samples for this study were industrial AM50 die-cast magnesium alloys received from General Motors India Private Limited. The chemical composition of the alloy is predominately Mg with the following minor components (in wt.%): 4.9 Al, 0.45 Mn, 0.2 Zn, <0.05 Si, <0.01 Ni, <0.008 Cu, <0.004 Fe, and 0.001 Be [32]. The AM50 samples were successively polished with 800 and 1200 silicon carbide grinding papers using water as a lubricant prior to cold mounting in epoxy resin (Struers Epofix, Ontario, Canada). The mounted samples with the exposed surface area of 1 cm<sup>2</sup> were then finely polished to achieve a mirror finish using an established protocol [33]. The microstructure of the die-cast AM50 alloy was analyzed using a light microscope (Zeiss Axio-plan 2 Imaging microscope, with a Hal 100 halogen lamp) and at higher magnification with a dual-beam scanning electron microscope/focused ion beam (SEM/FIB) (a Zeiss NVision 40).

### 2.2. SECM apparatus and procedure

The SECM experiments were carried out using a HEKA scanning electrochemical microscope ELPro scan 1 integrated with shear force unit (HEKA Elektronik, Germany). The cell was made from Teflon with a small opening in the middle into which the epoxy mounted alloy sample was tightly fitted. A platinum microelectrode (ME) was utilized as the working electrode, a chloridized silver wire as a quasi-reference electrode (Ag/AgCl QRE) and a 0.5 mm diameter platinum wire as a counter electrode (Goodfellow Cambridge Limited, Huntingdon, England). MEs were fabricated in-house by sealing Pt wires (25  $\mu\text{m}$  diameter, Delta Scientific Laboratory Products Ltd., Canada) into borosilicate glass capillaries with outer diameter of 1.5 mm, inner diameter of 0.7 mm (Sutter Instrument, USA) and sharpening the probe end to a ratio  $RG = r_{\text{glass}}/r_T \approx 10$ , where  $r_{\text{glass}}$  is the radius of the insulating sheath and  $r_T$  is the radius of the active ME. The resulting Pt MEs were polished on a microcloth pad (Struers MD Chem cloth) using a series of water-based alumina slurries (1  $\mu\text{m}$ , 0.3  $\mu\text{m}$  and 0.05  $\mu\text{m}$ ). Electrochemical cleaning was performed in  $\text{H}_2\text{SO}_4$  (0.1 M) cycling between 1 V and  $-0.5\text{ V}$  vs. Ag/AgCl until well-defined typical features of platinum were recognized, including  $\text{H}_2$  adsorption/desorption, and platinum oxidation/reduction [34]. All electrochemical measurements for the local detection of dissolved  $\text{H}_2$  were performed in freely aerated 0.6 M aqueous NaCl solution. We have chosen this concentration, which is standard for Mg alloy corrosion tests by General Motors, to obtain industrially relevant data. The approach curves were measured over the same location on the alloy surface at different immersion times. Line scan experiments were performed using SECM in shear force distance control mode to decouple the effect of surface topography from the reactivity on ME current. In this mode, the Pt ME is scanned at a constant distance above the sample enabling exclusive surface reactivity measurement. The amplitude controlled shear force scan parameters used in this experiment were; stimulation amplitude = 120 mV, stimulation frequency = 317 kHz, scan speed = 0.2  $\mu\text{m s}^{-1}$ , and piezo step size = 3 nm. Time-dependent 3D SECM maps were acquired in constant height mode over the corroding alloy surface at a translation speed of 20  $\mu\text{m s}^{-1}$ . The ME was biased at  $E_T = -0.05\text{ V}$  vs. Ag/AgCl in order to fully oxidize  $\text{H}_2$ .

Numerical simulations were performed using the finite element method (FEM) modeling package, Comsol Multiphysics 4.3a (Comsol AB, Sweden) with the Livelink for MatLab R2012b (MathWorks,

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