



Scanning Electrochemical Microscopy (SECM) Study of the Electrochemical Behavior of Anodized AZ31B Magnesium Alloy in Simulated Body Fluid

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In this work, scanning electrochemical microscopy (SECM) was employed to study the corrosion behavior of anodized AZ31B magnesium alloy exposed to simulated body fluid. SECM measurements were carried out in surface generation/tip collection mode. The hydrogen evolution flux caused during corrosion of the magnesium alloy was oxidized at the ultra-microelectrode (UME). Thus, this experimental procedure allowed evaluating the effect of the anodic protection in this alloy from the SECM analysis of Z-approximation curves, cyclic voltammograms and topographic maps. The results evidence differences in the local electrochemical response of magnesium alloy in the anodized and pristine conditions. The main sites of H₂ evolution were verified in the magnesium alloy without anodizing at short exposure times.

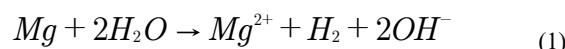
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1. Introduction

Magnesium alloys have recently gained increasing attraction as biodegradable and biocompatible materials for resorbable medical implants. However, one drawback of these alloys is that they present high degradation rates when are exposed to biological environments, being prone to localized corrosion¹⁻⁷.

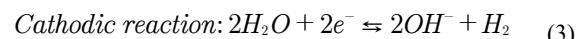
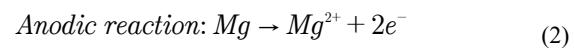
There are evidence that magnesium alloy corrosion process is initiated at heterogeneous sites in the microstructure which are mainly due to localized variations in the chemical composition of the alloy formed during the casting process^{8,9}.

Several works showed that one of the simplest and most effective methods for studying the corrosion rates of magnesium in aqueous solutions is by measuring hydrogen gas evolution associated with the magnesium corrosion process as shown in Eq. (1)¹⁰⁻¹³.



According to it, for each Mg²⁺ ion produced from the corrosion of Mg metal, one molecule of H₂ is evolved.

Normally, magnesium and its alloys produce magnesium hydroxide (Mg(OH)₂) and molecular hydrogen (H₂) when are exposed to aqueous environments, where the main cathodic reaction is water reduction, with hydrogen evolution and local alkalization, as shown in Eqs. (2) to (4)^{14,15}.



H₂ is produced at the cathodic sites of the magnesium surface and can be oxidized at a platinum ultra-microelectrode (UME) as follows:



Thus, H₂ generation can be sensed in an oxidation reaction at the UME probe potential of 0.0 V versus Ag/AgCl. Several researchers studied the flux of H₂ gas evolving from the surface of magnesium based materials^{10,14,16-19}.

For instance, Jamali et al.¹⁸ studied the hydrogen gas (H₂) evolution on a corroding surface of AZ31 alloy in simulated body fluid (SBF). It was found that the main domains of H₂ evolution are associated with lower insulating properties of the surface as well as higher local pH. Additionally, the SECM technique was implemented for studying H₂ evolution at the surface of AZ31 as a model Mg alloy. SECM results revealed that local domains of higher H₂ evolution on the surface of AZ31 are in close proximity of the observed pitting sites¹⁰.

Recently, the SECM technique was employed to map and assess the initial stages of electrochemical degradation of AZ91D Mg alloy exposed to simulated body fluid. The results indicate dynamic electrochemical activity on the AZ91D substrate at short exposure times, suggesting a rapid pit nucleation and changes in hydrogen evolution intensity¹⁹.

Therefore, for a better understanding of the degradation of magnesium alloy, different techniques are required to describe the phenomena involved in this process. In this context, scanning electrochemical microscopy (SECM) is a well-established high resolution scanning technique to monitor corrosion processes *in situ*. The UME is positioned close to a substrate surface for localized detection of electrochemically active species, thus producing valuable information on their local electrochemical activities²⁰⁻²³. This technique has been successfully applied to study magnesium alloys in different solutions²⁴.

The SECM technique can provide an understanding about local corrosion reactions at different exposure times of AZ31B alloy in the anodized state. Anodization is a powerful method to control the degradation rate of different metals. It consists of an electrolytic oxidation process that has been conventionally used to produce thick and stable films on metals for industrial applications, mainly aiming to increase corrosion resistance^{25,26}. Previous studies have highlighted the use of anodizing treatments to produce protective layers on magnesium alloys²⁷⁻²⁹.

Although anodization has been the target of extensive research, the application of SECM to explore the influence of anodizing treatment in the local corrosion processes of magnesium alloys is still scarcely reported in the literature.

Thus, the aim of this work was to investigate the local corrosion processes of anodized AZ31B magnesium alloy using SECM. The measurements were made in SBF, by means of the substrate generation/tip collection (SG/TC) mode, in order to detect hydrogen evolution generated in this process.

2. Experimental

2.1 Samples and solutions

Measurements were performed on AZ31B substrates (nominal composition wt%: Al 2.54, Zn 1.1, Mn 0.39, Mg balance).

All solutions were prepared with analytical grade reagents and ultra-pure water purified with a Milli-Q system from Millipore. All samples were abraded successively with 220, 600, 800, 1200 and 2500 grit emery paper and polished with diamond paste up to 1 µm. Simulated body fluid (SBF) was prepared using analytical grade reagents (8.2 g/L NaCl, 1.05 g/L Na₂HPO₄ and 0.355 g/L NaH₂PO₄) (pH 7.2).

2.2 Anodizing procedure

The anodizing experiments were performed using a power supply source (Maisen MP3003D), a stainless steel container as the cathode and AZ31B magnesium alloy specimen as the anode. The sample was galvanostatically anodized in 1.0 M NaOH + 0.5 M Na₂SiO₃ electrolyte at room temperature. Anodizing time was set at 5 minutes and at constant current density of 20 mA·cm⁻².

2.3 Scanning Electron Microscopy (SEM)

Surface micrographs of the polished and anodized samples were obtained by SEM (Jeol JSM-6010LA).

2.4 SECM: Instrumentation and measurements procedure

Scanning electrochemical microscopy (SECM) was performed using a microscope built by Sensolytics (GmbH Bochum, Germany). An electrochemical cell was employed using 25 µm Pt disk ultra-micro-electrode (UME) as working electrode, Pt as auxiliary-electrode and Ag/AgCl/KCl (3M) as reference electrode (Fig. 1).

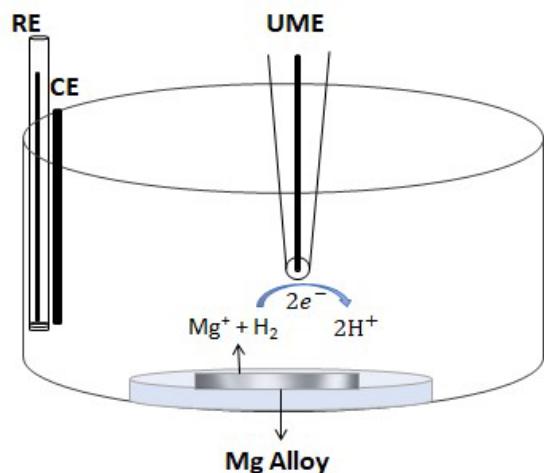


Figure 1. Schematic representation of the electrochemical cell of SECM set up in SG/TC mode.

Measurements were made at room temperature and at the open circuit potential (OCP). The AZ31B alloy was cut into strips and then embedded in epoxy resin to expose a working area of approximately 0.25 cm². The experiments were performed at selected heights of the tip above the surface. The operating height was set after recording *z*-approach curves, with the tip adjusted to ~10 µm above the surface. All experiments were performed using the surface generation/tip collection (SG/TC) mode. In the SG/TC mode,

H_2 generation from corrosion of magnesium alloy was sensed in an oxidation reaction at the UME probe potential of 0.0 V versus Ag/AgCl (Equation 5).

2.4.1 Cyclic voltammograms

Cyclic voltammograms of Pt UME above AZ31B surface in the as-polished and anodized conditions at the OCP were recorded after 10 minutes of immersion in SBF solution at a scan rate of 25 mV s⁻¹.

2.4.2 SECM Z- approach curves

Z-approach curves for a 25 μ m Pt UME were recorded in SBF solution at a starting distance of 100 μ m above the surface in the as-polished and anodized conditions at the OCP. The Z-Approach curves were acquired after 20 minutes of immersion at a scan rate of 5 μ m s⁻¹ and step size of 1 μ m.

2.4.3 SECM maps

SECM maps in constant height mode were obtained by scanning the UME tip in the x-y plane and recording the tip current as a function of its location. The maps were recorded after 30 and 80 minutes of immersion in SBF solution. A working area of 400 μ m x 200 μ m was examined in each specimen with the Pt UME biased at 0.0 V versus Ag/AgCl using a scan rate of 100 μ m s⁻¹ and increment of 25 μ m. These parameters were used considering the high surface reactivity, where in that way each mapping was quickly obtained in approximately 5 minutes.

3. Results and Discussion

3.1 Surface morphology

SEM micrographs of the AZ31B alloy surface in the as-polished and anodized conditions are shown in Figure 2.

The morphology surface of the magnesium alloy before the exposure to SBF is shown in Figure 2a. A cellular-shaped corrosion product is rapidly observed in localized areas on the surface of the freshly polished metal after 30 minutes (Fig. 2c) of immersion in SBF, as similarly found by Nordlien et al.³⁰. Clusters of needle or flower-like crystals are developed after 80 minutes of immersion (Fig. 2e), as also observed by other authors^{31,32}. According to the literature, these corrosion layers have the ability to slow down the dissolution process³⁰⁻³⁴. Meanwhile, the anodized layer (Fig. 2b) has not been substantially affected by the SBF electrolyte during the same periods of immersion (Fig. 2d and 2f). In this way, the artificially grown oxide film promotes the protection of the substrate by acting as a barrier, limiting the evolution of the corrosion process.

3.2 H_2 generation studied in substrate generation/Tip collection mode

3.2.1 Cyclic voltammograms

Initially, cyclic voltammograms of the AZ31B magnesium alloy in the as-polished and anodized conditions were recorded in SBF using the 25 μ m UME (Fig. 3).

When the UME was positioned at 10 μ m above the surface of the as-polished magnesium alloy, an oxidation current around 900 nA was observed at height of the peak, which is attributed to the oxidation of hydrogen (H_2) generated on its surface. However, when the UME was positioned in the same distance above the anodized magnesium alloy the current value was greatly reduced, which is associated to the local protection effect provided by the anodized layer. No oxidation peak was observed and the current was substantially reduced when the UME was positioned at longer distances from the surfaces.

3.2.2 SECM Z- approach curves

Figure 4 shows the Z-approach curves for a 25 μ m Pt UME recorded in SBF solution at a starting distance of 100 μ m above the surface.

Near to the magnesium alloy surface, H_2 evolution was significantly reduced for the anodized AZ31B alloy. It is clearly observed that there is a lower H_2 current evolution in Figure 4b compared to Figure 4a. Moreover, in Figure 4a an increase in current can be perceived, which is related to intense gas generation from the AZ31B Mg surface in the as-polished condition. The anodizing process dramatically decreases the current near the surface of AZ31B Mg alloy.

3.2.3 SECM maps

The SG/TC SECM mode was also applied to map hydrogen released from the AZ31B Mg alloy surface in the as-polished and anodized conditions when immersed in SBF solution. The maps were recorded 30 and 80 minutes of immersion (Fig. 5).

In Figure 5, the upper and lower color scales are an indicative of different current intensities for hydrogen evolution in the AZ31B Mg alloy surface in the as-polished and anodized conditions. The upperscale colors (red and yellow) indicate the areas with high H_2 evolution rate whereas the lowerscale colors (blue and green) represent the relatively passive areas with incipient H_2 formation.

After 30 minutes of immersion the current response was significantly higher in the AZ31B Mg alloy surface in the as-polished condition (Fig. 5a). The same behavior was observed after 80 minutes of immersion. However, the current

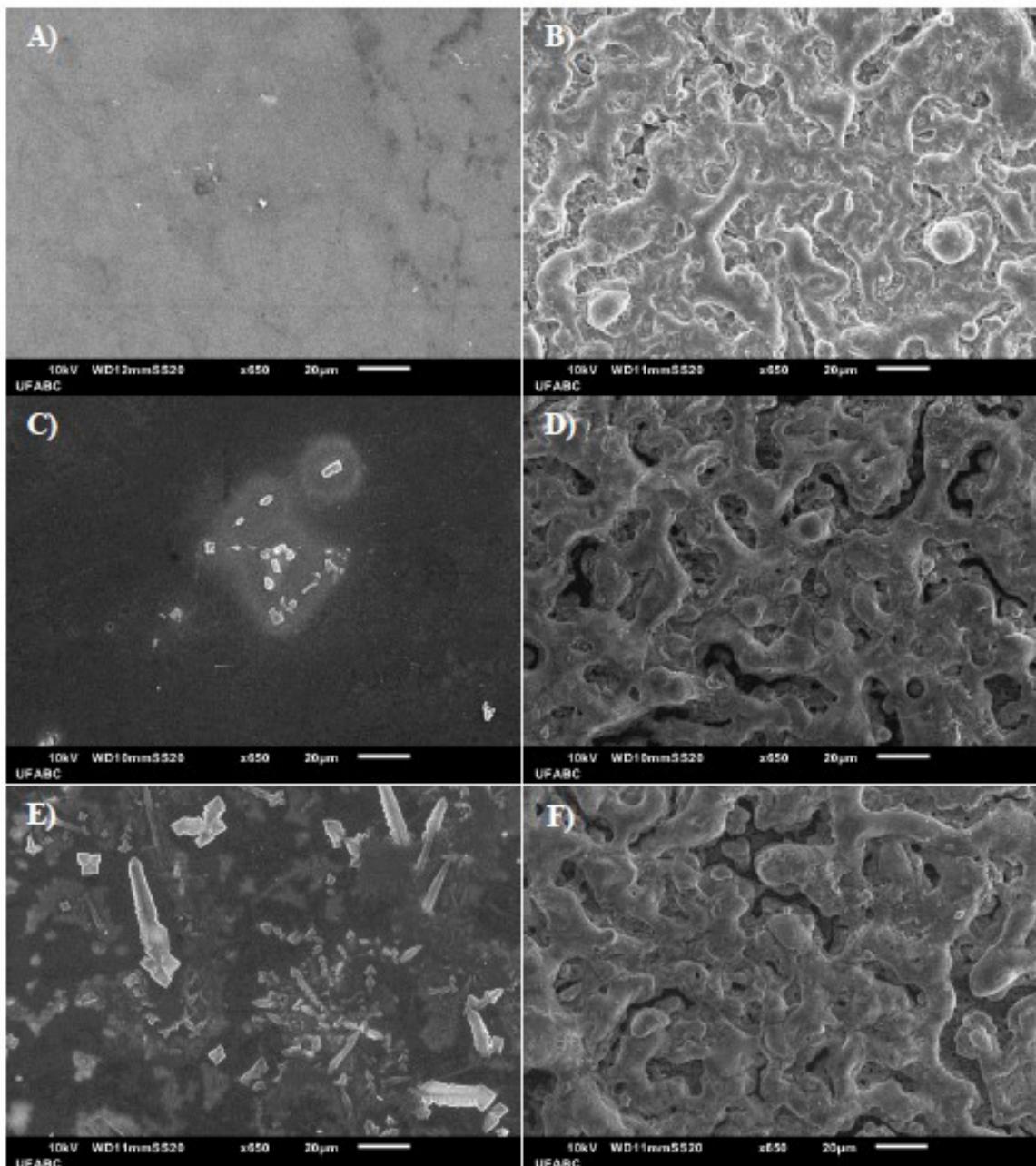


Figure 2. SEM images of AZ31B alloy surface: a) as-polished; b) anodized film; c) as-polished after 30 min; d) anodized film after 30 min; e) as-polished after 80 min; f) anodized after 80 min immersed into SBF.

values measured at 30 and 80 minutes indicate that hydrogen evolution is higher at the beginning of the experiments and decreases over time. This behavior may be attributed to the early formation of a magnesium oxi-hydroxide film over the surface exposed to SBF (Fig. 2c and 2e). The formation of a magnesium oxi-hydroxide film over magnesium alloys surface has been reported^{19,35-38}.

For instance, the SG/TC SECM mode was applied by Mena-Morcillo et al.¹⁹ to map the hydrogen released from AZ91D magnesium alloy surface at short periods of immersion in simulated body fluid. The current values measured at 10 min, 1 h, and 2 h indicated that hydrogen evolution was higher at the beginning of the experiments, diminishing over time due to the possible early formation of corrosion products¹⁹.

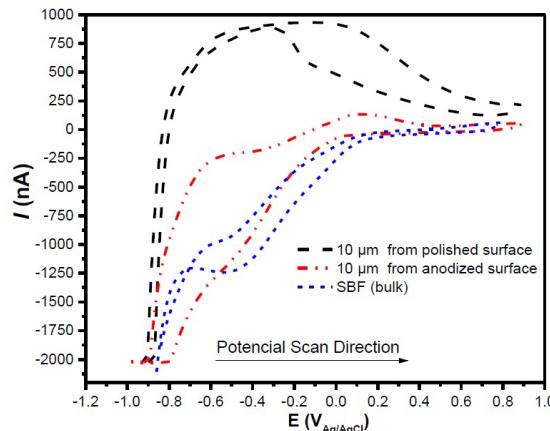


Figure 3. Cyclic voltammograms of Pt UME above AZ31B surface at the OCP after 10 minutes of immersion in SBF solution at a scan rate of 25 mV s^{-1} .

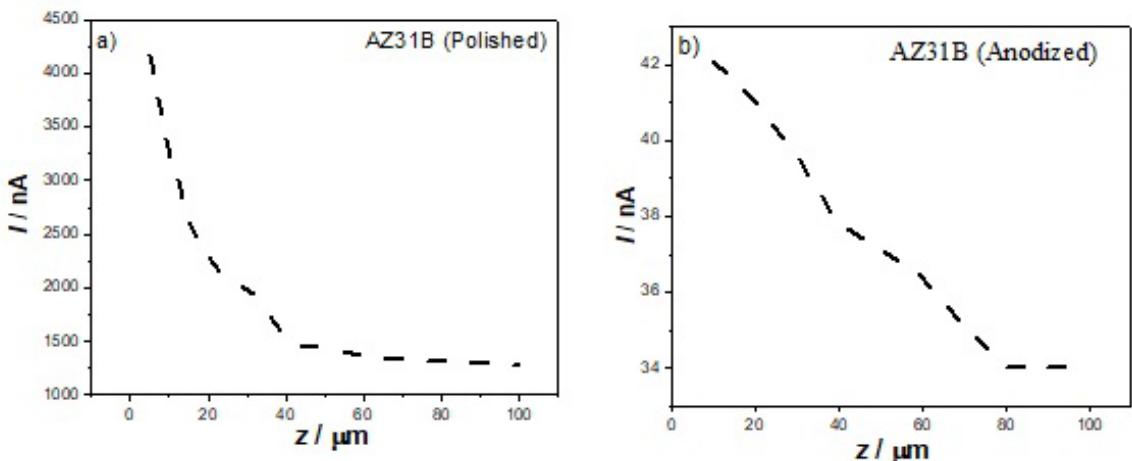


Figure 4. Z-Approach curves for a $25 \mu\text{m}$ Pt UME biased at 0.0 V on the AZ31B alloy at the OCP: polished (a) and anodized (b) conditions in SBF solution. The Z-Approach curves were acquired after 20 minutes of immersion at a scan rate of $5 \mu\text{m s}^{-1}$.

Here, this effect was more evident in the AZ31B Mg alloy surface in the as-polished condition. For the anodized surface, after 80 minutes, no significant variation of current values was observed (Fig. 5d). This behavior may be attributed to the protection ability of the anodized layer that hinders the local corrosion reactions and, consequently, decreases hydrogen generation.

SECM proved to be an effective tool to assess the protective ability of the anodized layer formed on the AZ31B alloy. By sensing the hydrogen evolution reaction at the specimen's

surface local corrosion processes could be successively mapped using the SG/TC mode. Up to the author's knowledge the successful use of SECM to examine local corrosion spots of anodized magnesium surfaces is reported for the first time in the current literature. It opens an extensive research frontier for examining the effectiveness of anodized layers in protecting magnesium alloys from corrosion over time, correlating anodizing parameters, surface defects and local corrosion spots. This research is currently ongoing by our group and will be published in a near future.

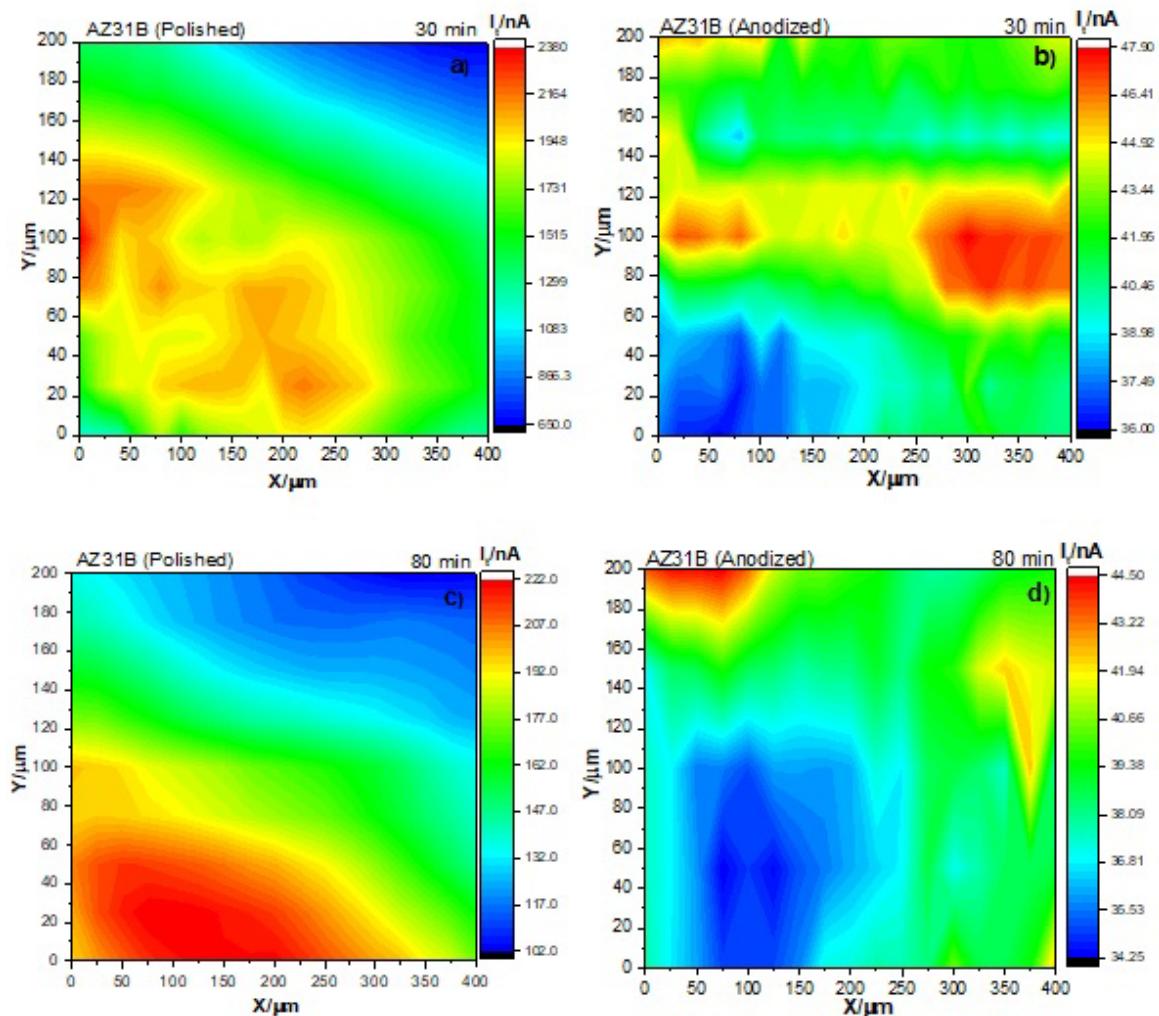


Figure 5. Hydrogen evolution (HE) maps of AZ31B alloy immersed in SBF. HE maps were acquired by SG/TC mode of SECM using a 25 μm Pt UME biased at 0.0 V versus Ag/AgCl. The SECM maps of AZ31B surface were acquired at the open circuit potential after 30 minutes of immersion for the as-polished (a) and anodized conditions (b), and after 80 minutes of immersion for the as-polished (c) and anodized conditions (d).

4. Conclusions

The present study demonstrates that SECM in the SG/TC mode is an ideal tool to investigate the difference in spontaneous corrosion activity of anodized and polished AZ31B Mg alloy at short periods of immersion in simulated body fluid. The different SECM measurements showed that a higher H_2 evolution flux, sensed in an electro-oxidation reaction at the SECM probe, produced a significantly higher current in the polished AZ31B alloy surface when compared to the anodized alloy. It was found that the anodizing process decreases the hydrogen evolution on the surface, and consequently, the current obtained near the surface dramatically decreases. Hydrogen evolution (HE) maps indicated a higher H_2 generation at the beginning of the experiments and lower

generation over time, associated with the early formation of a film of corrosion products. This effect was more evident in the AZ31B Mg alloy surface in the as-polished condition. For the anodized surface, no significant variation of current values was observed, indicating a protective effect that decreases the local corrosion reactions.

5. Acknowledgements

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