Electrochemical testing, hydrogen collection and on-line inductively coupled plasma mass spectroscopy are used to assess the dissolution of high purity magnesium and the attendant hydrogen evolved in solutions containing ferrous ions. It was revealed that ferrous ions in solution had a minimal effect on the hydrogen evolved upon anodically polarized magnesium. The results show that deposition of ferrous ions could not account for enhanced hydrogen evolution during anodic polarization of magnesium. Further analysis of the results obtained under the testing conditions in this study show that the anomalous hydrogen evolution exhibited by dissolving Mg was associated with the regions of anodic dissolution.

The effect of noble metal impurities has attracted attention as one of the most studied for Mg but has been observed on other active metals such as Al. The anomalous HE on anodically polarized Mg has been rationalized on the basis of an enhanced HER rate in response to anodic dissolution – whereby the HER remains a cathodic reaction.

In this context, the increase in cathodic reaction rates on previously anodically dissolved metals (i.e., cathodic activation) has also been shown to be less unique a phenomenon than previously considered.

A number of different theories have been proposed to explain anomalous HE on anodically polarized Mg. The unipositive Mg (Mg⁺) theory, which was first invoked by Turrentine in 1907, persisted for decades after Petty et al. reported indirect evidence of the existence of monovalent (n=1) Mg⁺ and was further developed by Song and Atrens. This theory was discredited after it was shown that the observations of Petty et al. did not support evidence for the existence of Mg⁺ and that numerous independent studies have revealed that n (the number of electrons transferred during anodic dissolution of Mg) equals 2. The effect of noble metal impurities has attracted attention as one rationale for the anomalous HE observed during anodic polarization of Mg. The importance of impurities on Mg corrosion under open circuit conditions has been known since the work by Boyer and later by Hanawalt and McNulty. However, the idea that the accumulation of noble metal impurities due to incongruent dissolution of Mg may be responsible for the HE observed during anodic polarization of Mg is more recent. In brief, this hypothesis considers the regions enriched with noble metals to be the primary source for anomalous HE due to higher catalytic properties toward the HER than Mg and the overpotential for HE shown by these metals at the low potentials reached during Mg dissolution. Brady et al. indicated that alloying elements such as Al and Zn can concentrate in the inner MgO corrosion product layer formed on Mg alloys. The enrichment of iron impurities on Mg specimens (unalloyed with the exception of deliberate Fe impurities) was modelled by Lysne et al., who reported poor enrichment efficiencies that could not account for the large amount of H₂ exhibited at potentials above the OCP. Trace analysis using Rutherford backscattering spectroscopy (RBS) and particle induced X-ray emission (PIXE) confirmed that, even though noble metal enrichment indeed occurs as a consequence of Mg dissolution, the enrichment process has a low efficiency. Finally, it has been shown that, even though impurities affect the kinetics of the HER, the influence is small relative to the total HE rates measured during anodic polarization.

Recently, Høche et al. proposed an impurity-based mechanism in which Fe impurities present in the Mg electrode leave the surface as a consequence of non-faradaic release, and then re-plate in their metallic form after ‘self-corrosion’ in solution at their OCP. In this model, analogous to that exhibited by Cu-containing particles in Al alloys, Fe electrodeposition would form thin regions of metallic iron on the electrode surface that may act as reactive cathodic sites for the HER following the Heyrovsky pathway (H₂O + H₂O + e⁻ → H₂ + OH⁻, where H₂O is a reduced hydrogen atom adsorbed on the electrode surface). This concept was further developed by Lamaka et al., who evaluated the impact of Fe sequestration on Mg corrosion by exposing commercially pure Mg (220 ppm Fe) to different strong Fe-complexing agents. Hydrogen collection measurements under open circuit conditions showed decreased rates of HE in NaCl solutions containing species such as cyanide, salicylate, oxalate, methylsalicylate and thiocyanate that can complex ferrous ions and thus prevent iron replating. However, cyanide, which provided the highest corrosion inhibition, poisons the HER by strongly adsorbing on surfaces and suppressing hydrogen recombination. Additionally, cyanide has also been reported to increase hydrogen permeation into α-Fe by promoting hydrogen entry into the metal and decreasing the number of reduced hydrogen atoms available for chemical recombination via the Heyrovsky pathway. It is possible that cyanide and the other complexing agents studied may cause the same effect on Mg. Therefore,
even though additions of these species decreased the rates of HE (and the concomitant Mg oxidation), it is not clear that this was due to suppression of Fe electrodeposition on the Mg surface. Furthermore, electrodeposition of metallic Fe is a complex process that can be influenced by several factors, such as concentration of Fe ions and pH.33–35 On this matter, the concentration of ferrous ions close to the electrode surface will vary with pH as the result of hydrolysis reactions. The HER produces hydroxyl ions that alkalinize the environment, favoring hydrolysis of ferrous ions and therefore decreasing the efficiency of electrodeposition. It should be mentioned that the Heyrovsky pathway has been suggested by other authors to be favored versus the Tafel pathway. Yuwono et al.36 used first principles density functional theory (DFT) simulations to study the electrochemical stability of Mg surfaces in aqueous environments and found that, under open circuit conditions, the thermodynamically predominant pathway for the HER is the Volmer-Heyrovsky reaction. However, among the different possible reactions that may occur on Mg, it was reported that neither the Tafel nor Heyrovsky reaction can fully explain the phenomenon of cathodic activation.36 As a consequence, further investigation is needed to confirm the validity of this mechanism to explain the enhanced rates of HE exhibited by anodically polarized Mg surfaces.

Mercier et al.37 reported that metallic impurities present in a commercially pure Mg specimen such as Fe, Mn and Al segregate at the grain boundaries (GBs) after chemical etching in a strong acidic solution. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis of anodically polarized surfaces after chemical etching revealed a homogeneous distribution of Fe, which was interpreted according to the model proposed by Höche et al.28 The ToF-SIMS analysis of anodically polarized surfaces after chemical etching showed a low concentration of metallic Fe (lower than that in the absence of polarization) covered by a uniform oxide/hydroxyde Mg layer, with GBs virtually unidentifiable. Therefore, it is not clear if the small amount of Fe detected originated from electrodeposition of previously detached iron from the surface, or if the very low concentrations detected are able to explain the extremely high rates of HE on Mg at potentials above its OCP.

Recently, Michaillardou et al.37 studied the role of electrodeposition of transition metal ions such as Mn2+, Fe2+, Zn2+ and Cu2+ in the cathodic activation of dissolving Mg. Using methods including volumetric H2 collection and the scanning vibrating electrode technique, the addition of transition metal ions enhanced the cathodic activity of the surface and the concomitant oxidation of Mg at open circuit. To explain this behavior, they invoked the mechanism originally proposed by Höche et al., suggesting that transition metal ions released through the self-corrosion could contribute to cathodic activation after being electrodeposited as metal on the Mg at the OCP.38 However, it is not clear if this mechanism applies for anodically polarized Mg since the vast majority of hydrogen originated at the corrosion front when no metallic cations were externally introduced into the test solution.

The aim of the present work is to contribute to clarifying the effect of Fe ions in solution on the anomalous HE exhibited by anodically polarized Mg surfaces and to critically investigate the Fe electrodeposition mechanism originally proposed by Höche et al.28 For that purpose, HE rates were measured on high purity (HP) Mg specimens at different anodic current density values during 1 minute in all cases. The applied current densities were 1, 5 and 10 mA/cm² with a total net charge density passed of 0.06, 0.3 and 0.6 C/cm², respectively. Prior to application of the current, the samples were left at their open circuit potential (OCP) for 10 min, which was the time needed for the OCP to reach a stable value.

Polarization measurements were conducted using a three-electrode configuration with the HP Mg acting as the working electrode, a Pt mesh acting as the counter electrode and a silver/silver chloride (SSC) electrode acting as the reference electrode. A Gamry Instruments Interface 1000E potentiostat/galvanostat controlled by the Gamry Framework was used to polarize the specimens.

**Scanning flow cell coupled to inductively coupled plasma mass spectrometry (ICP-MS).**—With the aim of investigating the effect of ferrous ions and the dissolution of Fe during anodic polarization of Mg, an electrochemical flow cell combined with inductively coupled plasma mass spectrometry (ICP-MS) was used. This technique is derived from the AESEC method developed by Ogle.40 The coupling of a three-electrode electrochemical flow cell (012799, ALS Co. Ltd, Tokyo Japan)41 consisting of an SSC reference electrode, a Pt counter electrode and a Perking Elmer NexION 2000 ICP-MS was used to quantitatively measure the dissolution rate of Mg and Fe. Detailed information on the flow cell that was used in this work and the operating principles of the online ICP-MS measurements can be found elsewhere.41 For the measurements, the following masses were monitored: 24Mg, 57Fe and the corresponding calculated detection limits (Cld), were 2.6 ppb for Mg and 1.3 ppb for Fe. For this experiment, the electrolyte was transported through the electrochemical flow cell at a rate of 0.13 ± 0.03 mL min⁻¹ and injected to the ICP-MS.

The concentration of the released elements (C_M, in ppm) was calculated according to Equation 1, as previously reported by Ogle:40

$$C_M = \frac{(1 - \Gamma)}{k}$$  

[1]

where I is the measured intensity, Γ is the background intensity and k is the sensitivity factor determined from the calibration. As in the hydrogen volume collection experiments, the applied anodic current densities were 1, 5 and 10 mA/cm². Prior to current application, the samples were left at their OCP during 10 min. As described in the previous section, this was the time needed for the potential to reach
Electrodeposition, even if it occurs, is responsible for the anomalous HE exhibited by Mg under anodic polarization. One would expect that increasing concentrations of metallic Fe should electrodeposit on the Mg surface as polarization time progresses, creating larger regions to sustain the faster HER. Accordingly, the rates of HE should increase with time. However, the HER rate, given by the slope in Fig. 1, was found to be constant with time for all applied current densities.

Cathodic potentiodynamic polarization measurements after anodic galvanostatic polarization.—To study the catalytic properties of the previously corroded HP Mg surfaces at different anodic current densities, both in the absence and the presence of ferrous ions, cathodic potentiodynamic polarization measurements were performed after the anodizing treatment. These experiments were carried out after the anodic galvanostatic polarization experiments finished. The cathodic potentiodynamic polarization measurements were performed in 0.1 M NaCl even for samples that were anodically polarized in solutions containing 1 mM FeCl₂ to avoid the presence of Fe ion during cathodic polarization, which could enhance the measured current densities. Consequently, after the anodic galvanostatic polarization experiment finished, the cell was emptied, the cell and the sample surface thoroughly rinsed with deionized water to wash off any trace of ferrous ions, and fresh 0.1 M NaCl electrolyte was poured into the cell before the start of the potentiodynamic experiments. Cathodic polarization measurement were performed after a steady OCP value was achieved (10 min) scanning downwards from the OCP to \(-2.2\ V_{\text{SSC}}\) at a scan rate of 1 mV/s.

Results and Discussion

Gravimetric hydrogen volume collection under galvanostatic polarization.—Fig. 1 shows the volume of hydrogen collected using the gravimetric method as a function of time for the HP Mg electrode in 0.1 M NaCl and 0.1 M NaCl + 1 mM FeCl₂ solutions under the application of different anodic current densities. Data from triplicated experiments are presented.

![Figure 1](image1.png)

**Figure 1.** Volume of \(H_2\) determined using the gravimetric method as a function of time for the HP Mg electrode in 0.1 M NaCl and 0.1 M NaCl + 1 mM FeCl₂ solutions under the application of different anodic current densities. Data from triplicated experiments are presented.

A stable OCP value is observed, indicating that dissolution achieved steady state conditions. Galvanostatic polarization was performed with a Biologic VMP3 potentiostat/galvanostat. All experiments were carried out in duplicate and similar trends were observed, indicating a good reproducibility.

**Cathodic potentiodynamic polarization measurements after anodic galvanostatic polarization.**—To study the catalytic properties of the previously corroded HP Mg surfaces at different anodic current densities, both in the absence and the presence of ferrous ions, cathodic potentiodynamic polarization measurements were performed after the anodizing treatment. These experiments were carried out after the anodic galvanostatic polarization experiments finished. The cathodic potentiodynamic polarization measurements were performed in 0.1 M NaCl even for samples that were anodically polarized in solutions containing 1 mM FeCl₂ to avoid the presence of Fe ion during cathodic polarization, which could enhance the measured current densities. Consequently, after the anodic galvanostatic polarization experiment finished, the cell was emptied, the cell and the sample surface thoroughly rinsed with deionized water to wash off any trace of ferrous ions, and fresh 0.1 M NaCl electrolyte was poured into the cell before the start of the potentiodynamic experiments. Cathodic polarization measurement were performed after a steady OCP value was achieved (10 min) scanning downwards from the OCP to \(-2.2\ V_{\text{SSC}}\) at a scan rate of 1 mV/s.

**Gravimetric hydrogen volume collection under galvanostatic polarization.**—Fig. 1 shows the volume of hydrogen collected using the gravimetric method as a function of time for the HP Mg electrode in 0.1 M NaCl and 0.1 M NaCl + 1 mM FeCl₂ solutions under the application of different anodic current densities. Data from triplicated experiments are presented.
The points where the Mg oxidation reaction intersects the cathodic lines for HE on Mg and Fe define the open circuit corrosion current densities when the electrode surface is Mg ($i_{\text{corr,Mg}}$) and when it is Mg fully covered with electrodeposited metallic Fe ($i_{\text{corr,Mg-Fe}}$), respectively. Fig. 3b shows a magnified view of this region where a hypothetical cathodic Tafel line associated with the HER on a partially-covered Mg-Fe surface is plotted as a red dashed line. Due to the higher exchange current density of Fe for the HER ($i_{0,\text{H,Fe}}$), the Mg-Fe surface will promote the evolution of H$_2$ at faster rates than the pure Mg surface, and thus will exhibit a higher corrosion current density, as shown in previous works where Mg with different Fe nominal concentrations were studied. This difference is shown in Fig. 3b as $\Delta i_{\text{HE}}$.

When an anodic current is applied galvanostatically, a net anodic current of a certain value flows through the electrochemical cell in addition to the corresponding $i_{\text{corr}}$. Associated with this applied anodic current will be HE from the anomalous HE phenomenon, $i_{\text{AHE}}$. It is reasonable then that under the application of a net anodic current for the two cases, $\Delta i_{\text{HE}}$ should affect the amount of HE an H$_2$ collection measurement. Schematically, the total HE detected on a surface with both Mg and Fe ($i_{\text{HE,Total}}$) should be the sum of $\Delta i_{\text{HE}}$ and $i_{\text{AHE}}$:

$$i_{\text{HE,Total}} = \Delta i_{\text{HE}} + i_{\text{AHE}}$$  \[2\]

The fact that the measured HE current densities in the iron containing solution shown in Fig. 2 (i.e. $i_{\text{HE,Total}}$) do not exhibit this extra difference is consistent with the notion that either no Fe electrodeposition occurs or that it happens to a very low extent, having an insignificant impact on the catalytic activity of anodically polarized Mg surfaces toward the HER. Furthermore, it is possible that the ferrous ions hydrolysed in the electrolyte (even if the pH was adjusted to 3 it is likely that the solution near the electrode surface locally reached higher values) and precipitated out as oxides, depositing onto the dissolving Mg surface or embedding into the corrosion product film. The chemical composition of previously polarized Mg surfaces will be analyzed in future work to fully elucidate if Fe (not from accumulation of impurities) is found and, in the case it is, in which state.

Additionally, a positive polarization for Mg would result in a lower overpotential for the HER on Fe, leading to decreased HE rates associated with the virtual Fe-rich regions of the surface. This behavior is shown in Fig. 4, where the HE current density values in Fig. 2 are plotted as a function of the measured potential during the galvanostatic polarization experiments together with the cathodic potentiodynamic polarization curve of pure Fe (99.95% wt of Fe, Alfa Aesar) in the same electrolyte. A limiting current density associated with oxygen reduction is found at potentials above about −1 $V_{\text{SSC}}$ followed by HE at lower potentials. As predicted by the standard electrochemical theory, the HE rate on Fe increased with decreasing applied potential. Fig. 4b shows a closer view of the potential region where the HER dominates the cathodic kinetics. It can be seen that current density values associated with HE on Mg increased with potential whereas the opposite behavior was observed on Fe.

It is possible that area effects play a role and the anomalous HE rates measured on HP Mg may be limited by the fraction of the surface covered with Fe. However, this could only explain the anomalous HE rates observed on HP Mg at 1 mA/cm$^2$. For the applied current densities of 5 and 10 mA/cm$^2$ the results are not consistent with the Fe electrodeposition mechanism. In the case of 5 mA/cm$^2$, the metallic Fe should have covered the entire Mg surface (which is very unlikely within only 1 min of anodic polarization), whereas the rates associated with anomalous HE at 10 mA/cm$^2$ exhibited values nearly two orders of magnitude greater than those of HE on pure Fe. Furthermore, the anomalous HE rates in FeCl$_2$ containing solution were virtually identical to those in 0.1 M NaCl, suggesting that the presence of Fe ions in the test solution do not present any effect on the anomalous HE mechanism. This supports the notion that the catalytic activity of dissolving Mg surfaces is greater than that of noble impurities present in the material above certain values of polarization.

Even though operating under current control is a common practice in the study of the anomalous HE on Mg, it is possible that potentiostatic polarization would result in different results. It has been shown that under potential control Mg surfaces undergo polarity reversal when anodically polarized for a certain period of time. This is due to an enhancement in the cathodic kinetics during anodic polarization that turns the electrode surface into a net cathode. Therefore, under such circumstances electrodeposition would be favored. Furthermore, corrosion products deposited as a consequence of dissolution are likely to partially protect the Mg surface, decreasing the anodic current associated with Mg oxidation. However, in the present investigation much shorter times of polarization were used and variations in the anomalous HE rates (i.e. galvanostatic vs potentiostatic polarization) are expected to be minimal. Nonetheless, more investigation under potential control is needed to fully clarify the influence of ferrous ions.
in the test solution on the anomalous HE exhibited by dissolving Mg surfaces.

In summary, gravimetric H₂ collection measurements are not consistent with the notion that Fe-rich regions, whether coming from noble impurity enrichment or the hypothetical electrodeposition of Fe ions²⁸ are responsible for causing the enhanced rates of anomalous HE on anodically polarized Mg.

**Online ICP-MS measurements during anodic polarization.**—To further investigate the effect of Fe ions in the electrolyte on Mg subjected to anodic polarization, the concentration of Fe ions detected in the downstream electrolyte during galvanostatic polarization at different anodic current densities of 1, 5 and 10 mA/cm² was measured using online ICP-MS. For that purpose, a solution with a known concentration of cationic Fe was passed through a flow cell where the working electrode was HP Mg and the concentration of Fe in the electrolyte was measured after leaving the cell. If Fe ions were to electrodeposit onto the Mg surface during polarization,²⁸ decreased concentrations of Fe should be detected. Additionally, a 1 mM NaCl solution with no added Fe ions was also passed through the electrochemical flow cell in separate experiments using the same HP Mg material for comparative purposes.

Fig. 5 shows the concentration of Fe as a function of time of polarization at different anodic current densities as well as at the OCP prior to the galvanostatic current application for the HP Mg in 1 mM NaCl solution. The concentrations of Fe measured under open circuit conditions prior to any anodic polarization was applied to the Mg surface were in the range of near to zero to approximately 20 ppb. Note that the Fe concentration plotted in Fig. 5 corresponds to the Fe signal detected by the ICP-MS after the background signal (electrolyte not previously passed through the electrochemical cell) was subtracted. Consequently, the Fe depicted in Fig. 5 is associated with Mg dissolution and therefore, comes from the small amount of Fe in the HP Mg electrode. Considering that the initial parts of these experiments were performed under nominally identical conditions, using the same material and electrolyte, it is likely that this difference in Fe concentration is due to the presence of H₂ gas formed inside the cell when the surface was in contact with the electrolyte. The formation of a hydrogen bubble that may remain on the surface despite the flowing test solution would decrease the exposed surface, thus leading to decreased concentrations of the Fe measured.

Once anodic polarization was applied to the HP Mg, the concentration of Fe leaving the cell exhibited a small increase, as determined by the online ICP-MS measurements and shown in Fig. 6. This was attributed to a more rapid release of Fe to the electrolyte coming from the electrode as a consequence of enhanced dissolution kinetics. However, the increment in Fe concentration observed for the applied anodic current densities of 1 and 5 mA cm⁻² was rather insignificant (approximately 7 ppb). For the case of an applied current density of 10 mA cm⁻² the highest increase was shown. Nevertheless, this increase was only of about 18 ppb.

Fig. 7 shows the concentration of Fe profile as a function of time of polarization at different anodic current densities as well as at the OCP prior to the galvanostatic current application for the HP Mg in 1 mM NaCl solution in the presence of 1 ppm Fe. As previously commented, it was rationalized that in the case that Fe electrodeposition occurs on Mg under anodic polarization, decreased concentrations of Fe should be measured with increased values of anodic polarization. However, such behavior was not observed and no significant variations in the amount of Fe leaving the cell were exhibited, as shown in Fig. 7. These data also suggest that in the case that the ferrous ions hydrolysed in
solution, Fe oxides did not deposit on the Mg surface or were retained into the corrosion product film under anodic polarization either.

In summary, online ICP-MS measurements on Mg during anodic polarization in the presence of an Fe-containing electrolyte suggest that Fe (whether deposited as an oxide, embedded in the corrosion product film or electrodeposited as metallic iron) did not remain on the Mg surface during anodic polarization. This is in agreement with the H2 volume collection measurements, which showed that the presence of ferrous ion in the electrolyte did not cause any impact on the rates associated with HE under the application of different anodic current densities.

Cathodic polarization experiments after anodic galvanostatic treatment.—Fig. 8 shows the cathodic potentiodynamic polarization curves of the HP Mg after galvanostatic polarization measurements were carried out at different anodic current densities (i.e., 1, 5 and 10 mA cm\(^{-2}\)) for 1 min. For comparative purposes, cathodic potentiodynamic polarization curves were also performed on HP Mg surfaces that were immersed for 10 min both in the 0.1 M NaCl and the 0.1 M NaCl + FeCl\(_2\) solutions. It can be observed that, whereas the appearance of the surfaces without any prior polarization and the one that was polarized at 10 mA cm\(^{-2}\) showed almost no variation, greater amounts of corrosion products were observed on the HP Mg surface with increased applied current densities, as has been reported previously.\(^{26,27,42}\) These observations are in perfect agreement with the cathodic kinetics depicted in Fig. 8a. Fig. 8b shows that in the presence of ferrous ions all polarization curves exhibited enhanced cathodic current density values. However, it is interesting to note that the surface with no prior anodic treatment and those that were anodically polarized at 1 and 5 mA cm\(^{-2}\) showed similar kinetics. In fact, the Mg surface previously polarized at 10 mA cm\(^{-2}\) presented slightly lower current density values that that without prior polarization. The highest cathodic kinetics were observed for the HP Mg surface previously polarized at 10 cm\(^{-2}\).

It is possible that the enhancement in the cathodic current densities of the samples that were subjected to anodic polarization in FeCl\(_2\) was due to the presence of ferrous ions during prior Mg dissolution. However, in the absence of prior anodic polarization the increased cathodic kinetics is also consistent with the greater surface coverage of corrosion products shown by the HP Mg that was immersed in 0.1 M NaCl + 1 mM FeCl\(_2\) with respect to that in 0.1 NaCl solution. Even though all solutions were freshly made and immediately used before each experiment, it is possible that some ferrous ions further oxidized to ferric ions during the measurement. Consequently, ferric ions may have acted as powerful oxidizing species under the open circuit period, enhancing Mg dissolution and indirectly contributing to the deposition of greater amounts of corrosion products on the electrode’s surface. It is not clear if these ferric-to-ferrous ions further reduced to electrodeposit on the HP Mg in the form of metallic Fe or they hydrolysed to form iron oxides that may have precipitated in the test solution. However, the fact that two different oxidizing species likely coexisted in the electrolyte is consistent with a higher Mg oxidation rate.

Furthermore, it can be observed in Fig. 9 that the surface appearance of the HP Mg samples that were tested in the presence of FeCl\(_2\) showed similar amount of corrosion products. The exception to this observation was the sample that was anodically polarized at 10 mA cm\(^{-2}\), which showed dark corrosion product covering almost the entire surface. This sample exhibited the highest cathodic kinetics in Fig. 8a. In brief, it is possible that the enhanced cathodic current densities observed for the HP Mg surfaces tested in the presence of FeCl\(_2\) were due to an increased surface coverage of corrosion products (more catalytic toward the HER than the bare Mg surface) and not to the presence of ferrous ions in the electrolyte during prior anodic polarization.

As proposed previously, the total current density associated with the anomalous HE can be expressed as the summation of the individual contributions to the HE current density of all the local sites that may

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**Figure 6.** Variation of Fe concentration leaving the flow cell between open circuit conditions and galvanostatic anodic polarization measured as a function of the applied current density for the HP Mg in 1 mM NaCl solution.

**Figure 7.** The \(^{57}\)Fe ICP-MS concentration profile measured as a function of time during open circuit galvanostatic polarization of HP Mg in 1 mM NaCl solution containing 1 ppm of Fe at different anodic current densities.
support the evolution of H$_2$ according to the following expression:

$$i_{TOT} = i_{Anod} + i_{Film} + i_{Imp}$$  \[3\]

where $i_{TOT}$ is the total HE current density determined using the gravimetric method for H$_2$ volume collection (see Fig. 2) and $i_{Anod}$, $i_{Film}$ and $i_{Imp}$ are the contributions of the anodic regions, the corrosion product film and the noble impurities on the electrode surface to the total HE current density, respectively. In the context of the present study, it is proposed that $i_{Imp}$ can be separated into the contribution of noble metal impurities enriched on the Mg surface ($i_{imp}$), and the hypothetical contribution of deposited Fe as a consequence of ferrous ions reduction during anodic polarization ($i_{Fe}$). It is possible to determine the contribution of the corrosion product and the presence of Fe on the surface (accumulated, deposited, embedded or hypothetically electrodeposited) to the total HE current density on the HP Mg surfaces during anodic polarization in 0.1 M NaCl with and without ferrous ions. This procedure, described in detail previously,$^{26}$ involves analysis of the cathodic potentiodynamic polarization curve measured after anodic polarization. In brief, extrapolation of the Tafel region of the cathodic curve to the potential reached during anodic polarization provides a measure of the HE expected from the corrosion products and noble metal on the sample surface. This method assumes that the corrosion film and the accumulated/deposited impurities are relatively unchanged during subsequent cathodic polarization, and that the HE mechanism during anodic and cathodic polarization are similar. Although this method was criticized by Cain et al.,$^{47}$ experimental validation using the gravimetric method for H$_2$ collection and the scanning vibrating electrode technique (SVET) has been provided.$^{27}$

An example of the analysis for the case of prior anodic polarization at 5 mA cm$^{-2}$ in the presence of FeCl$_2$ is shown in Fig. 10. The determination of the part of the curve that represents the Tafel region is complicated by the large ohmic potential drop caused by the intense ohmic drop.
The polarization at 5 mA cm$^{-2}$ is the IR-corrected potential that was measured during prior anodic extrapolation method. The total HE current density values determined in Fig.11 shows HE current density values associated with the corrosion product or the presence of Fe on the surface for the HP Mg electrode in 0.1 M NaCl under the application of different anodic current densities. Determination consisted in extrapolating the cathodic Tafel line to the potential reached during anodic polarization.

HE. In the present analysis, the Tafel regions were determined using the potential range between $-50$ mV and $-250$ mV from the Ecorr for the cathodic curves, where ohmic effects are expected to be minimized. The same protocol was followed for the other applied anodic current densities by extrapolating the Tafel regions of the respective cathodic polarization curves to the appropriate steady state anodic potentials. The IR correction was performed by the current interrupt method during anodic polarization.

Fig. 11 shows HE current density values associated with the corrosion product and the presence of Fe on the surface for the HP Mg electrode in 0.1 M NaCl + 1 mM FeCl$_2$ under the application of different anodic current densities, determined by the cathodic curve extrapolation method. The total HE current density values determined from the gravimetric H$_2$ volume collection measurements shown in Fig. 2 as well as values determined by extrapolation the HE current densities in the absence of prior anodic polarization (i.e. HP Mg immersed for 10 min in the test solution at the OCP before replacing the electrolyte by fresh 0.1 M NaCl solution and starting the cathodic potentiodynamic polarization measurement) are also plotted for comparative purposes. It is not possible from this approach to distinguish the separate effects of the corrosion product, noble metal enrichment and the effect of ferrous ions in solution; only their combined contribution to the total anomalous HE will be considered. Nonetheless, it is reasonable to assume that $i_{\text{Enrich}}$ will be similar for both systems (i.e. in the absence and presence of FeCl$_2$) as the same HP Mg material and identical applied anodic current densities were used. Consequently, it is expected that noble metal enrichment is not the cause of the differences observed in the HE current density values associated with the corrosion product and the presence of Fe on the surface between the results in the Fe-containing and not containing solutions in Fig. 11.

Even though higher HE current density values were exhibited in the presence of FeCl$_2$, an identical trend was shown by the HP Mg in both electrolytes with a slight increase in the HE current density with the applied current density. Interestingly, the current density values associated with the corrosion product and the presence of Fe on the surface in both electrolytes for the lowest current density applied (i.e. 1 mA cm$^{-2}$) were lower than the surfaces that were not anodically treated, as it has been reported in a previous work using ultra-high purity Mg in 2 M NaCl. Similar values to those in the absence of prior polarization were observed when an anodic current density of 5 mA cm$^{-2}$ was applied to the HP Mg in the 0.1 M NaCl solution with and without ferrous ions. However, an increase in the current density values associated with the corrosion product and the presence of Fe on the surface with respect to the unpolarized HP Mg surfaces were shown upon the application of the highest current density of 10 mA cm$^{-2}$.

With the aim of further investigating if the increased HE current density values between the previously polarized HP surfaces in 0.1 M NaCl + 1 mM FeCl$_2$ are associated with the corrosion product or the presence of Fe on the surface, the analysis in Fig. 12 is provided. Fig. 12 shows the ratio of the HE current densities on the HP Mg calculated by Tafel extrapolation of the cathodic curves after the application of an anodic galvanostatic treatment at different current densities by those in the absence of any prior anodic polarization in 0.1 M NaCl and 0.1 M NaCl + 1 mM FeCl$_2$ solutions. Fig. 12 shows that, independently of the absolute current density values with and without Fe ions in the test solution, the HE current densities increased with the applied current density by similar factors. Each current density was applied to the HP Mg in both electrolytes for the same amount of time, meaning that an identical net anodic charge was passed. This is consistent with a similar amount of corrosion product formed on the electrode surface during the anodic treatment for a given applied current density. In the absence of FeCl$_2$ in the test solution (where Fe ion dissolution was determined to be insignificant, as shown in Fig. 5) the HE current density increased on the HP Mg by a similar amount as that observed in the presence of 1 mM FeCl$_2$ at each applied current density. This is consistent with the idea that, regardless of the initially higher HE current density measured in the presence of ferrous ion, the corrosion product (or noble metal enrichment) formed during anodic polarization may be responsible for the enhanced catalytic properties toward the HER calculated in Fig. 11. Furthermore, it is possible that, as rationalized above, the enhanced cathodic current densities observed for the HP Mg surfaces tested in the presence of FeCl$_2$ without prior anodic polarization were due to an increased surface coverage of corrosion products (see Fig. 9) resulting from the presence of more than one
 oxidizing species in the electrolyte and not to any effect associated with ferrous ions in the test solution.

Finally, from Fig. 11 it is possible to discriminate the HE current density associated with the actively dissolving anodic regions by subtracting the corrosion product/metal enrichment HE current densities to those calculated from the gravimetric H$_2$ volume collection measurements.\textsuperscript{26,27} This is based on the idea that the total current density associated with the HER can be described by the summation of the individual contributions to the HE current density of all the local sites that may support anomalous HE (i.e. anodic regions, corrosion product film and noble metal impurities). Following this protocol, it was determined that in the absence of ferrous ions in the test solution the HE current densities associated with the anodic regions was greater than the 90% of the total HE rates. However, slightly lower values were calculated in the presence of FeCl$_2$, where the contribution of the anodic regions to the total HE rates measured was about 80%. As rationalized above, this difference may be due to a greater contribution of the corrosion product film in the electrolyte with Fe ions, where the electrode surface was precorroded prior to the application of any anodic current density. A significantly different behavior was observed for the lowest anodic current density applied (i.e. 1 mA cm$^{-2}$). In this case, the contribution of the actively dissolving regions to the total HE rate exhibited decreased values, which is consistent with previous observations.\textsuperscript{26,27} While further investigation is needed to fully explain this difference, it provides evidence that the primary source for anomalous HE are the regions dominated by the Mg dissolution.\textsuperscript{6,23,27,48}

The results presented in this paper show that it is possible to explain the anomalous HE on anodically polarized Mg, as well as the cathodic activation of corroded Mg surfaces, without the need to invoke electrodeposition of Fe ions, as proposed by other authors.\textsuperscript{19,28,30,37,49} Furthermore, the experimental data indicate that the majority of anomalous HE originates at the actively dissolving anodic regions for the test conditions herein.

Conclusions

The effect of Fe ions in acidic solution in the anomalous HE on anodically polarized HP Mg was studied and the following conclusions can be drawn:

- The gravimetric H$_2$ collection measurements during galvanostatic polarization showed that the volume of anomalous hydrogen increased linearly with time in both electrolytes for all the applied anodic current densities, indicating that the rates associated with anomalous HE were constant. Furthermore, the anomalous HE current densities measured in the presence of FeCl$_2$ were virtually identical to those in the absence of ferrous ion. This behavior is not consistent with the notion that electrodeposition of Fe ions, even if it may occur, is the source for anomalous HE on HP Mg during anodic polarization.
- The current density values associated with anomalous HE on Mg polarized at different anodic current densities increased with potential, whereas the opposite behavior was observed on pure Fe. Even though area effects may play a role, the anomalous HE rates at 10 mA cm$^{-2}$ exhibited values nearly two orders of magnitude greater than those of HE on pure Fe, indicating that, for the test conditions studied, the catalytic activity of dissolving Mg surfaces is greater than that of noble impurities present in the material above certain values of polarization.
- Inductively coupled plasma mass spectrometry results on HP Mg showed that during anodic polarization in the presence of an Fe-containing electrolyte negligible Fe remained on the Mg surface. Furthermore, it showed that the concentration of Fe leaving the electrochemical flow cell was independent of the amount of polarization applied. This is in agreement with the H$_2$ volume collection measurements and further supports that anomalous HE is independent of the presence of ferrous ions in the electrolyte.
- Cathodic potentiodynamic polarization curves after galvanostatic anodic treatment at different current densities showed that cathodic activation of HP Mg was enhanced after prior polarization in the presence of FeCl$_2$. However, this could also be explained in terms of the greater amounts of corrosion products covering the surface.
- The presence of ferrous ion in the electrolyte had no influence in the anomalous HE on anodically polarized HP Mg. Furthermore, it is possible to account for the cathodic activation on previously polarized Mg surfaces by alternate explanations such as the corrosion product film surface coverage, indicating that there is no need to invoke the Fe electrodeposition mechanism.
- For the test conditions used in this study, the majority of anomalous HE on anodically polarized HP Mg originated at regions undergoing active dissolution, supporting previous observations that revealed the anodic areas (or their close vicinity) as the sites of anomalous HE.

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