Reducing the corrosion rate of magnesium alloys using ethylene glycol for advanced electrochemical imaging

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Abstract

The corrosion of an AM50 Mg alloy was studied in ethylene glycol using electrochemical and electron microscopy techniques. Switching from H2O to ethylene glycol, it was shown that the corrosion of the AM50 alloy was significantly suppressed thereby slowing H2 evolution. The corrosion of the AM50 alloy was mapped using scanning electrochemical microscopy in the feedback mode. Ferrocenemethanol can be used to expose the reactive anodic areas on the Mg alloy. These studies confirmed that studies in ethylene glycol can be used to elucidate reaction features obscured by rapid corrosion in H2O without significantly altering the mechanism and damage morphology.

1. Introduction

Mg alloys possess several desirable properties for use in the automotive and aerospace industries, such as their high strength to weight ratio and good castability [1]. A deterrent to their application is their high corrosion rates in aqueous media. Driving the corrosion of Mg alloys is the microgalvanic coupling between the α-Mg matrix and the secondary microstructural constituents, such as β-phase and intermetallic particles [2] with the cathodic reactivity of the latter increased if it contains contaminant elements such as Fe [3]. Understanding the behavior of these microstructural features during corrosion is essential if alloys with improved corrosion properties are to be developed. Separating the responses of individual microstructural components acting as cathodes is inherently difficult using standard electrochemical measurements.

Scanning probe techniques provide valuable insights on a microscale with high spatial resolution. Such techniques have been applied to study the corrosion of Mg alloys including localized electrochemical impedance spectroscopy (LEIS) [4,5], scanning Kelvin probe force microscopy (SKPFM) [6,7], the scanning vibrating electrode (SVET) technique [8–12], and different modes of scanning electrochemical microscopy (SECM) [13–17]. Monitoring corrosion processes above Mg alloys in an aqueous environment with these techniques is challenging because of large H2 fluxes evolving as corrosion progresses which can interfere with mediator detection at the microelectrode tip and create a convective medium at the corroding surface [18]. Recently, these fluxes of H2 have been used to monitor the corrosion process on Mg alloys [19,20].

To overcome this issue we have focused on controlling the corrosion rate, and hence, the amount of H2 produced, using ethylene glycol as the corrosion medium since it limits the availability of H2O, the primary cathodic reagent during corrosion. The corrosion of Mg alloys in ethylene glycol solutions has previously been investigated with a primary focus on their behavior as potential engine block materials which use ethylene glycol-based coolants [21–23]. In these studies increasing the ratio of ethylene glycol to H2O was found to decrease the corrosion rate of the Mg alloys, although little detail was paid to pure ethylene glycol or to this solvent containing only small percentages of H2O. Corrosion was also not investigated on the microscale.

Here, we present a study of the corrosion of the AM50 Mg alloy in ethylene glycol using a range of electrochemical techniques, including SECM, to compare the corrosion behavior to that observed in aqueous solution. Scanning electron microscopy (SEM) and energy dispersive X-ray analyses (EDS) were used to locate and elementally analyze the alloy microstructure, and to locate and correlate surface microstructural features with an in-situ SECM map. Confocal scanning laser microscopy (CLSM) was used to observe the locations of corrosion damage.

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2. Experimental procedures

2.1. Materials

Bulk AM50 sand cast and graphite cast Mg alloy rods were received from General Motors Canada and machined into 1 cm × 1 cm × 0.7 cm size samples. For SECM measurements the AM50 sand cast alloy was machined into 4 mm × 4 mm × 0.5 cm samples. All samples were threaded on the backside to allow connection to external circuitry, and Struers EpoFix epoxy resin was used to seal the samples allowing only the exposure of a single face to the aqueous solution. Solutions were prepared with ethylene glycol (ACP), reagent grade NaCl (Caledon), ferrocenemethanol (FcMeOH) (97% Sigma Aldrich Canada), and NanoPure® (18.2 MΩ cm) H2O.

2.2. Sample preparation

The mounted AM50 samples were ground successively with 800, 1200, 2400 grit SiC paper with a 50:50 ethanol/isopropanol solution as a lubricant, and subsequently polished with a Struers DP-Dur cloth saturated in 3 μm Struers DP-Suspension A for 5–10 min with the ethanol/propanol mixture once again used as a lubricant. A final 2–3 min polish was performed on a Struers OP-Chem cloth using an equal volume mixture of Struers OP-S Suspension and ethylene glycol, as an abrasive. The polished sample was then rinsed and sonicated in anhydrous ethanol for 2 min, Ar dried, and stored in a desiccator.

2.3. Electrochemical measurements

Electrochemical measurements were carried out in a standard three electrode cell with a Pt-mesh counter electrode and a saturated calomel reference electrode (SCE) (with a Luggin capillary placed 2 mm from the working electrode) in aerated solutions at ~22 °C. Electrochemical responses were measured with a Solartron® 1287 potentiostat coupled to a Solartron® 1255B frequency response analyzer for electrochemical impedance spectroscopy (EIS) measurements.

For corrosion potential (Ecorr) measurements the samples were placed in solution, face down for selected durations. Potentiodynamic polarization (PDP) scans were performed following a 2 h exposure to solution by scanning (at 0.167 mV/s) from −200 mV below Ecorr to either −800 mV (vs. SCE), or until a current density of 0.05 mA/cm² was measured to limit the extent of surface damage to the sample. EIS measurements were performed by potentiostatically fixing the potential and applying a sinusoidal potential perturbation of ±10 mV vs. Ecorr. The current response was recorded over the frequency range, 10⁵ Hz to 10⁻⁴ Hz, and a one point per decade reverse scan was recorded from 10⁻² to 10⁵ Hz to ensure steady-state was maintained throughout the measurement.

2.4. Electron microscopy

Scanning electron microscopy (SEM) images were collected in secondary electron (SE) and back scattered electron (BSE) modes on either a LEO 440, Hitachi 3400-N Variable Pressure SEM, LEO 1540 XB SEM, or a Hitachi SU6600 Field Emission SEM. X-ray energy dispersive spectroscopy (XEDS) maps were collected using a Quartz XOne XEDS system. Confocal laser scanning microscopy (CLSM) was performed by measuring the reflected light intensity from a Zeiss 510 confocal with a HeNe 633 nm laser.

2.5. Scanning electrochemical microscopy (SECM)

Prior to SECM measurements, a montage image of a polished 4 mm × 4 mm area on an AM50 sand cast alloy sample was collected at 150× magnification using a Hitachi SU6600 Field Emission SEM. A complete map of the surface was produced by stitching the images using Image-Pro Plus 7.0®. SECM characterization was performed using an ELPProScan 1 system (HEKA, Germany; bipotentiotstat model PG340) by positioning a 25 μm Pt microelectrode over the alloy surface immersed in 1 mM FcMeOH solution (Sigma Aldrich) in ethylene glycol (Fisher Scientific). An approach curve was performed using feedback current from the FcMeOH mediator at an approach speed of 1 μm/s in order to position the microelectrode at a known distance of 10 μm from the surface. The microelectrode tip was polarized to 500 mV (vs. Ag/AgCl) and rastered at 5 μm/s over an area of interest (A0I). A 0.5 mm diameter (as drawn) Pt counter electrode (99.99%, Goodfellow Cambridge Limited, Huntingdon, England) and a Ag/AgCl quasi-reference wire electrode (fabricated as reported elsewhere [24] using a Ag wire of 1.0 mm diameter, annealed 99.99% from Goodfellow) were employed to record electrochemical data.

3. Results

3.1. AM50 alloy microstructure

The microstructural constituents of the AM50 alloy are shown in the SEM micrograph in Fig. 1a, in which one of the many β-phase particles (Mg12Al14) is marked with a green arrow and an AlMn intermetallic with a red arrow. The compositions of individual phases were confirmed in the XEDS maps for Mg, Fig. 1b, which show the general distribution of Mg throughout the alloy matrix. The Al was present in both the β-phase and the intermetallic, Fig. 1c, with some enrichment in the network running between the β-phases corresponding to eutectic α-Mg. The Mn was present within the ten AlMn intermetallic particles in the imaged region, Fig. 1d.

3.2. Electrochemical behavior

The electrochemical behavior of the AM50 sand cast alloy was investigated in 3 mM NaCl in both NanoPure®H2O and ethylene glycol. The chloride was added to enhance solution conductivity. Fig. 2 shows the Ecorr measured in 3 mM NaCl + H2O (black) and 3 mM NaCl + ethylene glycol (red). In H2O, Ecorr initially rose over the first 2 h of immersion from −1.56 V (vs. SCE) to −1.50 V (vs. SCE), and then increased slowly over the 24 h to −1.49 V (vs. SCE) accompanied by a number of small fluctuations. This final value was in the range expected for AM50 in aqueous chloride solutions [25]. In ethylene glycol Ecorr initially decreased from −1.05 V (vs. SCE) to −1.4 V (vs. SCE) over the first 2 h of immersion before increasing to a final steady-state value of −1.26 V (vs. SCE) after 24 h.

The PDP behavior of the alloy in both solutions is shown in Fig. 3. As expected the cathodic current at potentials less than Ecorr was considerably higher in H2O than in ethylene glycol. In H2O (black), once the net current became anodic at −1.45 V (vs. SCE) it increased (region I). For higher potentials the current increased sharply (region II). These features were typical of the behavior observed on this alloy [25] with an attempt to grow a partially protective film in region I followed by film breakdown and the onset of rapid dissolution in region II. In ethylene glycol (red), a similar initial event was observed with region I persisting to a potential of −1.10 V (vs. SCE). The subsequent increase in reactivity was minor, currents <1 μA/cm² being maintained before final film breakdown.
for $E > -0.80$ V (vs. SCE) (region II). Only at these high potentials did the current approach that observed in region I in H$_2$O when the surface is partially protected by corrosion product. For all potentials anodic to $E_{CORR}$, the currents measured in ethylene glycol were $\sim 10^3$ less than those observed in H$_2$O. The solution conductivities were different for the two solutions, with the 3 mM NaCl in H$_2$O having a conductivity of 320 $\mu$S/cm and the 3 mM NaCl in ethylene glycol having a conductivity of 19.3 $\mu$S/cm. These conductivities correlated to iR drops of 13 mV in the aqueous environment and 20 mV in the glycol at the highest currents shown in the PDP scans. The suppression of corrosion rate in ethylene glycol compared to H$_2$O was evident in the Nyquist plots in Fig. 4a, which were recorded after 20 h of immersion, and the Bode plots in Fig. 4b and c. In glycol, the $E_{CORR}$ was $-1.31$ V (vs. SCE) and in H$_2$O $-1.52$ V (vs. SCE) prior to the EIS measurements. Extrapolation of these plots at the low frequency limit to the real axis yielded a measure of the polarization resistance ($R_P$) which is inversely proportional to the corrosion rate. The value obtained for $R_P$ in H$_2$O was nearly two orders of magnitude lower than that in ethylene glycol. The Nyquist plot recorded in H$_2$O exhibited two capacitative responses (I and II), the one at high frequencies being shown in the inset to Fig. 4a. The plot recorded in ethylene glycol exhibits two, possibly three capacitative responses (I, II and III) although whether or not the response at high frequencies (I) was a true response or a result of a combination of the dielectric properties of the solvent and the cell geometry remains to be determined. The characteristic frequency of the low frequency response in H$_2$O (0.5 Hz) was approximately the same as the characteristic frequency of the low frequency response in ethylene glycol, a possible indication that the signals arose from the same process at the electrode surface.
3.3. Corrosion process control

The addition of H₂O to the ethylene glycol system has an intriguing effect. Fig. 5. The $E_{\text{CORR}}$ of the sand cast AM50 alloy in the ethylene glycol solution initially increased to $1.32 \text{ V}$ (vs. SCE) and appeared to be approaching the same steady-state value previously observed (Fig. 2). On addition of 2 mL of H₂O (to 400 mL of ethylene glycol) after 2 h, $E_{\text{CORR}}$ immediately dropped to $1.66 \text{ V}$ (vs. SCE) before recovering to a value of $1.45 \text{ V}$ (vs. SCE) over the next 24 h, which was within the range expected in H₂O (Fig. 2). A second addition of 2 mL of H₂O induced a similar drop in $E_{\text{CORR}}$ although the recovery over the subsequent 24 h was similar but not as complete as observed after the first H₂O addition.

Fig. 6a shows the $E_{\text{CORR}}$ behavior of the sand cast AM50 alloy in 3 mM NaCl + ethylene glycol. Prior to the addition of 25 mL of H₂O (to 400 mL of ethylene glycol) after 2 h, $E_{\text{CORR}}$ immediately dropped to $-1.66 \text{ V}$ (vs. SCE) before recovering to a value of $-1.45 \text{ V}$ (vs. SCE) before recovering to a value of $-1.25 \text{ V}$ (vs. SCE); i.e., a value close to that measured in ethylene glycol with no H₂O addition (Fig. 2). A second addition of 2 mL of H₂O induced a similar drop in $E_{\text{CORR}}$ although the recovery over the subsequent 24 h was similar but not as complete as observed after the first H₂O addition.

Fig. 6b shows the $E_{\text{CORR}}$ behavior of the sand cast AM50 alloy in 3 mM NaCl + ethylene glycol. Prior to the addition of 25 mL of H₂O (to 400 mL of ethylene glycol) after 2 h, (a larger addition of H₂O was used to ensure that the effect was sustained for the duration of EIS measurements) $E_{\text{CORR}}$ was more negative than measured in the previous experiment (Fig. 2). Since the $E_{\text{CORR}}$ measured in H₂O is significantly lower than the $E_{\text{CORR}}$ in ethylene glycol (Fig. 2), and upon the addition of H₂O to ethylene glycol a decrease in $E_{\text{CORR}}$ was observed, the lower $E_{\text{CORR}}$ seen in Fig. 6a suggested that, in this case, the ethylene glycol contained more H₂O than in the previous experiment, a likely result of its hygroscopic nature.

This sensitivity to H₂O content of the ethylene glycol was further indicated by a comparison of the impedance spectra recorded in the two experiments, the overall impedance of the alloy/solution interface being considerably lower in this second experiment. This can be appreciated by a comparison of the Nyquist plots in Figs. 4 and 6. In the first experiment in which the H₂O content of the ethylene glycol appeared to be low, extrapolation of the low frequency
response to the real axis would yield an $R_p$ value of $\sim 67 \text{k} \Omega \text{cm}^2$ compared to $\sim 35 \text{k} \Omega \text{cm}^2$ in this second experiment.

In the second experiment (Fig. 6a), EIS measurements were performed just prior to and following the addition of H$_2$O, Fig. 6b–d. Comparison of the characteristic frequencies for the two capacitive responses observed showed they were the same for both spectra and similar to the spectrum in ethylene glycol in Fig. 4. This similarity in response was confirmed by the Bode plots in Fig. 6c and d which showed only a small change in both time constants after H$_2$O addition. The key difference was in the overall impedance which decreased by a factor of ~2 on the addition of H$_2$O. In both cases the spectra showed a low frequency response at $<10^{-1}$ Hz which suggested some contribution from diffusion, most likely of H$_2$O in the glycol.

3.4. Microstructure behavior in ethylene glycol

Our previous results show that AlMn intermetallic particles can act as cathodes in the corrosion of AM50 alloys in saline aqueous environments [26–27], and that the presence of an accumulated dome of corrosion product (predominantly Mg(OH)$_2$) is evidence of this function [27]. This corrosion product is formed as a consequence of the alkalinity generated by H$_2$O reduction to H$_2$ gas on the intermetallic particles which leads to the precipitation of soluble Mg$^{2+}$ transported to this location from adjacent anodically dissolving areas of the surface. Fig. 7a shows a backscattered SEM image of the freshly polished alloy. The $\beta$-phase network was clearly visible as irregularly shaped light strips in the image, and a large bright AlMn intermetallic was visible in the top right corner. A magnified image of this particle is shown in Fig. 7c. Fig. 7b and d show the same particle after 72 h of exposure to 3 mM NaCl + ethylene glycol solution. The low magnification image, Fig. 7b showed slight corrosion damage of the $\alpha$-Mg matrix had occurred as indicated by the green arrow. No observable change in the $\beta$-phase network was visible. The AlMn intermetallic particle, which appears dark in Fig. 7b, had accumulated a deposit of corrosion product, Fig. 7d, clearly indicating its function as a cathode actively supporting the corrosion of the surrounding $\alpha$-matrix.

3.5. Scanning electrochemical microscopy in ethylene glycol

Fig. 8 shows a 4 mm $\times$ 4 mm area of the surface of the AM50 alloy which was montage imaged to identify the area to be mapped by SECM. This imaging process allows us to identify an area within which we could cross-correlate the SECM measurements with the distribution of microstructural features in the surface. The selected AOI for SECM measurements is marked with the red box.

In SECM experiments, the sample was exposed to a 1 mM solution of FcMeOH in ethylene glycol. A cyclic voltammogram recorded with a 25 $\mu$m Pt microelectrode in this solution at a scan rate of 10 mV/s is shown in Fig. 9a. A steady state current (for the oxidation FcMeOH $\rightarrow$ FcMeOH$^+$ + e$^-$) was observed for $E > 400$ mV (vs. Ag/AgCl) and 500 mV (vs. Ag/AgCl) was selected as the micro-electrode potential during SECM measurements. To position the probe at a 10 $\mu$m tip to substrate distance, feedback current probe approach curves with an approach speed of 1 $\mu$m/s were recorded, Fig. 9b, at the locations marked 1 and 2 in Fig. 10a.

Following positioning, the microelectrode was rastered over a 500 $\mu$m $\times$ 500 $\mu$m area at a scan rate of 5 $\mu$m/s with a potential of 500 mV (vs. Ag/AgCl) applied to the tip while keeping the alloy surface at $E_{CDER}$. The SECM map recorded, Fig. 10a, showed clearly distinguishable regions with the microelectrode tip current varying between 300 and 400 pA.

The approach curve recorded at location 2 yields slightly negative feedback behavior indicating low reactivity while that at location 1 yields slightly positive feedback behavior Fig. 9b. Due to a
regeneration of the oxidized mediator at the microelectrode tip, \( \text{FcMeOH}^+ \) diffused toward the surface being reduced back to \( \text{FcMeOH} \). Heterogeneous rate constants \( (k_o) \) were extracted to quantify the rate at which the mediator was regenerated at these locations. By fitting the approach curves to an analytical approximation \[ k_1 = 1.02 \times 10^{-2} \text{ cm/s} \] and \[ k_2 = 3.13 \times 10^{-2} \text{ cm/s} \] were obtained, clearly demonstrating the difference in reactivity between these locations. For comparison, the analytical approximation for full positive (diffusion controlled reactivity) and negative (no reactivity on an insulating surface) feedback are also shown, plots (I) and (II) in Fig. 9b, respectively.

Fig. 10b shows the SECM image (Fig. 10a) superimposed on the SEM image of the polished AM50 sample with the red arrow highlighting two AlMn intermetallic particles and a circular arrangement of \( \beta \)-phase. These overlaid images show that the reactive areas (faster kinetics in the probe approach curve) were associated with the \( \alpha \)-Mg locations on the surface and the regions of low reactivity (slower kinetics) with \( \beta \)-phase ligaments and surrounding eutectic regions.

Following the SECM experiment the AOI was re-examined and both BSE and SE micrographs are shown in Fig. 11a and b, respectively. To assist in image comparison, the same two AlMn intermetallic particles identified in Fig. 10b are indicated by the red arrow. The SE image in Fig. 11b showed the collection of some corrosion product (identified as the slightly lighter regions) on the \( \alpha \)-Mg areas of the surface.

The 3D CLSM image in Fig. 12a shows an area of an AM50 alloy surface imaged after exposure to ethylene glycol solution for 24 h, and Fig. 12b the AOI imaged by SECM after exposure to the ethylene glycol + \( \text{FcMeOH} \) solution. The red arrow again identifies the location of the two Al–Mn structures highlighted in Figs. 10 and 11. It is clear from these images that the surface was much more extensively damaged after exposure to the ethylene glycol containing \( \text{FcMeOH} \) than it is in the ethylene glycol alone. The darker areas in the CLSM image in Fig. 12b coincided with the corrosion product-covered \( \alpha \)-Mg areas (dark since the laser beam was scattered rather than reflected) and the lighter areas with the less corroded \( \beta \)-phase/eutectic skeletal-like structure. Comparison of this CLSM image with the overlaid SEM/SECM map (Fig. 10b) confirmed that \( \text{FcMeOH}^+ \) was active in corroding the alloy surface and that it was consumed primarily at \( \alpha \)-Mg locations.
Fig. 9. (a) A cyclic voltammogram recorded on a Pt microelectrode in 1 mM FcMeOH in ethylene glycol at 10 mV/s, the arrow represents the initial scan direction: (b) approach curves recorded at locations 1 and 2 labeled in Fig. 10a (Δ and ○). I and II show the calculated approach curves for a diffusion limited reaction and an insulating unreactive surface, respectively.

Fig. 10. (a) SECM map recorded on a sand cast AM50 Mg alloy in 1 mM FcMeOH + ethylene glycol using a Pt microelectrode polarized at 500 mV located 10 μm above the surface and rastered across the surface at 10 μm/s: (b) an overlay of SEM and SECM images of the same area. The red arrow indicates two Al–Mn particles used to relocate this area in the images. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 11. (a) SEM BSE micrograph of the AOI on the sand cast AM50 Mg alloy following the SECM measurement shown in Fig. 10; and (b) SEM SE micrograph of the AOI. Red arrows identify the same AlMn intermetallic particles in each micrograph. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
4. Discussion

In the aqueous corrosion of pure Mg or Mg alloys, the oxidation of α-Mg regions is coupled with H2O reduction, the two reactions occurring at equal rates, as demonstrated recently by a multitude of techniques [29,30]. A detailed summary of the overall corrosion mechanism in aqueous environments leading to Mg(OH)2 deposits has recently been published [31]. The cathodic half reaction occurs predominantly on the most kinetically active locations, not necessarily the most noble with respect to the Mg matrix, (i.e. impurities, intermetallic particles, secondary phases) [32] and, if these sites are limited, the corrosion rate is reduced. This can be achieved through alloy purification [33] or the inclusion of cathodically inept secondary phases [34]. The goal of this project was to demonstrate whether or not the corrosion of a Mg alloy, which proceeds by the influence of adding small amounts of H2O on n intermetallic particles, secondary phases) and, if these sites are not necessarily the most noble with respect to the Mg matrix, (i.e. impurities, intermetallic particles, secondary phases) [32] and, if these sites are limited, the corrosion rate is reduced. This can be achieved through alloy purification [33] or the inclusion of cathodically inept secondary phases [34]. The goal of this project was to demonstrate whether or not the corrosion of an Mg alloy, which proceeds rapidly in aqueous solution with the production of copious quantities, is coupled with H2O reduction, the two reactions occurring at equal rates, as demonstrated recently by a multitude of techniques [29,30]. A detailed summary of the overall corrosion mechanism in aqueous environments leading to Mg(OH)2 deposits has recently been published [31]. The cathodic half reaction occurs predominantly on the most kinetically active locations, not necessarily the most noble with respect to the Mg matrix, (i.e. impurities, intermetallic particles, secondary phases) and, if these sites are limited, the corrosion rate is reduced. This can be achieved through alloy purification or the inclusion of cathodically inept secondary phases. The goal of this project was to demonstrate whether or not the corrosion of an Mg alloy, which proceeds by the influence of adding small amounts of H2O on intermetallic particles, secondary phases) and, if these sites are limited, the corrosion rate is reduced. This can be achieved through alloy purification or the inclusion of cathodically inept secondary phases.

In ethylene glycol, which will contain only small amounts of H2O, the cathodic reactions have been reported to be oxygen reduction and the less likely reduction of the ethylene glycol [37]. However, the large positive shift in E\text{CORR} (Fig. 2) and \sim 10^2 drop in cathodic current in the PDP scans (Fig. 3) on switching from an aqueous solution to the ethylene glycol solution suggest that H2O, even when present in small amounts in ethylene glycol, was the dominant cathodic reagent. This appeared to be confirmed by the influence of adding small amounts of H2O on \text{E}\text{CORR} and the EIS spectra. The immediate drop in \text{E}\text{CORR} (Fig. 5) confirmed the spontaneous effect of H2O on the corrosion process. The subsequent rise in \text{E}\text{CORR} over a period of \sim 22 h to the value expected prior to H2O addition, suggested the H2O was being consumed in the corrosion process. A subsequent addition of H2O led to similar behavior.

A possibility on switching from H2O to ethylene glycol, when the conductivity of the solution was considerably lower, is that the lower conductivity was the primary influence on the corrosion process, not a distinct suppression of the cathodic kinetics due to a lack of H2O. However, the iR drops in the electrochemical measurements were minimal for the potential ranges investigated, and any effect of the solution conductivity would be in the ability of the cathodes in the alloy to microgalvanically couple to the α-Mg matrix.

This influence of changing from H2O to ethylene glycol on the impedance of the alloy/solution interface is clear in Fig. 4, the polarization resistance (estimated by extrapolating the spectra to the zero frequency limit) increasing by approximately two orders of magnitude. Despite this change, the Nyquist plots in aqueous solution and ethylene glycol both exhibited two capacitative responses, comparable features to previously reported systems in H2O and ethylene glycol [5,38]. In aqueous systems, the high frequency response has been attributed to the charge transfer process (Mg → Mg^{2+}) and film capacitance at the alloy surface, and the lower frequency response to the diffusion of Mg^{2+} through the thickening MgO/Mg(OH)2 corrosion product film [5]. If these assignments are accepted, then the Nyquist plots show the characteristic frequency for the charge transfer process (an indication of the time constant of the response) was considerably larger in H2O (~3000 Hz) than in ethylene glycol (~400 Hz); i.e., the kinetics of the initial charge transfer process were considerably faster in H2O. By contrast the characteristic frequencies for the lower frequency response were approximately the same despite the large increase in overall resistance.

The significant increase in \text{E}\text{CORR} combined with a decrease in corrosion rate indicated by the impedance measurements was consistent with a combination of suppressed cathodic kinetics and the formation of a more coherent protective film. This claim was clearly supported by the polarization curves which show a very significant suppression of both the cathodic and anodic kinetics. The considerably larger influence (of switching from H2O to ethylene glycol) on the anodic reaction compared to the cathodic reaction, apparent in the PDP scans (Fig. 3), suggested that lowering the amount of available H2O can lead to improved cohesiveness and protectiveness of the anodically-formed film.

This claim, that the protectiveness of the corrosion product film was improved on switching from H2O to ethylene glycol, was also supported by the impedance data. When \text{E}\text{CORR} in ethylene glycol was high in the first experiment (~1.26 V vs. SCE), the impedences associated with both the interfacial charge transfer (II in Fig. 4a) and the film properties (III in Fig. 4a) were substantially increased. In the second experiment, when the presence of more H2O was suspected, \text{E}\text{CORR} was considerably more negative (~1.45 V vs. SCE) and the two impedances considerably lower. That H2O content is the primary feature controlling the...
corrosion rate is then confirmed by the reduction in both imped-
apances on the further addition of H₂O (Fig. 6). The electrochemical
data thus supports two effects of changing from an aqueous elec-
trolyte to ethylene glycol: (1) a reduction in the kinetics of the
cathodic half reaction by limiting access to H₂O as an oxidant, and (2) an improvement in the properties of the film formed on the
alloy surface.

The SEM micrographs in Fig. 7 confirmed that corrosion in eth-
ylene glycol proceeded via the same microstructural processes observed for the corrosion of this alloy in aqueous chloride solu-
tions, but with a much lower rate of damage accumulation. The
graphite cast AM50 alloy used in this exposure showed identical
corrosion damage morphology, albeit on a smaller scale, to that
observed on the sand cast AM50 alloy [25]. Damage generally
accumulated on the α-Mg grains (Fig. 7b) with the Al–Mn interme-
talic particles acting as microgalvanically-coupled cathodes (Fig.
7d) [26,27]. The extent of damage to the α-Mg grains was minimal after 72 h of exposure consistent with SEM observations (seeFig. 11b below) that these areas, while corroded, were uni-
formly covered with a thin layer of corrosion product. In addition, the β-phase regions and the areas of surrounding eutectic
remained uncorroded, which was also observed after corrosion in
aqueous solutions [26]. In the case of the eutectic regions, this
was attributed to their higher Al content compared to the core of
the α-matrix which led to their protection by the enrichment of
Al at the alloy/oxide interface [26].

With the corrosion rate suppressed in this manner, as demon-
strated by the electrochemical measurements, the H₂ production
was also suppressed making it possible to map the corrosion pro-
cess using SECM, distinct differences in feedback current being
observed on the different microstructural regions on the surface.
The observed spatial variations in current could have arisen from
two scenarios; (1) the migration of the FcMeOH⁺ species from
the microelectrode tip to a region based on the Volta potential of
that region, or (2) the function of FcMeOH⁺ as an oxidant involved
in the corrosion of the α-Mg when generated at the microelectrode
tip. As discussed above, the alloy surface contained a number of
phases for which different average Volta potentials have been
reported relative to the α-Mg matrix phase, i.e., AlMn + 257 mV, β-phase + 152 mV [39]. These differences could cause the preferen-
tial migration of the FcMeOH⁺ to the less noble regions, and would
lead to an SECM map in which the relative feedback currents
reflected the Volta potential differences. However, if such a con-
tribution to the tip current existed, it was minimal since no difference in
current detection was detected between the β-phase and the
AlMn in the system, the regions surrounding these features all
showing low currents, Fig. 10.

The CLSM evidence in Fig. 12 confirmed that the presence of
FcMeOH⁺ was driving a slow but significant corrosion process,
an influence requiring further investigation. However, as opposed to
H₂O, which is reduced predominantly on features such as the AlMn
particles leading to corrosion of the α-matrix by microgalvanic
coupling, the generated FcMeOH⁺ at the microelectrode tip was
reduced at the most anodically reactive locations. According to the
SECM and SEM maps in Fig. 10, this order of reactivity is
α-Mg matrix > Al-containing eutectic > β-phase/Al–Mn
In this regard, SECM provided a map of the anodic reactivity of
the surface. While this may be intuitively surprising since FcMeOH⁺ is a
localized cathodic reagent, it most likely reflected two features: (i)
the rapid kinetics of the FcMeOH⁺/FcMeOH couple which dictated
that reduction occurred on the most conductive location rather than
on a catalytic secondary phase location; and (ii) the more limited
range of microgalvanic coupling possible in the less conductive eth-
ylene glycol solution. In this somewhat surprising manner, SECM
using an FcMeOH⁺ mediator gave an excellent indication of the
corrosonivity of individual surface locations. A comparison of the
SECM map to the CLSM image obtained for the corrosion of this
alloy in an aqueous system confirmed that the corrosion damage
morphology and roles played by the microstructural features, while
muted by the reduced conductivity in ethylene glycol, are the same as in H₂O [26].

5. Conclusions

The corrosion of a sand cast AM50 Mg alloy was studied in eth-
ylene glycol with and without added H₂O. A combination of elec-
trochemical and microscopic investigations showed similar
 corrosion processes occurred in ethylene glycol as in H₂O but con-
siderably slower. Experiments in which H₂O was added to the eth-
ylene glycol demonstrated that H₂O is the key cathodic reagent in
this solvent, not oxygen reduction or reduction of the ethylene gly-
col. By slowing the corrosion process and avoiding excessive H₂
production, it was possible to map the corrosion response of the
alloy by SECM using the redox mediator FcMeOH⁺. The FcMeOH⁺
was also suppressed making it possible to map the corrosion pro-
cess of the alloy by SECM using the redox mediator FcMeOH⁺
confirming that the corrosion process of the alloy is the same
in ethylene glycol as in H₂O. Reducing the corrosion rate of Mg alloys,
without a large alteration in the roles played by the microstruc-
tural features, through solvent selection presents a potentially
valuable approach to analyzing the corrosion processes on Mg
alloys with increased resolution and detail.

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