Mg and Mg alloys have been shown to be susceptible to the formation of laterally-spread corrosion products, which tend to form thread-like “filaments” or radially-expanding “discs” in neutral-pH sodium chloride (NaCl) solutions with concentrations ranging from 0.01 M to 0.86 M.1–12 Williams et al. have employed the scanning Kelvin probe (SKP)1 and the scanning vibrating electrode technique (SVET)1,5,9 to show that this behavior is driven by a “differential electrocatalytic” mechanism, whereby areas consumed by the corrosion products catalyze the cathodic hydrogen evolution (HE) reaction. The HE reaction has been proposed to be catalyzed by non-alloy-specific mechanisms including undissolved metallic Mg “chunks” and a significantly roughened surface film,1,13 in addition to alloy-specific mechanisms including enrichment of noble (relative to Mg) alloy constituents.5,9,14,15 However, a consensus has not been reached in the literature to date regarding the dominant source(s) of cathodic activity.

Williams et al.9 proposed that the main source of cathodic activation on corrosion filaments formed on as-cast Mg alloy AZ31B were Al-Mn intermetallic particles which were originally present in the alloy microstructure and were left behind as the Mg matrix phase was selectively dissolved. Al-Mn phases are well-known to promote cathodic activity, then the cathodic current density measured over a corrosion filament was argued to be indicative of a solute enrichment mechanism being a significant factor in this process.

The AZ31B alloy used in this work was received as 2.0 mm thick wrought sheet in the H24 temper, the chemical composition of which was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), as shown in Table I. The composition of the alloy was within the range outlined by its nominal specification.19 A near-neutral aqueous 0.05 M NaCl solution was used as the electrolyte for all experiments. This solution was used in the previous TEM investigation12 and allowed for the spontaneous (i.e. at the open circuit potential (OCP)) initiation of corrosion filaments within a convenient time period with filament propagation occurring sufficiently slowly to allow for spatially-resolved SVET measurements to be acquired. The solution was prepared from NaCl powder (Fisher Scientific, 99.0% min. assay) and deionized water naturally aerated in room temperature laboratory air. For each test, the corrosion cell (with all electrodes in position) was filled with approximately 800 mL of electrolyte immediately prior to the beginning of electrochemical measurements.

For OCP and potentiodynamic polarization measurements, Al tape was used to attach steel wires to 5 mm × 5 mm plan-view sections of the AZ31B-H24 alloy. The samples were individually mounted in cold-mounting epoxy such that only the plan-view surface opposite the surface attached to the wire was exposed to the electrolyte. The exposed surface was polished to a 1200-grit finish using SiC paper and an ethanol lubricant. Fast-curing epoxy was applied around the edges of the exposed surface to prevent preferential localized corrosion at the sample/epoxy mount interface. OCP and potentiodynamic polarization measurements were conducted on the mounted filaments of cathodic activity under conditions known to promote a Zn-enriched layer should be valuable nonetheless. The purpose of this work was to re-investigate the electrochemical behavior of filiform-like corrosion on AZ31B, in this case using the same wrought AZ31B-H24 sheet material employed in the reported TEM investigation.12 To realize this objective, sequential potentiodynamic polarization and SVET measurements were made on AZ31B-H24 electrodes immersed in a 0.05 M NaCl solution.

### Experimental

The AZ31B alloy used in this work was received as 2.0 mm thick wrought sheet in the H24 temper, the chemical composition of which was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), as shown in Table I. The composition of the alloy was within the range outlined by its nominal specification. A near-neutral aqueous 0.05 M NaCl solution was used as the electrolyte for all experiments. This solution was used in the previous TEM investigation and allowed for the spontaneous (i.e. at the open circuit potential (OCP)) initiation of corrosion filaments within a convenient time period with filament propagation occurring sufficiently slowly to allow for spatially-resolved SVET measurements to be acquired. The solution was prepared from NaCl powder (Fisher Scientific, 99.0% min. assay) and deionized water naturally aerated in room temperature laboratory air. For each test, the corrosion cell (with all electrodes in position) was filled with approximately 800 mL of electrolyte immediately prior to the beginning of electrochemical measurements.

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### Table I. Chemical composition of the AZ31B alloy as determined by ICP-OES

| Alloy   | Al wt% | Zn wt% | Mn wt% |
|---------|--------|--------|--------|
| AZ31B   | 3.08   | 2.81   | 1.16   | 0.44   | 0.293  | 0.131 |

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samples using a standard three-electrode configuration. The exposed face of the sample acted as the working electrode, while a saturated calomel electrode was used as the reference electrode. Two graphite rods positioned on opposite sides of the sample were used as counter electrodes. The electrodes were positioned in a Uniscan Instruments Environmental TriCell with a mount holder fixed to its base, as shown schematically in Figure 1a. This corrosion cell was chosen in order to maintain a consistent configuration with the SVET measurements, which required the sample to lie in a horizontal plane. All OCP and potentiodynamic polarization measurements were conducted with a Solartron 1287 potentiostat.

The OCP was determined for an immersion period of 24 h. The exposed surface was also monitored with a high-resolution video camera positioned directly above the corrosion cell. Potentiodynamic polarization measurements were conducted after 1 h and 24 h immersion at the OCP for the purpose of investigating the anodic and cathodic kinetics at two different stages of corrosion: (i) prior to the initiation of localized corrosion and (ii) after significant localized corrosion. For the 1 h polarization measurements, anodic and cathodic scans were completed separately using freshly-prepared solutions and sample surfaces. For the 24 h polarization measurements, the anodic scans were completed following the cathodic scan on the same sample with an immersion period of 1 h at the OCP between the two scans. The electrode potential was swept from the OCP to –1.75 V\text{SCE} for the cathodic scans and from OCP to –1.35 V\text{SCE} for the anodic scans, using a scan rate of 0.1667 mV/s for all measurements. Each OCP and polarization measurement was repeated three times using freshly-prepared solutions and sample surfaces to ensure data consistency.

For the SVET measurements, 10 mm × 10 mm plan-view sections of the AZ31B-H24 alloy were mounted in epoxy and polished to a 200 μm/s with a data point collected at 150 μm intervals. The probe was vibrated in the vertical direction with an amplitude of 30 μm and a frequency of 80 Hz. The gain of the electrometer was set to 10^6, and the full scale sensitivity of the lock-in amplifier was set to 160 μV. The 24 h immersion test was repeated three times using a freshly polished surface for each experiment to evaluate data repeatability. The exposed surfaces were monitored with a high-resolution video camera positioned at approximately 45° to the vertical during each test to relate the local ionic activity with the visual development of localized corrosion.

A calibration test similar to the one outlined by Williams and McMurray was performed to convert the measured voltages to ionic current density values. The vibrating probe was first placed inside a tube with a known inner area. Using a polished gold (Au) working electrode immersed in a 0.05 M NaCl electrolyte, a series of known current densities. A more detailed explanation of the SVET technique is available elsewhere.

**Results**

Microstructural examination.— The plan-view grain structure of the as-received alloy (Figure 2a) was revealed by etching in a solution of 25 mL ethanol, 5 mL acetic acid and 2.1 g picric acid for approximately 3–5 s. The mean grain size (with 95% confidence) was 13 ± 2 μm, as determined using the ASTM E112-10 linear

![Image](https://example.com/image1.png)
Al-Mn intermetallic particles, distinguishable by their bright atomic number contrast, were observed under back-scattered electron SEM imaging (Figure 2b). Semi-quantitative EDS analysis using the built-in standards (i.e. k-factors) of the resident EDS software revealed that the average Al:Mn ratio of the particles in the AZ31B-H24 alloy was approximately 2.7. This ratio is close to that expected for the Al₁₁Mn₄ phase, and was also consistent with prior TEM-EDS analysis of the alloy.

**OCP transient measurements.**— An OCP transient for AZ31B-H24 immersed in a 0.05 M NaCl solution is shown in Figure 3 and summative OCP data in Table II. The OCP typically increased from approximately −1.7 V_SCE to −1.6 V_SCE within the first 100 s after immersion and subsequently increased at a more gradual rate. After an immersion time of 2–5 h, the OCP suddenly decreased. This event coincided with the initiation of a corrosion filament on the exposed surface and the observation of H₂ bubbles evolving from the same location. After this initiation (i.e. breakdown) event, relatively large OCP fluctuations were observed as the surface became increasingly covered by corrosion filaments. Figure 3 corresponds to the sample that displayed the longest breakdown initiation time in order to demonstrate that a stable OCP was not observed prior to breakdown.

A sequence of images of the AZ31B-H24 surface during corrosion is shown in Figure 4. These images were taken while recording the OCP values plotted in Figure 3. The exposed surface became lighter in color within the first 30 min. of immersion, coinciding with the large initial increase of the OCP (Figure 3). This was attributed to the replacement of the initial air-formed film with an aqueous-formed film. Corrosion filaments were initially observed at the top-left edge of the exposed surface following 6 h of immersion (Figure 4). These filaments continued to propagate until the majority of the surface was covered following 12 h of immersion. However, a second, darker set of corrosion filaments were observed following 16 h of immersion (Figure 4). Continued filament initiation and propagation was observed from this time onwards, with the new filaments appearing progressively darker and wider, as can be observed for the 20 and 24 h exposures shown in Figure 4.

**Table II.** Average corrosion parameters with 95% confidence intervals for the AZ31B-H24 alloy determined from OCP and potentiodynamic polarization measurements in a 0.05 M NaCl solution. The time until breakdown is presented as individually determined values because the confidence interval for this quantity was unacceptably large.

|                          | 1 h at OCP          | 24 h at OCP         |
|--------------------------|---------------------|---------------------|
| Final OCP (V_SCE)        | −1.527 ± 0.005      | −1.499 ± 0.008      |
| Time until breakdown (h) |                     |                     |
|                          | 3.22, 2.44, 4.66     |                     |
| E_b (V_SCE)              | −1.417 ± 0.131      | −1.412 ± 0.131      |
| \( i_\text{corr} (\text{A/cm}^2 \times 10^{-6}) \) |                 |                     |
|                          | 12.7 ± 5.4          | 54.5 ± 22.0         |
| \( i_\text{corr} \) at −1.6 V_SCE (A/cm² \times 10^{-6}) |                 |                     |
|                          | 47.4 ± 15.0         | 158 ± 38.7          |

**Potentiodynamic polarization measurements.**— Representative potentiodynamic polarization curves following 1 h and 24 h of immersion are presented in Figure 5 and a summary of the determined electrochemical kinetic parameters derived from them is provided in Table II. The 1 h polarization curve provided the anodic and cathodic kinetics prior to breakdown, since no corrosion filaments had initiated prior to polarization. The anodic polarization curve for the 1 h measurements displayed a breakdown potential (E_b) of −1.417 ± 0.131 V_SCE (see Table II), above which the anodic current density rapidly
Figure 5. Representative potentiodynamic polarization curves for AZ31B-H24 recorded after 1 h and 24 h at the OCP in a 0.05 M NaCl solution. The average corrosion current density ($i_{corr}$) was calculated by extrapolating the linear portion of the cathodic curves to the corrosion potential ($E_{corr}$) of each sample. As can be seen in Table II, at 95% confidence, the average $i_{corr}$ values for the 1 h and 24 h measurements were significantly different, being $(12.7 \pm 5.4) \times 10^{-6} \text{ A/cm}^2$ and $(54.5 \pm 22.0) \times 10^{-6} \text{ A/cm}^2$, respectively. The average cathodic current density ($i_c$) at a potential chosen within the linear portion of the cathodic curves (i.e. –1.6 V SCE) was also significantly different at 95% confidence between the 1 h measurement ($[47.4 \pm 15.0] \times 10^{-6} \text{ A/cm}^2$) and the 24 h measurement ($[158 \pm 38.7] \times 10^{-6} \text{ A/cm}^2$) (see Table II).

SVET measurements — Selected SVET maps recorded as a function of immersion time are presented in Figure 6. Images of the scan area at the corresponding immersion time are provided alongside the SVET maps. It is important to note that the SVET maps presented in this work are not completely time-resolved, since the anodic and cathodic locations sometimes moved appreciably during the time required to complete a scan (approximately 25 min.). In light of this,
either the SVET scan immediately after or prior to each indicated immersion time was selected for presentation based on whether the bottom half of the scan area (i.e. the first half scanned) or the top half (i.e. the second half scanned) was of higher interest. In addition, it was noted during SVET testing that the initiation of corrosion filaments generally occurred earlier than during the OCP measurements discussed above. This may have been due to the increased solution convection caused by the scanning of the SVET probe, as well as the fact that the Pt tip on the probe tended to remove H2 bubbles adhering to the alloy surface that would have otherwise prevented direct contact between the alloy surface and the electrolyte. However, the morphology and linear propagation rates of the corrosion filaments following localized breakdown did not appear to be affected by the SVET probe movement.

The localized corrosion sites were initiated within the first 30 min. of immersion, as evidenced by the appearance of local anodic peaks accompanied by HE at the same location (Figure 6a). Multiple corrosion filaments propagated laterally from these initiation sites toward the bottom half of the scan area, with anodic peaks and HE observed at the fronts of the propagating corrosion filaments (Figures 6b, 6c). In addition, cathodic currents were observed in the dark areas behind the propagating corrosion filaments (Figure 6c). After an immersion time of approximately 8 h, a second set of corrosion filaments propagated laterally from these initiation sites toward the bottom half of the scan area, with anodic peaks and HE observed at the same location (Figure 6a). Multiple corrosion filaments generally occurred earlier than during the OCP measurements discussed above. This may have been due to the increased solution convection caused by the scanning of the SVET probe, as well as the fact that the Pt tip on the probe tended to remove H2 bubbles adhering to the alloy surface that would have otherwise prevented direct contact between the alloy surface and the electrolyte. However, the morphology and linear propagation rates of the corrosion filaments following localized breakdown did not appear to be affected by the SVET probe movement.

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The average values of the anodic and cathodic current densities within the 0.6 mm × 0.6 mm area outlined by the small frame in the scan area images of Figure 6 are shown in Figure 7. It can be seen that after the first pass of filaments (indicated by the large average anodic current densities) from approximately 0–4 h immersion, the assessment area became dominated by cathodic currents with relatively stable values as a function of immersion time. After the second pass of filaments for immersion times of approximately 10–12 h, comparatively larger cathodic currents dominated the assessment area until a third set of filaments passed for immersion time of greater than 20 h.

Individual current densities for each SVET map were integrated according to the formalisms of Williams and McMurray:5

\[ I_a = \int_0^Y \int_0^X [i_{a(x,y)} > 0] \, dy \, dx \]  
\[ I_c = \int_0^Y \int_0^X [i_{c(x,y)} < 0] \, dy \, dx \]

where \( I_a \) and \( I_c \) are the total integrated anodic and cathodic currents across the scan area at a given immersion time, respectively, and \( X \) and \( Y \) are the dimensions of the scan area and \( i_{a(x,y)} \) corresponds to the SVET-measured current density at a co-ordinate \((x,y)\) within the scan area. Use of this integration allowed for the construction of plots of the total ionic current across the SVET scan area versus immersion time, as shown in Figure 8. It should be noted that the data presented in Figure 8 span three repeats of the integration for freshly prepared samples. The anodic currents in these plots should ideally be equal to the cathodic currents at each time in order to satisfy the conservation of charge. However, transient inequalities in the respective integrated currents likely resulted from the limited spatial resolution of the SVET measurements (i.e. cathodic currents were often “drowned out” by nearby intense anodes) as well as the fact that the SVET scan area did not encompass the entire exposed sample area. Points with higher anodic currents than cathodic currents typically represent situations where one or more large anodic peaks block measurement of surrounding cathodic currents, while points with higher cathodic currents represent situations where anodic peaks are partially or fully

![Figure 7](image-url)  
**Figure 7.** Average current density values within the area outlined by the small frame in the scan area images in Figure 6, as a function of immersion time in a 0.05 M NaCl solution.

![Figure 8](image-url)  
**Figure 8.** Integrated currents across the SVET scan area for AZ31B-H24 as a function of immersion time in a 0.05 M NaCl solution. Current values were normalized by dividing by the scan area (6 mm × 6 mm). Each plot was derived from a separate 24 h immersion test of a freshly polished alloy surface. The first plot was derived from the same test as shown in Figure 6 and Figure 7.
outside of the scan area dimensions. Nevertheless, it can be observed in Figure 8 that the integrated anodic and cathodic currents generally increased comparably with immersion time for each of the immersion periods. As can be seen from Figure 8, this trend was consistent for all of the 24 h immersion tests.

It should be noted that no steps were taken to maintain a constant electrolyte resistivity, pH and SVET probe-to-sample distance throughout the 24 h immersion tests. However, these factors are not believed to have influenced the major observations of sustained local cathodic activity (Figure 7) and the time-dependent increases of overall anodic and cathodic currents (Figure 5, Figure 6, Figure 8) on AZ31B-H24, since the same trends were not observed for an AM30 alloy recently characterized using the sample experimental procedures.21

Discussion

The initial rise of the OCP followed by a sudden decrease (Figure 3) at the AZ31B-H24 passivation breakdown was fundamentally similar to the OCP transients recorded by Williams et al.9 for as-cast AZ31B in NaCl solutions ranging in concentration from 0.034 M to 0.86 M. The sudden OCP decrease is thought to result from the high anodic current densities associated with localized corrosion (i.e. corrosion filament) initiation where the OCP fluctuations following the breakdown event were reflective of the transient nature of corrosion filament propagation. The potentiodynamic polarization results (Figure 5) were also comparable to those obtained by Williams et al.,9 since both showed an increase in cathodic current density following significant surface coverage by the corrosion filaments — i.e. the 1 h vs. 24 h potentiodynamic polarization curves.

The SVET results revealed that the increased cathodic activity originated from the surfaces consumed by the propagation of corrosion filaments (Figure 6), which was also in agreement with the previous SVET investigation of as-cast AZ31B by Williams et al.24 However, it was shown in this work that the cathodic current density above a defined region of filaments was relatively stable with respect to immersion time when using a 0.05 M NaCl electrolyte (Figure 7), whereas Williams et al.24 noted that the average cathodic current density for a defined region of corrosion filaments diminished with increasing immersion time for a 0.86 M NaCl solution. The relatively stable cathodic current density observed above a defined region of filaments in the present work resulted in a continuous increase of the integrated anodic current throughout the 24 h immersion period (Figure 8), arising from the continuous appearance of new cathodic filaments during this period (Figure 4, Figure 6). Conversely, the integrated anodic current across the as-cast AZ31B surface investigated by Williams et al. was stable after an immersion time of approximately 2 h in a 0.86 M NaCl solution.9 It should be noted that the current variations within the stabilized period observed by Williams et al. were larger than the maximum currents measured in the present investigation; however, this can be attributed to the higher NaCl concentration in the former investigation. Additional tests at lower NaCl concentrations by Williams et al.9 produced current variations more in line with those in the present investigation. The lack of anodic current stabilization in the present investigation cannot be attributed to differing NaCl concentrations, since Williams et al. also demonstrated that the time required for the integrated anodic current to stabilize on as-cast AZ31B was proportional to the NaCl concentration in the solution (from their results, the integrated anodic current stabilized after approximately 0.5 h in a 0.17 M solution and appeared to be immediately stable in a 0.034 M NaCl solution).9 Williams et al. attributed this dependence on electrolyte concentration to the throwing power of the electrolyte, whereby a relatively low NaCl concentration limited the distance that a cathodically-activated filament tail could galvanically couple with the anodic filament head. The contrasting results in the present investigation using a relatively weak NaCl concentration (0.05 M NaCl) thus demonstrated the strong cathodic throwing power of AZ31B-H24 corrosion filaments relative to as-cast AZ31B corrosion filaments, which is argued to be linked to its differing microstructure.

AZ31B in the as-cast condition often has a dendritic microstructure with significant segregation of Al (and by proxy, Zn)25,26 as opposed to the more homogeneous α-Mg solid solution microstructure of the alloy in the H24 temper (Figure 2). The dendritic appearance of the corrosion filaments observed by Williams et al.7 suggests that they followed the dendritic microstructure of the as-cast surfaces. In this case, it would be expected that the corrosion filament propagation would follow the Mg-rich primary dendrites, since these would represent the most anodically-susceptible pathways. Several past investigations of multi-phase Mg alloys provide evidence to support this hypothesis in the form of optical and SEM images showing the primary alpha-Mg phase to have been preferentially corroded.26,27 By contrast, the more homogeneous distribution of alloying elements in the H24 alloys likely promoted corrosion filament propagation along some anodically-susceptible pathways, which can include grain boundaries, twin boundaries and other microstructural defects in addition to being favored by particular grain crystallographic orientation.2,3,29

Although the formation mechanism of the previously reported metallic Zn-enriched layer at the base of a corrosion filament on AZ31B-H24 is not yet clear,12 it is reasonable to assume that the availability of solute Zn in the vicinity of the locally corroded region was required for it to appear. Thus, if the corrosion filaments on as-cast AZ31B preferred to propagate along anodically-susceptible Mg-rich dendrites, the formation of a Zn-enriched layer might not be expected in this case. A cross-sectional microscopic examination of the corrosion filaments formed on as-cast AZ31B will be required to confirm this hypothesis. Given that Zn metal and Zn-alloyed Mg have been shown to be more cathodic toward the cathodic HE reaction than pure Mg,31,32 the sustained cathodic activity revealed by the SVET results in the present investigation of AZ31B-H24 could be attributed to the Zn-enriched layer at the base of the filaments. Although the Zn-enriched layer was observed to be present underneath a reasonably dense corrosion filament, the presence of through-thickness cracks in the filaments could provide pathways for the electrolyte to be in direct contact with the Zn-enriched surface.12

Conclusions

The filiform-like corrosion behavior of Mg-alloy AZ31B-H24 was investigated in a 0.05 M NaCl solution using OCP measurements, potentiodynamic polarization and the scanning vibrating electrode technique (SVET). The results were discussed in the context of a previously reported TEM examination of the corrosion filaments.12 The key conclusions from the present study are as follows:

1. The corrosion filaments supported the enhanced cathodic activity necessary to provide the driving force for filiform-like corrosion propagation.
2. The SVET-measured cathodic current density remained relatively stable, resulting in an increase in the total anodic current measured across the exposed surface for the 24 h immersion period.
3. Once initiated, the sustained cathodic activation is hypothesized to be directly linked to the metallic Zn enrichment observed at the corrosion filament/alloy interface in the wake of a propagating corrosion filament.

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