The fraction of the surface corroded is quantitatively tracked during the corrosion process. The small electrode in close proximity to the defined surface where essentially the whole surface undergoes corrosion after about one minute. The small electrode in close proximity to the defined surface where essentially the whole surface undergoes corrosion after about one minute.

Hydrogen Evolution during the Corrosion of Galvanically Coupled Magnesium

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In this study, the impact of galvanic coupling of magnesium to steel on the corrosion rate, surface morphology, and surface film formation was investigated. In particular, experiments were performed to examine and quantify the role of self-corrosion (also called negative difference effect (NDE) or anodic hydrogen) during the corrosion of galvanically coupled Mg. It was found that galvanic coupling at high cathode-to-anode area ratios resulted in high rates of corrosion that impacted hydrogen evolution on the Mg surface. Self-corrosion accounted for, on average, approximately one-third of the total observed corrosion. The self-corrosion fraction varied with time and was found to reach values in excess of 50%. Surface film formation was observed, and approximately 30% of the Mg lost to corrosion was found in the film at the end of our experiments. The surface morphology observed during galvanic corrosion was dramatically different from the filiform structures associated with free corrosion of our samples, but showed similarities to the morphology observed previously for anodically polarized samples. Film formation appeared to slow the rate of self-corrosion with time. These results complement previous studies of Mg corrosion and add important insight into the role of hydrogen evolution on the Mg surface during galvanic corrosion.

New environmental regulations, good mechanical properties, abundant availability and reasonable cost have generated renewed interest in the wider use of magnesium (Mg), especially for automobile and aerospace applications.1–4 There has also been growing interest in the use of Mg for batteries and in hydrogen generation systems.5–8 A key obstacle to the use of Mg is its corrosion susceptibility. Consequently, several previous studies have focused on understanding the corrosion mechanisms that control the dissolution rate and surface morphology of Mg during corrosion. Both disk-shaped and filiform corrosion have been observed for unalloyed Mg, depending on the concentration of impurities in the metal and the concentration of Cl\textsuperscript{−} in the electrolyte.9–11 In both cases, the morphology is strongly influenced by the cathodic reaction, which limits the rate of corrosion.11,12

The situation changes dramatically when Mg is coupled to another metal because of the increased cathodic area that significantly diminishes limitations due to the cathodic reaction on the Mg surface. Although most hydrogen evolution occurs on the coupled metal, hydrogen evolution on the Mg surface does not cease. The purpose of this paper is to investigate the impact of galvanic coupling on Mg corrosion that is associated with hydrogen evolution on the Mg surface, and the extent to which such coupling influences both the morphology and rate of Mg self-corrosion.

In this paper, we use the term “self-corrosion” to refer to the dissolution of Mg that is not associated with the galvanic current that passes between the coupled metal and the Mg, similar to the definition used previously by others in galvanically coupled studies of Mg.13,14 The high rate of self-corrosion of Mg during anodic polarization is widely referred to as the negative difference effect (NDE) or anodic hydrogen evolution, and has been a topic of study for quite some time.15–21 Most NDE studies have been performed on uncoupled polarized Mg samples. While polarization of Mg samples is a convenient method for studying NDE, our galvanically coupled experiments have advantages that make them a useful complement to the previous experiments. For example, we use a relatively small Mg electrode to provide a well-defined surface where essentially the whole surface undergoes corrosion after about one minute. The small electrode in close proximity to the external steel cathode serves to minimize ohmic losses and leads to high current densities at very moderate potentials. In addition, the fraction of the surface corroded is quantitatively tracked during the initial period in order to aid in quantifying the results. The coupled experiment represents a practical corrosion scenario that involves a natural balance of the anodic and cathodic reactions. It is well-defined owing to direct measurement of the galvanic current, total dissolution rate and potential. Such an experiment differs from experiments that artificially constrain the potential or current, and can therefore provide a different perspective and additional insight. Pragmatically, it is possible to insert a submerged camera without significantly impacting current flow since the field lines remain close to the surface in our experiments. Thus, galvanically coupled experiments permit investigation of self-corrosion in a practical environment. Moreover, galvanic corrosion is usually assessed by the galvanic current or by overlay of the polarization curves; however, these methods will not provide accurate analysis without considering hydrogen evolution on the anode.

Studies of galvanically coupled Mg have focused on the factors influencing the corrosion rates and comparison of experimental results with models. It has been shown that a higher ratio of cathodic-to-anodic area, a greater depth of electrolyte solution and a smaller insulating distance between the anode and cathode all result in higher corrosion rates.12,22 Moreover, the type of metal coupled with Mg also significantly impacts the rate of corrosion. Song et al. examined the galvanic coupling of AZ91D with zinc, Al380 and steel, and found that the corrosion rate was significantly higher with steel than with the other two metals.23 This was due to the higher cathodic current density on the steel, which led to a higher corrosion potential and an increased rate of corrosion.

The comparison of numerical simulations with experimental results helps to provide important insight into the mechanisms that control the corrosion rate. In addition, such simulations have the long-term potential to predict critical aspects of the corrosion behavior of galvanically coupled Mg.13,14,24–26 Jia et al. used the Boundary Element Method (BEM) to calculate the corrosion rate of a galvanically coupled Mg alloy with use of a measured polarization curve, and compared the calculated results with their experimental measurements.13,14 Overall, they observed that the model adequately predicted the corrosion distribution for different anode-to-cathode area ratios and electrolyte thicknesses.14 However, in some instances the model was observed to underpredict the experimental dissolution rate by more than 50%.15 They interpreted the underprediction as the evidence for self-corrosion, which they estimated to be up to 230 mm/year.13,14 Similarly, Deshpande et al. compared experimental results from the galvanic corrosion of Mg under a variety of conditions with calculations based on the secondary current distribution.24 They, like Jia, used measured polarization curves. Their model included a moving boundary...
and was capable of tracking the position of the corroding Mg surface with time. Comparison of the local corrosion rates obtained from the numerical model with measurements from immersion experiments showed that the model underpredicted the measured corrosion rates by 20% and 47% for the AE44-mild steel and the AE44-AA6063 couples, respectively.\textsuperscript{24} It is likely that self-corrosion contributed to this underprediction. As mentioned above, both of these studies used measured polarization curves, which do not account for corrosion associated with H\textsubscript{2} evolution on the Mg surface (self-corrosion). Where significant, inclusion of self-corrosion in simulations is needed to accurately predict the total corrosion rate.\textsuperscript{13,24}

Self-corrosion of galvanically coupled Mg is especially important because of the high anodic dissolution rate of Mg when coupled. Previous studies have shown enhanced catalytic activity on corroding Mg surfaces.\textsuperscript{15,18–20,26} Frankel et al. suggested that the hydrogen exchange current density on a corroding Mg surface increased with an increasing rate of Mg dissolution, leading to a very large increase in the hydrogen evolution rate on the Mg surface.\textsuperscript{19} In another study, Birbilis et al. showed increased cathodic reaction rates (up to an order of magnitude higher) on Mg surfaces as a result of prior anodic dissolution.\textsuperscript{20} Curioni et al. also observed substantially higher hydrogen evolution rates on dark corroded Mg surfaces relative to rates observed on the uncorroded silvery surface of Mg.\textsuperscript{15} Based on these results, it is likely that the high anodic dissolution rate of galvanically coupled Mg will catalyze hydrogen evolution on the Mg surface, leading to an increased rate of self-corrosion. In this paper, we examine, quantify and evaluate the importance of self-corrosion (i.e., NDE or anodic hydrogen evolution) during the corrosion of galvanically coupled Mg. We do so in the context of results from previous studies on polarized and on freely corroding Mg samples that explore possible causes of enhanced HER activity.\textsuperscript{18,20,26–30}

**Experimental**

The samples tested consisted of the exposed end of a magnesium rod (99.95%, GalliumSource), 3 mm in diameter, that was electrically insulated from and surrounded by a mild steel (A36, Metals Depot) electrode. Heat shrink tubing with a thickness of approximately 0.2 mm was used to electrically insulate the Mg from the steel. The principal impurities in the Mg were Zn (0.005%), Mn (0.005%), Si (0.004%), Fe (0.003%), Ca (0.003%) and Al (0.002%). The steel electrode was a hollow cylinder with an inside diameter of 3.8 mm, just large enough to accommodate the insulated Mg rod, and an outer diameter of either 8, 12 or 16 mm. This geometry was chosen in order to change the rate of galvanic corrosion by varying the cathodic area relative to a fixed anodic area. This structure (Mg surrounded by steel) was cast into epoxy (EpoThin 2 Epoxy System, Buehler) for testing. After casting, the sample was cross-sectioned with an Isomet 1000 precision diamond saw (Buehler), and the surface was polished (to 1 micron paste) prior to submersion in the 5 wt% NaCl electrolyte. Experiments used a 50 mL volume of solution with an initial pH of 4. The concentric Mg and steel electrodes were galvanically coupled by electrically connecting them external to the solution through a potentiostat (263A, Princeton Applied Research) in a zero resistance ammeter (ZRA) mode, which also permitted direct measurement of the galvanic current. The metal potential relative to a saturated calomel reference electrode (SCE) was also measured. A schematic diagram of the experimental set up is shown in Figure 1a. The cross section of the working surface is shown in Figure 1b.

Experiments were designed to study the impact of coupling Mg to steel electrodes of different sizes on the processes that control Mg corrosion. In particular, the goal was to quantify the role of self-corrosion and to examine changes in the morphology of the corroding surface due to galvanic coupling. Each experiment was run for 10 minutes. As soon as the solution was poured in the cell, the two metals were connected through the ZRA, which served to measure the galvanic current. The time that elapsed between the addition of the solution to the cell and connection of the metals was less than 2 seconds. An immersible microscope was used to monitor the electrode surfaces during the course of some experiments. At the end of each experiment, the amount of Mg dissolved during the experiment was determined with Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) in order to quantify the total amount of corrosion that occurred as described below. For some experiments, a graduated cylinder was placed on the top of the electrode surfaces to capture the total amount of hydrogen evolved (from both the Mg and steel surfaces). These hydrogen measurements provided an independent measure of the total corrosion rate.

Any precipitate in the solution at the end of the experiment was dissolved for analysis using 2 mL of 1.2 M hydrochloric acid (HCl), which decreased the pH to 1–1.5. The film observed on the Mg surface was also dissolved using 10 wt% chromic acid. Chromic acid corrodes Mg at a very low rate and is often used to remove corrosion products from Mg without significantly attacking the substrate metal.\textsuperscript{2} As mentioned above, ICP-MS was used to directly measure the amount of Mg dissolved during the experiment; this measurement included any Mg in solution, in the homogeneous precipitate, and in the surface film. The difference between the total corrosion (as measured by the amount of Mg dissolved) and the total amount of galvanic corrosion (from the integral of the galvanic current) provided the amount of self-corrosion. The galvanic current was measured as a function of time, fit to a cubic-spline function, and then integrated numerically to get the total charge passed between the steel and Mg. The total moles of Mg lost by galvanic corrosion were determined from the total charge via Faraday’s law with n = 2.\textsuperscript{18}

To study the surface morphology, images were taken at various time intervals using an inverted optical microscope (Axio Vertical A1, Zeiss). The samples were taken out of solution to capture the images under the microscope at various times during the course of the experiment. The images were analyzed with ZEN software (compatible with above mentioned microscope) in order to measure, for example, the dimensions of corrosion pits formed. In order to quantify the fraction of the Mg surface that was corroded, image processing via Matlab was used to segment the surface images into black and white pixels, where the black pixels corresponded to the corroded
areas and the white pixels to the uncorroded areas. The level of intensity was chosen from the valley separating the two peaks of the bimodal gray-scale histogram. The ratio of black pixels to total pixels (black + white) provided the fraction of surface that was corroded.

**Results and Discussion**

The immersible microscope used to monitor the electrode surface showed vigorous hydrogen evolution on the steel metal surface as soon as the metals were connected. Considerable hydrogen evolution appeared on Mg surface as well. The pH quickly increased from 4 to 10.4–10.9 within the first minute. The final solution pH for all the samples was between 11.7 and 11.9. This suggests that ambient conditions for precipitating a film were achieved. The initial clear solution became cloudier with time due to homogeneous precipitation of corrosion products. The Mg surface showed dark areas of active corrosion that increased in size with time until the entire surface was actively corroding. A film was observed to form on the corroding surface, which grew in thickness and turned milky-white with time. Microscopic observation at the end of experiments revealed the presence of several “large” cracks in the films. Mg loss due to corrosion was measured directly with ICP-MS. In addition, the volume of hydrogen gas evolved was also measured for several of the experiments.

**Current-voltage behavior during galvanic corrosion.—**In order to examine and quantify self-corrosion for galvanically coupled Mg, it was first necessary to establish the baseline behavior. To that end, the measured galvanic current and corresponding voltages are reported in this section as a function of time and the size of the external cathode.

Figure 3 shows an example of the galvanic current as a function of time for each of the three cathode sizes tested. These experiments were repeated several times with similar results. As shown in the Figure 3, the current decreased gradually with time. For some samples, a short initial increase in current was observed (e.g., see 12 mm line in Figure 3). In general, the magnitude of the current at a given time increased with increasing cathode size, although the 12 mm and 16 mm results were quite close. In contrast, a clear difference between the 8 mm results and the others was observed.

Similarly, Figure 4 shows the corresponding potentials vs. an SCE reference electrode for the same three experiments. The potential decreased quickly at the beginning of each experiment and then increased gradually with time. A distinct difference in the measured potentials was observed for each steel size tested, with the smallest steel electrode having the lowest potential.

Figure 4 shows a clear increase in the potential with time for all three cathode sizes. Simultaneously the galvanic current decreased with time as shown in Figure 3. A higher potential would typically be associated with an increased rate of metal dissolution; however, in our experiments, metal dissolution appeared to be inhibited at the higher pH. The high rate of hydrogen evolution observed experimentally caused the solution pH to quickly increase from 4 to greater than 10 during the first minute of each experiment for all of our galvanically coupled samples. After that, the pH increased slowly to 11.9. Because the pH was nearly constant throughout most of a given experiment, the steady decrease in the corrosion rate is not due to changing pH, but is likely connected to the higher pH. Surface films on Mg have been shown to slow the corrosion rate, and may contribute to the observed decrease in the measured galvanic corrosion rate with time.

The impact of the steel area on both the galvanic current and the measured corrosion potential (vs SCE) demonstrates the importance of the cathodic reaction during galvanic corrosion of Mg, even at high cathode-to-anode area ratios; conversely, it shows the potential of Mg to undergo rapid corrosion. The observed increase of the galvanic current density with increasing cathode area is due, of course, to the availability of additional surface area for H₂ evolution, which evolution also occurs more readily on the steel than on the Mg surface, at least initially, due to faster kinetics. The change in the galvanic current density and the corrosion potential was greater for a change
in the steel area from 8 mm to 12 mm than it was for a change from 12 mm to 16 mm. There are at least two reasons for this; 1) the percent difference in cathode area between the 8 mm and 12 mm electrodes is substantially higher than that between the 12 mm to 16 mm electrodes; 2) as the cathode size increases, the solution resistance becomes more important and eventually dominates, diminishing the impact of cathode size. The solution resistance effect is reflected in a non-uniform distribution of hydrogen evolution on the steel electrode. Indeed, the rate of hydrogen evolution observed via the submerged microscope was much higher near the Mg-steel interface. However, the fact that the size of the steel continues to make a difference implies that the rest of the cathode is also playing a part. This trend will not continue indefinitely, and the solution resistance will eventually limit change beyond a certain size of cathode. The comparable values of the galvanic current for the 12 mm and 16 mm samples indicate that this size has nearly been reached. In contrast, the difference between the measured potentials of these two electrodes shows that the limit was not yet reached. For reference, the area ratio of steel to Mg for the 8 mm, 12 mm and 16 mm electrodes is 5.5, 14.4 and 26.8, respectively.

The rates of galvanic corrosion reported here are higher than any of the corrosion rates that we found reported previously for Mg. The fact that such high rates of corrosion can be obtained at moderate potential values of $-1.45$ to $-1.34$ V is significant. These experiments allow us to study enhanced cathodic activity on Mg under more practical conditions and at higher rates, where the rates are controlled by the cathode size. 

**Impact of galvanic coupling on self-corrosion.**—Figure 5 shows the average total, galvanic and self-corrosion current densities for the three different cathode sizes after corrosion for 10 minutes. The total current densities reported here are from ICP-MS measurements, although hydrogen gas measurements yielded similar results (Figure 2). We first note that the corrosion rates are quite high (>2000 A/m²), significantly higher than rates typically reported for anodically polarized samples and two orders of magnitude higher than reported free corrosion rates. These high rates are possible at very moderate potential values of $-33$ to $-35$%. The observation that self-corrosion represents a significant fraction of the total corrosion rate implies that the reaction kinetics for hydrogen evolution are comparable on the two surfaces. This result is in contrast to the situation on the native Mg surface where the exchange current density for hydrogen is orders of magnitude lower than that on steel.

In the absence of galvanic coupling (i.e., during free corrosion), the current densities for Mg corrosion were significantly lower ($<26$ A/m²), in agreement with values reported previously in the literature. In contrast, the rate of hydrogen evolution on the surface of galvanically coupled Mg was approximately 30 times higher than that evolved during free corrosion. Clearly, hydrogen evolution on the Mg surface (and hence the rate of corrosion associated with H₂ evolution on the magnesium rather than on the steel) is strongly influenced by the coupling of Mg with steel.

As seen in the average corrosion rates above, the coupling of Mg with steel greatly enhances the total corrosion rate, which is expected to impact hydrogen evolution on the surface. Figures 6 and 7 show the corroding surface as a function of time under both free and coupled conditions (note the difference in the times at which the images were taken). It is evident from these figures that corrosion propagates much faster when Mg is coupled. To quantify this observation, Matlab was used to segment the images and determine the fraction of the surface that was corroded as a function of time (see Figure 8). The
impurities. Clearly, impurity enrichment due to selective corrosion contributes to the high rate of self-corrosion reported in Figure 5. As seen in Figure 8, the self-corrosion fraction was lower for the 8 mm sample from Table I, and assuming a linear increase in the fraction corroded with time, the instantaneous self-corrosion rate at the end of the first minute would be 1340 A/m² (twice the average value) if the rate scales linearly with the corroded surface area fraction. In addition, the self-corrosion rate would stop changing significantly with time once the entire surface was corroding (after approximately one minute) if the change from “non-corroded” to “corroded” surface processes related to dissolution would be much faster for the coupled sample, and likely contributes to the high rate of self-corrosion reported in Figure 5.

We also see from Figure 8b that the rate at which the surface corrodes for coupled Mg is higher for the larger steel electrodes. Thus, surface processes related to dissolution would also be enhanced by the larger cathodes. Consequently, self-corrosion rates were observed to increase with the increasing cathodic area for coupled Mg (Figure 5). However, the self-corrosion fraction was independent of cathode size. This is a significant result, but further work is needed to determine if similar results can be obtained at other conditions and with different geometries.

**Self-corrosion with time.**—From the results above, it is clear that self-corrosion plays a significant role for galvanically coupled Mg. The self-corrosion rate reported above was the average value for the 10-minute duration of the experiments. However, the Mg surface undergoes various changes during the experiment, changes that may impact the rate of self-corrosion. The initial polished, oxidized surface is gradually replaced by an actively corroding surface when the Mg is coupled to steel in a chloride-containing electrolyte. A film forms on the corroding surface that is likely influenced by the solution pH. Film growth has been shown to decrease the galvanic corrosion rate. Changes such as these are expected to cause the self-corrosion rate to change with time as well. To explore this time variation, experiments similar to those reported above were performed for run times of 1, 3, 5 and 10 minutes. Time dependent values of the self-corrosion rate and the fraction of the total corrosion rate attributable to self-corrosion are given in Table I and Figure 9, respectively, where each value represents the average obtained from three repetitions of the experiment. Also, since these experiments provide average rates for the entire time period, the values from the earlier time periods were subtracted off in order to estimate the change that occurred in a given time interval.

As seen in Figure 9, the self-corrosion fraction was lower for the one minute experiments, but was still a significant fraction of the total corrosion. The self-corrosion fraction reached a maximum between one and three minutes, and appeared to decrease after that. A similar trend was observed for the total corrosion rate.

Replacement of the native oxide with a corroded surface has been shown to enhance the rate of hydrogen evolution, as the HER is readily supported by the corroded surface. Therefore, one important factor that influences the self-corrosion rate is the fraction of the surface that is corroded. That fraction was quantified and found to vary approximately linearly with time for corrosion times less than one minute as shown in Figure 8. Given the average value of the self-corrosion rate for the first minute of the experiment (e.g., 670 A/m² for the 8 mm sample from Table I), and assuming a linear increase in the fraction corroded with time, the instantaneous self-corrosion rate at the end of the first minute would be 1340 A/m² (twice the average value) if the rate scales linearly with the corroded surface area fraction. In addition, the self-corrosion rate would stop changing significantly with time once the entire surface was corroding (after approximately one minute) if the change from “non-corroded” to “corroded” were the dominant factor influencing the change in the self-corrosion rate.

Examination of the data in Table I indicates that the average self-corrosion rate for the second time interval was significantly greater than twice that observed after one minute for all three samples. Consequently, an increase in the corroded fraction of the surface does not appear to account fully for the self-corrosion rate observed between 0-1 min and 1-3 min.
1 and 3 minutes. Rather, these data appear to be consistent with increased hydrogen evolution due to both 1) the increasing fraction of corroded area with time and 2) additional acceleration of hydrogen evolution in the corroded areas with time. The corrosion potential did not contribute to the increase in the self-corrosion rate since the potential increased with time, as shown in Figure 4, resulting in a reduction in the driving force for the hydrogen reaction. The most likely explanation is that the hydrogen reaction was catalyzed due to the high rate of Mg dissolution. Frankel et al. showed that the hydrogen exchange current density on a corroding Mg surface increased with an increasing rate of Mg dissolution, leading to a very large increase in the hydrogen evolution rate on the Mg surface.\(^{15}\) In another study, Birbilis et al. showed increased cathodic reaction rates (up to an order of magnitude higher) on Mg surfaces as a result of prior anodic dissolution.\(^{20}\) We also note that the absolute self-corrosion rate (per Mg area) for our coupled samples was higher than that reported for samples coupled at a lower cathode-to-anode area ratio.\(^{13,14}\)

Thus, the high anodic dissolution rates observed for our galvanically coupled Mg samples appear to have been effective in increasing the self-corrosion rate by enhancing the HER on the Mg surface.

Recent studies suggest that during anodic polarization both surface enrichment and film growth sustain hydrogen evolution, resulting in NDE.\(^{15–17}\) It has been reported that enrichment of surface impurities alone cannot account for the observed NDE since substantial enhanced catalytic activity was observed even for ultra-high purity Mg.\(^{20}\) Recently, Mg surface films have been shown to sustain HER and may also contribute to increased rates of self-corrosion.\(^{19,21,28,31,36}\) Studies also suggest that the impurities trapped in the film may provide cathodic sites to sustain HER.\(^{16,27,37}\) We note that these mechanisms may have played a role in the high rates of self-corrosion observed, and that acceleration was likely facilitated at the high dissolution rates observed in our experiments.

However, the reduction in the fraction of the Mg dissolution due to self-corrosion after 3 minutes needs further attention. Figure 4 shows that the potential increases with time, indicating greater polarization of the Mg electrode. Previous studies have shown pH dependent film growth and enhanced HER on Mg surface upon increased anodic polarization.\(^{31}\) While film growth with time was observed, the decrease in the self-corrosion fraction after 3 minutes suggests a negative impact on the HER for galvanically coupled Mg. Thus, for the conditions examined, it appears that galvanic coupling may impact the mechanism of enhanced HER on Mg surfaces, leading to a reduction in self-corrosion with time. The mechanisms that control this may differ from those relevant to uncoupled samples. Alternatively, the results presented here may represent accelerated progress along a common trajectory.

Importantly, self-corrosion fraction was significant throughout the entire period of the experiment. An increase in hydrogen kinetics\(^{19,20}\) and an increase in the corroded area both contributed to the increasing self-corrosion fraction observed for the first 3 minutes. The self-corrosion fraction subsequently decreased due to the increase in the pH and the formation of a surface film (see Figure 9). Running experiments for longer time may provide further insights into the stability of surface film and its effect on self-corrosion. Our results not only show a significant self-corrosion fraction, but also its variability with time, and are important to understanding the corrosion behavior of coupled Mg.

Surface film formation during galvanic corrosion.—A film with several cracks was observed on the Mg surface after galvanically coupled corrosion for 10 min. Images of the Mg surface before and after an experiment are shown in Figures 10a and 10b, respectively. The surface after film removal is shown in Figure 10c.

For the purpose of determining the total amount of Mg corrosion, it was important to include any Mg present in the film. To do this, the film was dissolved using 10 wt% chromic acid, and ICP-MS was used to analyze the resulting solution. Table II summarizes the results of experiments for each of the three steel cathode sizes.
(in-situ) to continue on the Mg surface after film formation. The concentration of Mg in the solution also continued to increase in the form of a homogeneous precipitate. Additional characterization of the dynamic composition and morphology of film is needed and will be the topic of a future publication.

**Surface morphology.**—Previous studies have shown that the surface morphology of freely corroding Mg depends on factors such as metal impurities (acting as cathodic sites) and Cl\(^{-}\) concentration.\(^{5-11}\) In particular, two types of surface morphologies are seen, namely disk-shaped corrosion and filiform corrosion. In both cases, the corrosion geometry is determined by the cathodic reaction, which is severely limiting. Our study showed that the corrosion morphology of galvanically coupled Mg was quite distinct from that of uncoupled Mg (see Figures 6 and 7).

For freely corroding Mg, corrosion initiated with small crack-like structures that lengthened with time and took the form of filiform-type corrosion.\(^{10,12}\) This type of corrosion appeared to be initiated randomly on the metal surface. As shown earlier, the average cathodic current density on Mg surface during free corrosion was approximately 26 A/m\(^2\) and was associated with filiform-type corrosion. Williams et al. also observed filament-like structures and current densities of \(\sim 10-15\) A/m\(^2\) for high purity samples, in good agreement with our uncoupled results.\(^{11}\) The low impurity concentration (30 ppm Fe) in the samples tested contributed to slow hydrogen evolution and the low corrosion rate observed for uncoupled Mg.

Radial growth or disk-type corrosion has also been observed for freely corroding Mg.\(^{9,11,15}\) Williams et al. reported such corrosion for commercially pure Mg in a concentrated NaCl (\(\geq 0.1\) M) solution with iron impurity levels higher than our samples (\(\geq 280\) ppm).\(^{11}\) However, even at those impurity levels, the morphology of attack changed from disk-shaped to filament when the NaCl concentration was reduced from 0.1 M to 0.01 M, presumably due to increased ohmic constraints.\(^{11}\) In all cases, disk-shaped structures produced cathodic current densities (SVET) of 100 A/m\(^2\) or higher and filament structures produced cathodic current densities of 10 A/m\(^2\) or lower. In another study, Curioni et al. observed disk-shaped corrosion for higher purity Mg (99.95%) in \(\sim 0.6\) M NaCl, although the concentration of specific impurities was not reported.\(^{16}\) In both cases, the anodic dissolution led to enhanced rates of hydrogen evolution in the corroded area. As a result, the corroded area became predominantly cathodic, and anodic dissolution took place primarily in a ring that surrounded the corroded area. This led to a large, shallow disk of corrosion that moved across the Mg surface.\(^{9,11}\) The disk geometry was made possible by the enhanced rate of the cathodic reaction caused by the higher impurity concentration. The corrosion was cathodically limited and remained shallow because of the cathodic nature of the area inside the disk.

When Mg was coupled to steel, the addition of a separate steel cathode removed the severe cathodic limitation and dramatically changed the morphology. The corrosion of coupled Mg started with small pits that increased in size and depth with time, and eventually coalesced so that the entire surface was corroding. We observed pit initiation that was generally random, although preferred initiation at scratch defects was observed for some samples where the polishing was less satisfactory. Even small pits present on the surface after only 10 seconds had an appreciable depth of approximately 20 microns. Because of the steel electrode, the anodic reaction was not limited to a specific area (e.g., ring or track) and aggressive corrosion of the entire surface was observed. While the entire surface corroded, a cross-section of the corroded sample showed that the local rate of corrosion was highest near the Mg-steel interface. The high rate of anodic dissolution enhanced the hydrogen evolution rate on the Mg surface and led to the high rates of self-corrosion measured in this study. Anodic polarization of Mg also removes the severe cathodic limitations observed for freely corroding samples. Corrosion morphologies similar to those observed in this study for galvanically coupled samples have also been observed for anodically polarized Mg samples.\(^{16,18,20,29}\) However, the current densities for anodically polarized samples are typically much lower than those observed for our galvanically coupled samples owing to high IR losses.\(^{18}\)

**Conclusions**

In this paper, the role of hydrogen evolution during the corrosion of galvanically coupled Mg has been examined. In particular, the importance of self-corrosion (i.e., NDE or anodic hydrogen evolution) has been evaluated and quantified. Mg coupled to steel at high cathode-to-anode area ratios resulted in high corrosion rates at moderate potentials. The high anodic dissolution rates enhanced hydrogen evolution on the Mg surface and resulted in high rates of self-corrosion. Specifically, the observed rate of self-corrosion for coupled Mg was, on average, one third of the total corrosion rate for all three of the cathode sizes tested. The self-corrosion fraction varied with time and was found to reach values in excess of 50% (Figure 9). On average, the rate of self-corrosion increased with increasing cathode size and, therefore, with increasing rate of anodic dissolution (Figure 5). This increase in self-corrosion with cathode size was in spite of the fact that the measured potential was higher for the larger cathodes.

A significant fraction of corroded Mg was found in the surface film that formed during corrosion. For our coupled experiments, the film formed on the metal surface during the first three minutes. At the end of 10 minutes, we found that about 30% of the Mg removed as corrosion product was present in the film. Importantly, the film contributed to the reduction of the corrosion rate with time that was observed experimentally. Microscopic examination of the film revealed several cracks that were likely formed as a result of hydrogen evolution on the Mg surface.

The surface morphology observed during galvanic corrosion was dramatically different from the filament structures associated with free corrosion, which were observed in uncoupled experiments with our samples, and are consistent with previous studies done on Mg under similar conditions.\(^{10,13}\) The lack of severe cathodic limitations, avoided with the use of relatively large steel cathodes, was responsible for this difference in morphology. The morphology observed for galvanically coupled corrosion was also different from the disk-shaped corrosion observed for freely corroding samples at open-circuit potential.\(^{9,11,15}\) In contrast, similarities were observed between the morphology from coupled samples and that seen for uncoupled samples that were anodically polarized.\(^{16,18,20,29}\)

The enhanced HER for polarized Mg samples is well known. Our results document similar behavior for galvanically coupled Mg, and demonstrate the importance of self-corrosion under such conditions. These results complement previous studies of anodically polarized samples, while providing additional insights from a system corroding under more practical conditions.

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### Table II. Mg content in the surface film.

| Cathode Size (mm) | Total Amount of corroded Mg (g) | Amount of Mg in film (g) |
|------------------|---------------------------------|-------------------------|
|                  | Experiment 1                    | Experiment 2            |
| 8                | 1.1E-03                         | 1.2E-03                 |
| 12               | 1.4E-03                         | 1.4E-03                 |
| 16               | 1.4E-03                         | 1.5E-03                 |
|                  | Experiment 1                    | Experiment 2            |
|                  | 2.9E-04                         | 3.3E-04                 |
|                  | 4.4E-04                         | 4.0E-04                 |
|                  | 4.0E-04                         | 4.0E-04                 |
|                  | Mg fraction in film (wt%)       |
|                  | 27%                             | 30%                     |
|                  | 28%                             | 27%                     |

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