Galvanic Corrosion of Magnesium Coupled to Steel at High Cathode-to-Anode Area Ratios

Dila Ram Banjade

Brigham Young University - Provo
Galvanic Corrosion of Magnesium Coupled to Steel at High Cathode-to-Anode Area Ratios

Dila Ram Banjade

A thesis submitted to the faculty of Brigham Young University in partial fulfillment of the requirements for the degree of Master of Science

John N. Harb, Chair
Dean R. Wheeler
W. Vincent Wilding

Department of Chemical Engineering
Brigham Young University
December 2015

Copyright © 2015 Dila Ram Banjade
All Rights Reserved
ABSTRACT

Galvanic Corrosion of Magnesium Coupled to Steel at High Cathode-to-Anode Area Ratios

Dila Ram Banjade
Department of Chemical Engineering, BYU
Master of Science

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, the role of self-corrosion was quantified as previous studies showed discrepancies between model predictions and experimental results that were likely due to significant self-corrosion. This experimental study examined the corrosion of Mg coupled to steel in 5 wt% NaCl at cathode-to-anode area ratios that ranged from 5 to 27. Results showed that self-corrosion was significant and accounted for, on average, one-third of total corrosion. Moreover, self-corrosion varied with time and cathode size, and was accelerated by the high dissolution rate. Film formation was observed on the magnesium surface that inhibited the corrosion rates. This film contained approximately 30% of the Mg lost to corrosion. The morphology of the coupled Mg showed the rapid formation of pits with considerable depth, and was quite distinct from previously studied filiform and disk corrosion for uncoupled Mg. This study demonstrates the important role of self-corrosion during galvanic corrosion of Mg and the need to account for such corrosion when predicting corrosion rates. This study also provides important insight into the processes that control Mg corrosion under several conditions.

Keywords: magnesium corrosion, galvanic corrosion, self-corrosion, surface film, surface morphology, high cathode-to-anode ratio, high anodic dissolution, galvanic couple, magnesium-steel couple
ACKNOWLEDGEMENTS

First of all, I would like to thank and express my deepest appreciation to my advisor, Professor John N. Harb, who mentored and guided me throughout this project. I truly appreciate his patience, willingness to help, thoughtful feedback and positive attitude that have helped me become a better researcher and an engineer. I am also grateful for my committee members, Professor Dean R. Wheeler and Professor W. Vincent Wilding, for their valuable feedback to my work. I would also like to thank my undergraduate students, Steven D. Porter, Brian M. McMullan and KC Maughan, for their input and hard work into this project. I am thankful for the Department of Chemical Engineering (BYU) for providing an incredible quality of education that I could implement in my research.

I am very grateful towards my family and friends who have been very supportive throughout this journey. I am thankful for my wife, Mahima Joshi, who has been my biggest supporter. I would not have accomplished this without her love and support. I am grateful for my parents, Dak Prasad and Durpata, who continue to provide unconditional love and encouragement to me on a daily basis.

Lastly, but certainly not the least, this work would not have been possible without the generous funding of CD-adapco.
TABLE OF CONTENTS

LIST OF TABLES .................................................................................................................. vi
LIST OF FIGURES .............................................................................................................. vii

1 INTRODUCTION ............................................................................................................. 1

2 BACKGROUND AND LITERATURE REVIEW ........................................................ 4

3 OBJECTIVES AND SCOPE ......................................................................................... 15
   3.1 Objectives ................................................................................................................. 15
   3.2 Scope ......................................................................................................................... 16

4 MATERIALS AND METHODS ................................................................................... 18
   4.1 Sample preparation .................................................................................................. 18
   4.2 Cutting and polishing of sample .............................................................................. 18
   4.3 Corrosion cell ........................................................................................................... 19
   4.4 Experimental set up ................................................................................................. 20
   4.5 Experimental methods ............................................................................................ 21
   4.6 Measurement and data analysis technique .............................................................. 23
LIST OF TABLES

Table 2-1: Equilibrium potential (vs. H$_2$ electrode) of different metals ........................................5
Table 6-1: Magnesium content in surface film ................................................................................39
LIST OF FIGURES

Figure 1-1: Relationship between vehicle mass and fuel consumption ........................................2

Figure 2-1: Pourbaix diagram for the Mg-H2O system at 298 K .................................................7

Figure 2-2: A) Disk-type corrosion B) Filiform Corrosion ..........................................................12

Figure 2-3: Morphology of a disk for a freely corroding Mg .....................................................12

Figure 4-1: A) Schematic of corrosion cell made of Teflon B) Top view of the corrosion cell. The opening on the bottom contained O-ring to seal the sample from leaking out solution ..............................................................19

Figure 4-2: Schematics of experimental set up ............................................................................20

Figure 4-3: Cross section of sample showing Mg wire insulated and surrounded by steel cast in epoxy ..........................................................................................................................21

Figure 4-4: A) Original image B) Black and white image obtained with Matlab. Please note that the area other than Mg surface was masked with red color to account for the black and white pixels of Mg surface only .....................................................22

Figure 4-5: Bimodal histogram of grayscale image ........................................................................23

Figure 5-1: Comparison of measurement of Mg using ICP and hydrogen collection .................25

Figure 5-2: Galvanic current as a function of time for three different cathode (steel) sizes. The anode diameter (3mm) was constant for all experiments ..............................................26

Figure 5-3: Corresponding potential variation with time for results shown in Figure 5-2 ..........27

Figure 5-4: pH increase during the course of the experiment .....................................................28

Figure 5-5: Average current densities for total, galvanic and self-corrosion for three different sized cathode samples for 10 min experimental time. Self-corrosion was 35, 33 and 33 percent of total corrosion for 8 mm, 12 mm and 16 mm samples respectively .................................................................30
Figure 5-6: Surface morphology of A) freely corroding Mg at 5 min B) galvanically corroding Mg at 40 sec .................................................................32

Figure 5-7: Fraction of Mg surface corroded during A) galvanic and free corrosion for three different samples. Only one set of data for free corrosion is shown as the outer cathodic area had no impact on it. B) Plot in A) with free corrosion data removed .................................................................33

Figure 5-8: Fraction of self-corrosion at various time intervals for different samples ..........35

Figure 5-9: Average mass of Mg lost from self-corrosion ...............................................36

Figure 6-1: A) Polished Mg surface B) Mg Surface after galvanically corroded for 10 min C) Mg surface after film removal .................................................................38

Figure 6-2: Surface morphology of freely corroding Mg at A) 5 min B) 10 min C) 15 min D) 20 min. Note that only top half of Mg surface is shown at each time .................................................................41

Figure 6-3: Surface morphology of galvanically corroding Mg at A) 10 sec B) 20 sec C) 30 sec D) 40 sec. Note that only top half of Mg surface is shown at each time.................................................................43

Figure 6-4: A) Polished surface with imperfections (scratches) B) corrosion disk attacking the imperfections in Mg surface .........................................................43
1 INTRODUCTION

Magnesium (Mg) is the lightest of all structural metals. With a density of 1.75 g/cm³, it is much lighter than other widely used structural metals such as aluminum (2.7 g/cm³) and steel (7.86 g/cm³)[1, 2]. Other than being light, it is also one of the most abundantly found metals. The majority of Mg is found in seawater in the form of magnesium chloride (MgCl₂). A cubic meter of seawater roughly contains 1.3 kg of Mg [1, 2].

The use of Mg is increasing in the automobile and aerospace industries due to its light weight. Recent environmental regulations have stricter policies limiting emissions. Use of lightweight materials such as Mg will decrease vehicle weight and, consequently, fuel consumption and greenhouse gas emissions (see Figure 1-1). An average vehicle in North America uses only 0.25 wt% of Mg [1]. Thus, wider use of Mg could significantly reduce fuel consumption and greenhouse gases.

Apart from being light weight, Mg also has good ductility, high stiffness to weight ratio and excellent castability. In addition, it has better noise and vibration dampening characteristics than aluminum [1-4]. New environmental regulations, good mechanical properties and abundant availability have generated renewed interest in the wider use of Mg, especially in the automobile and aerospace industries.
The main obstacle to the use of Mg is its corrosion susceptibility. Mg ranks highly anodic in the electrochemical series of structural metals and is thus susceptible to corrosion. For this reason, Mg is often used as sacrificial anode to prevent corrosion of other metal such as steel. Poor design, surface contamination, poor surface treatment (polishing and protection) and the presence of galvanic couples all serve to increase corrosion problems [2, 4]. Mg can corrode freely; however, the rate of corrosion increases significantly when it is galvanically coupled to another metal such as steel [4, 5] because of the increased cathodic area and, likely, the increased rate of the cathodic reaction on the other metal. Although hydrogen evolution on the coupled metal dominates the cathodic reaction, hydrogen evolution on the Mg surface does not stop. The purpose of this work is to investigate the impact of such coupling on the self-corrosion of Mg (i.e., corrosion that is associated with hydrogen evolution on the Mg surface), and the extent to which galvanic coupling influences both the morphology and rate of Mg self-corrosion.
We provide background information and discussion of important terms involved with our research in Chapter 2. Chapter 3 includes the objective and scope of our research. Chapter 4 outlines the experimental procedure established for sample preparation, data collection and analysis. Chapters 5 and 6 provide the discussion of results for the role of self-corrosion and surface morphology for galvanically coupled Mg respectively. In Chapter 7, we provide conclusions and describe potential future work.
2 BACKGROUND AND LITERATURE REVIEW

2.1 Current and future applications of Mg

The use of Mg in automobiles is not new. Volkswagen and Porsche first used Mg in cars as early as 1928 [1]. GM has been offering cast Mg wheels for the Corvette since 1998[1]. Recent developments of Mg alloys and stricter environmental regulations have caused wider use of Mg in last few years. BMW was able to reduce the fuel consumption of cars by 30% between 1990 and 2007 by using a composite Mg-Al alloy engine, R6[1]. The use of Mg in the American auto-industry has also risen recently due to regulations required reduced emissions and driving forces to increase fuel economy. The amount of Mg in the automotive industry is expected to rise by significant amounts in the next decade. Therefore, research studies to improve its mechanical and electrochemical properties are expanding rapidly.

2.2 Physical and electrochemical properties of Mg

Mg is a light weight metal with a density of 1.7 g/cm$^3$ [4]. It is more than 1.5 times lighter than aluminum (2.7 g/cm$^3$) and over four times lighter than steel (7.86 g/cm$^3$) [1]. It is the eighth most abundant element and is mainly isolated from MgCl$_2$ in seawater [1]. It has a better stiffness to weight ratio than both aluminum and steel. Although its lower melting point and creep susceptibility present challenges for use of high purity Mg, alloying it to another metal such as
aluminum or steel has been shown to significantly improve its mechanical properties. The price of Mg has also decreased in recent years where it sells at $0.90/lb (data as of Oct, 2015) compared to $1.09/lb in 2014 [6]. The reasonable price and attractive physical properties are expected to increase the use of Mg in the automobile and aerospace industries.

Although the mechanical properties of Mg make it an attractive metal for automobile and aerospace industries, its electrochemical properties impede wider application. Mg is highly anodic with a standard potential of -2.36V (see Table 2-1) [7]. The standard potential is the potential relative to a standard hydrogen electrode (SHE, 0 V) and measures the tendency of an element to be reduced or oxidized. A positive standard potential with respect to SHE means that element is likely to be reduced, and a negative standard potential means it is likely to be oxidized. The lower the standard potential, the greater the thermodynamic driving force for oxidation.

Table 2-1: Equilibrium potential (vs. H₂ electrode) of different metals [7].

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Reaction</th>
<th>Potential, V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li, Li⁺</td>
<td>Li⁺ + e⁻ → Li</td>
<td>-3.02</td>
</tr>
<tr>
<td>K, K⁺</td>
<td>K⁺ + e⁻ → K</td>
<td>-2.92</td>
</tr>
<tr>
<td>Na, Na⁺</td>
<td>Na⁺ + e⁻ → Na</td>
<td>-2.71</td>
</tr>
<tr>
<td>Mg, Mg²⁺</td>
<td>Mg²⁺ + e⁻ → Mg</td>
<td>-2.37</td>
</tr>
<tr>
<td>Al, Al³⁺</td>
<td>Al³⁺ + e⁻ → Al</td>
<td>-1.71</td>
</tr>
<tr>
<td>Zn, Zn²⁺</td>
<td>Zn²⁺ + e⁻ → Zn</td>
<td>-0.76</td>
</tr>
<tr>
<td>Fe, Fe²⁺</td>
<td>Fe²⁺ + e⁻ → Fe</td>
<td>-0.44</td>
</tr>
<tr>
<td>Cd, Cd²⁺</td>
<td>Cd²⁺ + e⁻ → Cd</td>
<td>-0.40</td>
</tr>
<tr>
<td>Ni, Ni²⁺</td>
<td>Ni²⁺ + e⁻ → Ni</td>
<td>-0.24</td>
</tr>
<tr>
<td>Sn, Sn²⁺</td>
<td>Sn²⁺ + e⁻ → Sn</td>
<td>-0.14</td>
</tr>
<tr>
<td>Cu, Cu²⁺</td>
<td>Cu²⁺ + e⁻ → Cu</td>
<td>0.34</td>
</tr>
<tr>
<td>Ag, Ag⁺</td>
<td>Ag⁺ + e⁻ → Ag</td>
<td>0.80</td>
</tr>
</tbody>
</table>
For this reason, Mg oxidizes easily. Under atmospheric conditions, an oxide layer protects the Mg surface from further corrosion. Under immersed conditions and in the presence of an electrolyte that contains Cl⁻, the oxide layer is easily penetrated and Mg corrodes freely [2]. The electrons released from Mg react with water to evolve hydrogen gas.

The overall reaction of Mg corrosion is shown below.

**Anodic Reaction:** \[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \]

**Cathodic Reaction:** \[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \]

**Overall Reaction:** \[ \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Mg}^{2+} + 2\text{OH}^- \]

\( \text{Mg}^{2+} \) and \( \text{OH}^- \) are the products of the corrosion reaction and can further react to form Mg (OH)₂, which becomes significant as the pH increases. The impact of pH on the rate of corrosion will be discussed in the next section. Magnesium hydroxide is only slightly soluble and readily precipitates out of solution.

It has been shown that the cathodic (H₂ evolution) reaction is the limiting reaction and that it controls the rate of anodic dissolution of Mg during free corrosion [5, 8]. Birbilis et al. showed that when Arsenic was alloyed with Mg, the Mg corrosion significantly decreased because Arsenic poisoned the H₂ evolution [8]. H₂ evolution causes the solution pH to significantly increase providing favorable environment for formation of corrosion products and surface that influence Mg corrosion.
2.3 The effect of pH and surface films on Mg corrosion

Both pH and surface films affect the corrosion of Mg in aqueous solution. Figure 2-1 is the Pourbaix diagram for Mg and it demonstrates stability of different Mg species under aqueous conditions. The Pourbaix diagram is a potential vs pH diagram that maps out possible stable phases for an aqueous electrochemical system. Mg is immune to corrosion below its standard potential of -2.36V, and this region is called immunity. At a pH higher than 11, Mg(OH)$_2$ is the stable reaction product, which may form a protective passive layer that prevents Mg from further corrosion. Apart from these two regions, Mg corrodes freely. The stability of different species is shown in the diagram below.

Figure 2-1: Pourbaix diagram for the Mg-H$_2$O system at 298 K [17].
The Pourbaix diagram is solely based on the thermodynamics of the species considered, and does not account for kinetic effects or presence of other species such as Cl\textsuperscript{-}. Rossrucker \textit{et al.} studied the effect of electrolyte pH on the hydrogen evolution rate [9]. They clearly found that the hydrogen evolution rate increases with decreasing electrolyte pH. As described earlier, hydrogen evolution during Mg corrosion will increase the solution pH and its role will be important as we analyze and discuss our results in the subsequent chapters.

When exposed to aqueous solution, Mg develops a surface film. It has been shown that the film is composed of two layers, MgO and Mg(OH)\textsubscript{2} [10]. A study by Santamaria \textit{et al.} used in situ (Photocurrent spectroscopy) and ex situ (X-ray photoelectron spectroscopy) techniques to study the film for a freely corroding 99.9 wt\% Mg in a neutral electrolyte. They found that the external layer consisted of Mg(OH)\textsubscript{2} and its thickness is a function of immersion time, while there is a ultra-thin internal layer of MgO probably of constant thickness. Previous studies have shown that the surface films reduce the corrosion rate of Mg [11]. When Mg is not exposed to the aqueous environment, the natural oxide layer protects Mg from undergoing corrosion [4]. When immersed, especially in a chloride containing solution, the native oxide film is broken and the surface is exposed, contributing to corrosion. As the solution pH increases, another film, likely containing layers of Mg(OH)\textsubscript{2} and MgO forms on the Mg surface [10]. This film, although not completely passivating, has been shown to reduce the rate of corrosion significantly [11]. This work will address the role of surface film and report what fraction of total corroded Mg goes to the film for galvanically coupled Mg. This will provide a clearer picture to the corrosion behavior of coupled Mg.
2.4 Corrosion of Mg

Mg corrodes freely or when galvanically coupled with another metal. Free corrosion occurs when Mg is immersed in a conductive electrolyte. This corrosion is caused by the hydrogen evolution on impurities that act as cathode and form micro-galvanic couple with Mg [12]. During free corrosion, the rate depends on the Cl⁻ concentration [13] in the electrolyte and the impurities in the metal. Cl⁻ breaks down natural oxide and the surface impurities provide cathodic sites for hydrogen evolution, resulting in an increased corrosion rate. Free corrosion of Mg is cathodically limited and the rate of corrosion is controlled by the rate of hydrogen evolution [14, 15]. Other factors such as pH changes, surface film formation and corrosion products also alter the free corrosion rate [9-11, 16].

Galvanic corrosion occurs when two dissimilar metals are immersed in the same electrolyte and are electrically connected. The electrolyte provides an ionic path for current flow, in addition to the flow of electrons between the metals. Galvanically coupling of Mg to steel increases the cathodic reaction (hydrogen evolution) due to increased cathodic areas and surface availability for H₂ evolution. The coupling increases the anodic dissolution rate of Mg; however the free corrosion under this situation does not stop. This additional corrosion during galvanic couple is referred to as self-corrosion [17].

Galvanic corrosion is found to be concentrated near the interface between the anode and cathode metals because the potential field from the current is highest near the interface. Jia et al. observed that the galvanic corrosion was confined to 1 - 2 cm radial distance from the interface of
a steel rod (10-30 mm diameter) inserted to a Mg plate (11 cm x 12 cm) [17]. Corrosion pits were also observed at random locations over the entire surface as a result of self-corrosion.

Studies of galvanically coupled Mg have focused on the factors influencing the corrosion rates and validation 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 in solution all result in higher corrosion rates [18, 19]. Moreover, the type of metal coupled with Mg also significantly impacts the rate of corrosion. Song et al. showed that when the Mg alloy AZ91D was coupled with zinc, Al380 or steel, the corrosion rate was significantly higher with steel than with the other two metals [20]. This was due to the higher cathodic current density on the steel, leading to a higher corrosion potential and an increased rate of corrosion.

The coupling 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 the critical aspects of the corrosion behavior of galvanically coupled Mg from first principles [17, 19, 21, 22]. Jia et al. used the Boundary Element Method (BEM) to calculate the corrosion rate of a galvanically coupled Mg alloy with use of a polarization curve, and compared the calculated results with their experimental measurements. Overall, they observed that the model adequately predicted the corrosion distribution for different anode-to-cathode area ratios and solution depths. However, in some instances the model was observed to significantly underpredict the experimental data. This underprediction was likely due to self-corrosion, which they estimated to be up to 230 mm/yr [17]. 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 [21]. 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 rates by 20% and 47% for the AE44-mild steel and the AE44-AA6063 couples, respectively [21]. 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$_2$ evolution on the Mg surface (self-corrosion). Where significant, inclusion of self-corrosion in simulations is needed to accurately predict the total corrosion rate [17, 21].

### 2.5 Increased cathodic activity on Mg surface due to anodic dissolution

Self-corrosion for galvanically coupled Mg is especially important because of the high anodic dissolution rate of Mg when coupled. 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 [23]. In another study, Birbillis et al. showed increased cathodic reaction rates (up to an order of magnitude higher) on Mg surfaces as a result of prior anodic dissolution [24]. 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. Thus, the need to quantify self-corrosion is important. This will be discussed in detail in section 5.2.
2.6 Morphology of Mg corrosion

Mg exhibits both general and localized corrosion. Under immersed conditions, it mostly undergoes localized corrosion [25]. Filiform (worm-track) and disk-type corrosion are common localized corrosion under immersed conditions.

![Figure 2-2: A) Disk-type corrosion B) Filiform corrosion [26, 27].](image)

![Figure 2-3: Morphology of a disk for a freely corroding Mg [27].](image)
Mg undergoes disk type corrosion at its free corrosion potential usually in a neutral or alkaline salt solution. As shown in Figure 2-2A Williams et al. reported dark circular spots on a commercial purity (99.9%) Mg within minutes of immersion in a 5% (w/v) NaCl solution. These dark spots grew radially with time to form disk-like structures [15, 27]. SVET analysis of surface showed the corroded areas behaved as cathodic areas while the outer ring behaved as anodic areas as shown in Figure 2-3. High metal impurities (>280 ppm Fe) in Mg and transition metals in Mg alloys promote this type of corrosion. A high concentration of Cl- in the electrolyte may also lead to disk corrosion. Disk corrosion is often associated with a high current density (~100 – 150 A/m²) on the metal surface that can sustain the radial propagation of the disks [15].

Filiform or worm track corrosion has been mostly seen under protective coatings. However, uncoated Mg with low impurities immersed in electrolyte containing lower concentration of Cl- has also shown filiform-type corrosion. As shown in Figure 2-2B, dark, thread-like tracks that evolve hydrogen and lengthen with time are described for high-purity Mg (<80 ppm Fe) immersed in chloride-containing solution. This type of morphology is associated with a low current density (~10 A/m²) on the metal surface that cannot sustain the radial propagation of corrosion [15].

In both cases, the morphology is strongly influenced by the cathodic reaction, which limits the rate of corrosion [8, 15]. The corrosion morphology of galvanically coupled Mg has been sparsely researched and the impact of coupling and cathode size on surface morphology needs to be studied in detail. Our work will study the morphological changes caused due to the coupling of Mg to steel.
After carefully reviewing the literature, we have outlined the properties, significance, application and challenges of Mg. The physical properties of Mg are attractive while the electrochemical properties are the limiting factor to its wider use. The rate of Mg corrosion is affected by many factors such as impurities, the type of metal to which Mg is alloyed or coupled, Cl⁻ concentration in electrolyte, geometry and so on. The corrosion morphology also depends on various factors. For this reason numerical prediction of Mg corrosion can be particularly challenging. The discrepancy between numerical models and experimental results in the literature are mainly due to the role of self-corrosion. The self-corrosion during galvanic coupling is important due to the enhanced cathodic activity of Mg especially during high anodic dissolution. In this work we look to quantify the role of self-corrosion and study the morphology of Mg galvanically coupled to steel cathodes of various sizes.
3 OBJECTIVES AND SCOPE

3.1 Objectives

The first objective of this project is to study and quantify the role of self-corrosion of Mg galvanically coupled to steel. Galvanic coupling of Mg to another metal such as steel increases the corrosion rate of Mg due to increased hydrogen evolution. Although galvanic corrosion dominates this process, self-corrosion does not entirely stop. When Mg is galvanically coupled to steel, most of the hydrogen evolves on the steel surface; however, we have observed that substantial hydrogen evolution is seen on the Mg surface as well. This indicates that there is an important contribution of self-corrosion even when the metal is galvanically coupled. While many researchers assume the self-corrosion to be negligible compared to galvanic corrosion, no quantitative analysis has been done. Previous studies have shown that the hydrogen evolution reaction is catalyzed at high metal dissolution rates [23, 24]. Therefore, the role of self-corrosion for coupled Mg may be significant. It is also evident from the literature that models developed to address the galvanic corrosion have often underestimated the total corrosion rate [17, 21]. This also suggests that self-corrosion may play an important role in such systems, and provides motivation for a detailed study of self-corrosion for galvanically coupled Mg.
The second objective of this project is to study how the surface morphology is impacted by corrosion when Mg is galvanically coupled to steel. 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 [15, 26, 27]. 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. However, this limitation is significantly reduced when Mg is coupled to steel due to increased cathodic area for hydrogen evolution. Thus, galvanic coupling of Mg changes drastically the mechanisms that control the corrosion rate. Therefore, it is likely that the morphology of attack will be different for coupled Mg. Studying the morphology of galvanically coupled Mg will provide in-depth knowledge of how corrosion starts and what form it takes under different conditions. Such knowledge may provide insights into corrosion prevention of galvanically coupled Mg.

In summary, the purpose of this research 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.

3.2 **Scope**

This is an experimental study designed to examine the role of self-corrosion of pure (99.95 wt\%) Mg galvanically coupled to mild steel. Different steel (cathode) sizes will be used to study the influence of changing cathodic area on the self-corrosion. Moreover, the behavior of self-corrosion with time will be explored. In addition, we will also study surface film formation and
the surface morphology. The results obtained here will be for short-term corrosion experiments (≤ 10 min).
4 MATERIALS AND METHODS

4.1 Sample preparation

The samples tested consisted of the exposed end of an Mg rod (99.95%, GalliumSource), 3mm in diameter, that was electrically insulated from and surrounded by a mild steel (A36, Metals Depot) electrode. The insulator around Mg wire was a heat-shrink material with a thickness of roughly less than 0.2mm. The main 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 16mm. This geometry was chosen in order to study the effect of 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 a diamond saw (Buehler Isomet 1000), and the surface was polished (to 1 micron paste) prior to submersion in the 5 wt% NaCl electrolyte.

4.2 Cutting and polishing of sample

The samples were first cut by the Buehler Isomet 1000 precision saw to form a uniform sample surface to be polished. The cuts were made with 350 g/cm² pressure at 700 RPM. Once cut, the samples were polished using a Buehler Ecomet 2 polishing wheel equipped with a Buehler
Automet 2 attachment head. The samples were first polished with a 600 grit silicon carbide sandpaper for 10 minutes with the polishing wheel rotating at 240 RPM and the head containing sample at 120 RPM in the same direction with 10 pounds of force. The polisher was lubricated with a 1:1 by volume ethanol and ethylene glycol mixture at a rate of approximately 5mL per minute. After the initial grinding/polishing, the samples were then polished with a 3 micron diamond paste obtained from Ted Pella Inc. for 7:30 minutes at 120 contra RPMs with 10 pounds of force. Lastly, the samples were polished with a 1 micron diamond paste (Ted Pella Inc.) for 5 minutes at 120 RPM, with the head and wheel rotating in the opposite direction with 10 pounds of force.

4.3 **Corrosion cell**

The cylindrical corrosion cell was made out of Teflon with an internal diameter of 4.2 cm, a height of 5 cm and a capacity of up to 70 mL of electrolyte. The cell contained a small O-ring lined opening (2.4 cm diameter) at the bottom into which the sample was inserted. This arrangement prevented leaking throughout the course of experiment (see Figure 4-1 below).

![Figure 4-1: A) Schematic of corrosion cell made of Teflon B) Top view of the corrosion cell. The opening on the bottom contained O-ring to seal the sample from leaking out solution.](image-url)
The electrode was mounted in the cell “face up,” which allowed us to conveniently capture hydrogen for volumetric measurements and to observe morphological changes on the surface during the course of experiment.

4.4 Experimental set up

A 5 wt% NaCl solution with a starting solution pH of 4 was used for all experiments. The concentric Mg and steel electrodes were galvanically coupled by electrically connecting them external to the solution through a zero resistance ammeter (ZRA), which also permitted direct measurement of the galvanic current. A saturated calomel reference electrode (SCE, BioLogic) was used. The experimental set up along with cross section of working surface are shown in Figures 4-2 and 4-3, respectively.

![Schematics of experimental set up.](image)

**Figure 4-2: Schematics of experimental set up.**
4.5 **Experimental methods**

Experiments were designed to study the impact of coupling Mg to steel electrodes of different sizes. 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 second. A waterproof immersed camera was used to monitor the electrode surfaces during the course of some experiments. It provided a closer look at hydrogen evolution and morphological changes.

To study the surface morphology, samples were taken out of solution at various time intervals during the course of the experiment and the images were taken using an inverted optical microscope (Axio Vertical A1, Zeiss). This microscope used a software (ZEN) that allowed us to analyze the captured image with ease. For example, the radii and depths of the pits were measured using this software. In order to quantify the fraction of the Mg surface that was...
corroded, image processing via Matlab was used to segment the surface images (Figure 4-4A) into black and white pixels (Figure 4-4B), where the black pixels corresponded to the corroded areas and the white pixels to the uncorroded areas. Appendix A provides the Matlab code for converting the original image (Figure 4-4 A) to black and white (Figure 4-4 B). Appendix B provides Matlab code to obtain the fraction of black pixels (representing corroded areas) on Mg surface.

The level of intensity was chosen from a valley separating two peaks of bimodal gray scale histogram as shown in Figure 4-5. The area other than the Mg surface was masked with red color as shown in Figure 4-4B for one such picture.

Figure 4-4: A) Original image B) Black and white image obtained with Matlab. Please note that the area other than Mg surface was masked with red color to account for the black and white pixels of Mg surface only.
The ratio of black pixels to total pixels (black + white) provided the fraction of surface that was corroded.

4.6 Measurement and data analysis technique

Any precipitate in the solution at the end of the experiment was dissolved for analysis using 1mL 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

Figure 4-5: Bimodal histogram of grayscale image.
very low rate and is often used to remove corrosion products from Mg without significantly attacking the base metal [4]. As mentioned above, Inductively Coupled Plasma-Mass Spectroscopy (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 using a Potentiostat (263A, Princeton Applied Research) in the ZRA mode, fit to a cubic-spline function, and then integrated numerically to get the total charge passed between the steel and Mg as established by equation 4-1 below. The total moles of Mg lost by galvanic corrosion were determined from the total charge via Faraday’s law as established by equation 4-2 below.

\[ Q = \int I dt \]  

\[ m(\text{mol of Mg lost}) = \frac{Q (C)}{n_{\text{mol of Mg lost}} F \left( \frac{C}{e_q} \right) \text{eq}} \]  

where \( Q \) is total charge, \( I \) is galvanic current, \( t \) is time, \( m \) is moles of Mg lost by galvanic corrosion, \( n \) is equivalent number of electrons per each mole of Mg lost, and \( F \) is Faraday’s constant. The number of electrons \( (n) \) is 2 as shown in reaction mechanism in section 2.2 and clearly established in the literature [5, 14, 24, 28]. Total current density was obtained by converting Mg lost in solution to current density, using Faraday’s equation. Galvanic current density was obtained by converting total charge to current density.
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 final solution pH for all the samples was between 11.7 and 11.9. A film with several cracks was present on the Mg surface at the end of the experiment. Measurements of the Mg lost using two different techniques, a) ICP-MS and b) volume of hydrogen gas, were in good agreement as shown in Figure 5-1.

![Figure 5-1: Comparison of measurement of Mg using ICP and hydrogen collection.](image)
5.1 Impact of cathode size on the galvanic current

Figure 5-2 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 5-2, 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 5-2). 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.

Figure 5-2: Galvanic current as a function of time for three different cathode (steel) sizes. The anode (Mg) diameter was constant (3mm) for all experiments.
Similarly, Figure 5-3 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 decreased 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 5-3 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 5-2. A higher potential would typically be associated with an increased rate of metal dissolution; however, in our experiments, other factors such as the higher solution pH and the formation of a surface film...
slow the corrosion rate. Metal dissolution is also inhibited by both the increased pH and the surface film [9-11, 29]. The high rate of hydrogen evolution 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. This is shown in Figure 5-4.

![Figure 5-4: pH increase during the course of the experiment.](image)

After that, the pH increased slowly to 11.9. Stability of surface film on Mg surface has been shown to be dependent on the pH [30]. At lower pH the film dissolves easily but at higher pH, the film is not only stable but continues to grow. Stable surface films on Mg have been shown to slow the corrosion rate [11, 29], and are most likely responsible for 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. The observed increase of the galvanic current density with increasing cathodic area is due 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. This is because, the influence outside cathode is highest near the 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 we are not there yet. For reference, the ratio of the steel to Mg for the 8mm, 12mm and 16mm electrodes are 5.5, 14.4 and 26.8, respectively.
5.2 Impact of coupling and cathode size on self-corrosion

Figure 5-5 shows the average total, galvanic and self-corrosion current densities for the three different cathode sizes at the end of a 10 min experiment. The total current densities reported here are from the ICP-MS measurements, although hydrogen gas measurement yielded similar results (Figure 5-1). The total, galvanic and self-current densities all increased with the cathode size. As observed with the galvanic current (Figure 5-2), change in current density between the 8 mm and 12 mm samples was greater than that observed between 12 mm and 16 mm samples. It is important to note that self-corrosion represented a significant fraction of total corrosion.

Figure 5-5: Average current densities for total, galvanic and self-corrosion for three different sized cathode samples for 10 min experimental time. Self-corrosion was 35, 33 and 33 percent of total corrosion for 8 mm, 12 mm and 16 mm samples respectively.
Self-corrosion accounted for more than one-third of the total corrosion. It increased with cathodic area; however, the fraction of self-corrosion stayed relatively constant (33-35%). The corrosion rates observed for our samples are higher than most values reported in the literature. The principal reason for the higher rates is the high ratio of cathode to anode area used in our experiments, which ranged between 5 and 27. Others have also observed corrosion rates that increased with increasing cathode area [18, 19]. However, it is interesting to note that the corrosion rate continued to increase with cathode area even at the high area ratios used in this study. The use of pure Mg rather than an alloy and the initiation of experiments at pH 4 may also have contributed to the higher rates [7, 9]. Finally, we note that the time period examined in this study was relatively short and may have been a contributing factor to corrosion rates that were different than those observed previously by others over longer periods of time.

In the absence of galvanic coupling (free corrosion), the current densities for Mg corrosion were significantly lower (26 A/m²), and in agreement with values reported previously for Mg of similar purity [15]. However, the rate of self-corrosion for coupled Mg was approximately 30 times higher than the free corrosion rate. Clearly, the self-corrosion rate 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 corrosion rate, which is expected to impact hydrogen evolution on the surface [23, 24]. Variation of the corrosion rate with time under both free and coupled conditions was approximated by examining the fraction of the surface that was corroded as shown in Figure 5-6.
It is evident from these figures that corrosion propagates much faster when Mg is coupled than during free corrosion. 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 5-7). Note that the observed morphology differences will be discussed in Chapter 6.

Figure 5-6: Surface morphology of A) freely corroding Mg at 5 min B) galvanically corroding Mg at 40 sec.
Figure 5-7: Fraction of Mg surface corroded during A) galvanic and free corrosion for three different samples. Only one set of data for free corrosion is shown as the outer cathodic area had no impact on it. B) Plot in A) with free corrosion data removed.
As obvious from Figure 5-7A, most of the surface was corroded within the first minute for coupled Mg. For uncoupled Mg, just over half of total surface was corroded in 20 minutes (Figure 5-7A). Clearly, impurity enrichment due to selective dissolution would be much faster for the coupled sample. Such enrichment due to high dissolution rates could be responsible for the high rate of self-corrosion reported in Figure 5-5.

We also see from Figure 5-7B 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 5-5).

5.3 **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 [31]. Then, as the pH of the solution increases, a film forms on the corroding surface. This film has shown to decrease the galvanic corrosion rate [20]. Both of these changes are expected to cause the self-corrosion rate to change with time as well. To explore this time variation, the experiments similar to those reported above were performed for run times of 1, 3, 5 and 10 minutes. The results are shown below in Figure 5-8, where each experiment was repeated 3 times.
As seen in Figure 5-8, the fraction of self-corrosion was lower for the 1 min experiments, but was still a significant fraction of the total corrosion. The fraction of self-corrosion reached a maximum between one and three minutes, and appeared to decrease after that. This pattern is also evident from Figure 5-9, where the rate of absolute values of self-corrosion changes with time. It can be seen from figure 5-9 that the slope of the graph is significantly higher at 1-3 min time interval than at other time intervals.

Figure 5-8: Fraction of self-corrosion at various time intervals for different samples.

As seen in Figure 5-8, the fraction of self-corrosion was lower for the 1 min experiments, but was still a significant fraction of the total corrosion. The fraction of self-corrosion reached a maximum between one and three minutes, and appeared to decrease after that. This pattern is also evident from Figure 5-9, where the rate of absolute values of self-corrosion changes with time. It can be seen from figure 5-9 that the slope of the graph is significantly higher at 1-3 min time interval than at other time intervals.
The lower fraction of self-corrosion observed during the initial period was due to the influence of the native oxide film on the Mg surface [31]. However, as shown in Figure 5-7, the native oxide was either completely gone, or nearly so, by a corrosion time of 1 minute, assuming that the observed linear trend continued. Consequently, a decrease in the fraction of the surface covered by the native oxide cannot account for the significant increase in the self-corrosion rate observed between 1 and 3 minutes, particularly in the case of the 12 mm and 16 mm cathodes. The corrosion potential did not contribute to the increase in the self-corrosion rate since it increased with time as shown in Figure 5-3. 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 [23]. In another study, Birbillis et al. showed increased cathodic reaction rates (up to an
order of magnitude higher) on Mg surfaces as a result of prior anodic dissolution [24]. Although there has been quite a few studies on the enhanced cathodic activity on Mg surface due to prior dissolution, the exact mechanism is yet to be found[30, 32-36]. However, most studies suggest that, catalysis of the hydrogen reaction is likely due to enrichment of impurities in the Mg owing to selective dissolution of the Mg [23, 24, 32-34, 36]. As a result, 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 [17, 19]. Thus, the high anodic dissolution rate observed for our galvanically coupled Mg catalyzed hydrogen evolution on the Mg surface, leading to an increased rate of self-corrosion, especially between 1 and 3 minutes.

It is important to note that the fraction of self-corrosion was significant throughout the entire period of the experiment. The increase in hydrogen kinetics [23, 24] contributed to the increasing fraction of self-corrosion observed for the first 3 minutes. The fraction of self-corrosion subsequently decreased due to the increase in the pH and the formation of a surface film (see Figure 5-8). Our results not only show the significant fraction of self-corrosion, but also its variability with time, and are important to understanding the corrosion behavior of coupled Mg.
6 IMPACT OF GALVANIC COUPLING ON SURFACE FILM AND MORPHOLOGY

6.1 Surface film-formation during corrosion

A film with several cracks was observed on the Mg surface after galvanically coupled corrosion for 10 min. The images of the Mg surface before and after the experiment are shown in Figure 6-1A and 6-1B, respectively. The surface after film removal is shown in Figure 6-1C.

Figure 6-1: A) Polished Mg surface B) Mg surface after galvanically corroded for 10 min C) Mg surface after film removal.
Although, figuring out exact composition of the film is not the scope of this project, previous studies have clearly suggested that a film layer consisting of Mg(OH)$_2$ and possibly MgO forms on the Mg surface as the electrolyte goes in the alkaline pH range [10, 11, 37]. For the purpose of determining the total amount of Mg corrosion, it was important to include the 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 6-1 summarizes the results of experiments for each of the three steel cathode sizes.

**Table 6-1: Mg content in surface film.**

<table>
<thead>
<tr>
<th>Cathode Size</th>
<th>Total Amount of Mg corroded (g)</th>
<th>Amount of Mg in film (g)</th>
<th>Average Mg in the film (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Experiment 1</td>
<td>Experiment 2</td>
<td>Experiment 1</td>
</tr>
<tr>
<td>8 mm</td>
<td>$1.1 \times 10^{-3}$</td>
<td>$1.2 \times 10^{-3}$</td>
<td>$2.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>12 mm</td>
<td>$1.4 \times 10^{-3}$</td>
<td>$1.4 \times 10^{-3}$</td>
<td>$4.4 \times 10^{-4}$</td>
</tr>
<tr>
<td>16 mm</td>
<td>$1.4 \times 10^{-3}$</td>
<td>$1.5 \times 10^{-3}$</td>
<td>$4.0 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

For the 8 mm sample, the total amount of Mg and the amount of Mg in the film were both lower than the corresponding values for the other two samples. In contrast, the results for the 12 mm and 16 mm samples were essentially the same, given the accuracy of the experiments. Approximately 30% of total corroded Mg resided in the film for the experiments carried out for the full 10 minutes.

As shown in Figure 6-1B, several cracks were apparent in the film. It is likely that hydrogen evolution on Mg surface contributed to the formation of these cracks. In-situ examination with a submerged video camera indicated preferential evolution of hydrogen at the cracks. Figure 6C shows the surface after removal of the film. Although the entire surface underwent corrosion,
nonuniformities were observed, which may reflect local differences in the film that covered the surface (e.g., the presence of cracks, etc.).

Although the film appeared to slow the corrosion rate, it did not completely passivate the surface. Hydrogen evolution was observed (in-situ) to continue on the Mg surface after film formation. The concentration of Mg in the solution also continued to increase. Additional characterization of the dynamic composition and morphology of film is needed and will be the topic of a future publication.

6.2 Surface morphology of galvanic and free corrosion

Previous studies have shown that the surface morphology of freely corroding Mg depends on factors such as the metal purity and Cl\textsuperscript{−} concentration [15, 26, 27]. In particular, two types of surface morphologies are seen, namely disk and filiform, that are governed by the magnitude of current density on the corroded surface [15]. Our study showed that the corrosion morphology of galvanically coupled Mg was quite distinct from that of the uncoupled Mg (see Figures 6-2 and 6-3).

For freely corroding Mg, corrosion initiated with small crack-like structures that lengthened with time and took the form of filiform-type corrosion [26]. This type of corrosion appeared to be initiated randomly on the metal surface (see Figure 6-2).
As shown earlier, the average cathodic current density on Mg surface during free corrosion was approximately 26 A/m² and was associated with filiform-type corrosion. Williams et al. also observed filament-like structures and current densities of ~10-15 A/m² for high purity samples, in good agreement with our results [15]. The samples used in this study were 99.95 wt% Mg with an iron content of ~30 ppm. Impurities such as iron increase the rate of hydrogen evolution. Consequently, the low impurity concentration in the samples tested contributed to slow hydrogen evolution and a low corrosion rate for uncoupled Mg. The low rate of the cathodic reaction in our samples was not sufficient to sustain the radial growth observed for Mg with a higher impurity content [7], yielding the observed filiform corrosion.

Figure 6-2: Surface morphology of freely corroding Mg at A) 5 min B) 10 min C) 15 min D) 20 min. Note that only top half of Mg surface is shown at each time.
Radial growth or disk type corrosion was observed for freely corroding Mg with iron impurity levels higher than our samples (≥280 ppm) [15]. In those samples, 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 [15, 27]. 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.

In both of the above situations (filiform and disk corrosion), the corrosion geometry was determined by the cathodic reaction, which was severely limiting. In contrast, the addition of a separate cathode in galvanic corrosion removes the severe cathodic limitation and dramatically changes 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 (see Figure 6-3).
Pit initiation was generally random, although preferred initiation at scratch defects was observed for some samples where the polishing was less satisfactory (see Figure 6-4).

Figure 6-3: Surface morphology of galvanically corroding Mg at A) 10 sec B) 20 sec C) 30 sec D) 40 sec. Note that only top half of Mg surface is shown at each time.

Figure 6-4: A) Polished surface with imperfections (scratches) B) corrosion disk attacking the imperfections in Mg surface.
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.
7 CONCLUSIONS AND FUTURE WORK

7.1 Conclusions

1. When Mg was galvanically coupled to steel, self-corrosion contributed to more than one third of total corrosion. Previous attempts to model Mg corrosion have noted a discrepancy between the measured and predicted corrosion rates [17, 19, 21, 22]. One possible reason for this might be the influence of the self-corrosion, which represented a significant fraction of the corrosion rate for galvanically coupled systems. Previous studies have shown increased hydrogen kinetics on Mg surface due to prior anodic dissolution [23, 24]. Consistent with previous studies, our results also showed that the rate of catalysis for H₂ evolution on Mg surface (self-corrosion) increased with the rate of anodic dissolution (seen with larger steel cathodes samples). The sample with the largest cathode area had the highest potential that would have the lowest driving force for hydrogen. However, the driving force for H₂ evolution was controlled by the surface kinetics that increased with anodic dissolution rate [23, 24]. This resulted in significant amount of self-corrosion, as seen with our results. The important role of self-corrosion, discussed here, will help to precisely predict the total corrosion rate of galvanically coupled Mg.
2. Self-corrosion varied with time. The fraction of self-corrosion was lower for the one minute experiments, but was still a significant fraction of the total corrosion. The fraction of self-corrosion reached a maximum between one and three minutes, and appeared to decrease after that. The initial polished surface of Mg has a native oxide film that is generally resistant to the corrosion, resulting in a low initial rate of self-corrosion. As soon as the film broke down, the dissolution rate significantly increased, catalyzing the hydrogen reaction on Mg surface. For this reason, significant increase in self-corrosion rate was seen between one and three minutes. The pH increased quickly and surface film formed on the Mg surface in the first few minutes. An increased pH, and more importantly the surface film, however, slowed this process. Our results showed both self-corrosion and galvanic corrosion changed with time. While galvanic corrosion decreased with time, self-corrosion rate was initially low, increased to a maximum value and decreased thereafter. It is important to consider the dynamic behavior of self-corrosion to fully understand the corrosion behavior of galvanically coupled Mg.

3. 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 of experiment. 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.

4. The surface morphology during free corrosion was different from that present during galvanic corrosion. Uncoupled Mg showed filiform corrosion, consistent with previous studies for Mg, with similar Mg purity and electrolyte concentration. Free corrosion of Mg was cathodically limited that caused slow H₂ evolution and resulted in filiform type corrosion. For coupled Mg, corrosion started with small pits that gained significant depth with time. For coupled Mg, the cathodic limitation on Mg surface was greatly reduced due to presence of the outer cathode. Because of this, the anodic reaction was not limited by the cathodic reaction on the Mg surface (e.g. ring or track). As a result, pits with appreciable depths were seen at the end of the experiment. The surface morphology of corrosion provides fundamental knowledge of corrosion propagation on the Mg surface. Understanding phenomenon of Mg surface corrosion may contribute to controlling Mg corrosion.

In this work we have shown how coupling of Mg to steel cathodes of different sizes impacts the rate self-corrosion, galvanic corrosion and surface morphology. In particular, the role of self-corrosion for a galvanically coupled Mg is quantified. Although, galvanic corrosion dominates the overall corrosion process, self-corrosion plays a significant role. In fact, the fraction of self-corrosion approached 50% in our time-dependent experiments (Figure 5-8). It is important to understand that it is the high anodic dissolution rate (caused due to galvanic coupling) that leads to increased hydrogen kinetics on Mg surface, resulting in significant amount of self-corrosion and
observed morphology. This study also provides important insight into the processes that control Mg corrosion under several conditions, such as, high cathode-to-anode ratios, low electrolyte pH, surface film etc.

7.2 Future work

There are various opportunities for future work related to this project. We will discuss two possible future efforts related to this study: 1) role of oxygen in a thin electrolyte film and its impact on Mg corrosion and 2) numerical modeling of current and future results.

Studying Mg corrosion under a thin electrolyte film is of particular interest due to its practical significance. In most of the real world applications, the corrosion of Mg takes place under an electrolyte film. The cathodic reaction of Mg corrosion is H₂ evolution; however, the change in electrolyte thickness may affect the processes such as the mass transport of dissolved oxygen, pH changes and accumulation of corrosion products. Under a thin film electrolyte, oxygen consumption may compete with hydrogen evolution. It is, therefore, possible that oxygen may play a role for thin electrolyte film. Exploring the role of oxygen for Mg corrosion under for thin electrolyte film is significant because it may change the cathodic reaction. From a practical scenario, thin electrolyte films are important to study because most applications of Mg are exposed to such films caused by rain water and atmospheric moisture.

Numerical modeling of Mg corrosion is particularly difficult due to the complexity of the corrosion phenomenon caused by the corrosion products, pH changes, etc. Despite such difficulties, recent studies have clearly shown satisfactory prediction of Mg corrosion via
simulation under some conditions. However, the self-corrosion, i.e. the kinetics of H\textsubscript{2} evolution on Mg surface were not considered in those studies. As a consequence, some of the models significantly under predicted the experimental results. Our results have shown significant self-corrosion. We will use STAR CCM+ software from CD-Adapco to create the geometry (discussed in chapter 4). We plan to input hydrogen kinetics on Mg surface in the simulation to see if the model predicts the experimental results more precisely. As the use of Mg increases in automobile and aerospace industry, modelling of Mg corrosion will become increasingly important. Developing a numerical model that predicts Mg corrosion precisely would allow us to explore situations where experimental results are difficult to obtain.
Appendix A - Matlab code for converting image to black and white

```matlab
Image = imread(“specify image file location”);
imshow(Image);
%%
Image_original=Image;
Image(:,:,3)=0;
%%
Image_adjusted=imadjust(Image, stretchlim(Image, 0.1));
imshow(Image_adjusted);
%%
Im_int=rgb2gray(Image_adjusted);
imshow(Im_int);
figure, imhist(Im_int)
%%
M=mean2(Im_int);D=std2(Im_int);
%%
Bsize=[3 3];
k=[0.4 0.02 0.4];
E=4.0;
fsem_enh=nlfilter(Im_int,Bsize,@mylocstat,M,D,E,k); 
t_nlfilter=toc
Isem_enh=im2uint8(mat2gray(fsem_enh));
%%
imshow(Isem_enh);
%%
K = wiener2(Isem_enh,[3 3]);
imshow(K);
%%
level_k = graythresh(K);
Image_k_bw=im2bw(K, level_k);
imshow(Image_k_bw);
imwrite(Image_k_bw,filename{1});
return;
```
Appendix B - Matlab code to calculate the fraction of black pixel in the image from Appendix A

```matlab
filename = uigetfile({ '*.jpg; *.jpeg; *.png'}, 'image files (*.jpg, *.jpeg, *.png)');
I = imread(filename);

%%
black_pixels = 0;
white_pixels = 0;
red_pixels = 0;

for i=1:size(I,1)
    for j=1:size(I,2)
        if (I(i,j,1)>150 && I(i,j,2)<50);
            red_pixels = red_pixels + 1;
            continue;
        end;
        if (I(i,j,1)>200 && I(i,j,2)>200 && I(i,j,3))
            white_pixels = white_pixels + 1;
            continue
        end
        if (I(i,j,1)<150 && I(i,j,2)<150 && I(i,j,3)<150)
            black_pixels = black_pixels + 1;
            continue
        end
        I(i,j,:);
    end
end
area_ratio = black_pixels/(white_pixels + black_pixels);
fprintf('area ratio is %f\n',area_ratio);
```

51
REFERENCES


