Developing scanning electrochemical microscopy method for studying bio-corrosion of magnesium alloys and protective surface treatments

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Developing scanning electrochemical microscopy method for studying bio-corrosion of magnesium alloys and protective surface treatments

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This thesis is submitted in fulfilment of the requirements for the award of the degree
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Declaration

I, Sina S Jamali, declare that this thesis, submitted in partial fulfilment of the requirements for the award of doctor of philosophy, of the School of Chemistry, University of Wollongong, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other academic institution.

Sina S Jamali

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ABSTRACT

Ways of implementing scanning electrochemical microscope (SECM) for studying corrosion and degradation of Mg in simulated biological solution has been studied in this thesis. SECM was first employed in more conventional mode of operation, namely feedback mode, to provide a baseline for comparison with other imaging modes of SECM. Four modes of SECM were in total exploited including feedback, AC, potentiometric and surface generation/tip collection modes. In feedback and AC modes electro-activity and insulating properties of surface were examined at a local scale. In the AC mode variation in conductivity of solution that was caused by corrosion reactions was also examined. A solid-state pH sensing microelectrode based of iridium/iridium oxide was fabricated and used in potentiometric mode of SECM for measuring the near surface pH during corrosion of Mg.

A new method of sensing H$_2$ at a solid surface has been introduced herein which is implemented to evaluate the H$_2$ evolution during corrosion of Mg as a tool for acquiring mechanistic information about the corrosion process as well as measuring H$_2$ evolution as an indicator of corrosion rate. Also a new Mg alloy named AZNd was specifically designed by Boston Scientific, funding body of this research, for use in fabrication of biodegradable coronary stents. Corrosion of AZNd in buffered media as well as effective of surface treatments for protection against corrosion was investigated using SECM and other electrochemical and analytical methods.

Chapter 4 and 5 of this thesis were case studies showcasing capabilities of SECM as a powerful characterization tool for studying corrosion of Mg and protective properties of surface treatments. In chapter 4 effect of protein (i.e. albumin) on the corrosion of Mg in buffered media was investigated and it was shown that presence of protein may reduce the corrosion rate in the early stages of contact with corrosive media via formation of a barrier layer on the surface of Mg. However in the long term presence of protein may be detrimental due to formation of inhomogeneous surface layer and/or chelation of metal ions thus promoting localized corrosion. In chapter 5 surface treatments based on praseodymium conversion coating and a biodegradable conducting polymer were applied on AZNd and corrosion protection afforded by these surface treatments were investigated.
Publications arising from/during the course of this thesis

Journal papers


Conference contributions


**Forthcoming publications**


Chapter 1

Mg corrosion and its biomedical applications


1.1 Coronary stents

Coronary angioplasty is a medical procedure used to treat narrowing of the arteries that supply blood to the heart. This is accomplished by inflating a small balloon inside the artery to increase the blood flow to the heart [1]. It may be performed on an emergency basis following a heart attack or on an elective basis when conservative treatment measures have failed to relieve symptoms of coronary artery disease such as chest pain and shortness of breath. Similar procedure may be implemented for relief of poor blood flow in other body parts such as legs which is called peripheral angioplasty. During the procedure, a thin, flexible catheter (tube) with a balloon at its tip is threaded through a blood vessel to the affected artery. The balloon forces expansion of the inner white blood cell/clot plaque deposits and the surrounding muscular wall, opening up the blood vessel for improved flow, and the balloon is then deflated and withdrawn. Although angioplasty restores blood flow and relieves symptoms in over 90 percent of patients, there is a risk of recurrent symptoms often due to recurrent narrowing (restenosis) of the artery [2]. Restenosis that is severe enough to cause original symptoms recurs in approximately 30 percent of people who have balloon angioplasty without stent placement.

The immediate result of coronary angioplasty is mainly influenced by both plastic (irreversible) and elastic (reversible) changes of the vessel wall [3]. Coronary stents are the small mesh-like scaffolds placed inside the arteries following the balloon angioplasty surgery (Figure 1.1) to provide mechanical opening support and avoid the elastic arterial recoil [4,5]. The desired effects are achieved within weeks after angioplasty. Stents were first introduced in 1979 for relief of coronary vascular obstructions by Sigwart et al. [6]. In 1991, the use of stent angioplasty to deal with congenital heart defects was introduced. Since then, the uses of stents have been widespread and they are applied in numerous locations of the vascular system [7]. Angioplasty using stents is a common procedure in Australia, with over 30 000 cases performed each year and new reports show marked increase in the use of coronary stents in the recent years. In the process, the stent is mounted on the balloon and is expanded and positioned by inflating the balloon. The expansion of the stent opens
up the artery wall to restore the effective blood stream [6]. These steps are schematically shown in Figure 1.1.

![Figure 1.1](image)

**Figure 1.1** Steps involved in stent angioplasty including (a) placing the stent within the narrowed area of artery using stent delivery device (catheter), (b) inflation of balloon inside the stents and (c) removing the catheter and balloon to restore the normal blood stream.

Generally, stents are laser cut from metal mini-tubes with special designs to impart an expandable characteristic [8]. Laser cutting allows precise cutting of stent designs from tubes and because of its computer controlled mechanism, it is flexible in stent designs. Stent designs are unique (and patented) for each stent manufacturer. It has been shown that while the stent surface material plays the major role in occurrence of thrombosis, geometric configuration of stents plays a significant part in determining the stent-induced vascular injury and restenosis [9]. Two typical designs for cardiovascular stents, before and after expansion, are shown in Figure 1.2.
Figure 1.2 Two typical designs of cardiovascular metal stents: Slotted tube stent before (a) and after (b) expansion; corrugated ring stent before (c) and after (d) expansion [9].

Using stent can considerably reduce the risk of restenosis (recurrence of arterial narrowing) after the angioplasty, however, in about 25% of stent recipients, the problem of restenosis still remains in the form of so-called in-stent restenosis [10]. Currently most stents consist of a 316L grade stainless steel framework. However, this 316L steel is not fully biocompatible and has been shown to induce high occurrences of in-stent restenosis [11,12] and thrombosis [13,14], schematically illustrated in Figure 1.3.

Figure 1.3 Illustrative presentation of late stage thrombosis (a) and in-stent restenosis (b) cause by permanent stents.
It has been elucidated that the artery’s wall remodels within weeks after stent-angioplasty as a consequence of the mechanical stresses generated by the deployed stent [15]. In order to help eliminate in-stent restenosis, thrombosis and need for prolonged anti-platelet therapy caused by permanent stenting the idea of using a biodegradable material has been introduced [16,17]. During the arterial remodelling process the temporary implant may gradually lose its mechanical integrity (due to degradation) until the arterial tissue gradually regains enough strength to remain patent without requiring support. The concurrent degradation of the stent with the gradual remodelling of an artery is shown in Figure 1.4.

![Remodelling Diagram](image)

**Figure 1.4** Illustration of an ideal compromise between mechanical integrity and degradation of a biodegradable implant [18].

Replacing these bio-stable stents (stainless steel) with degradable stents allows for the therapeutic benefits of the stent to take place which is then followed by degradation of stent that obviates the long term complications. Degradable stents would also permit alternative therapeutic strategies: They would eliminate the ongoing process of interference of an artificial material with the blood vessel wall, and could serve as a carrier of drugs applied to the implantation site. In addition, they would open the possibility of re-dilatation at the same location. This is
significant since while a stent addresses the negative consequences of a diseased vessel section, it does not address the initial cause of the disease which may reappear, requiring reintervention at the same location in some patients. A non-degradable stent would remain in this location, hence restricting the ability to treat the location successfully. Another potential benefit of degradable stents is the lack of interference with potential subsequent surgery on the stented vessels [19].

Development of degradable metal stents is a new area of research, with the two metals of choice currently being magnesium (Mg) and iron (Fe). Metal alloys based on Mg [20] or Fe [21] have been shown to be biocompatible and possess the mechanical properties required for stents. The early clinical studies on bioabsorbable metal stents (BMS) have shown promise indicating good mechanical scaffolding and biocompatibility of magnesium in animals [22,23] and human trials [24,25]. However, the rapid bio-corrosion process of Mg alloys produces extensive amounts of Mg(OH)₂ and H₂ which are not conducive to cell growth [26]. The work presented in this thesis has been financially supported by Boston Scientific, one of the world leading companies in the field of biomedical devices and, in particular, developing novel biodegradable coronary stents. The main focus of this thesis is developing scanning electrochemical microscopy (SECM) as a tool for studying corrosion behaviour of Mg alloys in an in vitro environment. Simulated biological fluid (SBF) has been used throughout the thesis as the buffered in vitro environment. Chapters 2 and 3 are dedicated to the advancement in SECM and the technique is implemented in combination with other analytical and electrochemical methods in the following chapters for corrosion studies. Chapter 4 will address the important contribution of protein in physiological environment on the corrosion behaviour of Mg. In chapter 5 rare earth compounds are studied as anti-corrosion treatment for Mg and in chapter 6 the corrosion protection afforded by two biodegradable polymer coatings have been investigated. In chapters 5 and 6, a new Mg alloy (AZ80X) which was designed by Boston Scientific for stent applications was used.
1.2 Mg alloys composition

The aim of this section is to provide readers with the principles of labelling Mg alloys and assist readers to identify the approximate composition of Mg alloys throughout the thesis from their name.

The American society for testing and materials (ASTM) specification B275 * classifies magnesium alloys based on maximum of two letters that represent the percentage of two major alloying elements (all in %Wt/wt) used in greatest amounts in the alloy composition. These ranged in order of decreasing percentages or in alphabetical order (if of equal percentages), followed by the respective percentages rounded to whole numbers. The code AZ91 therefore signifies an Mg alloy with roughly 9% Wt/wt aluminium and 1% zinc. Exact composition should be confirmed from reference standards. Table 1.1 lists the associated letters for the common alloying elements used in Mg alloys. It is noteworthy that almost all commercial Mg alloys contain more than two alloying elements while the alloy codes only specify the two major elements. The exact composition of a given alloy can only be obtained from the manufacturer or by analytical methods.

Table 1.1 Letter codification used to represent the alloying elements

<table>
<thead>
<tr>
<th>Letter</th>
<th>Alloying element</th>
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<tbody>
<tr>
<td>A</td>
<td>Aluminum</td>
</tr>
<tr>
<td>B</td>
<td>Bismuth</td>
</tr>
<tr>
<td>C</td>
<td>Copper</td>
</tr>
<tr>
<td>D</td>
<td>Cadmium</td>
</tr>
<tr>
<td>E</td>
<td>Rare earths</td>
</tr>
<tr>
<td>F</td>
<td>Iron</td>
</tr>
<tr>
<td>H</td>
<td>Thorium</td>
</tr>
<tr>
<td>J</td>
<td>Phosphorus</td>
</tr>
<tr>
<td>K</td>
<td>Zirconium</td>
</tr>
<tr>
<td>L</td>
<td>Beryllium</td>
</tr>
<tr>
<td>Z</td>
<td>Zinc</td>
</tr>
<tr>
<td>M</td>
<td>Manganese</td>
</tr>
<tr>
<td>N</td>
<td>Nickel</td>
</tr>
</tbody>
</table>

* Standard Practice for Codification of Certain Nonferrous Metals and Alloys, Cast and Wrought
The elements are generally added into the Mg alloys composition to improve mechanical properties and/or corrosion resistance. In biomedical applications it is important that the alloying elements have no toxic effect within the range they are presented. Effect of common alloying elements on corrosion behaviour of Mg alloys will be further discussed in sections 1.3 and 1.4.1.

The codification may be expanded to provide additional information or variants by adding a letter after the last composition number, to describe an important manufacturing process. Fabrication information can be coded as shown in table 1.2 [27]. To differentiate from the other information a hyphen is inserted, for examples ZK 61A−T5 or AM 100A−T61.

<table>
<thead>
<tr>
<th>General divisions</th>
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<tr>
<td>F As fabricated</td>
</tr>
<tr>
<td>O Annealed recrystallised (wrought products only)</td>
</tr>
<tr>
<td>H Strain hardened</td>
</tr>
<tr>
<td>T Thermally treated to produce stable tempers. Other than F, O or H</td>
</tr>
<tr>
<td>W Solution heat treated (unstable temper)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Subdivisions of H</th>
</tr>
</thead>
<tbody>
<tr>
<td>H1, plus one or more digits Strain hardened only</td>
</tr>
<tr>
<td>H2, plus one or more digits Strain hardened and then partially annealed</td>
</tr>
<tr>
<td>H3, plus one or more digits Strain hardened and then stabilised</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Subdivisions of T</th>
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</thead>
<tbody>
<tr>
<td>T1 Cooled and naturally aged</td>
</tr>
<tr>
<td>T2 Annealed (cast products only)</td>
</tr>
<tr>
<td>T3 Solution heat treated and then cold worked</td>
</tr>
<tr>
<td>T4 Solution heat treated</td>
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Intermetallic phases can be found in almost every magnesium alloy as the secondary phases within the main Mg matrix with high enrichment of one or more alloying elements. These intermetallic compounds play a very important role in optimizing the microstructure and mechanical properties \[28\]. The stability of this phase increases with the electronegativity of the alloying element. Perhaps the most important of all intermetallics are the Al enriched intermetallic forming within AZ alloys. Due to its low mechanical properties, unalloyed Mg is rarely used as a structural material, while the family of AZ alloys represents the majority of the used Mg products. The AZ Mg alloys present a good combination of properties, such as good tensile strength, cast-ability and corrosion resistance. When the Al content is higher than 6\% an intermetallic phase consist of Mg$_{17}$Al$_{12}$ is formed which is called β phase and has better corrosion stability compared to the matrix (α phase) \[29\]. Formation of this β phase has a beneficial impact on tensile strength of Mg alloy. Intermetallic may precipitate discontinuously along the grain boundaries or within the grain matrix. All Mg alloys exhibit a hexagonal crystal structure. The boundary between one grain (crystallites*) and its neighbour is a defect in the crystalline structure. Grain boundaries are associated with a higher level of energy (compared to grain matrix) due to localised slip and build-up of stresses at the grain boundaries in locations where the localised deformation occurs \[30\]. Grain boundaries therefore provide higher affinity for precipitation of intermetallic phases.

### 1.3 Aqueous corrosion of Mg and its alloys

Magnesium alloys are resistant against atmospheric corrosion because of a protective oxide film that forms in a process similar to the formation of films on other active

---

*Crystallites are small, often microscopic, crystals that are held together through highly defective boundaries and constitute a polycrystalline solid.
metals such as aluminium. When corrosion occurs, it is the result of breakdown of this protective film [31]. Mg dissolves in aqueous environments as a consequence of an electrochemical reaction with water that produces magnesium hydroxide and hydrogen gas. The overall reaction may be expressed as:

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \quad (1.1)
\]

The overall reaction may include the following partial reactions [18]:

\[
\text{Mg (s) } \leftrightarrow \text{Mg}^{2+} (\text{aq}) + 2e^- \quad (1.2) \quad \text{(anodic reaction)}
\]

\[
2\text{H}_2\text{O (aq)} + 2e^- \leftrightarrow \text{H}_2 (\text{g}) + 2\text{OH}^- (\text{aq}) \quad (1.3) \quad \text{(cathodic reaction)}
\]

\[
\text{Mg}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \leftrightarrow \text{Mg(OH)}_2 (\text{s}) \quad (1.4) \quad \text{(product formation)}
\]

Unlike most other structural metals, reduction of O\textsubscript{2} plays no part in cathodic reactions during aqueous corrosion of Mg and its alloys. As expressed by equation 1.4, dissolution of Mg is a pH dependent process and can be controlled by changing the electrochemical potentials and pH. Pourbaix (potential-pH) diagram in Figure 1.5 illustrates the corrosion, immunity and passivation regions for a simple system of pure Mg in water at 25°C. Pourbaix diagrams have been used commonly to evaluate the corrosion tendency or trend of metals in a given environment. These diagrams take into consideration the electrochemical potentials and the chemical equilibriums between the different species in solution as applied in the Nernst equation, equation 1.5:

\[
E = E_0 - \frac{RT}{nF} \ln \frac{a_{\text{Red}}}{a_{\text{Ox}}} \quad (1.5)
\]

where \(E\) is the cell potential, \(E_0\) the standard cell potential, \(R\) the universal gas constant (8.314 J K\(^{-1}\)mol\(^{-1}\)), \(T\) the absolute (K) temperature, \(a\) the chemical activity/concentration for the relevant species, \(F\) the Faraday constant (9.648 C mol\(^{-1}\)) and \(n\) the number of moles of electrons transferred in the half-cell reaction. For
aqueous corrosion, $E$–$pH$ diagrams should present in the background of the diagram the cathodic reactions involving water, $H_2$, and $O_2$. For example, for $H_2$ evolution reaction, applying reaction 1.3 to the Nernst equation at $25^\circ C$ and atmospheric pressure yields equation 1.6 that defines $pH$ and potential dependence of $H_2$ evolution half-cell reaction (shown as a dashed line on Figure 1.5).

$$E_{H^+/H_2}^o = E_{H^+/H_2}^{\circ} + \frac{0.0592}{2} log \left( \frac{\alpha_{H^+}}{pH} \right) = -0.0592 \ pH \quad (1.6)$$

Similarly the potential and $pH$ dependence of all other reactions participating in corrosion of Mg (e.g. reactions 1.2 and 1.4) can be calculated and plotted on a Pourbaix diagram. Further information on construction of Pourbaix diagrams and active/passive regions of Mg-aqueous systems can be obtained from references [32–34].

In theory, Mg can be cathodically protected against corrosion by coupling it with another (sacrificial) metal that has a more negative corrosion potential. However, it is highly impractical as no other structural metal can afford such a negative potential. In fact, the corrosion attack of an Mg alloy in an aqueous environment is often facilitated by microgalvanic coupling between anodic (Mg rich phase in the alloy) and cathodic (intermetallic phase in the alloy) areas which will be further discussed in section 1.3 in this chapter.
Figure 1.5 Potential-pH (Pourbaix) diagram presenting equilibrium regions for the system of magnesium and water at 25 °C and showing the theoretical domains of corrosion, immunity, and passivation.

The corrosion model presented in Figure 1.6, proposed by Song [18], illustrates the electrochemical reactions during corrosion of magnesium in aqueous media resulting in hydrogen evolution at both anodic and cathodic sites, namely anodic hydrogen evolution (AHE) and cathodic hydrogen evolution (CHE) respectively. This model proposes dissolution of Mg in the form of both divalent and monovalent cations.

Figure 1.6 Schematic illustration of anodic and cathodic reactions involving cathodic H2 evolution (CHE) and anodic H2 evolution (AHE) in the self-corrosion of pure magnesium according to the model suggested by Song from reference [18].
Aqueous corrosion of Mg involves an unusual electrochemical phenomenon known as negative difference effect. For most metals that involve H₂ evolution (HE) as the cathodic reaction, the rate of HE decreases when the metal is anodically polarised (referred to as anodically forced dissolution) whereas in the case of Mg HE increases during dissolution in an anodically polarised state. This effect is called the “negative difference effect” (NDE) and has been a controversial subject of a number of fundamental studies on Mg corrosion. As a result, several theories have emerged to explain this effect including; the existence of unipositive Mg⁺ [35], multi-step cathodic process [36], partial breakdown of protective film [37,38], enhanced catalytic activity of Mg surface [39] and formation of magnesium hydride [40]. The theory based on the existence of Mg⁺ has particularly been subject of debate with a number of published works in favour [35,41–43] and against it [44–47]. Regardless of the source of NDE, the phenomenon is widely blamed for a major issue in electrochemically determining Mg corrosion rates. It has been frequently reported that the corrosion rate measured by electrochemical methods such as potentiodynamic polarisation is lower than that determined experimentally by the weight loss measurement or H₂ collection. One of the aims of this thesis, addressed in Chapter 3, is to introduce a reliable alternative way of determining corrosion rate by direct measurement of HE using scanning electrochemical microscopy (SECM).

According to Song [18], in the early stages of corrosion, before the formation of hydroxide film, the concentration of metastable Mg⁺ controls the rate of corrosion. In the long term the dominant mechanism changes to the rate of surface coverage by an oxide film [48]. An insulating layer of Mg(OH)₂ forms on the surface in aqueous environments which protects the metal from rapid corrosion. The Pilling-Bedworth ratio (P-B ratio) is the ratio of the volume of the metal oxide molecule to the volume of the corresponding metal atom (from which the oxide is created). Therefore a P-B ratio close to 1 corresponds with a consistent and dense oxide layer which can efficiently protect metal from further corrosion [49]. The P-B ratio of 1.77 for Mg(OH)₂/Mg indicates a porous oxide film (illustrated in Figure 1.7) under compression which slows down the diffusion process to some extent resulting in a
slower corrosion rate [50]. The composition of oxide layer depends on the chemical species present in the corrosive media [51] and alloying components [52].

![Formation of oxide layer in aqueous corrosion of Mg](image)

**Figure 1.7** Formation of oxide layer in aqueous corrosion of Mg

A natural oxide layer mainly composed of MgO rapidly forms on Mg surface as soon as the clean surface is exposed to air. This oxide form is unstable in aqueous environment and turns into Mg(OH)₂. The natural oxide layer also breaks down in physiological environment, e.g. simulated biological fluid, as a consequence of the chloride ion turning the Mg oxide into the highly soluble MgCl₂ [53,54]. Oxide dissolution at selective locations takes place at chloride concentrations exceeding 30 mmol/L [55]. Preferential oxide dissolution introduces high susceptibility of the Mg to pitting corrosion at its free corrosion potential*, E₉₀₀, in biological environments where the chloride concentration reaches up to 150 mmol/L [56,57]. Pitting corrosion is referred to as the form of corrosion in which corrosion pits (holes) are formed into the metal by highly localized dissolution of metal. Inclusion of alloying components with different free corrosion potentials introduces surface heterogeneity and therefore promotes non-uniformity or localization of corrosion [34]. Alloying compounds such as Al may also contribute into heterogeneous formation of passive oxide layer which further enhances localized corrosion of Mg alloy [58].

Alloying components also govern the micro-structure and mechanical properties of Mg alloys to a large extent. Magnesium and its alloys have the most active potentials

*Free corrosion potential is referred to the open circuit potential of corroding metal as measured by a voltmeter. The metal in open circuit state has no galvanic coupling with another metal nor is polarised by an external source of potential.
of all structural metals in the electromotive force (EMF) series, presented in tables 1.3. It is because of such oxidation activity that magnesium and its alloys are commonly employed as sacrificial anode in designing cathodic protection systems for protecting other metals against corrosion [59].

Table 1.3 Standard reduction potentials [55].

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Reaction</th>
<th>Potential, V</th>
</tr>
</thead>
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<tr>
<td>Li, Li⁺</td>
<td>Li⁺ + e⁻ → Li</td>
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</tr>
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</tr>
<tr>
<td>Na, Na⁺</td>
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</tr>
<tr>
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<td>-2.37</td>
</tr>
<tr>
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<td>-1.71</td>
</tr>
<tr>
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<tr>
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<td>-0.24</td>
</tr>
<tr>
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</tr>
<tr>
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<td>Cu²⁺ + e⁻ → Cu</td>
<td>0.34</td>
</tr>
<tr>
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<td>Ag⁺ + e⁻ → Ag</td>
<td>0.80</td>
</tr>
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Another form of corrosion is caused by hydrogen stress cracking of Mg and is a process in which Mg grains are mechanically detached from the metal lattice by evolving hydrogen and results in fast structural deterioration. It has been shown that most Al containing Mg alloys are not prone to stress corrosion cracking [60] because in almost all Mg-Al alloys, the grain boundary is more cathodic than the grain and anodic dissolution occurs inside individual grains resulting in pitting corrosion [61]. Under mechanical stress, cracks initiate from the corrosion pits which eventually propagates resulting in collapse of the load bearing structure [62]. The principal rate-limiting factors in the aqueous corrosion of magnesium alloys are associated with the breakdown of the surface film and the rate of its reformation [63]. Depending on the composition of Mg alloy, a passive layer may form on the surface in biological environments where more complex chemicals are present [64,65]. These layers may significantly alter the corrosion rate by introducing a diffusion barrier against the corrosive species.
In the field of biomedical engineering, corrosion of biomaterials is of paramount importance as most biomaterials are required to be reliably and permanently functional for the survival of the human beings suffering from acute heart diseases, arthritis, osteoporosis and other joint complications [66]. In addition to structural failure, dissolution of the metallic ions that leaches away from the metallic implants due to corrosion in the human body can cause several serious biological complications such as skin inflammation (due to nickel dissolution), anemia (due to cobalt dissolution), neurological disorders (due to chromium and aluminium dissolution) and cytotoxicity (due to vanadium dissolution) [66]. Exceptions for the cases where permanent implants are not required consist of the arterial stents and orthopaedic scaffolds where only a temporary functional structure is required.

Biodegradable polymers such as poly-L-lactic acid (PLLA), polyglycolic acid (PGA), poly (D,L-lactide/glycolide) copolymer (PDLA) and polycaprolactone (PCL) have been widely investigated for degradable stent fabrication [67]. However, insufficient mechanical strength of polymeric stents to effectively provide scaffolding support have appeared to be a serious drawback [68]. Recently Mg alloys are emerging as a promising alternative material for use in these temporary biomedical implants [69]. A comparative illustration of mechanical properties of PLA polymer, Mg alloy AZ61 and 316L stainless steel is given in Figure 1.8. Mg has a mechanical advantage over other existing biodegradable materials such as polymers, ceramics or bioactive glasses. In the case of orthopaedic implants, Mg alloys present mechanical properties that is closest to that of the bone, unlike the other biodegradable materials that pose a mismatch in mechanical properties between the bone and implant [70].
Studies in this thesis aim at characterizing Mg alloys for stents application, however all technical advancements developed in this thesis are also applicable to both orthopaedic and stent Mg based implants. Final application of Mg implant, i.e. vascular stents or orthopaedic implants, also governs the choice of \textit{in vitro} environment in which the corrosion behaviour is studied. Simulated biological fluid is the recommended environment for testing \textit{in vitro} performance of stents and is used as the test solution throughout this thesis.

\textbf{1.4.1 Bio-absorbable metal stents (BMS)}

Early clinical studies on bioabsorbable metal stents (BMS) have shown good biocompatibility of magnesium in animals [22,23,71,72] and human trials [24,25]. Magnesium as a degradable implant material provides both biocompatibility and suitable mechanical properties in \textit{in vitro} and \textit{in vivo} and it has been shown that Mg is suitable to be used for degradable implants as they exhibit good cell attachment and tissue growth [53,73,74]. Biocompatibility of Mg alloys with certain cells associated with each particular application (bone or blood vessel) to a large extent depends on the corrosion products on the surface of Mg and can be best controlled by careful choice of alloying components [75].

\begin{figure}
\centering
\includegraphics[width=\textwidth]{Figure1.8.png}
\caption{Comparison between mechanical properties of the conventional 316L stainless steel, Mg alloy and PLA polymer.}
\end{figure}
One of the corrosion products of Mg alloys are Mg\(^{2+}\) ions which is an essential element and present in large amounts (the fourth most abundant cation) in the human body [76]. Daily intake of Mg for a normal adult is about 300–400 mg and redundant magnesium cations can be harmlessly and efficiently excreted in the urine [77]. However, rapid corrosion of magnesium produces hydrogen cavities in the alloy which may result in necrosis of tissues or in the extreme situation can interrupt the blood stream and cause death. Also the surface alkalization due to the fast corrosion reaction (reactions 1.2 to 1.4) can introduce inflammatory effects and cause disorder to the pH dependent physiological reactions [52] in the vicinity of the magnesium implant or in the worst case scenario lead to an alkaline poisoning effect [78]. Therefore, it is essential to carefully control the rate of degradation (i.e. corrosion) to avoid extensive hydrogen evolution and alkalization and provide adequate time for arterial remodelling. Therefore, special attention must be given to the alloy design both to avoid toxicity caused by some of the alloying components [75] and also to achieve a slower rate of corrosion [79]. It has been shown that the corrosion rate of Mg alloys may be altered by up to 3 orders of magnitude by inclusion of different alloying elements [80].

### 1.4.2 Effect of biological parameters on Mg corrosion

Implants that function as supporting structures for bone and blood vessels, i.e. bone scaffolds and vascular stents, are usually used under severe cyclic loading conditions, such as tension, compression and bending. It has been found that a material very often fails at a cyclic load well below the threshold to produce failure in the absence of the mechanical stress, which is called fatigue failure [81]. For orthopaedic implants, the ultimate implant failure is usually associated with corrosion fatigue, which is the synergetic effect of electrochemical corrosion and cyclic mechanical loading [82,83]. The fatigue life of Mg alloys has been shown to be mainly related to their alloying elements, micro-structures, surrounding environment and cyclic loading. Studies by Gu et al. [62] on two experimental Mg alloys showed that the corrosion rate increases under cyclic loading compared to that of under the static immersion test. Under the combined conditions of cyclic loading and a corrosive environment, the corrosion cracks initiate from the corrosion pit also
resulting in the release of mechanical stress. Corrosion testing in biological environments involves a complex media containing a wide range of organic and inorganic compounds, with additional complication arising from the relationship between corrosion mechanism and the biological host response. For example degradation processes and corrosion products can induce local inflammation and the products of inflammation can in return enhance the degradation process [84].

One such biological host response is the formation of amorphous calcium phosphate or magnesium calcium apatite (known as hydroxyapatite or \((\text{Ca}_{1-x}\text{Mg}_x)_{10}(\text{PO}_4)_6\text{OH}_2)\) which has been found to be beneficial to cell attachment and cell growth on the surface of Mg implants by providing a bone-like structure [72]. As the bio-corrosion proceeded, the Mg(OH)_2 film on the surface of Mg alloy provides favourable sites for hydroxyapatite nucleation [85,86]. Precipitation of hydroxyapatite film on the surface is catalysed by anodic dissolution of Mg as a result of the alkaline local pH and by consuming the calcium and phosphate ions from the surrounding fluid [87]. Formation of a phosphate layer on Mg surface has also been found to act as a semi-protective layer that reduces corrosion rate [88]. Similar phosphate layers have been found \textit{in vitro} [86] and \textit{in vivo} [89]. The exact composition and morphology of the phosphate layer depends on the alloy composition as well as the solution in which the Mg alloy in immersed. In \textit{in vitro} studies it is critical to choose a suitable pseudo-physiological environment that mimics the target \textit{in vivo} environment best. Several \textit{in vitro} solutions that have been frequently used in the literature are Hanks solution, simulated biological fluid (SBF), cell culture media, phosphate buffered solution (PBS) and Dulbecco’s Modified Eagle’s cell culture medium (DMEM) [90]. These solutions contain different amount of ions, in particular chloride (the most significant to corrosion behaviour), and may also contain added proteins.

In addition to inorganic compounds, biological environments contain organic compounds which may adhere or adsorb to the implant surface and change the corrosion behaviour. For example, studies of the effect of glucosamine sulphate on the corrosion rate of Mg alloys AZ31E and AZ91E in Hanks solution has shown a
reduced rate of corrosion as a result of contribution of glucosamine sulphate in formation of a more resistive oxide film [91]. Glucosamine sulphate is a naturally occurring compound found in the human body and consumed by the body to produce a variety of other chemicals that are involved in building tendons, ligaments, cartilage and the thick fluid that surrounds joints. It is also commonly used as a drug for arthritis.

Albumin as the most abundant blood protein in the range of 3.5-5 g.dl⁻¹ is one of the key components playing a significant role in determining bio-corrosion rate of Mg [92]. The effect of albumin has been found to be greatly dependant on the alloy composition and albumin concentration [93]. Also there have been evidence suggesting that the albumin forms a barrier film on the Mg in the early stages of contact which slows down the corrosion to some extent [64,94]. This film can be destroyed in the long term due to surface alkalization and/or dissolution of corrosion deposits underneath the albumin film. Muler et al. reported a rise in the corrosion rate of Mg alloy LAE442 as a consequence of adding albumin into the PBS. They suggested that the discontinuous protein film does not provide effective protection and also it may hinder the surface passivation by avoiding the pH change near surface [54]. On the contrary, the corrosion inhibitive effect of albumin has been reported on the aluminium containing Mg alloy (AZ91) and Mg-Ca alloy in simulated biological fluid (SBF) [94,95]. It was suggested that the adsorbed layer of protein interacts with aluminium oxide and forms a protective layer which impedes the diffusion of corrosion reactants. It has been also reported that the corrosion rate will be further reduced in vivo after implantation due to adherent proteins and inorganic salts such as calcium phosphates which stabilizes the corrosion layer [89]. It has also been reported that protein can chelate metal ions such as Fe, Ti, Zn, Cr, Ni, Co and Cu and enhance the corrosion rate [96–100]. Effective removal of the protective corrosion deposits and increasing the dissolution rate of metal through chelation a process are suggested as the main mechanisms. A similar mechanism could be responsible for increasing the rate of Mg corrosion in presence of protein. In vitro studies of the effect of living cells on corrosion of AZ91D has shown that living cells form a barrier layer to slow down the corrosion in the early stages,
however the cell adhesion was greatly influenced by near surface alkalization in the long term resulting in cells death and detachment [101]. It was shown that cell death was followed by break down of the barrier layer resulting in an increased corrosion rate.

The somewhat controversial reports on the effect of protein on bio-corrosion of Mg inspired the work described in Chapter 4 in this thesis. Bovine serum albumin was added in SBF to investigate the effect of protein on corrosion behaviour of AZ31. A range of analytical and electrochemical methods are used to elucidate the mechanism in which albumin affects bio-corrosion of Mg.

### 1.5 Effect of structural heterogeneity

According to what the EMF series (Table 1.3) suggests, Mg is anodic when galvanically coupled to any other structural metals and therefore Mg is specifically susceptible to galvanic corrosion. Figures 1.9a and b show the macro-galvanic and micro-galvanic models, respectively, of the galvanic corrosion cells forming when Mg is coupled with other metals.

![Figure 1.9](image)

**Figure 1.9** (a) Macro-galvanic corrosion and (b) micro-galvanic corrosion cells forming on magnesium and alloys as a result of difference in corrosion potential with other metals [102]. α and β phases are the Mg rich matrix and intermetallic phases,
respectively, and I is the local corrosion current flowing from anodic areas to cathodic areas.

Refining the microstructure of Mg alloys has a drastic influence on the corrosion behaviour of Mg and in particular localised corrosion. Therefore, currently a major focus in manufacturing advanced Mg alloys is to reduce the size of metallic particles in the alloy structure with the aim to reduce the corrosion rate and achieve uniform corrosion characteristics. Alloying elements are primarily added to Mg in order to achieve the mechanical characteristics required in a specific application despite their potential role in formation of the micro-galvanic corrosion cells. Figure 1.10 shows the effects of 14 elements on the corrosion performance of Mg in binary alloys in 3% NaCl solution.

![Figure 1.10](image)

**Figure 1.10** Effect of alloying metals on the corrosion rate of Mg alloys in 3% NaCl solution [103]. The alloying metals (i.e. Cu, Fe, Ni, Co, Na etc) were added in different concentrations to Mg to produce binary Mg alloys.

Many elements such as aluminium, manganese, sodium, silicon, tin, and lead (included in Figure 1.10) as well as thorium, zirconium, beryllium, cerium, praseodymium, and yttrium [104], have little deleterious effect on the corrosion
performance of pure magnesium when present at levels exceeding their solid solubility. This threshold is important because beyond this threshold intermetallic particles of these secondary elements will begin to form within the alloy structure and facilitate micro-galvanic corrosion cells formation. In other words, thorium, zirconium, beryllium, cerium, praseodymium, and yttrium do not act as effective cathodic sites to accelerate micro-galvanic corrosion. Four elements in Figure 1.10, namely cadmium, zinc, calcium, and silver, have mild-to-moderate accelerating effects on corrosion rates, whereas iron, nickel, copper, and cobalt that have extreme deleterious effects because of their low solid-solubility limits and their ability to serve as effective cathodic sites for the reduction of water and formation of active micro-galvanic corrosion cells.

1.6 Ways of protecting Mg against corrosion

Proper reduction of the corrosion rate decreases the release of corrosion products and surface alkalization and provides a more stable interface for cell growth, leading to improved cytocompatibility of Mg alloy [105]. Any discussion which considers the prevention of aqueous metallic corrosion usually takes as its starting point the electrochemical model of the corrosion of metal with the four important processes involved linked in series namely; the anodic reaction, the cathodic reaction and the conductive pathways for ions and electrons [106]. Inhibition of the anodic or cathodic reactions or an interruption of the ionic flow are the three key elements that could cause a significant reduction of the corrosion rate [107]. Thus, all corrosion prevention measures are aimed at removing or suppressing one of these three. There are, in general, three strategies for providing corrosion protection to a given metal. These strategies are cathodic protection, corrosion inhibitors and protective coatings. The first approach, cathodic protection, would be impractical for protection of Mg and its alloys because of the very active potential that renders Mg anodic to all other structural metals. Corrosion inhibitors are often added into the surrounding environment to form and maintain a passive layer on the surface of active metal. This approach would also be impractical for biomedical applications of Mg, however, inhibitors can be incorporated into a secondary matrix, e.g. polymer film,
to support a consistent supply of the inhibitor and maintain the surface passivation. Polymer films can also be used (without inhibitors) as protective coatings to insulate Mg from corrosive media and reduce corrosion rate.

1.6.1 Alloy engineering

Corrosion behaviour of a base metallic alloy can be adjusted, to a large extent, by an appropriate alloy design (as discussed above). The corrosion behaviour of Mg alloys is greatly dominated by alloying composition and its microstructure [108]. The atomic diameter of magnesium is 0.320 nm, so there is a favourable size factor facilitating the blending of Mg with a diverse range of the solute elements such as aluminum (Al), zinc (Zn), cerium (Ce), yttrium (Y), silver (Ag), zirconium (Zr), and thorium (Th). Kirkland et al. reported over three orders of magnitude variation in corrosion rate as a result of alloying with elements such as Al, Zn, Ca, Ce, La, Nd and Y in MEM physiological fluid [80]. A study of the effect of 14 elements on the saltwater corrosion performance of magnesium in binary alloys showed the following trends:

- aluminium, manganese, silicon, tin, lead, thorium, zirconium and cerium had little or no deleterious effect on the basic saltwater corrosion performance of magnesium at levels either up to and exceeding their limits of solubility in magnesium or up to a maximum of 5% Wt/wt.
- Cadmium, zinc, calcium and silver had mild-to-moderate accelerating effects on corrosion rates
- whereas iron, cobalt, nickel and copper had extremely deleterious effects on saltwater corrosion.

The deleterious effect these latter elements on the corrosion properties of Mg is a function of the basic alloy composition and the composition of the corroding medium [18]. Tunold et al.[56] found that the corrosion of commercially pure Mg was usually via transgranular fracture (alongside the grain boundaries), while the corrosion of Mg alloys was more uniform. Similarly, Makar and Kruger [109] reported that the corrosion of pure magnesium was non-uniform, giving an etched appearance, but AZ61 was relatively uniformly attacked, and alloys formed through
rapidly solidification were attacked more uniformly than conventional alloys. This was attributed to the formation of refined metallic particle size due to rapid solidification process. The mechanism in which the alloying components accelerate or impede corrosion is believed to be based on providing stable cathodic sites (thus accelerated galvanic corrosion) and formation of passive surface layers composed by inert oxide forms of the alloying elements, respectively. The former is similar to the influence of the presence of metals such as copper, nickel, and iron in solution where a severe corrosion of magnesium alloys may occur due to the deposition of salts on the surface and formation of active cathodic sites on the anodic magnesium alloy surface. It was shown that Al enrichment of the oxide layer in aqueous corrosion of AZ91 plays a key role in reducing the corrosion intensity [110].

Dissolved ions from metal implants are always a concern due to the possibility of inducing hypersensitivity and/or allergies in an in vivo situation. Mg alloys AZ31, AZ91, WE43 and LAE442 have been shown to be non-allergenic in an epicutaneous patch test* [111]. Moreover, high extracellular Mg concentrations have been found beneficial for cartilage tissue engineering [112]. Animal trials with a range of Mg alloys elucidated that addition of rare earth elements, e.g. cerium, praseodymium and lanthanum, increases the biocompatibility of Mg alloy, reduces corrosion rate and enhances homogeneous degradation, therefore resulting in healthier tissue regeneration and better toleration of the Mg implant [113].

1.6.2 Surface modification

Controlling the corrosion rate of an Mg alloys can also be achieved through modifying the alloy surface chemistry. This approach provides some level of control over the surface electrochemical reactions and therefore bio-corrosion of Mg. While the mechanical properties of an Mg implant are mainly governed by the bulk properties of the material, the biological responses depend on the surface characteristics [114–116]. Surface properties play a major role in determining both the biological response to implants and the material response to the physiological

* A clinical method of defining allergic inflammation response of skin occurred due to contact with a substance.
condition. Surface modification for biomedical Mg alloys is aimed to impart biocompatibility and corrosion resistance and can be performed by several methods such as chemical and electrodeposited conversion coatings, thermal treatment, organic coatings as well as physiological and biomimetic surface treatments.

1.6.2.1 Hard coatings (i.e. anodizing and conversion layers)

The method of anodizing (by galvanic or applied current) results in the formation of a hard, abrasion and corrosion-resistant surface layer which has been shown to provide corrosion protection. The anodized films are porous and in order to mask this porosity the films may be further modified by immersion in an appropriate solution, such as organic resins (i.e., epoxy). Due to the limited biocompatibility of the elements used in anodized hard coatings, these surface treatments have not found considerable application in biomedical Mg corrosion protection.

An alternative cost-effective method to assist in the corrosion protection of Mg and its alloys is through the formation of chemical conversion coatings. These chemical treatments form an inert surface film that results in improving the corrosion resistance. Conversion coatings based on chromate (VI) have been used for many years as one of the most effective corrosion inhibitors for the protection of Mg alloys [117]. However the hexavalent chromium is highly toxic [118,119], and thus an extensive effort in the past decade has gone into developing new classes of conversion coating in order to replace the toxic but very effective chromate conversion coatings. Consequently a wide range of “green” conversion coatings have been developed to satisfy specific requirements in a variety of Mg end-use applications. In general, it has been postulated that factors such as film thickness, defectiveness, adherence to the substrate and resistance to the chemical attack in solution play major roles in the corrosion protection afforded by the conversion coatings [120]. A conversion layer consisting of MgF₂ formed on Mg alloys by pretreatment in hydrofluoric acid was shown to significantly reduce the corrosion resistance in cell culture medium [121] and Hanks solution [122]. Calcium phosphate conversion coating was also found to significantly improve corrosion resistance with a direct relationship between corrosion resistance and the thickness
of conversion layer [123]. However a discontinuous layer of calcium phosphate, formed by inappropriate treatment, was found to be detrimental to protection due to the cracks producing corrosion initiation sites [124].

Robustness and biocompatibility of rare earth based conversion coatings such as Pr and Ce based conversion coatings encouraged the research presented in the Chapter 5 of this thesis. Here conversion coatings of rare earth compounds were formed on the surface of Mg alloy in a robust chemical process that allows for easy adjustment of coating properties such as thickness. Chapter 5 also outlines a study on protective performance of rare earth compounds when used as corrosion inhibitor dissolved in the surrounding media.

1.6.2.2 Organic coatings

The simplest way of protecting Mg against corrosion is to coat it’s surface with an insulating organic coating to prevent contact with the corrosive environment [125]. Organic coatings are extremely versatile particularly in terms of the method of application and the level of corrosion protection. Provided an appropriate surface pre-treatment method is developed to encourage interfacial bonding between the alloy and organic coating they afford effective corrosion protection [126]. It is firmly acknowledged that all polymeric coatings are relatively permeable to water and oxygen and corrosion protection is normally afforded by isolation of metal from corrosive ions of the surrounding media [127]. Effective protection facilitated by barrier mechanism requires that coatings impede the ionic conduction and remain adherent to the substrate in the presence of water and the metallic corrosion products [127,128]. Biocompatible coatings that can delay the onset of corrosion would ensure that the mechanical integrity of the implant remains intact in the early stages of healing. The effect of protecting Mg surface with poly(L-lactic acid) (PLA) and poly(desaminotyrosyl tyrosine hexyl carbonate) [poly (DTH carbonate)] (an amino acid based biocompatible polycarbonate polymer) has been studied by Gray-Munro et al. [129]. Their results indicate approximately an order of magnitude reduction in corrosion rate of AZ31 in the long term when protected by these organic coatings.
Also an improved cell attachment and cell growth on poly(lactide-co-glycolide) (PLGA) coated Mg-6Zn alloy was reported by Li et al. [130].

1.6.2.3 Effect of surface pre-treatment

Surface preparation of metal prior to application of organic coating is a crucial step to achieve efficient interaction between protective coating and the metal surface [126,131]. Metal surfaces can be prepared by mechanical, electrochemical [132] or chemical methods to obtain effective adhesion of the organic coating on metal surface. Surface pre-treatment improves the interfacial bonding by strengthening the electrostatic bonds (Van der waals) as well as the mechanical interlocking between the coating and substrate irregularities [133]. In most cases coating detachment starts from the edges of corroding area where the alkali, generated by cathodic reaction, hydrolysis the polymeric bonds. It is noteworthy that although the surface activation promotes electrostatic bonds it also produces higher affinity for polar water molecules to penetrate and breakdown the interfacial bonding between the metal and the coating.

An effective surface pre-treatment removes the impurities and secondary phase elements from the alloy and leaves a passive surface layer that enhances interfacial bonding with the subsequent polymer coating [134]. For example, surface modification with calcium phosphate or etching with 90% (v/v) phosphoric acid was shown to significantly reduce the corrosion rate [129]. Such passive substrates can serve as an effective platform for the subsequent organic coating film. Also pre-treatment by silane coupling agents was found to improve the adherence and homogeneity of adsorbed layer of albumin and significantly reduce the corrosion rate [135]. Studying the protective action of silane compounds as a pre-treatment layer for subsequent organic coating [136] and as a free standing layer [137] have revealed significant protection enhancement. Adhesion improvement and barrier action of a silane layer against ionic conduction are suggested as the main protective mechanisms. Silane layers have been also investigated as single protective layers for inhibition of Mg corrosion [138].
1.6.2.4 Conducting organic coatings

Conducting polymers are a unique group of organic polymer capable of electronic, chemical and/or electrochemical interaction with active metals. The mechanisms in which the conducting polymers protect active metal from corrosion is not fully understood, however a number of mechanisms have been proposed [139]. Altering the corrosion potential, creating a diffusion limiting electro-magnetic field, barrier protection and gradual release of dopant* to act as corrosion inhibitor are the main suggested mechanisms [140,141]. Tallman et al. showed the protection of aluminium may be afforded only by galvanic coupling of polypyrrole [142]. The significant role of polypyrrole (PPy) in growth of an adhered stable oxide layer was also suggested elsewhere [143]. Turhan et al. suggested that the release of dopant ions from PPy is the dominant mechanism of protection of AZ91D alloy [144]. Further surface modification of PPy with a biomimetic albumin monolayer was found to significantly improve the corrosion resistance. Corrosion protection was also enhanced by incorporation of PPy micro-sized particles in an acrylic matrix [145]. Changing the redox state of Mg and catalytic action of PPy was suggested as the protection mechanism afforded by the PPy particles. Also pigmentation of acrylic coating with polyaniline phosphate was shown to remarkably increase the protection afforded to Mg alloy ZM21 [146]. In contrast, Song et al. reported increased corrosion of Mg when coated with Nafion/PPy films [147]. It has been suggested that the electronic conductivity of these coatings and the electrical contact between the coating and the area of metal to be protected plays a major role in protection afforded by conducting polymer coating [139]. Therefore incorporation of a discontinuous phase of conducting polymer into insulating polymeric films, such as acrylic, may reduce the corrosion protection afforded by conducting polymers.

The unique advantage of conducting polymers in biomedical applications lies within the biocompatibility of these materials [148]. However, the controversial results

* Dopants are the chemicals added to the base polymer with opposite charge to the monomeric unit to assist the polymer growth and also in most organic conducting polymers dopant imparts the conductive characteristic.
reporting acceleration of Mg corrosion with conducting polymer coatings [147] may have prevented these materials from being developed further as corrosion protection coatings. In theory, a stable conducting surface coupled with Mg can provide an effective cathodic surface that facilitates cathodic reactions and increases the corrosion rate. Also the entire class of conducting polymers reported in the literature for the purpose of protecting Mg against corrosion are non-degradable. In biomedical applications of Mg, i.e. cardiovascular stents and orthopaedic bone fixation implants, the ultimate goal must be the complete degradation of the implant which cannot be achieved with non-degrading conducting polymers.

1.6.2.5 Smart multi-functional coatings

Organic coatings afford effective protection of the underlying substrate against corrosion as long as the coating provides a flawless barrier against diffusion of aggressive ionic species. In applications such as arterial stenting, the extensive deformation of the metal stent during angioplasty surgery (illustrated in Figure 1.11) induces cracks and structural defects to the organic coating. These defective areas provide ionic pathways towards the underlying substrate where the corrosion is initiated.
Figure 1.11 Structural deformation of cardiovascular stents during balloon angioplasty surgery [149].

Figure 1.12 illustrates how localized corrosion initiated from the defective areas of the coating may cause premature recoil of the stent and drastically reduces its service life [149]. Inset images (i) and (ii) represent schematic models for a stent with localized and uniform corrosion attacks, respectively. It is therefore crucial to implement a strategy to protect the metal at defective areas of the coating as uniformly as those areas protected by the intact coating.

Figure 1.12 Early recoil of the stent caused by localized (pitting) corrosion [149].

A solution to this problem is the addition of corrosion inhibitors which protect the damage zones through the so-called “self-healing” effect through the formation of another protective layer [150]. The self-healing effect is generally defined as the ability of a coating to recover after mechanical damage and effectively continue protecting the underlying substrate. In most cases this is achieved by replenishing the
damaged area with reactive chemicals being stored in the coating layer. However in anticorrosive coatings the recovery of coating integrity is not obligatory as long as the metallic substrate is kept under protection [151].

A self-healing coating may be loaded with corrosion inhibitors such as cerium compounds to be release to the defected areas and passivate the uncoated metal surface [152,153]. It has been suggested that cerium participates in the formation of insoluble oxide/hydroxide compounds that effectively blocks ionic pathways [154] and passivates the active dissolution sites [155]. Montemor and Ferreira [155] reported about an order of magnitude improvement in corrosion resistance of silane coating when it is loaded with cerium nitrate. Zheludkevich et al. reported a biodegradable self-healing protective coating based on a chitosan layer loaded with cerium nitrate [152,153]. The protective action of this coating on an aluminum substrate was studied in dilute NaCl solution. Their results revealed self-healing characteristics of coating due to the controlled release of cerium. The efficiency of corrosion inhibitors in preventing near surface alkalization of AZ31 was studied by Karavai et al. using scanning probe techniques, i.e. SVET & SIET [156]. Their results revealed that the increase of pH in defective areas of the coating can be effectively prevented with corrosion inhibitors such as Ce\(^{3+}\), F\(^-\) and 1,2,4-triazole.

Eventually the challenge remains to design a biocompatible Mg alloy with slow corrosion characteristics and a temporary corrosion protection mechanism. Meanwhile it should be kept in mind that the temporary implant needs to degrade completely, otherwise parts of it may remain and create long-term complications. The work described in Chapter 5 of this thesis tried to address this issue by combining the advantages received from rare-earth conversion coatings with robustness of organic coatings. PLGA and a novel polythiophene based coating with proven biodegradable and biocompatible characteristics are investigated.
1.7 Methods of corrosion monitoring

A firm understanding of the corrosion mechanism and the effective measurement of its rate is critical to the successful development and implementation of biodegradable Mg-based biomaterials. Corrosion of metal, as described above, is an electrochemical process involving anodic and cathodic reactions that leads to oxidation and deterioration of metallic structure. Electrochemical techniques will be the main tools used throughout this Thesis to characterize the corrosion process of Mg alloy and measure the efficiency of protection strategies employed. A range of electrochemical techniques will be used to look at both the local and global corrosion behaviour of Mg alloys. Also a range of analytical techniques will be utilized to study the chemistry of corrosion products and mechanism of protection afforded by organic coatings.

1.7.1 Open circuit potential (OCP)

When cathodic and anodic reactions occur on a metal surface, individual potentials corresponding to each reaction cannot be measured. In this situation a polyelectrode or mixed electrode forms with an electrolytic potential between cathodic and anodic reversible potentials. This mixed potential is so called open circuit potential (OCP) (also known as rest corrosion potential) at which the total rate of oxidation is equal to the total rate of reduction [157,158]. The corrosion potential measured at an open electric circuit (OCP) is used as a thermodynamic measure of corrosion process on a metal surface. The corrosion potential is measured in comparison with a reference electrode such as calomel, silver/silver chloride or copper/copper sulphate electrodes. Equation 1.7 [159] explains how the change in anodic/cathodic area alters the corrosion potential.

\[ f_a \neq 0 \text{ or } 1 : E_{corr} = E_{0.5} - \left[ \frac{1}{\beta_a} + \frac{1}{|\beta_c|} \right] \log \frac{f_a}{f_c} \]  \hspace{1cm} (1.7)
where \( f_a \) and \( f_c \) are the fractions of anodic and cathodic area respectively so that \( f_a + f_c = 1 \). \( \beta_a \) and \( \beta_c \) are the anodic and cathodic slopes* and \( E_{0.5} \) represents the corrosion potential when anodic and cathodic area are equal (\( f_a = f_c = 0.5 \)). According to this equation a rise in the ratio of anodic/cathodic area results in decreasing the OCP and vice versa. In practice cathodic reactions generally take place at the stable areas and anodic areas are the sites at which active dissolution of metal or corrosion occurs. Therefore an increasing OCP value is considered as spreading the passivation and confinement of dissolution sites. In contrast, breakdown of oxide layer in neutral or acidic solutions provides a larger number of anodic sites thus reduction of the OCP value occurs. It should be noted that while OCP is a reliable measure of corrosion thermodynamic it does not necessarily correspond with corrosion kinetic of metal [158,160].

### 1.7.2 Potentiodynamic polarization (PDP) and linear polarization resistance (LPR)

Potentiodynamic polarization technique is a unique electrochemical technique often used for measuring the instantaneous corrosion rate of metals. Other methods of measuring corrosion rates such as sample weight loss and hydrogen gas collection may be used to measure the cumulative corrosion rate. The corrosion current is the sum of current flowing between cathodic and anodic area when sample is at OCP hence OCP is also known as \( E_{corr} \). Corrosion current cannot be directly measured because at OCP all electrons produced in the anodic process are consumed in the cathodic process, and therefore no net current flows from the system that can be directly measured. However, the corrosion current can be determined by polarizing the natural corrosion potential of a sample via applying a cathodic potential and gradually increasing it towards anodic values. For the purpose of measuring corrosion current a polarising potential in the range of \( \pm 250 \) mV (relative to OCP) is usually applied after measuring OCP in a two electrode arrangement against a reference electrode [160]. Potentiodynamic polarisation is performed in a three

* \( \beta_a \) and \( \beta_c \) are calculated from linear parts of anodic and cathodic branches on polarisation curves. Further detail is given in section 1.5.2.
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A typical polarisation curve for Mg corrosion with anodic dissolution of Mg as sole anodic reaction and hydrogen evolution as the sole cathodic reaction is shown in Figure 1.13. Using the linear parts (red dashed lines) of the cathodic and anodic curves (Tafel slopes), the corrosion current ($I_{corr}$) can be calculated as the current density at which cathodic and anodic branches intercept at $E_{corr}$. Also anodic and cathodic reactions and the rate controlling mechanism of corrosion (diffusion or activation) can be studied using anodic and cathodic Tafel constants [161–163].

![Figure 1.13](image-url) Calculating the corrosion rate, $I_{corr}$, of Mg from an experimental polarization curve (black solid line) using the Tafel slopes (red dashed lines) and extrapolation towards $E_{corr}$.

It should be noted that polarization is a destructive electrochemical technique since it intensifies the driving force for corrosion reactions by providing extra electrons for anodic reaction (anodic polarization relative to OCP) or accelerating cathodic reactions by demanding more electrons (cathodic polarization relative to OCP). By studying the corrosion current flow at potentials more positive and negative to OCP, active-passive behaviour, corrosion resistance and anodic-cathodic reactions can be
studied [160]. The Stern and Geary equation (equation 1.8) [164] defines the inverse correlation between corrosion current, \(i_{\text{corr}}\), and polarization resistance, \(R_p\):

\[
i_{\text{corr}} = \frac{B}{R_p}
\]  

(1.8)

The proportionality constant \(B\) (mV) is called Stern–Geary constant and depends on the type of the metal and environment. For a given anodic and cathodic Tafel constants, \(\beta_a\) and \(\beta_c\) respectively, \(B\) can be calculated according equation 1.9:

\[
B = \frac{1}{2.3R_p} \left( \frac{\beta_a \beta_c}{\beta_a + \beta_c} \right)
\]  

(1.9)

1.7.3 *Electrochemical impedance spectroscopy (EIS)*

EIS studies the detailed response of an electrochemical system to an applied sinusoidal AC signal. Measurements are carried out over a range of AC frequencies with small amplitude of polarizing potential (e.g. \(\pm 10\) mV) around the OCP in order to minimize destructive impact of the externally applied potential. Analysis of the system response provides detailed information about individual electrochemical components of the system that can impede the current flow generated from AC potential perturbation. This applies to electrochemical processes at the metal-electrolyte interface, oxide layer and corrosion products, barrier layers (e.g. organic coatings) and electrolyte resistance. Each of these elements affects the alternating current at a certain frequency range and so can be characterized separately. The corroding system can be then simulated with an electrical equivalent circuit (EEC) where each electrical element of circuit represents a part in the actual electrochemical process. Capacitance and resistance are the two typical electrical elements used to simulated electrochemical features. Similar to an electrical capacitor, insulating characteristic of polymer coatings creates a capacitor in which the coating capacitance value is given by equation 1.10:

\[
C_c = \frac{\varepsilon \varepsilon_0 A}{d}
\]  

(1.10)
Where, ε is the dielectric constant of the coating, ε₀ is the dielectric constant of vacuum, A is the area of the coating and d is the coating thickness. This capacitive aspect of organic coatings introduces a time lag and a measurable phase shift to the applied AC signal in a discrete frequency range different from those frequencies affected by the electrical double layer (EDL). Figure 1.14 shows the phase shift due to the AC current passing through an insulator.

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![Figure 1.14](image.png)

**Figure 1.14** Current phase shift caused by a capacitor.

Change in capacitance value of organic coating is typically connected with water-uptake which increases its dielectric constant, while change in capacitance value of electrical double layer (EDL)\(^*\) is normally a result of chemical change in composition of EDL at metal-electrolyte interface and/or change in thickness of diffusion layer [165,166]. Typical dielectric constants of coatings are in the range 3-4 and of water around 80. When water penetrates a coating, its dielectric constant increases, resulting in an increased coating capacitance. Hence, the capacitance value of coating (\(C_C\)) can be used to measure the water absorbed by the coating. EIS has been extensively used in literature to study the corrosion behaviour of Mg alloys and mechanisms associated with its degradation in biological environments [74,101,167–169].

\* An electrical double layer exists at the electrode/electrolyte interface. This double layer is formed as ions with the opposite charge to that of substrate accumulate at the electrode surface. This charge separation forms a capacitor at the interface with a value dependent on electrode potential, temperature, ionic concentrations, types of ions, oxide layers, electrode roughness and impurity adsorption.
With aid of accurate EIS analysis programs and sensitive AC response analysers, detailed information on the permeability of coatings, delaminated areas and delamination rate, the formation and density of the oxide film beneath the coating and diffusion mechanism can be studied [170,171]. Precise selection of equivalent electrical circuit to simulate the actual elements of electrochemical system and fit the experimental spectrum is the essential key to effective data analysis [172]. The amount of water up-taken by coating is an important parameter that can be determined by EIS using the capacitance element of coating extracted from EIS data [173–176]. EIS is uniquely capable of determining the extent of coating disbondment from a metal substrate by breaking up a complex electrochemical system to individual elements [177].

1.7.4 Scanning Electrochemical Microscopy (SECM)

Scanning electrochemical microscopy (SECM) uses an ultra-micro-electrode (UME) as sensing probe to collect electrochemical information. The UME is rastered above the surface within a close range, e.g. 5-10 µm, and probe reading is recorded as a function of probe location which results is construction of a three dimensional map. The probe may read electrochemical current, potential or AC components which defines the operation mode of SECM. Despite the unique capabilities of SECM as a characterization method for corroding metal surfaces, there have been limited reports of its application for characterizing Mg corrosion in recent years [178–180].

A major focus of this PhD is to develop and adjust this powerful technique for studying localized corrosion of Mg. As described earlier, intense localized corrosion of Mg in biomedical applications such as stent causes premature recoil of the stents and loss of load bearing characteristics much quicker compare to a uniform corrosion attack [149]. This exemplifies the necessity of studying localization during corrosion of Mg which has only been practiced so far by other scanning techniques such as scanning vibrating electrode technique, scanning kelvin probe and localized EIS.

The primary aim of this PhD is to introduce a implement powerful capabilities of SECM to attain detailed information about the corrosion behaviour of Mg. Chapters
2 and 3 of this thesis describe the work that has been undertaken to develop SECM as an assessment tool for Mg corrosion in a buffered media. SECM in four modes of operation, namely feedback, generation/collection, AC and potentiometry, is utilized to acquire in-depth mechanistic information during corrosion of Mg.
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Using SECM for studying corrosion of Mg in SBF

(feedback, AC and potentiometric modes)
2.1 Background

Scanning electrochemical microscopy (SECM) (this abbreviation is also used for the device) is a follow-up development by Prof. Alan J. Bard at University of Texas in 1989 after the Nobel Prize winning invention, Scanning Tunneling Microscopy (STM). His experiments using an Electrochemical Scanning Tunneling Microscope (ESTM) demonstrated current at large probe-to-sample distances that was inconsistent with electron tunneling range [1]. This phenomenon was attributed to Faradaic current, compelling a more thorough electrochemical analysis which established the basis of SECM. SECM involves the measurement of an electrochemical parameter (e.g. current) through an ultra-micro-electrode (UME) (an electrode with a radius in the order of a few nm to 25 µm) when it is held or moved in a solution in the vicinity of a substrate. The local probe in SECM is often called a “tip”, although in most cases disk-shaped UMEs are used. Substrates, which can be solid surfaces of different types or liquids, perturb the electrochemical response of the tip, and this perturbation provides information about the nature and properties of the substrate [2]. SECM has several advantages over other scanning based characterization techniques such as STM and AFM. While STM can image with astounding resolution, and in ideal cases atoms can be “seen”, it cannot be used with insulating substrates, and it does not yield information about the chemical nature of a surface. While other scanning microscopes, such as the atomic force and the ion-conductance microscopes, can image insulators, they are not “chemically sensitive”. In SECM the substrate and the tip are part of an electrochemical cell that also contains reference and auxiliary electrodes and the imaging process depends on the interaction of the substrate with a species electro-generated at the tip [3].

In the field of biodegradable metal implants it is particularly important to study the degradation or bio-corrosion behaviour because the metal structure loses its mechanical integrity and load bearing characteristics much quicker when the corrosion is highly localized compared to a uniformly corroding structure [4]. The significance of localized corrosion has been addressed in more detail in section 1.4 in chapter 1 of this thesis. Scanning techniques are essential tools for examining the localized corrosion behaviour or the protection afforded by an anti-corrosion coating.
at a defective area of coatings [5]. Local corrosion behaviour of Mg alloys has been studied using scanning techniques such as localized EIS [6–8], scanning vibrating electrode technique [9,10] and scanning Kelvin probe [11,12]. Among the methods used to enable local detection of microscopic processes, SECM has the unique capability to recognise active/passive regions and allows for surface characterization with a resolution in the micrometre range or below [13]. SECM has shown great promise as an effective tool for studying localized degradation in a coated metal [14–16] and evaluating the self-repairing properties of coatings [17]. Using this technique, one can not only acquire microscopy data on distribution of active species at the surface affected by corrosion but also measure local differences in electrochemical reactivity. For example the release of metal ions at anodic sites and the consumption of oxygen at cathodic sites can be monitored as direct measure of corrosion kinetic.

In SECM, electrochemical data may be collected in three main modes namely amperometric, potentiometric and AC modes. Two distinctive modes of SECM data collection, namely feedback and generation/collection modes, are possible when current (amperometric) is measured as the tip function. SECM when operated in feedback mode utilizes an electron mediator whilst in surface generation/tip collection (SG/TC) mode no mediator is required. The feedback and potentiometric modes have been used previously to study the passive layers [18,19] and organic films on metal [20–23] as well as defects and pitting [24–26] and sensing local pH on a corroding metal surface [27,28]. The recently introduced AC mode (AC-SECM) has been proven to be useful for studying the insulating/conducting domains as well as ionic activity of electrolyte near a corroding metal surface [29–31]. In AC-SECM, the AC signal is most responsive to the changes in solution resistance at high frequencies, while at lower frequencies the capacitive/resistive behaviour of the surface and the electrical double layer make the major contributions to the impedance [29,32].

Despite the proven usefulness of SECM in studying corrosion behaviour of metals, a survey of the literature returns a limited number of published studies on
characterizing Mg alloys surface using SECM*. Also, despite the advancements in understanding the corrosion behaviour of Mg and its alloys in simple chloride containing media, there is still essential need for better understanding of corrosion mechanism in physiological buffered environments [33]. The primary aim of this thesis is to develop and utilize SECM for characterizing the local corrosion processes, in real time, on the surface of Mg alloys in SBF. The work presented in this chapter covers the implementation of feedback, AC and potentiometric modes of SECM for studying active/passive domains on the surface of Mg as well as capacitive behaviour and local pH. Chapter 3 of this thesis is dedicated to generation/collection mode of SECM where a novel and unique method of measuring local corrosion of Mg is introduced and calibrated. SECM in these robust modes of operation will be the main characterization method used in the next chapters for studying corrosion behaviour and performance of protective layers on Mg surface.

2.2 Experimental

2.2.1 Materials and sample preparation

Simulated biological fluid (SBF) was prepared using analytical grade reagents (from Sigma) consisting of 5.403 g/l NaCl, 0.504 g/l NaHCO₃, 0.426 g/l NaCO₃, 0.225 g/l KCl, 0.230 g/l K₂HPO₄·3H₂O, 0.311 g/l MgCl₂.6H₂O, 0.8 g/l NaOH, 0.293 g/l CaCl₂, 0.072 g/l Na₂SO₄ and 17.892 g/l HEPES (4-(2-Hydroxyethyl)piperazine-1-ethanesulfonic acid or C₈H₁₈N₂O₄S) as buffer agent. The pH was adjusted to 7.40 ± 0.05 using 1 M NaOH solution. This SBF recipe was recommended by Boston Scientific, the industrial partner and financial supporter of this research.

Ferrocenemethanol (FcMeOH) with chemical formula C₁₁H₁₂FeO, Hydroquinone (HQ) with chemical formula C₆H₄(OH)₂, Potassium ferrocyanide with chemical formula K₄[Fe(CN)₆], Potassium ferricyanide with chemical formula K₃[Fe(CN)₆], Iodine/Potassium iodide with chemical formula I₂/KI (or 3I⁻/I₃⁻), Ruthenium

* At the time of commencing this PhD study in May 2011, no previously published study was found on application of SECM to Mg surfaces.
hexammine trichloride (Ruhex) with chemical formula Ru(NH$_3$)$_6$Cl were analytical grades purchased from Sigma and were used as redox mediators in this study.

Mg alloy AZ31 (3% Al, 1% Zn and 0.3% Mn, and the balance Mg all in Wt%) was purchased from Goodfellow in the form of sheet with 0.5 mm thickness. Mg coupons were abraded successively using 600, 1200 and 4000 grit emery and cleaned with isopropanol before exposure to electrolyte.

2.2.2 Instrumentation

Scanning electrochemical microscopy (SECM) was performed using CH Instruments SECM model 920D utilizing CHI integrated software version 12.26. 10µm and 25 µm diameter disk Pt UMEs, purchased from CH Instruments Inc., were used as SECM probe (also known as tip or working electrodes). Pt mesh and Ag/AgCl were used as auxiliary (counter) electrode (AE) and reference electrode (RE), respectively. A three dimensional SECM image in constant height mode can be obtained by scanning the tip in the x-y plane and recording the tip function against tip location [2]. Depending on the operation mode of SECM, the tip function can be current (in feedback and generation/collection modes), AC components (AC mode) and potential (potentiometric mode). The optimised (resolution vs. noise) signal was acquired using the 10µm UME in amperometric modes and 25µm UME in AC mode. AC mode scan was performed at a single frequency based on the response of surface to different applied frequencies as measured by AC mode approach curves. Further detail on the choice of frequency and significance of response at each frequency is given in section 2.4 of this chapter. Figure 2.1 demonstrates a schematic representation of SECM set-up used in this study.
Figure 2.1 Schematic representation of SECM set-up with Mg sample as substrate and Pt UME as working electrode (WE). In this study Pt mesh was used as counter electrode (CE) and Ag.AgCl was used as reference electrode (RE).

Adjusting the distance between tip and substrate for SECM imaging is often done by performing several approach curve measurements which consists of measuring tip function while the tip approaches the substrate. The Z coordinate of the substrate is detected as the tip location in which the tip function (e.g. current) shows a sharp change with the change of Z. However, in the case of Mg corrosion in a corrosive media such as SBF, vigorous H$_2$ evolution in the form of H$_2$ bubbles does not allow a stable approach curve to be measured. An example of the H$_2$ evolution on the surface of Mg alloy AZ80X after 10 sec, 2 min and 10 min immersion in SBF is shown in Figure 2.2. To overcome this problem, throughout this thesis a digital microscope was assembled on the SECM set up for the precise adjustment of tip distance over substrate. The distance between tip and substrate was generally adjusted to 5µm (unless otherwise stated) using a zoom digital microscope,
manufactured by MEIJI Techno model MS50. The area of surface not being examined was always masked with tape to eliminate interference.

All experiments were performed at room temperature, ca. 22 °C.

![Figure 2.2](image)

**Figure 2.2** (a) Mg alloy AZ80X before immersion in SBF and (b), (c) and (d) H₂ evolution on the surface of Mg alloy AZ80X after 10 sec, 2 min and 10 min immersion in SBF, respectively. The surface was ground successively with 240, 600, 1200 and 4000 grit emery and degreased with isopropanol before immersion.

### 2.3 Amperometric Feedback mode

#### 2.3.1 Data collection principle

Data collection in feedback mode involves an electron redox mediator that changes in oxidation state in contact with the appropriately biased UME tip and substrate. The potential of the tip is maintained constant by a potentiostat and the substrate is at the OCP, which is dictated by the concentration of ions and the redox species in the electrolyte (according to the Nernst equation, equation 1.5). Only the tip current
from a reaction such as $O \rightarrow R$ (where $O$ is an appropriately chosen mediator) is measured. The tip current is perturbed by the presence of the substrate.

In the bulk solution, because of the small dimension of microelectrode, mass transfer is controlled solely by hemispherical diffusion of the redox mediator towards the microelectrode tip. Therefore, at sufficiently far distance from surface, in bulk solution, the steady-state current measured at UME, ($I_\infty$), is proportional to bulk concentration of redox mediator, ($C_\infty$), diffusion coefficient of the redox mediator, ($D$), and number of electrons involved in redox reaction, ($n$), according to the equation 2.1 [34]:

$$I_\infty = 4nFDc^{\infty}a$$  \hspace{1cm} (2.1)

where $a$ is the UME radius and $F$ is the Faraday constant. When the tip is moved toward the surface of an insulating substrate, the diffusion flux of mediator from bulk solution is blocked by the insulating nature of the substrate and the sheath around the UME tip, resulting in a decrease in the feedback current or $I < I_\infty$. This effect, schematically shown in Figure 2.3a, is called “negative feedback”. Conversely, if the substrate is a conductive or electrochemically active surface, the reduced mediator generated by the tip can be oxidized back (or recycled, since the substrate is poised at a sufficiently positive potential by the bulk redox species), producing an additional flux of mediator to the tip and, hence, an increase in tip current or $I > I_\infty$. This effect, schematically shown in Figure 2.3b, is called “positive feedback” effect.
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**Figure 2.3** Schematic representation of the SECM operation principle in feedback mode based on negative feedback (a) and positive feedback (b) effects when SECM tip is positioned close to an insulating and conductive substrate, respectively (reproduced from Ref. [35]).

Mg and its alloys form a passive a film consisting of an oxide or hydrated oxide layer of limited ionic conductivity that adheres to the metal and provides a semi-barrier film reducing the metal dissolution rate. Formation of the passive layer on the Mg surface has a major impact on the corrosion mechanism and its localization. A stable and inhomogeneous surface layer leads to preferential dissolution of Mg and promotes localized corrosion at these sites. Using SECM in feedback mode, active/passive domains can be sensed due to the variation in electrochemical reactivity of the surface and its role in the redox regeneration of the redox mediator. Figure 2.4 illustrates the principle of positive feedback effect by FcMeOH in contact with Mg surface where the passive layer does not cover the underlying metal. In theory, the oxidized mediator by the tip can be reduced when in contact with active surface of Mg resulting in a positive feedback effect (Figure 2.4a). At those areas, covered with the inert surface layer, the redox mediator is not reduced therefore a negative feedback effect is observed (Figure 2.4b).
Figure 2.4 Schematic representation of SECM probe in feedback mode showing redox activity of ferrocenemethanol (FcMeOH) in contact with Mg substrate and cathodically (oxidative) biased Pt probe.

2.3.2 Experimental parameters

2.3.2.1 Redox mediator

The primary requirement for an electrochemical redox mediator, in order to detect changes in the active/passive state of the Mg substrate is to undergo a fast reversible oxidation or reduction reaction when in contact with the active (non-covered) Mg surface. In other words, the Mg surface should be an effective catalyst for the redox reaction. Herein six redox mediators that are often used in feedback mode data collection have been studied to identify a compatible and consistent redox mediator capable of interacting with active/passive sites on Mg surface. The six mediators were FcMeOH, HQ, K₃[Fe(CN)₆], K₄[Fe(CN)₆]⁺, I₂/KI and ruthenium hexamine trichloride (Ruhex). The K₃[Fe(CN)₆] and Ruhex are found in the oxidized state (O group) in the bulk solution while the other four FcMeOH, HQ, K₄[Fe(CN)₆] and I₂/KI are in reduced state (R group) in the bulk solution. This means that for example, when using K₃[Fe(CN)₆], the SECM tip should be cathodically polarized to be able to reduce the ferricyanide ([Fe(CN)₆]³⁻) according to the reaction 2.2 and transforms into the reduced form, ferrocyanide.

*Note that K₃[Fe(CN)₆] and K₄[Fe(CN)₆] present two redox intermediates of one specie (Fe(CN)₆) but because their initial oxidation state is different in the solution, they were studied as two different mediators. In the long term storage either of these solutions will reach an equilibrium between K₃[Fe(CN)₆] and K₄[Fe(CN)₆].
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\[ \text{[Fe(CN)₆]^{3-} + e^-} \leftrightarrow \text{[Fe(CN)₆]^{4-}} \] \hspace{1cm} (2.2)

Ferrocyanide, in order to be able to sense active sites on the Mg surface, should be oxidized back to ferricyanide in contact with Mg. Since the OCP of Mg in solution is very negative, it is less likely to provide an effective oxidizing potential for the group O mediators (it more tends to reduce other species). Also the potential at which these mediators are detected (reduced) at the tip interferes with the potential at which \( \text{H}_2 \) and \( \text{O}_2 \) are electrochemically sensed (in other word, the electroactivity of these mediators overlaps the electroactivity of \( \text{H}_2 \) and \( \text{O}_2 \)). At appropriately biased tip potential, active species such as \( \text{O}_2 \) and \( \text{H}_2 \) can be sensed via electro-reduction and electro-oxidation reactions, respectively. This forms the principle for \( \text{H}_2 \) detection in generation/collection mode of SECM which will be discussed in detail in chapter 3 of this thesis.

Interference between electrochemical reactions of \( \text{H}_2 \) and \( \text{O}_2 \) with that of the redox mediator at the SECM tip introduces an ambiguity in the current measured by the potentiostat. Figure 2.5 illustrates the cyclic voltammograms (CV) of the six redox mediators in SBF performed using a 10\( \mu \)m Pt UME. There was no magnesium or any other source of \( \text{H}_2 \) present in the solution for these six measurements. Note that the solution was open to air hence the \( \text{O}_2 \) was available to SECM tip. It also shows the CV of the UME without redox mediator in SBF solution with and without a Mg specimen in solution. In the SBF solution without mediator and without Mg specimen the only electrochemical active species is \( \text{O}_2 \) which is reduced at potentials negative to -0.2 V (Ag/AgCl) resulting in a negative current shown in “SBF (background)” curve in Figure 2.5. In the presence of an Mg sample (“SBF 2000\( \mu \)m from Mg” and “SBF 8\( \mu \)m from Mg” curves in Figure 2.5), \( \text{H}_2 \) is also present in the solution and is oxidized at potentials negative to 0.3 V (Ag/AgCl). This results in a positive current which increases as the tip moves closer to the substrate (higher positive current at 8\( \mu \)m compared to 2000\( \mu \)m distance from Mg specimen). In order to avoid interferences from these reactions (reduction of \( \text{O}_2 \) and oxidation of \( \text{H}_2 \)) the
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Tip potential in feedback mode must be positive to 0.3 V. In other words, the redox mediators from O group cannot be used for SECM experiments on Mg in feedback mode.

Figure 2.5 Cyclic voltammograms of FcMeOH, HQ, $K_4[Fe(CN)_{6}]$, $K_3[Fe(CN)_{6}]$, $I_2/KI$ and Ruhex redox mediators in SBF. No mediator was present in the solution in cases of SBF (background) and 8 µm and 2000 µm from Mg. Working electrode was a 10µm Pt UME. Except for the two cases of 8 µm and 2000 µm distance from Mg surface, no Mg was present in the solution. Concentration of redox mediators in SBF were Ruhex 1mM, HQ 1mM, FcMeOH 1mM, $K_4[Fe(CN)_{6}]$ 2mM, $K_3[Fe(CN)_{6}]$ 2mM and $I_2$ 0.5mM/KI 5mM.

The redox electron mediator, in order to be effective for SECM feedback mode imaging, apart from a fast redox kinetic, should measure a stable steady-state current ($I_\infty$ in equation 2.1) in bulk solution. It should also have minimal interaction with the active substances on the surface to minimize the interference with natural electrochemical processes. In studying the corrosion of Mg, it is important to make
sure that the redox kinetics is not influenced by the high pH and Mg\(_{2+}\) dissolution in close vicinity of the surface. Herein, the four redox mediators from group R have been studied by measuring the steady-state current at a 10\(\mu\)m Pt UME in bulk electrolyte as a function of time. An example of such measurement for KI/I\(_2\) mediator is shown in Figure 2.6. This was performed in SBF containing a given concentration of mediator and also in SBF+mediator solutions with added 10 mM MgCl\(_2\) or NaOH (to adjust the pH to 10). The aim was to find the redox mediator which produces the most stable \(I_\infty\) and is least effected by an excess Mg\(_{2+}\) concentration and high pH.

![Figure 2.6 Measuring the steady-state \((I_\infty)\) current at a 10 \(\mu\)m Pt UME as a function of time in SBF containing 0.5mM I\(_2\) / 5mM KI. Tip potential was 0.6 V (Ag/AgCl).](image)

Results of \(I_\infty\)-t measurements for four redox mediators (group R) are presented in Figure 2.7. \(I_\infty\) is calculated as the mean value of the measure current during 1024 second measurement time. The error bars present the standard deviation of \(I_\infty\) fluctuation (exemplified by Figure 2.6) during the measurement as a measure of \(I_\infty\) stability. Results show a significant influence of pH on \(I_\infty\) when measured in HQ mediator and significance influence of excess MgCl\(_2\) on \(I_\infty\) when measured in I\(_2\)/KI.
mediator. The \( I_\infty \) in either of FcMeOH and \( K_4[Fe(CN)_6] \) is relatively unaffected by adding extra MgCl\(_2\) and NaOH while FcMeOH shows superior level of stability. Therefore, the FcMeOH with one-electron oxidation at potentials positive to 0.2 V (Ag-AgCl), is used throughout this thesis as the redox mediator for collecting the feedback mode data on the Mg surface.

![Graph showing steady-state current](image)

**Figure 2.7** Results of measuring steady-state current for a 10µm Pt UME in SBF containing different redox mediators as well as the SBF+mediator electrolyte plus 10 mM MgCl\(_2\) or NaOH (to adjust pH to 10). Concentration of redox mediators in SBF were HQ 1mM, FcMeOH 1mM, \( K_4[Fe(CN)_6] \) 2mM, and \( I_2 \) 0.5mM/KI 5mM.

### 2.3.4 Implication of feedback mode data for corrosion behaviour of Mg

In the context of corrosion of Mg, the feedback mode SECM can be particularly useful to obtain information about formation and breakdown of passive surface layers. It is well known that corrosion behaviour of Mg alloys to a large extent is driven by the formation and stability of the passive layer that forms on the surface in
which media the Mg is immersed [36–38]. Figure 2.8a shows the conducting/insulating domains acquired by SECM in feedback modes on the surface of AZ31 after 1 hr immersion in SBF. Upper scale colors indicate the areas with higher conductivity versus the lower scale colors that represent areas with relatively more insulating properties (e.g. covered with insulating surface layer). Figure 2.8b presents the optical micrograph of the same surface after experiment (1 hr immersion in SBF). It is notable that the areas with higher insulating properties in Figure 2.8a, correlate well with the darker colored areas in the Figure 2.8b. The highly protective characteristic of similar black corrosion product layer on AZ31 in SBF has been revealed elsewhere [39]. This result suggests formation of the micro-galvanic corrosion cells which has also been shown by other researchers in buffered media [40] and chloride containing solutions [41] caused by intermetallic particles. Micro-galvanic corrosion mechanism has been described earlier in section 1.3 in chapter 1 of this thesis.

**Figure 2.8** (a) SECM image of AZ31 surface in feedback mode after 1 hr immersion in SBF and (b) optical micrograph of the same surface after immersion and SECM imaging. For the SECM experiment FcMeOH was used as redox mediator with the tip potential of 0.55 V (Ag/AgCl) and a 10µm Pt UME.
The results acquired by SECM in feedback mode can also be used as complementary data with other modes of SECM operation to obtain an in-depth understanding of the formation of corrosion product layer on Mg surface and its role in the corrosion mechanism.

2.4 AC mode

When precursor regions which are susceptible to pitting corrosion exist due to local inhomogeneities, these areas often show a higher conductivity and thus allow a higher electron transfer rate \([42]\). While SECM in feedback mode is a feasible tool to measure local conductivities, it may cause complications in certain situations as the redox mediator used in feedback mode may interfere with the natural corrosion process or alter the passive film. Electrochemical impedance spectroscopy (EIS) does not bear these problems, although it usually works integrally for a quite large substrate region and cannot identify microscopic inhomogeneities. Ballesteros Katemann et al. \([29]\) combined the advantages of SECM and impedance spectroscopy through application of an alternating voltage between the UME and the counter electrode. This method bears the advantage that measurements are performed in a solution without requiring a redox mediator and therefore eliminates the complications that may arise from its interference with corrosion process. In order to use these AC measurements for analysing local corrosion phenomena, it is essential to identify the origin of the contrast in AC signals by means of modelling AC response with appropriate electrical equivalent circuits \([43]\). The equivalent circuits are defined considering the physical elements in the system (e.g. passive surface layer, solution resistance etc) that affect AC response in the given AC frequency range \([44]\).

In order to better understand how frequency affects the AC path, response of a simple Randles equivalent circuit is presented in Figure 2.9. At low frequencies the double layer capacitance \((C_{dl})\) is impermeable and the current flows exclusively via the Faradaic branch of the circuit (case i in Figure 2.9). The diffusion is the slowest event and therefore the Warburg impedance, \(Z_W\), which represents the diffusion
phenomena, dominates the impedance at low frequencies. At frequencies around $f_{\text{max}}$ (case ii in Figure 2.9) the current can pass via both the Faradaic and the capacitive branches. At high frequencies the electrolyte resistance ($R_S$) becomes the dominating component to the overall impedance. The current does flow via the capacitive pathway, but the double layer capacitance itself does not contribute to the impedance because above a certain threshold frequency it is permeable to the alternating current. In other words, at sufficiently high frequencies $R_{\text{ct}}$ and $Z_W$ do not contribute to the overall impedance. Therefore, high frequency (i.e. $\geq 100$ kHz) AC-SECM experiments can be used for probing the ionic activity of solution near the substrate surface; the higher the ionic activity the lower the solution impedance is.

![Figure 2.9](image)

**Figure 2.9** Contribution of the Randles equivalent circuit components to the Nyquist plot by the frequency range [32].

### 2.4.1 Data acquisition and electrical model

AC-SECM data should be obtained in dilute solutions (i.e. low ionic activity) in order to drive the AC signal towards the substrate and maximize the contribution of substrate surface to the AC response. Figure 2.10 illustrates the electrical model for SECM data acquisition in AC mode at conducting and insulating domains of a Mg
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In this thesis AC-SECM experiments are performed in 100 times diluted SBF. Also a 25µm Pt UME has been used instead of 10µm Pt UME in order to reduce the contribution of tip impedance and maximize the signal-to-noise ratio.

**Figure 2.10** Electrical model of AC mode data acquisition at conducting and insulating parts of Mg surface. $R_{sol}$ represents the solution resistance. $R_{sl}$ and $C_{sl}$ represent the resistive and capacitive characteristics of the surface layer, respectively. $R_{mg}$ and $C_{mg}$ represent resistive and capacitive characteristics of the magnesium surface, respectively.

To better understand the influence of AC frequency on the measured impedance by a 25 µm Pt UME, electrochemical impedance spectroscopy (EIS) measurements were performed using a 25 µm Pt UME in dilute SBF in bulk solution and in close vicinity of Mg surface. Results of the measurements are presented in Figure 2.11 and show the frequency dependence of AC response in three distinct frequency domains. At the high frequency domain, e.g. 100kHz, the UME exhibits a relatively insensitive impedance to the change of frequency whereas the impedance measured in close vicinity of surface which shows a significant dependence to the frequency. At high frequencies, solution resistance is the only parameter affecting the AC response. This is because of the high permittivity of interfacial elements such as double layer capacitance and surface layer capacitance to the high frequency AC resulting in the

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* The presented electrical equivalent circuit has been adopted for Mg from the model proposed by Eckhard et al. [44] for an inhomogeneous active/passive surface.
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The majority of AC to transmit through solution towards counter electrode. Therefore, the differences observed at these high frequencies are attributed to the difference in solution conductivity or in other word differences in local concentration of ions in the solution near the surface. In the bulk solution, in presence of a consistent ionic activity, relatively steady impedance is observed at high frequencies. In close proximity to the Mg surface, due to the small gap between the tip and substrate (i.e. small volume of solution) the solution resistance increases resulting in a larger AC impedance to be measured. This characteristic (distance dependence of AC impedance) in AC mode SECM at high frequency ranges has been successfully implemented for studying in-situ surface profile [32,45,46].

**Figure 2.11** Impedance measurements (Bode plot) of a 25µm Pt UME in dilute SBF in 5µm distance from AZ31 surface and in the bulk solution (∞ distance from Mg surface). Pt mesh and Ag.AgCl served as counter and reference electrodes respectively. AC perturbation amplitude was ±50 mV relative to OCP.
In the intermediate frequency range, e.g. 1 kHz > f > 100 kHz, other elements at the interface begin to contribute to the overall impedance when UME is close to the substrate. In the bulk solution the impedance from electrical double layer formed at the surface of UME becomes significant giving rise to the overall impedance while in close vicinity to the Mg surface, the insulating surface layer presents an additional impedance that adds to the UME double layer impedance. As frequency decreases to less than 1 kHz, the capacitive impedance of UME becomes increasingly more dominant due to the small (25 μm diameter) size of Pt UME. Therefore at these low frequencies similar impedance is measured for both electrodes in the bulk solution and in close distance to the Mg surface.

2.4.2 AC approach curves

AC approach curves are measured similar to those measured in feedback mode however in AC mode the AC components (i.e. real and imaginary impedance and phase shift) are recorded as a function of tip-to-substrate distance (Figure 2.12). AC approach curves are normally obtained over a range of frequencies to determine the response of the surface film as a function of the frequency of excitation amplitude [30]. Approach curves presented here are collected by approaching a 25 μm Pt UME from 75 μm distance above the Mg substrate down to <1 μm probe-substrate separation while a set frequency is applied to the tip. Normalized impedance is calculated using equation 2.3;

\[
\text{normalized impedance} = \frac{Z_L}{Z_\infty} \quad (2.3)
\]

where \(Z_L\) is the impedance at distance \(L\) from substrate and \(Z_\infty\) is the bulk impedance at 75 μm distance from Mg substrate. Normalized tip-substrate distance, \(NL\), is calculated as:

\[
NL = \frac{L}{D} \quad (2.4)
\]
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where \( L \) is the tip-to-substrate distance in \( \mu m \) and \( D \), the tip diameter in \( \mu m \). Figure 2.12 shows the normalised approach curves on the surface of Mg alloy AZ31. The sample (prepared according to the procedure outlined in section 2.2.1) was immersed in SBF for 1 hr before it was transferred to a diluted SBF solution for AC mode experiments. A positive feedback (increasing impedance as the tip approaches the substrate) was observed at lower frequencies \((f \leq 15 \text{ kHz})\) and negative feedback (decreasing impedance as the tip approaches the substrate) was observed at higher frequencies \((f > 42\text{kHz})\).

As explained earlier, in sufficiently high frequencies all capacitive elements of the system are *permeable* against the AC signal and the solution resistance is the sole element reflected in the AC response. This results in a lower impedance values which is seen as negative feedback at high frequency range in Figure 2.12. Presence of an insulating layer on the substrate surface (such as the surface layer shown in Figure 2.10) introduces additional impedance which is measureable at low frequencies and contributes to the overall impedance of system. This results in a higher impedance value which is seen as positive feedback at low frequencies in Figure 2.12.
Figure 2.12 Normalized approach curves at a range of frequency from 75kHz to 1kHz towards the surface of AZ31 in diluted SBF. AZ31 was at open circuit potential. The probe was a 25µm Pt UME at OCP with excitation signal amplitude of ±100 mV.

In principle, positive feedback effect is observed when the frequency of the applied signal is smaller than the reciprocal of the time constant for the interfacial impedance, whereas negative feedback is observed for higher frequencies [31]. Equation 2.5 shows the relationship between the time constant, RC\(^\ast\), and the cut-off frequency, \(f_c\):

\[
 f_c = \frac{1}{2\pi RC} \tag{2.5}
\]

As a surface film grows (R ↑ and/or C ↑) on the bare Mg surface, the time constant associated with the surface film increases (\(R.C\), resulting in a lower frequency threshold \((\frac{1}{2\pi RC})\) at which the positive to negative feedback transformation occurs [31]. Thus, the frequency at which a distinct differentiation is observed between bare Mg surface and covered Mg, will decrease. This also indicates the insulating nature of the surface film that forms on Mg in SBF solution.

If the substrate presents a conductive surface, the AC transmittance will be facilitated by the conductive path near the substrate surface which will result in a negative feedback. Approach curves shown in Figure 2.12 suggest that adequate sensitivity of AC signal to insulating properties of the Mg surface layer is obtained at low frequencies such as 1 kHz. Similar frequency has also been used elsewhere for AC-SECM imaging of active pitting corrosion [47,48]. This frequency will be used as the set frequency for AC-SECM imaging in this thesis.

\* The RC time constant is the time constant (in seconds) of an RC circuit and is equal to the product of the circuit resistance (in ohms) and the circuit capacitance (in farads).
2.4.3 AC mode imaging

SECM imaging in AC mode comprises recording impedance (imaginary and real) and phase shift via counter electrode (CE) as a response to the excitation AC signal applied by UME at a set frequency. Good resolution with high sensitivity towards the surface layer was observed at 1 kHz with 100 mV amplitude of excitation voltage (Figure 2.13) and shows the local impedance and phase shift at the surface of an AZ31 Mg alloy obtained by AC-SECM. The Mg sample was immersed in SBF for 1 hr before it was transferred to dilute SBF for AC mode experiments. Upper scale colors in Figure 2.13a (magenta and blue) represent the relatively insulating areas versus lower scale colours (red and yellow) that indicate relatively conductive areas. In Figure 2.13b, upper scale colors indicate domains with higher capacitive behaviour whereas the lower scale colors that indicate lower capacitive characteristic.

Figure 2.13a shows locally isolated more conductive domains while the majority of surface exhibits more insulating characteristic. This is consistent with the feedback mode imaging result (Figure 2.8) where inhomogeneous formation of a surface layer with isolated local areas of higher activity were observed. Furthermore, Figure 2.13b shows higher capacitive (or higher phase shift) properties at those domains marked as higher insulating domains in Figure 2.13a. Assuming a uniform oxide/hydroxide chemical composition of surface layer over the entire surface, the differences in capacitive characteristics can only be attributed to the difference in thickness and density of the surface layer. Equation 2.6 presents the relationship between the capacitive value of a capacitor, $C$, and dielectric constant and thickness of the insulating material,

\[ C = \frac{\varepsilon A}{d} \quad (2.6) \]

Where $\varepsilon$ is the dielectric constant of insulating material, $A$ the capacitor surface area and $d$ thickness of the insulating material.
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Figure 2.13 AC-SECM images at the surface of an AZ31 Mg alloy after 1 hr immersion in SBF showing local (a) impedance and (b) phase shift. AC mode experiments were performed in diluted SBF using a 25µm Pt UME with excitation signal amplitude of 100mV at 1 kHz.

Considering equation 2.6, stronger localised capacitive behaviour cannot originate from or be dominated by a thinner surface layer because in that case those domains with stronger capacitive property should have exhibited higher conductivity which is the opposite of what is observed in Figures 2.13a and 2.13b. Therefore, it can be postulated from these Figures that the surface layer at the domains with higher phase shift have a more dense structure.

Figure 2.14 shows the AC-SECM image of the same surface, studied in Figure 2.13, with excitation AC frequency of 100 kHz. At this frequency the local ionic concentration of solution within the gap between the substrate surface and the UME
dominates the AC response. Comparing Figure 2.14 with 2.13, it elucidates high local ionic activity at those areas of surface with higher conductivity. This is most likely due to the dissolved Mg$^{2+}$ ions from anodic reaction (reaction 1.2) and/or OH$^{-}$ ions from cathodic reaction (reaction 1.3).

![Figure 2.14](image)

**Figure 2.14** AC-SECM images at the surface of an AZ31 Mg alloy after 1 hr immersion in SBF showing local (a) impedance and (b) phase shift. AC mode experiments were performed in diluted SBF using a 25µm Pt UME with excitation signal amplitude of 100mV at 100 kHz.

Here the AC mode SECM is shown to be a useful method for studying resistive properties of the surface layer that forms on Mg during corrosion. While the impedance map at low (1kHz) frequency differentiates domains of low conductivity from those of higher conductivity, more information about capacitive properties of the surface layer at a certain area may be achieved by AC approach curves over a range of frequencies and also by phase shift data. AC-SECM at high frequency scan can be used to look at the local ionic activity at the Mg surface as a result of ongoing
corrosion reactions. The main advantage of the AC mode is the elimination of the redox electron mediator that in some cases may interfere with the natural corrosion process or may react with active/passive domains on the surface. It is also noteworthy that phase shift data acquired in AC mode is nearly independent from the excitation amplitude of the AC signal and for that matter it may be considered as a more reproducible parameter for studies using AC-SECM [29].

2.5 Potentiometry mode for local pH sensing

Electrolyte pH is an important parameter in corrosion studies as it has a profound influence on the rate of corrosion of most metals, primarily by affecting the solubility of native oxide films. Potential and pH conditions of where corrosion, passivation and stability are thermodynamically favoured may be predicted from Pourbaix diagrams as shown earlier in chapter 1, section 1.2. Both anodic and cathodic processes occurring during the corrosion of Mg can affect the electrolyte pH near the surface and the proximity of anodic and cathodic sites can enhance localized corrosion. The cathodic reaction (namely the reduction of water and evolution of H$_2$) produces hydroxide ion and directly increases the pH. The anodic reaction with the corrosion model that traditionally assumes dissolution of Mg in the form of Mg$^{2+}$ can lower the pH due to the hydrolysis of metal ions with water. However the more recent corrosion model advanced by Song and Atrens [49] includes multi stage formation of Mg$^{2+}$ and involves dissolution of Mg in the form of Mg$^{+}$ unipositive cation in the first step of Mg corrosion. The model that is also presented in Figure 1.6 accounts for H$_2$ evolution and increase of pH at the anodic sites.

2.5.1 Data acquisition principle

Potentiometric mode is basically a two electrode configuration of SECM in which the open circuit potential of UME tip is measured against the reference electrode as a function of tip location. The thermodynamic basis of measuring ions concentration based on Nernst equation (equation 1.5) is well defined by Bard and co-workers
There have been major advancements in the area of potentiometric measurement of pH using miniaturized ion sensitive electrodes (ISE) in the past decade [52]. However, there has been limited number of reports on using UME based ISEs for SECM imaging of local pH on the surface of corroding Mg [27]. This is mainly due to the generally slow response time (compared to what is expected for a SECM probe, e.g. <0.1s) and interference with H₂ evolution during corrosion of Mg [53].

![Figure 2.15](image)

Figure 2.15 Schematic of (a) SECM set up in potentiometric mode using an ion selective microelectrode and (b) the flow of active ionic species from a substrate source towards the potentiometric tip. The concentration profile of the product that develops is monitored by measuring the potential of ion sensitive micro-electrode (ISME) against a reference electrode (RE) (placed in the bulk solution) [51].

One of the most common methods for fabricating a miniature pH sensitive electrode is using a pulled glass capillary filled with a pH sensitive ionophore. This method facilitates rapid electrode preparation and achieves widespread use in biological applications. However, the ionophores have a limited pH range, the tips are mechanically fragile and the electrodes have a short lifespan [28]. A class of electrode that does not display these limitations are the solid state metal oxide sensors. The pH sensitive metal oxide electrodes have been successfully prepared
from tungsten [54], palladium [55], iridium [56–58], antimony, [51][59,60], zirconium [61] and lead [62] oxides. Antimony and iridium oxide electrodes have been consistently cited to exhibit a wide operating range, good stability and rapid response times. Furthermore these electrodes may be used at high temperature, high pressure and in aggressive electrolytes. However, Antimony pH electrodes have exhibited interference with H$_2$ evolution and therefore are not appropriate for measuring pH on the surface of corroding Mg [53]. Therefore, Iridium was chosen for the localised micro-pH sensing work conducted in this thesis.

Preparation of stable, pH sensitive iridium oxide films have been done by molten salt immersion [59,63,64], thermal oxidation [57,65–67] and electrochemical oxidation methods [56,58,67–72]. A thorough survey of miniature iridium oxide based pH sensing electrodes has been given in ref. [68]. In a previous study by Lowe [28], the electrochemical method more appropriate for constructing the electrodes used as SECM probes. The ease of constructing micron size UME through the electrochemical method and good stability and reproducibility of these electrodes are the main reasons for using electrochemically made iridium oxide UMEs for the work reported in this thesis.

The iridium oxide film produced electrochemically appears to be composed of a multi-valent, hydrous oxide structure in which iridium exists in the film in the +3, +4 and +5 oxidation states. An increasing concentration of higher oxidation states is observed with increasing potential [73]. A model for the pH response of the electrode has been proposed by Hitchmann et al. [58,72]. This model proposes that the proton and electron transfer reactions happen in the hydrated, porous outer oxide layer, rather than the compact anhydrous inner oxide layer. The near Nernstian electrode response means that proton and electron transfer reactions must occur simultaneously in the film. Applying the electrochemical equilibrium for Ir$^{3+}$ and Ir$^{4+}$ species to the Nernst equation (equation 1.5) produces the equilibrium equation shown in Equation 2.7, which describes the relationship between the electrode potential, the concentration of Ir$^{3+}$, Ir$^{4+}$ oxides as well as H$^+$ and OH$^-$ [56,72].
\[ E = E^0 + \frac{2.3RT}{2F} \log \left[ \frac{[IrO_2(OH)_{2-x}(2+x)H_2O]^{(2-x)-}}{[IrO_3(OH)_{3-}3H_2O^{3-}]} \right] + \frac{2.3(3-2x)RT}{2F} \log[H^+] \] (2.7)

2.5.2 Fabrication of IrOx ultra-microelectrode

pH responsive microelectrode probes were constructed from 75 μm diameter high purity Iridium wire purchased from American Elements. In order to increase the sensitivity and also to reduce the response time of the electrode it was essential to reduce the size of sensing tip. This was achieved by etching a 10 mm long Ir wire in 0.5M H_2SO_4 under a 5 V DC anodic polarisation against another Ir wire. The Ir wire was previously point-welded to a large Cu wire to make electrical connection. The solution discoloured during etching, turning dark purple, indicating dissolution of Ir. Etching continued for 20 min* producing a tapered end. The tapered wires were cleaned ultrasonically in distilled water, washed with ethanol and dried in air.

The wires were encapsulated in glass by melting a glass capillary (2 mm outer diameter) on the bunsen burner with the wire placed in the glass capillary. Special care was taken to eliminate air entrapment next to the Ir wire and inside the melted glass. Before any further procedure the Cu wire and the end of electrode was glued to the glass capillary to secure the Ir wire and its electrical connection with Cu. The tip was then sharpened and ground flat on 1200 grit and 4000 grit SiC paper to expose an iridium disc electrode, which was polished using a 0.05 μm silica slurry on a polishing cloth. An optical image of the tip is shown in Figure 2.16. Tips with iridium microelectrodes ranging from 7 μm to 75 μm in diameter were prepared in this manner. The results in this thesis were obtained using tips that were 16 μm diameter.

* Note that the length of Ir wire exposed to the etching solution has a direct relationship with the time required to etch the wire. The longer the wire exposed to etching solution, the more time is required to etch the wire.
Figure 2.16 Optical micrographs of the Ir UME fabricated by etching the Ir wire and insulation in glass sheath.

The tip was cleaned in 0.5 M $\text{H}_2\text{SO}_4$ by stepping the potential between -0.3 V and +1.6 V for 2 s each (3 cycles). The iridium oxide (IrOx) film was grown by cycling the potential of the iridium UME between -0.25 V and +1.25 V at 3000 mV s$^{-1}$ in 0.5 M $\text{H}_2\text{SO}_4$ electrolyte for 10000 cycles [72]. An example of the current from oxide growth is shown in Figure 2.4. The progressively increasing current, shown by the broken arrow in Figure 2.4, is associated with the growth of the IrOx. There is evidence suggesting that thicker films are more suited for analytical applications as they usually provide greater sensitivity, less drift and dissolution of the oxide does not affect the electrode response [72]. Also it has been shown that low scan rates (100 - 500 mV s$^{-1}$) produce thin films with poor response, while at higher scan rates (3000 mV s$^{-1}$ – 6000 mV s$^{-1}$), the oxidation currents exceed the reduction currents, resulting in thicker films [28].
Figure 2.17 Potential-current plot from electrochemical growth of IrOx film on Ir surface by cycling the potential of the iridium UME between -0.25 V and +1.25 V at 3000 mV s⁻¹ in 0.5 M H₂SO₄ electrolyte for 10000 cycles. Each colour domain represents 2000 cycles.

The Ir tip was stored in SBF overnight at room temperature (ca. 22°C) prior to being used in the experiment. The pH response of a freshly formed iridium oxide film is known to drift to more negative potentials over time and this was observed primarily in the first few hours following preparation [68,70]. Storage for 24 hours prior to measurements alleviated this drift. For calibration of the electrode, the pH of a SBF solution was altered using 0.1M HCl and 0.1M NaOH with these solutions used to produce the calibration curve, shown in Figure 2.18. Similar method was used in a previous study to sense pH on Al-Zn in un-buffered media [74]. The H₂ interference was ruled out by measuring OCP in SBF solution with and without dissolved H₂. The response times for alkaline pH were less than 1s and for acidic pH the response time varied from 1s to up to 5s.
Figure 2.18 Calibration curve correlating Ir.IrO$_2$ potential to the pH of a SBF solution. Alkaline and acidic pH was adjusted using 1M NaOH and 1M HCl solutions, respectively.

2.5.3 Local pH detection

Figure 2.19 shows individual pH values at certain points of interest on an impedance map. In order to measure local pH an impedance map (shown in Figure 2.14a) was first produced in AC mode (according to the section 2.4.3). The impedance map was then used as a guide to find the domains with different levels of conductivity. The Ir.IrOx electrode was then moved precisely above the points of interest and OCP was measured against an Ag/AgCl electrode at approximately 20µm distance away from Mg surface. The calibration curve (Figure 2.18) was used to convert the OCP values to pH. The pH of bulk buffered solution (i.e. SBF) was 7.4 at the time of measurement. As illustrated in Figure 2.19, the near surface pH is significantly higher than that of bulk with local pH at highly conductive areas reaching up to 12.1.
Figure 2.19 Local (single point) pH values in SBF solution shown on a local impedance map (Figure 2.14a). A 16µm dia. Ir.IrO₂ UME was positioned precisely above the points of interest and the OCP potential was recorded against an Ag/AgCl reference electrode. Individual pH values were converted from OCP values using the calibration graph (Figure 2.18).

The near surface pH plays an essential role in determining the formation and stability of the surface layer as well as inducing inflammatory effects. It is well known that most magnesium hydroxide and calcium phosphate layers that form on the surface of Mg are stable at high pH and tend to break down at low or neutral pH [33]. On the other hand, in the context of biomedical implants, it is known that extreme pH is generally not tolerated by surrounding tissue and causes inflammation [75,76]. It is believed that near surface pH measured by Ir.IrOx microelectrode in this study can provide valuable information that helps to provide a better understanding of the formation of the surface layer and potential cytocompatibility of Mg alloys in physiological media.
2.6 Summary

In summary, SECM in three modes of operation (i.e. feedback, AC and potentiometric) was used for in-situ characterisation of Mg surface during corrosion in a biological buffered solution. Combining the variables measured in different modes of SECM gives new insight into the complex corrosion mechanism of Mg in a buffered media.

In feedback mode an electron-mediator is used to reveal the active/passive domains of the surface. In performing SECM feedback imaging it is essential that much care must be taken in selecting the probe potential in order to avoid interference between H$_2$ detection range and the electron-mediator redox potential.

It was shown that AC mode holds promise in visualizing the areas that are covered with an insulating surface film, with high sensitivity in differentiation at low frequency. AC mode at low frequency confirmed feedback mode results revealing isolated conducting areas on the surface while the rest of surface (also comprising the majority of surface) exhibited a rather capacitive behaviour. These isolated active areas are where hypothetically anodic dissolution of Mg takes place. The AC results in high frequency elucidated that a significantly higher ionic concentration at these active domains which is consistent with occurrence of corrosion reactions, increasing the ionic activity, at the active areas of the Mg surface.

The near surface pH was found to be alkaline despite the SBF solution being buffered to 7.4. This has significant impact on the mechanisms involved in formation of surface passive layer as well as the cytocompatibility of magnesium. The regions of highest pH coincided with the domains showing lower surface resistivity. This implies that anodic dissolution of Mg at the active areas of surface either involves dissolution of Mg in form of Mg$^+$ or it takes place at the very close vicinity of isolated cathodic areas. This also rules out the corrosion mechanism by anodic
dissolution at independent sites that produces local acidic pH by water hydrolysis of Mg cations.
2.7 References


Developing SECM for studying corrosion of Mg in SBF


Chapter 3

Using SECM for studying corrosion of Mg in SBF:

Surface generation / tip collection (SG/TC) mode
3.1 Background

One of the simplest and most accurate methods for measuring corrosion rates of magnesium in aqueous media is by measuring the rate of hydrogen gas (H$_2$) evolution associated with the Mg corrosion process. According to Equation 3.1 [1–3], for each Mg$^{2+}$ ion produced from the corrosion of Mg metal, one molecule of H$_2$ is evolved (i.e. one mol (i.e. 24.31 g) of Mg metal corrodes for each mol (i.e. 22.4 L) of hydrogen gas produced).

$$Mg + 2H_2O \rightarrow Mg^{2+} + H_2 + 2OH^-$$  \hspace{1cm} (3.1)

Therefore, in the absence of any other cathodic reaction, the hydrogen evolution rate is equivalent to the metal corrosion rate. For Mg corrosion, an excellent agreement [1,3] is found between the corrosion rate measured by the weight loss and that calculated from the H$_2$ evolution. However, the H$_2$ collection technique is a cumulative method that affords corrosion rate data after a certain period of immersion. Therefore, it has limited ability in studying spontaneous corrosion phenomena. Additionally, this method is susceptible to error due to the solubility of H$_2$ in aqueous media, particularly when measuring short term or slow corrosion rates [4]. Potentiodynamic polarisation (PDP) is an electrochemical method commonly used to determine corrosion rates by Tafel extrapolation at the cathodic branch of the polarisation curve, giving the corrosion current, $i_{corr}$, which is related to the average corrosion rate [5]. However, this technique is a destructive measurement method that can change the surface properties considerably after a single scan. In addition, this electrochemical technique is susceptible to errors such as uncompensated IR drop or generalized assumptions (e.g. uniform corrosion) that leads to unreliable values for Mg corrosion rate [1,6]. Nevertheless the electrochemical technique of Tafel extrapolation is still widely used for the evaluation of Mg alloy corrosion, mainly because it is the only quick and easy technique for assessing spontaneous corrosion rates.
Scanning electrochemical microscopy (SECM) is a high resolution scanning technique that allows for chemical interaction with electroactive species, thus producing valuable information on local concentration of certain species. SECM in generation/collection (G/C) mode relies on electrochemical detection of species generated at the SECM tip or at the substrate. If species are generated at the tip and sensed at the substrate the method is called tip generation/substrate collection (TG/SC) mode and vice versa. In surface generation/ tip collection (SG/TC) mode of SECM, electrochemically oxidisable or reducible species produced at the substrate surface can be sensed via an electrochemical reaction at the SECM tip. In theory, the evolved H$_2$ can be sensed in SG/TC mode, providing the ability to investigate localised corrosion and to determine the corrosion rate distributions on a Mg alloy surface.

There have been a limited number of studies reporting the application of SECM to investigate corrosion of Mg, in part due to the difficulty of precisely positioning an UME tip over a surface in the presence of evolving H$_2$ bubbles. SECM has been applied to Mg substrates previously for determining the concentration profile of Mg$^{2+}$ and pH (in potentiometry mode) [7–10], as well as assessing the uniformity of surface treatments (in feedback mode) [11,12]. However, at the time this PhD project started the unique capability of SECM to electrochemically measure H$_2$ evolution from the corroding surface of Mg had not been studied. Such measurements can be particularly advantageous for evaluating the instantaneous corrosion rate of Mg with a localised approach, as no other technique is capable to do so. The importance of monitoring localised corrosion of Mg is highlighted by the great impact that corrosion has on the mechanical integrity and load bearing characteristics of biomedical implants [13]. The use of surface generation/tip collection (SG/TC) mode for sensing H$_2$ evolution as a measure of corrosion behaviour of Mg in a simulated biological environment was first reported by Jamali et al [14]. Further studies highlighted the significance of major domains of H$_2$ evolution as the domains with lower local resistance of surface and higher pH [15]. The SG/TC mode of SECM has been applied elsewhere for screening hydrogen oxidation reaction (HOR) [16,17] where the H$^+$ generated electro-catalytically at the substrate was reduced to H$_2$ at the
tip and thus electrochemically detected. A recent study by Tefashe [18] utilized SG/TC mode of SECM for studying the time dependence of corrosion behaviour by imaging \( \text{H}_2 \) flux during corrosion of AM50 Mg alloy.

Despite recent reports on the successful implementation of SECM in SG/TC mode for measuring \( \text{H}_2 \) evolution at the surface of Mg [14,15,18], fundamental questions such as the responsiveness of the tip, image resolution, effect of pH on tip current and the correlation of localised \( \text{H}_2 \) evolution with corrosion pit formation have not been addressed. This chapter outlines a mechanistic study on sensing \( \text{H}_2 \) and its implications for Mg corrosion. Sensing \( \text{H}_2 \) is first evaluated on a Pt substrate in order to validate the approach and check the influence of corrosion reactions, such as surface alkalization, on the HOR. This study then utilized the SG/TC mode of SECM in a case study to probe the evolution of \( \text{H}_2 \) at the Mg substrate via hydrogen oxidation reaction (HOR) at a UME tip to investigate localised Mg corrosion. The SECM results in SG/TC mode is then compared to other modes of SECM (i.e. feedback, AC and potentiometric modes) and correlation is made between \( \text{H}_2 \) evolution at the Mg surface and its insulating properties.

### 3.2 Experimental

#### 3.2.1 Materials and sample preparation

Simulated biological fluid solution and AZ31 Mg specimens were prepared similar to the procedure described earlier in chapter 2 (section 2.2).

Pt line arrays were fabricated by placing 35µm thick Pt foil between 1mm thick glass slides using epoxy glue. The cross-section that was exposed to solution was polished successively using 600, 1200 and 4000 grit emery (Figure 3.6a) while the opposite end was attached to a Cu wire using silver paint and sealed using epoxy glue.
Pt micro-substrate was made by mounting a Pt wire with 65 µm in epoxy. The cross-section of Pt wire that was exposed to solution was abraded successively using 600, 1200 and 4000 grit emery and cleaned with isopropanol. The other end of Pt wire was left protruding outside of epoxy for further electrical connection.

3.2.2 Methods

Scanning electrochemical microscopy (SECM) was performed using a CH instruments SECM model 920D utilizing CHI integrated software version 12.26. A Pt UME (10µm and 25µm diameter), Ag/AgCl (3M NaCl) and Pt mesh were used as working and reference electrodes, respectively. A SECM image in constant height mode was obtained by scanning the UME tip in the x-y plane and recording the tip current as a function of tip location. The distance between tip and substrate was adjusted to 5µm using a digital microscope manufactured by MEIJI Techno model MS50.

All experiments were performed at room temperature, ca. 22 °C. In the manuscript all voltages are stated versus the Ag/AgCl reference electrode unless otherwise stated.

Surface profiles were examined using a Wyko NT9100 optical profilometer (Veeco instruments Inc.). Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) studies were performed using a JEOL 7500FA field emission scanning electron microscope.

3.3 Data acquisition principle in SG/TC mode

In the SG/TC mode of SECM, the tip and substrate potentials can be independently controlled by a bipotentiostat such that a species generated at the substrate (e.g., R from the reaction O → R) is collected (detected) at the tip by forcing the reverse reaction (R → O) at the tip. An approach curve scan (where the SECM tip is
advanced towards the sample surface) in the $z$ direction can produce the concentration profile of the species of interest, while a scan over the surface can be used to identify the areas where reactions occur at a higher rate. SG/TC mode can also be implemented in potentiometric state where the tip is a potentiometric sensor detecting specific ions generated at the substrate. In this thesis, the term “SG/TC mode” is regarded as amperometric measurement of species detected at the tip.

In the potentiometric mode SG/TC mode, the tip/substrate separation should be large enough in order to avoid the feedback effect. The feedback effect occurs in short distance from substrate when species are reoxidized (or rereduced) at the tip return to the substrate and increase the local concentration of the detectable species. The same principle applies to amperometric SG/TC mode. It should also be noted that increasing the tip/substrate separation will have negative effect on the resolution acquired by SECM imaging. Therefore, in adjusting the tip/substrate distance, there is a trade-off between interfering feedback effect in SG/TC mode and the methods resolution.

In a SG/TC experiment, when a UME with a surface area $a_T$ is placed above a substrate with a surface area $a_S$ and $a_S/a_T \gg 1$, the diffusion layer generated by the substrate is much thicker than that at the tip electrode [19]. It can be assumed that no feedback effect occurs (i.e., the substrate current is not affected by the tip process) if either $d/a \gg 1$ ($d$ is the tip/substrate separation and $a$ is the UME diameter) or when the product of the tip process does not react at the substrate. There are in particular three factors making it difficult to measure the accurate concentration profile in SG/TC mode including (i) the moving tip stirring the substrate diffusion layer; disturbances are especially significant when the tip is an amperometric sensor and has its own diffusion layer; (ii) when the substrate is large, no true steady state can be achieved; and (iii) the tip blocks the diffusion to the substrate surface, and this screening effect is hard to take into account.
SECM in SG/TC mode was historically first used with an amperometric tip in order to probe the diffusion layer generated by a large substrate electrode using a much smaller amperometric sensor [20]. Consequently simple theories were advanced to predict the concentration profile following the substrate potential perturbation at a planar electrode based on the tip/substrate separation, \( d \), and time after potential perturbation [20–23]. When the separation distance is sufficiently large to eliminate feedback to the substrate, the diffusion of species between two electrodes can be probed by transient SG/TC measurements. The tip current transient following the application of a short potential pulse to the substrate electrode is peak shaped. The time corresponding to the maximum tip current, \( t_{\text{max}} \), is independent of the tip size and can be expressed as [24]:

\[
t_{\text{max}} = \frac{0.111d^2}{D}
\] (3.2)

If the tip/substrate distance, \( d \), is known, one can use equation 3.2 to evaluate the diffusion coefficient \( (D) \) [51].

In many of the SECM studies using SG/TC mode, the species collected (detected) at the tip is electrochemically generated at the substrate by applying a controlled current or potential through the bipotentiostat [25]. However, more commonly in corrosion studies, SG/TC mode is also used to detect electroactive species naturally generated or consumed at the substrate [26]. Main body of the literature reporting the use of SECM in SG/TC mode in corrosion studies, implemented the method in a so-called “oxygen competition mode” for resolving oxygen consumption at the surface of metal as a measure of cathodic activity. This is essentially due to the predominance of oxygen reduction as the major cathodic reaction in corrosion of most metals. SECM in oxygen competition mode applies a cathodic potential at the UME tip for reducing the dissolved oxygen. At the cathodic sites on the metal surface, due to consumption of oxygen in corrosion half-cell reaction, there will be a lower concentration of oxygen which can be detected by SECM tip. However, as
explained earlier in chapter one (section 1.2), oxygen reduction plays no part in aqueous corrosion of Mg and its alloys.

Among the species produced or consumed during the corrosion of Mg (see equation 3.1), Mg$^{2+}$ cannot be electrochemically detected due to its very negative redox potential which exceeds that of water reduction. H$_2$ is, however, an electroactive species that can be electrochemically sensed in an oxidation reaction, $H_2 \rightarrow 2H^+ + e^-$. Sensing H$_2$ evolution can provide valuable information about the corrosion rate of Mg given that evolved H$_2$ from corrosion of Mg is equimolar of dissolved (corroded) Mg (equation 3.1). Also mapping the distribution of H$_2$ at the surface of Mg can provide useful information about corrosion mechanism of Mg in a given solution. Prior to any empirical measurement of H$_2$ evolving from a corroding Mg surface, the current measured by SECM tip via H$_2$ oxidation reaction should be calibrated in respect to the source of H$_2$ generation. This is mainly due to the known fact that collection efficiency in SG/TC mode is less than 1, particularly when the substrate is much larger than the tip.

### 3.3.1 Source of H$_2$ evolution from Mg corrosion

Electro-oxidative detection of H$_2$ using SECM has also been previously applied to aluminium corrosion by Dufek and Buttry [27]. They biased aluminium to artificially produce H$_2$ and studied the areas that showed active H$_2$ generation. However, in the case of Mg corrosion, H$_2$ is a natural product of the aqueous corrosion (equation 3.1) that is detectable at the SECM microprobe in an oxidation reaction.

Equation (3.2) expresses the oxidation reaction of H$_2$ at the SECM UME in neutral and acidic electrolytes.

$$H_2 \rightarrow 2H^+ + 2e^- \quad (3.2)$$
Under alkali conditions (as a result of OH\(^-\) generation – equation 3.1) near the Mg surface, Equation (3.2) may be more appropriately written as Equation (3.3):

\[
H_2 + 2OH^- \rightarrow 2H_2O + 2e^- \tag{3.3}
\]

At higher pH, Equation (3.3) dominates. The Nernst equation for either of these reactions (at standard atmospheric pressure) will result in Equation (3.4), where the pH dependence of the reduction potential is defined as:

\[
e_{H^+/H_2} = e^{o}_{H^+/H_2} - 0.059 \, pH \quad (25\, ^\circ C, \, p = 1 \, atm) \tag{3.4}
\]

Therefore, H\(_2\) can be oxidized at the SECM tip, theoretically at -0.44 V NHE at the pH of 7.4 (pH of SBF). At a pH as high as 12 (as shown in chapter 2 of this thesis) in close proximity of the Mg surface the oxidation potential of H\(_2\) can be as negative as -0.7 V NHE (~ -0.9 V vs. Ag/AgCl). Therefore any potential higher than -0.7 V NHE may be set as tip potential to sense the H\(_2\) evolution. However, as a result of the oxidation reaction of water interfering with the anodic current from oxidation of H\(_2\) at low potentials, the potentials lower than -0.7 V (Ag/AgCl) should not be used. Operating principles of SECM in SG/TC mode is schematically shown in Figure 3.1 where the H\(_2\) generated at Mg surface (either from anodic or cathodic sites) is directly sensed by the SECM tip in a reverse electro-oxidation reaction.
Figure 3.1 Schematic principle of $\text{H}_2$ probing in SG/TC mode of SECM using a polarized Pt UME to oxidize $\text{H}_2$ over the corroding surface of Mg.

### 3.4 Calibration of SECM in SG/TC mode for $\text{H}_2$ detection

#### 3.4.1 Sensing $\text{H}_2$ on a homogeneous Pt substrate and responsiveness of tip

The ability of the SECM technique used in SG/TC mode to detect $\text{H}_2$ generation through the electro-oxidation of the $\text{H}_2$ at the UME tip is assessed in this section using a Pt substrate in place of the Mg alloy. A Pt substrate provides an inert surface whereby application of a suitable reducing current will generate $\text{H}_2$ from the surface. This approach ensures that the only detectable species evolving from the substrate is $\text{H}_2$ and therefore eliminates the possibility of interferences (e.g. by $\text{Mg}^{2+}$) to $\text{H}_2$ detection at the UME tip.

The substrate was a Pt disk with 2000 $\mu$m diameter polished down to 4000 grit emery. In order to generate $\text{H}_2$, the Pt substrate was cycled between -0.75 and -1.15 V at a scan rate of 5 mV s$^{-1}$ in NaCl solution (Figure 3.2a). The potential was scanned from -0.75V down to -1.15V with the current becoming more negative (reducing current) at approximately -0.9V and continues until the potential reaches -1.15V. As the voltage is reversed back to -0.75V the current started to become less negative with a positive or oxidative current observed at approximately -0.95V. The reduction current is associated with the reduction of both the dissolved oxygen in the NaCl solution was well as the water [28] thus generating $\text{H}_2$. Vigorous $\text{H}_2$ bubbling was observed at the Pt substrate at potentials more negative than -0.9V, with these bubbles dislodging from the substrate and moving into the bulk solution.

The $\text{H}_2$ generated at the Pt substrate (as a result of the reduction of water) was subsequently oxidized at the 10 $\mu$m Pt UME (which was biased at a range of potentials and positioned 5$\mu$m above the Pt substrate), Figure 3.2b. The scan rate
used in Figure 3.2a was 5 mV s\(^{-1}\) and the time taken to cycle the potential from -0.75 to -1.15V and back to -0.75V was 160 sec with this represented in the x-axis of Figure 3.2b. Time 0 sec in Figure 3.2b corresponds to the potential at the Pt substrate being -0.75V and therefore since no H\(_2\) is generated at the Pt substrate there is no observable H\(_2\) oxidation current recorded at the UME (Figure 3.2b). The current in Figure 3.2b remains at zero until approximately 40 sec (indicated by an asterisk) upon which time there is a sudden increase in current. This increase in current also corresponds with the onset of the generation of a reduction current from the Pt substrate (Figure 3.2a - asterisk). As the reduction current in Figure 3.2a increased so too did the oxidation current recorded at the UME (Figure 3.2b) and this is attributed to the increased amount of H\(_2\) generated from the Pt substrate. As the potential was cycled back to -0.75V in Figure 3.2a the amount of H\(_2\) generated from the Pt substrate decreases and this is reflected in the decline of the oxidation currents recorded by the UME tip (Figure 3.2b). This illustrates the responsive nature of the UME in SG/TC mode for detecting H\(_2\) evolution at the substrate. This responsive property is critical for a scanning mode approach whereby the tip moves rather fast across the sample surface and is therefore only at a fixed point on the sample for a very short time (e.g., milliseconds time scales).
**Figure 3.2** Cyclic voltammetry (a) of the Pt substrate in 5.4 g.l\(^{-1}\) NaCl solution at a scan rate of 5 mV s\(^{-1}\). The arrows show the direction of the potential scan. The H\(_2\) oxidation current generated at the UME at a range of tip potentials (b). The diameter of the Pt UME was 10µm and was positioned at a constant height of 5µm above the Pt substrate. The asterisks indicate the onset of H\(_2\) generation from the Pt substrate (a) and the onset of H\(_2\) detection at the UME (b).

The magnitude of the oxidation current in Figure 3.2b varies with the biased potential applied to the UME. In general, a more negative potential at the UME tip results in an increase in the magnitude of the H\(_2\) oxidation current. This indicates that
application of a negative bias potential increases the oxidation efficiency of the H\textsubscript{2} at the UME tip. Since the solution was not buffered, the negatively polarised Pt substrate would generate reasonably high local pH that can influence the kinetics of HOR. This suggests that negative potentials of the probe might afford a higher sensitivity for detection of H\textsubscript{2} in high pH conditions. However, potentials more negative than -0.2 V must be avoided in order to eliminate interference of O\textsubscript{2} reduction processes with H\textsubscript{2} oxidation at the UME tip. The tip potential range at which O\textsubscript{2} reduction occurs and interferes with HOR will be further discussed in this chapter in section 3.5.1.

3.4.2 Effect of ions and varying pH on HOR detection

When using the SECM technique with corroding Mg alloys there is the possibility of local interfering species such as Mg\textsuperscript{2+} ions as well as localised increase in pH. To ensure that the increasing solution pH and the increased concentration of Mg\textsuperscript{2+} ions in the solution (caused by Mg corrosion) do not interfere with the H\textsubscript{2} sensing capabilities of the SECM in SG/TC mode, a series of experiments were performed using the inert Pt disk substrate. Cyclic voltammograms, shown in Figure 3.3, were recorded using the SECM UME positioned 5 µm above the Pt disk substrate that was biased at -1.0 V. The Pt disk substrate was biased at -1.0V in order to generate H\textsubscript{2} from the reduction of water. The CVs were recorded in a solution of 5.4 g l\textsuperscript{-1} NaCl with varying amounts of added MgCl\textsubscript{2} and NaOH (to investigate the effects of Mg\textsuperscript{2+} and pH, respectively). The CVs presented in Figure 3.3 show H\textsubscript{2} oxidation centred at approximately -0.40V detected by the 10 µm Pt UME. These results indicate that alkaline pH and increased concentration of Mg\textsuperscript{2+} ion has no detrimental effect on HOR at the UME.

\* NaCl is the major component of SBF solution used in this thesis with concentration of 5.4 g l\textsuperscript{-1}.
Figure 3.3 Cyclic voltammograms recorded using a 10 µm Pt UME positioned above a Pt disk substrate with tip-substrate distance of 5 µm in 5.4 g l⁻¹ NaCl. The arrows indicate the direction of the scanned potential. The Pt substrate was biased at -1.0 V while the UME potential was scanned at a rate of 10 mV s⁻¹. The dashed box represents the potential range at which hydrogen can be detected.

Although the cyclic voltammograms shown in Figure 3.3 does not show negative (reduction) current at potentials above -0.7 V, it is assumed that some O₂ reduction current is generated. However this current is superimposed and masked by the strong positive current associated with the oxidation of H₂. Therefore, in order to eliminate contribution to the tip potential from O₂ reduction, a potential in the range of -0.2 to +0.1 V (dashed box in Figure 3.3) was considered appropriate for mapping the H₂ evolution. Extending the UME tip voltage down to -0.8 V (Figure 3.3) shows a negative current which is associated with reduction of water. At potentials higher than +0.1 V, the probe current decreases with increasing potential indicating that the
HOR may diminish at positive potentials due to passivation of the Pt microelectrode itself via the loss of metal sites for H\textsubscript{2} adsorption [29].

Figure 3.4 shows the approach curves recorded in 5.4 g l\textsuperscript{-1} NaCl for a 25 \textmu m Pt UME approaching the Pt substrate (biased at -1.0 V). The Pt UME tip was also biased at a range of different potentials. Negative feedback (current decrease as the tip approaches the substrate) was observed at all probe potentials. This is in spite of the expected positive feedback in the vicinity of the Pt substrate due to the increase in local H\textsubscript{2} concentration [16]. The negative feedback effect is most likely due to the very high local pH in the vicinity of the Pt substrate [30].

![Figure 3.4](image-url)

**Figure 3.4** Current recorded at the UME tip in 5.4 g l\textsuperscript{-1} NaCl as it approaches the Pt disk substrate. The UME was biased at -1.0 V.

At a Pt substrate the hydrogen oxidation reaction (HOR) and its reverse reaction are both fast in an acidic electrolyte, but significantly slower in an alkaline electrolyte (H\textsubscript{2} + 2OH\textsuperscript{-} $\leftrightarrow$ 2H\textsubscript{2}O + 2e\textsuperscript{-}) [30]. In acidic electrolytes, hydrogen is produced by hydronium ion reduction (Equation 3.5) while in alkaline electrolytes, hydrogen is produced by water reduction (Equation 3.6).
It is known that, HOR is diffusion controlled in acidic and neutral media whereas in alkaline media the reaction becomes electron transfer (kinetically) controlled [30]. Also it has been reported that, in alkaline media, it is more difficult to oxidise H₂ [31] which explains the negative feedback shown in Figure 3.4. This theory was further investigated in Figure 3.5. It shows the approach curves for a 25 µm Pt UME on a large Pt disk substrate in buffered SBF solution (pH 7.4). In contrast to the NaCl solution, the response is a positive feedback (increase in current at the UME approaches the Pt substrate). This is consistent with the above hypothesis about HOR being harder in alkaline media and suggests that surface alkalization is not as strong in buffered SBF compared to the un-buffered NaCl solution.

![Figure 3.5](image-url)  

**Figure 3.5** SECM tip approach curves towards Pt disk electrode biased at -0.95V in SBF.
3.4.3 Spatial Resolution of SG/TC mode SECM image

The spatial resolution attainable with SECM depends on several factors such as the UME diameter and the proximity of the UME tip to the substrate. In principle, a small tip/surface separation is desirable to minimize non-perpendicular diffusion of reactants from the substrate towards the probe and enhance the resolution. An empirical approach has been chosen here to examine the SECM spatial resolution by probing H$_2$ generation in 5.4 g l$^{-1}$ NaCl from biased (at -1.0 V) Pt line arrays 35 µm wide and spaced approximately 1000 µm apart (Figure 3.6a). The substrate was polished down to 4000 grit with emery to achieve a uniform surface and the SECM images obtained by monitoring H$_2$ oxidation (Figure 3.6b). The current generated from the Pt lines varies from line to line (Figure 3.6c). Thus the H$_2$ generation appears to be non-uniform across this array. This difference is most likely associated with the variation in the individual Pt lines themselves. The results in Figure 3.6b and 3.6c show a broadening of H$_2$ detection that spreads outside the 35 µm Pt line arrays with maximum detection occurring above the Pt line. This suggests that the generated H$_2$ diffuses spherical to the substrate. The significantly higher detection peak at the centre of each Pt line that is presented in Figure 3.6b produces a high spatial resolution acquired by this technique.
Figure 3.6 Optical micrograph (a), SECM image (b) and SECM line scan (c) of 35 μm wide Pt line array spaced approximately 1000μm apart. Current generated from the oxidation of H$_2$ generated from the biased (-1.0V) Pt lines recorded using a 10 μm Pt UME (biased at 0.0 V) positioned at a distance of 5 μm above the substrate rastered across the Pt lines in the direction of the dashed arrow in (a). The electrolyte used was 5.4g l$^{-1}$ NaCl at pH 7.4.

Further studies were conducted to illustrate the diffusion profile of H$_2$ and its significance to the resolution acquired by SECM in HOR mode. Figure 3.7a illustrates the distribution of H$_2$ concentration that is generated at a 65μm diameter Pt disk substrate at different tip/substrate separations. The micro Pt substrate (Figure 3.7b) was biased at -1.0 V (Ag/AgCl) to produce a consistent rate of H$_2$ generation.
It is evident from Figure 3.7a that H₂ permeates spherical from its source towards the bulk electrolyte. An important implication of Figure 3.7a for H₂ sensing using SECM in HOR mode is the loss of resolution as tip/substrate separation increases.

![Figure 3.7](image)

**Figure 3.7** (a) Distribution of H₂ concentration versus distance from a 65µm diameter Pt disk substrate biased at -1.0 V (Ag/AgCl). (b) Optical micrograph of the Pt micro-substrate. SECM probe was a 10µm Pt UME biased at 0.0 V (Ag/AgCl). The tip/substrate separations were 2µm, 5µm, 10µm, 20µm and 30µm.

### 3.4.4 Correlation between H₂ electro-oxidation current and H₂ generation rate

In order to use SECM in H₂ detection mode as a quantitative measure of Mg corrosion, it is essential to calibrate the oxidative current measured by the UME with reference to the reduction current generating H₂ at the substrate. In tip generation/substrate collection (TG/SC) mode with large substrates (relative to the
tip size) the collection efficiency is essentially 1, meaning that the entire electroactive species generated at the tip is electrochemically converted and sensed at the substrate [19]. However, in the reverse situation, SG/TC mode, because of disproportional size factor between tip and substrate, only a fraction of electroactive species generated at the substrate is detected at the tip. It is also suggested that in small tip/substrate separation, the feedback effect may also contribute to the current being measured by the SECM tip.

Herein the relationship between HOR current measured at the SECM tip and the hydrogen evolution reaction (HER) current consumed at the substrate is studied. Figure 3.8 shows a cyclic voltammogram of a 10µm Pt UME at 5µm distance from a 65µm diameter Pt disk substrate. Substrate was biased at -1.0V (Ag/AgCl) to generated H₂ and UME was biased at 0.0V (Ag/AgCl) to electro-oxidize the H₂. Figure 3.8 indicates that the oxidative current measured by the tip (Figure 3.8a) is significantly larger than the associated H₂ reduction current consumed by the substrate (Figure 3.8b). One explanation for this can be the H₂ from surrounding domains (not directly below the tip) permeating towards the UMPE which is oxidized and contributes to the current measured by the UME tip. Earlier findings (Figures 3.6 and 3.7) showing spherical diffusion of H₂ are consistent with this hypothesis. The second contributing phenomenon is the feedback effect cause by H₂/H⁺ redox regeneration within the small separation gap between substrate and the UME probe.

Figure 3.8 also shows variation in substrate reduction current (Figure 3.8b) when the tip potential is cycled between -0.8 V and 0.5 V. The maximum reduction current (larger negative current in Figure 3.8b) is produced when the tip is biased within -0.4V to -0.2V which is the most efficient range of tip potential for HOR. At this range the HOR happens more effectively resulting in a less alkaline pH as explained earlier in section 3.4.2 (see reactions 3.5 and 3.6). This is also in favour of HER taking place at the substrate resulting in more effective reduction and larger current measured at the substrate.
Figure 3.8 (a) Cyclic voltammetry using a 10µm Pt UME as SECM tip at 5µm distance from a 65µm diameter Pt disk substrate and (b) the reduction current measured at the substrate. Substrate was biased at -1.0V(Ag.AgCl) to generated H₂. Current generated by substrate is calculated per surface area of UME tip (approx. 78.5µm²).

A further experiment was conducted to study the effect of permeating H₂ from surrounding domains (not directly below the UME) and also the feedback effect from H₂/H⁺ regeneration on the HOR current measured by the tip. In case the former
phenomenon dominates, the oxidative current should decrease when reducing the gap between tip and substrate. In contrast, if the feedback effect from \( \text{H}_2/\text{H}^+ \) regeneration plays the major part then reducing the gap between tip and substrate should increase the oxidative current exponentially. Figure 3.9 shows the approach curve of a 10µm Pt UME measured on a 65µm Pt disk substrate. The substrate was biased at -1.0V to generated \( \text{H}_2 \) and the tip was biased at 0.0V to oxidise the \( \text{H}_2 \). This result shows that feedback current from \( \text{H}_2/\text{H}^+ \) redox regeneration is the dominant contribution to HOR current measured by the tip in close proximity of substrate (e.g. <10µm). The \( \text{H}_2 \) permeation from the surrounding domains towards the tip is probably more important at higher tip/substrate separation.

![Figure 3.9 Amperometric approach curve using a 10µm Pt UME as SECM tip biased at 0.0V(Ag/AgCl) and a 50µm dia. Pt disk biased at -1.0V(Ag/AgCl) as substrate and source of \( \text{H}_2 \) generation.](image)

The electrochemical system proposed in Figure 3.10 illustrates how \( \text{H}_2 \) generation from surrounding domains contributes to the HOR current that is measured at the UME probe (solid radial arrows). It also demonstrates the redox regeneration of \( \text{H}_2/\text{H}^+ \) within the separation gap between substrate and the UME probe (broken arrows). This redox regeneration may also influence the substrate reduction current.
when the probe is appropriately biased to effectively oxidize H₂. This increase of reduction current can be seen as more negative current at the substrate in Figure 3.8b. The solid vertical arrow shows the H₂ generated at the substrate which is directly detected (collected) at the UME probe.

![Figure 3.10 Schematic representation of electro-oxidative H₂ sensing showing the contribution of a large area in H₂ supply at the Pt probe and redox regeneration of H₂/H⁺ within the separation gap between substrate and the probe. Pt substrate is negatively biased (e.g. -1.0 V (Ag/AgCl)) to generate H₂ while the probe is biased positive to H₂/H⁺ reduction potential (e.g. 0.0 V (Ag/AgCl) to electro-oxidize H₂.](image)

Due to the contribution of other phenomena (i.e. multi-directional diffusion of H₂ and feedback effect of H₂/H⁺) it is very difficult (if not impossible) to isolate the H₂ collection from a certain spot directly underneath the SECM tip and independently measure its current. It should also be noted that the feedback effect of H₂/H⁺ between two Pt surfaces, a Pt substrate and a Pt UME, studied here is different from (and most probably stronger than) the same feedback effect between a Pt and a Mg surface. This is due to different catalytic properties of Pt and Mg for H₂ reduction reaction. Therefore, H₂ detection using SECM in SG/TC mode cannot be utilized as a quantitative measure of corrosion for determining the absolute value of corrosion rate. However, as a qualitative and comparative tool it introduces new opportunities for studying and understanding the mechanism of Mg corrosion.
3.5 Detection of H\textsubscript{2} evolution on Mg surface

In this section, SECM in SG/TC mode is applied for the detection of H\textsubscript{2} at the surface of corroding Mg and relationship between domains of H\textsubscript{2} evolution, insulating properties and local pH at these domains and localized corrosion is studied.

3.5.1 Detection range

The results presented above demonstrate the ability of the SECM technique used in SG/TC mode to detect H\textsubscript{2} generated from a substrate via its oxidation at the UME. The sensitivity of this technique is shown to not suffer significantly from varying pH or increased concentration of Mg\textsuperscript{2+} ions and a high spatial resolution by detecting H\textsubscript{2} is obtained. Therefore, the suitability of this electrochemical technique to study the generation of H\textsubscript{2} from a corroding AZ31 Mg alloy surface in simulated body fluid (SBF) is presented below.

Figure 3.11 shows cyclic voltammograms recorded for a 10 µm Pt UME in SBF (pH 7.4) at a distance of 5 µm and 2000 µm above the surface of AZ31 Mg alloy as well as in SBF solution without dissolved H\textsubscript{2}. The anodic peak current centred at -0.3V corresponds to oxidation of the H\textsubscript{2} that is generated from the Mg surface due to the corrosion process (Equation 3.1). The magnitude of this current significantly drops as the distance between the UME and the Mg surface increases which is due to the decreasing concentration of H\textsubscript{2} further away from the corroding surface. In the absence of an Mg sample there is no source of H\textsubscript{2} generation resulting in the disappearance of H\textsubscript{2} oxidation peak (SBF (background) in Figure 3.11) in SBF.

As the potential is swept to voltages more positive than -0.3V the current associated with H\textsubscript{2} oxidation decreases. The decrease of current at highly positive potentials (i.e. > +0.3V) is most likely due to passivation of the Pt UME [29]. The loss of Pt UME sensitivity at positive potentials could also be due to formation of an inorganic
surface layer in complex electrolytes (e.g. calcium phosphate due to high pH) thus passivating the UME.

Figure 3.11 Cyclic voltammograms of Pt UME above an AZ31 surface in SBF and comparison with the redox behaviour of FeMeOH. The Mg substrate was held at OCP while the UME potential was swept at a scan rate of 10 mV s\(^{-1}\). The red dashed box represents the optimal potential range at which hydrogen oxidation is detected with no interference from O\(_2\) reduction. SBF background was obtained with no Mg alloy present in the solution.

The cyclic voltammogram of Pt UME in fresh SBF (“SBF background” in Figure 3.11) shows an increasing negative (reduction) current at potentials negative to -0.1 V which is related to the reduction of dissolved O\(_2\) in the SBF. In standard condition, at potentials negative to -0.2 V the reduction of O\(_2\) \((O_2 + 2H_2O + 4e^- \rightarrow 4OH^-)\) occurs in the solution open to air [32]. Mapping the O\(_2\) has been used previously in corrosion studies of metals [32,33], however it is a well-known fact that O\(_2\) plays no
role in corrosion of magnesium [34] and therefore should not be considered in SG/TC mode for studying Mg corrosion. In order to avoid any potential interference from O$_2$ reduction, a UME potential negative to -0.1 V was not used. The red-dashed box represents the range of probe potential at which H$_2$ oxidation can be sensed at the probe without interference from O$_2$ reduction. Although the cyclic voltammograms in presence of Mg specimen (Figure 3.11) does not show negative (reduction) current in the range of -0.1 V to -0.7 V, it is assumed that the O$_2$ reduction current is superimposed and masked by the strong positive oxidation current of H$_2$. Therefore, in order to eliminate contribution to the tip current from O$_2$ reduction, a potential in the range of -0.1 to +0.2 V was considered appropriate for mapping the H$_2$ evolution. Extending the tip voltage down to approximately -0.8 V (Figure 3.11) shows an exponential increase in reduction current which is associated with reduction of water. Similar to Pt array substrate (Figure 3.6), a good resolution and high sensitivity was observed at tip potential of 0.0 V which is the bias potential for tip used throughout this thesis for SECM experiments in SG/TC mode.

### 3.5.2 Implication of H$_2$ evolving areas relative to anodic/cathodic activity

In this section, SECM in SG/TC mode was performed to study the localised corrosion of an AZ31 alloy and provide insight into the H$_2$ generating domains and their relevance to the localized corrosion process. A 25µm Pt UME biased at 0.0 V (this bias voltage was chosen as it falls within the red box region shown in Figure 3.11 and shows acceptable sensitivity and resolution for H$_2$ oxidation) was used as SECM tip. The aim of this work was to further understand the local H$_2$ evolution and its relationship with the anodic/cathodic domains on an AZ31 surface. By scanning an area of the Mg sample using SECM in SG/TC mode, it is possible to generate a H$_2$ evolution map (Figure 3.12a). The versatility of this technique also allows for a bias potential to be applied to the Mg substrate which provides the opportunity to investigate corrosion processes under polarised conditions. The OCP of the Mg sample was measured to be approximately -1.7V at the time of acquiring the H$_2$ evolution map shown in Figure 3.12a. Subsequently the Mg substrate was polarised...
H2 detection using SECM in surface generation/tip collection mode

Chapter 3

Figure 3.12 Hydrogen evolution maps (a-c) and the associated surface profile (d) of AZ31 immersed in 10 times diluted SBF. HE maps were acquired by SG/TC mode of SECM using a 25 µm Pt tip biased at 0.0 V. The potential of AZ31 substrate was (a) unbiased (OCP), (b) polarised anodically relative to OCP at -1.5 V, and (c) polarised cathodically relative to OCP at -1.8 V. Note the different scales between (a) and (c).

The negative difference effect (NDE) describes the increase in H2 evolution from the Mg surface in an anodically polarised state and is clearly observed with the larger H2 evolution current in Figure 3.12b compared to Figure 3.12a and agrees with previously published data [35,36]. It is evident from the increase in current observed...
in Figure 3.12c that there is also an increase in the generation of H$_2$ from the Mg surface under cathodically polarised conditions.

It is anticipated that the regions of the Mg surface that possess better conductivity or cathodic catalytic properties should dominate the H$_2$ evolution reaction [37]. Major domains of H$_2$ evolution at OCP (Figure 3.12a – the example is indicated by the black arrow) remain the same when the Mg is polarised positive to the OCP (Figure 3.12b). However, the activity of these same domains is significantly diminished in the more cathodically polarized state (Figure 3.12c - the example is indicated by the black arrow) and become the sites with the least H$_2$ evolution. The profilometry result (Figure 3.12d) reveals that the original domains of H$_2$ evolution (at OCP) are associated with regions of both negative (white arrow) and positive (black arrow) profiles with the corrosion pits being associated with the negative profiles. This indicates both pit formation and a build-up of corrosion product deposits in the areas where the H$_2$ evolution is dominant.

Theoretically, corrosion pits form at the anodic sites by active dissolution of Mg and build-up of corrosion product is more often observed at cathodic sites where higher pH triggers precipitation of calcium phosphates and magnesium hydroxide. However, further investigation with complementary methods such as scanning Kelvin probe (SKP) and scanning vibrating electrode technique (SVET) is required to determine the exact relevance of H$_2$ evolution sites to their anodic/cathodic activity. SKP is a scanning technique capable of determining distribution of electrochemical potential on the surface and SVET is able to measure local current densities thus identifying local anodes and cathodes.

Figure 3.13 shows the SEM micrograph and EDXS elemental maps from the lower left corner (approximately 900µm×700µm) of the area shown in Figure 3.12a (black dashed box). Comparing the profile map (Figure 3.12d) and EDXS elemental map for Al, it appears that pit formation occurs in close proximity of Al inclusions. This is consistent with the findings of Williams and McMurray [38] who studied a single
corrosion pit. However, the results presented here show that pit formation and domains of H$_2$ evolution are not limited to the areas with Al inclusion and are also found randomly distributed on the Mg surface. The heterogeneous nature of electrochemical activity at corrosion pits has also been shown previously by Lamaka et al. [9] using ion selective and vibrating electrode scanning techniques.

Figure 3.13 SEM micrograph and elemental analysis results for Al, O, Mg and P from the lower left corner of the AZ31 surface subjected to SECM experiments (shown in Figure 8a).

3.5.3 Relevance of H$_2$ evolution sites to their insulating/conducting properties

In this section, the same Mg surface that was investigated by AC and potentiometric modes in section 2.4.3 and 2.5.3 is studied in SG/TC mode. The purpose was to understand whether there is a relationship between domains of H$_2$ evolution and their insulating properties as well as local pH. Figure 3.14a shows the H$_2$ map from the same surface studied in Figures 2.13, 2.16 and 2.19. Figure 3.14b shows the optical micrograph of the sample after experiment. Upper scale colors (magenta and blue) indicate the areas with high H$_2$ evolution rate whereas the lower scale colors (red and
yellow) that represent the relatively passive areas with low H$_2$ evolution. Comparing Figures 2.13 and 3.14a, a relatively higher activity/conductivity is observed at the main domains of high H$_2$ evolution. This result is in line with the micro-galvanic corrosion mechanism (discussed in section 1.3) in buffered media [39] and chloride containing solutions [40] caused by intermetallic particles.

![Image](image.png)

**Figure 3.14** (a) H$_2$ map on the surface Mg alloy AZ31 in SBF after 1 hr immersion acquired by SECM in SG/TC mode and (b) optical image of the surface after immersion. A 10$\mu$m Pt UME was used as SECM probe at 5$\mu$m distance from the substrate (Mg) surface. Probe potential was 0.0V (Ag/AgCl).

Corrosion properties of Mg alloys to a large extent depend on the formation and stability of the passive surface layers. Combining the results shown in Figure 2.13 and 3.14a, it is postulated that the local formation of surface layer in SBF is connected to de-activation of those domains of surface for H$_2$ evolution. The particularly high pH at H$_2$ evolving sites shown by comparing Figures 2.19 and 3.14a, can be explained using two different theories. The first theory is based on the proximity of cathodic and anodic sites resulting in formation of corrosion pits close to intermetallics (e.g. Al intermetallic inclusions). The high pH measured at the corrosion pits can then be explained by $OH^-$ generated in cathodic process near the
anodic sites. The second theory is based on existence of Mg unipositive cation or Mg$^+$. This theory considers corrosion of Mg in a two steps process involving dissolution of Mg to Mg$^+$ in the first step followed by further oxidation of Mg$^+$ to Mg$^{2+}$ in the second step. The second step also involves reduction of water and evolution of H$_2$ as well as alkali production as detailed in Equation 3.7.

$$Mg^+ + H_2O \rightarrow Mg^{2+} + \frac{1}{2} H_2 + OH^- \quad (3.7)$$

The high local pH consistent with domains of high H$_2$ evolution can therefore be explained by the second theory or taking into account the existence of Mg$^+$. However, there is major ongoing debates in the recent literature over the existence of Mg$^+$ and source of H$_2$ evolution during the corrosion of Mg [35,37,41–46]. It is believed that H$_2$ detection using SECM in SG/TC mode has a great potential for future research and clarification in this area particularly if combined with other scanning methods.

### 3.6 Conclusion

SECM in SG/TC mode presents a novel way of studying corrosion rate with a local approach. Due to contribution of other sources of H$_2$ (i.e. radial diffusion of H$_2$ from surrounding area and the feedback effect by H$^+/H_2$ redox regeneration) to HOR, H$_2$ measurement in SG/TC mode cannot directly be used to calculate absolute dissolution rate of metal. However, it is believed that the technique holds great promise as a qualitative and comparative method for studying the corrosion rate of Mg. SG/TC mode SECM allows for instantaneous measuring of the H$_2$ evolution as a direct measure of corrosion rate. Also combining the data with that acquired by other modes of SECM (feedback, AC and potentiostatic modes), it helps in better understanding the corrosion mechanism of Mg.
Special care must be taken in setting the bias potential at the UME tip as this will dominate what is oxidized or reduced (and therefore measured) at the tip. At potentials positive to +0.3V the Pt tip becomes insensitive to H$_2$ and therefore this is the appropriate potential range to perform feedback mode imaging with no interference from H$_2$ oxidation. At potentials negative to -0.1V there is interference from oxygen reduction and therefore this range should also be avoided.

H$_2$ sensing was performed in a controlled environment with H$_2$ generated at a Pt substrate to further understand the effect of near surface high pH and dissolved Mg$^{2+}$. It was found that high pH in close vicinity of the substrate reduces the sensitivity of the Pt UME due to the change in mechanism of H$_2$ electro-oxidation. Such loss of sensitivity was not found in buffered media, SBF. H$_2$ sensing was implemented to study the local H$_2$ evolution on the surface of AZ31 Mg alloy. Explicit regions of H$_2$ evolution were found associated with Al intermetallic particles as well as domains of Mg dissolution.
References


Chapter 4

Studying the effect of protein on the corrosion of AZ31 using EIS and SECM in simulated biological fluid
4.1 Background

The principal rate-limiting factors in the aqueous corrosion of magnesium alloys are associated with the breakdown of the surface film and the rate of its reformation [1]. Depending on the composition of the Mg alloy and its surrounding environment, a complex surface layer may form on the alloy surface in biological environments containing complex chemical species [2,3]. This surface layer breaks down in a physiological environment in the presence of chloride ion [4–7]. Biological environments also contain organic compounds which may adhere or adsorb to the implant and alter the corrosion behaviour. The protein albumin is the most abundant blood protein and plays a significant role in the degradation rate of Mg alloys. There has been evidence showing that albumin forms a layer on the Mg surface in the early stages of contact which can be destroyed in the long term [2,8]. Mueller et al. [7] observed an increase of corrosion rate as a consequence of adding albumin into the media. They suggested that the discontinuous protein film formed on Mg surface does not provide effective protection and intensifies the localized corrosion. On the contrary, the presence of albumin has been reported to inhibit corrosion on AZ91 and Mg-Ca alloys in SBF [9,10]. It was suggested that the adsorbed layer of protein interacts with aluminium oxide and forms a protective layer which impedes the diffusion of ions. More recently Yang et al. [11] showed that the protein may increase or decrease the corrosion rate depending on the composition of the alloy or the composition of buffer used for the in vitro studies. They observed increased corrosion rate of Mg-Dy (Dysprosium) alloys in cell culture media as a result of added protein and attributed this to the binding of Mg$^{2+}$ and Ca$^{2+}$ ions to the serum albumin molecule. It has been reported that protein can chelate metal ions such as Fe, Ti, Zn, Cr, Ni, Co and Cu and enhance the corrosion rate [12–16].

The ability to probe the localised corrosion of Mg alloys will provide invaluable insights into the early stages of corrosion process and such knowledge is essential in determining and controlling the service life [17]. Among the scanning electrochemical based techniques, SECM has the unique capability of interacting with electroactive species that participate in corrosion reactions with the ability to locate active dissolution sites [18]. The high spatial resolution achieved by precise
positioning of an ultra-microelectrode above the corroding surface of metal elucidates the corrosion regime at different stages and helps to better understand bulk corrosion characteristics. The aim of this study is to utilize EIS and SECM together with SEM to investigate the corrosion behaviour of AZ31 in SBF with and without the presence of protein. Several parameters have been extracted from EIS experiments including the constant phase element or CPE (shown by symbol $Q$) with the exponent $n$ (also shown by $\alpha$ in some literature) that is attributed to the consistency of electrochemical properties across the surface [19,20]. By definition, a $n$ value of 1 represents an ideal capacitor and a value of 0 represents an ideal resistor. For a simple $RQ$ circuit the pseudo-capacitance associated with $Q$ can be determined by $C = Q^{1/n}R^{(1-n)/n}$, where $R$ is the resistance parallel with the $Q$ forming the time constant $RQ$ and $n$ is the non-linearity exponent. These elements have been used in analysing the results of EIS measurements. Given the good mechanical properties, market availability and relatively low Al content, the AZ31 has been widely studied as a biocompatible/biodegradable Mg alloy in the literature and will be looked at in this study. The effect of albumin on the corrosion of AZ31 in buffered electrolyte is examined using bulk and local electrochemical techniques.

4.2 Experimental

4.2.1 Material and sample preparation

Mg alloy AZ31 (3% Al, 1% Zn and 0.3% Mn) was supplied by Goodfellow in the form of sheet with 2 mm thickness. Electrochemical impedance spectroscopy (EIS) and open circuit potential (OCP) measurements were conducted using samples 5 mm in length. SECM experiments were performed using 5 x 5 mm sheets. All specimens were abraded using 600, 1200 and 4000 grit emery consecutively to a gloss finish and cleaned with acetone before exposure to electrolyte.

Simulated biological fluid solution and AZ31 Mg specimens were prepared similar to the procedure described in Chapter 2 (section 2.2).
The protein used was bovine serum albumin (BSA), fraction V from Sigma and used as received. Concentration of serum albumin in the human body is in the range of 3.5-5 g dl\(^{-1}\) [21]. In addition concentration of albumin at 4 g dl\(^{-1}\) (4% w/v) has been used elsewhere as a realistic concentration in \textit{vitro} [2,10,22] and is therefore was used in this study. The SBF and SBF containing 4% w/v BSA solutions were stored at 4 °C when not in use. Throughout this paper A-SBF represents the SBF solution containing 4% w/v BSA and SBF represent the simulated biological fluid without protein.

4.2.2 Methods

Open circuit potential (OCP) was measured against the Ag/AgCl (3M NaCl) reference electrode. OCP data was collected with 0.1Hz sampling rate so that any potential transients could be detected. Electrochemical impedance spectroscopy was performed using a standard 3-electrode set-up, employing a 10 kHz-10 mHz frequency range and a ±5 mV (rms) perturbation around the OCP. A Pt mesh served as the auxiliary electrode and Ag/AgCl (3M NaCl) served as the reference electrode. All OCP and EIS experiments were conducted using the automated CH instruments electrochemical workstation model 660D with CHI integrated software version 11.17.

SECM experiments in SG/TC mode were performed according to the method described in Chapter 3 for detecting H\(_2\) evolution from corroding surface of AZ31.

Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) studies were performed using a JEOL 7500FA field emission scanning electron microscope. Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy was performed using Shimadzu AIM8000 FT-IR with a germanium ATR attachment.
4.3 Results and discussion

4.3.1 Surface characterization
Scanning electron microscopy utilizing energy-dispersive X-ray spectroscopy (SEM/EDS) characterization of freshly prepared AZ31 (Figure 4.1) reveals the heterogeneous distribution of Al intermetallic inclusions. The higher concentration of O at the Al inclusion spots is due to the pre-existing oxide that forms rapidly in air on the surface of both Al and Mg. These intermetallic phases can potentially act as galvanic cathodes and accelerate the alloy’s corrosion process [23].

![Figure 4.1 SEM micrograph of fresh prepared AZ31 (a) and SEM/EDS elemental mapping for Mg (b), Al (c), O (d).](image)

The cross-section of the oxide layer that formed on the AZ31 after 2 days immersion in the SBF was subjected to SEM-EDS elemental mapping (Figure 4.2). The results
demonstrate a relatively heterogeneous structure of surface deposits rich in Ca, P, Al and O.

**Figure 4.2** SEM micrograph of a cross section of AZ31 after 2 days immersion in SBF (a) SEM/EDS elemental mapping for Mg (b), Al (c), Ca (d), C (e), O (f) and P (g).

In order to ascertain the possible source of these elements ATR-FTIR analysis was performed on the AZ31 surface after immersion in the SBF (Figure 4.3). Two ATR-FTIR spectra were recorded from different locations on AZ31 after 1 day immersion in SBF. Figure 4.3a shows characteristics of an apatite type film with the bands at 864 cm\(^{-1}\) and 1026 cm\(^{-1}\) associated with PO\(_4^{3-}\) and 1400 cm\(^{-1}\) and 1454 cm\(^{-1}\) associated with the CO\(_3^{2-}\) incorporated into the apatite structure [24]. The bands at 1612 cm\(^{-1}\) and 3329 cm\(^{-1}\) are bending and stretching modes of OH from the intercalated water [24]. Spectra recorded from other regions of the sample did not
show bands associated with CO$_3^{2-}$ suggesting other forms of calcium phosphate are present on the sample surface (Figure 4.3b). The bands at 1157 cm$^{-1}$ and 779 cm$^{-1}$ are associated with P-O. The broad band at 3545 cm$^{-1}$ region and 1658 cm$^{-1}$ were assigned to O-H stretching and bending of H$_2$O. The bands at 852 cm$^{-1}$ and 1411 cm$^{-1}$ regions were ascribed to CO$_3^{2-}$ vibration mode. The differences between these two spectra indicate that the surface film after 24 hr immersion in the SBF is in fact heterogeneous in nature, being a mixture of hydroxyapatite and hydrated calcium phosphates.

Figure 4.3 ATR-FTIR spectra of the AZ31 surface taken at two separate locations of the sample. The spectra were taken in air at room temperature. The AZ31 sample was immersed in SBF for 24 hrs then dried in air prior to the ATR-FTIR analysis.
4.3.2 Effect of adding protein to SBF

SEM micrographs and SEM-EDS analysis of AZ31 sample immersed in A-SBF solution are shown in Figures 4.4a and 4.4b. EDS analysis of the surface of the sample was performed with the results of the chemical composition displayed in Table 4.1. Nitrogen (N) is detected in the sample immersed in A-SBF whilst in Figure 4.2 (immersed in SBF alone) there was no N detected. The presence of N is attributed to adsorbed protein (N arising from the amine components of BSA) as indicated by point 4 in Figure 4.4a. This protein deposit is observed to cover the surface as a discontinuous layer. Whilst the compound HEPES, present in SBF, also contains N the lack of N in Figure 4.2 (AZ31 immersed in SBF only) supports the claim that the N is arising from the adsorbed BSA.

Further elemental analysis of the cross-section of the surface film (Figure 4.4b-4.4i) reveals the presence of N also within the surface film. The appearance of the nitrogen in this composite layer is also attributed to the amine groups of the adhered protein. The nature of the protein contained in this composite layer is unknown, however given the potentially high pH near the Mg surface [25] it is expected that the protein is in its denatured state as proteins have been shown to denature in high pH environments [26]. There are two types of distinct deposits identifiable in Figure 4.4a, namely at points 1 and 3. Point 1 represents the relatively dense and adherent surface layer. Point 3, in comparison, shows a porous structure deposited discontinuously with higher percentage of C and less O. The presence of C in the surface layer formed on Mg alloy in SBF and A-SBF has been shown elsewhere [8] and it is likely to originate from the carbonate content of SBF. The cracked mud shape of the surface film (Figure 4.4a) is due to the dehydration of surface film after the sample was dried for SEM. Point 2 shows a very high percentage of Mg compared to all other points and is attributed to the magnesium beneath the cracked surface layer.
Effect of protein on corrosion of AZ31

Figure 4.4 SEM micrograph from oxide surface formed on AZ31 after 2 days immersed in A-SBF (a). The numbers refer to points on the sample where elemental analysis was performed using EDS and shown in Table 4.1. SEM cross section (b) and elemental mapping for Mg (c), Al (d), Ca (e), C (f), N (g), O (h) and P (i).

Table 4.1 Elemental analysis results associated with the points shown in Figure 4.4a.

<table>
<thead>
<tr>
<th>Elements</th>
<th>C (%)</th>
<th>N (%)</th>
<th>O (%)</th>
<th>Mg (%)</th>
<th>Al (%)</th>
<th>P (%)</th>
<th>S (%)</th>
<th>Ca (%)</th>
<th>Zn (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Point 1</td>
<td>19.8</td>
<td>-</td>
<td>51.4</td>
<td>17.6</td>
<td>2.62</td>
<td>3.64</td>
<td>-</td>
<td>2.45</td>
<td>0.21</td>
</tr>
<tr>
<td>Point 2</td>
<td>8.9</td>
<td>-</td>
<td>5.9</td>
<td>82.4</td>
<td>2.11</td>
<td>-</td>
<td>0.11</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>Point 3</td>
<td>27.2</td>
<td>44.78</td>
<td>18.67</td>
<td>1.55</td>
<td>3.41</td>
<td>-</td>
<td>3.07</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>Point 4</td>
<td>32.4</td>
<td>11.8</td>
<td>44</td>
<td>4.3</td>
<td>0.31</td>
<td>2.77</td>
<td>0.16</td>
<td>3.26</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 4.5 shows the ATR-FTIR spectra from the surface of the AZ31 surface after (a) 1 hr and (b) 24 hr immersion in A-SBF. In Figure 4.5a, the band at 1396 cm⁻¹
region may be assigned to CO$_3^{2-}$ but also to albumin [27]. The bands at 999 cm$^{-1}$ and 848 cm$^{-1}$ are associated with PO$_4^{3-}$ and HPO$_4^{2-}$ from the calcium phosphate. The 3356 cm$^{-1}$ and 1612 cm$^{-1}$ bands are assigned to the OH stretch and bending mode for intercalated water, respectively [24]. The ATR-FTIR spectrum of AZ31 after 24 hr in A-SBF shows a composition relatively similar to the sample immersed in SBF for 24 hr (Figure 4.3b).

![ATR-FTIR spectra](image)

**Figure 4.5** ATR-FTIR spectra of the AZ31 surface after (a) 1 hr and (b) 24 hr immersion in A-SBF at room temperature.

### 4.3.3 Bulk electrochemical properties

The Nyquist plots of AZ31 immersed in SBF and A-SBF for different immersion periods is shown in Figure 4.6a and 4.6b respectively. The equivalent electrical circuits (EEC) are included in Figure 4.6a and were used to fit the experimental data
and extract the individual components of the corroding system. EECs where chosen based on the physical state of the surface and in respect to the number and shapes of the detected time constants. The EIS data presented in Figure 4.6a shows the diameter of MF capacitive loop increasing for the duration of experiment, in addition a distinct inductive loop is shown at MF range at 48 hr immersion. In A-SBF up to 14 hr, the plots consisted of one high frequency (HF) capacitive loop, one medium frequency (MF) capacitive loop and one low frequency (LF) inductive loop. After 14 hr, the inductive loop disappeared while the diameter of both HF and MF capacitive loops kept increasing up to 24 hr. Subsequently, the MF capacitive loop shrunk and then disappeared after 28 hr and HF capacitive loop also began to shrink. Medium (374 Hz) and low (11 Hz) frequencies shown in Figure 4.6b represent the lower limits of the first capacitive loop and the lower limit of the EIS scan, respectively.

The HF capacitive loop is attributed to a charge transfer process at the interface between the metal surface and the corrosive medium [28]. The MF capacitive loop is related to the mass transport, i.e., the diffusion of ions through the corrosion product layer [29]. The LF induction loop has been attributed to various origins, including the existence of the metastable species [1,30,31], passivating oxide [32], discontinuous surface and roughness [33] and adsorption/desorption processes [34,35]. The inductive loop observed after long immersion time has also been attributed to pitting corrosion and discontinuity of surface film [31,36]. Given the physical evidence by SEM micrographs Figures 4.2, 4.4, 4.10 and 4.11 (later in this chapter), the discontinuity of surface layer and surface roughness are likely causes for appearance of inductive loop in EIS results.
Figure 4.6 Nyquist plots of AZ31 at different immersion periods in SBF (a) and A-SBF (b). The EIS data was obtained under OCP conditions.

Resistance data including charge transfer resistance or $R_{ct}$ (obtained at HF domain) and diffusion resistance or $R_{diff}$ (obtained at LF domain) were extracted from the EECs and are presented in Figure 4.7. The first 8 hrs of immersion is magnified in the Figure 4.7b for better illustration of changes in the early stages.
Throughout the duration of the experiments, as long as the two HF and MF capacitive time constants are detectable, the charge transfer resistance was always larger than diffusion resistance (Figure 4.7). This suggests that a major fraction of the surface is covered with adherent and dense surface film, limiting the exposed area at which the charge transfer takes place. Formation of a denser surface film also has an impact on the diffusion resistance which is observed as the increase of $R_{\text{diff}}$.

**Figure 4.7** Changes of $R_{\text{ct}}$ and $R_{\text{diff}}$ during 42 hr (a) immersion in SBF and A-SBF solutions and an expanded view of the first 8 hr of immersion (b).
There is an initial sharp increase in both the $R_{ct}$ and $R_{diff}$ domains when immersed in A-SBF compared to SBF. The resistance increases for approximately 1.5 hr then reaches a steady state. Subsequently, $R_{ct}$ and $R_{diff}$ recorded in A-SBF begin to increase after 5 hrs, exhibiting values similar to those observed in the SBF. After approximately 24 hr the $R_{ct}$ and $R_{diff}$ drop in A-SBF, whilst $R_{ct}$ remain constant and $R_{diff}$ increases further after 24 hrs immersion in the SBF.

The sharp increase of $R_{ct}$ and $R_{diff}$ in A-SBF in the early stages of immersion (Figure 4.7) might be due to the quick formation of a resistive layer of protein on the Mg surface, thereby hindering the diffusion process and confining the areas at which charge transfer takes place. In contrast, a consistent build-up of deposits on the AZ31 in the SBF leads to a gradual increase of $R_{ct}$ and $R_{diff}$. Similar behaviour has been reported by Wang et al., indicating rapid adsorption of albumin on the Mg surface in the early stages of immersion, resulting in a lower corrosion rate [8]. In the latter stages of immersion, albumin could chelate the corrosion product as reported by Yang et al. [11], lowering the $R_{diff}$ and $R_{ct}$ by forming a more porous and permeable surface film.

Capacitance values were obtained from the constant phase elements (CPE) in the EEC model shown in Figure 4.6a at both HF and LF domains. The changes of CPE exponent $n$ at HF and LF domains in both SBF and A-SBF solutions are given in Table 4.2. The exponent $n$ increases slightly at HF and decreases significantly at LF in both solutions as immersion time increases with no significant difference between SBF and A-SBF solutions. The LF capacitive loop disappeared after 28 hr therefore no data is presented in Table 4.2. The small variation of exponent $n$ at HF is attributed to the experimental error while the values indicated a relatively ideal capacitor for the HF domain. The large decrease of $n$ exponent in the LF domain could be attributed to the decrease in the continuity of the surface layer as anodic and cathodic sites establish in the long term. The observed increase of surface roughness with increasing immersion time could change the diffusion profile which is reflected as decrease of LF exponent $n$ in the Table 4.2.
Table 4.2  CPE exponent $n$ at HF and LF domains in SBF and A-SBF as a function of immersion time.

<table>
<thead>
<tr>
<th>Immersion time</th>
<th>HF in SBF</th>
<th>HF in A-SBF</th>
<th>LF in SBF</th>
<th>LF in A-SBF</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min</td>
<td>0.84</td>
<td>0.89</td>
<td>0.96</td>
<td>0.92</td>
</tr>
<tr>
<td>1.5 hr</td>
<td>0.89</td>
<td>0.88</td>
<td>0.87</td>
<td>0.88</td>
</tr>
<tr>
<td>9 hr</td>
<td>0.89</td>
<td>0.88</td>
<td>0.89</td>
<td>0.89</td>
</tr>
<tr>
<td>28 hr</td>
<td>0.90</td>
<td>0.91</td>
<td>0.67</td>
<td>0.68</td>
</tr>
<tr>
<td>40 hr</td>
<td>0.91</td>
<td></td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The capacitance values obtained from the EECs shown in Figure 4.6a are presented in Figure 4.8. Double layer capacitance ($C_{dl}$) was obtained from the HF domains whilst the diffusion capacitance ($C_{diff}$) was obtained from the LF domain. The $C_{diff}$ is attributed to the dielectric characteristic of the surface film in which the formation of a dense film with insulating characteristic results in higher $C_{diff}$. An increase of $C_{diff}$ in the LF domain is observed after 24 hr immersion (Figure 4.8). The slow increase of $C_{dl}$ is associated with the increasing surface roughness (more effective in the early stages of corrosion) and formation of a surface film with higher dielectric constant (more effective in the long term). These results are consistent with the $R_{ct}$ and $R_{diff}$ results presented above for immersion times greater than 24 hrs.
Figure 4.8  Pseudo-capacitance at high and low frequency for AZ31 immersed in SBF and A-SBF. Note different scales in y-axis. $C_{\text{diff}}$ data could only be obtained for immersion time up to 29hr.

The OCP was measured against Ag/AgCl during 48 hrs immersion in SBF and in A-SBF solutions with results presented in Figure 4.9. It shows a shift to more noble potentials due to the addition of albumin to the SBF in the early stages (first 2 hr) of corrosion. This potential shift in A-SBF could be associated with formation of a porous layer of protein that confines the dissolution of Mg and hence, renders the surface less active and is in line with the results of Liu et al. [9,10]. Liu et al. suggested that electrostatic bonding between negatively charged amino acid groups (present in albumin) and metal cations may form a relatively stable layer which impedes the dissolution of the native oxide layer, resulting in a more positive potential. However, in the long term the specimen in contact with BSA acquires a relatively more active potential, which is consistent with the formation of a less protective film. Alternatively, it could be a result of a larger fraction of anodic area for the specimen in contact with BSA [37]. The pH of both solutions were measured throughout the immersion period and showed a slight increase from the original pH of 7.4 after 24 hrs to 7.6 for SBF and 7.5 for A-SBF which was considered insignificant.

It is reasonable to assume that a relatively more discontinuous surface film forms in contact with BSA where the areas free of deposition form a larger anode, resulting in a shift towards more anodic potentials. The potential transients in SBF after 24 hrs immersion could be associated with meta-stable pitting [38].
Figure 4.9 OCP recorded in SBF and A-SBF.

4.3.4 Local electrochemical activity using SECM

SECM experiments were conducted to study the local H$_2$ evolution (HE) from the AZ31 alloy immersed in SBF and A-SBF solution for 24 hrs. The HE maps of the AZ31 surface in SBF and in A-SBF solutions after 10 min, 1 hr, 7 hr, 18 hr and 24 hr immersion periods are shown in Figure 4.10. The current (colour) scale was unified for both SBF and A-SBF at each immersion time in order to make the comparison easier. Significantly lower HE in A-SBF solution compared to SBF (as indicated by the lower currents generated) is observed throughout the entire immersion times. Figure 4.10 imply a relatively lower corrosion rate of AZ31 in A-SBF compared to SBF during the 24 hrs immersion. This supports the hypothesis of protein film formation in the early stages of corrosion as suggested by Retting et al. [2] and by Wang et al. [8] using bulk corrosion measures. Formation of an insulating protein layer may reduce both the H$_2$ generation and the feedback effect, resulting in remarkably lower tip current density.
The number of active sites (regions of higher current) decreased over the immersion period in SBF while it remained unchanged in A-SBF after the initial first 10 min. Reduction in the number of active sites in SBF could be a result of corrosion undercutting of intermetallic inclusions or their coverage with passive deposits. The location of well-established active sites in presence of protein remained relatively unchanged after 24 hrs immersion.
Figure 4.10 HE maps of AZ31 during 24 hrs immersion in SBF and A-SBF. Images were acquired by SG/TC mode of SECM with 25 µm Pt tip biased at 0.0 V (Ag/AgCl). The AZ31 substrate was unbiased.
The isolated sites with relatively high tip current density are most likely cathodic sites producing hydrogen (e.g. at noble intermetallic inclusions). The increased dissolution of Mg in the form of Mg$^{2+}$ when coupled to Al and Fe has been previously shown by Souto et al. [39]. From the optical micrographs (Figures 4.11a and 4.11b) and profilometry maps (Figure 4.11c and 4.11d) of the specimens, it appears that highly active HE domains are located on the non-corroded part of the samples. Profilometry results also clearly show smoother profile associated with less corrosion of the AZ31 after immersion in A-SBF compared to the specimen immersed in SBF. Both specimens have undergone localized corrosion as shown in Figure 4.11c and 4.11d, while HE maps generated by SECM in SG/TC mode (Figure 4.10) show limited ability to distinguish the corrosion pattern.
Figure 4.11 Optical micrographs and profilometry maps of the AZ31 samples (from the same area that was subjected to SECM mapping, Figure 13) after 24 hr immersion in (a and c) SBF and (b and d) A-SBF. Optical micrographs were produced while the specimens were immersed.

It has been suggested that surface alkalization in the long term decomposes protein structure and releases amino acids that can act as effective chelating agents [2,8], causing an increase in corrosion rate. However, due to the increased surface roughness after long term corrosion and the high sensitivity of SECM to the surface roughness, the SECM analysis was not continued after 24 hrs immersion.

4.4 Conclusion

The effect of protein on the corrosion of AZ31 in simulated biological fluid was studied. The theory based on formation of a layer of protein on the surface of Mg in the early stages of corrosion is also supported by the data presented here. It is suggested that the protein layer forms a relatively resistive layer which reduces the corrosion rate. The early formation of protein film renders the surface more anodic in the long term accompanied with the lower $R_{ct}$. It remains unclear whether this is due to the formation of a thinner and/or more porous film or to enhanced removal of corrosion product in the presence of protein.

SECM was successfully utilized to look at the local hydrogen generation on the surface of AZ31 in SBF and A-SBF solutions. The HE maps produced by SG/TC mode of SECM may be used as a direct measure of corrosion. It was shown that adsorption of protein confines the $H_2$ generation in the early stages of corrosion. In the long term though, it resulted in stabilized cathodic/anodic areas which can potentially enhance localized corrosion. In the context of load bearing biodegradable Mg implants it is crucial to ensure that mechanical integrity of implant remains intact for the duration that scaffolding support is expected from the implant. This study
showed that the presence of protein does not lead to less localized degradation which is detrimental to the structural strength of Mg.
References


[26] G. Mermigidis, pH-spectrum of bovine albumin, pH-Spectra Database,


Chapter 5

Corrosion protection afforded by rare earth (RE) compounds on AZNd alloy
5.1 Background

Studies have gone on in the past decade to improve bio-corrosion properties of magnesium alloys through alloy engineering [1–3] and surface modifications [4–6]. Apart from the rapid corrosion of magnesium, its tendency for localized corrosion in presence of chloride [7,8] is a serious drawback that significantly reduces the in-vivo service life [9]. The vulnerability to localized corrosion is even more pronounced in applications such as arterial stenting where the extensive deformation of metal structure during angioplasty induces internal stress and structural defects [10].

Corrosion inhibitors have been widely used to afford a uniform corrosion pattern and avoid early failures due to highly localized corrosion [11]. Rare earth (RE) based corrosion inhibitors have gained increasing attraction as a replacement for the toxic chromate based inhibitors in the last decade [12]. The inhibitive properties of RE compounds were first discovered by Hinton et al. on corrosion protection of aluminium in saline media [13] with the effectiveness of rare earth compounds as green corrosion inhibitors being demonstrated for ferrous metals [14–16], zinc [17] and aluminium [18–20]. The high efficiency of rare earth elements (REE) in inhibition of localized corrosion is also reported [21]. They are widely added as alloying component into Mg alloy composition to improve the mechanical properties [22,23] and degradation/corrosion rate of alloys [24]. In biomedical application, use of any chemical compound should also be considered from the perspective of their potential cytotoxicity. In the case of RE compounds, anti-carcinogenic properties of many REs has been evidenced in number of studies [25–28], however some studies have shown cytotoxic and hepatotoxic effects at elevated dose of Gd, Y, Ce and Pr [29–32]. It has been shown that rare-earth alloying elements including Ce, Nd, Y, and Yb have no adverse effect on growth of living cells but they can induce inflammatory effects at high concentration [33]. In vitro cytotoxicity of 10 REEs was performed by Feyerabend et al. on primary human and mouse cells [34]. Their results demonstrated highest relative cytotoxicity of La and Ce while good cell viability was achieved in presence of Eu, Nd and Pr.
Inhibitive effect of RE compounds as a conversion coating for protection of Mg was first studied by Rudd et al. [35]. They observed an improved corrosion properties for pure Mg and WE43 alloy treated by La(NO$_3$)$_3$, Ce(NO$_3$)$_3$ and Pr(NO$_3$)$_3$ in the early stages of contact with borate buffered media followed by breakdown of passivation and rise of corrosion in the long term. They attributed the short term protective characteristics of conversion layers to formation of mixed magnesium/RE oxide/hydroxide film while the long term deterioration was attributed to penetration of electrolyte underneath the conversion layer and increase of film porosity due to corrosion of Mg. Improved corrosion properties of AZ31 in dilute saline media was reported by Montemor et al. by application of La and Ce conversion layers [36]. Short term protection afforded by conversion layer was attributed to the cathodic inhibition due to deposition of insoluble RE oxide/hydroxide. Improved corrosion resistance of AZ91, AM50 and AZ63 alloys with Ce conversion layer was also reported elsewhere [37,38]. A more homogeneous conversion layer was formed by CeCl$_3$/H$_2$O$_2$ when acid pickling was applied as a surface pre-treatment. It has been shown that good corrosion protection with a dynamic self-healing characteristic is afforded as long as the active (trivalent RE cation) corrosion inhibitor is available to Mg surface [39]. However, the protection afforded by the conversion layer deteriorates by removing the inhibitor from corrosive media. Similar instability of REE conversion layer was also reported by Zucchi et al. [40]. They investigated Ce conversion layers produced by Ce$_2$(SO$_4$)$_3$ and CeCl$_3$ which revealed an unstable conversion layer without sufficient protective characteristics in the long term. These studies indicate a requirement for a complementary protection mechanism to stabilize the inhibition afforded by REEs.
A different approach to obtain consistent and uniform corrosion protection with REE inhibitors has been the incorporation of REEs into stable polymeric matrixes which results in longer lasting self-healing characteristics [41]. Incorporation of RE inhibitors into organic coatings to improve protection properties on aluminum [42], Zinc [43], stainless steel [44] and galvanized steel [45,46] has been successfully implemented. Significant improvement of silane coating with Ce and La nitrate for protection of AZ31 alloy has been reported by Montemore et al. [47]. Biocompatibility, good adherence and chemical stability of silane coatings in addition to the extensive range of possible structures and functional groups make them an ideal choice as tie-layer between Mg surface and protective layer. Also silane treatment as an stand-alone anti-corrosive layer for Mg has been shown previously with the barrier effect being the main protection mechanism [40]. Biodegradation is the basic requirement for the coating to be used to temporary protect a biodegradable metal implants. Use of chitosan as polymeric layer with long term release of Ce³⁺ corrosion inhibitor to obtain self-healing ability over aluminium has been recently reported by Zheludkevich et al. [48,49]. Biocompatibility and flexible biodegradation properties of poly(lactide-co-glycolide) or PLGA has been shown elsewhere [50,51]. Biodegradable PLGA and a novel chitosan based polymer are used in this study as reservoir for REE corrosion inhibitors to formulate self-healing coatings with uniform protection of Mg alloy AZ31 for biomedical applications.

In the present chapter, inhibitive performance of two REEs, praseodymium and cerium, in form of inorganic chloride and nitrate salts for protection of Mg alloy will be investigated. The study includes inhibition efficiency of RE compounds in form of dissolved salt in SBF, as a passivation conversion coating on Mg surface as well as organic coating doped with RE compounds applied on Mg surface. This chapter focuses on the use of SECM as the main technique of studying corrosion behaviour in simulated biological environment coherent to the rest of this thesis.
5.2 Experimental

5.2.1 Materials

AZNd was designed and supplied by Boston Scientific with the approximate composition of Al 7.26%, Zn 0.59%, Mn 0.10%, Nd 0.66% (all in Wt%) and the balance Mg. XRF analysis measured the composition as Al 7.3%, Zn 0.32%, Mn 0.024%, Nd 0.63% and the balance Mg. The first composition detailed above is the actual quantities of elements used during the casting of the AZNd alloy. The XRF analysis was performed to investigate if contaminants entered the alloy composition during the casting process. The mismatch between the two compositions arises because the XRF results are collected at random locations on the surface of the alloy and do not match the average bulk composition. Further detail regarding the composition and corrosion properties of this alloy may be found in Ref. [52].

Mg alloy AZ31 (3% Al, 1% Zn and 0.3% Mn, and the balance Mg all in Wt%) was purchased from Goodfellow in the form of sheet with 0.5 mm thickness.

Simulated biological fluid was prepared using analytical grade reagents with the recipe given in the previous chapters.

Ce(NO$_3$)$_3$, CeCl$_3$, Pr(NO$_3$)$_3$, PrCl$_3$ were analytical grade purchased from Sigma.

All specimens were abraded using 600, 1200 and 4000 grit SiC emery consecutively and ultrasonically cleaned in isopropanol before exposure to electrolyte.

5.2.2 Methods

Scanning electrochemical microscopy (SECM) was performed using CH instruments SECM model 920D. 10µm and 25 µm Pt microelectrodes and an Ag/AgCl were used as working and reference electrodes. A three dimensional SECM image in constant height mode was obtained by rastering the tip in the x-y plane and recording the tip function against its tip location. The distance between tip and substrate was adjusted using an integrated digital microscope manufactured by MEIJI Techno model MS50. An area of 2000x2000 µm was examined and the rest of surface was masked with tape to eliminate interference. In the generation/collection mode, the probe was
biased at 0.0 V(Ag/AgCl) for direct detection of H₂ evolution via the H₂ electro-oxidation at the probe. Figure 5.1 illustrates the laboratory configuration for SECM experiment (Fig. 1a) and basic principles of data acquisition in SG/TC and AC modes (Figure 5.1b and 5.1c, respectively). Further details of the experimental procedure and data acquisition are given in chapters 2 and 3 of this thesis.

**Figure 5.1** (a) Schematic representation of SECM set-up and (b) principle of data acquisition for hydrogen probing in SG/TC mode and (c) measuring local resistivity of surface in AC mode. A 25µm Pt UME was used as WE at 5µm distance from Mg substrate. R_T and C_T are resistance and capacitance of the tip, respectively; R_Sol is the solution resistance; R_{mg} and C_{mg} are the resistance and capacitance of the magnesium surface and R_{ce} and C_{ce} are the resistance and capacitance of the cerium conversion layer.
Electrochemical impedance spectroscopy (EIS) was performed using a CH Instruments electrochemical workstation model 660D. Pt mesh and Ag/AgCl were used as working and reference electrodes respectively. Frequency range of scan was 10 kHz to 10 mHz with 10 mV perturbation around OCP.

Surface profile was examined using a wyko NT9100 optical profilometer (Veeco instruments Inc.). Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS) studies were performed using a JEOL 7500FA field emission scanning electron microscope.

All experiments were performed at room temperature, 22±2 °C.

5.3 Results and discussion

Structural and electrochemical characterization of Pr conversion film presented here aims at examining the level of corrosion protection afforded by the surface treatment and understanding the protection mechanism.

5.3.1 Corrosion inhibition by dissolved rare-earth compound in solution

The simplest way to examine efficiency of an inhibitor is to measure the passivation afforded by that inhibitor when the active inhibitor is in an electrolyte in contact with the metal surface. Information acquired from this examination will help in understanding the mechanism of corrosion protection by that inhibitor when it is incorporated in a polymeric layer and applied to the metal surface. The latter will provide a longer lasting supply of active inhibitor to the metal but at the same time due to a more complex protection mechanism (i.e. barrier protection as well as active corrosion inhibitor) it will be more difficult to understand the significance of corrosion inhibitor independently from the barrier characteristic of coating. Therefore it is important to examine the protective efficiency of inhibitor without
presence of a polymeric phase in aqueous electrolyte. Figures 5.2 and 5.3 compares the impedance spectrums (Nyquist plots) of AZNd alloy in SBF solution (Figure 5.2) with AZNd alloy in SBF containing 1 mM Pr(NO$_3$)$_3$ (Figure 5.3). These EIS results indicate an evolution of a more resistive passive layer on AZNd surface in presence of 1 mM Pr(NO$_3$)$_3$ compared to the AZNd surface in SBF without Pr(NO$_3$)$_3$. Both the charge transfer (high frequency domain) related impedance and the surface layer impedance (low frequency domain) grew larger in presence of Pr(NO$_3$)$_3$. Higher charge transfer impedance is an indicative of better coverage of metal surface with passive layer leaving less unprotected/non-covered area exposed to corrosive media. The higher impedance in low frequency domain (surface layer related) is indicative of a denser and more impermeable layer forming in presence of Pr(NO$_3$)$_3$.

![Nyquist plots](image)

**Figure 5.2** Nyquist plots from EIS experiments on AZ80X during 58 hr immersion in SBF
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Figure 5.3 Nyquist plots from EIS experiments on AZ80X during 58 hr immersion in SBF+1mM Pr(NO$_3$)$_3$.

Figure 5.4 shows changes of OCP values for AZNd samples in SBF and SBF+1 mM Pr(NO$_3$)$_3$ solution. The more positive OCP values in presence of Pr(NO$_3$)$_3$ and in particular the relatively quick shift of OCP towards positive values in the first 6 hours of immersion indicates formation of a more stable surface layer in presence of RE corrosion inhibitor. This early established stable layer maintains its more positive potential throughout the measurement for 58 hours.
Figure 5.4 OCP value of AZNd during 58 hours immersion in SBF and SBF + 1mM Pr(NO₃)₃ Solution.

Figure 5.5a-f presents SECM images of AZNd surface in surface generation / tip collection and AC modes of operation for mapping hydrogen evolution (HE map) and insulating properties of the surface layer, respectively. Data was collected using a 25 µm Pt microelectrode. For the purpose of comparison, HE map for AZNd in SBF solution without Pr(NO₃)₃ after 45 min immersion which was acquired using similar microelectrode and settings (e.g. tip-substrate separation, bias potential etc) is also given in Figure 5.5g. An immediate implication of HE map results of SECM is the significantly lower corrosion rate of AZNd in presence on Pr(NO₃)₃ indicated by lower H₂ electro-oxidation current.
Figure 5.5 SECM imaging results in SG/TC and AC modes on AZNd alloy surface in SBF with (a-f) and without (g) 1mM Pr(NO$_3$)$_3$ in the solution. Sequential images of H$_2$ evolution (HE map) were acquired in SG/TC mode of SECM in presence of Pr(NO$_3$)$_3$ after (a) 15 min, (b) 45 min, (c) 1.5 hr, (d) 2.5 hr and (e) 3.5 hr immersion. Phase map (f) from AC-SECM imaging was acquired after 5 hr immersion in SBF containing Pr(NO$_3$)$_3$. HE map on AZNd in SBF without Pr(NO$_3$)$_3$ after 45 min immersion is also acquired for the purpose of comparison as a control specimen. SECM tip was a 25 µm Pt Microelectrode. In SG/TC mode the tip was biased at 0.0 V (Ag,AgCl) to detect H$_2$ evolution via electro-oxidation of H$_2$. Scan frequency in AC mode was 1000 Hz with 50 mV perturbation around OCP.

Sequential HE maps presented in Figure 5.5 show a consistent decrease in H$_2$ evolution (as indicated by the decreasing current) over the period of immersion in SBF + 1mM Pr(NO$_3$)$_3$ indicating reduction in corrosion rate over time. This is believed to be due to formation of a passive oxide layer which improves the protective properties due the presence of Pr(NO$_3$)$_3$. The phase map (from AC-SECM imaging) presented in Figure 5.5f shows an inhomogeneous formation of passive layer on the surface of AZNd. Lower phase value\(^1\) is associated with larger local impedance. Note the phase map (Figure 5.5f) and HE maps (Figures 5.5a-e) were not acquired from the same location on the surface of AZNd sample.

5.3.2 Conversion coating

Chemically formed conversion layers are inert forms of metal oxide precipitated by reaction between active compounds and the metal surface. The process usually involves formation of a complex intermediate including hydroxide forms of REE [53] which precipitates on the metal surface and then further oxidation of REE resulting in formation of an insoluble RE oxide on the surface [54]. Conversion coatings based on lanthanum (La), cerium (Ce) and praseodymium (Pr) has been shown to provide levels of corrosion protection to the underlying metal substrate and

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\(^1\) Phase shift component of AC response from AC-SECM measurements. Refer to section 2.4.3 of this book for further explanation of the significance of phase shift value.
their protective properties have been studied for number of Mg alloys such as WE43 [35] AZ31 [36], AZ91, AM50 [37], AZ63 [38] and WE43 [40]. Majority of these studies have shown effective corrosion protection afforded by the REE conversion coating in the short term (e.g. under 24 hr) that tends to deteriorate as exposure time to corrosive environment increases. The corrosion inhibition mechanism of REE is often attributed to the deposition of an insoluble passive RE oxide/hydroxide film at cathodic domains [36,55]. The process is facilitated by high pH near the metal surface as the intermediate and oxide forms of REE become less soluble in alkaline pH [56]. Use of nitrate salts of REEs is a popular method of deposition of RE based conversion coating on metal since the oxidizing nature of nitrate facilitates oxidation of REE from trivalent state (soluble) to tetravalent state (insoluble) and provision of an alkaline near surface environment.

Preliminary studies were conducted to find the optimum concentration of Pr(NO$_3$)$_3$ in the conversion bath and immersion time as well as the pre-treatment of Mg coupons. It was found that low concentrations of Pr(NO$_3$)$_3$ (Figure 5.6a) or too short immersion time (Figure 5.6b) tend to produce a discontinuous PrOx film while using high concentrations (e.g. > 0.5 M Pr(NO$_3$)$_3$) or long immersion time (Figure 5.6c) tend to severely attack the Mg substrate and produce a rough surface which was confirmed by optical profilometry method.
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Figure 5.6 Optical micrograph of AZNd surface after formation of conversion layer in (a) 0.05 M Pr(NO$_3$)$_3$ for 2 min, (b) 0.2M Pr(NO$_3$)$_3$ for 30 s and (c) 0.2 M Pr(NO$_3$)$_3$ for 5 min.

Also it was found that surface pre-treatment by 0.2 M NaOH for 2 min resulted in a more uniform PrOx film and less corrosion attack during immersion in the conversion bath. The effect of the alkali pre-treatment in the NaOH solution has been extensively studied elsewhere [57–59] and shown to produce a dense and passive Mg(OH)$_2$ layer. The role of Mg(OH)$_2$ passive layer in formation of a more uniform and less defective PrOx conversion coating is believed to occur due to controlling the rise of pH and localized attack at the surface of Mg. It has been shown that precipitation of intermediate compounds during the formation of rare earth oxide at the surface of Mg is facilitated by an increased pH [36,53,60]. An unprotected Mg surface will undergo a severe localized attack in the presence of a strong oxidizing agent such as NO$_3^−$. It is believed that the alkali pre-treatment in a NaOH solution provides a moderately protective layer that controls the pH and minimizes the localized corrosion during formation of the conversion coating.
To produce a more uniform conversion coating, AZNd specimens were immersed in 0.2M NaOH solution for 2 min. Conversion layers were then deposited on the surface by immersing the Mg alloy in 0.2M RE(NO₃)₃ solution for 30 sec. Specimens were then rinsed with DI water and dried with N₂. This method produced a film with 700 nm to 1µm thickness confirmed by SEM analysis at the cross-section of samples (Figure 5.7). Pr treated samples were sputter coated with a 15 nm layer of Pt to minimise beam charging and heating effects and cast into epoxy resin in preparation for cross sectioning. Cross sections were analysed using back scatter SEM at an accelerating voltage of 15 kV and a spot size setting of 14. The brighter areas in Figure 5.7 correspond to the higher atomic numbers which is attributed to Pr conversion coating.

Figure 5.7 SEM micrograph (in back scatter mode) from cross-section of AZNd treated in 0.2M Pr(NO₃)₃ solution for 30 sec to form a Pr₂O₃ conversion coating on the surface. The specimen was mounted in epoxy for the purpose of sample preparation.

SEM micrographs shown in Figure 5.8a and 5.8b illustrate the nano-porous structure of the Pr treated AZNd surface. EDX analysis (Figure 5.9 and Table 5.1) identified the chemical composition of surface layer as Pr₂O₃. The cracks in the Pr₂O₃ film
shown in Figure 5.8a were not observed under optical microscope examination (Figure 5.8g) before the SEM analysis and therefore appearance of these cracks were attributed to the dehydration of the conversion film in vacuum chamber during SEM analysis.
Figure 5.8 SEM micrographs (a and b) and elemental mapping (c-f) showing morphological structure of Pr$_2$O$_3$ layer on AZNd surface treated for 30 sec in 0.2 M Pr(NO$_3$)$_3$. The optical image (g) shows the Pr treated AZNd surface prior to undergoing SEM analysis.

![SEM micrographs and elemental mapping](image)

Figure 5.9 EDX elemental analysis of PrOx conversion layer on AZNd surface formed via immersion in 0.2M Pr(NO$_3$)$_3$ solution for 30 Sec. Quantified data are presented in table 1.

Table 1 Results of elemental and component analysis of Pr based conversion layer on AZNd surface confirming formation of Pr$_2$O$_3$ compound.

<table>
<thead>
<tr>
<th>Element</th>
<th>[norm. wt.%]</th>
<th>Compound</th>
<th>[norm. wt.%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>16.82</td>
<td>Compound</td>
<td>0.00</td>
</tr>
<tr>
<td>Magnesium</td>
<td>4.06</td>
<td>MgO</td>
<td>6.73</td>
</tr>
<tr>
<td>Aluminium</td>
<td>0.94</td>
<td>Al$_2$O$_3$</td>
<td>1.77</td>
</tr>
<tr>
<td>Praseodymium</td>
<td>78.18</td>
<td>Pr$_2$O$_3$</td>
<td>91.50</td>
</tr>
</tbody>
</table>
Further elemental analysis was performed on randomly found defective areas of the conversion coating such as the area shown in red-dashed box in Figure 5.10a. Figure 5.10a and 5.10b show a defective domain of the surface treatment where the Pr conversion layer did not completely cover the Mg surface.
Figure 5.10 AZNd surface treated for 30 sec in 0.5M Pr(NO$_3$)$_3$, (a & b) morphological structure of Pr$_2$O$_3$ layer by SEM showing the porous structure and (c-g) elemental mapping by EDXS showing a defective layer formed at the location of Al intermetallic inclusion.
EDX elemental mapping (Figures 5.10 c-g) at this location reveals high percentage of Al content and also an inclusion of Nd with no Pr conversion coating within the detection limits of EDX. This indicates that Pr conversion layer may have a selective affinity for growth on different phases of Mg alloy and may preferentially not grow as a uniform film on Al or Nd containing intermetallics.

The insulating properties of the Pr conversion film on the surface of AZNd was examined using SECM in AC mode by producing AC approach curves and maps of local impedance before and after immersion in SBF. Corrosion resistance of Pr conversion film is studied using SECM in the SG/TC mode for measuring $H_2$ evolution from the Mg surface as a direct measure of corrosion rate. Comparison between $H_2$ maps and phase maps are made to further understand the protection mechanism.

Figure 5.11 shows the local impedance and $H_2$ evolution domains for a Pr treated (Figures 5.11a and 5.11c) and non-treated (Figures 5.11b and 5.11d) AZNd in dilute SBF. In Figures 5.11c and 5.11d upper scale colours (e.g. dark brown) represent higher rate of $H_2$ evolution while lower scale colours (e.g. dark green) represent lower rate of $H_2$ evolution. Comparison between Figure 5.11a and 5.11b (note different scale bars) reveals a more insulating characteristic of the Pr treated AZNd surface due to the formation of PrOx layer [36]. Further comparison between the two surfaces can be made via $H_2$ evolution rate shown in Figures 5.11b & 5.11c. Figure 5.11c shows a significantly lower rate of $H_2$ evolution (note the different scale bars) at the surface of the Pr treated AZNd, indicating a significantly lower rate of corrosion, correlating with the more resistive surface measured in Figure 5.11a, presumably due to the formation of a Pr rich conversion film. It is also clear that the domains on the surface which are less insulating result in the greatest $H_2$ evolution. For example, on the non-protected surface localized currents as high as 9nA (Figure 5.11d) are recorded when the surface impedance is at its lowest value (Figure 5.11b).
Figure 5.11 Local impedance and H$_2$ evolution on the surface of (a & c) a Pr treated AZNd and (b & d) a non-treated AZNd in dilute SBF obtained by SECM in AC and SG/TC modes. SECM tip was a 25µm Pt UME. AC mode was performed with ±200mV AC excitation amplitude at 1kHz and 5µm tip-to-substrate distance. Tip potential in SG/TC mode was 0.0V. Impedance map and H$_2$ evolution map of each sample were collected from the same location.

Two locations (marked as A and B in Figure 5.11a) on the surface of Pr treated AZNd were selected as representative domains for contrasting levels of insulating properties. AC approach curves were produced at A and B and are shown in Figures 5.12a and 5.12b, respectively. An AC approach curve on the surface of non-treated
AZNd was also produced and is shown in Figure 5.13. Positive feedback (i.e., increasing normalised impedance as the UME tip approaches the AZNd surface) was observed for the treated surface (Figure 5.12a and 5.12b) at low frequencies (i.e. \( f \leq 42\text{kHz} \)) while slight negative feedback (i.e., decreasing normalised impedance as the UME approaches the AZNd surface) was observed at high frequencies (i.e. \( f > 42\text{kHz} \)).

The positive feedback observed at low frequencies was stronger at location B (Figure 5.12b) compared to A (Figure 5.12a), consistent with the higher impedance measured here. The slightly stronger negative feedback at higher frequencies at location A (Figure 5.12a) indicates higher ionic content of the electrolyte at this location resulting from the corrosion process. It should be noted that similar to conventional AC impedance spectroscopy, the impedance in AC-SECM at sufficiently high frequencies is mainly dominated by the solution resistivity \[61\]. Details on the elements playing a part in defining the AC impedance at each frequency domain is given in Ref. \[61\]. This observation is also consistent with results of a previous study \[62\] that showed correlation between areas of higher conductivity, higher \( \text{H}_2 \) evolution and greater ionic (OH\(^-\)) content.

AC approach curves at the surface of the non-treated AZNd (Figure 5.13) show significantly weaker positive feedback at low frequencies, again consistent with lower impedance values measured for this surface, while stronger negative feedback at high frequencies indicates generation and accumulation of ionic species at the surface, most likely due to increased corrosion products from the AZNd surface.
Figure 5.12 AC (impedance) approach curves on Pr treated AZNd recorded in dilute SBF. (a) is associated with location A in Figure 5.11a and (b) is from location B in Figure 5.11a. Approach curves were obtained using a Pt UME (25µm diameter tip) SECM probe with applied AC excitation amplitude of ±200mV starting from a tip-to-substrate distance of 75µm.
Figure 5.13 AC (impedance) approach curves on AZNd recorded in dilute SBF obtained using a Pt UME (25µm diameter tip) SECM probe with applied AC excitation amplitude of ±200mV starting from a tip-to-substrate distance of 75µm.

Results of the local impedance and H₂ evolution for the Pr treated and non-treated samples after 2hrs immersion in SBF are shown in Figure 5.14. The H₂ evolution maps were acquired in non-dilute SBF in order to examine the performance of the Pr conversion layer in a highly corrosive medium. The horizontal lines observed in Figures 5.14c and 5.14d are believed to be due to excessive H₂ evolution in non-diluted SBF and small H₂ pockets occasionally attaching to the UME tip. It is noteworthy to mention that these lines are consistent with the horizontal direction of scan and that these lines were not observed in the images acquired in dilute SBF. The same regions of the AZNd samples displayed in Figure 5.11 are also displayed in Figure 5.14. Comparisons of Figures 5.11a and 5.11b with Figures 5.14a and 5.14b illustrate that the major domains of low impedance (e.g. top right corner in Figure 5.11a and 5.11b) remain at the same location after 2h of exposure to highly corrosive SBF media. However, some other domains which initially showed high impedance now show less insulating characteristics after 2 hours immersion in this more aggressive medium. It has been suggested that the porous structure of PrOx films allows for penetration of corrosive ions [35] such as chloride and leads to under-film corrosion of Mg. Nevertheless, the hydrogen evolution reaction still appears...
suppressed on the treated AZNd with the untreated sample when the absolute currents are noted in Figures 8c and 8d, indicating an effective corrosion protection afforded by the Pr treatment surface probably due to formation of a Pr conversion layer.

Passivation of less insulating domain and formation of insulating areas is most likely due to precipitation of calcium phosphate from SBF at high pH near Mg surface. Given the extremely low solubility of RE oxide/hydroxides in alkaline pH [56] it is highly unlikely that formation of insulating domains on Pr treated AZNd after exposure to SBF be due to dissolution of Pr species and then precipitation at another area. The correlation between insulating property and H\textsubscript{2} evolution remains the same in SBF, compared to the dilute SBF, with domains of lower insulating properties being the major areas of H\textsubscript{2} evolution. Also comparison between Figures 5.11c and 5.11d reveals significantly lower levels of H\textsubscript{2} evolution on the AZNd surface that was treated by Pr conversion film indicating an effective corrosion protection afforded by the Pr treatment.
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Figure 5.14 Local impedance (a and b) and H₂ evolution (c and d) obtained on the surface of a AZNd sample, treated (a and c) with Pr and untreated (b and d) after immersion in SBF for 2hrs. SG/TC (H₂ evolution) measurements were performed in non-dilute SBF and then the samples were transferred to dilute SBF to perform the AC mode measurement. AC maps were obtained with ±200mV AC excitation amplitude applied to the tip at 1kHz and 5µm tip-to-substrate distance. The SG/TC maps were obtained using a 25 µm Pt UME with bias tip potential of 0.0V (Ag.AgCl).

The inhomogeneity of surface treatment and its protective performance can be explained by the inhomogeneous nature of the Mg alloy. Al rich intermetallic particles often serve as cathode in micro-galvanic corrosion cells on Mg alloys [63,64]. The inhibition mechanism of REE is often attributed to the deposition of an
insoluble passive RE oxide/hydroxide at cathodic domains, e.g. Al rich intermetallic particles [36,55]. However, Pr treatment with nitrate salt solution results in defective growth of Pr₂O₃ on Al/Nd containing intermetallic particles. It has been shown that precipitation of passive oxide is facilitated by increased pH at the surface of Mg. It is plausible that intermetallic particles are passivated immediately after exposure to Pr(NO₃)₃ solution and make no significant contribution towards cathodic process. This could be either by formation of a very thin film of Pr₂O₃ or Al oxide/hydroxide on the intermetallic particles. Thereby the local pH does not increase at these domains resulting in no further PrOx film deposition. It does not seem that corrosion protection in the short term immersion is influenced by the micro-defects in PrOx film at the location of intermetallics as evident by no significant contribution of these domains in H₂ evolution. It seems more likely that nano-porous structure of PrOₓ film allows an effective penetration of corrosive ions [35], e.g. Chloride, thus leads to under-film corrosion of Mg.

5.3.3 Self-healing corrosion protection using RE compounds

In principle a defectless organic coating with high level of barrier characteristics can effectively protect the underlying metal substrate against corrosion. However in practice deformation of metal, handling and friction induce cracks and structural defects to protective layer where corrosive species can access the underlying metal and initiate corrosion. Thus a strategy to protect the metal at defective areas is also crucial. A solution to the problem is the addition of corrosion inhibitors to the protective organic coating which protect the damage zones through the so-called “self-healing” effect to enable the formation of another protective layer [65]. Self-healing effect is generally defined as the ability of coating to recover after a mechanical damage and effectively continues protecting the underlying substrate. In most cases this is achieved by replenishing the damaged area with reactive chemicals being stored in the coating layer. However in the concept of anticorrosive coatings the recovery of coating integrity is not obligatory as long as the metallic substrate is kept under protection [41]. Organic coatings may be loaded with corrosion inhibitors such as RE compounds to release to the defected areas and passivates the exposed
metal surface once a defect is induced [48,49]. RE compounds also participates in formation of insoluble oxide/hydroxide compounds that effectively blocks ionic pathways [66] and passivates the active dissolution sites [47]. Figure 5.15 demonstrates a proposed mechanism for corrosion inhibition of Ce\(^{3+}\) triggered by increased pH at cathodic site.

**Figure 5.15** Proposed mechanism of corrosion inhibition for Ce\(^{3+}\) doped organic coating at defect area [67].

It is generally acknowledged that RE based conversion coatings have no self-healing characteristic due to the very low solubility of RE oxide and hydroxide forms [56]. However, it has been suggested that damaged RE oxide film can be replenished if active (soluble trivalent cation) RE compound is available in the environment. Experiments detailed in this section focus on the self-healing ability of the Pr oxide conversion coating. Conversion coating was prepared according to the method outlined in section 5.3.2. AZNd substrate was masked with tape before deposition of conversion coating in order to produce an artificial defect. Figure 5.16 shows the optical image of specimen with 300µm wide uncovered surface. Neighbouring the Pr treated and non-treated surface also brings about the possibility of immediate
comparison between surfaces in terms of corrosion activity. Specimen was immersed in both dilute SBF and standard (non-dilute) SBF solutions and corrosion behaviour was looked at by imaging H$_2$ evolution in SG/TC mode of SECM. As shown in Figure 5.17, the non-treated part of Mg surface (light brown area in both images) exhibited significantly higher level of H$_2$ evolution which indicates more intense corrosion occurring where the surface is not protected by PrOx film.

**Figure 5.16** Optical image of AZNd surface, partially covered by Pr oxide conversion coating.
Figure 5.17 SECM image of local impedance H₂ evolution in SG/TC mode on the surface of AZNd, partially treated with Pr conversion coating immersed in dilute SBF after (a) 10 min and (b) 3 hr immersion. The SG/TC maps were obtained using a 25 µm Pt UME with bias tip potential of 0.0V (Ag.AgCl).

After 6 hours immersion in dilute SBF, the solution was changed to dilute SBF containing 1mM Pr(NO₃)₃. H₂ imaging was conducted successively (Figures 5.18a-5.18d) to examine local changes in corrosion activity. As shown in Figures 5.18a-5.18d, during 6 hrs immersion in a solution containing active corrosion inhibitor, 1mM Pr(NO₃)₃, corrosion rate in the (initially) non-treated part of surface decreased. This is evident by less H₂ evolution compared to the part that was originally coated by PrOx conversion coating. The mechanism of this transformation is most likely attributed to more alkaline condition at the non-treated part of surface that underwent more intense corrosion when exposed to corrosive media. More intense corrosion results in a highly alkaline pH near the surface resulting in precipitation of the intermediate species (Pr oxide/hydroxide) and subsequent deposition of Pr₂O₃. Coverage of AZNd surface by the oxide film can be observed as significant reduction in H₂ evolution rate and transformation of the areas with originally higher H₂ evolution into areas with less H₂ evolution compared to the rest of surface after immersion in electrolyte containing Pr³⁺. It is also noteworthy that overall level of H₂ evolution reduced significantly (note the difference in current scale bars) as a result of active inhibitor being present in the environment.
Figure 5.18 Successive H$_2$ imaging of partly Pr treated AZNd in dilute SBF solution containing 1mM Pr(NO$_3$)$_3$ after (a) 5min, (b) 1hr, (c) 5.5hr and (d) 8hr immersion.

Impedance imaging by SECM in AC mode was conducted after 6 hrs immersion in dilute SBF containing 1mM Pr(NO$_3$)$_3$ in order to confirm formation of a resistive layer at the originally unprotected area. Figure 5.19 present the local impedance map of surface. Phase value associated with each domain of impedance is also given. Figure 5.19 shows presence of a domain with higher local resistivity where the surface was not originally treated, confirming formation of insulating layer at this domain.
Figure 5.19 Local impedance map acquired by SEM in AC mode at the surface of partially Pr treated AZNd after 12 hrs immersion in dilute SBF. AC map was obtained with ±200mV AC excitation amplitude applied to the tip at 1kHz and 5µm tip-to-substrate distance. SECM tip was a 25 µm Pt UME.

5.3.4 Polythiophene based conducting polymer

In order to further improve anti-corrosion performance and cyto-compatibility of AZNd and Pr conversion coating, surface treatment and combination of Pr conversion coating with biodegradable conductive polymers was investigated. The main challenge in this approach is to find an appropriate polymeric material with high level of cyto-compatibility and appropriate degradation rate. A high level of bio-compatibility is crucial for any material that is used as arterial stent in order to reduce inflammatory effects and rejection of stent by artery tissue following stent angioplasty. Such successful biodegradable implant requires a scaffold compatible with surrounding cells but should eventually disintegrate leaving the appropriate cellular structure in place. While the polymeric scaffold needs to retain its integrity for a suitable period of time, it must eventually break down into components that can be eliminated from the body without toxic effects. To this effect, conducting polymers (CPs) have been extensively researched as platforms or components of platforms to promote cell adhesion and proliferation with [68,69] and without
electrical stimulation [70,71]. However, majority of CPs are stable polymers that do not break down in aqueous biological environments. A recently developed polythiophene based composite (PTC) by Mawad et al [72] with promising cell compatibility and degradation rate (3-4 month in PBS) was selected and studied in regards to its anti-corrosion properties. PTC was formed on AZNd using aqueous solutions containing 0.1 wt% poly[ammonium (3-thienyl) ethoxypropanesulfonate] (SPT) and 0.025 wt% PEI according to the procedure outlined in ref. [72]. Figure 5.20 represents the chemical structure of SPT and PEI and a schematic for formation of layer-by-layer film deposition. SPT was synthesized as described in the literature [73] by chemical oxidation using FeCl₃. To reduce the synthesized polymer, it was treated with 10% ammonia in water. The solution turned red. It was filtered and the filtrate was evaporated under vacuum to obtain a red product (SPT).

![Figure 5.20 Chemical structure of SPT and PEI and schematic representation of layer-by-layer (LBL) deposition of PTC on the AZNd surface (figure reproduced from Ref. [72]).](image)

Red color appeared after 6-7 bi-layer (BL) deposition indicating growth of PTC film on the surface. Figure 5.21a shows optical image of AZNd surface coated with 40 BL system of PTC. In order to compare the effect of number of BLs, 20 and 40 BL systems were deposited on AZNd surface. Also AZNd pre-treated by Pr(NO₃)₃
conversion coating was used as substrate and coated with 20 BL coating in order to investigate the synergistic effect of PrOx film and the conducting polymer (Figure 5.21b). The areas shown in Figure 5.21 were then studied using SECM. The top-right-corner of image shows the SECM tip (a 25 µm Pt UME) that was used in SECM experiments.

**Figure 5.21** AZNd samples (a) coated with 40 BL PTC and (b) Pr treated AZNd coated with 20 BLs.

Morphological and elemental analyses of specimens were conducted using SEM and EDX elemental mapping. Figure 5.22 presents cross-section of AZNd coated with 40 BLs of PTC with about 1µm thickness.

**Figure 5.22** SEM micrograph (in back scatter mode) from cross-section of AZNd coated with 40 BLs of PTC. The specimen was mounted in epoxy for the purpose of sample preparation.
Thickness of the PTC layer was measured using line-scan mode of SECM in back scatter mode at the cross-section of AZNd specimen. Sulphur (S) is the signature element for PTC layer as other elements in PTC (e.g. C, N and H) are also present in abundance in epoxy. Result presented in Figure 5.23 indicates a sulphur rich layer with less than 2 µm thickness.

Figure 5.23 Line-scan results with SEM in back scatter mode from the cross-section of PTC coated AZNd.
Figure 5.24 presents physical evidence of formation of PTC film on top of Pr conversion coating. Oxygen (O) and praseodymium (Pr) rich layer indicates the Pr conversion film.

**Figure 5.24** SEM micrograph and EDX elemental map from cross-section of AZNd treated with Pr conversion coating and then coated with 20 BLs of PTC. The specimen was mounted in epoxy for the purpose of sample preparation.

Samples were immersed in dilute SBF and SBF solutions and H₂ evolution was studied using SECM in SG/TC mode. Figures 5.25a and b show the local H₂ evolution for AZNd coated with 20BL in dilute SBF and standard (non-dilute) SBF solutions respectively. Figures 5.25c and d show H₂ the local H₂ evolution for AZNd coated with 40BL in dilute SBF and standard SBF solutions respectively. Figures 5.25e and f show the local H₂ evolution for Pr treated AZNd coated with 20BL in dilute SBF and standard SBF solutions respectively. It is evident from these results
that a 20 BL coating has improved the corrosion resistance compared to the plain non-protected AZNd surface. Level of protection afforded by the conducting polymer improves as number of BLs increases from 20 to 40. AC mode approach curve experiments (results not presented) revealed improvement of conductivity as number of BLs increased from 20 to 40. Striking result was observed with the combined Pr treatment/conducting polymer system with H₂ electro-oxidative current level in the order of $10^{-12}$ A in dilute SBF.
Figure 5.25 H$_2$ evolution imaging for AZNd surface treated by (a and b) 20BL PTC, (c and d) 40BL PTC and (e and f) Pr conversion film then 20BL PTC, in dilute SBF and standard SBF solutions respectively.

Further characterization of surface treatments was conducted using SECM in AC mode to examine stability of the coating layer and its degradation after exposure to corrosive media. Results presented in Figure 5.26 show the impedance map of the surface before exposure to SBF (images are acquired in a 100 fold diluted SBF) and after 2 hr immersion in SBF. Figure 5.26 shows a relatively more uniform impedance across the entire surface after 2 hr immersion in corrosive SBF. This is most likely due to precipitation of calcium phosphate in the areas with lower corrosion protection (i.e. lower impedance) at the early stages of immersion. In all cases the impedance has decreased after 2 hr immersion in SBF which is attributed to ingress of ions in the protective layer. In comparison, the combined Pr conversion film/20BL PTC exhibited the slightest decrease in the impedance indicating its high stability and resistance to corrosive environment.
Figure 5.26 AC SECM images of AZNd surface treated by (a&b) 20BL PTC, (c&d) 40BL PTC and (e&f) Pr conversion film then 20BL PTC, prior to and after 2 hr immersion in SBF. Images a, c and e were acquired before contact with SBF and images b, d and f were acquired after 2 hr immersion in SBF. Measurements were made in dilute SBF using a 25 μm Pt UME as SECM probe. AC scans were performed with ±200 mV AC excitation amplitude applied to the tip at 1 kHz and 5 μm tip-to-substrate distance.
Further insight into the protection mechanism afforded by PTC layer was obtained by measuring conductivity of surfaces after treatment using SECM approach curves in AC mode. Figures 5.27a-c present AC approach curve results for AZNd surface treated with 20BL PTC (5.27a), 40BL PTC (5.27b) and Pr conversion film then 20BL PTC (5.27d). It is evident from Figures 5.27a and 5.27b that increasing the number of BLs in PTC coating enhances the conductivity of coating. This is observed as negative feedback at low frequencies (e.g. 4kHz and 8kHz) for the 40BL PTC coating while positive feedback was observed at these frequencies for the PTC coating with 20BL. In the case of combined Pr conversion film then 20BL PTC coating, strong positive feedback is observed, Figure 5.27c, indicating dominant insulating characteristics of the surface comparable with the insulating characteristics of Pr conversion coated AZNd as exhibited in Figure 5.12. It is hypothesized that the insulating layer of PrOx in between the conducting PTC coating and AZNd surface interrupts any electrical connection between the PTC and AZNd while the thin PTC coating alone does not have required conductivity characteristics to carry the AC signal.

There are a number of mechanisms proposed in the literature as the mechanism by which the conducting polymer coatings may protect active metal from corrosion [74]. Altering the corrosion potential, creating a diffusion limiting electro-magnetic field, barrier protection and gradual release of dopant to act as corrosion inhibitor are the main suggested mechanisms [75,76]. Since the PTC coating used in this study does not contain a dopant that can be released and act as corrosion inhibitor, the last mechanism cannot be responsible for corrosion protection afforded by the PTC coating. Also as evident from approach curve results, Figure 5.27, there is no electrical connection between the PTC coating and AZNd surface which is the necessary condition for mechanisms based on altering the corrosion potential and creating a diffusion limiting electro-magnetic field. Therefore, it is concluded that barrier action is the mechanism responsible for the corrosion protection afforded by the PTC coating.
**Figure 5.27** AC (impedance) approach curves on AZNd with (a) 20 BLs of PTC, (b) 40 BLs of PTC and (c) Pr conversion coating then 20 BLs of PTC deposited on the surface. Approach curves were obtained in dilute SBF using a 25 µm Pt UME as SECM probe with applied AC excitation amplitude of ± 200 mV starting from a tip-to-substrate distance of 75 µm.

### 5.4 Conclusion

Morphological and elemental analysis of the surface layer after formation of Pr conversion coating in 0.2 M Pr(NO₃)₃ solution revealed formation of a porous layer of Pr₂O₃ on the AZNd Mg alloy with a lack of consistency over ceratin secondary phases and/or intermetallic particles.

AC-SECM results showed that Pr treatment using nitrate salt solution results in formation of an inconsistent PrOₓ conversion layer on the AZNd Mg alloy with a variation of insulating properties across the surface. Sensing H₂ evolution by means of SECM in SG/TC mode was used as a method of examining the corrosion behavior of Mg and obtaining comparative measures of corrosion rate between a non-treated and a Pr treated Mg surface. It was shown that corrosion resistance of AZNd during a short term immersion in SBF is improved by Pr treatment. However, it was observed that some insulating domains of the PrOₓ film broke down after 2h immersion and showed higher H₂ evolution activity.

It is postulated that Pr conversion film does not have self-healing characteristics as the oxide layer breaks down in a corrosive environment in the absence of active Pr compounds. However, such conversion film showed significant corrosion protection properties when compared with non-treated plain Mg surface. Also it was shown that Pr(NO₃)₃ serves as an active corrosion inhibitor for Mg when it is present in the environment. It was exhibited that defective areas of Pr conversion coating can be replenished if active inhibitor is present in the environment which produces a self-healing protective layer with effective and dynamic protection against corrosion.
It was shown that the conducting polymer based on polythiophene/PEI composite holds promise as a degradable biocompatible protective layer for temporary corrosion protection. Corrosion resistance was significantly improved when conducting polymer was applied on Pr treated AZNd surface. This implies that the conducting polymer may afford protection by serving as a barrier layer rather than altering the corrosion potential or creating a diffusion limiting electro-magnetic field. The latter two mechanisms require electrical connection between conducting polymer and metal substrate which in this case was lost due to the insulating layer of PrOx pre-treatment between AZNd and PTC film.
References


[27] I. Kostova, G. Momekov, P. Stancheva, New samarium (III), gadolinium (III), and dysprosium (III) complexes of coumarin-3-carboxylic acid as antiproliferative agents, Met. Based Drugs. (2007) 15925.


Corrosion protection of AZNd using rare earth inhibitors

Chapter 5


Corrosion protection of AZNd using rare earth inhibitors

Chapter 5


Chapter 6

Conclusion and future work
The major findings of this study are reviewed in the first part of this chapter. In a nutshell, this thesis focused on developing SECM as a tool for studying corrosion of magnesium alloys in a simulated biological environment. Novel advancements that have been made in this area throughout this PhD will be discussed. Also case studies that have been conducted using the new developed method will be summarized. In the second part of this chapter suggestions are made for the future work and potentially valuable advancements in the area of implementation of SECM for studying corrosion of bio-materials as well as ways for corrosion control of active metals in a biological environment.

6.1 Major remarks

Capabilities of SECM were exploited for examining corrosion of Mg alloys in a buffered simulated biological solution. SECM in feedback mode was implemented for initial assessment of the Mg surface in SBF and to provide a baseline for the subsequent imaging modes of SECM. It is noteworthy that SECM technique was first developed (By Prof A.J. Bard) [1,2] through observation of feedback effect with electron redox mediators and this mode of operation is relatively well established and standardized. Consequently, other modes of SECM operation including AC-SECM, potentiometric and surface generation/tip collection were explored to gain further insight into the localized corrosion process on the surface of Mg.

The major contribution in the development of AC-SECM for corrosion studies have been made by Prof Wolfgang [3–7] and his co-workers at Ruhr University (Germany) in the past 10 years and also by Prof. Ricardo and his co-workers [8–12] (Spain) in more recent years. The AC-SECM results presented in this thesis is, in principle, implementation of the technique developed by Schuhmann and Souto in a new application which is measuring impedance measurement at the surface of Mg. In general, the AC-SECM results confirmed the results of feedback mode operation.
showing relatively conductive and insulating domains at the locations where it was indicated earlier by the feedback mode imaging. AC-SECM at high frequency was used as an indication of solution resistance which then showed higher conductivity of solution at the domains of surface with more active/conductive characteristics. This was to be expected because hypothetically dissolution of Mg takes place at anodic areas with no insulating surface layer and this increases ionic content of solution at those areas.

Potentiometric mode of SECM was employed to measure the local pH near the surface of corroding Mg in the solution. Solid state pH sensing iridium/iridium oxide microelectrodes were fabricated for this purpose and calibration curves were produced in SBF with added HCl or NaOH to alter pH to specific values. Potentiometric SECM measurements revealed that the near surface pH can increase to as high as 12 at the active corrosion spots. This explained the passivation mechanism of Mg in simulated biological solution where species such as calcium phosphate precipitate at alkaline pH and form an inert layer on the surface of Mg. Also by superimposing results from potentiometric mode of SECM and other data (e.g. feedback and AC) higher pH was observed at the active corrosion/dissolution sites. This is a significant observation proving that either anodic dissolution of Mg involves H$_2$ evolution (and alkaline production) or active anodic and cathodic areas are very close on the surface of Mg with an emphasis on the existence of micro-galvanic cells. Micro-galvanic corrosion cells were described in the first chapter of this thesis.

The major contribution of this work is perhaps introducing a new method for local detection of H$_2$ on a solid surface using SECM in surface generation/tip collection (SG/TC) mode. During the early stages of this work, unusual SECM images were acquired that should not have been observed given the redox mediator and the bias potential of the tip that were used in those experiments. Consequently experiments were repeated without the use of redox mediator and yet similar results were obtained. It was first suspected that Mg$^+$ is finally being discovered/detected through an oxidation reaction at the SECM tip to Mg$^{2+}$ but then soon it was realized that tip potential required for such reaction is beyond the oxidation potential of water and therefore it could not be
Mg\(^+\) that was being oxidized at the tip. Further control experiments on an inert (i.e. Pt) substrate and in a range of buffered and unbuffered solution revealed that H\(_2\) is the specie that is electro-oxidized at the tip and therefore it can be detected at the surface of Mg during corrosion in SG/TC mode of SECM. The early results were presented at the Corrosion and Protection conference in 2012 Melbourne, Australia [13] and then followed up by publications in the top scientific journals of the field [14–16].

Immediate implication of SECM results in SG/TC mode was that H\(_2\) evolution occurs primarily at the active corrosion sites where the surface impedance is low (conductive surface) and the pH is high. This rules out the corrosion mechanism by anodic dissolution at independent sites far from cathodic sites that produces local acidic pH at anodic sites by water hydrolysis of Mg cations as suggested in some literature. Also this provides further support for the micro-galvanic cell mechanism or the unipositive Mg cation theory because it again shows that H\(_2\) which is believed to be a bi-product of cathodic reaction is mainly detected at the anodic sites. The author is aware of an ongoing debate regarding the very existence of Mg\(^+\) species and its role in the corrosion of Mg. So far there have been numerous publications in the favour [17–21] and also against [22–27] the idea of Mg\(^+\) idea mainly from Prof A. Atrens group (University of Queensland) in the favour of Mg\(^+\) and Prof G. Frankel (Ohio State University) against it. The author has been fortunate to discuss the matter also in person with these scientists and it appears as so there is so far no hard evidence to prove the existence of Mg\(^+\) nor to reject it. The experimental work and conclusion presented in this thesis does not rely on this theory and also it does not support either of these theories in particular as the close proximity of H\(_2\) evolution sites and anodic areas can also be explained by the micro-galvanic cells with size smaller than it could be resolved by the SECM imaging.

SECM in these four modes operation (feedback, AC, potentiometric and SG/TC) turned into a powerful tool to study the corrosion behaviour of Mg and effectiveness of surface treatments for protection of metal against corrosion. In chapter 4 of this thesis, SECM in combination with other electrochemical and analytical techniques was employed to look at the effect of protein on corrosion of AZ31 Mg alloy in SBF. It was shown that protein
(i.e. albumin) forms a resistive layer on the surface of Mg in the early stages of contact with metal resulting in lowering the corrosion rate. However in the long term it renders the surface more anodic with highly stabilized anodic/cathodic areas which in theory would result in severe localized corrosion damage. In the context of load bearing biodegradable implants it is very important that mechanical integrity of the structure is kept intact and degradation to occur uniformly to avoid premature failure of the implant. Therefore it was concluded that presence of protein will promote localized corrosion which is detrimental to structural integrity of Mg. It remains unclear whether long term increase in the corrosion rate in presence of protein is due to the formation of a thinner and/or more porous film or because of enhanced removal of corrosion product in the presence of protein. The latter mechanism has been described in the literature by chelation tendency of albumin with metal ions.

In chapter 5 of this thesis two type of surface treatments by praseodymium conversion coating and a biodegradable conducting polymer were investigated for corrosion protection of Mg in SBF. Protection mechanism of Pr$^{3+}$ in dissociated form in solution was elucidated with the aid of SECM. It was shown that Pr oxide conversion coating is an inert and stable layer with insulating characteristics that does not possess self-healing ability while presence of Pr$^{3+}$ cation in the solution can replenish the defect in the protective layer and provide a high level of corrosion protection. These results were presented at the 19th International Corrosion Congress in Jeju, Korea 2014 [28]. Similar to other rare earth based corrosion inhibitors, praseodymium is a cathodic inhibitor that passivates cathodic areas of the metal surface by formation of an insulating layer. Measuring pH in potentiometric mode of SECM, it was revealed that alkaline pH at the active corrosion sites plays a major part in deposition of passive Pr oxide film. Second surface treatment studied in chapter 5 was a polythiophene based composite that was deposited on the Mg surface using a layer-by-layer deposition method. It was shown that increasing the number of layers of coating increases the conductivity of film as well as corrosion protection afforded by the surface treatment. Eventually, the conductive polymer coating was combined with the Pr oxide conversion coating as a second coat on top of conversion coating and corrosion behaviour was examined using SECM. A
significant reduction in corrosion was observed which is believed to be due to the passivation by the Pr oxide conversion coating and further barrier protection obtained by the conductive polymer film. Regarding the mechanism by which the conducting polymer afforded corrosion protection, mechanisms based on altering the corrosion potential and creating a diffusion limiting electro-magnetic field were ruled out as these mechanisms required electrical coupling between the conductive polymer and metal surface while in presence of Pr oxide tie layer such connectivity was lost.
6.2 Future work

Applications of SECM are not limited to corrosion studies. Throughout the course of this PhD, SECM was also implemented in other studies such as characterizing polypyrrole surface designed for accelerated growth of human neural stem cells [29]. In another study SECM was applied to investigate electro-activity of nano features formed by Pt based ink and nano-lithography on the surface of ITO glass [30]. These studies exploited SECM in feedback mode which is a more standard operation mode of SECM. Capabilities of SECM as a characterization tool is certainly not limited to feedback mode and it is, in particular, suggested to take advantage of the developments made in this thesis for detection of hydrogen at a local scale and apply the method in other areas of research such as fuel cell studies or physiological studies were generation or consumption of hydrogen at a surface or by certain microorganisms are important.

In the field of Mg based degradable biomaterials, hydrogen evolution combined with the near-surface alkaline condition remains to be a major issue that has to be carefully monitored and controlled. This is because of the potential physiological complications that might occur by H$_2$ cavities or inflammatory effect of alkaline pH to the surrounding tissue of the metal implant. Throughout this thesis, it was shown that SECM holds great promise as an ideal characterization method for monitoring hydrogen evolution as well as measuring the pH of solution near to the surface of Mg. Further developments in this area might involve more efficient ion-selective microelectrodes for measurement of pH that perform the measurement at each single point faster and more accurate so that a map of pH can be acquired.

Some efforts have also been made towards re-arranging the electrodes configuration and the use of conductive substrate (Mg itself) as a counter electrode to increase sensitivity and resolution of measurement with some promising preliminary results but a throughout study in this area was not possible within the time frame of this PhD. As an interesting future work it is suggested to explore alternative electrode arrangements for SECM.
In the third chapter of this thesis it was found that highly alkaline pH reduces sensitivity of Pt microelectrode for detection of H₂ due to change in mechanism of H₂ electro-oxidation at the surface of Pt. It would be beneficial to explore microelectrodes other than Pt such as gold, iridium or carbon fibre microelectrodes to find out if these would perform better than Pt in detecting (electro-oxidizing) H₂ at high pH with more stable sensitivity.

Complementary use of other scanning techniques, in particular scanning Kelvin probe (SKP) and scanning vibrating electrode technique (SVET), will help understanding what cannot be confirmed via the sole use of SECM. SVET can be used to identify anodically and cathodically active sites via measuring local current densities and correlate the H₂ evolution and metal dissolution with the type (thermodynamic) and intensity (kinetic) of activity at a given domain. SKP can be used to gain more knowledge on the formation of anodes and cathodes in the early stages of corrosion as well as in the long term via measuring local Volta potential at the surface. This could in particular benefit the research into designing new alloys with refined microstructure and improved homogeneity. SKP could also be very useful in the research on corrosion inhibitors and protective organic coatings for Mg alloys by indicating the level of passivation provided by the protective mechanism and localized information on the interfacial bonding.
References


Conclusion and future work


