Surface Modification of Mg and Mg Alloys
(Oberflächenmodifizierung von Mg und Mg-Legierungen)

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Can Metehan Turhan
Dedicated to my mother and father...
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Abstract:

Progressively, the well explored and studied mechanical properties of a bulk metal are compared with the corrosion behaviour obtained from its surface, which enables promising improvements in desired applications. An example is magnesium metal: where, by developing new types of surface modifications by understanding its inconsistent corrosion behaviour, it would be possible to apply this engineering metal safely as a biocompatible metal, in addition to its widely used application areas such as the automobile and aerospace industries. Accordingly, many scientists worldwide have focused their attention on new approaches either to fabricate anti-corrosive coatings or tailor the corrosion rate of magnesium for industrial and biomedical applications.

This work covers different types of surface/bulk modification of magnesium or magnesium alloys with different surface pre-treatments, polymer coatings, nanostructuring and composite formation. For instance, the first part of this thesis explores the chemistry of a very common surface pre-treatment technique, fluoride activation by ammonium fluoride (NH₄F) on a dual phase Mg alloy (AZ91D) surface to enhance its corrosion resistance. NH₄ treatment was applied after samples were etched by H₂SO₄ and it is found that acidic pickling has a detrimental effect on coating adhesion and uniformity by removing the non-stable, native oxide layer. Additionally, acidic pickling time was also found to be a very important parameter resulting in changes in the different distribution of phases on the surface. Therefore corrosion protection of such a dual phase alloy can be significantly enhanced by optimizing acidic etching and F-treatment conditions.

The formation of a conducting polymer coating (polypyrrole –PPy-) on Mg alloy AZ91D is reported for the first time from aqueous solutions of sodium salicylate by cyclic voltammetry (CV) method. PPy films are characterized by surface analytic techniques and electropolymerization conditions such as scan rate- and potential range, while monomer and salicylate concentration are optimized to achieve adhesive PPy films on Mg alloy AZ91D. Moreover, corrosion behaviour of PPy/Mg AZ91D alloy in simulated body fluid (SBF) solutions is also reported. Results show that the adherent PPy coatings hinder the anodic dissolution of Mg substrate and enhance the corrosion resistance by releasing dopant anions. Furthermore, functionalization of PPy layers with Albumin (Alb) monolayers provides better salicylate release profile over 20 days with zero order kinetics and
shows the most effective corrosion performance. Such salicylate doped PPy layers have a high potential for tailoring the degradation rate of Mg alloys, and therefore could be used as biomedical components.

Further on, a small example of potentiostatic anodisation of a biorelevant Mg alloy WE43 in hydrofluoric acid (HF) containing non-aqueous electrolyte shows growth of self-ordered nanostructures. The morphology of the surface structures varies with applied potential and anodization time whereby tubular or porous structures with different sizes and orientation can be grown. Formation of these structures was found to be potential- and time-dependent. In view of practical applications, these nanostructured layers may also have considerable potential to help formation of further biocompatible coatings (i.e. hydroxyapatite) or enhance cell adhesion, as nanotubes on Ti have an influence on these effects.

In the end, an example related to bulk modification of Mg metal is given and corrosion behaviour of carbon nanotube (CNT)/Mg composites is demonstrated. Due to the coupling effect between cathodic CNTs and the anodic Mg alloy, the corrosion rate is increased by adding increasing amounts of CNTs. Moreover, surface pre-treatment and dispersion of CNTs was also found to be critical on the corrosion performance. Therefore, in order to exploit the outstanding mechanical properties of these composites, additional corrosion protection methods are required.
Zusammenfassung:

Die gut erforschten mechanischen Eigenschaften eines Bulk-Metalls werden in zunehmendem Maße mit dem auf seiner Oberfläche basierenden Korrosionsverhalten kombiniert, was vielversprechende Verbesserungen für viele Anwendungen ermöglicht.


Des Weiteren wird erstmalig die Bildung einer leitfähigen Polymerschicht (Polypyrrol –PPy) aus einer wässrigen Lösung von Natriumsalicylat auf der Magnesiumlegierung AZ91D mittels zyklischer Voltammetrie (CV) gezeigt. Die Ppy-Filme werden mit Oberflächenanalysetechniken charakterisiert und Elektropolimersationsbedingungen wie Scan-Rate, Spannungsbereich und Monomer- sowie Salicylatkonzentration werden optimiert, um haftende Ppy-Filme auf der Magnesiumlegierung AZ91D zu erhalten. Auch wird über das


Schließlich wird ein Beispiel betreffend die Bulkmaterial-Modifikation von Magnesium gegeben und das Korrosionsverhalten von Kohlenstoffnanoröhren (carbon nanotubes – CNTs)/Magnesium-Kompositen wird demonstriert. Wegen der gemeinsamen Verwendung kathodischer CNTs und der anodischen Magnesiumlegierung wächst die Korrosionsgeschwindigkeit mit der Zugabe von CNTs. Außerdem wurde gezeigt, dass die Oberflächenvorbehandlung und die Dispersion der CNTs entscheidend für das Korrosionsverhalten sind. Deswegen werden zusätzliche Methoden des Korrosionsschutzes dringend benötigt, um die herausragenden mechanischen Eigenschaften dieser Komposite nutzen zu können.
1 INTRODUCTION:
CORROSION OF MAGNESIUM AND MAGNESIUM ALLOYS

1.1 Abstract

In this chapter, a general overview of the corrosion mechanism of magnesium and its alloys is reported including summary of recent research achievements during industrial and academic studies. This chapter also covers “anodic hydrogen evolution”, corrosion rate estimations with the aim of deepening the understanding of corrosion and protection of magnesium and its alloys and provides a base for later chapters.
1.2 Corrosion of magnesium

After discovery of elemental Magnesium (Mg) by Sir Humphrey Davy in 1808, his assistant, Michael Faraday achieved the production of metallic Mg by electrolysis in 1833. This invention was followed by the first attempt of commercial production of Mg by Robert Bunsen in 1852. Afterwards, magnesium was produced for use in flash lights in Europe and America and also suggested for use as ligatures to stop bleeding by the physician Edward C. Huse [1]. These were the first signs of this metal’s use in promising areas of science and technology. In the 1920’s, the first magnesium parts were produced for race cars and this commercialization followed with the release of the Volkswagen Beetle in 1936, which had 20 kg of magnesium within its powertrain. In the following century, interest in Mg has grown and now this metal is a strong competitor, along with its alloys, for many applications in many fields in industry.

Magnesium has been used as a “structural” component in aerospace, automotive [2-5], electronic [6-7] and other performance based industries such as powertrain applications [8-14] due to its superior mechanical properties as a lightweight metal. On the other hand, due to its very low electrode potential ($E_{\text{SHE}} = -2.37 \, \text{V}$), it can also be used as a sacrificial anode to protect other metals [15-18]. But, most of the engineering applications of magnesium are limited due to its corrosion rate. Therefore a significant and detailed understanding of the reasons behind its corrosion is needed to minimize this drawback.

Upon all engineering metals used in industry, magnesium is the most active metal and therefore corrodes very readily in many environments (Figure 1). Despite this major drawback of magnesium, unprotected magnesium may also be more resistant to atmospheric corrosion as compared to mild steel. This is mainly because of air formed magnesium oxide which forms on exposure to the atmosphere at room temperature.

There are two major reasons for the poor corrosion resistance of magnesium. Firstly, the very electronegative potential of Mg makes it very prone to galvanic corrosion that can be initiated by internal coupling components with more noble potential (e.g. impurities [19] or second phases) or by external coupling with
dissimilar metals. Therefore analysis of these secondary phases as well as full chemical composition is very important.

![Galvanic series of most used engineering metals](image1)

**Figure 1:** Galvanic series of most used engineering metals

Secondly, the quasi-passive hydroxide [20] film with a formula of Mg(OH)$_2$ is not found to be as stable as other metal oxide films such as aluminum, nickel and chromium oxide that provide better corrosion properties. Passivation of magnesium with only this layer shows poor pitting resistance for both pure magnesium and magnesium alloys. The Pourbaix diagram of magnesium in water is shown in Figure 2. The stability domain of magnesium is always found to be below that of water and therefore magnesium dissolves in water with hydrogen evolution as Mg$^{+}$ (aq) and Mg$^{+2}$ (aq).

![Potential-pH (Pourbaix) diagram for pure magnesium in water at 25 °C.](image2)

**Figure 2:** Potential-pH (Pourbaix) diagram for pure magnesium in water at 25 °C.
The passive film, Mg(OH)$_2$ is found to be slightly soluble in water and does not provide protection over long periods. However, it also breaks down in the presence of aggressive ions like chlorides [21-24]. Formation of Mg(OH)$_2$ and magnesium dissolution in aqueous environments proceeds electrochemically accordingly to the following reactions;

$$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2(\text{g}) \quad (\text{cathodic partial reaction})$$

$$2\text{Mg} \rightarrow 2\text{Mg}^+ + 2\text{e}^- \quad (\text{anodic partial reaction})$$

$$2\text{Mg}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{Mg}^{++} + 2\text{OH}^- + \text{H}_2 \quad (\text{chemical reaction})$$

$$2\text{Mg} + 2\text{H}^+ + 2\text{H}_2\text{O} \rightarrow 2\text{Mg}^{++} + 2\text{OH}^- + 2\text{H}_2 \quad (\text{overall reaction})$$

$$\text{Mg}^{++} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \quad (\text{product formation})$$

During corrosion of magnesium, there are two important key points; firstly, hydrogen evolution is observed that (4) is associated with both the cathodic partial reaction (1) which balances the anodic reaction of magnesium dissolution (2) and the chemical reaction of Mg$^+$ with water (3). Overall in reaction (4), one mole of hydrogen gas is generated for one mole of magnesium dissolved. Secondly, in net reaction (4), H$^+$ is consumed and OH$^-$ is formed favouring the formation of Mg(OH)$_2$ and shifting the Mg to its passive domain in Figure 2 by alkalization of the medium [25].

**1.3 Corrosion rate measurements**

Side products generated during corrosion of magnesium are helpful for analyzing corrosion experiments. For instance, in addition to polarisation curves and other electrochemical techniques, corrosion rate can be estimated more reliably by collection of H$_2$(g) simply using a burette and funnel as shown in Figure 3. As already mentioned above, 1 mole of H$_2$(g) is generated when 1 mole of Mg corrodes. Therefore, by a simple calculation, it can be said that 0.92 ml of H$_2$(g) is produced from the corrosion of 1 mg of magnesium. Or, if a volume change of 1 ml is achieved on the burette, this corresponds to corrosion of 1.08 mg of magnesium.
But this is not always found to give accurate results because of leaking or the presence of other dissolved gases in the electrolyte. In these cases, the corrosion rate can also be calculated from weight loss measurements and both of these results should be compared for better accuracy.

Figure 3: Setup using for collection of H\textsubscript{2}(g) during magnesium corrosion.

The corrosion layer of magnesium, namely Mg(OH)\textsubscript{2}, is slightly soluble in water. Therefore the removal of the corrosion products before weight loss measurements is essential. To remove the corrosion products a mixture of 400 g/l CrO\textsubscript{3} + 20 g/l AgNO\textsubscript{3} solution at room temperature is used [26]. The corroded specimen is soaked in the mixture for 5 minutes and the corrosion products were removed and weight loss values recorded (Figure 4).

Figure 4: Optical image of pure magnesium specimen surface a) before, b) after removal of corrosion products.
But in this case, other experimental difficulties occur: if the immersion time of the specimen is too long, chemical etching of the magnesium substrate result; or if the soaking time is too short, the complete removal of corrosion products is not achieved. Therefore an experimental error always exists and should be reported for corrosion of magnesium (Figure 5).

**Figure 5:** Comparison of corrosion rates calculated from two different methods for pure magnesium exposed in 3.5% NaCl 1 week.

### 1.4 Anodic hydrogen evolution: negative difference effect

In principle, corrosion rate of magnesium can be adequately estimated by using polarisation curves and Tafel extrapolation. But in practice, the corrosion rates evaluated by this method do not agree with the corrosion rates calculated from weight loss and hydrogen evolution. Moreover, the deviation between these methods has been shown to be up to 48% or 96% [27]. The reason behind this is accompanied by different hydrogen evolution behaviour; more hydrogen is observed at more anodic potentials or current densities. This kind of behaviour is a common phenomenon and is called “negative difference effect” (NDE) [28].

For metals, all corrosion reactions take place in anodic and cathodic red-ox processes. Normally, the cathodic reaction rate is lowered and anodic reactions are more favoured by increasing the applied potential and therefore the anodic dissolution rates are lowered. However, for magnesium, the hydrogen evolution
behaviour is found to be very different [25] than other metals and this type of
behaviour is very contrary to the fundamentals of electrochemistry theory.

Figure 6: Schematic presentation of negative difference effect (NDE). Expected anodic ($I_{e,a}$) and
cathodic ($I_{e,c}$) current density values are shown on solid black lines. Dashed lines show measured
cathodic ($I_{m,c}$) and anodic ($I_{m,a}$) current density values.

Figure 6 shows the comparison of NDE with normal polarization curves. The
normal anodic ($I_a$) and cathodic ($I_c$) partial reactions are shown by solid black lines
and the system is assumed to follow Tafel kinetics. The rates of reactions are equal to
the intersection point that corresponds to corrosion potential ($U_{corr}$) and corrosion
current ($I_{corr}$), as expected. When the potential is increased to a more positive value
($U_{applied}$), the rate of the anodic reaction rate would be expected to increase to the
value of $I_{e,a}$. In parallel, the rate of cathodic reaction would be lower and decreased to
a value of $I_{e,c}$. However, for magnesium it is experimentally reported that [25] the
hydrogen evolution reaction, -cathodic reaction- rate increases (blue curve) rather
than decrease when higher potentials are applied. As a result, a significant increase of
the cathodic current value is observed ($I_{m,c}$). On the other hand, the anodic current
(red curve) values can also increase faster than expected ($I_{m,a}$). Therefore the
corrosion rates calculated from weight loss or hydrogen gas evolution methods differ
from the corrosion rates from polarisation curves at the applied currents by using Faraday’s Law.

There are four important mechanism proposed to explain NDE [28]. The first model [23, 29] postulates the breakdown of semi-protective film during anodic dissolution process. However, the model was criticized because there is no direct proof present showing this surface film is partially protective and it is not able to explain the NDE in neutral and acidic solution. In another model [30], unipositive Mg$^+$ ions are assumed to be produced electrochemically and these intermediate species can react chemically to evolve hydrogen. However, this mechanism is not able to explain the drop of the magnesium dissolution at potentials 1000 mV higher than the Mg$^+/\text{Mg}$ equilibrium potential. In the third model [31], NDE was explained by undermining and falling of second phase particles in magnesium alloys. More undermining would be expected at higher anodic current densities or potentials. But, this model was also found to be insufficient to explain the NDE phenomena at higher anodic potentials [32]. Lastly, a further model was postulated to explain the NDE effect by means of the formation of a MgH$_2$ layer on Mg substrates under certain conditions. According to this model, reactive MgH$_2$ decomposes into Mg$^{+2}$ and H$_2$ and therefore a significant amount of H$_2$ can be produced at potentials in the anodic direction.

Even though many mechanisms are postulated to explain the NDE effect, the corrosion mechanism of magnesium is still debated and a common mechanism is still not provided to cover this phenomenon for both magnesium and magnesium alloys over a wide range of over potential region.

1.5 Improving corrosion resistance of magnesium

In general, mainly two approaches exist to achieve better corrosion resistance for metals; alloying (e.g. stainless steel, Ni-based super alloys, hard metals) and surface treatments (e.g. zinc-phosphate coatings, lacquers, paints). It has been reported that alloying Mg with several metals such as Al, Be, Ca, Cu, Li, Mn, Ni, Re, Si, Ag, Th, Sn, Zn, Zr and Y changes both the mechanical properties and corrosion behaviour. These alloying elements either applied alone (binary alloys) or together with other metals (ternary alloys) are mainly aimed to change desired mechanical properties. Compared to all these alloying elements, aluminum has the most
significant effect on magnesium corrosion. It also improves the strength and hardness and makes the alloy easier to cast. Commercial Al-Mg alloys with a content between 3-9% Al show the optimum strength and ductility. Zinc, which is next to aluminum, is always used in conjunction with Al to improve the alloy’s room temperature strength. For instance, addition of 9% Al together with 1% Zinc gives the well known magnesium alloy AZ91D. Its combination with rare earth elements also gives better mechanical properties. Rare earths are usually added as a mixture of Ce, La and Nd to increase the strength at elevated temperatures.

Due to the fact that this approach is mainly aimed at achieving better mechanical properties, in general alloying Mg does not provide a sufficient corrosion protection in aggressive environments [33]. Therefore many industrial surface treatments are developed to increase its corrosion resistance. Due to its high tendency to galvanic coupling and its very anodic nature, these treatments have to be pore-free to avoid aggressive attacks of electronegative anions such as chlorides. One of these treatments involves coating of magnesium surfaces by other metals such as zinc [34-36], chromium [37-38], copper[38] and nickel [39-40] metals. Although these coatings are usually found to enhance corrosion resistance, due to their electrochemical activity, many challenges are reported for these processes. Therefore with these types of processes it is usually found to be very difficult to achieve compact and pore-free coatings with multi-step preparation. Another important challenge to consider is that the presence of heavy metals reduces the recyclability of the metal [41].

As another surface treatment strategy, environmentally friendly ceramic layers such as phosphate, stannate, silicate and rare earth metal coatings are reported to increase corrosion behaviour of magnesium, as summerized in a recent review [42]. Due to their insoluble nature in acidic solutions, phosphate coatings have been widely investigated since the 90s. During the conversion coating process of magnesium, magnesium substrate is immersed in a reactive solution that alters the metal ion concentration as well as the pH at the metal-solution interface. Change in composition leads to precipitation of the phosphate species onto the magnesium surface through formation of insoluble magnesium phosphate layers [42]. During these processes, many factors such as temperature, time, bath stabilizers (Zn, Mn, V, Ca, Mo, Sn, Co), substrate microstructure and surface state have many influences on the resulting coating. In addition to phosphate conversion coatings, micro-arc
oxidation of magnesium metal has been widely investigated to achieve compact and pore-free silicate and stannate ceramic layers and this method has become very popular in the last decade. Proper choice of electrical parameters such as anodisation potential/current, applied steps, duration and further anodisation in different electrolyte solutions is very important and therefore this approach very sophisticated [43].

In this work, in contrast to above mentioned traditional approaches, new types of surface modifications on the magnesium alloy AZ91D surface is carried out. For instance, in chapter 3, a very common surface pre-treatment technique, fluoride activation by ammonium fluoride (NH$_4$) is studied on Mg alloy (AZ91D) surfaces to enhance corrosion resistance. In chapter 4, a first time formation of conducting polymer coating (polypyrrole –PPy-) on Mg alloy AZ91D is reported from aqueous solutions of sodium salicylate by cyclic voltammetry (CV) method. In chapter 5, a small example of electrochemical formation of self-ordered nanotubular and nanoporous magnesium oxy-fluoride structures on a magnesium-based alloy are reported. In the end (chapter 6), influence of carbon nanotube (CNT) addition into Mg matrix and its effect on the corrosion behaviour is studied.
2 Experimental Methods

In this chapter, a main concept about experimental details is explained with a common overview. More details and specific explanation concerning how the experiments are performed will be explained in the experimental part of each chapter.
2.1 Electrochemical setup

For electrochemical experiments, three different types of electrochemical setups were used in order to meet the specific requirements of different works and reduce the side effects during corrosion tests. Figure 7 shows the electrochemical setups used during the study. Figure 7a shows a conventional three electrode system with an o-ring cell sealed to the working electrode (anode). A Cu back-plate was used to achieve the electrical contact by pressing against the o-ring to expose a defined electrode area to the electrolyte. Figure 7b shows the same three electrode system where a simple flask with a total volume of 200 ml replaced the o-ring cell to anodize bigger surfaces during experiments. A potentiostat/galvanostat Autolab PGSTAT 30 was used where a Pt foil or stainless steel (SS) sheet served as a counter electrode and an Ag/AgCl (3 mol dm$^{-3}$ KCl) with a second capillary filled with the electrolyte solution used as reference electrode to avoid attack of aggressive Cl$^-$ ions. Results were monitored by NOVA software (Official software of Autolab).

For experiments at higher potentials, a two electrode system was used either in a flask (Figure 7c) or in the o-ring cell and connected to Heinzerling 350-2 model DC-Voltage source that interfaced to a computer via a USB-GPIB controller (National Instruments) combined with a Keithley 188 model digital multimeter. The anodisation progress and curves were monitored by in-house software programmed in LabView.
Figure 7: Electrochemical setups used during the study; a) A conventional 3-electrode system with an O-ring cell, b) Same electrochemical 3-electrode system with a simple flask as electrochemical cell, c) 2-electrode system with a power source.
2.2 Electrochemical methods and corrosion tests

2.2.1 Cyclic and linear sweep voltammetry

Cyclic voltammetry is a powerful type of potentiodynamic method where the potential applied to the working electrode can be ramped linearly versus time like linear sweep voltammetry. Unlike linear sweep voltammetry, that ends when it reaches a set potential, the potential ramp of working electrode with respect to the reference electrode is reversed at a set potential where upon it is scanned linearly back to the initial potential again. This process is called a “cycle” and can be done multiple times during a single experiment by using a triangle shaped potential waveform.

The graph where the current measured passing through the working electrode is plotted versus the potential applied is called a “cyclic voltammogram” and generally used to study electrochemical analyses of red-ox active couples in an electrolyte solution. Moreover, this technique is also used for electrochemical electropolymerization of conductive polymers [44] and characterization of these materials in monomer free electrolyte solutions to analyze electronic properties of the polymer films [45-49].

In this work, cyclic voltammetry is used to obtain polypyrrole films on magnesium substrates and the linear sweep voltammetry for corrosion tests with the Tafel extrapolation method.

2.2.2 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy is a powerful emerging technique where the analyses of materials in which ionic conduction is strongly dominated such as fused salts, conductive polymers,  ionically bonded single crystals and metals. Because of its non-surface destructive background, this technique also helps to understand the trend of the surface resistance during corrosion tests.

Basically, electrochemical impedance of a system is obtained by applying an small excitation signal to have a pseudo-linear cell response [50];

\[ E_t = E_0 \sin (\omega t) \]
In a pseudo linear or linear system, the current response gained from the sinusoidal excitation potential signal is considered as a sinusoid function at the same frequency ($\omega$) but shifted in phase ($\Phi$) and shown as following:

$$I_t = I_o \sin (\omega t + \Phi)$$ \hspace{1cm} (7)

An expression analogous to Ohm's Law allows calculation of the impedance of the system by dividing equations 1 and 2.

$$Z = \frac{E_t}{I_t} = \frac{E_o \sin(\omega t)}{I_o \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)}$$ \hspace{1cm} (8)

Total impedance of a system is then presented as a complex number by using Euler’s relationship as following [50]:

$$Z(\omega) = \frac{E}{I} = Z_0 (\cos \phi + j \sin \phi)$$ \hspace{1cm} (9)

A typical presentation of impedance data, Nyquist plot, is obtained where the real part is plotted versus the imaginary part in reaction (4) as shown in Figure 8. For magnesium and magnesium alloys, polarization resistance ($R_p$: the difference along the real axis between the resistance at the highest and lowest frequencies) generally is not equal to the charge transfer resistance ($R_{ct}$ or $R_c$: the diameter of the Nyquist curve along the real axis) due to its pseudo-inductive nature in corrosive media (see chapter 3). Therefore the impedance spectra of magnesium and its alloys can not be explained easily as fundamental systems with one time constants where the corrosion process is lying with combination of a single capacitor and a resistor (i.e. corrosion of carbon steel).

Therefore in this study, further analysis of EIS data with equivalent circuit modelling is not studied. Instead, the direct relationships are carried out. Even though equivalent circuits in many cases are very valuable and helpful, the circuit elements do not have straightforward and simple physical explanations in the case of this work, as the electrochemical interface is quite complex and dynamic (e.g., corrosion of Mg leads to an increase of the pH value in the surroundings, and this can influence both the coating and the Mg substrate behaviour).
During EIS experiments, a sinusoidal perturbation of ±10 mV for 10 points per decade in a frequency range between 100 kHz and 10 mHz used.

![Nyquist plot of a magnesium alloy in 3.5% NaCl solution after 20 minutes of immersion.](image)

Figure 8: Nyquist plot of a magnesium alloy in 3.5% NaCl solution after 20 minutes of immersion.

2.2.3 Corrosion tests

Corrosion tests of magnesium specimens were performed by two methods;

a) A conventional gas evolution setup

b) Electrochemical polarization curves with Tafel Analyses

To determine the corrosion rates from hydrogen gas evolution, surfaces of the magnesium samples were sealed to expose a defined electrode surface to the electrolyte and placed in a beaker that is connected to a burette. The change of the electrolyte level on the burette was recorded every day. To validate the corrosion rates obtained from gas evolution setup, weight loss measurements were also performed. Samples were removed from the test medium and immersed into 400 g/l
CrO$_3$ + 20 g/l AgNO$_3$ solution at room temperature for 5 minutes and the corrosion products were removed and weight loss values were recorded [26].

Linear polarization curves were measured between -2.0 and -1.0 V by using a three electrode system (Figure 7a) with a scan rate of 1 mV/s and the Tafel analysis of the data was performed by Nova software. Tafel Plots can provide a direct measure of the corrosion current, which can be related to corrosion rate. Additionally with this technique, it is possible to measure extremely low corrosion rates, and it can be also used for continuous monitoring of the corrosion rate of a mixed electrode system.

2.3 Surface analytic methods

2.3.1 Scanning Electron Microscopy

In electron microscopy, electrons of the specimen surface are excited to high energy levels [51]. During this process, electrons absorb more energy than their work function and are ejected from the atomic shell. The energy of the emitted electrons changes by only changing frequency or energy of the incoming beam. If the excitation energy is too low, electrons can not escape. Interaction of the beam with specimen surface produces secondary, backscattered, Auger electrons as well as X-ray radiation and light (Figure 9).
Figure 9: Some atom-high energy electron interactions. The inner electron shells of atoms are labelled according to standard notation (K, L etc.). a) Electrons pass to next layer of atoms with little loss of energy - Low-angle scattering, b) Back-scattering, c) Characteristic X-Ray emission for secondary electron and d) Emission of a second electron and an Auger electron.

These different electrons ejected from the specimen surface are collected by different detectors to form images. The interaction volume of signals is shown in Figure 10. In SEM, secondary (SE) and backscattered electrons (BSE) are usually used to produce images. SEs are produced by inelastic interactions with an energy loss and produced by the interactions between valence electrons of insulators and semiconductors or weak conduction-band electrons in metals. These electrons usually escapes from energy levels below 50 eV and this provides highest spatial resolution images.
BSEs are produced by elastic interactions of beam electrons with nuclei (Figure 9b). The energy loss is usually less than 1 eV and gives slightly less spatial resolution than SEs since they come from deeper parts of the specimen (Figure 10). These electrons generally provide compositional and crystallographic information due to electron channeling. For elements with higher atomic numbers, more backscattered electrons are bounced back that makes the image brighter for atoms of higher atomic number [52].

During this work, a field-emission scanning electron microscope, Hitachi FE-SEM S4800, was used to investigate morphological characterization of the samples.

### 2.3.2 Auger Electron Spectroscopy (AES)

As shown in Figure 9d, Auger electrons are emitted from very close to the surface and gives information about surface chemistry. Different than secondary or backscattered electrons, Auger electrons are second ejected electrons. After the core electron is removed by leaving a vacancy, another electron fulfils by releasing energy. Sometimes this energy is transferred to a second electron and result in
ejection. This second ejected electrons are called Auger electrons [53]. Auger electrons have energy between 100 eV to 2 KeV and mainly absorbed by the specimen. Therefore, only Auger electron from the surface can be measured, making Auger Electron Spectroscopy (AES) a separate surface method.

Auger electron spectroscopy (AES) was performed in a PHI Model 670 instrument with primary electron beam voltage of 10 kV. Spectra were detected by using the manufacturer software and sensitivity factors.

2.3.3 Energy Dispersive X-ray Spectroscopy

When a high energy beam interacts and ejects an inner shell electron (Figure 9c), an outer shell electron moves into the empty orbit with a progression from higher to lower energy states with the excess energy emanating from the material as an X-ray of specific energy till all electron states are refilled. The specific energies of these X-rays are detected by an energy- or wavelength-spectrometer adapted in the SEM instrument. It usually provides rapid qualitative analyses [54]. On the other hand where it is the wavelengths of the X-rays that is detected this is referred to as wavelength dispersive X-ray spectroscopy (WDS), which provides greater elemental resolution but with a considerably longer analysis time.

In this work, EDAX Genesis, fitted in the same SEM chamber Hitachi FE-SEM S4800 was used for chemical analysis of the surface compositions.

2.3.4 Focused Ion Beam

The Focused Ion Beam (FIB) is an SEM technique that uses a Ga$^+$ ion beam in place of an electron gun in SEM. Generated secondary electrons or ions are used to produce images of surface morphology as previously explained. Differently than conventional SEM, Ga$^+$ ions allow selective milling or peeling-off of a desired area on the surface. It is usually used for cross sectional imaging, as well as modification of semiconductor devices and failure analyses. Additionally, it is also used for sample preparation for TEM analyses [55].

In this work, cross-sections of the samples were cut using a Zeiss brand focused ion beam (FIB), Cross-Beam 1540, at the chair of “Allgemeine Werkstoffeigenschaften” (WW1-Prof. Dr. Mathias Göken). Coarse millings of the
cross-sections and the final polishing processes were both executed at an acceleration voltage of 5 kV. An additional platinum layer was deposited to protect the surfaces from rounding-off effects.

2.3.5 X-Ray Photoelectron Spectroscopy

XPS, also known as ESCA –electron spectroscopy for chemical analyses-, is a widely used surface analytic technique because of its sensitivity and reliability. In XPS, specimen’s surface is irradiated with mono-energetic x-rays and photoelectrons (photoelectric effect) with different work functions (binding energy) are ejected. Binding energy and intensity of a photoelectron peak is characteristic for all elements and hence, XPS detects elemental composition of the surface (top 1–10 nm usually). It is widely used in surface science and technology applications including: polymers, catalysis, corrosion, adhesion, semiconductor and dielectric materials, electronics, magnetic media, and thin film coatings [56].

In this work, chemical composition was determined by employing X-ray induced photoelectron spectroscopy (XPS)-Phi 5600, using Al Kα radiation.

2.3.6 Time of Flight Secondary Ion Mass Spectroscopy (ToF-SIMS)

In ToF-SIMS, a pulse of ions is used and a cloud of atoms are sputtered. Some of the atoms are ionized and these particles of one polarity are accelerated into a spectrometer. After they travel through a tube, depending on the molecular mass of the particles, they arrive at an ion detector at different times. However, the lighter ones arrive at the detection system before the heavier ones. The "Time-of-Flight" of an ion is proportional to the square root of its mass, hence all the different masses can be detected individually [57]. The ToF-SIMS technique gives chemical composition of surfaces in ppm sensitivity. Transport of oxygen in ionic materials, reactions at interfaces, composition of quantum dots and their interfaces, multilayer structures and monolayers can be analyzed with this technique.

Positive and negative static time-of-flight secondary-ion-mass-spectroscopy (ToF-SIMS) measurements were performed with a ToF-SIMS V spectrometer from ION TOF, Münster). The samples were irradiated with a pulsed 25 keV Bi⁺ liquid-
metal ion beam. Spectra were recorded in the high mass resolution mode (m/Δm> 8000 at ²⁹Si).

2.3.7 Fourier Transform Infrared Spectroscopy

FTIR is a very powerful technique to identify the “fingerprint” of organic and inorganic chemicals. In principle, molecular bonds vibrate at various frequencies depending on their bonding energies. According to quantum principles, these frequencies correspond to lowest and higher frequencies between these two states (ground state (E₀) and the first excited state (E₁)); the difference in the energy must be equal to the energy of the detected light.

\[
E₁ - E₀ = \frac{hc}{l} \tag{10}
\]

Where; \(h\) = Plank’s constant, \(c\) = speed of light, and \(l\) = the wavelength of light.

The term Fourier Transform Infrared Spectroscopy (FTIR) refers to a recent development converting data to a spectrum which makes the technique more sensitive. FTIR is used to identify chemicals in paints, polymers, coatings and drugs for example [58].

In this work, functional groups were characterized with a Fourier-Transform Infrared Spectrophotometer from Bruker Instruments, Germany.
3 Effect of Acidic Etching and Fluoride Pre-Treatment on Corrosion Performance of Magnesium Alloy AZ91D

3.1 Abstract

Fluoride activation of Mg alloy surfaces by ammonium fluoride pre-treatment is an important procedure used in industry for the removal of the non-stable, native oxide layer from Mg alloys that can have a detrimental effect on coating adhesion and uniformity during industrial coating processes. Furthermore, the corrosion protection properties of the F-coated AZ91D surface can be significantly enhanced by optimizing the time of acid etching and F-treatment.

The present chapter explores the effect of a surface pre-treatment by acid etching in H2SO4 on the properties of such a F-coated Mg alloy AZ91D in 3.5% NaCl electrolytes.
3.2 Introduction

Despite their ultra lightness and high strength to weight ratio with a density that is two thirds of aluminum and one fourth of iron, application of magnesium and its alloys in a wide number of industrial fields is restricted by their poor corrosion resistance on which many reviews have been reported in literature [25, 28]. To overcome this problem, different types of coatings that enhance the corrosion resistance of Mg and Mg alloys have been developed. Even though a coating processes including hexavalent chromium (Cr$^{6+}$) [59] was widely used for producing conversion coatings, the use of Cr$^{6+}$ is reduced in recent years as it is found to be carcinogenic [60]. Afterwards, other alternative procedures have been used in producing eco-friendly corrosion protection coatings such as stannate[61-62], cerium oxide[63], phosphate[64-65] and silicate[66] treatments, and some of these including other industrial treatments have been summarized in recent reviews [41, 43, 67].

Along with the importance of these treatment methods, it has been also found that pre-treatment methods are very important for the protection of magnesium against corrosion. The importance of these pre-treatment methods originates in the need to remove the passive oxide-layer that forms easily due to the high reactivity of Mg [41] and has a detrimental effect on coating adhesion and uniformity. Industrial pre-treatment methods such as alkali cleaning[68], acid [69] or fluoride activation [70-71] are capable of removing this oxide layer. In the case of fluoride activation it was previously found that this oxide layer is replaced by magnesium fluoride, enabling further coatings on Mg or Mg dual-phase alloys.

Such a dual-phase alloy is die-cast AZ91D, which contains 9% Aluminum and 1% Zinc. Aluminum has the most significant effect on magnesium improving its strength and its hardness. Moreover, it widens the freezing range and makes the alloy easier to cast. However, zinc is often used with aluminum to improve room-temperature strength. Additionally, it also helps to overcome the harmful corrosive effect of iron and nickel impurities[72].

Figure 11a shows the phase diagram of the Mg–Al alloys which is generally characterized by solidification of aluminum in magnesium. These alloys have two phases: a Mg-rich $\alpha$ phase and an Al-rich $\gamma$ phase, which is also called $\beta$ phase. Figure 11b shows the intermetallic $\beta$ phase compound located at the grain boundaries with a stoichiometric composition of Mg$_{17}$Al$_{12}$ (at 43.95 wt.% Al) with an $\alpha$-Mn–
type cubic unit cell model that acts as a cathodic centre for the $\alpha$ phase [25, 73]. The inset EDAX spectra show two sharp peaks for Mg whereas the Al peak is only prominent for the spectra from the white regions of the SEM images. The spectra verify that the white regions in SEM images are the Al rich $\beta$ phase and the darker regions are the Mg rich $\alpha$ phase. In Mg-Al alloys $\alpha$ phase is found with a hexagonal closely-packed, hcp structure with a Young modulus value around 45 GPa, where the same value for the $\beta$-phase is about 80 GPa.

For Al-Zn alloys of magnesium in which the Al to Zn ratio is larger than 3:1, new phases do not appear with zinc. In this case, the zinc substitutes aluminum in the $\beta$-$\text{Mg}_{17}\text{Al}_{12}$ phase, creating a ternary intermetallic compound $\text{Mg}_{17}\text{Al}_{11.5}\text{Zn}_{0.5}$ or $\text{Mg}_{17}(\text{Al},\text{Zn})_{12}$ [74-79].

![Figure 11: a) Fragment of Mg–Al phase diagram (adopted from ASM Handbook Committee, 1986) b) EDAX spectra of $\alpha$- and $\beta$-phases of an AZ91D alloy surface after 5 s of etching in 2.5 wt% H$_2$SO$_4$.](image)
Song and co-workers have reported that the β phase located at the grain boundaries mainly serves as a galvanic cathode, where it couples with the α phase due to the higher cathodic activity of the β phase [32]. Furthermore, they postulated that, depending on its volume fraction, the β phase may also act as a surface barrier against corrosion as opposed to a galvanic cathode. Until now, there are no works that clearly report this postulated barrier-effect-against-corrosion of Mg in AZ alloys.

The main objective of the present chapter is to explore the effect of acidic etching of AZ91D Mg alloy on the electrochemical properties of the alloy, as well as on the nature of the F-coating formed on these etched surfaces during NH₄F steeping.

3.3 Experimental route

Magnesium AZ91D coupons with dimensions of 2 cm x 2 cm x 0.5 cm were mechanically ground with 1200 grit emery paper and then polished with 6-, 3-, and 1-µm diamond paste using ethanol as surfactant followed by cleaning in 1:1 ethanol:acetone mixture for 10 minutes in an ultrasonic bath.

After polishing, the first step of the pre-treatment process, chemical etching was employed in 2.5 wt.% H₂SO₄(aq) and the samples were subsequently sonicated in deionized (DI) water and in ethyl alcohol prior to SEM imaging. To allow for progressive imaging of the same surface area, SEM images were taken between etching steps. After the samples were removed from the SEM, they were etched again allowing the etching progress of the same position to be observed for approximately 1, 2, 3, 5 and 10 seconds of etching.

For the second step of the pre-treatment process, steeping in NH₄F(aq), samples of different etching durations were prepared and etched as described above. Etched samples were chemically treated by steeping in 2.5 mol dm⁻³ NH₄F (aq) solution (pH: 6.35±0.05, T: 80±5°C)[71]. After steeping, the samples were cooled down to room temperature with DI water and stored in high purity (99.9%) ethyl alcohol.

In addition to SEM, EIS analyses and OCP monitoring was carried out in 3-electrode setup with an O-ring cell as already described in section 3.1 and 3.2.2, respectively. To study the surface chemistry, F-species rich coatings were analysed with time-of-flight secondary-ion-mass-spectroscopy (ToF SIMS) to depend on the underlying phase of the alloy surface.
3.4 Results and Discussion

3.4.1 Etching Behaviour

To examine the effect of acid etching time on the electrochemical behaviour of the sample, open circuit potentials OCPs of samples etched for approximately 1, 2, 3, 5 and 10 seconds were recorded. Figure 12 shows the OCP-time curves of the samples over 20 minutes. After 20 minutes, there is small difference in OCP values with a value of $-1.535\pm0.004$ V for all samples so that the influence of the acidic etching onto the electrochemical behaviour was not clearly monitored. But on the other hand, these potentials are, as expected, between the corrosion potentials of $\text{Mg}_{17}\text{Al}_{12} (-1.17 \text{ V})$ and pure Mg ($-1.62 \text{ V}$) [25].

![OCP measurements of AZ91D alloy samples in 3.5% NaCl after different etching times of 1, 2, 3, 5 and 10 s in 2.5% by weight H$_2$SO$_4$.](image)

To examine the changes after etching, the surface morphology of a sample was monitored \textit{ex situ} by SEM on several occasions during etching. Figure 13a-d show SEM images of 1-, 2-, 3- and 5-s etched AZ91D samples allowing the relative degree of $\alpha$ (Mg rich: dark) and $\beta$ (Al rich: bright) phases to be observed. As is evident from the SEM images, the $\text{Mg}_{17}\text{Al}_{12}$ rich structures have irregular shapes and sizes. The results indicate that during the first five seconds of etching, the interconnected $\beta$–phase structures become more visible.
Figure 13: SEM images of the same region of an AZ91D alloy sample after different etching times of (a) 1 s, (b) 2 s, (c) 3 s and (d) 5 s, respectively in 2.5 wt% H$_2$SO$_4$.

Figure 14: SEM images of the same region of an AZ91D alloy sample after different etching times of (a) 3 s, (b) 5 s and (c) 10 s, respectively, in 2.5 wt% H$_2$SO$_4$. 
Figure 15: Left: peeling-off and undercutting mechanism for AZ91D alloy. Right: tilted SEM image of AZ91D alloy (at 45°) showing the undercutting of the β phase after 10 s of etching in H₂SO₄.

Figure 14a-c show SEM images of another area after 3, 5 and 10 seconds of etching, which are representative of the overall trend observed for α and β phase distribution. It is apparent, from the SEM images, that up until 5 seconds of etching time, the β phase structures stay attached to the surface. However, during further etching these structures are separated from the bulk alloy, and since they are only loosely interconnected with each other, they become disconnected from the sample surface (as shown in the model on the left of Figure 15) and fall into the solution. Therefore, due to this mechanical instability, a maximum surface fraction of β phase is obtained after 5 seconds of etching that reduces to a constant plateau for longer etching times.

In contrast to the sudden change in β-phase, the Mg rich α phase etches in a relatively constant manner. At the beginning of etching, dissolution of α phase results in the formation of cracks in the top layer that then peels off to the edge of the phase boundary revealing an underlying layer. This can be clearly observed in Figure 13c-d and Figure 14-a. This peeling-off step is followed by the formation of another crack on the freshly exposed surface. This crack then propagates beneath the surface resulting in the peeling off of another layer promoting a continuously repeating process that results in the formation of a cavity in the α phase and exposes the β phase so that it extrudes from the surface as shown in the tilted SEM image of
Figure 15. Taking into account this kind of $\alpha$-phase behaviour, the etching process can be characterized as a “peeling-off” mechanism that creates cavities with stepped edges. This mechanism has the properties that at the beginning of each stage a crack forms on the surface due to the etching agent. A layer then peels off via undercutting. Each step reveals more of the surface of each $\beta$ phase region till mechanical instability results in detachment from the surface as shown in schematic of Figure 15.

After SEM investigations, samples were also investigated by EIS so as to gain a better electrochemical understanding of the electrolyte-AZ91D interface. Spectra of 1-, 2-, 3-, 5- and 10-seconds etched surfaces (step 1) were recorded and the Nyquist plots for these samples are shown in Figure 16.

Figure 16: Nyquist plots of etched AZ91D alloy in 3.5% NaCl after different etching times in 2.5 wt% $\text{H}_2\text{SO}_4$.

EIS experiments show two capacitive loops in the high and middle frequency (HF and MF) domain. HF capacitive loops are usually attributed to both charge transfer and the double layer associated with the interface between the electrolyte and the alloy surface. Although, the capacitive loop in the MF region of all the curves is
small, it is always apparent. For MF capacitive loops, proposals are reported by Song et al. and Baril et al.: According to Song et al. [80], these loops are attributed to Mg⁺ concentration [73] within the broken areas of surface-oxide film; Baril et al. [81-82] proposed that these loops are the relaxation of mass transport in the growing solid oxide phase. In Figure 16, a clear trend is observed in the charge transfer resistance Rᵢ (i.e., the diameter of the Nyquist curve along the real axis). The value of Rᵢ increases from ~260 Ω for the 1-second etched sample to ~750 Ω for the 5-second etched sample. Although there is an increase of Rᵢ from the 3- to 5-second etched sample, a decrease in Rᵢ is observed for 10 seconds of etching time.

The polarisation resistance (i.e., the difference along the real axis between the resistance at the highest and lowest frequencies) is almost the same for all samples due to the presence of an inductive loop in the LF domain region of all the curves.

In the case of Mg, inductive loops are commonly reported for Nyquist curves in LF regions as scattered points [32, 82]. Inductive loops in EIS plots were firstly reported for corroding or dissolving systems [83] and can be explained by a faradaic impedance if the dissolution of the metal (Me) to solution (i.e., as Me⁺) involves an intermediate transition to, for example, (MeOH)ads. Where such an intermediate transition exists, the imaginary part of the complex representation of the faradaic impedance can either be capacitive or self-inductive. The nature of the imaginary part is dependent on which of the two intermediate reactions is greatest which is decided by the applied voltage. Inductive behaviour is generally assumed to be due to the presence of adsorbed surface species such as Mg(OH)⁺ads, Mg(OH)₂ads, [80-82] and Mg⁺ads [32]. For Magnesium and magnesium alloys, at open-circuit potential, inductive behaviour results at low frequencies and is observed as an inductive loop in Nyquist Plots [84]. In addition, strong inductive loops are also reported due to the high concentrations of Mg ions on relatively film-free surface [84-85]. However, Anik et al. [86] found that low-frequency inductive-loops have a tendency to disappear when the dissolution rate of the alloy decreases in the presence of a protective oxide layer.

For our results, the scattered points in the low frequency (LF) domain indicate that the slow reactions at the interface are not stable enough to allow smooth curves. In addition, the immersion time was less than 1 hour so the corrosion products did not completely cover the whole surface. An increase in inductance with etching time was observed for all samples as a corresponding increase in α-phase surface area was
observed in SEM images. Therefore, the increased inductance with increased duration of etching may be attributed to increased presence of absorbed Mg species on the electrode surface due to an increase in $\alpha$-phase surface area.

Up until a duration of 5 seconds of etching, the overall surface area increases at the same time as the area of $\beta$-phase surface increases. This etching also causes an absolute increase in the area of the $\alpha$ phase. Although the $\alpha$ phase surface area increases during this etching duration, the exposed surface area of the $\beta$ phase increases sufficiently so as to create a barrier effect that increases the overall charge transfer resistance. In addition, the exposed interconnected $\beta$ phase structures reach a maximum linkage and play an important role as active cathodic sites on the surface. For durations greater than 5 seconds the $\beta$-phase structures detach from the surface due to mechanical instability (Figure 14). Thus, for the 10-seconds etched sample, there is a decrease in charge transfer resistance but a continued presence of inductive behaviour.

3.4.2 Fluoride treatment optimization

After acid etching in $\text{H}_2\text{SO}_4$ for the optimum time of 5 seconds the treatment of samples was completed by steeping in ammonium fluoride solution of pH $6.30\pm0.05$ at $80\pm5^\circ\text{C}$. The EIS spectra for a range of different sample steeping durations from 1 minute to 2 hours are shown in Figure 17. For steeping times of 20 minutes or less no inductance effect is present and the polarisation resistance, $R_p$ (i.e., the difference along the real axis between the resistance at the highest and lowest frequencies), increases with increasing steeping time. Thus, for steeping of 20 minutes or less, the ammonium fluoride treatment forms a passive layer that protects the surface reducing the flow of current and halting the $\alpha$-phase dissolution of Mg to $\text{Mg}^{2+}$ via $\text{MgOH}$. For steeping times greater than 20 minutes the polarisation resistance diminishes and inductance effects reappear and grow as the steeping duration is increased. These reductions in the benefits of the treatment method after extended durations of steeping may be due to deterioration of the passive surface-layer from mechanical stress or chemical etching due to temperature and bubbling of the solution or chemistry of $\text{NH}_4\text{F}$, respectively.
Figure 17: Nyquist plots of AZ91D alloy samples in 3.5% NaCl for different fluoride treatment times after 5 s of etching in 2.5% by weight H$_2$SO$_4$.

Figure 18 shows SEM images of NH$_4$F treated surfaces that underwent the same treatment as the samples shown in Figure 6 for 20 and 120 minutes of steeping. In Figure 18a the layer that passivates the surface covers the $\alpha$ and $\beta$ phases. Contrary to this, in Figure 18b almost all of the chemically more stable $\beta$ phase has detached from the surface and unlike Figure 18a the layer that covers the surface has developed many cracks and fissures. Together these deteriorations in the surface of the 120-minute sample may facilitate the lower polarization resistance and the increased inductivity that are observed in the EIS Nyquist curves (Figure 17) of greater than 20 minutes steeping.
To further examine the effect of etching time on fluoride pre-treatment of the surface, EIS was performed on samples for the optimum steeping duration (step 2) but for different durations of step 1. The EIS results for the 1-second etched sample show a low $R_t$ of around 1 kΩ (Figure 19) with a complete circle characteristic indicating a large inductance. For the 2 seconds etched sample a larger $R_t$ value with relatively small inductance is achieved. This trend of decreasing inductance and increasing resistance was observed to continue for increased etching time in the case of 3-second and 5-second etched samples where $R_t$ values of approximately 6 kΩ and 9 kΩ, respectively, were achieved. However, for the 10-second etched sample, a dramatic decrease in $R_p$ was observed. As in the case of samples that were not steeped after etching (as shown in Figure 16), this decrease may be related to the mechanically unstable β phase as described in our model (Figure 15-left).
Figure 19: Nyquist plots of fluoride treated AZ91D alloys after different etching times in 2.5 wt% H$_2$SO$_4$.

Figure 20: Nyquist plots of AZ91D alloy in 3.5% NaCl after polishing (blue squares: both in the main image and magnified plot of the inset); after polishing and 5 s of etching (red circles); and after polishing, 5 seconds etching and 20 min steeping (black triangles).
The optimum conditions, found in our study, for the two steps of the treatment process (*i.e.*, H₂SO₄ etching and NH₄F steeping) have a progressive effect on charge transfer resistance and surface protection (Figure 16-17). For the polished sample the Rₜ is approximately 40 Ω (inset of Figure 20). By etching the surface for 5 s the Rₜ resistance increases to almost 1 kΩ (Figure 16). We propose that this increase is due to the increased surface fraction of β phase which increases the resistance significantly enough to compensate for the increase in surface area due to surface roughening. We further propose that since the α phase is still present the faradaic inductance also increases. Finally, through fluoride activation of the surface by steeping in NH₄F(aq) solution, which leads to the formation of a thin fluoride passivating layer, the α phase becomes insulated from the solution-surface interface removing the faradaic inductance (Figure 17). Furthermore, the F⁻ passivating layer creates a resistance in series with the original surface increasing the charge transfer resistance to approximately 8 kΩ.

### 3.4.3 Chemistry of fluoride layer

To analyze the morphology and elemental constituents of the fluoride layer, SEM and ToF-SIMS analyses were performed. These analyses where carried out on samples that where etched for various durations from 1 to 10 s and steeped for the optimum steeping duration of 20 min. To investigate the elemental constituents, ToF-SIMS spectra of both positively and negatively charged secondary ions were recorded for the different samples along with mapping of the distribution of the major spectral peaks. All observed ions are summarized in Table 1 and Figure 21 shows the most prominent peaks along with their corresponding assigned chemical formulae in order of increasing ion mass. The mass numbers marked with an asterisk indicate the peaks that were resolved clearly for the 5- and 10-second samples only. On the 1-s, 2-s and 3-s etched samples, characteristic multiplets of peaks resulting from the isotopic pattern of Mg can be assigned to a series of species consisting of MgₓF₂⁻ and MgₓOF₂⁻ in the positive and MgₓF₂⁺ and MgₓOF₂⁺ in the negative ion spectra. The counts per total Bi⁺ shots for these multiplets vary with increased etching time. An additional series of signals that can not be ascribed to Mg containing species (due to disagreement with the isotopic pattern of Mg) are obtained for the 5- and 10-second etched samples. These signals occur as single spectral
peaks and are attributed to Al containing species. They were assigned to $\text{Al}_x\text{F}_{3x-5}(\text{OH})_2^+$ and $\text{Al}_x\text{F}_{3x+1}^+$ in the positive, and $\text{Al}_x\text{F}_{3x-3}(\text{OH})_2^-$ and $\text{Al}_x\text{F}_{3x-1}^-$ in the negative, ion-spectra.

<table>
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<th>Mass</th>
<th>Fragment (Positive ToF SIMS)</th>
<th>Origin</th>
<th>Mass</th>
<th>Fragment (Negative ToF SIMS)</th>
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<td>$\text{Al}_3\text{F}_9(\text{OH})_2^+$</td>
<td>$\text{Al}<em>x\text{F}</em>{3x-5}(\text{OH})_2$</td>
<td>245</td>
<td>$\text{Mg}_3\text{OF}_7^-$</td>
<td>$\text{Mg}<em>3\text{OF}</em>{2x-1}$</td>
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<tr>
<td>291</td>
<td>$\text{Mg}_3\text{F}_9^+$</td>
<td>$\text{Mg}<em>3\text{F}</em>{2x-1}$</td>
<td>271*</td>
<td>$\text{Al}<em>3\text{F}</em>{10}^+$</td>
<td>$\text{Al}<em>x\text{F}</em>{3x+1}$</td>
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<tr>
<td>317*</td>
<td>$\text{Al}<em>3\text{F}</em>{11}^+$</td>
<td>$\text{Al}<em>3\text{F}</em>{2x-1}$</td>
<td>267</td>
<td>$\text{Mg}_3\text{F}_8^-$</td>
<td>$\text{Mg}<em>3\text{F}</em>{2x+1}$</td>
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<tr>
<td>331</td>
<td>$\text{Mg}_3\text{OF}_9^+$</td>
<td>$\text{Mg}<em>3\text{OF}</em>{2x-3}$</td>
<td>307</td>
<td>$\text{Mg}_3\text{OF}_9^-$</td>
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<tr>
<td>353</td>
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<td>$\text{Mg}<em>3\text{F}</em>{2x-1}$</td>
<td>313*</td>
<td>$\text{Al}_3\text{F}_9(\text{OH})_2^+$</td>
<td>$\text{Al}<em>x\text{F}</em>{3x-5}(\text{OH})_2$</td>
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<tr>
<td>359*</td>
<td>$\text{Al}<em>3\text{F}</em>{10}(\text{OH})_2^+$</td>
<td>$\text{Al}<em>x\text{F}</em>{3x-5}(\text{OH})_2$</td>
<td>329</td>
<td>$\text{Mg}<em>3\text{F}</em>{11}^+$</td>
<td>$\text{Mg}<em>3\text{F}</em>{2x+1}$</td>
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<tr>
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<td>$\text{Al}<em>3\text{F}</em>{14}^+$</td>
<td>$\text{Al}<em>3\text{F}</em>{2x-1}$</td>
<td>355*</td>
<td>$\text{Al}<em>3\text{F}</em>{13}^+$</td>
<td>$\text{Al}<em>x\text{F}</em>{3x+1}$</td>
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<tr>
<td>415</td>
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<td>$\text{Mg}<em>3\text{F}</em>{2x-1}$</td>
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<td></td>
<td>391</td>
<td>$\text{Mg}<em>3\text{F}</em>{13}^-$</td>
<td>$\text{Mg}<em>3\text{F}</em>{2x+1}$</td>
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<td></td>
<td>397*</td>
<td>$\text{Al}<em>3\text{F}</em>{12}(\text{OH})_2^+$</td>
<td>$\text{Al}<em>x\text{F}</em>{3x-5}(\text{OH})_2$</td>
</tr>
</tbody>
</table>

Table 1: Table containing all relevant species detected in ToF-SIMS analysis.
Figure 21: Representative section of ToF-SIMS spectra of fluoride pre-treated AZ91D alloy samples after different etching times of 1, 2, 3, 5 and 10 s in 2.5 wt% H$_2$SO$_4$.

Figure 21 shows a section of the negative spectra illustrating the variation in spectral counts for the Mg$_3$F$_7^-$ multiplet at 205 u (unified atomic mass unit) and the Al$_2$F$_7^-$ and Al$_3$F$_6$(OH)$_2^-$ single spectral lines at 187 and 229 u, respectively. For the 1-s curve only the Mg associated multiplet is observable. As etching time is increased, the counts per total number of Bi$^+$ shots decreases for this multiplet until 5 s and then increases slightly for 10 s. Furthermore, for the 5-s etched sample, Figure 21 also shows the maximum spectral-line counts for the masses associated with Al species. For etching times less than 5 s these peaks are almost indistinguishable from the background noise, probably due to a combination of the low penetration depth of the ToF-SIMS technique and a smaller apparent surface fraction. In addition, for longer etching times the peak counts decrease slightly, in agreement with the decrease of β phase on the surface as observed in SEM images.
FIGURE 22: Left: Positive ion ToF-SIMS image of AZ91D alloy after fluoride pre-treatment. Right: ToF-SIMS mapping results for the cavity, indicated by the box in the left image, for (a) Mg, (b) F and (c) NH₄⁺ positive ions, and (d) O, (e) OH and (f) F negative ions.

Smaller cavities were also investigated on the 3-s and 5-s etched samples and they show comparable results. However, larger cavities are represented.

Figure 23: High-magnification SEM images of the steeped edge of a cavity in a pre-treated (5 s 2.5 wt% H₂SO₄ etched and 20 min fluoride steeped) AZ91D alloy surface.

Figure 22 shows a ToF-SIMS positive ion image for all ion masses of the overall surface and several higher magnification mappings for the distribution of
selected mass values across a cavity (the location of which is marked by a box on the overall map). The investigated cavity has a relatively large diameter of 50 µm. The most pronounced signals originating from the large cavity of the 3-s etched sample of Figure 22 are Mg⁺, MgF⁺, NH₄⁺, O⁻, OH⁻ and F⁻. The signal of Mg⁺ is most abundant in the positive ion detection while NH₄⁺ yields a comparatively small signal. In negative ion detection mode, F⁻ has the most prominent signals originating from the cavity. The reason for lack of Mg observed within the cavity can be due to a higher formation probability for negative ions of the species in the cavity or due to a topography effect.

![Figure 24](image)

**Figure 24**: Effect of extraction bias on topography in ToF-SIMS

The applied bias to the extractor in this mode can bend the path of the incident Bi⁺ beam, resulting in only few incident ions hitting the actual cavity in the positive detection mode; in negative detection, the beam path is bent in a way that many incident ions hit the cavity interior. Rossi et al. [87] also observed less contrast for ToF-SIMS images of cavities recorded by negative-ion detection.

Figure 23 shows a high-resolution SEM image of the edge of a cavity after 5 seconds of H₂SO₄ etching and 20 minutes of NH₄F steeping. The image shows only the α phase. A highly structured network can be found on the top layer (on the right of the image) but this coating becomes less visible on approaching the centre of the cavity. This indicates that the structured coating formed on the cavity circumference.
is thicker than that formed in the cavity. According to ToF-SIMS mapping results, these networks correspond to chemically bonded Mg-F structures.

Progressing from the edge of the cavity to the cavity centre the fluoride containing species disappear from ToF-SIMS analysis (Figure 22f) and the structured network reduces in density in SEM images (Figure 23). Figure 22d and Figure 22e show O\(^-\) and OH\(^-\) species positioned in the middle of the figure indicating an unstable oxide layer is still located mainly at the centre of the cavity. This film may be the result of the formation of a large degree of Mg-OH species on the \(\alpha\) phase at the cavity bottom during the etching step or, indeed, during the steeping step itself, or indeed it may be due to a thinner coating at the centre that allows the detection of an underlying O\(^-\) or OH\(^-\) species. Oxygen is also observed by EDX measurements (EDX results in Figure 11 after etching but oxygen peaks were mainly removed from EDX measurements after fluoride steeping (EDX spectra not shown here).

In the literature it has been reported that a mixed oxide/hydroxide layer is the favoured product on magnesium alloy surfaces in solutions containing water [88]. Furthermore, it has been proposed that the fluoride layer may be a fluoride substituted magnesium hydroxide layer with a formula of \(\text{Mg(OH)}_{2-x}\text{F}_x\) or a mixture of \(\text{Mg(OH)}_2\) and \(\text{MgF}_2\) but not of \(\text{Mg}_x\text{OF}_{2x-3}\) [89]. Our results support a mechanism including substitution or exchange of hydroxyl ions with fluoride ions, that takes place after \(\text{Mg(OH)}_2\) formation, resulting in magnesium fluoride (\(\text{MgF}_2\)) or magnesium-oxo-fluorides (Mg-O-F) formation, depending on the nature of the alloy [71]. Where this formation of \(\text{Mg(OH)}_2\) is greatest (\(e.g.,\) in the centre of the cavity), it may not be completely replaced by a fluoride layer during steeping. Alternatively, it is also possible that Mg-F species may be formed by anodic dissolution of magnesium followed by a reaction with the fluoride ions in solution, without the formation of an intermediate \(\text{Mg(OH)}_2\) stage [41].

### 3.5 Conclusions

In this chapter, dependence of the corrosion behaviour of AZ91D alloy on the \(\beta\) phase was investigated in respect to acid etching time. The etching time was found to be a very important parameter resulting in changes to the different distribution of \(\alpha\) and \(\beta\) phases on the surface. Where samples are only etched, the distribution of \(\alpha\) and \(\beta\) phases changes with increasing etching time and these changes result in
increases of both charge transfer resistance and faradaic inductance. In addition, SEM investigations showed that the etching proceeded via a peeling-off mechanism that creates cavities with stepped edges on the freshly exposed surface.

Steeping of samples for up to 20 min in NH₄F solution removes inductance in EIS spectra. However, for longer steeping durations, inductance effects reappear. This reappearance may be due to exposure to solution of the α phase because of either mechanical instability of the β phase or surface cracking in the protective fluoride layer.

SEM and ToF-SIMS were used to give a detailed description of the fluoride layer and highly structured Mg-F networks were found on the top layer of the α (Mg) phase. According to mapping results, the centre of the cavity showed a drop in F intensity and a very strong O²⁻/OH⁻ signal that belongs to a mixed oxide/hydroxide layer. The SEM and ToF-SIMS characterization indicate that the surface layer formed in NH₄F is non-homogenous in thickness and chemical composition.

In parallel to results obtained for NH₄F pre-treatment in literature [71], a systematic investigation of experimental parameters showed that optimum conditions could be achieved for etching and steeping durations of 5 s and 20 min, respectively. For industrial applications, combination of two steps can significantly affect the ultimate durability of any surface treatment as the total corrosion performance is mostly based on the quality of the pre-treatment. In view of modifying magnesium surface with a thin layer mixture of magnesium oxides/hydroxides or fluorides, it would be interesting to explore its effect after a zinc-phosphate coating or hard anodisation process. It would also be of interest to clarify, if a time limit for the pre-treatment conditions reported here exist- for instance during rapid growth of silicate coatings during arc-oxidation process.
4 Electrochemical Polymerization of Polypyrrole on Mg Alloy AZ91D

Part 1: Characterization and Optimization of Electropolymerization Parameters

4.1 Abstract

In this chapter, a first time formation of conducting polymer coating (polypyrrole –PPy-) on Mg alloy AZ91D is reported from aqueous solutions of sodium salicylate by cyclic voltammetry (CV) method. The polymeric films of PPy are directly coated onto AZ91D substrates without any pre-treatment or intermediate steps. The electrochemically formed PPy films are characterized by surface analytic techniques. Electropolymerization conditions such as scan rate, potential range, monomer and salicylate concentration are found to play an important role on the adhesion and hence the corrosion performance of PPy films.
4.2 Introduction

4.2.1 Synthetic metals and doping

Since their discovery in 70s [90] by Shirakawa, Heeger and MacDiarmird, intrinsically conducting polymers (ICP)s such as polythiophene (PT), polyaniline (PANI) and polypyrrole (PPy) and their derivatives have been explored to be promising nominees in the development of semiconductor technologies such as biosensors [91], actuators [92], fuel or bio-fuel cells [93-94], light emitting diodes (LED) [95] and supercapacitors [96-98].

Semiconductor materials have electrical properties between conductors and insulators (Figure 25) because of their free electrons in crystalline patterns. However, electrical conductivity of semiconducting materials can be further improved by adding certain impurities to increase the number of free electrons and thereby conductivity. These doping agents can be donor or acceptor atoms depending on whether they produce electrons or holes that is so called doping. Doping can be achieved by two possible ways; for instance addition of Antimony (Sb) into a Silicon (Si) matrix (Figure a) allows four of the five electrons to bond with silicon atoms leaving one free electron. In this case, positively charged donor atoms lead to ejection free electrons when a potential is applied (n-type doping). This could be also achieved when covalent bonds of the silicon matrix are excited by a sufficient energy. In the second case in Figure b, if Boron (B) with only three valence electrons is introduced into the crystal structure, a fourth covalent bond cannot be formed. This leads to the formation of positively charged carriers known as "holes" in the crystal structure. When the hole is occupied with an adjoining free electron, the electron filling the hole leaves another as it moves (p-type doping). Doping of ICP polymer backbones shows the same properties as metallic doping. For instance, p-type doping is dominant for semi-conductive polymers such as PPy and electron transfer is achieved by alternation of double bonds in the $\pi$-conjugated polymer backbone followed by delocalization. Transfer of charged species through the carbon chain therefore allows for electron transport and gives an electronically conductive material.
Dopant molecules remove or add electrons play an important role during doping of ICP molecules. For example, when polyacetylene (Figure 26a) is doped with iodine ($I_2$), it abstracts an electron from the valence band of the polymer and forms $I_3^-$ (Figure 26b). This leads to formation of a hole that does not delocalise completely and the charge is carried along the chain (Figure 26c-d). But, due to low mobility of the $I_3^-$ counter ions as compared to the positive charge carriers, higher concentration of $I_3^-$ is required to move the polaron close to counter ions. Therefore doping concentration is found to be very important in the case of conducting polymers [99-100].
4.2.2 Pyrrole and electropolymerization of conductive polymers

Among the conductive polymers, PPy is found to be one of the most suitable candidates for corrosion protection because of its relatively easy preparation from aqueous solution and stability at oxidized state. The electropolymerization mechanism of ICPs is a complicated subject as there have been many different mechanisms proposed till now. One of the difficulties is the determination of the different stages of reaction because of the polymerization. However, the insolubility of the PPy along with its non-crystalline nature makes the characterization difficult. As a result, there has not been an agreement among researchers concerning the electropolymerization mechanism of PPy.

Amongst the many polymerization mechanisms, the most discussed mechanism was proposed by Diaz et al. [101] and confirmed by Waltman and Bargon [102-103]. The first step of this mechanism implies the oxidation of monomer M at the electrode to form cation radical M⁺ (Scheme 1).

In the second step, because of a greater unpaired electron density in the α-position of the radical cation, coupling of two radical cations results in the formation
of the dihydromer-dication (Scheme 2). In the stabilization (third) step of electropolymerization, loss of two protons forms the aromatic dimer of pyrrole (Scheme 3)

![Scheme 3](image)

In the next step of the polymerization reaction, oxidation of the dimer results in the formation of pyrrole trimer (Scheme 4) and propagation of the polymer chain takes place (Scheme 5).

![Scheme 4](image)

![Scheme 5](image)

Electrochemical polymerization of Py always gives PPy in its oxidized conducting form (doped) and the resulting polymer chain carries a positive charge every 3 or 4 repeating pyrrole units which are balanced by counter anions. Studies showed that the composition of PPy chains consist of 65% polymer and 35% counter anion in weight [104]. Reasons supporting the relevance of Diaz’s mechanism is believed to be the best one for number of reasons. Firstly, the mechanism is in agreement with EPR (Electron Paramagnetic Resonance) results. Moreover, the elimination of H\(^+\) is in agreement with the observed drop in pH of the solution during polymerization [105].
Among all other mechanism that are summerized in a recent review [104], the one proposed by Diaz which features a combination of several successive reactions (radical cation formation, radical coupling, and deprotonation) is certainly the most probable due to explained reasons above.

4.2.3 Conducting polymers on magnesium

Because of its relatively easy preparation from aqueous solutions and stability at oxidized state, PPy and its derivatives are reported to be one of the most important candidates for corrosion protection. (Details of corrosion protection by ICPs will be discussed in next chapter). This biocompatible ICP [106-107] is also the most widely explored one as a drug delivery material with many advantages as summarized in a recent review [108].

Although there are many studies on the electrochemical polymerization of pyrrole on widely used metals such as zinc [109], aluminum [110], iron [111], copper [112] and these works report that PPy coatings show good mechanical stability and corrosion protection in corrosive media, only a few attempts were aimed to achieve ICP coatings on Mg substrates. Guo et al. [113] showed electropolymerization of aniline on AZ91D alloy surface using an electrochemical pulse method in alkaline solutions, and Jiang et al. [114] reported electropolymerization of pyrrole on a Cu-Ni plated Mg AZ91D surface. Even less information is available on direct electrochemical deposition of PPy on Mg [115] surfaces. This type of surface modification with ICPs may be promising for many applications of Mg alloys, including their usage as drug eluting stents or other types of self degradable metallic implant materials. In these applications, surface modification techniques are of interests which are able to slow down the dissolution rate of Mg, but not completely stop corrosion.

Due to its fast dissolution rate and very negative corrosion potential of Mg, direct polymerization of conducting polymers on the Mg surface is difficult. To overcome this problem, surface passivation is required [112] prior to initiation and attachment of conductive polymer coating. In a different approach, Petitjean et al. [116] and Hermelin et al. [117] recently showed electropolymerization of PPy coatings from sodium salicylate solutions on zinc without any pretreatment. However, Cascalheira et al. [118] determined the oxidation peak of salicylate at
around 1 V and showed the formation of a Cu(II)-salicylate film is favoured at the electrode surface and contributes to its passivation.

Taking the advantage of sodium salicylate, film formation occurs in a one-step process, and does not need any preliminary treatment of the metal. They also claimed that in aqueous media, sodium salicylate is the most suitable candidate that allows the formation of an adherent and homogeneous PPy film on active metals without pre-treatment.

Moreover, sodium salicylate is reported to be a drug in medicine as replacement of Aspirin (Figure 27) and also reported to have analgesic, antipyretic and non-steroidal anti-inflammatory (NSAID) properties that lower the level of apoptosis [119-120] in cancer cells.

![Figure 27: Molecular structures of a) Sodium salicylate and b) Aspirin.](image)

**4.3 Experimental route**

Magnesium AZ91D coupons (2 cm × 2 cm × 0.5 cm) were ground with 1200 grit emery paper and then were cleaned in 1:1 ethanol : acetone mixture for 10 min in an ultrasonic bath. Electrochemical analyses were performed using an o-ring cell (See 2.1 Electrochemical setup) with a three-electrode system.

PPy films were synthesized from 0.1 mol/l pyrrole (Py) containing aqueous solutions of 0.5 mol/l carboxylic acid salts, sodium oxalate (Sigma), sodium malonate (Sigma) and sodium salicylate (Sigma) (pH=6.50) using cyclic voltammetry (CV) between -0.5 V and +1.0 V at 20 mV s⁻¹ scan rate for 20 cycles. It is also possible to use conventional methods for electropolymerization. Electrolytes of 0.5 M sodium oxalate, sodium salicylate and sodium malonate with addition of 0.1 M Py were used. Formation of a black film (pyrrole black) was obtained only from
0.5 M sodium salicylate + 0.1 M Py solution. Where the other electrolytes were used, either corrosion of AZ91D resulted or no surface coverage was obtained.

Afterwards, electrochemical characterization of thin PPy films was performed in monomer-free solutions of the same electrolyte via CVs. EIS measurements were performed in 0.1 M NaSO₄ with a sinusoidal perturbation of ±10 mV for 10 points in each decade over the frequency range from 100 kHz to 10 mHz. Functional groups were characterized with a Fourier-Transform Infrared Spectrophotometer (Bruker Instruments - Germany). The chemical composition was investigated by employing X-ray induced photoelectron spectroscopy (XPS)-Phi 5600. Also, positive and negative static time-of-flight secondary-ion-mass-spectrometry (ToF-SIMS) measurements were performed on a ToF SIMS V spectrometer (ION TOF, Münster). A field-emission scanning electron microscope (Hitachi FE-SEM S-4800) was used to investigate surface morphology.

After the characterization of PPy films by several surface analytic techniques, electropolymerization parameters such as scan rate, dopant concentration and potential region were optimized. Resulting PPy films were tested by a sticky tape from Tesa (Germany) that was used during pull-off tests to determine the level of adhesion of PPy coatings.

The electrical conductivity of the coated samples was measured using a four-probe D.C. technique; constant current was applied to the sample through connecting probes and the potential drop was measured by means of a multimeter. Then the current was and the potential was measured again. From a series of such measurements, a regression value of the resistance and hence of the electrical conductivity was obtained.

4.4 Results and discussion
4.4.1 Electrochemical polymerization and characterization of pyrrole

Electropolymerization of pyrrole in the presence of salicylate ions has been studied previously. Cascalheira et al.[118] determined the oxidation peak of salicylate at around 1 V and showed the role of salicylate ions in the anodic behavior of copper where formation of a Cu(II)-salicylate film is favoured at the electrode surface and contributes to its passivation. In references [116-117] it is claimed that in aqueous media, sodium salicylate is the most suitable candidate that allows the
formation of adherent and homogeneous PPy films without pre-treatment on active metals.

Figure 28: Cyclic voltammogram of AZ91D in 0.5 M sodium salicylate solution, scan rate 20mVs⁻¹. Inset: First cycle

Figure 28 shows the electrochemical behaviour of a magnesium AZ91D electrode in 0.5 M sodium salicylate solution. It is clearly seen that the surface of Mg AZ91D alloy can not be passivated easily due to anodic dissolution of Mg ranging from -0.5 to 0 V (inset figure). However, a drop of current density around 0 V is observed suggesting lowering of the anodic dissolution rate. At the end of the forward scan, a decrease of the current drop is obtained with a corresponding peak in the reverse scan direction at around 0.9 V. This reversible red-ox couple is attributed to oxidation-reduction of sodium salicylate. At the beginning of the 2nd cycle, the current density value does not reach as high a value in the potential range of -0.5 / 0 V as in the 1st cycle, probably indicating partial passivation of the surface, but the current density values are still high. Repetitive 20 cycles in Figure 28 show a shift of
current density to more anodic values, suggesting that reversible red-ox behaviour of salicylate takes place, and dissolution of the AZ91D surface is dominant.

Figure 29: Cyclic voltammogram of AZ91D in 0.5 M Sodiumsalicylate + 0.1 M Pyrrole, scan rate 20mVs$^{-1}$. Total Charge; $Q_{dep} = 4.995$ C Inset: First cycle.

Figure 29 shows electrochemical polymerization of Py on AZ91D surface from sodium salicylate solution. Oxidation potential of Py - that is reported around 0.8 V - can not be detected due to overlapping with the oxidation peak of sodium salicylate. However, in contrast to the first cycle (inset figure of Figure 28) of monomer free solution, the intensity of the oxidation peak around ~0.8 V sharply decreases at the end of the first cycle in Py containing electrolyte (inset figure of Figure 29). This strong drop of the peak intensity upon addition of pyrrole is a result of pyrrole being involved in the passivation process and the current decrease continues in repetitive cycles in Figure 29. A slight current increase was observed at the end of the each cycle that is attributed to a monomer oxidation process by step by step polymer film growth.
Figure 30: Cyclic voltammogram of PPy film (deposited from 0.1 M pyrrole in 0.5 M sodium salicylate, at a scan rate of 20mVs⁻¹; \( Q_{dep} = 4.995 \) C) in a monomer free solution of 0.5 M sodium salicylate at scan rates of (a)10, (b) 20, (c) 30, (d)40, (e) 50 mV s⁻¹.

Figure 30 shows the scan rate dependence of the PPy films in monomer-free solution. One broad oxidation peak is observed during anodic scanning that is associated with overlapping of the PPy and salicylate peaks. On the cathodic part, a wide reduction peak is observed. Anodic and cathodic peak current densities are related to the oxidation and reduction of PPy. The electrochemical process is diffusion controlled, as both the anodic and cathodic peak intensities are increased with increasing scan rate.
Figure 31: Nyquist plots of bare and PPy coated AZ91D alloy samples in 0.1 M Na$_2$SO$_4$ solution. Inset: Open circuit potentials of bare and PPy coated AZ91D alloy samples recorded in 0.1 M Na$_2$SO$_4$ solution during 24 hours.

Figure 31 compares the electrochemical impedance of bare AZ91D alloy with fresh PPy coatings. Electrochemical impedance spectroscopy of pure magnesium in sodium sulfate solutions has been previously studied [81, 84]. The Nyquist plots were characterized by two well-defined capacitive loops followed by an inductive loop [33, 121] (Detailed information about these loops are found in Chapter 4.4). The PPy coated AZ91D clearly shows a significant increase of the polarization resistance ($R_p$) as compared to the bare sample, indicating a protection with a barrier effect of PPy [121]. Moreover, the inset figure of Figure 31 shows the open circuit potential (OCP) recorded during 1 day in the same electrolyte. PPy coated samples did not show noisy oscillations as compared to bare AZ91D, also suggesting that the PPy coating decreases the dissolution of Mg in Na$_2$SO$_4$ electrolyte.
5.4.2. FTIR-ATR, XPS, ToF-SIMS measurements and SEM analyses

FT-IR spectra of a salicylate copper complex have been reported previously [122]. Santos et al. [123] also showed FT-IR spectra of PPy molecules in sodium salicylate medium and determined the characteristic peaks with a shift of wave numbers due to a copper-salicylate complex. In addition, C=O stretching of aromatic carboxylic acid was not detected in the 1700–1650 cm\(^{-1}\) region as a strong band. Instead, characteristic salicylate peaks were detected as a \((\nu_s(COO^-))\) band around 1377 cm\(^{-1}\) and shifted to 1392 cm\(^{-1}\), in the case of copper salicylate by splitting into two components. Similarly, for PPy/Mg AZ91D system, these characteristic \((\nu_s(COO^-))\) bands were detected around 1597 and 1556 cm\(^{-1}\) in Figure 32, probably due to formation of a Mg salicylate complex. In addition, characteristic bands of the ring stretching are found between 1400 and 1500 cm\(^{-1}\). The characteristic peaks of PPy were detected around 1300 cm\(^{-1}\), 1185 cm\(^{-1}\) and 1035 cm\(^{-1}\), according to references [124-127].

Figure 32: FTIR-ATR spectra of PPy coated Mg AZ91D.
Figure 33: XPS survey spectra of PPy polymer.

Figure 33 shows an XPS survey spectrum of PPy/AZ91D surface containing mostly C (63.43%), O (28.00%) and N (3.42%). The presence of nitrogen atoms is a further indication of PPy coating. Additionally, the surface coverage of PPy is relatively high as the signals from the substrate (Mg, Al, Zn) are very low. Figure 34-a and -b show SEM pictures of PPy coated Mg AZ91D alloys with a typical cauliflower type morphology of PPy grains [128] with a diameter ranging between 500nm to 800nm. As the grind striations are still visible on the surface, the passivation process leads to a very thin film formation in sodium salicylate medium.
Figure 34: SEM pictures of fresh PPy surface; a) Lower magnification image with grinding striations are visible. Inset: Higher magnification image showing usual PPy morphology b) High magnification of cauliflower like PPy structures.

Figure 35: ToF-SIMS spectra of Mg AZ91D alloy before (top) and after (bottom) PPy coating. a) Mg$^+$, b) CN$^-$ ions, c) C$_3$H$_3$O$_2^-$ and d) C$_5$H$_4$NO$^+$, C$_6$H$_8$N$^+$. ToF-SIMS investigation revealed the successful formation of a PPy layer. Figure 35a-d shows characteristic fragments after electrochemical treatment in sodium salicylate (top) and a solution of PPy in sodium salicylate (bottom). Panel a shows a decrease of the Mg$^+$ signal, indicating a larger film thickness and better coverage of the coating containing PPy. Panel c shows the fragment of C$_3$H$_3$O$_2^-$, which is related to salicylate. A relative decrease of the signal upon addition of PPy is observed. The ratio of C$_3$H$_3$O$_2^-$ to Mg$^+$ stays approximately constant. This implies that salicylate also incorporates into the PPy layer. Furthermore, an increase in the appearance of PPy specific fragments (C$_6$H$_8$N$^+$, CN$^-$) is shown in panels b and d. Also, the signal of C$_5$H$_4$NO$^+$ (panel d) appears only in the PPy containing sample, indicating a possible reaction of salicylate and PPy.
4.4.3 Optimization of electrochemical parameters

4.4.3.a Optimization of salicylate concentration and scan rate

First, the effect of salicylate concentration (0.5M, 1.0 M and 3.0 M) on the resulting coating properties was studied in 0.1 M Py containing salicylate solutions, while keeping a fixed scan rate (20 mV s\(^{-1}\)) and cycle numbers (20 cycles) in the potential region between -0.5 V and 1.0 V. Figure 36 shows the EIS spectra measured after coating AZ91D in solutions of varying salicylate concentration. The variation of the salicylate concentration did not lead to a significant change of the polarization resistance (R\(_p\)) (i.e., the difference along the real axis between the resistance at the highest and lowest frequencies) of the coated samples. Nevertheless, PPy films which are synthesized from 0.5 M salicylate + 0.1 M Py solution show the best corrosion resistance, without any sign of inductive effect in the impedance spectra. In the case of Mg and Mg alloys, these inductive loops appearing in LF regions as scattered points and are commonly reported as a sign of active dissolution [30-32]. This behaviour is generally assumed to be due to the presence of adsorbed surface species such as Mg(OH)\(^+\)\(_{ads}\), Mg(OH)\(_2\)\(_{ads}\) or Mg\(^+\)\(_{ads}\) [33,34]. Therefore, even though only a minor effect on the R\(_p\)-values is found for different salicylate

Figure 36: Determination of optimum sodium salicylate concentration by using EIS technique.
concentrations in the PPy synthesis solution, the absence of an inductive loop (or even any scattered data points in the region of the inductive loops of the spectra) is an indication for somewhat better protective properties of this coating as compared with those synthesized with higher salicylate concentrations.

![Graph showing EIS examination](image)

**Figure 37:** Determination of optimum scan rate by using EIS technique.

Using this optimum salicylate concentration, optimum scan rate was examined at different scan rates of 10, 20 and 50 mV s\(^{-1}\) in the potential region between -0.5 V and 1.0 V at a fixed cycle number (20 cycles) from 0.1 M Py containing 0.5 M sodium salicylate solution. Figure 37 shows the EIS examination to determine the optimum scan rate for PPy films. It is found that AZ91D surfaces look brown in color instead of “pyrrole black” after electrodeposition at scan rates greater than 50 mVs\(^{-1}\). At this scan rate, the coating time is not sufficient to achieve a thick enough PPy layer on AZ91D surface. Hence, samples do not show good corrosion behaviour with \(R_p\) values very close to the bare AZ91D sample. On the other hand, when a scan rate of 10 mVs\(^{-1}\) is chosen, the propagation of Py molecules does not take place and acidic etching of the electrolyte removes freshly formed nucleation sites and the corrosion occurs instead of electrodeposition of a PPy layer. Compared
to others, only PPy films synthesized with a scan rate of 20 mV s\(^{-1}\) lead to corrosion protection of AZ91D in Na\(_2\)SO\(_4\) solutions with a R\(_p\) value \(~25\) kOhm.

### 4.4.3.b Optimization of potential region

**Figure 38:** Cyclic voltammograms of AZ91D in 0.5 M Sodiumsalicylate + 0.1 M Pyrrole, between different initial and end potential ranges (a-f) at scan rate 20 mV s\(^{-1}\). Inset figures of a-f shows the first cycles during electropolymerization.
In order to investigate the optimum potential range, experiments of different initial (-0.5 V and 0.0 V) and upper potentials (1.0 V, 1.2 V and 1.5 V) were carried out, while keeping the above mentioned parameters fixed (a scan rate of 20 mV s\(^{-1}\), cycle number of 20 cycles in 0.1 M Py containing 0.5 M sodium salicylate). After that, PPy films were again tested by EIS.

Figure 38 shows electrochemical polymerization of Py on AZ91D with different potential region variations between -0.5 V and 1.5 V. Cyclic voltammograms with similar shapes were obtained for each condition. However, due to overlapping of oxidation peaks of sodium salicylate and of Py around 0.8 V, separate peaks were not observed. In all inset figures of Figure 38, independent of initial and end potentials, the oxidation peak around ~0.8 V sharply decreases at the end of the first cycle. This is a sign of pyrrole being involved in the surface passivation process without oxidative degradation, and the current decrease continues in repetitive cycles. A slight current increase was observed after each cycle that is attributed to the oxidation process of Py by step by step polymer film growth.

Figure 39 shows the EIS results of freshly coated PPy films on AZ91D electrodes prepared by cycling between the different potential regions. All PPy coatings provide some corrosion protection to the bare AZ91D electrode. However, change of initial and end potential values during electropolymerization of PPy did not lead to a very significant improvement of the polarisation resistance of freshly coated AZ91D samples. Nevertheless, for all end potential values, an initial potential of -0.5 V was found to provide higher \(R_p\) values as compared to the initial potential value of 0.0 V.
Figure 39: Nyquist plots of bare and PPy coated (fresh) AZ91D alloy samples in 0.1 M Na$_2$SO$_4$ solution.

After 24 hours in Na$_2$SO$_4$ solutions, EIS tests were repeated. Results in Figure 40 show that for all PPy coated samples, the $R_p$ values were increased after 24h in solution. The most significant increase of $R_p$ value was found for two coatings: 1) $U_{in}$ (Initial potential): -0.5V, $U_{f}$ (Final potential): 1 V; and 2) $U_{in}$: 0.0V, $U_{f}$: 1 V. For these coating parameters, $R_p$ values of ~50 and 60 kOhm were observed after 24 hour immersion. This increase in the $R_p$ values with immersion time can result from precipitation of corrosion products in the defects of the coatings, as the initial $R_p$ values for freshly coated samples clearly indicate only weak barrier properties. The precipitation of corrosion products leads to additional (weak) corrosion protection. In addition, for these samples the PPy coatings were well adhered on the surface after 24 hours of immersion, whereas coatings prepared with other potential ranges resulted to peeling-off of the PPy. This is in contrast to freshly prepared coatings which all showed very good adhesion. Due to these observations, the adhesion properties of the coatings were further explored, as described in the next section.
4.4.3.c Influence of electrochemical parameters on adhesion and conductivity of the coatings

Figure 41 demonstrates the relationship between applied potential and level of adhesion by pull-off tests. The level of adhesion decreases after 24 hours of immersion in Na$_2$SO$_4$ (from a-e, or from b-f) when wider ranges are chosen during electropolymerization of Py. Moreover, an increase of initial potential from -0.5V to 0 V results with more adhesive PPy coatings on Mg AZ91D surface.
Figure 41: Mechanical adhesion test of PPy films after 1 day immersion in 0.1 M Na$_2$SO$_4$ solution.

Figure 42: SEM images (top-view) of PPy films (a-f) on AZ91D Mg alloys prepared in different potential regions. Inset pictures shows higher magnification images.
Figure 43: Tilted SEM images of PPy films (a-f) on AZ91D Mg alloys prepared in different potential regions showing the change of surface roughness by means of applying different potential regions.

SEM images of the coated samples (Figure 42 and Figure 43) indicate that change of surface morphology can—at least partially—explain the different adhesion behaviour. For example, when higher initial and end potential values are chosen during electropolymerization of Py, the level of coating roughness increases (Figure 42a-c Figure 43a-c and Figure 42d-f and Figure 43d-f) and irregular surface morphologies (inset Figure 42a-f) are obtained. Similar to the results of adhesion tests in Figure 41, this type of surface morphology shows worse adhesion behavior after 1 day of immersion in Na$_2$SO$_4$.

<table>
<thead>
<tr>
<th>$U_{f}$ (V)</th>
<th>$U_{in}$ (V)</th>
<th>-0.5</th>
<th>0.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td></td>
<td>16.834 S cm$^{-1}$</td>
<td>22.312 S cm$^{-1}$</td>
</tr>
<tr>
<td>1.2</td>
<td></td>
<td>1.980 S cm$^{-1}$</td>
<td>0.459 S cm$^{-1}$</td>
</tr>
<tr>
<td>1.5</td>
<td></td>
<td>0.096 S cm$^{-1}$</td>
<td>0.681 S cm$^{-1}$</td>
</tr>
</tbody>
</table>

Table 2: 4-probe conductivity measurement results (through the film—horizontal direction—) of PPy films synthesized onto Mg AZ91D alloys in between different potential regions (All values are reported with an experimental error of ±10%).
Another interesting finding is that the change of initial and end potential values also affect the conductivity of the resulting PPy. Table 2 shows the relationship between conductivity of the PPy coating and the chosen potential regions during electropolymerization. For both initial potential values (0.0V and -0.5V), as compared to end potentials of 1.2 and 1.5V, highly conductive PPy films are obtained when an end potential of 1.0 V is chosen. However, initial potential value of 0.0 V is found to give a relatively high conductive PPy film with smoother surface morphology (Figure 42d). It can be concluded that more adhesive and high conductive PPy films are synthesized when a relatively short potential range is chosen during electropolymerization.

![Figure 44: Charge values of PPy films on AZ91D Mg alloys in between different potential ranges by cyclic voltammetry. Inset table shows the total charge of corresponding samples.](image)

Interestingly, the coating parameters leading to enhanced adhesion and reduced coating roughness are found to be related to an increase of total charge. It is found that the total charge is increased when a smaller potential range is chosen during the electropolymerization (Figure 44). For all conditions, the observed decrease of charge as a function of cycle number indicates a surface passivation that corresponds to current drop of the anodic peak around 0.8V. This, moreover,
increases the conductivity of the coatings. The resulting more uniform surface morphology may therefore originate from an increased number of nucleation sites; as a result better corrosion protection is achieved.

From all above mentioned results, the relationship between adhesion, conductivity and corrosion resistance is explained with overoxidation of PPy films. Kaplin [129] et al. showed that overoxidation of PPy films occurs when the end potential exceeds 1.0 V. Similar results for 0.1 M Py concentration were reported by Otero [130] et al. By controlling the magnitude of the electrical field, some effects are obtained over the morphology of the freshly formed polymer. It is reported that PPy films prepared at lower anodic potentials are found to be denser and homogeneous. But, PPy films grown at higher anodic potentials form less regular surfaces [131-132]. Besides, if the potential range chosen is too high, overoxidation can occur which reduces the electrochemical activity and conductivity of the polymer film with decreased adhesion to the substrate and loss of mechanical properties [133-134]. A similar behaviour of PPy films was also found on Mg AZ91D alloy surface in our work.

![Figure 45: FIB-cut measurements showing the film thickness values varying between ~300 and ~1000 nm.](image)

On the other hand, applying different potential regions did not affect the film thickness values. Figure 45 shows a cross-sectional focused ion beam (FIB-Cut) measurement performed on a PPy coating (U_{in}: 0 V, U_{f}: 1 V). Cauliflower like surface structures were found to have cavities within, and the thickness values varied
between ~300 and ~1000 nm. These values do not change by changing the potential range applied.

Depending on above mentioned results and corrosion tests, two PPy/AZ91D electrodes (coated in potential ranges of 0.5/1.0 and 0.0/1.0V) are chosen for long term corrosion tests, as these coatings show better corrosion protection (Figure 40), mechanical adhesion (Figure 41) and higher electrical conductivity (Table 2) as compared to others.

### 4.4.4 Long Term Corrosion performance of PPy/Mg AZ91D

![Nyquist plots of PPy coated AZ91D Mg alloy in 0.1 M Na$_2$SO$_4$ during 10 days. Potential region: 0.0V/1.0V](image)

Figure 46: Nyquist plots of PPy coated AZ91D Mg alloy in 0.1 M Na$_2$SO$_4$ during 10 days. Potential region: 0.0V/1.0V
Figure 47: Nyquist plots of PPy coated AZ91D Mg alloy in 0.1 M \( \text{Na}_2\text{SO}_4 \) during 10 days. Potential region: -0.5V/1.0V.

Figure 46 and Figure 47 show the Nyquist plots of two PPy coated samples in \( \text{Na}_2\text{SO}_4 \) during 10 days. The long term corrosion protection of PPy film prepared in the shorter potential range (higher initial potential) is found to be more durable as compared to the one in Figure 47. Even though PPy/Mg AZ91D in Figure 47 shows slightly better \( R_p \) values up to first 5 days, a drastic decrease takes place between 5 and 7 days due to peeling-off of the surface film, and results in strong corrosion of Mg AZ91D substrate. Moreover, the PPy/Mg AZ91D samples coated between 0.0/1.0 V in Figure 46 do not peel-off and show better protection during 10 days, with only a slight decrease of \( R_p \) values.

4.5 Conclusions

This chapter demonstrates direct growth of a conductive polymer (polypyrrole) thin film on a magnesium alloy (AZ91D) without any pretreatment for the first time. Fourier-Transform Infrared Spectroscopy (FT-IR), X-Ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (ToF-SIMS) and scanning electron microscopy results shows that the magnesium...
AZ91D surface is covered by a thin PPy film. Electrochemical impedance spectroscopy results (EIS) demonstrate that this sodium salicylate doped PPy layer has a corrosion protection property in NaSO₄ solutions.

Effect of electrochemical coating parameters such as scan rate, sodium salicylate concentration and potential range on the corrosion behaviour of the PPy films was studied with electrochemical impedance spectroscopy (EIS). It is found that the resulting surface morphology and the conductivity are highly affected by the potential range chosen to deposit PPy on Mg AZ91D alloy surface. For long term (10 days) immersion periods, PPy coatings electrodeposited in between 0.0/1.0 V were most effective in reducing corrosion rate of Mg. The PPy coatings prepared under optimized conditions remained well adhesive over this period; no peeling-off was observed.

In view of practical applications, for instance in biomedical applications of Mg and its alloys, such salicylate doped PPy layers on Mg alloys have a high potential for tailoring the degradation rate, since all components (substrate, passivating agent, coating) of the resulting system are non-toxic. Therefore, these coatings may have potential for tailoring the degradation rate of Mg alloys for biomedical and drug-releasing applications.
5.1 Abstract

In this chapter, corrosion behaviour of PPy/Mg AZ91D alloy is studied in simulated body fluid (SBF) solutions at body temperature, Hydrogen gas collection measurements, polarisation curves and EIS results showed that the adherent PPy coatings hinder the anodic dissolution of Mg substrate and enhance the corrosion resistance by releasing dopant anions. Moreover, further functionalization of PPy layers with Albumin (Alb) monolayers also provides a better controlled release profile over 20 days with zero order kinetics.
5.2 Introduction

5.2.1 Corrosion control with ICPs

Corrosion protection by ICP coatings has been reported to be not favorable under practical conditions [135-136], as has been discussed in a recent review [137]. However, a good corrosion protection can be achieved in practical applications if these coatings are applied together with other coatings in sandwich like structures. For instance, an effective coating against corrosion consists of several layers: a primer that enhances the adhesion to the metal (~1µm) followed by a thick polymer layer (~20 µm) containing anticorrosion pigments. Finally, a thin top-coat is applied [138]. The most important property of a coating is the barrier effect and the electrochemical inhibition. However, an electrochemical process of anodic and cathodic reactions takes place on substrate surface [139];

\[ M \rightarrow M^{+n} + ne^- \] ......................................................... (11)

As a counter reaction, \( O_2 \) is reduced, according to either;

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- (pH \geq 7) \] ................................................ (12)

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O (pH < 7) \] ............................................... (13)

Reaction (11) corresponds to dissolution of metal substrate that can be reduced if either a sacrificial coating (e.g. zinc deposition on steel) is employed or potential of the metal is shifted into the passivation domain by formation of a metal-oxide layer. Formation of insoluble compounds attached to the metal surface, resulting from chemical or electrochemical treatment of the metal [139], contribute to its passivation. However, hindering the diffusion of \( O_2 \) and \( H_2O \) by increasing the thickness of the coating also increases the protection efficiency. Addition of corrosion inhibitors such as chromate salts, [140-142] is also found in general to maintain good corrosion properties in metals. Even though chromate-based techniques provide excellent passivation of metals, they are now prohibited due to environmental regulations and replaced with alternative solutions as recently summerized in several reviews [143-144].
The use of ICPs against corrosion of the metals was firstly investigated in the 80’s, after DeDerry [145] showed a polyaniline (PANi) film obtained by electrochemical oxidation of aniline on stainless steel (SS) and mild steel (MI) surfaces. This work was followed by electropolymerization of Py in neutral medium on the same metals. First reports [146-147] of the resulting PPy films were not found to adhere to metal surface. Because of the oxidation potential of the metals is lower than the oxidation potential of monomer, hence a considerable amount of metal dissolution was observed during electropolymerization. But this problem was overcome by changing the rates of electropolymerization. For instance, using solvents slightly alkaline of water [148] or pre-treatment of metal surfaces [149] result in more adhesive PPy films. Additionally, choice of electrolytes including proper anion groups to form insoluble metal-salt layers [150] is found to be another important way to obtain better PPy films on active metals as shown in Figure 48. This metallic salt layer only partially passivates the metal by hindering its electrochemical activity.

![Figure 48: Figure shows effect of metallic salt onto adherence of resulting polymer. Dissolution of the metal is favoured (a) if the anions in electrolyte have no ability to form an insoluble metallic complex. In b), more homogenous films are obtained in the presence of a metallic salt layer (b).](image)

The use of ICPs brings an original concept to the protection of metals. Although the way the ICPs work to protect metals against corrosion is different than the mechanisms accepted for polymeric coatings in general, the protection mechanism is still debated. But till now, four main mechanisms [139] are reported to explain their working principles during corrosion process:
a) Displacement of the electrochemical interface,
b) Ennobling the metal by polymer in its oxidized state,
c) Self-healing properties,
d) Barrier effect.

5.2.1. a Displacement of the electrochemical interface

When a metal is coated with another noble one, for instance when iron is coated with nickel, the electrochemical interface moves from oxidizable metal (Fe)-electrolyte interface to noble metal (Ni)-electrolyte interface and prevents the corrosion of Fe substrate. The underlying metal escapes from the aggressive environment if the top Ni layer is free from any defect (pinholes or scratches). When an oxidizable metal is coated by ICPs, the same situation is observed if the ICP remains in its oxidized state. Therefore the electrochemical interface moves to the polymer-electrolyte interface and the underlying metal is no longer in contact with the electrolyte as illustrated in Figure 49.

Figure 49: a) Corrosion of a metal in corrosive media by dissolution of metal. b) Displacement of the electrochemical interface to electrolyte/ICP by reducing of polymer.

This effect was reported by Lacroix et al. [151] for a bilayer structure of PPy/PANi to show the displacement of the electrochemical interface. Direct electrochemical deposition of PANi onto zinc fails and large amounts of metal dissolves. But, if a zinc electrode is firstly coated by a thin layer of PPy from aqueous electrolytes of salicylate, the metal dissolution is not observed during PANi coating. The film is found to be very stable in acidic electrolytes indicating that the underlying metal is fully protected. This confirms the displacement of the
The electrochemical interface to polymer-electrolyte region from its usual location. The same concept is also reported by Iroh et al. [152-153] by showing that bilayer structures also lower the porosity and provide better protection compared to single layer coatings [154].

Recently, Michalik and Rohwerder [155] showed that oxygen reduction is very crucial to determine the shift of the electrochemical interface. They showed that the oxygen reduction process can take place at the metal-electrolyte interface again if the resulting polymer is fully reduced in the presence of small surface defects. Therefore O₂ and H₂O can reach the metal surface through the porous surface of ICP coating by diffusion. On the other hand, they showed that fast reducing of ICP coatings is also needed in the case of these surface defects. Because the redox potential of the polymer is generally above that of the metal and thus it is capable of oxidizing the metal by reducing itself. In this case, the electrochemical interface is not displaced, but a barrier effect is obtained. Therefore open circuit potential (OCP)–time curves are generally used to understand the efficiency of the ICP during corrosion tests as the kinetics of reduction reactions of O₂ and H₂O is also depends onto OCP value of the bare metal.

When a metal is coated with a highly doped ICP, and as long as the ICP remains in its conductive state, OCP of the ICP/Metal system is always above that of the bare metal electrode. When the ICP is reduced, the potential value drops to a lower value. For instance, for PPy, the redox potential of O₂/H₂O is always more positive than the PPy and hence the reduction of O₂ always takes place at the polymer surface and produces OH⁻ ions [139]. These OH⁻ species are reported to be responsible for delamination [151-155] in many cases.

As a conclusion, displacement of the electrochemical interface can only delay the corrosion process for a certain time by reducing the ICP coating through reduction of O₂ on the polymer surface.

5.2.1.b Ennobling the metal by polymer in its oxidized state

The main idea of ennobling the metal surface by ICPs is that the metal surface is set to a potential within its passive range if it couples with an ICP at its oxidized state as shown in Figure 50. In general, an oxidizable metal has 3 different electro kinetic regions: active, passive and trans-passive. When the sample is in contact with
a weak oxidant, a counter electrochemical reaction, namely reduction reaction may correspond to active region with a high corrosion current value. In this region, the metal has no ability to form an insoluble isolating layer as it has in a passive region and hence a corrosion process takes place (Red line in Figure 50).

Figure 50: Schematic representation of ennobling mechanism of metal surface that have a passive region.

On the other hand, if the metal is coupled with strong oxidants (blue curve in Figure 50) such as ICPs, the corrosion current density values correspond to the passive region and are relatively lower than the first case [139]. In this case, the width of the passivation range is very important. Because when a metal is coated by an ICP at its oxidized state, a mixed OCP value is obtained due to galvanic coupling between the metal and polymer. However, the resulting current corresponds to the net reaction from the reduction of the polymer and the oxidation of the metal. Therefore, the most favorable situation is the fact that the reduction of the polymer falls within the passive area of the metal.

The ennobling effect by ICPs is widely studied with different ICPs coatings [111, 156-162] In most cases, good protection was reported with the ennobling mechanism for PANi coatings [111, 160]. However, for PPy, this mechanism has also been widely investigated. Recently, Michalik and Rohwerder showed that [155]
PPy could protect small surface defects easily. But for large defects, PPy was considered not to have enough capability to passivate iron and ennobling was not successful [139].

As compared to displacement of the electrochemical interface, it could be concluded that the ennobling effect is applicable for systems where small scratches occur during the corrosion. This effect also would be more expected within the metals that have large passive potential areas.

In view of non-passivating metals such as magnesium, this mechanism can not be discussed since magnesium metal does not have a passivation region like other metals (e.g. steel, Al). Therefore, when magnesium is coated by an ICP at its oxidized state, the resulting current from the reduction of the polymer can not fall within any passive area of magnesium.

5.2.1.e Self-healing effect by release of dopant anions

As already mentioned with the mechanisms above, due to galvanic coupling between the metal and ICP, reduction of the polymer and oxidation of the metal surface is interlinked. In this special case, reduction of $O_2$ can occur either at the polymer surface or at a scratch and result in formation of $OH^-$ (Figure 51). Depending on the metal substrate, two mechanisms can be predicted: either the metal initiates the formation of a metal oxide, or the doping anions are released and act as inhibitors [139, 163]. However, these molecules can only be released when the corrosion starts [164-166].

![Figure 51: Schematic representation of oxygen reduction on PPy surface in neutral solutions.](image)
This property of ICPs is described by Chang and Miller [167] for drug release applications and further details such as mobility, size and valance of the dopant anions were reported by Weidlich et al. [168].

The self healing effect of the ICPs is generally assumed as an extension of the ennobling mechanism. But in this case, doping of the polymer is found to be very important for drug delivery applications. Therefore, choice of a suitable dopant molecule is very crucial for use of these materials in drug delivery applications [169].

5.2.1.d Barrier effect of the polymer

As previously explained in chapter 6, investigations including electrochemical polymerization of conducting polymers on active metals such as iron [111, 170], copper [150], aluminum [110] and zinc [109, 171] report that these coatings show good adherence on surface and good performance in corrosive media [139, 172]. Good adherence of ICPs onto the metal substrates acts as a simple paint layers in general and shows barrier properties. The barrier effect slows down the corrosion by hindering diffusion of \( \text{O}_2 \) and \( \text{H}_2\text{O} \) to reduce the corrosion at the interface[173]. However, in the presence of very aggressive anions such as chlorides, diffusion of these anions must be prevented in the barrier effect.

For ICPs, independently of whether the polymer is conductive or not, diffusion rates of these species are mainly dependent on the porosity of the polymer. Therefore decrease of the film porosity [174] and changing the surface hydrophobicity [154-155] is generally reported to enhance barrier properties.

5.2.2 PPy in biomedical research

Among all other ICPs, Py is reported as a strong candidate for biomedical applications with a soluble nature in neutral or weakly acidic conditions. However, its low oxidation potential and environmentally friendly nature as compared to aniline and thiophene make PPy very promising for a wide range of biomedical applications including the development of artificial muscles [175], neural recording [176], sensors [91, 177], actuators [178] stimulation of nerve regeneration [179] and controlled drug release [171, 180].
Among all of these applications, controlled drug release applications by PPy is very promising. The release of dopant anions from the PPy backbone has been reported to promote cell survival and growth for biomedical implants [181]. However, it has also been reported that these systems could be used as suitable platforms for the delivery of a wide range of biomolecules [182] such as glutamine [183], ATP [184], salicylate[132] and dopamine [185] in the presence of different dopant anions. On the other hand, dopant anions themselves can also act as drugs if they have healing properties in biological environments. For instance, sodium salicylate is reported as a suitable replacement of Aspirin (Figure 27) because of its analgesic, antipyretic and non-steroidal anti-inflammatory (NSAID) properties. These properties are also known to lower the level of apoptosis [119-120] in cancer cells. Therefore use of salicylate during electropolymerization processes may give an opportunity afterwards for healing by releasing of the dopant anion. Healing ability of a drug eluting system is related to its drug elution kinetics as shown in Figure 52. In most cases, zero order kinetics is preferred with a reservoir system showing a constant release rate. This is mostly obtained if a constant drug source such as pure liquid drugs or dispersed particles are provided. If the drug source is a non-constant source (dissolved drug in solution), it usually gives first order (Fickian) release rates [186]. In this case, the dose released does not provide a constant healing rate and therefore is not stabilized as like in the zero order kinetics.

Figure 52: Two patterns of drug delivery; a) Fickian and b) Zero order kinetics.
5.2.3 Mg and its alloys in biomedical research

In medical science, one of the most promising areas is the development of biodegradable implant materials and drug eluting stents (DES). As compared to traditional implant materials such as Ti and stainless steel, biodegradable materials do not cause long-term irritation or incompatibility with the biologic environment. Biodegradable implants are mainly made of polymers, such as poly-lactic acid and derivatives [187-188]. But, these materials are usually found to have limited mechanical properties and therefore can not meet with the requirements of the desired applications [189-190].

On the other hand, Mg and its alloys have been regarded as potential biodegradable materials. In 1878, Mg wires to stop bleeding vessels were first introduced by Edward Huse [1]. Since then, many researches have been reported about these materials being used as biodegradable components [191-196].

Although mechanical properties of Mg are found to be very close to human bone [195], the use of this metal as bio-degradable orthopedic implants is limited due to its inhomogeneous corrosion. Additionally, alkalization and H$_2$(g) production during corrosion of Mg [25] is reported to be critical for the biological environments. Therefore many attempts including physicochemical surface modifications, bioactive, biomimetic or self-assembled monolayer coatings have been reported to tailor the magnesium corrosion [197-199]. For instance, albumin attachment onto Mg surfaces [200-201] is reported to increase corrosion resistance of magnesium in simulated body fluid (SBF) solutions. Additionally, it is also shown that the surfaces modified with this most abundant blood protein has a tendency to have antithrombogenic properties [202-203]. Therefore, these types of protein coatings could be helpful for further improvement of the Mg surfaces to tailor the corrosion rates.

In the previous chapter, the direct electrochemical polymerization of PPy on Mg alloys AZ91D [204-205] from aqueous electrolytes of sodium salicylate was presented. Results showed that optimization of coating parameters is found to be critical to achieve adhesive PPy films and Mg surfaces with good mechanical and corrosion properties. In this part, corrosion behaviour of PPy/Mg AZ91D alloy is studied in simulated body fluid (SBF) solutions at body temperature. Corrosion behaviour of PPy/AZ91D system is studied by hydrogen gas collection
measurements, EIS and polarisation curves during 1 week of immersion. It is found that the adherent PPy coatings (1st step) hinder the anodic dissolution of Mg substrate and enhance the corrosion resistance by releasing dopant anions. Moreover, further functionalization of PPy layers with Albumin (Alb) monolayers (2nd step) also provides a better controlled drug release profile over 20 days with zero order kinetics.

5.3 Experimental route

Magnesium AZ91D coupons (2 cm × 2 cm × 0.5 cm) were ground with 1200 grit emery paper and then were cleaned in 1:1 ethanol : acetone mixture for 10 min in an ultrasonic bath. Electrochemical analyses were performed using an o-ring cell (See 2.1 Electrochemical setup with a three electrode system)

PPy films (step 1) were synthesized from 0.1 mol/l pyrrole (Py) containing aqueous solution of 0.5 mol/l sodium salicylate (Sigma) (pH=6.50) by using cyclic voltammetry (CV) in the potential region between 0.0 V and +1.0 V at 20 mV s⁻¹ scan rate. Different numbers of cycles of 5, 10, 20, 30, 40 and 50 were performed to optimize mechanical adhesion. Further surface modifications of PPy layers with albumin monolayers (second step) were achieved by immersion of PPy/AZ91D electrodes in 1 mM aqueous solution of Bovine Serum Albumin (Sigma) during 1 day. Characterization of Albumin modified electrodes were performed by positive and negative static time-of-flight secondary-ion-mass-spectrometry (ToF-SIMS) (ION TOF, Münster).

H₂ gas evolution, polarization and electrochemical impedance spectroscopy measurements were performed in SBF5 solutions [206] at body temperature. (see Figure 53 and Table 3).

<table>
<thead>
<tr>
<th>Ion</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Mg²⁺</th>
<th>Ca²⁺</th>
<th>Cl⁻</th>
<th>H₂CO⁻</th>
<th>HPO₄²⁻</th>
<th>SO₄²⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma</td>
<td>142.0</td>
<td>3.6-5.5</td>
<td>1.0</td>
<td>2.1-2.6</td>
<td>95.0-107.0</td>
<td>27.0</td>
<td>0.6-1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>SBF5</td>
<td>142.0</td>
<td>5.0</td>
<td>1.0</td>
<td>2.5</td>
<td>131.0</td>
<td>5.0</td>
<td>1.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Table 3: Composition of SBF 5 in comparison with human blood plasma.

EIS measurements were performed with a sinusoidal perturbation of ±10 mV for 10 points in each decade over the frequency range from 100 kHz to 10 mHz. Polarization tests were performed between -2.0 and -1.0 V with a scan rate of 1
mV/s. A simple flask attached with a funnel was used to investigate the H$_2$(g) evolution measurements. A field-emission scanning electron microscope (Hitachi FE-SEM S-4800) was used to investigate surface morphology.

A UV-visible spectrophotometer was used to quantitatively analyze drug release profiles of the specimens. As a drug release medium, phosphate buffered saline (PBS) is used. The characteristic salicylate peak at 295nm wavelength is measured.

![Figure 53: Preparation of SBF according to [206]](image)

### 5.4 Results and Discussion

#### 5.4.1 Optimization of mechanical stability and adhesion: Effect of different cycles

In order to investigate optimum adherence, experiments of different cycle numbers (5, 10, 20, 40 and 50) were carried out, while keeping the other electrochemical polymerization parameters fixed (between 0.0 / 1.0 V scan range with a scan rate of 20 mV s$^{-1}$ in 0.1 M Py containing 0.5 M sodium salicylate). Afterwards, adherence of PPy films was tested by double side tapes.
Figure 54 demonstrates the relationship between cycle numbers and level of adhesion by pull-off tests. For 5-, 10- and 20-cycle coated electrodes (a, c and e), homogenous PPy films were observed. After 20 cycles, adherence of PPy films is decreased. However, electrodes coated for 5, 40 and 50 cycles also show poor adherence after peel-off test (b, h and i). On the other hand, samples coated during 10 and 20 cycles are not completely peeled-off from the surfaces (d and f). This could be explained by increase of total charge during the electropolymerization process.
Figure 55: Graph shows the increase of total charge during electropolymerization of PPy on Mg alloy AZ91D.

The increase of total charge during electropolymerization is shown in Figure 55. The charge rapidly increases after 20 cycles and the resulting PPy layer peel off the surface for cycle numbers greater than 20 (Figure 54g-j). During electropolymerization of PPy, the total charge obtained is a combination of the charge used to build a PPy layer and simultaneous oxidation of the PPy layer itself after initial stages of electropolymerization. During the initial stages, most of the total charge is transferred firstly to build a PPy layer by red-ox process of the Py monomer and therefore follows a linear increase. The total charge increases especially after 20 cycles because of a systematic doping-dedoping process of PPy polymer with salicylate counter ions. Therefore, in addition to a simultaneous electropolymerization process of PPy, PPy/AZ91D system also has a charge limit to obtain good adherence till 20 cycles of coatings (from Figure 54g, i and Figure 54h, j). When number of electropolymerization cycles is increased, a rapid increase of charge also results in poor mechanical adherence.
Figure 56 shows the surface morphology of the PPy coated electrodes up to 20 cycles. For 5 cycles, it is found that the Mg AZ91D surface is not completely covered by the PPy layer (dashed circles in a) and do not adhere onto surface (Figure 56a). Moreover, a cauliflower surface morphology is not present (inset of Figure 56a) as already confirmed by mechanical pull-off tests of the corresponding sample where the PPy layer completely peeled off of the surface (Figure 54a). When the cycle number is increased to 10, formation of typical PPy morphology is slightly observed (inset of Figure 56b) but a complete coverage is not observed, too (dashed circles in Figure 56b). However, when the cycle number is increased to 20, the surface is fully covered with PPy molecules (Figure 56c) with cauliflower structures (inset figure of Figure 56c) with a film thickness around 1 µm [204].

On the hand, if the cycle number greater than 20 is chosen, the level of coating roughness increases and very irregular surface structures are obtained (Figure 57a-c). Similar to the results of adhesion tests in Figure 54, this type of surface morphology shows decreased adhesion during mechanical pull-off test.
From all of the above mentioned results, the relationship between adhesion and cycle number is explained with similar results as already explained for overoxidation of PPy films [129-131, 184, 204]. In this case, similar to the present results, an increase of the surface roughness is obtained with poor mechanical properties of polymer.

Due to these observations, AZ91D samples coated during 10 and 20 cycles are used in the further corrosion tests.

5.4.2 Corrosion behaviour of PPy/AZ91D system in simulated body fluids

Figure 58 shows the corrosion rates of PPy/AZ91D electrodes exposed in SBF5 during 1 week. Corrosion rates were calculated by $\text{H}_2(g)$ evolution during corrosion of PPy/AZ91D electrodes and results were compared with bare AZ91D. It is found that the formation of a PPy layer on AZ91D decreases the corrosion rate and, moreover, the rate does not increase rapidly as compared to that of the bare electrode. On the other hand, daily corrosion rate increases with immersion time for all electrodes. The increase of the corrosion rate with time is most probably due to
defects on the PPy surface leading to an increase of the effective surface area by dissolution-induced roughening of the Mg surface.

Figure 58: Corrosion rates of AZ91D and PPy/AZ91D electrodes exposed in SBF5 during 1 week.

Additionally, electrochemical impedance spectra of coatings were measured in SBF5 during 1 week (Figure 59). In the beginning of the corrosion tests, a trend of increase of the polarization resistance ($R_p$) is observed for both the 10- and 20-cycles coated AZ91D electrodes. For instance, for 10 coating cycles, the $R_p$ value increases up to $\sim 20$ kOhm after 1 day. But, a significant decrease is observed during 1 week of immersion and, in addition, inductive loops are observed after 3 days of immersion. For 20 cycles of coating, a similar trend and character is observed, too. In this case, increase of $R_p$ values up to $\sim 17$ kOhm is found and decrease of the $R_p$ value is observed after 3 days. For both samples, in parallel to increase of the corrosion rates in Figure 58, inductive loops are observed during 1 week which is also typical for magnesium dissolution [73, 80-82].
Figure 59: Nyquist plots in SBF5 during 1 week show long term corrosion tests of PPy coated AZ91D Mg alloys coated with different cycles; a) 10 cycles and b) 20 cycles.

Figure 60 shows the mechanical adhesion and pull-off tests of PPy/AZ91D electrodes. Results imply that inhomogeneous corrosion of magnesium substrates during 1 week immersion takes place for both the 10 (Figure 60a) and the 20 (Figure 60b) cycles coated electrodes. Both electrodes show partial and random peeling off of PPy during corrosion.
Additionally, pull-off tests of both electrodes (Figure 60b and d) show that the mechanical adherence of the PPy films is decreased by means of diffusion of aggressive anions through the polymer/metal interface which initiate the corrosion.

<table>
<thead>
<tr>
<th>Cycles</th>
<th>As-coated</th>
<th>Pull-Off</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td><img src="image1.png" alt="image" /></td>
<td><img src="image2.png" alt="image" /></td>
</tr>
<tr>
<td>20</td>
<td><img src="image3.png" alt="image" /></td>
<td><img src="image4.png" alt="image" /></td>
</tr>
</tbody>
</table>

Figure 60: Mechanical adhesion test of PPy films after 1 week immersion in SBF5 solution; a) 10 cycles, b) 10 cycles after pull-off tests, c) 20 cycles and d) 20 cycles after pull-off tests.

Figure 61 shows the SEM image of corroded surface morphologies for 10 and 20 cycles. For both electrodes, similar types of surface structures were observed. In general, Figure 61a shows that PPy molecules with typical cauliflower surface morphology disappear most probably due to reducing of polymer from its oxidized state. This also results in highly porous surface morphology (Figure 61a) enabling diffusion of water through polymer/metal interface. After the polymer is reduced, it only acts as a non-specific barrier and loses its electrochemical protection mechanism. On the other hand, it is well known that for PPy coatings the reduction of O\textsubscript{2} to give OH\textsuperscript{-} always takes place on the PPy layer. These OH\textsuperscript{-} are also reported to be suspect for delamination of surface layers and hence increase the corrosion rate (Figure 58).

On the other hand, Figure 61b and d show formation of nano-whiskers and hollow structures that are most probably formed during passivation of magnesium surface in SBF5. This also could be explained by self healing property of ICPs by releasing dopant counter ions from its backbone.

Figure 62 shows the release profile of salicylate during 3 days. The amount of salicylate released from a 20 cycle coated electrode is slightly higher than 10 cycles.
However, the release kinetics for both electrodes show Fickian distribution after 3 days immersion in PBS. It is also worthwhile to stress that the inductive loops are observed after 3 days during EIS measurements (Figure 59) when the all salicylate is released from the PPy/AZ91D electrode. Therefore, self healing effect by release of dopant ions is provided for a temporary period. After all amount of salicylate is released, dissolution of magnesium takes place and corrosion rate is increased.

![Figure 61: SEM images of PPy/AZ91D electrodes after 1 week immersion in SBF5 solution.](image)

On the other hand, salicylate could be of interest in applications that require the controlled delivery of drugs. To achieve this, the Fickian type of drug release profile and inhomogeneous corrosion of Mg substrates could be improved by further functionalization of PPy layer. As already explained above, ICPs could show better corrosion protection behaviour if they were applied together with other layers in sandwich type systems. Therefore the PPy layer could be covered to achieve better corrosion protection and drug release profile.
5.4.3 Modification of PPy layers with Albumin monolayers

Further surface modification of PPy/AZ91D electrodes is done by immersion of these electrodes in 1 mM Albumin solutions during 24 hours. Afterwards, albumin layers are characterized by ToF-SIMS that provides information about chemical structures within the protein and consequently may be a promising tool for surface protein analysis. The fragment pattern generated by amino acids allows for the confirmation of the attachment of proteins on the surface, determination of their orientation, and distinguishing of specific proteins deposited from mixtures as well as to observation of denaturation of protein coatings [207-223].
Figure 63: ToF-SIMS spectra and ratios of ToF-SIMS signals after the different treatment steps: bare AZ91D - AZ; pyrrole covered AZ91D - AZ-P; AZ91D covered with pyrrole and albumin subsequently - AZ-PA; AZ91D steeped in albumin - AZ-A; a) Mg$^+$ - substrate, b) CNO$^-$ - protein backbone, c) C$_4$H$_3$N$^+$ - pyrrole monomeric unit, d) C$_4$H$_3$N$^+$ / CNO$^-$ - pyrrole monomeric unit in ratio to protein backbone, e) C$_4$H$_8$N$^+$ - valine / proline, f) C$_5$H$_8$N$_3^+$ / Mg$^+$ - valine / proline in ratio to the substrate.

In Figure 63a-f characteristic fragments for albumin, the pre-treatment and substrate are displayed. Upon protein adsorption a variety of amino acid signals is observed, e.g., m/z 70.07 u: C$_4$H$_8$N$^+$ – proline, valine; m/z 84.04 u: C$_6$H$_6$NO$^+$ – glutamine, glutamic acid; m/z 84.08 u: C$_5$H$_10$N$^+$ – lysine, leucine and m/z 110 u: C$_3$H$_8$N$_3^+$ – histidine. A systematic assignment of typical fragments of amino acids to their mass spectral signals can be found elsewhere [210, 217, 222].

From Figure 63a, it can be seen that the amount of magnesium decreases upon coating with pyrrole and albumin. After albumin adsorption only small amounts of Mg$^+$ could be detected. CNO$^-$, the signal produced by the peptide bonds of the protein is only clearly visible after albumin adsorption (cf. Figure 63b). A higher
amount of CNO$^-$ is present on the pyrrole pre-coated surface, indicating better coverage of the latter. On the pure AZ91D substrate and the pyrrole pre-coated sample no peptide fragments could be detected. Figure 63c displays m/z = 65, which contains the fragments C$_4$NH$_3^+$ (monomeric repeat unit of pyrrole, m/z = 65.00) and C$_3$N$_2$H$^+$ (m/z = 65.01). The pyrrole monomeric unit is dominant on AZ-P and a signal at the same position occurs on the albumin coated samples AZ-PA and AZ-A.

On these two samples the signal has comparative intensity, indicating that it is a fragment of the protein (possibly originating from tryptophane) and not the pyrrole layer showing through. Figure 63d shows the C$_4$NH$_3^+$ signal in ratio to the peptide backbone and reinforces the observations from Figure 63c.

Figure 63e and Figure 63f show that the fragment C$_4$H$_8$N$^+$ produced by the amino acids valine and proline is not observed on AZ and AZ-P, but increases significantly upon attachment of albumin (AZ-PA / AZ-A). A better coverage of the substrate with pre-treatment by pyrrole is obvious.

As it has been a common observation that proteins tend to adsorb in monolayers, i.e. proteins do not adsorb non-specifically onto their own monolayers [212, 223] and magnesium signals were still observed in low yields after the reaction sequence, we expect monolayer (or sub-monolayer) coverage of the AZ91D surface.

![Figure 64: ToF-SIMS spectra and ratios of different amino acids for the treatment steps. a) histidine signal, b) histidine in ratio to magnesium, c) glutamic acid / glutamine, lysine/leucine.](image-url)
A further observation is that fragments produced by aromatic amino acids, e.g. histidine, are more pronounced on the AZ-A sample (cf. Figure 64a; all spectra normalized to total count rate), whereas other amino acids, e.g. glutamine / glutamic acid, are only detected in lower yields than on the pyrrole pre-treated sample. This indicates that the albumin possibly adsorbs via $\pi-\pi$ interactions to the pyrrole coating. Figure 64b confirms that the amount of histidine compared to magnesium still is higher on the pre-treated surface, even though the extent is smaller than for valine/proline (cf. Figure 63f).

![Figure 65: Mechanical adhesion test of Albumin modified PPy films](image)

Moreover, it is clear from the optical microscope images that the adhesion of PPy layers does not deteriorated during immersion of electrodes in aqueous solutions of albumin (Figure 65a and c). However, after pull-off tests (Figure 65), Alb/PPy/AZ91D electrodes do not peel-off of the surface and a good attachment of albumin onto PPy is achieved.

### 5.4.4 Corrosion behaviour of Alb/PPy/AZ91D system in simulated body fluids

Figure 66 shows the corrosion rates of Alb/PPy/AZ91D electrodes in SBF5 during 1 week. It is found that further functionalization of PPy layer significantly decreases the corrosion rate of AZ91D substrate and, moreover, does not increase rapidly as compared to bare electrode. However, 10 cycles coated Alb/PPy/AZ91D electrode shows slightly higher increase of the corrosion rate during the first day (marked as region I in Figure 66). Afterwards, it stabilizes as with the 20-cycle
coated electrode. On the other hand, similar to the electrodes without albumin modification, daily corrosion rate increases with immersion time for all electrodes mainly due to diffusion of corrosive species through the metal/polymer interface.

Corrosion rates from $H_{2(g)}$ measurements are summarized in Table 4. As compared to bare AZ91D electrode, corrosion rates decrease when a PPy coating is applied to AZ91D. Moreover, when the electrodes are further modified with albumin monolayers, a drastic decrease of corrosion rate is observed for both 10- and 20-cycle coated electrodes and corrosion rate is reduced by ~70 times that of bare AZ91D.

Additionally, electrochemical impedance spectra of Alb/PPy/AZ91D electrodes were measured in SBF5 during 1 week (Figure 67). For both samples, an increase of $R_p$ values is observed. But, for 10 cycles of coating, a rapid increase of $R_p$ value up to ~12 kOhm is found after the 1st day of immersion. On the next days, impedance of the system did not change significantly. But a decrease of $R_p$ value with an inductive loop is observed after the 6th day of immersion. For a 20-cycles coated electrode, systematic increase of $R_p$ is obtained. This increase continues during 1 week starting from ~9.0 kOhm to ~17.5 kOhm without inductive loops.

Figure 66: Corrosion rates of albumin modified PPy/AZ91D electrodes exposed in SBF5 during 1 week.
Moreover, the second capacitive loops at the middle frequency region start to disappear, which is also an indication of corrosion inhibition of AZ91D substrate without adsorbed electroactive species [224]. Therefore, after albumin coating, 20 cycles coated electrode found to show slightly better corrosion performance in SBF5 solutions.

<table>
<thead>
<tr>
<th>Step 1 (PPy)</th>
<th>Step 2 (Albumin)</th>
<th>Corr Rate* (mg.cm(^{-2}).day(^{-1}))</th>
<th>Corr Rate** (mg.cm(^{-2}).day(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>-</td>
<td>2.31</td>
<td>-</td>
</tr>
<tr>
<td>10 cycles</td>
<td>-</td>
<td>0.79</td>
<td>-</td>
</tr>
<tr>
<td>10 cycles</td>
<td>Albumin</td>
<td>0.60</td>
<td>0.07</td>
</tr>
<tr>
<td>20 cycles</td>
<td>-</td>
<td>0.56</td>
<td>-</td>
</tr>
<tr>
<td>20 cycles</td>
<td>Albumin</td>
<td>0.03</td>
<td>-</td>
</tr>
</tbody>
</table>

Corrosion rate of 10 cycle coated sample with albumin coating was calculated separately from two different regions (I and II) of Figure 66: * from region I and ** from region II.

Table 4: Average corrosion rates calculated from Figures 58 and 66 for bare AZ91D, PPy/AZ91D and Albumin modified PPy/AZ91D electrodes, exposed in SBF5 during 1 week.
Figure 67: Nyquist plots in SBF5 during 1 week show long term corrosion tests of PPy coated AZ91D Mg alloys coated with different cycles; a) 10 cycles and b) 20 cycles.

After EIS measurements, surface adhesion of albumin modified samples are also investigated by pull-off tests again. Figure 68 shows that both of the samples are not heavily corroded as compared to PPy/AZ91 electrodes in Figure 60. However, very light corrosion is observed for the 20-cycle coated electrode after albumin coating. As compared to 10 cycles, this electrode also shows better adherence after pull-off tests (Figure 68 b and d)
Figure 68: Mechanical adhesion test of Albumin modified PPy films after 1 week immersion in SBF5.

Figure 69 shows the surface morphology of albumin modified 20-cycle electrode. In general, surface structures (whiskers in Figure 61) as obtained for the same electrode without an albumin layer are not observed (Figure 69a). However, small surface defects (Figure 69b, marked as I in Figure 69a and d marked as II) are generally found that are most probably formed during the corrosion process. On the other hand, on defect free surfaces (Figure 69c, marked as III Figure 69a), PPy is present with typical cauliflower like surface morphology. This may be an indication of that reducing of the PPy layer does not take place because of sufficient surface coverage by the albumin monolayer. Therefore diffusion of water through the polymer/metal interface does not take place and the polymer stays at its oxidized state. Moreover, the reduction reaction rate of O$_2$ on PPy layer and corrosion of Mg substrate to give OH$^-$ is significantly reduced.
In parallel with the findings as explained above, the protection mechanism is also explained by the releasing profile of dopant counter ions. Figure 70 shows the release profile of salicylate during 20 days in PBS solution. Both electrodes show the same type of drug release profiles in orders of μg which is found to be 100 times lower than that of PPy/AZ91D electrodes in Figure 62. However, the reason of low amount of dopant present in Figure 70 is that most of salicylate is already released during the coating of PPy layers during soaking in albumin solutions.

When the electrodes are coated by an albumin layer, drug release profiles become more durable and follow zero-order kinetics over 20 days with a constant release of salicylate. It is also worthwhile to stress that the inductive loops are not observed during EIS measurements for 20 cycles in Figure 67. This may be due to a self healing effect through the release of dopant ions that is generally provided when samples are further functionalized by albumin monolayers.
To understand the corrosion inhibition mechanism and the effect of the coatings on the kinetics of electrochemical reaction rates, polarization curves of bare and modified AZ91D electrodes were compared when measured directly (Figure 71a) and after 1 week (Figure 71b) of immersion in SBF5 solution.

The values of $E_{\text{corr}}$, $i_{\text{corr}}$, Tafel constants ($\beta_a$ and $\beta_c$), corrosion rate (CR) (calculated by AutoLab® software, NOVA©), and polarization resistance $R_p$ (calculated from the Stearn–Geary equation) [225] (6) are given in Table 5. Corrosion rates were obtained from these curves.

A parallel trend to EIS results is observed from polarisation curves. As compared to bare AZ91D, decrease of corrosion current densities with a positive shift of $E_{\text{corr}}$ is observed for all coated samples. Additionally, all samples show small regions of passivation. The strongest effect is found for the Alb/PPy/AZ91D electrodes. Moreover, after albumin coating, the 20-cycles coated electrode shows better corrosion protection as compared to the 10 cycles one. The corrosion
The protection effect of all coatings is clearly related to inhibition of anodic reactions, as cathodic reactions easily take place on the coated electrodes.

**Figure 71**: Polarisation curves of bare AZ91D, PPy/AZ91D and Albumin modified PPyAZ91D electrodes in SBF5.
Table 5: Potentiodynamic polarization measurement results of pure AZ91D and modified electrodes in SBF5 solution.

<table>
<thead>
<tr>
<th>Step 1</th>
<th>Step 2 (Albumin)</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ ($\mu$A/cm$^2$)</th>
<th>$\beta_a$ (mV)</th>
<th>$\beta_c$ (mV)</th>
<th>Corrosion Rate (mm/year)</th>
<th>$R_p$ (k$\Omega$. cm$^2$)</th>
<th>$X^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-</td>
<td>-1.63</td>
<td>78</td>
<td>220</td>
<td>312</td>
<td>4.09</td>
<td>0.7</td>
<td>1.44 x 10$^{-10}$</td>
</tr>
<tr>
<td>10</td>
<td>-</td>
<td>-1.48</td>
<td>9</td>
<td>181</td>
<td>134</td>
<td>1.87</td>
<td>3.7</td>
<td>2.49 x 10$^{-12}$</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
<td>-1.47</td>
<td>6</td>
<td>141</td>
<td>97</td>
<td>1.03</td>
<td>4.3</td>
<td>2.12 x 10$^{-12}$</td>
</tr>
<tr>
<td>10</td>
<td>Alb.</td>
<td>-1.41</td>
<td>2</td>
<td>136</td>
<td>95</td>
<td>0.09</td>
<td>12.5</td>
<td>9.86 x 10$^{-16}$</td>
</tr>
<tr>
<td>20</td>
<td>Alb.</td>
<td>-1.36</td>
<td>1</td>
<td>127</td>
<td>82</td>
<td>0.08</td>
<td>18.1</td>
<td>7.73 x 10$^{-14}$</td>
</tr>
</tbody>
</table>
6.4.6 Surface characterization of PPy/AZ91D and Alb/PPy/AZ91D electrodes

<table>
<thead>
<tr>
<th>Element</th>
<th>Py/AZ91D Wt%</th>
<th>Py/AZ91D At%</th>
<th>Alb/PPy/AZ91D Wt%</th>
<th>Alb/PPy/AZ91D At%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C K</td>
<td>10.88</td>
<td>16.83</td>
<td>36.15</td>
<td>50.25</td>
</tr>
<tr>
<td>N K</td>
<td>1.18</td>
<td>1.57</td>
<td>3.32</td>
<td>3.95</td>
</tr>
<tr>
<td>O K</td>
<td>45.21</td>
<td>52.51</td>
<td>16.60</td>
<td>17.33</td>
</tr>
<tr>
<td>Zn L</td>
<td>1.36</td>
<td>0.39</td>
<td>1.39</td>
<td>0.36</td>
</tr>
<tr>
<td>Mg K</td>
<td>21.87</td>
<td>16.71</td>
<td>32.58</td>
<td>22.37</td>
</tr>
<tr>
<td>Al K</td>
<td>9.62</td>
<td>6.62</td>
<td>6.54</td>
<td>4.05</td>
</tr>
<tr>
<td>P K</td>
<td>5.40</td>
<td>3.24</td>
<td>2.04</td>
<td>1.10</td>
</tr>
<tr>
<td>S K</td>
<td>0.16</td>
<td>0.09</td>
<td>0.16</td>
<td>0.08</td>
</tr>
<tr>
<td>Cl K</td>
<td>0.51</td>
<td>0.27</td>
<td>0.18</td>
<td>0.09</td>
</tr>
<tr>
<td>Ca K</td>
<td>3.81</td>
<td>1.77</td>
<td>1.04</td>
<td>0.43</td>
</tr>
</tbody>
</table>

*Table 6:* Table shows distribution of the elements on PPy and Alb modified electrodes after 1 week immersion in SBF5 electrolyte.

Additionally, chemical composition of surfaces is determined by EDAX analysis after 1 week immersion in SBF5 (Table 6). As compared to PPy/AZ91D electrode, more carbon (C) and nitrogen (N) signal is detected for the albumin modified electrode. This is most probably due to the albumin layer on the PPy. Moreover, oxygen (O), calcium (Ca), phosphorous (P), chloride (Cl) and sulphur (S) signals are also found to be less on the albumin modified electrode indicating that the level of corrosion and formation of corrosion layers including phosphates, chlorides, sulphates and oxide layers proceeds slowly as compared to PPy/AZ91D electrodes.

5.5 Conclusions

This chapter demonstrates corrosion behaviour of polypyrrole thin films on magnesium alloy (AZ91D). Electrochemical impedance spectroscopy (EIS) and corrosion test results show that sodium salicylate doped PPy layers have a corrosion protection property in SBF5 solutions.

It is also found that PPy layers can be further functionalized by albumin layers. The resulting surface layers show the most effective corrosion performance by release of dopant anions. In both cases, PPy layers act as anodic barrier during corrosion and the corrosion protection mechanism is achieved by release of dopant anions. The prepared PPy coatings adhered well throughout the period of testing: i.e. no peeling-off was observed.

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Dopant release profiles are further improved in addition to the corrosion performances after the electrodes are coated by albumin monolayers. In addition, zero order drug release is achieved.

For biomedical applications of Mg and its alloys, such as salicylate doped PPy layers on Mg alloys, there is a high potential for tailoring the degradation rate, since all components (substrate, passivating agent, coating) of the resulting system are non-toxic. Moreover, these coatings have potential for tailoring the degradation rate of Mg alloys for biomedical applications.
6 Anodic Growth of Self-Ordered Nanoporous/Tubular Layers on Magnesium Alloy

6.1 Abstract

In the present chapter, electrochemical formation of self-ordered nanotubular and nanoporous magnesium oxy-fluoride structures on a magnesium-based alloy are explored. The morphology of the surface structures varies with applied potential and anodisation time. Tubular and porous structures with different sizes and orientation can be grown.
6.2 Introduction

Over the past several decades, a variety of self ordering processes by electrochemical [226] or photoelectrochemical [227] methods such as rapid breakdown anodisation (RBA) [228], atomic layer deposition (ALD) [229-230] with or without templates (sol-gel or hydro/solvothermal) [231-232] have been found to produce oxide nano-structures. These tubular or porous oxide layer structures (Figure 72) can be obtained by anodization of a suitable metal from aqueous or non-aqueous fluoride-containing solutions by chemical etching of the metal substrates [233] as summarized in a recent review [234].

![Figure 72:](image)

When metals are exposed to a sufficiently anodic voltage in an electrolyte, depending on the anodization parameters, an oxidation reaction of metal is initiated where mainly three possibilities exist. The first possibility is that the $M^{n+}$ ions are either solvatized in the electrolyte or the metal substrate continuously dissolved resulting in electropolishing of the metal (Figure 72a). The second possibility is formation of an insoluble metal oxide (MO) layer when metal cations ($M^{n+}$) react with $O_2$ from the $H_2O$ in the electrolyte (Figure 72b). In some very special circumstances a third possibility, competition between solvatization and oxide
formation resulting in the formation of porous MO layers by chemical etching (Figure 72c-d).

Over 5 decades ago, anodic growth of porous Al₂O₃ (Figure 73a) on aluminum was first reported and this system was found to have a perfect self organization of pores in the oxide layer [235]. Since then, anodic treatment of other metal surfaces were studied by many researchers with a growing interest worldwide became established in many industrial applications or research areas such as photocatalysis [236-241], solar cells[242-247], dye sensitized solar cells (DSSC) [245, 248-249], electrochromic devices[250-253], implant materials (cell interactions and biomedical coatings) on [254-259], drug delivery systems [260-261] and sensing [262-265] applications.

![Figure 73](image)

Figure 73: Cross-sectional and top view (inset) images of; a) porous alumina [266] and b) TiO₂ [267] nanotubes.

Formation mechanisms of these structures and models provide better understanding for the occurrence of self-organization of these porous networks. These models are mainly based on stress formation at the metal–oxide interface, optimization of current-flow conditions and attraction of the electric fields as summerized in a recent review [234]. For instance, electrochemical anodization of metals in different electrolytes results in different current-time (i-t) characteristics as overviewed in Figure 74. These curves differ depending on the F⁻ concentration used for solvatization and result in different types of MO layers. For a widely
investigated metal, Ti (Figure 73b), HF is the most used complexing agent which forms water-soluble $[\text{TiF}_6]^{2-}$ structures and complexation occurs with Ti$^{4+}$ at intermediate concentrations. The restriction of porous or tubular MO layer formation to these concentrations is due to the necessity for competition between solvatization and oxide formation is provided. Else, if the concentration of HF is very low or very high, either a compact oxide is formed or no-oxide film formation is observed and electropolishing of the metal surface results.

![Figure 74: Typical I–t transitions for different type of metal oxide surface morphologies[234].](image)

An I–t curve for conditions that lead to nanotube formation has three stages: I) During the initial stage of formation, the curve usually follows the fluoride-free case and forms an compact oxide layer. In the intermediate stage, stage II, irregular pores are formed monitored by an current increase that corresponds to increase of the effective surface area. In the last step, current drops and a regular nano-pores or -tubes are formed [234].

In addition to porous alumina and tubular TiO$_2$ [234, 267-269], there are also many works reported in the literature on the formation of ordered porous oxides of other metals including valve metals, Fe[270-271], Ta [272], Zr [273-274], Nb [275] and Hf [276], but only a few attempts can be found based on Mg and Mg alloys. Since magnesium hardly forms defined oxide films in aqueous solutions, it may be a promising approach to use non-aqueous solutions for anodisation, particularly with the aim of reducing chemical dissolution during anodisation.
Brunner et al. [277] showed the formation of a black, porous oxide-layer on Mg from water free methanol or ethanol electrolytes containing nitrate ions. Ono et al. [278-279] studied anodisation of pure Mg [280] in non-aqueous solutions where they showed the formation of a barrier layer in a solution consisting of a mixture of amine, ethylene glycol and water. They also investigated the formation of anodic oxide-films on magnesium surfaces in alkaline-fluoride solutions [281] and for the first time, using alkaline aluminate solutions, they reported formation of cylindrical cellular structures [282].

Such surface modifications might be especially interesting for utilizing of Mg alloys in biomedical applications, as a biodegradable metallic implant material: a subject of steadily growing interest [195]. In order to optimize the biological performance, the corrosion behaviour of the material as well as its interactions with cells need to be tailored. In view of biomedical applications, it is interesting to mention that on TiO$_2$ nanotubes adhesion, proliferation and differentiation of cells has been demonstrated to be controlled by the morphology (tube diameter) of nanotubular layers [283-286]. For Mg alloys, simple chemical surface treatments such as chemical passivation or biofunctionalization by soaking in simulated body fluids were recently shown to drastically influence adhesion and survival of cells on corroding Mg surfaces [287], but specific surface nanostructuring of Mg alloy surfaces has not been studied in this context.

![Figure 75: Backscattered SEM image of the WE43 magnesium alloy.][288]

The alloy selected (WE43) in this chapter is a wrought Mg alloy including Yttrium (Y), Zirconium (Zr) and Neodymium (Nd). Yttrium has a high solubility in magnesium and usually added with other rare earth elements to increase creep
resistance at high temperatures (300°C) and also to reduce weld cracking [72]. The microstructure of WE43 alloy consists of different and irregular precipitates of Mg-Nd or Mg-Y particles precipitated at grain boundaries and the grain interiors [289-290] as shown in Figure 75. On the other hand, this alloy is one of the likely candidates for biodegradable implants [201, 291-293]

6.3 Experimental route

Since HF acts as a weak acid and does not dissociate in non-aqueous solvents such as EG, electrolyte was aged (see below). During the aging of the solution, titanium was dissolved and therefore the conductivity was increased by formation of $(\text{TiF}_6)_{2-}$ ions [267]. Electrolytes of ethylene glycol (EG) were prepared with addition of hydrofluoric acid (HF): of 500 ml volume and 0.2 M HF concentration. From this solution 50 ml was ‘aged’ by anodising of Ti overnight for 12 hr at a constant potential of 120 V in a two electrode cell with the solution as the electrolyte. The Ti working electrode was sealed to the cell by an o-ring, to expose $1 \text{ cm}^2$ of the electrode surface to the electrolyte, by pressing a Cu plate, which acted as electrical contact, to the back of the electrode. A platinum foil was used as the counter electrode. After aging, the aged solution (50 ml) was stirred together with the rest of the solution (450 ml, non-aged) for 10 minutes. This mixture was found to have the optimum conductivity to obtain porous surface layers. WE43 Mg alloy samples – cut from a rod with a diameter of 25 mm – were anodised in the resulting electrolyte using the same electrochemical cell and counter electrode as used for electrolyte aging. Prior to anodising, the samples were ground with 1200 grit emery paper. The chemical composition of WE43 alloy consists of 3.7-4.3% Y with 2.2-4.4% rare earth elements (Nd) and 0.4% Zr with the balance being Mg.

To investigate the effect of applied potential on the resulting surface morphology, potential ramp experiments were performed. The potential ramps were from the 0 V to a maximum potential, $V_{\text{max}}$, (of 20, 40, 70, 120, 160, 200, 240 and 300 V) at a sweep rate of 1 V s$^{-1}$ after which the potential was held constant at $V_{\text{max}}$ for 1 additional hour. In addition, effect of the anodisation duration was investigated for potential ramp experiments with a $V_{\text{max}}$ of 70 V by applying the same initial sweep to $V_{\text{max}}$ (70 V) and by varying the duration the experiment was held at $V_{\text{max}}$. 
A two-electrode setup (Figure 7c) was used as explained in a previous section (2.1 Electrochemical setup). A field-emission scanning-electron-microscope (Hitachi FE-SEM S-4800) equipped with an energy dispersive X-ray analyser (EDAX) was used to investigate the morphology and composition of the surface layers.

### 6.4 Results and Discussion

#### 6.4.1 Optimization of anodisation potential

Anodisation of the Mg WE43 samples at different potentials indicates the formation of a compact layer of magnesium fluorides or magnesium oxy-fluorides (SEM and EDX results, not shown) with some incomplete passivation for potentials up to $V_{\text{max}} = 40$ V, which is followed by a drop in current containing a shoulder. On such samples randomly distributed surface features such as macro pitting was observed, but no nano porous or tubular surface morphology could be detected. Figure 76 shows the top view of an anodized WE43 magnesium alloy surface. The surface anodized at 20 V shows two remarkable regions under SEM: highly charging white and relatively less charging black regions. High magnification images (inset figures of Figure 76) of these areas do not impart either pore or tube formation on the surface. Only a compact layer of magnesium fluorides or magnesium oxy fluorides is detected as suggested by EDAX measurements (Figure 77). When the anodisation potential is increased to 40 V, the same surface morphology is observed (Figure 78). However, it was found that the white regions have started to crack (Inset bottom-left, and inset top-left) and a compact oxide layer has started to form at the edge of these cracks while the compact film on the black regions is thickening.
Figure 76: SEM image of WE43 magnesium alloy anodized at 20 V during 1 hour. Inset top-a-) High magnification SEM image of non-charging (black) areas. Inset bottom-b-) High magnification SEM image of charging (white) areas.

Figure 77: EDX spectra of WE43 alloy surface after anodisation by ramping the potential from 0 to 20 V and then holding it at this potential for 1 h in Ti aged 0.2 M HF ethylene glycol solution. Inset bottom-left: Overlay mapping image of O and F. Inset bottom-right: Overlay mapping image of O, F and Mg. Inset Table: Weight and atomic percentage ratio of the elements on the surface.
The surface morphology for 70 V and 120 V anodisation, however, drastically differs from anodisation at lower potentials. At 70 V elongated nanoporous structures (nanopores/nanotubes) on the Mg alloy surface are observed (Figure 79). At this potential, some large recessed areas are formed on the surface; focusing in these regions reveals nanostructures of both nanopores and nanotubes on the surface (Figure 79a-f). For example, Figure 79a shows highly packed nanotubular structures with an average diameter of 100 nm. Porous structures near these tubes with an average pore diameter of 70 nm are shown in Figure 79b. Moreover, well defined and separated nanotubes are also found in these regions having an average diameter of 70 nm (Figure 79c). Lastly, different types of long columns are also detected (Figure 79d). Among all these different types of surface structures, tubular forms are the most frequently occurring structures. EDX measurements indicate that in this case passivation is possible not only by oxide formation but also by formation of Mg fluorides or oxy-fluorides (Figure 77).
When the applied potential is increased to 120 V, the resulting surface morphology displays a lesser presence of elongated porous structures as compared to surface structures formed at 70 V but still displays tubular (Figure 79e) and pore like (Figure 79f) features. This may be an indication of excess field supported chemical etching at higher anodisation potentials, in accordance with the slower decrease of current with time. This effect becomes even more significant at even higher potentials. Although under the present conditions structures as ideal as grown for Al or Ti could not be attained; the experiments at 70 V represent an optimum potential for obtaining of well defined tubular structures on Mg.

This type of surface morphology with more than one kind of structures suggest that chemical etching and anodisation potential may act as important
parameters in the case of magnesium anodisation. Rather than these parameters, also the type of chemical, solvent used or water addition may influence the surface morphology such as has been observed for aluminum or titanium. For example, increase in potential leads to increase in the pore diameter and interpore distance [294-295] of titanium or amount of HF [275] may also influence surface morphology. In addition, water addition has an influence on the thickness of oxide layers [296] in the case of Nb. In addition, an effect due to temperature is also found to be critical for transition of porous structures to tubular forms for Fe [270]. Although the morphology of oxide layer on these valve metals can be modified by such parameters, an apparent change of magnesium surface is not observed by changing these parameters.

During this work, to obtain more ordered nanostructures, many other experimental parameters were changed as following;

1) Type of base electrolytes (aged with different conductivities with Ti or Mg, 5µS-10mS).

2) Different chemicals as additives (ionic liquids, aluminates, water, different fluoride sources, NaF, NH₄F).

3) Different solvents (methanol, ethanol, glycerol, water, acetone, acetonitrile, propylene carbonate or their mixtures).

4) Different anodisation temperatures (between -50 to 150 °C)

5) Different types of surface preparation or pretreatments (ground, etched, polished surfaces or NH₄F, NaOH and polymer pre-treated)

6) Area of working electrode, cathodes, continuous stirring or ultrasonication during anodisation.

All these parameters were tried either separately or in combination with others to achieve better self-ordered nanostructures. But, these changes resulted in irregular etching of surface morphologies with formation of a compact oxide layer similar to those in Figure 77 and Figure 78. Moreover, addition of different complexing agents (EDTA, oxalates, CN⁻), annealing of the samples between 300-600°C on different Mg substrates such as AZ31, AZ91, WE43 and pure Mg also did not give any self-ordered porous or tubular surfaces. These nanostructures always took place and tubular forms are only detected in the large pits formed at 70 V under the previously explained conditions.
The morphology in general is found to be similar to TiO$_2$ nanotubes; however, it is not entirely clear yet, if indeed a barrier layer is present at the bottom of the tubes. Although under the present conditions structures as ideal as grown for Al or Ti could not be attained, the experiments at 70 V represent an optimum potential for obtaining of well-defined tubular structures on Mg.

![Figure 80](image)

**Figure 80**: Current transient as a function of time recorded during electrochemical anodisation of WE43Mg alloy at different potentials in 0.2 M HF/EG with a sweep rate of 1 V s$^{-1}$.

Figure 80 shows the current density as a function of time for samples anodized between 20 and 300 V. After the potential is increased to the desired potential by a sweep rate of 1 V s$^{-1}$, a drop in current density occurs due to oxide layer formation. After this drop of current density, the plot has a shoulder shape and reaches to low current densities. At higher potentials more than 120 V (inset Figure 80), after the initial decrease of current density, it again increases which may be due to temperature increase by high potential. This results to a highly with highly etched surface morphology dissolution or degradation of tubular or porous structures (SEM images of 160, 200, 240 and 300 V are not shown here). Afterwards, current decreases again, probably due to re-passivation of the surface by fluorides. In addition, at all potentials the current density values are to be found very similar after 1 hour of anodisation which may indicate that the system is diffusion controlled as in the titanium case [294].
6.4.2 Effect of anodisation time

For valve metals, anodisation time is an important parameter influencing the nanotube layer morphology (i.e. nanotube length). From SEM results and i-t curves above, an applied potential around 70 V is found as the optimum anodisation potential to have well defined tubular structures on WE43 magnesium alloy surface and hence the effect of anodisation time was investigated at this potential. Figure 81a shows SEM images of a 30 min anodised WE43 surface showing well-ordered tubular structures of diameter between 50-80 nm (inset figure of Figure 81a). When the anodisation time is increased to 1 hour (Figure 79a-d), overall surface appearance looks almost the same but with porous structures of a diameter between 60-100 nm. A slight increase of pore diameter is observed when the anodisation potential is increased but the general appearance of resulting surface is found smoother for shorter time as compared to the 1 hour anodised surface (Figure 79a-d). An increase of anodisation time to 2 hours leads to the start of chemical etching of the porous surface (Figure 81b), and after more extended time of 6h all structures are dissolved due to excess chemical etching, and granular surface morphology results (Figure 81c).

Figure 81: SEM image of WE43 magnesium alloy anodized at 70 V during top left-a) 30 min, top-right-b) 2 hours bottom-c) 6 hours. High magnification image of figure of 7 (top-left-a).
6.4.3 Initiation of porous layer

In order to study the initiation phase of nanotube formation, a potential ramp to $V_{\text{max}} = 70$ V followed by a short anodisation time of 3 minutes at $V_{\text{max}}$ was carried out. Figure 82 and the details in its insets show four different structural layers: the first layer (I) is a compact layer (top), the second layer (II) is porous and the third layer (III) is the propagation layer, i.e., the initiation of these structures is in agreement with a sequence frequently observed for self-organizing oxide growth [233]: I, compact layer formation; II, penetration and pore formation underneath the compact layer; III, ordered pore growth. The growing pores finally lead to a dimpled scalloped surface (IV).

![Figure 82: SEM image of a WE43 magnesium alloy surface anodised in 0.2 M HF ethylene glycol solution at 70V for 3 min. along with a) an inset figure of surface region II; b) an inset figure of surface region III; and c) an inset figure of surface region IV.](image)

With increasing anodisation time, the surface shows well-ordered tubular structures with diameters of between 50 and 80 nm (as shown for 1 h anodisation in Figure 79) Overall, anodisation time increases tube order and abundance but for durations greater than 2 h an increasing loss of the porous structures is observed. This can be attributed to dissolution processes that begin to dominate the anodisation reaction.

The mixed type of surface morphology (tubular and porous) and the loss of the tubular layers after extended anodisation suggest that oxide formation and
chemical etching play important interacting roles in the formation of self-ordered oxide features. This suggests that the anodisation potential, the type of chemical solvent used, or the addition of water to solution may influence the surface morphology in a similar way to what has been observed in the case of aluminum and titanium anodisation, and the effect of these parameters on Mg anodisation will require further exploration so as to achieve a greater degree and range of ordering.

6.5 Conclusions

Potentiostatic anodisation of a biorelevant magnesium alloy (WE43) in HF containing non-aqueous electrolyte, after an initial potential sweep, can lead to growth of ordered oxy-fluoride nanostructures (nanopores and nanotubes). Optimum conditions for the formation of porous/tubular structures were found to be potential- and time-dependent. In particular, it should be noted that an optimum parameter window exists. When the anodisation time or potential is too high, the resulting surface morphology is destroyed by excess chemical etching. In view of practical applications, these nanostructured layers on Mg alloys have a considerable potential in functionalising the surface, for instance in biomedical applications of Mg and its alloys.
7 Corrosion Behaviour of Carbon Nanotube Modified Magnesium and Magnesium Alloy AZ91D

7.1 Abstract

Carbon nanotubes (CNTs) have been confirmed as good reinforcements for the improvements of mechanical properties of light metal matrixes such as magnesium and magnesium alloys. However, the corrosion behaviour of CNT/Mg composites has hardly been investigated.

This chapter explores the influence of CNT addition on the corrosion behaviour of pure Mg and Mg alloy AZ91D composites. The corrosion rate is drastically increased with increased addition of CNTs to the composite matrix due to the coupling effect between cathodic CNTs and anodic Mg. Additionally, surface pre-treatment was also found to be critical on the corrosion performance (especially in low CNT content composite). Moreover, better dispersion of CNTs leads to reduced corrosion resistivity.
7.2 Introduction

Magnesium and magnesium alloys, with a low density of 1.738 g/cm³, exhibit good mechanical and physical properties. These properties are of interest for use of Mg alloys in transportation, automobile, electronics and machine tool applications. However, application of these materials in a wide number of fields is restricted by their poor corrosion resistance [25, 80].

However, these materials are found to suffer from moderate and high temperature creep resistance in applications such as gearbox and engine block components [297]. For instance, for powertrain applications, an elevated temperature performance at service conditions of 150-200°C and stresses in the range of 50-70 MPa is required where the commercial AM and AZ type of magnesium alloys do not possess these properties [10].

In order to further improve high-temperature strength and creep resistance of these materials, development of new types of alloys is the main scope of many scientists worldwide. But due to high production costs, complexity and their poor machinability, reinforcing magnesium with nanoparticles or carbon materials instead of alloying was found to be an alternative solution while preserving the low density of the material. For example, magnesium or its alloys reinforced with inorganic nanoparticles such as SiC [298-300], Al₂O₃ [301-302], Y₂O₃ [303-304] and SiO₂ [305] are reported to increase both high-temperature performance and mechanical properties.

To further improve the mechanical properties, carbon reinforced magnesium composite materials also have been developed [306]. Hall [307] and Bakkar et al. [308] have studied the effect of carbon fibre addition into the Mg matrix and showed that even though the mechanical properties are improved, the formation of galvanic cells between the Mg matrix and the carbon fibres reduces the corrosion resistance of the composites.

Since their discovery in 1991 [309], another carbon material, carbon nanotubes have attracted remarkable interest due to their excellent mechanical, electrical and physical properties. There are mainly two types of nanotubes available; single walled (SWNT) and multi-walled (MWNTs) nanotubes [310-312]. SWNTs are made of a single sheet of graphene rolled to form a cylinder and MWNTs consist of multiple rolled layers of graphene or rolled graphite. Depending on the relationship
between rolling direction and the unit vectors of the graphene sheets, CNTs can be metallic or semi-metallic [313]. Semi-conducting nanotubes have bandgaps ranging between approximately 1.8 eV and 0.18 eV [314]. On the other hand, metallic carbon nanotubes are extremely conductive, as their one-dimensional nature allows their charge carriers to carry very large current densities of up to 100 MA/cm² [315]. For semi-conducting nanotubes, carrier mobilities are reported as 105 cm²/V s [316]. It has also been reported that SWNTs show superconductive properties around temperatures of 5 K [317].

These properties make them very unique materials with a whole range of promising applications such as in electron gun components in vacuum microelectronics [318] (in electron microscopes or in microwave amplifiers), in flat panel displays [319-320], in gas-discharge tubes in telecom networks [321], and in energy storage [322-324] as summarized in a recent review [313, 325]. CNTs are also considered as ideal reinforcements for their high strength, light weight, high performance composites [313] due to their favorable geometrical (high aspect ratio, high specific surface area) and excellent mechanical properties (very high strength modulus, extreme rupture strength). Theoretical simulation [326-327] and experimental results [328-330] have indicated their extraordinary strength (about 150 GPa) and Young’s modulus (about 1 TPa).

Even though the mechanical properties of nanotube modified light metal composites are in general found to be enhanced, the corrosion behaviour of these materials has not yet been explored in detail. Due to the very low standard electrode potential of -2.36 V, and due to the poor protective properties of Mg oxide/hydroxide layers in many environments, Mg alloys show a very low corrosion resistance. The low standard potential of Mg of course makes the material very prone to galvanic corrosion, when coupled to almost any other technologically interesting conducting material. The first study on the corrosion behaviour of CNT reinforced Mg AZ91D alloy composites, recently presented by Endo et al. [331], claimed that CNTs act as good mechanic fillers in Mg AZ91D alloy and reduce the corrosion rate of Mg. On the other hand, Fukuda et al. [332] also showed the formation of galvanic cells between the Mg matrix of a AZ31B alloy and CNTs with a high (-surface – Kelvin Probe) potential difference of 1.1 V. Similar effects of increased corrosion due to microgalvanic action between CNTs and the Mg matrix were reported by Aung et al. [333] for Mg/CNT composites.
Even though these first reports on the corrosion behaviour of Mg/CNT composites indicate that CNTs are deleterious due to internal galvanic corrosion, these studies are still rather preliminary in nature. In the present chapter, the corrosion process of CNT-reinforced Mg and Mg alloy AZ91D composites is explored in more detail and over a large time period, from initiation of corrosion until extended durations of one week. Using a combination of electrochemical and surface characterization techniques, the aim of the present chapter is to provide further understanding of the role of MWNTs during Mg corrosion. Even though similar galvanic corrosion effects are expected to take place as has been reported for Mg/carbon fiber composites, the nanoscopic size of the local cathodes may lead to a different behavior than for larger cathodic sites in the material.

7.3 Experimental

A two-step process is applied to produce the MWNT/Mg composites: first, a pre-dispersion step was performed on MWNTs to avoid formation of large agglomerates followed by fabrication of MWNT/Mg composite by melt stirring technique. By using the pre-dispersion step, a relatively homogenous dispersion of MWNTs in Mg matrix could be achieved that was expected to affect the corrosion behaviour. The block copolymer Disperbyk-2150 (BYK Chemie GmbH) was first dissolved in ethanol, which has been proven to be a good dispersing agent to improve the dispersion of CNTs [334]. MWNTs (Baytubes® C 150P) were added to the as-prepared solution. This mixture was put into an ultrasonic bath and stirred 30 minutes. After adding Mg (Chempur) or Mg alloy AZ91D (ECKA) chips, the suspension was further stirred until the ethanol was evaporated. The MWNT coated chips were then placed in a cylindrical sample crucible in an oven to heat up to 670°C.

Different percentage of MWNTs (0.1 wt%, 1 wt% and 5 wt%) were used to produce MWNT/AZ91D and 0.1 wt% of MWNTs was used to produce MWNT/Mg composites. When the Mg chips were molten, the melt was mechanically stirred at 350 rpm during 30 minutes to further disperse MWNTs. After stirring, the molten MWNT/Mg (MWNT/Mg –dispersed) composite was poured into a mould. A pure Mg sample was also produced without MWNT addition by the same technique. In order to check the influence of the pre-dispersion process, the reference samples
(MWNT/Mg and MWNT/AZ91D – non-dispersed) were produced using the same technique without the pre-dispersion step.

Corrosion tests were performed in 3.5% NaCl solution (Sigma-Aldrich, purity >99.5) that was refreshed daily (250 ml/day) as described in section 2.2.3 Corrosion tests.

Further analysis by SEM, FIB and AES were also performed (2.3 Surface analytic methods).

7.4 Results and Discussion

7.4.1 Corrosion behaviour of MWNT reinforced AZ91 composites

Figure 83 shows the corrosion behaviour of MWNT reinforced AZ91D composites (1 and 5%) after different surface pretreatments. Inset images in Figure 83 show the corresponding corroded surfaces of the composites after 1 day of immersion in 3.5% NaCl. The effect of MWNT additions can be observed from the images but also visually during the experiment by the hydrogen gas bubbling level. It is obvious that 5 wt% MWNT/AZ91D were highly corroded compared to 1 wt% MWNT/AZ91D samples. The corrosion rates concur with these results. Corrosion rates of the composites were found between 9-18 g/m² day⁻¹ with 1 wt% MWNTs and ~24 g/m² day⁻¹ with 5 wt% MWNTs.
Montemor et al. [335] have shown that adding Ce or La-modified CNTs into an amino silane film on AZ31 induced significant reduction of both anodic and cathodic activity at the metallic surface. However, until now no study has been carried out to check whether adding “clean” CNTs (i.e. without any pre-treatment) in the metal alloys could lead to galvanic coupling, which can increase the corrosion rate of the Mg phase. In our experiments, a strong gas bubbling was observed proportional to the MWNT amount in the matrix, which could be explained by the coupling leading to faster dissolution of the Mg phase.

Additionally, surface preparation was also found to be an important factor. In 1 wt% MWNT/AZ91D composite, the highest corrosion rate was measured on the chemically etched surfaces. The origin of this effect is not yet clear; however surface pre-treatment seems a critical parameter for the low MWNT-containing composite. On the other hand, surface pre-treatment was not critical for 5 wt% MWNT/AZ91D composites. Weight loss of different samples was also measured for 7 days.
hydrogen bubbling was also observed during the experiments, especially for the 5 wt% MWNT/AZ91D composite.

For improved mechanical properties, it is known that a homogenous dispersion of CNTs in a material matrix is important. Without a homogenous dispersion of CNTs, the excellent properties of CNTs can not be exploited and CNTs would act as defects rather than reinforcements in the matrix. In order to understand the influence of the CNT dispersion on the corrosion behaviour of the CNT magnesium composite, two different samples were prepared. One sample was produced by using the two step process [336], which has been confirmed that more homogeneously dispersed MWNTs in AZ91D composite can be achieved; another sample was produced without a pre-dispersion process, so MWNTs are mainly in bundles in the AZ91D matrix. Figure 84a-c shows the optical microscopy on the surfaces of the different samples after 1 day immersion in 3.5% NaCl. The effect of CNT dispersion can be easily observed even at low MWNT contents. A bigger and more evenly dispersed corrosion pattern can be observed in Figure 84a (with pre-dispersion process) compared to a smaller corrosion corner in Figure 84b (without pre-dispersion process). With well-dispersed MWNTs in AZ91D, formation of galvanic couples takes place everywhere on the composite surface, hence strongly increasing the corrosion rate of the alloy. Without pre-dispersion, MWNTs exist mainly in bundles in the composites, so the coupling effect only takes place at MWNT agglomerates (as suggested by Figure 84b). Figure 84c exhibits the pristine AZ91D alloy corroded surface. Corrosion only takes place on a small area (seen in the circle) and the corrosion level after 1 day is quite low compared to the MWNT/AZ91D composites.

Figure 84d shows the weight loss for 5 wt% MWNT/AZ91D composites with and without pre-dispersion. Clearly, a much higher weight loss of the more homogeneously dispersed CNT/AZ91D composite (with pre-dispersion process) compared to the less homogeneously dispersed CNT composite (without pre-dispersion process) is observed confirming that the better the dispersion, the worse the corrosion behaviour.
Figure 84: Optical microscopy of 0.1 wt% MWNT/AZ91D with a) pre-dispersion process, b) without pre-dispersion and c) pristine AZ91 sample after 1 day immersion in 3.5 % NaCl; d) weight loss results of 5 wt% MWNT/AZ91D in 3.5 % NaCl during 1 week with/without pre-dispersing MWNTs. The circle in c) shows the corrosion takes place only in a small area on the pristine AZ91D surface.

The corrosion product of the 5 wt% MWNT/AZ91D sample in 3.5% NaCl solution was collected and dried after the corrosion test, and the residue was observed under SEM as seen in Figure 86. The pattern in the circle looks very different from Fig. 4b, which presents a typical corroded AZ91D composite surface with short, sharp and needle-shaped crystals. The materials in the circle rather look like to have relatively long and cylindrical shapes with a smooth surface, which is more like pristine MWNTs (Figure 85c) and pre-dispersed MWNTs on AZ91D chips (Figure 85d). Therefore, we assume that they are CNT-like materials. This finding suggests that the CNTs themselves are not dissolved, supporting the proposal that they act as local cathodes in the composite. (More detailed explanation of the corrosion products as well as corrosion mechanism will be presented in next section).
7.4.2 Corrosion behaviour of MWNT reinforced Mg composites

In this section, the influence of the MWNT addition into the pure Mg matrix is explained by electrochemical means in more detail. Further characterization of MgH$_2$/Mg(OH)$_2$ layer is also provided by surface analytic techniques.

7.4.2.a Influence of MWNT addition on the electrochemical behaviour of Mg

The OCP of pure Mg and MWNT/Mg composites was measured over 30 minutes in 3.5% NaCl solutions (inset of Figure 86). In the first 5 minutes, the potential for all samples shifts towards less negative values very fast, indicating rapid formation of a partially protective Mg(OH)$_2$ layer on the surface. After 5 minutes, the formation rate of the Mg(OH)$_2$ oxide layer is lowered and the slope of the OCP/time curves is decreased. Finally, OCP values reach slightly different steady-state values around -1.65 V. The OCP values are quite similar for all the samples which is not surprising considering the small area fraction of the MWNTs on the sample surfaces.
After OCP measurements, electrochemical impedance spectra were measured (Figure 86). Addition of (only 0.1 wt-%) MWNTs to the Mg matrix leads to a measurable and significant increase of the dissolution rate. The corrosion behaviour of pure Mg has been frequently studied by EIS, and interpretation of the behaviour has been provided for example by Baril et al. [81-82] and Song et al. [80]. According to Baril et al., capacitive loops in the EIS spectra are the relaxation of mass transport in the growing solid oxide phase on the Mg surface. Song et al. proposed that these loops are attributed to unipositive Mg\(^+\) ion concentration within the cracked areas [73] of a surface oxide layer. Most recently, Swiatowska et al. [337] reported that dissolution of Mg in both NaCl and Na\(_2\)SO\(_4\) electrolytes takes place with no evidence for the often invoked Mg\(^+\) intermediate. Independent of the detailed interpretation of the origin of some of the spectral features, the most straightforward observation in our case is evidenced by the decrease of the charge transfer resistance (R\(_t\)) (i.e., the diameter of the Nyquist curve along the real axis) due to the addition of MWNTs in Mg.

![Figure 86: Nyquist plots of pure Mg and MWNT/Mg composites in 3.5% NaCl after 30 minutes at open circuit potential. Inset: Open Circuit Potential versus time curves of pure Mg and MWNT/Mg composites in 3.5% NaCl.](image-url)
The value of $R_t$ is $\sim 2.0$ kOhm, $\sim 2.5$ kOhm and $\sim 3.0$ kOhm for dispersed MWNT/Mg, non-dispersed MWNT/Mg and pure Mg, respectively. Clearly, addition of a small amount of MWNTs into the Mg matrix decreases the corrosion resistance and the corrosion resistance becomes even smaller, when a pre-dispersion step is applied during preparation of the composites. This is in line with findings on MWNT/AZ91D composites in which MWNT dispersion was shown to significantly increase the dissolution rate as already explained in a previous section. The polarisation resistance ($R_p$) values - the difference along the real axis between the resistance at the highest and lowest frequencies – show the same trend as the $R_t$ values, with an inductive loop in the low frequency (LF) regions. For Mg and Mg alloys, inductive loops have been attributed to adsorbed surface species such as $\text{Mg(OH)}^+_{\text{ads}}$ and $\text{Mg(OH)}_{2\text{ads}}$ [73, 81-82, 337]. Additionally, these inductive loops are also attributed to Mg ions on relatively film-free surfaces [84, 338].

The reaction of pure Mg in aqueous solutions is given by the equations below [28]:

$$\text{Mg}_{(s)} \rightarrow \text{Mg}^{2+}_{(aq)} + 2e^- \ \text{(anodic reaction)} \quad \ldots \quad (14)$$

$$2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-_{(aq)} \ \text{(cathodic reaction)} \quad \ldots \quad (15)$$

$$\text{Mg}^{2+}_{(aq)} + 2\text{OH}^-_{(aq)} \rightarrow \text{Mg(OH)}_{2} \ \text{(corrosion product)} \quad \ldots \quad (16)$$

According to these reactions, and as is well-known, dissolution of Mg leads to pH increase in the surroundings. Figure 87 shows the change of pH values for all samples during 90 minutes of immersion. A rapid increase of pH is achieved during the first 5 minutes in 3.5% NaCl. After 5 minutes, pH/time curves of different samples continue to increase with different slopes, indicating different dissolution rates. The highest pH value is obtained for dispersed MWNT/Mg composite followed by the non-dispersed one. The pure Mg shows the relatively slowest rate of pH increase, indicating less dissolution in this time period. This is in good agreement with the EIS results, and again confirms that the addition of MWNTs leads to increased dissolution of Mg. As can be seen from the optical inset images of Figure
When a pre-dispersion step is applied, rate of corrosion also increases and leads to a macroscopically more uniform corrosion process.

Figure 87: The pH change of each sample in 50 ml 3.5% NaCl during 90 minutes. Inset: Optical images of specimens after 1 day immersed in 50 ml 3.5% NaCl.

In order to better understand the effect of the CNT addition on the corrosion rate of Mg, potentiodynamic polarization curves were measured (Figure 88). The polarization curves demonstrate that an acceleration of the cathodic hydrogen evolution kinetics is observed when MWNTs are added to Mg, but the kinetics of the anodic dissolution are not significantly influenced by the presence of carbon nanotubes in the material. Hence, the influence of the MWNTs on the electrochemical behaviour of Mg is similar to the well-known effects of impurities, such as Fe, in accelerating kinetics of the hydrogen evolution (see e.g. [339-340]). It is noteworthy that the composites contain only 0.1 wt-% MWNTs; hence the MWNTs can be considered as efficient cathodes, as their influence is well observed even with this small concentration (n.b. the polarization curves are very reproducible).
Moreover, polarization curves of pure Mg and the Mg/MWNT composites were compared when measured directly after immersion, and after 6 h of immersion in 3.5% NaCl solution (see Figure 89) and the results are summarized in Table 7. The values of $E_{\text{corr}}$, $i_{\text{corr}}$, Tafel constants ($\beta_a$ and $\beta_c$), corrosion rate (CR) (calculated by AutoLab® software, NOVA©), and polarization resistance $R_p$ (calculated from Stearn–Geary equation )[225] (17) are given in Table 7. Corrosion rates were obtained from these curves.

$$R_p = \frac{\beta_a \cdot \beta_c}{2.3 i_{\text{corr}} (\beta_a + \beta_c)} \quad \ldots (6)$$

In all cases, the cathodic current densities are increased with immersion time, but the effect is the strongest for the composite with dispersed carbon nanotubes (Figure 89c). Similar effects of faster hydrogen evolution on pre-corroded surfaces have been previously observed for pure Mg and some Mg alloys [341]. The higher cathodic currents after 6 h of immersion can result from a larger cathodically active area after corrosion, as corrosion leads to roughening of the surface. This may also lead to exposure of a higher number of CNTs on the surface, as the CNTs are expected to be chemically and electrochemically stable under these conditions. With
the progress of dissolution of the Mg matrix, the remaining CNTs probably become detached but at the same time, new CNTs can become exposed. Moreover, with time, the surface becomes increasingly covered by corrosion products layers. Therefore, the corroding surfaces of the Mg/CNTs composites are highly dynamic. The finding that this immersion-induced increase of the cathodic currents is the strongest for the composite with dispersed nanotubes is logical in that a fine distribution of the carbon nanotubes leads to creation of a large number of local galvanic couples on the surface; hence, dissolution on the microscopic scale can be expected to be highly non-uniform and to lead to the largest increase of the electrochemically active surface area. The anodic parts of the polarization curves suggest a slight decrease of anodic dissolution with time, which may result from the growth of corrosion product layers on the surface. Overall, however, for all materials the corrosion rates increase with time indicating the poor protective properties of the formed corrosion product layers.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$E_{corr}$ (V)</th>
<th>$i_{corr}$ (µA/cm²)</th>
<th>$\beta_a$ (mV)</th>
<th>$\beta_c$ (mV)</th>
<th>Corrosion Rate (mm/year)</th>
<th>$R_p$ (Ω. cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Mg (0h)</td>
<td>-1.627</td>
<td>36.477</td>
<td>31.335</td>
<td>186.540</td>
<td>1.668</td>
<td>635.790</td>
</tr>
<tr>
<td>Pure Mg (6h)</td>
<td>-1.531</td>
<td>28.168</td>
<td>58.245</td>
<td>246.000</td>
<td>1.288</td>
<td>726.100</td>
</tr>
<tr>
<td>Non-disp. (0h)</td>
<td>-1.607</td>
<td>63.185</td>
<td>39.302</td>
<td>230.970</td>
<td>2.890</td>
<td>465.500</td>
</tr>
<tr>
<td>Non-disp.(6h)</td>
<td>-1.499</td>
<td>71.965</td>
<td>31.342</td>
<td>304.820</td>
<td>3.292</td>
<td>341.370</td>
</tr>
<tr>
<td>Dispersed (0h)</td>
<td>-1.618</td>
<td>98.291</td>
<td>49.123</td>
<td>281.290</td>
<td>4.469</td>
<td>368.200</td>
</tr>
<tr>
<td>Dispersed (6h)</td>
<td>-1.520</td>
<td>280.390</td>
<td>151.430</td>
<td>372.990</td>
<td>12.825</td>
<td>332.830</td>
</tr>
</tbody>
</table>

*Table 7: Potentiodynamic polarization measurement results of pure Mg and MWNT/Mg composites in 3.5% NaCl solution.*
7.4.2.b Characterization of the corrosion product layers

To observe the initial formation of the corrosion layer on MWNT/Mg, SEM images of the samples were taken after 90 seconds of immersion in 3.5% NaCl. As compared to pure Mg (Figure 90a), SEM images of both MWNT/Mg composites (non-dispersed, figures Figure 90b and dispersed, Figure 90c) show higher surface coverage by corrosion products even after short (90 seconds) immersion times. Additionally, dispersion of the MWNTs in (Figure 90c) seems to lead to more homogeneous corrosion product formation over the surface. However, in all cases an incomplete and inhomogeneous coverage of the surface is observed after 90 s immersion.
Figure 90: SEM images showing surfaces covered with Mg(OH)$_2$ species after exposed in 3.5% NaCl after 90 seconds; a) pure Mg, b) non-dispersed MWNT/Mg and c) dispersed MWNT/Mg.

To elucidate the effect of MWNTs in the corrosion process in more detail, laterally resolved AES measurements were performed. These analyses were carried out on samples that were soaked in pure water for 12 h, to simplify the chemical analysis of the surface. Figure 91a-c shows the carbon signals from AES mappings and corresponding SEM images (Figure 91d-f) for pure Mg and MWNT/Mg composites. It is worthwhile to emphasize that even though MWNTs are absent in the pure Mg matrix, weak carbon signals were detected, mostly due to carbon contamination (Figure 91a). If pure Mg is selected as a background image, one can conclude that the high intensity of C signals (yellow pixels in Figure 91b) is attributed to non-dispersed MWNT agglomerations. Additionally, formation of Mg(OH)$_2$ layers is also favoured on these MWNT bundles; this could be attributed to formation of C-Mg red-ox couples and therefore to galvanic corrosion process. Similar clusters of corrosion products are also observed for the dispersed MWNT/Mg sample (Figure 91c). However, in this case localized clusters of carbon signals (yellow) are not detected, indicating that the MWNTs were successfully dispersed during production of composites (hence, the signals from dispersed MWNTs are below the detection level of the measurement).
Figure 91: AES results (a-c) with corresponding SEM images (d-f) showing distribution of MWNTs through the Mg(OH)\(_2\) layers after exposed in pure water after 12 hours; a,d) pure Mg, b,e) non-dispersed MWNT/Mg and c,f) dispersed MWNT/Mg.

The corrosion product layers were further analyzed by FIB-cut SEM images. Figure 92 shows the cross-section of the corrosion product layers formed during 90-min immersion in 3.5% NaCl. In all cases, an inner compact and an outer porous layer is observed. The thickness of the corrosion product layer very strongly varies for pure Mg and for the composite samples: for pure Mg, an ~1100-nm thick layer is observed (Figure 92a), a layer thickness of ~510 nm is found for non-dispersed MWNT/Mg (Figure 92b), and ~350 nm for dispersed MWNT/Mg (Figure 92c). The higher the corrosion rate, the thinner the corrosion product layer. The origin of this behaviour may be related to the vigorous H\(_2\) gas production on the Mg composites.
Figure 92: FIB-cut SEM images showing composite cross-section surfaces covered with Mg(OH)$_2$ film after being exposed in NaCl for 90 minutes; a) pure Mg, b) non-dispersed MWNT/Mg and c) dispersed MWNT/Mg.

The strong H$_2$ bubbling enhances transport of dissolution products (e.g. Mg$^{2+}$ ions) away from the surface. Therefore, precipitation of the corrosion products is decreased. In addition, H$_2$ bubbling may partially detach the growing corrosion product layer. This could result not only in thinner corrosion product layers, but moreover in different surface morphologies as shown in Fig. 8a-c. In the case of dispersed MWNTs in the composite, a smoother morphology of the corrosion product layer is observed in the top-view image. A schematic illustration of the influence of clustered and finely-distributed carbon nanotubes on the anodic and cathodic reactions on the composite surface is included in Figure 93.
7.4.2.c Long term corrosion measurements

Figure 94 shows the average corrosion rates of dispersed MWNT/Mg, non-dispersed MWNT/Mg and pure Mg exposed in NaCl during 1 week. Average rates were calculated and compared by using two methods; 1) weight loss calculations, and 2) hydrogen gas collection measurements. These two methods were used together to check validity of the measurements, as both methods have their strengths and challenges (e.g., proper removal of the corrosion product layers is crucial for correct weight loss measurement). A small difference between the results of the two methods was indeed observed, probably due to corrosion products that were not completely removed during immersion in CrO$_3$ + AgNO$_3$ solution. However, the general agreement between the two methods was good as shown in Figure 94.
Figure 94: Change of average corrosion rates of pure Mg, dispersed MWNT/Mg and non-dispersed MWNT/Mg that were each exposed in NaCl during 1 week.

Similar to the initial stages of corrosion as discussed in Section 5.4.2.a, Figure 94 indicates that the addition of MWNTs into Mg increases the corrosion rate, and moreover, the daily corrosion rate increases with immersion time (the trends for the corrosion rate follow the same behaviour both for the weight loss and for the volume of produced hydrogen gas). The increase of the corrosion rate with time is most probably due to an increase of the effective surface area by dissolution-induced roughening of the surface, similarly as was discussed in the case of short-term immersion effects on the cathodic current densities (Figure 89).

Qualitatively this increase of the corrosion rate with time is the strongest for the sample containing well-dispersed MWNTs (see dotted lines in Figure 94 which are drawn as a guide to the eye), which is in agreement with the formation of a high number of well-distributed galvanic couples on the surface (i.e., finely distributed localized dissolution leads to the strongest roughening of the surface). As discussed previously, the corrosion product layers forming on the surface do not provide high corrosion protection; hence the surface roughening effects in increasing the corrosion rate overrun the small barrier effect of the corrosion products in decreasing the dissolution rate. It is noteworthy that the effect of CNTs on the corrosion behaviour
prevails over extended times of dissolution, in spite of the low concentration and the small size of the local cathodes in the matrix.

7.5 Conclusions

In contrast to the previous report by Endo et al. [331], the present chapter clearly demonstrates that reinforcement of pure Mg and Mg alloy AZ91D by multi wall carbon nanotube (MWNT) addition leads to a strong increase of the corrosion rate by formation of galvanic couples between the pure Mg matrix and multi wall carbon nanotubes (MWNT). Moreover, pre-dispersion of MWNTs increases the number of galvanic couples and therefore increasing the corrosion rate.

However, addition of MWNTs into the pure Mg matrix plays an important role in the formation of the corrosion product layers in the early stage of corrosion, but even more significantly increases the corrosion rate over extended exposure periods. Therefore, in order to exploit the outstanding mechanical properties of MWNT reinforced Mg (alloy) composites, additional corrosion protection measurements are required.

In regards of modifying bulk structure of magnesium material, it would be aimed to have controlled and homogenous corrosion morphology (not localized) as it is demonstrated that the corrosion rate of magnesium increases in presence of CNTs. Thus, different types of CNTs (e.g., single-wall vs. double-wall carbon nanotubes) or surface-modified CNTs would be of interest to tailor corrosion properties. Additionally, it would also be of interest to focus on surface modification of CNTs by electrically insulating or dispersing layers without deteriorating their mechanical properties as the distribution of the CNTs in the matrix is randomly and the CNTs have a tendency to cluster in the present case.
8 Conclusions And Outlook
This work covers new types of surface and bulk modifications of magnesium and its alloys with the aim of tailoring its corrosion rate. In general, it is found that surface pre-treatments have a significant effect on corrosion behaviour of magnesium. For instance, in chapters 3, 4 and 5, two different types of surface pre-treatments are reported; a conventional NH$_4$F pre-treatment and polypyrrole (PPy) coatings as a new approach. In chapter 3, it is presented that acidic etching and NH$_4$F steeping durations are very sensitive parameters with respect to the increase of corrosion resistance. For instance, although short durations of treatment have a beneficial effect, longer durations of etching and steeping results in dissolution of magnesium and does not provide a protection, as the chemical etching starts to take place.

As another pre-treatment strategy, in chapter 4 and 5, a first time formation of conducting polymer coating (polypyrrole –PPy-) on Mg alloy AZ91D is reported from aqueous solutions of sodium salicylate by cyclic voltammetry (CV) method. In contrast to findings from NH$_4$F steeping, these thin films show better protection and corrosion resistance. It is also worthwhile to stress that these electrically conductive and organic layers can be further functionalized by additional functional groups. For instance, in chapter 5, it is demonstrated that further modification of PPy layers with albumin layers shows even better corrosion performance by release of dopant anions. In both cases, PPy layers act as anodic barriers and the corrosion protection is achieved by release of dopant anions. Moreover, these layers remained very adhesive over the corrosion period and no peeling-off was observed.

In addition to surface pre-treatment approaches, a small example about tuning of surface morphology of magnesium alloy WE43 is given in chapter 6. It is presented that anodisation of a biorelevant magnesium alloy (WE43) in HF containing non-aqueous electrolyte can lead to growth of self-ordered nanostructures such as nanopores and nanotubes. These structures have considerable potential in tailoring and functionalising the surface, for instance in biomedical applications of Mg and its alloys.

In chapter 7, bulk modification of Mg and Mg alloy AZ91D with multiwall carbon nanotubes (CNTs) is carried out. Results reveal that although CNTs have been confirmed as good reinforcements to improve the mechanical properties of light metal matrixes, addition of these materials into a Mg matrix drastically increases the corrosion rate as the coupling effect between cathodic CNTs and anodic Mg
increases. Moreover, better dispersion of CNTs leads to even more corrosion rates and reduced corrosion resistivity.

In general, surface modification of magnesium is very open to new approaches and strategies. To use this metal as a biomedical component or in industry, a proper coating or surface treatment can be achieved by multi steps of coatings, as every coating step has its individual protection mechanism and property. For instance it would be of interest to use acidic etching or ammonium fluoride treatment before a zinc-phosphate coating or a hard anodisation process. Additionally, further modification of porous/tubular Mg surfaces or PPy layers with other biocompatible ceramic layers or biopolymers (e.g., bioglass, chitosan) would be of interest to extend these approaches to a wide scale of applications.
References:


35. Gvozdenovic, M., et al., *Corrosion behavior of magnesium, aluminum and zinc as anodic materials in chloride based electrolytes for use in primary and


248. Schmuki, P., et al., *Fast formation of aligned high-aspect ratio TiO(2) nanotube bundles that lead to increased open circuit voltage when used in


List of Abbreviations:

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>Alb</td>
<td>Albumin</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic Layer Deposition</td>
</tr>
<tr>
<td>ATP</td>
<td>Adenosine Triphosphate</td>
</tr>
<tr>
<td>BSE</td>
<td>Back-Scattered Electrons</td>
</tr>
<tr>
<td>CNT(s)</td>
<td>Carbon Nanotube(s)</td>
</tr>
<tr>
<td>CR</td>
<td>Corrosion Rate</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
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<tr>
<td>DES</td>
<td>Drug Eluting Stent</td>
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<tr>
<td>EDAX</td>
<td>Energy Dispersive X-Ray Spectroscopy</td>
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<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
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<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>HF</td>
<td>High Frequency</td>
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<tr>
<td>ICP(s)</td>
<td>Intrinsically Conductive Polymer(s)</td>
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<tr>
<td>LF</td>
<td>Low Frequency</td>
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<tr>
<td>MF</td>
<td>Middle Frequency</td>
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<tr>
<td>MO</td>
<td>Metal Oxide</td>
</tr>
<tr>
<td>MS</td>
<td>Mild steel</td>
</tr>
<tr>
<td>MWNT(s)</td>
<td>Multi-wall Carbon Nanotube(s)</td>
</tr>
<tr>
<td>NDE</td>
<td>Negative Difference Effect</td>
</tr>
<tr>
<td>NSAID</td>
<td>Non-steroidal Anti-inflammatory Drug</td>
</tr>
<tr>
<td>OCP</td>
<td>Open Circuit Potential</td>
</tr>
<tr>
<td>PAni</td>
<td>Polyaniline</td>
</tr>
<tr>
<td>PPy</td>
<td>Polypyrrole</td>
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<tr>
<td>PT</td>
<td>Polythiophene</td>
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<tr>
<td>SBF</td>
<td>Simulated Body Fluid</td>
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<td>SE</td>
<td>Secondary Electrons</td>
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<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
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<tr>
<td>SS</td>
<td>Stainless steel</td>
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<tr>
<td>SWNT(s)</td>
<td>Single-wall Carbon Nanotube(s)</td>
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<tr>
<td>ToF-SIMS</td>
<td>Time of Flight Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>USB-GPIB</td>
<td>Universal Serial Bus - General Purpose Interface Bus</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectroscopy</td>
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List of Symbols:

\( E_{\text{SHE}} \) : Standard Electrode Potential
\( I_a \) : Anodic Current Density
\( I_c \) : Cathodic Current Density
\( U_{\text{corr}} \) : Corrosion Potential
\( U_{\text{applied}} \) : Applied Potential
\( I_{e,a} \) : Expected Anodic Current Density
\( I_{e,c} \) : Expected Cathodic Current Density
\( I_{m,c} \) : Measured Cathodic Current Density
\( I_{m,a} \) : Measured Anodic Current Density
\( E_t \) : Potential Applied at \( t \)
\( E_0 \) : Initial Potential
\( I_t \) : Measured Current Density at \( t \)
\( I_0 \) : Initial Current Density at \( t \)
\( Z \) : Impedance
\( \Phi \) : Phase Angle
\( \omega \) : Frequency
\( t \) : Time
\( R_p \) : Polarisation Resistance
\( R_{\text{CT}}, R_T \) : Charge Transfer Resistance
\( E_0 \) : Ground State
\( E_1 \) : First Excited State
\( h \) : Planck’s Constant
\( c \) : Speed of Light
\( \Omega \) : Ohm
\( \beta_a \) : Anodic Tafel Constant
\( \beta_c \) : Cathodic Tafel Constant
\( u \) : Mass unit
\( V_{\text{max}} \) : Maximum Potential