



UNIVERSITÀ DEGLI STUDI DI PALERMO

PhD Course in Chemical, Environmental, Biomedical, Hydraulic and Materials Engineering
Dipartimento di Ingegneria
Settore Scientifico Disciplinare ICHI-01/A

Electrochemical surface engineering of biomedical metal alloys

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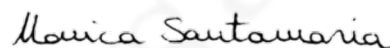


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XXXVIII CYCLE

GRADUATION YEAR 2026

CODICE BORSA PNRR 38-411-20-DOT204NJ79-2020 – CUP B76E22000080007

Summary

Metallic biomaterials have traditionally been designed to remain stable in the physiological environment for long periods, ensuring mechanical reliability and corrosion resistance. However, the need to avoid secondary removal surgeries and long-term complications has driven increasing interest toward biodegradable metals. Among them, magnesium and its alloys represent particularly promising candidates for temporary orthopedic and cardiovascular implants due to their low density, elastic modulus close to that of natural bone, and intrinsic biocompatibility. Nevertheless, their rapid and often uncontrolled corrosion in chloride-rich physiological environments remains the major limitation to their widespread clinical adoption.

This research project focuses on understanding and tuning the biodegradation behavior of magnesium alloys, with particular emphasis on the AZ31 alloy, through a combined experimental and modelling approach. The work is structured to move from the study of magnesium corrosion in simulated physiological environments, to the development of surface engineering strategies aimed at tuning degradation kinetics, and finally to the formulation of a semi-empirical predictive model.

A first critical aspect investigated in this thesis concerns the influence of electrolyte composition on the corrosion behavior of AZ31. Magnesium degradation was systematically studied in four simulated body fluids: saline solution (0.9% NaCl), Hank's Balanced Salt Solution (HBSS), Kokubo solution, and Dulbecco's Modified Eagle Medium (DMEM). These media differ in terms of ion concentration, buffering capacity, and presence of organic components. The corrosion rate was evaluated using a combination of electrochemical techniques (open circuit potential monitoring, electrochemical impedance spectroscopy, polarization curves), hydrogen evolution measurements via gas chromatography, and gravimetric mass loss analysis.

The results show that electrolyte composition strongly affects both the corrosion rate and the degradation mechanism. HBSS, characterized by a relatively high phosphate concentration, promotes the formation of a protective phosphate-based conversion layer that significantly slows down corrosion. DMEM, containing organic species and amino acids, modifies the degradation behavior, leading to a different dissolution mechanism. Kokubo solution, with limited buffering capacity, results in the highest corrosion rates and pronounced localized attack. In saline solution, the absence of protective species leads to significant pitting, although partial passivation occurs due to local pH

increase. These findings highlight the intrinsic limitations of bare AZ31 in physiological environments and underline the necessity of tailored surface treatments.

The second part of the work is dedicated to the development of surface modification strategies aimed at controlling early-stage degradation and mitigating the initial burst of hydrogen evolution. Three main approaches were investigated: stannate-based chemical conversion coating, electrodeposition of hydrophobic manganese stearate, and UV-induced grafting of polydimethylsiloxane (PDMS). The stannate conversion coating leads to the formation of a MgSn(OH)_6 layer. Structural and compositional analyses (SEM, EDX, XRD, FT-IR) confirmed the formation of a hydroxystannate layer uniformly covering the surface. Although the coating is hydrophilic, it improves corrosion resistance when full coverage is achieved, while insufficient coverage may promote localized corrosion. This treatment represents a cost-effective and scalable alternative to chromate-based coatings, which are unsuitable for biomedical applications due to toxicity. To further enhance corrosion resistance and reduce initial degradation rates, a hydrophobic manganese stearate layer was electrodeposited. The hydrophobicity of the coating reduces electrolyte penetration, limiting the access of aggressive species to the magnesium surface. This approach effectively decreases hydrogen evolution in the early immersion stage, which is critical for minimizing gas pocket formation in vivo. An additional strategy consisted of UV-grafting PDMS molecules onto the magnesium surface. The grafted PDMS layer introduces strong hydrophobicity and acts as a barrier to electrolyte ingress, significantly delaying the initial corrosion process. By minimizing direct contact between the metallic substrate and the physiological medium, this functionalization reduces the early-stage burst release of magnesium ions while preserving the biodegradable nature of the alloy. Beyond corrosion rate reduction, the work also addresses the importance of corrosion morphology. For biodegradable implants subjected to mechanical loads, generalized corrosion is preferable to localized attack, which may lead to premature mechanical failure. Surface treatments were therefore evaluated not only in terms of overall degradation rate but also in terms of their ability to modify corrosion mode.

The final part of the thesis integrates experimental results into a semi-empirical model for predicting magnesium alloy biodegradation. Given the well-known discrepancies between electrochemical estimations (e.g., Tafel extrapolation) and actual degradation rates - particularly due to the negative difference effect in magnesium - the model is based on more reliable hydrogen evolution data. The objective is to establish a framework capable of correlating material composition, surface state, and environmental conditions with expected degradation kinetics. Such predictive tools can be used to accelerate material screening and optimize implant design before in vivo testing.

Overall, this work demonstrates that the biodegradation behavior of magnesium alloys is the result of a complex interplay between alloy composition, surface condition, and physiological environment. By combining electrolyte-dependent corrosion analysis, chemical and electrochemical surface engineering, and semi-empirical modelling, this thesis aims to contribute to the design of biodegradable magnesium-based implants. The proposed strategies focus on achieving resorption rates aligned with tissue healing timelines, minimizing hydrogen evolution and ion burst release, and promote safer clinical translation of next-generation bioresorbable metallic devices.

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1 Introduction

Biomaterials can be universally defined as those materials, either natural or synthetic, designed to interact with biological system [1,2]. The scope of such interactions may vary broadly, biomaterials are engineered to replace, repair or augment organs and tissues, to support them in the healing process following trauma, defects or disease. Starting with such definition of biomaterials, they include ceramics, polymers, composites and even biological substances, but metals are the most common and suitable choice for applications requiring high mechanical strength, durability, and processability [3,4].

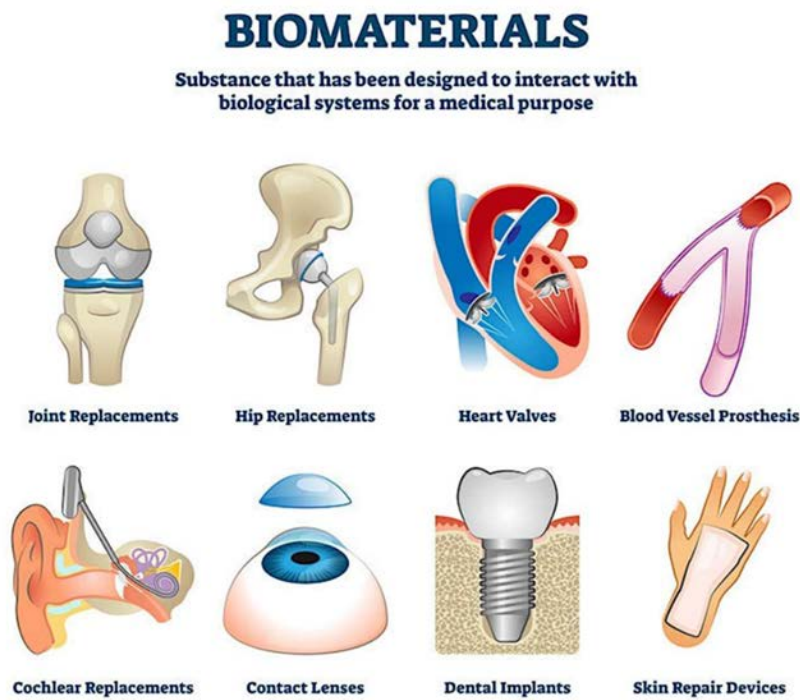


Figure 1. Biomaterials application examples.

The interaction of biomaterials with biological tissue requires in first place their biocompatibility, or the ability to maintain their functionality without harming the surrounding biological environment. Biocompatibility is achieved thanks to different properties, a biomaterial must not only avoid toxic or allergic reactions, but also integrate successfully with tissues, resist degradation in hostile

environments, and, in some cases, gradually dissolve at a controlled rate. The implementation of biocompatibility as an actual material property has evolved through the years, progressively shifted from simple inertness toward active interaction with biological systems. Engineered materials today aim to achieve additional functionality like osteointegration, antibacterial behavior, and controlled drug release [5,6].

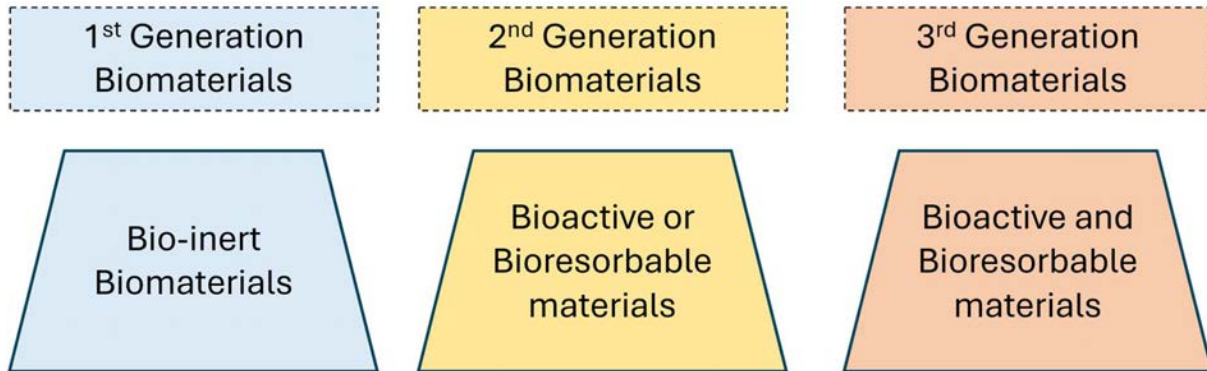


Figure 2. Evolution of the biocompatibility paradigm from bioinert to bioactive and bioresorbable biomaterials.

The use of metals in clinical medicine dates back to the 19th century, beginning with their use as fixation for fractured long bones. Their success, however, was severely limited before the advent of aseptic surgery. Implantation of foreign materials almost always led to infection and failure until the introduction of sterile surgical techniques, when metals were more safely used in the orthopedic field. The use of metals in this early stage was limited to temporary devices (plates, screws, pins) and later they were adopted as permanent replacements such as joint prostheses. Originally, metallic alloys were directly repurposed for medical use. At first, Stainless steels were chosen for their mechanical robustness and apparent corrosion resistance. In the 1930s, cobalt–chromium alloys, originally developed as dental casting materials, were adapted to orthopedics, providing improved wear resistance, very important for application such as hip replacements. In the second half of the 20th century, titanium and Ti–6Al–4V alloys established themselves as gold standards due to their superior corrosion resistance, and excellent bone integration [7,8]. The diversification of metallic biomaterials has continued ever since, i.e. with the introduction of NiTi shape-memory alloys and the recent research of biodegradable metals. The first enabled minimally invasive cardiovascular devices, while the use of magnesium, iron, and zinc alloys represent a paradigm shift: implants designed to disappear once healing is complete [9,10].

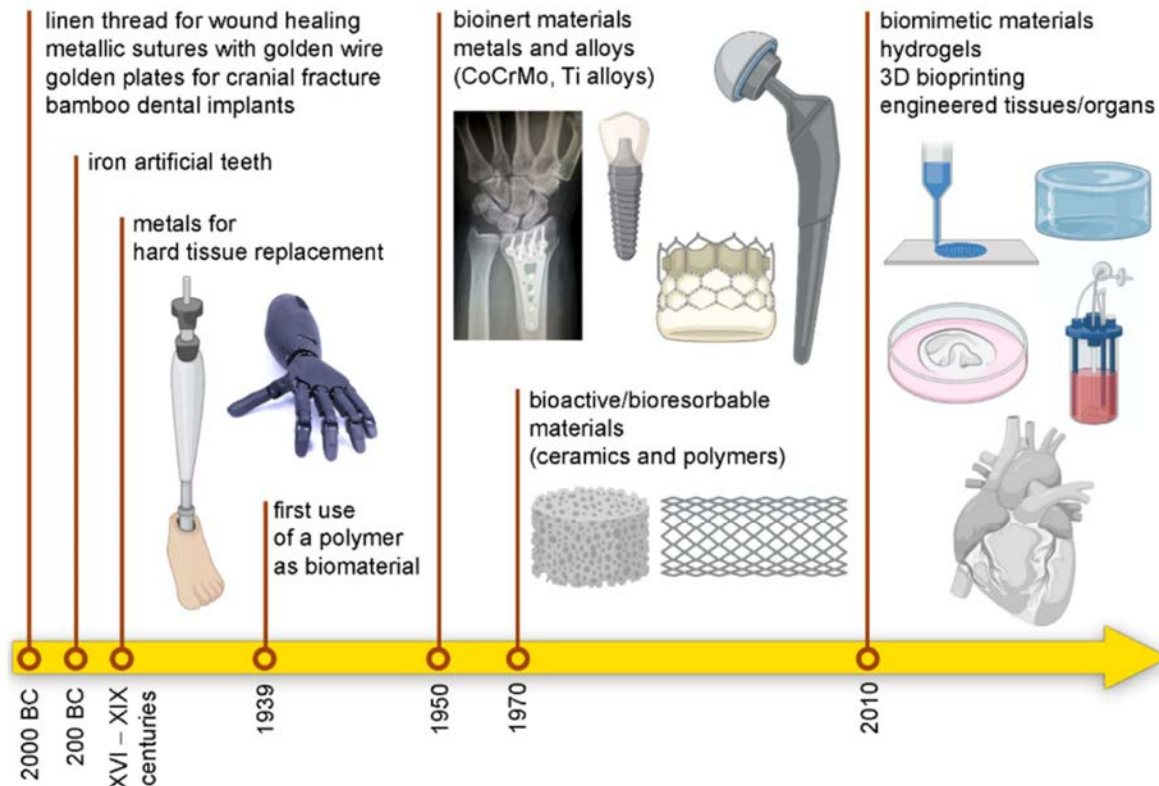


Figure 3. Historical progression of biomaterials used in medical applications [11].

To understand the requirements imposed on metallic implants, it is essential to consider the composition of the human body. Approximately 95% of body mass consists of just four elements: oxygen, carbon, hydrogen, and nitrogen. The remaining fraction includes calcium and phosphorus (key for bone mineralization), sodium, potassium, chloride (main electrolytes in extracellular fluids), magnesium, and trace elements such as iron, zinc, copper, and manganese.

Element	Wt. %	At. %
O	65.0	25.5
C	18.5	9.5
H	9.5	63.0
N	3.3	1.4
Ca	1.5	0.31
P	1.0	0.22
K	0.4	0.06
S	0.3	0.05
Na	0.2	0.3
Cl	0.2	0.03
Mg	0.1	0.1
Trace element	<0.01	<0.01

Table 1. Elements in the human body. Table taken from [12].

These trace elements, though present in very small amounts, play critical physiological roles. Iron is central to oxygen transport through hemoglobin; zinc is required for enzymatic function and DNA binding; copper and manganese are cofactors in antioxidant enzymes. However, at excessive concentrations, many of these elements become toxic. This duality is crucial in biomaterial design: the use of elements naturally present in the human body generally enhances biocompatibility, but their uncontrolled release may disturb local or systemic homeostasis [13].

Human body fluids constitute a highly aggressive environment for metals. Blood plasma and interstitial fluids are essentially aqueous electrolytes containing a mixture of inorganic ions (Na^+ , Cl^- , Ca^{2+} , Mg^{2+} , K^+ , phosphate, bicarbonate, sulfate), amino acids, and proteins. The temperature is maintained around 37 °C, while oxygen partial pressure is lower than in ambient conditions, reducing the stability of passive films on metals. The pH of physiological fluids normally ranges between 7.2 and 7.4. However, in specific pathological or post-surgical conditions, this value can change drastically. During inflammation reactive oxygen species (ROS) are released, and the pH can locally fall to values as low as 3. Under these highly aggressive acidic and oxidative conditions, corrosion rates accelerate, and even stable alloys may release significant amounts of ions [14–16].

Furthermore, implants are rarely at rest. Mechanical stresses from load bearing, cyclic fatigue, and micromotions at interfaces contribute to phenomena such as stress corrosion cracking, fretting corrosion, and tribocorrosion. The simultaneous action of electrochemical and mechanical degradation is often the limiting factor in the longevity of metallic implants [17,18].

Metallic biomaterials can be divided into two broad categories:

- Metals for permanent prostheses: stainless steels, cobalt–chromium alloys, titanium and titanium alloys. These are expected to remain in the body even for decades, requiring long-term corrosion resistance, mechanical durability, and minimal ion release.
- Metals for biodegradable prostheses: magnesium, iron, zinc and their alloys. These are designed to provide mechanical support only during the healing time, gradually corroding until their complete absorbance or disappearing, in order to avoid secondary removal surgeries.

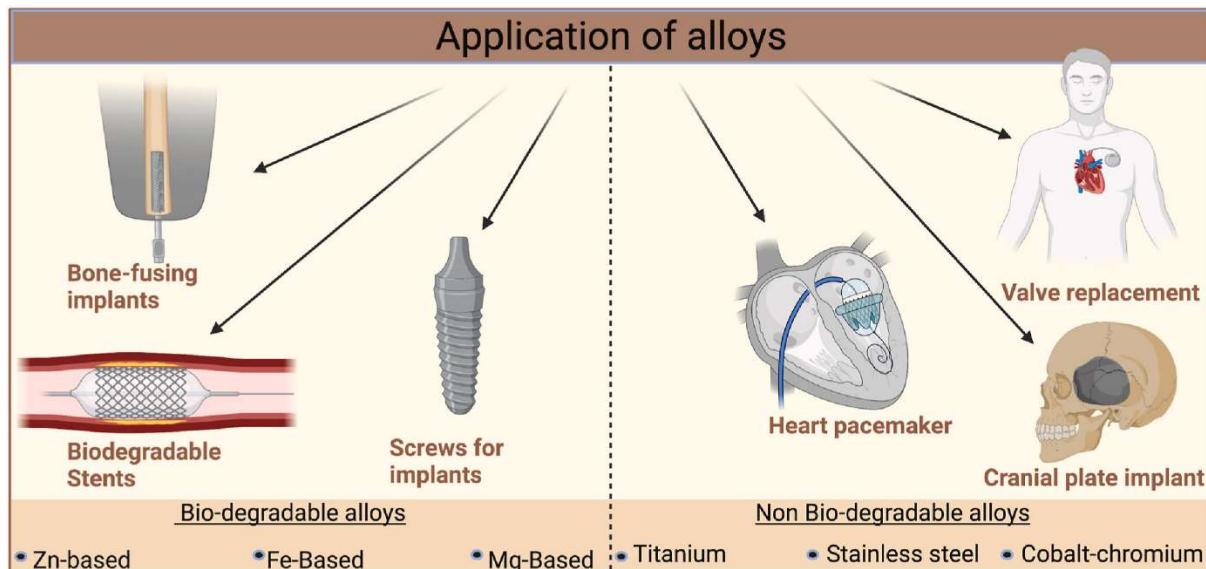


Figure 4. Typical applications of permanent and biodegradable metallic alloys in biomedical devices [19].

Within the two categories, different alloys have been optimized for specific applications. For example, austenitic stainless steel like 316L are widely used in temporary fracture fixation, while Ti–6Al–4V is common in dental and orthopedic implants. Magnesium alloys have been explored for biodegradable screws and plates, whereas zinc alloys are emerging as candidates for biodegradable cardiovascular stents.

Permanent implants are biomedical devices designed to remain in the body for decades, sometimes for the entire lifespan of the patient. Such stringent requirements impose strict properties:

- High corrosion resistance in chloride-rich physiological environments, to prevent ion release.
- Mechanical reliability, including strength, toughness, fatigue resistance, and wear resistance.
- Minimal ion release, especially for alloying elements known to be toxic or allergenic.

- Good biocompatibility, allowing integration with surrounding tissues.
- Adequate osteointegration, particularly for orthopedic and dental devices.

Failure of permanent implants is usually associated with a combination of electrochemical and mechanical processes: localized corrosion, fretting, wear-assisted degradation, or fatigue. Biological complications such as chronic inflammation, fibrous encapsulation, and bacterial colonization further compromise performance [20,21].

Stainless steels were among the first metallic alloys used in biomedical applications. The austenitic grade AISI 316L, containing chromium, nickel, and molybdenum, became the reference due to its good mechanical properties, low cost, and relative corrosion resistance. The corrosion resistance of stainless steels relies on the formation of a thin passive film enriched in chromium oxides. However, in physiological conditions, especially under low pH or in crevices, this film may locally break down. Chloride ions play a central role in pitting and crevice corrosion, particularly at interfaces such as the underside of screws or plates. One of the limitations of stainless steel is due to the possibility of an excessive release of nickel, chromium, and iron ions. Nickel is associated with allergic reactions and toxic effects, while hexavalent chromium is carcinogenic. These risks, combined with the high elastic modulus of stainless steel (~200 GPa) compared to cortical bone (20–30 GPa), which may cause stress shielding, have limited their use to temporary fixation devices rather than permanent implants [22–25]. According to Wolff's law, bone tissue adapts to mechanical loading by increasing its mass and strength under elevated stress conditions, while reduced mechanical stimulation leads to bone weakening. In this context, stress shielding refers to the resorption of bone surrounding implant regions that are insufficiently loaded [26].

Today, stainless steels are widely used for fracture fixation plates, screws, and intramedullary nails that are removed after healing. For long-term implants, they have been largely replaced by titanium and cobalt-based alloys.

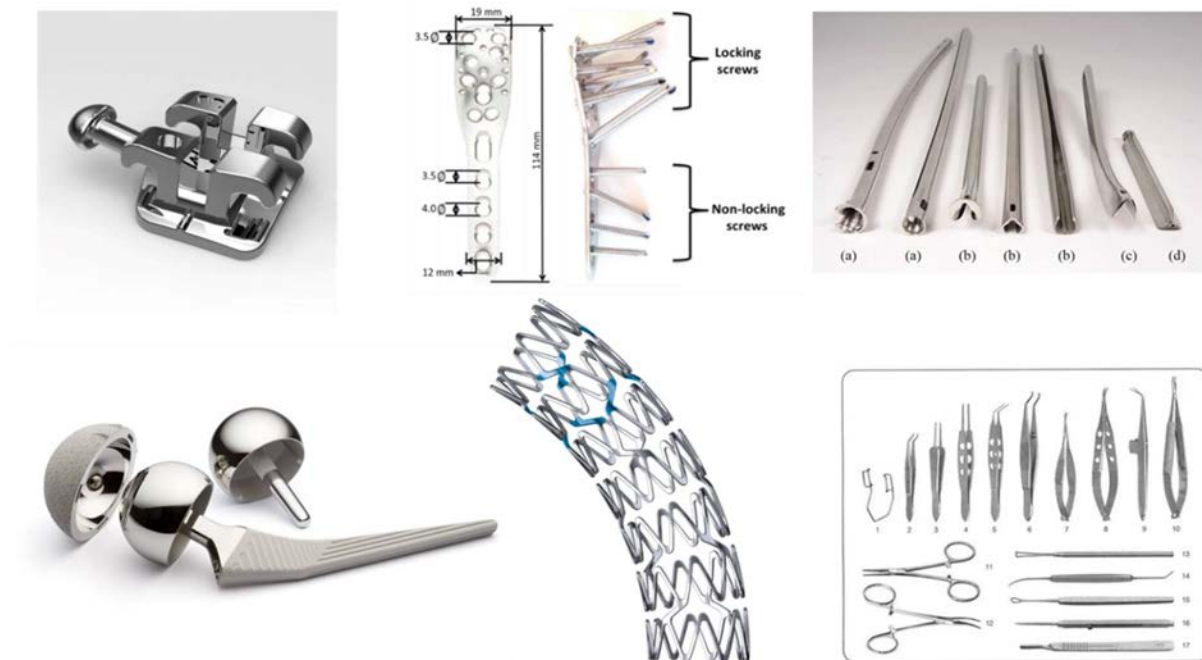


Figure 5. Typical biomedical applications of stainless steel alloys, including orthopaedic fixation devices (plates, screws, and nails), joint replacement components, orthodontic brackets, vascular stents, and surgical instruments.

Cobalt–chromium–molybdenum alloys (Co–Cr–Mo) were introduced in the 1930s. Initially used in dental restorations (with the most common Vitallium alloy), they were soon adapted to orthopedic prostheses. Their superior wear resistance and fatigue strength made them especially suitable for articulating surfaces in joint replacements. Co–Cr alloys exhibit very high strength and hardness, and their corrosion resistance is even higher than that of stainless steels, mainly due to chromium and molybdenum. However, their elastic modulus ($\sim 220\text{--}230$ GPa) is higher than steel, thus worsening stress shielding. The main alloy constituent, Cobalt, is present in the human body almost only in the B-12 vitamin but becomes toxic at high concentrations. Particles released from wear or corrosion of Co–Cr implants have been linked to local tissue reactions and, in some cases, systemic effects such as neurological symptoms. Nickel, in small concentration, is also present in some Co–Cr alloys, adding some allergenic risk. Despite these concerns, in vitro and clinical studies have shown that Co–Cr alloys are generally less toxic than pure cobalt or nickel due to their passivity. Co–Cr alloys are currently widely used in total hip and knee replacements, particularly for femoral heads and articulating components. They are also used in dental prostheses and some cardiovascular devices. However, their high cost, ion release risks, and mechanical mismatch with bone (stress shielding) limit broader applications [27,28].

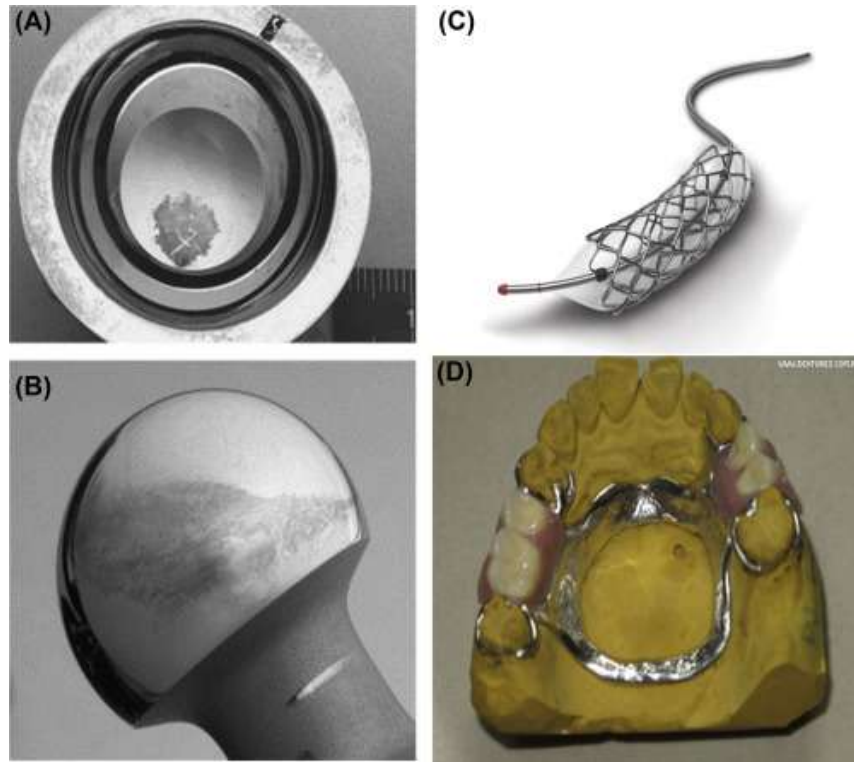


Figure 6. Representative biomedical applications of cobalt–chromium (Co–Cr) alloys: (a,b) McKee–Farrar hip prosthesis, (c) vascular stent, and (d) orthodontic appliance [29].

Titanium emerged in the mid-20th century as an innovative biomaterial. Its density (4.5 g/cm^3) is significantly lower than that of steel or Co–Cr, reducing implant weight. Its elastic modulus ($\sim 110 \text{ GPa}$) is lower than the mentioned alloys, closer to bone, and its corrosion resistance is exceptional due to the spontaneous formation of a stable TiO_2 passive film. Titanium is considered bioinert: it elicits little or no adverse tissue reaction. More importantly, bone can grow directly on titanium surfaces, a process called osseointegration, which ensures stable anchoring of implants. This favorable property is one of the main reason titanium is the most widely used metal in dental and orthopedic implants. The most adopted titanium alloy is Ti–6Al–4V, while it offers superior mechanical strength, concerns have been raised about the release of vanadium (for its cytotoxicity) and aluminum (potentially neurotoxic). These issues have driven the development of a second-generation of alloys such as *β -titanium alloys* (Ti–Nb, Ti–Mo, Ti–Ta, Ti–Zr), which eliminate vanadium and aluminum in favor of more biocompatible elements. Titanium and its alloys dominate the fields of orthopedics, with hip and knee stems, plates, screws, spinal implants; dentistry, with root-form implants, abutments, prosthetic components; cardiovascular devices, such as heart valve housings, pacemaker cases. Despite its advantages, titanium has some drawbacks. Its wear resistance is lower than Co–Cr alloys, making it less suitable for articulating surfaces. It also lacks inherent

antibacterial properties, increasing the risk of infection at implant sites. Moreover, in vitro studies suggest that titanium particles may affect stem cell differentiation and connective tissues at high concentrations [8,18,30,31].

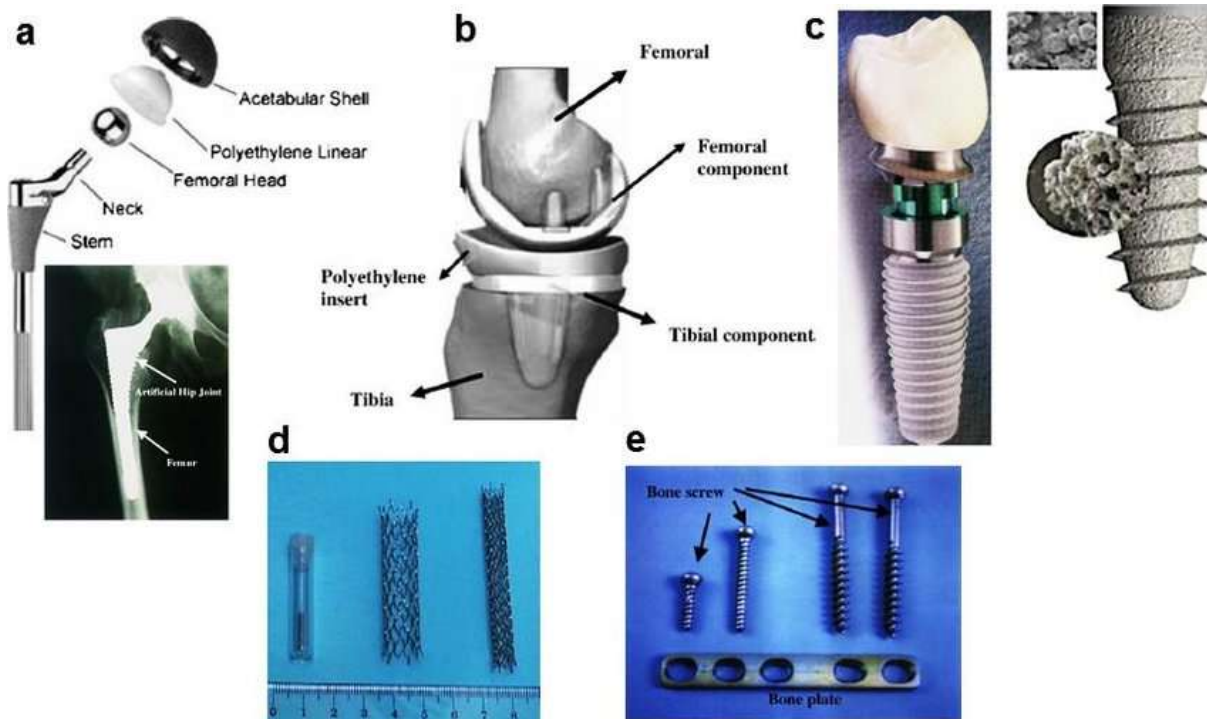


Figure 7. Representative biomedical applications of titanium and its alloys: (a) hip joint prosthesis, (b) knee joint prosthesis, (c) dental implant, (d) vascular stent, and (e) screws and plates for bone fixation.

Stainless steels, cobalt–chromium alloys, and titanium alloys are the main materials that constitute the family of metallic biomaterials for permanent devices. Each has distinct strengths and weaknesses:

- Stainless steel has low cost, good workability, but limited corrosion resistance and high ion release.
- Co–Cr alloys show excellent wear resistance, good corrosion resistance, but high modulus and potential toxicity.
- Titanium alloys have superior biocompatibility and corrosion resistance, but wear limitations and issues with alloying elements.

The continued challenge in the field of biomedical metal implants is to balance mechanical reliability with biological safety, minimizing ion release while maximizing integration with tissues. In addressing these challenges, surface engineering plays a key role, as will be discussed later.

For decades, the paradigm of metallic biomaterials has been based on the search for maximum corrosion resistance and long-term durability. Stainless steels, cobalt alloys, and titanium have been engineered to remain stable in the physiological environment for years, minimizing their corrosion and ion release. However, this paradigm presents two significant drawbacks, permanent implants inherently carry the risk of chronic inflammation and local complications due to their long-term presence in the body; moreover, many devices (particularly fracture fixation systems in orthopedics) are required only for a limited time, necessary for tissue healing. Once the bone has consolidated, the implant is no longer needed, and the removal surgery is invasive, costly, and not without risk. These considerations have driven the development of a new class of biomaterials: biodegradable metals. The concept is to design implants that provide mechanical support only during the healing period, then gradually corrode in the body, releasing biocompatible products and leaving no permanent material behind [32–35].

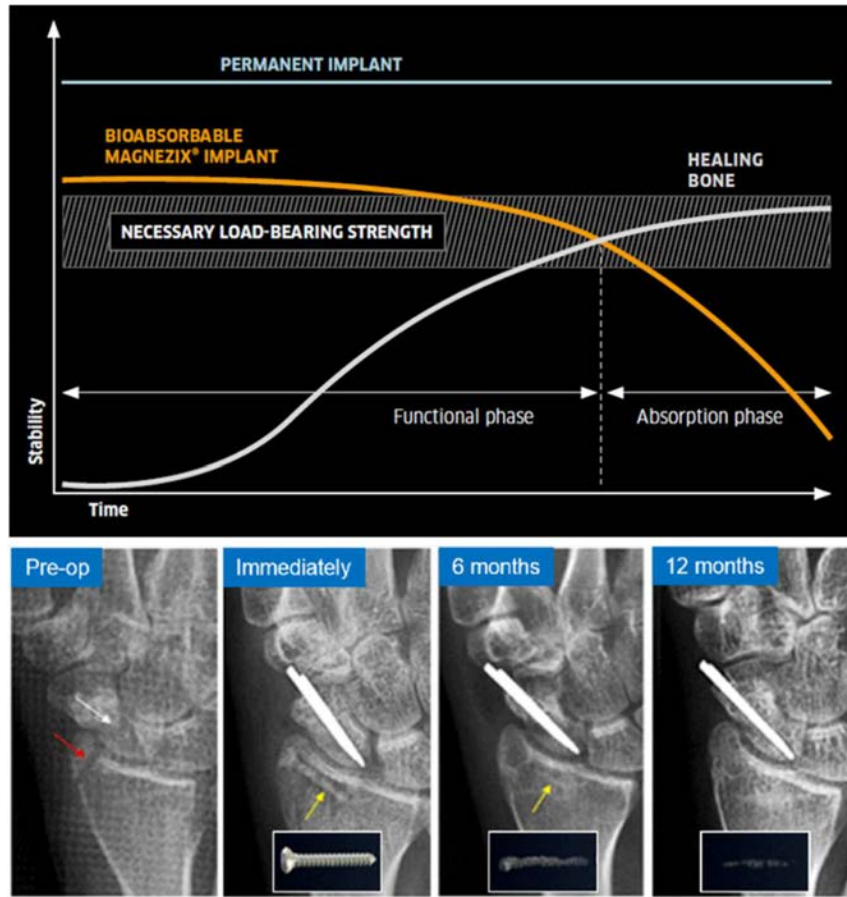


Figure 8. Conceptual illustration of degradation time matching tissue healing time for a Magnezix® biodegradable magnesium-based implant (top), and radiographic images showing the biodegradation process at different time points after implantation (bottom) [36].

This strategy avoids the need for removal surgery, reduces the long-term risk of complications, and aligns the material's lifetime with the healing kinetics of tissues. Biodegradable metals must satisfy three key requirements: biocompatibility, controlled biodegradation and adequate mechanical properties. The biocompatibility required for degradable implants means that degradation products must be tolerated or metabolized by the body. Such degradation must occur at a rate that match the healing process: for bones, this means maintaining mechanical support for 3-6 months, while for cardiovascular stents support is required for 3-4 months. At the beginning of its service life, the biodegradable implant must withstand physiological loads, then gradually weaken as tissues recover. If corrosion is too slow, the implant persists unnecessarily, negating the benefit of biodegradability, achieving the right balance is therefore critical. The metals mainly studied for these applications are magnesium-, iron- and zinc- based [37,38].

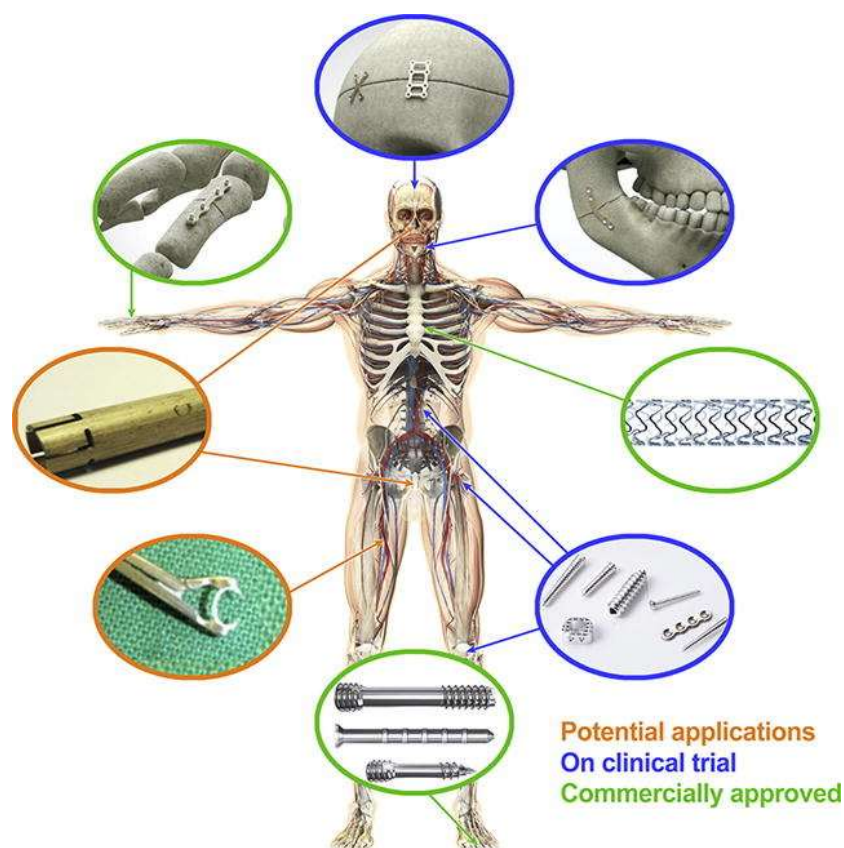


Figure 9. Biodegradable metallic implants and their applications [32].

Magnesium was the first metal to be considered for producing biodegradable implants, thanks to its favorable properties: density and elastic modulus close to bone, reducing stress shielding; high biocompatibility and ability to promote new bone formation; non-interference with magnetic resonance imaging (MRI) due to low magnetic susceptibility. However, magnesium corrodes too rapidly in physiological environments. The oxidation of Mg leads to the formation of $\text{Mg}(\text{OH})_2$, this process produces hydrogen gas, leading to bubble formation near the implant and increasing local pH, which can damage surrounding tissues. These issues have limited clinical adoption of Mg based implants. To slow down degradation, two parallel strategies have been investigated: alloying (with rare earths, aluminum, zinc, calcium) and surface coatings. Commercial examples include the MAGNEZIX® screw, a MgYREZr alloy device certified in Europe, and the Magmaris® stent, a drug-eluting magnesium alloy scaffold used in cardiology. Despite these successes, widespread use of Mg remains limited by its aggressive corrosion behavior [9,13,39–44].

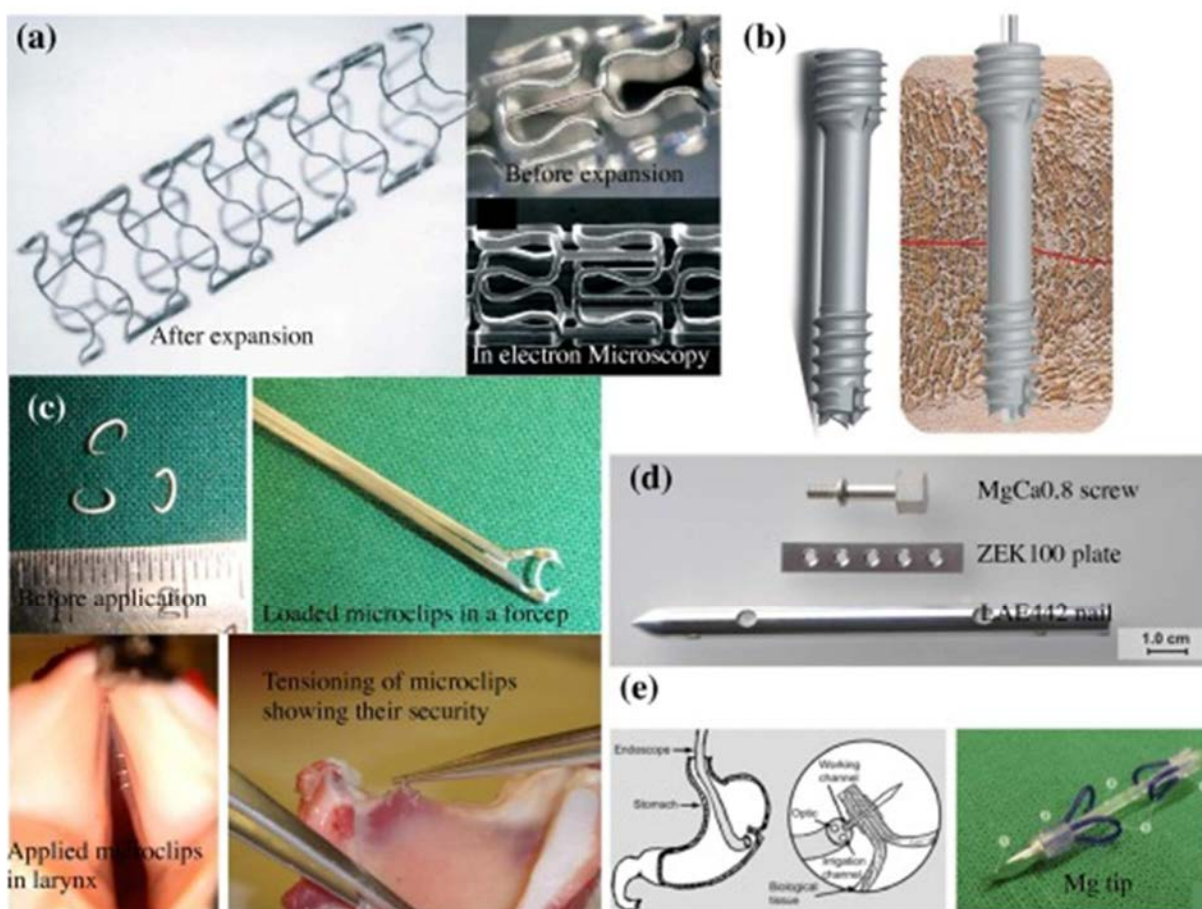


Figure 10. Representative applications of biodegradable magnesium-based implants [9].

Iron is another essential element in the body, central to hemoglobin and cellular metabolism. Pure iron exhibits good strength and ductility, making it a candidate for stents and load-bearing implants. However, in contrast to magnesium, the main limitation of this material lies in its slow degradation rate. In physiological conditions, iron corrodes at rates below 0.1 mm/year, insufficient for timely resorption. Additionally, its ferromagnetic nature interferes with magnetic resonance imaging (MRI) diagnostics. To overcome these issues, iron-based alloys such as Fe–Mn have been proposed. The purpose of adding manganese is not only to accelerate corrosion but also eliminate ferromagnetism, making this alloy safer for imaging. Composite systems combining iron with bioceramics (e.g., iron + tricalcium phosphate) have also been studied to promote controlled degradation. Animal trials have shown promising results, though no Fe-based devices are yet commercially available [45,46].

Zinc has recently emerged as one of the most promising biodegradable metals. It occupies an intermediate position between magnesium and iron in terms of standard electrode potential (-0.76 V vs the standard hydrogen electrode (SHE)), and therefore in degradation rate. Pure zinc corrodes at

0.1–0.3 mm/year, which matches the healing times of bone and vascular tissues. In addition, zinc is present in the human body as an essential trace element, involved in numerous enzymatic processes; It is non-ferromagnetic and thus it doesn't interfere with MRI; its degradation does not produce hydrogen gas, unlike magnesium. The main limitation of pure zinc is its relatively low mechanical strength and ductility, that may be insufficient for high-load applications. Alloying strategies have been developed to improve strength without compromising biocompatibility, alloying elements like Mg, Ca, Li and Mn. Other than this, processing techniques such as extrusion, rolling, and more recently additive manufacturing are also being explored to optimize microstructure and properties. In terms of biological response, zinc ion release must be carefully controlled. While Zn^{2+} is necessary for cell proliferation and bone metabolism, excessive concentrations can be cytotoxic. Surface modifications, such as conversion coatings or polymer grafting, have proven effective in reducing the initial burst release of zinc ions and in promoting more uniform degradation [47,48].

Biodegradable metals must be carefully designed to match the specific timelines required for tissue healing and implant resorption. Magnesium alloys exhibit excellent biocompatibility and an elastic modulus close to that of natural bone; however, their degradation occurs too rapidly, often accompanied by the undesirable hydrogen evolution. In contrast, iron-based alloys provide high mechanical strength and structural stability, but their corrosion rate is excessively slow, and their ferromagnetic nature can interfere with MRI. Zinc and its alloys, on the other hand, represent an appealing compromise: their degradation kinetics are more compatible with the desired time frames for temporary implants. Nevertheless, they still require optimization through alloying strategies and surface modifications to enhance their mechanical performance and minimize potential cytotoxic effects. In conclusion, biodegradable metals represent a paradigm shift in biomaterials science, aiming not for maximum durability but for controlled resorption aligned with tissue healing. Their successful application depends not only on alloy development but also on precise surface engineering strategies that tune degradation rates and biological interactions.

For both permanent and biodegradable implants, alloy selection is crucial, but the surface of the implant is the true interface with the body. Properties such as corrosion resistance, osteointegration, antibacterial activity, and protein adsorption are largely governed by surface chemistry and morphology. For this reason, surface engineering has become a central strategy to tailor implant behavior [49,50]. Electrochemical treatments, such as anodizing and electrodeposition, offer scalable routes to functional coatings that can enhance corrosion resistance, tune degradation rates, and improve biological response. The goals of surface modification are multiple:

- Increase corrosion resistance and reduce ion release.

- Promote osteointegration and bioactivity.
- Provide antibacterial properties to reduce infection risk.
- Tune degradation rates of biodegradable metals.
- Control surface wettability and topography to influence cell behavior.

Electrochemical processes have attracted particular interest because they are cost-effective, scalable, and applicable to complex geometries [51,52].



Figure 11. Scalable electrochemical surface treatments: laboratory-scale experimental setup (left) and industrial bath processing line (right).

Chemical conversion coatings are obtained by immersing the material in a reactive solution that promotes the formation of a protective film through surface transformation. Typical examples include phosphate-, stannate-, and titanium-based conversion layers, they act as diffusion barriers, reducing the access of aggressive species and thereby slowing down corrosion processes while modulating ion release [53–55]. Acid etching represents another well-established chemical treatment, particularly for titanium and additively manufactured components: controlled etching can smooth surface irregularities, remove residual powders, and increase surface wettability, all of which contribute to improved osteointegration [56,57]. Chemical grafting techniques allow the attachment of functional molecules to the surface, in order to impart specific properties such as hydrophobicity or bioactivity. For instance, the grafting of long-chain organic molecules onto zinc surfaces can reduce the initial

corrosion rate by limiting electrolyte penetration, whereas the incorporation of bioactive species such as peptides can enhance cell adhesion and proliferation [58,59].

Electrochemical surface treatments offer a higher degree of control over the morphology and composition of the modified layer, through the adjustment of parameters such as potential, current density, electrolyte composition, and temperature. Among these, anodizing is one of the most widely employed techniques, producing a stable oxide layer that enhances corrosion resistance and serves as an ideal substrate for further functionalization such as hydroxyapatite nucleation [60–62]. By tuning process parameters, it is possible to obtain nanostructured oxide films capable of influencing cellular response. Plasma electrolytic oxidation (PEO), a high-voltage variant of anodizing, generates porous, ceramic-like oxides with improved wear and corrosion resistance. Other electrochemical techniques include electrodeposition, which enables the controlled deposition of metallic or composite coatings - such as silver layers for antibacterial functionality or calcium phosphate films to promote bone-like mineralization - and electrophoretic deposition (EPD), which is particularly effective for applying bioceramic particles such as hydroxyapatite onto complex geometries. The uniformity and versatility of EPD make it especially suitable for orthopedic and dental applications [63,64]. Electrochemical methods can also be combined in multistep processes, like a first anodizing step to create a porous oxide, then electrodeposition or EPD as a sealing step. This modularity enables precise tailoring of multifunctional surfaces.

Beyond chemical and electrochemical routes, physical surface treatments further expand the range of achievable functionalities. Techniques such as physical vapor deposition (PVD), ion implantation, and laser texturing enable precise modification of surface composition and topography, introducing hard, wear-resistant layers or defined micro-patterns that can direct cell behavior [60]. Mechanical finishing processes, including polishing or shot peening, are often employed as complementary steps to tune surface roughness and residual stresses, improving both fatigue strength and the reproducibility of subsequent coatings [65,66]. Although these physical approaches can yield excellent performance, their implementation is often limited by cost, process complexity, and the difficulty of treating intricate implant geometries. For these reasons, chemical and electrochemical methods remain more versatile and scalable options for biomedical applications.

Regardless of the chosen technique, the final surface state strongly dictates the biological response of the host tissue. The initial events following implantation are governed by the interaction between the modified surface and the surrounding physiological environment: protein adsorption, cell adhesion, and bacterial colonization occur within minutes and are highly sensitive to surface chemistry and wettability. Controlled roughness or porosity enhances osteointegration by providing anchoring sites

for osteoblasts and by promoting mineral nucleation, while bioactive coatings containing calcium phosphates or hydroxyapatite can further stimulate osteogenic differentiation. Conversely, hydrophilic or bacteriostatic surfaces help limit bacterial attachment, particularly when combined with antibacterial agents such as silver, copper, or zinc [65,67–71].

In biodegradable systems, achieving a uniform and gradual degradation profile is essential to ensure mechanical stability throughout the healing process, allowing the surrounding tissue to gradually take over the mechanical load as the implant resorbs. In titanium alloys, anodizing in phosphoric acid solutions produces stable oxide films capable of withstanding the oxidative conditions typical of inflammatory environments, while simultaneously promoting hydroxyapatite nucleation. When coupled with electrodeposited silver nanoparticles, such surfaces combine corrosion resistance, bioactivity, and antibacterial functionality in a single system. Additively manufactured titanium components, which often exhibit irregular and contaminated surfaces, particularly benefit from this sequence: acid etching removes residual powders and smooths asperities, while anodizing restores the protective oxide and improves the homogeneity of the surface response. A similar rationale applies to zinc-based materials, where phosphate and stannate conversion coatings effectively reduce degradation rates and control the early burst of Zn^{2+} release. The subsequent grafting of hydrophobic organic molecules can further restrict electrolyte access, improving short-term stability without compromising biocompatibility. For 3D-printed zinc, the same chemical treatments are advantageous because they uniformly conform to complex geometries, enhancing both corrosion behavior and mechanical integrity [72,73].

Overall, the combination of chemical, electrochemical, and physical strategies provides a powerful framework for designing multifunctional implant surfaces. Yet, maintaining coating stability *in vivo* and reconciling multiple performance requirements - corrosion resistance, osteointegration, and antibacterial activity - remain major challenges. Furthermore, the translation of laboratory-scale treatments into industrially reproducible processes is still limited by cost and standardization issues. Despite these limitations, electrochemical surface modification represents one of the most promising approaches due to its intrinsic versatility, scalability, and ability to generate multifunctional interfaces in a single step.

Through the analysis of their electrochemical behavior and biological interactions, this work aims to elucidate the relationship between alloy composition, surface modification, and physiological environment, ultimately identifying strategies for optimizing biodegradable metallic implants.

As discussed before, one of the major challenges in design of biodegradable implants is achieving degradation rates that match healing processes. In vitro experiments may provide inconsistent results due to the variability of simulated body fluids and testing conditions. In-vivo tests are more representative but also costly and time-consuming [37,74]. These variabilities introduce the need for predictive models, capable of linking material properties and surface characteristics with expected degradation rates. Electrochemical principles provide a foundation for such models, parameters such as the corrosion current density can be correlated with degradation kinetics. Advanced modelling can incorporate factors like localized corrosion, the influence of proteins and cells, and dynamic physiological conditions. A predictive approach could enable faster material screening, a rapid evaluation of new alloys before animal testing; surface treatment optimization via tailoring of the parameters to achieve target degradation rates; design of personalized implants by adjusting material and surface treatments to patient-specific healing profiles.

The integration of alloy design, additive manufacturing, surface engineering, and predictive modelling is paving the way toward multifunctional implants. A good device should simultaneously:

- Provide mechanical support.
- Promote osteointegration and tissue regeneration.
- Deliver antibacterial activity.
- Degrade at a controlled rate matched to healing.
- Adapt geometry and stiffness to individual patient anatomy.

The evolution of metallic biomaterials reflects a trajectory from adaptation of industrial alloys to purpose-designed systems for medical use. Stainless steel and cobalt alloys laid the foundations, titanium alloys became the gold standard, and biodegradable metals such as magnesium, iron, and zinc represent the frontier of temporary implants. Surface engineering has emerged as the key strategy to tailor properties at the interface with the body, while additive manufacturing and predictive modelling expand the design space toward personalized and multifunctional devices. This approach represents a convergence of materials science, electrochemistry, biomechanics, and computational modelling. By addressing the challenges of durability, biocompatibility, and controlled resorption, next-generation metallic implants can effectively move from the inert materials of the beginning to become an active tool in the healing process.

Considering the scientific and technological challenges associated with biodegradable magnesium-based implants, this thesis aims to provide a comprehensive investigation of their corrosion behavior in simulated physiological environments and to develop strategies for controlling their degradation

kinetics. The first objective is to understand how electrolyte composition influences corrosion mechanisms, surface film formation, hydrogen evolution, and overall degradation rate, highlighting the complexity and variability of in vitro degradation assessment. A second objective is to design and optimize surface treatments capable of modulating early-stage corrosion, reducing localized attack, and improving degradation uniformity. Particular attention is devoted to surface functionalization approaches, including chemical conversion coatings, hydrophobic electrodeposition, and UV-induced grafting techniques, with the aim of limiting the initial burst degradation and controlling ion release. Finally, this work seeks to propose a semi-empirical modelling framework able to correlate electrochemical parameters with long-term biodegradation behavior, providing a predictive tool to support the rational design of magnesium-based biodegradable implants with degradation rates tailored to tissue healing processes.

2 Materials and Methods

This section describes materials and procedures used for all the experimental tests mentioned in the thesis, unless differently indicated in the respective chapter. The selected magnesium alloy was the AZ31 (as designated in the Standard Specification ASTM B90/B90M [75]), purchased from Goodfellow, with the following nominal composition: Mg 96%, Al 3%, Zn 1%. After cutting the samples in suitable shape and dimensions, the surfaces were prepared with mechanical grinding, using silicon carbide paper (Buehler) with progressively higher grit number, up to P2500. During this process, samples were quenched in ethanol ($C_2H_6O \geq 99.5\%$ - Emplura). Afterwards, AZ31 coupons were cleaned in an ultrasonic bath with ethanol for 10 minutes and finally dried in air.

The simulating solutions used for all the experimental activities are reported in Table 2. Four different physiological solutions were adopted, to account the effect of organic species (proteins and amino acids) and inorganic ions (chloride, calcium, carbonate, phosphates and sulphate). The mentioned solutions were prepared in our laboratory, except for the Dulbecco's Modified Eagle Medium (DMEM with stable Glutamine, with 1.0 g L^{-1} Glucose – Genaxxon bioscience). All solutions were maintained at 37°C for the whole duration of the tests in order to mimic physiological environment.

Saline solution		HBSS		Kokubo		DMEM	
<i>substance</i>	<i>conc.</i> (mg L ⁻¹)	<i>substance</i>	<i>conc.</i> (mg L ⁻¹)	<i>substance</i>	<i>conc.</i> (mg L ⁻¹)	<i>substance</i>	<i>conc.</i> (mg L ⁻¹)
NaCl	9000	NaCl	8000	NaCl	7990	NaCl	6400
		KCl	400	KCl	230	KCl	400
		(*) NaHCO ₃	300	(*) NaHCO ₃	350	CaCl ₂	200
		(*) Na ₂ HPO ₄	60	(*) K ₂ HPO ₄ 3H ₂ O	230	MgSO ₄ 7H ₂ O	200
		(*) NaH ₂ PO ₄ H ₂ O	250	MgCl ₂ 6H ₂ O	300	(*) Na ₂ HPO ₄	124
		MgCl ₂	190	CaCl ₂ 2H ₂ O	360	D-Glucose	1000
		CaCl ₂ 2H ₂ O	190	Na ₂ SO ₄	70	Fe(NO ₃) ₃ H ₂ O	0.1
		MgSO ₄ 7H ₂ O	60	HCl (1M)	≈40 mL	Na-Pyruvate	110
		Glucose	1000	(*) Tris	6044.7	Phenol red	15
						(*) NaHCO ₃	3700
						L-Arginine HCl	84
						L-Cysteine	48
						L-Glutamine	580
						L-Histidine HCl	42
						L-Isoleucine	106
						L-Leucine	106
						L-Lysine HCl	146
						L-Methionine	30
						L-Phenylalanine	66
						L-Threonine	95
						L-Tryptophan	16
						L-Tyrosine	72
						L-Valine	94
						Glycine	30
						L-Serine	42
						Cholinchloride	4
						Folic acid	4
						Myo-Inositol	7.2
						Nicotinamide	4
						Da-Ca-	4
						Pantothenate	4
						Pyridoxal HCl	4
						Riboflavin	0.4
						Thiamine-HCl	4

Table 2. Testing solutions compositions. (*) participating in the pH buffer mechanism.

The crystalline structure was investigated with a diffractometer (PANalytical Empyrean) with a Cu anode (Cu K α radiation, $\lambda = 0.15405$ nm) equipped with PIXCellD detector and 10°–90° as angle range. The adopted operating parameters were 40 V and 40 mA, chosen to maximize the signal-to-noise ratio.

The morphology of the samples was analysed by Scanning Electron Microscopy (SEM), by using a FEI Quanta 200 FEG SEM instrument combined with an X-ray energy dispersive system (EDX). Testing parameters were the accelerating voltage of 30 keV, in high vacuum mode.

Fourier Transform Infrared spectroscopy (FTIR) was adopted to identify organic species, by using a Spectrum One PerkinElmer instrument. IR spectra were recorded with 8 scans between 4000 and 400 cm⁻¹, at 4 cm⁻¹ resolution.

Metal ions released in the different testing solutions were estimated by using a PerkinElmer Optima 2100 DV ICP-OES. For each metal detected, a calibration line was recorded before the analysis using the respective standard solution.

The wettability properties of the samples were assessed by measuring the contact angles. Static contact angles were measured using an FTA 1000 optical tensiometer, by depositing 5 μ L droplets of deionized water. Measurements were repeated at least three times in different positions on the sample.

Information about the corrosion behavior of the samples in the simulating testing solutions was assessed with the use of electrochemical techniques, such as the measure of open circuit potential, electrochemical impedance spectra (EIS) and polarization curves.

Electrochemical Impedance spectra were recorded by imposing a sinusoidal voltage over the set constant electrode potential. The frequency of the alternated signal varies between a determined range (i.e. 10 mHz – 100 kHz). The sinusoidal voltage signal can be written as:

$$E = E_0 \sin(\omega t) \quad (1)$$

where ω is the angular frequency, obtained as the frequency expressed in Hz times 2π . Expression (1) can also be used to describe a rotating vector (*phasor*), whose length corresponds to the amplitude E , and ω is the rotating frequency [76]. By imposing the described voltage signal, the recorded output will be another phasor, related to the current response, typically not in phase with potential. The current phasor can be expressed as follows:

$$I = I_0 \sin(\omega t + \phi) \quad (2)$$

Where ϕ represents the phase angle. Impedance Z is then defined as a generalized form of resistance, expressed by:

$$Z = \frac{E}{I} \quad (3)$$

Impedance can also be separated into real and imaginary components and written in its rectangular representation:

$$Z = Z_{Re} + jZ_{Im} \quad (4)$$

When voltage and current signals are in phase, the imaginary part of the impedance is zero, so the total impedance will be purely real ($Z = Z_{Re}$). Conversely, if the input and output signal are out of phase, the real part vanishes and the impedance is entirely imaginary ($Z = jZ_{Im}$). The relation between impedance and phase angle ϕ is better illustrated by writing it in its exponential representation:

$$Z = |Z|\exp(j\phi) \quad (5)$$

where $|Z|$ is the modulus of the impedance vector and ϕ is the phase angle. The frequency dependence of impedance can be visualized in different ways. In a Bode plot, $\log|Z|$ and ϕ are plotted against $\log(\omega)$, whereas the representation when the imaginary part Z_{Im} is plotted versus the real part Z_{Re} is known as the Nyquist plot [76]. A key challenge in interpreting EIS data lies in identifying an appropriate equivalent circuit capable of reproducing the impedance behavior, and in assigning physical meaning to the passive elements included in the model [77–79]. The fundamental passive components of electrical circuits are resistors, capacitors, and inductors. The impedance of a resistor is purely real and equal to its resistance value; under an applied potential, the current through it is in phase with the voltage. Capacitors introduce capacitance into a circuit and store electrical energy in the form of an electric field. Their impedance is entirely imaginary and increases as either capacitance or signal frequency decreases, while the current has 90° delay with respect to the voltage. Inductors, on the other hand, store energy in a magnetic field and have impedance that rises with frequency; in this case, the current is 90° earlier than the voltage. If the active surface of the electrode is not uniform, a 2D distribution of time-constant can be observed: this can be caused by reactivity or current/potential variations along the surface of the electrode. When the time-constant dispersion is caused by the distributing of a local property of the electrode, it can result in a 3D distribution. These variations can be modelled with a specific circuit element known as constant phase element (CPE), that can be expressed as:

$$Z_{CPE} = \frac{1}{(j\omega)^{\alpha}Q} \quad (6)$$

with ω the frequency of the signal. The CPE assumes units of a capacitance when α equals one, and it represents the capacity of the interface. For values of $\alpha < 1$, the CPE has units of $s^{\alpha}\Omega^{-1}cm^{-2}$, the modelled behavior is that of a heterogeneous surface or the presence of continuously distributed time constant due to charge-transfer reactions (see figure 12). Notably, both α and Q are not dependent on the frequency ω . Values of $\alpha < 1$ are usually related to variation in passive film resistivity in the region between the metal and the electrolyte [80–82].

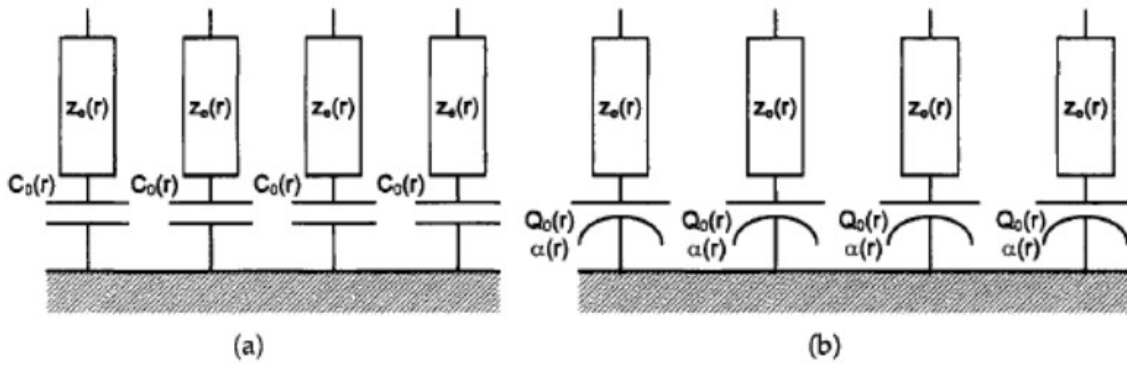


Figure 12. Time constant distribution for a blocking electrode in 2D and combined 2D and 3D distribution [76].

Polarization curves are an exceptional tool for those who study corrosion processes and electrochemistry in general. They provide information about the kinetics of electrode reactions occurring on a metal's surface immersed in an electrolyte. Polarization curves are recorded under a controlled variation of imposed potential (potentiodynamic polarization - PDP) or current at the electrode, and measuring the corresponding output. Results are usually visualized by plotting the potential against the current density logarithm: such representation allows to obtain the characteristics of anodic and cathodic reactions (Evans diagram), thus the system operating conditions. Evans diagram shows the relationship between the metal electrode potential and the current density through the electrolyte-metal interface [53]. While Evans diagram represents the reaction rates, polarization curves show applied current density i_{app} , that is the difference between total anodic and cathodic current densities at a given potential:

$$i_{app} = i_a - |i_c| \quad (7)$$

where the cathodic current density i_c is assumed negative. The corrosion potential E_{corr} is when cathodic and anodic rates are the same, which corresponds to an applied current density of zero. An example of an active corrosion behavior exhibited by a metal can be studied considering a system with iron immersed in an acidic solution. Here, the surface reactions are the anodic dissolution of iron and the reduction of water, thus the hydrogen evolution (see Fig. 13).

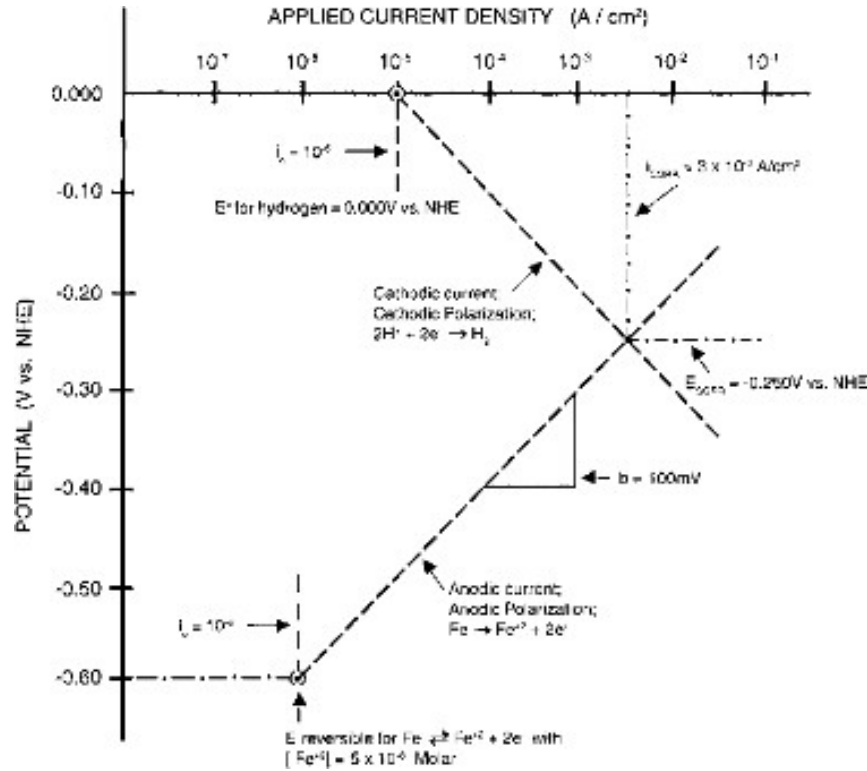


Figure 13. Evans diagram for Fe in acidic solution. Image taken from ref [83].

The anodic branch of the polarization curve is generated when an anodic current density is imposed on the system by an external source (e.g. a potentiostat). An increase in applied anodic current decreases the reduction reaction rate, because of the positive polarization of the surface. When the cathodic reaction is negligible with respect to the anodic current density, the applied current density can be considered equal to the anodic one. Similar consideration can also be done for determining the cathodic current density: measurements carried out using these assumptions allow the determination of the Tafel slope.

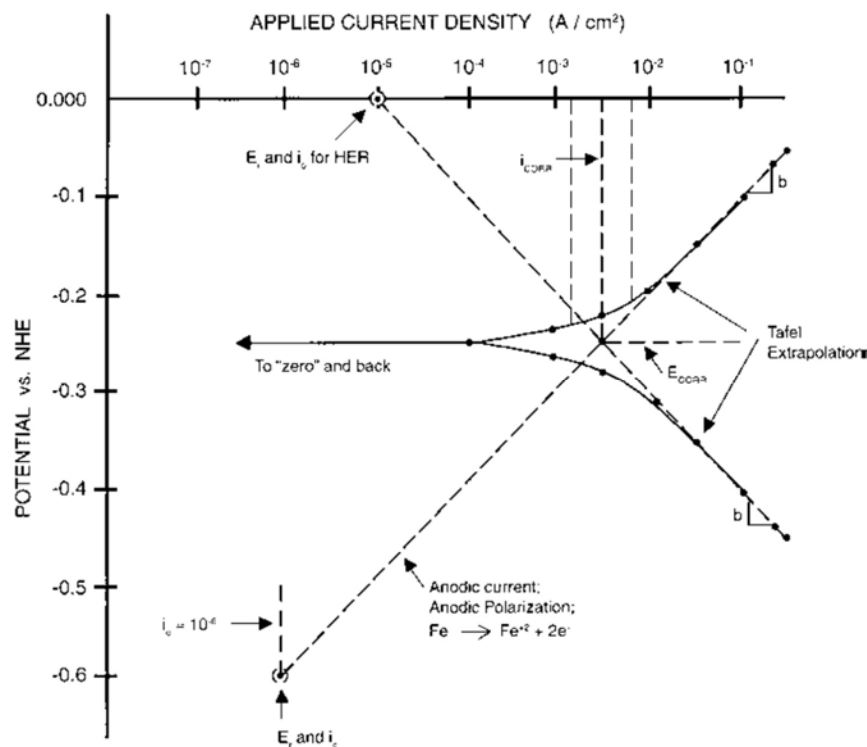


Figure 14. Polarization curve that would result for Evans diagram, see **Figure** . Image taken from ref [83].

When potential is far enough from E_{corr} , the applied current density reflects the kinetics of only the anodic or cathodic reaction, in these regions (see Figure 14) the linear portion of the polarization curve can be extrapolated, leading to an intersection in (i_{corr}, E_{corr}) [83].

Electrochemical measurements were carried out on at least 3 identical samples, by using a Parstat 2273 potentiostat and an electrochemical cell with a three-electrode configuration. An Ag/AgCl/sat. KCl reference electrode and a platinum mesh as the counter. Open circuit potential (OCP) was measured over time, electrochemical impedance spectroscopy (EIS) was adopted, EIS was measured at the OCP, varying the potential in the range ± 10 mV; and investigating frequencies between 10 mHz and 100 kHz. For each sample, polarization curves were obtained with a single scan, using a 5 mV/s scan rate and a potential sweep between -0.15 V vs OCP and -0.50 V vs SSC. The scan rate was selected in this study to minimize excessive surface alteration and hydrogen evolution during testing of highly reactive magnesium alloys. Slower scan rates may lead to significant surface modification and accumulation of corrosion products, which could mask the intrinsic electrochemical behavior of the material.

Hydrogen evolution rate evaluation was carried out by immersing samples individually in closed bottles, with a stopper in bromobutyl rubber (DURAN®) for effective sealing and reliable self-sealing after needle piercing. Gas samples were collected with a 500 μL Hamilton gastight syringe. The bottles were kept at the physiological temperature of 37 $^{\circ}\text{C}$. For each experiment, the ratio between electrolyte volume and immersed area was 25 ml/cm^2 , the solutions were changed every 3.5 days and gas samples were collected periodically. Sampling frequency was adjusted depending on the observed hydrogen evolution rate: measurements were initially performed more frequently (6-12 times per day) to detect possible rapid changes, and subsequently stabilized to approximately two measurements per day when the evolution rate became steady. All collected gas samples were analyzed using an HP 6890 Series gas chromatograph to quantify hydrogen concentration.

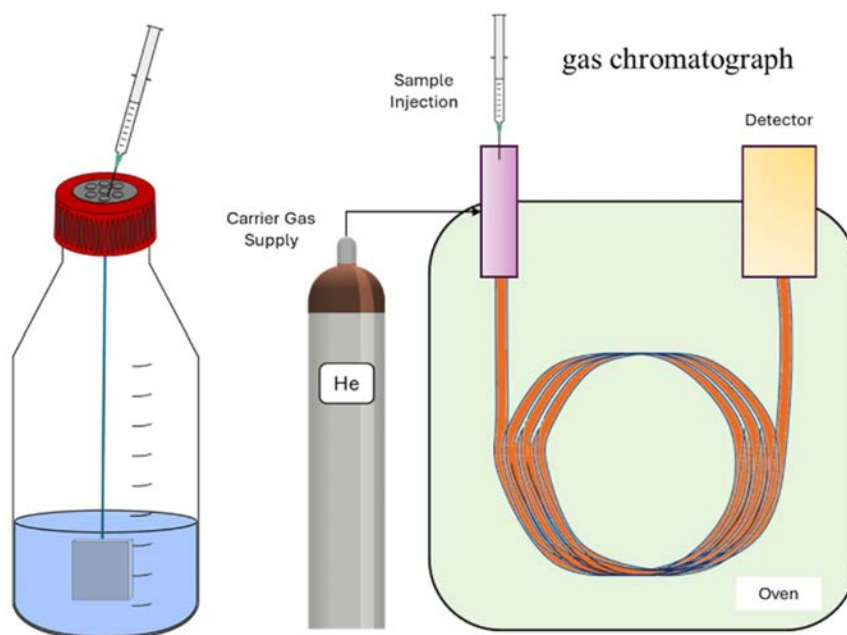


Figure 15. Setup used for the direct estimation of hydrogen evolution rate.

Before the immersion of the metallic sample in the respective bottle, and during the electrolyte change after 3.5 days of immersion, pH measurements were carried out using a (HANNA Instrument HI2020) pH-meter.

A gravimetric analysis was also conducted. The mass of the samples was measured with a (Kern analytical balance ACS 120-4) scale before the immersion and after the removal of corrosion product (see detailed procedure in Chapter 3).

For the cytotoxicity tests, samples were sterilized by incubation in 70% ethanol for 24 hours, followed by a UV treatment for 2 hours (1 hour per side) in a laminar flow hood. They were then placed into a petri dish and treated with complete medium, composed of DMEM high glucose (Sigma-Aldrich), 10% Fetal Bovine Serum (FBS), 100 µg/ml Penicillin/Streptomycin (Sigma-Aldrich), and 2 mM L-glutamine, with a surface/volume ratio of 3 cm² ml⁻¹. After 24 hours of incubation, the medium was used to treat cells. Specifically, 7·10³ MC3T3 pre-osteoblastic cells were cultured in a 96-well plate with 150 µl of complete medium. After 24 hours, the medium was replaced with the conditioned medium derived from the samples or with the normal medium (as a positive control named CTRL). After 24- and 48-hours cell viability was assessed using Alamar Blue cell viability reagent (Thermo-Scientific), which is based on resazurin. Essentially, live cells metabolize resazurin into resorufin, which displays intrinsic fluorescence. The medium was replaced with 100 µl of the reagent diluted 1:10 with a complete medium. Cells were incubated for 2 hours at 37°C in a humidified incubator with 5% CO₂. Fluorescence intensity, directly correlated with cell viability, was measured using a plate reader (BioTek Sinergy HT) at an emission wavelength of 530/25 nm and an emission peak at 590/35 nm. A schematic representation of the experimental setup is shown in Figure 16.

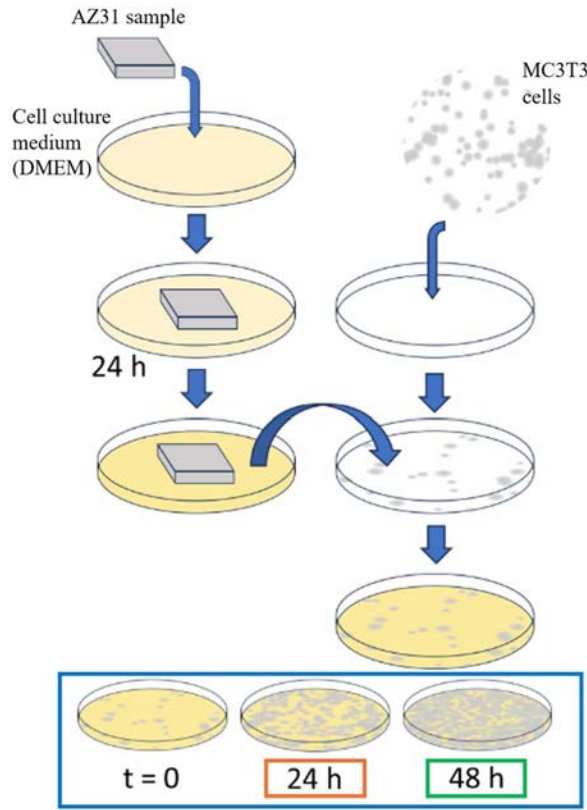


Figure 16. Viability assay: experimental setup.

3 Magnesium Alloy Biodegradation: Influence of Electrolyte Composition

Metallic biomaterials are extensively used as temporary or permanent implants in orthopedic and cardiovascular applications, such as bone plates, screws, and vascular stents [84–88]. However, permanent metallic implants can lead to long-term complications, including chronic inflammation, thrombosis, restenosis, and the need for additional surgery to remove the implant once healing is complete [89–91]. In contrast, biodegradable metals, particularly magnesium and its alloys, have emerged as promising candidates for next-generation bioresorbable implants due to their favorable mechanical properties (e.g., low density, elastic modulus close to that of bone) and their ability to gradually corrode in the physiological environment, eliminating the need for implant removal [92–97].

Despite their potential, the clinical translation of magnesium-based implants remains limited, primarily due to their rapid and uncontrolled corrosion in chloride-rich environments like simulated body fluids (SBFs) [98–101]. The high degradation rate can compromise the mechanical integrity of the implant before tissue healing is completed. Moreover, the hydrogen gas evolution accompanying the corrosion process can result in gas pocket formation and localized alkalization, both of which may be detrimental to surrounding tissues [102–105].

Accurate estimation of the corrosion or dissolution rate of Mg alloys is therefore crucial for the design and safe application of biodegradable implants. Traditional electrochemical methods such as Tafel extrapolation are often used to evaluate corrosion kinetics. However, in the case of magnesium, these methods tend to underestimate the actual degradation rate due to the so-called negative difference effect (NDE), wherein the hydrogen evolution rate increases with anodic polarization—a behavior not captured by Tafel analysis [106–111].

In addition, an often overlooked but critical factor is the composition of the electrolyte used to simulate the physiological environment. Various simulated body fluids (such as Dulbecco's Modified Eagle Medium [DMEM], Hank's Balanced Salt Solution [HBSS], saline solution or Kokubo solution) differ significantly in ion concentrations, buffering capacity, and organic content, all of which can strongly influence the degradation mechanisms and rates of Mg alloys [112,113]. Consequently, data obtained in one simulated fluid may not be directly transferrable to another, emphasizing the necessity

for experimental validation in multiple relevant media. To address these challenges, gas collection methods, particularly hydrogen evolution rate measurements using gas chromatography (GC), provide a more direct and reliable estimate of the degradation behavior of Mg alloys in vitro. A systematic experimental investigation of Mg alloy degradation in various simulated body fluids was performed, including commonly used solutions such as Saline solution, Dulbecco's Modified Eagle Medium, Hank's Balanced Salt Solution, and Kokubo solution. Hydrogen evolution rates were measured using gas chromatography, providing accurate, quantitative data on the dissolution kinetics of Mg in each medium. This approach aims to overcome the limitations of electrochemical methods such as Tafel extrapolation.

3.1.1 Additional Experimental Details

Squared samples of AZ31 Mg alloy were obtained from a 1 mm thick sheet. The surface of the samples was prepared as explained in Chapter 2.

Corrosion products were removed from the surface of the samples after the H₂ evolution test, in accordance with ASTM G1-03 [114]. Samples were first rinsed in DI water, then they were immersed in an aqueous solution of 200 g L⁻¹ chromium (VI) oxide (Sigma Aldrich, ≥98.0%) and 2 g L⁻¹ silver nitrate (VWR Chemicals, ACS analytical reagent) for 5 minutes, then cleaned in an ultrasonic bath for 5 minutes in DI water and finally rinsed in ethanol and left to dry at room temperature.

Each sample was analyzed by means of scanning electron microscopy, using a FEI Quanta 200 FEG SEM instrument, with an EDX probe. SEM micrographs were acquired before and after the removal of corrosion products from the surface of the samples.

3.1.2 Results and Discussion

3.1.2.1 Testing solutions composition

The corrosion rate of AZ31 samples was estimated using various physiological solutions, since the solution selection significantly affects corrosion experiment results [115]. Saline solution, Kokubo solution, Hank's Balanced Salt Solution (HBSS), and Dulbecco's Modified Eagle Medium (DMEM) were employed. Saline solution (the simplest physiological medium) contains only 9 g L⁻¹ of NaCl and lacks buffering agents to stabilize local pH. Both Kokubo solution and HBSS contain calcium ions, carbonates, phosphates, and sulphates. Kokubo solution utilizes Tris/HCl as a buffering agent, though it has been shown to be ineffective at stabilizing local pH [116]. In contrast, HBSS contains

a high amount of phosphate ions, which are capable of stabilizing local pH. Finally, DMEM is a highly complex cell culture medium, which, in addition to inorganic ions, also contains amino acids, vitamins, glucose, and other essential nutrients for cell growth.

3.1.2.2 Morphology

The morphology of samples surface after 7 days immersion in the different testing solutions has been analyzed by SEM. Figure 17 shows the micrographs of AZ31 samples immersed for 168 hours in the four testing solutions. For samples immersed in HBSS a characteristic “mud” structure is visible, consisting of a cracked layer of corrosion products [112,117]. Also, it can be seen that the degradation of the surface was mainly due to a general form of corrosion, and its products covered the sample with uniformly distributed particles agglomerate. EDX analysis (Table 3) shows that the corrosion product layer is mainly constituted by Ca, P and C.

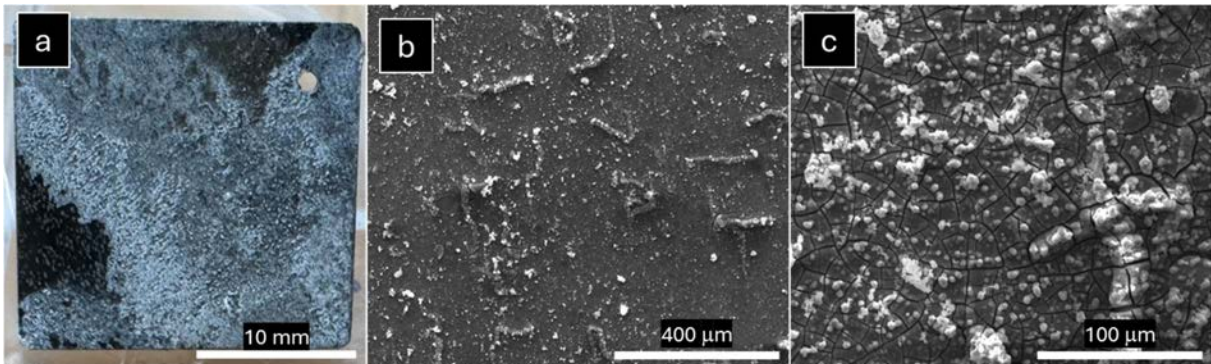


Figure 17. Picture (a) and SEM micrographs (b, c) of AZ31 samples after 7-days immersion in HBSS.

	HBSS	DMEM	Kokubo	NaCl 0.9%
At. %	<i>t = 168 h</i>			
C	16.9	18.34	17.01	-
O	37.68	35.29	50.47	63.08
Zn	0.29	0.4	0.51	0.17
Mg	28.17	36.87	10.8	35.87
Al	0.62	3.23	3.17	0.15
Na	0.64	0.49	1.31	0.36
Cl	-	-	-	0.38
P	9.02	3.99	10.22	-
Ca	6.67	1.40	6.51	-

Table 3. EDX analysis of AZ31 samples after 168 hours of immersion in the four testing solutions.

SEM micrograph of sample immersed in DMEM also shows mud structure, with uniform degradation and corrosion product distribution. Notably, particle agglomeration was almost absent on these samples (Figure 18).

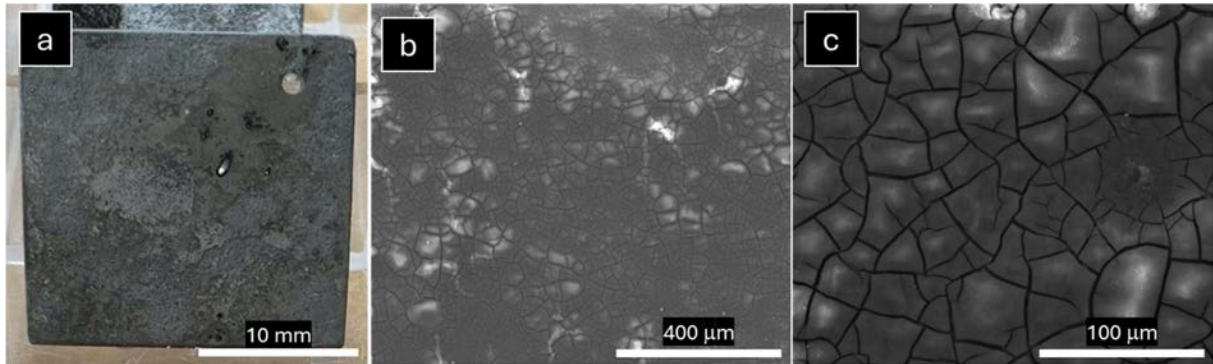


Figure 18. Picture (a) and SEM micrographs (b, c) of AZ31 samples after 7-days immersion in DMEM.

SEM micrographs of samples immersed in Kokubo solution for 7 days reveal the presence of both a mud-like structure and a limited number of particle agglomerates. In addition, a significantly higher degree of degradation is observed. In particular, micrograph 19b shows a pronounced loss of material, characterized by valley-like features, which are also partially visible on the surface in Figure 19a. These morphological features are not observed in samples immersed in Hanks' or DMEM solutions.

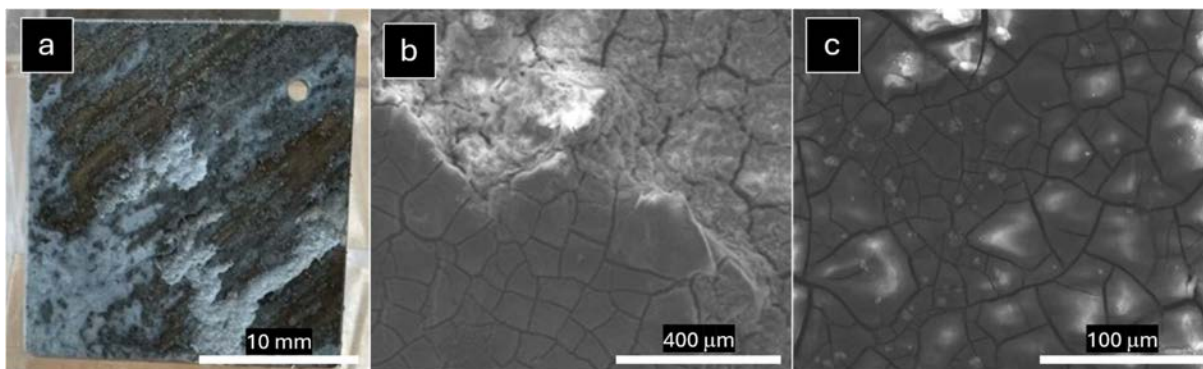


Figure 19. Picture (a) and SEM micrographs (b, c) of AZ31 samples after 7-days immersion in Kokubo solution.

Conversely, samples immersed in 0.9% NaCl solution do not exhibit such valley-like structures; instead, an extensive presence of corrosion products is observed, with no evident mud-like morphology (Figure 20).

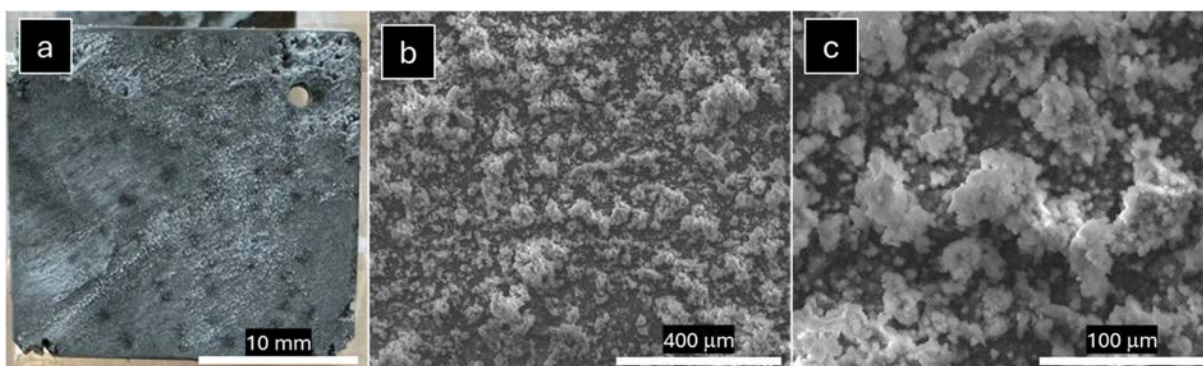


Figure 20. Picture (a) and SEM micrographs (b, c) of AZ31 samples after 7-days immersion in NaCl 0.9%.

FT-IR spectra for samples after 7-days immersion at 37°C in physiological solutions are shown in Figure 21. The spectra reveal strong bands at 1020 cm^{-1} and at 570 cm^{-1} corresponding to PO_4^{3-} stretching and bending modes, respectively, indicating the precipitations of phosphate layers. The latter is further confirmed by the presence of a band at 1630 cm^{-1} that according to the literature can be associated with the presence of water in phosphates [118]. For AZ31 immersed in DMEM the asymmetric stretching vibrations of CO_3^{2-} at 1485 cm^{-1} and 1426 cm^{-1} are evident [119], suggesting the precipitation of carbonate in agreement with the high concentration of NaHCO_3 in this solution

(see table 2). Smaller bands at the same wavelengths are also present for HBSS and Kokubo, i.e. in the physiological media containing a lower concentration NaHCO_3 .

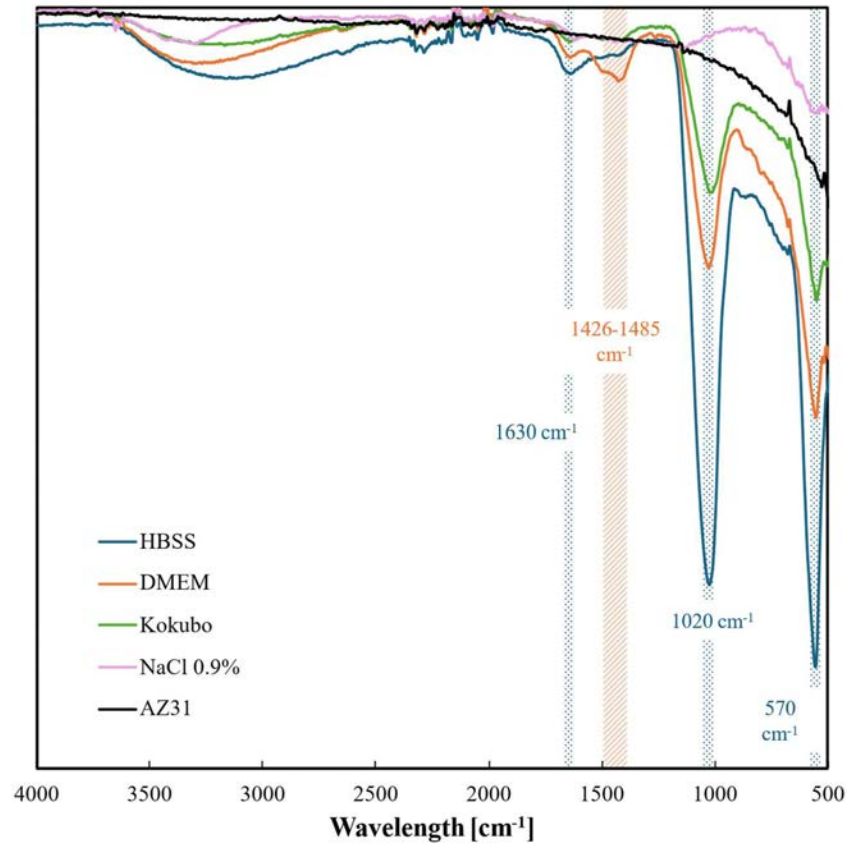


Figure 21. FT-IR analysis on AZ31 samples, before and after 168 hours of immersion.

3.1.2.3 Electrochemical characterization

In order to assess corrosion behavior of tested samples in the different simulating solutions, electrochemical testing techniques were adopted. The electrochemical measurements for samples that had been immersed for 7 days were conducted immediately after removing the samples and placing them in a new solution with the same composition as the immersion test solution. Open circuit potential was recorded over time for AZ31 samples in the respective solution, the values reported in table 4 were reached after a 1h stabilization time.

<i>OCP [V vs SSC]</i>	HBSS	DMEM	Kokubo	NaCl 0.9%
t = 1h	-1.52	-1.69	-1.63	-1.54
t = 7 days	-1.52	-1.62	-1.51	-1.50

Table 4. Recorded open circuit potential of AZ31 samples.

Samples immersed in HBSS showed the highest OCP, with no changes after the immersion period.

The impedance spectra displayed in Figure 22, presented in the Nyquist format, exhibit at least two distinct time constants along with an inductive loop. Interpreting such complex spectra requires kinetic models that describe reactions involving the formation of adsorbed intermediates followed by its subsequent oxidation, as extensively detailed in reference [76]. These kinetic models are preferable to electrical circuit analogues because they can reliably account for the metal's varying behavior depending on the electrolyte composition. In the case of magnesium alloys, the interpretation of EIS spectra becomes even more challenging since the formation of adsorbed intermediates has been reported for both the anodic half-cell reaction (magnesium oxidation, [120]) and the cathodic half-cell reaction (hydrogen evolution, [111]). Due to the complexity of the EIS spectra, fitting them with equivalent electrical circuits would require numerous circuit elements, which could render the analysis somewhat trivial. Therefore, the present study limits the analysis to a qualitative level.

The presence of phosphates led to the formation of a conversion coating that protects the surface, as it can be seen with the increasing overall impedance after 7 days immersion (~ 6 to $\sim 20 \text{ k}\Omega \text{ cm}^2$). OCPs in DMEM were the lowest, with no significant changes over the 7 days. Nyquist plots for samples immersed in DMEM are reported in figure 22b. Here it can be seen that no substantial variation occurred after 7 days, being the overall impedance around $2 \text{ k}\Omega \text{ cm}^2$, with a non-entirely formed inductive loop at low frequencies. Samples immersed in Kokubo solution showed the highest variation in recorded OCPs (+120 mV) and the lowest corrosion resistance (i.e. overall impedance) among the different solutions (figure 22c). A second time constant appeared in the Nyquist representation of the EIS spectra, both before and after the 7-days immersion, with an increase of one order of magnitude of the overall impedance (120 to $1000 \text{ }\Omega \text{ cm}^2$), and with the clear presence of the inductive loop at the low frequencies in these plots. Sample tested at $t = 1\text{h}$ in NaCl 0.9% solution showed the clearest inductive loop at low frequencies as well as a capacitive loop, with an overall impedance of less than $350 \text{ }\Omega \text{ cm}^2$ (figure 22d) and an OCP of -1.54 V. After 7 days of immersion, the inductive loop nearly disappeared, accompanied by an increase in overall impedance to approximately $2500 \text{ }\Omega \cdot \text{cm}^2$ and a recorded OCP of -1.50 V.

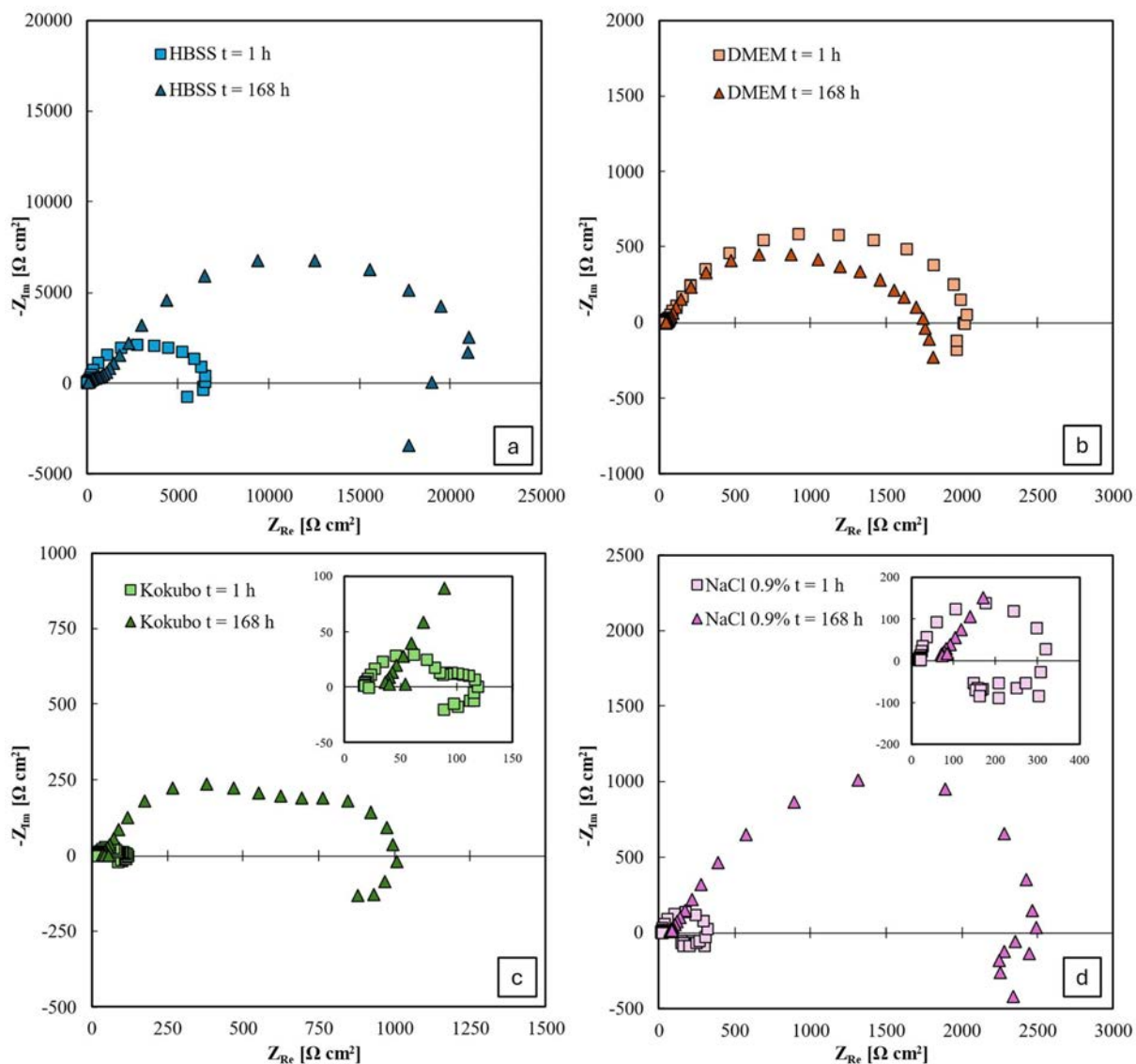


Figure 22. Nyquist representation of EIS of AZ31 samples in testing solutions before and after 168 hours of immersion in: a) HBSS, b) DMEM, c) Kokubo, d) NaCl 0.9%.

Polarization curves recorded in HBSS (Figure 23) after 7 days of immersion indicate a reduction in current density in the anodic branches, which can be attributed to the formation of a thick phosphate conversion coating. This is accompanied by a shift in corrosion potential by almost 100 mV, along with an increase in pitting potential. In contrast, curves recorded in DMEM solution (Figure 23b) show minimal changes in current densities across both the anodic and cathodic branches after 168 hours. However, there is an increase of approximately 100 mV in both corrosion and pitting potentials following the 7-day immersion. Polarization curves obtained in Kokubo solution (Figure 23c) reveal the most significant variation, with the current density in the anodic branch changing by more than an order of magnitude. This is coupled with an almost 100 mV increase in both corrosion and pitting

potentials. Lastly, polarization curves for samples immersed in 0.9% NaCl solution (Figure 23d) show a decrease in corrosion potential of approximately 100 mV, along with an increase in pitting potential in the anodic region.

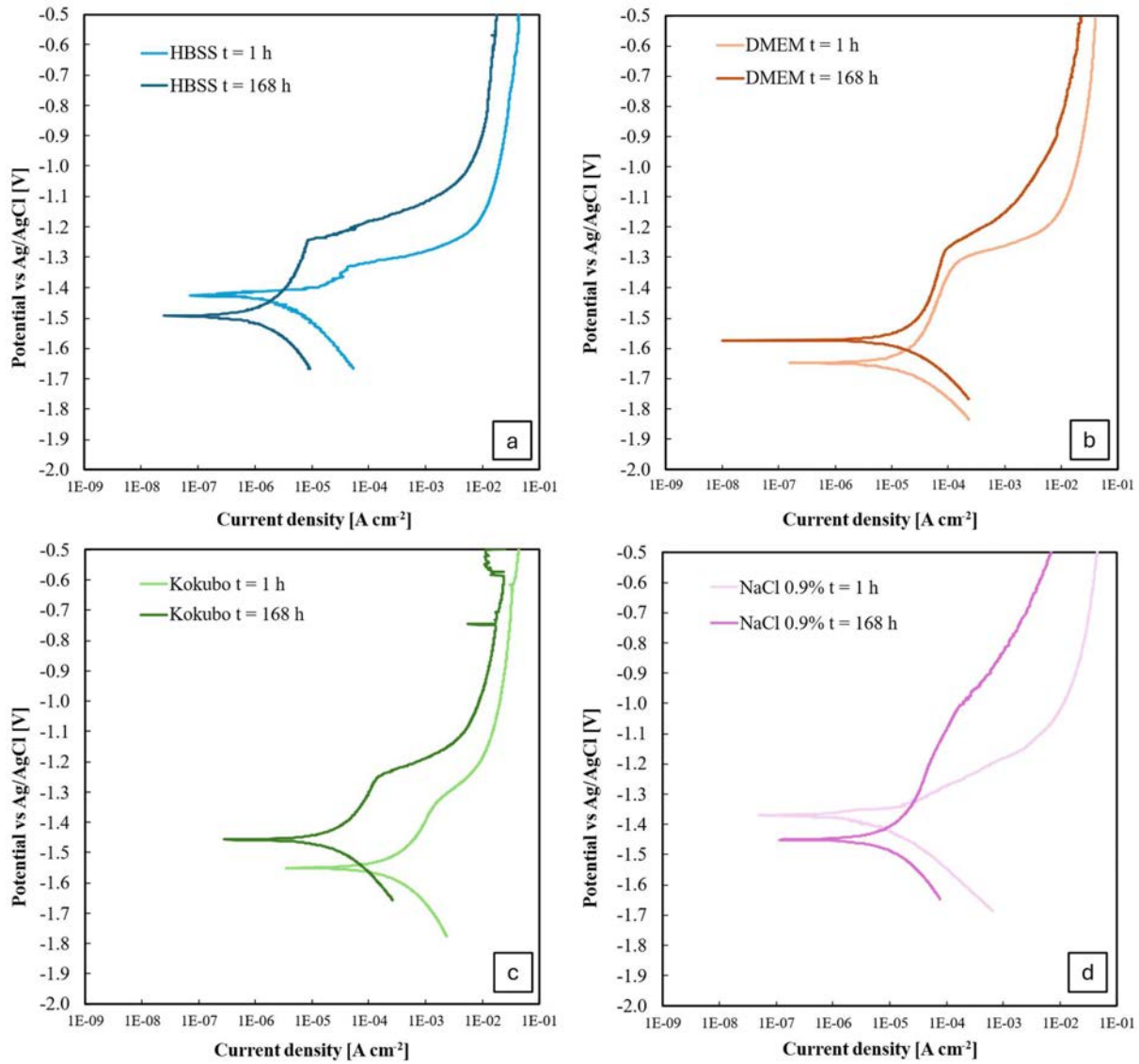


Figure 23. Polarization curves of AZ31 samples in testing solutions before and after 168 hours of immersion: a) HBSS, b) DMEM, c) Kokubo, d) NaCl 0.9%.

3.1.2.4 Corrosion products removal

After the removal of corrosion products from the surface of samples immersed in the different solutions, EDX analysis was carried out in order to verify the effectiveness of the procedure. EDX results are reported in table 5, where no other elements were present other than oxygen and the alloy

constituents. These results can also be confirmed by SEM micrographs of the samples (figure 24-27). A comparison with table 3 and figure 17-20 shows that corrosion product (mainly phosphate and carbonate), were effectively removed from the surfaces.

At. %	HBSS	DMEM	Kokubo	NaCl 0.9%
O	2.93	3.57	2.83	3.91
Mg	94.77	94.45	94.63	93.21
Al	1.90	1.63	2.27	2.46
Zn	0.39	0.36	0.27	0.42

Table 5. EDX analysis of AZ31 samples after the removal of corrosion products.

SEM micrographs of samples in HBSS solution after corrosion products removal (figure 24) confirmed the effects of a mostly generalized corrosion attack on the surface, along with the presence of a few pits. Such behavior is probably due to the formation of a protective layer (the thick mud structure seen in figure 17), that prevents a more aggressive form of corrosion.

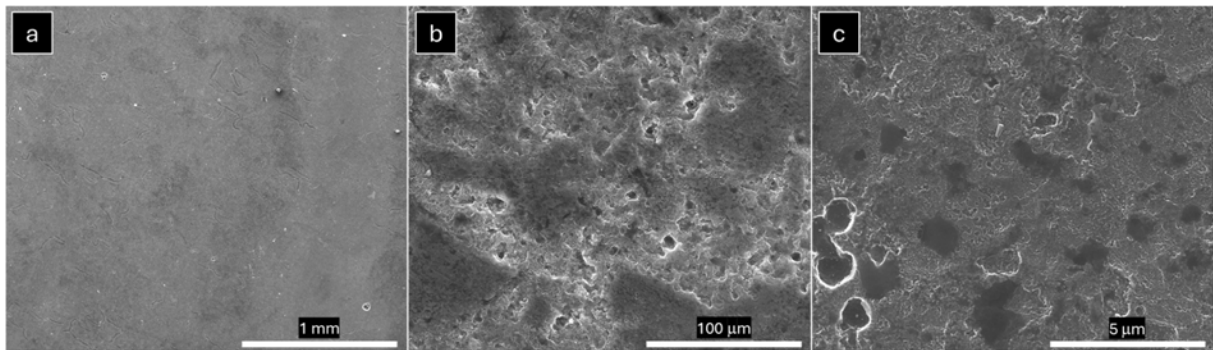


Figure 24. SEM micrograph of AZ31 after immersion in HBSS and removal of corrosion products.

Immersion in DMEM led to a more pronounced degradation of the samples with respect to HBSS's, as it can be seen in figure 25, with the formation of a rough but still homogeneous surface.

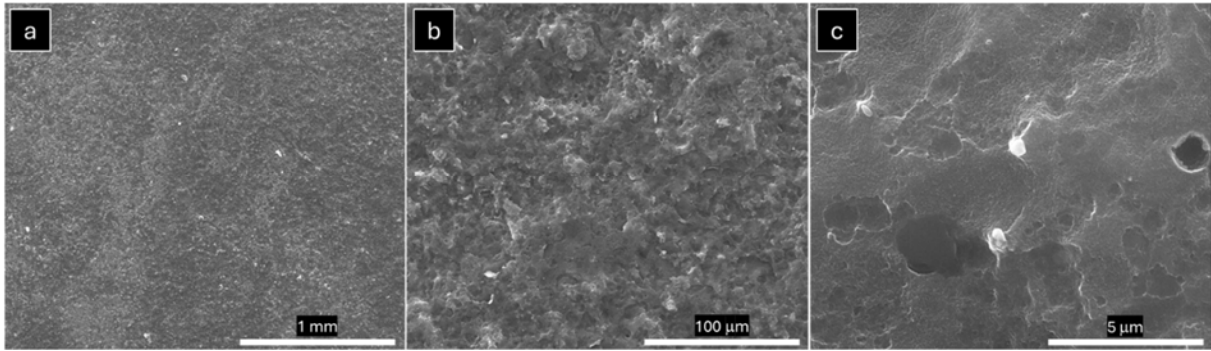


Figure 25. SEM micrograph of AZ31 after immersion in DMEM and removal of corrosion products.

Micrographs in figure 26 show the widely degraded surface of a sample immersed in Kokubo solution for 7 days after corrosion product removal. On the surface it can be seen a large number of pits, which grew larger and merged together forming deep cavities. This phenomenon was significantly more pronounced compared to what was observed in the other testing solutions.

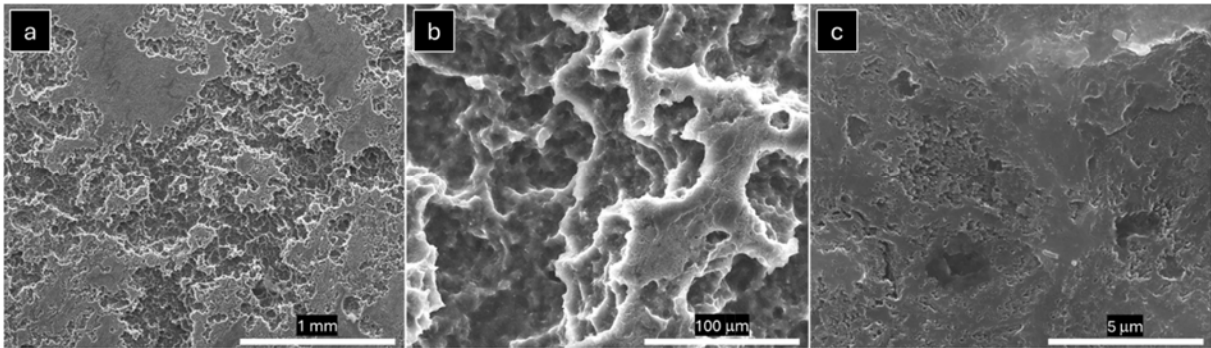


Figure 26. SEM micrograph of AZ31 after immersion in Kokubo solution and removal of corrosion products.

In figure 27 the surface of a sample immersed in NaCl 0.9% is shown after corrosion product removal. It can be seen that also here many pits are present, but they appear smaller than what observed in the Kokubo solution. Such pits formation and distribution led to a slightly more regular surface than with Kokubo's, even with the presence of numerous deep cavities.

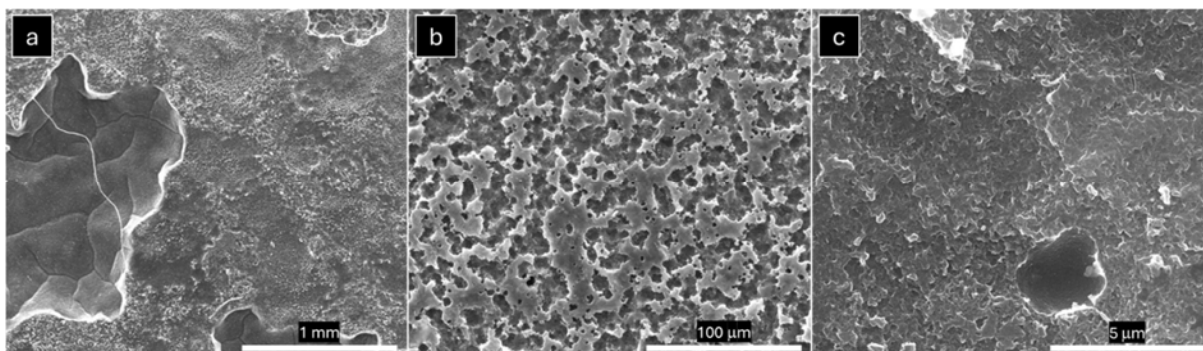


Figure 27. SEM micrograph of AZ31 after immersion in NaCl 0.9% and removal of corrosion products.

The removal of corrosion products allowed us to identify a localized form of corrosion in Kokubo and NaCl solutions.

3.1.2.5 *Hydrogen evolution estimation*

Hydrogen evolution is the primary cathodic reaction occurring during Mg alloys corrosion, thus obtaining a precise evaluation of its entity is of great importance in assessing corrosion behavior. The corrosion rates were calculated as the slope of the interpolating straight line obtained plotting the hydrogen evolution (ml cm^{-2}) measured in the gas samples collected at different times (expressed in days) (see figure 28).

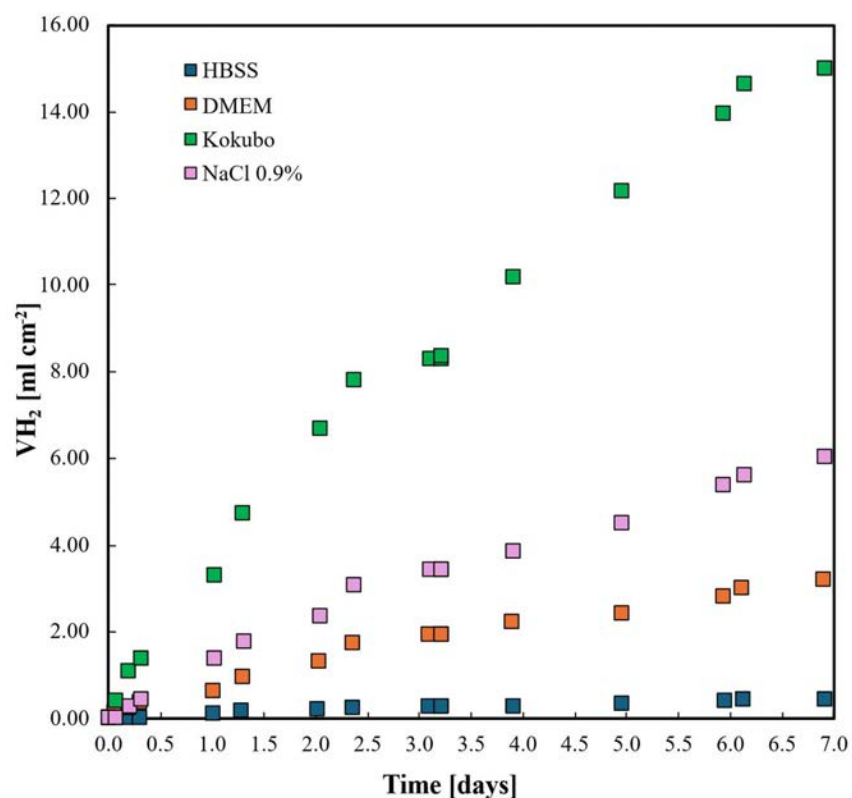


Figure 28. Evolved hydrogen collected with GC during 7-day immersion period.

In figure 29 the H₂ evolution rates are reported, here it can be seen that in HBSS almost no H₂ evolution is recorded in the first 6 hours, while the corrosion rate has a maximum during the first day and then starts to decrease. The hydrogen evolution data for samples in DMEM show that the highest rate is recorded in the first 6 hours, then it rapidly reduces until after 7 days when it's less than half the initial value. This trend is not observed in the measured overall impedance, since it is related to the formation of a thin conversion coating layer, thus confirming that estimating corrosion rates by electrochemical measurements only could be misleading.

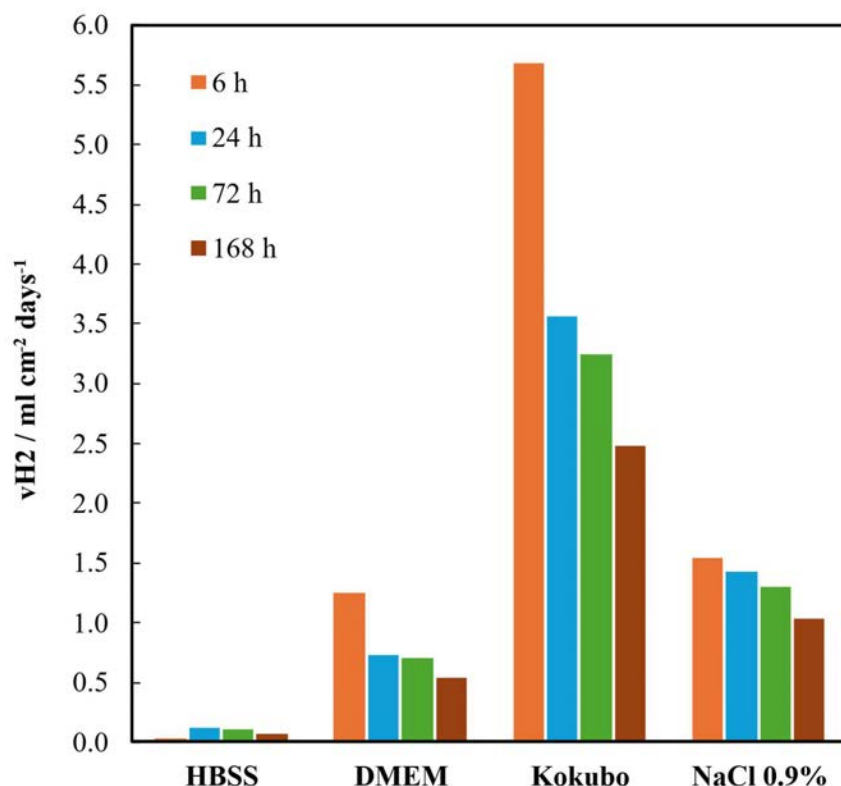


Figure 29. Hydrogen evolution rate in HBSS evaluated with GC measurements.

Electrochemical measurements showed the highest corrosion rate in Kokubo solution, which is attributed to its lower concentration of phosphate ions and reduced buffering capacity compared to DMEM and HBSS media. Such behavior is reflected also in the hydrogen rates. After an initial burst in the first six hours, where the measured HER was nearly $6 \text{ ml cm}^{-2} \text{ days}^{-1}$, the evolution rate decreases with a halving time of ~ 7 days.

In NaCl solution, the rate of H_2 evolution is higher than that observed in HBSS and DMEM, due to the complete absence of phosphates and other species capable of forming a protective layer. However, this rate is lower compared to that measured in Kokubo solution, due to the lack of buffering agents to mitigate pH increase. Consequently, the pH in NaCl solution rises rapidly, resulting in partial passivation of the sample surface (see Figure 30).

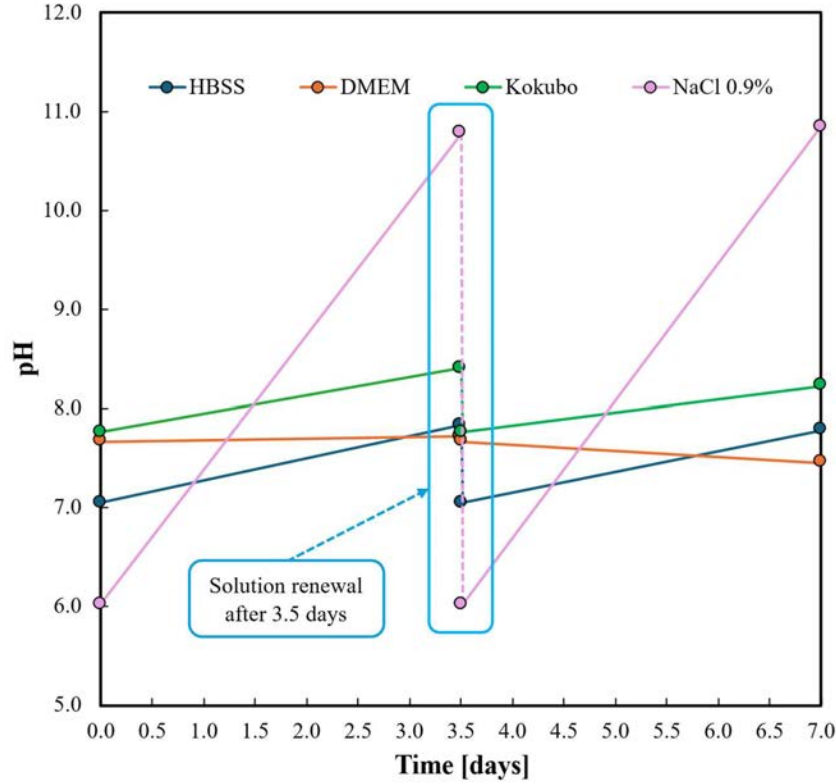


Figure 30. pH values over 7 days immersion time.

3.1.2.6 Mass loss evaluation

The hydrogen evolution rates obtained for samples in the different testing solutions were used to evaluate the corresponding expected mass loss due to Mg oxidation during the 7-day immersion period, with the hypothesis of no other concurring reactions. This is calculated by assuming that all the hydrogen detected with the gas chromatograph originates from Mg dissolution, according to the following reactions:



Magnesium mass loss is calculated by multiplying n_{Mg} ($= n_{\text{H}_2}$, the number of H_2 moles detected) and MW_{Mg} (24.305 g/mol the molecular weight of Mg), then dividing by the surface area of the immersed sample A .

In addition, the gravimetric analysis of the samples allowed us to compare the mass loss estimates with the actual mass variation after corrosion product removal. These results are reported in figure 31, where *indirect* Δm are obtained with GC and *direct* Δm are the mass losses measured with the

scale. It can be seen that mass losses estimated by GC measurements were in good agreement with those measured after corrosion products removal. Moreover, Figure 31 further confirms that the estimated corrosion rate is strongly affected by the physiological media used, since the different compositions can affect the corrosion mechanisms.

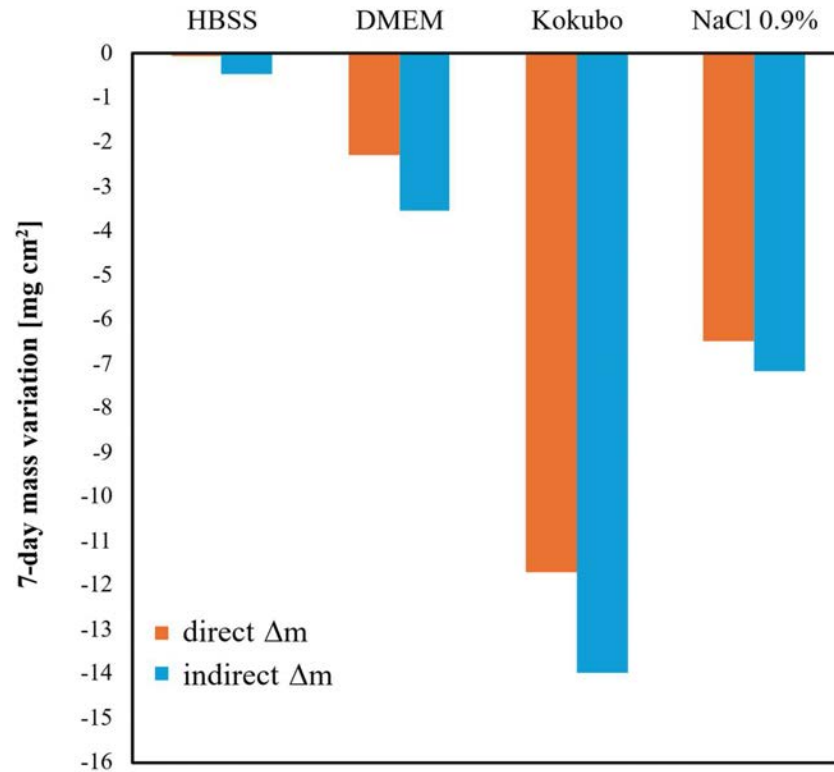


Figure 31. Mass variation of AZ31 samples after 7 days of immersion as evaluated with gravimetric analysis and with gas chromatograph measurements.

3.1.3 Conclusions

The corrosion behavior of AZ31 alloy was investigated in four different simulated body fluids by combining electrochemical testing with direct hydrogen evolution measurements (via gas chromatography) and mass loss analysis after removal of corrosion products. The findings highlight the significant impact of the physiological medium's composition on both the corrosion rate and the underlying corrosion mechanisms. In particular, the high phosphate concentration in HBSS promotes the formation of a protective conversion layer, which slows down corrosion. SEM imaging after corrosion product removal revealed generalized corrosion in HBSS and DMEM, while localized corrosion was observed in Kokubo and saline solutions.

The electrolyte-dependent degradation mechanisms discussed in this chapter highlight the intrinsic limitations of bare AZ31 when exposed to physiological media. Each solution interacts with the alloy in a specific way: HBSS promotes the precipitation of magnesium phosphates on the surface; Kokubo solution remains highly aggressive and does not form stable protective layers; and DMEM components tend to complex released Mg^{2+} ions, leading to a different dissolution behavior compared to purely inorganic media. Overall, the degradation trends observed in this chapter justify the adoption of both electrochemical and chemical surface treatments presented in Chapter 4, which are specifically designed to control the early-stage dissolution rate and tailor the biodegradation behavior of AZ31 in physiological environments.

4 Tuning Magnesium Alloy Biodegradation: Surface Modification

Compared with traditionally employed stainless steels, titanium alloys and chromium-cobalt based alloys, magnesium and its alloys show special mechanical and chemical properties. Indeed, Mg alloys have low density ($1.74 - 2.0 \text{ g cm}^{-3}$) and an elastic modulus between 41 and 45 GPa, very well matching with that of natural bone. Moreover, Mg ions released by these alloys as a consequence of corrosion as well as wear processes are not harmful to the body [121–125]. Therefore, magnesium and its alloys are promising candidate materials for biodegradable implants for orthopedic applications and vascular stents [126–129]. However, due to the very low reduction potential and to the poor corrosion resistance in chloride containing environments (as human body fluids or blood plasma), the degradation rate of magnesium and its alloys is so high that the mechanical integrity before the diseased or damaged bone tissue healed is not always maintained [130,131]. Moreover, since water reduction is the common cathodic process during corrosion of Mg and its alloys, the high corrosion rate implies a high H_2 evolution rate. An overabundant hydrogen formation may lead to detrimental gas pockets around the implant, and it may also cause alkalization in the vicinity of the corroding surface, discussed as possibly being deleterious for the surrounding biological environment [132–134].

The simplest way to slow down corrosion is to form a coating on the magnesium substrate to provide a barrier toward the contact between the substrate and the environments. There are many coating technologies which can be used to coat the magnesium substrate, such as electrochemical plating, chemical conversion coating, physical vapor deposition, laser surface treatment and anodic oxidation [135–142]. Among these technologies the latter is one of the most effective and employed processes, even if the growth of protective anodic layers on Mg and Mg alloys is difficult due to the unfavorable Pilling-Bedworth (PB) ratio [143–149]. The PB ratio is defined as the ratio of the volume of the elementary cell of a metal oxide to the volume of the elementary cell of the corresponding metal oxidized to produce the oxide, that is 0.8 for MgO. This would cause the formation of a porous and/or cracked and thus unprotective layer. Chemical conversion treatments are easy to apply and cost-effective, since they are electroless processes generally carried out in mild conditions (moderate temperature and atmospheric pressure). However, the composition of the conversion bath must be properly selected to avoid the formation of compounds detrimental for human body, thus excluding

the possibility to use surface treatments relying on chromates, which are very effective in corrosion inhibition but are toxic and carcinogenic [150–152]. Stannate conversion coatings are a good alternative to chromate coatings although they provide less corrosion resistance to Mg alloys [153–157]. On the other hand, another promising method to grow corrosion resistant coating is the electroplating, a process traditionally used for the deposition of metallic layers but that can be also used to induce the formation of functional hydrophobic coating preventing corrosion and biofouling [158–161]. However, they suffer adhesion problems with a strong impact on their durability. Another approach to protect the surface of a metallic implant is to employ chemical grafting techniques: functional hydrophobic molecules can decrease the initial burst of degradation occurring after implantation, by preventing corrosive environment from reaching the surface. UV grafting of polydimethylsiloxane (PDMS, silicon oil) can greatly delay the initial corrosion of biodegradable alloys [58].

In the process of studying and designing a protective or functionalizing coating, it is important to mention that other than the corrosion rate, also the form of corrosion plays a crucial role in determining feasibility and duration of a biodegradable implant. Particularly when the device is subjected to mechanical stresses, the occurrence of a general, instead of a localized form of corrosion can avoid the failure of the implant.

4.1 Stannate based Conversion Coating

4.1.1 Additional Experimental Details

AZ31 Mg alloy (Mg 96%, Al 3%, Zn 1%, Goodfellow) 20x20 mm coupons were cut and mechanically grinded with silicon carbide grinding papers (Buehler) up to P2500 grit, while quenching in ethanol ($C_2H_6O \geq 99.5\%$ - Emplura). Then, samples were ultrasonically cleaned in ethanol for 10 minutes and dried at room temperature.

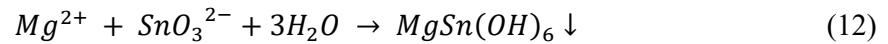
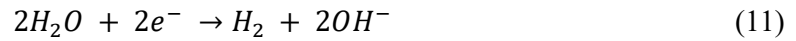
Tin based conversion coating was obtained by immersion of samples in a water-based solution containing 9.95 g/L sodium hydroxide (NaOH - Fluka), 49.87 g/L potassium stannate ($K_2SnO_2 \cdot 3H_2O$ – Thermo-Scientific), 9.95 g/L sodium acetate ($NaC_2H_3O_2 \cdot 3H_2O$ – Carlo Erba Reagents), 49.87 g/L sodium pyrophosphate tetrabasic ($Na_4P_2O_7$ - Sigma-Aldrich) [58]. During the conversion process, temperature was controlled and maintained at 82 ± 5 °C, without stirring. Different immersion time were investigated, samples subjected to 30 minutes conversion coating are named AZ31/CC30, while those subjected to 60 minutes conversion coating are named AZ31/CC60.

After immersion, converted samples were rinsed in DI water and dried at room temperature. Open circuit potential (OCP) was recorded over time during the chemical conversion process by using a three-electrode cell configuration with Ag/AgCl/sat. KCl as a reference electrode (0.197 V vs SHE), and a Pt mesh as counter electrode. Gravimetric experiments were carried out in order to measure mass gain due to the stannate based conversion coating. For each immersion time the mean value between at least 5 samples was calculated.

Electrochemical and H₂ evolution rates measurements were carried out according to the procedures described in chapter 2. The adopted testing solution was Dulbecco's Modified Eagle Medium (DMEM with stable Glutamine, with 1.0 g L⁻¹ Glucose – Genaxxon bioscience), maintained at 37 °C in order to mimic physiological environment (composition reported in Table 2).

4.1.2 Results and Discussion

AZ31 coupons were immersed in the conversion bath (T = 82°C) to induce the growth of hydroxystannate layer on their surface, according to the following reactions:



Indeed, due to its very low equilibrium reduction potential, magnesium is oxidized by water with simultaneous release of Mg²⁺ and OH⁻ ions and consequent MgSn(OH)₆ precipitation. The conversion process was followed as a function of time with a specific focus on open circuit potential and mass gain (see Figure 32).

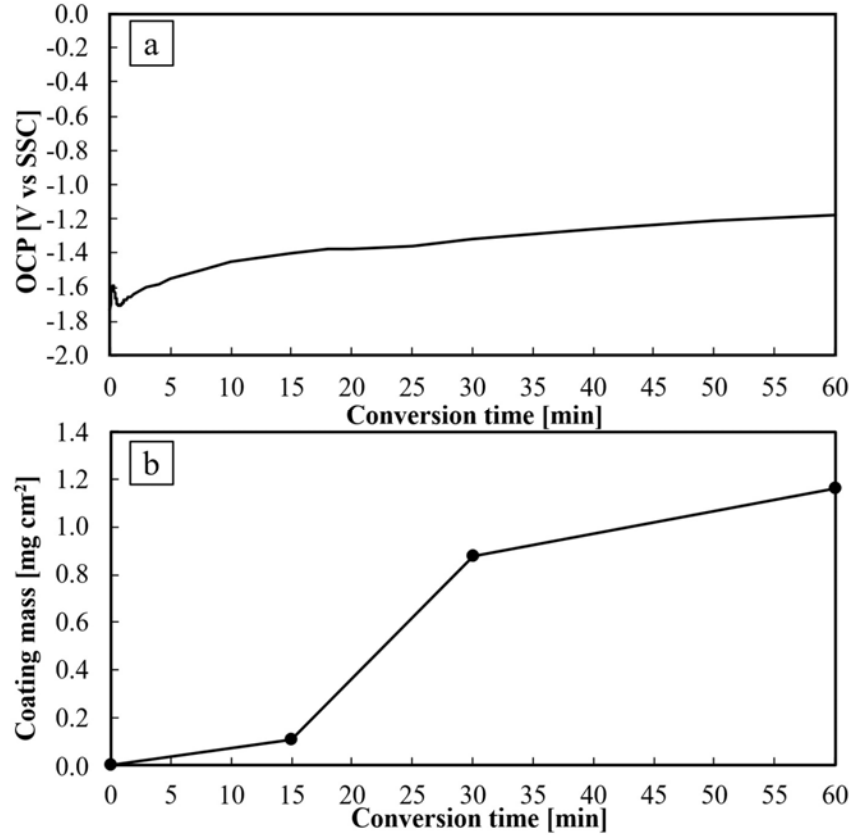


Figure 32. a) Open circuit potential recorded during chemical conversion; b) Conversion coating mass gain at different immersion time.

OCP raises during conversion in agreement with the formation of a protective coating and reduction of bare magnesium alloy surface exposed to the conversion bath and, simultaneously, the total mass increases due to the formation of the coating.

Figure 33 shows SEM analysis of the surface of samples AZ31/CC30 and AZ31/CC60 and discloses the formation of a coating constituted by closely packed spheres. Such spheres, according to the EDX analysis contain Mg, Sn and O (see Table 6).

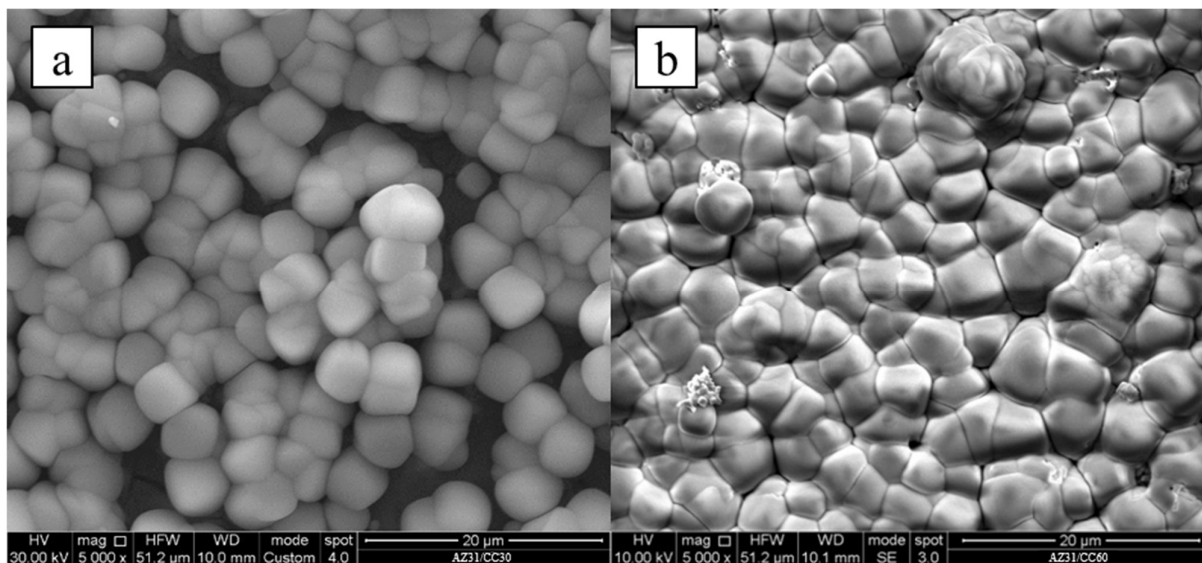


Figure 33. SEM images of conversion coating at different immersion time: a) 30 minutes, b) 60 minutes.

At. %	O	Mg	Sn
AZ31/CC30	74.97	10.50	14.53
AZ31/CC60	74.46	11.85	13.69

Table 6. EDX analysis of the coated samples.

Notably, the longer the conversion time the higher is the coverage degree (see Figures 33a and 33b). After the growth of the coating some samples were bent and partially scratched in order to measure the thickness of conversion coating, that was estimated to be $\sim 5 \mu\text{m}$ (see Figure 34).

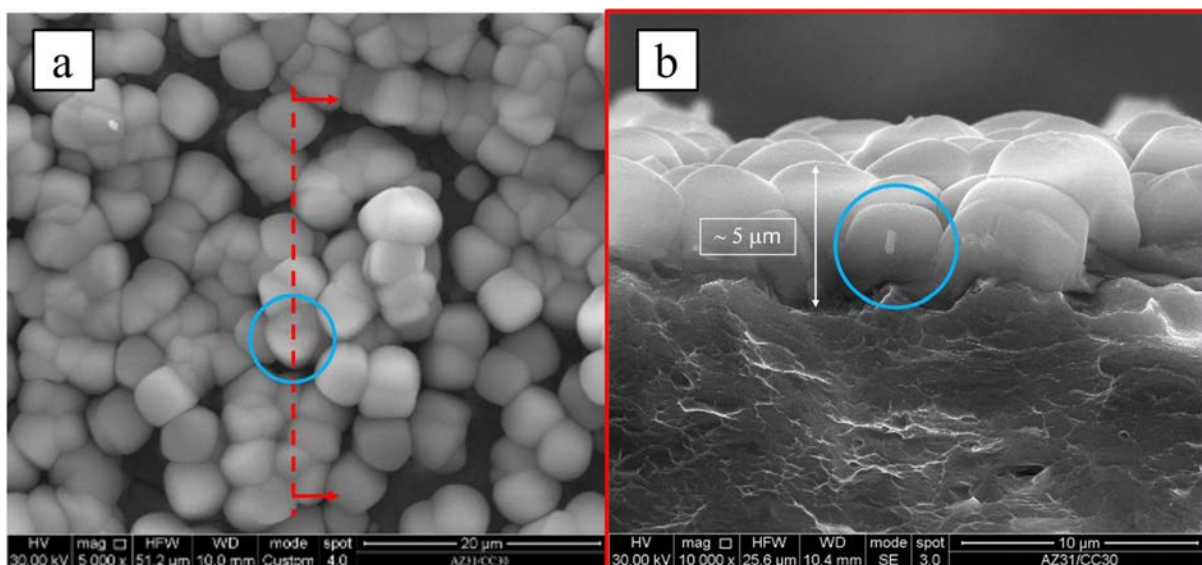


Figure 34. Thickness of $\text{MgSn}(\text{OH})_6$ coating on AZ31/CC30 sample.

XRD diffraction pattern for coated alloys revealed the presence of reflections attributed to crystalline $\text{MgSn}(\text{OH})_6$ (see Figure 35) confirming the successful formation of magnesium hydroxystannate layer.

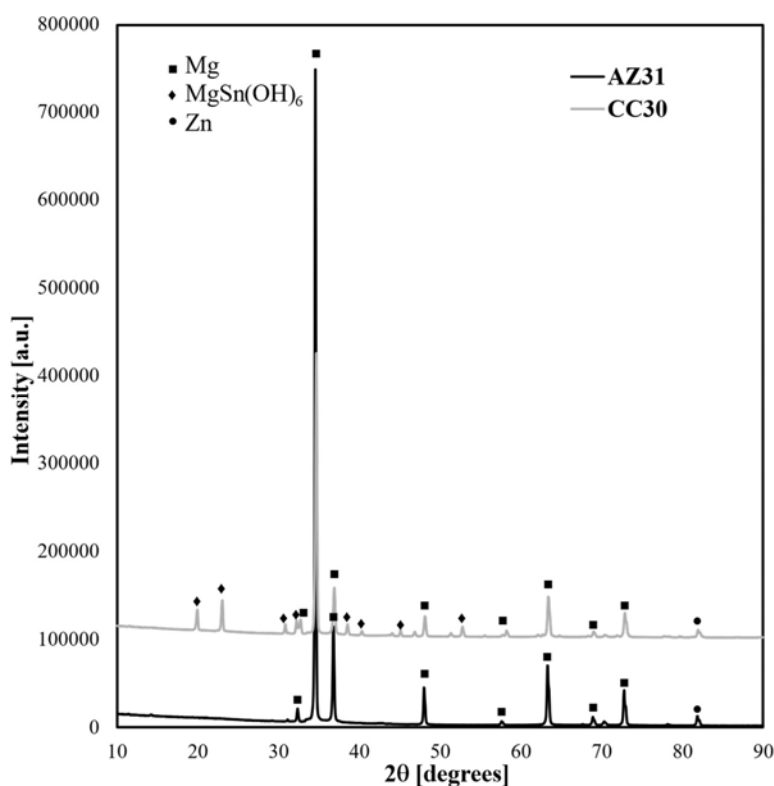


Figure 35. XRD spectra of bare AZ31 and sample with 30 minutes conversion coating

The chemical conversion (i.e. the growth of MgSn(OH)_6) makes the surface strongly hydrophilic, showing contact angles lower than 30° , as can be seen in table 7.

Sample	AZ31	AZ31/CC30	AZ31/CC60
Water contact angle	61	30	20

Table 7. Contact angle measurements.

In the FT-IR spectrum (figure 36) peaks related to the conversion coating can be seen: a wide absorption band in the range $2800\text{--}3600\text{ cm}^{-1}$ and a peak at 1175 cm^{-1} are related to O-H stretching and lattice modes respectively; Mg-O and Sn-O stretching show absorption bands in $500\text{--}1000\text{ cm}^{-1}$ range [162]

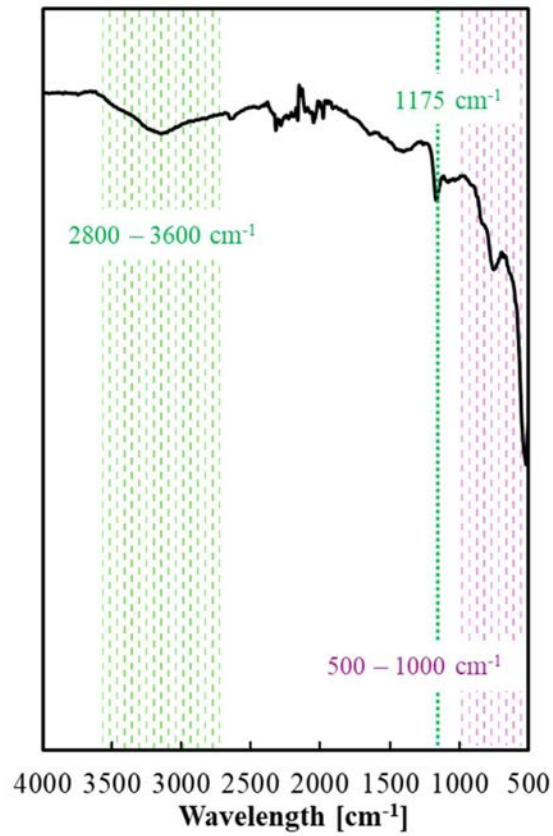


Figure 36. FT-IR spectra for AZ31 samples with conversion coating (AZ31/CC30).

EIS spectra in the Nyquist representation recorded at open circuit potential are reported in Figure 37. For bare AZ31 and AZ31 after 30 and 60 minutes of chemical conversion, a low frequency inductive loop is present associated with a strong hydrogen evolution and, thus, with a high corrosion rate [163]. Notably, for short conversion time the overall impedance is even lower than that measured for $\text{MgSn}(\text{OH})_6$ -free sample. Indeed, the uncoated parts of the alloy are prone to localized corrosion, and this explains why the corrosion resistance of this sample is even worse than that of bare alloy.

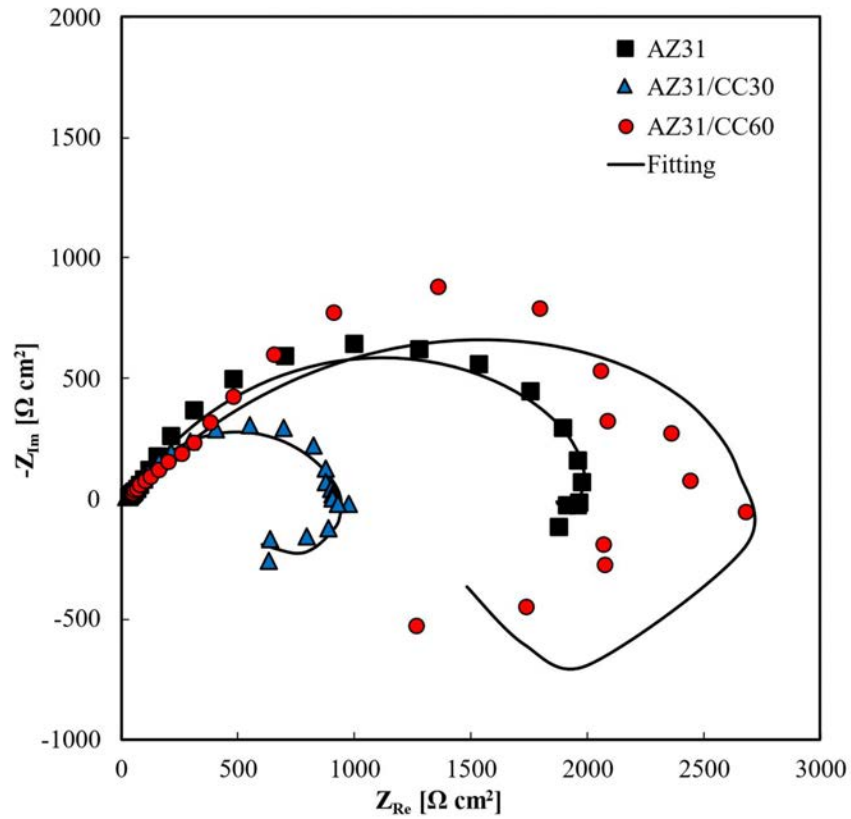


Figure 37. Nyquist representation of EIS spectra recorded at the open circuit potential in DMEM.

To get quantitative information from impedance measurements, the EIS spectra were fitted according to the equivalent circuit reported in Figure 38. The equivalent circuit was used to model the interfaces of uncoated and coated samples, where R_{el} is the electrolyte resistance, Q_{dl} is a constant phase element (CPE) modelling the not ideal behavior of the double layer capacitance, R_T accounts for the charge transfer kinetic of both half-cell reactions on coated and uncoated regions of the alloy, while the L - R_i series accounts for superfluous hydrogen evolution [163]. The fitting parameters are reported in

Table 8. R_T in order of $10^3 \Omega \text{ cm}^2$ and L in the order of 10^4 H cm^2 are in agreement with results reported in previous work, taking into account the chloride ion concentration [163].

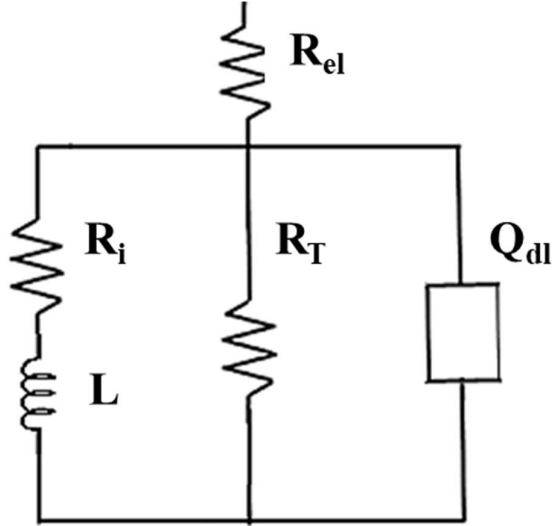


Figure 38. EEC used to model samples.

	R_{el} [$\Omega \text{ cm}^2$]	Q [$\text{S s}^n \text{ cm}^{-2}$]	n	R_T [$\Omega \text{ cm}^2$]	R_i [$\Omega \text{ cm}^2$]	L [H cm^2]	χ^2	OCP [V vs SSC]
AZ31	30.00	6.6E-05	0.63	2.2E+03	1.2E+04	2.2E+04	1.4E-02	-1.71
CC30	30.00	3.4E-05	0.69	9.3E+02	9.7E+02	1.6E+04	1.7E-02	-1.43
CC60	30.00	7.5E-05	0.52	3.1E+03	2.4E+03	2.2E+04	2.3E-02	-1.43

Table 8. EIS spectra fitting parameters.

Figure 39 shows the polarization curves recorded by scanning the potential at 5 mV s^{-1} in DMEM at 37°C . The cathodic branches of the polarization curves are due to both oxygen reduction and hydrogen evolution, while the anodic current is associated to the metal oxidation. The presence of the coating reduces the current density in the anodic branches and shifts the pitting potential to more positive values. However, for alloys after chemical conversion the shift in the corrosion potential is so high that it is coincident with the pitting potential, thus explaining their very high pitting susceptibility.

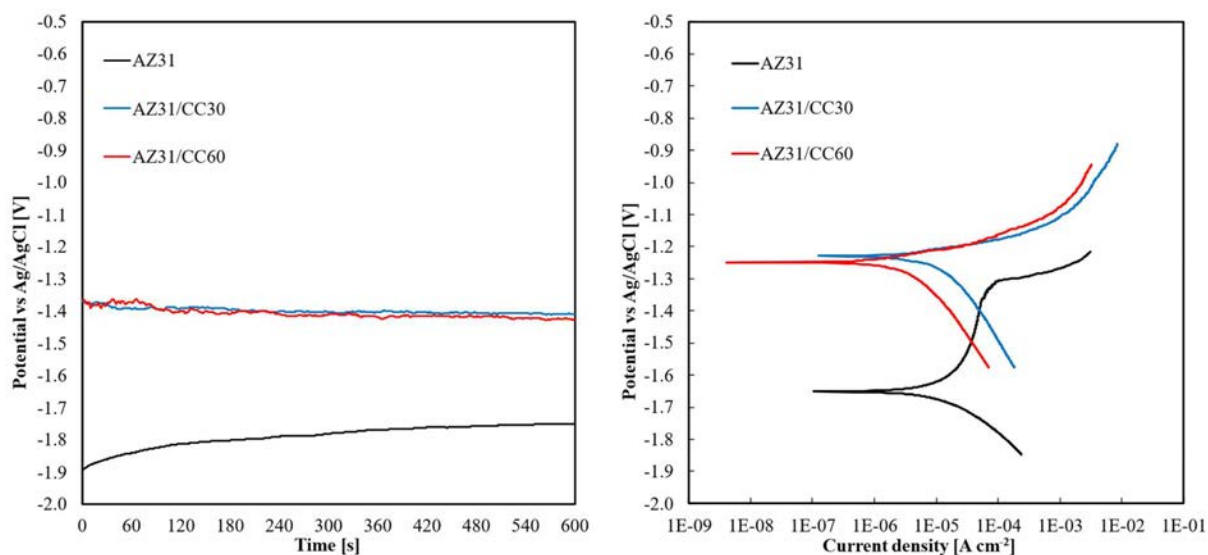


Figure 39. Open circuit potential and polarization curves of samples in DMEM solution.

It is crucial to remember that Mg and Mg alloys show a characteristic behavior known as negative difference effect (NDE), with the consequence that during an anodic polarization over their corrosion potential, dissolution rates increase together with hydrogen evolution rate (HER) [164]. This leads to uncertainty in the evaluation of hydrogen evolution rate from the corrosion current density estimated by fitting polarization curves, and it requires the introduction of a different experimental approach. Different methods have been adopted to evaluate HER, like measuring hydrogen accumulation in closed containers thanks to the weight change in a buoyant system, or by indirect evaluation with pressure sensors and O₂ sensors [165,166]. The method used in this study allows the direct measurement of H₂ concentration, collecting a gas sample directly from the closed container where the metallic sample is corroding, namely DMEM solution at 37°C in this work. The gas sample is then analyzed by a gas chromatograph, providing precise concentration values representative of the atmosphere in the head volume of the container. H₂ concentration values were collected regularly over 168 hours, allowing to measure the amount of hydrogen evolved over time. In figure 40 are reported the collected data in $ml\ cm^{-2}$, and the time in *days*, HER could then be estimated as the slope of the interpolating straight line.

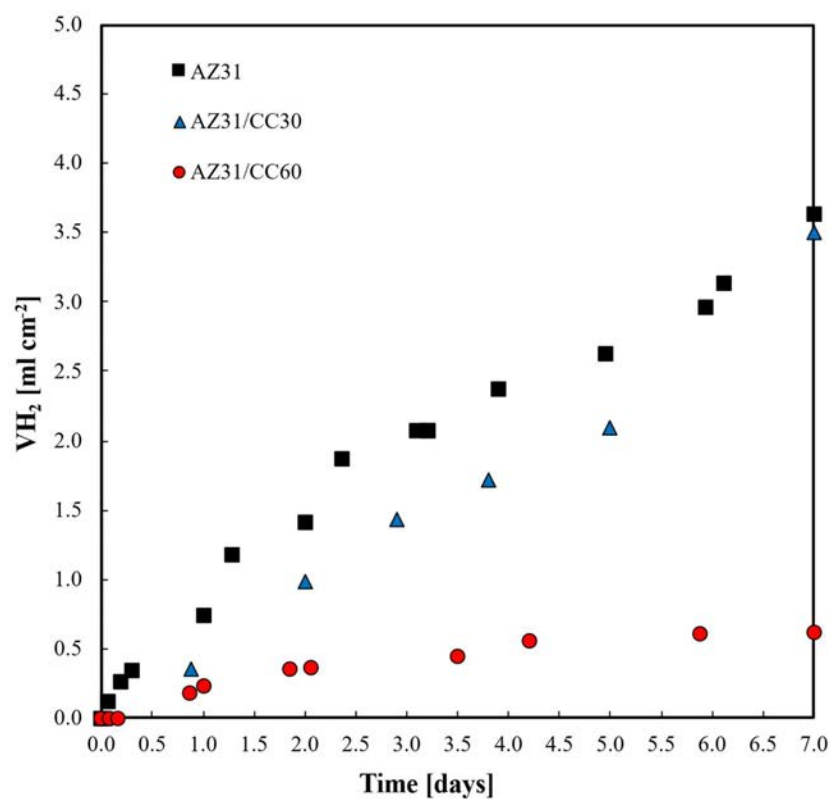


Figure 40. Evolved hydrogen collected with GC during 7-day immersion period.

Slope values are reported in Figure 41, where it can be seen that a strong reduction of hydrogen evolution rate with respect to bare AZ31 can be provided by a 60-minute chemical conversion coating. Notably, the amount of H_2 collected after 6 hours was small enough to be undetectable by the instrument.

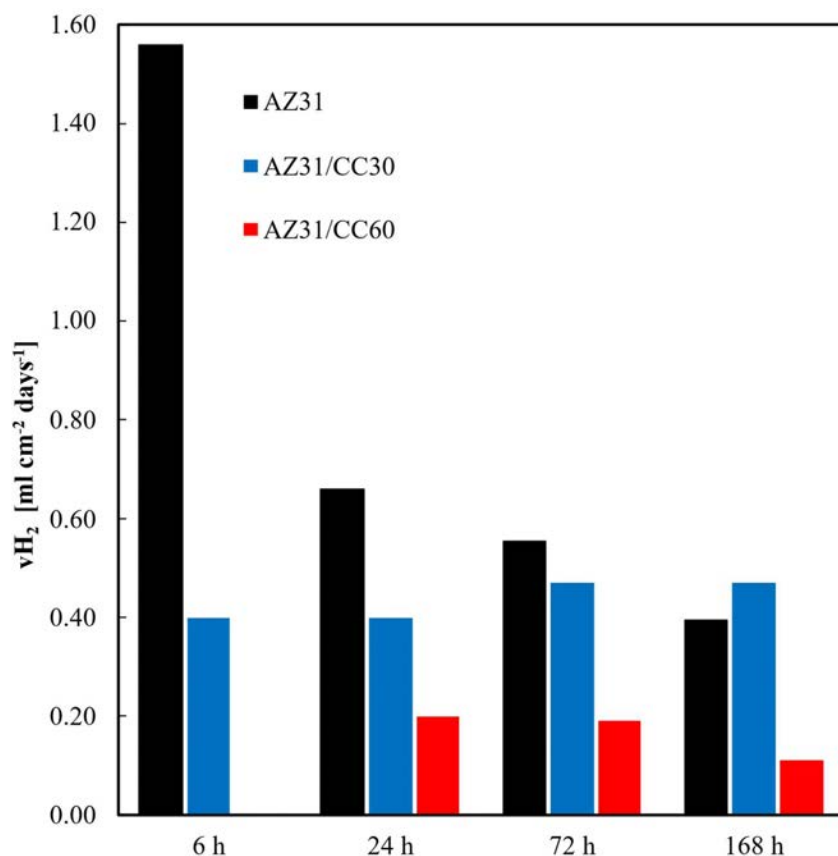


Figure 41. Direct estimate of hydrogen evolution rate during 168 h.

4.1.3 Conclusions

It is important to note that conversion coating wasn't meant to be used as a standalone protection strategy for magnesium alloys in biomedical application, as their intrinsic morphology necessarily leaves nano- and micro-scale uncovered regions. This behavior, however, can be either detrimental or advantageous depending on the subsequent processing. In the next sections it will be discussed that, when electrodeposition is required, partial coverage (CC30) is desirable to ensure sufficient current pathways. Conversely, for UV-grafting of PDMS-based polymers, an electroless process, the highest possible coverage (CC60) is preferred, as it maximizes the number of hydroxylated sites available for covalent grafting and minimizes electrolyte accessibility.

4.2 Electrodeposition of a Hydrophobic Manganese Stearate Coating

In this section a new strategy is proposed to grow an efficient coating able to tune the biodegradation rate of AZ31 alloy by carrying out the mentioned stannate based chemical conversion followed by the electrodeposition of a functional hydrophobic layer of manganese stearate. The goal is to reduce the corrosion rate of AZ31 by preventing corrosive environment from reaching the surface. The presence of a textured conversion coating will improve the adhesion of the hydrophobic layer with consequent beneficial effect on its stability.

Structure, morphology and composition of the coatings will be studied by X-ray diffraction, Scanning Electron Microscopy and FT-IR, while their corrosion resistance will be assessed by recording polarization curves and electrochemical impedance spectra in Dulbecco's Modified Eagle Medium (DMEM) solution (composition in Table 2). To avoid misleading estimates due to negative difference effect [167–171], direct measurements of hydrogen evolution rate will be carried out by following the concentration of evolved H_2 in the environment by gas chromatography, while cytocompatibility tests will allow to assess the biocompatibility of the coated alloys.

4.2.1 Additional Experimental Details

AZ31 Mg alloy (Mg 96%, Al 3%, Zn 1%, Goodfellow) 20x20 mm coupons were cut and mechanically grinded with silicon carbide grinding papers (Buehler) up to P2500 grit, while quenching in ethanol ($C_2H_6O \geq 99.5\%$ - Emplura). Then, samples were ultrasonically cleaned in ethanol for 10 minutes and dried at room temperature.

Electrodeposition process was carried out in ethanol ($C_2H_6O \geq 99.5\%$ - Emplura), with 0.1 M stearic acid ($CH_3(CH_2)_{16}COOH$ - Sigma-Aldrich) and 0.05 M manganese chloride ($MnCl_2 \cdot 4H_2O$ – Carlo Erba Reagents). The solution was prepared at 50 °C, such temperature was maintained during the process and samples were immersed for 15 minutes prior to the beginning of the deposition. A two-electrode configuration was adopted, imposing a range of different potentials between cathode (AZ31 sample) and anode (two rectangular sheets of carbon paper): potential in the range -5V / -20V were investigated. Samples were then rinsed in ethanol and dried at room temperature for 24h.

The degradation of the obtained coating was assessed by estimating Mn and Sn release after immersion in testing solution for 24 hours, using a PerkinElmer Optima 2100 DV. ICP-OES analyses

were performed on solutions diluted 1:10 with 2 wt. % nitric acid (65% Suprapur, Sigma-Aldrich) aqueous solution.

The procedures each sample has undergone are summarized in Table 9.

sample name	I step: Conversion coating	II step: Hydrophobic coating
AZ31	-	-
AZ31/CC30	30 min.	-
AZ31/MnST	-	0.5 C cm ⁻²
AZ31/CC30/MnST	30 min.	0.5 C cm ⁻²

Table 9. Samples treatment summary and names used.

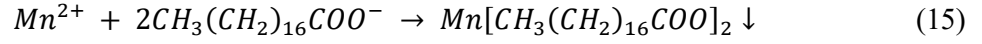
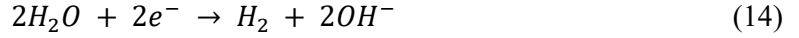
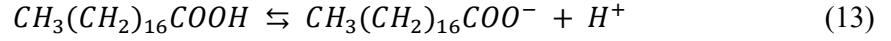
Bare AZ31 and coated samples were studied by means of OCP measurement over time, EIS spectra and polarization curves. Testing solution was DMEM, maintained at 37 °C in order to mimic physiological environment [122].

Cytotoxicity test were also performed in order to assess the impact of the proposed coating on the surrounding tissue after the implantation of the device (see details in chapter 2).

Samples with the complete coating were also studied after 24h immersion in DMEM (named AZ31/CC30/MnST 24h): contact angle, EIS spectra, EEC modeling and SEM micrographs are reported.

4.2.2 Results and Discussion

An electrochemical deposition step was carried out on converted alloys to further improve their corrosion resistance, in the attempt to seal the remaining exposed metal surface with a hydrophobic compound. Therefore, magnesium alloys after the growth on its surfaces of MgSn(OH)₆ by conversion coating process were immersed in a fatty acid (stearic acid) and manganese salt containing ethanol solution, and they were cathodically polarized (at -10 V) to induce the precipitation of manganese stearate according to the following reactions:



The electrodeposition potential was selected after a preliminary optimization within the range -5 V to -20 V, based on coating adhesion and deposition stability. At lower absolute potential (e.g., -5 V), the deposited layer exhibited poor adhesion and tended to spontaneously detach in the form of flakes or powder, indicating insufficient driving force for stable film formation. Conversely, at higher absolute potential (e.g., -20 V), the overpotential for hydrogen evolution was excessive, leading to intense gas formation at the electrode surface. The vigorous hydrogen evolution disrupted the deposition process, resulting in non-uniform coatings with compromised integrity. Therefore, -10 V was identified as an optimal compromise, providing sufficient cathodic driving force to ensure good adhesion while limiting hydrogen evolution to a level that did not significantly interfere with film growth.

For matter of comparison, this electrodeposition step was also carried out on bare AZ31 to highlight the role of the conversion coating on the corrosion rate of the samples. Figure 42 shows the current density transients recorded for both bare and converted alloy. In both cases the absolute value of the current density decreases as a function of time suggesting that the deposited layer covers the metallic surface. The process was stopped after the circulation of $\sim 0.5 \text{ C cm}^{-2}$.

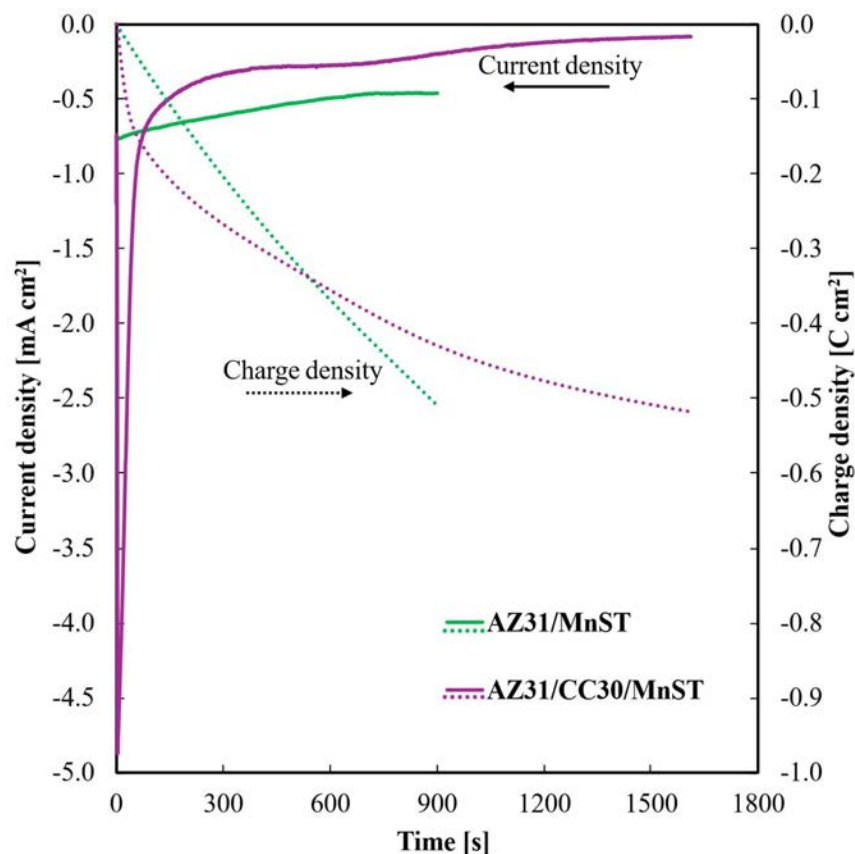


Figure 42. Stearate deposition curves obtained on AZ31 bare and on AZ31/CC30 substrate samples.

Under the same applied potential, the circulating current per unit geometric surface is different, since the bare alloy is highly conductive and its geometric surface is almost coincident with its real surface. In the case of AZ31 after chemical conversion, the active metal surface is that below the coating (i.e. in the parts not yet covered by $\text{MgSn}(\text{OH})_6$ layer). This explains why the target charge density was reached sooner in case of MnST deposited directly on AZ31 bare surface.

The successful deposition of manganese stearate on AZ31 was confirmed by analyzing the morphology of the coating soon after electrodeposition by SEM and by analyzing surfaces composition by EDX and FTIR (see table 10 and figure 43).

At. %	O	C	Mg	Sn	Mn
AZ31/MnST	2.34	77.85	19.49		0.32
AZ31/CC30/MnST	60.48	10.32	19.52	9.08	0.60

Table 10. EDX analysis of the coated samples.

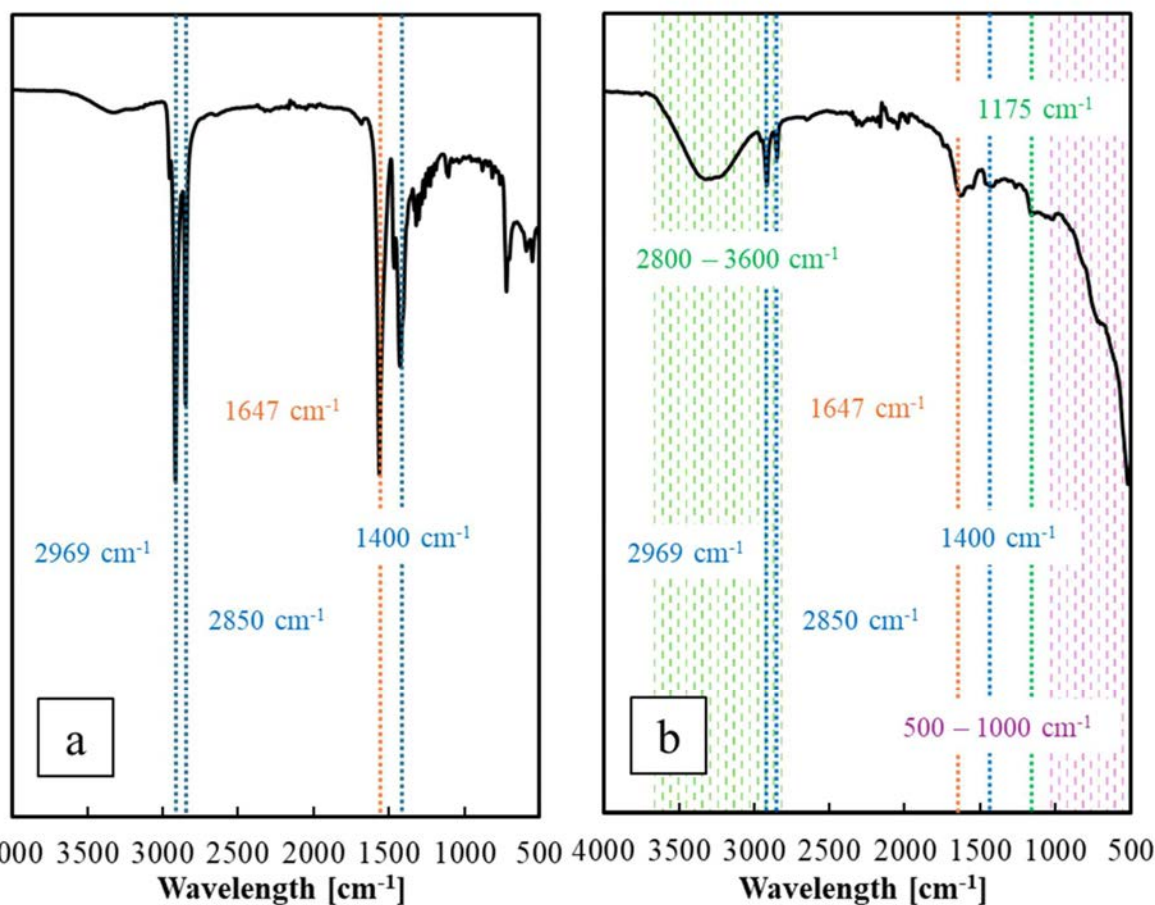


Figure 43. FT-IR spectra for AZ31 samples with: a) hydrophobic coating on bare substrate (AZ31/MnST); b) hydrophobic coating on 30 minutes conversion coating (AZ31/CC30/MnST).

Figure 44 shows the surface morphology of stearate manganese deposited on bare AZ31, constituted by quasi-spherical structures with smaller spiky extremities (see Figure 44c), that cause a great increase in specific surface area. EDX analysis reveals a high carbon content and the presence of manganese.

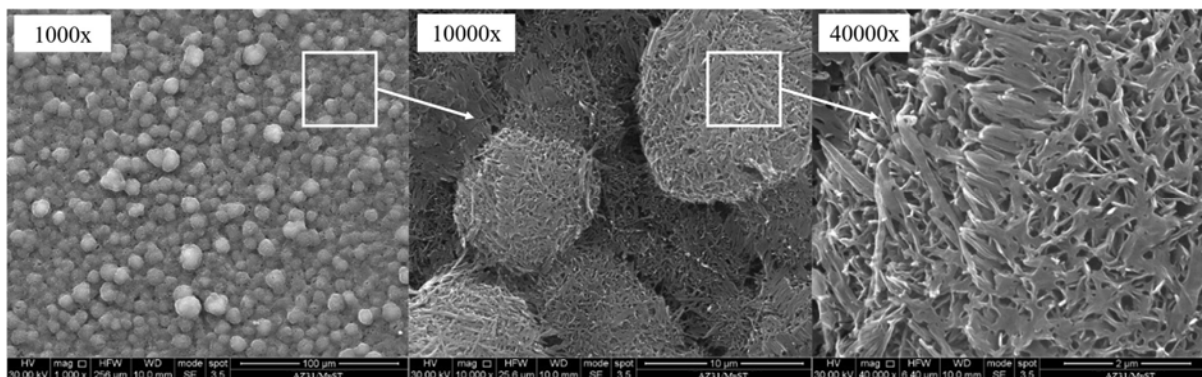


Figure 44. a, b, c) SEM images of AZ31/MnST at different magnification.

From the cross section of Figure 45, the coating appears to be constituted by spherical structures embedded in a flat MnST layer, with a thickness ranging between 3 and 8 μm .

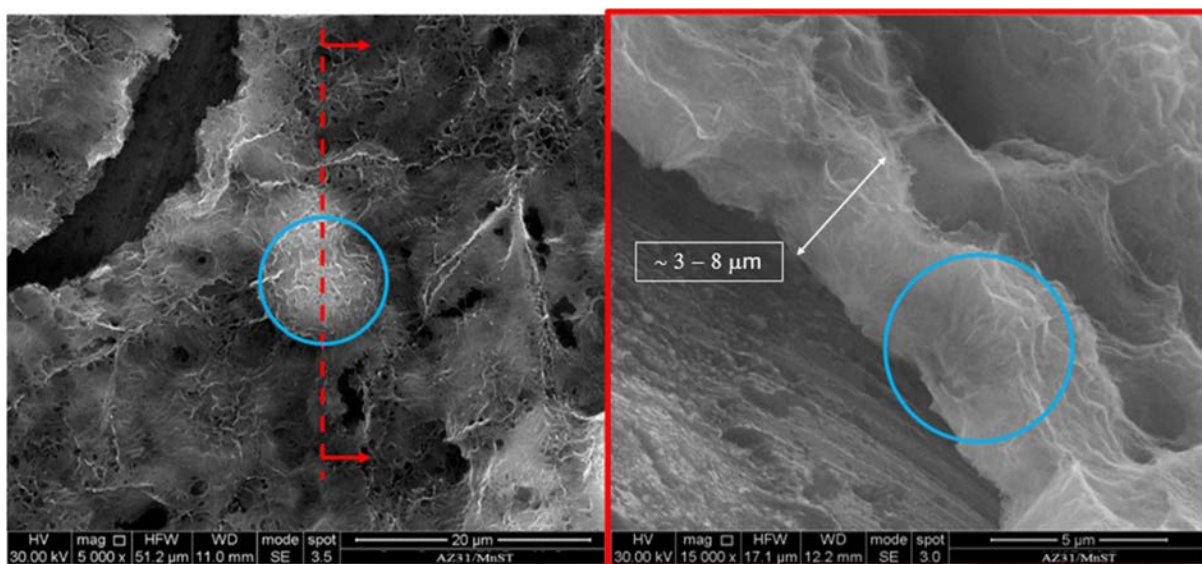


Figure 45. Thickness of stearate coating on AZ3/MnST sample.

FT-IR spectra for this coating (AZ31/MnST - Figure 43a) reveal absorption bands in the range 2850-2969 cm^{-1} that can be attributed to C-H group symmetric and asymmetric vibration, and another peak at 1400 cm^{-1} related to C-H bending. A peak at 1647 cm^{-1} can be attributed to COO-, due to the formation of the stearate salt [172]. The contact angles on such coating showed hydrophobic behavior, with measured angles of $\sim 147^\circ$ (see Figure 46).

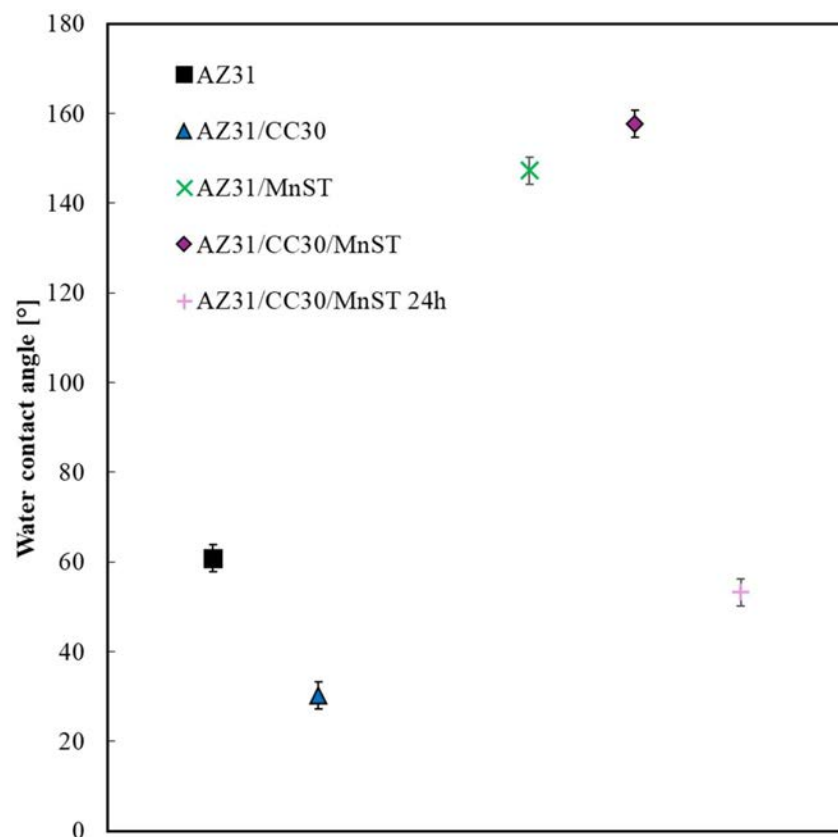


Figure 46. Static contact angles measured on the samples.

It is important to mention that stearate coating electrodeposited on bare samples appears to have a poor adhesion since it can be easily detached releasing powder.

A different morphology is shown by coating on AZ31 after 30 minutes of chemical conversion. (AZ31/CC30/MnST - see Figure 47).

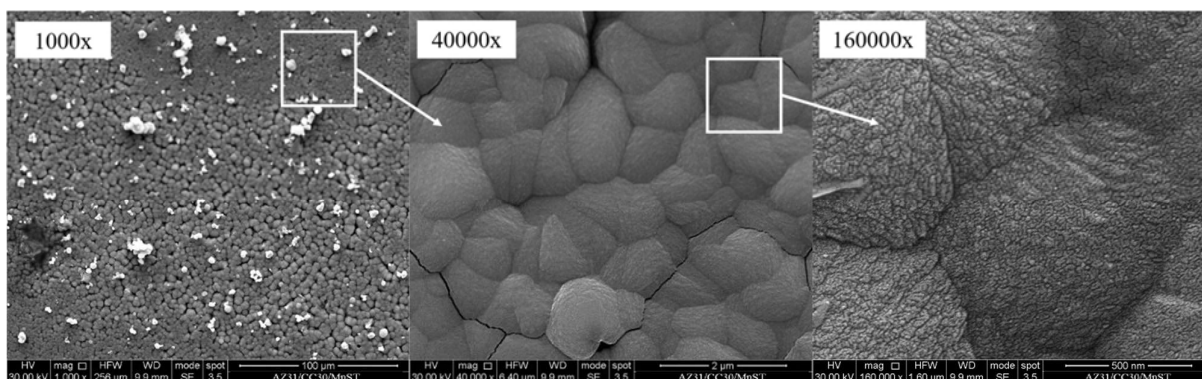


Figure 47. SEM images of AZ31/CC30/MnST at different magnification.

In this latter case manganese stearate seems to wrap the existing magnesium hydroxystannate spheres, generating a very rough layer covering all the spheres. Notably, manganese stearate seals the space among the $\text{MgSn}(\text{OH})_6$ spheres (compare Figure 47b with Figure 33a), thus inhibiting the contact between the alloy and the aggressive environment. Moreover, in some areas MnST is present as bridges between spheres (see Figure 48 below).

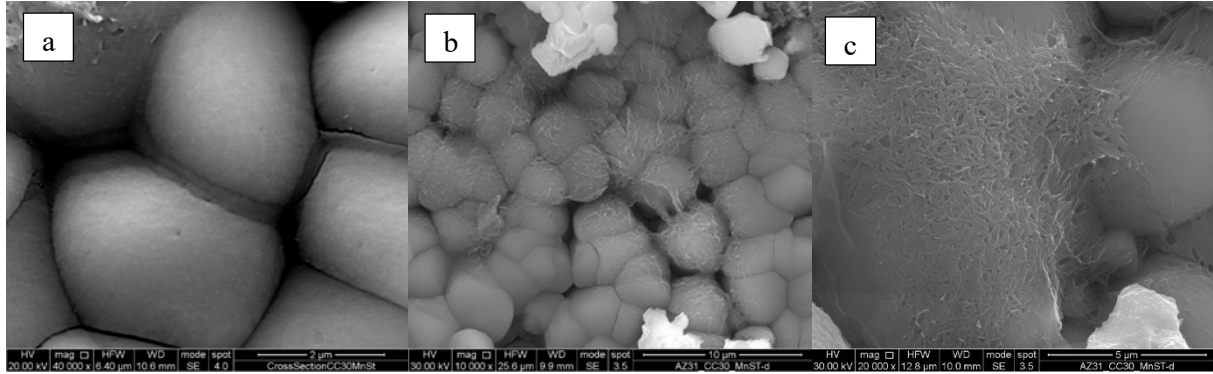


Figure 48. Details of MnST coating grown on CC30 substrate.

Additionally, by analyzing the surface of cracked coated samples, it was possible to estimate the MnST layer thickness on top of the conversion coating, that resulted to be $\sim 10 - 30 \text{ nm}$ (see Figure 49).

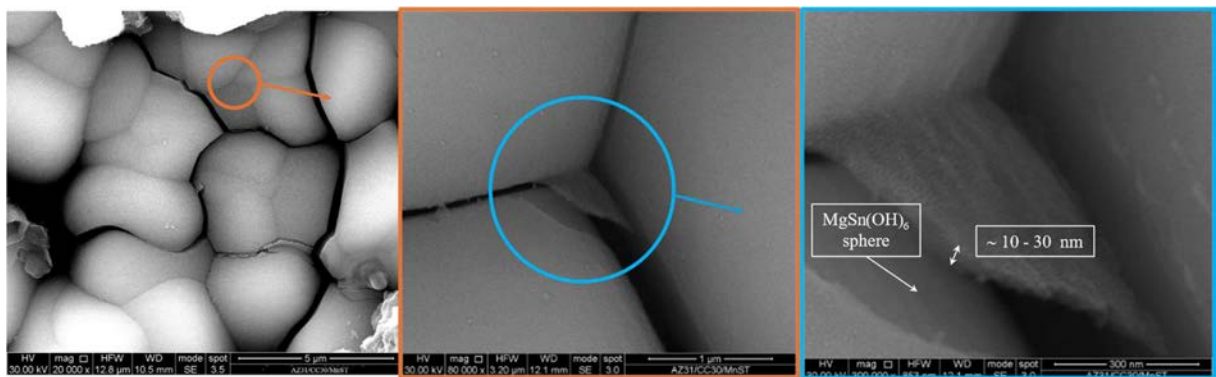


Figure 49. Thickness of the coating on AZ31/CC30/MnSt sample.

EDX analysis confirmed the presence of C and Mn, but also the signal arising from Mg and Sn beneath. FT-IR spectrum for the samples with complete coating (Figure 43b) shows the peaks related to the stearate (C-H and COO-), and in addition other bands and peaks related to the conversion

coating substrate. The measured contact angles on such coating resulted to be $> 150^\circ$, revealing superhydrophobic behavior.

For both AZ31/MnST and AZ31/CC30/MnST the increased specific surface area with a hierarchical structure as well as the low surface free energy characteristic of manganese stearate (24.5 mJ m^{-2} as reported in [173]) explain the high contact angles, greatly reducing the wettability and thus improving corrosion resistance. Indeed, in agreement with the Cassie-Baxter model, the contact angle (θ_R) on a rough surface can be determined by the corresponding static angle (θ) on a flat surface, as expressed in the following equation:

$$\cos\theta_R = f_s (\cos\theta + 1) - 1 \quad (16)$$

with f_s denoting the fraction of the surface effectively in contact with the liquid. By using $\theta = 101^\circ$ for Mn stearate, as reported in [173], the values of $f_s = 0.20$ and $f_s = 0.09$ for AZ31/MnST and AZ31/CC30/MnST respectively were calculated.

However, after 24 h of immersion in DMEM solution, the contact angle decreases to 53° (see Figure 46) suggesting that the coating loses its superhydrophobicity thus allowing to not repel cells. Indeed, during immersion in the physiological environment, the stearate layer slowly dissolves exposing the beneath MgSn(OH)_6 spheres. This finding is confirmed by ICP measurements (see Figure 50), revealing that Mn ions are released from stearate hydrophobic coating ($\sim 1 \mu\text{g cm}^{-2}$ after 24 hours), while no Sn ions were detected suggesting that MgSn(OH)_6 is stable.

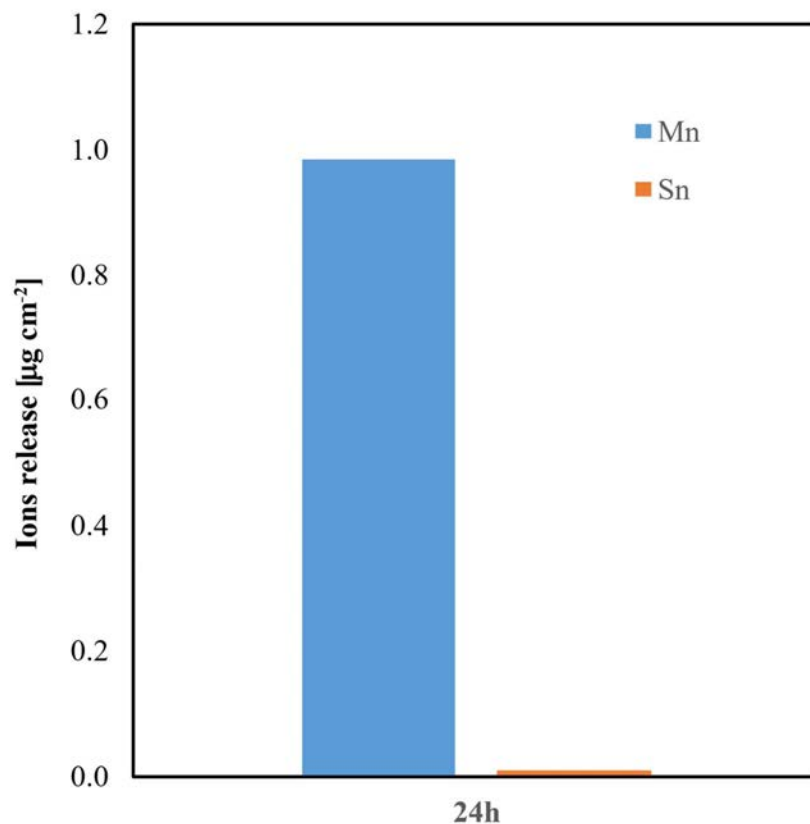


Figure 50. a) ICP-OES measurements.

This is also confirmed by SEM micrographs of the coating after 24 hours of immersion in DMEM solution. The degradation of hydrophobic coating occurs by losing both stearates that fill the space among the $\text{MgSn}(\text{OH})_6$ spheres (see Figure 51a) and stearates covering the surface on the same spheres (see Figure 51b).

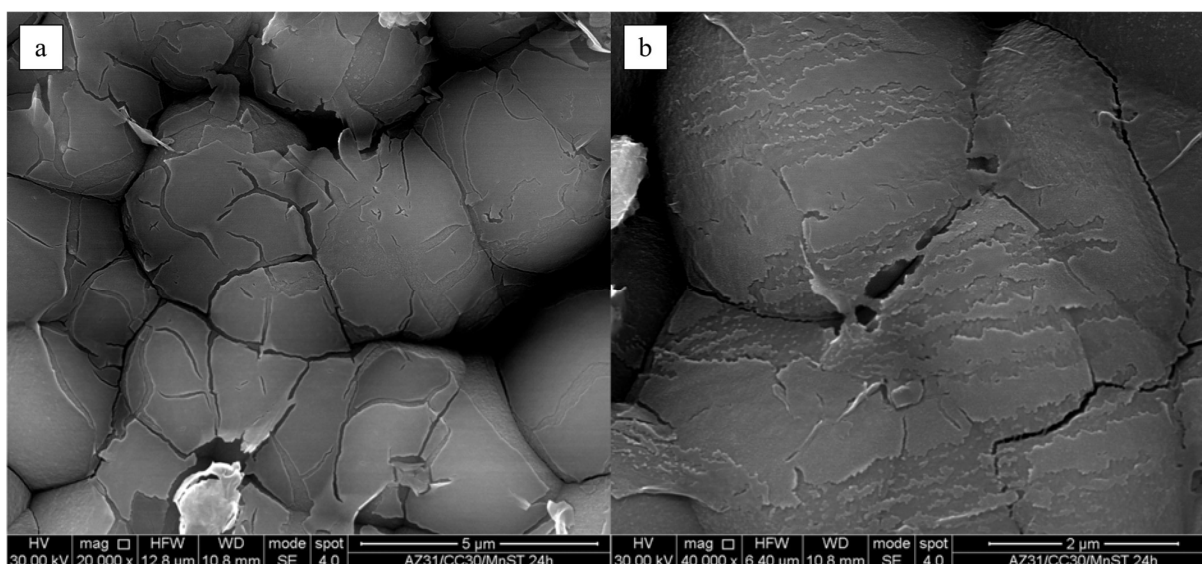


Figure 51. a, b) SEM micrographs of degraded coating after 24 hours of immersion in DMEM.

Electrochemical characterization of not coated and coated AZ31 was carried out in DMEM solution at 37°C in order to evaluate corrosion resistance in a physiologic-simulating environment. The uncoated and coated AZ31 alloys were left for 30 minutes at 37°C at the open circuit potential (figure 54a). The latter resulted in being below the equilibrium potential for hydrogen evolution reaction at pH 7, thus suggesting that the cathodic processes coupled to magnesium oxidation were both oxygen reduction and hydrogen evolution. EIS spectra in the Nyquist representation recorded at open circuit potential are reported in Figure 52.

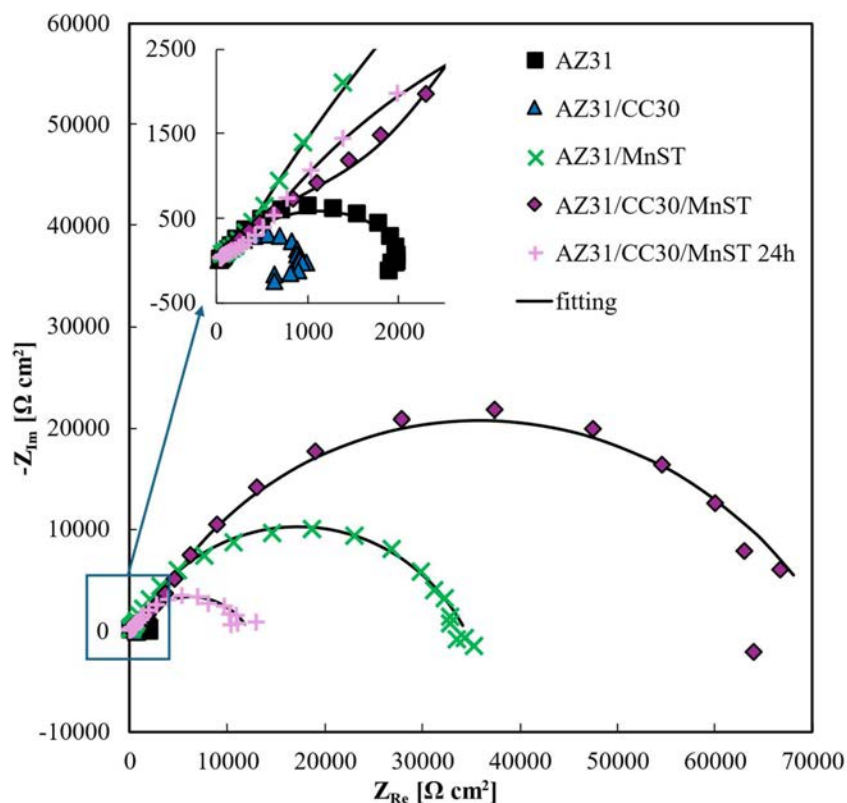


Figure 52. Nyquist representation of EIS spectra recorded at the open circuit potential in DMEM.

As soon as manganese stearate grows on the surface of the samples and in agreement with the higher water contact angles, the inductive loop present in AZ31 and AZ31/CC30 disappears and the overall impedance raises significantly. AZ31/MnST samples show a higher impedance than bare AZ31 and the alloys with conversion coating, without the presence of inductive loop at the lower frequencies in the Nyquist plot. The overall impedance of the hydrophobic coating on the bare samples is lower than that of the coating grown on conversion coating, probably because of the worse adhesion on the substrate. However, the coating on the bare samples is compact and adherent enough to reduce considerably the exposed metal surface, thus the absence of the inductive loop.

Samples with the complete hydrophobic coating grown on the stannate based substrate (AZ31/CC30/MnST) show the highest overall impedance, being almost 35 times higher than bare AZ31, and such impedance is maintained at the same order of magnitude even after 24h of immersion in DMEM.

From these results it appears that the morphology obtained with 30 minutes of immersion in the conversion bath plays an important role in the proper interlocking of the hydrophobic electrodeposited coating.

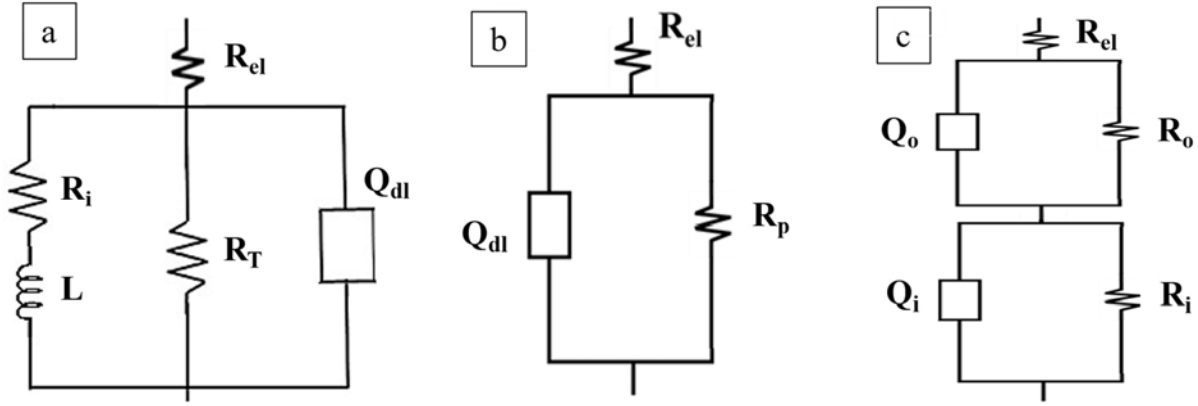


Figure 53. Equivalent electric circuits adopted to model EIS spectra of the samples.

	R_{el} [$\Omega \text{ cm}^2$]	Q_{dl} [$\text{S s}^n \text{ cm}^{-2}$]	n	R_T [$\Omega \text{ cm}^2$]	R_i [$\Omega \text{ cm}^2$]	L [H cm^2]	χ^2	OCP [V vs SSC]
AZ31	30	6.6E-05	0.63	2.2E+03	1.2E+04	2.2E+04	1.4E-02	-1.71
CC30	30	3.4E-05	0.69	9.3E+02	9.7E+02	1.6E+04	1.7E-02	-1.43

	R_{el} [$\Omega \text{ cm}^2$]	R_p [$\Omega \text{ cm}^2$]	Q_{dl} [$\text{S s}^n \text{ cm}^{-2}$]	n	χ^2	OCP [V vs SSC]
AZ31/MnST	30	3.7E+04	4.9E-06	0.60	2.2E-02	-1.65

	R_{el} [$\Omega \text{ cm}^2$]	R_o [$\Omega \text{ cm}^2$]	Q_o [$\text{S s}^n \text{ cm}^{-2}$]	n	R_i [$\Omega \text{ cm}^2$]	Q_i [$\text{S s}^n \text{ cm}^{-2}$]	n	χ^2	OCP [V vs SSC]
AZ31/CC30/MnST	30	2.0E3	7.2E-6	0.58	6.7E4	8.2E-6	0.73	3.4E-3	-1.52
AZ31/CC30/MnST 24h	30	2.5E2	6.6E-6	0.66	1.1E4	3.0E-5	0.67	3.4E-3	-1.44

Table 10. Fitting parameters of the equivalent electric circuits used to model EIS spectra.

Bare samples and samples with 30 minutes conversion coating were fitted as explained in section 4.1.2. For MnST coated bare AZ31 the employed equivalent circuit is reported in Figure 53b, where Q_{dl} models the not ideal double layer capacitance and R_p accounts for the polarization resistance. For the AZ31 alloys with MnST deposition after $\text{MgSn}(\text{OH})_6$ conversion layer two time constants are necessary (EEC in Figure 53c) to account for the presence of MnST grown on uncoated bare alloy and sealing the empty space between $\text{MgSn}(\text{OH})_6$ spheres (see Figure 48). Indeed, R_i and Q_i account for the non-ideal capacitance and for the resistance of the manganese stearate layer electrodeposited on uncoated regions beneath and/or among the $\text{MgSn}(\text{OH})_6$ spheres, while R_o and Q_o account for the non-ideal capacitance and for the resistance of the outer manganese stearate in direct contact with the

electrolyte. It is important to mention that the contribution to the measured impedance of magnesium hydroxystannate is in parallel with that of the MnST layer, but it is negligible due to the insulating character of $\text{MgSn}(\text{OH})_6$, that is a quaternary metal hydroxide with a dielectric behavior and a wide band gap [174,175].

Figure 54b shows the polarization curves recorded by scanning the potential at 5 mV s^{-1} in DMEM at 37°C . For alloy directly coated by manganese stearate (AZ31/MnST) the corrosion potential and the corresponding corrosion current density are reduced by the layer, but the pitting potential is coincident with that of the bare alloy. This could be also because of the poor adhesion of the coating on the bare alloy. For hydrophobic Mn stearate layer deposited directly on bare AZ31 the coating showed lower mechanical stability than with the conversion coating used as substrate, leading to a lower corrosion resistance. The AZ31/CC30/MnST samples show the best performance in terms of reduction of corrosion current density with a pitting potential far enough from the corrosion potential (more than 250 mV).

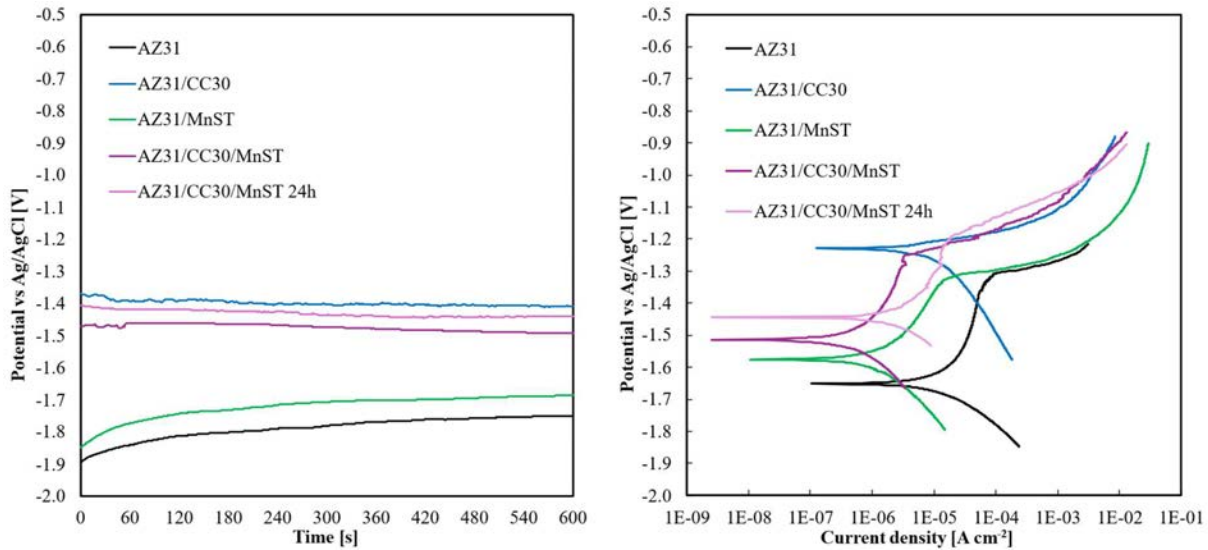


Figure 54. Open circuit potential of samples (left) and polarization curves (right) in DMEM solution.

As regards AZ31/CC30/MnST samples, the good corrosion behavior is confirmed since the evolved H_2 cannot be appreciated after 24 hours (see Figure 55) in agreement with the recorded EIS spectra and remains constant under $0.08 \text{ ml cm}^{-2} \text{ days}^{-1}$ up to 168 hours of immersion.

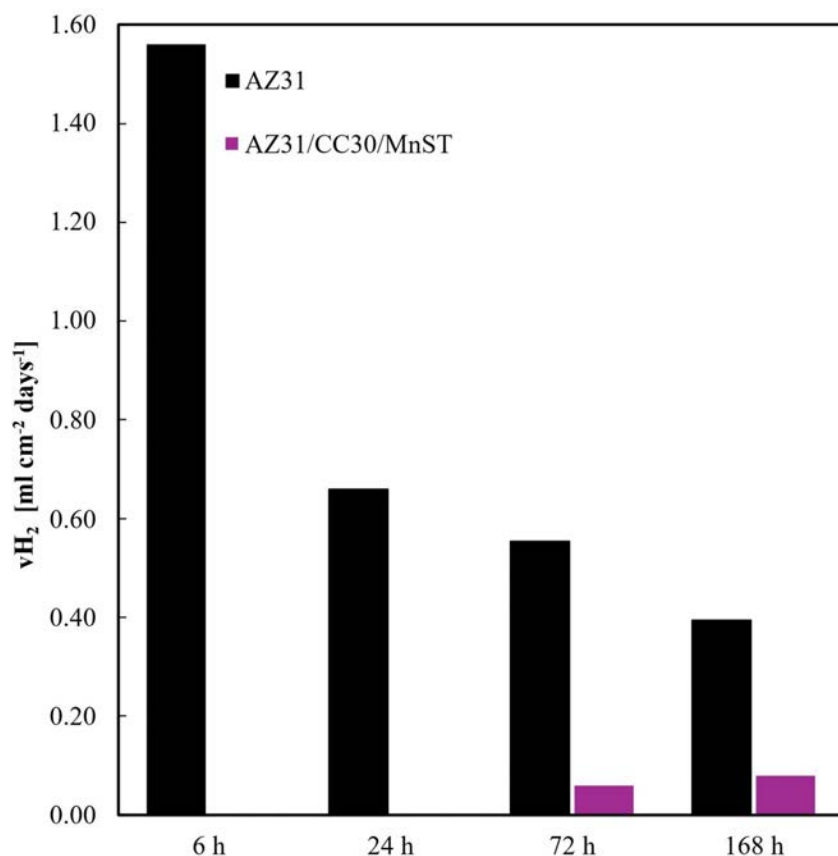


Figure 55. Direct estimate of hydrogen evolution rate during 168 h.

4.2.2.1 Cytotoxicity Tests

Cytotoxicity tests were carried out to evaluate the potential of stannate conversion coating and Mn stearate coating as biomaterial for biomedical applications. Figure 56 shows the percentage of viable cells grown in each conditioned medium with respect to the control (i.e. cells grown in normal medium). After 24 hours, the viability of cells exposed to AZ31-, AZ31/CC30-, and AZ31/CC30/MnST-treated samples was 89.6%, 85.9%, and 83.5%, respectively. All samples exhibited over 70% viability, indicating non-toxicity after 24 hours. At 48 hours, the AZ31/CC30/MnST-treated samples maintained a high viability, 78.7%, confirming their cytocompatibility, whereas lower values were recorded for AZ31 (73.2%) and AZ31/CC30 (61.2%).

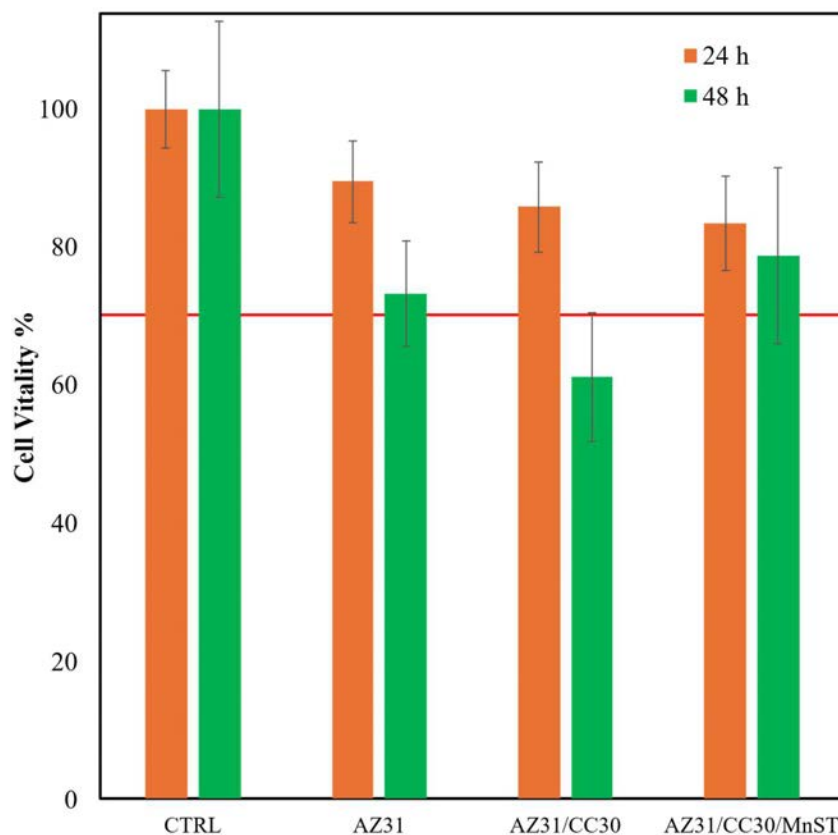


Figure 56. Cell viability after 24 and 48 hours of treatment with normal medium (CTRL) or with AZ31, AZ31/CC30, and AZ31/CC30/MnST conditioned medium.

Additionally, growth rates were calculated by comparing for each sample the value of fluorescence (directly proportional to the number of viable cells) at 24 and 48 hours. Results in Table 11 show a 9% decrease, in terms of viable cells, for cells exposed to AZ31/CC30-medium and a slight increase (4.2%) of cells treated with AZ31-medium. Interestingly, cells treated with AZ31/CC30/MnST-medium showed a 20.3% increase, the closest to that observed in the control (27.5%). Overall, these results not only highlight the cytocompatibility of MnST coated samples, but also suggest a positive effect on cell growth with respect to the bare metal.

Sample	Fluorescence at 24h	Fluorescence at 48h	Cells Growth %
CTRL	2440	3111	27,5
AZ31	2186	2279	4,2
AZ31/CC30	2095	1905	-9,0
AZ31/CC30/MnST	2037	2450	20,3

Table 11. Percentage of cells growth from 24 to 48 hours.

4.2.3 Conclusions

A double step process, consisting of a first stannate based chemical conversion followed by manganese stearate electrodeposition, was employed in order to slow down the magnesium corrosion rate in DMEM. The hydrophobic coating obtained in the second step was successfully optimized for the stannate based substrate, ensuring a good adhesion and a great improvement in the overall impedance with respect to the bare alloy. The recorded EIS spectra show the absence of inductive loop, suggesting the formation of a compact and protective layer on the AZ31 substrate. The gas chromatography measurements for the direct estimation of H₂ evolution allowed to confirm this result, reaching a hydrogen evolution rate of 0.08 ml cm⁻² days⁻¹ even after 168 hours. Furthermore, cytocompatibility of the coating was confirmed by the vitality test, maintaining acceptable values even after 48 hours.

4.3 UV-Grafting of Polydimethylsiloxane Molecules

Hydroxystannate conversion coatings represent an effective strategy to mitigate the initial corrosion rate of magnesium alloys in physiological environments by forming a compact, hydroxyl-rich layer capable of partially blocking electrolyte penetration. However, despite their beneficial effect, these coatings remain intrinsically porous, and the aggressive ionic species present in simulated body fluids, especially chloride, may still reach the metallic substrate during the early immersion stages. Surface grafting of polymeric molecules is increasingly explored as a method to enhance the performance of conversion coatings by adding an additional barrier layer tailored through appropriate chemical functionalities. Polydimethylsiloxane (PDMS) is widely used for its low surface energy, hydrophobicity and chemical stability, and can be covalently attached to oxide- or hydroxyl-terminated surfaces through UV-induced cleavage. Functional derivatives of PDMS, such as fluorinated PDMS (PDMS-F) or polyethylene glycol-terminated PDMS (PDMS-PEG), provide additional degrees of tunability: fluorinated chains typically increase hydrophobicity and reduce ionic permeability, whereas PEG-based chains create hydrophilic, protein-repellent interfaces capable of altering ion-surface interactions. In this work, three molecular systems, PDMS, PDMS-F and PDMS-PEG, were grafted onto $\text{MgSn}(\text{OH})_6$ coatings grown on AZ31 Mg alloy. The objective was to investigate how different PDMS functional end groups influence surface chemistry, wettability, corrosion resistance and degradation stability in Kokubo solution, hydrogen evolution behavior, and cytocompatibility, with particular attention to differences between short-term protection and long-term immersion performance.

Part of the data reported in this chapter were obtained by the writer during his period abroad at the *Surface Science and Corrosion* laboratory (FAU, Erlangen – Germany), under the supervision of Professor Sannakaisa Virtanen.

4.3.1 Additional Experimental Details

After the chemical conversion coating, carried out for 60 minutes (AZ31/CC60), in order to increase coverage samples were placed in a glass Petri dish, and covered with:

- polydimethylsiloxane silicon oil (PDMS, 500 cSt – Carl Roth)
- PEG-terminated PDMS (PDMS-PEG, 400 cSt – Gelest Inc.)
- fluorinated PDMS (PDMS-F, 80-120 cSt – Gelest Inc.)

The polymers were pipetted over the samples in order to completely cover the surface, then, a quartz cover was placed over the Petri dish and the samples were irradiated with a medium-pressure UV lamp (1 kW mercury lamp, UVAPRINT HPV, Hönle AG, Germany) (see experimental setup in Figure 57). The working distance was 20 cm, the samples were illuminated for 30 minutes. The remaining, nongrafted polymer was removed with toluene, and samples were cleaned in ethanol and dried.

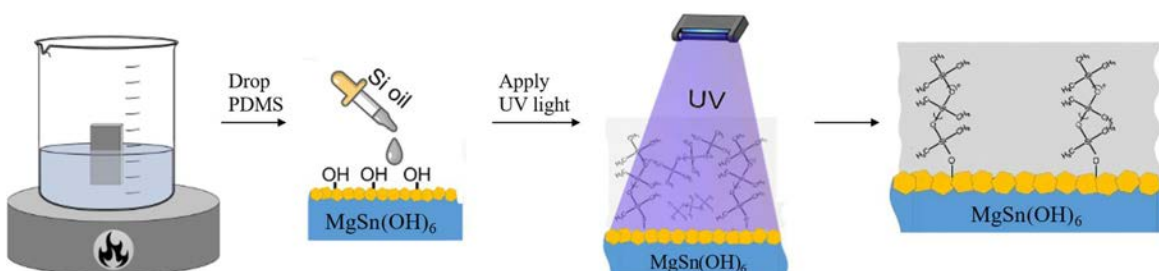


Figure 57. UV grafting setup adopted for polymer deposition.

To mimic physiological conditions, the chosen testing electrolyte was the Kokubo solution, prepared in our laboratory according to [176] (composition in Table 2). Temperature of the electrolyte was maintained at 37 °C for both electrochemical and hydrogen evolution tests.

4.3.2 Results and Discussion

To achieve further functionalization to the $\text{MgSn}(\text{OH})_6$ surface formed through the conversion coating process, PDMS molecules were UV-grafted (see structural formulas in Figure 58).

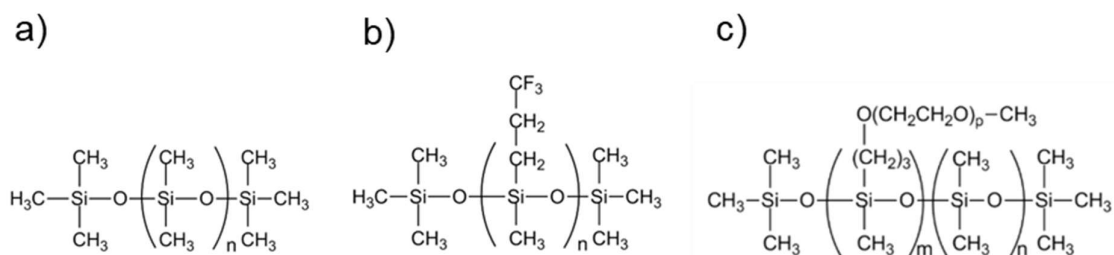


Figure 58. Structural formulas of a) PDMS, b) PDMS-F and c) PDMS-PEG molecules.

Plain PDMS imparts a highly hydrophobic behavior to the surface, effectively avoiding contact between the electrolyte and the underlying metallic substrate. The formation of a PDMS layer on the AZ31 alloy via UV-induced grafting represents a simple and nondestructive approach, which can be efficiently employed as a sealing step following the first hydroxystannate conversion coating [58].

The morphology of the samples was analyzed by SEM (Figure 59). The underlying hydroxystannate conversion coating consisted of compact, closely packed spherical particles as previously shown. After the UV-grafting treatment, SEM imaging confirmed that the morphology of the conversion coating was preserved: PDMS formed a continuous ultrathin film conformally wrapping the MgSn(OH)_6 spheres without altering their geometry (Figure 59e-j and 60).

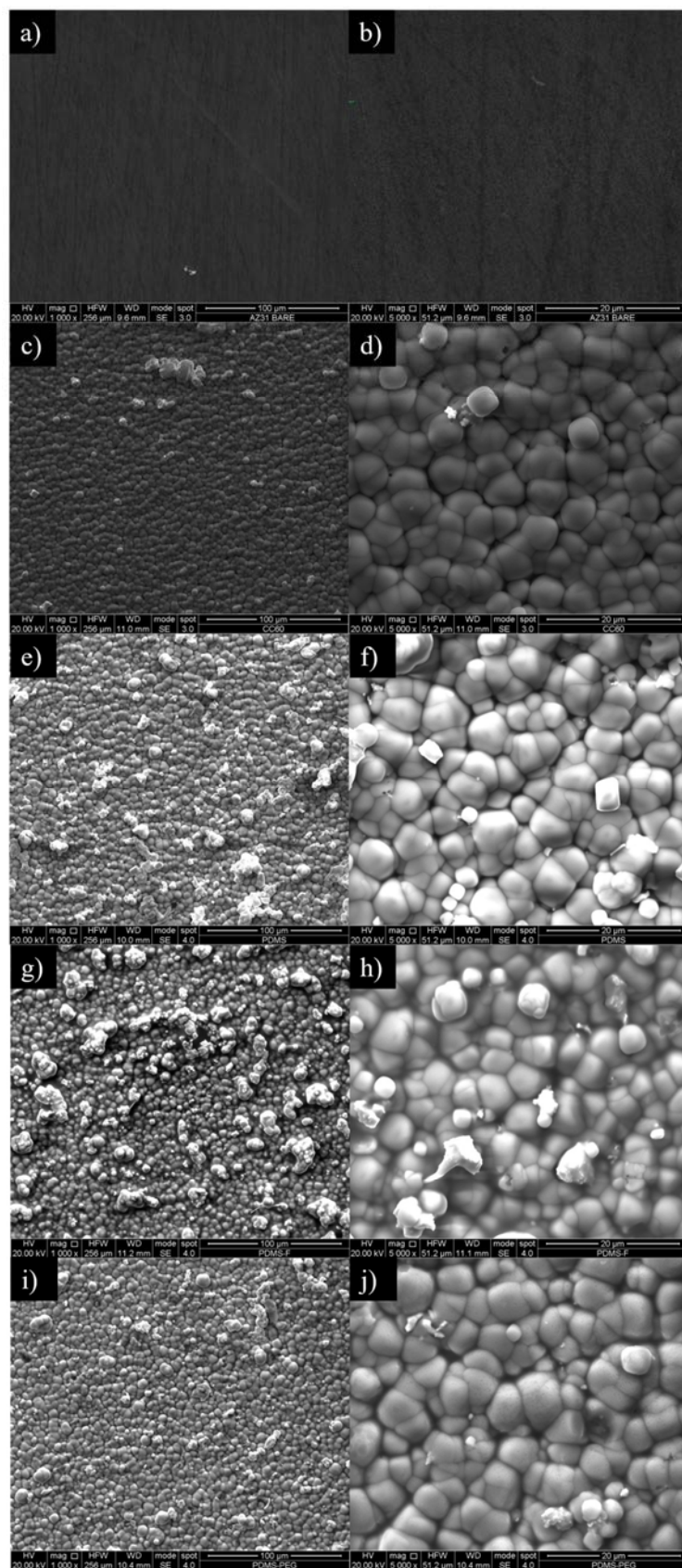


Figure 59. SEM images related to a, b) bare AZ31, c, d) CC60 sample and after the UV grafting of e, f) PDMS, g, h) PDMS-F and i, j) PDMS-PEG.

At higher magnification, thin polymeric bridges were observed between adjacent particles, filling interstitial spaces and sealing the porous paths through which the electrolyte could reach the metallic substrate, as shown for PDMS covered samples in Figure 60. This sealing effect is expected to significantly decrease the accessibility of aggressive ions to the AZ31 alloy.

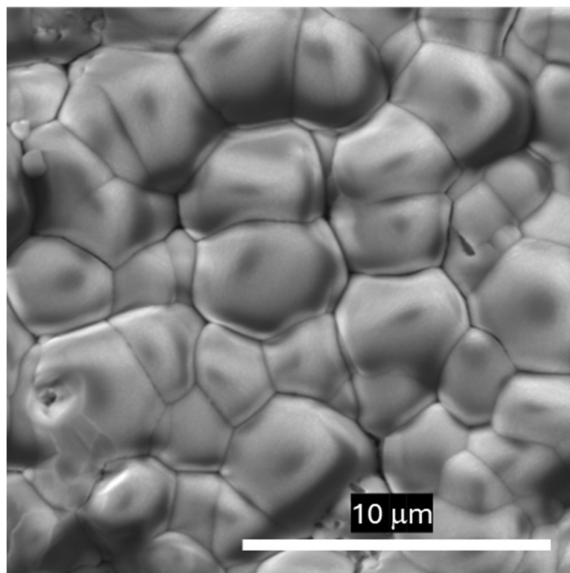


Figure 60. SEM image of PDMS thin layer grafted on MgSn(OH)_6 spheres.

EDX analyses reported in Table 12 confirm the presence of silicon-based molecules on the surface, indicated by the detection of characteristic elements including as Si, O, and C. For the PDMS-F-grafted samples, the additional presence of fluorine provides further evidence of the successful grafting of the fluorinated silicone layer.

	At. %	Mg	Al	Zn	O	Sn	C	Si	F
AZ31	91.42	1.94	0.91	5.73	-	-	-	-	-
AZ31/CC60	12.36	-	0.35	73.21	14.08	-	-	-	-
AZ31/CC60/PDMS	9.97	0.09	0.46	69.96	10.91	7.72	0.90	-	-
AZ31/CC60/PDMS-F	4.11	0.06	0.45	34.31	6.67	30.89	4.90	18.63	-
AZ31/CC60/PDMS-PEG	9.38	-	0.40	62.18	8.78	17.82	1.45	-	-

Table 12. EDX analysis related to AZ31 sample reported in Figure 58 at 5000x of magnitude.

FT-IR spectra confirmed the presence of grafted PDMS molecules (Figure 60). A broad absorption band spanning $2800\text{--}3600\text{ cm}^{-1}$, together with a signal at 1175 cm^{-1} , is associated with O–H stretching vibrations and lattice-related modes, respectively, while absorptions observed in the $500\text{--}1000\text{ cm}^{-1}$ region originate from Mg–O and Sn–O stretching vibrations [177]. The appearance of distinct bands at 1258 , 1083 , 1014 , and 788 cm^{-1} provides clear evidence of PDMS on the surface. In particular, the band at 1258 cm^{-1} and the shoulder near 788 cm^{-1} are attributed to CH_3 deformation and rocking modes of the Si– CH_3 groups, whereas the bands at 1083 and 1014 cm^{-1} correspond to asymmetric stretching of the Si–O–Si backbone [58,177]. Additionally, symmetric and asymmetric CH_3 stretching vibrations are observed at 2902 and 2961 cm^{-1} , respectively, as shown in Figure 61. For the PDMS-F-modified samples, the emergence of a band at approximately 1210 cm^{-1} indicates the incorporation of $-\text{CF}_3$ groups [163]. Similarly, PDMS-PEG-grafted surfaces exhibit characteristic absorptions near 1250 and 1100 cm^{-1} , which are consistent with C–O–C stretching vibrations and confirm successful PEG grafting [178].

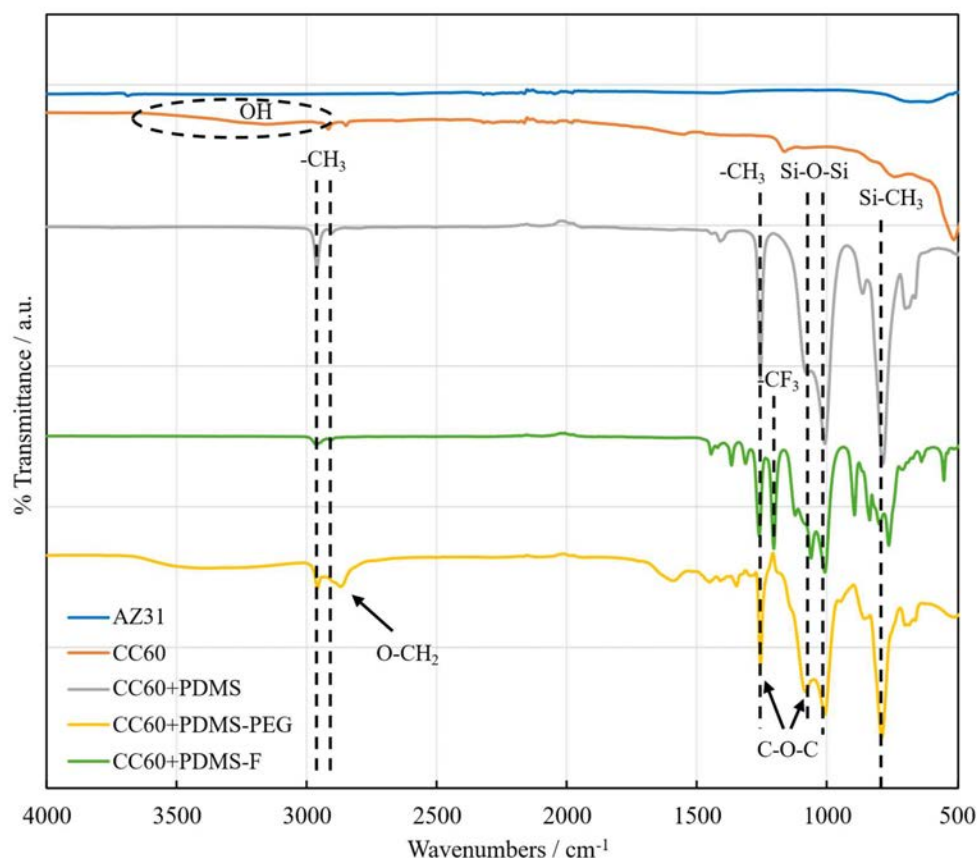


Figure 61. FT-IR spectra related to AZ31 sample after different surface treatments.

The presence of silicon oil with different side chains on the surface leads to changes in surface wettability, which in turn can be used to modulate the corrosion rate. Figure 62 reports the static water contact angles measured on AZ31 samples after different surface treatments.

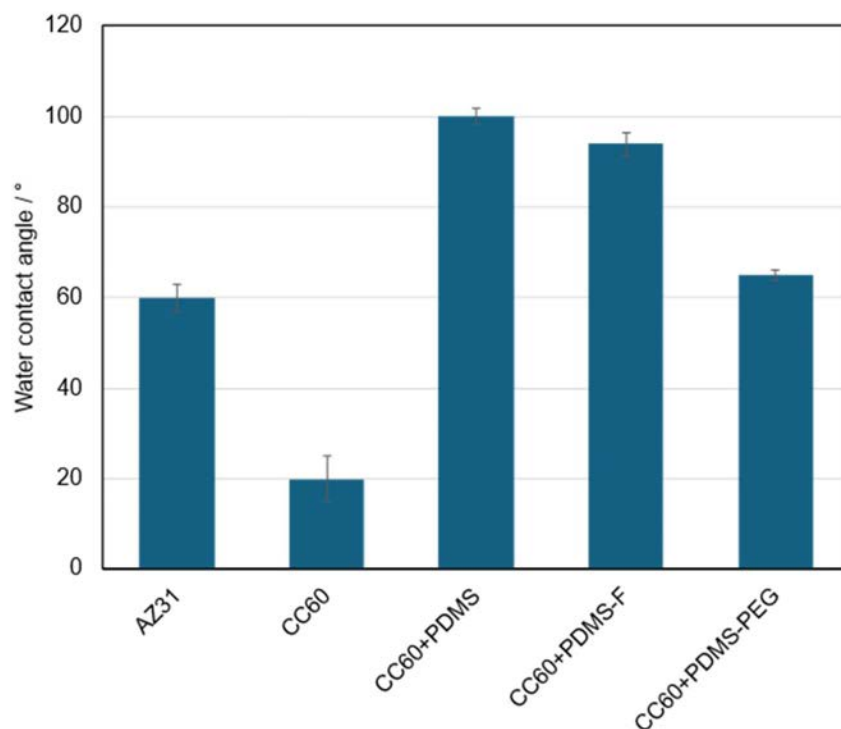


Figure 62. Water contact angle measured for AZ31 sample after different surface treatments.

The untreated AZ31 substrate shows a relatively low contact angle, reflecting the inherently high surface energy of magnesium alloys and the presence of a native oxide/hydroxide layer that favors hydrophilicity. Following the stannate-based chemical conversion treatment, the contact angle decreases significantly, due to the formation of a surface enriched in –OH functional groups. Grafting silicon molecules onto the conversion coating increases the contact angle: after PDMS-PEG grafting the angle reaches 65°, which can be attributed to the polar and hydrogen-bond-accepting nature of its side chain, whereas surfaces modified with PDMS or PDMS-F exhibit pronounced hydrophobicity.

Cytotoxicity tests were conducted to evaluate the compatibility of the stannate conversion coating and the silicon-based surface modifications for biomedical applications. As shown in Figure 63, cell viability is expressed as a percentage relative to the control, which consists of cells cultured in standard medium. After 24 hours of incubation, all treated samples retained viabilities above 70%, indicating that none of the coatings caused cytotoxic effects.

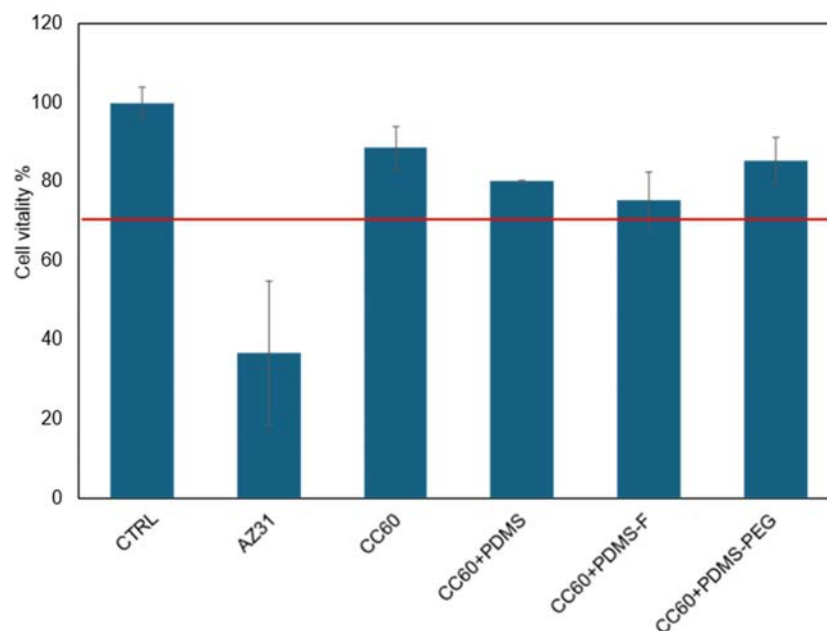


Figure 63. Cell viability after 24 of treatment with normal medium (CTRL) or with treated-AZ31 conditioned medium.

In order to compare AZ31 samples with conversion coating only, and with the three different grafted polymer, EIS measurements and PDP curves were collected in Kokubo solution. The EIS data were recorded at the respective open-circuit potentials and are presented in Bode plots in order to better visualize the differences between samples with varying frequency. EIS spectra, along with the corresponding polarization curves, are displayed in Figure 64. These electrochemical results provide insight into the corrosion resistance imparted by the various surface modifications under simulated physiological conditions.

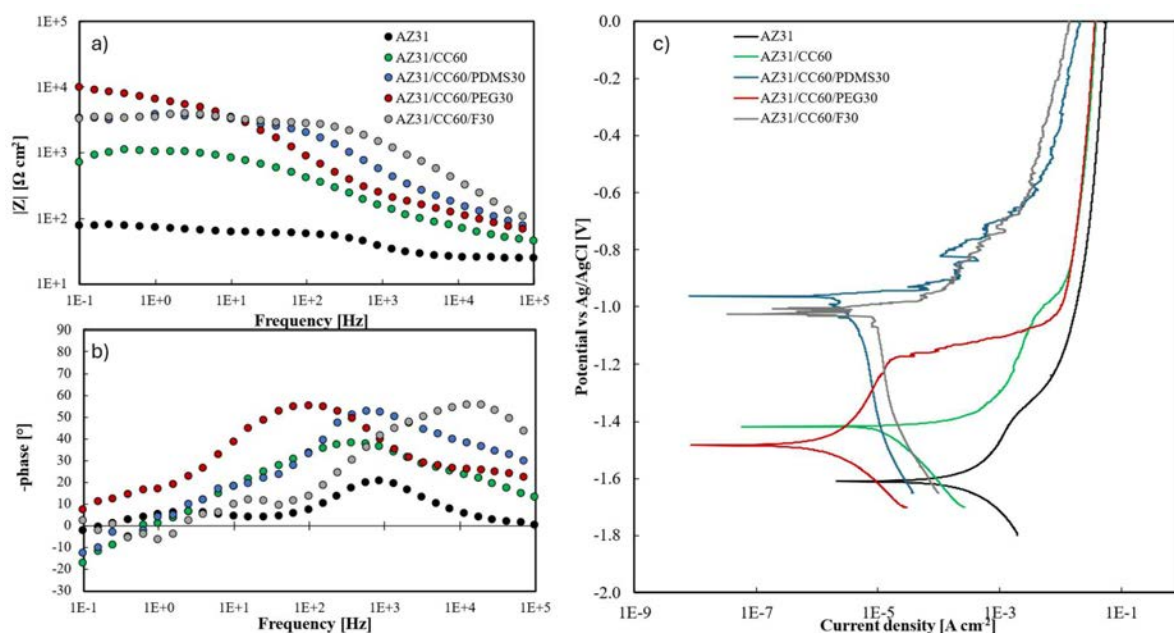


Figure 64. a, b) EIS spectra and c) polarization curves recorded in Kokubo solution at 37°C.

The impedance modulus plots shown in Figure 64a highlight distinct differences in overall impedance, indicating the significant impact of surface treatment on electrochemical behavior. The untreated AZ31 sample displays the lowest overall impedance reflecting active corrosion limited surface stability in the electrolyte. Following the stannate conversion treatment, the CC60 sample exhibits a notable increase in low-frequency impedance, suggesting the formation of a protective layer. Samples functionalized with PDMS display an additional rise in overall impedance. The increased complexity of these surfaces often results in EIS spectra that would require highly intricate equivalent circuit models with numerous elements, which may provide limited physical insight. Therefore, in this study, the EIS results are interpreted qualitatively rather than through detailed circuit modeling.

The trends observed in the EIS spectra are consistent with the contact-angle measurements, indicating that the organic molecules effectively hinder electrolyte diffusion through the hybrid inorganic–organic system, thereby enhancing corrosion resistance in a physiological environment.

Figure 64c shows the PDP curves of AZ31 in Kokubo's solution. The bare AZ31 sample displays highly active behavior, characterized by a negative corrosion potential and elevated anodic and cathodic current density, reflecting rapid magnesium dissolution and hydrogen evolution. The stannate conversion coating shifts the corrosion potential toward more noble values and significantly lowers the corrosion current densities in both anodic and cathodic branches. Grafting with PDMS molecules further decreases the current density, with the degree of protection dependent on the

terminal functional group. The lowest current densities are observed for the most hydrophobic PDMS-modified surfaces, consistent with the contact-angle and EIS findings.

Traditional electrochemical methods, such as Tafel extrapolation, are commonly used to evaluate corrosion kinetics. However, for magnesium-based materials, these approaches often underestimate the actual degradation rate, primarily because of the negative difference effect. Given these limitations, measuring hydrogen evolution through gas chromatography provides a more direct and reliable assessment of the degradation behavior of magnesium alloys in physiological environments.

Figure 65 shows the measured H_2 evolution rates for all samples.

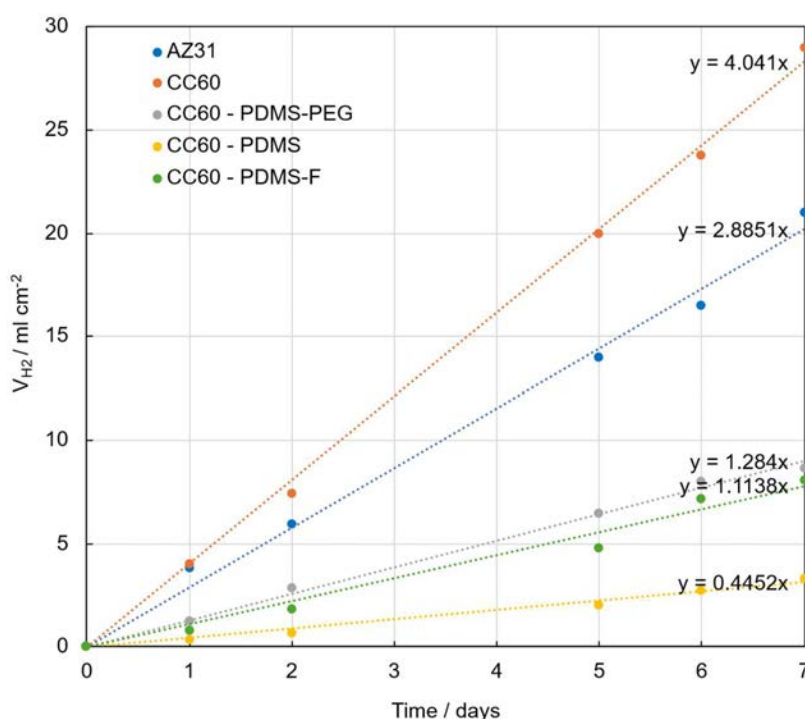


Figure 65. Hydrogen evolution as a function of time in Kokubo's solution evaluated with GC measurements.

The results indicate that the hydrogen volume measured by gas chromatography is strongly affected by the different surface treatments. The hydrogen evolution rate, estimated from the slope of the curves, shows that the presence of PDMS molecules enhances corrosion resistance. Specifically, PDMS-modified AZ31 samples exhibit a hydrogen evolution rate approximately one order of magnitude lower than that of AZ31 samples treated only with the chemical conversion coating.

The morphology of AZ31 samples was studied by scanning electron microscopy and EDX analysis even after 7 days of immersion in physiological media and the results are shown in Table 13 and Figure 66.

At. %	Mg	Al	Zn	O	Sn	C	Si	Ca	Cl	P
AZ31	7.61	4.23	0.47	55.66	-	16.15	-	6.32	-	9.56
AZ31/CC60	12.96	-	0.17	66.13	6.94	11.69	-	1.18	-	0.94
AZ31/CC60/PDMS	9.23	0.25	0.28	68.43	10.55	9.35	0.27	0.97	0.08	0.58
AZ31/CC60/PDMS-F	9.69	0.20	0.44	68.28	9.93	9.51	0.35	0.86	0.17	0.58
AZ31/CC60/PDMS-PEG	19.87	-	0.29	64.67	3.35	9.98	0.22	0.35	1.06	0.21

Table 13. EDX analysis in atomic percentage (at.%) related to AZ31 sample reported in Figure 66 at 1000x of magnitude.

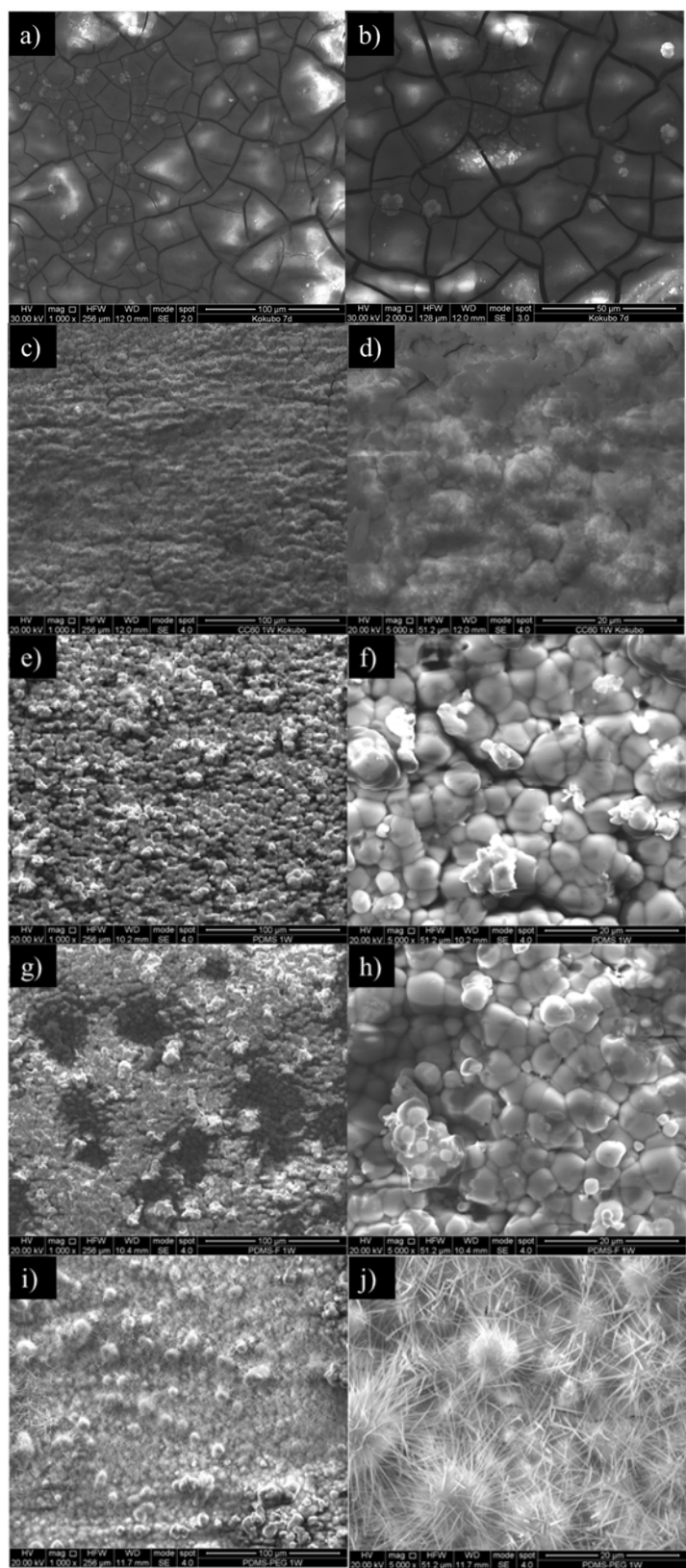


Figure 66. SEM images related to a, b) bare AZ31, c, d) CC60 sample and after the UV grafting of e, f) PDMS, g, h) PDMS-F and i, j) PDMS-PEG after 7 days of immersion in Kokubo's solution.

The bare AZ31 substrate (Figure 66a, b) after 7 days of immersion in Kokubo's solution, displays a characteristic "mud-like" structure, corresponding to the formation of a calcium- and phosphorus-rich corrosion product layer [179,180], as confirmed by EDX analysis (Table 13).

The CC60 sample (Figure 66c, d) shows partial surface damage following immersion. Although the Sn-containing coating remains, it exhibits visible cracking. EDX data (Table 13) also reveal the deposition of calcium- and phosphorus-containing corrosion products.

By contrast, the PDMS-grafted surface (Figure 66e, f) shows the lowest degree of degradation among all samples. The surface remains relatively compact and homogeneous, with no significant cracks, consistent with the hydrogen evolution rates and electrochemical characterizations. These observations suggest that PDMS forms a uniform, stable polymer layer that effectively shields the substrate from corrosion. The PDMS-F sample (Figure 66g, h), however, presents surface cracks and a pronounced light-dark contrast in the SEM images. This contrast suggests non-uniform polymer degradation, exposing localized areas of the underlying substrate and reducing corrosion protection relative to PDMS. On surfaces with comparable composition and irregular morphology, such as the conversion layers, a less viscous fluid like PDMS-F likely spreads more quickly. Consequently, during UV irradiation there is less time to crosslink locally, resulting in a less uniform coating compared to a more viscous polymer. Finally, the PDMS-PEG sample (Figure 66i, j) exhibits extensive surface damage after 7 days of immersion. EDX analysis reveals exposure of the underlying conversion layer, with the surface largely covered by corrosion products. This behavior suggests that, despite an initially high overall impedance, the amphiphilic nature of PDMS-PEG and the presence of side chains hinder effective and uniform grafting, ultimately leading to limited corrosion protection during immersion in Kokubo's solution.

4.3.3 Conclusions

In this study, a hybrid inorganic-organic surface modification strategy was developed to tailor the corrosion behavior of AZ31 magnesium alloy for biodegradable implant applications. A MgSn(OH)_6 hydroxystannate conversion coating was successfully formed on AZ31 and subsequently functionalized via UV grafting of silicon-based molecules with different side chains on a common siloxane backbone. SEM, EDX, and FT-IR analyses confirmed the successful grafting of PDMS, PDMS-F, and PDMS-PEG molecules onto the conversion layer.

The grafted silicone layers strongly influenced surface wettability and, consequently, the corrosion behavior in Kokubo's solution. Electrochemical measurements, hydrogen evolution tests, and long-

term immersion studies consistently showed that hydrophobic PDMS and PDMS-F coatings effectively restricted electrolyte diffusion, substantially enhancing corrosion resistance and reducing the hydrogen evolution rate by approximately one order of magnitude compared to the conversion-coated alloy. In contrast, the amphiphilic PDMS-PEG coating exhibited lower stability over prolonged immersion. The hydrophilic PEG chains likely facilitated electrolyte uptake and ion transport, promoting penetration of aggressive species and accelerating degradation of the underlying hydroxystannate layer after one week. Although fluorinated compounds are chemically persistent and may raise environmental concerns, in the applications presented in this chapter only small amounts are used, and the polymer is covalently grafted to the surface, minimizing the risk of leaching. Therefore, PDMS-F may provide performance benefits with a controlled and limited environmental impact, while future work could explore fluorine-free alternatives for broader sustainability considerations. All surface-treated samples demonstrated good cytocompatibility, indicating the absence of toxic effects associated with both the conversion coating and the grafted silicone molecules. Overall, these findings demonstrate that UV-grafting of tailored silicon molecules onto hydroxystannate conversion coatings provides a versatile and effective approach to control the degradation kinetics of magnesium alloys. By selecting appropriate organic functional groups, the corrosion rate of AZ31 can be finely tuned, offering promising perspectives for the design of next-generation bioresorbable magnesium-based implants.

5 A Semiempirical Model for Predicting Magnesium Alloy Biodegradation

The biodegradation of magnesium alloys in physiological environments results from the concurrent action of electrochemical dissolution, surface film precipitation and breakdown, ionic transport and evolving local chemistry. As demonstrated in the previous chapters, the degradation rate of AZ31 depends strongly on the electrolyte composition and on the presence of surface treatments that influence the stability of corrosion layers. Predicting the long-term corrosion behavior of magnesium remains challenging, as the dissolution rate seldom follows simple analytical laws and evolves dynamically with immersion time. Mechanistic modelling approaches, which incorporate ionic migration, buffer equilibria, film growth/dissolution and pH changes, can in principle capture these processes in detail, but require many input parameters that are difficult to measure experimentally and often lead to computationally demanding simulations. On the other hand, empirical fits based solely on mass loss or hydrogen evolution provide limited mechanistic insight and cannot be readily applied to complex geometries such as orthopedic implants.

In this chapter, a semiempirical model is developed to predict the biodegradation kinetics of AZ31 and its mechanical implications. The approach is simple and fully grounded in experimentally accessible quantities. Hydrogen evolution measurements are converted into material loss, and the resulting degradation profile is interpolated using a power-law function. This function is then used to generate geometrically degraded implant models through a surface-offset procedure, which realistically reproduces uniform material loss without distorting the internal features of the implant. These degraded geometries are finally analyzed through finite element modelling (FEM) to determine how corrosion progression affects the mechanical performance of the device.

The method is additionally extended to a conversion-coated alloy (CC60), allowing assessment of the protective duration of the coating and its influence on structural integrity. Overall, the chapter integrates electrochemical kinetics, geometric modelling and mechanical analysis into a unified predictive framework.

5.1.1 Additional Experimental Details

Hydrogen evolution measurements were acquired by gas chromatography during static immersion of AZ31 samples in four physiological solutions: NaCl 0.9 wt.%, HBSS, Kokubo and DMEM. At each immersion time, the accumulated hydrogen volume was converted into moles of gas through the ideal gas law. Because magnesium dissolution proceeds predominantly via the Mg oxidation / hydrogen evolution reaction, one mole of hydrogen corresponds to one mole of magnesium dissolved. This allowed extraction of the mass and volume of magnesium lost at each time point, using the density of bulk AZ31.

For each electrolyte, the resulting degradation points were fitted with a power-law function of the form:

$$\Delta m(t) = at^b \quad (17)$$

which provided a continuous representation of mass loss over 180 days.

The model of an orthopedic fibula plate was created and subjected to a simulated four-point bending test, in accordance with ASTM F382 [181]. The test was performed using finite element analysis (FEA) software to simulate static structural conditions. Multiple geometric variations of the 3D model were tested to assess the plate's mechanical properties over its expected service life. The design of the fibula plate was based on a simplified version of commercially available plates [182–184], with the dimensions and bending test parameters detailed in Figure 67.

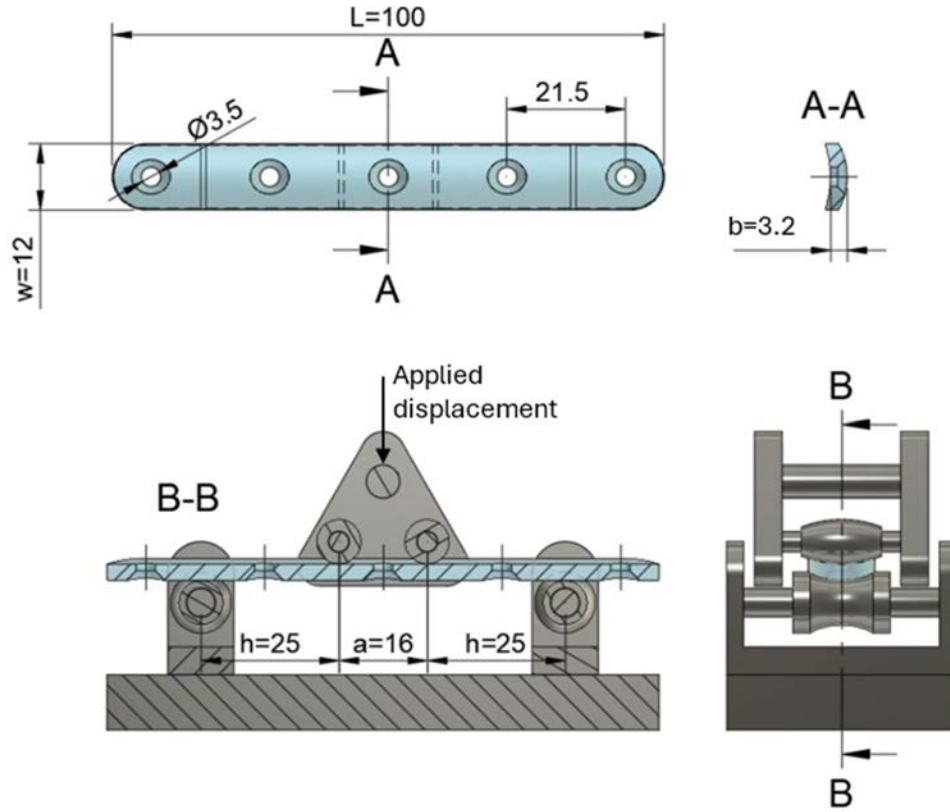


Figure 67. Fibula plate dimensions and four-point bending test setup as described in ASTM F382 (length are expressed in *mm*).

A high-resolution three-dimensional model of the plate was generated and used to construct degraded geometries corresponding to selected volume fractions. Instead of uniformly scaling the model, which would artificially shrink internal features such as screw holes, the external surface of the implant was offset inward along its normal directions. A parametric offset was applied and iteratively adjusted until the total volume of the modified plate matched the target volume fraction derived from the power-law degradation curve. Finite element simulations were performed in ANSYS using tetrahedral 0.2 mm elements, resulting in more than 130000 elements with an average skewness of $S_{avg}=0.43$. Material properties for AZ31 were taken from the software database (see table 14).

Material properties		
Density	1770	kg m ⁻³
Young's Modulus	45	GPa
Poisson's Ratio	0.35	
Bulk Modulus	50	GPa
Shear Modulus	17	GPa
Yield Strength	193	MPa
Tangent Modulus	920	MPa

Table 14. AZ31 mechanical properties adopted in the FEM model.

The bending strength and bending structural stiffness were calculated according to the ASTM F382 four-point bending guidelines, and compared to the required FDA thresholds (2.3 N·m for bending strength and 0.17 N·m² for stiffness – see table 15).

1. **Test name:** Static Four-Point Bending
Methodology: FDA-recognized version of ASTM F382 *Standard Specification and Test Method for Metallic Bone Plates*. The worst-case bone plate(s) for each anatomic region should be selected for mechanical testing.
Performance Criteria:

Intended Anatomical Location of Bone Plate		Minimum Bending Strength (N·m)	Minimum Bending Structural Stiffness (N·m ²)
Upper Extremity	Humerus	11.6	4.39
	Elbow (Distal Humerus and Ulna)	6.7	0.89
	Hand, Wrist and Forearm	1.6	0.18
Lower Extremity	Femur & Proximal Tibia	26.3	8.66
	Distal Tibia	11.9	3.49
	Fibula	2.3	0.17
	Foot	1.2	0.13
Other	Clavicle	11.9	1.69

Table 15. Static Four-Point Bending thresholds according to FDA.

In order to do so, a simulated 4-point bending test was modeled in the software, adopting suitable boundary conditions (see inset in figure 68).

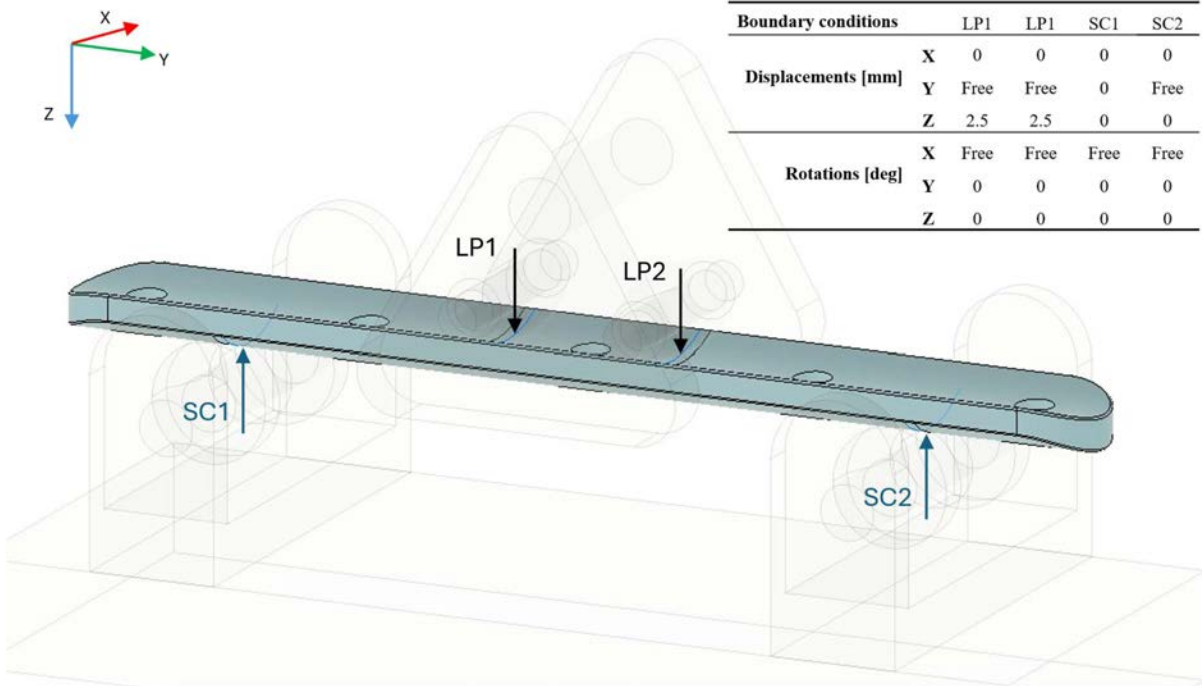


Figure 68. Boundary condition adopted in the 4P bending test.

For the coated alloy, the CC60 conversion coating thickness ($\approx 5 \mu\text{m}$) previously measured by SEM (Chapter 4) was used as a threshold. Degradation followed the CC60 power-law until the cumulative dissolved thickness reached $5 \mu\text{m}$, after which the degradation rate switched to that of bare AZ31 in the same electrolyte.

5.1.2 Results and Discussion

The hydrogen evolution measurements showed significant differences among the four electrolytes. Kokubo induced the fastest degradation, with a rapid increase in hydrogen volume during the first days of immersion. NaCl 0.9 wt. % exhibited intermediate behavior, while HBSS and DMEM produced slower corrosion kinetics. The interpolated power-law functions accurately reproduced these trends in figure 69, allowing prediction of material loss in the first weeks after implantation.

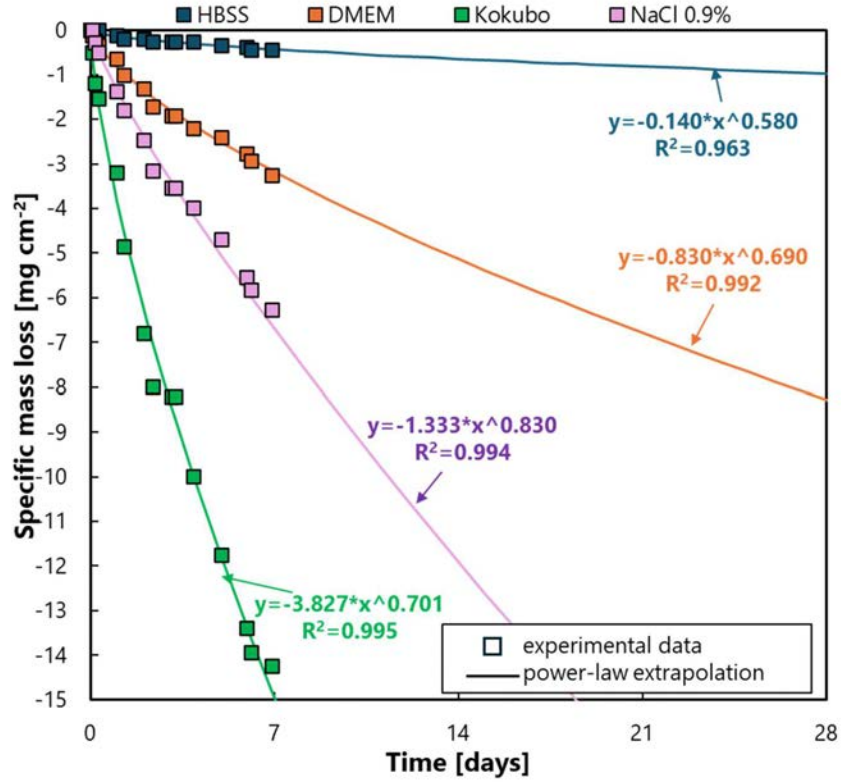


Figure 69. Specific mass loss calculated for the first 28 days from H₂ evolution data reported in figure 28.

The volume fractions corresponding to the selected degradation levels were extracted directly from the fitted power-law curves. The results reflect the stabilizing influence of organic components in DMEM and the aggressive behavior of Kokubo, which lacks buffering mechanisms and promotes rapid Mg dissolution.

The parametric surface-offset procedure successfully generated degraded geometries corresponding to the experimentally derived volume fractions. This approach preserved the topology of the implant and maintained realistic evolution of screw holes and internal channels. Mechanical simulations revealed a progressive reduction in bending strength as degradation increased, while the original intact plate exceeded the FDA bending strength requirement for fibula plates (see table 16 below).

Offset	Volume	Bending	Bending Structural
[mm]	[%]	Strength [N·m]	Stiffness [N·m ²]
0.000	100.00	2.74	1.30
-0.001	99.91	2.74	1.29
-0.01	99.05	2.69	1.27
-0.1	90.66	2.23	1.02
Minimum acceptable value		2.3	0.17

Table 16. Mechanical properties of the simulated fibula plate with decreasing resisting volume.

The predicted time at which each electrolyte caused the plate to reach the critical volume fraction was consistent with the electrochemical expectations: rapid failure in Kokubo (<7 days), intermediate performance in NaCl and DMEM, and prolonged survival in HBSS (see figure 70).

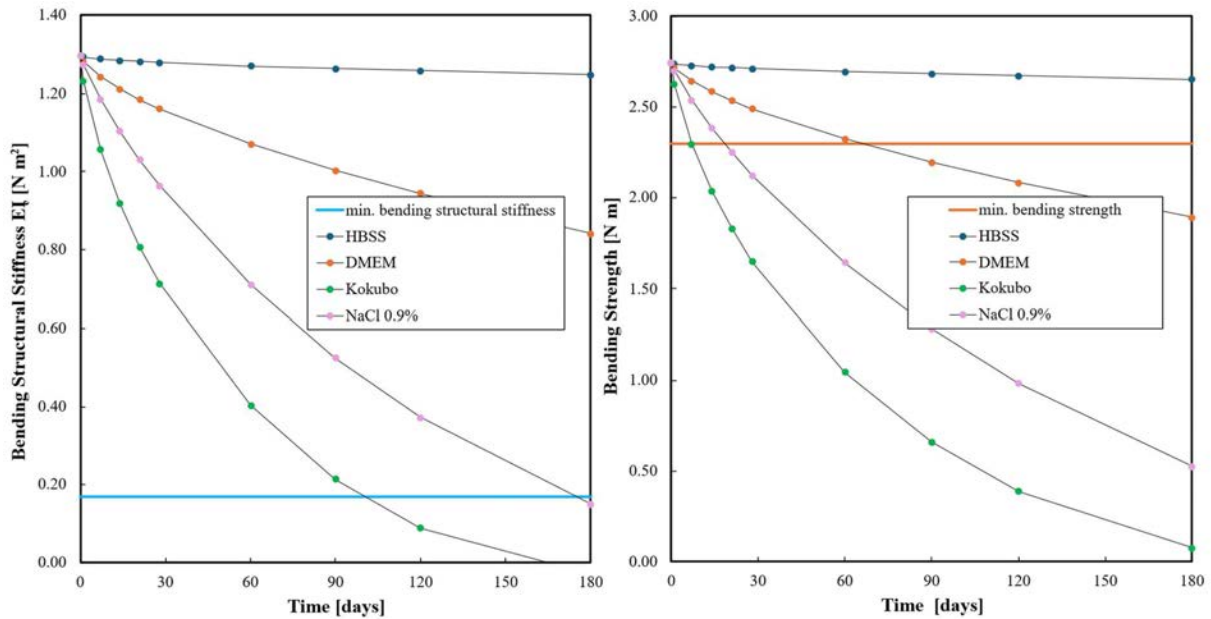


Figure 70. Estimated mechanical properties of the simulated fibula plate during 180 days immersion in different solutions.

The CC60-coated alloy exhibited slower early-stage degradation in DMEM, and was studied by applying a two-stage model: initially, the degradation follows the CC60 power-law, until 5 μm of material is dissolved, then switches to AZ31. With such approach, the protective duration of the coating was quantified (figure 71).

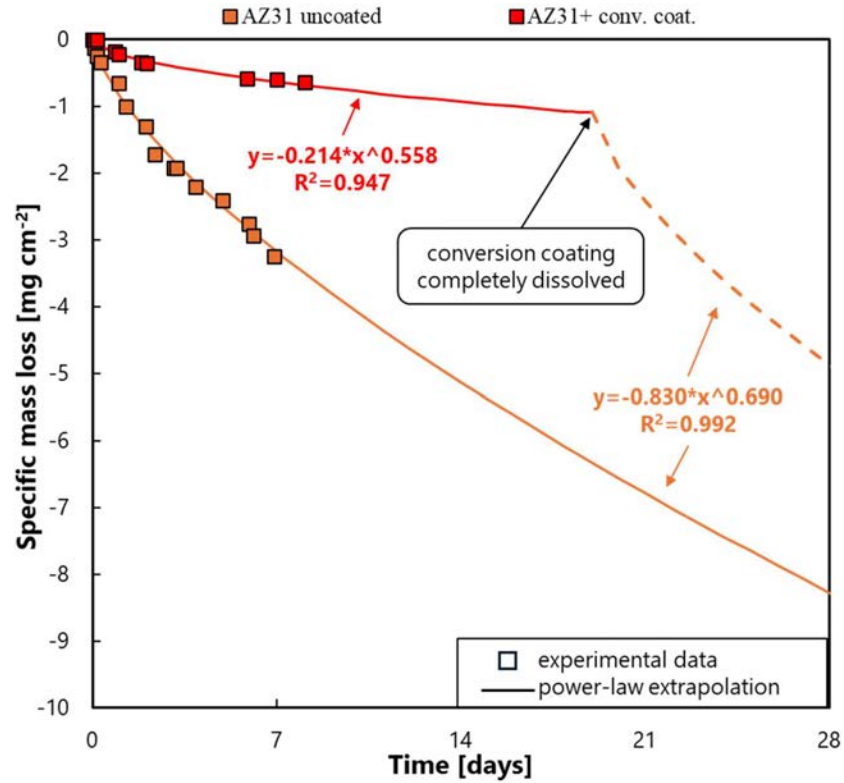


Figure 71. Mass loss of uncoated and CC60 coated samples in DMEM.

The coating prolonged the time required to reach critical volume loss by approximately two weeks compared to bare AZ31 in the same solution (see figure 72). FEM analysis of CC60-based degraded geometries showed that the coated plate retained acceptable bending strength for longer immersion times in DMEM, highlighting the beneficial effect of the coating on implant lifespan during the early postoperative period.

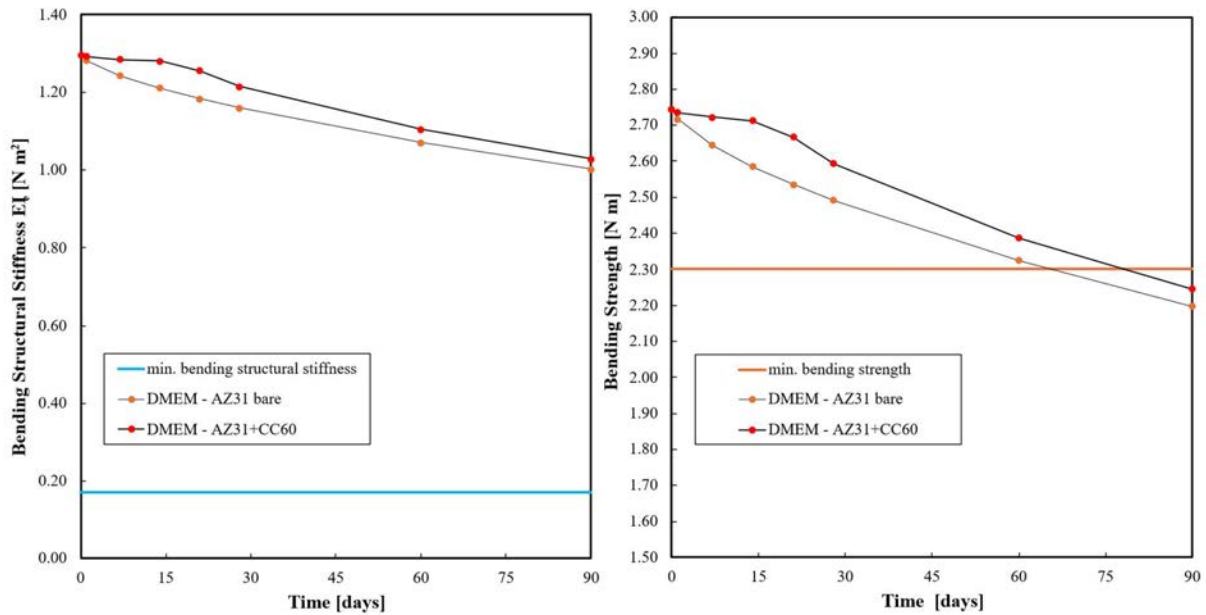


Figure 72. Estimated mechanical properties of the simulated fibula plate, with and without the stannate based conversion coating, during 90 days immersion in DMEM.

Overall, these findings demonstrate the ability of the semiempirical model to integrate electrochemical kinetics with structural performance and to capture the influence of surface treatments on implant degradation.

5.1.3 Conclusions

A semiempirical model for predicting the biodegradation of AZ31 was developed by combining hydrogen evolution measurements, power-law interpolation and finite element analysis. The model successfully translates experimental dissolution data into meaningful predictions of material loss, which are then used to generate geometrically consistent degraded implant models through a surface-offset method. Although the simulated data closely match the experimental results, the duration of the immersion test used as reference limits the applicability of the model: a longer-term experimental campaign, considering different coatings and their degradation mechanisms, would enhance both the usefulness and applicability of the model. Mechanical simulations performed on these geometries demonstrate how corrosion progression affects the bending performance of an AZ31 fibula plate under physiological conditions. The model captures the different degradation behaviors of the four tested electrolytes and quantifies the protective effect of the CC60 conversion coating. This approach

provides a practical framework for assessing implant lifetime, comparing surface treatments and guiding the early design of biodegradable magnesium devices.

6 Conclusions

The work presented in this thesis explored the biodegradation behavior of AZ31 magnesium alloy in physiological environments and demonstrated how electrochemical and chemical strategies can be used to tune surface corrosion kinetics for biomedical applications. By integrating experimental electrochemistry, morphological characterization, surface functionalization and semiempirical modelling, this study provides a comprehensive view of the relationships between electrolyte composition, surface chemistry and long-term mechanical performance.

The systematic investigation of degradation in four simulated physiological solutions revealed that the corrosion behavior of AZ31 is strongly medium-dependent. HBSS promoted the precipitation of protective phosphate layers, resulting in limited hydrogen evolution and predominantly general corrosion. DMEM, owing to its organic components and buffering species, moderated the early corrosion rate and produced uniform surfaces with minimal particle agglomeration. In contrast, Kokubo and saline solutions led to more aggressive attack: the former due to limited buffering capacity and insufficient phosphate availability, and the latter due to the absence of stabilizing ions. After corrosion product removal, SEM analysis highlighted the transition from general corrosion (HBSS, DMEM) to strongly localized attack (Kokubo, NaCl), demonstrating that the electrolyte composition not only affects the rate of degradation but also its morphology. These results reinforce the necessity of evaluating magnesium alloys in multiple relevant media, as no single simulated body fluid can reproduce all features of the physiological environment.

Building on these findings, Chapter 4 explored a set of surface engineering strategies aimed at modulating AZ31 degradation. Stannate-based conversion coatings successfully formed MgSn(OH)_6 layers with a characteristic spherical morphology and thickness of approximately 5 μm . Although inherently porous, these coatings altered the surface chemistry and significantly influenced the early corrosion response. Their role as substrates for further functionalization was subsequently demonstrated through two distinct approaches. First, manganese stearate electrodeposition produced hydrophobic and superhydrophobic films capable of suppressing the inductive loop associated with hydrogen evolution and markedly increasing overall impedance. The coating decreased early hydrogen release by more than an order of magnitude and maintained cytocompatibility over 48 hours. Second, UV-grafting of PDMS and functional derivatives (PDMS-F, PDMS-PEG) produced ultrathin polymeric films conformally wrapping the MgSn(OH)_6 spheres and sealing interstitial

pathways. Despite the hydrophobic behavior expected from PDMS-based systems, the PEG-terminated variant, nominally hydrophilic, offered the best corrosion protection, highlighting the role of molecular uniformity and polymer–substrate interactions. All grafted surfaces exhibited good cytocompatibility, further supporting their biomedical relevance. Collectively, these results demonstrate that surface chemistry is a powerful and tunable lever for controlling magnesium degradation, and that properly designed coatings can address both corrosion and biological performance.

In Chapter 5, a semiempirical model was developed to bridge the gap between electrochemical dissolution and structural integrity of real implants. Hydrogen evolution data were converted into mass loss and interpolated using power-law expressions to derive continuous degradation profiles in each electrolyte. These profiles enabled the construction of geometrically consistent degraded models of an AZ31 fibula plate through a surface-offset procedure that preserves topology and internal features. Finite element simulations showed that even modest reductions in volume can lead to significant decreases in bending performance, defining a time-dependent window of mechanical reliability. When applied to the CC60-coated alloy, the model reproduced the two-stage degradation behavior, initially governed by the coating, then by the bare substrate, and quantified the extension of mechanical functionality provided by the coating. This simple modelling framework effectively integrates electrochemical kinetics with mechanical performance and provides a practical tool for evaluating implant lifespan and for guiding material and surface design.

Overall, this thesis demonstrates that the biodegradation of AZ31 in physiological environments is not an intrinsic material property but the result of a complex interplay between medium composition, surface state and time-dependent electrochemical reactions. Surface engineering, through both inorganic and polymeric coatings, offers powerful means to tune this interplay, enabling control over corrosion rate, morphology and biological response. The semiempirical model developed herein further provides a quantitative link between dissolution kinetics and mechanical integrity, paving the way toward predictive design of biodegradable implants.

While the experimental setup was designed to reproduce conditions as close as possible to the real implant environment, further optimization can still be adopted. Extending the immersion time would provide additional insight into the long-term applicability of the predictive model. Moreover, the present study was conducted exclusively under static conditions. In vivo, however, fluid dynamics can significantly influence coating behavior, particularly in cardiovascular stents, but also in orthopedic applications. These aspects may affect corrosion and degradation mechanisms. Improvements to the experimental protocol addressing dynamic conditions have already been

planned and will follow a systematic approach similar to that proposed by Zheludkevich et al. for corrosion studies under controlled flow conditions [185].

7 Scientific output

Publications in International Journals

Chemical and electrochemical surface treatments to grow magnesium hydroxystannate/manganese stearate coating for tuning biodegradation rate of AZ31 for bioresorbable implants. **V. Verro**, F. Di Franco, F. Carfi Pavia, F. La Monica, M. Santamaria. *Electrochimica Acta* 525 (2025) - <https://doi.org/10.1016/j.electacta.2025.146159>.

A Semiempirical Model for Predicting Magnesium Alloy Biodegradation in Simulated Body Fluids: Influence of Electrolyte Composition and Implant Geometry.

V. Verro, F. Di Franco, D. Pupillo, M. Santamaria. *Electrochimica Acta* - <https://doi.org/10.1016/j.electacta.2025.148093>.

Other papers

Biodegradation Control of AZ31 Magnesium Alloy through UV-Grafted Silicon on Hydroxystannate Conversion Coatings. D. Pupillo, **V. Verro**, F. Di Franco, M. P. Bruns, A.B. Tesler, F. Carfi Pavia, S. Virtanen, M. Santamaria - submitted.

Corrosion behaviour of 316L stainless steels in physiological solutions and under inflammatory conditions. S. Dinolfo, F. Di Franco, **V. Verro**, M. Santamaria - in preparation.

Conference Contributions

Electrochemical processes on metallic bioimplants for tuning their corrosion resistance and for providing specific functionalities. M. Santamaria, D. Pupillo, **V. Verro**, M.L. Lazzara, S. Dinolfo, A. Zaffora, F. Di Franco (76th ISE annual meeting, 7-12 September, Mainz, Germany).

Tuning the biodegradation rate of Mg alloys for bioresorbable implants. M. Santamaria, D. Pupillo, **V. Verro**, G. Tranchida, A. B. Tesler, S. Virtanen, F. Di Franco (75th ISE annual meeting, 18-23 August, Montreal, Canada).

Chemical conversion coatings on AZ31 Magnesium alloys for biodegradable implants. G. Tranchida, **V. Verro**, F. Di Franco, M. Santamaria (Giornate dell'Elettrochimica Italiana (GEI), 17-23 September 2023, Cefalù, Italy).

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