

Investigation of the corrosion behavior of phosphate coated magnesium in a Kokubo Solution.

H. Quintana-Camacho¹, J. L. Ramírez-Reyes¹, A. L. Medina-Almazán³, N. García-Navarro², G. Galicia-Aguilar^{1,*}

¹ Instituto de Ingeniería, Universidad Veracruzana Av. Juan Pablo II s/n Frac. Costa Verde, Boca del Río Ver., C. P. 94294, México.

² Facultad de Ciencias Químicas, Universidad Veracruzana. Av. Venustiano Carranza s/n Col. Revolución, Poza Rica, Ver., C. P. 93396, México.

³ Departamento de Tecnología de Materiales, Instituto Nacional de Investigaciones Nucleares. Carretera México – Toluca s/n, La Marquesa, Ocoyoacac, Estado de México, C. P. 52750, México.

*E-mail: gogalicia@uv.mx

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Magnesium is a biocompatible element. Nevertheless, in order for it to be used as a prosthesis or implant, it is necessary that the organism is able to assimilate it. Thus, it is essential to control its degradation rate. There are two means so as to reach this objective. The former consists in looking for one element to alloy it. As for the latter, a compound precipitation could be induced by means of a chemical conversion treatment. In the present work, we focused on the induction of $Mg_3(PO_4)_2$ precipitation on a Mg surface from a phosphate solution of pH 10. The obtained compound was characterized by means of Scanning Electron Microscopy (SEM), X-Ray diffraction (XRD) and ellipsometry. Corrosion rate (CR) of Mg with the obtained precipitate was measured in a Kokubo solution by means of Linear Polarization Resistance (LPR); the capacitor at the metal-electrolyte interphase was determined using Electrochemical Impedance Spectroscopy (EIS) experimental data by varying the stabilization and exposition time. Results reveal the presence of $Mg_3(PO_4)_2$ and $Mg(H_2PO_4)_2$ on the Mg surface. It is suggested that the presence of MgO and $Mg(OH)_2$ favors the precipitation of $Mg_3(PO_4)_2$ on the surface of pure Mg exposed to a Kokubo solution. In the presence of $Mg_3(PO_4)_2$ precipitate, the CR of Mg in a Kokubo solution decreases in an order of magnitude.

Keywords: Magnesium, Biomaterials, Phosphate Coating.

1. INTRODUCTION

Magnesium and its alloys are appealing materials for the transport industry, mainly due to their

weight/mechanical properties relation. However, in the orthopedic area, some decades ago interest arose within numerous research groups. After iron and oxygen, magnesium is one of the most abundant elements on earth; the second one in the sea and the fourth one in the human body, where it is necessary for metabolic functions [1- 3]. Mg is an element that can be absorbed by the human body; moreover, it is vital for the assimilation and fixation of calcium in bones [3]. Due to the biocompatibility with the human body, its use as a prosthesis or implant could avoid a second surgery. Notwithstanding the advantages, Mg application in the medical area will be limited until a solution is found to its rapid degradation in the human body, which could lead to hemolysis, above all if we consider that one of the main compound in our organism is NaCl 0.9 wt. %. In order to combat this issue, multidisciplinary research groups have proposed new alloys with aluminum, calcium, zinc, manganese, cadmium, bismuth among other elements [3, 5]. Nonetheless, some of these alloys present possible risks to health, such as aluminum, which is associated with Alzheimer, as well as rare earth elements. In the case of pure Mg, it is important to recognize the need of alloying it to another element so as to increase its mechanical properties while decreasing the CR. Another way of mitigating its rapid metallic degradation is by means of chemical conversion treatments, which are recognized for their practicality and low cost. In the medical area, it is imperative to consider that the coating needs to be biocompatible as well as nontoxic. In the case of Mg, literature reports the use of phosphate based solutions, manganese-phosphate [6], micro arc oxidation as well as hydroxyapatite application [5, 5 – 8]. Some authors [7, 8] report that using a fluoride based conversion coating, the CR of pure Mg was mitigated in a physiological solution of pH 7.4. The EIS values obtained from this treatment are $1.5 \times 10^6 \Omega \text{ cm}^2$ after the first day of exposure and $6 \times 10^6 \Omega \text{ cm}^2$ after the eighth day of exposure, whilst the capacitance values are in the order of $10^{-9} \text{ F cm}^{-2}$. On their behalf, Zhou [9] report a coating of uniform thickness of $1.5 \mu\text{m}$ with the same treatment and impedance values of $5 \text{ K}\Omega \text{ cm}^2$. In [6] it is proposed the use of phosphates as a possible candidate for mitigating the CR of Mg in physiological solutions. The coatings obtained in [9] are typified by a crystal structure and a well-defined flower shape. It is important to recognize that the objective of chemical treatments, as well as alloying, is not to stop CR, but to decrease Mg degradation so that it could be used by the organism. Literature [10] reports storage of 1 g of Mg for a person that weighs 70 Kg, whilst in [2] it is reported a daily consumption of 375 mg. During the corrosion process of Mg, numerous authors agree with the formation of a thin and compact film identified as MgO as well as a porous and low-adherent film of Mg(OH)₂. However, the formation of such compounds depends on the environment where they are formed. In the case of an aqueous media, MgO and Mg(OH)₂ are easily formed; but in air, their formation is a slow process.

In the present article, we obtained and characterized a Mg₃(PO₄)₂ coating precipitated on the surface of Mg by means of a chemical conversion treatment. The CR of the interphase with a Kokubo solution [11] was obtained by means of the LPR technique. In order to determine capacitance behavior, EIS experiments were carried out in the coating as a function of the immersion time. A Kokubo solution is a simulated body fluid (SBF), with ion concentration close to that of human blood plasma.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of pure Mg samples

Samples of 99.97 wt. % Mg of 1.5 x 1.5 x 1 cm were mechanically polished with SiC paper varying from grit 80 to 600. Afterwards, samples were rinsed with distilled water and cleaned by means of ultrasound. Lastly, samples were dried with acetone.

2.2. Precipitation of $Mg_3(PO_4)_2$ coating

The precipitation treatment consisted in the immersion of the Mg samples in a phosphate solution (pH = 10). Such phosphate solution was prepared using 85 wt % phosphoric acid (H_3PO_4), to which it was added 1M sodium hydroxide (NaOH) in order to adjust the pH to 10. Different immersion times were studied (1, 5 and 30 days). During the immersion time, the container was kept closed and temperature was maintained constant at $25\text{ }^\circ\text{C} \pm 1\text{ }^\circ\text{C}$.

2.3. Electrochemical evaluation in a Kokubo solution

For having the ion concentration almost equal to those of human blood plasma, the composition of one liter of Kokubo solution is as follow [12, 13]:

NaCl : 8gr,

NaHCO₃ : 0.35 gr,

KCl : 0.22 gr,

K₂HPO₄ · 3H₂O : 0.23 gr,

MgCl₂ · 6H₂O : 0.21 gr,

1 kmol/m³ HCl : 40 ml,

CaCl₂ : 0.28 gr,

Na₂SO₄ : 0.07 gr,

(CH₂OH)₃CNH₂ : 6.06 gr.

pH was adjusted to 7.25 with 1 mol HCl.

Samples of Mg and Mg with $Mg_3(PO_4)_2$ coating were electrochemically evaluated in a Kokubo solution by EIS technique. Additionally, Mg samples were also evaluated by means of LPR technique. Electrochemical evaluation was carried out using a Bio-logic SP-150 potentiostat coupled to a desk station. LPR electrochemical measurements were performed after two stabilization times, 1 and 24 hours. The employed voltage interval was $\pm 25\text{ mV}/E_{\text{corr}}$ and 0.1667 mV/s was set as the scanning speed.

EIS measurements were carried out at open circuit potential, (E_{corr}), in a frequency range from 30 KHz to 10 mHz with a 10 mV/rms signal perturbation and 7 points per decade. The capacitance of the interphases was determined from the Brug's equation [13].

$$C = Q^{1/\alpha} [R_s^{-1} + R_{ct}^{-1}]^{\alpha-1/\alpha} \tag{1}$$

where:

C = Capacitance (Farad)

Q = Brug constant

α = Linear parameter from log f vs log Zim

R_s = Electrolyte resistance (Ohms)

R_{ct} = Charge transfer resistance (Ohms)

Electrochemical techniques were carried out in a three electrode electrochemical cell with standard conditions for temperature and pressure. As the working electrode, a 99.97 wt. % Mg plate with a controlled exposition area (0.78 cm²) was used in static conditions; a graphite rod was used (15 cm long with a 0.6 cm diameter) as the counter electrode. All overpotentials were referred to a saturated Ag/AgCl reference electrode.

2.4. Superficial Characterization

The surface of samples was studied with a Jeol JSM 6610LV scanning electron microscope. The XRD characterization was carried out using a Siemens D-5000 diffractometer, with a Cu K α ($\lambda=1.54178 \text{ \AA}$) radiation at 35 KV and 25 mA.

Surface ellipsometry was carried out using a Dektak 150 surface profiler, on a 1:1 scale with a needle of 2 μm of diameter and a force of 2 mN.

3. RESULTS AND DISCUSSION

3.1. Mg in a Kokubo solution

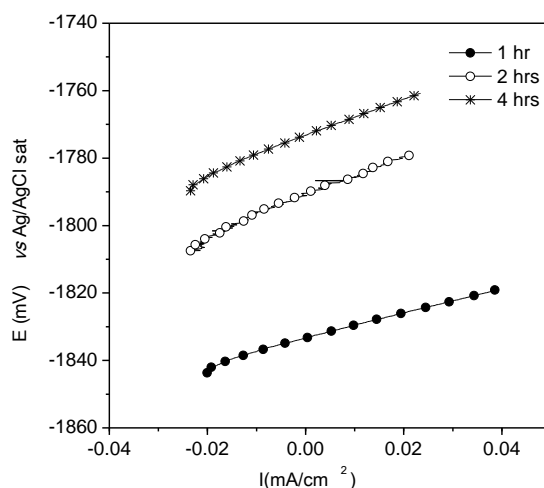


Figure 1. Linear Polarization resistance of Mg in a Kokubo solution as a function of immersion time (1, 2 and 4 hours).

In Figure 1, it is observed that the Mg potential moves to less electronegative values as the immersion time increases, which is accompanied by a slight increase in the Polarization Resistance (R_p), and a decrease in CR.

Thermodynamic and kinetic data are summarized in Table 1 and Table 2 for Mg immersed in a Kokubo solution after 1 hour and 24 hours of stabilization, respectively. A decrease in CR values is noticeable when immersion time increases. This behavior is followed by a displacement in E_{corr} to less negative values.

Table 1. E_{corr} , R_p and CR values determined from experimental data of Mg immersed in a Kokubo solution with a stabilization time of 1 hour.

Time (min)	E_{corr} (mV) vs Ag/AgCl sat.	R_p ($\Omega.cm^2$)	Corrosion Rate (mm/year)
0	-1964	321	2.36
30	-1942	352	2.16
60	-1931	386	1.97
90	-1940	301	2.53
120	-1943	278	2.73
150	-1937	254	2.99
180	-1932	264	2.88

Table 2. E_{corr} , R_p and CR values determined from experimental data of Mg immersed in a Kokubo solution with a stabilization time of 24 hours.

Time (min)	E_{corr} (mV) vs Ag/AgCl sat.	R_p ($\Omega.cm^2$)	Corrosion Rate (mm/year)
0	-1837	369	1.22
30	-1791	600	0.75
60	-1790	589	0.76
90	-1789	619	0.73
120	-1787	563	0.80
150	-1775	545	0.82
180	-1774	606	0.74

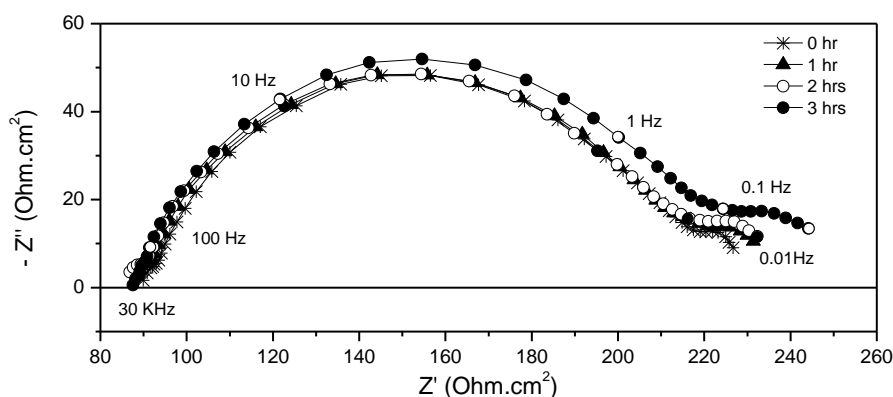


Figure 2. Nyquist diagrams of 99.97 wt % Mg in a Kokubo solution. Stabilization time: 1 hour.

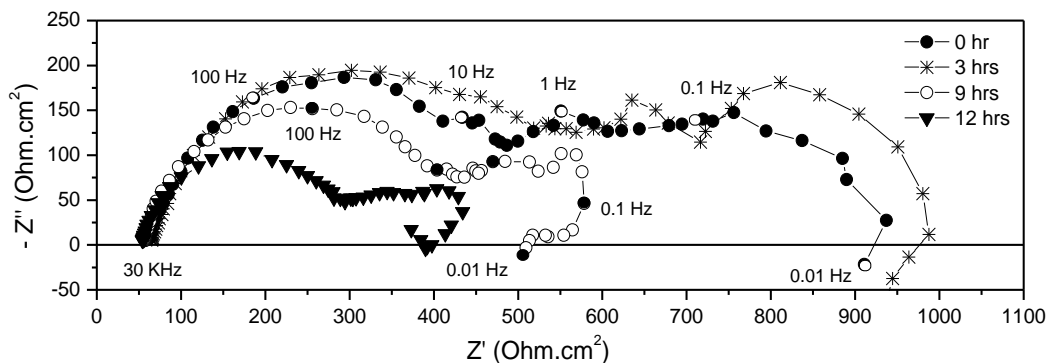


Figure 3. Nyquist diagrams of 99.97 wt. % Mg in a Kokubo solution. Stabilization time: 24 hours.

The observed behavior has been explained by Baril [14, 15], who appoint the formation and growth of Mg(OH)₂ on a Mg surface, as the responsible of such behavior. The presence of an oxide determines the electric conduction properties at the metal / electrolyte interphase. From EIS experimental data, such as the ones shown in Figure 2 and Figure 3, capacitance values were obtained by employing equation (1). Table 3 and Table 4 summarize α , Q and C values corresponding to 1 and 24 hours of stabilization, respectively.

Table 3. Capacitance values of 99.97 wt. % Mg after 1 hour of stabilization in a Kokubo solution.

Immersion time (hours)	A	Q	C (F/cm ²)
0.0	0.67	1.97×10^{-04}	4.3×10^{-05}
0.5	0.70	1.51×10^{-04}	3.5×10^{-05}
3.0	0.66	3.03×10^{-04}	4.6×10^{-05}
3.5	0.73	1.19×10^{-04}	3.2×10^{-05}

Table 4. Capacitance values of 99.97 wt. % Mg after 24 hours of stabilization in a Kokubo solution.

Immersion time (hours)	A	Q	C (F/cm ²)
0.0	0.75	6.70×10^{-05}	1.6×10^{-05}
3.0	0.72	8.89×10^{-05}	2.0×10^{-05}
9.0	0.77	7.32×10^{-05}	1.65×10^{-05}
12.0	0.74	9.65×10^{-05}	1.78×10^{-05}

An impedance increase is clearly observed in Figure 2 and Figure 3 at a long stabilization time (24 hrs) rather than a short stabilization time (1 hr), which is attributed to the increase in MgO and Mg(OH)₂ on the Mg surface. Overall, capacitance values determined at a short stabilization time (1 hr) decrease when the immersion time increases. It is assumed that after 24 hrs of stabilization, the formation of corrosion products (MgO and Mg(OH)₂) has practically finished. As a consequence, capacitance values at different immersion times are close to 1.75×10^{-05} F/cm² (Table 4) and are smaller than the ones obtained after 1 hr of stabilization (3.9×10^{-05} F/cm²), see Table 3. According to

equation (2), an increase in thickness leads to a decrease in capacitance values, and consequently to an increase in impedance diagrams.

$$C = \frac{\varepsilon\varepsilon^0 A}{\delta} \quad (2)$$

where:

C = Capacitance

ε^0 = Vacuum permittivity

ε = Dielectric material

A = Area of the Plates

δ = Thickness

As the Nyquist diagrams increase, the impedance increases, thus corrosion decreases [16]. The Nyquist diagrams (Figure 2 and Figure 3), are characterized by the presence of two time constants at high and medium frequencies (30 KHz to 0.1 Hz), which correspond to charge and mass transfer, respectively [14, 16]. At a short stabilization time (1 hr), the impedance of the second semicircle is smaller in comparison with the first semicircle, which means that the mass transfer process is carried out in a relatively easy manner. As the immersion time increases, the mass transfer process slows down, possibly due to an increase in the thickness of $\text{Mg}(\text{OH})_2$, which agrees the behavior over time of the capacitance values in Table 3 and Table 4.

3.2. Mg with $\text{Mg}_3(\text{PO}_4)_2$ coating: surface analysis and electrochemical behavior in a Kokubo solution

In Figure 4 we observe the surface of a magnesium sample treated in the phosphate solution (pH = 10) after 24 hours of stabilization. Flower and granule shaped structures are present on the chemical treated Mg surface. Such structures are described in literature as orthorhombic, trigonal and triclinic crystal structures [5, 17, 18]. The distribution of such structures is not uniform on the Mg surface, leaving some Mg areas in direct contact with the electrolyte. Such precipitate has electrical properties as the ones of a semiconductor [19], which blocks the charge transfer at the metal / electrolyte interphase. Results from the ellipsometry analysis show that the phosphate coating has a thickness of 13.5 μm and a roughness of $7.84 \pm 0.98 \mu\text{m}$. The thickness obtained is thicker than others obtained on Mg alloys, for example, in [9] it is reported a conversion coating in die cast AZ91D magnesium alloy in a phosphate bath of about 10 μm in thickness. According to [20], a rough surface facilitates adhesion and promotes cellular growth in implants, thus the roughness of the coating obtained here is suitable for such purposes. The XRD pattern shown in Figure 5 confirms the presence of $\text{Mg}_3(\text{PO}_4)_2$.

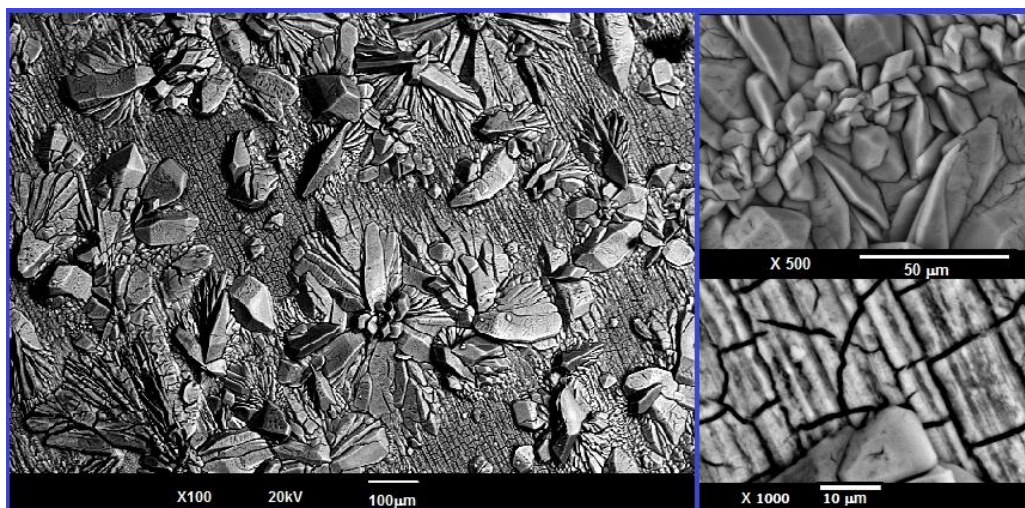


Figure 4. SEM image of the surface of Mg sample treated in a phosphate solution (pH = 10).

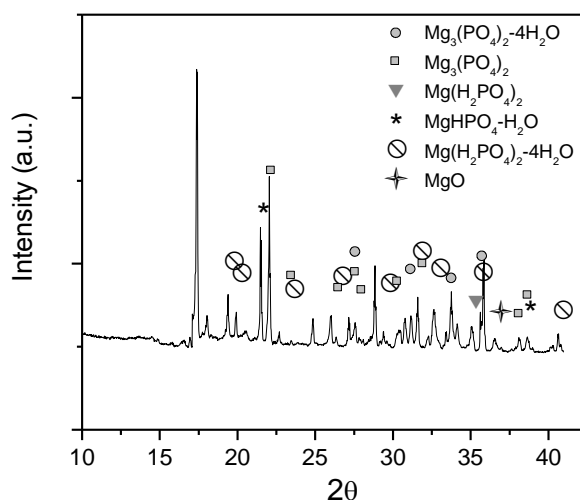


Figure 5. XRD pattern of the surface of Mg sample treated in a phosphate solution (pH = 10).

Equations 3 to 8 explain the formation of $Mg_3(PO_4)_2$ on the surface of the Mg samples treated in a phosphate solution (pH = 10).

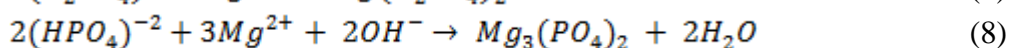
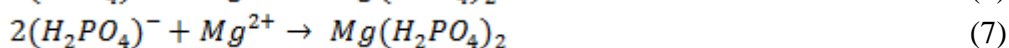
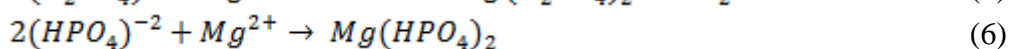
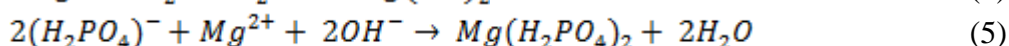
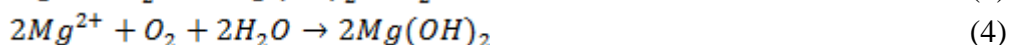


Figure 7 presents the Nyquist diagrams of the Mg / phosphate coating / electrolyte interphase after 30 exposure days to a Kokubo solution as a function of the immersion time in phosphate solution

(pH = 10) (1, 5 and 30 days). The presence of a time constant in the interval of high to low frequencies is clearly observed. A second semicircle appears at very low frequencies ($f < 10$ mHz). This last one is associated to Mg^+ adsorption [21].

When comparing the Nyquist diagrams of 99.97 wt. % Mg (Figure 2 and Figure 3), to the ones of Mg/ $Mg_3(PO_4)_2$, presented in Figure 7, an impedance increase in the presence of $Mg_3(PO_4)_2$ coating is clearly observed. Such increase leads to a decrease in corrosion, as a result of the precipitation of the phosphate coating on the 99.97 wt. % Mg surface. According to Equations 3 to 8, and Figure 5 (XRD), the principal compound that is formed is $Mg_3(PO_4)_2$, nevertheless, the XRD pattern evidences the presence of $Mg(HPO_4)_2$, in a smaller fraction. Likewise, in Figure 4 we can observe some zones without coating. The decrease and increase of impedance as a function of immersion time, observed in Figure 3 and Figure 7, could be explained considering the species diagram of Figure 6, and the alkalization reactions as a result of Mg oxidation as it follows: the impedance obtained after one day of immersion in phosphate solution (pH = 10) is higher than the impedance of 99.97 wt. % Mg. After 5 days of immersion, the impedance decreases as a consequence of an increase in the Mg oxidation reaction. According to Equations (3) and (4), Mg oxidation promotes the alkalization of the interphase, which favors the formation of $Mg(HPO_4)_2$ by Equation (3).

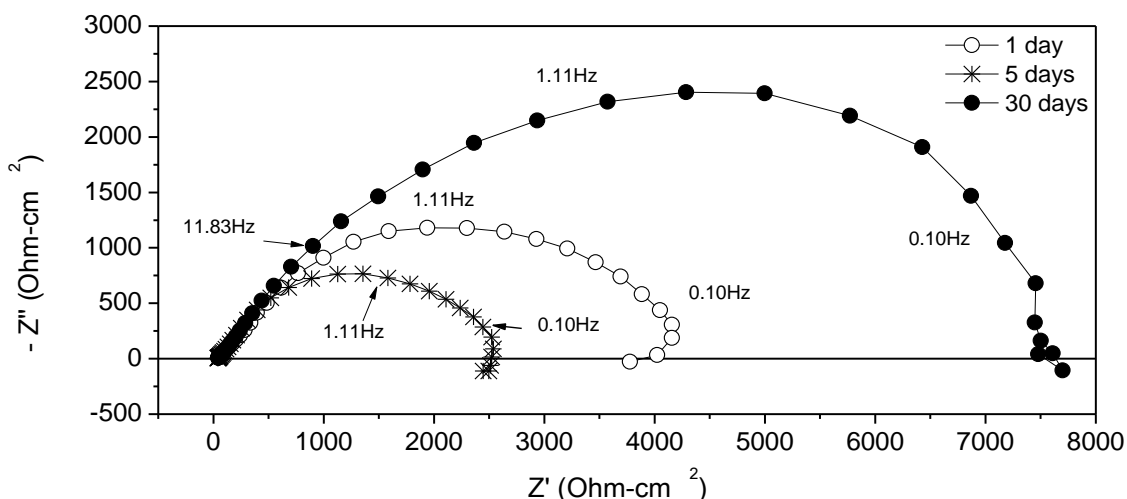


Figure 7. Nyquist diagrams of 99.97 wt. % Mg with $Mg_3(PO_4)_2$ coating immersed in a Kokubo solution for 30 days.

Table 5. Parameters from EIS data of 99.97 wt. % Mg with $Mg_3(PO_4)_2$ coating immersed in a Kokubo solution for 30 days.

Immersion time in phosphate solution (pH = 10) (days)	E_{corr} (mV) vs Ag/AgCl sat.	Re (Ω cm ²)	C F/cm ²	CR mm/year
1	-1839	37.7	8.83×10^{-6}	0.18
5	-1762	38.2	1.43×10^{-5}	0.17
30	-1526	40.4	5.58×10^{-6}	0.04

Table 5 presents values obtained from the EIS measures. As a function of the immersion time in

phosphate solution (pH = 10), the E_{corr} values experience a displacement to less electronegative values, as we previously saw in 99.97 wt. % Mg (Figure 1). As aforementioned, the exposure time of Mg to phosphate solution promotes the formation of $\text{Mg}(\text{OH})_2$, which decreases CR. The growth of $\text{Mg}(\text{OH})_2$ occurs at free $\text{Mg}_3(\text{PO}_4)_2$ areas. However, in order for this to happen, the oxidation of Mg through Equation (3) is necessary. This process suggests the decrease of impedance at the 5th day ($Z_{\text{real}} = 2500 \Omega \cdot \text{cm}^2$, see Figure 7). As it is seen in Equations (4) to (8), the Mg oxidation locally increases the pH at the interphase, which is responsible for $(\text{HPO}_4)^{-2}$ to chemically react in order to form phosphates on the surface. Therefore, the phosphate free zone decreases as the impedance increases ($Z_{\text{real}} = 7500 \Omega \cdot \text{cm}^2$ after 30 days of immersion in phosphate solution (pH = 10), see Figure 7). This asserts the increase in $\text{Mg}_3(\text{PO}_4)_2$ thickness, which corresponds to an increase in the capacitor's thickness. Consequently, according to Equation (2), leading to a decrease in its values as it is seen in Table 5. The 2D and 3D growth of coating results in an increase in total impedance, thus leading to a decrease in CR. When comparing CR of Mg with (Table 5) and without phosphate coating (Table 1 and Table 2) a decrease in CR in presence of the coating can be clearly seen. The decrease obtained is at least an order of magnitude lower than the CR in its absence.

4. CONCLUSIONS

During the stabilization process of Mg in a Kokubo solution, we observed an increase in R_p , which suggests the formation and growth of $\text{Mg}(\text{OH})_2$, which partially protects Mg from a corrosion process. It is proposed that the presence of both, MgO and $\text{Mg}(\text{OH})_2$, is responsible for the displacement of E_{corr} to less electronegative values and a decrease in the CR. The values of capacitance determined by the Brug Equation, drive us to postulate that the increase in thickness of $\text{Mg}(\text{OH})_2$, as a function of exposure time to the electrolyte, is responsible for the observed behavior.

By means of the chemical treatment used in this work, immersion in phosphate solution (pH = 10), we obtained the decrease in CR of 99.97 wt. % Mg in a Kokubo solution.

As a function of the immersion time, it was observed that the degradation of Mg promotes the formation of $\text{Mg}_3(\text{PO}_4)_2$, by means of the alkalization of the metal/electrolyte interphase.

The obtained chemical coating, exhibited a dielectric character, as well as a roughness of 8 μm and a thickness of 10 μm . The coating does not cover the entire Mg surface, remaining some areas exposed to direct contact with the electrolyte.

The chemical coating obtained on 99.97 wt. % Mg is made up of $\text{Mg}_3(\text{PO}_4)_2$, $\text{Mg}(\text{H}_2\text{PO}_4)_2$ and $\text{Mg}(\text{HPO}_4)_2$.

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