

# Corrosion study of anodes for magnesium air batteries

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**Abstract**— This thesis aims at studying corrosion phenomena in magnesium alloys that can be used as anodes in magnesium air batteries, and how to possibly control it. The experimental part of the dissertation project consists on the description of four electrochemical techniques: Open Circuit Voltage, Electrochemical Impedance Spectroscopy, Galvanostatic Discharge and Potentiostatic Polarization that are used to characterize the corrosion processes at the Mg anode. These techniques will be used to study the anode response in blank electrolyte ( $\text{NaNO}_3$ ). These techniques were also used to study the effect of an added inhibitor (sodium phosphate) in the electrolyte in order to determine how the corrosion behavior changed and how this could benefit magnesium air batteries. The obtained results suggest that the usage of proper inhibitor concentration can increase the cell voltage but there is evidence of the formation of a resistive layer that creates unwanted diffusion overpotential and negative current response.

**Keywords:** Magnesium air battery; anode; corrosion; inhibitor; electrolyte.

## I. INTRODUCTION

The battery as we know it today was invented over 200 years ago by a scientist named Alessandro Volta [1]. There are two main types of batteries: primary and secondary. A primary cell is designed to be used only one time and it cannot be recharged, while secondary cells are designed to be electrically recharged many times during their lifetime. An electrochemical battery is able to store energy by holding certain electro-chemically active materials in the same cell setup [1]. The battery main function is to generate and store electrons, which will be delivered when needed. Many technologies that are commonly used today are powered by batteries, including smartphones, computers and cars.

Metal air batteries have a metal anode and an air cathode. The metal air battery cathode uses oxygen from the air for the oxidation process, and this will lead to an important reduction of the battery weight. Metal air batteries present one other big advantage, they are cheaper than most of its competitors, especially Lithium batteries. The price is lower due to the abundance of the low-cost metals used in the anode, such as Aluminum, Magnesium or Zinc. The cathode source is oxygen from air which is also contributing to the overall low price of this type of battery. [2]

One of the more promising materials to use in the anode of metal air batteries is magnesium. Mg-air batteries have very high theoretical energy density of around 6800 Wh/kg [3]. In terms of specific capacity Mg-air batteries have around 2200 Ah/kg and a theoretical cell voltage of 3.1 V, even though actual cell

voltages will be approximately half of that value [3]. These numbers are similar or even superior to that of a Lithium ion battery [4]. A global use of Mg-air battery, like it is found with Li-ion batteries, is not possible now due to several factors. These 4 are the most important ones:

- Narrow operating voltage of around 1.2 V, due to high polarizability of the electrodes [4].
- Low faradaic efficiency due to unwanted parasitic reactions such as hydrogen evolution or formation of thick corrosion layers [4].
- Sluggish oxygen reduction reaction kinetics at the cathode [4].
- Poor recharge ability due to uneven Mg deposition and formation of corrosion layers [4].

The main objective of this thesis is to control the corrosion process in the anode of magnesium air batteries. Magnesium has a lot of energy density potential and advantages over other anode materials used for the purpose, but its biggest drawback is how fast corrosion occurs and the occurrence of unwanted reactions that happen at the surface of the anode when in contact with the electrolyte.

For this reason, the experimental part of this project is going to be divided between experiments done in blank electrolyte and experiments done with an added corrosion inhibitor. First, the corrosion process in the anode will be studied when it is immersed in a blank electrolyte using four different electrochemical techniques that will be thoroughly discussed and explained in the methodology part: Open Circuit Voltage, Electrochemical Impedance Spectroscopy, Galvanostatic Discharge and Potentiostatic Polarization

The results obtained using the blank electrolyte will be compared with results obtained using the same electrolyte plus a corrosion inhibitor. The four same electrochemical techniques used in the first part will be repeated in order to obtain a proper comparison of the results.

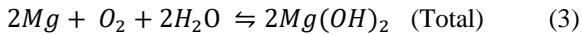
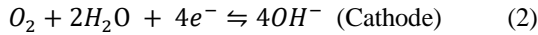
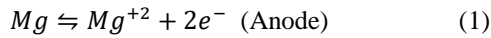
Even though the most used electrolyte for magnesium air batteries is NaCl, it was decided that in this project  $\text{NaNO}_3$  is going to be used instead. The selected corrosion inhibitor is sodium phosphate.

## II. MG AIR BATTERY - STATE OF THE ART

Mg air batteries have a very similar behavior to the conventional primary batteries. The biggest difference is that the cathode will be made of a conductive carbon layer where reduction of oxygen from external air takes place. Since the

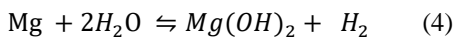
oxygen reactant is not stored in the battery, there is a reduction of the volume and mass needed and this increases the specific capacity and energy density of the battery (this is a common feature with the other metal air batteries). During discharging of a metal–air electrochemical cell, the reduction reaction involves the reduction of oxygen from ambient air at the cathode and in the meantime the metal anode is oxidized.

The reactions that can be found in a typical magnesium air battery are shown in Equations 1, 2 and 3:



The electrode that is more of interest for this project is the anode and the reactions that occur around it. During the discharge process, the magnesium found in the anode is dissolved to produce ions. The standard potential in the anode's reaction is -2.37 V and can produce up to 2.2 A h g<sup>-1</sup>. [4]

Corrosion is a side reaction that greatly influences the overall performance of the cell and thereby must be taken into consideration. The overall corrosion reaction equation of the magnesium air battery cell is a combination of the anode, cathode and product reactions and can be seen in Equation 4:



#### A. Anode magnesium alloys

It is a common practice to introduce alloying metal elements, like aluminum, zinc, manganese, tin and indium in order to decrease corrosion rate produced in the Mg anode. In this thesis, and due to availability and academic reasons, AZ31 is used, although using different electrolyte solutions and inhibitors, researchers have found that AZ61 alloy to be superior to AZ31 regarding cell voltage and hydrogen evolution rate. More alloying elements have also been tested, such as heavy metals like cesium, lead and gallium, and also light metals like aluminum, lithium and calcium [5]. Some of these alloys, such as Mg–14Li–1Al–0.1Ce have presented higher operating voltage, anode utilization efficiency and lower self-discharge than AZ31 alloy and even pure magnesium. Other studies show that adding Ca helps the alloy Mg–6Al–0.3Mn–2Ca get a higher capacity as well as efficiency, especially with low operating current. A recent study found the optimal composition of Al, Sn and Mn in a magnesium alloy anode using orthogonal design and showed that the proportions of composition Mg–6Al–1Sn–0.4Mn give the higher discharge potential as well as corrosion resistance. [5]

Hydrogen evolution reaction, which takes place in the metal anode during the charge and discharge processes of the cells, is known to decrease the overall Coulombic efficiency because it consumes otherwise useful electrons found in the metal anode. Another negative side effect of hydrogen evolution is the diffusion of hydrogen inside the electrolyte which can increase the internal pressure of the battery and creates possible explosion danger. [6]

Another unwanted side reaction is passivation. Passivated electrodes are unable to properly charge and discharge due to an insulating layer or film (called passivation layer) that blocks the

exchange of ions necessary for completing the discharge process. Corrosion is also a problem as it accelerates anode dissolutions and decreases battery life. In some cases, corrosion leads to the formation of a passivation and resistive layers. This depends on the metal and electrolyte nature. [6]

The last side reaction that will be mentioned in this section is dendritic formation and deformation. This reaction is the gradual change of the anodes metal shape, where its surface tends to become uneven and rough. This process happens when the metal ions released during discharge deposit on the anode during the charging process. After several battery cycles, the anode will accumulate dendrites and the cell will become more and more unstable.[6]

#### B. Electrolyte

The main function of the electrolyte in metal air batteries is to transport the ions from one electrode to the other to make sure that the oxidation and reduction reactions happen. Two main types of electrolytes will be discussed in this section, the aqueous electrolyte and the non-aqueous electrolyte.

The aqueous electrolyte is the most commonly used electrolyte, these are the three main solutions found:

**Alkaline solutions:** the alkaline electrolytes will have a pH above 7 but not above than 14, being the less acidic solutions for aqueous electrolytes. A lower overpotential and faster kinetic reactions make oxygen reduction more favourable and this is why alkalines are usually favoured for aqueous based electrolytes in metal air batteries. The biggest drawback of these solutions is that CO<sub>2</sub> found in the ambient air will react with the electrolyte and create unwanted carbonate around the cathode. This carbonate, when found in large amounts, can block the cathode material and severely decrease the cell efficiency. [7]

**Neutral salt solutions:** as the name indicates, these solutions have a pH close to 7. This type of electrolytes is usually used in aluminum air battery, due to the lower corrosion rate that they generate compared to the alkaline electrolytes.

**Acidic solutions:** these solutions will have a pH lower than 7. Acidic electrolytes are demonstrated to accelerate H<sup>+</sup> production which translates into a reduced battery efficiency. This is why they are not commonly used in actual metal air cell setups. [7]

There are three main types of non-aqueous electrolytes:

**Solid-state electrolyte:** This type of electrolytes differs from the aqueous electrolytes mainly in ion conduction and wettability. In a solid-state electrolyte, the three phased interface reaction can be restrained due to the low wetting property of the electrolyte, and this can facilitate the transportation of OH<sup>-</sup> compared to an aqueous system. Alkaline gel electrolytes have been developed (especially for primary lithium air batteries) in order to reduce this phenomenon. This gel has low molecular weight and low acidity. [7]

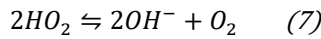
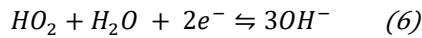
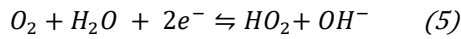
**Ionic liquid electrolyte:** This type of electrolytes has few applications due to the formation of carbonates and the lack of information and research done regarding the oxygen reaction in

an ionic liquid. The main agent in these electrolytes are large organic cations with both organic and inorganic anions and alkali ions inside a solvent. [7]

**Polymeric (organic) electrolytes:** Polymeric electrolytes have the potential to reduce several drawbacks such as hydrogen evolution, dendrite formation, unwanted extra water evaporation in the electrolyte, and carbonation [8]. They also typically provide higher and wider temperature range, which can be very useful for specific applications. On the other hand, it is important to decide which composition to use in order to avoid problems like volatility, flammability and toxicity. Those are the main reasons why traditionally the metal-air battery's electrolyte has been an aqueous solution that enables ion's transportation between anode and cathode. [8]

### C. Air cathode

When a neutral solution is used in the cell,  $O_2$  is transformed to  $OH^-$  at the interface of the gas–solid–liquid ternary phases located in the air electrode. Complex chemical reactions occur when the Oxygen Reduction Reaction happens in the three-phase interface [4]. Typically, the reactions involved in the Oxygen Reduction Reaction in a neutral electrolyte are Equations 2, 5, 6 and 7:



The standard electrode potential of ORR, which can be seen in Equation 2 is 0.44 V. However, a high overpotential and polarization are typically seen in the ORR, which ultimately leads to a bad cell performance due to the sluggish kinetics of the reaction. In order to achieve lower overpotential, efficient catalysts are needed as explained in the previous section. The direct four electron process seen in Equation 6 is the most efficient, so having a four-electron catalytic ability is a desirable quality in an optimal catalyst material. [4]

## III. METHODOLOGY

### A. Sample preparation

The sample preparation will be equal for all the tests in order to achieve maximum reliability. First of all, a plate (4x3 cm, 2 mm of thickness) of alloy Mg AZ31 is polished using four different sandpapers in a polishing machine. SiC papers of four different grit sizes were used: 280, 360, 600 and 1200 of the European FEPA or P-Grading.

The composition of the magnesium alloy AZ31 is 97% Magnesium, 2.5-3.5% Aluminum, 0.6-1.4% Zinc, 0.2% Manganese, 0.1% Silicon, 0.05% Copper, 0.04% Calcium, 0.005% Iron and 0.005% Nickel. All the percentages are calculated in weight. [9]

An exposed area of 3.65 cm<sup>2</sup> was defined thanks to glued acrylic tubes onto the metal surface. In order to make sure that the setup is completely sealed, the immersions in electrolyte will be held 24 hours after.

The blank electrolyte consisted of an aqueous solution with 0.5 M of  $NaNO_3$ , and approximately 10 mL of solution were used in each sample.

### B. Electrochemical techniques

These are the four techniques used in the experimental section:

The **Open Circuit Potential** (also known the equilibrium potential, the rest potential, or the corrosion potential) is the potential at which no current is flowing, so experiments based on the measurement of the open circuit potential are considered potentiometric experiments. Such measurements are very basic and simple, they have many important applications, which will be discussed briefly in this section.

The basic equation of potentiometric concentration measurements is the Nernst equation, which relates the concentration of electroactive species at the electrode surface to the potential at that electrode.

**Electrochemical Impedance Spectroscopy** (EIS) is a powerful technique that utilizes a small amplitude, alternating current (AC) signal to probe the impedance characteristics of a cell. The AC signal is scanned over a wide range of frequencies to generate an impedance spectrum for the electrochemical cell under test. EIS differs from direct current (DC) techniques since it allows the study of capacitive, inductive, and diffusion processes taking place in the electrochemical cell. EIS has far reaching applications including coatings, batteries, fuel cells, photovoltaics, sensors, and biochemistry.

EIS is most commonly run in 3 electrode mode. In this configuration there is a working electrode (the Mg sample), counter electrode (graphite and platinum are commonly utilized), and an independent reference electrode--Saturated Calomel Electrodes (SCE) or Silver/Silver Chloride (Ag/AgCl) which are the most common.

**Linear polarization resistance** (LPR) is a quick, nondestructive testing technique (unless conditions are too harsh, and/or the processes are irreversible) commonly used in material corrosion studies to gain corrosion rate data. For this method the material is polarized, typically on the order of  $\pm 10$ mV, relative to its Open Circuit (OC) potential—the potential measured when no [net] current is flowing. As the potential of the material (working electrode) is changed, a current will be induced to flow between the working and counter electrodes, and the material's resistance to polarization can be found by taking the slope of the potential versus current curve.

In **Galvanostatic Discharge**, the working electrode is introduced into the electrolyte and subjected to an initial potential, corresponding to the electric double layer potential formed between the electrode and dissolution. When the potential jump occurs, the double layer has to adjust to a new potential, so that, when collecting the variation of the current density over time, a large initial peak is obtained.

## IV. RESULTS AND DISCUSSION

### A. Potentiostatic Polarization

Potentiostatic Polarization results are shown first in the experimental part as it provides useful information. Both anodic and cathodic obtained Tafel curves can be obtained. In this case the technique was used to assess the best inhibitor concentration to be used in the rest of the experiments.

The first results were obtained in blank  $\text{NaNO}_3$  electrolyte in order to have a benchmark to compare the inhibitor results when sodium phosphate is added. Three different inhibitor concentrations will be tried in the second part: 0.05 M, 0.01 M and 0.005 M.

Figure 1 show the anodic and cathodic polarization resistance curves in blank electrolyte. The voltage range for both sides is 0.3 V from the OCP values determined before for each sample. This means that for the anodic curve will move, from the OCP value into the positive direction 0.3 V, while the cathodic one will move 0.3 V into the negative range. The scan rate was 0.15 mV/s in each case.

It is important to mention that the anodic and cathodic curves were obtained in different samples and the results are plotted together. This is the right procedure to avoid interferences of the cathodic curve in the anodic response.

In this plot the voltage in the y axis is plotted against the logarithm of the intensity over the area. This is very useful as it eliminates the total area factor when comparing different samples.

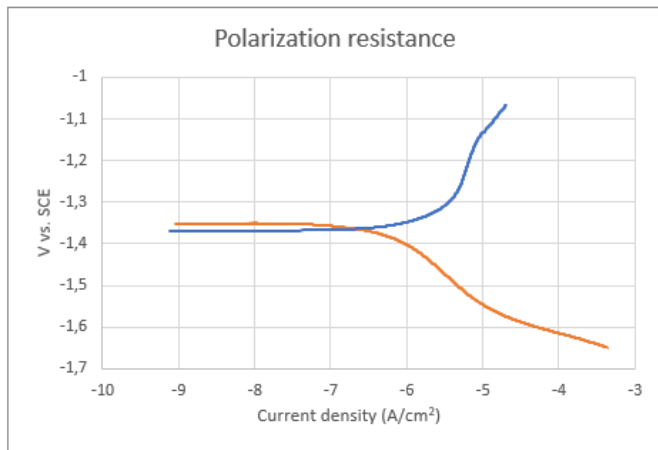


Figure 1. Anodic and Cathodic Polarization resistance curves using blank electrolyte.

Both anodic curves reveal a regular increase of the current density with potential and both curves are under charge transfer kinetic control because the currents increase regularly with potential. No relevant diffusional effects could be observed in the cathodic curve. It is worth to mention that extraction of quantitative parameters from polarization curves obtained on Mg samples is not an accurate procedure due to the specificities of the corrosion mechanism and intense gas release. Therefore, only comparative discussion will be made in this section.

Literature on the usage of  $\text{NaNO}_3$  as electrolyte for magnesium air batteries show that the results obtained using

blank  $\text{NaNO}_3$  electrolyte are in good agreement with previous work [10], and that the OCP of the Mg electrode is higher than when NaCl is used. The values found in various articles are more or less -1.4 V for  $\text{NaNO}_3$  and -1.6 V for NaCl [10].

This is negative for the battery as having a higher potential in the anode using this electrolyte will result in a lower discharge voltage. The negative increase found in the OCP using Potentiostatic Polarization suggests that a different corrosion reaction is occurring. Nitrate to nitrite corrosion is considered to be the principal cause of this secondary corrosion, as experiments on  $\text{NO}_2^-$  titration show an increase of  $\text{NO}_2^-$  when  $\text{NaNO}_3$  is used [10].

In Figure 2, the anodic curve of all three inhibitor concentrations: 0.01 M, 0.05 M and 0.005 M are shown. The anodic curve of the sample that used only blank electrolyte is also shown for better visualization and comparison of the samples.

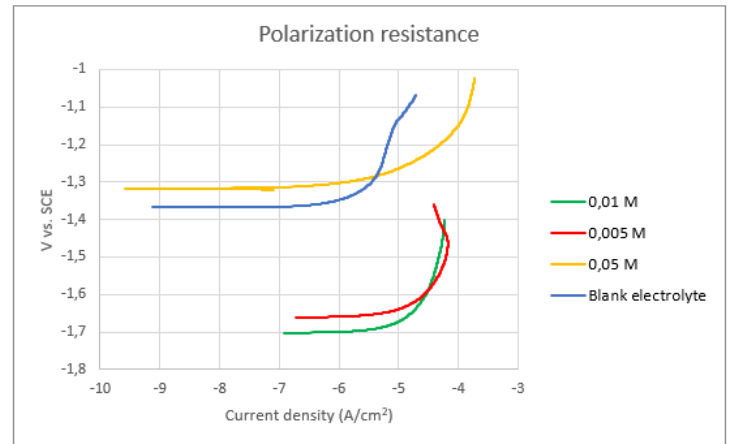


Figure 2. Anodic curves, with and without inhibitor, plotted together.

Clearly, lower concentrations induce an important decrease of the OCP benchmark value that is obtained prior to the polarization of the samples, towards more cathodic values, evidencing that in this case the cathodic reaction is strongly polarized. The anodic current densities are very similar and one order of magnitude lower than the ones in the presence of 0.05 M, which is closer to the behaviour in the blank solution.

The most important conclusion is that decreased inhibitor concentrations cause an important cathodic polarization effect and increase the anodic current density and also a significant increase of the corrosion current. This may also account for easier and faster Mg dissolution. Contrarily the highest concentration places the curve closer to that of Mg in the blank electrolyte, with identical corrosion potential and identical corrosion rate.

It is known for sodium phosphate to decrease OCP in the magnesium anode when added as corrosion inhibitor in the electrolyte, as it prevents the erosion of  $\text{Cl}^-$  [11]. Experiments show that it can decrease around 0.1 V when an AZ91 Mg alloy is immersed in a solution of NaCl with sodium phosphate. In this experiment, using AZ31 Mg alloy and  $\text{NaNO}_3$  solution, it decreases almost 0.4 V.

### B. Open Circuit Potential

The main purpose of the Open Circuit Potential was to observe the anode behaviour during the first 24 h of immersion and to determine at which moment the sample was already stable so it would also be easier to conduct other experimental techniques that required stabilized samples were corrosion had already created a passivated layer on top of the magnesium anode. Furthermore, a comparison of these parameters between blank electrolyte and adding inhibitor will be conducted. The open circuit potential evolution is an indicator of the Mg alloy response in the electrolyte. Typically, an increase reflects formation of a more protective layer whereas sudden fluctuations may account for corrosion activity. Figure 3 shows the behavior of the open circuit voltage of AZ31 in 0.5M NaNO<sub>3</sub> in an aqueous solution.

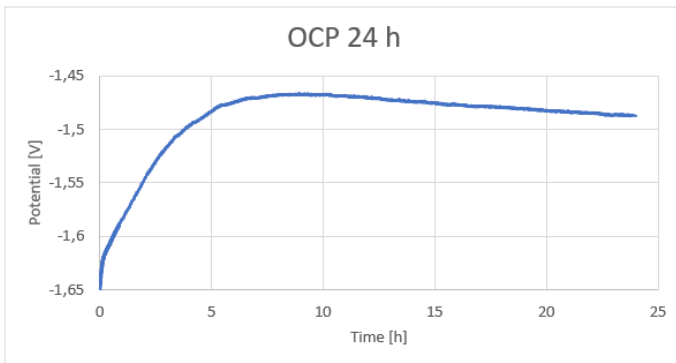


Figure 3. OCP using blank electrolyte during the first 24 h of immersion.

The behavior of AZ31 immersed in NaNO<sub>3</sub> is similar as if it was immersed in NaCl solution, but it seems to stabilize a bit later [12]. This means that it takes more time to create the passivation layer or it makes a thicker one. On the other hand, when compared to the samples that are immersed in a KOH solution, the ones using either NaNO<sub>3</sub> or NaCl present a much smoother curve, without the characteristic falls that appear in the OCP tests that run Mg alloys with KOH electrolyte solutions [13].

Now, 0.01 M of sodium phosphate concentration is used in the electrolyte, as it showed during the polarization test that it seems the most ideal of the three different concentrations of inhibitor substance that were tested during this experimental part. Figure 4 shows the behavior of the first 24 h of immersion:

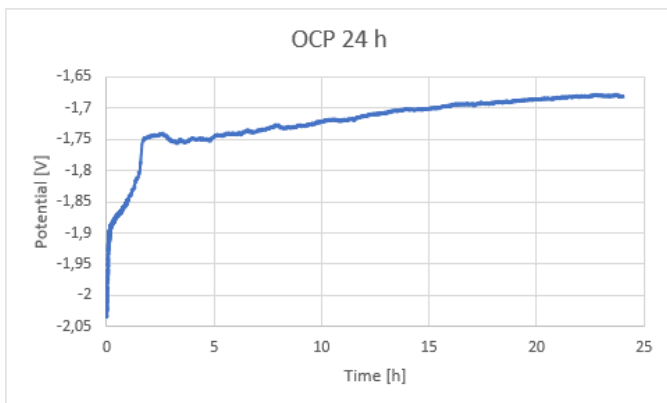


Figure 4. 24 h OCP with inhibitor.

The most important feature is a drop of the corrosion potential at early stages of immersion that was more negative than in the absence of inhibitor. Over time, potential increased, similarly to the what was observed for Mg in the blank solution. As it can be observed, the tendency line could also be identified as logarithmic, but it is definitely more irregular than the one obtained using only blank electrolyte.

It is very interesting to observe that the OCP obtained when an inhibitor was used is more negative than the one obtained using only electrolyte, in both the first moment of immersion and after 24 h, when the sample in both cases is stabilized already.

This pinpoints that the presence of inhibitor affects the cathodic reaction, i.e the oxygen reduction. This follows the trends shown when Mg alloys are immersed in a NaCl solution with sodium phosphate [11], although as mentioned in the Potentiostatic Polarization section, the decrease when this inhibitor is combined with NaNO<sub>3</sub> is even larger than the ones using NaCl [11].

The inhibitor was likely to accelerate Mg dissolution at early stage, leading to the formation of a compact corrosion layer that appeared right after immersion in the sample exposed to inhibitor.

This phenomenon was observed constantly during the experimental part and could explain this initial voltage drop and the previously mentioned less smooth behaviour of the curve. In order to show what could be visually seen during the experiment, the samples were taken to the microscope in order to compare the two samples.

Both of these factors can be explained more easily when looking at the image of the two samples (Figure 5):

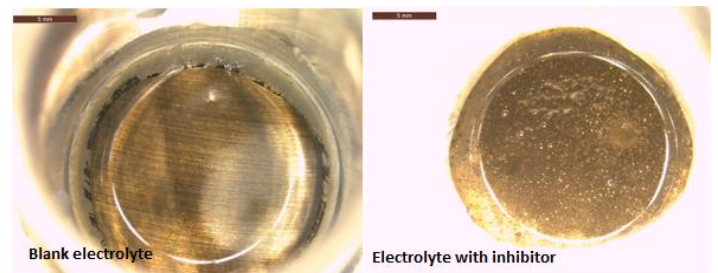


Figure 5. Optical comparison between the two samples.

It can be seen that a thick surface layer is formed when the inhibitor is used. Over time this layer forms a protective cape that will difficult contact between the original electrode surface and the electrolyte.

Thus, it can be concluded that the presence of the corrosion inhibitor decreases the open circuit potential to more negative values promoting the formation of a layer of magnesium compounds, likely Mg(OH)<sub>2</sub> that forms a stable, but probably porous barrier.

### C. Electrochemical Impedance Spectroscopy

EIS is a powerful technique because it allows to understand the mechanism of the processes occurring at the surface and at extracting important information such as the protectiveness of the layers formed at the surface and how this change over time. Moreover, fitting of spectra can allow determining quantitative parameters.

The experiments were conducted during a time span of 7 days. During these 7 days, four measurements were made in order to see how EIS was evolving with time. Results are shown in the form of a Nyquist plot in Figure 6:

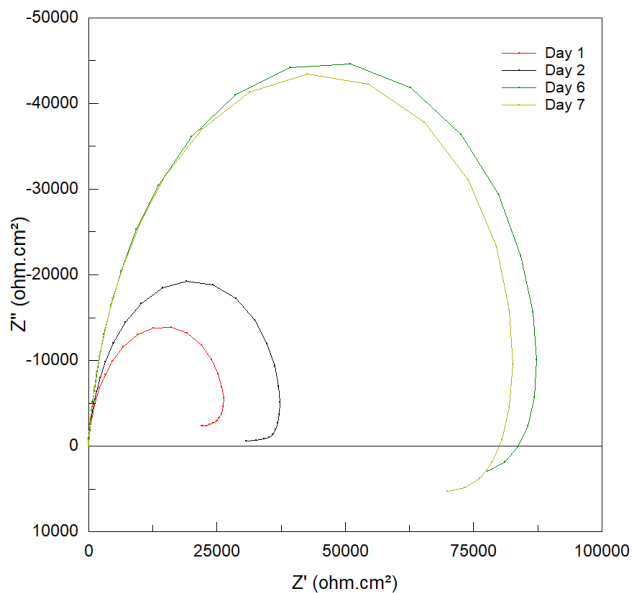


Figure 6. Impedance Nyquist plot using blank electrolyte.

These results clearly show an increase of the capacitive impedance loop over time and the formation, in the low frequency range of an inductive loop. The impedance changes were notorious during the first days but become attenuated from 6 to 7 days, reaching a more stable condition. The presence of the inductive loop is related to corrosion activity and formation of intermediate Mg ions ( $Mg^+$ ) that are released from the surface.

The impedance results obtained in the Nyquist plot and the Bode magnitude plot are much higher, around two orders of magnitude, compared to the research done with AZ31 anodes immersed in NaCl that are done right after immersion [10], [14]. Impedance greatly increases with time, especially in Mg alloys compared, for example, to Al alloys [15].

Now, 0.01 M Sodium Phosphate will be added to the previously used electrolyte and the experiment will be repeated. EIS measurement were taken after days 1, 2, 6 and 7 days of immersion.

Figure 7 shows again a Nyquist plot, where the real and imaginary part of the impedance are plotted together:

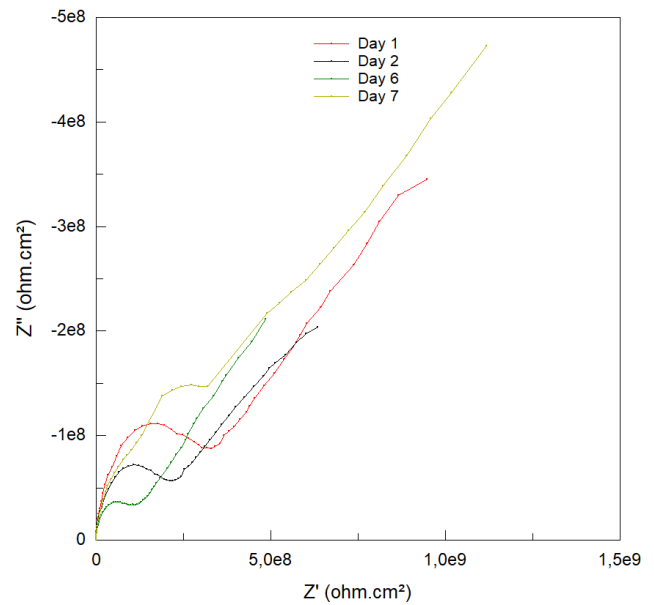


Figure 7. Nyquist plot using sodium phosphate as corrosion inhibitor.

The first noticeable result is that the impedance response has greatly increased when an inhibitor has been used. The spectra reveal a loop at high frequency and then a slope that can be assigned to mass transport controlled phenomena. The inductive loop has disappeared. This low frequency process is due to mass transfer, of charged species, and the process is now mass controlled. Charged species take more time to pass through the protective layer created by the inhibitor and this slow down the corrosion rate over time.

In practical terms this would decrease the active area exposed to the electrolyte and would introduce diffusional effects in the response of the Mg anode over time.

Even though inhibitors typically increase impedance in the electrode when added in NaCl [11], [16]–[18], the combination of  $NaNO_3$  and sodium phosphate shows a magnitude of impedance that does not appear so far in the literature. A fast, thick, protective layer that introduces a mass controlled process that greatly increases the impedance that isolates the electrode and makes current flow more difficult.

### D. Galvanostatic Discharge

This first set of chrono amperometry experiments (discharge curves) represent three different currents applied consecutively in the same sample, which was immersed 24 hours before the experiment was held in order to achieve an acceptable OCP stabilization. The currents applied to the electrode are 2.5, 5 and 10 mA respectively and are applied in this same order, from lower to the highest to avoid extra corrosion and unwanted reactions in the sample from the same beginning. The total area of the exposed sample had to be input in the used software, so the current mentioned in this paragraph is already divided by the area of the sample.

2 samples are tested after 24h of immersion in the blank electrolyte for each applied current. For comparative purposes a

“fresh” sample was also prepared and submitted to the highest applied current. To discard the effect of consecutive polarizations at different current densities a sample immersed for 24 h was immediately subjected to the highest applied current.

Electrode materials that exhibit more negative discharge potential during the discharge test are able to supply higher voltage when serving as anodes in fully assembled Mg air batteries.

The results depicted in Figure 8 show that all the discharge potentials show a very sudden drop during the first 100 seconds and then the values stabilize keeping constant and between -1.1 and -1.4 V. This is characteristic of Mg air batteries and corresponds to the accumulation of discharge corrosion products at the electrode as soon as the current is imposed. No relevant changes were observed over time and, furthermore, the effect of the applied current do not have a significant effect on the potential of the electrode under applied current, as expected in typical Mg air batteries using NaCl [14], [17].

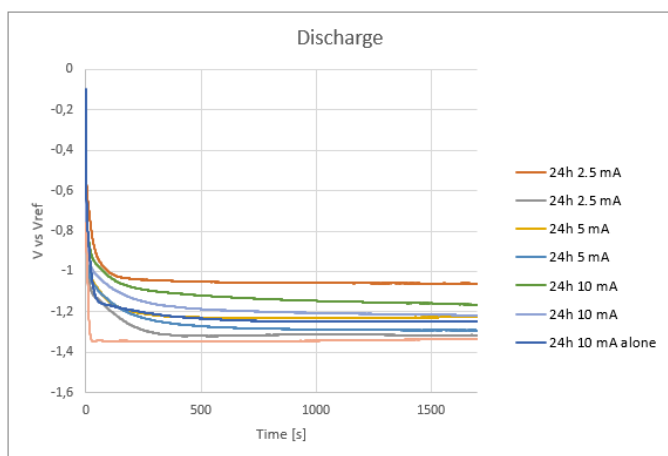


Figure 8. Galvanostatic discharge curves using blank electrolyte

Interestingly, the fresh sample revealed a faster decay, probably due to the absence of the corrosion layer that was formed during the 24h immersion period. In practice the presence of this corrosion layer is the typical situation as the anode is expected to be in contact with the electrolyte even when the battery is not on.

Also, another conclusion is that the applied current do not affect the electrode voltage and the response is reliable even when increasing the applied current. This reveals that the electrode presents a stable electrochemical performance under different applied currents and that the voltage of the electrode remains stable in these various conditions.

A set of chronoamperometry experiments using different inhibitor concentrations is obtained at the current intensity of 2.5 mA. In order to see if the concentration amount of sodium phosphate would have any effect on the electrode discharge, the three different concentrations have been tested twice. All samples were immersed in the electrolyte with its respective inhibitor concentration 24 h before the test was done. This procedure allows the sample to stabilize and avoids any

unwanted reactions that can hide the electrode response during chronoamperometry.

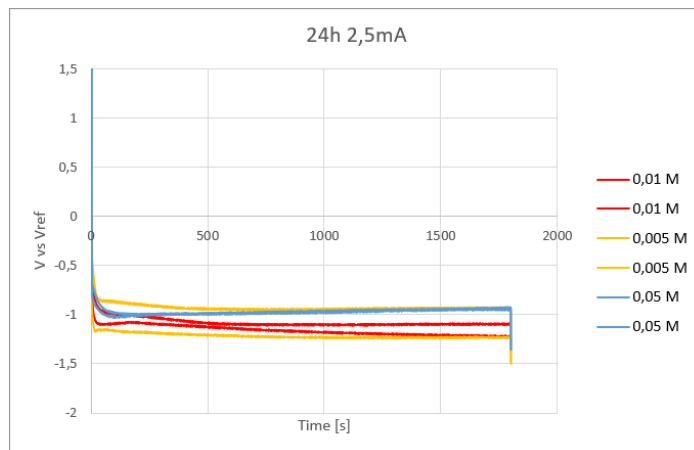


Figure 9. Discharge curves at 2.5 mA using different inhibitor concentrations

As it can be observed in Figure 9, the red curves correspond to a concentration of 0.01 M of sodium phosphate. The yellow and the blue curves correspond to a concentration of 0.005 and 0.05 M respectively. Two samples of each concentration are plotted in order to check how behaviour changes between concentrations and to see if the results of each concentration remain similar.

The results evidence a sudden decrease of the potential towards values slightly below -1.0 V and the inhibitor effect is not relevant. However, the general trend suggests that the two lowest concentrations induce slightly lower potentials, while the highest inhibitor concentration provides less negative values. Overall, it can be said that the presence of inhibitor, for the same applied current, decreases the electrode potential. This might be due to the fact that the inhibitor changes the corrosion process rate and mechanism. EIS have shown much higher impedances and mass transfer controlled reactions that might be responsible for the lowest potential of the electrode during discharge.

This is important because in the cell, the electrode potential can be affected by the charge transfer overpotential ( $\eta_{ct}$ ), by the diffusion overpotential ( $\eta_{diff}$ ) and by the  $iR$  drop ( $R$  is the electrolyte resistance). Since for all electrodes  $iR$  is the same (the same cell arrangement is used) the differences are related to the mechanism. In fact, it can be said that the diffusional polarization can reduce the final voltage of the Mg anode and this is more likely for the electrodes tested in the presence of the largest amount of inhibitor.

## V. CONCLUSIONS

There main conclusions that can be extracted after finishing the experimental part:

- A  $\text{NaNO}_3$  electrolyte was chosen to evaluate the performance of a Mg AZ31 anode in the absence and presence of sodium phosphate as corrosion inhibitor. This is a new approach compared to the actual state of art.
- There is a significant decrease in OCP from the samples that were naturally immersed in an aqueous solution of  $\text{NaNO}_3$  compared to the ones that were immersed in an

electrolyte that contains sodium phosphate as an inhibitor. A lower OCP suggests that the overall potential of the cell will be higher.

- The discharge voltage remains similar for the different applied currents. Even though different concentrations and different currents were tested, there is no evidence that any of the parameters tried can have a significant impact on the resulting discharge curves. This evidences good stability of the electrode even under high current demands an effect that can be advantageous for the Mg air battery.
- There is a very important increase in the impedance when the inhibitor is added to the electrolyte. Visually it can also be seen the rapid formation of a passivation layer that blocks the active areas of the electrode changing the mechanism to a mass controlled condition. This increases the diffusion overpotential that, in turn decreases the electrode potential. Both these factors may have a negative impact on the electrode resistance and current response in the presence of the largest concentration of sodium phosphate as inhibitor.
- Although d.c. polarization (faster experiment) did not evidence relevant mechanism changes in the Mg electrodes in the presence and absence of inhibitor, thanks to electrochemical impedance spectroscopy (EIS), a resistive electrode was formed accompanied by mass transfer control. This can slowdown the response of the electrode compared to a condition using lower inhibitor concentrations. This may also affect the time response of the anode.
- After studying the effect of three different concentrations, 0.01 M of sodium phosphate is found to be a good concentration to be further tested in this project, mainly due to the lower OCP obtained in the potentiostatic polarization and open circuit potential experiments. It is also observed that 0.005 M shows decent potential and reliable discharge curves, making it a plausible option prior to further experiments.
- Even though the usage of 0.01 M sodium phosphate seemed to have some beneficial aspects, the very large increase of low frequency impedance might make the usage of these inhibitor unsuitable for commercial purposes. Further experiments should be held in order to see how this would affect the final battery and its viability.

After finishing the experiments, analyzing the results and extracting some conclusions it is clear that more research needs to be done, especially because Mg air batteries still have a lot of potential to improve its performance and characteristics. Some of the points that should follow this work are:

- Test in more detail EIS of all inhibitor concentrations and enlarge the range of concentrations to be studied
- Test different inhibitors

- Assemble a cell and run discharge curves and calculate both capacity and capacity retention under different current densities.
- Determine the capacity and resistance over the time in presence and absence of inhibitor

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#### REFERENCES

- [1] M. Sedacca, "Better batteries," *Sci. Am.*, vol. 317, no. 4, p. 23, 2017.
- [2] Y. Li and J. Lu, "Metal-Air Batteries: Will They Be the Future Electrochemical Energy Storage Device of Choice?," *ACS Energy Lett.*, vol. 2, no. 6, pp. 1370–1377, 2017.
- [3] J. Ma, G. Wang, Y. Li, F. Ren, and A. A. Volinsky, "Electrochemical performance of Mg-air batteries based on AZ series magnesium alloys," *Ionics (Kiel)*, vol. 25, no. 5, pp. 2201–2209, 2019.
- [4] T. Zhang, Z. Tao, and J. Chen, "Magnesium-air batteries: From principle to application," *Mater. Horizons*, vol. 1, no. 2, pp. 196–206, 2014.
- [5] Y. Sun *et al.*, "Recent advances and challenges in divalent and multivalent metal electrodes for metal-air batteries," *J. Mater. Chem. A*, vol. 7, no. 31, pp. 18183–18208, 2019.
- [6] X. Zhang, X. Wang, Z. Xie, and Z. Zhou, "ScienceDirect Recent progress in rechargeable alkali metal air batteries," *Green Environ. Engin.*, pp. 1–14, 2016.
- [7] C. Wang *et al.*, "Recent progress of metal-air batteries-A mini review," *Appl. Sci.*, vol. 9, no. 14, pp. 1–22, 2019.
- [8] A. R. Mainar *et al.*, "An overview of progress in electrolytes for secondary zinc-air batteries and other storage systems based on zinc," *J. Energy Storage*, vol. 15, pp. 304–328, 2018.
- [9] S. You, Y. Huang, K. U. Kainer, and N. Hort, "Recent research and developments on wrought magnesium alloys," *J. Magnes. Alloy.*, vol. 5, no. 3, pp. 239–253, 2017.
- [10] F. W. Richey, B. D. McCloskey, and A. C. Luntz, "Mg anode corrosion in aqueous electrolytes and implications for Mg-air batteries," *J. Electrochem. Soc.*, vol. 163, no. 6, pp. A958–A963, 2016.
- [11] Y. Li, J. Ma, G. Wang, F. Ren, Y. Zhu, and Y. Song, "Investigation of sodium phosphate and sodium dodecylbenzenesulfonate as electrolyte additives for AZ91 magnesium-air battery," *J. Electrochem. Soc.*, vol. 165, no. 9, pp. A1713–A1717, 2018.
- [12] S. A. Salman, R. Ichino, and M. Okido, "A comparative electrochemical study of AZ31 and AZ91 magnesium alloy," *Int. J. Corros.*, vol. 2010, pp. 1–8, 2010.
- [13] K. M. Ismail and S. Virtanen, "Electrochemical behavior of magnesium alloy AZ31 in 0.5 M KOH solution," *Electrochem. Solid-State Lett.*, vol. 10, no. 3, pp. 2006–2008, 2007.
- [14] D. Höche *et al.*, "Performance boost for primary magnesium cells using iron complexing agents as electrolyte additives /639/638/675



- /639/301/299/161/891 /128 /123 /132 article,” *Sci. Rep.*, vol. 8, no. 1, pp. 1–9, 2018.
- [15] J. Genescà Ferrer and J. Juárez, “Development and testing of galvanic anodes for cathodic protection,” *Contrib. to Sci.*, vol. 1, no. 3, pp. 331–343, 2000.
- [16] M. A. Deyab, “Decyl glucoside as a corrosion inhibitor for magnesium-air battery,” *J. Power Sources*, vol. 325, pp. 98–103, 2016.
- [17] Y. C. Zhao, G. S. Huang, G. L. Gong, T. Z. Han, D. B. Xia, and F. S. Pan, “Improving the intermittent discharge performance of Mg-air battery by using oxyanion corrosion inhibitor as electrolyte additive,” *Acta Metall. Sin. (English Lett.)*, vol. 29, no. 11, pp. 1019–1024, 2016.
- [18] S. V. Lamaka, B. Vaghefinazari, D. Mei, R. P. Petrauskas, D. Höche, and M. L. Zheludkevich, “Comprehensive screening of Mg corrosion inhibitors,” *Corros. Sci.*, vol. 128, no. September, pp. 224–240, 2017.