Original Article

Role of turbulent flow seawater in the corrosion enhancement of an Al–Zn–Mg alloy: an electrochemical impedance spectroscopy (EIS) analysis of oxygen reduction reaction (ORR)

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1. Introduction

Oxygen reduction reaction (ORR) is the main cathodic reaction influencing the corrosion processes in natural environments. Oxygen reduction is a complex process that involves the transfer of 4 electrons. As the reaction is normally diffusion-controlled, the implementation at the experimental level of diverse hydrodynamic conditions allows for a broader understanding of the behavior of technologically important materials, such as aluminum alloys, in common application environments such as seawater. Contrary to the sluggish mechanism of ORR acting as key barrier in, for example, solid oxide fuel and electrolysis cells, in some cases, the flow rate, unpredictably, enhances the corrosion mechanisms up to levels which were not originally expected. Hence, the effect of well-controlled hydrodynamic conditions needs to be considered.

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In a previous paper, the effect of turbulent flow on the corrosion kinetics and mechanisms of an Al–Zn–Mg alloy in synthetic seawater was analyzed by the potentiodynamic polarization technique [1]. A small effect of electrode rotation on the anodic behavior of Al-alloy can be observed, Fig. 1. The anodic branch of the polarization curve displayed typical resistive behavior due to the formation of a corrosion-products layer. On the other side, the cathodic branch of the polarization curve showed the typical and expected diffusion-control behavior, Fig. 1. A strong effect of flow on cathodic polarization was also observed, as oxygen reduction facilitated dissolution dominates the cathodic reactions. This is due to the decrease of double-layer thickness because of turbulent flow.

Two limiting current density regions appeared before the onset of water reduction, Fig. 1. Both plateaus (diffusion-limited current) were observed in the cathodic region for all the RCE rotation rates tested. The first one was assigned [1] to the reduction of O$_2$ diffusing either through the boundary layer only, or through the boundary layer and a partially reduced surface film (depending on the value of the RCE rotation rate). In both cases, the plateaus are controlled by mass transfer. The reasons that could explain the presence of these two plateaus have not yet been fully investigated.

One of the most technologically important Al alloys is AA2024. Some studies have been recently published about the ORR on AA2024-T3 (93.5 Al, 4.4 Cu, 1.5 Mg, 0.6 Mn) or on arrays of copper electrodes embedded in AA2024. In contrast, the Al–Zn–Mg alloy studied in the present work has not been used commercially. It was developed by Barbucci et al. [2] and proposed as a promising material for galvanic anodes for CP purposes to mitigate environmental concerns. In their paper, they studied the effect of the alloy morphological structure on its electrochemical behavior, with special attention to the influence of the secondary phases. They furthermore performed diverse heat treatments to ensure the dispersion of the fine intermetallic phases [3–5]. Of special interest was the influence of the Ca–Zn and Al–Mg–Zn intermetallic phases on the activation of the aluminum anode materials.

The present work complements the aforementioned studies as it evaluates the potential use of these Al-alloy anodes for marine applications. Preliminary results have demonstrated the key role played by the intermetallic compounds, identified as Al2Mg3Zn3 and Mg7Zn3 in the α-Al matrix, on the activation process of this Al-alloy [6–8]. The metallurgical microstructure leads to a uniform dissolution of the Al-anode, thus preventing the formation of a protective oxide film. Such film slows down the O$_2$ reduction reaction (ORR) occurring at the first plateau of the cathodic polarization curve, in the potential range between −1.0 and −1.2 V (sce) [1].

$$
\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-
$$  

(1)

Fluid hydrodynamics could play a significant role in the oxide-film formation and then in the Al-alloy passivity. An increase in the electrode rotation would enhance the mass-transfer rate of solution, and consequently the oxygen diffusion toward the metal surface for reduction reaction. The generated hydroxide ions are favorable to the formation of an Al oxide film on the electrode surface.

The fact that Al is a poor catalyst for O$_2$ reduction, in aerated solutions, may be explained by the high resistivity of aluminum oxide, restricting electron migration through the passive film.

In the present work, the new experimental evidence is discussed. Besides, an interpretation of the electrochemical impedance spectroscopy (EIS) response, obtained by studying the same system at the corrosion potential, $E_{corr}$, and at −1200 mV (sce) potential at which ORR occurs, is performed. It is clear the need to continue studying the cathodic contributions in this alloy system, specifically the effect of flow on the kinetics and mechanism of ORR, where the surface plays an important role due to the formation of a protective oxide.

2. Experimental

The experimental details concerning the preparation of the Al–Zn–Mg test-alloy and its resulting microstructure are reported in a previous paper [1]. Electrochemical impedance spectroscopy (EIS) measurements were conducted with a Gill AC potentiostat (ACM Instruments) at two potential values. One set of measurements was acquired at the corrosion potential, $E_{corr}$, and the second one at a cathodic potential of −1.2 V (sce). The impedance spectra were performed by scanning the frequency from 10 kHz to 10 mHz (10 data points per decade) applying a small AC signal amplitude of 10 mV/rms between the working and reference electrodes.

The aqueous solution was synthetic seawater prepared according to ASTM D1141 standard [9]. All electrochemical experiments were conducted at atmospheric pressure (Mexico City) and room temperature, 20°C, and carried out at least three times to confirm reproducibility. As the experimental error of the series was minimal, only single spectra of each run are presented. The open circuit potential, $E_{corr}$, was measured for a minimum period of ~45 min to reach steady-state conditions.

An air-tight three-electrode electrochemical cell was used [10]. The working electrode (WE) was machined from the
Fig. 2 – Nyquist impedance diagrams of Al–Zn–Mg alloy at the corrosion potential, $E_{\text{corr}}$, in synthetic seawater at different RCE rotation rates. (a) Impedance diagrams under laminar, 0 rpm and turbulent conditions, 1000, 3000 and 5000 rpm. (b) Impedance diagrams under turbulent flow conditions, 1000, 3000 and 5000 rpm.

Parent material, the as-cast Al-alloy ingot, and had a diameter of 1.2 cm and an exposed area of 3.071 cm². The counter electrode was a rod of sintered graphite and a saturated calomel electrode (SCE) was used as the reference electrode. Prior to each run, the Al-alloy surface was first polished with 600-grit SiC paper, then cleaned and degreased with acetone and finally rinsed with distilled water.

3. Results and discussion

3.1. Electrochemical impedance spectroscopy

3.1.1. Corrosion potential

The characteristics of the impedance spectra varied with rotation rate. Fig. 2 shows the Nyquist diagrams obtained at the corrosion potential value for the Al–Zn–Mg test-alloy immersed in synthetic seawater at room temperature. Significant differences can be noticed between laminar and turbulent flow regimes. Two features are observed. The Nyquist diagram exhibits a first capacitive semicircle in the high and medium frequency ranges, and an extending ill-defined segment or tail, not so well defined, at the lowest frequencies tested. The lowest impedance measurement performed was, however, at 131 mHz, which is not particularly a low frequency in EIS.

The diameter of the first semicircle (the larger arc at high and medium frequencies) is rotation rate dependent. This clearly indicates that the electrochemical reaction corresponding to this arc is due to the oxygen-reduction charge-transfer process. The corrosion potential, $E_{\text{corr}}$, is a mixed potential at which the anodic, corrosion reaction, and cathodic, oxygen reduction reaction, ORR, occurs at the same rate. Then, the charge-transfer resistance, $R_{\text{ct}}$, at $E_{\text{corr}}$ is the polarization resistance, $R_p$.

This charge-transfer resistance, $R_{\text{ct}}$, is higher in the laminar than in the turbulent regime. Under laminar flow conditions, $R_{\text{ct}}$ reaches values of 12,000 $\Omega$ cm², while $R_{\text{ct}}$ values decrease significantly under turbulent conditions to 650, 400, 180 and 120 $\Omega$ cm² for the rotation rates of 1000, 3000, 5000 and 7000 rpm, respectively.

At the lower frequencies, the ill-defined segment may be attributed to the mass transfer process. In any case, at the corrosion potential, the EIS measurement has contributions due to the anodic and cathodic processes involved.

An analysis of the impedance spectrum obtained at $E_{\text{corr}}$, Fig. 2, and specially the charge-transfer arc observed in the high and medium frequencies range, allow determining that, at the low frequencies range, the effects of diffusion predominate. Fig. 3 shows a plot of the impedance modulus as a function of the square root of the rotation rate, $|Z_W|$ vs $\omega^{-1/2}$. These $Z_W$ values are related to frequency according to the following equation [11,12]

$$|Z_W| = \sigma \omega^{-1/2}$$  (2)

It would be expected that as the frequency decreases, even further, finite-diffusion effects would be observed due to the finite thickness of the diffusion layer. The predominant effect of diffusion at low frequencies could be clearly observed in Fig. 3, in which a linear relationship between $|Z_W|$ and $\omega^{-1/2}$ is shown.

Since the impedance response of several equivalent circuits can follow exactly the same function of frequency, as pointed out by Sluyters-Rebach in the IUPAC Recommendations 1994 [13], several electric circuits were considered to fit the EIS data. It is important to point out that the physics model should be according with the kinetics of the involved electrochemical reactions. This includes Al-alloy dissolution, oxygen
The circuit elements, $R_s$, $R_{ct}$, $C_{dl}$ are respectively, the solution resistance, the charge-transfer resistance and the double-layer capacitance. A $C_{dl}$ instead of $C_{dl}$ accounts for the depression in the semicircular arc observed in the Nyquist plot in Fig. 2. Properties of the double-layer are heterogeneous among studied Al-alloy surface, resulting in a capacitance dispersion. Depressed semicircles are common in the impedance plots of several heterogeneous materials. The finite-length Warburg element, $W$, accounts for the diffusional impedance.

Taking into account that the dc measurement reveals an important diffusion process in the cathodic reaction, electrochemical impedance measurements were carried out at a cathodic potential of $-1.2$ V (sce), just in the zone in the cathodic polarization curve, Fig. 1, in which ORR prevail, in order to demonstrate the mass-transfer control by a diffusion process [1].

### 3.1.2. Cathodic polarization

EIS measurements were performed at a potential inside the limiting current plateau. The impedance data is reported in the form of Nyquist plots, Fig. 6, as this representation is more easily influenced by differences between model and experiment than typical Bode plots [16]. Fig. 6 shows the impedance response of the tested Al-alloy at the imposed cathodic potential, $-1.2$ V (SCE). A decrease in impedance is observed as the rotation rate increases. At constant ambient temperature, this effect is attributed to the increase of the oxygen concentration at the metal/electrolyte interface. The impedance is lower (impedance decreases as a function of oxygen concentration) at higher oxygen concentration. Under stationary conditions,

Fig. 4 – The equivalent circuit at $E_{corr}$, using the finite-length Warburg element.
impedance diagrams show what appears to be two capacitive semicircles. However, at 1000 rpm, a single one is observed.

At 3000 and 5000 rpm, a second and very small arc appears at the high frequency end, Fig. 6a. Fig. 6b enlarges the diagram obtained at a rotation rate of 3000 rpm. A remnant of the charge-transfer semicircle is seen at the highest frequencies. Because of the higher cathodic overpotential, −1.2 V, the diameter of this very small arc is considerably diminished, as reduced charge-transfer resistances could be expected due to the relatively large cathodic overpotential imposed. As the frequency decreases, diffusion effects become more predominant. This is confirmed by the linear segment in the Nyquist plot, Fig. 7, representative of a semi-infinite linear diffusion condition, typical of the Warburg-diffusion element [17]. The impedance diagram exhibits a linear behavior characteristic of a diffusion impedance, Z_0. The arc-shaped termination of such segment could be due to a finite-diffusion effect associated with the finite thickness of diffusion layer within the electrolyte [18]. The proximity to 45° at intermediate frequencies can be observed from the Bode representation of the data, Fig. 8. The ending of the line is noticeable by the phase approaching 0° at low frequencies.

It does not seem possible to model all the processes that take place on the metal/solution interface. Therefore, a simplified equivalent circuit is proposed using constant phase element, CPE, as a representation of the surface dispersion of the double-layer capacitance. An R_C(PCE_d(R_CW)), Fig. 4, is used for data analysis. The quality of fitting to the equivalent electrical circuit was judged by the χ^2 values [15,16]. χ^2 provides an estimation of the difference between the real and the simulated data. The obtained χ^2(2) values (0.1095–0.09814) indicate an acceptable fitting to the proposed circuit, as shown in Fig. 9.

The impedance response of the Al-alloy suggests the electrode surface processes control the behavior at the high frequency region while the electrode surface and bulk electrolyte diffusion dominate the low frequency one. Thus, the oxygen reduction reaction at this cathodic potential seems to be influenced by both the formation of aluminum hydroxide (main corrosion product) and the electrolyte layer thickness (which itself depends on the rotation rate). As the rotation rate is increased, the oxygen reduction current rises (oxygen diffusion is enhanced in thin electrolyte layers).

The impedance measurements reveal that the corrosion is controlled by the mass-transfer process involved in the cathodic oxygen reduction (cathodic control), with the highest rate of 7000 rpm, corresponding to a shorter electrolyte layer thickness. The corrosion rate of these Al-alloys in aerated solutions could then be controlled by oxygen diffusion from the bulk of the solution toward cathodic sites through pores in corrosion films.

The elucidation of the mass transfer effects influencing Al-Zn-Mg alloy behavior in seawater is extremely important if the electrochemical corrosion mechanism is to be determined. Quantitative analysis of both, charge and mass-transfer controlled components of the cathodic polarization characteristics within a turbulent fluid flow is possible using the established RCE geometries [19].

The Nyquist plots presented in Figs. 2 and 6 reflect data collected from two different Al-alloy probes, each examined as a function of applied voltage, corrosion potential, E_corr, and −1.2 V, respectively. In both cases, the total polarization resistance, as Fig. 10 shows, is a function of bias (cathodic potential), changing at 0 rpm from 12,000 Ω (E_corr) to 5500 Ω (−1.2 V). The total polarization resistance (obtained as the sum of low- and high-frequency processes) also presents a strong dependence on rotation rate, specially at high bias, decreasing, for example, from 5500 Ω to 20 Ω at −1.2 V. This dependence is evident in the semi-log plot of Fig. 10. R_0 values of less than 100 Ω could indicate that the layer of the corrosion products film was completely removed. The diffusion layer thickness at the metal/solution interface depends on the conductivity of the environment. The excess of hydroxyl ions produced at the surface of Al-alloy, because of oxygen reduction, influence the thickness of the diffusion layer and electrolyte conductivity. Current density increases occur, and consequently, the decrease of charge-transfer resistance due to the decrease of double layer thickness. As a result, there is usually an increase of corrosion rate in the presence of OH⁻ ions.

3.2. Analysis of ORR

The cathodic response in the potentiodynamic polarization curves of the Al-alloy is due to the electrochemical reaction of interest, ORR, Eq. (1), Fig. 1. While these polarization curves were obtained at sufficiently slow scan rates to
minimize capacitive and other transient effects, they can still be employed for a quantitative analysis of oxygen reduction kinetics. For such an analysis, it must be considered that the ORR occurs on an oxidized Al-alloy surface, thus oxygen reduction is assumed to occur on the partial electrode surface (exposed surface regions).

The cathodic behavior revealed a reduction process dominated by a single wave for oxygen reduction in the potential range −1000 mV to −1200 mV vs SCE. Additionally, no significant production of hydrogen peroxide was observed, supporting a 4-electron transfer mechanism. The somewhat irreversible initial potential region of charge-transfer-controlled O₂ reduction leads to limiting-current density values which showed definite dependency on rotation velocity. This dependency was in quantitative agreement with Eisenberg equation [20].

The behavior revealed in Fig. 10 suggests that the dc current across the Al-alloy/NaCl solution interface should display, like the ac resistance, a quasi-exponential dependence on bias within an appropriate range of voltages. A rotation-rate-dependent polarization resistance is a typical feature of a mass-transport-controlled electrochemical reaction.

At potentials more positive than the diffusion controlled region, the cathodic process was controlled by both diffusion and activation kinetics. At the pure charge-transfer-controlled O₂ reduction reaction region occurring at low overpotentials, close to corrosion potential (Fig. 1) selected for the analysis performed here, only the cathodic part of the Butler–Volmer
charge-transfer-controlled $O_2$ reduction was extracted from the linear Tafel region (range $-1.3$ to $-1.5$ V vs SCE at 0 rpm, and $-1.1$ to $-1.5$ V vs SCE at 1000 rpm), Fig. 1. From the Tafel slope values obtained in this region, 22 mV decade$^{-1}$ and 44 mV decade$^{-1}$ for 0 and 1000 rpm respectively, it is possible to estimate the exchange (cathodic charge transfer) coefficient, $\alpha$. This parameter provides a measure of the symmetry of the activation barrier for the charge-transfer process. The values of 0.67 and 0.34 obtained for $n=4$, fall within the range observed in aqueous electrolyte systems ($\nu = 0.3–0.7$).

The limiting current density, $j_l$ for an RCE can be expressed by the Eisenberg equation [20],

$$j_l = 0.0791nFCO_2d_{RCE}^{-0.30}v^{-0.344}D^{0.644}v_{RCE}^{-0.7}u_{RCE}^{-0.7}$$  \hfill (4)

where

$$A = 0.0791nFCO_2d_{RCE}^{-0.30}v^{-0.344}D^{0.644}$$  \hfill (5)

with $CO_2$ the oxygen concentration, $d_{RCE}$ the diameter of the RCE, $v$ the kinematic viscosity, $D$ the diffusion coefficient, and $u$ the rotation rate.

To describe the cathodic reactions on this Al-alloy in the charge transfer, mixed and mass transport regimes for ORR, an analysis was performed considering the equations and analytical method suggested by Gabe [21] and Kear [22], which allowed to connect the Eisenberg-type mass transport correlation and the classic Wagner and Traud equation [23] for electrochemical kinetics for corrosion processes controlled by a charge-transfer step. Considering both activation, and mass transfer processes, the expression for the total current equation is as follows:

$$\frac{1}{j} = \frac{1}{j_{act}} + \frac{1}{j_l} - \frac{1}{j_{act}}\frac{1}{A_{RCE}^{0.7}} = \frac{1}{j_{act}} + b$$  \hfill (6)
Fig. 11 – Current density as a function of rotation rate, as obtained from the data in the potentiodynamic polarization curves of Al-alloy, Fig. 1.

where

\[ b = \frac{1}{A} = \frac{1}{0.0791 n FC_{O_2} d^{-0.30} \rho^{-0.34} P^{0.644}} \]  

with \( j_{act} \) the current density for the activation process.

Substituting values for the parameters, one can obtain

\[ b = \frac{1}{5.33 n CO_2} \]  

Moreover, it is possible to calculate the number of electrons involved (transferred),

\[ n = \frac{1}{5.33 b CO_2} \]  

The linear behavior of \( j^{-1} \) versus \( u^{0.7} \), curve, Fig. 11, allowed calculating \( n \), the number of electrons that were involved in the ORR. The \( n \) value was 4.07, thus confirming a direct pathway involving a 4-electron transfer mechanism, as previously stated in Eq. (1).

4. Conclusions

Experimental evidence supports the influence of turbulent flow conditions on the corrosion rate of the Al–Zn–Mg alloy investigated which is influenced to a significant degree by a mass-transfer process, the oxygen reduction reaction, ORR.

The cathodic response of Al–Zn–Mg alloy in artificial seawater has been examined under conditions of controlled turbulent flow using potentiodynamic polarization technique, where irreversible reduction of oxygen dominates the cathodic process at applied potentials more negative than approximately −1.0 V vs. SCE.

It has been demonstrated that in hydrodynamic conditions of turbulent flow that the cathodic reaction on the Al-alloy surface is the reduction of oxygen which controls the overall corrosion rate.

The oxygen reduction reaction, ORR, is a mass-transfer-controlled regime that proceeds mainly through a pathway reduction mechanism involving a four-electron process. The mass-transfer-controlled ORR rate is a complex function inversely related to the boundary layer thickness.

Impedance spectra recorded during the mass-transfer limited oxygen reduction reaction, ORR, process on Al-alloy in synthetic seawater can be adequately fit an equivalent electrical circuit, which assumes the presence of a mass transfer impedance or semiinfinite Warburg impedance, \( Z_W \).

Conflicts of interest

The authors declare no conflicts of interest.

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