Study of the electrochemical behavior of Al-Zn-In based sacrificial anodes in sea water

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ABSTRACT

Cathodic protection is one of the most commonly used methods to protect steel structures immersed in seawater. This mode of protection may be used alone or associated with a coating, such as paint systems. This work aims to determine the durability of this protection system. We have studied the sacrificial nature of anodes made from Al-Zn alloy. The different materials used have been subjected to stationary and non-stationary electrochemical tests, especially electrochemical impedance spectroscopy (EIS), which is then characterized by EDX and SEM. In the case of sacrificial anodes, the results have highlighted the conditions of activation and passivation of these anodes, which are of particular industrial interest. A relationship has been established between the functioning of the studied anodes and the nature of the corrosion products.and revealing three areas of resistance and suggesting complex mechanisms for localized corrosion.

1. INTRODUCTION

Corrosion is an undesirable phenomenon that reduces the lifespan of metallic materials while destroying their brilliance and purity. Metals deteriorate through corrosion, which results from their contact with the environment. It is a chronic problem that cannot be entirely ignored. Metals' chemical and physical characteristics deteriorate in such hostile settings [1-2]. For the objective of avoiding corrosion in metals, many methods are employed. An appropriate inhibitor provides a number of benefits, including strong inhibitory effectiveness, cheap cost, minimal toxicity, and ease of manufacture . In general, inhibitors have been utilized to minimize metal loss in corrosive environments.

Many industries, including the chemical and petrochemical ones, use metal in a variety of ways. One of the most practical ways to prevent the corrosion of metals in an acidic medium is to use corrosion inhibitors [3]. The most practical and economical method of mitigating corrosion is the use of a protective coating or paint. Coatings and paints, despite being very thin, can be rapidly placed over large areas and offer protection. The price of labor and materials is typically less than the worth of the thing being safeguarded. Over the past century, corrosion-resistant coating and paint technology has improved steadily, yielding a wide range of options for maintaining a variety of substrates in a variety of conditions.

The mature field of coatings is always creating new substrates and application techniques to address evolving needs. In the past thirty years, coating technology has evolved significantly in response to environmental concerns. New coating systems and application techniques are being developed as a result. Cathodic protection is regarded as the most dependable and effective strategy for controlling corrosion, particularly in various marine conditions. Cathodic protection systems often fall into one of two categories: 1) sacrificial anode cathodic protection; and 2) impressed current cathodic protection. The first system has been extensively used, although maintaining it is challenging and occasionally constrained by the availability of an electric power supply . The second approach seems more practical because it doesn't require external wiring or an extra power source [4]. However, it cannot supply the desired current or voltage for the best protection and is not changeable after installation. Therefore, there is a great need for a straightforward sacrificial anode technology that can effectively provide cathodic protection for reinforced concrete. An ideal sacrificial anode needs to provide adequate cathodic protection current and exhibit a very low rate of self-decomposition or corrosion. Because of their high current efficiency, low activity potential, inexpensiveness, aluminum sacrificial anodes are widely employed for cathodic protection of structures in marine environments [5]. Yet, during actual use, sacrificial anodes may be exposed to the impact of microbial life activities, significantly reducing their effectiveness.

The performance of anti-microbial attachment of aluminum sacrificial anodes has been the subject of numerous investigations, and numerous studies have demonstrated a clear correlation between the performance of anti-microbial attachment and the composition of alloy components [6]. There is little doubt that commercially available aluminum sacrificial anodes do not function as well as Al-Zn-In base anodes in Zn and in, the activator elements, ensure uniform anode dissolution and avoid polarization. The material's great current efficiency, though, is a benefit. Numerous researchers are attempting to enhance the electrochemical characteristics of Al-Zn-In alloys [7].

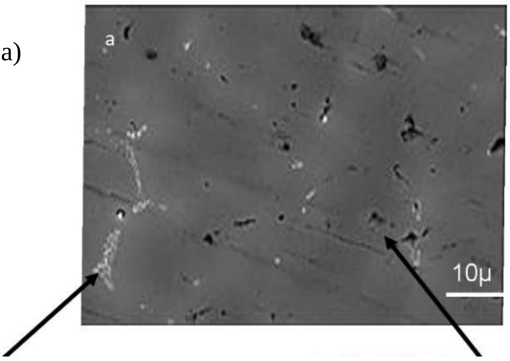
The electrochemical behavior of Al-Zn-In alloys was previously investigated [9-11]. While precipitates received less attention, the majority of them concentrated on the effect of trace elements on the electrochemical properties of an anode. In the case of Al-Zn-In alloys, Bessone et al. noted that the amount of In^{3+} present at the interface determines the level of activation obtained in the Al anode [12,13]. The material that is most frequently used for developing sacrificial anodes for averting corrosion in steel structures is aluminum. But in aluminum, pitting corrosion rather than uniform corrosion takes place. This is because the passive layer on the aluminum surface naturally develops quickly. Microstructural defects in the oxide film could lead to film breakdown [11] Pit corrosion arises when Al alloy is exposed to aggressive electrolytes, resulting in localized ion penetration through the film at the locations of the microstructural defects [15]. This is the circumstance to take into account for pit initiation. Despite the fact that the Al-Zn-In sacrificial anode offers fantastic electrochemical qualities, but little is known about how it behaves as it corrodes. Graver et al. proposed that indium segregation on the alloy surface was what induced aluminum activation in chloride solution, and annealing at 300 °C proved that this was indeed the case [14]. In order to better comprehend the corrosion mechanism, this study investigated the corrosion behavior of the alloy Al-Zn-In in a seawater solution.

2. EXPERIMENTAL

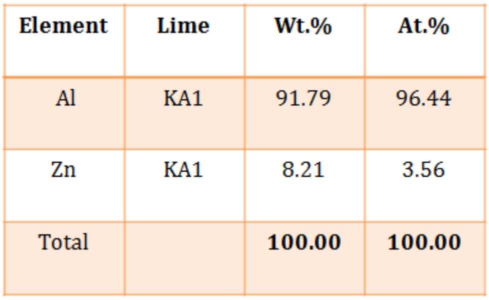
Electrochemical experiments is being carried out in a three-electrode cell using a VoltaLab 40 potentiostat/galvanostat operated by a PC. A platinum wire and a saturated calomel electrode (SCE) serve as the counter and reference electrodes, respectively. The working electrode in this case is a revolving disc electrode. This system has the benefit of achieving uniform and steady stirring in the region of the electrode, allowing the hydrodynamic conditions to be determined.

The electrodes are 5 mm diameter cylinders installed on a door steel sample. The device is then coated with epoxy resin and covered with cataphoresis to isolate the unexposed portions and adapt to the sample cell (diameter ≈ 18 of the cylinder, 30 mm). The electrodes were performed and the material is made of an aluminum-zinc-indium alloy; its chemical composition is illustrated in tables in Figure 1.

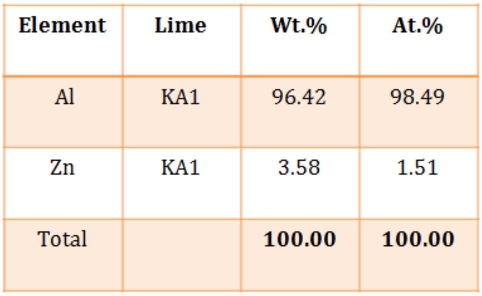
(a)



(b)



Element	Lime	Wt.%	At.%
Al	KA1	91.79	96.44
Zn	KA1	8.21	3.56
Total		**100.00**	**100.00**



Element	Lime	Wt.%	At.%
Al	KA1	96.42	98.49
Zn	KA1	3.58	1.51
Total		**100.00**	**100.00**

Figure 1**.** (a) SEM observation, (b) EDX analysis of the aluminum anode surface after preparation surface.

The electrodes are polished on abrasive sheets of silicon carbide SiC grain in 1000 (≈ 20 microns grain) and 4000 (≈ 5 microns grain), then placed in ethanol and sonicated, passed back to the ultrasonic bath, and rinsed with water. A scan rate of 30 mV/mn was used to obtain the potentiodynamic polarization curves. Because of this speed, quasi-stationary settings were obtained and the results achieved good reproducibility. The plot of the polarization curves in the potentiostatic regime seeks to investigate the behavior of the anode in the areas bounded by the potential feature values E_{corr}, E_{rup}, and E_{pass}. After each polarization in chloride media, impedance measurements are taken at 25 °C.

At frequencies ranging from 100 kHz to 1 MHz, the amplitude of the applied sinusoidal potential drop is 10 mV peak to peak, with 10 points per decade. The simple method of parameter tweaking was applied to simulate the results of electrochemical impedance spectroscopy. Z. VIEW for equivalent circuits is the software program that has been developed. The electrode surface is characterized by SEM (ultra 55).

3. RESULTS AND DISCUSSION

3.1. Polarization curves

The polarization curves generated in seawater and potentiocinetic chloride media are shown in Figure 2, where a plateau is followed by a last, abrupt current. Similar gaits were detected in other experiments [16], which are suggestive of a metal's tendency to passivation [17-19]. In the presence of chlorides, these alloys are subjected to a localized attack for all potential values greater than the Pourbaix et al [20]. breakdown potential. The breakdown potential is correlated with a sharp and final current.

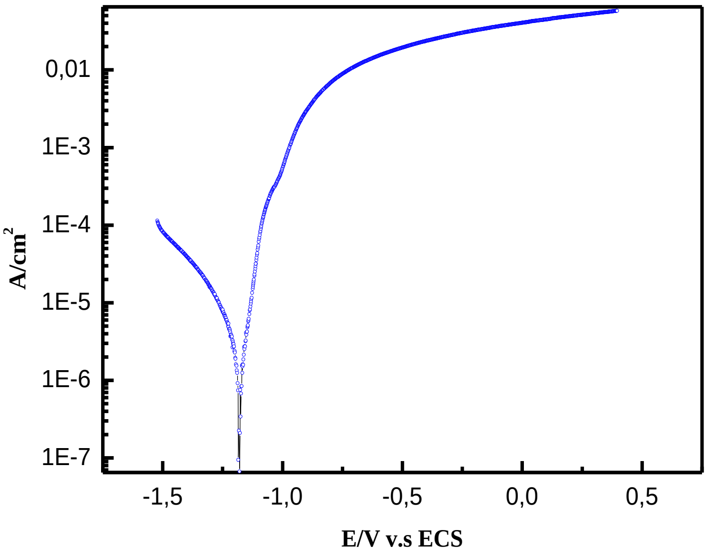
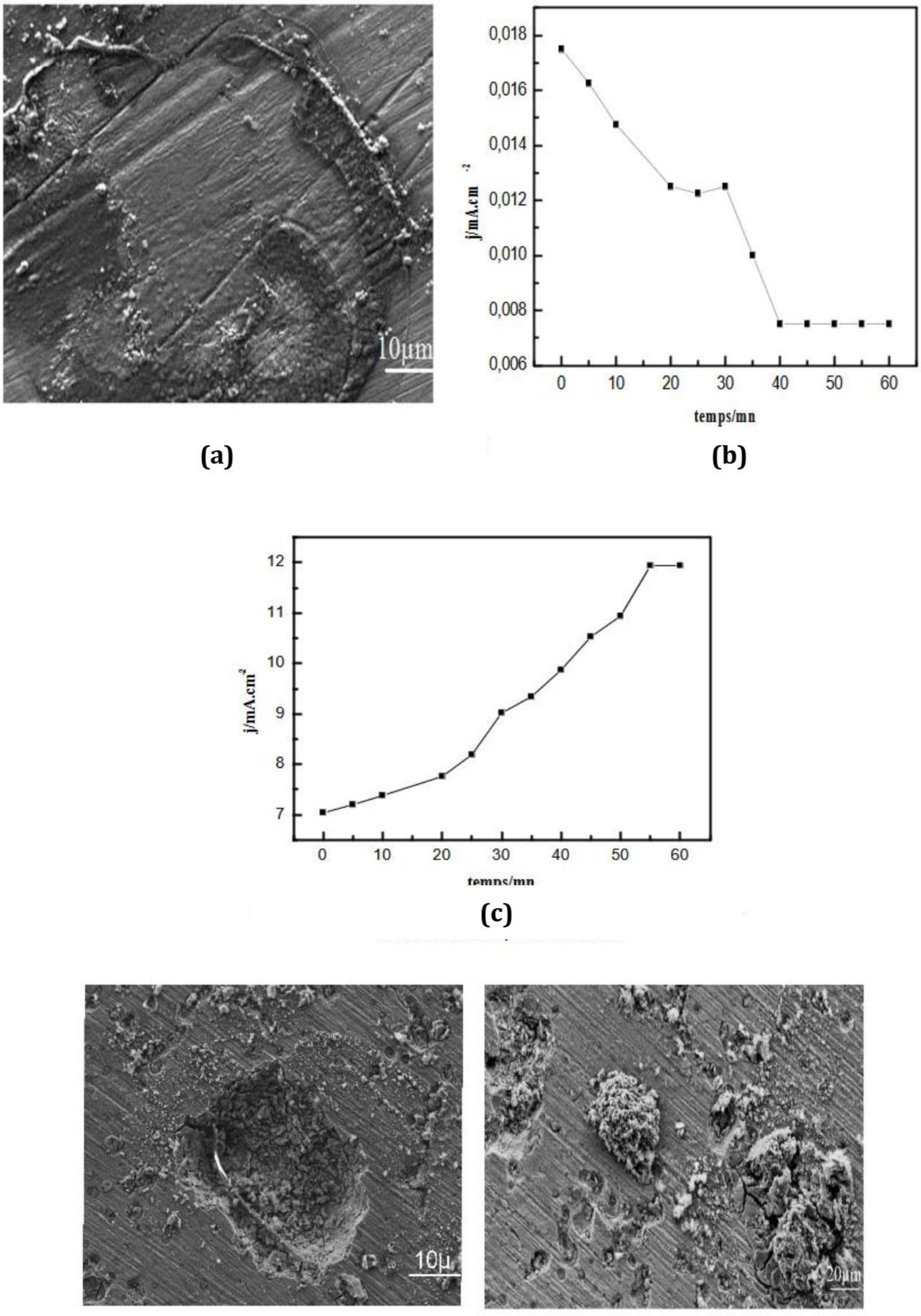


Figure 2. Potentiocinetic polarization curves of Al-Zn-In



(a) **(b)**

(c)

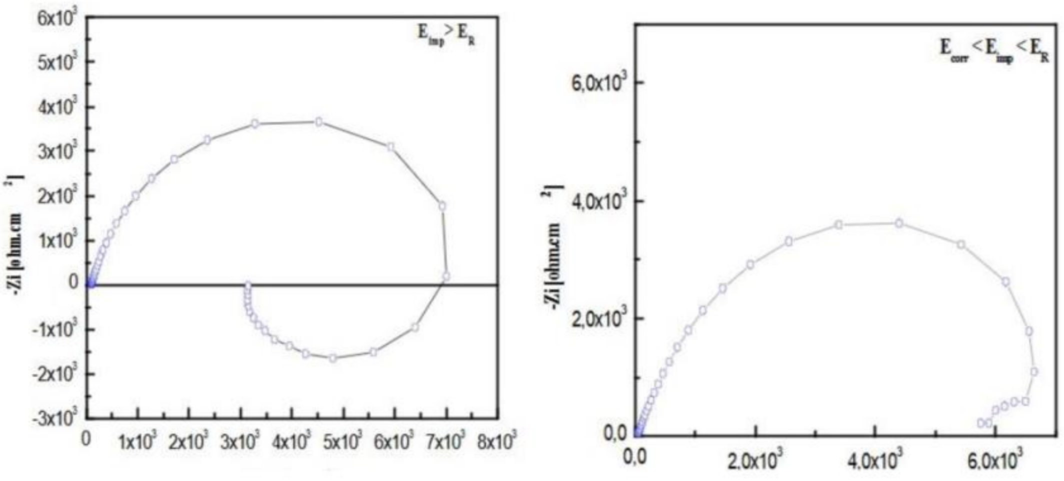
(d)

Figure 3. Potentiostatic polarization curves of Al-Zn-In : (a) passive state of the Al-Zn-In andoe SEM observation, (b) Potentiostatic polarization curves of Al-Zn-In at 1050 mV/ECS at (E_{corr}<E_{imp}<E_R), (c) Potentiostatic polarization curves of Al-Zn-In at 1050 mV/ECS at (E_{imp}>E_R), d) Active state of the Al-Zn-In andoe SEM observatrion.

The potentiostatic polarization curves in the passive and active state was illustraterd in Figure.3 , where Passive state of Al-Zn-In anode depicted in Figure 3.(b) and were displayed at potential levels measured in several characteristic domains where the curve was gradually decrease, and this highlited at SEM observation if Figure3.(a) where surface was not damaged. And when the imposed potential exceeds the rupture potential (Eimp > ER), the anode current gradually increases Figure 3.(c), which is linked to an active dissolution that results in the formation of pits highlighted by SEM observations Figure 3.(d). Surface activation is attributed to indium which enhances chloride adsorption, is involved in activation, and is implicated in local acidity [15,16, 19,21].

3.2. Impedance diagrams

The impedance diagrams recorded in the Nyquist representation after each polarization test in the potentiostatic regime as shown in Figure. 4 and as a function of immersion time as highlited in Figure 5. Under pitting conditions (E> ER) and long immersion times (3–5 days), the impedance diagram reveals two high-frequency capacitive loops and a very low-frequency inductive loop ($f < 10^{-1}$). The first high-frequency loop is caused by the double-layer capacitance in parallel with the transfer resistance, while the second is most likely caused by the disintegration of the passive layer and an acceleration of the material's degradation. This conclusion has been reported in other publications and is compatible with diffrents works [18-22]. The pitting behavior seen by other researchers is linked to the inductive component of the impedance diagrams. There is a huge dispersion of the points under passivation circumstances and at very low frequencies, and the inductive loop no longer occurs. The scattering of the dots can be attributed to a surface metastable state represented by current variations.



(a) **(b)**

Figure 4. Impedance diagram of Al-Zn-In in sea water under different conditions : (a) : Pitting conditions, (b): Passivation conditions.

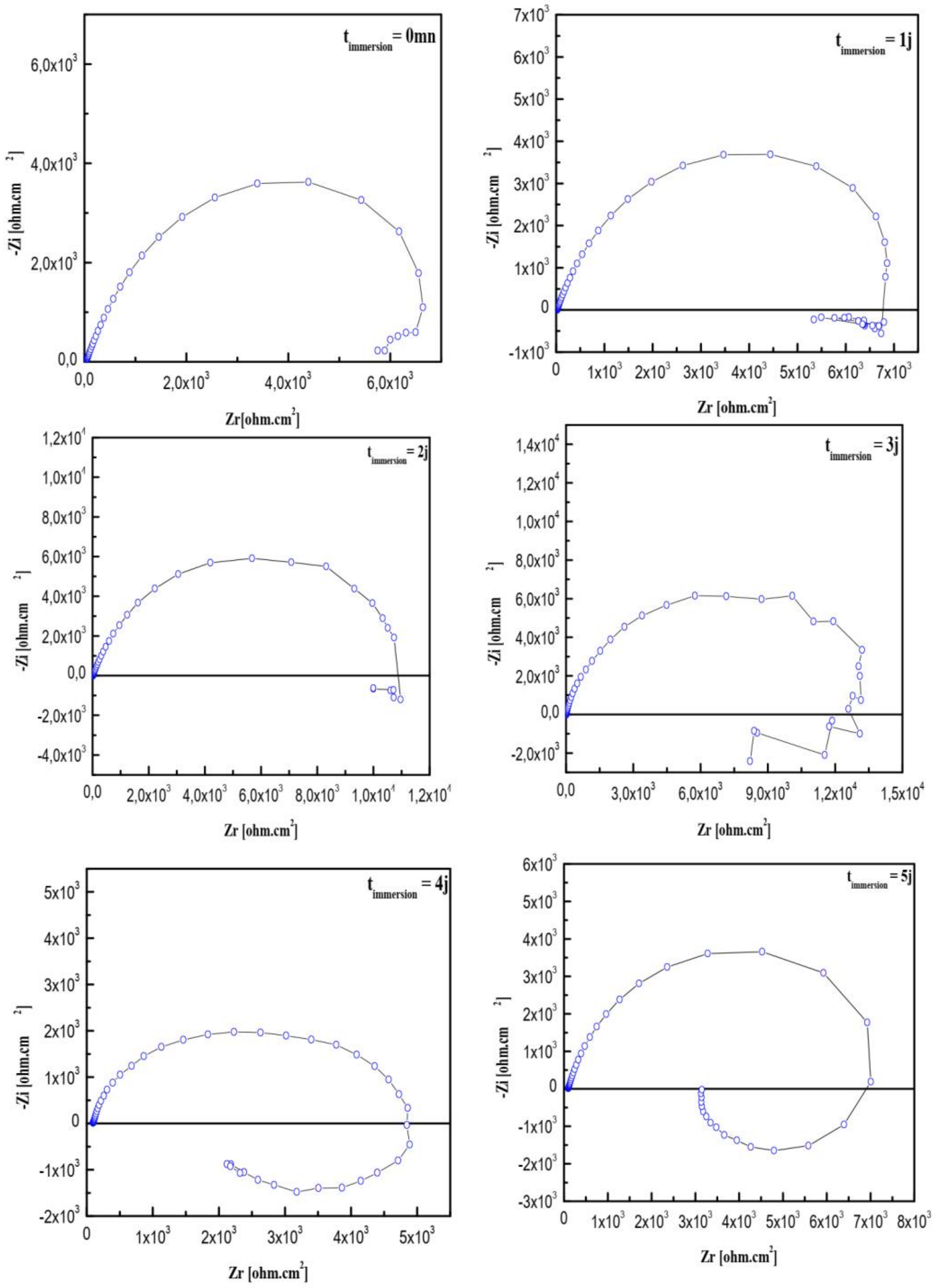


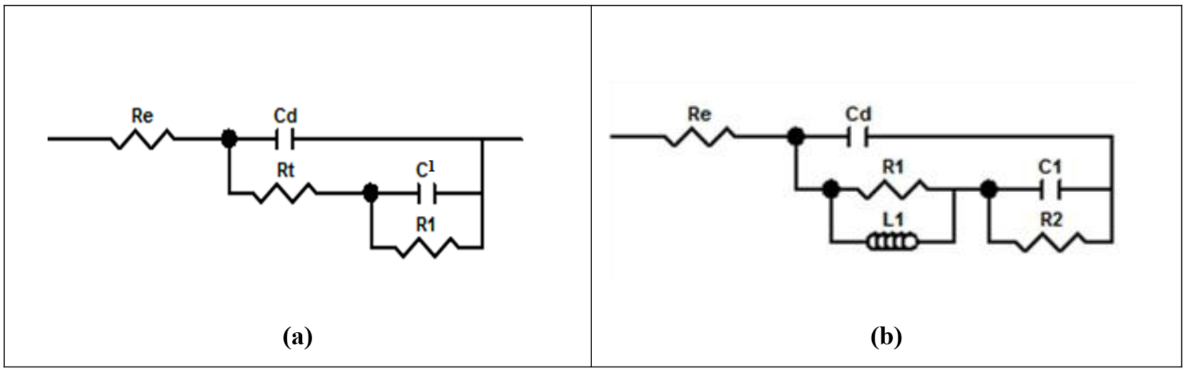
Figure 5. Impedance diagrams of Al-Zn-In in sea water as a function of time

3.3. Electrical circuit proposed models

The program ZView was utilized to choose models and alter electrical parameters in the instance of electrochemical sacrificial anodes. The comparable circuit under passivity is given by two parallel RC components. The inductive loop formerly attributed to the presence of Bite is no longer observable under these conditions.

In this circuit illustrated in Fig. 6.a, rerepresents the electrolyte resistance; Cd is the double-layer capacitance, and Rt transfer resistance, while C1 and R1 represent the capacitance and resistance of the passive film, respectively.

The diagram obtained under the conditions of pitting is a circuit-2RC RL illustrated by the Figure. 6.b below. In this circuit, the Re represents the resistance of the electrolyte, Cd the double-layer capacitance, and resistance Rt transfer, C1 and R1 represent respectively the capacitance and resistance of the passive film.



(a) **(b)**

Figure 6. Electrical circuit proposed models.

Table 1: electrical parameters in the conditions of pitting

Re ($\Omega.cm^2$)	Cd (μFcm^{-2})	Rt ($\Omega.cm^2$)	L1	C1 (μFcm^{-2})	R1 ($\Omega.cm^2$)
24	**0.010842**	**1.48**	**0.13245**	**0.046416**	**1.288**

Table 2: electrical parameters in the passivation conditions

Re ($\Omega.cm^2$)	Cd (μFcm^{-2})	Rt ($\Omega.cm^2$)	C1 (μFcm^{-2})	R1 ($\Omega.cm^2$)
26	**0.026984**	**2.654**	**5.26657E14**	**1.77E9**

These results are similar to results obtained by other researchers Xudong Li.et al, [22] who studied the effect of precipitates on the performance of sacrificial anodes based on aluminum.

4. CONCLUSION

In this study, the corrosion resistance of an Al-Zn-In sacrificial anode in seawater is examined. The resulting potentiodynamic polarization curves identified three areas: a cathode region for $E< E_{corr}$, a passivity range for $E_{corr} <E <E_R$, and field training bites for $E> E_R$.

The impedance measurements revealed two-time constants in passivation conditions and three-time constants in pit formation situations. Equivalent circuits could reproduce the experimental patterns founded, taking into account the electrochemical behavior as a function of applied voltage and surface state. These findings suggest that localized corrosion is triggered by a local breakdown of the passive film. It occurs via complex mechanisms that are not always clear to comprehend. To preserve electroneutrality, the mechanism stared by a mid-chloride ion adsorption of Cl in the natural oxide layer, followed by a rupture with the problems (grain boundaries) at the bottom of the injection. This is the phase of propagation. Complexes are formed of metal chlorides that are then hydrolyzed.

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