Development of an Al-Zn-Bi alloy sacrificial anode for the protection of steel in artificial Seawater: An electrochemical analysis

M. H. Qureshi¹, A. Farooq¹, M. Wasim², K. M. Deen³*
¹Corrosion control Research Cell, Institute of Metallurgy & Materials Engineering, University of the Punjab, Lahore, 54590, Pakistan
²Engineering & Development, Millat Tractors Limited, Lahore, 54000, Pakistan
³Department of Materials Engineering, The University of British Columbia, Vancouver, V6T 1Z4, Canada

Abstract

The Al-Zn sacrificial anodes are widely used for cathodic protection in marine steel structures. This study evaluates the impact of bismuth addition on the electrochemical properties of the Al-Zn sacrificial anode in artificial seawater. The microstructure analysis confirms the presence of uniformly distributed intermetallic β-AlFeSi and spherical Bi particles within the α-Al matrix. The open circuit potential (OCP) comparison between Al-Zn-Bi and carbon steel reveals a potential difference of approximately 400 mV, indicating sufficient cathodic protection for the steel. Electrochemical impedance measurements indicate the initial hindered dissolution of the anode due to surface film formation, which later dissociates due to the aggressive attack of Cl⁻ species in the electrolyte. The sufficiently negative surface potential (−0.875 V vs. Ag/AgCl) observed at 10 mA/cm² demonstrates the suitability of anode for fulfilling the cathodic protection criteria of steel structures.

Keywords: Sacrificial anodes; Al-Zn-Bi anodes; Corrosion; Cathodic protection; Aluminum anodes

*Corresponding Author (kashifmairaj.deen@ubc.ca)

1. Introduction

Steel is a widely used material in the construction of large infrastructures. It serves as a primary component in the building of various structures, including offshore drilling platforms, steel-cast docks, pipelines laid on the seabed, coastal bridges, and ship hulls [1]. However, the corrosion of these offshore structures poses a significant concern, as they are constantly exposed to a corrosive electrolyte such as seawater. The corrosion process in seawater can cause severe degradation and deterioration of these structures. It can lead to the development of fatigue cracks, which can compromise the structural integrity over time. Corrosion-induced brittle failure and unstable failure are also potential risks associated with the corrosion of offshore structures in seawater [2]. Therefore, effective corrosion protection measures are crucial to
ensure the longevity and safety of these steel structures in such corrosive environments. Cathodic protection is a cost-effective and commonly used technique for mitigating corrosion in aggressive marine environments, as compared to the use of corrosion-resistant nickel-based alloys [3]. There are two main types of cathodic protection techniques: Impressed Current Cathodic Protection (ICCP) and Sacrificial Anode Cathodic Protection (SACP). In ICCP, the required current to mitigate corrosion is supplied from an external DC power source. The structure to be protected is connected to the negative terminal of the DC source, making it the cathode, while a noble element such as Mixed Metal Oxides (MMO) or platinized titanium anode is connected to the positive terminal. This method is suitable for large structures with significant corrosion issues and a projected service life of more than 25 years [4, 5]. On the other hand, SACP involves the use of galvanic anodes that are electrochemically more active, having a more negative reduction potential. These anodes are directly attached to the structure, providing the required current for corrosion protection. This method is applied in cases where the budget is limited and the expected service life of the structure is around 10 years [6, 7].

Aluminum-based sacrificial anodes are extensively employed for the cathodic protection of metallic structures in seawater due to several advantageous properties. These include the abundance of aluminum in Earth's crust, its non-toxic nature, more negative reduction potential, high current density, and greater protection efficiencies [8]. However, aluminum is prone to the formation of a protective oxide layer on its surface, known as the passivation effect. This oxide layer shifts the corrosion potential towards a more noble state, which hampers the dissolution process [8-10]. Furthermore, chloride ions present in seawater can attack areas of the aluminum anode where the oxide layer is depleted or defective, leading to localized corrosion in the form of pitting corrosion. This selective corrosion reduces the efficiency of the anode [11].

To counteract this problem, the passive oxide layer on the aluminum sacrificial anode needs to be removed or modified by incorporating alloying elements that act as activators. Commonly used modifiers include zinc (Zn), magnesium (Mg), cadmium (Cd), and barium (Ba). Additionally, elements such as indium (In), tin (Sn), titanium (Ti), mercury (Hg), gallium (Ga), bismuth (Bi), and silicon (Si) are added to enhance the de-passivation effect [12-17].

Various ternary alloys of aluminum find application due to their specific properties. Al-Zn-In alloys demonstrate superior electrochemical properties, such as high current efficiencies reaching up to 85% and an actual current capacity of 2600Ah/kg. However, they exhibit low operating potentials, which can lead to stress corrosion cracking or hydrogen embrittlement [18, 19]. Al-Zn-Sn alloys are used in seawater applications but show lower current efficiency and often require heat treatment for improved performance [20]. Al-Zn-Mg alloys are effective for cathodic protection; however, they have high hydrogen...
overpotential and form MgZn2 intermetallic compounds, where the intermetallic acts as an anode and the aluminum matrix serves as a cathode, resulting in the fast dissolution of the sacrificial anode. On the other hand, Al-Zn-Mg-Mn alloys exhibit lower protection efficiency, around 83% [21]. Although Al-Zn-Hg alloys demonstrate high current efficiencies, the environmental pollution caused by mercury led to its elimination from competition [22]. Each sacrificial anode alloy system possesses its advantages and disadvantages, which determine its usage in specific environments.

However, the electrochemical behavior of 0.195% Bi in Al-4.22%Zn alloy researchers has not yet been studied. Therefore, our objective is to investigate the properties of this alloy and determine the impact of Bi as a modifier in Al-Zn-based sacrificial anodes. We aim to assess their suitability for practical application in the cathodic protection of steel structures in marine environments.

2. **Materials and Methods**

The Al-Zn-Bi alloy was developed via melting and casting. The chemical composition of the alloy is given in the following **Table 1**. The casted Al-anode and carbon steel billet were then cut in the required dimensions to perform electrochemical tests.

**Table 1**: Chemical composition of the as-casted Al-Zn-Bi anode in wt(%)

<table>
<thead>
<tr>
<th>Si</th>
<th>Fe</th>
<th>Cu</th>
<th>Zn</th>
<th>Ti</th>
<th>Bi</th>
<th>Ga</th>
<th>In</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0160</td>
<td>0.140</td>
<td>0.0204</td>
<td>4.22</td>
<td>0.0421</td>
<td>0.195</td>
<td>0.0129</td>
<td>0.0159</td>
<td>Bal</td>
</tr>
</tbody>
</table>

The composition of carbon steel used in this study is given in **Table 2**.

**Table 2**: Chemical composition of carbon steel in wt (%)

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.146</td>
<td>0.275</td>
<td>0.139</td>
<td>Bal</td>
</tr>
</tbody>
</table>

The electrolyte (artificial seawater) used for weight loss and electrochemical testing was prepared according to the standard ASTM D1141. The composition of artificial seawater is given in **Table 3**.

**Table 3**: Composition of artificial seawater

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>NaCl</th>
<th>MgCl2</th>
<th>CaCl2</th>
<th>KCl</th>
<th>NaHCO₃</th>
<th>H₃BO₃</th>
<th>NaF</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/L</td>
<td>24.53</td>
<td>5.20</td>
<td>1.16</td>
<td>0.695</td>
<td>0.201</td>
<td>0.027</td>
<td>0.003</td>
</tr>
</tbody>
</table>

2.1 **Microstructural Analysis**

Small samples of Al-alloy and carbon steel were mounted and ground using emery paper up to P1200 grit. They were then polished with corundum paste in a range from 1 to 0.25 µm to achieve a smooth and scratch-free surface, following the ASTM G01 standard. After polishing, the samples were rinsed with...
distilled water, dried, and then etched using Keller's reagent for the Al-anode and 2% Nital for the carbon steel. The microstructure of the samples was analyzed using an optical microscope. The Al-anode was examined at a magnification of 500X, while the carbon steel was examined at a magnification of 50X.

2.2 Weight Loss Analysis
Samples were cut into dimensions of 1cm x 1cm x 0.2cm for the Al-anode and carbon steel, and ground up to P1200. Cylindrical glass jars were used, and 100ml of artificial seawater (with the composition specified in Table 3) was added to each jar. A hole was drilled in the cap, and the samples were hung using threads. The samples were periodically removed from the electrolyte and cleaned using different cleaning solutions. For the Al-anode, concentrated HNO$_3$ was used as the cleaning solution, while for the carbon steel, a 5% HCl solution was used. These solutions were used to remove corrosion products from the surface of the samples. After cleaning, the samples were washed with distilled water, dried, and then weighed to calculate the mass loss. The testing was conducted for 30 days, and the weight loss of the samples was measured at regular intervals of time.

2.3 Electrochemical Testing
For electrochemical testing, samples of Al-anode and carbon steel were cut into dimensions of 1 cm x 1 cm x 0.2 cm and ground up to P1200. A hole with a diameter of 2 mm was drilled in the samples through which a wire was passed to provide an electrical path. Only a 1 cm$^2$ area of the samples was exposed, and the remaining area, including part of the exposed wire, was covered using epoxy resin. Open circuit potential (OCP), Electrochemical impedance spectroscopy (EIS), Linear polarization resistance (LPR), and Potentiodynamic polarization (PD) of Al-anode and carbon steel were conducted to evaluate the corrosion behavior of both Al anode and steel samples. The galvanostatic testing of Al-anode was also conducted using a three-electrode assembly. In this setup, the Al-anode sample served as the working electrode, a graphite rod was used as the counter electrode, and Ag/AgCl saturated KCl was used as the reference electrode. Artificial seawater, with the composition specified in Table 3, was used as the electrolyte. The OCP measurement was conducted for 1000 seconds, while the EIS test covered a frequency range of $10^5$ to 10 mHz with an AC potential amplitude of $\pm 5$ mV$_{\text{rms}}$. The LPR test was performed within a potential range of $-0.25$ V to 0.25 V. An anodic impressed current density of 0, 0.1, 1, 10, and 100 mA/cm$^2$ was applied to the Al-anode to estimate its cathodic protection capacity.

3. Results

3.1 Microstructural Analysis
The microstructures of Al-anode and carbon steel obtained after etching with Keller’s reagent (10 ml HNO₃, 10 ml HCl, 2.5 ml HF and 10 ml deionized water) and 2% Nital, respectively are given in Figure 1.

![Microstructures of Al-Zn-Bi and Carbon Steel](image)

Figure 1. Microstructures of (a) Al-Zn-Bi (b) Carbon Steel

Bismuth has a solubility of <0.1 wt. % at 660 °C in the Al matrix and a melting point of 271 °C. This indicates that it will solidify last and form a solid solution with Al. As Bismuth has a standard reduction potential of 224 mV vs. SHE, the spherical Bi-particles observed in the microstructure, act as cathode to Al and Zn [23]. These Bi-particles are uniformly distributed, ensuring the uniform distribution of cathodic sites that may facilitate the dissolution of the alloy matrix. Additionally, flakes of Al-Zn intermetallic were observed at the grain boundaries, and the fine AlFeSi particles (β-phase) were present in the Al-Zn-Bi matrix phase. On the other hand, Figure 1b showed a typical pearlite and ferrite grain structure of the normalized carbon steel.

3.2 Weight Loss Testing
The corrosion rates of both Al-anode and carbon steel were individually measured as a function of time in artificial seawater according to standard ASTM G31.
The weight loss of the samples was measured at regular intervals over a total exposure period of 648 hours, and the corrosion rates were calculated in grams per square meter per day (gmd). These corrosion rates are presented in Figure 2.

Initially, the Al-Zn-Bi anode exhibited a relatively high corrosion rate of 3.5 gmd under ambient conditions. However, this corrosion rate gradually decreased to less than 2 gmd after 100 hours of exposure and remained relatively constant throughout the total exposure period of 648 hours. In contrast, the corrosion rate of carbon steel was significantly higher than that of the Al-anode. It increased from 11.32 gmd after 24 hours of immersion to 42.58 gmd after 648 hours.

The corrosion rate results indicate that no passive film formed on the surface of the carbon steel, which could have acted as a physical barrier to limit the active dissolution process. The high dissolution rate observed for carbon steel suggests that unprotected steel structures in the marine environment are highly susceptible to destructive failure. The presence of corrosion products on the surface of carbon steel, as shown in Figure 3, further supports the prediction of significant corrosion in the marine environment. At potentials more positive than −1.0 V vs. SHE, the dominant cathodic reaction is oxygen reduction.
At potential, $< -1.0 \text{ V vs. SHE}$, water reduction on the surface of steel could generate hydrogen evolution as per reaction 2.

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \quad (2)$$

**Figure 3.** Post surface features of Al-anode and steel substrate obtained during weight loss measurements

The oxidized species i.e., $Al^{3+}$ released from the Al-anode surface could react with hydroxide ions generated on the cathode (steel surface) and may form $Al(OH)_3$ as per reaction 3.

$$Al^{3+} + 2OH^- \rightarrow Al(OH)_3 \quad (3)$$

This aluminum hydroxide could deposit on the surface as a film, which provides a physical barrier to seawater, thus reducing the dissolution rate of Al-anode. Moreover, in actual seawater, the presence of dissolved $Ca^{2+}$ and $Mg^{2+}$ ions could precipitate on the anode surface by forming a thick layer by reducing its dissolution and cathodic protection efficiency [24-28]. Calcium hydroxide could precipitate under alkaline conditions (between pH 8 – 10) however, magnesium starts precipitating beyond a threshold pH (> 9.3) [29, 30]. The discoloration of the Al-anode and deposition of barrier layers was visible on the surface of the pre-cleaned Al-anode surface even after 24 hours of exposure to artificial seawater as shown in **Figure 3**.

Due to the formation of the hydroxide surface layer on the Al-anode surface reduced its dissolution rate (3.61 to 1.44 gmd) resulting in a decrease in weight loss (**Figure 2**) in artificial seawater. The formation of the surface film slows down the diffusion of $Al^{3+}$ species from the surface to the electrolyte resulting in the accumulation of cations at the metal/hydroxide layer interface. The net positive
charge increases under the surface layer could attract highly electronegative Cl$^-$ ions at the defect sites via migration and diffusion thus enhancing the localized corrosion of the Al-anode. The Cl$^-$ species could form complexes with Al$^{3+}$ and Al(OH)$_3$, which are soluble species (reactions 4 – 5). The hydrolysis of soluble AlCl$^{2+}$ species could form a solid species (reaction 6). However, these species are unstable and could act as a defect with the Al(OH)$_3$ surface layer causing localized dissolution of the Al-anode. The combination of these processes could accelerate the dissolution of Al-anode thus facilitating the cathodic protection [31-34].

\[
\begin{align*}
\text{Al}^{3+} + \text{Cl}^- & \rightarrow \text{AlCl}^{2+} \quad (4) \\
\text{Al(OH)}_3 + \text{Cl}^- + 2\text{H}^+ & \rightarrow \text{Al(OH)Cl}^+ + 2\text{H}_2\text{O} \quad (5) \\
\text{AlCl}^{2+} + 2\text{H}_2\text{O} & \rightarrow \text{Al(OH)}_2\text{Cl} + 2\text{H}^+ \quad (6)
\end{align*}
\]

After immersion in the marine environment, the formation of corrosion products, specifically iron hydroxide, was observed on the surface of the steel. The presence of these corrosion products was evident by changes in color, indicating different oxidation states of the iron species. During the initial 168 hours of exposure, the surface of the steel was partially covered by oxides. This non-uniform surface layer exhibited high porosity, which accelerated the corrosion process. Figure 3 provides visual evidence of the surface condition of the steel after 648 hours of exposure. The image reveals the highly rough surface and the presence of large shallow pits, which further indicate the extent of corrosion and the degradation of the steel structure. These observations highlight the detrimental effects of corrosion on the steel surface in the marine environment, emphasizing the need for effective corrosion protection strategies to mitigate the accelerated corrosion and potential structural failures associated with it.

3.3 Electrochemical characterization of Al-anode and Carbon steel

A more negative OCP indicates that the material or structure is thermodynamically more active, meaning it is more likely to undergo corrosion in that specific environment. It signifies that the material has a higher tendency to undergo anodic reactions and undergo corrosion. In the context of sacrificial anode cathodic protection, the potential of the sacrificial anode must be lower than the potential of the structure being protected (the cathode). This potential difference creates a driving force for anodic and cathodic reactions, effectively diverting the corrosion process from the protected structure to the sacrificial anode. However, it is important to note that if the potential difference between the anode and cathode is too large, it can lead to increased hydrogen evolution. In the case of steel, this can result in hydrogen embrittlement, where hydrogen atoms diffuse into the steel matrix and cause a loss of mechanical strength. Moreover, excessive hydrogen evolution can also damage the protective coating of the structure and lead to blistering, which further accelerates the corrosion rate.
Therefore, it is necessary to carefully consider the potential difference between the sacrificial anode and the structure being protected to ensure effective corrosion protection without introducing detrimental effects such as hydrogen embrittlement or coating damage.

Too low a potential difference between the anode and cathode can negatively impact the cathodic protection system. In other words, the insufficient potential difference would compromise the efficiency of cathodic protection and may pose a threat to the stability of the structure being protected.

**Figure 4** presents the Open Circuit Potential (OCP) values for both the Al-alloy and carbon steel samples. The samples were immersed in the electrolyte (artificial seawater) and allowed to stabilize for 60 minutes before measuring the OCP. This resting period ensures that the system reaches a stable state before recording the OCP values.

The initial OCP of the Al-alloy sample after immersion was measured at -796 mV. Over time, a significant change in potential towards the active direction is observed, with the potential shifting from -825 to -937 mV after 48 hours of immersion. The potential change slows down thereafter, and the OCP stabilizes at approximately -978 mV after 600 hours of immersion. In contrast, the OCP of the carbon steel sample remains relatively stable throughout the 600-hour immersion period, with a value of approximately -580 mV.
Pure aluminum, in its pristine state, exhibits an OCP of around -1460 mV vs. Ag/AgCl and possesses a high current capacity of 2980 Ah/kg [32]. However, when exposed to a marine environment, aluminum develops a thin, adherent, and passive oxide layer (gamma-Al2O3) on its surface. This oxide layer reduces the surface activity of aluminum and shifts its potential towards a more noble direction, approximately -740 mV vs. Ag/AgCl [33,34]. It is important to note that this potential of aluminum is relatively positive compared to the potential required for effective cathodic protection of offshore carbon steel structures. *Figure 5* depicting the electrochemical cell of the three-electrode system provides a visual representation of the setup used in the study. It is worth noting that hydrogen evolution is observed on the Al-anode sample, which is a typical side reaction in cathodic protection systems.

![Image of electrochemical cell](https://doi.org/10.26434/chemrxiv-2023-tmq4b)

**Figure 5:** Formation of hydrogen bubbles in a three-electrode electrochemical Cell

When zinc (Zn) is added to aluminum (Al), the potential of the alloy shifts towards the active direction, typically by around 100-300 mV. However, even with the addition of zinc, the potential of the alloy remains relatively positive. The OCP value of pure zinc is approximately -560 mV vs. Ag/AgCl. Although the addition of zinc helps to make the alloy more active, the potential shift may not be sufficient to achieve a significant dissolution of the anode [35, 36]. In the given scenario of Al-5 wt. % Zn alloy immersed in a 3 wt. % NaCl solution, the open circuit potential (OCP) measured was E = -1002 mV vs. Ag/AgCl. This potential indicates that the alloy is relatively more active in the solution compared to the reference...
electrode (Ag/AgCl). The negative potential suggests that the alloy tends to undergo corrosion in artificial seawater [37].

From the provided information, it is clear that the Al-alloy (Al-Zn-Bi) exhibits a more negative potential (E = -978 mV) compared to carbon steel (E = -580 mV). This indicates that the Al-alloy is more active than carbon steel and can act as a sacrificial anode for cathodic protection.

Furthermore, the addition of Bi to the Al-4.22 wt% Zn alloy causes the potential of the anode to shift toward the noble direction (-978 mV) after 600 hours of immersion in artificial seawater. This suggests that the Al-Zn-Bi alloy can mitigate the risk of hydrogen embrittlement and is a promising candidate for applications requiring low-potential sacrificial anodes. The average potential difference of approximately 400 mV between the carbon steel and Al-Zn-Bi anode further supports the effectiveness of the Al-Zn-Bi alloy as a sacrificial anode for steel cathodic protection.

In Figure 6(a), the Nyquist plot displays the capacitive loop of the carbon steel substrate and the values of the real impedance at a low frequency representing the charge transfer resistance (R_{ct}). Initially, at 0 hours of immersion, R_{ct} measured was 3080 ohm.cm², but within 24 hours, it sharply decreased to 1520 ohm.cm² (as given in Table 4). This decline in R_{ct} can be attributed to the heightened activity of carbon steel in artificial seawater, primarily caused by the presence of aggressive ions such as chloride ions (Cl⁻).
The value of $R_{ct}$ further decreases to 261 ohm.cm$^2$ after 576 hours of immersion. Also, from the frequency vs. impedance plot in Figure 6 (b), it is evident that the resistance to corrosion decreases gradually as the immersion time increases. The phase angle $Z_{phz}$ in the frequency vs. phase angle diagram of the Bode plot shown in Figure 6 (c) continuously decreases from -690 to -530 (Table 4). This indicates the depletion of the double layer over the surface of the steel with increasing immersion time, and it suggests that no adherent passive film develops on the surface of carbon steel in artificial seawater to protect it from corrosion. The resistance of the alloy decreases with time making the dissolution process easier, hence exhibiting a high corrosion rate. No inductive loop has been observed therefore we can infer that there are no adsorbed species on the surface of the substrate that can affect the electrochemical behavior. The
equivalent electrical circuit model used for the fitting of impedance spectra of carbon steel is shown in Figure 6 (d), where $R_s$ represents the solution resistance, $R_{ct}$ represents the charge transfer resistance, and CPE represents the constant phase element associated with the formed double layer on the rough surface [38]. An appreciable decrease in $R_{ct}$ (from 3080 to 261 ohm.cm$^2$) during 576 hours of exposure indicated the enhanced corrosion rate of the carbon steel.

**Table 4. Parameter of the carbon steel obtained by fitting the EEC to the impedance spectra**

<table>
<thead>
<tr>
<th>Exposure Time (hrs)</th>
<th>$R_{ct}$ (ohm.cm$^2$)</th>
<th>$R_s$ or $R_u$ (ohm.cm$^2$)</th>
<th>$(-Z_{img})$</th>
<th>$Z_{phz}$</th>
<th>Frequency (Hz)</th>
<th>n</th>
<th>CPE (F/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3080</td>
<td>4.06</td>
<td>42.08</td>
<td>-69.66</td>
<td>31.25</td>
<td>0.774</td>
<td>0.000929</td>
</tr>
<tr>
<td>24</td>
<td>1520</td>
<td>2.53</td>
<td>35.59</td>
<td>-71.37</td>
<td>38.42</td>
<td>0.793</td>
<td>0.000758</td>
</tr>
<tr>
<td>96</td>
<td>814</td>
<td>3.20</td>
<td>35.40</td>
<td>-67.89</td>
<td>15.62</td>
<td>0.754</td>
<td>0.002131</td>
</tr>
<tr>
<td>168</td>
<td>817</td>
<td>3.28</td>
<td>20.78</td>
<td>-60.53</td>
<td>15.62</td>
<td>0.672</td>
<td>0.005946</td>
</tr>
<tr>
<td>528</td>
<td>272</td>
<td>2.76</td>
<td>120.96</td>
<td>-53.15</td>
<td>0.05</td>
<td>0.590</td>
<td>0.116535</td>
</tr>
<tr>
<td>576</td>
<td>261</td>
<td>2.17</td>
<td>100.09</td>
<td>-53.31</td>
<td>0.06</td>
<td>0.592</td>
<td>0.112960</td>
</tr>
</tbody>
</table>

**Figure 7 (a)** shows the Nyquist plots of Al-anode obtained after different exposure durations. These EIS curves were obtained at regular time intervals of 96 hours, 168 hours, 264 hours, 336 hours, and 576 hours of immersion in artificial seawater. In the initial immersion of 96 hours, the $R_{ct}$ was 3716 ohm·cm$^2$, which increased to 5071 ohm·cm$^2$ after 264 hours of immersion (as given in Table 5).
Figure 7. EIS graphs of Al-anode (a) Nyquist plot (b) Frequency vs. impedance (c) Frequency vs. phase (d) Equivalent circuit model.

This behavior can be attributed to the deposition of insoluble corrosion products, such as Al(OH)$_3$, on the surface of the alloy. These corrosion products act as a physical barrier, impeding the transfer of ions and increasing the resistance during the initial stage of exposure to seawater. After 336 hours of exposure, the $R_{ct}$ decreased from 5071 to 3720 ohm·cm$^2$. This decrease in $R_{ct}$ after 576 hours further validates the aggressive attack of Cl$^-$ species and the formation of local defects within the oxide film.
Table 5. Quantitative values of impedance spectra of Al-anode obtained after fitting as per EEC

<table>
<thead>
<tr>
<th>Exposure Time (hrs)</th>
<th>Rct (ohm.cm²)</th>
<th>Rs or Ru (ohm.cm²)</th>
<th>-Zimg (ohm.cm²)</th>
<th>Zphz (°)</th>
<th>Frequency (Hz)</th>
<th>n</th>
<th>CPE (F/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96</td>
<td>3716</td>
<td>4.06</td>
<td>88.48</td>
<td>-66.48</td>
<td>62.91</td>
<td>0.738</td>
<td>0.0004401</td>
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<tr>
<td>168</td>
<td>4115</td>
<td>2.99</td>
<td>89.86</td>
<td>-63.54</td>
<td>62.91</td>
<td>0.706</td>
<td>0.0006128</td>
</tr>
<tr>
<td>192</td>
<td>4218</td>
<td>3.97</td>
<td>114.31</td>
<td>-65.74</td>
<td>49.86</td>
<td>0.730</td>
<td>0.0004711</td>
</tr>
<tr>
<td>264</td>
<td>5071</td>
<td>3.36</td>
<td>164.86</td>
<td>-59.36</td>
<td>38.42</td>
<td>0.659</td>
<td>0.0009248</td>
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<tr>
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<tr>
<td>576</td>
<td>3720</td>
<td>5.9</td>
<td>202.80</td>
<td>-50.82</td>
<td>31.25</td>
<td>0.564</td>
<td>0.0025242</td>
</tr>
</tbody>
</table>

During 264 hours of exposure, the increase in Rct (from 3716 to 5071 ohms.cm²) was attributed to the formation of a barrier surface layer, which could deteriorate due to the Cl⁻ ions attack thus increasing the corrosion rate as evident from the decrease in Rct to 3720 ohm.cm² [39]. This behavior of the Al-anode in which resistance first increases and then decreases by the action of Cl⁻ is indicated in the Bode plots as shown in Figure 7 (b). The decreasing phase angle of the Al-anode (Figure 7 (c)) is indicated by the decrease in the relaxation coefficient (n) attributing to the non-uniformity of the surface due to localized corrosion. This formation of a rough surface was associated with the aggressive attack of the Cl⁻ species that has created local defects within the oxide layer as discussed above.

A linear polarization resistance (LPR) test was conducted on Al-alloy and carbon steel in artificial seawater for 264 hours as shown in Figure 8. The LPR test is a corrosion rate monitoring method that provides an indication of the corrosion resistance of materials in an aqueous environment [40]. Upon exposure, Al-anode exhibited low polarization resistance (Rp) which increased significantly during the 246 hours. This increase in Rp was associated with the formation of an oxide film on the surface of the Al-anode, which impeded its dissolution during the initial stage of immersion. However, the carbon steel sample showed a small increase in Rp, attributed to the formation defective oxide layer on its surface.
The LPR can be interpreted as the inverse of the corrosion rate at the time of measurement. As depicted in Figure 8, it is observed that the $R_p$ of the Al-alloy increases steadily during the immersion period of up to 264 hours. This trend is consistent with the EIS quantitative data, providing further evidence of the increasing polarization resistance over time due to the formation of surface oxide film.

The anodic and cathodic polarization of the Al-anode and carbon steel, respectively, was conducted using a three-electrode system, and the corresponding graph is shown in Figure 9. The samples were polarized to 0.25 V in the anodic direction for the Al-anode and the cathodic direction for the steel. The anodic curve of the Al-anode exhibits a low polarization, indicating the accelerated and uniform dissolution of the Al-anode. The point of intersection between the anodic curve of the Al-anode and the cathodic polarization curve of carbon steel corresponds to the mixed potential ($E_{corr}$) and mixed current ($i_{corr}$) for the Al-anode/steel system in seawater. The significantly negative $E_{corr}$ (~0.983 V) value compared to the OCP of the carbon steel sample, along with an $i_{corr}$ of 119.5 $\mu$A/cm$^2$, confirms the effectiveness of the Al-anode in protecting the steel substrate by preferentially dissolving at the rate of $1.254 \times 10^{-8}$ mpy (mils per year), as calculated based on the $i_{corr}$, using the following relationship.
Weight Loss  = \( M_{i_{corr}} / nF \)

Where “M/n” is the equivalent weight of the Al-anode, “\( i_{corr} \)” is the corrosion current density, and “F” is Faraday’s constant (96485 C/g-eq.).

\[
E_{corr} = -0.983 \text{ V} \\
I_{corr} = 119.5 \text{ mA/cm}^2
\]

**Figure 9.** Anodic and Cathodic Polarization of Al-Zn-Bi & Carbon Steel

The stability of the Al-Zn-Bi anode and its polarization behavior is evaluated by applying various currents (from 0 to 100 mA) for 16 ks as shown in **Figure 10.**
Figure 10. Galvanostatic Test of Al-Zn-Bi at various anodic impressed current densities

The results indicate that at 0 mA/cm² current (i.e. surface potential) was measured to be −0.97 V, which shifts towards the positive potential as the applied current increases. A negligible change in the surface potential was observed with an order of magnitude increase in current (0.1 & 1 mA/cm²). Compared to the free corrosion condition (at 0 A applied current), approximately 65 mV of shift in the positive direction i.e. −0.912 V vs. Ag/AgCl was observed. With a further increase in current to 10 mA/cm², the surface potential increase increased to −0.875 V, which still falls within the specified range of cathodic protection potential as recommended by ASTM. However, at 100 mA/cm² the potential shift was very large and a potential of −0.176 V was observed, which exceeds the cathodic protection criteria for steel structures. On the other hand, the significantly negative potential of the Al-anode at 10 mA/cm² is considered optimal and validates the effectiveness of the designed alloy for the cathodic protection of steel.

4. CONCLUSIONS

The microstructure analysis of the Al-anode indicates the presence of well-distributed spherical Bi particles in addition to the dispersed β-particles. The well-distributed second-phase particles suggest that the corrosion process of the Al-anode is relatively uniform, meaning that the dissolution of the anode material occurs evenly across its surface. This is a desirable characteristic for sacrificial anodes, as it
ensures effective and consistent protection of the structure being preserved. On the other hand, the corrosion rate obtained from the weight loss measurements of the carbon steel sample highlights the high susceptibility of unprotected carbon steel structures to corrosion in marine environments. Overall, based on the OCP values, it can be inferred that Al-Zn-Bi-based alloys have potential advantages in terms of protecting structures from corrosion and mitigating hydrogen-related issues such as hydrogen embrittlement in carbon steel, making them suitable for specific applications where low potential sacrificial anodes are required. The impedance results indicated that the initial hindered dissolution of the developed Al-anode during immersion was attributed to the formation of a surface barrier layer. However, over time, this barrier layer could dissociate in the presence of Cl\(^{-}\) species, leading to increased dissolution. Furthermore, the significantly negative surface potential of \(-0.875\) V observed at an applied current of 10 mA/cm\(^2\) confirmed the efficacy of the designed alloy for providing cathodic protection to steel structures.

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