Efficiency and characterization study of low voltage current sacrificial anode on Al-Zn-Cu and Al-Zn-Si alloy

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Abstract. The sacrifice of the anode is the cathodic protection used to prevent corrosion. Al-Zn-In alloys are often used it causes excessive protection that can increase the possibility of hydrogen embrittlement in high-strength steel. Therefore, the solution is to use aluminum alloys with low voltage current. The purpose of this research is to know the efficiency of aluminum sacrificial anode with alloy elements Zn, Si and Cu as low voltage current. As well as studying the potential of Al alloys with elements Zn, Cu and Si can be used as sacrificial anodes at sea water conditions. Testing methods performed are Optical Emission Spectroscopy testing, weight loss testing, efficiency testing, Electrochemical Impedance Spectroscopy testing, and metallographic testing. From this research, we found the result of Al-Zn-Cu alloy which has electrochemical capacity and best efficiency is Al-5Zn-0,1Cu Alloy for 2795 Ah / kg with 98% efficiency and Al-Zn-Si alloy with capacity value electrochemistry and the best efficiency is Al-5Zn-0,1Si alloy for 2808 Ah / kg with 98% efficiency. The lowest value of transfer resistance is found in Al-5Zn-0.1Cu alloy and Al-5Zn-0.1Si alloy with the value of 1012.7 Ω and 1092.9 Ω and the double capacitance value in the smallest Al-Zn-Cu alloy is Al-5Zn-0.5Cu with the value of 13.2 μMho while in Al-Zn-Si alloys are present in Al-5Zn-0.5Si with the value of 19 μMho. With the structure obtained is the greater the addition of Cu and Si, the more rough and corroded surface sacrificial anodes.

1. Introduction
Corrosion is a very important problem throughout the world that greatly affects the natural and industrial environment. Corrosion and pollution are interconnected where more pollution accelerates corrosion and results as rust where both of these will affect the efficiency of industrial development and the resilience of infrastructure asset [1]. Corrosion prevention can be done in various ways such as inhibition, cathodic protection of the material, material selection, coating and so forth. Cathodic protection is the reduction or elimination of corrosion by making metals into cathodes by impressed currents [2]. The sacrifice of the anode means sacrificing the anode so the anode is corroded and protect the cathode metal. The addition of alloying elements to aluminum will change sacrificial anodes properties. Addition of indium to aluminum alloy will make the electrode potential more negative and current efficiency will decrease more. The indium contained in the aluminum anode will also increase its activity, so that its electrochemical performance will improve [3]. However, the
addition of Ti and Zr as a very high quantity purifying counter is contra-productive. Bifilms are precipitated prematurely from molten alloys with excess Ti or Zr prior to pouring, exhaust alloying and corrosion distribution in corrosion areas [4]. The addition of Ga or / and Bi into Al-Zn-Sn alloys can improve the uniformity distribution of the compacted structure. In addition, the addition of Ga or / and Bi can improve the efficiency of current in Al-Zn-Sn [5]. Furthermore, the addition of copper in Al-5Zn alloy showed that copper will increase the corrosion rate and the potential of the alloy, and also will reduce the charge transfer of the Al-5Zn alloy [6]. In this research we will use weight loss testing method and efficiency test to find the efficiency that can be produced by low voltage current anode at Al-Zn-Cu and Al-Zn-Si alloy, material characterization by optical emission spectrometer to know chemical composition of sacrificial anode as well the electrochemical impedance spectroscopy test and metallography to determine the value of electrical elements and the morphological structure of low voltage current anodes on Al-Zn-Cu and Al-Zn-Si alloys.

2. Experimental

2.1. Materials
The material used for this research was cast from high purity Al, Zn and Cu ingot with 99% grade and also Si and In in graphite crucible under atmospheric condition. The material that will be prepared for are Al-5Zn-0.5Cu, Al-5Zn-0.3Cu, Al-5Zn-0.1Cu Al-5Zn-0.5 Si, Al-5Zn-0.3 Si, Al-5Zn-0.1 Si and Al-5Zn-0.02 In. The aluminum is fed into the graphite crucible and fused in a furnace with a temperature of 750°C for 90 min. After the aluminum melting, furnace temperature is decreased to 710°C follow by alloying process by weighted amount of Zn, Cu, and Si added to the molten aluminum. During the blending process, the melted metal is stirred manually for 20 seconds after 15 minutes it is poured into mold.

2.2. Materials Characterization
The alloying will be characterized for the chemical composition, metallographic test and electrochemical impedance spectroscopy (EIS). Chemical composition was performed by using optical emission spectrometer (OES). After that, the sample preparation will be performed for metallographic testing according to the standard. The corrosion behavior of the alloys was also tested by using electrochemical test technique in seawater at room temperature. EIS were performed at range of frequency of 100 kHz-10mHz.

2.3. Efficiency Testing
This efficiency test was performed using DNV RP-B401 standard. The circuit is composed of Al alloy anodes, steel cathodes, aerators, and seawater. The sacrificial anode shall be positioned at the center of the steel cathode as well as the temperature for this test shall be maintained, at 20°C with a tolerance of 3°C. The principle of weight loss was used for testing this efficiency, so that the initial and final weights are calculated and can be determined. Measurements of potential values were performed according to DNV RP - B401 standard, where the current is given from the power supply and the measurement is carried out for 24 hours for 4 days. After the efficiency testing is completed, the specimen will be cleaned again with running water and soaked in a solution of 20 grams of chromium trioxide and 30 ml of phosphoric acid per liter of water for 10 minutes at a temperature of 80°C. The specimen is then washed with water and alcohol and then dried again. The final weight calculation is performed after the cleaning of the specimen is performed. The weight calculation was performed on each specimen of Al-sacrificial anode Al, Cu rod, Cu plate on coulometer to know the final weight and can be calculated to lose weight.
3. Result and Discussion

3.1. Electrochemical Impedance Spectroscopy

EIS test was performed to analyze the surfaced electrochemical behavior. In Figure 1 show the nyquist plot result from this research.

![EIS result from Al-Zn-Cu, Al-Zn-Si and Al-Zn-In Alloy.](image)

Table 1. EIS Fitting Circuit Result.

| Alloy         | $R_{ct}$ (Ω) | N    | $C_{dl}$/CPE (μMho) |
|---------------|--------------|------|---------------------|
| Al-5 Zn-0.5 Cu | 6623.4       | 0.90722 | 13.2               |
| Al-5 Zn-0.3 Cu | 8770.5       | 0.83448 | 22.5               |
| Al-5 Zn-0.1 Cu | 1012.7       | 1.1   | 40.4               |
| Al-5 Zn-0.5 Si | 10887        | 0.81177 | 19                 |
| Al-5 Zn-0.3 Si | 1189.9       | 0.9768 | 33.8               |
| Al-5 Zn-0.1 Si | 1092.9       | 0.051251 | 108              |
| Al-5 Zn-0.02 In| 692.43       | 0.8651 | 35.7               |

Based on the graph of nyquist plot Figure 1 we can see that the more elements of Cu and Si, the greater the impedance value obtained in each sacrificial anode. This proves that the more addition of Cu and Si elements in the aluminum sacrificial anode make corrosion resistant of the material higher. We observed a semicircle curve in the plot nyquist graph where the larger the diameter of the semicircle curve the greater the value of charge transfer resistance ($R_{ct}$) in the sacrificial anode. The value of the electrical elements obtained can be seen in Table 1.
3.2. **Metallographic Examination**

The aluminum sacrificial anode microstructure was observed using an optical microscope in as-cast condition. Figure 2 shows the microstructure formed on the aluminum sacrificial anode with the variation of Cu and Si concentrations and the sacrificial anode of aluminum with the addition of the In element. From the microstructure we can see that bright color is the grain boundary of the sacrificial anode alloy, while the aluminum has a darker color than the grain boundary. The precipitates formed at the grain boundary have white color. Because of the addition of elements Cu and Si, the formation of precipitate appear in the grain boundary, where the more precipitate appear in the material, the material will be more easily corroded.

**Figure 2.** Metallographic result of a) Al-5Zn-0.1Cu b) Al-5Zn-0.3Cu c) Al-5Zn-0.5Cu d) Al-5Zn-0.1Si e) Al-5Zn-0.3Si f) Al-5Zn-0.5Si that showed precipitation (200x magnification).
3.3. Efficiency Testing

The sacrificial anode efficiency testing was performed using the sacrificial anode samples after casting with diameter of 10 mm and length of 50 mm. The external electric current applied to the sacrificial anode is determined using the surface area of the victim anode sample. From Table 2 it can be seen that the increasing levels of Cu and Si in the alloy composition decrease the electrochemical capacity. The value of electrochemical capacity is the sacrificial anode’s performance capability in protecting or protecting a protected structure. The higher the electrochemical capacity, the better the sacrificial anode protects the structure. In Al-Zn-Cu alloys, the highest and best value electrochemical capacity is the Al-5Zn-0.1Cu alloy with the value of electrochemical capacity of the test of 2795 Ah/kg, while in Al-Zn-Si alloy, the electrochemical capacity value highest and best is Al-5Zn-0.1Si alloy with electrochemical capacity test value of 2808 Ah / kg.

![Table 2. Value of Electrochemical Capacity Testing, Theoretical Capacity and Efficiency of Sacrificial Anodes.](image)

| Alloy      | Theoretical Capacity (A.h/kg) | Electrochemical Capacity Testing (A.h/kg) | Anode Efficiency (%) |
|------------|-------------------------------|------------------------------------------|----------------------|
| Al-5Zn-0.5Cu | 2847                          | 1853                                     | 65                   |
| Al-5zn-0.3Cu | 2860                          | 2024                                     | 71                   |
| Al-5Zn-0.1Cu | 2867                          | 2795                                     | 98                   |
| Al-5Zn-0.5Si | 2877                          | 2035                                     | 71                   |
| Al-5Zn-0.3Si | 2870                          | 2676                                     | 93                   |
| Al-5Zn-0.1Si | 2867                          | 2808                                     | 98                   |
| Al-5Zn-0.02In | 2872                          | 2399                                     | 84                   |

4. Conclusion

Al-Zn-Cu alloy which has the best value of electrochemical capacity and efficiency is Al-5Zn-0.1Cu alloy for 2795 Ah / kg with 98% efficiency and Al-Zn-Si alloy which has the best electrochemical capacity and efficiency value. The lowest charge transfer resistance is found in Al-5Zn-0.1Cu alloys and Al-5Zn-0.1Si alloys of 1012.7 Ω and 1092.9 Ω. The double capacitance value of the smallest Al-Zn-Cu alloy is Al-5Zn-0.5Cu of 13.2 μMho while in Al-Zn-Si alloys are present in Al-5Zn-0.5Si of 19 μMho. The addition of Cu and Si elements affects the alloy grain shape and gives rise to precipitates. Higher additions of Cu and Si elements make the grain shape smoother and makes precipitates appear more at grain boundaries.

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