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# ANODIZING PROCESS FOR ENHANCING CORROSION RESISTANCE OF ALUMINIUM ANODES IN 1M NaOH ALKALINE SOLUTION

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**ABSTRACT**

Corrosion electrochemical behaviour of aluminium anodes coated with various coating processes, such as nickel electroplating, nickel and copper electroplating, zinc flake coating, and anodizing, in 1M NaOH alkaline solution were studied by electrochemical impedance spectroscopy (EIS) in Aluminium air batteries. The impedance spectra of the four coating samples of aluminium anode during immersion in alkaline solution were analysed and their surface morphology was studied using SEM. The findings from the experiments showed that the Ni-Cu plated aluminium anode sample had the highest protection characteristics in the four coating samples in 1M NaOH alkaline solution. Ni-Cu plated aluminium shows outstanding resistance to stress corrosion cracking, is more uncomplicated and efficient, and increases the mechanical strength of the aluminium alloy sample in an alkaline solution for an aluminium air battery.

**Keywords:** Aluminium–Air Battery, Corrosion Resistance, Coating Processes, Impedance Spectroscopy, Hardness, Cost-Effective.

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## INTRODUCTION

A great deal of work has been put into developing batteries of the future over the past ten years. A lot of interest has been shown in different types of Metal Air batteries based on different metal anodes like Li, Zn, Mg, Al, Fe, and Na in either aqueous or nonaqueous electrolytes, for use in electric vehicles.[1] The battery has a greater equilibrium potential (2.96 V) and specific capacity (3,842 mAh/g), making it equivalent to petrol and far higher than current Li-ion batteries.[2] Li-$O_2$ batteries, therefore, may provide a viable substitute for the current Li-ion battery technology.[3] Nonaqueous Li-air batteries do, however, have several practical issues that need to be resolved before they can be sold. The most severe disadvantage of Li-$O_2$ batteries is the phenomenon known as "abrupt death," which occurs when a passivation layer forms in the cathode during discharge.[4,5] Therefore, Al metal-based air batteries represent some of the most appealing substitutes for present chemical processes in all non-rechargeable (primary) and rechargeable batteries (secondary) because of Al's excessive natural abundance, widespread accessibility, ease of process (which comprises reuse), affordable price, and enormous theoretical volumetric capacity (8056 mAh $cm^{-3}$) and gravimetric (2981 mAh $g^{-1}$) capacity. An analysis of some key characteristics of metals that make them desirable choices for energy storage solutions.[6] The practical measured energy density of an Al-air battery is 4.30 kWh/kg. It is significantly greater than Zn-air battery, (1.08 kWh/kg) and less than Li-air batteries, which have a practical measured energy density is 5.20 kWh/kg.[7] The primary drawback of these alloys is their poor resistance to corrosion in harsh conditions, necessitating the application of a surface protective layer to the parts made from them. In addition to corrosion resistance, other desirable qualities of a good coating include good adhesion, consistency, and reliability.[8] Certain issues regarding aluminium-air batteries still need to be resolved. The two most important problems with aluminium-air batteries' design flaws are the $H_2$ gas emission and corrosive reactivity with the electrolyte, which have caused rapid anode degradation. This makes it hard to generate energy from aluminium in aluminium air batteries with an elevated level of performance.[9] These needs led to the development of aluminium electrodes with various


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coating treatments, and different coating procedures were used to examine the influence of these treatments on battery performance, such as (a) Nickel electroplating: Due to its qualities and widespread industrial application, nickel is a viable option that satisfies the requirements for a high-quality coating. For many years, nickel metals have been effectively utilised to protect MS from corrosion. It offers a surface that is both ornamental and corrosion-resistant.[10] (b) Nickel and Copper electroplating: Ni-Cu plated aluminium alloys are employed because they are corrosion-resistant. When Ni-coated aluminium has been electroplated with Cu Metal. It forms a strain-free film on Ni-coated aluminium alloy since they have virtually comparable lattice characteristics and the same crystal structure.[11,12] (c) Zinc flake coating is frequently required for steel in the wind turbine, aerospace, automotive, heavy truck, marine, and construction equipment industries[13]. (d) Anodizing of Aluminium- The anodizing process is controlled oxidation of the aluminium, is sustainable and gives a surface with exceptional beauty, longevity, and reliability. Anodized aluminium produces a surface that is three times tougher than ordinary aluminium and will not break, crumble, or peel, even when treated to add colour.[14] In this paper, we investigate these different coatings on aluminium and measure their electrochemical properties on aluminium air batteries along with their surface morphology. The electrochemical behaviour of electrodes has been examined by cyclic voltammetry and Linear sweep potential. To calculate corrosion for aluminium and coated aluminium anode, a mass loss test was performed whereas SEM was used to analyse morphologies of the surface of these samples.

## EXPERIMENTAL

### Electrode Preparation

To generate catalytic activity, the surfaces of aluminium plates were pre-treated and surface imperfections were eliminated using acetone. The anodes are composed of commercial 3003 aluminium alloy. Before electroplating, the aluminium plates (purity 98.17%, dimensions 1.5 cm x 1.5 cm, thickness 0.2 cm) were agitated in a weak HCl solution to stimulate the materials. The nickel bath was heated to between 60 and 70 degrees for 15 minutes while the activated plate was submerged in it at 10 volts. An aluminium plate serves as the cathode in a nickel bath, which contains a nickel electrode as the anode and nickel chloride salt and water as the bath solution. Following the procedure, the aluminium plate is rinsed with regular water and allowed to dry at room temperature. Ni-coated Al plates were subjected to copper plating using a bath solution that contained 11.10% $H_2SO_4$ solution and 2.85% $CuSO_4.5H_2O$ (weight percentage). Ten minutes of room temperature plating were conducted at a constant voltage of ten volts.

### Corrosion Rate Test

To determine the rate of corrosion in 1 M NaOH over 60 Minutes (Table-1), sheet samples with regulated sizes were submerged. The samples were washed, and then their weights were compared before and after immersion. This equation can be used to determine the corrosion rate[15].

$$\text{Corrosion rate}(mgcm^{-2}h^{-1}) = 87.6 \times [W/Dat]$$

Where,
W = weight loss in milligrams
D = density in grams/ $cm^3$
A = surface area in $cm^2$, and
T = time in hour

Table-1: Rate of Corrosion in 1 M NaOH Over 60 Minutes

| Metal | The corrosion rate in 1M NaOH (mg $cm^{-2}h^{-1}$) (60 Minutes) |
|---|---|
| Al plate Aluminium Plate | $0.1495*10^{-3}$ |
| Ni-Cu Coated Aluminium Plate | $0.0300*10^{-3}$ |
| Ni Coated Aluminium Plate | $0.1110*10^{-3}$ |
| Zn Flake Coated Aluminium Plate | $0.3330*10^{-3}$ |
| Anodized Aluminium Plate | $0.1993*10^{-3}$ |

We calculate the corrosion rate for NaOH at various molar solutions (0.8M, 0.9M, 1.0M, 1.1M, and 1.2 M) and time intervals (30, 60, and 90 minutes) using the weight loss method. In comparison to aluminium and

other coated aluminium samples, Ni-Cu-coated aluminium plates show a lower rate of corrosion in 1M NaOH solution after 60 minutes.

## RESULTS AND DISCUSSION

### Cyclic Voltammetry

Cyclic voltammetry was used to assess the Metal Anode's electrochemical stability. The sweep potential was initially scanned in a positive direction and subsequently in a reverse direction during the cyclic voltammetry test. Single electron reduction and oxidation are the first steps in cyclic voltammetry. When all of the $O_2$ has been reduced, the cathodic peak potential (Epc) is reached, and when all of the Al substrate has been oxidised at the electrode's surface, the anodic peak potential (Epa) is reached.[16] The cyclic voltammograms of Zn, Al, Al-Ni/Cu, and Al are shown in Figure 1. In an alkaline solution of 1 M NaOH, samples of flake and anodised aluminium were scanned at a rate of 100 mV/s throughout a potential range of -1.0 through +1.0 V. During the first forward scan, the nickel-plated aluminium sample displayed, a minor cathodic peak near around 0.2V showing the reduction of the Nickel-plated aluminium alloy than current residually decreases from the same way on sweep reversal resultant formed an anodic peak at a potential around -0.3V and for Zn Flake aluminium anode & Anodized aluminium sample show cathodic peak near 0.5V and 0.2V and their anodic peak is observed at same voltage after that current sweep decreases.[17] There is no difference observed between cathodic and anodic potential peaks for the Zn Flake aluminium anode & Anodised aluminium sample. Cyclic voltammograms of pure aluminium samples do not clearly show a cathodic or anodic peak and Ni-Cu coated aluminium exhibits a large cathodic peak around 0.4v. Below are some likely reactions of aluminium alloys covered with nickel copper.

$$Cu + OH^- \rightarrow Cu\,(OH) + e^-$$
$$Cu + 2OH^- \rightarrow Cu\,(OH)_2 + 2e^-$$

When scanned in the opposite direction, a reverse anodic peak was seen at -0.2V. Copper hydroxides typically turn into copper oxides during the oxidation process. The probable reaction is as follows.

$$2Cu\,(OH) \rightarrow Cu_2O + H_2O$$
$$Cu\,(OH)_2 \rightarrow CuO + H_2O$$

The difference between both peaks is larger for Ni-Cu Coated aluminium anode than other coated aluminium samples in 1M NaOH. It implies that Al-Ni/Cu metal has higher electrochemical stability towards the oxidation-reduction pair in 1M NaOH solution than Aluminium and other coated aluminium samples. It has been shown by Rasiha Nefise Mutlu *et al.* (2018) that electrodeposited Cu on Ni-coated aluminium results in improved electrochemical stability than direct Cu deposition on aluminium. The underlying mechanism of strengthening in Cu-Ni-Al alloys is accomplished by generating nanoscale $Ni_3Al$ (γ') phase precipitates. Due to the passivating effect of aluminium, two of these alloys have been commercialized and show greater corrosion resistance to maritime settings than normal cupronickels. These materials' primary characteristics are their outstanding resistance to stress corrosion cracking, high impingement resistance, immunity to hydrogen embrittlement, excellent elasticity modulus, low magnetic susceptibility, anti-biofouling characteristics, and machining simplicity. They also exhibit excellent anti-galling properties.[18,19,20]

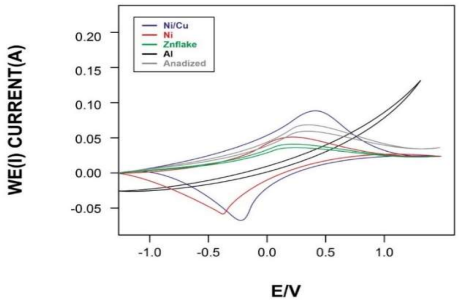



Fig.-1: Voltammograms of Al, Al-Ni/Cu, Al-Ni, Zn Flake in an Alkaline Solution of 1 M NaOH

## Linear Sweep Potential

To assess the electrical window (EW) of the aluminium electrode and other plated aluminium electrodes in 1M alkaline NaOH electrolyte solution, linear sweep voltammetry (LSV) experiments were performed. The aluminium electrode's cathodic stability in the alkaline solution (1M NaOH) at the anode side was found to be approximately 0.8 V compared to the standard hydrogen electrode (SHE). The cathodic stability of the Ni-coated electrode, Ni-Cu-coated anodised electrode, and Zn flake aluminium electrode exhibit cathodic stability of 0.3V, 0.87V, 0.7V, and 0.65V, respectively. The Al electrode (Ni/Cu plated) in 1M NaOH showed the largest electrochemical shift (ESW) (Fig.-2). The Ni-Cu plated aluminium electrode must be stable against anodic dissolution within the battery's operational voltage range in 1M alkaline NaOH solution to be used as the current collector in the Aluminium Air Battery.[21]

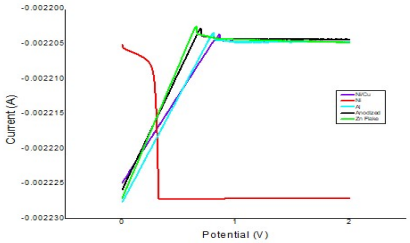
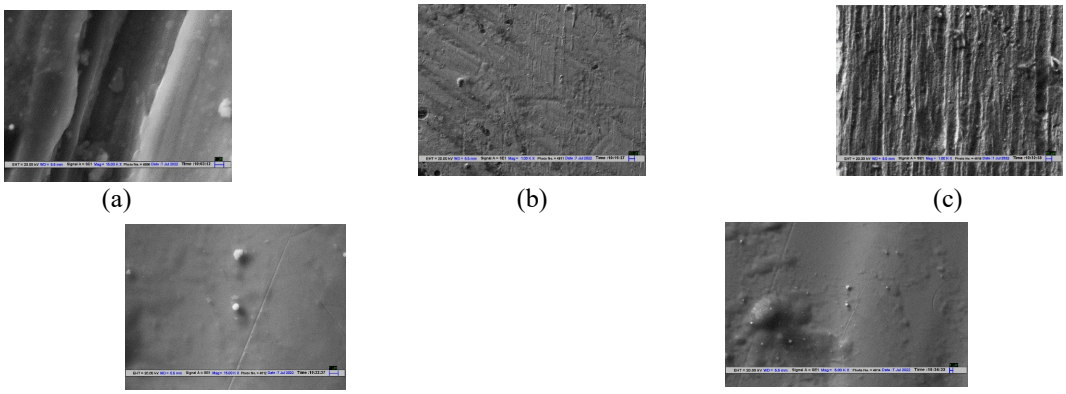



Fig.-2: Linear Sweep Voltammetry of Al, Al-Ni, Al-Ni/Cu, Zn Flake in an Alkaline Solution of 1 M NaOH

## Surface Characterization

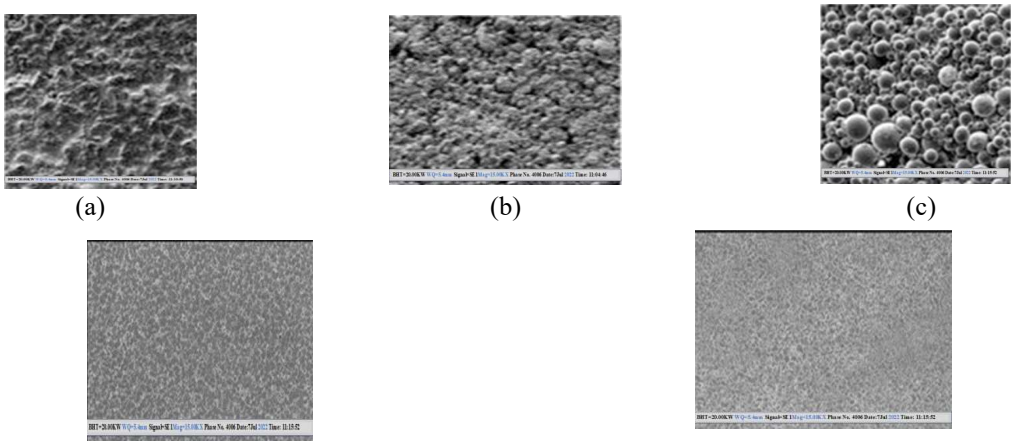
Anodised aluminium, zinc flake coated alloy electrodes, Aluminium, Aluminium-Nickel and Aluminium – Nickel Copper electrodes were all shown in their structure and morphology using SEM. Before and during the galvanostatic discharge test in 1M NaOH, 3600 s at 50 mA $cm^{-2}$ electrode SEM images were acquired. The surface of the pure aluminium anode is smooth in Fig.-3, but the anodised aluminium, zinc flake-coated alloy electrodes, and Ni-coated, Ni-Cu-coated aluminium alloy exhibit symmetrical thick coatings before the discharge process.[22–23] SEM pictures of aluminium alloy samples taken following a galvanostatic anodic dissolution test in 1M NaOH are displayed in Fig.-4. Following a galvanostatic anodic dissolution test, the surfaces of pure aluminium, anodised aluminium, and alloys coated with zinc exhibit broad, shallow corrosion pits with a more compact pit formation. After being subjected to a galvanostatic anodic dissolving test in a 1M NaOH solution, the aluminium anodic oxidation results in a rough surface with numerous voids. The Ni-plated aluminium electrode's SEM picture in 1M NaOH solution shows a distorted, scratch-free surface with a uniform distribution of dancing dark dots, suggesting that oxide compounds are precipitating on the anode surface. The Ni-Cu plating on the aluminium electrode indicates that the oxide products that precipitate on the anode surface do not obstruct the discharging process. This is supported by the SEM image of the Ni-Cu plated aluminium electrode, which displayed a more polished appearance and smaller white scratches on the surface. In a 1M NaOH solution, Ni-Cu plating on an aluminium electrode prevents the Al from corroding towards itself 24-25.



(a) (b) (c)

(d) (e)

Fig.-3: SEM image of (a) Al (b) Anodized Al (c) Zn Flake Coated Al (d) Al-Ni (e) Al-Ni/Cu



(a) (b) (c)

(d) (e)

Fig.-4: SEM Image of (a) Al (b) Anodized Al (c) Zn Flake Coated Al (d) Al-Ni (e) Al-Ni/Cu after Galvanostatic Discharge Test in 1M NaOH during 3600s at 50mACm$^{-2}$

## CONCLUSION

The alloy aluminium surface was processed with different electrodepositions of Ni, Ni-Cu, anodized, and Zn Flake to create an efficient, useful, and reasonably priced aluminium anode for the aluminium-air battery in 1M NaOH. Not only does nickel-copper coating save money, but it also increases efficiency on aluminium surfaces by lowering alkali corrosion. The amoral redox reaction between Ni-Cu coated aluminium metal and 1M NaOH was proposed by cyclic voltammetry studies to contribute to the corrosion prevention mechanism, along with superior electrochemical stability. Robust Ni-Al surface contact was shown in the SEM images.

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## CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

## AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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