



# Aluminium Anode Activation Research – A Review

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## ABSTRACT

The aim of this paper is to review aluminum anode formulation and activating elements till date and discuss the possibility of further work based on recent trends in the use of nano or agro based materials. The performance of aluminum anodes is largely dependent on alloy composition and a good understanding of the relationships between the metallurgy and the anodic response of the alloys. Recent researches show that microalloying aluminum anodes with certain metallic composite oxides can significantly improve anode life and reduce costs. Suggestions for further work are also presented.

**Keywords:** Aluminum anode, nano materials, microalloying, composite oxides

## 1. INTRODUCTION

Presently, the most commonly employed sacrificial metals for cathodic protection systems are alloys of magnesium (Mg), zinc (Zn) and aluminium (Al). Aluminium has attained considerable merit as the basis for a galvanic anode in oil and gas environments mainly due to its low density, large electrochemical equivalent, availability, thermal and electrical conductivity, high current capacity, low specific weight and reasonable cost [1]. Aluminium anodes are readily adaptable to a variety of saline environments such as seawater, marine muds and brackish waters. Pure and unalloyed aluminium adopts a relatively noble solution potential in saline media as a result of the formation of a thin, continuous, adherent and passive layer of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on its surface [1], hence it cannot be used as a sacrificial anode. This  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> compound is the cause of rapid polarization when aluminium is placed under a corrosion load in a cathodic protection circuit. Nevertheless, the success of the aluminium anode depends upon the alloying of certain metals whose primary role is to ultimately prevent the formation of a continuous, adherent and protective oxide film on the surface of the alloy, thus permitting continuous galvanic activity of the Aluminium [2], [3]. Numerous research works considering the influence of alloying elements such as Zinc (Zn), titanium (Ti), mercury (Hg), and indium (In) on aluminium alloys for sacrificial anodes have been carried out [4], [5]. The employment of each of these alloying elements is used in order to shift aluminum towards sufficiently electronegative values and to produce a more uniform attack morphology.

The quest for better surface activation, slower metal dissolution, greater protective output current, longer anode life and recent breakthroughs in the development of functional nano based materials may have renewed interest in the development of cost effective, environmental friendly and high performance aluminium sacrificial anodes [6]. To achieve this goal, it is important to obtain a microstructure of  $\alpha$ -Al with a good distribution of fine intermetallic compounds on it, in the as – cast or heat – treated condition.

## 2. HISTORY OF GALVANIC ANODES

The first practical use of cathodic protection is generally credited to Sir Humphrey Davy in the 1820s. Davy's advice was sought by the Royal Navy in investigating the corrosion of copper sheeting used for cladding the hulls of naval vessels. Davy found that he could preserve copper in sea water by the attachment of small quantities of iron or zinc; the copper became, as Davy put it, "cathodically protected" [7], [8]. Subsequently, galvanic zinc anodes evolved and, until several decades ago, were widely employed in marine service. Though zinc maintains a closed-circuit potential with steel of approximately -1.04 V, has an efficiency as high as 99%, exhibits a relatively uniform corrosion morphology and is self-cleaning, it however provides a relatively low theoretical capacity of 795 Ahr/kg at an efficiency of 100% [6]. Hence, aluminum has become an advantageous and substitute material for galvanic anodes due to its relatively high theoretical capacity of about 2980 Ahr/kg, low density and cost.. Presently, the Al/Zn/In alloy is the most widely employed galvanic anode for marine service [9], [10]. Table 1 below shows alloying compositions and potentials from electrochemical tests proposed by researchers till date.

## 3. INFLUENCE OF ACTIVATORS ON ALUMINUM ANODES

In the early 1960's, Schreiber and Reding [12], performed comprehensive tests on Aluminum alloys; and in 1966 an Al/Zn/Hg anode, which maintains a relatively negative potential and a reported electrochemical efficiency of 95% was introduced. Sakano et al. [13] developed concurrently an Al/Zn/In anode which provided an efficiency as high as 90%.

However, Schrieber and Reding's [12] development of the (Al–Zn–Hg) alloy with mercury as an activator was not without environmental concerns. Though this alloy became popular soon after this investigation and marketed under the trade name "Galvalum", some aluminum anode users however prefer



not to use it due to the effects of mercury on the environment, particularly with growing calls on environmentally clean and safe technologies.

According to Gurrappa [5], this aspect made Cathodic Protection Engineers find an alternative to mercury and successfully developed some anodes with indium, bismuth, tin, mercury, metallic oxides as activators. Some of these studies are presented in the following broad categories;

- (i) tin-activated aluminium alloy anodes,
- (ii) bismuth-activated aluminium alloy anodes and
- (iii) indium-activated aluminium alloy anodes.
- (iv) Metal Oxide-activated aluminum alloy anodes
- (v) Mercury-activated Aluminum alloy anodes

### 3.1 Tin-Activated Aluminium Alloy Anodes

These anodes with a composition of (Al + 5% Zn + 0.12% Sn) and a reported anode efficiency of 70% were first developed by Keir et al. [14]. The effectiveness of tin is attributed to reduced ionic resistance of oxide films on Al–Sn alloys. The results from tests show that anode capacities depended on various compositions of tin-activated aluminium alloy anodes. There are different views on the role of tin, but it is generally accepted that the creation of additional cation vacancies by entering tin as uadravalent  $\text{Sn}^{4+}$  is responsible for improving the Cathodic protection properties. It was clearly shown that decrease in surface free energy with the addition of tin to (Al + 5% Zn) and after the heat treatment is the principal reason for increasing the cathodic protection properties of these alloys.

**Table 1: Aluminium Anodes Compositions Researched till Date (Source: [11])**

WP = Working potential, OCP = Open circuit potential, SSCPP = Steady state critical pitting potential, PP = Pitting potential, CP = Coupled potential, FP = Free potential, CCP = Closed circuit potential.

Al alloy composition (wt.%)	Medium	Potential (V) Vs SCE	Type of potential
100% Al	pH 8	-2.3	WP
100% Al	0.5 M NaCl soln. at 25 °C	-0.8	OCP
99.9933% Al, 0.0005% Mg, 0.0039% Cu, 0.0007% Fe, 0.0016% Si	0.5 M NaCl at 25 °C	-0.741	SSCPP
99.9933% Al, 0.0005% Mg, 0.0039% Cu, 0.0007% Fe, 0.0016% Si	1 M NaCl at 25 °C	-0.721	SSCPP
98.689% Al, 1.3%Mn, 0.001% Mg, 0.006% Cu, 0.002% Fe, 0.002% Si	0.1 M NaCl at 25 °C	-0.691	SSCPP
97.04% Al, 0.02% Mn, 2.43% Mg, 0.23% Cr, 0.04% Cu, 0.16% Fe, 0.08% Si	0.1 M NaCl at 25 °C	-0.681	SSCPP
99.9933% Al, 0.0005% Mg, 0.0039% Cu, 0.0007% Fe, 0.0016% Si	0.1 M NaCl at 0 °C	-0.651	SSCPP
99.3336% Al, 0.004% Mn, 0.0004% Mg, 0.002% Cr, 0.1% Cu, 0.48% Fe, 0.08% Si	0.1 M NaCl at 25 °C	-0.651	SSCPP
99.9933% Al, 0.0005% Mg, 0.0039% Cu, 0.0007% Fe, 0.0016% Si	0.1 M NaCl at 25 °C	-0.641	SSCPP
99.9933% Al, 0.0005% Mg, 0.0039% Cu, 0.0007% Fe, 0.0016% Si	1 M KBr at 25 °C	-0.591	SSCPP
99.9933% Al, 0.0005% Mg, 0.0039% Cu, 0.0007% Fe, 0.0016% Si	0.1 M NaBr at 0 °C	-0.561	SSCPP
99.9933% Al, 0.0005% Mg, 0.0039% Cu, 0.0007% Fe, 0.0016% Si	0.1 M NaBr at 25 °C	-0.531	SSCPP
99.9933% Al, 0.0005% Mg, 0.0039% Cu, 0.0007% Fe, 0.0016% Si	1 M KI at 25 °C	-0.441	SSCPP
99.9933% Al, 0.0005% Mg, 0.0039% Cu, 0.0007% Fe, 0.0016% Si	0.1 M NaClO <sub>4</sub> at 25 °C	-0.241	SSCPP
99.8443% Al, 0.013% Zn, 0.0227% In, 0.08% Fe, 0.04% Si	Artificial sea water/ room temp.	-0.813/-0.828	WP/PP
99.86597% Al, 0.014% Zn, 0.00003% In, 0.08% Fe, 0.04% Si	pH 8	-0.729/-0.73	WP/PP
98% Al, 2% Zn	Substitute ocean water at 300 °C	-0.924/-0.925	CP/FP
96% Al, 4% Zn	Substitute ocean water at 300 °C	-0.953/-0.975	CP/FP
95.453% Al, 4.3% Zn, 0.02% In, 0.007% Cu, 0.12% Fe, 0.1% Si	0.5 M Cl <sup>-</sup> soln., pH 3, 25 °C	-1.5	OCP
95.0699% Al, 4.8% Zn, 0.0201% In, 0.07% Fe, 0.04% Si	Artificial sea water/ room temp.	-1.103/-1.078	WP/PP
94.867% Al, 4.97% Zn, 0.025% Pb, 0.003% Cd, 0.021% In, 0.022% Cu, 0.077% Fe, 0.015% Si	pH 5 / 0.5 M NaCl soln. / N <sub>2</sub> saturated atm. / 25 °C	-1.1	WP
94.9% Al, 5% Zn, 0.1% Se	3% NaCl soln.	-1.02/-1.035	CCP/OCP
94.91997% Al, 5% Zn, 0.0003% In, 0.04% Fe, 0.04% Si	Artificial sea water/ room temp.	-0.955/-0.943	WP/PP
95% Al, 5% Zn	3% NaCl soln.	-0.925/-0.93	CCP/OCP
99.8% Al, 0.2% Ga	Substitute ocean water at 30 °C	-0.84/-1.108	CP/FP
97.8% Al, 2% Zn, 0.2% Ga	Substitute ocean water at 30 °C	-0.95/-1.011	CP/FP
97.8% Al, 4% Zn, 0.2% Ga	Substitute ocean water at 30 °C	-0.964/-0.999	CP/FP
99.5% Al, 0.5% Ga	Substitute ocean water at 30 °C	-0.9505/-1.25	CP/FP
97.5% Al, 2% Zn, 0.5% Ga	Substitute ocean water at 30 °C	-0.987/-1.036	CP/FP
97.5% Al, 4% Zn, 0.5% Ga	Substitute ocean water at 30 °C	-0.992/-1.014	CP/FP
99% Al, 1% Ga	Substitute ocean water at 30 °C	-0.928/-1.288	CP/FP
97% Al, 2% Zn, 1% Ga	Substitute ocean water at 30 °C	-1.009/-1.05	CP/FP
95% Al, 4% Zn, 1% Ga	Substitute ocean water at 30 °C	-1.016/-1.03	CP/FP
99.98% Al, 0.02% Sn	0.5 M NaCl soln. at 25 °C	-0.85	OCP
99.91% Al, 0.09% Sn	0.5 M NaCl soln. at 25 °C	-1.02	OCP
94.3% Al, 5% Zn, 0.1% Sn, 0.5% Se, 0.1% Bi	-	-1.12/-1.12	CCP/OCP
94.7% Al, 5% Zn, 0.1% Sn, 0.1% Se, 0.1% Bi	-	-1.112/-1.116	CCP/OCP
94.75% Al, 5% Zn, 0.1% Sn, 0.05% Se, 0.1% Bi	-	-1.048/-1.05	CCP/OCP
94.8% Al, 5% Zn, 0.1% Sn, 0.1% Bi	3% NaCl soln. at 30 °C	-1.024/-1.025	CCP/OCP
94.79% Al, 5% Zn, 0.1% Sn, 0.01% Se, 0.1% Bi	-	-1.018/-1.022	CCP/OCP
99.873% Al, 0.12% Sn, 0.004% Fe, 0.003% Si (homogeneous solid solution)	0.1 N NaCl soln. 25 °C	-1.341	CCP
99.88% Al, 0.12% Sn	0.1 N NaCl soln. 25 °C	-1.321	CP
99.873% Al, 0.12% Sn, 0.004% Fe, 0.003% Si (As cast condition)	0.1 N NaCl soln. 25 °C	-1.241	CCP
99.64% Al, 0.2% Sn, 0.16% Bi,	0.1 N NaCl soln. 25 °C	-1.401	CP
99.8% Al, 0.2% Sn, 0.012% As	0.1 N NaCl soln. 25 °C	-1.351	CP
98.7% Al, 0.2% Sn, 1.1% Mg	0.1 N NaCl soln. 25 °C	-1.331	CP
99.706% Al, 0.2% Sn, 0.094% Zr	0.1 N NaCl soln. 25 °C	-1.331	CP
99.779% Al, 0.2% Sn, 0.021% Co	0.1 N NaCl soln. 25 °C	-1.311	CP
99.8% Al, 0.2% Sn	0.5 M NaCl soln. at 25 °C	-1.3	OCP
99.755% Al, 0.2% Sn, 0.045% Sb	0.1 N NaCl soln. 25 °C	-1.271	CP
99.704% Al, 0.2% Sn, 0.096% Ni	0.1 N NaCl soln. 25 °C	-1.201	CP
99.6% Al, 0.4% Sn	0.5 M NaCl soln. at 25 °C	-1.4	OCP



### 3.2 Bismuth-Activated Aluminium Alloy Anodes

Murai et al. [15] reported that 0.005–1.0% bismuth addition is helpful in enhancing the anode efficiency of (Al + 5% Zn) from 65 to 71%. Gurrappa et al. [5] successfully added small amounts of bismuth to (Al + 5% Zn + 0.25% Sn), thus avoiding heat treatment. The effect of bismuth in improving the polarization behaviour of basic composition (Al + 5% Zn + 0.25% Sn) was studied [5]. It was reported that bismuth helps in expanding the aluminium matrix and thereby increases the tin solubility in aluminium. For seawater applications, suitable addition of bismuth was identified and the anode efficiency of (Al + 5% Zn + 0.2% Bi) was improved to 83% by the addition of 2% magnesium [5].

Shibli and Gireesh [16] explored the feasibility of effective aluminium activation by selenium and bismuth incorporation. The electrochemical performance of these anodes were evaluated by galvanic and galvanostatic polarization, OCP and CCP measurements etc. The selenium incorporated anode showed improved galvanic efficiency of around 70%. This can be attributed to the size and uniformity of the grains produced which are normally predicted to yield high coulombic efficiency. The best activator combination was found to be 0.5%Se + 0.1%Sn + 0.1%Bi. This combination of activator in aluminium alloy anodes showed a galvanic efficiency of 90%.

### 3.3 Indium-Activated Aluminium Alloy Anodes

Sakano et al. [13] developed indium-activated aluminium alloy anodes with a composition of (Al + 5% Zn + 0.03% In) and a high anode efficiency of 80%. These anodes were reported to perform satisfactorily. Often times, once indium is dissolved, it is immediately reduced at localised sites and thus promotes activation. Researchers have also found out that chloride ions present in solution is essential for indium to activate aluminium [2]. The reduced indium ions produce a highly polarizing condition, which promote chloride migration and adsorption, thereby enhancing aluminium dissolution by forming complex chlorides.

Zazoua and Azzouz [17] obtained results from tafel curves and Evans diagrams which revealed that indium favours significantly the reactivity of aluminium in natural sea water, which in turn gives the anode a better yield in the cathodic protection of immersed marine installations. Tamada and Tamura [18] have confirmed that magnesium addition to (Al + 5% Zn + 0.03% In) is helpful in improving the cathodic protection properties. It was reported that the homogenization of (Al + 5% Zn + 0.03% In) [19] and (Al + 5% Zn + 0.03% In + 2%Mg) [20] exhibited improved anode performance.

Junguang He. et al [21], studied the influence of precipitates on the electrochemical performance of Al-Zn-In alloys. The solution treatment and the aging process were used to change the size, morphology and distribution of precipitates. Their results showed that the anodes with spherical or discal precipitates in their matrix had high current efficiencies and even corrosion morphology; while those with rod – like precipitates easily corroded along grain boundaries resulting in low current efficiencies caused by serious grain loss.

Juba Wen et al, [22] studied extensively the influence of silicon on the behavior of Al-5Zn-0.03In-1Mg-0.05Ti (wt%) sacrificial anode. The reduction in density, thermal expansion coefficient, improvement in hardness, ambient temperature, mechanical properties, wear resistance and excellent castability of Si addition to aluminium alloy probably formed the basis for this research. They found out that the microstructure, electrochemical characteristics and corrosion uniformity significantly improved after adding 0.1 wt % Si. Bruzzone, G, et al [23], [24], studied the effects of Ca-Zn, Ca-In and Al-Mg-Zn intermetallics activation of aluminum anodes with particular interest on the relationship between the morphological structure and the electrochemical results. The results showed that calcium had an anodic depolarizing effect on aluminum and that stabilizing aluminum with zinc achieved its passivity breakdown. They considered the  $Al_{90}Mg_5Zn_5$  alloy as a more promising material for the production of a new generation of anodes. Sherif Zein and Frank [25], investigated on the electrochemical behaviour of Al, Al-In and Al-Ga-In alloys in 0.6 M NaCl solutions. The study was performed by means of potentiodynamic polarization, potentiostatic current-time and electrochemical impedance spectroscopy measurements. They established that Al-In alloy exhibited the highest negative breakdown potential in 0.6 M NaCl and the corrosion resistance of the tested electrodes decreased in the following order: Al > Al-Ga-In > Al-In. The greater activity of Al-In alloy was interpreted on the basis of the autocatalytic attack by indium. Accordingly, the initial dissolution of Al-In alloy led to the increase in concentration of  $In^{3+}$  ions in the electrolyte, thus allowing for the redeposition of In at active sites on the electrode surface leading to the enhanced activity.

### 3.4 Metallic Oxide Activated Aluminum Anodes

The inclusion of metal oxides can significantly suppress the grain boundary corrosion of the anodes resulting in the improvement of the anode performance [1]. During fabrication of the aluminium alloy with oxides, the infiltration of the reinforcement network by molten aluminium and the homogeneity of the matrix are partially governed by the wetting nature of the metallic oxide composite and the chemical interaction between the reinforcement and the aluminium matrix.



Shibli and George [26], [27], undertook EIS studies on the uniform surface activation characteristics of ruthenium oxide ( $\text{RuO}_2$ ) – coated – Al – Zn – sacrificial anodes. This was another dimension in researchers quest to yet find ways of improving the aluminum anodes as  $\text{RuO}_2$  is an excellent catalytic transitional metal oxide possessing a rutile structure. The results obtained from this study revealed sustained catalytic activity of  $\text{RuO}_2$  on the anode surface even after a large extent of galvanic dissolution. Shibli et. al [1], developed a high performance aluminum sacrificial anode by incorporating metal composites of alumina and zinc oxides into an Al + 5% Zn alloy. The results showed that galvanic efficiencies as high as 83% was achieved when 0.5% ZnO was incorporated in the metal matrix as the incorporation of alumina led to adverse effects. They inferred that the good wettability and the presence of an optimum amount of ZnO in the alloy matrix prevented precipitation of the composite but suggested that the anodes would have exhibited better performance if the anodes were cast at very high temperature.

Shibli and Gireesh [28], explored and evaluated the feasibility of effective aluminum activation in Al + 5%Zn alloy anode by Iridium oxide ( $\text{IrO}_2$ ) surface coatings. The anodes according to the study were found to possess good surface interaction, low surface resistivity and facilitated interlayer diffusion of aluminum ions. The porous cracked  $\text{IrO}_2$  layer was found to persist on the electrode surface even after the electrode size was substantially reduced as a result of long period of galvanic exposure.

Mixed oxides of cerium and zinc in their nano forms were researched by Shibli et al [29] as been able to confer uniform dissolution properties on the Al-Zn matrix and good protection against bio-corrosion. Microstructural observation using SEM showed clearly that the insoluble cerium oxide migrated effectively to the grain boundaries helping to reduce corrosion. Electrochemical characterization of the anodes showed relatively good performance of 78.62% at an optimized nano cerium oxide content of 0.2%.

### 3.5 Mercury Activated Aluminum Anodes

Bessone, J.B, [4] reported that the presence of Hg at concentration less than 300 ppm in Al base alloys causes their passivation breakdown and a major lowering of (>0.3 V) in the operational potential of alloys used as sacrificial anodes in chloride media. He also corroborated reports that Mercury as trace constituent in natural gas streams cause severe damage to cryogenic heat exchangers. The results he obtained from open circuit potential–time responses, scanning microscopy and EDAX/X-Ray analysis demonstrated that immediately after immersion, the initial air-formed oxide film underwent a dynamic crack–healing process at flaws in the film, possible associated to grain boundaries.

### 3.6 Rare Earth Element activators

Rare earth (RE) elements have high chemical activity and special physical & chemical properties. Metallic structures of some alloys get pure and homogeneous because rare earth elements are added into them and so have effect on integrative electrochemical properties of aluminum anodes [30]. Hou Delong et al [31] researched on a novel Al-Sn-Bi anode with and without lanthanum (La). Constant current and dynamic loop tests were carried out to determine the efficiency and corrosion rate of the anodes. Their results from Optical microscopy (OM), transmission electron microscopy (TEM) and energy spectrum analysis techniques showed that the Al-Sn-Bi anodes with La additions revealed higher current efficiency. Segregation phase of anodes with La additions got more homogenous than that without La additions, its grains were fined and the amount of segregation Fe-phase was reduced.

## 4. CONCLUDING REMARKS

The development of a new generation of Aluminum anodes will be quite a daunting task, since the number of permutations of alloying additions is vast; it seems improbable that significant improvements in anode performance can be achieved from further trial-and-error procedures [2]. Rather, a fundamental understanding of the relationships between the anodic response of these alloys (related to the operating potential) and the metallurgy (related to the attack morphology and therefore to the current capacity) is needed [2]. The use of metallic activators like Zn, Sn, Hg, In, Bi and Ga have been very well researched, with obvious advantages and limitations. The available literature show that while good activation is achieved, current capacities and anode efficiencies can still be improved upon. However, some of these metal activated anodes have also been shown to undergo pitting corrosion in chloride environments [27]. Therefore further developments can be made with the use of nano synthesized materials and other possible renewable materials, which is the main thrust of this research as not much literature is available on their use.

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