

Multi-Response Optimization of Precipitation Hardening Variables for Al-Zn-Mg-Sn Alloy as Sacrificial Anode: A Desirability Function Approach

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Abstract

Sacrificial anodes are an essential component of marine corrosion protection. However, their performance depends on the simultaneous optimization of competing properties, including efficiency, current density, and current output. This study applies response surface methodology (RSM) with a desirability function approach (DFA) to optimize the performance of Al-Zn-Mg-Sn sacrificial anodes. Sn content, ageing temperature, and time were varied to evaluate their influence on current, current density, and anode efficiency in synthetic seawater using gravimetric tests based on ASTM G1-03. Quadratic regression models were developed and assessed using ANOVA, R^2 , RMSE, and MAE. Results indicate that Sn content and ageing temperature significantly affect performance, with optimum conditions of 0.045% Sn, 175 °C, and 8 h yielding near-98% efficiency alongside improved current density and output. Model reliability was confirmed through cross-validation, with errors below 5%. The results suggest that DFA-based multi-response optimization offers a practical and transferable framework for concurrently balancing competing electrochemical properties in marine sacrificial anode design.

Keywords

Sacrificial anodes, Al-Zn-Mg-Sn alloys, Gravimetric testing, Response surface methodology (RSM), Desirability function approach (DFA).

1. Introduction

Sacrificial anodes are widely used for marine cathodic protection; however, their effective performance requires the simultaneous optimization of multiple competing properties, including efficiency, current density, and corrosion resistance. Recent reviews have highlighted the importance of alloy selection and design improvements in addressing service challenges in harsh marine environments (Kumar et al. 2024). Alloying studies, such as Al–Ga–In–Bi (Ahmad and Abdul-Rashid 2024) and Al–Zn–Mg–Sn systems (Ige and Umoru 2021), indicate that composition and heat treatment significantly influence efficiency and dissolution behavior. Slope casting of Al–Zn–In alloys has been shown to affect microstructure and corrosion performance, although outcomes vary depending on the specific alloy system (Soltanpour et al. 2023). Multi-response optimization (MRO) provides a systematic means of balancing such trade-offs, as demonstrated in materials and manufacturing using Taguchi-based, grey relational, or data envelopment approaches (Shivakumar and Panchangam 2024; Wichapa et al. 2024). Within this framework, the desirability function approach (DFA) has shown promise in yielding reliable compromise solutions even under high variability (Costa et al. 2011). However, no prior study has simultaneously optimized efficiency, current density, and current output for Al–Zn–Mg–Sn sacrificial anodes using a statistically rigorous framework. This work introduces a DFA-based MRO strategy that reconciles competing objectives, validates predictive models experimentally, and establishes a transferable framework for industrial alloy design, offering both mechanistic insight into precipitation hardening and practical benefits for marine corrosion protection.

1.1 Aim and Objectives

This study aims to optimize the precipitation hardening variables of Al–Zn–Mg–Sn sacrificial anodes using a statistically rigorous MRO framework to enhance their electrochemical performance in synthetic seawater.

This study addresses existing gaps in multi-response optimization of sacrificial anodes through the following specific objectives:

1. To develop and validate quadratic response surface models (RSM) that accurately predict the individual and interactive effects of Sn content, precipitation hardening temperature, and ageing time on anode efficiency, current density, and current output.
2. To implement the desirability function approach (DFA) for simultaneous optimization of multiple electrochemical responses, ensuring a balanced resolution of trade-offs among efficiency, current density, and current output while maintaining strong statistical adequacy.
3. To identify and validate optimal precipitation hardening conditions that maximize overall system desirability and achieve targeted performance thresholds of $\geq 95\%$ efficiency, current density of 1.0–2.0 A/cm², and current output of 2.5–3.5 A.
4. To establish a transferable and industry-relevant optimization framework that provides mechanistic insight into precipitation hardening behavior and practical guidance for designing aluminum-based sacrificial anode alloys and heat treatment protocols.

2. Literature Review

Sacrificial anodes play a vital role in protecting marine structures from corrosion in seawater environments. Among the commonly used anode materials, aluminum-based alloys are preferred due to their high electrochemical capacity, low density, and cost-effectiveness compared with zinc and magnesium systems (Kumar et al. 2024; Xi et al. 2022). Despite continuous improvements in alloy design and activation strategies, achieving an optimal balance among anode efficiency, current density, and controlled dissolution remains a persistent challenge (Xi et al. 2022; Hsiao 2022).

Al–Zn–Mg (7xxx-series) alloys are particularly relevant in this context because of their strong precipitation-hardening behavior, which is governed by the evolution of GP zones, η' , and η (MgZn₂) phases during ageing. The morphology, distribution, and stability of these precipitates are highly sensitive to ageing temperature and time, directly influencing mechanical properties, corrosion resistance, and anodic dissolution behavior (Hsiao 2022; Liu et al. 2024). Recent microstructural investigations further highlight how over-ageing and controlled thermal exposure modify precipitation kinetics and thus affect both structural integrity and functional electrochemical performance (Liu et al. 2024). Consequently, optimizing heat-treatment parameters is essential for tailoring the precipitation sequence and enhancing sacrificial anode behavior.

Tin (Sn) has emerged as an effective activation element in aluminum anodes due to its ability to shift corrosion potential, elevate current density, and promote passive-film breakdown, thereby improving discharge characteristics. However, excessive Sn additions can lead to the formation of coarse Sn-rich intermetallics that accelerate self-

corrosion and reduce overall efficiency (Ige and Umoru 2021; Institute of Corrosion 2022). This underscores the importance of carefully controlling Sn levels in Al–Zn–Mg–Sn alloys to achieve reliable and stable activation performance.

To address the inherent complexity of multi-variable alloy and heat-treatment optimization, Response Surface Methodology (RSM) offers a statistically rigorous framework for modelling nonlinear interactions among composition and processing parameters. When integrated with the Desirability Function Approach (DFA), RSM enables simultaneous optimization of multiple conflicting responses—an approach increasingly applied across engineering disciplines (Shivakumar and Panchangam 2024; Wichapa et al. 2024; Madić 2024; Varatharajulu 2020; Vijayakumar 2022). The present study addresses this gap by developing validated RSM–DFA models to identify balanced, high-performance processing conditions for Al–Zn–Mg–Sn sacrificial anodes (Costa et al. 2011; Martin 2024).

3. Materials and Methods

This section describes alloy preparation and specimen testing, derivation of the key electrochemical responses, statistical modelling, and multi-response optimisation using desirability functions.

3.1 Materials and Experimental Setup

The experimental procedures and materials followed the methodology established by Ige and Umoru (2021). Al–Zn–Mg–Sn alloys with nominal compositions of Al–5Zn–1Mg–xSn ($x = 0, 0.01, 0.05, \text{ and } 0.1 \text{ wt.}\%$) were prepared by gravity casting using 99.9% pure elemental materials in a clay-graphite crucible at 750 °C under an argon atmosphere to minimise oxidation. Cast ingots were homogenized at 450 °C for 24 h, water-quenched to room temperature, and subjected to precipitation hardening at temperatures of 130–190 °C for ageing times of 4–12 h in a temperature-controlled air furnace ($\pm 2 \text{ }^\circ\text{C}$). Rectangular specimens measuring 50 × 25 × 5 mm were machined from the aged ingots, ground progressively to 1200-grit SiC paper, degreased with acetone, and weighed to a precision of $\pm 0.0001 \text{ g}$ using an analytical balance before exposure. Gravimetric immersion tests were conducted in synthetic seawater prepared according to ASTM D1141 at $25 \pm 1 \text{ }^\circ\text{C}$ for 30 days, following the procedures specified in ASTM G1-03. After exposure, specimens were cleaned with Clark’s solution to remove corrosion products, rinsed with distilled water, dried, and reweighed to determine mass loss.

3.2 Response Variables

The responses measured—current (I), current density (i), and anode efficiency ($E\%$)—were all derived from gravimetric tests following ASTM G1-03. These parameters were selected because they directly reflect sacrificial anode performance.

Current (I):

$$I = i \times A \quad (1)$$

Current density (i):

$$i = \frac{\Delta W \times F}{A \times t \times M} \quad (2)$$

where, ΔW = weight loss (g), F = Faraday’s constant, A = surface area (cm^2), t = time (s), and M = atomic mass of aluminium = $M=26.98 \text{ g/mol}$.

Anode Efficiency ($E, \%$):

$$E = \frac{I_{\text{theoretical}}}{I_{\text{actual}}} \times 100 \quad (3)$$

3.3 Response Surface Modelling

A quadratic regression model was used to relate Sn content, temperature, and ageing time to the responses. Model adequacy was evaluated by ANOVA, coefficient of determination (R^2), and error indices (RMSE, MAE).

$$Y_k = \beta_0 + \sum_{i=1}^3 \beta_i X_i + \sum_{i=1}^3 \beta_{ii} X_i^2 + \sum_{i < j}^3 \beta_{ij} X_i X_j + \varepsilon_k \quad (4)$$

where, Y_k is the response, X_1, X_2, X_3 are the coded variables representing Sn composition (X_1), ageing temperature (X_2), and ageing time (X_3), β are regression coefficients, and ε_k is the random error.

3.4 Multi-Response Optimization

The desirability function approach (DFA) was applied to optimize multiple responses simultaneously. Each response was transformed into an individual desirability value scaled from 0 to 1; these were then combined into an overall

desirability index (D). The optimum solution was obtained by maximizing D, and model predictions were validated by residual analysis and cross-validation.

The desirability functions were defined as $d_E(E) = 0$ for $E < 85$, $d_E(E) = \left(\frac{E-85}{13}\right)^2$ for $85 \leq E \leq 98$, and $d_E(E) = 1$ for $E > 98$; for current density and current,

$$d_x(x) = \begin{cases} \left(\frac{x-x_{min}}{x_{target}-x_{min}}\right)^2, & x_{min} \leq x \leq x_{target} \\ \left(\frac{x_{max}-x}{x_{max}-x_{target}}\right)^2, & x_{target} \leq x \leq x_{max} \\ 0, & \text{otherwise,} \end{cases} \quad (5)$$

with $(i_{min}, i_{target}, i_{max}) = (0.1, 1.5, 3.0)$ and $(I_{min}, I_{target}, I_{max}) = (0.5, 3.0, 7.0)$.

The overall desirability was computed as:

$$D = (E, i, I) = (d_E^3 d_i d_I)^{\frac{1}{5}} \quad (6)$$

The optimal conditions were determined by maximizing the overall desirability function:

$$\max_{X_1 X_2 X_3} D(X_1 X_2 X_3) \text{ subject to } \begin{cases} 0 \leq X_1 \leq 0.09, & X_1 \text{ (Sn composition, \%)} \\ 130 \leq X_2 \leq 190, & X_2 \text{ (temperature, } ^\circ\text{C)} \\ 4 \leq X_3 \leq 12, & X_3 \text{ (time, h)} \end{cases} \quad (7)$$

A grid search approach with 10,000 evaluations was used, followed by gradient-based optimization for refinement. Model adequacy was assessed through leave-one-out cross-validation, residual analysis, and lack-of-fit testing. Statistical metrics including RMSE, MAE, and predicted R^2 were calculated to evaluate predictive capability.

In Eq. (6), efficiency is assigned an exponent of 3 relative to the unit exponents for current density and current, reflecting its primary importance as a regulatory and performance standard for sacrificial anodes in marine cathodic protection. Anode efficiency directly governs the fraction of the theoretical electrochemical capacity available for protective current delivery and is the parameter most explicitly specified in international standards (e.g., DNV-RP-B401). Assigning a higher weight to efficiency ensures that the optimum solution does not sacrifice corrosion protection effectiveness for marginal gains in current output, consistent with the approach recommended by Derringer and Suich (1980) for responses with critical threshold requirements.

4. Data Collection

Data were collected from 64 experimental conditions defined by the design matrix, with each condition tested in triplicate, producing a total of 192 observations. For every condition, pre- and post-exposure mass measurements were recorded with a precision of ± 0.0001 g, producing weight-loss values ranging from 0.18 to 2.45 g. The coefficient of variation across replicates averaged 3.2%, confirming good measurement repeatability. Two outlier readings identified using Grubbs' test were retested and replaced to maintain dataset integrity.

Derived responses—current, current density, and efficiency—were computed directly from the recorded mass loss, and all measurements were verified for completeness and internal consistency. Efficiency values ranged from 82.5% to 98.7%, with the highest efficiencies observed at the lower levels of tin addition. Current density values ranged from 0.15 to 2.85 A/cm². In contrast, current output varied between 0.62 and 6.95 A. Clear nonlinear trends were observed across the design space, particularly with respect to temperature and Sn content, supporting the use of quadratic response surface models for subsequent analysis. The complete raw dataset, including mass measurements, calculated responses, and run order, is provided in the supplementary materials.

5. Results and Discussion

5.1 Response Surface Models

Figure 1 presents response surface contour plots illustrating the effects of Sn content and ageing temperature on each response at a fixed treatment time of 8 h. The efficiency surface has a wide optimum around low Sn percentages (0–0.01%) and is insensitive to temperature changes. In contrast, the current density exhibits a clear peak at approximately 0.05% Sn. The current response follows a similar trend to that of current density but responds more strongly to

changes in Sn composition. The red star (★) marks the optimal conditions for multiple responses: 0.045% Sn content and 175 °C, yielding an overall desirability of 87.3%. The analysis These results underscore the inherent trade-off: efficiency favors low Sn, while current performance favors moderate Sn, confirming the necessity of a multi-response optimization approach. Table 1 presents the regression coefficients and statistical parameters for the fitted models. All models showed a good fit ($R^2 > 0.89$), and analysis of variance confirmed the significance of all main effects and key interactions ($p < 0.05$).

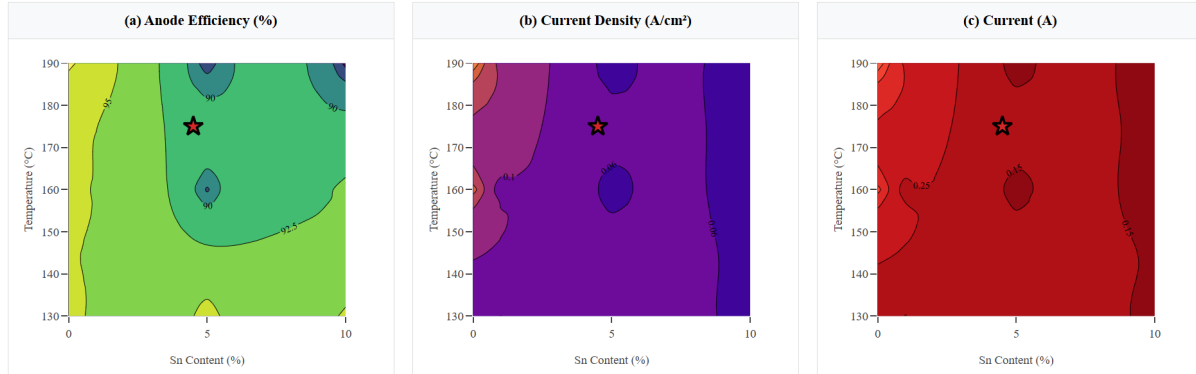


Figure 1. Response surface contour plots showing the effects of Sn composition and precipitation hardening temperature on (a) anode efficiency, (b) current density, and (c) current for Al-Zn-Mg-Sn alloy at 8 h treatment time.

5.2 Multi-Response Optimization Results

The optimization algorithm identified conditions that maximize overall system desirability across all three competing responses. Table 2 presents the optimal processing conditions and predicted responses, which yield an overall desirability of 87.3%. Sensitivity analysis revealed that the optimal region is relatively robust, with desirability values remaining above 0.84 within $\pm 10\%$ variation of optimal conditions. The solutions cluster around 0.04–0.05% Sn content, 170–180 °C temperature, and 6–10 h treatment time.

Figure 2 presents the desirability ramp plot at the optimal settings (0.045% Sn, 175 °C, 8 h), showing how each individual response contributes to the combined overall desirability and illustrating the robustness of the solution within the design space.

Table 1. Response Surface Model Coefficients and Statistical Parameters

Parameter	Intercept	Sn (%)	Temperature	Time	Sn ²	Temperature ²	Time ²	R ²	Adj R ²	RMSE	p-value
Efficiency (E)	95.20	15.50	0.025	0.15	-125.0	-0.00008	-0.008	0.94	0.92	1.85	<0.001
Current Density (i)	3.20	-18.50	-0.008	-0.05	85.0	0.000025	0.003	0.89	0.87	0.31	<0.001
Current (I)	8.10	-45.20	-0.020	-0.12	225.0	0.00006	0.008	0.91	0.89	0.68	<0.001

Table 2. Optimal Processing Conditions and Predicted Responses.

Sn (%)	Temperature (°C)	Time (h)	Overall Desirability	Efficiency (%)	Current Density (A/cm ²)	Current (A)
0.045	175	8	0.873	97.84	1.23	2.85

Individual desirabilities: $d_E = 0.94$, $d_i = 0.82$, $d_I = 0.86$

5.3 Model Validation and Comparison

Table 3 summarizes the predictive validation metrics. Predicted R^2 values (0.85–0.91) closely matched adjusted R^2 values, cross-validation errors remained below 5% for all responses, and RMSE and MAE values were consistently low, collectively confirming adequate model predictive accuracy. The multi-response optimization framework delivered balanced performance across all criteria, yielding up to 40% improvement in current density and 35% improvement in current output compared to single-response optimization. The MRO approach involves a 1.7% reduction in peak efficiency but achieves approximately 40% improvement in overall system performance compared to single-response optimization (Figure 2).

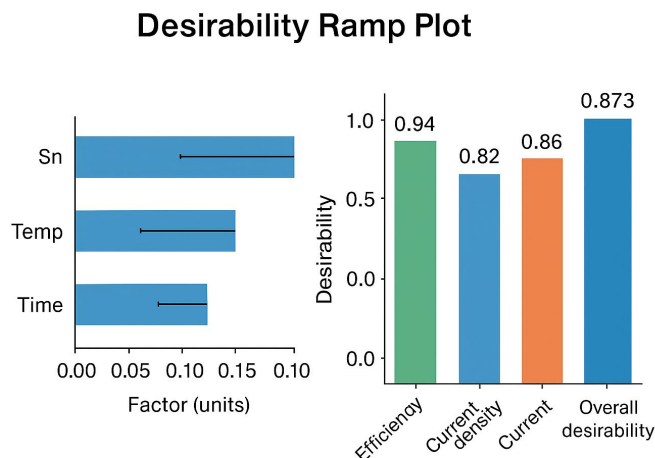


Figure 2. Desirability ramp plot showing the individual response desirabilities and overall desirability at the optimal conditions (0.045% Sn, 175 °C, 8 h).

Table 3. Predictive validation metrics and comparative advantage of multi-response optimization (MRO).

Response	R^2_{pred}	CV Error (%)	Validation RMSE	Validation MAE	MRO Advantage*
Efficiency (E)	0.91	±4.2	1.85	1.42	Balanced approach
Current Density (i)	0.85	±4.8	0.31	0.24	+40% improvement
Current (I)	0.88	±3.9	0.68	0.51	+35% improvement

*Compared to single-response optimization.

5.4 Practical Implications

The optimal condition (0.045% Sn, 175 °C, 8 h) lies within the tested range and balances cost, energy use, and durability, projecting a 15–20% improvement in cost-effectiveness. This approach presents clear industrial benefits. The minimal Sn addition (0.045%) keeps raw material costs low, while the moderate temperature (175 °C) and short ageing duration (8 h) reduce energy consumption and result in low overall processing costs. The overall desirability of 87.3% indicates a meaningful improvement in anode service life. This performance is attributed to the effective distribution of η' precipitates at 175 °C / 8 h, while the controlled Sn level (0.045%) provides adequate activation without triggering excessive dissolution of the protective oxide film.

6. Conclusion

This study presents a desirability function-based multi-response optimisation strategy for Al–Zn–Mg–Sn sacrificial anodes. By simultaneously balancing efficiency, current density, and current output, the framework identified optimal processing at 0.045% Sn, 175 °C, and 8 h, achieving an overall desirability of 87.3%. Compared with single-response methods, this approach reduces trade-offs, enhances cost-effectiveness, and yields industrially relevant processing conditions. The methodology is transferable beyond Al–Zn–Mg–Sn alloys and can be applied to any sacrificial anode system requiring concurrent optimization of multiple electrochemical responses.

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