



Nickel Entrapped K₁₀-Montmorillonite Composite Incorporated Al Alloy for Cathodic Protection

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The galvanic performance of aluminum sacrificial anodes, which are extensively used for cathodic protection of steel structures in sea water, can be significantly improved by the presence of nickel. However the fabrication of such an alloy evenly distributed with nickel is very difficult. In the present case, Ni(0) was entrapped into montmorillonite (MMT) to prevent the agglomeration of metal nanoparticles. The resultant composite was incorporated into Al + 5 wt % Zn alloy for enhanced galvanic performance. The metallurgical characteristics of the metal-metal matrix were improved by the incorporation of nickel entrapped K₁₀-MMT nanocomposite. Enhanced interfacial activation was achieved as evidenced from the results of impedance spectroscopic analysis. The Ni-MMT composite facilitated enhanced chloride ion adsorption from the solution of high chloride ion concentration. The developed anode possessed very high galvanic efficiency even under aggressive chloride concentration.

Keywords: Aluminium alloy, Galvanic efficiency, Pitting corrosion, Sacrificial anode.

INTRODUCTION

The most commonly used sacrificial anodes are alloys of Mg or Al, which can be applied to protect steel structures especially in corrosive aqueous environments like marine environment or moist soil [1,2]. Aluminium alloy anodes, due to their advantages such as low cost, long life, high energy capacity and light weight are highly renowned as an effective sacrificial anode [3]. Nevertheless the protective layer of γ -Al₂O₃ formed on the surface of Al inhibits the sacrificial action of the anode by shifting its potential to more passive direction. This activity inhibition can be prevented by resisting the formation of protective oxide layer. This can be achieved in three ways, such as, addition of alloying elements to Al, internal activation of Al by the incorporation of metal oxides or composites and external activation by catalytic coating on the metal surface. By employing these methods the equilibrium potential of Al can be shifted to more active direction.

Among the Al alloy sacrificial anodes, Al-Zn alloy is the commonly used base material with concentration of Zn varying in the range of 2-5 %. Literature survey reported that when Al is alloyed with 5 wt % Zn, phase saturation is attained with the possible incipient β -phase formation [4]. The most commonly used Al alloy anode is Al-Zn-In anode and which presents the best performance in seawater with an average potential of -1.1

V_{SCE}. Efficiencies over 90 % have been reported, related to a quite uniform attack [5,6]. The activation potential is sustained by the chloride adsorption assured by the presence of indium [7-10].

The inclusion of nano metal oxides and composites synergistically and significantly improves the metallurgical characteristics of anodes [4,11,12]. Recently catalytic activity of Ni nanoparticle has gained significance in many fields. A number of methods have been devised for the preparation of Ni nanoparticles, both in solution as well as in heterogeneous media. Literature survey reported that incorporation of nickel into aluminium alloy sacrificial anode matrix can improve its efficiency to a great extent [13]. The fabrication of the Al alloy anode with a uniform distribution of Ni is difficult to attain. Usually metal nanoparticles agglomerate under non-ideal natural conditions leading to an increase in their particle size, which reduces their catalytic activity. It has been reported that montmorillonite clay (MMT) can increase the catalytic activity of nickel by preventing agglomeration of the composite material. Clay minerals have been extensively used as reinforcement material for composites [14-17] due to its properties such as layered structure, large surface area and high cation exchange capacity [18]. Montmorillonite pillared with different metal compounds possesses additional functions. Hence, montmorillonite clay can also be used to stabilize particle size of nickel [19].

In the present study, Ni-MMT composite was explored as an activator for the sacrificial action in Al-Zn alloy anode. Ni(0) was entrapped into montmorillonite and the resultant composite was incorporated into aluminium alloy matrix to improve its galvanic performance. All these details and the performance of activation of the aluminium alloy as a sacrificial anode under aggressive conditions are reported in this work.

EXPERIMENTAL

Synthesis of nickel entrapped K₁₀-montmorillonite composite: Nickel entrapped K₁₀-montmorillonite composite was synthesized by chemical reduction with hydrazine hydrate in an aqueous alkaline medium containing Ni²⁺-exchanged K₁₀-MMT precursor [13]. This method consisted of two steps:

(i) Preparation of Ni²⁺-exchanged K₁₀-montmorillonite:

K₁₀-montmorillonite clay (Sigma-Aldrich) was used as received. The nickel(II) ions were exchanged into the clay (10 g) by stirring with NiCl₂·6H₂O (1M in 25 mL H₂O for 1 g of clay) solution at room temperature for 72 h. The precipitate was filtered, washed thoroughly using distilled water and then dried.

(ii) Preparation of nickel entrapped K₁₀-montmorillonite composite:

The Ni²⁺-exchanged clay (500 mg) was suspended in 1 mL of 25 % aqueous NH₃ solution. Then 2 mL of hydrazine hydrate was added into the solution and the mixture was stirred for 3 h at 60 °C. It was cooled and centrifuged with continuous washing using distilled water until the mother liquor became neutral. The precipitate was then dried at 150 °C for 0.5 h in the oven. The reducing agent hydrazine hydrate generated an inert atmosphere by releasing nitrogen. The most significant advantage of this method was that it avoided the risk of handling external molecular hydrogen. The reliability of method and the reproducibility of characteristics were also ensured before casting the composite incorporated anode.

Characterization of Ni²⁺-entrapped K₁₀-MMT composite:

Ni-MMT composite was subjected to X-ray diffraction analysis using CuKα radiation (λ = 1.54439) of 35 kV. The samples were scanned from 0°-80° at a scan rate 1.2°/min.

$$\text{Particle } D_{\text{XRD}} = 0.9 \lambda / \beta \cos \theta$$

where, λ = wavelength of radiation, θ = diffraction angle and β = full width half maximum (FWHM). The XRD analysis of K₁₀-MMT was also carried out for comparison.

Anode fabrication: Commercially available aluminium (purity index of 99.75 %) and zinc (purity index of ≈ 99.95 %) ingots were used for the fabrication of anodes. The ingots were weighed as per the requirement and melted in a graphite crucible in a muffle furnace at 720 °C. Ni-MMT composite were added into the molten alloy at different predetermined ratios. The molten mixture is stirred well using a silicon carbide rod and heated again to ensure homogeneity. The molten metal is then cast to pre-prepared reusable graphite die of dimension 5.5 cm × 3.5 cm × 0.5 cm. All the anodes were mechanically polished using emery paper of grit size varying from 100 to 2000 and suitably cut small pieces as per requirement.

Physico-chemical characterization

The anodes were subjected to Vicker's micro-hardness test as per ASTM-E-384-05 using a Shimadzu HMV-2000 machine. A Hitachi S-2400 instrument was used to record scanning electron

micrograph (SEM) and FEI Model: NOVA NANOSEM 450 was used to record field emission scanning electron micrograph (FESEM) of the anode surface. The anodes were finely ground in sequence up to 1000 grits with SiC paper and then mirror polished successively with 0.1 μm and 0.05 μm alumina pastes. During the polishing step the metal was protected from galvanic deterioration by means of dehydrated ethanol for lubrication and cleaned the surface ultrasonically in acetone. Then the samples were etched by dipping in 1 wt % NaOH solution for a period of 30-60 s, washed with distilled water, dried and were examined by secondary electron signal. The SEM and FESEM micrographs recorded at different magnifications were compared to analyze the morphological characteristics. EDS analysis was conducted for the elemental characterization and atomic absorption spectroscopy (AAS) was used for detecting the presence of nickel in the alloy matrix. The morphology of anodes was also studied after they were subjected to accelerated galvanostatic dissolution at a current density of 10 mA cm⁻² for 20 min.

Electrochemical characterization: The open circuit potential (OCP) of the test anodes having different compositions of Ni-MMT composite was monitored with respect to a SCE for a period of four months. The studies were carried out in 3, 5 and 10 wt. % NaCl solutions kept at 30 ± 2 °C under stagnant condition. The OCP measurements were also conducted during the sequential addition of 10 wt % NaCl into the electrolytic solution to evaluate the nature of chloride adsorption by the composite. Anodic current density was measured in a galvanic couple of anode and a cathode having surface area 1:10 ratio. This was made in order to measure the potential of Ni-MMT incorporated anode when it is being consumed due to anodic dissolution during the cathodic protection of the coupled steel (closed circuit potential-CCP). The current density generated at the anode surface was constantly maintained during the CCP measurements using a controlled variable resistance box. The CCP was measured by fixing the current density as 0.1, 1, 10 and 15 mA cm⁻². For all these experiments, different batches of the coupons were tested and the average values are reported here. There were no significant variations in the results among the individual batch of anodes normally.

The test anode and a steel cathode having surface area 1 and 10 cm², respectively were coupled and immersed in 3 wt % NaCl solution at 30 ± 2 °C for a period of 90 days. The weight of the anode in galvanic couple before and after the immersion were determined after cleaning the anode by following a standard procedure (ASTM G 31). From the weight loss measurement, the theoretical current to be produced by the anode was calculated. Thus the galvanic efficiency (η) was determined by the relation:

$$\text{Galvanic efficiency } (\eta) = \frac{\text{Effective current capacity}}{\text{Theoretical current capacity}} \times 100$$

where the effective current capacity of anode was the total coulombic charge (current × time) produced by unit mass of anode as a result of the electrochemical dissolution and the theoretical current capacity was calculated as per Faraday's law. The rate of current flow between the sacrificial anode and the protected mild steel structure in a simulated marine corrosive

condition was monitored *via* zero resistance ammeter and recorded over a continuous time period. The current yield of the sacrificial anode was tabulated from the current *versus* time plot.

The corrosion rate of anodes was also determined by measuring the weight loss after immersing the anodes in 3 wt % NaCl for a period of 90 days. For all these experiments, different batches of the coupons were tested and the average values are reported here. There were no significant variations in the results among the individual batch of the anodes normally.

$$\text{Corrosion rate} = \frac{\text{Weight loss}}{\text{Surface area}} \times \text{Time}$$

To understand the behaviour of Ni-MMT composite in the interior layer, the test anodes were subjected to anodic dissolution for 3 h under an anodic current density of 5 mA cm⁻² after coupling with cathodes having surface area in the ratio 1:10.

Detailed electrochemical measurements were carried out using an electrochemical analyzer (BioLogic Science Instruments, SP 200 using EC-Lab software, version 10.38). The electrolyte used was 3.5 wt % NaCl. Ag/AgCl/KCl (satd.), Pt mesh and anode having 1 cm² exposed area were used as reference, counter and working electrodes, respectively. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements were used to reveal the electrochemical characteristics of anodes. The polarization studies were carried out immediately after the EIS studies on the same exposed electrode surface without any additional surface treatment.

Potentiodynamic polarization was performed with a potential scanning rate of 1 mV/s. The measurements were carried out ranging from -1.5 to -0.5 V *versus* open-circuit potential (OCP). Impedance measurements were performed at open circuit potential (OCP) by the application of a periodic small amplitude (10 mV) ac voltage signal with a wide spectrum of frequency ranging from 1 MHz to 0.1 Hz after 15 min exposure in the electrolyte. The impedance data were analyzed using Nyquist and Bode plots and fitted using a non-linear least square (NLLS) method. All the experiments were repeated with different specimens to confirm reproducibility of the results.

RESULTS AND DISCUSSION

Synthesis and characterization of Ni entrapped K₁₀-MMT: In the present study, Ni entrapped K₁₀-MMT was prepared and the experimental parameters and reproducibility was checked by several attempts of different sets of preparation. The chemical sequence predicted in the synthesis process can be explained as follows:

Montmorillonites are hydrated aluminum silicates represented by the formula NaCa(AlMg)₆(Si₄O₁₀)₃(OH)₆.nH₂O. The Al³⁺ or Si⁴⁺ locations in montmorillonites can be replaced by lower valent cations, which cause the MMT structure to have an excess of electrons [20,21]. This negative charge is fulfilled by loosely held cations from the associated water. The layers of MMT have a periodical spacing of about 1 nm and are called the gallery spacing. The hydration of clay results an increase in inter-gallery spacing depending upon the cation exchange capacity of the clay [22].

The possible mechanism to deposit nickel metal in the interlayer spacing of MMT can be explained as follows: By

stirring with NiCl₂·6H₂O, the inter layer spacing of MMT was widened without changing its ordered structure. The hydration of clay increased the inter-gallery spacing which gave way to impregnate Ni²⁺ into the interlayer spacing of MMT. Then Ni²⁺ exchanged MMT was reduced with hydrazine hydrate and converted to Ni entrapped K₁₀-MMT. This was revealed from XRD analysis. The powder X-ray diffraction patterns of K₁₀-MMT and Ni-MMT composite are shown in Fig. 1. The peak obtained at 2θ of 8.8° on the XRD pattern of sample A was assigned as the basal spacing of (001) reflection of MMT observed to be shifted to a low diffraction angle of 5.994° while the shape became wider and the intensity decreased. This increased basal spacing is a clear signal that Ni has been intercalated in the inter-platelets space of K₁₀-MMT. K₁₀-MMT shows a peak corresponding to a *d*-spacing value of 9.8 Å, whereas Ni-MMTs show basal spacing value 12.39 Å. This revealed that the layered structure was retained and the interlayer space got wider during the course of synthesis process. This yielded the ease to impregnate Ni into the interlayers of MMT. Three characteristic peaks of Ni in 2θ range of 40-80° (2θ = 44.5°, 55.8° and 76.4°) could be indexed as face centered cubic Ni [(111), (200) and (222)]. The crystalline size of Ni-MMT composite, calculated from the Scherrer formula was 16.33 nm.

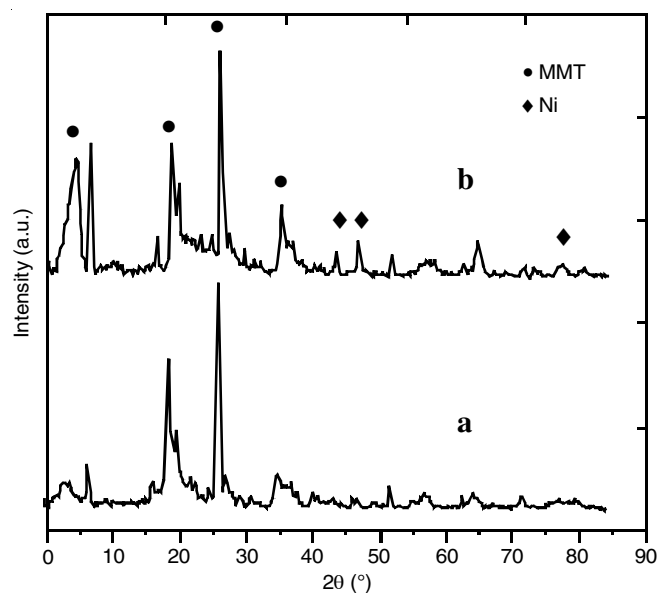


Fig. 1. XRD patterns of (a) K₁₀-MMT and (b) Ni entrapped K₁₀-MMT

Morphological and compositional characteristics of anode: The anodes were subjected to SEM analysis in order to understand the morphological characteristics. The SEM micrographs of Al + 5 % Zn and 0.2 % Ni-MMT composite incorporated Al alloy anodes are shown in Fig. 2. The microstructure consisted of an intermetallic high strength Al-Zn phase (β-phase) embedded in an aluminum solid-solution α-phase (more ductile). These micrographs revealed better grain refinement with slight segregation of Ni-MMT composite on the alloy surface. FESEM images in Fig 2 (B), (C) and (E), (F) gives the evidence of better grain refinement by composite incorporation. The grain size and its uniform distribution have a large influence on galvanic performance. Small grains and their uniform distribution are normally yield high coulombic

efficiency [23]. Al-Zn anodes are generally corroded along grain boundaries, resulting in low self corrosion *i.e.*, non-coulombic efficiency, due to serious grain loss [24]. The Ni-MMT composite may probably exist at the grain boundaries and improves the metallurgical properties of anode by suppressing the grain boundary corrosion. Grain boundaries are thermodynamically active sites and the precipitation of corrosion product in this region reduces the corrosion attack [25].

The compositional analysis of Ni-MMT composite incorporated anodes were carried out using EDAX analysis. EDAX spectrum of Ni-MMT composite incorporated anode was compared with the bare anode surface in Fig. 2 (G) and (H). The peaks of varying intensity corresponding to the elements such as Al (63.73 wt %), Si (1.82 wt %), O (31.72 wt %), K (0.93 wt %), Ni (0.24 wt %) and Zn (1.57 wt %) could be seen from the spectrum. The effective incorporation of catalytic Ni on the anode surface was thus confirmed. The Ni content of these anode samples

was found to be 0.24 wt %. The absence of chlorine in the sample revealed that entrapped Ni was zero-valent. The percentage of Ni in the alloy matrix was confirmed by conducting AAS analysis and found to be 0.27 % Ni in Al + 5 wt % Zn + 0.2 % anode and 0.58 % Ni in Al + 5 wt % Zn + 0.5 % anode. This is well consistent with the results of EDS analysis.

The SEM micrographs (Fig. 3) revealed the corroded surfaces of Al alloy after dissolution. Breslin *et al.* [26,27] and El-Shayeb *et al.* [28] reported that the presence of zinc, either as an alloying element or as cations in the electrolyte, promoted the nucleation of ZnAl₂O₄ spinel which gave rise to increased defects and cracking of the protective layer. The probable mechanism of action could be explained as follows: Once Ni-MMT nanocomposite is deposited at the newly generated defects, it may diffuse into the bulk material owing to its high mobility, enabling true composite Al contact and facilitates the adsorption of chloride ions at the surface (*i.e.*, activation) due to its greater affinity to nickel.

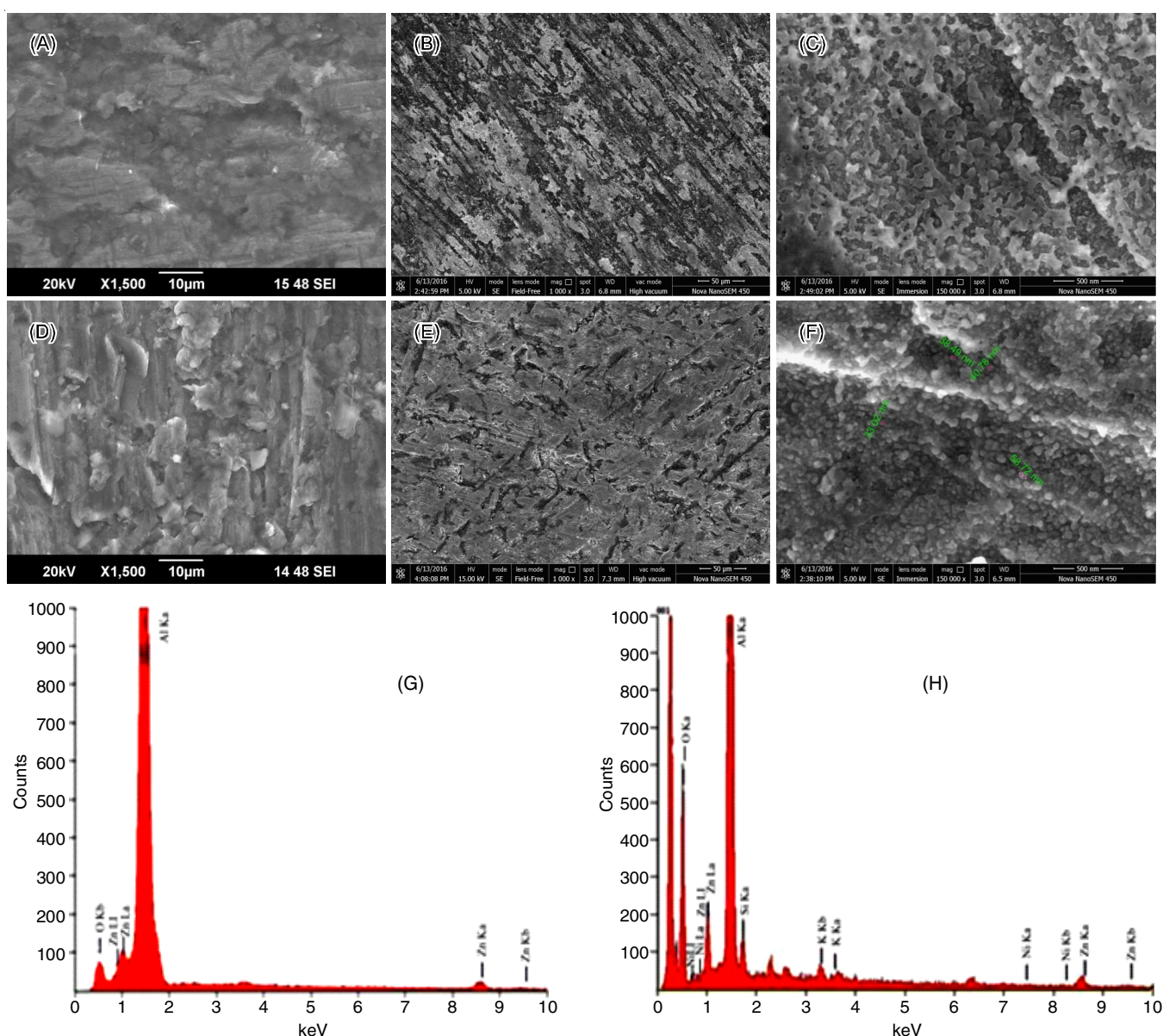


Fig. 2. SEM micrographs of (A) Al + 5 % Zn alloy and (D) 0.2 % Ni entrapped K₁₀-MMT incorporated Al + 5 % Zn alloy anodes, FESEM images of (B) and (C) Al + 5 % Zn alloy and (E) and (F) 0.2 % Ni entrapped K₁₀-MMT incorporated Al + 5 % Zn and EDAX spectra of (G) 0 % and (H) 0.2 % Ni-MMT composite incorporated Al + 5 % Zn anodes respectively

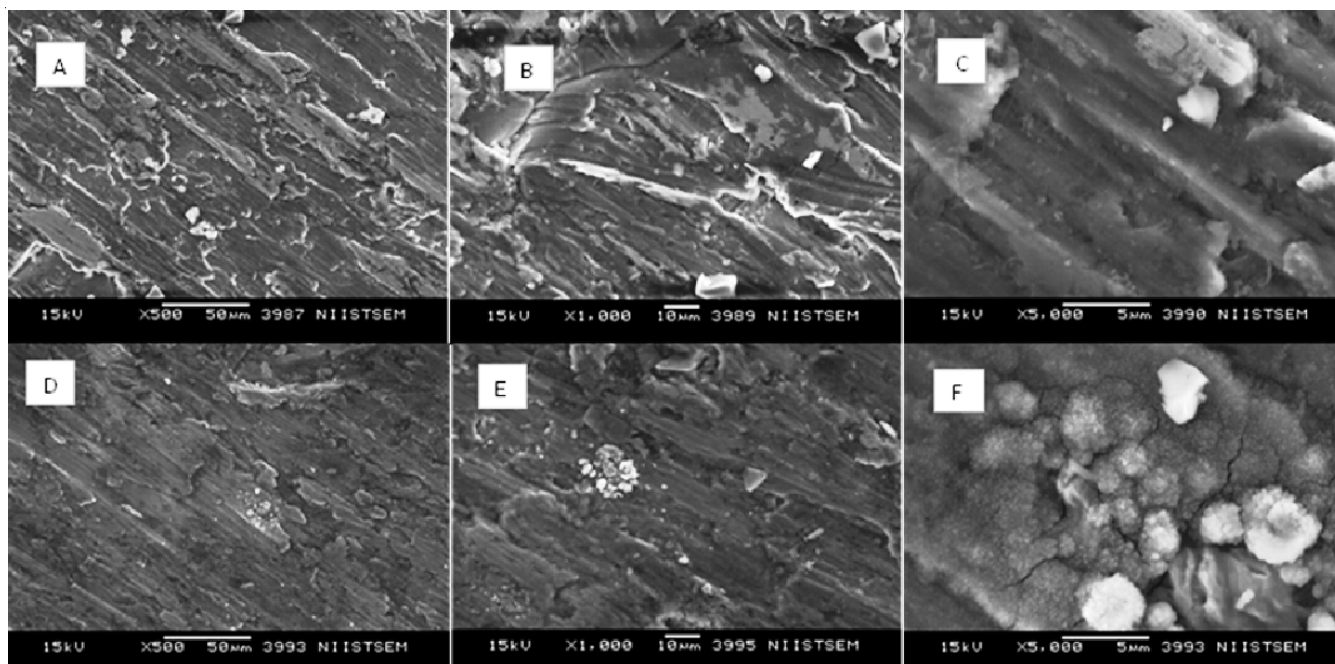


Fig. 3. SEM micrographs of (A), (B) and (C) Al + 5 % Zn alloy and (D), (E) and (F) 0.2% Ni entrapped K₁₀-MMT incorporated Al + 5 % Zn alloy after anodic dissolution at different magnifications

Metallurgical characteristics of anode: The effective incorporation of Ni-MMT composite into Al matrix has improved the metallurgical characteristics of the anodes. By incorporating Ni-MMT composite, the hardness of anode was also slightly improved. The hardness values of Al + 5 % Zn anodes with 0, 0.05, 0.1, 0.2, 0.5 and 1.0 % Ni-MMT composite were 34 ± 2.7 , 31 ± 2.2 , 35 ± 2.4 , 36 ± 2.2 , 42 ± 2.3 and 62 ± 2.3 HVN, respectively. This revealed that the hardness values were generally increased due to the composite incorporation while it also improved the metallurgical characteristics of the anodes.

Galvanic performance: The open circuit potential is a reliable parameter that indicates the tendency of an electrode to corrode. The initial OCP value of Ni-MMT composite incorporated anode showed more negative than Al + 5 % Zn anode. The initial OCP value of Al + 5 % Zn anode was found to be $0.943 V_{SCE}$. After one month of immersion, the potential shifted to $0.956 V_{SCE}$. The initial OCP values of different compositions of Ni-MMT composite incorporated anodes were found to be in the range of -0.957 to $-0.972 V_{SCE}$. The more negative initial OCP value was exhibited by the anode incorporated with 0.2 % composite. The OCP values slowly shifted to more cathodic region with more time of immersion (Fig. 4). There was no remarkable difference in potential of the anodes after 1 month. After 4 months, the OCP value for 0.2 % anode showed a remarkable shift to $-1.026 V_{SCE}$. All the Ni-MMT incorporated anodes showed more negative OCP values than the blank anode. The 0.2 % composite incorporated anode exhibited more active behaviour among the tested anodes. For all these experiments, different batches of the coupons were tested and the average values are reported. There were no significant variations in the results among the individual batch of anodes normally.

The trend of closed circuit potential (CCP) variation of Al + 5 % Zn anodes incorporated with different compositions of Ni-MMT composite are shown in Fig. 5. The current density was 1 mA cm^{-2} during the CCP studies. The closed circuit potential

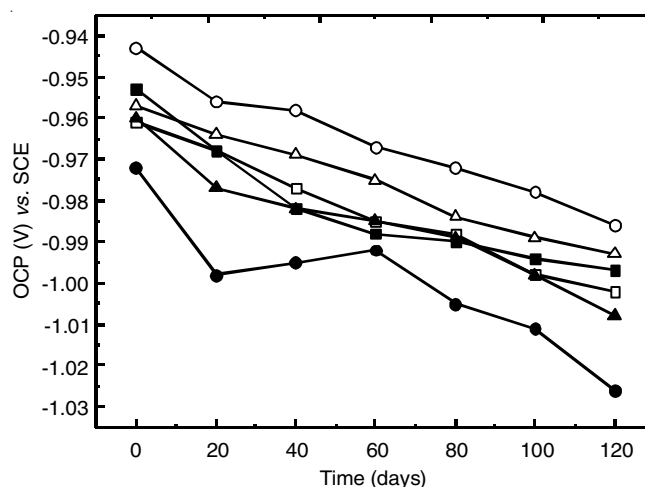


Fig. 4. variation of OCP with time of different compositions of Ni-MMT composite incorporated sacrificial anode. [(○) - 0 %, (△) - 0.05 %, (□) - 0.1 %, (●) - 0.2 %, (▲) - 0.5 %, (■) - 1 %]. (Electrolyte: 3 wt% NaCl, temperature: $30 \pm 2 ^\circ\text{C}$, under stagnant condition)

is the potential of anode when it is being consumed as a sacrificial anode for cathodic protection. All the Ni-MMT composite incorporated anodes exhibited high cathodic initial CCP values in the range of -0.825 to $-0.932 V_{SCE}$, which were substantially higher than that of pure Al + 5 % Zn anode. The anode incorporated with 0.2 % Ni-MMT composite exhibited more active behaviour, in accordance with the CCP results. An active OCP and CCP are desirable for an efficient sacrificial anode because a relatively noble potential indicates passivation. The anodes must also possess high galvanic efficiency in order to avoid frequent anode replacement. Duplicate experiments were conducted and the average values of efficiency of 0, 0.05, 0.1, 0.2, 0.5 and 1.0 % Ni-entrapped K₁₀-MMT incorporated anodes were 47.5, 56.3, 60.4, 79.2, 68.3 and 54.4%, respectively. The Al and Al alloys generally suffer from pitting and

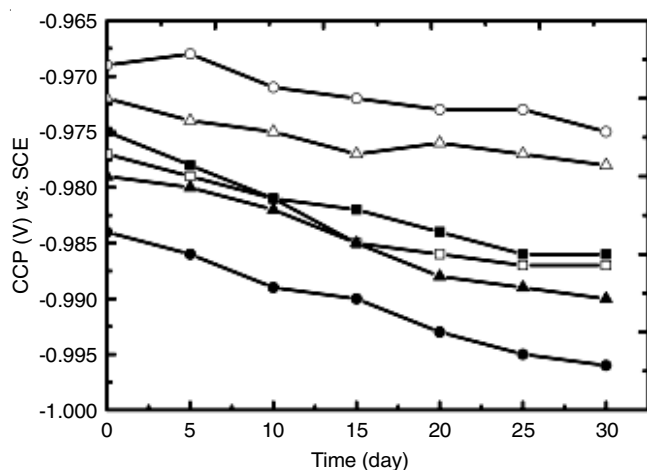


Fig. 5. Variation of CCP with time of different compositions of Ni-MMT composite incorporated sacrificial anode [(○) - 0 %, (Δ) - 0.05 %, (□) - 0.1 %, (●) - 0.2 %, (▲) - 0.5 %, (■) - 1 %]. (Electrolyte: 3 wt% NaCl, temperature: 30 ± 2 °C, under stagnant condition)

localized corrosion in 3 wt % NaCl solution which is the main cause of low efficiency of Al + 5 % Zn anode [29-32]. 0.2% Ni-MMT incorporated anode exhibited the highest efficiency. This improved efficiency of anodes revealed uniform anodic dissolution during the galvanic exposure by Ni-MMT composite present in the interior of anode. The self corrosion of anodes was determined to assess the non-columbic loss. An efficient sacrificial anode must possess low self corrosion value in order to avoid frequent anode replacement. All the Ni-MMT composite incorporated anodes exhibited self corrosion values in the range of 21.23 to $20.62 \mu\text{g cm}^{-2} \text{h}^{-1}$ which were remarkably lower when compared with that of pure Al + 5 % Zn anode. The reduction in self-corrosion values of the anode could be attributed to the reduction in grain boundary corrosion. The 0.2 % Ni-MMT composite incorporated anode exhibited lowest self-corrosion value. The overall galvanic performances of the anodes are compared in Table-1. Actually, the efficiency was found to be little higher with respect to a current impression of 0.1 mA cm^{-2} when compared with that calculated at 1 mA cm^{-2} .

Anodic dissolution: To understand the role of Ni-MMT composite during casting of the interior layers of the anode, they were subjected to continuous dissolution for 3 h. Anodic dissolution test was conducted in order to study the behaviour of Ni-MMT composite in the interior mass of bulk anode. The nature of dissolution as well as the resultant surface morphology during the test will reveal the interior nature of anode mass. The extent or aggressiveness of anodic dissolution will depend

on the current density as well as the environment in which it is dissolved. Any metal or alloy having good metallurgical characteristics would have uniform morphology of the resultant (interior) surface after anodic dissolution. Any defects as well as the compactness can also be assessed after analyzing the interior mass after anodic dissolution. The role of composite in improving the metallurgical characteristics of the interior mass is convinced from comparing the SEM images (Fig. 3). The Al + 5 % Zn anode exhibited a rise in potential when compared with the composite incorporated anodes. The 0.2 % Ni-MMT composite incorporated anode exhibited relatively good tolerance behaviour. While incorporation of the composite improved the metallurgical characteristics of anode, its excess amount yielded adverse effect facilitating more non-columbic loss and low stability. Hence, the content of composite was optimized to yield better metallurgical and electrochemical characteristics.

Potentiodynamic polarization: The potentiodynamic polarization measurements of different concentrations of Ni-MMT composite incorporated anodes carried out in 3.5 % NaCl are shown in Fig 6. The passive region in all cases extends up to a certain critical potential at which the anodic branches showed the inflection to potentials more positive than corrosion potential (E_{corr}) possibly due to the initiation of pitting corrosion. The presence of Ni-MMT composite decreased the polarization resistance (R_p) and increased the corrosion potential E_{corr} in the negative direction. The E_{corr} value are obtained in between -1.0007 V

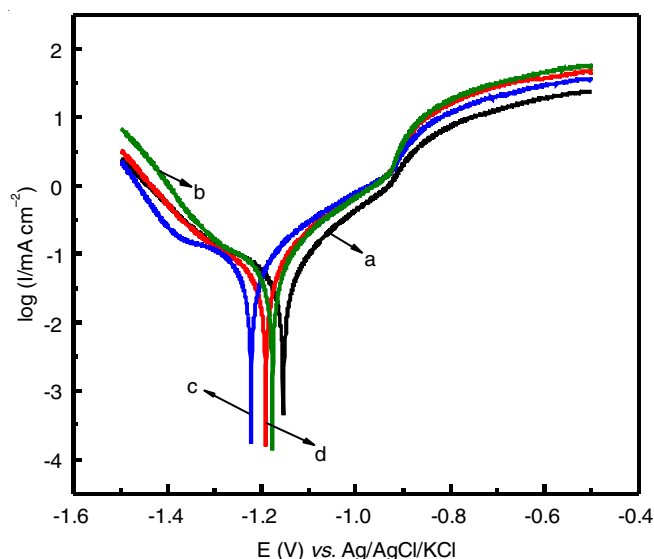


Fig. 6. Potentiodynamic polarization curves of different amount of composite incorporated anode [(a) 0 %, (b) 0.1 %, (c) 0.2 % and (d) 0.5 %] performed with a potential scanning rate of 1 mV/s

TABLE-1
GALVANIC PERFORMANCE OF Al + 5 % Zn ANODE INCORPORATED WITH DIFFERENT COMPOSITIONS OF Ni-MMT COMPOSITE (ELECTROLYTE: 3 wt % NaCl, TEMPERATURE: 30 ± 2 °C, UNDER STAGNANT CONDITION)

S. No.	Compositions of K ₁₀ -MMT entrapped Ni (%)	OCP vs. SCE (V)	CCP (V) vs. SCE, different current densities (mA cm^{-2})				Self-corrosion $\times 10^{-6} (\text{g cm}^{-2} \text{h}^{-1})$	Efficiency (%)
			0.1	1	10	15		
1	0.00	-0.943	-0.984	-0.969	-0.944	-0.915	21.93	47.5
2	0.05	-0.957	-0.993	-0.972	-0.928	-0.896	20.25	56.3
3	0.10	-0.961	-0.968	-0.977	-0.939	-0.902	19.12	60.4
4	0.20	-0.972	-0.998	-0.984	-0.961	-0.946	11.52	79.2
5	0.50	-0.960	-0.987	-0.979	-0.953	-0.926	17.81	68.3
6	1.00	-0.953	-0.988	-0.975	-0.948	-0.918	20.62	54.4

and -1.0436 V *versus* Ag/AgCl/sat. KCl electrode and I_{corr} of different concentrations of composite incorporated anodes are within the range of 16.654×10^{-6} to 20.445×10^{-6} A cm². The polarization resistance (R_p) values are obtained between 866.50 and 1068.5 Ω/cm^2 . The high E_{corr} , low R_p , high I_{corr} and high corrosion rate (0.6685 mm/year) were observed for 0.2 % Ni-MMT composite incorporated Al alloy sacrificial anode which is suitable for a good sacrificial anode and this concentration was selected as optimum.

The anodic slope β_a decreases due to composite addition (0.0738 V/dec to 0.0571 V/dec), which indicates the enhanced dissolution of anodes. Compared to Al, Zn is more electro-negative and it may dissolve at anodic potentials. The Ni-MMT composite enhances the chloride adsorption and later increases the dissolution process of Zn. Breakdown of the passive state of aluminium in chloride medium occurs by the interaction between $\text{Al}(\text{OH})_3$ film and Cl^- ions and generate AlCl_3 which dissolves as $[\text{AlCl}_4]^-$ above the pitting potential [33].

Electrochemical impedance spectroscopy (EIS): The EIS plots of Al alloy sacrificial anodes incorporated with Ni-MMT composite are shown in Fig 7a. An equivalent circuit for simulating this process is shown in Fig. 7b. In this, R_s is the solution resistance, CPE is the constant phase element, R_t is the charge transfer resistance, L and R are inductive elements related to the adsorption process. The EIS diagram of anodes shows a capacitive loop at high frequency and an inductive loop at low frequency region. The capacitive loop at high frequency is attributed to the charge transfer reaction in the electric double layer formed at the interface between metal surface and corrosive medium [25,34], which can be described by polarization resistance (R_t) and constant phase element (CPE). The R_t is inversely related with the electrochemical corrosion rate. The double layer capacitance (C_{dl}) value is affected by imperfections of the surface and this effect is simulated *via* a constant phase element (CPE) [35]. A CPE is substituted for the capacitive element to give a more accurate fit, as the Nyquist plot obtained for this presents depressed semicircles. The CPE is given as follows:

$$Z_{\text{CPE}} = A^{-1} (i\omega)^{-n}$$

where A is the CPE constant, ω is the angular frequency in rad/s, n is the CPE exponent and related to the roughness of surface. Depending upon the value of n, CPE can represent resistance ($n=0$, $A=R$), capacity ($n=1$, $A=C$), inductance ($n=-1$, $A=L$) or Warburg impedance ($n=0.5$, $A=W$). The interfacial double layer capacitance values were obtained by determining the frequencies at which the imaginary component of the impedance is maximum $f(-Z_{\text{max}})$ from the following equation [36]:

$$C_{\text{dl}} = 1/2\pi f_{\text{max}} R_t$$

The inductive loop at low frequency is probably due to the relaxation processes in adsorbed species formed during dissolving at the interface oxide/electrolyte, which define the faradaic processes in the system examined [33]. The χ^2 is the precision of the simulated data. It can be seen that the χ^2 values are small, reflecting the fact that the simulated data have good agreement with the experimental ones. The entire anodes showed similar trends in the general shape of impedance diagrams and the diagrams were validated with the Kramers-Kronig relations.

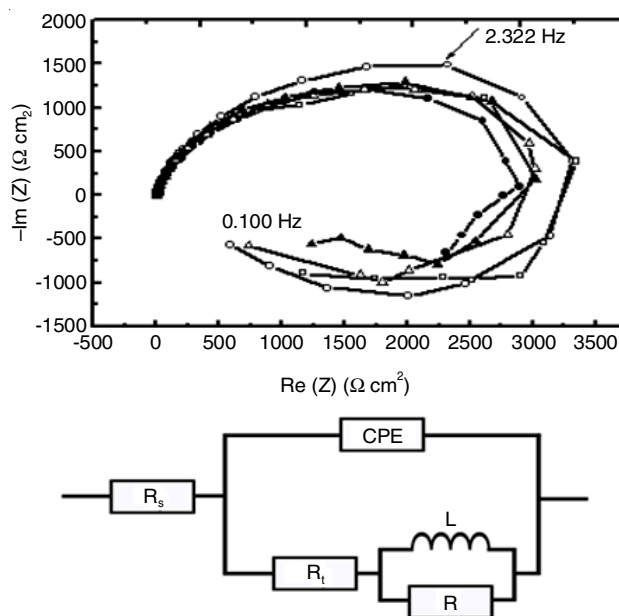


Fig. 7. (a) Impedance plots of Ni-MMT composite incorporated sacrificial anode [(○) - 0 %, (▲) - 0.05 %, (□) - 0.1 %, (●) - 0.2 %, (▲) - 0.5 %] frequency ranging from 1 MHz to 0.1 Hz and equivalent circuit model used to fit the EIS diagrams

The obtained data reveals that R_t of composite incorporated anodes varied from 703.3 to 3375 $\Omega \text{ cm}^2$. Maximum R_t value is obtained for 0 % and minimum for 0.2 % composite incorporated anode. There is observed a decrease in R_t by the addition of Ni-MMT composite, which revealed the less passive nature of the electrodes. In opposite to R_t , C_{dl} values increases due to the addition of composite. C_{dl} value for 0 % composite incorporated anode is least (20.32 $\mu\text{F cm}^2$) and a maximum value of 97.49 $\mu\text{F cm}^2$ was observed in the case of 0.2 % composite incorporated anode. C_{dl} is associated with water/electrolyte uptake through the pores/defects of surface. An increase in C_{dl} implies the increase in defects of oxide film and which increases diffusion reaction [25]. Compared to other anodes 0.2 % Ni-MMT composite incorporated anode showed better performance due to its low R_t value and high double layer capacitance which indicates the active nature of composite incorporated sacrificial anodes. The appearance of a low frequency inductive loop is related to relaxation of the adsorbed anions on the surface of metal [25,33]. This gives the evidence of enhanced adsorption of Cl^- on anode matrix.

Performance of anode under different aggressive chloride environment

Normally corrosion of aluminium alloy anode in 3 wt % NaCl proceeds through pitting since chloride ion is easily adsorbed into the defect site of aluminum alloy surface [22]. The behaviour of the Al + 5 % Zn and 0.2 % Ni -MMT composite incorporated Al alloy anode in different chloride concentration were also studied. The trend in variation of OCP and CCP were compared for the above two anodes in 3, 5 and 10 wt % NaCl and are shown in Table-2. The OCP and CCP values were shifted to more negative region on increasing concentration of NaCl solution from 3 to 10 %. Even then, the potential values were found to be more negative in the case of Ni-MMT composite incorporated Al + 5 % Zn anode when compared with pure Al + 5 %

TABLE-2
COMPARISON OF GALVANIC PERFORMANCE OF Al + 5 % Zn ANODE AND 0.2 % Ni-MMT COMPOSITE INCORPORATED Al + 5 % Zn ANODE IN DIFFERENT CHLORIDE CONCENTRATIONS (TEMPERATURE: 30 ± 2 °C, UNDER STAGNANT CONDITION)

Al + 5 % Zn anode with of K ₁₀ -MMT entrapped Ni (%)	Concentration of NaCl solution (%)	OCP vs. SCE (V)	CCP vs. SCE (V) at 0.1 mA cm ⁻²	Self-corrosion $\times 10^{-6}$ (g cm ⁻² h ⁻¹)	Efficiency (%)
0.0	3	-0.985	-0.968	16.28	58.73
0.0	5	-0.998	-0.973	11.65	54.15
0.0	10	-1.010	-0.988	11.16	62.49
0.2	3	-1.018	-0.990	8.630	79.23
0.2	5	-1.022	-0.997	8.320	80.16
0.2	10	-1.037	-1.007	8.730	83.45

Zn anode. The interaction between chloride anions and passive Al₂O₃ film made it unstable and led eventually to the dissolution of anode. As suggested elsewhere, the change in potential could be attributed to the enhanced adsorption of chloride ions by Ni-MMT composite in Al + 5 % Zn matrix [32]. The surface properties of modified clays seem to play an important role for the adsorption of chloride ions [34,37]. This was further proved by analyzing the behaviour of anodes while increasing the chloride concentration by sequentially adding 10 mL of 10 wt % NaCl solution into 3 wt % NaCl solution as shown in Fig. 8. The adsorption capacity of clays may be affected by the interlayer spacing and the surface properties. As the chloride concentration increases the potential of composite incorporated anode changes from -0.9884 to -1.022 V_{SCE} while the potential of the blank anode changes from -0.9658 to -0.9703 V_{SCE}. The increase in potential of composite incorporated anode was due to increased adsorption of chloride ions. The overall galvanic performances of Al + 5 % Zn anode and 0.2 % Ni-MMT composite incorporated Al + 5 % Zn anode in 3 wt % NaCl, 5 wt % NaCl and 10 wt % NaCl are compared in Table-2. The anode current efficiency maximized (83.45 %) at 10 wt % NaCl and the current efficiency started to decrease with decreasing the chloride concentration. The composite incorporated anode also exhibited low self-corrosion value relatively, in the aggressive chloride environments. For all these experiments, different batches of the coupons were tested and the average values are reported. There were no significant variations in the results among the individual batch of anodes normally.

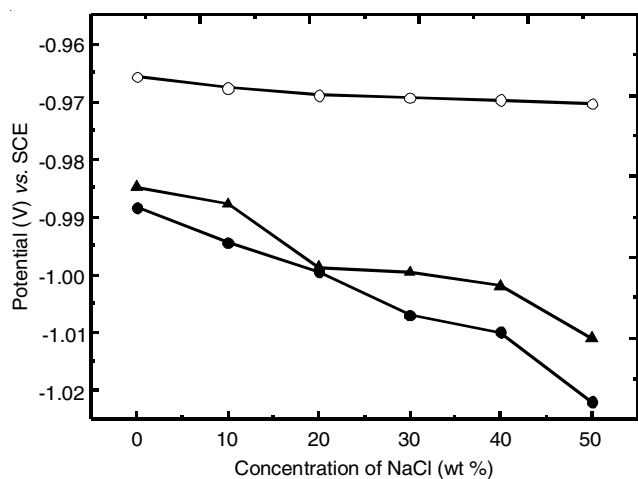


Fig. 8. Variation in potential of Al + 5 % Zn anodes incorporated with different compositions of Ni-MMT by increasing the chloride concentration [● - 0 %, ▲ - 1 % and ■ - 0.2 %] (Temperature: 30 ± 2 °C, under stagnant condition)

Conclusion

Nickel entrapped K₁₀-montmorillonite composite was explored as an activator for the sacrificial action in Al alloy anode. The composite incorporated anode exhibited low self corrosion value and high galvanic efficiency (83.45 %) relatively, in the aggressive chloride environments. Based on the preliminary evaluations and polarization measurements, the percentage weight of Ni-MMT composite in Al + 5 wt % Zn alloy anode was optimized to be 0.2 wt %. The grain refinement of alloy anode after the incorporation of composite was attributed to the inter-particle interaction between the composite and the matrix. The decrease in R_i by the addition of Ni-MMT composite revealed the active nature of electrodes. The anode corresponding to the Ni-MMT composite loaded with the optimized content of 0.2 % exhibited the highest performance. The anode had low R_i value and high double layer capacitance. The appearance of a low frequency inductive loop was attributed to the relaxation of the adsorbed anions on the surface of anode. This was the evidence of enhanced adsorption of Cl⁻ ion on anode matrix. Thus, it was proved that the microstructure, metallurgical properties, electrochemical characteristics and corrosion uniformity can be improved significantly by adding Ni-MMT composite into Al + 5 wt % alloy matrix.

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REFERENCES

1. T. Kaewmaneeekul and G. Lonthongkum, *Corros. Sci.*, **66**, 67 (2013); <https://doi.org/10.1016/j.corsci.2012.09.004>.
2. W. Xiong, G.T. Qi, X.P. Guo and Z.L. Lu, *Corros. Sci.*, **53**, 1298 (2011); <https://doi.org/10.1016/j.corsci.2011.01.001>.
3. I. Gurrappa, I.V.S. Yashwanth, I. Mounika, *Proc. Natl. Acad. Sci. India Sect. A: Phys. Sci.*, **85**, 1 (2015); <https://doi.org/10.1007/s40010-014-0182-0>.
4. I.L. Muller and J.R. Galvele, *Corros. Sci.*, **17**, 191 (1977); [https://doi.org/10.1016/0010-938X\(77\)90044-0](https://doi.org/10.1016/0010-938X(77)90044-0).
5. J.B. Bessone, R.A. Suarez Baldo and S.M. de Micheli, *Corrosion*, **37**, 533 (1981); <https://doi.org/10.5006/1.3580802>.
6. J.B. Bessone, D.O. Flamini, S.B. Saidman, *Corros. Sci.*, **47**, 95 (2005); <https://doi.org/10.1016/j.corsci.2004.05.002>.
7. A.G. Munoz, S.B. Saidman and J.B. Bessone, *J. Electrochem. Soc.*, **146**, 2123 (1999); <https://doi.org/10.1149/1.1391902>.
8. A.G. Munoz and J.B. Bessone, *Electrochim. Acta*, **43**, 1067 (1998); [https://doi.org/10.1016/S0013-4686\(97\)00279-X](https://doi.org/10.1016/S0013-4686(97)00279-X).

9. A.G. Munoz, S.B. Saidman and J.B. Bessone, *Corros. Sci.*, **44**, 2171 (2002); [https://doi.org/10.1016/S0010-938X\(02\)00042-2](https://doi.org/10.1016/S0010-938X(02)00042-2).
10. J. He, J. Wen and X. Li, *Corros. Sci.*, **53**, 1948 (2011); <https://doi.org/10.1016/j.corsci.2011.02.016> 1948-1953.
11. S.M.A. Shibli, S.R. Archana and P.M. Ashraf, *Corros. Sci.*, **50**, 2232 (2008); <https://doi.org/10.1016/j.corsci.2008.06.017>.
12. S.M.A. Shibli and K.K. Binoj, *J. Appl. Electrochem.*, **39**, 159 (2009); <https://doi.org/10.1007/s10800-008-9659-3>.
13. S.M.A. Shibli, V.S. Dilimon and A. Mohan, *Appl. Electrochem.*, **37**, 1015 (2007); <https://doi.org/10.1007/s10800-011-0301-4>.
14. H.L. Hsu, J.M. Jehng and Y.C. Liu, *Mater. Chem. Phys.*, **113**, 166 (2009); <https://doi.org/10.1016/j.matchemphys.2008.07.067>.
15. J.R. Sohn and S.I. Lee, *Langmuir*, **16**, 5024 (2000); <https://doi.org/10.1021/la980637k>.
16. K.G. Fournaris, M.A. Karakassides and D. Petridis, *Chem Mater.*, **11**, 2372 (1999); <https://doi.org/10.1021/cm981140z>.
17. I. Isik, U. Yilmazer and G. Bayram, *Polymer*, **44**, 6371 (2003); [https://doi.org/10.1016/S0032-3861\(03\)00634-7](https://doi.org/10.1016/S0032-3861(03)00634-7).
18. C.R. Reddy, G. Nagendrappa and B.S. Jai Prakash, *Catal. Commun.*, **8**, 241 (2007); <https://doi.org/10.1016/j.catcom.2006.06.023>.
19. A. Dhakshinamoorthy and K. Pitchumani, *Tetrahedron Lett.*, **49**, 1818 (2008); <https://doi.org/10.1016/j.tetlet.2008.01.061>.
20. P.B. Messersmith and E.P. Giannelis, *Chem. Mater.*, **6**, 1719 (1994); <https://doi.org/10.1021/cm00046a026>.
21. J.J. Lin, Y.N. Chan and Y.F. Lan, *Materials*, **3**, 2588 (2010); <https://doi.org/10.3390/ma3042588>.
22. R.A. Horch, T.D. Golden, N.A. D'Souza and L. Riester, *Chem. Mater.*, **14**, 3531 (2002); <https://doi.org/10.1021/cm010812+>.
23. K.D. Ralston, D. Fabijanec and N. Birbilis, *Electrochim. Acta*, **56**, 1729 (2011); <https://doi.org/10.1016/j.electacta.2010.09.023>.
24. M. Zhao, H. Song, J. Li, G. He and Y. Gui, *Comput. Mater. Sci.*, **102**, 78 (2015); <https://doi.org/10.1016/j.commatsci.2015.02.020>.
25. I.B. Singh, M. Singh and S. Das, *J. Magn. Alloys*, **3**, 142 (2015); <https://doi.org/10.1016/j.jma.2015.02.004>.
26. C.B. Breslin, L.P. Friery and W.M. Carroll, *Corros. Sci.*, **36**, 85 (1994); [https://doi.org/10.1016/0010-938X\(94\)90111-2](https://doi.org/10.1016/0010-938X(94)90111-2).
27. C.B. Breslin, L.P. Friery, *Corros. Sci.*, **36**, 231 (1994); [https://doi.org/10.1016/0010-938X\(94\)90155-4](https://doi.org/10.1016/0010-938X(94)90155-4).
28. H.A. El-Shayeb, F.M. Abdel-Wahab and S.J. Zeinel-Abedin, *Appl. Electrochem.*, **29**, 473 (1999); <https://doi.org/10.1023/A:1003425306696>.
29. J. Ma and J. Wen, *J. Alloy. Compd.*, **496**, 110 (2010); <https://doi.org/10.1016/j.jallcom.2010.02.174>.
30. J. Ma, J. Wen, W. Zhai and Q. Li, *Mater. Charact.*, **65**, 86 (2012); <https://doi.org/10.1016/j.matchar.2012.01.003>.
31. D.R. Salinnas and J.B. Bessone, *Electrochim. Acta*, **42**, 413 (1997); [https://doi.org/10.1016/S0013-4686\(96\)00236-8](https://doi.org/10.1016/S0013-4686(96)00236-8).
32. M. Jingling, W. Jiuba, L. Xudong, Z. Shengli and Y. Yanfu, *Rare metals*, **28**, 187 (2009); <https://doi.org/10.1007/s12598-009-0037-z>.
33. S. Khireche, D. Boughrara, A. Kadri, L. Hamadou and N. Benbrahim, *Corros. Sci.*, **87**, 504 (2014); <https://doi.org/10.1016/j.corsci.2014.07.018>.
34. D.O. Flamini and S.B. Saidman, *Mater. Chem. Phys.*, **136**, 103 (2012); <https://doi.org/10.1016/j.matchemphys.2012.06.036>.
35. J. Li, K. Wan, Q. Jiang, H. Sun, Y. Li, B. Hou, L. Zhu and M. Liu, *Metals*, **65**, 1 (2016).
36. H. Zarrok, A. Zarrouk, R. Salghi, M.E. Touhami, H. Oudda, B. Hammouti, R. Tourir, F. Bentiss, S.S. Al-Deyab, *Int. J. Electrochem. Sci.*, **8**, 6014 (2013).
37. J.Q. Jiang and Z. Zeng, *Chemosphere*, **53**, 53 (2003); [https://doi.org/10.1016/S0045-6535\(03\)00449-1](https://doi.org/10.1016/S0045-6535(03)00449-1).