

Article

A Comprehensive Evaluation of Electrochemical Performance of Aluminum Hybrid Nanocomposites Reinforced with Alumina (Al₂O₃) and Graphene Oxide (GO)

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Abstract: The electrochemical performance of in-house developed, spark plasma-sintered, Aluminum metal–matrix composites (MMCs) was evaluated using different electrochemical techniques. X-ray diffraction (XRD) and Raman spectra were used to characterize the nanocomposites along with FE-SEM and EDS for morphological, structural, and elemental analysis, respectively. The highest charge transfer resistance (R_{ct}), lowest corrosion current density, lowest electrochemical potential noise (EPN), and electrochemical current noise (ECN) were observed for GO-reinforced Al-MMC. The addition of honeycomb-like structure in the Al matrix assisted in blocking the diffusion of Cl^- or SO_4^{2-} . However, poor wettability in between Al matrix and Al₂O₃ reinforcement resulted in the formation of porous interface regions, leading to a degradation in the corrosion resistance of the composite. Post-corrosion surface analysis by optical profilometer indicated that, unlike its counterparts, the lowest surface roughness (R_a) was provided by GO-reinforced MMC.

Keywords: aluminum metal–matrix composites; hybrid nanocomposites; graphene oxide (GO); Spark Plasma Sintering (SPS); electrochemical corrosion



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1. Introduction

Aluminum-based metal–matrix Composites (Al MMCs) are finding increased applications in industries such as automobiles, aviation, and marine to name a few, due to their lightweight as well as high strength, high thermal conductivity, and high stiffness, along with excellent corrosion and wear resistance properties [1–3]. Al MMCs that are utilized in high temperature applications ought to have competent mechanical properties and resilience to chemical degradation under severe conditions; therefore, enhancing their corrosion resistance using different reinforcements has recently gained considerable attention [4,5]. Many studies have reported an improvement in strength and wear resistance of Al MMCs by incorporating different reinforcements such as alumina, silicon carbide, titanium carbide, tungsten carbide, titanium diboride, boron nitride, and B₄C [6–10]. Among the various available reinforcements, alumina is the most generally utilized due to its phenomenal mechanical properties and high-temperature strength [11–17]. However, research on alumina-reinforced MMCs is mainly focused on their manufacturing methods and mechanical aspects [11–15]. The effect on the corrosion resistance is rarely reported; therefore, the corrosion mechanisms of such MMCs are not well understood, and there are conflicts in the reported literature with regard to the corrosion initiation sites and the role of alumina in corrosion susceptibility [16–19]. Alaneme et al. [20] investigated the corrosion behavior of alumina-reinforced Al (6063) MMCs using different techniques and reported a discrepancy in the results. Nanjan et al. [21] used the weight loss technique to analyze the corrosion phenomenon of alumina-reinforced MMCs and reported no phenomenal effect of alumina

on the corrosion of aluminum-based MMCs. Kargul et al. [22] reported improved corrosion resistance due to the Al_2O_3 particulate distribution of the reinforcement with intact matrix-reinforcement bonding. In the recent past, different researchers tried carbon-based reinforcements in Al-based MMCs and reported improvements in corrosion resistance of the MMCs. Reinforcements such as carbon fibers [23,24], graphite [25,26], carbon nanotubes (CNTs) [27,28], graphene (G) [29,30], and graphene oxide (GO) [31,32] have been used as reinforcements in Al-MMCs. Among all these, graphene, a carbon allotrope, has emerged as an excellent reinforcement for superior performance in futuristic materials in view of its chemical stability and excellent thermal, electrical, and mechanical properties. However, the usage of graphene has been restricted due to its high manufacturing cost, poor dispersibility, and susceptibility to get agglomerated in the matrix [33,34]. To overcome these issues, graphene oxide came into being as an alternative because of its characteristic resemblance with graphite structure, with excellent strength and stability to chemical and thermal degradation. However, most of the research has been conducted on MMCs reinforced with reduced-graphene-oxide (RGO) with very limited research on graphene oxide (GO) reinforced MMCs [35,36]. Furthermore, a majority of these studies on GO-reinforced Al MMCs are directed towards understanding their mechanical properties [37,38]. Corrosion resistance properties of these composites are rarely reported; therefore, one of the objectives of this work is to systematically investigate the corrosion phenomenon of GO-reinforced Al MMCs using state-of-the-art electrochemical techniques such as EIS, EPN, ECN, and PDP in different solutions.

On the other hand, though MMCs reinforced with ceramic oxides have many advantages, they suffer from a serious limitation of lower fracture toughness, which is limiting the utilization of alumina-reinforced MMCs in a wide scope of applications [11]. Therefore, to overcome this constraint, micro/nano-sized reinforcements such as CNT, CNF, SiC, G, and GO are mixed with an alumina matrix to form hybrid nanocomposite materials with enhanced fracture toughness [39]. Graphene additionally forms aluminum carbide during the fabrication process of Al-G composites and subsequently brings down the hardness. This could be due to the defective nature of graphene produced through the reduction process (thermal exfoliation) of graphite. Based on the literature discussed above, it can be deduced that reinforcement of Al-MMCs with monolithic types of materials contributes in both positive and negative ways. For instance, reinforcement of Al-MMCs with ceramic inclusions resulted in improved hardness and stiffness, but at the expense of ductility and fracture toughness [40]. In order to overcome these challenges, hybrid composites such as Al-MMCs reinforced simultaneously with both ceramics and carbon allotropes are receiving attention [41–45]. However, the main focus of these studies was to improve the mechanical properties of Al-MMCs, and only a few studies evaluated their corrosion performance [46,47]. Moreover, composite processing methods play a considerable role in determining their properties, and spark plasma sintering (SPS) is believed to have a significant positive impact on the properties. Among the various techniques available for synthesizing the Al-MMC's, such as casting, roll bonding, etc., research has shown that consolidation and sintering stages are integrated through SPS with a high heating rate and at a relatively lower sintering temperature, thus shortening the processing times [48–50].

Based on the discussed literature, it is evident that most of the electrochemical corrosion studies on composite materials are conducted basically to evaluate the reinforcement loading (%) in Al matrix. Based on our knowledge, the mechanistic electrochemical investigations revealing the fundamental causes behind the enhanced or degraded corrosion performance of GO or Al_2O_3 based (hybrid-)nanocomposite prepared by spark plasma sintering (SPS) has never been reported. There are many questions that require in-depth investigations, such as how GO reinforcement will affect the corrosion properties of Al-based MMCs (Al-GO) and what would be the combined effect of GO and alumina (Al_2O_3) on the corrosion performance of hybrid Al MMCs (Al- Al_2O_3 -GO). So the objective of this study is to conduct a systematic electrochemical performance evaluation of the in-house SPS

GO-reinforced aluminum nanocomposite and aluminum hybrid nanocomposite reinforced both with alumina (Al_2O_3) and graphene oxide (GO).

2. Experimental

2.1. Material Specifications

Aluminum (Al) powder of 99.5% purity and 30 μm particle size was procured from Alpha chemicals to be used as a matrix. Alpha alumina (Al_2O_3) having a particle size of 300 nm and surface area of 85–115 m^2/g with 99.8% purity was obtained from Union Carbide corporation for Buehler Ltd., Lake Bluff, IL, USA, to use as a reinforcement. Graphene oxide (GO) having a surface area of 250 m^2/g with 99.8% purity was obtained from ADNano Company, Shimoga, India, to use as a second reinforcement.

2.2. Material Processing

Fabrication of nanocomposite (Al-10V% Al_2O_3) and hybrid nanocomposite (Al-10V% Al_2O_3 -0.25 wt% GO) samples involved many steps, including ultrasonication, ball milling, and SPS, which are discussed below in detail. The 10V% of Alumina and 0.25 wt% of GO are based upon a previous study wherein they were optimized after a comprehensive experimental evaluation [51].

2.2.1. Ultrasonication of Al_2O_3 and GO Powders

To achieve a uniform distribution of the reinforcements (Al_2O_3 and GO) within the Al matrix, the reinforcements were sonicated individually at room temperature in ethanol for 10 min and 1 h, respectively, using a probe sonicator (Sonics VCX 750, Newtown, CT, USA), where the On/Off cycle was set to 20/5 s and the amplitude was fixed to 45%. The volume of Al_2O_3 was 10%, whereas the graphene oxide (GO) weight was 0.25%, and sonication was conducted under similar conditions in all the cases to prepare different sets of materials.

2.2.2. Ball-Milling Procedure

Aluminum powder (Al) was mixed with 10 volume % of the ultra-sonicated Al_2O_3 in a zirconia vial for 24 h, using a ball mill attritor (HD/HDDM/01, Union process, Inc. Akron, OH, USA). Argon (Ar) was continuously supplied to hinder the oxidation process, and to avoid excessive cold welding and agglomeration, ethanol was used as a process control agent (PCA). Zirconium oxide (ZrO_2) balls having a diameter of 5 mm were used by setting the ball-to-powder weight ratio (BPR) to 10:1, and powder mixing speed was set to 200 rpm. To avoid the sticking of the powder to the walls of the vial, the milling process was stopped after every hour. After 24 h of ball milling, the powder mixture was kept inside the oven at 80 $^\circ\text{C}$ for 12 h for drying. The ball milling procedure was repeated to mix Al-0.25% GO powders and the Al-10% Al_2O_3 -0.25% GO hybrid powders for an additional 24 h (total 48 h) to obtain a well-mixed homogeneous mixture. Mixing parameters used for the synthesis of (hybrid-) nanocomposites powders are illustrated in Table 1.

Table 1. Nanocomposite and hybrid nanocomposite powders mixing parameters used in ball milling operation.

Material	Speed (RPM)	BPR	Mixing Time (h)	PCA	Atmosphere
Al-10V% Al_2O_3	200	10:1	24	Ethanol	Argon
Al-0.25wt% GO	200	10:1	24	Ethanol	Argon
Al-10V% Al_2O_3 -0.25wt% GO	200	10:1	48	Ethanol	Argon

2.2.3. Spark Plasma Sintering (SPS) Procedure

Aluminum-based composite powders were put in a graphite die having 20 mm diameter. A graphite sheet of 0.35 mm thickness was placed among the die, powder, and punch in such a way that the powder acted as a sandwich in between the graphite sheets.

This sort of arrangement helps in the easy removal of samples as well as helps in avoiding the wear of the punch. The SPS machine from the FCT group, System GMBH, (Rauenstein, Germany), was used to sinter the Al, Al-10% Al₂O₃, Al-0.25% GO nanocomposite, and Al-10% Al₂O₃-0.25% GO hybrid nanocomposite samples, respectively. The SPS was conducted at a temperature of 500 °C, under a pressure of 50 MPa, with a holding time of 10 min and a heating rate of 200 °C/min for all the samples. Additional parameters, such as a cooling rate of 100 °C/min, were set to room temperature (20–35 °C), and pulse: pause was applied as 1:0 ms, and the number of pulse = 1. The SPS process provided disk-shaped nanocomposite samples having a diameter of 20 mm and height of 6 mm were also implemented. Figure 1 represents the schematic illustration of the synthesis of nanocomposite and hybrid nanocomposites from raw nanomaterials.

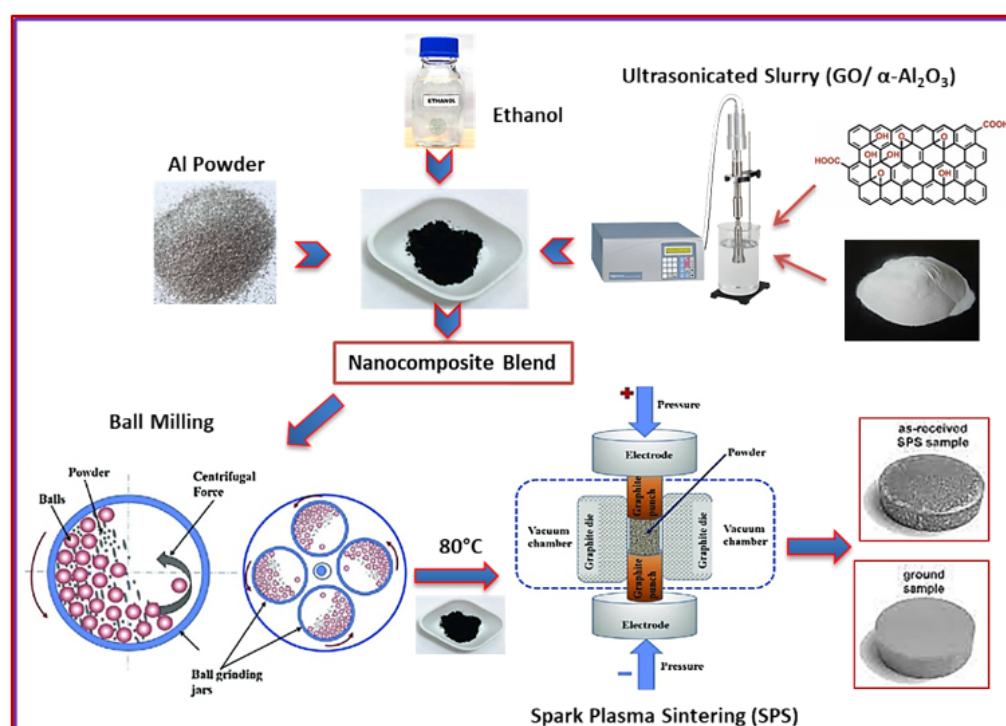


Figure 1. Schematic illustration of the synthesis of nanocomposite and hybrid nanocomposite from raw nanomaterials through spark plasma sintering.

2.3. Material Characterization

2.3.1. Sample Preparation

The sintered samples were epoxy-mounted and used subsequently for SEM, XRD, hardness testing, and electrochemical performance evaluation. These mounted samples were ground using different SiC grit papers ranging from 240 to 1200, followed by fine polishing using 0.3 µm alumina paste. Finally, the samples were ultrasonically cleaned for 10 min to remove any debris prior to performing any further characterizations.

2.3.2. Characterization and Imaging

The density of sintered examples was estimated following the Archimedes rule (Kern ABT weighing scale, 320 g capacity, Balingen, Germany). Micro-hardness was tested by applying a load of 500 gf through Zwick Roell Vickers hardness tester (Ulm, Germany). A total of 10 measurements were taken, and an average was calculated for each sample. Surface morphologies were observed through scanning electron microscopy (SEM), whereas elemental analysis was carried out by energy dispersive x-ray (EDX) (Quanta FEG 250, Thermo Fisher Company, Waltham, MA, USA). XRD was performed (Rigaku Miniflex X-ray diffractometer, Cedar Park, TX, USA) using Cu Kα radiation ($\lambda = 0.15416$ nm) using

a scanning range (2θ) of 5° – 120° and a scanning speed of $2^\circ/\text{min}$. Raman spectra were collected using a DXRTM microscope (Thermo Fisher Scientific, Waltham, MA, USA) with an argon-ion laser with a power of 2 mW, laser wavelength (λ_{ex}) = 455 nm, aperture = 50 mm, and beam spot size = 0.6 mm. On average, three spectra were collected for each sample. Water contact angle measurements were carried out using Kyowa Contact Angle Meter DM-501 (Takasaki, Japan). A 0.5 μL of deionized water droplet was placed on the surface for each of the test, and angles were measured. A total of five independent measurements were performed randomly at different locations on the samples, and an average value was taken for every sample. The measurement error was within $\pm 3^\circ$.

2.3.3. Electrochemical Evaluation

The electrochemical performance of nanocomposites was evaluated using Gamry 3000 potentiostat (Warminster, PA, USA). In a conventional three-electrode cell, composite samples were set as working electrode (WE), graphite rod was set as a counter electrode (CE), and saturated calomel electrode was set as reference electrode (RE). Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) techniques were used for evaluating the corrosion performance of Al and its composites in chloride (0.1 M, 0.3 M, 0.6 M) and acidic (0.5 M H_2SO_4) solution. Before electrochemical testing, composite samples were degreased with ethanol and subsequently rinsed with deionized water. Open circuit potential (OCP) was monitored until potential stability was achieved before electrochemical evaluations. EIS spectra were obtained by applying a sinusoidal voltage of 10 mV amplitude, and frequency was set in a range of 100 K to 10 mHz. PDP plots were obtained by applying potential in a range of -0.1 to 1 V vs. OCP, whereas the scan rate was fixed to 0.5 mV/s.

Electrochemical noise measurements (ENM) were performed using a Gamry ESA 410 data acquisition system (Version 7.10) under the ZRA mode. Potential and current fluctuations were measured simultaneously in a standard three-electrode arrangement using two similar working electrodes and a SCE reference electrode. The electrochemical current noise (ECN) was recorded between the two working electrodes, whereas the electrochemical potential noise (EPN) was recorded between the working and reference electrodes. A nested Faraday cage was used to place the ENM experimental setup in order to isolate it from the environmental noise. Five points per second were obtained during a time period of 1800 s, which fixed the frequency in the region between 0.1 Hz and 2.5 Hz. A low-pass output filter of 0.1% was set with a cut-off frequency of 5 Hz in order to attenuate the frequencies above the Nyquist frequency.

3. Results and Discussion

3.1. Density and Hardness

The density of nanocomposites was measured using the Archimedes method and is shown in Figure 2a. It can be seen in Figure 2 that Al exhibited the highest density of 99.7%, followed by Al-0.25% GO (99%), Al-10% Al_2O_3 (97.5%), Al-10%, Al_2O_3 -0.25% GO (96.8%) nanocomposite, respectively. The reduction in density can be attributed to the loss of wettability between the Al matrix and Al_2O_3 and GO reinforcements, respectively, and the reduction was more significant between Al- Al_2O_3 and Al-GO nanocomposites [51]. It seems logical because, in Al- Al_2O_3 composites, the amount of Al_2O_3 reinforcement was high (10%) as compared to that of 0.25% GO in Al-GO composites. It can be concluded that due to the high quantity of Al_2O_3 reinforcement, the agglomeration of alumina particles could have contributed to the reduction in density. A rule of mixtures was used to obtain the theoretical densities as well and is shown in Figure 2a (Inset).

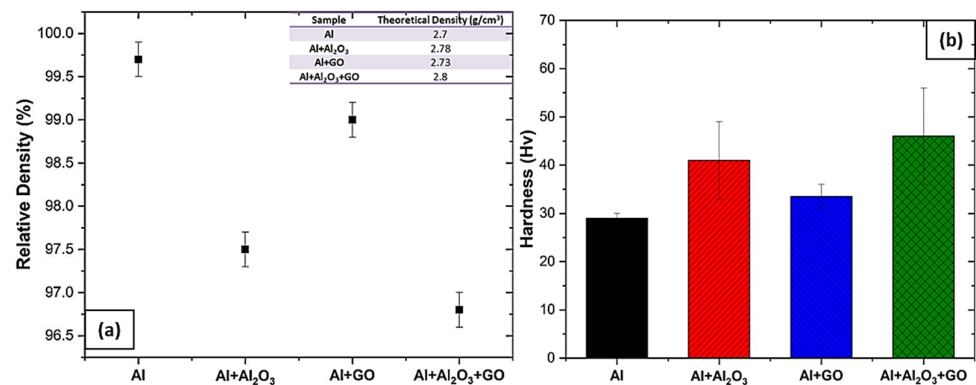


Figure 2. (a) Relative and theoretical densities, (b) Hardness of pure Al, Al-0.25% GO, Al-10 vol% Al₂O₃, and Al-10% Al₂O₃-0.25% GO.

Figure 2b shows the Vickers hardness of Al MMCs, and it is clear that the highest hardness was observed as expected for the Al₂O₃-GO-reinforced hybrid nanocomposite. The increase in the hardness of sintered Al from 29 HV to 33.5 HV by the addition of just 0.25% GO was observed and is mainly credited to the uniform distribution of graphene oxide (GO) throughout the Al matrix, which helped in restricting the slip motions. The discrepancy in hardness values was found to be minuscule, as is shown by the error bar, and provides evidence of the uniform dispersion of GO in the Al matrix. On the other side, a significant increase in hardness (42 HV) due to 10% Al₂O₃ reinforcement was observed, indicating more restriction in slip motion due to the higher Al₂O₃ volume and also due to the inherent hardness of the alumina particles. However, a huge discrepancy in hardness values was measured through the error bar, signifying the agglomeration of Al₂O₃ particles in the Al matrix. Agglomeration of Al₂O₃ separated it from the Al matrix, thus forming a binary phase structure. It is evident from the SEM images (Section 3.3) that metallic Al was noticed to be separated from the Al-Al₂O₃ nanocomposite by forming a distinctive interface region. This is why metallic Al around such interface regions provided low hardness, whereas Al-Al₂O₃ nanocomposite provided higher hardness, and this discrepancy was translated to the enlarged error bar. The combined reinforcement of Al₂O₃-GO to Al matrix increased both the average hardness (46 HV) and discrepancy (error bar), which could be attributed to the combined effect of both of the reinforcements. One other indirect factor that may have contributed to the increase in the hardness is the prolonged time of ball milling of 48 h for the hybrid composite, which may have resulted in a grain size reduction leading to an increase in the hardness.

3.2. Characterization

The X-ray diffraction (XRD) pattern of spark plasma-sintered (SPS) nanocomposite and hybrid nanocomposite specimens is shown in Figure 3a. A narrow peak broadening of both Al₂O₃ and Al was observed for Al-Al₂O₃ nanocomposite in comparison to that of hybrid nanocomposite (Al-Al₂O₃-GO), signifying a uniform dispersion of the fillers within the parent matrix. No GO peak was detected in XRD patterns in both Al-GO or Al-Al₂O₃-GO nanocomposites, possibly due to its small content (0.25%). Furthermore, no evidence of any chemical reaction between Al, Al₂O₃, and GO, as an intermetallic phase such as aluminum carbide (Al₄C₃) was absent from the XRD pattern of (hybrid-) nanocomposites.

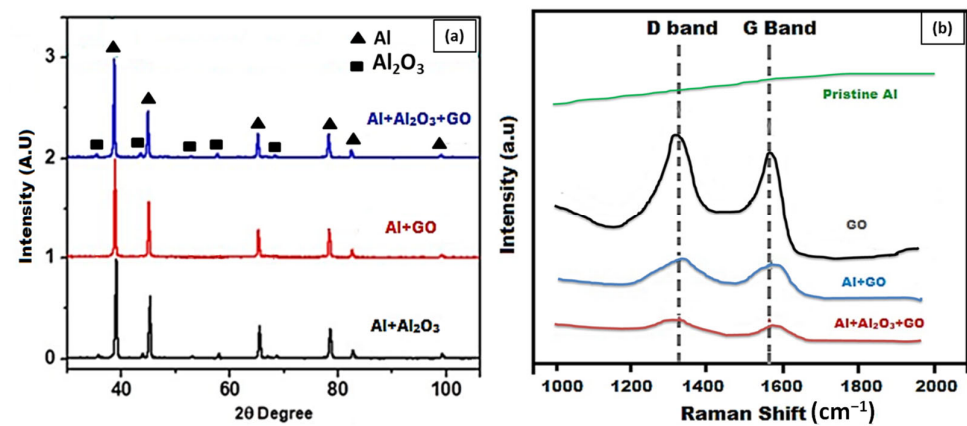


Figure 3. (a) X-ray diffraction (XRD), (b) Raman spectra of metallic Al, Al-0.25% GO, Al-10% Al₂O₃, and Al-10% Al₂O₃-0.25% GO (hybrid-) nanocomposites.

Raman spectra of pure Al, GO, GO-reinforced Al-MMC, and Al₂O₃-GO-reinforced Al-MMC are shown in Figure 3b. Two signature peaks of GO were detected, first approximately at 1580 cm⁻¹, which corresponds to the G-band and is possibly generated by the stretching of the C–C bond in graphene oxide (GO). The second peak was detected approximately at 1350 cm⁻¹, which corresponds to the D-band, and is associated with the disorders or defects. These defects could be generated from the resonance spectra of Sp² hybridized carbon. G- and D-bands are evident through the Raman spectra and can be seen against pure GO, nanocomposite, and hybrid nanocomposite.

3.3. Surface Analysis

3.3.1. Morphology and Elemental Analysis

Scanning electron microscopic (SEM) images of the powders utilized in fabricating composite materials, i.e., pure Al, alumina (Al₂O₃), and graphene oxide (GO), are shown in Figure 4a–c. Clustering of both alumina (Al₂O₃) and graphene oxide (GO) particles was observed; however, no such clustering was observed against Al powder particles. Three-dimensional structures of the nanocomposite and hybrid nanocomposite were generated from the SEM images for a better understanding and assessment and are shown in Figure 5a–d. SEM microstructures may reveal a discrete amount of information about the pore density, distribution, alignment, and nature of pores, along with the matrix–reinforcement bonding.

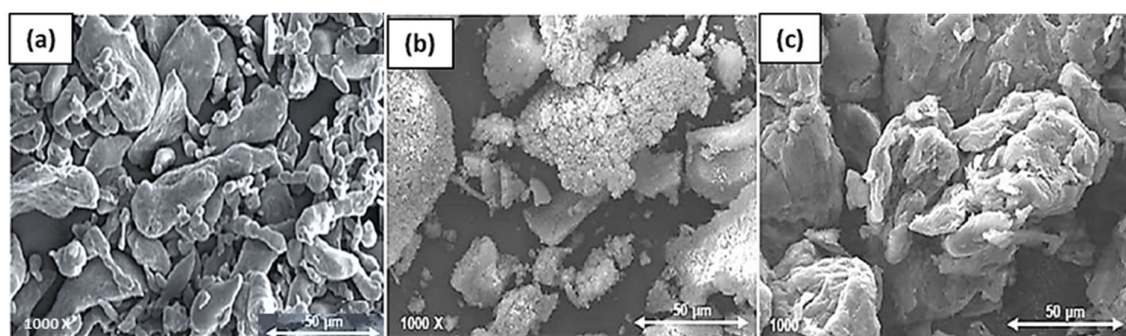


Figure 4. SEM for the as-received powders of (a) Al, (b) Al₂O₃, (c) GO.

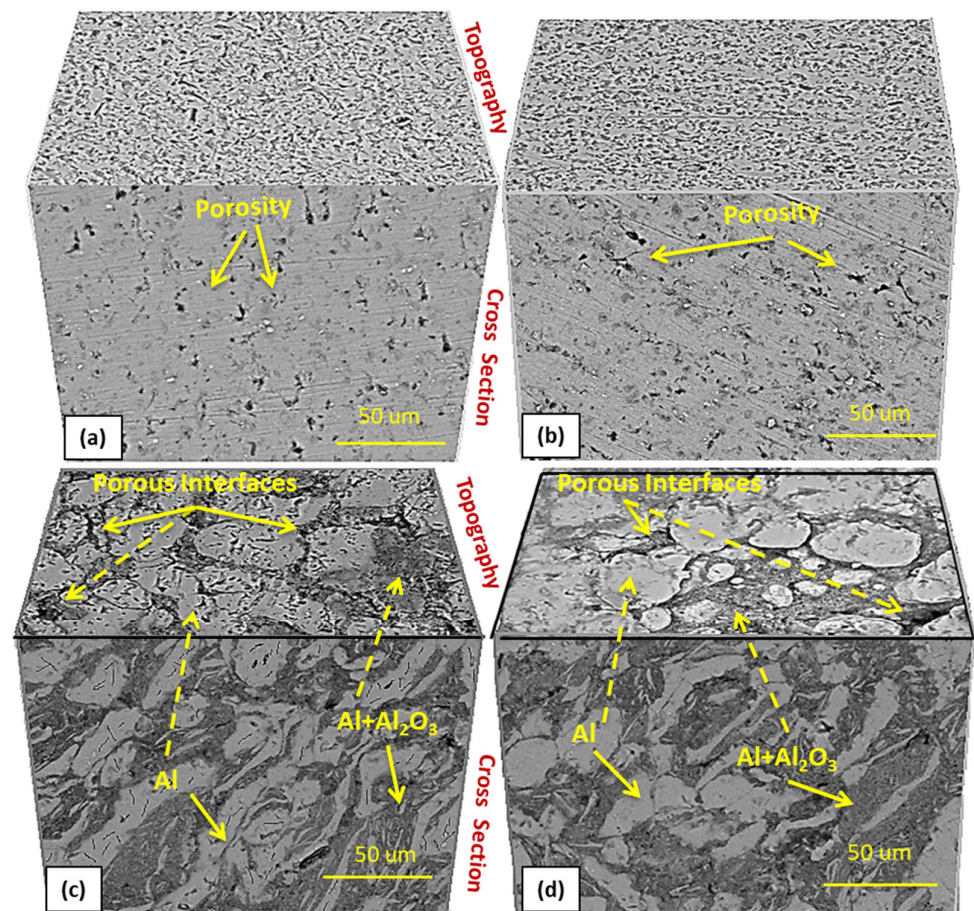


Figure 5. The 3D-SEM images of the Al based nanocomposites after SPS. (a) Pure Al, (b) Al-0.25% GO, (c) Al-10% Al_2O_3 . (d) Al-10% Al_2O_3 -0.25% GO.

It can be noticed from Figure 5a,b that both the metallic Al and Al-0.25% GO nanocomposite samples exhibited nearly similar types of surface and cross-sectional morphologies. This could be because of the insignificant GO content (0.25%) in the Al matrix and thus apparent morphology was seen unchanged. Since dispersion of GO in the Al matrix, is hard to predict through the topography and cross-sectional SEM images (Figure 5b), the dispersion phenomenon will be discussed later on through the fractography carried out by SEM analysis in the discussion section. However, it is believed that pure graphene has high surface energy but a low wetting tendency for Al. Surface energy can be reduced by the formation of GO, which can increase its wetting tendency along with Al to have good interface bonding with uniform dispersion. Interface bonding with higher wettability could be achieved due to the possible mismatch in between the higher thermal expansion coefficient (CTE) of the Al matrix and the lower CTE of GO reinforcement. With the increase in temperature, the thermal stresses generate dislocation at the matrix-reinforcement interface. Consequently, an increase in dislocation density contributes to the pinning of the grain boundaries by restricting the grain growth of the Al matrix, thus contributing to achieving interfacial bonding and strength at the same time [52].

However, structural morphology was noticed to be totally changed due to the presence of 10% Al_2O_3 as a reinforcement in both Al- Al_2O_3 and Al- Al_2O_3 -GO (hybrid-) nanocomposites, and is shown in Figure 5c,d. A binary structure was formed through the interface regions distinctively separating the metallic Al (light grayish) from the Al- Al_2O_3 nanocomposite (dark grayish). The SEM micrographs of the nanocomposites suggest the presence of a network of alumina particles within the intergranular spaces of the aluminum matrix. The initial fusion phenomenon may have resulted in plasma formation at interparticle interfaces at the time of sintering, resulting in a well-bounded nanocomposite. Another

reason behind the well-bounded nanocomposite structure could be the smaller size of the reinforcement particles (Al_2O_3) as compared to that of the matrix particle size (Al), and hence the inter-particle voids created by the consolidation of aluminum (Al) particles may have been occupied by the alumina (Al_2O_3) nanoparticles. The bonding of Al_2O_3 nanoparticles with the Al matrix particles could also be due to the higher atomic diffusivity of the Al_2O_3 nanoparticles in micron-sized Al particles [53].

Though the proximate level of affinity of Al_2O_3 nanoparticles for Al matrix has resulted in well-distributed bonded nanocomposite structures, poor wettability in between Al_2O_3 and Al was seen that provided porous and unbounded Al- Al_2O_3 interface regions throughout the composite structure. This could be due to: (1)—The differential wettability between Al_2O_3 reinforcement nanoparticles and Al matrix [48], leading to the agglomeration of alumina (Al_2O_3). Agglomeration could be minimized if the ratio of reinforcement particle size to the matrix particle size (PSR) is close to 1 [54]. Agglomeration of Al_2O_3 nanoparticles most probably might have increased the particle size because of the disproportionate temperature zones in the sintering process and thus deviated the PSR ratio from 1 and caused clustering. At the earlier stage, when temperature was high, these clustered Al_2O_3 particles could be intact within the intergranular regions of Al, but the possible contraction in volume with the decrease in temperature might have lowered the wettability and thus resulted in voids and porosity in the composite structure. (2)—The clustered alumina (Al_2O_3) particles are larger in size in comparison to the Al_2O_3 nanoparticles, so they might have generated an extra space, not letting them fit into the matrix. The grain growth of the Al matrix is likely to occur to a greater extent around the porous regions surrounded by the clustered alumina (Al_2O_3) particles. This phenomenon could be attributed to the inability of the clustered alumina (Al_2O_3) particles to hinder the grain boundary growth via Zener pinning in a larger proportion.

EDS mapping of the metallic Al and its nanocomposites is shown in Figure 6a–d. EDS mapping of the metallic Al and 0.25% GO-reinforced nanocomposite reveals no difference in view of Al or O distribution, as can be seen in Figure 6a,b. Since Al was reinforced with just 0.25% GO, no significant difference in carbon elemental density was observed between pure Al and Al-0.25% GO nanocomposites. However, only a negligible amount of carbon clustering was evident in Figure 6b (encircled) depicting the GO agglomeration, leading to the conclusion that GO was uniformly dispersed throughout the Al matrix. On the other hand, the systematic elemental distribution of Al and O for the Al_2O_3 - or Al_2O_3 -GO-reinforced (hybrid-) nanocomposites was found to be in agreement with the SEM morphologies, as can be seen in Figure 6c,d. Both metallic Al and composite of Al- Al_2O_3 could be observed to be distinctively separated from each other. However, the C distribution in Al_2O_3 -GO reinforced hybrid nanocomposite was found to be potentially different compared to that of Al_2O_3 -reinforced Al-MMC. GO agglomeration was observed (Figure 6d) in Al_2O_3 -GO-reinforced Al-MMC (encircled in Figure 6d), which could be attributed to the predominant agglomerating tendency of Al_2O_3 . In other words, Al_2O_3 presence suppressed the homogeneous dispersion of GO in the Al matrix, thus forcing it to be agglomerated in localized regions.

3.3.2. Wettability

Contact angle measurements of aluminum and its nanocomposites are shown in Figure 7. The contact angle of Al was observed to increase from 80.2° to 102.8° with the addition of 0.25% GO. The increase in contact angle of 0.25% GO-reinforced Al MMC proves it to be hydrophobic in nature in contrast to pure Al, which acted as a hydrophilic surface. The shift from hydrophilic to hydrophobic tendency results in a decrease in surface energy due to the reinforcement of GO in Al matrix, which can be attributed to the high wettability (adhesion tendency) between Al matrix and GO reinforcement [55]. However, the contact angle of Al_2O_3 -reinforced Al MMC was observed to decrease from 80.2° to 72.7° , which signifies that composite was formed with higher surface energy compared to that of pure Al. Poor wettability between Al_2O_3 reinforcement and Al matrix can be

seen in Figure 5c through the open interface regions, and hence, an increase in free surface energy was expected. Contact angle decreased even further to 69° with the introduction of GO along with Al_2O_3 in the Al matrix, as revealed in Figure 5d, signifying that wettability between reinforcements and matrix in hybrid MMC remained poor and GO was found ineffective in the presence of Al_2O_3 .

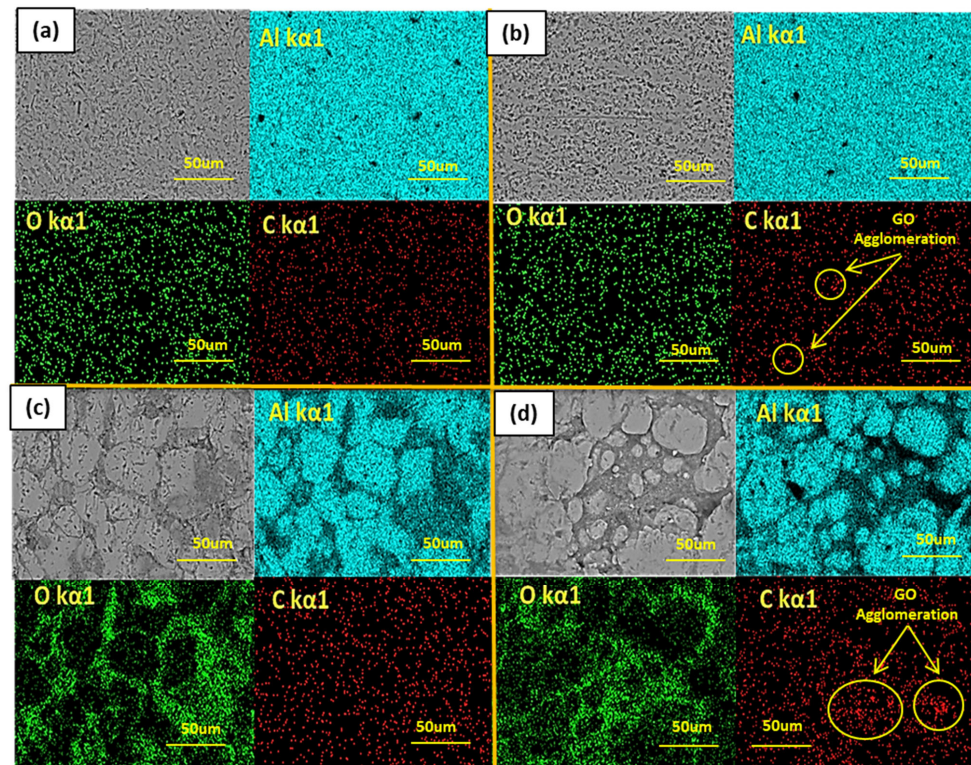


Figure 6. EDS of the Al-based nanocomposites after SPS. (a) Pure Al, (b) Al-0.25% GO, (c) Al-10% Al_2O_3 . (d) Al-10% Al_2O_3 -0.25% GO.

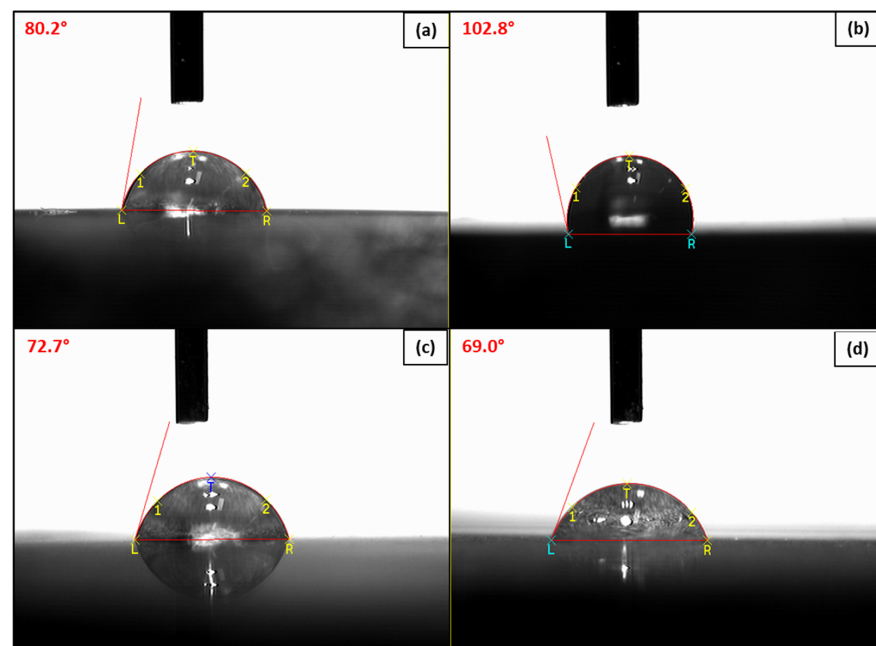


Figure 7. Contact angles measured on (a) Al, (b) Al-0.25% GO, (c) Al-10% Al_2O_3 , (d) Al-10% Al_2O_3 -0.25% GO.

3.4. Electrochemical Evaluation

3.4.1. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was conducted on Al-MMC samples in chloride (0.1 M, 0.3 M, 0.6 M NaCl) and acidic (0.5 M H₂SO₄) solutions at room temperature. The experimental data were fitted using three different types of equivalent circuits shown in Figure 8a–c. In each equivalent, the solution resistance is represented by R_s , R_{ct} is charge transfer resistance, and R_{po} depicts pore resistance. Two constant phase elements (CPE) were used in equivalent circuits, signifying the non-ideal behavior of the double layer appearing due to thickness variation of inhibitory film, non-uniform surface corrosion product, unequal charge distribution density, or variation in surface roughness. CPE can be represented by Equation (1).

$$Z_{CPE} = [Y_o^{-1} (j\omega)^{-n}] \quad (1)$$

where Z_{CPE} is the impedance of CPE ($\Omega \text{ cm}^{-2}$), Y_o is a numerical value of the admittance ($1/|Z| = s^n \Omega^{-1} \text{ cm}^{-2}$), $j = (-1)^{1/2}$, ω is the angular frequency (rad s^{-1}), and n is the deviation factor from ideal behavior ranging from 0 to 1. CPE acts as an ideal capacitor if $n = 1$, or as resistor if $n = 0$. Z_w represents Warburg element (used for diffusion-controlled mechanism at low frequency), and L acted as an inductor. Nyquist and Bode plots are shown in Figure 9a–h, whereas EIS extracted parameters are given in Tables 2–5.

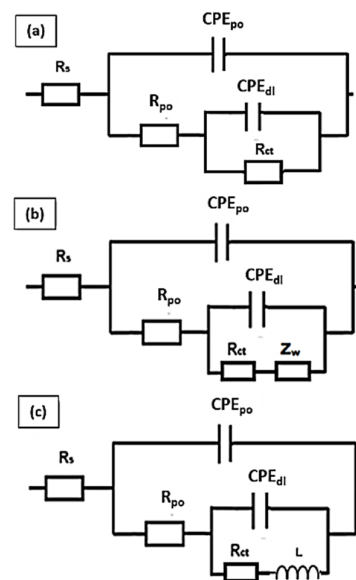


Figure 8. Electrochemical equivalent circuits used for fitting the experimental data to obtain impedance parameters. (a) without diffusion consideration. (b) with diffusion by adding Z_w in the circuit. (c) to simulate corrosion product effect by adding inductor (L) in the circuit.

A Nyquist plot of Al and its nanocomposites in a 0.1 M NaCl solution is shown in Figure 9a. A reasonable impedance was provided by the metallic Al, but its reinforcement with Al₂O₃ or GO exhibited opposing effects, i.e., Al₂O₃ decreased the impedance while GO increased it. EIS parameters in Table 2 reveal that metallic Al provided charge transfer resistance (R_{ct}) of $1.82 \times 10^5 \Omega \cdot \text{cm}^2$ and pore resistance (R_{po}) of $1.76 \times 10^4 \Omega \cdot \text{cm}^2$. The reinforcement of 10% Al₂O₃, however, was found to be detrimental, and both R_{ct} and R_{po} were dropped to $3.68 \times 10^4 \Omega \cdot \text{cm}^2$ and $1.31 \times 10^4 \Omega \cdot \text{cm}^2$, respectively. On the other side, the reinforcement of 0.25% GO to metallic Al increased the R_{ct} and R_{po} values up to $4.74 \times 10^6 \Omega \cdot \text{cm}^2$ and $5.46 \times 10^4 \Omega \cdot \text{cm}^2$, respectively. However, the addition of Al₂O₃-GO together in the Al matrix to form a hybrid nanocomposite was found to be more detrimental than the Al₂O₃-reinforced MMC, as both the R_{ct} ($6.16 \times 10^3 \Omega \cdot \text{cm}^2$) and R_{po} ($1.02 \times 10^3 \Omega \cdot \text{cm}^2$) values

decreased. In other words, GO alone was found to be effective in improving the corrosion resistance; however, it was ineffective in the presence of Al_2O_3 .

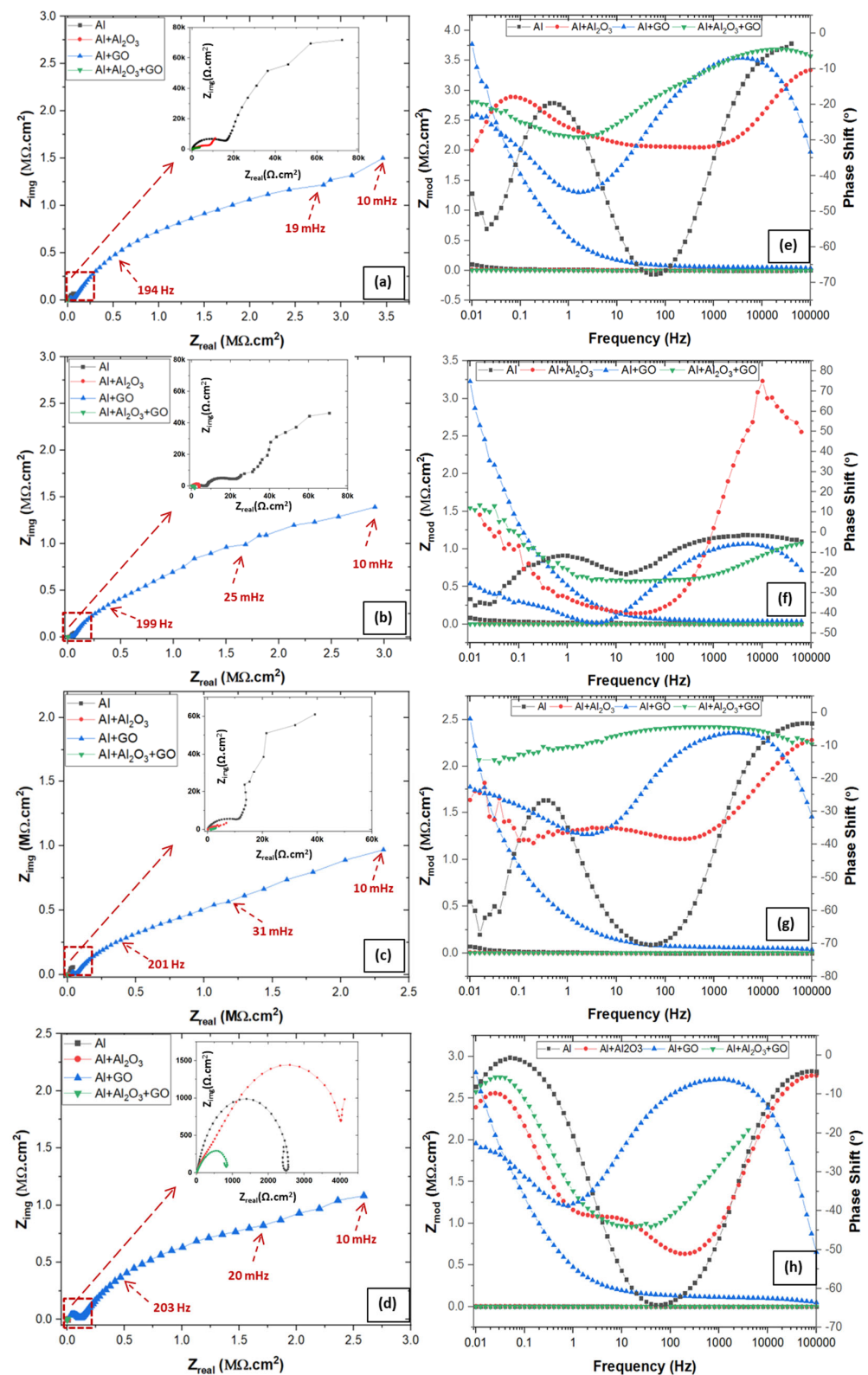


Figure 9. Nyquist and Bode plots of Al, Al-10% Al_2O_3 , Al-0.25% GO, and Al-10% Al_2O_3 -0.25 GO nanocomposites tested in (a,e) 0.1M NaCl, (b,f) 0.3M NaCl, (c,g) 0.6M NaCl, (d,h) 0.5M H_2SO_4 electrolytes at room temperature.

Table 2. Impedance parameters of Al MMCs obtained in 0.1 M NaCl solution.

Specimen	R_{soln} ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	R_{po} ($\Omega.cm^2$)	Dbl Layer Capacitance ($\mu F/cm^2$)	Dbl Layer Thickness ($\delta = nm$)	Film Capacitance ($\mu F/cm^2$)	Film Thickness ($\delta = nm$)	W ($S \times s^{1/2}$)
Al	7.6	1.82×10^5	1.76×10^4	7.1×10^1	11.27	3.64×10^1	21.85	-
Al + Al ₂ O ₃	8.9	3.68×10^4	1.31×10^4	1.6×10^3	0.51	5.94×10^1	13.42	-
Al + GO	5.4	$4.74E \times 10^6$	5.46×10^4	3.1×10^1	25.81	8.65×10^0	92.11	2.91×10^{-6}
Al + Al ₂ O ₃ + GO	6.6	$6.16E \times 10^3$	1.02×10^3	4.1×10^3	0.19	1.28×10^2	6.23	-

Table 3. Impedance parameters of Al MMCs obtained in 0.3 M NaCl solution.

Specimen	R_{soln} ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	R_{po} ($\Omega.cm^2$)	Dbl Layer Capacitance ($\mu F/cm^2$)	Dbl Layer Thickness ($\delta = nm$)	Film Capacitance ($\mu F/cm^2$)	Film Thickness ($\delta = nm$)	W ($S \times s^{1/2}$)
Al	7.2	1.02×10^5	1.16×10^4	1.5×10^2	5.20	5.76×10^1	13.83	-
Al + Al ₂ O ₃	8.1	2.28×10^4	5.22×10^3	2.5×10^3	0.32	1.55×10^2	5.13	-
Al + GO	4.5	2.58×10^6	5.19×10^4	4.7×10^1	16.89	2.04×10^1	39.06	2.69×10^{-6}
Al + Al ₂ O ₃ + GO	8.5	2.67×10^4	7.40×10^2	5.9×10^3	0.13	2.90×10^2	2.74	-

Table 4. Impedance parameters of Al MMCs obtained in 0.6 M NaCl solution.

Specimen	R_{soln} ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	R_{po} ($\Omega.cm^2$)	Dbl Layer Capacitance ($\mu F/cm^2$)	Dbl Layer Thickness ($\delta = nm$)	Film Capacitance ($\mu F/cm^2$)	Film Thickness ($\delta = nm$)	W ($S \times s^{1/2}$)
Al	4.3	9.95×10^4	1.35×10^4	2.8×10^2	2.85	9.04×10^1	8.81	-
Al + Al ₂ O ₃	8.6	9.86×10^3	5.80×10^2	4.4×10^3	0.18	2.04×10^2	3.91	-
Al + GO	6.7	1.90×10^6	3.87×10^4	5.5×10^1	14.40	3.57×10^1	22.30	3.67×10^{-6}
Al + Al ₂ O ₃ + GO	6.9	5.83×10^3	1.15×10^3	7.2×10^3	0.11	4.47×10^1	17.81	-

Table 5. Impedance parameters of Al MMCs obtained in 0.5 M H₂SO₄ solution.

Specimen	R_{soln} ($\Omega.cm^2$)	R_{ct} ($\Omega.cm^2$)	R_{po} ($\Omega.cm^2$)	Dbl Layer Capacitance ($\mu F/cm^2$)	Dbl Layer Thickness ($\delta = nm$)	Film Capacitance ($\mu F/cm^2$)	Film Thickness ($\delta = nm$)	W ($S \times s^{1/2}$)	L (H)
Al	5.3	2.41×10^3	3.13×10^2	2.0×10^2	3.93	3.55×10^1	22.47	-	567.7
Al + Al ₂ O ₃	8.2	3.38×10^3	7.86×10^2	3.7×10^2	2.17	1.12×10^2	7.14	6.37×10^{-3}	-
Al + GO	9.1	3.11×10^6	1.11×10^5	4.3×10^1	18.70	1.00×10^1	79.50	6.47×10^{-6}	-
Al + Al ₂ O ₃ + GO	9.7	8.09×10^2	1.25×10^3	3.6×10^2	2.20	2.33×10^2	3.42	-	102.4

The impedance performance of Al and its nanocomposites, i.e., Al-10% Al₂O₃, Al-0.25% GO, and Al-10% Al₂O₃-0.25 GO in other solutions (0.3 M NaCl, 0.6 M NaCl, and 0.5 M H₂SO₄) was found to be consistent with that of 0.1 M NaCl electrolyte. However, increasing the chloride concentration (0.3 M NaCl and 0.6 M NaCl) degraded the corrosion performance due to the intensive chloride ingress and diffusion [56]. The impedance plots of each material in different test solutions can be seen in Figure 9b,c,f,g. The extracted impedance parameters in each test solution are given in Tables 2–4.

The EIS spectra of metallic Al and its nanocomposites in H₂SO₄ are shown in Figure 9d,h and the impedance parameters are given in Table 5. The trend was found to be similar to one obtained in chloride solution, and it was found that the highest R_{ct} ($3.11 \times 10^6 \Omega.cm^2$) and R_{po} ($1.11 \times 10^5 \Omega.cm^2$) values were observed for Al-GO nanocomposite. The charge transfer resistance (R_{ct}) of Al and its nanocomposites is shown in Figure 10a. It can be seen that, in each test solution, the highest charge transfer resistance (R_{ct}) was provided by the

GO-reinforced Al-MMC, followed by the metallic Al. However, the incorporation of alumina (Al_2O_3) as reinforcement in the Al matrix dropped the R_{ct} values significantly.

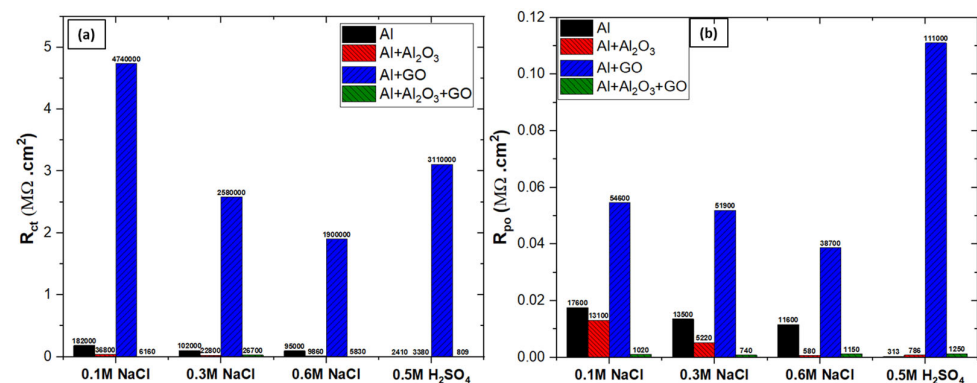


Figure 10. (a) Charge transfer resistance (R_{ct}) and (b) pore resistance (R_{po}) of Al, Al-10% Al_2O_3 , Al-0.25% GO, and Al-10% Al_2O_3 -0.25 GO nanocomposites tested in different test solutions at room temperatures.

Double layer capacitance and film capacitance was measured using Brug's [57] formula given in Equation (2) and, Hsu and Mansfeld [58] formula given in Equation (3), respectively.

$$C_{dl} = Q_{dl}^{(1/\alpha)} (1/R_e + 1/R_{ct})^{(\alpha-1)/\alpha} \quad (2)$$

$$C_f = Q_f^{(1/\alpha)} R_f^{(1-\alpha)/\alpha} \quad (3)$$

where Q_{dl} and Q_f represent CPE of double layer and film, respectively. R_e , R_{ct} and R_f are known as ohmic resistance, charge transfer resistance, and film resistance, respectively. From capacitances values, thicknesses of the double layer (δ_{dl}) and the film (δ_f) were estimated using the following expression;

$$C = \epsilon \epsilon_0 / \delta \quad (4)$$

where ϵ is the dielectric constant for aluminum oxide ($\text{Al}_2\text{O}_3 = 9$) and ϵ_0 is the vacuum permittivity ($8.85 \times 10^{-14} \text{ F}\cdot\text{cm}^{-2}$). Pore resistances (R_{po}) of the film formed on the Al and its nanocomposites in different test solutions is shown in Figure 10b. It can be seen that the highest pore resistance (R_{po}) of $5.46 \times 10^4 \Omega \cdot \text{cm}^2$ was achieved against the GO-reinforced Al-MMCs in 0.1 M NaCl solution, whereas the lowest R_{po} of $1.02 \times 10^3 \Omega \cdot \text{cm}^2$ in 0.1 M NaCl was provided by the hybrid nanocomposite (Al- Al_2O_3 -GO). Pore resistance (R_{po}) of the composites is found to be in true agreement with the estimated double layer thickness (δ_{dl}) and film thickness (δ_f). It can be seen that maximum double layer thickness ($\delta_{dl} = 25.81 \text{ nm}$) and film thickness ($\delta_f = 92.11 \text{ nm}$) was achieved at Al/GO nanocomposite anode. The lowest double layer thickness ($\delta_{dl} = 0.19 \text{ nm}$) and film thickness ($\delta_f = 6.23 \text{ nm}$) was achieved at Al- Al_2O_3 -GO nanocomposite anode. However, the comparison of pore resistance (R_{po}) of Al-GO nanocomposite in each test solution indicates that maximum R_{po} was achieved in 0.5 M H_2SO_4 followed by 0.1 M NaCl solution, and it started to decrease further with the increase in Cl ion concentration. Higher pore resistance (R_{po}) in H_2SO_4 compared to that of 0.1 M NaCl signifies that chlorides are more detrimental in reducing the film resistance, possibly due to their aggressive ingress.

The electrochemical equivalent circuit shown in Figure 8b with Warburg impedance was used for the fitting of Al-GO nanocomposite EIS data. Warburg impedance exists in low-frequency regions where oxygen diffusion mechanisms are involved [55]. A typical mass-transfer process is indicated during this step, which plays an important role in the electrode process. Cathodic reaction ($\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$) in a certain potential zone is purely a diffusion-controlled process where reduction and diffusion of the dissolved oxygen are dominated. If the rate of reaction at the cathode surface is significantly fast

enough, oxygen concentration at the electrode surface can deplete compared to that of the bulk solution. As a result, the gradient to oxygen diffusion is set, and the rate of diffusion may become a limiting factor. Lower oxygen availability at the cathode surface slows down the cathode reaction, and so does happen with the anodic reaction to conserve electrons. This could be the reason that the lowest release of electrons happened from the Al-GO nanocomposite anode surface, as is evident from the highest charge transfer resistance ($R_{ct} = 4.74 \times 10^6 \Omega \cdot \text{cm}^2$) [59].

3.4.2. Electrochemical Noise Analysis (ENA)

Pitting mechanisms as a result of some physical and chemical processes can give rise to random low-frequency signals. The potential and/or current fluctuations from these stochastic processes are referred to as electrochemical noise (EN). Since chlorides play a detrimental role in pitting mechanisms, so EN data of Al and their composites were collected in 0.6M NaCl using ZRA mode, where potential is applied between two identical electrodes so that the anodic corrosion process of one electrode tends to shift towards the positively polarized electrode. The collected electrochemical noise (EN) data (Figure 11a,b) were transformed into power spectral density (PSD), from which spectral noise impedance plots were obtained as shown in Figure 11c–f.

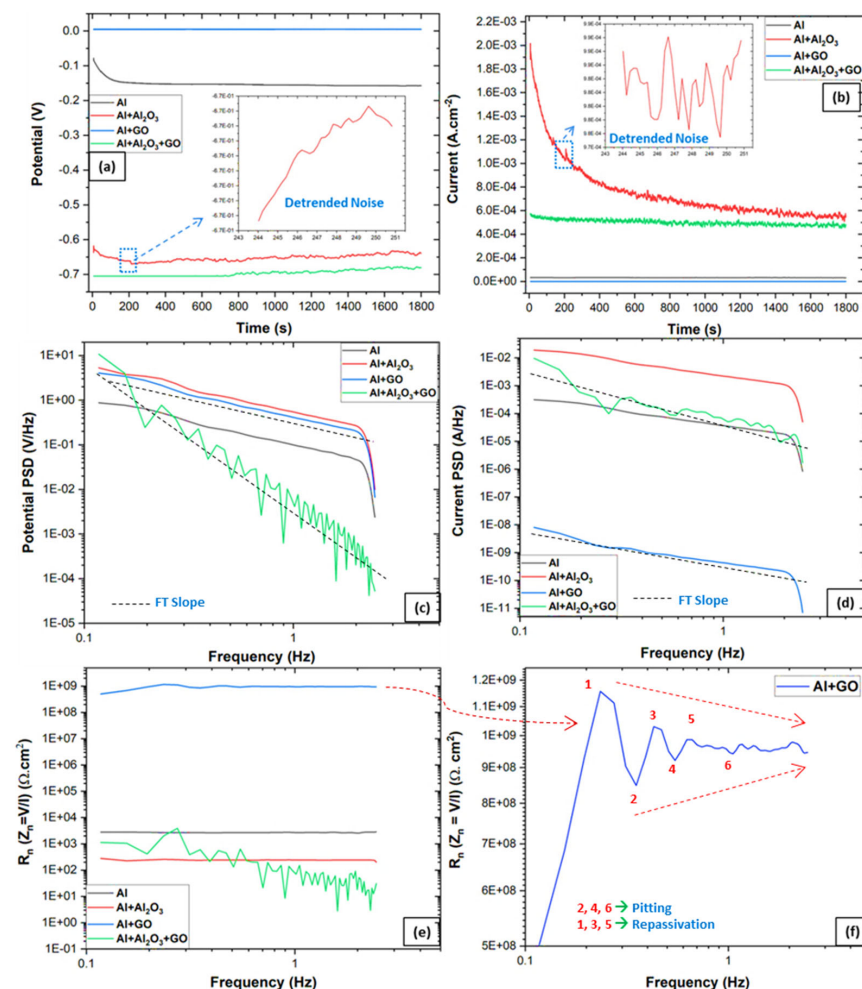


Figure 11. Electrochemical noise analysis (ENA) of Al, Al–10% Al_2O_3 , Al–0.25% GO, A–10% Al_2O_3 –0.25% GO in 0.6 M NaCl. (a) potential time record, (b) current time record, Fast Fourier Transformation (FFT) PSD of- (c) Potential, (d) Current, (e) Resistance (V/I), (f) Resistance (V/I) for Al-0.25% GO.

Electrochemical potential noise (EPN) and electrochemical current noise (ECN) were observed in alumina (Al_2O_3)-containing nanocomposites, as shown in Figure 11a,b. The incorporation of 0.25% GO in pristine Al lowered the mean current density from 1.25×10^{-5} (A/cm^2) to 3.6×10^{-10} (A/cm^2) as shown in Table 6. However, a higher mean ECN (7.5×10^{-4} A/cm^2) was observed with the addition of alumina (Al_2O_3) in the Al matrix. In the frequency domain, a highest –ve slope ($m = -2.4$) of PSD for Al- Al_2O_3 -GO nanocomposite was observed as shown in Figure 11c (Table 6), and it clearly shows the severity of physio-chemical process, which resulted in severe pitting in the presence of chlorides and a similar trend is observed in Figure 11d. However, Al-GO nanocomposite was found resistant to pitting as minimal EPN and ECN were observed with PSD, as shown in Figure 11c,d.

Table 6. Real-time statistics calculated by Gamry ESA 410 analyzer on EPN and ECN data streams in time and frequency domain.

Potential (V)					Fourier Transformation		
Sample	Mean	RMS	Skewness	Kurtosis	Resistance ($\Omega.\text{cm}^2$)	Slope (m)	y-Intercept
Al	-2.9×10^{-2}	5.2×10^{-2}	-5.1×10^{-1}	-1.7×10^0	2.8×10^3	-1.1×10^0	-1.3×10^0
Al + Al_2O_3	3.4×10^{-1}	4.1×10^{-1}	-4.8×10^{-1}	-1.8×10^0	2.4×10^2	-3.2×10^{-1}	-1.3×10^0
Al + GO	-1.4×10^{-1}	2.2×10^{-1}	-2.1×10^{-1}	-1.9×10^0	9.7×10^8	-4.4×10^{-1}	-1.3×10^0
Al + Al_2O_3 + GO	-7.0×10^{-1}	7.0×10^{-1}	1.5×10^{-2}	-1.1×10^0	4.6×10^{-2}	-2.4×10^0	-3.4×10^0
Current (A/cm^2)					Fourier Transformation		
Sample	Mean	RMS	Skewness	Kurtosis	Resistance ($\Omega.\text{cm}^2$)	Slope (m)	y-Intercept
Al	1.2×10^{-5}	2.0×10^{-5}	5.2×10^{-1}	-1.7×10^0	2.8×10^3	-4.5×10^0	-1.3×10^0
Al + Al_2O_3	7.5×10^{-4}	1.2×10^{-3}	5.0×10^{-1}	-1.7×10^0	2.4×10^2	-2.7×10^0	-1.3×10^0
Al + GO	3.6×10^{-10}	4.0×10^{-10}	-2.1×10^{-1}	-1.9×10^0	9.7×10^8	-9.4×10^0	-1.3×10^0
Al + Al_2O_3 + GO	6.1×10^{-4}	6.1×10^{-4}	-3.8×10^{-1}	-1.6×10^0	4.6×10^{-2}	-4.2×10^0	-1.8×10^0

In the same frequency domain, the ratio of potential to current PSD provided spectral noise impedance plots and is given in Figure 11e,f. The highest average spectral noise impedance of 9.7×10^8 ($\Omega.\text{cm}^2$) with a stable EN was achieved for Al-GO nanocomposite, whereas the lowest average spectral noise impedance of 4.6×10^{-2} ($\Omega.\text{cm}^2$) was achieved for Al- Al_2O_3 -GO nanocomposite, as shown in Figure 11e and Table 6, respectively. The magnified spectral noise impedance plot of Al-GO is separately shown in Figure 11f, revealing that the addition of 0.25% GO in Al matrix provided a significantly higher metastable pitting resistance.

3.4.3. Potentiodynamic Polarization (PDP)

Potentiodynamic polarization (PDP) tests were conducted in 0.1 M, 0.3 M, 0.6 M NaCl, and 0.5 M H_2SO_4 at room temperature, and results are presented in Figure 12a–d. It can be seen in Figure 12a that, in 0.1 M NaCl, metallic Al provided a current density of 3.87×10^{-7} (A/cm^2); however, the reinforcement of alumina (Al_2O_3) increased the current density to 8.75×10^{-7} (A/cm^2). Surprisingly, the induction of just 0.25% graphene oxide (GO) to the metallic Al remarkably lowered the current density to 1.91×10^{-9} (A/cm^2). Nevertheless, the highest current density of 2.46×10^{-6} (A/cm^2) was observed for Al_2O_3 -GO-reinforced hybrid Al-MMCs. It is obvious from Figure 12a that metallic Al formed a protective passive film at a current density (i_{pass}) of 8×10^{-7} (A/cm^2); however, Al_2O_3 reinforcement degraded the passive film-forming ability of the composite due to the presence of ceramic particles [60,61]. Hence, a partially protected surface remained electrochemically active all the time, causing a continuous increase in current density. On the other side, passive

film current density of GO-reinforced Al-MMC was also observed to be stable like that of metallic Al, indicating the formation of a stable protective film.

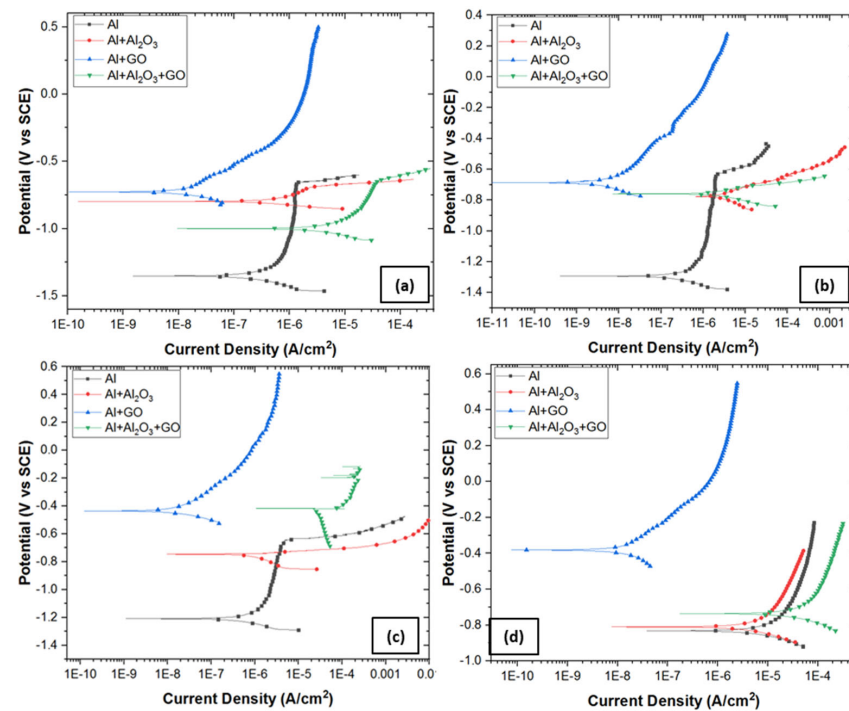


Figure 12. PDP plots of Al, Al–10% Al_2O_3 , Al–0.25% GO, and Al–10% Al_2O_3 –0.25% GO nanocomposites tested in (a) 0.1 M NaCl, (b) 0.3 M NaCl, (c) 0.6 M NaCl, (d) 0.5 M H_2SO_4 electrolytes at room temperature.

An increase in Cl concentration of the test solution increased the corrosion rate (Figure 12b,c); however, Al-GO nanocomposite was least affected, as its corrosion rate was the lowest among all the composites. Similarly, unlike the other composites, reinforcement of just 0.25% GO in Al-GO nanocomposite was found equally effective against the acidic solution (H_2SO_4), as shown in Figure 12d. The corrosion rates of the composites are summarized in Figure 13.

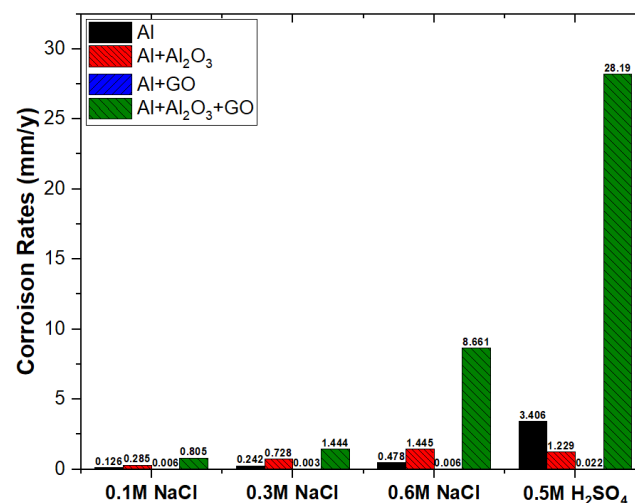


Figure 13. Corrosion rates comparison of Al, Al–10% Al_2O_3 , Al–0.25% GO, and Al–10% Al_2O_3 –0.25% GO nanocomposites samples in different test solutions.

4. Post-Corrosion Analysis

4.1. Increased Corrosion Resistance of GO-Reinforced Al-MMC

Unlike alumina (Al_2O_3) or hybrid (Al_2O_3 -GO)-reinforced Al-MMC, the 0.25% GO reinforcement improved the corrosion resistance significantly. It can be seen from Figure 13 that the lowest corrosion rate was achieved against GO-reinforced Al-MMC in comparison to Al, Al- Al_2O_3 , and Al- Al_2O_3 -GO nanocomposites. Improved corrosion resistance due to the reinforcement of 0.25% GO could be observed from the post-corrosion SEM analysis given in Figure 14. In the case of pure Al, its thin protective oxide film could be attacked and broken down in the first place by the chlorides (Cl^-) or sulfates (SO_4^{2-}) ions. Due to its porous structure, Al could not hinder the diffusion of corrosive species like Cl^- or SO_4^{2-} , and possibly a straight path might be offered to them in reaching the metal–film interface, thus an aggressive pitting could start as shown schematically in Figure 15a. As a result, the dissolution of Al could start forming $\text{Al}(\text{OH})_3$ product.

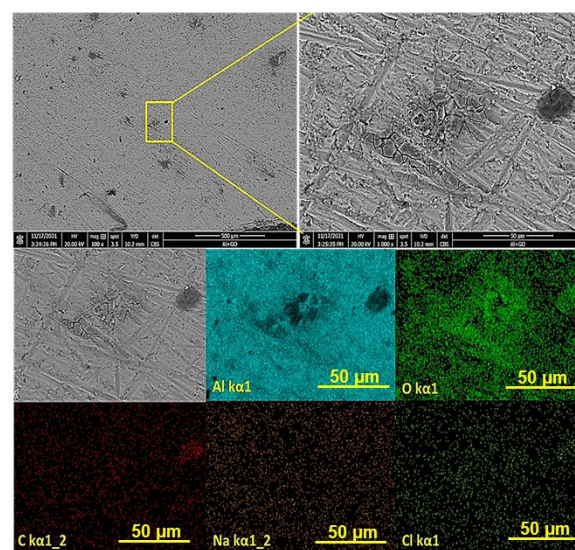


Figure 14. SEM images and EDS mapping of the post-corrosion surface morphology of Al-0.25% GO nanocomposite tested in 0.6 M NaCl.

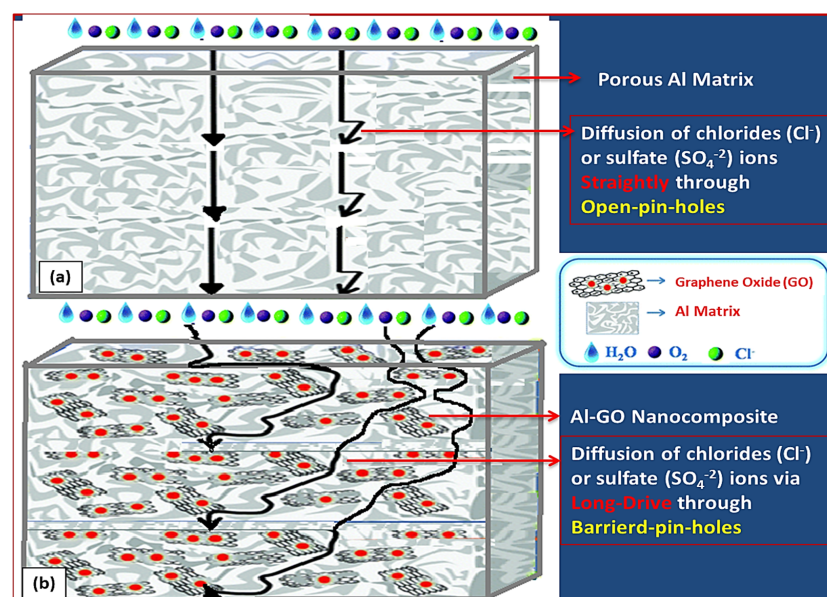


Figure 15. Schematic illustration of chlorides or sulfate ions diffusion mechanism penetrating (a) Al matrix, (b) graphene oxide (GO)-reinforced Al MMCs.

Contrary to pure Al, reinforcement of 0.25% GO in the Al matrix assisted in gaining film thickness to a significant extent, and so increased corrosion resistance was observed. For instance, in Table 4, the charge transfer resistance of 0.25% GO-reinforced Al MMC in 0.6M NaCl was improved 19 times as the double layer thickness was increased from 2.85 nm to 14.4 nm, which is nearly 5 times higher in comparison to the pure Al. Another reason behind the robust corrosion resistance performance of 0.25% GO-reinforced Al MMC is the formation of the thicker oxide film over its surface. In Table 4, it can be seen that an oxide film of 22.08 nm thickness was observed on GO-reinforced Al MMC, which was 2.5 times thicker than that of pure Al (8.81 nm). This reveals that GO in the Al matrix helped in the formation and growth of a more protective and stable film.

GO also assisted in blocking the porous sites available in pure Al and made it difficult for the diffusion of (Cl^-) or (SO_4^{2-}) ions to resist the pitting mechanism. Blockage of the discussed porous sites due to the presence of a honeycomb-like structure of graphene oxide (GO) at the intergranular regions of the Al matrix could be seen from the fractured surface analysis of the Al-GO nanocomposite in Figure 16 (and schematically in Figure 15b). Subsequent to pores blocking, very few openings might have remained active, and thus corrosive species (Cl^- and SO_4^{2-}) were forced to cover a long path. By this mechanism, diffusion could only be possible through the barrier-pin-holes which also increased the penetration time. Resistance to pitting with the presence of GO in the Al matrix could be validated from the electrochemical potential noise (EPN) and electrochemical current noise (ECN) in Figure 11c,d, and from the impedance noise spectrum in Figure 11f, which confirms that Al-GO nanocomposite was found to be extremely resistant to metastable pitting in the presence of chlorides.

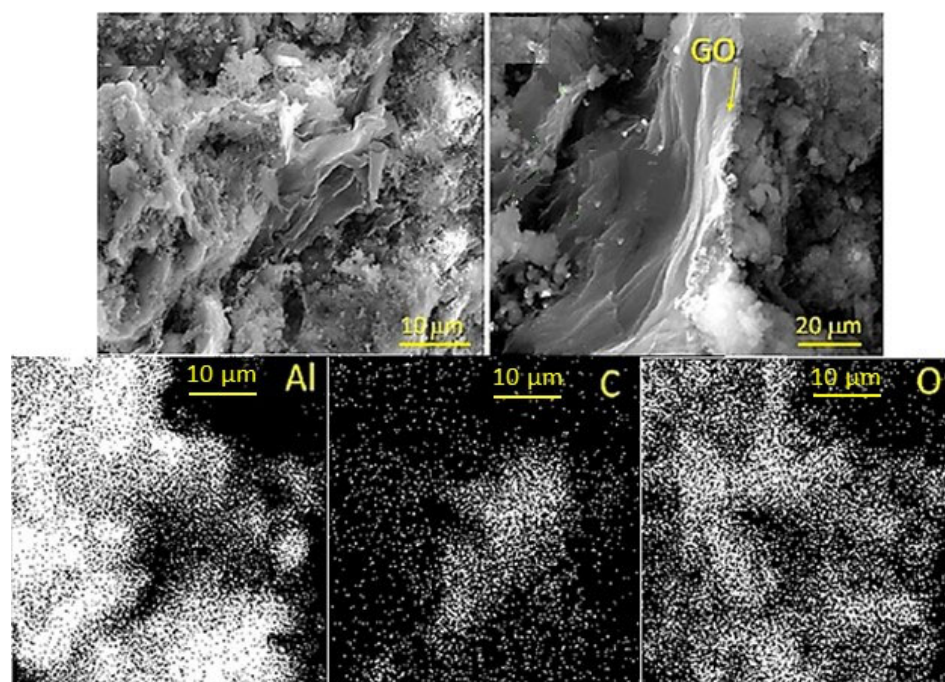


Figure 16. SEM images and EDS mapping of the fractured Al-0.25% GO nanocomposite surface reveal the distribution of GO at the grain boundaries of the Al matrix.

Moreover, the improved wettability (adhesion) in between Al matrix and GO reinforcement is evident from the higher contact angle measurement of 102.8° at Al-0.25% GO nanocomposite in Figure 7, which confirms its hydrophobic nature. Thus, the lower surface energy is reflected by the hydrophobic behavior of Al-0.25% GO nanocomposite, which signifies that Al and GO were well adhered to each other. Subsequently, minimum pore opening sites could be available for penetration of the corrosive ions (Cl^- or SO_4^{2-}), thus leading to the improved corrosion resistance. On the other side, Raman spectra in Figure 3b

confirm that low intensity of D- and G-bands were recorded against GO/ Al_2O_3 -reinforced Al-MMC in comparison to that of GO-reinforced Al-MMC. The intensities ratio (ID/IG) of GO/ Al_2O_3 -reinforced Al-MMC was also found to be lower than that of GO-reinforced Al-MMC. The relationship between ID/IG ratio helps in quantifying the defects present in the carbon structure [62], which in other words is the extent of functionalization. The higher ID/IG ratio of GO is attributed to the presence of oxygenated functional groups linked to the carbon structure [61]. Thus, $(\text{ID/IG})_{\text{GO}/\text{Al}_2\text{O}_3} < (\text{ID/IG})_{\text{GO}}$ implies that oxygenated functional groups in GO could have decreased the mean crystallite size of the graphene network by forming new graphitic domains [63]. Consequently, this may have set the basis for agglomeration-free distribution of GO throughout the Al-matrix, and hence chloride or sulfate diffusion was restricted due to the blockage of porous sites, leading to achieving efficient corrosion resistance.

4.2. Surface Topography

Post-corrosion surface topography of Al and its composites was conducted using an optical profilometer as shown in Figure 17. For better understanding, 3D profiling of the total groove diameter was collected by stitching method.

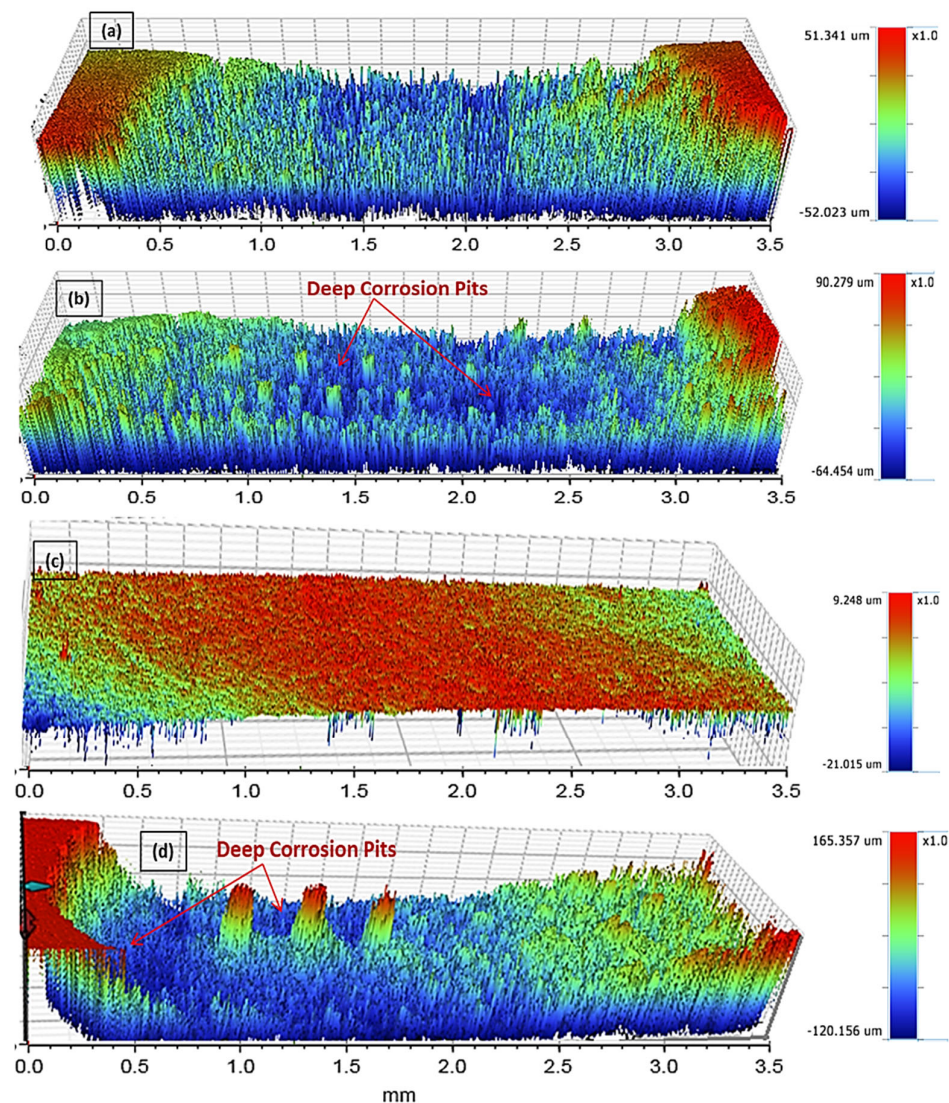


Figure 17. The 3D-optical surface profiling of post corrosion grooves developed on (a) Al, (b) Al- Al_2O_3 , (c) Al-GO, (d) Al- Al_2O_3 -GO (hybrid-) nanocomposites tested in 0.6 M NaCl.

Surface profiling inside the corrosion groove of pure Al in Figure 17a indicates an average surface roughness (R_a) of 16.4 μm and maximum pitting depth of 52 μm (Figure 18). Reinforcement of Al-matrix with Al_2O_3 increased the surface roughness (R_a) to 17.8 μm and pitting depth was extended to 64.5 μm (Figure 17b). This is in true agreement with the electrochemical results, where it was observed that Al_2O_3 reinforcement to Al-matrix increased the corrosion rate because of the poor wettability between the matrix and the reinforcement. Similarly, the combined Al_2O_3 -GO reinforcement in the Al-matrix resulted in an increased surface roughness (R_a) of 48.4 μm , which is comparatively 3 times higher than that of Al and Al_2O_3 -reinforced Al-MMC due to aggressive corrosion. A maximum pitting depth of 120 μm was observed, which is also nearly twice compared to its discussed counterparts. Aggressive pitting mechanism was found in agreement with the EPN, ECN in Figure 11c,d, and spectral noise impedance in Figure 11e. On the other hand, the corroded surface of GO-reinforced Al-MMC provided clear evidence of the absence of any groove formation in Figure 17c. Variation in surface roughness was noted to be very narrow, and average surface roughness (R_a) of 0.5 μm was recorded. A thorough analysis of the 3D surface profile indicated that GO-reinforced Al-MMC was overall found to be pitting resistant. Unlike its counterparts, no severe pits were noticed, except in some localized areas where minuscule pits were seen. Thanks to the honeycomb-like structure of GO, which hindered the diffusion of ionic species by its agglomeration-free distribution at the intergranular spaces of the Al matrix in achieving the robust electrochemical performance against GO-reinforced Al-MMC.

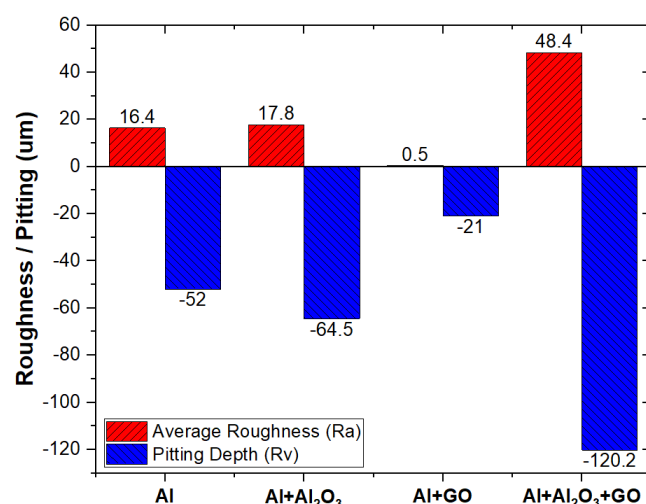


Figure 18. Graphical illustration of average surface roughness and pitting depth obtained by optical profilometer of aluminum and its composites.

5. Conclusions

The Al matrix was reinforced with 10 V% Al_2O_3 and 0.25% GO to manufacture Al- Al_2O_3 , Al-GO, and Al_2O_3 -GO (hybrid-) nanocomposites using spark plasma sintering (SPS) technique. Characterization of the nanocomposites was carried out through XRD and Raman spectra, whereas their morphological, structural, and elemental analysis was conducted through FE-SEM and EDS. Electrochemical studies were conducted using EIS, EPN, ECN, and PDP techniques in different test solutions containing chloride or sulfate. Surface topography was conducted using an optical profilometer. Based on the experimental data, the following conclusions can be drawn;

- (1) The metallic Al phase was noted to be segregated from the composite phase of Al- Al_2O_3 due to the poor wettability, thus forming the porous interface regions.
- (2) The possible galvanic coupling effect between Al matrix and Al_2O_3 reinforcement became dominant with the diffusion of chlorides (Cl^-) or sulfates (SO_4^{2-}) through

the available open sites, leading to aggressive pitting and dealuminization of Al₂O₃-reinforced Al MMC.

- (3) Absence of a double layer and the formation of a very thin oxide film over Al₂O₃-reinforced nanocomposite provided low charge transfer resistance, and thus the corrosion rate in 0.6 M NaCl was increased from 0.48 to 1.45 mm/y.
- (4) Contrarily, reinforcement of just 0.25% graphene oxide (GO) in the Al matrix did not cause any agglomeration in between intergranular regions of the Al matrix. The honeycomb-like structure of GO blocked the open sites of the Al matrix by hindering the chloride (Cl[−]) or sulfate (SO₄^{−2}) diffusion, thus compelling them to take a long drive through the available pin-holes.
- (5) Significantly thickened double layer and oxide film formation over GO-reinforced Al MMC provided a robust charge transfer resistance, and thus, the corrosion rate in 0.6 M NaCl was decreased from 0.48 to 0.006 mm/y.
- (6) The combined reinforcement of Al₂O₃ and GO in the Al matrix (hybrid MMC) provided poor wettability in between the Al matrix and Al₂O₃-GO reinforcements thus, the formation of voids allowed the aggressive diffusion of corrosive species through the open sites, which results in an increased corrosion rate from 0.48 to 8.66 mm/y.
- (7) Electrochemical noise (EN) analysis revealed that highest and lowest pitting resistances were achieved for the Al-GO and Al-Al₂O₃-GO nanocomposites, respectively.
- (8) Optical profilometry results confirmed that GO-reinforced Al-MMC was found to be pitting resistant, unlike its counterparts, as the lowest surface roughness (Ra) of 0.5 μm was observed for GO-reinforced Al-MMC.

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