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Enhancing the corrosion resistance of aluminum by graphene oxide and reduced graphene oxide films

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Abstract
This study is carried out with the goal of improving the corrosion resistance of aluminum in a saline solution through coating with graphene oxide (GO) and reduced GO (ERGO). The GO layer was applied on an aluminum substrate and then electrochemically reduced by cyclic voltammetry in 0.01 M K$_2$HPO$_4$ solution to form a reduced graphene oxide layer. The surface morphology, structure, and crystallinity of the coated materials were characterized using scanning electron microscope (SEM), x-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy techniques. To study the electrochemical corrosion behavior of the coated aluminum substrate, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods were performed in 3.5 wt% NaCl solution. The results showed that both GO and ERGO films uniformly covered the surface of the aluminum substrates with layered structures. A noteworthy elimination of oxygen-containing functional groups (OFGs) occurred upon the electrochemical reduction of the film, yielding a highly-reduced ERGO layer on the substrate. Furthermore, the electrochemical reduction process significantly increased the thickness of the GO coating. The electrochemical test results exhibited that both GO, and ERGO layers improved the corrosion resistance of the bare aluminum substrate. However, electrochemical reduction of the GO layer had adverse effects on the corrosion barrier properties of the GO coating.

1. Introduction
Graphene is a two-dimensional material which consists of interconnected hybrid sp$^2$ carbon atoms laid out in a hexagonal pattern. In monolayer graphene, each carbon atom is connected to three other atoms via covalent bonds since the existing bonds between graphene layers are weak van der Waals bonds [1]. Due to this unique structure, graphene possesses a combination of exceptional properties including, low density, high strength and modulus of elasticity, good resistance to deformation, remarkable transparency, excellent electrical and thermal conductivities, bacterial toxicity, resistance to gas permeability, and corrosion resistance which grow its applications in different fields [2, 3]. The synthesis of graphene can be accomplished via several approaches including, chemical vapor deposition (CVD), micro-mechanical exfoliation of graphite, epitaxial growth, organic synthesis, and chemical methods [4]. The most common route for the large-scale synthesis of graphene is based on the exfoliation of graphite in which the common principle is to eliminate the bond between the graphene layers in the graphite and to separate them to achieve single-layered graphene [5]. In the chemical exfoliation, first, graphite is intensely oxidized in the presence of strong acids and oxidants mainly through Hummers, Brodie, and Staudenmeier methods to form graphite oxide. During the oxidation stage, the interlayer spacing of graphite is increased by intercalation of oxygen-containing functional groups (OFGs) on the main surface and the edge of layers, thereby the van der Waals forces are weakened, and the exfoliation is facilitated [6]. Using ultrasonic waves or intense mixing for an extended period, can fully exfoliate graphite oxide and result in a colloid suspension of graphene oxide (GO) sheets. Finally, for the restoration of the graphene structure and
removal of the OFGs, GO should be reduced using thermal, chemical, electrochemical, or photocatalytic reduction methods [7].

Aluminum is an active metal with a remarkable tendency to react with the environment. That is to say, aluminum surface is rapidly covered with a thin oxide layer when exposes to the air, which protects the metal from the subsequent corrosion attack. Nevertheless, when aluminum is placed in proximity to oxygen or corrosive media like sea-water, or even undergoes thermomechanical treatment, various types of corrosion, including atmospheric corrosion, local corrosion especially pitting and intergranular corrosion, stress corrosion cracking, and fatigue cracking can occur [8].

Recently, graphene has been proposed as an effective coating for preventing metal from corrosion due to its non-toxicity, chemical inertness, impermeability to chemical ions and gas molecules, and environmental friendly [9, 10]. Prasai et al [11] reported that the CVD-coated copper with a single layer of graphene corrodes seven times slower than the uncoated copper in a Na2SO4 solution. The evaluation of the corrosion current of CVD-grown graphene on the 304 stainless steel in a 3.5 wt% saline, indicated fivefold improvement relative to the corrosion current of the uncovered stainless steel [12]. Lih et al [13] deposited GO on the surface of a copper substrate through electrophoretic deposition method, and then reduced the film using electrochemical reduction technique. The corrosion test results in a NaCl solution indicated that the corrosion resistance of the metallic substrate was significantly enhanced in the presence of reduced GO (rGO) coating. Singhbabu et al [14] coated steel plates with oil-based GO through dip coating method followed by curing at 350 °C, and stated that the corrosion rate of the bare steel in the brine (3.5% NaCl) decreased about 10000 times in the presence of GO coating. It was also affirmed by Liu et al [10] that the corrosion resistance of aluminum substrate coated by GO through dip coating in a NaCl solution was improved about threefold in comparison to the uncoated aluminum. Rahimi et al [15] investigated the changes in the corrosion current density of electroplated nickel-graphene composite coating on the copper substrate at different temperatures. Their results indicated that this coating exhibited desirable corrosion resistance up to 50 °C, but with further increase of temperature, the corrosion resistance was lowered.

These studies indicated that graphene and its derivatives are promising materials for protection of metals from corrosion in harsh conditions, but it is not clear that which one of them, i.e., GO or rGO/graphene, shows higher barrier performance in a corrosive media. Therefore, in this work, the surfaces of aluminum were coated by GO to improve the corrosion resistance of the substrate. The produced film was then reduced through electrochemical reduction method. The effectiveness of GO or electrochemically-reduced GO (ERGO) coating on the aluminum substrate against corrosion in a 3.5%M NaCl solution was examined.

2. Material and methods

0.5 mm thickness aluminum sheets were first cut into 10 mm × 10 mm square pieces and then ground with SiC sandpapers. For cleaning and removing natural oxide, the aluminum samples were immersed in a 0.5 M NaOH solution at 50 °C for 40 s and then in a 30% HNO3 solution for 40 s. All the samples were washed with distilled water and dried at ambient temperature.

The GO colloidal suspension with a concentration of 5 mg ml−1 was purchased from API Technology Pioneers Co. (Iran). After ultrasonication of the GO colloidal suspension for 10 min, 0.1 ml of the suspension was drop-casted on each aluminum sample and kept for 24 h at ambient temperature for drying. The reduction of GO films was carried out via electrochemical reduction method. To this end, cyclic voltammetry (CV) was performed in 0.01 M K2HPO4 solution in a standard three-electrode cell with the Saturated Calomel Electrode (SCE) and a platinum sheet as the reference and counter electrodes, respectively. CV scans were recorded for 30 cycles using an Origa flex 01 A galvanostat/potentiostat.

The morphology of GO powder and GO/ERGO coatings was observed by a LEO 440i scanning electron microscope (SEM). X-ray diffraction (XRD) analysis was performed using a STOE STADI Diffractometer with Cu Kα, radiation source. A Bruker Tensor 27 was utilized for Fourier transformation infrared spectroscopy (FTIR) of the samples. The Raman measurements with the excitation laser of 532 nm were performed using a Teksan (Tekram P50COR10) Raman microscope.

Electrochemical experiments were performed using an Origa flex 01 A potentiostat in a three-electrode glass cell. Each of the samples was immersed in a 3.5% NaCl solution for one h to reach the stable open-circuit potential (OCP). The Tafel corrosion test was performed in the potential range from −250 mV to +250 mV versus SCE with the scan rate of 0.5 mV s−1. Electrochemical impedance spectroscopy (EIS) measurements were carried out from an initial frequency of 100 kHz to a final frequency of 100 mHz through an AC sine wave. The Impedance data were analyzed using Zview 2 software.
3. Results and discussion

3.1. Electrochemical reduction of GO

It is known that the reduction of OFGs from GO can be attained through applying a high negative potential [16]. The GO film was electrochemically reduced using potential cycling in K$_2$HPO$_4$ solution from 0 to $-1.5$ V versus Hg/HgO at a scan rate of 50 mV s$^{-1}$. Figure 1 shows the cyclic voltammogram of the GO film during the electrochemical reduction process from the 1st to 30th cycle. The high reduction current starting at about $-0.9$ V is caused by electrochemical reduction of OFGs from the surface of GO [17, 18]. Other redox peaks approximately appeared at $-0.6$ V can be attributed to the activity of OFGs as well [18, 19]. As can be observed in figure 1, the current of redox peaks first increases and then decreases (to disappear) as the potential cycling proceeds. After 25 scans, the CV curves were stabilized representing that the reduction of GO to ERGO was accomplished.

The exact mechanism of electrochemical reduction of GO is still unclear. One possible mechanism proposed by Zhou et al [20] can be expressed by the following reaction:

\[
\text{GO} + \text{aH}^+ + \text{be}^- \rightarrow \text{ERGO} + \text{cH}_2\text{O}
\] (1)

As GO sheets are coated on the surface of Al substrate, OFGs are absorbed on the Al atoms. The fast electron transportation between the GO film and the surface of working electrode is essential for the electrochemical reduction of GO. Due to the high electrical conductivity of the Al substrate, electrons can be quickly transferred to the reaction sites. Gue et al [21] have shown that more OFGs can be removed on copper electrode (conductive) in comparison with glass carbon electrode (non-conductive) during the electrochemical reduction of GO nanosheets. On the other hand, the ionization of water molecules to hydrogen and hydroxyl ions is taken place during the electrochemical process [22]. According to the reaction (1), hydrogen ions from the aqueous electrolyte are critical in the electrochemical process.

3.2. Surface morphology observations

A SEM micrograph of GO sheets after freeze-drying of the colloidal suspension is shown in figure 2. It is obvious that the GO sheets are thin and wrinkled. Figure 3 illustrates the observed SEM images of GO and ERGO films. It can be seen that both GO, and ERGO films uniformly covered the surface of the aluminum substrate (figures 3(a), (b)). Also, the coatings possess the wrinkled structure. The ERGO film shows fewer wrinkles and smoother surface than the GO film. The examination of the cross-section of the fractured edges of the coatings indicated a layered structure (figures 3(c), (d)). Moreover, the GO film exfoliated during the electrochemical reduction. During the electrochemical reduction, electrons transport from the aluminum substrate surface to both GO sheets and hydrogen ions in the K$_2$HPO$_4$ solution, forming ERGO and H$_2$ gas, respectively. The hydrogen gas bubbles can be clearly seen in figure 3(d). The generated bubbles at the ERGO film/electrode interface increase the interlayer spacing of ERGO layers and promote the film delamination [23].
3.3. Chemical structure and phase analyses
The structural changes after the coating of GO suspension on the aluminum substrate and further electrochemical reduction were examined using Raman spectroscopy (figure 4). The Raman spectrum of the samples displays two intense peaks at \( \sim 1570 \text{ cm}^{-1} \) (G band) and \( \sim 1350 \text{ cm}^{-1} \) (D band). The G peak is due to the first-order scattering from the doubly degenerate \( E_{2g} \) phonon modes of graphite in the Brillouin zone center and the bond stretching of sp\(^2\) carbon pairs in both rings and chains [24]. The G band of the ERGO layer was shifted to a lower frequency than that of the GO film, exhibiting the successful reduction of GO after the electrochemical reduction method [25]. On the other hand, the D peak originating from the breathing mode of aromatic rings resulted from the structural imperfections [26]. It is clear that the intensities of D- and G-bands for films were
raised in comparison to the suspension. The integrated intensity ratio of the D-band to the G-band ($I_{D}/I_{G}$) points out the oxidation degree and the size of sp$^2$ ring clusters in a sp$^3$/sp$^2$ hybrid network of carbon atoms [24]. Generally, $I_{D}/I_{G}$ increases in the wake of reduction of GO owing to increasing the number of imperfections and disorders which comes out from the connection of OFGs on the graphene surfaces during the oxidation and remaining of the binding sites and vacancies after reduction [27]. The $I_{D}/I_{G}$ for the GO suspension, GO layer, and ERGO film was determined to be 0.9, 1, and 1.37, respectively, confirming the partial reduction of GO upon coating and the efficient elimination of OFGs in the sake of the electrochemical reduction. This observation is in agreement with several previously-reported investigations [28–30]. The high $I_{D}/I_{G}$ value for the ERGO layer was related to the formation of numerous smaller sp$^2$ carbon lattice clusters upon the electrochemical reduction [28]. Two broad peaks at ∼2645 cm$^{-1}$ (2D band) and ∼2878 cm$^{-1}$ (D + G band) were also detected in the Raman spectra. The 2D peak is attributed to double resonance transitions resulting in the production of two phonons with opposite momentum [24]. This peak is an indicative of the number of graphene layers; the high $I_{2D}/I_{G}$ discloses the low number of graphene layers. Here, $I_{2D}/I_{G}$ was enlarged after electrochemical reduction, revealing a decline in the stacking of graphene layers on each other. The combination mode (D + G band) is caused by the presence of disorder in the system [31]. The D + G band in GO and ERGO films is more intense than the GO suspension owing to the higher intensity of D- and G- bands.

The changes of the chemical structure of coatings regarding OFGs were investigated using FTIR spectroscopy (figure 5). The broad signal between 3200 cm$^{-1}$ and 3700 cm$^{-1}$ is attributed to O–H stretching vibration and adsorbed water molecules. The intensity of O–H bond was decreased, and its position was transferred to the lower wavenumbers in the case of GO and ERGO coatings in comparison to that of the GO suspension. More decline in the intensity of O–H signal in the ERGO layer is also noticed. Two weak peaks at about 2926 cm$^{-1}$ and 2866 cm$^{-1}$ in the FTIR spectrum of the coatings have originated from asymmetric and symmetric vibrations of CH$\_2$ groups, respectively [3]. The peak at approximately 1698 cm$^{-1}$ is assigned to C–O stretching vibration [32]. The peaks which appeared in the range of 1641–1657 cm$^{-1}$ and 1535–1556 cm$^{-1}$ are attributed to the C=C stretching vibration [33]. The peak at 1047 cm$^{-1}$ in the FTIR spectrum of the coatings belongs to the C–O stretching vibration. The intensity of C–O bond was weakened after the electrochemical reduction. The signal that is seen at 671 cm$^{-1}$ is due to the C–H bending vibration [34]. The intensity of this peak was decreased after coating.

According to the Raman and FTIR spectroscopy results, it can be deduced that partial reduction of some OFGs occurred after the coating of GO on the aluminum substrate. A similar result has been previously reported by Liu et al [10]. The partial reduction of GO sheets on the surfaces of aluminum powder particles has been stated as well [32, 35]. The mechanism of the partial reduction of GO can be explained as follows. In an aqueous solution, the GO sheets are negatively charged due to the functionalization of GO with various OFGs [36]. On the other hand, the surface of the aluminum substrate is ionized to Al$^{3+}$ in contact with the GO aqueous solution. The electrostatic attraction force stimulates the interaction between negatively-charged GO and positively-charged Al, and thus, the electron transfer from the Al/Al$^{3+}$ interface to the GO coating gives rise to the elimination of some OFGs and the partial reduction of GO. Further reduction of partially-reduced GO was

![Figure 4. FTIR spectra of GO colloidal suspension, and GO and ERGO coatings.](image-url)
obtained through the electrochemical reduction process, as realized from figures 4 and 5. It is known that during the electrochemical reduction, the interface charge transfer between the aluminum substrate and the GO coating results in the effective elimination of OFGs and thus the formation of highly-reduced graphene oxide [23].

The XRD patterns of GO and ERGO films in the range of 2θ from 5° to 40° are shown in figure 6. In the XRD pattern of the GO film on the aluminum substrate, the broad peak at 2θ = 11.7° corresponds to (002) plane of GO with the interlayer spacing of 0.76 nm. It should be noted that the presence of aluminum and Al2O3 peaks in this pattern, which is originating from the substrate material, significantly attenuated the (002) peak of GO. To remove the sharp peak of Al, the XRD pattern of the ERGO film was recorded after peeling off the coating from the substrate. After electrochemical reduction, the (002) peak of GO disappeared while a broad and low-intensity peak centered at 2θ = 24° shows up. The appearance of the characteristic peak of graphene in the XRD pattern of the ERGO film again confirms the efficient reduction of GO upon the electrochemical reduction process.
3.4. Corrosion resistance of the coatings

The corrosion resistance of the aluminum substrates coated with GO and ERGO was evaluated and compared with the bare aluminum. Figure 7 displays the electrochemical polarization plots for the coated and uncoated aluminum specimens measured in 3.5% NaCl solution. The calculated corrosion parameters including, corrosion potential, corrosion current density, and corrosion rate are given in Table 1. It can be deduced from Table 1 that both GO and ERGO layers improved the corrosion resistance of the aluminum substrate among which the GO film had superior barrier properties. The calculated $E_{corr}$ value for the aluminum substrate shifted from $-657.07$ mV to $-597.85$ mV (a 10% increase) in the presence of the GO layer, whilst a 15% decrease in the corrosion potential (from $-508.24$ mV to $-597.85$ mV) of the GO layer was observed when it was electrochemically reduced (ERGO layer). In contrast to the corrosion potential, in the presence of the GO layer, the corrosion current density of the aluminum substrate decreased from $2.5 \mu\text{A cm}^{-2}$ to $1.55 \mu\text{A cm}^{-2}$ (a 38% drop) whereas the ERGO deposit increased the $I_{corr}$ to $1.74 \mu\text{A cm}^{-2}$ (an increase of 10% compared to the GO coating). The corrosion rate for the GO-coated aluminum was also 18 $\mu$m per year which was higher than the corresponding value for both the bare substrate (30 $\mu$m per year) and the ERGO-coated aluminum (21 $\mu$m per year).

The corrosion resistance enhancement of aluminum in the presence of a GO and ERGO layer can be attributed to the chemical inertness of GO and ERGO nanosheets deposited on the surface of the aluminum substrate. These layers act as barriers inhibiting the penetration of corrosive electrolyte to the metallic substrate [37]. Therefore, these layers increase the corrosion resistance of aluminum by preventing the direct contact of the substrate and the corrosive electrolyte [38]. Moreover, in our research, the GO coating yielded higher corrosion resistance than the ERGO layer. Superior corrosion resistance of epoxy coating filled with GO than hydrazine-reduced GO has also been reported by Ghauri et al [39]. This observation is probably due to the differences in the structural properties of GO and ERGO coatings, as described in 3.3 section. Since GO possesses a higher amount of OFGs, it has a lower electrical conductivity which cannot provide adequate electrons for the advancement of the corrosion [40]. Also, the OFGs on the GO layer would trap the aggressive Cl$^{-}$ ions within the GO network preventing these ions from reaching the underlying metal [39]. It has also been shown that the ERGO coating has more water uptake and therefore less isolation from NaCl solution than the GO layer [41, 42]. In a saline solution, the corrosive Cl$^{-}$ ions eventually reach the metal/electrolyte interface,

![Figure 7. Potentiodynamic polarization curves for bare Al and Al coated by GO and ERGO.](image)

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<th>Table 1. The calculated corrosion parameters for the Al substrate coated with GO and ERGO.</th>
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<td>$I_{corr}$ ($\mu\text{A cm}^{-2}$)</td>
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<td>$E_{corr}$ (mV)</td>
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and the conductive nature of ERGO layers conduct electrons provided by anodic reactions of the underlying substrate. This will enhance the cathodic reactions to complete the corrosion cycle.

To further support our electrochemical polarization findings and attaining more accurate mechanistic information on the metal/electrolyte and metal/coating interfaces, the electrochemical corrosion behavior of the GO- and ERGO-coated samples was assessed by using a non-destructive EIS technique. Here, the EIS data are presented as Nyquist, and Bode plots. The Nyquist plots (figure 8) display the imaginary part of the impedance versus the real component, whereas the Bode plots (figure 9) shows the logarithm of the impedance modulus $|Z|$ as a function of the logarithm of frequency. It is clear from Nyquist plots (figure 8) that the semicircle diameter for the Al/GO sample is larger than that of the Al/ERGO and the bare aluminum which specifies the superior corrosion resistance of the GO coating. In general, an increase in the semicircle arc radius is normally indicated by an increase in the charge transfer resistance ($R_{ct}$) value which is inversely proportional to the corrosion rate of the system [43]. This is also well correlated with the electrochemical polarization measurements (figure 7). It is pertinent to point out that the occurrence of two single semicircles in the Nyquist plots indicates that the corrosion processes involved two single time-constants probably related to the electrolyte/coating and metal/coating interactions [44]. This observation was further confirmed by the Bode plots which are shown in figure 9. The time-constant, i.e., the semicircle in Nyquist plots, appearing at the high.
frequency represented the solution/coating interface, while the one at low frequency corresponded to the metal/coating interface. In Bode plots, the impedance modulus at the lowest measured frequency (most commonly log Freq = −1 Hz) indicates the sample’s barrier performance [45]. According to the Bode plots shown in figure 9, the Al/GO sample showed a higher impedance modulus than that of the Al/ERGO and the bare aluminum samples. This meant that the GO coating could be served as an effective corrosion barrier layer.

In general, the equivalent circuit modeling is utilized to calculate the electrochemical parameters related to the impedance spectroscopy analysis [46]. In this research, the Nyquist plots were fitted using the circuits shown in figure 10. In this figure, Rs represents the electrolyte resistance between the SCE electrode and the coated or uncoated aluminum substrates, and Rct shows the charge-transfer resistance at the substrate/electrolyte interface. W and C are also used to determine the Warburg impedance element, and the capacitance of the interface, respectively [46, 47]. It can be seen from the fitted results summarized in table 2 that the Rct for Al/ERGO was lower than that of the Al/GO which indicates a higher diffusion of ionic species and charge transfer across the ERGO/solution interface [48]. Moreover, both capacitance values, i.e., the double layer capacitance (Cdl) and the coating capacitance (Ccoat), for the Al/GO sample were lower than those of for the Al/ERGO sample implying the higher resistance of the GO layer against the destructive corrosion phenomenon.

### 4. Conclusions

Graphene oxide suspension was coated on an aluminum substrate and electrochemically reduced by cyclic voltammetry to form a reduced graphene oxide layer. The produced films had layered structure and uniformly covered the surface of the aluminum substrate. As a result of electrochemical reduction, an increase in the thickness of the GO film was observed which was probably due to the accumulation of H2 gas bubbles generated at the ERGO film/electrode interface. According to the Raman and FTIR spectroscopy results, it can be deduced that partial reduction of some OFGs occurred after the coating of GO on the aluminum substrate whilst further structural modifications and removal of OFGs were taken place during the electrochemical reduction of the GO film. The corrosion resistance of bare aluminum substrates in 3.5% NaCl solution was significantly improved after coating with GO and ERGO layers. The electrochemical polarization test results showed that the corrosion current density of the aluminum substrate decreased 38% and 30% through coating with GO and ERGO, respectively. The higher corrosion resistance of GO/ERGO-coated aluminum was also confirmed by Nyquist and Bode plots. However, because of the differences in the conductivity of the layers, the ERGO film indicated inferior corrosion barrier performance than the GO coating.

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