Corrosion inhibition properties of graphene oxide on mild steel in 3.5% NaCl

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Abstract. In this work the corrosion inhibition of mild steel in 3.5% Sodium chloride (NaCl) solution at ambient conditions by Graphene Oxide (GO) has been studied. Graphene oxide was prepared by Modified Hummers Method and characterized by Fourier Transform Infrared spectroscopy (FTIR), UV-Visible spectroscopy (UV-Vis), X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), and Thermo-Gravimetric Analysis (TGA). The electrochemical corrosion behaviour of mild steel has been studied in the absence and presence of GO coatings by Tafel polarization and impedance analyses. The modified electrode has 44.8mV potential shift in the cathodic direction and reduction in current by 41.9 µA (61%). This indicates the strong protection offered by graphene oxide film. The obtained impedance spectra also clearly show that the charge transfer resistance of graphene oxide film is much higher than that of the uncoated steel electrode, demonstrating the strong protection offered by graphene oxide films for mild steel.

Keywords: (Corrosion, Graphene Oxide, Coating, Marine Environment, Electrochemical Impedance Spectroscopy)

1. Introduction

Corrosion of iron and steel is a major worldwide problem. The estimated cost of corrosion in India is ~ Rs. 4.283 trillion (approximately 1% of gross national product) [1]. Corrosion is primarily the formation of ions and oxides due to localized anodic dissolution or passivation, which degrades the material and the structures built from it. Such degradation has significant impact on various industries, environments or products such as petroleum refineries, automobiles, and marine environments. Common corrosion prevention methods include coatings on metal surfaces such as paints, primers, polymer coatings, and films of different substances including metal oxides. These films form passive layers, increase the resistance for charge transfer involved in anodic dissolution of the metals, and thereby provide corrosion protection. The films may be bonded to the metal surface by physisorption or chemisorption.
Graphene is a novel sp\textsuperscript{2}-hybridized form of carbon, with exceptional mechanical, thermal, and electrocatalytic properties. It is typically synthesized from graphite by chemical oxidation [2], or from deposition processes using carbon precursors [3]. Chemical oxidation of graphite results in different oxidized states of graphene, which could be reduced using appropriate reducing agents. Recently, there is an increasing interest in exploring the corrosion resistance properties of graphene and its oxides. Studies have been carried out on corrosion prevention of copper [4,5], mild steel [6], carbon steel [7], stainless steel [8] by various modifications. Modifications studied include those with graphene [9], metal-graphene [10], metal [11], metal oxides [12], polymers [13,14], and polymer-graphene [15,16]. However, to the best of our knowledge, the applicability of graphene oxide films for corrosion protection of mild steel in marine environments has not been studied so far. This study is a preliminary exploration in this direction. Graphene oxide dispersions have been prepared and drop cast into films on well-polished mild steel coupons and their corrosion inhibition properties have been studied electrochemically.

2. Experimental procedure

2.1. Chemicals, instruments and reagents

Sodium chloride (AR, 98%) was procured from Avra chemicals, acetone (AR, 99%) from Fisher Scientific, dimethylformamide (DMF) (99.8%) from Rankem, and used without further modifications. Mild steel coupons were prepared of size in 1mm thickness. All the solutions were prepared from ultrapure water (Millipore water systems). Mild steel coupon was used as the working electrode, Pt wire as the counter electrode and saturated calomel electrode as the reference electrode (SCE).

2.2. Synthesis of graphene oxide

Graphene oxide (GO) was synthesized by an in-house modification of Hummers method [2,17]. Two grams of graphite powder was mixed with 50 ml of 95% sulphuric acid and the mixture was stirred for 30 minutes in an ice bath. To this mixture, 6 g of KMnO\textsubscript{4} was added followed by vigorous stirring for 2 hours. The rate of addition of permanganate was gradually slowed down so as to maintain temperature below 20°C. This mixture was subsequently stirred at room temperature for 8 hours. At this juncture, 100 ml of ultrapure water was slowly added along with the gradual increase of the solution temperature to 98°C. The solution effervesced and its color became yellow, which was then stirred at the same temperature for 12 hours. Finally, 20 ml of the oxidizing agent 30% H\textsubscript{2}O\textsubscript{2} was added. The mixture was rinsed and centrifuged with 5% HCl. It was then repeatedly washed with ultrapure water until the pH became neutral. The wet powder was dried in an oven maintained at 60°C and brown-colored GO powder was synthesized.

2.3. Preparation of GO suspension and GO-modified mild steel electrode

The synthesized GO was dispersed at a concentration of 1 mg/ml in DMF and sonicated for 30 minutes. The mild steel coupon surface (1 cm × 1 cm) was polished with emery sheets from 120 to 2000 grade to obtain mirror finish. The coupons were then wiped with acetone, and the GO dispersion was drop cast, and dried at 80°C for 15 minutes.
3. Results and discussion

3.1. Characterization of graphene oxide

The synthesized GO was characterized by UV-Visible spectroscopy (UV-Vis), Fourier Transform Infrared spectroscopy (FTIR), Field Emission Scanning Electron Microscopy (FESEM), X-ray diffraction (XRD), and Thermogravimetric Analysis (TGA). UV-Vis studies was carried out on a Shimadzu UV 1800 spectrometer, FTIR studies were conducted on a Thermo Nicolet iS10 spectrometer, and SEM analysis was carried out on a Hitachi S-4800 FESEM microscope. XRD studies were carried out using a Bruker D8 Advance diffractometer equipped with Cu anode and a Cu Kα source of the wavelength of 1.5406 Å with the scanning speed of step time = 61.2, and step size = 0.0341526. TGA study was done using TA instruments, SDT Q600 35°C to 800°C at 10°C/minute. Electrochemical experiments were carried out using a workstation (CHI604E, CH instruments).

Figure 1a shows the UV-Vis spectrum of GO, with a strong peak at 226 nm due to ($\pi$-$\pi^*$) transition for C-C aromatic bonds and a peak at 300 nm assigned for n-$\pi^*$ for C=O bonds [18]. Figure 1b shows the FTIR spectrum of GO obtained. It indicates the presence of different functional groups in GO, namely $\text{C} - \text{O}$ stretching (1078 cm$^{-1}$), $\text{C} - \text{C}$ (1127 cm$^{-1}$), $\text{C} - \text{O}$ stretching (1738 cm$^{-1}$), $\text{C}$–$\text{H}$ stretching (2924 cm$^{-1}$) and $\text{O}$–$\text{H}$ stretching (3406 cm$^{-1}$) [18,19].

![Figure 1](image1.png)

**Figure 1.** UV-Visible and FTIR spectra of the synthesized graphene oxide. (a) UV-Vis spectrum, (b) FTIR spectrum.

XRD spectrum shown in Figure 2a clearly indicates a strong and prominent peak at 11.33°, which confirms the presence of GO [20,21] with a corresponding interlayer distance of 7.8 Å. The TGA data in Figure 2b shows 2 to 5% weight loss at 90°to 100°C due to removal of water molecules (moisture) and a significant weight loss (70%) between 190°to 240°C due to the decomposition of oxygen-containing functional groups [22,23,24]. Together with the XRD and FTIR spectra, this result indicates strong oxidation of graphite into oxygenated groups.
Figure 2. X-ray diffraction spectrum and thermogravimetric analysis of graphene oxide. (a) XRD, (b) TGA.

Figure 3a shows the SEM image of graphene oxide indicating flaky nature, randomly folded, few-layered and exfoliated structure. Thus, the synthesized GO has the ability to form thin-film coatings on substrates, which is of interest in the present study. The same sample was also analysed by Energy Dispersive X-ray Spectroscopy (EDS) for its composition. The results, shown in Figure 3b, indicate a carbon-to-oxygen weight ratio of 56.93 to 43.07, and an atomic C/O ratio of 1.76:1. This further shows strong oxidation of graphite by the in-house-modified Hummers method.

Figure 3. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy Analysis of graphene oxide. (a) SEM (b) EDS

3.2. Electrochemical corrosion studies
The corrosion protection property of the synthesized graphene oxide was studied electrochemically. Bare and modified mild steel working electrodes were used for this purpose. Electrochemical impedance spectra were recorded for both bare mild steel and GO-coated mild
steel electrodes in 3.5 wt% NaCl solution, which is representative of marine environment. A Nyquist plot of the impedance, i.e., the real part ($Z'$) of the impedance plotted against the negative value of the imaginary part ($-Z''$), is presented in Figure 4. Qualitatively it is clear that the GO film provides excellent corrosion protection for the underlying substrate by preventing charge transport between the sodium chloride solution and the mild steel substrate. This increase in charge transfer resistance is nearly seven-fold.

![Figure 4. Electrochemical impedance spectra for bare mild steel and GO-modified mild steel electrodes.](image)

To further evaluate the corrosion protection efficiency, the corrosion potentials and currents were evaluated using a Tafel polarisation study, with the results shown in Figure 5. The corrosion current of bare mild steel coupon was ($I_{corr}^0$) 68.75 µA/cm² while that of GO-mild steel coupon ($I_{corr}$) was 26.85 µA/cm², with a 61% corrosion inhibition efficiency. Further evidence of corrosion protection was seen from the nearly 45 mV positive shift of the corrosion potential from –692.5 mV for bare mild steel electrode to –647.4 mV for the GO-coated mild steel electrode. The corrosion inhibition efficiency was calculated from the equation given below.

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Efficiency = \left( \frac{I_{corr}^0 - I_{corr}}{I_{corr}^0} \right) \times 100,
\]
Figure 5. Tafel polarisation study of bare mild steel electrode and GO-modified mild steel electrode, at a scan rate of 1 mV/s.

Table 1. Corrosion potential and corrosion currents from Tafel polarisation study

| S. No | Surface       | $E_{\text{corr}}$ (mV) | $I_{\text{corr}}$ ($\mu$A/cm$^2$) | Corrosion Inhibition Efficiency |
|-------|---------------|-------------------------|----------------------------------|--------------------------------|
| 1     | Bare Mild steel | $-692.5$              | 68.75                            | -                              |
| 2     | GO-Mild steel  | $-647.7$              | 26.85                            | 61%                            |

4. Conclusions
In this study, graphene oxide has been synthesized using an in-house modification of the Hummers Method and was characterized using UV-Visible spectroscopy, FTIR spectroscopy, X-ray diffraction, Thermogravimetric analysis, Scanning Electron Microscopy, and Energy Dispersive X-ray Spectroscopy. Well-exfoliated, few-layers of graphene oxide with a C:O ratio of 1.76:1, with hydroxyl, epoxy, and carbonyl groups was obtained. Thin films of GO were cast on well-polished mild steel electrode surfaces. These films were found to reduce the corrosion of mild steel in 3.5% NaCl significantly, with 61% corrosion inhibition efficiency, and a seven-fold increase in charge transfer resistance. These preliminary results indicate significant promise for the use of graphene oxide as coating material in marine environments.

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