Graphene oxide-based nanomaterial as a coating with anti-corrosion properties

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Abstract. In this work, the synthesis of reduced graphene oxide (rGO) and its incorporation into a hybrid organic-inorganic matrix is reported. The hybrid matrix was obtained from Bisphenol A diglycidyl Ether (DGEBA) and tetraethylorthosilicate (TEOS) as the organic and inorganic phase, respectively, up to have an optimal hybrid matrix (HYBRID) having both good adherence on steel surface and good microhardness. In addition, the rGO was added to HYBRID (HGO). DGEBA, HYBRID and HGO were used as coatings on the surface of different 1018 carbon steel coupons. The coupons were immersed in a H₂SO₄ solution, then electrochemistry impedance spectroscopy (EIS) measurements were carried out. The corrosion current density, the corrosion rates, and the inhibition efficiency were estimated. The results show that the addition of rGO to HYBRID contributes to obtain a coating with good corrosion protective properties.

1. Introduction

In 1859, B. Brodie described the highly laminar structure of graphite using different oxidative methods, obtaining changes in the concentration of oxygen in the material and being one of the pioneers in the background to obtain graphene oxide by oxidative methods. Established the X-ray diffraction technique, in 1916, P. Debye and P. Scherrer reported the structure of the graphite. Using this technique, Kohlschütter and Haenni studied graphite in detail in 1918 and described the properties of what they called graphite oxide paper. In the theoretical field, P. Wallace considered the existence of graphene in 1947. The development of the electron microscope allowed the first few graphite images to be reported in 1948, followed closely by the observation of individual graphene layers by Ruess and Vogt. Due to its great theoretical importance and promising use in various applications, the task of isolating graphene began, and A. Geim and C. Novoselov reported this isolation in 2004, an issue that earned them the Nobel Prize in physics in 2010 [1]. One of the perspectives of graphene from the own vision of the discoverers was its enormous potential in applications as composite materials [2]. It has been found that one of the materials associated with graphene, graphene oxide (GO), is considerably attractive for countless applications coming from the possibility of modulating its physical and chemical properties by controlling the degree of oxidation and the type of functional groups present in its structure [3]. In the field of the science and technology of corrosion, GO has been reported as a promising solution [4,5].
Recently, a methodology for the direct synthesis of reduced graphene oxide (rGO) has been reported [6]. In this work, the synthesis of rGO from the chemical exfoliation of graphite and its incorporation into a hybrid organic-inorganic matrix, is reported. In addition, the rGO-based material was used as a coating layer on carbon steel surfaces, the coated materials were submitted to corrosion tests in a solution of H$_2$SO$_4$ and the corrosion rates were measured. A remarkable improvement in the protection character against corrosion was found.

2. Materials and methods
The synthesis of rGO starts with the addition of 0.4 grams of graphite to a concentrated solution of H$_2$SO$_4$:HNO$_3$ (with a 3:1 volume ratio). This mixture was sonicated for 90 minutes at constant temperature of 60 °C before starting the oxidation process. Then, the temperature was risen to 70 °C in order to avoid compression of the graphene layers. This step improves the action of the oxidizing agents in the insertion of the sulphates between the carbon layers. Subsequently, the oxidation starts with an intense and constant stirring at 100 °C for 24 hours. At the end of the oxidation, the mixture was cooled to room temperature and sonicated for 30 minutes. Finally, a neutralization process is carried out in which the oxidized solution is added in a separating funnel containing 50% of volume of NH$_4$OH at 26% v/v. In order to establish if the final product was rGO, a proper number of analytical techniques were used. However, Raman spectroscopy was a key technique in this purpose. Figure 1 shows the Raman spectra of the synthesized material and the D and G$_{app}$ bands with their deconvolution, where “app” stands for apparent. As reported by King et al. [7], if the conditions $0 < \omega_{D'} - \omega_{G_{app}} < 25$ cm$^{-1}$ and the atomic ratio carbon to oxygen $10 < C/O < 500$ are satisfied, the sample consists in rGO. In our case the difference $\omega_{D'} - \omega_{G_{app}}$ was around 6.0 cm$^{-1}$ even though the C/O ratio was estimated in 4.27 as obtained from SEM-EDX measurements. However, some authors mention that the C/O ratio could be around or be higher than 5 for rGO depending of the synthesis process. All the details on the synthesis and characterization of the product can be found in the reference [6].

![Figure 1. Deconvolution of the D and the G$_{app}$ Raman bands.](image-url)

In order to have a corrosion protective graphene oxide-based material, the rGO was incorporated into an organic-inorganic matrix. Bisphenol A diglycidyl Ether (DGEBA) and tetraethylorthosilicate (TEOS) as the organic and inorganic phase, respectively, were mixed up to have an optimal hybrid matrix (HYBRID). Both the highest adhesion and microhardness were obtained with 70% and 30% w/w of DGEBA and TEOS, respectively. Under these conditions, the microhardness and adhesion on steel for HYBRID, were 0.272 MPa and 4.9 GPa, respectively. Then, 0.01% wt of rGO was added to the HYBRID, and finally, a curing agent, KCA-4303 modified cycloaliphatic amine, was added to accelerate the polymerization processes of the DGEBA.

After submitting the steel coupons to a sandblasting and washing them with acetone procedure, four types of 1018 carbon steel samples were prepared: bare, DGBEA coated, HYBRID coated and HGO coated. Four coupons of each sample were analyzed for statistical studies. A SILAR Coating System
Model HO-TH-03B, was used to produce the protective layers on the steel surfaces. The coating immersing and emerging speeds were 5 mm/s and 3 mm/s, respectively. Figure 2. shows this system and the three different coated coupons. Afterward, the bare coupons and the different coated coupons, were separately submitted to corrosion tests.

![Figure 2. The system used for coating the steel coupons (a) and the steel coated coupons (b).](image)

3. Corrosion tests and results
In order to explore the protective character of the rGO-based material, HGO, and compare with other coating, a set of corrosion tests were performed.

As it was said before, the bare, DEGEBA coated, HYBRID coated and HYBRID matrix plus rGO (HGO) coated were separately immersed in a 0.5M solution of H2SO4 with pH = 1. The samples were labelled as Steel, DGEBA, HYBRID and HGO, respectively. Electrochemical impedance spectroscopy (EIS) measurements were carried out by using a conventional 3-electrode cell configuration. The coated steel specimens were used as the working electrodes. A saturated calomel electrode (SCE) and a platinum mesh were used as reference and counter electrodes, respectively. A potentiostat galvanostat SOLARTRON SI 1260 was utilized. A 10 mV of amplitude signal with a frequency sweeping in the range from 10 mHz to 10 kHz, was used in all measurements. In Figures 3 and 4, the Nyquist plots and the Bode plots are shown, respectively. From both plots, it is evident that the impedance of the electrochemical system is increasing in the order of HGO > HYBRID > DGEBA.

![Figure 3. Nyquist plots for all the samples.](image)

![Figure 4. Bode plots for all the samples.](image)

In order to determine the protective character of the different coatings, the polarization resistance, $R_p$, in each case was estimated from the EIS data. Then, following a simplified model, the corrosion current ($I_{corr}$), the corrosion rate (C.R.) and the inhibition efficiency (I.E.), were calculated.
The calculation model is based on the possibility to obtain $I_{\text{corr}}$ measured in $\mu A/cm^2$ from the so-called Stern-Gerar coefficient, $B$ and the polarization resistance $[8]$. The Equation (1) is

$$I_{\text{corr}} = 10^6 B/R_p$$

where $B$ is related to the anodic and cathodic Tafel coefficients $\beta_a$ and $\beta_c$, respectively by the Equation (2),

$$B = \frac{\beta_a\beta_c}{2.3(\beta_a+\beta_c)}$$

From Equation (1) and Equation (2), the corrosion rate measured in millimetre per year (mm/y) can directly be obtained by the Equation (3),

$$C.\ R. = 3.27 \times 10^{-3}I_{\text{corr}} \frac{W}{\rho}$$

where $W$ and $\rho$ are the equivalent weight and the density of the corroding material, respectively. For 1018 carbon steel these values are 27.92 g/cm³ and 7.87 g/cm³, respectively [8]. In this work, the values for $\beta_a$ and $\beta_c$ were 0.10 V and 0.068 V, respectively, which are consistent with the conditions of our experiments [9].

The inhibition efficiency of the coating was estimated by the Equation (4),

$$\text{I.E.} = (1 - I_{\text{corr}}/I_{\text{corr}}^0) \times 100$$

being $I_{\text{corr}}$ the corrosion current in each material and $I_{\text{corr}}^0$ the corrosion current in the bare steel.

The polarization resistance $R_p$ was estimated from the EIS data, as the respective values of the real part for the impedance at the smallest frequency. Then, From Equation (1) to Equation (4) the calculations were carried out and the results are presented in Table 1. As it can be seen, the results for the corrosion rates are order in the following way: HGO < HYBRID < DGEBA < Steel. Additionally, the inhibition efficiency is higher for HGO and decreases in the order HGO > HYBRID > DGEBA > Steel. These results are consistent with the behavior of the Nyquist and Bode plots (see Figure 3 and Figure 4). It is important to remark, that the conditions of corroding environment in the carried-out experiments were too much aggressive. However, a corrosion rate of 1.04 mm/year obtained with the HGO coating is considerably lower than other recently reported for the same material and in the same corrosive medium [10]. In addition, an I.E. of 97.1% was higher than that of 82% reported by Valle-Quintana et al. using phthalocyanine blue as inhibitor of corrosion of 1018 carbon steel in a solution of 0.5M of H₂SO₄ [11]. The Figueredo’s work [12], shows that the chlorine ions and gaseous molecules of CO₂ accelerate the corrosion on surface steel. In this way, the results of the present research suggest the coating developed with graphene oxide contributes to avoid the contact between Cl⁻ ions and the steel surface, decreasing the corrosion rate. Hence, it is expected that the developed material could be promising as a corrosion protector for steel submitted to a lower corrosive environment as the case of saline solutions.

| Sample | $R_p$ (Ω·cm²) | $I_{\text{corr}}$ (µA/cm²) | C.R. (mm/y) | I.E. (%) |
|--------|---------------|-----------------------------|-------------|---------|
| Steel  | 7.29          | 3124.1                      | 36.2        | 0       |
| DGEBA  | 68.1          | 334.92                      | 3.89        | 89.3    |
| HYBRID | 191           | 119.24                      | 1.38        | 96.2    |
| HGO    | 253           | 90.017                      | 1.04        | 97.1    |
4. Conclusions and perspectives
A type of reduced graphene oxide-based material was synthesized. The material, consisting in reduced graphene oxide incorporated into an organic-inorganic hybrid matrix was used as a coating on steel. Corrosion tests were carried out and the developed material presented an acceptable performance as a corrosion protector for 1018 carbon steel immersed in a 0.5M H₂SO₄ solution.

The protective material continues to be improved and other studies are being carried out in order to have a better performance, both in acidic and saline environment.

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