TUNING THE PROPERTIES OF ELECTROCHEMICALLY REDUCED GRAPHENE OXIDE FILMS FOR THEIR USE AS ANTICORROSIVE-COATINGS FOR STEEL PROTECTION

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Introduction

Due to the excellent barrier properties of graphene-based materials, several studies have focused on their implementation as anticorrosive-coatings, most of them involve the use of reduced graphene oxide (rGO) due to the advantages that it brings for films and coatings assembly. Recent studies have shown the corrosion-promoting, or galvanic, effect of CVD graphene films on certain metals; however, there are no studies addressing if rGO promotes corrosion as CVD grapheme films do.[1] On the other hand, most of the time no accurate justification of the reduction methodology used to remove O-groups in graphene oxide (GO) is given (*i.e.* thermal, chemical, electrochemical). This is of great importance, since different defects are introduced during GO, affecting its performance as anticorrosive coating.[2] In this work, the electrochemically reduced graphene oxide (ErGO) was correctly tuned, *i.e.* chemical properties and defects, for this application. To achieve this, the electrochemical reduction mechanism of GO and the galvanic effect of ErGO films on carbon steel was investigated considering FTIR, Raman spectroscopy, XPS and electrochemical studies. Moreover, an attempt to avoid the galvanic effect by achieving low-conductivity/insulator ErGO-films with alkyne chains is presented.

Materials and Methods

GO films were assembled by drop-coating 100 μL of an aqueous suspension of GO onto carbon steel pieces. Cyclic voltammetry (CV) was used to reduce the GO films. The relationship between the electrolyte composition and the resulting properties of the ErGO films was studied. For this, 0.1 M phosphate buffer solutions of different pH and an organic media free of H^+ were employed. The resulting ErGO-films were characterized by FT-IR, Raman spectroscopy, XPS and electrochemically. The anticorrosive performance was measured electrochemically by linear polarization and electrochemical impedance test, and galvanic current measurements, all of them in a 0.6 M NaCl electrolyte solution.

Results and Discussion

According to our results, H^+ concentration in the electrolyte used to reduce GO has an important role for tailoring the properties of ErGO. The reduction was more efficient (higher C/O ratio) when protons were present in the electrolyte media, pH 2 (Table 1). Even tough lower C/O ratios were achieved when using the organic electrolyte, the characterization showed that the graphitic carbon sp^2 domains were restored to a larger extent, as described by the lower I_D/I_G ratios (Table 1). The results point out that the electrochemical reduction mechanism consists in the removal of O-groups by hydrogenation/hydrolysis reactions. At the same time, hydrogenation reactions of the graphitic sp^2 domains occur, causing a higher abundance of C-C bonds in sp^3 hybridization (Table 1). Due to these defects, and despite of exhibiting higher C/O ratio, the film reduced in acidic electrolyte displayed a lower electron transfer in comparison to the ErGO sample reduced in an organic electrolyte, as described by a larger ΔEp in the ferrocyanide redox-probe (Table 1).[3] These defects play an important role for the performance of an ErGO film as an anticorrosive-coating, since, unlike other defects such as vacancies, introduced by other reduction methods,[3] the former doesn't compromise the capacity of ErGO to work as a barrier. Additionally, due to the hydrogenation of sp^2 domains, the ErGO-pH 2 showed a conductivity of 13 S cm^{-1}, much lower than those obtained through other reduction methodologies.[4] This film was further modified by an electrochemical oxidation (CV) in an electrolytic solution containing 4-pentynoate. The electrochemical oxidation of the carboxylic acid groups formed a radical C atom that bonded covalently with the carbon atoms in a sp^2 configuration in ErGO-pH2. During this process some of the remaining O-groups were removed. The modified film (HrGO) showed a lower conductivity of 1.3 S cm^{-1} and an increased hydrophobicity. As anticorrosive coatings, average anodic currents of 3.17, 0.12 and 0.03 mA cm^{-2} were measured for the bare steel, ErGO-pH2 and HrGO coated pieces, respectively. The galvanic current measurements showed that both films do not have a corrosion-promoting effect on the steel. The latter was attributed to the low conductivity of both films, hindering the electric contact between the steel and the coating, which is one of the necessary conditions for the occurrence of galvanic corrosion.

Table 1. Different parameters obtained from XPS, Raman and electrochemical characterization.

Sample	C=C sp^2 abundance (%)	C-C sp^3 abundance (%)	C-O abundance (%)	C=O abundance (%)	O-C=O abundance (%)	C/O ratio	I_D/I_G ratio	ΔEp (mV)
GO	12.7	28.7	36.7	15.1	6.8	0.71	0.87	---
ErGO-pH2	47.7	31.9	7.7	8.2	4.6	3.89	1.43	318
ErGO-org	39.4	20.2	25.6	11.1	3.7	1.47	0.80	138
HrGO	3.55	42.55	47.39	2.66	3.83	4.8	1.76	---

Conclusions

The electrochemical reduction of GO in presence of H^+ improves the removal of oxygenated groups and cause the hydrogenation of sp^2 domains. While detrimental to most applications, these defects are beneficial when the films are used as anticorrosive coatings. Our results show no galvanic effect with carbon steel when the metal is coated with ErGO or HrGO films, which is of great significance for engineered anticorrosive-coatings of metals made of graphene-based materials.

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