Protection and Functionalizing of Stainless Steel Surface by Graphene Oxide-Polypyrrole Composite Coating

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Abstract: The corrosion inhibition of metallic substrates is a prime issue for many potential applications where corrosion plays a crucial role. The development of carbon based on functionalized coatings could increase the lifetime of metallic substrates by inhibiting the corrosion process. Present work is an effort to develop a corrosion inhibiting composite coating of graphene oxide and polypyrrole for AISI (American Iron and Steel Institute) type 304 stainless steel substrates. The electrochemical galvanostatic deposition process was applied for coating development. The coating morphology and ability to cover the substrate surface was analyzed with a high-resolution scanning electron microscope. The coating’s structural and electronic properties were analyzed with Raman spectroscopy. The investigation of corrosion inhibition involved open circuit potential, Tafel, and voltammetry analysis. The standard salt test ASTM (American Society for Testing and Materials) G48A for stainless steel substrate has also been studied. Significant enhancement of corrosion potential as well as pitting potential for the composite coated substrates has been noted. Furthermore, corrosion and breakdown potential increased upon changing the material from graphene oxide to its composite coating. During the salt test analysis, the durability of the composite coating was noted up to 72 h, which is the standard time scale. Based on experimental analysis, this composite material can be used as an effective carbon based on functionalized corrosion inhibitor for stainless steel substrates to increase their lifetime.

Key words: Graphene oxide, graphene oxide-polypyrrole composite, corrosion inhibition.

1. Introduction

There is a constant effort underway to find or develop better and more effective corrosion inhibiting materials that can inhibit corrosive phenomenon, and increase a metal and its alloy’s lifetime. The use of carbon based on functionalized composite coatings [1-5] to prevent corrosive processes is an area got increased attention among researchers and industrialists. Recently, developed materials graphene oxide and graphene may greatly contribute to the solution of this problem. The barrier properties of these materials already have been proven and reported in the Refs. [6-10].

The usage of these materials in the field of corrosion inhibition is underway. Researchers are trying to find the best inhibition efficiency. In our early study [11], we investigated whether GO (graphene oxide) or rGO (reduced graphene oxide) nanoplatelets were the better corrosion inhibitor. Surprisingly, both of them showed great potential. However, due to the small size of nanoplatelets, developing nonporous coating was a bit challenging. Therefore, our primary interests are to minimize the number of pores and prepare better effective coatings using these materials. The application of conductive polymer PPy (polypyrrole) and its composites for corrosion inhibition are already known in the literature and the attention to it among researchers is still increasing [12-14]. Recently, the GO-PPy composite was developed using different
techniques, with a variety of applications. So far, numerous aspects of this material have been reported in the literature, e.g., supercapacitor [15], energy storage [16], electrically switched ion exchanger [17], biosensors [18], enzyme immobilization [19], drug delivery [20], etc. Therefore, our initial study involved applying this GO-PPy composite material in the field of corrosion inhibition. In this paper, we described a valuable application of this material as an effective corrosion inhibitor.

2. Experiments

The graphite oxide and GO were prepared by modification of Hummer’s method [21-23]. The details of this procedure have been reported in our early study [24]. The Raman scattering of these materials was studied with μ-Raman spectrometer (inVia Raman microscope, Renishaw). The measurements were conducted with a laser of 514 nm wavelength at 10% of its maximum intensity.

The AISI (American Iron and Steel Institute) type 304 SS (stainless steel) (Goodfellow) substrates of surface dimensions 15 mm × 15 mm were polished with abrasive paper P500 and cleaned for 30 min in an ultrasonic bath using isopropanol (Alfa Aesar) as a cleaning solvent. The deposition of GO-PPy composite was carried out in a three-electrode cell system at room temperature (22 ± 1 °C) using Reference 600 potentiostat/galvanostat (Gamry). The SS substrate was used as a working electrode, where the GO-PPy composite was deposited. Pt wire and a SCE (saturated calomel electrode) were used as counter and reference electrodes, respectively. In a typical experiment, 10 mL aqueous GO solution of 0.5 mg·mL⁻¹ concentration was mixed with 10 mL aqueous Py (pyrrole) solution of 0.1 M concentration. The mixed solution was sonicated for 5 min in order to achieve homogeneous dispersion. The Py solution (Fluka) was prior purified in the laboratory by distillation over calcium hydride in a vacuum setup and stored in the dark under Ar (99.999%, AGA Eesti) atmosphere at a low temperature. To the 20 mL of the previously mentioned sonicated mixture, 10 mL aqueous solution of oxalic acid (Sigma Aldrich) of concentration 0.1 M, pH ≈ 1.3 was added and placed in the above described electrochemical cell system. The coating deposition process was carried out for 10 min with a constant current density of 0.5 mA·cm⁻².

The prepared coating was washed with de-ionized water and dried in the air. All of the electrochemical corrosion analyses were carried out in 3.5% NaCl aqueous electrolyte. The tested area of each sample of 1 cm² was fixed by using special 3M™ electroplating tape masks (Gamry). The Tafel scan was performed after stabilization of the OCP (open circuit potential). Each Tafel plot was obtained within the potential range starting from -250 mV to +250 mV relative to OCP. The typical scan rate of 0.125 mV/s was applied for Tafel plots. The voltammetry scans were carried out with a scanning rate of 10 mV/s within the potential range from -1 to +1 V with respect to SCE. Finally, the samples were tested using the standard ASTM (American Society for Testing and Materials) G48A salt test analysis (a test for pitting and crevice corrosion resistance of stainless steel alloys). The samples were immersed into 6% ferric chloride (FeCl₃·6H₂O, Sigma Aldrich) aqueous solution, the pH of which was adjusted to 1 with adding HCl acid. The test was carried out for six days. The tested substrates were examined with HR-SEM (high-resolution scanning electron microscope—Helios Nanolab 600, FEI).

3. Results and Discussion

The GO as prepared is largely soluble in water and polar organic solvents. Due to the presence of a large variety of oxide functional groups in the GO structure, the material becomes polar and hydrophilic in nature, enabling a solubility of GO in water [22, 24]. In Fig. 1, the Raman spectrum of the graphite powder (curve 1) G band was observed at ~ 1,580 cm⁻¹, which was
up-shifted to ~ 1,588 cm\(^{-1}\) for GO (curve 2), indicating the presence of isolated double bonds, that resonate at the frequencies higher than the graphite G band [25]. The prominent D band was observed for GO and graphite at ~ 1,363 cm\(^{-1}\), reflecting the presence of structural imperfections [26]. The low intensity S3 peak observed is a reflection of the D + G peak. The ratio of the integrated intensities of the D and G bands (\(I_D/I_G\)) is usually taken as an indication of the relative disorder presented in graphitic structures. In the present case, the \(I_D/I_G\) ratio of graphite and GO were found at 0.97 and 0.90, respectively. This decreased ratio upon oxidation of graphite indicates a decrease of structure defectiveness in the GO structure. The Raman spectrum of the GO-PPy composite material is shown in inset of Fig. 1. The Raman spectrum of PPy (not shown) is characterized by two broad peaks near 1,355 cm\(^{-1}\) and 1,582 cm\(^{-1}\), respectively. These two peaks correspond to the ring stretching of the polymer backbone and the \(\pi\)-conjugated structure [27, 28]. In the Raman spectra of GO-PPy composite, the G and D peaks of GO nanoplatelets are not clearly visible due to overlapping with a high intensity broad peaks of PPy.

The electrochemical GO-PPy composite deposition mechanism was compared with the PPy deposition mechanism. During electro-deposition, the depositional potentials for both were recorded and shown in Fig. 2. For PPy coating (Fig. 2, curve 1), the depositional potential increased to 0.73 mV, which was the peak potential, then dropped rapidly to 0.68 mV, and increased again to 0.73 mV, which was the polymerization potential. Whereas, during GO-PPy deposition (Fig. 2, curve 2), the potential of the system slightly decreased and then reached to polymerization potential, which was 0.70 mV. This lower polymerization potential of the GO-PPy composite system compared with the PPy system is likely due to the presence of charge carriers on GO sheets that indicate the involvement of GO sheets in the polymerization reaction [15, 29-31]. It is expected that, during ultra-sonication, the positively charged Py cation radicals could first attach at the basal planes and edges of a negatively charged GO surface, and then polymerization of Py would occur on the surface of GO sheet. There is a strong \(\pi\)-\(\pi\) stacking interaction between the GO sheet [29] and the electronic structures of the conjugated backbones of PPy. For

Fig. 1 Raman spectrum of raw graphite powder (curve 1), graphene oxide (curve 2) and graphene oxide-polypyrrole composite (inset).
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Fig. 2  Galvanostatic electrochemical deposition of polypyrrole (curve 1) and graphene oxide-polypyrrole composite (curve 2) on AISI type 304 stainless steel substrates.

that reason, the parts of the composite are well bonded and the coating adheres strongly with the metal surface.

Fig. 3 represents the morphology of the GO (inset) and the composite coated substrate that were examined with HR-SEM. Both surfaces show homogeneous coverage, the GO coated substrate is a bit rough in morphology when compared with the GO-PPy composite coated one. Although some pores were noticed in the GO coated substrate. From the coating composition analysis, a homogeneous distribution of the GO nanoplates in the composite was noticed. However, we have to remember that some oxide groups in the GO structure can be reduced as the current density of 0.5 mA·cm\(^{-2}\) was used during composite deposition. The coating thickness was obtained around 10 µm, and was measured with a focused ion beam cross-section prepared by the FIB-SEM (focused ion beam-scanning electron microscope). The Tafel plot and voltammetry analysis give information about the extent of corrosion inhibition ability of the composite coating by measuring corrosion potential (\(E_{\text{corr}}\)), corrosion current density (\(I_{\text{corr}}\)) and pitting potential (\(E_{\text{pit}}\)). In order to inhibit the corrosion process, the nature of the coating or protective layer should be more passive. We studied \(E_{\text{corr}}\), \(I_{\text{corr}}\) and \(E_{\text{pit}}\) of the GO, GO-PPy composite coatings by Tafel plot (Fig. 4) and

Fig. 3  HR-SEM image of graphene oxide-polypyrrole composite coating on AISI type 304 stainless steel surface electrodeposited by galvanostatic technique; in the inset figure: surface of a graphene oxide coated stainless steel substrate.
voltammetry scans (Fig. 5). Determined from the Tafel plot, value of $E_{\text{corr}}$ for the GO-PPy composite coated surface was $+48$ mV, which was most anodic value, if compared to the ones for the GO coated and bare surfaces, $+32$ mV and $-9$ mV, respectively. The $I_{\text{corr}}$ density for the composite coating was observed 6.0 nA/cm$^2$, which is much lower than the bare and GO coated substrates. The $E_{\text{pit}}$ for the uncoated, GO and GO-PPy coated samples were observed from the Fig. 5 at 243, 300 and 360 mV, respectively. These analyzed experimental findings reflect a better and improved passivity of the composite coating over others. The details of these data have been analyzed and presented in Table 1. Furthermore, to investigate the stability of the GO-PPy composite coating in a highly corrosive environment, we tested the coating according to salt test standard ASTM G48A salt test for six days and examined the substrate with an HR-SEM study. In Fig. 6, HR-SEM images of the composite coating are shown after 72 h and 144 h (inset) of immersion. We observed that, the coating was stable more than 72 h (which is the standard testing time). At 144 h immersion, the coating structure deteriorated and in some places a breakdown of the coating was noticed. To increase stability for a longer period of time in a corrosive environment, some modification is needed, and we are currently researching for a solution.
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Fig. 6  HR-SEM image of graphene oxide-polypyrrole composite coated stainless steel substrate after 72 h immersion and after 144 h (inset) standard ASTM G48A immersion test.

Table 1  OCP (open circuit potential), corrosion potential ($E_{corr}$), corrosion current density ($I_{corr}$) and pitting potential ($E_{pit}$) measured from Tafel plot and voltammetry scan analysis.

<table>
<thead>
<tr>
<th>Sample</th>
<th>OCP (mV)</th>
<th>$E_{corr}$ (mV)</th>
<th>$I_{corr}$ (nA/cm²)</th>
<th>$E_{pit}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare SS</td>
<td>2</td>
<td>-9</td>
<td>29</td>
<td>243</td>
</tr>
<tr>
<td>SS/GO</td>
<td>112</td>
<td>32</td>
<td>223</td>
<td>300</td>
</tr>
<tr>
<td>SS/GO-PPy</td>
<td>147</td>
<td>48</td>
<td>6</td>
<td>360</td>
</tr>
</tbody>
</table>

4. Conclusions

The graphene oxide-polypyrrole composite was effectively electrodeposited onto a 304 stainless steel substrate using the galvanostatic deposition technique. The morphology of the composite coating reveals homogeneous distribution of GO over the composite with great surface coverage ability. The Tafel and voltammetry tests exhibit better and enhanced corrosion inhibition ability with the composite technique compared with the graphene oxide coated one. The Tafel and voltammetry analyses reflect better and more effective corrosion inhibition by improving corrosion potential, breakdown potential and lowering corrosion current density. The standard ASTM G48-A salt test further supports the above results. We would emphasize that, this material can be used as an effective corrosion inhibitor. However, further modification and research are needed to reach its best inhibition efficiency as well as to increase stability in highly corrosive environment. We are researching ways to increase the maximum inhibition efficiency.

Based on our experimental findings and analysis, we conclude that, this graphene oxide-polypyrrole composite material can act as a better corrosion inhibitor, which can be used to prepare better and more effective corrosion inhibition compared with graphene oxide nanosheets alone.

Acknowledgments

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