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Effect of graphene oxide nanoplatelets on electrochemical properties of steel substrate in saline media

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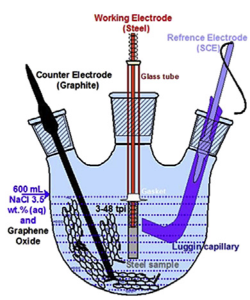
HIGHLIGHTS

- Electrochemical properties of steel in saline media containing nano graphene oxide.
- Effect of concentration of graphene oxide on electrochemical properties.
- Mechanism of corrosion reduction due to the presence of graphene oxide.

GRAPHICAL ABSTRACT



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ABSTRACT

There has been increased interest in using graphene oxide (GO) in various industrial applications such as working fluids, lubricants, oil and gas fields, heavy metal removal from water, anticorrosion paints and coatings etc. We studied electrochemical properties of steel in the presence of suspended GO in saline media. GO suspension has been characterized using Transmission electron microscopy (TEM) and X-ray diffractometer (XRD). We measured the effect of the GO concentration (0–15 ppm) on electrochemical properties of steel using different techniques: open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR) and potentiodynamic (PD) methods. Results indicate that the suppression of corrosion is directly proportional to increasing GO concentrations in saline environments. Surface morphology of corroded samples was examined using Scanning Electron Microscopy (SEM). Identification of the elements at accumulated layer was estimated from peaks of energy dispersive x-ray spectroscopy (EDX) and XRD. Increased protection abilities with increasing GO concentration have been attributed to the domination of salt layer presence at the surface of steel which occurs via precipitation of sodium chloride. Surface analysis confirm that there is no direct effect of GO on the protection behavior of steel. The presence of GO in the solution can enhance the precipitation of NaCl due to the decreased solubility NaCl which further slows down the corrosion. The pourbaix diagram shows that GO forms an anionic compound with sodium which may enhance the precipitation at working electrode.

1. Introduction

Graphene oxide (GO) comprised of two dimensional hydrophilic oxygenated layered sheets has attracted attention due to many

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factors such as its very large surface area [1], ease in solution processing [2], good physical and mechanical properties [3]. Further deoxygenation leads towards improvements in the aforementioned properties of GO. Dreyer et al. reported many types of functional groups at basal planes and including epoxy, hydroxyl, carboxylic and alcohols [3]. Fig. 1 represents Hummer's method for synthesis of GO. This produces an intercalated structure of oxidized sheets of graphite with the aid of strong oxidizing agent and concentrated sulfuric acid [4]. The anchored oxygenated GO to produce stable dispersion in many polar and non polar solvents [5] including water which is the most important and widely used medium for many industrial applications. The dispersing ability of GO in many solvents more specifically in water is because of the ionizable carboxylic acid at the edges act as hydrophilic whereas phenol hydroxyl and epoxide groups at basal planes act as a hydrophobic area [6]. The properties such as large surface area and amphiphilic nature makes GO suitable for various industrial applications. It includes the stabilization of multiphase system like oil and water interface [7,8] enhanced oil recovery, stabilization of CO_2 foam [9], surfactant for detergents and emulsifiers, dispersing agent [10], desalination and water purification [11], and for delivery purposes of nanoparticles in deep oil reservoirs [1].

Recently, Yoon et al. reported the stabilization of oil and water emulsion in 5 wt % NaCl using GO at a low concentration. This behavior of GO was attributed towards the presence of high charge density at the edges due to the presence of carboxylic anions. These anions slightly extend out in to the water phase and stabilize the interface. It was also presented that GO adsorbs at the oil/water interface and promotes the stabilization [1].

Corrosion is an electrochemical process having deterioration effect on the metal or alloy. For iron, corrosion produces porous and pervious film which is composed of different forms of iron oxide It can be seen from Fig. 2 that redox reactions are occurring on the surface. The presence of sodium and chloride ions acting as electrolyte, where chloride ions accelerating the corrosion process by destroying any type of passivity which the active corrosion rate. In this case, the accelerating corrosion process involves the dissolution of iron oxide film and in addition sodium and chloride ions also enhance the transportation of electrons [12].

In recent literature, anti-corrosion properties of graphene oxide and reduced graphene oxide (rGO) have also been reported for different metals. The main associated protection mechanism was barrier to the corrosive media. Recently, polystyrene/graphene nano-composites showed superior anti-corrosion properties with the incorporation of 2 wt. % of modified reduced (r-GO) owing to excellent barrier properties [13]. Similar results, were shown for the composites of silane modified r-GO/poly vinyl butyral (PVB) [14] and graphene/pernigraniline/PVB [14,15].

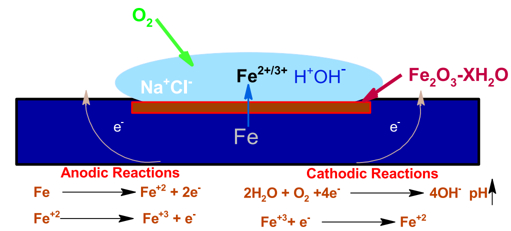

Fig. 2. Schematic diagram of iron corrosion process, production and consumption of electrons resulting corrosion products.

With so many potential and possible solution based applications of GO, it is necessary to see the effect of GO on corrosion properties of metals in the presence of corrosive media such as saline solution. In this work solution based electrochemical testing of dispersed GO were observed using carbon steel as working electrode in 3.5 wt. % NaCl solution containing various concentration of GO.

2. Materials and methods

2.1. Materials

Nano Graphene Oxide aqueous solution (concentration: 1 g/L, pH: 2.90 diameter: 90 nm, +/−15 nm, thickness: about 1 nm, single layer ratio: >99%, Purity: >99% as provided by supplier) was purchased from Graphene supermarket, USA and used as received. The industrial steel used in this study was cut from pipe line. API-5L X80 steel coupons (elemental composition (wt%): C0.07, Mn1.36, Ti0.008, S0.003, P0.004, Cr0.45 + Ni and remaining Fe), were machined to 10 × 10 × 4 mm dimensions and a tap and drill hole of 3–48 tpi (threads per inch) was drilled to one long side of the coupon. Machined carbon steel is used as the working electrode and the exposed surface area was 3.4 cm^2. The specimens were surface finished using different grades of SiC grit papers up to 240 grit to ensure the same surface roughness [16,17], followed by cleaning and degreasing with industrial grade acetone and ethanol followed by drying in air. In order to evaluate the protection behavior of Nano-GO, solution were prepared in 3.5 wt. % NaCl with varying concentration of GO i.e. 0–15 ppm. Table 1 shows the pH of GO solution with 3.5 wt. % NaCl. The decreasing trend in the pH of the GO solution was due to the higher pH of original solution.

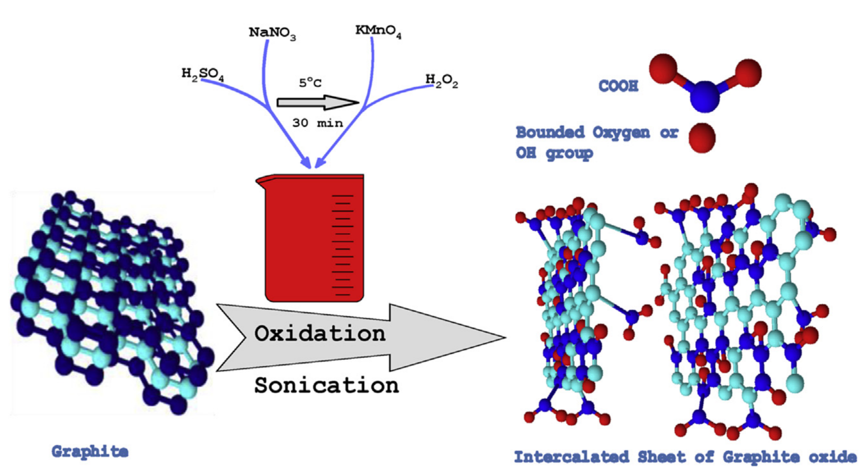

Fig. 1. Graphene oxide synthesis and structure.