



# Steel surface pre-treated by an advance and eco-friendly cerium oxide nanofilm modified by graphene oxide nanosheets; electrochemical and adhesion measurements



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## ABSTRACT

In this research the silane-functionalized graphene oxide (GO) nanosheets were utilized for modification of an eco-friendly cerium conversion coating and its effect on the cathodic disbonding, corrosion protection and adhesion properties of the epoxy coating was investigated. For this purpose, the cerium coating was modified by GO nanosheets functionalized with 3-(Triethoxysilyl) propyl isocyanate (TEPI, IGO nano-fillers). The Electrochemical Impedance Spectroscopy (EIS) showed that the addition of IGO nano-fillers in the cerium coating resulted in improved anti-corrosion properties of cerium coatings. The adhesion and anti-corrosion performance of the steel-cerium/epoxy system were also investigated. Results showed that inclusion of IGO nano-filler into the cerium matrix significantly improved the corrosion resistance, cathodic disbonding and adhesion properties of the top epoxy coating.

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## 1. Introduction

One of the most common and effective methods for corrosion protection of buried or immersed metals is cathodic protection along with organic coatings. The organic coatings, due to barrier properties, prevent the direct contact of the corrosive electrolyte to the metal surface and reduce the amount of current required for cathodic protection of the metal substrate. One of the major problems in cathodic protection of coated structures is cathodic disbonding or cathodic delamination. This phenomenon occurs due to the cathodic reaction, i.e. oxygen reduction and  $\text{OH}^-$  ion production, in the areas where the coating is damaged and subsequently leads to the adhesion loss of the organic coating from the metal surface [1–6]. In fact, the increase in pH, as a result of  $\text{OH}^-$  ion generation, leads to the destruction of the organic coating adhesion bonds and cathodic delamination [7–10]. This is one of the most important mechanisms of protection failure for cathodic

protection system of coated structures. Research has shown that improving the adhesion among the metal substrate and organic coatings decreases the cathodic delamination rate and adhesion loss in corrosive environment [11]. In fact the adhesion strength is one of the most important factors for corrosion protection when two materials are kept together in close inter-molecular contact and the adhesion loss is directly related to (electro) chemical degradation at the substrate/organic coating interface [11,12]. There are several methods to improve the adhesion among the organic coating and metal surface for example, acid washing, sand blasting, conversion coatings and sol-gel based silane coatings [13–19]. The conversion coatings (for example chromate and phosphate coatings) are the most widely used pre-treatments for the improvement of adhesion strength among organic coatings and metal substrates and therefore the improvement of the anti-corrosion performance. This is due to the increase of surface free energy and surface roughness after applying a conversion coatings [20]. Chrome-based conversion coatings are widely used due to excellent anti-corrosion properties, self-healing capacity and favorable adhesion strength to top organic coating. However, the use of these coatings has been recently limited due to the environmental problems, and chrome-free conversion coatings have been developed as their alternatives [21–23]. Recently the cerium conversion

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coatings due to promising features such as being environmentally friendly, increasing the adhesion strength between the organic coating and the metal substrates and improving the anti-corrosion performance have been widely considered as a suitable alternative to chromate conversion coatings. The formation of these coatings is through the steel substrate immersion in an aqueous solution containing cerium salts and  $\text{H}_2\text{O}_2$  accelerator or direct spraying the solution onto the substrate in a short time. During the coating process, the steel substrate is sequentially corroded and an increase in pH over the cathodic regions causes the deposition and island growth of cerium compounds. However, these coatings have some disadvantages such as low corrosion resistance and highly cracked morphology. In recent years studies were devoted to improve the anti-corrosion properties of cerium-based coatings on steel substrates [24–26]. Kobayashi et al. [27] studied the influence of  $\text{SO}_4^{2-}$  ions on the corrosion behavior of cerium-based conversion coatings on galvanized steel. They showed that formation of a complex between  $\text{Ce}^{3+}$  and  $\text{SO}_4^{2-}$  causes the incorporation of  $\text{SO}_4^{2-}$  in the cerium conversion coatings, which leads to creation of a grained conversion layer and enhancement of the corrosion resistance. Onofre-Bustamante et al. [28] investigated the role of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the formation of cerium conversion coatings and found that  $\text{H}_2\text{O}_2$  acts as an oxidant, complexing agent and a source of  $\text{OH}^-$  ions. In this way, the presence of  $\text{H}_2\text{O}_2$  can improve the roughness, adhesion strength, corrosion resistance and the speed of precipitation process. Ramezanzadeh et al. [29] studied the effect of zinc phosphate conversion post-treatment as sealing agent on the corrosion protection performance of cerium conversion coatings. They showed that the post-treatment of the cerium coatings creates a more compact layer with less cracks and better anti-corrosion performance. Also in another work [30], they compared the adhesion strength and anti-corrosion performance of the epoxy coating applied on the steel surface treated with cerium, zinc phosphate and cerium post-treated by zinc phosphate coatings. The results revealed that the cerium post-treated by zinc phosphate coatings offers better features. Mahidashti et al. [31] improved the anti-corrosion performance of cerium conversion coatings by heat treatment of coatings. They showed that the post-heating of cerium coatings significantly reduces the amount of micro-cracks in coating structure and enhances its anti-corrosion performance and adhesion strength. In another study, Ramezanzadeh et al. [32] studied the effect of cerium conversion pre-treatment on the cathodic delamination and anti-corrosion performance of carbon steel/fusion-bonded epoxy (FBE) coating systems. They showed that the cerium conversion pre-treatment compared to the phosphoric acid washing method significantly increased the surface free energy of steel substrate, decreased the cathodic delamination rate, improved the adhesion properties and enhanced the anti-corrosion performance of FBE. Graphene oxide (GO) nanosheets have many functional groups (including hydroxyl, carboxylic and epoxide), which are suitable sites for the covalent functionalization by various compounds [33]. Functionalization of GO with silane coupling agent causes the increase in its compatibility with other systems, and increasing its adhesion strength with the metallic substrate, other GO nanosheets, and the organic coatings. Recently, the GO nanosheets in a lot of research have been used to enhance the corrosion resistance of metallic substrates. But so far these nanosheets have not been used as filler in the surface pre-treatment baths of cerium. As the carbon steel plays an important role in various industries, investigation on its behavior during cerium conversion pre-treatment and its influence on the subsequent epoxy coating is still important. In this work, the role of adding silane-functionalized graphene oxide nanosheets in the cerium conversion coatings on the adhesion strength, corrosion protection and cathodic disbonding of the epoxy coating on the

pre-treated steel surface was studied. Covalent functionalization of GO nanosheets was done by 3-(Triethoxysilyl)propylisocyanate (TEPI) silane coupling agent which provides strong covalent bondings between the GO nanosheets and the epoxy matrix. So first the GO nanosheets were functionalized by TEPI (named IGO nanosheets) and then were added to the cerium chemical bath to prepare the cerium conversion coating co-deposited with IGO nanosheets on the steel surface. After pre-treatment of steel surface in different cerium baths, the samples were coated with the epoxy coating. The silane-functionalized GO nanosheets were characterized by Fourier transform infrared spectroscopy (FT-IR) analysis. The cerium based nano-composite coatings deposited on the steel surface was studied by field emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), contact angle measurements and electrochemical impedance spectroscopy (EIS). The effect of cerium pre-treatment modified via IGO nanosheets on top epoxy coating properties was studied by EIS, pull-off, salt spray and cathodic delamination tests.

## 2. Experimental

### 2.1. Materials

For synthesis of graphene oxide nanosheets, the expandable graphite powder (with grain size of  $80\% > 300 \mu\text{m}$ ),  $\text{H}_2\text{SO}_4$  (98%),  $\text{KMnO}_4$  and  $\text{H}_2\text{O}_2$  (30%) were purchased from Aldrich Co. (Germany). Also 3-(Triethoxysilyl) propyl isocyanate (TEPI,  $(\text{C}_2\text{H}_5\text{O})_3\text{Si}(\text{CH}_2)_3\text{NCO}$ ) and N,N-dimethyl formamide (DMF) were prepared from Kropfmuehl Graphite Co. (Germany) and Merck Co, respectively, for functionalization of the graphene oxide. In order to prepare cerium chemical bath,  $\text{Ce}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ , HCl (37 wt %) and NaOH were purchased from Merck Co. Araldite GZ7 7071X75 as epoxy resin and CRAYAMID 115 as amido polyamide curing agent were purchased from Saman and Arkema Co., respectively. The St-37 type steel panels with dimensions of  $80 \times 70 \times 2 \text{ mm}$  and the composition of 0.04 wt% Al, 0.05 wt% P, 0.05 wt% S, 0.34 wt% Si, 0.32 wt% Mn, 0.19 wt% C and 99.01 wt% Fe were purchased from Foolad Mobarakeh Co, Iran. Before coating, the selected substrates were sanded by SiC papers to 1200 grit, and subsequently degreased by acetone and rinsed with distilled water.

### 2.2. Synthesis and functionalization of graphene oxide nanosheets and cerium pre-treatment process

Graphene oxide (GO) nanosheets were synthesized through oxidizing and exfoliating the graphite powder by modified Hummer's method according to previous work [34]. To functionalize the GO nanosheets by TEPI silane, 50 mg of GO was added to a round bottom flask containing 5 mL DMF solvent and 2 mmol TEPI. The brown solution of the dispersed GO was stirred with a rate of 600 rpm and heated at  $85^\circ\text{C}$  for 2 h. After that, the color of the reaction mixture changed to black, indicating the successful functionalization of the GO and formation of IGO nanosheets. In order to remove the unreacted TEPI silanes, it was centrifuged and washed three times by distilled water.

In order to prepare the cerium chemical solution,  $\text{Ce}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  (2 g/L),  $\text{H}_2\text{O}_2$  (1 g/L) and HCl (11 mL/L) were mixed in water and then the pH of the solution was adjusted at 3 using NaOH 5 wt % solution. To prepare cerium-IGO composite, 0.2 g/L of IGO nanosheets was added to the above cerium solution. Then the solution was centrifuged for 5 min. For surface pre-treatment of steel substrates by cerium based coatings, the solutions of cerium and cerium-IGO were sprayed on the substrates for 45 s. The cerium treated substrates were then washed with distilled water and dried by warm air.

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