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Original Article

# Poly(ophenylenediaminecoaniline)/ZnO coated on passivated low nickel stainless steel

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ABSTRACT

Iron and its alloys are broadly used in many applications, which have strengthened the research in corrosion resistance in various neutral and provoking environments. Almost all powerful corrosion inhibitors may have unsafe and effects on both environment and health. Therefore, there is a need for a primer that provides outstanding adherence and corrosion resistance, and is environmentally safer. The conducting polymer coating on metals was found to offer the anti-corrosion. In this work, the electrochemical synthesis of Poly(o-phenylenediamine-co-aniline) copolymers (P(Popd-co-Ani)) and Poly(o-phenylenediamine-co-aniline)/ZnO (P(Popd-co-Ani)/ZnO) composite was accomplished by using the electrochemical techniques on borate passivated low nickel stainless steel (LN SS) electrode from lithium perchlorate in acetonitrile solutions containing a fixed concentration of monomer and different concentrations of zinc oxide (ZnO). The structural and morphological analyses of the copolymer and composite coatings were executed using various analytical techniques, for example Fourier transform-infrared spectroscopy (FT-IR), X-ray diffraction method (XRD), field emission scanning electron microscopy (FE-SEM), elemental mapping and energy dispersion X-ray spectroscopy (EDX). The surface topography was assessed with using an atomic force microscope (AFM) corrosion protection behavior of these copolymer-coated stainless steels was investigated in 0.5 M $H_2SO_4$ solution by potentiodynamic polarization (Tafel) method and electrochemical impedance spectroscopy methods. Among the as developed protective copolymer coatings, the P(Popd-co-Ani)/ZnO composite exhibited the best corrosion protection.



## 1. Introduction

Stainless steel is of great interest in industrial applications owing to the union of exceptional resistance to corrosion, good mechanical properties, intrinsic durability, ductility and good workability [1–5]. Anti-corrosion is essential by many industries via, oil and gas exploration and production, chemical manufacture, petroleum refining and product additives [6–8]. For this reason, the stainless steel, in which the nickel content is partly replaced with other elements (low-nickel stainless steel (LN SS)), is being evaluated as a possible alternative to traditional carbon steel. This LN SS could mean a saving of about 15–20% in contrast to the conventional austenitic stainless steel [9–11].

Although the influence of chemical and atmosphere can be negligible, LN SS is susceptible to corrosion in the aggressive environment. To tailor the corrosion rate of LN SS, different approaches have been developed such as use of inhibitors, protective coatings, etc. One of the ideal ways to improve the corrosion resistance of LN SS is to apply the protective coatings [12–14]. To protect the metals from corrosion, organic conducting polymer coatings were found to be more effective than other protective coatings [15–18]. Additionally, polymers are with the aim of they can be evenly and electrochemically deposited the metal surface with easiness of control over the extent of the polymer coatings and irrespective of the surface roughness and shape [19].

Phenylenediamine (Popd) is inspect as one of the most examine conducting polymers and also advantages much interest in several studies with a choice of practical applications for the reason that of its high conductivity, outstanding air stability [20,21], and special physical and chemical properties compared to other conducting polymers [22]. Also, the rigid backbone structure of o-aniline

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attributed [23–26] to the extensive delocalization of π–electrons. The copolymers have a stand of special properties for instance enhanced chemical, thermostability and good barrier properties etc [27,28].

Conducting polymer/inorganic oxide nanocomposites have a little while back attracted great attention caused by their unique micro and nano shape, electrooptical, physiochemical properties and a wide-range of their potential treatment in battery cathodes and in the structure of nanoscopic assemblies in sensors and microelectronics. It is believed that, with the development of material science, ZnO has found applications in many fields such as the chemical industry, electronics, optics, and number of areas because of its catalysis, optical, magnetic, and mechanical special features [29]. The nanocomposites consisting of polymers and ZnO have attracted lots of interest in their magnificent properties and potential applications. The Numerous researches investigated conducting polymer/ZnO nano-composites, and a number of research groups have focused their research on the investigation of PVC/ZnO nanocomposites and their applications [30]. To the best of our knowledge, there are no reports on the electrochemical synthesis of nanocomposite coating consisting of PoPd, PAni and ZnO by CV technique on borate passivated LN SS material. In the present work the structure and properties of P(Popd-co-Ani)/Zno nanocomposite coating were studied and the anticorrosive property of P(Popd-co-Ani)/Zno nanocomposite coating on metal sample was investigated in 0.5 M $H_2SO_4$ at room temperature.

## 2. Experimental

In this work, The LN SS (size of 1 cm × 1 cm × 0.3 cm) samples were embedded in epoxy resin with suitable electrical make contact with to have an exposed area of 1 $cm^2$. The substrates were polished with a 200 to 1500 series of emery papers, the specimens were cleaned by ultrasonication and followed by thorough rinsing in acetone and DI-water and dried in air [1]. Passivation of LN SS surface was done in the borate buffer solution [31]. and under potentiostatic conditions for 1 h at potentials of 0.64 V according to procedure declared by our previous work. The polymer composite coatings were electrosynthesized on the passivated LN SS by using cyclic voltammetry [32,33]. The Ani, Popd and ZnO monomers were double distilled prior to their use. The electrochemical polymerization was complete in a one compartment three electrode chamber with working electrode (LN SS), reference electrode (SCE) and counter electrode (platinum). The cyclic voltammetric setting were maintained using a CHI Electrochemical Workstation (CHI 760C, CH Instruments, USA). After deposition, the working electrode (LN SS metal) was removed from the electrolyte and rinsed with DI water and dried in air.

## 3. Result and discussion

### 3.1. Preparation of P(Popd-co-Ani)/Zno composite

The cyclic voltammetric (CV) curves recorded for P(Popd-co-Ani)/Zno copolymer composite coating on passivated LN SS from ACN-$LiClO_4$ containing solution (Fig. 1). The equal ratio of monomer in the presence and absence of ZnO nanoparticles were taken in arrange to compare the morphology, shape and corrosion resistance of composite coating with P(Popd-co-Ani) the figure represents (CV) between −0.8 to 2.0 V at a scan rate of 100 mV $s^{-1}$ at room temperature (28 ± 1 °C) and for 20 cycles. In CV studies well defined oxidation and reduction peaks of P(Popd-co-Ani)/Zno copolymer composite between −0.4 and + 2.0 V vs. SCE appear to indicating the formation of homogenous and strong adherent P(Popd-co-Ani)/Zno copolymer composite coating occurs over the passivated LN SS surface.

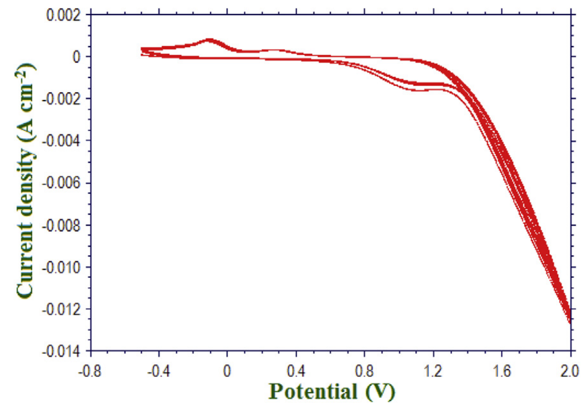


**Fig. 1.** Cyclic voltammograms of P(Popd-co-Ani)/ZnO copolymer nanocomposite coating on passivated LN SS for cycle numbers 1–20 at a scan rate of 100 mV $s^{-1}$.

### 3.2. Phase structure and morphological characterization

The electropolymerized P(Popd-co-Ani) in the presence and absence of ZnO on the passivated steel surface was scraped off and their Fourier transform infrared spectroscopy (FT-IR) spectrum were recorded (Fig. 2). The Fig. 2a,b gives the FT-IR spectra of pure P(Popd-co-Ani) and P(Popd-co-Ani)/ZnO composite [23]. The P(Popd-co-Ani) peaks are present in the composite and the peak appeared at 578 $cm^{-1}$ confirms the presence of ZnO composite coating formed on LN SS surface. Fig. 3 shows the XRD patterns for P(Popd-co-Ani) and P(Popd-co-Ani)/ZnO nanocomposite. The peaks for P(Popd-co-Ani) (Fig. 3a) is found around the 2θ values of 20–25, respectively. Similarly the XRD pattern of nanocomposite (Fig. 3b) shows the corresponding peaks for copolymer along with the peaks for ZnO (31, 34, 36, 47, 56, 62, and 67). Hence, the XRD pattern supports for the formation of P(Popd-co-Ani)/ZnO nanocomposite [30].

The FE-SEM morphological study of CV electrodeposited P(Popd-co-Ani) and P(Popd-co-Ani)/Zno composite coatings obtained at 20 segments above condition shown in Fig. 4. The Fig. 4a shows the non-uniform structure for P(Popd-co-Ani) coating whereas a flower-like morphology is obtained for the P(Popd-co-Ani)/Zno coating (Fig. 4b) which covers the entire surface of the anticorrosion. P(Popd-co-Ani)/Zno composite coating consisted reveals that the ZnO particles were distributed randomly into the net lines among P(Popd-co-Ani). The morphologies of the obtained

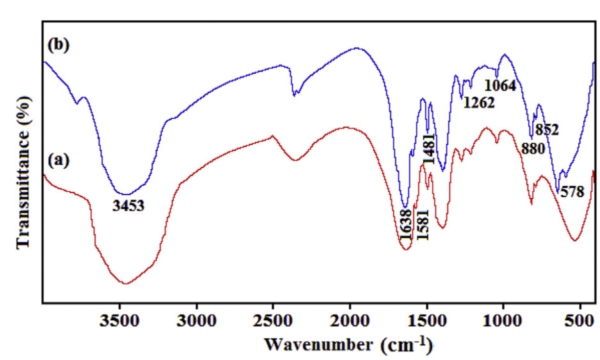


**Fig. 2.** FT-IR spectra of (a) P(Popd-co-Ani) copolymer and (b) P(Popd-co-Ani)/ZnO nanocomposite.