

Protection of type 430 stainless steel against pitting corrosion by ladder conductive polymer

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Abstract

Poly(*o*-phenylenediamine) (PoPD) was electropolymerized by cyclic voltammetry (CV) on 430 stainless steel from sulfuric acid solution containing *o*-phenylenediamine monomer. The formation of the polymer film is slower than that of polyaniline (PANI) film. Transparent and compact layers ($\sim 1.0 \mu\text{m}$) of PoPD deposited after 100 cycles, while thicker ($\sim 3 \mu\text{m}$), grainy and porous layers of PANI formed after 50 cycles. The PoPD layers protect the steel substrate from pitting in 3% NaCl but the layers of PANI fail, and pitting and crevice corrosion were observed on the steel surface. Both polymers keep the steel substrate in a passive state in sulfuric acid. After aging in acid solution the underlying oxides were investigated after peeling off the polymer layers; this showed an excellent passive film formed under PoPD. The passive steel was completely free from pitting after immersion in the chloride solution for 1 week.

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1. Introduction

Stainless steels belong to a class of metals and alloys which protect themselves by forming passive films on their surface. However, in the presence of chloride ions, localized corrosion such as pitting and crevice corrosion is still a serious problem for this type of steel. For this reason the study of corrosion involving stainless steels in chloride media has technological importance [1].

Conductive polymers (CPs) are materials with promising properties. One of the important new applications of conductive polymers is their use as surface coatings to protect metals against corrosion; it is an environment friendly and effective method. Passivation of stainless steels by coating chemically or electrochemically with CP has been studied previously [2–8]. DeBerry [8] found that electrodeposited polyaniline (PANI) enhances the corrosion protection of stainless steel in strong acid. Wessling [9] indicated that the protection brought by PANI depends on the underlying passive layer that it stabilizes through a ‘quasipotentiostatic’ effect. The passivation of stainless steel is achieved by

partial coating of the electrode surface with PANI. It is considered that the polymer film passivates the SS by simply holding the potential in the passive region, forming a Cr-enriched passive film [7]. The passive films of SS under layers of CP were found to have different characters than those formed by applied positive potential [2–4].

Aging of SS in the passive state by anodic polarization in H_2SO_4 solution without and with chlorides below the pitting potential is beneficial for pitting resistance. This is attributed to the enrichment in chromium oxide in the oxide layer which increases with increasing polarization time, forming a more protective layer [10]. Recent studies showed that the stability of passive films under CPs increases with increasing immersion time in H_2SO_4 and the films have higher corrosion resistance than those formed by anodic polarization under the same conditions of immersion [2–4]. PoPD enhances the formation of excellent passive films on 304 SS [2].

The electrochemical properties of PoPD differ significantly from those observed for polymers which are prepared from aniline and its other derivatives [11]. PoPD has been an active area of research recently [12–14]. It is readily electropolymerized on platinum [15], indium tin oxide (ITO) [16] and glassy carbon [17] electrodes from sulfuric acid solutions containing *o*-phenylenediamine monomer. PoPD was first electrodeposited on 304 SS from aqueous solutions of phosphoric acid and sulfu-

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ric acid by D'Elia et al. [6] and by Hermas et al. [2], respectively. In this work, PoPD layers were used for protection of less resistance commercial stainless steel (430 ferritic SS) against pitting corrosion, and the results were compared with those of PANI layers and by anodically passivation (applied positive potential).

2. Experimental works

The electrodeposition process was carried out in a one-compartment three electrodes cell. The working electrode was 430 SS plate (1.5 cm^2). The counter and reference electrodes were Pt mesh and Ag/AgCl (saturated KCl), respectively. The steel surface was polished using emery paper of successive grades up to 600. The steel electrode was washed thoroughly with redistilled water and acetone before immersion in the electrolytic solution. *o*-Phenylenediamine 99% (Wako) and the other chemicals were of reagent grade and used as received. PoPD was synthesized on SS by CV between -0.5 and 1.2 V (Ag/AgCl) with a scan rate of 50 mV s^{-1} from 0.1 M sulfuric acid solution of pH 1.0 and containing 0.05 M *o*-phenylenediamine at room temperature. The PoPD-coated sample, before use in other experiments, was thoroughly washed with $0.1 \text{ M H}_2\text{SO}_4$ solution and rinsed with distilled water. The electrochemical equipment consisted of a potentiostat (Hokuto Denko HA-301) and a function generator (Hokuto Denko HB-104). The electrochemical measurements (corrosion tests) were carried out at 35°C . The underlying oxides (modified SS) were investigated after peeled off the polymer from the steel surface with a tape paste and then washing by redistilled water and finally with acetone in ultrasonic bath.

Field emission scanning electron microscope (FE-SEM) data were obtained by using Hitachi S-4700Y SEM. X-ray photoelectron spectroscopic (XPS) of the surface oxide film on SS were carried out. The preparation of steel sample was finished a few minutes before the measurement. XPS spectra were collected using a Fisons Escalab 210 spectrometer, with an unmonochromatized Al K α X-ray source. The source was operated at 15 kV and 20 mA with a take off angle $\theta = 35^\circ$ (relative to the sample normal). The binding energy scale was calibrated with respect to the C 1s (284.5 eV). Spectra of Fe $2p_{3/2}$, Cr $2p_{3/2}$ and O 1s were recorded. Curve fitting of the spectra was done by a mixture of Gaussian and Lorentzian functions on a Shirley-type background [18].

3. Results

3.1. Electrodeposition of CP films on stainless steel

As the bare stainless steel is immersed in aerated solution of $0.1 \text{ M H}_2\text{SO}_4$ (pH 1) containing 0.05 M *o*-phenylenediamine, the potential-sweep electrolysis is carried out. In Fig. 1, the curves 1–3 are represented the initial three successive cycles while curve 4 is represented the last three successive cycles of 100 cyclic voltamograms for the electrodeposition of PoPD on the stainless steel. With potential scanning, the *o*-phenylenediamine is electro-oxidized irreversibly in a potential region higher than 1.0 V (Ag/AgCl), which is accompanied by the formation of red

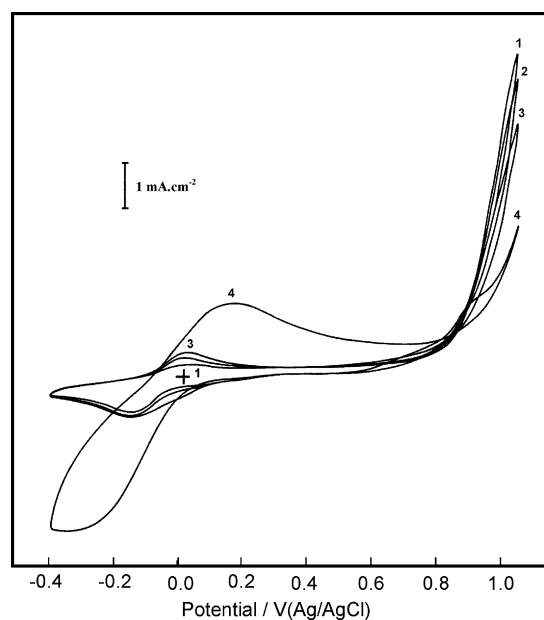


Fig. 1. Cyclic voltammetry for electrodeposition PoPD (100 cycles) on 430 SS from $0.1 \text{ M H}_2\text{SO}_4$ (pH 1) with 0.05 M *o*-phenylenediamine, first (curves 1–3) and last (curve 4) cycles.

powdery products near the electrode surface, soluble oligomers might occur. On the first reverse scan, cathodic current peak appears around -0.2 V and then anodic peak on the second forward scan is around 0.02 V which varied with cycling. The current response increases with successive potential scans, indicating the growth of the electroactive PoPD film on the stainless steel surface. Dai et al. [19] estimated that, the current efficiency for formation of PoPD on gold electrode reached to maximum (100%) in the third cycle during electropolymerization in $0.1 \text{ M H}_2\text{SO}_4$ solution. It was attributed to a significant increase in the concentration of oligomers near the electrode surface. After 50 cycles, the increase of current is becoming very small and the potential of cathodic and anodic peaks is -0.4 and 0.18 V , respectively. A thin adherent layer was formed on the steel surface after these cycles. Similar electrodeposition of PoPD was carried out on austenitic stainless steel of type 304 from H_2SO_4 solution and the formed polymer was found to have ladder structure by using FTIR [2].

Fig. 2 shows the successive cyclic voltamograms for electrodeposition of PANI on the surface of 430 SS from $0.1 \text{ M H}_2\text{SO}_4$ (pH 1) containing 0.2 M aniline. The formation of PANI film is faster than that of PoPD. Two redox peaks are shown, they are related to the oxidation states of PANI, leucoemeraldine (amine (NH,NH)), emeraldine (radical cation $[(\text{NH},\text{NH})\text{H}]^+\text{X}^-$) and permigraniline (quinone diimine (N,N)).

3.2. Morphological study of CP films

The morphology and thickness of PoPD layers on SS was investigated by SEM as shown in Fig. 3. A transparent and compact polymer layer ($\sim 1.0 \mu\text{m}$) formed after 100 cycles as shown in Fig. 3A. The layer of PoPD is the characteristic by a net of broad lines ($0.3\text{--}0.8 \mu\text{m}$) or fiber-like which are shiny silver and

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