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Electrosynthesis of poly(aniline-co-o-phenylenediamine) film on steel and its corrosion protection performance

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ABSTRACT

Poly(aniline-co-o-phenylenediamine) (Ani-co-oPD) has been electrosynthesized on steel surface by cyclic voltammetry technique from an aqueous oxalic acid electrolyte. The copolymer film was characterized by FTIR, UV, TGA, and SEM techniques. The corrosion protection performance of poly(Ani-co-oPD) film on steel was found out by impedance and Tafel polarization methods in 1% NaCl. The copolymer film was found to be highly corrosion resistant and a suitable mechanism for corrosion protection is suggested.

1. Introduction

The electropolymerization of conducting polymer on suitable electrode surface is an active area of research [1–3]. Greater attention has been paid due to large number of potential applications of conducting polymers in batteries, electro chromic devices, microelectronic devices, photo electronic devices, display devices, chemically modified electrodes, sensors, corrosion protection, etc. [4–9]. Recently it has been reported that conducting polymers can also be electrodeposited on non-noble electrodes such as iron, aluminium, etc. [10,11]. It has been shown that conducting polymer coating on non-noble metals can either act as physical barrier towards corrosive agents or as inhibitor by shifting the corrosion potential to a value where their corrosion rate is reduced [12–16]. Among the electrically conducting polymers, polyaniline (PANI) is considered as one of the most attractive materials used as coating for corrosion control. M. Rashid et al. reported the coatings containing polyaniline/palm oil blend could provide excellent protection when coated on to mild steel exposed to the saline environment [17]. Corrosion protecting primer coating system based on poly-acrylic acid doped PANI was reported by T. PAN [18]. P. Muthirulan et al. [19] reported the corrosion protection behaviour for PoPD nano fibre coated 316L SS in 3.5% NaCl by observing shift in the corrosion potential towards nobler direction. However, the studies of Nagels et al. [20], Sekine et al. [21] and Kamaraj et al. [22] have shown that the electropolymerized PANI films alone on steel do not satisfactorily protect the surface against corrosion. Reports have shown that the co-polymerization of aniline with substituted anilines, which bear various functional groups leads to modified copolymers. The copolymers exhibited better properties than the homo polymers and it is true in offering corrosion protection. Copolymer films on steel have been found to offer higher corrosion protection [22] due to compact film formation. B. Yazici et al. reported synthesis of poly(pyrrole-co-2-amino-4-methyl-pyridine) film on 7075 aluminium (Al) substrate from aqueous oxalic acid solution by employing cyclic voltammetry technique [23]. Uniform and strongly adherent PNDMA-SDS/PANI coatings on Cu were synthesized by electrochemical method and the corrosion rate of PNDMA-SDS/PANI coated copper was found to be nearly 40 times lower than that which can be observed for uncoated copper in 0.5 M H_2SO_4 solution [24]. Electropolymerization of copolymers of aniline and o-phenylenediamine has been successfully attempted and its spectroelectrochemical characterization [25], degradation chemistry [26] have also been reported. In this work, we report the results on electrosynthesis of poly(aniline-co-o-phenylenediamine) on mild steel from aqueous oxalic acid bath using cyclic voltammetry technique. The copolymer film

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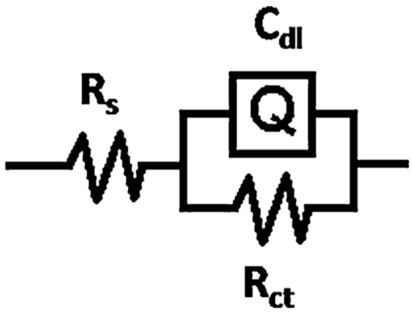

Fig. 1. Equivalent circuit for intact electrosynthesized films.

thus obtained was characterized by Fourier transform infrared spectroscopy (FTIR), UV–vis spectroscopy, TGA, SEM. Besides, the corrosion resistance of homo and copolymer films was studied.

2. Experimental

2.1. Materials

o-phenylenediamine (Merck Schuchardt, Germany) was purified twice by recrystallization from distilled water as described elsewhere. Aniline, Oxalic acid and Anhydrous sodium chloride were supplied by SD-Fine chemicals, Mumbai. All the solutions were prepared using Millipore double distilled water (resistivity 18.2 MΩ cm^2).

2.2. Electrosynthesis of homo and copolymers

Commercial steel sample of 1 cm^2 area with the elemental composition of C-0.1, Mn-0.45, S-0.035, P-0.06, Si-0.01, Al-0.05, Cu-0.2, and Fe-balance, was used. Before each experiment, the steel electrodes were polished using 1/0 to 4/0 grade emery papers sequentially and degreased with acetone. An electrolyte solution of 0.3 M oxalic acid + 0.2 M aniline + 0.05 M o-phenylenediamine was used for electrosynthesis of copolymer. The deposition of homo and copolymer films on steel electrodes was carried out by cyclic-voltammetry technique by scanning potential between −0.5 and 1.4 V vs SCE for 15 cycles with a scan rate of 10 mV s^{-1}. All the experiments were carried out using the electrochemical measurement unit (Solartron −1280B).

2.3. Characterization of homo and copolymers

2.3.1. FTIR spectroscopy

The FTIR spectra of electrosynthesized homo and copolymer films on mild steel were recorded using Nicolet 380 (Thermo, USA) FTIR instrument having ATR attachment.

2.3.2. UV–vis spectroscopy

The films of homo and copolymer films were scratched out and dispersed in NMP (N-methyl 2-pyrrolidone) solution. The absorption spectra were recorded by using UV–vis double beam spectrophotometer (Evolution 600, Thermo Scientific Ltd., USA).

2.3.3. Morphology studies

The morphology of the electrosynthesized homo and copolymer films deposited on steel was analysed using Hitachi (model S3000H) scanning electron microscope.

2.3.4. Thermal studies

The thermal gravimetric analysis of homo and copolymer films has been done using a thermal analyzer (STA, 1500), Polymer Laboratory, Thermo Science Ltd.

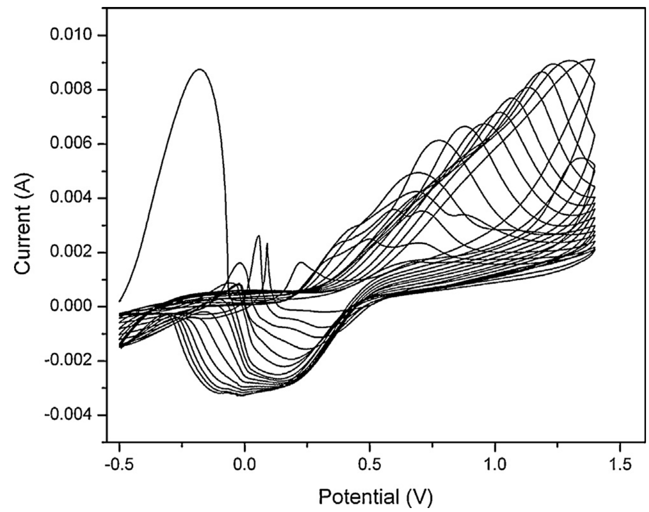

Fig. 2. Cyclic voltammograms of electrosynthesized PANI on steel surface.

2.4. Corrosion protection evaluation of electrosynthesized homo and copolymer films deposited on steel

2.4.1. EIS method

Zplot software was used for data acquisition of impedance measurements. AC signals of 20 mV amplitude of spectrum of frequencies from 10 kHz to 0.1 Hz were impressed to the coated steel at open circuit potential. From the Nyquist plots, the charge transfer resistance (R_{ct}) and the double layer capacitance (C_{dl}) values were calculated using ZsimpWin 3.21 software using the equivalent circuit (Fig. 1) where R_s is the solution resistance, R_{ct} is the charge transfer resistance and Q is the constant phase element of the double layer capacitance.

For the description of a frequency independent phase shift between an applied AC potential and its current response, a constant phase element (*CPE*) is used which is defined in impedance representation as

$$Z(Q) = Y_0^{-1}(j\omega)^{-n}$$

where Y_0 is the *CPE* constant, ω is the angular frequency (in rad s^{-1}), $j^2 = -1$ is the imaginary number and '*n*' is the *CPE* exponent ($n > 0$, for

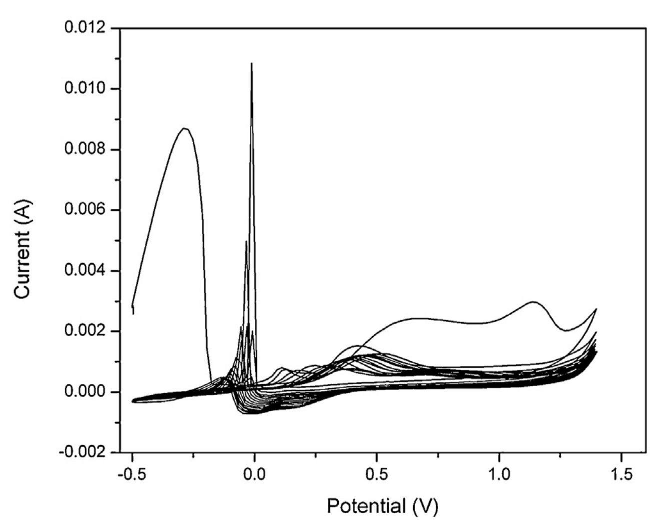

Fig. 3. Cyclic voltammograms of electrosynthesized PoPD on steel surface.