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Anticorrosive properties of electrosynthesized poly(*m*-aminophenol) on copper from aqueous phenylphosphonic acid solution

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ABSTRACT

Electropolymerization of *m*-aminophenol (MAP) on copper from aqueous phenylphosphonic acid (PPA) medium was achieved using cyclic voltammetry by applying three different scan rates namely 10 mV s^{-1}, 50 mV s^{-1} and 100 mV s^{-1}. Characterization of obtained poly(*m*-aminophenol) (PMAP) films were done by FTIR, SEM and AFM methods. FTIR data reveal the presence of C—O—C linkage in the polymer and suggest that monomer polymerized through –OH group. Corrosion performance of PMAP films was investigated in 0.1 M H_2SO_4 using potentiodynamic polarization and EIS methods. Results show that corrosion performance of PMAP films depends on the scan rate used for electrodeposition. It was found that for short immersion periods PMAP films synthesized at 50 mV s^{-1} scan rate (PMAP(50)) to have the highest performance, PMAP films synthesized at 10 mV s^{-1} (PMAP(10)) to have moderate protection performance and that of PMAP films synthesized at 100 mV s^{-1} (PMAP(100)) to have least corrosion performance. However for long immersion periods the order of the performance was found to be as PMAP(100) > PMAP(10) > PMAP(50).

1. Introduction

Thin polymeric films synthesized by electropolymerization of various compounds present diverse applications in advanced technology and corrosion control. Phenols and anilines have established a place in the field of electropolymerization [1–3]. 3-Aminophenol is a monomer containing both –OH and $–NH_2$ groups in non-interaction position. Electropolymerization of *m*-aminophenol was studied on Pt electrode in acetonitrile and methanol using $NaClO_4$ as supporting electrolyte [4] and from aqueous $HClO_4$ solutions [5]. Polymer films produced from either neutral non-aqueous or acidic aqueous solutions lead to the formation of C—O—C bond while $–NH_2$ groups are preserved. Oxidation and polymerization of 3-aminophenol on gold electrode in neutral medium was studied by Kennedy et al. From XPS analysis they recorded formation of etheric bonds [6]. However electropolymerization of 3-aminophenol on carbon graphite electrode using cyclic voltammetry in different pH conditions leads to formation of conducting polymeric films suggesting that polymerization occurs through the NH_2 group [7]. Electropolymerization of *m*-aminophenol by cyclic voltammetric method was also carried out on mild steel in basic alcoholic medium and surface analysis method indicates the presence of C—O—C polyoxide state as well as free amine groups [8]. Achievement of thin highly cross-linked poly(phenylene oxide) that contains retained amine surface functionality has been of high interest as a reactive pre-treatment for subsequently applied organic coatings [9]. We have also managed to synthesized poly(*m*-aminophenol) using cyclic voltammetric, chronoamperometric and chronopotentiometric methods on mild steel in alkaline hydroalcoholic medium. Corrosion performance of poly(*m*-aminophenol) films in 3.5% NaCl solution were also tested by potentiodynamic polarization and electrochemical impedance spectroscopy [10].

The aim of this work is to electropolymerize *m*-aminophenol in aqueous acidic solution on copper and investigate corrosion performance of polymer coatings, poly(*m*-aminophenol), in 0.1 M H_2SO_4 solution using potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

2. Experimental

2.1. Chemicals and apparatus

3-Aminophenol (MAP), phenylphosphonic acid (PPA) and other chemicals used in this study were all purchased from Aldrich Chemical Company. The chemicals are analytical grade and used without any further purification. In all electrosynthesis experiments an aqueous solution of MAP (0.1 M) and PPA (0.1 M) were prepared by

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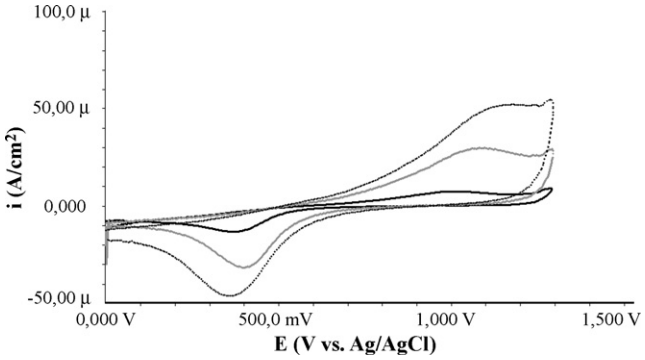

Fig. 1. Cyclic voltammograms of Pt electrode in solution containing 0.1 M PPA, (—) $\nu = 10\,mV\,s^{-1}$, (▬) $\nu = 50\,mV\,s^{-1}$, (. . .) $\nu = 100\,mV\,s^{-1}$ scan rates.

using ultra pure deionized water. All the experiments were carried out at room temperature and open to the atmosphere.

Electropolymerization and subsequent electrochemical studies were carried out in a conventional three electrode cell with Cu as working electrode, platinum wire as counter electrode and Ag/AgCl

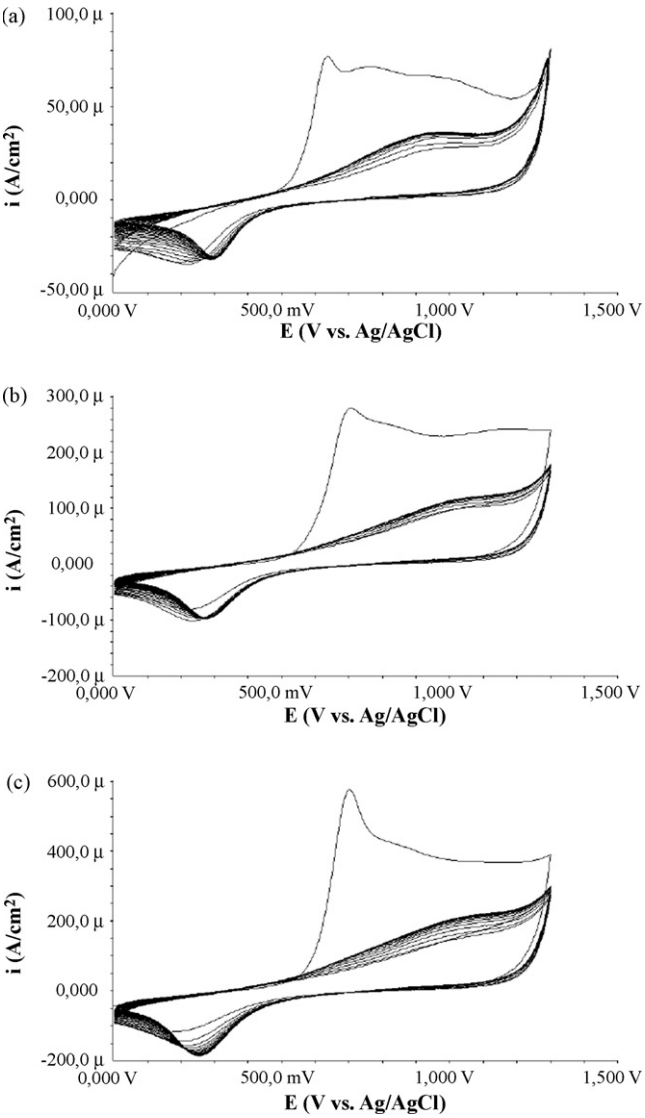

Fig. 2. Cyclic voltammograms of Pt electrode in 0.1 M PPA solution containing 0.1 M MAP (a) $\nu = 10\,mV\,s^{-1}$, (b) $\nu = 50\,mV\,s^{-1}$, and (c) $\nu = 100\,mV\,s^{-1}$ scan rates, 25 cycles.

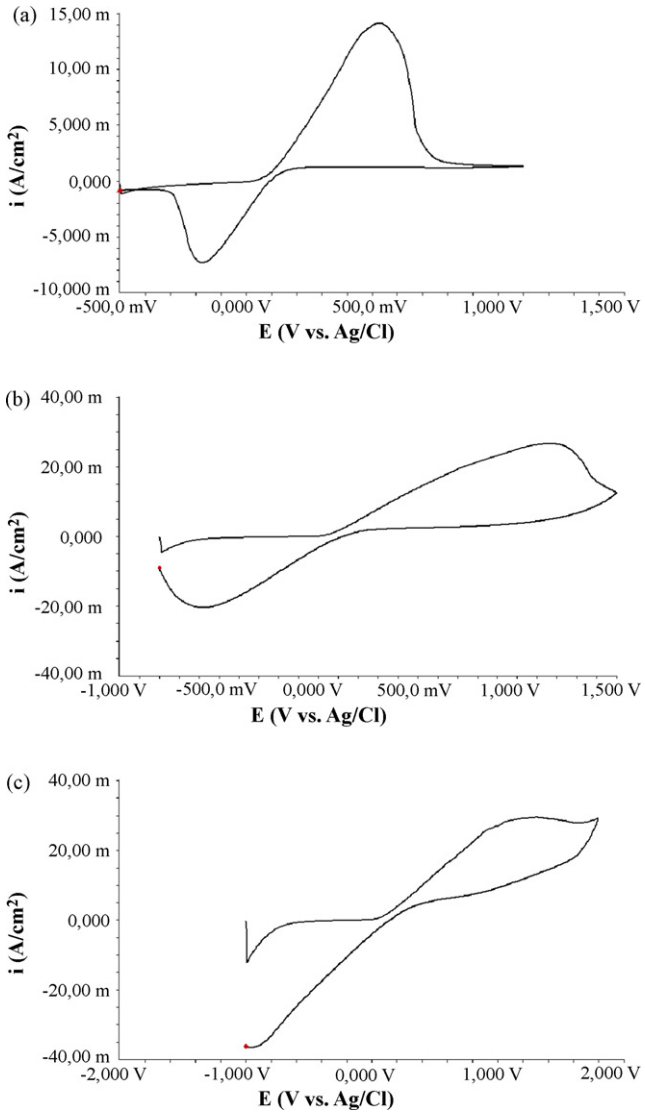

Fig. 3. Cyclic voltammograms of Cu electrode in solution containing 0.1 M PPA, (a) $\nu = 10\,mV\,s^{-1}$, (b) $\nu = 50\,mV\,s^{-1}$, and (c) $\nu = 100\,mV\,s^{-1}$ scan rates.

as reference electrode. All potentials given here are referred to this electrode. The working electrode was copper (99.98% purity) rod (with 3.5-mm diameter embedded in Teflon holder) or rectangular sheet (size ~10 mm × 20 mm and 0.5 mm thick). Rod and sheet electrodes were used in corrosion and AFM measurements, respectively. Prior to each electrochemical experiment copper electrodes were mechanically polished with abrasive paper (1200 grade) and cleaned in 1:1 acetone/ethanol mixture in an ultrasonic bath to remove impurities than rinsed with water and dried in air.

A Gamry PC3/600 potentiostat/galvanostat/ZRA system (Wilmington, USA) was used for electrosynthesis and corrosion studies. This system was interfaced to a personal computer to control the experiments and the data were analyzed using Gamry CMS-300 (version 5.30) framework/analysis software. The analysis of the impedance spectra was done by fitting the experimental results to equivalent circuits using ZSimpWin 3.21 software. The quality of fitting to equivalent circuit was judged by chi-square value.

2.2. Preparation of PMAP electrodes

The poly(*m*-aminophenol) (PMAP) films were synthesized by electropolymerization of *m*-aminophenol on Cu substrates from