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Corrosion protective poly(*o*-ethoxyaniline) coatings on copper

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Abstract

Poly(*o*-ethoxyaniline) (POEA) coatings were synthesized on copper (Cu) by electrochemical polymerization of *o*-ethoxyaniline in aqueous salicylate solution by using cyclic voltammetry. These coatings were characterized by cyclic voltammetry, UV–vis absorption spectroscopy, Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM). The performance of POEA as protective coating against corrosion of Cu in aqueous 3% NaCl was assessed by the potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The results of the potentiodynamic polarization and EIS studies demonstrate that the POEA coating has ability to protect the Cu against corrosion. The corrosion potential was about 0.330 V versus SCE more positive in aqueous 3% NaCl for the POEA coated Cu than that of uncoated Cu and reduces the corrosion rate of Cu almost by a factor of 140.

Keywords: Corrosion resistant coatings; Conducting polymers; Poly(*o*-ethoxyaniline); Electrochemical polymerization; Cyclic voltammetry; Copper

1. Introduction

Electrically conducting polymers have attracted a great deal of attention during last decade and even now, because of their unusual electronic properties. A number of potential device applications have emerged based on these materials, particularly in rechargeable batteries [1,2], sensors [3,4], electromagnetic interference (EMI) shielding [5,6], electrochromic display devices [7,8], smart windows [9], molecular devices [10], energy storage systems [11] and membrane gas separation [12]. Recently, conducting polymers have received considerable interest as corrosion protective coatings for oxidizable metals. It is now well established that the electrochemical polymerization is a simple and most convenient method for the synthesizing novel conducting polymers on metallic surfaces [13,14]. Mengoli et al. [15] was the first to examine the protective behavior of polyaniline on stainless steel and then in 1985, DeBerry [16] showed that the electrochemically synthesized polyaniline acts as corrosion protective layer on stainless steel in 1 M H_2SO_4. Since then, several research groups [17–21] have systematically investigated the electrochemical synthesis of various conducting polymers on oxidizable metals for corrosion protection purposes. The common feature of these investigations is that the electrochemical synthesis of conducting polymer coatings on oxidizable metals is preceded by the dissolution of the base metal at a potential lower than the oxidation potential of monomer. Thus, the oxidation of the metal appears as a simultaneous and competitive process at the potentials adequate for the formation of polymer. Hence, a successful electrochemical synthesis of conducting polymer coatings on oxidizable metals demands a careful choice of the solvent and/or supporting electrolyte and the establishment of electrochemical parameters, which will strongly passivate the metal without impeding the electropolymerization process.

Copper (Cu) is widely used reactive metal in electrical and electronic devices. It is rapidly replacing aluminum as the interconnect material of choice in integrated circuits, particularly microprocessors, because of its low resistivity and its improved electromigration performance [22]. Despite the fact that copper is noble, it readily corrodes in a variety of environments [23]. However, only very few studies [24–26] have been carried out on the corrosion protection of copper by conducting polymer coatings inspite of its use in wide range of technological applications. There are only two reports dealing with the

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direct electrochemical polymerization of pyrrole on pure Cu. Fenelon and Breslin [24] have successfully electropolymerized the pyrrole on Cu from a near-neutral sodium oxalate solution to generate a homogeneous and adherent polypyrrole films. It was observed that these films exihibit significant corrosion protection properties in acidified and neutral 0.1 M NaCl solution. Cascalheira et al. [25] recently reported the formation of strongly adherent polypyrrole coatings on Cu from an aqueous salicylate solution. In most of the other studies, the conducting polymers were first synthesized chemically and then deposited on the metal surface. For example, Brusic et al. [26] have deposited the films of polyaniline and its derivatives on Cu by spin coating technique and studied the corrosion protection properties as a function of the applied potential and temperature.

Our group has reported the electrochemical polymerization procedures to synthesize strongly adherent poly(*o*-anisidine) (POA) [27,28], poly(*o*-toluidine) (POT) [29] and poly(2,5-dimethylaniline) (PDMA) [30] coatings on Cu substrates. It was shown that these coatings have remarkable capability to protect Cu against corrosion. More recently, we have also synthesized the poly(anisidine-*co*-*o*-toluidine) coatings on Cu from aqueous salicylate solution using cyclic voltammetry and investigated the corrosion properties of these copolymer coatings in aqueous 3% NaCl [31]. It was found that the poly(*o*-anisidine-*co*-*o*-toluidine) coatings provide better protection for Cu against corrosion than corresponding homopolymer coatings. The corrosion rates of POA, POT and poly(*o*-anisidine-*co*-*o*-toluidine) (with feed ratio of *o*-toluidine as 0.5) coated Cu are found to be ∼9, 27 and 720 times lower than that observed for uncoated Cu. Further, the corrosion protection properties of the copolymer coatings are observed to depend on the feed ratio of *o*-toluidine used for their synthesis.

With the objective to search for new conducting polymers applicable for corrosion protection of oxidizable metals, we have made an attempt to synthesize strongly adherent POEA coatings on Cu substrates by electrochemical polymerization from aqueous salicylate medium and examined the ability of these coatings to serve as corrosion protective coatings on Cu. To the best of our knowledge, there are no reports in the literature dealing with the direct deposition of POEA coatings on Cu from aqueous salicylate medium.

2. Experimental

2.1. Materials

All chemicals were of analytical grade. The monomer, *o*-ethoxyaniline was procured from Fluka and it was doubly distilled prior to being used for the synthesis. Sodium salicylate ($NaC_7H_5O_3$) was procured from Merck and used as-received without further purification. Bi-distilled water was used to prepare all the solutions.

2.2. Substrate preparation

The Cu (99.98% purity) substrates (size ∼10 mm × 15 mm and 0.5 mm thick) were cut from a piece of Cu plate. The substrate were polished with a series of emery papers of different grit size (180, 400, 600, 800, 1200), followed by thorough rinsing in acetone and double distilled water and dried in air. Prior to any experiment, the substrates were treated as described and freshly used with no further storage.

2.3. Synthesis of POEA coatings on Cu

The POEA coatings were synthesized by the electrochemical polymerization of *o*-ethoxyaniline on Cu substrates from aqueous salicylate solution using cyclic voltammetry. The aqueous solution containing 0.1 M sodium salicylate and 0.05 M *o*-ethoxyaniline was used as the electrolyte for the synthesis of the coating. The electrochemical polymerization experiments were carried out using the set-up as described in our previous paper [28]. The cyclic voltammetric conditions were maintained using a SI 1280B Solartron Electrochemical Measurement System (UK) controlled by corrosion software (CorrWare, Electrochemistry/Corrosion Software, Scribner Associates Inc. supplied by Solartron, UK). The synthesis was carried out by cycling continuously the electrode potential between −1.0 and 1.8 V at a potential scan rate of 0.02 V/s. After deposition the working electrode was removed from the electrolyte and rinsed with double distilled water and dried in air.

2.4. Characterization of the POEA coating

The FTIR transmission spectra were recorded with a Perkin-Elmer spectrometer (1600 Series II, USA) in horizontally attenuated total reflectance (HATR) mode in the spectral range 4000–400 cm^{-1}. The UV–vis absorption spectroscopy study was performed ex situ in the wavelength range 300–1100 nm using microprocessor controlled double beam UV–vis spectrophotometer (Model U 2000, Hitachi, Japan). SEM images were recorded with a Leica Cambridge 440 Microscope (Cambridge, England, UK). The adhesion of the coating was determined by the standard sellotpe test (TESA-4204 BDF) which consists of cutting the coating into small squares, sticking the tape and then stripping it. The percentage adherence was calculated by taking the ratio of the number of the remaining adherent coating squares to the total number of the squares. The thickness of the coatings was measured by a conventional magnetic induction based microprocessor controlled coating thickness gauge (Minitest 600, ElectroPhysik, Germany). The error in the thickness measurements was less than 5%.

2.5. Evaluation of corrosion protection performance

The corrosion protection performance of the POEA coatings was evaluated in aqueous 3% NaCl solution by using potentiodynamic polarization measurements and EIS. For these measurements, a Teflon holder was used to encase the polymer coated Cu substrates so as to leave an area of ∼40 mm^2 exposed to the solution. All the measurements were repeated at least four times and good reproducibility of the results was observed.

The potentiodynamic polarization measurements were performed by sweeping the potential between −0.25 and 0.25 V