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Electrochemical synthesis and corrosion behaviour of poly (pyrrole-*co*-*o*-anisidine-*co*-*o*-toluidine)

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ABSTRACT

In this study, a ter-polymer film of pyrrole, *o*-anisidine and *o*-toluidine has been electrochemically synthesized on low carbon steel. The synthesis solution was aqueous oxalic acid containing 2:1:1 monomer feed ratio between pyrrole, *o*-anisidine and *o*-toluidine, respectively. The characterization of synthesized ter-polymer film was realized with help of UV–Vis absorption, Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM) and differential scanning calorimetry (DSC) techniques. The stability of this ter-polymer film as a coating material has also been investigated on steel, in 3.5% NaCl solution. Under such severe conditions, the ter-polymer film was found to exhibit low permeability against water ingress. It was able to exhibit protective coating behavior on steel, even after 72 h exposure time. The DSC results revealed that the ter-polymer film had better thermal stability with respect to single polypyrrole film. The synthesized ter-polymer film was completely different in aspect of morphology, stability and other structural properties when compared to single polypyrrole film. This highly stable and extremely thin (0.80 μm) film can find application for various purposes (anticorrosive, electrocatalytic, etc.), at where the stability of polypyrrole like films constitutes a drawback.

1. Introduction

The intense attention and research on conducting polymers have resulted with number of practical applications because of their distinct electronic properties, diversity, ease of fabrication and potentially low cost [1,2]. Electrochemical polymerization of conducting polymers is simple and most convenient method for preparation of a film on the metal surface [3]. Among the large number of polymers have been studied so far; polypyrrole, polyaniline and derivatives have gained prime importance. Since, they can be easily obtained on various oxidizable metals such as carbon steel, zinc, aluminum and copper.

There have been innumerous studies subjecting potential applications of conducting polymers for various purposes; corrosion protection, electrocatalysis, energy storage, sensors and microelectronics [4–11]. However, the required stability (mechanical, thermal) and efficiency may not be offered by simple conducting polymers, for specific purposes. This fact motivates the studies subjecting to develop new design polymeric materials with desired properties; co- and ter-polymer films have been studied for various purposes. Electrochemical synthesis of co- and ter-polymer films employing diverse monomers types offers effective solution to furnish physical–chemical properties [12]. In recently, Brole et al. have reported the preparation of a glucose oxidase electrode based on a ter-polymer of poly (aniline-*co*-anisidine-*co*-*o*-toluidine) [13]. Especially, low thermal stability of conducting polymer films is marked as considerable drawback for potential practical applications involving noteworthy temperature changes. For example, fuel cells necessitate materials (bipolar plates) with high stability at elevated temperatures and good electrical conductivity, as much as catalytic efficiency; anticorrosive coatings for outdoor conditions [14,15].

Owing to its good conductivity and ease of synthesis, polypyrrole has long been marked as one of the most promising polymers [16], while polyaniline and derivatives are frequently emphasized with high stability [17]. In the Literature, poly (*o*-anisidine) film on copper has been reported to protect copper successfully against corrosion under severe conditions [18]. Also, poly (*o*-anisidine) has higher solution processability, with respect to other aniline family polymer films. As well, another aniline derivative coating poly (*o*-toluidine) has been performed on copper and reported to provide significant protection efficiency against copper corrosion in chloride media [19]. Another study reported electrosynthesis of poly (pyrrole-*co*-N-methyl pyrrole) on steel, which showed better quality coating properties with respect to single polypyrrole and poly (N-methyl pyrrole) films [20]. The studies aiming to improve the quality of conducting polymer coatings are still favourable, as a result of extensive potential application area. In this

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study, the electrosynthesis and characterization of a ter-polymer film consisting of pyrrole, *o*-anisidine and *o*-toluidine was aimed. Oxalic acid solution has been chosen as the electrolyte for the deposition of ter-polymer in view of the results reported in the Literature. This solution medium was provided some advantages that conducting polymer films formation on the oxidizable metal surfaces as mild steel and copper. For example; mild steel interacts with the oxalate ions to form a passive layer of iron (II) oxalate prior to the formation of the polymer. This layer is strongly influenced by the electrochemical parameters of deposition [9,19,21].

The synthesized ter-polymer film was characterized by FT-IR, UV–Vis spectroscopy. It was also examined by electrochemical techniques, thermal stability and protective behavior against steel corrosion.

2. Experimental

Mild steel (W%: 0.082 C, 0.621 Mn, 0.181 Si, 0.0129 P, 0.0162 S, and Fe) samples were cylindrical rods measuring 0.40 cm in the radius, with the working surface area of 0.5024 cm^2. The isolation of the rest surface area was provided with thick polyester coating. The electrochemical cell was consisted of a platinum counter electrode (2 cm^2 surface area), Ag/AgCl reference electrode and the working electrode. The chemical substances (sodium chloride, oxalic acid, pyrrole, *o*-anisidine, and *o*-toluidine) were purchased from Merck. The monomer reagents were freshly distilled before use. The mild steel sample surface were polished with abrasive papers (600–1200 grade), prior to coating procedure.

The ter-polymer coatings were electrochemically synthesized by cyclic voltammetry technique on mild steel electrodes, under 20 ± 1 °C temperature conditions and open to the atmosphere. All the electrochemical measurements were realized with CHI604 model electrochemical analyzer. The composition of synthesis solution was 0.3 M $H_2C_2O_4$ + 0.05 M pyrrole + 0.025 M *o*-anisidine + 0.025 M *o*-toluidine, the ratio of pyrrole/*o*-anisidine/*o*-toluidine (2:1:1), the total concentration of monomers was constant; 0.1 M. The applied monomer ratio was determined after various attempts for obtaining a stable ter-polymer film on the working electrode. The thickness of ter-polymer film was measured to be 0.80 μm, with an ElectroPhysik product coating thickness measuring device which conforms the ASTM standards.

The Fourier transformed infrared (FT-IR) spectroscopic measurements were realized for polypyrrole, poly (*o*-anisidine), poly (pyrrole-*co*-*o*-anisidine), poly (pyrrole-*co*-*o*-toluidine) and poly (pyrrole-*co*-*o*-anisidine-*co*-*o*-toluidine) ter-polymer films. For this aim their pellets (KBr-pressed) have been prepared and the measurements were conducted with a Perkin-Elmer spectrum RX1 FT-IR system instrument. The characterization of each of sample in ultraviolet–visible (UV–Vis) region has also been examined with a Perkin-Elmer Lambda 25 UV–Vis spectrophotometer. For this purpose, the polymer films were dissolved in dimethyl sulfoxide (DMSO), with help of ultrasonic bath.

The morphology of the polymer films obtained was also illuminated with help of scanning electron microscopy (SEM) technique. Also, DSC measurement was performed at a heating rate 10 °C/min with a sample size of 5–6 mg, using a Perkin-Elmer Diamond Pyris Thermal Analyzer.

Electrochemical Impedance spectroscopy (EIS) and anodic polarization curves were used to investigate the corrosion performance of the ter-polymer in aqueous 3.5% NaCl solution. The EIS measurements conducted at instantaneously measured open circuit potential values, in a frequency range of 1 m Hz −100 K Hz, using the amplitude 7 mV. The anodic polarization curves were recorded in anodic direction, with 2 mV/s scan rate, after 2 h of immersion time to corrosive solution for reaching the steady state.

3. Results and discussion

3.1. Synthesis

Cyclic voltammetry technique has been utilized to investigate the oxidation behavior of employed monomers separately and together. The successive voltammograms recorded in pyrrole, *o*-anisidine and *o*-toluidine containing solutions are given in Fig 1. The typical oxidation – passivation behavior of MS appeared as broadened anodic peak starting at −0.6 V, during the first forward scans. This event is known to be related to iron dissolution leading to Fe(II) ions which provide surface passivation via forma-

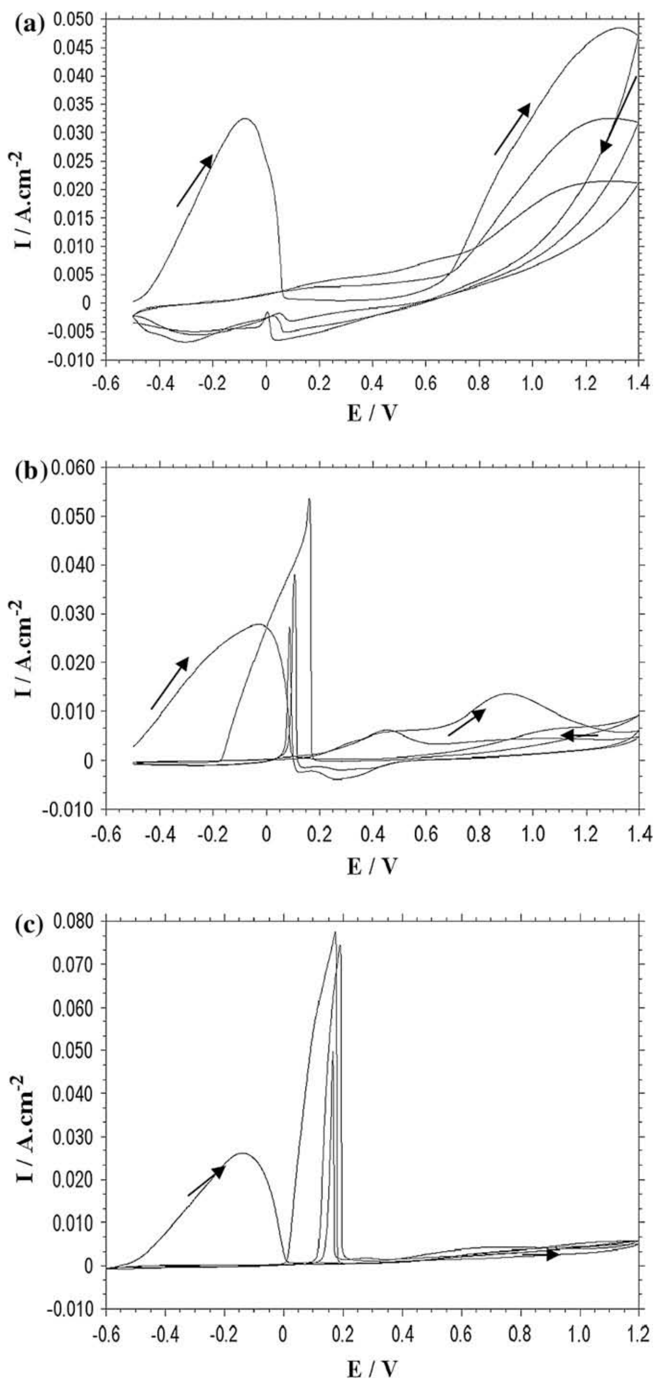

Fig. 1. The voltammograms recorded for MS electrode in (0.3 M oxalic acid + 0.1 M pyrrole) (a), (0.3 M oxalic acid + 0.1 M *o*-anisidine) (b) and (0.3 M oxalic acid + 0.1 M *o*-toluidine) (c), scan rate 50 mV/s.