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Electrochemical synthesis of poly(o-anisidine)/chitosan composite on platinum and mild steel electrodes

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ABSTRACT

In this study, poly(o-anisidine)/chitosan composite film was electrochemically synthesized on the platinum and mild steel electrodes. Electrochemical synthesis of the composite film was carried out by cyclic voltammetry technique. The synthesized composite film was characterized by FT-IR, UV–Vis, cyclic voltammetry, SEM and TGA. The SEM micrographs showed that the composite film homogeneously covered the surfaces of platinum and mild steel electrodes. The TGA results proved that the composite film does not degrade until 648 °C while the poly(o-anisidine) film is decomposed between 190 and 432 °C. Also, electrochemical studies showed that poly(o-anisidine) and the composite films have good stability and electroactivity.

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1. Introduction

Conducting polymers are called synthetic metals and they have similar properties of metals or semiconductors including electric, electronic, magnetic, and optical properties. However, the mechanical properties of these polymers are deficient [1]. These polymers can be synthesized either chemically or electrochemically as powder or a film [2–4]. The electrochemical synthesis is a simple, relatively not expensive and most convenient method for the preparation of a thin film. Also, electrochemical synthesis takes place directly on the metal surface [5].

Conducting polymer films are widely used in protection against corrosion, photoelectrochemistry, electroanalysis, electrocatalysis, biosensors, battery and materials science, electrochromic devices, capacitor, anti-static coatings, and electromagnetic shielding devices [6–12]. Polypyrrole, polyaniline and its derivatives are the substances which have been mostly studied in this area [13]. It was reported that the polymer films of aniline and aniline derivatives are known to have better environmental and thermal stability than other conducting polymer films [14,15].

Poly(o-anisidine) homopolymer film has good stability, electroactivity, and higher solution processability with respect to the other aniline family polymer films [16]. Recent studies show that poly(pyrrole-co-o-anisidine), poly(pyrrole-co-o-anisidine-co-o-toluidine) and poly(aniline-co-o-anisidine-co-o-toluidine) films have been synthesized by electrochemical method on mild steel and platinum electrode. Poly(pyrrole-co-o-anisidine) and poly(pyrrole-co-o-anisidine-co-o-toluidine) films show better protection for the corrosion of mild steel (MS) [17,18]. Poly(aniline-co-o-anisidine-co-o-toluidine) film on platinum electrode was used as glucose oxidize electrode [19]. Also, Dogru et al. prepared a poly(pyrrole-co-o-anisidine) coating on 3102 aluminum alloy from 0.1 M monomer (pyrrole and pyrrole:o-anisidine, 8:2) containing oxalic acid by using the cyclic voltammetry technique [20].

Chitosan has long been marked as one of the most promising natural polymers. This natural polymer is very interesting due to its chemical characteristics such as biodegradability, chemical inertness, biocompatibility and good film-forming properties [21,22]. Also, chitosan films are homogeneously prepared with high mechanical strength by chemical method [23]. Since chitosan film has very low electrical conductivity, it cannot be formed as a film on the metal surfaces via electrochemical way. Despite having good conductivity, the conducting polymer films are porous and their mechanical properties are relatively limited. Therefore, composites have been attempted by incorporating a rigid conducting polymer into chitosan to combine the good mechanical strength of chitosan and electrical conductivity of conductive polymer [22]. Because of these properties, conducting polymer/bio-polymer composites can be used as a supporting agent for sensor applications and material for removal fluoride ions from water [24,25].

In this study, poly(o-anisidine)/chitosan composite film was electrochemically synthesized in aqueous oxalic acid solution on the platinum and mild steel electrodes via cyclic voltammetry technique. It was aimed to obtain a film which is conductive and has

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good mechanical and thermal properties. The characterization of the composite film was carried out using CV, UV–Vis, FT-IR, SEM micrographs, and TGA techniques.

2. Experimental

The monomer o-anisidine was distilled before it was used. Chitosan with high molecular weight (75% deacetylated) was purchased from Aldrich. Electrochemical synthesis of the composite films was carried out by using cyclic voltammetry technique. All the electrochemical studies were carried out in a conventional three electrode set-up, open to the atmosphere, by using CHI 606 model electrochemical analyzer. The counter electrode was a platinum foil with 2 cm^2 surface area and Ag/AgCl electrode was used as the reference (all the potential values were referred to this electrode). Mild steel samples were cylindrical rods measuring 0.40 cm in the radius and with the following composition (wt.%) 0.082 C, 0.621 Mn, 0.181 Si, 0.0129 P, 0.0162 S, 99.0866 Fe, the working electrode was 0.5024 cm^2 while rest of electrode was masked with thick polyester block.

The synthesis solution was prepared by dissolving 0.2 g chitosan in 50 ml aqueous solution of 0.3 M oxalic acid and stirred for 24 h, and then 5 mmol o-anisidine (as monomer) was added to the final solution.

The solubility of the composite film was examined in various organic solvents: DMSO (dimethylsulfoxide), DMF (dimethylformamide), chloroform, NMP (N-methylpyrolidone) and THF (tetrahydrofuran).

The characterization of poly(o-anisidine)/chitosan composite film in ultraviolet–visible (UV–Vis) region was examined with a Perkin Elmer Lambda 25 UV–Vis spectrophotometer. For this purpose, the composite film was dissolved in dimethylformamide (DMF).

The Fourier transform infra-red (FT-IR) spectroscopic measurements were conducted with a Perkin Elmer spectrum RX1 FT-IR system instrument and KBr pressed pellets.

The morphological analysis of the composite films was investigated by using scanning electron microscopy (SEM) technique. Thermogravimetric analyses (TGA) of the samples were performed with DuPont 951 thermal analyzer under air atmosphere at a heating rate of 10 °C min^{-1} with a sample size of 5 mg.

3. Results and discussion

3.1. Synthesis

The successive voltammograms recorded for Pt electrode in chitosan, o-anisidine and chitosan + o-anisidine containing solutions were given in Fig. 1. The cyclic voltammogram of solution containing chitosan was given in Fig. 1a. It was observed that the oxygen gas evolution process was found to start at around +0.9 V. A chitosan film was not obtained on the platinum electrode (Fig. 1a) [26]. In the voltammogram of o-anisidine (Fig. 1b) and o-anisidine + chitosan (Fig. 1c) solutions, the o-anisidine monomer oxidation and composite formation process were observed beyond +0.6 V. The voltammogram of o-anisidine solution showed similar mode with voltammogram of o-anisidine + chitosan solution. But, the o-anisidine monomer oxidation peak was broader than the peak of composite film formation. It should be noted that the oxidation and reduction waves of poly(o-anisidine) and composite films were observed at 0.0–0.4 V.

Fig. 2 shows the cyclic voltammograms recorded during the film growth of poly(o-anisidine) (Fig. 2a) and composite (Fig. 2b) on the platinum electrode after three cycles. The synthesis of poly(o-anisidine) and the composite films were carried out by 20 cycles.

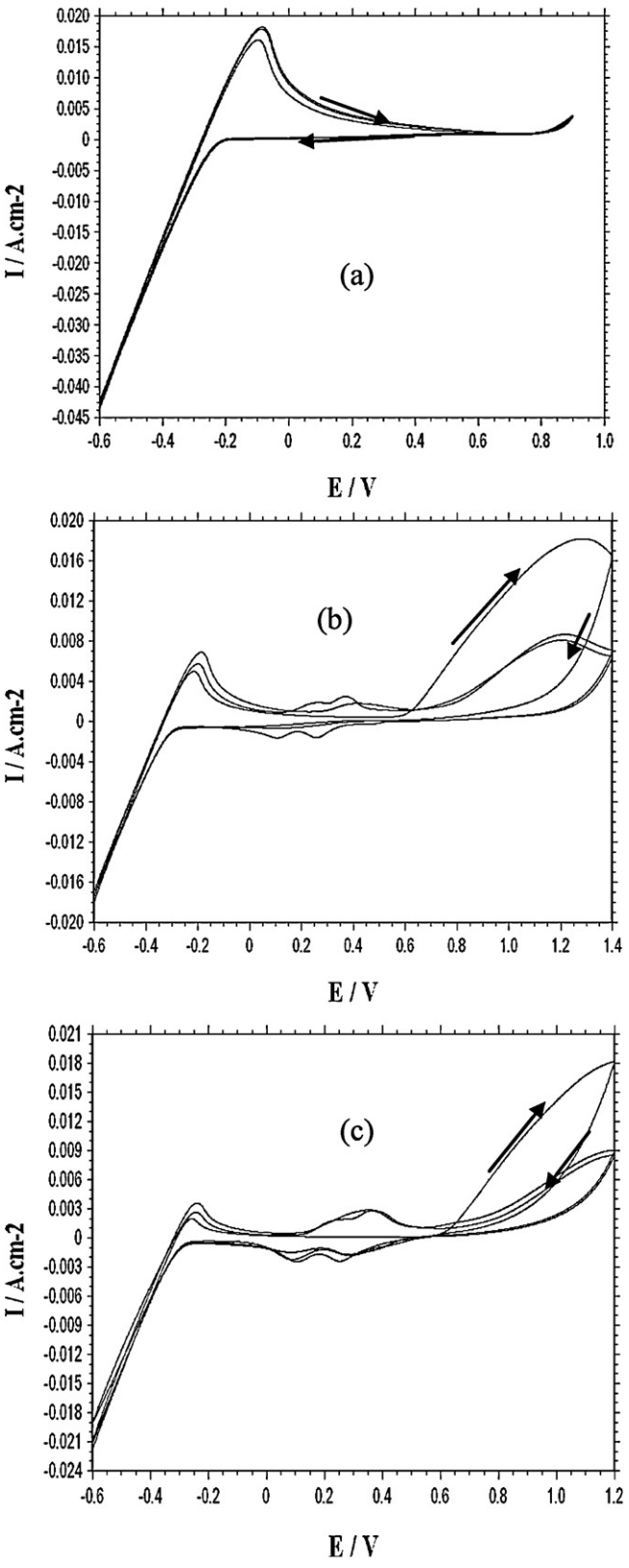

Fig. 1. The voltammograms recorded for Pt in oxalic acid solution of chitosan (a), o-anisidine (b), chitosan and o-anisidine (c), 50 mV/s.

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