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Electrochemical synthesis and characterization of poly(pyrrole-*co*-*o*-toluidine)

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ABSTRACT

The electrochemical polymerization of *o*-toluidine has been investigated in oxalic acid solution. It was shown that the oxidation of monomer could be achieved but this process does not yield a stable, homogenous polymer film on either platinum or mild steel electrodes. Therefore the copolymerization between pyrrole and *o*-toluidine has been studied as an alternative method for obtaining good quality coating (low permeability and water mobility, high stability), which could also be easily synthesized on steel. For this aim, various monomer feed ratio solutions of pyrrole:*o*-toluidine 9:1, 8:2 and 7:3 have been examined, in aqueous oxalic acid solution. By using cyclic voltammetry technique, copolymer films were realized on platinum and steel, successfully. The temperature of synthesis solution was found to have a vital role on polymerization and film growth, as much as the monomer feed ratio. The synthesis of homogenous copolymer film could only be achieved under ≤25 °C conditions with using the 9:1 ratio, while the 8:2 ratios could only produce stable films below 5 °C. As the amount of *o*-toludine increased the required temperature value decreased further, 7:3 ratio could only give a stable copolymer film below 2 °C. The characterization of deposited copolymer coating has been realized by using SEM micrographs, UV–vis and FT-IR spectroscopy techniques and cyclic voltammetry. The protective behaviour of these coatings was also investigated against mild steel corrosion in 3.5% NaCl solution, by means of electrochemical impedance spectroscopy (EIS) and anodic polarization curves. It was found that the monomer feed 8:2 ratio gave the most effective coating against the corrosion of mild steel.

1. Introduction

The studies aiming to develop conducting polymer films for various applications (electrochromic devices [1], photoelectrochemical devices [2], rechargeable batteries [3], sensors [4,5] and corrosion protection [6–9]) frequently involve structural modification of the polymer backbone to enhance the properties, e.g. incorporation of various functional groups changes conductivity and porosity. Polyaniline, polypyrrole and their derivatives have been regarded as the most important conducting polymers, owing to their stability and synthesis advantages [10,11]. The electropolymerization of aniline (and its derivatives) brings about some difficulties like slow nucleation and film growth, but its high stability and interesting electrochemical properties have attracted much attention [10]. On the other hand, polypyrrole films generally exhibit better conductivity and are more easily synthesized by electropolymerization, when compared to polyaniline [12,13].

The role of anticorrosive polymer coatings on oxidizable metals is to hinder the attack of corrosive environment and reduce the corrosion rate [14,15]. The conducting polymer films generally have nobler reduction potentials with respect to mild steel and this give rise to an interesting phenomena; the anodic protective effect of conducting polymer films. The protection comes from formation of more stable ferric compounds under oxidizing and stabilizing effect of polymer film [16–18]. On the other hand, the hydrophilic and porous nature of conducting polymer films lead to serious drawbacks for anticorrosive applications under severe conditions. The copolymerization has long been utilized to improve various properties (conductivity, stability, porosity, etc.) of polymer films [19]. The similar structural properties of pyrrole and aniline allow the copolymerization between these species. It was reported that this process undergoes exothermically. Li et al. have reported that copolymer film of pyrrole–toluidine (feed ratio of 3:7) could be realized at 2 °C temperature, with chemical synthesis technique [20].

Poly(*o*-toluidine) homopolymer film exhibit good stability. Vandana et al. have reported that electrochemically synthesized poly(*o*-toluidine) could protect copper against corrosion in chloride media, successfully [21]. However, the attempts aiming the electrosynthesis of poly(*o*-toluidine) film on mild steel surface have failed. This was attributed to slow nucleation and low surface coverage. Therefore the anodic oxidation of steel continues at monomer oxidation region and inhibits the formation of stable-adherent film on the surface. In order to obtain a film which combines the

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advantages of pyrrole (ease of synthesis and conductivity) and *o*-toluidine (low permeability and high stability), poly(pyrrole-*co*-*o*-toluidine) coating have been electrosynthesized on mild steel. The copolymer films were characterized by FT-IR, UV–vis spectroscopy, cyclic voltammetry measurement and SEM micrographs. The corrosion behaviour of poly(pyrrole-*co*-*o*-toluidine) copolymer was investigated in 3.5% NaCl solution.

2. Experimental

All the electrochemical studies were carried out in a conventional three-electrode set up, open to the atmosphere, by using CHI604 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 (*W*%) 0.082, C; 0.621, Mn; 0.181, Si; 0.0129, P; 0.0162, S; 99.0866, Fe, the working are 0.5024 cm^2 while rest of electrode was isolated with thick polyester block.

The copolymer films were electrochemically synthesized by using cyclic voltammetry technique. The synthesis solution (all chemicals were purchased from Merck) composition was 0.1 M oxalic acid +0.1 M monomer, varying the ratio pyrrole:*o*-toluidine (9:1, 8:2, 7:3) but keeping constant the total concentration of monomers. Each monomer feed ratio was studied for a set of temperatures, then the most appropriate values were determined and applied, these temperatures were 25, 5 and 2 °C for 9:1, 8:2 and 7:3 monomer feed ratios, sequentially. These temperatures were yielding stable copolymer films on mild steel surface. The solution of 8:2 monomer feed ratio did not give a stable polymer film above 5 °C, while the ratio of 7:3 involved lower temperature like 2 °C. There was a monomer oxidation which was observed as current increase, but this process could not lead to a sufficiently thick and homogenous film. The thickness of coatings was approximately the same, by balancing the CV numbers and passing charges within monomer oxidation potential regions. The applied charge density value was 1.17 C/cm^2 for each sample.

UV–vis spectra of the copolymer solution in dimethyl sulfoxide (DMSO) were recorded on a PerkinElmer Lambda 25 UV–Vis spectrophotometer. FT-IR spectra measurements were conducted using a PerkinElmer spectrum RX1 FT-IR system instrument. For this aim, the polymer coatings electrosynthesized on mild steel were peeled off the surface and their pellets were prepared with bulk KBr. Electrochemical impedance spectroscopy (EIS) and anodic polarization curves were used to investigate the corrosion performance of these coatings.

3. Results and discussion

3.1. Synthesis

Fig. 1 shows the cyclic voltammograms recorded for platinum (Pt) electrode in 0.3 M oxalic acid +0.1 M *o*-toluidine (at 25 °C) by

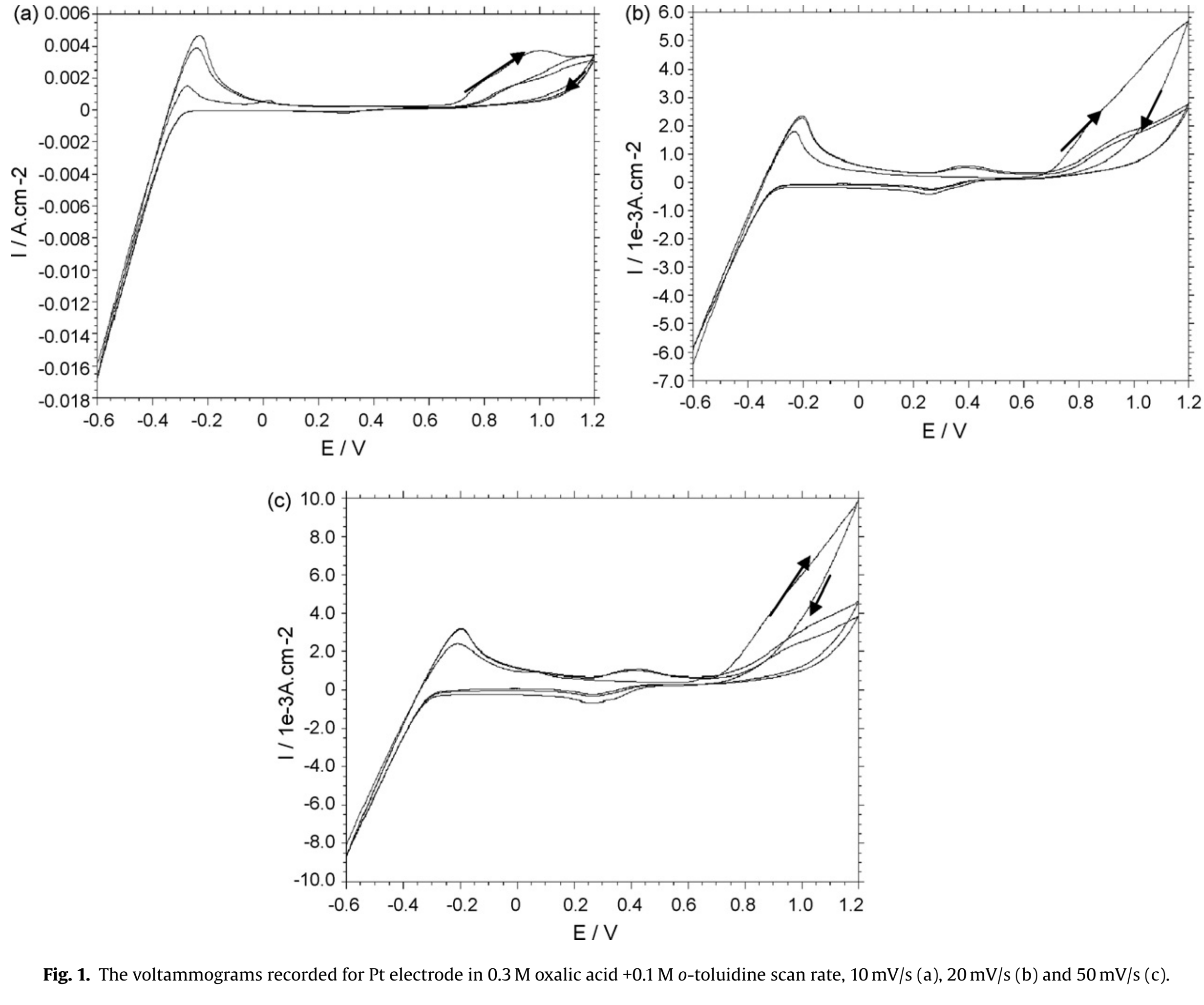

Fig. 1. The voltammograms recorded for Pt electrode in 0.3 M oxalic acid +0.1 M *o*-toluidine scan rate, 10 mV/s (a), 20 mV/s (b) and 50 mV/s (c).