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Effect of saccharin addition on the corrosion resistance of polypyrrole coatings

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ABSTRACT

Electropolymerization baths for polypyrrole coating typically consist of two main constituents: monomer and counter-ion. By adding saccharin as the third constituent, a new branch emerges in electropolymerization that will yield coatings with modified properties. In the present study, polypyrrole is galvanostatically deposited onto carbon steel in an aqueous solution containing 0.2 M pyrrole and 0.1 M oxalic acid as the supporting electrolyte with (0.25, 0.5, 2.5 g/l) and without saccharin addition. Determination of the corrosion resistance of coatings in 0.1 M NaCl solution shows that in the presence of 0.5 g/l saccharin, a more noble corrosion potential and a greater corrosion resistance are obtained. Electrochemical impedance spectroscopy (EIS) revealed that the corrosion process was under infinite diffusion control of ions during prolonged immersion. The results indicate that the lower diffusion rate of ions in the coating produced in the presence of 0.5 g/l saccharin is responsible for its better corrosion resistance. Atomic force microscopy (AFM) shows that greater compaction of the coating produced in the presence of 0.5 g/l saccharin could be the reason for its higher corrosion resistance.

1. Introduction

Protective coatings on active metals represent one of the most promising applications of conductive polymers since the work of DeBerry [1]. He reported on the catalytic ability of polyaniline in forming a passive oxide layer on stainless steel in perchloric acid solution. Many studies have been conducted on pyrrole electropolymerization because of its high conductivity, stability, and ease of synthesis. Electropolymerization of pyrrole was first performed in organic solutions [2–5]. Its disadvantages (toxicity, high inflammability, and high cost), however, led investigators to study electropolymerization in aqueous solutions [6–11].

Beck et al. [9] reported that strongly adherent and smooth polypyrrole (PPy) coatings on steel could be obtained by electropolymerization in oxalic acid solutions. Su and Iroh [10] examined the effect of electrochemical process parameters on the properties of PPy coatings produced from aqueous oxalate solutions onto carbon steel. They reported that coherent, smooth, tough, and strongly adherent coatings are obtained in low-pH media at low current densities, while brittle and poorly adherent coatings are generally obtained in alkaline solutions at high current densities [11]. The authors also investigated the effect of benzene sulfonate counter-ion concentration and reported that smoother and more compact PPy coatings formed at lower electrolyte concentrations while, at higher concentrations, the deposit became spongy and porous [11].

One of the desirable properties of PPy is its reversible oxidation/reduction behavior. During polymerization, an oxidized form of the polymer forms on steel due to ion doping (ex. oxalate ion). In contrast, when PPy-coated steel is immersed in an aggressive solution, PPy reduction is caused by the release of counter-ion [12]. Progression of this process leads to passivation of the underlying metal substrate. The passive layer consists of a metallic or a complex oxide on steel surface [13–17]. Therefore, PPy coating not only shifts the corrosion potential of the substrate surface anodically [15,18,19] but can also act as a barrier coating by hindering the transport of cathodic or anodic agents towards the metal substrate [20,21]. The degree of corrosion protection afforded by the coating depends on both structural and electronic properties. Many attempts have been made to optimize the protection efficiency of these coatings [22–27].

Tuken et al. [24] electropolymerized a top polyaniline coat onto a thin PPy primer coating from $LiClO_4$ in acetonitrile (ACN) solutions to produce a more compact coating with low-permeability against the removal of doping anions from pores. Tamer et al. performed energy-dispersive X-ray analysis of electropolymerized sulfonated PPy (SPPy) films produced on Pt and confirmed the incorporation of covalently bonded sulfonate groups in the polymer films [25].

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Hur et al. [26] electropolymerized an adherent and homogeneous SPPy film onto stainless steel from a fluorosulfonic acid (FSO_3H) in acetonitrile solution. They reported that SPPy prepared at lower FSO_3H concentrations could provide much better protection than those prepared at higher concentrations. The film could also inhibit the pitting corrosion of stainless steel [26].

Bazzaoui et al. [27] reported successful electropolymerization of homogeneous PPy films in alkaline aqueous solutions of sodium saccharinate. X-ray photoelectron spectroscopy of the elemental composition of PPy coatings confirmed the presence of sulfonyl groups ($-SO_2-$) and oxidized sulfur in the coatings. The authors proposed that residual corrosion products themselves constitute a physical barrier against electrode dissolution.

The use of additives in aqueous electrodeposition solutions is extremely important because of interesting and important effects on growth and structure of deposits, including brightening of the deposits and reducing their grain size, stress and pitting corrosion. The striking effects of low concentrations (10^{-4} to 10^{-2} M) of additives on electrodeposition processes point to their adsorption on a high-energy surface and on growth sites. Consequently, this has a poisoning or inhibiting effect on the most active growth sites [28]. To suppress the growth of existing grains, addition of an organic inhibitor such as saccharin (benzoic acid sulfimide, $C_7H_5NO_3S$) to the electrolyte has been a common practice in modifying the electrodeposition of metallic coatings [29]. The additive acts as a grain refiner because of its effect on electrode kinetics and structure of the electrical double layer at the plating surface [30]. It was recently demonstrated that saccharin addition improved the structure of electroless Ni–Cu–P deposits on an Al substrate. It was also reported that a lower concentration of additive had a greater influence [31]. Additives are usually consumed in decomposed products and incorporated in the deposit. For example, the possible decomposed products of saccharin include benzamide, toluene, and *O*-sulfamidobenzoic acid [28].

The major interest shown by authors in the literature is focused on the effect of electrochemical parameters and chemical composition of the bath in modifying the polypyrrole coatings. This work is devoted to evaluate the effect of saccharin on the corrosion behavior of polypyrrole coatings. For the purposes of the present study, adherent PPy coatings were electropolymerized from an aqueous oxalic acid solution with and without saccharin addition. The coatings were characterized and their corrosion resistance examined in 0.1 M NaCl solution in terms of their open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS) measurements.

2. Experimental procedures

The chemicals used in this study were purchased from Merck. Pyrrole was distilled before use. The electrochemical process was carried out in a conventional cell with three electrodes. A platinum rod was used as the auxiliary electrode and saturated calomel as the reference electrode. Mild steel was used as the substrate, prepared in square sheets with an area of 6.9 cm^2 to be suitable for characterization. One side of each specimen was connected to an insulated wire and then mounted in epoxy resin. Samples were mechanically polished using abrasive paper down to 1200 grit, degreased by stirring in tetrachloroethylene for approximately 30 min, washed in ethanol and then in distilled water, and finally dried in warm air.

The bath contained initially pyrrole monomer and oxalic acid at concentrations of 0.2 and 0.1 M, respectively, in double-distilled water. Electropolymerization of pyrrole onto mild steel was performed galvanostatically at a current density of 2 mA/cm^2 using an EG&G potentiostat/galvanostat (model 263A). In order to produce a constant coating thickness, the electropolymerizating charge, which corresponds to the positive potential plateau, was kept constant at 4.6 C/cm^2. In this case, the thickness of dry films was around 15 μm as measured by Elcometer thickness meter (model no. 456). Coating was carried out in solutions with (0.25, 0.5 and 2.5 g/l) and without saccharin addition. Each coating was rinsed with double-distilled water and methanol followed by drying in a stream of warm air.

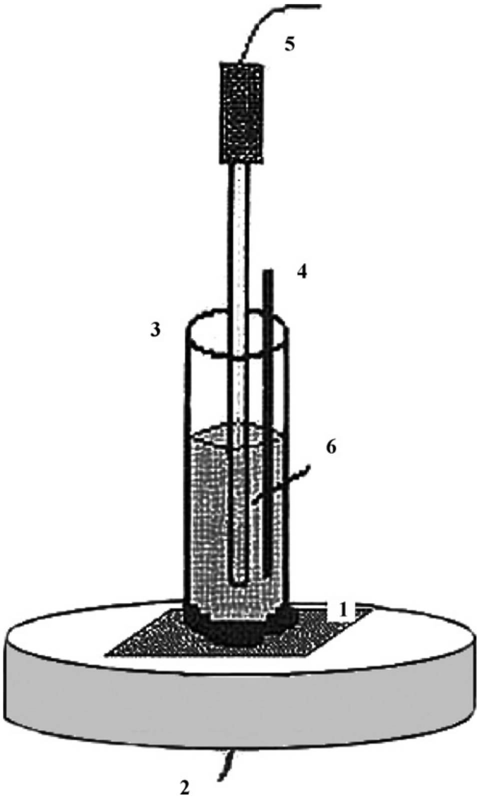

Fig. 1. Electrochemical test cell: (1) PPy coating samples, (2) electrical wire joint, (3) glass tube, (4) platinum rod supporting electrode, (5) SCE reference electrode and (6) test solution.

To mark off a smaller working area for corrosion experiments, a glass tube of approximately 2.5 cm^2 in area was fixed onto coated samples using a sealing adhesive binder. The glass tube was filled with 0.1 M NaCl solution and used as a corrosion cell. The auxiliary and reference electrodes were placed inside the cell as shown in Fig. 1. This assembly was used for OCP and EIS readings.

AC impedance measurements were carried out using an EG&G model 1025 frequency response analyzer coupled to the potentiostat/galvanostat. The voltage amplitude was 5 mV with respect to the open circuit potential. Impedance values were recorded in the frequency range from 100 kHz to 10 mHz. Nyquist and Bode phase diagrams of impedance spectra were plotted and analyzed using the ZVIEW program to estimate the parameters of electrical equivalent circuits.

Elemental analysis of various coatings, scraped from their steel substrates, was performed on an Elementar vario EL II system. Atomic force microscopy (AFM) images were obtained using a model DME DS95-50 scanning probe microscope (Dual Scope C-26) in non-contact mode.