Role of supporting electrolyte on the corrosion performance of poly(carbazole) films deposited on stainless steel

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ABSTRACT

This work presents a comparative study of supporting electrolyte effect on the protection ability of poly(carbazole) films deposited on 304 stainless steel. Tetrabutylammonium, sodium and lithium perchlorate salts were used as supporting electrolyte in the investigation. Poly(carbazole) films were synthesized by electropolymerization of carbazole using cyclic voltammetry from acetonitrile medium containing monomer and supporting electrolyte. Protective properties of poly(carbazole)s were investigated in 1 M H_2SO_4 solution using E_{ocp}–t curves, Tafel polarization and electrochemical impedance spectroscopy. Corrosion test results revealed that supporting electrolyte affects conductivity of deposited films. Poly(carbazole) synthesized from tetrabutylammonium perchlorate exhibited better protection performance than the other poly(carbazole)s.

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1. Introduction

Iron and its alloys are widely used in many applications and diversity of these applications have intensified the researches relating to enhancement of corrosion resistance of iron based metals in various neutral or aggressive environments [1–7]. Protection of these metals against corrosion by using polymeric coatings has been subject of the many studies [1,3,4,8–11]. Lately, it has been reported in literature that stainless steels are utilized in proton exchange membrane fuel cells as metallic bipolar plates due to their high electrical conductivity, acceptable material cost and high strength properties [12–19]. Conducting polymer coatings, especially poly(pyrrole) and poly(aniline) have been deposited on stainless steel bipolar plates in order to improve its corrosion resistance [14–16]. In the past decade researches are focused to develop new conducting polymer coatings for corrosion control of various metals [20–24].

Conducting polymers have attracted considerable interest as advanced materials and sometimes these materials can be called as "synthetic metals" due to their metallic like conductivities [25–27]. They have been proven to be efficient protective films against corrosion of metals since they produce a galvanic effect characterized as an anodic protection where the oxidizing power of the conducting polymer is able to set the metal in the passive state. This case is valid, in particular for iron and ferrous metals [28].

Poly(aniline), poly(pyrrole) and their derivatives have been regarded as the most important conducting polymers, owing to their stability and synthesis advantages [29–31] and they have been extensively studied for their synthesis, characterization and applications [32–34]. Recently, other classes of polymers like poly(carbazole) are gaining considerable attention due to its potential applications in electrochromic devices, sensors and rechargeable batteries. Electrochemical deposition of poly(carbazole) has been performed onto tin oxide coated glass, platinum and carbon fiber microelectrodes [35–38]. Although electropolymerization of substituted carbazole derivatives was introduced to the literature for the purpose of corrosion protection of stainless steel [39,40]; the use of poly(carbazole) as protective coating for the corrosion of active metals has not been reported so far.

The film forming ability of conducting polymers has been found to be more convenient through the electrodeposition process especially on metal surface and this approach has opened up another technologically important area of corrosion protection by conducting polymers [41]. Many properties of conducting polymers can be controlled by varying the characteristics of dopant ions [8]. Effect of doping ions on various properties (structure, electroactivity, crystallinity, thermal stability) of deposited polymer was demonstrated in an early investigation of poly(carbazole) film deposited on platinum electrode by means of selected two different electrolytes such as tetrabutylammonium perchlorate and tetrabutylammonium tetrafluoroborat [35]. Role of doping ions on the corrosion protection was explored for iron in NaCl solution by duplex type poly(pyrrole) films and it was shown that the doping anion has an influence on the protective performance of the polymer due to the permselectivity of the resulting film [28].

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In this work, apart from the doping anion, effect of counter cation of the dopant on the protective property of the resulting polymer was explored for the first time by means of poly(carbazole) films deposited on 304 stainless steel. Corrosion performances of the coatings deposited from lithium perchlorate, sodium perchlorate and tetrabutylammonium perchlorate electrolytes were examined in 1 M H_2SO_4 corrosive test solution.

2. Experimental

2.1. Materials

Carbazole (Cz, 95%) monomer, acetonitrile (ACN, 99.9%), electrolytes lithium perchlorate (LP, 99.9%), sodium perchlorate (SP, 98%), tetrabutylammonium perchlorate (TBAP, 99%) and other chemicals used throughout this study were purchased from Sigma–Aldrich Chemicals and they were used as received. Platinum sheet (99.99%) and Ag wire (99.99%) were also supplied from Aldrich as electrode materials whereas 304 stainless steel (SS) rods were obtained locally.

Electropolymerization and corrosion tests were performed at room temperature in single-compartment glass cell using three electrode configurations. Cylindrical type 304 stainless steel rod (0.6 cm in diameter) was mounted into a Teflon holder and used as working electrode. Before electropolymerization, the exposed steel surface (0.2827 cm^2) was mechanically ground with different grit abrasive papers (800–1200) by Forcipol 1 V grinder/polisher; subsequently ultrasonically cleaned in 1:1 (v/v) acetone/ethanol mixture to remove residues, then rinsed with acetonitrile and freshly used. Platinum sheet with 2 cm^2 surface area and Ag wire were used as counter and pseudo reference [37] electrode, respectively. In corrosion studies Ag/AgCl (3 M KCl, Gamry) electrode was used as the reference electrode.

2.2. Instruments

Electropolymerization and corrosion studies were carried out using a computer controlled Gamry Reference 600 potentiostat/galvanostat/ZRA system with Gamry Framework/Echem Analyst (Version 5.50) software. Morphologies of the polymer coated stainless steel surfaces were investigated via Jeol-JSM 5600LV model scanning electron microscope (SEM).

Thickness values of the produced films were determined by a conventional magnetic induction based microprocessor controlled coating thickness gauge (ElektroPhysik, Minitest 730 FN 1.5) coating thickness gauge. Conductivity measurements of the polymer coated samples were conducted by means of conventional four-probe method (Keithley 2400 multimeter). The analysis of the impedance spectra and fitting of the experimental results to equivalent circuits were performed by using ZSimpWin (Version 3.21) software from the Princeton Applied Research. The quality of fitting to equivalent circuit was judged firstly by the chi-square value (χ^2, i.e. the sum of the square root of the differences between theoretical and experimental values) and secondly by comparing the experimental data with the simulated data.

2.3. Coating process

The polymerization solution containing 0.01 M Cz and 0.1 M supporting electrolyte (TBAP, SP and LP) was prepared by using ACN as solvent. Different cyclic voltammetric synthesis parameters (potential range, scan rate and cycle number) were tested and optimized conditions were applied for the poly(carbazole) (PCz) synthesis in order to find out the effect of the supporting electrolyte on the nature of the resulting PCz film. The PCz films were electro-chemically synthesized by cyclic continuously the electrode potential between +0.3 V and +1.4 V (vs Ag) at 50 mV/s scan rate by applying 10 cycles. After electrodeposition of the PCz films, polymer coated electrodes (SS/PCz) were removed from the polymerization medium and immersed in ACN to remove adsorbed electrolytes and dried at room temperature before the corrosion tests.

2.4. Corrosion tests

Corrosion tests of PCz coated and uncoated steel electrodes were carried out in aerated 1 M H_2SO_4 solution by open circuit potential–time (E_{ocp}–t) curves, Tafel polarization and electrochemical impedance spectroscopy (EIS) techniques. The substrates were allowed to stabilize in the corrosive test solution for 30 min, prior to the anodic polarization and impedance measurements. Tafel polarization curves were recorded from −400 to +400 mV with respect to the open circuit potential at a constant scan rate of 1 mV/s. Impedance measurements were carried out at open circuit potential with the ac amplitude of 10 mV within the frequency range of 100 kHz–10 mHz.

3. Results and discussion

3.1. Electrochemical synthesis of PCz films on stainless steel

Electropolymerization of Cz has been carried out at optimum conditions, which have been deduced from the corrosion tests of PCz coated steel electrode prepared in presence of TBAP electrolyte by applying different cyclic voltammetric synthesis parameters (final potential, initial potential, scan rate and cycle number). Synthesis parameters giving the best protective PCz(TBAP) coating were applied to PCz synthesis for other supporting electrolytes.

Fig. 1 shows successive cyclic voltammograms corresponding to the electropolymerization of Cz from TBAP, SP and LP supporting electrolytes on the SS electrodes in the potential region between +0.3 and +1.4 V (vs Ag) with a scan rate of 50 mV/s by applying 10 cycles.

The monomer oxidation process was observed as current increase at around +1.1 V (vs Ag) in the first forward scan and the oxidation current value increased for the following cycles. This oxidation process leads to the formation of stable and homogeneous PCz film on the SS-304 surface from the forward scan of the first cycle. During repeated scans, reduction and oxidation peaks of the freshly produced PCz films were appeared as new cathodic and anodic broad redox waves at lower potentials. Reduction of the PCz films can be seen from the first reverse scans approximately at +0.9 V (vs Ag) potential; whereas the oxidation of PCz films can be seen from the second forward scans at around +0.8 V (vs Ag). These broad peaks also develop gradually due to the polymer growth on the SS-304 substrates. In all cases, stainless steel surface was coated with dark green and homogeneous PCz films.

3.2. Characterization of PCz films

The average thickness values of the synthesized PCz films were determined as 32.4, 33.5 and 34.6 (±0.3) μm for PCz(TBAP), PCz(SP) and PCz(LP) coatings, respectively. It is seen from these values that the difference between the thickness values of these coatings is approximately 1 μm and this small difference in the thicknesses can cause different corrosion performance of these coatings, as confirmed by the following corrosion test results. In other words, the thickness of the resulting polymer is affected by type of the supporting electrolyte used in polymer deposition process even if