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Electropolymerized bilayer coatings of polyaniline and poly(N-methylaniline) on mild steel and their corrosion protection performance

B. Narayanasamy [a,*], S. Rajendran [b]

[a] Department of Chemistry, Thiagarajar College of Engineering, Thirupparankunram, Madurai 625015, India
[b] Department of Chemistry and Corrosion Research Center, GTN Arts College, Dindigul 624005, India

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ABSTRACT

Polyaniline (PANI) and poly(N-methylaniline) (PNMA) have been electrodeposited on mild steel from oxalic acid bath using cyclic voltammetric technique. Pretreatments like passivation and primer polymer coatings were required for effective coating. Differently stacked composite polymer layers on the metal surface by layer-by-layer approach have also been obtained and their properties have been compared with their corresponding copolymer coatings. FTIR study confirms the formation of electroactive polymer compounds on mild steel. Evaluation of these coatings in 3.5% NaCl solution by potentiodynamic polarization and electrochemical impedance spectroscopy reveals significant corrosion resistant behavior. Relatively higher corrosion protection is exhibited by copolymer coatings and composite-bilayer coatings than the corresponding homopolymer coatings. The composite metal–PANI–PNMA layer shows higher stability and better protection than the metal–PNMA–PANI layer.

1. Introduction

Electrochemical synthesis of conducting polymers using active metals as electrodes has become a subject of multidisciplinary interest. Economically viable large-scale production of electroactive polymers using low cost metal-electrodes and corrosion protection of widely used active metals using electroactive polymer coatings are worth mentioning areas. A successful electropolymerization on active metals generally requires a passive layer to prevent the dissolution of the metal and at the same time to oxidize monomers into polymers. Sometimes, a primer polymer coating has also been needed to ensure a firm binding deposit onto the base metal. Polyaniline and polypyrrole and their derivatives have been widely investigated because of the low potential for polymer formation and easy preparation and stability of the formed films. Aqueous electrochemical polymerization has been preferred to give primer-base coatings on metals for obvious advantages. Electroactive polymer coatings have emerged as successful alternatives to harmful chromium based corrosion inhibitors in combating corrosion [1–11].

Bi- and multilayer coatings of conducting polymers have also been reported in the literature in recent times. Camalet et al. have electrosynthesized polyaniline on mild steel in a two-step process from aqueous electrolytes. The first step, which acted as a pretreatment of the surface, was the deposition of a thin polypyrrole (PPy) film, which could be achieved in less than 3 s. It was followed by the electrodeposition of a PANI film of controllable thickness. Bilayer systems are thus generated. They showed electroactivity in acidic electrolyte similar to that of PANI deposited on platinum, which indicates that the underlying oxidizable metal is fully protected [12].

Tüken et al. synthesized polyaniline on mild steel (MS) in acetonitrile–$LiClO_4$ for corrosion protection. Polyaniline film could not be obtained on mild steel by direct electrooxidation of aniline in $LiClO_4$ containing acetonitrile medium, because sufficient passivity of the surface could not be achieved. This non-passivated metal underwent intense dissolution, in potential region at which the monomer oxidation happened and this event prevented the formation of a stable polymer film on the surface. Therefore, the electrode surface was coated with very thin PANI, PPy primer coatings, in monomer containing aqueous oxalic acid solution and then the synthesis of top PANI film was achieved in aniline containing ACN–$LiClO_4$ successfully. The corrosion behavior of PANI\PANI and PPy\PANI coated MS samples was investigated in 3.5% NaCl solution. Anodic polarization curves and electrochemical impedance spectroscopy (EIS) techniques were mainly used. It was shown that PPy\PANI coating could provide much better protection for longer periods than PANI\PANI coating against the corrosion of MS. This behavior was explained with better barrier property of PPy\PANI [13].

* Corresponding author.
E-mail address: bnschem@tce.edu (B. Narayanasamy).

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Hasanov et al. [14] have studied on monolayer and bilayer conducting polymer coatings for corrosion protection of steel in 1 M sulphuric acid solution. In this study, monolayer PPy, PANI and bilayer PPy\PANI, PANI\PPy coatings were deposited onto steel electrodes by electropolymerization from 0.1 M monomer and 0.3 M oxalic acid solution. Bilayer coatings displayed better corrosion inhibition than monolayer coatings. Furthermore, the PPy\PANI coatings offered superior corrosion protection than the PANI\PPy coatings.

Tüken et al. have successfully synthesized polyindole on mild steel after giving a primer coating of polypyrrole in presence of oxalic acid solution by cyclic voltammetry technique. The corrosion performance of this PPy\PI coating was investigated in 3.5% NaCl solution by using anodic polarization and open circuit potential (E_{ocp})–time curves and electrochemical impedance spectroscopy (EIS). This coating exhibited excellent barrier efficiency for a long time (about 190 h) and it was also able to provide a certain anodic protection [15].

Gao et al. have carried out cyclic voltammetric and ac impedance studies on PPy–PANI bilayer films. Cyclic voltammograms of the bilayers showed additive properties of the individual polymers. The ac impedance studies of the bilayers showed that when PPy is the outer layer, oxidation of the inner PANI layer is mediated. The largest difference between the impedance plots of the PPy\PANI and PANI\PPy bilayers is observed at 0 V, where PPy already was in its conducting state but PANI first started to become oxidized [16].

Yağan et al. have carried out electrochemical synthesis of PNMA and poly(*N*-ethylaniline) (PNEA) coatings on mild steel in aqueous oxalic acid solutions by potentiodynamic synthesis technique. The effects of monomer and electrolyte concentrations on electrochemical growth of PNMA and PNEA coatings on mild steel substrates were investigated. Repassivation peak did not appear during electrosynthesis of PNMA and PNEA coatings from solutions containing 0.1 M monomer and 0.1 M electrolyte. The tests for corrosion protection of the polymer coated and uncoated mild steel substrates were done in 3% NaCl solutions by dc polarization and EIS techniques. Corrosion tests revealed that PNMA and PNEA coatings exhibited effective anticorrosive properties. The acidity of the polymerization solution was found to influence the anticorrosive behavior of the polymer [17].

Meneguzzi et al. have deposited electroactive poly(aromatic amine) films on mild steel from aqueous $HClO_4$ medium. The medium allowed passivation of the substrate followed by oxidation of the monomer. PANI film and poly(1,5-diaminonaphthalene) (poly(1,5-DAN)) film as well as their composite films with excellent adhesion properties were formed on mild steel [18].

Tan et al. have reported on corrosion protection on mild and stainless steels by multilayered coatings, consisting of combinations of the conducting polyaniline and polypyrrole. Potentiodynamic polarization was used to assess the ability of these copolymers to provide an effective barrier to corrosion in chloride environments. For mild steel the performance of these multilayered coatings on mild steel was not sufficiently better than for single PANI coatings to justify their more complicated deposition procedures. However, in the case of stainless steels the new multilayered coatings proved to be significantly better than previously reported single PANI coatings. It was found that the degree of protection was a function of the deposition-order of the bilayer system, with films consisting of a PANI layer over the top of a PPy layer yielding the best results. The results suggested that the ability of a conducting polymer film to act as electronic and chemical barriers was more important in providing corrosion protection than its ability to act as a physical barrier [19].

Tüken et al. have reported on the corrosion protection of mild steel by polypyrrole\polyphenol multilayer coatings formed by cyclic voltammetric techniques. The corrosion performance was investigated in 0.05 M H_2SO_4 solution by using electrochemical impedance spectroscopy, anodic polarization curves and open circuit potential (E_{ocp})–time curves. It was found that the multilayer coating could provide much better protection than the single PPy coating. It was proposed that the very thin PPhe film coated on top of PPy coating lowered the porosity and improved the barrier effect of the coating significantly [20].

Yağan et al. [21] have carried out the study on inhibition of corrosion of mild steel by homopolymer and bilayer coatings of PANI and PPy. The monomers were electropolymerized by potentiodynamic synthesis from their respective aqueous monomer solutions in the presence of oxalic acid. Characterization was carried out by cyclic voltammetric technique and corrosion behavior was studied by Tafel test and electrochemical impedance spectroscopy (EIS) techniques in various aqueous corrosive solutions. They have reported that PANI and PPy did not exhibit better combined corrosion resistant property than the individuals. PPy, a very good conducting polymer, exhibited the best corrosion resistant property.

Yano et al. [22] have studied on bilayer conducting polymer coating on iron for corrosion protection. They formed electrochemically a poly(2-*N*-phenylamino-4,6-dimercapto-S-triazine) (PPDT) layer first on an iron surface and then PANI layer next. They have observed the anti-corrosion ability due to a hybrid effect of the PANI–PPDT layers, which are individually noted for *in situ* oxidation and diffusion barrier behavior respectively.

Ananda Kumar et al. [23] have reported on anti-corrosion behavior of bilayer PANI–metal coatings formed cyclic voltammetrically on mild steel substrate. The corrosion resistant behavior was evaluated using potentiodynamic polarization and electrochemical impedance spectroscopic techniques. PANI–Zn was found to offer the maximum protection than Zn–PANI, PANI–Ni and Ni–PANI and mild steel–PANI offered the least.

Polyaniline has been electrodeposited on AA 7075 alloy and its corrosion protection ability has been studied by Tafel and impedance techniques in 1% NaCl. Pure polyaniline film was not found to protect the aluminium alloy due to galvanic interaction of polyaniline and aluminium surface exposed through pinholes and cracks. However, it was found that the corrosion resistance property of the polyaniline film can be substantially increased by post-treatment in cerium salt solution [24].

Infrared spectroscopy has been used in the literature to explain the chemical structure of the coating and the effect of substitution. It has been found that the adhesion of the coatings to the substrate depends on the electrodeposition parameters and the structure of the polymer.

There have been no reports at all on the synthesis of poly(N-methylaniline) as well as its composite-bilayer coating with polyaniline on mild steel. This paper reports a study on the electrodeposition of five sets of different conducting polymer coatings of aniline and N-methylaniline on pretreated mild steel and their corrosion resistant property by polarization and EIS techniques in a 3.5% NaCl solution.

2. Experimental

Mild steel was procured with the following percentage composition: C 0.140, S 0.026, P 0.060, Mn 0.401 and Fe rest. Samples of cylindrical discs with cross-sectional area of 0.5 cm^2 were used. Oxalic acid, aniline, N-methylaniline and sodium chloride used in this study for passivation, electropolymerization, characterization and evaluation were of AR grade chemicals. Electrochemical experiments were carried out using CHI-Electrochemical workstation with AC impedance (Model 660A). Surface polished and cleaned mild steel specimens were used as working electrodes in the conventional 3-electorde assembly having platinum foil