

# Polypyrrole modified nickel coating on mild steel

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## Abstract

Electrochemical synthesis of polypyrrole (PPy) film was achieved on mild steel (MS) which has been previously coated with various thicknesses of nickel coatings. Electrodeposition of nickel coating on MS was carried out galvanostatically and the PPy top coating was synthesized by using cyclic voltammetry technique, in monomer containing oxalic acid solutions. The corrosion performances of single nickel coating (with different thicknesses from 0.5 to 4  $\mu\text{m}$ ) and PPy top coated nickel coatings have been investigated, in 3.5% NaCl solution. For this aim, electrochemical impedance spectroscopy (EIS) and anodic polarization curves were used. It was shown that the PPy modified nickel coatings could provide much better protection for mild steel, for longer periods when compared to single nickel coating. The polymer film exhibited simple physical barrier behaviour on top of Ni layer and hindered the attack of corrosive species. It was also shown that the polymer film enhanced the protection efficiency and life time of nickel layer, by accelerating and stabilizing the formation of protective oxide layer.

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## 1. Introduction

Electrochemically synthesized conducting polymer coatings (polypyrrole, polyaniline, etc.) have long been investigated for their potential use against the corrosion of commercial metals. They are able to exhibit effective physical barrier behaviour against corrosive species (such as  $\text{O}_2$ ,  $\text{H}^+$  and  $\text{Cl}^-$ ) and provide anodic protection to metal, under various conditions [1–8]. However, some serious problems could arise in their practical use, because of the variety and complexity of corrosive environments. In order to improve their protection efficiencies and to obtain better quality coatings, their blends, composites and copolymers have been investigated. Also, their possible use as primary or top coating has been studied by various authors [9,10].

On the other hand, various metal coatings (nickel, chrome, zinc, etc.) have long been used successfully for protection of mild steel against corrosion. Especially, nickel coating has found wide application area, because it provides a surface that is resistant to corrosion and gives decorative appearance [11–14]. In general, 5–40  $\mu\text{m}$  thick Ni coating is applied for decorative purposes, but about 0.5  $\mu\text{m}$  thickness is usually sufficient under a top coat of chromium. On the other hand, electrochemical deposition technique is preferred for such thin Ni films and the quality of coating is strictly related to the porosity [15]. Because, the initiation and continuation of corrosion at the surface of underlying metal strongly depends on physical barrier efficiency of the coating against the attack of corrosive environment.

The objective of this study was to synthesize adherent and homogenous polypyrrole (PPy) film on nickel coated MS and investigate the possibility of this PPy modified Ni coating for the prevention of MS. For this aim, various thicknesses (0.5–4  $\mu\text{m}$ ) of nickel coatings

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were obtained on mild steel surface. Then, the synthesis of PPy top coating has been achieved on nickel coated MS electrodes. The corrosion performance of single Ni coated and PPy modified nickel coated MS were investigated, in 3.5% NaCl solution.

## 2. Experimental

All the chemicals were purchased from Merck; pyrrole was distilled before use and all the solution were prepared with bi-distilled water. The electrochemical cell is consisted of a three-electrode cell where the auxiliary electrode was a platinum sheet and a Ag/AgCl (KCl sat.) electrode was used as the reference. All the potential values are referred to this electrode. Mild steel samples were cylindrical rods measuring 0.47 cm in the radius and with the following composition (wt.%): 0.098 C, 0.35 Mn, 0.031 S, 0.017 P and 99.334 Fe. The working area was 0.694 cm<sup>2</sup> while the rest of electrode was embedded in a thick polyester block. The exposed surfaces were polished to a 1200 grit finish using SiC paper, degreased with 1:1 ethanol/water mixture and washed with bi-distilled water.

The electrodeposition of nickel (Ni) film was carried out from a bath with the following composition (by wt.%): 30 NiSO<sub>4</sub>, 1.0 NiCl<sub>2</sub>, 1.25 H<sub>3</sub>BO<sub>3</sub>; pH: 5.6–6.2. The thickness of Ni layer was controlled by monitoring the amount of passing charge for the deposition under 7 mA constant current. A nickel electrode with 0.64 cm<sup>2</sup> surface area (99.9% purity) was used as anode for the coating process was carried out open to atmosphere and under stirring conditions.

The PPy film was synthesized electrochemically by using cyclic voltammetry technique from monomer containing 0.3 M oxalic acid solution. Electrochemical impedance spectroscopy (EIS) and anodic polarization curves were used to investigate the corrosion performances of these coatings. The Nyquist plots recorded at instantaneous open circuit potential values, in a frequency range of 1 mHz to 100 kHz, the amplitude was 7 mV.

## 3. Results and discussion

The cyclic voltammograms recorded for mild steel (MS) and platinum (Pt) electrodes in monomer free and 0.1 M pyrrole containing oxalic acid solutions are given in Fig. 1. The peak potential values ( $E_p$ ) for oxidation–passivation (in the forward scan) and re-passivation peak (at the reverse scan) of MS were observed at –0.2 and +0.150 V, respectively. Oxygen gas evolution process was found to start at around +0.9 V on Pt electrode, where the same event could not be observed on MS electrode up to 1.40 V. But, the monomer

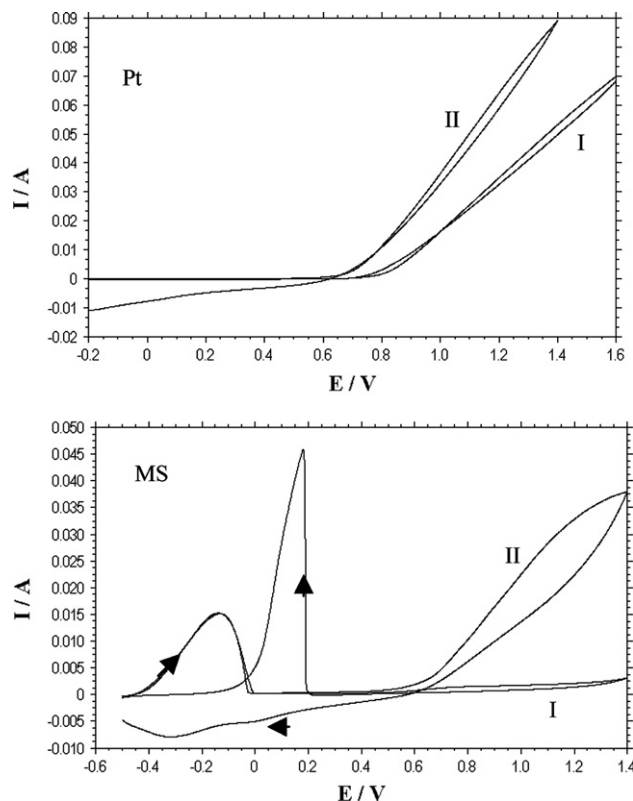
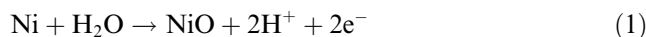


Fig. 1. Cyclic voltammograms recorded for Pt and MS electrodes in monomer free (I) 0.3 M oxalic acid solution and in presence of 0.1 M pyrrole (II), scan rate: 50 mV/s.

oxidation potential value on MS electrode was almost the same as it was on Pt electrode, +0.70 V. This event could not be identified as a well resolved anodic oxidation peak on either electrode, instead an insistent current increase was observed. It must be noted that the re-passivation peak disappeared in the first reverse scan due to the presence of freshly produced polypyrrole (PPy) film. Also, a cathodic reduction peak appeared at around –0.35 V (during the reverse scan), this was related to reduction of freshly produced PPy film.

Fig. 2 shows the voltammograms recorded for nickel coated MS (MS/Ni) electrodes in oxalic acid solutions, in the absence and presence of 0.1 M pyrrole. Regardless of the Ni thickness, the oxidation–passivation peak of electrodes was observed at around +0.10 V and the re-passivation peak disappeared.



$E = +0.20$  V (for studied conditions)



The charge amounts involved in oxidation–passivation process decreased regularly with increasing Ni coating thickness (Table 1).

Electrodeposited Ni film has a porous structure and this porosity plays an important role during the oxidation–passivation process. The underlying MS electrode

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