



ENGINEERING

# ELECTRODEPOSITION AND ANTI-CORROSIVE PROPERTIES OF POLYPYRROLE COATINGS ON STAINLESS STEEL

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## Abstract

Electrochemical deposition of polypyrrole coatings on stainless steel was carried out by the constant potential technique. This study will provide a better understanding of the corrosion protection mechanism of the polypyrrole coating. The structure of the coating was determined by using Reflection Absorption Infrared Spectroscopy (RAIR). The RAIR peaks ratios of the characteristic peaks were used to monitor the changes in the structure of polymer with respect to the process parameters. The change in corrosion current with process parameter was correlated with the extent of oxidation of the polymer. The mean roughness, rms roughness and the 3-D morphology of the coatings obtained from Atomic Force Microscopy (AFM) were used to correlate the surface energy changes of the coatings.

**Keywords:** Polypyrrole, Conducting polymer, Corrosion, Reflection Absorption Infrared spectroscopy (RAIR), Atomic Force Microscopy (AFM)

## Introduction

In recent years, intrinsic conducting polymers with conjugated double bonds have been attracted much attention as advanced materials. Among those conducting polymers, polypyrrole (PPY) is especially promising for commercial applications because of its good environmental stability, facile synthesis, and higher conductivity than many other conducting polymers. PPY can often be used as biosensors (Vidal et al. 1999), gas sensors (Kincal et al. 1998), wires (Jerome et al. 1999), micro actuators (Smela et al. 1999), antielectrostatic coatings (Gautron et al. 2003), electrochromic windows and displays, and packaging, polymeric batteries, electronic devices and functional membranes, etc. (Skotheim et al. 1998, Wallace et al. 1997). PPY coatings have an excellent thermal stability and are good candidate for use in carbon composites (Iroh et al. 1997). Furthermore, the electrochemical process parameters affecting the properties of the PPY coatings are also investigated (Su et al. 1998). PPY can be easily prepared by either an oxidatively chemical or electrochemical polymerization of pyrrole. However synthetically conductive PPY is insoluble and infusible, which restricts its processing and applications in other fields. The problem has been extensively investigated and new application fields have also been explored in the past several years. For example, PPY-based polymers can be used to load and release drugs and biomolecules (Reynolds et al. 1999).

The electrochemical generation of polypyrrole presents some other advantages with respect to the chemical methods of synthesis. It permits direct

grafting of the conducting polymer onto the electrode surface, which is of special interest for applications such as modified electrodes, batteries or protective coatings. Polypyrrole was examined in recent years by several different spectroscopic techniques with the aim to understand the chemical and electronic structure of the conducting polymers. In spite of considerable effort there is still some uncertainty about the structure of polypyrrole since extreme insolubility of polypyrrole in organic solvents hinder detailed structural analysis. Besides this, the actual structure of polypyrrole appears to be more complicated than the ideal structure. Thus, it is very important to obtain exact structural information for polypyrrole to clarify the relationship between the structure and physical properties such as electrical conductivity, mechanical property, thermal and environmental stability for developing and designing high-performance polypyrrole based polymers.

Conductive polymers can be synthesized chemically or electrochemically. Chemically synthesized polymer is deposited from dispersion (Wessling 1994) or solution (Wei et al. 1995). Electrochemical synthesis of conducting polymers has its advantages; it permits the synthesis without oxidizing agent together with doping with different organic and inorganic ions. Also, electrochemical synthesis takes place directly on the metal surface and is expected to have better adherence than in the case of chemically synthesized conducting polymers.

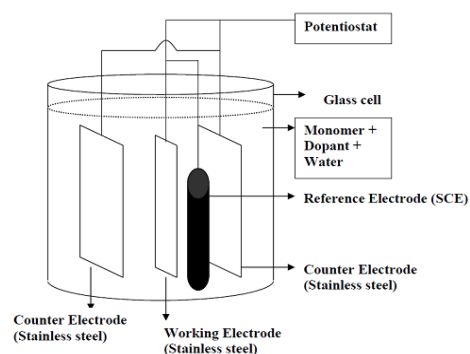
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## Materials and Methods

The monomers used in electrochemical deposition were pyrrole (98%). This chemical was bought from Aldrich chemicals. Two stainless steel electrodes (0.9 x 25 x 76 mm) were used as the counter electrodes. The reference electrode used in the experiment is the saturated calomel electrode (SCE), which was purchased from Fischer Scientific Company. Stainless steel coupon (0.9 x 70 x 70 mm) was the working electrode for all the experiments. Oxalic acid was used as the electrolyte. It was purchased Fluka chemical company. The electrolyte concentration was kept constant at 0.2 M. All aqueous solutions used in the experiment were prepared by using double distilled water.

Electrochemical reaction was performed in a glass beaker. Figure 1 shows a schematic representation of an electrochemical cell. An EG&G Princeton Applied Research Potentiostat/Galvanostat Model 363 was used for electrochemical polymerization. The stainless steel samples were rinsed thoroughly with double distilled water, hexane and dried by using kim wipes. About 300 ml of electrolyte was used for each experiment. The initial monomer concentration was varied from 0.1 M to 0.3 M. Concentration higher than 0.3 M did not dissolve in the solution. Oxalic acid was used as the electrolyte. The concentration of oxalic acid was also systematically varied between 0.1-0.3 M. The concentration of oxalic acid used was such that the PH of solution is maintained around 1.5-1.7. The deposition of polypyrrole coating on stainless steel alloy SS-304 takes place at this lower PH (range 1 to 2). The ferrous oxide layer is not stable in the PH range 1 to 2 and allows the deposition of conducting polymer layer onto the substrate. Oxalic acid was also used to in-situ clean the SS-304 substrate. Galvanostatic polymerization (constant current technique) was used to electrodeposits the conducting polymer coating onto SS-304 coupon. The applied current was varied between 2-6 mA/cm<sup>2</sup>. The deposition time was varied between 30 sec-3 minutes. Thus by varying the electrochemical deposition parameters like monomer concentration, electrolyte concentration, applied current density and deposition time the primer properties were optimized. After electro deposition the SS-304 coupons were rinsed with deionised water and heated to 100 °C for 1 hr. The thickness of the primer coating was controlled by changing the deposition time and the applied current density. The thickness of the primer coat varied between 0.5-2 microns.

Figure 1: Sketch of Electrodeposition setup



## Results and Discussions

### Electrochemical deposition

Constant potential method was employed for electrochemical deposition of polypyrrole. As soon as the experiment started, coating was visible on the stainless steel substrate within few seconds. It was only from 30 seconds deposition that the stainless steel substrate was fully covered by polypyrrole coatings. The polypyrrole coating has a very good adhesion onto stainless steel substrate. If the coating is too thick, coating may act as a physical barrier instead of chemical or electronic diffusion barrier. It was interesting to see change in color of the coating with change in the deposition time and concentration of the monomer. Polypyrrole coatings showed green and black colors with change in concentration and deposition time.

### Reflection Absorption Infrared Spectroscopy

The chemical structure and composition of the resulting coatings were determined by using RAIR spectroscopy at a resolution of 8 cm<sup>-1</sup>. A total of 256 scans were carried out over a scan range of 4000 to 400 cm<sup>-1</sup>. A background spectrum of bare stainless steel was subtracted from the sample spectrum.

Infrared spectroscopic analysis was performed to study the structure of the electro polymerized polymer coatings on stainless steel substrate. Figure 2 & 3 shows the IR spectrum of the polypyrrole deposited on stainless steel at different deposition times. The peaks at 1570, 1025 and 940 cm<sup>-1</sup> are the characteristic peaks of polypyrrole, in agreement with the literature (Davidson et al., 1995). The peak at 1590 cm<sup>-1</sup> is due to C=N stretch. The peak at 1140 cm<sup>-1</sup> is due to the presence of dopant. The peaks at 1025 and 940 cm<sup>-1</sup> are due to the pyrrole ring vibrations. Table 1 shows the characteristic peaks of polypyrrole coating.

Figure 2. Infrared spectra of polypyrrole formed on stainless steel, 0.1 M pyrrole at 30 seconds deposition time

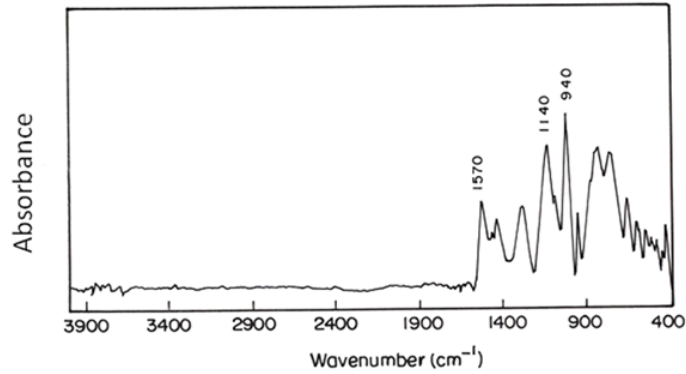


Figure 3. Infrared spectra of polypyrrole formed on stainless steel, 0.1 M pyrrole at 3 minutes deposition time

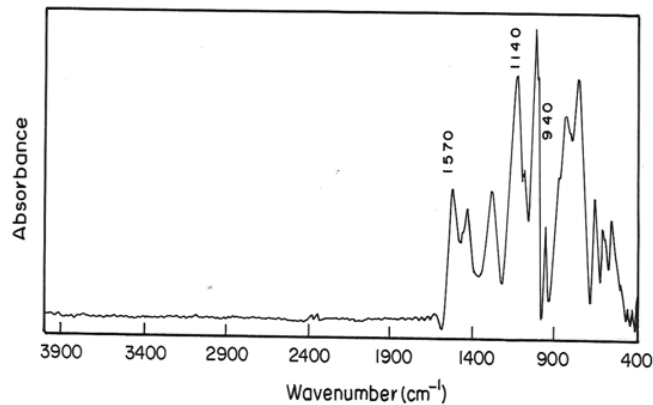


Table 1. Characteristic peaks of polypyrrole coating

Peaks (cm <sup>-1</sup> )	Functional groups
1570	C=N stretch
1140	Sulfonic group (dopant)
1025	Pyrrole ring vibration
930	Pyrrole ring vibration

### Atomic Force Microscopy

The morphology and the roughness of the coatings were determined by using AFM at a scan size of 20  $\mu\text{m}$ . The approximate thickness of the coatings can also be obtained from AFM. The roughness and rms values are noted for each coating that was tested.

Atomic Force Microscopy was used to study the change in morphology of the coatings with process parameters and compare the surface roughness of the coatings. The change in morphology with concentration of pyrrole is shown in Figure 4 & 5. The change in

mean roughness and the rms roughness of polypyrrole coatings with concentration of the monomer is shown in Table 2. With increase in concentration of the coatings the cone shape of coatings gets broader and longer. The change in morphology with deposition time of polypyrrole coatings on stainless steel is shown in Figure 6 & 7. The change in mean roughness and the rms roughness of polypyrrole coatings with deposition time is shown in Table 3. Roughness values increased with increase in pyrrole concentration and deposition time.

Figure 4. AFM picture of polypyrrole coating on stainless steel at 0.1 M pyrrole, 2 minutes deposition

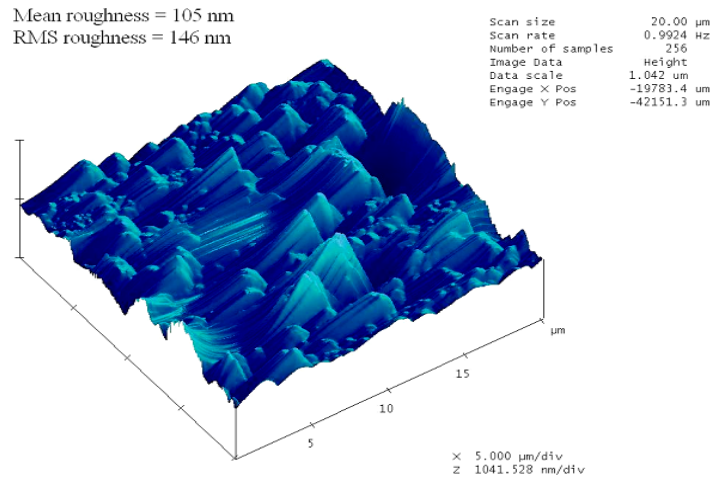


Figure 5. AFM picture of polypyrrole coating on stainless steel at 0.2 M pyrrole, 2 minutes deposition

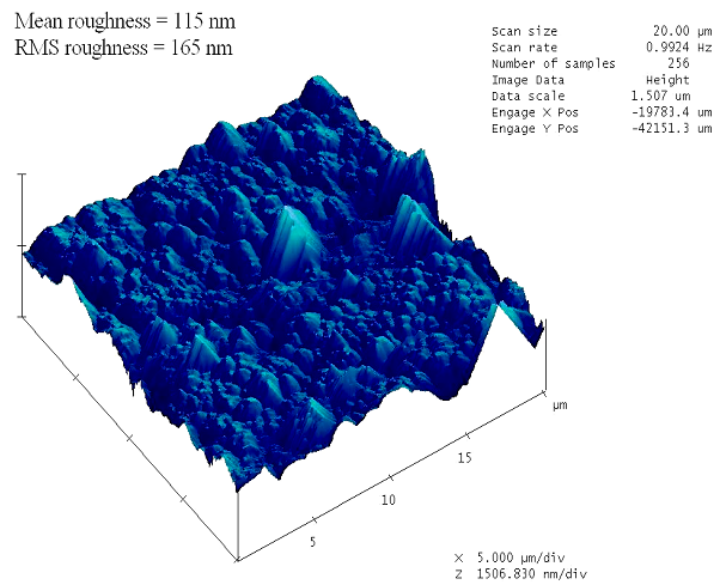


Figure 6. AFM picture of polypyrrole coatings on stainless steel at 30 seconds deposition, 0.1 M pyrrole

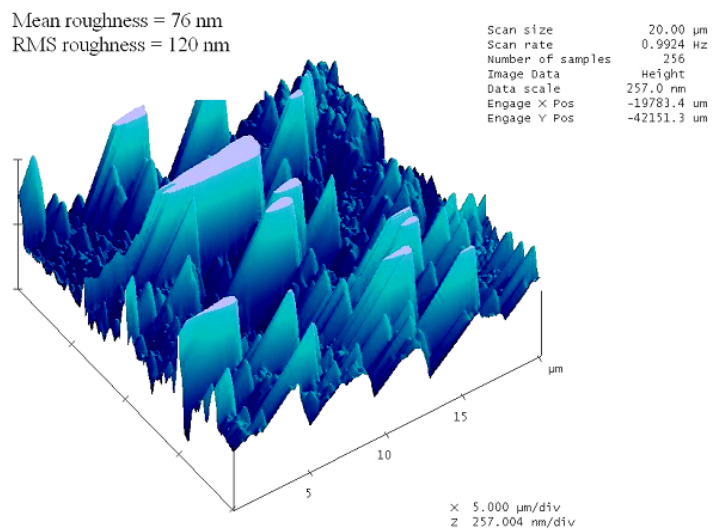


Figure 7. AFM picture of polypyrrole coatings on stainless at 2 minute deposition, 0.1 M pyrrole.

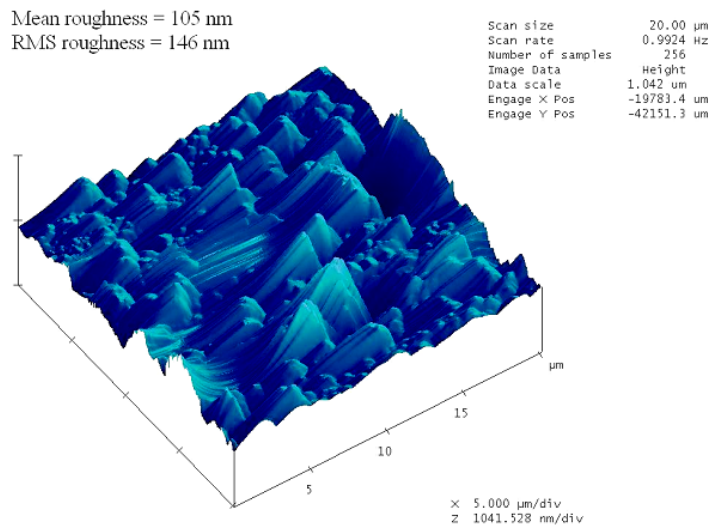


Table 2. Roughness of polypyrrole coatings on stainless steel with change in concentration of the monomer

Polypyrrole coatings	Mean roughness (nm)	RMS roughness (nm)
0.1 M Pyrrole at 2 min	105	146
0.2 M Pyrrole at 2 min	115	165

Table 3. Roughness of polypyrrole coatings on stainless steel with change in deposition time

Polypyrrole coatings	Mean roughness (nm)	RMS roughness (nm)
0.1 M Pyrrole at 30 sec	76	120
0.1 M Pyrrole at 2 min	105	146

### Conclusion

The formation of polypyrrole coatings on stainless steel was successfully achieved by the constant potential method. Electrochemical deposition was carried out at different deposition times and concentrations of monomers. The effect of these parameters was studied by using RAIR and AFM. Infrared spectroscopy was used to understand the structure of the coatings. Atomic force microscopy was used to study the morphology of the coating formed on stainless steel. IR spectra showed that extent of oxidation. The oxidation changes systematically with change in process parameters. As the concentration of the monomer increases, the extent of oxidation was shown to decrease. As the deposition time increases, the extent of oxidation was shown to increase. Since the oxidizing form is the conducting form of these polymers, extent of oxidation might affect the corrosion current of the coating. Atomic force microscopy showed the three dimensional morphology of the

Polypyrrole coatings. The roughness values were also obtained from AFM. In polypyrrole coatings showed a decrease in roughness with increase in concentration of monomer.

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