

CONDUCTING POLYPYRROLE COATING OF STEEL IN AQUEOUS SOLUTIONS

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Abstract. Polypyrrole films were deposited galvanostatically (2 mA/cm^2) on steel electrodes at a temperature of -5°C from the solution of 0.2 M pyrrole and 0.1 M sodium *p*-toluenesulphonate in an ethanol/water solvent system. It was found that this polymer coating remarkably increases corrosion resistance of steel when exposed to saline environments. A pronounced and reproducible shift in the direction of noble metals for electrochemically coated steel was observed. Potentiodynamic polarization measurements confirm the corrosion protective effect of the polypyrrole coatings.

Key words: conducting polymers, polypyrrole, corrosion.

INTRODUCTION

In recent years electrodes modified with a new type of electroactive materials, electrically conducting polymers (CP), have attracted considerable fundamental and technological interest [1, 2]. Since polyacetylene, the first polymer discovered to exhibit a high conductivity, there has been rapid growth in research on conjugated heterocyclic (polypyrrole, polythiophene) and aromatic (poly *p*-phenylene, polyaniline) polymers [3]. Research is fast moving on to open up new areas of application. More and more sophisticated materials, chemically functionalized to add new properties (redox catalysis, electrochromism, asymmetrical recognition, etc.) or composites to improve the intrinsic (mechanical, electrical, optical, electrochemical) properties have been developed. A variety of potential applications have been proposed: sensors, surgical plasters containing active ingredients, membranes, electrodes, electromagnetic interference shielding, deposition for antistatic finishing, optical storage systems, etc. [4]. A steadily increasing interest

has been shown in the research of novel potential applications as corrosion protective materials.

In 1985 DeBerry [5] observed the passivation of stainless steel electrochemically coated with a CP, polyaniline (PAn) in 0.2 M H₂SO₄. Beck & Barsch investigated the mechanism for the corrosion of polypyrroles [6] and polythiophenes [7] electrodeposited galvanostatically on an inert electrode material (platinum). Recent studies have been focused on more active substrates like steel, iron, and copper [8, 9]. Wessling [10] demonstrated the corrosion protection performance of the non-electrochemically coated PAn in 1 M NaCl solution and concluded that coatings lead to practically useful improvements in protection if a corrosion potential shift has occurred. The protective effect was attributed to the formation of passive metal oxide layers. Most of these investigations have been focused on PAn. Polypyrrole (PPy) and polythiophene have been much less studied. The protective effect of these coatings has been observed but the mechanism of this process and especially the influence of different media are still open.

In this work, the steel was electrochemically coated with a conducting PPy film and the influence of saline conditions (0.2 M NaCl) was investigated.

EXPERIMENTAL

Electrochemical syntheses were performed in a four-electrode glass cell (Fig. 1). The working and counter electrodes were steel sheets (Fe37) with a thickness of 0.8 mm from Rautaruuki OY, Finland. The working electrode was placed between two parallel counter electrodes at 10 mm distance. The coated surface areas varied from 2 to 12 cm². A saturated calomel electrode (SCE) was used as reference. Before the electrochemical synthesis electrodes were prepared as follows: (i) wet grinding with P800/1200 abrasive paper, (ii) polishing with AP-paste, (iii) rinsing with ethanol (ultrasonic cleaner). Electrolyte was prepared by dissolving the 0.1 M sodium *p*-toluenesulphonate (NaToS) (Aldrich) as a doping agent in the mixture of water and ethanol (6.5 M). Pyrrole (0.2 M) (Aldrich) was distilled under reduced pressure. All the other chemicals were used as received.

Prior to each experiment, the electrolyte was deaerated by passing nitrogen through the solution for 20 min. A steady flow of nitrogen was maintained over the solution surface during the synthesis. All syntheses were performed galvanostatically at a current density of 2 mA/cm², at a temperature of -5°C, without stirring. Films of different thickness were obtained by varying the polymerization time.

The conductivity of the PPy/ToS films was determined by the conventional four-probe method. Films were peeled off the electrode and a rectangular fragment was placed on an insulating substrate. Graphite contacts were used.

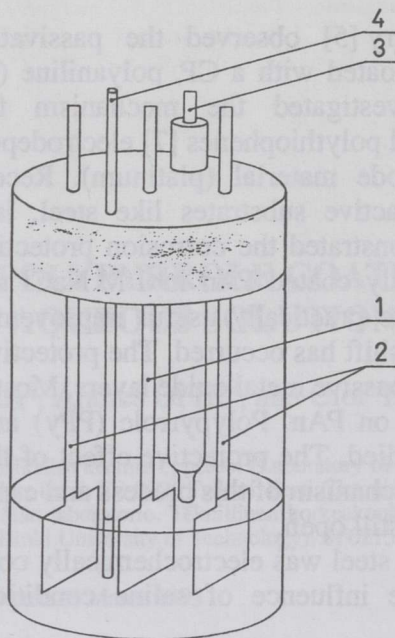


Fig. 1. The four-electrode cell for the electrochemical synthesis. 1, working electrode; 2, counter electrodes; 3, reference electrode; 4, gas inlet.

For the electrodeposition and electrochemical measurements a Parc Model 273 potentiostat/galvanostat under a direct computer control was used. Electrochemical measurements were performed in a standard three-electrode glass cell. The surface area of the test samples was 0.5 cm^2 . Potentiodynamic polarization measurements in 0.2 M NaCl solution at room temperature were always started from the corrosion potential value (E_{corr}) in the anodic direction at the scan rate $1 \text{ mV}/6 \text{ s}$. Scanning electron microscope (SEM) studies were performed using a JEOL JXA-840 apparatus.

RESULTS AND DISCUSSION

Deposition and characterization of the films

Conductive films of PPy grow directly on the surface of anode by electrochemical polymerization. A typical potential vs. time curve for galvanostatic polymerization of PPy is shown in Fig. 2. A sharp oxidation peak was observed signalling the start of PPy deposition. After that the potential decreased with time and stabilized approximately at 1.3 V vs. SCE. Anodic dissolution of the substrate has been mentioned as one disadvantage during this process in some studies [9]. In our system no anodic dissolution of the substrate was observed and films covered the

electrode entirely. Films of different thicknesses in the range of 0.2–30 μm were deposited by varying the synthesis time. The thickness was calculated from the electrical charge consumed during the deposition [11]. For example, films with a thickness of approximately 1 μm were deposited by using a charge density of 0.24 C/cm^2 . It was observed that the adhesion of the films to the substrate depended on the film thickness. For example, it was not possible to remove thin (200–1000 nm) films from the substrate in any other way than by grinding. Thick films were less adherent and it was possible to remove them as continuous sheets from the metal surface. Lateral conductivity of the films measured by the four-probe method was in the range of 20–100 S/cm .

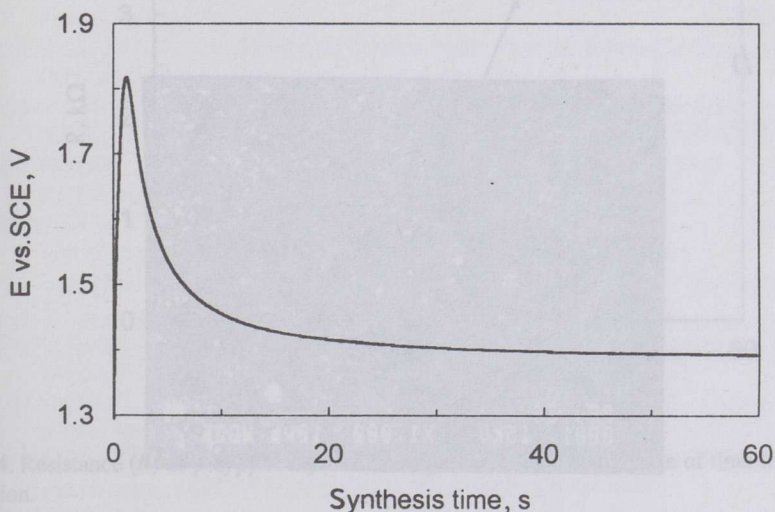
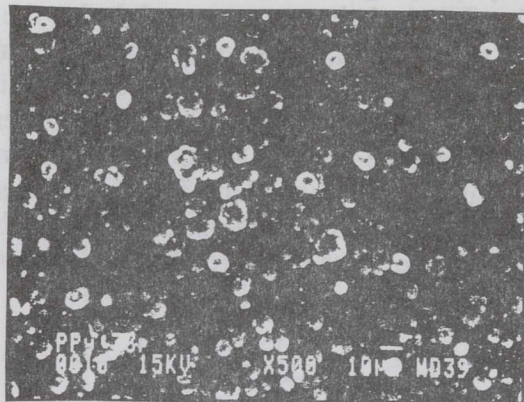


Fig. 2. Potential time curve for the galvanostatic ($2 \text{ mA}/\text{cm}^2$) synthesis of polypyrrole on steel in 0.1 M sodium *p*-toluenesulphonate in an ethanol/water solvent system at a temperature of -5°C (monomer concentration: 0.2 M).

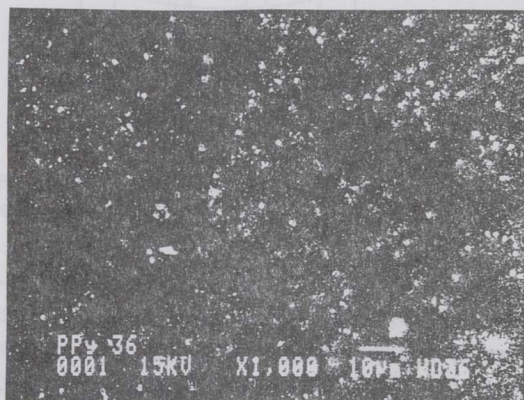
SEM studies

SEM examination of PPy/ToS-coated steel was conducted to further characterize the material. Typical micrographs for the samples are presented in Fig. 3. As observed, the coatings are continuous and fine grained (Fig. 3a, 3b). The micrograph of the coating from the metal side shows that the base of the coating is highly continuous, no pores were observed (Fig. 3c). SEM studies of the profile of the coatings reveal that the coating structure depends on the film thickness: monolayers of PPy films are continuous and smooth, after that a layered porous structure appears, and finally the fine-grained nodular growth is apparent.

a



b



c



Fig. 3. Scanning electron micrographs of polypyrrole/*p*-toluenesulphonate (PPy/ToS) films of different thickness (*d*) galvanostatically (2 mA/cm^2) deposited from an aqueous (water/ethanol) solution at a temperature of -5°C . *a*, PPy/ToS film on steel, from the surface side; $d_{\text{theor}}=30 \mu\text{m}$; magnification $\times 500$; *b*, PPy/ToS film on steel, from the surface side; $d_{\text{theor}}=0.5 \mu\text{m}$, magnification $\times 1000$; *c*, PPy/ToS film, from the electrode side; $d_{\text{theor}}=22.5 \mu\text{m}$; magnification $\times 1000$.

Resistance vs. time measurements

A rectangular standardized PPy piece with two terminal isolated contacts was embedded into the NaCl solution for the resistance measurement. The typical change of the resistance as a function of time is shown in Fig. 4. An increase occurred in the resistance during the first 50 h. The same behaviour was observed in the NaCl solutions with different concentrations and in distilled water.

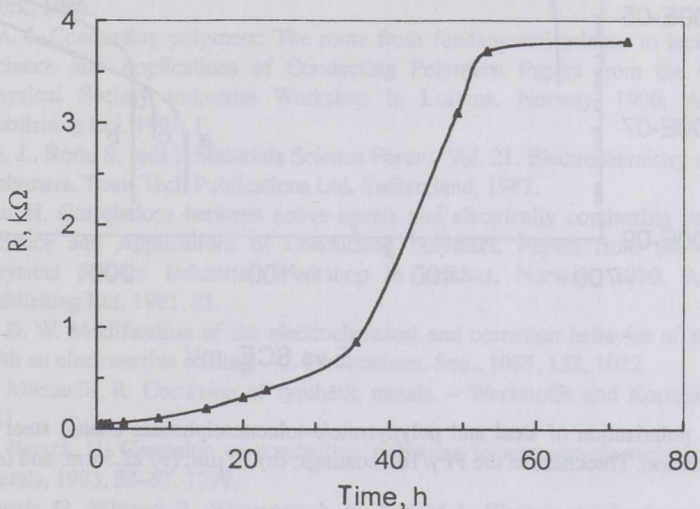


Fig. 4. Resistance (R) of polypyrrole/*p*-toluenesulphonate film as a function of time in 0.2 M NaCl solution.

Anodic polarization measurements

The electrochemical behaviour of the films was characterized by polarization curves of coated steel in 0.2 M NaCl. Typical polarization curves of the change of the redox current as a function of the applied voltage obtained for the steel of different thickness of the PPy/ToS coating are shown in Fig. 5. Polarization characteristics derived from these curves by the Tafel linear extrapolation method are listed in the Table. Remarkably lower redox currents (i_{redox}) were found for PPy/Tos-coated samples. From the polarization data it can be seen that a marked decrease of the redox current occurs together with a change of the corrosion potential values in the direction of noble metals. The maximum shift was +800 mV compared to the corrosion potential of steel. This result is in accordance with the studies of Wessling [10] concerning chemically deposited PAN coatings on steel. A description of the observed corrosion protection mechanism is complicated because of the interactions of the different processes. Our studies of the influence of the coating thickness

on the protection effect of steel are inconclusive. We did not observe any strong correlation between the thickness and the values of i_{redox} . The protective effect depends on the quality of the coating (deposition process) rather than on its thickness.

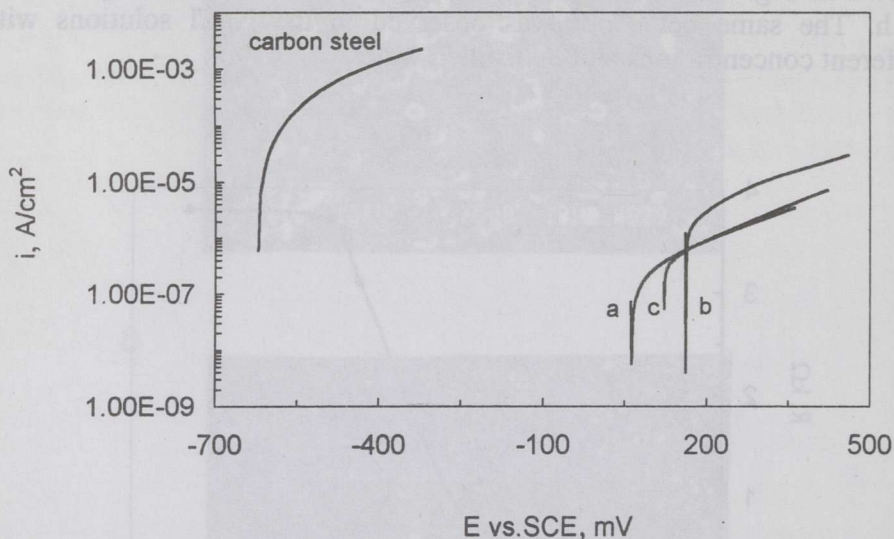


Fig. 5. Anodic polarization of steel and polypyrrole/*p*-toluenesulphonate coated steel samples in 0.2 M NaCl solution. Thickness of the PPy/ToS coatings: (a) 15 μm , (b) 22.5 μm , and (c) 30 μm .

Corrosion potentials (E_{corr}) and redox current (i_{redox}) values for polypyrrole/*p*-toluenesulphonate (PPy/ToS)-coated steel

Calculated from the anodic polarization curves by the Tafel equation

System	Thickness of the coating, μm	E_{corr} , V	i_{redox} , $\mu\text{A}/\text{cm}^2$
Steel		-0.620	93.71
Steel//PPy/ToS	15.0	0.064	0.19
Steel//PPy/ToS	22.5	0.162	3.41
Steel//PPy/ToS	30.0	0.121	0.44

CONCLUSIONS

Our results of the anodic polarization measurements of the PPy/ToS coatings on steel confirm the protective effect of these coatings. The corrosion protection of steel of our PPy coatings is more effective than the results of electrochemically deposited PAN coatings investigations [8] show.

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TERASE ELEKTROKEEMILINE KATMINE JUHTIVA POLÜPÜRROOLKILEGA

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On uuritud juhtivast polümeerist, polüüpürroolist (PPy), teraselektroodide pinnale elektrokeemiliselt sadestatud katete käitumist NaCl vesilahuses. Pürrooli elektrokeemiline polümeerisatsioon viidi läbi 0,2 M pürrooli ja 0,1 M naatrium *p*-tolueensulfonaadi (NaTs) vee ja etanooli segus konstantsel voolutugevusel (2 mA/cm^2) ja temperatuuril (-5°C) inertgaasi (N_2) keskkonnas. Pinnauuringud skaneeriva elektronmikroskoobi abil näitasid, et sünteesi tulemusel saadud polümeeri pind on polü-

kristalse ehitusega ning koosneb üksteisega tihedalt kokkukasvanud graanulitest. Sünteesitud PPy/Ts kilede juhtivus, mis määrati pärast nende eemaldamist metallelektroodilt nelja sondi meetodil, on vahemikus 20–100 S/cm. PPy/ToS kilega kaetud teraselektroodide korrosioonipotentsiaal on märkimisväärselt positiivsem terase korrosioonipotentsiaaliga võrreldes. Terasse korrosioonipotentsiaal uuritavas lahuses oli –640 mV küllastatud kalomelelektroodi suhtes, PPy/Ts kilega kaetud teraselektroodidel aga vahemikus +50 kuni +180 mV. Kilede kaitseefekti kvantitatiivseks hindamiseks polariseeriti uuritavaid elektroode potentsiodünaamilisel meetodil. Tulemused näitavad oluliselt väiksemaid korrosioonivoolu väärtusi, kinnitades seega juhtivate polümeeride kasutamise võimalikkust korrosioonikaitsel.

ПРОВОДЯЩИЕ ПОЛИПИРРОЛОВЫЕ ПОКРЫТИЯ ДЛЯ ЗАЩИТЫ СТАЛИ ОТ КОРРОЗИИ

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Исследована возможность использования проводящих полимеров для защиты стали от коррозии. Электрохимический синтез проводящих пленок полипиррола проводился гальваностатическим методом (2 mA/cm^2) в системе вода–этанол с легирующей солью паратолуолсульфоната натрия (0,1 М) на стальных электродах при температуре -5°C . Потенциал коррозии стали, покрытой проводящим полимером в 0,2 М растворе хлорида натрия, составил относительно потенциала каломельного электрода 50–180 мВ. Приведены результаты электронной микроскопии и анодной поляризации.