

A STUDY OF THE ELECTROCHEMICAL SYNTHESIS OF POLYPYRROLE FROM AQUEOUS SOLUTION ON STAINLESS STEEL ELECTRODE

Jekaterina REUT, Katrin IDLA, and Andres ÖPIK

Tallinna Tehnikaülikooli keemiaminstituut (Department of Chemistry, Tallinn Technical University), Ehitajate tee 5, EE-0026, Tallinn, Eesti (Estonia)

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Abstract. Polypyrrole (Ppy) electrocoatings on stainless steel with electrochemical and spectroscopic methods were studied. Electropolymerization was carried out from an aqueous solution containing 0.1 M pyrrole and 0.1 M sodium dodecylsulphate (DS) with phosphate buffer solution (pH 4) and without buffer (pH 6) at room temperature. Cyclic voltammetry was employed to examine the polymerization potential of Ppy. The obtained results showed that electroactive polymer films can be obtained at the values not higher than 1.4 V vs. SCE. UV-VIS spectra showed peaks at different energy values for reduced and oxidized Ppy. A scanning electron microscopy study showed the polycrystalline structure of Ppy/DS and the most homogeneous surface for films synthesized at 1.3 V vs. SCE. The structure of polymer films was characterized with IR spectrometry.

Key words: polypyrrole, dodecylsulphate, electrochemical synthesis, stainless steel.

REFERENCES

INTRODUCTION

Polypyrrole (Ppy) is an attractive electrically conductive polymer because of the ease of its synthesis, non-toxicity, and high electrical conductivity (up to 100 S cm^{-1}) [1]. It has a number of potential applications in areas of energy storage [2], sensors [3], and electronic devices [4]. In recent years interest in the application of electrically conductive polymers as anti-corrosion materials has increased [5, 6]. In our previous work [7] it was shown that Ppy films synthesized in aqueous sodium *p*-toluenesulphonate protect mild steel in saline solutions.

It is well known that polymerization conditions, e.g. the material of substrate, electropolymerization potential, current density, and the nature and concentration of the electrolyte solution, affect strongly the properties

of the resulting film [1, 8]. Considering the possibility to use Ppy as an anti-corrosion coating, electrochemical synthesis was performed from aqueous solution directly onto a stainless steel electrode. Sodium dodecylsulphate (NaDS) was chosen as electrolyte because Ppy films obtained in the presence of long-chain organic anions (surfactants) have been found to be flexible and with good mechanical properties [8]. The electropolymerization process of pyrrole was studied with cyclic voltammetry (CV). *In situ* UV-VIS spectrometry, IR spectrometry, and scanning electron microscopy (SEM) were used for the characterization of the obtained Ppy/DS films.

EXPERIMENTAL

Cyclic voltammetry was carried out in a classical three-electrode cell (volume 10 ml) connected with a potentiostat PAR 173 and a function generator PAR 175. A stainless steel working electrode ($d = 3$ mm), a glassy carbon auxiliary electrode, and a saturated calomel electrode (SCE) were employed for the CV study. Cyclic voltammograms were recorded with an XY Sefram type TGM 164 recorder.

In situ UV-VIS spectra during the oxidation of the Ppy films from -0.6 to 0.8 V vs. SCE were obtained using a spectroelectrochemical cell and an optical fibres spectrophotometer Model 150 (Guided Wave Inc. Corporation). A polished curved platinum mirror with a diameter of 6 mm was used as a working electrode.

The potentiostatic electropolymerization of 0.1 M pyrrole (Aldrich) was carried out in a two-compartment cell (volume 180 ml) in aqueous solution of 0.1 M NaDS (Aldrich). A number of syntheses were carried out in the phosphate buffer solution with pH 4. All syntheses were performed at room temperature, in the atmosphere of Ar. Working and auxiliary electrodes were stainless steel sheets with an area of 10 cm². The synthesis time was 1 hour and the thickness of the deposited Ppy/DS films varied from 50 to 80 μ m. After synthesis the Ppy film was removed from the electrode, washed with distilled water, and dried in air.

The IR spectra were recorded through the Ppy/DS film with an FT-IR spectrometer Nicolet 205. A scanning electron microscope JSM 840A was employed to characterize the surface morphology of the polymer.

ELECTROPOLYMERIZATION OF PYRROLE

Figures 1–3 illustrate the CV in 0.1 M pyrrole and 0.1 M NaDS aqueous solution. A loop is seen at the peak for the oxidation of pyrrole on the first sweep (Fig. 1). This behaviour is well known for pyrrole electro-

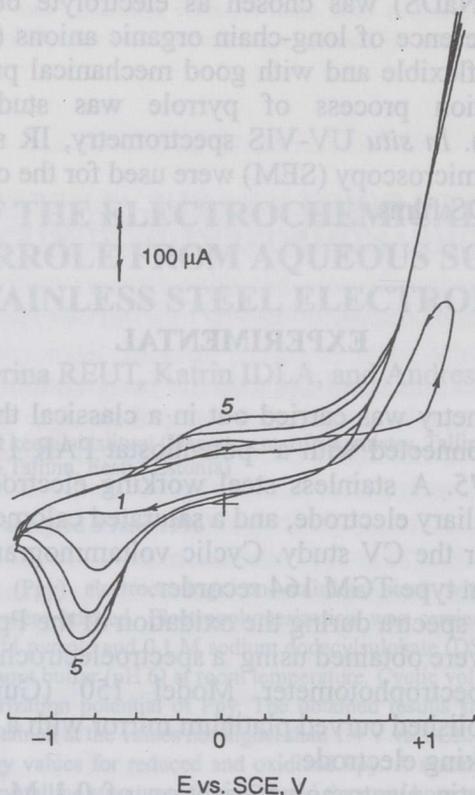


Fig. 1. Cyclic voltammograms of 0.1 M pyrrole in aqueous 0.1 M NaDS; sweep rate 100 mV/s, anodic potential 1.1 V.

polymerization and has been explained as an indication of a nucleation step in the first stage of the formation of Ppy [9]. Further, polymerization onto an already deposited polymer layer proceeds more easily. Nucleation is more intense in the solution without buffer solution (Fig. 2). The formation of black polymer film on the electrode surface in the unbuffered NaDS solution occurs at the potential 0.8 V vs. SCE, but in the presence of a buffer black film appears at 1.0 V vs. SCE. Reversible anodic and cathodic peaks (Fig. 1) correspond to the formation of electroactive polymer film [10]. After increasing the oxidation potential to 1.4 V vs. SCE, the reversible peaks disappear (Fig. 3). This indicates the decrease of the electroactivity of the resulting film.

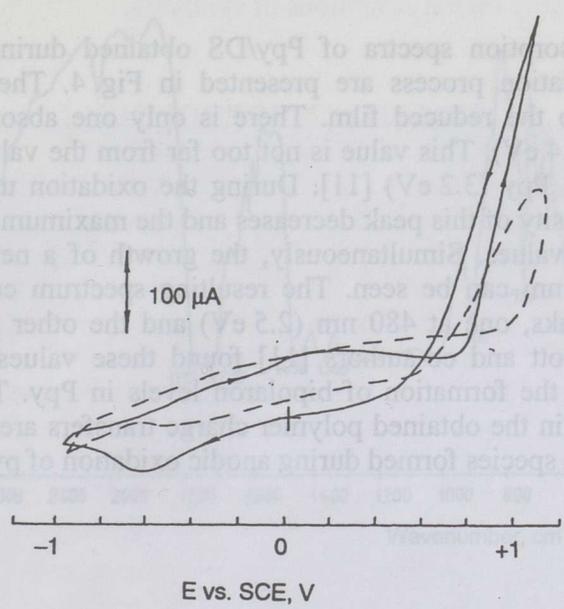


Fig. 2. Cyclic voltammograms of 0.1 M pyrrole in aqueous 0.1 M NaDS; the first sweep: dashed line, with buffer solution; solid line, without buffer solution.

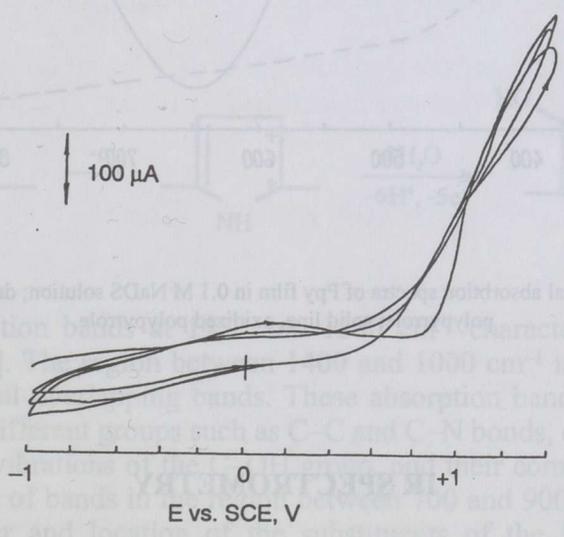


Fig. 3. Cyclic voltammograms of 0.1 M pyrrole in aqueous 0.1 M NaDS; sweep rate 100 mV/s, anodic potential 1.4 V.

IN SITU UV-VIS SPECTRA

Optical absorption spectra of Ppy/DS obtained during the electrochemical oxidation process are presented in Fig. 4. The dotted curve corresponds to the reduced film. There is only one absorption peak at $\lambda = 350$ nm (3.4 eV). This value is not too far from the value of the band gap of neutral Ppy (3.2 eV) [11]. During the oxidation up to 0.8 V vs. SCE, the intensity of this peak decreases and the maximum shifts towards lower energy values. Simultaneously, the growth of a new peak in the range of 800 nm can be seen. The resulting spectrum consists of two absorption peaks, one at 480 nm (2.5 eV) and the other at $\lambda > 900$ nm (< 1.3 eV). Scott and co-authors [11] found these values of energy to correspond to the formation of bipolaron levels in Ppy. Thus it can be supposed that in the obtained polymer charge transfers are accomplished with bipolaron species formed during anodic oxidation of pyrrole.

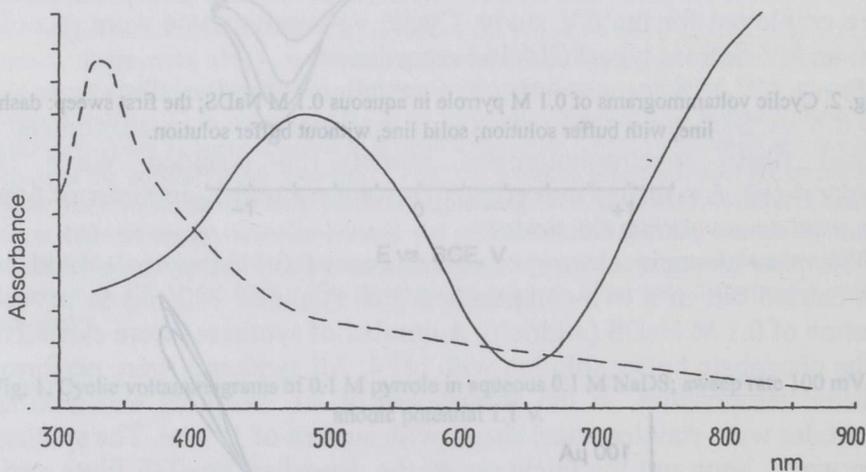


Fig. 4. *In situ* optical absorption spectra of Ppy film in 0.1 M NaDS solution; dashed line, reduced polypyrrole; solid line, oxidized polypyrrole.

IR SPECTROMETRY

We analysed Ppy/DS films prepared under different conditions of synthesis (potential, pH). The natural complexity of the IR spectra of Ppy/DS (Fig. 5) makes it impossible to identify differences in the molecular weight or its distribution of those films. However, according to literature [12, 13] it is possible to identify a number of characteristic bands.

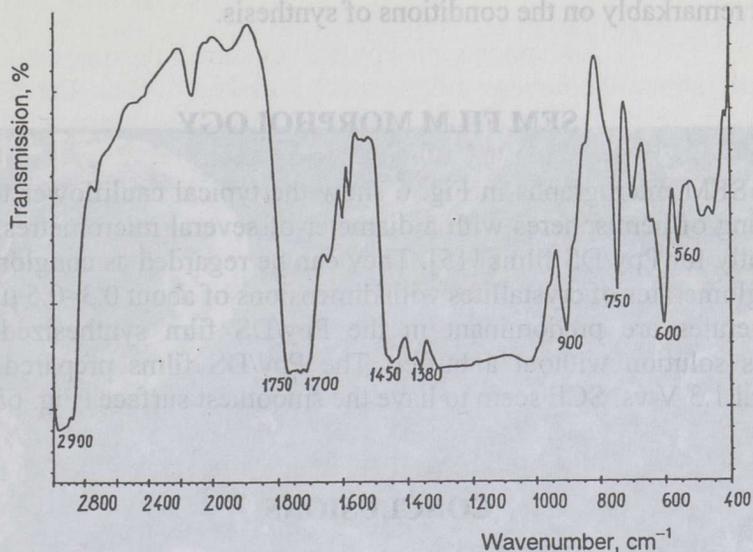
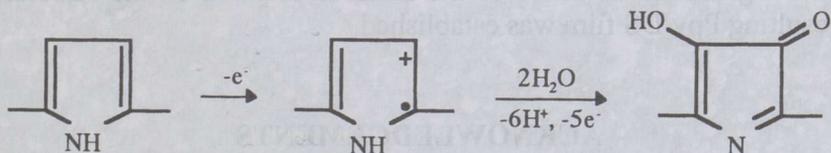


Fig. 5. IR spectra of Ppy/DS film polymerized from aqueous solution of 0.1 M NaDS.

The band observed at 1700–1800 cm^{-1} possibly corresponds to the carbonyl group that appears during the overoxidation of polymer according to the following scheme [14]:



The absorption bands at 1450 and 1380 cm^{-1} characterize Ppy ring vibrations [12]. The region between 1400 and 1000 cm^{-1} is complex and contains several overlapping bands. These absorption bands characterize vibrations of different groups such as C–C and C–N bonds, deformation of the Ppy ring, vibrations of the C–OH group, and their combinations. The exact situation of bands in the region between 700 and 900 cm^{-1} depends on the number and location of the substituents of the Ppy ring. The character of this part of the spectrum depends slightly on the conditions of synthesis and on the presence or absence of a buffer. Principal differences are revealed by a comparison of the intensities of absorption bands near 2900 cm^{-1} , which correspond to the CH_2 and CH_3 stretching vibrations in alkyl groups of DS. Bending vibrations of some groups appear at 1450 and

1380 cm^{-1} . However, the basic character of Ppy itself does not seem to depend remarkably on the conditions of synthesis.

SEM FILM MORPHOLOGY

The SEM micrographs in Fig. 6 show the typical cauliflower textures consisting of hemispheres with a diameter of several micrometres, found frequently for Ppy/DS films [15]. They can be regarded as conglomerates and agglomerates of crystallites with dimensions of about 0.3–0.5 μm . The agglomerates are predominant in the Ppy/DS film synthesized in an aqueous solution without a buffer. The Ppy/DS films prepared at the potential 1.3 V vs. SCE seem to have the smoothest surface (Fig. 6b).

CONCLUSIONS

– Electroactive polypyrrole films onto stainless steel from aqueous solution of 0.1 M NaDS can be obtained at the potentials not higher than 1.4 V vs. SCE. Electrochemically inactive films form at higher potentials.

– An absorption peak at 3.4 eV was found for the reduced Ppy/DS. Two peaks at a lower energy values (2.5 and 1.3 eV) were found for the oxidized polymer.

– No remarkable structural changes of the polymer synthesized under different conditions can be seen from the IR spectra. Carbonyl groups are present in the polymer.

– Ppy/DS films synthesized at 1.3 V vs. SCE have the most homogeneous surface.

– No significant influence of the buffered solution on the structure of the resulting Ppy/DS film was established.

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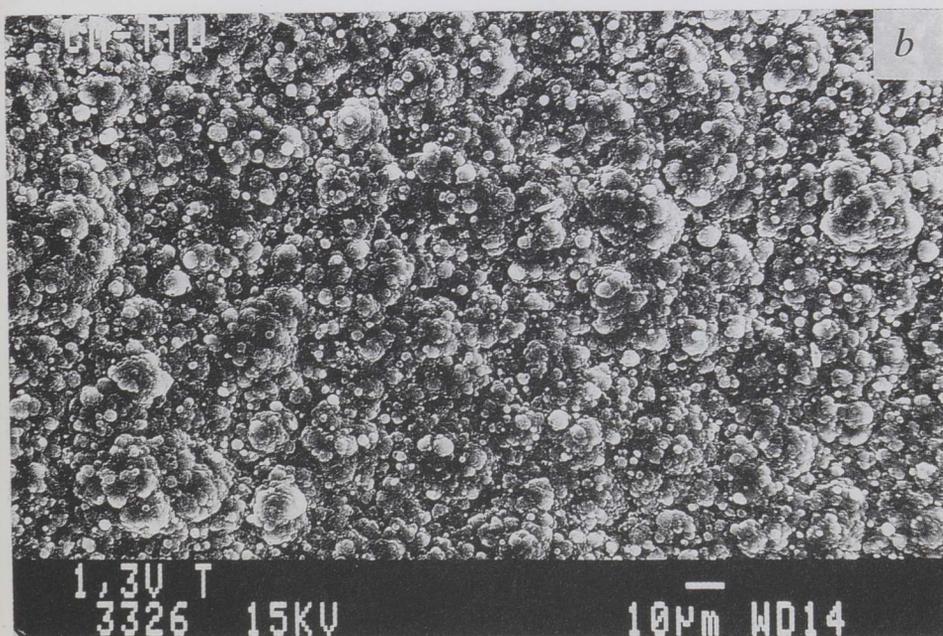
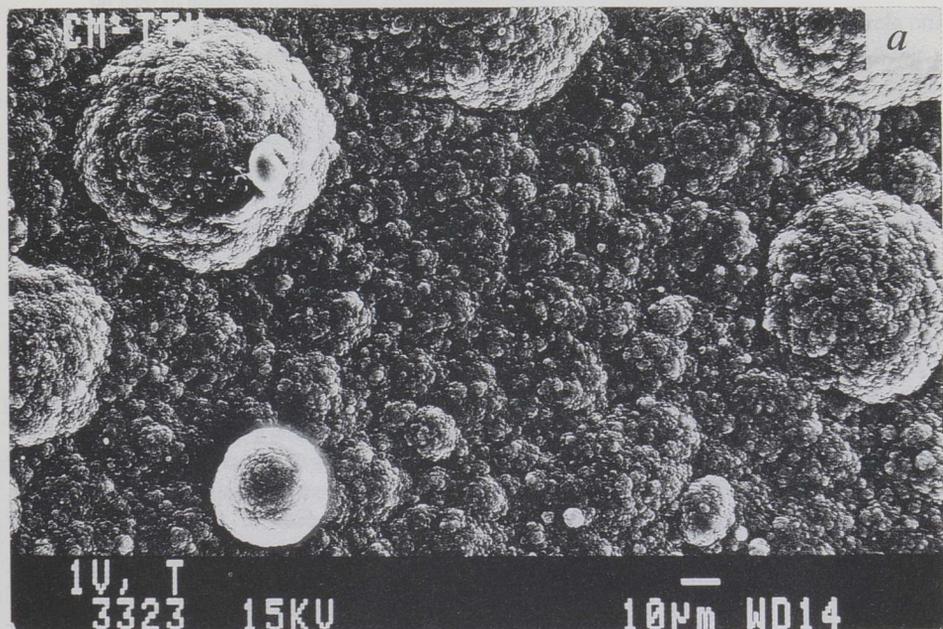


Fig. 6. SEM micrographs of Ppy films prepared in aqueous 0.1 M NaDS solution, anodic potential 1.0 V (a) and 1.3 V (b).

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POLÜPÜRROOLI ELEKTROKEEMILINE SÜNTEES VESILAHUSTES TERASELEKTROODIL

Jekaterina REUT, Katrin IDLA, Andres ÖPIK

Töö eesmärk oli uurida polüpürrooli (Ppy) elektrokeemilise sünteesi võimalusi vesilahustest teraselektroodi pinnale ning iseloomustada saadud polümeerse kile omadusi. Pürrooli (0,1 M) polümeerisatsioon toimus 0,1 M Na-dodetsüülsulfaadi vesilahuses toatemperatuuril. Polümeerisatsiooni-protsessi uurimiseks kasutati tsüklilist volt-amperomeetria meetodit ning leiti, et elektroaktiivse materjali saamiseks peab Ppy sünteesipotentsiaal olema väiksem kui 1,4 V (küllastatud kalomelektroodi suhtes). *In situ* UV-VIS-spektritel tuvastati ultraviolettkiirguse neeldumistüübi muutus polümeeri oksüdeerimisprotsessi tulemusel (redutseeritud vormi neeldumismaksimum 3,4 eV juures asendus kahe neeldumismaksimumiga: 2,5 ja 1,3 eV juures). IR-spektri analüüs osutas, et polümeeri ahel sisaldab karbonüülühmi. Pinnauuringud skaneeriva elektronmikroskoobi abil näitasid, et sünteesitud Ppy-kilede pind on polükristalse ehitusega ja et kõige homogeensemata struktuuriga Ppy-kiled sünteesiti potentsiaalil 1,3 V.