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Characterization and electrocatalytic application of silver modified polypyrrole electrodes

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Abstract: Silver modified polypyrrole electrodes were prepared with the aim of testing them for the electrooxidation of formaldehyde in alkaline solution. The modification of polypyrrole by immersion in aqueous $AgNO_3$ solution was studied by cyclic voltammetry and vacuum techniques (AES and XPS). The influence of time of immersion and the thickness of the polypyrrole film, prepared by electrochemical polymerization, on the modification of the polymer were examined. The results acquired from both electrochemical and spectroscopic examinations show that immersion of a polypyrrole electrode in a $AgNO_3$ solution results in its modification with silver, which is deposited in the elemental state on the surface. The quantity of silver deposited depends not only on the immersion time but also on the thickness of the polymer film. A modified PPy/Ag electrode exhibits catalytic activity for the electrooxidation of CH_2O in NaOH. In spite of the low quantity of silver, the activity of the electrode for this reaction is comparable to that of a polycrystalline silver electrode.

Keywords: polypyrrole, modification by immersion in $AgNO_3$, AES and XPS techniques, electrooxidation of formaldehyde.

INTRODUCTION

Conducting polymers, due to their remarkable properties, offer a whole new range of potential electrode materials. In recent years, the possible applications of these materials have been intensively studied, such as electrodes for batteries,[1] in corrosion as protective films,[2] as electrochemical sensors[3] but also as high surface area supports in electrocatalysis.[4–9] Polyaniline and polypyrrole have been used the most as such supports for metallic (mostly Pt but also Pb, Ru, Pd, Rh, Au) or bimetallic (such as Pt/Pd, Pd/Rh, Pt/Sn) catalysts. The conducting polymers were modified mainly by electrodeposition of catalyst particles on a preformed polymer[4–6,8] or by their incorporation during monomer polymerization.[8,9] The deposition of metal or bimetal particles was also achieved by subsequent reduction of a polymer film previ-

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ously immersed in a solution containing the metal ions in question.[6,7] The modified electrodes showed electrocatalytic activity for the oxidation of small organic molecules, such as methanol, formic acid or other organics,[5–7] oxidation of hydrogen[8] and reduction of oxygen.[4] Although not so widely, the electrochemical or chemical deposition of silver into polymer films have been studied as well.[10–16]

It was shown earlier that glassy carbon (a product of the carbonization of polymer resins) was modified with silver particles simply by its immersion in aqueous $AgNO_3$ solution.[17] The modified electrode exhibited high catalytic activity for the oxidation of small organic molecules in alkaline solution even at low quantities of silver.[18]

The aim of this work was to investigate both the possibility of modifying polypyrrole in a similar manner and the activity of such an electrode for the electrooxidation of formaledehyde in sodium hydroxide solution.

EXPERIMENTAL

All chemicals used were of p.a. purity and the solutions were prepared with high purity water (Millipore, 18 MΩ cm resistivity). Pyrrole was redistilled before use, while the formaldehyde was used as refluxed. The electrolytes were purged with nitrogen before each experiment. All the experiments were performed at room temperature.

Pyrrole was electrochemically polymerized in a three electrode/three compartment cell with a glassy carbon (GC) working electrode, Pt as the auxiliary and SCE double junction (in acid) or Hg/HgO (in alkali) as the reference electrode. The potentials are given *versus* corresponding reference electrode.

The electrochemical polymerization of pyrrole was carried in 0.1 M HNO_3 solution with a monomer concentration of 0.1 M Py or 0.05 M Py. Cyclic voltammetry was applied in the potential range between – 0.6 V to 0.8 V *vs.* SCE at a sweep rate of 50 mV/s. The potential was cycled for 15 or 30 min. The rinsed electrode was then checked in electrolyte free of pyrrole and the thickness of the film was determined only by the charge passed corresponding to the oxidation and reduction of polypyrrole. After this, the electrode was transferred in 0.1 M NaOH and the potential was cycled between –0.6 V and 0.8 V *vs.* Hg/HgO till steady state.

Modification of the obtained electrode was performed by immersion in 0.1 M $AgNO_3$ solution for 10 or 20 min. In this way a total of 4 types of electrodes were prepared:

– electrode designated as A (0.1 M Py, polymerization time 15 min, immersion time 10 min),
– electrode designated as B (0.1 M Py, polymerization time 30 min, immersion time 10 min),
– electrode designated as C (0.1 M Py, polymerization time 30 min, immersion time 20 min),
– electrode designated as D (0.05 M Py, polymerization time 15 min, immersion time 10 min).

The silver modified polypyrrole (PPy/Ag) electrodes were examined in 0.1 M NaOH by cyclic volatmmetry in the potential range from –0.6 V to 0.9 V *vs.* Hg/HgO at a sweep rate of 50 mV/s.

PPy/Ag electrodes were tested for electrooxidation of 0.1 M CH_2O in 0.1 M NaOH by cyclic voltammetry (potential range from –0.6 V to 0.9 V *vs.* Hg/HgO, sweep rate 50 mV/s) using a stationary or a rotating electrode (rpm 1600).

Voltammograms were recorded using standard set – up with PAR Model 273 potentiostat and Philips Model 8033 X-Y recorder.

Another set of as prepared PPy/Ag electrodes was used for vacuum characterization techniques (Auger-electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS)). The AES spectra were recorded using a RIBER spectrometer with a primary electron beam acceleration voltage of 3 keV and an absorbed beam current of 3 μA. The XPS spectra were recorded using a RIBER OPX 150 photoelectron spectometer with an Al Kα X-ray source with a power of 50 W. All the spectra presented were obtained by 20 moving-point average curve smoothing.

RESULTS AND DISCUSSION

Earlier studies showed that simple immersion of glassy carbon in an aqueous solution of $AgNO_3$ results in the deposition of Ag metal particles[17] and the electrode obtained was active for the oxidation of small organic molecules.[18,19] In the present work, with the aim of investigating the oxidation of formaldehyde in basic solution, similar electrodes based on polypyrrole instead of glassy carbon were prepared.

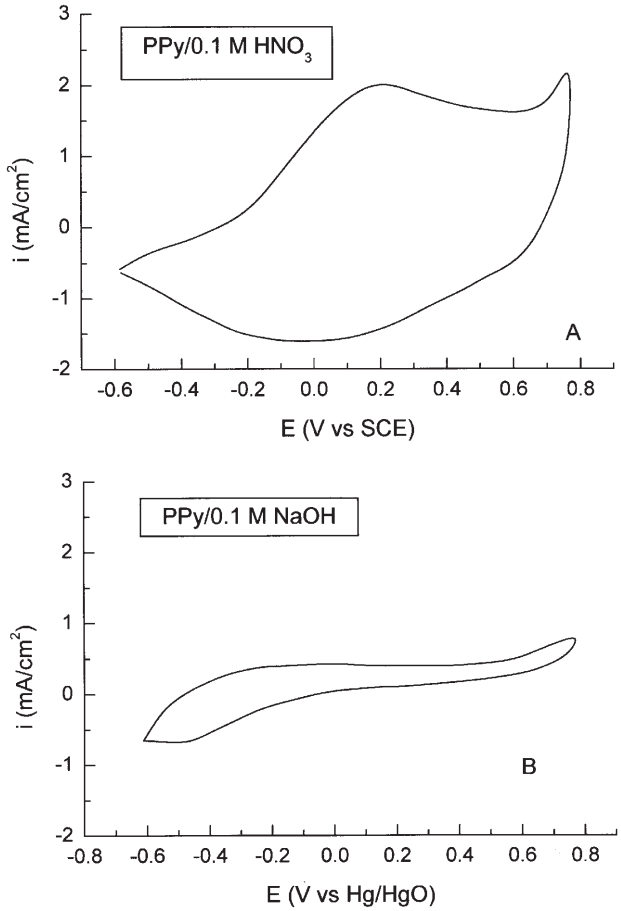

Fig. 1. Cyclic voltammogram for a polypyrrole covered GC electrode in: a) 0.1 M HNO_3 solution; b) 0.1 M NaOH solution (sweep rate 50 mV/s).

Two procedures are described in the literature[11,16] regarding the immersion of polypyrrole films in $AgNO_3$ solutions for the extraction of silver. Pickup *et al.*[11] extracted silver by acid-base treatment of polypyrrole. This treatment of the polymer results in its deprotonation/protonation.[20] Thus, the procedure applied by Pickup and coworkers[11] included galvanostatic polymerization of pyrrole in acetate buffer soltion, treatment of the polymer in NaOH for 5 h and immersion of the polymer in silver solution in HNO_3. Another group, F.-Y. Song and coworker,[16]

polymerized pyrrole in KNO_3 solution applying chronocoulometry and the obtained PPy-NO_3 film was immersed in $AgNO_3$ solution under the open-circuit potential. The procedure used in this work is, in some respects, a modified combination of these two. It enables the simple preparation of stable silver modified polypyrrole (PPy/Ag) electrodes for application in alkaline solutions.

Pyrrole was polymerized in 0.1 M HNO_3 by cyclic voltammetry. The CV recorded in HNO_3 free of pyrrole, presented in Fig. 1a, is similar to the CV of a PPy electrode prepared in 0.1 M KNO_3 solution[3] and is characteristic for polypyrrole doped with NO_3^- anions. As the aim of this work was to prepare electrodes for the oxidation of CH_2O in basic solution, the PPy electrode was cycled in 0.1 M NaOH (the CV recorded is presented in Fig. 1b). During this cycling, the exchange of dopant anion with OH^- ions should occur.[21] Treatment of the polymer film in base decreases the conductivity of the film,[22,23] but as can be seen from Fig. 1b, the electrode is still active enough for further applications. The thoroughly rinsed electrode was then immersed in 0.1 M $AgNO_3$ solution. In this way, using the monomer concentration, polymerization time and immersion time as variables, in total four types of electrodes (designated A – D) were prepared.

The modified electrodes were characterized by voltammetry in 0.1 M NaOH. The procedure applied was as follows: PPy/Ag electrode, after having been in contact with 0.1 M $AgNO_3$ solution, was thoroughly rinsed and immersed under a potential of 0.1 V *vs.* Hg/HgO (a value between the reduction and oxidation of silver) in 0.1 M NaOH, and scanning of the potential was started in the anodic direction. As shown in Fig. 2a (for electrode B), already in the first cycle, an anodic peak of the oxidation of silver was recorded, which means that silver is deposited in the zero valent state which is in agreement with Pickup[11] and Song.[16] Also, a somewhat lower quantity of silver was detected in this first cycle in comparison with the subsequent cycles, with a cathodic potential limit at – 0.6 V *vs.* Hg/HgO. This is due to the reduction of silver cations which remained in the film after rinsing either as Ag^+ from $AgNO_3$ or as AgOH (subsequently Ag_2O) precipitated in a reaction between OH^- from and within the PPy film and Ag^+ from the solution. The cyclic voltammogram in Fig. 2a (for electrode B), displays oxidation peaks for $Ag \rightarrow Ag_2O$ (A_1) and reduction peak $Ag_2O \rightarrow Ag$ (C_1) which resembles the one for a GC/Ag electrode with a small quantity of Ag.[17] The poorly defined peaks (A_2) and (C_2) should correspond to the further oxidation of Ag and $Ag_2O \rightarrow AgO$ and the reduction $AgO \rightarrow Ag_2O$ and Ag, respectively. However, while the cathodic peak (C_1) is recorded at practically the same potential for a PPy/Ag as for a GC/Ag electrode, the anodic peak (A_1) recorded for a PPy/Ag is at a less positive value by some 200 mV and thus the peak separation is smaller. These differences between a PPy/Ag and a GC/Ag electrode might be due to the nature and morphology of the substrates being different, leading to a different distribution and size of the Ag particles.

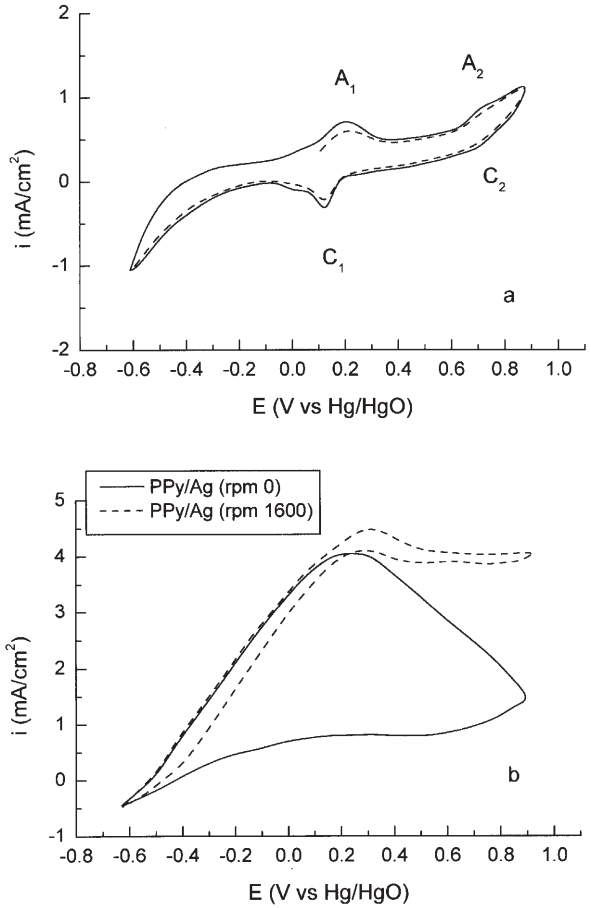

Fig. 2. Cyclic voltammogram for PPy/Ag – B electrode in: a) 0.1 M NaOH solution; b) 0.1 M NaOH + 0.1 M CH_2O solution (sweep rate 50 mV/s, rotation rate 1600 rpm for - - -).

TABLE I. Double layer charge of the PPy electrodes determined in 0.1 M HNO_3 and 0.1 M NaOH solutions and the quantity of silver deposited on the PPy/Ag electrodes

Electrode	q/mC cm^{-2} (HNO_3)	q/mC cm^{-2} (NaOH)	m Ag mol cm^{-2}
PPy/Ag – A	19.2	3.1	9.8×10^{-10}
PPy/Ag – B	28.8	5.6	7.3×10^{-9}
PPy/Ag – C	30.4	6.0	3.8×10^{-8}
PPy/Ag – D	13.7	2.4	traces

With GC/Ag electrodes, the quantity of silver deposited depends not only on the immersion time but also on the pretreatment of the GC electrode.[17] In the case of phlypyrrole, besides the immersion time, the thickness of the film and the monomer concentration were examined as variables that might effect the quantity of Ag

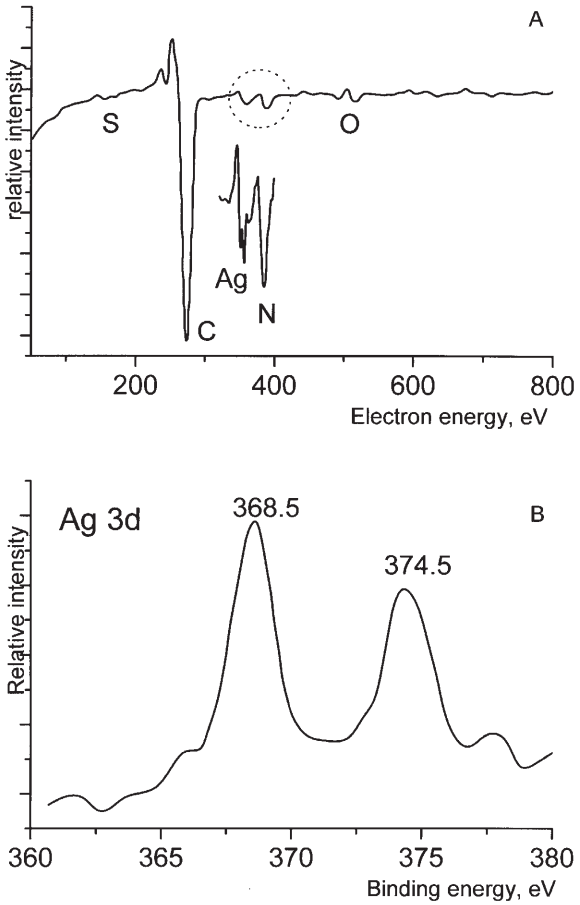

Fig. 3. AE spectra (a) and XP spectra (b) of PPy/Ag – B electrode (insert in Fig. 3a is the enlarged encircled part of the spectra).

deposited. The quantity of Ag was calculated by integration of the anodic peak (A_1) on the CV. The calculated values for each electrode are given in Table I. Hence, for the same immersion time (10 min), the quantity of Ag was higher on the electrode formed with a higher monomer concentration (0.1 M Py), only traces of Ag being found when 0.05 M Py was polymerized (electrodes A and D, respectively). Also, a smaller quantity of Ag was deposited on the thinner film than on the thicker one (electrodes A and B, respectively), which is in accordance with Song *et al.*[16] As expected, a longer time of immersion enabled a higher quantity of Ag to be deposited (electrodes B and C, respectively).

The modified PPy/Ag electrodes, except electrode D, were also examined for the oxidation of 0.1 M CH_2O in 0.1 M NaOH. The oxidation of formaldehyde at the PPy/Ag – B electrode is presented in Fig. 2b. The reaction starts at –0.5 V *vs.* Hg/HgO, but the peak maximum is reached at 0.2 V, *i.e.*, at the potential of Ag → Ag_2O oxida-

tion. Reversal of the direction of the voltage scan on a stationary electrode results in the loss of its activity and the electrode is blocked with gas dubbles. These bubbles are probably hydrogen as the electrooxidation of CH_2O in NaOH at a Au electrode is also accompanied with the evolution of hydrogen.[24] However, if the next sweep is recorded at a rotating PPy/Ag electrode, then the curve during the reverse sweep is practically superimposed on the curve recorded during the sweep in the positive direction. This should mean that no significant poisoning of the active sites of the electrode occurs. Similar results were obtained with the electrodes A and C.

Although the oxidation of CH_2O takes place at pure Ag (not on a surface covered with oxides), this reaction has been examined at the PPy/Ag electrodes over a wide potential range which, by comaprison with GC/Ag electrodes, includes the potentials of oxide formation. Namely, the oxidation of CH_2O on bulk Ag proceeds before the oxide formation and if the potential range includes the potentials of oxide formation the electrode will gradually lose its activity. In contrast, the GC/Ag electrode is active even over this wide range of potentials in both the positive and negative sweep direction.[19] The results described here, however, show that the PPY/Ag electrodes are similar to a polycrystalline Ag electrode. The CV recorded on a stationary electrode is similar to that of the rough surface of polycrystalline silver.[18] This is not surprising, as PPy/Ag is a high surface area supported electrode.

The surface of PPY/Ag electrodes was characterized using the AES (Auger-electron sprectroscopy) and XPS (X-ray photoelectron spectroscopy) methods as well. AE and XP spectra were recorded at four different points on the surface of the sample and were similar at all points. The presented spectra are the average spectra for these four points. The AE spectra of the surface composition of the PPY/Ag – B electrode, oxhibited in Fig. 3a, shows that silver is present on the surface. The XP spectra for the same electrode (Fig. 3b) shows that the $Ag_{3d5/2}$ transition occurs at 368.5 eV ($\pm$ 0.1 eV for the four different points) and the spin orbital separation of the Ag_{3d} level is 6.0 eV (and a Ag MVV Auger peak at 358.4 eV – not presented). These are statistical values for silver in the metallic form[25,26] and are in accordance with those from the literature.[16] Thus, the results obtained confirm the conclusion gained from cyclic voltammetry that simple immersion in $AgNO_3$ solution results in polypyrrole modified with silver in the zero valent state, deposited in the polymer film as a result of electroless reduction of silver ions.[11,14–16]

CONCLUSION

The above-described preliminary examinations gave some new results regarding the modification of polypyrrole with silver particles simply by immersion in $AgNO_3$ solution. The silver is deposited in the zero valent state and its quantity depends on the immersion time, thickness of the polymer film and concentration of monomer used for the polymerization. The conclusions based on the electrochemi-

cal characterization of the PPy/Ag electrode are confirmed also by AES and XPS surface examination. The modified PPy/Ag electrode is active for the oxidation of CH_2O in NaOH in spite of the rather low quantity of silver and is comparable with a polycrystalline Ag electrode.

Based on the preliminary results, we believe that it might be possible to improve the activity of the PPy/Ag electrode for the oxidation of CH_2O by optimizing the conditions applied during the polymerization of pyrrole and the modification of the polymer with silver.

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И З В О Д

КАРАКТЕРИЗАЦИЈА И ЕЛЕКТРОКАТАЛИТИЧКА ПРИМЕНА ПОЛИПИРОЛА МОДИФИКОВАНОГ СРЕБРОМ

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Електроде од полипирола модификованог сребром (PPy/Ag) испитиване су за електрооксидацију формалдехида у натријум-хидроксиду. Полипирол је модификован само урањањем у раствор сребро-нитрата, а добијене електроде су испитиване цикличном волтаметријом и вакуум техникама (AES и XPS). Полипирол је добијен електрохемијском полимеризацијом пирола, а испитиван је утицај времена урањања и дебљине полимерног филма на модификацију полимера сребром. Резултати добијени електрохемијским и спектроскопским испитивањима су показали да се полипирол уроњен у раствор сребро-нитрата спонтано модификује сребром које се таложи у елементарном облику. Количина наталоженог сребра зависи не само од времена урањања већ и од дебљине полимерног филма. Модификоване електроде PPy/Ag показују каталитичку активност за електрооксидацију формалдехида у натријум-хидроксиду. Активност ових електрода и при малим количинама спонтано наталоженог сребра, упоредива је са активношћу поликристалне сребрне електроде.

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