

Copper-modified conducting polymer layers for electroanalytic applications in neutral solutions

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Specific effects, observed in the studies of three different reactions (reduction of nitrate ions, oxidation of ascorbate ions and oxidation of dopamine) on copper-modified polyaniline (PANI), poly-*o*-methoxyaniline (POMA) and poly-3,4-ethylene-dioxythiophene (PEDOT) layers are discussed. It is shown that copper deposition on PANI results in blocking of the pores in the polymer structure and impeding reactions, involving the diffusion of small ionic species through the polymer layer. The comparative study of ascorbate oxidation on POMA, PANI and PEDOT points to the fact that the conjugated polymer (CP) layers conductivity is not always playing a crucial role in electrocatalytic applications. The weak electrocatalytic response, observed for dopamine oxidation on Cu-modified PANI, indicates the role of specific surface interactions impeding the access of the dopamine species to the copper surface.

Key words: polyaniline, PEDOT, copper, dopamine, ascorbic acid.

INTRODUCTION

Since the discovery of the electronic conductivity in conjugated polymers (CP), metal particles deposition on these materials has attracted much interest due to the possible use of metal modified polymers in electrocatalytic, electroanalytic and sensor applications. The initial purpose was to use the CP layer as a conducting matrix for dispersing metal catalytic sites. Meanwhile it was found out that the conducting polymers have intrinsic electro-catalytic activity with respect to oxidation reactions involving various analytes, e.g. catechols [1–6], ascorbic acid [5–9], uric acid [8, 9], etc. Thus, the next step in this direction was to try combining the electrocatalytic activity both of the CP matrix and deposited metallic sites.

Copper-modified electrodes are well known for their electrocatalytic activity in non-acidic solutions for electrooxidation of carbohydrates, organic acids, diols and amines [1–6]. Electrochemical reduction of nitrate ions has also been studied on copper and copper modified electrodes mainly in acidic solutions [10–14]. Recently it was shown [15] that copper electrodes were also effective for nitrate reduction in neutral solutions.

A first attempt to employ copper modified polyaniline electrodes for the oxidation of a number of amino acids and polyhydric compounds in alkaline solutions was carried out by Casella *et al.* [16]. In a

recent investigation [17] we studied the oxidation of ascorbate ions on PANI and POMA modified electrodes at pH 5.9.

The purpose of this investigation is to present exemplary results obtained in the studies of three different reactions (reduction of nitrate ions, oxidation of ascorbate ions and oxidation of dopamine) on copper-modified polyaniline, poly-*o*-methoxyaniline and poly-3,4-ethylenedioxythiophene layers and to focus on some specific effects due to the use of various Cu/CP systems. All three reactions are studied in neutral solutions.

EXPERIMENTAL

All electrochemical measurements were carried out in three-electrode cells, equipped with platinum plate counter electrodes and mercury sulphate reference electrodes. A platinum single crystal bead with surface area of $2 \times 10^{-3} \text{ cm}^2$ was used as working electrode. The electrolyte solutions are deaerated by bubbling argon prior to the electrochemical measurements. Details on the electrosynthesis of the polymer layers are available in our previous works [17–22]. Copper deposition is carried out in 0.033 M CuSO_4 and 0.5 M H_2SO_4 solutions under galvanostatic conditions ($j = -0.17 \text{ mA} \cdot \text{cm}^{-2}$) for PANI [18, 19] and POMA [17, 20] and under potentiostatic conditions ($\eta = 70 \text{ mV}$) for PEDOT [21, 22]. All potentials in the text and figures are given with respect to SHE.

Nitrate reduction was studied in 0.1 M NaClO_4 solution. Ascorbate oxidation was studied in 0.1 M phosphate buffer solution at pH 5.9 [17] and pH 7.

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Dopamine oxidation was studied in 0.1 M phosphate buffer solution at pH 7. In all cases before making the voltammetric measurements in the presence of the corresponding analyte (nitrate, ascorbate or dopamine) several scans were carried out in the corresponding supporting electrolyte (buffer or NaClO₄) till a stable response was obtained.

RESULTS AND DISCUSSION

Reduction of nitrate ions

Polyaniline and its derivatives, e.g. poly-*o*-methoxyaniline, are known for their pH- and potential-dependent conductivity. In neutral solutions and in the potential window, where nitrate reduction should be expected PANI, is in its low conducting state. Nevertheless, even under such conditions electrochemical reactions, involving small electroactive species such as H⁺, may proceed due to the porous polymer structure and the access of the reacting ions to the underlying metal surface. The initiation of the hydrogen reduction reaction on a PANI-coated electrode (Fig. 1, dashed grey line) was observed at about -0.65 V vs SHE. In the presence of nitrate ions no effect was found on the reduction current measured on the polymer coated platinum electrode (Fig. 1, grey line).

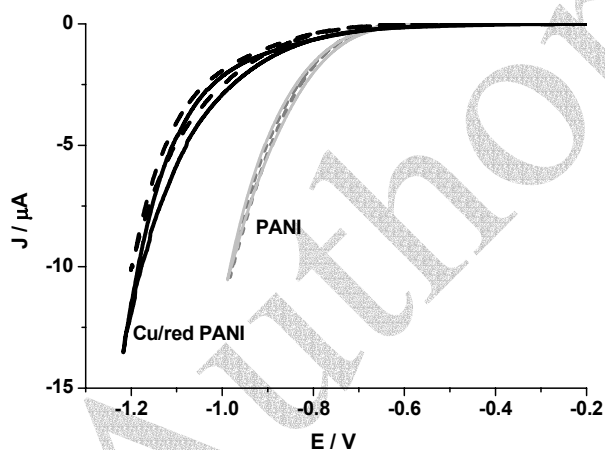


Fig. 1. Cyclic voltammograms measured in the absence (dashed lines) and presence of 5 mM NaNO₃ (full lines) in 0.1 M NaClO₄ solution on PANI (grey lines) and Cu-modified PANI (black lines) electrodes. $m^{\text{Cu}} = 23 \mu\text{g}\cdot\text{cm}^{-2}$; $v = 5 \text{ mV}\cdot\text{s}^{-1}$

A different behaviour was observed with the copper-modified PANI electrode (Fig. 1, black lines). For this electrode the hydrogen reduction became significantly (by more than 100 mV) inhibited. In the presence of a small amount of nitrate ions the reduction currents in both forward and backward directions were slightly shifted to more positive potentials (Fig. 1, black lines), indicating a

possible contribution of the nitrate reduction reaction to the overall reduction current. According to the proposed model [15, 18, 23] for copper deposition in the two different oxidation states of PANI, the inhibition of the hydrogen reaction on the Cu-modified PANI electrodes should be due either to filling of the porous polymer structure by the metal phase (in the case of copper deposition in the reduced PANI state) or to partial blocking of the pores on the polymer surface by copper crystallites (in the case of copper deposition in the oxidized PANI state). In both cases, the access of hydrogen ions to the underlying platinum surface is impeded.

Further experiments were carried out by increasing both the amount of deposited copper and the concentration of nitrate ions. In the case of copper deposited in the initially reduced PANI layer [18] the currents due to nitrate reduction became clearly discernible (Fig. 2, black line). The nitrate reductive wave was found in the potential window, where nitrate reduction is observed on bulk copper [15]. A less pronounced reductive response due to nitrate reduction was observed with electrodes obtained by copper deposition in the oxidized PANI state (Fig. 2, dashed line). In this case, the major part of the copper crystallites should be located on top of the polymer surface. Bearing in mind that the nitrate reduction experiments were carried out under conditions, where PANI is low conducting and most of the copper crystallites would be in contact only with the polymer phase, they would remain inactive for nitrate reduction.

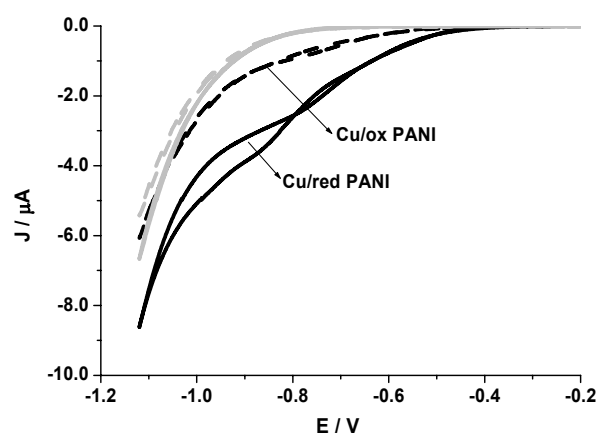


Fig. 2. Cyclic voltammograms measured in the absence (grey lines) and presence (black lines) of 20 mM NaNO₃ in 0.1 M NaClO₄ solution at Cu/PANI electrodes. Cu deposited in reduced (full lines) and oxidized (dashed lines) PANI layers. $m^{\text{Cu}} = 46 \mu\text{g}\cdot\text{cm}^{-2}$; $v = 20 \text{ mV}\cdot\text{s}^{-1}$.

Oxidation of ascorbate ions

In our previous study on ascorbate oxidation on polyaniline and poly-*o*-methoxyaniline coated elec-

trodes it was shown that both types of layers are electroactive for ascorbic acid oxidation at pH 5.9. Although *in-situ* measurements of the conductivity [24] indicated that POMA had lower conductivity than PANI, POMA coated electrodes showed higher ascorbate oxidation currents [17]. This result implied that the conductivity of the polymer coating was not of primary importance for its electrocatalytic performance. In the present study, we offer an additional argument in support of this suggestion.

Fig. 3 shows voltammetric curves measured in the presence of ascorbic acid (AA) at pH 5.9 on three different polymer modified electrodes: PANI, POMA and PEDOT. Among the three polymers PEDOT is the material with the highest (not pH dependent) conductivity.

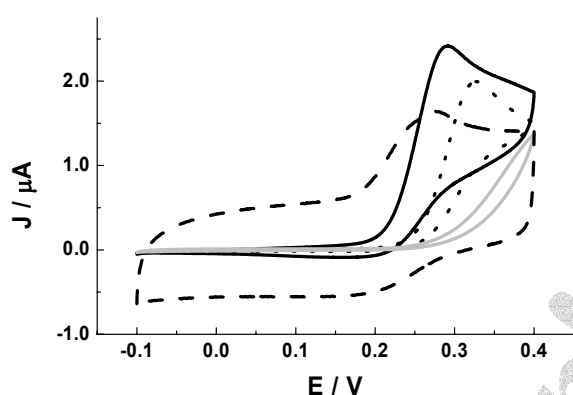


Fig. 3. Cyclic voltammograms measured in the presence of 5 mM ascorbic acid in PBS buffer solution (pH 5.9) at PANI (···), POMA(—) and PEDOT(---) coated electrodes. The grey line denotes the curve measured on the non-coated platinum electrode. $v = 5 \text{ mV}\cdot\text{s}^{-1}$.

As it is seen PEDOT and POMA enable the AA oxidation reaction at roughly the same potential, but POMA, although having much lower conductivity, provides higher AA oxidation currents. On the other hand, due to the low intrinsic capacitive current measured with POMA, this material would provide a better sensitivity for AA concentration measurements than PEDOT.

The comparison of the performance of the copper modified polymer coated electrodes (Fig. 4) shows, in all cases, an increase in the AA oxidation currents due to the involvement of the copper particles in the oxidation reaction. The much lower conductivity of PANI and POMA in comparison to PEDOT obviously did not limit the transport of electrons to the copper crystallites and their involvement in the AA oxidation reaction.

Oxidation of dopamine

Dopamine (belonging to the group of catecholamines) is a neurotransmitter playing an important

role in the human nervous and cardiovascular systems. Most of the work in the field of analytic detection of dopamine is directed towards finding selective electrocatalytic materials, able to discriminate between dopamine and other organic compounds, e.g. ascorbic acid, simultaneously present in the biological liquids. One of the proposed principles of discrimination relies on the charge characteristics of the reacting electrode surface [5, 25]. Positively charged surfaces or electrocatalytic centres should favour anion oxidation, e.g. ascorbate, whereas negatively charged surfaces or electrocatalytic centres should repel anions and favour the oxidation of the positively charged species, e.g. dopamine.

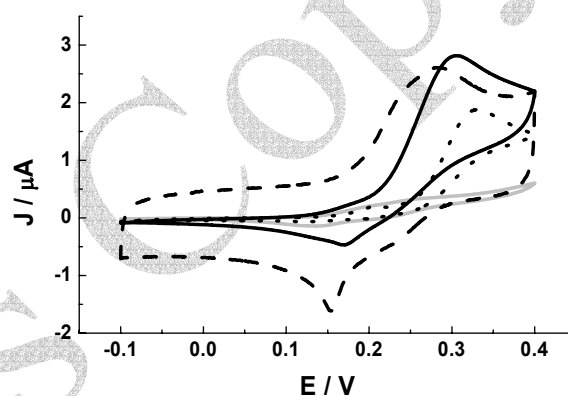


Fig. 4. Cyclic voltammograms measured in the presence of 5 mM ascorbic acid in PBS buffer solution (pH 5.9) on Cu-modified PANI (···), POMA (—) and PEDOT (---) coated electrodes. The grey line denotes the curve measured on the Cu-coated platinum electrode. $m^{\text{Cu}} = 34 \mu\text{g}\cdot\text{cm}^{-2}$; $v = 5 \text{ mV}\cdot\text{s}^{-1}$. (Copper deposited in the reduced state of PANI and POMA.)

Our experiments have shown that polyaniline alone has no intrinsic electroactivity for dopamine oxidation at pH 7. On the other hand, dopamine oxidation on a copper-coated platinum electrode showed a single well defined peak (Fig. 5, solid line) dominating over the ascorbate oxidation peaks (Fig. 5, dashed line).

Surprisingly, although copper is a good catalyst for dopamine oxidation, copper modified PANI layers exhibited only very low dopamine oxidation currents (Fig. 6). The weak response of the Cu-modified PANI electrodes to the dopamine oxidation reaction, observed also with notably increased copper loadings, indicates that in contrast to the ascorbate case dopamine has impeded access to the copper crystallites surface. This could be explained in terms of the already mentioned effects of surface charge interactions, involving repulsion of the dopamine species by positively charged centres of the polymer surface. On the other hand, the signifi-

cantly decreased ascorbate oxidation signal, observed in this case, should be ascribed to the much lower conductivity of the PANI matrix at this pH value [24].

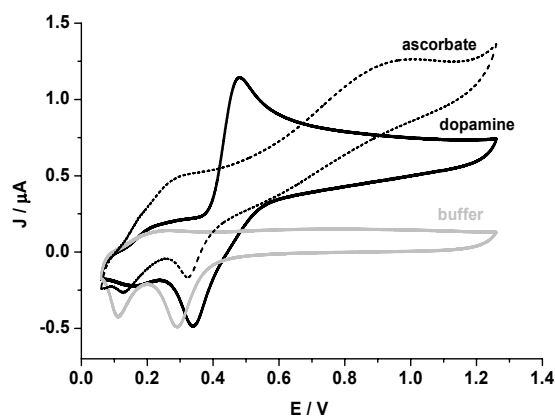


Fig. 5. Voltammetric curves measured in 0.1 M PBS (pH 7) (grey line) and in the presence of 5 mM ascorbic acid (dashed line) and of 2 mM dopamine (full line) using a copper-coated platinum electrode. $v = 20 \text{ mV}\cdot\text{s}^{-1}$.

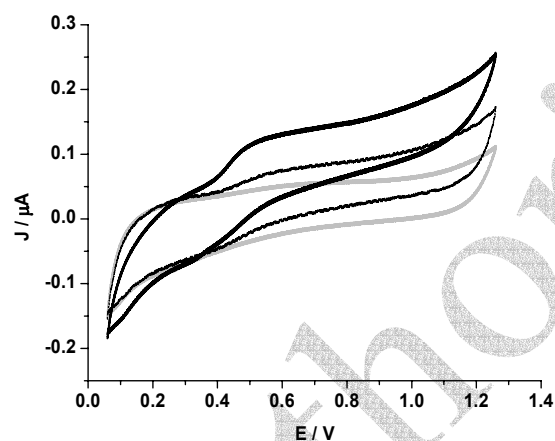


Fig. 6. Voltammetric curves measured in 0.1 M PBS (pH 7) (grey line) and in the presence of 5 mM ascorbic acid (dashed line) and of 2 mM dopamine (full line) using a copper-modified PANI electrode. $m^{\text{Cu}} = 46 \mu\text{g}\cdot\text{cm}^{-2}$; $v = 20 \text{ mV}\cdot\text{s}^{-1}$. (Copper deposited in the reduced state of PANI.)

CONCLUSIONS

In the present communication, we focused on some specific effects observed in the course of investigations of Cu-modified conducting polymers in three different electrocatalytic reactions. It was shown that copper deposition in PANI results in blocking of the porous polymer structure and impeding of reactions, involving small ionic species, which are able to diffuse through the polymer membrane and react on the underlying metal substrate. Thus side reactions (e.g. hydrogen reduction) going in parallel with the main reaction

investigated (e.g. nitrate reduction) are suppressed. Even when the polymer structure is in the low conducting state (as is the case of PANI at pH 7) the copper crystallites deposited under specific conditions (use of initially reduced PANI layers) provide the necessary electronic contact to the underlying metal electrode and are active for reactions, which proceed electrocatalytically on Cu.

A similar situation arises in the case of dopamine oxidation on PANI-coated electrodes. The polymer layer is again in the low conducting state and does not show any electrocatalytic activity in this reaction, whereas copper alone shows a well defined dopamine oxidation peak. The current response of the Cu-modified PANI electrode in this reaction is however strongly suppressed, indicating, very probably, an impeded access of the dopamine species to the dispersed copper crystallites. Most likely, this is due to the irreversible adsorption of the positively charged dopamine oxidation products on the polymer surface. Indication in this respect was obtained by comparing the voltammetry of the Cu-modified PANI electrodes in buffer solution before and after measurements carried out in the dopamine containing solution, showing a change in the polymer pseudocapacitive behaviour. Repulsive interaction of the adsorbed oxidation products with the diffusing dopamine species will limit their transport to the copper crystallites.

Finally, it is worth emphasising that the conductivity of the CP layers is not always playing a crucial role in electrocatalytic applications. Small conductivity may be still combined with high electrocatalytic activity as in the case of ascorbic acid oxidation on POMA. Although having high conductivity, the PEDOT layers do not provide a better ascorbate oxidation response. The low conductivity state of the polymer layer is in fact suitable for electroanalytic applications of metal/polymer composites materials due to the suppressing of the intrinsic capacitive currents of the CP layers. This would provide a better sensitivity of the metal/polymer composite materials in applications aimed at amperometric or voltammetric sensing of small analyte concentrations.

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МОДИФИЦИРАНИ С МЕД ПРОВОДЯЩИ ПОЛИМЕРНИ СЛОЕВЕ ЗА ЕЛЕКТРОАНАЛИЗ В НЕУТРАЛНИ РАЗТВОРИ

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(Резюме)

Обсъдени са специфични ефекти, наблюдавани при изследването на три електрохимични реакции (редукция на нитратни иони, окисление на аскорбатни иони и на допамин) върху модифицирани с мед слоеве от полианили (ПАНИ), поли(орто-метоксианилин) (ПОМА) и поли(3,4-етилендиокситиофен) (ПЕДОТ). Показано е, че електроотлагането на мед в полианилин води до блокиране на порите в полимерната структура и затрудняване на реакции, свързани с дифузията на малки иони през полимерния слой. Сравнителното изследване на окислението на аскорбатни иони върху ПАНИ, ПОМА и ПЕДОТ показва, че електрическата проводимост на полимерните слоеве не винаги играе решаваща роля при електрокаталитични приложения. Слабият електрокаталитичен сигнал, наблюдаван в случая на окисление на допамин върху модифицирани с мед слоеве от ПАНИ показва ролята на специфичните повърхностни взаимодействия, затрудняващи достъпа на допаминови молекули до медната повърхност.