



Electrochemical synthesis of polypyrrole films doped by ferrocyanide ions onto iron substrate: Application in the electroanalytical determination of uric acid



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ABSTRACT

Hollow spherical micro-particles of polypyrrole film doped by ferrocyanide anions $\text{Fe}(\text{CN})_6^{3-}$ were synthesized by chronoamperometric mode at 750 mV/(Ag/AgCl) onto iron substrate from an aqueous solution containing pyrrole monomer, potassium hexacyanoferrate $\text{K}_4\text{Fe}(\text{CN})_6$ and potassium tetraoxalate ($\text{C}_4\text{H}_3\text{KO}_8$). The modified electrode PPy/FCN/Fe was characterized by XRD, FEG-SEM and EDX techniques and its electrochemical behavior toward uric acid oxidation was studied by cyclic voltammetry. The results show that the incorporation of $\text{Fe}(\text{CN})_6^{3-}$ anions into the polypyrrole matrix improves significantly the electrocatalytic activity of this film. The plot of the catalytic oxidation peak current as function of uric acid concentration gives rise to the obtaining of straight line with a correlation coefficient of 0.983 and a good sensitivity of 4.46 $\mu\text{A}/\text{mM}$. The detection limit was found to be equal to 23 μM in a wide range of uric acid's concentration.

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1. Introduction

Uric acid (UA) is a principal and final product of purine metabolism. It was reported in the literature that the concentration of uric acid in serum is about 240–520 $\mu\text{mol L}^{-1}$ and the urinary excretion is 1.49–4.46 mmol L^{-1} during 24 h for a healthy person [1]. The increase of uric acid concentration in urine and serum cause several diseases. Thus, the determination of UA in body fluids is one of the most frequent analyses in clinical laboratories. Different methods such as colorimetric, enzymatic and electrochemical techniques have been widely used to determine the concentration of UA [2–4]. The electrochemical methods are more selective, less expensive and less time consuming than those based on colorimetric and enzymatic methods [5,6]. Conducting polymers exhibit catalytic effects for any redox reactions, e.g. oxidation of hydrazine on polyaniline [7], oxidation of ascorbic acid and hydrazine on polypyrrole [8,9]. The catalytic activity of the conducting polymers

can be improved by the incorporation of chemical species such as enzymes, metal particles [3,9] or doping ions [8], into the polymer matrix which can mediate the electron transfer process.

Among the conducting polymers, polypyrrole was chosen owing to its convenience of preparation, high stability and proton conductivity [8–10]. Its thickness can be roughly controlled by the electrolysis conditions and its oxidized form is positively charged and requires the incorporation of doping anions in order to maintain its electroneutrality [11]. Generally, the materials used as substrate in the preparation of polypyrrole modified electrodes are platinum, gold, glassy carbon and carbon paste electrode (CPE) [12,13], but the research area has known a real extension widening the choice of substrates in which the polymer is deposited, touching metals less noble as aluminum, copper, or iron [8,9,14].

Present paper deals with the preparation of polypyrrole films doped by ferrocyanide ions modified iron electrode by electropolymerization of pyrrole from an aqueous solution containing $\text{K}_4\text{Fe}(\text{CN})_6$, and $\text{C}_4\text{H}_3\text{KO}_8$ in order to study its electrocatalytic activity toward uric acid ($\text{C}_5\text{H}_4\text{N}_4\text{O}_3$) oxidation.

The modified electrode thus obtained was characterized by a Field Emission Gun-Scanning Electron Microscope (FEG-SEM), Energy Dispersive X-ray elemental analysis (EDX), and X-ray powder diffraction (XRD) techniques.

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2. Experimental

2.1. Reagents

All the solutions were prepared using distilled water. Uric acid ($C_5H_4N_4O_3$), potassium hexacyanoferrate $K_4Fe(CN)_6$, and potassium tetraoxalate $C_4H_3KO_8$ were of analytical grade supplied by Merck. Pyrrole was purchased from Fluka and was distilled before use. The pH of the solutions was adjusted with phosphate buffer solution prepared from potassium dihydrogenophosphate (KH_2PO_4) (99%, purity) and dipotassium hydrogenophosphate (K_2HPO_4) (97%, purity) purchased from Prolabo.

2.2. Preparation of the modified electrode PPy/FCN/Fe

Prior to synthesis, the iron electrode was polished with emery paper to 2400 grit, rinsed with distilled water and finally dried. The PPy/FCN film modified iron electrode was synthesized from an aqueous solution containing 0.05 M pyrrole, 0.05 M $K_4Fe(CN)_6$, and 0.05 M $C_4H_3KO_8$, used as electrolyte, by chronoamperometric mode at an imposed potential of 750 mV/(Ag/AgCl) during an electrolysis time of 5 min. Finally, the obtained modified electrode was rinsed with distilled water before each experiment.

2.3. Apparatus

Electrochemical measurements were run using a Tacussel PGP 201 potentiostat/galvanostat coupled with an HP personal computer under "Voltmaster software". The experiments were done in an electrochemical cell containing three electrodes. The working electrode was an iron of 0.196 cm^2 (99.99%, purity), a platinum wire as counter electrode and a double junction Ag/AgCl/KCl_{sat} (metrohm) as reference electrode. A pH-meter (Inolab) was used to read the pH of the buffered solutions.

A Field Emission Gun-Scanning Electron Microscope (FEG-SEM Ultra 55 Zeiss), coupled with Energy Dispersive X-ray elemental analysis (EDX), was used to visualize the morphology of the modified electrode PPy/FCN/Fe while the XRD technique was used to study its structure.

3. Results and discussion

3.1. Electrochemical preparation of the modified electrode PPy/FCN/Fe

3.1.1. Electrochemical behavior of iron and iron modified electrodes in potassium tetraoxalate medium

Iron is an oxidized metal and its oxidation potential is much more negative than that of pyrrole, which makes difficult the electrodeposition of polypyrrole on account of the dissolution of iron. As reported in our previous paper [8], the existence of a passive film on the iron substrate is necessary to the electrochemical synthesis of the polypyrrole film. The passive film is formed from an acidic medium where the nature of the anion influences its structure and chemical properties which determine the conditions to have strong bonds with the polymer film [15].

The anodic behavior of iron in the tetraoxalate medium is favorable to the synthesis of polypyrrole film comparatively to other acids such as sulfuric acid, acetic acid and citric acid [16]. Indeed, the potential of iron passivation in the potassium tetraoxalate is

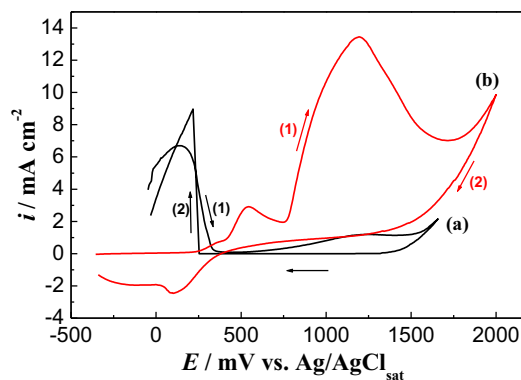


Fig. 1. Cyclic voltammograms obtained in 0.05 M $C_4H_3KO_8$ solution (pH 2.5) at 500 mV min^{-1} for (a) Fe electrode and (b) PPy/FCN/Fe modified electrode (prepared in 0.05 M pyrrole, 0.05 M $Fe(CN)_6^{4-}$).

much lower than that of pyrrole polymerization, which leads to the synthesis of an adherent and conductive polypyrrole film [16–19]. As reported by Mengoli and Musiani [20], the mechanism of the polypyrrole electrodeposition on iron electrode is strongly influenced by the chemical properties of oxalates anions.

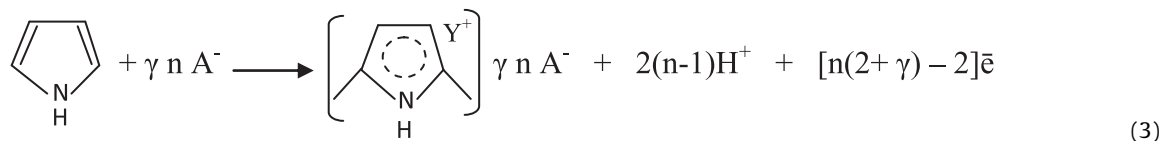
The results corresponding to the electrochemical behavior of the iron electrode in aqueous solution of $C_4H_3KO_8$ (0.05 M, pH 2.5) were first presented. The cyclic voltammogram presented at Fig. 1a corresponding to the first cycle reveals the presence of four different regions:

- In the anodic scan, the active dissolution of the iron electrode at a potential lower than 150 mV vs. Ag/AgCl according to the following reaction:

$$Fe \rightarrow Fe^{2+} + 2e^- \quad (1)$$
- Passivation of the iron substrate recorded in the range of 350–1500 mV vs. Ag/AgCl, which corresponds to a process of precipitation on the surface of the iron electrode due to the low solubility of the ferrous oxalate which forms according to the following reaction [21]:

$$Fe^{2+} + C_2O_4^{2-} \rightarrow FeC_2O_4 \quad (2)$$
- Region of trans-passivation at potential higher than 1500 mV where the current increases again slightly with the polarization (trans-passivation current), which is due to the attack of iron oxalate layer and to the oxygen evolution.
- Region of iron de-passivation at the potential of 250 mV vs. Ag/AgCl during the reverse scan.

In the presence of $Fe(CN)_6^{4-}$ ions and pyrrole monomer in the solution of $C_4H_3KO_8$, the cyclic voltammogram shows that the simultaneously electrodeposition of FCN and PPy is situated in the iron passivation zone (Fig. 1b). As can be observed, the oxidation peak of $Fe(CN)_6^{4-}$ ions occurs at a potential of 550 mV vs. Ag/AgCl which is less positive than the oxidation potential of pyrrole that starts at around 750 mV vs. Ag/AgCl. The oxidation of $Fe(CN)_6^{4-}$ ions was characterized by a blue deposit onto iron electrode followed by a black deposit of PPy covering the whole electrode surface. The general electropolymerization of pyrrole occurs according to the following reaction:



where γ is the doping level ($\gamma = 0.25\text{--}0.33$) [20].

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