

ELECTROCHEMISTRY OF METAL HEXACYANOFERRATES AND CONDUCTING POLYMERS BILAYER STRUCTURES DEPOSITED ON CONVENTIONAL SIZE ELECTRODES AND ULTRAMICROELECTRODES. I. CONVENTIONAL SIZE MODIFIED ELECTRODES

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Received May 28, 2007

Electrochemical preparation and characterization of hybrid inorganic-organic films consisting of iron (III) hexacyanoferrate, well known as Prussian Blue (PB), and of organic conducting polymers, on a platinum electrode, are reported. The organic conducting polymers poly-[3,4-ethylenedioxythiophene] (PEDOT), polyazulene (PAZ) and poly-2-[(E)-2-azulen-1-ylvinyl] thiophene (PAVT) have been used for the preparation of hybrid films in various configurations, such as PB/PEDOT, PB/PAZ, and PB/PAVT. The PB/PEDOT coating is prepared electrochemically by a two-step method. Firstly, a PB layer is electrodeposited onto a platinum electrode in aqueous solution. In the second step, the electrochemical deposition of PEDOT film over the Pt/PB modified electrode was carried out. The PB/PAZ and PB/PAVT coatings have been prepared in a similar manner. Thereafter, the electrochemical behaviour and the stability of the hybrid coatings were studied in aqueous solutions. The electrochemical response of PB/PEDOT, PB/PAZ and PB/PAVT coatings is based mainly on the Prussian Blue/Everitt Salt redox wave.

INTRODUCTION

During the last two decades, much progress has been made with developing modified electrodes, for instance based on transition metal hexacyanoferrates and conducting polymers.^{1,2} The electrode surface can be deliberately modified by different procedures, such as: adsorption, electroadsorption, electropolymerization, physical coverage and chemical bonding of specific species. Among these procedures, electropolymerization of the monomer on electrode surface is the most used method for conducting polymers modified electrodes preparation. The modification of electrodes with Prussian blue (PB, ferric ferrocyanide ($\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3$), has attracted a great deal of interest. In fact, PB or other metal hexacyanoferrates have been the subject of studies by many research groups involved in the preparation of electrochemical sensors as well as amperometric biosensors.³⁻⁶ The conducting polymers, such as polypyrrole, polyaniline,

polythiophene, polyazulene, and their derivatives, are usually prepared through an electropolymerization procedure and used as modifiers for the construction of the chemically modified electrodes. For instance, polymers of azulene and its derivatives have received much attention due to their good electrochemical properties and possible applications to various practical devices.⁷⁻⁹ The preparation of the electrodes modified with thin, but robust and highly conducting films capable of fast bulk and interfacial electron transfers during redox reactions are of great importance to electroanalysis. The conducting polymer can be used as a matrix to facilitate the flow of charge to spatially distributed redox centers, which could improve the performances of such electrochemical sensors based on modified electrodes. Recently, hybrid inorganic-organic coatings containing transition metal hexacyanoferrates and conducting polymers have been prepared as bilayer structures on electrode surfaces.¹⁰⁻¹² The role of the inorganic

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compound is mainly that of a redox mediator, while the organic component acts as a matrix or a permselective membrane. In this way, most stable and highly conducting coatings can be prepared on electrode surfaces.

This paper deals with the elaboration of new electrodes modified with spatially organized multilayers containing PB, PEDOT, and polyazulene derivatives. The electrochemical properties of these hybrid inorganic-organic structures have been investigated by using cyclic voltammetry.

EXPERIMENTAL

All chemicals: FeCl₃ (Merck), K₃[Fe(CN)₆] (Feinbiochimica), HCl (Aristar), KCl (Aldrich), 3,4-ethylenedioxythiophene (EDOT, Aldrich), acetonitrile (Sigma-Aldrich), tetrabutylammonium hexafluorophosphate (TBAPF₆, Fluka), and azulene (99%, AZ, Merck) were used without any further purification. 2-[(E)-2-azulen-1-ylvinyl]thiophene (AVT) was synthesized and purified according to the method reported in the literature.¹³ Doubly distilled water was always used to prepare aqueous solutions. The electrochemical experiments were carried out with an Autolab PGSTAT 20 or μAutolab potentiostat (Ecochemie) coupled to a PC running GPES software, using a single-compartment, three-electrode cell, at room temperature. A 3-mm diameter Pt disk electrode (Metrohm) was the working electrode, a saturated calomel electrode was the reference electrode, and a platinum wire (Metrohm) was the auxiliary electrode. All electrode potential values through this paper are expressed versus saturated calomel reference electrode. When a silver-silver chloride electrode was used as reference electrode, this is mentioned in text and caption of figures. Before each electrochemical test the surface of the working electrode was polished subsequently with 1, 0.3, and 0.05 μm alumina powder to a mirror finish, and rinsed with doubly distilled water.

Deposition procedure of PB, PEDOT and PAZ films

The modified electrodes have been prepared electrochemically by a two-step method. In the case of the PB|PEDOT coating, first a PB layer has been electrodeposited onto a Pt electrode. In the second step, the electrochemical polymerisation of PEDOT film over the Pt|PB modified electrode has been carried out. The PB film has been prepared from an aqueous solution containing 1 mM FeCl₃, 1 mM K₃Fe(CN)₆, 0.1 M KCl and 0.01 M HCl. The deposition electrode potential was +0.4 V vs. SCE and the charge consumed was 2 mC. In the case of the potentiodynamic procedure, the electrode potential was scanned in the potential range 0.0 – 1.0 V vs. SCE at a scan rate of 0.05 V/s. The PB deposition takes place during the first 10 successive potential cycles. After the deposition of PB layer, the modified electrode was washed with doubly distilled water. Then, an outer layer of organic conducting polymer was deposited on top of the Pt|PB modified electrode. The outer layer of PEDOT was prepared by potentiostatic electrochemical polymerisation of the monomer from an aqueous solution containing 0.01 M 3,4-ethylenedioxythiophene and 0.1 M

KClO₄. The deposition potential was 0.82 V vs. SCE and a deposition charge of 3.5 mC has been consumed. After the deposition of the conducting polymer, the modified electrode Pt|PB|PEDOT was washed with doubly distilled water and immersed in the transfer solution where it has been investigated by using cyclic voltammetry. The Pt|PB|PAZ modified electrodes were prepared in a similar manner, except that the deposition of the outer PAZ layer has been carried out by potential cycling in the range -0.6 – 1.8 V vs. Ag/AgCl, at a scan rate of 0.05 V/s, for 6 successive potential scans.

RESULTS AND DISCUSSION

Conventional-size electrodes modified with PB and PB/PEDOT structures

The PB layer was deposited onto Pt disk electrode surface by using the potentiostatic procedure at a potential of +0.4 V vs. SCE. The electrolysis was prolonged until a charge of 2 mC was consumed. The thickness (*d*) of the PB film was estimated using equation (1):

$$d = \frac{Q \cdot l^3 \cdot N_A}{4nFA} \quad (1)$$

where *Q* is the charge consumed for deposition, *l* the length of the PB unit cell, in centimetres (*l* = 10.28 · 10⁻⁸ cm), *N_A* the Avogadro's number, *n* the number of electrons (*n* = 1 in this case), *F* the Faraday's constant, and *A* the area of the Pt disk electrode surface coated with the PB film, in square centimetres (*A* = 0.071 cm² in the case of Pt disk electrode of 3 mm diameter).¹⁴ The thickness of freshly deposited films was 477.5 nm, assuming that all the charge is consumed for the deposition of PB. After the deposition of PB, the modified electrode was washed with doubly distilled water and immersed in the transfer solution where it has been investigated by using cyclic voltammetry. The cyclic voltammograms of the freshly prepared Pt|PB modified electrode in the transfer solution are depicted in Fig. 1. The Pt|PB modified electrode displays two redox waves situated at ca. 0.2 V and 0.9 V vs. SCE, respectively. These waves correspond to the reduction of PB to Everitt Salt (ES) and to the oxidation of PB to Berlin Green (BG), respectively. These redox processes can be described by using the two formula of PB, *i.e.* the soluble form (equations 2 and 4) and the insoluble form (equations 3 and 5), respectively, according to the following reactions:

- redox wave corresponding to the PB/SE system:



- redox wave corresponding to the PB/BG system:

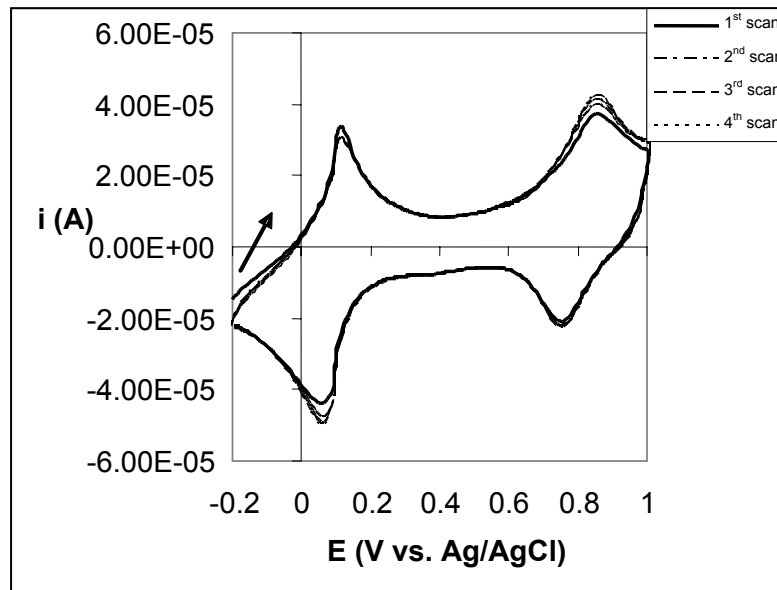
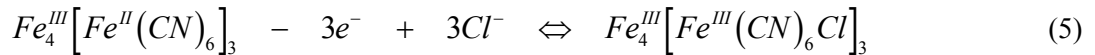


Fig. 1 – Cyclic voltammograms of Pt/PB electrode ($q = 2 \text{ mC}$; $d = 477.5 \text{ nm}$) in the transfer solution containing 0.1 M KCl and 0.01 M HCl . Potential scan rate: 0.05 V/s . The first 4 scans are represented.

The modified electrode shows the electrochemical features of PB films often reported in the literature, and therefore our interest was to investigate the deposition of the PEDOT outer layer on top of Pt/PB electrode. The deposition of EDOT was achieved by potentiostatic electrochemical polymerization of the monomer at $+0.82 \text{ V vs. SCE}$. A charge of 3.5 mC was consumed during the electropolymerization. The Pt/PB/PEDOT modified electrode was then investigated in aqueous solution by using cyclic voltammetry. Fig. 2 reports cyclic voltammograms recorded at the modified electrode for different potential ranges. The hybrid PB/PEDOT coating displays the redox wave corresponding to the PB/ES system. No redox wave can be observed when the anodic potential limit is extended to $+1.0 \text{ V}$, which clearly suggests that under these experimental conditions the occurrence of the reactions (4) and (5) is hindered. The hybrid coating is very stable when the electrode potential is scanned in the negative direction for electrode potential values as high as $(-1.0) \text{ V}$.

The shape of these cyclic voltammograms demonstrates that the outer conducting polymer layer allows the transport of potassium ions from the electrolyte solution in and out of the inner PB film. As regards the electrochemical features of the outer PEDOT layer, it is difficult to observe the redox wave corresponding to the polaron formation. However, this wave can be seen when ultramicroelectrodes are used. The values of the electrical charges used for the deposition of each layer on conventional size electrodes are small enough to allow the formation of very thin films onto the electrode surface. Therefore the diffusion path length of both electrons, for electron hopping between neighbour redox centers, and counter ions is short enough that a reversible behaviour prevails. The electrochemical responses of this hybrid coating demonstrate that: (i) PB is able to conduct electrons through the outer organic polymer layer and (ii) potassium cation transport to the PB is not impeded by the presence of the outer organic layer.

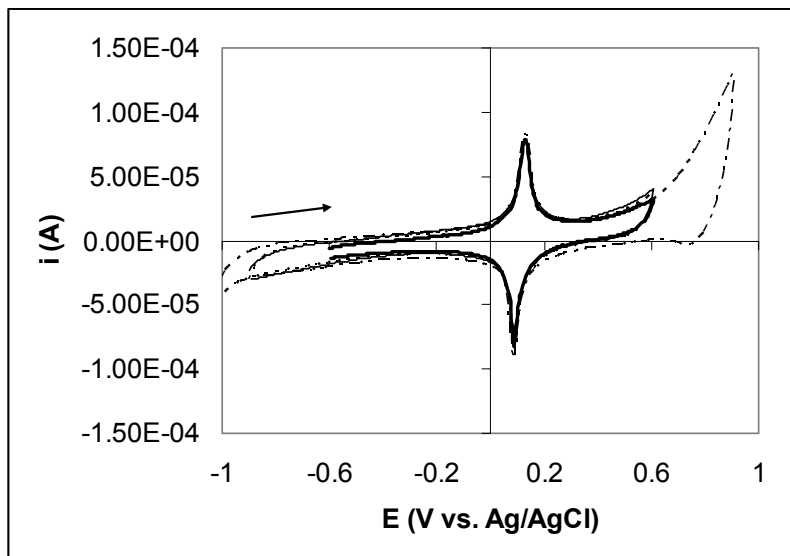


Fig. 2 – Cyclic voltammograms of Pt/PB/PEDOT modified electrode (2 mC / 3.5 mC) in aqueous solution containing 0.1 M KCl. Potential scan rate: 0.05 V/s.

Conventional-size electrodes modified with PB/PAZ coatings

Hybrid PB/PAZ coating have been prepared in a similar manner onto Pt disk electrodes by a two step method. Firstly, a PB layer is formed onto Pt electrode surface by cycling the electrode potential from O.C.P to 0.0 V and reversing back the scan to +1.0 V vs. SCE at a scan rate of 0.05 V/s. The composition of the solution was as follows: 0.5

mM FeCl₃, 0.5 mM K₃ Fe(CN)₆, 0.1 M KCl, and 0.01 M HCl. The cyclic voltammograms recorded during the PB deposition are depicted in Fig. 3. The PB deposition occurs for the first 8 successive scans, as indicated by the increase of both cathodic and anodic peak currents, for each redox wave.

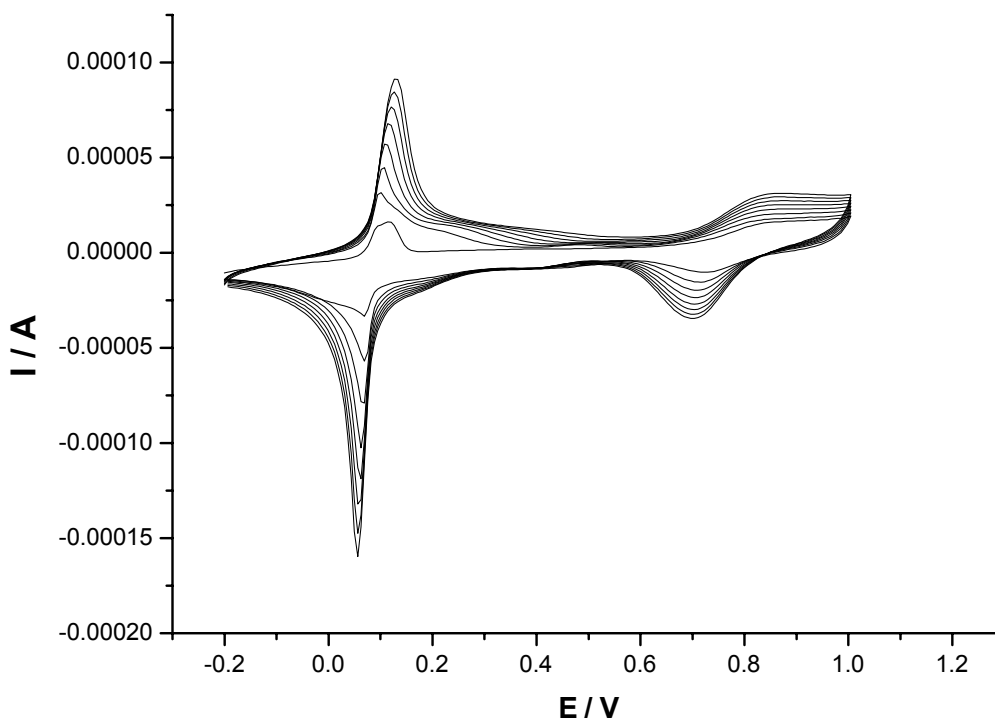


Fig. 3 – Cyclic voltammograms recorded at Pt electrode during the PB deposition from a solution containing 0.5 mM FeCl₃, 0.5 mM K₃ Fe(CN)₆, 0.1 M KCl, and 0.01 M HCl. Potential scan rate: 0.05 V/s. The first 8 successive scans are represented.

After the PB deposition, the modified electrode was washed with deionized water and the PAZ film was generated on top of this electrode by potentiodynamic electropolymerization from a solution in acetonitrile containing 0.01 M azulene and 0.1 M TBAPF₆. Fig. 4 reports the cyclic voltammograms recorded during the electropolymerization of azulene on top of Pt/PB modified electrode.

The electropolymerization of azulene occurs at a potential value of ca. +0.9 V vs. Ag/AgCl. The first scan in anodic direction shows a diffusional shape, while the following scans are broadening. The anodic peak current increases with the potential scan number and the anodic peak potential shifts slowly to more positive values. These electrochemical features demonstrate that the PAZ film grows during the potential scanning and the inner PB layer acts as a redox mediator for the electropolymerization process. The Pt/PB/PAZ modified electrode was then investigated in transfer solution by using cyclic voltammetry (see Fig. 5).

From Fig. 5 it can be seen that the peak to peak potential separation of the PB/SE redox wave is larger than in the case of Pt/PB/PEDOT modified electrode. This behaviour suggests that the PAZ film has high thickness and this does not allow rapid transport of potassium ions in and out of the inner PB layer. The redox wave corresponding to

the PB/BG system can not be observed for this modified electrode. The effect of scan rate on the oxidation and reduction of PB/PAZ bilayer was investigated. The anodic and cathodic peak currents increase linearly with the scan rate up to 0.5 V/s. A good linearity between the scan rate and peak currents was obtained within the range of 50-500 mV/s, suggesting a surface-controlled process on the modified electrode. The linear equation was $I_{pa} = 2.7965 \nu \text{ (V/s)} + 0.2668$, ($R^2 = 0.9888$) and $I_{pc} = -3.3883 \nu \text{ (V/s)} - 0.3895$, ($R^2 = 0.9923$), respectively.

Another hybrid coating containing an inner PB layer and an outer PAVT layer has been prepared in a similar manner. The cyclic voltammograms recorded during the electrochemical deposition of PAVT layer on top of Pt/PB modified electrode are presented in Fig. 6. The electrochemical polymerization of AVT at Pt/PB modified electrode occurs at a potential value of ca. +0.6 V vs. Ag/AgCl. The PAVT film grows during the anodic scan, as indicated by the increase of the anodic peak current during potential cycling. The deposition of PAVT film clearly demonstrates that the inner PB layer is capable to conduct electrons even in the organic media containing acetonitrile.

The Pt/PB/PAVT modified electrode was then characterized in free monomer acetonitrile solution (see Fig. 7).

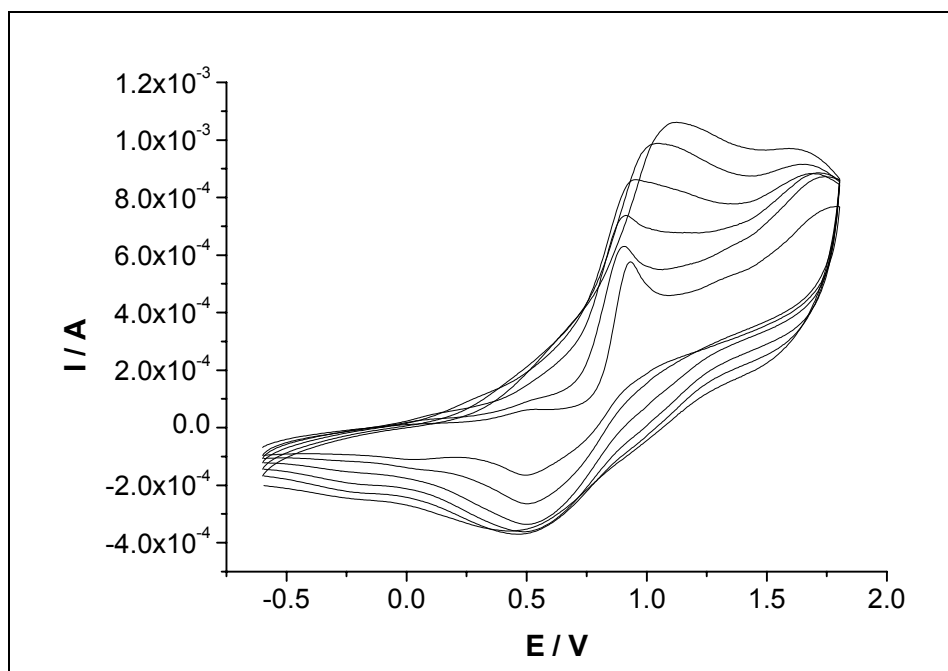


Fig. 4 – Cyclic voltammograms recorded at a Pt/PB modified electrode during the electropolymerization of azulene from 0.01 M azulene and 0.1 M TBAPF₆, acetonitrile solution. Potential scan rate: 0.05 V/s. The first 6 successive scans are depicted.

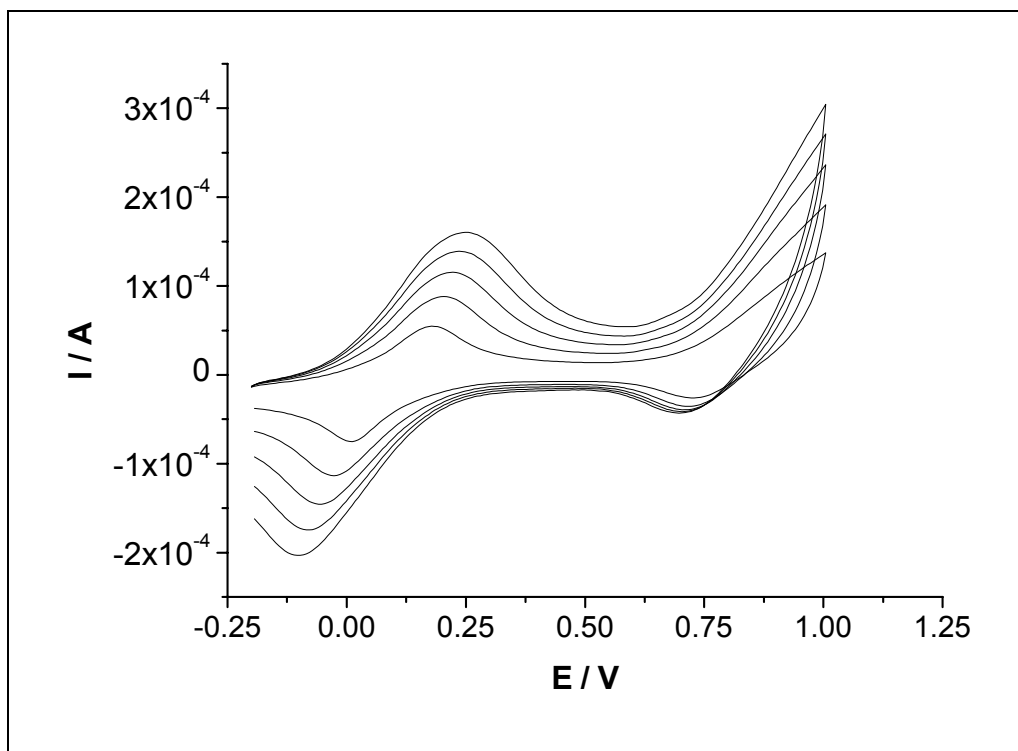


Fig. 5 – Cyclic voltammograms of Pt/PB/PAZ modified electrode recorded in 0.1 M KCl, 0.01 M HCl aqueous solution. Potential scan rates: 0.1, 0.2, 0.3, 0.4 and 0.5 V/s.

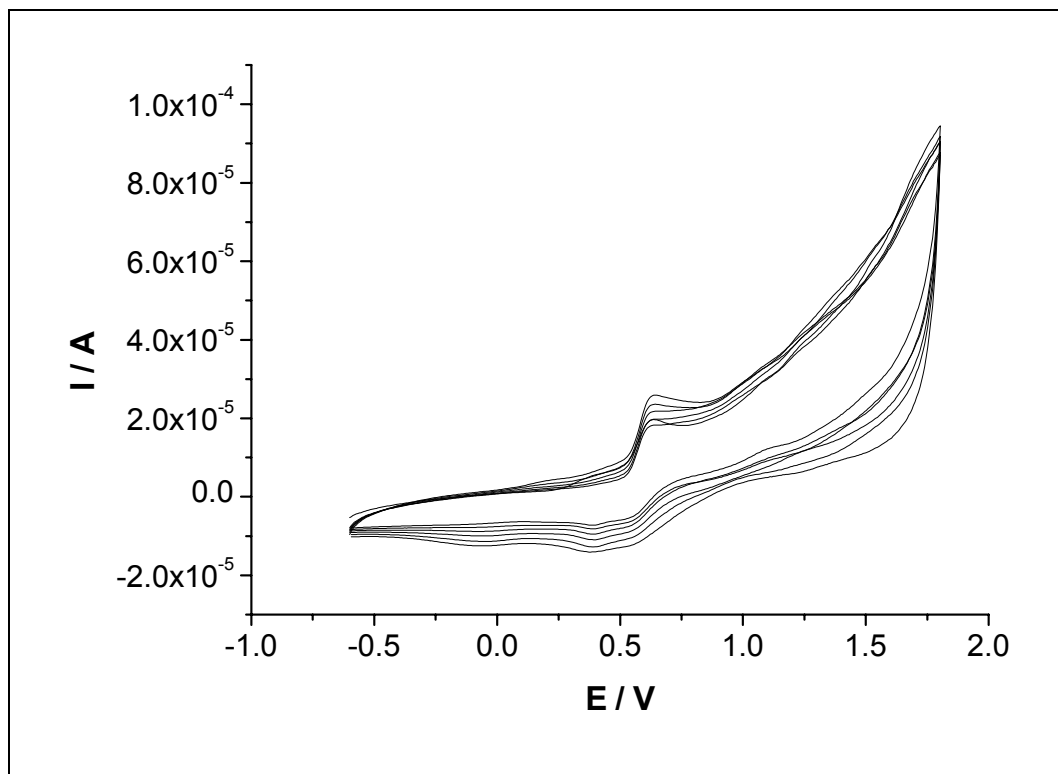


Fig. 6 – Cyclic voltammograms recorded at a Pt/PB modified electrode during the electropolymerization of AVT from 0.01 M AVT and 0.1 M TBAPF₆, acetonitrile solution. Potential scan rate: 0.05 V/s. The first 6 successive scans are depicted.

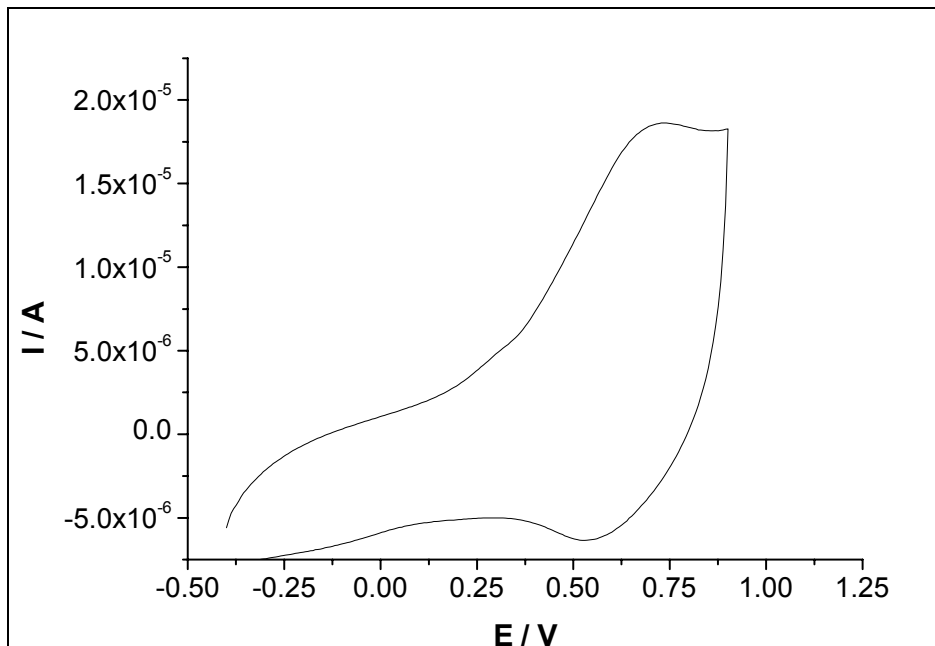


Fig. 7 – Cyclic voltammogram of Pt/PB/PAVT modified electrode in 0.1 M TBAPF₆, acetonitrile solution. Potential scan rate: 0.05 V/s.

The cyclic voltammogram shows a redox wave situated at ca. 0.6 V vs. Ag/AgCl, which corresponds to the polaron formation on the PAVT backbone. In this organic media the redox wave of PB/SE system can not be observed because of the

absence of potassium ions in the solution. When the modified electrode is transferred in aqueous solution containing KCl, the characteristic redox wave of PB/SE system could be observed at ca. 0.2 V vs. Ag/AgCl, as can be seen from Fig. 8.

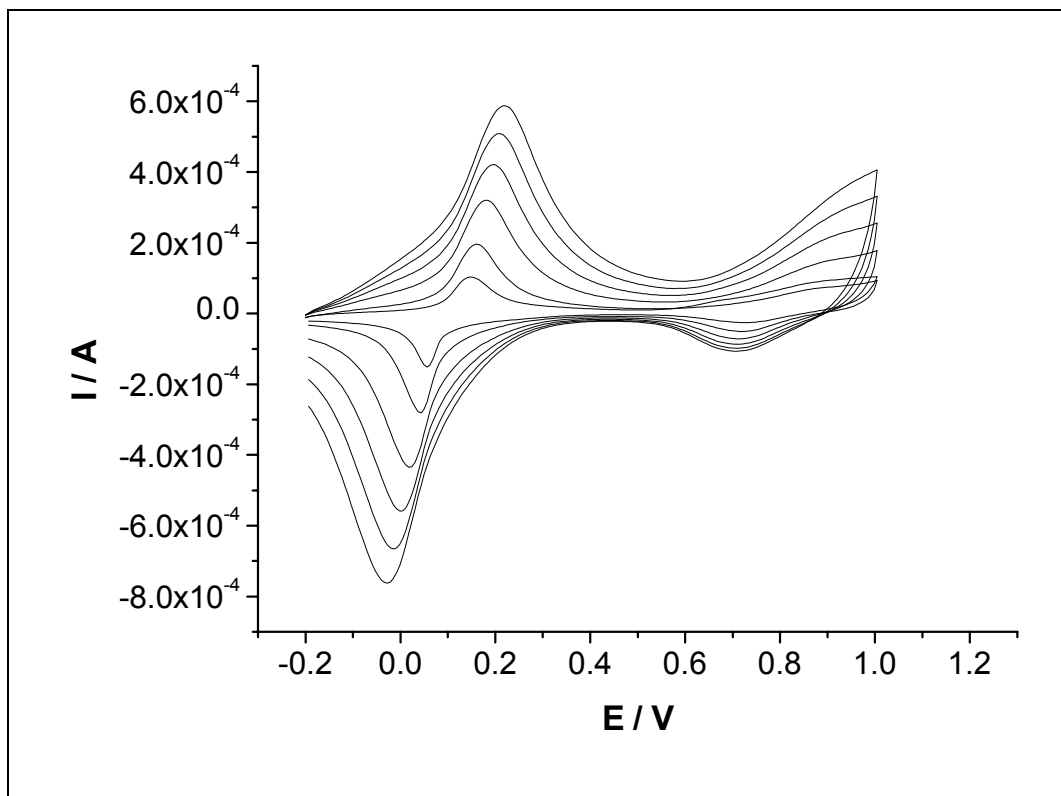


Fig. 8 – Cyclic voltammograms of Pt/PB/PAVT modified electrode recorded in aqueous solution containing 0.1 M KCl and 0.01 M HCl. Potential scan rates: 0.1, 0.2, 0.3, 0.4 and 0.5 V/s.

CONCLUSIONS

The hybrid inorganic-organic coatings prepared in various experimental conditions exhibit good electrochemical properties. The PB/PEDOT bilayers present the redox wave corresponding to the PB/SE system. The thickness of PB inner layer could be controlled by the electrical charge consumed during the deposition. Very thin PB films with thickness less than 500 nm can be prepared by potentiostatic method. The inner PB layer acts as a redox mediator during the deposition of the outer conducting polymer layer. The stability and electrochemical features of these hybrid inorganic-organic coatings could be exploited in the preparation of electrochemical sensors.

Acknowledgements: Financial support from the Ministry of Education, Research and Youth through grant no. 2 CEEEX 06-11-43/25.07.2006 is greatly acknowledged. The authors thanks Mr. A. C. Razus for the synthesis of 2-[(E)-2-azulen-1-ylvinyl]thiophene.

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