

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

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Electrochemical preparation and characterisation of composite films consisting of iron (III) hexacyanoferrate, well known as Prussian Blue (PB), and of organic conducting polymer, such as poly-[3,4-ethylenedioxythiophene] (PEDOT), on a platinum ultramicroelectrode, are reported. The inorganic-organic hybrid PB/PEDOT films have been prepared electrochemically by a two-step method. Firstly, a PB layer is electrodeposited onto a platinum ultramicroelectrode in aqueous solution, and thereafter the electrochemical deposition of PEDOT film over the Pt/PB modified electrode was carried out. The electrochemical behaviour and the stability of the hybrid coatings were studied in aqueous solutions. The electrochemical response of PB/PEDOT coatings is based both on the Prussian Blue/Everitt Salt (PB/ES) redox wave and polaron formation redox wave, respectively. The surface coverage for each redox couple was computed as follows:  $2.68 \times 10^{-10}$  mol cm<sup>-2</sup> for the PB/ES anodic wave,  $2.60 \times 10^{-10}$  mol cm<sup>-2</sup> for the cathodic PB/ES wave, and  $2.36 \times 10^{-10}$  mol cm<sup>-2</sup> in the case of the polaron formation redox wave, respectively. These surface coverage values attest that the hybrid bilayer coating contains very thin PB films.

### INTRODUCTION

Modification of electrode surfaces with composite coatings of inorganic and organic materials has been shown to exhibit a lot of functional characteristics, which are valuable for the preparation of electrochemical sensors. In a previous paper, the electrochemical preparation and characterization of conventional size electrodes modified with transition metal hexacyanoferrate and various conducting polymers has been discussed.<sup>1</sup> The classic approach was to develop modified electrodes, for instance based only on transition metal hexacyanoferrates or conducting polymers.<sup>2,3</sup> The electrode surface can be deliberately modified by different procedures, such as: adsorption, electroadsorption, electropolymerization, physical coverage and chemical bonding of specific species. Electropolymerization of the monomer on electrode surface has become the method of choice for conducting polymers

modified electrodes preparation. On the other hand, the deposition of Prussian blue (PB, ferric ferrocyanide (Fe<sup>III</sup>[Fe<sup>II</sup>(CN)<sub>6</sub>]<sub>3</sub>) as thin films onto electrode surface for electrochemical sensors and biosensors preparation has attracted a great deal of interest.<sup>4-7</sup> Recently, hybrid inorganic-organic coatings containing transition metal hexacyanoferrates and conducting polymers have been prepared as bilayer structures in various configurations on electrode surfaces.<sup>8-13</sup> The inorganic compound acts as a redox mediator, while the role of the organic conducting polymer is that of a matrix or a permselective membrane. This results in most stable and highly conducting coatings deposited on electrode surfaces.

The use of ultramicroelectrodes in electrochemistry has become widespread only in the past 15 – 20 years. Ultramicroelectrodes have been constructed in a variety of geometries including disk, line, cylinder, and ring electrodes. The most widely used geometry is the disk type,

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because it is relatively simple to fabricate and easy to use.<sup>14</sup> Ultramicroelectrodes offer several advantages over electrodes of conventional size. One obvious advantage is that their small size allows their use in very small sample volumes. Another advantage is that of the use of ultramicroelectrodes for *in vivo* electrochemical measurements. Considerable attention has been devoted to measurements of neurotransmitters and associated compounds in the brain.<sup>15</sup> The small size of ultramicroelectrodes also results in small currents, which means that these electrodes can be used without any alteration of the sample. This feature is very important when considering biological samples or *in vivo* measurements, where such destruction should be minimized. The use of ultramicroelectrodes in cyclic voltammetric experiments is now common. The benefits of undertaking cyclic voltammetric experiments at ultramicroelectrodes are: fast time scale, enhanced mass flux and current density, low  $IR_u$  drop.<sup>16, 17</sup> The combination of these benefits with electrode surface modification results in powerful electrochemical sensors.

In this paper, the preparation of new ultramicroelectrodes modified with spatially organized bilayers containing PB and PEDOT is presented. The electrochemical properties of these hybrid inorganic-organic coatings have been investigated in aqueous solution by using cyclic voltammetry.

## EXPERIMENTAL

All chemicals:  $FeCl_3$  (Merck),  $K_3[Fe(CN)_6]$  (Merck), HCl (Merck), KCl (Aldrich),  $KClO_4$  (Merck), and 3,4-ethylenedioxythiophene (EDOT, Aldrich), were used without any further purification. De-ionised water was always used to prepare aqueous solutions. The electrochemical experiments were carried out with an Autolab PGSTAT 20 (Ecochemie) coupled to a PC running GPES software, using a single-compartment, three-electrode cell, at room temperature. A Pt inlaid disk ultramicroelectrode with diameter of 125  $\mu m$  was the working electrode, a saturated calomel electrode was the reference electrode, and a platinum wire was the auxiliary electrode. Before each electrochemical test the surface of the working electrode was polished with 0.3  $\mu m$  alumina powder to a mirror finish, and rinsed with doubly distilled water.

### Deposition procedure of PB/PEDOT hybrid films

The modified ultramicroelectrodes have been prepared electrochemically by a two-step method. Firstly, a PB layer has been electrodeposited onto a Pt ultramicroelectrode. In the second step, the electrochemical polymerisation of PEDOT film over the Pt/PB modified ultramicroelectrode has been carried out. The PB film has been prepared by using a

potentiodynamic procedure from an aqueous solution containing 1 mM  $FeCl_3$ , 1 mM  $K_3Fe(CN)_6$ , 0.1 M KCl and 0.01 M HCl. 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 ultramicroelectrode was washed with doubly distilled water. Then, an outer layer of organic conducting polymer was deposited on top of the Pt/PB modified ultramicroelectrode. 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  $KClO_4$ . The deposition potential was 0.82 V vs. SCE and a deposition charge of 0.1 mC has been consumed. After the deposition of the conducting polymer, the Pt/PB/PEDOT modified ultramicroelectrode was washed with doubly distilled water and immersed in the transfer solution where it has been investigated by using cyclic voltammetry.

## RESULTS AND DISCUSSION

The electrochemistry of hybrid inorganic-organic coatings has been investigated at Pt inlaid disk ultramicroelectrode with diameter of 125  $\mu m$ . Fig. 1 reports the cyclic voltammograms recorded at a Pt disk ultramicroelectrodes ( $d = 125 \mu m$ ) during the deposition of PB.

The cathodic and anodic peak currents for both redox systems increase linearly with the number of potential scan, as indicated in figure by arrows. Both redox waves are well defined and the cathodic part of the redox wave corresponding to the PB/SE system is very narrow, demonstrating that a very thin film is formed onto the electrode surface. After the deposition of PB layer, the modified electrode was investigated in transfer solution by using cyclic voltammetry. In Fig. 2, the first and the fifth scan are represented. These scans are very well overlapped attesting an excellent stability of the PB layer. This result is remarkable taking in consideration that the so called “PB activation” is performed usually on a narrow potential range where the anodic scan limit does not reach the formal potential of the PB/BG redox system.

The outer PEDOT layer has been deposited by potentiostatic polymerization from an aqueous solution containing 0.01 M EDOT and 0.1 M  $KClO_4$ , at a potential value of +0.82 V vs. SCE. The charge used in the electropolymerization process was of 0.1 mC. The Pt/PB/PEDOT modified ultramicroelectrode has been lately immersed in 0.1 M  $KClO_4$  aqueous solution. The first 5 scans of the cyclic voltammograms recorded at this modified electrode are represented in Fig. 3.

It can be seen that all the cyclic voltammograms are very well overlapped, which attests for a high stability of the hybrid coating. Two redox waves are observed in the potential range from (-1.0) to +0.6 V vs. SCE. The wave located at ca. (-0.6) V vs. SCE is attributed to the polaron formation on the outer PEDOT backbone. It should be noted that this wave is not evident in the case of the macroscopic conventional-size modified electrodes.<sup>1</sup> The advantages of ultramicroelectrodes result in more well shaped cyclic voltammograms. The

second redox wave situated at ca. +0.2 V vs. SCE corresponds to the PB/SE redox system.<sup>1</sup> This wave is not narrow and the peak to peak potential separation suggests the presence of a thick PEDOT layer on top of the PB inner layer. However, the PEDOT outer layer allows the transport of potassium ions in order to maintain the electroneutrality and for the proper functioning of the PB inner layer. Furthermore, the PB layer is able to mediate the electron transfer required for the polaron formation.

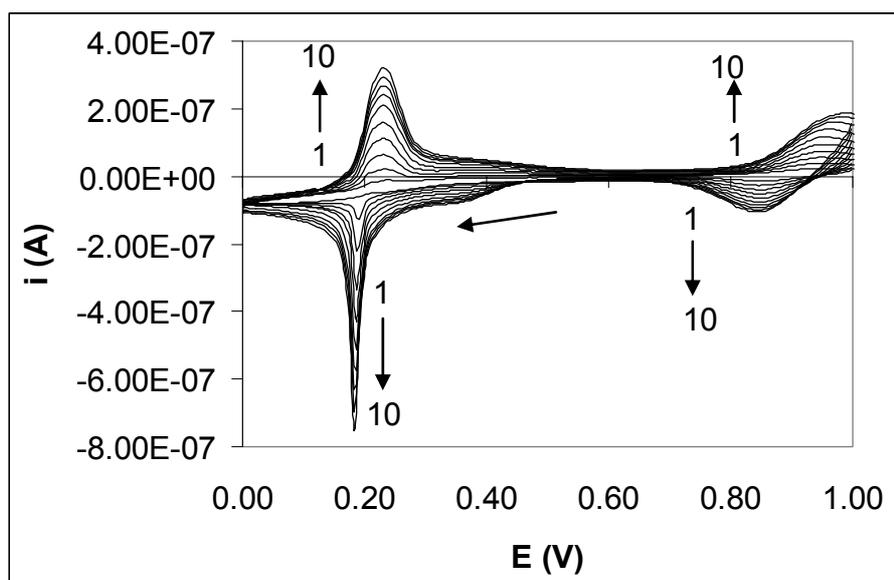


Fig. 1 – Cyclic voltammograms recorded during the PB deposition onto Pt disk ultramicroelectrode ( $d = 125 \mu\text{m}$ ). Composition of the deposition solution: 1 mM  $\text{FeCl}_3$ , 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$ , 0.1 M KCl and 0.01 M HCl. Potential scan rate: 0.05 V/s. The first 10 successive scans are depicted.

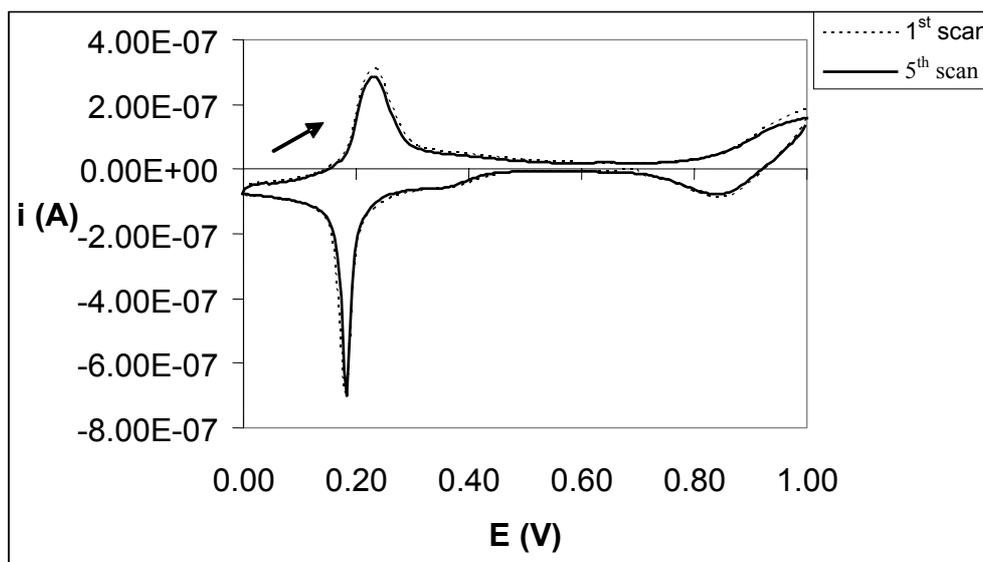


Fig. 2 – Cyclic voltammograms of Pt/PB modified ultramicroelectrode ( $d = 125 \mu\text{m}$ ) in the transfer solution containing 0.1M KCl and 0.01M HCl. Potential scan rate: 0.05 V/s. The 1<sup>st</sup> and 5<sup>th</sup> scans are depicted.

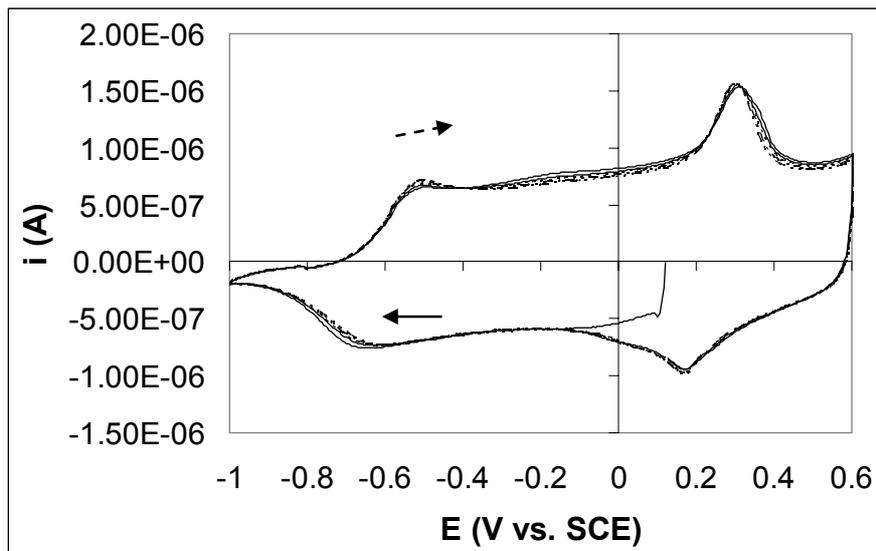


Fig. 3 – Cyclic voltammograms of Pt/PB/PEDOT modified ultramicroelectrode ( $d = 125 \mu\text{m}$ ) in transfer solution containing 0.1 M  $\text{KClO}_4$ . Potential scan rate: 0.05 V/s. The first 5 successive scans are shown.

Both inorganic and organic layers work properly under these experimental conditions. The influence of the counter anion needed during the p-doping process in the PEDOT outer layer was

studied by investigating the modified electrode in KCl aqueous solution. The cyclic voltammograms recorded at different scan rates are depicted in Fig. 4.

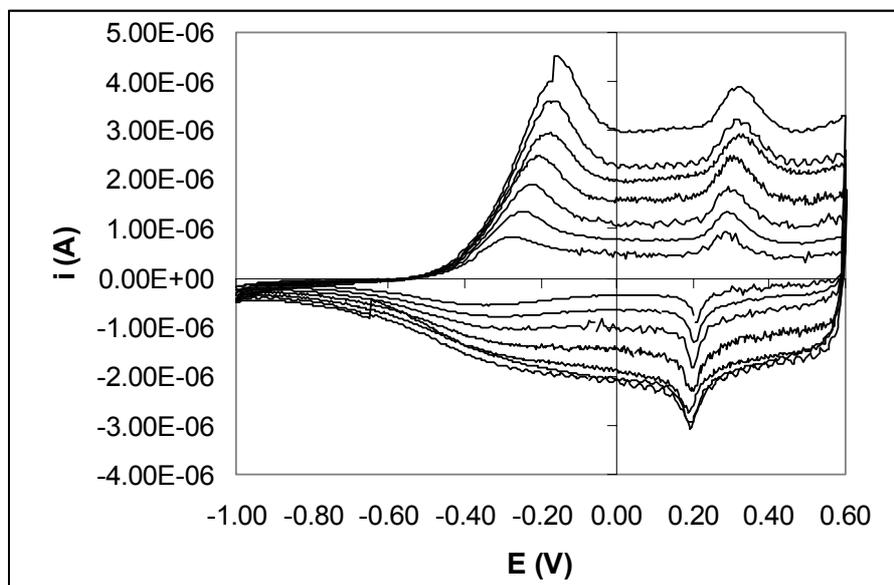


Fig. 4 – Cyclic voltammograms of Pt/PB/PEDOT modified ultramicroelectrode ( $d = 125 \mu\text{m}$ ) in transfer solution containing 0.1 M KCl. Potential scan rate: 0.05, 0.075, 0.1, 0.125, 0.15, 0.175 and 0.2 V/s.

The shape of the cyclic voltammograms is similar to those recorded in  $\text{KClO}_4$  aqueous solution, except for the polaron wave which is shifted to more positive potential value of ca. (-0.3) V vs. SCE. The cathodic counterpart of this redox wave is not well defined. The shift of the polaron redox wave to

positive values can be attributed to the swelling of the outer PEDOT layer, which increases the electron transfer mediation capability of the inner PB layer. The anodic peak current corresponding to the polaron formation increases linearly with the scan rate, as can be seen from Fig. 5.

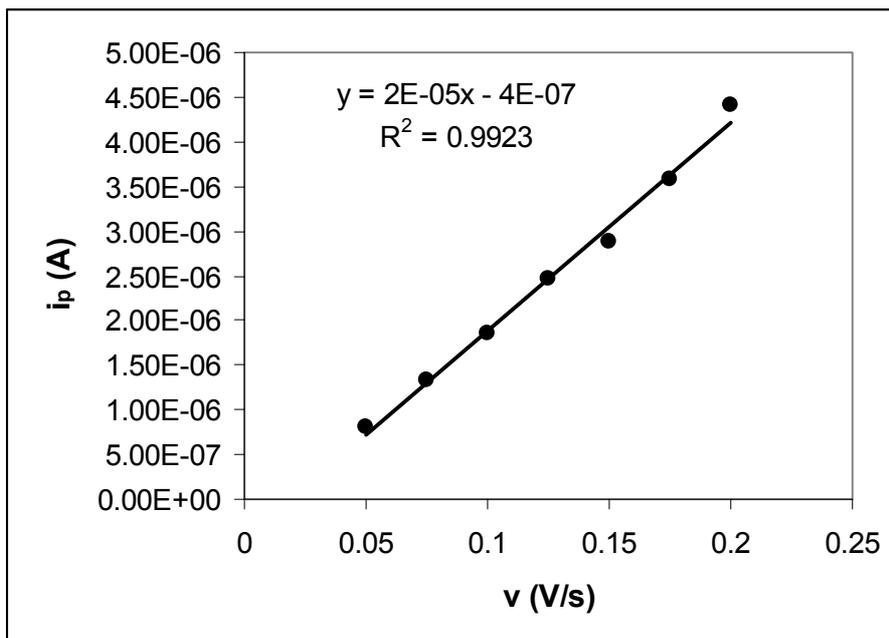


Fig. 5 – Dependence of the anodic peak current of the polaron formation on the scan rate.

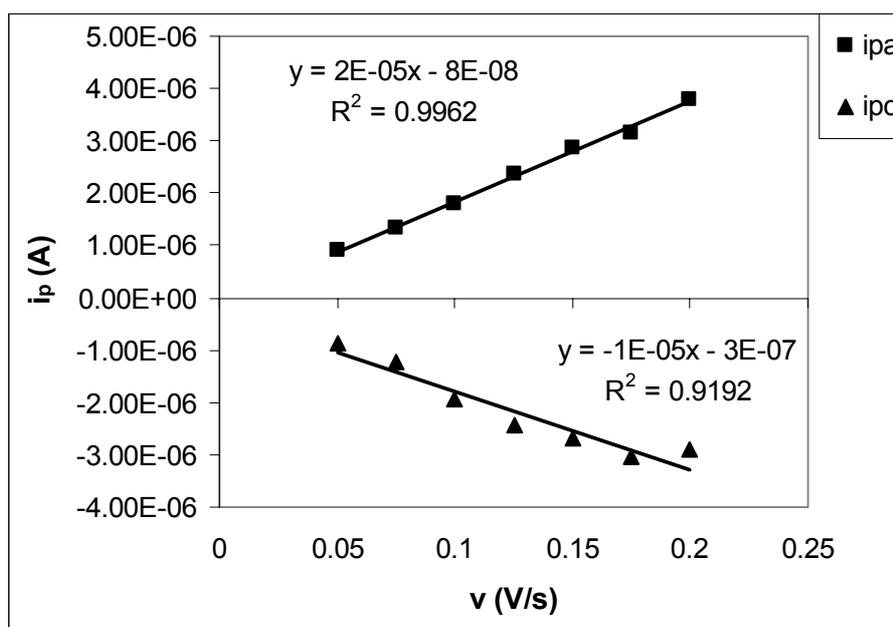


Fig. 6 – Dependence of the anodic and cathodic peak currents of the PB/ES and respectively PB/BG system on the scan rate.

A similar behaviour is observed for both anodic and cathodic peak currents for the PB/SE redox wave (see Fig. 6). It is well known that for redox species confined into a very thin layer close to the electrode surface, the peak current becomes linear with respect to the scan rate. These redox species can be described by the surface coverage,  $\Gamma_0$ . The surface coverage for each species involved in the redox processes occurring in the bilayer coating can be calculated by using the following equation:

$$I_p = \frac{n^2 F^2}{4RT} \nu A \Gamma_0 \quad (1)$$

where  $I_p$  is the peak current,  $n$  is the number of electrons transferred ( $n = 1$  in this case),  $F$  stands for the Faraday's constant,  $R$  is the gas constant,  $T$  is the temperature,  $\nu$  is the scan rate and  $A$  represents the electrode surface area.<sup>18</sup>

By using the equation (1), the surface coverage for each redox couple was computed as follows:  $2.68 \times 10^{-10} \text{ mol cm}^{-2}$  for the PB/ES anodic wave,  $2.60 \times 10^{-10} \text{ mol cm}^{-2}$  for the cathodic PB/ES wave, and  $2.36 \times 10^{-10} \text{ mol cm}^{-2}$  in the case of the polaron formation redox wave, respectively. These surface coverage values attest that the hybrid bilayer coating contains very thin PB films.

## CONCLUSIONS

The PB/PEDOT hybrid coating presents the redox wave corresponding to the PB/SE system and polaron formation redox wave, respectively. The polaron formation redox wave can be seen when the bilayer structure is deposited on ultramicroelectrodes, taking benefits from the special features of these electrodic substrates. Very thin PB films can be prepared by using the reported preparation procedure. The inner PB layer acts as a redox mediator during the deposition of the outer conducting polymer layer. The stability and electrochemical features of this hybrid inorganic-organic coating could be exploited in the preparation of electrochemical sensors.

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## REFERENCES

1. S. Lupu, C. Lete, M. Marian and N. Totir, *Rev. Roum. Chim.*, **2007**, *53*, 539-546.
2. R.W. Murray (Ed.), "Molecular Design of Electrode Surfaces", Wiley, New York, 1992, Vol. 22.
3. J. Roncali, *J. Mater. Chem.*, **1999**, *9*, 1875-1893.
4. S. S. L. Castro, V. R. Balbo, P. J. S. Barbeira and N. R. Stradiotto, *Talanta*, **2001**, *55*, 249-254.
5. S. Lupu, C. Mihailciuc, L. Pigani, R. Seeber, N. Totir and C. Zanardi, *Electrochem. Comm.*, **2002**, *4*, 753-758.
6. I. Luiz de Mattos, L. Gorton, T. Ruzgas, *Biosens. Bioelectron.*, **2003**, *18*, 193-200.
7. S. De Luca, M. Florescu, M. E. Ghica, A. Lupu, G. Palleschi, C. M. A. Brett and D. Compagnone, *Talanta*, **2005**, *68*, 171-178.
8. V. Noel, H. Randriamahazaka and C. Chevrot, *J. Electroanal. Chem.*, **2000**, *489*, 46-54.
9. P. J. Kulesza, K. Miecznikowski, M. A. Malik, M. Galkowski, M. Chojak, K. Caban and A. Wieckowski, *Electrochim. Acta*, **2001**, *46*, 4065-4073.
10. P. Somani and S. Radhakrishnan, *Mater. Chem. Phys.*, **2002**, *76*, 15-19.
11. L. V. Lukachova, E. A. Kotelnikova, D. D'Ottavi, E. A. Shkerin, E. E. Karyakina, D. Moscone, G. Palleschi, A. Curulli and A. A. Karyakin, *Bioelectrochemistry*, **2002**, *55*, 145-148.
12. H. Zhao, Y. Yuan, S. Adeloju and G.G. Wallace, *Anal. Chim. Acta*, **2002**, *472*, 113-121.
13. V. S. Vasantha and S-M. Chen, *Electrochim. Acta*, **2005**, *51*, 347-355.
14. J. O. Howell and R. M. Wightman, *Anal. Chem.*, **1984**, *56*, 524-529.
15. M. L. A. V. Heien, P. E. M. Phillips, G. D. Stuber, A. T. Seipel and R. M. Wightman, *Analyst*, **2003**, *128*, 1413-1419.
16. C. Amatore in "Physical electrochemistry – principles, methods and applications", I. Rubinstein (Ed.), Marcel Dekker, New York, 1995, p. 163.
17. C. Amatore, Y. Bouret, E. Maisonhaute, H. D. Abruña and J. I. Goldsmith, *C. R. Chimie*, **2003**, *6*, 99-115.
18. F. Marken, A. Neudeck and A.M. Bond in "Electroanalytical Methods – Guide to Experiments and Applications", F. Scholz (Ed.), Springer-Verlag, Berlin, 2002, p. 65.