Improved Stability and Catalytic Activity of Screen Printed Electrode Modified with PB in the Presence of Anionic Surfactant

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In this article is reported the effect of anionic surfactants AOT (dioctyl sulfosuccinate) in the electrodeposition of Prussian Blue (PB) onto screen-printed carbon electrodes (SPCE). The SPCE/PB/AOT electrode displayed a significant improvement of its electrochemical properties and of its stability compared with PB modified SPCE formed in absence of surfactant. The effects of AOT concentration and applied potential on the sensor response to H_2O_2 are discussed. The PB film stabilized with AOT, were characterized by Scanning electron microscopy (SEM), and Raman spectroscopy. The new electrodeposed PB/AOT film proved excellent electroanalytic properties for H_2O_2 determination and is a promising material for assembling biosensors based on oxidoreductase enzymes.

Keywords: Prussian blue, electrochemical, AOT, hydrogen peroxide, screen printed carbon electrode

Prussian blue is a material which has been extensively investigated due to its electrochemical, photophysical, and magnetic properties and potential analytical applications [1-3]. In 1978, Neff [4] reported for the first time the successful deposition of Prussian blue on a platinum foil as well as its electrochemical behaviour [5-7]. From thereon, enormous number of studies has used different methods for preparation of PB-modified electrodes which have been reported in the literature [8]. The PB modified electrodes developed by Karyakin et al. [9] is based on the reduction of H_2O_2 rather than on its oxidation. Using iron hexacyanoferrate (Prussian Blue - PB) as an electrocatalyst, H_2O_2 can be detected at potentials below 0 mV (vs. SCE) with high sensitivity and specificity thus eliminating problems with interfering compounds [9-11]. Itaya and co-workers reported an electrochemical method of PB films preparation, which is based on the electrochemical reduction of a solution of ferric ferricyanide under galvanostatic conditions on platinum, glassy carbon and SnO_2 electrodes [12-13]. The surfactants have been employed in a great number of applications in chemistry [14], exploiting their tendency to accumulate at a surface or interface between two different phases, such as the electrode-solution. This property has been utilized in recent years in the surface modification of electrodes with PB and other hexacyananoferrates, where the presence of added surfactant offers enhanced film, improved stability and excellent electrochemical reversibility [15-18]. Although, studies to date have focused mainly on the use of cetyltrimethyl ammonium bromide (CTAB), we have recently shown the other cationic surfactants such as benzethonium chloride (BZTC) may also be used successfully [19].

The aim of this article was to optimize the electrodeposition of PB in presence of AOT and to study the electrochemical and analytical properties of different modified AOT/PB films. The improved electro-deposition methods, permeability of the optimized AOT/PB provide a further boost in its sensitivity for H_2O_2 detection, which can be a critical parameter in biosensor design and application.

Experimental part

Equipment, materials and methods

Apparatus

Electrochemical measurements were carried out using a Autolab potentiostat/galvanostat computer controlled by the GPES software and a PARSTAT 4000 potentiostat/galvanostat controlled via VersaStudio software with FRA module.

The morphology of the samples were investigated by scanning electron microscopy (SEM) using a high-resolution microscope, FEI Quanta 3D FEG model, at an accelerating voltage of 5 kV, in high vacuum mode with Everhart-Thornley secondary electron (SE) detector.

Unpolarized solid state Raman spectra were recorded by means of a LabRam HR spectrometer (Jobin-Yvon-Horiba) over 50-2400 cm^{-1} range. The 514 nm line of an Ar^+ laser was used as exciting radiation with the power within 4-6 mW. The backscattered light was collected through the x 50 objective of an Olympus microscope at a confocal hole of 200 μm. The diameter of the laser spot on the sample surface amounted to 2-3 mm providing a spectral resolution better than 2 cm^{-1}.

Electrodes

Screen-printed carbon electrodes (SPCE) model DRP-110 purchased from DropSens (Spain) were used for electrochemical measurements. In this case the electrochemical cell is composed by a graphite working electrode (d = 4 mm), a graphite auxiliary electrode and a silver pseudo-reference electrode, with silver electric contacts deposed on a ceramic substrate.

Reagents

All chemicals from commercial sources were of analytical grade. Iron chloride ($FeCl_3$), potassium ferricyanide $K_3[Fe(CN)_6]$, HCl 37%, sodium chloride, hydrogen peroxide (30%) and Dioctyl sulfosuccinate sodium salt (AOT), Sodium dihydrogen phosphate $Na_2HPO_4 \cdot 2H_2O_2$, disodium hydrogen phosphate KH_2PO_4, KCl were purchased from Sigma-Aldrich.

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Preparation of modified electrodes

Electrochemical deposition of Prussian Blue

Shortly, prior to Prussian Blue modification, screen-printed electrodes were pre-treated in 50 mM phosphate buffer in 0.1 M KCl solution, *p*H 7.4, by applying a potential of + 1.7 V versus Ag/AgCl for 3 min [7]. The potentiostatic technique was used for the electrochemical deposition of PB, in a mixture of 2.5 mM $K_3[Fe(CN)_6]$, 2.5 mM $FeCl_3$ and various AOT concentrations prepared in 100 mM KCl and 100 mM HCl solution, by applying a step potential of + 0.4 V for 40 s [7]. After a gentle rinsing with water, the electrode was placed in a solution of 100 mM KCl in 100 mM HCl and a number of 20 cycles, between - 0.2 and 0.4 V, at a scan rate of 50 mV was run. The films were stabilized by keeping the electrodes at 100° for 90 min.

Results and discussions

Electrochemical characterization

The deposition of PB on different substrates is usually accomplished by the electrochemical reduction of a mixture of ferric and ferricyanide ions [11]. In this work we applied the electrochemical synthesis of PB onto SPE electrodes in the presence of an anionic surfactant (AOT). The influence of AOT on the PB film characteristics was tested for the three concentrations 1, 2 and 5 mM of surfactant. The results are shown in figure 1. The optimum concentration of surfactant for PB deposition was chosen 2mM AOT. Taking into consideration that the charge from the cronoamperometric curve (curves not shown) is a measure of the amount of PB deposited, these results indicate that the presence of this surfactant promote the PB on the SPE surface.

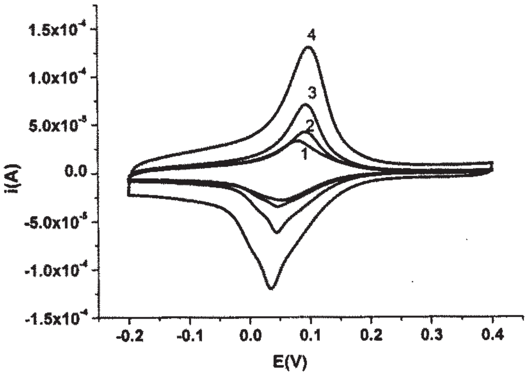

Fig.1. Cyclic voltammograms recorded on: (1) SPCE/PB; (2) SPCE/PB (AOT 1mM); (3) SPCE/PB_AOT 5mM and (4) SPCE/PB_AOT 2mM; in 50 mM phosphate buffer pH 6.5 and 0.1 M KCl, scan rate = 50 mV/s

All electrodes modified with PB in the presence of AOT showed the characteristic peaks around -0.05 V. These peaks were studied because are involved in the electrocatalytic detection of H_2O_2 [19]. In table 1 are presented the voltammetric parameters of SPE electrode modified with PB in absence or presence of AOT characterised in KCl+HCl 0.1M solution. The SPE electrodes modified with PB in the presence of AOT displayed (fig. 2) a higher value of ΔE_p that is correlated well with the amount of PB deposition.

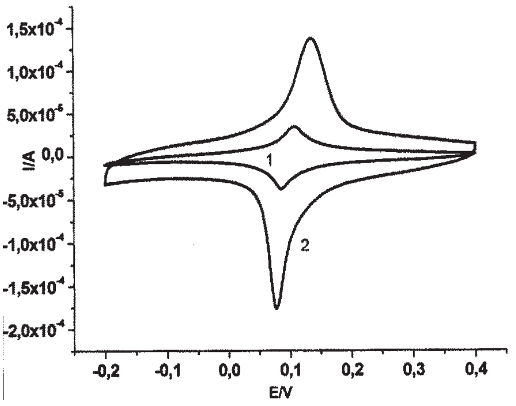

Fig. 2. Cyclic voltammograms of (1) SPCE/PB and (2) SPCE/PB_(AOT 2mM) in 0.1M KCl and 0.1M HCl; scan rate = 50 mV/s.

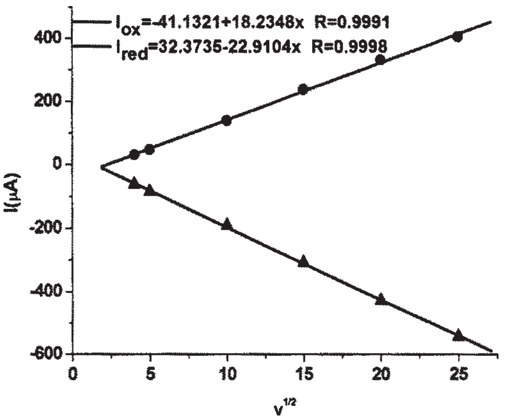

Fig. 3. Variation of I_{ox} and I_{red} vs. square root of scan rate in electrolyte solution 0.1M KCl and 0.1M HCl for the SPCE/PB_AOT 2 mM

The amount of charge associated with the anodic (Q_{ox}) and cathodic (Q_{red}) peaks also has increased (4 times) when the surfactant was used. The PB film formed in presence of AOT presented much higher anodic and cathodic currents, indicating also a more reversible behaviour than for PB without AOT. These results suggest that the surfactant improved the PB electrodeposition by 75%.

The effect of potential scan rate on the oxidation I_{ox} and reduction I_{red} peak currents was studied in the potential range at -0.5 to 0.7V. From figure 3 one can observe the linear proportionality of the I_{ox} and I_{red} to the square root of scan rate, which is expected for a diffusion limited process. However, the greater ΔE_p values obtained at higher scan rate could be result from limiting charge transfer kinetics. The figure 4 shows a linear dependence for E_{ox} and E_{red} versus logυ at high υ. These results are in good agreement with the literature [18].

In order to provide the fingerprint of interface region, the EIS method can be used. The EIS spectra were recorded to E= 0.0 V vs. Ref. The Nyguist plots of the electrodes SPE modified with PB are presented in figure 5. For these electrodes two regions could be distinguished: a semicircle part at higher frequencies corresponding to the electron charge transfer, and a linear part at lower frequencies corresponds to the diffusion-controlled process. The equivalent circuits were used for model electrode SPCE and SPCE/PB interface are presented in figure 6. For SPCE electrode the EIS spectra are indicative of a single time-

Table 1

VOLTAMMETRIC PARAMETERS FOR PB FILMS OBTAINED IN 0,1M KCl AND 0.1M HCl SOLUTION SCAN RATE = 50 mV/s

	Q_{dep} (mC)	Q_{ox} (mC)	Q_{red} (mC)	E_{ox} (V)	E_{red} (V)	ΔE_p (V)	I_{ox} (μA)	I_{red} (μA)	Q_m (μC)	Q_m/Q_{mAOT}
PB	2.2	$1x10^{-4}$	$-1x10^{-4}$	0. 108	0.086	0.022	35.3	-36.9	0.1	0.25
PB-AOT	10.5	$3.7x10^{-4}$	$-4.2x10^{-4}$	0.135	0.077	0.058	138.2	-175.3	0.395	1

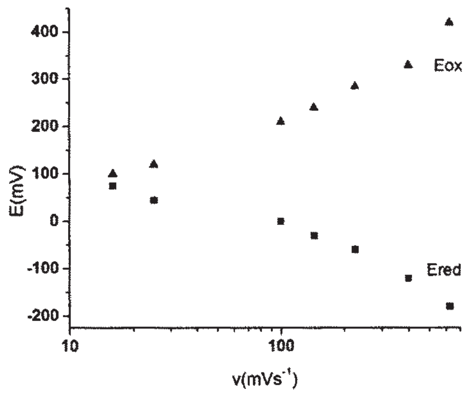

Fig 4. Variation of E_{ox} and E_{red} vs. log v in 0.1M KCl + 0.1M HCl solution for the SPCE/PB electrode with AOT 2 Mm

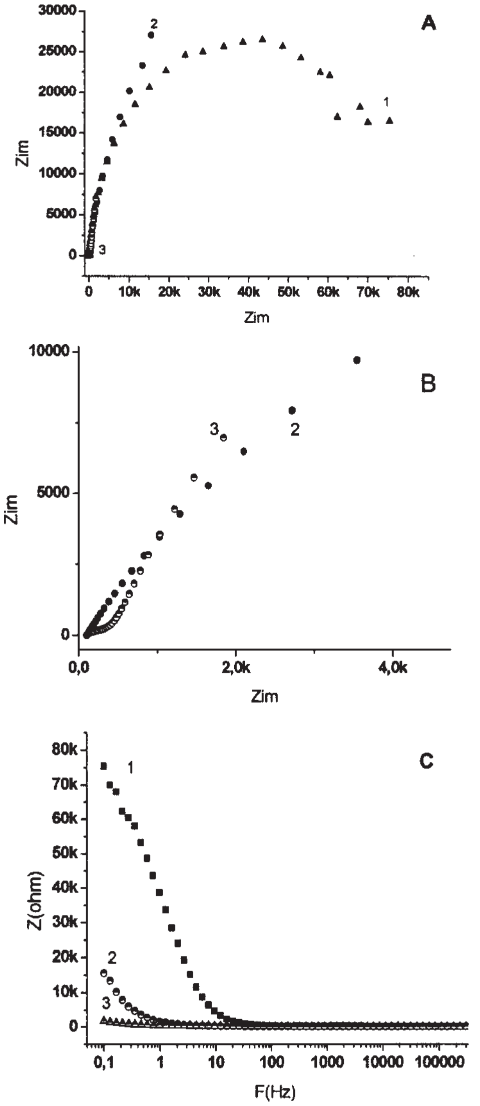

Fig. 5. Complex plane impedance spectra for SPCVE electrode modified with PB: (A)-Nyquist plane for (1) SPCE; (2) SPCE/PB; (3) SPCE/PB with AOT; (B) - detail at high frequencies; (C) - Bode plane for (1) SPCE; (2) SPCE/PB; (3) SPCE/PB with AOT, recorded at 0.0V vs.Ag/AgCl, in KCl+HCl 0.1M, amplitude 10mV

constant electrode process and can be modelled by an electric equivalent circuit (A in fig. 6) consisting of a cell resistence Rs, in series with a parallel CPE-R2, with R2 representing the charge transfer resistence. The CPE is assumed to be a non-ideal capacitance. Using this approach, values of Rs is 200Ω, and Rct is 80kΩ are obtained and the phase angle exponent is 0.85 as is usually found at different types of carbon electrode [20-21].

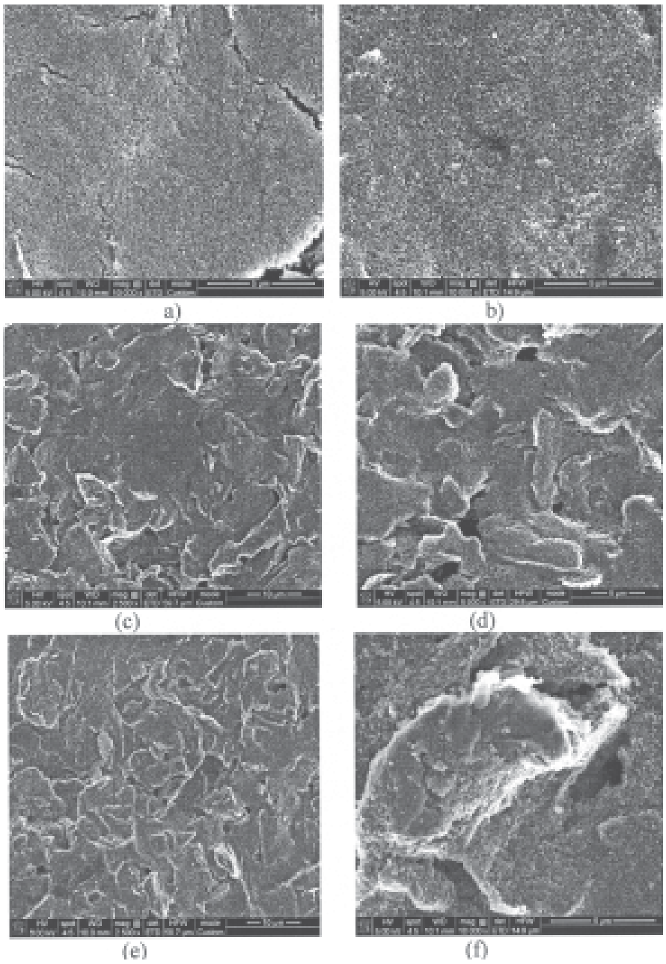
a) b) (c) (d) (e) (f)

Fig. 6. SEM images of (a) - SPCE; (b), (c) and (d) SPCE/PB (large scale 5-10 μm); (e) and (f) SPCE/PB_AOT (large scale 5-10 μm)

The spectra for the electrodes modified with PB can be modelled with the same equivalent circuit with the addition of a second constant phase element, CPE2 representing a second capacitance in series with the R1CPE1 parallel combination. This element (CPE1) represents processes at the Pb/electrolyte interface and CPE2, charge separation within the conducting film. Values of CPE and Rct are different for the SPCE/PB and SCPE/PB_AOT. For the SPCE/PB electrode the Rct values are 20kΩ, respectively 500 Ω for SPCE/PB_AOT, while the phase angle exponent is 0.35 for the first electrode and 0.65 for the SPCE/PB_AOT. From these values it is assumed that a series charge separation occurring, presumably at the PB film/electrolyte interface owing to the discontinuities in the crystal structure [22]. The small values of phase angle indicate the increase of the surface roughness.

For SPCE/PB obtained in presence of AOT surfactant this behaviour is more evident than SPCE/PB electrode. These results are in a good agreement with the voltammetric results.

Morphological characterization

The morphological features of SPE electrodes modified with Prussian blue were analyzed by Raman spectroscopy and Scanning Electronic Microscopy.

SEM pictures revealing visual differences of the structure of the surface of the two different SPCE/PB electrodes are shown in figure 4 (a) and (c). However, some porosity of SPCE can be noticed. From these pictures it is evident that the surface characteristics of the two electrodes are different after modification with Prussian Blue (fig. 6). The SEM image at 5 μm, show the Prussian blue aggregates of

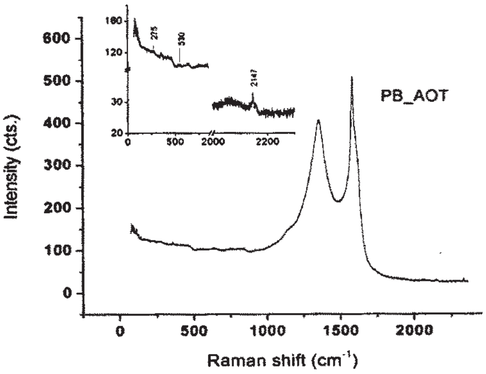

Fig. 7. Raman spectra recorded on SPCE/PB_AOT

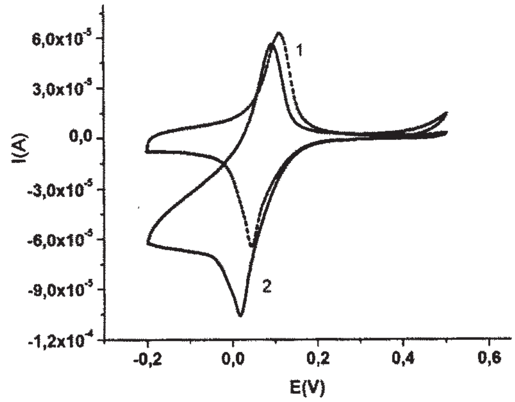

Fig. 8. CVs recorded with SPCE/PB_AOT in buffer phosfate in KCl 0.1M solution, pH=6.5. Scan rate v = 50 mVs^{-1}. (1) buffer phosfate; (2) buffer phosfate + H_2O_2 3mM.

high dimension with no precise shape, the presence of these aggregates on the surface could possibly be the reason for the improved electrochemical activity. These results are supported by the Raman spectra recorded on SPE/PB electrode modified in the presence of AOT.

The Raman spectra of Prussian blue presented in figure 7, shows that there is a vibrational band at 2147 cm^{-1} characteristic to the streaching vibration of C≡N group of Prussian blue. Because carbon presents the strong vibrations at 1325 cm^{-1} and 1620 cm^{-1}, vibrations of Prussian blue are faded in intensity. The other peaks present to 275 and 530 cm^{-1} are expected to have relation to the presence of ferricyanide ions [23].

In order to assess the electrocatalytic activity of SPE/PB modified electrode, cyclic voltammetric curves were recorded in presence of 3 mM H_2O_2 in 50 mM phosphate buffer, *p*H 6.5 with KCl 0.1M. Figure 8 shows the catalytic effect of Prussian Blue obtained in the presence of surfactant (AOT), on the reduction of H_2O_2. The typical two pairs of redox waves showing the oxidation and the reduction of PB are present. Therefore, the significant increase of the cathodic peak current at around 0.1V in presence of H_2O_2 can be noticed like a catalytic activity of the SPE/PB electrode.

To obtain the best sensitivity and selectivity for the electrochemical detection for H_2O_2, the effect of the applied potential was studied using the amperometry technique. Potentials ranging from -100 mV to +200 mV were applied. For a selected concentration of hydrogen peroxide (100μM) we have plotted the current intensity *vs.* applied potential (fig. 9). The lowest background noise and the highest signal for H_2O_2 measurement was recorded for the SPCE/PB/AOT electrode obtained by electrochemical procedure. From amperometric response of SPCE/PB_AOT to H_2O_2 (fig. 9) a potential of -50 mV was selected as the working potential considering both the response intensity and operational stability.

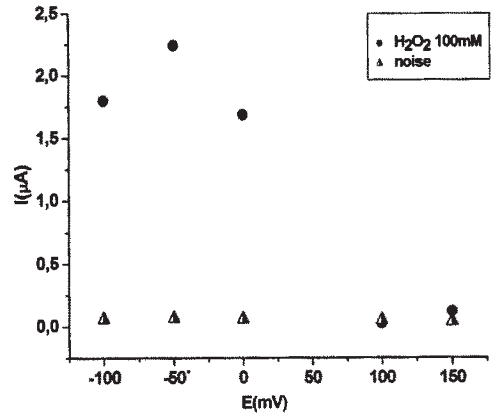

Fig. 9. Amperometric response of SPCE/PB_AOT to 100 μM H_2O_2 in 50 mM phosphate buffer solution, pH 6.5, at different applied potentials

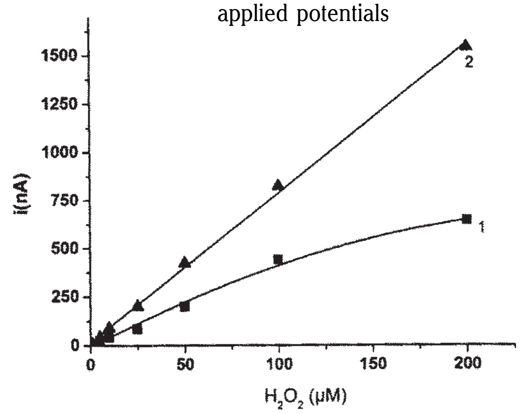

Fig.10. Calibration plot for detection of H_2O_2, using chronoamperometry, applied potential E = -50 mV in phosphate buffer and KCl 0.1 M. (1) SPCE/PB; (2) SPCE/PB_AOT 2 mM

The influence of several AOT concentration (1 mM, 2 mM and 5 mM) on the analytical performances of the PB sensor for H_2O_2 sensing were evaluated. The calibration graphs obtained by chronoamperometry are very similar for all three AOT concentrations (data not shown), showing a sensitivity higher with around 75 – 80 % than of the PB sensor prepared without AOT. For exemplification, in figure 10, are presented the calibration graphs for H_2O_2 determination obtained with the SPCE/PB and SPCE/PB_AOT 2 mM. The calibration equation obtained for SPCE/PB_AOT 2 mM electrode is I (nA) = 14.67 + 7.74 · C_{H2O2} (μM) with a correlation coefficient R= 0.9993 for a much larger concentration range (up to 200 μM) comparing with the equation calculated for the SPCE/PB which is I (nA) = - 4.53 + 4.33 · C_{H2O2} (μM) with R = 0.9915 for a concentration range up to only 100 μM H_2O_2.

The detection limit calculated for the SPCE/PB/AOT 2 mM electrode was of 0.27 μM H_2O_2 (S/N=3) and the RSD = 1.53 % for 50 μM μM H_2O_2 (n=10).

The stability of the SPCE/PB/AOT 1 mM sensor under storage conditions (dried, at room temperature, darkness) was assessed for a period of 90 days using a solution of 50 μM H_2O_2 by making a determination in triplicate at least twice on week. The AOT has induced a remarkable stability of the SPCE/PB response. After 90 days the response of sensor was around 87 % of the initial response.

Conclusions

In this work, for the first time it was optimized a new method for PB deposition in the presence of the anionic surfactant AOT.

The results showed, also, that the anionic surfactant highly improves the operational stability of the PB film.

The SPCE/PB_AOT electrode has an excellent electrocatalytic activity for the reduction of H_2O_2 and exhibited almost a double sensitivity and a larger linear concentration range up to 200 μM for H_2O_2 determination comparing with the SPCE/PB without AOT and is a promising material for assembling biosensors based on oxidoreductase enzymes.

Acknowledgments: The authors acknowledge to the project POSDRU/CPP107/DMI1.5/S/78534 for financial support, and the SEM and Raman measurement support of the EU (ERDF) and Romanian Government that allowed for acquisition of the research infrastructure under POS-CCE O 2.2.1 project INFRANANOCHEM Nr. 19/01.0.3. 2009 is gratefully acknowledged.

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Manuscript received: 12.07.2013