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COMPOSITE CARBON ELECTRODES WITH ENHANCED STABILITY BASED ON POLYANILINE INCORPORATING PRUSSIAN BLUE FOR AMPEROMETRIC DETECTION OF H_2O_2

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ABSTRACT. The obtaining of composite glassy carbon modified electrodes based on a conducting polymer (polyaniline, PANI) matrix entrapping a polynuclear inorganic compound (Prussian Blue, PB) with redox properties is reported. The electrocatalytic activity towards H_2O_2 reduction of PB+PANI modified glassy carbon electrodes and their electrochemical stability were studied and compared to those of PB modified electrodes prepared through simple electrodeposition of the inorganic compound onto glassy carbon (GC/PB). It was confirmed that the GC/PB+PANI modified electrodes present stable electrochemical behavior and showed good electrocatalytic efficiency for H_2O_2 reduction.

Keywords: composite electrodes, Prussian Blue, polyaniline, cyclic voltammetry, amperometric detection, hydrogen peroxide

INTRODUCTION

The development of amperometric sensors/biosensors on the basis of Prussian Blue (PB) modified electrodes aims to valorize the excellent catalytic efficiency of this inorganic mediator, comparable to that of biological catalysts, towards the reduction of both O_2 and H_2O_2 [1-3]. However, these modified electrodes still face some drawbacks with regarding the long-term stability and sensitivity to pH changes [4].

Among various techniques for increasing the electrodes stability, the mediator entrapment in an electrogenerated polymer film appears a simple and attractive method for fabricating PB modified electrodes [5]. Such one-step immobilization procedure allows the facile functionalization of electrode surfaces [6] as well as the electrochemical control of polymer film thickness [7].

Polyaniline (PANI) is one of the most studied and promising conducting polymers due to its chemical stability, easy polymerization, high electronic conductivity following partial oxidation, good protonic conductivity and a relatively long period of stability in acid media [8, 9]. The great interest in this polymer stems from its ability to be rapidly and reversibly cycled between the differently colored conductive (partially oxidized, emeraldine) and insulating (completely reduced and oxidized, leucoemeraldine and pernigraniline, respectively) states [10]. Additionally, in the case of PB, a hexacyanometallate, it is supposed to act the concept of electrostatic stabilization originating from the ability of the positively charged conducting polymer backbone (PANI) to attract the negatively charged cyanometallate [9].

In this context, in the present work, we propose to prepare composite glassy carbon (GC) modified electrodes based on a conducting polymer (PANI) matrix into which a polynuclear inorganic compound (PB) with redox properties is

introduced. The electrochemical stability of glassy carbon electrodes modified with PB and PANI (GC/PB+PANI) and their electrocatalytic activity towards H_2O_2 reduction were studied and compared to those of GC/PB modified electrodes prepared through simple electrodeposition of the inorganic compound on GC.

EXPERIMENTAL SECTION

Reagents

Hydrogen peroxide was purchased from Merck (Darmstadt, Germany). All other reagents were of analytical grade and used as received. The solutions were prepared using distilled water.

Preparation of modified electrodes

Prior to surface modification, the glassy carbon electrode of ~ 3 mm diameter, was mechanically wet polished with fine grade aqueous alumina slurry (grain size, 0.25 μm) on a polishing cloth.

The electrodeposition of Prussian Blue on glassy carbon was accomplished in a solution containing 2 mM $FeCl_3$ + 2 mM $K_3[Fe(CN)_6]$ + 0.5 M KCl + 1M HCl as described in [9]. Typically, 20 full potential cycles were applied in the potential range from −0.10 to 1.0 V, at a scan rate of 50 mV/s. The GC/PB modified electrodes were then carefully washed with water and dried 1h at 100 ^oC.

Similarly, PANI was electrogenerated on the CV substrate from a solution containing 0.22 M aniline and 0.5 M KCl + 1 M HCl in the potential range from −0.10 to 1.0 V, at a scan rate of 50 mV/s.

The composite PB-PANI films were electrodeposited from a solution containing 2 mM $FeCl_3$ + 2 mM $K_3[Fe(CN)_6]$ +0.22 M aniline in 0.5 M KCl + 1M HCl through potential scanning in the same potential range as mentioned above.

Electrochemical measurements

Electrochemical measurements were performed using an electrochemical analyzer (Autolab-PGSTAT10, Eco Chemie, Utrecht, The Netherlands) connected to a PC for potential control and data acquisition. The electrochemical deposition of PB onto the GC electrode and the voltammetric investigation of the modified electrodes were carried out using a typical three-electrode electrochemical cell. The modified electrodes were used as working electrodes, a platinum ring as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

For each electrode, the surface coverage (Γ, mol cm^{-2}) was estimated from the under peak areas, recorded during the cyclic voltammetry (CV) measurements at a low scan rate ($v < 10$ mV s^{-1}), and considering the surface redox valence equal to unity [11]. All presented results are the average of at least 3 identically prepared electrodes, if not otherwise mentioned.

Amperometric batch measurements were carried out with the modified electrodes at an applied potential of - 50 mV *vs.* SCE and under constant magnetic stirring, in the presence of various concentrations of H_2O_2.

Stability measurements were carried out for GC/PB and GC/PB+PANI modified electrodes under potentiodynamic conditions. The electrode potential was cycled continuously at 50 mV/s, within the potential range covering the mediator redox activity (± 120 mV relative to its standard formal potential), during 80 cycles, in a 0.5 M KCl + 1M HCl solution.

RESULTS AND DISCUSSION

Preparation of modified electrodes

The cyclic voltammograms recorded during GC modification with PB in a solution containing 2 mM $FeCl_3$ + 2 mM $K_3[Fe(CN)_6]$ in 0.5 M KCl + 1 M HCl (figure 1a) exhibited two peak pairs corresponding to the following redox processes [13]:

$$KFe^{III}Fe^{II}(CN)_6 + e^- + K^+ \rightarrow K_2Fe^{II}Fe^{II}(CN)_6 \qquad (E^{0'})_I = 0.2 \text{ V/SCE} \qquad (I)$$

$$KFe^{III}Fe^{II}(CN)_6 \rightarrow Fe^{III}Fe^{III}(CN)_6 + e^- + K^+ \qquad (E^{0'})_{II} = 0.9 \text{ V/SCE} \qquad (II)$$

The formal standard potentials were estimated as the average of the cathodic and anodic peak potentials [12]. All following results will refer to the first peak pair, due to its redox formal potential, well placed in the optimal potential domain for amperometric detection [14]. The electrochemical parameters of this voltammetric wave ($\Delta E_{peak,\ I}$ = 60 mV; Γ = 3 nmol cm^{-2}) point to a monoelectronic, quasi-reversible couple. The increase of peak currents with the number of cycles confirms the increase of film thickness during electrodeposition.

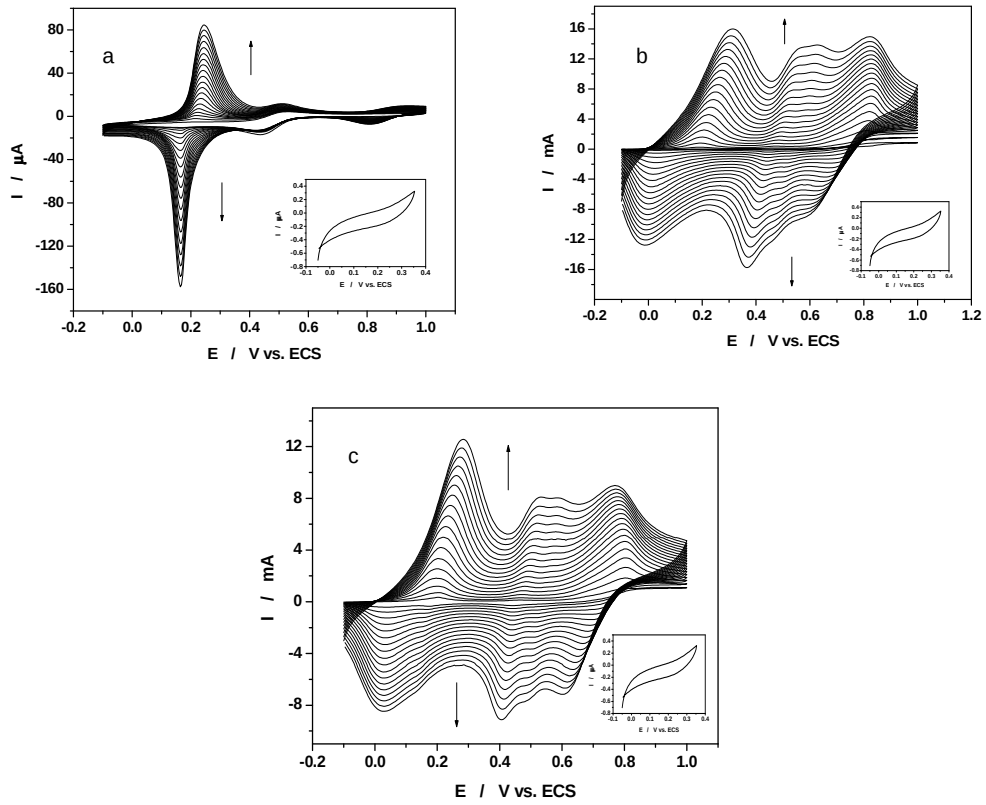
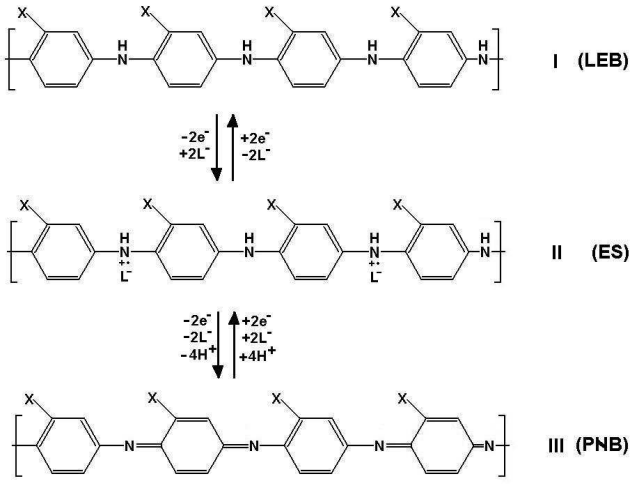


Figure 1. The CVs corresponding to (a) PB; (b) PANI and (c) PB+PANI film formation on a GC surface. Scan rate: 50 mV /s. *Insets*: The CV for GC in 0.5 M KCl + 1 M HCl.

The growth of PANI on the GC surface during electro-polymerization is slow at the beginning of the polymerization, but increases considerably after the first cycles. In the corresponding cyclic voltammogram, (figure 1b), the first redox couple with $E^{0'}$= 153 mV *vs.* SCE is attributed to the Leucoemeraldine (LEB)-Emeraldine salt (ES) transition from Scheme 1 [10]. The second redox couple with $E^{0'}$= 464 mV *vs.* SCE is usually associated with a degradation product of PANI. The third redox couple at $E^{0'}$> 600 mV *vs.* SCE corresponds to the ES- Pernigraniline (PNB) transition [9].



Scheme 1. The redox behavior of PANI

The only electrically conducting form is, the emeraldine salt form (ES), which is the protonated form of LEB. The protonation process is reversible and represents the basis for the pH sensitivity of PANI [10].

The voltammograms corresponding to the composite PB-PANI films electro-deposition from a solution containing 2 mM $FeCl_3$ + 2 mM $K_3[Fe(CN)_6]$ +0.22M aniline in 0.5 M KCl + 1M HCl are presented in Figure 1c. As expected, the peak currents systematically increase in the course of voltammetric potential cycling. The result is consistent with the view that, as usual, organic polymer (PANI) layers are generated on the electrode surface during positive potential scans, whereas polynuclear PB microstructures are electrodeposited during negative potential scans [9].

It should be noticed that the anodic peak potentials characteristic of PANI behavior in composite film are slightly shifted towards more negative values when compared to their position in PANI (PB-free) film investigated in the same electrolyte. The most likely explanation of this observation lies on the existence of electrostatic attraction forces between the negatively charged PB and the positively charged PANI fragments. Another argument in this sense is the decrease of width at half height of the voltammetric peaks (results not shown), pointing to the existence of

lateral interactions between the species inside the film [15]. Consequently, regardless of the nature of interactions between PB and PANI, the composite PB/PANI system cannot be considered as a simple mixture of single components, PB and PANI.

Electrocatalytic activity for H_2O_2 electro-reduction

In order to check the electrocatalytic activity of the above-mentioned modified electrodes towards H_2O_2 reduction, their amperometric responses were recorded in the absence and in the presence of different concentration of H_2O_2 in an electrolyte containing 0.5 M KCl + 1M HCl (pH 0), at E = -0.05 V *vs.* SCE.

Contrarily to GC/PB and GC/PB+ PANI modified electrodes, GC/PANI modified electrode exhibited no activity towards H_2O_2 reduction. The analytical parameters for H_2O_2 detection extracted from the amperometric calibration curves for GC/PB and of GC/PB+PANI modified electrodes, in the presence of different concentrations of H_2O_2 (figure 3) are presented in Table 1.

Table 1.

The analytical parameters of amperometric calibration curves for GC/PB and GC/PB+PANI modified electrodes in the presence of H_2O_2 at different pH values. Electrolyte: 0.5 M KCl + 1M HCl; E = -0.05 V *vs*. SCE.

Electrode	pH	Sensitivity (μA/mM)	Detection limit (mM)	R / No. points
GC/PB	0	4.75 ±0.66	0.417	0.9967 / 6
GC/PB + PANI	0	28.38 ±2.78	0.294	0.9994 / 9
	3	15.43 ± 1.84	0.359	0.9982 / 8

As it can be observed, the slope of the amperometric curves (equal to the electrode sensitivity) is higher in the case of composite GC/PB+PANI electrodes than in the case of GC/PB electrodes. As expected, taking into account the pH sensitivity of polyaniline, based on the protonation-deprotonation equilibrium and the decrease of PB activity at higher pH values, the GC/PB+PANI electrode sensitivity decreases at increasing pH. For the same reasons, the detection limit is improved at more acid pH values and in presence of the polymer.

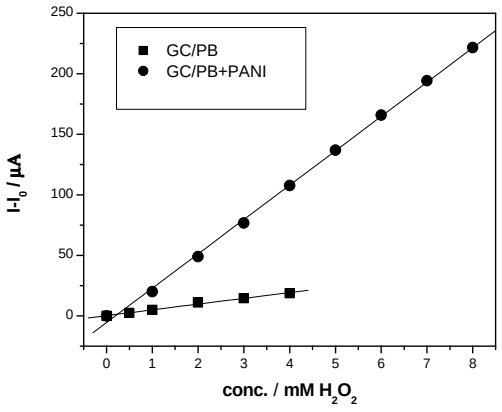


Figure 3. Amperometric calibration curves for GC/PB and GC/PB+PANI modified electrodes. E = -0.05 V *vs*. SCE; Supporting electrolyte: 0.5 M KCl + 1M HCl (pH 0).

Electrochemical stability measurements

Stability tests were carried out for all modified electrodes under potentiodynamic conditions. The electrode potential was cycled continuously at 50 mV/s, within the potential range covering the mediator redox activity (± 120 mV relative to its standard formal potential), during 80 cycles, in 0.5 M KCl + 1M HCl solution. Monitoring the surface coverage, a progressive decrease was observed (results not shown). The electrode deactivation process obeys first-order kinetics as confirmed by the ln I_a *vs.* t dependence analysis (figure 4).

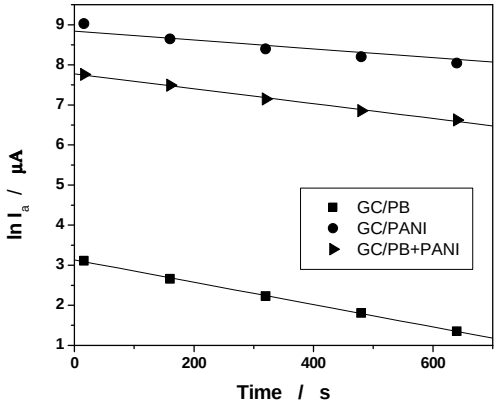


Figure 4. Experimental dependence of ln I_a *vs.* time for GC/PB, GC/PANI and GC/PB+PANI modified electrodes cycled in 0.5 M KCl + 1M HCl.

The relatively low values of the deactivation rate constants (Table 2), expressed as the slope of ln I_a *vs.* t dependence, proved a good stability of GC/PB + PANI modified electrodes in the investigated potential range, as well as an enhancement of stability in comparison with GC/PB electrodes.

Table 2.

The parameters of ln I_a *vs.* t dependence for GC/PB, GC/PANI and GC/PB+PANI modified electrodes

Electrode	Deactivation constant (s^{-1})	R / No. of points
GC/PB	0.0028 ± 0.0224	0.9996 / 5
GC/PANI	0.0011 ± 0.1446	0.9673 / 5
GC/PB + PANI	0.0018 ± 0.0381	0.9979 / 5

CONCLUSIONS

In the present study, the stabilization of Prussian Blue modified electrodes for electroanalytical purposes was achieved by mediator entrapment in an electroconductive polymer (PANI). The attractiveness of this composite system concerns the fact that the formal potential of the Prussian Blue redox process lies in the potential range where PANI is conductive.

The investigated modified electrodes showed good electrocatalytic efficiency and a high electrochemical stability.

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