Carbon Black as electrode modifier in Prussian Blue Electrodeposition for H_2O_2 sensing

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Abstract. Carbon Black Nanoparticles (CBNPs) onto Screen-Printed electrodes (SPE) are proposed as an electrode modifier for assisting electrodeposition of PB for non-enzymatic hydrogen peroxide electrochemical sensing. CBNPs allows an effective PB electrodeposition on SPE modified electrodes and enhance the electrochemical rate constant for the reduction of hydrogen peroxide (H2O2) compared to bare SPE.

Keywords: Carbon Black, Prussian Blue, Screen-Printed Electrodes, Hydrogen Peroxide.

1 Introduction

Nowadays nanomaterials used as sensitivity, stability and selectivity enhancers are widespread in electroanalytical chemistry [1]. In the last years Carbon Black (CB) has been used in Screen-Printed Electrodes (SPE) to modify the surface for analytical purposes. CB is a product of different industrial processes [2], which is formed by a primary structure made of spherical carbon nanoparticles with a diameter ranging from 30 to 100 nm and a secondary structure of aggregates of 100 to 600 nm. It has several applications in the industry as reinforcement material for rubber and plastic, as black dye and as a capacitor due to its electrical properties. The low cost, compared to other carbonaceous material like graphene and carbon nanotubes, and its versatility makes CB ideal in the electrochemistry field. Good examples are reported in the literature on the use of CB electrodes: electrochemical sensing of antioxidants [3,4], dopamine [5], pesticides [6] and relevant biological molecules [7]. On the other hand, Prussian Blue (PB) is one of the most know electrocatalyst for H_2O_2 reduction and has been widely used for non-enzymatic sensing of H_2O_2. PB allows low potential and interference-free detection of H_2O_2 in oxygenated environment, nonetheless it has some disadvantages such as stability at physiological pH and high crystallization rate. The latter hinder potential nanostructuring of the surface and application in biological media [8]. To overcome these shortcomings modification of the electrode with soft or hard templates, polymers, carbonaceous materials or different metals are used in different combinations to design specific analytical platforms for each application. In this work we report the use

of Carbon Black (CB) as electrode modifier with electrosynthesis of PB on SPE's surfaces; this resulted in improved hydrogen peroxide electrocatalysis.

2 Materials and methods

2.1 Materials

Experiments were carried out with MilliQ water from a Millipore MilliQ ((Millipore, Bedford, MA, USA), system. All inorganic salts, organic solvents and hydrogen peroxide (30% solution) were obtained at the highest purity from Sigma-Aldrich. SHSY5Y cells were obtained from Sigma (Sigma–Aldrich). H_2O_2 concentration was periodically standardized by titration with $KMnO_4$. Screen-Printed electrodes (SPE) were purchased from Dropsens S.L. (ref. SPE).

2.2 Instrumentation

All electrochemical measurements were carried out in Autolab PGSTAT 12 potentiostat from Metrohm (Utrecht, The Netherlands) connected to a personal computer. The software used was Nova 2.1 (EcoChemie B.V.). The flow injection (FIA) system consisted on a Minipuls 3 (Gilson Inc., Middleton, WI, USA) peristaltic pump, wall-jet cell (ref. FLWCL) (Dropsens, Spain). Sample volume was 50 µL, the working electrode potential chosen was -50 mV (vs internal reference). The running buffer solution in FIA experiments was 0.05 M phosphate buffer pH 7.4 containing 0.1 M KCl.

2.3 Preparation of SPE-PB and SPE-CB-PB electrodes

A CBNPs dispersion of 1 mg/mL in water and dimethylformamide (DMF) (1:1 ratio) was prepared. The dispersions were obtained using a bath sonicator for 30 min. SPE-CB electrodes were prepared by drop-casting 10 µL of CBNPs. Prussian Blue electrodeposition was carried out cycling the potentials between +400 and +800 mV (vs int. ref) for different number of cycles in a solution containing 0.1 M KCl, 0.1 M HCl and 5mM concentration of Fe^{3+} and $[Fe(CN)_6]^{3-}$. When the electrodeposition is carried out on bare SPE we obtain SPE-PB, in the case of using SPE-CB we obtain SPE-CB-PB. The potential of the internal reference electrode against an Ag|AgCl|KClsat reference electrode was measured as -120 mV. Electrodes were further modified with 2 µL of a Nafion ethanolic solution (0,5% v/v). Current density was calculated considering the geometrical area of SPE.

3 Results and discussion

PB is usually synthetized using Fe^{3+} and $[Fe(CN)_6]^{3-}$ anions as precursors. Usually, ferric ions are selectively reduced to form Prussian Blue on common electrode's sur-faces such as platinum, gold or glassy carbon. The selection of the potential at which PB is electrodeposited is crucial to allow the selective reduction of the precursors since the

reduction of both anions at the same time leads to an irregular structure of PB, hindering its potential for the electroreduction of H_2O_2. As shown in the voltammogram of Fig. 1, the reduction peaks of Fe^{3+} and $[Fe(CN)_6]^{3-}$ are not resolved using SPE. Interestingly, in the case of CB-SPE the peak potential of Fe^{3+} is anodically shifted of 280 mV, and peak current is increased by a 1.5 factor confirming an electrocatalytic behavior of CB toward Fe^{3+} reduction. On the other hand, for the reduction of $[Fe(CN)_6]^{3-}$, only a slight increase of peak intensity was observed, keeping the peak potential at the same value of unmodified SPE. A study on the effect of electrode surface coverage on the electrocatalytic rate was then run cycling the potential between +400 and +800 mV for different times to obtain different surface coverage of PB.

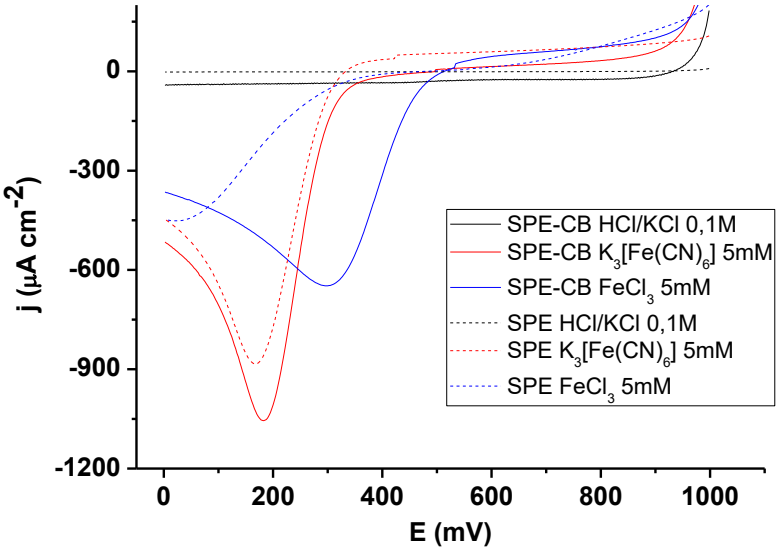

Fig. 1. LSV of LSV of $K_3[Fe(CN_6]$ and $FeCl_3$ on SPE and SPE-CB in HCl/KCl 0,1 M solutions

The bare (SPE) and CB-modified SPE (CB-SPE) were modified using 5 to 20 electrodeposition cycles. The electrocatalytic properties of these electrodes were evaluated considering the electrochemical rate constant (k) calculated using a wall-jet electrode configuration in continuous flow. This experimental approach uses a semi-empirical model which allows to separate the kinetic and mass transport terms contribution to total current density [9]. Eq 1 shows the relationship between the kinetic term (expressed as the kinetic constant (k)) and the mass transport term (expressed as the effective mass transfer coefficient (k_D)). As shown in Eq. 2, k_D is proportional to the ¾ power of the flow rate and to a b parameter dependent on the flow cell geometry (for further information, lector is referred to ref. 9).

$$\frac{1}{j} = \frac{1}{nFC_0}\left(\frac{1}{k_D} + \frac{1}{k}\right) \quad (1)$$

$$k_D = bV^{3/4} \quad (2)$$

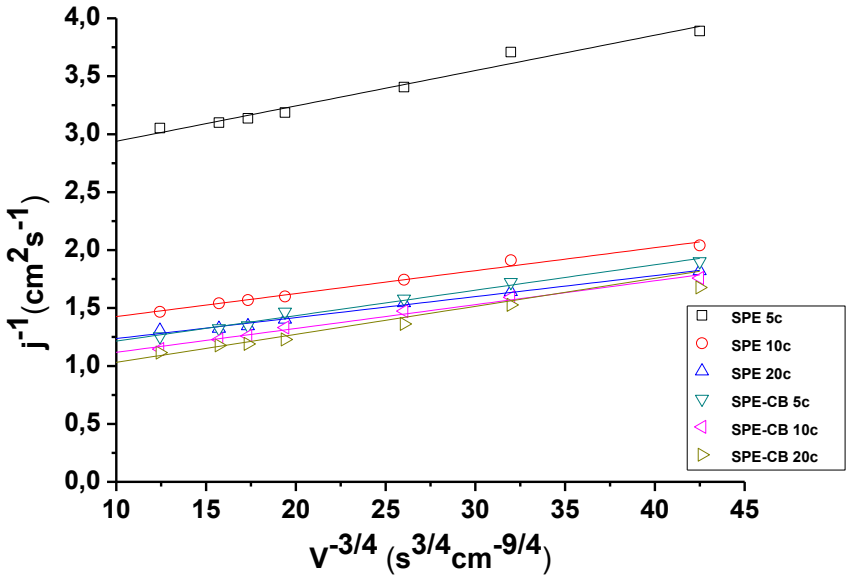

Fig. 2. Dependence of the current density on the flow rate for different electrodes

Thus, one can obtain k by the intercept of the regression of j^{-1} vs. $V^{-3/4}$, Fig. 2 shows the linear regression for different electrodes. As seen in Table 1, the electrochemical rate constant is higher for SPE-CB for a given cycle number. Even, SPE with 20 cycles has a k comparable to SPE-CB with only 5c.

Table 1. Electrochemical rate constant of each electrode

Electrode	k ($cm \cdot s^{-1}$) 10^3
SPE-PB 5c	0,39
SPE-PB 10c	0,84
SPE-PB 20c	0,98
SPE-CB-PB 5c	1,04
SPE-CB-PB 10c	1,14
SPE-CB-PB-20c	1,42

This highlights the advantage of using CB as an effective SPE modifier for PB electrodeposition and further electrocatalysis of H_2O_2. Calibration curves obtained with SPE-PB 20c and SPE-CB-PB 20c gave a linear range of 0.5 to 500 μM, detection limits of 0.11 and 0.09 μM and sensitivities of 0.27 and 0.47 $\mu A\ \mu M^{-1}\ cm^{-2}$ respectively.

4 Conclusions

CBNPs were successfully employed as SPE modifier for electrodeposition of PB from the precursors Fe^{3+} and $[Fe(CN)_6]^{3-}$. The CB-SPE were able to shift the reduction potential of ferricyanide 280 mV, allowing the selective electroreduction of the two precursors. As previously reported in literature, the reduction of both precursors at same time leads to an irregular crystalline structure of PB, lowering it electrocatalytic performance towards H_2O_2 reduction. In fact, a higher electrochemical rate constant was found when PB was electrodeposited on CB-SPE-PB in contrast to SPE-PB. Thus, a higher electrocatalytic activity in CB-SPE-PB was demonstrated. These results are the basis for further developing of these electrodes for non-enzymatic electrochemical sensing of H_2O_2 and biosensing of analytes of interest linking peroxidase enzymes to electrode's surface.

5 Bibliography

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