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Application of Prussian Blue electrodes for amperometric detection of free chlorine in water samples using Flow Injection Analysis

Pedro Salazar [a,*], Miriam Martín [b], José Luis González-Mora [b], Agustín R. González-Elipe [a]

[a] Laboratory of Nanotechnology on Surfaces, Institute of Materials Science of Seville (CSIC-Univ. Sevilla), Calle Américo Vespucio 49, 41092 Sevilla, Spain
[b] Neurochemistry and Neuroimaging Group, (Laboratory of Sensors, Biosensors and Materials) Faculty of Medical Sciences, University of La Laguna, Campus de Ofra s/n, Tenerife, 38071 La Laguna, Spain

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ABSTRACT

The performance for free chlorine detection of surfactant-modified Prussian Blue screen printed carbon electrodes (SPCEs/PB-BZT) have been assessed by cyclic voltammetry and constant potential amperometry. The characterization of SPCEs/PB-BZT by X-ray photoemission, Raman and infrared spectroscopies confirmed the correct electrodeposition of the surfactant-modified PB film. These electrodes were incorporated in a Flow Injection device and the optimal working conditions determined as a function of experimental variables such as detection potential, electrolyte concentration or flow-rate. The sensor presented a linear response in the range 0–3 ppm free chlorine, with a sensitivity of 16.2 µA ppm^{-1} cm^{-2}. The limit of detection (LOD) ($S/N=3.3$) and the limit of quantification ($S/N=10$) amounted to 8.25 and 24.6 ppb, respectively, adequate for controlling tap and drinking waters. To demonstrate the feasibility of using this free chlorine sensor for real applications possible interferences such as nitrate, nitrite and sulfate ions were successfully tested and discarded. Real free chlorine analysis was carried out in spiked tap water samples and commercial bleaches.

1. Introduction

Quality of drinking water represents a great concern for scientists, authorities and consumers. Sodium hypochlorite (NaOCl) solution is a strong oxidizer, currently used as disinfectant or bleaching agent. It is also used in water works for the chlorination of water and as disinfectant in swimming pools, waste and drinking waters [1–7].

When NaOCl is added to water it creates hypochlorous acid (HClO) and hypochlorite ion (ClO^-) which are linked by the following equilibrium equations at 25 °C [1,6]:

$$NaClO \rightarrow Na^+ + ClO^- \tag{1}$$

$$HClO \leftrightarrow ClO^- + H^+ \quad pKa = 7.5 \tag{2}$$

These species are generally known as *free chlorine* species and the presence of trace amounts of these substances in water is generally taken as a guarantee of microbial safety in water distribution systems. However, excess of free chlorine may have negative effects on the human health and its monitoring is critical for the whole cycle of water treatment, water distribution and water consumption [8,9].

In the pH dependent equilibria (1) and (2), the hypochlorous acid is the dominant species at pHs lower than 7.5. This means that a significant change in the $HClO/ClO^-$ ratio occurs between pH 6 and 9, i.e., within the typical pH range for drinking and tap waters. This variation is significant for sanitation purposes because HClO is a stronger disinfectant than ClO^-. Various analytical methods such as, interferometric [10], spectrophotometric [11,12], potentiometric [13], amperometric [1,3,6,7,14], green methods [15], etc. are currently used to determinate free chlorine in water. Among them, electroanalytical procedures are advantageous [1,6,16,17] because of their simplicity, high sensitivity and selectivity, low cost, real-time output and the possibility to develop user-friendly and wireless integrated devices suitable for on-line monitoring, i.e., the so-called Flow-Injection Systems implementation [1,4,6,18].

Prussian Blue (PB), $Fe_4[Fe(CN)_6]_3$, is the most representative compound of the transition metal hexacyanometallate family. It has so high electrocatalytic activity and selectivity towards the detection of H_2O_2 by reduction [16,19,20] that some authors have named it "*artificial enzyme peroxidase*" [21]. As such, this compound has been used for biosensor and inmunosensor applications coupled with oxido-reductase enzymes [16,20]. The electrocatalytic activity of PB and its analogues have been also proved with other molecules such as vitamin B-6, thiocholine, dopamine,

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* Corresponding author.
E-mail address: psalazar@icmse.csic.es (P. Salazar).

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epinephrine, morphine, cysteine, methionine and ascorbic acid [16]. In this line, we have recently developed a novel surfactant-modified PB Glassy Carbon Electrode (GCE) which, acting as free chlorine sensor in tap water, presented a detection performance comparable to that of standard colorimetric methods [22].

In the present work we report the development of a surfactant-modified PB Screen Printed Carbon Electrode (SPCE) and their incorporation into a FIA device for the quantitative determination of free chlorine in water. These PB-modified SPCEs are fully characterized by X-ray photoemission, Raman and infrared (IR) spectroscopies and their sensor performance tested using cyclic voltammetry and chronoamperometry. In addition, the effect of experimental variables such as detection potential, electrolyte concentration and flow-rate has been systematically investigated to define the optimal working conditions of the system. Finally, to demonstrate its reliability for the intended application, the flow injection device is successfully tested with real tap water samples and commercial bleaches.

2. Experimental

2.1. Reagents and solutions

Sodium hypochlorite (4.00–4.99%), $FeCl_3$, $K_3[Fe(CN)_6]$, benzethonium chloride (BZTC) and other chemicals were purchased from Sigma and used as supplied. Stock solutions were prepared in doubly distilled water (18.2 MΩ cm, Millipore-Q) and stored at 4 °C when not in use. The stock chlorine solution (100 ppm) was prepared in water every day and used to prepare different chorine solutions just before carrying out the different essays.

2.2. Instrumentation

Screen Printed Carbon Electrodes (SPCEs) DRP-100, were purchased from Dropsens (Spain). They have a conventional three-electrode configuration printed on ceramic substrates (3.4 cm × 1.0 cm). Both working (disk-shaped 4 mm diameter) and counter electrodes were made of carbon inks, whereas the pseudo reference electrode and electric contacts were made of silver. Electrochemical measurements were performed with a DRP-μSTAT400 potentiostat and the data were acquired with the Dropview software (DropSens). Raman and IR spectra were taken with a HORIBA HR-800-UV microscope and a JASCO FT/IR-6200 spectrophotometer under Attenuated Total Reflection (ATR) mode, respectively. X-ray photoelectron spectroscopy (XPS) measurements were taken in a Phoibos 100 spectrometer working in the pass energy constant mode and using the Mg Kα as excitation source. The binding energy (BE) scale was referenced to the C1s signal taken at 284.6 eV for the spurious carbon contaminating the sensor surfaces. To compare the concentration of commercial bleaches, we applied the N, N-diethyl-p-phenylendiamine (DPD) method using a VARIAN Cary-100-UV/Vis spectrophotometer.

2.3. PB electrodeposition

The background electrolyte solution for electrodeposition consisted of 0.02 M HCl and 0.1 M KCl. The deposition of the PB-surfactant composite film onto SPCEs was done by firstly dropping the precursor solution (background electrolyte solution containing 1.5 mM $FeCl_3$ + 1.5 mM $K_3[Fe(CN)_6]$ + 2 mM surfactant) onto the working, pseudo-reference and counter electrodes, followed by cycling between −0.2 and 1 V at a scan rate of 0.1 V s^{-1} (default 20 cycles) (*see the optimization of the electrodeposition step in our previous publications*, [17,22,23]). Unmodified PB film was prepared under the same conditions except for that the solution was free of surfactant. For XPS analysis the surfactant-modified PB was electrodeposited on a Ti foil using a similar methodology with Ag/AgCl (3 M KCl) and Pt as reference and counter electrodes, respectively.

2.4. Electrochemical characterization

Electrochemical characterization was done by cyclic voltammetry (CV) in the presence of the background solution. Chronoamperometry and Constant Potential Amperometry (CPA) were employed to study the sensitivity against free chlorine using different configurations and experimental conditions.

2.5. Free chlorine sensor calibrations

Free chlorine sensitivities were determined with a Flow Injection Analysis (FIA) system supplied by Dropsens, using CPA as electroanalytical technique. The system was equipped with a flow-through cell for screen-printed electrodes, a manual sample injection valve with a sample loop of 0.5 mL and a peristaltic pump. The influence of experimental variables such as potential work, electrolyte concentration, pH and flow injection rate was carefully studied to optimize the sensor response. All experiments were performed at room temperature. Unless otherwise stated, the background solution employed for chlorine calibration was PBS (0.1 M KCl, pH 5.2) and free chlorine was in the form of HClO. Tap water (collected in our laboratory) was supplemented with 50 mM KCl and used to study the matrix effect in real samples (Section 3.4). In addition, commercial bleaches were obtained from local markets and their composition evaluated by comparison against a standard DPD colorimetric method [22].

3. Results and discussions

3.1. Characterization

Fig. 1(a) and (b) shows the CVs recorded for 20 cycles during film formation onto the SPCEs for unmodified (PB) and surfactant-modified (PB-BZT) films, respectively. Just from the first cycle the CV response was greater for PB-BZT than for the unmodified film. More details about film formation may be found in our previous publications [17,22,23]. CV for both configurations, Fig. 1(c), confirmed that a higher amount of PB is deposited in the presence of surfactant.

The surface coverage ($\Gamma^0_{Fe^{3+}}$) was determined according to Eq. (3) using the peak centered at ca. +0.1V in the presence of the background electrolyte:

$$\Gamma^0_{Fe^{3+}} = Q_{ox}/nFA \tag{3}$$

where Q_{ox} is the charge associated with the anodic peak, n the number of electrons exchanged in the reaction (n=1), F the Faraday constant and A the geometrical area of the working electrode (A=0.126 cm^2). The PB-modified electrode, SPCE/PB, gave a $\Gamma^0_{Fe^{3+}}$ value of 5.23 × 10^{-9} mol cm^{-2}, while the SPCE/PB-BZT electrode displayed a consistently higher value of 6.85 × 10^{-8} mol cm^{-2}, indicating an enhancement by one order of magnitude in the PB deposition when BZT was used. The thickness of the film, d, was estimated according Eq. (4) by considering the number of unit cells on the electrode surface, geometrical parameters of the PB cell and the working electrode area [17,23]:

$$d = \Gamma^0_{Fe^{3+}} \times (l^3 N_A/4) \tag{4}$$

where N_A is the Avogadro's number and l is the length of the unit