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Dedicated to the memory of Prof. dr. Ioan Silaghi-Dumitrescu marking 60 years from his birth

CARBON NANOTUBES-GRAPHITE PASTE ELECTRODE MODIFIED WITH Cu(II)-EXCHANGED ZEOLITE FOR H_2O_2 DETECTION

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ABSTRACT. Modification of a natural zeolite from Macicas (Cluj County, Romania) with copper(II) (Z-Cu), followed by its incorporation in carbon paste, made of carbon nanotubes and graphite powder as conductive matrix (Z-Cu-G-CNT-CPEs), lead to a stable modified electrode. The Z-Cu-G-CNT-CPEs electrodes show significant electrocatalytic activity toward H_2O_2 reduction. The rate constant for catalytic H_2O_2 reduction, estimated from rotating disk electrode measurements, extrapolated to zero H_2O_2 concentration was found to be 74.4 M^{-1} s^{-1} (pH 7). The amperometric detection of H_2O_2, at -400 mV *vs.* Ag/AgCl/KCl_{sat} is characterized by the following electroanalytical parameters: sensitivity of 15.33 mA M^{-1}, detection limit of 0.24 mM and linear domain up to 10 mM H_2O_2.

Keywords: *carbon paste electrodes, zeolite, hydrogen peroxide, carbon nanotubes*

INTRODUCTION

Hydrogen peroxide is an important analyte in food, pharmaceutical, clinical, industrial and environmental analyses [1]. H_2O_2 can be determined using different analytical methods such as: chemiluminometry [2], spectrophotometry [3], titrimetry [4], enzymatic [5], acoustic emission [6] and electrochemical methods [7].

Among the new materials used for H_2O_2 electrochemical detection, zeolite-modified electrodes are of high interest, due to the fact that zeolites offer the most complete range of interesting properties required at an electrochemical interface [8]. These properties can be greatly improved by metal ions incorporation, as zeolites are versatile cation-exchangers [9].

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In last years, modified electrodes based on carbon nanotubes received considerable attention for determination of H_2O_2, due to the possibility to obtain a good detection limit and a wide linear range [10-13].

The aim of this work was to explore the possibility of using Cu(II)-exchanged zeolitic volcanic tuff (Z-Cu) from Macicas (Cluj County, Romania) containing 70-80% clinoptilolite [14], for preparation of an amperometric sensor for H_2O_2 detection. The electrochemical reduction of H_2O_2 was investigated using a carbon paste electrode based on Cu-modified natural zeolite, incorporated in carbon nanotube-graphite paste conductive matrix. The electrochemical behavior of the modified electrode has been characterized by using cyclic voltammetry at different scan rates and pH values. The electrocatalytic efficiency toward H_2O_2 reduction was estimated, using amperometry and rotating disk electrode measurements.

RESULTS AND DISCUSSION

Electrode material characterization

According to compositional investigations, performed previously, the zeolitic volcanic tuff sample, Macicas (Cluj County), contains 70-80% clinoptilolite, present as tabular crystals. The zeolitic volcanic tuff sample shows a remarkable homogeneity in its mineralogical and chemical composition and has specific surface area of 35 m^2/g [14-16].

Using ESEM technique we were able to analyze the surface morphology (figure 1A) and also to determine surface composition of the zeolitic volcanic tuff sample (figure 1B). Mass percent composition for the elements present is as follows: O-57.08%, Na-0.90%, Al-5.23%, Si-28.96%, K-1.91%, Ca-2.33%; Fe-3.60%. The elements distribution maps (results not shown) indicate a uniform distribution on the solid surface sample.

TEM images of the copper modified zeolite (figure 1C) show darker regions on the surface of the solid samples, which could be attributed to the presence of the metal on the surface. Due to the high concentration of the copper solution used during the modification treatment, part of the metal ions were deposited on the surface and probably transformed in copper oxide during the calcination process. On the TEM images of the electrode material Z-Cu-G-CNT (figure 1D), it is easy to observe the carbon nanotubes as fine lines and the graphite used as a conductive material as black dots on the investigated surface.

As can be observed from figure 2, the electrochemical behavior of Z-Cu-G-CNT-CPEs modified electrodes show a well shaped voltammetric response. In a first attempt, the redox peaks pair ($E^{0'}$ of -165 mV *vs.* $Ag/AgCl/KCl_{sat}$) for obtained modified electrodes was attributed to cooper ions, immobilized on the natural zeolite.

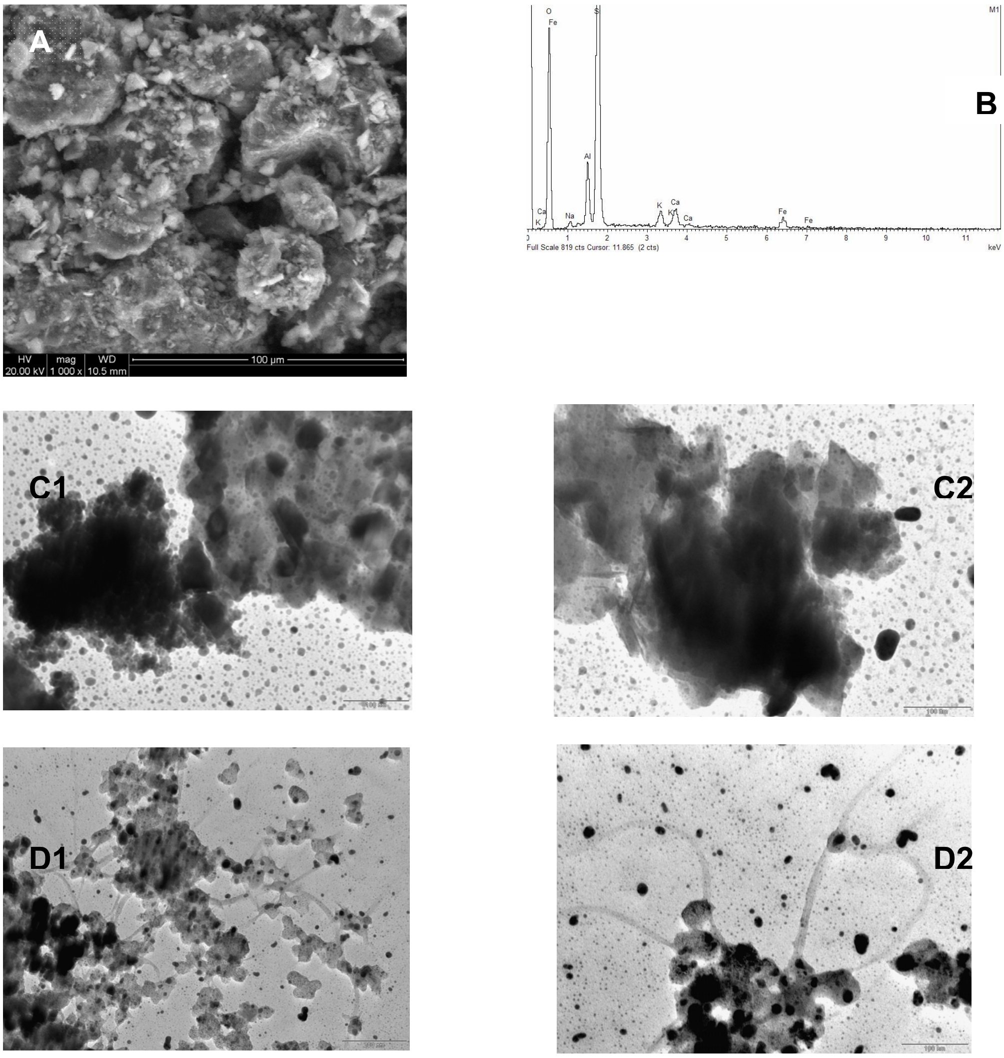

Figure 1. Electron microscopy images of zeolitic volcanic tuff (A), copper(II) modified zeolite (C1, C2) and electrode material (D1, D2). Note: (A) ESEM images; (B) ESEM spectra; (C) TEM images of different regions on copper(II) modified zeolite; (D) TEM images of the same region on Z-Cu-G-CNT material.

The redox response of the Z-Cu-G-CNT-CPEs was affected by pH (results not shown). Indeed, the formal standard potential, $E^{0'}$ (estimated as the average of the cathodic and the anodic peak potentials, recorded in the pH range from 3 to 9), changes with pH. This behavior suggests that the voltammetric response is a combined one, involving oxygen and Cu redox couples.

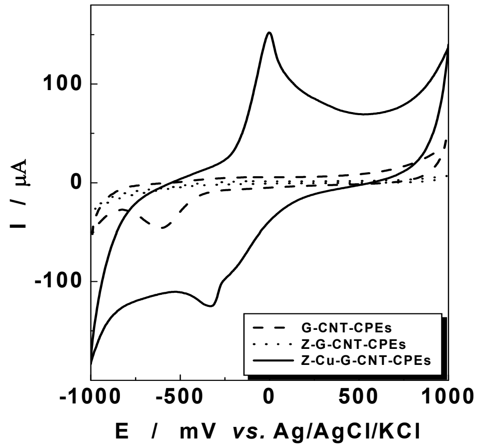

Figure 2. Cyclic voltammograms corresponding to obtained modified electrodes. Experimental conditions: starting potential, -1000 mV *vs.* Ag/AgCl/KCl$_{sat}$; potential scan rate, 10 mV s^{-1}; supporting electrolyte, 0.1 M phosphate buffer, pH 7.

Cyclic voltammetric measurements were performed in a wide range of potential scan rate (from 10 mV s^{-1} to 2 V s^{-1}), when the Z-Cu-G-CNT-CPEs electrodes were in contact with phosphate buffer solutions of different pH values (from 3 to 9). The slopes of the log–log peak current *vs*. potential scan rate dependence were close to 0.5 (Table 1), indicating the existence of a diffusion process of ions from zeolite to electrode surface, combined with the diffusion of counterions from solution, in order to maintain the electroneutrality.

Table 1. Parameters of the log-log linear regression corresponding to the peak current dependence on the potential scan rate for Z-Cu-G-CNT-CPEs. Experimental conditions: as in figure 2.

pH	**Slope**		**R/N**	
	oxidation	**reduction**	**oxidation**	**reduction**
3	0.61 ± 0.005	0.67 ± 0.02	0.999 / 12	0.993 / 12
5	0.75 ± 0.01	0.71 ± 0.01	0.999 / 7	0.999 / 7
7	0.44 ± 0.01	0.77 ± 0,03	0.997 / 11	0.994 / 9
9	0.67 ± 0.04	0.89 + 0.29	0.984 / 7	0.833 / 6

From the dependence of the peak potentials on the potential scan rate (results not shown), the heterogeneous electron-transfer rate constant (k_s, s^{-1}), for the redox process corresponding to Z-Cu-G-CNT-CPEs electrode was estimated to be 0.31 s^{-1} at pH 7 (figure 3A) using the Laviron treatment [17].

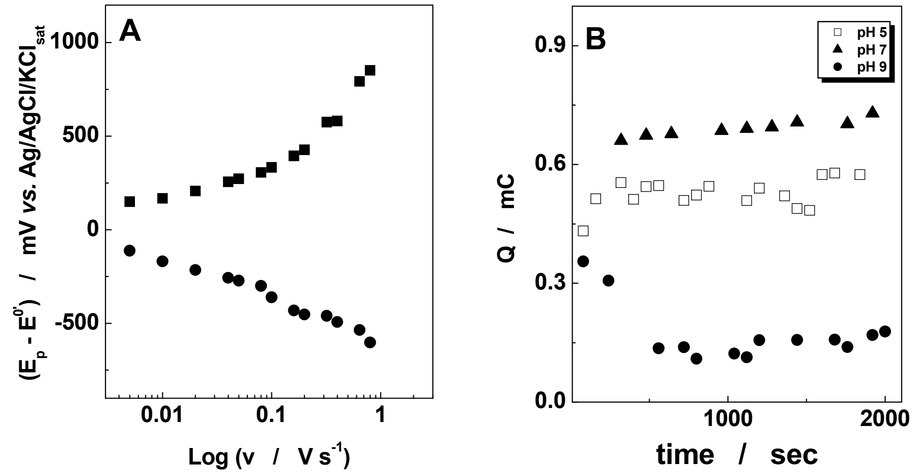

Figure 3. Experimental dependence of (Ep - $E^{o'}$) *vs.* logarithm of the scan rate (A) and time dependence of the charge amount (B) for Z-Cu-G-CNT-CPEs. Experimental conditions: scan rate, 50 mV s^{-1}; potential range, -1000 to 1000 mV *vs.* Ag/AgCl/KCl_{sat}.

The stability of the Z-Cu-G-CNT-CPEs electrodes was examined by continuous cycling of the electrode potential within the range covering the Z-Cu-G-CNT-CPEs redox activity, at different pH values of the surrounding solution, and the corresponding cyclic voltammograms were recorded. During such experiments, the charge amount (Q) involved in the redox process slightly decreases (figure 3B), while the shape of the voltammograms remained invariant (results not shown), except when the supporting electrolyte was pH 9. The best electrochemical stability was obtained at pH 7, which is the most used pH value for amperometric sensors for H_2O_2 detection. Considering that the decrease of the charge amount obeys zero order kinetics, the deactivation rate constant of the electrode response was estimated at pH 7 (3.50 10^{-8} C s^{-1}). This very low value proves at the same time, that copper is strongly retained in the zeolite framework and it has high electrochemical stability.

Comparing the cyclic voltammograms recorded in phosphate buffer (pH 7) for a Z-Cu-G-CNT-CPEs electrode, in the absence and in the presence of 5 mM and 10 mM H_2O_2 (figure 4A), a good electrocatalytic activity for H_2O_2 reduction is shown. The Z-Cu-G-CNT-CPEs electrodes exhibit significant electrocatalytic efficiency, characterized by: (i) the decrease in overpotential for H_2O_2 reduction (~200 mV, estimated as the difference between the cathodic peak potentials observed on the Z-Cu-G-CNT-CPEs electrode and on Z-G-CNT-CPEs electrode); (ii) the electrocatalytic efficiency is improved when Cu-exchanged zeolite is used (63.2 for the Z-Cu-G-CNT-CPEs and 34.7 for

Z-G-CNT-CPEs, estimated as the ratio $((I_{peak})_{[H2O2]=5mM} - (I_{peak})_{[H2O2]=0})/(I_{peak})_{[H2O2]=0}$, at an applied potential of -400 mV *vs*. Ag/AgCl/KCl$_{sat}$). This good electrocatalytic activity is due to the presence of a high quantity of copper in the zeolite structure (1.9515 mg Cu^{2+}/g zeolite), knowing that copper is an efficient mediator for H_2O_2 reduction.

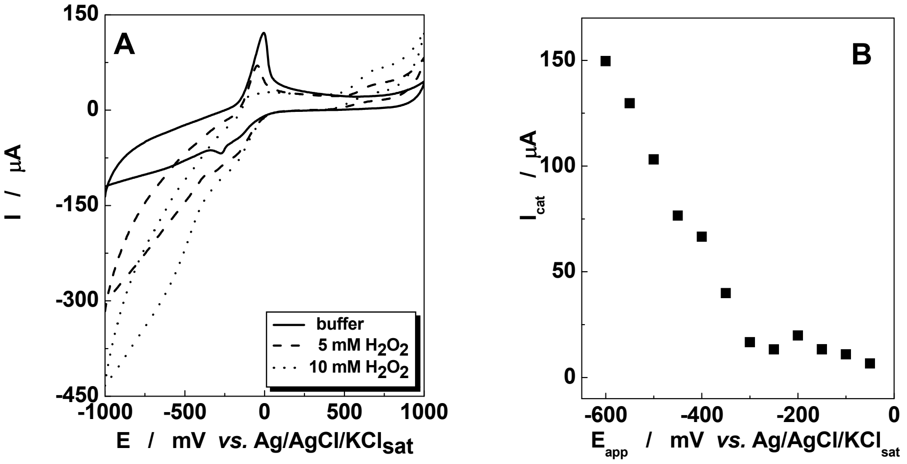

Figure 4. (A) Electrocatalytic activity of Z-Cu-G-CNT-CPEs electrode for H_2O_2 reduction, in absence and in presence of H_2O_2. Experimental conditions: starting potential, −1000 mV *vs*. Ag/AgCl/KCl$_{sat}$; scan rate, 10 mVs^{-1}; supporting electrolyte, 0.1 M phosphate buffer (pH 7.0).
(B) Effect of the applied potential on the electrocatalytic current recorded at Z-Cu-G-CNT-CPEs electrode, in presence of 5 mM H_2O_2. Experimental conditions: supporting electrolyte, 0.1 M phosphate buffer (pH 7.0); rotation speed, 800 rpm.

Rotating disk electrode measurements were employed to investigate the kinetics of the electrocatalytic reduction of H_2O_2 on the Z-Cu-G-CNT-CPEs electrodes. First, in order to find the optimal applied potential, its effect on the reduction electrocatalytic current was examined (figure 4B). Consequently, for all further measurements, the applied potential selected was -400mV *vs*. Ag/AgCl/KCl$_{sat}$.

Using the Koutecky–Levich treatment, applied for H_2O_2 reduction kinetics, the observed rate constants for H_2O_2 electrocatalytic reduction (k_{obs}) were evaluated at different H_2O_2 concentrations, at pH 7. The linear dependence between $1/I_{cat}$ and $1/\omega^{1/2}$ allowed calculation of k_{obs} values at different H_2O_2 concentrations. Supposing that the reduction reaction of H_2O_2 at the Z-Cu-G-CNT-CPEs obeys Michaelis–Menten kinetics, a plot of the reciprocal value of the observed rate constant *vs*. H_2O_2 concentration, results in a straight line (results not shown). From the slope and the intercept of this straight line, the extrapolated values of k_{obs} to zero H_2O_2 concentration ($k_{obs,\ [H2O2]\ =\ 0}$ = 74.4 M^{-1} s^{-1}, for Γ = $2.5\cdot 10^{-7}$ mol cm^{-2}), the apparent Michaelis–Menten constant (K_M = 1.1 mM) and the turnover number for the electrocatalytic reaction (k_{+2} = 0.08 s^{-1}) were estimated.

Finally, using amperometric measurements, performed in the optimal experimental conditions mentioned above, the amperometric response of Z-Cu-G-CNT-CPEs to increasing concentrations of H_2O_2 was recorded. By plotting the steady-state current values *vs.* H_2O_2 concentration, two calibration curves were obtained at -400 and -150 mV *vs.* Ag/AgCl/KCl_{sat} (figure 5).

As can be seen from figure 5, the kinetic parameters are better when the applied potential was -400 mV *vs.* Ag/AgCl/KCl_{sat}. By fitting the amperometric calibration curve to Michaelis–Menten equation, the following kinetic parameters were found: K_M = 60.51 mM and I_{max} = 920 μA. At the same time, the electroanalytical parameters of Z-Cu-G-CNT-CPEs electrodes for H_2O_2 determination were estimated: the sensitivity (calculated as I_{max}/K_M ratio) was 15.33 mA M^{-1}; the linear range was up to 10 mM; the detection limit was 0.24 mM (signal to noise ratio of 3); the response time was less than 10 s. It can be observed that this detection limit is improved by using cooper in comparison with other modified electrodes that used carbon nanotubes [13].

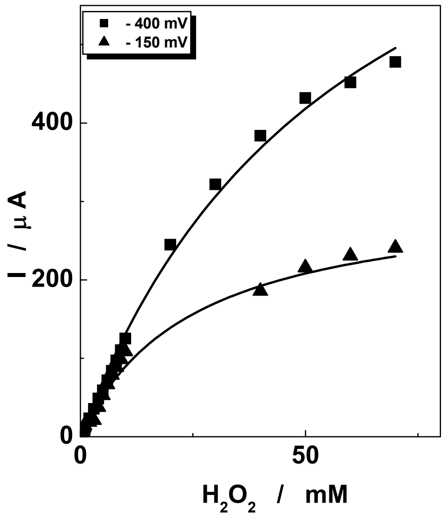

Figure 5. Calibration curves for H_2O_2 of Z-Cu-G-CNT-CPEs electrodes. Experimental conditions: applied potential, -400 mV and -150 mV *vs.* Ag/AgCl/KCl_{sat}; supporting electrolyte, 0.1 M phosphate buffer (pH 7.0); rotation speed, 800 rpm.

CONCLUSIONS

A new electrocatalytic system for mediated reduction of H_2O_2 based on carbon paste electrodes modified with a Cu-exchanged zeolite, using carbon nanotubes and graphite powder is proposed and investigated from physical-chemical, electrochemical and electrocatalytic point of view. Under operation in optimal conditions, the Z-Cu-G-CNT-CPEs electrodes exhibit a good electrochemical stability at pH 7 and electrocatalytic efficiency towards H_2O_2 reduction.

EXPERIMENTAL SECTION

Chemicals

Single-walled carbon nanotubes (CNT) were obtained from Sigma (St. Louis, MO, USA), graphite powder and paraffin oil from Fluka (Buchs, Switzerland) and hydrogen peroxide, $K_2HPO_4 \cdot 2H_2O$ and $KH_2PO_4 \cdot H_2O$ from Merck (Darmstadt, Germany). NaCl, $Cu(SO_4)_2 \cdot 5H_2O$, ammonium solution 25% were purchased from Reactivul Bucharest.

All reagents were of analytical grade and used as received. The supporting electrolyte was 0.1 M phosphate buffer solution, obtained by mixing appropriate solutions of $K_2HPO_4 \cdot 2H_2O$ and $KH_2PO_4 \cdot H_2O$.

Preparation of modified zeolite

A zeolitic volcanic tuff sample from Macicas (Cluj County), Z, granulation d < 0.2 mm, brought in –Na form was contacted with a solution containing copper in order to obtain the required modification.

Certain stages were involved in the zeolitic volcanic tuff preparation. First, solid samples were subjected to a mechanical treatment consisting of crushing, grinding and size separation. Next, samples were washed with distilled water and dried. A chemical treatment consisting of a contact with an alkaline solution, NaCl, pH 10, followed. After this last treatment, the zeolitic volcanic tuff sample was washed again with distilled water, until chlorine ions were no more detected in the washing water, and dried. [15] The zeolitic volcanic tuff sample is now prepared for the next stage, the ionic exchange with the desired metallic ion, in our case copper. The established quantity of zeolitic volcanic tuff prepared as described above, was brought in Z-Cu form using a $CuSO_4 \cdot 5H_2O$ 0.5N solution. The ionic exchange process (Na^+ ions from the zeolite structure were replaced with Cu^{2+} ions from aqueous solution) was realised in a batch reactor with solid and liquid phases as immobile phases, using a solid: liquid ratio of 1:10. Solid and solution were kept in contact for 24 hours. After this time interval, the copper modified zeolitic volcanic tuff sample was separated by filtration, dried for 6 hours at 105°C and then roasted at 400°C for 4 hours. In this way was obtained the M-Cu modified zeolitic volcanic tuff, containing 1.9515 mg Cu^{2+}/g zeolite. The initial and final concentrations of copper ions in solution, used to establish the quantity of copper retained in the zeolitic volcanic tuff sample, were determined using a JENWAY 6305 spectrophotometer, 25% ammonium solution at $\lambda = 440$ nm.

Electrode Preparation

The modified electrodes, Z-G-CNT-CPEs and Z-Cu-G-CNT-CPEs were prepared by hand mixing the unmodified or modified zeolites with CNTs, graphite powder (2:1:1, w/w) and paraffin oil. The resulting pastes were packed into a cavity at the end of a Teflon tube. Electrical contact was established *via* a copper wire connected to the paste. The electrode surface was smoothed by rubbing on a filter paper just prior to use.

Physical-chemical and electrochemical measurements

Zeolitic volcanic tuff samples morpholgy was investigated using environmental scanning electron microscopy (ESEM, INCAx-sight 6427 Oxford Instruments) and transmision electron microscopy (TEM, Jeol JEM1010 with a MegaViewIII CCD camera - SIS-Olympus). Using ESEM techniques we also could determine the superficial composition of the zeolitic volcanic tuff sample.

Electrochemical experiments were carried out using a typical three-electrode electrochemical cell. The modified carbon paste electrode was used as working electrode, a platinum ring as counter electrode and an $Ag/AgCl/KCl_{sat}$ as reference electrode. Cyclic voltammetry experiments were performed on a PC-controlled electrochemical analyzer (Autolab-PGSTAT 10, EcoChemie, Utrecht, The Netherlands).

Steady state amperometric measurements at different rotating speeds of the working electrode were performed using an EG&G rotator (Radiometer) and the same carbon paste as disk material. The current–time data were collected using the above-mentioned electrochemical analyzer.

Batch amperometric measurements at different H_2O_2 concentrations were carried out at an applied potential of -400 mV *vs.* $Ag/AgCl/KCl_{sat}$, under magnetic stirring, using 0.1 M phosphate buffer solution as supporting electrolyte. The current-time data were collected using the above-mentioned electrochemical analyzer.

The pH of the phosphate buffer solutions was adjusted using NaOH or H_3PO_4 and a pH-meter (HI255, Hanna Instruments, Romania), with a combined glass electrode.

The experimental results are the average of at least three identically prepared electrodes, if not otherwise mentioned.

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