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# CARBON PASTE ELECTRODE INCORPORATING A SYNTHETIC ZEOLITE EXCHANGED WITH Fe(III) FOR AMPEROMETRIC DETECTION OF ASCORBIC ACID

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**ABSTRACT.** A new modified electrode was obtained by incorporating a synthetic zeolite exchanged with Fe(III) in carbon paste. The electrochemical behavior of the modified electrode (Fe13X-CPE) was investigated using cyclic voltammetry. The modified electrode was successfully tested for electrocatalytic oxidation of ascorbic acid (AA) in phosphate buffer (pH 7.0), at an applied potential of +0,15 V *vs.* Ag/AgCl/$KCl_{sat}$. The amperometric sensor for ascorbic acid was characterized by a linear concentration range of 0,05 mM to 0,4 mM AA The theoretical detection limit, calculated from the slope of the regression equation and standard deviation of the calibration curve, was $5.8 \cdot 10^{-5}$ M.

**Keywords:** ascorbic acid, electrocatalytic oxidation; Fe-exchanged zeolite; modified carbon paste electrode.

## INTRODUCTION

One of the most flexible ways to obtain chemically modified electrodes with zeolites is their incorporation in carbon paste [1]. Carbon paste electrodes (CPEs) are popular because they are easily obtainable at minimal costs and are especially suitable for preparing an electrode material modified with admixtures of various compounds, thus giving the electrode certain pre-determined properties. Other advantages of CPEs are low background current, wide potential window and versatility.

Zeolite-modified carbon paste electrodes (ZME-CPEs) keep all these advantages, and in addition, they exhibit a number of chemical, physical and structural characteristics of high interest in the design of electroanalytical systems: shape, size and charge selectivity, physical and chemical stability, high ion-exchange capacity and hydrophilic character due to the presence of zeolites [2,3].

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Among the chemical species that can be determined by using ZME-CPEs, ascorbic acid (AA), known also as Vitamin C, is of particular interest, due to the fact that it is playing a key role in living bodies, being an antioxidant that protects cells against damage by free radicals, which are reactive by-products of normal cell activity. This is the reason why L-Ascorbic acid is widely used as a dietary supplement and is also added to manufacture foods as an antioxidant for preservation [4]. Consequently, measuring ascorbic acid content is very important for assessing food product quality.

Electrochemical methods for AA determination are based on different amperometric [5-9] potentiometric [10,11], and voltammetric [12-14] sensors, or on the use of biosensors [15-21]. Among these methods, those based on the utilization of zeolite modified electrodes have attracted much of attention, due to the fact that several mediators can be easily immobilized in the zeolitic matrix. For example, carbon paste electrodes incorporating synthetic zeolites modified with Methylene blue [22] and sensors in which a Fe(III) exchanged zeolite Y is dispersed on the surface of glassy carbon were successfully used for AA detection [23].

In this context, a new sensor incorporating a synthetic mesoporous zeolite (13X, Aldrich) exchanged with Fe ions embedded in a carbon paste matrix was designed and tested for ascorbic acid amperometric detection. The proposed AA sensor possesses high sensitivity and operational stability due to the strong affinity between zeolite and iron(III) and to the efficient immobilization technique.

## RESULTS AND DISCUSSIONS

### Electrochemical characteristics of Fe13X-CPEs

The presence of Fe(III) ions in the matrix of the carbon paste electrodes was put on evidence by cyclic voltammetry in the potential range from -200 at +1000 mV *vs.* Ag|AgCl/$KCl_{sat}$ (Figure 1).

As can be seen, in the case of Fe13X-CPE, a well-defined peak pair was observed on the cyclic voltammograms, with the formal standard potential ($E^{0'}$) at about 100 mV. The peak pair was attributed to the reduction / oxidation of Fe(III) ions embedded in the zeolitic matrix.

The peak separation, $\Delta E_p$, was found to be 45 mV at a scan rate of 50 mV/s, and increases with the scan rate (results not shown) indicating a quasi-reversible redox process. This is an indication that the kinetic of electron transfer on the electrode surface is not very fast, as consequence of the nature of the matrix, whose resistance is considerable [5].

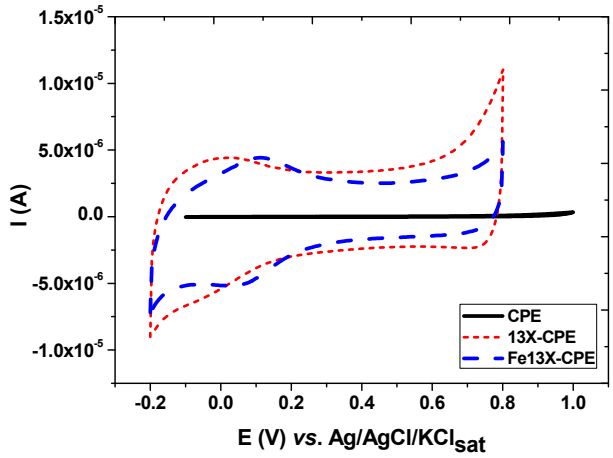


**Figure 1.** Cyclic voltammograms forFe13X-CPE. Experimental conditions: potential scan rate, 10 mV $s^{-1}$; supporting electrolyte, 0.1 M phosphate buffer, pH 7.0.

The cyclic voltammograms, recorded in a wide range of potential scan rates (0.01–1.6$Vs^{-1}$) for two pH values presented a linear dependence of peak current intensities ($I_p$) on scan rate ($v$). The slopes of log $I$ *vs.* log $v$ dependencies were close to the theoretical value 1, confirming the immobilization of the redox species generating the electrode response, (the Fe ions) on the electrode surface (Figure 2). As expected, the pH does not influence the electrochemical response of the Fe(III) / Fe(II) redox couple.

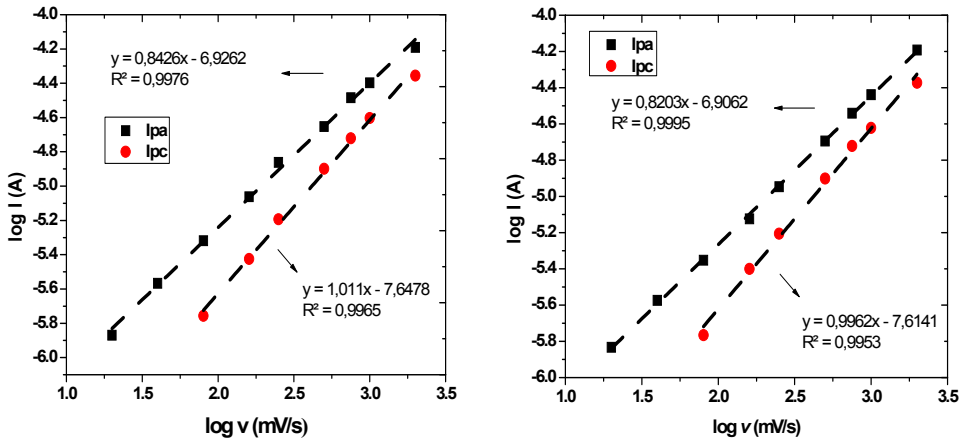


**Figure 2.** LogI *vs.* log v dependencies for Fe13X-CPE. Experimental conditions: supporting electrolyte, 0.1 M phosphate buffer, pH 7 (left) and pH 3 (right).

## Electrocatalytic oxidation of ascorbic acid

The cyclic voltammograms recorded in 0.1 M phosphate buffer pH 7 at Fe13X-CPE in the presence of different concentrations of AA are depicted in Figure 3. As it can be observed, when AA is present, the anodic current strongly increases and the oxidation potential of peak 1 (corresponding to the catalytic oxidation of AA on the Fe-exchanged zeolite) is much lower than peak 2 corresponding to AA oxidation on unmodified carbon paste (Figure 3b), indicating the existence of an electrocatalytic effect. The reason is a chemical interaction between AA and iron(III) loaded in the zeolite.

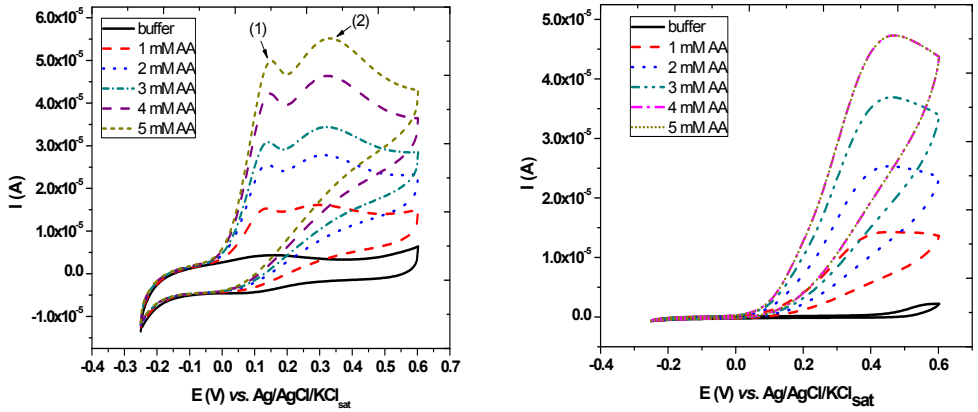


**Figure 3.** Cyclic voltammograms obtained at Fe13X-CPE in the absence and in the presence of different concentrations of AA on Fe13X-CPE (a) and on unmodified CPE (b). Experimental conditions: potential scan rate, 50 $mVs^{-1}$; starting potential, -250 mV *vs.* Ag|AgCl/$KCl_{sat}$; supporting electrolyte, 0.1 M phosphate buffer, pH 7.0.

For peak 1, the reaction taking place at the electrode-solution interface (esi) and into the zeolite modified electrode (z) can be written as follows [23]:

$$Fe^{3+}_{(z)} + 3C^{+}_{(s)} \leftrightarrow Fe^{3+}_{(esi)} + 3C^{+}_{(z)}$$

$$2Fe^{3+}_{(esi)} + C_6H_8O_{6(s)} \leftrightarrow 2Fe^{2+}_{(esi)} + C_6H_8O_{6(s)} + 2H^{+}$$

$$Fe^{2+}_{(esi)} + C_6H_8O_{6(s)} \rightarrow [FeC_6H_8O_6]^{2+}_{(esi)}$$

$$[FeC_6H_8O_6]^{2+}_{(esi)} - 3e^{-} = Fe^{3+}_{(esi)} + C_6H_8O_{6(esi)} + 2H^{+}$$

where C stands for a cation present in the buffer solution (s) and $H^{+}$ is originating from the zeolite matrix.

Batch amperometric measurements at constant applied potential (+0,15 V *vs.* Ag|AgCl/$KCl_{sat}$.) proved that Fe13X-CPE works well as amperometric sensor for AA. The reproducibility of the electrocatalytic effect of Fe13X-CPE

was confirmed by repetitive amperometric measurements (~ 3 measurements). A typical example of stable and fast amperometric response to successive injections of 500 µL $10^{-4}$ M AA is presented in Figure 4A and the resulting calibration curve, in Figure 4B.

The response time of the sensor is relatively short (~ 25s). As can be observed, the relationship between the steady-state current and the concentration of AA was linear in the range from 0.05 mM and 0.4 mM and the sensitivity, calculated as the slope of the calibration curve, was $6{,}9.10^{-3}$ A / M. The detection limit, calculated from the slope of the linear portion of the calibration curve (b) and the standard deviation (σ) with the formula ($3\sigma/b$) was $5{,}8.10^{-5}$ M. The analytical parameters of the Fe(III)-zeolite modified carbon paste electrodes are similar to those of other AA sensors reported in the literature [23].

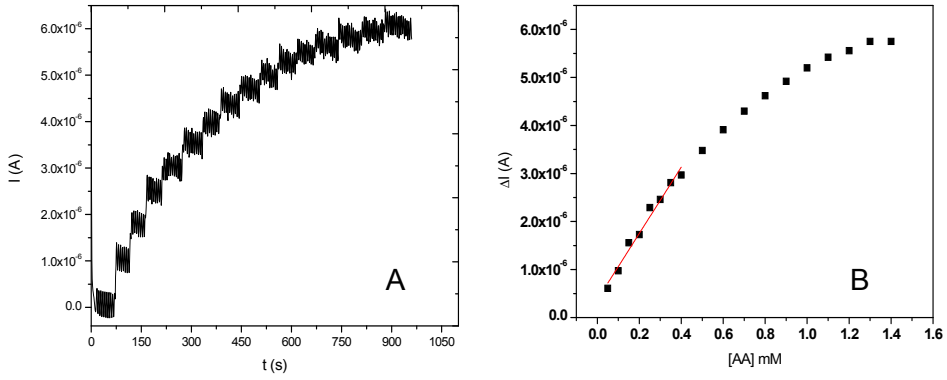


**Figure 4.** Amperometric response to successive increments of 500 µL $10^{-4}$ M AA (A) and the calibration curve for AA (B) at Fe13X-CPEs. Experimental conditions: applied potential, +0,15 V *vs.* Ag|AgCl/$KCl_{sat.}$; supporting electrolyte, 0.1 M phosphate buffer, (pH 7.0), dearated solution; magnetic stirring.

In a next step, by using Fe13X-CPE, AA was determined in a real sample, by using the standard addition method (Figure 5).

For this purpose, one tablet (0.5846 g) of a pharmaceutical product (Propolis C) was dissolved in 20 ml distilled water. Three successive additions of 500 µl solution containing Propolis C, followed by three additions of 500 µl standard solution $5.10^{-3}$M AA were performed in 10 ml phosphate buffer (pH 7) and the resulting current was recorded using Fe13X-CPE (Figure 5 A) at a constant potential value (+0.15 V *vs.* Ag/AgCl/ $AgCl_{sat}$).

From the $I = f(c_{AA})$ dependence, the unknown concentration of AA in the sample was determined by extrapolation ($c_{AA}$ =4.3 $10^{-3}$ M). Taking into account the dilution factor, 100.97 mg AA were found in a tablet, which is a very satisfactory result if compared to the content declared by the producer (100 mg AA / tablet).

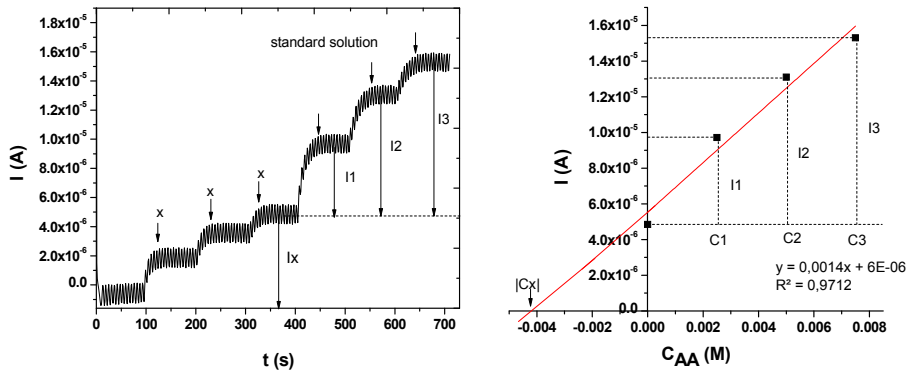


**Figure 5.** Standard addition method applied for determining AA concentration in a real sample (Propolis C). Experimental conditions: see Fig.4

## CONCLUSION

A new electrode based on synthetic mesoporous zeolite modified with Fe(III) incorporated in carbon paste was obtained and characterized. The modified electrodes presented good electrocatalytic effect toward ascorbic acid oxidation in neutral aqueous solution, at an overpotential with more than 500 mV lower than that observed on unmodified electrodes. The Fe13X-CPEs offer the advantages of easy fabrication and cleaning, fast response time, high sensitivity, a low background current and detection limit, which are suitable for routine determinations.

## EXPERIMENTAL SECTION

### Chemicals

The 13X type zeolite, $1Na_2O:1Al_2O_3:2.8\pm0.2\ SiO_2 \times H_2O$ (particle size, 3-5μ; pore diameter, 10 Å; specific surface area 548.69 $m^2/g$; bulk density 480.55 $kg/m^3$; Si/Al ratio 1.5) was purchased from Aldrich (Germany).

Ascorbic acid (AA) was purchased from Sigma (SUA), $K_2HPO_4 \cdot 2H_2O$ and $KH_2PO_4 \cdot H_2O$ were purchased from Merck (Darmstadt, Germany). All other reagents were of analytical grade and used as received.

The supporting electrolyte was a 0.1 M phosphate buffer solution. The pH was adjusted in the interval 3-7 using appropriate $H_3PO_4$ or NaOH solutions.

### Electrode preparation

The carbon paste was prepared by thoroughly mixing of 50 mg graphite powder with 60 μl paraffin oil (Fluka) until homogenization.

In parallel, a 0.01M $FeCl_3$ aqueous solution was purged with $N_2$ for 30 minutes. 1 g of NaY zeolite was lightly ground and immersed to 250 mL 0.01M $FeCl_3$ solution for 24 h. The modified zeolite was filtered, carefully washed with pH 2 HCl to remove occluded material and surface-adherent salt, and then washed with doubly distilled water till free of $Cl^-$ ions. Finally, the Fe(III) exchanged zeolite was dried in air.

For the preparation of the carbon paste electrode incorporating the modified zeolite (Fe13X-CPEs), 25 mg of the modified zeolite were mixed with 25 mg carbon paste and then incorporated in a cylindrical tube (3 mm inner diameter and 5 cm length). The electrode surface was finally polished on paper.

The preparation of Fe13X-CPEs was reproducible when the experimental conditions and variables were maintained constant during the preparation period. The current response of the electrodes did not change significantly by storing them in air for several days.

### Electrochemical measurements

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).

Batch amperometric measurements at different AA concentrations were carried out at an applied potential of 0.15 V *vs.* $Ag|AgCl/KCl_{sat}$, under magnetic stirring, using 0.1 M phosphate buffer solution (pH 7) as supporting electrolyte. The current-time data were collected using the above-mentioned electrochemical analyzer.

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