

Review article

New Electrodes Based On Garlic for the Inhibition of the Free Radicals Effects

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Abstract

A new electrode based on garlic is prepared to inhibit the effect of oxidative stress, often linked to the presence of an excess of free radicals. The electrode paste was prepared as a mixture of finely powdered of garlic together with graphite powder. The influence of variables such as the garlic loading and free radicals concentration was tested by Square Wave Voltammetry (SWV), Cyclic Voltammetry (CV) and Electrochemical Impedance Spectroscopy (EIS). The obtained results were found in good correlation with garlic reputation.

Keywords: Garlic; Oxidative Stress; SWV; CV; EIS; Modified Electrodes

Introduction

Oxidative stress is defined as an imbalance between the production of free radicals and the ability of the body to counteract or detoxify their harmful effects through neutralization by antioxidants. Free radicals play an essential role in the biochemical processes of living beings. They are continuously produced by the body's normal use of oxygen such as respiration and some cell mediated immune function. At high concentrations, free radicals generate oxidative stress, a deleterious process that can damage all cell structures [1-8]. Oxidative stress can develop of chronic and degenerative diseases such as cancer, arthritis, aging, autoimmune disorders, cardiovascular and neurodegenerative diseases. Antioxidant compounds in food are found to have a health protecting factor. Primary sources of naturally occurring antioxidants are whole grains, fruits and vegetables. Garlic (*Allium sativum*) is an herb. It is best known as a flavoring for food [9]. But over the years, garlic has been used as a medicine to prevent or treat a wide range of diseases and conditions. Garlic consists of more than 250 genera and 3700 species. The potential antioxidant properties of garlic are related to its phenolic and flavonoid fractions [10].

Several amperometric biosensors have already been proposed for antioxidant capacity determination [11-14]. Most of them are based on the amperometric detection of H₂O₂, resulting from the

catalyzed dismutation of superoxide radicals (O₂⁻) in presence of superoxide dismutase. In this work we prepared and characterized the garlic modified carbon-paste electrode, which successfully exploits the favorable mechanical and electrochemical properties of carbon-paste electrodes. Our work develops the electrochemical technology of the inhibition of effects of free radicals.

Experimental

Instrumentation and software

Square-wave voltammetry was performed with a voltalab potentiostat (model PGSTAT 100, Eco Chemie B.V., Utrecht, The Netherlands) driven by the general purpose electrochemical systems data processing software (voltalab master 4 software) connected to Pentium III computer run under Windows 98. The electrochemical cell contains a HAp- modified carbon paste working electrode, a platinum counter electrode and a saturated calomel reference electrode (SCE). The pH-meter (Radiometer Copenhagen, PHM210, Tacussel, French) was used for adjusting pH values.

Preparation of the modified electrode Garlic-CPE

Garlic-modified carbon-paste electrode was prepared according the following procedure [15-17]. The modified carbon-paste electrode was prepared by mixing the graphite powder with the garlic to give an appropriate ratio Garlic/CP. The mixture was grinding in amortar agate and then a portion of the resulting

composite material was housed in PTFE cylinder. The geometric surface area of the working electrode was 0.1256 cm². A bare of carbon vitreous inserted into carbon paste provided the electrical contact.

Results and discussion

The effect of the carbon paste composition in the voltammetric response of the electrode modified with Garlic was evaluated by cyclic voltammetry in 0.10 mol L⁻¹ NaCl media (Figure 1). The anodic peak current increased with the amount of garlic in the paste up to 30% (w/w). Beyond the anodic peak current decreased significantly, this probably occurs due to a decrease in the conductive area at the electrode surface (Figure 2). According by these results a carbon-paste composition of 30% (w/w) by weights was used in further experiments.

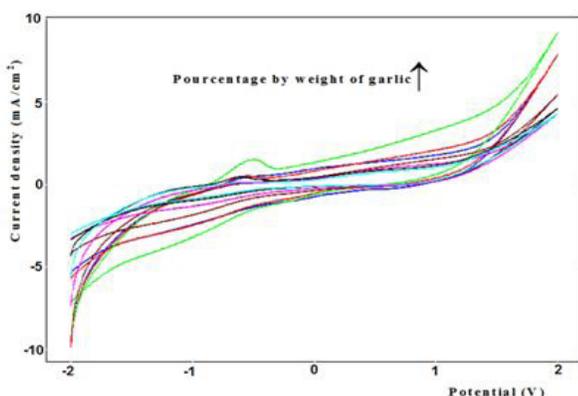


Figure 1: Cyclic voltammograms recorded at Garlic-CPE in 0.1 mol/L NaCl. Effect of Garlic content in carbon paste mixture.

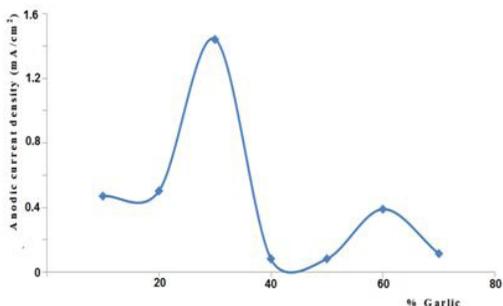


Figure 2: Influence of the content of Garlic in carbon-paste mixture % (w/w) on CV anodic peak currents density.

On the cyclic voltammogram recorded on the electrode (30% Garlic) - CPE (Figure 1), we notice the appearance of a well-defined anodic peak at about -0.3 V. This peak corresponds to the oxidation of garlic.

Calibration graph of H₂O₂

In this work we chose hydrogen peroxide (H₂O₂) as a free radical. The reduction of H₂O₂ was studied on a carbon paste

electrode (CPE) in 0.1M NaCl solution by SWV (Figure 3). The concentration range of H₂O₂ from 4.28.10⁻² mmol/L NaCl to 0.86 mmol/L was examined, firstly at CPE. The linear calibration plot (Figure 4) was obtained under optimal conditions. The regression straight line has the following equation:

$i_p = - 18.10^{-4} \times [H_2O_2] + 6.10^{-3}$, where i_p is the reduction current density of hydrogen peroxide expressed in mA/cm² and the concentration in mL/100ml NaCl.

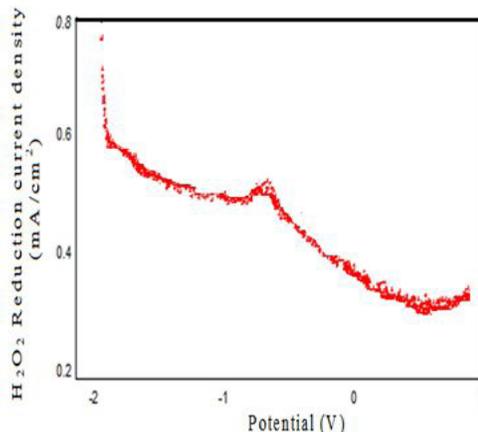


Figure 3: SWV recorded at CPE in 0.1 M NaCl containing 0.51 mmol/L of H₂O₂.

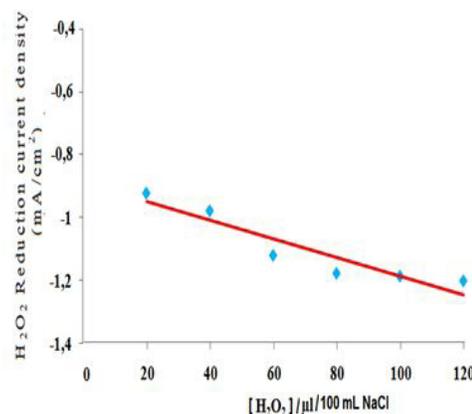
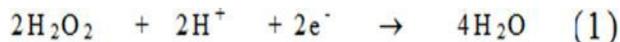


Figure 4: Influence of concentration of hydrogen peroxide on the reduction peaks intensity at CPE under the optimized conditions

Figure 5 shows the CVs recorded, respectively on the CPE (curve a) and in CPE modified by 30% of the garlic, in 0.1M NaCl solution. The CV recorded at CPE in 0.1M NaCl solution containing H₂O₂ shows clearly one reduction peak at about -0.3V, which corresponds to the following reaction:



When the CPE is replaced by the modified garlic / CP electrode, we can see clearly the disappearance of this reduction peak,

and thereafter the total stoppage of the reduction reaction of hydrogen peroxide (1). This leads us to conclude that the presence of the garlic on the matrix of the carbon paste electrode inhibits remarkably the effects of H_2O_2 .

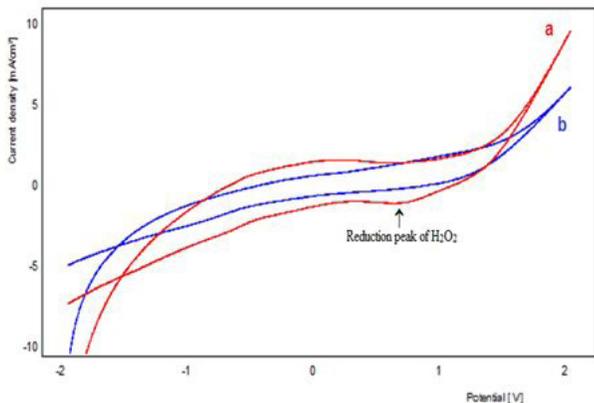


Figure 5: CV's recorded respectively, at a-CPE and b- 30% garlic/CPE in 0.1M NaCl solution containing H_2O_2 .

The same behavior was observed in SWV technique, where we can distinguish the disappearance of the reduction peak of H_2O_2 , when CPE is replaced by garlic / CPE (Figure 6).

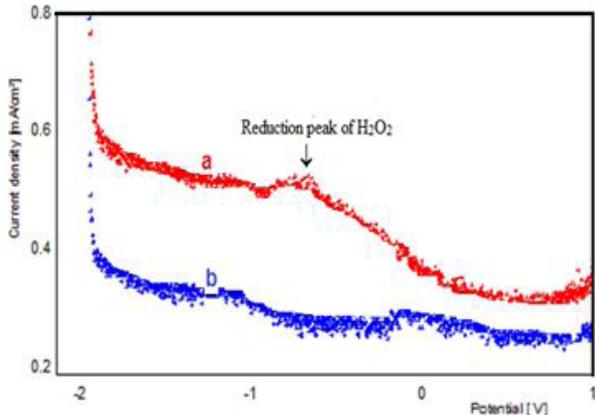


Figure 6: SWV's recorded respectively, at a-CPE and b- 30% garlic/CPE in 0.1M NaCl solution containing H_2O_2 .

The results of EIS tests are presented through Nyquist diagrams. These diagrams for the CPE (curve a) and garlic/CPE (curve b) surfaces in 0.1 M NaCl containing H_2O_2 are shown in Figure 7. When CPE is the working electrode, EIS spectra exhibit a half circle in the high-frequency region; it corresponds to the electrochemical reduction of the hydrogen peroxide. Further-

more, this data was changed when CPE is replaced by garlic/CPE, The half circle disappeared from the diagram, indicating that the reduction reaction of H_2O_2 is stopped.

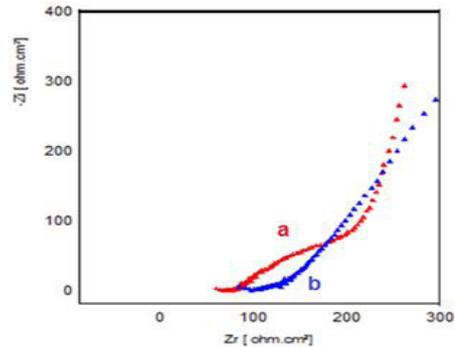


Figure 7: Impedance data recorded respectively on CPE (curve a) and garlic/CPE (curve b) in 0.1M NaCl containing H_2O_2 .

Figure 8 shows the evolution of the reduction current density of the H_2O_2 as a function of the concentration of the hydrogen peroxide, deduced from the SWV's recorded respectively, on CPE (curve b) and on garlic / CPE (curve a). The presence of the garlic in the matrix of the carbon paste, results in a remarkable drop in the H_2O_2 reduction current densities, which exceeds 80%.

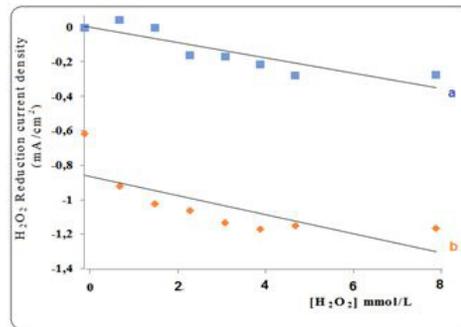


Figure 8: Influence of the hydrogen peroxide concentrations on the reduction peaks intensity, respectively, at a- Garlic/CPE and b- CPE in 0.1M NaCl.

The corresponding antioxidant capacity values (AOC), was calculated using the relation:

$$AOC = \frac{\text{Reduction } I_{H_2O_2} \text{ (CPE)} - \text{Reduction } I_{H_2O_2} \text{ (Garlic/CPE)}}{\text{Reduction } I_{H_2O_2} \text{ (CPE)}} \times 100$$

The results are illustrated by the following histogram:

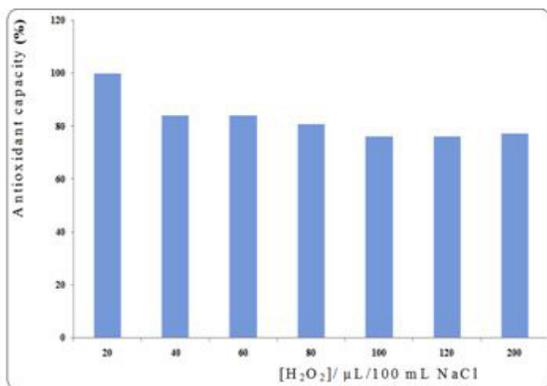


Figure 9: Evolution of the AOC percentage as function of the hydrogen peroxide concentration.

The antioxidant capacity of the garlic approaches 100%, indicating for the same occasion, that the prepared electrode (garlic / CPE) can totally inhibit the effects of the free radicals.

Conclusion

For a long time, garlic has been used as an additive in food in various cultures. Garlic is a natural medicine used to treat many diseases, is a powerful stimulant of the immune system. In this work, the garlic was used as a modifier of the carbon paste electrode to inhibit the reduction reaction of hydrogen peroxide often considered a powerful free radical. The composition of the electrode materials that gave the best result is 30% garlic and 70% carbon graphite. The antioxidant capacity of the garlic was evaluated, its value exceeding 80%, and its ability to inhibit the H₂O₂ reduction reaction may reach 100%.

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