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Nanostructured silver and platinum modified carbon fiber microelectrodes coated with nafion for H_2O_2 determination

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Abstract

Carbon fiber microelectrodes equipped with nanostructured metals (platinum and silver) and covered with a Nafion layer constitute sensitive H_2O_2 sensors. Metallic layers on carbon fibers were prepared by surfactant assisted electrodeposition. In the case of silver, the procedure leads to coating which is composed of porous, partially aggregated and crystalline deposits containing silver nanoparticles. The electrodeposition of platinum leads to carbon fiber decorated with clusters of platinum nanoparticles. After coating the electrodes with protective and antiinterference barrier made of Nafion, the sensing properties of the prepared microelectrodes towards hydrogen peroxide are investigated.

Keywords: Carbon fiber, microelectrode, platinum nanoparticles, silver nanoparticles, Nafion, amperometric sensor

Introduction

Carbon fiber electrodes represent an advantageous platform for amperometric sensors fabrication, since they combine microelectrode properties (i.e. enhanced diffusional transport of the analyte onto the electrode surface) with relatively high analytical current signals. Their disadvantage is, however, a slow charge transfer kinetics for some analytes requiring the modification of these electrodes.

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Electrodes containing platinum as an active material are frequently used to determine hydrogen peroxide in anodic region of potentials due to the relatively rapid electrode kinetics of hydrogen peroxide electrooxidation on platinum oxides (Hall et al.1998). The mechanism of hydrogen peroxide oxidation on platinum involves the adsorption of intermediate and therefore the dependence of limiting current (for the experiment with rotating platinum electrode) has the character of adsorption isotherm (Hall et al.1998). For this reason, the calibration curve for hydrogen peroxide on smooth platinum electrode deviates from linearity at H_2O_2 concentration as low as 5 $mmol{\cdot}dm^{-3}$. Nanostructuring of platinum enables to overcome this problem. A one approach to achieve nanostructuring of the electrode surface is the electrodeposition from the mixture of target metal salt and a suitable structure directing agent. This technique was first described by Evans et al (2002) who prepared platinized platinum electrode from the aqueous solution containing K_2PtCl_6 and octaethyleneglycol monohexadecyl ether and shown that the electrode enables determination of H_2O_2 over a wide concentration range upto 0.1 M.

Nanostructured silver electrodes have recently gained a great deal of interest as sensors for H_2O_2 amperometric determination in the cathodic region of potentials (e.g. Welch et al. 2005; Guascito et al. 2008). Cathodic regime is convenient especially for hydrogen peroxide determinations in biological matrices, since this potential region is usually free from interferences caused mainly by ascorbate and urate, often present in high quantities in biological samples, e.g. body fluids, tissue homogenates, cell lysates etc Kohen et al (2000); Hrbac et al (2000). In this contribution we used polyol – based nonionic surfactants Triton-X100 and Pluronic F127 as structure directing agents for coating carbon fiber microelectrodes with platinum and/or silver. We have found that Pluronic F127 is an effective structure directing agent for coating carbon fiber microelectrodes with silver. On the other hand, Triton-X100 gives optimum results for platinum coatings. In this contribution advantageous properties of silver and platinum material for H_2O_2 sensing are combined with advantages of carbon fiber microelectrodes, i.e. enhanced mass transfer by radial diffusion and relatively large surface area resulting in sufficiently high currents to be monitored using conventional potentiostats.

Materials and methods

For electrochemical measurements the CH Instruments 660C workstation was used in a three-electrode circuit with Pt wire as an auxilliary, Ag/AgCl as a reference and microelectrode sensor as a working electrode. Amperometry in stirred solution was used to test the microelectrode sensors. H_2O_2 aliquots were introduced into the cell using an autosampler. For testing the selectivities of the sensor, aliquots of selected interference compounds were introduced into the cell using Hamilton microsyringes.

Results and discussion

In our efforts to find optimum coating method, we tested a range of surfactants including Triton X100 and Pluronic F127 as additives into platinum and silver plating solutions. The electrodeposition of silver onto carbon fiber was performed from 0.08 M silver nitrate solution containing 25 % of Pluronic F127 at –300 mV vs. Ag / AgCl for 60 sec in quiescent solution. The electrodeposition of platinum onto carbon fiber was performed from 0.01 M K_2PtCl_6 solution containing 25 % of Triton X 100 at –200 mV vs. Ag / AgCl for 60 sec in quiescent solution. The amperograms recorded during the electrodeposition processes are shown in Fig 1 a,b. Fig 2 a,b and 3 a,b show the morphologies of metals electrodeposited onto carbon fibers. In the case of platinum the fiber is decorated with nanometer-sized platinum structures. Similar procedure for silver leads to coverage of the whole of carbon fiber with micron-sized silver crystallites. A closer look at the silver layer reveals that silver nanoparticles can be found attached to the crystallites.

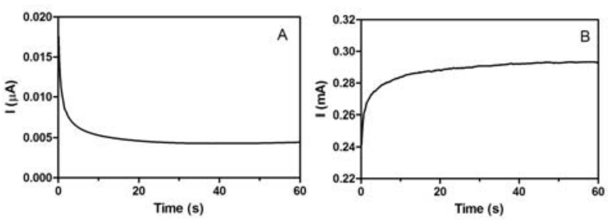

Figure 1: amperograms recorded during electrodeposition processes. A: platinum, deposition process proceeded at -200 mV vs. Ag/AgCl from the solution of K_2PtCl_6 (0.01 M) in the presence of Triton X100 (25 % (w/w)). B: silver, deposition from $AgNO_3$ (0.08 M) in the presence of Pluronic F127 (25 % (w/w))

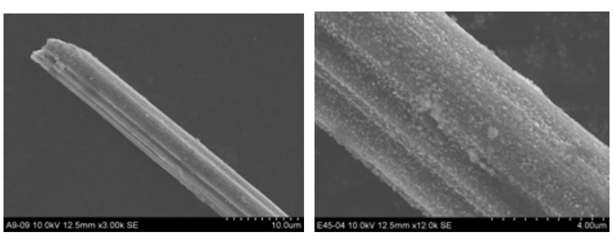

Figure 2: A,B SEM images of carbon fiber decorated with platinum particles

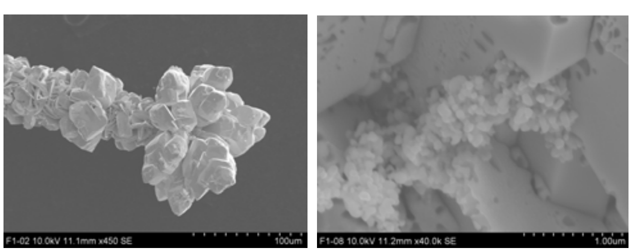

Figure 3: A,B SEM images of carbon fiber covered with silver layer

Coated carbon fibers were tested on their H_2O_2 sensing properties using amperometry at +700 mV vs. Ag/AgCl (platinum covered electrode) and –400 mV vs. Ag/AgCl (silver coated electrode). The resulting performances for electrodes prepared using deposition from solution of target metal salt without structure directing agent (A), Pluronic F127 (B) and Triton X100 (C) are shown in Fig 4 & Fig 5.

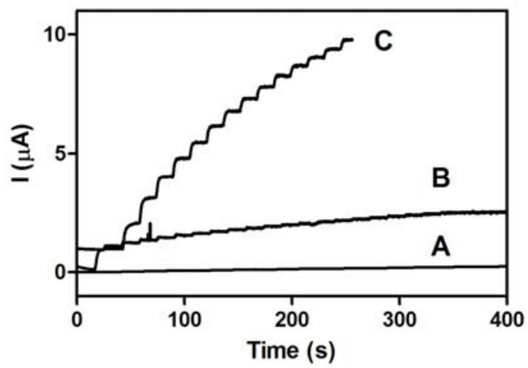

Figure 4: Amperometric curves of hydrogen peroxide for platinum coated carbon fiber electrode prepared prepared using deposition from solution of K_2PtCl_6 without structure directing agent (A), in the presence of Pluronic F127 (B) and Triton X100 (C). Every current step corresponds to the addition of H_2O_2 giving 1 mM increase in H_2O_2 concentration. The measurements were carried out in Britton-Robinson buffer (pH 7) at 700 mV vs. Ag/AgCl.

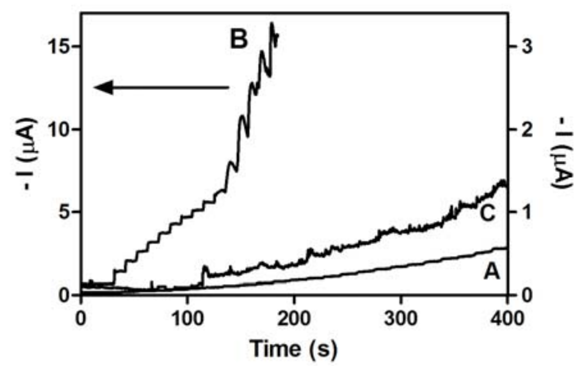

Figure 5: Amperometric curves of hydrogen peroxide for silver coated carbon fiber electrode prepared prepared using deposition from solution of $AgNO_3$ without structure directing agent (A), Pluronic F127 (B) and Triton X100 (C). Every current step corresponds to the addition of H_2O_2 giving 1 mM increase in H_2O_2 concentration. The measurements were carried out in Britton-Robinson buffer (pH 7) at -400 mV vs. Ag/AgCl.

The performance of silver coated electrode depends on chosen operational potential. Amperometric curves for H_2O_2 reduction are shown in Fig 6 for –400 and 0 mV. When the electrode is biased at 0 mV, broader usable concentration range is achieved, at the expense of some current sensitivity.

Long-term (tens of minutes) stabilities of H_2O_2 amperometric responses of both electrode types are rather poor and can be significantly improved by adding protective Nafion layer using a “dip-dry“ method (the electrodes were dipped into solution of Nafion and then dried at 80°C for 1h). In Fig 7 the response stability of platinum coated electrode is shown, the corresponding experiment for silver coated electrode is shown in Fig 8.

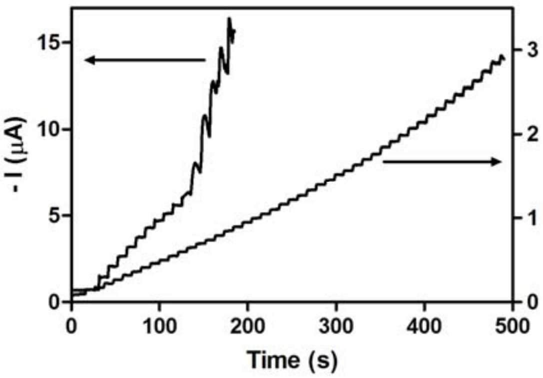

Figure 6: Amperometric response curves of carbon fiber microelectrodes covered with silver and Nafion at - 400 mV (left axis) and 0 mV (right axis) in stirred BR buffer (PH=7), each addition corresponded to 1 mM H_2O_2.

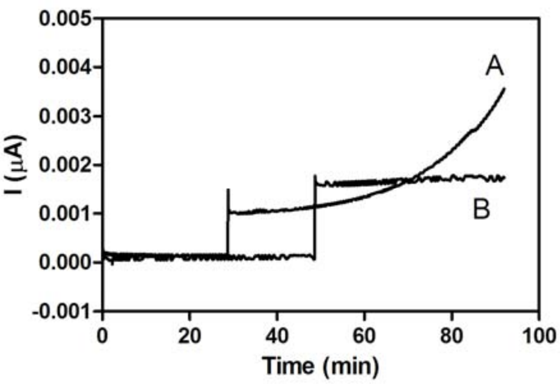

Figure 7: Amperometric response to 20 mM of hydrogen peroxide. A: platinized carbon fiber. B: Electrode prepared the same way equipped with protective layer of Nafion. The measurement was carried out in stirred Britton-Robinson buffer (pH 7) at 700 mV vs. Ag/AgCl.

Carbon fiber microelectrodes covered with silver and Nafion were tested for interferences from easily oxidizable species. Due to the protective layer of Nafion possessing well-known anion-repelling property, ascorbic acid and uric acid do not produce significant interferences. Fig 9,10. The selectivity towards paracetamol (acetaminophen) is lower for platinum-Nafion covered microelectrode.

Conclusion

We have shown that carbon fibers coated with platinum and/or silver and subsequently stabilized by Nafion layer can be used as sensors for hydrogen peroxide amperometric monitoring. The electrodeposition of metallic layers from solutions of platinum and silver salts proved itself to be a suitable coating method. Long-term stable and interference-free operation, as well as a broad range of concentrations, within which the response is linear was achived for both platinum and silver coated carbon fiber microelectrodes.

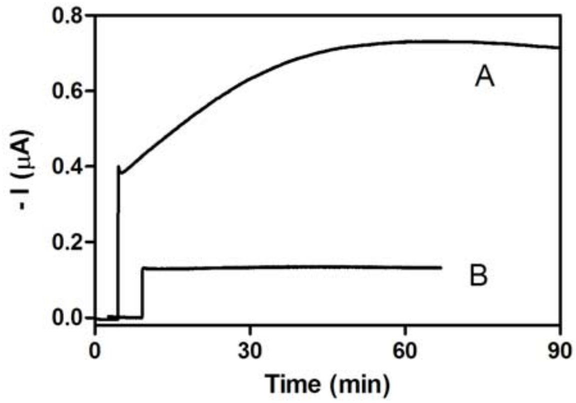

Figure 8: Amperometric response to 20 mM of hydrogen peroxide. A: silver coated carbon fiber. B: Electrode prepared the same way equipped with the protective layer of Nafion. The measurement was carried out in stirred Britton-Robinson buffer (pH 7) at 0 mV vs. Ag/AgCl.

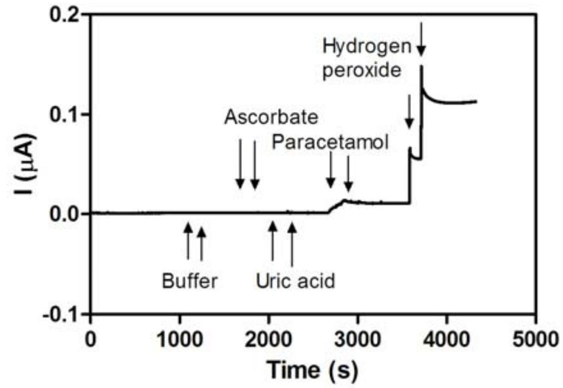

Figure 9: The response of platinum-Nafion coated microfiber to the additions of ascorbate, uric acid, acetaminophen and hydrogen peroxide (each addition indicated by arrow corresponded to 1.00 mM final concentration of each compound). BR buffer, pH=7.0, applied potential: 700 mV vs. Ag/AgCl.

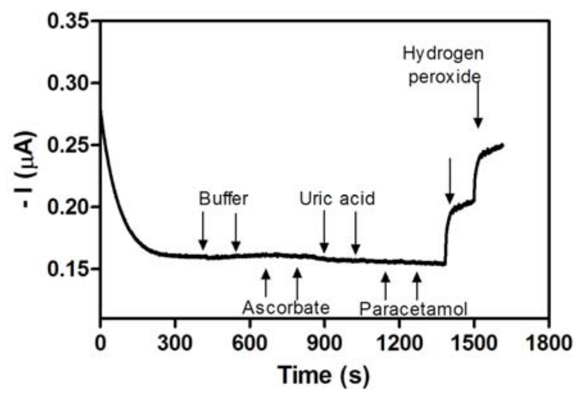

Figure 10: The response of silver-nafion coated microfiber to the additions of ascorbate, uric acid, acetaminophen and hydrogen peroxide (each addition indicated by arrow corresponded to 1.00 mM final concentration of each compound). BR buffer, pH=7.0, applied potential: 0 mV vs. Ag/AgCl.

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