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Silver-Nafion coated cylindrical carbon fiber microelectrode for amperometric monitoring of hydrogen peroxide heterogeneous catalytic decomposition

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ABSTRACT

Cylindrical carbon fiber microelectrode coated with a silver layer electrodeposited from silver nitrate solution containing Pluronic F127, a surface active agent, and also a Nafion layer prepared using a dip-dry method forms a sensitive, selective and stable amperometric hydrogen peroxide sensor, operating in the cathodic region of potential. The layer formed at the electrode is composed of porous, partially crystalline silver deposits with a significant fraction of attached silver nanoparticles. Using amperometry in stirred solution at 0 mV (vs. Ag/AgCl), the electrode is capable to monitor hydrogen peroxide over its wide concentration range (1×10^{-5} up to 0.1 M). The response of the electrode is sufficiently time-stable to enable the monitoring of hydrogen peroxide heterogeneous decomposition over manganese dioxide catalyst including the conditions where higher decomposition rates are observed, impossible to be monitored using batch titration.

1. Introduction

Electrodes containing silver as an active material have recently gained a great deal of interest as sensors for the cathodic determination of hydrogen peroxide by amperometry. Nanoparticles of silver, deposited on carbon surfaces either directly or embedded in various matrices have been used as active parts of most of these sensors. In an early study by Welch et al. [1] it was shown that the deposition of silver layer on a glassy carbon electrode followed by its partial stripping leads to the formation of silver nanoparticle-modified glassy carbon surface. The sensitivity of this electrode towards hydrogen peroxide reduction was demonstrated by series of cyclic voltammograms of hydrogen peroxide in millimolar concentration range. Guascito et al. [2] described the fabrication of a platinum electrode covered with a polyvinyalcohol layer loaded with silver nanoparticles and tested its amperometric response to hydrogen peroxide. The current response of freshly prepared electrode varied linearly from 45 μM to 6 mM (determined at −500 mV vs. Ag/AgCl), however, severe irregularities in current occur above 1 mM H_2O_2. In similar studies, poly (3,4-ethylenedioxythiophene) and mesoporous silica matrix have been successfully tested as a support for silver nanoparticles at −0.45 V vs. Ag/AgCl with detection limits of hydrogen peroxide 7 μM [3] and 12 μM ($S/N = 3$) [4], respectively. The linear ranges were up to 1.2 mM H_2O_2 for the first case and 48.5 μM to 0.97 M for the second case (broadest linear range published so far for silver-based sensor). In constructing a hydrogen peroxide sensor, Yang et al. [5] combined the electrocatalytical effect of silver nanoparticles with multi-walled carbon nanotubes. The sensor was characterized using differential pulse voltammetry and the obtained detection limit was 2×10^{-4} M H_2O_2 ($S/N = 3$), the response linear range was found to be up to 5 mM H_2O_2. The combination of silver nanoparticles with horseradish peroxidase supported by dendritic silica on gold electrode is another example of this approach [6]. The amperometric response of this sensor determined at −0.2 V vs. Ag/AgCl was linear from 3.3 μM to 9.4 mM H_2O_2. The fabrication of silver nanoparticle-modified electrode may, however, be a cumbersome procedure as it requires a number of steps i.e. the synthesis of nanoparticles, their purification, mixing with a suitable inert matrix, coating, curing etc. To simplify the preparation procedure of a silver electrode with a high surface area, Lian et al. [7] have roughened the bulk silver electrode by potential cycling between 0.3 and −0.3 V vs. Ag/AgCl in potassium chloride solution and demonstrated the resulting electrocatalytical activity towards hydrogen peroxide reduction. The detection limit of hydrogen peroxide, determined at −300 mV vs. Ag/AgCl), was found to be 6 μM ($S/N = 3$). The authors claimed that the linear

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range of H_2O_2 detection ranged from 10.0 μM to 22.5 mM, however, the amperometric curve presented in their paper is ending at 0.8 mM H_2O_2.

In this paper, we describe a new preparation procedure of a cylindrical carbon fiber electrode coated with nanosized silver particles and present its analytical application for the determination of hydrogen peroxide over extended H_2O_2 concentration range. Cylindrical microelectrodes in general and cylindrical carbon fiber microelectrodes in particular combine microelectrode properties (i.e. contribution of radial diffusion mass transfer to Faradayic current resulting in improved Faradayic to non-Faradayic current ratio) with relatively high currents, which make these electrodes well suited to amperometric measurements, namely due to lower sensitivity of the electrode response to irregularities in stirring compared to conventional millimeter-sized voltammetric electrodes [8]. Nanostructuring of an electrode surface is achieved by the electrodeposition of a high surface area film from a mixture of silver nitrate salt and Pluronic F127 as a structure directing agent. This technique was first described by Evans et al. [9], who prepared platinized platinum electrode by the electrodeposition of platinum layer on smooth platinum surface from the aqueous solution containing hexachloroplatinic acid and octaethylene glycol monohexadecyl ether. The surface active agent forms a hexagonal rod-like liquid crystalline phase, where the rods originate at the electrode surface and extend out towards the solution. After electrodeposition, which occurs only within the space between the rods and removal of the surfactant film by extensive washing, a high area honeycomb-like nanostructured platinum is formed. This high area platinum electrode was used as a sensor for anodic amperometric determination of hydrogen peroxide with broad linear range – up to 100 mM (the amperometric response on polished platinum electrode is linear only up to 5 mM). Similar results were obtained by Park et al. [10] when octaethylene glycol monohexadecyl ether was replaced by TritonX-100.

The same approach, applied by us to carbon fiber coating with silver yields heterogeneous silver layer containing micrometer-sized porous crystalline deposits with a significant amount of relatively monodisperse silver nanoparticles attached. The formed silver layer exhibits favourable electrocatalytical properties towards hydrogen peroxide reduction. The microelectrode was successfully used to monitor the kinetics of heterogeneous catalytic decomposition of hydrogen peroxide by manganese oxide at relatively high hydrogen peroxide concentration level (tens of millimoles per liter).

2. Experimental

2.1. Reagents

Silver nitrate, Pluronic F127, hydrogen peroxide 30% aqueous solution, ascorbic acid, uric acid (2,6,8-trihydroxypurine) and acetaminophen (4-acetamidophenol) were purchased from Sigma–Aldrich. Nafion 117, (5% solution in lower aliphatic alcohols and water, cat. No. 70160) was obtained from Fluka. Electrolytic manganese dioxide (β-MnO_2, BET area = 30 m^2/g) was purchased from Lachema (Brno, Czech Republic). All chemicals were of reagent grade and were used as received without further purification. All solutions were prepared in de-ionized water (Millipore). Britton–Robinson (B–R) buffers, in which the majority of measurements was carried out, contained 0.04 M boric acid (H_3BO_3), 0.04 M phosphoric acid (H_3PO_4) and 0.04 M acetic acid, the desired pH values were adjusted with 0.2 M NaOH.

2.2. Instruments

Electrochemical measurements were performed using CH-Instruments Model 660C electrochemical workstation in a three-electrode configuration. Ag/AgCl was used as a reference electrode (CHI111, CH Instruments, Inc.), platinum wire served as an auxiliary and carbon fiber microelectrodes as working electrodes. Scanning electron microscopy images (SEM) were obtained on Hitachi SU-6600 (FEG, SE image resolution 1.2 nm at 30 kV). The pictures were collected with a high voltage of 10 kV at working distance ranging from 10 mm to 22 mm. Sample material was fixed on carbon conductive discs. No coating method was used.

2.3. Microelectrode fabrication

Carbon fiber (diameter 7 μm, Ten Cate Advanced Composites, Amsterdam, Netherlands) was glued using conductive silver epoxy (Epotek H20E, Polytec, Germany) onto a copper wire; the junction was then cured at 170 °C for 10 min. The fiber with copper contact attached was fitted into the glass capillary, about 5 mm of the fiber was left protruding from its contracted end. Both ends of the capillary were sealed using epoxy resin (CHS Epoxy 1200, Sindat Pilsen, Czech Republic). Prior to use, the protruding fiber was cut to the length of approx. 1 mm by lancet and the fiber end of the electrode was briefly sonicated in dichloromethane in order to remove grease. Silver was then electrochemically deposited by applying a reduction potential of −300 mV (vs. Ag/AgCl) to a carbon fiber microelectrode in a 0.08 M silver nitrate solution containing 25% (w/w) Pluronic F127 for 60 s. After washing the electrode by copious amount of water the electrode was allowed to dry in the air and then coated with Nafion layer produced from 5% Nafion solution using a “dip-dry” method.

2.4. Sensor testing

Amperometry at a constant potential of −0.4 V or 0 V vs. Ag/AgCl in 25 mL of B–R buffer was used to characterize the microelectrode sensors. In these experiments, the buffer was stirred using a magnetic stirrer rotating at approximately 300 rpm. Background current obtained was allowed to decay until a stable baseline was achieved (usually approximately 1–5 min). Hydrogen peroxide aliquots were introduced into the cell using an auto sampler. For testing the selectivity of the sensor, aliquots of selected interference compounds (ascorbic acid, uric acid and paracetamol) were introduced into the cell using Hamilton microsyringes. All measurements were performed at room temperature (25 °C).

3. Results and discussion

3.1. Electrodeposition of silver onto carbon microfiber and coating with Nafion

Electrodes made of carbon in its various forms generally exhibit slow charge transfer kinetics for hydrogen peroxide reduction, therefore high overpotentials are required, in many cases oxygen reduction precedes the onset of hydrogen peroxide reduction wave. To overcome this obstacle, carbon surfaces are modified by various electrocatalytical layers in the case of solid carbon electrodes, or bulk modification is used for carbon paste, screen printed and composite electrodes. As discussed in Section 1, silver represents a powerful electrocatalyst of hydrogen peroxide reduction, especially when present in the form of silver nanoparticles. Carbon fiber is almost insensitive to hydrogen peroxide when employed as amperometric sensor. The carbon fiber microelectrodes were therefore equipped by electrochemically deposited silver layer by applying a reduction potential of −300 mV (vs. Ag/AgCl) for 60 s in a 0.08 M silver nitrate solution eventually containing surfactant. A range of surfactants such as SDS, TWEEN 40, Triton X-100, octaethylene glycol monohexadecyl ether and Pluronic F127 was tested in order to find an optimum structure tuning agent. The electrodes

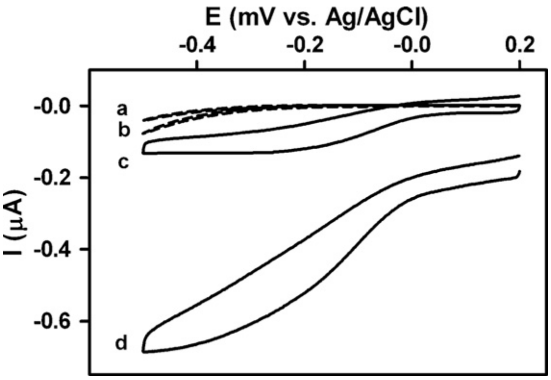

Fig. 1. Cyclic voltammograms of hydrogen peroxide (c = 5 mM, curves b and d) and associated background voltammograms (a and c) of air-saturated B–R buffer, pH = 7. Bare carbon fiber (dashed line) and silver coated fiber, prepared by electrodeposition from $AgNO_3$ solution (full line). Scan rate: 50 mV/s.

were characterized by cyclic voltammetry and constant potential amperometry in stirred solution. Representative cyclic voltammograms of hydrogen peroxide in air-saturated B–R buffer, pH = 7.0 along with the voltammograms recorded in air saturated B–R buffer without H_2O_2 are shown in Figs. 1 and 2.

A negligible response of plain carbon fiber microelectrode towards H_2O_2 reduction (Fig. 1, traces a and b) is observed, as only the onset of hydrogen peroxide reduction peak at ca. −300 mV is traceable on voltammogram 1b. The electroreduction of hydrogen peroxide occurs on all silver coated microelectrodes, the shapes of voltammograms (waves rather than peaks) indicate the H_2O_2 reduction current is governed by radial diffusion mode of transport of the electroactive substance into the electrode surface. The heights of H_2O_2 waves depend on the composition of silver plating solution (Fig. 2). The highest electrocatalytical actions towards H_2O_2 reduction have the microelectrodes prepared by using Pluronic F127 as an additive into the silver plating solution. For all silver covered microelectrodes, a background voltammetric response attributable to the reduction of dissolved oxygen is observable. The oxygen reduction occurs is shifted to slightly more negative (ca. 50 mV) potentials compared to the reduction of H_2O_2. Amperometric curves of hydrogen peroxide reduction on electrodes coated with silver layers prepared as mentioned above determined at −400 mV vs. Ag/AgCl are shown in Fig. 3.

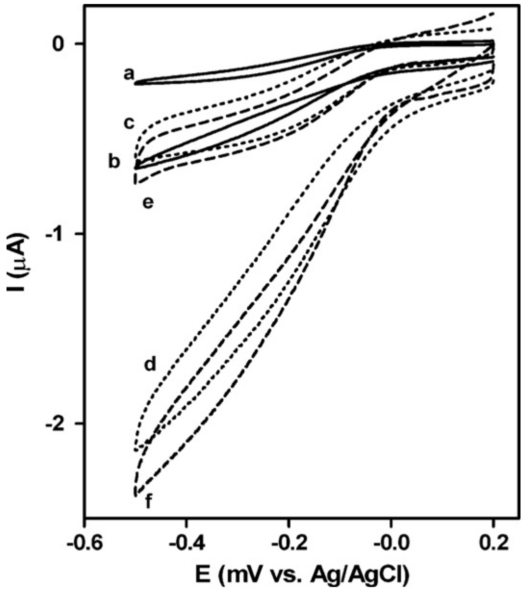

Fig. 2. Cyclic voltammograms of hydrogen peroxide (c = 5 mM, curves b, d, f) and associated background voltammograms (a, c, e) of air-saturated B–R buffer, pH = 7. The voltammograms were obtained on silver coated fibers, prepared by electrodeposition from $AgNO_3$ solution in the presence of TritonX100 (full line), Pluronic F127 (dashed line) and Pluronic F127 with additional coating with Nafion (dotted line). Scan rate: 50 mV/s.

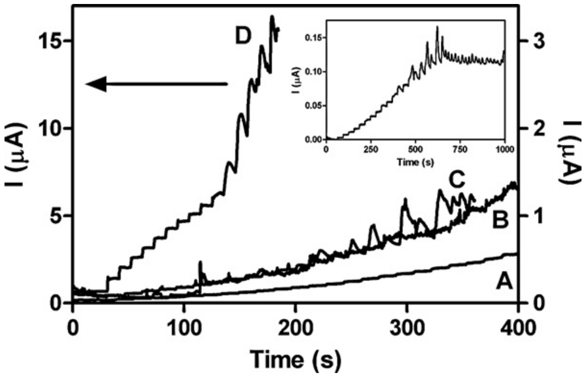

Fig. 3. Amperometric response curves of carbon fiber microelectrodes covered with silver layer deposited from solutions of $AgNO_3$ in the absence of surfactant (A) and in the presence of surfactants such as Triton X-100 (B), octaethylene glycol monohexadecyl ether (C), TWEEN 40 (inset) and Pluronic F 127 (D, left axis). The applied potential was −400 mV vs. Ag/AgCl and measurements were performed in stirred B–R buffer, pH = 7. Each addition corresponded to 1.0 mM H_2O_2.

Similar to the results of cyclic voltammetry investigations, highest amperometric responses were achieved with Pluronic F127 and therefore, next experiments were done using this surfactant. Silver coatings with the best performances were achieved when only silver nitrate and Pluronic F127 were present in the plating solution. The optimum concentrations for silver nitrate and Pluronic F127 were 0.08 M and 25% w/w, respectively. Increasing the ionic strength of the solution by the addition of an inert electrolyte (potassium nitrate) substantially decreased the final electrode performance (i.e. sensitivity and response linearity, data not shown). Furthermore, it proved beneficial to allow the plating solution to undergo aging process. For this purpose, the prepared plating solution was allowed to age for 20 days at ambient temperature. This resulted in ca. twofold increase in the electrode sensitivity towards hydrogen peroxide reduction (data not shown). We suppose that Pluronic F127 behaves as a weak reducing agent forming seeding nanoparticles, which catalyze subsequent electroreduction. The formation of ultra small (3 nm, mean size) silver nanoparticles, enlarging towards 15 nm after 5 days was observed by Lee et al. for $AgNO_3$ solution in Triton X-100 hexagonal phase [11]. Both Triton X-100 and Pluronic F127 molecules contain free hydroxyl groups, capable to reduce $AgNO_3$. Despite similarities in Triton X-100 and Pluronic F127 chemical structures, the performances of microelectrodes covered with silver layer deposited from Pluronic F127 are much better. This may be due to difference in morphologies of microheterogeneous domains between Pluronic F127 and Triton X-100. While Triton X-100 forms hexagonal liquid crystalline phase in concentrations in the range of 30–50% (w/w) and temperatures below 30 °C [12], solutions of Pluronic F127 above concentrations of 20% (w/w) exhibit well known anomalous behavior of being liquid at temperatures below 15 °C and gel at higher temperatures [13]. The formation of thermoreversible gel is associated with the transformation of the cubic structure of closely packed Pluronic F127 micelles into hexagonal-packed cylindrical micelles. Due to the fact, that the plating solution containing 25% (w/w) of Pluronic F127 and 0.08 M $AgNO_3$ is liquid at room temperature (25 °C), we suppose that silver ions can stabilize the cubic micellar structure which is unique for Pluronic F127. The electrodeposition of silver onto carbon fiber was performed by constant potential electrolysis (60 s at −300 mV vs. Ag/AgCl) in quiescent plating

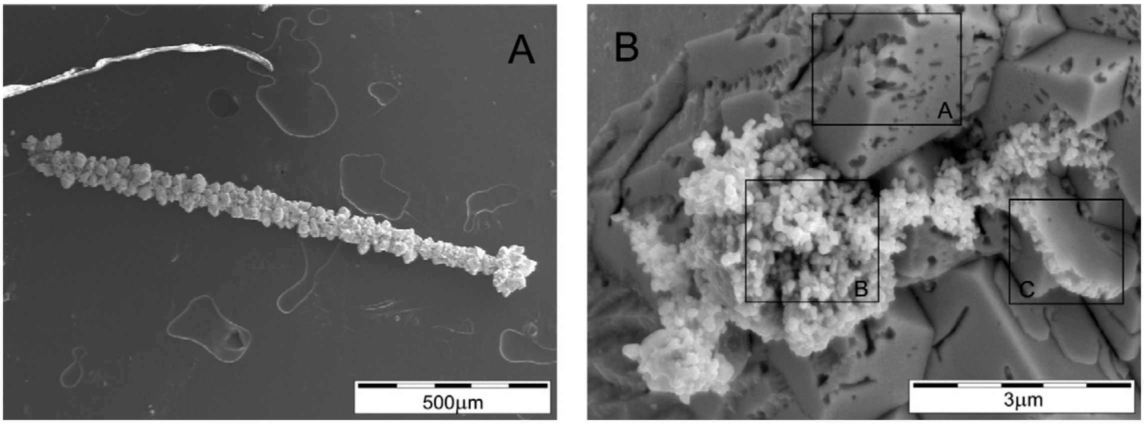

Fig. 4. (A) SEM picture of silver coated carbon fiber electrode. The carbon fiber is covered with silver crystallites of ca. 20 μm size. (B) SEM picture of silver coated carbon fiber electrode A. A closer look at the silver layer reveals that crystallites contain pores (area A) and spherical silver nanoparticles with diameters of about 100 nm (area B). At some parts of the silver layer (area C) it is obvious that silver crystallites are in fact the ordered assemblies built from the above mentioned nanoparticles.

solution. This procedure gave optimum and well reproducible results. The SEM image of the resulting silver coating is shown in Fig. 4.

Fig. 4A represents a general view of silver-coated carbon fiber. Notably, the fiber is covered with silver crystallites of ca. 20 μm size. A closer look at the silver layer (Fig. 4B) reveals that crystallites contain pores (area A) and spherical silver nanoparticles with diameters of about 100 nm (area B). At some parts of the silver layer, where crystals are probably fractured, it is obvious that silver crystallites are in fact the ordered assemblies built from the above mentioned nanoparticles (area C). After the carbon fiber was covered with silver layer, the electrode was coated by Nafion using a dip-dry method and then cured at 40 °C for 1 h. Nafion layer aids to mechanical stability of the coated fiber and contributes to response stability and selectivity properties of the sensor.

3.2. Hydrogen peroxide monitoring using silver coated carbon fiber electrode

Constant potential amperometry in stirred solution, which we used for testing the practical usability of our silver based sensor for hydrogen peroxide determination, requires a high stability of the sensor parameters, especially if long-term measurements are to be performed and their repetition is required. There are two attractive application areas in which amperometric hydrogen peroxide sensor can be targeted. Firstly, it is utilized in design of many oxidase-based biosensors. For this purpose, sensors working in the cathodic region of potentials have an inherent advantage of their insensitivity to easily oxidisable compounds (e.g. ascorbic acid, uric acid, polyphenols etc.), often present in high quantities in biological matrices. Secondly, amperometric sensing represents an attractive alternative to titration based methods for monitoring the kinetics of hydrogen peroxide catalytical decomposition. Sensors, suitable for the above mentioned kinetic measurements, must possess broad linear concentration range for hydrogen peroxide (tens of millimoles per liter) and high response stability (hours). As mentioned in the Introduction of this paper, these requirements are not met by most of the silver-based sensors published in the literature so far [1–7]. We have found that problems with response stability, linearity and limited usable concentration range of silver based sensors can be overcome by coating the sensor surface with Nafion and working in the less cathodic potential than optimum one, at the expense of sensor's current sensitivity. These improvements are documented in Fig. 5, which shows the amperometric measurements performed at pH = 7 in stirred solution with silver-Nafion coated carbon fiber electrode biased at 0 mV vs. Ag/AgCl and the response of the same electrode at −400 mV for comparison. At both potentials, the detection limits for H_2O_2 at $S/N = 3$ were in the range of 5 ± 2 μA ($N_{\text{electrodes}} = 5$, not shown), the current sensitivities for H_2O_2 are approx. three times lower at 0 V vs. Ag/AgCl. The response time of the sensors are <10 s, intraelectrode reproducibility is <3%, determined by repeated ($N = 5$) measurements of 1 mM H_2O_2. The electrode to electrode reproducibility is ±30 %, this parameter is, however, affected by the uniformity of the lengths of individual carbon fibers. The working potential of 0 mV vs. Ag/AgCl was chosen with respect to the fact that oxygen reduction does not interfere significantly with H_2O_2 determination at this potential. This process would complicate the application of the electrode for monitoring of H_2O_2 catalytic decomposition on MnO_2 described further in this manuscript. However, the catalytic decomposition of hydrogen peroxide by silver to water and oxygen is probably responsible for the change in the slope of the calibration curve at higher (>30 mM) hydrogen peroxide concentrations (i.e. the upright curvature of the amperograms in Fig. 5). The process of silver catalysed H_2O_2 splitting to water and oxygen was suggested in [1] to explain a shoulder in H_2O_2 voltammogram on silver nanoparticle modified glassy carbon electrode. The effect of Nafion layer on the sensor response stability is shown in Fig. 6, in which amperograms recorded at 0 V vs. Ag/AgCl within the period

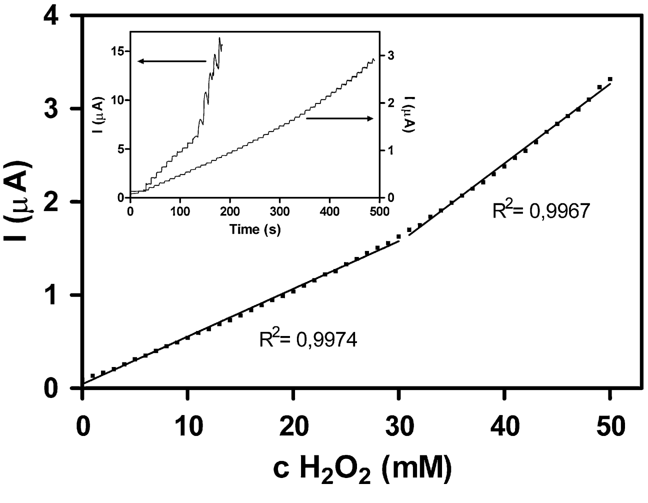

Fig. 5. Calibration curves for hydrogen peroxide determination on silver coated carbon fiber electrode. Inset: actual amperometric response curves determined in stirred B–R buffer, pH = 7. Each addition corresponded to 1.00 mM H_2O_2. Applied potential: 0 mV (right axis) and −400 mV vs. Ag/AgCl (left axis).

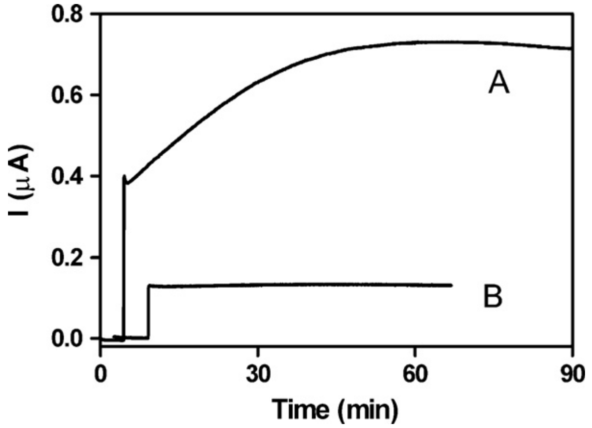

Fig. 6. Amperometric responses to addition of 20 mM hydrogen peroxide on bare silver coated carbon fiber microelectrode (A) and electrode stabilized with additional Nafion layer (B). The measurements were performed in stirred B–R buffer, pH = 7. Applied potential: 0 mV vs. Ag/AgCl.

of ca. 1 h are presented for two silver coated electrodes – bare and equipped with Nafion layer.

In addition to stabilizing effect on long-term amperometric response the Nafion serves as a protective coating in the process of monitoring of hydrogen peroxide heterogeneous catalytical decomposition. Without protective layer the catalyst particles would block the sensing surface of the sensor and alter its sensing properties. Nafion layer also aids to anti-interference properties of silver-based microelectrodes due to its well-known ion exchange property. This can be illustrated by the observation that ascorbic acid, uric acid and acetaminophen do not cause significant interferences despite the potential employed (0 mV vs. Ag/AgCl) is less cathodic than the value of −400 mV vs. Ag/AgCl used by most of the authors working in the field, Fig. 7. A set of calibration curves for hydrogen peroxide measured amperometrically over a wide pH range (pH 4–12) determined at 0 mV vs. Ag/AgCl is shown in Fig. 8. An increase in the sensor sensitivity with increasing pH is an advantageous feature of silver coated electrodes over widely used Prussian Blue and/or ferric oxide based hydrogen peroxide sensors [14]. These electrodes also work in the cathodic region of potentials, their sensitivities, however, decrease with increasing pH.

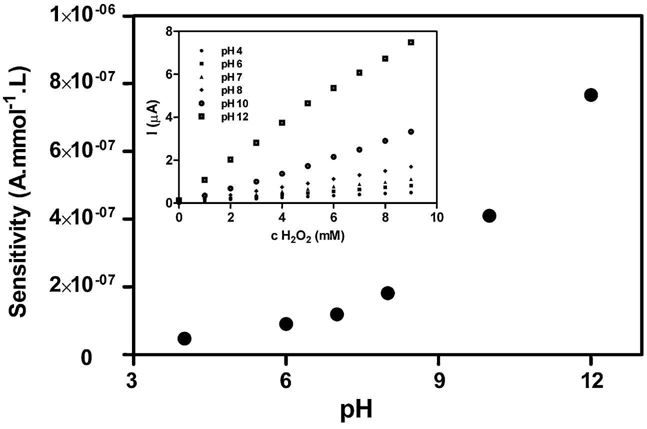

Fig. 7. The response of silver-Nafion coated microfiber to the additions of ascorbate, uric acid, acetaminophen and hydrogen peroxide (each addition indicated by arrow corresponded to 1.00 mM final concentration of each compound). B–R buffer, pH = 7.0, applied potential: 0 mV vs. Ag/AgCl.

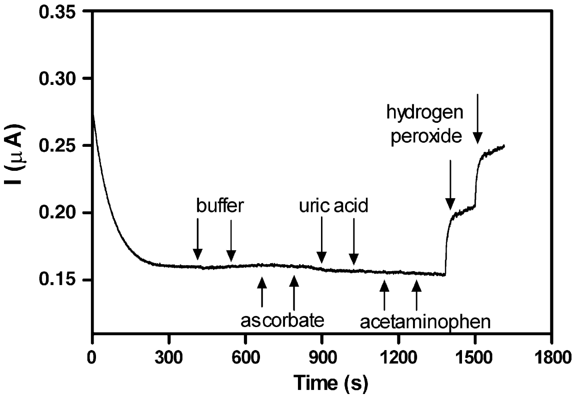

Fig. 8. pH dependence of silver coated carbon fiber electrode sensitivity for hydrogen peroxide determination. Y-axis data correspond to slopes of hydrogen peroxide calibration curves determined in the concentration range of 0–9.00 mM. Inset: hydrogen peroxide calibration curves at various pH values. All measurements were performed at a single electrode in stirred B–R buffers of individual pH values at 0 mV vs. Ag/AgCl.

3.3. Amperometric monitoring of hydrogen peroxide decomposition by manganese dioxide

Hydrogen peroxide heterogeneous catalytical decomposition is intensely researched in connection to the degradation of organic pollutants in wastewaters and contaminated soils [15,16]. During this process a highly reactive hydroxyl radical ($HO^\bullet$) is formed which is able to decompose a wide range of organic pollutants, including dyes and even highly biotoxic aromatic compounds [17]. To study hydrogen peroxide decompositions over heterogeneous catalysts, permanganate titration is used to monitor hydrogen peroxide consumption (in this case, concentration of hydrogen peroxide and amount of catalyst used are chosen so that the reaction is completed within tens of minutes to few hours). If faster kinetics are to be monitored, i.e. higher amounts of catalysts and hydrogen peroxide are employed, the time dependent measurement of oxygen volume evolved during the course of the decomposition reaction is usually done. However, this methodology usually requires high concentrations of hydrogen peroxide (moles per liter) in order to obtain measurable quantity of oxygen.

In our studies, we have used commercial β-manganese dioxide as a model catalyst to test our silver coated carbon fiber microelectrode due to the fact that manganese oxidic materials are among the best heterogeneous hydrogen peroxide catalysts. Hydrogen peroxide decomposition over manganese dioxide based catalysts obeys pseudo-first order kinetics in most cases [18]. If significant deviations are found, or more rigorous treatment is necessary, kinetic models involving adsorption are used, e.g. the Langmuir–Hinshelwood model [19]. The capability of our silver-Nafion electrode to monitor hydrogen peroxide concentration in the presence of manganese dioxide has been confirmed by recording the electrode response after repeated additions of hydrogen peroxide into the reaction mixture (Fig. 9). After separation of the amperogram into individual kinetic curves (first 15–20 data points obtained immediately after each H_2O_2 addition were discarded) the obtained data were statistically treated using the formalism of first-order kinetics. The rate constant of hydrogen peroxide decomposition, determined from this experiment was $k_{obs} = 0.030\ s^{-1}$ with SD = 0.00252.

Fig. 10 shows amperograms (solid lines) reflecting hydrogen peroxide decomposition kinetics over various amounts of manganese dioxide. In parallel experiments, the decomposition reactions were monitored using permanganate titration (Fig. 10, points). A reasonable agreement in pseudo-first order rate con-

Table 1
Observed pseudo first-order (k_{obs}) and second order rate constants k_{MnO_2} for hydrogen peroxide decomposition on manganese dioxide.

C_{MnO_2} (g/L)	$C_{H_2O_2}/C_{MnO_2}$	k_{obs} (min^{-1}) titration	k_{MnO_2} (L mol^{-1} min^{-1})	k_{obs} (min^{-1}) amperometry	k_{MnO_2} (L mol^{-1} min^{-1})
0.125	14	0.0048	3.34	0.0050	3.48
0.5	3.5	0.0238	4.14	0.0245	4.26
1.25	1.4	0.1038	7.22	0.0981	6.82
2.5	0.7			0.4319	15.02
5	0.35			0.9252	16.09
10	0.17			4.13	35.91

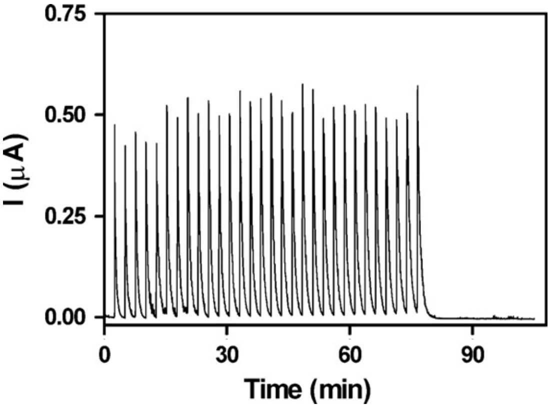

Fig. 9. Electrode response after repeated ($N = 30$) additions of hydrogen peroxide into stirred B–R buffer, pH = 7 containing 7.5 g/l MnO_2. Each addition corresponded to 20.00 mM H_2O_2. Applied potential: 0 mV vs. Ag/AgCl.

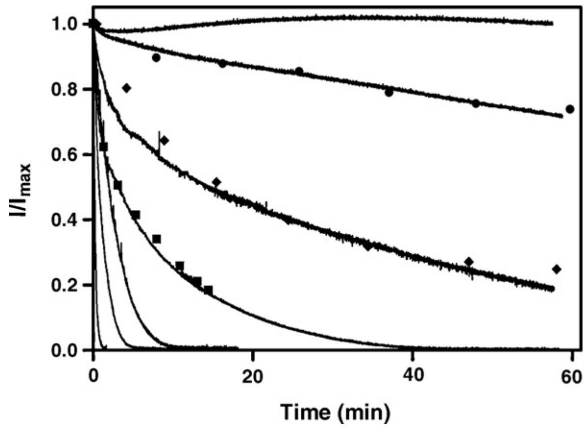

Fig. 10. Set of kinetic curves of hydrogen peroxide decomposition over different amounts of manganese dioxide. B–R buffer, pH = 7.0, 20.00 mM H_2O_2, 0, 0.125, 0.5, 1.25, 2.5, 5 and 10 g MnO_2/l (top to bottom). Solid lines: normalized amperometric curves determined at 0 mV vs. Ag/AgCl, points: H_2O_2 concentrations determined by manganometric titration relative to H_2O_2 initial concentration.

stants was found between the results of amperometry and titrimetry. Moreover, as confirmed experimentally, amperometry provides a distinctive advantages in terms of working with higher amounts of MnO_2 and consequently higher decomposition rates, which are difficult to be monitored using batch titration. The observed pseudo-first order and second order rate constants are summarized in Table 1. The results are characterized by an increase in values of second order rate constants with increasing amount of manganese dioxide, following the same trend as was observed in [18].

4. Conclusions

We have shown that carbon fiber coated with a silver layer electrodeposited from silver nitrate/Pluronic F127 solution and subsequently stabilized by Nafion layer can be used as sensor for long-term hydrogen peroxide amperometric monitoring. Favourable properties of these modified electrodes, namely response stability, broad linear range and mechanical stability make these electrodes suitable for monitoring the kinetics of hydrogen peroxide decomposition over heterogeneous catalysts. The results indicate that electrochemical monitoring represents a reliable alternative to titration method. Furthermore, it enables to work under the conditions where higher decomposition rates are observed, impossible to be monitored using batch titration.

Acknowledgement

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