VILNIUS UNIVERSITY
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AMPEROMETRIC RESPONSES OF SOME BIOSENSOR-RELATED ANALYTES AT ELECTRODES COATED WITH SEMIPERMEABLE POLYMER LAYERS: A COMPARATIVE STUDY

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VILNIAUS UNIVERSITETAS
FIZINIŲ IR TECHNOLOGIJOS MOKSLŲ CENTRO
CHEMIJOS INSTITUTAS

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MODIFIKUOTŲ ELEKTRODŲ ELEKTROCHEMINIO ATSAKO Į BIOLOGIŠKAI SVARBIŲ ANALIČIŲ PALYGINAMASIS TYRIMAS

Daktaro disertacijos santrauka

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CONTENT

INTRODUCTION

Sensors are essential components for all measurement and control systems. Sensors are classified according to the measured parameter: they are physical, chemical, biological.

The measurands in physical sensors include temperature, voltage, power, pressure, bias, position, speed, acceleration, optical radiation flux, density and electromagnetic fields. Temperature sensors (primary measurement parameter is the temperature) are very important in many control, environmental control systems. Several change mechanisms are required for temperature settings. The most commonly used electrical signal generating temperature sensors are thermocouples, thermistors and resistance measuring thermometers.

The measurands in chemical sensors include the concentration of ions, atomic weight, reaction speed, oxidation potential and gas concentration. The examples of chemical sensors are ion selective electrodes and gas chromatographs. Ion selective electrodes are used for the determination of specific ion-ion concentration in the solution. The membrane material is used for selective generation of the potential that depends on the concentration of determinable ions.

The measurand in biosensors is an amount of biologically generated material produced, such as antibodies, metabolites, hormones and enzymes. Biosensors are particularly important due to the high selectivity of biological reactions. The highest class of biosensors is enzymatic biosensors. Several signal modems can be used during the development of these biosensors. According to this, the biosensors can be divided into optical, gravimetric and electrochemical. Electrochemical sensors can be divided into two broad categories: potentiometric sensors for voltage measurement, and amperometric sensors for the measurement of electrical current. Both types of sensors comprise of at least two electrodes separated by a seal from the ion-conductive solution or solid electrolyte.

THE AIM AND OBJECTIVES OF THE WORK

The aim of the work

To carry out a comparative study of biologically important analytes on the electrodes modified with polymer layers.

Objectives of the work:

1. To choose similar conditions for the research of electroconductive polymers.

2. To examine and compare the permeability of inter-biologically important analytes through the precipitated layers on the electrode in the amperometric systems.

3. To compare the permeability of analytes through electrochemically polymerized and precipitated layers from the solution.

SCIENTIFIC NOVELTY OF THE WORK AND DEFENSIVE STATEMENTS

Scientific novelty of the work:

The electrochemical or chemical precipitation of single substance are usually described in scientific articles and studies; further research in different systems, solutions and conditions have been carried out as well. For my work I chose several substances which I provided with similar research conditions at the same operating potential. My main task was: to investigate and carry out a comparative study of selected substances having chosen similar conditions for electrochemical precipitation.

Defensive statements of the work:

1. The thickness of PANI, polypyrrole layer depends on the length of electropolymerization.

2. Electrooxidation of ascorbic acid on PANI electrode in neutral solution is of autocatalytic nature: loosened protons during its process increase the electroconductivity of PANI, and the subsequent anodic oxidation of ascorbic acid is already catalyzed by PANI itself.

3. Ascorbic acid molecular diffusion takes place without any hindrance.

4. Nafion layer coat is characterized by a high efficiency.

5. POPD layer is characterized by a relatively low conductivity.

1. EXPERIMENTAL TECHNIQUES

1.1. Reagents and electrodes

For the preparation of the solution 0.1 M pyrrole solution, poly (o-phenylenediamine), aniline, pyrrole, 3% hydrogen peroxide, ascorbic acid, paracetamol (was purchased in a pharmacy), and especially pure H_2SO_4, KCl, $NaH_2PO_4*H_2O$, Na_2HPO_4, 5% nafion solution in aliphatic alcohol solution and distilled water were used. 0.1M pH = 7 phosphate buffer was produced from KCl, $NaH_2PO_4*H_2O$, Na_2HPO_4.

1.2. Equipment

The BAS-Epsilon model potentiostat with C3 electrode cell (Bioanalytical Systems Inc., West Lafayette, USA) was used in this work. 15ml electrochemical cell which hosted three electrodes was used for experiments. Working Pt wire electrode was mounted into a plastic housing (1.6 mm in diameter (2 mm^2 surface area)), the auxiliary - glass graphite electrode, comparative - Ag/AgCl/saturated KCl. All potentials presented in the work were measured in respect of Ag/AgCl/saturated KCl electrode, the potential of which in respect of hydrogen electrode is +0, 20 V. Before the experiment, working Pt electrode was polished with aluminium oxide powder and washed with distilled water. During the experiments, the electrolyte solution was continuously stirred with a magnetic stirrer.

1.3. Preparation of electrode

Polyaniline modified Pt electrode was prepared for the work in two ways. Electropolymerization was performed in 0.5 M sulphuric acid solution containing 0.05 M aniline. In the first case, the electrode potential was maintained at a constant 0.8 V, and electropolymerization time from 3 to 20 minutes was being changed as well. After the polymerization within the defined time, the electrode was washed with distilled water and transferred to a sulphuric acid solution. Cyclic voltammogram in the range [-0.1, +0.5] V at emission rate of 50 mV/s was recorded in sulphuric acid solution. Then the modified electrode was washed with water and transferred to 0.1 M phosphate buffer solution (pH 7.0). During the experiments, a portion of corresponding analyte was instilled in a buffer solution in small portions with a microsyringe (hydrogen peroxide,

ascorbic acid, paracetamol). The electrode was kept at a constant potential of 0.6 V. Before each experiment, the tests with clean Pt electrode were carried out.

The electrodes modified with polypyrroles and the o-phenylenediamines were prepared analogously.

During the preparation of nafion plated electrode for the work, nafion solution in aliphatic alcohols solution was applied onto a clean Pt electrode (100 µl) inverted upside down and left to dry at a room temperature. In some experiments, two droplets of nafion solution were dripped successively, allowing each of them to dry separately. Thus prepared electrode was washed with distilled water and transferred to H_2SO_4 0.5 M solutions and the cyclic voltammogram was recorded. Then the modified electrode was washed with water and transferred to 0.1 M phosphate buffer solution (pH 7.0). During the experiments, a portion of corresponding analyte was instilled in a buffer solution in small portions with a microsyringe (hydrogen peroxide, ascorbic acid, paracetamol). The electrode was kept at a constant potential of 0.6 V. Before each experiment, the tests with clean Pt electrode were carried out. Cyclic voltammogram of Pt electrode was recorded [0; 1.5 V] in the range of 50 mV/s at emission rate.

2. RESULTS AND THEIR CONSIDERATION

2.1 Electrochemical polymerization of aniline: cyclic voltammetry method, the constant potential method. Ascorbic acid, paracetamol and H_2O_2 response study.

Polyaniline modified Pt electrode was prepared in two ways. Electropolymerization was performed in 0.5 M sulphuric acid solution containing 0.05 M aniline.

In the first case, the electrode potential was kept at a constant 0.8 V, and the electropolymerization time from 3 to 30 minutes was changed. After the polymerisation within the indicated time, the electrode was washed with distilled water and transferred to a sulphuric acid solution. Cyclic voltammogram the range [-0.1, +0.5] V at emission rate of 50 mV/s was recorded in sulphuric acid.

Thus obtained PANI layer depends largely on the duration of electropolymerization. It is known that polymerization of aniline is of autocatalytic in nature, so the amount of precipitated PANI and duration of precipitation is not of linear

dependence [167-170]. Fig. 1 shows the PANI cyclic voltammograms of modified Pt electrode at different time of electropolymerization. One anodic and one cathodic pair of peaks are observed in cyclical voltammogram. The sum of potential peaks is (Epa + Epc) = 0.16 and the peak is biased in respect of each other by 0.11 V. With increasing time of electropolymerization, the peak value is growing rapidly. In particular, the rapid increase of peaks is observed by increasing the number of electropolymerization cycles from 7 to 20 cycles. Thereby a slower growth of peaks is noticeable through the electropolymerization of Pt electrode for longer period of time (up to 27 or 41 cycle).
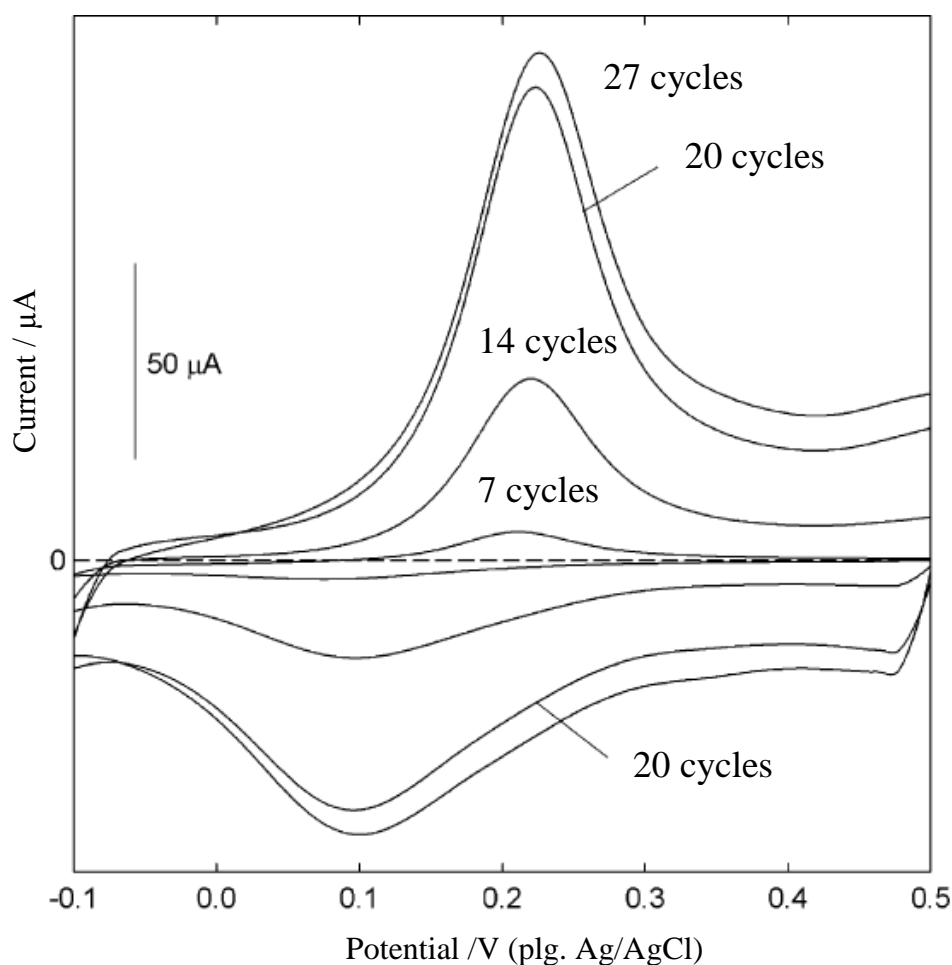

Fig. 1. Cyclic voltammograms were obtained on Pt electrode modified PANI 0.5 M sulphuric acid solution containing 0.05 M aniline. Potential emission limits [-0.1; 0.5] V. The potential emission rate was 50 mV s -1. The electrode potential was kept at constant 0.8 V. Modification time was from 4 to 41 of cycle.

Then the modified electrode was washed with water and transferred to 0.1 M phosphate buffer solution (pH 7.0). During the experiments, a portion of corresponding analyte was instilled in a buffer solution in small portions with a microsyringe (hydrogen

peroxide, ascorbic acid, paracetamol). The electrode was kept at a constant potential of 0.6 V. Before each experiment, the tests with clean Pt electrode were carried out.

When introducing small portions of hydrogen peroxide into the buffer solution, first, the anodic current grows and reaches a constant value. Constant current of unmodified electrode stabilizes after about 10 seconds, while it takes more time for the modified electrode. For example, the time for hydrogen peroxide and paracetamol is from 10 to 20 seconds, depending on the PANI film thickness. The thicker the film, the longer the settling time is.

A different phenomenon is observed after adding ascorbic acid into a buffer solution. Having instilled the first dose of ascorbic acid into the buffer solution, slow growth of anodic current is observed. Anodic current reaches its constant value only after 3 minutes or more. Introducing the second and subsequent portions of the analyte, the current growth is faster, and the maximum value is reached faster (Fig. 2).

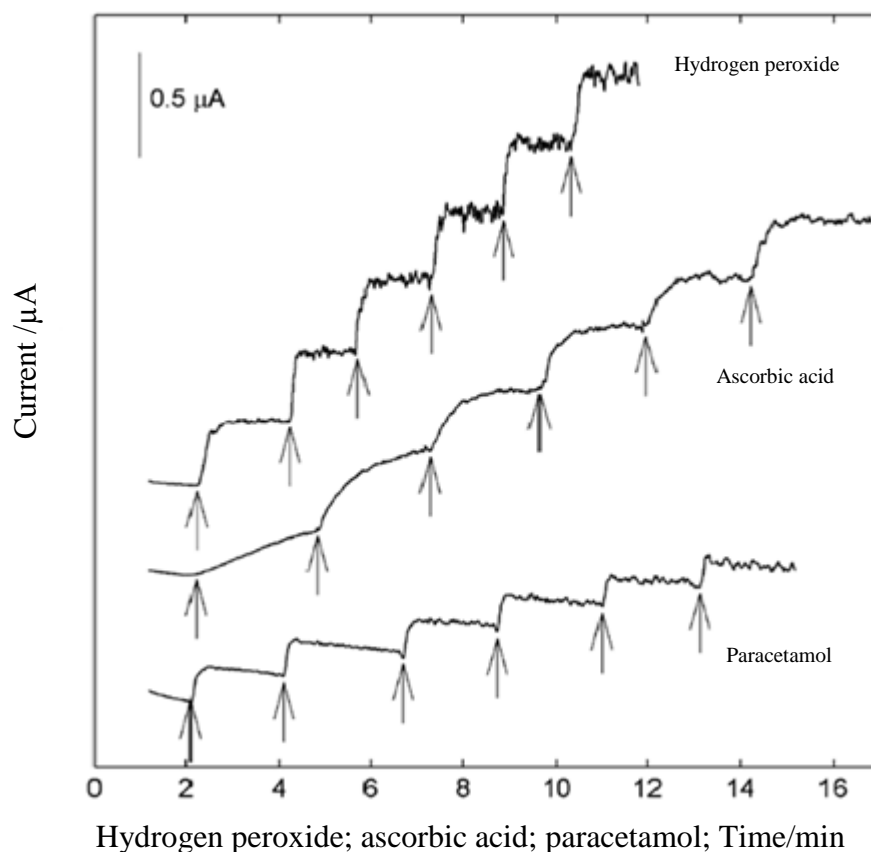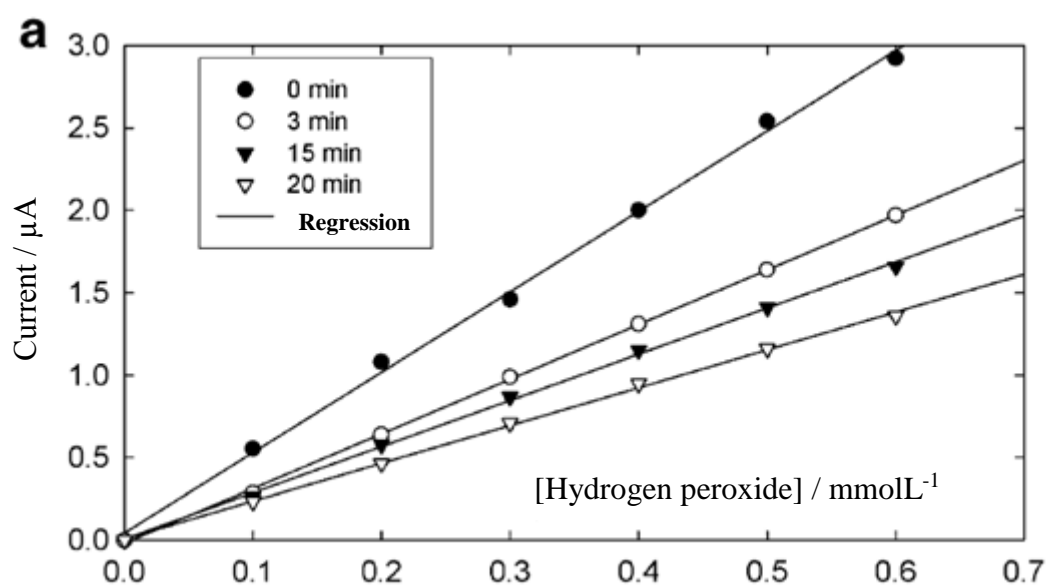Hydrogen peroxide; ascorbic acid; paracetamol; Time/min

Fig.2. Response of anodic current to hydrogen peroxide, ascorbic acid, paracetamol on polyaniline modified Pt electrode (under the same conditions). Electropolymerization was performed at a constant potential of 0.8 V, and the modification time of 10 minutes 0.5 mol L_{-1} in sulphuric acid solution containing 0.1 mol L^{-1} of aniline. A further test was carried out in a buffer pH7 solution, containing 0.1 mol L^{-1} of KCl at a constant potential of 0.6 V. The

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corresponding analytes were introduced into the solution in small portions of 0.1 ml L$_{-1}$. (Introduction time is displayed with arrows).

Earlier this behaviour has been interpreted as of autocatalytic ascorbic acid nature [171.172]. At neutral pH of solution, polyaniline is present in its deproteinized non-conductive shape, so no electrocatalytic reactions can take place. Since electrically precipitated PANI has a porous structure, ascorbic acid diffuses through the pores at the Pt electrode surface, where the electrooxidation process starts. As a result of this electrode reaction, the protons are released in equimolar amounts in respect of oxidized ascorbic acid, and this causes a decrease of pH inside the PANI layer. The pH decrease results in conversion of non-conductive deproteinized PANI form into protonated conductive PANI form (emeraldine). Further anodic oxidation of ascorbic acid is already catalyzed by PANI itself. The results obtained indirectly confirm our theory. Data presented in Fig.2 for hydrogen peroxide, ascorbic acid and paracetamol were obtained for the same polyaniline film.

Thus, porous polyaniline film obtained under these conditions not only allows the diffusion of hydrogen peroxide molecules, but also much bigger paracetamol molecules. Since ascorbic acid and paracetamol molecules are similar in size, the diffusion of ascorbic acid molecules takes place without a hindrance.
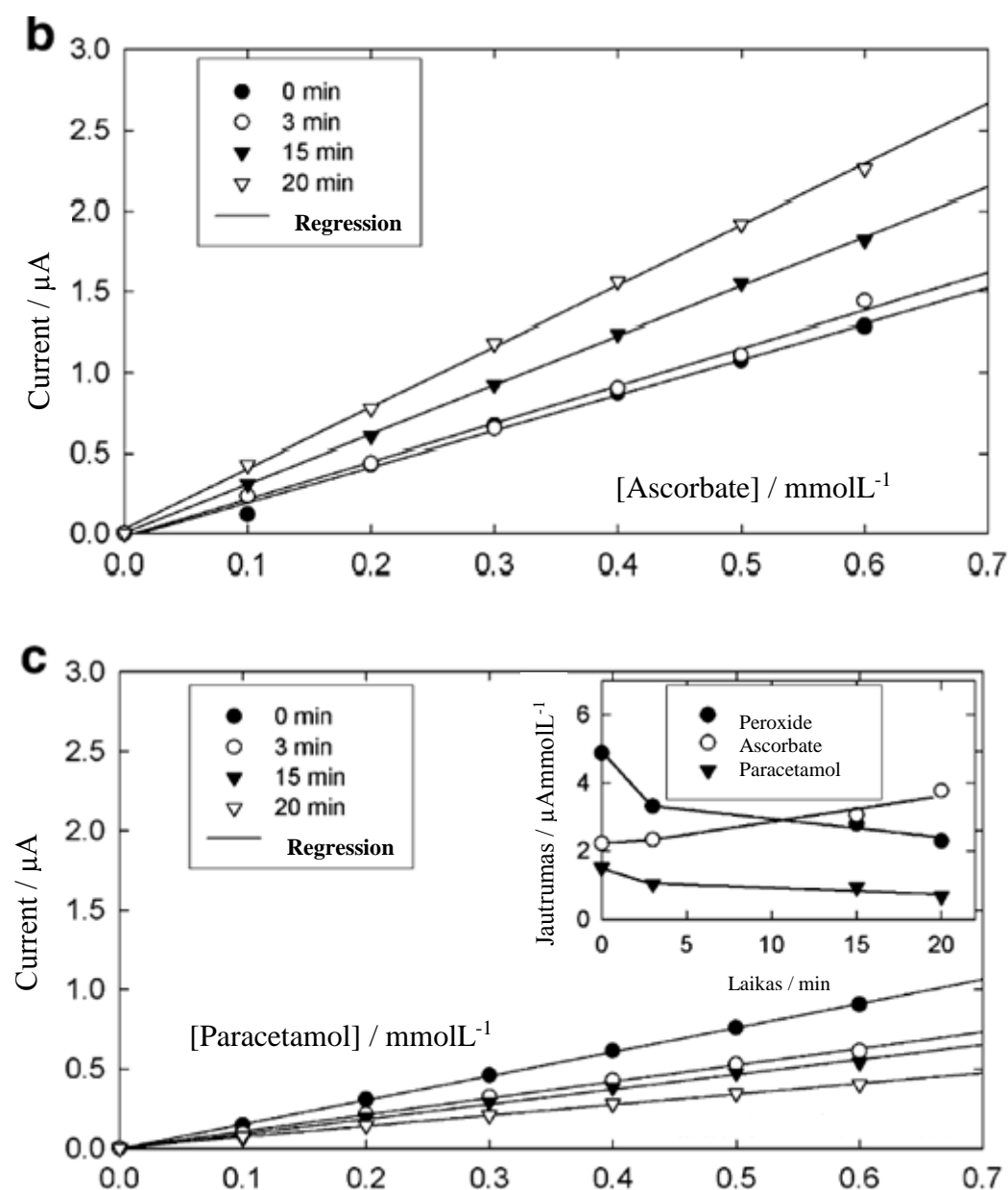
Fig.3. Dependence of anodic current function on the concentration of hydrogen peroxide (A, above), ascorbic acid (B, centre), paracetamol (C, below) on a Pt electrode modified polyaniline. Polymerization of Pt electrode was carried out in 0.5 mol L^{-1} solution of sulphuric acid containing 0.05 mol L^{-1} of aniline at a constant potential of 0.8 V, with different modification times (3,15 and 20 min). For clean Pt electrode - 0 min. Part C shows the Pt electrode sensitivity to different analytes, which were used during the electropolymerization.

All three analytes have a linear anodic current dependence from analyte concentration determined (Fig. 3). Based on these dependencies, several conclusions can be made. The maximum inclination of the calibration curve for hydrogen peroxide and the maximum sensitivity of the electrode have been recorded on an unmodified platinum electrode. After the increase of aniline electropolymerization time from 4 to 27 cycles, the sensitivity of platinum electrode decreases by 1.5 and 2.1 times respectively. As

expected, the indicator for ascorbic acid increases by contraries. Even the precipitation of thinner PANI layer (5 μC cm^2) on platinum electrode increases the sensitivity of the electrode by 1.1 times. The sensitivity for the thickest PANI coating (400 μC cm^2) increases by 1.7. In paracetamol case, as in the case of hydrogen peroxide, the decrease in sensitivity after the modification of the electrode with PANI layer is observed. For the thinnest and thickest PANI coating, the sensitivity to paracetamol reduces by 1.46 and 2.27 times respectively.

In the second case, the cyclic voltammograms were recorded in a 0.5M H$_2$SO$_4$ solution containing 0,05M aniline through the emission of potential at rate of 50 mV/s in the range from -0.1 to +1.0 V. Emission time of potential was changed from 4 to 41 of cycle. After the polymerisation within the indicated time, the electrode was washed with distilled water and transferred to a sulphuric acid solution. The cyclic voltammogram in the range of [-0.1, +0.5] V at emission rate of 50 mV/s was recorded in sulphuric acid.
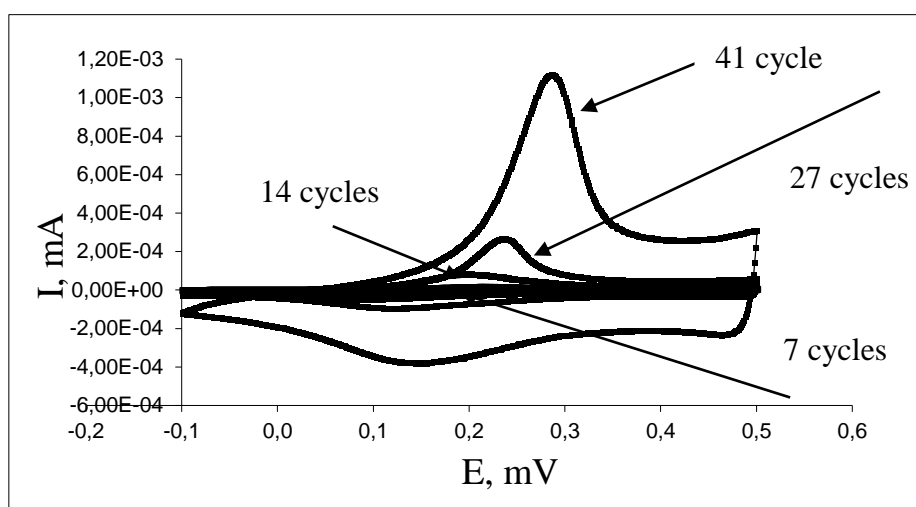

Fig.4. Cyclic voltammograms were obtained on Pt electrode modified PANI 0.5 M sulphuric acid solution containing 0.05 M of aniline. Potential emission limits - [-0.1; 0.5] V. The potential emission rate was 50 mV s -1. Modification time was from 3 to 30 minutes.

Thus obtained PANI layer also depends on the duration of electropolymerization. Fig. 4 shows the PANI cyclic voltammograms of modified Pt electrode at different time of electropolymerization. One anodic and one cathodic pair of peaks are observed in cyclical voltammogram. The sum of potential peaks is (Epa + Epc) = 0.2 and the peak is biased in respect of each other by 0.15 V. With increasing time of electropolymerization, the peak value is growing rapidly. In particular, the rapid increase of peaks is observed by increasing the number of electropolymerization cycles from 27 to 41 of cycle.

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Thereby a slower growth of peaks is noticeable through the electropolymerization of Pt electrode for shorter period of time (up to 14 cycles). This can be explained by the fact that in such a short time oxidation-reduction of aniline lags on the Pt electrode surface.

Then the modified electrode was washed with water and transferred to 0.1 M phosphate buffer solution (pH 7.0). During the experiments, a portion of corresponding analyte was instilled in a buffer solution in small portions with a microsyringe (hydrogen peroxide, ascorbic acid, paracetamol). The electrode was kept at a constant potential of 0.6 V. Before each experiment, the tests with clean Pt electrode were carried out (Fig. 5).
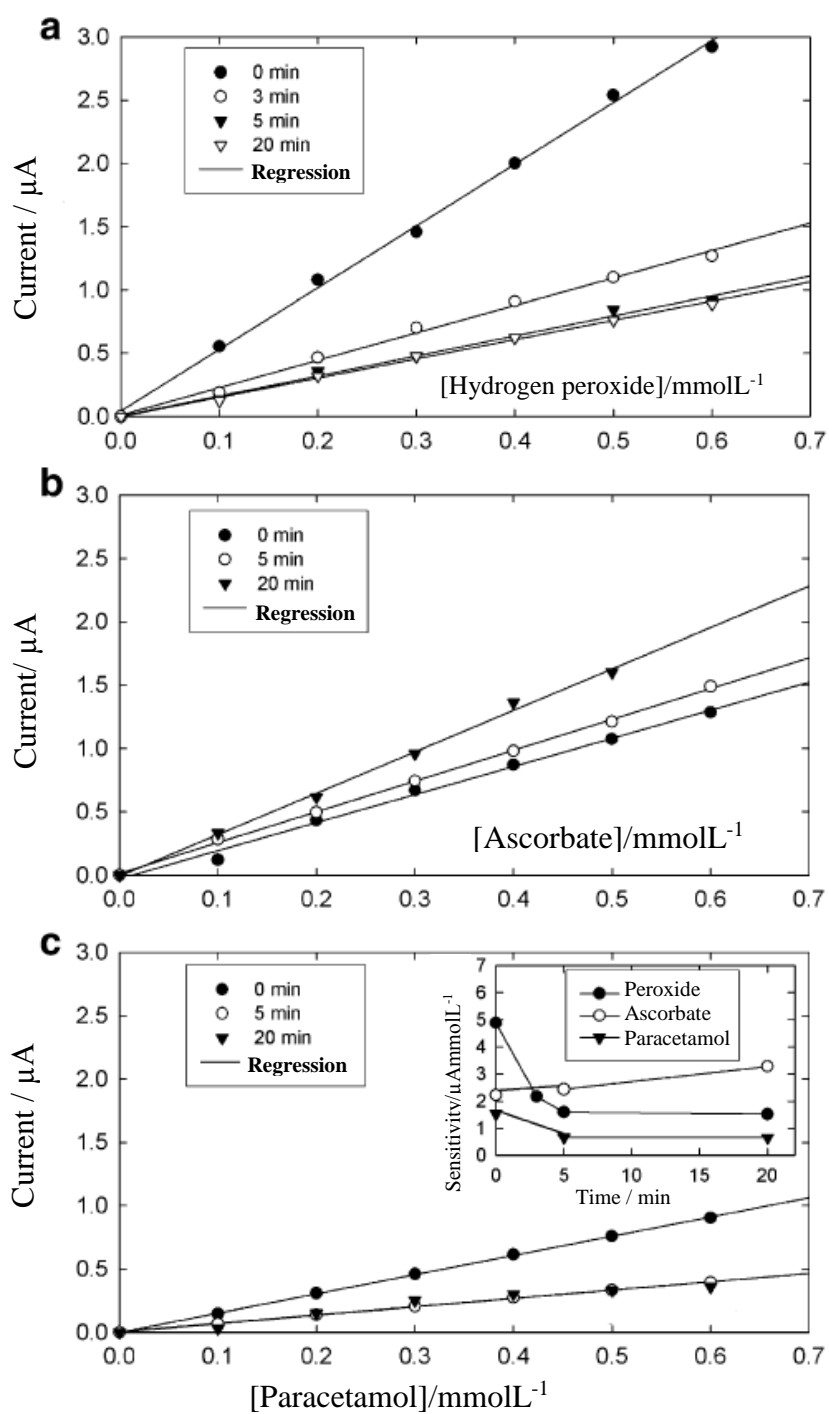
Fig.5. Dependence of anodic current function on the concentration of hydrogen peroxide (A, above), ascorbic acid (B, centre), paracetamol (C, below) on a Pt electrode modified polyaniline. Polymerization of Pt electrode was carried out in 0.5 mol L-1 solution of sulphuric acid containing 0.05 mol L-1 of aniline. Cyclic voltammograms were recorded at [-0.1: +1.0 V] potential in the range for different lengths of time (from 3 to 30 min). Pure Pt electrode - 0 min. Part C shows the sensitivity of Pt electrode to different analytes, which were used during the electropolymerization.

Two accomplished experiments lead us to several conclusions. All three analytes are characterized by a linear dependence of the anodic current from the concentrations of analytes. The maximum inclination of hydrogen peroxide calibration curve and the maximum sensitivity of the electrode were obtained on non-modified platinum electrode. Increase of aniline electropolymerization time from 3 to 20 minutes leads to the reduction of platinum electrode sensitivity by 1.5 and 2.1 times, respectively, keeping the potential of platinum electrode constant. An even greater reduction in the sensitivity of the electrode is observed when carrying out the emission of the potential – 2.2 and 3.2 and times, respectively, by increasing the electropolymerization time from 4 to 27 cycles. It follows that the emission of the potential is more compact and PANI film transmits the hydrogen peroxide less. Quite the opposite phenomenon is observed in the tests on the ascorbic acid (Fig.3 and 5). Even the thinnest PANI layer ($5\mu C$ sm^{-2}) increases the sensitivity of platinum electrode by 5 or 6% depending on the polymerization method applied. For the thickest PANI coating ($400\mu C$ sm^{-2}) electrode sensitivity increased by 1.7 times. Sensitivity of paracetamol electrode decrease is observed after the modification of platinum electrode with a polyaniline layer. For the thinnest and thickest PANI coating the sensitivity reduces by 1.46 and 2.27 times respectively. It follows that polyaniline modified platinum electrode shows practically no difference between the analyte (hydrogen peroxide) and disruptive analyte (paracetamol) to be determined.

2.2. Electrochemical polymerization of pyrrole: cyclic voltammetry method, the constant potential method. Ascorbic acid, paracetamol and H_2O_2 response study.

Polypyrrole modified Pt electrode was prepared in two ways. Electropolymerization was performed in 0.1 M KCl solution containing 0.1M of pyrrole.

In the first case, cyclic voltammograms were recorded in 0.1M KCl solution containing 0.1M pyrrole, emitting potential at 50 mV/s rate in the range of -0.4 to +1.0 V for different time from 3 to 10 minutes. After the polymerisation within the indicated time, the electrode was washed with distilled water and transferred to KCl solution. The cyclic voltammogram in the range of [-0.4, +1.0] V at emission rate of 50 mV/s was recorded in KCl solution (Fig.6).
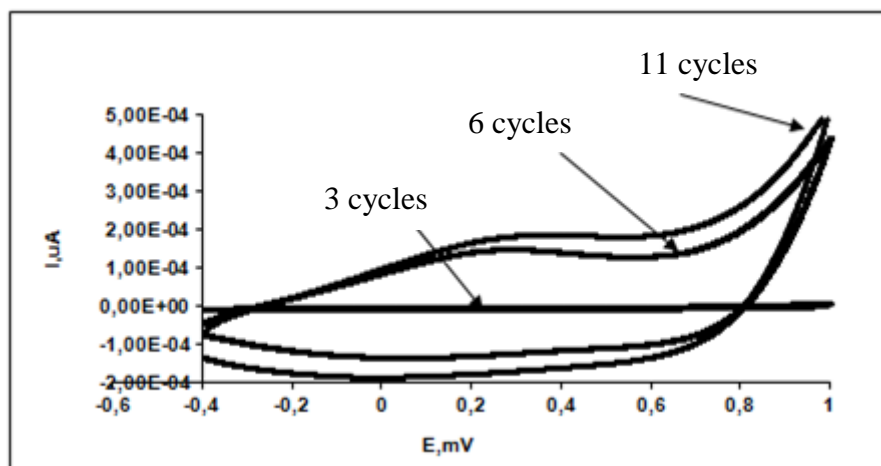

Fig.6. Cyclic voltammograms were obtained on Pt electrode modified with polypyrrole in 0.1 M KCl solution containing 0.1 M of pyrrole. Potential emission limits - [-0.4; 1.0] V. The potential emission rates - 50 mV s -1. Modification time – from 3 to 10 minutes.

Thus obtained polypyrrole layer thickness depends on the duration of electropolymerization. Fig. 6 shows the PANI cyclic voltammograms of Pt electrode modified at different times of electropolymerization. Increasing electropolymerization time results in rapid growth of the area of cyclic voltammograms. In particular, the rapid increase in the area size is observed by increasing the number of cycles of cyclic voltammograms recorded from 3 to 6 cycles. While smaller area is observed during the electropolymerization of Pt electrode for a longer period of time (up to 11 cycles). This can be explained by the fact that during that time, a large amount of pyrrole practically has already become polymeric.

Then the modified electrode was washed with water and transferred to 0.1 M phosphate buffer solution (pH 7.0). During the experiments, a portion of corresponding analyte was instilled in a buffer solution in small portions with a microsyringe (hydrogen peroxide, ascorbic acid, paracetamol). The electrode was kept at a constant potential of 0.6 V. Before each experiment, the tests with clean Pt electrode were carried out.
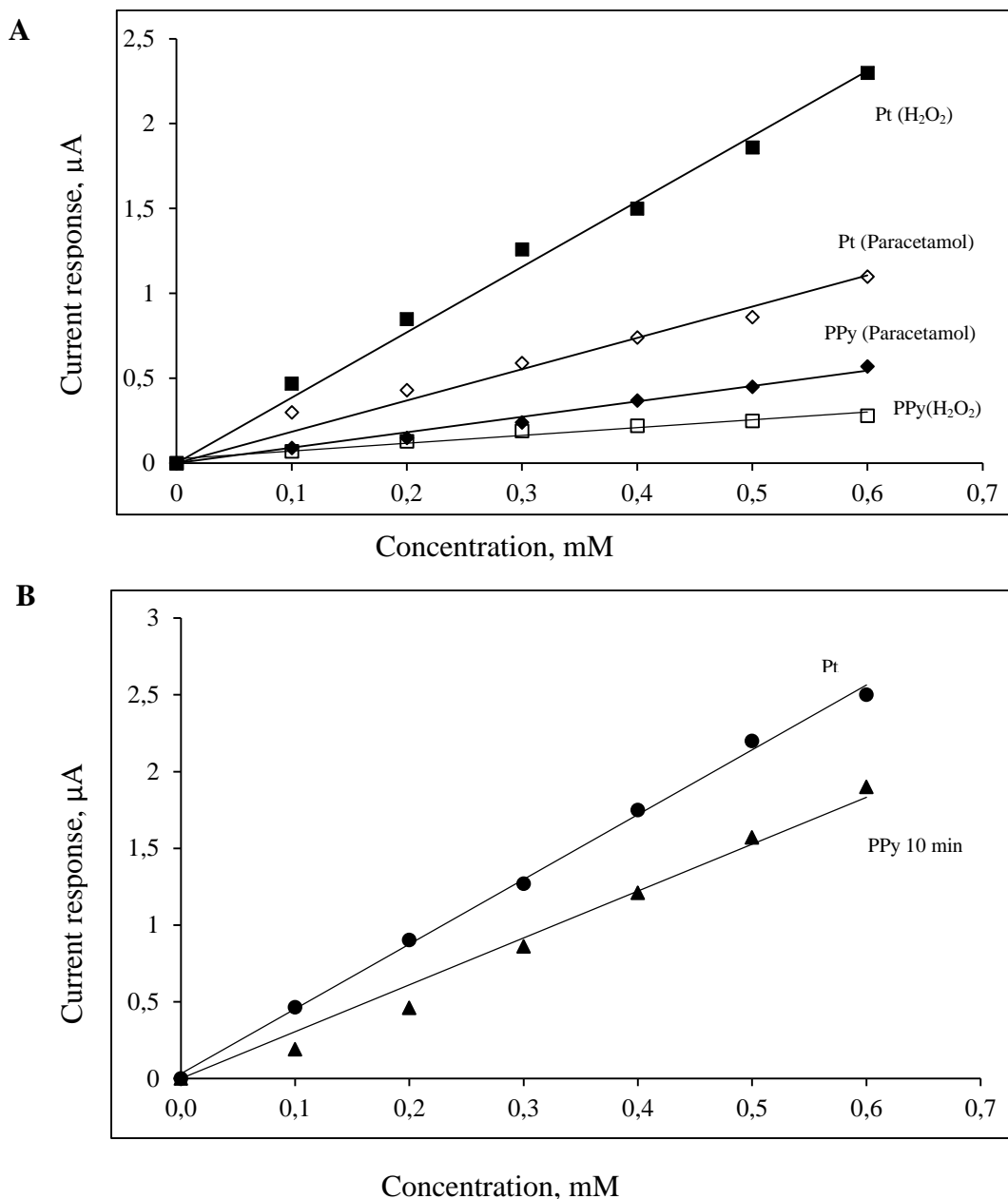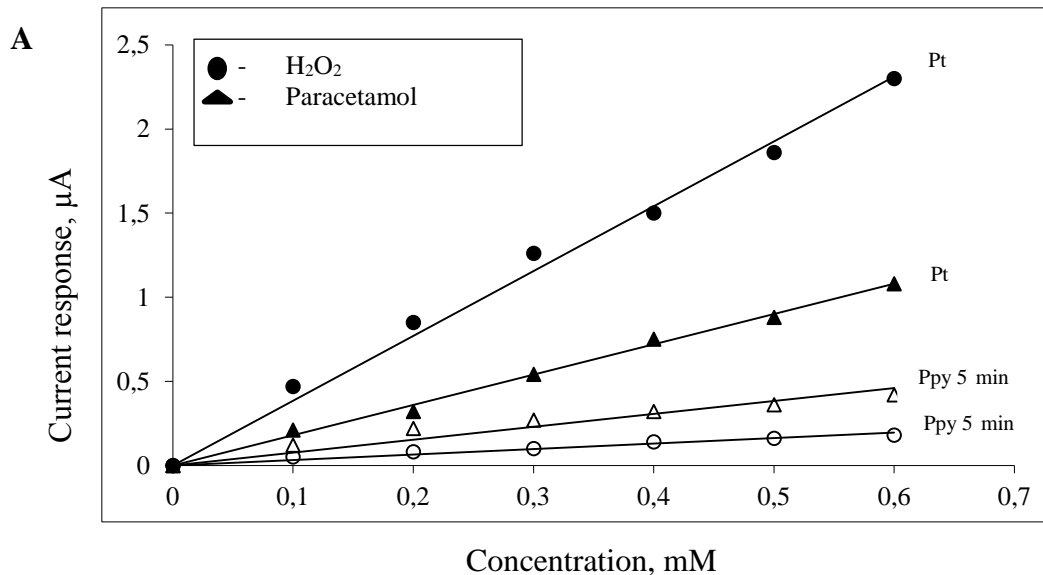
Fig.7. Dependence of anodic current from concentration of hydrogen peroxide and paracetamol (A, above), electropolymerization time - 3 min, ascorbic acid (B), and polypyrrole modified Pt. Cyclic voltammograms were recorded at [-0.4: +1.0 V] potential in the range during different time (from 3 to 10 min).

All three analytes have a linear anodic current dependence from analyte concentration determined (Fig. 7). Based on these dependencies, several conclusions can be made. The maximum inclination of the calibration curve for hydrogen peroxide and the maximum sensitivity of the electrode have been recorded on an unmodified platinum electrode. After the increase of aniline electropolymerization time from 3 to 10 minutes, the sensitivity of platinum electrode decreases by 8.3 and 11.6 times respectively. The indicator for ascorbic acid decreases as well. Even the precipitation of thinner PANI

layer (14 µC cm^2) on platinum electrode increases the sensitivity of the electrode by 1.11 times. The sensitivity for the thickest PANI coating (84 µC cm^2) increases by 1.13. In paracetamol case, as in the case of hydrogen peroxide, the decrease of sensitivity after the modification of the electrode with polypyrrole layer is observed. For the thinnest and thickest polypyrrole coating, the sensitivity to paracetamol reduces by 1.9 and 2.9 times respectively.

In the second case, the electrode potential was kept at a constant 0.8 V, and the electropolymerization time was changed from 3 to 10 minutes. After the polymerisation within the indicated time, the electrode was washed with distilled water and transferred to a sulphuric acid solution. The cyclic voltammogram in the range of [-0.4, +0.5] V at emission rate of 50 mV/s was recorded in sulphuric acid.

Then the modified electrode was washed with water and transferred to 0.1 M phosphate buffer solution (pH 7.0). During the experiments, a portion of corresponding analyte was instilled in a buffer solution in small portions with a microsyringe (hydrogen peroxide, ascorbic acid, paracetamol). The electrode was kept at a constant potential of 0.6 V. Before each experiment, the tests with clean Pt electrode were carried out (Fig. 8).

B Ascorbic acid
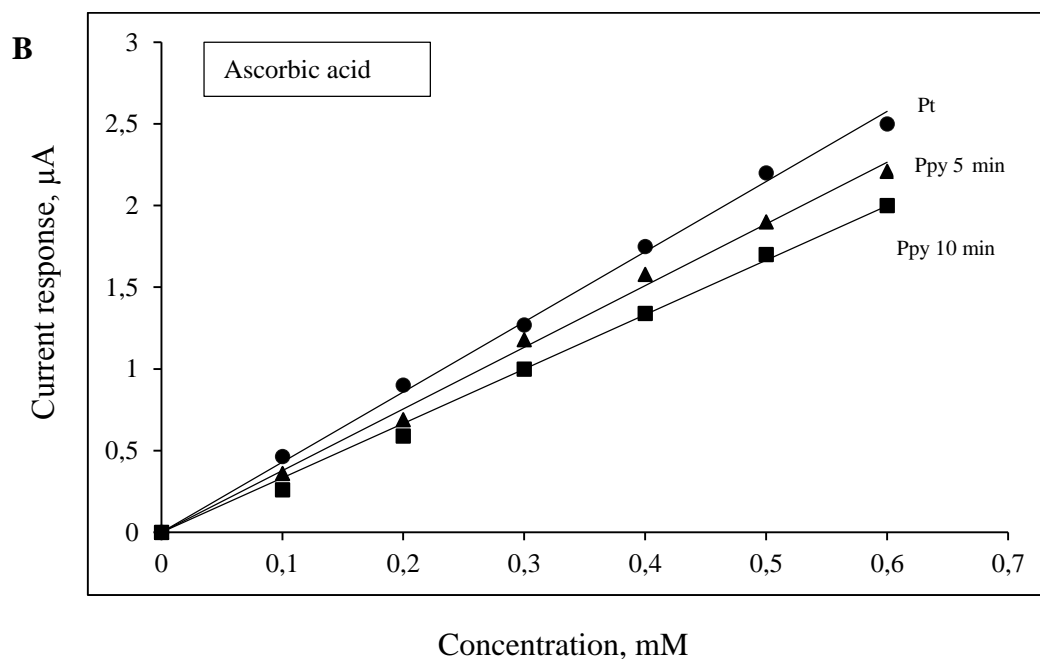
Current response, µA

Concentration, mM

Fig.8. Dependence of anodic current function on the concentration of hydrogen peroxide and paracetamol (A, above), ascorbic acid on a Pt electrode modified with polypyrrole. Polymerization of Pt electrode was carried out in 1M KCl solution containing 0.1M of pyrrole at 0.8V potential during different modification time (from 3 to 30 min).

Two accomplished experiments lead us to several conclusions. All three analytes are characterized by a linear dependence of the anodic current from the concentrations of analytes. The maximum inclination of hydrogen peroxide calibration curve and the maximum sensitivity of the electrode were obtained on non-modified platinum electrode. Increase of polypyrrole electropolymerization time from 3 to 10 minutes leads to the reduction of platinum electrode sensitivity by 10.9 and 11.6 times simultaneously recording cyclic voltammograms respectively. Greater reduction in the sensitivity of the Pt electrode is observed when carrying out the polymerization at constant potential – 8.3 and 11.6 and times, respectively, by increasing the electropolymerization time from 3 to 10minutes. It follows that the method of constant potential is more compact and polypyrrole film transmits the hydrogen peroxide poorly. After the tests with ascorbic acid (Fig. 7 and 8), decrease in sensitivity is also observed. Even the thinnest polypyrrole film layer (5.64µC sm^{-2}) reduces the sensitivity of platinum electrode by 93 or 114% depending on the polymerization method applied. For the thickest polypyrrole coating (38.5µC sm^{-2}), electrode sensitivity decreases by 1.11 – 1.13 times respectively. Sensitivity of paracetamol electrode decrease is observed after the modification of platinum electrode with a polyaniline layer. Polypyrrole film reduces the diffusion of

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ascorbic acid. Decrease of paracetamol Pt electrode sensitivity is observed after the modification of the platinum electrode with polypyrrole layer. For the thinnest and thickest polypyrrole coating the sensitivity reduces by 2.9 times respectively, depending on the modification method applied. Polypyrrole film badly conducts paracetamol molecules. It follows that polypyrrole shows no between the determined analyte (hydrogen peroxide) and disruptive analytes (paracetamol) and ascorbic acid. In hydrogen peroxide case, the area of active slightly reduces, and hydrogen peroxide does not have space for discharge. Due to their size, paracetamol and ascorbic acid molecules are trapped in the polymer matrix in the formation of hydrogen bonds.

2.3. Electrochemical polymerization of o-phenylenediamine: cyclic voltammetry method, the constant potential method. Ascorbic acid, paracetamol, H_2O_2 response study.

Orthophenylenediamine modified Pt electrode was prepared in two ways. Electropolymerization was performed in 0.5 M sulphuric acid solution containing 0.05 M of orthophenylenediamine.

In the first case, cyclic voltammograms were recorded in 0.5 M H_2SO_4 solution containing 0.05M orthophenylenediamine, emitting potential at 50 mV/s rate in the range from -0.2 to +1.2 V. 5.10 and 15 cycles were recorded. After the polymerisation within the fixed cycle, the electrode was washed with distilled water and transferred to sulphuric acid solution. The cyclic voltammogram in the range of [-0.1, +0.5] V at emission rate of 50 mV/s was recorded in sulphuric acid solution.

One oxidation peak at 1.1 V, which originates due to orthophenylenediamine polymerization, is observed in the cyclic voltammogram. And reduction peak at 0.05 V. The oxidation peak is clearly declining and peak potential is shifting toward the positive potential with each cycle. This indicates the relatively low conductivity of the polymer film (Fig. 9). After 15 cycles the curve changes.
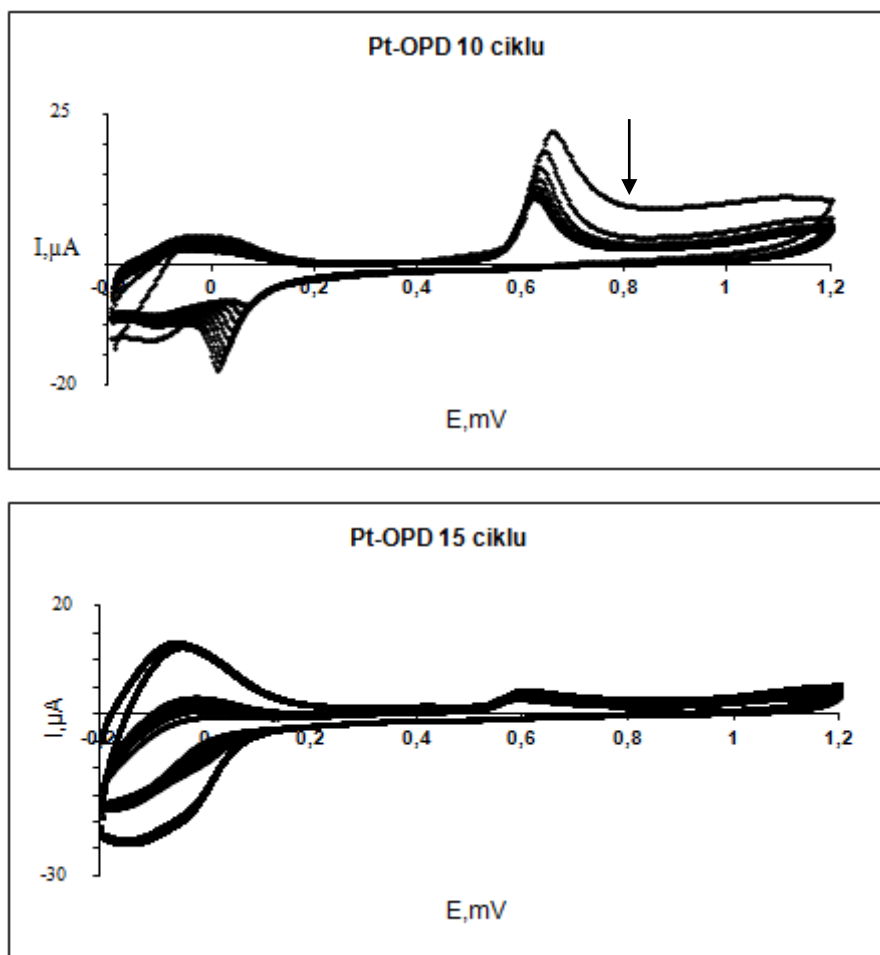
Fig.9. Cyclic voltammograms were obtained on Pt electrode modified with orthophenylenediamine in 0.5 M sulphuric acid solution containing 0.05 M orthophenylenediamine. Potential emission limit - [-0, 2; 1.2] V. The potential emission rate - 50 mV s^{-1}.

Then the modified electrode was washed with water and transferred to 0.1 M phosphate buffer solution (pH 7.0). During the experiments, a portion of corresponding analyte was instilled in a buffer solution in small portions with a microsyringe (hydrogen peroxide, ascorbic acid, paracetamol). The electrode was kept at a constant potential of 0.6 V. Before each experiment, the tests with clean Pt electrode were carried out (Fig. 9). Since orthophenylenediamine is not distinguished by enough good stability, so the modification of platinum electrode with freshly precipitated orthophenylenediamine was performed prior to each experiment with a new analyte.
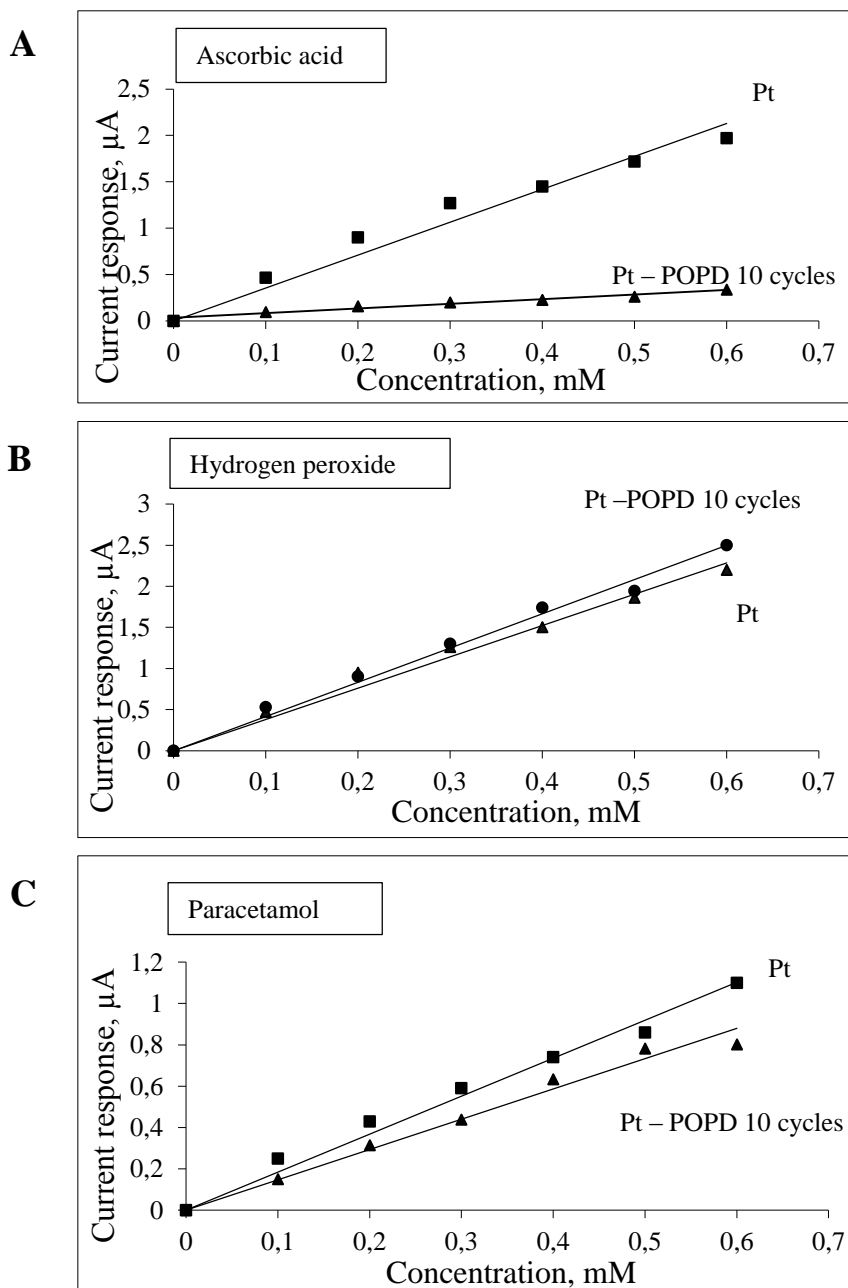
Fig.10. Dependence of anodic current on the concentration of hydrogen peroxide (A, above), hydrogen peroxide (B, centre), paracetamol (C, below) on a Pt electrode modified with orthophenylenediamine. Polymerization of Pt electrode was carried out in 0.5 mol L-1 solution of sulphuric acid containing 0.05 mol L-1 of orthophenylenediamine. Cyclic voltammograms were recorded at a potential of [-1.2: +0.2 V] in different times (from 5 to 15 cycles). Pure Pt electrode - 0 min.

All three analytes have a linear anodic current dependence from analyte concentration determined (Fig. 10). Based on these dependencies, several conclusions can be made. The maximum inclination of the calibration curve for hydrogen peroxide and the maximum sensitivity of the electrode have been recorded on an unmodified platinum electrode. After the electropolymerization, the sensitivity of platinum electrode

orthophenylenediamines increases 1.1 times. On the contrary, the indicator for ascorbic acid greatly decreases. Even the precipitation of thinner orthophenylenediamine layer (0.04 μC cm^2) on platinum electrode decreases the sensitivity of the electrode by 92%. The sensitivity for the thickest orthophenylenediamine coating (2.5 μC cm^2) decreases by 8.6 times. In paracetamol case, as in the case of ascorbic acid, the decrease of sensitivity after the modification of the electrode with orthophenylenediamine layer is observed. For the thinnest and thickest orthophenylenediamine coating, the sensitivity to paracetamol reduces by 1.4 and 2.9 times.

In the second case, the electrode potential was kept at a constant 0.8 V, and the electropolymerization time was changed from 5 to 15 minutes. After the polymerization within the indicated time, the electrode was washed with distilled water and transferred to a sulphuric acid solution. The cyclic voltammogram in the range of [-0.1, +0.5] V at emission rate of 50 mV/s was recorded in sulphuric acid.

Then the modified electrode was washed with water and transferred to 0.1 M phosphate buffer solution (pH 7.0). During the experiments, a portion of corresponding analyte was instilled in a buffer solution in small portions with a microsyringe (hydrogen peroxide, ascorbic acid, paracetamol). The electrode was kept at a constant potential of 0.6 V. Before each experiment, the tests with clean Pt electrode were carried out (Fig. 11).

B

Hydrogen peroxide

Pt-POPD 10min

Pt

Current response, μA (y-axis)
Concentration, mM (x-axis)

C

Paracetamol

Pt

Pt-POPD10 min

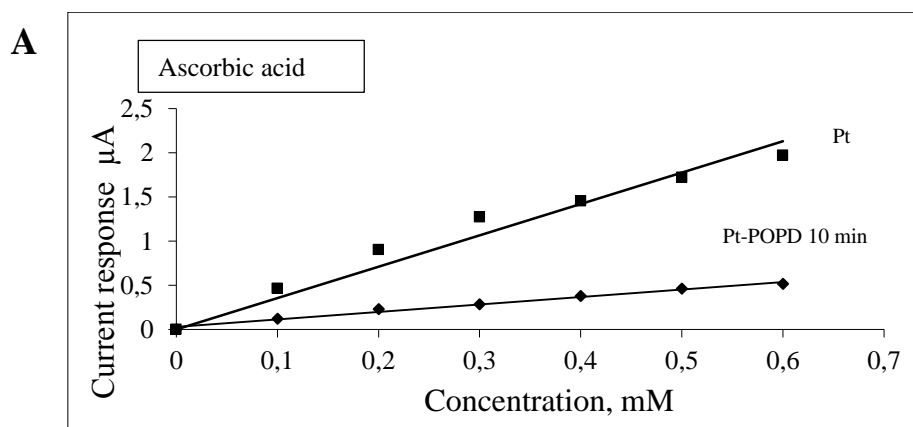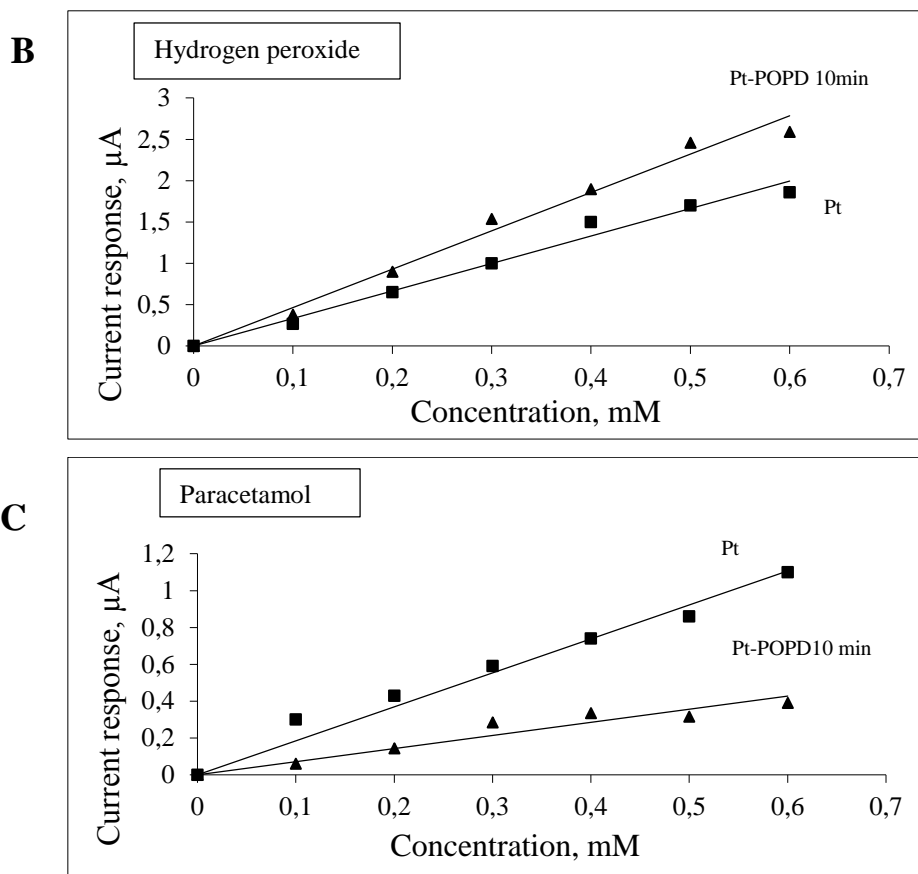Current response, μA (y-axis)
Concentration, mM (x-axis)

Fig.11. Dependence of anodic current on the concentration of hydrogen peroxide (A, above), hydrogen peroxide (B, centre), paracetamol (C, below) on a Pt electrode modified with orthophenylenediamine. Polymerization of Pt electrode was carried out in 0.5 mol L^{-1} solution of sulphuric acid containing 0.05 mol L^{-1} of orthophenylenediamine. The electropolymerization was carried out at constant potential of 0.8 V, at 5 and 10 minutes.

Two accomplished experiments lead us to several conclusions. All three analytes are characterized by a linear dependence of the anodic current on the concentrations of analytes. The maximum inclination of hydrogen peroxide calibration curve and the maximum sensitivity of the electrode were obtained on non-modified platinum electrode. After the modification of the platinum electrode with orthophenylenediamine layer, the sensitivity of platinum electrode increases by 1.1 and 1.4, depending on the type of electropolymerization method used. This means that the orthophenylenediamine film does not hinder free diffusion for hydrogen peroxide. Quite the opposite phenomenon was observed in the tests on the ascorbic acid (Fig.10 and 11). Even the thinnest orthophenylenediamine film layer (2.1μC sm^{-2}) reduces the sensitivity of platinum electrode by 92 or 79% depending on the polymerization method applied. For the thickest orthophenylenediamine coating (6.5μC sm^{-2}), electrode sensitivity decreases by

13.3 times. Orthophenylenediamine film does not conduct ascorbic acid. Sensitivity decrease of Pt electrode to paracetamol is observed after the modification of platinum electrode with orthophenylenediamine layer. The sensitivity to thinnest and thickest orthophenylenediamine coating decreases by 2.8 and 1.4 times, respectively, depending on the type of the modification method applied. Orthophenylenediamine film is practically impermeable to paracetamol molecules.

2.4. Nafion coated Pt electrode layer reception. Ascorbic acid, paracetamol, H_2O_2 response study.

Pt wire electrode was fixed onto the holder by inverting it upside down. One drop was instilled on Pt surface with a microsyringe (*ca*. 100 µl) in the solution of aliphatic alcohols of nafion solution. The electrode was left to dry at room temperature. In other experiments, 2 and 3 drops of nafion solution were instilled, allowing each of them to dry separately. After the drop has dried, modified Pt electrode was transferred to a 0.5 M H_2SO_4 solution, where the cyclic voltammogram in the range of [0:1V] at emission rate of 50 mV/s was recorded (Fig. 12).
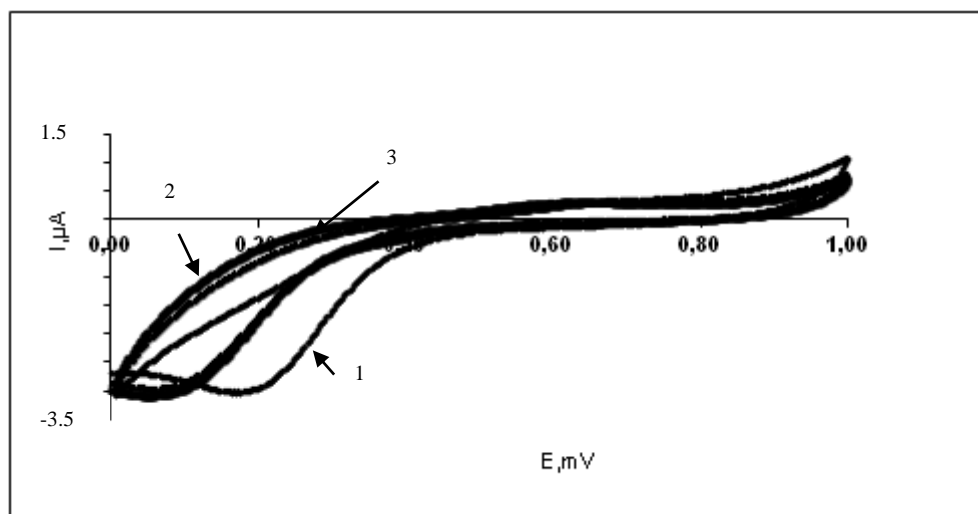
Fig.12. Cyclic voltammograms were obtained on Pt electrode modified with the solution of aliphatic alcohols of nafion solution. Potential emission limit – [0:1] V. The potential emission rate - 50 mV s^{-1}.

Subsequently, modified Pt electrode was washed with distilled water and transferred to a phosphate buffer pH 7.0, containing 0.1 M KCl. The electrode was kept at a constant potential of 0.6 V. Analyte solution was instilled into the buffer solution in small portions with a microsyringe (*ca*. 100 µl).

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Hydrogen peroxide is one of the most important analytes in biosensors. Oxidase biosensors are used for the determination of hydrogen peroxide during the enzymatic (catalytic) reaction. Hydrogen peroxide is determined amperometrically, maintaining a constant potential of 0.6 V in respect of the comparative electrode. Figure 13 shows the dependence of hydrogen peroxide concentration on the current on a clean and nafion-modified Pt electrode. Linear dependence is observed up to a concentration limit of 0.6 mM. This dependence does not practically differ from both for clean and modified electrode. The sensitivity of Pt and nafion-modified electrode is 6.65 µ/mm (or 332 µ/cm 2 mM) and 6.37 µ/mm (or 318 µ/cm 2 mM), respectively. It follows that nafion polymer layer slightly slows down the permeability of hydrogen peroxide. Polymeric nafion layer only slightly reduces the sensitivity of Pt electrode to hydrogen peroxide - just by 4-5%. Moreover, after the modification of Pt electrode with nafion, current noises significantly decreased, compared with clean Pt electrode (Fig. 13 insertion).
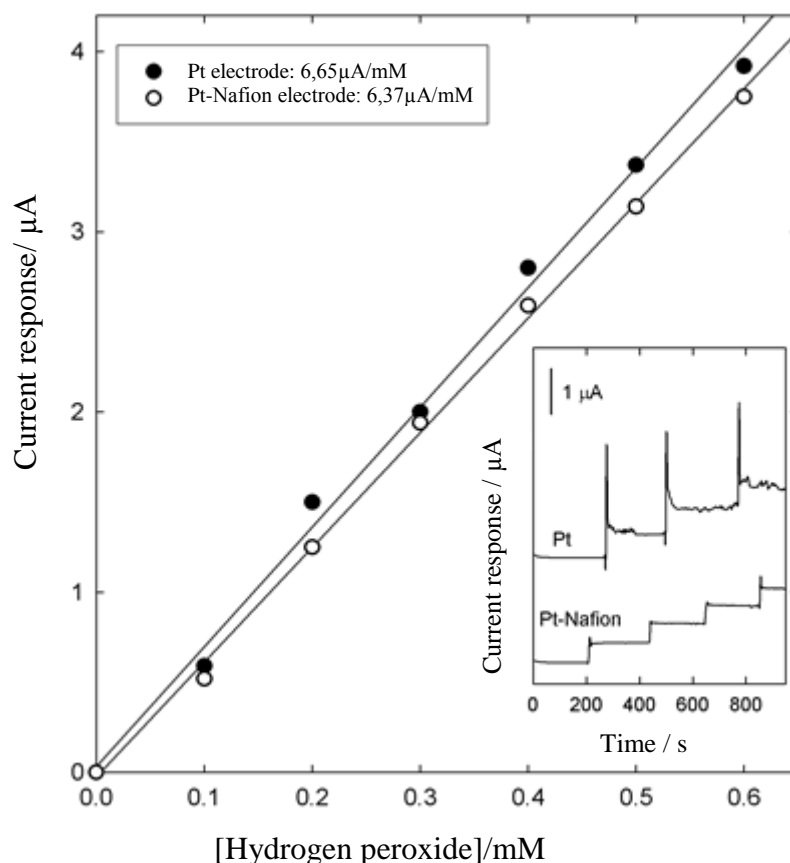

Fig.13. Comparison of the dependence of hydrogen peroxide concentration on the current on nafion-modified Pt electrode (curve 2) and on non-modified Pt electrode (curve 1).

Experiments with ascorbic acid also show a linear dependence of concentration within the measurement range (up to 0.6 mM), maintaining the Pt electrode at a constant potential of 0.6 V. After the instillation of 2 drops of nafion, the sensitivity of Pt and nafion-modified electrode decreased up to 0.075 µA/mM (3.75 µA/cm^2 mM) for thinner coating, and 0.021 µA/mm (1:05 µA mM/cm^2) for thicker coating (Fig. 14). Nation layer significantly reduces the diffusion of the ascorbic acid from about 4 to 1.1% in case of two drops of nafion. Ascorbic acid sensitivity on a clean Pt electrode was 3.3 times lower than in the case of hydrogen peroxide, which is 1.88 µA/mM (94 µA/cm^2 mM).

As in the case of hydrogen peroxide, the growth of output current is rapid after the instillation of a portion of ascorbic acid; low current noise are also observed. They decrease with increasing nafion layer thickness.

The results obtained show that nafion layer coating is characterized by a high efficiency. This is due to the negative vitriolic groups present in the composition of nafion polymer. These groups resist negatively charged anions of ascorbic acid with their electrostatic charge.
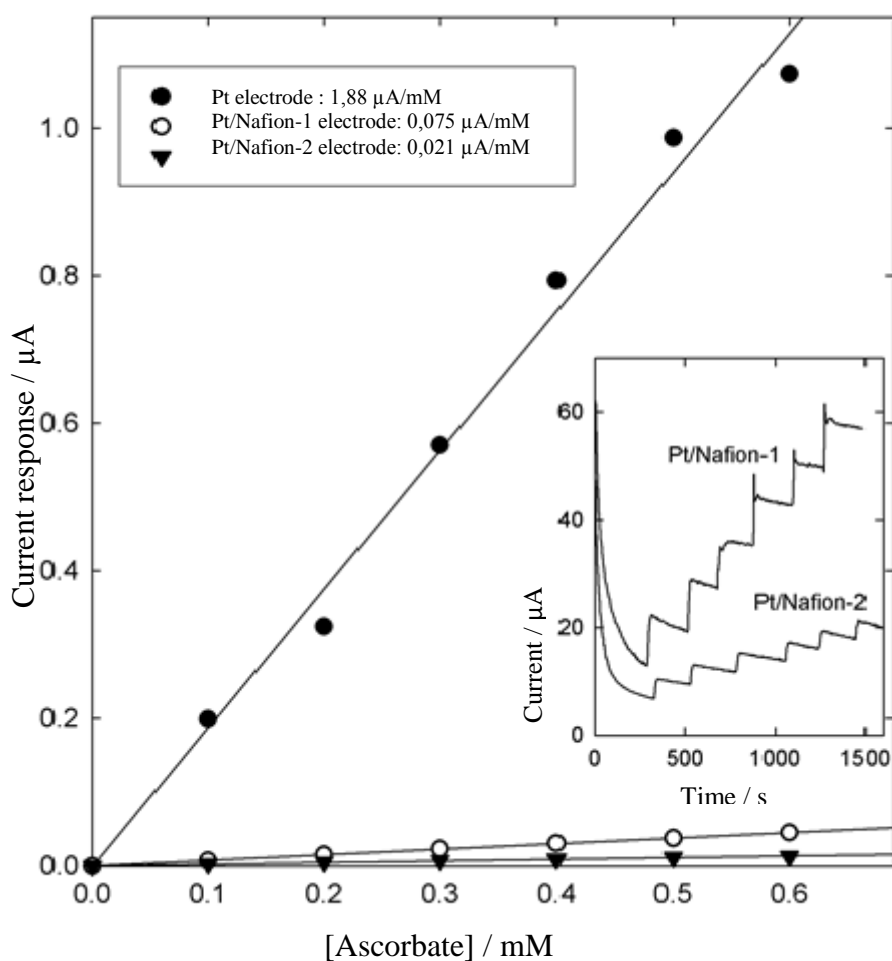
Fig. 14. Dependence of ascorbic acid concentration on non-modified Pt electrode and on Pt electrode modified using 1 and 2 drops of nafion. Insert: Dependence of the current on time with 1 and 2 drops of nafion (each step represents increase of ascorbic acid concentration by 0.1 mM).

Like in ascorbic acid and hydrogen peroxide, a linear dependence of concentration on the output current is observed in paracetamol (acetaminophen) case, too. For it was also analyzed under the same conditions. Sensitivity of Pt electrode to paracetamol is 1.67 $\mu\mu A/mm$ (83.5 $\mu A/cm^2$ mM). After the modification of the Pt electrode with nafion layers, the sensitivity decreased up to 0.77-0.78 $\mu A/mM$ (38-39 $\mu A/cm^2$ mM), which is up to 46% from the initial value (Fig. 15).

Since paracetamol does not contain negative ionizing group, this separation according to molecular size can be one of main reasons for decrease of current response.

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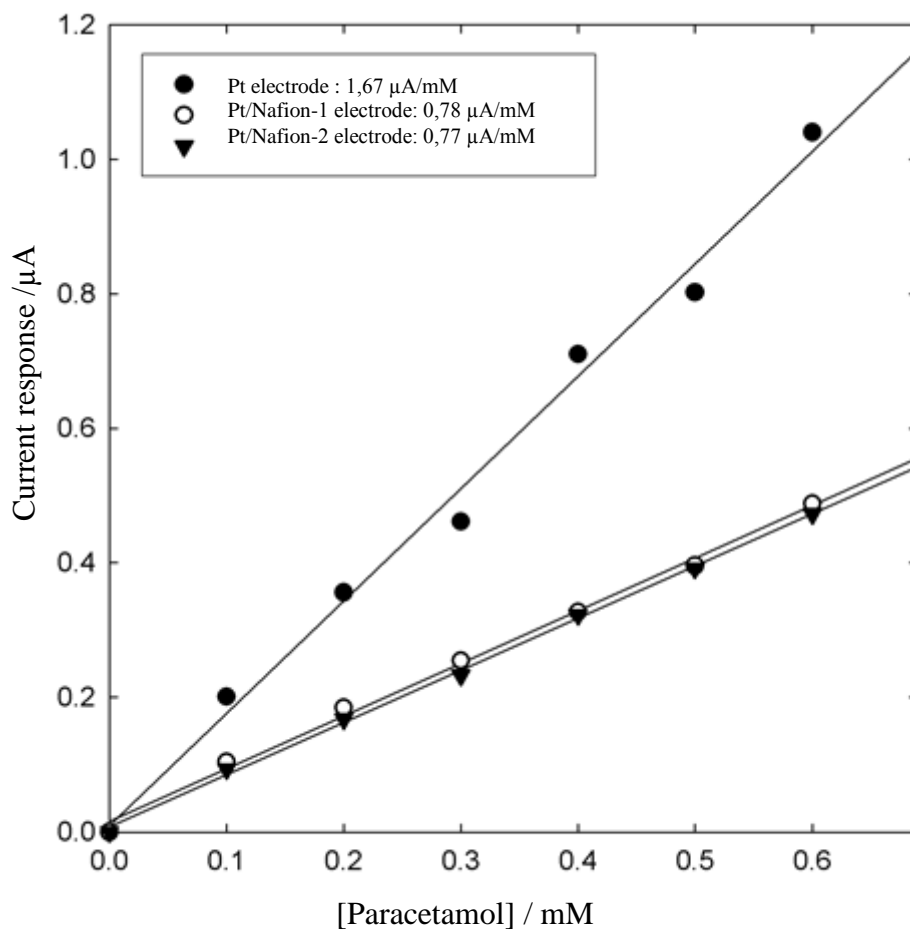
Fig.15. Dependence of paracetamol concentration on the current on Pt electrode unmodified and modified with nafion layers.

During the work the following tests were carried out: Three drops of nafion solution were instilled, but we only managed to record the cyclic voltammogram in sulphuric acid. After washing with distilled water, it was clear that the layer has crumbled. Moreover, each experiment with nafion was performed only with freshly instilled 1 or 2 drops of nafion. This was done because the lifetime of nafion layer is not long. After the tests with hydrogen peroxide, the layer began to disintegrate, so the tests with ascorbic acid or paracetamol were carried out with freshly modified Pt electrode.

3. CONCLUSIONS

Electropolymerized poly (o-phenylenediamine) layer has good permeability to peroxide and keeps ascorbate well, and electropolymerized polypyrrole layer almost does not show any difference between the determinable analyte (hydrogen peroxide) and disruptive analytes (ascorbic acid, paracetamol). Current response to hydrogen peroxide and paracetamol for polyaniline modified electrode anodic is practically the same. In order to use PANI film production in the production of biosensors, it should be noted that, although the PANI is often considered to be suitable matrix for the enzyme immobilization, it does not show any difference between the hydrogen peroxide, as enzyme catalysis of reaction product, and paracetamol. Conversely, increase of current response for ascorbate when covering the electrode with PANI layer is observed. As a result, PANI modified electrode shows high sensitivity to ascorbate compared with clean platinum electrode. This allows using this modified electrode as an amperometric ascorbate sensor. Nafion coating is the best for the production of biosensors for the determination of hydrogen peroxide.

MODIFIKUOTŲ ELEKTRODŲ ELEKTROCHEMINIO ATSAKO Į BIOLOGIŠKAI SVARBIŲ ANALIČIŲ PALYGINAMASIS TYRIMAS

Santrauka

Polianilinu modifikuotas Pt elektrodas buvo ruošiamas darbui dviem būdais. Elektropolimerizacija buvo atliekama 0,5 M sieros rūgšties tirpale, turinčiame 0,05 M anilino. Pirmu atveju, elektrodo potencialas buvo palaikomas pastoviu 0,8 V, keičiamas buvo elektropolimerizacijos laikas nuo 3 iki 20 min. Atlikus polimerizaciją per nustatytą laiką, elektrodas buvo nuplaunamas distiliuotu vandeniu ir perkeliamas į sieros rūgšties tirpalą. Sieros rūgšties tirpale buvo užrašoma ciklinė voltamperograma intervale [-0,1;+0,5] V skleidimo greičiu 50 mV/s. Toliau modifikuotas elektrodas buvo nuplaunamas vandeniu ir perkeliamas į 0,1 M fosfatinį buferinį tirpalą (pH 7,0). Eksperimentų metu mikrošvirkštu mažomis porcijomis į buferinį tirpalą buvo įlašinama atitinkamos analitės porcija (vandenilio peroksidas, askorbo rūgštis, paracetamolis). Elektrodas buvo laikomas esant pastoviam 0,6 V potencialui. Prieš kiekvieną eksperimentą buvo atliekami tyrimai su švariu Pt elektrodu.

Polipirolų ir o-fenilendiaminų modifikuoti elektrodai buvo ruošiami analogiškai.

Ruošiant darbui nafionu padengtą elektrodą, nafiono tirpalas alifatinių alkoholių tirpale buvo užlašinamas ant aukštyn kojomis apversto švaraus paruošto darbui Pt elektrodo (100 μl) ir paliekamas džiūti kambario temperatūroje. Kai kuriuose eksperimentuose, buvo užlašinami du lašeliai nafiono tirpalo iš eilės, leidžiant kiekvienam iš jų išdžiūti atskirai. Taip paruoštas elektrodas nuplaunamas distiliuotu vandeniu ir perkeliamas į H_2SO_4 0,5M tirpalą, ir užrašoma ciklinė voltamperograma. Toliau modifikuotas elektrodas buvo nuplaunamas vandeniu ir perkeliamas į 0,1 M fosfatinį buferinį tirpalą (pH 7,0). Eksperimentų metu mikrošvirkštu mažomis porcijomis į buferinį tirpalą buvo įlašinama atitinkamos analitės porcija (vandenilio peroksidas, askorbo rūgštis, paracetamolis). Elektrodas buvo laikomas esant pastoviam 0,6 V potencialui. Prieš kiekvieną eksperimentą buvo atliekami tyrimai su švariu Pt elektrodu. Ciklinė Pt elektrodo voltamperograma buvo užrašoma [0; 1,5 V] intervale 50 mV/s skleidimo greičiu.

Buvo ištirtos ir nustatytos optimalios elektrolaidžių polimerų nusodinimo sąlygos. Polianilinu modifikuotas Pt elektrodas buvo ruošiamas dviem būdais. Elektropolimerizacija buvo atliekama 0,5 M sieros rūgšties tirpale, turinčiame 0,05 M anilino. Pirmu atveju, elektrodo potencialas buvo palaikomas pastoviu 0,8 V ir buvo keičiamas elektropolimerizacijos laikas nuo 3 iki 20 min. Didėjant elektropolimerizacijos laikui, smailių dydis sparčiai auga. Ypač spartus smailių padidėjimas yra stebimas, pailginus elektropolimerizacijos laiką nuo 5 iki 15 min. Tuo

pat metu lėtesnis smailių augimas pastebimas, elektropolimerizuojant Pt elektrodą ilgesnį laiką (iki 20 arba 30 min). Antru atveju 0,5 M H_2SO_4 tirpale, turinčiame 0,05M anilino, buvo registruojamos ciklinės voltamperogramos, skleidžiant potencialą 50 mV/s greičių intervale nuo –0,1 iki +1,0 V. Buvo keičiamas potencialo skleidimo laikas nuo 3 iki 30 min. Didėjant elektropolimerizacijos laikui, smailių dydis sparčiai didėja. Ypač spartus smailių padidėjimas yra stebimas, pailginus elektropolimerizacijos laiką nuo 20 iki 30 min. Kuomet lėtesnis smailių augimas pastebimas, elektropolimerizuojant Pt elektrodą trumpesnį laiką (iki 10 min).

Nafiono atveju Pt vielos elektrodas buvo įtvirtinamas laikiklyje, apverčiant jį aukštyn kojom. Ant Pt paviršiaus mikrošvirkštu buvo užlašinamas vienas lašas (*ca.* 100 μl) nafiono tirpalo alifatinių alkoholių tirpale. Elektrodas paliekamas džiūti kambario temperatūroje. Kituose eksperimentuose buvo užlašinami 2 ir 3 lašai nafiono tirpalo, leidžiant kiekvienam iš jų išdžiūti atskyrai. Buvo bandoma užlašinti 3 Nafiono lašus. Bet jau po pirmojo ciklo sluoksnis sutrupėdavo.

Ortofenilendiaminu modifikuotas Pt elektrodas buvo ruošiamas dviem būdais. Elektropolimerizacija buvo atliekama 0,5 M sieros rūgšties tirpale, turinčiame 0,05 M ortofenilendiamino. Pirmu atvejų 0,5 M H_2SO_4 tirpale, turinčiame 0,05M ortofenilendiamino, buvo registruojamos ciklinės voltamperogramos, skleidžiant potencialą 50 mV/s greičiu intervale nuo –0, 2 iki +1, 2 V. Buvo užrašomi 5,10 ir 15 ciklai. Ciklinėje voltamperogramoje yra stebimas vienas oksidacijos pikas prie 1.1 V, kuris atsiranda dėl ortofenilendiamino polimerizacijos, ir redukcijos pikas prie 0,05 V. Oksidacijos pikas su kiekvienu ciklu aiškiai mažėja, ir piko potencialas pasislenka teigiamo potencialo link. Tai rodo santykinai mažą polimerinės plėvelęė laidumą. Antru atveju elektrodo potencialas buvo palaikomas pastoviu 0,8 V ir buvo keičiamas elektropolimerizacijos laikas nuo 5 iki 15 min. Palyginus šios du eksperimentus, galima padaryti išvadą, kad atliekant polimerizaciją esant pastoviam potencialui, kreivės gaunasi gražesnės, aiškiai atskirtos viena nuo kitos. Naudojant potencialo ciklinimą, kreivės susilieja.

Polipirolu modifikuotas Pt elektrodas buvo ruošiamas dviem būdais. Elektropolimerizacija buvo atliekama 0,1M KCl tirpale, turinčiame 0,1M pirolo. Pirmu atveju 0,1M KCl tirpale, turinčiame 0,1M pirolo, buvo registruojamos ciklinės voltamperogramos, skleidžiant potencialą 50 mV/s greičiu intervale nuo –0,4 iki +1,0 V skirtingą laiką nuo 3 iki 10 min. Antru atveju elektrodo potencialas buvo palaikomas pastoviu 0,8 V ir buvo keičiamas elektropolimerizacijos laikas nuo 3 iki 10 min.

Buvo ištirtas pasirinktų analičių atsakas ant modifikuotų elektrodų. Anodinės srovės atsakas tiek vandenilio peroksido tiek paracetamolio atveju yra atsilikęs beveik tuo pačiu

laipsniu ant PANI modifikuoto platinos elektrodo. Nors PANI yra dažnai laikomas geriausia matrica fermentų imobilizavimui, jis beveik nerodo jokio skirtumo tarp vandenilio peroksido, kaip fermentų katalizės reakcijos produkto, ir paracetamolio. Askorbato atveju, priešingai, padengiant Pt elektrodą PANI sluoksniu, yra stebimas srovės augimas. Kaip rezultatas PANI modifikuotas elektrodas rodo didelį jautrumą askorbatui, palyginti su švariu platinos elektrodu. Tai leidžia naudoti šį modifikuotą elektrodą kaip amperometrinį askorbato jutiklį.

Nafion lašu dengtas Pt elektrodas turi labai aukštą pralaidumą peroksidui ir yra beveik visiškai nepralaidus askorbatui.

Ortofenilendiamino plėvelė gerai praleidžia vandenilio peroksidą ir beveik nepraleidžia paracetamolio ir askorbo rūgšties molekulių.

Polipirolo plėvelė sulaiko vandenilio peroksidą. Polipirolo plėvelė stabdo askorbo rūgšties difuziją ir nepraleidžia paracetamolio molekules. Esant aukštam potencialui oksiduotas polipirolas (OPpy) geriau sulaiko vandenilio peroksidą. OPpy plėvelės įtaka askorbo rūgščiai ir paracetamoliui nėra iki galo aiški. Tai yra dėl pasikeitusio plėvelės laidumo, plėvelės struktūros. Elektropolimerizuotas poli (o-fenilendiamino) sluoksnis turi gerą pralaidumą peroksidui ir gerai sulaiko askorbatą, o elektropolimerizuotas polipirolo sluoksnis beveik nerodo jokio skirtumo tarp nustatomosios analitės (vandenilio peroksido) ir trukdančių analičių (askorbo rūgštis, paracetamolis). Polianilinu modifikuotam elektrodui anodinės srovės atsakas vandenilio peroksidui ir paracetamoliui yra praktiškai vienodas. Siekiant panaudoti PANI plėvelę biojutiklių gamyboje, reikėtų pažymėti, kad, nors PANI yra dažnai laikomas tinkama matrica fermento imobilizavimui, jis nerodo jokio skirtumo tarp vandenilio peroksido, kaip fermentų katalizės reakcijos produkto, ir paracetamolio. Askorbatui, priešingai, padengiant elektrodą PANI sluoksniu, yra stebimas srovės atsako padidėjimas. Kaip rezultatas, PANI modifikuotas elektrodas rodo didelį jautrumą askorbatui, palyginti su švariu platinos elektrodu. Tai leidžia naudoti šį modifikuotą elektrodą kaip amperometrinį askorbato jutiklį. Gaminant biosensorius vandenilio peroksido nustatymui, geriausiai tinka Nafiono danga.

Published works of the dissertation topic and conference list

Scientific articles in journals, included in the Institute for Scientific Information (ISI) list:

1. S. Kozlovskaja, R. Garjonytė and A.Malinauskas Response of hydrogen peroxide, ascorbic acid, and paracetamol at a platinum electrode coated with microfilms of polyaniline. Microhim Acta, 2009,166:229-234

2. S. Kozlovskaja, R. Garjonytė, and A.Malinauskas Amperometric responses of some biosensor –related analites at electrodes, coated with semipermeable polimer layers: a comparative study. CHEMIJA, 2012, Vol. 23,7-11

Conference proceedings:

1. Svetlana Kozlovskaja. Dodekavolframokobaltato (III) imobilizavimas stikliškosios anglies elektrodo paviršiuje. Neorganinių junginių chemija ir technologija, KTU, Kaunas, 2009 m.

2. Svetlana Kozlovskaja · Gintaras Baltrūnas · Albertas Malinauskas. Amperometric responses of some biosensor – related analites at electrodes, coated with semipermeable polimer layers: a comparative study. Chf, VU, 2011

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6. Reikšmingiausi moksliniai, metodiniai darbai (parengti per paskutinius 5 metus, ne daugiau kaip 5 darbai)
Malinauskas, Albertas, Garjonytė, Rasa, **Kozlovskaja, Svetlana** (2012). Amperometric response of some biosensor-related analytes at electrode coated with semipermiable polymer layers: a comparative study // Chemija. Vol. 23 No.1, p. 7-11.
Malinauskas, Albertas, Baltrūnas, Gintaras, **Kozlovskaja, Svetlana** (2009). Response of hydrogen peroxide, ascorbic acid and paracetamol at a platinum electrode coated with microfilms of polyanaline // Microchim Acta. Vol. 166, p. 229-234
Svetlana Kozlovskaja · Gintaras Baltrūnas · Albertas Malinauskas. Amperometric responses of some biosensor – related analytes at electrodes, coated with semipermeable polymer layers: a comparative study. Chf, VU, 2011
Svetlana Kozlovskaja. Dodekavolframokobaltato (III) imobilizavimas stikliškosios anglies elektrodo paviršiuje. Neorganinių junginių chemija ir technologija, KTU, Kaunas, 2009 m

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Date	**Institution**	**Position**
Nuo 2007	UAB "Vilniaus Ventos puslaidininkiai"	Engineer-technologist
2007	IĮ "Ekolabora"	Chemist-analyst
2006	UAB "Soveta Baltika"	Ombudsman
2005	National Public Health Laboratory	Laboratory assistant

5. Research areas
Biochemistry, biosensors, active electrodes, physical chemistry

6. The most significant scientific, methodical work (completed within the last 5 years, not more than 5 works)
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Svetlana Kozlovskaja · Gintaras Baltrūnas · Albertas Malinauskas. Amperometric responses of some biosensor – related analytes at electrodes, coated with semipermeable polymer layers: a comparative study. Chf, VU, 2011
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