VILNIUS UNIVERSITY
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STUDY OF ELECTROCATALYTIC PROCESSES AT PRUSSIAN BLUE MODIFIED GLASSY CARBON ELECTRODE

Summary of Doctoral dissertation
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VILNIAUS UNIVERSITETAS
CHEMIJOS INSTITUTAS

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ELEKTROKATALIZINIŲ PROCESŲ TYRIMAS ANT BERLYNO MĖLYNUOJU MODIFIKUOTO STIKLO ANGLIES ELEKTRODO

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INTRODUCTION

Electrocatalysis is an acceleration of electrochemical reactions using specific materials that are present either in a solution or bound to the surface of an electrode. By changing the nature of electrode material or physical – chemical properties of its surface, it is possible to change the rate of electrochemical processes. Use of various electrocatalytic processes of electrochemical synthesis and clarification of vital reactions in which biologically active materials (enzymes) participate are expanding nowadays.

Amperometric hydrogen peroxide sensor is an important part of glucose biosensor. Glucose biosensor, in which glucose oxidase (GOD) is incorporated, is used to measure the amount of glucose in blood, other biological fluids, food products and drinks. Hydrogen peroxide sensor is based on electrochemical (anodic or cathodic) detection of this analyte, formed in the course of enzyme catalysed oxidation of enzyme substrate by dissolved oxygen [1,2].

Different techniques have been proposed to develop efficient and interference-free amperometric sensors for hydrogen peroxide. From these, the use of an electrocatalytic layer which enables the detection of peroxide at a low electrode potential seems to be very promissing. Among many electrocatalysts, transition metal hexacyanoferrates are often considered as most prominent substances.This work is focused on glassy carbon electrode (GCE) modified by iron hexacyanoferrate (Prussian blue, PB).

Many scientists that worked with electrodes modified by Prussian blue concluded that this electrocatalytic layer is gradually decomposed in pH neutral solutions during cathodic reduction of hydrogen peroxide. Prussian blue (PB) is also unstable in alkaline solutions, therefore gradually losing electrocatalytic activity. This characteristic was emphasized by many scientists, including ourselves[3]. Another problem with electrode modified by Prussian blue is that response of hydrogen peroxide cathodic current diminishes in solution containing ascorbate and is dependent on ascorbate concentration[4].

It is clear that a deeper analysis on hydrogen peroxide reduction mechanism on PB modified electrode is necessary in order to evade known obstacles of this important and perspective process. For this purpose, a detailed study of electrochemical reduction of hydrogen peroxide, as well as of oxidation of ascorbate at Prussian blue modified electrode, along with the study of its stability and decomposition kinetics, are necessary.

It is essential to ascertain the selectivity, sensitivity and stability of Prussian blue modified electrode to abovementioned analyte and species. Hopefully, these studies would lead to a better understanding of electrode processes taking place at Prussian blue modified electrode, and to development of an efficient and interference-free detection system for hydrogen peroxide as a part of enzyme-based biosensors.

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[1] A.A. Karyakin, O.V. Gitelmacher, E.E. Karyakina. *Anal. Lett.* 27 (**1994**) 2861-2869.
[2] A.A. Kayakin, O.V. Gitelmacher, E.E. Kayakina. *Anal.Chem.* 67 (**1995**) 2419-2423.
[3] A. Malinauskas, R. Araminaitė, G. Mickevičiūtė, R. Garjonytė. *Mater. Sci. Eng. C*, 24 (**2004**) 513–519
[4] A. Malinauskas, G. Mickevičiūtė, R. Araminaitė, R. Garjonytė. *Chem. Anal. (Warsaw)* 51 (**2006**) 809-818.

The main purpose of this work:

Study of electrochemical hydrogen peroxide and ascorbate reactions on electrodes modified by Prussian blue, with the aim to apply these electrodes in creation of sensors and biosensors.

Goals:

- ✓ To study of hydrogen peroxide and ascorbate electrochemical behavior on PB modified electrode in pH 5.5 and pH 7.3 phosphate solution applying cyclic voltamperometric (CV) analysis.
- ✓ To study the cathodic reduction of hydrogen peroxide using rotating disk electrode.
- ✓ To study the anodic oxidation of ascorbate using rotating disk electrode.
- ✓ To study the stability of PB modified electrode during cathodic reduction of hydrogen peroxide.
- ✓ Preliminary studies on the applicability of Prussian blue modified electrode for biosensors.

SCIENTIFIC NOVELTY OF THE WORK

For the first time, a detailed study of electrocatalytic reduction of hydrogen peroxide and ascorbate oxidation has been provided with the use of a rotating disk electrode.

The kinetics of decomposition of PB modified electrode in the course of a cathodic reduction of hydrogen peroxide has been studied, and the influence of different factors to this process has been determined.

Prototypes of sensors and biosensors, for different analytes have been elaborated and tested.

Approbation and publication of the work

Material presented in the thesis is based on 5 papers published in the international scientific journals. The results were also presented at 2 Lithuanian scientific conferences.

Structure of the dissertation

The dissertation is written in Lithuanian language, it consists of four chapters. It consists of 104 pages, of 38 figures and of 8 tables.

1. MATERIALS AND METHODS

1.1. Preparation of electrode modified by Prussian blue

1.1.1. Preparation of glassy carbon electrode

Glassy carbon electrode (GCE) rod (ø 3 mm) from „Sigradur K, HTW“ (Germany) was positioned in a plastic tube or in case of RDE – in teflon. Before each new electrode preparation the surface of glassy carbon electrode has been polished by 1 μm and then by 0.3 μm Al_2O_3 paste until mirror-like shining was induced. Polished

electrodes were placed into ultrasound bath for 3 minutes to remove any dirt from the surface.

1.1.2. Electrodeposition of a PB layer at glassy carbon electrode

We employed BASi-Epsilon potenciostat (from Bioanalytical Systems Inc., USA) connected to a computer. Standard trielectrode scheme was used in amperometric measurements. In this work glassy carbon electrode was employed as working electrode, BASi RE-5B Ag/AgCl, 3M NaCl electrode as a reference electrode, with potential of 0.209 V *vs.* NHE and glassy carbon electrode, in which glassy carbon rod is protruded 6 mm from the tube as a couter elctrode.

Glassy carbon electrode was placed in 2.5 mM $FeCl_3$ and 2.5 mM $K_4[Fe(CN)_6]$ solution, and an electrode potential of 0.4 V has been applied for 60 s. This way a layer of Prussian blue is deposited on glassy carbon electrode.

After preparation, PB modified electrode has been conditioned by potential cycling procedure in a solution of 0.1 M of HCl and 0.1 M of KCl from -0.05 to 0.35 V. At an optimum, the cycling has been performed for 76 cycles at a potential scan rate of 50 mV/s. As a result, the electrode showed stable electrochemical behavior, and has been characterised by the midpoint potential of 0.178 V, and a peak separation of 56 mV.

1.2. Biosensor preparation

Glassy carbon electrode modified by Prussian blue is submerged into GOD solution, containing 350 µl/ml chitosan (Chi) + 100 mg/ml GOD + 50 µl/ml 2.5% hydrogen glutaraldehyde (Gla). Then GOD solution excess is gently shaken off the electrode and the electrode is dried in room temperature for approximately an hour. Glucose oxidase from *Aspergillus niger* from „Merck“ (Germany) with a specific activity of 90 U/mg has been used. Following this way, a GCE/PB/0.35Chi-GOD-Gla electrode has been prepared.

Similarly, GCE/PB/0.4Chi-GOD-Gla and GCE/PB/0.5Chi-GOD-Gla electrodes have been prepared by using 400 µl/ml Chi and 500 µl/ml Chi solutions. For some electrodes, a dialysis membrane has been placed over an enzyme layer.

After the modifications all electrodes were carefully washed using distilled water and stored in phosphate buffer pH 7.3 in a refrigerator at 4°C, while not in use. The electrodes prepared have been tested for biosensor applications in an usual three-electrode cell.

1.3. Electrochemical study

1.3.1. Amperometric measurements

Amperometric measurements utilize standard trielectrode system, as described in 1.1.2. section.

1.3.1.2. Stability study of PB modified electrode

Two 0.1 M phosphate buffer solutions are chosen for measurments, pH 5.5 and pH 7.3, both containing 0.1 M KCl. Aliquots of hydrogen peroxide stock solutions have

been added to 15 ml buffer solution, to achieve concentration ranging from 0.01 to 1.0 mM. During the experiment solution was stirred with magnetic stirrer at a constant speed, while working electrode potential of 0.0 or 0.1 V has ben applied.

1.3.1.3. Study of biosensor stability

Evaluation of biosensor stability over time were conducted in electrochemical three-electrode system. Biosensors prepared have been stored in pH 7.3 buffer solution at 4 ºC, and their response to a definite glucose concentration has been recorded at a definite time intervals.

1.3.2. Voltamperometric analysis

1.3.2.1. Hydrodynamic voltamerometric analysis

BASi-Epsilon potenciostat and BASi RDE-2 rotating disk electrode system (both from „Bioanalytical Systems“, USA) were employed here. Rotating disk electrode is composed of glassy carbon electrode rod (ø 3 mm) press-fitted into teflon holder. During the experiments, potential sweep rate ranging from 1 to 5 mV/s has been used.

2. RESULTS AND DISCUSSION

2.1. Prussian blue modified glassy carbon electrode

2.1.1. Reduction of hydrogen peroxide at Prussian blue modified rotating disk electrode

When the electrode is non-rotated in hydrogen peroxide pH 5.5 solution, a cathodic potential scan results in cathodic peak of Prussian blue reduction near 0.16 V (Fig. 1, left). In pH 7.3 solution of hydrogen peroxide this cathodic peak is observed around 0.08 V (Fig. 1, right). In presence of hydrogen peroxide, cathodic current is observed at a potential more negative than the peak potential. This cathodic process can be described by equations (1) and (2):

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4\bar{e} + 4K^+ \leftrightarrow K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 \quad (1)$$

$$K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 + 2H_2O_2 \rightarrow Fe_4^{III}[Fe^{II}(CN)_6]_3 + 4K^+ + 4OH^- \quad (2)$$

By equalizing both equations we would have the final equation of hydrogen peroxide cathodic reduction [5].

$$H_2O_2 + 2\bar{e} \rightarrow 2OH^- \quad (3)$$

[5] A.A.Karyakin, E.E.Karyakina, L.Gorton. *Electrochem. Commun.* 1 (**1999**) 78-82.

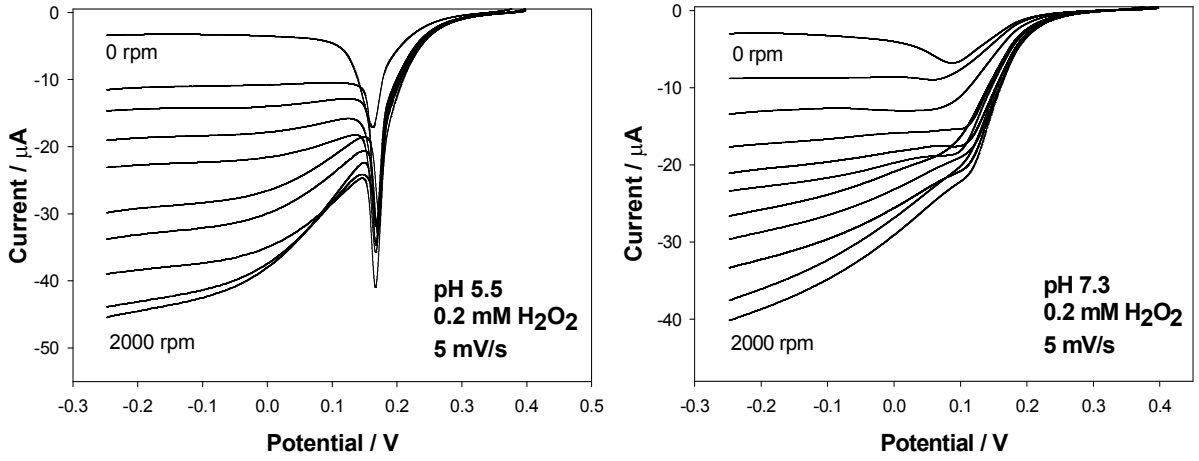

Fig. 1. Voltammograms of Prussian blue modified rotating disk electrode, obtained within scan limits of 0.4 to -0.25 V at a scan rate of 5 mV/s in pH 5.5 (left) and pH 7.3 (right) phosphate buffer solution containing 0.2 mM hydrogen peroxide. Voltamperograms were generated with different speeds of electrode rotation (0, 50, 100, 200, 300, 400, 600, 800, 1100, 1700, 2000 rpm).

In pH 5.5 solution, cathodic current is observed at electrode potential below 0.1 V (at potentials more negative than the peak potential) within a wide rotation speed range (Fig. 1, left). In pH 7.3 solution, the rise of cathodic current starts at around 0.0 V (Fig. 1, right).

When comparing both buffer solutions which have been examined, it seems that under equivalent conditions cathodic current is slightly lower in pH 7.3 solution than in pH 5.5 buffer solution (Fig. 1).

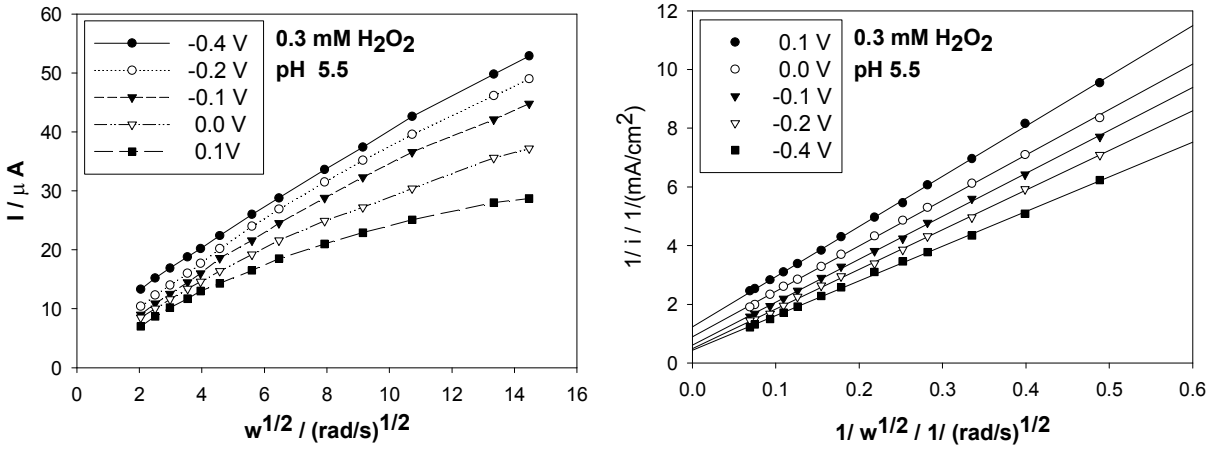

Fig. 2. Dependence of cathodic current on the square root of rotation speed, as obtained for Prussian blue modified glassy carbon electrode (left) in pH 5.5 phosphate buffer solution containing 0.3 mM hydrogen peroxide, as obtained at different electrode potentials (indicated). Data is also indicated in reverse coordinates according to Koutecky-Levich equation (right).

Fig. 2 (left) shows the dependence of cathodic current on the square root of rotation speed, which was acquired by using constant 0.3 mM hydrogen peroxide concentration in pH 5.5 buffer and altering rotation speed of the electrode in wide range

(from 40 to 2000 rpm). It is seen that cathodic current appears to be higher at more negative potentials. When potential is shifted from 0.1 to -0.4 V almost double current increase is observed for each given rotation speed. Rotating disk electrode current is expressed by Koutecky-Levich equation[6]:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_l} = \frac{1}{i_k} + \frac{1}{0.620nFAD^{2/3}\omega^{1/2}\nu^{-1/6}c} \qquad (4)$$

where i is a total current, i_k is the kinetic current (in absence of any mass transfer effects), i_l – is the mass transfer limited cathodic current.

Fig. 2 (right) depicts processed data, acquired in reverse coordinates according to Koutecky-Levich equation. Attained lines had good correlation (R = 0.999). When extrapolating this data to indefinitely high rotation speed ($1/\omega^{1/2} \rightarrow 0$), an intercept at inverse current axis is obtained, from which kinetic current (i_k) can be calculated. Under certain conditions, specified in Fig. 2, calculated i_k values vary from 0.796 to 2.658 mA/cm^2 depending on electrode potential within the limits of 0.1 and -0.4 V respectively

Similarly, the results obtained at different peroxide concentrations are presented in Table 1.

Table 1. Values of i_k as obtained in solutions of different pH at selected electrode potentials for different concentrations of hydrogen peroxide at electrode rotation speed ranging from 40 to 2000 rpm.

c(H_2O_2), mM / **E, V**	**i_k, mA/cm^2**								
	0.8*	**0.4**		**0.3**		**0.2**		**0.1**	
	pH 5.5	pH 5.5	pH 7.3	pH 5.5	pH 7.3	pH 5.5	pH 7.3	pH 5.5	pH 7.3
- 0.4	6.209	2.999	1.423	2.658	1.293	1.978	0.742	1.168	0.533
- 0.2	4.953	2.299	1.291	2.052	1.177	1.453	0.710	0.897	0.524
- 0.1	3.764	1.947	1.192	1.733	1.031	1.175	0.652	0.693	0.480
0.0	2.902	1.315	0.987	1.181	0.844	0.955	0.488	0.537	0.411
0.1	1.895	0.910	0.738	0.796	0.578	0.546	0.354	0.355	0.269

* - declinations from linear dependence. This subject will be covered later.

For biosensor applications, it is more important to perform the studies in nearly pH-neutral solutions. The corresponding data, obtained in pH 7.3 solution, are presented in Fig. 3. Within the potential window of 0.1 to -0.4 V, nearly twofold increase of catalytic current has been observed. Treatment of the data obtained according to Koutecky-Levich equation leads to i_k values varying from 1.85 to 3.56 mA/cm^2·mM, as recalculated for 1 mM of peroxide concentration. When comparing pH 5.5 buffer solution with pH 7.3 one, it appears that the density of kinetic current is roughly 1.5 – 2.5 times lower in pH 7.3 solution. This shows a slightly lower efficiency of electrocatalytic hydrogen peroxide reduction in pH-neutral solution than in lightly acidic solution.

[6] A. J. Bard, L. R. Faulkner, Electrochemical methods. Fundamentals and applications. 2nd ed., *Wiley*, New York, **2001**, pp. 331-367.

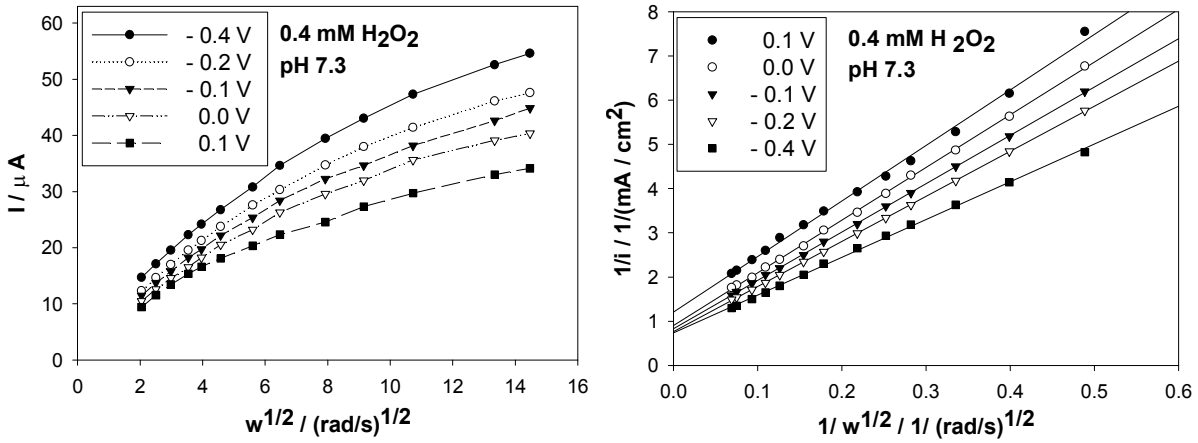

Fig. 3. Same as Fig. 2, except pH of the solution is 7.3, and it contains 0.4 mM hydrogen peroxide.

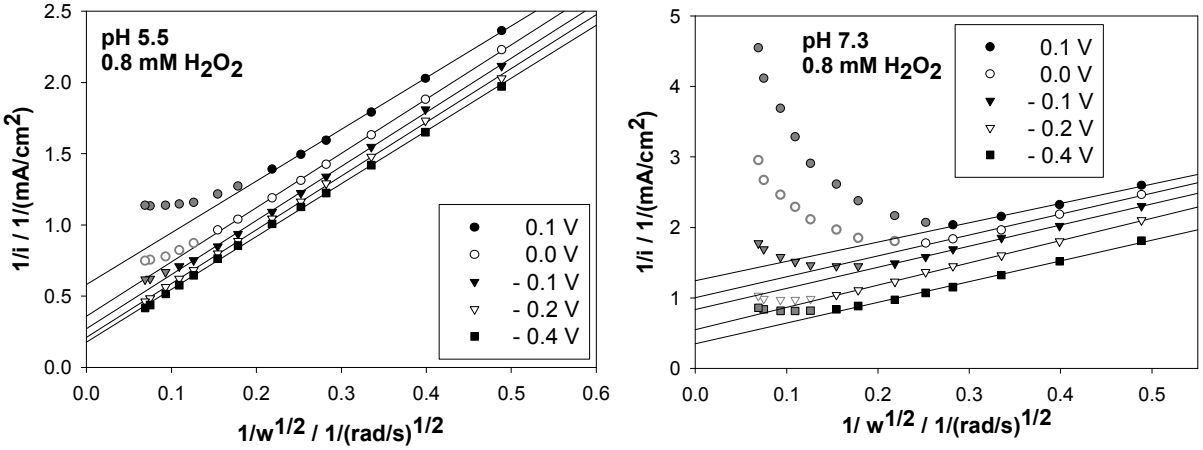

Fig. 4. 0.8 mM hydrogen peroxide cathodic reduction on rotating disk electrode modified by Prussian blue at various electrode potentials (indicated). Data is portrayed in reverse coordinates according to Koutecky-Levich equation in pH 5.5 (left) and pH 7.3 (right) buffer solutions.

In both pH 5.5 and pH 7.3 solutions, good linearization of the data (with correlation coefficient of 0.995 or even more) in accordance with Koutecky-Levich equation has been obtained at relatively low peroxide concentrations, not exceeding 0.3 or 0.4 mM. With concentrations higher than 0.6 mM, a clear deviation from linearity is observed (Fig. 4). Data, acquired in both aforementioned buffer solutions, when hydrogen peroxide concentration is 0.8 mM is presented in Koutecky-Levich coordinates in Fig. 4. A substantial deviation from linear dependence is observed with higher electrode potentials and rotation speed of the electrode. Also more significant deviations were attained while using pH 7.3 buffer solution compared to pH 5.5 one. Similar deviations from Koutecky-Levich coordinates were reported while performing oxygen reduction to HO_2^- on gold electrode[6], however, reasons of such deviations have not been explained. Density of kinetic current can be evaluated from the linear parts of these dependences, obtained at a relatively low electrode rotation speed. When recalculated to

1 mM peroxide concentration, i_k values ranging from 2.37 and 7.76 mA/cm^2·mM have been obtained within the potential limits of 0.1 to -0.4 V for pH 5.5 solution. For pH 7.3 solution, i_k values range between 1.01 and 3.36 mA/cm^2·mM under same other conditions. Calculated results are indeed slightly inferior than corresponding results attained while using lower concentrations of hydrogen peroxide. Inaccuracy that turned up due to data deviation from linear part might be the reason for this (Fig. 4).

In a physical sense, deviation from linearity, attained with high concentration of hydrogen peroxide, corresponds to decline of cathodic current with increasing rotation speed of the electrode. This might be attributed to the mechanism of electrochemical reaction of hydrogen peroxide on PB modified electrode. In a net reaction, two electrons are accepted per one molecule of hydrogen peroxide in a cathodic process (3). It is known that the mixed potential of hydrogen peroxide is pH-dependent and described by the equation[7]:

$$E = 0.84 - 0.059 \cdot pH \tag{5}$$

Potential-determining reactions are as follows:

$$H_2O_2 + \bar{e} \rightarrow OH^- + OH\cdot \tag{6}$$

$$OH\cdot + \bar{e} \rightarrow OH^- \tag{7}$$

According to this reaction scheme, peroxide molecule is reduced in two one-electron steps with the formation of intermediate short-living species, most probably OH· radicals. Alternatively, a cathodic reduction of peroxide is supposed to proceed via a chemical and the next following electrochemical steps. In the first step, peroxide is adsorbed at an electrode surface, followed by the split of peroxide molecule into two OH· radicals[7]:

$$H_2O_{2(aq)} \rightarrow 2\ OH\cdot_{(ads)} \tag{8}$$

In the second step, cathodic reduction of adsorbed OH· to hydroxyl anions proceed:

$$2\ OH\cdot_{(ads)} + 2\ \bar{e} \rightarrow 2\ OH^-_{(aq)} \tag{9}$$

It is clear that in case if the reduction of OH· radicals proceeds much faster than the dissociative adsorption of hydrogen peroxide, the linearity between an inverse cathodic current and $1/\omega^{1/2}$ should be retained even at the highest rotation velocity. In an opposite case, *viz.* at a slow electron transfer to OH· radicals, it is probable that, at a high rotation velocity, the OH· radicals are removed from electrode surface by the centrifugal force without being electrochemically reduced to hydroxyl anions. In this case, a decrease of cathodic current at elevated rotation should be observed. Thus, taking into account the present model, consisting of dissociative adsorption (8) and electron transfer (9) steps, it could be concluded that an overall reduction process is probably limited by the rate of electron transfer to OH· radicals. Alternatively, supposing a one-by-one electron transfer mechanism as described by (6) and (7) to be valid, it also could be concluded that the transfer of the second electron (*viz.*, cathodic reduction of OH· radicals to hydroxyde anions) becomes rate limiting. Obviously, the rate of this limiting step depends on electrode potential (being remarkably higher for lower electrode

[7] A. J. Bard, L. R. Faulkner. Electrochemical Methods. Fundamentals and Applications. 2nd ed., *Wiley*, New York, **2001**, pp. 331-367.

potentials), and on solution pH (being lower for higher pH value), as it follows from the data presented in Fig. 4.

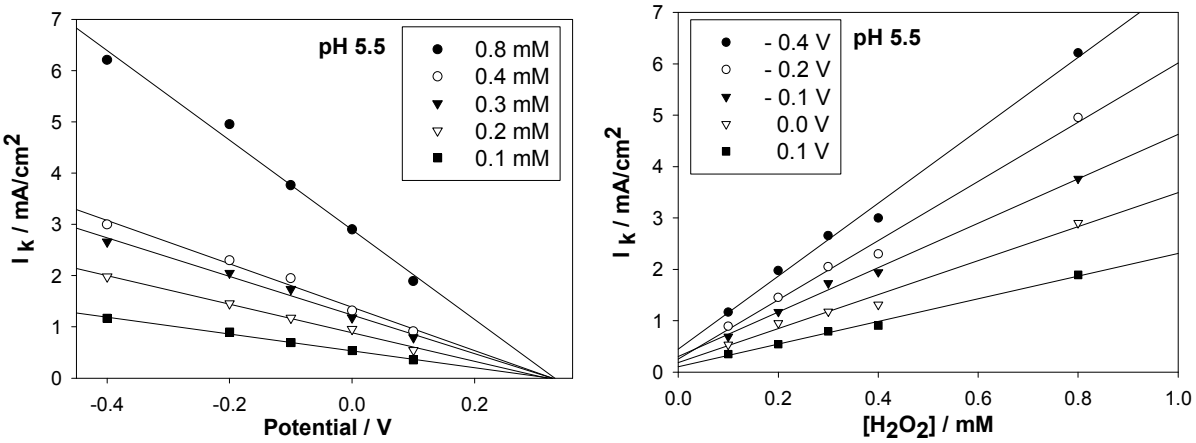

Fig. 5. i_k dependence on the potential, as obtained for different concentrations of hydrogen peroxide (left), and on hydrogen peroxide concentration with different potentials (right), in pH 5.5 buffer solution.

The values of kinetic current density obtained depend on electrode potential. For pH 5.5 solution, nearly linear dependence of i_k on electrode potential is observed, as presented in Fig. 5 (left). Extrapolation of these dependences, obtained at higher peroxide concentrations (0.3-0.8 mM), to zero kinetic current ($i_k \rightarrow 0$) yields a mean value for electrode potential of 0.33 V. This potential presents an upper potential limit for cathodic reduction of peroxide to proceed. In accordance with (10), the mixed potential for hydrogen peroxide at pH 5.5 should be 0.52 V, *i.e.* approx. 0.32 V *vs*. Ag/AgCl reference. Thus, the value of an upper potential limit for peroxide reduction, obtained from extrapolation of the data to $i_k \rightarrow 0$, coincides within error limits with the mixed potential known[8]. Also, nearly linear dependence of kinetic current on peroxide concentration has been obtained within an entire potential window studied, as presented in Fig. 5 (right). From these dependencies, a linear dependence of normalized kinetic current (the ratio of $i_k/[H_2O_2]$) on electrode potential has been obtained, as presented in an inset of Fig. 5. The latter dependence could be described by the correlation as follows:

$$\frac{i_k}{c} = \left(\frac{i_k}{c}\right)_0 + aE \qquad (10)$$

where i_k/c presents normalized kinetic current (in mA/(mM·cm^2)), $(i_k/c)_0$ – its value at a zero potential, $(i_k/c)_0 = (4.13\pm0.20)$ mA/(mM·cm^2), E – electrode potential (in V *vs*. Ag/AgCl reference), a – an empiric coefficient, presenting the slope of linear dependence, $a = (-13.54\pm1.51)$ mA/(mM·cm^2·V).

[8] A.Damjanovic, in: J.O'M.Bockris, B.E.Conway (Eds.), Modern aspects of electrochemistry, vol. 4, *Plenum Press*, New York, **1969**.

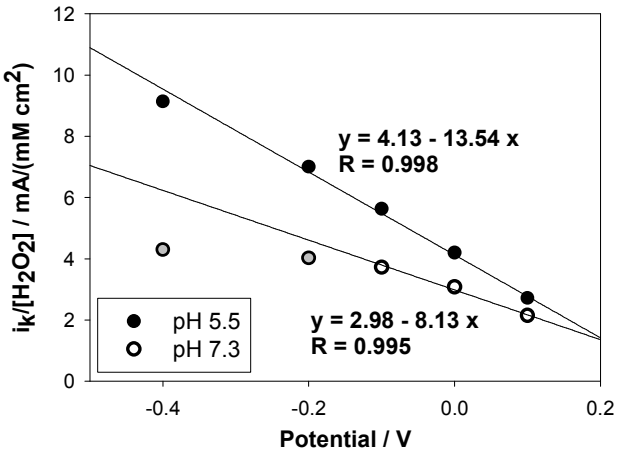

Fig. 6. $i_k/[H_2O_2]$ ratio dependence on the potential of the electrode.

Extrapolation of the data obtained in pH 5.5 solution according to the latter equation to zero current yields a zero-current potential of 0.31 V (Fig. 6). This value does not significantly differ from the potential calculated earlier (0.33 V) and from known mixed potential of hydrogen peroxide (0.32 V).

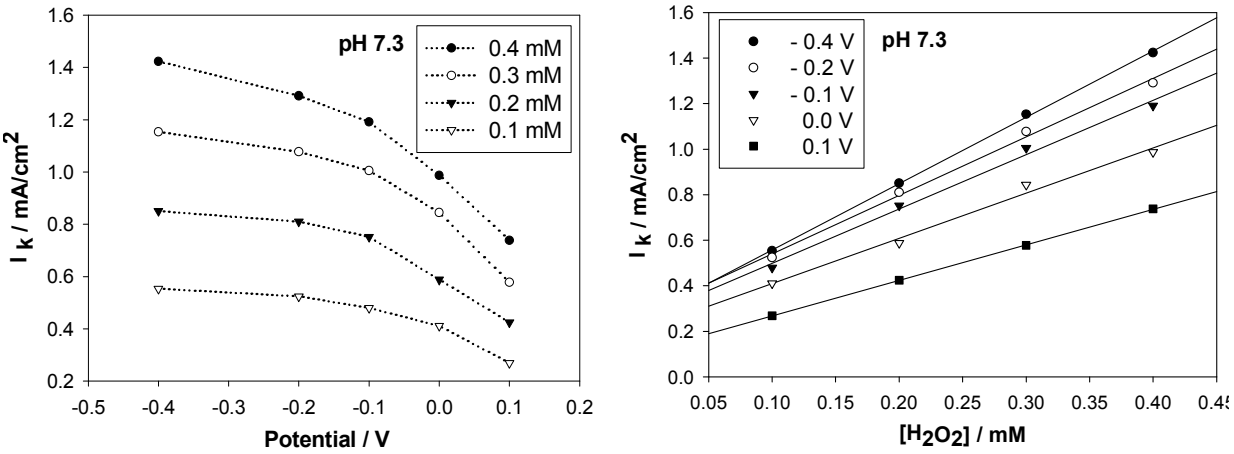

Fig. 7. Same as Fig. 5, except pH 7.3 buffer solution is used.

However in pH 7.3 solution linear dependence of kinetic current on the potential of the electrode was not obtained (Fig. 7, left). A probable reason for this is a limited rate of charge transfer, as discussed above. This deviation is clearer in pH 7.3 solution than in pH 5.5 (Fig. 4), therefore data acquired when using 0.8 mM concentrations of hydrogen peroxide was not applied in calculations. In an entire examined region of potentials almost linear dependence of kinetic current on the concentration of hydrogen peroxide (from 0.1 to 0.4 mM H_2O_2) was attained. This is presented in Fig. 7 (right). In this case linear dependence of normalized kinetic current on the potential of the electrode was attained in a narrower range of electrode potentials (from -0.1 to 0.1 V) (Fig. 6), also smaller values of normalised kinetic current were acquired, $\left(\frac{i_{kin}}{c}\right)_0$ = (2.98 ± 0.07) mA/(mM·cm^2), a = (−8.13 ± 0.87) mA/(mM·cm^2·V).

2.1.2. Oxidation of ascorbate at Prussian blue modified rotating disk electrode

The standard potential of the quasireversible redox couple ascorbate-dehydroascorbate E_0'=0.058 V *vs*. RHE at pH 7.0, i.e. −0.151 V *vs*. Ag/AgCl (3 M NaCl). At a glassy carbon electrode, the onset potential for electrooxidation of ascorbate appears around 0.1 V both in pH 5.5 and pH 7.3 solutions, as obtained at a slow potential sweep of 5 mV/s. The oxidation current grows up by shifting the potential to higher values, and by increasing of electrode rotation velocity. For Prussian blue modified electrode, a substantial increase of anodic current at lower electrode potentials is observed. At a non-rotated PB modified electrode, two well defined anodic peaks are observed for pH 5.5 solution, located at 0.10 and 0.22 V (Fig. 8, left). From these, the second peak appears well developed even in the absence of ascorbate, thus, it corresponds to anodic oxidation of a reduced form Prussian white to oxidised form Prussian blue. Rotation of the PB modified electrode results in a gradual transformation (at increasing rotation velocity) of the first peak into a prewave, followed by the 2nd peak with unchanged position. Also, an increase of anodic current at potentials more positive than the potential of 2nd peak, is observed. In pH 7.3 solution, the onset potential for ascorbate oxidation at PB modified electrode appears around 0 V, while the only anodic peak at around 0.2 V is observed (Fig. 8, right). Again, the oxidation current at potentials more positive of this peak increase by increasing rotation velocity. For pH 7.3 solution, the oxidation currents appear to be somewhat lower than for pH 5.5 solution.

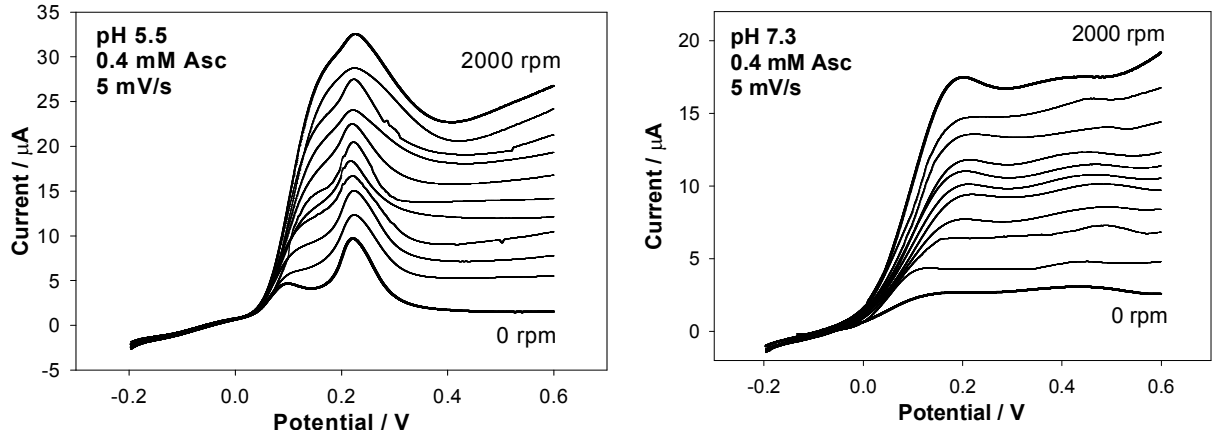

Fig. 8. Slow potential sweep (5 mV/s) voltammograms, obtained in pH 5.5 (left), and pH 7.3 solutions (rihgt) containing 0.4 mM of ascorbate, at Prussian blue modified glassy carbon electrodes at different electrode rotation velocities (0, 50, 100, 200, 300, 400, 600, 800, 1100, 1700, 2000 rpm).

The results obtained could be interpreted within the model of electrocatalytic oxidation of ascorbate at PB modified electrode. In aqueous solutions, ascorbic acid shows two reversible protonation steps, characterized by pK_1=4.17 and pK_2=11.57. In both the solutions at pH 5.5 and 7.3 ascorbic acid presents in its monoprotonated monoanion form, ascorbate. Since the redox potential for ascorbate/dehydroascorbate (Asc^-/DAsc) 2-electron redox couple is lower than the potential for Prussian blue –

Prussian white redox couple, ascorbate is able to reduce PB converting them into its reduced form Prussian white:

$$Fe_4^{III}[Fe^{II}(CN)_6]_3 + 2Asc^- + 4K^+ \rightarrow K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 + 2DAsc + 2H^+ \qquad (11)$$

Then, Prussian white is reoxidised electrochemically yielding an initial PB, provided that electrode potential is kept at an appropriate potential corresponding to oxidised form:

$$K_4Fe_4^{II}[Fe^{II}(CN)_6]_3 - 4\bar{e} - 4K^+ \rightarrow Fe_4^{III}[Fe^{II}(CN)_6]_3 \qquad (12)$$

In this sequence of redox processes, PB plays a role of a redox mediator–electrocatalyst shuttling electrons from ascorbate to electrode. Although electrooxidation of ascorbate proceeds even at an unmodified glassy carbon electrode (not represent), it is evident that a layer of PB, placed at electrode surface, increases the efficiency of this process by decreasing the overpotential for ascorbate anodic oxidation. According to the above reaction scheme, anodic oxidation of ascorbate would proceed within the potential limits corresponding to oxidised form of PB, *viz.* at E>0.22 V. However, it is seen from Fig. 8 that for pH 5.5 solution electrooxidation proceeds at potentials less positive than 0.22 V. Most probably, an anodic peak located at 0.10 V for non-rotated PB modified electrode corresponds to adsorption prewave. Anodic adsorption prewaves are usually observed for species with stronger adsorptivity for their reduced forms compared to oxidised ones[9].

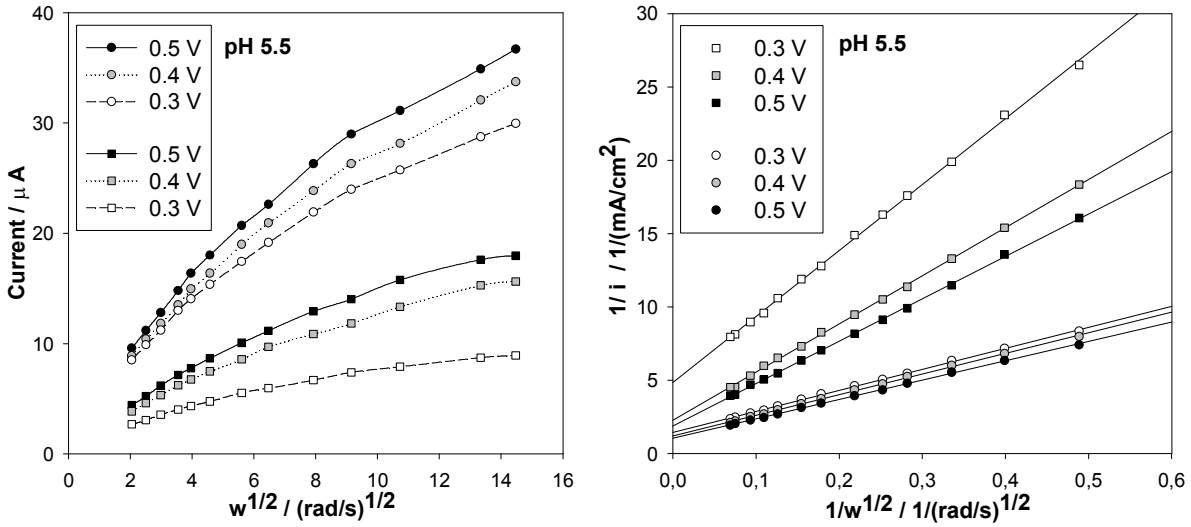

Fig. 9. Treatment of the data obtained at Prussian blue modified electrode in pH 5.5 solution for different ascorbate concentrations (● – 0,8 mM of ascorbate, ■ – 0,3 mM) and differentelectrode potentials (as indicated) in Levich (left) and Koutecky-Levich (right) coordinates.

In accordance with Levich equation[6], a linear dependence of limiting current for ascorbate electrooxidation on the square root of rotation velocity should be observed:

$$i_l = 0{,}620nFAD^{2/3}\omega^{1/2}\nu^{-1/6}c \qquad (13)$$

[9] Z. Galus, Fundamentals of Electrochemical Analysis. 2nd edn. *Ellis Horwood*, Chichester, **1994**.

where i_l is the mass transfer limited anodic current density, n is the number of transfered electrons, F is the Faraday constant, A is the rotating electrode area, D is the diffusion coefficient for hydrogen peroxide, ω is the rotation angular velocity, v is the kinematic viscosity of solution, and c is the hydrogen peroxide concentration.

Fig. 9 (left) shows that, in pH 5.5 solution, a linear dependence according to Levich equation is retained within a narrow range of relatively low rotation velocity, not exceeding *ca.* 200 rpm. Obviously, the deviation from linearity at higher rotation velocities is determined by limited rate of electron transfer reaction. In contrast to simple electron transfer processes at unmodified electrodes, there seems to be more factors that affect this rate at a PB modified electrode. At least three processes should be considered that could be responsible for kinetic limitation of electrocatalytic oxidation of ascorbate at this modified electrode:

i) electron exchange between ascorbate and PB, *viz.* the reduction of PB to Prussian white according to the above reaction (11),

ii) electron transfer through PB layer that proceeds presumably at a limited rate because of a limited electric conductivity (semiconductor-like behavior) of this electrode modifier,

iii) electron exchange between PB or Prussian white and electrode.

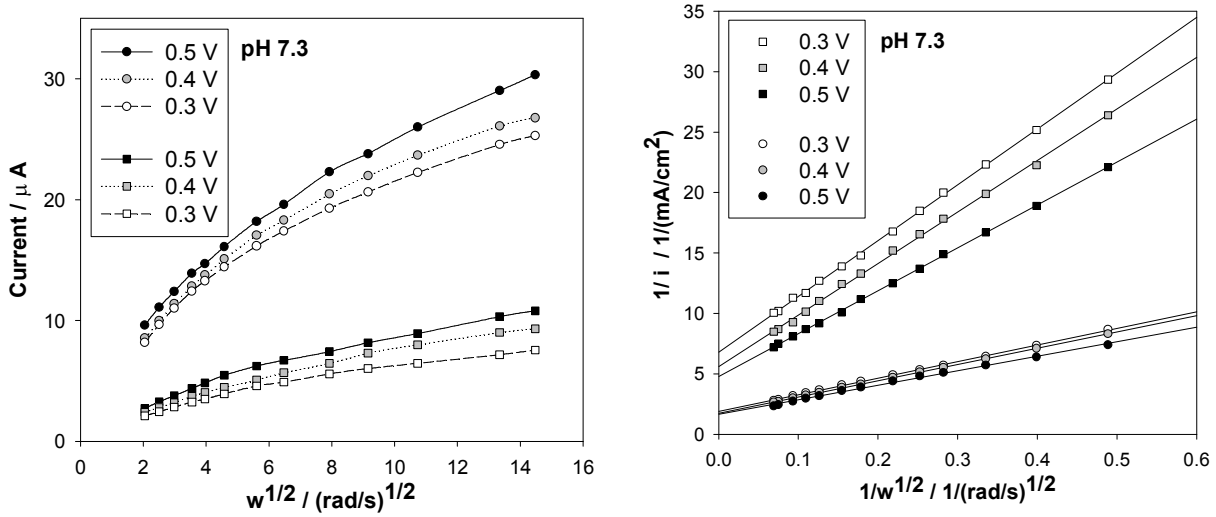

Fig. 10. Same as in Fig. 9, obtained in pH 7.3 phosphate buffer solution.

Based on RDE experiment, however, it cannot be determined what process appears rate limiting.

In any case, all factors mentioned above are included into kinetic current density, that can be attained at an indefinite high rotation velocity. In accordance with Koutecky-Levich equation (4), a net current can be divided into two components – mass transfer limited, and kinetic (or reaction limited) current.

Taking into account a linear dependence of i_l on square root of rotation velocity, as predicted by the Levich equation, a linear dependence of $1/i$ on $1/\omega^{1/2}$ could be expected. Treatment of the data obtained in these inverse coordinates is presented in Fig. 9 (right). It is seen that well-correlated linear dependencies have been obtained for electrode potentials ranging from 0.3 to 0.5 V, and for ascorbate concentrations ranging from 0.1 to 0.8 mM within an entire broad electrode rotation velocity range studied.

Similarly, the data obtained in pH 7.3 solution for different ascorbate concentrations and different electrode potentials, can be satisfactory linearized in Koutecky-Levich coordinates, as shown in Fig. 10 (right).

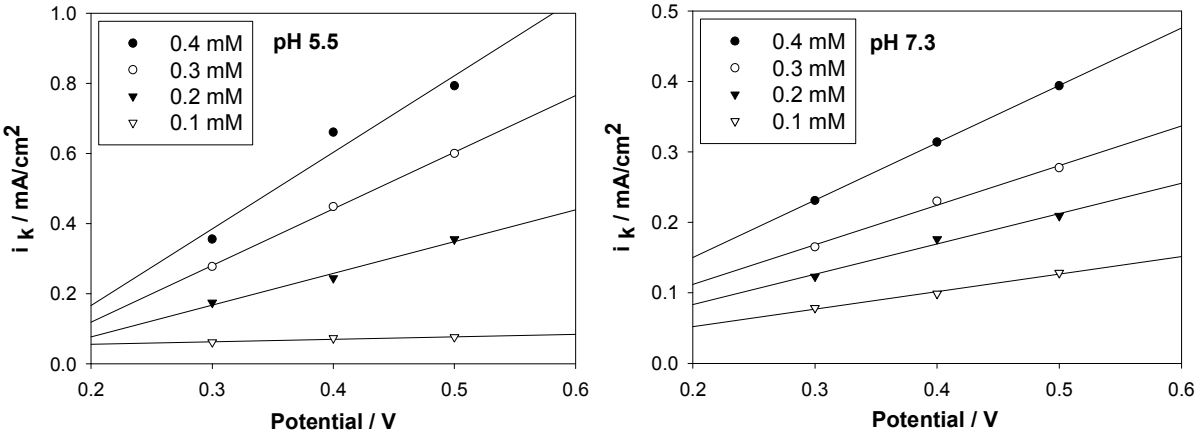

Fig. 11. i_k dependence on the potential, as obtained for different concentrations of ascorbate (as indicated). In pH 5.5 (left) and pH 7.3 buffer solution(right).

By extrapolation of linearized data (Figs. 9 and 10) to $1/\omega^{1/2} = 0$, *viz.* to indefinitely high electrode rotation velocity, the intercepts at $1/i$ axis are obtained. From these intercepts, kinetic current densities could be obtained.

Extrapolation of these dependences, obtained at ascorbate concentrations 0.2 to 0.4 mM, to zero kinetic current ($i_k \rightarrow 0$) yields a mean value for electrode potential of 0.1 V at pH 5.5 solution and at pH 7.3 should be 0.0 V (Fig. 11). Values of this potential should match the initial potential of ascorbate anodic oxidation. PB modified electrode sensitivity to ascorbate depends on the potential of the electrode.

Moreover it can be assumed from the inclination of curves that electrocatalytic oxidation of ascorbate is more effective in slightly acidic solutions than pH-neutral ones.

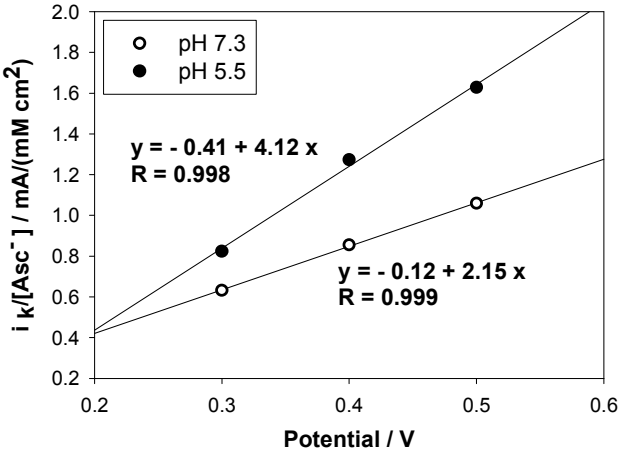

Fig. 12. $i_k/[Asc^-]$ ratio dependence on the potential of the electrode.

From these dependencies, a linear dependence of normalized kinetic current (the ratio of $\frac{i_k}{[Asc^-]}$) on electrode potential has been obtained, as presented in Fig. 12.

Linear normalized kinetic current dependence on electrode potential is shown in Fig. 12. Amplification of the current was attained by increasing the potential of the electrode. These linear dependences can be described using equation (10). *a* coefficient was calculated in pH 5.5 and pH 7.3 solutions, and is equal to 4.12 ± 0.26 and 2.15 ± 0.05 mA/(mM·cm^2·V) respectively. Therefore, sensitivity of kinetic current depends on electrode potental and is higher in pH 5.5 solution.

2.1.3. Decomposition of electrocatalytic layer of Prussian blue during cathodic reduction of hydrogen peroxide

Compact layer of Prussian blue, deposited on glassy carbon surface, provides good electrocatalytic activity for hydrogen peroxide.

The hydroxyl ions, formed in this reaction, cause a local increase of pH within or near of PB layer, leading to a gradual decomposition of PB layer. As a result, gradual decrease of cathodic current of electrocatalytic peroxide reduction is observed. It is well known that PB modified electrode possess good stability for peroxide reduction in acidic solutions, whereas, in pH neutral or slightly alkaline solutions, its stability appears to be limited.

Two hypothetical cases could be supposed regarding the decomposition of a PB layer during cathodic reduction of hydrogen peroxide.

First, there could be probably some definite “critical” value of solution pH for the decomposition rate. Over this value (i.e., in more alkaline solutions), the composition should proceed at a high rate, whereas no or slow decomposition proceeds below this critical value (in less alkaline solution). In this case, the decomposition rate should non-linearly depend on the concentration of hydrogen peroxide. At a low concentration, the rate of hydroxyl ions production is low, and, since hydroxyl ions diffuse out of a PB layer, the local pH within the PB layer does not reach or exceed the critical pH value. As a result, no or slow decomposition of this catalytic layer proceeds. At a high concentration of peroxide, however, hydroxyl ions are produced at a high rate, causing an increase of local pH up to a critical value. As a result, fast decomposition of PB layer should proceed.

In an opposite case, no critical pH value exists. Then, the rate of decomposition should be nearly proportional to the rate of hydroxyl ion production, which is proportional to the concentration of hydrogen peroxide. As a result, the rate of decomposition should be proportional to the concentration of hydrogen peroxide.

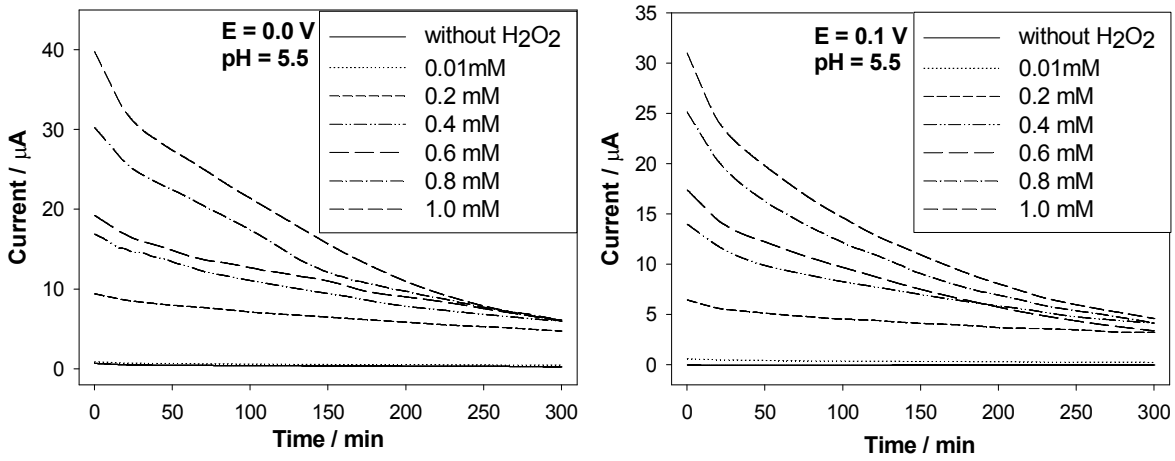

Fig. 13. The absolute decrease of cathodic current during electrolysis of hydrogen peroxide solution at different concentrations (as indicated), as obtained in pH 5.5 solution for Prussian Blue modified electrode at operating potential of 0.0 V (left) and 0.1 V (right).

Fig. 13 shows the decrease of cathodic current during prolonged electrolysis of hydrogen peroxide containing solution at pH 5.5. At a higher concentration of hydrogen peroxide, a higher initial current as well as higher absolute decomposition rate is observed (Fig. 13). Noteworthy, some residual current and its decay as well are observed even in the absence of hydrogen peroxide. Similar dependencies have been observed in pH 7.3 solution, as depicted in Fig. 14. Again, a higher initial current, and its decay rate as well are observed at higher peroxide concentration. Also, residual current and its decay are observed at pH 7.3. Obviously, the decay of cathodic current proceeds faster in pH 7.3 solution.

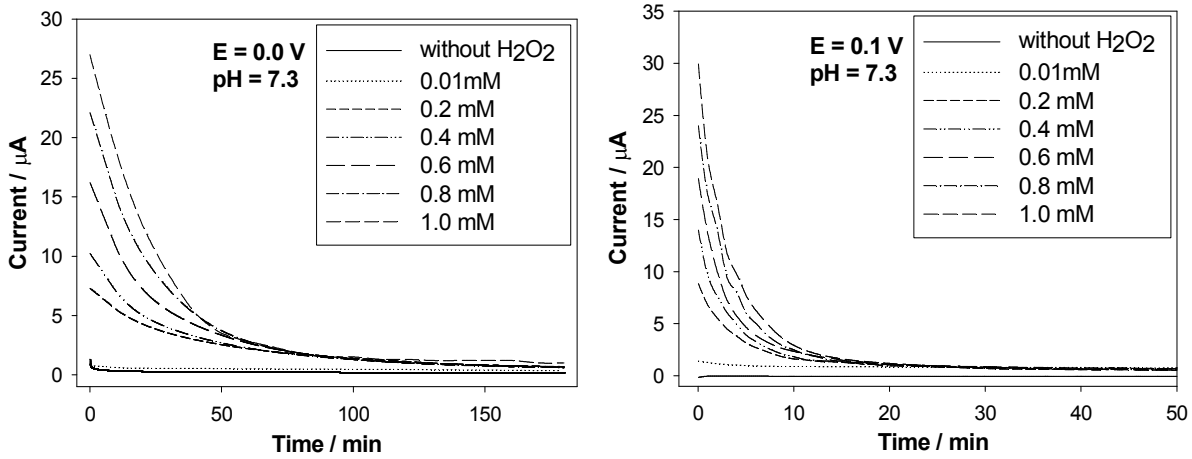

Fig. 14. Same as in Fig. 13, obtained in pH 7.3 solution.

When using higher hydrogen peroxide concentrations in pH 5.5 buffer solution higher decomposition rate and initial currents are attained, as shown in Fig. 13. When comparing acquired results with electrode potential, it is clear that the decline of cathodic current is faster at 0.1 V. Similar dependences were attained in pH 7.3 buffer solution and are displayed in Fig. 14. Higher initial currents and decomposition rate were acquired with higher concentration of hydrogen peroxide, as in case of pH 5.5. With

electrode potential of 0.1 V in pH 7.3 buffer solution a fast drop of cathodic current is observed during first 10 minutes, while with electrode potential of 0.0 V it expands up to 50 min. The rate of cathodic current decrease is higher in pH 7.3 solution.

Obviously, the electrocatalytic reduction of hydrogen peroxide at PB modified electrode and decomposition of a PB layer during electrocatalytic reduction present complex processes. A full kinetic analysis of decomposition process should include at least the following partial processes:

1. The diffusion of hydrogen peroxide to PB/solution interface or more precisely, to the reaction zone.

2. The diffusion of charge carriers (electrons) from the underlying electrode through the PB layer to reaction zone. This process should be taken into account because the PB presents a semiconductor with a limited mobility of charge carriers. Thus, under certain conditions (e.g., a thick layer of PB), the limited mobility could limit the overall rate of the electrocatalytic process.

3. The redox interaction between "active centers", if any, of PB, and hydrogen peroxide. This reaction leads to generation of hydroxyl anions and thus to an increase of a local pH that is responsible for decomposition rate.

Taking into account these partial processes, a kinetic scheme for the decomposition of PB layer could be composed, at least in principle. Because of *a priori* complications in deriving this kinetic scheme, any kind of a simple approximation in describing the kinetic dependencies would be very helpful. As a possible approximation, a simple first-order reaction kinetic scheme could be applied. The decay of cathodic current, which is related to the decomposition of catalytically active PB layer can be satisfactorily described as a firstorder kinetic process following the equation:

$$I = I_0 \cdot e^{-k \cdot t} \tag{14}$$

where I and I_0 are cathodic current and its initial value, respectively; t – the time and k – first-order current decay coefficient.

Treatment of the data obtained according to equation (14) yields first-order decomposition rate constants for particular peroxide concentration, working potential and solution pH values (Fig. 15). For a pH 5.5 solution, the decomposition rate constants vary between $2.16 \cdot 10^{-3}$ and $6.05 \cdot 10^{-3}$ min^{-1} for hydrogen peroxide concentrations of 0.2 and 1.0 mM, respectively and electrode potential of 0.0 V. This means that the half- life of decomposition varies between 321 and 115 min for the lower and upper concentrations, respectively. At 0.1 V potential, the decomposition rate constants vary from $2.18 \cdot 10^{-3}$ to $6.35 \cdot 10^{-3}$ min^{-1}. This means that the half-life of decomposition varies between 109 and 318 min, for hydrogen peroxide concentration of 0.2 and 0.8 mM, respectively.

For more alkaline solution (pH 7.3), the corresponding decomposition rate contants are higher by roughly one order of magnitude, ranging from $1.61 \cdot 10^{-2}$ to $3.76 \cdot 10^{-2}$ min^{-1} for peroxide concentrations ranging from 0.2 to 0.8 mM and electrode potential of 0.0 V, resulting in a half-life of decomposition of 43 to 18 min, respectively. At 0.1 V potential, the decomposition rate constants vary from $1.32 \cdot 10^{-1}$ to $2.49 \cdot 10^{-1}$ min^{-1}.

The results obtained show a limited stability of PB as electrode modifying material in electrocatalytic reduction of hydrogen peroxide.

Fig. 15 shows the dependence of decomposition rate coefficients on hydrogen peroxide concentration. For both pH tested, a linear dependence between these parameters is observed. In pH 7.3 solution, however, a deviation from linearity is observed at higher peroxide concentration and at a higher electrode potential (Fig. 15, right).

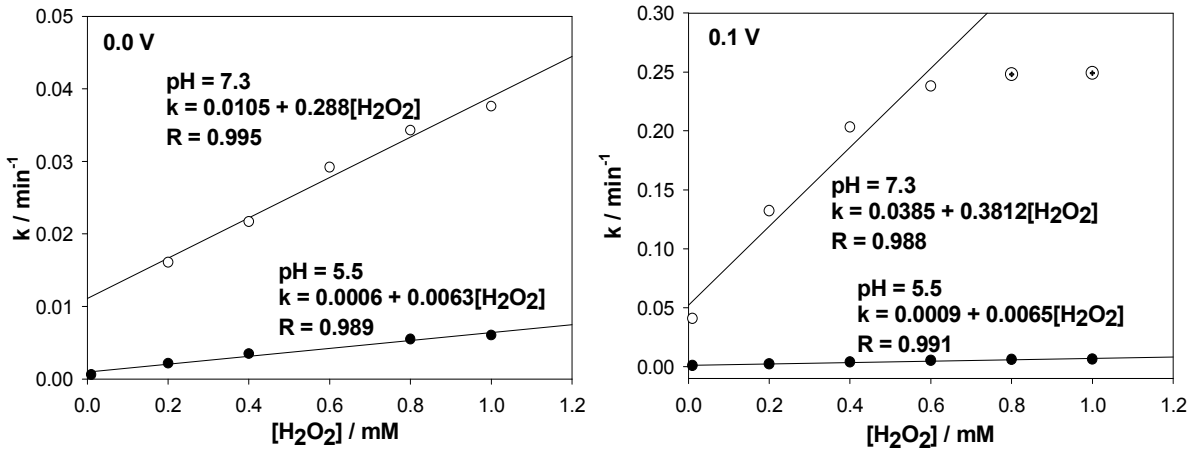

Fig. 15. Dependence of the first order cathodic current decay rate coefficient on the concentration of hydrogen peroxide, as obtained at solution pH of 7.3 and 5.5, electrode potential at 0.0 V (left) and 0.1 V (right).

The dependence obtained could be well approximated by the linear equation as follows:

$$k = a + b \cdot [H_2O_2] \tag{15}$$

where k is the first-order decomposition rate coefficient with a and b as empirical constants.

In this equation, the coefficient a presents the decomposition rate at a zero concentration of hydrogen peroxide, *i.e.* a "pure" electrochemical decomposition. This constant should depend on solution pH and on the operating potential. Also, this constant should include the decomposition at the expense of electrochemical reactions of molecular oxygen present in electrolyte. The constant b represents the sensitivity of the decomposition on hydrogen peroxide concentration therefore, should also depend on solution pH and probably on electrode potential.

The linear dependence obtained (Fig. 15, left) means that no "critical" peroxide concentration exists and the decomposition rate appears to be directly proportional to hydrogen peroxide content, except for higher peroxide concentrations in pH 7.3 solution and 0.1 V operating potential, as presented in Fig. 15 (right).

Extrapolation of linear dependencies obtained to the zero concentration of hydrogen peroxide yield the decomposition coefficients for PB layers in absence of peroxide. It could be concluded from the empirical constant a obtained from Fig. 15 (left) that in absence of peroxide, the decomposition of a PB layer proceeds *ca.* 17.5 times faster in pH 7.3 solution when compared to pH 5.5. Additionally, at 0.1 V, the process is about 43 times faster. The increase of the decomposition rate constant, b, by increasing peroxide concentration appears to be approx. 46 times higher for pH 7.3 than

for pH 5.5, at 0.0 V and approx. 59 times higher at 0.1 V. This shows a significant decrease of stability for PB layer with increasing solution pH.

2.2. Application of PB modified electrode for biosensor

Oxidase type enzymes catalyze the oxidation of various substrates by molecular oxygen. Many substrates are of high analytical interest. Among many oxidases, glucose oxidase is often used in development of new types of biosensors. Although glucose oxidase based biosensors have been commercialized long ago, they suffer from some demerits. From these, the influence of some interfering substances is of primary interest. In order to overcome this obstacle, electrocatalytic Prussian blue layers could be used. These layers enable the operation of electrode at a low electrode potential, thus excluding the influence of some most common interferents like e.g. ascorbate.

In the present work, we tried to test some prototypes of glucose sensors with the use of electrocatalytic PB layer. Over this layer, glucose oxidase has been immobilized by its crosslinking with chitosan using glutaraldehyde. Using this electrode configuration, hydrogen peroxide, that is a product of enzyme-catalyzed reaction, is electrocatalytically reduced at a PB layered electrode.

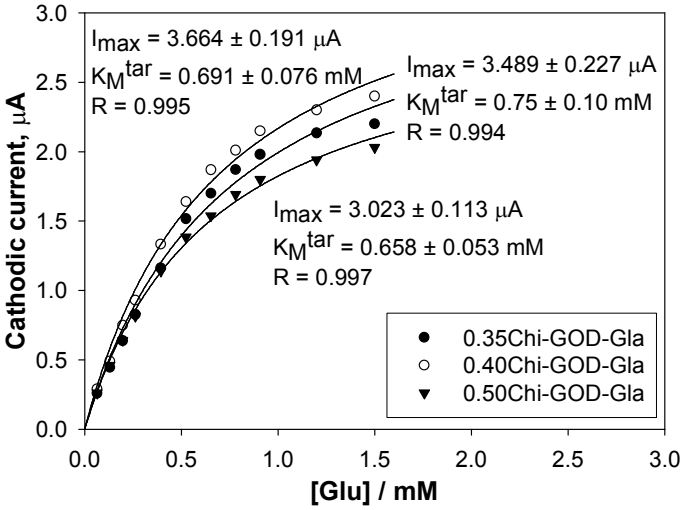

Fig. 16. GCE/PB/Chi-GOD-Gla biosensor's response to glucose. Biosensors have been prepared using different amounts of chitosan. 0,1 M phosphate buffer solution, pH 7,3;0,0 V electrode potential.

The electrodes thus prepared have been tested as biosensors for glucose. As expected, electrodes generate cathodic current that corresponds to peroxide reduction, at an operating potential as low as 0.0 V (Fig. 16). From the concentration dependencies of cathodic current, usual parameters for biosensors prepared have been obtained (Fig. 16).

Data averages were calculated with utilization of three equally modified electrodes. Maximum current was attained when 400 μl/ml Chi (52.47 ± 2.36 μA/(mM·cm^2)) was used for immobilization of GOD. Maximum currents of 46.20 ± 2.08 and 46.12 ± 2.08 μA/(mM·cm^2) have been obtained when using 350 and 500 μl/ml Chi for immobilization of GOD respectively.

For chitosan loading of 350, 400, and 500 µl/ml, K_M^{tar} of 0.75±0.10, 0.69±0.08, and 0.66±0.05 mM have been obtained, respectively, from treatment of the data obtained in Lineweaver-Burk coordinates.

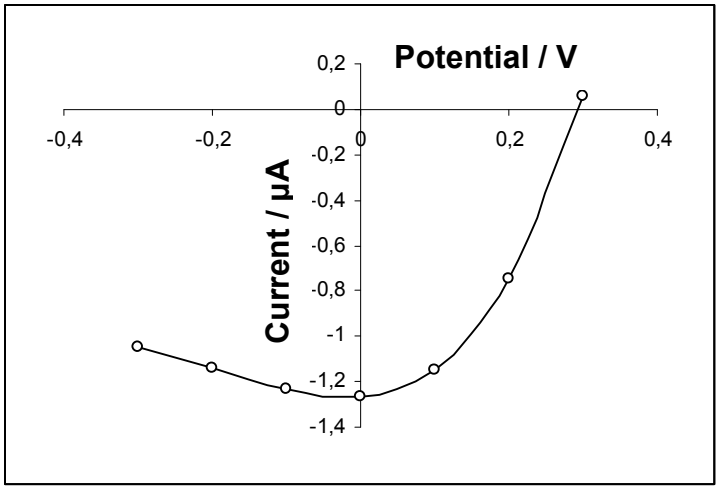

Fig 17. GCE/PB/0.4Chi-GOD-Gla electrode's current strength dependence on potential. 0.1 M phosphate buffer, pH 7.3; 0.5 mM of glucose.

Fig. 17 shows the dependence of relative biosensor output on operating potential. It is seen that the biosensor prepared could be operated in a broad window of operating potential ranging from 0.2 to -0.3 V. As compared to usual glucose biosensors based on peroxide detection at a high electrode potential (like 0.6 V or so), the present configuration enables the operation at a low potential, in an "ideal" electroanalytic window around 0.0 V. No electrochemical discharge of usual interferents like ascorbate or uric acid, present in biological fluids, could be detected at this operating potential, making the present biosensor configuration as "interference-free". Biosensors prepared show high sensitivity. At an optimum, a lower detection limit for glucose of 0.41 µM has been obtained.

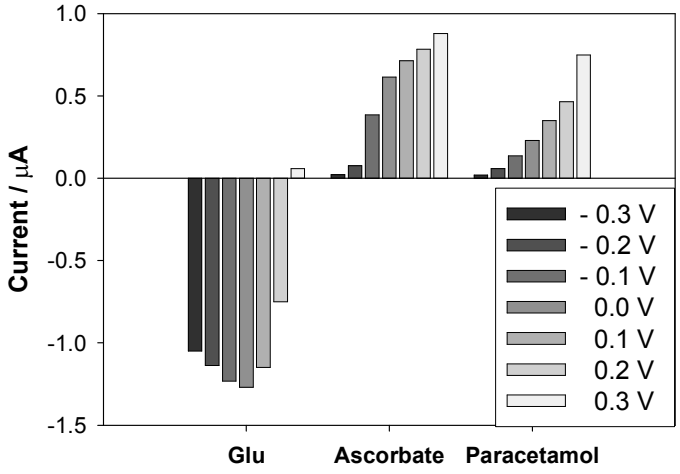

Fig. 18. Relative responses of GCE/PB/0.4Chi-GOD-Gla biosensor to glucose and interferences, as used in 0.5 mM concentration.

In order to evaluate some interferences, biosensor response to ascorbic acid and paracetamol have been evaluated. The results are pesented in Fig. 18.

Rotating disk electrode experiments with biosensors prepared have been done, and a sample of results obtained is presented in Fig. 19. It is seen that biosensor obeys dependencies, predicted by Koutecky-Levich equation within a broad glucose concentration range of 0.1 to 4.0 mM.

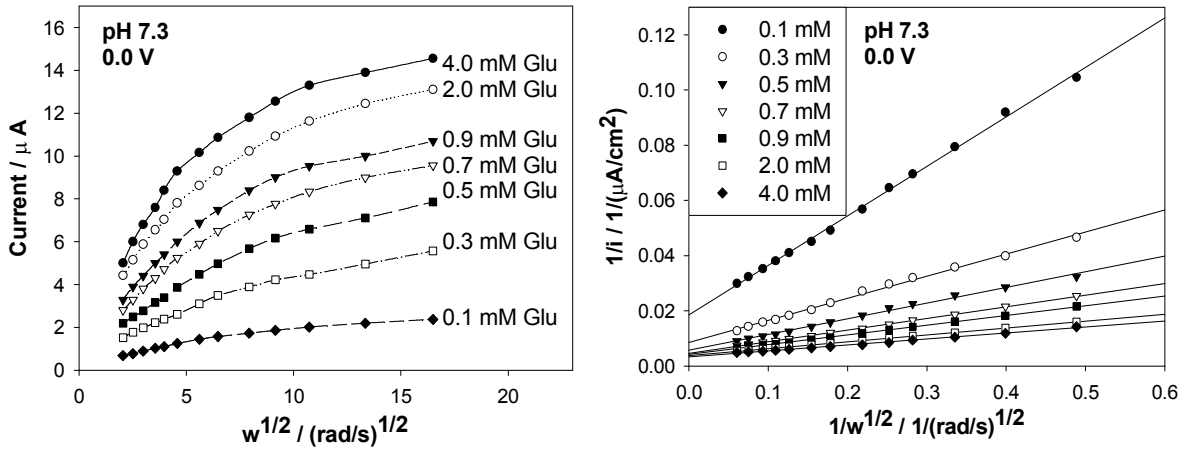

Fig. 19. Dependence of rotaing disk GCE/PB/0.4Chi-GOD-Gla electrode current on square root of electrode rotation speed, as obtained in pH 7.3 solution at 0.0 V operating potential for different glucose concentrations (left), and transformation of the data obtained according to Koutecky-Levich equation (right).

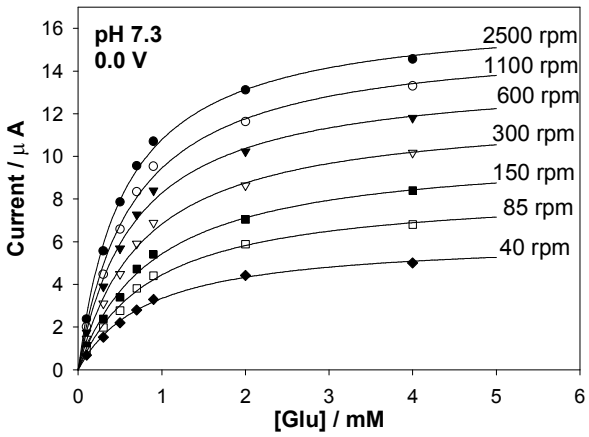

Fig. 20. Dependence of GCE/PB/0.4Chi-GOD-Gla biosensor's response on the concentration of glucose with different rotation speeds of the electrode (indicated) in 0.1 M phosphate buffer solution of pH 7.3 and 0.0 V potential of the electrode.

Fig. 20 presents the dependence of biosensor response to glucose at different rotation speed. From the dependencies obtained, some important parameters for biosensors have been calculated and presented in Table 3. From these data, some important consequences should be noted. The maximum current and the sensitivity of sensors increase with increasing rotation speed. Within the limits of 40-2600 rpm, nearly 3.5-4.0-fold increase of sensitivity occurs. It is important that the detection limit for

glucose diminishes from 0.36 to a very low value of 0.075 μM. Although not as drastical as for sensitivity, changes in an apparent Michaelis constant appear. Within same rotation speed limits, this constant diminishes roughly from 0.9 to 0.5-0.6 mM.

Table 2. Kinetic parameters of glucose oxidation on GCE/PB/0.4Chi-GOD-Gla biosensor with different rotation speeds of the electrode. Reaction was executed in 0.1 mM phosphate buffer solution of pH 7.3 and 0.0 V potential of the electrode.

Rotation speeds of the electrode, rpm	I_{max}, μA*	K_M^{tar}, mM*	Sensitivity, μA/(mM·cm^2)**
40	6.158 ± 0.155	0.906 ± 0.079	55.55 ± 4.04
60	7.415 ± 0.204	0.901 ± 0.074	58.57 ± 4.70
85	8.441 ± 0.901	0.895 ± 0.061	65.70 ± 5.35
120	9.367 ± 0.314	0.888 ± 0.074	74.22 ± 6.07
150	10.337 ± 0.365	0.874 ± 0.074	80.60 ± 6.58
200	11.403 ± 0.378	0.844 ± 0.054	89.35 ± 7.37
300	12.205 ± 0.394	0.789 ± 0.066	102.13 ± 8.45
400	12.906 ± 0.383	0.734 ± 0.058	112.75 ± 9.26
600	13.902 ± 0.444	0.680 ± 0.059	127.89 ± 10.36
800	14.740 ± 0.447	0.661 ± 0.055	146.57 ± 14.21
1100	15.594 ± 0.471	0.652 ± 0.054	156.12 ± 15.24
1700	16.234 ± 0.404	0.611 ± 0.043	168.80 ± 16.52
2600	16.775 ± 0.325	0.557 ± 0.031	183.64 ± 17.87

* parameters were acquired from data with good correlation (R was in limits of 0.997-0.999).
** sensitivity was calculated from data where R was in limits of 0.995-0.998.

3. CONCLUSIONS

1. Glassy carbon electrode, modified by Prussian blue, possesses electrocatalytic activity in reduction reactions of hydrogen peroxide and oxidation reactions of ascorbate. Catalysis of hydrogen peroxide cathodic reduction occurs effectively in wide range of electrode potential below the potential of Prussian blue reduction (approx. 0.2 V *vs*. Ag/AgCl). Oxidation of ascorbate on the electrode modified by Prussian blue occurs at electrode potentials, substantially (by 0.1-0.2 V) lower as compared to unmodified electrode.

2. At a low concentration of hydrogen peroxide (up to 0.3 mM), kinetic catalytic current appears to be about two times higher in pH 5.5 solution, as compared to pH 7.3 one, as determined with the use of a rotating disk PB modified electrode.

3. At a relatively high peroxide concentration, exceeding 0.6 mM, deviations from linearity of Koutecky-Levich equation have been observed. Based on this, a mechanism for hydrogen peroxide reduction at PB modified electrode has been proposed. In accordance with this mechanism, electron transfer appears to be rate-limiting step.

4. During electrocatalytic reduction of peroxide, PB layer undergo intense destruction processes. The calculated pseudo-first order degradation rate constants show a slower degradation in more acidic solutions.

5. With the use of PB modified electrode, prototypes of glucose biosensors were developed.

LIST OF PUBLICATIONS

1. A. Malinauskas, R. Araminaitė, G. Mickevičiūtė, R. Garjonytė. Evaluation of operational stability of Prussian blue- and cobalt hexacyanoferrate-based amperometric hydrogen peroxide sensors for biosensing application. *Mater. Sci. Eng. C* 24(4) (**2004**) 513–519.

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5. R. Araminaitė, R. Garjonytė, A. Malinauskas. Rotating disk electrode study of electrocatalytic oxidation of ascorbate at Prussian blue modified electrode. *Cent. Eur. J. Chem*. 7(4) (**2009**) 739–744.

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2. R. Araminaitė, A. Malinauskas. RDE study of electrocatalytic reduction of hydrogen peroxide and oxidation of ascorbate at Prussian blue modified elektrode. 9th National Lithuanian Conference, 2009, Vilnius, Lithuanian.

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ELEKTROKATALIZINIŲ PROCESŲ TYRIMAS ANT BERLYNO MĖLYNUOJU MODIFIKUOTO STIKLO ANGLIES ELEKTRODO

REZIUMĖ

Pasaulyje labai didelis skaičius žmonių serga cukriniu diabetu ir su kiekvienais metais šis skaičius tik didėja. Todėl šiai ligai teikiamas didelis dėmesys. Sergantys šia liga, kad galėtų gyventi pilnavertišką gyvenimą, privalo sekti gliukozės kiekį kraujyje. Leland C. Clark 1962 m. sukūrė pirmąjį gliukozės biojutiklį. Ir daugelį metų po to, šioje srityje, nebuvo patobulinimų. Kai 1995 m. A. A. Karyakin aprašė vandenilio peroksidui atrankų elektrokatalizinį Berlyno mėlynojo (BM) sluoksnį bei jį pritaikė biojutiklių kūrimui. Prasibėjo nauja biojutiklių era. Iki šių dienų tobulinamas elektrokatalizinių sluoknių, tokių kaip BM ir ne tik, naudojimas biojutiklių kūrime. Mano darbas ir buvo skirtas šio elektrokatalizinio sluoksnio tyrimui.

Pagrindinis darbo tikslas yra elektrocheminių vandenilio peroksido ir askorbato reakcijų tyrimas ant Berlyno mėlynuoju (BM) modifikuotų elektrodų, siekiant pritaikyti šiuos elektrodus jutiklių ir biojutiklių kūrimui.

Ištirta vandenilio peroksido redukciją ir askorbato oksidaciją naudojant sukamojo disko elektrodą. Gauti rezultatai galimai įrodo stadijinį vandenilio peroksido katodinės redukcijos mechanizmą vykstantį ant BM modifikuoto elektrodo. Askorbato elektrooksidacija išanalizavus duomenis yra efektyvesnė pH 5,5 tirpale bei esant didesniems elektrodo potencialams. Nustatyta, kad naudojant BM sluoksni elektrokatalizinė askorbato oksidacija prasideda 0,1 – 0,2 V žemesniame potenciale nei naudojant nemodifikuotą stiklo anglies elektrodą.

Detaliai ištirta BM sluoksnio irimo kinetika vandenilio peroksido elektroredukcijos metu, ir nustatyti faktoriai, įtakojantys irimo proceso greitį. Nustatyta, kad pH 5,5 tirpale BM sluoksnis pusę savo aktyvumo praranda per 321 ir 115 min. vandenilio peroksido koncentracijoms, atitinkamai, esant 0,2 ir 1,0 mM bei elektrodo potencialui 0,0 V. O pH 7,3 buferiniame tirpale – per 43 ir 18 min. nustatyta, kad BM sluoksnio stabilumas mažėja didinant tirpalo pH bei elektrodo potencialą.

Sukurti jutiklių ir biojutiklių prototipai, kurie galėtų būti panaudoti biologiškai aktyvių medžiagų (vandenilio peroksido, askorbato, gliukozės) nustatymui.

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I was born on February 9 in 1981 in the city Utena. In 1999, I was graduated from A. Šapokos gymnasium. In 1999 – 2003 I studied at the Faculty of Chemistry, Vilnius University, and obtained a Bachelor‘s degree (theme „The application of cobalt hexacyanoferrate modified electrode to amperometric determination of hydrogen peroxide“). In 2003 – 2005 I studied at the Faculty of Chemistry, Vilnius University, for a Master‘s degree (theme „Electrocatalytic properties of cobalt hexacyanoferrate modified electrode and application to electroanalysis“). From 2005 to 2009 years – post graduate studies at the Institute of Chemistry for a Doctor‘s degree.

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