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Rotating disk electrode study of electrocatalytic oxidation of ascorbate at Prussian blue modified electrode

Research Article

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Abstract: Electrooxidation of ascorbate has been studied with the use of a rotating disk electrode. The results obtained show an efficient electrocatalytic oxidation of ascorbate at the Prussian blue (PB) modified electrode to proceed in solutions of pH 5.5 and 7.3. Depending on solution pH, the onset potential for ascorbate electrooxidation at PB modified electrode appears shifted by 0.1-0.2 V to lower values, as compared to an unmodified glassy carbon electrode. Within the electrode potential window of 0.3 to 0.5 V *vs.* Ag/AgCl, and electrode rotation velocity of 50-2000 rpm, the catalytic current obeys Koutecky-Levich equation at a submillimolar ascorbate concentration. Kinetic current densities, obtained from the data treatment, are higher for a pH 5.5 solution, and also at higher electrode potential.

Keywords: *Electrocatalysis • Prussian blue • Ascorbate • Rotating disk electrode*

1. Introduction

Prussian blue (PB) has been widely studied during the past 15 years as electrocatalyst for oxidation or reduction of selected chemical species. The main aim of this study is the development of chemical sensors and biosensors for electroanalytical applications. Since the first report by Karyakin *et al*. in 1994 [1,2] on the use of PB modified electrode for amperometric detection of hydrogen peroxide and thus on its use in biosensors, a huge number of papers have appeared reporting on various uses and aspects of this and related metal hexacyanoferrate complex modified electrodes. The earlier studies have been well reviewed in a number of articles [3,4].

Along with the cathodic reduction of hydrogen peroxide, electrocatalytic oxidation or reduction of different species of electroanalytical interest is also known to proceed at PB modified electrodes. Both inorganic and organic substances have been shown to undergo electrocatalytic redox processes at the PB modified electrodes. Electrocatalytic reduction of nitric oxide at PB electrode has been reported to proceed at low electrode potentials, where PB is present in its reduced form Prussian white (PW) [5]. Electroreduction of carbon dioxide at a composite PB-polyaniline electrode has been found to proceed leading to complex C_2 and C_3 compounds [6]. Amperometric electrocatalytic detection of coenzyme NADH at a composite PB-polypyrrole electrode [7], and of morphine at PB modified indium tin oxide electrode [8] for electroanalytical applications has been demonstrated. Electrocatalytic oxidation of a series of organic thiols has been realized at a PB modified electrode, and used for the detection of these substances in liquid chromatography [9]. This ability of PB to catalyze electrooxidation of organic thiols has been later successively adopted for thiocholine and thus for pesticide detection, since thiocholine is a product of acetylcholinesterase catalyzed decomposition of acetylcholine [10,11]. Also, other substances of analytical interest have been shown to undergo electrocatalytic processes at PB and other metal hexacyanoferrate

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modified electrodes [3,4]. These findings show the potential of PB modified electrodes not only for amperometric detection of hydrogen peroxide, but also for electrocatalytic conversion of a broad range of chemical substances for electroanalytic applications.

Earlier, we studied electrocatalytic oxidation of ascorbate (Vitamin C) at the PB modified electrode [12]. In principle, electrooxidation of ascorbate at a PB modified electrode would be useful for the development of new amperometric sensors for this analyte. The present work has been aimed to more detailed study of electrocatalytic oxidation of ascorbate at a rotating disk PB modified electrode.

2. Experimental Procedures

A BASi-Epsilon potentiostat and BASi RDE-2 rotating disk electrode (both of Bioanalytical Systems Inc., West Lafayette, IN, USA) have been used in experiments. Electrochemical experiments were performed in a single-compartment 25 mL in volume three-electrode glass cell, containing glassy carbon rotating disk working electrode, 3 mm in diameter, press-fitted into a Teflon holder, a custom-built glassy carbon rod (Sigradur K, HTW, Germany) counter electrode, 3 mm in diameter and 10 mm in length, and RE-5B (Bioanalytical Systems Inc.) Ag/AgCl reference electrode, filled with 3 M NaCl solution. All potentials are referred below to this reference electrode.

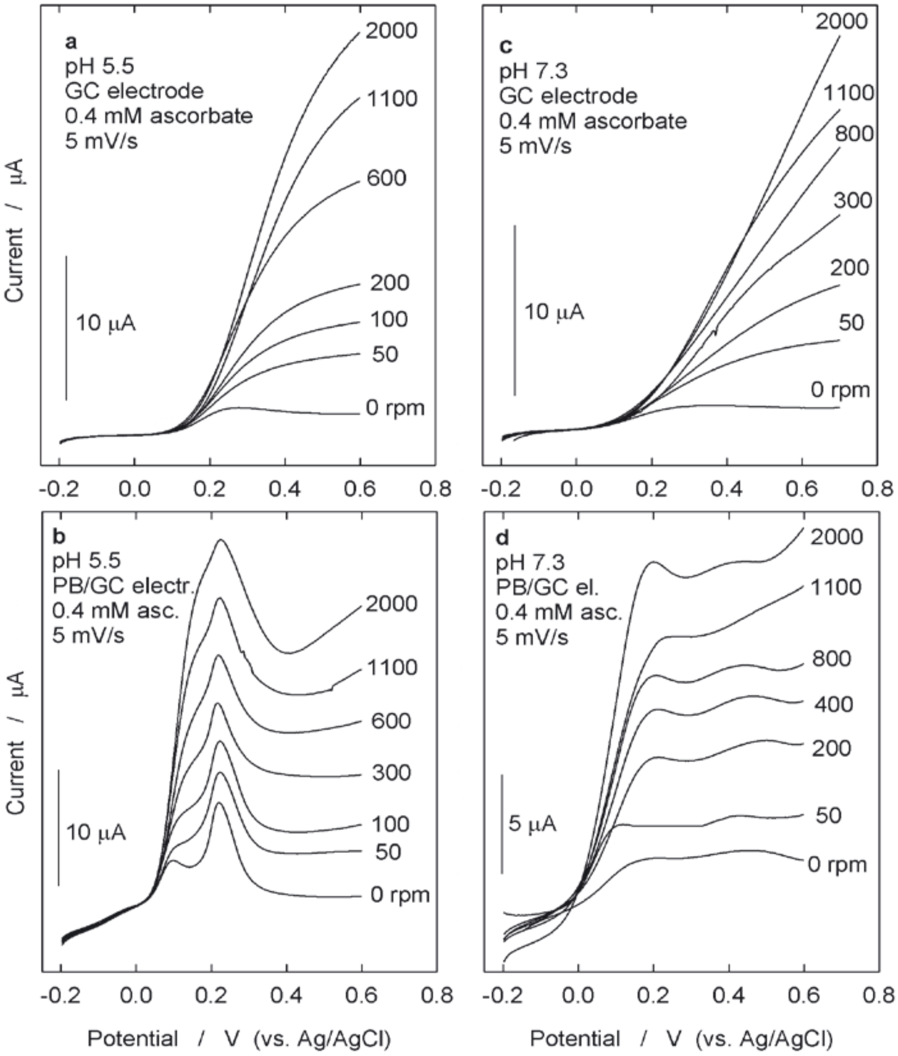

Figure 1. Slow potential sweep (5 mV s^{-1}) voltammograms, obtained in pH 5.5 (a, b), and pH 7.3 solutions (c, d) containing 0.4 mM of ascorbate, at a glassy carbon (a, c), and Prussian blue modified glassy carbon electrodes (b, d) at different electrode rotation velocities (as indicated).

Potassium chloride, potassium phosphates, and L-ascorbic acid (Fluka) were used as received. Electrodeposition of Prussian blue layer onto the working electrode was performed from the solution containing 0.1 M of KCl, 0.1 M of HCl, 2.5 mM of potassium ferricyanide, and 2.5 mM of $FeCl_3$. To perform electrodeposition, a potential of 0.4 V was applied for 1 min. RDE experiments were performed in 0.05 M phosphate buffer solution pH 5.5 or pH 7.3, containing 0.1 M of KCl.

3. Results and discussion

The standard potential of the quasireversible redox couple ascorbate-dehydroascorbate E_0'=0.058 V *vs*. RHE at pH 7.0, *i.e*. −0.138 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 solutions of PH 5.5 and 7.3 , as obtained using a slow potential sweep of 5 mV s^{-1} (Fig. 1). The oxidation current grows 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. 1). 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 the second 2nd peak, is observed. In a pH 7.3 solution, the onset potential for ascorbate oxidation at the PB modified electrode appears around 0 V, while the only anodic peak at around 0.2 V is observed. Again, the oxidation current at potentials more positive of this peak increase by increasing rotation velocity. For a pH 7.3 solution, the oxidation currents appear to be somewhat lower than for a pH 5.5 solution.

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:

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

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

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

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, 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, at *E*>0.22 V. However, it is seen from Fig. 1 that for a pH 5.5 solution electrooxidation proceeds at potentials less positive than 0.22 V. Most probably,

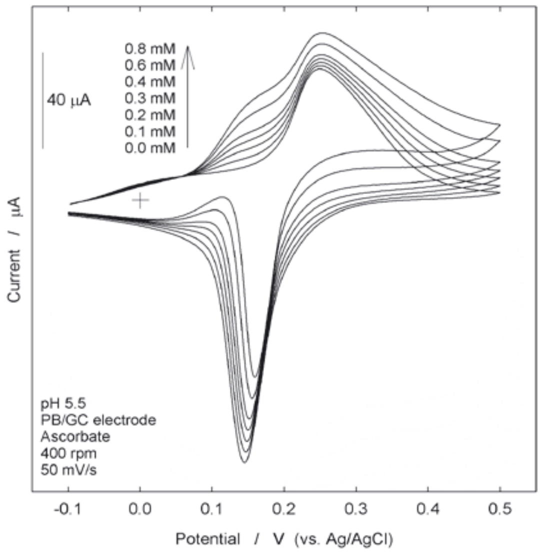

Figure 2. Cyclic voltammograms of Prussian blue modified glassy carbon rotating disk electrode, as obtained within potential scan limits of -0.1 to 0.5 V at potential sweep rate of 100 mV s^{-1}, and at rotating velocity of 400 rpm in pH 5.5 solution containing different concentrations of ascorbate ranging from 0.0 to 0.8 mM (as indicated). An inset shows cyclic voltammogram for high concentration (3.0 mM) of ascorbate.

an anodic peak located at 0.10 V for non-rotated PB modified electrode corresponds to the adsorption prewave. Anodic adsorption prewaves are usually observed for species with stronger adsorptivity for their reduced forms as compared to oxidised ones [13].

Fig. 2 shows potentiodynamic CVs for different concentrations of ascorbate at a constant rotation velocity. In the absence of ascorbate, a pair of anodic and cathodic peaks appears, characterized by the midpoint potential E_m=0.197 V, and peak potential difference ΔE_p=0.10 V for the given conditions. Within a relatively low ascorbate concentration range, not exceeding 3 mM, a nearly monotonic increase of anodic current at anodic peak potential, and at higher potentials as well, is observed with increasing concentrations of ascorbate. At increasing ascorbate concentration, the cathodic peak of the back potential scan shifts gradually to higher potential values, whereas the position of anodic peak remains almost unchanged. At the highest ascorbate concentration used of 3 mM, a shift of cathodic peak by 0.030 V has been observed. Also, an anodic prewave, located between 0.1 and 0.2 V, grows monotonically with increasing ascorbate concentration (Fig. 2).

In accordance with Levich equation [14], a linear dependence of limiting current for ascorbate electrooxidation on the square root of rotation velocity should be observed:

$$i_l=0.62nFAD^{2/3}\omega^{1/2}v^{-1/6}c$$

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

Fig. 3 (top) shows that, in a 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

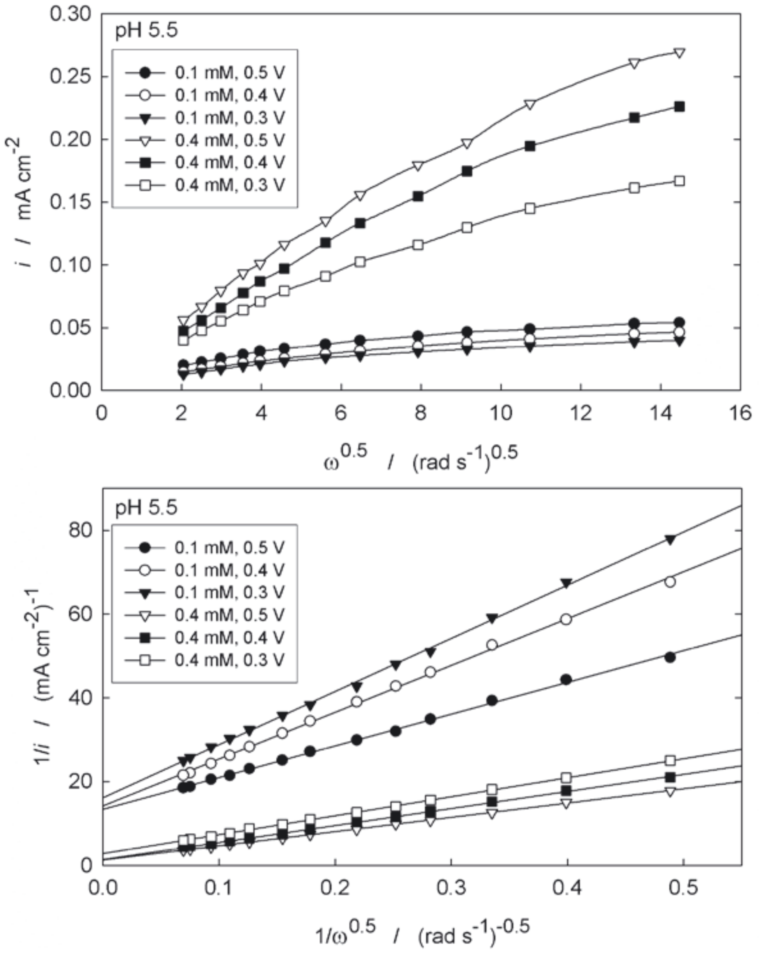

Figure 3. Treatment of the data obtained at Prussian blue modified electrode in pH 5.5 solution for different ascorbate concentrations and different electrode potentials (as indicated) in Levich (top) and Koutecky-Levich (bottom) coordinates.

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, 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, and iii) electron exchange between PB or Prussian white and electrode. Based on RDE experiment, however, it cannot be determined what process appears rate limiting. Recently, we presented a model that takes into account these three processes for a similar electrocatalytic system [15].

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, a net current can be divided into two components – mass transfer limited, and kinetic (or reaction limited) current:

$$\frac{1}{i}=\frac{1}{i_k}+\frac{1}{i_l}$$

where i, i_k, and i_l stand for a net, kinetic, and mass transfer limited current densities, respectively.

Taking into account a linear dependence of i_l on the square root of rotation velocity, as predicted by the Levich equation, a linear dependence of i^{-1} on $\omega^{-0.5}$ could be expected. Treatment of the data obtained in these inverse coordinates is presented in Fig. 3 (bottom). 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 0.4 mM within an entire broad electrode rotation velocity range studied. Similarly, the data obtained in a pH 7.3 solution for different ascorbate

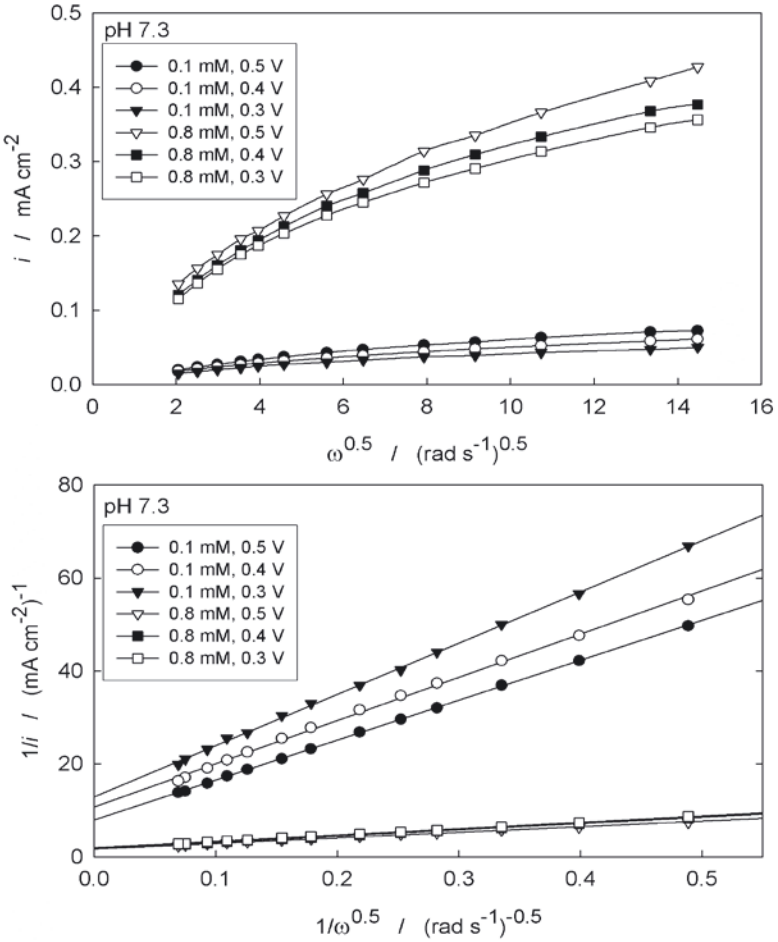

Figure 4. Same as in Fig. 3, obtained in pH 7.3 solution.

concentrations and different electrode potentials, can be satisfactory linearized in Koutecky-Levich coordinates, as shown in Fig. 4.

By extrapolation of linearized data (Figs. 3 and 4) to $1/\omega^{0.5} = 0$, *viz.* to indefinitely high electrode rotation velocity, the intercepts at $1/i$ axis are obtained. From these intercepts, kinetic current densities could be obtained. As an example, dependencies of kinetic current density on ascorbate concentration for both solutions has been studied and analysed for aselected electrode potential of 0.3 V. As expected, nearly linear dependencies have been obtained. The slope of these dependencies could be expressed by the correlation equation as follows:

$$i_k = a \times [\mathrm{Asc}] \quad (1)$$

where a represents an empirical coefficient, and [Asc] – ascorbate concentration solutions with pH 5.5 and 7.3, the coefficient a = (0.891±0.057) and (0.631±0.044) mA $\mathrm{cm^{-2}\ mM^{-1}}$, respectively. This shows that electrocatalytic oxidation of ascorbate proceeds more efficiently in slightly acidic than in pH-neutral solution.

The sensitivity of the PB modified electrode to ascorbate, and thus the coefficient a, depend on electrode potential. An increase of normalized kinetic current density (i_k/[Asc]) is observed at increasing electrode potential within the potential limits of 0.3 to 0.5 V. The nearly linear interdependence could be expressed as follows:

$$i_k/[\mathrm{Asc}] = a + b \times E \quad (2)$$

where a is normalized kinetic current density at a given potential as in (1) and b is an empirical coefficient.

For solutions of pH 5.5 and 7.3, the slope b = (2.45±0.55) and (0.625±0.118) mA $\mathrm{cm^{-2}\ mM^{-1}\ V^{-1}}$, respectively. It follows that the sensitivity of kinetic current to electrode potential is more pronounced in a pH solution of 5.5.

4. Conclusions

The results obtained show an efficient electrocatalytic oxidation of ascorbate at the Prussian blue (PB) modified electrode to proceed in solutions with a pH 5.5 and 7.3. Depending on solution pH, the onset potential for ascorbate electrooxidation at PB modified electrode appears shifted by 0.1-0.2 V to lower values, as compared to unmodified glassy carbon electrode. Within the electrode potential window of 0.3 to 0.5 V *vs.* Ag/AgCl, and electrode rotation velocity of 50-2000 rpm, catalytic current obeys Koutecky-Levich equation at a submillimolar ascorbate concentration. Kinetic current densities, obtained from the data treatment, are higher for solutions with pH 5.5, and at higher electrode potential.

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References

[1] A.A. Karyakin, O.V. Gitelmacher, E.E. Karyakina, Anal. Lett. 27, 2861 (1994)

[2] A.A. Karyakin, O.V. Gitelmacher, E.E. Karyakina, Anal. Chem. 67, 2419 (1995)

[3] F. Ricci, G. Palleschi, Biosens. Bioelectron. 21, 389 (2005)

[4] A.A. Karyakin, Electroanalysis 13, 813 (2001)

[5] K.C. Pan, C.S. Chuang, S.H. Cheng, Y.O. Su, J. Electroanal. Chem. 501, 160 (2001)

[6] K. Ogura, M. Higasa, J. Yano, J. Electroanal. Chem. 379, 373 (1994)

[7] H. Zhao, Y. Yuan, S. Adeloju, G.G. Wallace, Anal. Chim. Acta 472, 113 (2002)

[8] K.C. Ho, C.Y. Chen, H.C. Hsu, L.C. Chen, S.C. Shiesh, X.Z. Lin, Biosens. Bioelectron. 20, 3 (2004)

[9] W. Hou, E. Wang, J. Electroanal. Chem. 316, 155 (1991)

[10] E. Wilkins, M. Carter, J. Voss, D. Ivnitski, Electrochem. Commun. 2, 786 (2000)

[11] F. Ricci, F. Arduini, A. Amine, D. Moscone, G. Palleschi, J. Electroanal. Chem. 563, 229 (2004)

[12] A. Malinauskas, G. Mickeviciute, R. Araminaite, R. Garjonyte, Chem. Anal. (Warsaw) 51, 809 (2006)

[13] Z. Galus, Fundamentals of Electrochemical Analysis (Ellis Horwood, Chichester, 1976)

[14] A.J. Bard, L.R. Faulkner, Electrochemical methods. Fundamentals and applications, 2nd edition (Wiley, New York, 2001) 331

[15] R. Naujikas, A. Malinauskas, F. Ivanauskas, J. Mathemat. Chem. 42, 1069 (2007)