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BIOSENSORS

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HIGHLY SENSITIVE SENSOR FOR DETECTION OF VITAMIN B_1 ON THE NANOSTRUCTURAL SURFACE OF NICKEL

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Abstract. Vitamin B_1 (thiamine bromide) is a component of the ferments, which take part in the exchange of substances flowing in alive organisms and has a wide application in medical practices for medical treatment of different nerve illnesses. As alternative to polarograph detection of vitamin, we propose a voltamperometric chemosensor where nanostructured surface of nickel is used as indicator electrode. It claims that thiamine bromide has a significantly higher discharge intensity on the nanostructural nickel electrode than on the smooth one in 2–3 times and increases in the factor of tens as compared with mercury electrode. This significantly increases a sensitivity of sensor and make it application more safe.

Keywords: nanostrutured electrode, vitamin B_1, voltammetry, chemosensor, sensitivity

ВИСОКОЧУТЛИВИЙ СЕНСОР ДЛЯ ВИЗНАЧЕННЯ ВІТАМІНУ B_1 НА НАНОСТРУКТУРОВАНІЙ ПОВЕРХНІ НІКЕЛЮ

О. Шевченко, О. Лут, О. Аксіментьєва

Анотація. Вітамін B_1 (тіамін бромід) входить до складу ферментів, які беруть участь в обміні речовин в живих організмах, що зумовлює його широке застосування у медичній практиці для лікування різноманітних нервових хвороб. На відміну від полярографічного визначення вітаміну B_1, запропоновано вольтамперометричний хемосенсор, в якому як індикаторний електрод використовується наноструктурована поверхня нікелю. Встановлено, що інтенсивність розряду тіамін броміду на наноструктурованій нікелевій поверхні вища порівняно з гладким нікелевим електродом у 2–3 рази і збільшується у десятки разів порівняно з ртутним електродом. Це забезпечує значне підвищення чутливості сенсора і робить його використання більш безпечним.

Ключові слова: наноструктурований електрод, вітамін B_1, вольтамперометрія, хемосенсор, чутливість

ВЫСОКОЧУВСТВИТЕЛЬНЫЙ СЕНСОР ДЛЯ ОПРЕДЕЛЕНИЯ ВИТАМИНА B_1 НА НАНОСТРУКТУРИРОВАННОЙ ПОВЕРХНОСТИ НИКЕЛЯ

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Аннотация. Витамин B_1 (тиамин бромид) входит в состав ферментов, принимающих участие в обмене веществ в живых организмах, и широко применяется в медицинской практике для лечения разнообразных нервных заболеваний. В отличие от полярографического определения витамина B_1, предложен вольтамперометрический хемосенсор, в котором в качестве индикаторного электрода используется наноструктурированная поверхность никеля. Установлено, что интенсивность разряда тиамин бромида на нано-структурированной никелевой поверхности повышается в 2—3 раза по сравнению с гладким никелевым электродом и возрастает в десятки раз по сравнению с ртутным электродом. Это обеспечивает значительное повышение чувствительности сенсора и делает его использование более безопасным.

Ключевые слова: наноструктурированный электрод, витамин B_1, вольтамперометрия, хемосенсор, чувствительность

Introduction

Vitamin B_1 **(**thiamine bromide) is a component of the ferments, which take part in the exchange of carbohydrates**,** greases, proteins and water. It has a wide application in medical practices for medical treatment of different nerve illnesses. Study the chemical and electrochemical properties of this vitamin permit to widening a knowledge about the mechanism of the processes, flowing in the live organisms, therefore many physical and chemical methods (spectroscopy**,** chromatography, potentiometry, polarography, etc) are using for analytical detection of B_1 [1—4].

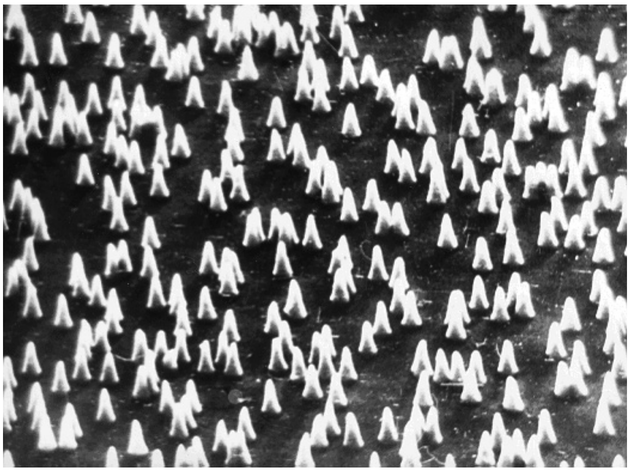
Voltammetry is one of the most universal electrochemical methods for investigation and detection of organic substances. As known voltammetry is characterized by simplicity, sensitivity, cost — efficiency, precision, accuracy and may be recommended for development a chemosensors for qualification analysis of vitamins and proteins in food products, biosystems, technological analysis of the run-off waters and in the medicine industry [5—7].

Many investigations of the last year are devoted to polarograph investigations of the vitamin water solution **by** means of toxic mercury or expensive platinum electrodes [1—3, 6]**.** But electro-chemical behavior of thiamine bromide on the nanostructured nickel electrode does not study. From the other hand the results of recent investigations show a promising application the electrodes with nanostructured surface for electrochemical investigations [6, 8].

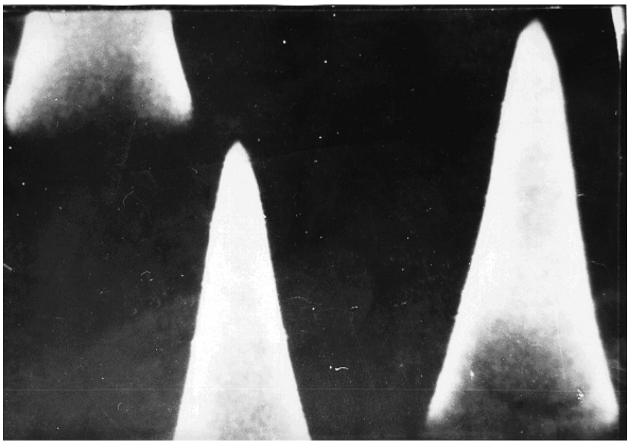
An aim of the present work is a study of electrochemical reduction of thiamine bromide on the nanostructured nickel surface and testing the possibility of the quantitative detection of vitamin B_1 with potential application of such electrode in electrochemical sensors.

Experimental

To investigate the processes of the thiamine bromide electroreduction a voltammetry method with linear and cyclic potential sweeping was used. Values of the current and electrode potential were registered with developed computer program Science Plotter. A sweeping of potential (E) to negative direction was carried out in the range of E from 0.0 to -1.4 V. Three compartment electrochemical cell before each measurement was bubbled by argon during 15 minutes for oxygen evacuation. As indicator electrodes the flat and nanostructured nickel electrodes by similar work area have been used. Nanostructured nickel electrode of the type «cluster — globule — surface» was fabricated in the shape of nickel plate with deposited from one side of plate uniform nanostructured elements in the vive of cones (Fig.1) with height and radius of curvature near the peak of 50 nm [9]. An area of the visible work electrode surfaces was $0.2375 \cdot 10^{-4}$ m^2. A surface concentration of elements in massive achieves 10^9 m^{-2}. As a counter electrode a platinum wire with visible surface of $7 \cdot 10^{-4}$ m^2 was used. A saturated silver-chloride electrode Ag/AgCl was used as a reference. Lithium perchlorate was a background electrolyte. All solutions were prepared on the bidistilled water, experiments were carried out at the temperature T = 298 K.



a)



b)

Fig. 1 (a) SEM image of the nanostructured surface of the nickel electrodes (x 1400); b — individual elements (x14300) in the vive of cones with height and radius of curvature near the peak of 50 nm.

Results and Discussion

Study the chemical and electrochemical properties of thiamine bromide permit to widening knowledge about the mechanism of the processes, flowing in live organisms. Depending on the value of pH thiamine may exists in molecular, cation and anion form [10]. At pH<6 thiamine in solution is in the form of stable salt of quaternary base. At pH = 6.8 a disclosing of thiazole cycle of molecule takes a place with formation of the open thiol form — RSH. At pH>8 it possible a formation of anion form of thiamine — RS^-, and in the interval of pH from 8.1 to 8.6 a protolytic equilibrium takes a place: $RSH = H^+ + RS^-$. With pH increasing a potential of peak current shifts to negative values [11] and over potential of vitamin reduction grows. We found that in the current dependence on pH a maximum at pH 7.5 — 8.5 are observed [12]. Peak current decreases with concentration of hydroxyl ions due to formation an insoluble compound on the electrode surface. Based on analyses of the obtained results the 0.5 M lithium perchlorate solution with pH near 6.0 was used as work background electrolyte.

Obtained in such conditions cyclic and linear voltammograms (Fig. 2 and 3) indicate that vitamin B_1 (thiamine bromide) electrochemically reduces on both smooth and nanostructured nickel electrodes. The electrochemical reduction of vitamin B_1 on the nickel nanostructural electrode starts at the potential $E > 0,5$ V and achieves a maximum in the interval of $E = -(0,92...0,97)$ V versus Ag/AgCl reference electrode.

Process of thiamine bromide electroreduction on the electrode with nanostructured surface is significantly lighting, potential of the cathode maximum shifts on 0.1 V in positive direction as compared with smooth nickel electrode at the same concentration of thiamine bromide in solution (Fig. 2), which may be explained by electrocatalytic action of nanostructured electrode surface.

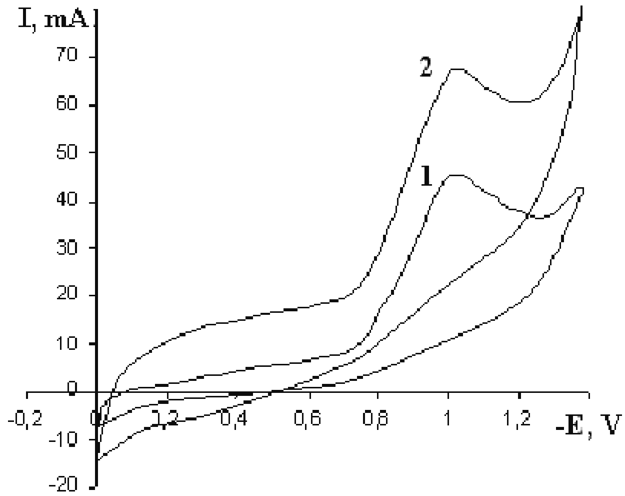


Fig. 2 Cyclic voltammogtams of thiamine bromide (TB) reduction on the smooth nickel electrode (1) and nonostructured nickel electrode (2) at $C_{TB} = 4{\cdot}10^{-2}$ M; $\upsilon = 5{\cdot}10^{-2}$ V/s.

In anodic part of cyclic voltammograms any peaks due to electrochemical activity of thiamine bromide or products of its reduction are absent in the investigated potential range, which indicates the irreversibility of the process [13]. Existence of a single clear maximum on the cathode branch line of potentiodynamic curves may be evidence to one step of electroreduction and suggested its one electron character. Increasing a rate of potential sweeping is accompanied by rising of reduction current and shifting of peak potential to the negative side which causes amplification of irreversibility of the process. As optimal sweep rate a value of $5\cdot10^{-2}$ V/s was chosen.

Displacement of peak potential in the negative side at the increasing of thiamine bromide concentration (Fig. 3) indicates a rising of the overpotential of electrochemical reaction. Such dependence is observed for both smooth and nonostructured electrode. It probably connected with adsorption of the products of thiamine bromide reduction on the electrode surface caused it passiveness.

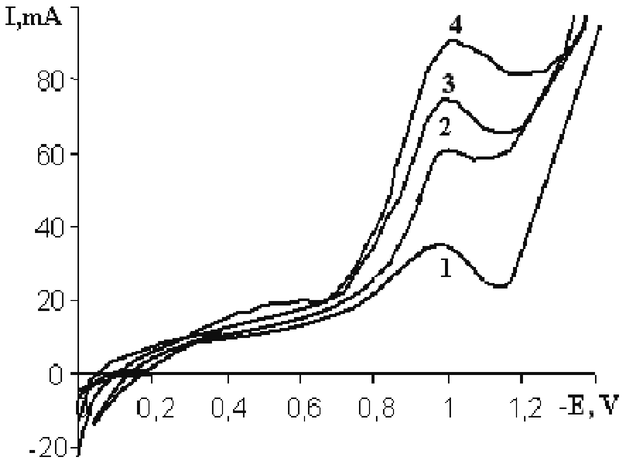


Fig. 3 Voltammograms of thiamine bromide (vitamin B_1) reduction on the nanostructured nickel electrode at concentration of thiamine bromide, M: 1- 0.02; 2. — 0.03; 3–0.04; 4–0.05. Electrolyte — 0,5 M $LiClO_4$; $\upsilon = 5\cdot10^{-2}$ V/s; T= 298±3K.

Cathode peak current (I_p, mA) linearly depends on the concentration (*c,* M) of vitamin B_1, which may be using for plotting the calibration curve. It has been found that calibration curve save a linearity up to vitamin concentration $c = 6\cdot10^{-2}$ M with low limit (throughout) of vitamin B_1 detection near $2\cdot10^{-7}$ M [14]. It proposed the linear equations $I_p = 1{,}86\cdot10^3 c$, which make it possible to quantity identification the thiamine bromide concentration in the solution.

As one can see from the Table, a nanostructured nickel electrode as compared to mercury indicator electrode or smooth nickel electrode is characterized by higher current of the response that confirms it higher sensitivity, caused by catalytic activity to the thiamine bromide electrochemical reduction. Due to high over potential of hydrogen evolution and stability of the nickel electrode in different mediums, a possibility of rapid regeneration the electrode surface by potential scanning in the range of E = -0.5...1.5 V, the merit and saving of vitamin B_1 detection become significantly increased.

Table

Futures of voltammetric detection of vitamin B_1 with different sensor electrodes

Sensor electrode	Hg, Mercury [7]	Smooth nickel	Nanostructured nickel
Peak potential, V	0.35–0.47	0.96–1.02	0.92–0.97
Peak current, mA	(1.7–3.5) $\cdot10^{-3}$	0.03–53	0.07–100
Concentration of B_1, M	(7.5–15.0)$\cdot10^{-5}$	$6.2\cdot10^{-5}$–$1.5\cdot10^{-2}$	$3.76\cdot10^{-5}$–$5\cdot10^{-2}$
Concentration of B_1, mg/ml	(3.26 –6.53)$\cdot10^{-2}$	2.95 10^{-2}–6.3	1.64 $\cdot10^{-2}$–23.442
Relative error, %	0.2–0.4	0.15–0.25	0.14–0. 21

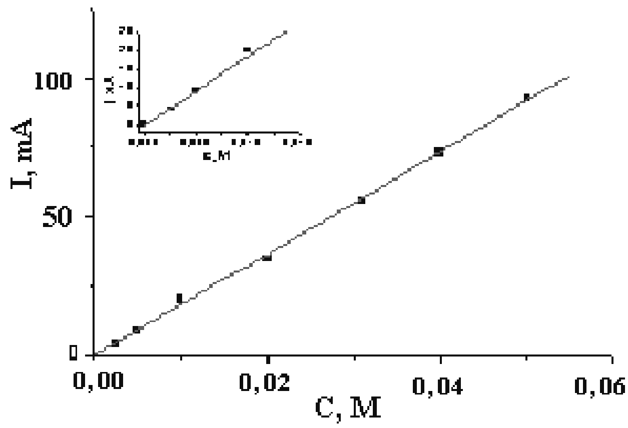


Fig. 4 Peak current dependence on concentration of vitamin B_1 on the nanostructuted nickel electrode in 0,5 M $LiClO_4$ aqueous solution.

Conclusions

It claims that thiamine bromide has a significantly higher discharge intensity on the nanostructure nickel electrode than on the flat one (2–3 times) and increases in the factor of 100 as compared with mercury electrode. This significantly increases a sensitivity of voltammetric sensor and makes it safer. Study the chemical and electrochemical properties of this vitamin permit to widening knowledge about the mechanism of the processes, flowing in the live organisms. Proposed nanostructured electrode may be used in chemo- and biosensors for analytical and biochemical investigations to quantitative detection of vitamins in food products, technological analysis of nature and run-off waters and in the medicine industry.

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