

Non-enzymatic Sensing of Glucose Using Glassy Carbon Electrode Modified with Organometallic Complex of Nickel

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A glassy carbon electrode(GCE) modified with organometallic complex of nickel: (S)-[O-[(N-benzylpropyl)amino](phenyl)methyleneiminoacetate(2-)-N,N',N''-nickel(II) (Ni-(S)BPB-Gly, irreversibly adsorbed on the electrode surface was investigated. The modified electrode shows an electrochemically reversible reaction due to a Ni(II)/Ni(III) redox couple and electrocatalytic activity toward glucose oxidation in alkaline solution. The electrochemical behaviors of the GCE modified with a redox film were investigated by cyclic voltammetry and chronoamperometry techniques. According to the voltammetric studies, the increase in the anodic peak current and subsequent decrease in the corresponding cathodic current, glucose was oxidized on the modified electrode surface via an electrocatalytic mechanism. The amperometric results indicate that glucose oxidation current response increases with increasing glucose concentrations. When this is high enough, the current tends to be stable, showing the characteristics of Michaelis-Menten kinetics. The Michaelis-Menten constant (K_M) and the maximum current density (i_{max}) were 2.3 mM and 4.6 mA cm⁻², respectively. The activation energy of the electrocatalytic reaction was estimated to be 42.1 kJ mol⁻¹.

Keywords: modified electrode, nickel, electrocatalysis, glucose

1. INTRODUCTION

Many simple carbohydrates, polyhydroxy compounds and other important organic solutes cannot be electrochemically oxidized because are very often hindered by their slow electron transfer kinetics at commonly used electrode materials. To overcome this drawback a chemically modified electrodes are often used; they offer an attractive solution for this and other limitation of ordinary electrodes. The preparation of a structure interface of deliberately designed character offers many promising prospects with regard to the development of an electrochemical detection methods. This idea is well-known for a long time ago, for example, the influence of surfactants on anodic stripping

voltammetric determination of many metal ions has been known almost since the static/hanging mercury drop electrode came into use [1-4]. Over the past few decades, substantial efforts have been devoted to the development of electrochemical sensors based on electrodes modified by electrosynthesized polymeric films [5,6]. Moreover, high attention has been focused for a long time on the use of macrocyclic complexes of some transition metals as modifiers in the form of conductive coatings generated from metallated porphyrins [7-9], phthalocyanines [10-12] and cyclic tetraamines [13-15], among other.

The polymeric metal complexes containing Ni(II)/Ni(III) redox couple have been attracting a lot of attention in the last years. This is due to mediate nature of nickel in alkaline solution which reminds a nickel oxyhydroxide species. It is well known that nickel oxyhydroxide species are considered to act as a redox mediator between a substrate and an electrode in many electrooxidation processes. Furthermore, the procedure of the polymeric film preparation into GCE is usually simple and the film properties can be controlled carefully. The electropolymerization procedure was used successfully for modifying GCE surfaces with Ni(II) complexes [16-17]. The obtained films were characterized by high catalytic activity toward electrooxidation of alcohols and/or other compounds with $-OH$ and $-NH_2$, respectively.

Electrocatalysis for the glucose oxidation is very important not only in medical technology for development of the new blood glucose monitoring sensors. It also may be applied to other areas, such as energy storage technology [18], industrial processes [19] and food industry [20]. Recent research on new electrocatalysts for glucose oxidation have been focused on non-enzymatic systems, which possess some advantages over the enzymatic systems. The non-enzymatic catalyst operates in accordance with the mediated electrocatalysis scheme, where direct glucose oxidation is possible because of the individual redox character of the electrode surface. The electrochemical oxidation of glucose molecules requires complex processes of adsorption, electron transfer, and subsequent chemical rearrangement, which are connected with the surface reactions on the electrode. Electrooxidation of glucose has been examined on various metals (copper, gold, platinum, iridium and rhodium) [21-23], on metal oxide electrodes (nickel, ruthenium and tungsten oxide) [24-27], in the recent time.

In this paper we report electrocatalytic glucose oxidation by a glassy carbon electrode (GCE) modified with adsorbed/polymerized organometallic nickel complex: poly-(S)-[O-[(N-benzylpropyl)amino](phenyl)methyleneiminoacetate(2-)-N,N',N''-nickel(II), Fig. 1 presents the structural formula of this complex. In our previous article [28] we studied the electrochemical properties of a GCE electrochemically modified by the above mentioned conductive, adsorbed/polymerized complex. Using Laviron's theory, the electron-transfer rate constant and the transfer coefficient were calculated and are $k = 1.94 \text{ s}^{-1}$ and $\alpha = 0.5$, respectively for the tested film on a GCE in 0.1 M NaOH solution. Its electrocatalytic activity toward the methanol oxidation in this solution expressed by the catalytic rate constant was determined to be $k_{\text{cat}} = 0.33 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

To the best of our knowledge, this is the second examination on electrocatalytic properties of the tested complex, which until today has been first used for synthesis of beta-hydroxy-alpha amino acids and then used in the synthesis (S)-alpha-amino acids [29-32].

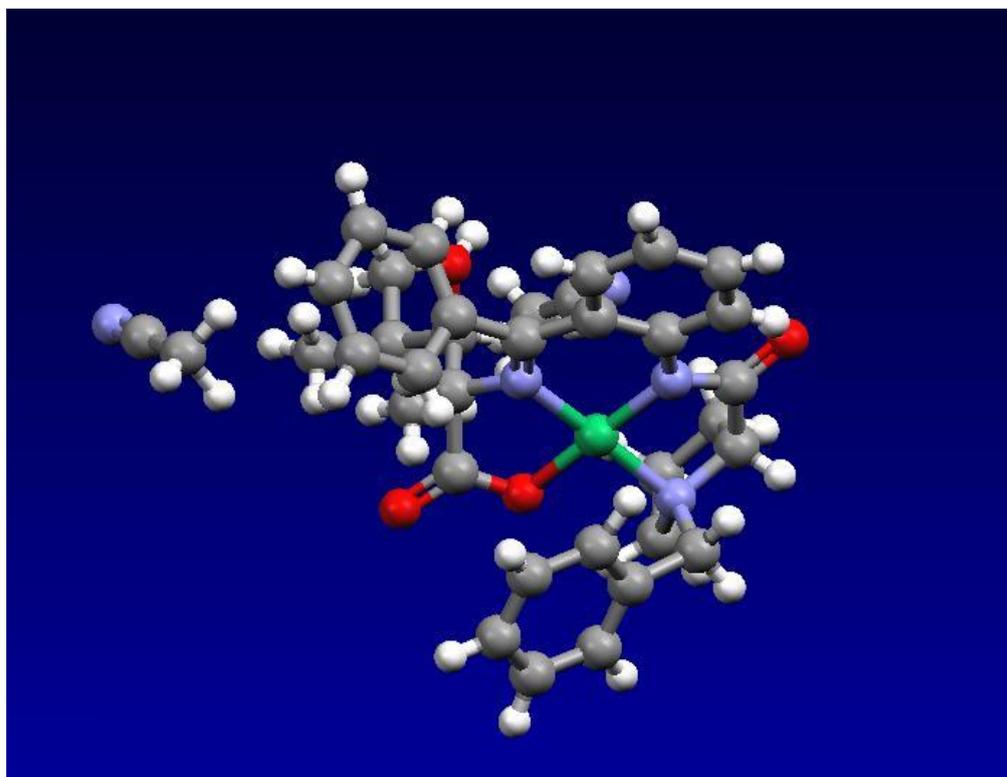


Figure 1. Schematic for the structure of Ni-(S)BPB-Gly complex. Nickel is shown in green color, nitrogen in blue color and oxygen in red color [33].

2. EXPERIMENTAL

2.1. Reagents

Organometallic nickel complex: (S)-[O-[(N-benzylpropyl)amino](phenyl)methyleneimino acetate(2-)-N,N',N''-nickel(II), sodium hydroxide (NaOH), acetonitrile (AN) and glucose (Glu) were purchased from ACROS and Merck. All the chemicals mentioned were all of analytical grade and used as received, without further purification.

2.2 Apparatus

All electrochemical experiments were performed using Palm-Sens electrochemical system (Palm Instruments VB, The Netherlands) in a conventional three electrode cell. The working electrode was a glassy carbon disc (GC - 3 mm diameter, Metrohm, Herisau, Switzerland), whereas an Ag/AgCl (saturated KCl) electrode and a Pt wire were used as the reference and counter electrodes, respectively. Most experiments were performed at room temperature, others in temperatures range from 25 to 40 °C.

2.3. Electrode modification

The electrode preparation and modification were carried out according the previously procedure described [28]. Prior to the modification, the surface of the GCE was polished on a polish pad with 0.05 μm alumina powder (Al_2O_3) and rinsed with distilled water several times. After pretreatment the electrode was placed in aqueous solution containing 10 mM of modifier in 0.1 M NaOH with acetonitrile (50:50 vol. %). The adsorption/polymerization was carried out using cycling voltammetric method by the film formation onto the electrode surface. The electrode potential was cycled between 0.0 and 0.8 V at a scan rate of 100 mV s^{-1} for 15 cycles. After that, the electrode was thoroughly rinsed with 0.1 M NaOH and cycled between 0.0 and 0.8 V until a reproducible cyclic voltammogram was obtained. Afterwards, the modified GCE was used in subsequent experiments.

3. RESULTS AND DISCUSSION

3.1. Formation of the modified electrode

The preparation of the modified electrode was carried out by adsorption/electropolymerization of the Ni-(S)BPB-Gly at a GCE in the mixture of 0.1 M NaOH and AN (50:50 vol. %) by using multiple scan cyclic voltammetry. CV is a common and convenient method to monitor the electrochemical behaviors of the modified electrodes. Fig. 2A presents the growth pattern for Ni(II)-complex in CV regime.

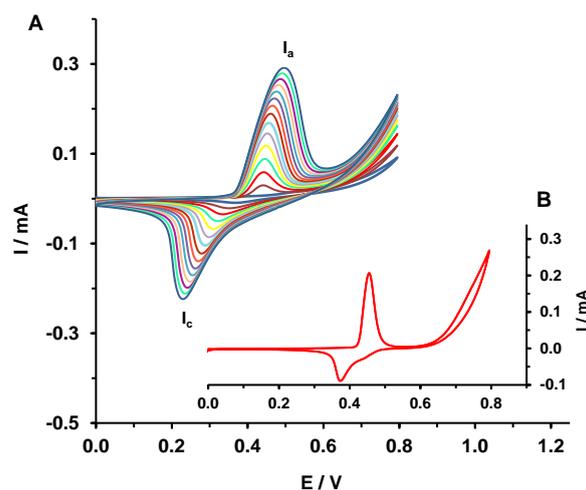


Figure 2. (A) Cyclic voltammograms of 10 mM of the Ni-(S)BPB-Gly complex at a GCE in 0.1 M NaOH + AN (50:50 vol. %) solution at a scan rate of 100 mV s^{-1} , during modification of electrode surface process. (B) Cyclic voltammogram of the poly-Ni-(S)BPB-Gly/GC modified electrode in 0.1 M NaOH solution at a scan rate of 20 mV s^{-1} .

This cyclic voltammograms clearly indicate film formation on the surface of the GCE (a couple of peaks I_a (oxidation) and I_c (reduction) are seen). The electroactive layer growth on the surface of

GCE is accompanied by increasing current for I_a and I_c peaks, which correspond to the Ni(II)/Ni(III) redox couple. The oxidation of Ni(II) to Ni(III) has been known to be very difficult due to the strong hydration of nickel ions, in aqueous media. However, the oxidation conditions for nickel can be changed significantly when nickel is coordinated in the hydrophobic film. Thereby, it is not surprising, that the Ni(II)/Ni(III) redox couple is observed in the tested film. The cathodic and anodic peaks shifted to more negative and more positive potentials with an increase in the number of scans, respectively. This is the indication of the increase in the electrical resistance of the film and that overpotential is needed to overcome the resistance. The deposit, which is formed demonstrates a high adherence to the GCE. When an electrode (with film, labeled as poly-Ni-(S)BPB-Gly/GC) is transferred into 0.1 M NaOH solution, only one reversible couple (Fig. 2B, peak $I_{a,c}$) is observed. The Ni(II)/Ni(III) couple redox potential estimated as the midpoint of the anodic and cathodic peak potentials was ca. 0.44 V. The surface coverage ($\Gamma_{Ni} = 4.4 \times 10^{-8} \text{ mol cm}^{-2}$), was determined from integration of the charge under the cyclic voltammetric peaks obtained at a slow potential scan rate. The peak current is directly proportional to the scan rate, as expected for surface immobilized reagents. It is worth noticing, that the height of the peak on the voltammogram which was obtained one day later was virtually the same to the one at the same scan rate in Fig. 2B. This result indicates that the modified electrode is stable, at least such time, under these conditions.

3.2. Mediated electrocatalytic oxidation of glucose

Before the discharge of the supporting electrolyte, oxidation does not occur and the electrochemical oxidation of glucose at a GCE in a basic media is poor. In contrary, oxidation of glucose at the poly-Ni-(S)BPB-Gly/GC modified electrode in an alkaline medium (0.1 M NaOH) appeared and it was connected with increasing anodic peak current while diminished in the cathodic peak current, as can be clearly seen in Fig. 3.

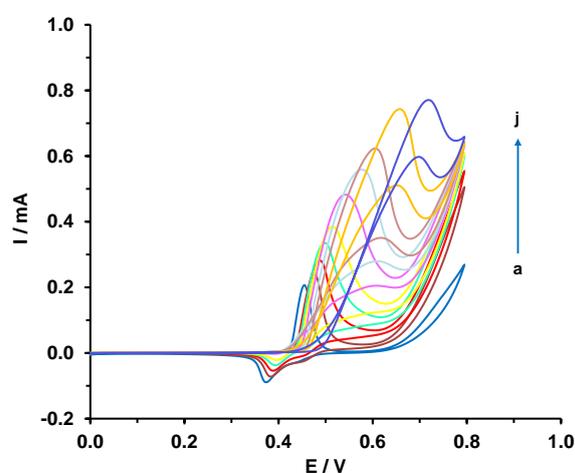


Figure 3. Cyclic voltammograms of the poly-Ni-(S)BPB-Gly/GC modified electrode in 0.1 M NaOH solution at different glucose concentration: (a) 0.0, (b) 0.5, (c) 1.5, (d) 3.5, (e) 5.5, (f) 7.5, (g) 9.5, (h) 11.5 (i) 15.0 and (j) 20.0 mM, at a scan rate of 20 mV s^{-1} .

These results indicate that the tested modified electrode is able to catalyze the electrooxidation of glucose. The reaction product of electrooxidation with the Ni(III) catalyst is still believed to form a gluconolactone, according to the following reactions:



and further hydrolysis to gluconic acid. The proposed mechanism for the oxidation of glucose at modified electrode with Ni(II)/Ni(III) redox couple consists of three steps: (i) Ni(II) is oxidized to catalytically active Ni(III), (ii) glucose undergoes hydrogen abstraction at the electrode surface to form a radical intermediate and reforming the Ni(II) species, (iii) hydroxyl anions in the solution rapidly complete the oxidation of the organic radical intermediate to form gluconolactone [34-37].

Fig. 4 shows the cyclic voltammograms of the poly-Ni-(S)BPB-Gly/GC modified electrode in 0.1 M NaOH in the presence of 2 mM glucose at various scan rates. Evidently, the peak potential for the oxidation of glucose moves increasingly to the positive potentials direction with an increasing scan rate. This outcome suggests a kinetic limitation in the reaction between the Ni(II)/Ni(III) redox sites of the poly-Ni-(S)BPB-Gly/GC modified electrode and glucose. Meanwhile, the anodic peak current is proportional to the square root of the scan rate (inset A), suggesting that the overall oxidation of glucose at this electrode might be controlled by diffusion of glucose from the solution to the redox sites of the surface. Moreover, the relationship between the reaction function ($i/v^{1/2}$) and v (inset B) indicates the independence of ($i/v^{1/2}$) from v , corresponding to a typical shape of an electrochemical-chemical (EC) catalytic process [38].

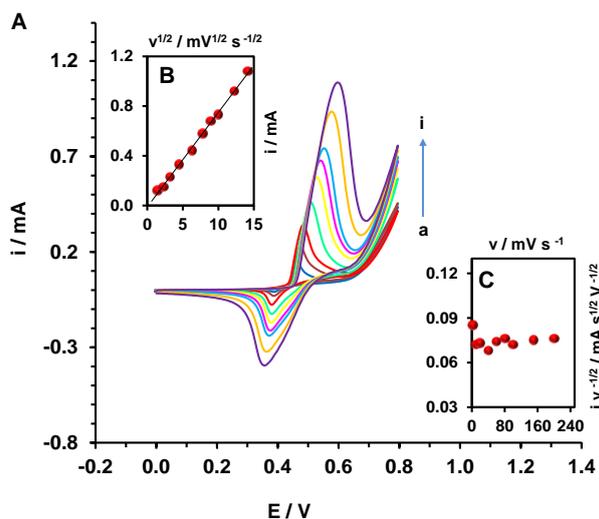


Figure 4. (A) Cyclic voltammograms of the poly-Ni-(S)BPB-Gly/GC modified electrode in 0.1 M NaOH solution in the presence of 2 mM glucose at different scan rates: (a) 5, (b) 10, (c) 20, (d) 40, (e) 60, (f) 80, (g) 100 (h) 150, and (i) 200 mV s^{-1} . (B) Plot of the anodic peak current versus $v^{1/2}$. (C) Plot of the anodic current function ($i/v^{1/2}$) versus a scan rate.

3.3. Chronoamperometric studies

Electrocatalytic oxidation of glucose by the GC modified electrode was also explored by chronoamperometric method.

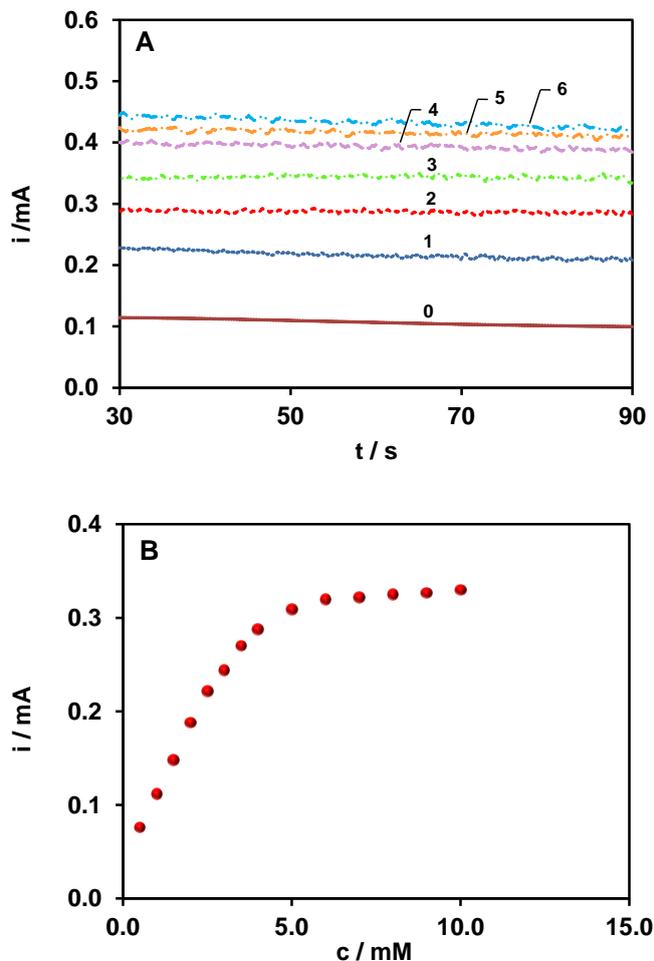
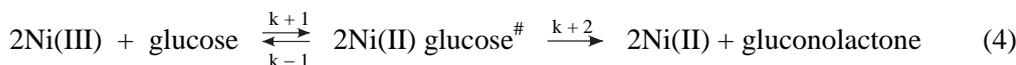


Figure 5. (A) Current-time curves recorded by holding the potential of the modified electrode at value of 0.75 V for 90 s for glucose concentrations of 0 (smallest), 1, 2, 3, 4, 5 and 6 mM (highest) in stirred 0.1 M NaOH solution. (B) Calibration curve of the steady-state current versus glucose concentrations.

The current-time profiles obtained in 0.1 M NaOH containing different glucose concentrations in the range 1 – 6 mM is presented in Fig. 5A. For all experiments, the potential was held at 0.75 V for a period of time 90 s, although the data is shown only for times of 30 – 90 s to emphasize the long-time behavior. As the glucose concentration was increased, the chronoamperometric current increased monotonically at first, but then its growth starts to level off. Fig. 5B demonstrates the resulting calibration curve of steady state current (i_{ss}) as a function of glucose concentration and shows that at higher glucose concentration a Michaelis-Menten type response is observed.

The catalytic reaction for the electrochemical oxidation of glucose may be described by the formation and decomposition of an intermediate charge transfer complex, similar to that of Michaelis-Menten kinetics:



where the apparent Michaelis-Menten constant, that is generally used to evaluate the biological activity of glucose oxidase, $K_M = (k-1) + (k+2)/(k+1)$ and the maximum current, $i_{\max} = nFA(k+2)$. In this case, the steady-state catalytic current, i_k , can be expressed as [39];

$$i_k = i_{\max}[G] / K_M + [G] \tag{5}$$

According to the Lineweaver-Burke equation [40], the apparent Michaelis-Menten constant (K_M) and the maximum current density (i_{\max}) of the catalytic reaction at the poly-Ni-(S)BPB-Gly/GC modified electrode can be calculated. In this case they are 2.3 mM and 4.6 mA cm⁻², respectively. These values are close to the reported values for free enzymes [41].

The evaluation of the effect of temperature on the modified electrode response to 3 mM glucose is presented in Fig. 6.

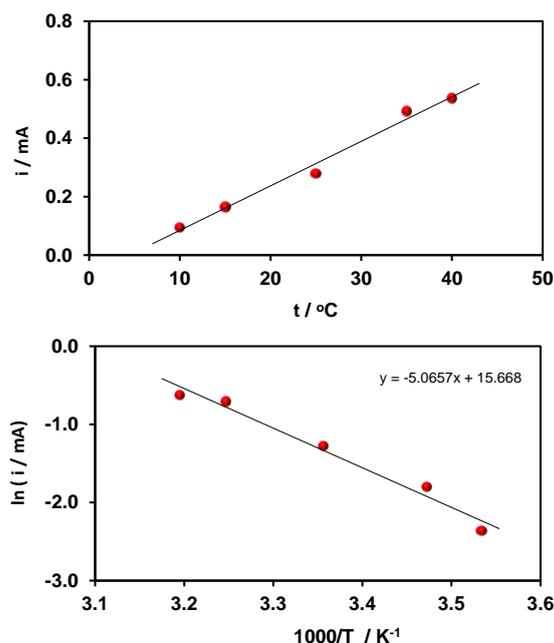


Figure 6. Temperature effect on the response current of poly-Ni-(S)BPB-Gly/GC modified electrode to 3 mM glucose. Inset: plot of the $\ln i$ versus T^{-1} ; other conditions are the same as those in Fig. 5A.

The response current increases when it changes from 10 to 40 °C, resulting from the rise of the catalytic reaction rate. This dependence can be expressed as an electrochemical version of the Arrhenius relationship: $i(T) = i_0 \exp(-E_a/RT)$. The plot extracted from the temperature dependency of the current signal showed a straight line (inset). The activation energy was calculated from the slope of this line and was found to be 42.1 kJ mol⁻¹. The found value was in accordance with those commonly encountered for glucose oxidase immobilized in different matrices: 22.5 – 50 kJ mol⁻¹, [42-45].

4. CONCLUSIONS

The GCE modified with organometallic nickel complex was formed using a cyclic voltammetry regime. The deposited film shows active Ni(II)/Ni(III) sites that promote the catalytic oxidation of glucose, for which this film exhibits a large response current in 0.1 M NaOH solution. The catalytic reaction may be described by the formation /decomposition of the intermediate charge transfer complex, similar to that of Michaelis-Menten kinetics. The apparent Michaelis-Menten constant (K_M) and the maximum current density (i_{max}) of the catalytic reaction are 2.3 mM and 4.6 mA cm⁻², respectively. The activation energy was found to be 42.1 kJ mol⁻¹. The investigated modifier appeared to be an effective electrocatalyst for the anodic oxidation of glucose. From the results presented above, it follows that the tested modifier offers a rather open structure allowing the penetration of a large quantity of supporting electrolyte and oxidized species.

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