Deposition of Nickel Hydroxide Nanoparticles Derivatized from Nickel Chitosan Complex on Glassy Carbon Electrode for Oxidative Electrocatalysis

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We demonstrate, for the first time, the chemical/electrochemical synthesis of uniformly dispersed nickel hydroxide nanoparticles (NPs) embedded in a chitosan (CH) membrane deposited on a glassy carbon (GC) electrode. The morphology of this composite was investigated by scanning electron microscopy (SEM). The SEM results show that NPs have a nano-globular structure in the range $10 \div 100$ nm. This composite displays electrocatalytic activity toward oxidation of methanol in alkaline solution. The electrochemical properties of the resulting material deposited as a redox film have been investigated by cyclic voltammetry and chronoamperometric techniques. Using Lavirin's theory the electron-transfer rate constant and the transfer coefficient were determined to be $k_s = 4.1$ s^{-1} and $\alpha = 0.42$, respectively, for a modifier film ($\Gamma_{Ni} = 7.1$ x 10^{-10} mol cm^{-2}) on a GC electrode in 0.1 M sodium hydroxide solution. Chronoamperometric studies were also used to determine the catalytic rate constant for the catalytic reaction of the tested modifier with methanol ($k_{ch} = 1.7$ x 10^4 cm^3 mol^{-1} s^{-1}). The dependence of the methanol oxidation current on alcohol concentration is discussed. The modified electrode for methanol oxidation is characterized by simple preparation, good stability and good reproducibility.

1. INTRODUCTION

Over the past decades great interest has been observed in bonding or coating monomolecular and multimolecular layers of chemicals on electrode surfaces in order to provide the electrode with special or distinctive characteristics. Such electrodes, called modified electrodes, have diverse applications, including electrocatalysis, electroanalysis and basic electron transfer chemistry [1-4]. Of particular interest in this regard is the immobilization of redox active materials that can alternate

between various valance states under the influence of external electric fields, and that are capable of mediating electrochemical reactions of substances dissolved in the contacting solution, which are electrochemically oxidized or reduced slowly or not at all at the naked electrode. Such mediated electrocatalysis is, for oxidation, represented by the general scheme (Scheme 1):
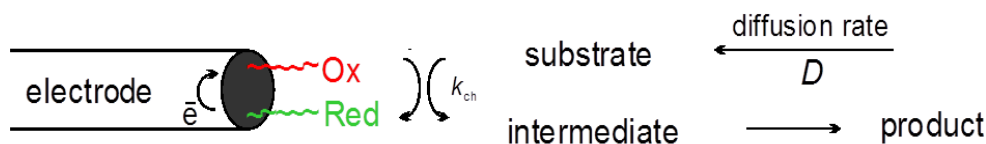
Scheme 1. Mediated electrocatalysis.

where Ox/Red is the immobilized redox couple, of which Ox reacts with the substrate at rate k_{ch} to give a product which is rapidly and irreversibly transformed into another product.

Among many possible electrocatalytic materials, particularly these with nickel redox couple: Ni(II)/Ni(III), are of great interest and have been the subject of much investigation. The literature survey shows that various studies have been devoted to investigations of electrochemistry of a nickel hydroxide/oxyhydroxide couple [5-8]; nickel oxyhydroxide strongly adsorbs some organic substances and has a high electrocatalytic efficiency toward the oxidation of an organic molecule via cyclic mediation electron-transfer processes in alkaline solutions. Recent research into developing new Ni-based redox modified electrodes for electrocatalytic applications seems to be directed toward the use of macrocyclic complexes of nickel in the form of multilayered conducting coatings [9-12] or the use of uniformly dispersed nickel oxide or nickel hydroxide nanoparticles onto electrode surfaces [13-16]. The main reason for the interest in redox chemistry of these coated electrodes is the expectation that they may combine the advantages of monolayer derivatized electrodes with those of a homogeneous catalytic system. Such redox electrodes as homogeneous catalytic systems offer a three-dimensional dispersion of the reacting centers, as opposed to the two-dimensional arrangement, prevailing at monolayer derivatized surfaces. From this fact it appears that the catalytic efficiencies of redox coatings are expected to increase with the amount of redox species deposited on the electrode surface. Thus, decorating supporting substrates with isolated nanoparticles or nanostructures is a good strategy to create efficient electrocatalysts. However, such a simple multiplication of the catalytic activity by a number of equivalent monolayers of the catalyst may be counteracted by limitations imposed by the rates of substrate diffusion and charge propagation across the coatings or other factors.

In this paper we report electrocatalytic oxidation of methanol, a substrate of great practical and analytical interest, by a glassy carbon (GC) electrode modified with the adsorbed/polymerized chitosan-nickel complex, which was then chemically/electrochemically derivatized to a chitosan-nickel hydroxide nanoparticle composite; chitosan (CH) [poly-β(1-4)-2-amino-2-deoxy-D-glucose], a polymer which derives from chitin deacetylation, the second most abundant polysaccharide in nature next to cellulose. To the best of our knowledge this is a first study on chemical/electrochemical properties of the tested complex, which up to the present was known as a generated and utilized product in the adsorption process to remove nickel(II) ions from aqueous solutions by different kind of

chitosan biosorbents [17-19]. Nevertheless, it must be pointed out that the literature sources contain few reports on using chitosan as a GC electrodes modifier for electrocatalysis and electroanalysis applications; the platinum-chitosan nano-composite was synthesized by electrochemical co-deposition at a GC electrode for fabrication of a nitrite sensor [20], the chitosan-modified screen-printed carbon electrode was used as a working electrode for the determination of selected metals [21] and the nano Bi_2O_3/chitosan-modified gold electrode was used as a biosensor for DNA hybridization [22].
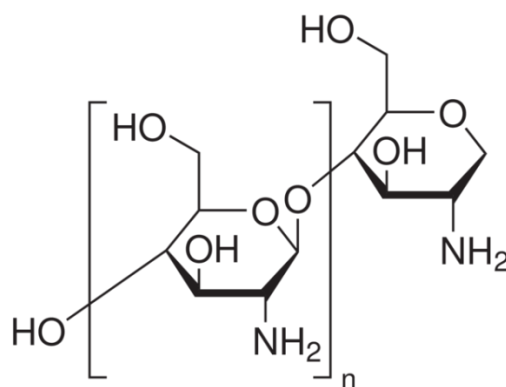
2. EXPERIMENTAL

2.1. Chemicals

Figure 1. Chemical structure of chitosan.

Chitosan (CH) [poly-β(1-4)-2-amino-2-deoxy-D-glucose] (DD = 75 ÷ 85 %,), (Fig. 1), acetic acid, nickel hydroxide, sodium hydroxide and methanol were obtained from Sigma-Aldrich. All chemicals were used as received. Redistilled water was used to prepare all solutions. All electrolyte materials were reagent grade and used without further purification.

2.2. Apparatus

All electrochemical experiments were performed in a conventional three-electrode cell powered by a Palm-Sens electrochemical workstation Palm-Sens (Palm Instruments BV, The Netherlands) controlled by a personal computer. A glassy carbon electrode (GC electrode, Metrohm, Herisau, Switzerland) of 3 mm in diameter (modified or otherwise), an Ag/AgCl saturated KCl electrode and a Pt wire were used as the working, reference and counter electrodes, respectively. All experiments were carried out at room temperature.

A scanning electron microscope and an energy dispersive X-ray spectrometer (SEM/EDS, Tescan, Vega 5135 with microanalyzer PGT, Avalon) was used to provide information on the morphological characteristics and composition of the tested modifier deposited on a GC electrode.

2.3. Preparation of chitosan nickel complex

Chitosan is insoluble in water, but with acetic acid it forms chitosan acetate, a water soluble salt. Tested chitosan in the form of dry powder was dissolved in 1% acetic acid to obtain 1% solution. The dissolution process took place at room temperature (ca. 20ºC) for 24 hours. The resultant bright yellow solution was then carefully filtered to remove various types of dust. In order to obtain the chitosan nickel complex known amounts of dry nickel hydroxide powder (insoluble in acetic acid) were placed in a glass-stoppered flask with 5 cm^3 of 1% acetic acid containing 1% chitosan and shaken at 100 rpm for 24 hours. After that the resulting transparent solutions (stock solutions) containing chitosan, the chitosan nickel complex and water were ready for further experiments.

2.4. Electrode modification
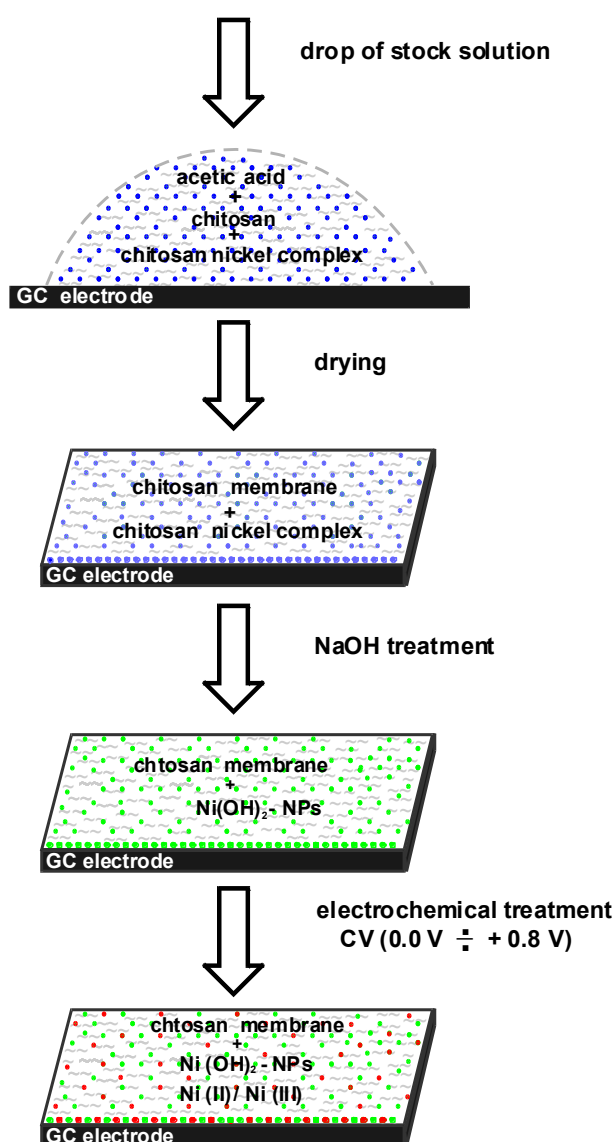
Scheme 2. Schematic illustration of the preparation of (CH)/Ni(OH)$_2$-NPs/GC electrode.

The surface of the GC electrode was polished using a polishing microcloth with 0.05 μm alumina powder and rinsed with distilled water several times prior to modification. The modified electrode was prepared by the drop-coating procedure; 5 μl of a selected stock solution was placed onto the surface of the GC electrode (diameter 3 mm) and it was allowed to dry (about 15 minutes at 50ºC). As a result the GC electrode covered with a chitosan membrane with uniformly dispersed and complexed nickel ions was obtained. After that the electrode was placed in the electrochemical cell with 0.1 M NaOH electrolyte and the electrode potential was cycled between 0.0 and 0.8 V at a scan rate of 100 mV s^{-1} in a cyclic voltammetry regime until a reproducible cyclic voltammogram was obtained, i.e. typically for 30 scans. Subsequently the modified electrode was used in different experiments.

Scheme 2 is a simple illustration of the preparation of the (CH)/Ni(OH)$_2$-NPs/GC modified electrode.

3. RESULTS AND DISCUSSION

3.1. Formation of the chitosan nickel complex

The binding mechanism of nickel ions to chitosan is not yet fully understood. Nevertheless, literature data shows that the binding of transition metal ions by chitosan is realized by coordination with the amino (–NH$_2$) and/or the hydroxy (–OH) groups on chitosan chains that serve as coordination sites. It is likely that the two –OH groups and the two –NH$_2$ groups are grabbed by one nickel and the chitosan-nickel complex is formed [23-25].

Preliminary tests had shown that the degree of Ni(OH)$_2$ dissolution in aqueous acetic acid solution containing chitosan depends on the mass ratio of nickel to chitosan used. The lower this ratio is, the faster the dissolution of solid hydroxide; this observation is not surprising, because chitosan used has its own coordination capacity that cannot be exceed. The binding of nickel ions by chitosan may formally be expressed by the equations:
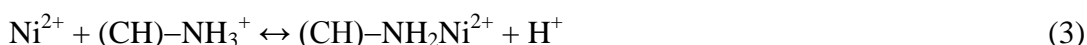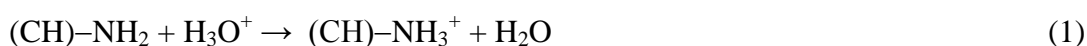
$$(CH)-NH_2 + H_3O^+ \rightarrow (CH)-NH_3^+ + H_2O \qquad (1)$$

$$Ni(OH)_2 \leftrightarrow Ni^{2+} + 2OH^- \qquad (2)$$

$$Ni^{2+} + (CH)-NH_3^+ \leftrightarrow (CH)-NH_2Ni^{2+} + H^+ \qquad (3)$$

Figure 2A shows the results of preliminary tests (dissolution of solid Ni(OH)$_2$ in 1% acetic acid containing 1% chitosan) expressed as a percentage of dissolved hydroxide versus the mass ratio of nickel to chitosan in a final solution. From this relationship the maximal content of nickel in the stock solution, at least under the conditions applied, was calculated to be 140 ± 5 mg/g of chitosan; this value is comparable with values reported in the literature concerning adsorption capacity for nickel ions from aqueous solutions by chitosan biosorbents: 120.5 mg/g [17], 114.9 mg/g [18] and

164.0 mg/g [26]. In our opinion the comparison of these values is plausible because the coordination capacity and the adsorption capacity are phenomena with similar mechanisms.

The maximal content of nickel in the stock solution was also confirmed by cyclic voltammetric measurements (see p. *3.3* and Fig. 2B).
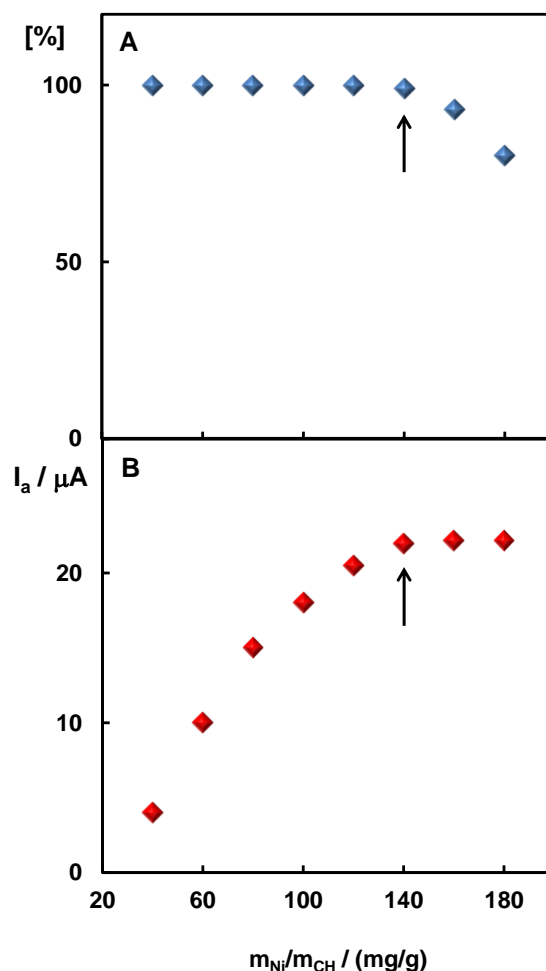

Figure 2. (A) A percentage of dissolved nickel hydroxide in 1% acetic acid solution containing 1% of chitosan versus the mass ratio of nickel to chitosan i tested solution. (B) Variation of the nickel(II) oxidation peak current during cyclic voltammetric measurements on its content in the modifier (membrane) expressed as the mass ratio of nickel to chitosan in the stock solutions used for the formation of modified electrodes; 0.1M NaOH. Scan rate 100 mV s^{-1}.

3.2. Formation of the modified electrode

The modified electrode was prepared by the drop-coating procedure as described in point *2.4*. Immersion of the GC electrode covered by a dry chitosan membrane with uniformly dispersed and complexed nickel ions into 0.1 M NaOH solution entail the drastic and irreversible changes in physical and chemical properties of the membrane in question. Firstly, the membrane becomes insoluble, and secondly dispersed nickel centers turn into insoluble nanoparticles of nickel hydroxide. These changes may formally be expressed by the equations:
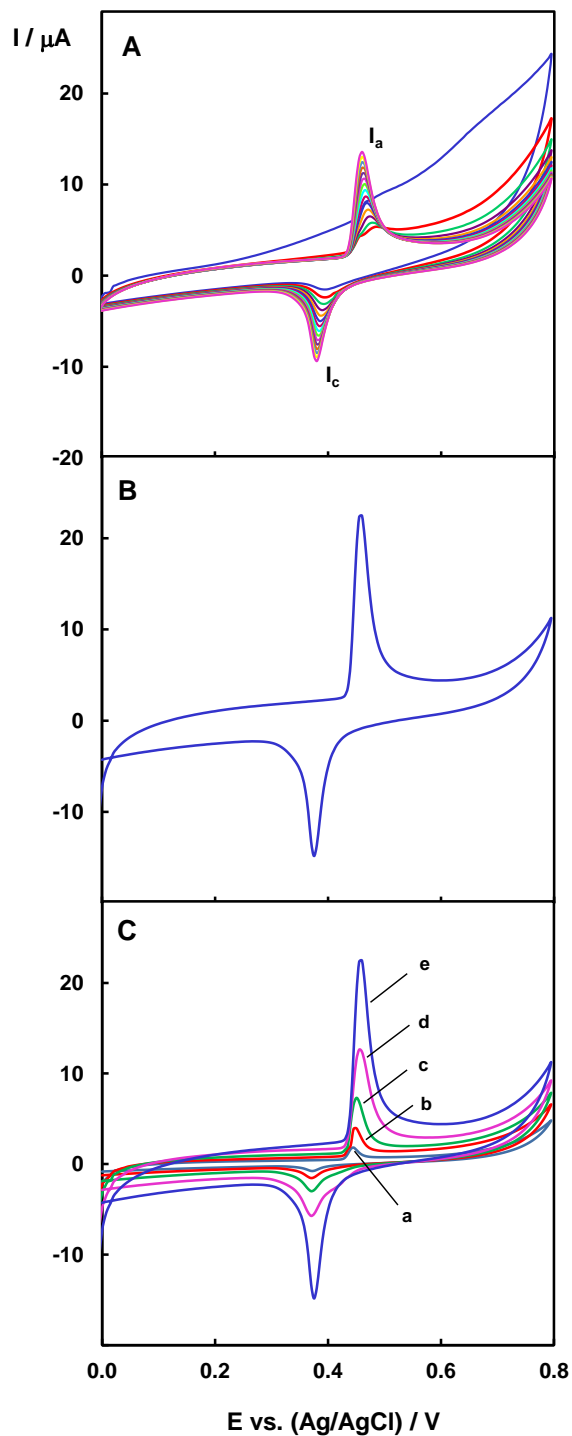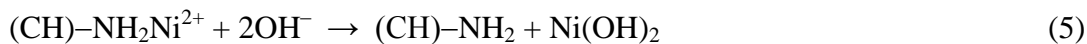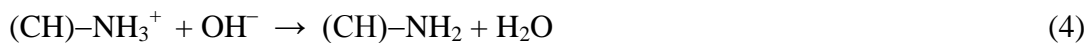
$$(CH)-NH_3^+ + OH^- \rightarrow (CH)-NH_2 + H_2O \tag{4}$$

$$(CH)-NH_2Ni^{2+} + 2OH^- \rightarrow (CH)-NH_2 + Ni(OH)_2 \tag{5}$$

Figure 3. (A) Repetitive cyclic voltammograms registered during electrochemical treatment of modified electrode [(CH)/Ni(OH)$_2$-NPs/GC] in 0.1 M NaOH (15 scans). Scan rate 100 mV s^{-1}. (B) Cyclic voltammogram of the stabilized modified electrode in 0.1 M NaOH (thickness of the film Γ_{Ni} 1.5 x 10^{-9} mol cm^{-2}). Scan rate 100 mVs^{-1}. (C) The same electrode at scan rates from 5 − 80 mV s^{-1}: (a) 5, (b) 10, (c) 20, (d) 50, (e) 80 mV s^{-1}

The final step in the formation of the modified electrode was carried out using a cyclic voltammetry regime with 0.1 M NaOH solution as an electrolyte; the electrode potential was cycled between 0.0 and 0.8 V at a scan rate of 100 mV s^{-1} until a reproducible cyclic voltammogram was obtained; Fig. 3A shows recorded curves. On the first and subsequent cycles a couple of I_a (oxidation) and I_c (reduction) peaks appeared. These couple of peaks corresponds to the oxidation of Ni(OH)$_2$ to NiOOH in accordance with the reaction [5,27]:

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \tag{6}$$
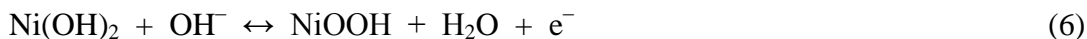
Increasing the number of potential sweeps results in a progressive increase of current values of the anodic and cathodic peaks because of the entry of OH$^-$ into the structure of Ni(OH)$_2$ nanoparticles, which leads to the progressive formation of a NiOOH corresponding to the Ni(OH)$_2$/NiOOH transition.

3.3. Morphological characterization of the modified electrode

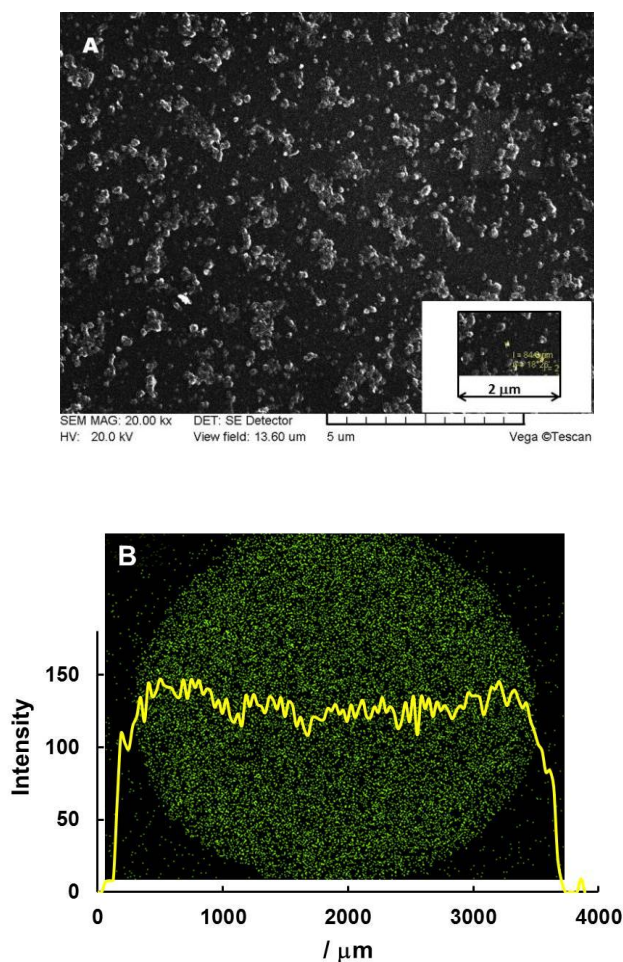**Figure 4.** (A) Typical field emission image obtained from (CH)/Ni(OH)$_2$-NPs (Γ_{Ni} 1.5 x 10^{-9} mol cm^{-2}); the inset is 2.0 μm x 2.0 μm. (B) EDS analysis of the line profile and mapping of nickel for tested film.

Figure 4 presents a typical scanning electron micrograph of (CH)/Ni(OH)$_2$-NPs film deposited onto a GC electrode. The field emission-SEM image (Fig. 4A) shows isolated NPs that are distributed uniformly over the electrode surface. The average size of NPs is around 50 nm, but there is evidence of some aggregation, as shown in the inset. Figure 4B shows EDS analysis of the line profiles and elemental mapping of nickel for (CH)/Ni(OH)$_2$-NPs film. The above data show that the presented modification route, described here, guarantees the production of uniformly dispersed Ni(OH)$_2$-NPs embedded in chitosan film on the GC electrode surface.

3.4. Voltammetric behavior of the modified electrode.

The cyclic voltammogram observed in 0.1 M NaOH for the freshly prepared modified electrode is illustrated in Fig.3B. Only one reversible couple is observed. The redox-potential of the Ni(II)/Ni(III) couple estimated at the midpoint of the anodic and cathodic peak potential was about 0.41 V. A similar shape of cyclic voltammetric curves has been recently observed for GC electrodes modified with several macrocyclic complexes of nickel [9-12], or with nickel oxide alone [13-16]. It should be noted that the peak height of the cyclic voltammogram obtained one day later was virtually identical to the one at the same scan rate presented at Fig. 3B. This indicates that the modified electrode is stable, at least over such a time period, under the conditions applied.

Figure 2B shows variation of the nickel(II) oxidation peak current during cyclic voltammetric measurements on its content in the modifier (membrane) expressed as the mass ratio of nickel to chitosan in the stock solutions used for the formation of modified electrodes. It may be seen from this figure that the nickel oxidation peak current linearly increases with an increasing nickel concentration up to about 140 mg/g, after which it reaches almost constant values independent of the concentration. Thus, a concentration of 140 mg/g represents a critical concentration, after which further dissolution of solid Ni(OH)$_2$ in 1% acetic acid containing 1% of chitosan *via* complexation of nickel ions by chitosan is not possible.

The voltammetric behavior of an electrode with a monolayer of a chemically stable redox couple and an electrochemically reversible system is characterized by symmetrical anodic and cathodic peaks with a difference ΔE_p in the peak potentials amounting to zero and a peak current directly proportional to the first power of the scan rate. Immobilized redox couples with slow charge-transfer kinetics exhibit higher ΔE_p values, which increase with the scan rate used. For relatively thicker coatings, further deviations from monolayer behavior normally occur, indicating the appearance of some mass transport limitation in the film [1].

Electrochemistry of Ni(OH)$_2$-NPs adsorbed on a GC electrode and embedded into the (CH) membrane was studied by cyclic voltammetry in 0.1 M NaOH. The cyclic voltammogram reaches a steady shape after ca. 30 scans and after that the peak currents show a linear dependence on scan rate as expected for surface-confined redox systems (Fig. 3C). Since the redox reaction of the modified electrode in question was that of a surface-confined redox system, the electron transfer rate constant, k_s, and the transfer coefficient, α, were determined from the relationship between ΔE [defined as $E_p - E^{o'}$; E_p is the peak potential value for the anodic or cathodic wave, and $E^{o'}$ is the formal potential taken

as the average of the anodic (E_a) and cathodic (E_c) peak potentials] and the log of potential scan rate (v) based on Laviron's theory [28].
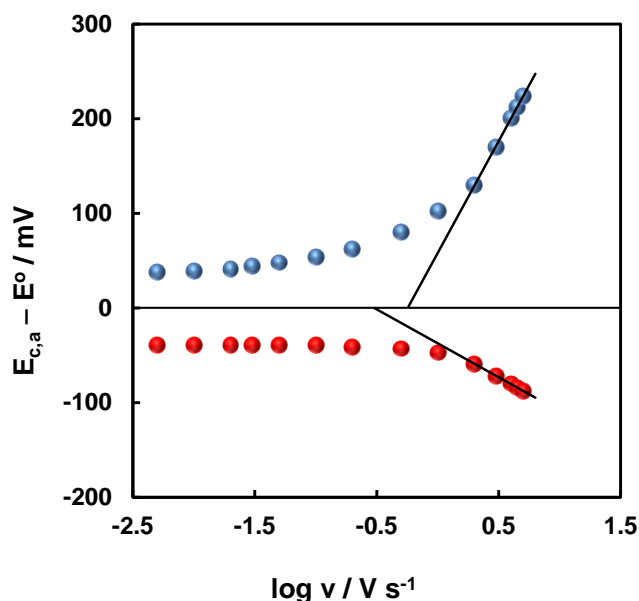

Figure 5. Laviron plot ($E_p - E^{o'}$ vs. log potential scan) of modified electrode in 0.1 M NaOH solution (Γ_{Ni} 7.1 x 10^{-10} mol cm^{-2}).

Figure 5 shows plots of ΔE vs. log(v) (Laviron plots) for the tested modifier film on the GC electrode (Γ_{Ni} = 7.1 x 10^{-10} mol cm^{-2}) in a 0.10 M sodium hydroxide aqueous solution; the surface coverage was determined from the integration of the charge under the cyclic voltammetric peaks obtained at a slow potential scan rate, where the peak current is directly proportional to scan rate, as anticipated for surface immobilized reagents. Interestingly, the peak separation is virtually constant (90 ± 10 mV) over the 5 to 100 mVs^{-1} scan rate range. Then the anodic and cathodic peaks start to move toward higher and lower potentials, respectively. For the highest scan rates a linear dependence is seen between the peak position and log(v). The two lines, assigned to anodic and cathodic peak positions, cross the $E^{o'}$ line at different points, indicating α to be different from 0.5, which is the value expected when the reversible oxidation and reduction processes have the same kinetics. From this plot the values of α and k_s were found to be 0.42 and 4.1 s^{-1}. We believe that the relatively small values of k_s and slowness of the electron-transfer kinetics is due, at least in part, to the fact that the electron-transfer reactions are hydroxide-coupled and, thus, k_s.

3.5. Mediated electrocatalytic oxidation of methanol

The electrochemical behavior of methanol at the GC electrode in basic media is poor, and oxidation does not occur prior to the discharge of the supporting electrolyte. Cyclic voltammograms recorded in 0.1 M NaOH in the absence and presence of 0.1 M methanol using the (CH)/Ni(OH)$_2$-NPs/GC electrode, at a scan rate of 5 mV s^{-1}, are shown in Fig. 6; as can be seen these curves show

that the redox coat mediates the oxidation of methanol. It is also clear that a reverse peak is absent, suggesting that the mediated reaction is irreversible.
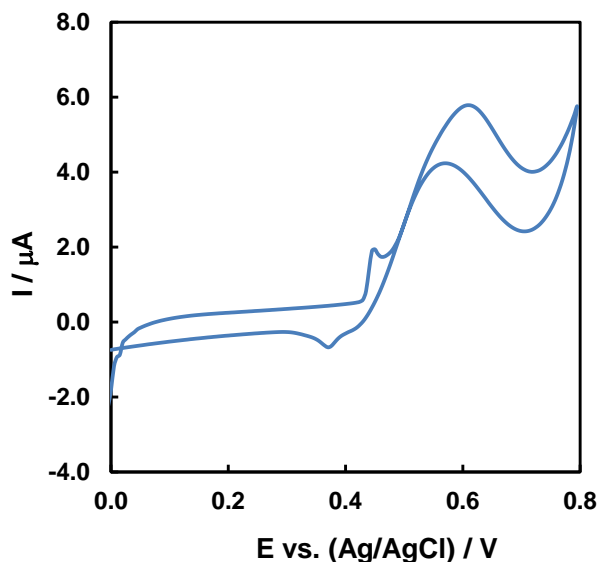

Figure 6. Electrocatalytic oxidation of methanol in 0.1 M NaOH on [(CH)/Ni(OH)$_2$-NPs/GC] modified electrode (Γ_{Ni} 1.5 x 10^{-9} mol cm^{-2}). Methanol concentration 0.1 M. Scan rate 5 mV s^{-1}.

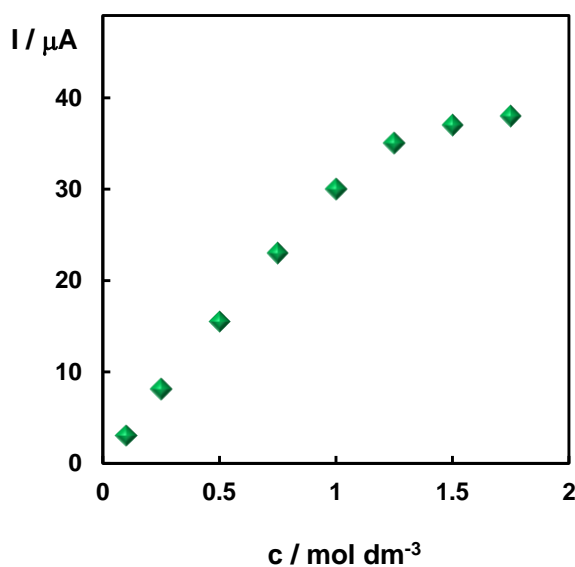**Figure 7.** The plot of methanol oxidation peak currents on modified electrode (Γ_{Ni} 1.5 x 10^{-9} mol cm^{-2}) vs. methanol concentration.

The oxidation peak of methanol appears at a potential of 0.61 V and also in the negative sweep methanol oxidation recommenced at the same potential; the height of the oxidation peak is stable on potential cycling. A similar shape of the cyclic voltammogram was observed recently by Taraszewska

et al. [29,30] for methanol oxidation in basic media on GC electrodes modified with nickel hydroxide formed by ex situ chemical precipitation or by tetraazamacrocyclic complexes of nickel.

Figure 7 illustrates the dependence of methanol electro-oxidation peak currents (recorded during the positive sweep in cyclic voltammetric measurements) on the modified electrode against methanol concentration. A nearly linear current-concentration dependence is observed up to 1 M of methanol. The current at higher methanol concentrations increases at first, but then its growth starts to level off. The significant deviation from linearity at higher methanol concentrations probably may not be attributed to the nature of the modifier, but it is rather a consequence of the change in the ratio of methanol and OH^- ion concentrations. The literature data show clearly the dependence of the kinetics of methanol electro-oxidation in basic media at nickel electrodes on the concentration of OH^- ions participating in the oxidation process [6,7]. Their excess or rather their insufficient concentration may disturb the whole process.
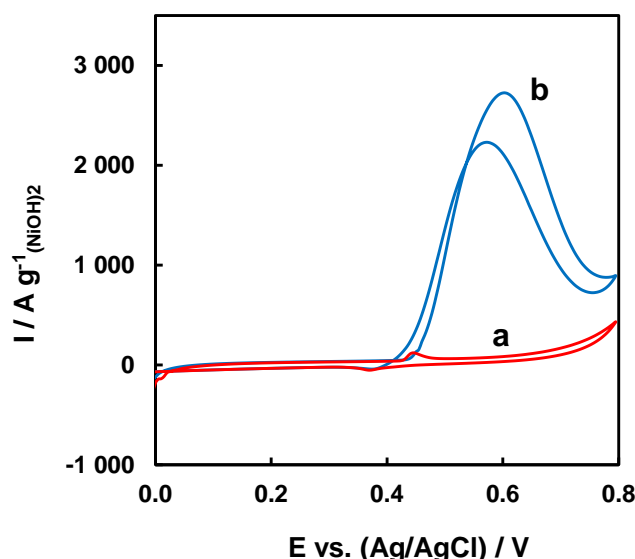

Figure 8. Cyclic voltammograms recorded at 5 mV s^{-1} at modified electrode (Γ_{Ni} 1.5 x 10^{-9} mol cm^2) recorded in 0.1 M NaOH in the absence (a) and presence (b) of 1.0 M methanol.

Cyclic voltammograms recorded in 0.1 M NaOH in the absence and presence of 1.0 M methanol, at a scan rate of 5 mV s^{-1}, are shown in Fig. 8. The currents were normalized by the mass of Ni(OH)$_2$ deposited on the electrode surface. Maximum normalized current of ~2700 A g^{-1} for methanol oxidation was found. It is worth noting that this value is much higher than the very recent reports using other nanostructured catalysts; ~450 A g^{-1} in an electrolyte solution containing 1 M methanol in 1 M HClO$_4$ using a Pt/MoO$_2$/carbon nanotubes modified electrode [31], ~300 A g^{-1} using 0.5 M H$_2$SO$_2$ as electrolyte and 1 M methanol with a carbon nanotube modified electrode decorated with Pt and PtRu NPs [32].

Methanol oxidation in basic media on electrodes modified with an Ni(II)/Ni(III) redox couple has been the subject of a number of papers [33-35]. These studies are of both theoretical and practical importance. Despite many attempts to determine the mechanism for the electro-oxidation of methanol,

surprisingly little is known with a reliable degree of certainty. Corresponding to the literature data it is evident that oxidation of methanol depends on the concentration of OH⁻, morphology of the modifying film, its thickness and permeability, surface concentration of active sites, and charge transport through the film.
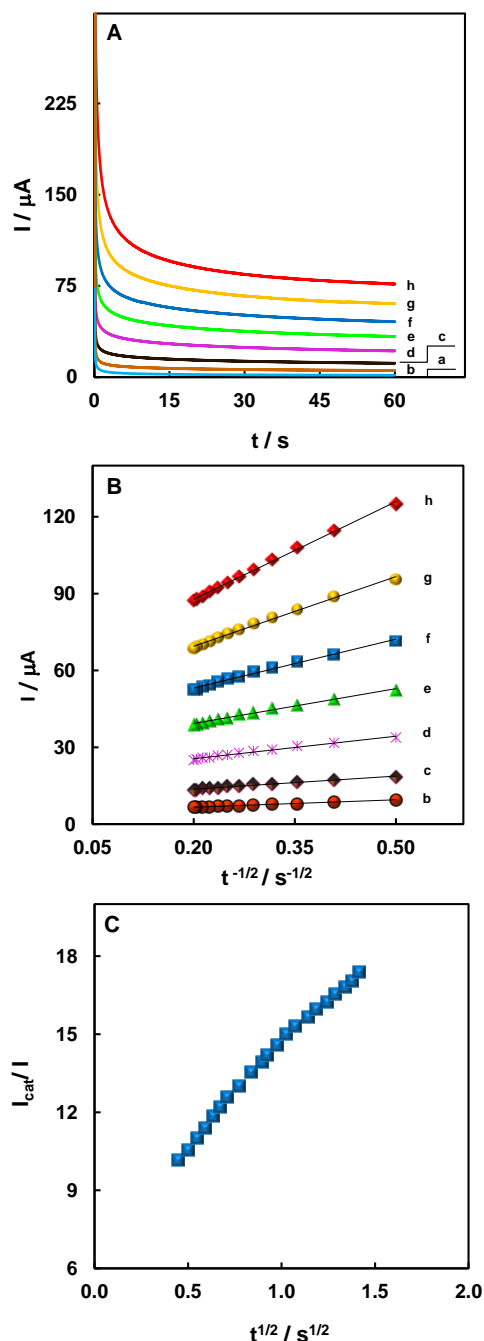
3.6. Chronoamperometric studies

Figure 9.(A) Chronoamperograms of modified electrode (Γ_{Ni} 1.5 x 10^{-9} mol cm^2) in 0.1 M NaOH solution containing (a) 0 M, (b) 0.1 M, (c) 0.25 M, (d) 0.5 M, (e) 0.75 M, (f) 1.0 M, (g) 1.25 M, and (h) 1.5 M methanol. (B) The plot of I vs. $t^{-1/2}$ from chronoamperogram data for different concentrations of methanol (Fig.9A)(C) The plot of I_{cat}/I vs. $t^{1/2}$, derived from chronoamperogram data in the absence and the presence of 1M methanol.

The catalytic oxidation of methanol by the tested modified electrode was also studied by chronoamperometry. Figure 9A shows the chronoamperometric measurements of methanol. The figure represents the current-time profiles obtained by setting the working electrode potential at 0.75 V for various methanol concentrations. For an electroactive material (methanol in this case) with a diffusion coefficient of D, the current response under diffusion control was described by the Cottrell equation [36]:

$$I = nFAD^{1/2}c\pi^{-1/2}t^{-1/2} \tag{7}$$

where D and c were the diffusion coefficient (cm^2 s^{-1}) and bulk concentration (mol cm^{-3}) of methanol, respectively; A was the electrode area (cm^2); and I was the current controlled by the diffusion of methanol from the bulk solution to the electrode/solution interface (in the presence of methanol at long experimental times, $t > 4$ s, the modifier oxidation is complete and the rate of electrocatalyzed methanol oxidation exceeds that of methanol diffusion from the bulk to the modifier/solution interface and therefore the current has a diffusional nature). The plot of I vs. $t^{-1/2}$ at various methanol concentrations was linear (Fig. 9B). From the slopes of the resulting straight lines and the methanol concentrations the average value of D was calculated to be 6.5 x 10^{-10} cm^2 s^{-1}. However, the recorded value of D was about two orders of magnitude lower than the diffusion coefficient of methanol in 0.1 M NaOH according to literature data [37,38]. This unexpected result becomes clear if someone takes into consideration that the determined diffusion coefficient in fact describes the methanol diffusion not in 0.1 NaOH solution, but in the (CH) membrane; not in the liquid phase, but in the solid state medium.

Chronoamperometry may also be used to evaluate the catalytic rate constant, k_{ch}, for the reaction between methanol and the surface-modified electrode. At intermediate times ($t = 0.2 - 2$s) the catalytic current I_{cat} is dominated by the rate of the electrocatalyzed oxidation of methanol and the rate constant for the chemical reaction between methanol and redox sites of the modifier, the catalytic current (I_{cat}) could be written as follows [39]:

$$I_{cat} / I = \pi^{1/2}(k_{ch} c_0 t)^{1/2} \tag{8}$$

where I was the current of the modified electrode in the absence of methanol, and I_{cat} was the catalytic current due to the addition of methanol. k_{cat}, c_0 and t were the catalytic rate constant (cm^3 mol^{-1} s^{-1}), bulk concentration (mol) of methanol and time elapsed (s), respectively. From the slope of the I_{cat} / I vs. $t^{1/2}$ plot (Fig. 9C), the k_{ch} value was calculated to be 1.7x 10^4 cm^3 mol^{-1} s^{-1} using $c_0 = 1.0$ M methanol, which is comparable with values reported in the literature concerning electrocatalytic oxidation of methanol in 0.1 M NaOH using different modifiers with a Ni(II)/Ni(III) redox couple [37].

4. CONCLUSIONS

A novel thin flat film deposited on a glassy carbon electrode, consisting of $Ni(OH)_2$ nanoparticles highly dispersed and homogenously embedded in the chitosan membrane, was successfully prepared by a simple chemical/electrochemical method. We characterized the surface morphology of the modifier and investigated its electrochemical behavior. An electrode made of this film was used in the electrocatalytic oxidation of methanol. From the results presented above it follows that the tested modifier (chitosan membrane with $Ni(OH)_2$-NPs) offers a rather open structure allowing the penetration of large amounts of the supporting electrolyte and oxidized species (methanol). These results also confirm that the electrocatalytic current depends on the rate of the catalytic reaction, and charge propagation and diffusion of oxidized species through the film are not limiting factors.

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