

Optimizing incorporation of nickel(II)–cyclam complex in poly(3,4-ethylenedioxythiophene) films for catalytic purposes

Krzysztof Maksymiuk · Marlena Puszcz ·
Katarzyna Szewczyk · Agata Michalska

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Abstract Poly(3,4-ethylenedioxythiophene) (PEDOT) films, due to their porous and open structure, as well as high stability, were chosen as a membrane for incorporation of Ni(II) ion complexes with 1,4,8,11-tetraazacyclotetradecane (cyclam) or deposition of electroactive films containing polymerized complex. Accumulation of the complex in PEDOT layers and its electrocatalytic activity was studied basing on voltammetric behavior of Ni(II)–cyclam and electrooxidation of a model reactant-methanol in alkaline solutions. Several modes of complex incorporation were tested, based on open circuit conditioning or polarization in the presence of nickel ions and cyclam. It was found that the most effective method was incorporation of cyclam in the course of PEDOT electrosynthesis, followed by potentiostatic accumulation of Ni(II) ions. This procedure resulted in around 50 times higher slope of dependence of methanol oxidation current on alcohol concentration than in the absence of PEDOT.

Keywords Nickel(II)–cyclam · Poly(3,4-ethylenedioxythiophene) · Methanol oxidation · Electrocatalysis

Introduction

Aza-macrocyclic ligands and their complexes with heavy metal ions gain growing popularity due to their potential versatile applications. One of the more interesting ligands is

neutral 1,4,8,11-tetraazacyclotetradecane (cyclam) that complexes various heavy metal cations [1], e.g., Ni²⁺. The importance of the Ni²⁺–cyclam complexes results, to some extent, from its significant role as electrode redox mediators (Ni(III)/Ni(II)) or catalyst for reduction of CO₂ [2], H₂O₂ [3], or oxidation of alcohols [4]. These catalytic processes can be applied, e.g., in fuel cells in the process of methanol oxidation, for sensing purposes or in reactions resulting in disposal of phenol derivative pollutants [4]. Ni²⁺–cyclam complexes can be easily obtained on electrodes in the form of conducting films by electropolymerization from aqueous solution of the complex [5]. In alkaline solutions, these electrodes behave similarly as electrodes modified by nickel hydroxide [6, 7].

From the point of view of tuning or enhancing mediating or catalytic properties of such complexes, efforts have been reported concerning incorporating/grafting cyclam Ni(II) complexes into conducting polymer layers: polypyrrole, polythiophene [8, 9], or modified polyaniline [5]. This form of catalyst dispersion is also advantageous to facilitate charge transfer between the electrode support and the reaction site.

Vilchez et al. [5] have applied copolymers of aniline and orthonilic acid to deposit Ni²⁺–cyclam complexes in polymer porous structure. This composite system has been studied in detail, and it was found to have good catalytic properties towards methanol oxidation in alkaline solutions. Higher currents recorded in the presence of the conducting polymer (sulfonated polyaniline) have been explained by its spongy morphology and more open structure [10]. Polyaniline coated also on nickel electrode has been used for electrocatalytic oxidation of methanol [11]. Gonzalez-Fuentes et al. [12] have introduced Ni²⁺–cyclam complexes into poly(amidoamine) dendrimers on gold electrode, resulting in a very efficient electrocatalytic system towards methanol oxidation.

K. Maksymiuk · M. Puszcz · K. Szewczyk · A. Michalska (✉)
Department of Chemistry, Warsaw University,
Pasteura 1,
02-093 Warsaw, Poland
e-mail: agatam@chem.uw.edu.pl

The aim of the present work was to incorporate Ni²⁺–cyclam complexes into a layer of a conducting polymer–poly(3,4-ethylenedioxythiophene) (PEDOT). This polymer belongs to the most stable conducting polymers [13] and also in alkaline solutions, and at higher potentials corresponding to Ni²⁺–cyclam complex electroactivity. As it is characterized by an open and porous structure [14], it is a promising candidate as a matrix for the effective catalyst dispersion and entrapment [15], enabling release and incorporation of larger ions, as e.g., Fe(CN)₆^{3–/4–} [16]. Moreover, PEDOT exhibits electroactivity in a wide potential range, where the current is only slightly dependent on electrode potential. Therefore, analysis of experimental data and separating the catalytic response from currents representing oxidation/reduction of the polymer is, in principle, easier.

The most effective method of cyclam complex incorporation in a conducting polymer is covalent binding of the complex with a monomer unit; this method has been also used to study properties of Ni–cyclam composites with PEDOT [17]. However, covalent binding requires, sometimes, a complicated synthetic procedure. Therefore, in this work, we discuss methods not requiring synthesis of a modified monomer; on the other hand, some procedures of effective catalyst incorporation into PEDOT films by simple conditioning will be checked. Our recent paper concerning incorporation of cyclam to a conducting polymer layer [18], on example of polypyrrole (in order to induce potentiometric sensitivity to Ni²⁺ ions) has shown, however, significant difficulties in this area. Incorporation of cyclam molecules in course of polymerization from a solution containing cyclam was not effective, most probably due to only weak physical entrapment of neutral or positively charged cyclam molecules (depending on pH). These difficulties can be omitted by variation of ion-exchange properties of the polymer, appropriate conditioning solution composition, and applied electrode potential.

The catalytic activity of Ni²⁺–cyclam complexes deposited on the electrode with PEDOT film will be checked on example of electrooxidation processes of a model reactant–methanol, important, e.g., for its applications in methanol fuel cells.

Experimental

Reagents

Distilled 3,4-ethylenedioxythiophene (Bayer) was stored in a refrigerator, and prior to use, it was purified by passing through a home-made alumina gel mini-column. All other chemicals including 1,4,8,11-tetraazacyclotetradecane

(cyclam) were p.a. products of Aldrich or Fluka, used as received. The complex Ni²⁺–cyclam was obtained in the solution by mixing equimolar (0.01 M) solutions of NiCl₂ and cyclam in the presence of 0.1 M NaOH.

Doubly distilled and freshly deionized water (resistance, 18.2 MΩcm, Milli-Qplus, Millipore, Austria) was used throughout this work.

Apparatus, electrodes, and synthesis of poly(3,4-ethylenedioxythiophene)

In electrochemical measurements, galvanostat–potentiostat CH-Instruments model 660A (Austin, TX, USA) was used.

The double junction silver/silver chloride reference electrode with 1 M lithium acetate in the outer sleeve (Möller Glasbläserei, Zürich, Switzerland) was used.

Platinum sheet of surface area 2 cm² served as counter electrode. Glassy carbon (GC) disk electrodes used as working electrodes (area 0.07 cm²) were polished with Al₂O₃, 0.3 μm.

PEDOT films were obtained from aqueous solution of 9 mM 3,4-ethylenedioxythiophene in the presence of 0.1 M electrolyte: either sodium poly(4-styrenesulfonate) (NaPSS), sodium dodecylsulfate (NaDS), or NaNO₃ to induce cation-exchanging (NaPSS, NaDS) or anion-exchanging (NaNO₃) properties of the polymer [16], respectively. Polymerization was carried out galvanostatically by applying current 1.4·10^{–5} A (current density, 0.2 mA·cm^{–2}). The applied polymerization charge was within the range from 2.5 to 30 mC corresponding to the approximate film thickness from 0.3 to 3 μm [19].

Mass spectrometry measurements with laser ablation of the sample were carried out in the way described elsewhere [20, 21]; the signal was recorded for the isotope ⁶²Ni.

Results and discussion

Electrodeposition of Ni²⁺–cyclam complex films

In these experiments, Ni²⁺–cyclam was obtained in the form of an electroactive film placed on the surface of a: (1) bare glassy carbon electrode or (2) glassy carbon electrode coated by a PEDOT layer. Electrodeposition of the complex was carried out from solution containing 0.1 M NaOH and 5 mM Ni²⁺–cyclam complex, under cyclic voltammetry conditions in the potential range from 0 to 0.900 V, with scan rate 50 mV s^{–1}. A pair of peaks, anodic at potential slightly above 0.6 V and cathodic at potential close to 0.45 V, was recorded, corresponding to oxidation/reduction for the Ni(III)/Ni(II) system, with current growing in the consecutive cycles. This is a typical behavior observed elsewhere [5]. Figure 1a, curve 1 presents voltammetric

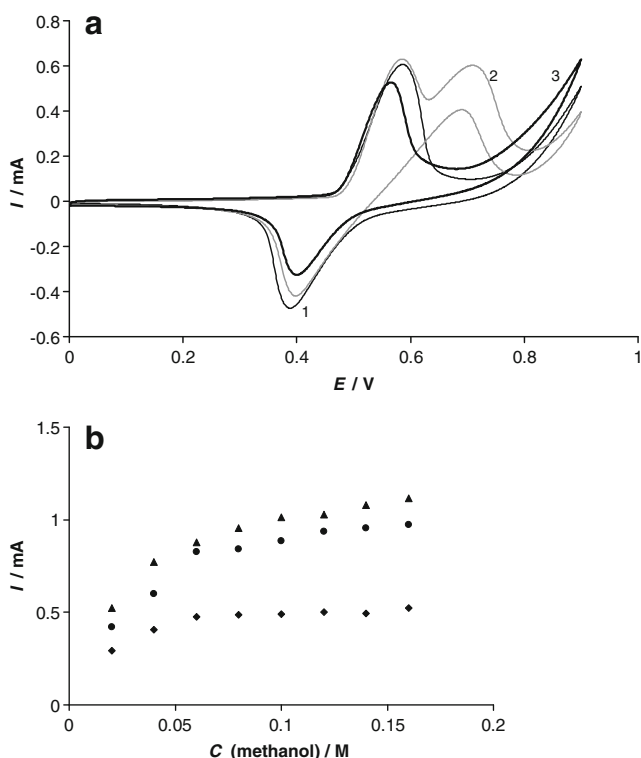


Fig. 1 **a** Voltammetric curves recorded for Ni(II)–cyclam complex polymerized on GC electrode (ten cycles) in 0.1 M NaOH solution in the absence (curve 1) and presence of 0.04 M methanol (curve 2), for Ni(II)–cyclam complex polymerized on electrode previously coated by PEDOT (doped by NO_3^-) ions, in the presence of 0.1 M NaOH (curve 3). Scan rate, 50 mV s^{-1} . **b** Dependence of methanol oxidation peaks on methanol concentration for various amounts of electroactive Ni(II)–cyclam film represented by number of cycles: five cycles (diamonds), ten cycles (circles), 20 cycles (triangles)

curve recorded in 0.1 M NaOH solution for such pretreated (ten cycles) bare GC electrode. The amount of the product on the electrode, estimated by integration of the voltammetric peak, was found to be around $10^{-7} \text{ mol cm}^{-2}$. The modified electrode was then used for the electrooxidation process of methanol. Portions of methanol were added to 0.1 M NaOH solution, and voltammetric curves were recorded (Fig. 1a, curve 2). In the presence of methanol, additional peaks were recorded at potential around 0.7 V, corresponding to oxidation process for both directions (anodic and cathodic) of the potential change. This shape of current vs. potential dependence points to electrocatalytic process of methanol oxidation in the presence of Ni^{2+} –cyclam complex film on the electrode surface (in the absence of this film, no oxidation process upon methanol addition was observed). These results, obtained both in the absence and presence of methanol are comparable with data reported by Vilchez et al. [5]. The results described in the manuscript refer usually to scan rate 50 mV s^{-1} , however, other scan rates were also used, within the range from 20 to

100 mV s^{-1} . A linear dependence of peak current of methanol oxidation on square root of scan rate pointed to a diffusion transport influence on the process, similarly as shown earlier for the same catalyst [4]. The methanol oxidation peaks were growing with increasing concentration of methanol, and Fig. 1b shows dependence of the peak height on methanol concentration in the range up to 0.16 M. This plot consists of two linear parts, with higher slope for concentrations below 0.06 M and lower slope for concentrations higher than 0.07 M; for the thinnest layer of the Ni^{2+} –cyclam film (five cycles), the recorded current is practically independent of methanol concentration higher than 0.06 M.

The influence of film thickness was also tested in more detail. The number of moles of the deposited complex is proportional to the number of cycles (Fig. 2), and the peak of methanol oxidation also increases with the number of cycles. However, this increase is not linear; the currents recorded for the films deposited in ten and 20 cycles do not differ considerably (Fig. 1b). This suggests also that, for thinner films, the whole layer can be penetrated by the reactant; however, for thicker layers, the reaction occurs mainly in the external part of such layer. This result suggests that effective distribution of the catalyst in the porous structure of a conducting polymer can be advantageous for the magnitude of the recorded current.

Detailed studies on Ni^{2+} –cyclam polymerization was rather outside the scope of our work, as it was studied earlier (e.g., [5, 10]). Our aim was mainly to show/highlight methods of simple and effective incorporation of Ni–cyclam into PEDOT, and in our case, methanol oxidation process served rather as a marker of this incorporation and catalytic efficiency.

Therefore, in the next step, the electrode was coated by a typical electropolymerized PEDOT layer first, and then the complex was deposited in the same way as described above. It is expected that, due to porous structure of this polymer, the Ni^{2+} –cyclam complex will fulfill the above-presented assumption of more effective dispersion, and thus, its catalytic influence will be more significant.

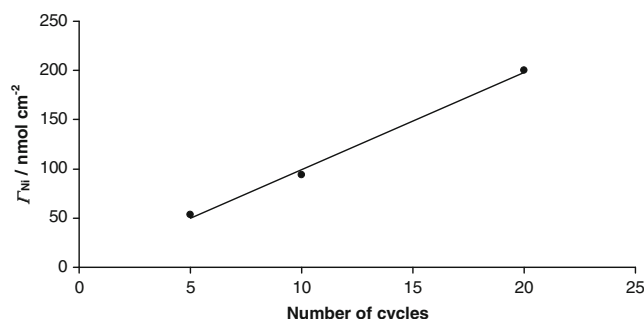


Fig. 2 Dependence of the amount of polymerized Ni(II)–cyclam on GC electrode on number of cycles

PEDOT layers were obtained by galvanostatic polarization, using three different values of polymerization charge: 13, 25, and 30 mC; different doping anions were applied (NO_3^- , PSS^-), resulting in anion- or cation-exchanging properties, respectively. Figure 1a, curve 3, shows an exemplary voltammetric curve obtained for the composite system: PEDOT(NO_3) (of polymerization charge 13 mC) and Ni^{2+} -cyclam film (ten cycles). A pair of peaks corresponding to Ni(III)/Ni(II) was added to the background current corresponding to oxidation/reduction of PEDOT. In the presence of PEDOT, a lower peak potential difference was observed than in the absence of PEDOT pointing to higher charge transfer rate. However, the currents peak for the Ni^{2+} -cyclam are slightly lower than recorded on PEDOT free electrode surface. In the presence of methanol in 0.1 M NaOH, oxidation current was also observed, and the observed dependence of current on methanol concentration was similar to that recorded in the absence of PEDOT, independently of the thickness of the conducting polymer layer and kind of doping anion. The independence of the PEDOT film thickness suggests that the complex accumulates rather on the film surface, although the conducting polymer layer is porous. Thus, the beneficial effect of catalyst dispersion was not obtained in this case.

The distribution of the electropolymerized complex was also studied using mass spectrometry with laser ablation of the solid sample. According to our experience [20], this method can bring more quantitative data than testing of the layer using scanning electron microscopy. The dependence of signal intensity on time can be easily transformed to signal intensity vs. penetration depth relation; as for longer exposition time the laser beam evaporates deeper parts of the PEDOT film. The recorded signal intensity for ^{62}Ni showed very rapid decrease with increasing penetration depth, pointing to accumulation of nickel species only on the PEDOT film surface.

Presence of the complex only in the surface part of PEDOT can be explained by competition between diffusion of the complex into the polymer and charge transfer reaction resulting in formation of immobilized electroactive film. The penetration depth, μ , of the polymer layer by the complex can be estimated from the formula [22]:

$$\mu = \frac{D}{k_{\text{ct}}} \quad (1)$$

where D is diffusion coefficient of the complex in the polymer layer, while k_{ct} is the charge transfer rate constant for the electroactive film formation. Basing on cathodic and anodic peak difference [23], the rate constant can be estimated as $\sim 10^{-3} \text{ cm s}^{-1}$, while D is around $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [19]. Therefore, μ thickness is below 1 μm , i.e., lower than thickness of PEDOT layer. This result suggests that effective

distribution of the complex in PEDOT film can be achieved in the absence of charge transfer reaction, e.g., under open circuit potential conditions or for potentials lower than 0.5 V, i.e., outside the potential range of electroactive film formation.

Conditioning in Ni^{2+} -cyclam solution

The above-described results show that electrodeposited film of Ni^{2+} -cyclam covers only the surface of either GC electrode or underlying PEDOT layer. Therefore, to obtain catalyst distribution in the PEDOT layer bulk, we were trying to incorporate Ni^{2+} -cyclam complex, now in the non-polymerized form, achieved by appropriate conditioning in a Ni^{2+} -cyclam complex solution. The first step was electrochemical preparation of a PEDOT layer on the electrode, doped either by NO_3^- or DS^- ions and following conditioning in a solution containing 0.01 M NiCl_2 , 0.01 M cyclam, and 0.1 M NaOH. The role of NaOH was to assure appropriate pH for complex stability, and moreover, it facilitates deprotonation of the polymer. This process is advantageous as it stimulates incorporation of cations [24]; in the present case, Ni^{2+} -cyclam cations can be absorbed in the conducting polymer phase. The conditioning time was a few days, and every day, the electrode was withdrawn from the conditioning solution, immersed in 0.1 M NaOH solution, and voltammetric curves were recorded. Then, conditioning process was continued. The voltammetric curves recorded for the electrode with PEDOT(DS) show presence of voltammetric peaks corresponding to Ni^{2+} -cyclam complex; however, the amount of the complex was much smaller than in the case described above, related to Ni^{2+} -cyclam complex film deposition on the PEDOT layer. After 1 day of conditioning, the peak was the highest, and the amount of the complex, determined by current peak integration, was close to $10^{-9} \text{ mol cm}^{-2}$. We were attempting to reduce uncertainty in charge determination by subtracting background current resulting from PEDOT oxidation/reduction and by comparing results for the same PEDOT layers but in the absence and presence of Ni-cyclam. On the other hand, ohmic drops in 0.1 M NaOH as supporting electrolyte, resulting from uncompensated resistance, are not significant, particularly for moderate scan rate as mainly used in this work. In course of following days, the current was decreasing; this can result from both decreasing electroactivity of the polymer in the alkaline medium and release of the complex from the polymer. After 3 days of conditioning, a voltammetric curve recorded for the electrode in the presence of methanol showed presence of anodic peak. This result confirms catalytic activity of the complex introduced in this way; however, the recorded current was low as result of low amount of the catalyst.

Analogous experiments were carried out for electrodes with PEDOT doped by NO_3^- ions. However, in this case, the voltammetric signals corresponding to Ni^{2+} -cyclam complex were much smaller. Most probably, PEDOT doped by nitrate ions, as anion exchanger, does not stimulate incorporation of cations in course of conditioning.

Because the open circuit conditioning did not result in high concentration of the complex in PEDOT film, the conditioning mode was changed to cyclic voltammetry conditions. It was shown earlier that this procedure is more effective for cation accumulation in polypyrrole in alkaline medium [18, 24], including Ni^{2+} -cyclam cation incorporation. In the present case, electrodes coated by PEDOT films of different thickness, doped either by PSS^- , NO_3^- , or DS^- ions were immersed in a solution containing 0.01 M NiCl_2 , 0.01 M cyclam, and 0.1 M NaOH and polarized within potential range from -0.5 to 0.5 V with scan rate 50 mV s^{-1} for 50 min. The potential range was selected to avoid oxidation of the complex and thus film formation inside PEDOT in course of conditioning. In all cases, voltammetric curves recorded then in 0.1 M NaOH solutions in the potential range from 0 to 0.9 V revealed presence of a pair of peaks corresponding to Ni^{2+} -cyclam complex. It was found that the amount of the complex (obtained by integration of the peak) was higher for thicker films. Figure 3 presents the dependence of the amount of accumulated Ni^{2+} -cyclam on PEDOT polymerization charge; it is linear for polymerization charge below 20 mC both for PEDOT(PSS) and PEDOT(DS). However, as shown in Fig. 3, for thicker PEDOT films, the amount of the complex decreases. The catalytic influence exerted on methanol oxidation was confirmed for these films; the oxidation current of methanol increased with the rising amount of the complex in PEDOT layer.

Synthesis of PEDOT from cyclam solution and following incorporation of Ni(II)

In another conditioning protocol immobilization of free cyclam and then Ni(II) ion incorporation steps were separated.

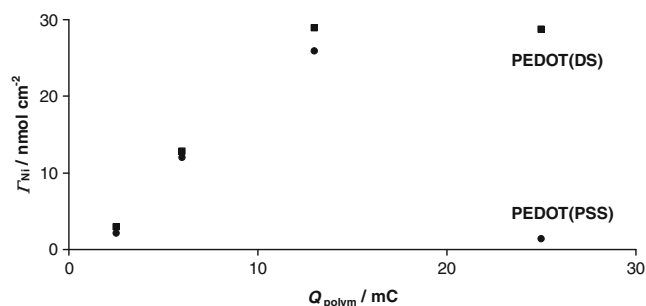


Fig. 3 Dependence of amount of Ni(II)-cyclam accumulated in PEDOT layer under voltammetric conditions on polymerization charge of PEDOT(PSS) (circles) and PEDOT(DS) (squares)

Since cyclam is a large molecule, there can be some steric hindrances in their effective diffusion into the PEDOT layer. Therefore, to facilitate incorporation, this process was coupled with electropolymerization, i.e., synthesis of PEDOT was carried out in solution containing both the monomer and cyclam, polymerization charge was 13 mC. Then, the electrode was rinsed with water and polarized under cyclic voltammetry conditions in solution containing Ni(II) ions. Non-complexed Ni(II) ions can easily penetrate the cation-exchanging PEDOT layer in course of its oxidation/reduction, this was confirmed by similar voltammetric curves of cation-exchanging PEDOT(PSS), recorded in KCl and NiCl_2 solutions (results not shown). Polymer films were doped either by DS^- or PSS^- ions and were obtained from solutions containing 0.01 M EDOT, 0.1 M NaPSS or NaDS and 0.01 M cyclam. Galvanostatic polymerization occurred at higher potential compared with cyclam-free solutions, particularly in the case of NaPSS, where a maximum on potential-time curves was observed. The observed overpotential results most probably from inhibiting influence of cyclam adsorbed on the GC electrode surface (confirmed by decrease of AC voltammetric current recorded for uncoated electrodes in 0.1 M KCl solution, in the presence of cyclam of concentration up to 0.01 M). In the presence of DS^- ions exhibiting high surface activity, the influence of cyclam adsorption on GC electrode can be lower. After polymerization, the electrodes were rinsed with water and then polarized in 0.1 M NiCl_2 solution under the same conditions as described above.

The voltammetric curves obtained for thus prepared films exhibit typically a pair of narrow peaks with peak potential separation close to 0.1 V and high peaks corresponding to methanol oxidation. For PEDOT(DS), the current for low methanol concentration (0.02 M) was slightly higher than recorded on GC electrode with Ni^{2+} -cyclam film (ten cycles), although the oxidation/reduction peaks corresponding to Ni^{2+} -cyclam complex were significantly lower.

The above-described method was then modified by replacing cyclic polarization in 0.1 M NiCl_2 solution by potentiostatic polarization at -0.7 V corresponding to partially reduced conducting polymer. This negative potential was expected to facilitate Ni(II) incorporation. Voltammetric curves recorded afterwards in 0.1 M NaOH solution revealed presence of peaks corresponding to Ni^{2+} -cyclam oxidation/reduction and also peaks corresponding to methanol oxidation in the presence of alcohol in the solution. Figure 4 shows exemplary data concerning Ni^{2+} -cyclam complex accumulation (calculated from integrated voltammetric peaks) in PEDOT(PSS) layers, obtained for various polarization times. With increasing polarization time, the complex amount increases as expected, however, for the time above 60 min, the increase approaches plateau.

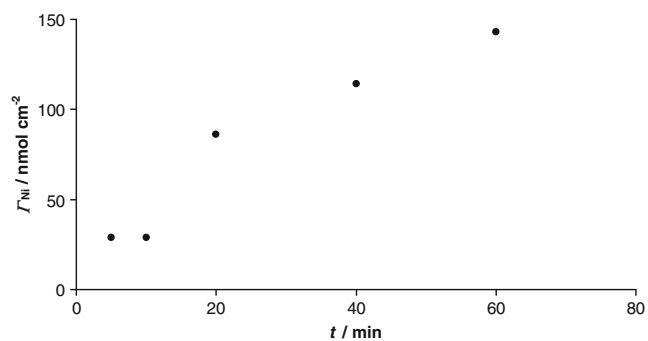


Fig. 4 Influence of polarization time at -0.7 V in 0.01 M NiCl_2 solution of electrodes with PEDOT(PSS) (polymerization charge, 4.5 mC) films containing cyclam on amount of accumulated complex

The time, t , required to obtain a uniform distribution of the complex in the polymer film can be approximately calculated basing on equation:

$$t = d^2/D \quad (2)$$

where d is film thickness, while D is diffusion coefficient of the complex in the layer. Assuming that d is slightly above $1 \mu\text{m}$ and D is of the order $10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [19], the estimated time is a few seconds.

Voltammetric curves obtained for PEDOT(DS) or PEDOT(PSS) and polarization time 60 min, show relatively high currents corresponding to oxidation/reduction of the complex in 0.1 M NaOH, in the absence of methanol, pointing to a complex amount close to $4 \cdot 10^{-7} \text{ mol cm}^{-2}$ in the case of PEDOT(DS). This value is higher than that obtained by electropolymerization on GC electrode (ten cycles) and higher than in the case of earlier-described methods, however, the peak potential difference was greater than in the absence of PEDOT. The catalytic influence on methanol oxidation was quite high; the current recorded, e.g., for methanol concentration 0.02 M or 0.04 M, was significantly higher than recorded in the absence of PEDOT (complex electrodeposited on GC electrode) and methanol oxidation currents were observed also for lower concentrations (~ 1 mM).

Figure 5 presents calibration plot (current vs. methanol concentration), recorded for PEDOT(DS) and PEDOT (PSS) films prepared as described above, in the range of lower concentrations of methanol (to 5 mM). In both cases, a linear dependence was observed with slope close to 0.8 mA/mmol , i.e., around 50 times higher than in the absence of PEDOT film (for the polymerized complex deposited on GC electrode, ten cycles). However, for concentrations higher than 5 mM, the current is no longer dependent on methanol concentration, and a constant value close to 2 mA was recorded. The voltammograms of methanol oxidation in this higher concentration range were slightly deformed and partly overlapped with the signal of

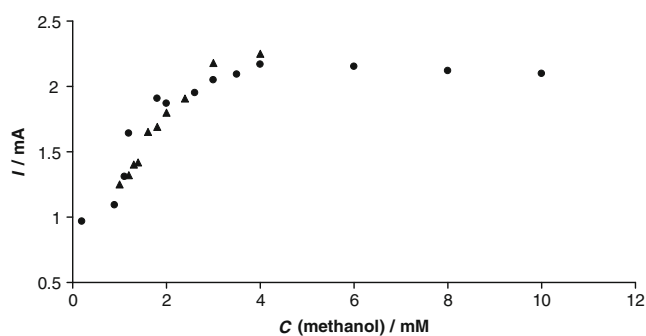


Fig. 5 Dependence of methanol oxidation current, I , on methanol concentration for electrodes with PEDOT(PSS) (circles) and PEDOT (DS) (triangles) containing cyclam and Ni(II) ions accumulated by potentiostatic polarization at -0.7 V for 60 min. Polymerization charge, 13 mC

the complex in the upper concentration limit. It seems that the limiting factor is maximal current (above 2 mA) which can be connected with availability of the complex–catalyst in the polymer layer and possible saturation resulting from methanol–complex interactions. The mechanism of these interactions requires more detailed studies and should be rather a subject of a separate paper. Here, our aim was mainly to show/highlight methods of simple and effective incorporation of Ni–cyclam into PEDOT.

As shown above, in general, the proposed sensors can operate in different methanol concentration ranges and also at concentrations much higher than 5 mM, where the electrodes were also stable (thus, the films do not undergo destruction in the presence of methanol). The observed sensitivity is dependent on the preparation mode, and the electrodes with low sensitivity, as, e.g., electroactive Ni–cyclam films on GC electrodes, can operate in a rather high methanol concentration, even above 0.2 M.

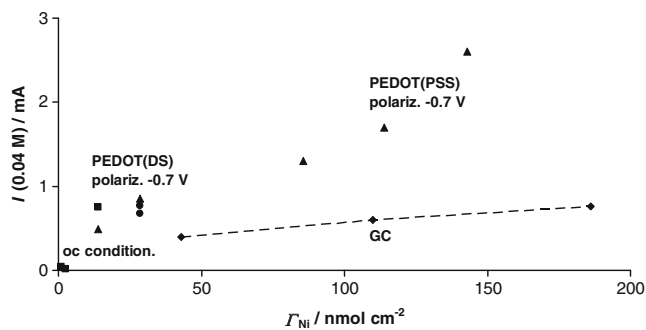


Fig. 6 Comparison of amount of Ni(II)–cyclam and methanol oxidation current, I , for 0.04 M methanol in 0.1 M NaOH for various methods of complex immobilization: polymerization on GC electrode (diamonds), open circuit conditioning (squares), polarization at -0.7 V for PEDOT (PSS) (triangles), polarization at -0.7 V for PEDOT(DS) (circles)

Relation between amount of Ni²⁺–cyclam and catalytic activity

The procedures of Ni²⁺–cyclam incorporation into the conducting polymer or on a substrate electrode resulted in different amounts of the complex on the electrode surface. Basing on these results, correlation between amount of the complex and its catalytic activity towards methanol oxidation can be discussed.

Figure 6 presents such relation, where the catalytic effect is represented by methanol oxidation current peak for methanol concentration 0.04 M. These results show that the catalyst located directly on the GC surface (in the absence of PEDOT, dashed line) exerts lower activity, compared with the systems with PEDOT. For the electrodes where the complex was incorporated in course of different forms of conditioning, the obtained catalytic currents were, generally, considerably higher. It can be noticed that, for the same amount of the catalyst (based on oxidation/reduction charge for the Ni(III/II) system) as coated directly on GC surface, the catalytic activity is higher. This is clear particularly for the case of potentiostatic polarization of PEDOT layer with cyclam in NiCl₂ solution. In this case, the concentration of methanol 0.04 M is rather high from the point of view of current vs. methanol concentration; already, for concentration above 5 mM, the current is no more dependent on methanol concentration. Therefore, analyzing catalytic effects for much lower methanol concentration the difference in this activity for GC electrode without PEDOT and for the electrode with PEDOT layer polarized potentiostatically would be significantly higher.

The beneficial effect of conditioning of the electrode with PEDOT film and appropriate incorporation procedure results probably from effective dispersion of the catalyst in the PEDOT film and other form of the catalyst (Ni²⁺–cyclam complex ions vs. electropolymerized film deposited on uncoated GC electrode). Moreover, in the case of Ni²⁺–cyclam electroactive film on the electrode, most probably, only the outermost part of the film is available for the reactant, as shown by dependence of the current on the thickness of the film.

Conclusions

Poly(3,4-ethylenedioxythiophene) films were used as support for Ni(II)–cyclam complexes, to enhance complex accumulation and increase its electrocatalytic activity, tested on a model example of methanol electrooxidation.

Deposition of Ni(II)–cyclam electroactive films occurs, however, mainly on PEDOT surface due to high rate of complex polymerization, compared with its diffusion

towards the membrane bulk. More effective methods, resulting in complex distribution within the PEDOT layer, were based on open circuit or voltammetric conditioning in solutions containing the complex. Better results were observed when cyclam incorporation and complexation were separated. The case of cyclam incorporation in the course of PEDOT synthesis, followed by potentiostatic Ni(II) ion accumulation resulted in about a 50 times higher current of methanol oxidation, compared with the reaction occurring directly on the glassy carbon electrode. This improvement can be explained both by enhanced complex accumulation and higher electrocatalytic activity, compared with electroactive Ni(II)–cyclam films deposited directly on the electrodes.

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