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Electrocatalytic oxidation of hydrogen peroxide by poly(Ni^{II}teta) modified electrodes[§]

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Abstract

[Ni^{II}(teta)]$^{2+}$ (teta = C-*meso*-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) was electropolymerized on glassy carbon (GC) and Nafion® coated GC electrodes (GC/Nf). These poly(Ni^{II}teta) modified electrodes showed 70 mV shift per pH unit and electrocatalysed the oxidation of H_2O_2. The thickness of the Nafion® film was found to influence the rate of the electrocatalytic reaction. A rate constant of 1.77×10^3 dm^3 mol^{-1} s^{-1} was observed at 1.0×10^{-5} cm thick Nafion® film, whereas a rate constant of 0.08×10^3 dm^3 mol^{-1} s^{-1} was observed at 3.6×10^{-5} cm thick film. At a plain GC electrode, a rate constant of 1.29×10^3 dm^3 mol^{-1} s^{-1} was observed. The poly(Ni^{II}teta) is stabilized in the Nafion® film when compared to the poly(Ni^{II}teta) coated on plain electrode.

1. Introduction

Much attention has recently been paid to the investigation of chemically modified electrodes due to their applications in electroanalytical techniques [1, 2]. Electrochemical methods based on the direct reduction or oxidation of substrate molecules at the bare electrodes are often not suitable for analytical applications as the electrode reactions are subjected to a large overvoltage. Modifying the surface of an electrode with a redox mediator is a well-established strategy for achieving wider applicability of electroanalytical methodology. Incorporation of a redox mediator into the polymer film can be achieved in different ways, possibly the simplest being the electropolymerization of the metal complex itself or the incorporation of a redox mediator in the polymer film [1–3]. The modified electrode surface usually shows improved electrocatalytic activity. In this respect an electrode modification obtained by electrochemical polymerization of metal complex is potentially appealing if the metal ion involved is catalytically active. Also, there has been an increasing interest in the study of electrocatalytic properties of macrocyclic complexes of cobalt [4–7] and nickel [3, 8–16]. In particular, Ni(II) and Co(III) with tetraazamacrocyclic ligands have been reported to be exceptionally efficient and selective electro- and photocatalysts for the reduction of CO_2 [17, 18], nitrate and nitrite [19, 20] and O_2 [4–7, 21, 22]. Catalytic activity towards alcohols and –NH_2 containing compounds was observed at electrodes modified with nickel(II)cyclam [15] and tetramethyldibenzo tetraaza(14)annulene complex [12]. The determination of H_2O_2 and organic peroxides is of great practical importance in clinical industries and environmental concern [23, 24]. In this paper, we report the stability and electrocatalytic behaviour of [Ni^{II}(teta)]$^{2+}$ (teta = C-*meso*-(5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) polymerized on a plain glassy carbon (GC) electrode and Nafion® coated GC electrode (GC/Nf) towards the electrocatalytic oxidation of hydrogen peroxide.

2. Experimental details

The [Ni^{II}(teta)](ClO_4)$_2$ was prepared according to a literature procedure [25]. The 5% Nafion® solution was purchased from Aldrich and diluted with methanol. Sodium hydroxide and hydrogen peroxide were purchased from Merck. All other chemicals and solvents were of reagent grade and used without further purification. Water was doubly distilled using an all glass apparatus under alkaline potassium permanganate solution. Cyclic voltammograms were recorded using an EG&G PAR 273A potentiostat/galvanostat equipped with a RE 0151 recorder. A three-electrode two-compartment cell with plain GC or Nafion® coated GC electrode (GC/Nf) as working electrode, a 1 cm^2 Pt flag as counter electrode and saturated calomel electrode (SCE) as reference were used for the cyclic voltammetric

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[§] This paper is dedicated to Professor P. Natarajan for the occasion of his 60th birthday.

studies. The rotating disc electrode experiments were done with an EG&G PARC model 616 rotating disc electrode set-up with GC as working electrode, platinum wire as counter electrode and SCE as reference electrode.

The poly(Ni^{II}teta) modified GC electrodes (represented as GC/Ni) was prepared by cycling the potential from 0.0 to 0.7 V vs SCE in a solution containing [Ni^{II}(teta)]$^{2+}$ and 0.2 M NaOH. To prepare the poly(Ni^{II}teta) incorporated Nafion® film coated GC electrode (represented as GC/Nf/Ni) a GC/Nf electrode was used. The GC/Nf electrode was prepared by casting a known volume of 0.5% Nafion® solution on the GC electrode [26]. The solvent was evaporated from the surface of the electrode at room temperature. Before the film was completely dried it was soaked in distilled water. The thickness of the Nafion® film was calculated from the cast solution volume and density of Nafion® film (1.58 g cm^{-3}) [27].

3. Results and discussion

3.1. *Film formation and characterization of modified electrode*

The electropolymerization of [Ni^{II}(teta)]$^{2+}$ complex was carried out at a GC electrode in an aqueous 0.2 M NaOH solution using multiple scan cyclic voltammetry. Typical continuous cyclic voltammograms of [Ni^{II}(teta)]$^{2+}$ are shown in Figure 1. Film growth is accompanied by increasing reversible peak currents which correspond to the Ni(II)/Ni(III) redox couple. The poly(Ni^{II}teta) film formed on the GC electrode demonstrates a high degree of adherence to the GC electrode. The cyclic voltammograms of poly(Ni^{II}teta) show an $E_{1/2}$ value of 0.42 V vs SCE indicating the formation of the poly(Ni^{II}teta) film on the GC electrode. According to Roslonek and Taraszewska [8], the film formation of nickel macrocycles (*cis*- and *trans*-aquo-5-aminomethyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecanenickel (II) and [Ni^{II}-*N*-tetramethylcyclam]$^{2+}$) and the attachment of the complex to the electrode surface is connected with the oxidation of the OH^{-} anions. They conclude that the coupling of the complex to the electrode surface 'S' takes place through an S–O–Ni^{II} bond. The attached Ni(II) complex undergoes oxidation to Ni(III) and binds with the Ni(III) complex via the formation of oxo-bridges [8, 28] (Figure 2).

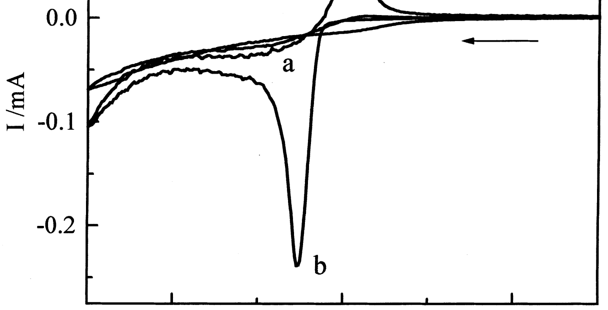

Fig. 1. Continuous scan cyclic voltammograms of 0.5 mM [Ni^{II}(teta)]$^{2+}$ complex at GC electrode in 0.2 M NaOH. Scan rate 20 mV s^{-1}. (a) First and (b) 15th scan (→ indicates the sweep direction).

The GC/Ni electrode shows a redox wave with an $E_{1/2}$ value of 0.42 V vs SCE and 60 mV peak separation (scan rate 20 mV s^{-1}). The plot of square root of scan rate ($v^{1/2}$) against peak current (I_p) shows a linear relationship. In Figure 3 the cyclic voltammograms of GC/Nf/Ni electrode in 0.2 M NaOH with different scan rates are shown. The GC/Ni and GC/Nf/Ni electrodes did not exhibit electrochemical response in other supporting electrolyte solutions (neutral pH). Similar behaviour has been reported for nickel hydroxide modified electrodes [11] and other nickel macrocycle modified electrodes [8]. This may be due to the compact nature of the film and the modification of polymeric film seems to be strongly favoured in high pH solutions. The ratio of anodic to cathodic peak currents (I_{pa}/I_{pc}) is always higher than unity for both GC/Ni and GC/Nf/Ni electrodes indicating the different kinetics for the oxidation and reduction processes [12]. These modified electrodes have shown increased peak separation (ΔE_p) on increasing the scan rate. The cyclic voltammograms exhibit ΔE_p values greater than 60 mV at scan rates greater than 20 mV s^{-1}. This indicates a relatively slow redox transition and/or electron exchange process at the interface between the electrode and the Ni(II)/Ni(III) redox centres. The anodic and cathodic peaks do not show symmetrical behaviour on increasing the scan rate, indicating that the kinetics of the forward and reverse processes are influenced differently by the counter-ion flux required to maintain electroneutrality inside the polymer film. The anodic peak potential has shifted towards the positive direction with increasing scan rate while the cathodic peak is slightly shifted towards more negative potentials. The voltammetric behaviour of an electrode coated with an electrochemically reversible redox couple can be characterized by ΔE_p values. Redox couples incorporated into thicker film and with slow heterogeneous electron-transfer kinetics exhibit increased ΔE_p values on increasing the scan rate [29].

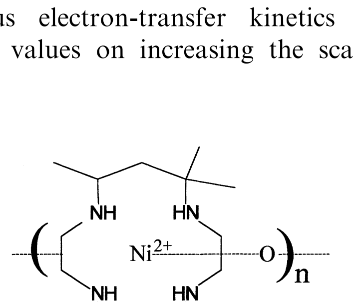

Fig. 2. Schematic structure of poly(Ni^{II}teta).

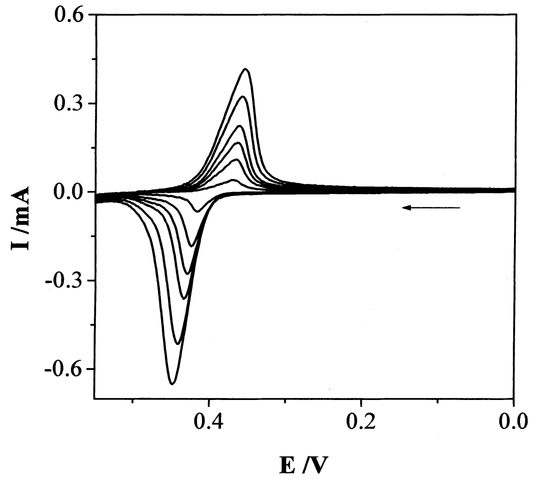

Fig. 3. Cyclic voltammograms of GC/Nf/Ni electrode in 0.2 M NaOH. Scan rates: 20, 50, 75, 100, 150 and 200 mV s^{-1} (→ indicates the sweep direction).

Using Equation 1 we can estimate the slow heterogeneous electron-transfer rate constant k° for the redox couple [29].

$$\log k^\circ = -4.24\,\Delta E_p + \log\left(\frac{vVF}{2ART}\right) \qquad (1)$$

where ΔE_p is the peak separation in V, v the scan rate (V s^{-1}), V the volume of the film (cm^3), A the area of the electrode (cm^2) and F/RT is 38.92 V^{-1} (25 °C). The calculated k° value for the GC/Ni electrode is 26.26×10^{-3} cm s^{-1} and for the GC/Nf/Ni electrode is 12.46×10^{-3} cm s^{-1}. The relatively lower heterogeneous electron-transfer rate constant observed at Nafion® film shows that the inclusion or exclusion of anions into the film is slower.

Figure 4 shows the voltammetric profiles against pH recorded for the poly(Ni^{II}teta) coated electrodes. Under these conditions, both anodic and cathodic charges did not significantly change with pH, whereas a significant displacement of the anodic and cathodic peaks towards positive potential values is noted as the pH of the solution decreases. The anodic and cathodic peak potentials plotted against pH of the solution show a slope of −70 mV and −76 mV per pH unit (insert of Figure 4). Similar behaviour was observed at nickel hydroxide and other Ni-complex modified electrode [11, 13].

3.2. *Electrocatalytic oxidation of H_2O_2 at modified electrodes*

Upon addition of H_2O_2 to a 0.2 M NaOH supporting electrolyte solution, the Ni-macrocycle modified electrode shows an increase in the anodic peak current (Figure 5). On increasing the concentration of H_2O_2, an increase in the catalytic current with a small positive shift in the peak potential is observed. The cyclic voltammograms of electrocatalytic oxidation of alcohols by the polymeric Ni-macrocycle complexes (Ni(cyclam) and Ni(TMPyP) where cyclam = 1,4,8,11, tetraazacyclotetradecane and TMPyP = tetrakis(*N*-methylpyridinium) porphyrin)) exhibit typical well-known voltammogram shape for the adsorption–desorption process on various electrode materials [15]. However, in the present study the electrocatalytic oxidation of H_2O_2 is not similar to that reported for the electrocatalytic oxidation of alcohols by polymeric Ni-macrocycle complexes [15]. Upon reversal of the potential scan direction, the cathodic peak intensity is slightly attenuated indicating that all the catalytic sites of Ni(III) are not completely reduced to Ni(II) by the H_2O_2 present in solution. Similar behaviour has also been reported for polyNi(cyclam) and polyNi(TMPyP) [15]. The current–potential curves for the oxidation of H_2O_2 recorded using the rotating disc electrode are shown in Figure 6 and the corresponding Koutecky–Levich plots are shown in Figure 7. The independence of the limiting current with rotation rate is reported for the electrocatalytic oxidation of glycine, lactic acid and ethanol [12] and

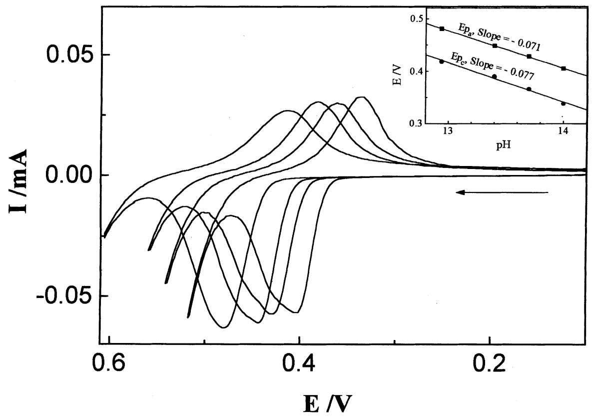

Fig. 4. Cyclic voltammograms of GC/Ni electrode at different pH (→ indicates the sweep direction). Inset: Dependence of anodic and cathodic peak potentials with pH.

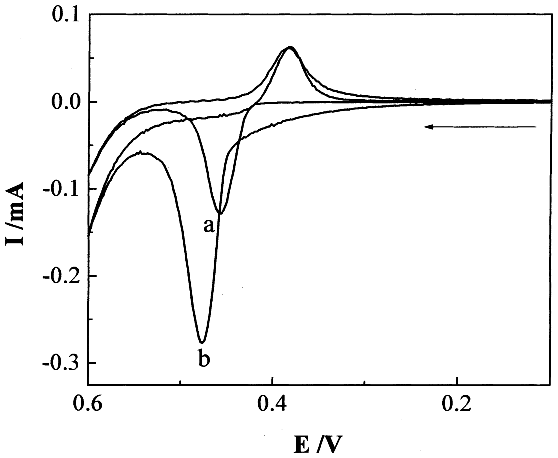

Fig. 5. Cyclic voltammograms of GC/Ni electrode in 0.2 M NaOH in the absence (a) and presence (b) of 12 mM H_2O_2. Scan rate 20 mV s^{-1} (→ indicates the sweep direction).

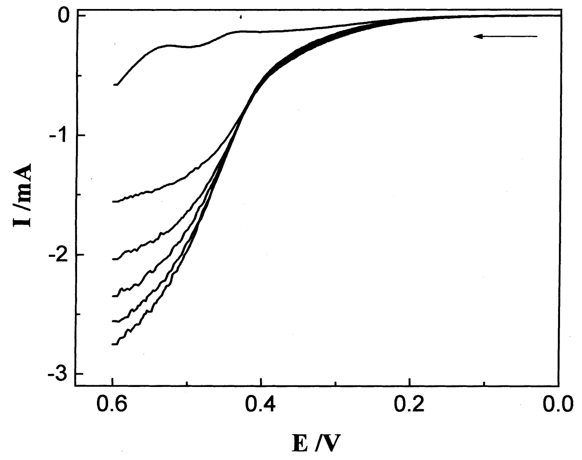

Fig. 6. Current–potential response of GC/Ni electrode in 0.2 M NaOH and 12 mM H_2O_2. (Rotation rates: 0, 500, 1000, 1500, 2000 and 2500 rpm). (→ indicates the sweep direction).

formaldehyde [16] by the polymeric Ni-macrocycle complexes. In contrast to the reported mechanism for alcohols and other organic substrates by the polymeric Ni-macrocycle complexes [12, 16], in the present case, the limiting current increases with increase in rotation rate (Figure 6) indicating that the mechanism of electrocatalytic oxidation of H_2O_2 by poly(Ni^{II}teta) complex is different. The linearity of the Levich plots at lower rotation rates indicates that the mass-transport limited kinetics and at higher concentrations of H_2O_2 with fast rotation rates, these plots deviated from linearity suggesting a kinetic limitation (Figure not shown). Under these conditions the Koutecky–Levich equation can be used to determine the rate constant. The limiting current is given by Equation 2:

$$\frac{1}{i_{\mathrm{lim}}} = \frac{1}{i_{\mathrm{Lev}}} + \frac{1}{i_{\mathrm{k}}} \tag{2}$$

where i_{Lev} is the Levich current and i_{k} is the kinetic current (current represented as the reciprocal of the intercept of the plot i_{lim}^{-1} against $\omega^{-1/2}$). i_{Lev} and i_{k} are defined by Equations 3 and 4.

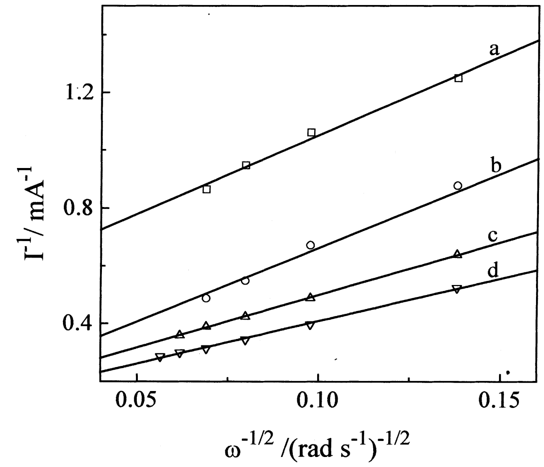

Fig. 7. Koutecky–Levich plots for the GC/Ni electrode in 0.2 M NaOH. [H_2O_2]: (a) 6.2, (b) 12, (c) 17 and (d) 24 mM.

$$i_{\mathrm{Lev}} = 0.62\,nFAD_{\mathrm{soln}}^{2/3}\nu^{-1/6}C^{b}\omega^{1/2} \tag{3}$$

where n is the number of electrons, D_{soln} the diffusion coefficient of the substrate (H_2O_2), F the faradaic constant, C^{b} the bulk concentration of the substrate (H_2O_2), A the electrode area, ν the kinematic viscosity of the solution and ω the rotation rate.

$$i_{\mathrm{k}} = nFAk\Gamma c^{\mathrm{b}} \tag{4}$$

where k is the rate constant (dm^3 mol^{-1} s^{-1}) governing the reaction of the catalyst with H_2O_2, and Γ is the quantity of the catalyst on the electrode (mol cm^{-2}). The intercepts of the Koutecky–Levich plots (Figure 7) represent the reciprocal of characteristic currents i_{k}. The intercept values plotted against concentration of H_2O_2 show a straight line (Figure 8) from the slope of which the k values were calculated and are summarized in Table 1. The k values for the GC/Ni electrode are higher when compared to that of the thicker Nafion® film (3.6×10^{-5} cm) coated electrode. However, for a Nafion® film coated electrode with a lower film thickness (1×10^{-5} cm), the k value is comparable to that of the GC/Ni electrode.

3.3. *Mechanism of electrocatalytic oxidation of H_2O_2 at modified electrodes*

A monomolecular film of a nickel(II) pentaazamacrocyclic complex has recently been used for the electrocatalytic oxidation of H_2O_2 [30] and the necessity of the presence of free coordination position for the oxidation of H_2O_2 has been discussed [30, 31]. In the present work, the plot of $1/I_{\mathrm{p}}$ against $1/C$ (Figure not shown) (where C is the concentration of H_2O_2) for the GC/Ni electrode does not exhibit a linear dependence and the voltammogram does not show any characteristic adsorption like behaviour, as observed in the case of methanol and other alcohols [15]. The O_2H^- species present in the

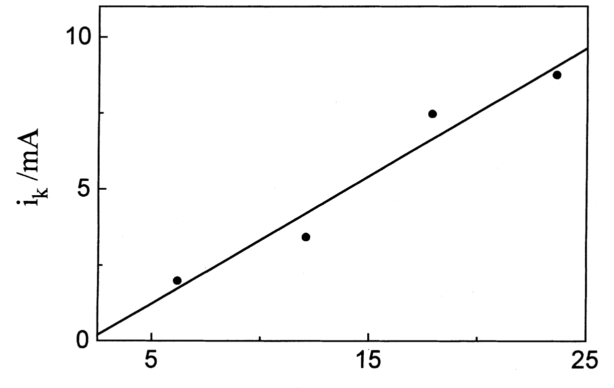

Fig. 8. Dependence of kinetic current i_{k} on the concentration of H_2O_2.

Table 1. Rate constants (*k*) for the electrocatalytic oxidation of H_2O_2 at poly(Ni^{II}teta) coated electrodes

Electrode	k/dm^3 mol^{-1} s^{-1}
GC/Ni	1.29×10^3
GC/Nf/Ni[a]	1.77×10^3
GC/Nf/Ni[b]	0.08×10^3

[a] Film thickness 1.0×10^{-5} cm, [b] 3.6×10^{-5} cm

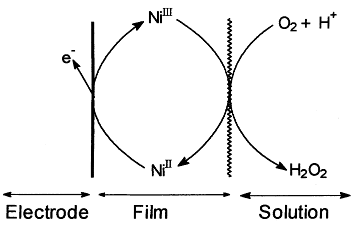

Fig. 9. Schematic representation of electrocatalytic oxidation of H_2O_2 at GC/Ni and GC/Nf/Ni electrodes.

basic solution will coordinate to the Ni(III) centre and undergo oxidation. The electrocatalytic oxidation of substrate occurring in the bulk of the polymer film is schematically shown in Figure 9. The oxidation of H_2O_2 at the modified electrode may be represented as given in Equations 5–8.

$$H_2O_2 \rightleftharpoons H^+ + O_2H^- \tag{5}$$

$$LNi^{II} \rightleftharpoons LNi^{III} + e^- \tag{6}$$

$$LNi^{III} + HO_2^- \rightleftharpoons [LNi^{III}O_2H^-] \tag{7}$$

$$[LNi^{III}O_2H^-] \longrightarrow LNi_i^{II} + O_2 + H^+ + e^- \tag{8}$$

3.4. *Influence of Nafion® film structure on the catalytic reaction*

The diffusion of O_2H^- species at the 3.6×10^{-5} cm thick Nafion® film results in a decrease in the *k* value (0.08×10^3 dm^3 mol^{-1} s^{-1}). When a lower thickness Nafion® film (1.0×10^{-5} cm) is coated on the electrode, a higher *k* value of 1.77×10^3 dm^3 mol^{-1} s^{-1} is observed. According to Fick's law, the rate is dependent on the concentration gradient meaning that the rate constant (*k*) depends on the thickness of the film. In the present case the *k* value decreases with increasing film thickness. In addition, due to the availability of free $-SO_3^-$ groups at the thicker Nafion® film (Nafion® film thickness = 3.6×10^{-5} cm, $-SO_3^-$ group = 3.63×10^{-9} mol and Ni^{II} species = 9.84×10^{-10} mol) the diffusion of anions may be hindered at the Nafion® film due to the excess $-SO_3^-$ groups and the *k* value may decrease. The stability of poly(Ni^{II}teta) coated on GC and GC/Nf electrodes were tested after the electrocatalysis studies. Freshly prepared GC/Ni and GC/Nf/Ni electrodes were used for the electrocatalytic oxidation studies of H_2O_2 and the cyclic voltammograms of these electrodes were measured by dipping in 0.2 M NaOH (Figure 10A(a) and B(a)). These electrodes were kept in distilled water for 24 h and then used for the electrocatalytic oxidation studies. After the catalytic experiment, the GC/Ni electrode showed a decrease in the peak currents (Figure 10A(b)). However, the GC/Nf/Ni electrode showed stable cyclic voltammograms after 24 h with improved film characteristics. A small increase in the peak currents but with constant coloumbic charges were noticed (Figure 10B(b)). All these observations clearly show that the poly(Ni^{II}teta) is stabilized in the Nafion® film and this improved stability of the

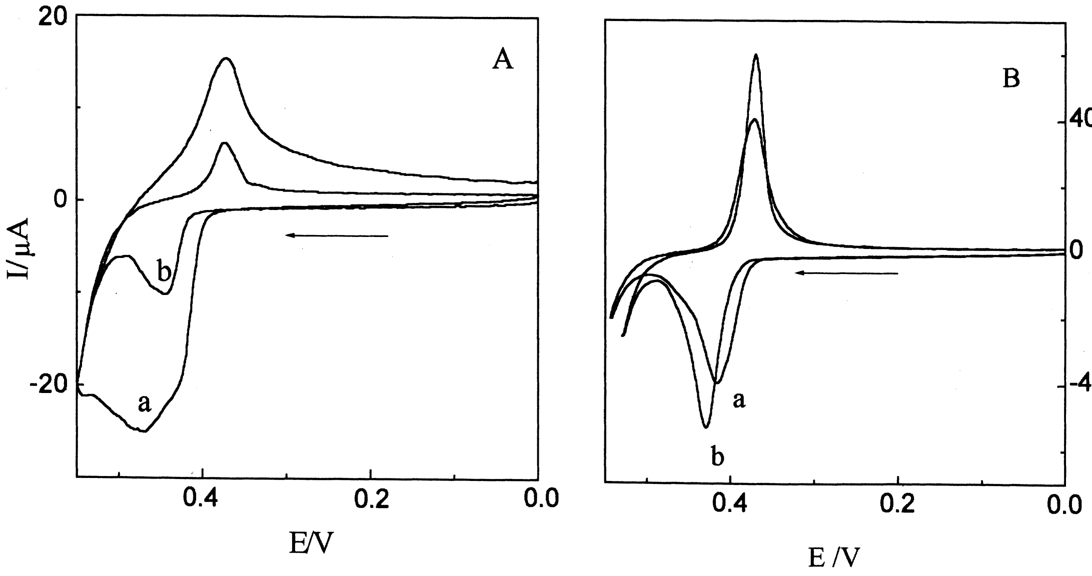

Fig. 10. Cyclic voltammograms of GC/Ni (A) and GC/Nf/Ni (B) electrodes in 0.2 M NaOH recorded after the electrocatalytic oxidation of H_2O_2. (a) Immediately after the preparation of electrode and (b) after one day (the electrodes were kept in distilled water for 24 h) Both the cyclic voltammograms (a) and (b) are recorded after the electrocatalytic oxidation of H_2O_2 experiment (→ indicates the sweep direction).

poly(Ni^{II}teta) complex is advantageous for electrocatalytic application.

Poly(Ni^{II}teta) film was electropolymerized on plain GC and Nafion® film coated GC electrodes which are found to electrocatalyse the oxidation of H_2O_2. The poly(Ni^{II}teta) showed better stability and reproducibility at a Nafion® film coated GC electrode when compared to poly(Ni^{II}teta) on a plain GC electrode. At relatively lower Nafion® film thickness (1×10^{-5} cm), an increase in the rate of electrocatalytic reaction was observed when compared to thicker Nafion® film (3.6×10^{-5} cm). The stable poly(Ni^{II}teta) incorporated Nafion® film coated electrode may find extensive application in other catalytic reduction and oxidation reactions.

Acknowledgements

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