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Electrocatalytic Oxidation of Formaldehyde on Ni/Poly(N,N-Dimethylaniline) (Sodium Dodecylsulfate) Modified Carbon Paste Electrode in Alkaline Medium[1]

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Abstract—In this work, an aqueous solution of sodium dodecylsulfate (SDS) surfactant is used as an additive for electropolymerization of N,N-dimethylaniline (DMA) onto carbon paste electrode (CPE), which is investigated as a novel matrix for deposition of nickel. The electrochemical oxidation of formaldehyde is studied at the surface of this modified electrode. The electrooxidation of formaldehyde was found to be more efficient on CPE modified with Ni/Poly(N,N-Dimethylaniline) (SDS), Ni/PDMA (SDS), than deposition Ni on CPE in alkaline solution. The electrochemical behavior and electrocatalytic activity of the electrode were studied using cyclic voltammetry and chronomethods studies. Also, the transfer second-order rate constant ($k = 5.5 \times 10^3$ cm^3 mol^{-1} s^{-1}) between formaldehyde and nickel hydroxide was calculated. Moreover, in order to optimize of electrode and variables for efficient performance of Ni/PDMA (SDS)/CPE towards formaldehyde oxidations, the effect of various parameters such as number of potential cycles for preparation of polymer, nickel and formaldehyde concentration and accumulation time have been investigated.

Keywords: formaldehyde, electrooxidation, polymer-modified electrodes, Ni modification, sodium dodecylsulfate

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1. INTRODUCTION

Formaldehyde is one of the toxic pollutants that poses a serious threat as it is a carcinogen. The extensive industrial applications of formaldehyde have resulted in an increased concentration above the tolerance level in industrial wastewater. Conventionally, effluents containing formaldehyde are treated by chemical and biochemical methods. Murphy et al. [1] have studied formaldehyde oxidation using Fenton's reagent and reported more than 90% oxidation. Garrido et al. [2] experimented oxidation of formaldehyde using the biochemical technique and observed that the formaldehyde degradation was effective only at lower concentration.

Knowledge of the reactivity of formaldehyde in an electrochemical environment is important for various applications including fuel cells and electrochemical detection. Therefore, electrochemical oxidation of formaldehyde at various electrodes has been receiving much attention. Pt [3, 4], polycrystalline palladium [5], gold [6], palladium nanoparticles electrodeposited on carbon ionic liquid composite electrode [7], binary and ternary alloys [8, 9] and nano-composites [10, 11] have been studied as anode catalysts for the formaldehyde oxidation. Besides, the high cost and short supply of these metals are not economical for practical and industrial application [12]. Thus, a great deal of interest has, recently, been focused on an alternative metal (non-noble metal) while maintaining the high catalytic activity and less expensive materials as anodes for formaldehyde oxidation. On the other hand, nickel is a low cost, relatively abundant material that is used extensively in numerous industrial applications. It is well established that Ni can be used as a catalyst due to its surface oxidation.

On the other hand, recent researches have demonstrated that coating the electrode surface with conducting polymers (CPs) is an attractive approach for enhancing the power and scope of electrochemically modified electrodes [13–15]. CP matrices have been employed as catalyst support materials for the oxidation of small organic molecules in place of conventional supports, because when catalyst is dispersed in carbon black, a part of the active sites remains inaccessible to the reactant molecules. The reason for incorporating metallic particles into the porous matrixes is to increase the specific area of these materials and thereby improve catalytic efficiency. Another reason is the higher tolerance of the metal particles to poisoning due to the adsorption of CO species, in comparison

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with the serious problem of bulk metal electrodes poisoning.

In our previous works, we used modified carbon paste electrodes with poly(1-naphtylamine)/Ni, poly(*o*-aminophenol)/Ni and PINA (SDS)/Ni–Co (with different percentages) for electrocatalytic oxidation of several carbohydrates [16–18]. These studies showed that the metal–polymer electrodes are easy to prepare, stable for long time periods with good detection limits and wide linear range responses. Also, we have demonstrated that the poly (1,5-Diaminonaphthalene)/Ni and poly(*o*-aminophenol)(SDS)/Ni modified carbon paste electrodes can successfully catalyze the oxidation of methanol in alkaline medium [19, 20]. Therefore in the present work, we dispersed a cheap catalyst, nickel ions, to an organic polymer, PDMA, which was electropolymerized on carbon paste electrode. This polymer film is considered to be a promising material in modification of electrode surface due to having some advantageous properties (e.g., strong attachment to the electrode surface, high chemical stability in air and good responsibility). Then, this modified electrode was used for electrooxidation of formaldehyde.

2. EXPERIMENTAL

2.1. Chemical Reagents

The solvent used in this work was double distilled water. Both sulfuric acid and sodium hydroxide from Merck were used as the supporting electrolytes. The $NiCl_2$, DMA monomer and SDS from Fluka and formaldehyde from Merck were used as received. High viscosity paraffin (density: 0.88 g cm^{-3}) from Fluka was utilized as the pasting liquid for carbon paste electrode. Graphite powder (particle diameter: 0.1 mm, from Merck) was employed as the working electrode (WE) substrate.

2.2. Instrumentation

The electrochemical experiments were performed at room temperature using a potentiostat/galvanostat (BHP 2063-C Electrochemical Analysis system, Behpajooh, Iran) coupled with a Pentium IV personal computer acquire gain the data. The working electrode was CPE with an area of 0.09 cm^2. CPE was prepared by blending a mixture of graphite powder and paraffin through hand mixing and the paste was then inserted in a glass tube with electrical contact. A layer of the CPE was removed with a spatula and smoothened on an emery paper to get a smooth and fresh surface. Pt wire and double junction Ag|AgCl|KCl (3 M) electrode acted as counter and reference electrodes, respectively.

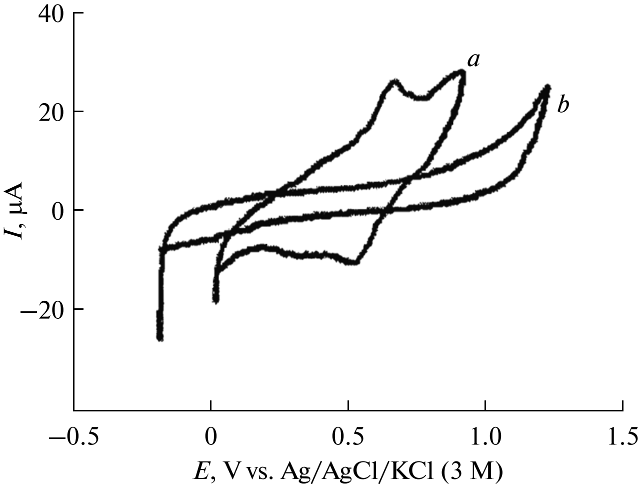

Fig. 1. Electrochemical responses of PDMA (SDS)/CPE in (*a*) 0.1 M H_2SO_4 and (*b*) 1 M NaOH solution at $v = 50$ mV s^{-1}.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of Ni/PDMA (SDS)/CPE

In this work, electropolymerization at the surface of CPE using consecutive cyclic voltammetry (15 cycles at potential scan rate, $v = 50$ mV s^{-1}) between 0 and 1.1 V vs. Ag|AgCl|KCl (3 M) was performed in an aqueous solution containing 1.0 mM DMA, 1.0 mM SDS and 0.1 M H_2SO_4. As can be seen in Fig. 1, the redox behavior of the polymeric film was strongly dependent on the pH of the electrolyte solution. Therefore, the obtained polymer shows a well-defined redox behavior (couple redox with $E_{pa} = 0.65$ and $E_{pc} = 0.5$ V) in an acidic solution (Fig. 1a). The response obtained in an alkaline solution shows a complete loss of electrode activity in the potential range from –0.2 to 1.1 V (Fig. 1b). This observation is as same as previous papers about aniline and derivatives [16, 21–23]. However, the film was not degraded under these experimental conditions, and its response was recovered when the electrode was immersed in an acidic solution.

In order to incorporate Ni(II) ions into the PDMA (SDS) film, the freshly electropolymerized CPE was placed at open circuit in a well stirred aqueous solution of 0.5 M $NiCl_2$. Accumulation of nickel ions was carried out by complex formation between Ni(II) with amine sites in the polymer backbone, for a given period of time ($t = 5$ min).

After incorporating of Ni^{2+} ions into the polymer films, the polarization behavior was examined in 0.1 M NaOH solution using cyclic voltammetry technique. This technique allows the hydroxide film formation in parallel to inspect the electrochemical reactivity of the surface. Cyclic voltammograms of Ni/PDMA (SDS)/CPE at anodic potentials in the potential range of 0.1–0.75 V with a potential sweep

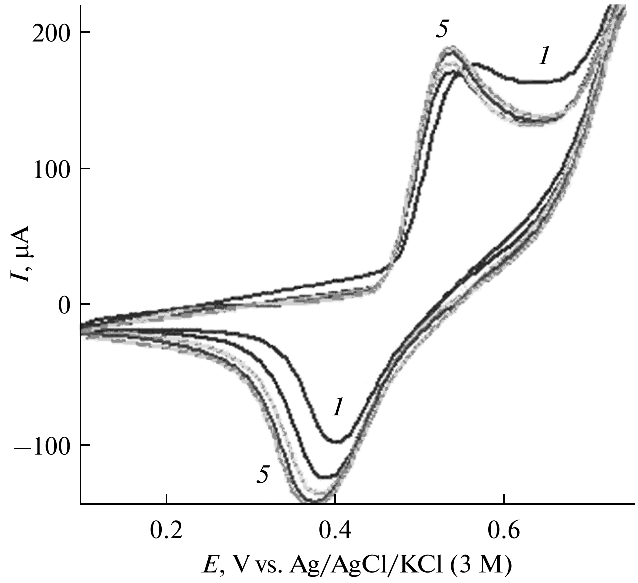

Fig. 2. Cyclic polarization behavior of Ni/PDMA (SDS)/CPE in 0.1 M NaOH solution at anodic potentials at $v = 50$ mV s^{-1} (number of cycles = 5).

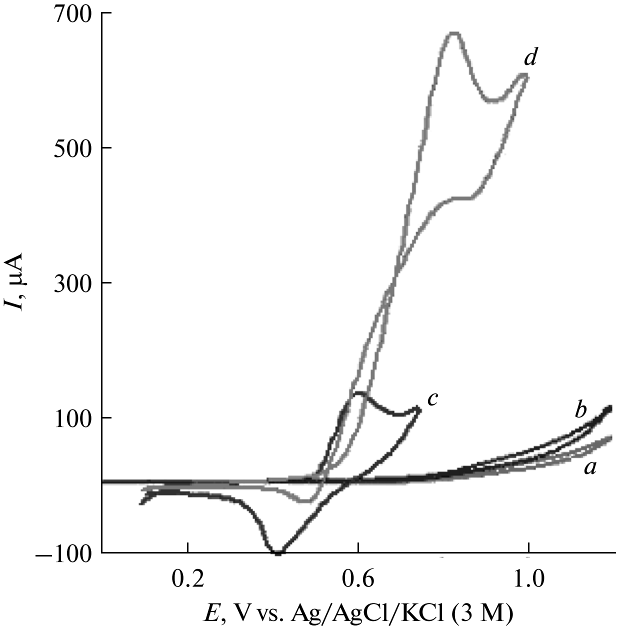

Fig. 3. Electrochemical responses of PDMA (SDS)/CPE in 0.1 M NaOH solution at v = 20 mV s^{-1} to: 0 M (*a*), 1 mM formaldehyde (*b*) and Ni/PDMA (SDS)/CPE to: 0 M (*c*), 1 mM formaldehyde (*d*).

rate of 50 mV s^{-1} are represented in Fig. 2. The current grows with the number of potential scans, indicating the progressive enrichment of the electroactive species Ni(II) and Ni(III) in the surface. The first positive potential scan generates a monotonically elevated current flow giving a peak at a potential more positive than in the subsequent potential cycles. The peak shift is indicative of an overpotential required for the nucleation and growth of [HOO(Ni/PDMA)]. The redox process of these modified electrodes is expressed as:

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e. \quad (1)$$

A pair of well-defined peaks with a half-wave potential of 460 mV vs. Ag|AgCl|KCl (3 M) appears in the voltammograms, and the peak-to-peak potential separation (at $v = 50$ mV s^{-1}) is 85 mV. In addition, the effect of the different scan rate of the potential (in the range of 10–1000 mV s^{-1}) on the electrochemical properties of this redox couple was studied. The anodic currents were linearly proportional to the scan rate up to 100 mV s^{-1} (Figure not shown). This can be attributed to an electrochemical activity of an immobilized redox couple at the surface. From the slope of this line and using equation [24]:

$$I_p = n^2F^2vA\Gamma^*/4RT, \quad (2)$$

where I_p, A and Γ^* are peak current, electrode surface area and surface coverage of the redox species, respectively, and taking the average of both cathodic and anodic currents, the total surface coverage of the immobilized active substance in the film of about 3.4×10^{-8} mol cm^{-2} is derived. In the higher range of potential scan rates (100–1000 mV s^{-1}) the peak currents depend on square root of the potential scan rate, signifying the dominance of the diffusion process as the rate limiting step in the total redox transition of the modifier film. The limiting diffusion process was also reported for other Ni-modified electrodes [17, 25, 26].

3.2. Electrochemical Behavior of Ni/PDMA(SDS)/CPE in Presence of Formaldehyde

Figure 3 shows the behavior of PDMA (SDS)/CPE and Ni/PDMA (SDS)/CPE in 0.1 M NaOH + 0.1 M formaldehyde at 20 mV s^{-1}. From CV of PDMA (SDS)/CPE, it is clear that this electrode exhibits no activity towards oxidation of formaldehyde. The electrochemical response of a Ni/PDMA (SDS)/CPE in alkaline solution (i.e., 0.1 M NaOH) exhibits well defined anodic and cathodic peaks (Fig. 3c) associated with the Ni(II)/Ni(III) redox couple. As can be seen, upon formaldehyde addition (1 mM) there is an increase in the anodic peak current and a decrease in the cathodic peak current (Fig. 3d). This indicates that formaldehyde is oxidized by active nickel moiety via a cyclic mediation redox process. Nickel species are immobilized on the electrode surface, and the one with a higher valence oxidizes formaldehyde via a chemical reaction followed by generation of low-valence nickel [27–29]. Accordingly, formaldehyde is oxidized via an EC' mechanism:

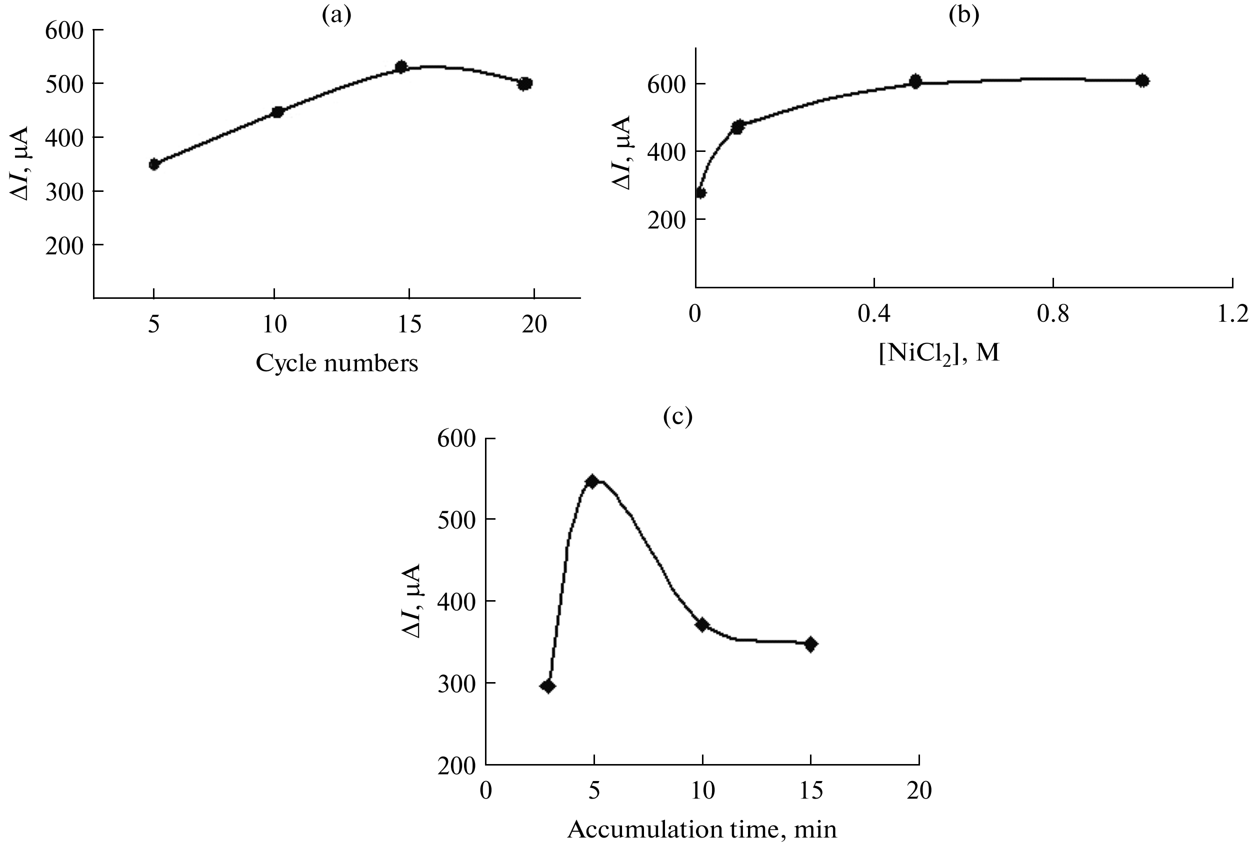

Fig. 4. Variation of currents for oxidation in presence and absence of 1 mM formaldehyde (ΔI) in 0.1 M NaOH for (a) different cycles of polymerization, (b) nickel concentration and (c) accumulation time at $v = 20$ mV s^{-1}.

$$Ni(OH)_2 + OH^- \longleftrightarrow NiOOH + H_2O + e \qquad E \qquad (3)$$

$$NiOOH + \text{formaldehyde} \longrightarrow Ni(OH)_2 + \text{products} \qquad C' \qquad (4)$$

It can be said that Ni/PDMA (SDS) modifying the electrode surface acts as a catalyst for the oxidation of formaldehyde in 0.1 M NaOH solution. The catalytic oxidation seems to be very facile, as shown by the elimination of the cathodic peak. The peak current of formaldehyde oxidation at the surface of Ni/PDMA (SDS)/CPE is greater than that at the Ni/PDMA/CPE (Figure not shown). The observations can explain clearly the role of the PDMA (SDS) on enhancement of the electrocatalytic oxidation currents of formaldehyde. Indeed this film is a good and proper bed for immobilization of nickel ions. It seems that the main and plausible reason for such an enhancement is the formation of a polymer film backbone at the surface of CPE that provides the facile arrival of formaldehyde on nickel catalytic centers.

3.3. Optimization of Electrode and Variables for Efficient Performance of Ni/PDMA (SDS)/CPE Towards Formaldehyde Oxidation

In order to optimize of electrode and variables for efficient performance of Ni/PDMA (SDS)/CPE towards formaldehyde oxidation, we studied variation of currents for oxidation in presence and absence of 1 mM formaldehyde (ΔI) for different cycles of polymerization, concentrations of nickel, NaOH and various times for nickel accumulation (Fig. 4).

3.3.1. Effect of cycles number. Electrochemical polymerization offers the possibility of controlling the thickness and homogeneity of PDMA film on the electrode surface. The influence of cycle numbers for preparation of the PDMA (SDS) films on the electrocatalytic oxidation of formaldehyde was investigated

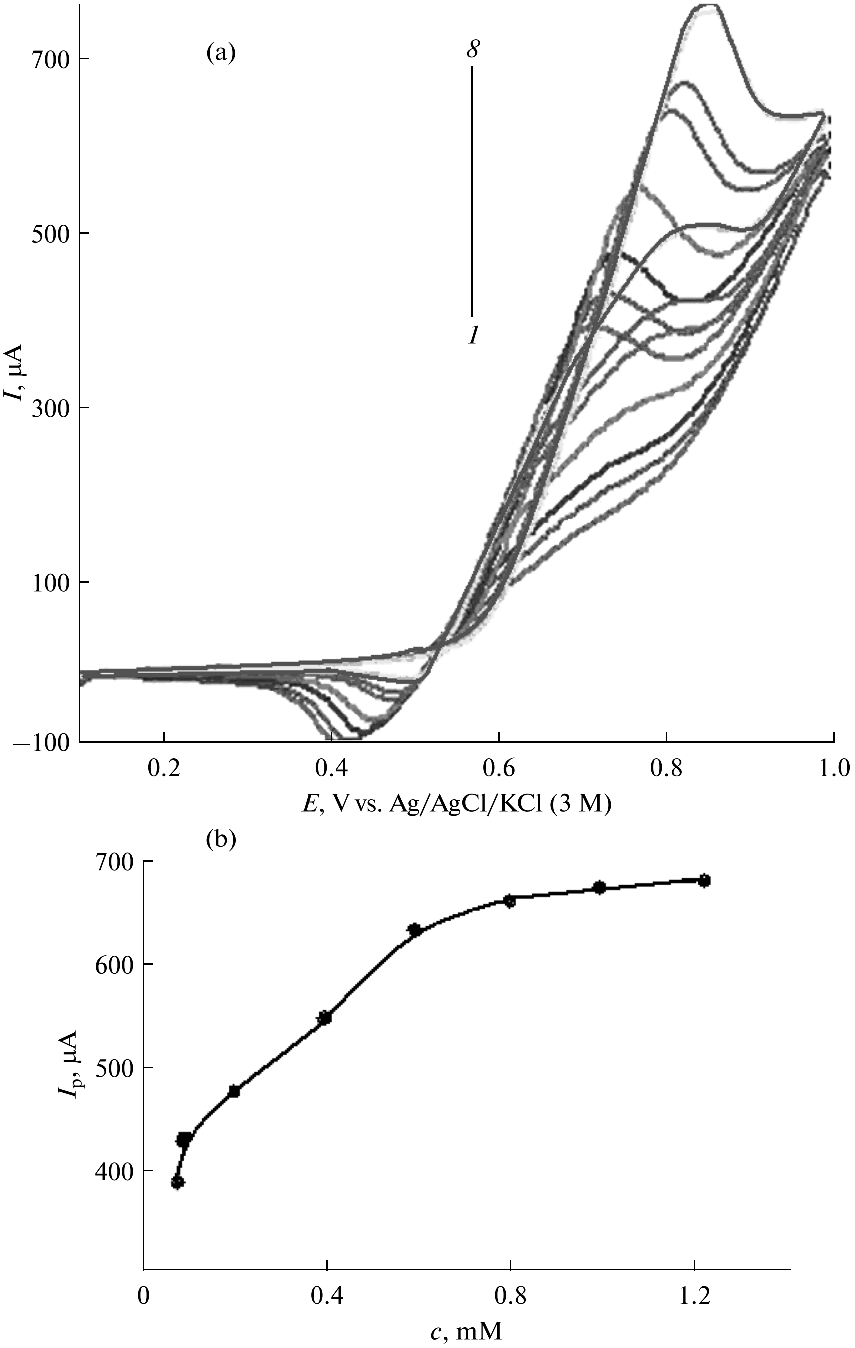

Fig. 5. (a) Current-potential curves of the Ni/PDMA (SDS)/CPE for electrocatalytic oxidation of formaldehyde at the scan rate of 20 mV s^{-1} in 0.1 M NaOH solution with different concentrations of formaldehyde: (*1*) 0.08, (*2*) 0.1, (*3*) 0.2, (*4*) 0.4, (*5*) 0.6, (*6*) 0.8, (*7*) 1 and (*8*) 1.2 mM, respectively. (b) The dependency of formaldehyde electrooxidation peak currents vs. formaldehyde concentrations.

and the corresponding results are shown in Fig. 4a. Under the constant accumulation time of Ni(II) ions, the anodic peak current rises progressively for cycle numbers up to 15 cycles and drops afterwards. This implies that the electrocatalysis of formaldehyde oxidation is sensitive to thickness of the polymer film. Increasing in the anodic peak current for cycle numbers up to 15 cycles may be due to the occupation of nickel in the pores of polymers with the real sizes. Decreasing in anodic peak current for formaldehyde oxidation beyond 15 cycles may be due to lessening of real surface area of nickel hydroxide by the excessive presence of polymers on the electrode surface.

3.3.2. Effect of nickel concentration. The effect of the amount of nickel was studied by varying the concentration of nickel chloride in the deposition bath. It

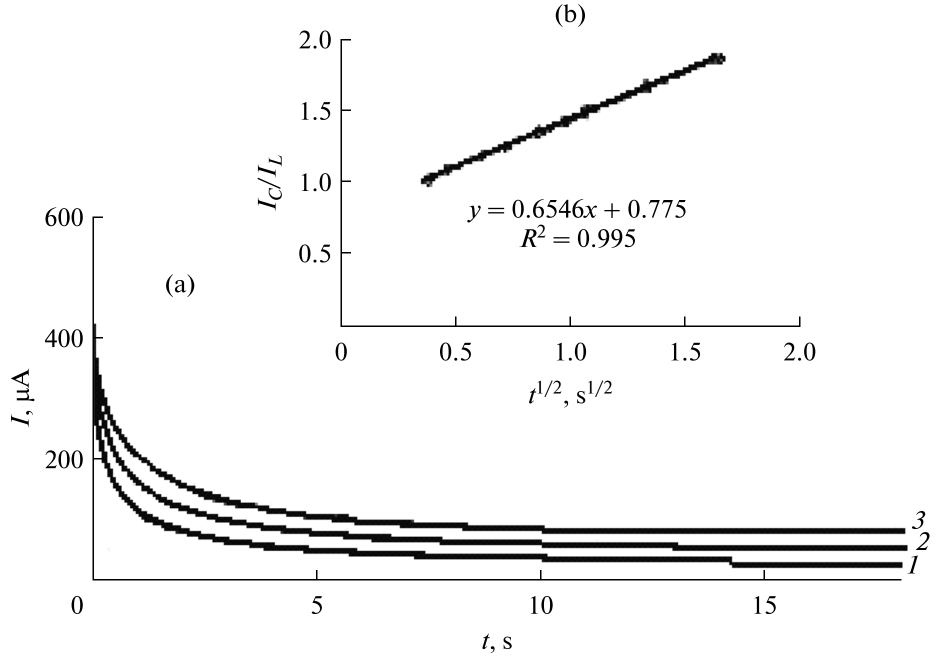

Fig. 6. (a) Double step chronoamperogram of Ni/PDMA (SDS)/CPE in 0.1 M NaOH solution with different concentrations of formaldehyde: (*1*) 0, (*2*) 0.1 and (*3*) 0.8 mM. (b) Plot of I_C/I_L vs. $t^{1/2}$ derived from the data of chronoamperogram of *3*.

was observed that as the concentration of Ni in the bath increased, the formaldehyde oxidation currents also increased up to 0.5 M; after which, it remained almost constant (Fig. 4b). This may be due to the fact that probably surface active sites of modified electrode get saturated at this concentration hinders further deposition of Ni.

3.3.3. Effect of accumulation time. The value of ΔI increased gradually with increasing of accumulation times. The maximum value was got at 5.0 min then leveled off, so 5.0 min was chosen as the optimum time, which indicated that saturated accumulation on the Ni/PDMA (SDS)/CPE had been achieved (Fig. 4c).

3.3.4. Effect of formaldehyde concentration. A set of experiments was carried out to study the effect of formaldehyde concentration. Cyclic voltammetric curves at a scan rate of 20 mV s^{-1} for formaldehyde concentrations ranging from 0.08 to 1.0 mM in 0.1 M NaOH were recorded in Fig. 5. Peak heights increase with the increase of formaldehyde concentrations up to 1.0 mM. It is observed from Fig. 5 that when formaldehyde concentration increases, the current density of the anodic peak increases significantly while the cathodic peak current decreases. This indicates an electrocatalytic oxidation of formaldehyde. The formaldehyde oxidation current increased steadily up to a concentration of 1 mM of formaldehyde after which it remained almost constant. It appears that the reaction sites get saturated at this concentration. In accordance with this result, the optimum formaldehyde concentration to obtain a higher current density may be considered as about 1.0 mM. Also, the onset potential of the Ni(II) oxidation moiety shifted to positive value and enhanced upon increasing the concentration of formaldehyde. In fact, this indicated a strong interaction of formaldehyde with the surface already covered by low valence nickel species. The anodic peak potential for formaldehyde oxidation is naturally shifted to the positive direction as a result of an *IR* drop arising from high current density values [27].

3.4. Chronoamperometric Studies

Chronoamperometry, as well as other electrochemical methods, was employed for the investigation of electrochemical processes at Ni/PDMA (SDS)/CPE. Figure 6 represents the current–time profiles obtained by setting the working electrode potential at 650 mV for various concentrations of formaldehyde. This technique can also be used for evaluation of chemical reaction between formaldehyde and the modifier layer (catalytic rate constant, k) according to [28]:

$$I_C/I_L = \pi^{1/2}\lambda^{1/2} = \pi^{1/2}(kc_0t)^{1/2}, \quad (5)$$

where I_C and I_L are the currents in the presence and absence of formaldehyde, k is catalytic rate constant; c_0 is the bulk concentration of formaldehyde and t is the elapsed time. From the slope of I_C/I_L vs. $t^{1/2}$ plot, presented in Fig. 6, the mean value of k was obtained as about 5.5×10^3 cm^3 mol^{-1} s^{-1}.

4. CONCLUSIONS

In this work, a novel electrode has been described herein, consisting of nickel ions loaded into a PDMA(SDS)/CPE by immersion of the polymeric modified carbon paste electrode in nickel chloride solution. This modified electrode was found to be capable of catalyzing the electrooxidation of formaldehyde very efficiently. Electrocatalysis of formaldehyde oxidation is sensitive to various parameters such as thickness of the polymer film, nickel concentration and accumulation time. The value of catalytic rate constant indicates that the modified electrode can overcome the kinetic limitation for formaldehyde oxidation by catalytic process and can decrease the oxidation overvoltage.

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