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ORIGINAL PAPER

Preparation of Ni/poly(1,5-diaminonaphthalene)-modified carbon paste electrode; application in electrocatalytic oxidation of formaldehyde for fuel cells

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Abstract This paper deals with electrochemical oxidation of formaldehyde in alkaline solution with a new electrocatalytic system composed of carbon paste electrode coated with poly (1,5-diaminonaphthalene) (P-1,5-DAN) film containing incorporated Ni(II)/Ni(III) redox ions. The modifier layer of (P-1,5-DAN-Ni)$(OH)_2$ at the electrode surface acts as a catalyst for the oxidation of formaldehyde in 0.1-M NaOH solution. Cyclic voltammetric and chronoamperometric experiments showed that the formaldehyde can be oxidized at the surface of Ni/P-1,5-DAN-modified carbon paste electrode. In cyclic voltammetry studies, the peak current of the oxidation of nickel hydroxide in the presence of formaldehyde increases and is followed by a decrease in the corresponding cathodic current. The rate constant (k) for the chemical reaction between the formaldehyde and nickel hydroxide has been evaluated by chronoamperometry method. This polymeric-modified electrode can oxidize the formaldehyde with high current density (over 7 mA cm^{-2}). Thus, it can be a candidate as an anode for fuel cell applications.

Keywords Formaldehyde · Electrocatalytic oxidation · Poly(1 · 5-diaminonaphthalene) · Carbon paste electrode · Fuel cell

Introduction

The development of chemically modified electrodes (CMEs) is at present an area of great interest. CMEs can be divided broadly into two main categories; namely, surface-modified and bulk-modified electrodes. Methods of surface modification include adsorption, covalent bonding, attachment of polymer films, etc. [1–4]. Polymer-film-coated electrodes can be differentiated from other modification methods such as adsorption and covalent bonding in that they usually involve multilayer as opposed to monolayer frequently encountered for the latter methods. The thicker films imply more active sites which lead to larger analytical signals. This advantage coupled with others, their versatility and wide applicability, makes polymer-film-modified electrodes particularly suitable for analytical applications. Recent research has demonstrated that coating the electrode surface with polymeric films is an attractive approach for enhancing the power and scope of electrochemically modified electrodes [5–8].

Electrochemical polymerization offers the advantage of reproducible deposition in terms of film thickness and loading, making the immobilization procedure of a metal-based electrocatalyst very simple and reliable [9, 10]. Also, it should be noticed that the nature of working electrode substrate in electropreparation of polymeric film is very important because properties of polymeric films depend on the working electrode material. The ease and fast of preparation and of obtaining a new reproducible surface, the low residual current, porous surface, and low cost of carbon paste are some advantages of carbon paste electrode (CPE) over all other solid electrodes [11, 12].

On the other hand, it has been shown that macrocyclic complexes of nickel are of interest as modifying agents because in basic media nickel redox centers show high catalytic activity towards the oxidation of small organic compounds [13–15]. It is well established that nickel can be used as a catalyst due to its surface oxidation properties. Many electrodes involving nickel as a component in their manufacture can be used as catalyst in fuel cells. One of the

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very important uses of nickel as a catalyst is for the oxidation of alcohols [16–18]. The high-valence species of Ni seem to act as strong oxidizing agents for low-electroactivity organic substrates.

Formaldehyde, as one of the organic intermediate products of methanol oxidation as well as formic acid, is important in investigating its electrochemical oxidation behavior. Several reports have been published on the oxidation of formaldehyde [19–24] but many of them were carried out with platinum electrodes [25, 26]. Until now, no sufficient investigation has been made for formaldehyde oxidation using polymeric films as the support materials compared to methanol or formic acid.

Previously, we combined the advantageous features of polymer modification, dispersion of metallic particles into an organic polymer and carbon paste technology by construction of poly(1-naphthylamine)/nickel-modified carbon paste electrode for electrocatalytic oxidation of some carbohydrates [27].

In this work, we decided to combine the above-mentioned advantageous features again for the aim of electrocatalytic oxidation of formaldehyde. In this context, we prepared poly (1,5-diaminonaphthalene) (P-1,5-DAN) films by electropolymerization at the surface of carbon paste electrode. Then, nickel ions were incorporated into the polymeric matrix by immersion of the polymeric-modified electrode in a nickel chloride solution. Suitability of this nickel-modified polymeric carbon paste electrode toward the electrocatalytic oxidation of formaldehyde in alkaline medium at ambient temperature was investigated. Our studies show that this polymeric-modified electrode can be a candidate as an anode for the fuel cell applications.

Experimental

Reagents and materials

The solvent used in this work was twice-distilled water. Sulfuric acid from Fluka was used as the supporting electrolyte. The 1,5-diaminonaphthalene from Merck was used as received. Sodium hydroxide and formaldehyde used in this work were analytical grade of Merck origin and used without further purification. High-viscosity paraffin (density 0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter 0.10 mm) from Merck was used as the working electrode substrate. All other reagents were of analytical grade.

Instrumentation

The electrochemical experiments were carried out using a potentiostat–galvanostat (BHP2063-C Electrochemical Analysis System, Behpajooh, Iran) coupled with a Pentium III personal computer. A platinum wire was used as the auxiliary electrode. A carbon paste electrode as working electrode and a double junction Ag|AgCl|KCl (3 M) electrode as reference electrode were used.

Preparation of working electrode

A 1:1 (*w*/*w*) mixture of graphite powder and paraffin was blended by hand mixing with a mortar and pestle for preparation of carbon paste. The resulting paste was then inserted in the bottom of a glass tube (internal radius 1.7 mm). The electrical connection was implemented by a copper wire lead fitted into the glass tube. A fresh electrode surface was generated rapidly by extruding a small plug of the paste with a stainless-steel rod and smoothing the resulting surface on white paper until a smooth shiny surface was observed.

Results and discussion

Preparation of poly(1,5-diaminonaphthalene)-modified carbon paste electrode (P-1,5-DAN/MCPE)

Previously, poly(1,5-diaminonaphthalene) (P-1,5-DAN) films were obtained at the surface of Au, Pt, and GC electrodes [28–32]. In this work, electropolymerization at the surface of CPE using consecutive cyclic voltammetry (for 15 cycles) between −0.2 and +1.0 V at 50 mV s^{-1} was performed in the sulfuric acid solution containing 5 mM 1,5-diaminonaphthalene. After this, the electrode was removed and rinsed with water and the sides were wiped with soft tissue paper. Redox properties of this polymer prepared at the surface of carbon paste electrode (a low-cost electrode) are completely comparable with other solid (Au, Pt, and GC) electrodes [28–32]. The redox behavior of the film was strongly dependent on the pH of the electrolyte solution [28]. As can be seen in Fig. 1 (a), obtained polymer shows a well-defined redox behavior in acidic-supporting electrolyte solution. The response obtained in an alkaline solution (0.1 M NaOH) showed a complete loss of electrode activity in the potential range from 0.0 to 0.9 V (Fig. 1 (b)). However, the film was not degraded under these experimental conditions and its response was recovered when the electrode was immersed in an acidic-supporting electrolyte solution.

Incorporation of Ni(II) ions into P-1,5-diaminonaphthalene film and electrochemical behavior of the Ni/P-1,5-DAN/MCPE

In order to incorporate Ni(II) ions into the P-1,5-DAN film, the freshly electropolymerized CPE was placed at open circuit in a

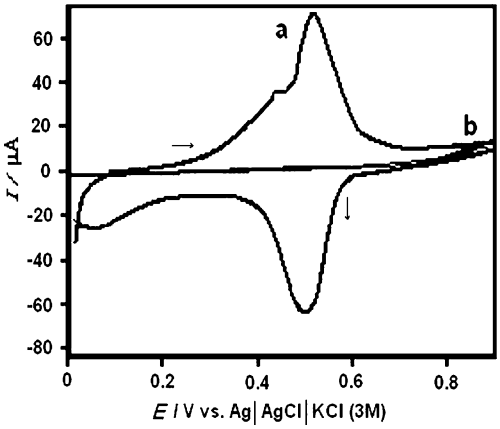

Fig. 1 Electrochemical responses of P-1,5-DAN/MCPE; *a* in 1.0 M H_2SO_4 solution; *b* in 0.1 M NaOH solution, υ=50 mV s^{-1}

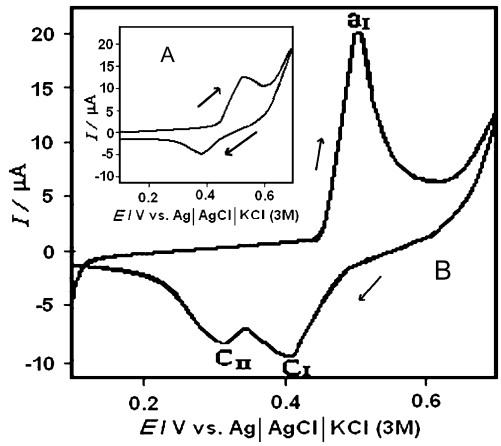

Fig. 2 Typical cyclic voltammograms of Ni/P-1,5-DAN/MCPE in 0.1 M NaOH solution: *A* first cycle and *B* 60th cycle, υ=50 mV s^{-1}

well-stirred aqueous solution of 1.0 M $NiCl_2$. Accumulation of nickel ions was carried out by complex formation between Ni (II) and amine sites in the polymer backbone, for a given period of time (t_a, accumulation time is 10 min with two time intervals 5 min). In practice, this electrode was transferred into a cell containing 0.1-M NaOH solution after 5 min which is placed in the 1.0-M $NiCl_2$ solution and two potential cyclings were performed. Then, this modified electrode was placed into the $NiCl_2$ solution for 5 min and again was transferred into cell containing 0.1-M NaOH solution.

The polarization behavior was examined in 0.1-M NaOH solution using cyclic voltammetry technique. This technique allows the oxide (hydroxide) film formation in parallel to inspecting the electrochemical reactivity of the surface. Consecutive potential-sweeping cycles results in a progressive increase of the current values of the anodic and cathodic peaks. Changes in the current of the peaks are likely due to the changes in the crystal structures of the nickel hydroxide and the nickel oxyhydroxide [16]. Typical first and 60th cyclic voltammograms of Ni/P-1,5-DAN/MCPE in potential range of 0.1 to 0.7 V with a potential sweep rate of 50 mV s^{-1} are represented in Fig. 2. As can be seen, 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 [(P-1,5-DAN-Ni)OOH]. Also, it can be seen that prolonged cycling (about 60 cycles) results in a new cathodic peak of C_{II}. Electrochemical behavior corresponding to the two peaks a_I and c_I is attributed to the redox couple Ni(II)/Ni (III) according to:

$$\left[(\mathrm{P}-1,5-\mathrm{DAN}-\mathrm{Ni})(\mathrm{OH})_2\right] + \mathrm{OH}^- \rightleftarrows [(\mathrm{P}-1,5-\mathrm{DAN}-\mathrm{Ni})\mathrm{OOH}] + \mathrm{H_2O} + \mathrm{e}^- \quad (1)$$

As has been reported [33–36], nickel hydroxide may generally exist in two different crystallographic forms designed α-$Ni(OH)_2$ and β-$Ni(OH)_2$ which are hydrous and anhydrous, respectively. In addition, the oxidation of nickel hydroxide gives two other varieties of oxyhydroxides, β and γ, which explains the existence of the two reduction peaks during the backward sweep [36, 37]. The α-form is known to be unstable and, when α-$Ni(OH)_2$ is formed at the initial stages, it is further slowly converted to the β-$Ni(OH)_2$. It was reported by Desilvestro et al. [38, 39] that both the electro-deposited nickel hydroxide and nickel oxyhydroxide phases are believed to be unstoichiometric. Therefore, the peak potentials changes with the increase of cycling numbers.

The surface coverage of the immobilized active substance (Ni(II)) in the films can be evaluated from the charge under the current-potential wave of Fig. 2 (B) with correction for the baseline according to the equation:

$$\boldsymbol{\Gamma = Q/nFA} \quad (2)$$

where $\boldsymbol{\Gamma}$ is the surface coverage in mole per square centimeter; $\boldsymbol{Q}$ is the charge under the oxidation peak (P_{aI}) for the voltammogram recorded in 0.1 M NaOH; $\boldsymbol{A}$ is the geometric surface area of carbon paste electrode and $\boldsymbol{n}$ is the number of electrons transferred in reaction 1. The value of Γ for Ni/P-1,5-DAN/MCPE was 4.94×10^{-9} mol cm^{-2}. Figure 3 (A) shows cyclic voltammograms of the (P-1,5-DAN-Ni)$(OH)_2$-modified carbon paste electrode from 0.1 to 0.7 V at various potential sweep rates in 0.1-M NaOH solution. As the scan rate increases, the anodic peak potentials shift to more positive and the cathodic peak potentials are converted to a slightly negative direction. At higher scan rates, a wider splitting appears indicating the limitation arising from the charge transfer kinetics. Inset 3 (B) indicates the plot of the anodic peak current I_{pa} in Fig. 3 (A) against the square root of the scan rate, $\upsilon^{1/2}$. As can be seen from the inset (B), the anodic peak currents I_{pa} are linearly proportional to $\upsilon^{1/2}$,

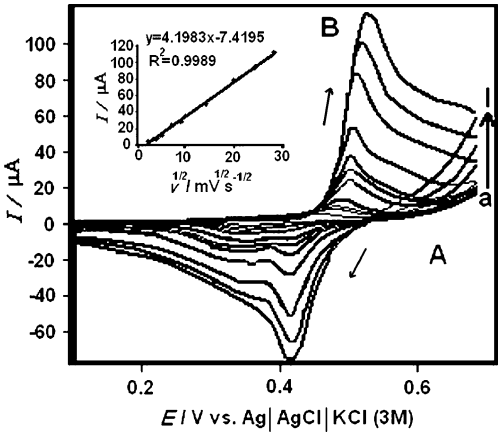

Fig. 3 *A* Scan rate dependence of the peak current for the Ni/P-1,5-DAN/MCPE after prolonged polarization (about 60 cycles), scan rates: *a* 5, *b* 10, *c* 15, *d* 20, *e* 25, *f* 50, *g* 80, *h* 100, *i* 200, *j* 400, *k* 600 and 1,800 mV s^{-1}; solution is 0.1 M NaOH. *B* The plot of I_{pa} vs. $\upsilon^{1/2}$

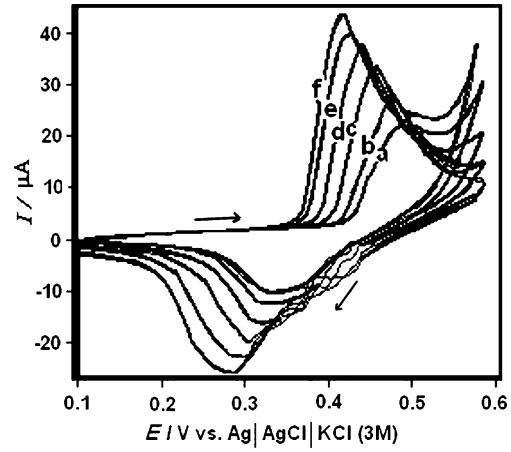

Fig. 4 Cyclic voltammograms of the Ni/P-1,5-DAN/MCPE in NaOH solutions with different concentrations: *a* 0.1, *b* 0.2, *c* 0.4, *d* 0.6, *e* 0.8 and *f* 1.0 M, respectively

showing the dominance of the diffusion-controlled process. This limiting diffusion process can be attributed to the hydroxide ion diffusion from the solution to film and vice versa during the oxidation–reduction process. However, in order to further investigation about the catalyst distribution place, we decided to check the influence of the polymer film thickness, but we have observed no significant changes in anodic peak current of Ni(II) to Ni(III) conversion. Thus, it seems that reaction occurs on the surface and catalyst distribution in the surface layer.

Effect of sodium hydroxide concentration

Sodium hydroxide concentration in the medium had considerable effects on the cyclic voltammetric behavior of the modified electrode. Figure 4 shows the cyclic voltammograms of the Ni/P-1,5-DAN-modified carbon paste electrode after transferring to aqueous solutions containing various concentrations of sodium hydroxide. As the sodium hydroxide concentration decreased, the anodic and cathodic peak currents decreased. Similarly, the peak separation between anodic and cathodic peaks was also increased with the decrease of NaOH concentration [40].

From the above results, it is understood that the species diffusing is the hydroxide ion that maintains the charge balance. As would be expected, at lower NaOH concentration, the increase in peak separation, cathodic peak broadening, decrease in peak currents indicating that the mass–charge transfer process in the cathodic process are slower and more affected by the decrease of NaOH concentration. This behavior is due to lower availability of hydroxide ion. The formal potential (the average of oxidation and reduction peak potentials) of Ni/P-1,5-DAN/MCPE shifted negatively with the increase of the sodium hydroxide concentration. It appeared that the concentration of OH^- took an important role in the voltammetry of the modified electrode.

Electrocatalytic oxidation of formaldehyde at the Ni(II)/P-1,5-DAN/MCPE in alkaline solution

The electrochemical behavior of formaldehyde at a bare carbon paste electrode in basic media is poor, and it does not undergo oxidation prior to the discharge of the supporting electrolyte.

In this work, the oxidation of formaldehyde was first studied at a P-1,5-DAN/MCPE by cyclic voltammetric technique in 0.1-M NaOH solution. Formaldehyde is electroinactive on the P-1,5-DAN/MCPE in the potential window of this study. Figure 5 presents the CVs of the Ni/P-1,5-DAN/MCPE in the presence of excessive concentrations of formaldehyde in 0.1-M NaOH solutions at the scan rate of 10 mV s^{-1}. In the presence of formaldehyde, it was observed that the anodic peak current increased drastically, while the cathodic peaks current decreased. This indicates that formaldehyde is oxidized by active nickel moiety via a cyclic mediation redox process. Nickel species is 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.

Accordingly, formaldehyde is oxidized via an EC' mechanism:

$$\left[(\mathbf{P-1,5-DAN-Ni})(\mathbf{OH})_2\right]+\mathbf{OH}^- \rightleftarrows \left[(\mathbf{P-1,5-DAN-Ni})\mathbf{OOH}\right]+\mathbf{H_2O}+\mathbf{e}^- \quad \mathbf{E}$$
$$\left[(\mathbf{P-1,5-DAN-Ni})\mathbf{OOH}\right]+\mathbf{CH_2O} \rightarrow \mathbf{products}+\left[(\mathbf{P-1,5-DAN-Ni})(\mathbf{OH})_2\right] \quad \mathbf{C'}$$

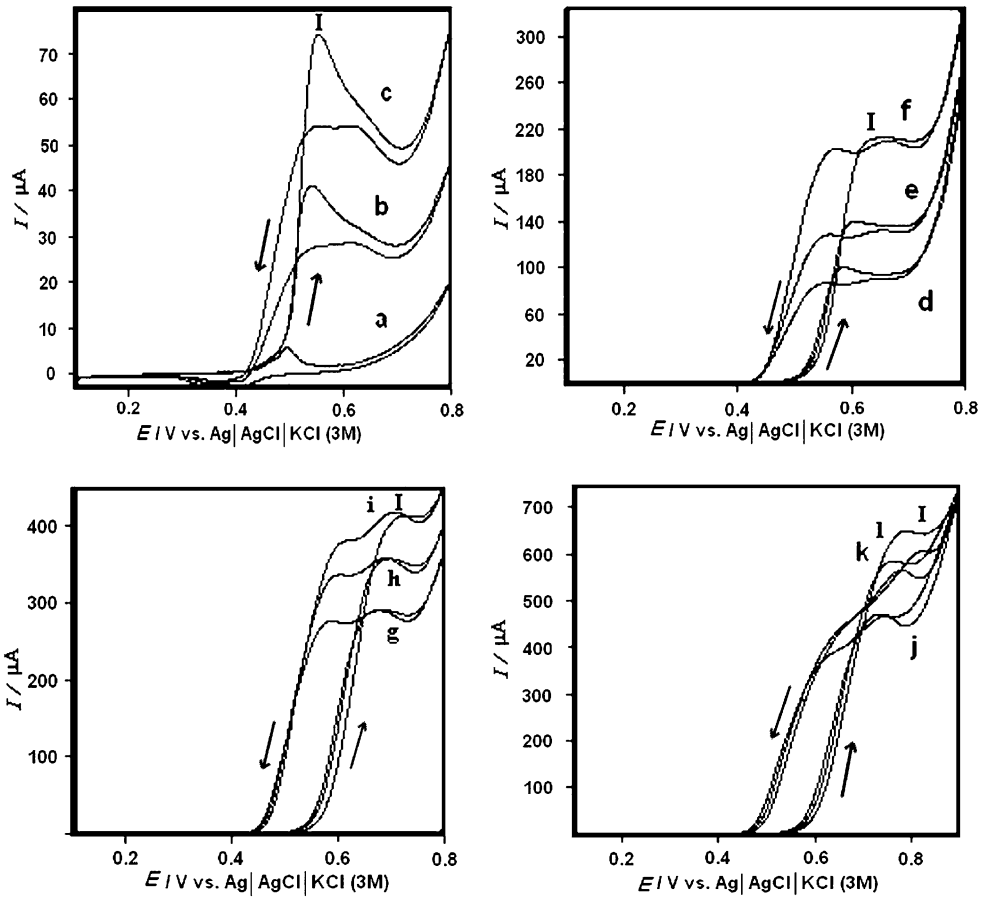

Fig. 5 Cyclic voltammograms of the Ni/P-1,5-DAN/MCPE in 0.1 M NaOH solution with different concentrations of formaldehyde: *a* 0.0, *b* 5.0, *c* 10.1, *d* 19.6, *e* 29.1, *f* 47.6, *g* 65.4, *h* 82.6, *i* 99.1, *j* 115.1, *k* 145.3, and l 173.6 mM, respectively, υ=10 mV s^{-1}

It can be said that the (P-1,5-DAN-Ni)$(OH)_2$ modifying the electrode surface acts as a catalyst for the oxidation of formaldehyde in 0.1-M NaOH solution. The oxidation current of formaldehyde (peak I in curves of Fig. 5) coincided exactly with that where Ni(III) species were produced. This coincidence, as well as the decrease of the reduction current of Ni(III) in the negative sweep, demonstrated clearly that the modifier examined here participates directly in the electrocatalytic process. There is a large increase in the anodic peak current and elimination of cathodic peak current in the presence of higher formaldehyde concentrations. The catalytic oxidation seems to be very facile, as shown by the elimination of the cathodic peak. Because the rate of chemical oxidation between the Ni(III) and formaldehyde was large enough, hence, no Ni(III) species remained to be reduced. Examination of Fig. 5 shows that, in the presence of formaldehyde, 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. So catalytic electrooxidation of formaldehyde on Ni/P-1,5-DAN/MCPE seems to be certain. The anodic peak potential for formaldehyde oxidation is naturally shifted to the positive direction as a result of an IR drop arising from a high current density values.

It is important to note unusual oxidation peaks appearing in the cathodic half cycle. To the best of our knowledge, this is the first time this result has been observed. Previously, the presence of an additional oxidation peak in the negative sweep was observed for the oxidation of formaldehyde on copper-based and palladium electrodes [24, 41, 42].

However, in this work, we have observed two additional peaks in the reverse scan. The Origin of these peaks is currently not fully understood, but possible explanations of this phenomenon may be the following:

1. A reversible poisoning of active sites by oxidation products which are released as the potential is swept negatively regenerating the catalyst; (2) a competition between formaldehyde oxidation and oxygen evolution whose ratio is a function of applied potential. The additional oxidation peaks is hardly seen in low concentrations of formaldehyde. It means that the lower the

formaldehyde concentration, the more process is matching typical mediated electrooxidation manifested by an increase of the anodic peak of the mediator redox couple and simultaneous suppression of the cathodic one. However, the (P-1,5-DAN-Ni)$(OH)_2$-modified carbon paste electrode is a good electrocatalyst for this reaction and high current density (over 7 mA cm^{-2}) for formaldehyde oxidation can be reached. This value is comparable with respect to other modified electrodes [43, 44]. So that, this amount of current is very larger than the value obtained by reference [43] (0.3–0.4 mA cm^{-2}) using GC electrode modified with porphyrin-Ni. In the reference of [44], with using palladium nanoparticles dispersed on the multiwalled carbon nanotubes, the maximum oxidation current that was observed is about the current observed in our work. Moreover, the ease and fast preparation and obtaining a new reproducible surface, the low residual current, porous surface, and low cost of carbon paste are some advantages of CPE over all other solid electrodes. Also, renewing and removing the polymer from surface of CPE is easier than Pt and GC electrodes. Hence, it can be a candidate as an anode for fuel cell applications.

Chronoamperometric studies

Double potential step chronoamperometry as well as other electrochemical methods was employed for the investigation of electrochemical processes. Figure 6a shows the double-step chronoamperograms for the modified electrode by setting the working electrode potential at 700 mV (firs step) and 300 mV (second step) versus Ag|AgCl|KCl (3 M) for various concentrations of formaldehyde. As can be seen, the forward and backward potential step chronoamperometry of the modified electrode in the blank solution showed an almost symmetrical chronoamperogram with almost equal charges consumed for the oxidation and reduction of surface-confined Ni(II)/Ni(III) sites (Fig. 6b (a′)). However, in the presence of formaldehyde, the charge value associated with the forward chronoamperometry is greater than that observed for the backward chronoamperometry (Fig. 6b (f′)). The current is negligible when potential is stepped down to 300 mV, indicating that the electrocatalytic oxidation of formaldehyde is irreversible.

Chronoamperometry can also be used for the evaluation of the chemical reaction between the formaldehyde and modified layer (catalytic rate constant, k) according to [45]:

$$\mathbf{I_C/I_L}=\gamma^{1/2}\left[\pi^{1/2}\mathbf{erf}\left(\gamma^{1/2}\right)+\mathbf{exp}(-\gamma)/\gamma^{1/2}\right] \quad (3)$$

Where I_C and I_L are the currents in the presence and absence of formaldehyde, and $\gamma = kct$ is the argument of the error function; k is catalytic rate constant; c is bulk concentration of formaldehyde and t is the elapsed time. In the cases where $\gamma > 1.5$, $\mathbf{erf}(\gamma^{1/2})$ is almost equal to unity and the above equation can be reduced to:

$$\mathbf{I_C/I_L}=\gamma^{1/2}\pi^{1/2}=\gamma^{1/2}(\mathbf{kct})^{1/2} \quad (4)$$

From the slope of the I_C/I_L versus $t^{1/2}$ plot, presented in Fig. 6c, the mean value of k for the concentration range of

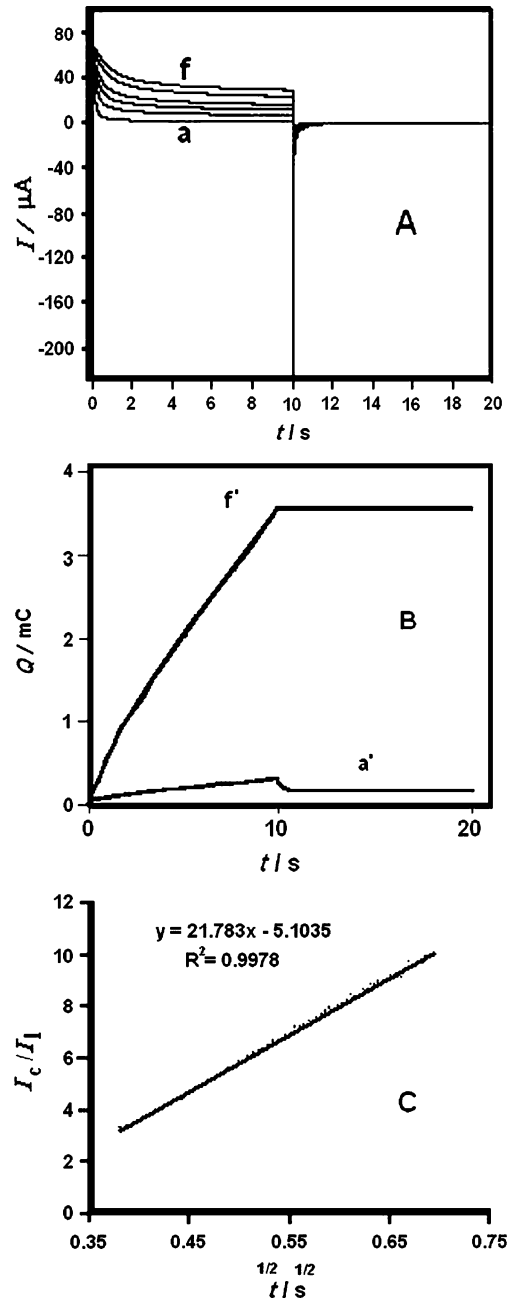

Fig. 6 **a** Chronoamperograms obtained at a Ni/P-1,5-DAN/MCPE in 0.1-M NaOH solution in the absence *a* and presence of *b* 10.1, *c* 19.6, *d* 29.1, *e* 47.6 and *f* 65.4 mM of formaldehyde; first and second potential steps were 700 and 300 mV vs. reference electrode, respectively. **b** Dependence of charge Q (mC) vs. t derived from the data of chronoamperograms of *a'* and *f'*. **c** Dependence of I_C/I_L on $t^{1/2}$ derived from the data of chronoamperograms of *a* and *f* in the main panel of **a**

10.1 to 65.4 mM of formaldehyde was obtained as 2×10^6 cm^3 mol^{-1} s^{-1}.

Conclusion

In the electrochemical oxidation of formaldehyde, the electrode material is clearly an important parameter where a high efficient electrocatalyst is needed. Because catalysis is a surface effect, the catalyst needs to have the highest possible surface area. For this reason, we have used carbon-supported electrodes as catalyst. In this work, we have shown the advantageous features of carbon paste technology, polymer modification and dispersion of metallic particles into an organic polymer. On the other hand, it is well established that nickel can be used as a catalyst due to its surface oxidation properties. The (P-1,5-DAN-Ni)$(OH)_2$ layer investigated in this study was found to be capable of catalyzing the electrooxidation of formaldehyde very efficiently. The oxidation process commences at a potential where the oxidizing Ni(III) species are generated. The value for the catalytic rate constant, k, obtained from the chronoamperometric method indicated that the modified electrode can overcome the kinetic limitation for the formaldehyde oxidation by a catalytic process and can decrease the overpotential for the oxidation reaction of formaldehyde.

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