

Electrocatalytic oxidation of some carbohydrates by poly(1-naphthylamine)/nickel modified carbon paste electrode

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Abstract

A method of generating a rapidly renewable and reproducible polymer coated electrode surface is proposed. This involves in situ electropolymerization at a monomer modified carbon paste electrode. A carbon paste electrode bulk modified with 1-naphthylamine was used to demonstrate this approach. Then Ni(II) ions were incorporated by immersion of the modified electrode in a 0.1 M Ni(II) ion solution. The electrochemical characterization of this modified electrode exhibits stable redox behavior of the Ni(III)/Ni(II) couple even after potential 500 cycles. Also, cyclic voltammetric and chronoamperometric experiments showed that glucose was oxidized at the surface of this Ni(II) dispersed polymeric modified carbon paste electrode. The electrode was successfully used in the electrocatalytic oxidation of various other carbohydrates. Finally, the electrocatalytic oxidation peak currents of all carbohydrates tested exhibited a good linear dependence on concentration and their quantification can be done easily.

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Keywords: Carbon paste electrode; 1-Naphthylamine; Carbohydrate; Electropolymerization; Cyclic voltammetry

1. Introduction

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 [1–4]. Polymers such as polypyrrole, polythiophene and polyaniline have been applied in electrochemical modification of electrodes [5–9]. This new class of electrode material has been found to improve the electrode sensitivity and selectivity, and to reduce fouling effects in many applications [10,11].

On the other hand, the electrochemical detection of carbohydrates, which are important in many medical, biological and industrial applications, because of its simplicity, selectivity and low cost [12,13], provides an alternative approach to absorption and fluorescence detection methods in the determination of carbohydrates in HPLC and FIA experiments. Various authors have shown that carbohydrates and specifically glucose,

can be oxidized directly at a variety of electrode materials, including metals such as platinum [14,15], gold [15,16], copper [15,17–19], indium [15], rhodium [15], nickel oxide [20], tungsten oxide [21], ruthenium oxide [22] or metallic complexes such as cobalt phthalocyanine [23]. Because of this, metal particles dispersed in thin organic films have been recognized as effective electrocatalysts with high activities for various electrode reactions [24,25]. Recently, modified electrodes with metallic microparticles electrodeposited into the polymeric matrix have been used for the oxidation of carbohydrates [26,27] and amino acids [28]. Kuwana and coworkers [26] prepared a copper-Nafion® modified electrode for catalytic oxidation of carbohydrates. Also, a poly-1-naphthylamine/copper modified glassy carbon electrode was successfully employed for electrocatalytic oxidation of various carbohydrates [29].

In this work, we decided to combine the advantageous features of polymer modification, dispersion of metallic particles into an organic polymer and carbon paste technology. We introduced 1-naphthylamine monomer into the carbon paste bulk and obtained a

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polymeric coated electrode in situ by electropolymerization of the monomer. In fact, this work showed that a renewable and reproducible polymeric coated electrode could be generated rapidly at the 1-naphthylamine modified carbon paste electrode (NAP/MCPE). Then, nickel ions were incorporated into the polymeric matrix by immersion of the polymeric modified electrode in a nickel chloride solution. This electrode was used for electrocatalytic oxidation of various carbohydrates.

2. Experimental

2.1. Reagents and materials

1-Naphthylamine from Fluka was sublimated at 40 °C under reduced pressure and kept under vacuum [30]. Perchloric acid from Fluka was used as the supporting electrolyte. All carbohydrates were from Fluka and were used as received. High viscosity silicon (density = 0.973 g cm⁻³) from Fluka was used as the pasting liquid for the carbon paste electrode. Graphite powder (particle diameter = 0.1 mm) from Merck was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

2.2. Working electrode

A 0.44% (w/w) mixture of 1-naphthylamine (NAP) to total weight of graphite powder was made by dissolving the given quantity of NAP in diethyl ether and hand mixing with the required graphite powder in a mortar and pestle. The solvent was evaporated by stirring. Silicon oil was then added and was blended by hand mixing until a homogeneous paste was obtained. For fabrication of the electrode, the prepared paste was tightly packed into one end of a glass tube (ca. 3.5 mm internal diameter) and a copper wire was introduced into the other end for electrical contact. 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.

2.3. Instrumentation

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP 2061-C Electrochemical Analysis System, Behpajoo, Iran) coupled with a Pentium II personal computer connected to an HP Laser jet 6L printer. A platinum wire was used as the auxiliary electrode. The 1-naphthylamine modified carbon paste electrode and a double junction Ag|AgCl|KCl(3M) (Behpajoo, Iran) electrode were used as the working and reference electrodes, respectively.

3. Results and discussion

3.1. Preparation of poly(1-naphthylamine) modified carbon paste electrode (P-NAP/MCPE)

Previously, poly(1-naphthylamine) (P-NAP) films were obtained at the surface of Au, Pt and GC electrodes by use of cyclic voltammetric methods [30,31]. Recently we have investigated the preparation of P-NAP at the surface and in the bulk of carbon paste electrodes in work submitted for publication [32]. So that the polymers obtained were completely comparable with those prepared at the surface of other electrodes [30,31], in this work, electropolymerization at the NAP/MCPE (0.44% NAP) was carried out in 0.2 M HClO₄ by holding the potential at 0.65 V for 200 s.

After this, the electrode was removed, rinsed with water and the sides wiped with soft tissue paper. The redox behavior of the film was strongly dependent on the pH of the electrolyte solution [29]. The response obtained in a 0.1 M NaOH solution showed a complete loss of electrode activity in the potential range from -0.15 to 0.65 V (Fig. 1(a)). However, the film was not degraded under these experimental conditions and its response was recovered when the electrode was immersed in a supporting electrolyte solution at pH 1.0 (Fig. 1(b)).

3.2. Incorporation of Ni(II) ions into P-NAP film and electrochemical response of the Ni(II)-P-NAP modified carbon paste electrode (Ni/P-NAP/MCPE)

In order to incorporate Ni(II) ions into the P-NAP film, the freshly electropolymerized NAP/MCPE was placed at open circuit in a well stirred aqueous solution of 0.1 M NiCl₂. Accumulation of nickel was carried out by complex formation between Ni(II) and amines site in

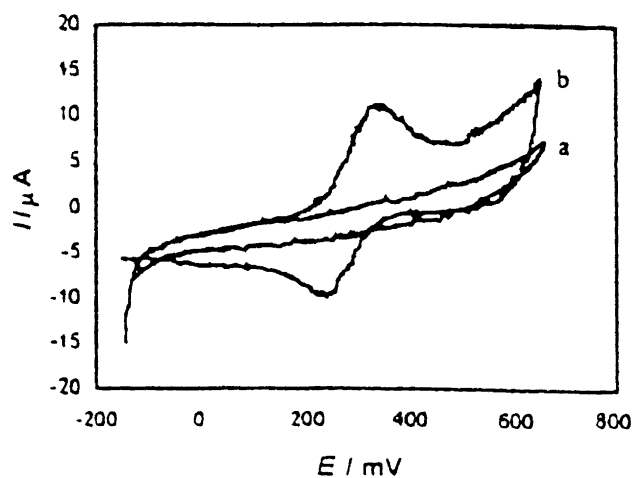


Fig. 1. Electrochemical responses of P-NAP/MCPE: (a) in 0.1 M NaOH solution; (b) in 0.2 M HClO₄ solution, scan rate = 50 mV s⁻¹.

the polymer backbone [29,33], for a given period of time (t_a , accumulation time). Fig. 2 shows the electrochemical response of the NAP/MCPE, P-NAP/MCPE and Ni/P-NAP/MCPE in 0.1 M NaOH solution. It can be seen from Fig. 2 that whereas neither oxidation nor reduction took place on the NAP/MCPE and P-NAP/MCPE, a well developed stable redox wave was observed on the Ni/P-NAP/MCPE when the potential was cycled between 0.0 and 0.6 V, which was related to the oxidation of Ni(II) to Ni(III) with a peak potential of 0.44 V and reduction of Ni(III) to Ni(II) with a peak potential of 0.35 V. The redox behavior is very stable, so no change in peak current is observed after 500 potential cycles. The surface coverage of the immobilized active substance (Ni(II)) in the films can be evaluated from the charge under the current–potential waves (Fig. 2) with correction for the baseline ($\Gamma = Q/nFA$). The value of Γ

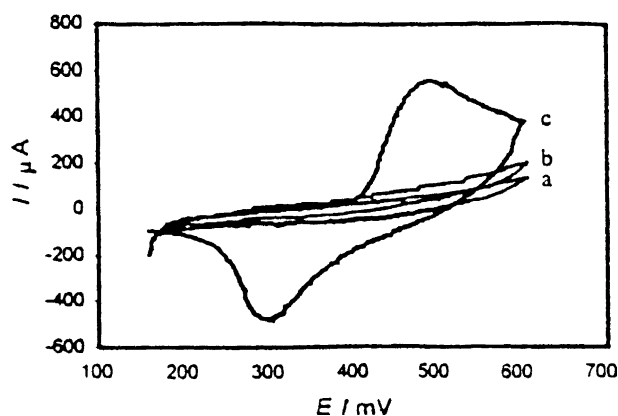


Fig. 2. Electrochemical responses of electrodes: (a) NAP/MCPE, (b) P-NAP/MCPE and (c) Ni/P-NAP/MCPE, in 0.1 M NaOH solution, scan rate = 50 mV s⁻¹.

for Ni/P-NAP/MCPE was 6.8 mmol cm⁻². Fig. 3(A) shows the cyclic voltammograms of Ni/P-NAP/MCPE in 0.1 M NaOH solution at different scan rates and Fig. 3(B) shows the plot of the oxidation peak current I_p vs. $v^{1/2}$, which is a straight line. The plot of I_p vs. $\log v$ has a slope of approximately 0.53 (not shown). The linear dependence and the slope of 0.53 indicate that the electrode reaction is diffusion controlled.

3.3. Electrocatalytic oxidation of carbohydrates on the modified electrode

3.3.1. Cyclic voltammetry studies

According to previous studies, carbohydrates are oxidized at high pHs [29,33]. In this work the oxidation of glucose was first studied at a P-NAP/MCPE electrode (without the incorporation of nickel) by cyclic voltammetric experiments in 0.1 M NaOH. Typical results obtained for a potential scan from 0.25 to 0.5 V vs. Ag/AgCl are shown in Fig. 4. The electrochemical response of P-NAP/MCPE in the absence of glucose is shown in Fig. 4(a); the addition of 1 mM glucose to the alkaline solution causes no effect on the electrochemical response of the P-NAP/MCPE (Fig. 4(b)).

The electrochemical response of a Ni/P-NAP/MCPE in alkaline solution (i.e. 0.1 M NaOH) exhibits well defined anodic and cathodic peaks (Fig. 4(c)) associated with the Ni(II)/Ni(III) redox couple. As can be seen, upon glucose addition (1 mM) there is an increase in the anodic peak current and a decrease in the cathodic peak current (Fig. 4(d)). This behavior is typical of that expected for mediated oxidation as follows:

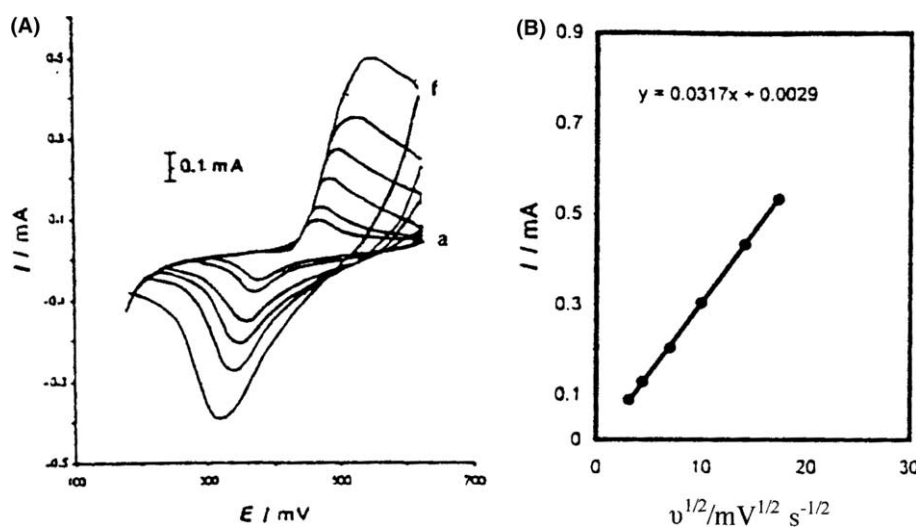
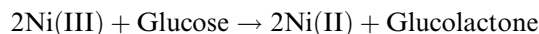


Fig. 3. (A) Scan rate dependence of the peak current, scan rates: (a) 10, (b) 20, (c) 50, (d) 100, (e) 153, (f) 300 mV s⁻¹ solution is 0.1 M NaOH. (B) Plot of I_p vs. $v^{1/2}$.

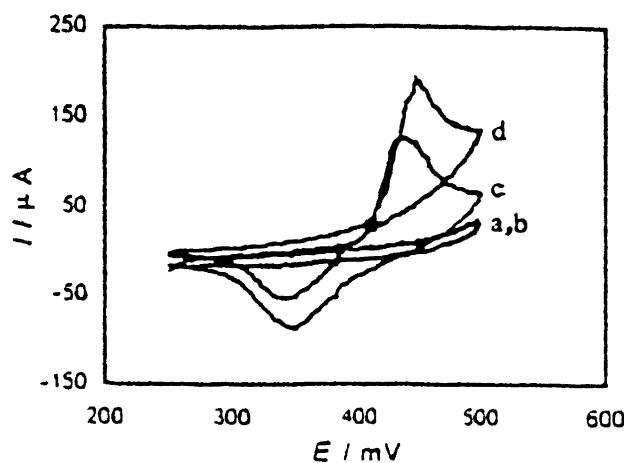


Fig. 4. Electrochemical responses of P-NAP/MCPE to: (a) 0, (b) 1 mM and Ni/P-NAP/MCPE to: (c) 0 and (d) 1 mM.

The results indicate that the Ni/P-NAP/MCPE can catalyze the electrooxidation of glucose to glucolactone [34] due to the existence of Ni(II) ions in the poly(1-naphthylamine) film. This modified electrode exhibited similar electrocatalytic responses for the other carbohydrates, exhibiting its capability for selective oxidation of carbohydrates both in the laboratory and on a technical scale. As is seen, the electrocatalytic oxidation of carbohydrates was very stable, without significant change in the current on subsequent cycles. Cyclic voltammograms of the P-NAP/MCPE in the presence of 0.24 mM glucose at various scan rates were recorded (Fig. 5). It can be seen from Fig. 5 that, with increasing scan rate, the peak potential for the catalytic oxidation of glucose shifts to increasingly positive potentials, suggesting a kinetic limitation in the reaction between

the redox sites of the Ni/P-NAP/MCPE and glucose. However, the oxidation current for glucose increased linearly with the square root of the scan rate (inset (A)), suggesting that the reaction is mass transfer controlled. Also, a plot of the scan rate normalized current ($I/v^{1/2}$) vs. scan rate (inset (B)), exhibits a shape typical of an EC' process. In order to obtain information on the rate determining step, the Tafel slope, b , was determined using the following equation, valid for a totally irreversible diffusion controlled process [35].

$$E_p = (b/2) \log v + \text{constant.}$$

On the basis of the above equation, the slope of E_p vs. $\log v$ plot is $b/2$, where b indicates the Tafel slope. The slope of the E_p vs. $\log v$ plot is $\delta E_p / \delta(\log v)$ which was found to be 0.0432 V for glucose in this work (Fig. 6(A)), so, $b = 0.0864$ V. This slope indicates that a one electron transfer process is the rate limiting step, assuming a transfer coefficient of $\alpha = 0.68$, for glucose. The number of electrons involved in the rate-determining step, can be obtained using another method. Tafel plots (Fig. 6(B)) were drawn using the data from the rising part of the current–voltage curve at a scan rate of 10 mV s^{-1} for 1 mM of glucose. A slope of 0.0869 V/decade or $11.5 \text{ (V/decade)}^{-1}$ was obtained indicating a one-electron process which was rate limiting, assuming a transfer coefficient of $\alpha = 0.68$. The results obtained from the two different methods are in good agreement. By use of this method, values of α for galactose, lactose, maltose, sucrose and sorbitol were calculated and are reported in Table 1.

3.3.2. Chronoamperometric studies

Chronoamperometry, as well as other electrochemical methods, was employed for the investigation of elec-

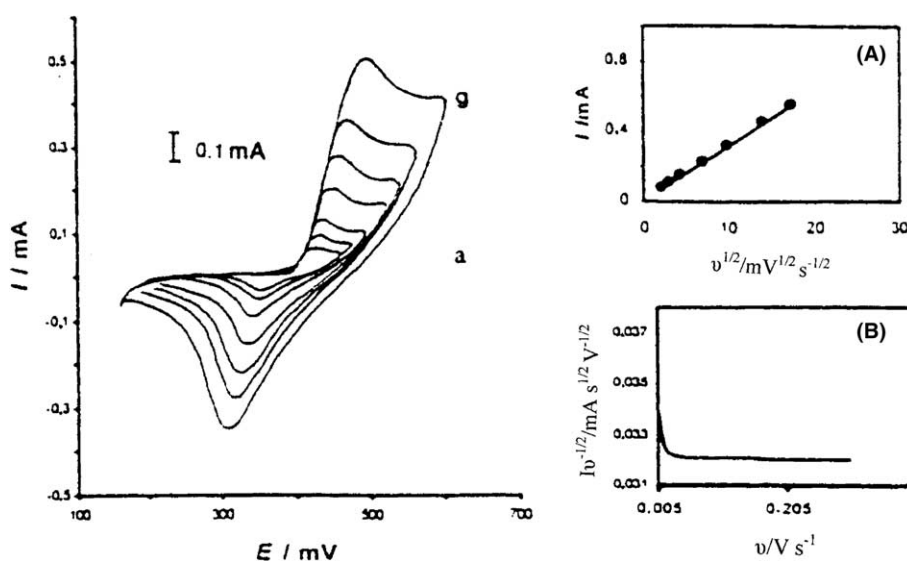


Fig. 5. Cyclic voltammograms of the Ni/P-NAP/MCPE in the presence of 0.24 mM glucose, scan rates: (a) 5, (b) 10, (c) 20, (d) 50, (e) 100, (f) 153, (g) 300 mV s^{-1} , respectively. Insets (A) and (B) represent the variations of the anodic peak currents and anodic current function vs. $v^{1/2}$ and v , respectively, solution is 0.1 M NaOH.

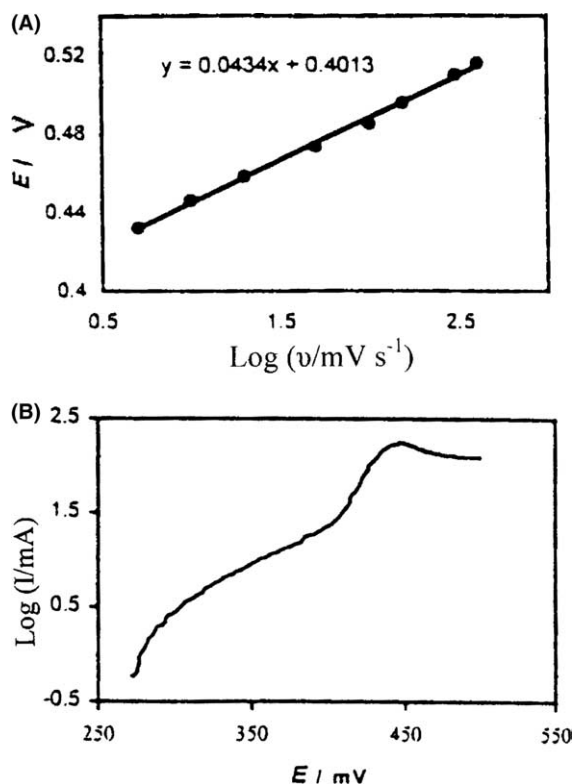


Fig. 6. (A) Dependence of the peak potential, E_p on $\log v$ for the oxidation of glucose at the Ni/P-NAP/MCPE obtained from the data of Fig. 5. (B) The Tafel plot derived from the current-potential curve obtained of the Ni/P-NAP/MCPE in the presence of 1 mM glucose at a 10 mV s^{-1} solution is 0.1 M NaOH.

trode processes at chemically modified electrodes. Fig. 7 shows chronoamperometric measurements of glucose at the Ni/P-NAP/MCPE. The main figure represents the current-time profiles obtained by setting the working electrode potential step at 450 mV for various concentrations of glucose. Inset (A) in Fig. 7 shows the plots of currents sampled at fixed time as a function of glucose concentration, added to the blank solution at different times after application of the potential step. Comparison of the plots (a), (b) and (c) in this inset suggests that in all cases, there is a similar connection between currents

measured at fixed times and glucose concentrations, but the slope of the calibration plot is increased with a decrease of the time elapsed after potential step application. 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. However, in the presence of glucose, the charge value associated with the forward chronoamperometry, Q is greater than that observed for the backward chronoamperometry (Fig. 7, inset (B)). Also, chronoamperometry was employed to investigate the electrode process at the modified electrode for galactose, lactose, maltose, sucrose and sorbitol. The rate constant for the chemical reaction between the carbohydrates and redox sites of Ni/P-NAP/MCPE, can be evaluated by chronoamperometry according to the method described in the literature [36].

$$I_C/I_L = \gamma^{1/2}[\pi^{1/2}\text{erf}(\gamma^{1/2}) + \exp(-\gamma^{1/2})\gamma^{1/2}],$$

where I_C is the catalytic current of the Ni/P-NAP/MCPE in the presence of carbohydrates, I_L is the limiting current in the absence of carbohydrates and $\gamma = kc_0t$ (c_0 is the bulk concentration of carbohydrate) is the argument of the error function. In the cases where γ exceeds 2, the error function is almost equal to 2 and the above equation can be reduced to:

$$I_C/I_L = \gamma^{1/2}\pi^{1/2} - \pi^{1/2}(kc_0t)^{1/2},$$

where k , c_0 and t are the catalytic rate constant ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), carbohydrate concentration (mol cm^{-3}) and time elapsed (s), respectively. From the slope of the I_C/I_L vs. $t^{1/2}$ plot we can simply calculate the value of k for a given concentration of substrate. Inset (C) of Fig. 7 shows one such plot, constructed from the chronoamperogram of the Ni/P-NAP/MCPE in the absence and presence of 0.05 mM glucose. The mean value for k , was found to be $229 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The values of k for galactose, lactose, maltose, sucrose and sorbitol were found by chronoamperometry according to the method describe in the above and are reported in Table 1. As can

Table 1
Analytical and electroanalytical parameters for oxidation of various carbohydrates at the Ni/P-NAP/MCPE

Compounds	α^a	α^b	K^c ($\text{cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$)	DR ^d (mM)	10^6LOD (M)	RSD% ($n = 5$)
Glucose	0.68	0.68	229	0.04–1	6	4.9
Galactose	0.58	0.55	275	0.02–1	7.7	4.4
Lactose	0.69	0.65	97	0.05–1	6.2	4.2
Maltose	0.67	0.64	98	0.04–0.82	8.9	3
Sucrose	0.7	0.7	22	0.35–0.7	8	3.2
Sorbitol	0.65	0.64	57	0.02–1	8.8	3.9

^a α was determined from the Tafel plot.

^b α was determined from the variation of peak current-potentials of electrocatalytic oxidation vs. $\log v$.

^c Catalytic rate constant.

^d Dynamic range.

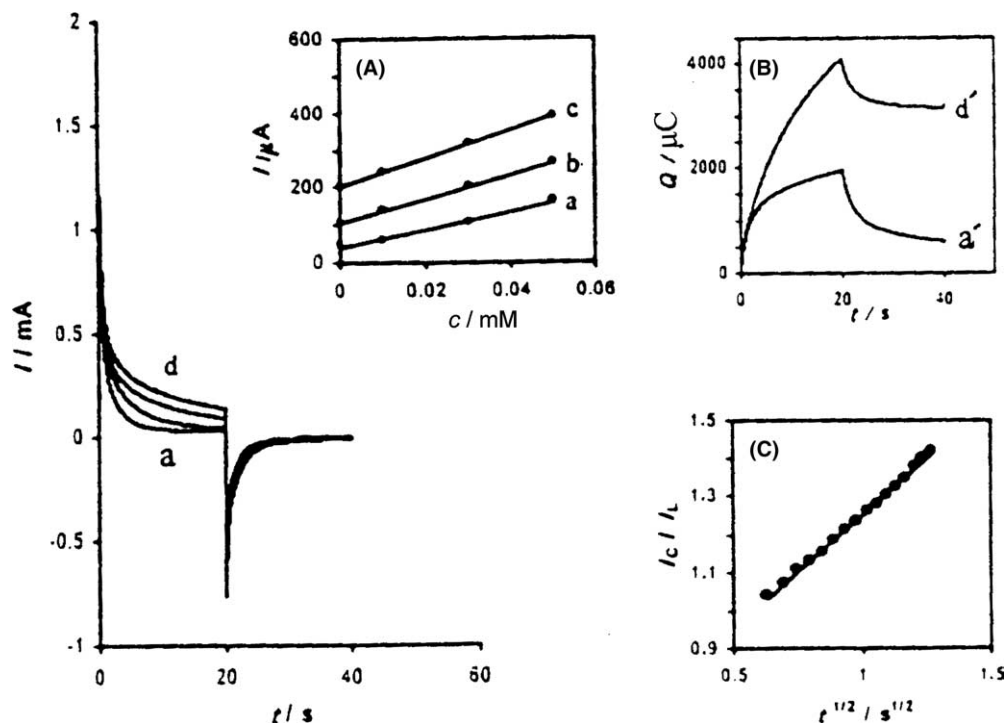


Fig. 7. Chronoamperograms obtained at the Ni/P-NAP/MCPE in the (a) absence and presence of (b) 0.01, (c) 0.03, (d) 0.05 mM of glucose, first and second potential steps were 0.33 and 0.45 V vs. Ag|AgCl, respectively, in 0.1 M NaOH solution. Inset (A) dependence of the fixed-time current observed (for (a) 2; (b) 4; (c) 8 s after the first potential step) vs. glucose concentration derived from the data of the main panel. Inset (B): dependence of Q (μC) vs. t derived from the data of chronoamperograms of (a) and (d). Inset (C): dependence of I_c/I_L on $t^{1/2}$ derived from the data of chronoamperograms of (a) and (d) in the main panel.

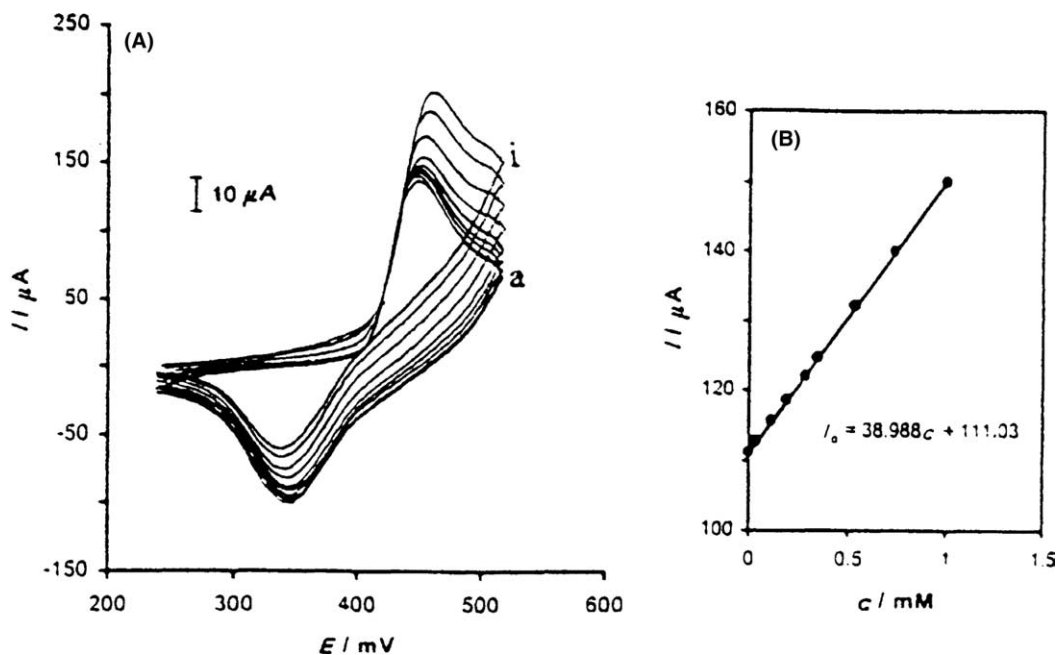


Fig. 8. (A) Current–potential curves for oxidation glucose at the Ni/P-NAP/MCPE in 0.1 M NaOH solution with different concentrations of glucose: (a) 0, (b) 0.04, (c) 0.11, (d) 0.19, (e) 0.28, (f) 0.35, (g) 0.54, (h) 0.75, (i) 1 mM. (B) Plot of I vs. c .

be seen, glucose and galactose (as monosaccharides) exhibit the highest values of k because of their high reducing powers and sucrose exhibits the lowest value for

k due to its non-reducing properties. However, disaccharides show behavior between the two above cases. It should be noted that sorbitol is a sugar alcohol.

Table 2
Some modified electrodes used in electrocatalytic oxidation of carbohydrates

Substrate	Modifier	Compound	Measurement method	LOD (μM)	Refs.
Glassy carbon electrode	Copper particles dispersed into a polyaniline film	Xylitol, sorbitol, glucosamine, glucose, lactose, sucrose	LC–EC ^a	0.25–0.75	[33]
Glassy carbon electrode	Copper/copper oxide particles dispersed into a Nafion [®] film	Glucose, fructose, rhamnose, maltose, lactose	LC ^b	0.5–6	[29]
Glassy carbon electrode	Copper particles dispersed into a poly(1-naphthylamine) film	Sorbitol, glucose, fructose, lactose sucrose, maltose	LC ^c	2.5–10	[30]
1-naphthylamine modified carbon paste electrode	Nickel particle dispersed into a poly(1-naphthylamine) film	Glucose, galactose, lactose, maltose sucrose, sorbitol	ED ^d	6–8.8	This work

^a Liquid chromatography–anion exchange chromatographic (applied potential, 0.55 V vs. Ag|AgCl; flow rate, 1.0 ml min⁻¹ carrier/electrolyte, 0.10 M NaOH; injection volume, 20 μL).

^b Liquid chromatography (applied potential, 0.48 V vs. Ag|AgCl; flow rate, 0.3 ml min⁻¹ carrier/electrolyte, 0.15 M NaOH; injection volume, 20 μL).

^c Liquid chromatography (applied potential, 0.50 V vs. Ag|AgCl; flow rate, 0.5 ml min⁻¹ carrier/electrolyte, 0.10 M NaOH; injection volume, 20 μL).

^d Electrochemical detection (cyclic voltammetry; sweep potential, 0.25 to –0.55 V vs. Ag|AgCl; scan rate, 10 mV s⁻¹ supporting electrolyte, 0.1 M NaOH; cell volume, 10 ml).

3.3.3. Electrocatalytic determination of carbohydrates

Fig. 8 shows the cyclic voltammograms of the P-NAP/MCPE in the presence of glucose. As is seen in Fig. 8(a), P-NAP/MCPE exhibits a well-defined catalytic oxidation current increasing linearly with increase in glucose concentration from 0.04 to 1 mM (Fig. 8). This modified electrode exhibited reproducible concentration dependent profiles for the carbohydrates. Calibration plots for analysis of carbohydrates show linear dependences of the anodic peak current with increasing carbohydrate concentrations in the solution. The analytical parameters are listed in Table 1. The electrocatalytic oxidation of carbohydrates has been investigated at the surface of other chemically modified electrodes by different measurement methods (see Table 2).

4. Conclusion

We have shown in this work, the advantageous features of carbon paste technology, polymer modification and dispersion of metallic particles into an organic polymer. A novel electrode has been described herein, consisting of nickel ions loaded into a poly-1-naphthylamine modified carbon paste electrode, by immersion of the polymeric modified electrode in a nickel chloride solution. The Ni/P-NAP/MCPE can catalyze the oxidation of carbohydrates via a surface layer mediated charge transfer. The kinetic process of the catalytic reaction can be explained using cyclic voltammetry and chronoamperometry. The values for the rate constant k obtained from the chronoamperometric method indicated that the modified electrode can overcome the kinetic limitations for carbohydrate oxidation by a catalytic process and can decrease the overpotential for the oxidation reaction of carbohydrates. This electrode is useful for the electrocatalytic quantitation of

several carbohydrate compounds in cyclic voltammetric studies. The method could be adapted for amperometric measurements using a flow-injection system.

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