

Performance of glucose electrooxidation on Ni–Co composition dispersed on the poly(isonicotinic acid) (SDS) film

Reza Ojani · Jahan-Bakhsh Raouf · Banafsheh Norouzi

Received: 18 October 2009 / Revised: 22 June 2010 / Accepted: 9 August 2010 / Published online: 1 September 2010
© Springer-Verlag 2010

Abstract Poly(isonicotinic acid) (PINA) film was electro-synthesized on carbon paste electrode (CPE) by using the repeated potential cycling technique in aqueous solution containing isonicotinic acid (INA), sulfuric acid and sodium dodecyl sulfate (SDS). Then, nickel and cobalt ions were incorporated by immersion of CPE/PINA prepared in the presence of SDS (CPE/PINA(SDS)) in a solution with different proportions of nickel chloride and cobalt chloride. The electrochemical characterization of mixed hydroxides containing cobalt and nickel at the surface of the modified electrode is presented. The modified electrodes were successfully used in the electrocatalytic oxidation of glucose. Finally, the electrocatalytic oxidation peak currents of glucose exhibited a good linear dependence on concentration, and its quantification can be done easily. The good analytical performance, low cost and straightforward preparation method make this novel electrode material promising for the development of an effective glucose sensor.

Keywords Poly(isonicotinic acid) · Modified electrode · Electrocatalysis · Glucose · SDS · Nickel hydroxide · Cobalt hydroxide

Introduction

The determination of glucose concentration is very important in many fields [1, 2]. For example, to date, clinical diabetes monitoring has been mainly based on blood glucose measurements [2]. In recent years, a number of studies have been conducted to develop new glucose detection methods. Some methods use glucose oxidase and show excellent sensitivity and high selectivity; however, there are still some disadvantages, such as low stability, high complexity, bad reproducibility and poor oxygen limitations [3–5]. Among them, the most serious drawback is insufficient stability originating from the intrinsic nature of the enzymes. Therefore, it would be most desirable to determine glucose concentration without using enzymes.

On the other hand, nickel hydroxide is commonly used as an active material for nickel positive electrodes in Ni-based rechargeable batteries [6–8], electrochromic devices [9], as promising catalysts for oxygen evolution reaction (OER) [10, 11], electrocatalytic oxidation of some analytes such as fructose [12], carbohydrates [13–17] and urea [18]. Some properties of nickel hydroxide electrodes (such as high power density, very good cyclability and high specific energy) have made them very viable for an extended range of applications [19].

The presence of certain metal cations such as cobalt in hydrated nickel oxides and oxyhydroxides, generically referred to as nickel hydrous oxides, can strongly affect the electrochemical characteristics of this interesting electrode material [20]. Cox and Pletcher [21] showed the use of Co–Ni oxides for catalytic oxidation of ethanol to acetic acid. In this way, the nickel hydroxide electrode has a great potential for application in sensing specific organic analytes, being suitable for urea determination [18].

R. Ojani (✉) · J.-B. Raouf · B. Norouzi
Electroanalytical Chemistry Research Laboratory,
Faculty of Chemistry, Mazandaran University,
Babolsar, Iran
e-mail: fer-o@umz.ac.ir

B. Norouzi
Department of Chemistry, Faculty of Industry and Engineering,
Islamic Azad University Ghaemshahr Branch,
Ghaemshahr, Iran

In our previous work, we used modified carbon paste electrodes (CPEs) with poly(1-naphthylamine)/Ni and poly(*o*-aminophenol)/Ni for electrocatalytic oxidation of several carbohydrates [16, 17]. These studies showed that the metal–polymer electrodes are easy to prepare, stable for long periods with good detection limits and wide linear range responses. Also, recently, we have demonstrated that poly-1,5-diaminonaphthalene/Ni and poly(*o*-aminophenol) (SDS)/Ni modified CPEs can successfully catalyze the oxidation of methanol in alkaline medium [22, 23]. In these studies, we have combined the advantageous features of polymer modification, dispersion of metallic particles into an organic polymer and carbon paste technology. All these results encouraged us to continue the studies with new polymer materials. In this work, we decided to combine the above-mentioned advantageous features, again, for the aim of electrocatalytic oxidation of glucose by use of poly(isonicotinic acid) (PINA) as a new polymer. We introduced an isonicotinic acid monomer in an acidic solution and obtained a polymeric coated electrode in situ by electropolymerization of the monomer in the presence and absence of SDS. Then nickel and cobalt ions were incorporated into the polymeric matrix by immersion of polymeric modified electrode in nickel chloride and cobalt chloride solutions with different percentages. Finally, we used CPE modified with PINA(SDS)/Ni(OH)₂ and PINA(SDS)/Ni₈₀Co₂₀(OH)₂ for electrochemical enzyme-free detection of glucose.

Experimental

Reagents and materials

The solvent used in this work was twice-distilled water. Sulfuric acid from Fluka was used as the supporting electrolyte. Isonicotinic acid and SDS from Fluka were

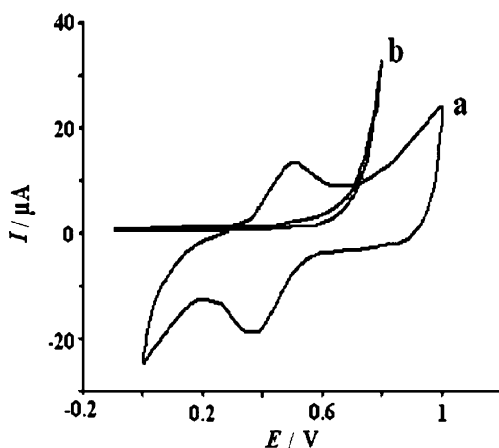


Fig. 1 Electrochemical responses of CPE/PINA(SDS) in: **a** 1 M H₂SO₄, **b** 0.1 M NaOH solution, $\nu=10 \text{ mV s}^{-1}$

used as received. Sodium hydroxide, nickel chloride, cobalt chloride and glucose used in this work were analytical grade of Fluka 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 CPE. Graphite powder (particle diameter=0.10 mm) from Merck was used as the working electrode (WE) substrate. All other reagents were of analytical grade.

Instrumentation

The electrochemical experiments were carried out using a Metrohm potentiostat/galvanostat model 764 VA trace analyzer instrument. Voltammetry was conducted using a three-electrode cell. A CPE, a platinum electrode and Ag|AgCl|KCl (3 M) were used as WE, counterelectrode and reference electrode, respectively.

Preparation of CPE

A mixture of graphite powder and paraffin were blended by hand mixing with a mortar and pestle for the 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 and smoothing the resulting surface on white paper until a smooth shiny surface was observed.

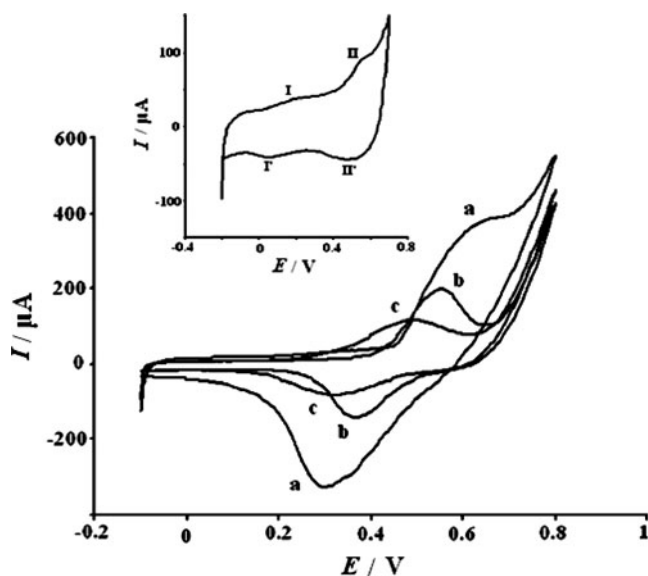
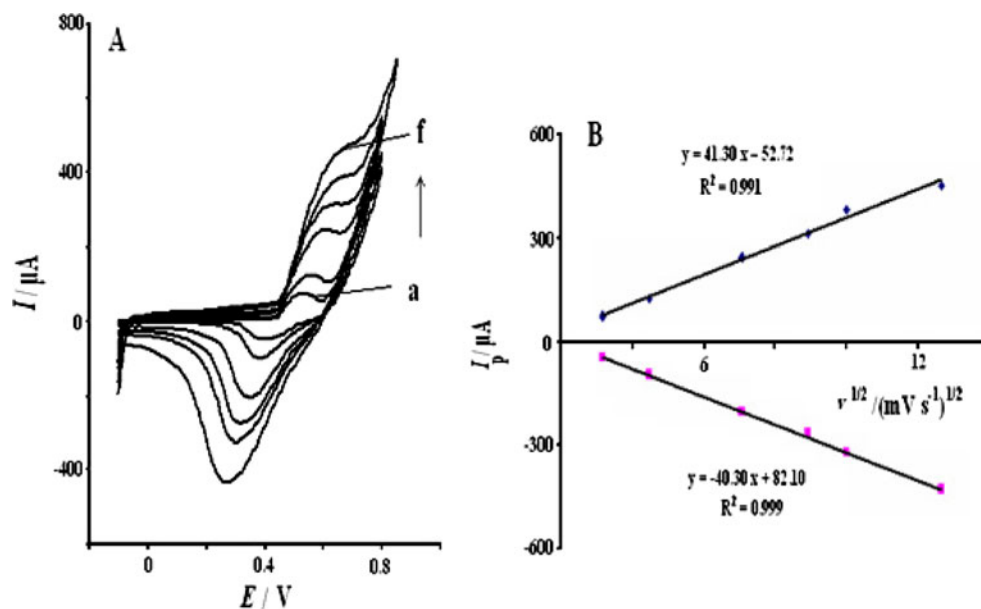


Fig. 2 Main panel: cyclic voltammograms for CPE/PINA(SDS) with **a** Ni(OH)₂, **b** Ni₈₀Co₂₀(OH)₂ and **c** Ni₅₀Co₅₀(OH)₂ in 0.1 M NaOH solution, $\nu=100 \text{ mV s}^{-1}$. Inset: cyclic voltammogram of CPE/PINA(SDS) with Co(OH)₂ in 0.1 M NaOH solution, $\nu=250 \text{ mV s}^{-1}$

Fig. 3 **a** Cyclic voltammograms of CPE/PINA(SDS)/Ni(OH)₂ film in 0.1 M NaOH as a function of the scan rate: *a* 10, *b* 20, *c* 50, *d* 80, *e* 100 and *f* 160 mV s⁻¹. **b** Plot of *I*_p vs. *v*^{1/2}

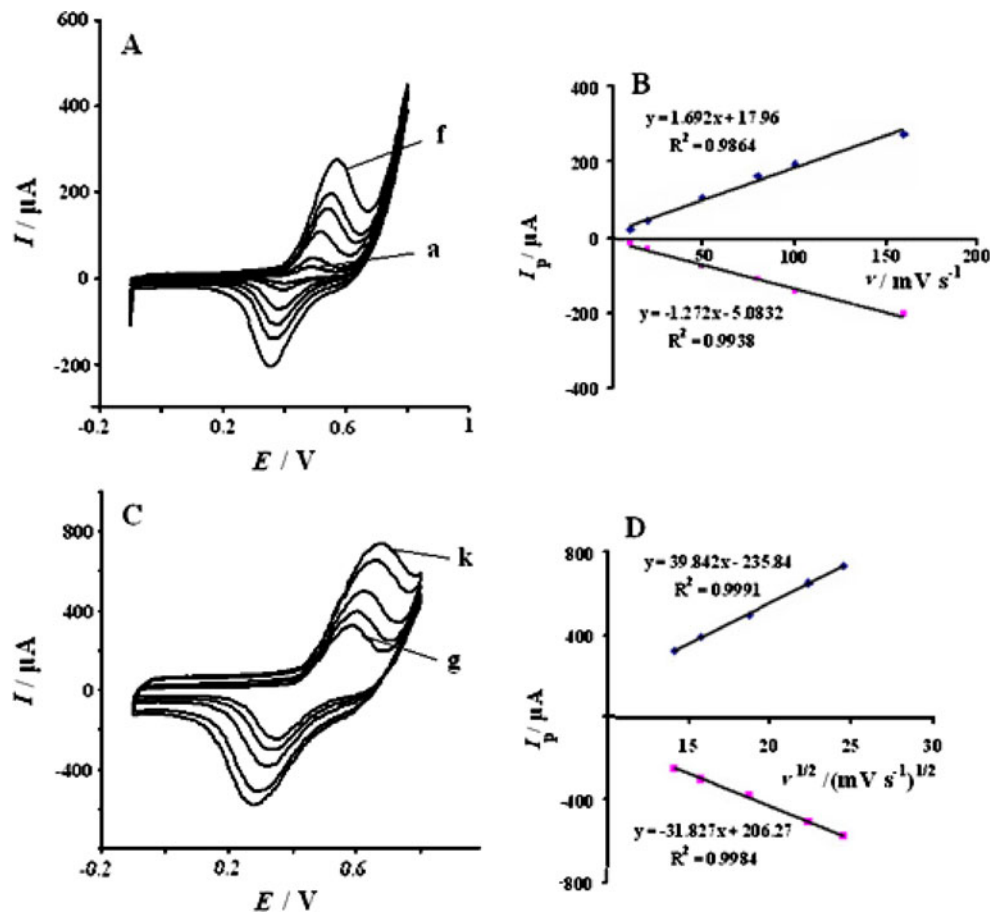


Electropolymerization procedure

PINA(SDS) films were synthesized using an isonicotinic acid monomer solution (1 mM isonicotinic acid in 1 M

H₂SO₄) in the presence of SDS (0.01 M). Electropolymerization was carried out by potential cycling (nine cycles at a scan rate of 50 mV s⁻¹) between 0 V and 1.2 V vs. Ag/AgCl.

Fig. 4 **a** Cyclic voltammograms of CPE/PINA(SDS)/Ni₈₀C₂₀(OH)₂ film in 0.1 M NaOH as a function of the scan rate *a* 10, *b* 20, *c* 50, *d* 80, *e* 100 and *f* 160 mV s⁻¹. **b** Plot of *I*_p vs. *v*. **c** As in **a** but at higher scan rates: *g* 200, *h* 250, *i* 350, *j* 500 and *k* 600 mV s⁻¹. **d** Plot of *I*_p vs. *v*^{1/2}



Incorporation of Ni(II) and Co(II) ions into a polymeric matrix

In order to incorporate Ni(II) and Co(II) ions into the PINA film, the freshly CPE electropolymerized with PINA(SDS) was placed at open circuit in a well-stirred aqueous solution with different percentages of nickel chloride and cobalt chloride (10 mL of an aqueous solution with 0.01 M NiCl₂, 0.008 M NiCl₂ and 0.002 M CoCl₂ (80:20 mol/mol), 0.005 M NiCl₂ and 0.005 M CoCl₂ (50:50 mol/mol) and 0.01 M CoCl₂), respectively. The accumulation of nickel and cobalt were conducted by complex formation between Ni(II) and Co(II) with amine sites in the polymer backbone [24–26] for a given period of time (t_a , accumulation time).

Results and discussion

Electrochemical behavior of polymeric films

We investigated the preparation of PINA on the surface of a CPE in the absence and presence of SDS. During the repetitive cycles, one redox peak (related to PINA) appeared at lower potential, and its current increased considerably with potential cycling. By adding 0.01 M anionic surfactant of SDS to the monomer solution, the oxidation current of monomer has been increased considerably. Moreover, the rate of polymerization increased considerably and the redox peaks due to PINA grew (not shown). These results show that, in the presence of SDS, the monomer can easily reach the electrode surface and produce more monocation radical. Moreover, a pair of shoulders was observed that can be attributed to the presence of SDS in the film. These results were compatible with our previous studies [23, 27, 28].

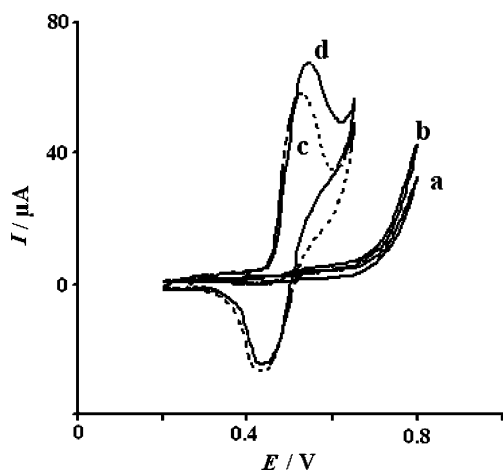


Fig. 5 Electrochemical responses of CPE/PINA(SDS) to: *a* 0 and *b* 2.35 mM glucose, and CPE/PINA(SDS)/Ni(OH)₂ to: *c* 0 and *b* 2.35 mM glucose

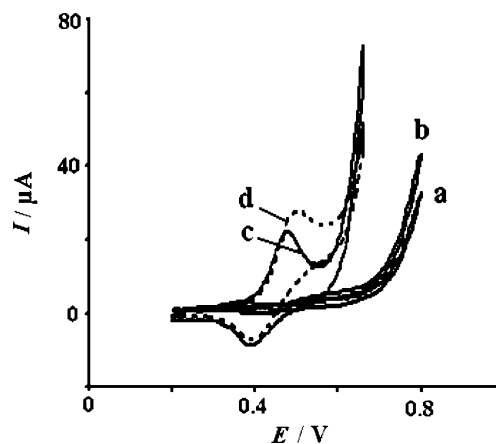


Fig. 6 Electrochemical responses of CPE/PINA(SDS) to: *a* 0 and *b* 2.35 mM glucose, and CPE/PINA(SDS)/Ni₈₀Co₂₀(OH)₂ to: *c* 0 and *b* 2.35 mM glucose

After preparing the PINA, the electrodes were removed and rinsed with water and the sides were wiped with soft tissue paper. The redox behavior of PINA and PINA(SDS) were investigated in the electrolyte solution. The cyclic voltammogram of the freshly prepared electrode (CPE/PINA) in 1 M H₂SO₄ shows redox couple at 0.42 V ($\nu = 0.05 \text{ V s}^{-1}$), which as discussed above are due to the PINA film (not shown). Also, the peak currents increase linearly with scan rates which are characteristic of electroactive species immobilized on the electrode surface. With the increase in ν , the oxidation peak potential is positively shifted and the reduction peak potential is negatively shifted, indicating that the redox reversibility of polymeric film was impaired. Also, the peak to peak potential separation (ΔE_p) for PINA is larger in comparison to that of the PINA(SDS) (e.g., ΔE_p is 0.24 V and 0.035 V for PINA and PINA(SDS), respectively, at $\nu = 50 \text{ mV s}^{-1}$) in 1

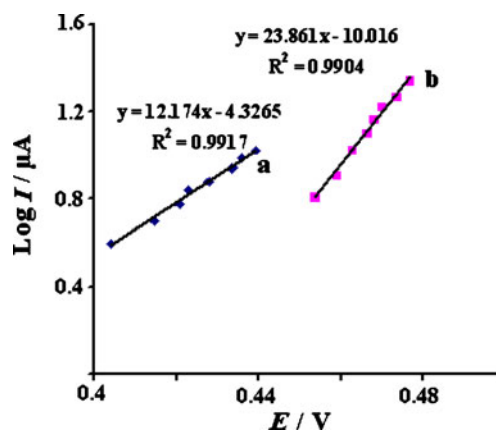


Fig. 7 Tafel plots for glucose electrooxidation in 0.1 M NaOH at the surface of *a* CPE/PINA(SDS)/Ni(OH)₂ and *b* CPE/PINA(SDS)/Ni₈₀Co₂₀(OH)₂ using data from the rising part of the current–voltage curve in Figs. 5 and 6

M H₂SO₄ solution. These results showed that the reversibility of PINA(SDS) film is more than that of the PINA film under the same conditions.

Also, 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 in an acidic solution (Fig. 1a). The response obtained in an alkaline solution (0.1 M NaOH) shows a complete loss of electrode activity in the potential range from 0 V to 1 V (Fig. 1b). However, the film was not degraded under these experimental conditions, and its response was recovered when the electrode was immersed in an acidic solution.

Electrochemical behavior of PINA(SDS) containing Ni and Co

After incorporating Ni and Co ions into the polymer backbone using the procedure discussed above, the polarization behaviors were examined in 0.1 M NaOH for PINA (SDS) with different proportions in Ni/Co content using cyclic voltammetry. This polarization allows for Ni and Co hydroxides (pure Ni(OH)₂, Ni₈₀Co₂₀(OH)₂, Ni₅₀Co₅₀(OH)₂ and pure Co(OH)₂) films formation in parallel

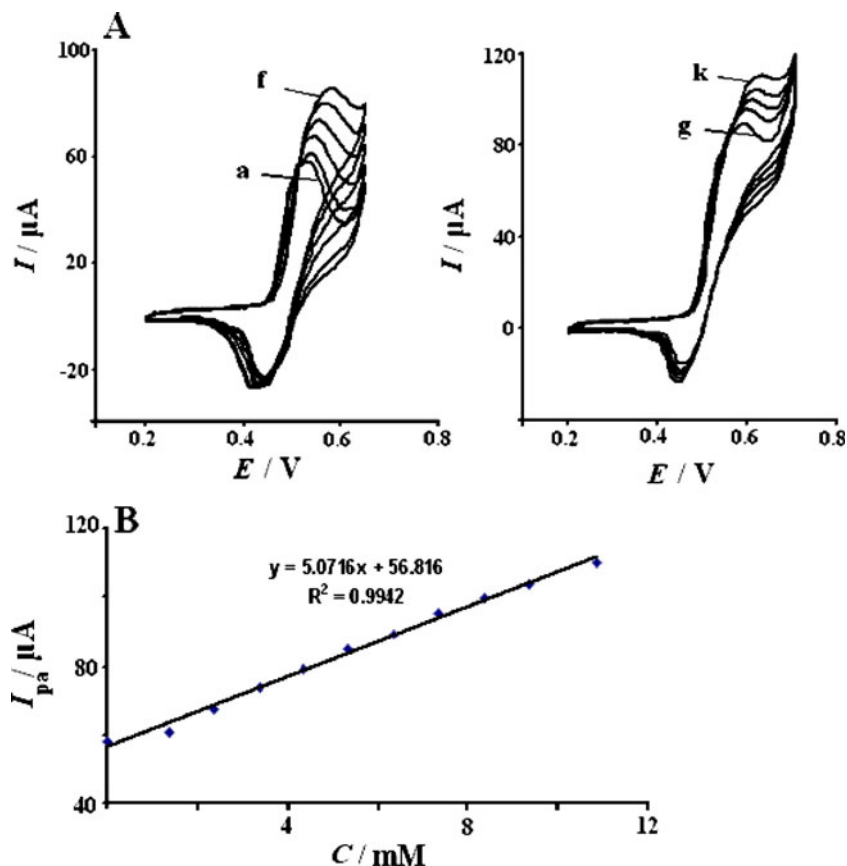
to inspecting the electrochemical reactivity of the surface [18, 29–31]. Voltammograms were recorded by cycling the potential between −0.1 V and 0.8 V at 50 mV s^{−1} until stable voltammograms were obtained.

Figure 2 shows the electrochemical response of the CPE/PINA(SDS) with different proportions in Ni/Co content after polarization in 0.1 M NaOH solution. In Fig. 1, it can be seen that, whereas neither oxidation nor reduction took place on the PINA(SDS), a well-developed redox wave was observed on the PINA(SDS) containing Ni, when the potential was cycled between −0.1 V and 0.8 V. This was related to the oxidation of Ni(OH)₂ to NiOOH and reduction of NiOOH to Ni(OH)₂.

On the other hand, the main limitation encountered in nickel hydroxide electrodes concerns the catalysis of oxygen ER in alkaline media [32]. One of the methods used is the inclusion of a foreign metal ion into the lattice of nickel hydroxide.

As shown in Fig. 2(b) and (c), it is also well known that the codeposition of Ni and Co hydroxides generates a mixed single-phase metal hydrous oxide in which Co ions occupy Ni sites in the lattice, and not two intermixed phases, each consisting of a single metal hydrous oxide [33]. Moreover, this excellent interaction between Ni and

Fig. 8 Cyclic voltammograms for electrooxidation of glucose at the surface of CPE/PINA (SDS)/Ni(OH)₂ in 0.1 M NaOH solution with different concentrations of glucose: *a* 0, *b* 1.35, *c* 2.35, *d* 3.35, *e* 4.35, *f* 5.35, *g* 6.35, *h* 7.35, *i* 8.35, *j* 9.35 and *k* 10.8 mM, $\nu=10$ mV s^{−1}



Co hydroxides could be explained by several similarities of these two elements: not only are the ionic radii very close in size (0.69 Å for Ni^{2+} and 0.63 Å for Co^{2+} [34]), but the bond strengths of the cations with oxygen (382.0 kJ/mol and 384.5 kJ/mol for Ni–O and Co–O [34], respectively) are also similar. Prepared hydroxides during polarization with different proportions (80:20 and 50:50) are $\text{Ni}_{80}\text{Co}_{20}(\text{OH})_2$ and $\text{Ni}_{50}\text{Co}_{50}(\text{OH})_2$.

The addition of different amounts of cobalt promotes a displacement of nickel hydroxide redox processes to less positive potentials. In the inset of Fig. 2, two pairs of redox peaks can be attributed to the conversion between cobalt oxidation phases of $\text{CoOOH}/\text{Co}(\text{OH})_2$ and $\text{CoO}_2/\text{CoOOH}$, which are stable at alkaline pH [35]. Although the displacement of nickel hydroxide redox peaks is an attractive characteristic, the presence of a high amount of cobalt atoms leads to an electrochemical irreversibility. By this method, the choice of modified electrodes with Ni(OH)₂ and $\text{Ni}_{80}\text{Co}_{20}(\text{OH})_2$ (this electrode showed a less irreversible behavior and the oxygen reaction is satisfactorily displaced in comparison with modified electrodes with $\text{Ni}_{50}\text{Co}_{50}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$) offers the most suitable proportions.

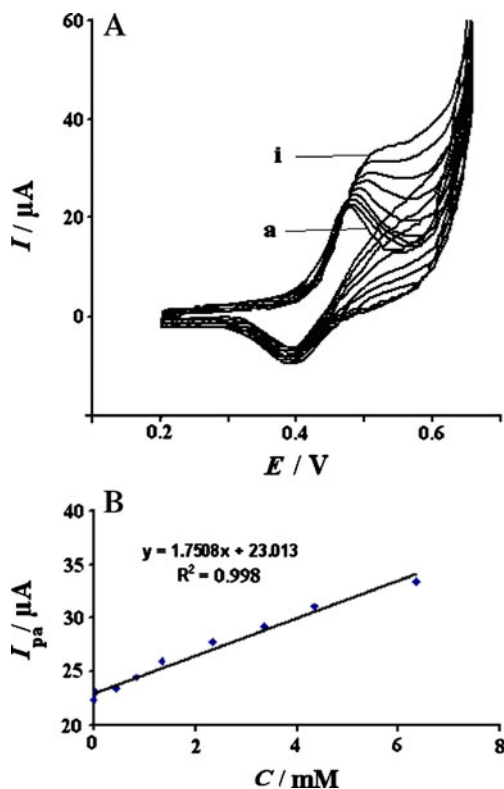


Fig. 9 Cyclic voltammograms for electrooxidation of glucose at the surface of CPE/PINA(SDS)/ $\text{Ni}_{80}\text{Co}_{20}(\text{OH})_2$ in 0.1 M NaOH solution with different concentrations of glucose: a 0, b 0.05, c 0.25, d 0.85, e 1.35, f 2.35, g 3.35, h 4.35 and i 6.35 mM, $v=10 \text{ mV s}^{-1}$

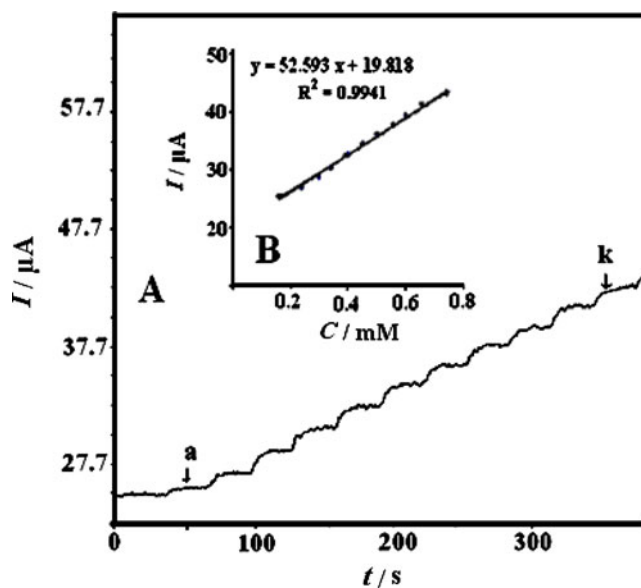


Fig. 10 a Amperometric responses of CPE/PINA(SDS)/ $\text{Ni}(\text{OH})_2$ in 0.1 M NaOH solution with different concentrations of glucose: a 0.16, b 0.24, c 0.30, d 0.34, e 0.40, f 0.45, g 0.50, h 0.55, i 0.60, j 0.65, k 0.75 mM, and b corresponding calibration curve. Applied potential: 0.57 V

Figure 3a shows the cyclic voltammograms of CPE/PINA(SDS)/ $\text{Ni}(\text{OH})_2$ in 0.1 M NaOH solution at different scan rates, and Fig. 3b shows the plot of the oxidation peak current vs. $v^{1/2}$, which is a straight line. The linear dependence indicates that the electrode reaction is diffusion

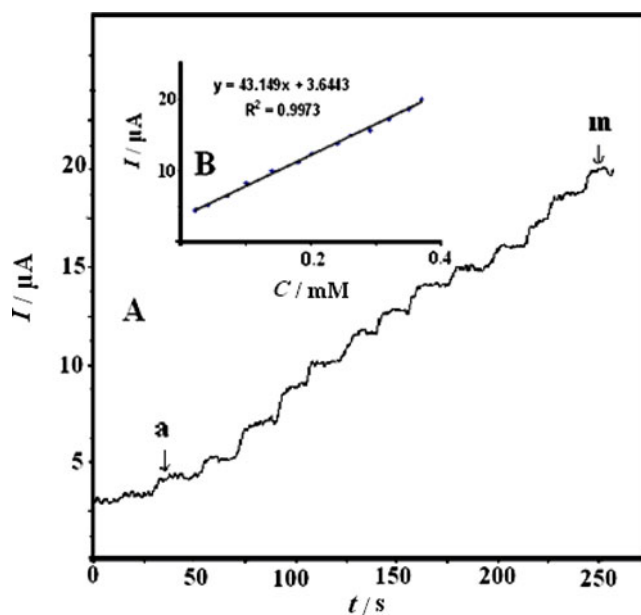


Fig. 11 a Amperometric responses of CPE/PINA(SDS)/ $\text{Ni}_{80}\text{Co}_{20}(\text{OH})_2$ in 0.1 M NaOH solution with different concentrations of glucose: a 0.01, b 0.04, c 0.07, d 0.10, e 0.14, f 0.18, g 0.20, h 0.24, i 0.26, j 0.29, k 0.32, l 0.35, m 0.37 mM, and b corresponding calibration curve. Applied potential: 0.54 V

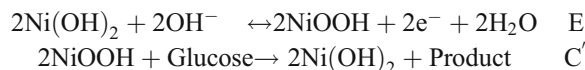
controlled. Figure 4a also shows the cyclic voltammograms of CPE/PINA(SDS)/Ni₈₀Co₂₀(OH)₂ in 0.1 M NaOH solution at different potential sweep rates; as can be seen, anodic and cathodic peak currents are linearly proportional to the potential sweep rate at low values ranging from 10 mV s⁻¹ to 160 mV s⁻¹ (Fig. 4b). This can be attributed to an electrochemical activity of an immobilized redox couple at the electrode surface. In the higher range of potential sweep rates (200–600 mV s⁻¹), the peak currents depend on the square root of the potential sweep rate, signifying the dominance of a diffusion process as the rate-limiting step in the total redox transition of the modifier film (Fig. 4c and d).

Electrocatalytic oxidation of glucose on the modified electrodes

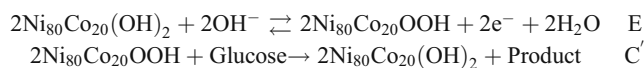
According to previous studies, carbohydrates are oxidized at high pH levels [24, 25]. In this work, the oxidation of glucose was studied at the surface of CPE/PINA(SDS)/Ni(OH)₂ and CPE/PINA(SDS)/Ni₈₀Co₂₀(OH)₂ by cyclic voltammetric experiments in 0.1 M NaOH. The results obtained for a potential scan from 0.2 V to 0.75 V vs. Ag AgCl are shown in Figs. 5 and 6.

The electrochemical response of CPE/PINA(SDS) in the absence of glucose is shown in Fig. 5a; the addition of 2.35 mM glucose to the alkaline solution causes no effect on the electrochemical response of the above modified electrode (Fig. 5b). The electrochemical response of CPE/PINA(SDS)/Ni(OH)₂ in the alkaline solution exhibits well-defined anodic and cathodic peaks (Fig. 5c) associated with the NiOOH/Ni(OH)₂ redox couple. Upon glucose addition (2.35 mM), there is an increase in the anodic peak current

and a few decrease in the cathodic peak current (Fig. 5d). This behavior is typical of that expected for mediated oxidation (EC' mechanism) as follows:



The results indicate that CPE/PINA(SDS)/Ni(OH)₂ can catalyze the electrooxidation of glucose due to the existence of Ni(II) ions in the PINA(SDS) film. Also, the electrochemical response of CPE/PINA(SDS)/Ni₈₀Co₂₀(OH)₂ in the alkaline solution exhibits well-defined anodic and cathodic peaks (Fig. 6c) associated with the Ni₈₀Co₂₀OOH/Ni₈₀Co₂₀(OH)₂ redox couple. Upon glucose addition (2.35 mM), there is an increase in the anodic peak current and small decreases in the cathodic peak current (Fig. 6d). It was because of the slow electrooxidation of glucose at the surface of electrode. This behavior is similar to the response described above, but with different percentages of Ni and Co in the backbone of polymer as follows:



In comparison with PINA(SDS)/Ni(OH)₂, the PINA(SDS)/Ni₈₀Co₂₀(OH)₂ film has low sensitivity, but its potential shifts to negative values (difference of potential shift between two electrodes was by almost 50 mV; see Figs. 5 and 6) by adding glucose concentration.

Figure 7 shows that the expected linear Tafel plots were drawn using the data from the rising part of the current–voltage curve at a scan rate of 10 mV s⁻¹ for 2.35 mM glucose. The slope of these lines is equal to $\alpha nF/2.3RT$

Table 1 Some modified electrodes used in electrocatalytic oxidation of glucose

Type of electrode	Sensitivity (μAmM ⁻¹ cm ⁻²)	LDR (mM)	LOD (mM)	References
Nickel electrode	–	0.1–2.5	0.04	[36]
Nanoscale Ni hydroxide modified CILE ^a	202	0.05–23	6.0 × 10 ⁻³	[37]
Ni powder modified electrode	40	0.5 × 10 ⁻³ –5.0	2.0 × 10 ⁻³	[38]
Cu nanoparticles	–	1.0 × 10 ⁻³ –5.0	0.5 × 10 ⁻³	[39]
Poly(1-naphthylamine)/Ni modified CPE	433	0.04–1	0.06	[16]
Poly(o-aminophenol)/Ni modified CPE	116	0.1–2.7	0.09	[17]
CoPcTs ^b /OPPyNF ^c modified GC	–	0.25–20	0.1	[40]
Boron-doped CNT modified GC	–	0.05–0.3	0.01	[41]
Ni nanoparticle modified CPE	–	1.0 × 10 ⁻³ –1.0	0.3 × 10 ⁻³	[42]
PINA(SDS)/Ni(OH) ₂ modified CPE	584	0.16–0.75	0.09	Present work
PINA(SDS)/Ni ₈₀ Co ₂₀ (OH) ₂ modified CPE	479	0.01–0.37	8.3 × 10 ⁻³	Present work

^a Carbon ionic liquid electrode

^b Co(II) phthalocyanine tetrasulfonate

^c Overoxidized polypyrrole nanofibers

(where α is the transfer coefficient, n is the number of electrons involved in the rate-determining step, F is the Faraday constant, R is the molar gas constant and T is temperature). The slopes of 12.17 and 23.86 decade/V were obtained. In addition, a greater Tafel slope for CPE/PINA(SDS)/Ni₈₀Co₂₀(OH)₂ than the other electrode implies an improved electrocatalytic performance of this modified electrode towards the electrocatalytic oxidation of glucose.

Determination of glucose on the modified electrodes

Figures 8 and 9 show the cyclic voltammograms of the CPE/PINA(SDS)/Ni(OH)₂ and CPE/PINA(SDS)/Ni₈₀Co₂₀(OH)₂ in the presence of glucose. Each of the two modified electrodes exhibit well-defined catalytic oxidation current increasing linearly with an increase in glucose concentration from 1.35 to 10.8 (limit of detection (LOD) (2 δ)=0.80 mM) and 0.05 mM to 6.35 mM (LOD (2 δ)=0.04 mM), respectively.

Based on the voltammetric results described above, it appears that amperometric detection of glucose using CPE modified with PINA(SDS)/Ni(OH)₂ and PINA(SDS)/Ni₈₀Co₂₀(OH)₂ is possible. Hydrodynamic amperometric responses (Figs. 10 and 11) were obtained by adding glucose to continuously stirred 0.1 NaOH solution. The insets of these figures show the calibration graphs for glucose at the modified electrodes. Their responses are linear for glucose within the concentration range 0.16–0.75 and 0.01–0.37 mM, respectively. The detection limits were 0.09 mM and 0.0083 mM, respectively, when the signal-to-noise ratio was 2.

This modified electrodes exhibited reproducible concentration-dependent profiles for glucose. Calibration plots for analysis of glucose show the linear dependence of the anodic peak currents with increasing glucose concentrations in the solution. The former modified electrode is more sensitive to concentration of glucose, whereas a wider concentration range and lower LOD are observed in the latter modified electrode. The analytical parameters are listed in Table 1. However, the electrocatalysis of glucose oxidation in this work has been compared with other research work.

Conclusion

A simple method was introduced to modify CPE with PINA(SDS). The results show that the presence of SDS as an anionic dopant in the polymer increased its reversibility. Also, codeposition of Ni and Co hydroxide films on the surface of CPE/PINA(SDS) was done by immersing CPE/PINA(SDS) in the solution containing different percentages of nickel and cobalt chloride. The

final composite electrodes were prepared in the forms of Ni(OH)₂, Ni₈₀Co₂₀(OH)₂, Ni₅₀Co₅₀(OH)₂ and Co(OH)₂. Modified electrodes with Ni(OH)₂ and Ni₈₀Co₂₀(OH)₂ showed electrocatalytic properties for nonenzymatic glucose oxidation. The sensitivity of the pure Ni(OH)₂ modified electrode was slightly higher when compared to Ni₈₀Co₂₀(OH)₂. However, a good linear range and lower LOD rates are observed for the modified electrode with Ni₈₀Co₂₀(OH)₂.

References

- Severcan F, Gorgulu G, Gorgulu ST, Guray T (2005) Rapid monitoring of diabetes-induced lipid peroxidation by fourier transform infrared spectroscopy. *Anal Biochem* 339:36
- Koschinsky T, Heinemann L (2001) Sensors for glucose monitoring: technical and clinical aspects. *Res Rev* 17:113
- Park S, Boo H, Chung TD (2006) Electrochemical non-enzymatic glucose sensors. *Anal Chim Acta* 556:46
- Wang J (2008) In vivo glucose monitoring: towards “sense and act” feedback loop individualized medical systems. *Talanta* 75:636
- Kang XH, Mai ZB, Zou XY, Cai PX, Mo JY (2007) A novel glucose biosensor based on immobilization of glucose oxidase in chitosan on a glassy carbon electrode modified with gold-platinum alloy nanoparticles/multiwall carbon nanotubes. *Anal Biochem* 369:71
- Desilvestro J, Haas O (1990) Metal oxide cathode materials for electrochemical energy storage: a review. *J Electrochem Soc* 137:5C
- Portemer F, Delahaye-Vidal A, Figlarz M (1992) Characterization of active material deposited at the nickel hydroxide electrode by electrochemical impregnation. *J Electrochem Soc* 139:671
- Krejci I, Vany'sek P (1994) Effect of zinc and iron ions on the electrochemistry of nickel oxide electrode: slow cyclic voltammetry. *J Power Sources* 47:79
- Maruyama T, Arai S (1996) Electrochromic properties of cobalt oxide thin-films prepared by chemical-vapor deposition. *J Electrochem Soc* 143:1383
- Nikolov I, Darkaoui R, Zhecheva E, Stoyanova R, Dimitrov N, Vitanov T (1997) Electrocatalytic activity of spinel related cobaltites M_xCo_{3-x}O₄ (M=Li, Ni, Cu) in the oxygen evolution reaction. *J Electroanal Chem* 429:157
- Cordoba SI, Carbonio RE, Lopez Teijelo M, Macagno VA (1986) The electrochemical response of binary mixtures of hydrous transition metal hydroxides co-precipitated on conducting substrates with reference to the oxygen evolution reaction. *Electrochim Acta* 31:1321
- Elahi MY, Mousavi MF, Ghasemi S (2008) Nano-structured Ni(II)-curcumin modified glassy carbon electrode for electrocatalytic oxidation of fructose. *Electrochim Acta* 54:490
- Elahi MY, Heli H, Bathaie SZ, Mousavi MF (2007) Electrocatalytic oxidation of glucose at a Ni-curcumin modified glassy carbon electrode. *J Solid State Electrochem* 11:273
- Zheng L, Zhang JQ, Song JF (2009) Ni(II)-quercetin complex modified multiwall carbon nanotube ionic liquid paste electrode and its electrocatalytic activity toward the oxidation of glucose. *Electrochim Acta* 54:4559
- Liu Y, Teng H, Hou HQ, You TY (2009) Nonenzymatic glucose sensor based on renewable electrospun ni nanoparticle-loaded carbon nanofiber paste electrode. *Biosens Bioelectron* 24:3329

16. Ojani R, Raoof JB, Salmany-Afagh P (2004) Electrocatalytic oxidation of some carbohydrates by poly (1-naphthylamine)/nickel modified carbon paste electrode. *J Electroanal Chem* 571:1
17. Ojani R, Raoof JB, Fathi S (2008) Electrocatalytic oxidation of some carbohydrates by nickel/poly (o-aminophenol) modified carbon paste electrode. *Electroanalysis* 16:727
18. Vidotti M, Silva MR, Salvador RP, de Torresi SI Cordoba, Antonia LHD (2008) Electrocatalytic oxidation of urea by nanostructured nickel/cobalt hydroxide electrodes. *Electrochim Acta* 53:4030
19. Provazi K, Giz MJ, Antonia LHD, de Torresi SI Cordoba (2001) The effect of Cd, Co and Zn as additives on nickel hydroxide opto-electrochemical behavior. *J Power Sources* 102:224
20. McBreen J (1990) In: White RE, Bockris JOM, Conway BE (eds) *Modern aspects of electrochemistry*, vol 21. Plenum, New York
21. Cox P, Pletcher D (1990) Electrosynthesis at oxide coated electrodes part 1 the kinetics of ethanol oxidation at spinel electrodes in aqueous base. *J Appl Electrochem* 20:549
22. Ojani R, Raoof JB, Hosseini SR (2008) Electrocatalytic oxidation of methanol on carbon paste electrode modified by nickel ions dispersed into poly (1, 5-diaminonaphthalene) film. *Electrochim Acta* 53:2402
23. Ojani R, Raoof JB, Fathi S (2009) Poly (o-aminophenol) film prepared in the presence of sodium dodecyl sulfate: application for nickel ion dispersion and the electrocatalytic oxidation of methanol and ethylene glycol. *Electrochim Acta* 54:2190
24. Eramo FD, Marioli JM, Arevalo AA, Sereno LE (1999) HPLC analysis of carbohydrates with electrochemical detection at a poly-1-naphthylamine/copper modified electrode. *Electroanalysis* 11:481
25. Casella IG, Cataldi TRI, Guerrieri A, Desimoni E (1996) Copper dispersed into polyaniline films as an amperometric sensor in alkaline solutions of amino acids and polyhydric compounds. *Anal Chim Acta* 335:217
26. Zhao H, Zhang Y, Yuan Z (2002) Poly (isonicotinic acid) modified glassy carbon electrode for electrochemical detection of norepinephrine. *Anal Chim Acta* 454:75
27. Ojani R, Raoof JB, Norouzi B (2009) Electropolymerization of n-methylaniline in the presence of sodium dodecylsulfate and its application for electrocatalytic reduction of nitrite. *J Mater Sci* 44:4095
28. Ojani R, Raoof JB, Norouzi B (2010) Carbon paste electrode modified by cobalt ions dispersed into poly (n-methylaniline) preparing in the presence of SDS: application in electrocatalytic oxidation of hydrogen peroxide. *J Solid State Electrochem* 14:621
29. Pham MT, Maitz MF, Richter E, Reuther H, Prokert F, Mucklich A (2004) Electrochemical behaviour of nickel surface-alloyed with copper and titanium. *J Electroanal Chem* 572:185
30. Jafarian M, Mahjani MG, Heli H, Gobal F, Khajehsharifi H, Hamed MH (2003) A study of the electro-catalytic oxidation of methanol on a cobalt hydroxide modified glassy carbon electrode. *Electrochim Acta* 48:3423
31. Casella IG (2002) Electrodeposition of cobalt oxide films from carbonate solutions containing Co(II)-tartrate complexes. *J Electroanal Chem* 520:119
32. Cordoba de Torresi SI, Provazi K, Malta M, Torresi RM (2001) Effect of additives in the stabilization of the α phase of Ni(OH)₂ electrodes. *J Electrochem Soc* 148:1179A
33. Kim S, Tryk DA, Antonio MR, Carr R, Scherson DA (1994) In situ X-ray absorption fine structure studies of foreign metal ions in nickel hydrous oxide electrodes in alkaline electrolytes. *J Phys Chem* 98:10269
34. Lide DR (1991) *Handbook of chemistry and physics*. CRC, Boca Raton
35. Vittal R, Gomathi H, Rao GP (2001) Derivatized nickel and cobalt oxide modified electrodes: effect of surfactant. *J Electroanal Chem* 497:47
36. Zhao CZ, Shao CL, Li MH, Jiao K (2007) Flow-injection analysis of glucose without enzyme based on electrocatalytic oxidation of glucose at a nickel electrode. *Talanta* 71:1769
37. Safavi A, Maleki N, Farjami E (2009) Fabrication of glucose sensor based on a novel nanocomposite electrode. *Biosens Bioelectron* 24:1655
38. You T, Niwa O, Chen Z, Hayashi K, Tomita M, Hirono S (2003) An amperometric detector formed of highly dispersed Ni nanoparticles embedded in a graphite-like carbon film electrode for sugar determination. *Anal Chem* 75:5191
39. Xu Q, Zhao Y, Xu JZ, Zhu JJ (2006) Preparation of functionalized copper nanoparticles and fabrication of a glucose sensor. *Sens Actuators B* 114:379
40. Özcan L, Sahin Y, Türk H (2008) Non-enzymatic glucose biosensor based on overoxidized polypyrrole nanofiber electrode modified with cobalt (II) phthalocyanine tetrasulfonate. *Biosens Bioelectron* 24:512
41. Deng C, Chen J, Chen X, Xiao C, Nie L, Yao S (2008) Direct electrochemistry of glucose oxidase and biosensing for glucose based on boron-doped carbon nanotubes modified electrode. *Biosens Bioelectron* 23:1272
42. Cheng X, Zhang S, Zhang H, Wang Q, He P, Fang Y (2008) Determination of carbohydrates by capillary zone electrophoresis with amperometric detection at a nano-nickel oxide modified carbon paste electrode. *Food Chem* 106:830