

Methanol electrooxidation on novel modified carbon paste electrodes with supported poly(isonicotinic acid) (sodium dodecyl sulfate)/Ni-Co electrocatalysts

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Abstract Poly(isonicotinic acid) (PINA) was formed by successive cyclic voltammetry in monomer solution in the presence of sodium dodecyl sulfate (SDS) on the surface of a carbon paste electrode (CPE). Ni(II) and Co(II) ions were incorporated into the electrode by immersion of the polymer-modified electrodes in Ni(II) and Co(II) ion solutions in different proportions. After the preparation of modified electrodes, their electrochemical behavior was studied by cyclic voltammetric experiments. Electrocatalytic oxidation of methanol at the surface of the modified electrodes was studied in 1 M NaOH solution. These modified electrodes exhibit high electrocatalytic activity and stability in alkaline solution, showing oxidation peaks at low potentials with high current densities. The electrooxidation of methanol was found to be more efficient on CPE/PINA(SDS)/Ni₈₀Co₂₀ than on CPE/PINA(SDS)/Ni and CPE/PINA(SDS)/Ni₅₀Co₅₀. The effects of various parameters such as scan rates and methanol concentration on the electrooxidation of methanol are also investigated.

Keywords Methanol oxidation · Polymer-modified electrode · Nickel hydroxide · Cobalt hydroxide · Carbon paste electrode

Introduction

Direct methanol fuel cells are recognized to be a promising power source for portable electronic devices and electric

vehicles [1, 2]. However, commercialization of these fuel cells has faced serious difficulties due to kinetic constraints of the methanol oxidation reaction (MOR) [3]. Pt-group metals and alloys are the most effective electrocatalysts for the MOR in acid solutions [3, 4]. However, high cost and limited resources [5] inhibit the use of Pt commercially (Pt could be used in some applications if loadings per kilowatt are small). In addition, Pt-based electrocatalysts, generally, undergo deactivation/poisoning by the reaction intermediates, particularly by adsorbed CO molecules in acid medium. In an alkaline electrolyte, instead of an acidic one, the kinetics would be significantly improved, and Pt-free electrocatalysts can then be used. Several nonnoble metals have recently been investigated as electrocatalysts for methanol oxidation reaction in alkaline media [6–8].

Ni is a suitable relatively low cost and highly active non-platinum catalyst [7, 9, 10]. The use of Ni electrodes for the oxidation of methanol is not new. In 1971, Fleischmann et al. [11] reported the efficient conversion of alcohols to carboxylic acids using a Ni anode and suggested that catalysis occurred through the formation of NiOOH. Abdel Rahim et al. [12] dispersed Ni on graphite electrodes and obtained high current densities for methanol oxidation reaction on these electrodes. Modification of a substrate such as glassy carbon (GC) with various Ni complexes appears to be a promising methodology for obtaining Ni-based electrode systems as anodes for the methanol oxidation reaction [13–16].

On the other hand, the presence of certain metal cations such as cobalt in hydrated nickel oxides and oxyhydroxides can strongly affect the electrochemical characteristics of this interesting electrode material. Cox and Pletcher [17] showed the use of Co-Ni oxides for catalytic oxidation of ethanol to acetic acid.

In our previous work, we used modified carbon paste electrodes with poly(1-naphthylamine)/Ni, poly(*o*-aminophenol)/

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Ni, and poly(isonicotinic acid) (PINA) (sodium dodecyl sulfate (SDS))/Ni-Co (with different percentages) for electrocatalytic oxidation of carbohydrates [18–20]. These studies showed that the metal-polymer electrodes are easy to prepare, are stable for long time periods with good detection limits, and possess wide linear range responses. Also, recently, 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 [21, 22]. In these studies, we have used carbon paste electrodes modified with PINA(SDS)/Ni-Co (with different percentages) for electrocatalytic oxidation of methanol.

Experimental

Reagents and materials

The solvent used in this work was twice-distilled water. Sulfuric acid, isonicotinic acid, SDS, sodium hydroxide, nickel nitrate, cobalt nitrate, and methanol used in this work were analytical grade of Fluka (Sydney, Australia) origin and used without further purification. High-viscosity paraffin (density=0.88 g cm⁻³) from Fluka (Sydney, Australia) was used as the pasting liquid for the carbon paste electrode (CPE). Graphite powder (particle diameter=0.10 mm) from Merck (New Jersey, USA) was used as the working electrode substrate. All other reagents were of analytical grade.

Preparation of working electrode

A 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 via 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 a white paper until a smooth shiny surface was observed.

The precursor modification of the carbon paste electrode with PINA(SDS) films was synthesized using an isonicotinic acid monomer solution (0.01 M isonicotinic acid in 1 M H₂SO₄) in the presence of SDS (0.01 M). The electropolymerization was carried out by potential cycling (nine cycles at a scan rate of 50 mV s⁻¹) between 0 and 1.2 V vs. Ag/AgCl. 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 nitrate and cobalt nitrate (10 mL of an aqueous solution with 0.1 M Ni(NO₃)₂, 0.08 M Ni(NO₃)₂ and 0.02 M Co(NO₃)₂ (80:20 mol/mol), 0.05 M Ni(NO₃)₂ and 0.05 M Co(NO₃)₂ (50:50 mol/mol), and

0.1 M Co(NO₃)₂). The accumulation of nickel and cobalt was conducted by complex formation between Ni(II) and Co(II) with amine sites in the polymer backbone [23–25] for a given period of time (*t*_a, accumulation time).

Instrumentation

The electrochemical experiments were carried out using a potentiostat/galvanostat (BHP 2063-C Electrochemical Analysis System, Behpajooh, Iran) coupled with a Pentium IV personal computer. Voltammetry was conducted using a three-electrode cell. A modified CPE, a platinum electrode from Azar Electrode (Urmia, Iran), and Ag/AgCl/3 M KCl from Azar Electrode (Urmia, Iran) were used as working electrode, counter electrode, and reference electrode, respectively.

Results and discussions

Electrochemical behavior of CPE/PINA(SDS)

Previously, we investigated the preparation of PINA on the surface of a carbon paste electrode in the presence of SDS [20]. The redox behavior of PINA(SDS) was investigated in the electrolyte solution. These results showed that the redox behavior of the polymeric film was strongly dependent on the pH of the electrolyte solution. Therefore, the polymer obtained shows a well-defined redox behavior in an acidic solution, but the response obtained in an alkaline solution (1 M NaOH) shows a complete loss of electrode activity in the potential range of 0 to 1 V (Fig. 1). 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, their polarization behavior was examined in 1 M NaOH for PINA(SDS) with different proportions of 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) film formation in parallel to inspecting the electrochemical reactivity of the surface [26–29]. Voltammograms were recorded by cycling the potential between 0 and 0.7 V at 50 mV s⁻¹ until stable voltammograms were obtained (not shown). We conclude that the states of the electrode surfaces reach a steady state after approximately five cyclic scans, and subsequent voltammetric curves are reproducible.

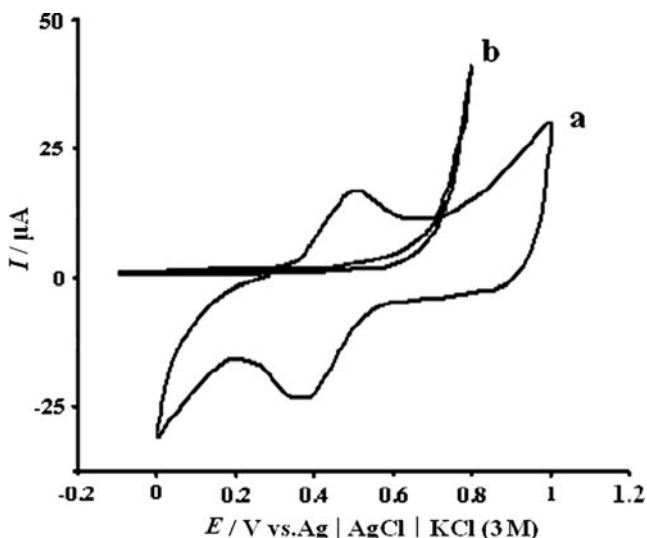


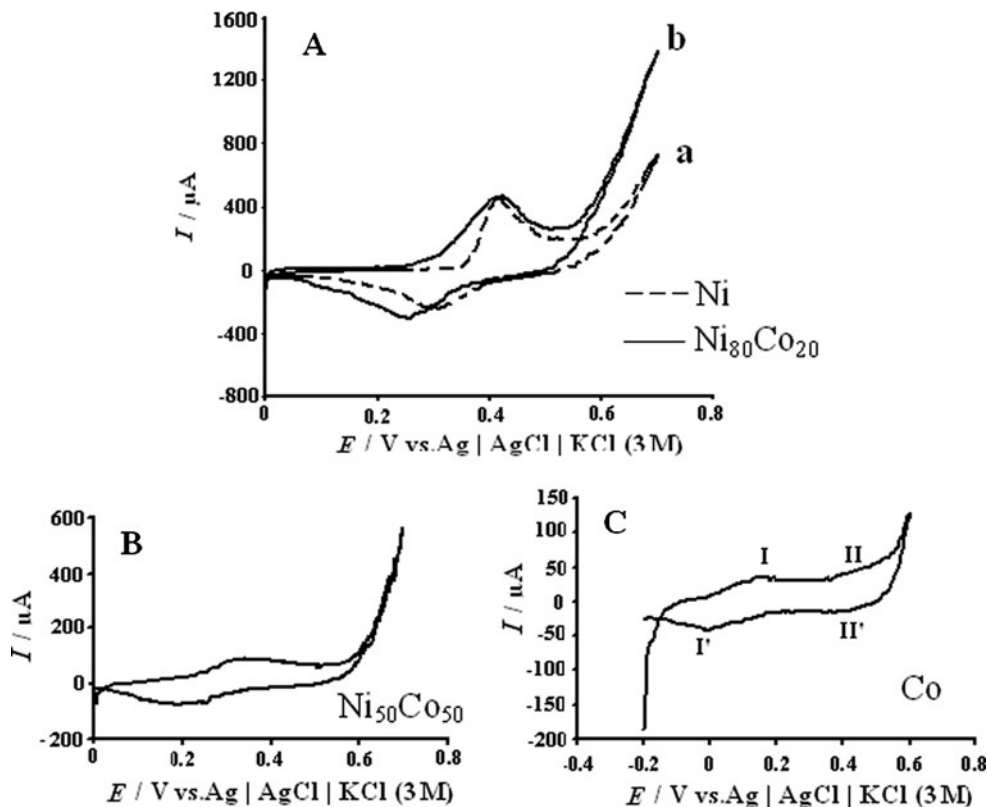
Fig. 1 Electrochemical responses of CPE/PINA(SDS) in *a* 1 M H_2SO_4 and *b* 1 M $NaOH$ solution, $v=20 \text{ mV s}^{-1}$

Figure 2 shows the electrochemical response of the CPE/PINA(SDS) with different proportional Ni/Co contents after polarization in 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 and 0.7 V. This was related to the

oxidation of $Ni(OH)_2$ to $NiOOH$ and reduction of $NiOOH$ to $Ni(OH)_2$. Anodic discharge of H_2O with concomitant production of O_2 is observed to occur for $E > 0.6 \text{ V}$. Also, a well-developed redox wave was observed on the PINA(SDS) containing Ni and Co with different proportions, when the potential was cycled between 0 and 0.7 V. No new anodic or cathodic waves appear in this potential range with addition of different amounts of cobalt. It is 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 [30]. In the inset of Fig. 2c, two pairs of redox peaks can be attributed to the conversion between cobalt oxidation phases of $CoOOH/Co(OH)_2$ (I/I') and $CoO_2/CoOOH$ (II/II') which are stable at alkaline pH [31].

Figure 3 shows the electrochemical behavior of CPE/PINA(SDS)/Ni and CPE/PINA(SDS)/ $Ni_{80}Co_{20}$ in 1 M $NaOH$ in the potential range of 0–0.7 V vs. $Ag/AgCl$ at different scan rates. As the scan rate is increased, the currents for the redox process also increased. As can be seen, anodic peak currents are linearly proportional to 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. This limiting diffusion process was also reported for other Ni-modified electrodes [32, 33].

Fig. 2 **a** Cyclic voltammograms for CPE/PINA(SDS) with *a* Ni (0.13 mg cm^{-2}) and *b* $Ni_{80}Co_{20}$ (0.21 mg cm^{-2}), cyclic voltammograms of CPE/PINA(SDS) with **b** $Ni_{50}Co_{50}$ (0.055 mg cm^{-2}) and **c** Co (0.015 mg cm^{-2}), in 1 M $NaOH$, $v=100 \text{ mV s}^{-1}$



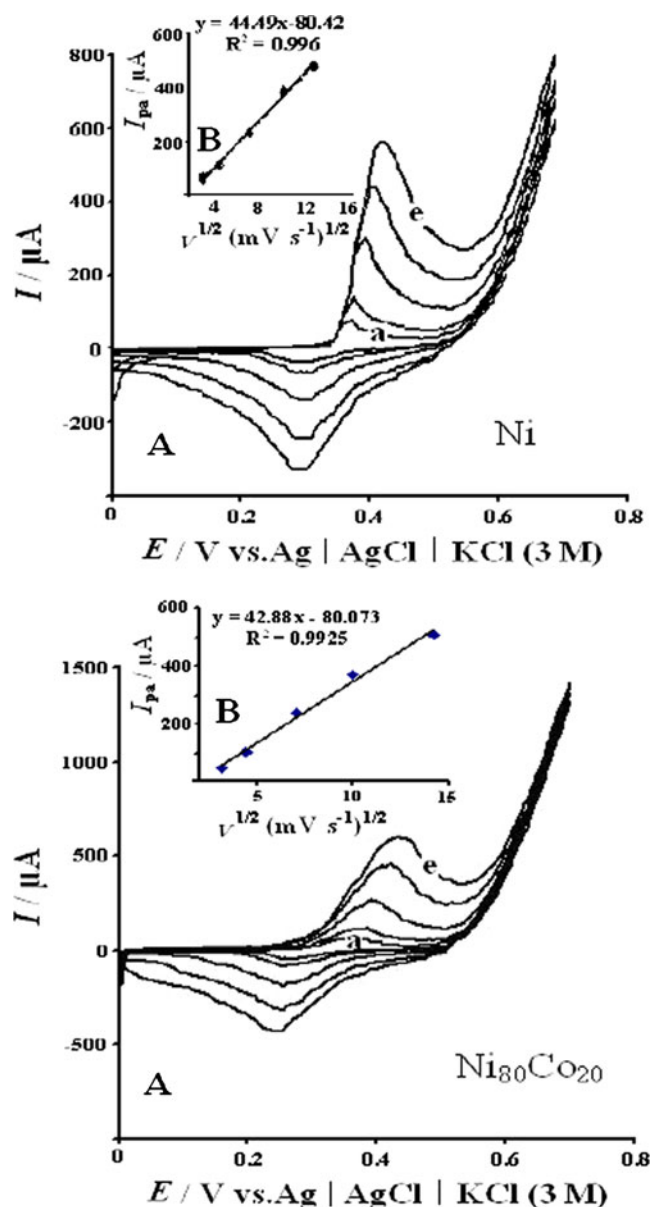
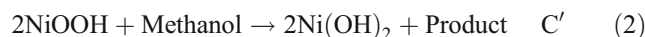


Fig. 3 A Electrochemical behavior of CPE/PINA(SDS)/Ni and CPE/PINA(SDS)/Ni₈₀Co₂₀ in 1 M NaOH at different scan rates: a 10 mV s⁻¹, b 20 mV s⁻¹, c 50 mV s⁻¹, d 100 mV s⁻¹, and e 160 mV s⁻¹. B The dependency of I_{pa} on $v^{1/2}$

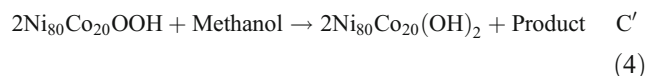
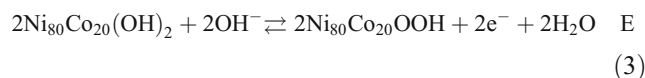
Electrochemical behavior of CPE/PINA(SDS)/Ni-Co in the presence of methanol

In this work, the electrochemical behavior of methanol was first studied at CPE/PINA(SDS) (without the incorporation of Ni and Co) by cyclic voltammetric experiments in 1 M NaOH. Typical results obtained for a potential range of 0–0.7 V vs. Ag/AgCl are shown in Fig. 4. The electrochemical response of CPE/PINA(SDS) in the absence of methanol is shown in Fig. 4c; the addition of 0.1 M methanol to the alkaline solution causes no effect on the electrochemical response of the CPE/PINA(SDS) (Fig. 4d). The electrochemical response of a

CPE/PINA(SDS)/Ni in alkaline solution (i.e., 1 M NaOH) exhibits well-defined anodic and cathodic peaks (Fig. 4a) associated with the Ni(II)/Ni(III) redox couple. As can be seen, upon methanol addition (0.1 M), there is an increase in the anodic peak current and a decrease in the cathodic peak current (Fig. 4b). This behavior is typical of that expected for mediated oxidation as follows:



As can be seen in Fig. 4, the oxidation current of methanol on the surface of CPE/PINA(SDS)/Ni appears at a potential slightly more positive than that of Ni(II)/Ni(III) oxidation. In fact, this peak is a new anodic peak. This is consistent with different redox potentials of α -Ni(OH)₂/NiOOH and β -Ni(OH)₂/NiOOH [34]. Also, Fig. 4 shows the cyclic voltammetric responses obtained at the surface of CPE/PINA(SDS)/Ni₈₀Co₂₀ and CPE/PINA(SDS)/Ni₅₀Co₅₀ in the presence and absence of methanol in 1 M NaOH, respectively. As can be seen, upon methanol addition (0.1 M), there is an increase in the anodic peak current and a decrease in the cathodic peak current. This behavior is similar to the response described above but with different percentages of Ni and Co in the backbone of polymer as follows:



The results showed that these modified electrodes were efficient catalysts for electrooxidation of methanol. But, the addition of methanol causes no effect on the electrochemical response of CPE/PINA(SDS)/Co (not shown).

In order to further clarify the electrochemical oxidation mechanism of methanol on the CPE/PINA(SDS)/Ni, the effect of methanol concentration and potential scan rates on cyclic voltammetric responses was investigated. Figure 5a represents the cyclic voltammograms (CVs) of the CPE/PINA(SDS)/Ni electrode in the range of 0–0.8 V at the scan rate of 20 mV s⁻¹. The concentration of methanol in 1 M NaOH solution is changed from 0 to 0.8 M. It is observed from Fig. 5b that when methanol concentration increases, the current density of the anodic peak increases significantly while cathodic peak decreases. The methanol oxidation current increased steadily up to a concentration of 0.6 M methanol after which it remained almost constant. It

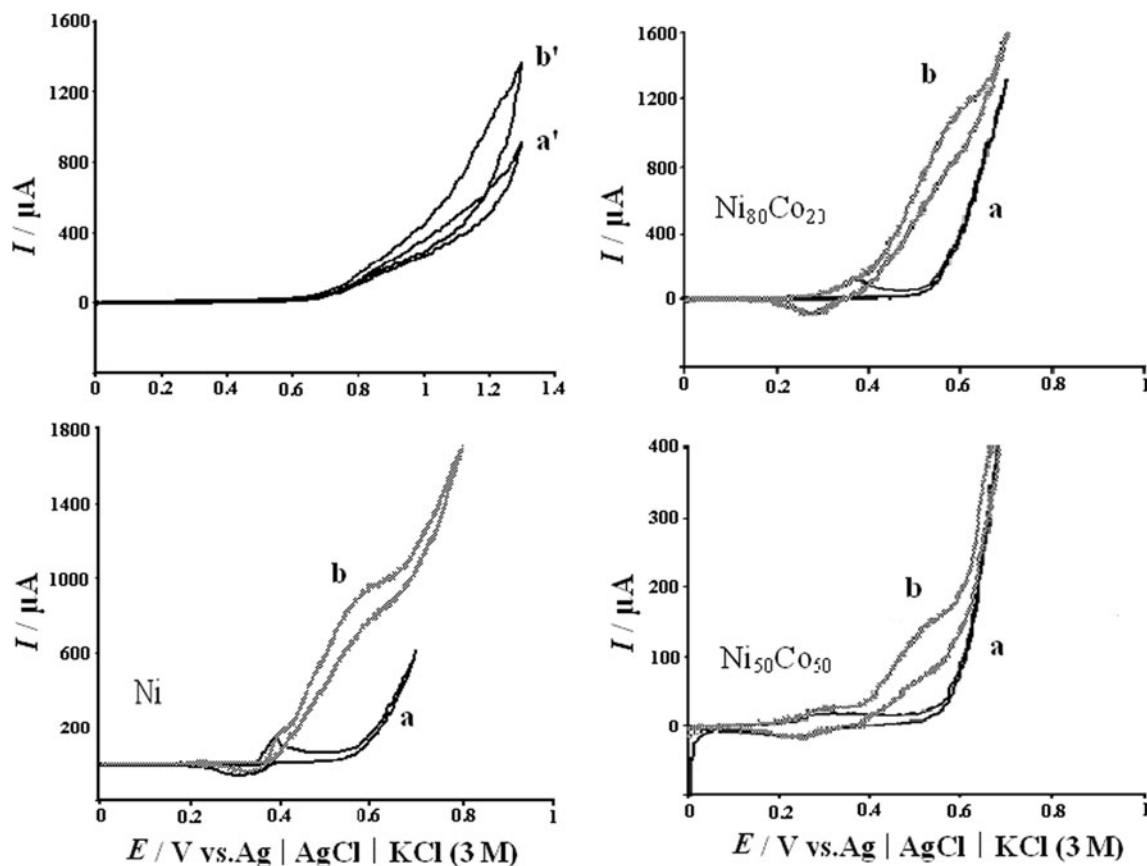


Fig. 4 Voltammetric responses for methanol obtained at the surface of CPE/PINA(SDS) with different proportions of Ni/Co content, solutions: *a* 1 M NaOH and *b* 0.1 M methanol in 1 M NaOH; *a'* and *b'* are the same as *a* and *b* but for CPE/PINA(SDS), $\nu=20 \text{ mV s}^{-1}$

appears that the reaction sites get saturated at this concentration, and hence, the constancy of current did not go beyond 0.6 M.

Also, Fig. 6a shows the CVs of the CPE/PINA(SDS)/Ni electrode in the presence of 0.1 M methanol at different potential scan rates. The height of the oxidation peak of methanol

increases with an increase in the scan rate, and a potential shift towards more positive values is observed. The positive shift in the peak potential may be due to the IR drop generated at high current density values. The increase in current density with square root of the potential scan rate indicates a diffusion-controlled process for methanol oxidation at this electrode.

Fig. 5 **a** Cyclic voltammograms of the CPE/PINA(SDS)/Ni (Ni loading= 0.13 mg cm^{-2}) in 1 M NaOH solution with different concentrations of methanol *a* 0 M, *b* 0.02 M, *c* 0.05 M, *d* 0.1 M, *e* 0.2 M, *f* 0.3 M, *g* 0.4 M, *h* 0.6 M, and *i* 0.8 M, $\nu=20 \text{ mV s}^{-1}$. **b** Plot of I_{pa} vs. methanol concentration

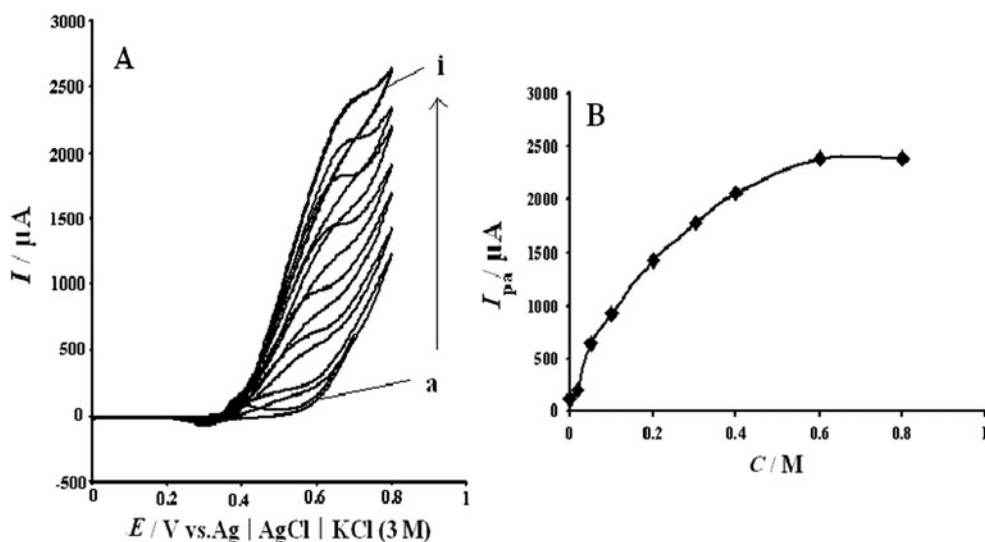


Fig. 6 **a** Cyclic voltammograms of the CPE/PINA(SDS)/Ni (Ni loading= 0.13 mg cm^{-2}) in the presence of 0.1 M methanol in 1 M NaOH solution, scan rates: *a* 10 mV s^{-1} , *b* 20 mV s^{-1} , *c* 50 mV s^{-1} , *d* 100 mV s^{-1} , and *e* 160 mV s^{-1} . **b** The dependency of I_p on $\nu^{1/2}$ and **c** variations of anodic current function vs. ν

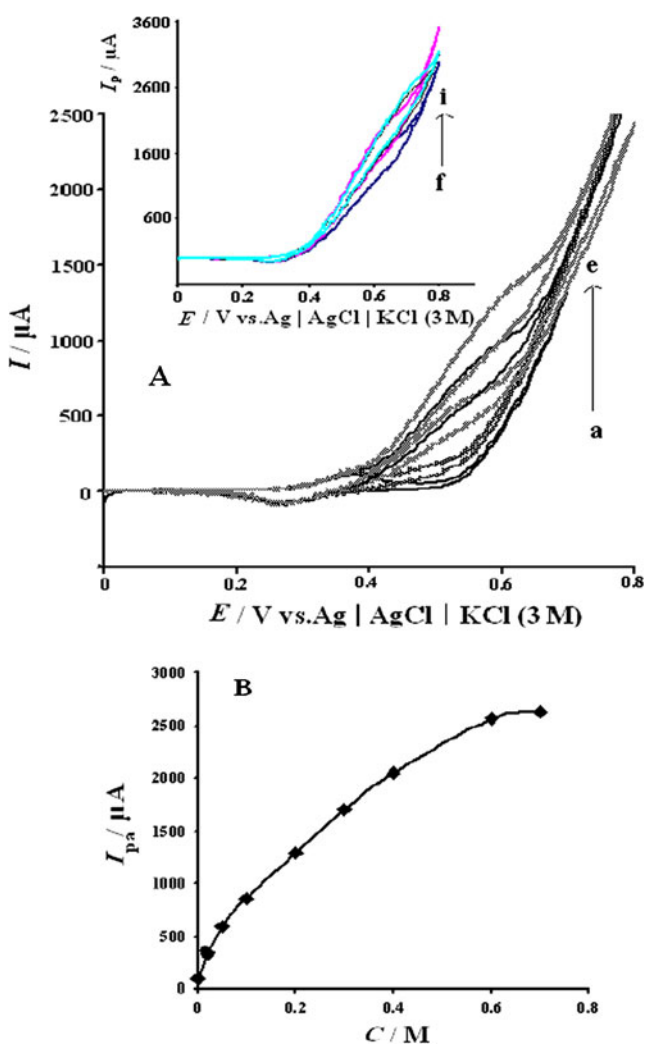
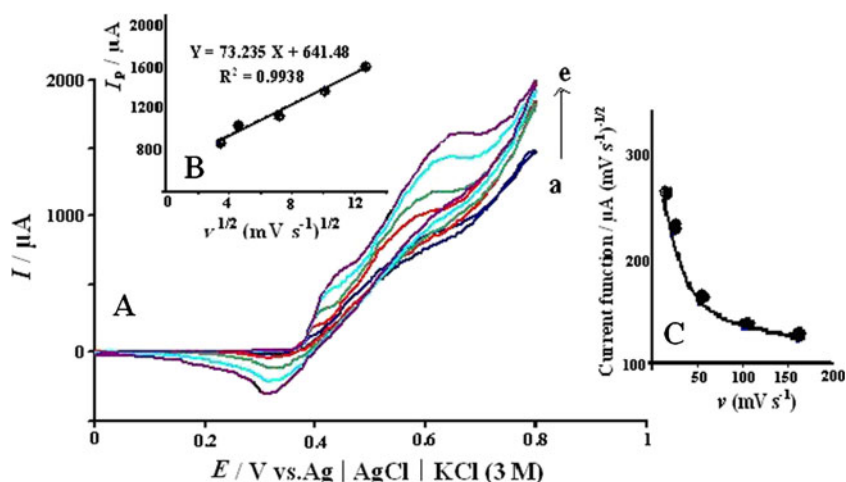


Fig. 7 **a** Cyclic voltammograms of the CPE/PINA(SDS)/Ni₈₀Co₂₀ (metal loading= 0.21 mg cm^{-2}) in 1 M NaOH solution with different concentrations of methanol *a* 0 M , *b* 0.02 M , *c* 0.05 M , *d* 0.1 M , *e* 0.2 M , *f* 0.3 M , *g* 0.4 M , *h* 0.6 M , and *i* 0.7 M , $\nu=20 \text{ mV s}^{-1}$. **b** Plot of I_{pa} vs. methanol concentration

These results and the current function of the anodic peak (Fig. 6c) show that oxidation of methanol follows a catalytic mechanism with the Ni(II)/Ni(III) redox couple acting as a mediator. In the redox system, $\alpha\text{-Ni(OH)}_2$ is first oxidized to NiOOH through the electrode reaction (1) in an alkaline medium; then, NiOOH generated is reduced to $\beta\text{-Ni(OH)}_2$ by methanol via reaction (2). Subsequently, this $\beta\text{-Ni(OH)}_2$ is converted to NiOOH at higher potentials through reaction (5), leading to the appearance of a new anodic peak.



Figures 7 and 8 show the behavior of CPE/PINA(SDS)/Ni₈₀Co₂₀ and CPE/PINA(SDS)/Ni₅₀Co₅₀ in the presence of different methanol concentrations at the scan rate of

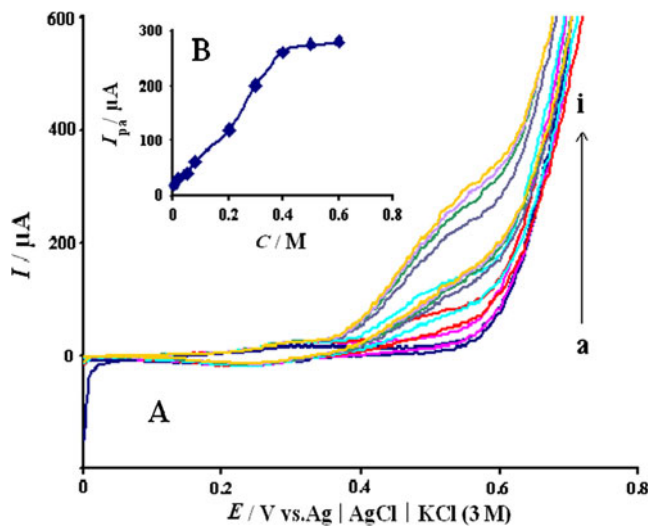


Fig. 8 **a** Cyclic voltammograms of the CPE/PINA(SDS)/Ni₅₀Co₅₀ (metal loading= 0.055 mg cm^{-2}) in 1 M NaOH solution with different concentrations of methanol *a* 0 M , *b* 0.02 M , *c* 0.05 M , *d* 0.08 M , *e* 0.2 M , *f* 0.3 M , *g* 0.4 M , *h* 0.5 M , and *i* 0.6 M , $\nu=20 \text{ mV s}^{-1}$. **b** Plot of I_{pa} vs. methanol concentration

20 mV s⁻¹. On the basis of these figures, it is observed that as the methanol concentration increases, the peak height increases linearly with methanol concentration up to 0.6 and 0.4 M, respectively. It can be assumed that the increase is due to the presence of a diffusion-controlled process that appears to play an important role at low methanol concentrations. While the methanol concentration exceeds from these limits, the rate of the whole oxidation process seems to be limited by that of the catalytic processes in origin, and its rate depends on the reaction between methanol and Ni(III)/Co(III) species (Figs. 7b and 8b).

A plot of log *I* vs. *E* (Tafel plot) is a useful device for evaluating kinetic parameters. The Tafel equation for anodic reactions is shown below [35]:

$$\log I = \log I_0 + (1 - \alpha)nFE/2.303RT \quad (6)$$

where α is the transfer coefficient, I_0 is the exchange current, 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. Figure 9 exhibits the Tafel plots derived from the upslope (rising current) of voltammograms recorded for the oxidation of 0.3 M methanol at the surface of CPE/PINA(SDS)/Ni and CPE/PINA(SDS)/Ni₈₀Co₂₀ at a scan rate of 20 mV s⁻¹. These plots give Tafel slopes of 126.69 and 149.21 mV dec⁻¹, respectively. Assuming one electron transfer to be the rate-limiting step, values of 0.64 and 0.6 are obtained for α .

Stability of CPE/PINA(SDS)/Ni-Co

We checked the long-term stability of CPE/PINA(SDS)/Ni-Co by measuring its responses for methanol oxidation after 2 weeks of storage under dry conditions. The electrodes retain

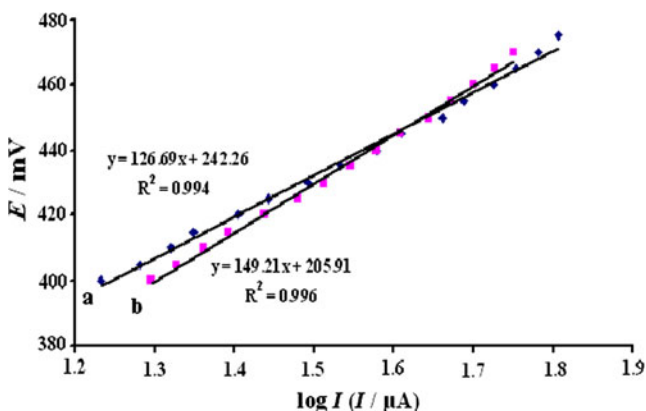


Fig. 9 Tafel plots for *a* CPE/PINA(SDS)/Ni and *b* CPE/PINA(SDS)/Ni₈₀Co₂₀ in the presence of 0.3 M methanol at a scan rate of 20 mV s⁻¹

about 90 % of its initial responses. Such stabilities seem to be acceptable for most practical applications.

Comparison of performance of modified electrodes

To assess the performance of CPE/PINA(SDS)/Ni-Co in relation to other electrode systems, methanol oxidation was compared on the surface of these electrodes. The relative oxidation currents and anodic peak potential (E_{pa}) of electrooxidation of methanol on different electrodes are presented in Table 1. Performance of modified electrodes in the present work is comparable with other electrodes. Also, among the electrodes tested, the CPE/PINA(SDS)/Ni₈₀Co₂₀ yields a significantly higher response for methanol than that observed for CPE/PINA(SDS)/Ni and CPE/PINA(SDS)/Ni₅₀Co₅₀. Also, there is a slight decrease in the E_{pa} from 0.60 to 0.55 V with an increase in the cobalt content of modified electrode from 0 to 50 %.

Conclusions

1. Ni-modified PINA(SDS) film on CPE substrates was found to be effective catalysts for methanol oxidation in alkaline medium.
2. Parameters such as the presence of SDS and methanol concentration influence the activity of the electrode towards methanol oxidation.
3. The mechanism of oxidation of methanol on dispersed Ni in PINA(SDS) in NaOH appears to be very similar to that on different Ni electrodes.
4. The performance of the electrode towards methanol oxidation is enhanced after partial chemical displacement of dispersed Ni with Co.

Table 1 Comparison of performances of some electrodes in electrocatalysis of methanol oxidation

Electrode	E_{pa}/V	$J/mA\ cm^{-2}$	Reference
GC/poly(Ni-curcumin)	0.70	17.14	[36]
CPE/1,5-diaminonaphthalene/Ni	0.64	1.6	[21]
CPE/P(<i>o</i> -aminophenol)-SDS/Ni	0.65	16.7	[22]
CPE/Poly(aniline)/Ni	0.65	18	[10]
GC/bis(1,2-phenylenediamine)-Ni	0.60	25.5	[37]
Cu/copper chloride	0.90	24	[38]
Pt/poly(<i>o</i> -phenylenediamine)/Pt	0.6	30.61	[39]
Gr/Poly(<i>o</i> -phenylenediamine)/Pt	0.6	12.74	[39]
CPE/PINA(SDS)/Ni	0.60	26.5	Present work
CPE/PINA(SDS)/Ni ₈₀ Co ₂₀	0.59	27.8	Present work
CPE/PINA(SDS)/Ni ₅₀ Co ₅₀	0.55	3.33	Present work

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