

Electrochemical behavior of Ni(II) incorporated in zeolite Y-modified carbon electrode: application for electrocatalytic oxidation of methanol in alkaline solution

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Abstract Nickel ions were incorporated in NaY zeolite according to cation exchange mechanism. Then NiY zeolite was used as modifier for preparation of modified carbon paste electrode. The electrochemical behavior of NiY-modified carbon paste electrode (NiY/CPE) was studied in alkaline solution using cyclic voltammetry method. Ability of different electrodes containing NiY/CPE, Ni-NiY/CPE, Ni-NaY/CPE, and Ni/CPE for electrocatalytic oxidation of methanol was compared (three last electrodes prepared by open circuit accumulation of Ni(II) ions on the surface of NiY/CPE, NaY/CPE, and bare CPE, respectively). Results show that Ni-NiY/CPE is best catalyst for the electrochemical oxidation of methanol in alkaline solution and both process of earlier Ni ion incorporation through cation exchange in NaY zeolite and open circuit accumulation of Ni ion on the surface of electrode are essential to have good catalyst. Effect of graphite–zeolite ratio on electrocatalytic current was studied and 3:1 ratio of graphite–zeolite was selected as optimum ratio for preparing electrode. Ni-NiY/CPE has very good stability toward the methanol oxidation in concentration range of 0.005 to 0.5 M. Finally, using

chronoamperometric method, the catalytic rate constant (k) for methanol was found to be $1.56 \times 10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Keywords Zeolite-modified electrode · NiY · Methanol · Electrocatalytic oxidation

Introduction

During the last 10 years, the characterization of chemically modified zeolites by electrochemistry has been widely described in the literature. They have many applications in the fields of electrocatalysis, molecular recognition—including size and chiral selectivity, amperometric determinations (electroanalysis), used in photocatalytic processes and electrochemical synthesis, and assembly of intrazeolite conductive polymers [1, 2]. Transition metal-containing zeolites exhibit high activity and selectivity in the catalytic reduction of NO with propane [3]. Ti-zeolite was used in the catalytic generation of hydrogen peroxide [4]. Ni, Co, Pt, and Pd supported on zeolites [5–7] are also known to be effective catalysts.

Zeolites are crystalline microporous solids that provide molecular-sized cages and passage ways for excellent steric control of reaction paths. The pore windows and cages or channel structures of zeolites result in physical exclusion or inclusion of molecules or ions according to their sizes relative to that of the pores. The primary building blocks of zeolites are SiO and AlO tetrahedra. These can link in several ways, resulting in arrays producing three-dimensional anionic networks. The presence of aluminum in the framework introduces a negative charge that is balanced by extra framework cation as a redox active guest. The framework Si to Al ratio can be controlled in the zeolite synthesis [1, 8].

Zeolites are best known as heterogeneous catalysts. They catalyze processes such as hydrocarbon cracking, methanol to

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gasoline conversion, and disproportionation and alkylation of aromatics. On the other hand, several examples of electrocatalysis at zeolite-modified electrodes have appeared in the literature [9, 10]. Rolison [1] had listed most of the methods used for the fabrication of zeolite-modified electrodes. In general, they are produced by forming a film containing the modifier on the electrode surface [11–15]. Variations involve the inclusion of the zeolite in a conductive composite with the use of conductive polymers as binders [15–21]. Some electrochemical examples were involved concerning the electrocatalytic use of porphyrins anchored to the external surfaces of zeolites [22] and the use of zeolite containing Pt (0) microstructures in water electrolysis [23]. The results showed improvements indicating the impact of a strong metal support on the electrochemistry.

The electrochemical oxidation of methanol is a main topic of research where noble metal catalysts particularly containing Pt are found to be the most effective and extensively investigated. Although metals such as Pt and Pt–Ru are very active in the anodic oxidation of methanol, they are too expensive for practical applications.

The use of Ni as the catalysts for alcohol electro-oxidation is of interest because it is an inexpensive metal. Many electrodes, including nickel, as a component in their manufacture can be used as catalysts in fuel cells. Nickel is commonly used as an electro-catalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis [24–27]. One of the most important uses of nickel as a catalyst is to oxidize alcohols. Several investigations on the electro-oxidation of alcohols on Ni have been reported [28, 29]. Previously, we used some nickel dispersed in polymer-modified electrodes for electrocatalytic oxidation of methanol [30–32].

In the present study, the preparation of the Ni-modified zeolite electrode and its use as an electro-catalyst for the anodic oxidation of methanol in alkaline media was described.

Experimental

Apparatus

Electrochemical experiments were performed on 746VA Trace Analyzer Metrohm potentiostat with a Metrohm voltammetry cell in a three electrode configuration. An Ag/AgCl was used as reference electrode and a platinum wire was the auxiliary electrode. Working electrode was carbon paste electrode modified with zeolite (ca. 3.4 mm internal diameter).

Chemicals

NaY zeolite was synthesized by a literature method [33]. Nickel nitrate and methanol prepared from Merck. Sodium hydroxide from Fluka was used as the supporting electrolyte.

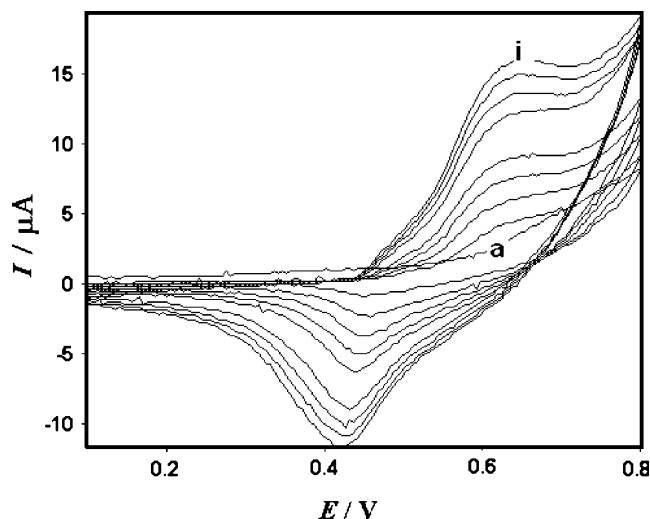


Fig. 1 Cyclic voltammograms of NiY/CPE in 0.1 M NaOH solution in different cycles: *a* first, *b* third, *c* fifth, *d* seventh, *e* ninth, *f* 11th, *g* 13th, *h* 15th, and *i* 17th. Scan rate 100 mV s^{-1}

Incorporation of Ni^{2+} in zeolite Y

NaY zeolite, 0.5 g, was mixed with 50 ml of 0.1 M nickel nitrate solution and stirred at room temperature for 3 h. After cation exchange, NiY was filtered and washed with water until colorless water was obtained, and then dried in air.

Electrode preparation

Carbon paste electrode containing NiY was obtained by homogeneously mixing of graphite particles and NiY in 6:1 mass ratio and then paraffin oil was added drop-wise until a uniformly wetted paste was obtained. A portion of prepared paste was packed into the end of a glass tube with a copper

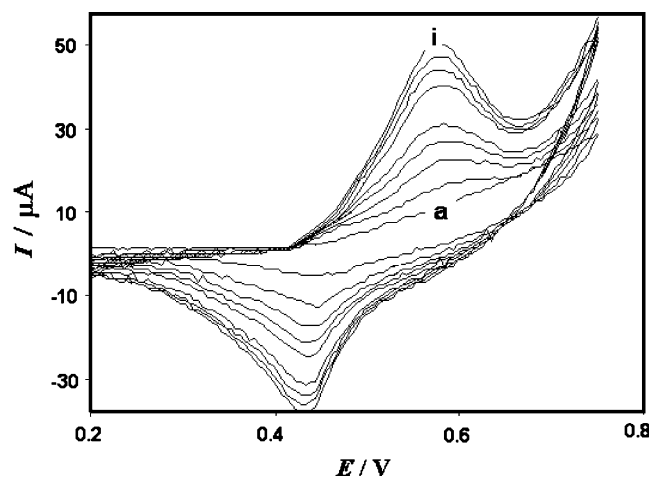
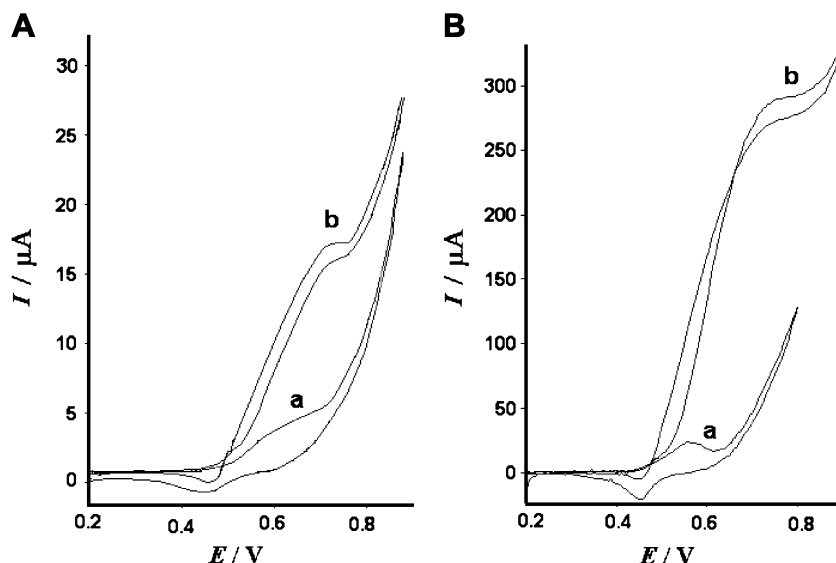


Fig. 2 Cyclic voltammograms of Ni-NiY/CPE in 0.1 M NaOH solution in different cycles: *a* first, *b* third, *c* fifth, *d* seventh, *e* ninth, *f* 11th, *g* 13th, *h* 15th, and *i* 17th. Scan rate 100 mV s^{-1}

Fig. 3 Electrochemical responses of **a** NiY/CPE and **b** Ni-NiY/CPE prepared with 6:1 ratio of graphite-zeolite to: *a* 0 and *b* 0.1 M methanol in 0.1 M NaOH solution, scan rate 20 mV s⁻¹

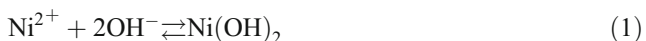


wire as electrical contact. The surface of paste was smoothed on a piece of paper. This electrode was named NiY/CPE. An electrode prepared with the same method but using NaY zeolite was named NaY/CPE. NiY/CPE, NaY/CPE, and bare CPE were placed at open circuit in a well-stirred aqueous solution of 0.1 M nickel nitrate solution. The obtained electrodes were named Ni-NiY/CPE, Ni-NaY/CPE, and Ni/CPE, respectively.

Results and discussion

Electrochemical behavior of NiY/CPE and Ni-NiY/CPE

Successive cyclic voltammograms of NiY/CPE in 0.1 NaOH solution is shown in Fig. 1. As can be seen in first scan, the amount of currents due to Ni(OH)₂/NiOOH redox couple is very low, but during cycling it increases which can be attributed to diffusion of hydroxide ion into zeolite and more conversion of Ni²⁺ to Ni(OH)₂ species according to the following reaction:



Such behavior was previously reported for Ni²⁺ incorporated in silicalite-1 zeolite [34]. For comparison, successive cyclic voltammograms of Ni-NiY/CPE in 0.1 M NaOH solution are shown in Fig. 2. As can be seen, the amount of current and current growth rate is more than NiY/CPE.

Electrocatalytic oxidation of methanol on the surface of different electrodes

Electrocatalytic oxidation of methanol on the surface of NiY/CPE

Figure 3a shows the cyclic voltammograms of NiY/CPE in 0.1 M NaOH solution, in the absence (Fig. 3a (a)) and presence (Fig. 3a (b)) of 0.1 M methanol.

An increment in the anodic peak current and a decrease of the cathodic peak current are the main effects observed upon the addition 0.1 M of methanol to the electrolyte which was previously reported in many literatures and also in our previous work [30–32]. This behavior is typical of that expected for mediated oxidation as follows:

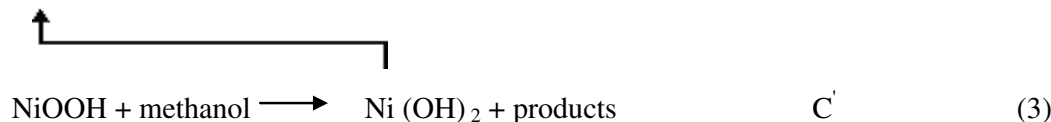
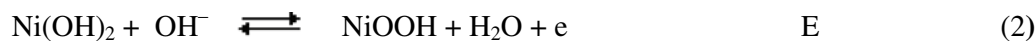
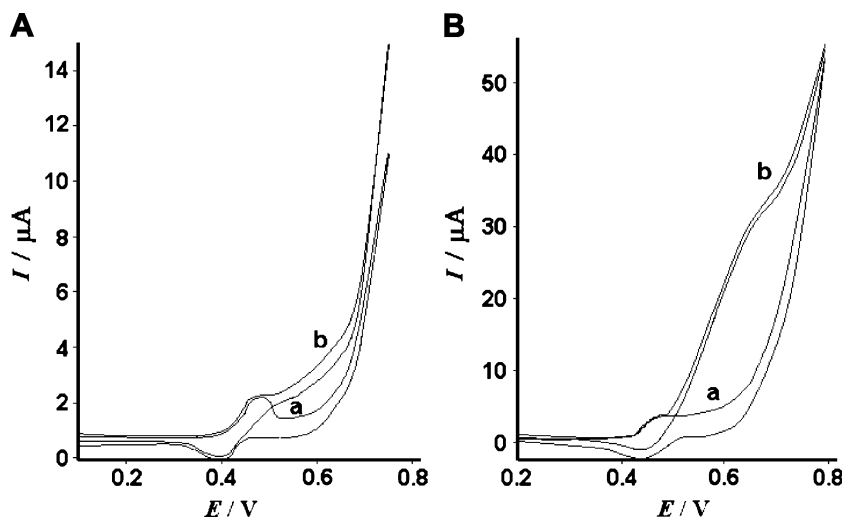


Fig. 4 Electrochemical responses of **a** Ni/CPE and **b** Ni-NaY/CPE prepared with 6:1 ratio of graphite–zeolite to: *a* 0 and *b* 0.1 M methanol in 0.1 M NaOH solution, scan rate 20 mV s^{-1}



As can be seen, the amount of anodic electrocatalytic current is very low and such current is not acceptable for fuel cell applications.

Electrocatalytic oxidation of methanol on the surface of Ni-NiY/CPE

Low current in NiY/CPE may arise from the following reasons:

1. The amount of nickel is not enough in the zeolite matrix.
2. Nickel ions incorporated in zeolite are not easily in the reach of methanol. Therefore, electrochemical behavior of Ni-NiY/CPE in the absence and presence of methanol was studied (Fig. 3b). As can be seen, the amount of currents significantly increased. It seems that preconcentration of Ni^{2+} on the surface of NiY/CPE is more effective than earlier cation exchange of Ni^{2+} with NaY. This question may be raised: is the earlier cation exchange step for incorporating Ni^{2+} ions in zeolite necessary? To answer this question, in the following section electrochemical behavior of Ni/CPE and Ni-NaY/CPE in the absence and presence of methanol will be studied.

Electrocatalytic oxidation of methanol on the surface of Ni/CPE and Ni-NaY/CPE

Figure 4a and b show respectively cyclic voltammograms of Ni/CPE and Ni-NaY/CPE in 0.1 M NaOH solution, in the absence and presence of 0.1 M methanol. These studies show that only preconcentration of Ni^{2+} ions on the surface of electrode is not sufficient and earlier cation exchange step for incorporating Ni^{2+} ions in zeolite is necessary and preconcentration step can improve the amount of currents.

Therefore, it seems that both steps (cation exchange and preconcentration) are necessary to have a good response to methanol.

Based on the above results, a schematic representation of the catalytic oxidation of methanol at the Ni-NiY/CPE is suggested and represented in Fig. 5. It is proposed that the catalytic oxidation reaction of methanol takes place when the oxy-hydroxide species (NiOOH) starts to be electrochemically formed by the anodic oxidation of nickel hydroxide (Ni(OH)_2) at the electrode surface and nickel species incorporated in zeolite act as an electron relay to the $\text{Ni(OH)}_2/\text{NiOOH}$ redox system. This might explain the low catalytic activity of Ni-NaY/CPE, which is free from incorporated Ni, towards methanol oxidation.

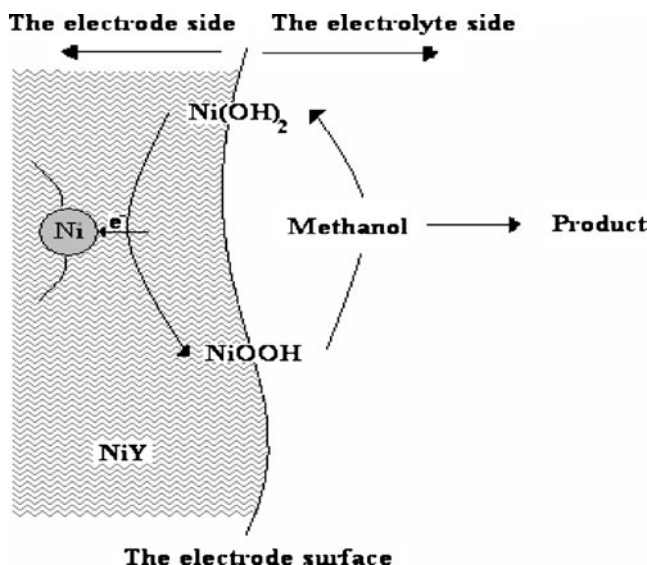


Fig. 5 Schematic representation of the electrocatalytic oxidation of methanol on the surface of Ni-NiY/CPE

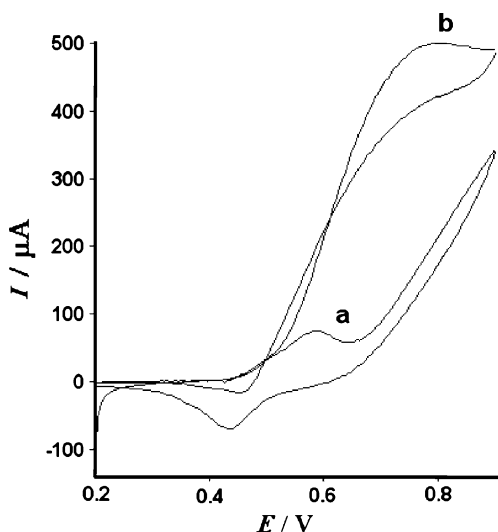


Fig. 6 Electrochemical responses of Ni-NiY/CPE prepared with 3:1 ratio of graphite–zeolite to: *a* 0 and *b* 0.1 M methanol in 0.1 M NaOH solution, scan rate 20 mV s⁻¹

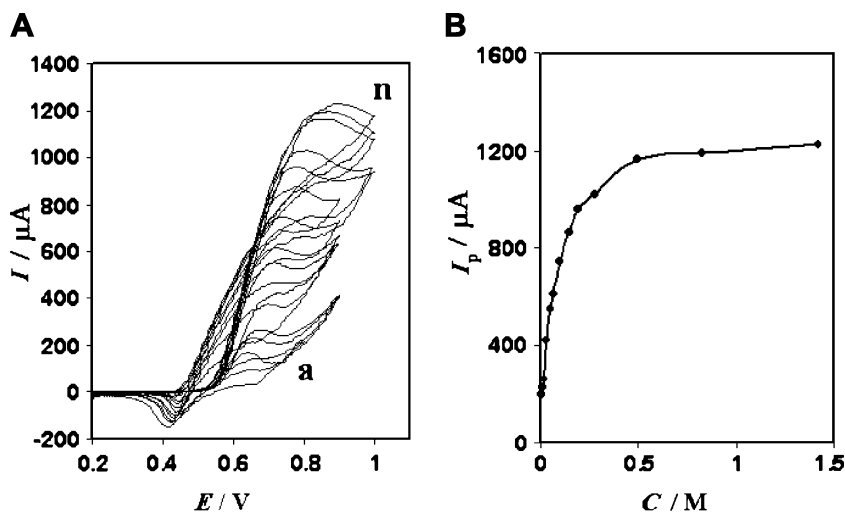
Effect of NiY percent on catalytic current

In order to study the effect of graphite to zeolite ratio on electrocatalytic current, a paste with 3:1 ratio was prepared. As it is seen in Fig. 6, with increasing the amount of NiY percent in paste, the amount of current increased. It must be noted that with more increasing the amount of NiY percent, the resulting paste would be physically unfavorable which cannot produce a smooth and shiny surface for electrode. Therefore, 3:1 ratio of graphite–zeolite was selected as optimum ratio.

Effect of methanol concentration

Figure 7a represents the CVs of the Ni-NiY/CPE in the range of 0–0.95 V at the scan rate of 20 mV s⁻¹. The

Fig. 7 a Cyclic voltammograms of the Ni-NiY/CPE in 0.1 M NaOH solution with different concentrations of methanol: *a* 0, *b* 0.005, *c* 0.01, *d* 0.02, *e* 0.03, *f* 0.05, *g* 0.07, *h* 0.1, *i* 0.145, *j* 0.192, *k* 0.28, *l* 0.5, *m* 0.83, and *n* 1.4 M, respectively. **b** Plot of catalytic peak current vs. methanol concentration



concentration of methanol in 0.1 M NaOH solution is changed from 0 to 1.4 M. It is observed from Fig. 7b that the amount of electrocatalytic current increases with increasing the concentration of methanol until 0.5 M, and for higher concentration this current level off due to the saturation of active sites on the surface of the electrode.

Chronoamperometric studies

Double potential step chronoamperometry, as well as other electrochemical methods, was employed for the investigation of electrochemical processes at Ni-NiY/CPE. The main panel of Fig. 8 represents the current–time profiles obtained by setting the working electrode potential at 700 mV (first step) and 350 mV (second step) for various concentrations of methanol. 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 Ni(OH)₂/NiOOH redox couple (Fig. 8a (a')). However, in the presence of methanol, the charge value associated with the forward chronoamperometry, *Q*, is greater than that observed for the backward chronoamperometry (Fig. 8a (f'))

The rate constant for the chemical reaction between the methanol and redox sites of Ni-NiY/CPE can be evaluated by chronoamperometry according to the method described in the literature [35].

$$I_C/I_L = \gamma^{1/2} \left[\pi^{1/2} \text{erf}(\gamma^{1/2}) + \exp(-\gamma)/\gamma^{1/2} \right] \quad (4)$$

Where *I_C* is the catalytic current of the Ni-NiY/CPE in the presence of methanol, *I_L* is the limiting current in the absence of methanol, and $\gamma = kc_0t$ (*c₀* is the bulk concentration of methanol) is the argument of the error function. In

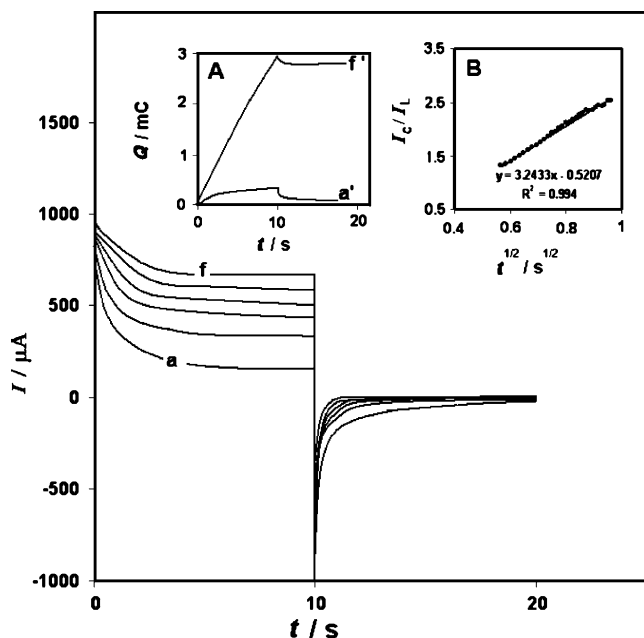


Fig. 8 Chronoamperograms obtained at the Ni-NiY/CPE in absence *a* and presence of *b* 0.05, *c* 0.075, *d* 0.1, *e* 0.15, and *f* 0.3 M of methanol, first and second potential steps were 0.7 and 0.35 V vs. Ag–AgCl, respectively, in 0.1 M NaOH solution. *Inset A* dependence of charge (*mC*) vs. *t*, *a'* and *f'*, respectively, derived from the data of chronoamperograms of *a* and *f*. *Inset B* dependence of I_c/I_L on $t^{1/2}$ derived from the data of chronoamperograms of *a* and *f* in the main panel

the cases where γ exceeds 2, the error function is almost equal to 1 and the above equation can be reduced to:

$$I_c/I_L = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (k c_0 t)^{1/2} \quad (5)$$

Where k , c_0 , and t are the catalytic rate constant ($\text{cm}^3 \text{mol}^{-1} \text{s}^{-1}$), methanol concentration (mol cm^{-3}), and time elapsed (s), respectively. From the slope of the I_c/I_L

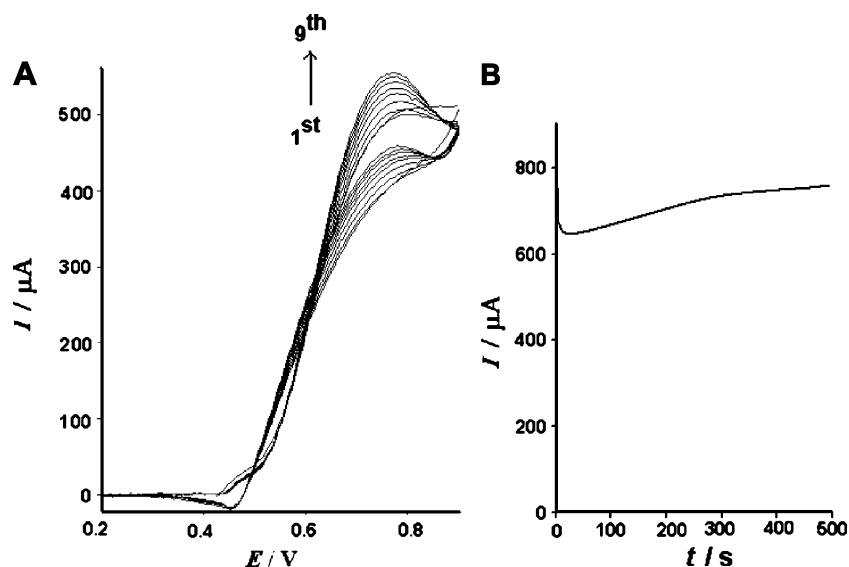
vs. $t^{1/2}$ plot, we can simply calculate the value of k for a given concentration of substrate. Inset (B) of Fig. 8 shows one such plot, constructed from the chronoamperogram of the Ni-NiY/CPE in the absence and presence of 0.3 M methanol. The mean value for k was found to be $1.56 \times 10^4 \text{ cm}^3 \text{mol}^{-1} \text{s}^{-1}$.

Stability of Ni-NiY/CPE

It is well known that the methanol oxidation current on a Pt polycrystalline electrode decays rapidly with time, and will reach 0 in a short amount of time [36]. The rapid current decay has been interpreted as the “self-poisoning” by CO-like intermediates formed during methanol activation. In order to investigate the stability of our modified electrode, successive cyclic voltammograms of modified electrode in presence of 0.1 M methanol were recorded (Fig. 9a). As can be seen in Fig. 9a, in presence of methanol in the electrolyte, the peak height of methanol oxidation increased with the increase of potential cyclization. The increase in peak height in successive cyclic voltammograms could be due to the increase of the amount of $\text{Ni}(\text{OH})_2$ resulted from more diffusion of hydroxide ion into zeolite and more conversion of Ni^{2+} to $\text{Ni}(\text{OH})_2$ species as inferred from the results of Fig. 1. This increase was also observed in chronoamperogram with a large time window of our modified electrode in presence of methanol (Fig. 9b).

We also verified the long-term stability of Ni-NiY/CPE by measuring its response to methanol oxidation after 2 and 4 weeks of storage in dry conditions. After this long period of times, the electrode shows 100% of its initial response. In other words, the amount of current does not decrease with the time. Such behavior seems to be more favorable for fuel cell applications.

Fig. 9 a Successive cyclic voltammograms of Ni-NiY/CPE in 0.1 M NaOH and 0.1 M methanol solution. Scan rate 20 mV s^{-1} . **b** $I-t$ transient for methanol oxidation on Ni-NiY/CPE in 0.1 M NaOH and 0.1 M methanol solution. The potential step was 0.7 V vs. Ag/AgCl



Conclusion

In this paper, Ni-NiY/CPE was prepared by immersion of a NiY-modified carbon paste electrode in 0.1 M nickel nitrate solution. In view of the results represented in this paper, it appears that both processes of earlier Ni ion incorporation through cation exchange in NaY zeolite and open circuit accumulation of Ni ion on the surface of electrode are essential to have a good catalyst for the electrochemical oxidation of methanol in alkaline solution. The experimental results led to the conclusion that nickel species incorporated in zeolite act as an electron relay to the Ni(OH)₂/NiOOH redox system were formed at the surface of Ni-NiY/CPE. Effect of graphite-zeolite ratio on electrocatalytic current was studied and 3:1 ratio of graphite-zeolite was selected as the optimum ratio for preparing electrode. Relatively, a good dependence of electrocatalytic current on methanol concentration was observed. Also this modified electrode has very good stability toward methanol oxidation. Finally, using chronoamperometric method, the catalytic rate constant (*k*) for methanol was estimated.

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