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Nickel modified ionic liquid/carbon paste electrode for highly efficient electrocatalytic oxidation of methanol in alkaline medium

Reza Ojani · Jahan-Bakhsh Raoof · Saeid Safshekan

Abstract In this study, the electrocatalytic oxidation of methanol at nickel modified ionic liquid/carbon paste electrode (Ni/IL/CPE) in alkaline medium is presented. The ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, is incorporated into the electrode as a binder. Electrochemical impedance spectroscopy is employed to evaluate the electron transfer rate of this electrode. Ni(II) ions are incorporated into the electrode by immersion of this electrode in 1.0 M nickel sulfate solution. Cyclic voltammetry and chronoamperometry techniques are used for the electrochemical study of this modified electrode in the absence and the presence of methanol. The effect of methanol concentration on the anodic peak current shows an increase in the anodic peak current up to 1.25 M. Current density of Ni/IL/CPE for methanol oxidation in alkaline media is investigated by comparison with some of the previously reported electrodes. Results show that this electrode exhibits a high efficient electrocatalytic activity toward the oxidation of methanol with the current density of 17.6 mA cm^{-2}. The rate constant for chemical reaction between methanol and redox sites of electrode is calculated. This new proposed electrode is simple and efficient enough, and it can be widely used as anode in direct methanol fuel cell.

Keywords Ionic liquid · Carbon paste electrode · Nickel ions · Methanol · Cyclic voltammetry

Introduction

Room temperature ionic liquids (RTILs) are stable salts, composed of an organic cation and either an organic or inorganic anion, and preserve in the liquid state over a wide temperature range [1, 2]. In the past few years, RTILs have emerged as a frontier and novel area of research because of their excellent chemical and physical properties such as good solvating properties, high chemical and thermal stability, non-flammability, low toxicity, almost negligible vapor pressure, high conductivity, and wide electrochemical window [3–9]. Recently, Di Wei et al. [10] and Simka et al. [11] reviewed the recent progress of RTILs in the field of electrochemical applications. As green solvents, RTILs can be used as the supporting electrolyte or the modified materials for electrode. RTILs have been proposed to be very interesting and efficient pasting binders in place of non-conductive organic binders for the preparation of carbon composite electrodes [12–14]. Using ionic liquid as a pasting binder in carbon paste electrode (CPE), we can construct a new generation of carbon composite electrodes with some advantages over CPEs such as high conductivity, fast electron transfer rates, and antifouling properties. There are various known hydrophobic ionic liquids that can be used as a binder for construction of this class of electrodes. These ionic liquids are mainly consist of bis(trifluoromethylsulfonyl)imide or hexafluorophosphate anions.

In the few past years, many carbon ionic liquid electrodes (CILE) have been applied in the electroanalytical community [15–23]. Liu et al. [24] reported a CILE constructed by graphite powder mixed with the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate that increased the sensitivity of the response toward potassium ferricyanide. Safavi et al. [25, 26] have reported a novel CILE based on the ionic liquid, *n*-octylpyridinum hexafluorophosphate as a binder for electrocatalytic and determination purposes.

To the best of our knowledge, carbon ionic liquid electrode modified with transition metal ions and its application for analytical purposes has not been reported. In the present

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

study, we combine the advantageous features of ionic liquids, electrocatalytic properties of transition metal ions, and carbon paste technology. At first, a type of ionic liquid/carbon paste electrode based on 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide was constructed and investigated. Then, we incorporated Ni(II) ions (as a cheap catalyst) at the surface of this electrode for application to electrocatalytic oxidation of methanol.

Experimental

Reagents and materials

The solvent used in this study was twice distilled water. Sodium hydroxide and methanol were of analytical grade (from Merck) and were used without further purification. Nickel sulfate was from Fluka, and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide from Aldrich. High-viscosity paraffin (density, 0.88 gcm^{-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 substrate.

Preparation of working electrode

A mixture of 0.15 mL paraffin and 0.10 mL ionic liquid (60:40 V/V) was added to 0.5 g of graphite powder and blended by hand mixing with a mortar and pestle for about 20 min for the preparation of carbon paste. A portion of the homogeneous paste was packed firmly into the bottom of a glass tube (internal radius, 1.7 mm). Electrical contact was provided by a copper wire connected to the paste in the inner hole of the tube. The conventional CPE was prepared in a similar way by mixing graphite powder with only paraffin oil. The surface of the electrode was smoothed on a white paper and rinsed with double-distilled water prior to each experiment.

Instrumentation

Cyclic voltammetry and chronoamperometry experiments were carried out using a potentiostat/galvanostat (Sama 500-C Electrochemical Analysis System, Sama, Iran). Electrochemical impedance spectroscopy (EIS) was performed by an AUTOLAB model PGSTAT 30 with FRA software version 4.9 (Eco Chemie, the Netherlands). The electrochemical cell was assembled with a conventional three-electrode system: a well-prepared ionic liquid/carbon paste electrode (IL/CPE) (3.4 mm in diameter) as the working electrode, an Ag/AgCl/KCl (3 M) as a reference electrode (Metrohm), and a platinum wire as a counter electrode.

Results and discussion

Electrochemical impedance spectroscopy studies

EIS is a simple and effective way to measure the charge transfer resistance (R_{ct}) of the electrochemical reactions [27]. The typical impedance spectrum (presented in the form of the Nyquist plot) includes a semicircle portion at higher frequencies corresponding to the electron transfer limited process and a linear part at lower frequencies representing the diffusion-limited process. The value of R_{ct} could be estimated by using the Randles equivalent circuit as the model, and fitting the impedance data into the model. This resistance controls the electron-transfer kinetics of the redox probe at the electrode interface. Therefore, R_{ct} can be used to describe the interface properties of the electrode. Its value varies when different substances are adsorbed onto the electrode surface [28, 29].

Figure 1 shows the Nyquist diagrams of CPE (curve a) and IL/CPE (curve b) in the presence of 1.0 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1)+0.1 M KCl solution. It can be seen that, while CPE exhibits a semicircle with R_{ct} equal to 11.5 kΩ, the IL/CPE revealed a very small semicircle domain implying a very low electron transfer resistance ($R_{ct}=$ 1.07 kΩ) of the redox pair in the solution. In fact, good conductive property of the ionic liquid plays an important role in improving the electron transfer rate between redox pair and electrode.

Incorporation of Ni(II) ions into the electrode

In order to incorporate Ni(II) ions into the surface of the electrode, the freshly prepared electrode was placed in a well-stirred aqueous solution of 1.0 M $NiSO_4$ at an open circuit for 10 min (accumulation time, t_a, is 10 min). Afterward, the
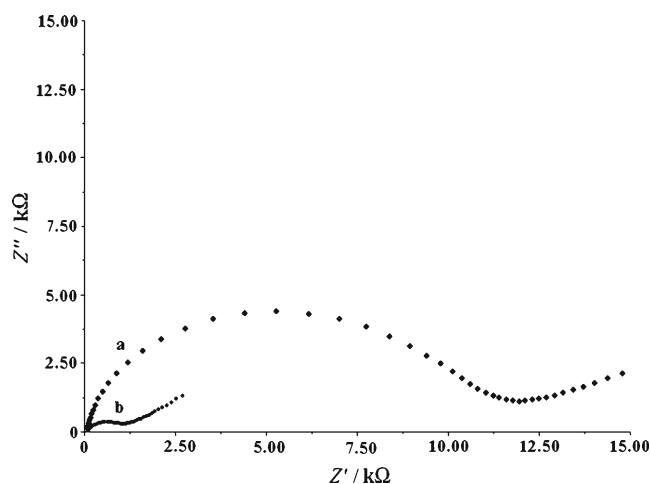

Fig. 1 Nyquist plots for the Faradaic impedance measurements of 1.0 mM solution of $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) and 0.1 M KCl performed on bare carbon paste (CPE) (*curve a*) and on IL/CPE (*curve b*)

electrode was transferred into a cell containing 0.1 M NaOH solution, and potential cycling was performed. This technique allows the oxide film formation in parallel to achieving the electrochemical reactivity of the surface (Eqs. 1 and 2):

$$Ni^{2+} + 2OH^- \rightarrow Ni(OH)_2 \qquad (1)$$

$$Ni(OH)_2 + OH^- \rightleftarrows NiOOH + H_2O + e^- \qquad (2)$$
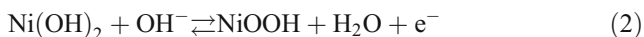
The polarization behavior of electrodes was examined in 0.1 M NaOH solution using cyclic voltammetry technique. Figure 2 shows cyclic voltammograms of Ni/CPE (a) and Ni/IL/CPE (b) in 0.1 M NaOH solution at the scan rate of 100 mV s^{-1} in the potential range of 0–0.75 V. As can be seen, at Ni/IL/CPE, a pair of well-defined anodic and cathodic peaks corresponding to the redox reaction of the NiOOH/Ni(OH)$_2$ couple in the surface of the electrode with a high anodic peak current (I_{pa}=193.3 μA) was observed. However, at Ni/CPE, the peak current (I_{pa}=24.8 μA) was much lower than that of Ni/IL/CPE. The shoulders in the cathodic peak of Fig. 2b can be attributed to different crystallographic forms of Ni(OH)$_2$, as previously reported in other articles[30, 31].

Effect of scan rate on the electrochemical behavior of Ni/IL/CPE

Figure 3 exhibits cyclic voltammograms of Ni/IL/CPE in 0.1 M NaOH solution at the different scan rates. With an increase in the scan rate, the peak current (I_p) increased and the anodic peak potentials shifted to more positive and the cathodic peak potentials shifted to more negative directions. Inset (B) in Fig. 3 indicates the plot of anodic peak current (I_{pa}) against the square root of the scan rate ($v^{1/2}$). It can be seen that the anodic peak currents are linearly proportional to $v^{1/2}$, indicating that the electrode reaction is diffusion controlled. This limiting diffusion process can be attributed to the hydroxide ion diffusion from the solution to film and vice versa during the oxidation–reduction process according to Eq. 2 [32, 33].

Electrocatalytic oxidation of methanol at the Ni/IL/CPE in alkaline solution

We have studied the electrocatalytic oxidation of methanol at the surface of IL/CPE and Ni/IL/CPE by cyclic voltam-
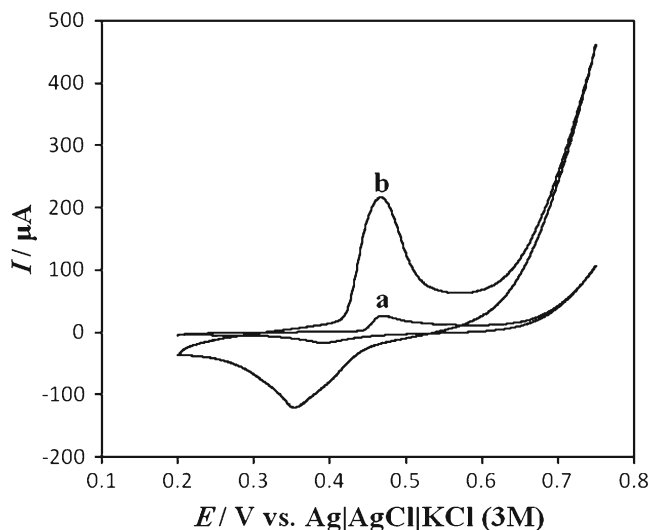

Fig. 2 Electrochemical responses of Ni/CPE (*a*) and Ni/IL/CPE (*b*) in 0.1 M NaOH solution at the scan rate of 100 mV s^{-1}

metry in 0.1 M NaOH solution. Typical results obtained for a potential scan from 0.0 to 0.75 V versus Ag|AgCl|KCl (3 M) are shown in Fig. 4. Curves 4a and 4c represent the electrochemical response of IL/CPE (4a) and Ni/IL/CPE (4b) in 0.1 M NaOH solution in the absence of methanol. It should be noted that, while the electrochemical response of the Ni/IL/CPE in alkaline solution (0.1 M NaOH) exhibits well-defined anodic and cathodic peaks associated with the NiOOH/Ni(OH)$_2$ redox couple, no anodic or cathodic peak was obtained for IL/CPE, and the addition of 0.1 M methanol to the alkaline solution causes no effect on its electrochemical response (Fig. 4b). This indicates that the bare IL/CPE has no electrocatalytic activity toward the methanol oxidation. Figure 4d shows the behavior of Ni/IL/CPE in the presence of 0.1 M methanol at the scan rate of 20 mV s^{-1}. An enhancement in the anodic peak current, the appearance of a new peak at a more positive potential, and a decrease in the cathodic peak current are the main effects observed in the presence of methanol. The relative decrease of the cathodic peak height is attributed to the partial consumption of nickel oxyhydroxide species for the oxidation of methanol.

Based on these evidences, catalytic electrooxidation of methanol on Ni/IL/CPE seems to be certain via an EC$^{'}$ mechanism as follows:

$$Ni(OH)_2 + OH^- \rightleftarrows NiOOH + H_2O + e \qquad E \qquad (3)$$

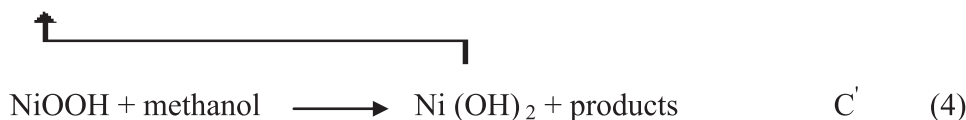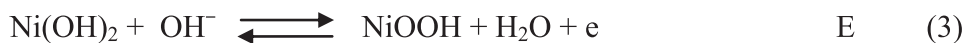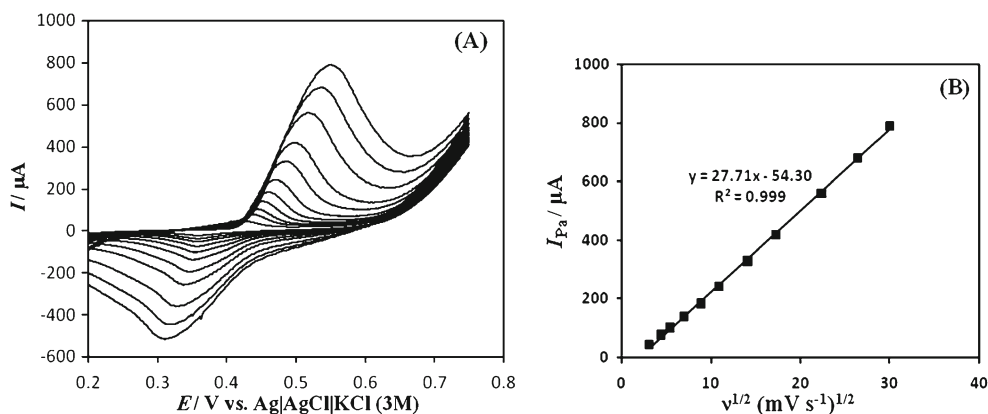$$NiOOH + methanol \rightarrow Ni(OH)_2 + products \qquad C^{'} \qquad (4)$$

Fig. 3 (**A**) Cyclic voltammograms of Ni/IL/CPE, at various scan rates: (a) 10, (b) 20, (c) 30, (d) 50, (e) 80, (f) 120, (g) 200, (h) 300, (i) 500, (j) 700 and (k) 900 mV s^{-1} in 0.1 M NaOH solution, (**B**) plot of I_{Pa} versus $v^{1/2}$

Nevertheless, the complete mechanism of methanol oxidation is complicated and it is not totally understood. However, as we have previously reported [34], we assume that the appearance of a new anodic peak at more positive potential is related to different crystallographic forms of Ni(OH)$_2$. In fact in the presence of methanol, NiOOH reduces to β-Ni(OH)$_2$ that is oxidized at a higher potential than α-Ni(OH)$_2$ oxidation.

Effects of methanol concentration on the oxidation of methanol

Figure 5 shows the voltammetric response of Ni/IL/CPE in the absence and presence of different concentrations of methanol at the scan rate of 20 mV s^{-1}. An increase in the concentration of methanol was followed by an increase in the anodic peak current up to the concentration of 1.25 M. In

the concentrations of more than 1.25 M, no significant change in the anodic peak current was observed. This can be due to the saturation of active sites of nickel catalyst on the surface of the electrode.

Table 1 shows a comparison between some of the previously reported nickel modified electrodes for electrocatalytic oxidation of methanol and the proposed electrode in this study. It is obvious that Ni/IL/CPE displays a comparable electrocatalytic behavior compared to many of these modified electrodes. These results indicate the remarkable electrocatalytic ability of this modified electrode for the oxidation of methanol in alkaline media.

Chronoamperometric study

We used a double potential step chronoamperometry study to achieve further perception about the electrocatalytic
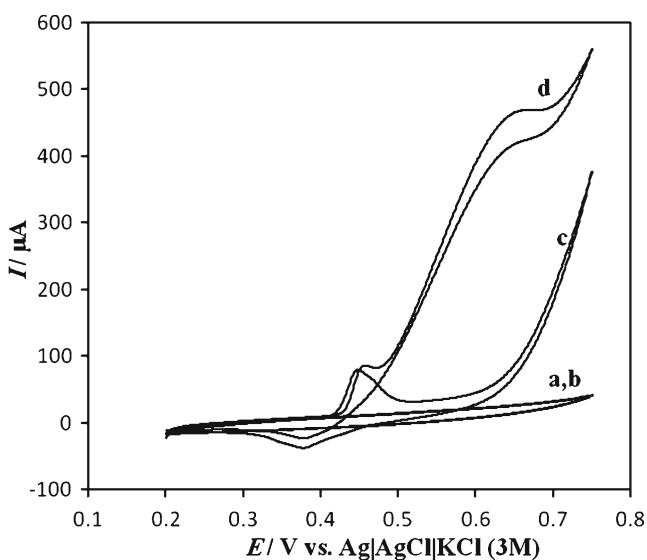

Fig. 4 Cyclic voltammograms obtained in 0.1 M NaOH solution at IL/CPE in the absence and the presence of 0.1 M methanol (*a, b*); and at Ni/IL/CPE in the absence (*c*) and presence (*d*) of 0.1 M methanol at the scan rate of 20 mV s^{-1}
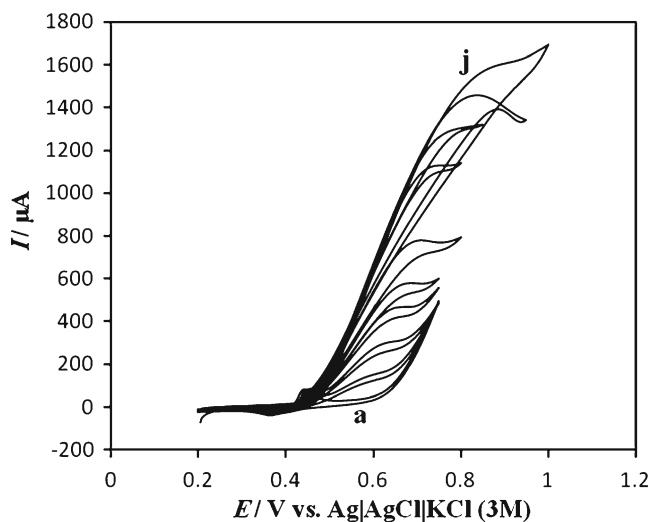
Fig. 5 Cyclic voltammograms of the Ni/IL/CPE in 0.1 M NaOH solution with different concentrations of methanol: *a* 0.0, *b* 0.02, *c* 0.06, *d* 0.1, *e* 0.18, *f* 0.25, *g* 0.32, *h* 0.49, *i* 1.0, and *j* 1.25 M respectively, at scan rate of 20 mV s^{-1}

Table 1 Comparison of the current density of Ni/IL/CPE with some of the previously reported electrodes for methanol oxidation in alkaline medium

Electrode	$C_{methanol}$ (mol L^{-1}) [a]	j (mA cm^{-2}) [b]	ν (mV s^{-1})	Reference
Ni(II)–Qu–MWCNT-CPE	0.4	4.7	20	[37]
Poly-[Ni^{II}-DHS]/GCE	0.373	6.3	20	[33]
Pd–Ni/GCE	1.0	12	50	[38]
Poly-Ni(II)curcumin/GCE	0.5	16.8	100	[39]
Ni/P-1,5-DAN/CPE	0.84	1.5	10	[40]
Ni/SDS–POAP/CPE	0.76	17.2	20	[41]
Ni/IL/CPE	1.25	17.6	20	This study

[a] Maximum concentration at which the electrode responds

[b] $j=I_{pa}/A$ (A=geometric surface area of substrate)

oxidation of methanol at the Ni/IL/CPE. Figure 6A shows the current–time curves obtained by setting the working electrode potential at 0.65 V (first step) and 0.3 V (second step) versus Ag|AgCl|KCl (3 M) for various concentrations of methanol. As seen from the figure, the forward and backward potential step chronoamperometry of the modified electrode in blank solution showed an almost symmetrical chronoamperogram with an almost equal charge which is consumed for oxidation and reduction of nickel species on the surface of the electrode (a′ in Fig. 6B). However, in the presence of 0.32 M methanol, the charge value associated with the forward chronoamperometry, Q, is much greater than that observed for the backward potential step (d′ of Fig. 6B). The rate constant for the chemical reaction between the methanol and redox sites of Ni/

IL/CPE can be evaluated by chronoamperometry, according to the method described in the literature [35]:

$$I_C/I_L = \gamma^{1/2}\left[\pi^{1/2}\mathrm{erf}\left(\gamma^{1/2}\right) + \exp(-\gamma)/\gamma^{1/2}\right] \quad (5)$$

where I_C is the catalytic current of the Ni/IL/CPE in the presence of methanol, I_L is the limiting current in the absence of methanol, and $\gamma=kc_ot$ is the argument of the error function. If γ exceeds 2, then the error function is almost equal to 1, and the above equation can be reduced to

$$I_C/I_L = \gamma^{1/2}\pi^{1/2} = \pi^{1/2}(kc_ot)^{1/2} \quad (6)$$

where k, c_o, and t are the catalytic rate constant (cm^3 mol^{-1} s^{-1}), methanol concentration (mol cm^{-3}), and time elapsed (s),

Fig. 6 (**A**) Chronoamperograms obtained at a Ni/IL/CPE in the absence of methanol (*a*) and the presence of (*b*) 0.1, (*c*) 0.25 and (*d*) 0.32 M methanol. (**B**) Plot of Q versus t derived from the data of chronoamperograms *a* and *d*. (**C**) Plot of I_C/I_L versus $t^{1/2}$ derived from the data of chronoamperograms *a* and *d*. (**D**) Plot of I versus $t^{-1/2}$ derived from the data of chronoamperogram of *b*
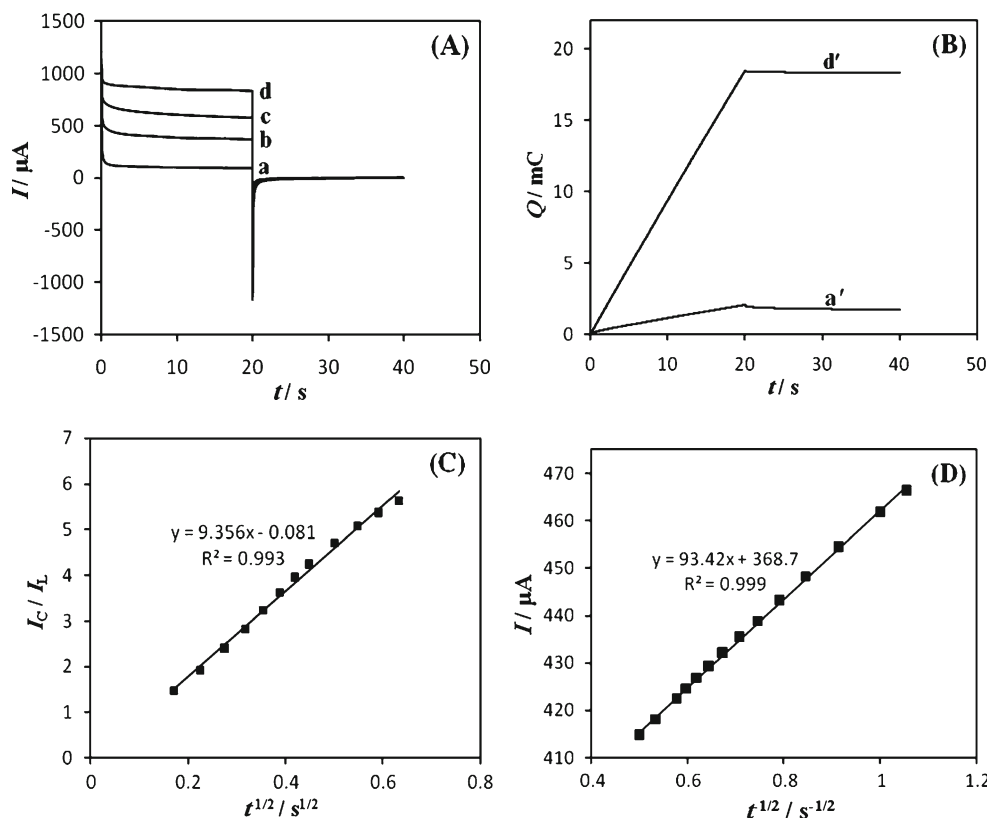
respectively. From the slope of the I_C/I_L versus $t^{1/2}$, we can calculate the value of k for a given concentration of substrate. Figure 6C shows one such plot, constructed from the chronoamperograms in the absence and the presence of 0.32 M methanol. The mean value for k was found to be 0.79×10^5 cm^3 mol^{-1} s^{-1} for Ni/IL/CPE and 0.12×10^4 for Ni/CPE. Chronoamperometry was also used to estimate the diffusion coefficient of methanol. For an electroactive material with a diffusion coefficient D, the current response under diffusion control was described by Cottrell equation [36]:

$$I = nFAD^{1/2}C\pi^{-1/2}t^{-1/2} \tag{7}$$

Where D is the diffusion coefficient (cm^2 s^{-1}), C is the bulk concentration (mol cm^{-3}) of methanol, and n is the total number of electrons transferred. Noting the assumption that 100% of the current is assumed to be methanol oxidation, from the slopes of I versus $t^{-1/2}$ (Fig. 6D), the value of D was calculated to be 8×10^{-5} cm^2 s^{-1}.

Conclusion

In this work, the electrocatalytic oxidation of methanol at the surface of nickel modified ionic liquid/carbon paste electrode in alkaline solutions was examined using voltammetry and chronoamperometry techniques. Electrooxidation of methanol occurs through a mediated electron transfer mechanism catalyzed by NiOOH/Ni(OH)$_2$ species. The catalytic rate constant and the diffusion coefficient for methanol were calculated using the chronoamperometry method. It was found that catalytic rate constant for methanol at Ni/IL/CPE was much higher than that of Ni/CPE. The proposed electrode exhibited an efficient electrocatalytic activity toward methanol oxidation up to the concentration of 1.25 M. This novel electrode was simple and efficient enough, and it can be expected to be widely useful for using as an anode in fuel cell. A comparison of the current density of Ni/IL/CPE for methanol oxidation with some of the previously reported electrodes in alkaline medium has shown that the current density of this electrode is large compared to other nickel-based modified electrodes.

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