CrossMark

ORIGINAL PAPER

Evaluation of sodium dodecyl sulfate effect on electrocatalytic properties of poly(1-naphtylamine)/nickel-modified carbon paste electrode as an efficient electrode toward electrooxidation of methanol

Reza Ojani[1] · Elahe Tirgari[1] · Jahan-Bakhsh Raoof[1]

Abstract In this work, 1-naphtylamine is electropolymerized at the surface of carbon paste electrode (CPE) using consecutive cyclic voltammetry in 15 mM monomer aqueous solution in the presence of 15 mM sodium dodecyl sulfate (SDS) as surfactant. Then, transition metal of nickel is incorporated into the polymeric electrode placing in 1.2 M $NiCl_2$ solution without applying any potential to the electrode for 7 min. In alkaline medium (i.e., NaOH 0.1 M), a good redox behavior of Ni(III)/Ni(II) couple at the surface of Ni/poly (1-naphtylamine) modified carbon paste electrode (Ni/PNAM/MCPE) in the absence and presence of SDS (Ni/SDS-PNA/MCPE) can be observed. Electrocatalytic oxidation of methanol has been studied on Ni/PNA/MCPE and Ni/SDS-PNAM/MCPE. The results show that SDS significantly enhances the catalytic efficiency of nickel particles on the oxidation of methanol in aqueous alkaline media. Moreover, the effects of various parameters such as concentration of SDS, concentration of methanol, film thickness, and monomer concentration on the electrooxidation of methanol as well as long-term stability of the Ni/SDS-PNAM/MCPE have also been investigated. This polymeric modified electrode can oxidize the methanol with high current density (over 3 mA).

Keywords Methanol oxidation · 1-naphtylamine · SDS · Electrocatalytic oxidation

✉ Reza Ojani
  fer-o@umz.ac.ir

[1] Electroanalytical Chemistry Research Laboratory, Department of Analytical Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar, Iran

Introduction

Fuel cells are entity considered as an important technology that can be used for various power applications [1]. In the past years, particular attention has been made to electrocatalytic oxidation of small organic molecules (CH_3OH, $HCHO$, $HCOOH$, etc.) on various modified electrodes. The reason for that is mainly dependent to their high energy density and their potential application as fuel in fuel cell systems [2]. Direct methanol fuel cell (DMFC) is considered a promising power source for electric vehicles and electronic portable devices due to its simple design, low operating temperature, and convenient fuel storage and supply [3]. However, the practical development of DMFCs is limited by poor activity of methanol electrooxidation and high cost of noble metal catalysts [4].

The development of chemically modified electrodes (CMEs) is at present an area of great interest. CMEs can be distributed broadly into two main categories, namely, surface-modified and bulk-modified electrodes. Methods of surface modification include adsorption, covalent bonding, attachment of polymer films, etc. [5, 6]. The electropolymerization of some monomers is particularly attractive because the polymeric deposits exhibit some very interesting properties. They are generally homogeneous, strongly adherent to the electrode and chemically stable [7]. In the electrochemical oxidation, the electrode material is a considerable parameter, and a high operative electrocatalyst is needed. An elegant way is to perform the electrocatalytic process with metallic microparticles electrodeposited into the polymeric film have been employed for electrooxidation of organic compounds containing OH and NH_2 groups, such as methanol [8, 9].

To increase the electrocatalytic oxidation of methanol, an enormous effort has been devoted toward the development of catalysts. In fact, the choice of suitable supporting material is an important factor that may affect the performance of

supported electrocatalysts owing to interaction and surface reactivity [10]. Pt and Pt-Ru electrodes have been reported to be most active for anodic oxidation of methanol in acidic medium [11] but they are too expensive for commercial applications. It is well known that some intermediates of methanol oxidation are strongly adsorbed at the surface of electrode, and leading to a loss of its electrocatalytic activity. Therefore, their activity is not satisfactory high [12].

Recent researches have demonstrated that coating the electrode surface with polymeric films is an attractive approach for enhancing the power and scope of electrochemically modified electrodes [1]. This new class of electrode material has been found to improve the electrode sensitivity and selectivity, and to reduce fouling effects in many applications [13]. Electropolymerization offers the advantage of reproducible deposition in terms of film thickness and loading, making the immobilization procedure of an electrocatalyst very simple and reliable [14].

Previously, we combined the advantageous features of polymer modification, dispersion of metallic particles into an organic polymer, and carbon paste technology by construction of a poly(m-toluidine)/nickel modified carbon paste electrode for successful electrocatalytic oxidation of hydrogen peroxide [15], and also we constructed carbon paste electrode modified by nickel ion dispersed into poly(1,5-diaminonaphthalene) film with capable of chelating nickel ions with an extra free amine group and this nickel-modified polymeric carbon paste electrode was useful toward the electrocatalytic oxidation of methanol in alkaline medium [16], Ni/poly(1-naphtylamine), and Ni/poly(o-aminophenol) modified carbon paste electrode for electrocatalytic oxidation of several carbohydrates [17, 18] and methanol [19] have been used. These studies showed that metal-polymer modified carbon paste electrodes are easy to prepare and stable for a long period of time with acceptable reproducibility, detection limits, and wide linear range responses. All these results encouraged us to continue the studies with new polymer materials. In addition, recently, much attention has been paid to using anionic surfactant, based mainly on sodium dodecyl sulfate (SDS), for electrosynthesizing conducting polymers, such as polypyrroles [20] and polythiophenes [21]. Adding SDS to the monomer solution leads to an increase of the polymer growth rate, and the observed rate of reaction depends on the association between the reactants and SDS. Also, SDS causes to decrease the monomer concentration which is in need for polymerization.

In this communication, we reported for the first time the effect of the presence of SDS on the behavior of poly(1-naphtylamine) (Scheme 1) at the surface of carbon paste electrode (not published). Nickel ions were incorporated into the polymeric matrix by immersion of the poly(1-naphtylamine)-modified electrode in a nickel chloride solution. Efficiency of this nickel modified polymeric carbon paste electrode toward the electrocatalytic oxidation of methanol was investigated.
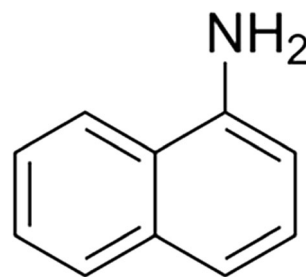
Scheme 1 Structure of 1-naphtylamine

Experimental

Reagents and materials

The solvent used in this work was twice distilled water. Perchloric acid (% 98, Fluka) was used for preparation of supporting electrolyte. 1-naphtilamine (NAM) from Fluka was used as monomer at the electrochemical polymerization. Sodium hydroxide and methanol used in this work were analytical grade of Merck origin and used as received without further purification. High viscosity paraffin (density, 0.88 g cm^{-3}) from Fluka was used as the pasting liquid for the carbon paste electrode. 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

Electrochemical experiments were performed on SAMA 500 potentiostat (from Iran) with a voltammetry cell in a three-electrode configuration. Ag/AgCl/KCl (3 M) was used as reference electrode; a platinum wire was the auxiliary electrode. Working electrode was homemade carbon paste electrode.

Working electrode

Graphite powder and paraffin were mixed by hand mixing with a mortar and pestle for preparation of carbon paste electrode. Then, the resulting paste was inserted in the bottom of a glass tube (internal radius, 1.7 mm). The electrical connection was implemented by copper wire lead matched into the glass tube.

Preparation of Ni/SDS-PNAM film

SDS-PNAM films were obtained at the surface of CPE by electropolymerization of 1-naphtylamine monomer solution (15 mM 1-naphtylamine in 0.5 M HCLO$_4$) in the presence of various concentrations of SDS (2–25 mM). Electropolymerization at the surface of CPE was performed by cyclic voltammetry (for 15 cycles) between −0.15 and 0.65 V vs. Ag/AgCl/KCl (3 M) (scan

rate = 50 mV s^{-1}). In order to incorporate Ni (II) ions into the PNAM film, the freshly electropolymerized PNAM was placed at open circuit in a well-stirred aqueous solution of 1.2 M NiCl$_2$. Accumulation of nickel was accomplished by complex formation between Ni (II) and amine sites in the polymer structure [22, 23] for a given period of time (t$_a$, accumulation time).

Results and discussion

Electrochemical polymerization

The poly(1-naphtylamine) film was prepared on the surface of carbon paste electrode in the absence and presence of SDS. Figure 1A shows the typical multi-sweep cyclic voltammograms during electropolymerization of 1-naphtylamine in the absence of SDS. As it is seen in this figure, 1-naphtylamine oxidizes irreversibly at 400 mV without corresponding cathodic processes in the reverse scan. During the next cycles, two redox peaks in lower potentials appeared and their current did not increase considerably with potential cycling. In order to grow polymer, often either high monomer concentration or long time of potential cycling can be conducted. After adding 15 mmol L^{-1} anionic surfactant of SDS to monomer solution (Fig. 1B), the rate of polymerization increased considerably and its growth did not stop.

Electrochemical properties of Ni/SDS-PNAM

After stabilization of Ni (II) into polymer, the electrochemical behavior of the SDS-PNAM/CPE and Ni/SDS-PNAM/CPE was examined in 0.1 M NaOH solution by cyclic voltammetry (Fig. 2). As can be seen, where as neither oxidation nor reduction happened on the SDS-PNAM, well-defined redox peaks were observed on the Ni/SDS-PNAM when the potential was scanned between 0 and 0.8 V, which was attributed to the oxidation of Ni(OH)$_2$ to NiOOH with a peak potential of 0.39 V and reduction of NiOOH to Ni(OH)$_2$ with a peak potential of 0.2 V. Therefore, the anodic and cathodic peaks that appeared in cyclic voltammogram of Ni/SDS-PNAM/CPE in the absence of methanol are related to the electrochemical reaction below [24]:

$$Ni(OH)_2 + OH \rightarrow NiOOH + H_2O + e^- \qquad (1)$$
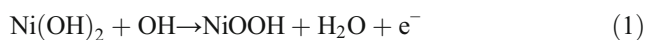
Characterization of Ni/P1NAM/SDS/MCPE

Scanning electron microscopy (SEM) was used to characterize and compare the morphologies of the different types of
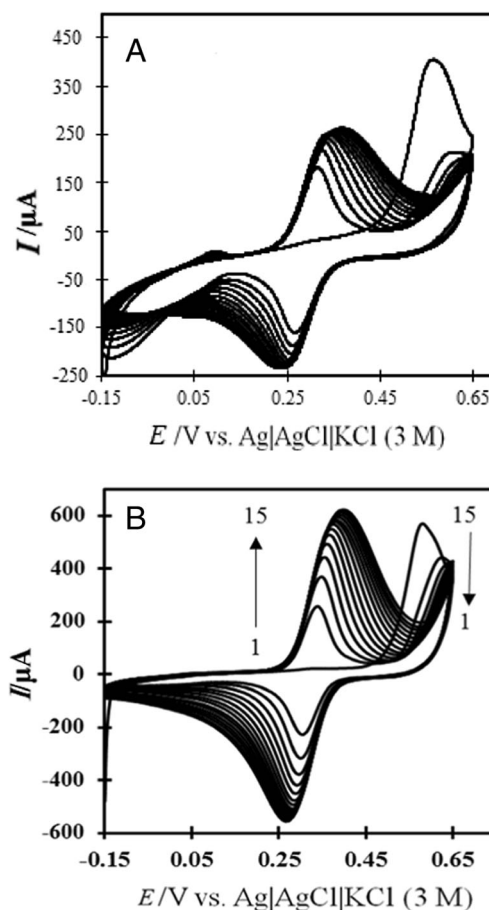

Fig. 1 Cyclic voltammograms 15 mM monomer (1-naphtylamine) in 0.5 M HClO$_4$ solution **a** in absence and **b** present of SDS On the surface of carbon paste electrodes at υ = 50 mV s^{-1}

modified electrodes with the results shown in (Fig. 3). The surface morphology of the CPE (a), Ni/CPE (b), Ni/P1NAM/MCPE (c), and Ni/P1NAM/SDS/MCPE (d) was characterized. At the traditional carbon paste electrode (CPE), the surface was formed by isolated and irregularly shaped carbon flakes and each layer could be distinguished clearly (Fig. 3a). The SEM image of the pure Ni catalyst
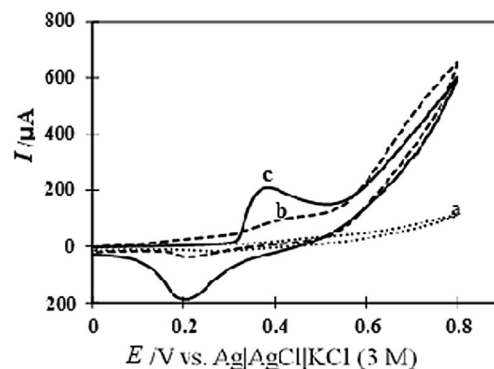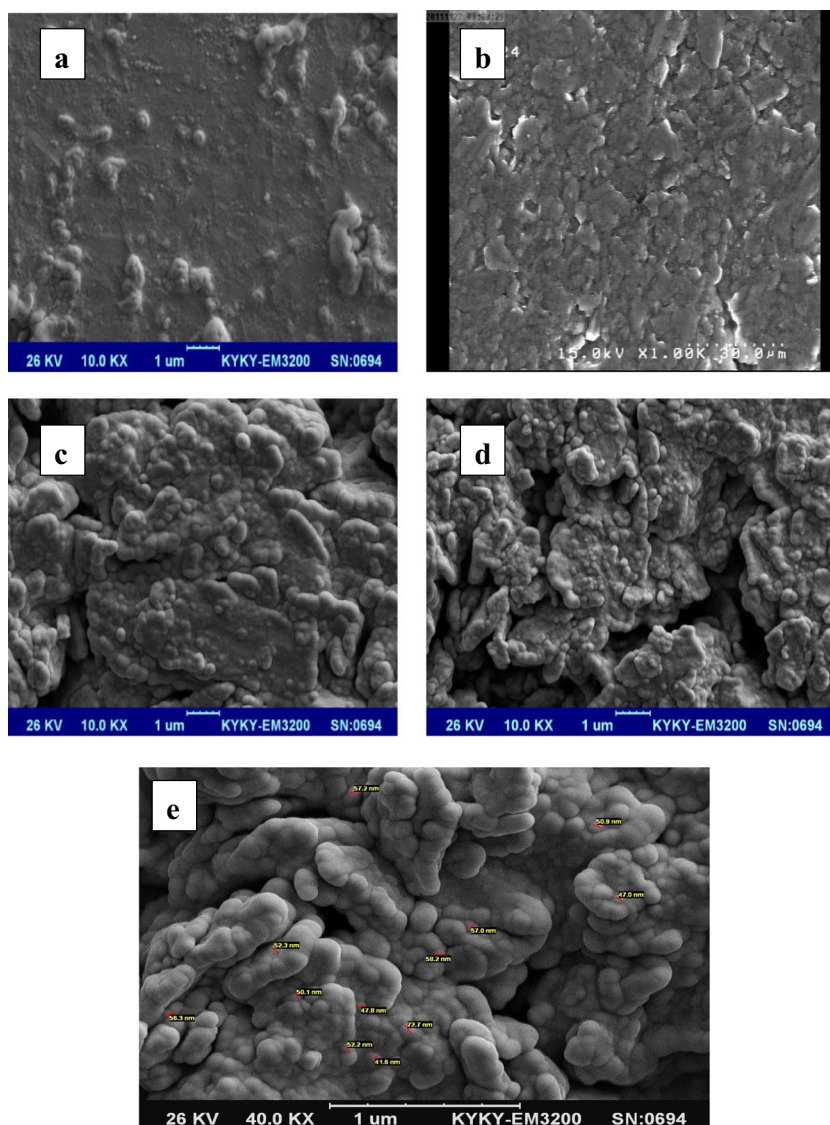

Fig. 2 Cyclic voltammograms of PNAM(SDS)/MCPE **a** absence of Ni, **c** presence of Ni, and **b** of nickel stabilized at the surface of carbon paste electrodes in the same condition. In the 0.1 M NaOH solution at = 50 mV s^{-1}

Fig. 3 SEM images of the CPE
(**a**), Ni/CPE (**b**), Ni/P1NAM/
MCPE (**c**), Ni/P1NAM/SDS/
MCPE (**d**) and (**e**). With different
magnifications

displays the aggregates of Ni particles (Fig. 3b). As shown in
trace (c), P1NAM film has a rough surface with many small
cavities and/or holes with no uniformity on the electrode sur-
face. The enlarged SEM shows that the P1NAM /MCPE film
is porous. Generally, the porous structure by micrometer-sized
pores allows the liquid fuel constituent better diffusion to in-
side the film; thus, maximum fuel molecules can be available
for the catalyst.

**Electrocatalytic oxidation of methanol
at Ni/SDS-PNAM/MCPE**

As can be seen in Fig. 4, by comparison, the peak cur-
rent of methanol oxidation at the surface of Ni/SDS-
PNAM/MCPE is about twofold greater than that at Ni/
PNAM/MCPE, which can be attributed to the faster
polymer deposition, high conductivity, and high real sur-
face area of SDS-PNAM/MCPE (Fig. 4). The

electrochemical behavior of these modified electrodes in
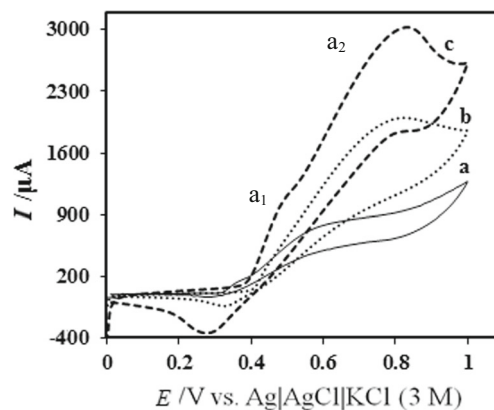the presence of methanol in 0.1 M NaOH solution shows

Fig. 4 Cyclic voltammograms of (**a**) CPE/Ni (**b**) Ni/PNAMM/MCPE
and (**c**) Ni/SDS-PNAMM/MCPE in the 0.1 M NaOH solution in the
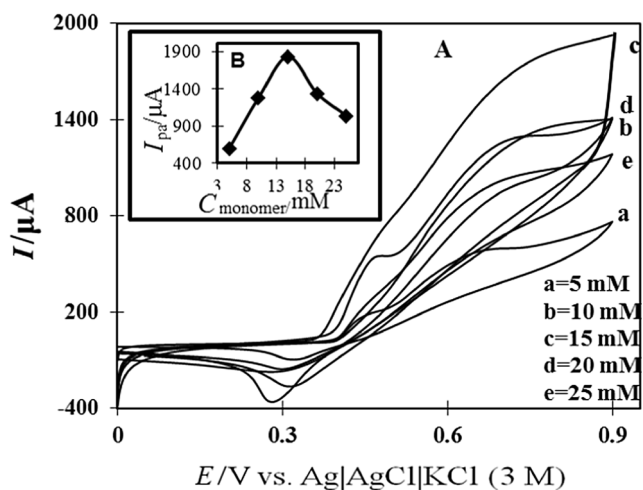presence CH$_3$OH 0.17 M at = 50 mV s^{-1}

Fig. 5 A Electrochemical responses of Ni/SDS-PNAM /MCPE electrode prepared in the presence of 0.1 M methanol with monomer concentration 5–25 mM in modification steps in 0.1 M NaOH. **B** Variation of the electrocatalytic peak current of methanol versus to monomer concentration (cycle numbers 15, SDS concentration 10 mM, NiCl$_2$ concentration 1 M, = 50 mV s^{-1})

Fig. 7 A Cyclic voltammograms of Ni/SDS PNAM /MCPE electrodes prepared in SDS concentration in range 2–25 in modification steps in the presence of 0.1 M methanol in 0.1 M NaOH. **B** Variation of the electrocatalytic peak current of methanol versus to SDS concentration (monomer concentration 15 mM, SDS concentration 10 mM, NiCl$_2$ concentration 1 M and = 50 mV s^{-1})

an increment in the anodic peak current for peak (a$_1$) followed by the appearance of a new oxidation peak (a$_2$) at more positive potential. The anodic peaks (a$_1$) and (a$_2$) demonstrate the existence of two different crystallographic structure of Ni(OH)$_2$ (α- Ni(OH)$_2$ and β-Ni(OH)$_2$) [25].

$$\alpha\text{-Ni(OH)}_2 + OH \rightarrow NiOOH + H_2O + e^- \qquad : E \quad (2)$$

$$NiOOH + methanol \rightarrow \beta\text{-Ni(OH)}_2 + product \qquad : C' \quad (3)$$

Therefore, the ffirst anodic peak current (a$_1$) is related to the oxidation of α- Ni(OH)$_2$ to NiOOH and in the presence of methanol, a new anodic peak (a$_2$) is appeared at more positive potential. It is related to the oxidation of β- Ni(OH)$_2$ that is oxidized at higher potential than α- Ni(OH)$_2$ and depends on methanol concentration.
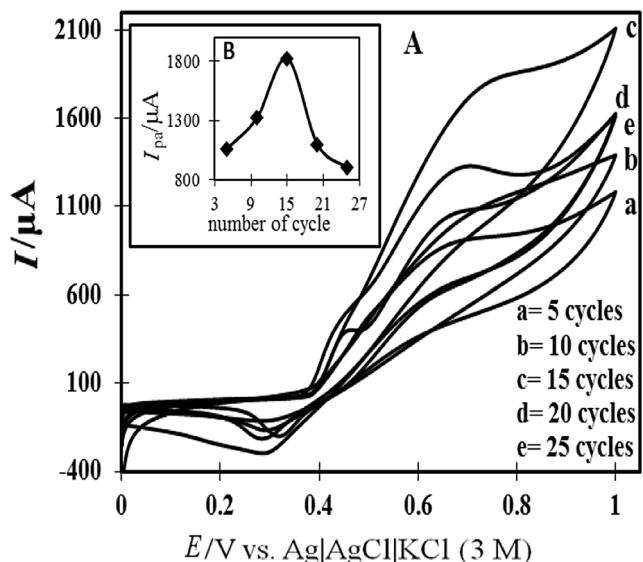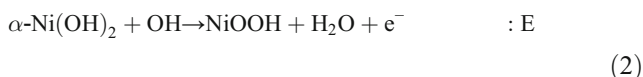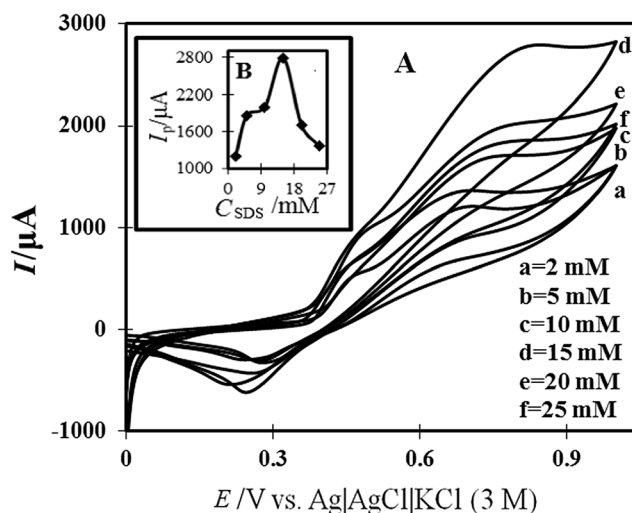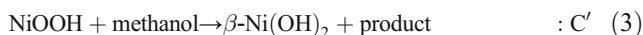

Fig. 6 A Cyclic voltammograms of Ni/SDS PNAM /MCPE electrodes prepared in cycle numbers in range 5–25 in modification steps in the presence of 0.1 M methanol in 0.1 M NaOH. **B** Variation of the electrocatalytic peak current of methanol versus to cycle numbers (monomer concentration 15 mM, SDS concentration 10 mM, NiCl$_2$ concentration
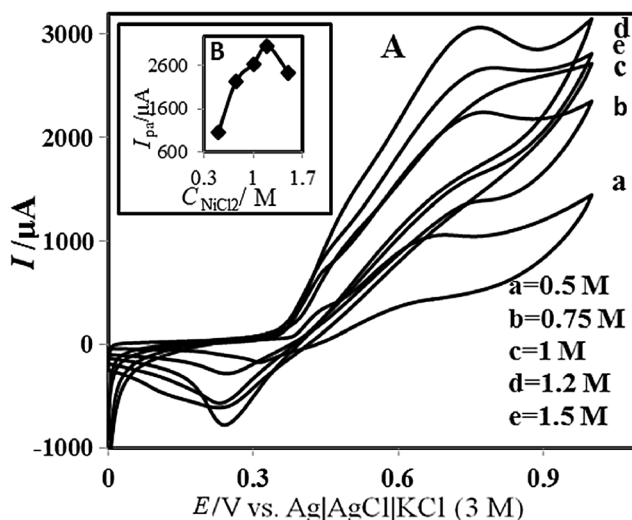

Fig. 8 A Current-potential curves of in 0.1 M NaOH for Ni/SDS-PNAM/MCP electrodes in the presence of 0.1 M methanol with NiCl$_2$ concentration in range 0.5–1.5 M in modification steps. **B** Variation of the electrocatalytic peak current of methanol versus to NiCl$_2$ concentration (monomer concentration 15 mM, SDS concentration 15 mM, cycle numbers 15, = 50 mV s^{-1})
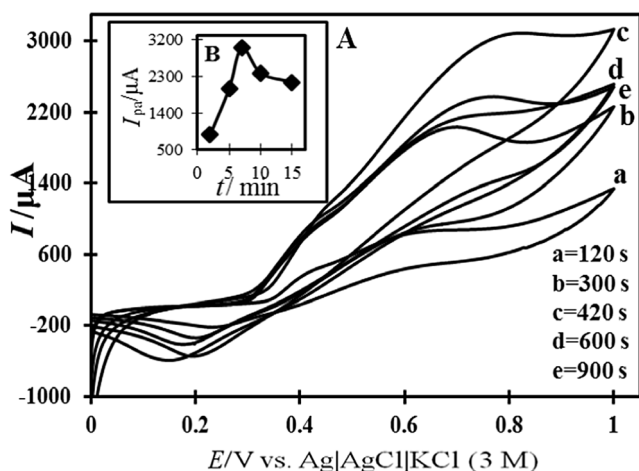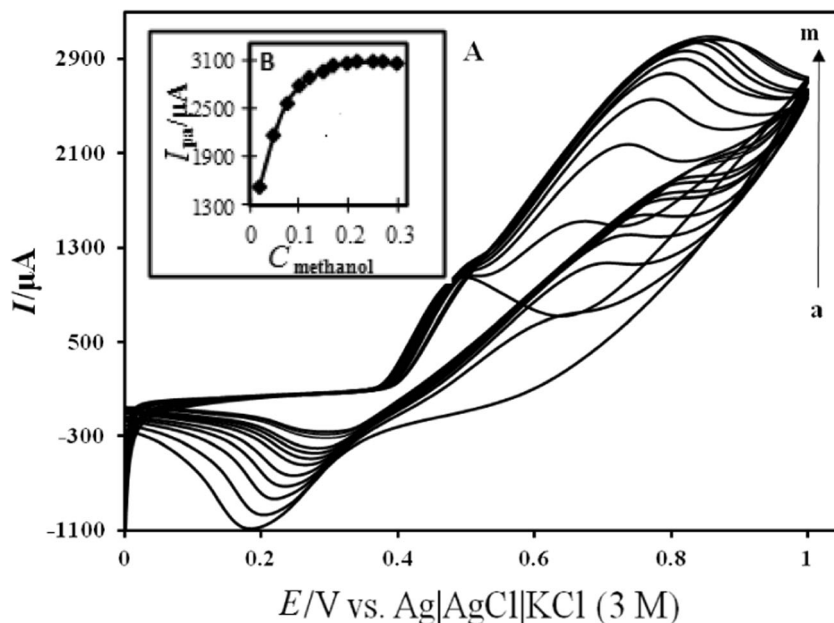
Fig. 9 **A** Cyclic voltammograms of Ni/SDS-PNAM/ MCP electrodes prepared at various electrodepositing time in 0.1 M NaOH solution in the presence of 0.1 M methanol. **B** Variation of the electrocatalytic peak current of methanol versus to time of plating (cycle numbers 15, monomer concentration 15 mM, SDS concentration 15 mM, NiCl$_2$ concentration 1.2 M, = 50 mV s^{-1})

Thus, methanol oxidation appears as an increasing in anodic peak (a$_1$) current accompanied by a decrease in cathodic peak current in the reverse scan rate of potential (as an EC' mechanism).

By appearance of a new anodic peak (a$_2$) at more positive potentials, it can be considered that methanol oxidation takes place mainly after the oxidation of Ni (II) to Ni (III) [26, 27]. As can be seen in (Fig. 4), methanol electrocatalytic oxidation takes place at potential about 0.8 V vs. Ag|AgCl|KCl (sat), where higher current and better signal to noise were achieved at the surface of Ni/P(1-NAM)SDS/MCPE.

Parameters affecting the electrode modification

Effect of monomer concentration

The influence of monomer concentration during the electropolymerization of 1-NAM films with certain thickness on the reactivity of the modified electrodes was investigated by varying the concentration of 1-naphtylamine from 5.0 to 25.0 mM. The results obtained for the peak currents related to the electrooxidation of methanol in this condition show that there is an increase in the electrooxidation peak current of methanol when there is an increase in the monomers concentration from 5.0 to about 15.0 mM (Fig. 5). A current decrease can be observed when the higher monomer concentrations are used. This may be attributed in one hand to the lower conductivity and poor electroactivity of thick film and in other hand to the simultaneous formation of some oligomers during the polymerization of 1-naphtylamine in the high concentrations. Thus, the formation of the oligomers affects the morphology of the polymer film, which decreases the amount of nickel particles dispersed in the film and effective surface area of the Ni and influences the poisoning extent of the dispersed nickel particles via the adsorption of some methanol oxidation intermediates.

Effect of cycles number

Electropolymerization offers the possibility of controlling the thickness and homogeneity of the conducting polymer film on the electrode surface. The influence of the cycle numbers for preparation of PNAM films on the electrocatalytic oxidation of methanol was investigated, and the corresponding results are shown in (Fig. 6). Under the condition of constant time of Ni

Fig. 10 **A** Current density-potential curves of 0.5 M HClO$_4$ solution with different concentrations of methanol (*a*) 0.02, (*b*) 0.05, (*c*) 0.075, (*d*) 0.1, (*e*) 0.12, (*f*) 0.15, (*g*) 0.17, (*h*) 0.2, (*i*) 0.22, (*j*) 0.25, (*k*) 0.27, (*l*) 0.3 M at the Ni/SDS-PNAM/MCPE, at = 50 mV s^{-1}. **B** oxidation peak current density on the methanol concentration

electrodepositing, the anodic current rises progressively for the cycle numbers up to 15 cycles and drops afterwards. This implies that the electrocatalysis of methanol oxidation is sensitive to thickness of the polymer films. The increase in the peak current for the cycle numbers up to 15 cycles may be due to the occupation of Ni particles in the pores of polymers with the real sizes. The decrease in anodic peak current for methanol oxidation beyond 15 cycles may be due to the lessening of real surface area of Ni particles and decrease of conductivity by the excessive presence of polymers on the surface of the electrode.

Effect of SDS concentration

In order to study the effect of varying concentration of SDS on methanol electrooxidation, the amount of anodic peak current (I_{pa}) was monitored as the index of finding of optimum concentration. It is evident from Fig. 7 that up to 15.0 mM SDS, I_{pa} increases and drops afterwards. Therefore, we used a concentration of 15.0 mM SDS to prepare the modified electrode.
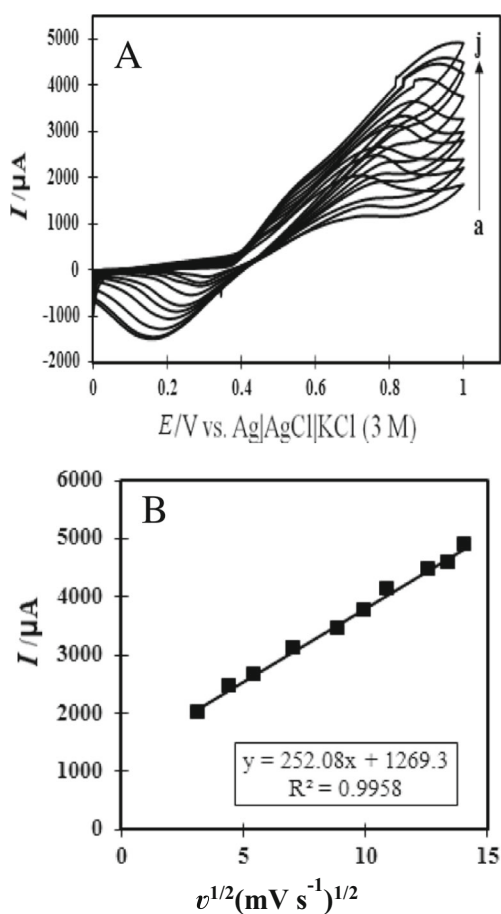
The effect of NiCl$_2$ concentration

The effect of nickel ions concentration was also examined by fixing the deposition time of the electrode in various concentrations of NiCl$_2$ in the alkaline medium, and the peak current density of methanol oxidation in 0.1 M NaOH solution is represented in Fig. 8. This result shows that, the peak height of methanol oxidation increases by increasing the NiCl$_2$ concentration in the alkaline medium up to 1.5 M which no appreciable change was observed in the peak height after 1.2 M. On the basis of this result, one may conclude that deposition the electrode in 1.2 M NiCl$_2$ solution for 420 s is quite enough to saturate the electrode surface by incorporated nickel ions that enhance the methanol oxidation process.

Fig. 11 A Cyclic voltammograms of 0.17 M methanol in 0.1 M NaOH solution at Ni/SDS-PNAM/MCPE at various scan rates: (a)10, (b)20, (c)30, (d)50, (e)80, (f)100, (g)120, (h)160, (i)180, and (j)200 mV s^{-1}, B the variation of I_{pa}.$^{-1/2}$ vs.
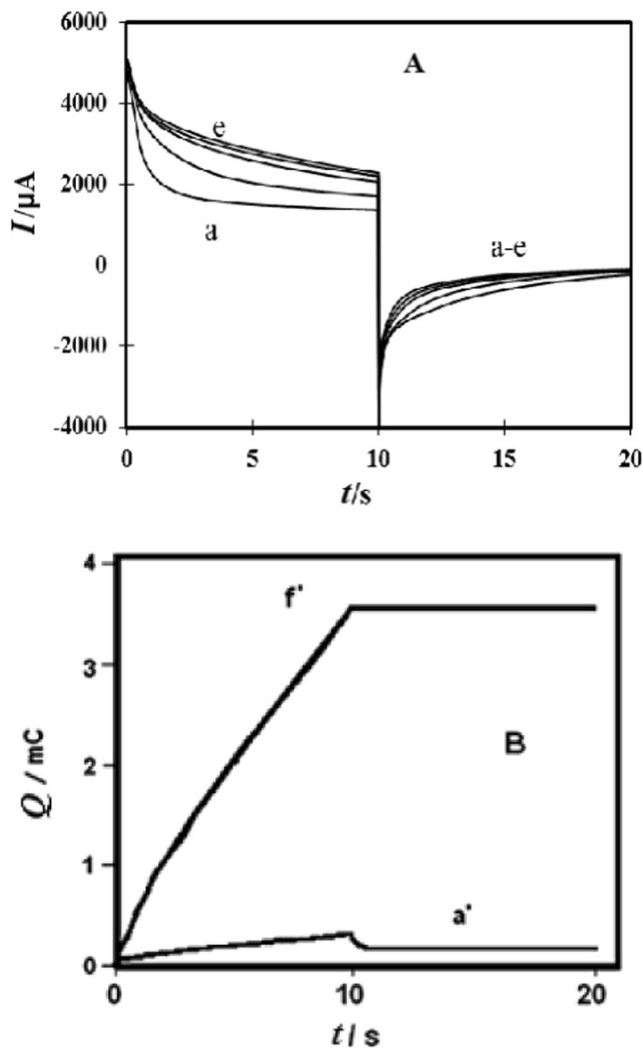

Fig. 12 Chronoamperograms obtained at a Ni/SDS-PNAM/MCPE in the absence (a) and the presence of (b) 0.05 M, (c) 0.1 M, (d) 0.14 M, and (e) 0.2 M of CH$_3$OH. B Dependence of charge Q (mC) vs. t derived from the data of chronoamperograms of a' and f'

Effect of Ni electrodepositing time

The anodic current of methanol oxidation depends on the amount of nickel incorporated in the film. The variation of the anodic peak current, which appear in the positive going scans, as a function of Ni electrodepositing time is given in Fig. 9 (at electrodes with the same thickness of polymers film). As is seen in Fig. 9, I_{pa} increases with increasing time of the Ni electrodepositing in the polymer film up to 7 min and drops afterwards. This observation can be attributed to the saturation of active sites of the electrode surface at higher times. Whereas, at the lower times, the area of Ni particles is increased in proportion to increasing Ni and the electrocatalytic activity of the modified electrodes is enhanced.

Effect of methanol concentration

Figure 10 shows the effect of methanol concentration on the anodic current of methanol oxidation at modified electrodes (Ni/SDS-PNAM/MCPE). It is clearly observed that the anodic current increases with increasing methanol concentration and levels off at concentrations higher than 2.0 M at electrode. We assume this effect may due to the saturation of active sites on the surface of the electrode. In accordance with this result, the optimum concentration of methanol to obtain a higher current density may be considered as about 0.17 M. As seen in this figure, the largest current for a given concentration of methanol was observed on the Ni/SDS-PNAM/MCPE electrode at optimum experimental conditions

Effect of scan rates of potential on the anodic peak current of methanol at modified electrodes

The electrochemical behavior of methanol studied at the surface of Ni/SDS-PNAM/MCPE in 0.1 M NaOH at various scan rates of potential. Figure 11A shows a typical cyclic voltammograms of 0.17 M of methanol at the surface of Ni/SDS-PNAM/MCPE at various scan rates of potential. As can be seen in this figure, the cathodic current would increase with increasing of , because in short time-scale experiments; there is not enough time for the catalytic reaction to take place completely. It can be noted from this figure, with an increasing in the scan rate of potential, the peak potential for the catalytic oxidation of methanol shift to more positive potential, suggesting a kinetic limitation in the reaction between redox sites of Ni/SDS-PNAM/MCPE and methanol. This finding reveals that the heterogeneous oxidation of methanol at the Ni/SDS-PNAM/MCPE is not a rapid reaction. A plot of the scan rate normalized current ($I_{pa}. ^{-1/2}$) vs. scan rate (Fig. 11B) exhibits the shape typical of an EC' process.

Chronoamperometric studies

Double potential step chronoamperometry is employed for the investigation of electrochemical processes at the Ni/SDS-PNAM/MCPE surface. Figure 12 shows the double-step chronoamperograms for the modified electrode by setting the working electrode potential at 0.8 V (first step) and 0.2 V (second step) vs. Ag|AgCl|KCl (3 M) for various concentrations of methanol. In all experiments, the working electrode was immersed in a 0.1 M NaOH solution containing 0.17 M CH_3OH. As can be seen, the forward and backward potential step chronoamperometry of the modified electrode in the blank solution showed an almost symmetrical chronoamperogram with almost equal charges consumed for the oxidation and reduction of surface-confined Ni(II)/Ni(III) sites (Fig. 12b (a')).

However, in the presence of methanol, the charge value associated with the forward chronoamperometry is greater than that observed for the backward chronoamperometry (Fig. 12b (f')).

Table 1 Comparison of the methanol oxidation with some modified electrodes

Electrocatalyst	$C_{Methanol}$ (M)	υ/mV s^{-1}	E_{op} /V	Current density/mA cm$^-$	Ref.
Pd-Ni/GCE[a]	1	50	−0.2	12	[28]
Ni/P(1,5-DAN)/MCPE[b]	0.84	10	0.68	1.4	[1]
Ni/SDS-POAP/CPE[c]	0.1	20	0.8	9.9	[19]
Ni(II)-Qu-MWCNT-CPE[d]	0.4	20	-	4.7	[29]
Cu/P(2ADPA)/MCPE[e]	0.5	10	0.85	46	[30]
Ni/SDS-1-NAM/MCPE	0.17	50	0.8	34.16	This work

[a] Pd/Ni

[b] Ni/poly1, 5diaminonaphthalene

[c] Ni/poly orthoaminophenol

[d] Ni/quercetin

[e] Cu/poly orto amino diphenylamine

Table 1 presents a comparison in terms of current density and onset oxidation potential between the proposed electrode and some available Ni modified electrodes. The results show that the Ni/P1-NAM/SDS/MCPE has good electrocatalytic activity.

Conclusion

In the electrochemical oxidation of methanol, the electrode material is clearly an important parameter where a high efficient electrocatalyst is needed. Because catalysis is a surface effect, the catalyst needs to have the highest possible surface area. For this reason, we have used carbon-supported electrodes as catalyst. In this work, the SDS-PNAM/MCPE was prepared by the electropolymerization of 1-naphtylamine on a carbon paste electrode in the presence of SDS. Addition of SDS to the monomer solution leads to an increase in the polymer growth rate. The electrochemical behavior of P(1-NAM)(SDS)/MCPE shows that, apart from the higher polymerization rate in the presence of SDS, the resulting polymer has good electrical conductivity, which can be due to the different morphology of poly(1-naphtylamine) in the PNAM (SDS)/MCPE. The Ni(OH)$_2$ layer investigated in this study was found very efficient for electrocatalytic effect of Ni particles in the electrooxidation of methanol. The oxidation process commences at a potential where the oxidizing Ni (III) species are generated. The stability of the Ni/SDS-PNAM/MCPE, stored in laboratory atmosphere, is more than 4 months.

References

1. Ojani R, Raoof JB, Zavvarmahalleh SRH (2008) Electrochim Acta 53:2402–2407
2. Jiang C, Chen H, Yu C, Zhang S, Liu B, Kong J (2009) Electrochim Acta 54:1134–1140
3. Zainoodin AM, Kamarudin SK, Daud WRW (2010) Int J Hydrog Energy 35:4606–4621
4. Wang S, Jiang SP, Wang X, Guo J (2011) Electrochim Acta 56:1563–1569
5. Zhang R, Zhang W, Gao L, Zhang J, Li P, Wang W, Li R (2013) Appl Catal A Gen 466:264–271
6. Pan C, Qiu L, Peng Y, Yan F (2012) J Mater Chem 22:13578–13584
7. Leclerc M, Guay J, Dao LH (1989) Macromolecules 22:649–653
8. Yan Z, He G, Zhang G, Meng H, Shen PK (2010) Int J Hydrog Energy 35:3263–3269
9. Martínez S, Martins ME, Zinola CF (2010) J Hydrog Energy 35:5343–5355
10. Lamy C, Belgsir EM, Leger JM (2001) J Appl Electrochem 31:799–809
11. El-Deab MS (2009) Int J Electrochem Sci 4:1329–1338
12. Habibi B, Pournaghi-Azar MH, Razmi H, Abdolmohammad-Zadeh H (2008) Int J Hydrog Energy 33:2668–2678
13. Wang J (2006) Analytical electrochemistry. Wiley, New York
14. Fathi S, Mahdavi MR (2014) Russ J Electrochem 50:1077–1084
15. Ojani R, Raoof JB, Babazadeh R (2010a) Electroanalysis 22:1607–1616
16. Entezami AA, Golabie SM, Raoof JB (1992) Iran J Polym Sci Technol 1:7
17. Ojani R, Raoof JB, Salmany-Afagh P (2004) J Electroanal Chem 571:1–8
18. Ojani R, Raoof JB, Zamani S (2010b) Talanta 81:1522–1528
19. Ojani R, Raoof JB, Fathi S (2009) Electrochim Acta 54:2190–2196
20. Barr GE, Sayre CN, Connor DM, Collard DM (1996) Langmuir 12:1395–1398
21. Bazzaoui EA, Aeiyach S, Lacaze PC (1996) Synth Met 83:159–165
22. D'Eramo F, Marioli JM, Arévalo AA, Sereno LE (1999) Electroanalysis 11:481–486
23. Casella IG, Cataldi TR, Guerrieri A, Desimoni E (1996) Anal Chim Acta 335:217–225
24. Jafarian M, Mahjani MG, Heli H, Gobal F, Heydarpoor M (2003) Electrochem Commun 5:184–188
25. Oliva P, Leonardi J, Laurent JF, Delmas C, Braconnier JJ, Figlarz M, De Guibert A (1982) J Power Sources 8:229–255
26. Robertson PM (1980) J Electroanal Chem Interfacial Electrochem 111:97–104
27. Raoof JB, Jahanshahi M, Ahangar SM (2010) Int J Electrochem Sci 5:517–530
28. Qiu C, Shang R, Xie Y, Bu Y, Li C, Ma H (2010) Mater Chem Phys 120:323–330
29. Zheng L, Zhang JQ, Song JF (2009) Electrochim Acta 54:4559–4565
30. Ojani R, Raoof JB, Ahmady-Khanghah Y (2011) Electrochim Acta 56:3380–3386