Highly improved methanol oxidation onto carbon paste electrode modified by nickel particles dispersed into poly (2,5-dimethylaniline) film

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Abstract: In this work, modification of carbon paste electrode surface with poly (2, 5-Dimethyl aniline) (P-2,5-DMA) by using electrochemical polymerization was described. Then, transition metal ions of Ni(II) were incorporated into the polymer film by two ways. At first way, the polymeric modified electrode was immersed in 0.2 M $NiSO_4$ solutions and the second way was carried out by electrodeposition of Ni from acidic $NiSO_4$ solution by using potentiostatically technique. The electrochemical characterization of both modified electrodes exhibit stable redox behavior of the Ni(III)/Ni(II) couple in NaOH solution. The results show that the Ni/P-2,5-DMA films prepared by electrodeposition route behaves as better electrocatalysts methanol oxidation in 1.0 M NaOH solution with respect to Ni/P-2,5-DMA prepared by accumulation of Ni(II) ions from the solution.

1. Introduction

Quantitative determination of methanol is of great interest in food, fermentation and wine industries as well as in clinical chemistry. Methanol is a notorious ingredient illegally used in the production of imitated spirits and wines. Intake of methanol will result in severe intoxication due to accumulation of toxic metabolites such as formic acid and formaldehyde [1]. In addition, methanol is one of the interesting future fuels for fuel cell applications. Compared with other fuel cells, direct methanol fuel cells (DMFCs) has several advantages such as high efficiency, very low polluting emissions, a potentially renewable fuel source and fast and convenient refueling. On the

other hand, the slow kinetics of methanol is one of the unsolved problems in development of the DMFCs [2] and represents a serious impediment in the use of electrochemical methods, based on the direct oxidation of this molecule on the electrode with analytical purposes. Thus, a large number of investigations have been carried out to diminish typically large overpotentials encountered in the direct oxidation of methanol at most unmodified electrode surfaces [3-6] or at chemically modified electrodes.

In the electrochemical oxidation of methanol, electrode material is clearly an important parameter where a high efficient electrocatalyst is needed. A considerable increase in power density and fuel utilization can be obtained by optimizing different components of fuel cells. Different electrode materials based on Pt [4] and Pt-binary electrodes [7], Pt-Ru and Pt-Ru-P/carbon nanocomposite [8], Pt/Ni and Pt/Ru/Ni alloy nanoparticles [9] were commonly used as catalysts for the electrochemical oxidation of methanol. It is well established that nickel can be used as a catalyst due to its surface oxidation properties. Many electrodes involving nickel as a component in their manufacture can be used as catalyst in fuel cells. It is commonly used as an electrocatalyst for both anodic and cathodic reactions in organic synthesis and water electrolysis [10-13]. One of very important uses of nickel as a catalyst is for the oxidation of alcohols. Several studies of the electrooxidation of alcohols on nickel have been reported [14,5]. Nickel-based electrodes obtained by chemisorptions of nickel oxide/hydroxide on glassy carbon have demonstrated long-term stability in alkaline solutions and excellent capability to catalyze the oxidation of organic molecules [15,16]. The high valence species of nickel seems to act as strong

oxidizing agents for low-electroactivity organic substrates. On the other hand, conducting polymers, a new class of electrode materials, are of considerable interest in the field of electrocatalysis. The polymers used are mainly polyaniline, polypyrrole and polythiophene [17-19]. These polymers offer great advantages due to their very good conducting and mechanical properties and the good adhesion to electrode substrate. Also, a significant way to get electrocatalyst with towering performance and low price is to disperse these compounds onto the supporters such as carbon. Finding an appropriate electrode material will be essential for financial reasons. Carbon paste is a promising material for DMFC due to its advantages.

Previously, we have reported that the poly (1,5-Diaminonaphtalene)/nickel modified carbon paste electrode display catalytic activity towards methanol oxidation [20]. Indeed, it is remarkable and important to find new supports for fuel cell applications. In this way, the use of conducting polymer as poly (2,5-Dimethylaniline) film for enhanced the activity of Ni particles is very interesting. In this work, we report the electrooxidation of methanol in alkaline medium solution by using two methods of nickel incorporation on CPE modified by P-2,5-DMA film. This polymeric modified electrode containing nickel can oxidize the methanol with high current density. Thus, it can be a candidate as an anode for DMFCs.

2. Experimental

2.1. Reagents and materials

The solvent used in this work was distilled water. Sulfuric acid (Fluka) was used as supporting electrolyte. The 2,5-Dimethylaniline (Fluka) was used as a monomer. Sodium hydroxide and methanol were analytical grade of Merck origin and used

without further purification. Graphite powder (particle diameter: 0.1 mm, Merck) was used as a working electrode substrate. High viscosity paraffin (density: 0.88 g cm^{-3}, Fluka) was used as pasting liquid for carbon paste electrode.

2.2. Working electrode

A 1:1 (w/w) 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 glass tube. The internal radius of glass tube for preparation of carbon paste electrode was 1.7 mm. The electrical connection was implemented by copper wire lead fitted into the glass tube.

2.3. Instrumentation

The electrochemical experiments were carried out using potentiostat/galvanostat (BHP 2063-C Electrochemical Analysis system, Behpajooh, Iran) coupled with a Pentium IV personal computer. A platinum wire was used as an auxiliary electrode. The carbon paste electrode and Ag│AgCl│KCl (3 M) (Azar electrode co., Iran) were used as working and reference electrodes, respectively. All potentials reported in this work were referenced to the Ag|AgCl|KCl (3 M).

3. Results and discussion

3.1. Preparation of poly (2,5-Dimethylaniline) modified carbon paste electrode (P-2,5-DMA/MCPE)

Previously, poly (2,5-Dimethylaniline) (P-2,5-DMA) films were prepared at the surface of Pt, LCS (Low Carbon Steel), LS (Langmuir-Scahefer) film on ITO glass plate by using cyclic voltammetry method [21-

23]. In this work, electropolymerization at the surface of carbon paste electrode (CPE) by using consecutive cyclic voltammetry (25 cycles) between 0.0 and 1.0 V at v=50 mV s^{-1} was performed in sulfuric acid solution containing 20 mM 2,5-Dimethylaniline. Figure 1 typically shows 10 cycles in 0.5 M H$_2$SO$_4$ solution. On the first positive potential sweep, 2,5-DMA is oxidized with an irreversible peak at about 0.90 V. On the negative sweep, this wave does not show a complementary peak, indicating the existence of very fast follow-up chemical reaction but appears a new redox peak and two shoulders at lower than 0.90 V related to the polymer formed on the electrode surface.
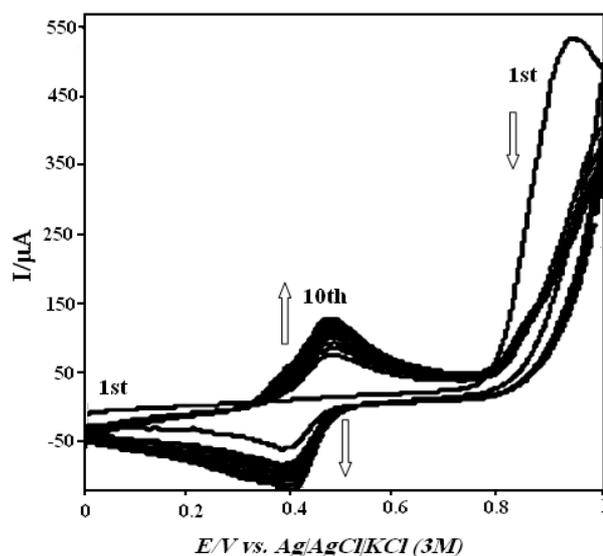
Fig. 1. Cyclic voltammograms of 20 mM 2,5-DMA in a 0.5 M H$_2$SO$_4$ solution at the surface of CPE at v= 50 mV s^{-1}.

After this, the electrode was removed and rinsed with water. The redox behavior of the film was strongly dependent on pH of the electrolyte solution [21].
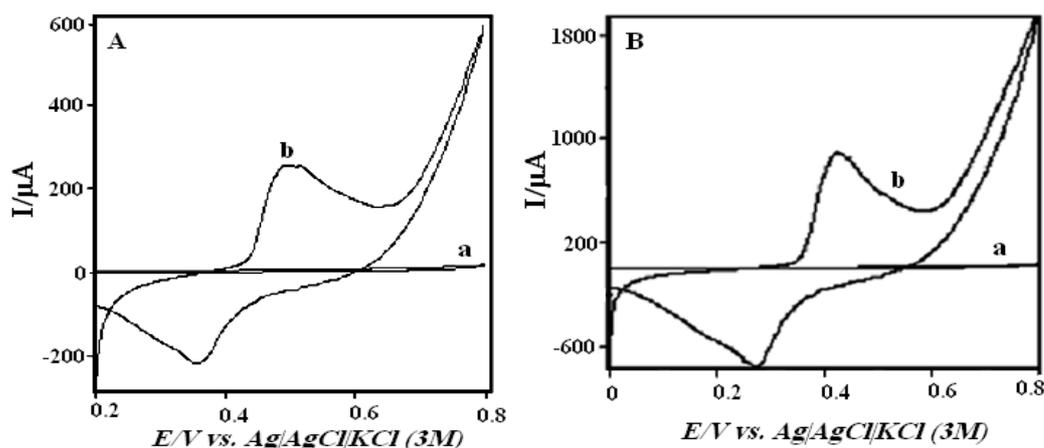
Fig. 2. (A) Electrochemical responses of: (a) P-2,5-DMA/MCPE and (b) accumulated Ni/P-2,5-DMA/MCPE after anodic polarization in 1.0 M NaOH solution at $v= 50$ mV s^{-1}. (B) Electrochemical responses of: (a) P-2,5-DMA/MCPE and (b) microparticle Ni/P-2,5-DMA/MCPE after anodic polarization, in 1.0 M NaOH solution at $v= 50$ mV s^{-1}.

According to our experiment, the obtained polymer shows a well-defined redox behavior in acidic supporting electrolyte. The response obtained in an alkaline solution e.g. 0.1 M NaOH showed a complete loss of the electrode activity in the potential range from 0.0 to 0.8 V. However, the film was not degraded under these experimental conditions and its response was recovered when the electrode was immersed in an acidic supporting electrolyte solution.

3.2. Incorporation of nickel on the P-2,5-DMA film

In order to incorporate the Ni into/onto the P-2,5-DMA film, we have used two different methods. At first, the freshly prepared P-2,5-DMA/MCPE was placed in a well-stirred solution of 0.2 M NiSO$_4$ at open circuit condition. Accumulation of nickel ions was carried out by complex formation between Ni(II) and amines sites in the polymer backbone, for a given period of time (accumulation time). Secondly, we dispersed nickel particles into the polymer backbone by electrodeposition method. Usually, the metal

electrodeposited into the polymer matrix appears as microparticles dispersed in a three-dimensional array confined to the organic film [24]. The electrodeposition of nickel was performed in a solution composed of 1.0 M NiSO$_4$ + 1.0 M H$_2$SO$_4$ by potentiostatically technique at -1.0 V vs. Ag│AgCl │KCl (3M) for 17 min. After the preparation of Ni microparticles on the P-2,5-DMA/MCPE, no further pretreatment of the electrode was necessary to avoid any changes in the substrate surface.

3.3. Electrochemical behavior of Ni(II)-P-2,5-DMA modified carbon paste electrode (Ni/P-2,5-DMA/MCPE)

Figure 2A shows the electrochemical response of the P-2,5-DMA/MCPE, and a freshly prepared Ni/P-2,5-DMA/MCPE after anodic polarization in 1.0 M NaOH solution. From this figure, it can be seen that whereas neither oxidation nor reduction took place on the P-2,5-DMA/MCPE, a well-developed redox pair was cycled between 0.2 and 0.8 V, which was related

to the oxidation peak of Ni(II) to Ni(III) with a peak potential of 0.49 V and reduction of Ni(III) to Ni(II) with a peak potential of 0.35 V. Also, it should be noticed that by electrodeposition of nickel in the P-2,5-DMA/MCPE, the anodic and cathodic peak potentials shifted to more negative directions with an enormous increase in peak currents (Fig. 2B). The surface coverage of the immobilized active substance (Ni(II)) in two films can be evaluated from the charge under the current-potential waves ($\Gamma = Q/nFA$). The value of Γ for the accumulated Ni/P-2,5-DMA/MCPE was approximately 4.8×10^{-8} mol cm^{-2} and for the microparticle Ni/P-2,5-DMA/MCPE was about 1.75×10^{-7} mol cm^{-2}. In order to test the influence of OH$^-$ concentration on the modified electrode behavior, the

electrochemical response of the microparticle Ni/P-2,5-DMA/MCPE was studied in the solutions with different pHs (different OH$^-$ concentrations) in the range from 12 to 14. It can be seen from Fig. 3A that by increasing hydroxide concentration, peak-to-peak potential separation (ΔE_p) decreases. From these results, it is understood that the diffusing species is the OH$^-$ that maintains the charge balance. The half-wave potential of the Ni(II)/Ni(III) redox couple shows a linear dependency on the pH with a slope of 0.085 V/pH (Fig. 3B). According to these results, one can affirm that the electrochemical behavior exhibited by the microparticle Ni/P-2,5-DMA/MCPE is quite similar to those previously observed by other authors for nickel hydroxide films [25-27].
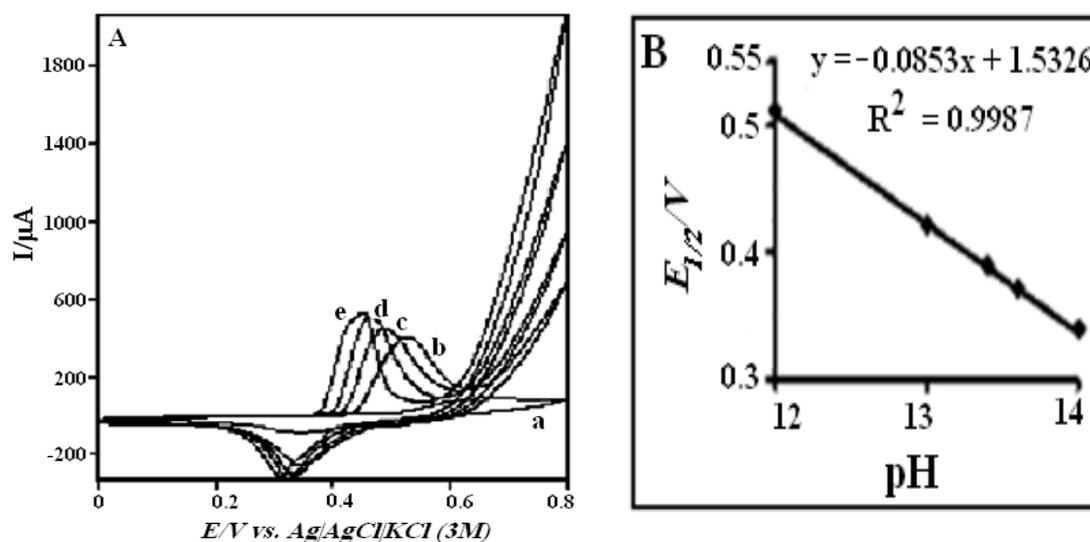
Fig. 3. (A) Cyclic voltammetric responses of the microparticle Ni/P- 2,5-DMA/MCPE conditioning at different pHs: (a) 12.0; (b) 13.0; (c) 13.4; (d) 13.6 and (e) 14.0 at v= 50 mV s^{-1}. (B) Plot of $E_{1/2}$ versus pH in the range of 12-14.

On the other hand, the theory predicts that the voltammetric behavior of an electrode modified with a monolayer of both chemically and electrochemically reversible system is characterized

by symmetrical anodic and cathodic peaks with ΔE_p close to zero and peak currents proportional to the potential scan rate. The electrodes modified with an electroactive film such as Ni/P-2,5-DMA/MCPE can

present some deviations from the normal behavior, indicating the presence of some mass transfer limitations towards the film. Figure 4A shows the cyclic voltammograms obtained for the

electrodeposited Ni/P-2,5-DMA/MCPE in 1.0 M NaOH solution at different potential potential scan rates in ranges 5-800 mV s^{-1}.
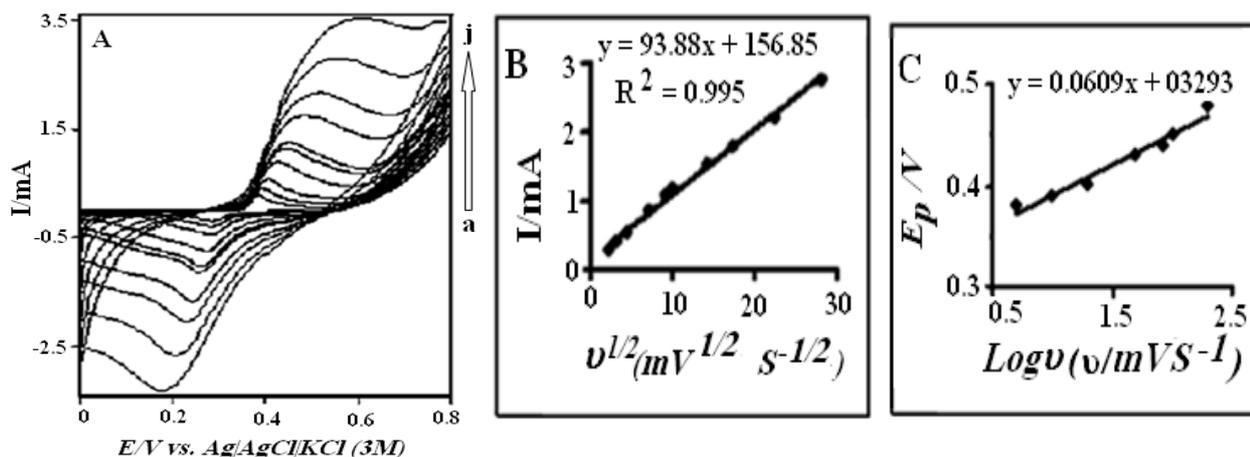
Fig. 4. (A) Scan rate dependence of the peak current for the microparticle Ni/P-2,5-DMA/MCPE, scan rates: (a) 5; (b) 10; (c) 20; (d) 50; (e) 80; (f) 100; (g) 200; (h) 300; (i) 500 and (j) 800 mV s^{-1}. (B) Plot of I_p vs $v^{1/2}$. (C) Plot of E_p vs log v.

As can be seen, the anodic peak potentials shift to more positive values with increasing of potential scan rate, while the cathodic peak potentials shift to more negative directions. In addition, the peak currents present a linear dependency with the square root of the scan rate (Fig. 4B). The linear dependence of the I_p with $v^{1/2}$ can be explained if we consider that the charge transfer is limited by the diffusion of OH$^-$ ions towards the film. Also, the value of electron transfer coefficient for the reaction can be obtained from the following equation which is valid for an irreversible diffusion-controlled process [28].

$$E_p = (RT/2\alpha F) \ln v + constant = (b/2) \log v + constant$$

Using the dependency of anodic peak potential on the logarithm of the potential sweep rate (Fig. 4C), the slope of E_p versus log v is 0.06 V, so, b=2×0.06=0.12 V. This slope indicates an one-electron transfer to be rate limiting step, assuming a transfer coefficient of α=0.49. We also carried out the same experiments for the accumulated nickel in the P-2,5-DMA film and the transfer coefficient (α) was equal to 0.52.

3.4. Electrocatalytic oxidation of methanol on the modified electrode

In this part, we observed an good catalytic activity for the nickel particles electrochemically deposited on the P-2,5-DMA film. Also, we found out that the Ni microparticles in the P-2,5-DMA/MCPE shows high catalytic activity towards methanol oxidation with respect to the Ni accumulated in the P-2,5-DMA

film. Figure 5(b) shows the cyclic voltammograms of the microparticle Ni/P-2,5-DMA/MCPE in the absence of methanol in 1.0 M NaOH solution which exhibits well-defined anodic and cathodic peaks associated with the Ni(II)/Ni(III) redox couple and oxygen evolution reaction at about 0.70 V. Figure 5(a) shows the behavior of the electrode in the presence of 0.4 M methanol. An increment in the anodic peak current for peak (P_{aI}) followed by the appearance of a new peak (P_{aII}) at more positive potential and a decrease of the cathodic peak (P_{cI}) during the reverse scan are the main effects observed upon the addition of 0.4 M of methanol to the supporting electrolyte.
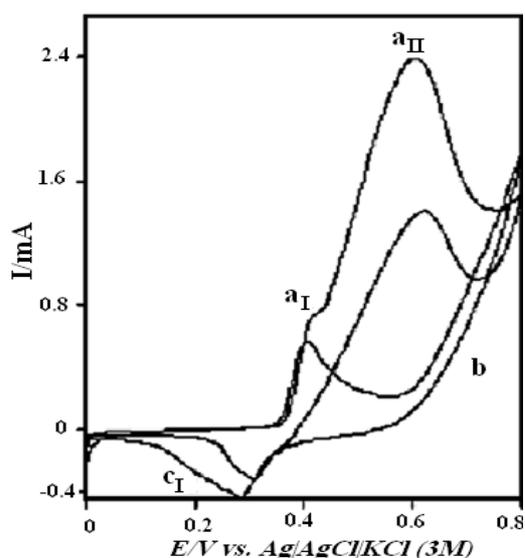
Fig. 5. Electrochemical response of the microparticle Ni/P- 2,5-DMA/MCPE in 1.0 M NaOH solution at v=20 mV s^{-1}to: (a) 0.4 M; (b) 0.0 M methanol.

The carbon paste electrode modified with the microparticle Ni/P-2,5-DMA presents electrocatalytic activity towards methanol oxidation in 1.0 M NaOH solution. The electrooxidation process takes place in two different regions of potential. The first one corresponds to the oxidation of Ni(II) to Ni(III) and appears as a sharp peak at 0.40 V (P_{aI}). At this potential, methanol oxidation appears as an increase in P_{aI} accompanied by a decrease in cathodic peak current in the negative sweep (an EC$'$mechanism).

$$Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \qquad fast$$
$$NiOOH + CH_3OH \rightarrow Ni(OH)_2 + product \qquad slow$$
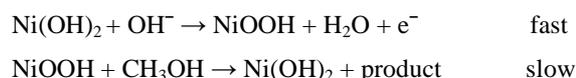
The relative decrease of the cathodic peak height in the presence of methanol is attributed to the partial consumption of nickel oxy-hydroxide species for methanol oxidation with formation of the nickel hydroxide. It is generally agreed that the Ni-based catalysts in a basic medium can catalyze methanol oxidation through an overall four electron process producing formate anion:

$$CH_3OH + 5OH^- \rightarrow HCOO^- + 4H_2O + 4e^-$$

This result clearly suggests an interaction between methanol and film redox centers confined at the electrode surface. At the second region of potential, a new catalytic wave (a_{II}) with a peak potential of 0.60 V and a significantly large peak current appears. This peak current increases linearly with methanol concentration suggesting that this is the region of potential in which the methanol is involved in the oxidation process. The appearance of the new anodic peak (a_{II}) at more positive potentials can lead to the conclusion that methanol oxidation takes place mainly after oxidation of Ni(II) to Ni(III) [29, 30].
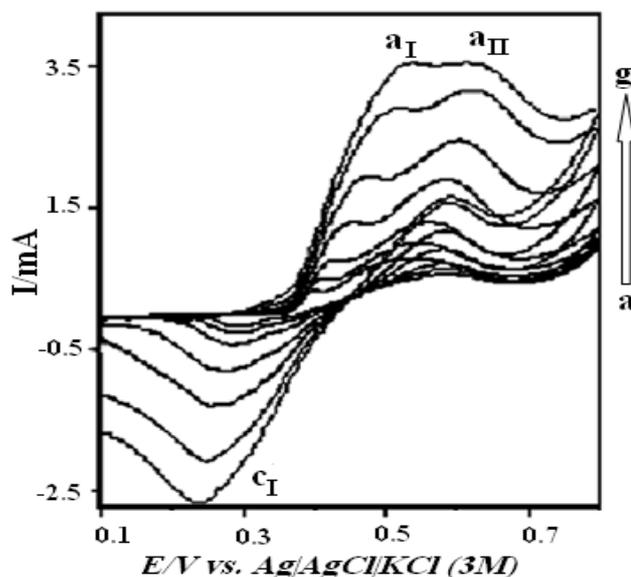
Fig. 6. Cyclic voltammograms of the microparticle Ni/P-2,5-DMA/MCPE in the presence of 0.2 M methanol in 1.0 M NaOH solution at v: (a) 5; (b) 10; (c) 20; (d) 50; (e) 100; (f) 200 and (g) 300 mV s^{-1}.

On the other hand, there is a separation of Ni(II)/Ni(III) oxidation peak from methanol oxidation peak. On the basis of this observation, the catalytic role of Ni(III) for methanol oxidation is obvious as proposed previously by Fleischmann et al. [5].

3.5. Effect of scan rate on the electrocatalytic oxidation of methanol

The effect of scan rate on the peaks current may contribute to give information about the electron-transfer kinetics. Figure 6 shows the cyclic voltammograms obtained when the microparticle Ni/P-2,5-DMA/MCPE is immersed in solution containing 0.2 M methanol + 1.0 M NaOH and the potential was swept at different scan rates. As can be seen, the methanol oxidation peak current (I_{paII})

decreases rapidly when the scan rate increases. However, the peak current corresponding to the oxidation of Ni(II) increases with increasing of the potential scan rate suggesting that the Ni(II)/Ni(III) transformation is much faster than the methanol oxidation on the Ni/P-2,5-DMA film. The decrease of the I_{paII} by increasing of the potential scan rate can be attributed to the decrease of time window for the ffective occurrence of the catalytic reaction between methanol and the nickel oxy-hydroxide species.

3.6. Effect of methanol concentration

Figure 7A (b-l) shows the cyclic voltammograms obtained when the microparticle Ni/P-2,5-DMA/MCPE was placed in 1.0 M NaOH solution with increasing of methanol concentration in the range of 0.022 - 1.02 M at v=20 mV s^{-1}.
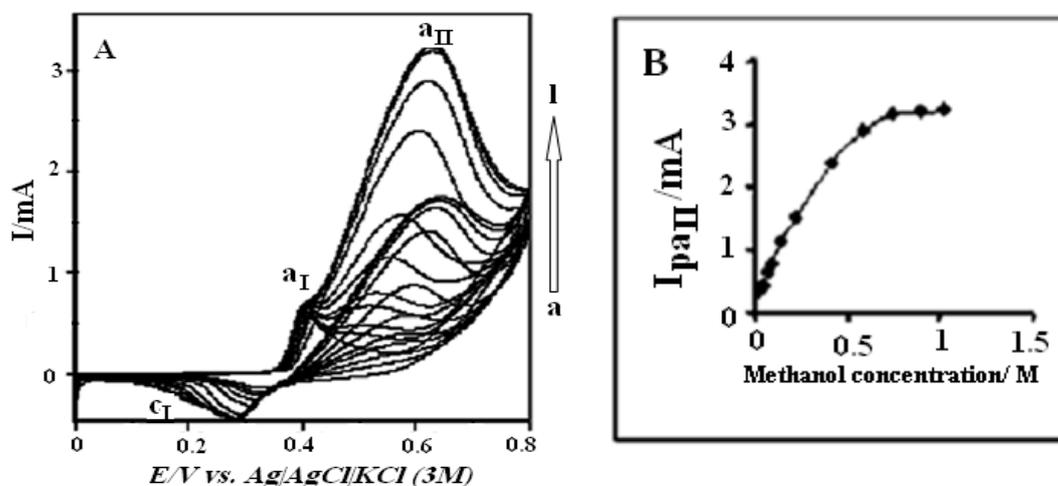
Fig. 7. (A) Current-potential curves of the microparticles Ni/P-2,5-DMA/MCPE for electrocatalytic oxidation of methanol at v=20 mV s^{-1} in 1.0 M NaOH solution with different methanol concentrations: (a) 0.0 M; (b) 0.022 M; (c) 0.045 M; (d) 0.067 M; (e) 0.089 M; (f) 0.132 M; (g) 0.216 M; (h) 0.41 M; (i) 0.585 M; (j) 0.744 M; (k) 0.888 M and (l) 1.02 M respectively. (B) Represents the dependency of methanol oxidation peak current on concentration.

Figure 7A (b-l) shows the cyclic voltammograms obtained when the microparticle Ni/P-2,5-DMA/MCPE was placed in 1.0 M NaOH solution with increasing of methanol concentration in the range of 0.022 - 1.02 M at v=20 mV s^{-1}. These curves reveal that the first anodic wave (a$_I$) shows a slight anodic shift in the peak potential concomitant with a gradual decay in the peak current which practically disappears at methanol concentration higher than 0.2 M. In addition, catalytic peak current (a$_{II}$) increase graduate. At low methanol concentrations, an anodic peak shift and peak current decrease was observed followed by disappear of the wave when the methanol concentration was higher than 0.2 M. In addition, the catalytic peak current (a$_{II}$) shows linear increase with the methanol concentration up to 0.6 M (Fig. 7B). This linear increase indicates that at low methanol concentration the catalytic process is controlled by a diffusion process. After 0.6 M, they

reach almost constant values independent of the concentration. At higher concentrations probably all the NiOOH catalytic centers present in the film, generated by the previous electrochemical oxidation of Ni(II), are interacting with methanol and the limiting step of the process is the rate of such interactions. This fact can explain the total disappearance of the a$_I$ and c$_I$ waves at high concentrations.

When we use the accumulated nickel in the P-2,5-DMA/MCPE as catalyst for methanol oxidation, the critical concentration was 0.1 M and a gradual decay in the peak current (a$_I$) occurs at concentration higher than 0.6 M. Also, with tantamount of methanol concentration, peak current for methanol oxidation by the nickel deposited in polymeric film is about 5 times greater than the accumulated nickel. The electrocatalytic oxidation of methanol at the electrodes modified with electropolymerized nickel

complexes, nickel electrode and polymeric film modified by nickel ions in alkaline media has been extensively studied [20,31,32]. In comparison with the previous works, it seems clearly that the microparticle Ni/P-2,5-DMA/MCPE can act as a better catalyst in methanol electrooxidation and peak current obtained by the nickel deposited in the polymeric film is significantly higher than what

previously observed by other authors and us (Table 1). Notably, comparison of the anodic peak current for methanol oxidation at the low cost modified electrode (I_P=1.13 mA) shows that this value is higher than that our previous work and comparable with the precious metal (i.e., Pt) modified electrodes. Besides, the surface modification is very simple and reproducible compared those other electrodes.

Table 1
Comparison of the efficiency of some modified electrodes used in the electrocatalysis of 0.1 M methanol in alkaline medium

Electrode	Modifier	I_p (mA)	scan rate (mV s^{-1})	Reference
Glassy carbon	Ni(II)-DHS	0.35	20	[33]
Nickel	NiODMG	0.25	20	[34]
Carbon paste	Ni/P-1,5-DAN	0.07	10	[20]
Carbon paste	Ni/P-2,5-DMA	1.13	20	present work

3.7. Chronoamperometry and chronocoulometry studies

Chronoamperometry was employed for investigation of the electrode process at chemically modified electrodes [33]. Figure 8A shows well-defined chronoamperograms of the microparticle Ni/P-2,5-DMA/MCPE in the (a) absence and presence (b-e) of methanol at applied potential steps of 0.70 V and 0.25 V for the forward and backward chronoamperometry, respectively. The forward and backward potential step chronoamperometry of the modified electrode in the blank solution showed an almost equal charges consumed for oxidation and

reduction of the surface confined Ni(II)/Ni(III) sites. Figure 8B shows the corresponding chronocoulograms of the fig. 8A. As can be seen from fig. 8B, the modified electrode in the absence of methanol exhibits a chronocoulogram with an almost equal charge for oxidation (Q_f) and reduction (Q_b) of the surface-confined Ni/P-2,5-DMA sites. However, in the presence of methanol, the Q_b is dramatically smaller than that the Q_f and tended to negligible values as the concentration of methanol increased. This behavior is typical of that expected for a mediated oxidation.
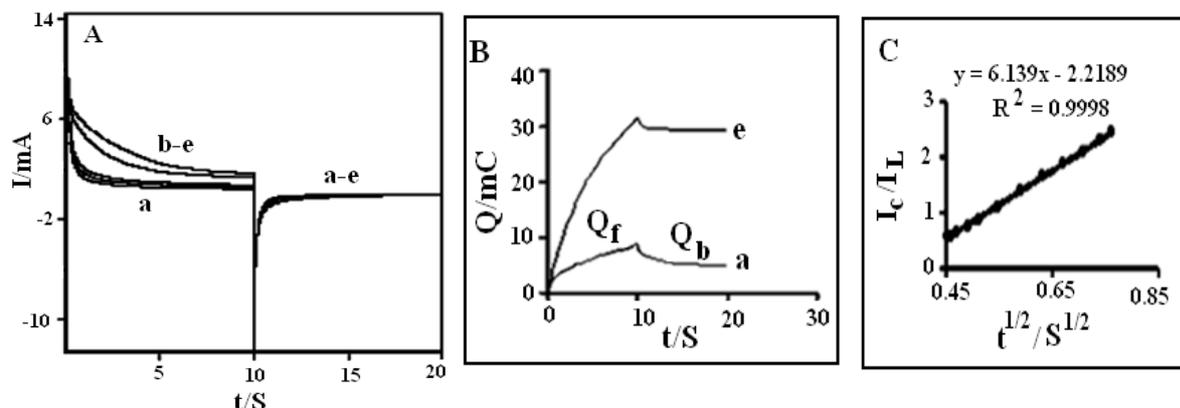
Fig. 8. (A) Chronoamperograms obtained for the microparticle Ni/P-2,5-DMA/MCPE in the (a) absence and presence of (b) 0.132 M; (c) 0.216 M; (d) 0.585 M and (e) 0.744 M of methanol. (B): Chronocoulograms obtained for the Ni/P-2,5-DMA/MCPE in (a) absence and (b) presence of 0.744 M methanol, derived from the chronoamperograms of part A. (C) Dependency of the I_c/I_L on $t^{1/2}$ derived from the data of chronoamperograms of part A.

Chronoamperometry was employed to investigate the electrode process at the modified electrode. The rate constant for the chemical reaction between methanol and redox sites of the microparticle Ni/P-2,5-DMA/MCPE can be evaluated by chronoamperometry according to the method described in the literature [34];

$$I_C/I_L = \gamma^{1/2}[\pi^{1/2} \, erf \, (\gamma^{1/2}) + exp \, (-\gamma)/\gamma^{1/2}]$$

Where I_C is the catalytic current of the Ni/P-2,5-DMA/MCPE in the presence of methanol, I_L is limiting current in the absence of methanol and $\gamma = kc_0t$ (c_0 is the bulk concentration of methanol) is the argument of the error function. In the case where γ exceeds 1.5, the erf ($\gamma^{1/2}$) is almost equal to unity and the above equation can be reduced to:

$$I_C/I_L = \gamma^{1/2} \, \pi^{1/2} = \pi^{1/2} \, (kc_0t)^{1/2}$$

Where k, c_0 and t are the catalytic rate constant (M^{-1} s^{-1}), methanol concentration (M), and elapsed time

(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 methanol. Figure 8C shows a such plot, constructed from the chronoamperogram of the microparticle Ni/P-2,5-DMA/MCPE in the absence and presence of 0.58 M methanol. The mean value for k was found to be 12.8 M^{-1} s^{-1} and during these experiments we reach the amount of 6.3 M^{-1} s^{-1} for the accumulated Ni/P-2,5-DMA/MCPE.

3.8. Long-term stability

The stability of the microparticle Ni/P-2,5-DMA/MCPE was studied by cyclic voltammetry for 1.0 M NaOH solution containing methanol. Our investigations indicate that this modified electrode exhibit well-defined cyclic voltammograms even after high numbers of cycles. So that, after 100 continuous cycles the electrode still retained near 90% of its initial current response to methanol oxidation but for the accumulated Ni/P-2,5-DMA/MCPE this amount is near 75%.

4. Conclusion

This work presents the advantageous features of carbon paste technology, polymer modification and dispersion of metallic particles into an conducting polymer. A novel electrode has been described herein consisting of nickel loaded into the poly (2,5-Dimethylaniline) modified carbon paste electrode, by two methods: (i) immersion of the polymeric modified electrode in a nickel sulfate solution and (ii) electrodeposition.

In both methods, the modified electrode only represent a redox activity that can be ascribed to the Ni(II)/Ni(III) couple. In the alkaline medium, the formed [NiOOH] present a potent and persistent electrtocatalytic activity towards methanol oxidation, but the electrodeposited nickel shows strongly higher electrocatalytic activity toward oxidation with respect to the accumulated nickel. At low methanol concentrations, the rate of the catalytic process is controlled by diffusion while at higher concentrations; the reaction is governed by kinetic of the interaction between alcohol and the oxidized nickel catalytic centers present in the film. Current-transient technique was employed to investigate the electrode process at the modified electrode for methanol oxidation. Higher rate constant was obtained in the electrodeposited electrode for the chemical reaction between methanol and redox sites of the microparticle Ni. These modified electrode exhibit well-defined cyclic voltammograms even after high number of cycles due to high stability of the electrodes in alkaline medium.

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