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Nickel Particles Dispersed into Poly (*o*-anisidine) and Poly (*o*-anisidine)/Multi-walled Carbon Nanotube Modified Glassy Carbon Electrodes for Electrocatalytic Oxidation of Methanol

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Poly (*o*-anisidine) (POA) and poly (*o*-anisidine) / multi-walled carbon nanotube (POA/MWCNT) films prepared upon glassy carbon electrode. Ni (II) is dispersed into POA and POA/MWCNT modified glassy carbon electrode by immersion of the modified electrode in nickel ions solution and used for electrooxidation of methanol in 0.1 M NaOH solution. The results demonstrate that each Ni-POA and Ni-POA/MWCNT modified glassy carbon electrodes behave as an efficient electrocatalyst for the electrooxidation of methanol in alkaline solution. The electrochemical behavior of methanol studied at the surface of Ni-POA and Ni-POA/MWCNT modified glassy carbon electrodes by cyclic voltammetry and chronoamperometry techniques. Combination of POA with MWCNT would offer an attractive support material based on morphological modification and electronic interaction between two components of films onto electrode. The electron transfer coefficient of methanol is determined herein on this two modified electrode by cyclic voltammetry. The generic application of carbon nanotube for electrocatalytic oxidation of methanol is discussed.

Keywords: Multi-walled carbon nanotube; Methanol; Electrooxidation; Poly (*o*-anisidine); Alkaline solution; Glassy carbon electrode

1. INTRODUCTION

Fuel cells are being considered as an important technology that can be used for various power applications. It is an attractive device to obtain directly electric energy from the combustion of a chemical product. In direct methanol fuel cells (DMFCs), methanol is used as a fuel. It is electrochemically oxidized at the anode containing electrocatalyst to produce electrons which travel through the external circuit to the cathode with electrocatalyst, where they are consumed together with oxygen in a reduction reaction. 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 [1, 2].

Pt and Pt-Ru electrodes have been reported to be most active for anodic oxidation of methanol in acidic medium [3-5]; they are too expensive for commercial applications. It is well known that some intermediates of this reaction are strongly adsorbed at the surface of electrode and leading to a loss of its electrocatalytic activity. Therefore, their activity is not satisfactory high [6-8]. On the other hand, the electrooxidation of methanol has large overpotential at the surface of ordinary electrodes. One promising approach for minimizing of overvoltage effects is in carrying out the electrocatalytic process at chemically modified electrodes.

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 [9-14]. This new class of electrode material has been found to improve the electrode sensitivity and selectivity, and to reduce fouling effects in many applications [15, 16]. Electropolymerization offers the advantage of reproducible deposition in terms of film thickness and loading, making the immobilization procedure of a nickel-based electrocatalyst very simple and reliable [17].

However, metal particles dispersed into conducting polymer support, not only provide access to large number of catalytic sites, but also offer the possibilities of spent catalyst recovery. Lamy and Co-workers first studied Pt micro particles deposition on polyaniline film for methanol oxidation by electrolysis at constant potential using acidic hexachloroplatinate solutions [18].

On the other hand, some new attempt have been recently made to design and synthesize of conducting polymer/carbon nanotube composite materials for various target applications namely electrochemical devices, light-emitting diodes, chromatography, electrostatic discharge protection and corrosion protecting paint [19-21].

Carbon nanotubes possess many special properties such as high electrical conductivity, high chemical stability as well as extremely high mechanical strength and modulus. They are of special interest due to their unique electronic, metallic and structural characteristic [22]. Both single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) have the ability to promote electron transfer reactions when used as an electrode material in electrochemical reactions [23, 24]. For instance, a composite made from SWCNTs and polyaniline (PANI) were synthesized through chemical routes and has been used as printable conductors for organic electronic devices [25]. The electrooxidation of methanol discussed on the Pt particles dispersed into PANI/SWNT composite film [26].

To the best of our knowledge, there have been no reports on the use of POA and POA/MWCNT film onto a glassy carbon electrode (GCE) as a supporting material in the electrocatalytic oxidation of methanol. Therefore, we prepared POA and POA/MWCNT modified GCE (POAMGCE, and POA/MWCNT/MGCE, respectively). Both of them could promote electrocatalytic oxidation of methanol in alkaline media and are investigated herein. The dispersed nickel particles into POA/MWCNT/MGCE may show better signal to noise properties. Therefore, it can be more promising for application as electrocatalyst for electrooxidation of methanol in alkaline solution.

2. EXPERIMENTAL PART

2.1. Reagent and materials

o-Anisidine from Fluka was used as a monomer. MWCNTs employed in this work were provided by CVD (chemical vapor deposition) method with ~95% purity and were obtained from Petroleum and Gas Institute of Iran. Further purification was accomplished by stirring of MWCNTs in 2.0 M nitric acid. Methanol, $NiCl_2$ and H_2SO_4 were from Fluka, ethanol (from Parsian Co. Shiraz, Iran) and nitric acid from Merck used in this work were analytical grade and were used without further purifications. Twice distilled water was used to prepare the reagent solutions.

2.2. Instrumentation

The electrochemical experiments were carried out using a potentiostat / galvanostat (BHP 2061-C electrochemical analysis system, Behpajooh, Iran) coupled with a Pentium III personal computer with a standard three electrode configuration cell. A platinum wire, double-junction Ag|AgCl|KCl (sat) and GCE were used as the auxiliary electrode, reference electrode and substrate of working electrode, respectively.

3. RESULTS AND DISCUSSION

3.1. Preparation of POAMGCE and POA/MWCNT/MGCE

Glassy carbon electrode was carefully polished with alumina powder on polishing cloth until a mirror finish was obtained. The electrode was placed in ethanol and sonicated for 5 minutes to remove of alumina residues. After this, the electrode was removed, rinsed with doubly distilled water and ethanol. Then, electropolymerization was carried out at the surface of GCE in 0.5 M H_2SO_4 solution containing of 2.0 mM *o*-anisidine using consecutive cyclic voltammetry (for 7 cycles) from -0.3 to +1.2 V vs. Ag|AgCl|KCl (sat) at 100 mV s^{-1} (Fig. 1). It is obvious that in the first cycle in the forward scan, the oxidation of monomer takes place at about 0.95 V vs. Ag|AgCl|KCl (sat) and in the reverse scan, one reduction peak appears at the potential 0.30 V vs. Ag|AgCl|KCl (sat) related to POA, respectively. At the second cycle, one new oxidation peak related to POA can be observed. As well it is obvious that in the higher cycles, the peaks height of the oxidation and reduction of polymer increase, while the height of the oxidation peak of monomer decreases.

After this, the electrode was removed and rinsed with distillated water. The redox behavior of POA on the surface of GCE was strongly dependent on the pH. As can be seen in Figure 2a, the polymer shows a well defined redox behavior in acidic media, whereas it behaves as a non-electroactive in 0.1 M NaOH solution in the potential range from -0.2 V to 0.8 V vs. Ag|AgCl|KCl (sat) (Fig. (2b)). However, the film was not degraded under these experimental conditions and the electrode response was recovered by immersion in 0.5 M H_2SO_4 solution.

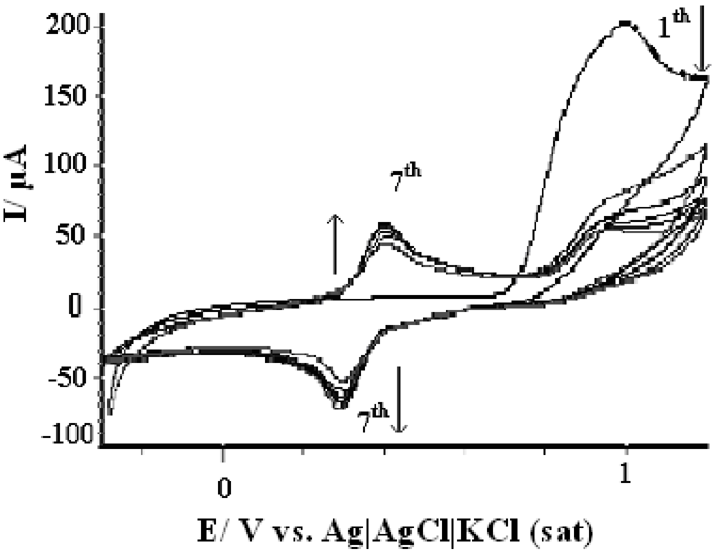

Figure 1. Cyclic voltammograms obtained during the electropolymerization of 2.0 mM *o*-anisidine monomer solution in 0.5 M H_2SO_4 on the surface of GCE in potentials between -0.3 – 1.2 V vs. Ag|AgCl|KCl (sat) at $\nu = 100$ mV s^{-1}.

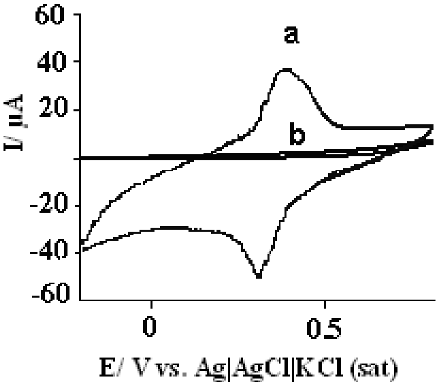

Figure 2. Electrochemical response of POAMGCE (a) in 0.5 M H_2SO_4 and (b) in 0.1 M NaOH solution at $\nu = 100$ mV s^{-1}.

In preparation of POA/MWCNT/MGCE, a 25 µL of DMF-MWCNT solution (2.0 mg MWCNT + 1.0 ml DMF) was dropped on the surface of GCE and was dried in room temperature to form a MWCNTs film at the surface of GCE. Electropolymerization of *o*-anisidine on the MWCNTs film at GCE was carried out in the same way for preparation of POAMGCE. Therefore, POA/MWCNT/MGCE was prepared. The redox behavior of this modified electrode is the same as POAMGCE, which is strongly dependent on the pH of solution. The cyclic voltammograms of

POA/MWCNT/MGCE and POAMGCE in 0.5 M H_2SO_4 solution are shown in Figure 3. The anodic and cathodic peak currents of POA/MWCNT/MGCE are significantly higher than that of POAMGCE, whereas, their peak potentials are the same (Fig. 3).

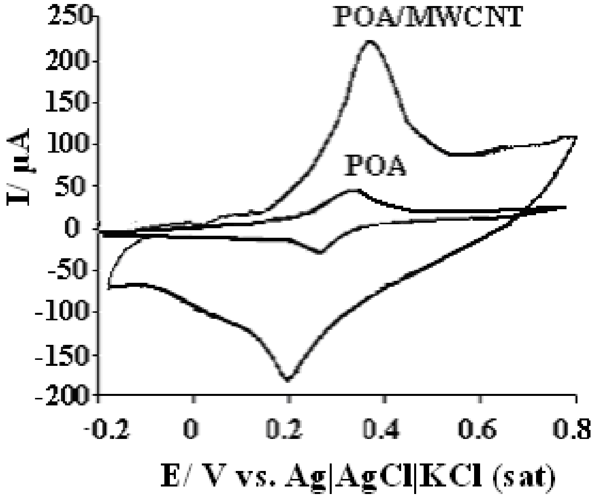

Figure 3. Cyclic voltammograms of POA and POA/MWCNT modified glassy carbon electrodes in 0.5 M H_2SO_4 solution at $\nu = 100$ mV s^{-1}.

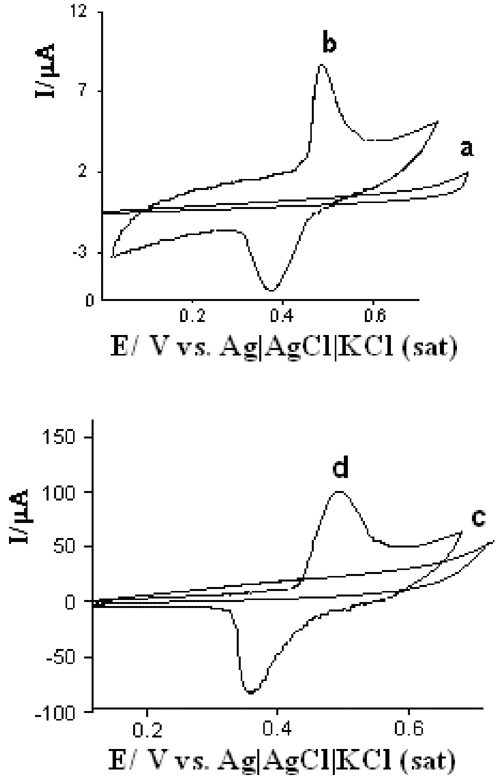

Figure 4. The electrochemical response of a) POAMGCE, b) freshly prepared Ni/POAMGCE, c) POA/MWCNT/MGCE and d) freshly prepared Ni/POA/MWCNT/MGCE in 0.1 M NaOH solution at scan rate 20 mV s^{-1}.

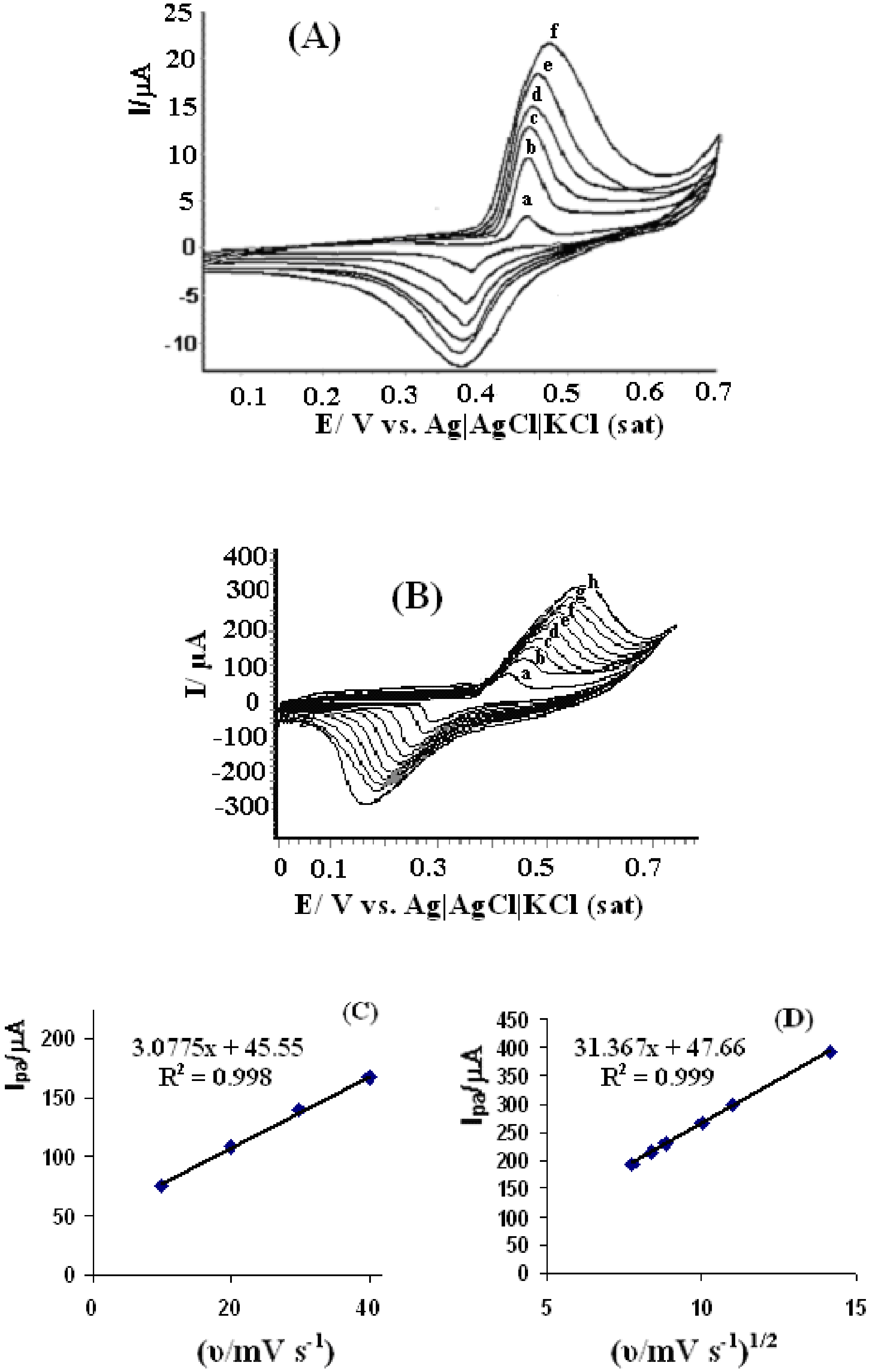

Figure 5. Cyclic voltammograms of A) Ni/POAMGCE at various scan rates:(a)10, (b)30, (c)50, (d) 70, (e)100 and (f) 120 m V $s^{-1}$and B) Ni/POA/MWCNT/MGCE at scan rates: (a)10, (b)20, (c)40, (d)60, (e)70, (f)90, (g)100 and (h)120 mV s^{-1} in 0.1 M NaOH. C) Plot of I_{pa} vs. ν and D) Plot of I_{pa} vs. $\nu^{1/2}$ (data obtained from (B)).

3.2. Incorporation of Ni (II) ions into POA and POA/MWCNT films

The POA/MWCNT/MGCE and POAMGCE were placed in a stirred 1.0 M $NiCl_2$ aqueous solution at open circuit for loading of Ni(II) into each modified electrodes. Accumulation of nickel (II) was carried out by complex formation between Ni (II) and amine sites in the polymer backbone for a given time. Therefore, Ni/POAMGCE and Ni/POA/MWCNT/MGCE were prepared. Figure 4 shows the electrochemical response of POAMGCE, POA/MWCNT/MGCE and freshly prepared Ni/POAMGCE, Ni/POA/MWCNT/MGCE in 0.1 M NaOH solution. It is clear that, a pair anodic and cathodic peak was appeared at the Ni/POAMGCE and Ni/POA/MWCNT/MGCE, which was related to oxidation of Ni(II) to Ni(III) and reduction of Ni(III) to Ni(II) as following equation:

$$[(POA\text{-}Ni)(OH)_2] + OH^{-} \leftrightarrow [(POA\text{-}Ni)OOH] + H_2O + e^{-} \qquad (1)$$

Whereas, neither oxidation nor reduction took place at the Ni(II) free modified electrodes in this condition. Therefore, Ni(II) was incorporated into polymeric matrix onto GCE in each modified electrode. Also, the redox peak current of $Ni^{II/III}$ at Ni/POA/MWCNT/MGCE is almost 12 times larger than that at Ni/POAMCPE, which is due to the fact that MWCNTs can increase the effective area of the electrode, so the resulted current value was significantly higher than that at Ni/POAMCPE. A decrease in the electroactive surface area of Ni/POAMGCE is mainly due to the lack of CNTs that acts as nanoconnectors between Ni/polymer and electrode.

Figures 5A and B shows the cyclic voltammograms of Ni/POAMGCE and Ni/POA/MWCNT/MGCE in 0.1 M NaOH solution at various scan rates of potential (υ). As can be seen, the anodic and cathodic peak potentials shift to more positive and negative potentials with increasing of scan rates of potentials, suggesting a kinetic limitation in the reaction between the redox sites and GCE. This potential shift is considerable at the Ni/POA/MWCNT/MGCE. Figures 5C and D show the plots of oxidation peak current (I_{pa}) vs. υ and $\upsilon^{1/2}$ for Ni/POA/MWCNT/MGCE. It was suggested that in the low scan rates of potential, the electrode reaction is adsorption controlled, while in high scan rates of potential, it is diffusion controlled.

3.3. Electrocatalytic oxidation of methanol at the modified electrodes

The oxidation of methanol studied at the surface of Ni/POAMGCE and Ni/POA/MWCNT/MGCE by cyclic voltammetry. The electrochemical response of each modified electrodes exhibits well defined oxidation and reduction peaks related to $Ni^{II\,/\,III}$ redox couple and oxygen evolution reaction in potential about 0.7 V vs. Ag|AgCl|KCl (sat) in the absence of methanol in 0.1 M NaOH (Fig. 6, curves (a) and (c)). The electrochemical behavior of these modified electrodes in the presence of methanol in 0.1 M NaOH solution show 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 and a decrease of the cathodic peak current (c_1) during the reverse scan rate of potential (Fig. 6, Curve (b) and (d)). Therefore, the anodic and cathodic peaks that appeared in cyclic voltammogram of

Ni/POAMGCE and Ni/POA/MWCNT/MGCE in the absence of methanol is related to the electrochemical reaction below [27]:

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \qquad (2)$$

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- $Ni(OH)_2$) [28]. Therefore, in the absence of methanol:

$$\alpha\text{-}Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \qquad (3)$$

And in the presence of methanol:

$$\alpha\text{-}Ni(OH)_2 + OH^- \rightarrow NiOOH + H_2O + e^- \qquad :E \qquad (4)$$

$$NiOOH + \text{methanol} \rightarrow \beta\text{-}Ni(OH)_2 + \text{product} \qquad :C' \qquad (5)$$

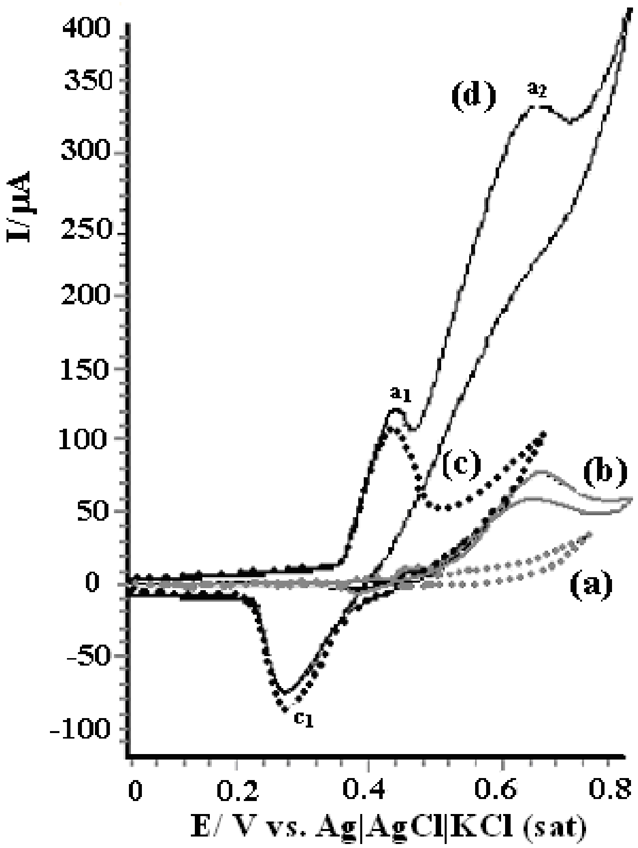

Figure 6. Electrochemical response of Ni/POAMGCE (a) and Ni/POA/MWCNT/MGCE (c) in the absence of methanol and (b) as (a) and (d) as (c) in the presence of 0.02 M methanol in 0.1 M NaOH solution at $\upsilon = 20$ mV s^{-1}.

Therefore, first 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 is depend on methanol concentration.

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) [29,30]. As can be seen in Fig. 6, methanol electrocatalytic oxidation takes place at potential about 0.65 V vs. Ag|AgCl|KCl (sat) in both modified electrode, where higher current and better signal to noise were achieved at the surface of Ni/POA/MWCNT/MGCE.

3.4. 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/POAMGCE and Ni/POA/MWCNT/MGCE in 0.1 M NaOH at various scan rates of potential. Figure 7A shows a typical cyclic voltammograms of 0.02 M of methanol at the surface of Ni/POAMGCE at various scan rates of potential. As can be seen in this figure, the cathodic current would increase with increasing of υ, 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/POAMGCE, Ni/POA/MWCNT/MGCE and methanol. This finding reveals that the heterogeneous oxidation of methanol at the Ni/POAMGCE and Ni/POA/MWCNTMGCE is not a rapid reaction. A plot of the scan rate normalized current ($I_{pa}.\ \upsilon^{-1/2}$) vs. scan rate (Fig. 7 B), exhibits the shape typical of an EC' process.

3.5. Effect of methanol concentration on the anodic peak current

The effect of methanol concentration on the anodic peak current of methanol has been studied at Ni /POAMGCE and Ni/POA/MWCNT/MGCE in 0.1 M NaOH solution. Figure 8A shows a typical cyclic voltammograms at the surface of Ni/POA/MWCNT/MGCE at $\upsilon = 20$ mV s^{-1}. It is obvious that the onset potential of Ni $^{II/III}$ redox is slightly delayed. This might be related to higher Ni(II)/polymer electron transfer resistance due to methanol adsorption on the Ni(II) active center. By this model, higher methanol concentrations result in greater numbers of Ni(II) active centers which absorbed with methanol, with increasing onset delay following from increasing of methanol concentration. However, this figure shows that the methanol oxidation potential increases with increasing of methanol concentration. The methanol oxidation peak current increases linearly with methanol concentration up to 0.1 M (Fig. 8B). This is due to the presence of diffusion-controlled process that appears to play an important role at low methanol concentrations. When the methanol concentration exceeds from this limit, the rate of the whole oxidation process seems to be limited by the catalytic process and its rate depends on the reaction between methanol and Ni(III) species, presenting in the polymeric film [31].

Tafel plots were drawn (data not shown) and derived from the date of the rising part of the current-voltage curves at $\upsilon = 10$ mV s^{-1}. Slopes of 5.46 and 7.36 were obtained at Ni /POAMGCE and Ni/POA/MWCNT/MGCE. If one electron is involved in rate determining step, $\alpha = 0.32$ and 0.43 were obtained for Ni /POAMGCE and Ni/POA/MWCNT/MGCE, respectively.

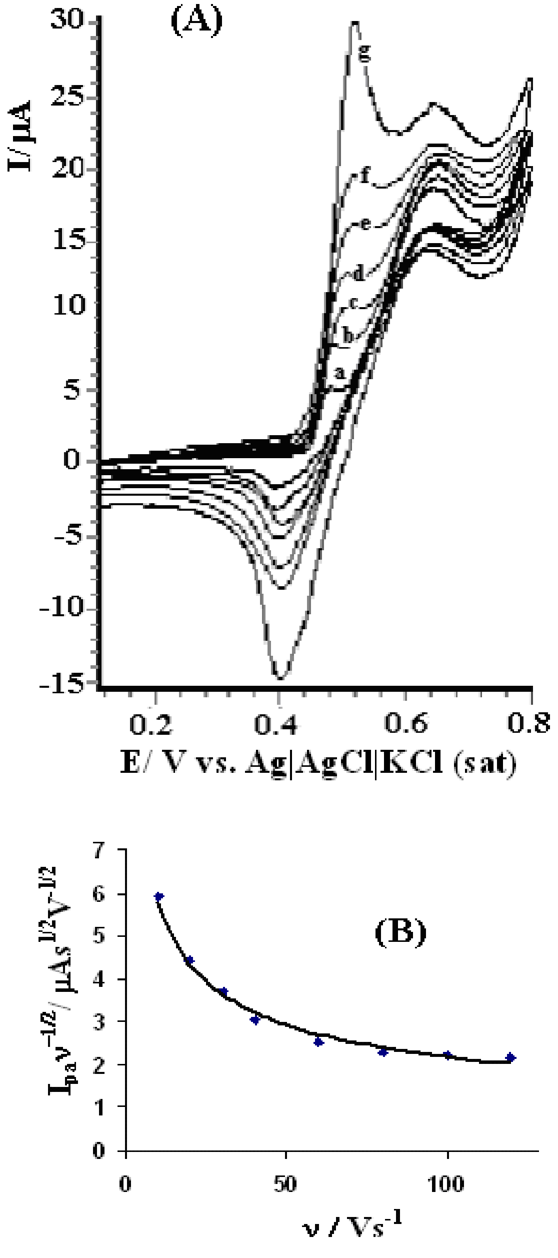

Figure 7. A) Cyclic voltammograms of 0.02 M methanol in 0.1 M NaOH solution at Ni/POA MGCE at various scan rates: (a)20, (b)40, (c)50, (d)80, (e)100, (f)200 and (g)300 mV s^{-1}, B) the variation of $I_{pa}.\nu^{-1/2}$ vs. υ.

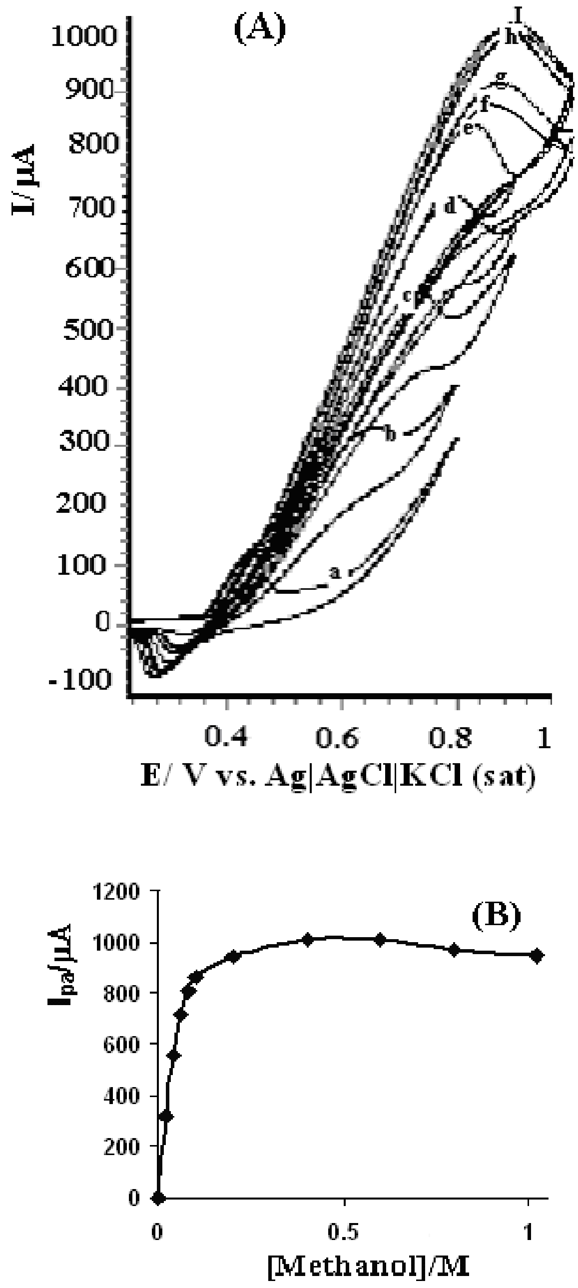

Figure 8. A) Cyclic voltammograms of various concentrations of methanol (a)0.0, (b)0.02, (c) 0.04, (d)0.06, (e)0.08, (f)0.10, (g)0.20, (h)0.40 and (i) 0.80 M in 0.1 M NaOH at the surface of Ni/POA/MWCNT/MGCE at $\upsilon = 20$ mV s^{-1}, B) plot of I_{pa} vs. concentration of methanol.

3.6. Chronoamperometric studies

Double step chronoamperometry, as well as other electrochemical method, were employed for the investigation of electrode processes at chemically modified electrodes. For example, Figure 9A shows double-step chronoamperograms for Ni/POA/MWCNT/MGCE in the absence (curve a) and presence (curves b-e)of methanol in 0.1 N NaOH solution with applied potential step of 350 mV and

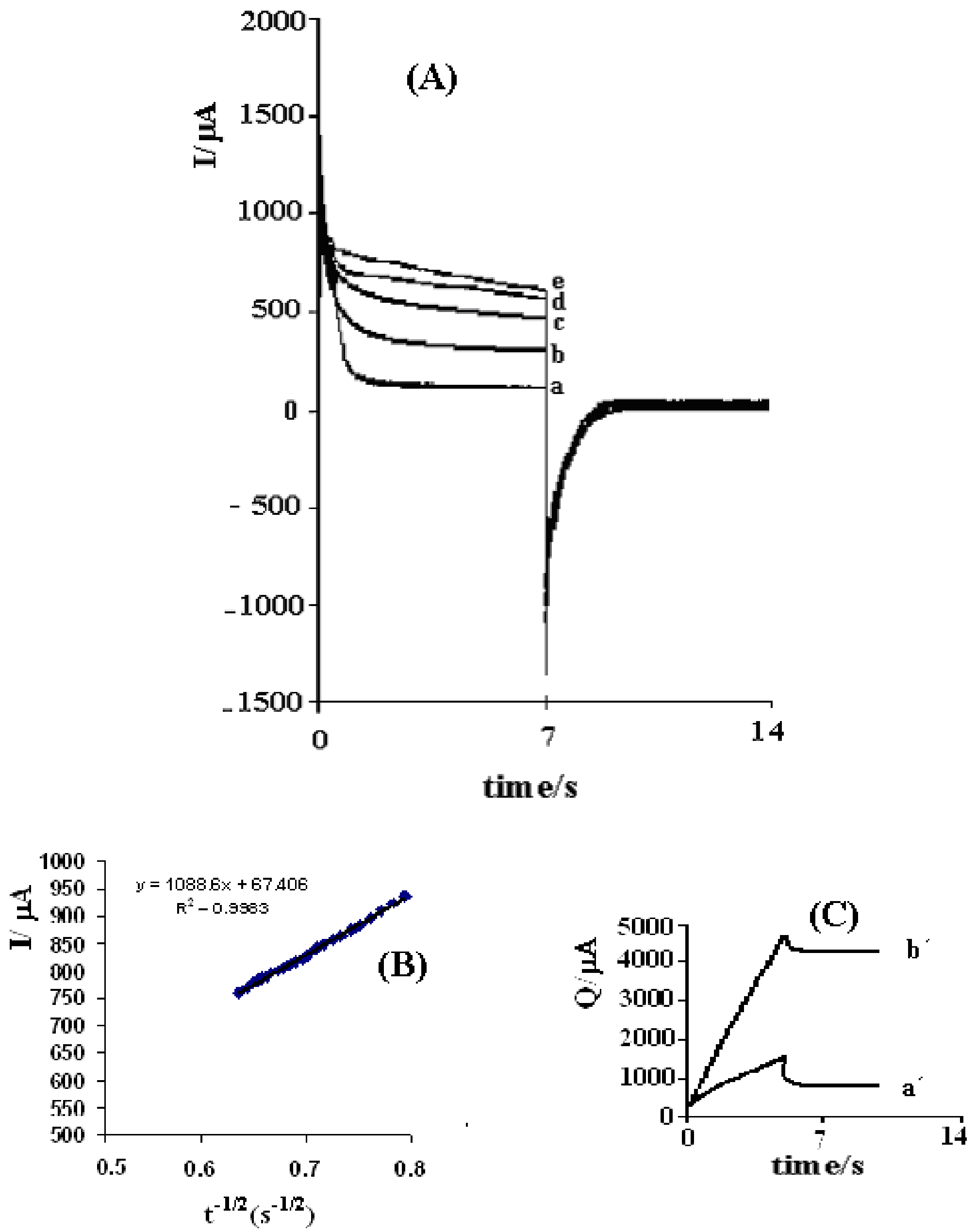

Figure 9. A) Double step potential chronoamperograms obtained at Ni/POA/MWCNT/MGCE in the absence (a) and the presence of (b)0.02, (c)0.06, (d)0.20 and e)0.40 M of methanol in 0.1 M NaOH solution, the first and second potential steps were 0.75 and 0.35 V vs. Ag|AgCl|KCl(sat), respectively. B) Cottrell plot and C) the charge-time curves (a′) for curve (a) and (b′) for curve (d).

750 mV vs. Ag|AgCl|KCl (sat), respectively. The forward and backward potential step chronoamperometry of modified electrode in the blank solution showed an almost equal charge consumed for the oxidation and reduction of surface confined Ni (II)/Ni (III) sites. However, in the presence of methanol, the charge value associated with the forward chronoamperometry, Q_a is greater than that observed for the back-ward chronoamperometry (Fig. 9B). The transition current is obviously

due to the mediated oxidation of methanol by NiOOH species and is substantiated upon increasing the concentration of methanol. Also, as the electrolysis potential is stepped down to 350 mV vs. Ag|AgCl|KCl (sat), no significant current is obtained indicating the irreversibility of the process. The net current (background subtracted) vs. $t^{-1/2}$ (Cottrell plot) has linear dependency (Fig. 9C), which demonstrates a diffusion-controlled process.

Additionally, the current density of methanol oxidation recorded at the surface of Ni/POAMGCE and Ni/POA/MWCNT/MGCE at t = 3 s and C = 0.04 M are 253.27 and 7991.29 μA cm^{-2}. It can be concluded that the current density recorded on Ni/POA/MWCNT/MGCE is significantly higher than that on Ni/POAMGCE.

4. CONCLUSIONS

In this work, POAMGCE and POA/MWCNT/MGCE were prepared and was shown that the mechanism of o-anisidine polymerization is not significantly affected by the presence of MWCNT on the surface of electrode. Subsequently, the incorporation of Ni(II) particles into POAMGCE and POA/MWCNT/MGCE were demonstrated, and the redox peak current of $Ni^{II/III}$ at POA/MWCNT/MGCE were almost 12 times larger than that at POAMGCE. In chronoamperometry technique, the current density recorded on Ni/ POA/MWCNT/MGCE was significantly higher than that on Ni/POAMGCE.

Both Ni/POAMGCE and Ni/POA/MWCNT/MGCE showed excellent electrocatalytic performance in methanol electrooxidation in alkaline medium. The methanol oxidation process at Ni/POAMGCE and Ni/POA/MWCNT/MGCE is diffusion controlled at low methanol concentrations while it was governed by the catalytic reaction between methanol and Ni(III) site prepared on polymer layer at higher methanol concentration.

The Ni/POA/MWCNT/MGCE shows better signal to noise ratio with large electrochemical accessible surface area and current density and higher peak current and is more promising for application in electrocatalysis of methanol oxidation.

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