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Electrocatalytic Oxidation of Hydrazine on the Nickel Particles Dispersed into Poly (*ortho*-anisidine) Modified Glassy Carbon Electrode

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Abstract- The advantageous features of polymer modification and dispersion of metallic particles into the organic polymer was studied by construction of poly *ortho*-anisidine (POA) film and Ni(II) were used in combination with POA films by immersion of the glassy carbon modified electrode in Nickel ions solution. This modified electrode exhibits good electrocatalytic activity toward the electrooxidation of hydrazine and has been studied by cyclic voltammetry (CV) and chronoamperometry techniques. The oxidation of hydrazine is occur at a potential about 140 mV less positive than that at unmodified electrode. The electron transfer coefficient (α) was determined and the electrocatalytic oxidation peak current of hydrazine showed a linear dependent on the hydrazine concentration and a linear calibration plot were obtained in the range of 5×10^{-5} M-1.4×10^{-2} M with cyclic voltammetry method. The detection limit (2σ) were determined as 3.9×10^{-5} M.

Key words- Hydrazine, Poly *ortho*-anisidine, Alkaline Solution, Electrocatalytic Oxidation

1. INTRODUCTION

Hydrazine is a substance anticipated to be carcinogenic, colorless, oily and liquid, (N_2H_4), and a powerful reducing agent or electron donor. It has been used as an oxygen scavenger in industry and has been found to have wide application as an antioxidant, a photographic developer and an insecticide [1,2].

It is also used as a fuel in fuel cells due to its high capacity and lack of contamination [3]. Hydrazine can be absorbed through skin; effects blood production, causes liver and kidney damages [4], so its detection has attracted considerable analytical interest. Hydrazine compound have large oxidation overpotential at ordinary carbon electrodes and one approach for minimizing over voltage effects is through the use of electrocatalytic process at chemically modified electrode (CMEs) [4].

Electrochemically pretreated glassy carbon electrode [5], carbon paste containing cobalt phtalocyanine [6], platinum and ruthenium particle dispersed in porous carbon films [7], or on carbon fiber [8], pyrogallol red [9] and pyrocatechol violet (PVC) chemically modified glassy carbon electrode [10], inorganic mixed-oxidation state prussian blue [11, 12], nickel ferricyanide [13] and hybrid hexacyanoferrate of copper and cobalt [14] modified glassy carbon electrodes have shown interesting catalytic properties toward the electrooxidation of hydrazine compound.

Recent research has demonstrated that coating the electrode surface with polymeric films is an attractive approach for enhancing the power and scope electrochemically modified electrode [15]. This new class of electrode material has been found to improve the electrodes sensitivity and selectivity and to reduce fouling effects in many applications [16].

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 [17]. For example, nickel porphyrins were used for electrocatalytic oxidation of H_2O_2, N_2H_4, NH_2OH and L-Cysteine [18].

Although metals such as Pt, Au, Ag and Ni are very active in the anodic oxidation of hydrazine, they are too expensive for practical applications [19-21] so, we use metal particles dispersed into conducting polymer for electrocatalytic oxidation of hydrazine.

The purpose of the present work is to study the electrooxidation of hydrazine on Ni/POA (Ni/ poly *ortho*-anisidine) modified glassy carbon electrode. The Ni/POA modified glassy carbon electrode can be used as an electrochemical sensor for determination of hydrazine in alkaline solution.

2. EXPERIMENTAL SECTION

2.1. 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} electrode and glassy carbon electrode (GCE) were used as the auxiliary electrode, reference electrode and substrate of working electrode**.**

2.2. Reagents and solutions

o-anisidine from Fluka was used as a monomer. Hydrazine mono-hydro chloride from Fluka), $NiCl_2$ (from Fluka), H_2SO_4 (from Fluka), ethanol (from parsian, Shiraz, Iran) used in this work without further purification.

3. RESULTS AND DISCUSSION

3.1. Preparation of poa modified glassy carbon electrode

In order to prepare POA modified glassy carbon electrode, GCE was carefully polished with polishing paper and subsequently with a little alumina powder until a mirror finish was obtained. After 5 min of sonication to remove the alumina residues, the electrode was rinsed by doubly distilled water and ethanol. Then electropolymerization of *o*-anisidine was carried out at the surface of GCE in 0.5 M H_2SO_4 solution containing of 2.0 mM of *o*-anisidine using consecutive cyclic voltammetry (for 7 cycles) between -0.3 and +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 take place at about 0.95 V and in the reverse scan, one reduction peak appears at the potential 0.3 V, which related to the polymer formed. At the second cycle, also one new oxidation peak related to the polymer oxidation can be observed. In the higher cycles, the peaks height of polymer is increased, whereas the oxidation peak height related to the monomer oxidation is decreased. After this, the electrode was removed and rinsed with water. The redox behavior of the polymeric film on the surface of working electrode was strongly dependent on the pH of electrolyte solution. The response obtained in 0.1 M NaOH solution showed complete loss of electrode activity in the potential range from -0.2 V to 0.8 V (Fig. 2b). However, the film was not degraded under these experimental conditions and the electrode response was recovered by immersion it in 0.5 M H_2SO_4 solution (Fig. 2a).

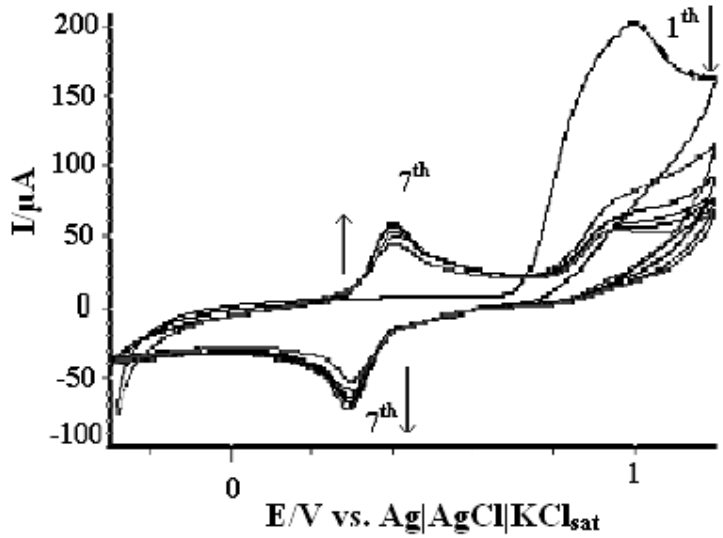

Fig. 1. Cyclic voltammograms obtained during the electropolymerization of 2.0 mM *o*-anisidine monomer solution in 0.5 M H_2SO_4 on the surface of GCE in potentials between-0.3–1.2 V *vs.* Ag|AgCl|KCl_{sat} at υ=100 mV s^{-1}

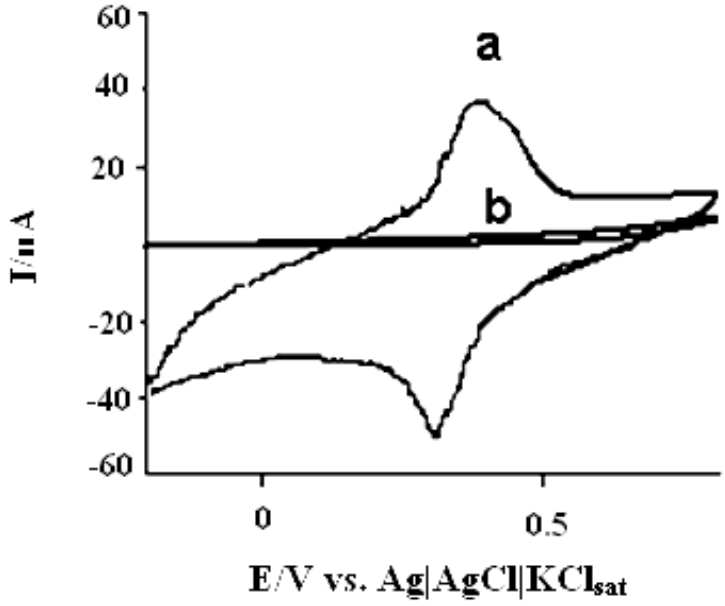

Fig. 2. Electrochemical response of POA: (a) in 0.5 M H_2SO_4, (b) in 0.1 M NaOH solutions, υ=100 mV s^{-1}

3.2. Incorporation of Ni (II) ions into POA

In order to incorporate of Ni(II) ions into the POA, the freshly modified electrode was placed at open circuit in a well stirred aqueous solution of 1.0 M $NiCl_2$. Accumulation of nickel was carried out by complex formation between Ni(II) and amine sites in the polymer backbone, for a given accumulation time. Fig. 3 shows the electrochemical response of POA and freshly prepared Ni/POA modified GCE in 0.1 M NaOH solution. As can be seen, a pair anodic and cathodic peak was appeared on the Ni/POA modified GCE, which was related to oxidation of Ni(II) to Ni(III) and reduction of Ni(III) to Ni(II) as following equation:

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

Whereas, neither oxidation nor reduction took place on the Ni(II) free modified electrodes in this condition. Therefore, Ni(II) was incorporated into polymeric matrix onto GCE.

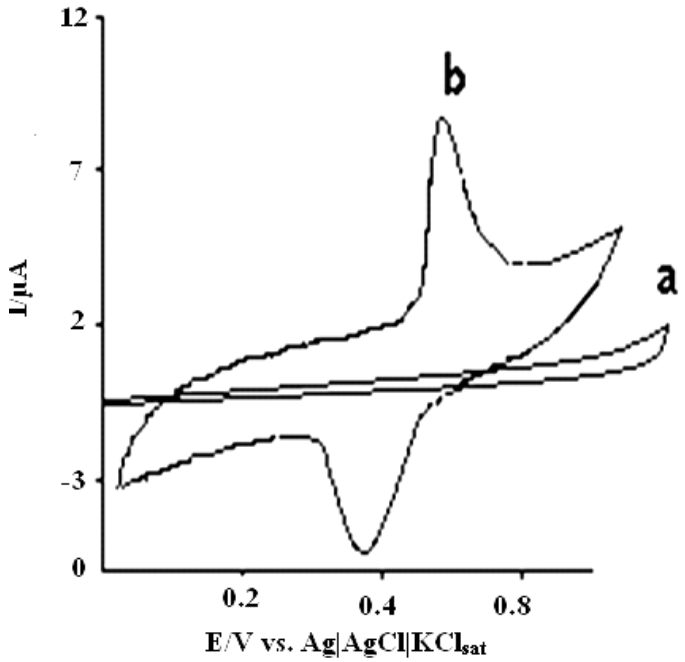

Fig. 3. The electrochemical response of a) POA, b) freshly prepared Ni/POA modified GC electrodes in 0.1 M NaOH solution at υ=20 mV s^{-1}

The effect of scan rate of potential (υ) on electrochemical behavior of Ni/POA modified GCE was studied in 0.1 M NaOH solution (Fig. 4A). As can be seen, the anodic and cathodic peak potentials shift to more positive and negative potentials with increasing of υ, suggesting a kinetic limitation in the reaction between the redox sites and GCE. The anodic peaks current are linearly proportional to υ up to 70 mV s^{-1} as shown in the Fig. 4B. At higher

sweep rates of potentials, the plot of peak current *vs*. υ deviates from linearity and the peak current becomes proportional to the square root of υ (not illustrated), which can be expected for a diffusion-controlled electrode process.

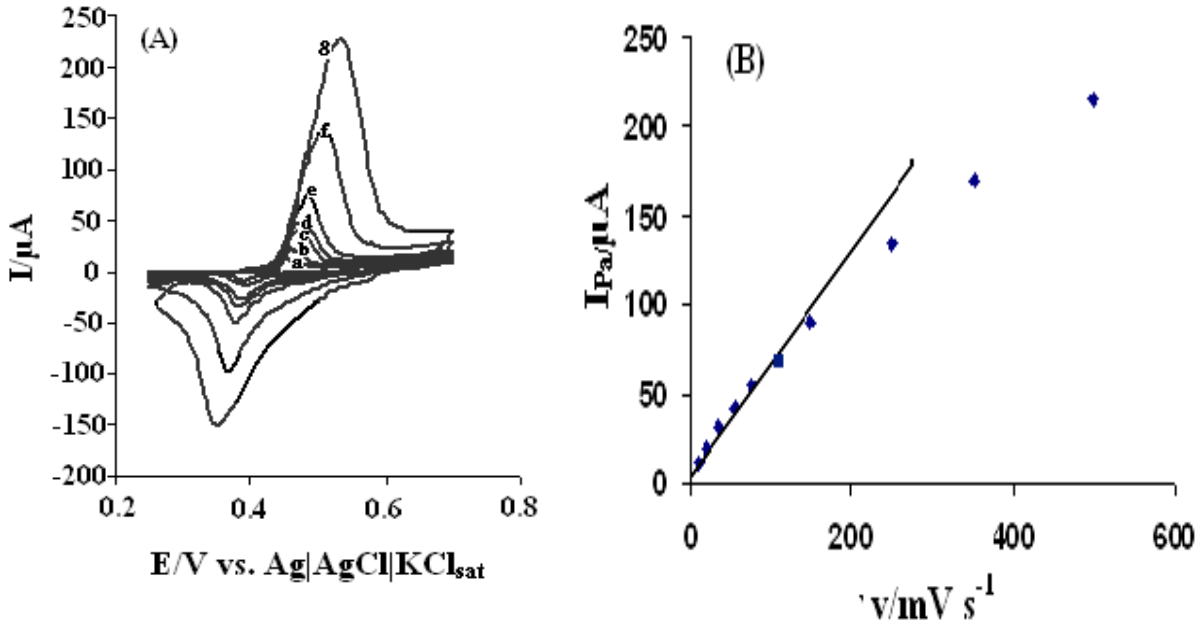

Fig. 4. Cyclic voltammograms of A) Ni/POA at various scan rates: (a) 20, (b) 30, (c) 50, (d) 70, (e) 100 and (f) 250 and (g) 500 m V s^{-1} in 0.1 M NaOH. B) Plot of I_{pa} *vs*. υ

3.3. Electrocatalytic oxidation of hydrazine on the Ni/POA modified electrode

The oxidation of hydrazine was studied at the surface of Ni/POA modified GCE using cyclic voltammetry method. Cyclic voltammograms of the bare and Ni/POA modified GCE in the absence and presence of hydrazine are shown in Fig. 5. As can be seen, the anodic peak current of Ni/POA modified GCE was greatly enhanced in the presence of hydrazine in compression that in the absence of hydrazine. Whereas, no cathodic peak current appear in the reverse sweep of potential at the surface of Ni/POA modified GCE in the presence of hydrazine (Fig. c). Also, the hydrazine electrooxidation is shifted about 140 mV toward less positive potential at the surface of Ni/POA modified GCE. The above results show that the oxidation of hydrazine is facilitated and catalyzed by the presence of Ni ions in polymeric film according to this purposed mechanism:

$$[(POA\text{-}Ni)(OH)_2] + OH^- \leftrightarrow [(POA\text{-}Ni)OOH] + H_2O + e^- \quad (E) \quad (2)$$

$$[(POA\text{-}Ni)OOH] + N_2H_4 \leftrightarrow [(POA\text{-}Ni)(OH)_2] + \text{product} \quad (C_i') \quad (3)$$

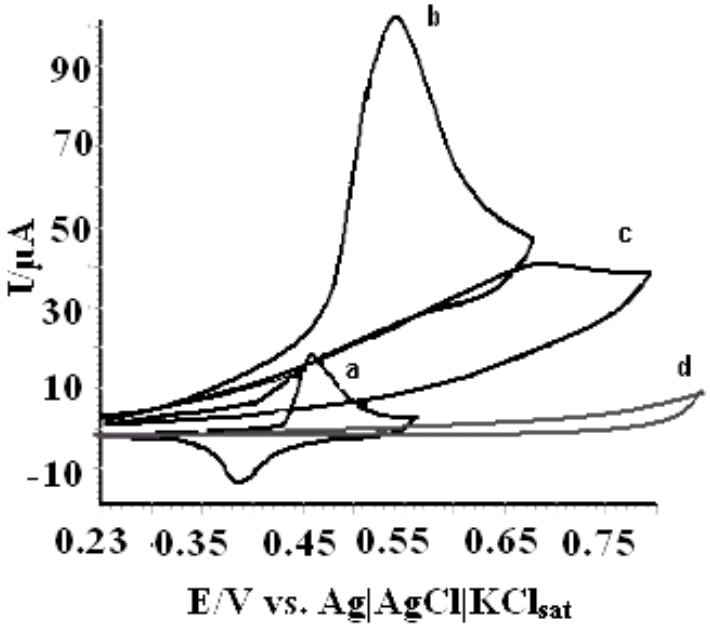

Fig. 5. Cyclic voltammograms of Ni/POA/MGCE in NaOH 0.1 M (a) without, (b) 10 mM hydrazine at scan rate of potential 20 mV s^{-1}. (c) as (a) and (d) as (b) for bare glassy carbon electrode

3.4. Effect of scan rate on the anodic peak height hydrazine

The effect of the potential scan rate on the electrocatalytic property of Ni/POA modified GCE toward hydrazine was studied by cyclic voltammetry. Fig. 6A shows the cyclic voltammograms of the Ni/POA at various scan rates of potentials (10-500 mV s^{-1}). This results show that, the peak potential for the electrooxidation of hydrazine shift to more positive potentials with increasing of υ. This phenomenon confirms a kinetic limitation in the reaction between the redox sites of Ni/POA and hydrazine. In addition, the cathodic current would increase with increasing of υ, because in short time-scale experiments, there is no enough time for catalytic current reaction to take place completely. However, the oxidation current of hydrazine increased linearly with the square root of scan rate of potentials (Fig. 6B), which demonstrates a diffusion controlled electrochemical process.

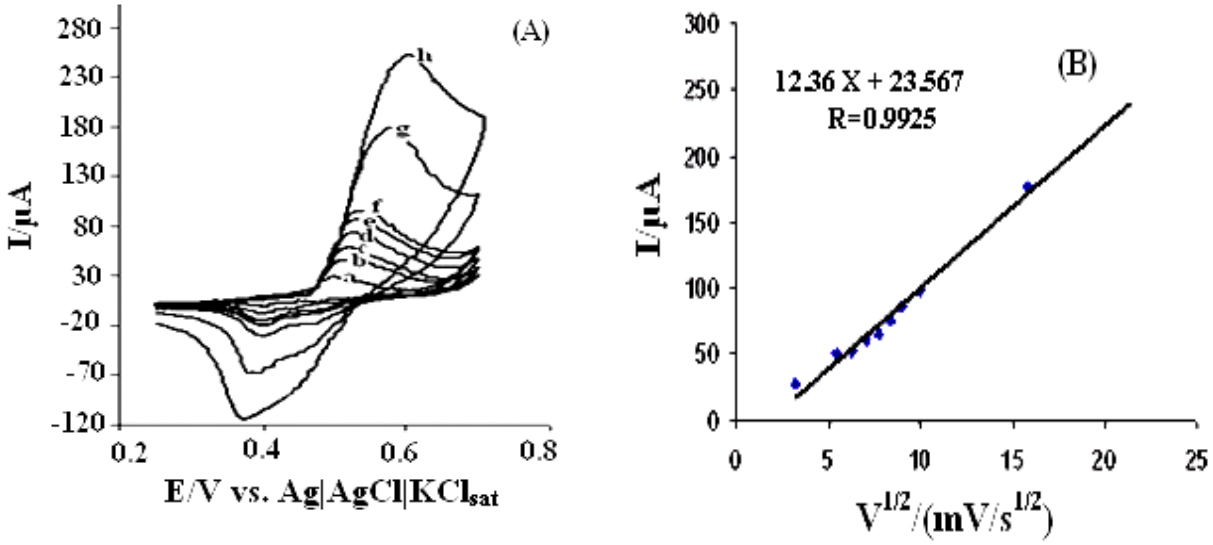

Fig. 6. (A) Scan rate dependence of peak current of Ni/POA/MGCE in 5 mM hydrazine in NaOH 0.1 M, scan rates: (a) 10, (b) 30, (c) 50, (d) 70, (e) 80, (f) 100, (g) 250, (h) 500 mV s^{-1} **(B)** Plot of I pa *vs*. υ1/2.

In order to get the information on the rate determining step, a tofel plot was drown by using the data derived from the rising part of the current-voltage curve at scan rate of 10 mV s^{-1} in 5 mM hydrazine in NaOH 0.1 M solution. The value of αn_α (where α is the transfer coefficient and n_α is the number of electrons involved in the rate determining step) was calculated equal to 0.95 from the slope of this plot.

Also, the values of αn_α were calculated for the oxidation of hydrazine in NaOH 0.1 M at modified electrode, according to the following equation [22];

$$\alpha n_\alpha = 0.048/ (E_p - E_{P/2})$$

Here, $E_{P/2}$ is the potential corresponding to $I_{P/2}$. The values for αn_α were found to be 0.96 for the oxidation of hydrazine at the surface of Ni/POA modified GCE. The results obtained from these two different methods have a good agreement.

The cyclic voltammograms obtained for a series of hydrazine solution with various concentrations are illustrated in Fig. 7A. The result show that electrocatalytic oxidation peak current of hydrazine at the surface of Ni/POA modified GCE was linearly dependent on the hydrazine concentration within the ranges 5.0×10^{-5} M -1.4×10^{-2} M using cyclic voltammetry method (Fig. 7B). The detection limit (2σ) was 3.9×10^{-5} M.

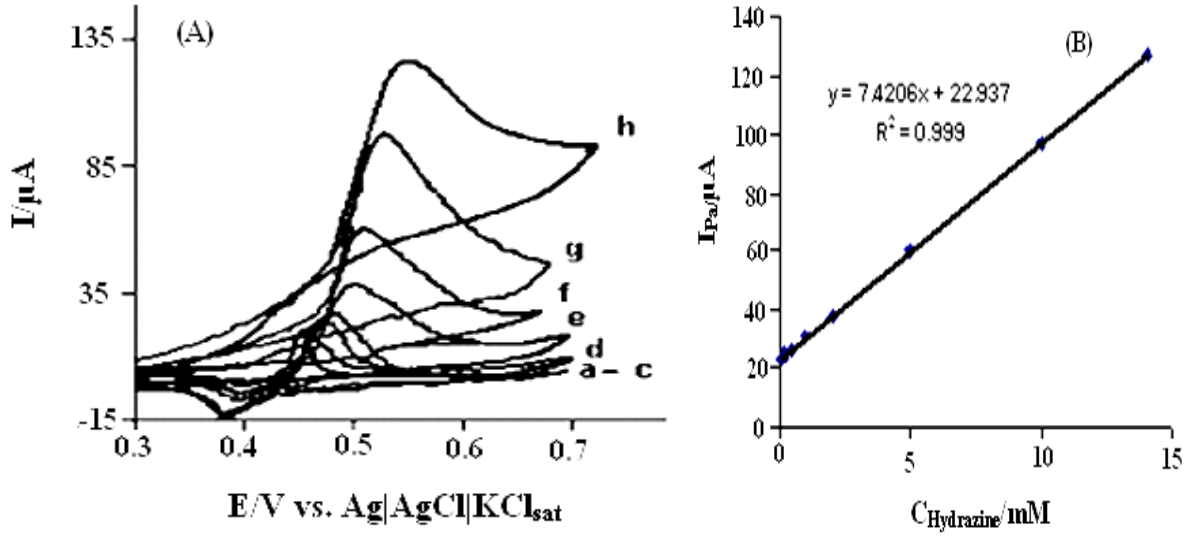

Fig. 7. (A) Current-potential curves for oxidation of hydrazine at the Ni/POA/MGCE in 0.1 M NaOH solution with different concentration: (a) 0.05, (b) 0.2, (c) 0.5, (d) 1.0, (e) 2.0, (f) 5.0, (g) 10.0 and (h) 14.0 mM of hydrazine. **(B)** The plot of I_{pa} *vs*. [hydrazine]

3.6. Chronoamperometric studies

Double step potential chronoamperometry was also employed for investigation of electrochemical processes at the chemically modified electrode. Therefore, double step potential chronoamperometric behavior of modified glassy carbon electrode was examined in the absence and presence of various concentration of hydrazine in NaOH 0.1 M aqueous solution by setting the working electrode potential at 0.75 V (at the first potential step) and 0.35 V (at the second potential step) *vs*. Ag|AgCl|KCl$_{sat}$ (Fig. 8A). As can be seen, in the presence of hydrazine, the charge value associated with forward chronoamperometry is significantly greater than that observed for backward chronoamperometry (Fig. 8B).

A plot of I *vs*. $t^{-1/2}$ for a Ni/POA modified electrode in the presence of hydrazine given a straight line (Fig. 8C), slop of such lines can be used to estimate the apparent diffusion coefficient of hydrazine (D_{app}). Therefore, the value of D_{app} found to be 2.8×10^{-5} cm^2 s^{-1}.

Chronoamperometry can be also used for the evaluation of the catalytic rate constant according to [23].

$$I_{cat} / I_l = \gamma^{1/2}[\pi^{1/2} \text{erf} (\gamma^{1/2}) + \exp (-\gamma) / \gamma^{1/2}] \quad (4)$$

where I_{cat} and I_l are the currents in the presence and absence of hydrazine and γ=kCt is the argument of the error function, k is catalytic rate constant, C is bulk concentration of hydrazine and t is the elapsed time. In the cases where $\gamma > 1.5$ and erf ($\gamma^{1/2}$) is almost equal to unity, the above equation can be reduced to:

$$I_c / I_l = \gamma^{1/2} \pi^{1/2} = \pi^{1/2} (kC_0 t)^{1/2} \quad (5)$$

From the slope of the I_{cat} / I_l *vs.* $t^{1/2}$ plot, presented in Fig. 8D, the mean value of k was obtained as 3523.89 $cm^3 mol^{-1} s^{-1}$.

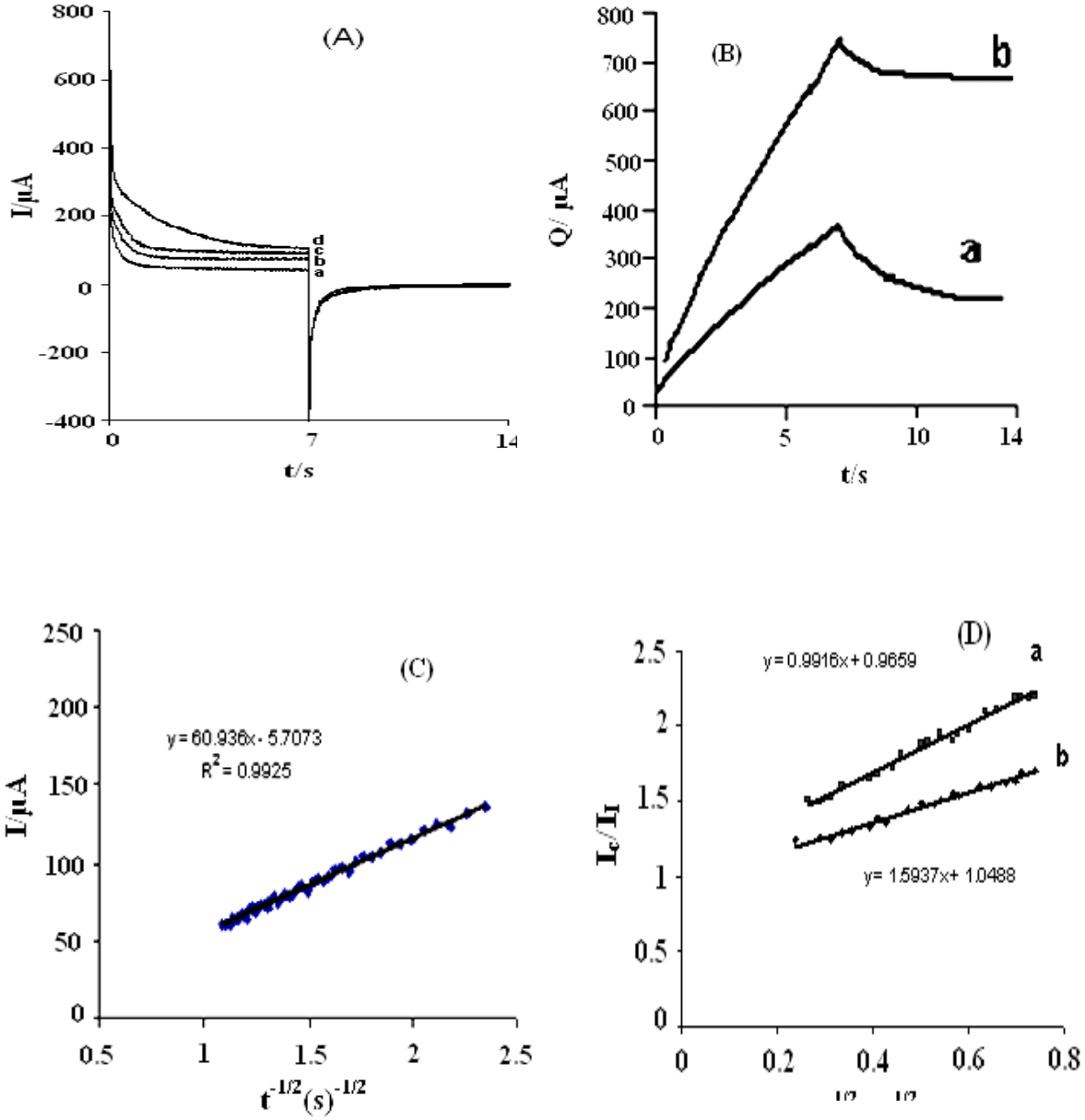

Fig. 8. (A) Chronoamperograms obtained at Ni/POA/MCPE in the (a) 0.0, (b) 0.05, (c) 1.0, (d) 5.0 M of hydrazine, first and second potential steps were 0.35 V and 0.75 V *vs.* Ag|AgCl|KCl_{sat} in 0.1 M NaOH solution, respectively. **(B)** Dependence of Q(µC) *vs.* t(s) derived from the data of chronoamprogram (a) and (c). **(C)** The Cottrell plot derived from the data of chronoamprogram (d). **(D)** Dependence of I_c/I_l *vs.* $t^{1/2}$

4. CONCLUSIONS

poly *ortho*-anisidine (POA) was prepared on GCE using consecutive cyclic voltammetry. The polymer films show one new redox couple and its formal potential is pH dependent when transferred to different solution. Then, the incorporation of Ni(II) ions into POA was demonstrated. As can be seen, Ni/POA modified GCE acts as an electrocatalyst for the oxidation of hydrazine in NaOH 0.1 M solution. The obtained result demonstrated that the electrooxidation of hydrazine at the surface of Ni/POA occurs at potential about 140 m V less positive than at bare glassy carbon electrode. The kinetic parameters such as charge transfer coefficient, α, and the catalytic reaction rate constant, k and the apparent diffusion coefficient of hydrazine, D_{app} of hydrazine, were determined. Finally, the electrocatalytic oxidation currents of hydrazine at the surface of modified electrode were linear to concentration of hydrazine.

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