

*Full Paper*

## **The First Use of Rh(III)-Complex Modified Carbon Ceramic Electrode for the Electrocatalytic Oxidation of Hydrazine**

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**Abstract-** A carbon ceramic electrode activated with MWCNTs and modified with [Rh(terpyridine)(bipyridine)Cl] (PF<sub>6</sub>)<sub>2</sub>, have been applied to the electrocatalytic oxidation of hydrazine which reduced the overpotential by about 165 mV with obviously increase the current response. Cyclic voltammetry was employed to characterize the electrochemical behavior of the chemically modified electrode. The electrocatalytic efficiency of the modified electrode towards hydrazine oxidation depends on solution pH, and optimum pH value for oxidation of hydrazine is 7.0. The overall number of electrons involved in the catalytic oxidation of hydrazine and the number of electrons involved in the rate-determining steps are 4 and 1, respectively. And diffusion coefficient of hydrazine was estimated using chronoamperometry.

**Keywords-** Carbon ceramic electrode, MWCNTs, [Rh(terpyridine)(bipyridine)Cl] (PF<sub>6</sub>)<sub>2</sub>, Electrocatalytic oxidation, Hydrazine

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### **1. INTRODUCTION**

The electrocatalysis of slow electron transfer reactions is maybe the main feature of chemically modified electrodes (CMEs). Such electrodes raise the rate of electron transfer by reducing the overpotential associated with a reaction. Therefore, such electrocatalysis enables

a high current density to be obtained for a poor kinetic reaction at a potential close to the equilibrium potential. In the past years, different CMEs have been prepared and applied in the determination of hydrazine, including cobalt phthalocyanine [1], cobalt proto porphyrin dimethyl ester [2] poly(4-vinyl) pyridine [3], nafion/ruthenium (III) [4], coumestan modified carbon paste electrode [5], 4-pyridil hydroquinone self-assembled platinum electrode [6], nickel hexacyanoferrate modified carbon ceramic electrode [7], hydroquinone salophen derivatives [8], 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy [TEMPO] [9], catechin [10] and metal hexacyanoferrates [11-13] modified glassy carbon electrode, palladium hexacyanoferrate modified aluminum electrode [14], platinum [15] and Rhodium [16] modified carbon fiber microelectrode. Hydrazine is widely used in industrial applications. Such as corrosion inhibitors, antioxidants, catalysts, emulsifiers, and reducing agent; as starting material in the production of some insecticides, herbicides, pesticides, dyestuffs, and explosive; and in the preparation of several pharmaceutical derivatives [17]. Hydrazine is also an ideal fuel for a direct fuel cell system because its fuel electrooxidation process does not suffer any poisoning effects [18,19]. However hydrazine is a toxic material that must be treated with care. Due to the reasons above, it is highly desirable to fabricate a reliable and sensitive analytical tool for the effective detection of hydrazine [20].

Sol-gel technology is very versatile in tailoring matrices for electrochemical studies [21-24]. This has led to an intensive research in this area particularly with regard to sensing and biosensing. A new type of composite electrodes called carbon ceramic electrodes (CCEs) was first constructed by Lev's et al. Using sol-gel technology [25]. A considerable feature of the CCEs is the ability to compose surface-renewable, bulk modified electrodes for electroanalytical and electrocatalytic applications. The preparation protocol of CCEs allows the linkage of other compounds during the preparation stage itself, and hence they can be bulk-modified. An additional advantage is that the electrochemically active, wetted surface of the electrode in aqueous solutions can be manipulated by the judicious choice of monomers used to prepare the silicate matrix. Sol-gel chemistry offers new and interesting possibilities in the fields of chemical sensors and biosensors owing to its simplicity, versatility, physical rigidity, transparency, porosity, efficient encapsulation and flexibility in the fabrication procedure [26-28]. Recently, the sol-gel derived ceramic carbon composite electrodes (CCEs) have become increasingly used for the fabrication of effective electrochemical sensors [29]. The composite electrodes are prepared by mixing carbon with organically modified silicates (ormosils) and the resultant mixture is packed into a tube or spread on a suitable surface. It is therefore possible to dope the ceramic composite with a wide variety of reagents or catalysts to fabricate the desired sensing material [25]. An interesting feature of the carbon ceramic electrodes (CCEs) is that due to the brittleness of the sol-gel silicate backbone, the active section of the electrodes is not clogged upon repeated polishing and thus the active section of the electrodes can be renewed by a mechanical polishing after each use or contamination. The

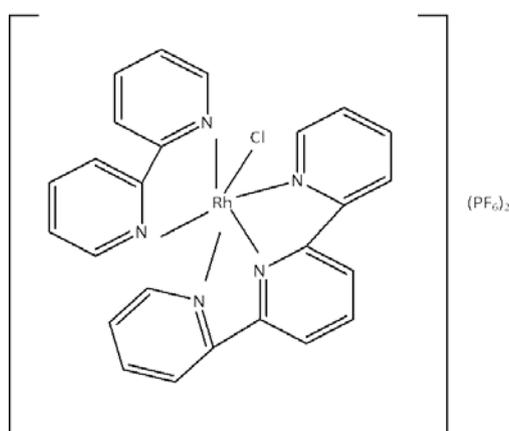
modified CCEs containing ruthenium metallodendrimer, manganese hexacyanoferrate and dirhodium-substituted polyoxometalate were fabricated by sol-gel techniques and used for voltammetric detection of L-methionine and L-cysteine [30-32]. Considering the chemically modified electrode containing  $[\text{Rh}(\text{tpy})(\text{bpy})\text{Cl}] (\text{PF}_6)_2$  was constructed by sol-gel technique, have been used here for electrocatalytic oxidation of hydrazine.

To our knowledge, several groups studied the voltammetric response of modified electrodes that were fabricated by sol-gel technique and several groups used terpyridine derivatives for modification of electrodes [33-38]. But up to now, the chemically modified electrodes containing  $[\text{Rh}(\text{tpy})(\text{bpy})\text{Cl}] (\text{PF}_6)_2$  that were fabricated by sol-gel technique have not been reported. In this paper, we used an electrode for electrocatalytic oxidation of hydrazine that was developed via an easy and effective sol-gel preparation method.

## 2. EXPERIMENTAL

### 2.1. Reagents and solutions

Hydrazine, methyltrimethoxysilane (MTMOS), methanol and HCl were of analytical grade supplied by Merck. High purity graphite powder was obtained from merck. Multi-walled carbon nanotubes (OD=10-30 nm, ID=5-10nm, length=0.5-500  $\mu\text{m}$ , 95%) were purchased from Aldrich. Deionized water was used for the preparation of all solutions. The background electrolyte solution was prepared from potassium chloride. The pH of solutions was adjusted to 7 with phosphate buffer. The ligand of  $[\text{Rh}(\text{tpy})(\text{bpy})\text{Cl}] (\text{PF}_6)_2$  (Fig. 1) was synthesized, purified and characterized as reported [39]. A Universal Buffer solution (0.1 M) was prepared from boric acid, acetic acid, phosphoric acid and sodium hydroxide with different pH Value was used for the study of the effect of pH. Solutions were deaerated by bubbling high purity (99.99%) nitrogen gas through them prior to the experiments and the electrochemical cell was kept under nitrogen atmosphere throughout the experiments.



**Fig. 1.** Molecular structure of  $[\text{Rh}(\text{tpy})(\text{bpy})\text{Cl}] (\text{PF}_6)_2$

## 2.2. Apparatus

Electrochemical measurements were performed with an Autolab potentiostat/galvanostat model PGSTAT 30 (Metrohm, Utrecht, Netherlands) and a system was run on a pc using GPES 4.9 software. A three electrode cell, consisting of a CCE, modified with Rh-complex as a working electrode, A platinum wire was employed as counter electrode and a saturated Ag/AgCl (saturated KCl) served as the reference electrode and all potentials in the text refer to it. The pH measurements were made with a Metrohm 632 pH meter using a combined glass electrode. A personal computer was used for data storage and processing. The morphology of CCEs modified with Rh- complex and MWCNTs surface was observed using a scanning electron microscope (SEM) from SERON technology AIS-2100. All electrochemical experiments were performed at room temperature ( $25\pm 0.5$ ) °C.

### 2.3. Preparation of bare and Rh(III)-complex/MWCNT modified CCE

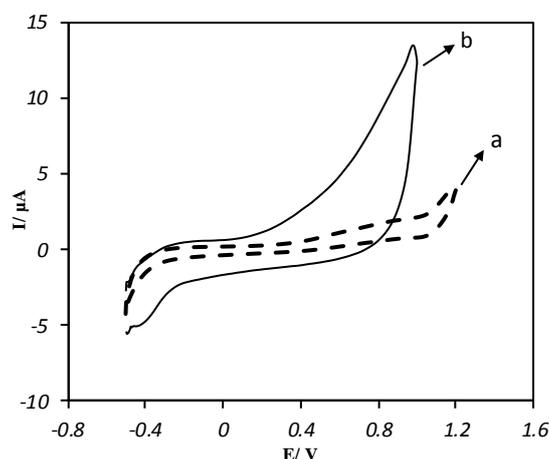
Carbon ceramic electrodes (CCEs) were prepared according to the procedure described by Lev and co-workers [25]. The fabrication of Rh(III)-complex/MWCNT modified carbon ceramic electrode is described briefly as follows. First 5 mg of Rh(III)-complex was dissolved in 1 ml methanol and homogenized thoroughly by sonication for 10 min until a clear solution was obtained. Then, 0.9 ml of this solution was mixed with 0.6 ml (MTMOS), and 0.1 ml hydrochloric acid (0.1 M) and stirred for 5 min until a homogeneous gel solution resulted. At the second stage, This ormosil was mixed well with 600 mg graphite powder and 4 mg MWCNT for 5 min. the mixture was added to Teflon tubes (with 2 mm inner diameter and 3 cm length, and the length of composite material in the tube was about 0.5 cm). In addition, a little extra mixture was needed to be retained on the top of the electrodes and the mixture in the tubes was slightly pressed on smooth plastic paper with a copper stick through the back. After drying at 25 °C for 48 h, the electrode was polished firstly with emery paper to remove extra composite material and then wiped gently with weighing paper until shiny surface was obtained. A copper wire was inserted through the opposite end to establish electrical contact. The modified electrode was rinsed with distilled water, and applied for electrochemical studies. The same procedure was used for preparing of bare carbon ceramic electrode and carbon ceramic electrode activated by MWCNT .

## 3. RESULTS AND DISCUSSION

### 3.1. Electrochemical behavior of the modified electrode

The electrochemical properties of the Rh(III)-complex/MWCNT modified carbon ceramic electrode with sol-gel technique were studied, using cyclic voltammetry. Fig. 2 shows typical cyclic voltammograms of the bare and Rh(III)-complex/MWCNT modified

carbon ceramic electrode by sol-gel techniques in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7) at scan rate 20 mV s<sup>-1</sup>. It shows that the oxidation peak areas of Rh(III)-complex/MWCNT modified electrode are much larger than the bare electrode. A small anodic peak current by the oxidation of hydrazine is observed but no cathodic peak is found, indicating an irreversible heterogeneous charge transfer in this system.

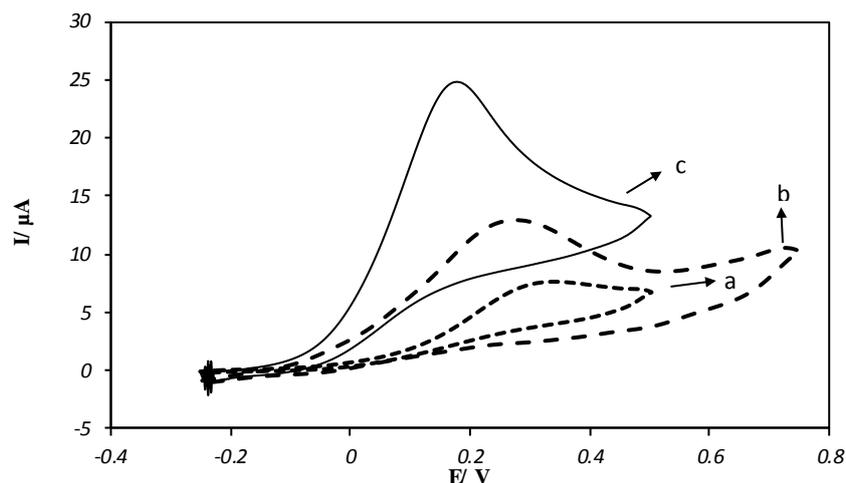


**Fig. 2.** Cyclic voltammograms of the (a) bare CCE and (b) Rh(III)-complex/MWCNT modified CCE in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7) at scan rate 20 mV s<sup>-1</sup>

### 3.2. Electrocatalytic oxidation of hydrazine

In order to evaluate the electrocatalytic activity of the Rh(III)-complex/MWCNT modified CCE toward oxidation of hydrazine, voltammograms were obtained in comparison with bare CCE electrode and carbon ceramic electrode activated by MWCNT in the presence of 1 mM hydrazine in 0.1 M phosphate buffer solutions (pH 7), as shown in Fig. 3. At bare carbon ceramic electrode, a small oxidation peak current was observed at about 320 mV (Fig. 3, curve a), a larger peak current was observed at about 255 mV (Fig. 3, curve b) and a well-formed sharp catalytic oxidation peak at about 155 mV was observed at Rh(III)-complex/MWCNT modified CCE (Fig. 3, curve c). Thus in comparison with the bare CCE and activated carbon ceramic electrode with MWCNT, an increase in peak current and a decrease in the overpotential of hydrazine were observed at the Rh(III)-complex/MWCNT modified electrode. This suggests an efficient oxidation reaction of hydrazine on the Rh-complex/MWCNT-

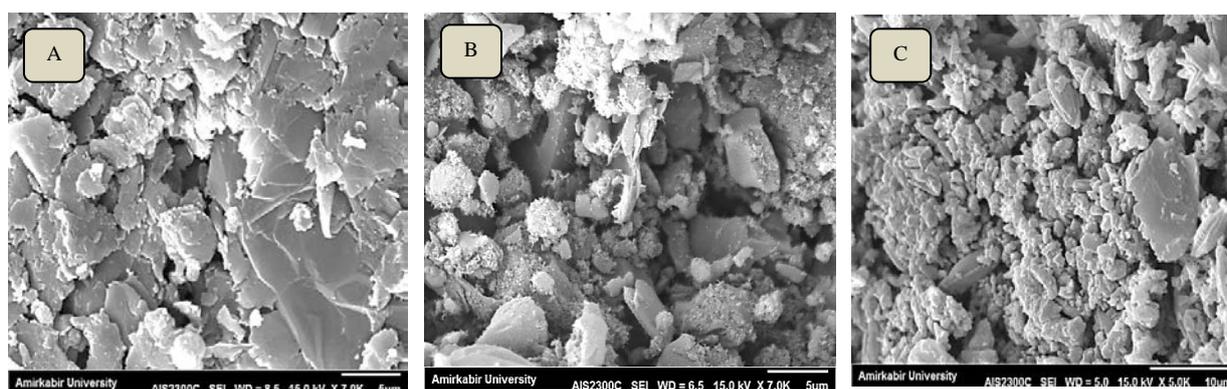
Modified carbon ceramic electrode. By using the Rh(III)-complex as an electron mediator into the carbon ceramic electrode, the overpotential for the anodic oxidation of hydrazine becomes considerably lower and the rate of the heterogeneous electron transfer is increased.



**Fig. 3.** Cyclic voltammograms of 1 mM hydrazine at (a) bare CCE (b) MWCNT modified CCE (c) Rh(III)-complex/MWCNT modified CCE in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7) at scan rate  $50 \text{ mV s}^{-1}$

### 3.3. Characterization of the Rh-complex/MWCNTs-modified carbon ceramic electrode

The Rh(III)-complex/MWCNT modified carbon ceramic electrode was first characterized by SEM. Scanning electron microscopy (SEM) has been an essential tool for characterizing the surface morphology and fundamental physical properties of the absorbent. A typical scanning electron micrograph image of the carbon ceramic electrode, MWCNT modified CCE and Rh(III)-complex/MWCNT modified CCE surface, are shown in Fig. 4.

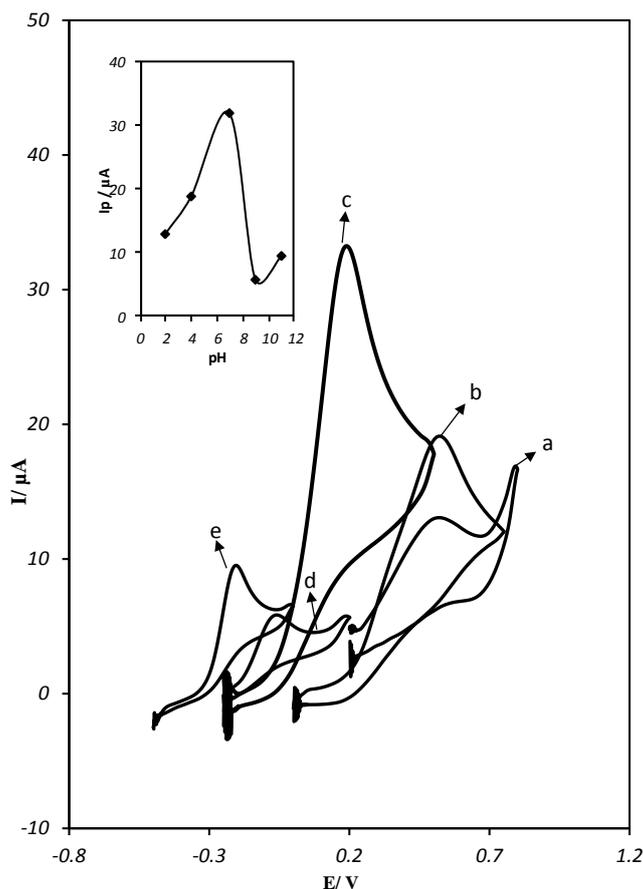


**Fig. 4.** SEM image of (A) bare carbon ceramic electrode (B) MWCNT modified CCE (C) Rh(III)-complex/MWCNT modified CCE

### 3.4. The effect of pH solution

The oxidation of hydrazine showed a strong dependence on pH, so pH be optimized for their catalytic determination. Therefore, we studied the electrochemical behavior of the hydrazine in buffered solutions with different pH values 2-11 (Fig. 5). From this figure it can

be concluded, for the oxidation of 1 mM hydrazine, the anodic peak potential shifts to more negative values with increasing pH and the catalytic oxidation is more favored at neutral pH. Thus the Rh(III)-complex has a better electrocatalytic activity for the oxidation of hydrazine in a basic solution with pH equal 7, and also the sensitivity is enhanced by working at this pH at which the current is in maximum. The decrease of current at lower and higher pH 7 can be due to the protonation or deprotonation of hydrazine, which causes a shift in the formal potential of hydrazine [40].



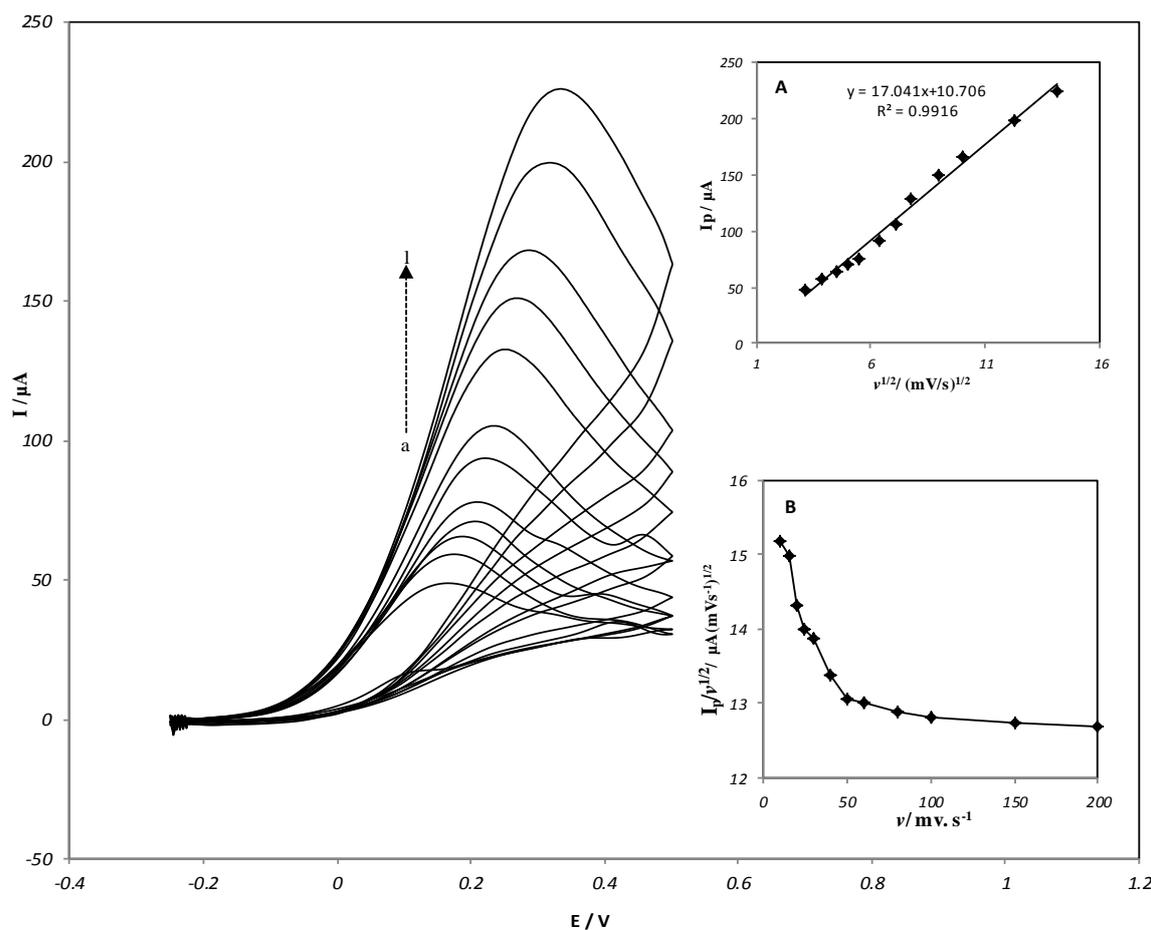
**Fig. 5.** Cyclic voltammograms of Rh(III)-complex/MWCNT modified CCE in 1 mM hydrazine solutions with different buffered pHs: (a) 2, (b) 4, (c) 7, (d) 9 and (e) 11. Scan rate was  $50 \text{ mV s}^{-1}$ . Inset shows dependence of the oxidation current of hydrazine on pH values

Fig. 6 shows the cyclic voltammograms of a Rh(III)-complex/MWCNT modified carbon ceramic electrode at various scan rates obtained in 0.1 M phosphate buffer solutions (pH 7) containing 1.0 mM hydrazine. The peak current for the anodic oxidation of hydrazine is proportional to the square root of scan rate (fig. 6.) the reaction involves mass transport. It can be noted from Fig. 4B that the anodic currents increase and the peak potential shifts as the scan rate increases. When peak current values were plotted against  $v^{1/2}$  (Fig. 3B), the following linear relationship was obtained:

$$I_p = 10.70 + 17.041 v^{1/2} \text{ (mV}^{1/2} \text{ s}^{1/2}\text{)}, \quad R^2 = 0.9916$$

This behavior suggests that the oxidation process is controlled by diffusion.

Also, a plot of the sweep rate-normalized current ( $i_p/v^{1/2}$ ) vs. sweep rate (Fig. 6 inset B) exhibits the characteristic shape typical of an electrochemical-chemical (EC') catalytic process. The slope of  $I_p$  versus  $v^{1/2}$  is  $17 \mu\text{A}/(\text{mV s}^{-1})^{1/2}$ .



**Fig. 6.** Cyclic voltammograms of modified carbon ceramic electrode in 0.1 M KCl solutions in phosphate buffer electrolyte solution (pH 7) containing 1 mM hydrazine at scan rates of a-l: (a) 10, (b) 15, (c) 20, (d) 25, (e) 30, (f) 40, (g) 50, (h) 60, (i) 80, (j) 100, (k) 150, (l) 200  $\text{mV s}^{-1}$ , insets: (A) dependence of the peak current with square root of the scan rate, (B) variation of the scan rate normalized current ( $I_p/v^{1/2}$ ) with scan rate

Thus, according to the following equation for a totally irreversible diffusive process [41]:

$$I_p = 3.01 \times 10^5 n [(1-\alpha) n_a]^{1/2} A c D^{1/2} v^{1/2}$$

And considering  $(1-\alpha)n\alpha=0.55$  (see below),  $D=3.31\times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  (see chronoamperometric studies),  $A=0.031 \text{ cm}^2$ , it is estimated that the total number of electrons involved in the anodic oxidation of hydrazine is  $n\approx 4$ .

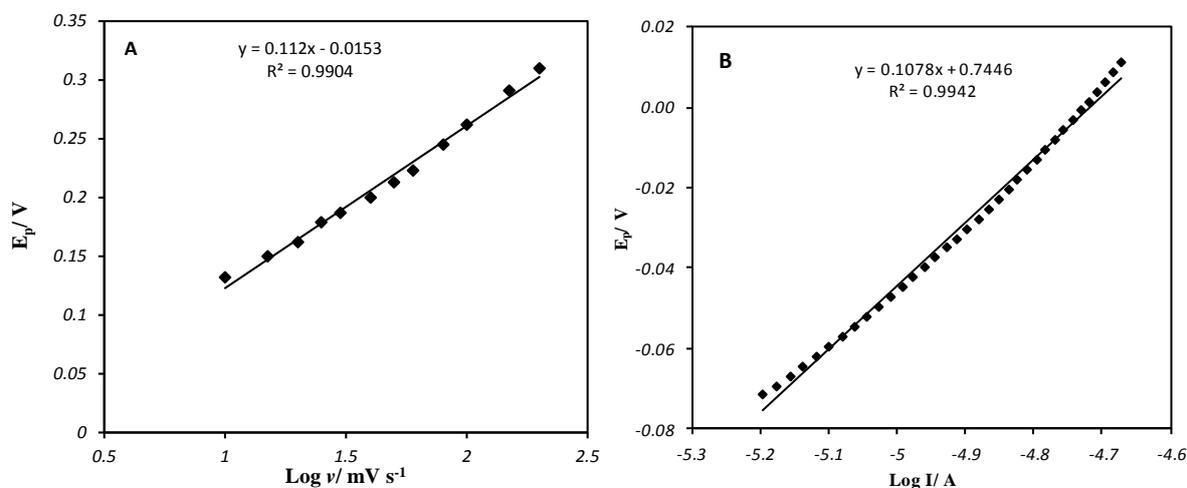
In order to get information on the rate determining step, The peak potential,  $E_p$ , is proportional to  $\log v$  as can be seen in Fig.4A. The slope of  $E_p$  versus  $\log v$  is 112 mV. The tafel slope may be estimated according to the equation for the totally irreversible diffusion-controlled process:

$$E_p = (b \log v)/2 + \text{constant} \quad (3)$$

So,  $b=224 \text{ mV}$ . This result is close to that obtained from polarization measurement [42].

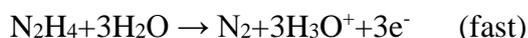
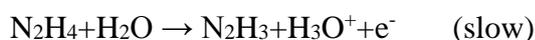
This slope indicates a one electron transfer to be rate limiting assuming a transfer coefficient of  $\alpha=0.73$

The tafel slope,  $b$ , can be obtained by another method. A tafel plot was drawn (Fig. 5B). Derived from data of the rising part of the current-voltage curve at a scan rate of  $10 \text{ mV s}^{-1}$ , A slope of  $107 \text{ mV decade}^{-1}$  is obtained which indicates that the rate limiting step is one electron transfer to be rate limiting assuming a transfer coefficient of  $\alpha=0.72$ .



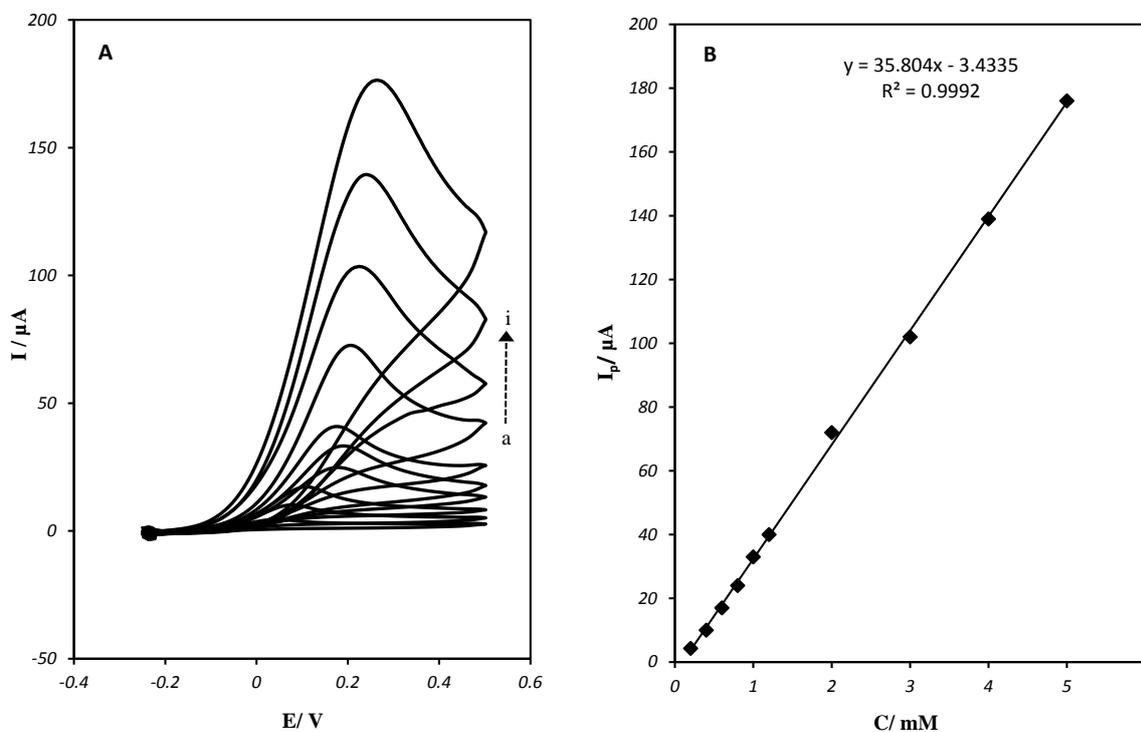
**Fig. 7.** (A) Plot of  $E_p$  versus  $\log v$ . (B) Tafel plot Derived from data of the rising part of the current-voltage curve at a scan rate of  $10 \text{ mV s}^{-1}$

Accordingly, the following mechanism can be proposed for the oxidation of hydrazine on a Rh(III)-complex/MWCNT modified carbon ceramic electrode in neutral solution:



In other words the rate-determining step is a one electron transfer followed by a three-electron process to give  $N_2$  as a final product.

The cyclic voltammograms at different concentrations of hydrazine are shown in Fig. 7B. A plot of the peak current values as a function of the concentration was drawn. The plot was linear in the concentration range of 0.2–5 mM hydrazine (Fig. 8B).



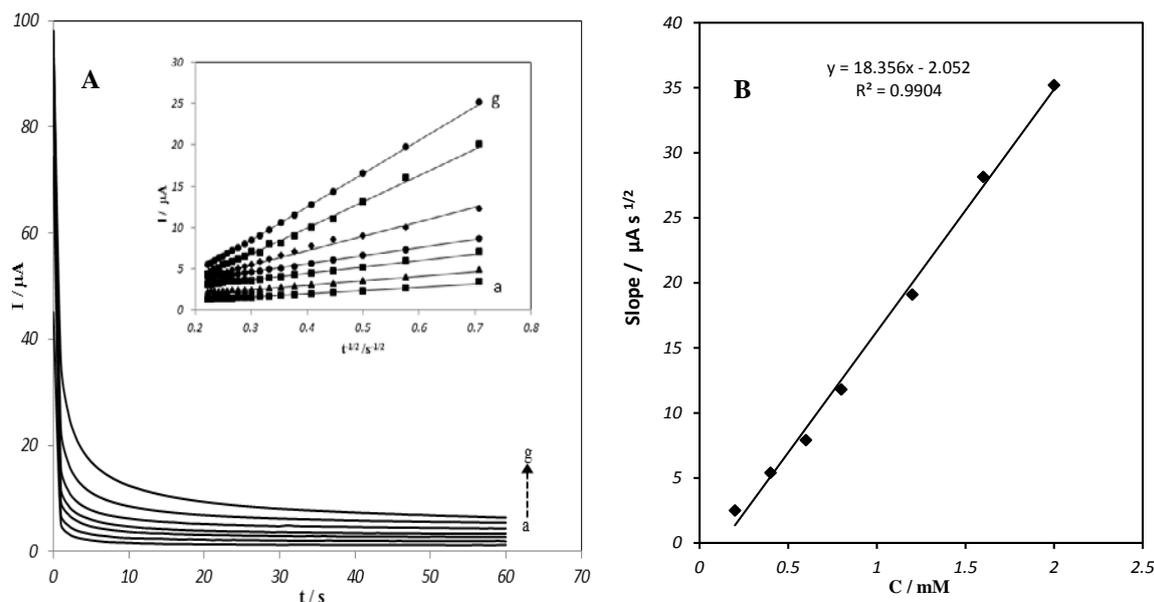
**Fig. 8.** (A) Cyclic voltammograms for increasing concentrations of hydrazine from 0.2 to 5 (a to i) mM in buffer solution (pH 7) containing 0.1 M KCl solutions on Rh(III)-complex/MWCNT modified CCE. Scan rate was  $50 \text{ mV s}^{-1}$ . (B) Calibration plot for concentrations of hydrazine from cyclic voltammograms

### 3.5. Chronoamperometric studies

The electrocatalytic oxidation of hydrazine at the Rh(III)-complex/MWCNT modified carbon ceramic electrode was studied by chronoamperometry. The chronoamperograms obtained for a series of hydrazine solutions with various concentrations as illustrated in Fig. 9. An increase in concentration of hydrazine was accompanied by an increase in anodic currents obtained for a potential step of 400 mV versus SCE. In addition, the level of the Cottrell current, which was measured for 60 s, increase with increasing concentration of hydrazine in the range of 0.2–2 mM. In chronoamperometric studies, the diffusion coefficient of hydrazine the modified electrode can be determined. The relationship between current and time can be described by the Cottrell equation [43]:

$$I = n F A D^{1/2} c / \pi^{1/2} t^{1/2} \quad (5)$$

Where  $D$  is the diffusion coefficient ( $\text{cm}^2\text{s}^{-1}$ ) and  $c$  is the bulk concentration ( $\text{mol cm}^{-3}$ ). The plot of  $I$  versus  $t^{-1/2}$  will be linear, and from the slope, the value of  $D$  can be obtained. Fig. 9 A, inset shows the experimental plots of the resulting straight line were then plotted versus the concentration of hydrazine (Fig. 9 B), from which we calculated a diffusion coefficient of  $D = 3.31 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$  for hydrazine.



**Fig. 9.** (A) Chronoamperometric response of a Rh(III)-complex/MWCNT modified CCE in 0.1 M phosphate buffer solution (pH 7.0) containing different concentrations of hydrazine for a potential step of 400 mV vs. SCE, in the range of 0.2, 0.4, 0.6, 0.8, 1.2, 1.6 and 2 mM. Inset shows Plot of plot of  $I$  versus  $t^{-1/2}$  obtained from chronoamperometric experiments. (B) Plot of the slope of linear segments against the hydrazine concentration

#### 4. CONCLUSIONS

The Rh(III)-complex/MWCNT modified CCE act as an electrocatalyst for oxidation of hydrazine. This electrode exhibits excellent electrocatalytic behavior toward hydrazine oxidation in aqueous phosphate buffer solution containing KCl as supporting electrolyte. The overall number of electrons involved in the oxidation of hydrazine, the number of electrons involved in the rate-determining step and the diffusion coefficient of hydrazine were calculated. Thus, the results obtained for hydrazine shows that terpyridine complex can be used for determination of other compounds.

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