Available online at www.sciencedirect.com
SCIENCE DIRECT®
Talanta 68 (2006) 1610–1616
Talanta
www.elsevier.com/locate/talanta

Amperometric detection of ultra trace amounts of Hg(I) at the surface boron doped diamond electrode modified with iridium oxide

Abdollah Salimi*, Vali Alizadeh, Rahman Hallaj

Department of Chemistry, Kurdistan University, P.O. Box 416, Sanandaj, Iran

Received 24 March 2005; received in revised form 27 July 2005; accepted 9 August 2005
Available online 22 September 2005

Abstract

Iridium oxide (IrOx) films formed electrochemically on the surface boron doped diamond electrode by potential cycling in the range −0.2 to 1.2 V from a saturated solution of alkaline iridium(III) solution. A strongly adherent deposit of iridium oxide is formed after 5–10 potential scans. The properties, stability and electrochemical behavior of iridium oxide layers were investigated by atomic force microscopy and cyclic voltammetry. The boron doped diamond (BDD) electrode modified with electrodeposition of a thin film, exhibited an excellent catalytic activity for oxidation of Hg(I) over a wide pH range. The modified electrode shows excellent analytical performance for Hg(I) amperometric detection. The detection limit, sensitivity, response time and dynamic concentration ranges are 3.2 nM, 77 nA μM^{-1}, 100 ms and 5 nM–5 μM. These analytical parameters compare favorably with those obtained with modern analytical techniques and recently published electrochemical methods.

Keywords: Boron doped diamond; Modified electrode; Iridium oxide; Hg(I); Amperometry

1. Introduction

Mercury is present as a trace contaminant in all environmental compartments as a result of both natural and anthropogenic activities. Determination of trace levels of this element in the environment is a highly important, yet challenging analytical problem. To determine the environmentally toxic trace levels of mercury, highly sensitive and selective methods need to be developed. Spectroscopic techniques such as cold vapor generation (CVG) followed by atomic absorption spectrometry [1], cold vapor atomic fluorescence spectrometry [2], liquid chromatography-inductively coupled plasma mass spectrometry [3], capillary zone electrophoresis-inductively coupled plasma mass spectrometry [4] and plasma atomic emission spectroscopy [5] have been used successfully for detection of mercury. These methods generally have good sensitivity, reproducibility and can meet practical requirements. However, they require expensive instruments, well-controlled experimental conditions, sample making and relatively large sample volumes for analysis. Also, they are not suitable for on-line monitoring.

Simple methods are highly required for rapid measurements of trace levels of mercury in industrial process control. Electrochemical detection offers several advantages, including remarkable sensitivity, inherent miniaturization and portability, independence of optical path length or sample turbidity, low cost, low power requirements and high compatibility with advanced micromachining technologies. Because of the simple procedure and high sensitivity of electroanalysis and electroactivity of mercury, studies of measurement of mercury with electrochemical methods were carried out. Various electrochemical methods have been applied to the determination of mercury, and significant improvements in both sensitivity and selectivity were gained by using chemically modified electrodes.

Several electrodes including a glassy carbon electrode modified with 2-mercaptobazimidazole [6], carbon paste electrode modified with silica particles [7], carbon paste electrode modified with thiolic resin [8], polymeric membrane ion selective electrode [9], modified screen printed electrode [10], anodic stripping voltammetry at the rotating gold electrode [11], amperometric detection by formation of complexes with l-tyrosine at the surface GC electrode [12] and other electrodes have been used for measuring mercury [13]. Unfortunately, most of the modified electrodes used for mercury detection have certain disadvantages such as considerable leaching of electron trans-

---

* Corresponding author. Fax: +98 871 6660075.
E-mail addresses: absalimi@yahoo.com, absalimi@uok.ac.ir (A. Salimi).

0039-9140/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.talanta.2005.08.048

fer mediators and poor long term stability. Furthermore, their preparation methods are more expensive and difficult and the irreversible adsorption behavior renders the routine analysis difficult. Also, some of them are not sensitive enough for real sample analysis. Hence, it is pertinent to explore and develop different electrode surfaces for mercury detection.

The use of boron doped diamond as a robust electrode substrate is well established due to its wide potential window in aqueous solutions [14], low background currents [15], long term stability and low sensitivity to dissolved oxygen [16]. Boron doped diamond (BDD) has recently been utilized electroanalytically as a suitable electrode substrate for determination of several metals such as Ag [17], Pb [18], Cu [19] and Mn [20]. Differential pulse anodic stripping voltammetry at the surface of the BDD electrode has been used for detection of mercury(II) [21]. The Hg_2^{2+} ion has been determined at the surface of the BDD electrodes by differential pulse voltammetry, and square wave voltammetry at the surface BDD electrode that it was conditioned at 1.5 V [22].

Although mercury species have been determined successfully at the surface of BDD electrodes but these methods cannot be used for rapid measurements of trace levels of mercury species and other cations can be reduced with Hg_2^{2+} ion over the range of potential used. The analytical properties of BBD electrodes modified with electron transfer mediators can be improved. Recently, the application of BDD electrodes modified with oxide layers of metals such as Ag, Sn, Bi and Pb have been reported [23–25]. Considering the fact that IrOx films are stable, reversible and a good electron transfer mediator, it can be used for modification of different electrode surfaces. The BDD electrode modified with iridium oxide layers has been used for detection of hydrogen peroxdie at low positive potential [26]. Recently, we reported the application of BDD electrodes modified with iridium oxide films for detection of ultra trace amount of As(III) [27]. In the present study, the possibility of BDD electrode modified with iridium oxide film for electrocatalytic oxidation of Hg_2^{2+} is investigated. The analytical performance of modified electrode respectively is described as an amperometric sensor for nanomolar detection of mercury.

2. Experimental

2.1. Reagents

All chemicals used were of analytical reagent grade and used as received without further purification. Mercury(I), nitrate and potassium hexachloroiridate(III) were obtained from Aldrich. The aqueous solutions were prepared using doubly distilled deionized water, and solutions were deoxygenated by purging with high purified argon gas. The electrochemical cell was kept under argon atmosphere throughout the experiments. Buffer solutions (0.1 M) were prepared from H_2SO_4, H_3PO_4, CH_3COONa and Na_2HPO_4. For adjustment of pH solution, HCl and KOH were used. The deposition solution of iridium was prepared according to the two-step procedure reported by Baur and Spaine [28]. The first step in the preparation is the formation of the diaquotetrachloroiridate(III) ion ($Ir(H_2O)_2Cl_4^-$) from $K_3Ir(Cl)_6$. A 1 mM solution of $K_3Ir(Cl)_6$ in 0.1 M HCl is dissolved by heating at 100 °C for 2 h. The second step in the preparation of deposition solution is the formation of iridium(III) oxide from $Ir(H_2O)_2Cl_4^-$ with added base based according to following reaction:

$$Ir(H_2O)_2Cl_4^- \xrightarrow{NaOH} Ir_2O_3 \cdot xH_2O \qquad (1)$$

Prior to the addition of base, oxygen must be removed because the iridium(III) oxide is unstable in the presence of oxygen [28]. After removing the oxygen from the acidic solution of, $Ir(H_2O)_2Cl_4^-$ the pH of solution was raised to 10.5 by adding anhydrous potassium carbonate, and this solution used for the deposition of iridium oxide onto the BDD electrode surfaces.

2.2. Apparatus

Cyclic voltammograms were recorded using an Autolab modular electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PSTA 20 module and driven GEPS software (ECO Chemie) was used for amperometric and voltammetric measurements. A BDD electrode (BDD, DeBeers Industry Diamond Division Ascot, supplied via Windsor Scientific, Slough, UK) is modified with electrodeposition of iridium oxide (prepared as follows) was used as the working electrode; a platinum wire and saturated calomel electrode (SCE, Radiometer, Copenhagen) were used as the counter and reference electrodes, respectively. The rotating disk electrode of BDD (3 mm × 3 mm BDD in Teflon) was made in the workshop of the Physical Chemistry Laboratory of Oxford University. A personal computer was used for data storage and processing. The BDD film electrode was housed in Teflon mounting with an electrical connection to the rear graphite side made via a brass road, attached using silver epoxy resin. The BDD electrodes modified with iridium oxide layers were characterized by atomic force microscopy (AFM). The AFM was a digital Instruments Multimode SPM, operating in ex situ Tapping Mode. A Methrom drive shaft was used for stirring solutions during amperometric measurements of mercury(I). The electrochemical measurements were carried out at thermostated temperature of 25 ± 0.1 °C. A personal computer was used for data storage and processing.

3. Results and discussions

3.1. Electrodeposition of IrOx at BDD electrode

Potential cycling was used in this study to form an iridium oxide layer at the surface of working electrode. For this purpose the potential was scanned between −0.2 and 1.2 V versus SCE at 50 mV s^{-1} for 10 cycles in a solution of 0.1 mM Ir^{3+} at a pH of 10.5. The currents on the consecutive scans increased (not shown) indicating formation of an electroactive deposit film of iridium oxide on the electrode surface. The oxidation of iridium(III) oxide and precipitate formation of iridium(IV) oxide films is known to be initiated electrochemically at the surfaces

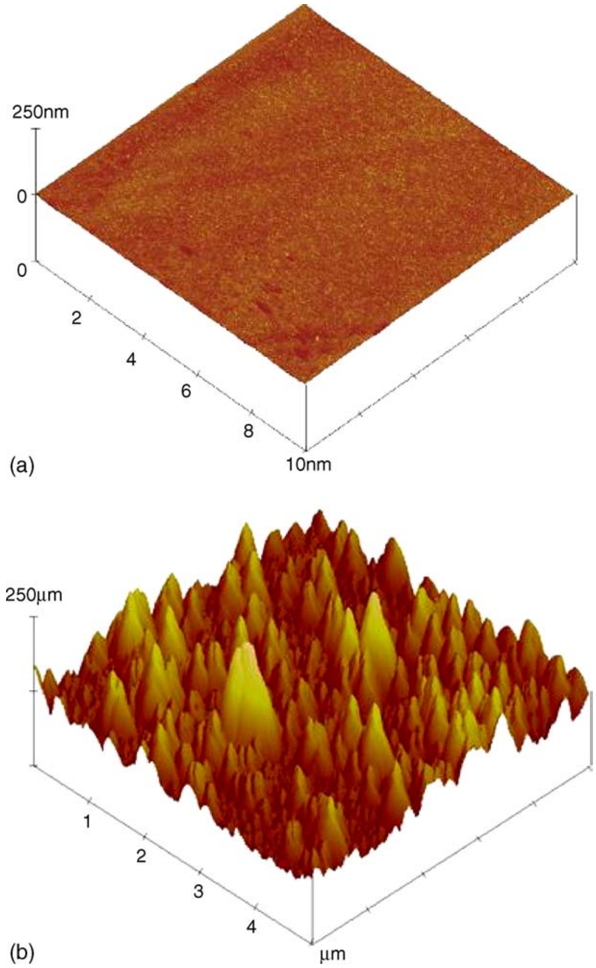

Fig. 1. AFM images of clean polished BDD electrode (a) and BDD electrode modified with iridium oxide film (b) (10 potential cycles in 0.1 mM deposition solution).

of working electrodes based on the following reaction [28]:

$$Ir_2O_3 \cdot xH_2O\,(aq) + 2OH^- \rightarrow 2IrO_2 \cdot xH_2O\,(s) + H_2O + 2e^- \qquad (2)$$

The modified electrodes were rinsed with distilled water, and used for electrochemical measurements. Fig. 1 compares atomic force microscopy images of a polished BDD and a BDD modified with an iridium oxide film. The figure indicates the formation of a uniformly distributed thin film of iridium oxide particles deposited on the electrode surface.

3.2. Electrochemical properties of IrOx modified boron doped diamond

Fig. 2 shows the cyclic voltammograms of BDD electrode modified with iridium oxide (10 potential cycles) in phosphate buffer solution (pH 4) at different scan rates. When the potential was scanned between 0.0 and 0.7 V, we found a single, well-defined redox couple with a formal potential of 0.4 V versus SCE, a low background current and low peak potential separation. This is typical of a surface immobilized redox couple, and corresponding to the Ir(III)/Ir(IV) system. The ratio of cathodic to anodic peak currents at various sweep rates was almost unity. As shown in inset of Fig. 2 the anodic and cathodic peak currents are directly proportional to the scan rate of potential as expected for a surface confined redox process [29]. The peak-to-peak potential separations (ΔE_p is about 50.0 mV) for sweep rate below 100 mV s^{-1}. This suggests facile charge transfer kinetics over this sweep range. The surface concentration of electroactive species, Γ, can be calculated from the following equation:

$$\Gamma = \frac{Q}{nFA} \qquad (3)$$

where Q is the charge obtained by integrating the anodic peak at low voltage scan rates and other symbols have their usual meaning. After cycling the electrode 10 times in 0.2 mM Ir^{3+} solution, the calculated surface coverage was found to equal 4×10^{-10} mol cm^{-2}. The stability and electrochemical properties of the modified electrode at different pHs have been reported [27]. Since the electron transfer rate constant for this redox couple is about 2.4 s^{-1} [27], it can be used as an excellent electron transfer mediator for electrocatalytic processes.

3.3. Electrocatalytic oxidation of mercury(I) on the IrOx modified BDD electrode

Due to the chemical stability and electrochemical reversibility of iridium couple, it is widely used in electrocatalysis as electron transfer mediator to shuttle electrons between analytes and substrate electrodes. As mentioned above, BDD electrodes modified with iridium oxide films had a very stable electrochemical behavior at wide pH range, therefore they can be used as a sensor for analytical applications. One of the objectives of this work was to fabricate a modified electrode with capability of the electrocatalytic oxidation of mercury(I). In order to test electrocatalytic activity of the modified electrodes, cyclic voltammograms were obtained in the presence of mercury(I) at the surface of bare and modified BDD electrodes. Fig. 3 shows cyclic voltammograms for the electrooxidation of mercury(I) at a bare and modified BDD electrode in buffer solution (pH 4).We can see at the surface of a bare BDD electrode, ${Hg_2}^{2+}$ is electroinactive in the potential range 0.1–0.8 V. At the surface of a modified BDD electrode, upon the addition of 8.35 µM ${Hg_2}^{2+}$, there is an enhancement of the anodic peak current. Thus, a decrease in overpotential and enhancement of anodic peak current for mercury(I) oxidation is obtained, indicating a strong catalytic effect of IrOx modified BDD electrode. The anodic response decreased slightly (10%) during 3 scans and remained stable and no shift of peak potential was detected even after 50 successive scans. The effect of aging on the performance of the modified electrode was studied by repeating the experiment after 2 weeks in 0.1 M phosphate electrolyte (pH 5) and the peak potential for mercury(I) oxidation remained unchanged. In addition, only less than 7% diminution of the current signals was observed compared to the initial response. The stability of the modified electrode and its catalytic activity for mercury oxidation was investigated by recording the cyclic voltammograms of iridium oxide modified BDD electrodes before and

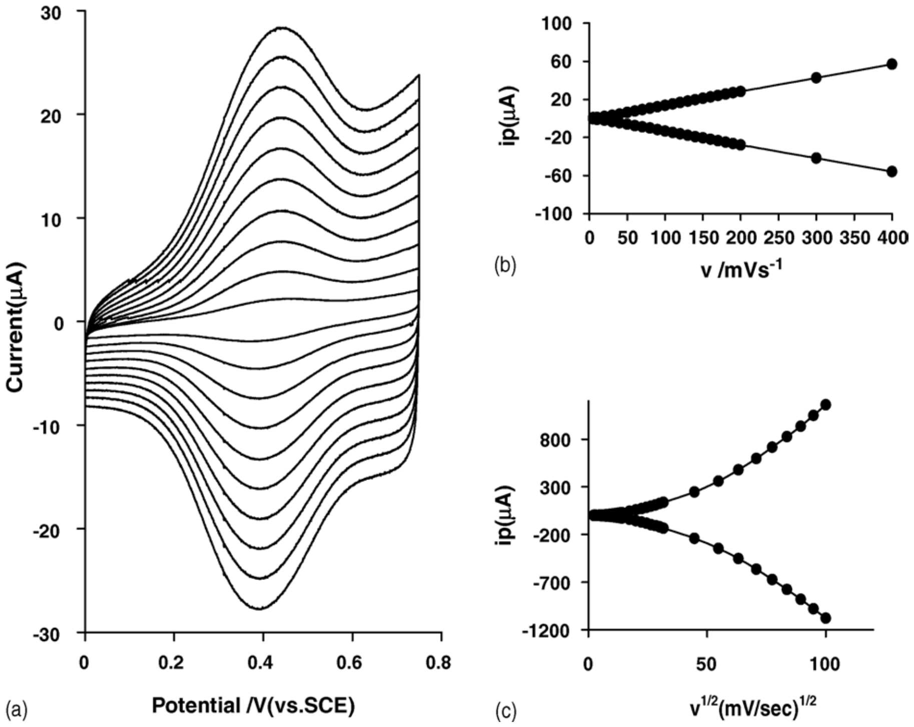

Fig. 2. Cyclic voltammetry response of a modified BDD electrode in 0.1 M phosphate buffer solution (pH 4) at scan rates from inner to outer, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55 and 60 mV s^{-1}. *Inset* (b and c): Plots of peak current vs. scan rate and square root of scan rates.

after using these electrodes in the presence of mercury(I). After 20 cyclings at scan rate of 20 mV s^{-1} in a solution containing 5 μM Hg_2^{2+}, and recording cyclic voltammograms in the presence and absence of mercury(I), the peak potentials remained unchanged and the currents decreased by less than 15% and 8%, respectively. The reproducibility (RSD) of the cyclic voltammogram currents for a 5 μM mercury(I) at pH 4 for eight replicate determination was <4%.

In order to optimize the electrocatalytic response of the modified IrOx BDD electrode toward mercury(I) oxidation, the effect of pH on the catalytic oxidation behavior was investigated. The cyclic voltammograms of modified electrode in 8.35 μM Hg_2^{2+} at different pH values were recorded (Fig. 4). Although, the modified electrode showed electrocatalytic activity at pH 2–6, higher peak current was observed at pH 4. Fig. 5 shows the dependency between the voltammetric responses of the modi-

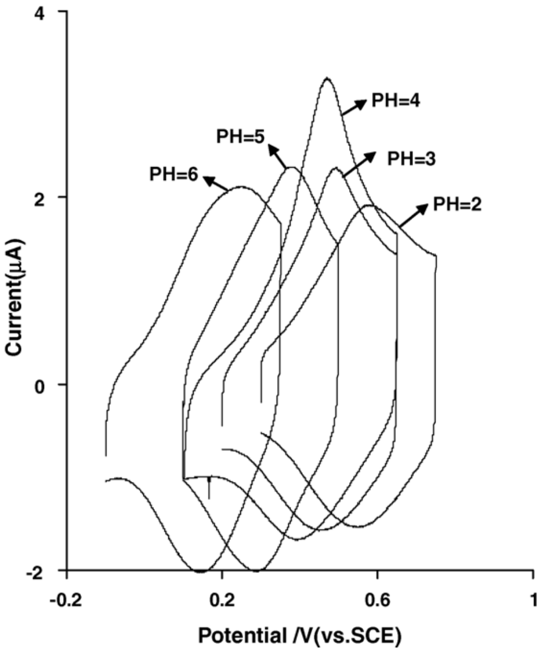

Fig. 3. Cyclic voltammograms of a modified BDD electrode in 0.1 M buffer solution (pH 4) at scan rate 20 mV s^{-1} in the absence (a) and presence 8.35 μM mercury solution (b); (c and d) as (a and b) for bare BDD electrode.

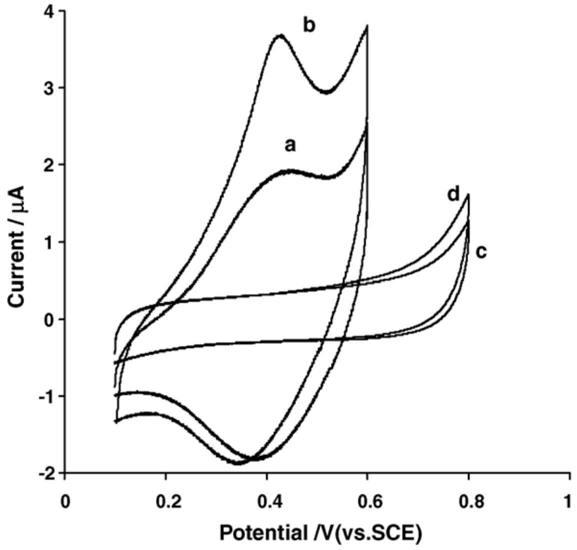

Fig. 4. Cyclic voltammograms of modified BDD electrode in 8.35 μM mercury(I) solution for pH values 2–6, scan rate 20 mV s^{-1}.

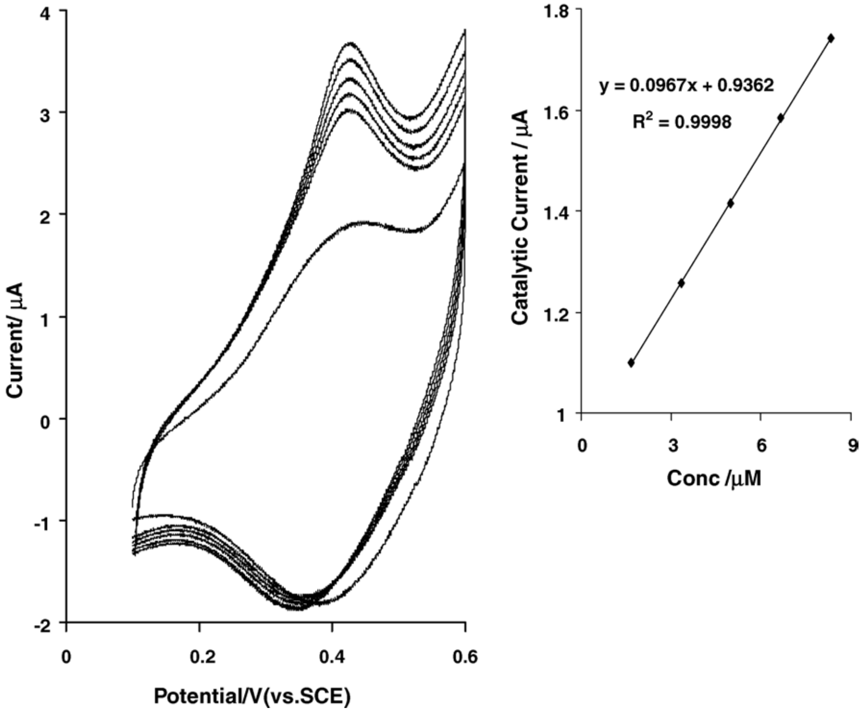

Fig. 5. Cyclic voltammograms of modified BDD electrode in pH 4 at scan rate 20 mV s^{-1}, with increasing the mercury(I) concentration 0.0, 1.65, 3.3, 4.95, 9.65 and 8.35 µM mercury(I). *Inset*: Plot of the catalytic peak current vs. mercury concentration.

fied BDD electrode on the addition of mercury(I) concentration. The anodic peak current increased by raising the concentration of mercury(I). The catalytic current values are linearly related to $Hg_2{}^{2+}$ concentration within the range of 1.65–8.35 µM (I (A) = 0.0967C (µM) + 0.9362 and $r^2 = 0.9998$). When the concentration of mercury(I) is more than 10 µM, the anodic peak currents start to decrease and the formation and deposition of calomel Hg_2Cl_2 (chloride diffuse from reference electrode to experimental solution) at electrode surface deactivate the electrocatalytic properties of iridium oxide film for mercury(I) oxidation. By recording the cyclic voltammograms of 8.35 µM mercury(I) solution at different scan rates (not shown), the peak currents for the anodic oxidation of mercury(I) were proportional to the square root of the scan rate. These results indicate that at sufficient positive potential, the reaction is controlled by diffusion of $Hg_2{}^{2+}$, which is the ideal case for quantitative applications. It can also be seen that by increasing the sweep rate, the peak potential for the catalytic oxidation of mercury(I) shifted to higher positive value, suggesting a kinetic limitation in the reaction between the redox sites of iridium oxide and $Hg_2{}^{2+}$. Based on these results the following catalytic scheme (EC′) showed that IrO_2 catalysed mercury(I) oxidation in the following electrochemical catalytic pathway:

$$\text{Ir (reduced form)} \rightarrow \text{Ir (oxidized form)} \tag{4}$$

$$\text{Ir (oxidized form)} + Hg_2{}^{2+} \xrightarrow{K_{cat}} \text{Ir (reduced form)} + 2Hg^{2+} \tag{5}$$

In order to obtain information on the rate determining step, a Tafel slope was determined by using the following equation [30]:

$$E_p = \frac{b}{2\log(v)} + \text{constant} \tag{6}$$

According to this equation, the slope of E_p versus log v plot is $b/2$, where b indicates the Tafel slope. The value of b which was found to be 84 mV in this experiment, suggesting a one electron transfer process in a rate limiting step, assuming a transfer coefficient of $\alpha = 0.31$. The catalytic rate constant for reaction (5) can be evaluated by cyclic voltammetry. Under the above conditions for EC′ mechanism, the Andrieux and Saveant theoretical model [31] can be used to calculate the catalytic rate constant. Based on this theory, there is a relation between the peak current and the concentration of substrate compound for the case of low scan rates and large catalytic rate constant.

$$I_p = 0.496nFAD^{1/2}\left(\frac{vF}{RT}\right)^{1/2} C_s \tag{7}$$

where D and C_s are the diffusion coefficient (cm^2 s^{-1}) and the bulk concentration (mol cm^{-3}) of substrate ($Hg_2{}^{2+}$), respectively, and other symbols have their usual meaning. Low value of K_{cat} gave coefficients lower than 0.496. For low scan rates (5–20 mV s^{-1}), the average value of this coefficient was found to be 0.26 for a IrOx modified BDD electrode with a coverage of 4.0×10^{-10} mol cm^{-2} and a geometric area (A) of 0.25 cm^{-2} in 5 µM mercury(I). The D values for mercury(I) was calculated by chronoamperometric method and found to be about 1.2×10^{-5} cm^2 s^{-1}. According to Andrieux and Saveant approach and using Fig. 1 in reference [31] the average value of K_{cat} was calculated to be 7.6 (±0.1) × 10^3 M^{-1} s^{-1}. The high

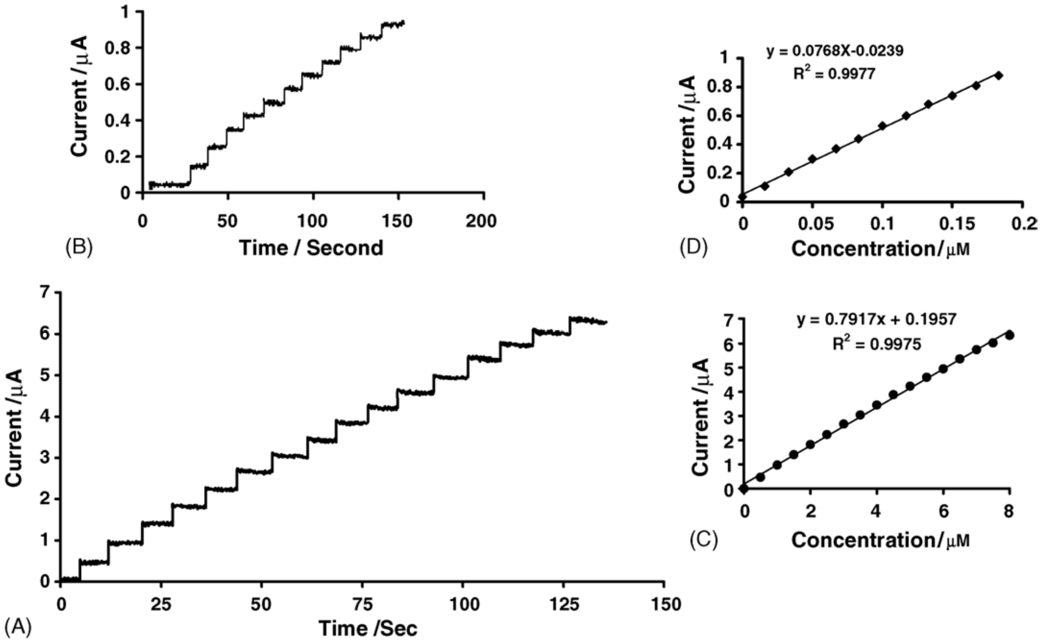

Fig. 6. Amperometric response at modified BDD electrode held at 0.4 V in stirred buffer solution (pH 4) for successive addition of (A) 0.5 μM and (B) 16 nM of mercury(I). (C and D) Plots of chronoamperometric currents vs. mercury concentrations.

value of catalytic rate constants indicate that the IrOx can be used as an excellent electron transfer mediator for electrooxidation of mercury(I).

3.4. *Amperometric measurements of Hg_2^{2+} at modified BDD electrode*

The passivation of reactants decreases the reproducibility of determinations at concentrations studied for cyclic voltammetry. In addition, the hydrodynamic amperometry under stirred conditions has a much higher current sensitivity than cyclic voltammetry. It was used to estimate the lower limit of detection of mercury(I) at IrOx modified BDD electrode. As shown above the iridium oxide film modified BDD electrode has excellent and strong electrocatalytic properties and facilitates the low potential amperometric measurement of Hg_2^{2+}. The applied potential for Hg(I) detection at this modified electrode is relatively low, which is great advantage since the number of interferences in electrochemical detection increases exponentially with increasing the applied potential value. Various possible interferents were evaluated by adding a specified concentration of interfering substances into phosphate electrolyte (pH 4) containing 8.35 μM of Hg(I). The experimental results showed that at least 50-fold of Mn^{2+}, Co^{2+}, Ni^{2+}, Cr^{3+}, Fe^{2+}, Cu^{+2}, Hg^{2+} and Sn^{2+} have no effect on the amperometric responses of mercury(I). Fig. 6 shows chronoamperograms recorded at stirred solution using constant potential (0.45 V) at the modified electrode in phosphate buffer solution with (pH 4) during successive addition of 16 nM and 0.5 μM mercury(I). A well-defined response is observed even for addition of 5 nM mercury (not shown). The response time measured in amperometric measurements was 1 s or less to 90% of the full signal. As shown in the inset of Fig. 6, the measured current increases with increasing mercury concentration in solution while for a high concentration, the plot of *I* versus mercury concentration deviates from linearity. The calibration plots for the mercury oxidation currents were linear for a wide range of concentration 5 nM–5 μM. Linear least squares calibration curves over the range of 16–175 nM (11 points) gave a linear dependence of current versus concentration of mercury which fitted the equation $I\,(\mu A) = 0.0768\ \mu A\ \mu M^{-1} - 0.0239\ \mu A$, sensitivity 77 nA μM^{-1} and a correlation coefficient of 0.9977. The electrode has a detection limit of 3.2 nM at signal to noise ratio of 3. High stability of amperometric response during long period of time toward Hg_2^{2+} oxidation is one of the advantages of this modified electrode for amperometric detection of mercury(I). The amperometric response of 8.35 μM mercury(I) was recorded over 15 min periods (Fig. 7). As shown in Fig. 7, the current reduced about 10% in the first minute of the measurement and then remained constant. For the evaluation of the reproducibility a series of replicate addition of Hg_2^{2+} was recorded (not shown). The relative standard deviation for six replicate addition of mercury(I) was less than 5%. Therefore, the modified electrode exhibits high sensitivity, stability at long period of time, reproducibility and fast response to oxidation mercury and it can be used as an amperometric detector for ultra trace determinations of mercury(I).

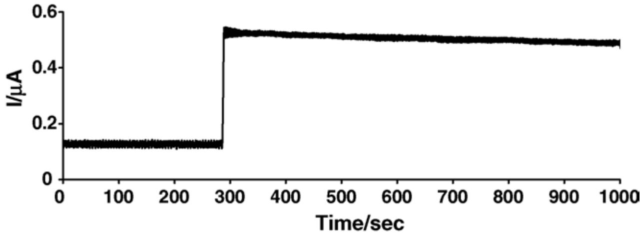

Fig. 7. Stability of the response of the modified BDD electrode in 8.35 μM mercury(I) solution, other condition as in Fig. 6.

4. Conclusion

Cyclic voltammetry in a saturated solution of alkaline iridium(III) was used for electrodeposition of electroactive iridium oxide film on a BDD electrode. A BDD electrode modified with iridium oxide film was found to be suitable for electrocatalytic oxidation of Hg_2^{2+} in the pH range 2–6. The results presented in this paper confirm that the IrOx modified BDD electrode enables very sensitive and stable amperometric measurements of mercury(I) at pH 4. The IrOx coating offers a significant increase in sensitivity and a marked decrease in the over voltage for mercury(I) oxidation. The catalytic response exhibits a linear dependence on the concentration of Hg_2^{2+} with a limit of detection 3.2 nM. The catalytic rate constant was determined by cyclic voltammetry is about $7.6(\pm0.1) \times 10^3\,M^{-1}\,s^{-1}$. The detection limit and the good long term stability confirm that this electrode can be a good candidate for many practical applications. It should also be mentioned that it is possible to fabricate miniature diamond electrode for electroanalytical detection of mercury(I) in ground water, plating solution and other aqueous solutions in hostile environments.

Acknowledgments

The authors are very thankful to Dr. Habibollah Daniali and Dr. Saied Soltanian for their discussions and helpful suggestions during the preparation of this manuscript and M.H. Hyde (Oxford University) for taking AFM images.

References

[1] M. Gallignani, H. Bahsas, M.R. Brunetto, M. Burguera, J.L. Burguera, Y.P. Pena, Anal. Chim. Acta 369 (1998) 57.
[2] K.C. Bowels, S.C. Apte, Anal. Chem. 70 (1998) 395.
[3] C.C. Wan, C.S. Chen, S.J. Jiang, J. Anal. At. Spectrom. 12 (1997) 683.
[4] Q. Tu, J. Qvarnstrom, W. Frech, Analyst 125 (2000) 705.
[5] C. Dietz, Y. Madrid, C. Camara, J. Anal. At. Spectrom. 16 (2001) 1397.
[6] M.F.B. Sousa, R. Bertazzoli, Anal. Chem. 68 (1996) 1258.
[7] A. Walcarius, J. Devoy, J. Bessiere, J. Solid State Electrochem. 4 (2000) 330.
[8] R. Agraz, M.T. Sevilla, L. Hernandez, J. Electroanal. Chem. 390 (1995) 47.
[9] M.H. Mashhadizadeh, I. Sheikhshoaie, Talanta 60 (2003) 73.
[10] P. Ugo, L.M. Moretto, O. Bertoncello, J. Wang, Electroanalysis 10 (1998) 1017.
[11] Y. Bonfil, M. Brand, E.K. Eisner, Anal. Chim. Acta 424 (2000) 65.
[12] S. Majid, M.E. Rhazi, A. Amine, C.M.A. Brett, Anal. Chim. Acta 464 (2002) 123.
[13] R. Agraz, M.T. Sevilla, L. Hernandez, J. Electroanal. Chem. 390 (1995) 47.
[14] J.W. Strojek, M.C. Granger, T. Dallas, M.V. Holtz, G.M. Swain, Anal. Chem. 68 (1996) 2031.
[15] S. Jolley, M. Koppang, T. Jakson, G.M. Swain, Anal. Chem. 69 (1997) 4099–4107.
[16] T.N. Rao, I. Yagi, T. Miwa, D.A. Tryk, A. Fujishima, Anal. Chem. 71 (1999) 2506.
[17] A.J. Saterlay, F. Marken, J.S. Foord, R.G. Compton, Talanta 53 (2000) 403.
[18] A.J. Saterlay, C. Agra-Gutierrez, M.P. Taylor, F. Marken, R.G. Compton, Electroanalysis 11 (1999) 1083.
[19] C. Prado, S.J. Wilkins, F. Marken, R.G. Compton, Electroanalysis 14 (2002) 262.
[20] A.J. Saterlay, J.S. Foord, R.G. Compton, Analyst 124 (1999) 1791.
[21] A. Manivannan, M.S. Seehra, A. Fujishima, Fuel Process. Technol. 85 (2004) 513.
[22] http://www.nasatech.com/briefs/Mar00/NPo20726.html.
[23] A.J. Saterlay, S.J. Wilkins, C.H. Goeting, J.S. Foord, R.G. Compton, F. Marken, J. Solid State Electrochem. 4 (2000) 383.
[24] M.E. Hyde, A.J. Saterlay, S.J. Wilkins, J.S. Foord, R.G. Compton, F. Marken, Solid State Electrochem. 6 (2002) 183.
[25] M.E. Hyde, R.G. Compton, J. Electroanal. Chem. 531 (2002) 19.
[26] C. Terashima, T.N. Rao, B.V. Sarada, N. Spataru, A. Fujishima, J. Electroanal. Chem. 544 (2003) 65.
[27] A. Salimi, M.E. Hyde, C.E. Banks, R.G. Compton, Analyst 129 (2004) 9.
[28] J.E. Baur, T.W. Spaine, J. Electroanal. Chem. 443 (1998) 208.
[29] A.J. Bard, L.R. Faulkner, Electrochemical Methods: Fundamentals and Applications, Wiely, New York, 2001.
[30] J.A. Harrison, Z.A. Khan, J. Eelectroanal. Chem. 28 (1970) 131.
[31] C.P. Andrieux, J.M. Saveant, J. Electroanal. Chem. 93 (1978) 163.