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SENSORS

Determination of Mercury Using a Novel Sonogel-Carbon 3-Methylthiophene Electrode

Hanane Zejli
Equipe de Recherché, Bioelectrochemie et Systèmes Interfaciaux,
University Abdelmalek Essaadi, Morocco

J. L. Hidalgo-Hidalgo de Cisneros and I. Naranjo-Rodriguez
Department of Analytical Chemistry, Faculty of Sciences,
University of Cádiz, Cádiz, Spain

Khalid Temsamani
Equipe de Recherché, Bioelectrochemie et Systèmes Interfaciaux,
University Abdelmalek Essaadi, Morocco

Abstract: A solid Sonogel-Carbon electrode was modified for the determination of Hg (II) in industrial waste water. 3-Methylthiophene (3MT), pyrrol, poly-3-methylthiophene (P3MT), polypyrrol, and C18 were used for the chemical modification. The obtained composite electrodes were tested for their response to Hg(II); the best results were observed for the 3MT monomer modification with a detection limit of $10^{-2}\,\mathrm{mg \cdot l^{-1}}$ and 3 weeks lifetime of use. A linear relationship between anodic peak height and concentration inside the range of $0.07–0.42\,\mathrm{mg \cdot l^{-1}}$ was obtained. A study of interferences due to other heavy metal is also included.

Keywords: 3-Methylthiophene, mercury(II), Sonogel-Carbon electrode

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Address correspondence to Hanane Zejli, Equipe de Recherché, Bioelectrochemie et Systèmes Interfaciaux, University Abdelmalek Essaadi, Morocco. E-mail: zejlih@yahoo.fr

INTRODUCTION

Mercury is one of the most well known toxic metals. Its toxicity is attributed to its harmful effects on the central nervous system that cause neuropsychiatric disorders (da Silva and Williams 1993). Mercury is usually present at low concentration levels in environmental samples as free metal or as complexes with inorganic and organic ligands (Das et al. 2001). Many analytical techniques have been employed for metal analysis, such as atomic absorption spectrometry (AAS) (Gadzekpo et al. 2000), X-ray fluorescence (Turyan and Mandler 1997), or UV spectrophotometry (Wittner and Riklin 1994), induced coupled plasma-atomic emission spectrometry (ICP-AES) (Krull et al. 1986), and induced coupled plasma-mass spectrometry (ICP-MS) (Harrington and Catterick 1997). These techniques commonly used for trace measurement of mercury in the laboratory, aside from their high cost, are not suitable for on-site monitoring. The portability and excellent sensitivity of electrochemical techniques make them very attractive for field monitoring of trace metals (Brett 1999).

On the other hand, the use of chemically modified electrodes for determination of mercury is an area of great interest. This has been encouraged by the complexation reactions with organic reagents as modifiers that have been widely applied. At the beginning, determination of mercury was successfully performed with carbon electrodes chemically modified with 1,5-diphenylcarbazide (Navratilova 1991), humic acid (Navratilova and Kula 1992), zinc diethyldithiocarbonate (Khoo and Cai 1996), and ion exchange amberlite LA2 (Cai et al. 1993). The detection limits obtained then were 5, 0.5, 0.8, and 50 nM, respectively.

Recently, some of us have developed a new type of graphite-based sol-gel electrode, named the Sonogel-Carbon electrode, which is obtained using high energy ultrasounds. Classical procedures for the synthesis of acid-catalyzed sol-gel-based electrode materials include the addition of an alcoholic solvent to the initial precursor mixture to make it homogeneous and the employment of an ultrasound bath for several minutes to promote the hydrolysis. Contrarily, by means of sonocatalysis, high energy ultrasounds are applied directly to the precursors, and ultrasonic cavitation is achieved so that hydrolysis with acidic water is promoted in a few seconds and in the absence of any additional solvent. Thanks to the phenomenon of ultrasonic cavitation, sol-gel reactions occur in a unique environment, leading to gels with special characteristics. These so-called sonogels are mainly of high density, with a fine texture and homogeneous structure. The mixture of sonogel with spectroscopic grade graphite leads to the Sonogel-Carbon electrode (Cordero-Rando et al. 2002; Hidalgo-Hidalgo-de-Cisneros et al. 2001).

These electrodes show very favorable electroanalytical properties when used as amperometric sensors and, furthermore, easily permit the incorporation of numerous receptor molecules at the Sonogel-Carbon materials

(Ballarin et al. 2002, 2003; Cordero-Rando et al. In press), which can notably improve the selectivity.

In the present paper, we propose a new application of Sonogel-Carbon electrodes based on the incorporation of 3-methylthiophene (3MT) for mercury. The developed electrode shows a good amperometric response. Hg(II) and also a great ability to preconcentrate the heavy metal, due to the well known affinity of 3-methylthiophene towards mercury (Zejli et al. 2004, In press).

EXPERIMENTAL SECTION

Reagents and Materials

Methyltrimethoxysilane (MTMOS), tetrabutylamonium, and all the reagents for the Britton–Robinson buffer solution (ortho-phosphoric acid, boric acid, acetic acid, and sodium hydroxide) were from Merck (Darmstad, Germany). The HCl was from Panreac (Barcelona, Spain), pyrrole, 3-methylthiophene (3MT), polyprrole, C18, were from Aldrich (Milwaukee, WI). Graphite powder was from SGL Carbon (Ringsdorff, Germany). The $Cr(NO_3)_3$, $Cd(NO_3)_2$, $CuSO_4$, $ZnCl_2$, $HgSO_4$, $PbNO_3$, and potassium dichromate were all purchased from Sigma (St. Louis, Missouri). All other chemical were of reagent grade and used as received. Nanopure water was obtained by passing twice-distilled water through a Milli-Q system (18 $M\Omega \cdot cm$, Millipore, Bedford, MA). Glass capillary tubes, i.d. 1.15 mm, were used as bodies for the composite electrodes.

Instrumentation

All electrochemical measurement were performed with an Autolab PGSTAT20 (Ecochemie, Utrecht, The Netherlands). The experiments were carried out in a three electrode cell at room temperature (25 ± 1°C) under nitrogen atmosphere; the counter electrode was a platinum wire and an Ag/AgCl, 3 M KCl electrode was used as the reference. The composite-filled capillary tubes were used as the working electrode. Differential pulse anodic stripping voltammetry (DPASV) and cyclic voltammetry (CV) were the electrochemical techniques applied to study the behavior of the Sonogel-Carbon electrodes. Instrumental parameters were as follows: pulse amplitude 60 mV, pulse repetition time 0.4 s, and pretreatment at −0.5 V for 12 s. The CV measurements were realized at a scan rate of $100\,mV \cdot s^{-1}$.

A 600-watt model, 20 kHz ultrasonic processor (Kontes, Dusseldorf, Germany) equipped with a 13 mm titanium tip was used. The ultrasonic processor was enclosed inside a sound-proof chamber during operation.

Electrochemical Impedance Spectroscopy Measurements

The electrochemical impedance spectroscopy (EIS) measurements were performed with a Voltalab 10 type PGZ 100 from Radiometer. The impedance spectra were set up as described previously (Zejli et al. 2004). The initial frequency used was 10 KHz and the final one was 10 MHz with AC amplitude from 5 to 10 mV. In order to ensure the inert effect of the modified electrode during the experiment, a potential of 1V was chosen. All other conditions were as described in the voltammetric procedure.

Sonogel-Carbon Electrode Preparation

To prepare the Sonogel carbon, 500 µL of MTMOS and 100 µL of 0.2 M HCL were mixed and insonated during 5 sec, then 1 g of graphite powder was added and homogeneously dispersed. To prepare the chemically modified electrodes, either 7.5% of liquid modifier (3MT, pyrrole, polypyrrole), or 7.5% of solid modifier (or P3MT) were added prior to the graphite powder to obtain the composite electrodes.

Procedure for Determination of Hg(II)

The determination of Hg(II) is carried out by the following three steps procedure: a) Accumulation step. The electrode is immersed in the sample solution for 30 min at open circuit; after this the electrode is rinsed thoroughly with deionized water, and transferred to a clean media; b) Voltammetric measurement is performed; c) Cleaning. The electrode is cleaned by immersing in 6 M HNO_3 for 2 min; in this way, the electrode is ready for the next experiment.

RESULTS AND DISCUSSION

Influence of Type of Modifier

Table 1 shows the regression equations, regression coefficients, and detection limits for an unmodified Sonogel-Carbon electrode and for several others modified Sonogel-Carbon electrodes. The modified electrodes containing one of the following modifiers at a percentage of 7.5%: 3MT, polypyrrole, C18, pyrrole, P3MT. The results (Table 1) show that the chemically modified electrode with 3MT presents the lower limit of detection. It was decided to continue the studies.

The detection limit was calculated, using a statistical procedure, as the signal of the blank plus three times its standard deviation.

Table 1. Regression equations, regression coefficients, and detection limits for an unmodified Sonogel-Carbon electrode and for several other 7.5% modified Sonogel-Carbon electrodes, for a 0.35 $mg \cdot l^{-1}$ Hg(II) concentration

Modifier	Equation (R^2)	Limit of detection ($mg \cdot l^{-1}$)
3-Methylthiophene	$Y = 2.1710^{-5} \times -1.510^{-6}$ (0.9992)	0.01
Pyrrole	$Y = 1.410^{-5} \times -1.011\ 10^{-6}$ (0.999)	0.03
Poly-3-methylthiophene	$Y = 8.7710^{-6} \times -410^{-7}$ (0.999)	0.1690
Polypyrrole	$Y = 8.7710^{-6} \times -3.6510^{-6}$ (0.997)	0.018
C18	$Y = 1.610^{-5} \times -1.01110^{-6}$ (0.999)	0.036
Unmodified electrode	$Y = 8.27310^{-6} \times -6.910^{-7}$ (0.998)	0.1

In this experiment, the electrode was immersed at open circuit into a solution of Hg(II) for 30 min, then rinsed with deionized water and put into an electrochemical cell that contained a 0.2 M Britton-Robinson solution. The DPASV mode was immediately applied and the instrumental parameters were as follow: pulse amplitude 60 mV, pulse repetition time 0.4 s, and pretreatment at −0.5 V for 12 s.

The differential pulse voltammograms (Fig. 1) clearly show improved electrochemical kinetics and sharper oxidation peaks that increase with Hg(II) concentration, varying from 0.07 to 0.42 $mg \cdot l^{-1}$. The chemically modified Sonogel-Carbon electrode used here could maintain its activity as a sensor for Hg(II) during 3 weeks. The reproducibility was evaluated by measuring the height peak. A relative standard deviation of 1.7% was obtained (for $n = 7$).

Cyclic Voltammetry

The 3MT-modified Sonogel-Carbon electrode showed no electroactivity in a potential range between 0 and 1 V when immersed in a blank solution. Also, under the experimental condition used, in a 0.2 M Britton-Robinson buffer media, the obtained signal was stable, without peaks, and with a low residual current. Prior to the study of the mercury response, the modified electrode was immersed in Britton-Robinson buffer; and a scan between 0 and 0.7 V was carried out. Cyclic voltammograms were recorded after 30 min preconcentration periods at open circuit in a solution containing 5 $mg \cdot l^{-1}$ of $HgSO_4$. The results (Fig. 2) show an anodic peak at 0.17 V

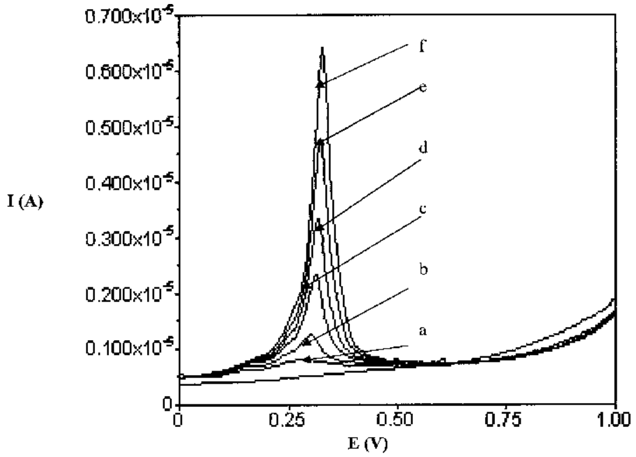

Figure 1. DPASV response of the 3MT Sonogel-Carbon electrode for Hg(II); the concentration of the mercury solution varies from a) 0.07 mg $\cdot$ l^{-1}, b) 0.14 mg $\cdot$ l^{-1}, c) 0.21 mg $\cdot$ l^{-1}d) 0.28 mg $\cdot$ l^{-1}, e) 0.35 mg $\cdot$ l^{-1}, f) 0.42 mg $\cdot$ l^{-1}.

(scan rate 100 mV $\cdot$ s^{-1}). These results indicate a possible accumulation of Hg(II) on the surface of the modified electrode, as a consequence of the affinity of mercury for the sulfur atom of 3MT. There is a cathodic peak at around 0.075 V but it is broader and smaller than the anodic one. The comparison between the two systems (3MT-modified electrode and unmodified electrode) shows relevant differences, both in peak sharpness and in peak potential. In fact, at the modified electrode the peak is sharper and significantly shifted towards a less negative potential value than the peak recorded at an unmodified electrode. The incorporation of 3MT into the Sonogel-Carbon seems to improve the analytical performance of the electrode towards Hg(II).

Effect of the Supporting Electrolyte and pH

The effect of the determination of Hg(II) on several experimental conditions and parameters was explored. First of all, several supporting electrolytes such as KCl, $LiClO_4$, NaCl, Britton-Robinson, and sodium acetate were tested at pH 2 and the concentration of Hg(II) was 0.35 mg $\cdot$ l^{-1}. Among those, the Britton-Robinson buffer was found to be the most suitable because it gave peaks that were well defined and higher than other buffers.

We have studied the influence of the pH of the supporting electrolyte on the voltammetric behavior of the chemically modified electrodes preconcentrated with mercury species. Table 2 summarize the voltammetric parameters under different pH conditions. It clearly appears that the pH of the supporting electrolyte plays a key role in the voltammetric behavior as is shown in

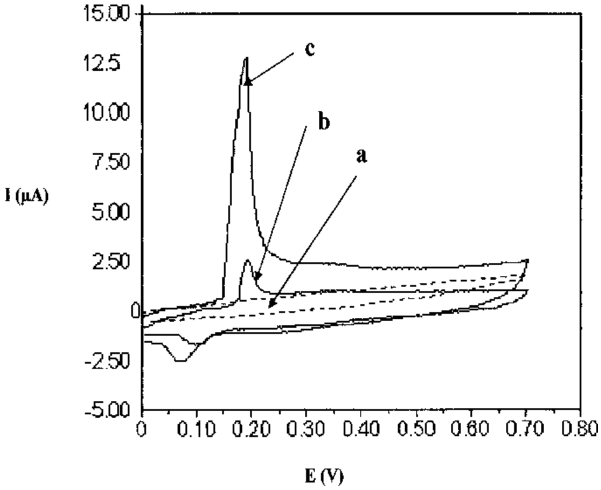

Figure 2. Cyclic voltammetric curves of 5 mg/L of Hg(II) after incubating during 30 min: (a) Background response, (b) Bare Sonogel-Carbon electrode, (c) Sonogel-Carbon electrode modified with 3-methylthiophene. Scan rate 100 mV/s. Supporting electrolyte, Britton-Robinson buffer solution of pH 2.

Table 2, in acidic media there is a unique and greater peak; from pH 3 to 7 there is also a unique but lower peak. No peak were observed at pH values from 8 to 10.

Influence of Percentage of Modifier

Percentages up to 7.5% were studied and higher values were not used because the mixtures obtained were less compact and leaked from the electrode. The

Table 2. Influence of pH on Ep and Ip for a 0.35 mg · l^{-1} Hg(II) concentration at a 7.5% modified electrode

pH	Ip (A)	Ep (V)
2	4.43 10^{-6}	0.315
3	2.33 10^{-6}	0.208
4	1.3 10^{-6}	0.238
5	8.6 10^{-7}	0.250
6	2.8 10^{-7}	0.260
7	1.8 10^{-7}	0.280
8	n.d.	—
10	n.d.	—

n.d.: Not detected.

Table 3. Influence of percentage of modifier on Ep and Ip for a $0.35\,mg \cdot l^{-1}$ Hg(II) concentration at a 7.5% modified electrode

Percentage	I_{1p} (A)	I_{2P} (A)	E_{1p} (V)	E_{2P} (V)
5%	$2.08\ 10^{-7}$	$5.34\ 10^{-8}$	0.232	0.393
7.5%	$4.43\ 10^{-6}$	n.d.	0.315	—
10%	$4.16\ 10^{-7}$	$8.39\ 10^{-7}$	0.226	0.327
15%	$6.76\ 10^{-7}$	$6.06\ 10^{-7}$	0.238	0.327

n.d.: Not detected.

highest peaks were obtained for 7.5% of modifier in the Sonogel-Carbon electrode; the results are shown in Table 3.

Electrode Cleaning

Two cleaning methods were tested: an electrochemical method and a chemical one. The electrochemical method involves an electrolysis process after each measurement by applying DASPV from 0 to 1 V for five cycles; the chemical one involves an immersion in 6 M HNO_3 solution for 2 min. Figure 3 shows the voltammograms at the modified electrode after electrochemical and chemical cleanings, respectively. The second method was found to be more efficient than the first one, considering the cleaning efficiency. Therefore, the chemical cleaning method was used after each measurement.

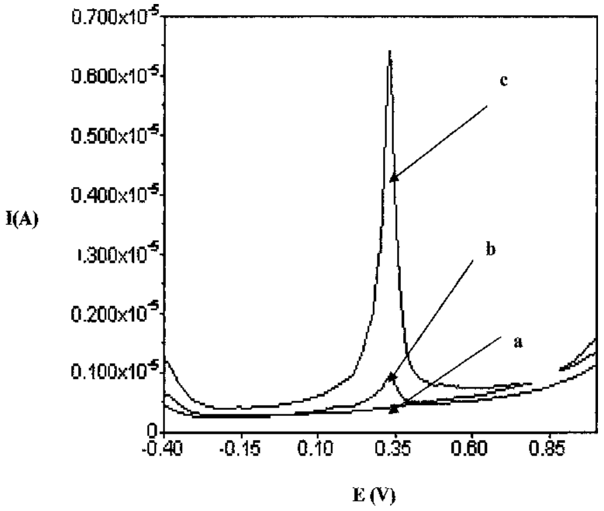

Figure 3. DPASV of a 3MT-modified electrode: a) after chemical cleaning, b) after electrochemical cleaning, c) $0.42\,mg \cdot l^{-1}$ of Hg(II).

EIS Measurements

The impedance spectra were collected at 1 V (vs. SCE) in a frequency range from 10 $\mathrm{KH_Z}$ to 10 $\mathrm{mH_Z}$ with an AC amplitude of 5 mV. The potential of 1 V was chosen in order to ensure the stability of the system during the measurements. Figure 4a shows that the chemically modified electrode has a small diameter arc If we admit the Randles equivalent circuit model, the calculated charge transfer resistance, R_{ct}, and the double layer capacitance C_d are successively 1.627 kohm $\cdot$ cm^2 and 195.5 $\mu F \cdot cm^{-2}$. These data are typical of metal electrodes covered with polymeric films.

On the other hand, Fig. 4b also exhibits an arc-like Nyquist plot for the chemically modified electrode preincubated with the 3MT/Hg(II) system. The electrical parameters calculated were: $R_{ct} = 1.3\,\mathrm{Kohm} \cdot \mathrm{cm}^2$ and $C_d = 258\,\mu F \cdot cm^{-2}$. It appears clearly from these data that the capacitance at the interface increases when the chemically modified electrode is exposed to Hg(II). This observation is in agreement with the literature in the case of adsorption phenomenon at the electrode surface. Our result gives another evidence for Hg(II) adsorption on the modified electrode as part of an integrated process leading to the electrolytic reduction of the heavy metal at the polymer surface. The observed decrease of the charge transfer resistance also means that the modified electrode in contact with Hg(II) becomes more conductive.

Study of Interferences

Several common metal ions were subject to DPASV under the same conditions described previously. The 3MT-modified Sonogel-Carbon electrode was tested.

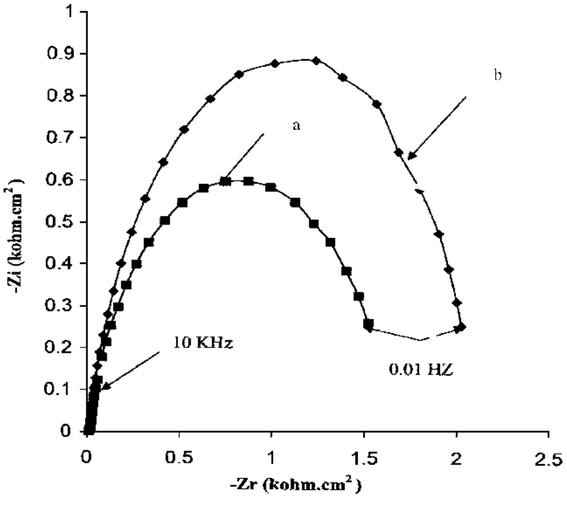

Figure 4. Electrochemical impedance spectroscopy (EIS) of (a) a 3MT-modified electrode, (b) 3MT modified electrode incubated with Hg(II).

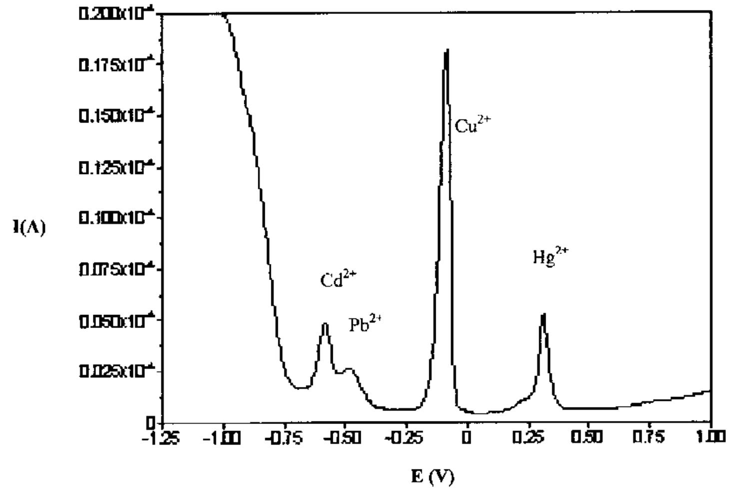

Figure 5. DPASV of a 3MT-modified electrode in a solution containing 0.35 mg $\cdot$ l^{-1} of Hg(II), and Cd(II), Cr(III), Zn(II), Pb(II), and Cu(II) at a concentration of 3.5 mg $\cdot$ l^{-1} of each one (10:1 interferent:analyte mass ratio).

The electrode was immersed in a mixture of Hg(II) (0.35 mg $\cdot$ l^{-1}), Cr(III), Cd(II), Cu(II), Zn(II), Pb(II), and Ni(II), (3.5 mg $\cdot$ l^{-1}) each. The voltammograms (Fig. 5) show the presence of other significant metal ion signals but none is disturbing the mercury peak. We can conclude that the proposed sensor is able to determine mercury even in the presence of principal water soluble.

The analytical performance of the novel electrode was explored further in the determination of Hg(II) on an industrial site at Cadiz Bay; the results of this study yields a concentration of 0.06 mg $\cdot$ l^{-1} of Hg(II).

SEM Measurement

In order to characterize our electrode better we have performed some scanning electron microscopy (SEM) measurements. The unmodified Sonogel-Carbon material shows a rough and perfect jagged structure and high surface porosity. The Sonogel-Carbon material modified with 3-methylthiophene shows a surface that is much smoother, revealing that this material is more compact and organized than the unmodified material.

CONCLUSIONS

In this work we prepared a new modified Sonogel-Carbon electrode based on the incorporation of 3-methylthiophene for the detection of Hg(II) in aqueous solution. This method is very simple and offers a relatively short analysis time, it is inexpensive and presents easy operability. It could be applicable for field use, the good selectivity and the detection limit of $0.01\,\mathrm{mg} \cdot \mathrm{l}^{-1}$ make it a promising tool for detection of heavy metals.

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