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Use of a polymer modified electrode for arsenic determination

M. Angélica del Valle*, Fabiola Bustos, Fernando R. Díaz, Gean C. Arteaga, Loreto A. Hernández, Andrea C. Ramos

Pontificia Universidad Católica de Chile, Facultad de Química, Laboratorio de Electroquímica de Polímeros (LEP), Vicuña Mackenna 4860, 7820436-Macul, Santiago, Chile

Correspondence to: M. Angélica del Valle (mdvalle@uc.cl; Phone: 56-2-23544405; Fax: 56-2-26864744)

ABSTRACT

This paper presents the optimization of a polypyrrole-modified steel electrode (SS/PPy) to be used as arsenic(V) amperometric sensor using electrochemical techniques. The electrode response is based on the doping/undoping ability of the polymer matrix that involves anions incorporation and removal, generating thus a charge or current that correlates to the analyte concentration.

Once the electrode was optimized, analytical parameters were established. A linear response in the range 5 - 250 ppm As(V) was found, with a response time 5 s. Besides, it is noteworthy that the response obtained with a freshly prepared SS/Ppy electrode before each measurement is highly reproducible. Therefore the SS/Ppy electrode is proposed as a sensor that may be utilized as disposable device.

KEYWORDS : polypyrrole electrode, arsenic, arsenic quantitation, amperometric sensor, arsenic sensor.

INTRODUCTION

Arsenic environmental pollution is a worldwide problem, with an increase of arsenic contamination in Bangladesh,[1] India, England, Thailand, Chile, California,[2] among others. Water pollution may be due not only to natural sources in soil, in which arsenic is present as oxysalt or sulfur mineral, but mainly by human activities, emphasizing its application in agriculture as herbicide, fungicide, insecticide, as preservative (copper chrome arsenate) in the wood industry, in the glass manufacture, in the micro-electronics industry (GaAs) etc. [3, 4] that causes arsenic levels in waters, mainly drinking, being of concern. This may provoke in short periods of time adverse health effects because of its unaware ingestion. Some of the demonstrated diseases suggest inhibition of a large number of biological functions, such as inhibition of pyruvate oxidation and beta-oxidation of fatty acids, inhibition of DNA damage repair by altering growth factors, increasing cell proliferation, suppressing the transcription of the p53 protein gene encoding (p53 is a protein that regulates cell cycle, programs the apoptosis when DNA damage is shown to be irreparable, and activates DNA repair when damage has occurred).[5]

A variety of spectrometric methods have been currently utilized for arsenic determination, namely UV-visible, atomic absorption with hydride generation, atomic fluorescence spectroscopy, inductively coupled plasma atomic emission spectrometry, among others. The methods based on these techniques require expensive instrumentation, complicated procedures and special sampling, in order to form either colored complexes or toxic compounds, such as arsine.[6] Consequently, development of a technique that allows the fast and in-situ determination of this pollutant is necessary. Electrochemical sensing devices offer a more economical solution than other analytical methods. Electrochemical techniques have the advantages of high sensitivity, excellent selectivity, low cost, and simple instrumentation and operation.[7-9]

In previous investigations of our group, the doping/undoping properties of conducting polymers were studied.[10, 11] It was established that they were useful for metals extraction.[12, 13] Among these polymers, polypyrrole (PPy), their derivatives and composites have been the most studied. [14,15] Therefore polypyrrole modified steel electrodes have been evaluated to adsorb arsenate ions from solutions, as a "sponge", and its use has been proposed as arsenic extractant.[16] Furthermore, a correlation between response and concentration of this ion was found.[17] Experimental evidence as extractant, based on the p-doping/undoping phenomenon, enabled corroborating the possibility of a reversible doping by observing the charges generated during the process of successive "electro-extractions" as a result of the ability to incorporate and remove ions, depending on the applied potential, that the poly(pyrrole) modified electrode possesses. This property could be exploited to develop an amperometric sensor for arsenate ion, since the current generated by the applied potential would be proportional to the anion concentration.[17]

EXPERIMENTAL

All solutions were prepared with 18.3 MΩ-cm specific resistivity ultrapure water, obtained from a Milli-Q system. The experiments were carried out in a three-compartment cell using 4 cm^2 geometric area AISI 316 steel sheets as working electrode, polished to a mirror finish utilizing 0.3 µm alumina slurry on a polishing pad.

A platinum wire coil of large area and an Ag|AgCl electrode in tetramethylammonium chloride solution, adjusted to match the potential of the SCE at room temperature (20 °C),[18] were the auxiliary and reference electrode, respectively. A potentiostat-galvanostat PGZ 201 Voltalab (Radiometer, Denmark) coupled to Voltamaster electrochemical software, was utilized throughout the electrochemical work.

To plot calibration curves, the following reagents were used: 1000.000 ± 0.002 ppm As(V) Merck Titrisol standard solution; pyrrole 98% Aldrich distilled under reduced pressure and then stored under refrigeration an inert atmosphere before use; 95-98% sulfuric acid and anhydrous sodium sulfate purchased from Merck.

Ppy modified electrodes, SS/Ppy, were prepared using chronoamperometry. The same technique was employed for Ppy undoping and subsequent doping in the presence of As.

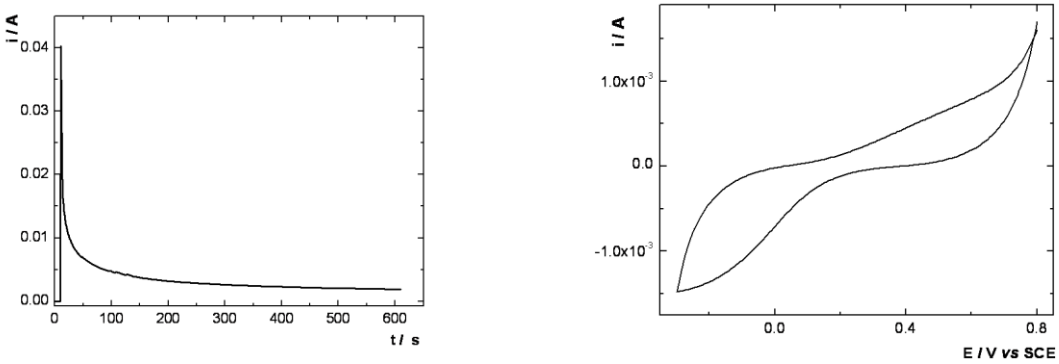
Electro-polymerization optimum conditions for preparing this electrode have been established in previous work of our group as well as the potential step program for incorporating the anionic species under survey into the polymer matrix from the solution and its subsequent release. Optimum monomer and supporting electrolyte concentration were determined too.[14, 17]

The modified electrode was prepared in a cell containing monomer solution and 0.05 mol•L^{-1} supporting electrolyte at pH 1.5 by applying an optimal polymerization potential of 0.98V vs SCE for 10 min. Subsequently a -0.2 V undoping potential was applied to the deposit.[19] Once the modified electrode was prepared, it was rinsed and dried before being immersed into an As solution of known concentration at pH and supporting electrolyte concentration as stated above. Subsequently, a potentiostatic perturbation of 0.7 V was applied and the respective transients, that record the current obtained at different times, were analyzed and plotted as a function of analyte concentration.

RESULTS AND DISCUSSION

Preparation, optimization and doping/undoping potential of the SS/PPy modified electrode

Preparation and optimization of the SS/PPy modified electrode have been established by our group in a previous work.[17] The suitable porosity of a SS/PPy modified electrode was found by applying a steady potential of 0.98 V during 10 min (Fig. 1a). The doping/undoping process takes place at 0.7 and -0.2 V respectively (Fig. 1b), the magnitude of the charges attributable to these processes in the presence of As being very similar to each other. This finding would corroborate the possibility of a reversible doping/undoping process, as verified when the device was tested as arsenic extractant.[17]



a **b**

Figure 1 (**a**) Current-time transient obtained during Py electro-polymerization on SS at 0.98 V *vs* SCE. (**b**) Voltammetric response of electro-deposited Ppy at SS in 0.5 mol·L^{-1} Na_2SO_4 and pH 1.5. v = 10 mV·s^{-1}.

It is noteworthy that the *doping* applied potential was 0.7 V that corresponds to a value lower than the optimum potential for monomer electro-polymerization, so that the polymer matrix undergoes no structural changes during the process.[11, 20] In turn, the applied *undoping* potential was -0.2 V, which corresponds to the lower potential that can be applied to achieve electro-neutrality without causing π modification of the system.

Optimization of the parameters involved in the development of the arsenic sensor

Electrode useful life

To determine the electrode useful life, analyte solutions between 50 and 750 ppm As(V) were prepared for the construction of calibration curves. Once the Ppy modified electrode was prepared according to the conditions previously established, the *doping* potentiostatic perturbation was applied in each solution containing a known As concentration and, between each measurement, the undoping potential -0.2 V was applied for 10 min in a solution containing just 0.5 mol·L$^{-1.}$ supporting electrolyte.

The recorded transient perturbations at 0.7 V are depicted in Fig 2. It can be seen that the signal corresponding to the current jump decreases as As(V) concentration increases when the same electrode is successively utilized.

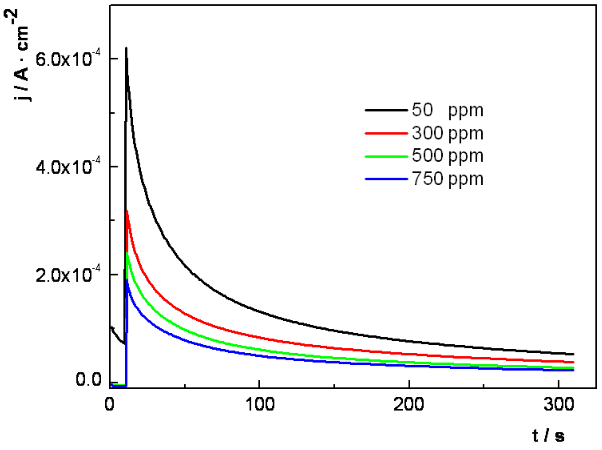


Figure 2 SS/Ppy j/t transient in solutions containing 50, 300, 500, 750 ppm As + 0.05 mol·L^{-1} Na_2S0_4 at pH 1.5 using the same electrode in successive measurements.

This could be ascribed to that, even if the undoping potential is applied for 10 minutes, not all counterions leave the polymer network, therefore it might be necessary to prepare a "fresh" SS/Ppy each time a new measurement is performed, *i.e*. the use of the SS/PPy electrode should be thought as a disposable device, which is not too expensive considering the low cost of the employed materials.

Limits of detection and quantification

The electrochemical perturbation was applied to a supporting electrolyte solutions, pH 1.5, in the absence of analyte, setting the *doping* potential at 0.7 V during 5, 10 and 20 s. Each measurement was repeated at least 7 times and the results are summarized in Table 1. In Table 2, standard deviation (s) of these blanks response was calculated as well as the minimum detectable signal (S_{min}), limit of detection (LOD) and limit of quantitation (LOQ).

Table 1 Blank amperometric response as a function of time.

t (s)				**j (A·cm^{-2})**			
5	$3.3\cdot10^{-4}$	$2.87\cdot10^{-4}$	$2.92\cdot10^{-4}$	$3.44\cdot10^{-4}$	$2.88\cdot10^{-4}$	$3.65\cdot10^{-4}$	$2.65\cdot10^{-4}$
10	$2.55\cdot10^{-4}$	$2.31\cdot10^{-4}$	$2.29\cdot10^{-4}$	$2.67\cdot10^{-4}$	$2.38\cdot10^{-4}$	$2.33\cdot10^{-4}$	$2.20\cdot10^{-4}$
20	$2.6\cdot10^{-4}$	$1.78\cdot10^{-4}$	$1.73\cdot10^{-4}$	$1.98\cdot10^{-4}$	$1.89\cdot10^{-4}$	$1.82\cdot10^{-4}$	$1.76\cdot10^{-4}$

Table 2 Statistical parameters, S_{blank}, S_{min}, LOD and LOQ.

t (s)	**S_{blank}**	**S_{min}**	**LOD**	**LOQ**
5	$2.59\cdot10^{-4}$	$1.10\cdot10^{-5}$	$2.89\cdot10^{-4}$	$3.60\cdot10^{-4}$
10	$2.39\cdot10^{-4}$	$1.64\cdot10^{-5}$	$2.88\cdot10^{-4}$	$4.30\cdot10^{-4}$
20	$1.64\cdot10^{-4}$	$6.54\cdot10^{-5}$	$3.60\cdot10^{-4}$	$8.18\cdot10^{-4}$

From the results in Table 2, it follows that the blank signals that produce the lowest standard deviation is the one obtained after applying the doping potential during 5 s. However, it is noteworthy that these data correspond to a modified electrode whose supporting area is 4 cm^{2,} because if this area varies, the obtained values would change either.

Response time of the modified electrode

From the j/t transients obtained in solutions containing known As(V) concentrations (Fig. 3), the response at 5, 10 and 20 s was determined. The results revealed that the arsenate sensor operates based on ions entry, for which purpose it must be allowed to stand for a while to partially oxidize the deposit before the anions enter as counter-ion, *i.e*. not only a diffusion time from the bulk electrolyte exists, but there is also an additional time corresponding to the oxidation of the polymeric matrix.[21] Measurements at times longer than 20 s were not conducted because this is an extremely long time for an application such as that designed in the current work.

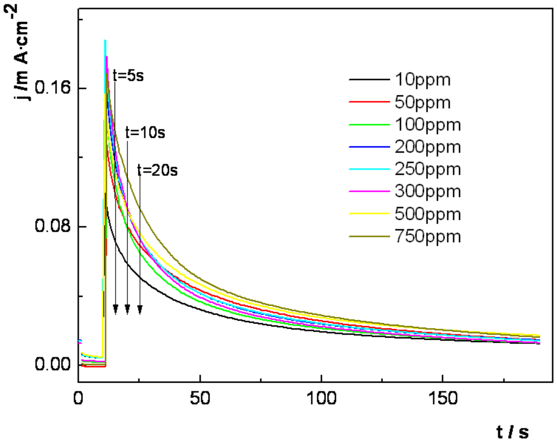


Figure 3 j/t transients obtained using the modified electrode in solutions of different As concentration. Interface: SS/Ppy, 0.05 mol·L^{-1} Na_2SO_4, pH 1.5, + As (concentrations exhibited in the inset).

Arsenic concentration linear range

Current density plots after the application of the *doping* potential (0.7 V) at each specified time (5, 10 and 20 s) *versus* As concentration showed a linear range below 100 ppm for all times. At higher concentrations slope jump along with matrix saturation was observed; this fact was evidenced by the formation of a *plateau* in the obtained plots (insert Fig. 4). From these results a comprehensive analysis was conducted between 10-100 ppm. A greater linearity was obtained, reflected in the value of r (correlation coefficient), for 5 s within this working range (Fig. 4).

When the response was analyzed as a function of the logarithm of analyte concentration, *i.e.* log(ppm As), more points could be included, therefore it is more appropriate to consider the sensor response as a function of log(ppm As). Thus, the sensor exhibits a linear response over the range 5-250 ppm As (Fig. 5).

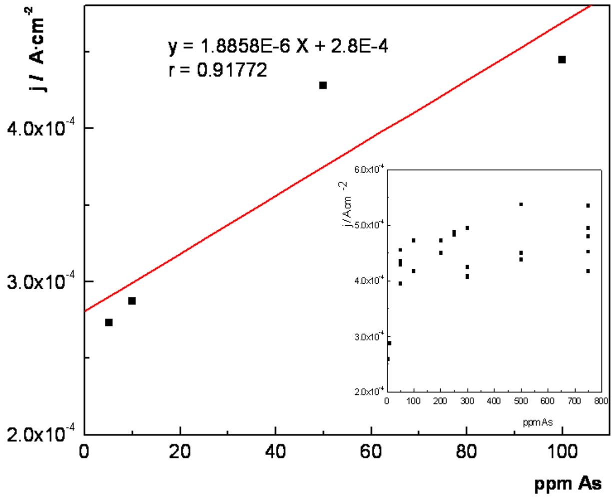


Figure 4 Measured current density after applying 0.7 V for 5s *vs* doping ppm As (range 5 to 100 ppm). Insert: current density after the application of 0.7 V for 5 s *vs* doping ppm As (range 5 to 750 ppm).

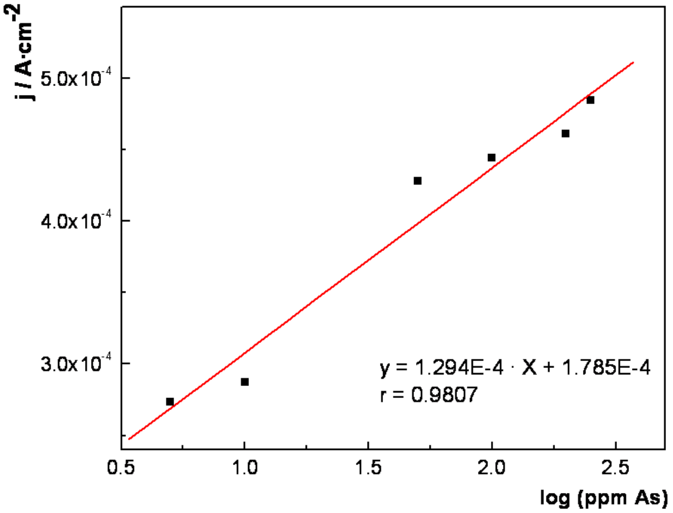


Figure 5 Current density after applying 0.7 V of doping for 5 s *vs* log(ppm As).

LOD and LOQ of SS/PPy for As(V) quantification

Using data from Figs. 4 and 5, the limit of detection and limit of quantification were worked out for the specified time. The results are set forth in Table 3.

t (s)	**j (A cm^{-2}) *vs* ppm As**		**j (A cm^{-2}) *vs* log(ppm As)**	
	LOD (ppm As)	**LOQ (ppm As)**	**LOD (ppm As)**	**LOQ (ppm As)**
5	23	109	27.5	*
10	293	*	*	*
20	4.7	42	4.9	14

* The blank standard deviation of these points is so large that extrapolation comes completely out of the range of the studied concentrations, affording, from an analytical viewpoint, meaningless or absurd limits of detection and quantification.

j × log(ppm As) plots extrapolation of the detection and quantification limit signals at each time showed that all the points are above the resulting measurements. It follows, therefore, that a blank correction would be a mistake, because, in the absence of analyte anions, an interaction between the electro-deposit and sulfate anions from the supporting electrolyte present in the blank exists and this interaction would be different in the presence of arsenate ions during the *doping* process.[21] On the other hand, in solutions containing the analyte a competitive effect of these anions with charges of the doped polymer would occur. In summary, the obtained response is clearly due to arsenate interaction with the doped polymer, making blank correction impossible.

Conclusions

A linear correlation was found between the logarithm of arsenate concentration and the current obtained at fixed potential, 0.7 V *vs* SCE. Consequently, the SS/Ppy modified electrode can be utilized as an arsenic amperometric sensor. A linear range between 5 and 250 ppm As(V) was found and the response time that yields the best detection and quantification limits was 5 s.

If a freshly prepared SS/Ppy electrode is employed for each determination or quantification, its response is fully reproducible and consequently the sensor can function as a disposable electrode.

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