DESIGN AND EVALUATION OF A Hg(II) SENSOR BASED ON THE RESPONSE OF A POLY(3,4-Ethylenedioxythiophene) MODIFIED ELECTRODE

M. A. DEL VALLE*, P. LLANQUILEO, F. R. DÍAZ, M. FAÚNDEZ, L. A. HERNÁNDEZ, B. GONZÁLEZ

Pontificia Universidad Católica de Chile, Facultad de Química, Departamento de Química Inorgánica, Laboratorio de Electroquímica de Polímeros, Av. V. Mackenna 4860, 7820436, Macul, Santiago, Chile

ABSTRACT

The electro-synthesis of poly(3,4-ethylendioxythiophene), PEDOT, has been widely studied due to its different and important applications. Considering that one of the most important electrochemical characteristics of this polymer is its ability to undergo p- and n-doping/undoping, our research group has tested its potential usefulness for cations extraction based on the n-doping/undoping process, hitherto almost unexplored. Therefore, in a first stage, EDOT was electropolymerized on AISI 316 stainless steel, SS, and the SS/PEDOT modified electrode was then obtained. Applying the n-doping potential to these SS/PEDOT electrodes immersed in Hg(II) solution at physiological pH (PBS) it was verified that the cation was incorporated into the polymeric matrix and, depending on the area of the working electrode and removal method (n-doping/undoping), its extraction parameter was established, namely linear response between 66.6 µmol·L\(^{-1}\) and 1.0 mmol·L\(^{-1}\). In turn, the electro-oxidized on various substrates such as Al, Pt, glassy carbon, etc. \(^{16-21}\), EDOT is electro-oxidized on a prominent place. The obtained conducting polymer has been extensively characterized and one of its remarkable properties is that presents the possibility of undergoing both p- and n-doping/undoping. In turn, the p-doping/undoping process has been thoroughly studied, while the n-doping/undoping was first mentioned only in 1994 \(^{22}\) and since then, only a few publications have addressed the subject \(^{22}\); as a consequence, this challenge has been tackled recently and together with EDOT, the electro-polymerization of several of its analogues has been studied in order to gain a deeper understanding of the n-doping/undoping process and the effect of monomer structure on this property. \(^{22}\) \(^{31}\) Ethylenedioxythiophene, \(^{31}\) Propylenedioxythiophene, \(^{31}\) 3,4-ethylenedioxythiophene, \(^{31}\) 3,4-propylenedioxythiophene, thiophene and pyrrole derivatives, were electro-polymerized by potentiodynamic and potentiostatic methods on AISI 316 stainless steel electrodes, using lithium perchlorate as supporting electrolyte in acetonitrile. In all cases electrodes modified with the respective polymeric deposit were obtained. One of the most relevant features of these polymers is that their voltammetric studies revealed that all presented reversible p- and n-doping/undoping processes. Consequently, we set out to exploit this last property, so little explored as far as the application of these materials is concerned, considering its prospective utility in the development of a device for cations extraction. \(^{24}\) To this purpose, it was born in mind previous results concerning the use of poly(pyrrole) p-doping/undoping for arsenate ion and copper complexes extraction \(^{23-25}\), proving that just as p-doping/undoping was suitable for anions removal or extraction, so was n-doping/undoping for cations. Furthermore, in the case of arsenic a sensor was designed to determine this element in its anionic form \(^{25}\) n-doping studies revealed that during Hg(II) cation removal, the recorded charge was directly proportional to the metal ion concentration, hence the design and evaluation of the electrode as sensor was proposed. Although all the analogous studied showed a similar n-doping/undoping process, EDOT was chosen because it was the most affordable.

Although currently different methods exist for determining mercury ions, e.g. atomic absorption spectrometry \(^{12,22}\), spectrofluorimetry \(^{23,24}\), atomic fluorescence spectrometry \(^{23}\), among others \(^{26}\), and since most of them are not only very time consuming but require costly and sophisticated instrumentation and/or expensive pre-treatment, the technique proposed in this work is quite simple and cheap. Consequently, the development of an approach that allows 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.

EXPERIMENTAL

All electrochemical measurements (polymerization and characterization) were performed on an AUTOLAB PGSTAT 20 potentiostat, at room temperature (20 °C) under high purity argon atmosphere in anchor-type three-compartment electrochemical cells, using a 0.07 cm\(^2\) geometric area AISI 316 stainless steel (SS) discs as working electrode, a platinum wire coil of large geometric area as counter electrode, and Ag/AgCl in tetramethylammonium chloride solution to match the potential of a saturated calomel electrode, SCE, as reference electrode. \(^{23}\) Unless otherwise stated, all potentials quoted in the current work are referred to this electrode at room temperature.

SS/PEDOT modified electrodes were prepared by electropolymerization of the monomer on SS discs under the previously established optimal working conditions \(^{24}\), i.e. 0.01 mol·L\(^{-1}\) Hg(II) chloride in PBS pH 7.4 (physiological buffer solution) and then diluting up to 100 mL with the same buffer. The following aliquots of this stock solution were taken: 5, 10, 50, 100, 250, 500, 750, 1000, 1250, 1500 and 2000 µL diluted up to 15 mL with PBS. To verify its voltammetric profile, cyclic voltammograms at the SS/PEDOT modified electrode were run, within the n-doping/undoping region, on each solution. It was established thereupon that the most suitable potential to perform amperometric and/or charge (i/t) measurements at this electrode was -0.4 V.

To study repeatability and reproducibility, each measurement was performed at least 5 times, using each time a freshly prepared electrode, or then, using the same sensor to measure successively the whole series of solutions.

The blank solution was prepared using lithium perchlorate (supporting electrolyte in acetonitrile) as solvent, giving a standard deviation (S\(_{0}\)) of 2.2 ± 0.10
RESULTS AND DISCUSSION

Firstly, EDOT electro-oxidation on steel under the previously described conditions to obtain a PEDOT deposit whose doping/undoping works properly for the proposed process, was corroborated. Figure 1 shows the voltammetric profile recorded for 50 successive voltammetric cycles under conditions established as optimum. Figure 1 reveals, on the one hand, a continuous current increase that accounts for the growth of the polymeric deposit and, on the other hand, the possibility of both n- and p-type doping/undoping at ranges between 0 and 1 V and 0 and -1 V, respectively. In addition, the potentiostatic obtention of the polymer modified electrode at ca. 1.4 V was confirmed. In such case, transients such as that in Fig. 2, highly reproducible and that allows verifying the proper obtaining of SS|PEDOT to be used as sensor, were recorded. An initial current rise is observed that drops exponentially until that, when nucleation that causes deposit growth (induction time) occurs, increases again in terms of such growth. Thus, it was confirmed that, as pointed out previously, 1.4 V is a suitable potential for EDOT potentiostatic electro-oxidation under the employed experimental conditions. Thereby, application of the potential for 1 min is enough to obtain a film of suitable thickness for further use; highly reproducible responses are obtained within the n-doping/undoping region in solution containing just supporting electrolyte (Fig. 3), which are used as “fingerprint” to check electrode preparation repeatability.

Analysis of the voltammetric response in the n-doping/undoping region of the SS|PEDOT electrode prepared under the optimum conditions set out herein, Fig. 3, revealed that, besides of high repeatability, reversibility of the process with respect to charge exists. So, it was precisely based on this response that the preparation of the modified electrode was optimized. It was also observed that when the measurement was accomplished in the same supporting electrolyte in which the deposit was prepared, the charge is much lower than in solutions containing Hg(II), which demonstrate the feasibility of using the SS|PEDOT device as sensor for this cation. Table 1 summarizes the charges obtained with the modified electrode under the above described experimental conditions.

Table 1. Charges of n-doping (n-Q_d) and n-undoping (n-Q_u) of electro-synthesized PEDOT on SS within the respective negative (E_n) and positive (E_p) limits.

<table>
<thead>
<tr>
<th>E_n (V)</th>
<th>E_p (V)</th>
<th>n-Q_d (C)</th>
<th>n-Q_u (C)</th>
<th>n-Q_u:n-Q_d (C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-1.0</td>
<td>0.0</td>
<td>4.0·10^{-4}</td>
<td>4.0·10^{-4}</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The recorded transient perturbation revealed that, when the same electrode is successively utilized, the signal corresponding to the current rise decreases as Hg(II) concentration increases. This finding could be ascribed to that, even if the undoping potential is applied for 10 minutes, not all counterions have left the polymer network; therefore it might be necessary to prepare a “fresh” SS|PEDOT each time a new measurement is performed, i.e. the use of the SS PEDOT electrode should be thought as a disposable device, which is not too expensive considering the low cost of the employed materials. It is noteworthy, though, that whenever a “fresh” electrode is prepared, exactly the same result is attained, so that repeatability is assured. Besides, if not used, the sensor exhibits the same response even 10 days after its preparation when the device is kept under laboratory environmental conditions. However, more time is required to set the maximum shelf life, although this is admittedly a stable polymer.

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To determine the sensor useful life, analyte solutions were prepared for the construction of calibration curves. Once the modified electrode was prepared according to the conditions previously established, the doping potentiostatic perturbation was applied to each solution containing a known Hg(II) concentration and, between each measurement, 0 V undoping potential was applied for 10 min to a solution containing just 0.1 mol·L^{-1} supporting electrolyte.
The electrochemical perturbation was applied to supporting electrolyte solutions, PBS, in the absence of analyte, setting the doping potential at -0.4 V during 2.5 and 10 s. Each measurement was repeated at least 5 times and the standard deviation (s) of blank responses was calculated as well as the minimum detectable signal (S_min), limit of detection (LOD), limit of quantification (LOQ) and linear range.

After ascertaining the optimum n-doping potential for the analytical measurement as -0.4 V during 5 s, the linear working range for Hg(II) quantification at physiological pH was established. For this study the set of solutions in Table 2, as described in experimental, was prepared.

As seen in Fig. 4, the calibration curve linear range was between 6.67·10^{-4} and 1·10^{-3} mol L^{-1}.

**Table 2.** Hg(II) stock solutions to determine the linear range from the calibration curve.

<table>
<thead>
<tr>
<th>stock</th>
<th>C_Hg(II) (mol·L^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.33·10^{-4}</td>
</tr>
<tr>
<td>2</td>
<td>6.67·10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>3.33·10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>6.67·10^{-4}</td>
</tr>
<tr>
<td>5</td>
<td>1.66·10^{-4}</td>
</tr>
<tr>
<td>6</td>
<td>3.33·10^{-4}</td>
</tr>
<tr>
<td>7</td>
<td>5.00·10^{-4}</td>
</tr>
<tr>
<td>8</td>
<td>6.67·10^{-4}</td>
</tr>
<tr>
<td>9</td>
<td>8.33·10^{-4}</td>
</tr>
<tr>
<td>10</td>
<td>1.00·10^{-3}</td>
</tr>
<tr>
<td>11</td>
<td>1.33·10^{-3}</td>
</tr>
</tbody>
</table>

At concentrations below 6.67·10^{-4} mol·L^{-1}, the signal presents no current jump consistent with the rest of performed measurements, being poorly reproducible and sometimes biased by the blank. It is quite possible this fact is due to matrix effect as a result of a competition between Li(I) ion from the supporting electrolyte and Hg(II). This behavior has been ascribed to the low concentration of the latter in the medium, giving currents close, or in some cases equal, to that of the blank.

![Figure 4. Hg(II) concentration vs current calibration curve (at -0.4 V after 5 s of SS/PEDOT immersion into the solution).](image)

At concentrations higher than 1·10^{-3} mol·L^{-1}, data points deviate from linearity and a poor fit of the regression line is observed, with r^2 less than 0.9996, calculated without considering the 1.33·10^{-3} mol·L^{-1} point.

From these results, it follows that the blank signals that produce the lowest standard deviation (S_min = 2.2·10^{-7}) is the one obtained after applying the n-doping potential during 5 s. However, it is noteworthy that these data correspond to a modified electrode with 0.07 cm^2 substrate area. If this area varies, so does the obtained signal value.

Analytical parameters obtained within the linear range, are summarized in Table 3.

**Table 3.** Analytical parameters of SS/PEDOT modified electrode used as amperometric sensor for Hg(II) determination.

<table>
<thead>
<tr>
<th>Linear regression</th>
<th>r^2</th>
<th>S_min</th>
<th>LOD (µmol·L^{-1})</th>
<th>LOQ (µmol·L^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>i = 0.0665·C + 2.88·10^{-4}</td>
<td>0.99955</td>
<td>2.2·10^{-7}</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>

Because of the existence of the aforementioned matrix effect at concentrations less than the LOQ, the dynamic working range has been shortened, allowing working with good precision and accuracy from 3.33·10^{-3} mol·L^{-1} upward.

It would be thus possible to have available for use, within the stated concentration range, a disposable, low cost Hg(II) sensor.

Although the dynamic range in the current work shows good analytical parameters, it would be interesting to conduct in the future a comprehensive analysis concerning selectivity, with a wide range of analytes that can be absorbed within PEDOT polymeric matrix and displays some degree of competition with Hg(II), to thereby verify whether the sensitivity can be improved for instance, using the standard addition method.

Indeed, a selectivity study is still lacking, considering that the n-doping/undoping process would respond to any cation, as already observed in studies conducted in LiClO₄, as supporting electrolyte. However, this can be controlled based on polymer morphology, especially, pore size. Consequently, this is the next logical step of the current study that would actually improve the sensitivity of the technique and therefore, lower the quantification and detection limits.

**CONCLUSIONS**

In this work the feasibility of using the proposed electrode as a likely amperometric sensor was corroborated. Analytical performance parameters, e.g. detection and quantification limits, respectively 10 and 15 mmol·L^{-1} and sensitivity 0.0665, were found.

Among the significant findings of this study, it has been established that if a freshly prepared SS/PEDOT electrode is employed for each determination or quantification, its response was fully reproducible; consequently, the sensor can be utilized as a disposable electrode, because of the low production costs this entails, taking a great first step forward for the rapid and economic quantification of a highly toxic ion such as Hg (II). In addition, a precedent for future quantification of pollutants from physiological media using electrochemical techniques is set.

**DEDICATION**

This work is dedicated to Dr. Luis Núñez Vergara (RIP), to whom we express our admiration and respect as a scientist and a great person.

**REFERENCES**