Int. J. Electrochem. Sci., 6 **(2011)** 5209 – 5218

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Mercury(II) Extraction Using a Poly(3,4-Ethylenedioxythiophene) Modified Electrode

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Received: 29 August 2011 / *Accepted:* 6 October 2011 / *Published:* 1 November 2011

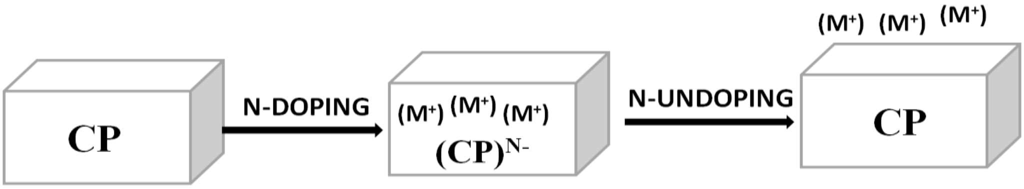
Poly(3,4-ethylenedioxythiophene), PEDOT, electro-obtention has been widely studied because of its variety of applications. One of its most relevant electrochemical characteristics is its ability of p- and n-doping (an almost unexplored property thus far), consequently in the present survey its potential use for mercury(II) extraction, based on n-doping process, was studied. To this end EDOT was potentiostatically electro-polymerized on steel (AISI 316, 6 cm^2) as substrate employing lithium perchlorate as supporting electrolyte and CH_3CN as solvent. Each extraction cycle consisted of immersing the PEDOT modified electrode into a solution made of 1 mM Hg(II) and phosphate buffer at physiological pH (PBS). The n-doping potential was then applied for 5 min to incorporate the cation into the polymer matrix. Subsequently, to remove the cation, n-undoping potential was applied for 5 min to the electrode immersed into another cell containing only PBS. In the current survey, the extraction process required 25 successive cycles to achieve 100% yield. XPS spectra confirmed that the metal was always in its +2 oxidation state, confirming that the extraction occurs only through a n-doping/undoping process. Thus, it was verified for the first time that this property of conductive polymers can be utilized to separate (extract or remove) cations (in this case Hg(II)), using a cheap and simple method that, among others, may have great utility in areas of environmental and/or toxicological interest.

Keywords: PEDOT, n-doping, extraction, mercury(II) ion

1. INTRODUCTION

Conducting polymers have a wide variety of applications, e.g. photocells, light emitting diodes, batteries, fuel cells, sensors, etc. [1-9]. Among these polymers, poly(3,4-ethylenedioxythiophene), PEDOT, obtained when 3,4-ethylenedioxythiophene (EDOT) is electro-oxidized at various substrates such as Al, Pt, glassy carbon, etc. stands out [10-13]. The conductive polymer obtained has been extensively characterized and found that may undergo both p- and n-doping. The p-doping has been widely studied, while the n-doping was first mentioned only in 1994 [10,14] and since then just a few publications have addressed the issue [15-19].

In the present work n-doping is proposed to develop a device that might be utilized to extract cations. To this purpose, the use of polypyrrole p-doping for arsenate ion and copper complexes removal [20-23] was taken as model, i.e. if p-doping was appropriate for anion removal or extraction, it may be assumed that n-doping would be suitable for cations according to the model depicted in scheme 1.



Scheme1. Schematic representation of the proposed model for cation extraction based on n-doping and n-undoping process of conducting polymers (CP)

The hypothesis illustrated in scheme 1 was confirmed in this early study by testing the use of a PEDOT coated steel electrode toward mercury ion extraction. Mercury is a well known neurotoxin that causes severe damage to the central nervous system, chiefly in fetuses and young children [24-27], therefore the presence of mercury in the environment is of global concern. The main activities that released or release more mercury into the enviroment, are gold extraction, chloro-alkali industry, batteries, household, hospital waste and industrial incinerators, and coal power plants. Released mercury, mainly as inorganic mercury, contaminates air, soil and water, and is highly mobile and persistent in the environment. That is the reason why the problem becomes a global one [28-31] and still calls for urgent solutions aimed at decontamination or detoxification of already affected persons.

Although many mercury determination methods are found in the literature, *e.g.* [32-37], methods regarding water Hg(II) remediation are scarce. The novel methodology proposed in this work, besides of completely removing the metal, employs steel as substrate of the polymer film electrode, turning the technique straightforward and very cheap.

2. MATERIALS AND METHODS

2.1 Reagents, Equipment, Preparation and Characterization of PEDOT Modified Electrodes

All solutions were prepared with freshly deionized water in a Heal Force (Smart Series) water purification system. The measurements were performed in an anchor-type three-compartment cell at room temperature (20 °C) under high-purity argon atmosphere. An AISI 316 steel disc 0.07 cm^2

geometric area and a coil of Pt wire were used as working and counter electrode, respectively. Ag|AgCl in tetramethylammonium chloride, whose potential matches that of a saturated calomel electrode at room temperature, was used as reference electrode throughout the work [38].

EDOT electro-oxidation on steel was optimized in order to obtain a PEDOT polymer deposit whose n-doping/undoping was suitable for the proposed process. EDOT (97%, Aldrich) electro-polymerization was accomplished on a Volta Lab PGZ 100 (Radiometer Analytical) potentiostat using cyclic voltammetry at various potential windows and scan rate 50 $mV \cdot s^{-1,}$ from solutions containing different concentrations of the monomer and diverse supporting electrolytes. The optima conditions for the achievement of the present work's goal were as follows: EDOT concentration 0.01 mol L^{-1}, lithium perchlorate ($LiCl_{4,}$ 99.99%, Aldrich) 0.1 mol L^{-1} as supporting electrolyte in CH_3CN, and scan potential range between -1.0 and 1.5 V.

The potentiostatic method was next attempted. The best potential to prepare satisfactory PEDOT on Stainless Steel modified electrodes (SS|PEDOT) was 1.4 V. In each case, to optimize the working conditions, SS|PEDOT stable electrochemical response was obtained in solution containing only supporting electrolyte. Also, the stable electrochemical response was recorded in different aqueous solutions of phosphate buffer at physiological pH (PBS) containing, respectively, lithium perchlorate, tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and mercury(II) diacetate (all high purity chemicals supplied by Aldrich) to determine the effect of Li^+, $TBAPF_6^+$ and Hg^{2+} cations in the PEDOT n-doping/undoping response.

2.2 Mercury(II) Extraction Process

Once the most suitable conditions to prepare SS|PEDOT to be utilized for Hg(II) extraction were stated, a BAS SP-2 potentiostat along with the abovementioned solutions, cells and electrodes, except the working electrode whose geometric area was increased to 6 cm^2, were employed to optimize the extraction method. A potential of 1.4 V was applied for 20 minutes. The prepared SS|PEDOT electrode was attempted for Hg(II) extraction employing extraction cycles, ExC. This approach consists in immersing the SS|PEDOT electrode in a Cell A, containing a 1 mM Hg(II) in PBS solution. Subsequently, the potential is stepped to -1.0 V (the polymer n-doping potential) for 5 min, after which the electrode is transferred to Cell B, containing only PBS, and potentiostatically disturbed at the n-undoping potential (0.3 V) for 5 min. This process (ExC), performed in succession, corresponds to the extraction approach proposed herein.

During each ExC stage the charge, Q, was recorded and after completion of each extraction process, Hg(II) concentration was determined in cells A and B, as described below.

2.3 Characterization by other Techniques

In addition to characterization by electrochemical techniques, already described, some additional tests were conducted, with some specific objectives: X-ray photoelectron spectroscopy (XPS) analysis was performed to the PEDOT of SS|PEDOT that had been doped in Hg(II) solutions and then undoped in PBS solutions. This was done specifically to establish whether or not mercury enters and leaves the polymer matrix and, if so, its oxidation state when trapped within the polymeric deposit. These measurements were performed on a Leybold LHS12 spectrophotometer, at Nantes University, with a magnesium source of X-ray (1253.6 eV) operating at 10 kV and 10 mA. During the measurements 10^{-7} Pa vacuum was used and the pass energy for high spectral resolution was 50 eV.

Finally, Hg(II) concentration in cells A and B was determined prior and after the extraction process by ICP-AES on a Varian Liberty Series II Spectrophotomer .

3. RESULTS AND DISCUSSION

3.1 Preparation of SS|PEDOT Modified Electrodes

The voltammetric profile in Fig. 1 accounts for the electrochemical oxidation of EDOT after 50 successive potentiodynamic cycles, under the experimental conditions (concentration, supporting electrolyte) and within the working window set forth herein as optimum. The increased current between successive cycles is an evidence of polymer growth, along with the clear presence of p- (between 0 and 1 V) and n-doping (between 0.0 and -1.0 V) processes.

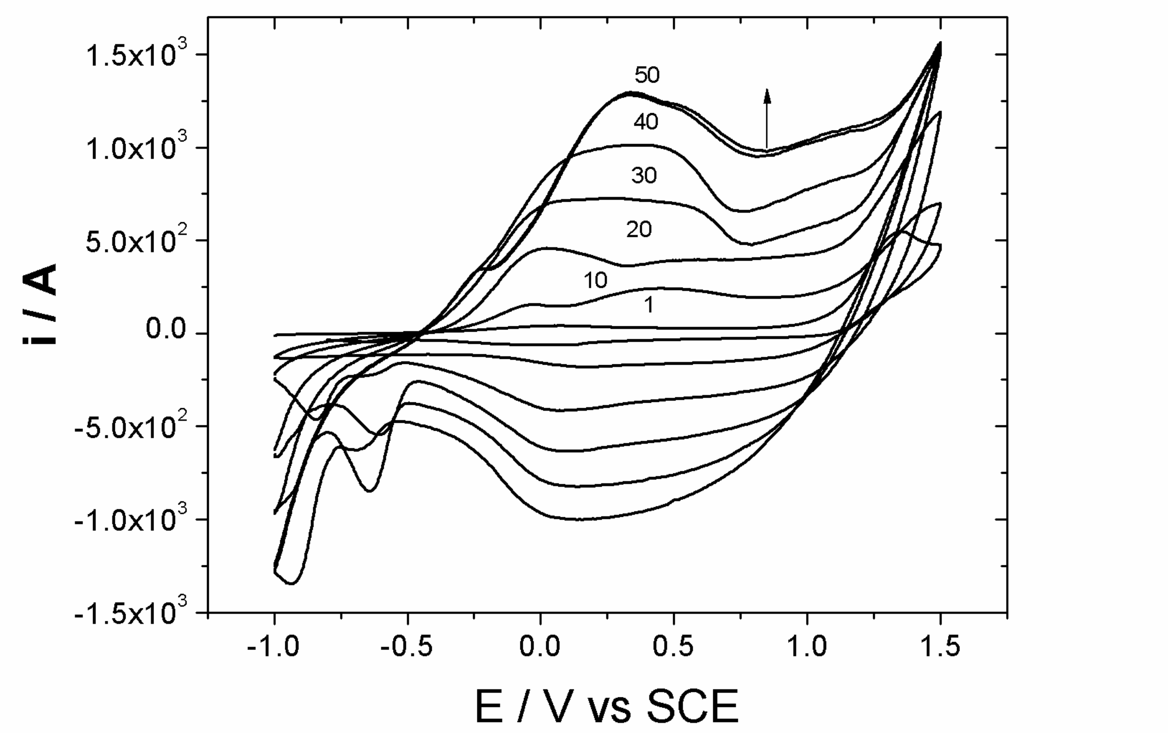


Figure 1.EDOT voltammetric profiles: 0.01 mol L^{-1} EDOT + $LiClO_4$ 0.1 mol L^{-1} in CH_3CN during the electro-polymerization on SS disc 0.07 cm ^{2} (v = 50 mV s $^{-1}$), by successive potentiodynamic cycles (number of cycles indicated on the respective responses).

Besides of evidencing the n-doping/undoping processes, these profiles allow establishing the zone of nucleation and growth, around 1.5 V. In this region the optimum working potential for the potentiostatic method should be found, Fig. 2.

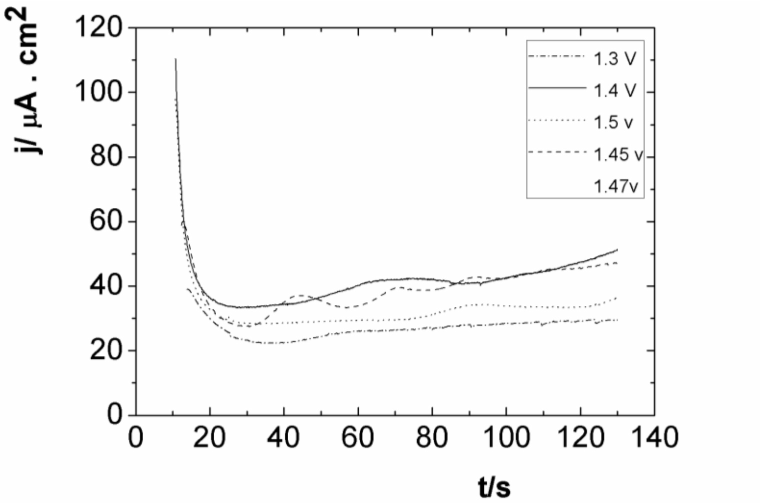


Figure 2. j/t transient recorded during EDOT electro-polymerization by potentiostatic method (E shown in the inset). Interface: SS|0.01 EDOT + 0.1 mol L^{-1} $LiClO_4$, CH_3CN.

Figure 2 shows, as example, j/t transients where a sudden increase of the initial current is observed, followed by an exponential drop to a minimum (induction time), were nucleation takes place, followed by a current increase accounting surface growth. Thus, it can be observed that under 1.4 V the induction time is very long, while at higher potentials is very short and erratic, lacking reproducibility, *i.e.* the film would be over-oxidized. This indicates, therefore, that 1.4 V, under the experimental conditions used herein, is the best suited potential for EDOT potentiostatic electro-polymerization.

Figure 3 illustrates the electrochemical responses in the n-doping/undoping region of SS|PEDOT electrodes prepared under the optimum conditions set forth herein. As can be seen, the response in aqueous solutions containing different ions demonstrated a clear effect of the cation on charge transfer during the n-doping/undoping process. This behavior is explained by the mobility and size of the respective cation and enables assessing the prospective use of this polymeric deposit in cation exchange. Based on this type of response the obtention of SS|PEDOT was optimized for the extraction or removal of mercury ions from solutions containing Hg(II) at physiological pH, in order to get the largest exchange capacity and reversibility. These are fundamental variables considering the use of this particular modified electrode.

As the n-doping/undoping occurs between 0.0 and -1.0 V, Fig. 3, the extraction method described in experimental was optimized by recording the respective n-doping and n-undoping charge during the application of the potentiostatic perturbation to cells A and B, as explained below.

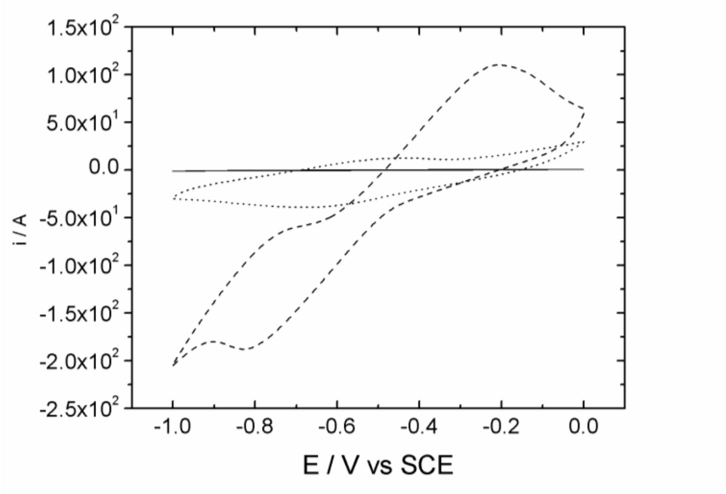
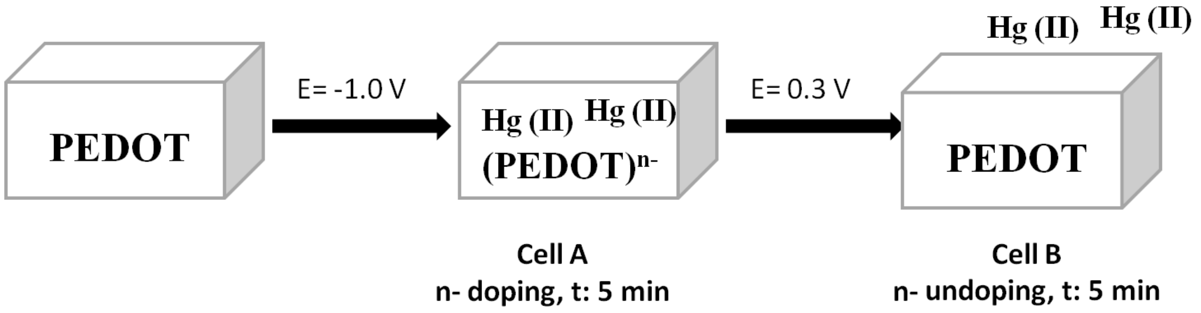


Figure 3. Response within the n-doping/undoping potential region of SS|PEDOT in PBS + $1{\cdot}10^{-3}$ mol L^{-1} of: TBA^+ (solid line), Hg (II) (dashed line), Li (I) (dotted line). Scan rate: 50 mV s^{-1}.

3.2 Hg(II) Extraction Process

Based on the above described background, Scheme 2 summarizes the conditions and methodology used to extract Hg(II) from a PBS aqueous solution.



Scheme 2. Schematic representation of Hg(II) extraction process

Table 1 summarizes the charge recorded after 25 successive extractions from a solution initially containing 10^{-3} mol L^{-1} = 228 mg L^{-1} Hg(II). It is noteworthy from these results that the charges are practically reversible, although the n-undoping is always somewhat lower than the respective charge of n-doping, suggesting that some of the metal cation is being held in the polymer matrix, as the same electrode is used in successive processes. However, it was found that this was not significant, at least in this case, since the behavior of SS|PEDOT was fully reproducible when using the 25 successive ExC for at least three extraction processes. This accounts for the stability of the modified electrode that, in addition, is stable at ambient conditions since it was found that its response is also reproducible when exposed to air for at least a week.

Perhaps the most remarkable feature of these results was the accomplishment of the proposed method for Hg(II) extraction: Hg(II) determination by ICP-AES in Cell A showed, within the limit of detection of the technique, the absence of the cation, while exactly 228 mg $L^{-1} = 1\cdot10^{-3}$ mol L^{-1} of Hg(II) was found in Cell B, which corresponds to 100% recovery.

Table 1. n-doping and n-undoping charge as a function of the number of extractions, ExC n°, for an initial concentration of Hg (II) = 10^{-3} mol L^{-1} = 228 mg $L^{-1;}$. Conditions as described in experimental.

ExC n°	$Q_{n\text{-doping}}$ / C	$Q_{n\text{-undoping}}$ / C	ExC n°	$Q_{n\text{-doping}}$ / C	$Q_{n\text{-undoping}}$ / C
1	-10.98	10.39	14	-11.02	11.00
2	-11.03	10.49	15	-11.10	10.95
3	10.82	10.80	16	-11.20	10.92
4	-11.03	10.85	17	-10.86	11.00
5	-10.92	10.90	18	-11.00	10.68
6	-11.02	11.00	19	-10.95	11.00
7	-10.85	10.78	20	-11.10	11.10
8	-10.95	10.89	21	-11.09	10.94
9	-10.89	10.78	22	-10.89	10.47
10	-10.79	10.80	23	-12.20	11.25
11	-10.86	10.76	24	-11.00	11.30
12	-10.90	10.80	25	-11.00	10.90
13	-10.92	10.85			

Another very relevant result can be observed by analyzing the recorded Q during the ExC: the sum of the n-undoping charge corresponds to 260.60 C. Using Coulomb's law for n = 2 (Hg(II)-Hg(0) = $2e^-$), gives precisely $1\cdot10^{-3}$ mol of Hg(II), that exactly matches the value obtained by ICP-AES, *i.e.* 100% extraction yield.

This outcome means that the SS|PEDOT electrode and the designed process are both effective for Hg(II) removal. This result is very important because indicates that the charge can be ascribed solely to Hg(II), the blank contribution being negligible, as it can be ascertained from Fig. 3.

The importance of the correlation between charge and the amount of Hg lies in the possibility of designing a Hg(II) sensor from this modified electrode. Despite the proven advantages of electrochemical techniques for this purpose, electrochemical approaches for this element are scarce. This study, however, is beyond the scope of this work, but will be dealt with in the near future.

Figure 3 also shows that attention must be paid on Li(I) interference. Li^+ charge is significant at equal Hg(II) concentration. Consequently, depending on the kind of sample, this ion might be an important interferent.

Consequently, this matter deserves to be studied in depth, chiefly by optimizing extraction performance and selectivity. This is another step to be taken very shortly. To this end, it is important to consider that performance success is assured by tailoring electrode area and ExC number. These parameters will be optimized, therefore, depending on the type of sample.

Some reports on Hg(II) extraction deal with the different Hg(II)- phase interaction [39-41]. Fisher et al 2011 stated that ionic liquids seem to be a good alternative for the extraction of analytes such as Hg (II). The use of conductive polymers (PEDOT) shares some of the advantages of ionic liquids, *e.g*. re-use and extraction efficiency. However, from the analytical standpoint, the preparation of modified electrodes is faster, simpler and more economic than ionic liquids. Furthermore, technically, the properties of conducting polymers (doping and undoping) are controlled by the mere application of a potential, becoming thus a simple, efficient and secure extraction method.

3.3. XPS Characterization

The proposed method postulates a cation exchange process. XPS was utilized to corroborate this aspect because it may have happened that Hg(II) was actually removed by reduction on the matrix in cell A and subsequently re-oxidized in cell B. The results bellow enable, at least with respect to this metal, to evaluate the hypothesis and the extraction model set forth in Scheme 2. Other cations should be studied to contrast the general model of Scheme 1.

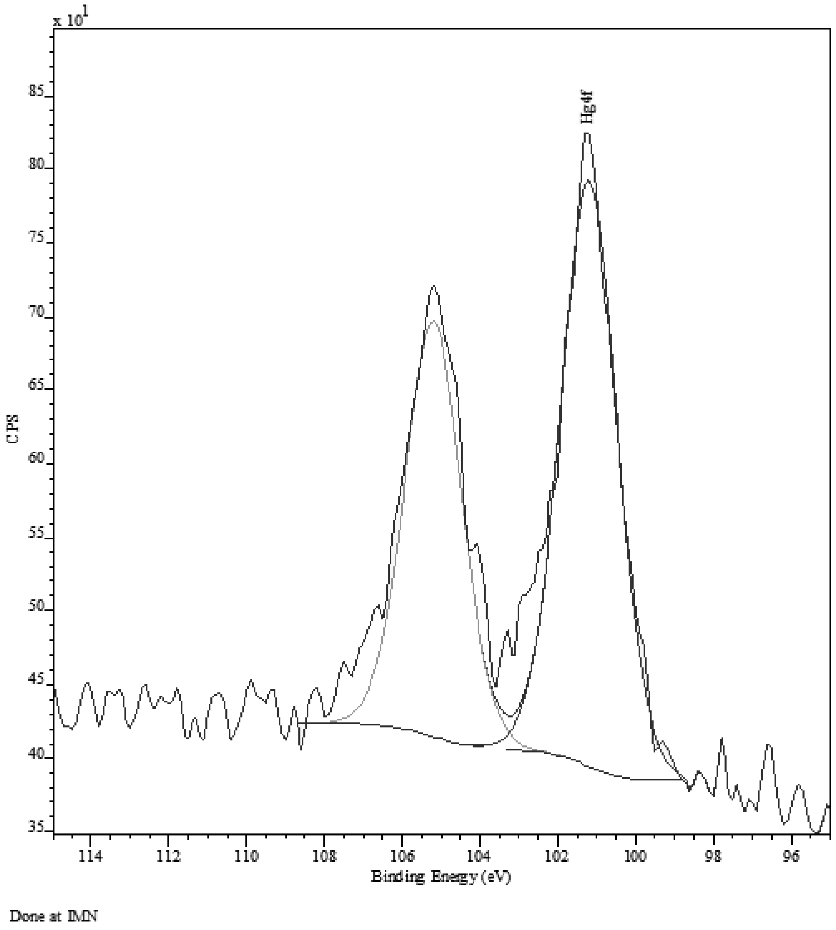


Figure 4. Mercury XPS spectrum (101 eV): - Hg-O (Hg 4f$_{7/2}$), - (Hg4f$_{5/2}$).

Hg4f doublet is clearly seen in Fig 4. The binding energy of $Hg4f_{7/2}$ is 101.20 eV, *i.e.* Hg is in an oxidized state [42-45]. Therefore Hg in the polymer matrix is present as Hg(II) (in its oxidized state). This implies Hg has not been reduced but incorporated into the polymer in its oxidized form (n-doping process) and then, when released, maintains the oxidation state in the solution.

In short, it was verified that PEDOT films on SS were appropriate, based on their n-doping-undoping properties, for cations extraction, such as Hg(II) ion.

Finally, it is noteworthy that this method is superior to any other available, because depending on the area of the supporting electrode and the number of "extraction cycles" it will always be possible to adapt the methodology to achieve, as in the current work, 100% efficiency, regardless of the sample. Besides, the presented results allow envisaging the use of such modified electrodes to quantify Hg(II) using the charge-concentration relationship.

4. CONCLUSIONS

In the present work 100% removal of Hg(II) was accomplished from synthetic samples. This is an outstanding result because for the first time the possibility of using conducting polymers showing n-doping as cation extractant was demonstrated. This opens up a broad research perspective that, in particular with respect to Hg(II) removal, can have a great environmental impacts due to the highly toxic and polluting characteristics of this ion.

The versatility of the approach is also remarkable because the electrode area and the number of extraction cycles can be optimized, depending on sample size and concentration, aimed at always achieving 100% yield. However, the challenge of making selective the method is raised. Perhaps this issue may be accomplished in terms of polymer porosity and chemical structure. Thus, it can be stated that the way has been paved for a significant number of research works, including the possibility of developing sensors based upon the same principles.

ACKNOWLEDGMENTS
We thank the financial support of CONICYT through FONDECYT Project 1100055 and ECOS-CONICYT through project E09C02. GCA thanks CONICYT scholarship Arteaga 2009, Folio 57090049.

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