

Short Communication

Polyanilines Modified Electrodes to be Assayed as Halides Sensors

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One of the new uses for polyanilines (PANIs) is as sensors, being able to measure the concentration of different types of compounds. As a positive charge exists on PANI's nitrogen, nucleophilic compounds can interact with the polymer leading to an observable and measurable change. In this case, modification of Pt electrodes with polymers derived from the linear structure of PANI previously reported by us, namely (poly [2,6-di(thiophen-2-yl)aniline]; poly (2,6-dibromoaniline); poly[N1-(2,6-di(thiophenyl-2-yl)phenyl)benzene-1,4-diamine] and poly[aniline/2,6-di(thiophen-2-yl)aniline (1: 1)]), display selectivity towards iodide over other halides, with good reproducibility and sensitivity, as evidenced by the linear relationship between concentration *vs* generated current measured at a fixed potential. Limit of detection (LOD) lower than $7.35 \cdot 10^{-5}$, limit of quantification (LOQ) below $7.43 \cdot 10^{-5}$ mol·L⁻¹ and linear regression $r^2 > 0.99$ were obtained. It is thus possible to develop with any of these polymers simple, very stable and inexpensive devices for the selective and direct quantification of halides, the most suitable being poly[N1-(2,6-di(thiophenyl-2-yl)phenyl)benzene-1,4-diamine], that produces the greatest current signals for iodide.

Keywords: polyanilines, sensors, halides, electropolymerization, modified electrodes.

1. INTRODUCTION

The structure of the polymers has been modified over time in order to improve their qualities with respect to classical conductive polymers, *e.g.* stability under different environmental conditions or to enhance specific characteristics, in the search of new materials for various applications. This has enabled finding uses as diverse as fabrication of solar cells [1-4], sensors [5-7], ion-extracting devices [8, 9], etc.

An outstanding application of conducting polymers is in the assembling of electrochemical sensors, since they offer the capability of interacting with various analytes and this interaction can be transduced into a measurable and quantifiable signal. Furthermore, they have a significant advantage over single molecules: an important sensitivity increase that enables envisaging their use in the fabrication of electrochemical and chemical sensors, due to their low cost and fast measuring rate [10, 11].

Among the polymers used as sensors thus far, polypyrrole (Fig. 1a), along with polyaniline (PANI) one of the first synthesized conducting polymers, have been used for the quantification of a variety of biological, organic and inorganic matrices; the former polypyrrole being the most vastly explored, due to the interaction of the amino groups found in biological plasmas with the aforementioned polymers. As for PANI, when attempting to determine the concentration of organic compounds such as methanol, ethanol, 1-propanol, 2-propanol, a wavelength decrease occurred, brought about by the interaction of alcohol's oxygen with the positive charge on nitrogen (Fig. 1b). This hypsochromic shift or blue shift is due to *band gap* increase, which significantly reduces the absolute coefficient of the solvent and causes the solvatochromic effect in measurements performed by UV-Vis spectroscopy [12]. Likewise, this polymer is also related to organophosphorus compounds measuring such as DMMP (dimethyl methylphosphonate), a neurotoxic compound, as well as to numerous papers for quantifying molecules, by sensing, for instance, humidity [13], ammonium ion [14,15], *para*-nitrophenol [16], etc. with appropriate correlation coefficients ($r^2 > 0.996$), which project them very strongly if this route is followed.

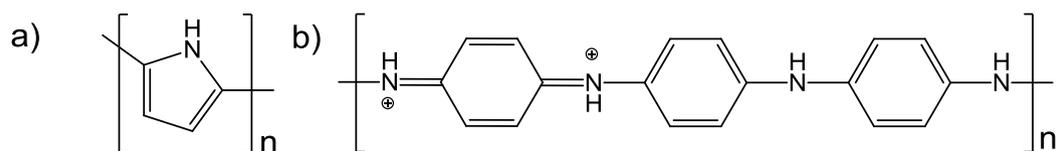


Figure 1. a) Polypyrrole; b) Polyaniline (Emeraldine).

In specific situations, electrochemical methods allow conducting polymers to be used as chemical sensors. Thus, conductimetric sensors show electrical conductivity changes following interaction with an analyte. These measurements can be easily performed by connecting two polymer-coated electrodes and measuring the conductivity of the film as a function of analyte concentration [17-20].

Thus, among the polymers utilized as sensors, polyanilines possess different properties, according to the substituent incorporated into the monomeric unit to modify their solubility and conductivity. In a previous work [21], a series of monomers were synthesized and characterized that enabled the synthesis of new modified polyanilines, namely poly-2,6-di(thiophen-2-yl)aniline (PDTA); poly-2,6-dibromoaniline (PDBA); poly-N1-(2,6-di(thiophenyl-2-yl)phenyl)benzene-1,4-di amine (PAFDOTA) and polyaniline/2,6-di(thiophen-2-yl)aniline (1:1) (CAD2), whose structures were corroborated by conventional techniques (Fig. 2).

Conductivity and solubility measurements allowed corroborating that bulky substituents decrease the conductivity as compared to PANI, reaching values of the order of $10^{-6} \text{ S} \cdot \text{cm}^{-1}$, however,

the solubility is enhanced. These findings lead to envisage the use of these polymers for electrodes modification employing the *spin coating* technique and to test the obtained device as electrochemical sensor. Consequently, in the current work, characterization of PDOTA, PDOBA, PAFDOTA and CAD2 deposits on Pt disk electrodes, with a view to its likely use for the development of halide electro-analytical sensors, is reported. Because of their negative charge, halides should be good candidates for interacting with the electrophilic nitrogen of the electrode coating, as mentioned above.

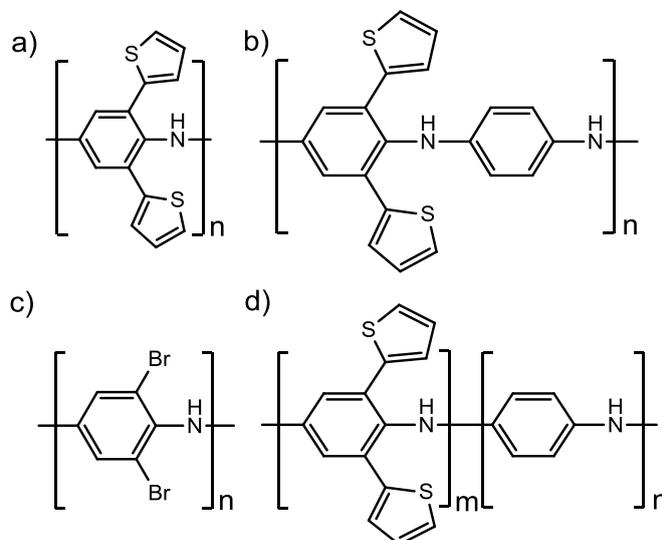


Figure 2. Polymers: a) PDOTA; b) PAFDOTA; c) PDOBA; d) CAD2.

2. EXPERIMENTAL

Monomers and polymers were chemically synthesized according to methods reported elsewhere [21]. The reagents were purchased from Aldrich and used as received.

All electrochemical work was conducted on a CH Instruments potentiostat coupled to a computer with appropriate software to control experimental conditions and data acquisition. Previous to the electrochemical measurements, 3-5 drops of a $2 \text{ mg}\cdot\text{mL}^{-1}$ polymer solution in acetone was deposited onto a 0.07 cm^2 geometric area Pt disk to form a thin film. The voltammetric response of the modified assembly was measured in an anchor-type three-compartment cell. Ag|AgCl in tetramethylammonium chloride solution, its potential adjusted to that of a saturated calomel electrode, SCE, was utilized as reference electrode [22] and a Pt wire of large geometric area was the counter electrode. All solutions were prepared with fresh Milli-Q grade deionized water obtained from a Heal Force (Smart Series) Deionizer. All experiments were performed at room temperature ($20 \text{ }^\circ\text{C}$) under argon atmosphere. A $1\cdot 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ tetrabutylammonium hexafluorophosphate, TBAPF₆, solution was used as supporting electrolyte. The optimum potential window was between -0.2 and 1.2 V for all the studied polymers. Subsequently, the voltammetric response of each modified electrode was studied, within the same potential window, utilizing $1\cdot 10^{-2} \text{ mol}\cdot\text{L}^{-1}$ aqueous solutions of the halide salts (NaF, KF, KCl, KBr and KI).

Calibration curves were constructed by measuring the current at the appropriate fixed potential for each polymer (indicated in Table 2). KI solutions, in concentrations between $1 \cdot 10^{-5}$ and $1 \cdot 10^{-2}$ mol·L⁻¹, were used to assess the respective figures of merit.

3. RESULTS AND DISCUSSION

The voltammetric profile of the polymer modified electrodes obtained in supporting electrolyte solution, showed no p-type doping/undoping process over a wide potential range, which allows thinking about their possible usefulness to study the redox response of other species at the same electrodes.

It is noteworthy that for each polymer, the voltammetric response in supporting electrolyte immediately reaches a stable profile (Fig. 3), when working within the optimal potential window, and is maintained for at least over 50 successive cycles, demonstrating thus the high stability of the modified electrodes.

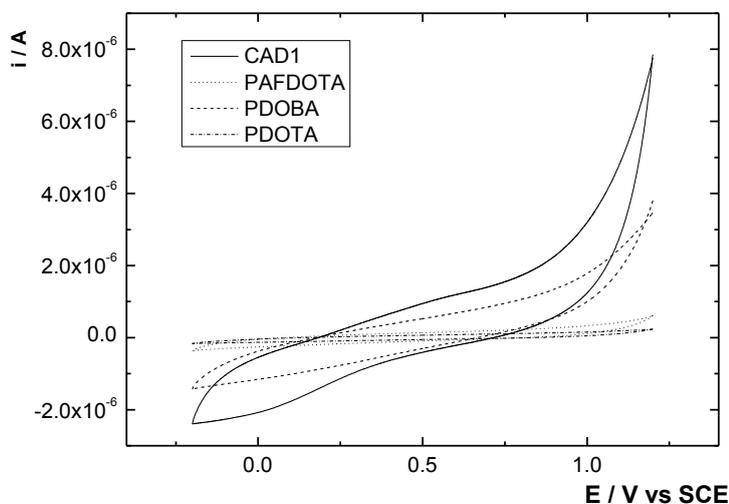


Figure 3. Polymers cyclic voltammetric profiles in TBAPF₆ supporting electrolyte solution.

Addition of the halide to the electrolytic solution showed that the electrochemical response for most of these ions remains the same, except for KI, Fig. 4, where a current variation for every single assay was observed. On the other hand, when fluoride or chloride is used, no oxidation or reduction process occurred, *i.e.* none of the modified electrodes is sensitive to these halides. Moreover, when sodium or potassium fluoride is utilized, the response is identical, indicating that the cation does not affect the measurement since neither reduction nor n-type doping is possible.

In contrast, for KI measurements on different polymer modified electrodes, a large oxidation peak current at potential close to 0.7 V, attributable to the halide redox process, is observed.

As for bromide ion, a slight redox process can be appreciated (Figs. 4a, 4b), however, the low intensity of the signal compared to the modified electrode in the absence of the salt precludes its

projection as a sensor for this anion. On the other hand, the peak potential is sufficiently far from that of iodide to enable a good resolution.

Based on the aforementioned behavior, quantification of iodide was accomplished by measuring the current, at a fixed potential, as a function of iodide concentration using the parameters summarized in Table 1. The results verified the feasibility of using these modified electrodes as sensors for the halide. As seen in Table 1, the obtained limit of detection (LOD) and quantification (LOQ) with all modified electrodes are very close between each other. However, a linear I vs. iodide concentration relationship, with a correlation coefficient of 0.9998, was found just when PAFDOTA was utilized, which proves this array is highly suitable as a prospective iodide sensor. In addition, this device provides the lower LOD and LOQ as compared with the other derivatives of the polyaniline family under survey. In other words, the other modified electrodes would allow detecting iodide and/or bromide at their respective peak potentials, while PAFDOTA may also be proposed for iodide quantification.

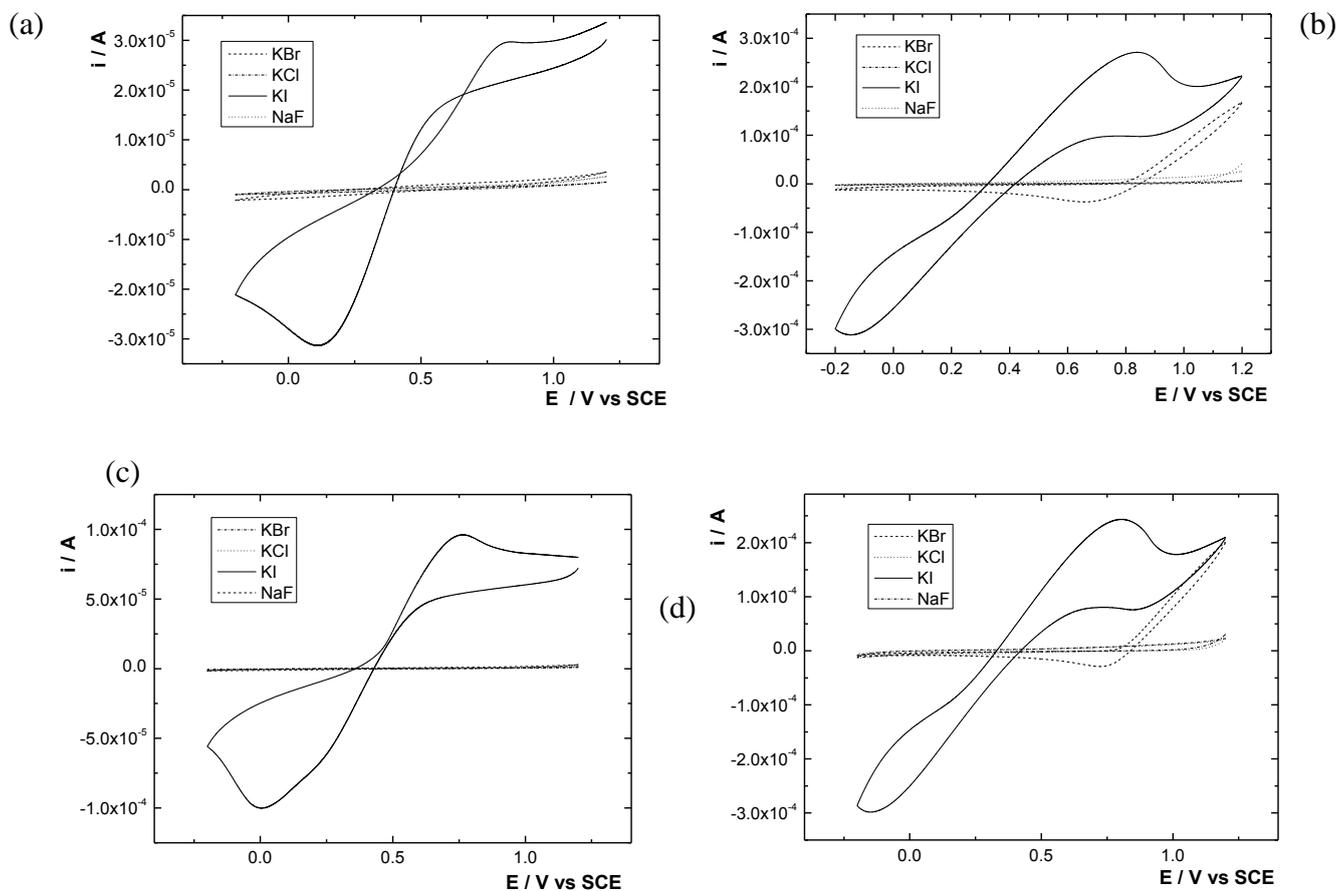


Figure 4. Voltammetric responses of the modified electrodes in halide solutions: a) Pt|CAD2; b) Pt|PAFDOTA; c) Pt|PDOBA; d) Pt|PDOTA.

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Table 1. Analytical parameters obtained in iodide analysis with different polymer-modified Pt electrodes.

Polymer	E (V)	linear regression	r^2	LOD ($\text{mol}\cdot\text{L}^{-1}$)	LOQ ($\text{mol}\cdot\text{L}^{-1}$)
CAD2	0.680	$y = 0.0076x + 5.49\cdot 10^{-8}$	0.9955	$7.35\cdot 10^{-5}$	$2.45\cdot 10^{-4}$
PDOTA	0.720	$y = 0.0180x + 2.1044\cdot 10^{-6}$	0.9910	$3.70\cdot 10^{-5}$	$1.24\cdot 10^{-4}$
PDOBA	0.700	$y = 0.0030x + 6.515\cdot 10^{-7}$	0.9953	$4.00\cdot 10^{-4}$	$1.33\cdot 10^{-3}$
PAFDOTA	0.730	$y = 0.0217x - 3.036\cdot 10^{-7}$	0.9998	$2.23\cdot 10^{-5}$	$7.43\cdot 10^{-5}$

It is likely that the obtention of a perfectly alternating and ordered polymer as PAFDOTA effectively regulate the amount of interactions between the concentration of iodide ion in solution and the amino groups of the polymer, decreasing, in turn, potential steric hindrance of pendant amino groups. On the other hand, corroborating the same hypothesis, PDOTA and PDOBA clearly seem less effective, finding greater hindrance into the polymeric matrix for the free interaction of the iodide anions.

Finally, the second polymer exhibiting acceptable analytical parameters was CAD2, a random polymer that could perhaps be in perfectly alternating small sections and, therefore, to exhibit a behavior very similar to PAFDOTA. Nevertheless, it has the disadvantage that its polymerization is random, is not highly reproducible in composition and, therefore, the analytical parameters can vary significantly between measurements.

Specific techniques for the detection of iodide ion have been reported by others, existing a variety of analytical techniques such as column chromatography [23], methods of multi syringe flow injection analysis (MSFIA) [24] or electrochemical techniques for not specific determination of ions [25], etc.

If electroanalytical techniques are compared with other conventional analytical techniques of quantification, as chromatographic techniques or MSFIA is possible to find limits of detection (LOD)

with two orders of magnitude lower. However, its implementation requires highly expensive specific ionic columns, plus the modification of this equipment for use only in these measures being prohibitive its implementation and projection on the quantification of iodide ion, for example in the industry. Moreover, in both cases longer times of analyte elution through columns are required, while electrochemical techniques provide an economical, rapid and highly sensitive alternative for projecting these modified electrodes in quantifying ions, as in this case, iodide.

In literature only an electrochemical method using conducting polymers for the determination of iodide ion and other ions of similar size is reported. It is based on the *doping/undoping* process of classical conducting polymers (polyaniline, poly(*o*-phenylenediamine), etc.) [25]. These highly porous polymers allow occluding different ions when applied one suitable potential, observing a change in the electrochemical response directly proportional to the concentration. However, this technique is not specific, since within the polymer matrix may occlude any ion with a suitable size, therefore, in a mixture of salts results could be biased or unreliable or would be required to perform separation techniques before ion quantification.

In the case reported here coating a platinum electrode with four different polymers obtained from monomers and polymers previously synthesized chemically, which are based on their structure aniline modified to improve their physicochemical properties is informed. These new polymers are stable at room temperature and soluble in suitable solvents for the selective detection and quantification of iodide ion. Furthermore, the solubility of these polymers is of great importance, since it is an odd feature, observed only in some few types of polymers, as modified polyacetylenes [26]. This advantage over other polymers, allows modifying any inexpensive electrode surface, such as steel, carbon, etc. Always give full recovery of the support-working electrode used, changing the solvent. It should be noted, finally, that the insolubility of these polymers in water make it stable and a good candidate for selective determination of iodide ion from complex matrices (where ions can be mixed), without pretreatment of the sample for determination.

However, a selectivity towards iodide by all the polymers should be assessed in further studies using the modified electrode in the presence of each of the investigated salts verifying the feasibility of using this sensor in real matrices.

Finally, since it has been corroborated the feasibility of using these polymers to modify Pt electrodes and use them as iodide sensor, future work entails the use of steel or PET (polyethyleneterephthalate coated indium tin oxide) electrodes seeking to reduce costs. In that case, for the optimization, the effect of the area of the substrate will be studied, and particularly the thickness of the polymer film.

4. CONCLUSIONS

All synthesized and tested polymers allowed preparing very stable, reliable and voltammetrically reproducible modified electrodes. The devices are sensitive and selective to iodide over the other halides, functioning as amperometric sensor when a constant potential of *ca.* 0.7 V is applied.

Furthermore, PAFDOTA and PDDOTA respond to bromide, but at higher potentials, which does not alter their selectivity.

PDDOTA is the most sensitive sensor to iodide, followed by CAD2, PAFDOTA and PDDOBA, however, the largest reproducibility and linearity was obtained with PAFDOTA; consequently, a comprehensive analytical evaluation of the latter device is justified (particularly with regard to selectivity) to propose it as sensor.

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