



**Thick-Film Organic Electrochemical Transistor (OECT) Sensors For
The Detection Of Hydrogen Peroxide**

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Abstract

Organic electrochemical transistors (OECTs) have gained great interest in the last few years as bio- and electrochemical sensors, due to their outstanding analytical performance, versatility, stability and easiness of fabrication. While thin-film OECTs have been studied extensively ever since the first device was reported more than three decades ago, thick film OECTs have not yet been explored. In this report, a simple approach for developing and testing thick-film OECT using a paper substrate is presented. The channel -cast by bar-coating the semiconducting polymer poly(3,4-ethylenedioxythiophene) doped with poly-styrene sulfonate (PEDOT:PSS) on a paper sputtered with gold- shows a thickness in the order of 10 μm , well above the conventional channels. This device is characterized by electrochemical techniques, displaying a high transconductance that exceeds 10 mS. The sensor was tested for the detection of H_2O_2 by building a transistor in a depletion mode where a Pt electrode was used as a gate. The outstanding analytical performance, as shown by the enhanced sensitivity and limits of detection, is presented and future applications of these type of devices are discussed.

Keywords

OECT, sensor, hydrogen peroxide, transconductance, thick film, PEDOT:PSS

1 INTRODUCTION

According to the World Health Organization (WHO), the first cause of death in the world is attributed to chronic diseases. In 2002, the WHO indicated that 60 % of the global deaths and 43 % of the healthcare expenses originate from four major diseases: diabetes, cardiovascular diseases, cancer, and obstructive pulmonary disease. By 2020, these numbers are expected to reach new alarming levels, 73 % and 60 % respectively [1, 2]. To assist both patients and physicists in managing and monitoring chronic diseases, new analytical platforms that combine simplicity, low-cost, accuracy and non-invasiveness are necessary.

A plethora of bio-electrochemical sensors exist nowadays for the diagnosis of a number of diseases and health conditions [3, 4]. The sensors detect specifically a biomarker in the biological fluids of the patients. In a plethora of cases, the indirect detection of a by-product of an enzymatic reaction, i.e. hydrogen peroxide (H_2O_2), is the basis of the electrochemical signal. For instance, glucose illustrates well this principle with the specific enzyme, the glucose oxidase (GOx). Several

electrochemical methods have been used for the detection of H_2O_2 , based mainly on active current approaches, such as amperometry, and to a much lower extent zero-current methods such as potentiometry. Amperometry requires a three-electrodes set-up as well as the use of a redox-mediator. Potentiometry may detect hydrogen peroxide directly without the use of additional components but the technique still suffers

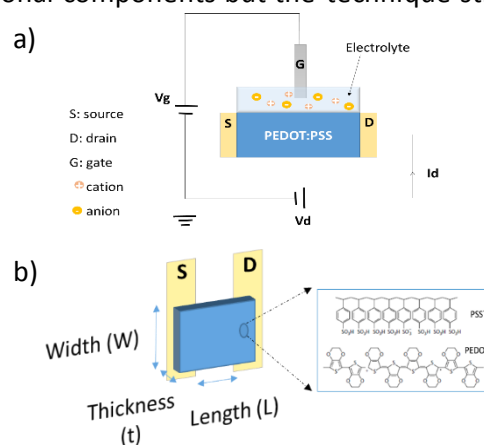


Figure 1. – a) Architecture and electrical circuit of an OECT, and b) geometrical parameters of the channel (in blue) and structure of PEDOT:PSS.

from limitations such as sensitivity and precision [5, 6]. In addition, in some biological fluids, the biomarkers maybe present in extremely low concentration (below the micromolar range for glucose in saliva, for instance) so that very low limit of detection is required.

Sensors based on organic electrochemical transistors (OECTs) appear as one of the promising solutions that are expected to play a major role in the future of disposable healthcare devices. An OECT is made of a thin film organic semiconductor material (channel) in contact with two metallic electrodes namely, the source and the drain (Fig.1-a). The channel and a third electrode (the gate electrode) are immersed in an electrolyte solution [7, 8]. Semiconducting polymers such as polypyrrole and polyaniline are among the first and most widely used polymers to build OECTs. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) (Fig. 1-b), however, is the most common semiconductor polymer employed essentially due to its high conductivity and stability in aqueous solutions [8-10]. Unlike organic field-effect transistors (OFETs), where the semiconductor is isolated from the solution using a dielectric material, the channel of the OECT is in direct contact with the solution. When a voltage is applied between the source and the drain (V_d), a source-drain current (I_d) flows through the channel. Applying a gate bias (V_g) causes ions from the electrolyte to be injected into the channel, which alters its conductivity [11]. As a result, this mechanism allows the modulation of I_d by a small change in V_g . The ability of V_g to modulate I_d is given by the transconductance:

$$g_m = - \frac{\Delta I_d}{\Delta V_g} \quad (1)$$

High transconductance is essential in order to have a sensor with enhanced performance, in particular with high sensitivity [12, 13].

In recent years, research on thin film OECT sensors for the detection of H_2O_2 has been very active. Y. Feng *et al.* have reported a highly sensitive and selective OECT sensor for the detection of glucose [14]. The gate electrode was prepared by modifying the surface of Pt with graphene, chitosan or nafion, and GOx, while the length and the width of the channel were 0.2 and 6 mm, respectively. The device demonstrated a linear range from 10 nM to 1 mM and a detection limit of 10 nM at $V_d = -0.05$ V and $V_g = 0.4$ V. L. Zhang *et al.* have constructed an OECT sensor with enhanced sensitivity and selectivity for the detection of ascorbic acid [15]. In this device, a gold electrode was coated with a polymeric film and imprinted with ascorbic acid molecule. The sensor displayed a sensitivity of 75.3

$\mu A/dec$, and low detection limit of 10 nM at V_d and V_g of -0.02 V and 0.6 V, respectively.

Evidently, since the performance parameters critically depend on the channel volumetric conductivity, one of the main factors that affect the transconductance is the device geometry [16, 17]. Several studies have demonstrated that the transconductance can be increased by carefully selecting the length (L), width (W) and thickness (t) of the channel (Fig 1-b) [18-20]. Bernardis *et al.*, based on the FET equations, showed that I_d and g_m scale with the width to length ratio (W/L), and the thickness [21]. Other parameters such as the gate material and geometry [22], doping level of the conductive polymer [23], have also been studied, and demonstrated to enhance the transconductance and the response time as well. In general, since these devices are mostly being developed for bio-electronic interfaces from the field of electronic engineering, very low response times are sought for. Thus, thin-film channels that facilitates the rapid exchange of ions with the solution have been traditionally used, since they allow response times in the μs time scale. For this reason, most of the work so far has been focused on optimizing the performance of thin film OECTs. Typically, in the majority of the devices investigated, the thickness was ranging from tens to few hundreds of nanometers [8, 18, 23]. The extent to which the thickness of the channel could be increased without loss of performance and sensitivity of the device, is still not well understood. In addition, the so far developed thin-film OECTs are confined to construction methodologies that require clean rooms. Therefore, the aim of this report is to characterize the electrical response of thick film OECTs sensors (superior to 10 μm), and the analytical parameters for the detection of H_2O_2 as a model for biosensors based on enzymatic reactions.

2 MATERIALS AND METHODS

2.1 Materials

High conductivity grade with 3-4% wt in water PEDOT:PSS aqueous solution was used. A stock solution of hydrogen peroxide 30% in water was used to daily prepare suitable fresh standards.

Nafion[®] solution used to make the gate electrode is composed of 5 % wt in aliphatic alcohols and water (15-20 % water).

Phosphate-buffered saline solution (PBS 0.1 M at pH = 7.4) was prepared from Na_2HPO_4 (57.6 % wt), NaCl (32 % wt), KH_2PO_4 (9.6 % wt), and KCl (0.8% wt).

All chemicals were analytical grade products and were purchased from Sigma-Aldrich. Finally, Milli Q water

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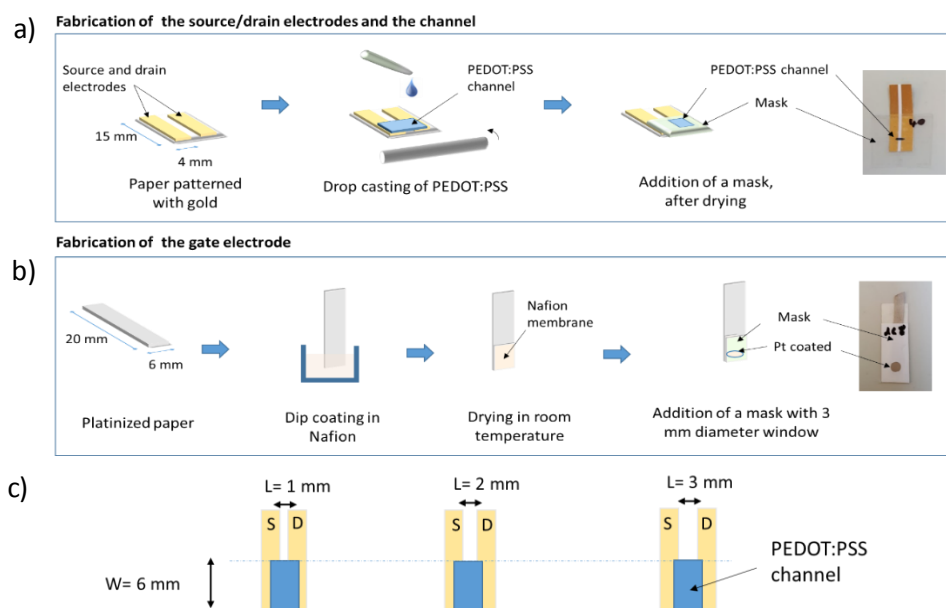


Figure 2. Fabrication process of *a)* source/drain and PEDOT channel and *b)* the gate electrode, and *c)* three channels with the same width (6 mm) and different lengths 1, 2 and 3 mm

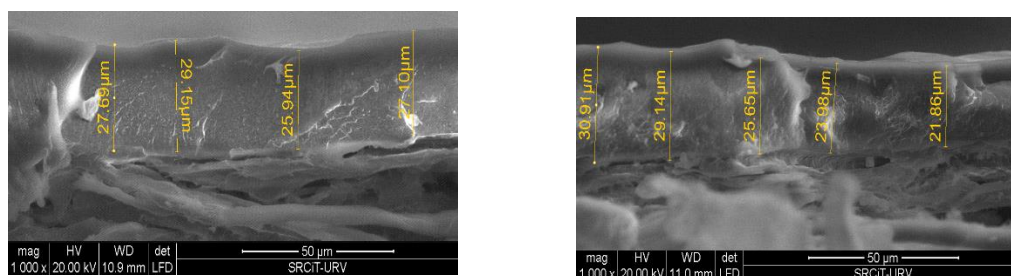


Figure 3. E-SEM Cross-section of two PEDOT:PSS channels with a length of *a)* 2mm and *b)* 3mm.

(18.2 MΩ/cm at 25 °C) was used to prepare all the solutions.

2.2 Fabrication of the sensor

The sensor was made in two major steps (Fig. 2). The first step consists of patterning the source/drain electrodes and the channel (Fig. 2-a). The electrodes are made by sputtering a 100 nm gold layer on top of a clean paper substrate. To create a gap between the source/drain electrodes, a mask was prepared from an adhesive tape, then fixed on the top of a clean substrate paper (before the sputtering process). Masks of different widths (1, 2 and 3mm) were used to evaluate the effect of the channel length. After removing the mask, the channel is deposited by casting a drop of PEDOT:PSS and rolling it using a glass bar. The PEDOT:PSS was then baked at 100 °C for 20 min. Finally, a mask was added to protect the source and drain electrodes, leaving only the channel exposed.

In a second step (Fig. 2-b), the gate electrode was built by sputtering a 100 nm platinum film on a substrate paper. Rectangular pads (6 mm × 20 mm) were then cut and dip coated in a Nafion® solution. The coated

electrodes were left drying at room temperature overnight. Finally, a mask with a circular window (R=1.5 mm) was applied over the coated area (Fig. 2-b).

2.3 Characterization of the sensor

2.3.1 SEM

The cross-sectional views of the PEDOT:PSS channel were analyzed using the Scanning Electrons Microscope (SEM) JEOL model JSM-6400. To prepare the cross-sections, the samples were frozen by dipping them into liquid nitrogen for few minutes, then sharply cut.

2.3.2 Electrical characterization

The measurements of the source-drain current (I_d) were taken using Keithley 6514 Electrometer (Keithley Instruments, Cleveland, OH, USA).

The gate and source drain voltages were applied using TENMA power supply (Element14®, Newark, New Jersey, US).

The channel and the gate electrodes were immersed in the PBS solution (0.1 M at pH = 7.4). Only the areas

delimited by the windows were in contact with the solution, while the rest of the electrodes was isolated from the solution by the mask.

3 RESULTS AND DISCUSSIONS

3.1 Characterization of the channel thickness

Bar coating is a simple and inexpensive technique for depositing planar films. In short, a drop of the film-forming solution is spread by rolling a suitable bar, which can be made out of metal, glass, etc. The thickness of the film depends on several parameters such as coating speed, density of the solution, and diameter and material of the bar. It is an ideal technique for creating films with a thickness of tens of microns [24, 25]. Fig.3 represents the cross-sectional views of two channels having a 6 mm width and a length of 2 and 3 mm. The average thickness of the channels is respectively $26.30 \pm 3.70 \mu\text{m}$ and $27.47 \pm 1.34 \mu\text{m}$. This confirms that the channels created using the process described in Fig. 2 have a high thickness with consistent uniformity, and that the process shows good reproducibility between sensors.

3.2 Ohmic region & Conductance

First, an electrical characterization to check the properties of the channel in terms of conductance was carried out. Three channels were prepared with similar width (6 mm) and different lengths 1, 2 and 3 mm as described in Fig.2-c. In other words, the channels had the width to length (W/L) ratios 6, 3 and 2, respectively. Fig.4 represents the $I_d - V_d$ output curves of the three devices. It shows that I_d changes linearly with the V_d applied. In other words, over the tested range of V_d , which is from -0.8 v to 0.8 v, the three channels act as a simple resistor [26-28]. The slope of each linear curve

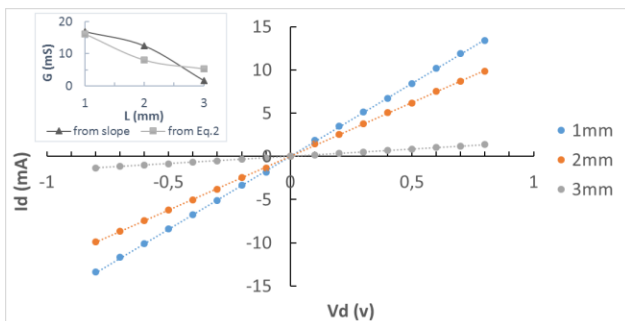


Figure 4. $I_d - V_d$ output curve of three channels with lengths 1, 2 and 3mm. The Inlet figure represents the plot of the dynamic and calculated conductance vs length of the channels.

represents the conductance of the corresponding channel. The conductance increases as the length of the channel decreases, as it can be seen in the inset curve. If we keep increasing the source-drain voltage, I_d will

eventually reach a saturation level, where the current becomes constant.

The conductance can also be calculated using the following equation :

$$G = \frac{\sigma \cdot W \cdot t}{L} \quad (2)$$

where σ is the conductivity of the PEDOT: PSS (1 S/cm), and L , W , and t ($27 \mu\text{m}$) are the length, width and thickness of the channel, respectively.

Despite of the differences between the values of the dynamic and the calculated conductance, Fig.4 inlet shows the inverse proportionality that exist between G and L .

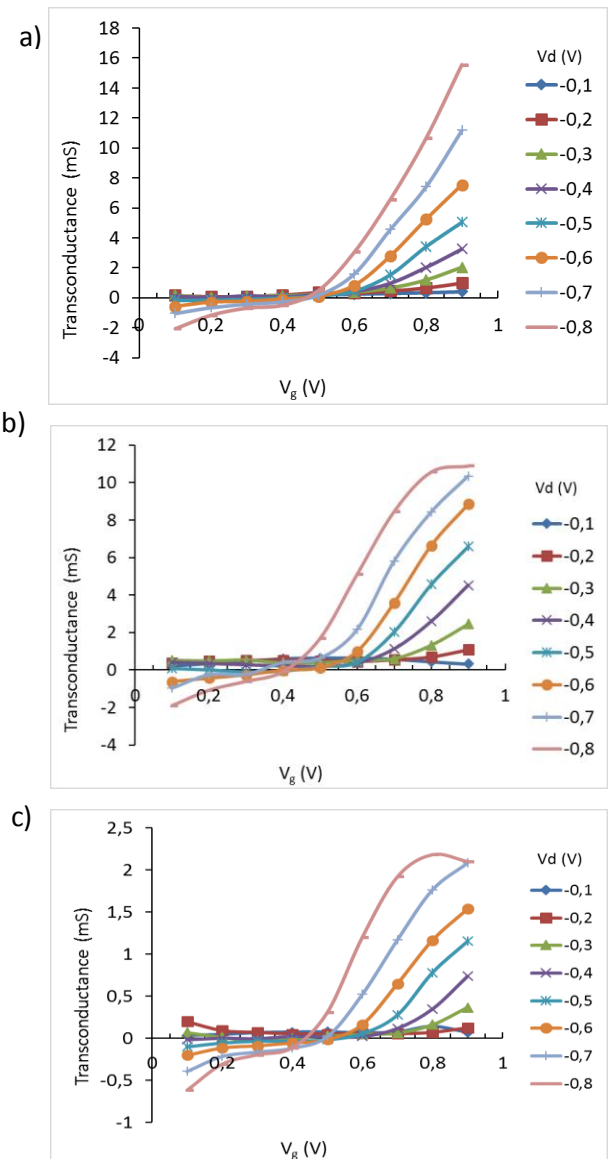


Figure 5. Transconductance vs V_g of three sensors with channel lengths a) 1mm, b) 2mm, and c) 3mm

3.3 Evolution of the transconductance

The test is performed by immersing the channel and the gate electrode in a PBS solution (0.1 M at pH= 7,4). First, a constant negative V_d is applied to generate a source-drain current (I_d); then, a gate bias is applied and the corresponding change in I_d is recorded. The same process is repeated for different values of V_d . The transconductance (g_m) is calculated using equation 1.

Fig. 5 represents the results of three devices with channel lengths 1, 2 and 3 mm. The most noticeable trend observed in the graphs is that the transconductance (g_m) increases with V_g and V_d , and is inversely proportional to the length of the channel. For example, at $V_d = -0.7$ V and $V_g = 0.7$ V, the transconductance of 1, 2 and 3 mm channels are 5.3 mS, 4.2 mS and 0.95 mS, respectively. All the devices demonstrate high transconductance values at high V_d and V_g . The highest transconductance (15 mS) is obtained at $V_d = -0.8$ V and $V_g = 0.9$ V for the device having the channel length 1 mm (Fig. 5-a). These relationships are compatible with what has been reported on the operation of OECTs. Bernards *et al.* describes the drain current (when $|V_d| < |V_g - V_p|$) as a function of the device geometry and the properties of the semiconducting polymer [21]:

$$I_d = \frac{G}{V_p} \left(V_p - V_g + \frac{1}{2.V_d} \right) V_d \quad (3)$$

where V_p is the pinch-off voltage, V_d and V_g are the drain and the gate voltages. The transconductance can be calculated by taking the first derivative of equation 3.

$$g_m = \frac{\partial I_d}{\partial V_g} = -\frac{G}{V_p} V_d \quad (4)$$

According to the equation 4, one way to increase the transconductance is by maximizing the conductance of the channel and operating at high V_d .

3.4 Stability of the sensor

The amount of time required for the drain current (I_d) to reach a steady state after applying V_d and V_g is an essential characteristic of OECTs, especially in applications where rapid detection of the analyte is equally important. In addition, signal-to-noise ratio (SNR) is a prerequisite to design OECTs sensors with high limit of detection [29, 30]. Fig. 6 represents the stability over time of the drain current of a sensor with a channel length 0.5 mm and width 1mm. The test was carried out by immersing the channel and the gate electrode in a PBS (0.1 M and pH= 7.4) at the operating conditions $V_d = -0.3$ V and $V_g = 0.3$ V. It shows that the sensor takes at least 20 min (1200 s) to reach a stable signal. This delay

is caused mainly by the slow movement of ions from the electrolyte into the channel. OECTs are modeled as two circuits: electronic and ionic. The electronic circuit

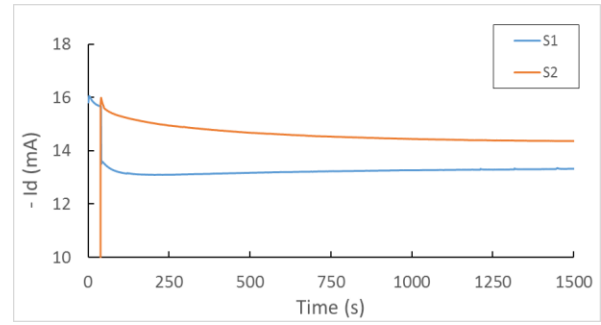


Figure 6. Time trace of $-I_d$ of two thick films sensors at $V_d = -0.3$ V and $V_g = 0.3$ V.

represents the flow of electrons/holes through the semiconducting material, which gives rise to the current I_d . On the other hand, the ionic circuit symbolizes the flow of ions from the electrolyte into the channel and vice-versa. The latter is a limiting factor because ions, compared to electrons, move with lower velocity [21]. The SNR of the two sensors tested were calculated for the last 100 points from the recorded I_d -Time data. They indicate that the two sensors (S1 and S2) are highly stable, having a SNR of 63.62 and 73.78 dB, respectively, which is higher than what is observed in thin film OECTs (52.7 dB) [31].

3.5 Calibration curve

To demonstrate the performance of the thick film OECT, the device is used to detect the hydrogen peroxide. Fig. 7-a shows the time plot of the response of a thick film sensor ($W = 1$ mm and $L = 0.5$ mm) at $V_d = -0.3$ V and $V_g = 0.3$ V, as the concentration of H_2O_2 increases from 10^{-7} to 10^{-5} M. When the analyte is added, the drain current (in absolute value) decreases. This response confirms that the OECT is operating in the depletion mode, as opposed to the accumulation mode where I_d increases with the concentration of the analyte [31]. To describe this behavior, equation 3 was modified by replacing V_g with the effective gate voltage (V_g^{eff}) in order to count for the contribution of the analyte. The response I_d is given by the following equation [32-34]:

$$I_d = \frac{G}{V_p} \left(V_p - V_g^{eff} + \frac{1}{2.V_d} \right) V_d \quad (5)$$

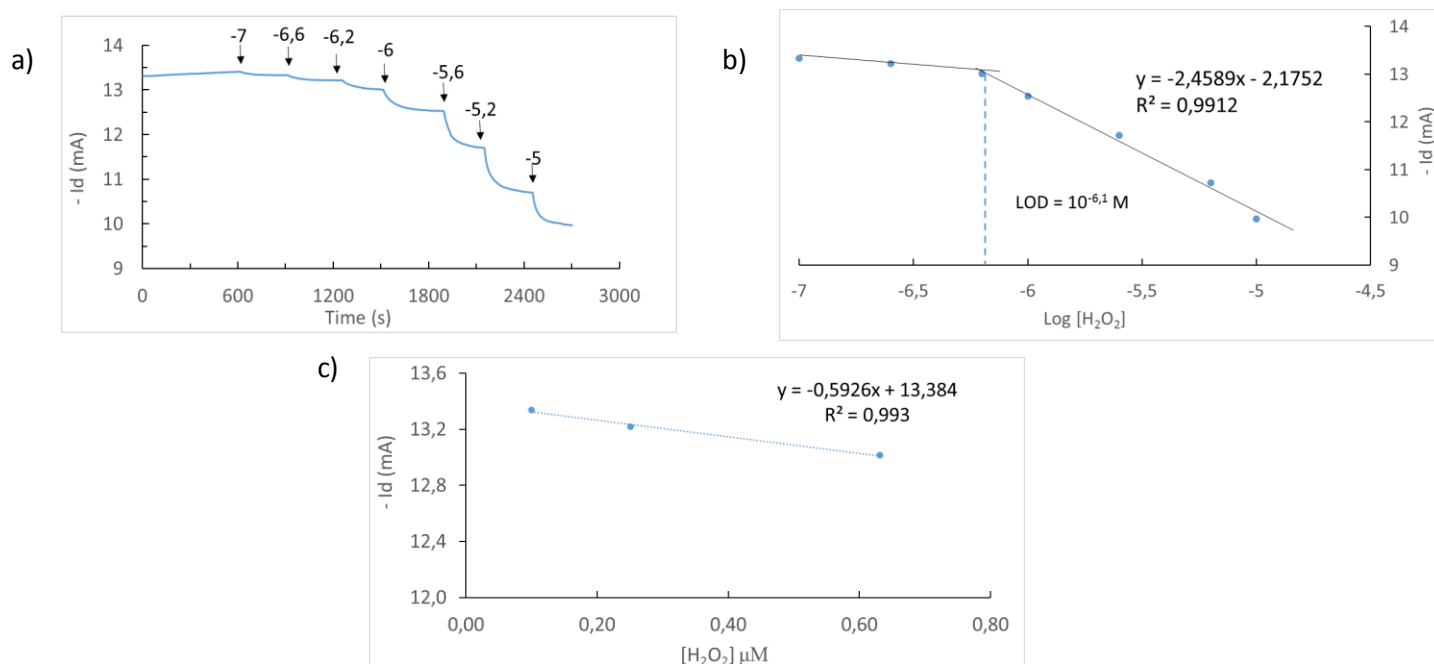


Figure 7. a) Time plot of the I_d responses of a thick-film sensor at $V_d = -0.3$ V and $V_g = 0.3$ V, for increasing concentrations of H_2O_2 , and b) the corresponding logarithmic calibration curve. c) calibration curve showing a linear relationship between $[H_2O_2]$ and I_d for concentrations between 10^{-7} M and $10^{-6.2}$ M.

In this sense, V_g^{eff} is the overall gate bias required to produce the same response in the absence of the analyte. V_g^{eff} is given by the following relationship :

$$V_g^{\text{eff}} = V_g + (1 + \gamma) \frac{kT}{2e} \ln[H_2O_2] \quad (6)$$

where γ is the gate to the channel capacitances ratio, k is Boltzmann constant, T is the absolute temperature, and e is the charge of an electron.

Fig. 7-b shows the calibration curve of the sensor. The limit of detection obtained is $10^{-6.2}$ M, which is comparable to what is achieved with thin film sensors. The sensor demonstrated a nernstian response with a narrow linear range from 10^{-6} to 10^{-5} M, and a sensitivity of 2,46 mA/dec. For small concentrations from 10^{-7} to $10^{-6.2}$ M (Fig.7-c), the response of the sensor is directly linear with respect to the concentration of H_2O_2 . The sensitivity in this region is 592.6 $\mu\text{A}/\mu\text{M}$.

As a final remark, it is important to stress that these results are showing that the OECT produce a power signal amplification, which is ideal from a detection point of view. To put this in perspective, the gate electrode is like a potentiometric sensor, but instead of monitoring the change in potential, it measures the variation that is produced on the source-drain channel. For example, a transconductance of 15 mS means that the system will change 15 mA for a 1 V change on the gate. Thus, by simple maths, if the gate was changing 60

mV (Nernstian change for 1 decade concentration) the drain current should be changing 0.9 mA. Since this is an actual current produced by a power supply, it can be run, for example, through a 1k Ω resistor, producing a voltage drop of 900 mV. This way to measure OECTs, which has been already reported, shows that this system should allow a sensitivity of 900 mV/decade, significantly higher than the Nernstian value, and with a noise level (considering typical fluctuations in the μA range) in the millivolt range.

4 CONCLUSION

Simple OECT sensor with a thick film channel was built and successfully tested. The electrical behavior of the device was investigated and evaluated for the detection of hydrogen peroxide. To build the channel, the semiconducting polymer PEDOT:PSS was deposited by a bar coating technique on a paper substrate patterned with gold. Pt coated with an ion-exchange membrane (Nafion) was used as the gate electrode because of its excellent electro-catalytic properties. The device demonstrated high transconductance and stability which are two requirements for the design of high performance OECTs. The analytical characteristics of the sensor in terms of sensitivity, limit of detection and linearity were determined. The sensor demonstrated a high sensitivity, and a good limit of detection towards hydrogen peroxide, which suggests it could be used, for instance, as a glucose enzymatic-based sensor in saliva or tears. To exploit the full potential of thick film OECTs,

further investigation is needed in order to understand the physics of their operation and the influence of the geometry on their performance.

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