



## Short Communication

# Biosensors 2020-Organic Electrochemical Transistors: versatile platforms for Bioelectronics

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### Abstract

In recent years, advancements in material research and technology have shed light on the disruptive impact of personalized diagnostic and therapeutic scenarios on the quality of life. Concomitantly, the need to bridge the gap between user-controlled electronics, such as sensors and actuators, and biology is evident. The design of effective interfaces allowing reliable interaction between electronics and biological entities is the ambitious purpose of Bioelectronics (1). Due to (i) the mechanical mismatch between abiotic hardware components and living, water-rich systems and (ii) the fundamental discrepancy in the nature of charge transport, the efficient transduction of the biological signal remains a major challenge. In this panorama, Organic electrochemical transistors (OECTs) (2) are electrochemical devices that are gaining momentum thanks to the unique combination of soft electronic components and the transistor configuration. On one hand, the transducing materials are typically soft conducting polymers capable of mixed conduction, that is, they can detect ionic fluxes and convert the bio-signal into an electronic output (or vice versa). On the other hand, the device benefits from intrinsic signal amplification and design versatility, thus realizing a high signal to noise ratio and adapting to a variety of geometries and substrates. In this contribution, the potentiality of OECT-based smart platforms will be presented, with particular focus on the realization of novel electrochemical sensors and biosensors for bio-signals transduction and highly sensitive and selective detection of medically relevant analytes, such as neurotransmitters (3,4).

### Keywords

OECT, bioelectronics, sensor, conducting polymer, mixed conduction, biological signals

## Introduction

Potentiometric sensors are important tools in analytical chemistry to quantify the concentration of chemical species in solution, however, some constraints hinder their low cost-fabrication, miniaturization, and thus their reliable use in some emerging fields such as wearable and lab-on-chip technologies (Sophocleous and Atkinson, 2017; Parrilla et al., 2019). A potentiometric measurement is performed with a high impedance voltmeter that measures a voltage difference in absence of a current flow between an indicator and a reference electrode, both dipped in the same solution (Skoog et al., 1992; Figure 1A). The circuit is very

simple and does not require other elements (Figure 1B). The response is controlled by the activity of the species that is quantified during the analysis, as ruled by Nernst equation. Among these sensors, the glass electrode for pH measurement has remained the gold standard for more than a century (Haber and Klemensiewicz, 1909; Skoog et al., 1992; Harris, 2016). Moreover, other potentiometric sensors have been developed for the detection of various chemical species such as fluoride and calcium, and these devices are now available on the market (Light and Cappuccino, 2009). Potentiometric measurements can be applied to very diverse fields in analytical chemistry due to their simplicity and fast response time, even if their use is limited by the difficulty in the fabrication of membranes able to selectively detect the target analyte.

## Materials and Methods

### Chemicals

CLEVIOS™ PH 1000 suspension (PEDOT:PSS) was bought from Heraeus (3-glycidioxypropyl)trimethoxysilane, dodecylbenzenesulfonic acid, potassium bromide, potassium iodide, potassium nitrate and potassium hydroxide were purchased by Sigma Aldrich. Potassium chloride was bought from Fluka. Ethylene glycol was obtained from Carlo Erba. Sodium hydroxide was purchased by Empura. All chemicals were of reagent grade or higher. The glass slides were obtained from Menzel-Gleaser. Polydimethylsiloxane (PDMS) was prepared using Sylgard 184 kit that was bought from Dow Corning.

### Apparatus

The electrochemical potentials were ideally applied with respect to a saturated calomel electrode (SCE) in a single compartment, three-electrode cell via a potentiostat (CH Instrument 660C). The gate electrode was connected to the working electrode output and a Pt wire was used as the counter electrode. It is worthy to note the difference between electrochemical potential and other applied voltage/potential. The electrochemical potential is measured or ideally applied with respect to a reference electrode, and as already stated, we used the symbol  $E$  to indicate it in this paper. This potential is strictly related to the thermodynamics of the different processes that can take place at the electrode surface. When the electrochemical potential is applied or measured at the gate electrode, the  $E_g$  symbol is used. Conversely, we use the symbol  $V$  to express a voltage that is applied/measured with respect to the ground or the source terminal, but it is not referred to an electrochemical interface with a reproducible and well-defined potential (measured with respect to a reference electrode).

During the transistor characterization a Keysight B2902 A source-meter unit applied the drain voltage, while the gate potential was applied by a potentiostat. The output and the transfer curves were

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recorded in 0.1 M KNO<sub>3</sub> solution.

The sensing experiments were performed while the Keysight B2902 A equipment applied the V<sub>d</sub> (0.01 V) and measured the I<sub>d</sub>, while the gate and the channel were dipped in 0.1 M KNO<sub>3</sub> and different amounts of the analytes were added to the electrolyte solution. In order to measure the gate electrochemical potential and compare it with the value estimated by the drain current, a reference electrode has been used.

## OEETs Fabrication

Gate, drain, and source contacts made of Cr/Au (50 nm) were deposited via thermal evaporation. The thickness of the Cr layer is 10 nm, while the Au one is 40 nm. PEDOT:PSS solution was prepared by adding 5% v/v ethylene glycol, 0.25% v/v dodecylbenzenesulfonic acid, and 1% v/v 3-glycidyloxypropyltrimethoxysilane to the CLEVIOS PH 1000 suspension. The mixture was filtered through a 1.2 μm cellulose acetate filter and spin coated between gold source and drain electrodes at 500 rpm for 3 s, and then annealed at 140°C for 1 h. The final thickness of the PEDOT:PSS channel was 800 nm. Afterward, the gate electrode of the transistor was modified with Ag/AgX (X = Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, and S<sup>2-</sup>). To this aim, the bottom part of the gate electrode was carefully dipped in the electrodeposition solutions in order to avoid the contact between the electrolyte and the channel. The gate electrode was connected to the working electrode terminal of the potentiostat. Firstly, silver was deposited on the electrode by applying 0.2 V using 0.1 M AgNO<sub>3</sub> as the electrodeposition solution. After washing with distilled water, the gate modification was completed by applying +0.6 V when the electrode was dipped in a 0.1 M solution of X<sup>n-</sup> anion (X<sup>n-</sup> is the analyte to be detected by the sensor). If the sensor was not used just after the preparation, it got dried. Before the use, the OEET was hydrated by soaking it in the electrolyte solution.

## Calculation of E<sub>g</sub> From I<sub>d</sub>

The E<sub>g</sub> values were calculated from the I<sub>d</sub> values recorded during an experiment for Cl<sup>-</sup> detection by exploiting the transfer curve as calibration plot of the transistor. In detail, the transfer curve was recorded before the chemical modification of the gate electrode with Ag/AgCl because the application of an E<sub>g</sub> would cause a current flow that changes the gate chemical composition. After that, the gate electrode was modified with the procedure described in the paragraph 2.3 and the obtained OEET was used for the Cl<sup>-</sup> detection. The sensing experiment was performed with the procedure described in the paragraph 2.2, and E<sub>g</sub> was measured with respect to a reference electrode. The I<sub>d</sub> values were extracted for every Cl<sup>-</sup> addition. The transfer curve was approximated to a line in the range of the observed I<sub>d</sub> values, where I<sub>d</sub> was the y-axis and E<sub>g</sub> the x-axis. The E<sub>g</sub> values were calculated from I<sub>d</sub> values by means of this line and were compared with the ones measured with respect to the reference electrode.

## Results

### OEET Characterization

The transistors were fabricated with a geometry that is ideally similar to the one proposed by Wrighton's group (Kittlesen et al., 1984; Paul et al., 1985) in the first articles describing OEETs, because the gate electrode is in electrical contact with the conductive polymer present in the channel (Figure 2A). The source and drain

terminals are the outer gold tracks, while the gate terminal is the inner gold track. The gold track of the gate is longer than source and drain ones in order to allow for the electrodeposition of the sensing material without immersing the conductive polymer. The channel is the PEDOT:PSS film connecting the drain and the source terminal. Consequently, the gate terminal can control the electrochemical potential of the conductive polymer when the device is dipped in a solution and connected to a potentiostat (Figure 2B). In order to complete the transistor architecture, a source-meter unit applies a voltage between the drain and source terminals and records the generated current (I<sub>d</sub>). Figure 2C shows the transfer curve of the transistor. As above described, the gate electrode is in direct electrical contact with the channel. Consequently, the two elements reach an equilibrium state, and thus they have the same potential. When a positive voltage is applied to the gate, also PEDOT:PSS acquires a positive voltage and the cations are pushed out causing holes injection. From an electrochemical point of view, PEDOT:PSS is converted in its oxidized state according to the reaction (1):



Since charge carriers are the oxidized centers of the polymer, the electrical conductivity of the polymer increases. On the other hand, if a cathodic/negative potential is applied to the gate, the reduction of the polarons and bipolarons takes place with a decrease of the charge carriers concentration, and thus of the source-drain current. The transistor behavior is in agreement with the observation of Wrighton's group (Kittlesen et al., 1984) which studied a transistor with a polypyrrole channel in direct contact with the gate electrode. The OEET output curves (Figure 2D) show the ability of the gate voltage to control the channel conductivity, demonstrating that the device works as a transistor.

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