EGFET-based pH Sensor coupled with Low-cost Electrochemical Screen-printed Electrodes

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Abstract. In this paper, we present an attractive EGFET-based pH sensor that integrates a n-channel metal-oxide-semiconductor field-effect transistor (MOSFET) as the transducer and low-cost electrochemical screen-printed electrodes (SPE) as the sensitive element. Our sensor is based on a metallic silver/silver-chloride (Ag/AgCl) reference electrode and an indium-tin-oxide (ITO) sensitive electrode, operating in the pH range of 2 to 9. Results show that the proposed sensor can measure pH with acceptable sensitivity and resolution.

1. Introduction
Sensing devices based on field-effect transistors (FET) have drawn significant attention as a promising tool for detecting chemical and biological phenomena [1]. A FET-based sensor comprises a sensitive electrode, a reference electrode (RE) and an electrochemical transduction stage; this latter can be seen as a trigger for the transistor given by either a chemical or a biological phenomenon, which changes the charge distribution and modifies the conductance of the FET [2]. Particularly, a potential for hydrogen (pH) sensor is an electrochemical device devoted to indicate the alkalinity or acidity of a solution by measuring the concentration of dissolved hydrogen ions [3]. The measurement of pH is widely found in several applications such as soil analysis, food quality and biofluid characterization, to mention only a few. Ion-sensitive FET (ISFET) is the most common FET-based pH sensor [4], it detects ionic activities due to the interaction of the sensitive electrode with an electrolyte. Nevertheless, ISFET major drawbacks are the poor long-term stability, the lack of insulation and encapsulation. To overcome this situation, the extended-gate FET (EGFET) based sensors [5] take on advantage a metal-oxide-semiconductor FET (MOSFET) device, such that, the gate region is preserved, and it is physically isolated from the sensing layer, thus providing advantages such as miniaturization, versatility, high-reliability and good detection limits [6]. Experimentally, an EGFET-based sensor requires a selective material as the recognition element and an external RE, which are part of the sensor device itself. Most common electrodes are, however, bulk, fragile and expensive devices, that are difficult to integrate within a single device for portable and in-situ experiments.

In this work, we introduce, to the best of our knowledge, a novel EGFET-based pH sensor that integrates a low-cost electrochemical electrode array for embedding both a metallic RE and an organic sensitive electrode, in a simple structure. The proposed device explores the advantages of screen-printing technology as a cost-effective solution to the conventional FET-based sensors but preserving enough sensitivity for detecting pH changes in a micro-volume.
The rest of the paper is organized as follows. In section 2 we introduce the operation principle of the sensor. Then, in section 3 an overview of the measurement setup is presented. Section 4 is devoted to showing the experimental results and its discussion. Ultimately, we present the conclusions in section 5.

2. Operation principle
The configuration of an EGFET-based sensor is shown figure 1. It is composed by three main elements. Firstly, a MOSFET device which can be a conventional n-channel MOSFET, which is in charge of the electrochemical transduction. The reference and sensitive electrodes, which are responsible for linking the electrical signals and the electrolyte under study (EUT). Finally, the underlying electrochemical phenomena of the sensor, which describes the overall relationship between sensing and transduction mechanisms.

2.1. MOSFET device
Similar to a conventional MOSFET, the output of an EGFET can be regarded as the drain-to-source current $I_{DS}$, which in the linear region is written as follows

$$I_{DS} = \mu C_{ox} \frac{W}{L} \left[ (V_{REF} - V_{th}^*) V_{DS} - \frac{1}{2} V_{DS}^2 \right],$$

where $\mu$ is the ion mobility, $C_{ox}$ is the gate oxide capacitance per unit area, $W$ and $L$ are the width and length of the channel, respectively, $V_{REF}$ is the reference voltage applied to the gate/ sensitive electrode pair and $V_{DS}$ is the drain-to-source voltage. Note that all the aforementioned parameters are related to the MOSFET device itself. Conversely, $V_{th}^*$ is the overall threshold voltage, which is a parameter that links the MOSFET to the EUT, thus being it the main source of transduction, as it relates the chemical reaction on the electrode with the potential at the gate of the transistor device.

2.2. Electrodes
The sensitive electrode of an EGFET is the element of recognition and it should be made of a specific material sensitive to a certain EUT [5]. We appeal to indium-tin-oxide (ITO) as the sensitive material due to its attractive characteristics. ITO exhibits high electrical conductivity with a highly transparent nature, thus avoiding photovoltaic effects; and furthermore, ITO allows to fabricate very low-cost conductive devices in an organic fashion for biocompatible applications [7]. The EGFET-based sensor requires a reference electrode, which is polarized with an external voltage $V_{REF}$ to excite the EUT. The RE provides a stable and well-defined potential, that establishes a zero-current condition. In such a sense, the Ag/AgCl electrode is the most common material used for the RE, as it is considered a non-polarizable electrode [8]. As a novelty of our contribution, in this work, we propose to embed both the sensitive and reference electrodes on a single planar structure, namely an array of printed electrodes.

![Figure 1. Schematic representation of an extended-gate field-effect transistor based sensor.](image)
2.3. Electrochemical transduction
Recalling equation (1), therein the threshold voltage \( V_{\text{th}}^* \) depends on the parameters of the chemical reaction among the electrolyte and the sensitive electrode as follows

\[
V_{\text{th}}^* = V_{\text{th}} + E_{\text{REF}} + \chi_{\text{EUT}} - \frac{U_M}{q} - \phi,
\]

where \( V_{\text{th}} \) is the threshold voltage of the MOSFET device, \( E_{\text{REF}} \) is the potential at which the reference electrode is polarized, \( \chi_{\text{EUT}} \) is the superficial dipole potential of the EUT, \( U_M \) is the work function of the RE, \( q \) is the electron charge and \( \phi \) is the potential of the surface at the EUT. Moreover, the potential \( E_{\text{REF}} \) can be expressed using the Nernst equation as

\[
E_{\text{REF}} = E_0 - \left( \frac{RT}{nF} \right) \text{pH}_{\text{val}},
\]

where \( E_0 \) is the standard potential of the Ag/AgCl electrode, typically 0.22 V at room temperature, \( R \) is the ideal gas constant, \( T \) is the absolute temperature, \( n \) is the number of electrons in reaction and \( F \) is Faraday constant. For pH sensing, the hydrogen ion concentration is defined as \( \text{pH}_{\text{val}} = -\log_{10}[H^+] \).

Finally, the potential \( \phi \) is defined as

\[
\phi = 2.303 \frac{kT}{q} \frac{\beta}{\beta + 1} (\text{pH}_{\text{PZC}} - \text{pH}_{\text{val}}),
\]

being \( k \) the Boltzmann constant, \( \beta \) is the buffer capacity which defined as an underlying property of the sensitive electrode material, and \( \text{pH}_{\text{PZC}} \) corresponds to the pH value for which the surface charge is null.

3. Measurement setup
In figure 2 we depict the block diagram of the measurement system for our EGFET-based pH sensor. It has four main stages, a data-acquisition device (DAQ), an array of screen-printed electrodes (SPE), a n-channel MOSFET and a transimpedance amplifier (TIA). The DAQ is in charge of generating and acquiring signals. It comprises a pair of 8-bit digital-to-analog converters (DAC) which generate the drain-source voltage \( V_{DS} \) and the reference voltage \( V_{\text{REF}} \). The former is applied to the EGFET at the drain terminal (D) of the MOSFET; whereas \( V_{\text{REF}} \) polarizes the RE. Regarding the electrode array, we fabricated it using low-cost screen printing technology over a polyethylene terephthalate (PET) substrate. The RE was made of Ag/AgCl; meanwhile, the electrode sensitive to pH values changes, was fabricated using ITO with a diameter of 4 mm. It is also worth mentioning that, the geometrical configuration of the SPE allowed to perform experiments with micro-volumes of the EUT, which was placed in such a way that it covered the surface of both the RE and the sensitive electrode. Our EGFET device was based on a conventional n-channel MOSFET device, with a channel width \( W = 100 \mu m \), length \( L = 5 \mu m \), threshold voltage around \( V_{\text{th}} = 0.8 \) V and gate oxide capacitance per unit area \( C_{\text{ox}} = 3.50 \times 10^{-3} \text{F/m}^2 \). These parameters were selected to provide enough sensitivity for the electrochemical transduction. Following equation(1), the output of the MOSFET is related to the pH value of the EUT, thus, the current \( I_{DS} \) was measured using a TIA with 1 T\( \Omega \) input impedance and noise of 45 nV/\( \sqrt{\text{Hz}} \). The transimpedance circuit converts the current \( I_{DS} \) into an output voltage \( V_o \), which is proportional to the input current by a feedback resistor \( R_f \), such that \( V_o = -R_f I_{DS} \). Finally, the voltage \( V_o \) is digitized by a 14-bit analog-to-digital converter (ADC) within the DAQ, which in turn acquires the data and sends it to a personal computer (PC) for storage and visualization.
4. Results and discussion

4.1. MOSFET characterization

For characterizing the n-channel MOSFET device, we investigated its electrical performance by measuring the output current $I_{DS}$, computed with the output $V_o$ of the TIA, and spanning the drain-to-source voltage $V_{DS}$, as well as the reference voltage $V_{REF}$. As shown in figure 3, the behavior of the MOSFET well agrees with the expected waveform for such kinds of semiconducting devices. In figure 3(a) we depict the output characteristic curves of the MOSFET given by the measured drain-to-source current $I_{DS}$ as a function of $V_{DS}$ for five values of $V_{REF}$ in the range from 2.0 V up to 4.0 V, which was applied to the gate terminal of the transistor. It is worth noticing that, the larger the value of the reference voltage, the larger the drain current saturation. This latter occurs when the $V_{DS}$ equals $V_{REF}$ minus the threshold voltage $V_{th}$. Moreover, Figure 3(b) shows transfer characteristics of the MOSFET relating the measured $I_{DS}$ response as a function of the input gate driving voltage $V_{REF}$ for different values of $V_{DS}$ in the range from 0.1 V to 1.5 V. In such a sense, it is possible to state a twofold remark, i) for values of $V_{DS} < 0.5$ V, the MOSFET operates in the Ohmic (linear) region, and ii) it is possible to straightforward obtain the value of $V_{th}$, which is reached as the drain current elevates. Finally, the MOSFET parameters are meaningful data for further EGFET-based pH sensing description.

![Figure 2](image_url)

**Figure 2.** Block diagram of the measurement setup for the proposed EGFET-based pH sensor.

![Figure 3](image_url)

**Figure 3.** Experimental characterization of the n-channel MOSFET device. (a) $I_{DS}$ current vs $V_{DS}$ output characteristics for different values of reference voltage $V_{REF}$. (b) $I_{DS}$ current vs $V_{REF}$ transfer characteristics for different values of $V_{DS}$.
4.2. pH measurements

The EUT used in this work were buffer solutions prepared by introducing an acid-basic pair into distilled water (DI). The proper concentrations of acid and conjugate base needed to make our buffer solutions were obtained by using the well-known Henderson-Hasselbalch equation. As a result, we obtained five different buffers at pH$_{\text{val}}$ = {2, 4, 5, 7, 9}. Experimentally, as the EUT, we placed a drop of 80 $\mu$L volume, taken from each buffer sample, in such a way that the drop covered the surface of the RE and the sensitive electrode. We measured the five EUT using the overall EGFET-based pH sensor as sketched in figure 2.

Figure 4 shows both the output and the transfer characteristic curves of our EGFET-based pH sensor. As depicted in figure 4(a), to obtain the output characterization, we measured the resultant current $I_{\text{DS}}$ as a function of $V_{\text{DS}}$, at a fixed value of $V_{\text{REF}} = 2.0$ V. From figure 4(a) it is possible to make the following remarks: i) one can notice that the measured current $I_{\text{DS}}$ decreases as the pH$_{\text{val}}$ increases, thus exhibiting an inverse relationship among them; and ii) the vertical dotted line denotes the value of $V_{\text{DS}}$ where the limit of the Ohmic region occurs. This latter allowed to fix the drain-to-source voltage to obtain the transfer characterization of the pH sensor. The results are shown in figure 4(b), where we swept $V_{\text{REF}}$ in the range from 0 V to 4 V and measured $I_{\text{DS}}$ for $V_{\text{DS}} = 0.2$ V. Interestingly, a shift to the right, on the threshold voltage, occurs as pH$_{\text{val}}$ becomes larger. It makes sense, by following equation (2), the overall threshold $V_{\text{th}}^*$ depends on the chemical reaction taking place at the sensitive electrode, as well as on the potential $E_{\text{REF}}$ at which the reference electrode is being polarized. As a result, the electrochemical phenomena are translated into a change in the MOSFET threshold voltage, which is measured at a current in the linear region, labeled by the horizontal dotted line in figure 4(b).

4.3. Sensor calibration

In order to assess the performance of the EGFET-based pH sensor, we used the output current $I_{\text{DS}}$ in the saturation region, as well as the shifted values of $V_{\text{REF}}$. Figure 5 shows the relationship of the drain-to-source current and the reference voltage in response to changes of pH$_{\text{val}}$ in the EUT. To determine linearity and compute the sensitivity of the sensor, we obtained the best model, in a least-squares sense, that fits the experimental data. In figure 5(a), a linear model inversely relates the square root of the output current and the pH of the EUT, exhibiting a sensitivity of 1.15 ($\mu$A)$^{1/2}$/pH$_{\text{val}}$ for fixed values of $V_{\text{DS}}$ and $V_{\text{REF}}$. Conversely, a direct linear relationship is shown in figure 5(b) among $V_{\text{REF}}$ and pH$_{\text{val}}$. Wherein, for fixed values of $V_{\text{DS}}$ and $I_{\text{DS}}$ the sensitivity is 52.2 mV/pH$_{\text{val}}$, which is close the Nernst’s limit, i.e.
59 mV/pHval [9]. Ultimately, the linearity of the proposed sensor exhibits a high linear behaviour as the coefficient of determination \( R^2 \) is 0.9936 and 0.9883, for \( I_{DS} \) and \( V_{REF} \), respectively.

![Figure 5](image)

Figure 5. Calibration of the EGFET-based pH sensor, symbols denote experimental data and solid line refers to the model describing them. (a) Sensitivity and linearity of the current \( I_{DS} \) as function of pHval. (b) Sensitivity and linearity of the voltage \( V_{REF} \) as function of pHval.

5. Conclusions

In this paper, we presented an attractive and cost-effective alternative sensor based on the EGFET operation principle. Converse to the conventional EGFET devices, our device integrates both the sensitive elements and the electrochemical transduction in a single structure, due to the advantages of the screen-printing technology. Furthermore, the proposed sensor was designed to operate on micro-volume samples with pH values ranging from 2 to 9 with a high linear behavior, and sensitivity of 52.2 mV/pHval in voltage and \( 1.15 \text{ (} \mu \text{A})^{1/2}/\text{pHval} \) in current. According to the results, this EGFET-based pH sensor could serve as a proof-of-concept to develop further robust tools with several chemical and biological applications.

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