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Driving Electrolyte-Gated Organic Field Effect Transistors with Redox Reactions †

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Abstract: Organic Electrochemical Transistors (OECTs) are now well-known, robust and efficient as amplification devices for redox reactions, typically biologically ones. In contrast, Electrolyte-Gated Organic Field Effect Transistors (EGOFETs) have never been described for that kind of application because field-effect transistors are known as capacitive coupled devices, i.e., driven by changes in capacitance at the electrolyte/gate or electrolyte/semiconductor interface. For such kind of transistors, any current flowing at the gate electrode is seen as a drawback. However, we demonstrate in this paper that not only the gate potential can trigger the source-drain current of EGOFETs, which is the generally accepted mode of operation, but that the current flowing at the gate can also be used. balabdyBecause EGOFETs can work directly in water, and as an example of application, we demonstrate the possibility to monitor microalgae photosynthesis through the direct measurement of photosynthetic O_2 production within the transistor's electrolyte, thanks to its electroreduction on the EGOFET's gate. This paves the way to the use of EGOFETs for environmental monitoring.

Keywords: Electrolyte-Gated Organic Field-Effect Transistor; Cyanobacteria; Photosynthesis; Gate current

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1. Introduction

Electrolyte-Gated Organic Field-Effect Transistors EGOFETs are original organic transistors for which the dielectric material in-between the gate and the semiconductor, mandatorily present in ISOFETs (Ion-Sensitive OFETs) is absent, so that the electrolyte is in direct contact with the semiconductor. In ISOFETs, the thickness of the dielectric governs the operating potential range of the device. Here, its absence allows particularly low operating potentials, of a few hundreds of millivolts. Another characteristic of EGOFETs compared to ISOFETs is that the gate is not necessarily a pseudo-reference electrode such as Ag/AgCl; it could be a simple metal wire such as Ti, Pt or Au, or even a carbon electrode. The electrolyte may be a solid one, as were designed the first EGOFETs, but could also be a liquid electrolyte such as DI water or current biological buffer such as PBS (phosphate Buffer Saline) [1] and are then operated at mild potentials, avoiding solvent oxidoreduction.

As for conventional FETs, EGOFETs are capacitance-driven devices. In practice, the current flowing through the semiconductor of these devices, called drain current and noted I_D, is directly proportional to the overall capacitance C_{G_OSC} between the gate and the semiconductor. This capacitance C_{G_OSC} comes from the series capacitances of both the gate/electrolyte (G_ELEC) and electrolyte/semiconductor (ELEC_OSC) interfaces, i.e., $1/C_{G\_OSC} = 1/C_{G\_ELEC} + 1/C_{ELEC\_OSC}$. Because the gate electrode and the OSC are dipping in an electrolyte, they are both subject to electrochemical reactions. One is the formation of an electrical double layer (EDL) corresponding to charge reorganization at the interfaces, directly related to the interfacial capacitances C_{G_ELEC} and C_{ELEC_OSC} and associated to interfacial potential drops. In short, a small capacitance is associated to a large potential drop while a large capacitance is associated to a small potential drop. It is known that organic semiconductors present EDL capacitances one order of magnitude lower than that of metals. As a consequence, for similar gate and OSC area, the potential drop is higher at the electrolyte/OSC interface and $1/C_{G\_OSC} \approx 1/C_{ELEC\_OSC}$, i.e., $C_{G\_OSC} \approx C_{ELEC\_OSC}$. Under this condition, the drain current I_D is independent on C_{G_ELEC}, i.e., is independent on the gate/electrolyte interface. On the contrary, for small gate areas, the gate/electrolyte interface can be used for biosensing, as demonstrated elsewhere [2–4].

The other reactions expected to occur at the interface are redox reactions, i.e., electron transfers, which then produce a gate current. This explain why EGOFETs are subject to high gate currents (I_G) compared to conventional OFETs. I_G comes from oxidation or reduction of the solvent or of dissolved species such as molecular oxygen. We will show here that a gate current leads to a change in voltage drop at the interface, so that a gate current I_G can be used to drive the drain current I_D of an EGOFET. In other words, an EGOFET can amplify a small gate current into a large drain current. As an example, we show that it is possible to amplify the reduction current of O_2 at a Pt gate into a larger drain current. An application could be the continuous monitoring of photosynthetic organisms present into the electrolyte.

2. Materials and Methods

Materials and fabrication procedures were described elsewhere [3,5]. The cyanobacteria *Anabaena flos-aquae* – *Af* – (strain ALCP B24) were provided by the National Museum of Natural History in Paris. For cyanobacteria growth, the Bold's basal medium (B_{3N}) was used, into which 2.97 μM of vitamin B1, 1.02 nM of vitamin H and 0.11 nM of vitamin B_{12} was added. A Pt microelectrode (diameter 100 μm) was used as gate. Electrical characteristics were acquired with a Keithley 4200 SCS source meter.

3. Results and Discussion

As preliminary experiment (not shown), oxygen or argon were alternately bubbled in the transistor's electrolyte while drain and gate currents were monitored, for a gate-source voltage V_{GS} = −0.8 V and a drain-source voltage V_{DS} = −0.6 V. Upon argon bubbling, the gate current decreased, while it increased upon oxygen bubbling. The amplitude of the gate current change was *ca.* 12 nA. We measured a parallel change of the drain current, with an amplitude of ca. 1000 nA. This experiment demonstrated that the EGOFET is able to amplify the current of a redox reaction occurring at the gate, into a more intense drain current. In another experiment, 10^6 per mL *Anabaena flos-aquae* cyanobacteria were then added into the electrolyte compartment of the transistor (total of 2×10^5 *Af* in 200 μL of B_{3N}). As all such photosynthetic organism, *Af* consumes carbohydrates and oxygen for its respiration, anytime, but produces carbohydrates and O_2 from CO_2 and H_2O during the light phase. O_2 is not captured inside de cyanobacteria but released into the external medium, where it dissolves, which increases its local concentration. Therefore, the continuous monitoring of oxygen concentration in the medium allows to follow the life cycle of the cyanobacteria over time. Under the same conditions as above, the drain and gate currents were recorded under alternated dark and illuminated periods (Figure 1, left). This result shows that oxygen produced under illumination by the cyanobacteria is reduced at the gate electrode, leading to a gate current then to a drain current increase (in absolute value). Under optimized experimental conditions, the amplitude of the drain current change upon illumination is ca. 70–80 nA while that of the gate is *ca.* 0.1 nA, corresponding to an amplification of two to three orders of magnitude. A control experiment without cyanobacteria in the electrolyte shows no gate current, but a small drain current change upon illumination, of ca. 10 nA, which is attributed to the photocurrent produced under semiconductor's illumination (Figure 1, right).

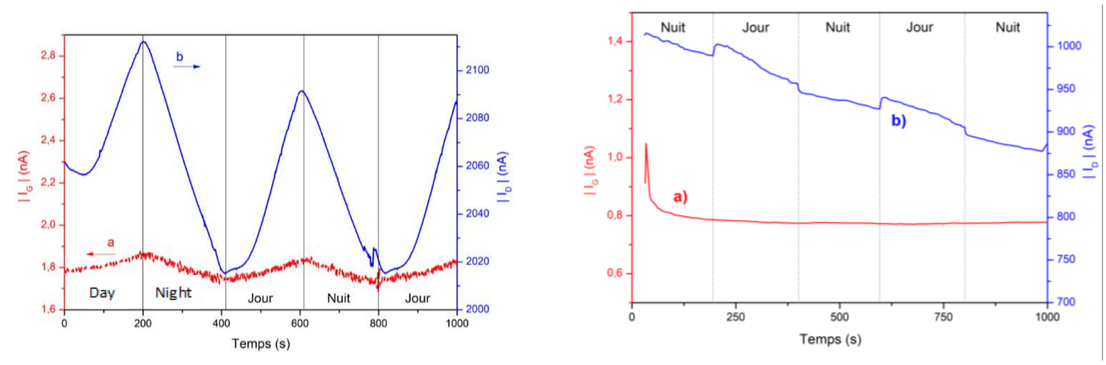

Figure 1. Left, gate current I_G (curve a) and drain current I_D (curve b) of an EGOFET containing 10^6 cyanobacteria per mL of electrolyte, under illumination cycles of 200 s each. Gate diameter = 110 µm. V_{GS} = −0.8 V; V_{DS} = −0.6 V. **Right**, gate and drain current under the same conditions, without cyanobacteria. Only the photocurrent appears on I_D.

4. Conclusions

In this work, we demonstrated that the gate current of an electrolyte-gated organic field-effect transistor is not necessarily a drawback resulting from undesirable electrochemical side-reactions which must be systematically minimized: it can be advantageously used to control the drain current. In other words, an EGOFET is able to amplify up to several orders of magnitude a gate current into a drain current. This is made possible if the gate/electrolyte capacitance C_{G_ELEC} is significantly lower than that of the electrolyte/semiconductor interface, C_{ELEC_OSC}, i.e., when the overall capacitance of the EGOFET is driven by C_{G_ELEC} rather than C_{ELEC_OSC}. For a given gate voltage, it corresponds to the situation where the potential drop between the gate and the semiconductor is concentrated at the electrolyte/semiconductor interface, maximizing the field effect. We applied this property to the monitoring of the photosynthetic activity of a cyanobacteria (*Anabaena flos-aquae*) directly added into the electrolyte compartment of the EGOFET. Compared to a regular amperometric O_2 sensor, the device is able to amplify the reduction current of several orders of magnitude, typically from a few nA at a ∅100 µm gate to a few µA at the drain. As an example, we applied the device for monitoring the production of O_2 from a cyanobacteria. A perspective could be to use such platform for monitoring the conditions of living organisms in surface waters, i.e., close by industrial areas.

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