

Extending Operational Voltage of Organic Electrochemical Transistors by Dual-Gate Configuration

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Abstract: A dual-gate configuration for organic electrochemical transistors allows the device to operate in a large potential window while maintaining the stability of the channel semiconductor. We present the relationship between the channel conductance and the potentials of the two gates. The large operational voltage window is useful for sensing applications that require high redox potential.

Keywords: organic electrochemical transistors, dissolved oxygen sensor, electrochemical stability, marine sensor

Organic electrochemical transistors (OECTs) offer the advantage of signal amplification in aqueous environments.¹ However, the operational voltage range of OECTs is limited by instability of semiconducting channels that typically restrict the applied bias to below 1 V, which is not sufficient to activate certain redox reactions for detection of analytes such as dissolved oxygen in seawater for ocean monitoring. In this work, we show an OECT design that uses two gate electrodes to achieve stable device operation at high voltages.

Fig 1 shows the device fabrication process. A facile stencil printing method was used for device patterning.^{2,3} A stencil mask was attached onto the glass substrate to define channel dimensions. The semiconductor PEDOT:PSS was spin-coated onto the substrate, followed by annealing and immersion in a concentrated sulfuric acid solution to remove the PSS component and enhance channel conductivity. Then

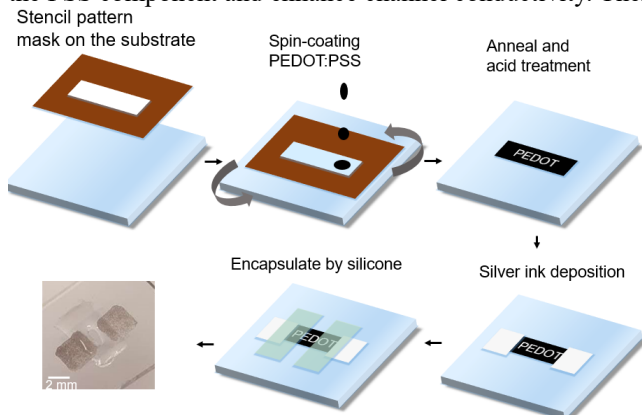


Figure 1. Device fabrication by stencil printing.

silver ink was deposited as source and drain electrodes. Silicone gel was stencil printed over the electrodes to pattern the analyte well. All the materials used here are compatible with roll-to-roll processing.

The structures of a conventional single-gate OECT and a dual-gate OECT are shown in **Fig 2**, along with diagrams of the potential drop between gate and channel. For a conventional OECT, the voltage bias between gate and source electrodes V_{GS} is limited to below 1 V, to keep the channel operating in the capacitive regime and avoid undesirable side reactions, for example, water electrolysis, over-oxidation and oxygen induced degradation. This design limitation cannot activate high redox potential reactions and is not compatible with analytes that require high redox potential for detection.

In dual-gate OECTs, an additional gate (denoted as the reference electrode) is incorporated and used as the ground^{4,5}. The applied potential (denoted as V_{SR}) between this ref gate and source will shift the potential of V_{GS} and V_{DS} at the same time. High redox potential reactions can be activated at the gate electrode by controlling V_{SR} . Meanwhile, the channel stays in the regime without side redox reaction. In this dual-gate configuration, we found that the gate biases have opposite

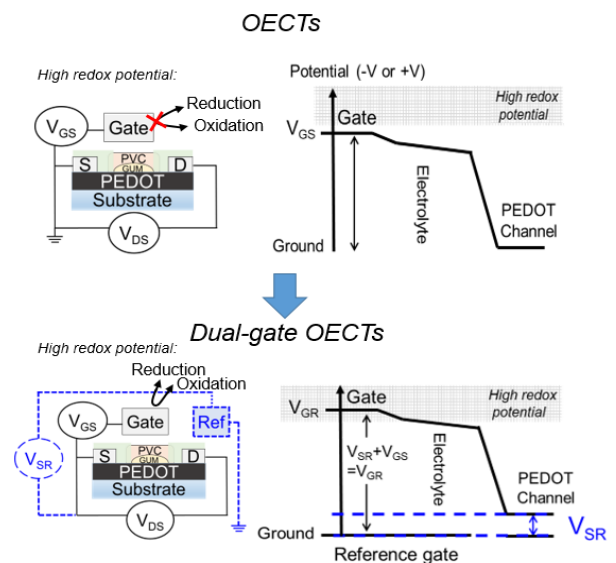


Figure 2. Potential diagrams of single-gate OECT (top) and dual-gate OECT (bottom).

modulation effect on the channel conductance, as evident from the transfer characteristics and described by equations below.

The relationship between gate, ref electrode, and channel can be expressed by the following equations:

$$I_{DS} = \frac{Wd}{L} \mu C^* (V_T - V_{eff} + \frac{1}{2} V_{DS}) V_{DS} \quad (1)$$

$$V_{eff} = -V_{SR} + V_{GS} \frac{(1+\beta)}{(1-\beta\gamma)} \gamma - \frac{kT}{ze} \frac{(1+\beta)(1+\gamma)}{(1-\beta\gamma)} \ln Q_r + \text{constant} \quad (2)$$

where Wd/L represents device dimensions, μ is the mobility, C^* is the volumetric capacitance. The coefficient $\beta = C_{\text{channel}}/C_{\text{ref}}$ and $\gamma = C_{\text{gate}}/C_{\text{ref}}$ is the capacitance ratios of gate/channel to the ref gate. V_{eff} is the effective bias applied on the channel that determines the doping state of channel, and in turn I_{DS} in **Eqn 1**. The derivation of these equations was explained in detail in Ref⁶. In **Eqn 2**, V_{eff} is the effective voltage influenced by the two gate biases (V_{GS} and V_{SR}), the analyte concentration (Q_r) and coefficients β and γ .

The transfer characteristic of a single-gate OECT and a dual-gate OECT are displayed in **Fig 3(a)**. The gate and ref gate used in this work were fabricated on a carbon cloth, the former with electrodeposited platinum and the latter with activated carbon. The gate capacitances were four orders of magnitude higher than the channel capacitance (so then the β term is negligible and can be discarded). The threshold voltage V_T of the dual-gate OECT ($V_{SR} = -0.6$ V, blue curve) shifts by around 1.5 V, a clear evidence of channel modulation with an applied V_{SR} .

In order to clarify the levels of modulation effect from the V_{SR} and V_{GS} , calculated ΔV_{eff} as a function of varying V_{GS} or V_{SR} is presented in **Fig 3(b)**. The blue curve represents with $V_{SR} = 0$ V as V_{GS} was varied, and the red curve is measured with $V_{GS} = 0$ V as V_{SR} was varied. The subthreshold slope of the red curve rose more sharply than blue one, indicating that the channel modulation from V_{SR} is more effective than V_{GS} . The value of the subthreshold slope ratio (slope of the blue curve over the red curve) matched well to the capacitance ratio of gate and ref gate ($\gamma \sim 0.3$) as measured by electrochemical impedance spectroscopy⁶.

As shown above, the channel modulation V_{eff} is affected by the parameter γ . Since γ is less than 1 and there are opposite signs in V_{SR} and V_{GS} in **Eqn 2**, the extended V_T of dual-gate OECT in **Fig 3(a)** is due to large negative modulation effect from V_{SR} , buffering the positive modulation from V_{GS} . The potential differences of gate and channel is not constrained by the range of V_{GS} as in traditional single-gate OECT.

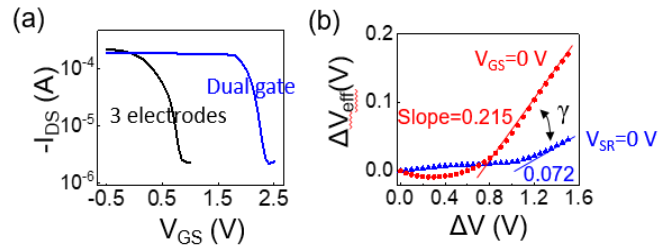


Figure 3. (a) Transfer characteristics and (b) the change in effective bias with respect to applied voltages in a dual-gate OECT.

In a typical single-gate OECT, the device behavior is dominated by channel capacitance when the channel capacitance is much less than the gate. The V_T indicates the transition of doping and dedoping processes on the channel as function of V_{GS} . The range of V_{GS} is limited by the channel intrinsic capacitance in OECT.

Transfer characteristics of a dual-gate OECT were recorded with varied V_{SR} from 0 to -0.8 V, as shown in **Fig 4(a)**. There is a slight change of V_T due to the voltage of transition point became more positive as more negative V_{SR} applied. The transition point was a function of the gate over-oxidation onset potential, correlated with the I_{GR} (current between gate and ref gate) verse V_{GS} shown in **Fig 4(b)**. In a dual-gate OECT, V_T became the function of the gate oxidation potential, controlled by V_{SR} in term of V_{GR} ($V_{GR} = V_{GS} + V_{SR}$), not limited by the channel capacitance. The p-type behavior in the extended V_{GS} indicates that the channel conductance is still modulated by different gate redox state, and range of gate potentials have been successfully expanded by the ref gate.

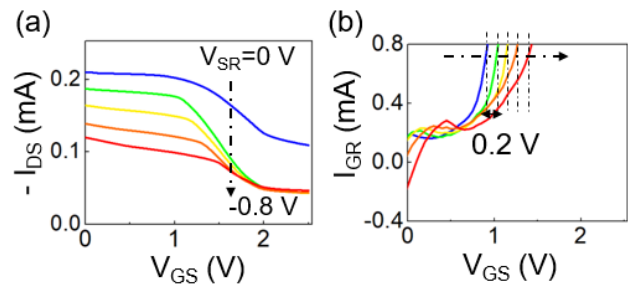


Figure 4. (a) Transfer characteristics in different applied V_{SR} . (b) onset of gate over-oxidation current with respect to V_{SR} .

In order to demonstrate the stability of dual-gate OECTs, we activated high potential oxygen reduction reactions to detect trace amount of dissolved oxygen in seawater. The instability of PEDOT channel in the existence of molecular oxygen has been a critical issue and discussed by ref⁷. Our dual-gate devices were submerged amid seaweeds to monitor oxygen release with or without light trigger as shown in **Fig 5**. The device was able to monitor dissolved oxygen variation in the level of 0~2 ppm with sensitivity $248 \mu\text{A}/\text{cm}^2$ per ppm. The increasing I_{DS} with rising oxygen level originated from the analyte concentration Q_r term in **Eqn 2**, which was based on

the Nernstian relationship. At higher oxygen concentration, V_{eff} became more negative and in turn higher I_{DS} in Eqn 1.

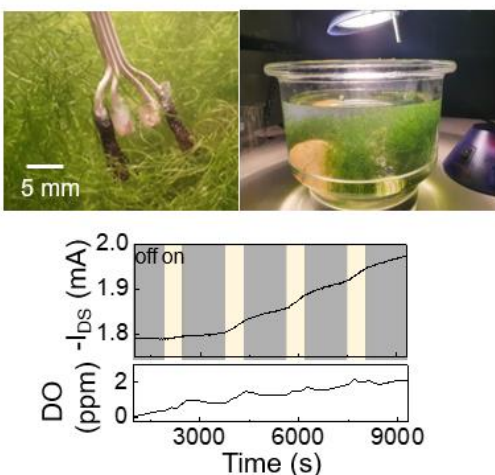


Figure 5. Our dual-gate OEET monitored the release of dissolved oxygen through photosynthesis in seaweed.

In summary, we present a dual-gate configuration for OEETs, allowing operation at large electrochemical potential while modulating channel with stability. The derived equations show the relationship between reference gate voltage and channel modulation, as demonstrated by the transfer characteristics. This configuration is simple and applicable to sensing events that require with high electrochemical potentials, such as in detection of dissolved oxygen in seawater.

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