

# Electrochemical and mathematical study of a Polythiophene-Electrolyte coupled device to understand the interaction occurring at abiotic/biotic interface

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## Abstract

The development of a fully organic photovoltaic prosthesis of poly(3-hexylthiophene) (P3HT) for subretinal implants was proposed to treat degenerative blindness [1,2]. Although the efficiency of organic polymer-based retinal devices in vivo has been proven, the interpretation of the working mechanisms that grant photostimulation at the polymer/neuron interface is still a matter of debate. In order to contribute solving this issue, we have first focused on the characterization of the interface between P3HT films and watery-electrolytes by the combined use of electrochemistry and mathematical modeling.

In particular, the electric behavior of P3HT is modeled through a system of time dependent Drift-Diffusion nonlinear partial differential equations. The model takes into account the working principles of the organic semiconductor in contact with the electrolyte solution, with a detailed description of its interaction with the dissolved oxygen through the use of a Marcus-Gerischer formula:

$$J_{\text{cat}} = \frac{qk_t c^{\text{ox}} N_A \sigma}{(\pi k_B T \lambda)^{\frac{1}{2}}} n \exp\left(-\frac{(E_L - E_F^{\text{OX}} - \lambda)^2}{4\lambda k_B T}\right) \quad J_{\text{cat}} = \frac{qk_t c^{\text{ox}} N_A \sigma}{(\pi k_B T \lambda)^{\frac{1}{2}}} n \exp\left(-\frac{(E_L - E_F^{\text{OX}} - \lambda)^2}{4\lambda k_B T}\right) \quad (1)$$

where  $q$  is the elementary charge [C],  $k_t$  the tunneling constant [ $\text{m}^4 \text{s}^{-1}$ ],  $c^{\text{ox}}$  the concentration of molecular oxygen at the interface [ $\text{mol m}^{-3}$ ],  $N_A$  the Avogadro constant [ $\text{mol}^{-1}$ ],  $\sigma$  the disorder parameter of P3HT [eV],  $k_B$  the Boltzmann constant [ $\text{J K}^{-1}$ ],  $T$  the room temperature [K],  $\lambda$  the width of the gaussian distribution of molecular oxygen states [eV].  $E_L, E_T$  is the energy of the LUMO of P3HT,  $E_F^{\text{OX}}, E_F^{\text{OX}}$  the energy corresponding to the potential of the oxygen reduction reaction.  $n$  is the electron number density at  $x = L$  [ $\text{m}^{-3}$ ]. By changing the value of  $c^{\text{ox}}$ , we have been able to simulate different oxygenating conditions. This effect has experimentally revealed to be crucial in the photoelectrical switch of P3HT, as visible in the photovoltage (PV) curves of Fig. 1.

In order to compare and validate the results of our mathematical model, we have performed several electrochemical measurements of PV on P3HT film deposited onto an ITO substrate samples, in different oxygenating conditions and with active layers of various thicknesses. Mathematical simulations well reproduce the experimental results upon illumination of the device in the various conditions.

Besides validation, the good agreement between measurements and simulations can be used to highlight the main effects, secondary to the illumination of the P3HT device, necessary to reproduce the experimental behaviour. Upon illumination, the essential unipolar transport in the photoexcited film leads in few  $\mu\text{s}$  to a drift-diffusion equilibrium associated to a space charge separation. Electron transfer reactions towards oxygen at the polymer/electrolyte interface extract negative charge from the polymer and are responsible for the positive signal that we observe after several  $\text{ms}$ . The quantitative description of the phenomena also permits the estimation of the charge accumulated at the interface, possibly responsible for an electrostatic interaction with a biological system.

In spite of the simple model studied, all these considerations shed light on the possible coupling mechanisms between the polymeric device and the living cell, supporting the hypothesis of pseudo-capacitive coupling arising from an electrostatic interaction between the polymeric film and the watery environment. In addition to this, once the fundamental mechanisms of P3HT have been quantitatively model, it is possible to start developing models to reproduce the effects of P3HT nanoparticles in a watery-electrolyte, a system whose electric properties are hard to characterize experimentally but which appears to be the new frontier of retinal devices.

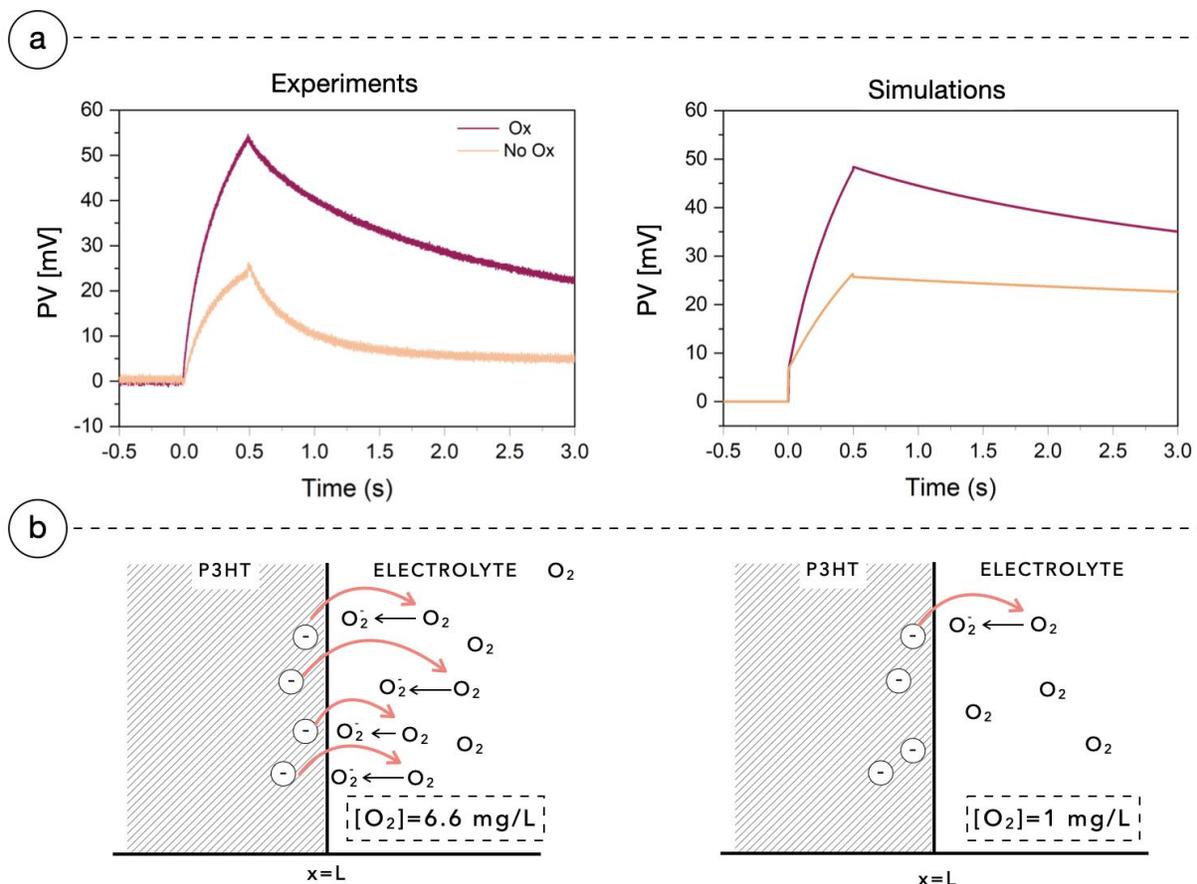


Figure 1: Faradaic oxygen reaction at P3HT/electrolyte interface and its effect on PV curves. Panel (a) shows the experimental PV measures (left) and PV simulation (right) varying the concentration of molecular oxygen dissolved in the electrolyte on a sample with 140nm of active layer. Light is switched on between 0 and 0.5 s and is impinging from the electrolyte side. The PV curves are decreasing in amplitude as the concentration of molecular oxygen is lowered. Panel (b) qualitatively shows how the different concentrations of molecular oxygen affects the exit of the electrons of the bulk and indirectly the amplitude of PV. In the two cases the oxygen concentration is  $c_{O_2} = 6.6 \text{ mg/L}$  and  $c_{O_2} = 1 \text{ mg/L}$ , respectively.

## References

- [1] Maya-Vetencourt, José Fernando et al. "A fully organic retinal prosthesis restores vision in a rat model of degenerative blindness." *Nature materials* vol. 16,6 (2017): 681-689. doi:10.1038/nmat4874
- [2] Maya-Vetencourt, J.F., Manfredi, G., Mete, M. et al. "Subretinally injected semiconducting polymer nanoparticles rescue vision in a rat model of retinal dystrophy." *Nature Nanotechnology* 15, 698–708 (2020). <https://doi.org/10.1038/s41565-020-0696-3>