Title:
Mathematical modeling of the photoactivation mechanisms of an organic photovoltaic retinal prosthesis in contact with an electrolyte solution

Purpose:
In 2017 the development of a fully organic photovoltaic prosthesis for subretinal implants was proposed to treat degenerative blindness (Maya-Vetencourt et al,2017). Despite its effectiveness, the working principles are still a matter of debate. In this work we address the theoretical study of the photoactivating effects of the Poly(3-hexylthiophene-2,5-diyl), known as P3HT: the goal of this preliminary study is to characterize the microscopic mechanisms occurring at the interface between the organic material and an electrolyte solution. Since the systematic study of polymer-electrolyte interfaces is far from trivial, the complex will be investigated through the combined use of electrochemistry and mathematical modeling. The final aim of the work will be to characterize the working principles of the device and its interactions with the biological environment.

Methods:
Photovoltage (PH) three electrode-measurements have been performed on samples of different thicknesses and with different oxygenation conditions, illuminating them by the two different sides of the device: when the sample is illuminated, it undergoes a redistribution of charges due to several mechanisms, the nature of which is the object of the study, and do create a PH, measured at the electrode contact, a crucial quantity that will also be the output of our models and used to validate our assumptions. To understand the physical mechanisms behind the experiments, we have developed a model of the electronic phenomena of P3HT through a system of time dependent Drift-Diffusion non linear partial differential equations: two continuity equations for free holes and electrons, and Poisson equation for the electric field. In order to solve the numerical problem we have adopted the Gummel Map decoupling algorithm, thus ensuring the positivity of the solutions for the concentration of carriers. The interfaces mechanisms with both electrolyte solution and conductive electrode are taken into account through the use of ad-hoc Robin-type boundary conditions.

Results:
In the attempt to reproduce the PH experimental curves, through the mathematical model we have developed a plausible physical picture: the impinging light leads to the creation of excitons, which, dissociating, create free photocarriers; the sudden availability of free carriers in the bulk, and particularly of electrons near the interface with the electrolyte, seems to trigger a chemical reaction of reduction of the molecular oxygen present in the solution, whose products accumulates on the surface attracting holes from the bulk, which recombine with the reduced oxygen, thus ensuring the overall electroneutrality of the polymer. The simulations and the connected physical assumptions have been validated against PH measurement on sample of different thicknesses and on sample immersed in electrolyte solutions with different oxygenation conditions.

Conclusions:

The proposed mathematical model allowed us to simulate device voltage output in different working conditions. Model simulations suggest that the PH curve is strongly affected by the presence of oxygen in the electrolyte solution: when it is present, oxygen starts reducing providing new surface recombination centers for holes. These preliminary results pave the way in understanding the main mechanisms of photoactivation of the prosthesis, both in in vivo and in vitro conditions.