

MODELING THE DOUBLE LAYER FORMATION FOR ELECTRICAL NEUROSTIMULATION AT THE ORGANIC POLYMER - ELECTROLYTE INTERFACE

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Abstract— *Electrical double-layer formation attracted significant interest more than a century ago and remains fundamentally involved in capacitive external stimulation of biological tissue. This work focuses on the study of the double layer characteristics at the interface formed between an electrolyte and polymer structures of organic photocapacitors for minimally invasive neurostimulation. Based on a combination of the Helmholtz and Gouy-Chapman methods, the Stern model is applied in COMSOL Multiphysics to investigate this electrical double layer formation. Simulations nicely highlight the importance of the electrolyte concentration and good cell adhesion.*

Keywords— *EDL, Stern model, photocap, organic photocapacitor, OEPC*

Introduction

Organic Photocapacitors (OEPCs)

Wireless light-sensitive semiconductors named organic electrolytic photocapacitor (OEPC) for cellular and tissue stimulation are currently attracting significant interest in the field of biomedicine [1][2]. This minimally invasive stimulation technique could be utilized to improve connectivity and tissue regeneration after peripheral or central nervous system injuries, such as cerebral injury. In using OEPCs for external stimulation of excitable cells, surpassing the threshold potential remains a major challenge, mainly due to an insufficient interface between the attached cell membrane and the electrode surface, which is caused by a small gap. This can electronically be described by an ideal capacitor acting in the intermediate layer [3]. The characteristic behavior within this cleft is essential to generate the required magnitude of stimulus to surpass the cells' threshold potential and can be described using models for the electrical double layer.

Double Layer Models

Many general studies have been published on the behavior of the electrolytic double layer (EDL). Helmholtz described the behavior of the electrolytic double layer for the first time in his seminal work in 1879 [4]. The model describes the linear potential curve across the "Helmholtz double layer", formed by ideally opposite charges between a metal electrode and the electrolyte. The double layer is bounded by the hydrate shells of the ions sitting on the electrode surface. The so-called outer Helmholtz plane (OHP) passes through the center of these ions. A major advance in the early 20th century was described by Louis Georges Gouy and David Leonard Chapman with the Gouy-Chapman double layer [5][6]. Their approach was an extended description of the Helmholtz theory, but Gouy and Chapman also considered the thermal motion and the ions forming a diffuse layer. Further findings from Otto Stern revealed that the electrolytic double layer can be described by a combination of the two previous models [7]. A rigid ion layer is assumed on the metal surface and an adjacent diffuse layer reaching deep into the electrolyte. Fig. 1 represents the double layer formed between the OEPC's surface and the electrolyte, where the OHP is limited by half of the K^+ -hydrated shell size, shown in the inset of this picture. A diffusive layer is adjacent to the Helmholtz layer, where the potential decreases against zero. Limitations are partially given by the Poisson-Boltzmann equation, where ions are treated as point charges and their physical size is ignored. Assumptions of point charges are mainly applicable for low ion concentrations and low electric potential changes. In other words, modeling EDL is often limited due to the simplification of the ionic structure.

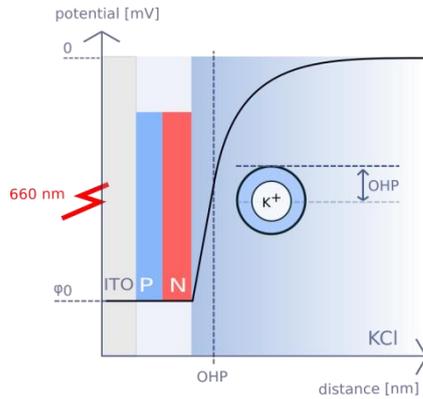


Figure 1: An electrochemical double layer schematic representing the OEPC-electrolyte interface illuminated with 660 nm light pulses. The initial surface potential ϕ_0 of the OEPC (ITO and PN layer) decreases against zero across the OHP and the diffusion layer. The OHP is limited by half of the K^+ -hydrated shell size, shown in the inset of this figure.

Methods

Double layer model

In order to describe the bilayer characteristics and subsequently evaluate whether optoelectronic neurostimulation is successful, it is necessary to take a detailed look at the mathematical descriptions of the double layer characteristics [8]-[13]. Focus is on the potential curve that arises between the electrode surface and the cell membrane. In this section, factors are pointed out essentially involved in the EDL formation. First, the linear Helmholtz potential distribution is described by Poisson's equation, shown in Eq. 1.

$$\frac{d^2\phi}{dx^2} = -\frac{\rho(x)}{\epsilon_r \cdot \epsilon_0} \quad (1)$$

ϕ_0 ... potential ϵ_r ... relative permittivity
 $\rho(x)$... charge density ϵ_0 ... electric field constant

Since there is a charge-free region between the metal surface and the ions, it follows for the Poisson equation that $\rho = 0$ at this point. The Helmholtz double layer capacity can be further calculated as shown in Eq. 2, where d equals the OHP distance.

$$C_H = \frac{\epsilon_r \cdot \epsilon_0}{d} \quad (2)$$

To explain the process in the diffusion layer, the Gouy-Chapman description is used. In addition, the Boltzmann distribution is considered in the Poisson equation for the potential field, see Eq. 3.

$$\rho(x) = \sum_i z_i \cdot e \cdot c_i \cdot \exp\left(-\frac{z_i \cdot e \cdot \phi(x)}{k \cdot T}\right) \quad (3)$$

z_i ... ion charge number k ... Boltzmann constant
 c_i ... ion bulk concentration [M] t ... temperature [K]
 e ... electron charge

For the calculation of the potential distribution, the linearized approach for solving the Poisson-Boltzmann equation is assumed as shown in Eq. 4, considering the Debye length κ^{-1} .

$$\phi(x) = \phi_0 \cdot \exp\left(-\frac{x}{\kappa}\right) \quad (4)$$

Hence, combining Eq. 1 and Eq. 3 yields the following expression, see Eq. 5:

$$\rho(x) = -\epsilon_r \cdot \epsilon_0 \frac{d^2\phi(x)}{dx^2} = -\frac{\epsilon_r \cdot \epsilon_0 \cdot \phi_0}{\kappa^2} \cdot \exp\left(-\frac{x}{\kappa}\right) \quad (5)$$

To describe the electrostatic ion interactions in electrolytes, the Debye-Hückel theory can be applied [14]. The thickness of the diffuse double layer, the so-called Debye length, can further be calculated considering the Avogadro constant (NA) and the ionic strength I_{str} see Eq. 6 and Eq. 7.

$$\kappa^{-1} = \sqrt{\frac{2 \cdot NA \cdot e^2 \cdot I_{str}}{\epsilon_r \cdot \epsilon_0 \cdot k \cdot T}} \quad (6)$$

$$I_{str} = \frac{1}{2} \left(\sum_i z_i^2 \cdot c_i \right) \quad (7)$$

The Gouy-Chapman bilayer capacitance is again related to the Debye length and is calculated as shown in Eq. 8, with σ representing the charge density.

$$C_{Gdiff} = \frac{d\sigma}{d\phi_0} = \frac{\epsilon_r \cdot \epsilon_0}{\kappa^{-1}} \cosh\left(\frac{z \cdot F \cdot \phi_0}{2 \cdot R \cdot T}\right) \quad (8)$$

Finally, the Stern model combines both theories and can be described electrically by the sum of the Helmholtz capacity together with the Gouy-Chapman capacity, as shown in Eq. 9.

$$\frac{1}{C_{stern}} = \frac{1}{C_H} + \frac{1}{C_{Gdiff}(\phi_0)} \quad (9)$$

Organic Photocaps

In this paper, an organic photocapacitor with the polymer layers H2Pc(p):PTCDI(n) is used. The OEPCs photo response is measured in a KCl electrolyte bath. For light stimulation, a 10 W LED with 660 nm is used.

Results

Analytical calculations were performed in MATLAB. Subsequently, both 1D and 2D models were set up in COMSOL Multiphysics using the AC/DC module.

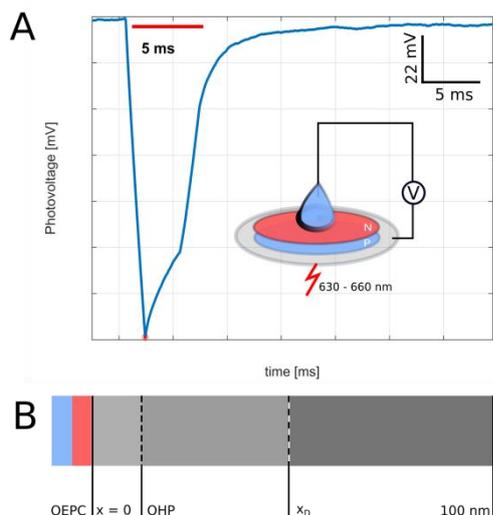


Figure 2: A. Electrical photo response measurement of an OEPC illuminated with a 5 ms light pulse, B. Model geometry with marked layer distances: $x = 0$, outer Helmholtz plane (OHP), Debye length (x_D) and the total length of 100 nm

The geometric model in COMSOL Multiphysics was set up as shown in Fig. 2 B, by inserting various layers with different thicknesses and distances, such as polymer-surface thickness, OHP, x_D and the total length.

A potential of -159 mV was set at the OEPC surface. The relative permittivity for the electrolyte was assumed with 78.4, the temperature with 293.15 K. The OHP is limited by the hydrated ion size of K^+ cations and was assumed with 0.315 nm [15]. The Debye length x_D was calculated with 3.01 nm for 0.01 M KCl and 0.95 nm for 0.1 M KCl. The total length was limited to 100 nm.

Fig. 2 A represents the measured photo response when illuminating the photocap for 5 ms. The inset part in Fig. 2 A represents the measurement setup for observing the photovoltage obtained from OEPCs using a KCl electrolyte. In the model, the potential decays to a steady-state starting from the polymer surface to a depth of about 100 nm into the electrolyte. Based on these assumptions and the equations listed in the methods section, the potential curves shown in Fig. 3 A are obtained for a temperature of 293.15 K. Furthermore, potentials maintained at prominent points within the double layer are represented in Tab. 1.

Table 1: Electrical potentials calculated within the double layer for different KCl concentrations.

distance x	potential $\phi(x)$ [mV]	
	0.01 [M]	0.1 [M]
0	-159.00	-159.00
OHP	-122.19	-90.62
x_D	-58.06	-50.72

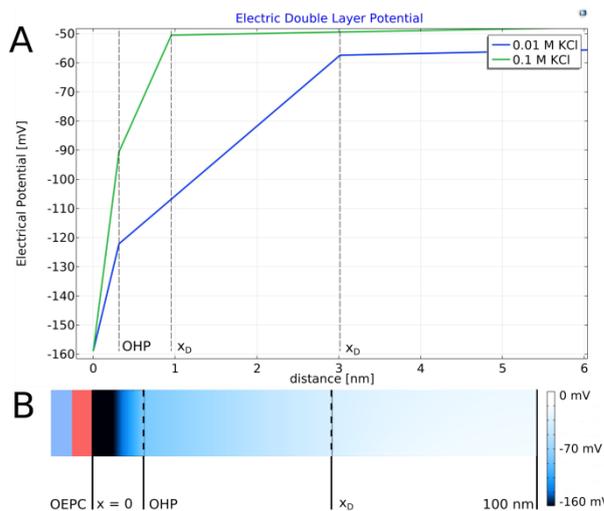


Figure 3: A. Electrical potential distribution for different electrolyte concentrations. The first dotted line represents the OHP distance, the second one the Debye length for 0.1 M KCl and the third one the Debye distance for 0.01 M KCl, B. Electrical potential distribution across the total length for 0.01 M KCl

The rapid potential drop between the OEPC surface and the OHP layer can be nicely seen in Fig. 3 B. In addition, the calculated capacities for various electrolyte concentrations are listed in Tab. 2.

Table 2: Calculated capacities for different electrolyte concentrations

	capacities [$\mu\text{F}/\text{cm}^2$]	
	0.01 [M]	0.1 [M]
C_H	220.37	220.37
C_{Gdiff}	39.98	112.70
C_{stern}	33.84	74.56

Discussion

There are significant advantages associated with the use of EDL models, especially since experimental methods are complex and often difficult to implement. They can be used to effectively investigate the double layer characterization, which reveals the interaction between the stimulation electrode and the cell behavior. Key parameters such as ion concentration, ion size, electrical potential, geometries, and many other factors pertaining to double layer characteristics can be quickly investigated and indicate the best way to improve cell measurements.

The simulation results presented in this paper show the rapid potential decrease within the outer Helmholtz layer. Furthermore, a strong dependence on the electrolyte can be observed. Thus, both the conductive medium and coating of the stimulating device intended to enhance cell attachment and thus essential for successful neurostimulation should be

taken into account. The distance between the cell membrane and the OEPC surface is of enormous significance. Variations in temperature are not a major factor here.

Beside the constant assumptions in the Stern model mentioned at the beginning, the model limitations are given by the linearization of the Poisson-Boltzmann equation. This approximation fits well for $\frac{\Delta\varphi}{kT} \leq 1$. Even though constraints arise with the linearized approach yielding the Debye-Hückel approximation, still good assumptions can be made with respect to a considerable number of cases. However, even in the case presented in this work, the approximation provides good assumptions despite small deviations. For larger potential changes improvements may be achieved by extending the Poisson-Boltzmann approach which can become complex quickly.

In conclusion, the model presented in this paper yields reasonable assumptions on parameters required to be adjusted to ensure successful external cell stimulation.

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