



Letter

A theoretical model for the time varying current in organic electrochemical transistors in a dynamic regime



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ABSTRACT

The dynamic interaction between cations and doped conductive polymer is at the basis of the working principles of organic electrochemical transistor devices. In this letter, we describe a theoretical model for the transport of saline ions in an electrolyte under the influence of an external voltage in a dynamic regime. We show how this scheme can be used to derive the time varying response and current generated by a conductive PEDOT:PSS polymer based OECT device interacting with those ions. The simulated output of the system displays a very high sensitivity on the parameters of the process including charge, size and concentration of the ions, and the frequency of operation of the device. The proposed model can be used to analyze the activity of an OECT device to derive the physical characteristics of individual species in a solution.

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1. Background and significance

Organic electrochemical transistors (OECTs) are an alternative transistor architecture in which a conductive polymer interacts directly with the electro-active medium, i.e., the electrolyte [1]. State-of-the-art OECTs are based on the conducting polymer poly(3,4-ethylenedioxythiophene) doped with polystyrene sulfonate (PEDOT:PSS) [2]. Due to bio compatibility, easy integration with mechanically flexible and conformable substrates, increased signal to noise ratio [1,3,4], OECTs have been extensively used for bio interfacing, bio sensing, and bio electronics [5–8]. OECT devices have been demonstrated in chemical and biological sensing [4,9], have been used to derive the size of individual ions in solution [10] and, integrated with a nano-scale architecture, they have been used to resolve simple [11] to complex mixtures [12].

In these and other similar applications, one necessitates theoretical models and simulation schemes that may correlate the measured output of a device to the physical characteristics of the solution at study. A fundamental model for charge transport in

organic electrochemical transistor has been proposed by Bernardis and Malliaras [13]. In the model, ionic transport in the electrolyte and hole transport in the PEDOT:PSS channel are considered separately and then superimposed to obtain the response of the system. While accurate in capturing the evolution of the system over time, the model disregards the effect of diffusion of the ionized species in the electrolyte. In Refs. [10], Coppedè and colleagues revised the model of Bernardis to consider the effect of diffusion. Using the formalism of the Nernst-Planck equations, they described the drain source current in an OECT in terms of the diffusivity and charge of species in the electrolyte. In all the considered models, the applied voltage is a constant function of time: the current flowing in the OECT smoothly transitions from zero to a constant final value that is proportional to the voltage and is inversely proportional to the impedance of the system.

Here, we introduce a model that describes the time varying response of an OECT device, where the driving voltage of the device is a periodic, alternate function of time. In simulations where the voltage sweeps upwards in frequency from 0.01 to 100 Hz, we observe that the behavior of the system transitions from a regime where the dedoping current balances the current predicted by pure Ohm's law, to a regime in which the system is purely resistive. The

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evolution from the first to the second regime depends on the operating frequency of the system, and on the size, charge and concentration of the ions in the electrolyte. Measured waveform matches the predictions of the model with a good level of accuracy. Coupled to experimental data, this template may be used to recover the physical characteristics of ions in an electrolyte.

2. The model

Consider the scheme in Fig. 1a. A silver electrode and a PEDOT:PSS polymer channel are buried in the electrolyte. The electrolyte is a saline species (MCl_n) dissociated into M^{n+} and Cl^- ions in water. Upon the application of a voltage at the gate, Cl^- ions react at the Ag electrode by an oxygen-reduction process, while M^{n+} ions are forced to the PEDOT:PSS channel. Interaction of M^{n+} with the PEDOT:PSS generates a faradaic current. In the present configuration the electrode and the channel are one-dimensional cylinders in which the sole important parameter is the distance l between those cylinders and the remaining lengths can be disregarded. Moreover, the external voltage ϕ is a periodic triangular function of time in which the period T and the amplitude ϕ_0 can be conveniently adjusted. Following the approach proposed by Bernardis and Malliaras in Refs. [13], the behavior of the device is here analyzed on dividing the system into an electronic and an ionic circuit. The electronic circuit consists of a p-type organic semiconductor film that transports holes between source and drain electrodes and is described by Ohm's law. The ionic circuit accounts for transport of ionic charge in the electrolyte. From the interaction of these two components results the behavior of the entire system.

Ionic circuit The ionic charge transported in the unit time from the electrolyte to the PEDOT/electrolyte interface is the ionic current $i(t)$. $i(t)$ may be determined from the analysis of the electrical equivalent circuit of the system, sometimes called Randles cell [14–16], as in Fig. 1c, in which R_S is the resistance of the electrolyte, R_{CT} is the charge transfer resistance, R_W is the Warburg or diffusion impedance, C_{dl} is the double layer capacitor. A description of these elements is provided in a separate Supporting Information file #1. Assuming $R_{CT} = 0$, simple electronics yields the impedance of the system as

$$Z_{eq} = \Xi + Yj = |Z_{eq}|e^{j\alpha} \quad (1)$$

where

$$|Z_{eq}| = \sqrt{\Xi^2 + Y^2}, \alpha = \arctan\left(\frac{Y}{\Xi}\right) \quad (2)$$

and

$$\begin{cases} \Xi = R_s + \frac{\Gamma}{\sqrt{f} + 2C_{dl}\Gamma f + 2C_{dl}^2\Gamma^2 f^{3/2}} \\ Y = -\frac{\Gamma(2C_{dl}\Gamma + 1/\sqrt{f})}{1 + 2C_{dl}\Gamma\sqrt{f} + 2C_{dl}^2\Gamma^2 f} \\ \Gamma = \frac{RT}{n^2 F^2 A c_0} \sqrt{2/D} \end{cases} \quad (3)$$

In Equations from (1) to (3), n is the charge number, $F = 9.64 \times 10^4 \text{ C/mol}$ is the Faraday constant, $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ is the universal gas constant, T is the absolute temperature of the system, A is the PEDOT/electrolyte interfacial area, c_0 the initial concentration, D the molecular diffusion of the ions in solution. Thus the magnitude and phase of the impedance depend on a non-linear combination of diffusivity, charge, and frequency. Fig. 2 reports the log plot of Z_{eq} and α as a function of frequency for different $D = (10^{-8}, 10^{-9}, 10^{-10}) \text{ m}^2/\text{s}$ and $n = (1, 2)$, for fixed $c_0 = 1 \text{ M}$ and $T = 298 \text{ K}$. At the limit of f going to infinity, the impedance is purely resistive ($Z_{eq} = R_S$, $\alpha = 0$) and would not depend on D nor n . Differently, at small f the impedance is influenced by D and n . $|Z_{eq}|$ is larger for smaller diffusion coefficients and charge numbers. This is easily explained considering that small D (thus, with the celebrated Stokes-Einstein relation, large ionic radius [17,18]) and small n would hamper the transport of charged species from the electrolyte to the PEDOT channel. Also notice that for smaller diffusion coefficients, that is for larger species, the time lag (α) between the driving voltage and the ionic current is increased. For vanishingly small ions, for which D goes to infinity, the transmission of ions from the electrolyte would be instantaneous. From the impedance, the total charge $Q(t)$ transported to the PEDOT organic film over time is readily derived, being

$$Q(t) = \int_0^t \frac{\phi(\tau)}{Z_{eq}} d\tau. \quad (4)$$

Electronic circuit the source-drain current $I(\tau)$ flowing in the OECT is given by the superposition of one term associated with the

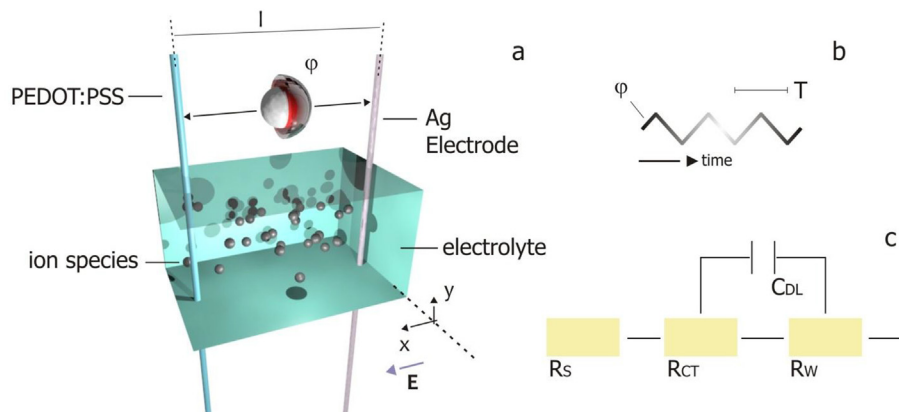


Fig. 1. Artist's impression of the model (a). A silver electrode and a PEDOT:PSS polymer are integrated in the electrolyte. Upon application of an alternate voltage at the gate (b), positive ions are transported to the PEDOT channel and a current is generated. The behavior of the device is here analyzed on dividing the system into an electronic and an ionic circuit. The ionic charge transported in the unit time to the PEDOT/electrolyte interface is determined from the analysis of the electrical equivalent circuit of the system, as in (c): R_S is the resistance of the electrolyte, R_{CT} is the charge transfer resistance, R_W is the Warburg or diffusion impedance, C_{dl} is the double layer capacitor.

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