Optical Measurements Revealing Nonuniform Hole Mobility in Organic Electrochemical Transistors

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Theoretical predictions and experimental results show that the carrier mobility in conjugated polymers depends on carrier concentration. However, existing models for organic electrochemical transistors (OECTs) assume uniform carrier mobility along the transistor channel despite variations in carrier concentration. Here, a model incorporating disorder-induced nonuniform mobility is developed to describe the steady-state behavior of OECTs. This model is tested using in situ optical measurements of an OECT channel to decouple the mobility and carrier concentration contributions to channel conductivity. It is found that unlike existing models, the nonuniform mobility model agrees with these measurements. Furthermore, it is found that the model matches current–voltage data over a wide range of device geometries and two different device architectures. Finally, it is shown that a 120% improvement of transconductance can be obtained by operating a sensor according to device parameters given by the nonuniform mobility model rather than those extracted from an existing model that assumes a uniform mobility. Ultimately, the model presented allows more accurate measurement of material properties via transistor characterization. This will enable better-informed material optimization, development of more accurate transient models for OECTs, and more effective use of OECTs made from existing materials.

1. Introduction

Because of their biocompatibility,[1] high transconductance,[2] and low operating voltage,[3] organic electrochemical transistors (OECTs) are promising solutions for a number of biosensing challenges.[4] For instance, they have been used in vitro to measure complementary DNA concentrations down to picomolar levels,[5] to monitor transepithelial cell integrity,[6,7] to locally stimulate hippocampal neurons,[8] and to detect glucose,[9] acetylcholine,[10] and lactate.[11] Additionally, they have been used in vivo as bioresorbable electrophysiological recording devices[12] and as sensors capable of detecting epileptic activity in rat brains.[13] While these devices have proven useful as biosensors, a better understanding of the device physics and material properties could lead to the development of more sensitive, accurate, and faster biosensors. In particular, a better understanding of the relationships between material properties and device performance will not only enable the development of better materials for OECTs but it will also lead to higher signal-to-noise ratios in OECT-based biosensors fabricated from existing materials.

The basic operating principles of OECTs and OECT-based biosensors are well described in the literature[6,14–17] and are reviewed here. A diagram of a lateral OECT is shown in Figure 1a,b. In this geometry, the gate, source, and drain electrodes are all in the same plane, and a thin film of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) connects the source and drain electrodes. Covering the entire device is an electrolyte gel containing mobile cations. Typically, these devices are operated in depletion mode with positive gate voltages and negative drain voltages. When the gate voltage is stepped to a positive value, cations drift in the applied electric field from the gel above the PEDOT:PSS into the PEDOT:PSS matrix. Once in the PEDOT:PSS, the cations compensate PSS\(^-\) acceptor ions, dedoping the PEDOT\(^+\) to its less conductive neutral state, PEDOT\(^0\), as described by Equation (1) and shown in Figure 1a,b. Therefore, the transistor’s channel conductivity is modulated by addressing the gate voltage.

\[
PEDOT^+ + PSS^- + Na^+ \leftrightarrow PEDOT^0 + Na^+ + PSS^- + h^+ \tag{1}
\]

As cations compensate PSS\(^-\) acceptors, holes (represented by h\(^+\) in Equation (1) are removed from the PEDOT. This causes a decrease in the number of polarons in the film and a resulting change in the film’s optical absorption. This electrochromic response of PEDOT:PSS has been characterized in the literature and is described in Figure 1d; as PEDOT is reduced to its...
low-conductivity state, optical absorption near 600 nm increases while near-IR absorption decreases.\cite{18,19} This allows one to optically measure the hole concentration in PEDOT:PSS.

In this article, we report measurements of optical absorption in an OECT channel during device operation, and we develop a simple electrostatic model to interpret these measurements. We find that the hole mobility in the channel is spatially nonuniform and dependent on the local hole concentration.

2. Development of a Nonuniform Mobility Model

While a basic understanding of OECT operating principles has allowed OECTs to be successfully used in numerous sensing\cite{5-7,9-13,16,20-23} and logic applications,\cite{24} understanding of the relevant device physics and material science is still limited. Existing models for OECTs either fail to provide quantitative predictions for actual devices or to account for well-known material properties of conjugated polymers. For instance, Bernard and Malliaras provided an early model for OECT behavior:\cite{14} This model modifies the standard treatment of long-channel depletion-mode inorganic field-effect transistors\cite{25} by incorporating an ionic coupling between the gate and channel. While this model has been used to explain OECT behavior in numerous applications,\cite{16,26,27} its accuracy is limited because it assumes that the OECT channel behaves as if it were a well-ordered, crystalline semiconductor. Therefore, this work, and much of the OECT literature,\cite{2,14,20,27,29} disregards the effect of carrier concentration on mobility. However, numerous theoretical\cite{30-32} and experimental\cite{30,32,33} studies have shown a dependence of mobility on carrier concentration and have found that it is due to the exponentially distributed density of states (DOS) near the band edges in disordered organic semiconductors. As the “trap states” near the band edge are filled, carriers begin to occupy states at higher energies, where the DOS is much larger. Because the DOS is larger, more sites are available for carriers to hop into. Consequently, carriers deeper into the DOS have a larger mobility than if they were near the band edge. According to this explanation, the dependence of mobility on carrier density should follow the relationship:

$$\mu(p) = \mu_0 \times \left(\frac{p}{p_0}\right)^{E_0/kT}$$

where $\mu$ is the hole mobility, $p$ is the hole concentration, $E_0$ is the disorder parameter describing the energetic width of the tail of the density of states, $k$ is Boltzmann’s constant, $T$ is temperature, and $\mu_0$ is a mobility prefactor that is independent of carrier concentration but may depend on other factors such as temperature, and $p_0$ is the zero-field hole concentration.\cite{30,34}

This effect has even been demonstrated in the OECT device configuration for several combinations of semiconductor and electrolyte materials.\cite{35} However, none of the authors of these reports integrates their empirical findings about carrier mobility into a closed-form expression for OECT channel current as a function of gate and drain voltage. Other authors, in particular, Berggren et al., do include a nonlinear conductivity versus hole concentration relationship in their current–voltage equations for OECTs. By assuming a conductivity of the form $\sigma = \sigma_0 \times (\epsilon + (p/p_0)\gamma)^\epsilon$, where $\epsilon$ and $\gamma$ are empirically determined constants, these authors have implicitly assumed a mobility with the form given by Equation (2). Berggren et al. show that their model predicts a voltage drop along the OECT channel that steepens as it nears the negatively biased drain electrode.\cite{15} Their spatially resolved voltage measurements and their optical measurements qualitatively agree with their predictions. However, their model contains too many free variables to quantitatively compare it to measurements or...
to extract meaningful device parameters.\textsuperscript{[14,15]} Furthermore, for a fixed gate voltage, their model fails to predict a decrease in the average carrier density as the drain voltage is made more negative. Later, the Berggren group developed a model for electrolyte-gated field-effect transistors that addressed these shortcomings, but they did not compare it to spatially resolved measurements along the transistor channel.\textsuperscript{[36]} Despite these weaknesses, their models demonstrate the importance of nonuniform hole mobility along the OECT channel.

In this article, we follow the previous work done by the Berggren and Malliaras groups and introduce a nonuniform mobility into the Bernards–Malliaras model.\textsuperscript{[14]} The resulting model is simpler than the Berggren models and quantitatively fits experimental current–voltage data. Furthermore, unlike the Bernards–Malliaras model, the nonuniform mobility model also explains spatially resolved optical data.

The Bernards–Malliaras model starts with the assumption that each injected cation removes one hole from the PEDOT:PSS. Thus the hole concentration in the channel can be found exactly as in the Bernards–Malliaras model, as shown in Equation (3)

$$dQ(x) = cWdx(V_c - V(x))$$

where $dQ$ is the injected cationic charge, $x$ is the distance along the OECT channel away from the source electrode, $c$ is the ionic capacitance per unit area, $W$ is the channel width, $h$ is the channel thickness, $V_c$ is the gate voltage, $V(x)$ is the voltage in the channel at position $x$, $p_0$ is the hole density before any cations are injected, and $V_p \equiv q_p h/c$ is the channel pinch-off voltage. The ionic capacitance, $c$, is given by the capacitance of two capacitors in series. One of these capacitors is at the gate/electrolyte interface, and the other is the capacitance of the OECT channel.\textsuperscript{[16,17]} Inserting Equations (2) and (3) into the differential form of Ohm’s law, $J = \sigma \frac{dV}{dx}$, yields

$$J = q_c p_0 \left(1 - \frac{(V_c - V(x))}{V_p}\right)^{E_c/kT} \frac{dV}{dx}$$

which is identical to Equation (5) of the Bernards–Malliaras model except for the $E_c/kT$ power that arises due to the inclusion of Equation (2) of this work.

Because the steady-state current density throughout the OECT channel is constant, the integration to obtain the current–voltage relationship is straightforward

$$\frac{J}{\sqrt{g_0p_0}} \int_{0}^{E_c/kT} \left(1 - \frac{(V_c - V(x))}{V_p}\right)^{E_c/kT} dV$$

$$I = \frac{GV_p}{E_0/kT + 1} \times \left[\left(1 - \frac{V_c - V_0}{V_p}\right)^{E_c/kT} - \left(1 - \frac{V_c}{V_p}\right)^{E_c/kT}\right],$$

where

$$G = \frac{q_p h_c W}{L}$$

is the channel conductance under zero applied field and $V_D$ is the drain voltage. When $V_D < V_{D, sat} = V_c - V_p$, the proposed model assumes the typical pinch-off behavior exhibited by long-channel transistors,\textsuperscript{[25]} as indicated by Equation (6). After obtaining the $I$–$V$ relationship given by Equations (5) and (6), we integrate Equation (4) from the source to an arbitrary distance $x$. This yields

$$Ix = GLV_p \left(\frac{E_0}{E_p/kT + 1} \times \left[\left(1 - \frac{V_c - V(x)}{V_p}\right)^{E_c/kT} - \left(1 - \frac{V_c}{V_p}\right)^{E_c/kT}\right]\right).$$

Using Equation (5) for the linear regime or Equation (6) for the saturation regime, this expression can be solved for \( \left(1 - \frac{V_c - V(x)}{V_p}\right) \), which can be substituted into Equation (3) to find the hole concentration as a function of position along the channel

$$p(x) = \frac{Ix(E_p / (kT) + 1) + \left(1 - \frac{V_c}{V_p}\right)^{E_c/kT} \int_{V_p}^{V(x)} kT \frac{dV}{V_p}}{p_0} \left[\left(1 - \frac{V_c - V(x)}{V_p}\right)^{E_c/kT} - \left(1 - \frac{V_c}{V_p}\right)^{E_c/kT}\right].$$

which is valid in both the linear and saturation regimes, as long as the appropriate expression is used for $I$.

### 3. Results and Discussion

#### 3.1. Optical Evidence for Nonuniform Hole Mobility

As shown in Figure 2a,b, the current–voltage data quantitatively fit both the Bernards–Malliaras model and the proposed nonuniform mobility model. Both models predict similar zero-field conductance of $\approx 0.65–0.75$ mS, but the nonuniform mobility model predicts an onset of saturation at 720 mV—about 40% higher than the value predicted by the Bernards–Malliaras model. In Figure 2c,d, we show the hole concentration predicted by the nonuniform mobility model as well as the response from our optical measurements. The optical data agree qualitatively with the proposed model; however, without a priori knowledge of how hole concentration and optical response are related, we cannot make a quantitative comparison. To examine this relationship, we plot optical absorption at every $V_D$ combination as a function of the predicted hole concentration parameterized by the position along the OECT channel. As shown in Figure 3a, the expected one-to-one relationship between the hole density predicted by the Bernards–Malliaras model and
the optical response does not result. However, if we take into account nonuniform mobility, all of the curves collapse onto a universal curve that holds for every combination of $V_D$ and $V_G$ (Figure 3b).

The lack of a universal curve in Figure 3a demonstrates that the Bernards–Malliaras model does not contain all of the relevant physics. As explained above, removing holes from the system reduces the number of polarons. Because decreases in the hole concentration should increase the visible absorption of PEDOT:PSS, there must be a one-to-one (but not necessarily linear) relationship between hole concentration and absorption, regardless of the drain and gate voltages. This is not experimentally observed unless energetic disorder in the density of states is accounted for by including a nonuniform mobility in the proposed model. Furthermore, we found that other modifications to the Bernards–Malliaras model, such as taking into account channel length modulation, contact resistance, or a voltage-dependent ionic capacitance all failed to generate such a universal curve (see the Supporting Information). However, a modification that assumes an exponential dependence of mobility (rather than the power law dependence described above) does yield a universal curve (see the Supporting Information). This supports the argument that the correct modification to the Bernards–Malliaras model involves a hole-concentration-dependent mobility. Although the exponential dependence gives results comparable to the power law dependence, we prefer the power law model because it is based on experimentally and theoretically justified physics. Moreover, the extracted disorder parameter of $\approx 2kT$ is consistent with typical experimental results for conjugated polymers.$^{[38]}$

A final element of interest in Figure 3 is the shape of the optical response versus hole concentration relationship shown in Figure 3b. If the change in the optical absorption does not depend on the energy of the hole removed,
there would be a linear relationship between absorption and hole concentration. From Figures 2d and 3b, it is clear that the relationship we find is linear (see the Supporting Information), as one would expect if the number of visible photons absorbed was directly proportional to the density of neutral PEDOT molecules. However, this linear relationship breaks down at high hole concentrations. This is likely due to the fact that at these carrier concentrations, the presence of bipolarons in addition to polarons and neutral PEDOT molecules complicates the absorption properties of the material. Although we do not have a detailed explanation for this departure from linearity, we note that similar behavior in the optical response at high conductivities has been reported by others.\[19,39\]

3.2. Geometrical Scaling of Transistor Parameters

To further test the validity of the nonuniform mobility model, we have checked to see if it holds for devices with different architecture and geometries. The device architecture for these experiments was different from the device used for Figures 2 and 3. Rather than the planar geometry and gel electrolyte shown in Figure 1, these devices used an Ag/AgCl gate electrode suspended in a liquid electrolyte (100 × 10^{-3} m NaCl in H_2O) above the channel. These changes lead to higher ionic mobility, the presence of mobile anions, and a gate electrode with greatly reduced polarizability. Despite these effects and others, the changes to our experimental system were not expected to invalidate the assumptions of our model. Therefore, using both sets of experimental conditions is a stringent test of our model. Furthermore, we not only tested a different overall architecture, but we also measured devices with six different channel width to length ratios ranging from 0.14 to 5.5. The \(I–V\) data for the devices with the smallest and largest width to length ratios are shown in Figure 4. Clearly the nonuniform mobility model yields an excellent fit to the \(I–V\) data even for devices with width to length ratios differing by more than an order of magnitude. Additionally, it is clear that the Bernards–Malliaras model fails to accurately describe the saturation behavior of these devices. On the other hand, the nonuniform mobility model fits the data well into the saturation regime. This distinction between the two models is most apparent at higher gate voltage values. Although Figure 4 clearly shows that the nonuniform mobility model fits device data for a wide range of geometries, the robustness of this model to geometry variations cannot be confirmed without analyzing the trends in the fit parameters. In Figure 5, each fit parameter is plotted as a function of the channel width to length ratio. Figure 5a shows that the extracted zero-field channel conductance, \(G\), scales linearly with \(W/L\). When the linear fit to these data is forced to cross the origin, the degree-of-freedom-adjusted coefficient of correlation is \(r^2 = 0.99\). The slope of this linear fit is 0.88 mS, and the dry-film thickness of the channel is \(≈ 100\) nm (the hydrated film is somewhat thicker). Thus we obtain a conductivity of \(≈ 90\) S cm\(^{-1}\), which is similar to previous measurements for the same PEDOT:PSS formulation.\[21\] In contrast to the linear relationship between channel conductance and \(W/L\), neither the pinch-off voltage nor the disorder parameter has a strong dependence on \(W/L\), as shown in Figure 5b,c.
These results demonstrate that the proposed model not only fits the data for a wide range of geometries, but it also extracts reasonable device and material parameters over this range. Furthermore, the geometry scaling of these parameters rules out several other possible explanations for the departure of device behavior from the Bernards–Malliaras model. For instance, if parasitic series resistance were responsible for the observed behavior, the departure from the Bernards–Malliaras model would be greatest for devices with large $W/L$, which is clearly not the case. Similarly, channel length modulation would affect short-channel devices the most, but as shown in Figure 5d, disagreement with the Bernards–Malliaras model tends to increase slowly with channel length. This tendency is not predicted by the proposed model and we cannot offer a theoretical explanation for this behavior. However, we note that even for an $\approx 400\%$ increase in channel length, the extracted disorder parameter varies by less than $40\%$. Moreover, even if the trend is extrapolated to $L = 0$, the disorder parameter would still be $90\%$ greater than what would be extracted if the Bernards–Malliaras model were valid.

3.3. Transconductance Optimization

In Section 3.1, we demonstrated that the pinch-off voltage provided by the nonuniform mobility model is substantially larger than that provided by the Bernards model. This discrepancy has significant implications for the use of OECTs as biosensors. It can be shown (see the Supporting Information) that the transconductance, $g_m = \frac{\partial I_D}{\partial V_G}$, increases monotonically as the drain voltage is made more negative, up to the saturation voltage. Because many OECT-based sensing platforms use a fixed drain voltage, the signal to noise ratio can be optimized by tuning the drain voltage. Setting the drain voltage at $V_D = V_{D,sat}$ maximizes the transconductance while minimizing bias stress on the device and damage to any biological systems being measured. As shown above, the Bernards–Malliaras model significantly underestimates the pinch-off voltage. Because $V_{D,sat} = V_C - V_P$, an underestimate of $V_P$ translates to an underestimate of $|V_{D,sat}|$ (for $V_P > V_C$) and leads to suboptimal transconductance. Figure 6a demonstrates this effect for a device at $V_G = 225$ mV. If the data for this device are fit using the Bernards–Malliaras model, the extracted pinch-off voltage is $V_P = 425$ mV; whereas, the nonuniform mobility model yields $V_P = 593$ mV. Therefore, at $V_C = 225$ mV, the saturation voltage is $V_{D,sat} = -200$ mV, according to the Bernards–Malliaras model, and $V_{D,sat} = -373$ mV, according to the nonuniform mobility model. One can define $\%$ improvement of the transconductance as

$$\%\text{Improvement} = \left( \frac{g(V_{D,sat}) - g(V_{D,sat}^{(\text{Bernards})})}{g(V_{D,sat}^{(\text{Bernards})})} \right) \times 100\%$$

where $V_{D,sat}$ is calculated with $V_P$ extracted from the fit to the nonuniform mobility model and $V_{D,sat}^{(\text{Bernards})}$ is calculated with $V_P$ extracted from the fit to the Bernards–Malliaras model.

With this definition, we find that operating the device at the saturation voltage given by the nonuniform mobility model results in a $19\%$ improvement in transconductance over what would be obtained if the device were operated at the saturation voltage given by the Bernards–Malliaras model. As shown in

**Figure 5.** Geometry scaling of fit parameters according to the nonuniform mobility model. Error bars are the 95% confidence intervals of the extracted parameters from the least squares fitting. The error bars are too small to be visible in panels (a) and (b).
disagreements in the literature between observations and theoretical predictions of transient behavior. While the nonuniform mobility model offers many improvements over existing models, it also has several limitations. In particular, although Equation (6) takes into account drain voltage saturation ($V_D < V_{D,sat}$), it does not describe depletive due to gate voltages greater than $V_p$. This puts an upper limit on the gate voltages over which our model is valid. Additionally, the model does not fit well to experimental $I–V$ curves when negative gate voltages are used. Because $V_C > V_p$ and $V_C < 0$ are outside the typical operating range of OECTs, understanding these limits is outside the scope of the current investigation. However, extending the proposed model to include these voltage ranges may be worthwhile to shed more light on the nature of carrier statistics and charge transport in conjugated polymers.

5. Experimental Section

Fabrication of Transistors with Gel Electrolyte: Chromium/gold electrodes (5 nm/100 nm) are evaporated on clean glass substrates and patterned using standard photolithographic lift-off. The channel length is 200 μm and the channel width is 100 μm. Next, an ~100 nm film of a PEDOT:PSS solution (89.66 wt% of Clevios PH-500, 6.87 wt% of ethylene glycol, 3.13 wt% of water, and 0.35 wt% of Zonyl FS-300 fluorosurfactant) is spun onto the chip. The PEDOT:PSS is patterned into transistor channels by scratching the film with a 20 μm radius tungsten tip controlled with a motorized micropositioning system. After patterning the PEDOT:PSS, an electrolyte gel (94.5 wt% water, 3.5 wt% glycerol, and 2.0 wt% sodium-PSS (Alfa Aesar, MW = 70 000)) is drop cast over the entire chip and allowed to dry for about 20 h in ambient conditions.

Fabrication of Transistors with Liquid Electrolyte: The transistors with liquid electrolyte were fabricated according to the parylene lift-off procedure outlined in Rivnay et al.[21] The PEDOT:PSS dispersion was spun at 3000 rpm for 30 s.

Electrical Characterization of Transistors with Gel Electrolyte: The current–voltage measurements are made using a Keithley 2636A SMU with custom-written control code. Although the response time of the device is ~30 ms (see the Supporting Information), the current is allowed to settle for 6 s before it is recorded after each gate voltage step. This guarantees that the response reaches a steady state and that the gate current is at least three orders of magnitude less than the drain current (see the Supporting Information). Between gate voltage steps, all electrodes are allowed to float for 3 min. Note that the gel electrolyte is rather transparent and its optical absorption is not affected by an applied voltage.[33]

Electrical Characterization of Transistors with Liquid Electrolyte: The transistors with liquid electrolyte were characterized with 100 × 10^-3 M NaCl contained in a poly(dimethylsiloxane) well. A Ag/AgCl pellet (2 mm diameter × 2 mm height) was used as the gate electrode. Because the liquid-electrolyte devices are much faster than the gel-electrolyte transistors (see the Supporting Information), the voltages are scanned at a rate of about 40 ms per step. The other details of the characterization are the same as in Rivnay et al.[21]

Optical Characterization: The optical measurements were only performed on the devices with the gel electrolyte and they were made at the same time as the electrical measurements. The optical
measurements were recorded with a monochrome, global shutter, complementary metal oxide semiconductor camera (Point Grey G3-U3-2356M) operated in 8-bit mode. The images were captured through a 10 ×/0.25 NA objective using transillumination supplied by a white light emitting diode with a spectral cut off near 650 nm (ThorLabs MCWHL2). The reported absorption increases are pixel intensities at each \( V_x \), \( V_y \) combination subtracted from the intensities when all electrodes are floating, and no pixels were ever saturated at 0 or 255. Due to interference ringing and shading effects near the electrodes, we do not record the optical response within 10 µm of the electrode edges. Additionally, two regions are cropped out of the images due to bubbles and wrinkles in the electrolyte (see the Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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