Chemical potential–electric double layer coupling in conjugated polymer–polyelectrolyte blends

Klas Tybrandt,* Igor V. Zozoulenko, Magnus Berggren

Conjugated polymer–polyelectrolyte blends combine and couple electronic semiconductor functionality with selective ionic transport, making them attractive as the active material in organic biosensors and bioelectronics, electrochromic displays, neuromorphic computing, and energy conversion and storage. Although extensively studied and explored, fundamental knowledge and accurate quantitative models of the coupled ion-electron functionality and transport are still lacking to predict the characteristics of electrodes and devices based on these blends. We report on a two-phase model, which couples the chemical potential of the holes, in the conjugated polymer, with the electric double layer residing at the conjugated polymer–polyelectrolyte interface. The model reproduces a wide range of experimental charging and transport data and provides a coherent theoretical framework for the system as well as local electrostatic potentials, energy levels, and charge carrier concentrations. This knowledge is crucial for future developments and optimizations of bioelectronic and energy devices based on the electronic-ionic interaction within these materials.

INTRODUCTION

The physics of intrinsic conjugated polymer (CP) semiconductors is well developed because of the major interest in light-emitting diodes (1), field-effect transistors (2), and organic solar cells (3). Heavily doped CPs, often in the form of poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS), have also been widely studied and explored for transparent electrodes (4), hole injection layers (3), and thermoelectrics (5). PEDOT:PSS is composites by the CP PEDOT and the polyelectrolyte (PE) PSS, in which the holes [positive (bi)polaronic charge carriers] on the PEDOT chains are electrostatically stabilized by the negatively charged sulfonate ions residing on the PSS chains (Fig. 1A). The surplus of sulfonate ions is compensated by positively charged mobile counterions, often in the form of protons or metal cations. After synthesis and processing into thin films, the PEDOT:PSS phase separates into PEDOT-rich regions of tens of nanometers in size, containing many 1- to 2-nm large crystallites (6), and a surrounding PSS-rich phase (4). In many applications, the moisture levels are relatively low, resulting in very low mobilities for the PSS counterions (7). Recently, there has been a significant interest in using and exploring CP-PE blends in aqueous applications for organic biosensors and bioelectronics (8), electrochromic displays (9), neuromorphic computing (10), and energy conversion (11) and storage (12). These applications use electrolytes or operate under elevated hygroscopic conditions, which render the counterions mobile and thus make the coupling of the electronic and ionic transport crucial (13). The electronic transport in organic electrochemical transistors (OECTs) (14, 15) has been quite successfully modeled for moderate carrier concentrations by the introduction of a volumetric capacitance in combination with the standard thin-film transistor equations (16, 17), although the used ideal capacitive charging approximation is simplistic and does not describe the charging behavior at lower carrier concentrations properly. Early models of dynamic systems with coupled electronic and ionic transport have typically been based on classical electrochemical Butler-Volmer models with an additional phenomenological term to account for the capacitive current (18–20). More recent works have been based on the drift-diffusion approach, which reproduces some dynamic current characteristics of CP-PE blends (21–23). However, these approaches fail to reproduce the experimentally observed volumetric capacitance of PEDOT:PSS (24), because the electronic and ionic charge carriers are treated as if they are existing in the same phase, with no electrostatic energy cost in charging the material, except from the contribution arising from diffusion gradients. This is not the case in reality because there is a spatial separation between the electronic and ionic charge carriers, similar to the electric double layers (EDLs) formed at the metal-electrolyte interfaces. Recent works argue that EDLs within CP-PE blends are responsible for the observed capacitive behavior (6, 25). The capacitive behavior of PEDOT:PSS has been qualitatively reproduced by explicit implementation of two-dimensional (2D) CP nanopores, although this approach is too computationally expensive to model realistic devices and did not consider the chemical potential of the holes. Overall, there exists no quantitative model that can relate the physical quantities to reproduce actual measurement data. Here, we present a novel drift-diffusion model of hydrated CP-PE blends, which provides a coherent theoretical framework that can reproduce a wide range of well-known experimental data. By introducing two distinct electrostatic potentials for the electronic and ionic phases, electronic properties such as the chemical potential of holes can be naturally coupled to the ionic phase through an EDL implemented by Poisson’s equation. This is done in a computationally inexpensive 1D manner, which allows for an accurate description of the charging behavior of CP-PE blends and modeling of OECTs and dynamic electrode systems of realistic dimensions.

RESULTS

Model of CP-PE blends

The CP-PE blend comprises two distinct phases on the nanoscale—the electronic CP phase (comprising crystallites) and the ionic PE phase (Fig. 1A). It has been experimentally shown that PEDOT:PSS contains PEDOT- and PSS-rich regions of different ionic conductivities (13); however, these variations are not considered in the present model. Assuming a Gaussian density of states (DOS), the chemical potential of the holes can be approximated by Eq. 1 (26, 27) (fig. S1)

$$\mu_p = k_BT \ln(p) + eB = (E_{DOS} - \sigma^2/(2k_BT) - \ln(p_i))/e \quad (1)$$

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charge. The work function of pristine PEDOT is lower than that of gold, giving rise to an interface potential difference and heavy doping at the system. A quasi-electric field term is included for the holes due to the shift in chemical potential. The Au-PEDOT boundary conditions are obtained by equating the Fermi level at the Au interface with the PEDOT phase ionic charge carriers. The polarons are electrostatically stabilized by the negative sulfonate groups, with the spatial separation of the electronic and ionic charge carriers creating an EDL.

Fig. 1. Charging of CP-PE blends. (A) PEDOT:PSS comprises two phases—the PEDOT phase with electronic charge carriers in the form of (bi)polarons (holes) and the PSS phase with ionic charge carriers. The polarons are electrostatically stabilized by the negative sulfonate groups, with the spatial separation of the electronic and ionic charge carriers creating an EDL. (B) Energy diagram of a PEDOT:PSS electrode immersed in a negative sulfate (PBS) with a Ag/AgCl reference electrode. VB, valence band; q, particle charge. The work function of pristine PEDOT is lower than that of gold, giving rise to an interface potential difference and heavy doping at the system. (C) For $V_{\text{app}} = -0.9$ V, the PEDOT is essentially doped, which increases the potential at the gold-PEDOT interface while the EDL is discharged. (D) The drift-diffusion–Poisson's equations and boundary conditions for the system. A quasi-electric field term is included for the holes due to the shift in chemical potential. The Au-PEDOT boundary conditions are obtained by equating the Fermi level and setting the space charge to 0. The electrolyte boundary conditions are the bulk concentration ($c_0$) and $V_c = 0$ V. (E) To measure the hole concentration dependence on the applied potential, $V_{\text{app}}$ was stepped from 0.3 V (blue circles) to $-0.85$ V (yellow circles) in 50-mV steps. The nonfaradic charge of each step was obtained by subtracting the linear faradic contribution. (F) The applied potential versus the measured hole concentration ($c$). Equation 12, which includes both the capacitive contribution of the EDL and the change in chemical potential, fits well (gray line). The previously reported purely capacitive model (16, 17) (red dashed line) deviates significantly at lower concentrations.

where $E_{\text{DOS}}$ is the center energy of the DOS, $p_i$ is the total available hole density (see Table 1 for quantities and constants). Here, although this approximation is only accurate for lower hole concentrations, it can also be used for higher concentrations because a capacitive term dominates the system in that regime (see below). The hole transport is described by the modified drift-diffusion equation (Eq. 2) (28), which includes the quasi-electric field arising from the shift in chemical potential due to changes in hole concentration. The ionic species in the PE phase are described by the classical drift-diffusion equation (Eq. 3), and the changes in concentrations are governed by the continuity equations (Eqs. 4 and 5)

$$j_p = -D_p (\nabla p + q p \nabla (V_p + \mu_p/e))$$

$$j_c = -D_c (\nabla c + q c \nabla V_{cc})$$

$$\nabla j_p = -\frac{dp}{dt}$$

$$\nabla j_c = -\frac{dc}{dt}$$

It should be stressed that the electrostatic potential has two different distinct values within the electronic ($V_p$) and ionic ($V_c$) phases.

This difference causes charging of the interface with holes and anions, thereby creating an EDL with the voltage-independent volumetric capacitance ($C_v$) implemented through Poisson's equation

$$-\frac{e}{e} \nabla^2 V_p = p - (V_p - V_c) C_v$$

Similarly, the PE phase is governed by Poisson’s equation (Eq. 7), with Eqs. 6 and 7 coupling the charging and transport of the electronic and ionic charge carriers

$$-\frac{e}{e} \nabla^2 V_c = p + c_+ - c_- - c_{\text{fix}}$$

One should notice that the hole concentration needs to be included in Eq. 7, because a portion of the anionic charges are compensating for the holes in the EDL.

Figure 1 (B and C) shows the energy diagrams for a PEDOT:PSS electrode immersed in an electrolyte [phosphate-buffered saline (PBS)] with a Ag/AgCl reference electrode for $V_{\text{app}} = 0$ and $-0.9$ V. The work function of the nonclean gold surface is set to $W_{Ag} = 4.5$ eV (29) and $W_{AgCl} = 4.7$ eV (30), and the remaining potential and concentration values follow from the analysis below. The vacuum level for the Ag/AgCl electrode is set to 0 eV as a reference. The system can be understood on the basis of three energy levels/potential differences, which depend on the doping level; the EDL potential difference, which causes

the charging of the interface and thereby doping of the semiconductor; the chemical potential of holes, which increases with doping level; and the gold-PEDOT interface potential difference caused by differences in the work function for gold and PEDOT. From the energy diagram, the standard boundary conditions for highly doped semiconductor-metal contacts are used for the gold-PEDOT contact \((x = 0)\) by equating the Fermi levels (electrochemical potentials)

\[
E_{F,Au} = W_{AgCl} + eV_{app} = E_{F,p}(0) = k_BT\ln(p(0))/e + eB + eV_p(0) \quad (8)
\]

\[
V_p(0) = -k_BT\ln(p(0))/e - B + W_{AgCl}/e + V_{app} \quad (9)
\]

and requiring charge neutrality in Eq. 6

\[
p(0) - (-k_BT\ln(p(0))/e - B + W_{AgCl}/e + V_{app} - V_c(0)) = 0 \quad (10)
\]

The full set of equations in the different domains is shown in Fig. 1D. At the steady state, the hole concentration is constant throughout the film, and \(V_c\) from Eq. 10 can be replaced by the Donnan potential \(V_D\) in Eq. 11. This requires knowledge about the concentration of fixed charges within the system, which was measured to be \(c_{fix} = 2400 \pm 400\) mol/m³. This yields Eq. 12, which relates the applied potential to the hole concentration

\[
V_D = -RT/F \arcsinh(c_{fix}/(2c_v)) = -72\text{ mV} \quad (11)
\]

\[
p/C_v - V_{app} - k_BT\ln(p)/e - B + W_{AgCl}/e - V_D = 0 \quad (12)
\]

### Charging characteristics

We can now determine the unknown parameters \(C_v\) and \(B\) by fitting Eq. 12 to the measurement data. Potential steps of \(-50\) mV (0.3 to \(-0.85\) V) were used to plot the extracted charge versus time for different voltages (Fig. 1E and fig. S2). Assuming that the faradaic current is kinetically limited and only depends on the applied voltage, it can be subtracted as a linear contribution from the curves. This was performed by fitting the function \(Q(t) = Q_{EDL} \cdot (1 - \exp(-t/T)) + I_p \cdot t\), where \(Q_{EDL}\) constitutes the charge in the PEDOT:PSS. From this data, \(p(V_{app})\) was calculated, and Eq. 12 was fitted, giving \(C_v = 19\) F/cm³ (Fig. 1F). This is about half the value in comparison of what has been previously reported (24), which is probably due to the relatively higher concentration of the cross-linker (30 volume percent) used in this work. Further, \(B = 4.0\) V gives \(\mu_p = 4.1\) and \(3.9\) eV for \(p = 100\) and \(0.01\) mol/m³, respectively. The work function of PEDOT:PSS is, in this context, given by the chemical potential and the EDL, that is, \(W_{P,P} = \mu_p + eV_{EDL}\).

### Organic electrochemical transistors

On the basis of the established relationship between carrier concentration and applied potential, we turn our attention to the electronic transport within the material by studying the characteristics of OECTs (Fig. 2A). The static characteristics \((I_G = 0)\) can be calculated from Eqs. 1, 2, 4, 9, and 10 by setting \(V_c = V_D\) (fig. S3). Because the hole mobility in CPs is known to increase with hole concentration, the first

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**Fig. 2. Modeling of OECT characteristics.** (A) The OECT comprises a PEDOT:PSS channel, gold source and drain terminals, and an Ag/AgCl gate electrode. (B) The model (line) was fitted to the measurement data (circles) for a low drain voltage (–20 mV) to minimize the nonlinearity of the channel. The obtained mobility (inset) shows the expected dependency on hole concentration. (C) With the model parameters set, the measured transfer curves for \(V_D = –0.3\) V (circles) and \(V_D = –0.5\) V (pentagons) could be accurately reproduced (lines). The curves show ideal organic field-effect transistor characteristics for \(V_G\) in [–0.1, 0.3] V. (D) Hole concentration in the channel for \(V_D = –0.5\) V and \(V_D = –0.3\) V (blue line) to 0.7 V (yellow). The hole concentration is depleted at the drain contact for higher gate voltages. (E) Effective potential \((W_{eff} = V_G + \mu_p/e)\) in the channel for \(V_D = –0.5\) V and \(V_D = –0.3\) V (blue line) to 0.7 V (yellow line). For higher gate voltages, most of the potential is dropped within the last micrometer of the channel next to the drain contact. (F) The output characteristics (circles) are accurately reproduced (lines) with the same parameter set as for the transfer curves.
step is to determine the parameter $D_p(p)$ from measured small signal data ($V_D = -20$ mV) (Fig. 2B). The Boltzmann function resulted in a good fit, giving $D_p(p) = D_{p,0} \cdot 0.93 - 1.1/\left(1 + \exp \left(\frac{p - 71}{23}\right)\right)$ with $D_{p,0} = 2.3 \times 10^{-5}$ m$^2$s$^{-1}$. The Einstein relation yields the mobility $\mu_p$, which shows the expected behavior from previously reported experimental and theoretical studies (26, 31, 32). With all parameters set, the transfer curves for $V_D = -0.3$ and $-0.5$ V can be calculated (Fig. 2C). For lower gate voltages, the hole concentration in the channel varies slowly, whereas for higher gate voltages, the hole concentration decreases rapidly at the drain contact (Fig. 2D). The drift is caused by variations in effective potential $V_{\text{eff}} = V_p + \mu_p/e$, which is plotted in Fig. 2E. For higher gate voltages, most effective potential is dropped at the drain contact. Diffusion plays an important role for higher gate voltages (fig. S4). Finally, the output characteristics of the OECT can also be accurately reproduced (Fig. 2F).

**CP-PE electrodes**

With both the static charging and transport processes established, we now address the coupled dynamic processes of CP-PE electrodes immersed in an electrolyte. To calculate the dynamic response of an electrode (Fig. 3A), we must solve the full set of equations in Fig. 1D. Figure 3B shows the calculated static concentrations of the system for $V_{\text{app}} = 0$ and $-0.7$ V. The concentration of holes is strongly affected by the applied potential, whereas the relative change in ion concentrations is less pronounced, because the concentration of mobile counterions is much higher. In addition, the electrolyte/PSS potential is nearly identical in both cases. The amount of electric charges stored in CP-PE films of different thicknesses is also calculated (Fig. 3C) and shows the expected linear relationship previously reported (24). Cyclic voltammetry (CV) is one of the most common electrochemical characterization techniques. In Fig. 3D, calculated and measured cyclic voltammograms at different scan rates for a 600-nm-thick PEDOT:PSS film are compared. The measured box-like shape with declining currents for negative potentials is reproduced, although there are some deviations for potentials $< -0.5$ V, probably due to faradaic side reactions. When the scan range is extended to $-1.2$ V, commonly observed peaks at $-0.5$ to $-0.4$ V in the forward scan direction emerge (Fig. 3E). These peaks are reproduced by our model if the hole mobility is reduced by seven orders of magnitude (see Discussion). Finally, the calculated electrochemical impedance spectroscopy (EIS) data (Fig. 3F and fig. S5) and the calculated pulse response (fig. S6) fit the experimental data very well.

Previous electrode characteristics implicitly probe the short-range vertical transport in the films. To explicitly probe the long-range lateral transport in the CP-PE blend, we used the device configuration shown in Fig. 4A. At $t = 0$, a potential of $-2$ V is applied to the electrode. This creates an optically measurable electrochromic reduction front at the electrolyte side of the device. The model was used to describe the behavior of the device as a function of time (0 to 45 s). The hole concentration starts to decrease at the electrolyte side and spreads with time into the film (Fig. 4B). The electrostatic potential in the PEDOT phase initially goes from 0.57 to $-1.43$ V but does not change much from there on due to the low potential gradient necessary to transport the holes (Fig. 4C). However, the electrostatic potential in the ionic phase changes significantly throughout the process. One should notice that most of the potential drop occurs in the electrolyte in the close vicinity of the electrode due to concentration polarization (fig. S7).

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**Fig. 3. Modeling of PEDOT:PSS electrode-electrolyte systems.** (A) The PEDOT:PSS electrode is electrically connected through a gold contact, and the electrolyte is grounded with a Ag/AgCl reference electrode. (B) Potentials and concentrations for $V_{\text{app}} = 0$ V (solid lines) and $-0.7$ V (dashed lines). The hole concentration (blue lines) markedly changes with the applied voltage, whereas relative changes in the cation (red lines) and anion (yellow lines) concentrations are small due to the high concentration of fixed charges (black line). The electrostatic potential in the PEDOT phase (blue lines) changes little, whereas the potential in the PSS and electrolyte phases (red lines) is nearly constant. (C) The model predicts the expected proportional relationship between stored charge and film thickness [50 nm (yellow line) to 500 nm (blue line)]. (D) The main features of the measured cyclic voltammograms ($\gamma = 1.0$ V/s; 0.5 V/s; and $\Delta = 0.2$ V/s) are predicted by the model. (E) By reducing the hole mobility, the commonly observed peaks in the forward scan direction can be reproduced. (F) The calculated EIS modulus and phase angles (lines) agree well with the measured data (○).
As the current decreases over time, so does the potential drop at the electrolyte interface. The calculated change in transmission at 600 nm for the device can be obtained by using experimental data relating the transmission to the hole concentration of the polymer (fig. S8) (33). The calculated optical response is in good agreement with the previously published data by Rivnay et al. (13) (Fig. 4D).

**DISCUSSION**

Capacitive-like charging of CPs is a well-known phenomenon. However, previous models have typically included capacitive charging as an additional phenomenological term in the expression for the total current without any clear physical justification. In our proposed model, the volumetric capacitance is a natural consequence of the electrostatic potential difference between the electronic and ionic material phases, resulting in an EDL, which is known to exhibit capacitive characteristics. The EDL is assumed to form around CP elements with no ionic conductivity, that is, CP chains and crystallites. Because the EDL introduces an energetic cost for charging up the material, our model does not need any of the artificially induced caps on local carrier concentrations often found in previous models (21–23) to prevent unphysically high values. Assuming that the PEDOT phase comprises cylindrical crystallites with a diameter of 2 nm (6) surrounded by an EDL with a surface capacitance of 10 μF/cm² (typical value for metals), the volumetric capacitance is estimated to be 40 F/cm³, which is reasonably close to the value of 19 F/cm³ from the fitted measurement data. By considering the influence of the chemical potential of the semiconductor, the charging behavior at lower hole concentrations can be accurately modeled. Here, a simplistic approximation of the chemical potential can be used, because the capacitive behavior of the EDL dominates for p > 20 mol/m³ (Fig. 1E). The work function of undoped PEDOT:PSS (W_{PEDOT}) is predicted to be W_{PEDOT} < 4 eV < W_{Au} (34); thus, there will be no injection barrier at the Au-PEDOT interface. The position and width of the DOS are not directly accessible from the model; however, the two orders of magnitude shift in mobility due to doping level are consistent with σ = 4k_B T ≈ 0.1 eV (26).

The low concentration regime is of particular importance for the modeling of electronic charge transport in OECTs, because much of their characteristics arise from this regime. We demonstrate this feature by accurately reproducing the well-known static OECT characteristics by a simplified static version of our model, which not only resembles the conventional thin-film transistor model but also takes into account the charge in chemical potential (that is, the "band bending"). Our model indicates that the electronic transport in the low concentration regime is dominated by the diffusion term (fig. S4). This raises the question of how well previous models, which have not taken diffusion effects into account, can represent the actual transport in these devices. By solving the full equation system, the dynamics of CP-PE electrodes immersed in an electrolyte was modeled. The standard characteristics of thin-film electrodes, such as cyclic voltammograms, pulse transients, and EIS data, could accurately be reproduced. Cyclic voltammograms of CP films are rich in features, that is, peaks and plateaus, which have been difficult to decouple in the past. The model offers explanations for three of these distinct features: (i) The box-like shape for higher potentials is due to the internal EDL within the material. (ii) The gradual decrease in current for lower potentials is a consequence of changes in the chemical potential of the semiconductor. This is, in turn, caused by the tail of the DOS. (iii) The asymmetry of the backward and forward scans for low potentials is explained by slow hole transport. This manifests itself as a delay followed by a peak in the forward scan current. It seems that large negative potentials induce a permanent change, probably loss of conductivity, in the films (fig. S9). Because this happens below the reduction potential of water, it might be caused by the generation of hydroxide ions, which are known to reduce the conductivity (34), although other mechanisms not included in the present model cannot be ruled out at this point.

Long-range coupled transport could also be accurately predicted by the model in comparison with the reported reduction front measurements. Because the ions are much slower than the holes, the reduction of PEDOT will start next to the electrolyte to minimize the length of the ion transport. Therefore, ion transport will limit the rate of the process, and the electrolyte next to the CP-PE interface imposes a significant limitation on the current due to concentration polarization. The
The overall behavior of the device can thus be expected to be sensitive to the particular geometry of this interface, because an extension of the CP-PE film away from the top insulator should provide significantly higher currents and faster reduction front movement.

CONCLUSIONS

We report on a model for CP-PE blends based on the coupling of the chemical potential of the semiconductor with the EDL of the semiconductor-electrolyte interface. Although the model is based on the classical drift-diffusion approach, it constitutes a significant departure from previous work (21–23) as it introduces two distinct material phases with different electrostatic potentials. Because this approach yields a coherent theoretical framework that quantitatively reproduces the well-known characteristics of CP-PE blends, it suggests that CP-PE blends should be viewed as two-phase materials comprising nanostuctured semiconductors embedded in PE matrices. This has significant implications on how the nature of electrochemical doping in CPs should be perceived, because it makes a strong argument for a view of spatially separated electronic and ionic charge carriers, in contrast to the classical view of doping as an electrochemical redox process (35). Although PEDOT:PSS, which is the most prevalent CP-PE blend, was used for comparison with the model in this work, other materials such as polypyrrole:PSS (36), polyaniline:PSS (37), and thiophene with glycolated side chains (38) show similar CV characteristics. The model is thus expected to be useful for a wider class of blends than just PEDOT:PSS. However, it may, in its current form, be limited to materials in which the stacking of the CP chain is not significantly altered by the doping level, because this process would likely be associated with an energetic cost. This issue, along with that of inhomogeneous ionic conductivity, is exciting venues for further refinements and extensions of the model. Because the model is computationally inexpensive, it can be applied to macroscopic 2D and 3D systems to improve the understanding or optimize the performance of a wide array of devices currently under investigation. The addition of faradaic reactions to the model should be straightforward, as the relevant physical quantities are available, and the reactants and products can be incorporated into the continuity equations. Within the growing field of energy conversion and storage, CP-PE blends are one of the premier candidates for supercapacitors, oxygen reduction electrodes, and cheap fuel cell electrodes. In the development of these kinds of applications, it will be invaluable to have access to the local concentrations, potentials, and energy levels of the systems to develop new concepts and optimize performance.

MATERIALS AND METHODS

Device fabrication

Titanium (5 nm) and gold (50 nm) were thermally evaporated onto glass substrates and patterned by photore sist and wet etching. PEDOT:PSS dispersion (Clevios PH 1000) was mixed with 6% (v/v) ethylene glycol (Sigma-Aldrich) and 0.5% (v/v) (3-glycidyloxypropyl)trimethoxysilane (Sigma-Aldrich) and filtered through a 0.45-μm polycarbonate filter. The mixture was then spin-coated (1000 rpm) on an 8-mm-diameter wafer. Spin coating was repeated for a total thickness of 100 nm. The film was then annealed at 150°C for 15 min, and the channels (20 μm long, 40 μm wide, and 60 nm thick) were patterned by Shipley s1813 photoresist followed by RIE dry etching (O2/CF4; at 150 W for 30 s) and stripping in acetone. A 2-μm-thick insulating layer of NanoTron SU-8 3000 was patterned to isolate the gold contacts from the electrolyte. Ag/AgCl paste was painted on the gate electrode and cured (at 110°C for 10 min).

Device characterization

All electrochemical measurements were performed in PBS buffer with a Ag/AgCl electrode as the reference electrode or gate electrode for OECT measurements. Three-electrode measurements were performed with a μAutolab III potentiostat in N2-purged electrolyte to reduce faradaic currents at negative working potentials. At least two CV scans were carried out on every sample before characterization to ensure stable performance. Scans were performed at 1, 0.5, and 0.2 V/s, and EIS measurements were taken at an effective amplitude of 10 mV. OECTs were characterized with a Keithley 4200A-SCS parameter analyzer. The concentration of fixed sulfonate groups within the PEDOT:PSS films was measured by ion exchange. First, the film was incubated in a 10 mM NaCl solution for 20 min to replace all mobile cations with sodium ions. Next, the film was incubated in 10 mM HCl for 20 min, after which the sample was quickly washed in deionized water and dried with a nitrogen gun to remove all liquid. Finally, the film was placed in a 10 mM NaCl solution for 20 min to extract the protons. The amount of extracted protons was determined by pH titration with NaOH.

Numerical simulations

Finite element calculations were carried out with the COMSOL Multiphysics 4.3a software on a standard laptop. For time-dependent simulations, the initial values were obtained from steady-state calculations. For the low hole concentrations, steady-state convergence was achieved by parametric sweep of the applied potential from a higher converging value down to the lower desired value. The specified mesh was fine (10−12 m) at the interfaces and coarser within the bulk of the materials to decrease computational cost. For simulations of the full PEDOT:PSS-electrolyte system, the extension of the PEDOT:PSS phase was controlled by setting ϵfix = Cv = 0 and εp = 10−5 in the electrolyte domain.

Table 1. Variables, parameters, and constants.

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<tr>
<th>Parameter</th>
<th>Description</th>
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<td>Cv</td>
<td>Volumetric capacitance</td>
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<td>p</td>
<td>Hole concentration</td>
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<td>cfix</td>
<td>PE fixed charge concentration</td>
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<td>μp</td>
<td>Hole chemical potential</td>
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<td>B</td>
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