Thermodynamics of Organic Electrochemical Transistors

matteo cucchi (✉ matteo.cucchi@tu-dresden.de)

TU Dresden

Anton Weissbach

TU Dresden

Lukas Bongartz

TU Dresden

Hsing Tseng

TU Dresden

Hans Kleemann

TU Dresden <https://orcid.org/0000-0002-9773-6676>

Richard Kantelberg

TU Dresden

Karl Leo

TU Dresden

Article

Keywords:

Posted Date: December 6th, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-1143463/v1>

License: This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Nature Communications on August 3rd, 2022. See the published version at <https://doi.org/10.1038/s41467-022-32182-7>.

Thermodynamics of Organic Electrochemical Transistors

Matteo Cucchi^{a*}, Anton Weissbach^a, Lukas M. Bongartz^a, Richard Kantelberg^a, Hsin Tseng^a, Hans Kleemann^a, Karl Leo^{a*}

^a IAPP, Technische Universität Dresden, Dresden

Abstract

Bioelectronics which bridge the gap between conventional electronics and biological systems are actively researched due to their fascinating perspectives in healthcare and other fields. A key element of future bioelectronics is the organic electrochemical transistor (OECT) that, by employing a mixed ion-electron conducting materials, can perform switching tasks in electrolytic environments and serve as sensoric or actinic element. OECTs differ substantially from their inorganic field-effect counterparts, mainly due to their electrochemical, rather than electrostatic, gate operation principle. However, the working mechanism of OECTs is modeled as the one of the field-effect transistor: this approach not only fails to give quantitative agreement with experimental observation, but also ignores the material properties of the channel and the chemical dynamics that stem for the operation of the device. Here, we present a new comprehensive unified model that can explain the behavior of OECTs across a broad range of materials, designs, and operation regimes. We treat the polymeric channel as a thermodynamic binary system and show that the entropy of mixing is the major driving force behind the operation of the OECT. We are able to quantify the entropic and enthalpic interactions between charged species for a variety of materials and solvents, and harness this knowledge to provide guidelines for material modeling and insights for device fine-tuning for targeted applications. Finally, our thermodynamic model provides a description of the intrinsic origin of the ubiquitous hysteretic behavior of OECTs.

1 Introduction

1 While conventional electronics are driven by electrons only, biological systems
2 use mixed ionic and electronic effects. Artificial systems which use both effects
3 have gained increasing attention in the last decade thanks to their operation
4 in electrolytic environments and their ability to transduce ionic into electronic
5 signal [1, 2, 3]. These appealing features, absent in traditional organic and
6 inorganic electronic devices, have been harnessed to design human-compatible
7 electronics, *e.g.*, circuits that can be implanted within an organism and interact
8 with tissues, neurons, blood, etc. [4, 5]. The most prominent device is the or-
9 ganic electrochemical transistor (OECT) [6], using modulation of the redox state
10 of a channel composed of an organic mixed ionic-electronic conductor (OMIEC)

Figure 1: a) Sketch portraying a typical OEFT measurement with a non-polarizable Ag/AgCl pellet as gate electrode. Such setup is used throughout this work too. b) OEFT transfer curve with a sketch of how the ions that mediate the doping/deoping accumulate in the channel and modulate the current. c) Key difference between the FET-based model for OEFTs and our thermodynamic model. The nonlinear charge accumulation resulting from the Gibbs free energy, in strong contrast with a (linear) accumulation typical of a capacitor.

[1]) immersed in an electrolytic solution. In a reversible and energy-efficient process, the accumulation of ions within the channel by means of a gate electrode controls transistor operation. The traditional OEFT architecture, sketched in Fig. 1a, can be employed for a broad spectrum of applications of technological interest as proven by the number of successful demonstrations of OEFT-based devices for biosensors [7], artificial synapses [8, 9], hardware capable of computing [10, 11, 12, 13], and wearable electronics for biofluid [14, 15] and biosignal monitoring [4, 16]. More recently, the application scope of OEFTs has been further expanded, entering *dry* electronics: using solid electrolytes, OEFT-based devices were shown to be an excellent candidate for non-volatile memories for machine-learning accelerators [17, 18] as well as a good alternative to traditional low-cost organic and inorganic digital circuitry [19]. Impressive performances have been demonstrated with OEFTs, *e.g.*, high transconductance [20], minimal subthreshold swing [21], and very large current densities [22].

Moreover, OEFTs have been employed as substrate for cell culture, although the electrostatic interactions that allow for successful bio-interfaces are still mysterious [23].

This multifaceted range of applications demands a detailed understanding of the physical and chemical processes underlying the OEFT operation, as well as a comprehensive electronic modeling. In their seminal paper, Bernardis *et al.* borrowed the mathematical framework of thin-film field-effect transistors (FETs) to describe the channel current I_d as a function of the gate voltage V_{gs} and drain voltage V_{ds} of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate

34 (PEDOT:PSS)-based OECTs, according to

$$I_d = \frac{Wt}{L} \Lambda_h [PSS^-]_0 \left(1 - \frac{V_{gs} - \frac{V_{ds}}{2}}{V_p}\right) V_{ds} \quad (1)$$

35 where V_p is the pinch-off voltage defined as $V_p = [PSS^-]_0 / C^*$, Λ_h is the hole
 36 mobility (we chose this uncommon notation to avoid confusion with the chemical
 37 potential μ extensively used below), C^* is the volumetric capacitance, $[PSS^-]_0$
 38 is the intrinsic charge density of dopants, and t , W and L are the geometrical
 39 channel thickness, width, and length. Bernards model is an elegant and often
 40 used framework to describe the operation OECTs. However, it does not allow
 41 for an accurate quantitative analysis of the important figures of merit of OECT
 42 operation (*e.g.*, transconductance, saturation in on- and off-state, subthresh-
 43 old behavior, etc.), nor for qualitative description of the OECTs IV curves,
 44 such as the peculiar S-shaped transfer curve (Fig. 1b), especially for high-
 45 performance devices. For this reason, several approaches have been proposed to
 46 extend Bernards model, usually adding parameters that capture OECT-specific
 47 properties not seen in conventional FETs, *e.g.*, ion concentration-dependent mo-
 48 bility [24], disorder [25], or ion diffusion [26]. On top of these effects, OECTs are
 49 often characterized by hysteresis, a feature that cannot be described by existing
 50 models.

51 A number of empirical models and numerical simulations were also proposed
 52 [27, 28, 29]. A detailed overview of the mathematical models of OECTs and
 53 their evolution over time was recently reported by Colucci *et al.* [30]. However,
 54 Bernards model and its extensions rely on the assumption that the accumu-
 55 lated ions in the channel can be calculated as a simple parallel-plate capacitor,
 56 similar to a metal-oxide-semiconductor FET, but experimental evidence shows
 57 a marked nonlinear potential-dependent capacitance, as shown in Fig. S1 and
 58 Ref. [31]. Moreover, the chemistry behind the redox process leading to the
 59 OECT switching is not taken into account: obviously, electrostatic interactions
 60 alone cannot comprehensively explain the basic mechanism that underlie the
 61 OECT operation.

62 Over the past years, new use cases shone light on these limits of the understand-
 63 ing of OECTs, exposing the weaknesses of the proposed approaches and calling
 64 for the need of finding a better description. Comprehensive models should not
 65 be restricted to the switching-off of the device and its linear regime, but rather
 66 be a comprehensive explanation of the variety of effects that OECTs show and
 67 that the FET-picture does not capture. A few studies put forth the idea, or
 68 the necessity, to investigate the metal/electrolyte/polyelectrolyte system on a
 69 thermodynamic basis. For example, thermodynamic notions (Nernst law and
 70 Boltzmann statistics) need to be integrated in the model in order to describe
 71 the concentration-dependent threshold voltage exploited in OECTs for ion sens-
 72 ing [7, 32]. Romele *et al.* investigated the transport properties of OMIECs and
 73 observed that the channel resistance and capacitance are independent of the elec-
 74 trolyte concentration, in contrast to the double-layer theory. This ionic buffering
 75 is explained in terms of Donnan's equilibrium [33]. Tybrandt *et al.* reasoned in

76 terms of chemical potential of the charged species within the polymeric chan-
 77 nel: their study results in accurate numerical drift-diffusion simulations and in
 78 the key observation that polyelectrolyte/conductive polymer blends should be
 79 viewed as two-phase materials [34]. Recently, Rebetez *et al.* investigated the
 80 temperature-dependence of the reaction equilibrium that drives the polaron and
 81 bipolaron formation and annihilation. In doing so, they revealed for the first
 82 time the importance of the entropy in the establishment of the redox equilib-
 83 rium, highlighting a key aspect of the kinetics of the doping mechanism [35].
 84 These approaches highlight new physical and chemical mechanisms behind the
 85 charging dynamics of OECTs and provide good tools to understand the inter-
 86 action at the gate/electrolyte and electrolyte/polymer interface. However, a
 87 fully-developed mathematical framework capable of reproducing experimental
 88 data while shining light on the material properties was never proposed.

89 Here, we propose a universal approach derived from thermodynamic axioms
 90 capable of explaining a plethora of OECT and OMIEC properties in a variety
 91 of applications. We argue that, although FET models can provide a useful and
 92 convenient tool to investigate the properties of OECTs, they fail in giving a real-
 93 istic physical and chemical picture of the system. Instead, we reason in terms of
 94 chemical equilibrium and electrochemical potential. Key in our approach is the
 95 fact that we do not rely on the direct proportionality between applied voltage
 96 and accumulated charge typical of a parallel-plate capacitor. Rather, a non-
 97 linear voltage-dependent charge accumulation (Fig. 1c) naturally derives from
 98 the treatment of the entropy and enthalpy of the system. We analyze the equi-
 99 librium that establishes between the conductive polymer and electrolyte, and
 100 how the gate-source voltage perturbs it. In doing so, key features of OECTs nat-
 101 urally emerge from the math without artificial parametrization. For example,
 102 previously overlooked peculiarities of OECTs, such as saturation in the on-state
 103 and the strong voltage-dependent capacitance are intrinsically captured by our
 104 model, and so is the effect on the device performance based on the doping level.
 105 We support our findings with experimental data employing PEDOT:PSS (the
 106 most widely employed OMIEC) OECTs as reference system, and with numer-
 107 ical simulations. We further analyze important findings reported in previous
 108 studies under a new light. We capitalize on the investigation and quantifica-
 109 tion of intrinsic material properties such as the interactions occurring between
 110 the polymer and ions mediated by the solvent. Finally, we extend our model
 111 to provide an intrinsic origin of the ubiquitous hysteretic behavior of OECTs,
 112 based on a two-phase system. Treating the channel as a thermodynamic binary
 113 system allows for an in-depth study of material-specific properties which might
 114 be the basis for either targeted circuit design or the development of tailor-made
 115 materials. The model exposes under a new light the role of the temperature,
 116 electrolyte, hysteresis, and interactions between the charged species that make
 117 up for the operation of OECTs.

2 Thermodynamics of OMIECs: redox-state equilibrium

When a PEDOT:PSS film is immersed in an aqueous electrolytic solution (*e.g.*, NaCl in H₂O), the polymeric matrix swells and ions can penetrate. Cations act as dedopants, reducing a fraction of the oxidized existing polarons PEDOT⁺ into PEDOT⁰ according to the reaction

sketched in Fig. 2a. This process happens spontaneously, without the need of external forces (*e.g.*, a gate potential), and it is proven by the conductance lowering of PEDOT:PSS when going from dry to liquid environment. Interestingly, the resulting amount of Na:PSS is independent on the concentration of salt in the bulk electrolyte, as shown experimentally by Romele *et al.* [33]. This appears evident looking at the equilibrium constant k_{eq}

$$k_{eq} = \frac{[\text{PEDOT}^0]}{[\text{PEDOT}^+]} \quad (3)$$

where the activity of the electrons provided by the electrodes is considered unitary. Here, we consider $[\text{PEDOT}^0]$ the relative concentration of PEDOT that reduces after the PSS moiety pairs with a cation and $[\text{PEDOT}^+]$ is the relative concentration in its oxidized state. Since the sum $[\text{PEDOT}^0] + [\text{PEDOT}^+] = 1$ is constant, and so are the temperature and the pressure, we treat the system as a canonical ensemble [36]. Obviously, even in absence of cations, not all the PEDOT units are doped. However, these cannot participate in the reaction and they do not contribute to the equilibrium. Eq. 3 provides a bridge between a chemical picture of the system, since it describes the chemical reaction, and an electronic picture, because it quantifies the doping level at a certain temperature. Hence, we use it as starting point for our analysis, which is schematically outlined in Fig. 2b. Based on the Gibbs free energy G , we compute the chemical potential as a function of the concentration of oxidized PEDOT. Having the chemical potential at hand, we build a bridge from the thermodynamic description to the electronic parameters of an OECT, *i.e.*, the transfer characteristics. We investigate the equilibrium between reduced and oxidized PEDOT in terms of Gibbs free energy G , by treating the channel as a binary mixture of the two species. The definition of Gibbs energy of a binary mixture is

$$G = H - TS_{mix} = H_0 + H_{mix} - TS_{mix}, \quad (4)$$

where H is the enthalpy, T the temperature, and S_{mix} the entropy of mixing. In the simplest approximation, the enthalpy of mixing H_{mix} is neglected and the only contribution to the enthalpy is H_0 , namely the sum of the enthalpies of the pure PEDOT⁰ and of pure PEDOT⁺ with the corresponding chemical potentials μ^{p0} and μ^{p+} , respectively [36]. By defining ϕ as the relative concentration of reduced PEDOT, defined as

$$\phi = [\text{PEDOT}^0] = 1 - [\text{PEDOT}^+], \quad (5)$$

154 which spans from 0 (purely oxidized phase) to 1 (fully reduced phase), we can
 155 describe the entropy of mixing [36]. Accordingly, Eq. 4 becomes

$$G(\phi, T) = \underbrace{\mu^{p0}\phi + \mu^{p+}(1 - \phi)}_{H_0} + \underbrace{k_B T \phi \log(\phi) + k_B T (1 - \phi) \log(1 - \phi)}_{TS_{mix}}. \quad (6)$$

156 where k_B is the Boltzmann constant. Eq. 6 is plotted in Fig. 2c for different
 157 temperatures. Since the pure phases are entropically unfavorable, the systems'
 158 equilibrium lays in its energetic minimum characterized by the coordinates ϕ_0
 159 and G_0 . ϕ_0 can be found by measuring the conductance of a PEDOT:PSS film
 160 in deionized water (DIW), where, in absence of a reducing agent, the charge
 161 concentration is $[PSS^-]_0$, and comparing it with its conductance in the so-
 162 lution containing the salt, where the charge concentration is $[PSS^-]_0(1 - \phi)$.
 163 By repeating this experiment at different temperatures, we can estimate the
 164 temperature-dependence of ϕ which, according to Eq. 6, for infinitely high
 165 temperature $\phi_0 \rightarrow 0.5$ (representing an ideally mixed system).

166 We found that the conductance of the PEDOT:PSS in the electrolytic so-
 167 lution decreases with temperature. As shown in Fig. S2, the reduced PEDOT
 168 concentration ϕ increase from 8% at room temperature to 11.5% at 60°C. The
 169 details of the calculations are reported in Note S1. A temperature-dependent
 170 doping concentration, linked to a higher entropic contribution ($\phi_0 \rightarrow 0.5$ for
 171 $T \rightarrow \infty$) is compatible with a thermodynamic picture. We now aim to generalize
 172 the mathematical framework in order to describe the behavior of PEDOT:PSS
 173 in the presence of an external gate electrode.

174 3 Thermodynamics of OECTs: entropy of mix- 175 ing

176 The derivative of the Gibbs energy is the chemical potential μ

$$\mu(\phi, T) = \frac{dG(\phi, T)}{d\phi} = \mu^{p+} - \mu^{p0} + k_B T \log\left(\frac{\phi}{1 - \phi}\right). \quad (7)$$

177 μ is plotted in Fig. 2d for different temperatures. The equilibrium state, char-
 178 acterized by $\mu_0 = \mu(\phi_0) = 0$, can be altered by an external stimulus *e.g.*, an
 179 electrical (gate) potential V_{gs} , hence introducing the electrochemical potential
 180 in the channel $\bar{\mu}$

$$\bar{\mu} = \mu + e(V_{gs} - V_{ch}), \quad (8)$$

181 with V_{ch} being the potential in the channel, which depends on the drain-source
 182 voltage V_{ds} according to Eq. S6. By plugging Eq. 8 into Eq. 7, combining it
 183 with Eq. S2, and integrating over the channel, we obtain the following expression
 184 for the current I_d flowing in the OECT channel for a given T , V_{ds} , and V_{gs}

$$I_d = A_h \frac{Wt}{L} [PSS^-]_0 k_B T \log\left(\frac{Ze^{-\beta(V_{gs} - V_{ds})} + 1}{Ze^{-\beta V_{gs}} + 1}\right) \quad (9)$$

Figure 2: a) Redox reaction between PEDOT⁰ and PEDOT⁺. The thermodynamic analysis of this equilibrium, composed of partly oxidized and partly reduced PEDOT in the channel highlights important OECT features, not considered in current models. b) Mathematical workflow leading to the voltage and temperature dependencies of the channel current of an OECT. Two stages can be distinguished: a first thermodynamic analysis of the chemical reaction (cyan box), and a following bridge between chemical potential and the charge accumulated in the channel q (yellow box). c) Gibbs free energy at different temperatures for the ideal gas model, with a sketch of a fully reduced PEDOT phase (pink) and fully oxidized phase (blue). Upon derivation, the chemical potential d) is obtained, and by introducing the electrochemical potential (See Note S2) a transfer curve can be extracted as shown in e). f) Transfer characteristics of a PEDOT:PSS OECT in 100 mM NaCl solution with $V_{ds} = -0.6$ V and -0.3 V. The experimental curves (red circles) have been fitted (solid lines) with f) the FET-based model (Bernards model), g) with the thermodynamic model in the ideal gas assumption, and h) with the thermodynamic model including the enthalpy of mixing. The device features $W = 50\mu\text{m}$, $L = 200\mu\text{m}$, $t = 200\text{nm}$. The parameters for the fits are: $V_p = 0.57\text{V}$ and $A_h C = 40\text{F/cm/s/V}$ for the FET model. For the ideal gas scenario: $\mu^{p^+} + \mu^{p^0} = 1 \cdot 10^{-21}\text{J}$, $A_h[PSS^{\text{I}}]_0 = 1.06 \cdot 10^{22}\text{C/cm}^2/\text{s/V}$, $T = 300\text{K}$, and $\alpha = 0.2$ (see Eq. S13). When adding the enthalpy: $h_1 = 0.20$, $h_2 = 0.18$, $h_3 = 0.20$.

185 where $\beta = q/k_B T$ is the ratio of the elementary charge to thermal energy and
 186 $Z = \exp(\frac{\mu^{p+} - \mu^{p0}}{k_B T})$ is a material-dependent constant that includes the chemical
 187 potential of the unmixed species. Refer to Note S2 for the full derivation of
 188 Eq. 9. In doing so, the crucial point distinguishing this model from FET-based
 189 models is the calculation of the accumulated charge in the channel: the charge
 190 accumulation is not directly proportional to the gate-source voltage as in a plate
 191 capacitor model. Rather, it is a nonlinear function of the gate potential (see
 192 Fig. 1c) that is derived directly from the equilibrium constant in Eq. 3. Under
 193 the condition that $H_{mix} = 0$, *i.e.*, when particle-particle interactions are
 194 neglected, the system is approximated to an ideal gas. While this seems a far-
 195 reaching simplification, it shines light on some basic features of OECTs as it
 196 can be seen in Figure 2e where we plot Eq. 9 as a function of the gate-source
 197 voltage. Firstly, Eq. 9 includes the linear proportionality with the geomet-
 198 ric parameters of the channel and with the hole mobility, as in the Bernards
 199 model. In contrast to it, it does not feature the capacitance, underscoring the
 200 fact that we did not consider the system as a plate-capacitor, and there is no
 201 pinch-off voltage, whose physical meaning in OECTs is unclear. Moreover, it
 202 captures the saturation in the off-state (due to the complete PEDOT reduction
 203 ($\phi = 1$) as well as the saturation in the on-state (complete oxidation ($\phi = 0$))
 204 as shown in Fig. 2c. The saturation in the on-state, relevant for analog cir-
 205 cuit applications, was never described in previous theories for OECTs. From
 206 a thermodynamic standpoint, $\mu(\phi = 0) \rightarrow -\infty$ and $\mu(\phi = 1) \rightarrow +\infty$ as
 207 shown in Fig. 2 and Eq. 7. This means that huge changes in chemical potential
 208 *i.e.*, large variation of V_{gs} , bring about small changes in cation concentration,
 209 hence saturation of the drain current. Furthermore, this simplified model fore-
 210 sees that, at room temperature, a gate voltage of less than 1 V is needed to
 211 drive a PEDOT:PSS-based OECT from the on-state to the off-state, in good
 212 agreement with state-of-the-art OECTs. We therefore conclude that the large
 213 transconductance typical of OECTs is a purely entropy-driven phenomenon, as
 214 also argued in Ref. [35]. Another important implication of the model is the
 215 explanation of the large transconductance that OECTs show for $V_{gs} \approx 0V$. As
 216 highlighted in Refs. [37, 38], this is of particular interest for applications such
 217 as biosignal monitoring (since biological signals are in the range of tens of mil-
 218 livolts), and for self-powered devices. According to the thermodynamic model,
 219 the derivative of the chemical potential is vanishing at ϕ_0 (*i.e.*, where the system
 220 spontaneously evolves towards, in absence of a gate voltage). As a result, for
 221 $V_{gs} \approx 0$, small ΔV_{gs} results in large changes in ionic content in the channel,
 222 which directly translates into the highest transconductance.

223
 224 In Figs. 2f-g, the transfer characteristics are fitted with the thermodynamic
 225 model and compared to the traditional FET-based model (Bernards model),
 226 revealing a much better agreement with experimental data even for the simplistic
 227 ideal gas model. Finally, a natural consequence of the thermodynamic model
 228 is the dependence of the transfer characteristics on the doping level and salt
 229 concentration. This dependence is included in the parameter Z (see Eqs. S16

and S17, and Fig. S3a). Increasing $[PSS^-]_0$ is reflected in a larger on-current, higher transconductance and larger V_p (as defined by the extrapolation of the transfer curve in the traditional MOSFET model). The alteration of the doping level was used, for example, by Keene *et al.* to produce PEDOT:PSS-based enhancement-mode transistors [39]. Their data can be fitted using Eq. 9, as shown in Fig. S4. Kim *et al.* reported a method to improve the structural order in a PEDOT:PSS film, with impressive consequences on its charge transport properties [40]. However, their data can be analyzed through the lens of our thermodynamic model. Namely, the 4.5-fold increase in on-current showed by the transistor after the treatment, combined with a shift in threshold voltage of 0.7 V is consistent with a 4.5 time increase of the doping concentration $[PSS^-]_0$ (see Fig. S5). Hence, we suggest that the increment in conductivity is primarily due to a larger doping level, rather than the transport improvement that Kim *et al.* suggest, which, however, can explain the improved long-term stability of the device. As for the salt concentration, the model reproduces the Nernstian dependence used in OECT-based ion sensors [7, 32], as shown in Fig. S3b.

4 Enthalphy of mixing

In order to achieve better quantitative agreement with experimental data, we must go beyond the ideal gas approximation and allow for enthalpic contributions H_{mix} arising from the interaction between reduced PEDOT pairs (interaction parameter h_1), between oxidized PEDOT pairs (interaction parameter h_2), or between each other (interaction parameter h_3) using the following term describing interactions as

$$H_{mix} = k_B T (h_1 \phi^2 + h_2 (1 - \phi)^2 + h_3 (1 - \phi) \phi). \quad (10)$$

Differently from the ideal gas scenario, $\phi(\mu)$ cannot be explicated if $H_{mix} \neq 0$. We need to resort to numerical simulations for the integration in Eq. S9 plotting and data fitting (see Note S3 for the full code). With this method, we fit the transfer characteristics as shown in Fig. 2f, decisively improving with respect to the ideal gas scenario, and obtaining excellent agreement with the experimental data.

The presence of an underlying S-shaped chemical potential can be directly probed by measuring a transfer curve for $V_{ds} \rightarrow 0$ (See Eq. S14). Lowering the drain-source voltage to such a low value makes the channel potential homogeneous and, mathematically speaking, reduces the integral along the channel length to a point (See Fig. S6). We do this for a number of material combinations, fit the data, and analyze the parameters used for the modeling.

For example, using larger cations (K instead of Na as in Figs. 3a-b), the charges are forced to stay further, lowering the Coulomb interaction energy (which we believe is mainly reflected in the decrease of the interaction parameters h_1 , h_2 , and h_3). Moreover, different solvents can be used to validate the model. If a water-free solvent is used, the enthalpy of mixing is larger than in

Figure 3: Investigation of the chemical potential and free energy underlying the transfer characteristics of an OECT immersed in a) 100 mM NaCl aqueous solution, b) 100 mM KCl aqueous solution, c) ionic liquid, d) 100 mM LiClO₄ in butanol, and e) 100 mM LiClO₄ in water. Experimentally determined curves (circles) are fitted with the blue solid curves. The histograms on the right display the parameters used for the fits.

the case of water. This is visible when employing an ionic liquid (Fig. 3c) or butanol (Fig. 3d) as electrolyte. Figs. 3d-e compare OECTs immersed in a solution of 100 mM LiClO_4 , first in butanol and then in water. Water, with its higher dielectric constant, significantly lowers the contribution of H_{mix} , again reflected in the decrease of the interaction parameters.

Besides the trend, it is worth discussing the absolute values of the H_{mix} contribution. It is important to state that its magnitude is a small correction to the ideal gas scenario, even though the electrostatic interaction that arise between holes, cations, and polyelectrolyte may make a larger effect be expected. This apparent paradox is readily resolved by reasoning in terms of energy variation ΔG : in the fully reduced phase, the PSS dopants are paired with positively charged polarons. When cations are injected, they replace the polaronic charge without altering dramatically the energetic landscape. This process is sketched in Fig. S7.

Therefore, the driving force behind the operation of an OECT is entropy, with small perturbations coming from the enthalpic terms. This insight is crucial for targeted material design as it foresees that modification to the material morphology or chemistry, which in turn affect the Coulomb forces, slightly alter the device properties (although they can be used to shift the threshold voltage). Instead, the entropic term must be targeted in order to change the device's figures of merit decisively. For example, the ionic presence in the channel, dominated by entropy, affects the electrolyte/polymer interface potential [33]. Such interface potential not only can improve the device performance, but can be rendered to enhance affinity to biological systems and viability for cell cultures [23, 41, 42],

5 Hysteresis and two-phase equilibria in OECTs

Hysteresis is ubiquitous in OECT IV-curves. A number of effects can cause hysteretic behavior, *e.g.*, trap states, channel charging with multiple time-constants, and capacitive currents. Hysteresis plays an important role in technological applications: for traditional circuit design, it is a property to be minimized; conversely, large and stable hysteretic behavior can become precious for long-term memory effects useful in neuromorphic devices. Despite the attempts to characterize and explain the origin of hysteresis in OECTs, its origin remains unknown. Here, we concentrate on the peculiar time-independent hysteresis that has been shown for OECTs with solid-state electrolyte [21].

We hypothesize that, under certain conditions, thermodynamic imposes a minimal hysteretic behavior of the devices, which may add to the other possible effects listed above. As explained in the previous sections, the transfer curve of an OECT is directly related to the chemical potential of the system, and can be obtained by integrating over the channel length. Thus, the shape of $\mu(\phi)$ governs the slope of the transistor when it switches from the on- to the off-state. However, depending on the parameters of the function $G(\phi)$ (given by the material system), the peculiar situation might occur that the slope of the

Figure 4: a) Free energy profile with $h_1 = h_2 = 0, h_3 = 1.54$, its derivative and the resulting (theoretical) transfer curve for $V_{ds}=100$ mV (dashed line). When the theoretical transconductance surpasses the thermodynamic limit of 60 mV/dec at room temperature, the current must follow a less steep path to turn on (yellow) and to turn off (orange line). b) Free energy profile with $h_1 = h_2 = 0, h_3 = 3.07$ showing two minima, its non-monotonic derivative and the resulting transfer curve for $V_{ds}=100$ mV (dashed line). c) Fit of a solid OECT showing the hysteretic behavior produced by the two-phase equilibrium. Circles are the experimental data, dashed line is the theoretical, underlying transfer curve.

314 chemical potential $\frac{d\mu(\phi)}{d\phi} \approx 0$, resulting in an almost perpendicular transition in
 315 the transfer curve of the OECT. Such a situation is shown in Fig. 4a. In this
 316 scenario, the trans-resistance is vanishing. However, such a sharp transition
 317 cannot be measured experimentally due to access resistance limitations (*e.g.*,
 318 contact resistance). Even under best experimental conditions, the slope of the
 319 transfer curve should be limited to the Boltzmann limit of 60 mV/dec at room
 320 temperature. Thus, implying that the slope is limited to this value, we conclude
 321 that the device would show a hysteresis when cycling between on- and off-state
 322 (see orange and yellow curves in Fig. 4a (right panel)). Even more peculiar, if
 323 – at a given temperature – the energy penalty coming from the particle-particle
 324 interaction is significant, Eq. 6 may feature two minima (Fig. 4b). This is a
 325 common scenario encountered in binary mixtures, where phase separation leads
 326 to the formation of two phases with different relative composition of its con-
 327 stituents. The interpretation of a two-minimum energy profile in the framework
 328 of this model for OECTs is not trivial: the chemical potential is not monotonic,
 329 therefore, the transfer curve is expected to show negative differential resistance.
 330 This scenario has already been analyzed in-depth in the framework of lithium
 331 batteries, where thermodynamics impose a minimal hysteretic behavior due to
 332 fast rearrangement of Li^+ [43]: while sweeping the voltage, the system follows
 333 either one of two meta-stable paths, hence leading to hysteresis as shown in Fig.
 334 4b. Similarly, in a PEDOT-electrolyte-PEDOT system, if fast ionic redistribu-
 335 tion occurs, as for example in the case of solid-state electrolytes [17, 44], the
 336 same effect is observed. It is worth highlighting that the hysteresis in insertion
 337 batteries amounts up to millivolts, while in OECTs it can be much larger. This
 338 is justified by the fact that small differences in the energy of the two equilibria
 339 in the gate current can translate into huge differences in the drain current due
 340 to the exceptional properties of OECTs as transducers of ionic currents.
 341 A number of hysteresis observations have been reported, but never explained in
 342 terms of two-phase system in the framework of OECTs. Rivnay *et al.* observed
 343 a long-term memory effect which they refer to as "memory level" that seems
 344 to stem from a permanent change of the channel's conductivity. They show
 345 how this mechanism can be harnessed to show synaptic properties of OECTs.
 346 Such mechanism is enabled when a particular current level, which they name
 347 "memory threshold", is reached, after which the channel seems to acquire this
 348 long-term memory effect [9]. Weissbach *et al.* observed very stable and repro-
 349 ducible hysteresis in solid-state electrolyte-gated OECTs without giving physical
 350 insights on its origin. In particular, a peculiar increase of hysteresis for slower
 351 sweeps has been observed, which is in contrast with a trap-release models or
 352 capacitive currents. The hysteresis width decreases only for sweeps slower than
 353 0.005 V/s [21].
 354 In Fig. 4c, we fit the hysteretic transfer curve of a solid-state electrolyte-gated
 355 OECT using the model proposed by Dreyer *et al.* [43] and adapted for OECTs.
 356 A very flat chemical potential in a wide range of ϕ is the root of such high
 357 transconductance of the device.

6 Conclusions

In this work, we develop a theoretical framework that explains a multitude of properties of organic electrochemical transistors. Our approach describes the chemical interactions that control OECT operation. Our model starts from the equilibrium constant of the redox reaction between dopant and conducting polymer, and argues with Gibbs energy and chemical potential in order to go beyond the simple plate-capacitor picture assumed in traditional OECT models. With the aid of numerical simulations and experimental data, we validate the main predictions of the model. We thus achieve a comprehensive picture that bridges the many and fragmented theoretical approaches proposed so far. These include the particular S-shape of the transfer curve that OECTs feature, their saturation in the on- and off-state, and their operation below 1 V. Moreover, we show how this model can be used to investigate materials properties in order to engineer devices with targeted figures of merit. Although our work focuses on the reference system PEDOT:PSS, we suggest the thermodynamic model can be generalized to any type of OECT because vastly different materials (*e.g.*, n-type [45] or normally-off [39] OECTs) show analogous shapes of the IV characteristics and on-to-off switch in a similar voltage range of around 1 V. After quantifying the enthalpic terms coming from the electrostatic interactions in the channel, we reveal that entropy is the main driver behind the operation of an OECT. Finally, we borrow the thermodynamics from the field of insertion batteries and propose an explanation for the often-reported peculiar hysteretic behavior of solid-state OECTs. We hope that our work will stimulate further research which extends our still simple theoretical model and allow quantitative comparison with various OECT devices.

Methods

Substrate patterning: starting from a glass 1 inch substrate, 3 nm of Cr and 50 nm of Au were evaporated, followed by the gold patterning using the positive resist AZ1518 (microchemicals). PEDOT:PSS (Clevios PH 1000 - Heraeus) (+5% EG, 0.5% (3-glycidyloxypropyl)trimethoxysilane (GOPS)) was spincoated at 3000 rpm, and then patterned with the orthogonal photoresist OSCoR 5001 (Orthogonal Inc.). Experiments were made with liquid electrolytic solutions or with solid electrolytes prepared as explained in Ref. [21]. All electrical measurements with liquid electrolytes, as well as the temperature control, were carried out with a parameter analyzer Keithley interfaced and controlled with the software SweepMe! (sweep-me.net) in ambient condition. Measurement for the solid electrolyte are carried out in glove-box. Numerical simulations were coded in Matlab, code in Note S3

References

- [1] Bryan D Paulsen, Klas Tybrandt, Eleni Stavrinidou, and Jonathan Rivnay. Organic mixed ionic–electronic conductors. *Nature Materials*, 19(1):13–26, 2020.
- [2] Jonathan Rivnay, Roisin M Owens, and George G Malliaras. The rise of organic bioelectronics. *Chemistry of Materials*, 26(1):679–685, 2014.
- [3] Pierre Leleux, Jonathan Rivnay, Thomas Lonjaret, Jean-Michel Badier, Christian Bénar, Thierry Hervé, Patrick Chauvel, and George G Malliaras. Organic electrochemical transistors for clinical applications. *Advanced Healthcare Materials*, 4(1):142–147, 2015.
- [4] Dion Khodagholy, Thomas Doublet, Pascale Quilichini, Moshe Gurfinkel, Pierre Leleux, Antoine Ghestem, Esma Ismailova, Thierry Hervé, Sébastien Sanaur, Christophe Bernard, et al. In vivo recordings of brain activity using organic transistors. *Nature Communications*, 4(1):1–7, 2013.
- [5] Xenofon Strakosas, Manuelle Bongo, and Roisin M Owens. The organic electrochemical transistor for biological applications. *Journal of Applied Polymer Science*, 132(15), 2015.
- [6] Jonathan Rivnay, Sahika Inal, Alberto Salleo, Róisín M Owens, Magnus Berggren, and George G Malliaras. Organic electrochemical transistors. *Nature Reviews Materials*, 3(2):1–14, 2018.
- [7] Peng Lin, Feng Yan, and Helen LW Chan. Ion-sensitive properties of organic electrochemical transistors. *ACS Applied Materials & Interfaces*, 2(6):1637–1641, 2010.
- [8] Matteo Cucchi, Hans Kleemann, Hsin Tseng, Giuseppe Ciccone, Alexander Lee, Darius Pohl, and Karl Leo. Directed growth of dendritic polymer

- networks for organic electrochemical transistors and artificial synapses. *Advanced Electronic Materials*, page 2100586, 2021.
- [9] Xudong Ji, Bryan D Paulsen, Gary KK Chik, Ruiheng Wu, Yuyang Yin, Paddy KL Chan, and Jonathan Rivnay. Mimicking associative learning using an ion-trapping non-volatile synaptic organic electrochemical transistor. *Nature Communications*, 12(1):1–12, 2021.
- [10] Yoei Van De Burgt and Paschalis Gkoupidenis. Organic materials and devices for brain-inspired computing: From artificial implementation to biophysical realism. *MRS Bulletin*, 45(8):631–640, 2020.
- [11] Sébastien Pecqueur, Maurizio Mastropasqua Talamo, David Guérin, Philippe Blanchard, Jean Roncali, Dominique Vuillaume, and Fabien Alibart. Neuromorphic time-dependent pattern classification with organic electrochemical transistor arrays. *Advanced Electronic Materials*, 4(9):1800166, 2018.
- [12] Matteo Cucchi, Christopher Gruener, Lautaro Petrauskas, Peter Steiner, Hsin Tseng, Axel Fischer, Bogdan Penkovsky, Christian Matthus, Peter Birkholz, Hans Kleemann, et al. Reservoir computing with biocompatible organic electrochemical networks for brain-inspired biosignal classification. *Science Advances*, 7(34):eabh0693, 2021.
- [13] Lautaro Petrauskas, Matteo Cucchi, Christopher Grüner, Frank Ellinger, Karl Leo, Christian Matthus, and Hans Kleemann. Nonlinear behavior of dendritic polymer networks for reservoir computing. *Advanced Electronic Materials*, page 2100330, 2021.
- [14] Luke J Currano, F Connor Sage, Matthew Hagedon, Leslie Hamilton, Julia Patrone, and Konstantinos Gerasopoulos. Wearable sensor system for detection of lactate in sweat. *Scientific Reports*, 8(1):1–11, 2018.
- [15] Scott T Keene, Daragh Fogarty, Ross Cooke, Carlos D Casadevall, Alberto Salleo, and Onur Parlak. Wearable organic electrochemical transistor patch for multiplexed sensing of calcium and ammonium ions from human perspiration. *Advanced healthcare materials*, 8(24):1901321, 2019.
- [16] Alessandra Campana, Tobias Cramer, Daniel T Simon, Magnus Berggren, and Fabio Biscarini. Electrocardiographic recording with conformable organic electrochemical transistor fabricated on resorbable bioscaffold. *Advanced Materials*, 26(23):3874–3878, 2014.
- [17] Armantas Melianas, TJ Quill, G LeCroy, Y Tuchman, H v Loo, ST Keene, Alexander Giovannitti, HR Lee, IP Maria, Iain McCulloch, et al. Temperature-resilient solid-state organic artificial synapses for neuromorphic computing. *Science Advances*, 6(27):eabb2958, 2020.

- [18] Yoeri van de Burgt, Ewout Lubberman, Elliot J Fuller, Scott T Keene, Grégorio C Faria, Sapan Agarwal, Matthew J Marinella, A Alec Talin, and Alberto Salleo. A non-volatile organic electrochemical device as a low-voltage artificial synapse for neuromorphic computing. *Nature Materials*, 16(4):414–418, 2017.
- [19] Peter Andersson Ersman, Roman Lassnig, Jan Strandberg, Deyu Tu, Vahid Keshmiri, Robert Forchheimer, Simone Fabiano, Göran Gustafsson, and Magnus Berggren. All-printed large-scale integrated circuits based on organic electrochemical transistors. *Nature Communications*, 10(1):1–9, 2019.
- [20] Jakob Lenz, Anna Monika Seiler, Fabian Rudolf Geisenhof, Felix Winterer, Kenji Watanabe, Takashi Taniguchi, and Ralf Thomas Weitz. High-performance vertical organic transistors of sub-5 nm channel length. *Nano Letters*, 21(10):4430–4436, 2021.
- [21] Anton Weissbach, Lukas M. Bongartz, Matteo Cucchi, Hsin Tseng, Karl Leo, and Hans Kleemann. Photopatternable solid electrolyte for integrable organic electrochemical transistors: Operation and hysteresis. *J. Mater. Chem. C*, in-press: DOI 10.1039/d1tc04230k, FOR THE REVIEWERS: PDF IS ATTACHED, 2021.
- [22] Jakob Lenz, Fabio Del Giudice, Fabian R Geisenhof, Felix Winterer, and R Thomas Weitz. Vertical, electrolyte-gated organic transistors show continuous operation in the mV regime and artificial synaptic behaviour. *Nature nanotechnology*, 14(6):579–585, 2019.
- [23] Marco Marzocchi, Isacco Gualandi, Maria Calienni, Isabella Zironi, Erika Scavetta, Gastone Castellani, and Beatrice Fraboni. Physical and electrochemical properties of PEDOT:PSS as a tool for controlling cell growth. *ACS Applied Materials & Interfaces*, 7(32):17993–18003, 2015.
- [24] Jacob T Friedlein, Robert R McLeod, and Jonathan Rivnay. Device physics of organic electrochemical transistors. *Organic Electronics*, 63:398–414, 2018.
- [25] Jacob T Friedlein, Jonathan Rivnay, David H Dunlap, Iain McCulloch, Sean E Shaheen, Robert R McLeod, and George G Malliaras. Influence of disorder on transfer characteristics of organic electrochemical transistors. *Applied Physics Letters*, 111(2):023301, 2017.
- [26] Francesco Gentile, Davide Delmonte, Massimo Solzi, Marco Villani, Salvatore Iannotta, Andrea Zappettini, and Nicola Coppede. A theoretical model for the time varying current in organic electrochemical transistors in a dynamic regime. *Organic Electronics*, 35:59–64, 2016.
- [27] Pushpa R Paudel, Vikash Kaphle, Drona Dahal, Raj Kishen Radha Krishnan, and Björn Lüssem. Tuning the transconductance of organic electrochemical transistors. *Advanced Functional Materials*, 31(3):2004939, 2021.

- 498 [28] Vikash Kaphle, Pushpa Raj Paudel, Drona Dahal, Raj Kishen Radha Kr-
499 ishnan, and Björn Lüssem. Finding the equilibrium of organic electrochem-
500 ical transistors. *Nature Communications*, 11(1):1–11, 2020.
- 501 [29] Marek Zdzisław Szymański, Deyu Tu, and Robert Forchheimer. 2-d drift-
502 diffusion simulation of organic electrochemical transistors. *IEEE Transac-*
503 *tions on Electron Devices*, 64(12):5114–5120, 2017.
- 504 [30] Renan Colucci, Henrique Frulani de Paula Barbosa, Florian Günther,
505 Priscila Cavassin, and Gregório Couto Faria. Recent advances in mod-
506 eling organic electrochemical transistors. *Flexible and Printed Electronics*,
507 5(1):013001, 2020.
- 508 [31] Sahika Inal, George G Malliaras, and Jonathan Rivnay. Benchmarking
509 organic mixed conductors for transistors. *Nature Communications*, 8(1):1–
510 7, 2017.
- 511 [32] Hsin Tseng, Matteo Cucchi, Anton Weissbach, Karl Leo, and Hans Klee-
512 mann. Membrane-free, selective ion sensing by combining organic electro-
513 chemical transistors and impedance analysis of ionic diffusion. *ACS Applied*
514 *Electronic Materials*, 2021.
- 515 [33] Paolo Romele, Matteo Ghittorelli, Zsolt Miklós Kovács-Vajna, and Fabrizio
516 Torricelli. Ion buffering and interface charge enable high performance elec-
517 tronics with organic electrochemical transistors. *Nature Communications*,
518 10(1):1–11, 2019.
- 519 [34] Klas Tybrandt, Igor V Zozoulenko, and Magnus Berggren. Chem-
520 ical potential–electric double layer coupling in conjugated polymer–
521 polyelectrolyte blends. *Science Advances*, 3(12):eaao3659, 2017.
- 522 [35] Gonzague Rebetez, Olivier Bardagot, Joël Affolter, Julien Réhault, and
523 Natalie Banerji. What drives the kinetics and doping level in the electro-
524 chemical reactions of pedot: Pss? *Advanced Functional Materials*, page
525 2105821, 2021.
- 526 [36] Ken A Dill, Sarina Bromberg, and Dirk Stigter. *Molecular driving forces:*
527 *statistical thermodynamics in biology, chemistry, physics, and nanoscience.*
528 Garland Science, 2010.
- 529 [37] Jonathan Rivnay, Pierre Leleux, Michele Sessolo, Dion Khodagholy,
530 Thierry Hervé, Michel Flocchi, and George G Malliaras. Organic elec-
531 trochemical transistors with maximum transconductance at zero gate bias.
532 *Advanced Materials*, 25(48):7010–7014, 2013.
- 533 [38] Songyan Yu and Erin L Ratcliff. Tuning organic electrochemical transistor
534 (oect) transconductance toward zero gate voltage in the faradaic mode.
535 *ACS Applied Materials & Interfaces*, 2021.

- [39] Scott T Keene, Tom PA van der Pol, Dante Zakhidov, Christ HL Weijtens, René AJ Janssen, Alberto Salleo, and Yoeri van de Burgt. Enhancement-mode pedot: Pss organic electrochemical transistors using molecular dedoping. *Advanced Materials*, 32(19):2000270, 2020.
- [40] Seong-Min Kim, Chang-Hyun Kim, Youngseok Kim, Nara Kim, Won-June Lee, Eun-Hak Lee, Dokyun Kim, Sungjun Park, Kwanghee Lee, Jonathan Rivnay, et al. Influence of pedot: Pss crystallinity and composition on electrochemical transistor performance and long-term stability. *Nature Communications*, 9(1):1–9, 2018.
- [41] Adrian Magaz, Ben F Spencer, John G Hardy, Xu Li, Julie E Gough, and Jonny J Blaker. Modulation of neuronal cell affinity on pedot–pss nonwoven silk scaffolds for neural tissue engineering. *ACS Biomaterials Science & Engineering*, 6(12):6906–6916, 2020.
- [42] Fabrizio Amorini, Isabella Zironi, Marco Marzocchi, Isacco Gualandi, Maria Calienni, Tobias Cramer, Beatrice Fraboni, and Gastone Castellani. Electrically controlled “sponge effect” of pedot: Pss governs membrane potential and cellular growth. *ACS applied materials & interfaces*, 9(8):6679–6689, 2017.
- [43] Wolfgang Dreyer, Janko Jamnik, Clemens Gohlke, Robert Huth, Jože Moškon, and Miran Gaberšček. The thermodynamic origin of hysteresis in insertion batteries. *Nature Materials*, 9(5):448–453, 2010.
- [44] Armantas Melianas, Min-A Kang, Armin VahidMohammadi, Weiqian Tian, Yury Gogotsi, Alberto Salleo, and Mahiar Max Hamedi. High-speed ionic synaptic memory based on two-dimensional titanium carbide mxene. *arXiv preprint arXiv:2104.05396*, 2021.
- [45] Hengda Sun, Jennifer Gerasimov, Magnus Berggren, and Simone Fabiano. n-type organic electrochemical transistors: materials and challenges. *Journal of Materials Chemistry C*, 6(44):11778–11784, 2018.
- [46] Olga Bubnova, Zia Ullah Khan, Hui Wang, Slawomir Braun, Drew R Evans, Manrico Fabretto, Pejman Hojati-Talemi, Daniel Dagnelund, Jean-Baptiste Arlin, Yves H Geerts, et al. Semi-metallic polymers. *Nature Materials*, 13(2):190–194, 2014.

Figure S1: Gate-dependent capacitance. a) electrochemical impedance spectroscopy of an OECT channel measured with an Ag/AgCl electrode with amplitude of 10 mV and varying bias. b) the extracted channel capacitance, showing that the capacitance of the channel is not fixed, rather strongly gate-dependent.

568 Supplementary Information

Figure S2: a) Temperature dependence of the Gibbs free energy according to the ideal gas theory ($\mu^{p+} = -60\text{meV/mol}$ and $\mu^{p0} = 0$). Higher temperatures shift the minimum towards $\phi_0 = 0.5$ and to lower energies. b) Measurement of the current flowing in a PEDOT:PSS thin-film at different temperature, in deionized (DIW) and DIW:NaCl (circles). Curves are fitted with a linear regression (solid lines). The experiment in DIW is used to estimate the contribution of the temperature-dependent mobility, which is then subtracted, leading to the blue dashed line. The same contribution is subtracted from the current measured in DIW:NaCl. The negative slope shows that, besides the increased mobility, the polaron density is lowered. c) Calculated concentration of reduced PEDOT⁰ and doped PEDOT⁺ in the film at different temperatures according to Eq. S3.

Figure S3: Dependence of the drain current on the a) doping level $[PSS^-]_0$ and b) cation concentration $[c^+]$ according to Eq. 9.

Figure S4: Data taken from [39]. The thermodynamic model can fit well (even in the ideal gas assumption) the transfer curve before and after the doping process. For the intrinsic device $\alpha = 0.28$ (see Eq. S13) while for the dedoped material $\alpha = 0.41$. The doping concentration is 6.5 times larger in the case of the intrinsic device.

Figure S5: Data taken from [40]. The thermodynamic model can fit well (even in the ideal gas assumption) the transfer curve before and after the acid treatment, using $\alpha = 0.7$ (see Eq. S13) and $[PSS^-]_0$ 7 times larger after the treatment. Note that the model captures both the increased transconductance due to the larger on-current, and the shift in threshold voltage.

Figure S6: Sketch of the mathematical treatment proposed in the main text, from Gibbs free energy to the transfer curve.

Figure S7: Scheme of the oxidation process. The circles indicate the charged species in play, namely PSS^- , holes and sodium cations, and the arrows indicate the Coulomb interaction, either attraction (green) or repulsion (red). In going from fully reduced to fully oxidized, despite the important changes related to the chemical reaction and electronic charge density, from a thermodynamic point of view the situation did not change dramatically. This explains why an OECT must be described in terms of entropy, and why enthalpy play a secondary role.

569 **Note S1: calculation of $\phi(T)$**

570 In DIW, the charge concentration of PEDOT:PSS is fixed at $[PSS^-]_0$. There-
 571 fore, the current I flowing through a PEDOT:PSS film immersed deionized
 572 water (DIW) is given by

$$I = \Lambda_h[PEDOT^+] \frac{Wt}{L} V = \Lambda_h(T)[PSS^-]_0 \frac{Wt}{L} V, \quad (S1)$$

573 where $V=10$ mV. Thus, by increasing the temperature of the solution, the
 574 temperature-dependent hole mobility $\Lambda_h(T)$ is found.

575 The situation is different in NaCl(aq), where the current is given by
 576

$$I = \Lambda_h[PEDOT^+] \frac{Wt}{L} V = \Lambda_h(T)[PSS^-]_0(1 - \phi(T)) \frac{Wt}{L} V. \quad (S2)$$

577 By changing the temperature, both ϕ and Λ_h are expected to change. In
 578 both cases, we observe an increase of the conductivity which we ascribe to a
 579 temperature-activated hopping mechanism [46]. However, the slope is different.
 580 We assume that $\Lambda_h(T)$ is the same for PEDOT:PSS in DIW and NaCl(aq). By
 581 combining Eqs. S1 and S2, $\phi(T)$ is obtained as

$$\phi(T) = [PEDOT^0](T) = 1 - \frac{I_{NaCl}(T)}{I_{DIW}(T)}. \quad (S3)$$

582 In Eq. S3, we used the linear fits showed in Fig. S2 as I_{DIW} and I_{NaCl} . In
 583 doing so, we are considering the hole mobility to be independent of the ion
 584 concentration. Although this effect exists, Friedlein *et al.* showed that its
 585 magnitude is weak and should not compromise our results in the small range of
 586 dedoping level *i.e.*, from 8% to 11.5%.

587 Accordingly, the doping level (defined as $1-\phi$) decreases, revealing that the
 588 doping concentration of PEDOT:PSS only changes by 3.2% in the investigated
 589 temperature range.

590 Note S2: calculation of the drain current

591 In order to find the number of charges accumulated in the channel by the gate
 592 voltage, Ohm's law (Eq. S2) must be integrated over the channel length from 0
 593 to L (or equivalently from V_{ds} to 0) as done normally for thin-film transistors.

$$\int_0^L I_d = eV_{ds}\Lambda_h \frac{Wt}{L} [PSS^-]_0 \int_0^L (1 - \phi(\mu)) d\ell \quad (S4)$$

594 yielding

$$I_d = -e\Lambda_h \frac{Wt}{L} [PSS^-]_0 \int_{V_{ds}}^0 (1 - \phi(\mu)) dV_{ch} \quad (S5)$$

595 after considering a linearly dropping potential V_{ch} along the channel length
 596 (direction ℓ)

$$V_{ch}(\ell) = V_{ds}(1 - \frac{\ell}{L}) \quad (S6)$$

597 and its differential:

$$dV_{ch} = -\frac{V_{ds}}{L} d\ell \quad (S7)$$

598 In doing so we are assuming i) that the gradual channel approximation is valid
 599 *i.e.*, the field across the channel/electrolyte interface is much higher than the
 600 field between source and drain across the channel, and ii) a linearly dropping
 601 potential across the channel. The former holds true thanks to the exponential
 602 decay of the field in the electrolyte. The second is not necessarily true and
 603 strongly depends on the gate voltage. However, the result of the integral is not
 604 expected to vary much depending on the charge distribution.

605 To solve Eq. S5, we need $\phi(\mu)$, that can be found by inverting $\mu(\phi)$ in Eq. 7:

$$\phi(\mu) = (Z \exp(-\frac{\mu}{k_B T}) + 1)^{-1}. \quad (S8)$$

606 In Eq. S8, $Z = \exp(\frac{\mu^{p+} - \mu^{p0}}{k_B T})$ is directly related to the concentration of the
 607 electrolyte $[c]$ and doping level $[PSS^-]_0$ as shown in Eq. S17.

608 The introduction of a gate potential has the effect of shifting the system from
 609 its chemical equilibrium. By introducing the electrochemical potential $\bar{\mu}$, μ
 610 becomes a function of the potentials applied as $e(V_{gs} - V_{ch})$ as explained in the
 611 main text.

612 Combining Eqs. S5 and S8

$$I_d = -e \frac{Wt}{L} \Lambda_h [PSS^-]_0 \int_{V_{ds}}^0 dV_{ch} (1 - \frac{1}{Z e^{-\beta(V_{gs} - V_{ch})} + 1}) = e \frac{Wt}{L} \Lambda_h [PSS^-]_0 \frac{1}{\beta} \log(\frac{Z e^{\beta V_{ds}} + e^{\beta V_{gs}}}{Z + e^{\beta V_{gs}}}) \quad (S9)$$

613 with $\beta = \frac{e}{k_B T}$ (elementary charge divided by thermal energy).

614 Thus, the current that flows in the channel of an OEET, assuming no en-
 615 thalpy of mixing, depends on V_{ds} , V_{gs} , and T as follows:

$$I_d = \Lambda_h \frac{Wt}{L} [PSS^-]_0 k_B T \log(\frac{Z e^{-\beta(V_{gs} - V_{ds})} + 1}{Z e^{-\beta V_{gs}} + 1}). \quad (S10)$$

616 The same analysis for an enhancement-mode OECT would result in

$$I_d = e\Lambda_h \frac{Wt}{L} [PSS^-]_0 (V_{ds} - \frac{k_B T}{e} \log(\frac{Ze^{-\beta(V_{gs}-V_{ds})} + 1}{Ze^{-\beta V_{gs}} + 1})). \quad (S11)$$

617 Accordingly, the transconductance $g_m = \frac{dI_d}{dV_{gs}}$ is

$$g_m = e\Lambda_h [PSS^-]_0 \frac{Wt}{L} Z (\frac{1}{e^{\beta V_{gs}} + Z} - \frac{1}{e^{\beta(V_{gs}-V_{ds})} + Z}) \quad (S12)$$

618 and has the typical (and peculiar) bell-shaped form of $g_m(V_{gs})$ of OECTs.
 619 A final note on the gate voltage: in order to fully capture the current dependency
 620 on the applied gate voltage V_{gs} one must take into consideration that the gate
 621 voltage applied differs from the effective gate voltage $V_{g,eff}$ "felt" by the channel
 622 that drives the device at the channel/electrolyte interface due to the drop at
 623 the gate/electrolyte interface and across the solution. In this work, since we
 624 focused on the modeling of the material parameters, we simplified it as

$$V_{gs,eff} = \alpha V_{gs} \quad (S13)$$

625 where $0 < \alpha < 1$ is the remaining percentage of potential applied after dropping
 626 across the electrolyte and at the gate/electrolyte interface. Although the volt-
 627 age drop from gate/electrolyte interface to electrolyte/PSS interface can have a
 628 more complex, nonlinear, voltage-dependent and concentration-dependent, we
 629 use a linear approximation for the sake of simplicity, and may be the root of
 630 the unmatching fit in Fig. 2 in the turning-off region. A detailed analysis of the
 631 voltage drop at the gate/electrolyte and electrolyte/channel interface is given
 632 by Romele *et al.* [33].

633
 634 For the transfer measurements in Fig. 3 with $V_{ds} = 5mV$, we exploit the
 635 fact that $V_{gs} - V_{ch} \approx V_{gs}$ in order to rewrite Eq. S5 as

$$I_d = -e\Lambda_h \frac{Wt}{L} [PSS^-]_0 \int_{V_{ds}}^0 (1 - \phi(V_{gs} - V_{ch})) dV_{ch} \approx \Lambda_h \frac{Wt}{L} [PSS^-]_0 V_{ds} (1 - \phi(V_{gs})) \quad (S14)$$

636 from which the material-specific property $\phi(\mu)$ can be extracted.

637
 638 As for the parameter Z

$$Z = \exp(\frac{\mu^{p+} - \mu^{p0}}{k_B T}). \quad (S15)$$

639 According to Nernst equation

$$\mu^i = \mu_0^i + k_B T \log([c_i]) \quad (S16)$$

640 and considering that for each PEDOT⁰ there is a paired cation, one can rewrite
 641 Eq. S15 as

$$Z = \frac{[PSS^-]_0}{[c^+]} \exp(\frac{\mu_0^{p+} - \mu_0^{p-}}{k_B T}) \quad (S17)$$

642 where $[c^+]$ is the cation concentration in the channel. Note that the ion con-
643 centration in the channel and in the bulk solution are not necessarily the same
644 due to the establishment of Donnan's equilibrium [33].

645 **Note S3: MatLab code for plotting the channel** 646 **current**

```

647     x=linspace(0,1,1000);
648     mu1mu2=1e-21;
649     g0=1;
650     alpha=1;
651     T=300;
652     kb=1.38e-23;
653     h1=1e-22;
654     mu=6.2e+18/alpha*(kb*T.*log(x./(1-x)) + mu1mu2 +2*h1.*x);
655     vg_new=linspace(-1,1, 1000);
656     id_new=interp1(mu(2:end-1),x(2:end-1),vg_new);
657     naan=find(isnan(id_new)==0);
658     id_new(1:naan(1))=0;
659     id_new(naan(end):end)=1;
660     dvg=vg_new(2)-vg_new(1);
661     vd=-.1;
662     for sweep=1:length(vg_new)
663         [yy,idx1]=min(abs(vg_new(sweep)-vg_new));
664         [yy,idx2]=min(abs(vg_new(sweep)-vd-vg_new));
665         q(sweep)=sum(id_new(idx1:idx2))/(idx2-idx1+1);
666     end
667     plot(vg_new,g0*vd*(1-q));

```

668 **Acknowledgments**

669 We thank Dr. Ron Dockhorn for the fruitful conversations about the ther-
670 modynamics of conductive polymers. HT thanks the financial support by the
671 European Social Fund (ESF) and the Free State of Saxony in the framework of
672 OrgNanoMorph (project number: 100382168). LMB and HK are grateful for
673 funding from the the German Research Foundation (DFG, KL 2961/5-1). AW
674 thanks the project ESF Re-Learning (cfaed), ESF Number: 100382146.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SIThermodynamicsofOECTs.pdf](#)