

# Advances in ion injection in organic electrochemical transistors

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## Abstract

Organic electrochemical transistors (OECTs) utilize conjugated polymer's ability to conduct both ions and electronic holes to create devices that can interface with biology along with being used in neuromorphic and memory applications. Improving OECT design means better understanding the physics of ion injection and the effects of hydration on different conjugated polymers. Recent studies have found that OECT performance benefits from hydrophilic side chains on conjugated polymers. Performance has also been found to decrease in highly crystalline polymers. Additionally, ionic liquids have been utilized either in doping a conjugated polymer or in creating an ion exchange gel interface to improve performance. Finally, certain polymers exhibit a phase change upon ion injection resulting in a sharp ion front.

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## 1. Introduction

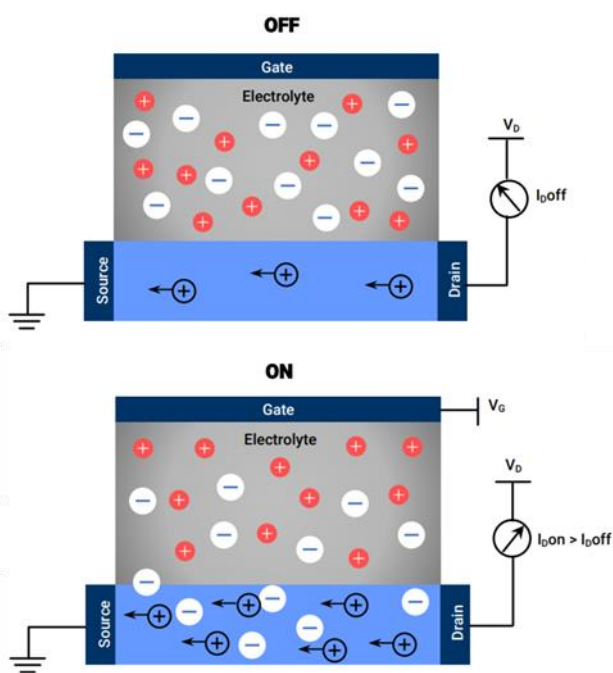
OECTs are a promising technology since they can interface with biology, turning the movement and concentration of ions into an electric signal. OECTs also have high signal amplification, operate at low voltages, and can be produced with simple low cost techniques. Although they have relatively low switching speeds in comparison with MOSFETs, OECTs have applications in bioelectronics like cell monitoring, neural interfacing, and electrophysiology [1].

Organic electrochemical transistors (OECTs) are transistors that use ion injection to modulate the bulk conductivity of an organic semiconductor [2]. Similar to a field effect transistor, a potential is applied from a source electrode to a drain electrode across the active material, in this case an organic semiconductor, (**Figure 1**). A gate potential is applied that modulates the conductivity and therefore the current across the active material in field effect transistors. In OECTs, an electrolyte is in contact with the organic semiconductor and, when a gate potential is applied across the electrolyte, ions are injected into the organic semiconductor and either decrease or increase the current depending on whether the OECT is depletion or accumulation mode.

Depletion-mode is how OECTs based on conducting polymers like poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate), (PEDOT:PSS), operate. PEDOT:PSS is composed of p-type doped PEDOT that allows for a current of holes to flow and sulfonate anions from PSS that compensate the charge. The depletion-mode OECT is on when no gate potential is applied, and the hole current moves freely from the drain to the source. The device reaches the off state once a negative gate potential is applied, driving cations from the electrolyte into the polymer and compensating the sulfonate anions which results in decreasing the hole current [2].

Accumulation-mode is how OECTs based on semiconducting polymers operate. The device is off when no gate potential is applied then reaches the on state as a larger positive gate potential is applied. The positive gate potential injects anions from the electrolyte into the polymer which induces a hole current along the backbone of the semiconducting polymer [2].

Transconductance is described as the relationship between the output current of a transistor and the input voltage. Transconductance can be found by taking the derivative of the transfer curve, i.e.  $g_m = \frac{\partial I_D}{\partial V_G}$  [2]. The response of an OECT



**Figure 1.** schematic of the off and on state of an accumulation-mode OEET.

can be described by Bernards model which yields equation 1 for the transconductance:

$$g_m = \frac{Wd}{L} \mu C^* (V_{th} - V_G) \quad (1)$$

where  $W$ ,  $d$ , and  $L$  describes the geometry of the transistor,  $\mu$  is the hole mobility,  $C^*$  is the volumetric capacitance, and  $V_{th}$  is the threshold voltage. Equation 1 is based on a depletion-mode OEET, for an accumulation-mode OEET the voltage terms would be swapped. The product  $\mu C^*$  is used to describe OEET performance, since the performance is dependent on both the hole mobility and ion injection. For most materials, hole mobility and ion injection are a compromise.

A barrier to improving OEET performance has been an incomplete understanding of ion injection and the effects an aqueous environment has on the organic semiconductor. Recent studies have focused on gaining a better understanding of the physics at play during ion injection in OEETs.

## 2. Aqueous Effects

Often, OEET materials are borrowed from organic field effect transistors (OFETs), a more common device, but OFETs do not operate in an aqueous environment and ions do not enter the material. Typical OFET organic semiconductors are conjugated polymers with side chains that are hydrophobic but enable better hole transport. Conjugated polymers like poly(3-hexylthiophene-2,5-diyl) (P3HT) have been altered to have more hydrophilic side chains into poly(3-([2-(2-methoxyethoxy)ethoxy)methyl]thiophene-2,5-diyl) (P3MEEMT) and have shown improved OEET performance [3]. Additionally, poly(2-(3,3'-bis(2-(2-(2-methoxy-

ethoxy)ethoxy)ethoxy)-[2,2'-bithiophen]-5-yl)thieno[3,2-b]thiophene) p(g2T-TT), a conjugate polymer with hydrophilic ethylene glycol side chains was tested at various ratios of ethylene glycol to hydrophobic aliphatic side chains and it was found to have the best OEET performance at 100% ethylene glycol side chains [4].

The effect of crystallinity on the hydrated semiconducting polymer has also been studied. More crystalline P3MEEMT was found to have good OFET performance but poor OEET performance [3]. Crystallinity improves the transport of holes in the dry polymer, but upon hydration, regions between the crystalline regions swell first disrupting the hole pathways between crystalline regions [3].

## 3. Phase Transition upon Ion Injection

Certain conjugated polymers have been found to undergo a phase change upon ion injection [5]. poly[2,5-bis(thiophenyl)-1,4-bis(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene] (PB2T-TEG) undergoes an 'unzipping' mechanism increasing the spacing between polymer backbones upon ion injection. Polymers like P3MEEMT display Fickian diffusion of ions, but PB2T-TEG displays a non-Fickian behavior with a sharp ion front [5]. The authors suggest this behavior could be exploited in computing applications or in improving energy storage in conjugated polymers.

## 4. Ionic Liquid and Gel Composites

Ionic liquids and ion exchange gels have been shown to improve performance when used in conjunction with hydrophobic conjugated polymers [6,7]. poly[2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-b]thiophene] (PBTTT) is a poor conductor of biologically relevant ions but a good conductor of large hydrophobic ions like bis(trifluoromethanesulfonyl)imide (TFSI-) [6]. A device architecture that places an ion exchange gel between the electrolyte and the polymer has shown improved performance [6]. A blend of poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) as the gel matrix and 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM TFSI) as the ionic liquid was the ion exchange gel used on PBTTT [6]. Upon

**Table 1.** Performance figures for conjugated polymers reviewed

Conjugated Polymer Studied	$\mu C^* (F \cdot cm^{-1} V^{-1} s^{-1})$
P3MEEMT, ethylene glycol-based side chains, accumulation-mode [3]	49.1±5.0
PEDOT:PSS, depletion-mode [3], most widely used	50
P(g2T-TT) [4], hydrophilic side chains	163
P(a2T-TT), hydrophobic side chains	9.88×10 <sup>-4</sup>
Ionic-liquid-doped PEDOT:PSS [7]	335
Ion exchange gel PBTTT [6]	179±40
PB2T-TEG, phase transition polymer [5]	25±4

applying a gate potential, the ions from the electrolyte enter the gel which then cause TFSI<sup>-</sup> ions to enter the polymer making it possible to detect other, more relevant ions.

Doping PEDOT:PSS with an ionic liquid has shown to dramatically increase OECT performance [7]. Where performance is usually a compromise between hole and ion mobility, ionic liquid in PEDOT:PSS improves both mobilities. Hole mobility is improved since it causes PEDOT:PSS to form a fibrillar structure that holes can easily follow [7]. Ion mobility is improved since the ionic liquid enhances the ionic character of PEDOT:PSS. Additionally, the ionic liquid acts as a plasticizer increasing the flexibility of the normally brittle PEDOT:PSS.

## 5. Conclusions

The ability of conjugated polymers to be both electronically and ionically conductive makes unique devices like OECTs possible. While the electronic conductivity of conjugated polymers has been well studied, the dual conductivity of ions and holes and the polymer's behavior in aqueous environments has been an active area of research in order to improve OECT performance. Further studies into electrical stability and environmental stability, along with a more complete understanding of structure-function relationships that could inform the design and synthesis of new materials, remain to improve the understanding of OECTs. Recent studies though have begun to shed light on how polymer structures and properties benefit OECT performance.

## Conflict of Interest

The author has no conflicts of interest.

## References

- [1] P. Romele, M. Ghittorelli, Z. M. Kovács-Vajna, and F. Torricelli, "Ion buffering and interface charge enable high performance electronics with organic electrochemical transistors," *Nat. Commun.*, vol. 10, no. 1, pp. 1–11, Dec. 2019. doi: 10.1038/s41467-019-11073-4.
- [2] J. Rivnay, S. Inal, A. Salleo, R. M. Owens, M. Berggren, and G. G. Malliaras, "Organic electrochemical transistors," *Nature Reviews Materials*, vol. 3, no. 2. Nature Publishing Group, pp. 1–14, 16-Jan-2018. doi: 10.1038/natrevmats.2017.86.
- [3] L. Q. Flagg, C. G. Bischak, J. W. Onorato, R. B. Rashid, C. K. Luscombe, and D. S. Ginger, "Polymer Crystallinity Controls Water Uptake in Glycol Side-Chain Polymer Organic Electrochemical Transistors," *J. Am. Chem. Soc.*, vol. 141, no. 10, pp. 4345–4354, Mar. 2019. doi: 10.1021/jacs.8b12640.
- [4] A. Savva et al., "Balancing Ionic and Electronic Conduction for High Performance Organic Electrochemical Transistors," *Adv. Funct. Mater.*, vol. 30, no. 11, p. 1907657, Mar. 2020. doi: 10.1002/adfm.201907657.
- [5] C. G. Bischak et al., "A Reversible Structural Phase Transition by Electrochemically-Driven Ion Injection into a Conjugated Polymer," *J. Am. Chem. Soc.*, Mar. 2020. doi: 10.1021/jacs.9b12769.
- [6] C. G. Bischak, L. Q. Flagg, and D. S. Ginger, "Ion exchange gels enhance organic electrochemical transistor performance in aqueous solution," Sep. 2019.
- [7] X. Wu et al., "Ionic-Liquid Doping Enables High Transconductance, Fast Response Time, and High Ion Sensitivity in Organic Electrochemical Transistors," *Adv. Mater.*, vol. 31, no. 2, p. 1805544, Jan. 2019. doi: 10.1002/adma.201805544.