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# TWO-TERMINAL ORGANIC ELECTROCHEMICAL TRANSISTORS AND THEIR APPLICATIONS

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# Two-terminal Organic Electrochemical Transistors and Their Applications

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A thesis submitted in partial fulfilment of the requirements for the degree of Master of Philosophy

August 2023

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## Abstract

Flexible bioelectronics is gaining interest as a vital medium for connecting electronics and biological systems. Organic electrochemical transistors (OECTs), a part of flexible electronics, are highly effective in constructing biochemical and bioelectric sensors due to their intrinsic amplification function and ion-to-electron conversion property. However, conventional OECT sensors seldom combine with other flexible components due to the lack of integration technology. Novel fabric OECT sensor has emerged as a versatile sensing platform due to its portability, low cost, and integration capabilities.

In this thesis, a literature review on the profiles and integration technologies of OECT will first be presented. The fundamental information about OECT, including typical three-terminal design, working principles, advantages, and functions, will be introduced in detail. Besides, a widely used theoretical model based on the depletion mechanism will be offered. Furthermore, the characteristics and integration technologies of flexible fiber-shaped and planar OECTs are summarized.

Secondly, a novel fabric two-terminal OECT by integrating gate and drain terminals is investigated thoroughly. This unique design combines the gate and drain terminals, allowing the sensor to be fabricated on a single wire rather than the multiple wires required by a typical three-terminal structure. This character significantly reduces fabrication complexities and reliability risks. The two-terminal design has an excellent on/off ratio, low subthreshold swing, and fast response for both P- and N-type OECTs. Besides, a general de-doping/doping model is built successfully to explain the underlying mechanism. Additionally, the fabric two-terminal OECTs are applied to fabricate high-gain inverters and fast-response rectifiers, showing their high potential for wearable electronic textile systems.

Lastly, a two-terminal n-type OECT sensor based on BBL organic semiconductor is developed to detect ion concentration. Different from conventional PEDOT:PSS based p-type OECT sensors, n-type sensors have an obvious advantage in low power consumption. The two-terminal configuration of the sensor avoids the decrease in conductivity at high gate voltage due to the anti-ambipolarity property of BBL material. This sensor has an impressive voltage response of nearly 100 mV/dec for NaCl and KCl electrolytes, which largely breaks the theoretical Nernst limit (59.2 mV/dec). Upon this foundation, a highly sensitive fiber-shaped K<sup>+</sup>-selective sensor has been demonstrated using PVC-based ion selective membrane and hydrogel. The design of this sensor is compatible with traditional weaving techniques and has shown potential for use in wearable electronics with multiple functions.

In summary, fiber-shaped OECT sensors with two terminals have been successfully created and used in bioelectronics. Remarkably, an impressive n-type OECT sensor

has been developed with low power consumption and high voltage response used for detecting  $K^+$  selectively. The fabric OECT sensors can be integrated into a multifunctional e-textile system by weaving them with other fiber-shaped components, such as energy-harvesting devices, energy storage devices, and displays. This development could potentially revolutionize current diagnostic and physiological monitoring methods.

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## **Chapter 1 Introduction**

There is important information about the physical state, health, and disease risk for living organisms within their physiological signals, including biochemical and bioelectric signals. Bioelectronics is a great tool that connects biology and electronics, providing a practical, easy-to-use, and non-invasive way to detect, monitor, research, and analyze biosignals. In wearable bioelectronics, biosensors that come into direct contact with the body are crucial for determining the sensitivity and comfort of the system.

The organic electrochemical transistor (OECT) is a top contender for advanced biosensing technology. It has garnered much interest lately for its ability to convert ions to electrons, low operating voltages (<1 V), and high sensitivity<sup>[1]</sup>. OECT biosensors have shown great potential in both biochemical and bioelectric applications, such as detecting ions, glucose, and viruses and monitoring electrocardiography (ECG), electromyography (EMG), and electroencephalography (EEG)<sup>[2]</sup>.

Advancements in flexible energy harvesting, storage, and display components have paved the way for developing a versatile wearable system that can self-power, sense biosignals, and display information<sup>[3]</sup>. To ensure flexibility and integration compatibility, OECT sensors are made in planar or fabric forms. Fabric sensors, in particular, are better suited to weaving technologies and offer superior liquid collection and breathability compared to planar sensors<sup>[4]</sup>.

The primary goals of this thesis are twofold. Firstly, to create a new two-terminal structure for OECTs that simplifies the fabrication process, reduces fragile connection points, and provides large transconductance and fast response. Secondly, optimize and functionalize OECT biosensors with high sensitivity and selectivity through structure design considerations such as gate material, area and distance, channel material, length, width, and thickness.

The organization of the thesis is as follows:

Chapter 1: Introduction. This chapter briefly overviews the background and development of wearable electronics. It also discusses the OECT-based sensor and its potential for wearable applications. Additionally, this chapter outlines the objectives and structure of the thesis.

Chapter 2: Literature review. This chapter provides an overview of OECTs, which introduces the typical three-terminal structure, working principles, features, and

functions, and then focuses on two flexible designs: planar and fabric-shaped OECTs that can be integrated into other devices. The chapter also briefly discusses connection technologies that can make OECTs more durable. Finally, it explores the potential for OECT biosensors in wearable electronics, highlighting the challenges and opportunities.

Chapter 3: Fabric two-terminal OECT. Two-terminal OECTs are developed where the gate and drain electrodes are integrated into one terminal. This design simplifies the weaving process of fabric OECTs and is available for microfabrication. Besides, the performances of the two-terminal OECTs can be elucidated through a general dedoping/doping model. Then, this chapter will demonstrate inverter and rectifier circuits using two-terminal OECTs that exhibit superior performance.

Chapter 4: Fabric two-terminal n-type OECT sensors with ultrahigh voltage response. This innovative n-type OECT is based on the BBL organic semiconductor and is designed in a fiber shape, making it low power consumption. The issue of current drop at high voltage caused by BBL material is resolved through a two-terminal configuration. As a BBL-based n-type OECT sensor, its voltage response to ion concentration is approximately 100 mV/dec, surpassing the Nernst limit of 59.2 mV/dec set by PEDOT:PSS-based p-type OECT sensors. The ion selectivity of the sensor is attained through the deposition of the ion-selective membrane and hydrogel layers. This research could lead the way for practical multifunctional woven textiles with high sensitivity and selectivity.

Chapter 5: Conclusions and Perspectives. This chapter summarizes the thesis work. In addition, it suggests further challenges and opportunities.

## **Chapter 2 Literature Review**

### **2.1 Abstract**

Flexible bioelectronics attracts great interest as an important medium to bridge electronics and biological systems. As an emerging part of flexible electronics, organic electrochemical transistors (OECTs) offer numerous benefits for biological sensing, such as ion-to-electron conversion property, low working voltage (<1 V), and large transconductance. The superiorities of OECTs have been successfully applied in constructing biochemical and bioelectric sensors. More importantly, significant progress has been made in integrating OECT technologies, opening up new possibilities for multifunctional and flexible bioelectronic systems. This review will first discuss the profiles of OECT, including typical design, working principles, advantages, challenges, and applications. Next, the characteristics and integration technologies of flexible fiber-shaped and planar OECTs are summarized. Last, major challenges for future high-performance OECT-based bioelectronics are discussed.

### **2.2 Introduction**

Valuable information pertaining to the physical state, health condition, and disease risk of a biological system is hidden in the physiological signals, consisting of biochemical and bioelectric signals. In the human body fluid (e.g., sweat and saliva), for example, Na<sup>+</sup>/K<sup>+</sup> concentration is closely tied to the hydration level and muscle activity<sup>[5, 6]</sup>; NH<sub>4</sub><sup>+</sup> concentration indicates whether the body is in an aerobic or anaerobic state<sup>[7]</sup>; and monitoring glucose levels is critical for assessing the risk of hypoglycemia or hyperglycemia<sup>[8]</sup>. Besides, bioelectric signals such as electrocardiography (ECG), electromyography (EMG), and electroencephalography (EEG) respond to the states of the heart, muscle, and brain separately<sup>[9, 10]</sup>. As an excellent bridge to connect biology and electronics, bioelectronics is a practical and effective platform for signal detection, monitoring, research, and analysis. In wearable bioelectronics, biosensors that make direct contact with the body are crucial as they play a significant role in determining the sensitivity and comfort of the system.

Lately, organic thin-film transistors (OTFTs) have made significant advancements, making them ideal devices for biochemical and bioelectrical sensing. They also show significance in wearable electronics for their structural flexibility, solution processability, and low cost<sup>[11]</sup>. Specifically, an organic electrochemical transistor (OECT) is a type of OTFT that shows distinct benefits for various sensing applications, such as good biocompatibility, ion-to-electron conversion property, low working voltage (< 1 V), and high transconductance<sup>[11]</sup>. The ion-to-electron conversion serves as the significant media for the information transformation in the biological system; The working voltage below 1 V helps to avoid the risk of water electrolysis;

And the high transconductance provides an increased sensitivity of the OECT biosensors. More importantly, OECTs show high compatibility with integration technologies in planar or fibrous shapes <sup>[4, 12]</sup>. It is convenient to fabricate a high-density OECT sensing array on flexible planar substrates through lithography or construct fabric OECT circuits through traditional weaving techniques. Innovations in connection technologies have strengthened the structure of OECTs and allowed them to merge with other flexible components while maintaining their flexibility<sup>[13, 14]</sup>. These exciting developments create opportunities to design multifunctional bioelectronic systems that perform tasks like signal detection, data processing, and power supply.

Several significant reviews have compiled the recent accomplishments of OECT, with particular emphasis on their working properties<sup>[1, 15]</sup>, popular organic p- and n-type semiconductors<sup>[16, 17]</sup>, and sensing ability<sup>[2, 18, 19, 20]</sup>. In addition, the function and position of OECT in flexible organic electronics are also summarized<sup>[21, 22]</sup>. However, more efforts are needed to provide a thorough and structured analysis of the integration technologies that combine OECT biosensors and other flexible components in a complete bioelectronic system, which is of great importance.

In this review, we will provide an introduction to the basic concepts of OECT and integration technologies commonly used in bioelectronics. Section 2 focuses on important information about OECT, such as its fundamental design, working principles, three types of organic semiconductors (p-type, n-type, and degenerately doped p-type), unique features, functions, and the underlying mechanism of sensing applications. Meanwhile, Section 3 delves deeper into the fiber-shaped and planar OECT sensors and their compatibility with integration. We will also summarize flexible connection technologies in terms of gate-channel connection and electrode connection. Finally, we will address the conclusions, challenges, and opportunities in this field.

### **2.3 OECT Profiles**

### 2.3.1 OECT Design and Working Principles

Generally, OTFTs consist of three electrodes (Source, drain, and gate), an organic active layer deposited on the channel (which connects the source and drain), and an electronic insulator (which separates the gate and channel). Since the circuit through the gate and electronic insulator can modulate the current density of the organic channel, the designs of the gate, the medium, and the organic channel play essential parts in the performance and the underlying working mechanism of the OTFT devices. Distinguished by the choice of electronic insulator and organic channel material, OTFTs can be further divided into three categories (Figure 2.1a), namely organic field effect transistors (OFETs), organic electrical double layer transistors (OEDLTs), and organic electrochemical transistors (OECTs)<sup>[20]</sup>.

For OFET, a solid dielectric electronic insulator is fabricated to separate the organic semiconductors from the gate electrode<sup>[23]</sup>. Similar to the traditional Si-based FET, the electric field from the gate electrode modulates the channel carrier density of an OFET, and a threshold voltage is needed to transition the transistor from the low "OFF" current to the high "ON" current. Compared to traditional inorganic channel material (e.g., Si, Ga, As, In, and Sb), the organic channel is easily affected by the aqueous or gas environment, which induces physical or chemical changes in the organic layer and influences the channel current<sup>[24, 25]</sup>. Upon this mechanism, OFET-based sensors are conveniently fabricated by surface and interface engineering aimed at the analyte of interest<sup>[26, 27, 28]</sup>.

When working with aqueous environments, the solid dielectric electronic insulator in an OFET can be substituted with an ionic conducting electrolyte to create an OEDLT (Figure 2.1b, also called electrolyte-gate OFET). Modulated by the gate electric field, the positive and negative ions in the electrolyte drift in opposite directions and accumulate at the electrolyte-gate and electrolyte-channel interfaces, establishing two electrical double layers (EDLs)<sup>[29]</sup>. It has been proved that electrolyte is a more potential electronic insulator for relatively large transconductance ( $g_m = \Delta I_{DS} / \Delta V_{GS}$ ) and low working voltage<sup>[29, 30]</sup>.

Unlike OFET organic channel materials, where ions in the electrolyte only accumulate at the interface, some organic semiconductors allow ions to penetrate the bulk<sup>[1]</sup>. This process usually involves a redox reaction that changes the carrier density and modifies the conductivity in the channel<sup>[31]</sup>. OTFTs that apply these organic materials as the channel are categorized as OECTs (Figure 2.1c). OECTs maintain the mechanism of two EDLs in OFET, but the volumetric capacitance of OECT materials is typically much higher than that in OFET<sup>[32]</sup> and OEDLT<sup>[33]</sup> materials, resulting in a larger transconductance g<sub>m</sub> under low gate voltage (typically < 1 V)<sup>[34]</sup>. The comparison of typical OFET, OEDLT, and OECT in the vision of transconductance and gate working voltage is shown in Figure 2.1d. Note that the aqueous electrolyte in OEDLTs and OECTs is sometimes replaced by a solid-state electrolyte (e.g., hydrogel and ion gel) to provide a constant humidity environment and enhance the device performance in practical applications<sup>[35, 36, 37]</sup>.

There are three kinds of organic semiconductors widely used in OECT devices. Poly (2-(3,3'-bis(2-(2-(2-methoxy)ethoxy)ethoxy)-[2,2'-bithiophen]-5-yl)thieno[3,2-b]thiophene), p(g2T-TT) and poly(benzimidazobenzophenanthroline), BBL are the representatives for P- and N-type OECT semiconductors separately<sup>[38, 39]</sup> (Figure 2.1e-

f). Typically, OECTs operate in the enhanced mode, which means negative gate voltage for P-type OECTs and positive voltage for N-type devices. In this mode, anions or cations from the electrolyte enter the channel, doping the polymer and enhancing the However, poly(styrene sulfonate)-doped current. poly(3,4-ethylenedioxythiophene), PEDOT:PSS is a unique degenerated doped P-type material that usually functions in the depletion mode (Figure 2.1g). The PEDOT:PSS film has high conductivity before applying a gate bias, making it capable of flexible conducting wire in some applications<sup>[40, 41, 42]</sup>. When a positive gate voltage is applied, cations from the electrolyte are injected into the PEDOT:PSS material and coupled with PSS anions. This causes a de-doping process that lowers the hole density and reduces the channel conductivity<sup>[43, 44]</sup>.



**Figure 2.1.** a–c) The device structures of (a) OFET, (b) OEDLT, and (c) OECT. d) Comparison of voltage and transconductance (g<sub>m</sub>) between OFET, OEDLT, and OECT. a-d) Reproduced from work<sup>[20]</sup>. e-g) Molecular structures and transfer characteristics of the (e) ptype polymer p(g2T-TT), (f) degenerately doped p-type polymer PEDOT:PSS, and (g) n-type polymer BBL. e) Reproduced from work<sup>[38]</sup>. f) Reproduced from work<sup>[39]</sup>. g) Reproduced

from work<sup>[45]</sup>.

Since PEDOT:PSS is one of the most extensively researched OECT materials, it is necessary to discuss further the operation mechanism of depletion mode operation OECT devices. According to the de-doping model (the derivation process will be provided in Section 3.7), the channel current is given by<sup>[43, 46]</sup>

$$I_{DS} = \frac{q_{\mu}p_{0}tW}{LV_{p}} \left( V_{p} - V_{g}^{eff} + \frac{V_{DS}}{2} \right) V_{DS} |V_{DS}| \ll |V_{p} - V_{g}^{eff}|$$
(2-1)

$$V_p = q p_0 T / c_d^{eff} \tag{2-2}$$

12

$$V_g^{eff} = V_G + V_{offset} \tag{2-3}$$

$$c_d^{eff} = \frac{1}{(1/C_g + 1/C_d)S}$$
(2-4)

where  $I_{DS}$  is the channel current;  $V_p$  is the pinch-off voltage;  $V_q^{eff}$  is the effective gate voltage;  $V_{DS}$  is the source-drain voltage;  $V_G$  is the gate voltage;  $V_{offset}$  is the offset voltage due to potential drop at the electrolyte (both determined by the electrolytegate and electrolyte-channel interfaces); q is the electric charge;  $\mu$  is the hole mobility;  $p_0$  is the initial hole density in the organic semiconductor film; t, W and L are the film thickness, width and length, separately;  $c_d^{eff}$  is the effective capacitance per unit area of the channel;  $C_g$  and  $C_d$  are the capacitances of electrolye-gate and electrolytechannel interfaces, separately; and S is the area of the channel layer. Ag/AgCl electrode shows efficient gating due to its unique faradaic operation property<sup>[47]</sup>. For Ag/AgCl gate, the gate capacitance  $C_g$  can be considered as infinite and the potential drop at the electrolyte is dominated by the electrolyte-channel interface. Recently, a thick PEDOT:PSS film with extremely large bulk capacitance is discovered to be a comparable gate as Ag/AgCl<sup>[48]</sup>. Other typical gate materials (e.g., small size Au, Pt and thin PEDOT:PSS film) on the other hand, show largely reduced gating due to the significant potential drop at the electrolyte-gate interface.

Besides, the transient behavior of OECT devices is primarily determined by the carriers drift transit time in the organic channel  $\tau_c$  and ions diffusion transport in electrolyte  $\tau_i$ , described as <sup>[43]</sup>

$$\tau_c = \frac{L^2}{\mu_c V_{DS}} \tag{2-5}$$

$$\tau_i \sim \frac{l}{\sqrt{c}} \tag{2-6}$$

where  $\mu_c$  is the carrier mobility, *l* is the distance between the organic film and the gate, and c is the electrolyte concentration. Note that the transient behavior principles are also observed and proved in non-PEDOT:PSS devices<sup>[49]</sup>, while the current calculation depending on the de-doping mechanism is mainly applied in PEDOT:PSSbased OECT because of its unique depletion operation mode at present.

#### **2.3.2 OECT Features**

OECT devices have been established as a preferred choice for flexible electronics due to their inherent advantages. Polymers comprise long chains that consist of repeating units called monomers. When in the state of solid membranes, they have strong intramolecular interactions. Thus, these chain conformations make polymers intrinsically flexible to mechanical stress<sup>[50, 51]</sup>. By applying flexible electrodes (e.g., PEDOT:PSS and silver nanowires<sup>[52]</sup>) and polymer channels, OECTs are ideal candidates for bendable and stretchable electronics. Besides, OECTs' ions doping/de-doping mechanisms realize the ion-to-electron conversion, creating a connection between biology and electronics<sup>[53]</sup>. Furthermore, compared to OFET and OEDLTs, OECTs display superior electrical performance with high transconductance at a low gate voltage, enabling them to operate with high sensitivity within a 1 V working voltage range. This property helps OECT devices avoid the risk of water hydrolysis and gain excellent biocompability<sup>[54, 55]</sup>. Finally, OECT devices are easy to fabricate at low cost via solution processes (e.g., spin-coating and printing)<sup>[56, 57]</sup>, which offers excellent opportunities in large-scale manufacture.

Despite progress, there are still obstacles to preventing the vast development of OECT devices. Compared to inorganic semiconductors, organic polymers have relatively low carrier mobilities and limited carrier densities, affected by various factors, such as chain growth mode, film morphology, and molecular interconnectivity<sup>[58]</sup>. These drawbacks lead to slower response and lower "On" current than silicon-based transistors. Besides, there is a performance mismatch between p-type and n-type organic semiconductors. So far, the conductivity and transconductance of p-type polymers are typically one order of magnitude larger than n-type polymers. Breaking this bottleneck is challenging due to numerous strict and occasionally contradictory requirements for creating n-type materials<sup>[17, 59]</sup>. The absence of high-performance n-type polymer brings difficulties in developing n-type enhanced mode OECT sensors and complementary circuits.

### **2.4 OECT Functions**

As stated above, OECTs have promising potential for biosensors. Depending on the target signals, OECT biosensors can be categorized into biochemical and bioelectrical

sensors.

#### 2.4.1 Biochemical OECT Sensor

Biochemical OECT sensors aim to detect the level of ions or biomolecules in the electrolyte through the modulation mechanism of two EDLs. The potential variations at two EDL interfaces are critical to the detection sensitivity. It is interesting to mention that both EDL interfaces can be modified to enhance the sensitivity and selectivity of the sensor.

Gate-modulated sensors are fabricated by gate modifications. These modifications are usually based on Au or Pt electrodes to increase the voltage variation range at the electrolyte-gate interface. These sensors have successfully detected glucose<sup>[60]</sup>, dopamine<sup>[61]</sup>, DNA<sup>[62]</sup>, and virus<sup>[63]</sup>. For example, in the case of virus detection, the Au gate is modified with the antigen (SARS-CoV-2 spike protein) to immobilize the virus and bovine serum albumin (BSA) to fill the vacancy left on the gate (Figure 2.2a). The antigen-virus immobilized protein can be charged under positive gate voltage, which induces an electric dipole on the electrolyte-gate interface and changes the effective gate voltage of the sensor (Figure 2.2b), while the nonspecific bondings between the Au gate and electrolyte contents are minimized by BSA occupation<sup>[63, 64]</sup>. Different from that, some channel-modulated sensors require channel modification, while others can even work without modification. These sensors prefer to apply the Ag/AgCl gate to have a larger voltage variation range within low gate voltage at the electrolyte-channel interface. In some cases, however, sensors can work at a relatively higher gate voltage, and they designedly apply a low capacitance electrode (Pt, thin PEDOT:PSS film) to reduce the gating. The representative channel-modulated sensor targets are humidity<sup>[65]</sup>, pH<sup>[66]</sup>, ions<sup>[66]</sup>, lactate<sup>[67]</sup>, and bacteria<sup>[68]</sup>. For example, the PEDOT:PSS channel is modified with the antibodies in a bacteria biosensor (Figure 2.2c). The antibody-bacteria combinations change the voltage drop at the electrolyte-channel interface so that it modulates the electric characteristics of the sensor (Figure 2.2d). When utilizing the Ag/AgCl gate, the voltage shift of the transfer curve caused by bacterial capture is approximately 14 mV at 0.4 V gate voltage. However, when using the Pt gate, the voltage shift increases to 55 mV at 1 V gate voltage.



Figure 2.2. a–b) Schematic diagrams for (a) gate modulated virus sensor and (b) change of potential drops in the double layer between gate and electrolyte. a-b) Reproduced from work<sup>[63]</sup>. c–d) Schematic diagrams for (c) electrolyte-channel modulated bacteria sensor and (d) change of potential drops in the double layer between electrolyte and channel. c-d) Reproduced from work<sup>[68]</sup>.

#### 2.4.2 Bioelectric OECT Sensor

Bioelectric OECT sensors utilize the outstanding feature of high trans-conductance at low gate voltage to record minuscule bioelectric signals for clinical applications, such as electrocardiography (ECG)<sup>[69]</sup>, electrocorticography (ECoG)<sup>[70]</sup>, electroencephalography (EEG)<sup>[71]</sup>, and electromyography (EMG)<sup>[72]</sup>. Around the gate voltage point of peak transconductance, slight voltage fluctuation can lead to a significant output variation. Thus, the bioelectric signals are adjusted to the voltage range with high transconductance and input as gate voltage to the sensor.

To further enhance the obtained bioelectric signal, inverter amplifier configurations with high gain are applied in some recording cases<sup>[73, 74, 75]</sup>. Potentially, a complementary inverter consisting of both p- and n-type OECTs could obtain a high gain (Figure 2.3a,b). However, due to the lack of high-performance n-type OECT material, it is challenging to match the mobility of p- and n-type OECTs<sup>[76]</sup>, resulting in an unsatisfactory gain (typically lower than 30<sup>[39, 73, 77]</sup>) with more complex fabrication processes. As a convenient way to avoid this problem, non-complementary inverters involving only p-type OECT are applied in some bioelectric sensors (Figure 2.3c-e). Note that inverter amplifier configurations can also be used to detect ions. These amplifier ion sensors have relatively large voltage changes per concentration at the expense of the detection limit<sup>[78, 79]</sup>.



 Figure 2.3. a) Schematic diagrams for complementary OECT-based inverters made with a pand n-type OECT. b) Voltage transfer characteristic of the complementary inverter. a-b)
Reproduced from work<sup>[39]</sup>. c-e) Schematic diagrams for non-complementary inverters made with p-type OECTs only, namely (c) resistive-ladder-based OECT inverter, (d) unipolar
OECT inverter, and (e) Common-source OECT amplifier. c) Reproduced from work<sup>[80]</sup>. d-e) Reproduced from work<sup>[81]</sup>

### 2.5 Flexible System Adapted OECT Structure

OECT biosensors are promising for wearable electronics because of their outstanding transfer characteristics and intrinsic flexibility. To meet the requirements of flexible electronics, two main OECT structures available to form flexible systems are widely investigated: fiber-shaped and planar OECTs.

### 2.5.1 Fiber-shaped OECT

Typically, a fiber-shaped OECT consists of source-drain fiber and gate fiber (Figure 2.4a). The organic semiconductor is deposited in the middle of the source-drain fiber, connecting separated source and drain electrodes. Another metal or polymer-modified fiber works as the gate electrode. Two fibers are assembled by electrolyte, where voltage drop modulates the transfer performance of the transistor. The flexible substrates of fiber-shaped OECTs can be Nylon<sup>[4]</sup>, cotton<sup>[82]</sup>, and silk<sup>[83]</sup> fibers.

When it comes to fiber-shaped devices and systems that may require long electrodes, the conductivity of the fiber electrodes is a crucial parameter. Conductive fibers are easily fabricated by coating conductive polymers on fiber substrate through a simple dip-coating process (Figure 2.4b). Pure conductive polymer fibers without substrate can also be manufactured by filament-spinning (Figure 2.4c)<sup>[84]</sup>. However, the
conductivities of polymers are several orders of magnitude lower than metals like Au, Ag, and Pt<sup>[85, 86]</sup>. When testing Cr/Au or Ti/Pt coated fiber, the resistance will significantly increase due to cracks in the metal film caused by bending. Applying an additional layer of PEDOT:PSS to the surface of the metal is an excellent strategy to connect the previously separated fractions of metal, resulting in a more consistent resistance for the fiber electrodes<sup>[4]</sup>.



Figure 2.4. a) Design of flexible fabric OECT sensor based on Nylon fiber substrate. This sensor can detect glucose, uric acid, and dopamine by different gate modifications. a)
 Reproduced from work<sup>[4]</sup>. b-c) Fabrication of fiber-shaped OECT sensors by (b) continuous dip-coating or (c) filament spinning process. b) Reproduced from work<sup>[87]</sup>. c)Reproduced from work<sup>[84]</sup>.

Fiber-shaped OECTs are ideal candidates for integration into the traditional weaving industry. The shape of the fiber can easily conform to the warp and weft during the

weaving process<sup>[4, 83]</sup>. By constructing functional weaving fibers (e.g., hydrophobic and hydrophilic) with fiber-shaped OECTs, a wearable textile system that integrates liquid transport, biosensing, and breathability functions can be fabricated<sup>[88, 89]</sup>.

There are some apparent issues with fiber-shaped OECTs. Specifically, the construction of two fibers assembled through electrolytes is unstable. It is because any deformation that occurs during practical use can alter the distance between the gate and channel of the transistor, which can impact the sensor's performance<sup>[90]</sup>. Additionally, fabricating fiber-shaped OECTs poses a challenge in applying elaborate processes such as lithography. It is difficult to create channels that are shorter than 10  $\mu$ m without the use of lithography. This limitation affects the channel current and transient response of the sensor, as stated in equations 2-1 and 2-5.

#### 2.5.2 Planar OECT

Planar OECT usually applies a classic three-terminal configuration consisting of source, drain, and gate electrodes (Figure 2.5a). Due to the positive correlation between surface stress and substrate thickness<sup>[91]</sup>, planar OECTs prefer to fabricate on flexible thin substrates such as poly(ethylene terephthalate) (PET)<sup>[62]</sup>, polyimide (PI)<sup>[92]</sup>, polydimethylsiloxane (PDMS)<sup>[93]</sup>, and parylene C<sup>[94, 95]</sup>. Every substrate has its unique advantages that make it a priority for specific fabrication processes. For

instance, PET exhibits exceptional chemical inertness<sup>[96]</sup>, PI remains stable over a broad temperature range<sup>[97]</sup>, PDMS adheres well under controlled temperatures ideal for transfer processes<sup>[93]</sup>, and parylene deposition can form a conformal configuration on any shape with a film thickness as low as a few micrometers<sup>[94, 95, 98]</sup>.

Flexible planar substrates use similar fabrication techniques as rigid substrates, allowing for detailed processes in planar OECTs. Through lithography, it is possible to create channels as small as 2  $\mu$ m in length<sup>[95]</sup>. This technique also offers a better encapsulation process with a minimal exposed window for the channel by using a permanent photoresist like SU-8, which is crucial in reducing leakage current. Solution processes such as spin-coating, 3D printing<sup>[99]</sup>, screen printing, and inkjet printing<sup>[57]</sup> provide great potential for producing elaborate large-scale planar OECTs (Figure 2.5b-d).



Figure 2.5. a) Design of flexible planar OECT sensors supported by parylene substrate. This sensor is capable of ECG wave capture. a) Reproduced from work<sup>[95]</sup>. b-d) Fabrication of planar OECT sensors by (b) 3D printing, (c) screen printing, or (d) inkjet printing. b) Reproduced from work<sup>[99]</sup>. c-d) Reproduced from work<sup>[57]</sup>.

Compared to fiber-shaped OECTs, planar OECTs encounter challenges with breathability and aqueous sample harvesting because of the low moisture permeability of flexible substrates, particularly  $PET^{[100]}$  and parylene  $C^{[98]}$ . Additionally, when analyzing dynamic aqueous solutions, planar OECTs have an obvious disadvantage compared to fiber-shaped OECTs. Although the distance between the gate and the channel is changeless in a planar device, electrolyte liquid is able to flow on its surface and potentially alter the contact area on the channel and gate. Furthermore, this liquid flow can result in a streaming potential between the gate and channel<sup>[101]</sup>. On the contrary, hydrophilic fiber-shaped OECTs can absorb liquid through a

capillary effect, which helps maintain relatively stable performance during dynamic measurements<sup>[4]</sup>.

#### 2.6 Connection Technologies with Flexibility

The flexible structure of OECTs has two vulnerabilities. The connection between the gate and channel through an aqueous electrolyte is unstable and at risk of geometry deviation due to deformation and liquid flow. Besides, the connection points in the electrodes of various flexible components (e.g., OECT sensors, power source, and chips) are also fragile. Strategies can be taken to strengthen these weak spots while maintaining the whole system's flexibility.

#### 2.6.1 Connection between Gate and Channel

A direct method to bypass the issues associated with liquid electrolytes and improve the connection between the gate and channel is by using a flexible solid-state electrolyte (Figure 2.6a). In some cases, solid-state electrolytes can also help enhance the sensors' sensitivity and selectivity. Commonly utilized solid-state electrolytes are Nafion<sup>[65]</sup>, ionogel<sup>[67]</sup>, hydrogel<sup>[13, 102]</sup>, and ion-conducting biomaterials<sup>[37, 71, 103, 104]</sup>.

Nafion is capable of transporting both protonic and cationic species. A critical characteristic of Nafion is that the mobility of ions is heavily influenced by the amount of water bonded within the membrane. Water can alter the microstructure of the Nafion membrane, potentially hindering the movement of ions within. This waterrelated change of ions transportation makes Nafion a sensitive electrolyte to the humity<sup>[65]</sup>; The ionogel conducting both positive and negative ions comprises a room temperature ionic liquid and gelating polymer. The block polymer forms a crosslinked network in the ionic liquid, offering the composite gel mechanical strength. The apparent advantage of ionogel is its large specific capacitance, which enhances the gating in the sacrifice of switching response<sup>[36, 67]</sup>; Different from ionogel, a hydrogel with a high content of water mainly transports metal ions. The hydrogel contains polymers that create a crosslinked network with the ability to retain water in the shape of solid gel<sup>[102]</sup>. Metal ions can exist and move within the hydrogel via water, making it an excellent solid-state electrolyte for detecting ions; Ion-conducting biomaterials are a big family that naturally exist in the biosystem, including melanin<sup>[103]</sup>, agar<sup>[104]</sup>, chitosan<sup>[71]</sup>, and gelatin<sup>[37]</sup>. Typically, they follow a similar working mechanism as hydrogel but excel in high proton transportation, low cost, high biocompatibility, and good processability<sup>[105]</sup>.

#### **2.6.2** Connection between Flexible Components

Due to concentrated stress, electronic connections in wearable devices are prone to breaking under excessive deformations. Electrically conductive adhesives (ECAs) with intrinsic flexibility are promising tools to strengthen the connections between flexible components in wearable systems. For example, PEDOT:PSS can be a good choice to connect different components for their conductivity and flexibility (Figure 2.6a). However, the adhesion of PEDOT:PSS may not be strong enough to tolerate large deformation.

Another outstanding representative with high stretchability and conductivity is the metal-polymer conductor (MPC), which consists of metal particles and elastic polymers (e.g., Polydimethylsiloxane, PDMS). It is interesting to note that the properties of MPC are tunable by adjusting the content ratio of the metal particles and polymers. Besides, the conductivity and mechanical strength of the MPC can be further improved by introducing the proper content of carbon nanotubes (CNTs)<sup>[14]</sup>.

In addition to ECAs, more convenient methods can be adopted according to the practice situations. For fiber-shaped OECTs, for example, reliable connections (both gate-channel and electrode connections) can be achieved by simple mechanical gripping, such as crimping, stapling, and embroidery (Figure 2.6b). It's important to

note that connections made by crimping and stapling can be inflexible and might break if the textile wrinkles<sup>[3]</sup>. As for planar OECTs with exposed Au electrodes on an ultra-flexible substrate (e.g., thin-film parylene), water vapor plasma–assisted bonding (WVPAB) technology is convenient for achieving direct bonding of Au electrodes (Figure 2.6c). This bonding process can be done at room temperature without any added pressure, which is friendly to most organic semiconductors. The bonding connection is flexible, firm, efficiently conducting, and highly stable even in a damp heat environment<sup>[106]</sup>.



Figure 2.6. a) OECT inverter in the shape of fiber mesh. Solid-state electrolyte PSS hydrogel was used to connect the channel and gate electrode. Conductive adhesive PEDOT:PSS was used to connect the circuit. a) Reproduced from work<sup>[13]</sup>. b) Combination of the channel and gate fibers by mechanical gripping. b) Reproduced from work<sup>[107]</sup>. c) Direct Au bonding on the flexible planar substrate by water vapor plasma–assisted bonding. c) Reproduced from work<sup>[106]</sup>.

### 2.7 Summary

OECTs have been proven as one of the most potential biosensors for their unique flexibility, ion-to-electronic conversion property, high transconductance, and low working voltage. Applications in biochemical and bioelectric sensing have achieved great successes, including the detection of humidity, ions, glucose, lactate, dopamine, DNA, bacteria, and viruses, as well as the monitoring of ECG, ECoG, EEG, and EMG. Besides, extensive research on using flexible substrates for integrating OECTs into wearable electronic systems is investigated. The fiber-shaped OECTs based on textile fibers adapt to the conventional weaving technology well but have difficulties in microfabrication. On the other hand, the planar OECTs based on flexible thin-film substrates can achieve high performance by elaborate fabrication but face challenges in dynamic liquid control and maintaining breathability. In addition, significant advancements have been made in connection technologies for flexible electronic systems. Solid-state electrolytes are investigated to improve the connection between the gate and channel, while conductive adhesives are developed to strengthen the electrode connections between different components. These technologies greatly enhance the stability and reliability of the flexible electronic system.

Despite progress, numerous challenges still exist for the widespread success of OECTs. First, the working principle of OECTs that are not based on PEDOT:PSS needs to be better understood. More efforts should be devoted to constructing the model for OECTs operating in the enhanced mode, which is of great importance to explain the performance of general P- and N-type OECTs addition to the PEDOT:PSS devices. Furthermore, the lack of high-performance N-type organic semiconductors is a major obstacle to developing OECTs in various logic circuits. The unmatched carrier mobility of current N-type and P-type materials greatly restricts the capabilities of complementary circuits. The shortage of N-type materials also results in the slow development of N-type OECT biosensors. These sensors generally operate in enhanced mode and offer advantages such as low static power consumption and improved noise immunity compared to sensors operating in depletion mode<sup>[17]</sup>.

It has been proved that OECTs can serve as an excellent medium for bridging the fields of electronics and biology. The progress of OECT integration technologies is also encouraging for paving the way for multifunctional flexible bioelectronics systems. Thus, we firmly believe that OECTs will play an essential part in the next-generation wearable biosensing platform.

# Chapter 3 Fabric Two-terminal Organic Electrochemical Transistors

#### **3.1 Abstract**

Flexible and wearable electronics based on functional fibers are widely discussed for their portability, convenience, and enormous market potential. However, the typical three-terminal structure of a transistor requires multi-wires, which brings complexities in fabrication and a high-reliability risk in practical situations. In this work, we develop a fabric two-terminal organic electrochemical transistor (OECT) by integrating gate and drain terminals. This design presents good performances in on/off ratio, subthreshold swing, and response for both P- and N-type OECTs. The underlying mechanism is elucidated successfully by the general de-doping/doping model. In addition, fabric two-terminal OECTs contribute to the high gain inverter and fast response rectifier, showing the broad applications in the functional integration of wearable electronic textile systems.

# **3.2 Introduction**

Wearable electronics have drawn the increasing attention of the public because they can potentially monitor health and motion state in real-time conveniently by detecting 32

various metabolites and physiological signals<sup>[49, 108, 109, 110, 111, 112]</sup>. The development of flexible energy harvesting and storage components brings the possibility of wearable self-powering systems <sup>[113, 114, 115]</sup>. Nonetheless, the functional integration of wearable electronics is facing challenges in connection. On the one hand, sensitive detection requires firm and stable connections in the system, even in a high-deformation state. On the other hand, the fixed weft or warp directions of the conventional weaving technology significantly limit the freedom of the circuit routing and connection. Therefore, a highly integrated electronics system with fewer connection points is significantly in need.

As an essential part of the circuit architecture, wearable transistors take on important tasks in transforming bio-signals into electronic signals or amplifying acquired small signals in the system. Three kinds of transistors were demonstrated to the wearable system: silicon-based field-effect transistor (FET), organic thin-film transistor (OTFT), and organic electrochemical transistor (OECT). Although the discrete integration of FET on textile allows slight deformation<sup>[116, 117]</sup>, the rigid component can not be tolerable in places that move substantially. Flexible OTFT has been proven to be capable of wearable displays<sup>[118]</sup>, memories<sup>[119]</sup>, and sensors<sup>[120, 121, 122]</sup>. As one variety of OTFT, OECT shows more potential as a wearable component for its low working voltage and promising bio-sensing performance<sup>[63, 123, 124]</sup>.

Wearable transistors are expected to be in the ideal shape of fiber so that they can meet the requirements of the conventional textile industry<sup>[4, 108]</sup>. However, the typical three-terminal structure of a transistor requires an individual gate or reference electrode fiber from the source-drain fiber. The complex connection processes and more fragile connection points they bring are not favored for wearable integrated systems. Besides, the two fibers are commonly weaved vertically or parallel to each other in the textile. The small interlaced area of two fibers in vertical relation has a high risk of disconnection in large deformation, while the large space between two fibers in parallel needs more electrolytes from the body to connect, which may cause more body fluid collection issues in practice. Twisting fibers together to combine a mixed fiber can be a way to solve the problems, but more complicated fabrication is needed to reduce the capacitive and inductive crosstalk induced by long parallel conductive fibers<sup>[3]</sup>.

In this work, we integrated drain and gate terminals in one electrode and developed a fabric two-terminal OECT that works without external gate fiber. This single-fiber construction adapts to energy storage fiber and has an obvious advantage for electronic textile integration by minimizing the connection points. Besides, the P- and N-type devices based on p(g2T-TT), and BBL showed advanced performance in high on/off ratio, low off current, giant subthreshold swing and fast response. The results were illustrated successfully by a general de-doping/doping model. The demonstration

applications on the high gain inverter and quick response rectifier indicate the significant influence it may have on wearable digital and analog electronic circuits.

#### **3.3 Experimental Section**

#### **3.3.1 Materials and Device Fabrication**

AZ5214 and SU-8 photoresists used in lithography were purchased from MicroChemicals GmbH. BBL, methanesulfonic acid (MSA), chloroform, acetone, and sodium chloride (NaCl) were purchased from Sigma-Aldrich Co. p(g2T-TT) were synthesized by Iain McCulloch's group.

Figure 3.1a, b demonstrates the design of fabric two-terminal OECT sensors. First, the PET film (0.1 mm thick) was prebaked at 150°C for 1 h under a flat weight so that it would not be deformed in the following process. After photo-etching a pattern onto the film, Au electrodes (Cr~10 nm; Au~40 nm) were prepared by magnetron sputtering deposition and the liftoff process. The channel was designed to be 10  $\mu$ m in length and 40  $\mu$ m in width. Next, a second photo-etching pattern was created to modify the gate. A layer of Ag or Pt (~100 nm thick) was deposited onto the drain electrode using the same process as the previous step, allowing it to act as a gate. For the Ag/AgCl gate preparation, the Ag layer was chlorinated by droplets of 0.2 M ferric

chloride (FeCl<sub>3</sub>.6H<sub>2</sub>O) for 15 mins. Then, an SU-8 photoresist insulating layer was patterned and solidified to protect the Au electrodes from the aqueous electrolyte. Last, a channel window was opened by a fourth layer of photoresist.

For P-type semiconductor sensors, a p(g2T-TT) film was spin-coated at the channel, followed by a liftoff process. p(g2T-TT) was first dissolved in chloroform at 2 mg/mL concentration at 40°C. Then, the solution was spin-coated at 1000 rpm for 15 s. Next, the film was heated at 100°C for 20 mins and cooled naturally to 40°C. The liftoff process was done after soaking the device in acetone for 30 mins. The thickness of the p(g2T-TT) film was approximately 40 nm. For N-type sensors, a BBL film was prepared, and a liftoff process was executed. BBL was dissolved in MSA at a concentration of 5 mg/mL, and the solution was stirred at 70°C until complete dissolution (approximately 1 h). Then, the solution was spin-coated at 1000 rpm for 1 min. Then, the BBL film was immersed in deionized water for 1 hour to eliminate MSA, followed by the liftoff process. Last, the film was dried on a hot plate at 150 °C for 1 hour. The final BBL film was approximately 20 nm thick.

#### **3.3.2 Device Characterizations**

The transfer characteristics of the devices were measured by Labview-controlled Keithley source meters (Keithley 2400). For assessing the transient response of the devices, an Agilent 33220A waveform generator was utilized to apply the input voltage ( $V_{D, G}$ ) pulse, and a Tektronix TBS2072 digital storage oscilloscope was connected to receive the output signals. An SR570 low-noise current preamplifier was also needed to convert the output current into voltage signals. This system could also measure the response of the rectifier.

The inverter was characterized by a semiconductor parameter analyzer (Keithley 4200). The drain voltage ( $V_{DD}$ ) was fixed at 0.4 V, and the input voltage was applied from 0 to 0.5 V with a variation interval of 0.5 mV. The transistor and diode were soaked in 0.1 M NaCl electrolyte during the measurement.

The thickness of the p(g2T-TT) and BBL films were tested by the Bruker DektakXT Surface Profiler. The films of different thicknesses were obtained by specific dissolution concentrations of p(g2T-TT) and BBL.

### **3.4 Results and Discussion**

For a fabric two-terminal OECT, the gate electrode was integrated into the drain terminal by depositing the gate directly onto the drain, as shown in Figure 3.1a, b. The drain and source terminal were shielded by the permanent SU-8 photoresist, except

for the gate area exposed to the environment. When the gate and channel are covered with electrolyte, the voltage applied to the drain terminal can efficiently conduct to the gate and govern the conductivity of the channel by forming the electric double layer<sup>[34]</sup> (EDL) on the surface of the gate and channel separately.

Theories on modeling the behavior of PEDOT:PSS-based OECT devices upon positive gate voltage have been widely discussed and successfully applied in previous works<sup>[18, 43, 46]</sup>. For a de-doping process ( $V_G > 0$  for P-type), cations in the electrolyte are pushed to inject into the organic film. They will be captured by the organic molecules via physical or chemical effects. Note that instead of participating in the transportation themselves, these cations are more likely to form an EDL on the outer surface of molecular bulk. To keep the molecular electric neutral, free hole carriers inside the bulk are compensated by the electrons from the source electrode, resulting in the decrease of hole carrier density. On the contrary, in a doping process ( $V_G > 0$ for N-type), cations injected in the film form an EDL and induce free electron carriers inside the molecular bulk. Here, the influence of the discontinuous de-doping/doping process is assumed to be negligible for ease. Then, an expression for the effective carrier density in the semiconductor material is<sup>[43]</sup>

$$N = N_0 \times (1 \mp \frac{Q}{qN_0 v}) \tag{3-1}$$

where N represents the average carrier density in the whole semiconductor (hole density for P-type or electron density for N-type semiconductors),  $N_0$  is the initial

carrier density, Q is the absolute total charge injected in the organic film from the electrolyte, q is the elementary charge, and v is the volume of the film. The subtraction refers to the carrier loss for de-doping, while the addition relates to the carrier gain for doping effect. Upon this foundation, the channel current of a fabric two-terminal OECT at steady-state under the condition of  $V_D = V_G = V_{D,G} > 0$  is given by

$$I_{DS} = G \left[ V_{D,G} \mp \frac{\left( V_{D,G} + V_{offset} \right)^2}{2V_p} \right]$$
(3-2)

$$G = N_0 \times q \mu W T / L \tag{3-3}$$

$$V_p = N_0 \times qT/c_d^{eff} \tag{3-4}$$

where G is the conductance of the P- or N-type organic semiconductor,  $V_{D,G}$  is the voltage applied at the drain-gate terminal. The derivation and further discussion of this model will be given in Section 3.7.

Using this framework, the off voltage for P-type transistors can be obtained by differentiating Equation 3-2 (set  $\frac{dI_{DS}}{dV_{D,G}} = 0$ ):

$$V_{D,G}^{off} = V_p - V_{offset} \tag{3-5}$$

When  $V_{D,G}$  of P-type device increases beyond  $V_{D,G}^{off}$ , the channel current will saturate due to the complete de-doping<sup>[43]</sup>, which determines the off current of the P-type device  $I_{DS}^{off}$  described by

$$I_{DS}^{off} = G_p \left(\frac{1}{2}V_p - V_{offset}\right)$$
(3-6)

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It is worth noting that the intrinsic electrons in the organic film determine the off current of N-type devices with positive applied voltage. Besides, the current of N-type devices will also saturate because of the complete doping, which is not discussed in this model.

To demonstrate the characteristics of fabric two-terminal OECTs, both P-type and Ntype devices were fabricated following the process outlined in Figure 3.1c. The channel was coated with polymer p(g2T-TT) for the P-type device, while BBL was coated for the N-type device. The spectroelectrochemical signatures of p(g2T-TT) and BBL show a gradual change in absorption under low working electrode bias (lower than 0.5 V)<sup>[38, 125]</sup>, indicating the continuous doping process. As a result, this model applies to them.



**Figure 3.1.** (a) The design of a two-terminal OECT fiber on the flexible PET substrate. (b) The cross-section of two-terminal OECT fiber with the potential drop through the electrolyte (black line) and across the channel (red line). (c) The fabrication process of a two-terminal OECT fiber.

Figure 3.2a,d shows the transfer characteristics of two-terminal OECT fibers with Au, Pt, and Ag/AgCl gates. According to equations 3-2 and 3-4, different effective gate capacitances due to the kinds of metal on the gate will affect the results of pinch-off voltage  $V_p$ , and thus influence the transfer performance of the devices. Besides, the gate modulation affected by the capacitance induces a change of the offset voltage with the relation of  $V_{offset} \sim c_d^{eff}$  [46, 66]. For the Au or Pt gate, a double layer between the gate and electrolyte will form a gate capacitance  $C_g$ , resulting in a smaller effective gate capacitance as  $c_d^{eff} = (C_d C_g) / [WL(C_d + C_g)]^{[46, 66]}$ . However, for the Ag/AgCl gate, there is no gate capacitance due to the faradaic effect at the interface<sup>[126, 127]</sup>. Agreed with the model, the experiments for P-type devices showed a minor off current  $I_{DS}^{off}$  of approximately  $5 \times 10^{-9}$  A by applying an Ag/AgCl gate. For N-type devices, the off currents for Au, Pt, and Ag/AgCl gate were all close to  $8 \times 10^{-9}$ A, but the shift of  $V_{D,G}^{off}$ , which induced by the change of  $V_p$  and  $V_{offset}$ , was significant. An optimized minor off voltage of around 0.05 V was observed by the Ag/AgCl gate. As a result, the Ag/AgCl gate was chosen for both P-type and N-type devices in the following experiments. It is noted that an undersized gate area operating at a non-faradaic (capacitive) regime will impair the gate modulation due to the lack of effective gate capacitance<sup>[48]</sup>. To ensure gate control, increasing the gate's length while the fiber limits the width is essential. Another approach is to produce nanoparticles on the gate surface (e.g., Pt nanoparticle by electrochemical deposition in  $H_2PtCl_6$ ·( $H_2O$ )<sub>6</sub> solution<sup>[128]</sup>).

Despite the gate, the thickness of the organic semiconductor film T is another critical factor affecting the performance of the fabric two-terminal OECTs. Figure 3.2b,d shows the devices' characteristics with different film thicknesses. Based on the proportional relation between conductance and thickness, it is evident that the magnitude of current in the channel  $|I_{DS}|$  will decrease as the film thickness reduces. It was worth mentioning that the ratios of saturation on currents for different thickness

BBL devices show the result of  $\frac{I_{DS,20nm}^{0n}}{I_{DS,10nm}^{0n}} \approx \frac{I_{DS,10nm}^{0n}}{I_{DS,5nm}^{0n}} \approx 2$ . This indicates that conductance  $G_n$  plays the majority role in the current saturation for BBL N-type devices. As proved by these experiments, the thicker film thickness can enlarge the currents for both the P-type and N-type devices and approach higher on/off ratios.

Experiments have been done for both P-type and N-type devices to discuss the influence of electrolyte concentration, as shown in Figure 3.2c,f. Typically, lower gate voltage is required to achieve the same channel doping level for higher electrolyte concentration in typical three-terminal devices<sup>[19, 66]</sup>, which can be explained by increasing of  $V_{offset}$ . Similar results were observed in two-terminal OECTs. In accordance with the model, a larger  $V_{offset}$  due to higher electrolyte concentration leads to a decrease in saturation off current for P-type devices. For N-type devices, larger  $V_{offset}$  with increasing concentration is also consistent with the left shift of the transfer curves. These experiments illustrate that the higher electrolyte concentration helps to decrease the off current of P-type devices and lower the off voltage of N-type devices.

Thoroughly considered, the on/off ratio can approach  $8.5 \times 10^5$  for a P-type device with Ag/AgCl gate, 40nm thickness p(g2T-TT) channel, and 1 M NaCl electrolyte, while  $1.1 \times 10^4$  for an N-type device with Ag/AgCl gate, 20 nm thickness BBL channel and, 1 M NaCl electrolyte. Both devices can achieve higher on/off ratio than

reported  $1.5 \times 10^5$  for the p(g2T-TT)<sup>[129]</sup> and  $6 \times 10^3$  for the BBL device<sup>[39]</sup> in 0.1 M NaCl solution.



**Figure 3.2.** The primary performance of p-type p(g2T-TT) and n-type BBL two-terminal OECT fiber. (a) and (d) are the transfer characteristics of two-terminal OECT fibers with different gate deposition. (b) and (e) are the transfer characteristics of two-terminal OECT fibers with different thickness p(g2T-TT) film. (c) and (f) show the on/off state for two-terminal OECT fibers with different NaCl concentrations. The OECT fibers default to be prepared by depositing ~ 40 nm p(g2T-TT) or ~ 20 nm BBL films with Ag/AgCl gate unless explicitly stated.

Super-low subthreshold swing is also observed for the design of fabric two-terminal OECTs. The subthreshold swing is defined as  $\frac{dV}{dlog(|I|)}$  reflects the modulation of input voltage to the output current. Figure 3.2c,f presents the subthreshold slope of P-type p(g2T-TT) and N-type BBL devices in the region of  $V_{D,G} \approx 0$ , where the lowest subthreshold swing was obtained. The magnitude of 6.7 mV/dec for the P-type p(g2T-TT) two-terminal OECT design is 10 times lower than the reported magnitude of 60 mV/dec for the typical three-terminal OECT at  $V_G \approx 0^{[74]}$ . This advantage of super-low subthreshold swing in two-terminal design benefits from the simultaneous increasing of  $V_d$  and  $V_g$ . Similarly, the N-type BBL two-terminal OECT design also shows an extremely low subthreshold swing of 16.4 mV/dec in this work.

Quick transient response is another critical parameter for OECT devices. Since the similarity of the de-doping and doping process, the transient responses of P-type and N-type devices share a close relation to the film thickness and electrolyte concentration, as shown in Figures 3.4 and 3.5. The transient behavior is primarily determined by the carrier drift transit time in the organic channel  $\tau_c$  and ion diffusion transport in electrolyte  $\tau_i$ . These two parameters are given by<sup>[43, 49]</sup>

$$\tau_c = \frac{L^2}{\mu_c V_{D,G}} \tag{3-7}$$

$$\tau_i \sim \frac{l}{\sqrt{c}} \tag{3-8}$$

where  $\mu_c$  is the carrier mobility, *l* is the distance between the organic film and the gate, and c is the electrolyte concentration. When applying pulse input voltage  $V_{D,G}$  (0 to - 0.6 V for p(g2T-TT) devices and 0 to 0.8 V for BBL devices), the transient response can be estimated by fitting the channel current curves with exponential decay function<sup>[130, 131]</sup>. Agree with the model, Figure 3.3a,b shows the slight change of transient responses for P-type devices with different film thicknesses, indicating the minor influence of film thickness. Similar results can be observed for N-type devices, as shown in Figure 3.4a,b.

The electrolyte concentration can significantly influence the transient response for a particular device with fixed geometry parameters, as stated in Equation 3-8. Figure 3.3c,d shows the quick transient response of a fabric P-type two-terminal OECT in different concentrations of NaCl electrolyte. In 0.1 M NaCl solution, p(g2T-TT) two-terminal device shows a response per channel length square of  $1.5 \times 10^{-5} s/\mu m^2$ , which is close to the reported magnitude of  $1.8 \times 10^{-5} s/\mu m^{2[132]}$  in a typical three-terminal device. In 1 M, 10 mM, and 0.1 mM NaCl electrolytes, the ratios of  $\frac{\tau_{n.10mM NaCl}}{\tau_{n.1M NaCl}} = 24$  and  $\frac{\tau_{n.01mM NaCl}}{\tau_{n.1M NaCl}} = 156$  are also close to the theoretical magnitude of approximately 10 and 100. Figure 3.4c,d shows an N-type two-terminal OECT transient response in 1 M, 10 mM, and 0.1 mM NaCl electrolyte, respectively. The ratios of  $\frac{\tau_{p.10mM NaCl}}{\tau_{p.1M NaCl}} = 4$  and  $\frac{\tau_{p.0.1mM NaCl}}{\tau_{p.1M NaCl}} = 22$  deviated from the ideal magnitude are probably related to the special doping process (anti-ambipolarity) of BBL observed in different concentrations<sup>[133]</sup>. Despite this, the transient response of the BBL N-type device also follows the trend that works faster under higher concentrations.



Figure 3.3. (a) and (b) show the transient responses for two-terminal OECT fibers with ~ 40,
~ 20, and ~ 10 nm thick p(g2T-TT) film on the channel. (c) and (d) are the transient responses for a two-terminal OECT fiber in 0.1 mM, 10 mM, and 1 M NaCl concentrations.



Figure 3.4. (a) and (b) show the transient response for two-terminal OECT fibers with ~ 20,
~ 10, and ~ 5 nm thick BBL film on the channel. (c) and (d) are the transient response for a two-terminal OECT fiber in 0.1 mM, 10 mM, and 1M NaCl concentrations.

The discussion above illustrates the great potential of fabric two-terminal OECTs with large on/off ratios, super-low subthreshold swing, and quick transient responses. Both devices work on low voltage (<1 V), capable of plenty of electronic or biosensing applications.

# **3.5 Electronic Applications of Fabric Two-terminal OECTs**

For example, the inverter depending on a typical three-terminal OECT  $(T_1)$  and twoterminal OECT  $(T_2)$  in series was prepared as shown in Figure 3.5a. To avoid the challenge of matching the mobility of P- and N-type OECTs in complementary inverters, a unipolar OECT inverter was applied by two P-type transistors developed by p(g2T-TT). As the simplest logic circuit, the inverter can invert the digital Hi or Lo input signal to the opposite output signal with a high gain. It can work as a digital amplifier to increase the biosignal for the electronics<sup>[74, 81]</sup>. Compared to previous works, introducing a two-terminal OECT instead of the resistor in the circuit can help increase the gain. In the low input voltage region ( $V_{input} < 0.3 V$ ),  $T_1$  has a relatively high conductance due to the high supply voltage  $V_{DD}$  set to be 0.4 V, and  $T_2$  working as a resistor with high resistance splits almost all voltage drop. When  $V_{input}$  increases, the resistance of  $T_1$  also increases gradually and reaches a close magnitude to the  $T_2$  at  $V_{input} \approx 0.3 V$ . Then, the voltage drop split to the  $T_1$  increase significantly with the decrease of the voltage applied on the  $T_2$ . This process is markedly accelerated by the decreasing of  $T_2$  resistance at the same time, which induces a high gain of 48.5. The super-low subthreshold swing of  $T_2$  when  $V_{D,G}$  close to 0 V further decreases the resistance of  $T_2$  and thus provides inverter the super-low output voltage ( $V_{output}$  = 0.57 mV) at  $V_{input} \approx 0.5 V$ . Because of the special mechanism of this design, the inverter has an excellent noise margin of 0.3 V for the digital Hi state by sacrificing the noise margin for the digital Lo state. Besides, benefiting from the large total resistance ( $\sim 8 \times 10^6 \Omega$ ) of this series circuit in both on and off states, the inverter has the apparent advantage of low power consumption<sup>[134]</sup>.

In addition to the inverter, fabric two-terminal OECTs have broad applications in analog and digital circuits for their similar two-terminal structure and one-direction switch characteristics to the diode. The high on/off ratio, low off current, and high response of two-terminal OECTs guarantee good performance when taking the role of the diode. P-type two-terminal OECT is capable of a diode that conducts at negative input voltage, and N-type is a diode conducting at positive voltage. As an essential part of modern electrical circuit architectures, diodes can build fundamental circuits like logic gates (AND, OR, and XOR) and rectifiers. As shown in Figure 3.5b,c, a full-wave rectifier circuit was implemented by four diodes based on P-type fabric two-terminal OECTs. When sinusoidal analog input voltage with an amplitude of 1 V and frequency below 500 Hz is applied, the wave can be fully rectified to positive polarity, agreeing with the transient response of the two-terminal transistors. This demonstration frequency is 5000 times higher than previous work<sup>[135, 136]</sup> and is fast enough for rectifying current in various energy harvesting components<sup>[137, 138, 139, 140]</sup>.



Figure 3.5. The fabric two-terminal OECTs in electronics. (a) Voltage transfer characteristic of an inverter with the application of two-terminal OECT. The circuit schematic of the inverter is shown in the inset. The inverter was soaked in 0.1M NaCl solution when testing. (b) The rectifier formed by four fabric two-terminal OECTs. (c) The rectifier output signals under 500, 1000, and 2000 Hz sinusoidal input voltage wave with amplitute of 1 V. The circuit schematic of the rectifier is shown in the inset.

# 3.6 Summary

In summary, we fabricated fabric two-terminal OECTs by integrating the gate and the source electrode. P-type p(g2T-TT) and N-type BBL materials were selected for the devices to realize a high on/off ratio, low off current, and fast response. A general de-

doping/doping model available for both P- and N-type devices under positive gate voltage was successfully developed to explore the key factors (gate, film thickness, and electrolyte concentration) that affect the device performances and support the advantages of this two-terminal design. High gain inverter enhanced by the two-terminal OECT and quick response rectifier based on it demonstrated the broad application in digital and analog bioelectronics or neuromorphic device arrays. The fabric two-terminal OECTs also have great potential on biosensors by modifying the gate or channel depending on the target.

# **3.7 Supporting Information**

In a PEDOT:PSS-based OECT, positive ions penetrate the film under positive gate voltage and react with the molecular described by the redox equation<sup>[44]</sup>:

$$n(\text{PEDOT}^+:\text{PSS}^-) + M^{n+} + ne^{-\frac{\text{Reduction}}{\text{Oxidation}}} n\text{PEDOT}^0 + M^{n+}:n\text{PSS}^-$$

where  $M^{n+}$  refers to a cation from the electrolyte, *n* is the charge number of the cation, and e<sup>-</sup> represents an electron from the source electrode. As the concentration of  $M^{n+}$ increases, it triggers a reduction reaction. During this reaction, oxidized PEDOT<sup>+</sup> is compensated by an electron and produces neutral PEDOT<sup>0</sup>, resulting in lower hole carrier density in the channel. Once the gate voltage is removed, the concentration of  $M^{n+}$  decreases via diffusion, and PEDOT<sup>0</sup> is restored to its oxidized state PEDOT<sup>+</sup> through an oxidation reaction. For evaluating the electric performance of PEDOT:PSS-based OECT, the OECT is considered as the combination of two equivalent circuits, namely the ionic circuit and the electronic circuit, as shown in Figure S3.1. The electronic circuit consisting of the drain, channel, and source is normally ohmic contact. The ionic circuit includes the gate, electrolyte, and organic semiconductor. Two EDLs between electrolyte and gate, as well as electrolyte and semiconductor, function as two capacitors in series, which are represented by an effective capacitor  $c_a^{eff}$ .



Figure S3.1. The equivalent circuits for a typical three-terminal OECT.

For ohmic contact electronic circuit, drift current is given by

$$I_{DS} = q\mu WTN \frac{dV}{dy}$$
(3-9)

Here, diffusion current and leakage gate current are neglected for ease. Under the influence of injected cations, the carrier density is described by

$$N = N_0 \left(1 \pm \frac{Q}{qN_0 LWT}\right) \tag{3-10}$$

The de-doping/doping process for N- or P-type semiconductors under different gate voltage is shown in Figure S3.2.



Figure S3.2. The de-doping/doping regions for N- or P-type semiconductors under different gate voltage.

For the ionic circuit, the voltage difference charges the effective capacitor. The charge of the effective capacitor reflects the amount of injected ions and offers the equation

$$Q(y) = c_d^{eff} W \left( V_g^{eff} - V \right) dy$$
(3-11)

where  $c_d^{eff}$  is the effective capacitance per unit area of the channel, *V* is the semiconductor voltage at the position *y*. Combining Equations 3-9, 3-10, and 3-11, we can express the differential equation as

$$I_{DS}dy = q\mu N_0 WT \left[ dV \mp \frac{c_d^{eff}(v_g^{eff} - v) dy dv}{qN_0 LT} \right]$$
(3-12)

In most cases of three-terminal devices, the effective gate voltage is much larger than the drain voltage  $(V_g^{eff} \gg V_{DS})$ , so the ions are injected into the film at the whole surface (from 0 to L). The integration of Equation 3-12 shows the result of

$$I_{DS}L = q\mu N_0 WT \left[ V_{DS} \mp \int \frac{c_d^{eff} (v_g^{eff} - v) dv}{q N_0 T} \right]$$
(3-13)

Simplification of Equation 3-13 offers the equation of

$$I_{DS} = G \left(1 \mp \frac{V_g^{eff} - \frac{1}{2}V_{DS}}{V_p}\right) V_{DS}, |V_g^{eff}| \gg |V_{DS}|$$

$$V_p = q N_0 T / c_d^{eff}$$

$$G = q \mu N_0 W T / L$$

$$V_g^{eff} = V_g + V_{offset}$$
(3-14)

which can also be written as Equation 2-1.

However, in the case of combining the drain and gate terminal together  $(V_g^{eff} \sim V_{DS})$ , the ions are injected into the film only at the area that  $V_g^{eff} > V$  (from 0 to  $y_0$ ).  $y_0$ represents the position where  $V_g^{eff} \sim V(y_0)$ . Then, the integration of Equation 3-12 shows the result that

$$I_{DS}y_{0} = q\mu N_{0}WT \left[ V_{g}^{eff} \mp \int_{0}^{V_{g}^{eff}} \frac{c_{eff} (V_{g}^{eff} - V) dV}{qN_{0}TL/y_{0}} \right]$$
(3-15)

Simplification of Equation 3-15 offers the equation of

$$I_{DS} = G \left( \frac{L}{y_0} V_g^{eff} \mp \frac{(V_g^{eff})^2}{2V_p} \right)$$
(3-16)

If the drain voltage drops linearly from the drain to the source terminal in the semiconductor, the position  $y_0$  has the relation of

$$y_0 = \frac{V_g^{eff}}{V_{DS}}L\tag{3-17}$$

Thus, Equation 3-16 can be further simplified as

$$I_{DS} = G \left( V_{DS} \mp \frac{(V_g^{eff})^2}{2V_p} \right)$$
(3-18)

For a two-terminal OECT,  $V_{D,G} = V_{DS} = V_g$ . Therefore, Equation 3-18 can be further written as

$$I_{DS} = G\left[V_{D,G} \mp \frac{\left(V_{D,G} + V_{offset}\right)^2}{2V_p}\right]$$
(3-19)

Specifically, the initial carrier density  $N_0$  can be negligible in some doping processes. Then, Equations 3-10 and 3-12 can be written as

$$N = \frac{Q}{qLWT} \tag{3-20}$$

$$I_{DS}dy = q\mu WT \left[ \frac{c_d^{eff} (v_g^{eff} - v) dy dv}{qLT} \right]$$
(3-21)

For  $V_g^{eff} \gg V_{DS}$ , the integration of Equation 3-21 gives

$$I_{DS} = G \left( \frac{V_g^{eff} - \frac{1}{2} V_{DS}}{V_p} \right) V_{DS} \approx G \left( \frac{V_g^{eff}}{V_p} \right) V_{DS}$$
(3-22)

And for  $V_g^{eff} \sim V_{DS}$ , result shows

$$I_{DS} = G \; \frac{(V_g^{eff})^2}{2V_p} \tag{3-23}$$

Notes that in the OFET, the channel current is given by<sup>[18]</sup>

$$I_{DS} = \frac{W}{L} \mu c_d^{eff} (V_g - V_t) V_{DS}, |V_{DS}| \ll |V_g - V_t|$$
(3-24)

$$I_{DS} = \frac{W}{2L} \mu c_d^{eff} (V_g - V_t)^2, |V_{DS}| \sim |V_g - V_t|$$
(3-25)

 $V_t = qNT/c_d^{eff}$ 

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where  $V_t$  is the threshold voltage that is normally changed due to doping effect of the analytes. The similarity of expressions for OECT and OFET explains their commonalities as transistors.

For the full-wave rectifier circuit shown in Figure 3.5b, an input signal up to 1000 Hz, close to the transient response limit of a fabric two-terminal device, will deform the rectified output wave. The two-terminal device will gradually lose its one-direction switch characteristics compared with markedly decreased conductance under much higher signal frequency (Figure S3.3a). The conductance will remain at a fixed value under different gate voltage when the frequency is up to 3000 Hz (Figure S3.3b), representing the same doping state of the organic channel.



Figure S3.3. (a) The response for a two-terminal OECT fiber in 500 Hz, 1000 Hz, and 1500 Hz. (b) The response for a two-terminal OECT fiber in high frequency.

# Chapter 4 Fabric Two-terminal N-type Organic Electrochemical Transistor Sensors with Ultrahigh Voltage Response

#### 4.1 Abstract

Organic electrochemical transistors (OECTs) have been proven a successful platform for multiple sensing applications. However, most of the reported OECT sensors are based on degenerately doped P-type PEDOT:PSS polymer as the channel material, which faces intractable dilemmas on high power consumption and limited voltage response. In this work, an N-type OECT sensor with a BBL channel is reported. The conductivity drop at high gate voltage due to the anti-ambipolarity property of BBL material is avoided by applying the two-terminal configuration, which integrates gate and drain electrodes into one terminal. This BBL-based two-terminal sensor has an impressive voltage response of nearly 100 mV/dec for NaCl and KCl electrolytes, which largely breaks the theoretical Nernst limit (59.2 mV/dec). Besides, a solid-state fabric K<sup>+</sup>-selective sensor is demonstrated with high sensitivity and selectivity. The proposed sensor design adapts to the traditional weaving technology well and shows promising potential in multi-functional wearable electronics.

#### **4.2 Introduction**

Nowadays, organic electrochemical transistors (OECTs) have attracted much attention as a promising candidate for multiple sensing applications. With the help of the unique ion permeation mechanism of the organic polymer<sup>[45, 76]</sup>, ions can be injected into the bulk of the channel and change the conductivity of the OECT device. Benefits from this working principle, OECT shows identifying features of high flexibility, ionto-electron conversion property, large transconductance, and low working voltage (<1 V)<sup>[21]</sup>, making it potential to realize different biological detections. In previous works, OECT-based biosensors have achieved great success in pH, ions<sup>[66]</sup>, glucose<sup>[60]</sup>, dopamine<sup>[61]</sup>, DNA<sup>[62]</sup>, bacteria<sup>[68]</sup>, and virus<sup>[63]</sup> detection.

At present, most of the bio-sensors rely on a degenerately doped P-type polymer Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) as channel material. The PEDOT:PSS has high conductivity without gate voltage, resulting in a large saturation on-state current. As the positive gate voltage grows, the current drops due to a simple de-doping process, which is highly related to the target concentration in the electrolyte<sup>[43, 46]</sup>. The mature study and stable performance of PEDOT:PSS-based OECT make it favorable in many sensing applications. However, these biosensors operating in depletion mode face obvious challenges with high static

power consumption and limited voltage response<sup>[17, 141]</sup>. A direct way to break these bottlenecks is to develop n-type OECT sensors, which work in accumulation mode.

In this work, we report a two-terminal N-type OECT sensor with a Poly(benzimidazobenzophenanthroline) (BBL) channel. The artful two-terminal configuration by integrating gate and drain electrodes into one terminal overcomes the conductivity drop caused by the anti-ambipolarity property of BBL material and helps to achieve an impressive high voltage response. Through the use of BBL two-terminal configuration, a practical application of ion-selective sensor in fiber shape is demonstrated, which adapts to the traditional weaving technology ideally.

#### **4.3 Experimental Section**

#### **4.3.1 Materials and Device Fabrication**

AZ5214 and SU-8 photoresists, BBL, and methanesulfonic acid (MSA) are stated above. Tetrahydrofuran (THF), high molecular weight polyvinylchloride (PVC), diisodecyl adipate, potassium tetrakis(4-chlorophenyl)-borate and potassium ionophore III for ion-selective membrane, agar and disodium ethylenediaminetetraacetic acid (Na<sub>2</sub>EDTA) for hydrogel are purchased from Sigma-Aldrich Co. Two-terminal OECT devices are fabricated following the previous steps. In short, the Au electrode was deposited on the PET substrate by sputtering and encapsulated by SU8 photoresist. Ag/AgCl gate was fabricated following the steps of Ag deposition and chlorination. A patterned channel with 10µm length and 40µm width was coated with 20nm BBL film by spin-coating.

For ion-selective property, ion-exchange hydrogel and potassium-selective membrane were prepared. First, agar (1 wt.%) was fully dissolved in DI water with KCl ( $10^{-3}$  M) and Na<sub>2</sub>EDTA (5×10<sup>-2</sup> M) by heating on a hot plate (105°C) in a sealed bottle. Then, the solution was slowly cooled to 60°C and maintained for use. After protecting the gate with weak sticky tape, the warm solution was spin-coated on the channel with an optimized speed of 2000 rad/s for 60 s. Then, a thin ion-exchange hydrogel film was formed at room temperature or in a fridge. Next, combining high molecular weight PVC (36.5 wt.%), diisodecyl adipate (60.5 wt.%), potassium tetrakis(4-chlorophenyl)borate (0.5 wt.%), and potassium ionophore III (2.5 wt.%) thoroughly in the organic solvent THF. The solution was spin-coated on the hydrogel film in the glove box with 500 rad/s to form a thin ion-selective membrane. Finally, the tape on the gate was carefully removed. It is worth noting that calibration was performed for all the devices by measuring the transfer characteristics in 10<sup>-5</sup> M KCl solution before preparing the hydrogel. This process can also help complete the first doping cycle from dry to wet film<sup>[142]</sup>.

#### **4.3.2 Device Characterizations**

The transfer characteristics of the devices were measured by Labview-controlled Keithley source meters (Keithley 2400). The ion concentration dependence of the device was measured from low  $(10^{-7} \text{ M})$  to high (1 M) separately. For typical three-terminal OECT sensors, a reference Ag/AgCl electrode was applied to contact the electrolyte. For two-terminal OECT sensors, the droplet of the corresponding concentration should cover both the gate and channel area. After each measurement, the gate and channel were rinsed with DI water for 2 mins and cleaned with nitrogen gas for another 2 mins. Repeated measurements from low to high concentration were done at an interval of 1 day. The measurement duration for each applied voltage was set to be 5 s to ensure the steady state of channel current in low-concentration electrolytes.

For assessing the selective property of the devices, transfer characteristics were measured with pure NaCl and KCl electrolytes separately after the deposition of hydrogel and selective membrane. Besides, continuous monitoring of the channel current  $I_{DS}$  for the increasing concentration of K<sup>+</sup> accompanied by a high concentration of Na<sup>+</sup> (10<sup>-2</sup> M) was demonstrated. The two-terminal OECT sensors were first soaked in a pure solution of 10<sup>-2</sup> M NaCl. Next, applied a fixed drain-gate voltage  $V_{D,G}$  of 0.4 V. Every 100 s, a concentrated solution (2 M KCl and 10<sup>-2</sup> M NaCl) was added, leading to an overall stepwise increasing concentration of K<sup>+</sup> (from 10<sup>-5</sup> to 1 M). The mixed solution was stirred at a constant speed during the measurement to accelerate the mixing process. Extra detailed measurement was done to test the selectivity of the sensor in human sweat content range (1 – 10 mM for K<sup>+</sup> and 10 – 100 mM for Na<sup>+</sup>). The sensor was first soaked in pure KCl solution varied from 1 mM to 5 and 10 mM. Then, highly concentrated pure NaCl (2 M) droplets were added to the solution, changing the Na<sup>+</sup> concentration from 0 mM to 10, 50, and 100 mM.

The bending tests of the fabric two-terminal sensors were conducted 200 times. The transfer characteristics of the sensors with different bending statues were measured in pure 0.1 M NaCl and 0.1 M KCl solutions separately, indicating the bending stability of the transistors, hydrogel, and selective membranes.

### 4.4 Results and Discussion

As a commercial N-type organic semiconductor, BBL is widely used in OTFTs and OECTs for its high electron conductivity and electron affinity<sup>[17, 143]</sup>. BBL-based OECT shows a relatively high current in N-type transistors and an impressive large voltage response to ion concentration, making it an ideal platform for ion-sensing applications. It was reported that there is an implausible voltage shift of nearly 100

mV/dec for NaCl concentrations in a typical three-terminal BBL-based OECT<sup>[144]</sup>, which largely breaks the classic theoretical Nernst limit of 59.2 mV/dec<sup>[104, 145]</sup>. One main impediment to this BBL-based ion sensor is the anti-ambipolarity property of BBL material. As shown in Figure 4.1, in a typical three-terminal BBL-based sensor, the electron conductivity will drop gradually with the increase of gate voltage when a high gate voltage is applied. Fortunately, the suitable electron affinity and ladder-like structure of BBL help to sustain the doping level, ensuring the anti-ambipolarity behavior is reversible<sup>[144, 146, 147]</sup>. Besides, the anti-ambipolarity response is tunable by the drain voltage. A higher drain voltage induces a larger saturate current, peak voltage, and full width at half maximum. This property naturally adapts to the two-terminal OECT design, which integrates gate and drain electrodes into one terminal. Taking advantage of the simultaneous increase of drain and gate electrodes, the two-terminal BBL-based sensor with a continuous on-state within low applied voltage (<1 V) can be fabricated.



Figure 4.1. The anti-ambipolarity behavior in BBL-based OECT sensor

Figure 4.2 shows the transfer characteristics of a BBL-based fabric two-terminal OECT sensor in NaCl and KCl solutions with different concentrations. The performances of the sensor in NaCl and KCl solutions are close, which are also observed in PEDOT:PSS-based sensor<sup>[66]</sup>. In classic Nernst theory, the similar sensitivity is explained by the simple redox process of PEDOT:PSS and the same monovalence of Na<sup>+</sup> and K<sup>+ [44, 46]</sup>. Although the outcome voltage shift of the BBL-based sensor (95 mV/dec for Na<sup>+</sup> and 99 mV/dec for K<sup>+</sup>) largely breaks the Nernst limit (59.2 mV/dec), the similar behaviors of PEDOT:PSS- and BBL-based sensors can indicate the close process of de-doping and doping to some extend. The outstanding voltage shift of the BBL-based device is probably due to its unique hydration and water injection process, which is not observed in PEDOT:PSS<sup>[142]</sup>.

Apart from the significant voltage shift, the BBL-based sensor also showed a high on/off ratio of about  $10^4$  with continuous saturation on-state current. The on-state current platform was not observed in low NaCl and KCl solution concentrations below  $10^{-6}$  M within 1 V applied voltage, indicating that the sensor was not saturated under these circumstances. Note that the leakage current can not be measured directly in the two-terminal design. Since the leakage current was two orders of magnitude lower compared to the drain current in a typical three-terminal BBL-based device and a much lower leakage current can be achieved by optimizing the water content in the hydrogel as reported in previous work<sup>[125]</sup>, it is reasonable to neglect the influence of leakage current within low applied voltage (<1 V) for ease.



Figure 4.2. The transfer characteristics of n-type two-terminal OECT fiber in (a) different NaCl concentrations and (c) different KCl concentrations. (b) and (d) are the changes of effective gate-drain voltage ( $\Delta V_{D,G}^{eff}$ ) versus NaCl and KCl concentrations, separately.

Similar to the three-terminal sensors, the two-terminal device can also achieve multifunction by modification on the channel or gate, as shown in Figure 4.3. For example, the ion-selective sensor can be fabricated by deposition of hydrogel and ion-selective membrane (ISM) on the channel<sup>[104]</sup>. Ag/AgCl gate is applied to minimize the potential drop at the interface of the gate and electrolyte<sup>[66]</sup>. The positive  $V_{D,G}$  forces K<sup>+</sup> ions penetrate the BBL film through ISM and hydrogel and thus significantly change the conductivity of the channel through the EDL effect, while

Na<sup>+</sup> ions are blocked. Glucose and dopamine detections can be realized by gate modification<sup>[60, 124]</sup>. In these cases, the Pt electrode is utilized to strengthen the gating. The selectivities of these sensors are provided by modifying the gate electrode with the biocompatible polymer film (Nafion or Chitosan) and glucose oxidase (for glucose sensing) or graphene nanomaterial (for dopamine sensing). The sensitivity of the sensor can be improved further by depositing Pt nanoparticles on the Pt gate before the modification. It is convenient to prepare Pt nanoparticles by electrodeposition of 5 mM H<sub>2</sub>PtCl<sub>6</sub> + 0.05 M HCl solution at -0.3 V (Ag/AgCl reference electrode) for 60 s<sup>[60]</sup>.



Figure 4.3. The design of fabric two-terminal OECT sweat biosensors. (a) Design of selective ion sensor enabled by channel modification. (b) Design of glucose sensor enabled by gate modification.

Here, we demonstrate a fabric  $K^+$  selective two-terminal OECT sensor based on the design shown in Figure 4.3a. The hydrogel consists of water, agarose, KCl (10<sup>-3</sup> M), and Na<sub>2</sub>EDTA (5×10<sup>-2</sup> M) are reported to have an enhanced response at the ISM without impairing its selectivity<sup>[148]</sup>. The PVC-based K+ selective membrane fabrication method can be expanded to Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, Li<sup>+</sup>, Ca<sup>2+</sup>, etc., by changing the content in PVC and THF solvents <sup>[149, 150, 151]</sup>. It is worth mentioning that the hydrogel and ISM films functioning in the wearable sensor will be under stress in practical use.

In a bending situation, the surface strain in the PET substrate can be calculated by<sup>[91]</sup>

$$\varepsilon = \frac{t_{structure} + t_{substrate}}{2r} \tag{4-1}$$

where  $\varepsilon$  is the bending induced strain,  $t_{structure}$  is the total thickness of the BBL, hydrogel, and ISM films,  $t_{substrate}$  is the thickness of the PET substrate, and r is the bending radius. Therefore, the mechanical stability of the sensor benefits from thinner substrate and active films. In this work, hydrogel and ISM were spin-coated on the channel to fabricate thin films. The spin speed should be carefully controlled for the conflict between film thickness and particle distribution<sup>[152]</sup>. The higher spin speed required by the thinner film will cause low particle concentration close to the rotation axis, which may influence the sensor's ion selectivity and conductivity performances. Besides, thinner ISM will induce higher gaps of the concentrations at the membrane surface and the bulk of the sample so that a stronger super-Nernstian effect will occur at higher electrolyte concentrations, significantly affecting the sensor's detection limit<sup>[148]</sup>. As a result, the optimized spin speeds of 2000 rad/s for hydrogel and 500 rad/s for ISM are introduced.

The transfer characteristics of the ion sensor after the deposition of hydrogel and ISM are shown in Figure 4.4a. It was observed that the conductivities of the sensor in different concentrations were lower with the presence of hydrogel and ISM. Besides, the voltage shift of 84.1 mV/dec was somewhat lower compared to the results of 99 mV/dec before the deposition. Even so, the intrinsic ion sensitivity of 84.1 mV/dec is

first realized by a single OECT element to the best of our knowledge. This performance has the potential to be further enhanced by applying current-driven or complementary amplifier configuration<sup>[153, 154, 155]</sup>. When estimating the K<sup>+</sup> selectivity of the sensor, it was noticed that the transfer response of 10<sup>-1</sup> M NaCl solution was close to the performance of 10<sup>-5</sup> M KCl, indicating the close doping state of the channel. In a simple definition of the selectivity coefficient as the concentration ratio of the primary ion (K<sup>+</sup>) and the interfering ion (Na<sup>+</sup>), which gives the same potential change<sup>[104]</sup>, the calculation result shows the value of  $-\log K_{K^+,Na^+} = 4$ . It is comparable to the reported value of 3.3 for the correspondent ion-selective electrode employing the close membrane composition<sup>[156]</sup>.

In practical situations, samples like sweat are usually mixed solutions containing both KCl and NaCl. This ion-selective sensor is expected to essentially block the response of NaCl if the gate voltage is set to 0.5 V. To explore the sensing applications of the fabric two-terminal K<sup>+</sup>-selective OECT sensor, the real-time monitoring of the drain current was done, as shown in Figure 4.4b. During the measurement, the concentration of K<sup>+</sup> was stepwise increased from  $10^{-5}$  M to 1 M, modulated by concentrated KCl (2 M) solution. Besides, consistent  $10^{-2}$  M interfering Na<sup>+</sup> was maintained to estimate the performance of the device in the mixed solution. The applied voltage was set at 0.5 V to block the response of NaCl. It was observed that the sensor achieved a high sensitivity in the range of  $10^{-3} - 1$  M KCl in the stirred

mixed solution. More specifically, the current variations were about 5.5, 5.2, and 5.8  $\mu$ A during the stepwise increased KCl concentration from 10<sup>-3</sup> M to 1 M separately. Since there was a gap of approximately 1.2  $\mu$ A from pure 10<sup>-2</sup> M NaCl solution to the mixed solution with 10<sup>-5</sup> M KCl, the detection limit of the K<sup>+</sup>-selective sensor was about 10<sup>-5</sup> M with the presence of 10<sup>-2</sup> M NaCl. Considering specific concentrations in human sweat (1 – 10 mM K<sup>+</sup> and 10 – 100 mM Na<sup>+</sup>), detailed measurement was done by continuously changing the electrolyte from pure KCl to KCl/NaCl mixed solution. First, concentrated KCl (2 M) solution was dropped into the solution, modulating the concentration of K<sup>+</sup> from 1 mM to 5 and 10 mM. Then, highly concentrated NaCl (2 M) solution was dropped into the solution, modulating the 30 mM to 50 and 100 mM. The gaps for K<sup>+</sup> were around 3.3 and 2  $\mu$ A separately, while there appeared to be no clear gap in Na<sup>+</sup> concentration variation across the range of sweat content, as shown in Figure 4.4c.





Figure 4.4. (a) The transfer characteristics of K<sup>+</sup> selective two-terminal OECT fiber sensor in pure KCl and pure NaCl solution separately. (b) The continuous monitoring of KCl concentration from 10<sup>-5</sup> M to 1 M with the presence of fixed 10<sup>-2</sup> M NaCl. (c) The continuous monitoring of the sensor in pure KCl to KCl/NaCl mixed solution.

The K<sup>+</sup>-selective OECT sensor exhibits good flexibility and robustness through the bending test conducted by rolling the fabric sensor over different cylinder diameters (a pen with a radius of  $\approx 0.5$  cm and a glass stick with a radius of  $\approx 0.5$  cm)<sup>[91]</sup>. The transform characteristics of the sensor with different bending radii are shown in Figure 4.5, indicating the stable performance of the sensor with functional selectivity property after 200 times bending. The bending tolerance of the sensor can be further enhanced if a layer of PEDOT:PSS is deposited on the Au electrode before encapsulation<sup>[4]</sup>. Note that the film thicknesses of hydrogel and ISM are critical to the flexibility of the sensor because cracks are more likely to appear after the bending test for the thick film.



Figure 4.5. Bending test of the K<sup>+</sup>-selective fabric OECT sensor. (a) Photograph of a fiber device with 0.5 cm and 0.2 cm bending radii. (b) The transform characteristics of the sensor were measured in pure 0.1 M NaCl and 0.1M KCl solutions separately.

To demonstrate the practical applications of the two-terminal fabric OECT sensor, we explore its potential in multi-functional textiles. The fabric sensor can be woven by a conventional weaving machine, as shown in Figure 4.6c. Thanks to the highly integrated design of two-terminal OECT, a single fiber is capable of its sensing property, which represents that only warp or weft weaving is needed. This advantage simplifies the weaving process by avoiding the gate and channel alignment step for a typical three-terminal design functioned by two fibers<sup>[4, 13]</sup>. Additionally, since the sweat harvest of the woven fabric is realized by constructing hydrophobic and hydrophilic fibers<sup>[88, 89, 157]</sup>, the single functional fiber in only one weaving direction is

more capable of sweat migration and collection constructions. For example, it is easier to manage a hydrophilic area (light pink area in Figure 4.6b) for parallel fabric sensors than cross-line construction, which is necessary for typical three-terminal sensors with a short distance between the gate and the channel. In the conventional weaving process, fibers will be rubbed by yarns frequently, which may degrade the performance of the sensors<sup>[21]</sup>. The protection method can be done by wrapping a layer of water-soluble polyvinyl alcohol (PVA) yarns on the fibers before weaving and wiping them out at last<sup>[4]</sup>. When integrated with the wearable power source and processing chip, the two-terminal sensor shows superiority for fewer connecting points and less chip terminal occupation<sup>[3]</sup>, which is of great importance, especially when multiple fabric sensors with different detection objects weave together.

Figure 4.6a demonstrates a multi-functional textile wristband. The signals of the fabric sensor can be conveniently monitored and recorded by a mobile phone through Bluetooth-integrated circuitry. Figure 4.6b presents a 15 cm  $\times$  20 cm woven with 20 fabric sensors in the hydrophilic area. The highly centralized construction of multiple sensors is rugged to realize if external gate fibers are required because one sensor's gate voltage may interfere with the signals of another sensor during the dynamic deforming process in practical use.



Figure 4.6. (a) Schematic of two-terminal OECT fibers integrated into a multifunctional textile wristband that a smartphone can control through Bluetooth. (b) Demonstration of 20 two-terminal OECT fibers integrated into a woven textile. (c) Picture of e CCI tech automatic dobby sampling loom system used to weave the integrated fabrics.

# 4.5 Summary

In summary, a fabric two-terminal OECT is successfully developed to save the drawback of noncontinuous on-state current brought by anti-ambipolarity behavior in BBL and take advantage of the BBL-based N-type device to fabricate a high on/off ratio, low power consumption, and high sensitivity sensor. The record-breaking

voltage responses of the sensor to K<sup>+</sup> concentration are first reported as 99 mV/dec before and 84.1 mV/dec after channel modification, significantly larger than the theoretical Nernst limit without any amplification. Close responses of Na<sup>+</sup> (95 mV/dec) and K<sup>+</sup> before the modification were separated by K<sup>+</sup>-selective membrane deposition on the channel. The all-solid-state K<sup>+</sup>-selective two-terminal sensor enabled by hydrogel and ISM deposition shows high flexibility and stability thanks to the optimized film thickness controlled by spin-coating speed. This ion-selective sensor can essentially block the response of  $10^{-2}$  M NaCl at the gate voltage of 0.5 V and achieves the low detection limit of  $10^{-5}$  M K<sup>+</sup>. For the range of sweat content, the device shows a large current gap for K<sup>+</sup>, which varies from 1 mM to 10 mM, and no apparent response to the Na<sup>+</sup> varies from 10 mM to 100 mM. The application demonstrations state the superiorities of the fabric two-terminal sensor for easy fabrication, sweat-harvest construction adaption, fewer connection points, and highly centralized feasibility, paving the way for practical multifunctional woven textiles with high-performance N-type OECT sensors.

# **Chapter 5 Conclusions and Perspectives**

In this thesis, it has been demonstrated that OECTs are highly promising biosensors due to their exceptional flexibility, ability to convert ions to electronics, high transconductance, and low working voltage. They have achieved great success in applications related to biochemical and bioelectric sensing. Moreover, researchers have extensively studied fiber-shaped and planar OECTs for their integration into wearable electronic systems. Additionally, significant progress has been made in connection technologies to improve the stability and reliability of these flexible electronic systems.

To simplify the fabrication process and reduce fragile connection points, we explore fabric two-terminal OECT configuration by integrating the gate and the source electrode. A de-doping/doping model that works for both p- and n-type devices under positive gate voltage was developed to investigate the main factors that impact device performance, such as gate, film thickness, and electrolyte concentration. By optimizing microfabrication based on the two-terminal configuration, we achieved a high on/off ratio, low off current, and fast response in both p- and n-type OECTs. In bioelectronics, these two-terminal OECTs are considered a top priority to achieve high-gain inverters and quick-response rectifiers.

Notably, an ion sensor has been developed using a two-terminal fabric OECT and BBL organic semiconductor. This sensor stands out due to its low power consumption and record-breaking voltage response of approximately 100 mV/dec. The sensor's selectivity is achieved through a K<sup>+</sup> ion-selective membrane and hydrogel layers. It is capable of detecting K<sup>+</sup> at concentrations as low as  $10^{-5}$  M in the presence of  $10^{-2}$  M Na<sup>+</sup>, and measuring K<sup>+</sup> in the human sweat by blocking the interference of Na<sup>+</sup>.

Bioelectronics and biosensor applications highlight the advantages of fabric twoterminal sensors due to their easy fabrication, adaptability for sweat harvesting construction, and fewer connection points. These characteristics make the twoterminal fabric OECTs potential for practical multifunctional woven textiles.

Although progress has been made, many challenges still need to be addressed to ensure the widespread success of OECTs. One of the main issues is that the working principle of OECTs still needs to be fully understood, particularly regarding the enhanced mode, which is especially important for n-type OECT sensors. Another obstacle is the lack of high-performance n-type organic semiconductors, which dramatically limits the capabilities of complementary circuits due to the unmatched carrier mobility of current p- and n-type materials. This shortage also hinders the development of n-type OECT biosensors, which typically operate in enhanced mode and offer benefits such as low static power consumption and improved noise immunity compared to sensors that operate in depletion mode. Therefore, efforts must be made to address these challenges to advance the development of OECTs further.

Finally, we urge increased focus on making wearable devices and external meters smaller and more integrated. These efforts will allow for affordable mass production and multiple detections. With the encouraging progress in various research topics, it is expected that OECTs will be vital in the upcoming generation of biosensing platforms for wearable technology.

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