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Fabric-Based Organic Electrochemical Transistor Towards Wearable pH Sensing Electronics

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Fabric-Based Organic Electrochemical Transistor Towards Wearable pH Sensing Electronics

by

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of the requirements for the degree of
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Dedication

This job is dedicated to my mother who has always fought for me and my brother to overcome all adversities even when the only money we had in the house was to survive and eat. My brother Saúl for being part of my life and teaching me that I failure only if I don’t stand up afterward. I dedicate this to my uncle, Jorge, my grandmother and grandfather, Luisa, and Vega for teaching me that education is the key to success, and I should try to learn as much as I can to be a good professional. I dedicate this to my fiancée, Ashley, for being always part of the process and be always with me, even in my bad moments, to my friends, for believing in me even when I did not. Also, I dedicate this to Jean C Arroyo, for being more than a coach, a big brother, for guiding me and helping me to start my university education with the best benefits possible. To Dr. Arash Takshi and Bernard Batson for helping me to pursue this degree and be the key to my success. Finally, I dedicate this to myself for working hard to achieve this degree.

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Abstract

Wearable electronics interest has attracted the attention of a few sectors because of their applicability in different areas like healthcare, military, and our daily basis. Still building circuits on fabrics to make these wearable electronics is challenging. As transistors are the building blocks of electronic circuits and most of the biosensors, recently, fiber-shaped electrochemical transistors have been studied extensively for a lot of applications including bioelectronics. Fiber-based devices are getting popular in different applications due to their low fabrication cost, lightweight, and flexibility without losing their properties. Additionally, they are potentially suitable for making sensors on garments.

In this work, we have studied various types of coating processes of PEDOT:PSS conducting polymer into different fabric types. After the coating, the conductive threads have been used to make organic electrochemical transistors (OECTs). Different studies before have shown the advantages of using dodecylbenzene sulfonic acid (DBSA) solution in PEDOT:PSS to improve conductivity. In this work, threads were tested with and without DBSA to make OECTs and the effects of conductivity change on these transistors performance have been studied. The results show the performance improvement in the treated thread with an acid. The transistor design is considered in the development for its application as a wearable pH sensor to monitor perspiration in the future wearable medical point-of-care systems.

In this work, we investigated the effect of thread materials on the performance of fiber-based OECTs made for wearable pH sensors. Three most commercially available threads were selected and tested in this research: 100% cotton, 25% cotton-75% polyester, and 32% cotton-68% polyester threads. Threads were coated with PEDOT:PSS polymer to use as the channel between the drain and source contacts. Then a silver-coated thread was used as the gate and a polyvinyl alcohol (PVA) gel electrolyte was used between the two threads. Devices were tested by applying different voltages to the transistor terminals and monitoring the current through the PEDOT:PSS channel. The best transistor was obtained with 25%cotton-75% polyester. The results obtained from the experiment show a promising approach toward wearable sensors.

Finally, we end up with the analysis of the transistor behavior when exposed to solutions of different pHs. Results showed a change in drain current after adding different solutions with different pH levels. The analysis revealed the effect of the pH on the PEDOT:PSS coating used as a semiconductor in the transistor that was made leading to results encouraging for the application of a new flexible bioelectronic device.

Chapter 1: Introduction

1.1 Justification of the Project

Wearable electronics have reached a way to form part of the human daily basis with a market size of 61.30 billion in 2022 and a compound annual growth rate (CAGR) of 14.6% by 2030. The dominant area is consumer electronics with a share of ~49% of the overall revenue with wristwear leading and driving the growth [1]. The second area with higher growth is healthcare due to their applicability of connecting doctors to patients, virtually allowing professionals to monitor patients remotely. The market size increase and interest in wearable electronics guided the interest in this area for the research explained here. However, wearable electronics can be divided into a lot of areas. This research focused on conductive textiles for wearable electronics.

Conductive textiles are attracting the attention of academy and the industry because of their applicability as wearable electronics. The interest of the industry in this can be seen in the market size since conductive textiles have experienced an increment in interest and demand not only in apparel companies but in military and defense, healthcare, and sports. The market size of conductive textiles was globally estimated at 1.37 billion by 2018 [1]. Meanwhile, it showed a CAGR of 16.5% from 2019 to 2025. By 2027 it is expected to reach 5.4 billion [2]. The major reason that is driving the market to grow in this area is the properties of the conductive textiles that include dimensional stability, and strength which is very beneficial since they are lightweight flexible, and versatile. The fact that they can be woven knitted or braided helps the development since adding a few different ways to have the type of product.

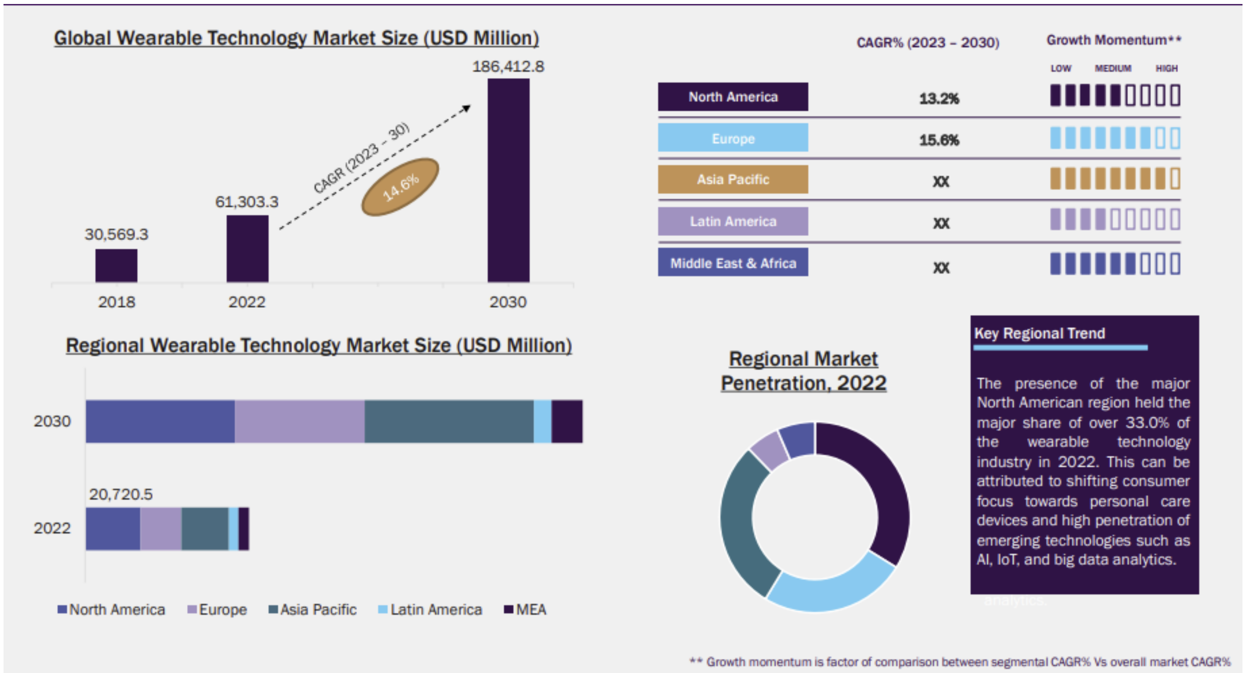

Figure 1.1 Market size of conductive textiles [1]. From *Conductive textiles market size, share & trends report, 2025*. The Grand View Research, 2023 Copyright 2023 by The Grand View Research, Inc. Reprinted with permission.

In this conductive textile, we have a few different types of products that may be found. Not only it is important to consider the product type that is used on fabric, but also, the fabric type is important to have specific properties. The most common fabric types are nylon, cotton, and polyester. Each of them represents an advantage. The nylon has abrasion resistance and high strength. The cotton is light and breathable. Polyester is strong with shrinkage and chemical resistance. Two of these materials that dominate the market are the ones used in this project to make wearable devices.

This research might lead to health applications and might be applicable or useful to military applications which are the two most areas of applications of conductive textiles. The Military emerged as the dominant area with 32.9% of the revenue share [1]. This area is expected to increase the use of these conductive textiles to make sensors that can monitor soldiers' health status and help in monitoring temperature and communication in battlefield. The next larger stakeholder, as shown in figure 1.2, is the healthcare industry. This area might use smart textiles to detect and treat chronic diseases like diabetes and respiratory problems.

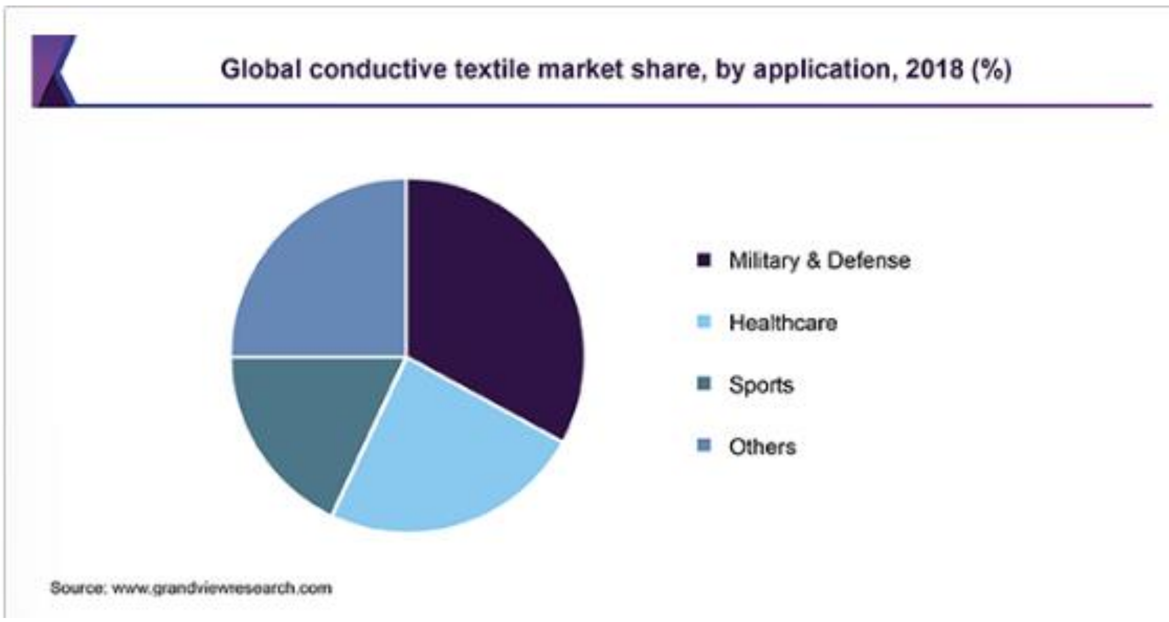

Figure 1.2 Market share of conductive textiles by shareholder [1]. From Conductive *textiles market size, share & trends report, 2025.* The Grand View Research, 2023 Copyright 2023 by The Grand View Research, Inc. Reprinted with permission.

Among all the studies done on wearable electronics not much is known about thread base as it is for thin film transistors. The characterization and their behavior in the presence of certain chemicals are topics that need further studies. The use of a transistor as a pH sensor is discussed in this work. Based on an idea that some diseases may change the pH of sweat, the transistors in this work were built with a vision to be used as a potential pH sensor for human perspiration in the future.

Organic electrochemical transistor uses an electrolyte between the gate and the source or the channel and the gate instead of using a dielectric. This electrolyte gives unique electrical characteristics such as a large electrolyte double layer capacitance and the ability of the ions in the solution to move and penetrate the organic semiconductor [3].

1.2 Research Objectives

Among different scientific reports, there is a lack of knowledge on which types of fabric are the best to make organic electrochemical transistors (OECTs). Therefore, in this work, we studied the effect of the thread materials on the performance of OECTs. This work shows the design process of different OECTs and their characterizations. Therefore, an analysis of the effect of the thread selection to make the transistor is done.

Another important thing that should be known that is unknown in the organic electrochemical transistor area is the aging effect of the transistor. To be able to use the transistor as a sensor, it is important to know the behavior of the transistor over time. The transistor behavior might change with time only by staying sitting on a shelf due to the chemical properties of some components of the device. In this work, we discuss the transistor aging effect to have a better idea of how it behaves over time.

In general, OECTs can be designed as sensors for different applications. It is common to have OECTs as saline or glucose sensors, but little is known about the transistor used as a pH sensor. Due to the characteristics of the transistor, it is possible to make it as a pH sensor. In this work, the possibility of the OECTs being used as a pH sensor on perspiration is discussed.

Geometry is very important for the behavior of each transistor. Unlike the solid-state Metal insulator semiconductor field effect transistor (MISFET), the OECTs geometry cannot be modified in the same way because is an electrolyte that is used instead of a solid glass or insulator. For that reason, the geometry is changed in the transistor designed to have the most efficient transistor possible.

The objectives of this research are 1) To determine the best materials and procedure to be used to design an efficient transistor. 2) To analyze the characteristics of the transistor by doing an IV curve and determine the threshold voltage of the OECTs. 3) To determine if the transistor can be used as a pH sensor by determining the change in threshold voltage and the impedance spectroscopy of the device. 4) To determine the behavior of this transistor embedded in a piece of cloth.

1.3 Thesis Outline

The thesis consists of 6 chapters. Chapter 1 analyzes the motivation and research objectives. Chapter two discusses the literature review related to OECTs. Chapter three describes the materials and methodology used to make the experiments to get the analysis done and the results obtained. Chapter 4 talks about the stability of the transistor which is a published conference paper based on an analysis of a fabricated transistor in the lab. Chapter 5 shows the results and analyzes them. Chapter 7 is the conclusion and future works.

Chapter 2: Background

2.1 Thin Film Organic Electrochemical Transistors

Some organic electrochemical transistors (OECTs) have a structure similar to that in organic field-effect transistors, but they utilize an electrolyte solution instead of a dielectric [3] Thin film-OECTs typically consist of metallic source, drain, and gate electrodes, with an electrolyte situated between the channel and gate. These transistors have the advantage of being able to operate at low voltages getting the current from ions on solution, making them ideal for organic bioelectronics and biosensors [3,4].

2.1.1 Flexible

Recently, there has been a growing interest in designing wearable biosensors and energy harvesting devices that can be applied directly on the skin [5,6]. In 2018, Seung Yun Oh and his team developed a flexible thin film sensor that can detect glucose and pH levels on the skin. The sensor was created by depositing carbon nanotubes (CNTs) layer by layer on top of patterned gold nanosheets. To detect the levels, they used $CoWO_4$/CNT and polyaniline/CNT coated with CNT-gold nanosheet. Although their sensor showed different results compared to a commercial one, they compensated for this through measurement [5].

When it comes to conductive polymers for organic sensor devices, PEDOT: PSS is a top choice. In a recent project by Y. Kim, et al., they blended PEDOT: PSS with highly stretchable nonionic waterborne polyurethane (WPU) and coated it with thermoplastic polyurethane to create a thin, flexible film. They discovered that the film with 2.0 wt% could stretch up to 400% of the electrode without being damaged. However, the electrical properties of the film decreased at higher content of WPU in the blend. [7].

2.1.2 Non-Flexible

Researchers have investigated the effects of using PEDOT:PSS film with liquids of varying polarities. Zhang Shiming and colleagues found that the thickness of the film decreases when exposed to more polar liquids. Additionally, the presence of these liquids leads to a decrease in the sheet resistance of the film [8].

The behavior of a device is greatly influenced by the crystallinity of the semiconductor, according to a study by Kim Seong-Min et al. They tested the performance and long-term stability of two types of channel material in an aqueous environment: crystallized PEDOT: PSS (Crys-P) and ethylene glycol-treated PEDOT:PSS (EG-P). The results indicated that Crys-P has better aqueous stability, 10 times higher on-state ID, and 4 times higher transconductance than EG-P [9].

Transconductance is a key measurement for thin film transistors. A team of French scientists created a transistor using PEDOT:PSS, which was deposited and patterned with photolithography. The transistor had gold for its drain and source contact, and the gate was made of Ag/AgCl wire with NaCl solution as the electrolyte. At a VG of 0.275V, the device had a transconductance of 2.7 mS, which remained constant at a frequency of around 1 kHz [10].

An important aspect of the research is to understand the behavior of PEDOT:PSS in different conditions. Thin films behave differently in different conditions depending on the compounds that compose that film. A group of scientist on Netherland studied the electrical properties of PEDOT:PSS thin film at different concentrations of sorbitol. It is known that sorbitol increases the conductivity of PEDOT:PSS but they discover that the way sorbitol increases the conductivity of PEDOT:PSS film is due to the evaporation of sorbitol on annealing process of

PEDOT:PSS/sorbitol. This way they demonstrate that sorbitol acts more like a process additive instead of a secondary dopant on the film. They found that the work function can be changed from 5.1 eV to 4.8 eV due to sorbitol. Also, sorbitol helps on the stability of the film [11]

The conductive polymer solution used is often a combination of ethylene glycol and PEDOT:PSS. J Rivnay et al., have found that adding ethylene glycol increases the aggregation of PEDOT:PSS film. This addition also aids in the hopping of charges at an intermolecular level, greatly improving electronic conductivity through an enhancement in hole mobility [12].

In an article from Gualandi et al., a new type of hybrid device sensor was demonstrated using a thin film with a fabric-based sensor made of PEDOT:PSS attached to glass. The sensor is composed of a two-terminal PEDOT:PSS stripe modified with Ag/AgCl nanoparticles. The signal obtained through the polymer is proportional to the logarithm of the concentration of chloride ions in the solution tested, working in the range of 10^{-4} to 1 M. The limit of detection obtained was $0.5x10^{-4}$ M, and the device showed a shorter response time than a transistor with an Ag/AgCl gate electrode without fabric. Overall, the geometry and composition of organic sensors have undergone changes in recent years [13].

2.2 Fiber Based Organic Electrochemical Transistors

The ideal smart clothing and wearable electronics should be based on flexible devices that can be woven into textiles. To solve this challenge fiber is used since the ideal electronic is difficult to obtain with planar and rigid structures devices [14]. The fiber base OECTs are transistors that are not made planar like the thin film but rather they use the 3D space by using the fabric threads by coating and functionalizing them with a conductive polymer. Monitoring the status of the body and flexibility is one of the most important advantages of designing these devices.

A group of scientists in Italy designed a fabric base transistor out of natural cellulose (cotton yarns). Like in the thin film transistor PEDOT:PSS, one of the most common conductive polymers is used to coat the tread to make the transistor using a silver wire as a gate. They analyze the functionalized thread-base transistor to use as saline sensing of sodium chloride (NaCl) concentration in water. They use no other electrolyte to know the concentration of salt, in other words, they use the analyte as the electrolyte between the gate and the drain and source [15].

In 2018, Anneng Yang and colleagues designed an OECT that serves as a biosensor for glucose in diapers. Nylon fiber was used to create the channel, which was then coated with layers of Cr/Au, Cr/Au/PEDOT:PSS, Ti/Pt, and Ti/Pt/PEDOT:PSS through deposition and magnetron sputtering. The researchers studied how bending the thread affected crack formation and measured glucose levels in the presence of synthetic urea [16].

As mentioned earlier, OECTs have multiple applications, such as in healthcare, medicine, and sports. In a scientific article by Gualandi Isacco et al., it was explained how textiles can be used as chemical sensors to analyze sweat. The study also discussed various techniques used to create textile sensors. One such approach was presented in a research paper by Shirley Coyle et al. They incorporated a pH-sensitive dye into a piece of fabric to create a textile sensor. The dye was placed inside a fluidic channel by screen printing a paste on the fabric. The dye used, called bromocresol purple, changes color from yellow to blue in response to a pH change. [16,17].

Another approach is done by Italian scientists. They made a textile sensor with ion-selective membranes. The yarn was immersed in PEDOT:PSS, baked for 3 hours and then soaked in a potassium ion membrane. The selectivity was due to the membrane and gate silver electrode. They created a sensor that was able to be highly selective of potassium and calcium in sweat. The membrane selectivity was tested in the presence of different ions, and it was able to discriminate among cations over from 10-3M to 1M although it was able to sense some difference modulation at 10-5 M to 10-3M concentration [16,18].

While there has been progress in recent years, there are still some areas that require further investigation. One such aspect, as discussed by Zhang Xiaoshuang and others, is the uniformity of films during preparation. This is a crucial factor as it impacts the stability and consistency of performance. Another significant area that requires further study is the enhancement of conductivity in PEDOT:PSS solid film[19]. Our work will focus on the uniformity of the thread to be used as a transistor, resulting in enhanced conductivity on the sensor substrate. The findings suggest the potential for a sensor embedded in the fabric to detect pH levels in human perspiration.

Chapter 3: Methodology

3.1 Operational Mechanism

The structure of the designed OECT consists of a conductive thread that works as the gate electrode, the second thread (parallel to the first one) coated with a conducting polymer as the transistor channel, and a gel electrolyte that bridges both threads. To make the channels, a conducting polymer (i.e., poly (3,4-ethylenedioxythiophene) doped with poly (styrene sulfonate), PEDOT:PSS) was used.

The majority of the designed OECTs with PEDOT:PSS are essentially depletion mode field-effect transistors in which the conductivity of the channel between the drain and source is controlled via the gate terminal. Hence, the drain current is a function of the drain-source voltage (V_{DS}) even in the saturation mode. PEDOT:PSS is a degenerated doped p-type polymer, application of a voltage to the gate drives holes toward the polymer channel. This makes the ionic interchange between the polymer and the electrolyte, consequently changing the conductivity of the channel. Regarding the polarity of dopants, a positive voltage at the gate ($V_g > 0$) forces the cations of the electrolyte to move towards the channel and de-dope the conductive layer [3].

3.2 Solution Synthesis

To make the conducting polymer solution, PEDOT:PSS was bought from Sigma-Aldrich and mixed with ethylene glycol from Sigma-Aldrich as well on a 15 mL tube. The solution consisted of 20% ethylene glycol on PEDOT:PSS. The solution was used to coat different threads, specifically 25%cotton-75% polyester, 32%cotton-68%polyesters, and 100%cotton. All these threads were bought from Walmart.

The electrolyte used to make the transistor was a polyvinyl alcohol gel (PVA gel) prepared by adding 1.5 g of PVA to 10 mL of DI water in a beaker. Then, 1 mL of phosphoric acid was added into the solution. The mixture was placed on a hotplate and stirred at 450 rpm at 90 C for 4 hours with a parafilm on top of the beaker to avoid evaporation of water from the solution. The solution was cooled down by leaving it for 3 days at room temperature. The procedure used is the same as Kareri et al. and provides a way to substitute the insulator layer on a MISFET for an electrolyte on a OECTs.[20]

To make the solution to be used as an analyte for sensing pH a 1.0 M Tris-buffer at pH of 7.5, 7.2, 6.9, 6.4 and 5.7 (HCl) were used. A stock solution of the buffer with a pH of 8 is lowered with HCl 1M and using a pH meter we add solution of HCl on tris-buffer until get the desire pH solution. This solution is placed on the channel of the transistor to use as a sensor.

3.3 Coating Process Selection

To determine which of the coating processes works better to get a reliable conductive thread, two different methods of coating (i.e., drop casting and dip coating) were practiced. The drop casting process was done by applying the PEDOT:PSS solution on a thread. To do this experiment, the solution was applied on a piece of 25% cotton-75% polyester thread using a micropipette. The 16 cm long piece of thread was positioned as seen in figure 3.1a and with a pipette add the solution. The coated thread was seated in its position so it could dry for 4 hours and then a second layer of the solution was applied on the thread. This process was repeated 3 times to get a coating layer.

The dip coating process was done with the same solution as drop casting. A 16 cm long thread was tied to an end to help retrieve the thread from the solution where the thread was sunk into. After tying the thread, it was submerged into the solution tube. The thread was left in the solution for 30 minutes. After removing, the thread was dried at room temperature for 8 hours in a vertical position as shown in figure 3.1b. This process was done two times to get the threads well coated with two layers of polymer.

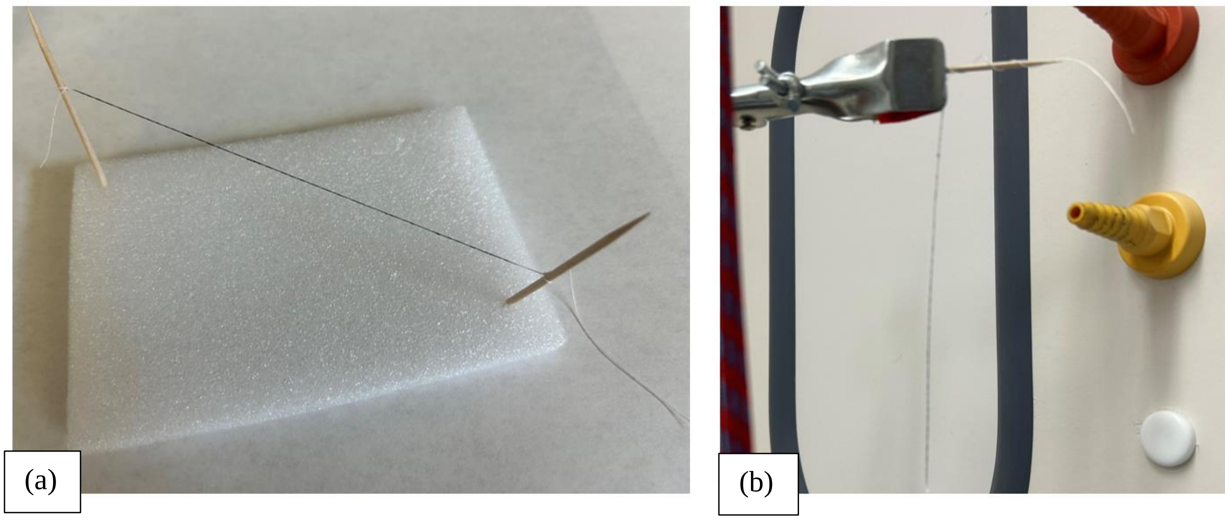

Figure 3.1 Thread drying to be used as channel for OECTs. Figure a) vertical position b) horizontal position.

3.4 Transistor Design

The fabrication steps for making an OECT from the coated threads are shown in figure 3.5. The transistors were built on a glass slide where the coated threads and contacts were placed. As shown in figure 3.2a, 1 cm long thread coated with PEDOT:PSS was stretched and taped down with two pieces of copper tape which also used as the drain and source contacts. Then to avoid any short circuit, a piece of Kapton tape was applied for passivation before a silver coated thread was positioned parallel to the PEDOT:PSS coated thread. A copper tape was put in the silver-coated thread as shown in figure 3.2d to be in contact with the silver thread. Since we aimed to fabricate an organic electrochemical transistor, unlike a MOSFET or MISFET that uses a dielectric layer between the gate and the channel, we completed the device by putting a droplet of the synthesized gel electrolyte between the threads. The overlapping area between the gel and the PEDOT:PSS thread is considered the channel of the transistor.

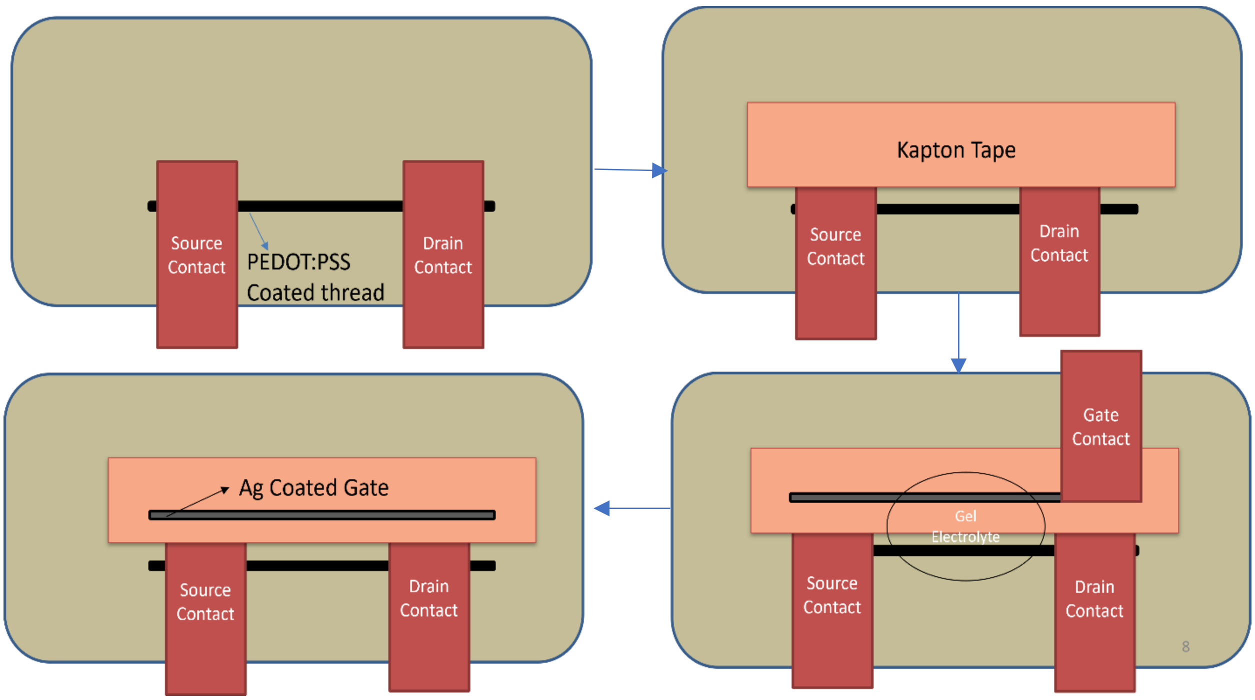

Figure 3.2 Building process for the fabric-based organic electrochemical transistor (OECTs)

3.5 SweepMe Analysis

To make the characterization of transistors, a two-channel source measure unit (SMU) Keithley 2602A instrument was used. The transistor was connected as in figure 3.2c. The drain and source contact are connected to the same channel, in this case, channel A and the gate of the transistor were connected to channel b of the SMU instrument. The reported testing results in chapter 4 were collected using Lab Tracer software and chapter 5 and 6 were using SweepMe software. This new software is used to make the analysis the best way possible. As reported in chapter 4, testing devices with Lab Tracer showed large displacement current at the gate terminal. The Lab Tracer does not have the delay option between measurements of different gate voltages. This makes the analysis inaccurate since the transistor needs delays time due to the ion movements taking time to go back to their original positions.

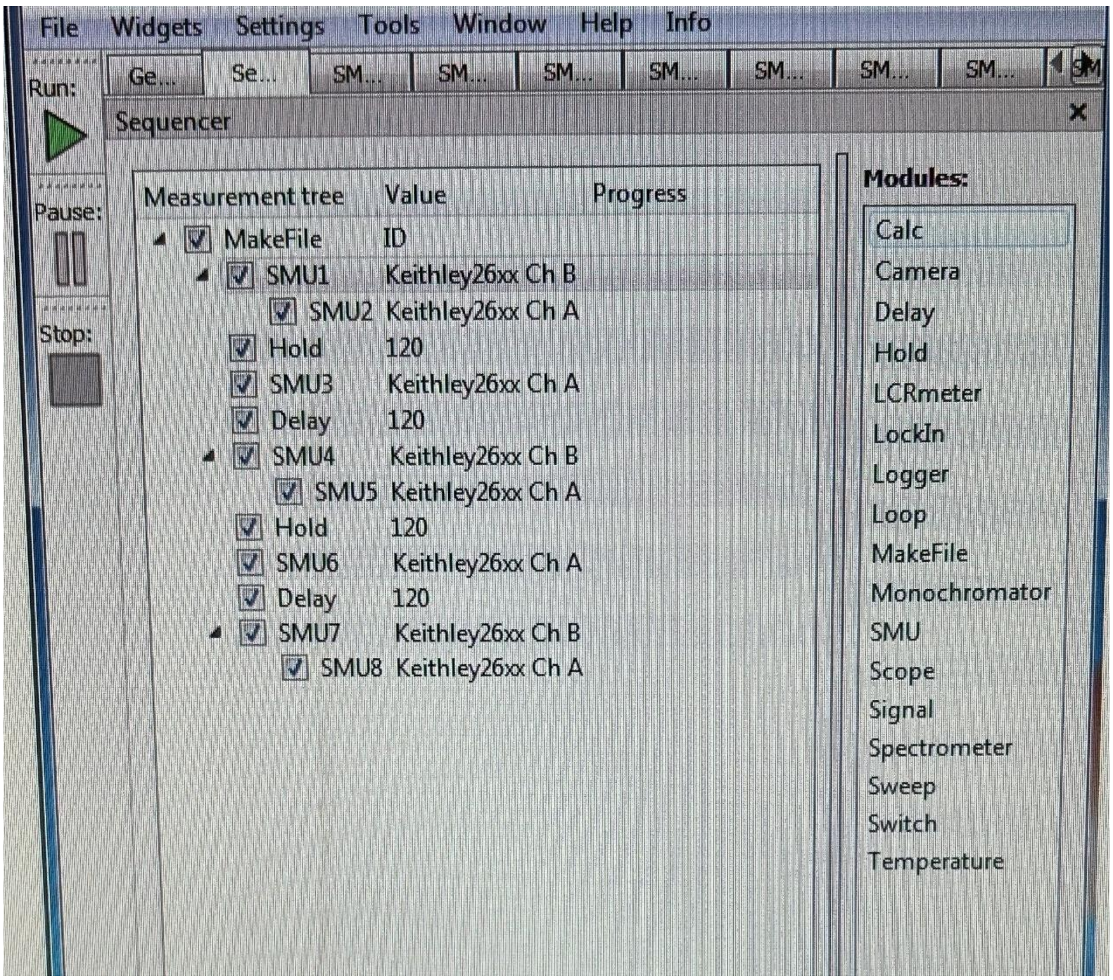

Figure 3.3 SweepMe software setup to make the output characterization analysis.

As can be seen in Figure 3.3, the analysis setup is done by coding the software in the shown way. A file is created to get the text file of each run. The SMU 1, SMU 4, and SMU 7 are channel

B of the Keithley instrument. Channel B controls the gate voltage that was applied to the transistor. To start the analysis 0 V was applied to the transistor and scan the drain and source voltage from 0 V to -0.8 V getting the current of the drain (I_d) vs the drain-source voltage (V_{ds}) as would be done on a solid state transistor. A 2-minute hold was placed to let the ions get back to their position in their steady state. To avoid any leakage current, we place the voltage on the drain and source to 0 V and place a hold for two more minutes. All this process ends the scanning of the transistor at 0 gate voltage (V_g).

To make the rest of the characterization at another V_g since we placed the transistor into its original state, we placed the channel B or SMU 4 into 0.2 V and make a scan from 0 V to -0.8 V on the drain and source getting the IV curve of the transistor at this gate voltage. Just like in the previous part at V_g =0 V, the hold is placed to give time to the ions to move to their position, and then channel A is putted into V_{ds}=0 V to warrantee we have the transistor in its original state. The same process is done to get the output characterization of the device at other V_{gs}**.**

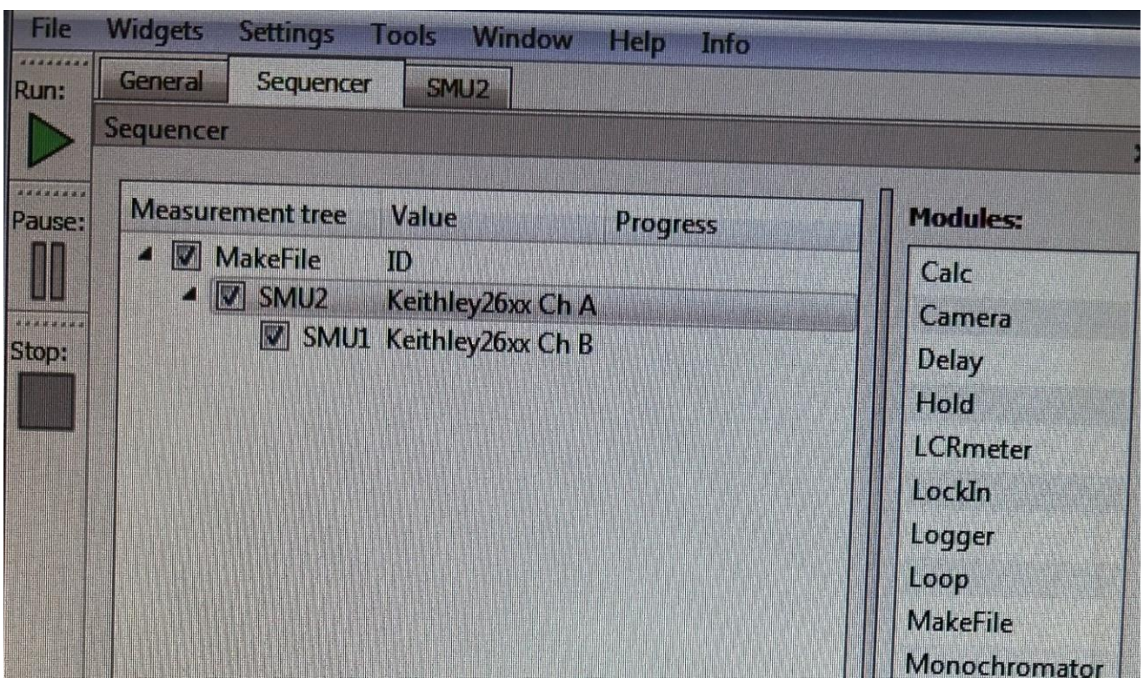

Figure 3.4 Setup of SweepMe software to make transfer characteristic of the device.

To make the analysis of the gate voltage the code changes a little to make the scanning and no hold or delay is placed since just one run is needed and the scan is from the gate instead of the drain and source. As seen in figure 3.4 it is needed to make a file like in the IV curve characterization to have the text file data. Just 2 SMUs were used to make the analysis. Channel A is for drain and source connection to the transistor and they are steady on -0.8 V and a scan is done on channel B which is the gate on the transistor.

3.6 Transistor use as a Sensor

In session 3.4, a transistor was created to serve as a pH sensor. To build the sensor, the same process was used to make the transistor in session 3.4 was followed, with the exception of using different threads. The transistor was constructed by altering the thread that served as a channel in session 3.4. After constructing the transistor, a buffer solution with varying pH levels was applied to observe how the transistor behaved. The solution was placed on top of the transistor gel, and transfer curves were taken for the added solution. The first solution had a pH of 7.5, then the transistor was washed with water droplets to add then the next solution which was a pH of 7.2. After the analysis of this new solution, the same washing procedure was done to do the next solution addition and add the subsequent solutions. The solutions were added at a decreased pH. We started with a pH of 7.9 as described and went to 7.2, 6.9, 6.4, and finally 5.7.

3.7 Potentiostat Analysis

To determine the impedance of the transistors the characterization was done by using a potentiostat instrument (VersaSTAT 4). The bode plot was collected using the transistor as a two-terminal device making an interconnection between drain and source and using it as a working electrode and the gate as a reference electrode. The data collected using the software was with a frequency of 1 to 0.1 MHz.

3.8 Making the Transistor on Fabric

To successfully integrate a transistor into wearable fabric technology, it is important to confirm that the previously utilized process operates effectively within the fabric. To perform this test, we fabricated the transistor directly onto a fabric piece of a shirt of 100%Cotton, utilizing the same procedure outlined in session 3.4. As previously explained, the PEDOTT:PSS thread that is coated is embedded within the fabric (as depicted in Figure 3.2), while the silver-coated thread serves as the gate and is sewn below it. Instead of copper tape, which was utilized in past samples, contact is established with a silver-coated thread that is sewn into the fabric to secure the PEDOT:PSS thread and function as both the drain and source contact for the transistor. Same analysis as the rest of the transistor is done.

Chapter 4: Stability of Fiber-Based Organic Electrochemical Transistors with Gel Electrolyte for Wearable Electronics[1]

4.1 Abstract

With the increasing interest in wearable electronics, still, building electronic circuits on fabrics is challenging. Among different approaches, fiber shape electrochemical transistors are potentially suitable for various applications, particularly for bioelectronics. Fiber-based devices are getting popular because of their low fabrication cost, lightweight, and mechanical flexibility without losing their properties as sensors and transistors. In this work, we have studied an organic electrochemical transistor made from two conductive threads with a gel electrolyte. The transistor was tested when it was exposed to an acidic solution which then showed a change in the drain current. The results from testing the conductive thread between the drain and source revealed the effect of the pH on the PEDOT:PSS coating used as the semiconducting material in the transistor design. The results are encouraging for the applications in new low-cost, flexible bioelectronics sensing devices.

4.2 Introduction

The organic chemical sensors and their developments as wearable electronic devices have attracted attention in both academia and industry because of their possible huge impact on personal healthcare, safety, and sports applications [15,21,22]. These sensors are electronic devices that can

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[1] This chapter was published before in SPIE (Nestor O. Marquez Rios and Arash Takshi "Stability of fiber-based organic electrochemical transistors with a gel electrolyte for wearable electronics", Proc. SPIE 12210, Organic and Hybrid Sensors and Bioelectronics XV, 1221004 (3 October 2022) Permission is included in Appendix A

be embedded in garments that might provide a non-invasive measurement while being designed with unique features such as flexibility, versatility, and low cost [15]. The sensors can be worn to provide information about the wearer's body by constantly monitoring signals and measurable parameters from their body.

In the past few years, there has been an increasing development in studies on organic electrochemical sensors specifically on the advancement of polymers with high conductivity [22]. These studies led us to design devices for energy harvesting and storage [20]. Cotton yarns have been functionalized to have conductive fibers. This functionalization has been done by coating using metal nanoparticles or carbon nanotubes (CNTs) [15]. Studies have been made to make nonconductive fabrics into conductive ones by coating them with different polymers like glycolated thiophene(g2T-T) polymers, poly(3-hexylthiophene) (P3HT), and poly(3,4-ethylenedioxythiophene) doped with poly (styrene sulfonate) (PEDOT:PSS), etc.[3]. While the majority of the designs work based on the resistance change of the functionalized materials for sensing the desired parameters, some devices have been designed in a form of a transistor [21]. The common sensor type is designed as organic electrochemical transistors (OECTs).

An OECT-based sensor can be designed to respond to sweat. The primary purpose of sweat in humans is thermoregulation in the body. However, the analysis of this fluid is valuable for the determination of some diseases like Cystic Fibrosis, or skin diseases that cause a change in pH of the skin like dermatitis or fungal infections [22,24]. The sweat contains metabolites and electrolytes which can be used as a tool for information about the health of the person and their fitness [23]. This perspiration is one of the body fluids that can be taken outside the body and do not require any implantation of a sensing device and can be collected in a non-invasive way. This led us to study the feasibility of using an OECT design as a wearable sensor for the pH measurements from sweat.

Although the application of OECTs could have a huge impact on medicine, we are still learning and working at the research level for producing preliminary results. To continue collecting information about this topic, we have studied an OECT that can potentially be used as a wearable pH sensor. Our device is based on the same properties as a field effect transistor (FET) with the difference of adding a layer of gel electrolyte instead of having a dielectric and using fabrics that have been functionalized with PEDOT:PSS conducting polymer as the channel and the gate as shown in Figure 4.1a. Other works have been done with PEDOT:PSS for sensing saline concentrations and glucose sensors [22]. To make the analysis, we built the transistor on a glass slide and analyze the transistor capability to determine the pH of phosphoric acid. Measurements were collected using a Keithley source-measure unit and a potentiostat instrument.

4.3 Materials

To make the gate of the organic electrochemical transistor, we bought Jameco thread. The thread that was used to make the channel of the OECT was 25% cotton and 75% polyester purchased from Walmart. The gel electrolyte was synthesized from polyvinyl alcohol (PVA) 87-89% hydrolyzed high molecular weight from Alfa Aesar, phosphoric acid (H3PO4) concentrated from Sigma Aldrich, and deionized water. The PEDOT:PSS polymer solution was synthesized by the addition of PEDOT:PSS, ethylene glycol from Sigma Aldrich, and dodecyl benzene sulfonic acid solution (DBSA) 70% in isopropanol from Sigma Aldrich.

4.4 Synthesis of Solutions

PEDOT:PSS polymer solution consisted of 5% dodecyl benzene sulfonic acid (DBSA) concentrated and 20% ethylene glycol. To prepare the solution, we added 4 mL of ethylene glycol and 1 mL of DBSA to 15 mL of PEDOT:PSS. To make the thread conductive, we coated the thread by deep coating [25] in the PEDOT:PSS solution. We submerged an 18 cm long thread solution into 10 mL of PEDOT:PSS solution in a glass petri dish that was placed on a hotplate for 30 min at 80 C. After the coating, we put the thread to dry at 60 C for 15 minutes in the oven. This process was repeated 2 times to make sure the thread was fully coated. After taking the thread out, we let it sit for 20 minutes so it can reach ambient temperatures before start using it.

The gel electrolyte was a polyvinyl alcohol gel (PVA gel) prepared by weighting 1.5 g of PVA and added to 10 mL of deionized water with an addition of 1 mL of phosphoric acid. The mixture was stirred at 450 rpm on a hotplate at 90 C for 4 hours with a parafilm layer on top of the beaker to minimize water evaporation. After stirring, we let the solution sit for 3 days at room temperature to have the gel consistency needed [26].

4.5 Transistor Design

For testing, prototype OECTs were made on glass slides by cutting 2 cm of the PEDOT:PSS conductive thread that was made. We placed the thread on the glass slide as shown in Figures 4.1a and 4.1b. Contacts were made at two ends of the thread with copper tape. The extension on the tape allowed us to make easy contact with the alligator clips while making solid contact with the threads. Kapton tape was put on top of the copper tape to passivate the surface of the copper and avoid any short circuit between the gate and the contacts. The transistor shown in Figure 4.1a-c was made with a 7 cm long Jameco thread as the gate which was placed ~4 mm away from the PEDOT:PSS thread sitting on top of the Kapton tape. We took another piece of the copper tape to put it on the Jameco thread to have a contact on the gate thread. We placed the 30 μL of the gel electrolyte on the channel area covering the gate and the exposed area of the PEDOT:PSS thread.

4.6 Data Collection

To characterize the OECT, we used a two-channel source Keithley 2602A instrument. The transistor was connected the same way as shown in the schematic in Figure 4.1a having the PEDOT:PSS contact as a drain and source on one channel of the source-measurement unit and the gate contact to the second channel. We applied 20 μL of acid on top of the gel electrolyte for the pH sensor testing. The data was collected every day letting the transistor dry from the analyte that was tested. The Software used was Versa Studio using the frequency from 10000 to 0.1 with a step of -0.5.

The second analysis was made using the potentiostat (VersaSTAT 4). To collect the bode plot we used a PEDOT:PSS thread the same way as the transistor but without using the gate contact (without the Jameco thread fiber). We used the working and counter electrodes connected to the drain and source contacts. Our analytes were phosphoric acids with different pHs ranging from 7.5 to 5.7 based on human sweat pH [27] and the same way as the transistor analysis on the Keithley, we added our analyte to the gel electrolyte, and we let the thread dry one day before testing different acids.

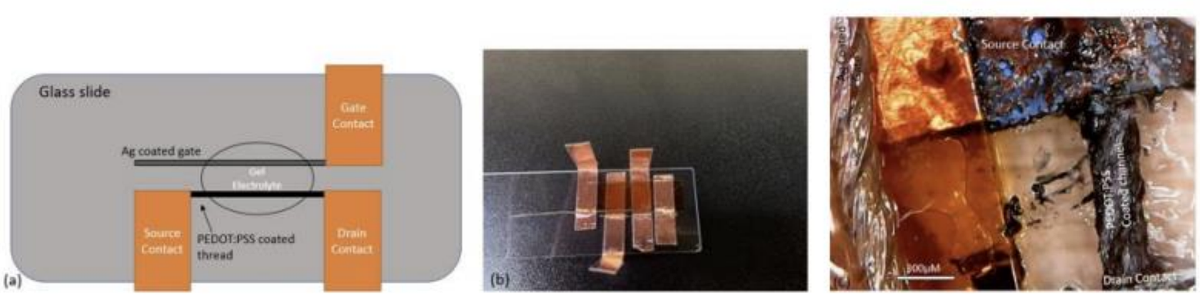


Figure 4.1 The organic electrochemical transistor design. The channel of the transistor is defined by the contact area between the gel electrolyte and the PEDOT:PSS thread. a) An schematic of the transistor. b) An image of the fabricated device. Kapton tape was used to avoid contact between the two threads. c) A zoom image of the transistor with gel on top of the gate and the channel.

4.7 Results and Discussion

The behavior of the OECT was studied by applying a constant gate voltage (V_g), scanning the drain-source voltage (V_{ds}), and measuring the drain current (I_d). The gate voltage was kept constant while scanning V_{ds} from 0 V to -0.8 V. The experiment was repeated 5 times each time at a different V_g. Since PEDOT:PSS is a p-type material, the OECT was a p-type transistor. However, in this configuration, the transistor operates at the depletion mode which required a positive voltage to the gate. The gate voltage makes the cations of the gel electrolyte move to the channel where the PEDOT:PSS polymer is. This makes the polymer change its conductivity as the oxidation state of the polymer changes:

$$PEDOT^{+}: PSS^{-} + M^{+} + e^{-} \leftrightarrow PEDOT + M^{+} :PSS^{-} \quad (1)$$

where M^+ is the cations in the gel electrolyte.

On the first day after the building of the transistor, the device was tested with the Keithley 2620A. As the curves in Figure 4.2 shows, there was a significant shift for $V_g \neq 0$, indicating a large leakage current through the gate terminal. This same performance was repeated one week after the transistor was built. Although, as shown it is not a perfect transistor, the device performed as a FET featuring both the triode and saturation modes.

Figure 4.2 shows the behavior of the OECT on day one that was tested after the built-up. A similar performance was observed during the first week of testing having reproducibility. The overlapping area between gel and PEDOT:PSS thread defines the channel in the transistor. As shown one of the signals started at 16μA and at V_{ds} = -0.6 V for the same V_g the drain currents was -7.3 μA which was different than the rest of the current with different V_g.

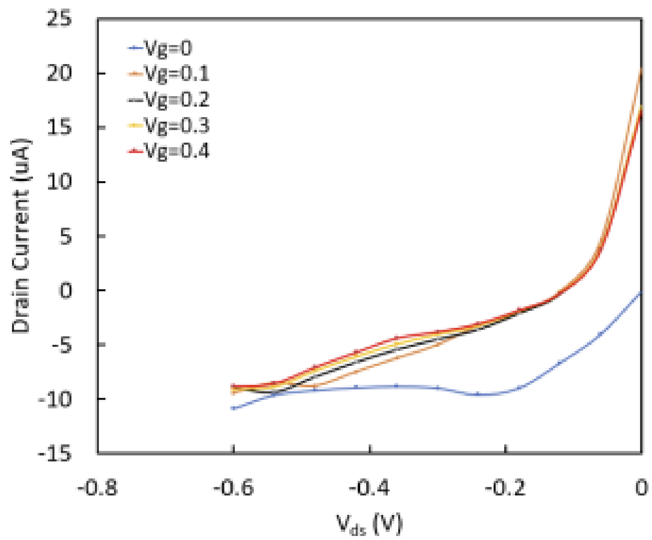


Figure 4.2 Transistor behavior day one after it was built.

A degradation in the device performance was observed as it aged. The OECT's behavior changed with time presenting a more resistive response a few weeks after the fabrication and storing of the sample in the lab. Figure 4.3 shows the behavior of the transistor after 3 weeks. The change in the OECT's response is likely due to the gel electrolyte drying over time.

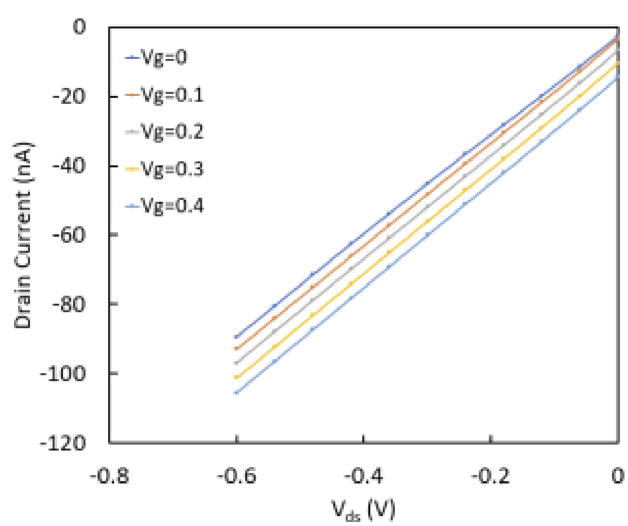


Figure 4.3 Transistor's output characteristic after 3 weeks.

The drain current demonstrates the loss in conductivity which is the signal of the OECT with more than 3 orders of magnitude. At V_{ds}=0.0 V the drain current shows a signal of -2.63 nA and at -0.6 V it shows a drain current of 90 nA changing linearly. The same feature was observed with different values showing a resistor-like signal. Compared to the first day, the drain current was reduced by two orders of magnitude. The fact that the electrolyte gel dries suggests that ions' mobility in the gel drops which consequently affected the conduction along the transistor channel. However, we observed that after the gel was dried, when the device was exposed to a liquid electrolyte, the drain current increased significantly, and the transistor performance started showing the triode and saturation modes again (Figure 4.4).

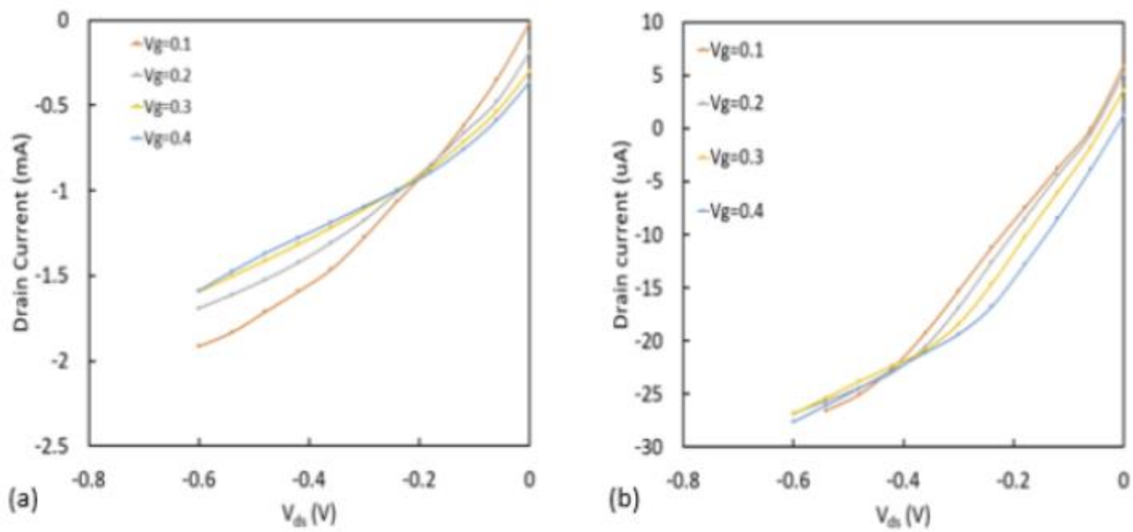


Figure 4.4 Transistor behavior after the addition of phosphoric acid. Figure a) phosphoric acid with a pH of 5.0 and b) phosphoric acid with pH of 6.8.

Figure 4.4 shows the results from the transistor being tested when it was exposed to two different buffer solutions one with a pH of 5.0 (Figure 4.4a) and the other pH of 6.8 (Figure 4.4b). The results show that for V_g=0.4 V, the drain current reached -1.5 mA at V_{ds}=0.6 V when it was exposed to the acidic solution of pH 5.0. However, the current value at V_g=0.4 V and V_{ds}=0.6 V was only -27 μA for the test with the neutral electrolyte (pH 6.8). Also, the data shows a significant reduction in the gate leakage current compared to the fresh OECT in Figure 4.2. The fact that a rejuvenating response was achieved after adding a neutral solution to the gel again implies that the aging effect was due to the dryness of the electrolyte. However, the significant boost in the current magnitude (2 orders of magnitude) in response to the acidic solution indicates the sensitivity of the device to the change in the pH level.

The acid used was phosphoric acid (H_3PO_4) which was added to the gel to see if it affects the transistor. To further investigate if the variation in the transistor response to an acidic solution was due to the gel electrolyte or the change in the conductivity of PEDOT:PSS, we designed a simple experiment by making a resistor-like device made from the PEDOT:PSS coated thread with no gel coating and no gate contact. The impedance of the resistor was then measured when it was exposed to the solutions with different pH. We ran the tests with five different solutions with pH of 7.5, 7.2, 6.9, 6.4, and 5.7. Purposefully, the pH range was limited between 7.5 and 5.7 to mimic the pH variation in human sweat [9]. For testing the resistor, we used the potentiostat.

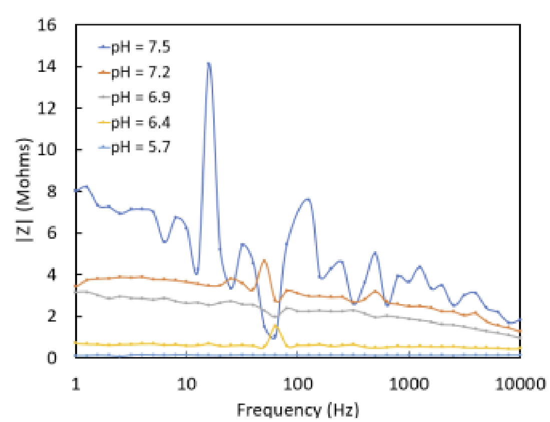


Figure 4.5 Bode plot for PEDOT:PSS thread as function of pH.

Figure 4.5 shows the results of the potentiostat analysis showing that the impedance decreases as the pH decreases. The data clearly shows that the impedance of the PEDOT:PSS thread is a function of pH. Also, this leads us to think that the important part of the transistor is the PEDOT:PSS thread since it shows an impedance decrease only by putting acid on the channel with no gate. We repeated the test with a thread coated partially with the gel. The results (not presented here) showed a much faster and more consistent change in the impedance when the acidic solution directly interacts with the exposed PEDOT:PSS part of the thread than the part was coated with the gel. Hence, we conclude that the observed changes in the drain current in the OECT (Figure 4.4) were due to the effect of the acidic solution on the PEDOT:PSS. Nevertheless, the transistor design allowed us to get an amplified signal which is more suitable for practical applications in wearable electronics. Further studies are planned on investigating the mechanisms that can improve the sensitivity of the OECT-based pH sensor and improve the stability of the device.

4.8 Conclusion

The results of this analysis demonstrate that the organic electrochemical transistor can be used as a pH sensor due to the properties of the PEDOT:PSS polymer thread. The transistor is capable of getting results for pHs similar to human perspiration. The limitation of the transistor is the aging process since the gel gets dry with time making the gel not functional for the sensor, affecting, therefore, the sensitivity of the transistor. Further studies are needed to have a wearable electronic device knowing the ability of the PEDOT:PSS thread.

Chapter 5: OECT Characterization

5.1 Introduction

The characteristic of OECT is not well known as field-effect transistors (FETs). Studies have shown that the materials and the fabrication process of FETs have direct effect on their behaviors [30]. However, little is known about the effect of the materials and the fabrication procedure on OECTs.

This chapter tries to determine which process is the most suitable for building an OECT using a selected thread. Since little is known about the process to build these devices, an analysis is conducted to get the best device possible based on the most commercially available threads on the market now. An essential feature is the coating process to convert the non-conductive thread to a conductive channel with source and drain contacts. Hence, the objective is to find a suitable coating method on various threads for the purpose of designing a thread-shaped OECT, characterize transistors with different types of thread to determine which is the most reliable and characterize transistor make in a sewed fabric.

5.2 Coating Process Selection

There are a few methods used to coat materials but not all of them are suitable for coating threads. For example, spin coating is a reliable method to make a thin-film on a planar substrate, but the method is not applicable for coating thread. Therefore, for the samples made and tested in this chapter, we tested dip coating and drop casting.

Based on the procedure discussed in chapter 3, two different coating processes were used to make the threads conductive. Figures 5.1a and 5.1b show the difference between the two different coating results on pieces of a commercially available thread made from 25% cotton-75% polyester. As explained in chapter 3, in the dip coating method, the thread was soaked into the solution while the drop casting was conducted by putting droplets of the PEDOT:PSS ink on the thread.

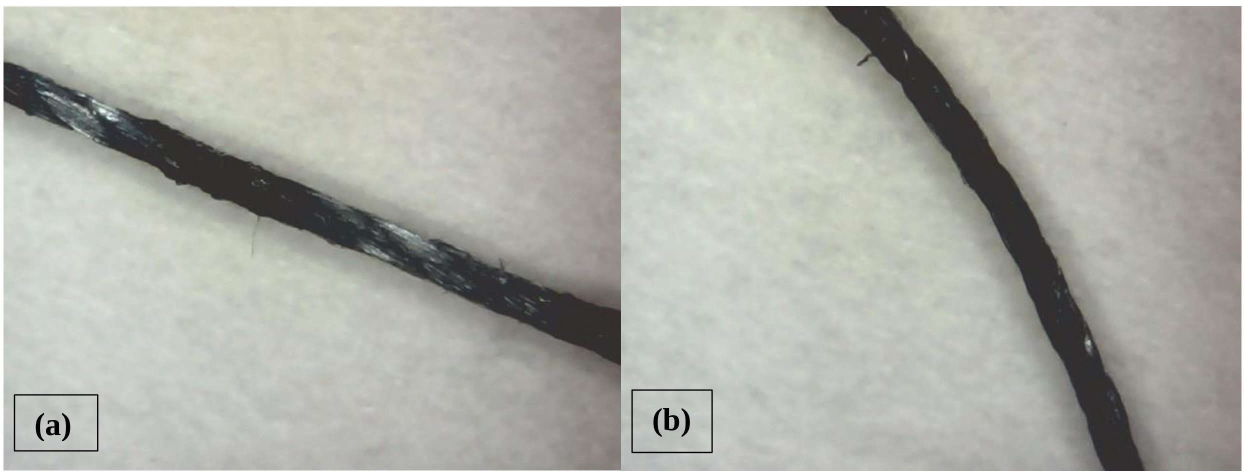


Figure 5.1 25% cotton-75% Polyester thread coated with PEDOT:PSS. Figure a) by drop casting and b) by dip coating

As shown in figure 5.1, the thread that was coated with the conducting polymer by drop casting did not get well coated even after three times of coating. The visual inspection of the thread with the naked eye (and the microscope image) shows a non-uniform coating. As shown in figure 5.2, the drop casting process produced chunks of the dried conducting polymer along the thread. The segments between the chunks were not coated properly. Since the thread is not well coated as seen in figure 5.1a white areas can be seen on the thread when solution dries, creating just non uniform layer of the polymer on the thread.

Figure 5.2 shows the problem that is caused by using drop casting over the thread leaving sections with poor coating. The problem was due to the motion of the liquid conductive ink along the thread when the droplets were applied. This created areas with droplets of ink and when they dried, chunks of the dried ink were formed. A probable explanation on the formation of the chunks is the cohesion of the solution which can be stronger than the adhesion of the same solution into the thread.

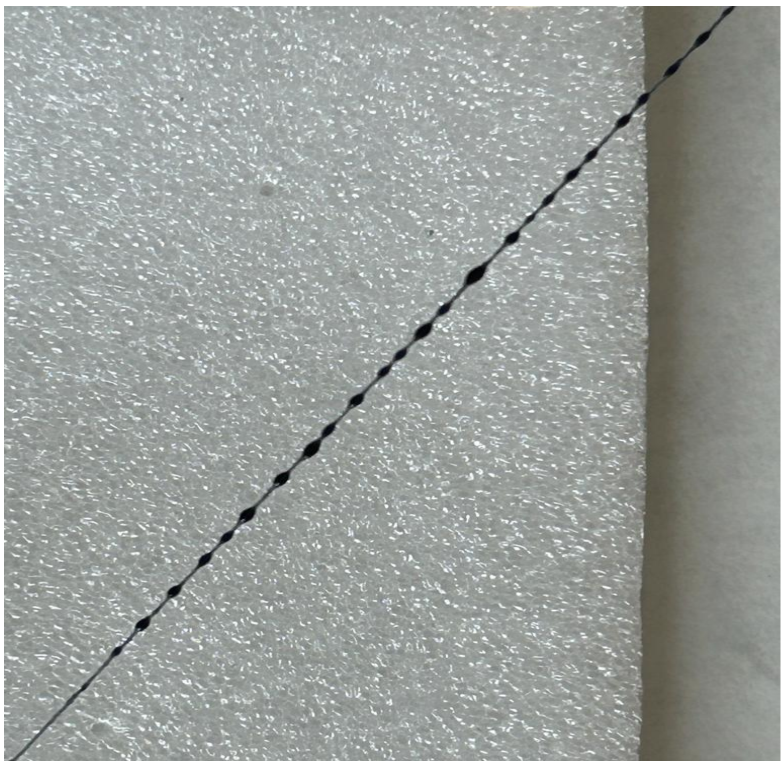


Figure 5.2 Droplets formed on the 25% cotton-75% polyester thread due to cohesion of the liquid.

Segments with high chunks of the polymer were inspected with SEM as shown in figure 5.3. However, the thread is not reliable to make transistors due to the non-uniform of the coating with the semiconductor polymer. By separating the well-coated areas with high density of the conducting polymer from the rest of the thread, we can get the image of how the tread looks on figure 5.3a. Figure 5.3b shows another side of the thread and more strings of the thread can be seen.

As expected, the segments with poor coatings were the ones with low conductivity or higher resistance with a difference of three orders of magnitude. Measuring the resistance across the chunks and between them with a multimeter also confirmed the non-uniform coating as the resistance values were almost two orders of magnitude different on a 1 cm length of the thread. As it can be seen, the difference in resistance in the same thread is too high to make a reliable transistor. However, if the channel of the transistor is larger than the chunks formed on the thread, we might have areas with higher conductivity.

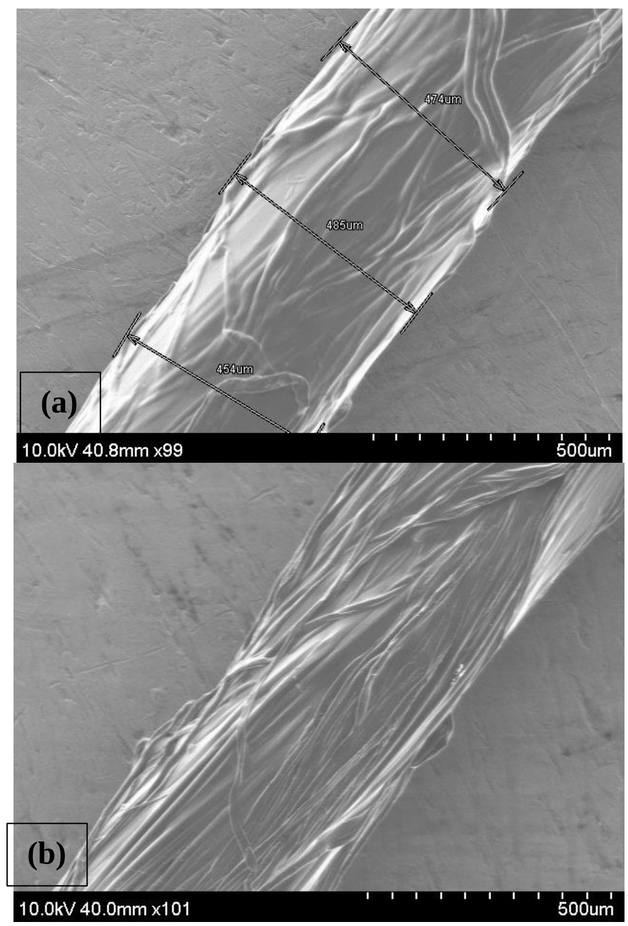


Figure 5.3 SEM image of thread treated by drop casting. Figure a) shows the well-defined part of the thread and b) shows the strings on an “almost” well coated area on that same thread.

In contrast to the drop casting, the dip coating resulted in a more uniform coating through the whole thread as shown in figure 5.3b. Since in the process of dip coating the thread was inserted in the solution vertically, no chunk was formed. As shown in figure 5.3b, the texture of the thread was changed significantly after dip coating which was different than that in the drop cast threads. The drop cast thread was dried horizontally. However, in the other method, the thread was dipped into ink and then took out to dry vertically. Apparently, these two major differences resulted in formation of no chunks (a more uniform coating) and a high density of the conducting polymer through the thread. As the SEM image (Figure 5.4) shows in the dip coating, the fibers of the thread were quite visible but uniformly coated.

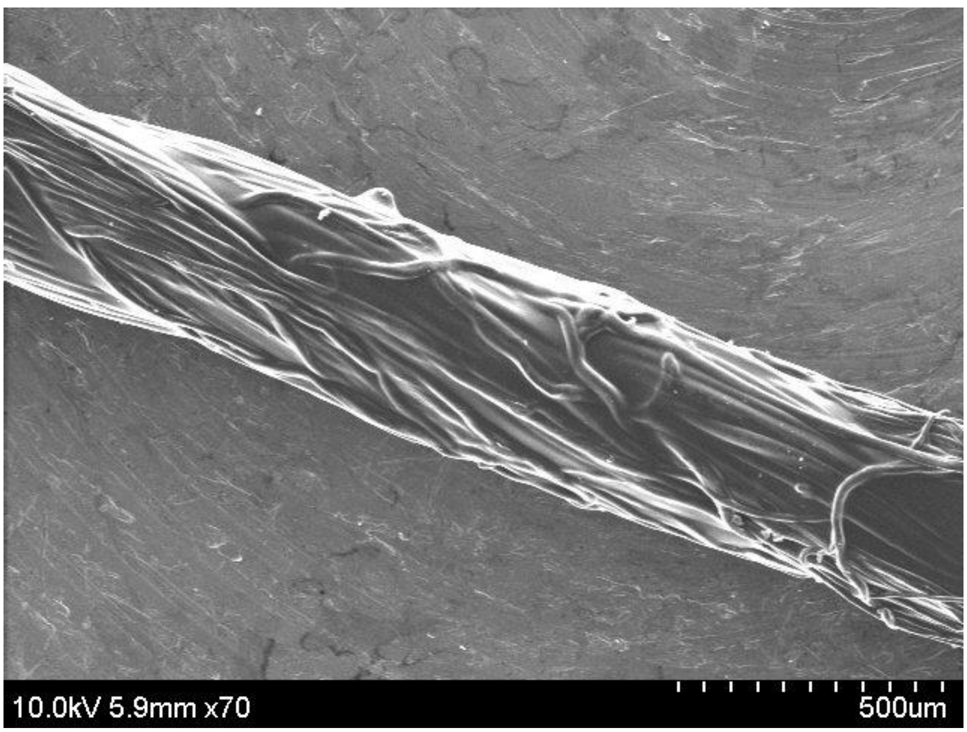


Figure 5.4 SEM image of dip 25% cotton-75%polyester thread.

As demonstrated, the most reliable way to convert a non-conductive fiber to a conductive one is by coating with PEDOT:PSS using the dip coating method. Soaking the thread into the solution and drying it vertically seems to work the best for a most uniform coating at least by inspecting the quality of the coating visually and with SEM. However, the drawback of the dip coating is the exact amount of the polymer being applied on a piece of thread.

5.3 DBSA Coating Effect on the 25%Cotton-75% Polyester Thread-Based Transistor

The coating process is important to get uniform layers of coating on threads since this may affect the overall conductance of the substrate to be used, which in this case is the thread. Previous works suggest improving the conductivity of a PEDOT:PSS coating by further treatment of the coating [8,15]. Following the recipe from Giuseppe et al. [15], the PEDOT:PSS coating was treated with DBSA to achieve a higher conductivity. As said by Zhang et al., high concentration of DBSA on PEDOT:PSS mixture is not good since it starts a phase separation and makes it difficult to coat [8], leading to a poor coating quality.

The quality of the threads being treated or not treated with DBSA was assessed by fabricating and testing OECTs. The transistors were made with the same procedure as described in chapter 3. We made a transistor by dipping the thread not only in PEDOT:PSS but also in DBSA (after it was dried). DBSA is a conductivity enhancement agent that enhances the coating of the thread and therefore the transistor. A separated transistor was made to see the effect of a lack of this agent on the transistor. The SEM images in Figures 5.5 and 5.6 show the effect of DBSA on the morphology of the threads.

As can be seen on figure 5.5 and 5.6 the DBSA adds an extra layer of coating on the thread that has been previously coated with PEDOT:PSS. The addition of such chemical increases the conductivity of the thread coated with PEDOT:PSS. This method helps increase the conductivity of the thread without creating any aggregation and separation of the PEDOT:PSS solution. If this separation happens it would decrease the conductivity instead of increasing, it.

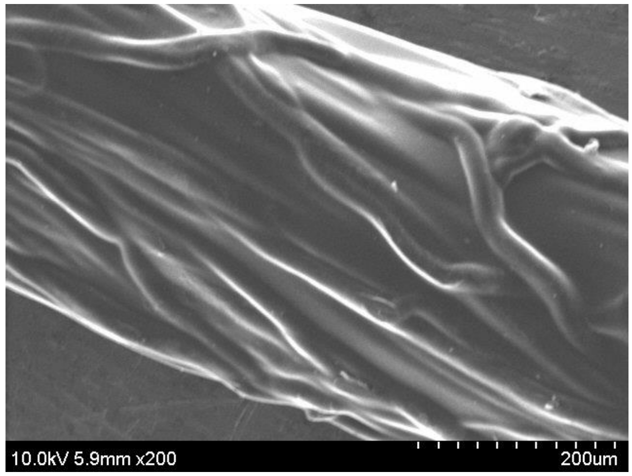


Figure 5.5 SEM image of PEDOT without DBSA

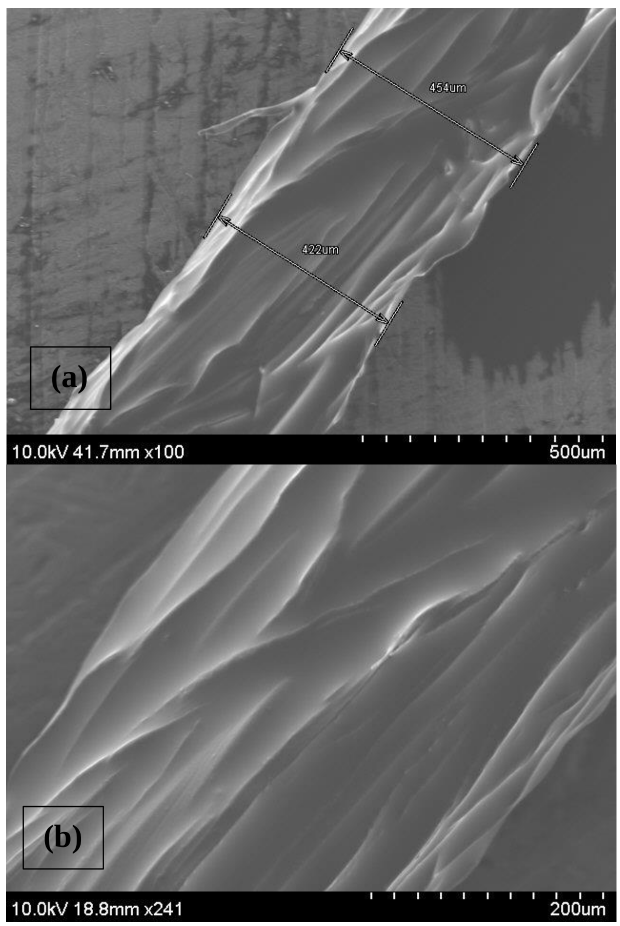


Figure 5.6 Figure a) SEM image of PEDOT:PSS thread treated with DBSA and figure b) shows the zoom image of the SEM image

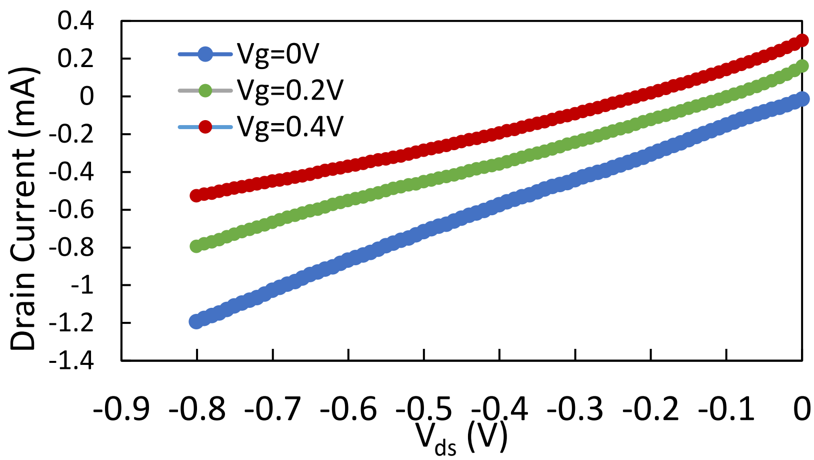


Figure 5.7 Output characteristics without DBSA

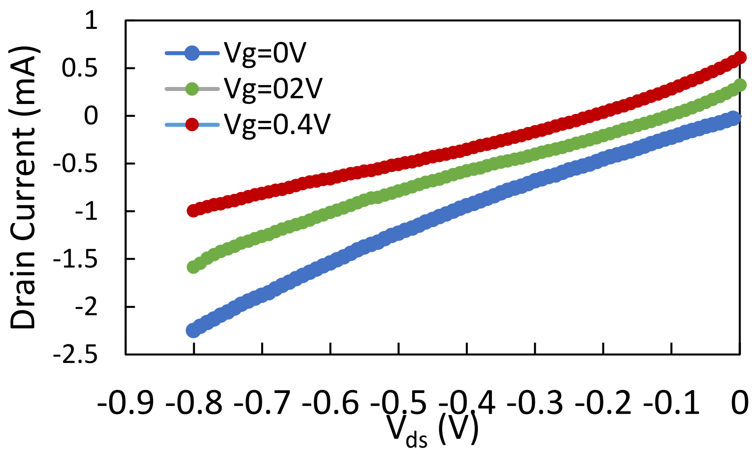


Figure 5.8 Output characteristics with DBSA

Figure 5.6 shows the visual effect of the DBSA on the thread. The image does not show the strings that were out layer of the thread. In other words, the whole thread was covered with an extra layer of agent. Most likely the DBSA makes the substrate more conductive providing extra help for any imperfection in the first coated layer of PEDOT:PSS. This effect can be seen in the characterization on 5.6. The threshold voltage was obtained for the thread with DBSA and the thread without DBSA to determine the effect of this agent on the transistor performance.

The threadhold voltage was measured by scaning V_{gs} while keeping the transistor in the saturation mode. The calculations are made to determine the treshold voltage, V_t. Using the equation of the transistor in solid state, we aproximate the transistor treshold voltage.

The equation in the saturation mode is defined as:

$$I_d = \frac{1}{2} K \frac{W}{L} (V_{gs} - V_t)^2 \quad (2)$$

where K is called the transistor transconductance parameter (μA/V^2) which is same as the product of the mobility (μ) and the gate capacitance (C_g), W is the channel width (μm), L is the channel length (μm), V_{gs} is the applied voltage to the gate and source (V), and I_d is the drain current (μA). Equation 2 can be converted to Equation 3 which shows that the square root of the current is a linear function of V_{gs} and the intercept to the voltage axis is same as V_t.

$$\sqrt{I} = \sqrt{(\frac{1}{2} K \frac{W}{L})} V_{gs} - \sqrt{(\frac{1}{2} K \frac{W}{L})} V_t \quad (3)$$

Using Equation 3, we can fit a linear curve (y=mx+b) to the data to obtain the slope (m) and the offset (b) values . From the fitted curve, we can find V_{gs}=V_t the sqrt(I_d) = 0. Therefore V_t=b/m. After getting this data using the solid-state equation led us to figures 5.9 and 5.10 where we can see the determination of the threshold voltage for both types of threads.

Comparing the two transistors, the one without a DBSA coating had a higher threshold voltage of 4.51 V, while the one with the coating had a lower threshold voltage of 1.18 V. The threshold voltage depends on both the PEDOT:PSS layer and the DBSA coating, which improves conductivity. As a result, the mobility also changes since both transistors have the same properties and were built in the same way. The difference in conductivity between the two transistors was significant, with the DBSA-coated transistor having three orders of magnitude higher conductivity.

It was observed that DBSA improves both the transistor and thread conductivity, so for future transistors, the thread was dipped in both PEDOT:PSS solution and DBSA solution.

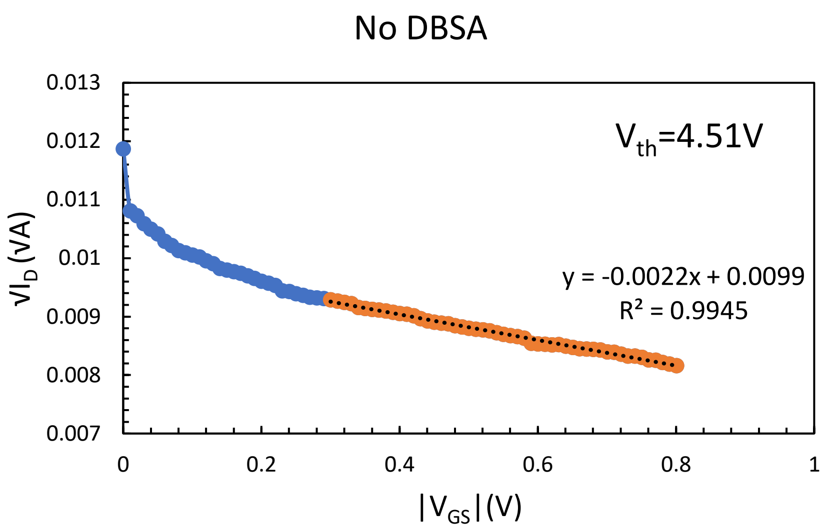


Figure 5.9 Threshold voltage of threads not treated with DBSA

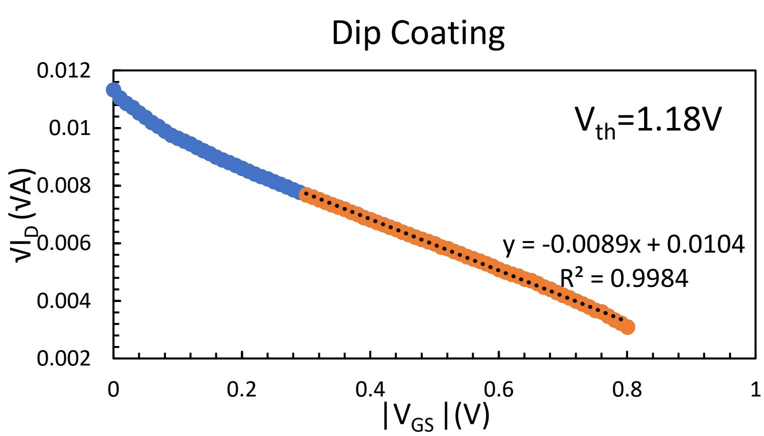


Figure 5.10 Threshold voltage of threads treated with DBSA.

5.4 Thread Effect Determination

5.4.1 Scanning Electron Microscope Results

Three different threads that are commercially available were used in this study. The threads were labeled as follows 100% cotton as 100C, 25%cotton-75%polyester as 25-75CP, and

32%cotton-68%polyester as 32-68CP. The cotton and polyester properties make it suitable to do the transistor with PEDOT:PSS as a conducting polymer to be used on the thread. The property of the cotton makes it important to do the transistor since cotton tends to be absolvent nontoxic and is stronger when gets wet [28]. This is important for further studies since this transistor might be used for sensor on sweat. Therefore, the transistor might be exposed to humidity and wet atmosphere. The flexibility of the transistor is also important to design comfortable wearable electronics. Generally, polyester is more flexible as it is resistant to stretching and shrinkage. The described threads were used to make OECTs.

5.4.1.1 100% Cotton Thread

The OECTs were made using the procedure explained in chapter 3, sections 3.3 and 3.4. In this study the thread-shaped transistors were made on a glass slide to test for characterization before designing a device that can be sewed on fabrics. Figure 5.11 shows the SEM image of the 100C thread before coating with PEDOT: PSS. Individual fibers that compose the thread can be seen on the figure.

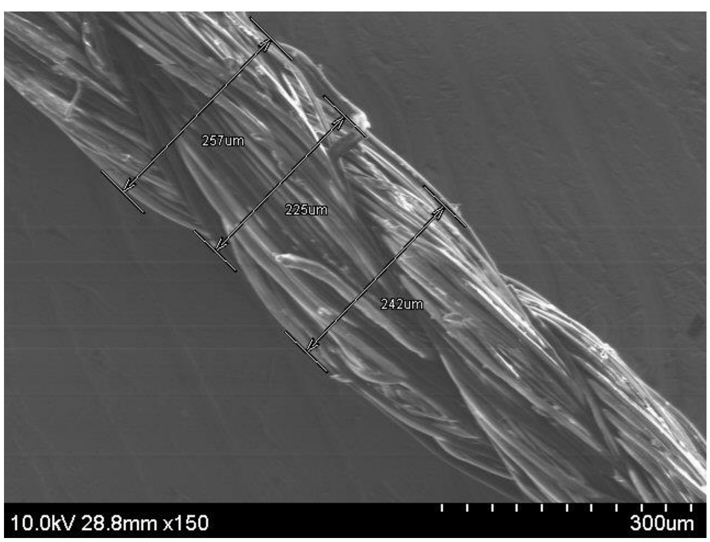


Figure 5.11 SEM image of 100C fabric before being coated with PEDOT:PSS conductive polymer.

The white thread was initially flexible, but it became somewhat rigid after being coated with polymer. Although the thread has a high absorption characteristic resulting in more polymer inside, the surface isn't entirely coated. A weight difference of 0.3 mg was observed between the coated and uncoated 100C thread samples. Figure 5.12a shows that there is a thickness difference of about 60 μm between the fully coated zones and those that are not coated properly.

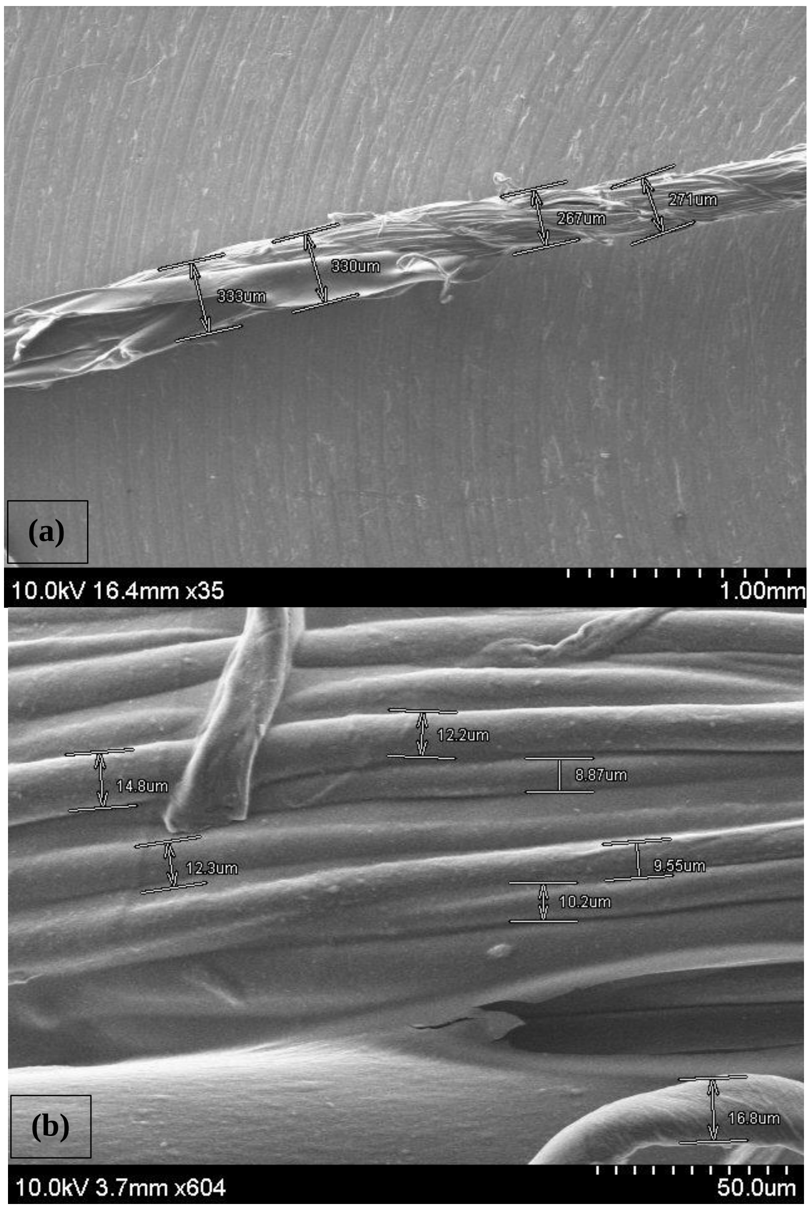


Figure 5.12 SEM image of 100C after being coated with PEDOT:PSS. a) shows imperfections of coating while b) shows the thickness of each string that forms the thread.

5.4.1.2 32% Cotton-68% Polyester

Another thread that was analyzed to determine its performance was the 32-68CP. In this one, we get some characteristics of polyester and cotton in the fabric. This provides a mixture of properties between the two types of thread. The SEM image in figure 5.13 shows the white thread with no PEDOT:PSS coated to this thread. The same procedure for coating process was made as the 100C thread to then make the OECT. The approximate thickness throughout the thread was 219 μm as seen on the image (Figure 5.13). The pattern at which this thread was made is not the same as the 100C sample since is not a braided shape. The effect of this pattern can be seen on the characterization of it by the IV output signal.

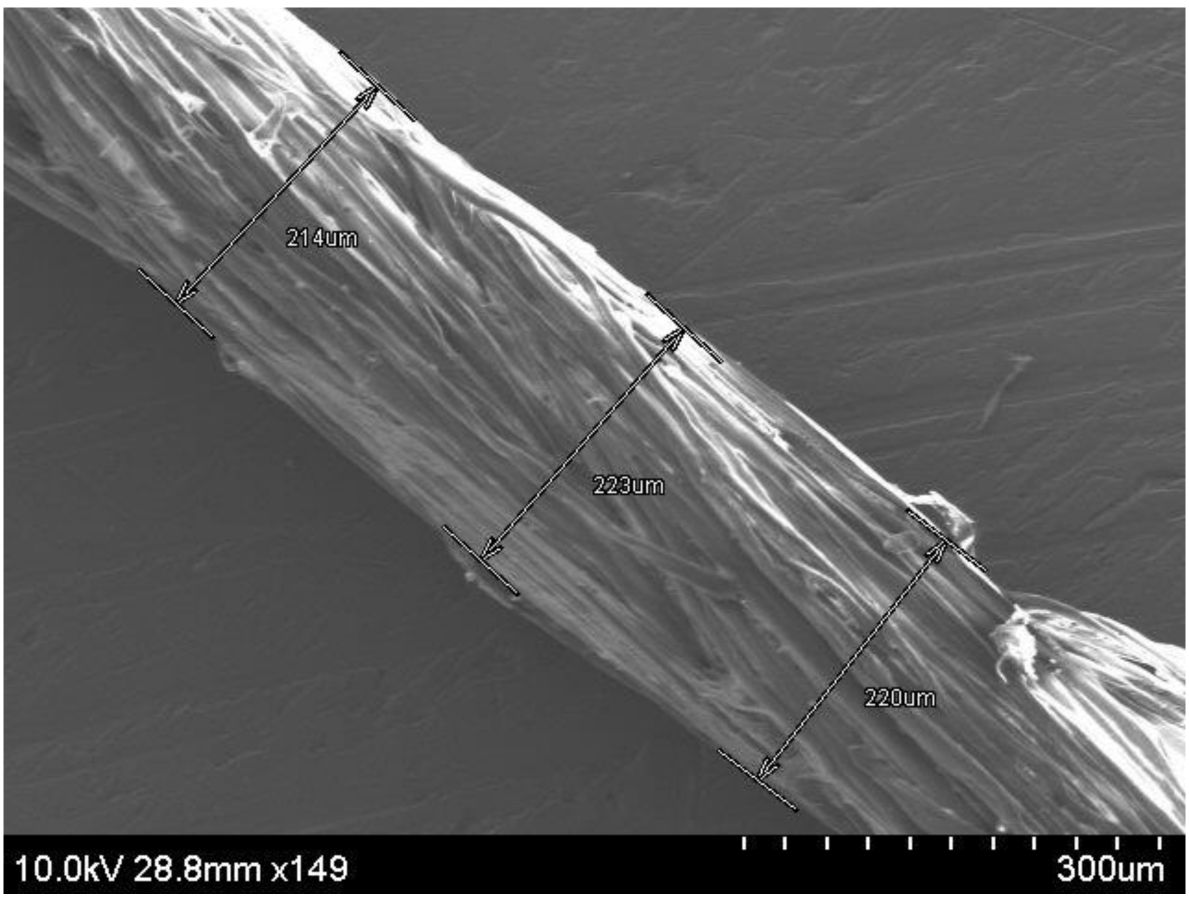
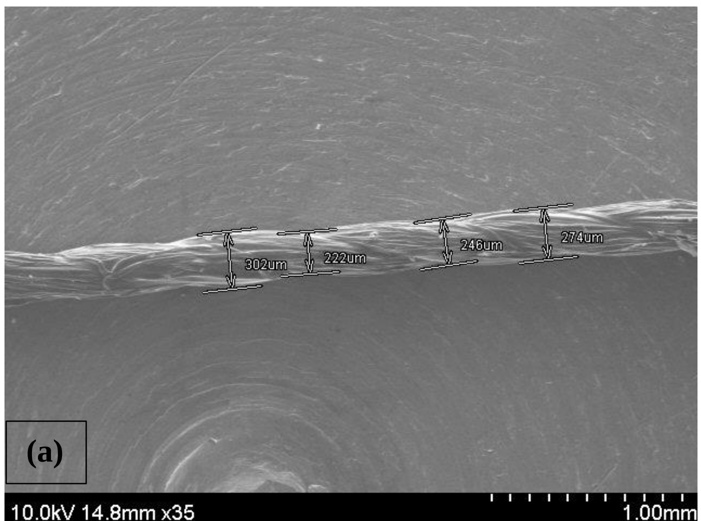


Figure 5.13 SEM image of 32-68CP sample before coating with PEDOT:PSS conductive polymer.

The SEM image of the same sample demonstrates that the coating process increases the thickness of the thread and shows the external strings of the thread. Based on the thickness of the thread, we can safely say that the fiber that composed the thread is thicker on this sample than in the 100C sample since no string is as thick as 24 μm like on 32-68CP. However, as seen on figure 5.14b there are still some non-uniform coatings on the thread. In contrast to sample 100C to get this imperfection, a bigger zoom was needed since at first sight it can be said that it is uniformly coated.



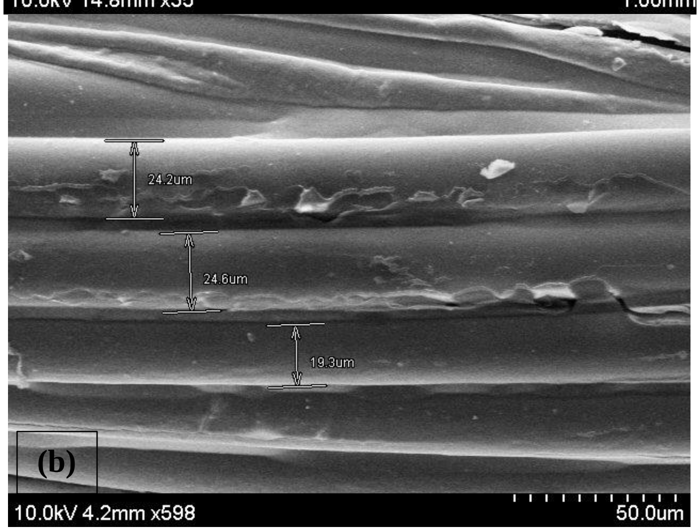


Figure 5.14 SEM image of the 32-68CP sample with different zooms. A) shows an uniform coating layer on top of the thread while b) shows that there are some imperfections per string of thread.

5.4.1.3 25% Cotton-75% Polyester

The third thread that was characterized was the 25-75CP. Figure 5.15 shows the SEM images of the threads with a uniform coating of PEDOT:PSS which also resulted in an increase in the overall thickness of the thread. However, the coated strings are similar to the 32-68CP thread sample. As can be seen on the zoomed image in figure 5.15b the thread is coated uniformly even on the strings. This lead us to think that this thread is the one that might have more uniform coating all over the thread and threfore, in the transistor's channel.

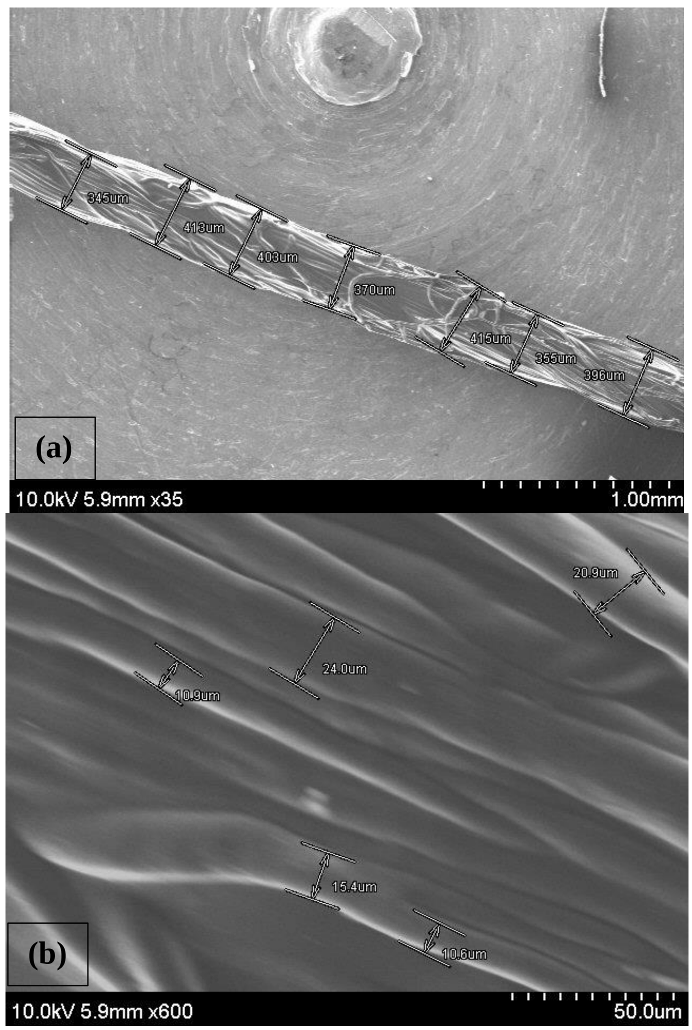


Figure 5.15 SEM image of the 25-75CP sample. Figure a) shows a uniform coating on the whole thread that is validated by the figure b) string coating of the thread.

5.4.2 Output Characterization of the Transistors

5.4.2.1 Output Characteristics of 100% Cotton

After SEM imaging, the threads were used to fabricate transistors as explained in chapter 3. The fabricated transistors were characterized through the IV measurements. As can be seen in figure 5.16a., the information was used to understand the effect of the thread on the threshold voltage.

The 100C sample showed some shift for $V_g \neq 0$ which tells us there is some current leakage through the gate. Besides that, there is no difference between the transistor behavior at V_g=0 V and V_g = 0.2 V. The drain current increases linearly with an increase on source drain voltage.

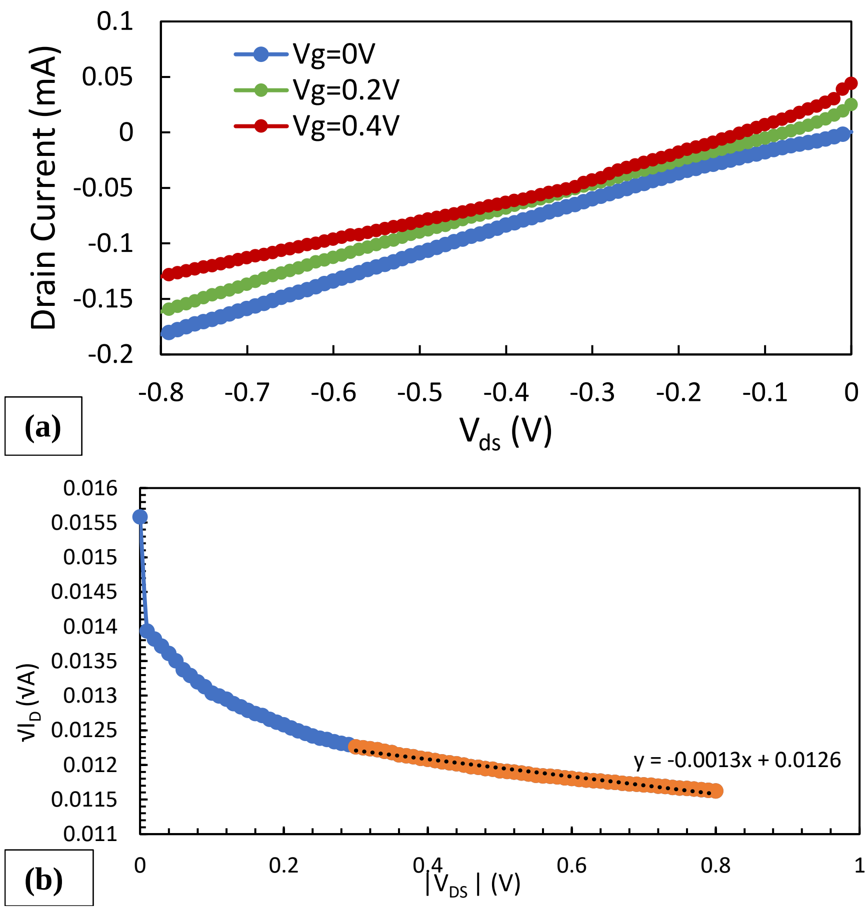


Figure 5.16 Figure a) shows IV curve of the 32-68CP thread and b) shows the determination of threshold voltage.

To determine the threshold voltage, it is important to take the linear zone of the graph starting at V_{ds}=0.3 V and ending at Vds = 0.8 V and extrapolate to the drain source to reach the intersession and get the threshold voltage of the transistor. Like in the previous section, the thread was measured from 0.0 V to -0.8 V sourece and drain scan at a 0 to -0.4 V gate voltage. The threshold voltage was estimated to be 9.6 V which is too high for an OECT. Data analysis can also reveal the difference in the mobility of charges in different transistors.

5.4.2.2 Output Characteristics of 32% Cotton-68% Polyester

The next method of characterization for this sample was the IV characteristic. As shown in figure 5.17, the device presented a relatively large amount of of leakage current mainly due to the current from the gate terminal. At zero voltage the current started at zero as it should be but when cranking up the gate voltage the current shifted up to possitive values even when is not in a reverse bias.

Nevertheless, the I_d-V_{gs} characteristic of the device was obtained for the transistor being in the saturation mode. Then, the threshold voltage was estimated to determine the difference between the two threads. The 100C sample showed a very high threshold voltage for a fabric based transistor. However, the result for this transistor showed a threshold voltage of 5.36 V.

The fact that is more uniformly coated than the previous sample helps to get a more reliable transistor. Based on the slope of the fitted curves, the results suggest that the mobility was higher in this transistor creating a higher Id on this sample than in the previuos one. This increase is due to the higher conductance on this sample by having a more uniform coating layer.

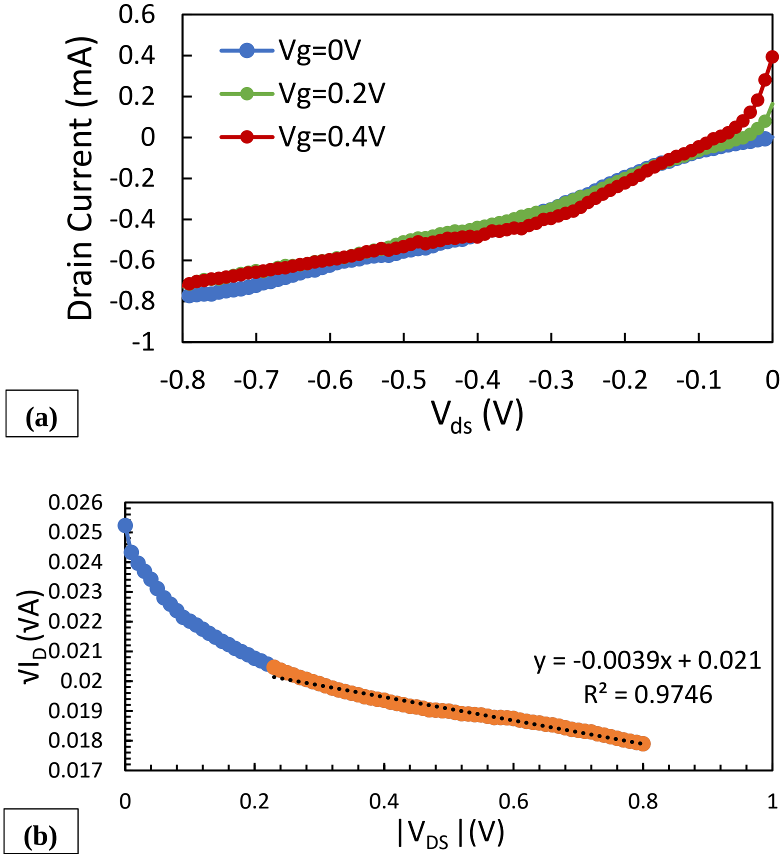


Figure 5.17 Figure a) IV characteristic of the 32-68CP thread and b) shows the threshold voltage determination.

5.4.2.3 Output Characteristics of 25% Cotton-75% Polyester

This transistor showed a better IV output characteristics as shown in the figure 5.18a. The transistor reaches a better threshold voltage getting 2.61V as seen in figure 5.18b. This is a decrease in threshold voltage of more than the half compared to 32-68CP sample and four times less than that in the 100C sample. In the next chapter, we discuss the effect of pH on the performance of 25-75CP transistor as a way to design a wearable sensor.

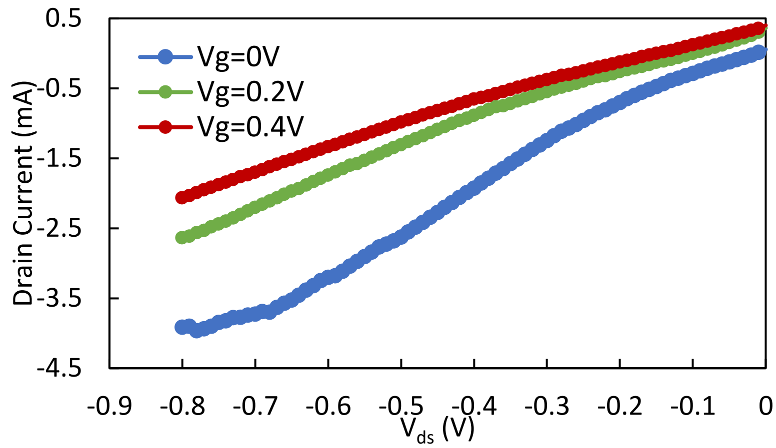


Figure 5.18 IV characteristic of 25-75CP transistor

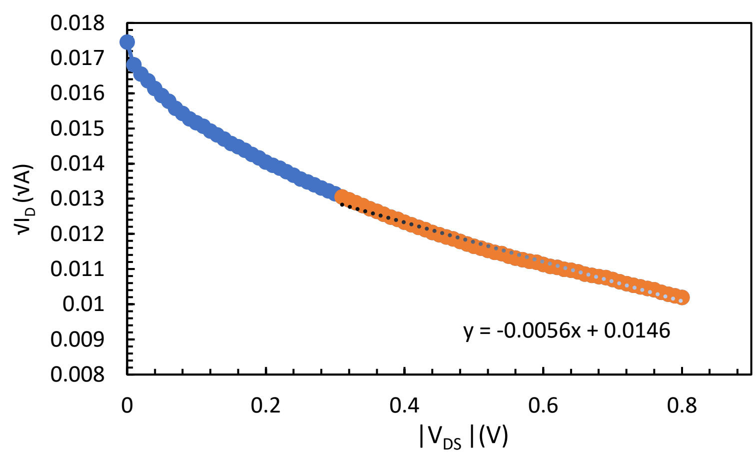


Figure 5.19 Threshold voltage of 25-75CP transistor

Table 5.1 Obtained data of the difference in thread used as substrate on the transistors.

Thread type	Coating uniformity	$\sqrt{(\frac{1}{2}\ muC\ \frac{W}{L})\ (\sqrt{(A)}/(V)}$	Threshold voltage
100 C	Not uniform	0.0013	9.6 V
32-68CP	Not fully uniform at micro scale	0.0039	5.36 V
25-75CP	Completely uniform	0.0056	2.61 V

5.5 Transistor as a Garment on Fabric Behavior

A new transistor sample was created using fabric instead of glass slide, following the process described in chapter 3. The transistor was built to match the characteristics of the most reliable sample and used 25-75CP thread. The transistor made from fabric showed good performance as expected, although there was a decrease in current output of approximately 1000 times compared to the glass slide transistor. Nonetheless, the transistor behaved consistently.

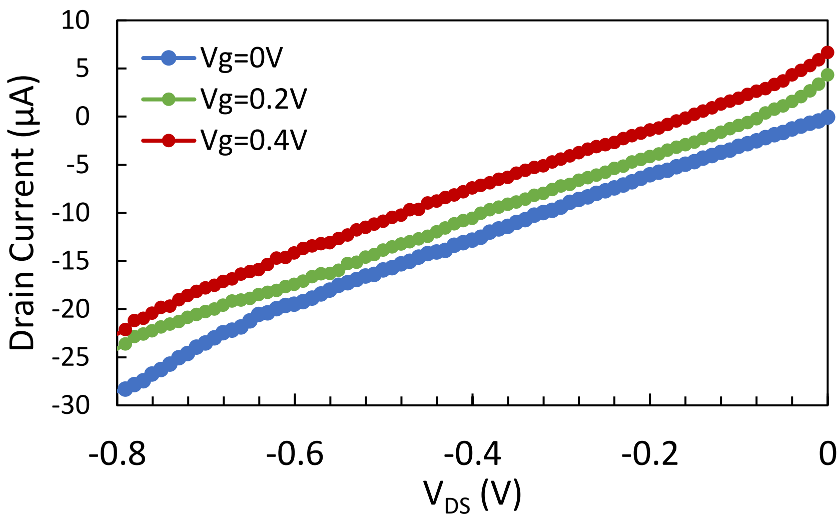


Figure 5.20 Transistor behavior in fabric

Although the scanning through the drain and source remains consistent, there is a noticeable shift in the output characteristics. Figure 5.20 displays that for V_g =0 V, the transistor current concludes at -30 µA and experiences greater leakage with every rise in gate voltage. However, this pattern indicates the potential for embedding the transistor into fabrics as a wearable electronic device.

5.6 Conclusion

The performance of different transistors studied in this chapter is summarized in Table 1. We have learned that the coating process plays a crucial part in the behavior of the transistors. It is necessary for the transistor to be fully coated to get good results. The presence of an enhancement agent helped increase the conductivity of the thread. The DBSA also helps reduce the threshold voltage of the transistor. Since the effect of this enhancement agent is in favor of designing a transistor with a lower threshold voltage, it is highly recommended for fabricating devices in the future. However, as explained by Zhang et al., there is a need to control the amount of DBSA as it may cause phase separation on PEDOT: PSS when the amount of DBSA is higher than 0.5% v/v in the PEDOT solution [8]. However, our method of treating the coated threads with DBSA is more practical with desired outcomes.

As it has been demonstrated the thread selection affects the transistor behavior. The I_d depends on the transistor thread chosen and their threshold voltage too. Based on the data collected we can see that at V_g =0 V,100C sample had an I_d of -0.2mA, the 32-68CP had a -0.8 mA and 25-75CP sample had -4mA. These transistors were made on the same conditions. So, we can have an idea on the effect of thread selection on their mobility on the substrate. The uniformity on coating the threads matters to get a more reliable transistor. The threshold voltage depends on this uniformity as seen in previous sections since the more uniform the coating on the thread, the better IV output characteristics and lower threshold voltage. The 25-75CP sample has the greatest I_d due to the uniformity of the coating. So, we can assume that if there is no uniform coating the overall conductance is less due to this non uniform coating limiting the overall response of the device.

Chapter 6: Transistor as a Prospective pH Sensor

6.1 Towards the Sensor

Tests have been conducted on OECTs to determine their applicability as a pH sensor for human perspiration. These transistors operate in depletion mode, exhibiting unique characteristics that change when exposed to a varying pH solution. The process for constructing these transistors is outlined in chapter 3, with the addition of pH solution to generate a transfer curve. The same threads utilized in session 5.3.2 are also used to build these transistors.

6.1.1 100% Cotton Transistor Sample

Figure 6.1 displays the transfer curves of the 100% cotton thread when exposed to various solutions. The curves illustrate the distinct behavior of the thread depending on the solution used. Notably, the threshold voltage does not follow a specific sequence, which could be attributed to the coating's unevenness, thereby limiting the transistor's overall behavior.

In Table 6.1, it is evident that there is a significant difference in slope. There doesn't seem to be a clear connection between the pH levels of the solutions used and the slopes and interceptions. For example, when a solution with a pH of 7.5 was used, the measured threshold voltage was 9.0 V. However, when a solution with a pH of 7.2 was used, the V_t changed to 1.7 V. The remaining solutions caused the threshold voltage to shift to 3.9, 2.8, and 2.0, respectively.

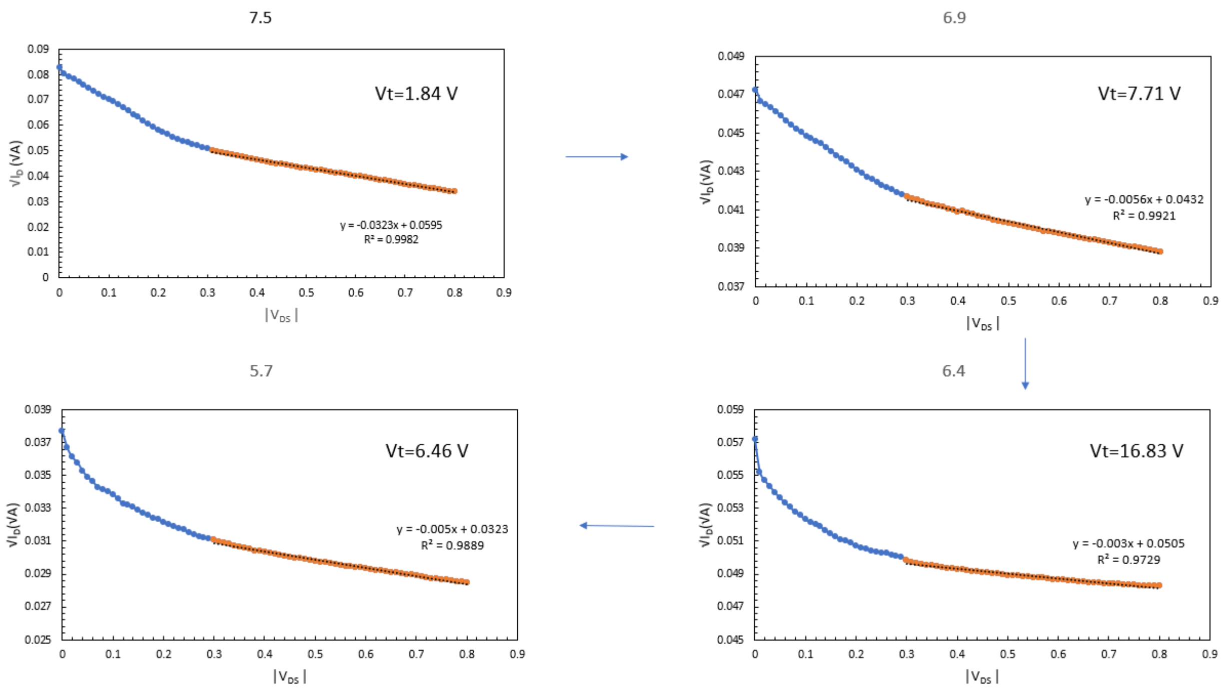


Figure 6.1 Transfer curves of the 100C transistor sample. There is no clear relationship between the threshold voltage and the pH solutions that it was exposed.

6.1.2 32-68CP Transistor Sample

The thread used in this transistor is coated better than 100% cotton, resulting in a more uniform coated channel. After conducting the transistor experiment and analyzing the transfer curves (as seen in figure 6.2), it was observed that the transistor operates in a depletion mode as it produces current at 0 *Vgs*. The curves are more consistent with each other, and the threshold voltage decreases more significantly compared to the 100C sample. The addition of solutions with lower pH levels resulted in a decreasing pattern on V_t. For instance, on the surface with a pH of 7.5, the threshold voltage was 3.0 V. However, as the pH decreased, the V_g changed to 2.5 V, 2.1 V, and eventually 1.0 V.

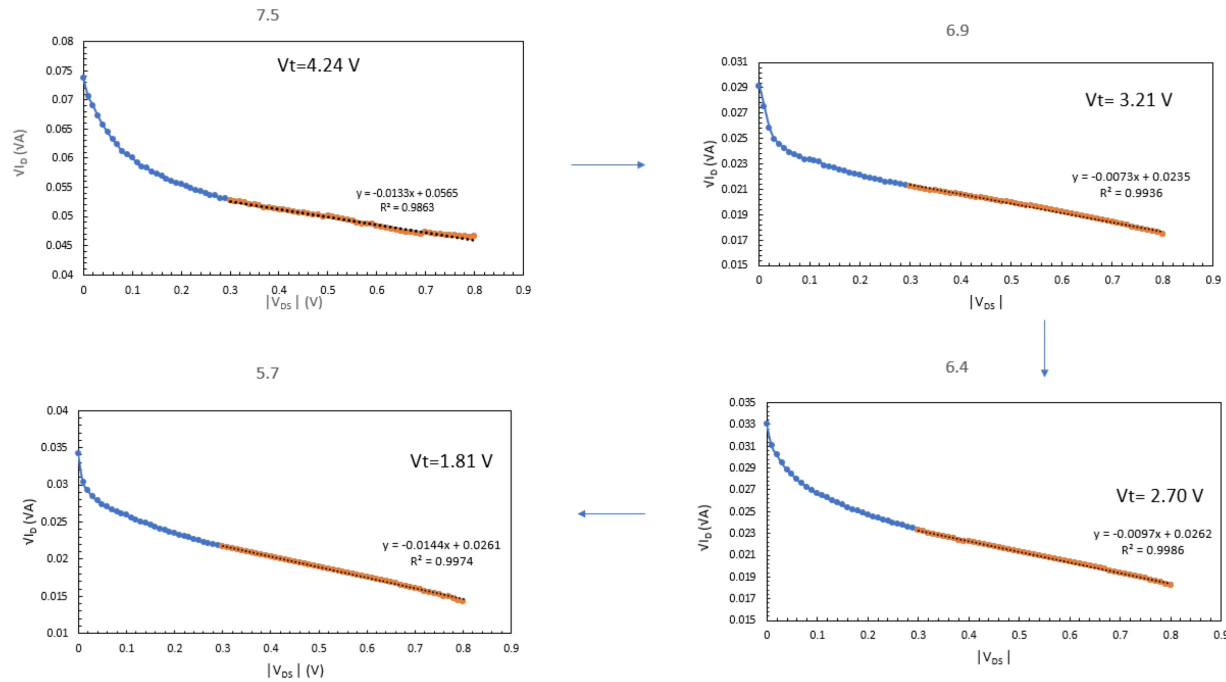


Figure 6.2 Transfer curves of the 32-68CP transistor sample. They show a decrease in threshold voltage as the pH solution they are exposed to decreases.

6.1.3 25-75CP Transistor Sample

Among the threads used, this particular thread had the best coating resulting in a more uniform transistor channel. It exhibited superior properties as a sensor, particularly in terms of a clear decrease in threshold voltage as the pH on the transistor surface decreased. This transistor shows great potential to be a sensor and its transfer characteristics are featured in Figure 6.3. Similar to the 32-68CP sample, it has a depletion mode characteristic and shows a current value at *Vgs*=0 V.

We conducted impedance spectroscopy on the transistor that showed the most potential for detecting changes in pH in sweat. The findings, presented in figure 6.4, indicate that the impedance decreases as the pH level on the transistor's surface decreases. This reduction in impedance may lead to a decrease in the threshold voltage. In other words, the lower the impedance, the lower the threshold voltage will be.

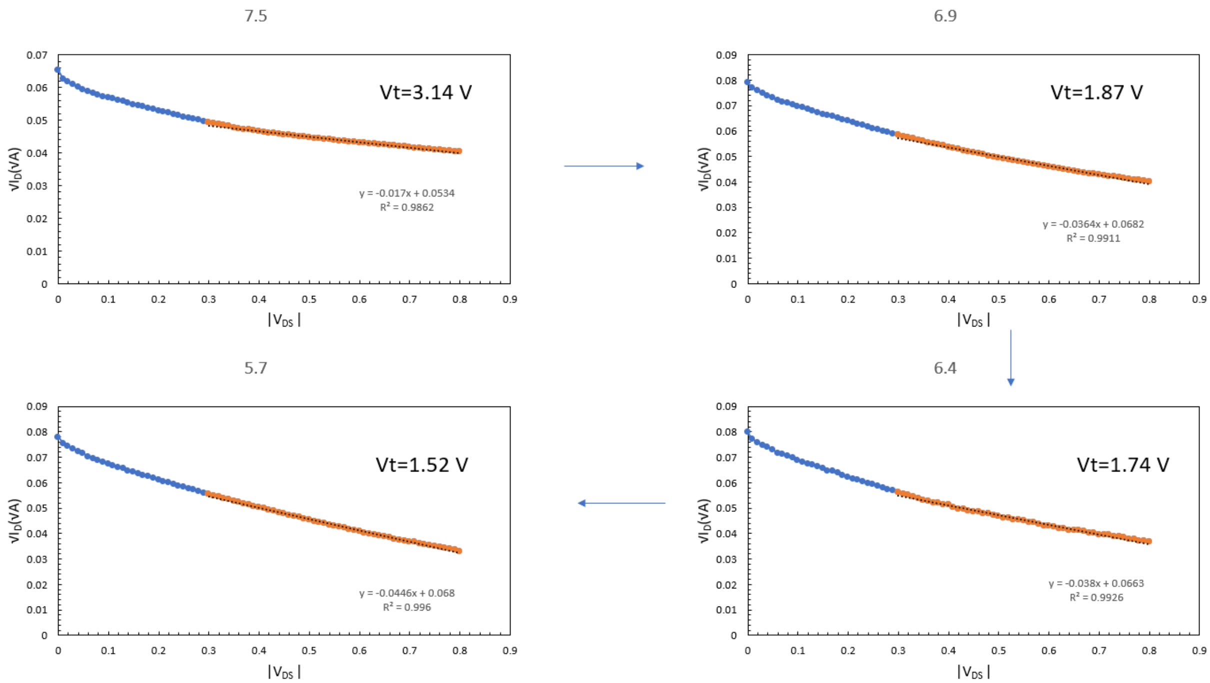


Figure 6.3 Transfer curves of the 25-75CP transistor sample. They show a decrease in threshold voltage as the pH solution they are exposed to decreases.

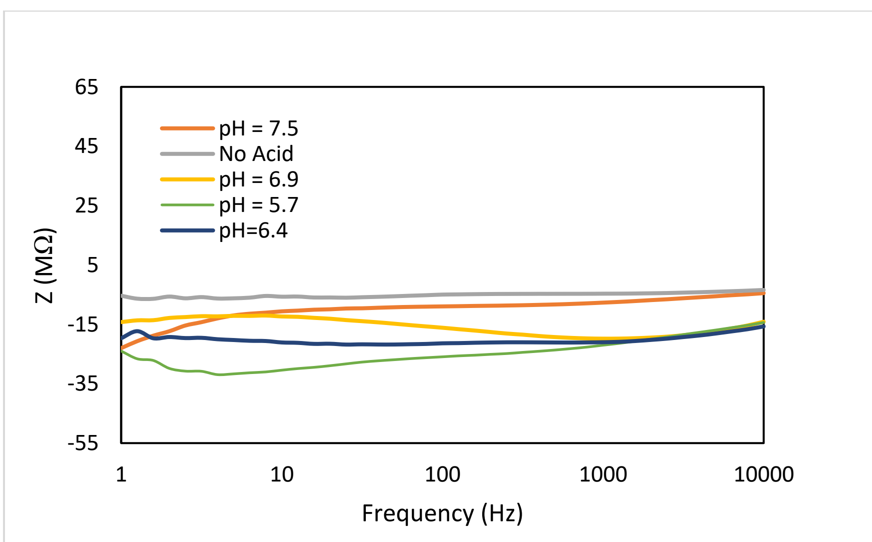


Figure 6.4 Impedance spectroscopy of 25-75CP transistor at different pH solutions.

6.2 Conclusion

When it comes to using transistors as a sensor, the 25-75CP sample is the best option. While the 32-68CP sample has potential, it may require additional processing to create a uniformly coated thread to serve as a substrate for the transistor. Unfortunately, the 100C sample did not work well as a possible sensor due to a lack of uniformity. Both the 32-68CP and 25-75CP samples have demonstrated good possibility to be a sensor by its characteristics through changes in transfer curves and V_t. In figure 6.4, the impedance displayed decreases as the pH level decreases, indicating potential for the transistor as a sensor. However, further research is needed to fully develop this device to make a sensor.

Table 6.1 Data of transfer curves obtained with the OECTs exposed to different pH solutions.

Thread type	pH level	$\sqrt{(\frac{1}{2}\, muC\, \frac{W}{L})}\ (\sqrt{(A)}/(V)$	V_t (V)
100 C	7.5	0.0133	1.84
	6.9	0.0073	7.71
	6.4	0.0097	16.83
	5.9	0.0144	6.46
32-68CP	7.5	0.0323	4.24
	6.9	0.0056	3.21
	6.4	0.003	2.70
	5.9	0.005	1.81

Table 6.1 (Continued)

Thread type	pH level	$\sqrt{(\frac{1}{2}\ muC\ \frac{W}{L})}\ (\sqrt{(A)}/(V)$	V_t (V)
25-75CP	7.5	0.017	3.14
	6.9	0.0364	1.87
	6.4	0.038	1.74
	5.9	0.0446	1.52

Chapter 7: Conclusion

In this work, we discussed the behavior of different OECTs due to the properties of a conducting polymer that has been used. As demonstrated, the organic electrochemical transistor highly depends on the quality of the coated layer on the thread. The thread has an important role in the coating and the casting process itself plays a major role in this analysis too.

The conductivity of the thread is greatly impacted by the coating process. To make the thread conductive, it is coated with polymer, which plays a key role in the transistor. However, an inconsistent coating can result in a poor-quality transistor with reduced reaction. Drop casting is not a suitable method for creating a uniform conductive thread as it often leaves white spots, as explained in chapter 5. Therefore, a bad coating can result in an insensitive transistor, and the white spots on the thread indicate areas where PEDOT: PSS is not present, leading to no reaction in those spots.

The thread that was exposed to dip coating showed a more uniform coating and therefore the best transistor can be obtained by this procedure. Since no spots are left blank the whole area of the thread is exposed to the chemical reaction of the conductive polymer and the gel electrolyte that is in contact with the thread. The other important thread-coating process that takes place is the addition of the enhancement agent through dip coating.

The DBSA plays a good role in this thread coating to get a good transistor. As explained in chapter 5.3 the DBSA is a good enhancement agent for the PEDOT: PSS. This agent reduces the resistance of the thread which helps for the enhancement mode transistor since it requires an on state at 0 Vg.

The thread plays a good role in transistor behavior too. The thread used to make a transistor is important since not all of them have the same properties. The 100% cotton thread has more absorbent properties but does not have a good coating compared to the other two samples. The 32% cotton-68% Polyester and the 25% cotton-75% polyester samples showed a more uniform coating and the most reasonable pH sensor properties as seen in chapter 6. As said in chapters 4 and 6 the fiber-based transistor that has been made has a good potential to be used as a sensor. Not only by taking the transfer characteristics but also, by taking the impedance of the sensor we can get the change in their characteristics in the presence of different pH solutions.

The transistor has potential as a pH sensor, but the characteristics of it need to be further studied to have a reliable sensor. The limit of detection, linearity, reliability, and other studies are further to be studied, furthermore, more studies are needed to determine the selectivity of the transistor and possible sensor towards pH change in sweat. There might be some interferences in sweat that might affect the transfer curve of the transistor like humidity, ions on sweat, sodium, or potassium selectivity are a big and important area to study. Although we do not have reach a stage of having a sensor yet, the transistor have a big potential to be a sensor.

Finally, the use of thread coated with conducting polymer as the channel for the OECTs provides advantages like flexibility, low cost, and biocompatibility. The transistor demonstrates a good response to pH differences on the channel. The results suggest a potential use of this sensor as a pH detector on sweat, opening new opportunities for developing low-cost and environmentally friendly sensors.

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