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Studying the effect of thread materials on the response of fiber-based Organic electrochemical transistors for pH sensing

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ABSTRACT

Among different conducting polymers, PEDOT:PSS has been used for making organic electrochemical transistors (OECTs) due to the remarkable stability and the electrochemical properties of the polymer. With the fast-growing market for wearable electronics, the application of OECTs has been proposed for wearable sensors. However, the majority of OECTs have a planar design. Recently, we have demonstrated the feasibility of fabricating OECTs on sewing threads. This work has focused on studying the effect of thread materials on the performance of fiber-based OECTs made for wearable pH sensors. Such sensors can be used to collect metabolic information from the body of a patient by analyzing the pH of perspiration. The three most commercially common different kinds of threads were used to make OECTs with polyvinyl alcohol (PVA) gel as the electrolyte. Using 100% cotton, 25% cotton-75% polyester, and 32% cotton-68% polyester threads were used to fabricate and then characterize the transistor. Threads were coated with PEDOT:PSS polymer to use as a channel then use a Silver coated thread as a gate and a PVA gel electrolyte. Devices were tested by applying different voltages to the transistor terminals and monitoring the current through the PEDOT:PSS. The best signal was obtained from the device made on 25% cotton-75% polyester thread. The experimental results showed a promising approach that can lead to a good wearable pH sensor on human perspiration.

Keywords: PEDOT:PSS, Organic electrochemical transistor, PVA gel, Electrolyte

1. INTRODUCTION

Conductive textiles are attracting the attention of the 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 with an increment in interest and demand not only in apparel companies but in military and defense, healthcare, and sports. 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 by adding a few different ways to have the type of product.

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 because of the difficulties related to the conformation of the conventional planar and rigid devices [1]. As the building block of electronics, transistors are needed for wearable devices. Among all the studies done on wearable electronics not much is known about thread base as it is for thin film transistors. A simple yet practical method of making a transistor for wearable applications is to coat threads with a conducting polymer as the channel and build an organic electrochemical transistor (OECT). OECTs use electrolytes between the gate (another conductive thread) and the channel instead of using a dielectric. This gives the electrolyte 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 [2]. Besides, the electrolyte can act as a chemically sensitive material for sensing applications. The characterization and the OECT's 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 the 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.

A group of scientists in Italy designed a fabric base transistor out of natural cellulose (cotton yarns). Learning from the conventional planar OECTs, PEDOT: PSS was used to coat the tread to make a 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

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between the gate and the drain and source [3]. In 2018, Anneng Yang and colleagues designed an OECT that served as a biosensor for glucose monitoring 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 the crack formation and measured glucose levels in the presence of synthetic urea [4].

OECTs can be used in different 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 [5]. In a different approach, Coyle et al. incorporated a pH-sensitive dye into a piece of fabric to create a textile sensor by monitoring its color change from yellow to blue in response to a pH change [6]. Another approach is done by Italian scientists. They made a textile sensor with ion-selective membranes. The yarn was immersed in PEDOT: PSS and 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 from 10^{-3} M to 1 M although it was able to sense some difference modulation at 10^{-5} M to 10^{-3} M concentration [4,7]. Our earlier works also show promises toward thread-based pH sensors [8].

While there has been progress in recent years, there are still some areas that require further investigation. One such aspect, as discussed by 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 [9]. Our work will focus on the uniformity of the tread 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.

2. METHODOLOGY

2.1 Materials and Equipment

To make the conductive ink, PEDOT: PSS was bought from Sigma-Aldrich and mixed with ethylene glycol (from Sigma-Aldrich). The ink solution consisted of 20% ethylene glycol on PEDOT: PSS. The solution was used to coat different threads, specifically 25% cotton-75% polyester (25-75 CtP), 32% cotton-68% polyester (32-68 CtP), and 100% cotton (100 Ct). All these threads were bought from Walmart. Also, Jameco conductive threads (Nylon coated with silver) were purchased from Jameco and used as the gate electrode.

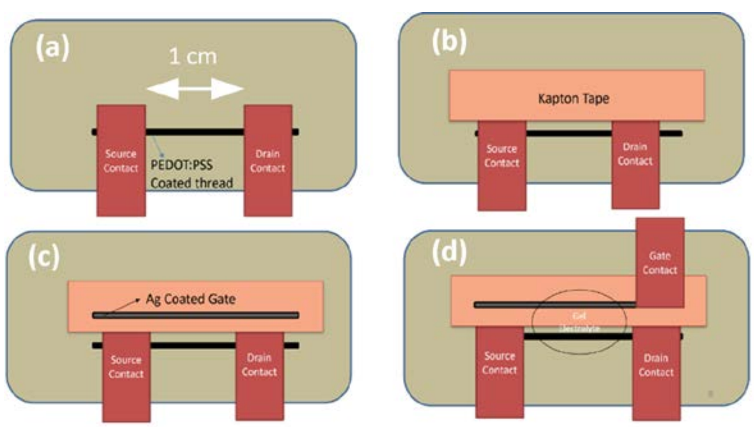

Figure 1. 4 steps of building fabric-based Organic electrochemical transistors (OECTs).

The electrolyte used to make the transistor was a polyvinyl alcohol gel (PVA gel) prepared as explained elsewhere [10]. Briefly, the gel was synthesized by adding 1.5 g of PVA to 10 mL of DI water in a beaker. Then, 1 mL of phosphoric acid was added to 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 the OECT.

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) was used. A stock solution of the buffer with a pH of 8 is lowered with HCl 1M and using a pH meter we add a solution of HCl on tris-buffer until get the desired pH solution. This solution is placed on the channel of the transistor to use as a sensor.

2.2 Transistor Design

To coat the threads, we used the dip coating method. A 16 cm long thread was tied to an end to help retrieve the thread from the solution where the thread was sunk into. The thread 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 being hung. This process was done two times to get the threads well coated with two layers of polymer.

The fabrication steps for making an OECT from the coated threads are shown in Figure 1. The transistors were built on a glass slide where the coated threads and contacts were placed. As shown in figure 1.a, 1 cm long thread coated with PEDOT:PSS was stretched and taped down with two pieces of copper tape which were 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 (i.e., Jameco thread) as shown in Figure 1.d 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.

2.3 Characterization

Hitachi SU-70 scanning electron microscope (SEM) was used to take images of the threads. we used the Ailigu ZP series digital push-pull force gauge dynamometer tester for tensile strength measurements. To characterize the devices, a two-channel source measure unit (SMU) Keithley 2602A instrument was used. One channel was used to bias the drain of the transistor and the other channel was connected to the gate. The source terminal was the common terminal between the two channels. SweepMe software was used to program Keithley for collecting the IV characteristics. Considering the aqueous-based gel and PEDOT:PSS being a p-type material, voltages between 0.0 V and -0.8 V were applied to the gate and drain with respect to the source. For the output characteristics, a constant voltage was applied to the gate and the drain voltage was scanned from 0.0 V to -0.8 V. For the trans-characteristics, the drain voltage was held at -0.8 V, when the gate voltage was scanned from 0.0 V to -0.8 V. The transistor response in the saturation mode was fit to the standard equation to derive the transistor parameters from their I-V curves:

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

where I_d is the drain current, V_{gs} is the applied gate-source voltage, V_t is the threshold voltage, and K is the transistor transconductance that includes geometrical factors (channel width and length). Due to the quadratic relationship of the current and voltage, equation (2) usually is plotted to find the linear response between $\sqrt{I_d}$ vs V_{gs}.

$$\sqrt{I_d} = \sqrt{(\frac{1}{2} K)} (V_{gs} - V_t) \qquad (2)$$

3. RESULTS and DISCUSSION

Figure 2 shows the SEM images of different threads before and after coating with PEDOT:PSS. The 25-75 CtP had an average diameter of 333 µm before coating (Figure 2.a) and the diameter was increased to 345-415 µm (Figure 2.b). The zoomed image in Figure 2.c shows fibers of ~24 µm thick. Among the three threads, 100 Ct had a different structure (Figure 2.g) with much thinner fibers of ~12 µm (Figure 2.i). The resistance of 1 cm long piece of the threads after coating was measured with a multimeter and also the tensile strength of the threads before and after coating was measured and reported in Table 1. The results show an incredible increase in the tensile strength of the cotton thread after coating while the lowest resistance was achieved from 25-75 CtP.

Table 1. Threads characteristics

Thread	**Average diameter before coating(µm)**	**Average diameter after coating (µm)**	**Average diameter of the fibers (µm)**	**Resistance after coating (Ω/cm)**	**Tensile strength before coating (kgf)**	**Tensile strength after coating (kgf)**
25-75 CtP	333	345-415	24	1400	2.02	2.23
32-68 CtP	223	246-302	24	2400	0.88	1.10
100 Ct	242	267-333	12	1600	0.61	2.64

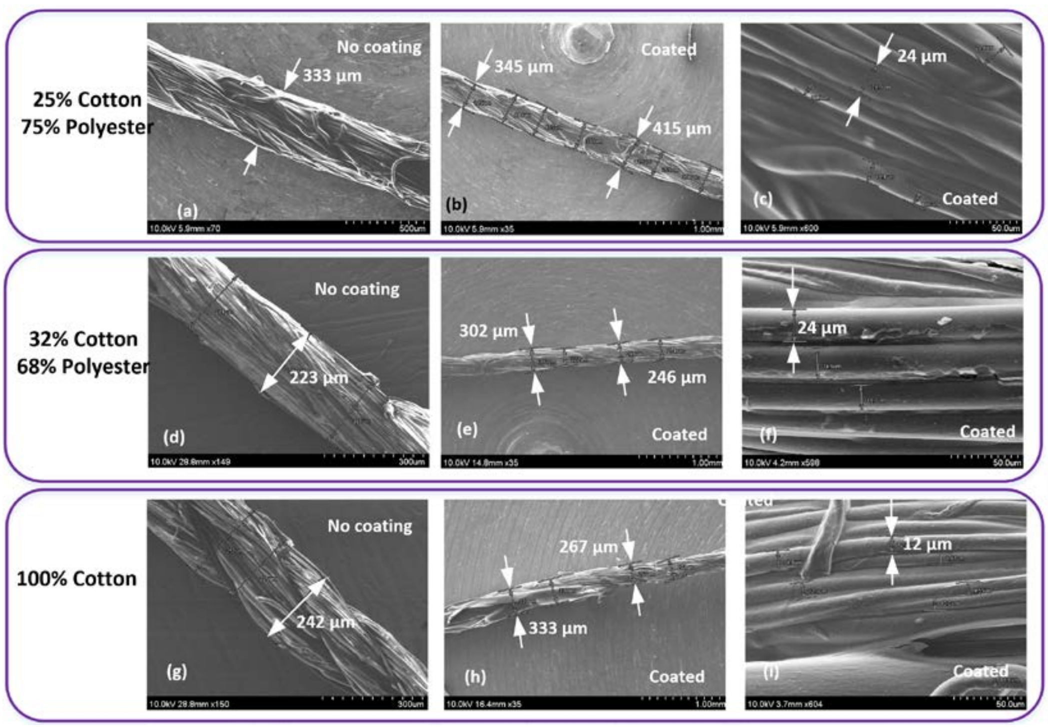

Figure 2. SEM images of three different threads before and after coating with PEDOT:PSS. (a-c) 25-75 CtP, (d-f) 32-68 CtP, and (g-i) 100 Ct.

The trans-conductance behavior of the three transistors when the drain voltage was kept at -0.8 V were measured and then $\sqrt{I_d}$ vs V_{gs} for the three transistors were plotted in Figure 3. The linear relationship between $\sqrt{I_d}$ and V_{gs} at larger voltages suggests the saturation mode that can be explained through equation (2). Therefore, the fitted curves can be used for the estimation of the threshold voltage as listed in Table 2. The results clearly show that 25-75 CtP has the lowest threshold voltage and the highest K which implies the highest mobility of charges.

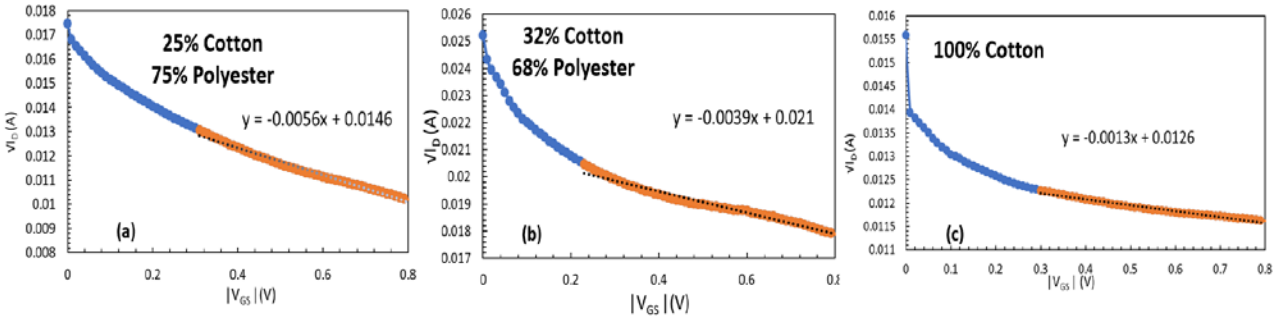

Figure 3. $\sqrt{I_d}$ vs V_{gs} of (a) 25-75 CtP, (b) 32-68 CtP, and (c) 100 Ct. The linear part of the curves were fitted with a linear function.

Table 2. Transistor parameters

Thread	$\sqrt{(\frac{1}{2}K)(\sqrt{(A)})}$	Threshold voltage
25-75 CtP	0.0056	2.61 V
32-68 CtP	0.0039	5.36 V
100 Ct	0.0013	9.6 V

Based on the properties of 25-75 CtP threads and its transistor response, we have tested the device for pH sensing. To study the effect of pH, when the gel electrolyte was exposed to the solutions with different pH, the trans-conductance property of the device was measured and then $\sqrt{I_d}$ vs V_{gs} was plotted in Figure 4. Since the pH level in human sweat varies between 7.5 and 5.7, in this study we considered 4 different solutions with pH in the same range [11]. The selected pH levels are: 7.5, 6.9, 6.4, and 5.7.

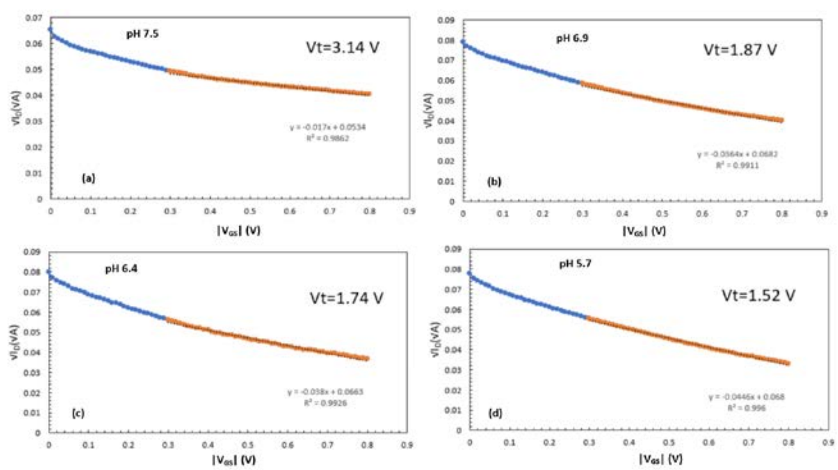

Figure 4. The $\sqrt{I_d}$ vs V_{gs} response of the OECT made from 25-75 CtP thread when being exposed to the solutions with (a) 7.5, (b) 6.9, (c) 6.4, and (d) 5.7 pH. The measurements were done at V_{DS}=-0.8 V

The results show that the transistor threshold voltage was 3.14 V when the device was exposed to a solution with pH of 7.5. The threshold voltage showed a consistent trend in response to a change in pH by reducing the threshold voltage with the reduction of pH. The results are promising for the application of the thread-based OECT as the pH sensor for monitoring perspiration. However, further studies are needed to examine the stability of the device and assess the pH sensitivity.

4. CONCLUSION

Testing three different threads, it was found that threads with 25% cotton and 75% polyester can be coated more uniformly with PEDOT:PSS to obtain the lowest resistance. The coating on 25-75 CtP shows a significant improvement in its tensile strength making it reliable for sewing with a sewing machine. Using the thread as a transistor, it was found that the device has the lowest threshold voltage that can be used in low voltage circuits. The OECT then was tested as a pH sensor to find that the threshold voltage of the device reduces with a decrease in the pH. The device's performance under different conditions has to be further studied before verifying its reliability for a wearable sensor.

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