PROCEEDINGS OF SPIE

SPIEDigitalLibrary.org/conference-proceedings-of-spie

Stability of fiber-based organic electrochemical transistors with a gel electrolyte for wearable electronics

Nestor Marquez Rios, Arash Takshi

Nestor O. Marquez Rios, 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); doi: 10.1117/12.2633175

SPIE.

Event: SPIE Organic Photonics + Electronics, 2022, San Diego, California, United States

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 15 Jan 2023 Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

Stability of Fiber-Based Organic Electrochemical Transistors with a Gel Electrolyte for Wearable Electronics

Nestor O. Marquez Rios[a], Arash Takshi[*a]
[a] Department of Electrical Engineering, University of South Florida, Tampa FL, U.S.A.

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 reviled 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.

Keywords: Electrochemical Transistors, PEDOT:PSS, Gel electrolyte, Wearable electronics, Bioelectronics.

1. 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 [1-3]. These sensors are electronic devices that can be embedded in garments that might provide a non-invasive measurement while being designed with unique features such as flexibility, versatility, and low cost [1]. 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 [3]. These studies led us to design devices for energy harvesting and storage [4]. Cotton yarns have been functionalized to have conductive fibers. This functionalization has been done by coating using metal nanoparticles or carbon nanotubes (CNTs) [1]. 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 [2]. 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 [3,6]. The sweat contains metabolites and electrolytes which can be used as a tool for information about the health of the person and their fitness [5]. 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 1a. Other works have been done with PEDOT:PSS for sensing saline concentrations and glucose sensors [3]. 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.

Organic and Hybrid Sensors and Bioelectronics XV, edited by Ioannis Kymissis,
Emil J. W. List-Kratochvil, Ruth Shinar, Proc. of SPIE Vol. 12210, 1221004
© 2022 SPIE · 0277-786X · doi: 10.1117/12.2633175

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 15 Jan 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

2. METHODOLOGY

2.1 Materials

To make the gate of the organic electrochemical transistor, we bought Jameco thread at (COMPLETAR). 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.

2.2 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 [7] 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 [8].

2.3 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 1a and 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 1 a-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.

2.4 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 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 [9] 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.

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 15 Jan 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

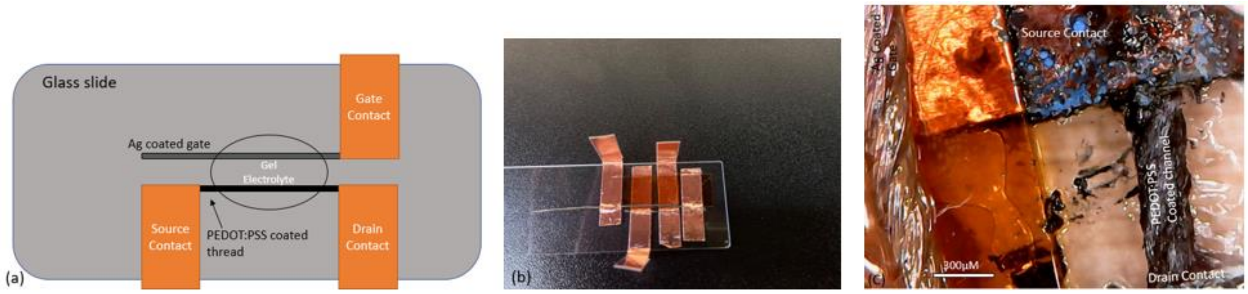

Figure 1. The organic electrochemical transistor design. The channel of the transistor is defined by the contact area between the gel electrolyte and the PEDOT:PSS thread. a) An schematic of the transistor. b) An image of the fabricated device. Kapton tape was used to avoid contact between the two threads. c) A zoom image of the transistor with gel on top of the gate and the channel.

3. 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 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.

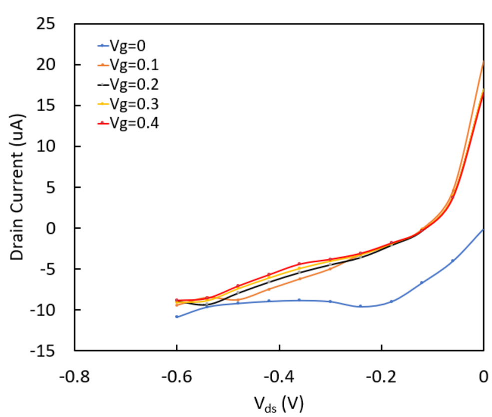

Figure 2. Transistor behavior day one after it was built.

Figure 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

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 15 Jan 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

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.

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 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.

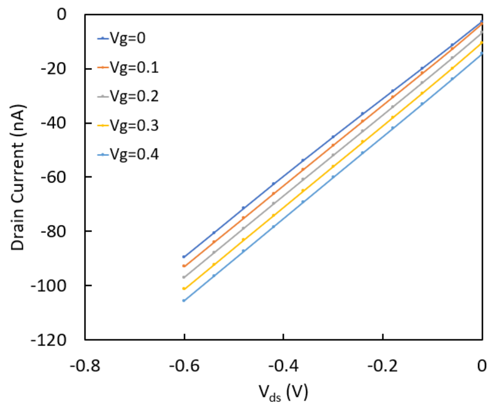

Figure 3. Transistor's output characteristic after 3 weeks.

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).

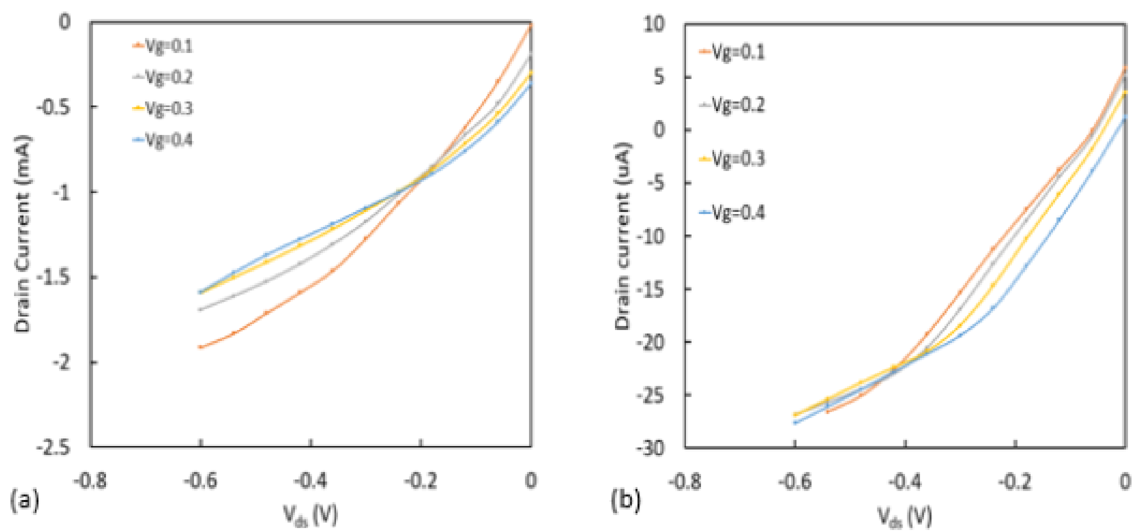

Figure 4. Transistor behavior after the addition of phosphoric acid at a. phosphoric acid with a pH of 5.0 and b. phosphoric acid with pH of 6.8.

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 15 Jan 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

Figure 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 4a) and the other pH of 6.8 (Figure 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 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.

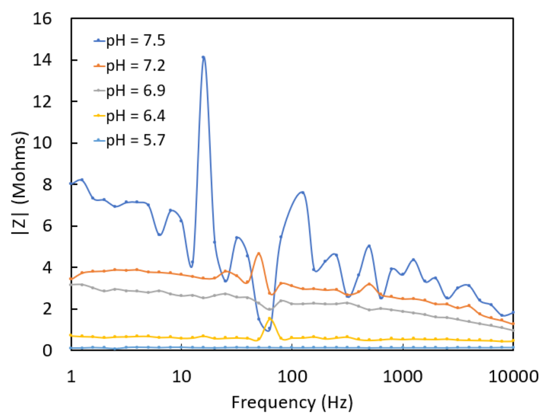

Figure 5. Bode plot for PEDOT:PSS thread as function of pH.

Figure 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) 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. 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.

ACKNOWLEDGEMENT

This work was supported by a grant from National Science Foundation (NSF 1953089) and Florida High Tech Corridor (Grant FHTC 21-19).

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 15 Jan 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use

REFERENCES

[1] Tarabella, G., Villani, M., Calestani, D., Mosca, R., Iannotta, S., Zappettini, A., & Coppedè, N., A single cotton fiber organic electrochemical transistor for liquid electrolyte saline sensing. Journal of Materials Chemistry, 22(45), 23830-23834 (2012)

[2] Gualandi I, Tessarolo M, Mariani F, et al. Textile Chemical Sensors Based on Conductive Polymers for the Analysis of Sweat. Polymers. Mar;13(6):894 (2021).

[3] Chen, S., Surendran, A., Wu, X., Lee, S. Y., Stephen, M., Leong, W. L., Recent Technological Advances in Fabrication and Application of Organic Electrochemical Transistors. Adv. Mater. Technol. 2020, 5, 2000523.

[4] Kareri, T, Hossain, MS, Ram, MK, Takshi, A. A flexible fiber-shaped hybrid cell with a photoactive gel electrolyte for concurrent solar energy harvesting and charge storage. Int J Energy Res. 2022; 1- 12.

[5] Possanzini, L., Decataldo, F., Mariani, F. et al. Textile sensors platform for the selective and simultaneous detection of chloride ion and pH in sweat. Sci Rep 10, 17180 (2020).

[6] Seung Yun Oh, Soo Yeong Hong, Yu Ra Jeong, Junyeong Yun, Heun Park, Sang Woo Jin, Geumbee Lee, Ju Hyun Oh, Hanchan Lee, Sang-Soo Lee, and Jeong Sook Ha, Skin-Attachable, Stretchable Electrochemical Sweat Sensor for Glucose and pH Detection, ACS Applied Materials & Interfaces, 10(16), 13729,-13740 (2018)

[7] Amirabad, R., Ramazani Saadatabadi, A. & Siadati, M.H. Preparation of polyaniline/graphene coated wearable thermoelectric fabric using ultrasonic-assisted dip-coating method. Mater Renew Sustain Energy 9, 21 (2020).

[8] Kareri, T., Yadav, R.L. & Takshi, A. Image processing analysis of supercapacitors with twisted fiber structures and a gel electrolyte. J Appl Electrochem, 52, 139–148 (2022)

[9] Lindsay B. Baker, Physiology of sweat gland function: The roles of sweating and sweat composition in human health, Temperature, 6:3, 211-259, (2019).

Downloaded From: https://www.spiedigitallibrary.org/conference-proceedings-of-spie on 15 Jan 2023
Terms of Use: https://www.spiedigitallibrary.org/terms-of-use