Fully Printed Organic Electrochemical Transistor on Paper for Glucose Sensing

Christopher Davidson
Biological Systems Engineering, University of Nebraska-Lincoln

NNIN iREU Site: Centre Microélectronique de Provence, École Nationale Supérieure des Mines de Saint-Étienne, France
NNIN iREU Principal Investigator: Dr. George Malliaras, Department of Bioelectronics, École Nationale Supérieure des Mines de Saint-Étienne
NNIN iREU Mentor: Eloïse Bihar, Department of Bioelectronics, École Nationale Supérieure des Mines de Saint-Étienne
Contact: cdavidson222@gmail.com, malliaras@emse.fr, bihar@emse.fr

Abstract:

Inkjet printing of conductive polymers is a versatile, low-cost, and non-contact fabrication method for bioelectronic devices. In this study, an all-plastic glucose biosensor based on an organic electrochemical transistor (OECT) was printed on a paper substrate. An aqueous bioelectronic ink consisting of the conductive polymer poly(3,4-ethylenedioxythiophene)-poly(styrene sulfonic acid) (PEDOT:PSS) was used to print the source, drain, channel, and gate of the transistor. An ink containing chitosan/ferrocene solution was also printed to functionalize the PEDOT:PSS gate. Bioenzymatic sensing of glucose was then completed with these devices by using glucose oxidase (GOx) and phosphate buffered saline (PBS) as the enzyme and electrolyte, respectively. Initial results show glucose detection between 2.70 and 10.00 millimolar, consistent with the concentration in human blood. These results pave the way to establishing a simple, low-cost, and paper based biosensing platform suitable for point of care diagnostics.

Introduction:

OECTs have recently gained great attention due to their high biocompatibility, ease of fabrication, and operation in low voltages, making them ideal candidates for bioelectronic applications. PEDOT:PSS is a conductive polymer ideal for fabricating OECTs due to its high conductivity, commercial availability, and its exceptional film forming properties [1]. In this study, we focused on inkjet printing a glucose sensing device. Inkjet printing is an ideal fabrication process as it presents advantages such as speed, flexibility, and low cost [2]. It can also successfully print on a multitude of substrates, including paper. Paper is an ideal substrate, as it is eco-friendly, disposable, and very inexpensive.

In this work, glucose is detected by inducing the enzyme specific reaction of glucose and GOx coupled with ferrocene, as shown in Figure 1. Ferrocene acts as an electron shuttle from the GOx to the PEDOT:PSS gate, causing de-doping of the channel and thus decreasing the drain current. This decrease is proportional to the concentration of glucose in the working solution [3].

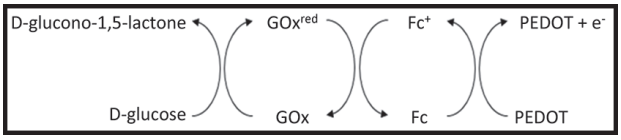

Figure 1: Reaction cycle for glucose detection using a ferrocene mediator.

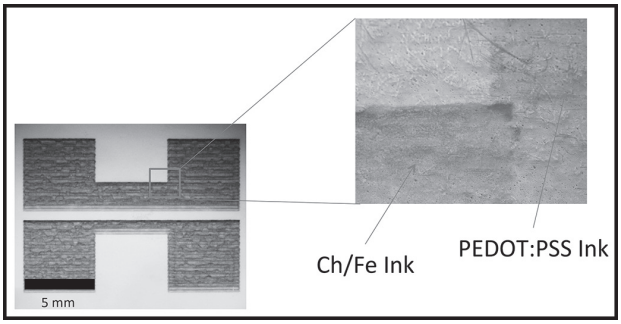

Figure 2: Fully printed OECT with zoom on gate.

Experimental Procedure:

A Dimatix Materials Printer (DMP) was used to print the device, and its dimensions are shown in Figure 2. The channel and gate dimensions (length and width) were 5 mm × 1 mm and 5 mm × 2 mm, respectively. We printed two layers of pre-developed PEDOT:PSS ink recipe to fabricate the channel, drain, source, and gate of the transistor.

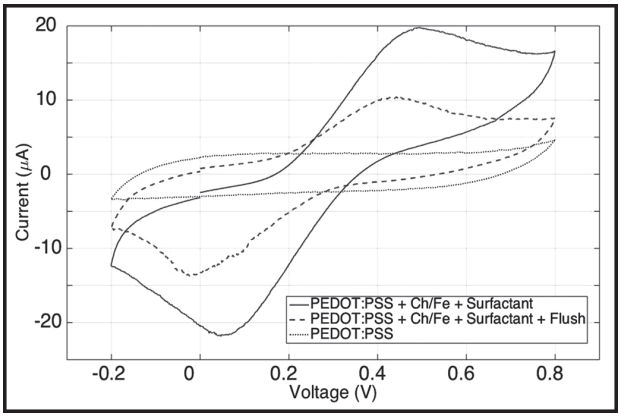

Figure 3: Cyclic voltammograms for different chitosan/ferrocene inks compared to PEDOT:PSS.

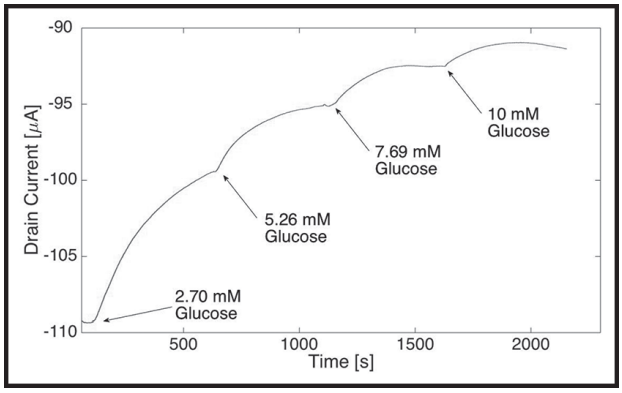

Figure 4: Device response to 2.70, 5.26, 7.69, and 10.00 mM glucose concentrations.

To make the electron mediator ink, a chitosan/ferrocene solution in acetic acid (0.3%wt) was first made by dissolving 15 mg of chitosan/ferrocene copolymer in 5 mL of 0.2 M acetic acid. To match this solution with the requirements of inkjet (rheological properties of the ink), we added a surfactant (Dynol 810) and a flush solution (water and ethylene glycol).

To assess the electrochemical performance of the ink in each step of its development, cyclic voltammetry was employed using a platinum wire as counter electrode, an Ag/AgCl reference electrode, and our ink as the working electrode, and can be seen in Figure 3.

Electrical characterization of the printed devices was carried out at a constant gate voltage of 0.5 V and a drain voltage of -0.7 V. In order to confine the electrolyte, a polydimethylsiloxane (PDMS) well was placed on top of the gate and channel, and the electrolyte (16 μL) and the enzyme (2 μL) were added. After stabilization of the drain current, different concentrations of glucose solutions were added. Figure 4 shows the device response to incremental steps in glucose concentration.

Results and Conclusion:

Figure 3 shows the cyclic voltammograms of the chitosan/ferrocene ink after addition of surfactant, after further addition of flush solution, and a control of PEDOT:PSS. Peaks can be observed at around 0.4 V and 0.1 V for both inks containing chitosan/ferrocene solution, confirming the electrochemical activity of ferrocene.

Figure 2 shows a fully printed device. There is a clear color change between the gate and the rest of the device, indicating that the chitosan/ferrocene ink was selectively printed onto the gate of the device.

Figure 4 shows the device response upon successive additions of different glucose concentrations onto the device. There are clear changes in the current values for a range of concentrations between 2.70 mM and 10 mM, which are consistent with those in human blood [4].

Conclusions and Future Work:

In this study, PEDOT:PSS and chitosan/ferrocene based inks were successfully printed on paper towards the development of an all printed paper OECT based glucose sensor. The detection of glucose was successful in a range of concentrations between 2.70 and 10.00 mM, similar to that in human blood. There is room for optimization, like immobilizing the enzyme on the gate and improving the sensor's sensitivity to the μM range, which is consistent with levels in human saliva. This work shows great potential as a disposable noninvasive sensing platform for point of care diagnostics.

Acknowledgments:

I would like to thank the NNIN iREU Program and NSF for funding this project (under Grant No. ECCS-0335765). I would also like to thank Eloïse Bihar, Anna-Maria Pappa, Xenofon Strakosas, Mary Donahue, Vincenzo Curto, and Dr. George Malliaras for their individual help and guidance.

References:

[1] Shim, N, et al. All-Plastic Electrochemical Transistor for Glucose Sensing Using a Ferrocene Mediator. Sensors 2009;9:9896-9902.

[2] Yun, YH, et al. A Glucose Sensor Fabricated by Piezoelectric Inkjet Printing of Conducting Polymers and Bienzymes. Anal. Sci. 2011;27:375-379.

[3] Strakosas X, Bongo M, Owens RM. The organic electrochemical transistor for biological applications. J. Appl. Polym. Sci. 2015;132:41735.

[4] Panchbhai, AS, et al. Correlation of Salivary Glucose Level with Blood Glucose Level in Diabetes Mellitus. J. Oral. Maxillofac. Res. 2012;3(3):e3.