Towards Ink-Jet Fabricated PEDOT:PSS Organic Electrochemical Transistors with Embedded Enzymes

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Abstract and Introduction:

Ink-jet printing is a promising method for the low cost fabrication of electronics and sensing devices. Indeed, its ease of processing includes additive patterning, simple modification of device geometry, non-contact processing, and diverse substrate possibilities.

Commercially available as an ink for printing, poly(3,4-ethylene dioxythiophene)-poly(4-styrenesulfonate) (PEDOT:PSS) is a degenerately-doped *p*-type organic semiconductor polymer which has been investigated extensively for the fabrication of organic electrochemical transistors (OECTs). Like other transistors, OECTs benefit from inherent signal amplification [1]. In contrast to traditional transistors, OECTs operate at biocompatible working voltages in electrolyte. OECTs are thus excellent candidates for biosensing and integration into *in vitro* and *in vivo* applications. In addition, a planar monolayer geometry is possible allowing simple fabrication by inkjet printing.

In the operation of an OECT, application of positive gate voltage increases cation concentration in the channel, which results in dedoping of the conducting polymer. The dedoped channel is less conductive resulting in a lower drain current. Thus, the change in gate voltage results in an amplified change in drain current.

Glucose sensing with an all-PEDOT:PSS OECT has been previously demonstrated with glucose oxidase (GOx) located in the electrolyte [2]. In this device design, electrons were shuttled by a mediator from the enzyme in solution to the PEDOT:PSS gate. Thus, the effective gate voltage and in result the drain current were modulated in response to changes in glucose concentration. Limitations of this device include the presence of reagents in the electrolyte. In contrast, Yun, et al., embedded GOx and horseradish peroxidase enzyme in a PEDOT:PSS electrode by inkjet printing a single bioelectronic ink consisting of the enzymes in an aqueous dispersion of PEDOT:PSS [3]. The aim of this project was to ink-jet print an OECT with GOx embedded in its PEDOT:PSS electrodes for glucose sensing. We report progress in the development of the fabrication of such devices.

Methods and Results:

Devices were printed with a Dimatix Materials Printer 2800 (DMP 2800). The DMP 2800 is a piezoelectric printer with a disposable cartridge that dispenses 10 pL drops of ink from 16 nozzles. Four layers were printed on glass slides coated in a vapor-deposited layer of Parylene-C that was treated with oxygen plasma just prior to printing (Figure 1).

The ink used in this project was a 1.8 wt.% dispersion of PEDOT:PSS in water with ethylene glycol and ethanol (Agfa Orgacon IJ-1005). Normal processing of this commercial ink entailed steps such as sonication and high-temperature annealing which would denature enzymes. Thus, modifications were necessary to preserve the activity of the enzyme while maintaining the desired electrical and mechanical properties of the conducting polymer.

PEDOT:PSS is normally annealed at temperatures exceeding 100°C for over 60 minutes, but native GOx is significantly denatured after 60 minutes at 60°C [4]. An alternative annealing process was therefore required to minimize enzyme denaturation. Drying the printed devices under vacuum at 25°C for 48 hours resulted in electrical properties very similar to those of devices baked at 150°C for one hour (Figure 2). While less mechanically robust than the devices baked at higher temperatures, the vacuum dried devices were sufficiently robust for characterization and testing.

Enzymes are also sensitive to salt concentration and pH. To achieve physiological salt concentration and to mitigate the ink pH of 1.5, the ink was mixed with 10X phosphate buffered saline (PBS) in a 10:1 volume ratio and then stirred overnight. In addition, extended sonication can damage the structure of the enzyme. The PEDOT:PSS-PBS ink was sonicated for one minute periods alternated with cooling at 4°C in a refrigerator. When prepared in this way the PEDOT:PSS-PBS ink was successfully jetted. While resistance of the final devices increased with addition of PBS, the modulation of the transistors was maintained (Figure 3).

In the next step of the project, GOx was added to the PEDOT:PSS-PBS ink. The enzyme was dissolved in 10X PBS before mixing with the PEDOT:PSS ink to result in a final concentration of 400 U GOx/mL. The ink was mixed overnight and sonicated as previously described. Jetting with the bioelectronic ink was poor or nonexistent even if the ink was filtered. Aggregates most likely blocked the cartridge nozzles or otherwise interfered with jetting. Such aggregates could be observed by optical microscope in a spuncoat film of the ink with enzyme (Figure 4).

Conclusions and Future Work:

A suitable annealing condition for printing PEDOT:PSS ink with enzyme was found. Mixing PEDOT:PSS ink with PBS resulted in a jettable ink that produced devices with lower current magnitude but modulation similar to that of devices printed with the original ink. Addition of GOx to PEDOT:PSS-PBS ink resulted in aggregation that prevented jetting.

Future work includes assessing the activity of the enzyme after ink preparation and reducing enzyme aggregation.

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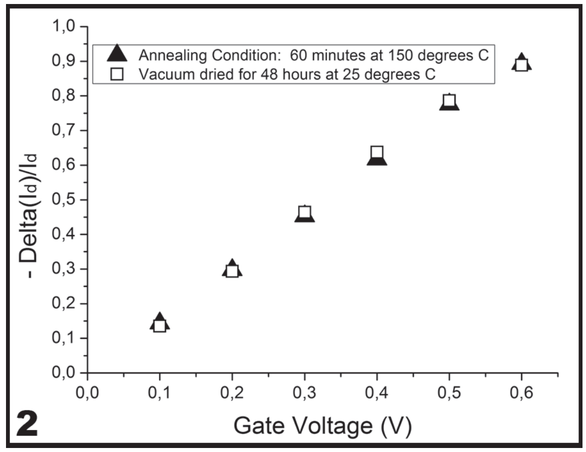

Figure 2: Normalized response for ink-jet printed OECTs fabricated with different annealing conditions.

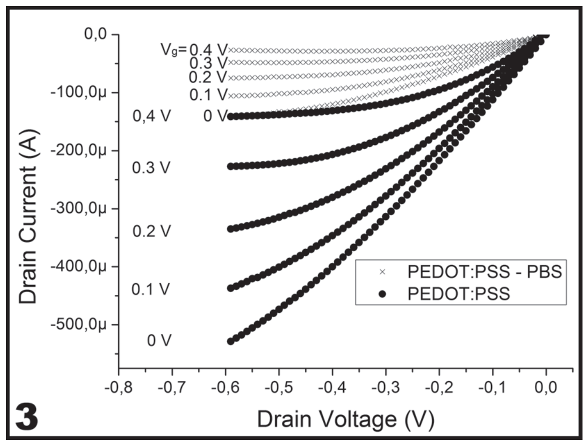

Figure 3: Output curves for OECTs printed with PEDOT:PSS and PEDOT:PSS-PBS inks.

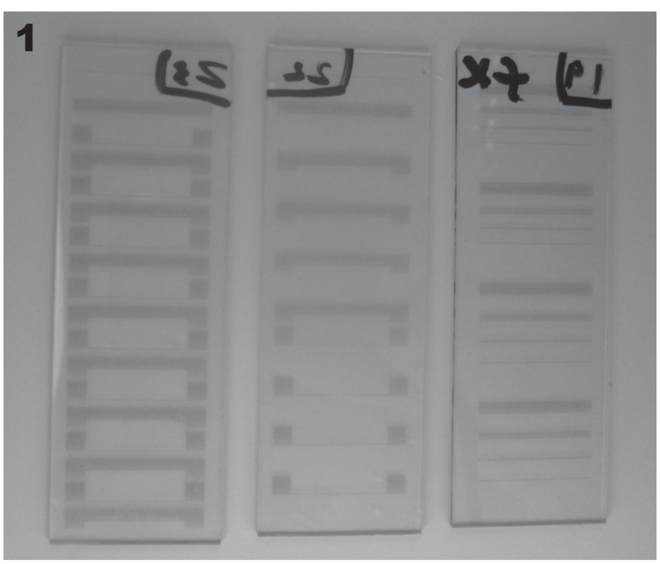

Figure 1: Inkjet-printed PEDOT: PSS OECTs on standard glass slide (26 mm by 76 mm).

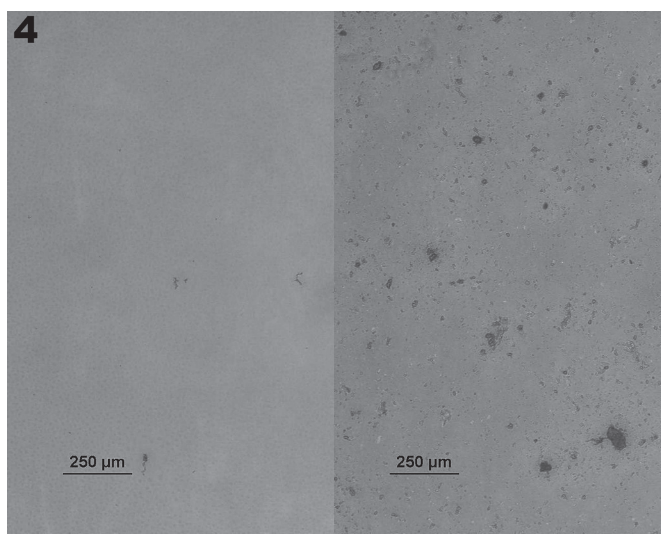

Figure 4: Left SEM, spincoat film of PEDOT:PSS-PBS ink. Right SEM, spincoat film of PEDOT:PSS-PBS-GOx ink.