TEXTILE-BASED ELECTROCHEMICAL SENSORS USING EMBROIDERED ELECTRODES

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ABSTRACT

Textile is an inexpensive, widely available material and offers unique advantages for disposable point-of-care diagnostics and wearable biosensors. Here, we report the first demonstration of a textile-based embroidered electrochemical sensor for analytical measurements. We have developed a simple method to generate conductive polyester threads which are used to fabricate flexible, mechanically robust electrodes on textiles. Proof-of-concept measurements of glucose show that this biosensor exhibits good specificity and linearity from 0 mg/dL to 720 mg/dL, which encompasses the clinically relevant concentration range in humans. Additionally, we demonstrate that this sensor can be easily fabricated in arrays using high-volume manufacturing processes for multiplexed measurements. Lastly, we show that this biosensor exhibits excellent resiliency against mechanical stress and good repeatability, which are important features for textile-based biosensors.

INTRODUCTION

Electrochemical sensors are a promising technology for analytical measurements due to their speed, small size, and high sensitivity [1]. Traditionally, electrochemical sensors are fabricated as multilayer laminate assemblies on rigid substrates, such as plastic or glass [2, 3]. However, these materials are too costly for point-of-care testing in the developing world and are difficult to dispose. Alternatively, the emerging era of wearable sensing requires sensor and sensor components that are flexible, robust and can be easily integrated with wearable materials. Textiles represent an excellent class of materials for point-of-care diagnostics and wearable sensing since they are inexpensive and widely used in the manufacturing of garments and clothing. In addition, the continuous contact of clothing with the wearer's skin facilitates the measurement of physiologically relevant data (e.g. pulse, skin temperature) and collection of bodily fluids (e.g. sweat). Furthermore, the large surface area of garments (e.g. undergarments, shirts, pants) provides substantial space for sensor placement at multiple locations and integration of corresponding electronic hardware. Previous efforts in textile electronics, such as woven transistors and printed sensors, have resulted in the development of wearable sensors for measuring skin temperature [4], heart rate [5, 6], and respiration [7]. With respect to chemical sensing, several groups have demonstrated screen-printed electrochemical sensors fabricated on textiles [8-10] and neoprene [11]. Recently, an electrochemical sensor was reported which employs conductive silk yarn woven into the fabric [12]. While this technique offers improved robustness compared with screen-printed sensors, it is limited to simple electrode geometries and substrates that are woven.

Here, we demonstrate a new type of embroidered electrochemical sensor that is mechanically robust, compatible with different types of fabrics, and offers custom electrode geometries. We also show that this embroidered sensor can be used for quantitative measurement of physiologically relevant analytes. Proof-of-concept measurements of glucose reveal that this embroidered sensor exhibits excellent specificity, linearity and repeatability. Furthermore, durability testing shows that this sensor can maintain measurement accuracy after repeated cycles of

mechanical deformation, making it a promising candidate for wearable applications.

MATERIAL AND METHODS

Materials and Reagents

Glucose, glucose oxidase, uric acid and L-lactate were purchased from Sigma-Aldrich (St. Louis, MO). Silver/silver chloride (Ag/AgCl) and carbon inks were purchased from Conductive Compounds Inc. (Hudson, NH). Blocker Casein in PBS was purchased from Thermo Scientific (Tustin, CA). Deionized (DI) water was generated using a Barnstead Smart2Pure water purification system. For electrochemical measurements, analytes were resolved in PBS at room temperature. Samples were freshly prepared prior to experiments and remaining biochemicals were used without further purification.

Thread Preparation

Each electrochemical sensor consists of three electrodes, a reference electrode (RE), working electrode (WE) and counter electrode (CE), which are fabricated using conductive threads. Briefly, polyester thread (Brothers International Corp., Bridgewater, NJ) was coated with carbon or Ag/AgCl ink and cured at 120 °C for 40 min. Thread coated with carbon ink was used for the WE and CE, and thread coated with Ag/AgCl ink was used for the RE. Glucose oxidase was immobilized onto the WE by immersing carbon-coated thread in a glucose oxidase solution (645 U/mL) and air drying overnight at room temperature.

Thread Characterization

Optical microscopy (Nikon Eclipse TS100-F trinocular microscope and DS Fi1 camera) and scanning electron microscopy (SEM) were used to characterize the thread coating process. SEM images were captured using a JEOL 6620LV scanning electron microscope at 12 kV and 170× magnification. The electrical properties of the threads were characterized by measuring their electrical resistance using a Fluke 87-V digital multimeter. Threads were cut into 1 m-long pieces and attached to the multimeter using alligator clips.

Sensor Design and Fabrication

Electrochemical sensors were designed using AutoCAD software (Autodesk, Vernon Hills, IL) and converted into an embroidery file using SewArt software (S & S Computing). The digitized image was uploaded to a Brothers SE400 embroidery machine and fabricated on polyester fabric stacked with a stabilizer film (World Weidner, Ponca City, OK). After the sensors were embroidered, the stabilizer was removed and individual sensors were cut and stored at ambient conditions prior to experiments.

Electrochemical Measurements

Amperometric measurements were performed using a Genefluidics electrochemical workstation (Irwindale, CA). For each measurement, 35 μ L of sample was dispensed onto the sensing region using a pipette and a bias potential of -200 mV (across the WE and RE) was used. Data was obtained 1 min after dispensing the sample. All measurements were performed at room temperature under ambient conditions.

RESULTS AND DISCUSSION

Thread Characterization

Conductive threads were characterized using optical microscopy and SEM to evaluate the effectiveness of the thread coating process. Optical images of uncoated thread (a) and thread coated with Ag/AgCl (b) are shown in Fig. 1. For the Ag/AgCl-coated sample, we can observe that the entire length of thread is uniformly coated with ink with negligible blotching or defects. Carbon-coated thread also exhibited similar surface coverage. SEM was used to further visualize the thread surface morphology after the coating process. A cross-sectional image of the thread shows that the ink permeates into the fibers at depths of $\sim 50\ \mu\text{m}$ (Fig. 1 (c)). These results also suggest that the enzyme coating process has negligible impact on the surface morphology and the coating thickness.

Figure 1. Optical micrographs of uncoated thread (a) and thread coated with Ag/AgCl (b). Scale bar, $500\ \mu\text{m}$. (c) Cross section SEM image of thread coated with Ag/AgCl. Scale bar, $50\ \mu\text{m}$.

The electrical properties of the thread influences the performance of the embroidered electrochemical sensor. Therefore, we measured the electrical resistance of the carbon and Ag/AgCl-coated threads. Ag/AgCl and carbon-coated threads exhibited resistances of $\sim 0.8\ \Omega/\text{cm}$ and $\sim 140\ \Omega/\text{cm}$ respectively, which is similar to values reported in literature [12]. To prevent the oxidation of Ag/AgCl ink, we applied flux to the Ag/AgCl-coated threads, which reduced its resistance to $80\ \Omega/\text{cm}$.

Sensor Embroidery

The embroidery process is an important part of sensor fabrication since there are several parameters that can affect the sensor performance. A few of these parameters, including the stitch separation distance and stitch length, were optimized to enhance the quality of the electrodes. For instance, decreasing the stitch separation distance resulted in a higher stitch density which improved electrode uniformity. However, using a higher stitch density required a larger amount of thread which increased the electrical resistance of the electrodes. We determined that a stitch separation distance of $0.2\ \text{mm}$ and stitch length of $0.5\ \text{mm}$ produced consistent uniformity while minimizing the electrode resistance.

Using the optimized embroidery parameters, we successfully fabricated embroidered electrochemical sensors with tightly-stitched, discrete electrodes (Fig. 2) allowing for excellent signal consistency and signal-to-noise ratio (SNR). The dashed circle indicates the sensing region, where the sample is dispensed, which encompasses all three electrodes. Fig. 2 also shows that we can easily fabricate sensor arrays for multiplexed measurements using this technique.

Figure 2. A 3×2 embroidered electrochemical sensor array fabricated on polyester. The dashed circle indicates the sensing region. Scale bar, $1\ \text{cm}$.

Sensor Characterization

We briefly investigated the electroactivity of the embroidered electrodes using cyclic voltammetry (CV). CV measurements of $0.1\ \text{mM}$ potassium ferrocyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) in $1\ \text{mM}$ of potassium chloride (KCl) were performed at various scan rates at room temperature. The resulting voltammograms are plotted in Fig. 3, which shows a positive correlation between the anodic peak current and scan rate, and good reversibility.

Figure 3. Cyclic voltammograms of $0.1\ \text{mM}\ \text{K}_3\text{Fe}(\text{CN})_6$ in $1\ \text{mM}$ of KCl at various scan rates using embroidered electrochemical sensors. Inset shows the relationship between anodic currents and the square root of the scan rate.

Glucose Detection

To demonstrate the utility of this platform for the detection of physiologically relevant analytes, we use it for amperometric measurements of glucose. Samples were prepared by dissolving glucose in PBS at increasing concentrations from $0\text{--}700\ \text{mg/dL}$. $35\ \mu\text{L}$ of sample was used for each measurement. Due to the high wettability of the sensor, the sample could be fully absorbed within $\sim 1\ \text{min}$ which also provided sufficient time for a stable electrochemical reaction to be generated. The electrochemical signal from the final $10\ \text{sec}$ was averaged and used to generate the dose-response profile shown in Fig. 4. The glucose assay exhibits a

highly linear response over the entire concentration range with a R^2 correlation coefficient of 0.996 and a lower limit of detection of 100 mg/dL. Additionally, the averaged data points exhibit very small standard deviations (SDs < 3%), which demonstrates the high accuracy and repeatability of this assay.

Figure 4. Amperometric measurements of glucose in PBS. Values are averaged over the final 10 sec of the detection signal. Each data point represents the mean $\pm$ standard deviation (SD) of three separate measurements using new sensors.

Assay Specificity

The specificity of the electrochemical sensor was briefly studied by performing independent measurements of glucose (100 mg/dL), lactate (100 mg/dL), uric acid (100 mg/dL) and PBS using glucose oxidase-immobilized sensors. The data is plotted as the SNR (Fig. 5). From this plot, we observe that a significant detection signal is generated only for the glucose sample (SNR = 3.2), while the irrelevant analytes generate SNRs similar to that of the PBS blank control. These results indicate that the sensor exhibits good specificity with minimal interference due to analyte cross-reactivity. They also suggest that this platform can be used for multiplexed detection with minimal modification to the sensor preparation or detection protocol.

Figure 5. Specificity of the glucose assay. Measurements were performed using glucose, lactate and uric acid diluted in PBS at a concentration of 100 mg/dL. Each bar represents the mean $\pm$ SD of three separate measurements.

Sensor Durability Testing

For textile-based sensors, an important factor that needs to be considered is the influence of mechanical deformation on the detection performance. Specifically, wearable sensors need to

maintain accurate and consistent detection response under repeated cycles of deformation caused by the wearer's movement. To mimic this effect, we manually folded and flattened the sensor for up to 100 times and performed measurements at intervals of 5, 10, 25, 50 and 100 bending cycles. By comparing the detection signals from mechanically folded sensors with those from control sensors that didn't undergo bending, we conclude that there is a negligible change in the signal after 25 cycles and a marginal decrease of ~9% after 100 cycles (Fig. 6). These results suggest that our embroidered sensor technology will be able to maintain its accuracy and exhibit high reproducibility under instances of repeated deformation, making it suitable for wearable applications.

Figure 6. Amperometric measurements of glucose (720 mg/dL) in PBS following cycles of bending. Each bar represents the mean $\pm$ SD of three separate measurements. Inset shows the mechanical bend testing of the sensors.

CONCLUSIONS

We demonstrate a unique textile-based embroidered electrochemical sensor for quantitative analyte detection. A simple method for generating conductive threads was developed and used to fabricate electrochemical sensors on textile. Cyclic voltammetry measurements showed that this embroidered sensor exhibits good reversibility. For proof of concept, this platform was used for amperometric measurements of glucose in PBS, which exhibited high linearity, repeatability and assay specificity. Studies to assess sensor durability revealed that this embroidered sensor generated consistent, stable and accurate measurements of glucose after repeated cycles of mechanical deformation. Furthermore, this sensor can be fabricated using automated, high-volume manufacturing processes on various types of textiles. Future work will focus on developing sensor arrays for simultaneous measurements of multiple analytes and detection using raw clinical specimens (e.g. serum, blood).

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