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Thread-Based Sensors †

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† Presented at the International Conference on the Challenges, Opportunities, Innovations and Applications in Electronic Textiles (E-Textiles 2019), London, UK, 12 November 2019.

Published: 20 January 2020

Abstract: Fiber and textile-based chemical sensors are emerging tools which target minimally invasive monitoring. Fiber-shaped electrodes are a versatile design for wearable applications since the fiber architecture allows for straightforward integration into textiles facilitating the principle of "wear-and-forget". Skin and wound care would benefit from real-time pH monitoring, which can indicate wound health and the physiological condition of the skin. A further application of wearable chemical sensors is therapeutic drug monitoring.

Keywords: fiber electrode; wearable sensor; pH measurements; lithium drug sensing

1. Introduction

Wristwatch biosensors are small, wearable devices that continuously monitor surrogate markers for sympathetic nervous system activity, namely electrodermal activity, skin temperature, blood oxygen levels and locomotion. The drive for improved wearability has led to the development of fully flexible components for wearable sensors. Fiber-based electrodes can be easily integrated into garments and therefore are an attractive option due to their electrically conductive and ductile nature.

Carbons such as carbon nanotubes (CNTs), graphene and conducting polymers such as polyethylene dioxythiophene (PEDOT) have been used to convert cotton fibers into conductive threads by dipping in conductive inks. Studies that have reported using conductive cotton in sensing platforms include PEDOT-coated cotton, which was used for stress-strain monitoring [1] and acetone vapor detection [2]. CNT-coated cotton was applied to pH, K^+ and NH_4^+ sensing [3]. This paper describes recent research at Surrey developing pH and lithium drug sensors, based on cotton threads [4,5]. Epidermal pH gives an indication of the skin physiology and the state of wound healing. Lithium is used to treat bipolar disorder and lithium drug monitoring is essential due to its narrow therapeutic range (0.4–1.0 mM) and the toxicity associated with drug-levels above this range.

2. Materials and Methods

2.1. Reagents

PEDOT:PSS (Clevios PH 1000; Heraeus, Leverkusen, Germany), thin multi-walled carbon nanotubes (MWCNTs) (95% purity; Nanocyl, Belgium) and single-walled carbon nanotubes (SWCNTs) (>70% purity; Nanocyl) and Ag/AgCl paste (C2130809D5; Sun Chemicals, Parsippany, NJ, USA) were used as received. All other chemicals were purchased from Sigma Aldrich.

2.2. Apparatus

Electrochemical measurements were performed using an eDAQ EA161 potentiostat with eDAQ e-corder 401 supported by EChem V2.1.16 software. Scanning electron microscopy (SEM) images were obtained using a JEOL USA JSM-7100 F field emission electron microscope.

2.3. Procedure

Cotton threads were dip-coated with a dispersion containing either 0.5 wt.% PEDOT:PSS and 1.5 wt.% MWCNT (for pH sensing) or 1.0 wt.% SDBS and 0.3 wt.% SWCNT (for Li^+ sensing). For pH-sensitive fibers, polyaniline (Pani) was coated onto PEDOT/MWCNT-cotton electrodes (1 cm length) using cyclic voltammetry between −0.2 to +1.0 V vs. Ag/AgCl for 10 cycles at 100 mV s^{-1} in solutions of aniline (0.1 M) in nitric acid (1.0 M). Potentiometry in Britton-Robinson pH buffered solutions was used for pH analysis and the potential of the Pani-PEDOT/MWCNT-cotton fiber electrodes (1 cm length) was measured against a fabric Ag/AgCl quasi-reference electrode. A wearable Ag/AgCl quasi-reference electrode was made by applying 0.2 g Ag/AgCl paste to one side of gauze fabric (1 cm^2 area) followed by curing at 80 °C for 20 min. The other side of the gauze was subsequently coated and cured.

A cotton fiber-based lithium sensor was fabricated by dip-coating cotton thread (5 mm) in SWCNT ink until a resistance of 500 Ω had been reached. The resulting dry conductive cotton fiber was further dip-coated 9 times with lithium membrane solution [5]. The lithium membrane solution was composed of 28 wt.% PVC, 68.5 wt.% NPOE, 1.5 wt.% Li ionophore VI, 0.5 wt.% lithium tetrakis(pentafluorophenyl)borate ethyl etherate (LiTPFPB) and 1.5% TOPO. After overnight drying, the resulting sensor could be used directly without preconditioning. To build a flexible fiber-based reference electrode, carbon fiber was dipped twice in Ag/AgCl ink and cured at 90 °C after each coating. The Ag/AgCl-coated carbon fiber was further coated 5 times by dipping in a reference membrane solution (78.1 mg of PVB and 50 mg of NaCl in 1 mL of methanol), left to dry overnight and used without any pre-conditioning the following day.

3. Results and Discussion

3.1. Sensor Fabrication and Characterisation

Cotton threads were made conductive by dip-coating with conductive inks. For pH sensing fibers, cotton threads were dip-coated with PEDOT/MWCNT dispersion a total of 10 times and dried. Pani was deposited onto PEDOT/MWCNT-cotton by electropolymerisation to make the fibers pH sensitive. In contrast, the cotton thread used in lithium drug sensing was dip-coated in a dispersion containing SWCNTs (with a water rinse after each coating to remove excess surfactant) until a resistance of 500 Ω had been reached. Li^+ sensing fibers were prepared by dip coating these SWCNT-cotton threads with a lithium selective membrane.

SEM images show the change in the surface morphology of the cotton threads when coated with different conductive inks (Figure 1). The PEDOT/MWCNT-cotton fiber has a smooth surface since it is completely coated with a conductive layer. Following Pani deposition on PEDOT/MWCNT-cotton fibers the surface morphology is noticeably rougher. In contrast, the individual fibrils of the cotton yarn are still evident after coating with SWCNT. This changes however once the SWCNT-cotton has been coated with the Li^+ sensing layer, which covers the thread with a smooth film approximately 15 μm thick.

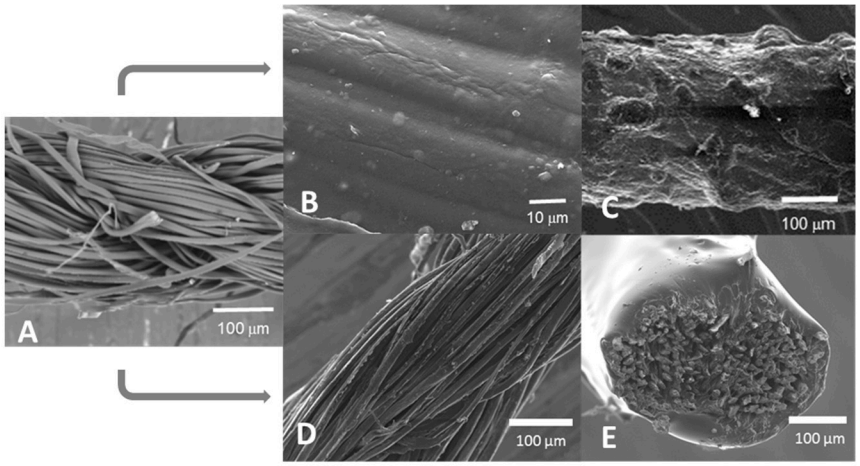
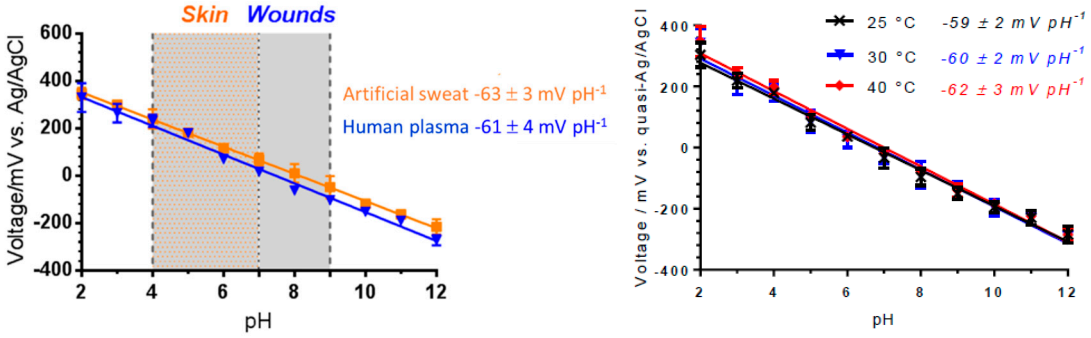


Figure 1. SEM images of cotton thread (**A**), PEDOT/MWCNT-cotton (**B**), Pani-coated PEDOT/MWCNT-cotton (**C**), SWCNT-cotton (**D**), cotton-based Li+ sensor (**E**).

3.2. pH Sensing

The application of a wearable sensor on skin or a wound requires the pH of small volumes of sweat/wound fluid to be measured. This necessitates a wearable quasi-reference electrode (e.g., Ag/AgCl on gauze fabric). The response of the pH fiber sensor vs. a fabric quasi-reference electrode was tested in 200 µL of pH-adjusted artificial sweat containing common sweat interferences. A response of −63 ± 3 mV pH^{-1} was achieved as shown in Figure 2a. The response time of the pH sensor was 59 ± 20 s, n = 3, demonstrating the electrode's capability for real-time monitoring.

The temperature of wounds and the skin surface varies between 31 to 37 °C. At temperatures ranging from 25 to 40 °C, a Nernstian response was obtained for the pH fiber sensor and a small increase in the slope was observed (ranging from −59 ± 2 mV pH^{-1} to −62 ± 3 mV pH^{-1} (n = 3) at 25 and 40 °C respectively (Figure 2b). These results correspond well with the ideal responses calculated from the Nernst equation of −59.2 mV pH^{-1} at 25 °C and −62.1 mV pH^{-1} at 40 °C.



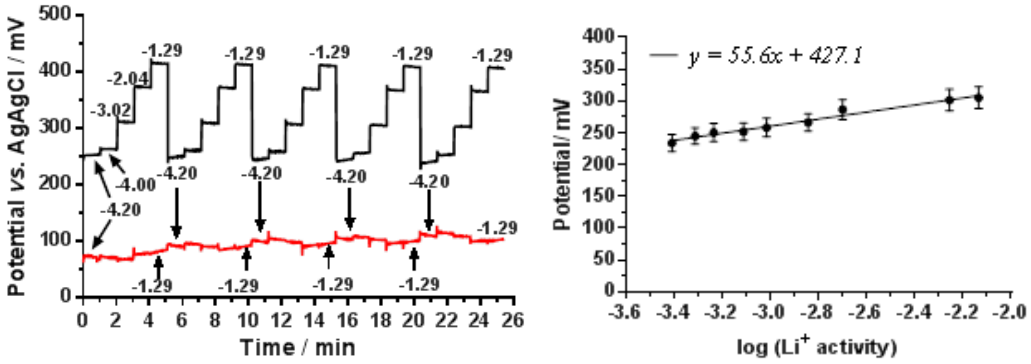
(**a**) (**b**)

Figure 2. (**a**) Potentiometric response of Pani-PEDOT/MWCNT-cotton in pH adjusted artificial sweat and plasma. N = 3; (**b**) potentiometric response of Pani-PEDOT-MWCNT-cotton in buffered solutions of varying pH levels between 25 and 40 °C, n = 3.

3.3. Li^+ Drug Sensing

The potentiometric response of the Li^+ sensor and fiber reference electrode vs. a double junction reference electrode was monitored in different concentrations of LiCl solution. Figure 3a shows how the fiber reference electrode response drifts during measurements especially when switching from a higher concentration LiCl solution to a lower concentration at the start of each run. In contrast, the behavior of the Li^+ fiber shows a very small drift over time (0.3% RSD).

The Li^+ sensor device (Li^+ fiber vs. fiber reference electrode) was tested in human plasma samples spiked with different concentrations of LiCl and the potentiometric response was measured. Figure 3 shows very promising responses for five different Li^+ sensor devices towards Li^+ concentration changes in plasma and the response of the Li^+ sensor spans over the clinically relevant therapeutic range and into the clinically toxic range.



(**a**) (**b**)

Figure 3. (**a**) The potentiometric response vs. time of the Li^+ sensor (black) and the fiber reference electrode (red) vs. Ag/AgCl double junction reference electrode with varying concentrations of LiCl solutions. The values on the plots are log (Li^+ activity); (**b**) the average potentiometric response of Li^+ sensor vs. the fiber reference electrode measured in LiCl solution (0.1–63.0 mM) in 0.1 ml spiked plasma (n = 5 devices).

4. Conclusions

A new pH sensing cotton-based electrode concept was developed from a PEDOT/MWCNT dispersion coated with pH sensitive Pani. These Pani-coated PEDOT-MWCNT-cotton fiber electrodes were used as pH indicator electrodes together with a Ag/AgCl quasi-reference electrode in an analogous configuration to smart dressings. This sensor achieved a rapid, selective, and Nernstian response (−61 ± 2 mV pH^{-1}) over a wide pH range (2.0–12.0). A proof-of-concept study for non-invasive therapeutic Li^+ monitoring highlights the promise of a miniaturized, flexible fiber-based potentiometric Li^+ sensor device. The potentiometric devices were able to determine Li^+ concentration in plasma as a complex biological fluid. Further work is underway to optimize these fiber-based chemical sensors.

Acknowledgments: The authors thank the University of Surrey and the Newton-Mosharafa PhD programme for providing funding for this work.

Conflicts of Interest: The authors declare no conflicts of interest and the funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the decision to publish the results.

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