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Textile sensor for chloride monitoring in sweat

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Summary. — Smart textile represents a novel and extremely fast-growing area in the well-established wearable sensors field. The possibility to integrate sensing and monitoring features to standard garments as shirts or bands using exclusively textile substrate is capturing a lot of attention. This article presents a good example of a compact, cost-effective, and comfortable textile thread sensor that can monitor the chloride concentration in human sweat for healthcare and sports applications. The single-thread sensor is based on conductive polymers poly(3,4-ethylene dioxythiophene):poly(styrene-sulfonate) (PEDOT:PSS) and nano-composite material (silver-silver chloride nanoparticles) deposited on a common cotton thread, and easily scalable for large-scale production. The sensitivity, selectivity, electrolyte volume independent performances, and reliability are evaluated in artificial human sweat showing the chance to achieve a point-of-care sweat analysis for a large textile multi-sensing platform.

1. – Introduction

In recent years, textile sensors are acquiring a lot of attention as a novel concept of non-invasive, real-time, and point-of-care biometric information monitoring. The textile substrates are flexible, stretchable, compatible with human skin, and industrially scalable. Among textiles, cotton is the most popular raw material since it is a natural fiber with outstanding properties such as high water absorptivity, breathability, and comfortability. Several examples of fully textile chemical sensors have been reported to monitor physiological parameters, biochemical markers as dopamine [1], glucose [2] or lactate [3], and electrolytes like chloride [4], sodium [5], potassium [6], and pH [7]. In addition, in 2018 Kim *et al.* [8] presented a two-terminal PEDOT:PSS thread able to sense the total cations concentration in artificial and human sweat while Xu *et al.* [9] in 2019 reported an electrochemically wearable Cl sensors able to detect in parallel also Ca^{2+} anion concentration in biofluids. Here, we present an example of a selective point-of-care device able to detect chloride levels in human sweat exploiting the electrochemistry transduction of a functionalized single-cotton thread with only two terminals. In this respect, the textile thread sensors are realized with a conductive polymer layer, and Ag/AgCl nanoparticles are electrochemically deposited. The sensors can be potentially applied to access the hydration status, fatigue [10], or cystic fibrosis pre-screening [11]. The high selectivity and sensitivity, combined with easy-integration features, allow to consider this non-invasive

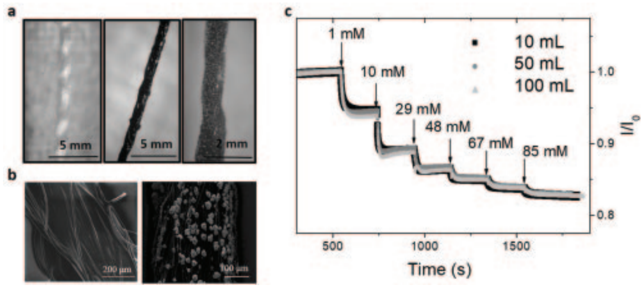

Fig. 1. – (a) Optical images of the cotton thread during the fabrication procedures; (b) SEM images of cotton thread coated with PEDOT:PSS polymers (left) and with Ag/AgCl nanoparticles; (c) sensor current response to Cl concentration in different solution volume of 0.1 M KNO3, adapted from [4].

sensor as a valid building block to achieve a textile multi-thread sensing platform for a complete bio-monitoring.

2. – Materials and methods

2˙1. *Chemicals*. – All chemicals were of reagent grade and used as received. CLEVIOS PH 1000 suspension (PEDOT:PSS) was purchased by Haraeus while (3-glycidyloxypropyl) trimethoxysilane (GOPS), ethylene glycol, silver nitrate, potassium chloride, potassium nitrate, L- histidine, sodium dihydrogen phosphate, sodium chloride by Sigma-Aldrich. The artificial sweat formulation (ISO pH 5.5) is prepared with 0.22%w/v NaH2PO4, 0.05% w/v L-histidine, and 0.5% w/v NaCl in DI water.

2˙2. *Characterization*. – All the measurements were carried out at room temperature and in air. Scanning electron microscope images have been obtained with the SEM, Cambridge Stereoscan 360; the electrochemical deposition has been performed using the Metrohm Autolab potentiostat in a three-electrodes cell (Pt wire, aqueous saturated calomel electrode (SCE) and PEDOT:PSS-coated threads as counter, reference, and working electrodes, respectively), and the sensor performance was evaluated with the Keysight B2912A to apply the required potentials, and measure the current response.

2˙3. *Fabrication procedure*. – A conductive solution was prepared as reported in our previous work [12]. After a washing cycle in acetone and distilled water, the cotton thread was covered for 2 cm with the conductive solution. The samples were dried at 70 °C in an oven achieving a conductive textile cotton thread. The surface functionalization procedure with Ag/AgCl nanoparticles consists of two consecutive electrochemical deposition steps using a three-electrodes cell: application of i) -0.2 V for 60 s in a 0.1 M AgNO3 solution, and ii) $+0.6$ V for 60 s in 1 M KCl solution. This procedure leads to the homogeneous formation of nanoparticles with a core of silver and an external shell of silver chloride.

3. – Results

Figure 1(a) shows three different fabrication steps of the textile thread sensor starting from bare cotton yarn, coated with the conductive polymer solution, and functionalized with the two-steps electrochemical deposition of Ag/AgCl nanoparticles to endow the thread with chloride sensing feature. The average electrical resistance of the conductive thread is $(56 \pm 9)\,\Omega$/cm. The SEM images reported in fig. 1(b) show the cotton thread before (left) and after (right) the nanoparticles deposition. This highlights their

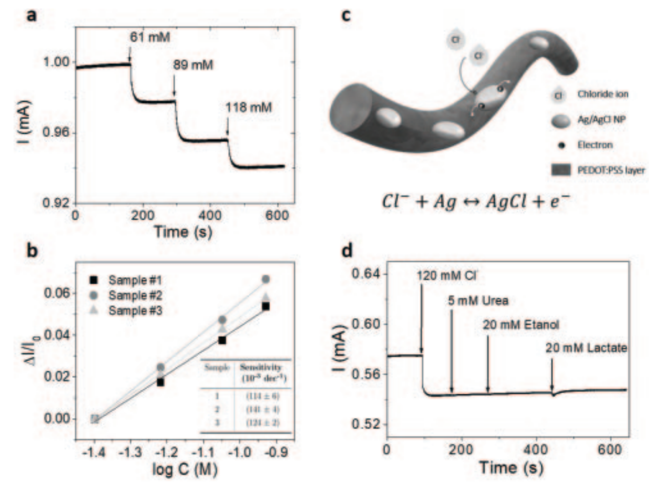

Fig. 2. – (a) Cotton thread sensor response varying the Cl concentration in 10 ml of artificial sweat; (b) calibration curve of three different sensors showing the high reproducibility; (c) schematic representation of electrons exchange between nanoparticles and PEDOT:PSS interface; (d) selectivity test in artificial sweat to investigate the possible interference of different compounds, adapted from [4].

homogeneous presence and their tight bond on the fiber surfaces. In every sensors characterization, the Cl concentration range has been varied from 0.1 to 120 mM to simulate the Cl content in human perspiration, which is between 10 and 120 mM [13]. To prove their stability and repeatability during the operation in different volumes, a thread sensor was tested successively in 10 ml, 50 ml, and 100 ml of 0.1 M KNO_3, changing the chloride anions concentration via the addition of suitable volumes of 2 M KCl. Three additions were performed in a baker under a soft stirring. From fig. 1(c) it is possible to assert the independence of the normalized current response (I/I_0) from the volume of the tested solution. The presented single-thread sensor's reliability and reproducibility were assessed characterizing three different devices in 10 ml of artificial sweat, which well reproduces the real sweat composition (ISO pH 5.5). Figure 2(a) reports the typical current response of the potentiometric-like devices with an externally applied potential of +0.1 V. After a 2 M of KCl addition, the average response time is (19 ± 6) s([1]). The current acquired at 40 mM Cl is used as I_0 to normalize the extracted values since it represents the lowest Cl concentration in human sweat. As reported in fig. 2(b), the normalized current variation ($\Delta I/I_0$) and the logarithm of chloride concentration are linearly dependent, and the similar sensitivity values (average (128 ± 6) 10^{-3} dec^{-1}) extracted from the calibration curve for different samples allow us to assert the samples reproducibility.

4. – Discussion and conclusion

The here reported textile single-thread sensor represents a good example of a stable and reproducible two-terminal device working in an aqueous solution. The absence of a gate or reference electrodes simplifies the device configuration concerning standard potentiometric or transistor structure. The Ag/AgCl nanoparticles attached on the PE-

([1]) Calculated as the time required to reach 90% of the total signal.

DOT:PSS surface of the cotton thread have a well-defined electrochemical potential described by the Nernst equation ($E = E_0 - (RT/nF)\ln[\mathrm{Cl}^-]$(2)) which can be varied by a reversible and spontaneous electrochemical reaction. The presence of Cl ions surrounding the NPs modifies their electrochemical potential that is responsible for the charge exchange and induces a current variation proportional to $\Delta I \propto kT/e \cdot \ln([\mathrm{Cl}^-]_2/[\mathrm{Cl}^-]_1)$, as reported in [12]. Figure 2(c) reports a schematic representation of the electrons exchanged between the nanoparticles and the conductive polymer layer that change the oxidation state of PEDOT:PSS leading to a conductance modulation responsible for the current variation. This current flows until the same potential is reached between the two materials.

Noteworthy, the high selectivity to chloride ions is demonstrated by the absence of interference after the addition of other compounds typically present in human sweat as urea, ethanol, and lactate (see fig. 2(d)).

By exploiting a new concept of electrochemical transduction, we have shown an example of a fully textile sensor for the continuous detection of chloride in human perspiration and, thanks to the easily scalable fabrication method, the possibility to integrate it in a multi-biosensing wearable platform incorporating other types of sensors for pH, glucose, lactate or ascorbic acid. This can pave the way for a wearable and textile device that can continuosly and remotely monitor the wearer's physiological parameters in a non-invasive manner.

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(2) Here E_0, R, T, n, F, $[\mathrm{Cl}^-]$ are the standard potential of the redox couple, the gas constant, the temperature, the number of exchanged electrons, the Faraday constant, and the chloride concentration, respectively.