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Highlights

Conductive fabrics electrodeposited with Iridium Oxide films can measure pH change.

A fully stretched Stainless steel mesh shows the best overall response to pH change.

A sweat pH measurement in human skin shows a relative error of 4% when compared with a standard method

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Potentiometric textile-based pH sensor

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Abstract

Determining the pH of sweat provides valuable information for athletes and patient monitoring. This work presents a textile-based, highly sensitive pH sensor for pH determination. Three conductive fabrics (Argenmesh, Ristop silver and Stainless steel mesh (SSM)) were modified with a pH sensitive electrodeposited Iridium Oxide Film (EIROF). The three electrodeposited fabrics were characterized by impedance measurements. The Stainless Steel Mesh showed the best sensitivity to pH changes and therefore was selected for further experiments. Two configurations of this fabric were evaluated, looking for improvement in pH sensitivity and temperature dependence. The best result was obtained with the configuration that maximizes the contact surface between the stainless steel fibers, showing an error of 0.15% in the pH measurement of a buffer solution. This configuration was also used to perform in vivo measurements, obtaining an error of 4% when compared to the measurements performed with a commercial pH test

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strip. The implementation of sensor into textiles brings some advantages such as comfort, biocompatibility and washability, among others; making the future incorporation of a sensor into a garment very possible.

Keywords: pH sensor, EIROF, Nanostructured electrode, Wearable, Athletes monitoring.

1. Introduction

Nowadays, the continuous monitoring of health status and, more specifically, physiological parameters is in growing demand among high performance athletes and the medical community. High performance athletes need an exhaustive control of their physiological variables in order to reach optimal performance, while patient monitoring would be very useful for early detection of pathologies and emergencies.

Sweat is a good option to monitor valuable information about the physiological status of the subjects [1]; being perspiration pH one important parameter to be evaluated. The information provided allows athletes to know when it is necessary to rehydrate themselves [2] [3] ; or it could be used to monitor chronic wounds, because pH provides wound condition information and can aid in determining wound response to a specific treatment [4]. In addition, changes in pH of the skin take part in the development of skin disorders such as dermatitis, ichthyosis and fungal infections [5].

In recent years, wearable technology has been the subject of much study due to the possibility of remotely and continuously monitoring a subject, allowing a rapid response to any change in physiological parameters. Wearable technology always includes one or several sensors incorporated into garments. Sweat-based

20 wearable sensors have emerged in the last few years for metabolites [6] [7], elec-
trolytes [8] [9] and pH measurements. Regarding pH measurements, Nakata et al.
[10] designed a flexible sweat chemical pH sensor sheet based on an ion-sensitive
field effect transistor. Although being a good option for low-cost, disposable and
wearable applications, this sensor requires sophisticated fabrication equipment
25 and temperature compensation. In the same year, Salvo et al. [11] presented an-
other pH sensor that used graphene oxide (GO) to detect the parameter changes;
the GO is coated over the working electrode of a commercially available screen
printed-board (C220BT, 33 x 10 x 0.5 mm, Dropsens). Nyein et al. [12] developed
a fully integrated wearable platform that includes measurement of pH in body flu-
30 ids using an ion-selective electrode (ISE) patterned on flexible PET substrate, that
detects H^+ by deprotonation of polyaniline. Bandonkar et al. [13] also designed
an ISE for pH detection based on polyaniline, but in this case the substrate was a
disposable tattoo. Another pH sensor was developed by Caldara et al. (Caldara et
al. 2012 [14] and 2016 [15]); they functionalized a cotton fabric with a colorimetric
35 and atoxic pH indicator and designed the electronics capable of monitoring the
fabric color. Other authors used flexible and adhesive microfluidic devices able
to harvest skin sweat to develop wearable pH sensors. Curto et al. [3] imple-
mented a colorimetric and disposable chemical barcode device that incorporates
ionic liquid hydrogels as sensitive element, while, the approach of Koh et al. [7]
40 consists of a paper-based colorimetric sensor. Although several approaches for
wearable pH sensors have been proposed, the state of the art of textile-based ones
is still poor, particularly if the desired features include low cost, simple hardware
requirements and reusability.

It has been demonstrated that Iridium Oxide is sensitive to pH [16]. In addi-
45 tion, electrodes modified with IrO_2 have been used in electrostimulation experi-

ments, which proves its biocompatibility. A recent work by Chen et al [17] presented iridium oxide coatings for neural interface applications. In this work, the authors obtained a cell viability close to 100%, which is higher than the viability obtained with indium tin oxide coated glass, also a biocompatible material. Furthermore, Göbbels et al showed the biocompatibility of iridium oxide by growing neuronal cells over coated electrodes [18].

The work presented here describes the design, development and evaluation of potentiometric textile-based pH (PTBpH) sensors that consist of a conductive textile material with an Electrodeposited Iridium Oxide Film (EIROF). The electrodeposition was achieved following a previously reported protocol [16]. Different conductive textile materials with EIROF (*Argenmesh*, *Ristop Silver* and *Stainless steel mesh*, LessEMF, Latham NY, USA) were analyzed in order to determine which one presents greater sensitivity to pH variations and how temperature affects them. Among the evaluated materials, Stainless steel mesh textile showed the best performance for in-vivo measurements, with a 4% relative error when compared with a standard method. The designed sensors are useful to carry out perspiration pH measurements and could be easily incorporated into wearables.

2. Materials and methods

2.1. Conductive textile material

Three different conductive textiles were used in this work: *Argenmesh*, *Ristop silver* and *Stainless steel mesh (SSM)*, all described by Goy et al. [19]. Briefly, *Argenmesh* fabric is composed of Nylon (Ny) threads where 55% of them are coated with Silver (Ag); *Ripstop* fabric is also made of Ny threads, but in this case, all of them are coated with Ag; and *Stainless steel mesh* fabric, which is composed

70 of 100% surgical stainless steel threads. It is remarkable that the wearability and comfort of conductive fabrics is very similar to traditional ones, which suggests that the sensors fabricated with these materials could be easily incorporated into garment without generating any disturb to the user.

Taking into consideration that SSM presents a low density of threads [19], this
75 textile was folded in order to form a double layer and present a higher density.

2.2. Electrodeposition

The electrodeposition was performed in a tripolar electrochemical cell, consisting of a hemispherical stainless steel counter electrode, an Ag/AgCl reference electrode and the conductive fabric as working electrode. These textiles were cut
80 into strips of approximately 10 cm long by 3 cm wide. They were adjusted on an acrylic cylinder by seals and an insulating material to delimit a circular area of approximately 1.5 cm² (See Figure 1). The acrylic cylinder is necessary in order to provide a mechanical support for the fabrics. This support allows immersing the fabrics into a solution, or placing them over the skin.

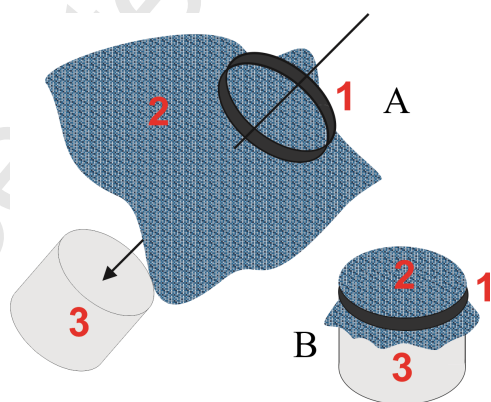


Figure 1: Configuration of the conductive fabrics (2) for electrodeposition and evaluation, where 1 is the non-conductive seal and 3 is the acrylic cylinder.

85 The whole procedure was performed using a potentiostat (Solartron®12508W,

Bognor Regis, UK), which consists of a Frequency Response Analyzer (Solartron®1250) and an electrochemical interface (Solartron ®SI1287).

The electrodeposition solution was prepared following the Yamanaka procedure [20] by dissolving 4 mM IrCl₄ in 40 mM oxalic acid, followed by a slow
90 addition of K₂CO₃ up to reaching a final pH of 10.3. The solution was then stirred until there was a complete dissolution of all materials. After this, the solution was kept in the dark for 8 days, until a blue color appeared. From this moment the solution was ready to be stored in the dark at 4 °C for two or three weeks prior to use.

95 Electrodeposition was made following a known potentiodynamic technique [21], which was slightly modified by Mayorga et. al. [16]. The modified technique consisted of a combination of a cyclic potential composed by a triangular wave (50 cycles between 0.0 and 0.55 V vs. Ag/AgCl reference electrode at a speed of 50 mV/s). This was applied to the fabric immersed in the previously described
100 solution, followed immediately by a rectangular potential pulsing (same potential limits for up to 3000 pulses of 0.5 s each). The initial triangular waveform is necessary to obtain adherent films. However, this initial potential cycling results in the deposition of less than 5 mC/cm² of EIROF [21]. The subsequent rectangular pulsing is necessary to obtain films with higher charge storage capacity (CSC).
105 The number of pulses will determine the CSC of the EIROF.

Electrodeposition was carried out in a water bath at 30°C. After the procedure was completed, the conductive textile was kept submerged for 45 minutes in the electrodeposition solution, and finally it was stored at room temperature in a dark place.

110 2.3. *Scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDS)*

The SEM and EDS studies were performed using a Zeiss Supra 55 VP scanning electron microscope gently provided by the Centro Integral de Microscopía Electrónica (CIME Universidad Nacional de Tucumán-CONICET).

2.4. *Impedance and pH measurements*

115 Impedance was measured before and after electrodeposition in the previously described tripolar cell by applying 10 mV AC (RMS), 0 V DC with a frequency sweep between 1 and 65 KHz. These measurements were performed using a Solartron®1250 Frequency Response Analyzer.

The pH calibration measurements were conducted using standard solutions of
120 pH 4, 5, 6, 7 and 8 (Cicarelli ®). These measurements were performed using an experimental set that consists of a XR38 multimeter to measure the open-circuit voltage variation of the working electrode vs. the Ag/AgCl reference electrode due to the pH changes. All the experiments were performed at 35°C, unless otherwise noted. The temperature was controlled using an LM35 temperature sensor
125 attached to the conductive textile and a water bath with controlled temperature. The impedance measurements were performed using the potentiostat previously described.

The sensor that presents the best overall response was selected by evaluating the calibration curves. Using this sensor, pH measurements were carried out in:
130 1) a saline solution of pH 7 with similar salt concentration of human sweat (Na 0.9 g/L, K 0.2 g/L, Ca 0.015 g/L and Mg 0.0013 g/L)[22] using the above described experimental set. 2) The lower back sweat of a 25-years-old male who rode a bicycle for 30 minutes. In this case, three bipolar measurements were performed using the PTBpH electrode as working electrode placed on a 5 cm thick acrylic

135 as a support, a commercial Ag/AgCl 3M electrode as reference, and the XR38
Multimeter to measure the open-circuit voltage (Figure 2). Commercial pH test
strips Macherey-Nagel (Düren, Germany) -pH range between 5.4 to 7 with 9 pH
steps- were used as reference method. The body temperature at the moment was
36.5 °C.

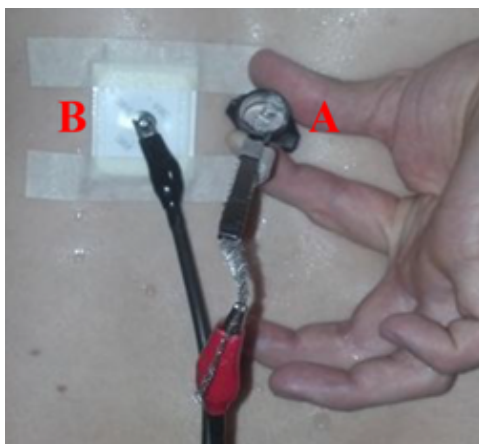


Figure 2: A) EIROF conductive fabric with the best overall response, B) Ag/AgCl 3M electrode used as reference.

140 3. Results and Discussion

3.1. SEM and EDS

In order to confirm the electrodeposition of iridium oxide over the fabrics, SEM and EDS studies were performed. Figure 3, 4 and 5 show Argenmesh, Ripstop and SSM fabrics before and after deposition of EIROF:

145 All these figures show a major change in the morphology of the fabric as a consequence of the IrO₂ electrodeposition. The presence of EIROF is confirmed with EDS, showing the Ir peaks in the modified fabrics (white arrows indicate the presence of these peaks).

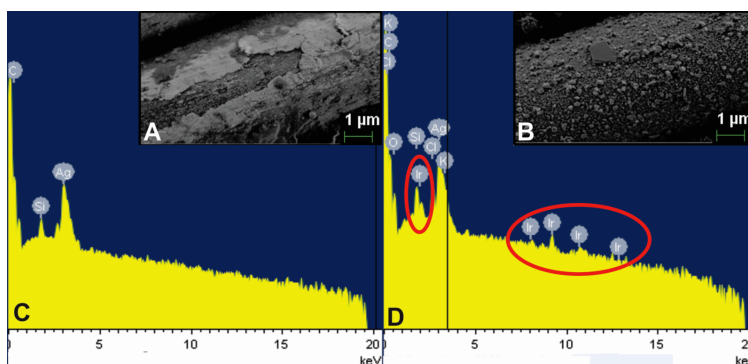


Figure 3: SEM and EDS for Argenmesh before electrodeposition (A and C) and after electrodeposition (B and D).

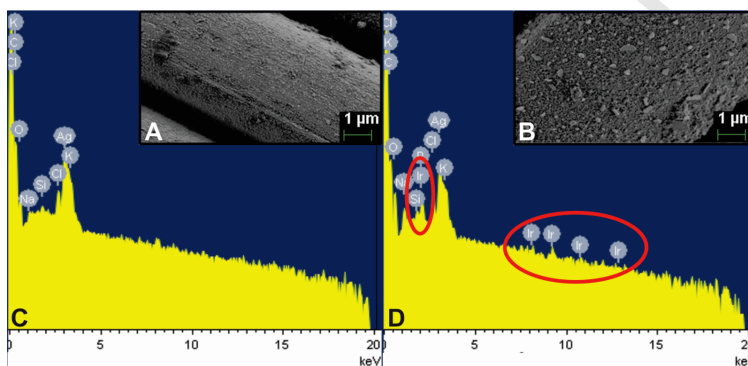


Figure 4: SEM and EDS for Ripstop before electrodeposition (A and C) and after electrodeposition (B and D).

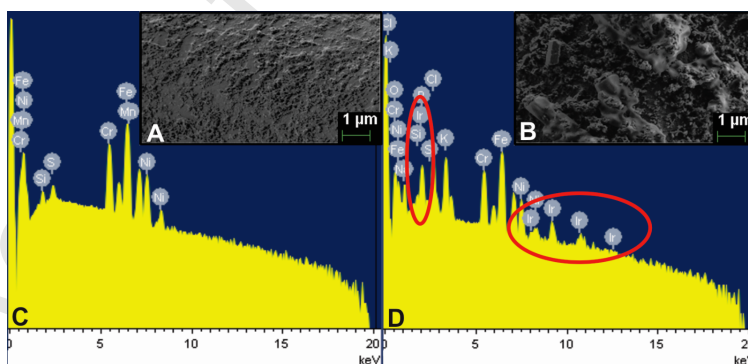


Figure 5: SEM and EDS for Ripstop before electrodeposition (A and C) and after electrodeposition (B and D).

Table I shows the differences in weight% of Ag and Ir of the fabrics before and
 150 after electrodeposition.

Fabric	Element	Weight% before deposition	Weight% after deposition
Argenmesh	Ag	36.37	30.34
	Ir	0	2.19
Ripstop	Ag	33.51	19.75
	Ir	0	0.01
SSM1	Ir	0	6.03

Table 1: Difference of the Weight% of Ag and Ir as a consequence of the electrodeposition conductive fabrics.

The analysis of SEM images and EDS results of Argenmesh and Ripstop fabrics (Figure 4B) suggest that the change in the surface morphology of these fabrics is more a consequence of the loss of silver than of the deposition of iridium oxide. Regarding Ripstop Silver, the great decrease of silver in EDS results reinforces this
 155 hypothesis (Table I).

3.2. Electrodeposition

This section presents the results of impedance measurements. Figure 6 shows the impedance for each textile before and after electrodeposition.

Figure 6A and 6B show an increase in the impedance magnitude after the electrodeposition, but for SSM the impedance decreases (figure 6C).
 160

The interpretation of impedance variation of the fabrics after IrO₂ electrodeposition is challenging since all fabrics does not have the same behavior. First, it must be noted that Argenmesh and Ripstop Silver are made of nonconductive threads with a silver coating, while Stainless Steel fabric is made of stainless steel
 165 threads without coating. According to Table 1, the amount of silver after electrodeposition is reduced from 36.37 to 30.4 weight% in Argenmesh while, in the case of Ripstop Silver, the Ag is reduced from 33.51 to 19.75 weight%. Therefore,

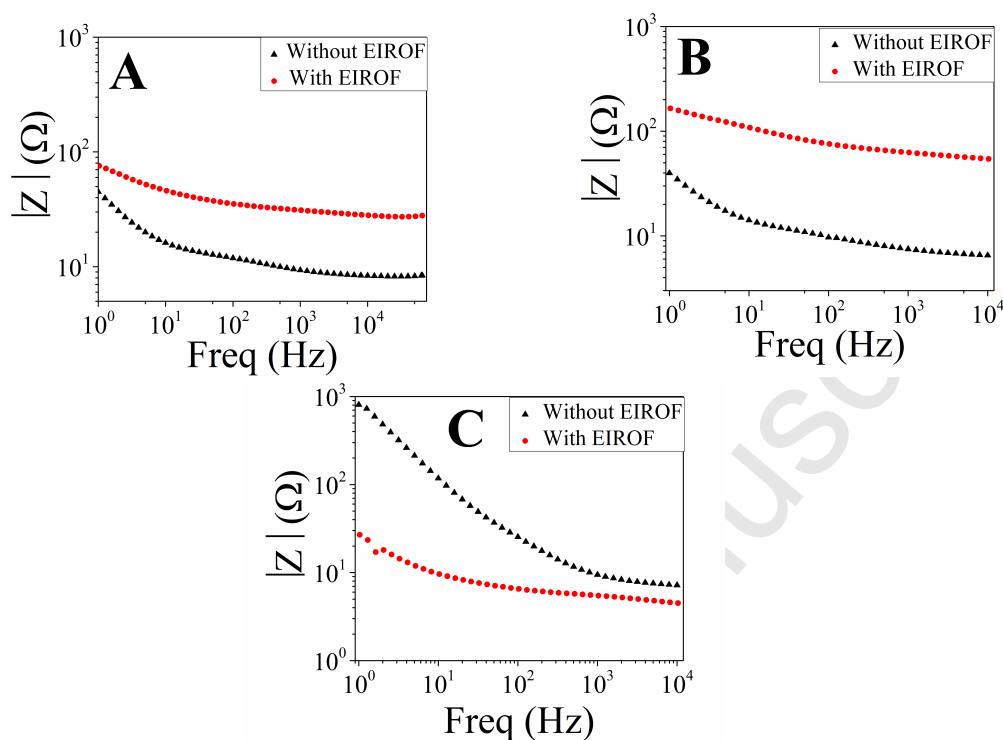


Figure 6: Variation of the impedance magnitude for A) Argenmesh, B) Ripstop Silver and C) SSM before and after electrodeposition.

some nonconductive threads could have been exposed after electrodeposition, which would lead to a reduction of the conductive surface of the fabrics. On the other hand, stainless steel threads were not modified, leading to a more effective electrodeposition (more IrO_2 was electrodeposited, Table 1), with the consequent impedance reduction (figure 6C).

Based on these observations and the results from EDS, it is hypothesized that:

- For Argenmesh and Ripstop Silver, the lower quantity of electrodeposited IrO_2 and the loss of Ag, lead to an impedance increase after electrodeposition; and
- For Stainless steel, the higher quantity of electrodeposited IrO_2 plus no surface modification produce a reduction of impedance. This last behaviour is expected,

as was previously reported [16] and [21].

It is remarkable that –to the best of our knowledge– there are as yet no reports
 180 of IrO₂ electrodeposition on Ag. Therefore, the deep and detailed study of this
 subject would be very interesting for future investigations.

3.3. Calibration

After electrodeposition, the textiles were calibrated to determine pH. Figure 7
 shows the obtained calibration plots.

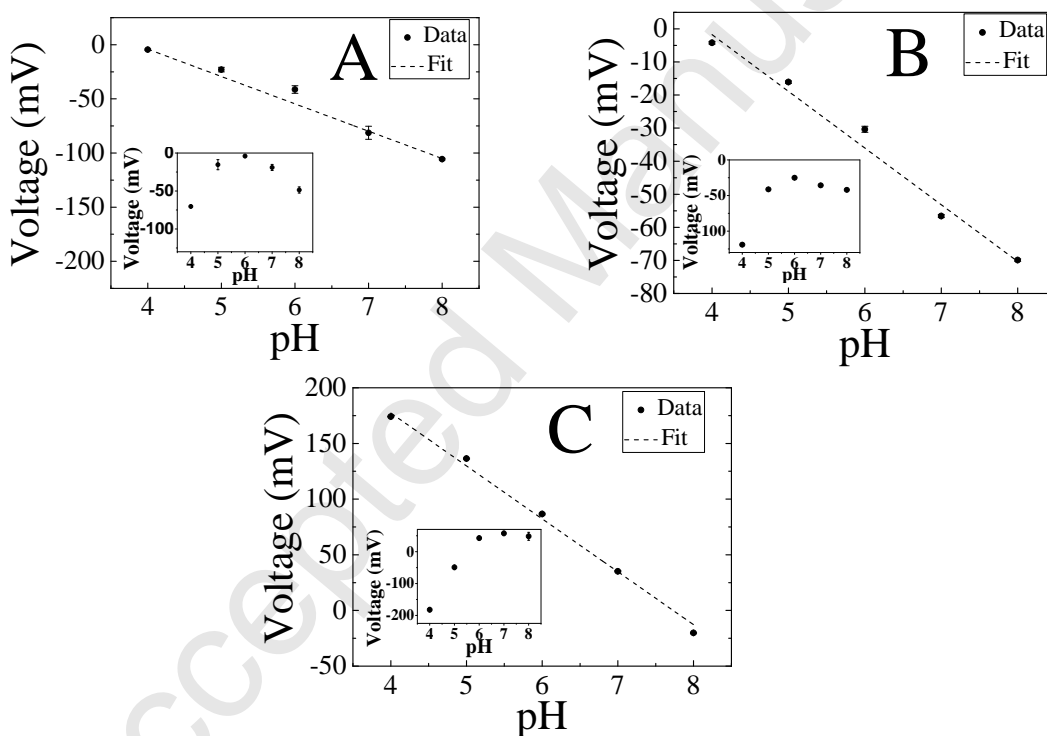


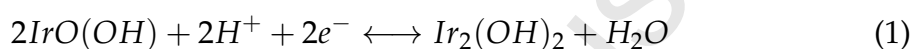
Figure 7: calibration plots for the three textiles immersed in buffer solutions with pH 4, 5, 6, 7 and 8. A) Argenmesh, B) Ripstop Silver, C) SSM. Insets show the response of the pure non-modified electrodes with pH.

185 SSM (Figure 7C) presents the highest sensitivity (-47.54 mV/pH) and also a
 very good correlation coefficient ($r^2 = 0,993$) (Table 2).

Fabric	Sensitivity (mV/pH)	r ²
Argenmesh	-25.25	0.997
Ripstop	-17.15	0.98
SSM1	-47.54	0.993

Table 2: Sensitivity and linear correlation factor

The reaction occurring at the interface of the electrodeposited electrode is the following (Mayorga Martinez et al., 2009) [23]:



The Nernst equation, which relates the involved species in the redox process, can be reduced to the following expression [23] :

$$E = E^\circ - 0.059pH \quad (2)$$

A slope of -0.059 V/pH implies a Nernstian behaviour. This sensor presents a sub-Nernstian response because the slope calculated from the calibration curve is -0.047 V.pH⁻¹ (Figure 7C).

The differences in sensitivity between the three fabrics can be explained considering the amount of electrodeposited IrO₂ showed in Table I. Table II shows that Ripstop Silver presents the lower sensitivity and, also is the one with the lower quantity of electrodeposited IrO₂. Surprisingly, a quantity as low as 0.01 Weight% of electrodeposited IrO₂ is enough to improve Ripstop pH sensitivity after deposition (Figure 7B). In the case of Stainless Steel fabric the highest quantity of electrodeposited IrO₂ leads to the highest pH sensitivity of all fabrics.

Since SSM presents the best overall response, a different configuration of this fabric was also tested. This configuration consists in fully stretch the conduc-

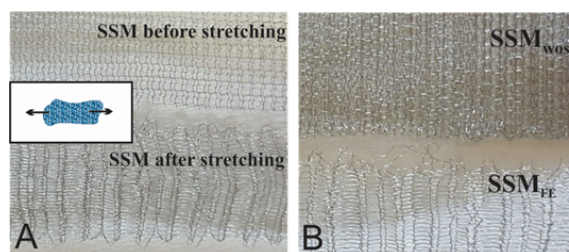


Figure 8: A) SSM before and after stretching. The arrows in the inset indicate the stretching direction. B) SSM_{WOS} and SSM_{FE} are presented for comparison.

tive textile in order to get a very good contact surface between the stainless steel threads (Figure 8). At this point, great care must be taken to not exert too much force that can distort the fabric. From now the SSM configuration without stretching will be named SSM_{WOS} in order to be compared with the fully stretched version (SSM_{FE}).

Figure 9 shows the calibration plot for the fully stretched SSM (SSM_{FE}) electrode in 5 different pH solutions.

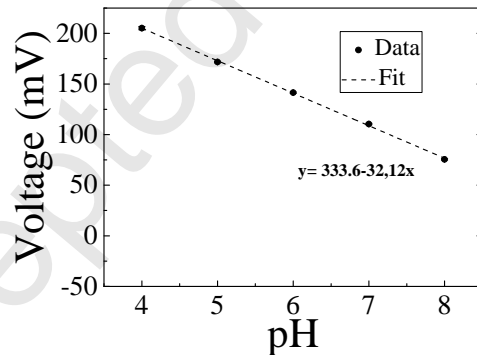


Figure 9: Calibration plot for the SSM_{FE} electrode.

Table 3 shows that SSM_{WOS} presents a higher sensitivity when compared with SSM_{FE} (-31,69 and -21,41 mV/pH respectively). One possible explanation of this behavior is that, since SSM_{WOS} is folded forming a double layer, it has more available surface for IrO₂ deposition than in the case of SSM_{FE}, which is expected tak-

ing into account the considerations made in Section 3.2. The highest sensitivity
 215 to pH occurs for the electrodes with the highest amount of electrodeposited IrO_2 .
 The r^2 of the two configurations are quite similar presenting only a small differ-
 ence.

Fabric	Sensitivity (mV/pH)	r^2
SSM_{WOS}	-47.53	0,993
SSM_{FE}	-32.11	0,998

Table 3: Sensitivity and linear correlation factor for the SSM_{WOS} and SSM_{FE} fabrics.

3.4. Influence of temperature over pH measurements

The core temperature of the body remains in a range from 35 to 40°C, and most
 220 physiological and pathological variations of body temperature are in this range
 [24]. Given that the temperature has an influence over the pH measurements,
 the same measurements performed with SSM_{WOS} and SSM_{FE} at 35°C, were also
 carried out at 40°C. The results are presented in Figure 10.

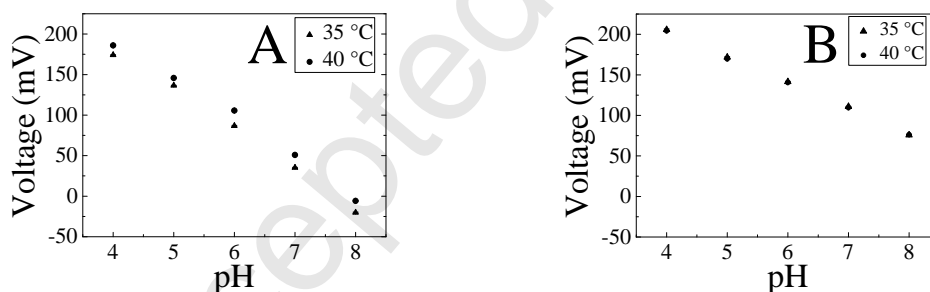


Figure 10: Response of the two SSM configurations at 35 and 40°C A) SSM_{WOS} , B) SSM_{FE}

This figure shows that the SSM_{WOS} configuration has a greater variation with
 225 temperature than the SSM_{FE} . Because of this, despite the fact that SSM_{WOS} has
 a higher sensitivity, SSM_{FE} was selected to perform the following pH measure-
 ment. This decision was taken in order to avoid temperature compensation in pH
 measurements.

3.5. pH measurements

230 Considering that the typical pH of a human sweat during exercise covers a range from 5 to 7 [3], the pH of a saline solution with a similar salt concentration of human sweat [22] (pH=7) was measured using the SSM_{FE} configuration. The sensor gave a response of 108.35 mV when submerged in the solution. The pH was calculated by using equation from Figure 9, obtaining a value of 7.011. The
 235 error in the measurement was calculated as:

$$Error : \frac{pH(sample) - pH(electrode)}{pH(sample)} \times 100 \quad (3)$$

An error of 0.15% was obtained, demonstrating the good response of the sensor.

Then, three pH measurements in real skin were performed using the SSM_{FE} electrode. The pH recording was carried out as previously described (section 2.4).
 240 An average voltage of 120.2 mV was obtained with a standard deviation of 1.32 mV. This voltage corresponds to a pH of 6.2, which was calculated by using the equation showed in Figure 9. In order to compare these results with a standard technique, the pH of sweat was measured with a commercial pH test strip. The pH measurement with this reference method, gave a pH value of 6.5, which implies
 245 a relative error (RE) of 4%. The pH readout obtained with the PTBpH sensor was achieved in a few seconds. The same RE was obtained by Curto et al. [3], but after a measurement time of 30 minutes. This fact is considered a very good advantage of the PTBpH sensors presented here.

It is important to remark that pH measurements are usually affected by ionic
 250 strength. It is well known that most pH test systems are designed for lab use where solutions are highly buffered. However, low ionic strength solutions are

poor conductors, and pH measurements could be inaccurate and noisy. In the present case the sensor was calibrated in a buffer solution. The human sweat has similar salt concentration to the buffer, making the ionic strength not an issue for sweat pH measurement in the present case.

As was mentioned, it is remarkable that the wearability and comfort of conductive fabrics is very similar to traditional ones, which suggests that they could be easily incorporated into garment. A possible configuration could be to incorporate the PTBpH sensor into a girdle, which gives the necessary mechanical support being comfortable and wearable. Figure 11 shows a prototype, which includes the PTBpH sensor, the reference electrode and the girdle. The Multimeter is only used for evaluation purpose, but the final design would include a small measurement interface and a wireless communication module, which is simple to implement.

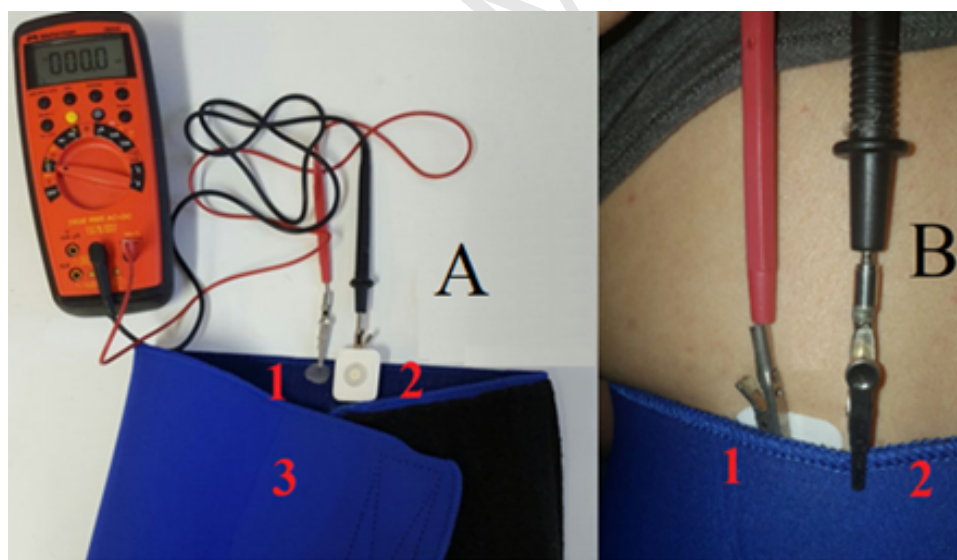


Figure 11: embodiment of the PTBpH electrode into a garment where A (left) shows the possible integration of the sensor into a garment: 1) PTBpH sensor, 2) commercial Ag/AgCl 3M electrode, and 3) girdle. B) Arrangement of the measurement set over the human skin, where 1) is the commercial Ag/AgCl 3M electrode and 2) is the PTBpH sensor.

It is noteworthy that, besides the sensor designed by Caldara et al. [14] [15],
265 there has not been reported in the bibliography another textile-based pH sensor.
An advantage of the PTBpH sensors here presented is that they are based on open
circuit voltage measurements, which could give a direct pH measurement, dif-
ferent from the colorimetric method needed by the Caldara sensor. Besides, us-
ing these sensors, the problem of sweat harvesting is solved without the need of
270 pumps or sophisticated system designs, since they work in direct contact with the
skin.

4. Conclusion

A pH sweat sensor was presented, which showed a good sensitivity and cor-
relation in pH measurements. Between the three IrO₂ modified fabrics, the SSM
275 presents the best response. This fabric was used in two different configurations,
SSM_{WOS} and SSM_{FE}, showing differences in sensitivity and temperature depen-
dence for pH response. The best result was obtained with the configuration that
maximizes the contact surface between the stainless steel fibers (SSM_{FE}), which
can measure sweat phantoms of different pH with an error of 0.15%. This config-
280 uration was also less affected by temperature. Measurements of the pH of sweat in
real skin exhibited good response, with an error of 4% compared with a reference
measurement made with a commercial pH test strip.

As was mentioned in the introduction of the manuscript, several approaches
for wearable pH sensors have been proposed. Nevertheless, the state of the art
285 of textile-based ones is still poor, moreover, if low cost, simple hardware require-
ments and reusability are desired features for them. The PTBpH sensor proposed
here presents some advantages over the sensors of the previous mentioned lit-
erature. The major ones are its low cost, simple hardware requirements and the

possibility to find a great number of SSM fabrics with different threads size in the
290 market. In addition, the biocompatibility characteristics of IrO₂ coatings allow
the PTBpH sensor to be used without major risks. Another great advantage when
compared against the other available wearable pH sensor is washability. Since
IrO₂ coating is firmly attached to the SSM fabric, it can be easily washed with DI
water.

295 Because of these features, the PTBpH is highly reusable and wearable, as was
previously showed with the sensor integrated in a sport belt. Finally, another
important fact to remark is the absence of potentiometric textile based sensors in
the bibliography, which increases the novelty and originality of this work.

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