



# Development of a wearable electrochemical sensor for voltammetric determination of chloride ions



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## ABSTRACT

This work describes the development of a disposable and wearable screen-printed electrochemical sensor for the determination of chloride ions. The sensor includes three screen-printed electrodes: a working, an auxiliary (both carbon paste electrodes), and an Ag/AgCl pseudo-reference electrode. The sensor works by measuring the Nernstian shift of the voltammetric peak potential of ferrocenemethanol in the presence of chloride ions, due to the use of a pseudo-reference electrode in the electrodic system. The measurements are easily taken by dropping the sample onto the electrodic surface.

Different flexible materials, including textiles, were studied as substrates of the electrodic system. A study of ink adherence and conductivity in these materials was carried out. The use of Gore-Tex® displayed good ink adherence, acceptable conductivity and waterproof properties. These features make it an excellent support for wearable sensors.

The reproducibility and repeatability, in terms of relative standard deviation values of the developed Gore-Tex sensor, were below 3% ( $n = 5$ ) and the detection limit was 0.2 mM ( $\alpha = \beta = 0.05$ ).

The sensor was successfully applied to determine the chloride content in sea water.

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## 1. Introduction

Since the mid-1980s, the screen printing technology has offered mass production of highly reproducible yet inexpensive electrode systems. The screen printing process involves the patterned deposition of conducting and insulating inks onto planar substrates by pressing the ink through a stencil or screen mask [1,2]. The basic composition for these inks includes a conductive material (i.e., graphite, gold, silver, etc.), a polymer or resin or epoxy, a binding agent and a solvent. Post-printing treatment varies by the formulation, but typically these thick-films are cured at high temperatures or dried at room temperature for a period of time. The electrodes can be easily modified, through the addition of specific functional materials to the ink formulation or in connection to different surface coatings.

Another variable in these thick-film electrodes, besides the material being printed, is the substrate itself. The adaptation of the screen-printing process for the preparation of wearable textile-based electrochemical sensors required a detailed understanding of the influence of manufacturing conditions and substrate properties

on the functionality of the resulting devices. The textile substrate itself must be compatible with the printing process and with the specific operational environment. Rigid solid supports (e.g., alumina, ceramic), which were used initially, are not suitable for use as wearable on-body sensors and are not compatible with current flexible-electronics and display systems. Polymeric substrates, such as flexible polyimides, or plastic PVC, have thus been introduced to meet the growing biomedical and industrial demands for more flexible and less rigid electrodes. These initial studies using polymeric substrates have spawned the recent development of flexible solar cells [3], implantable Kapton-based biomedical sensing devices [4], chemical sensors on flexible polyester films [5], or pressure sensors on flexible polyethylene naphthalate (PEN) [6]. Indeed, flexible devices are now widely sought in connection to flexible-electronics [7], organic field effect transistors [8], optical organic light emitting diodes [9], or flexible displays [10]. The major challenge to this surge is not only their manufacture, but in the stability of these devices in terms of mechanical, electrical, or electrochemical properties [11].

Fabrics represent an excellent class of substrates for developing wearable sensors because they can be in constant contact with the skin. Furthermore, the large surface area of textiles provides ample space for integrating the accompanying electronics. Various fabrics such as wool, cotton, nylon and polyester offer a rich

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variety of physical and chemical properties that can be utilized for incorporating chemical sensors within the fabric [12,13].

An optimal textile must possess inert properties, should not affect the electrochemical behavior of the analyte, and should be a suitable platform for integrating multiple sensors. The sensors should also adhere well to the textile and operate desirably under normal and heavy wear [14]. Additionally, liquid phase measurements require the utilization of water-proof fabrics, which would serve as excellent platforms for facilitating chemical reactions *in vitro* [12].

Electrochemical sensors are promising as wearable chemical sensors which are suitable for diverse applications because of their high performance, inherent miniaturization, and low cost. A wide range of wearable electrochemical sensors and biosensors have been developed for real-time non-invasive monitoring of electrolytes and metabolites in sweat [15–23], tears [24–31], or saliva [32–35] as indicators of a wearer's health status. Wearable electrochemical sensors, including amperometric and potentiometric sensors have already been described in literature concerning the determination of chloride ions [36–39].

With continued innovation and attention to key challenges, such non-invasive electrochemical sensors and biosensors are expected to open up new, exciting avenues in the field of wearable wireless sensing devices and body-sensor networks, and thus find considerable use in a wide range of personal health-care monitoring applications, as well as in sport, environmental and military applications [13].

This article examines the fabrication of wearable electrochemical sensors directly onto clothing structures or flexible substrates. In the following sections, we will describe their preparation and characterization taking into account some requirements that these supports have to fulfil to act as substrates in this kind of sensor.

Finally, we will propose a low-cost, disposable, highly-simple, wearable and voltammetric Gore-Tex® screen-printed sensor for the determination of chloride ions based on the shift suffered by the voltammetric peak potential of a control species (FeMeOH), when this ion is present in the solution.

## 2. Experimental

### 2.1. Reagents and solutions

All the reagents used were of analytical grade and Milli Q water (Millipore, Bedford, USA) was employed to prepare all solutions.

K<sub>2</sub>SO<sub>4</sub> and KCl were provided by Merck (Darmstadt, Germany). FeMeOH was obtained by Sigma-Aldrich, (Steinheim, Germany).

Sea water was collected from the Cantabrian Sea, Spain.

C10903P14 (carbon ink) and D2071120D1 (dielectric ink) were purchased from Gwent Electronic Materials (Torfaen, U.K). Electrodag 6037 SS (Ag/AgCl ink) and Electrodag 418 (Ag ink) were supplied by Acheson Colloiden (Scheemda, The Netherlands).

PET of 18 μm and paper were purchased from Hifi Industrial Films (France), greaseproof paper was obtained from Bosque Verde (Holland), adhesive label and cellulose acetate were provided by Apli Paper S.A. (Barcelona). Commercial polyester and nylon fabrics were supplied by a local shop, and 3-Layer Gore-Tex® laminate Waterproof Breathable Ripstop Nylon Fabric was supplied by Rockwoods (Loveland, USA). These flexible materials and fabrics were used as printing substrates.

### 2.2. Apparatus

Voltammetric measurements were performed with a μStat 200 bipotentiostat from Dropsens (Oviedo, Spain), using the DropView

**Table 1**

Resistance of the produced electrodes and precision values of manufactured sensors in different substrates. Precision calculated in terms of relative standard deviation (RSD) of cyclic voltammetric oxidation (**Pox**) and reduction (**Pred**) peaks of a 5 mM FeMeOH solution.

| Substrates        | Resistance (Ω) | RSD (n = 5)   |      |                 |       |
|-------------------|----------------|---------------|------|-----------------|-------|
|                   |                | Repeatability |      | Reproducibility |       |
|                   |                | Pox           | Pred | Pox             | Pred  |
| Cellulose acetate | 6.32           | 2.64          | 3.31 | 5.32            | 1.51  |
| PET of 18 μm      | –              | –             | –    | –               | –     |
| Paper             | 2.45           | 4.13          | 1.76 | 2.17            | 3.00  |
| Greaseproof paper | –              | –             | –    | –               | –     |
| Adhesive Label    | –              | –             | –    | –               | –     |
| Polyester fabric  | 0.22           | –             | –    | –               | –     |
| Nylon fabric      | 0.14           | 3.30          | 8.64 | 13.53           | 25.36 |
| Gore-Tex® fabric  | 0.01           | 2.63          | 2.85 | 3.21            | 3.42  |

software package to control the instrument register and perform the analysis of results.

Potentiometric measurements were made using chloride-selective electrode pH & ION-Meter GLP 22 + Crison (Crison Instruments, Barcelona).

### 2.3. Sensor manufacturing

Home-made SPEs, used in this work, consist of a carbon working electrode (area, 12.56 mm<sup>2</sup>), a carbon counter electrode and a silver/silver chloride as a pseudo-reference electrode (PRE). Carbon ink was used in conductive paths of SPEs. These electrodes were produced on a DEK 248 printing machine (DEK, Weymouth, UK) using different supports according to the procedure described elsewhere [1,40]. The fabrics were pre-heated to 120 °C for 1 h before the printing process.

### 2.4. Electrochemical measurements

Cyclic voltammetry (CV) experiments were performed between –0.4 V to 0.8 V vs. Ag/AgCl PRE, in a drop deposited onto the surface of an electrodic system, which contains FeMeOH 5 mM in KCl 0.1 M at a scan rate of 50 mV s<sup>–1</sup>.

Differential pulse voltammograms (DPV) were recorded from –0.4 V to 0.8 V vs. Ag/AgCl PRE, in a drop deposited onto the surface of an electrodic system. The sample droplet contains chloride ions, FeMeOH 5 × 10<sup>–5</sup> M and K<sub>2</sub>SO<sub>4</sub> 5 × 10<sup>–4</sup> M as supporting electrolyte. The scan rate was 20 mV s<sup>–1</sup> and the step potential was 5 mV.

## 3. Results and discussion

### 3.1. Study of manufactured flexible and wearable sensors

Firstly, a qualitative test of the ink adherences in the different substrates was carried out. This test consists of an adhesive tape which is habitually used to determine if the inks adhered properly to the substrates. When using PET of 18 μm, greaseproof papers or adhesive labels as a substrate, the resulting electrodes do not offer good adhesion to the support.

Afterwards, electric resistance of different inks printed in the rest of supports was studied by using a digital multimeter, and the values obtained are shown in Table 1. As the electrical conductivity is reciprocal of electric resistivity, and the resistance is proportional to resistivity, low resistance values indicate that a material readily allows the flow of electric current.

The tested materials which exhibit a good ink adhesion and possess suitable conductivity, could be used as electrochemical transducers.

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