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Simple modifications on Sonogel-Carbon electrodes to obtain new pH and T sensors. Target: reducing costs, not value.†

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Abstract: In this work two new different sensors are developed: a pH sensor and a temperature probe. The former is based on a polyaniline (PANI) layer electrodeposited employing sinusoidal voltages and optimizing the deposition time (10-20 min). On the other hand, the temperature probe was designed taking advantage of the carbon nanotubes temperature properties. Both sensors were built on Sonogel-Carbon electrodes seeking cost effective devices. In both scenarios, results were satisfactory, the repeatability and reproducibility with values below 5%. Additionally, an excellent selectivity of the pH sensor was evaluated with the challenging interstitial matrix, prospecting an adequate future employment in real clinical samples.

Keywords: Sonogel-Carbon electrodes; pH; temperature; polyaniline; sinusoidal voltages; multi-walled carbon nanotubes; cost effective sensor

1. Introduction

Great advances in modern medicine have been achieved thanks to the employment of powerful tools such as biostatistics and bioinformatics. In this sense, the assessment of trends in huge package of information is critical for early diagnosis and prevention. In order to improve and keep going forward, the deep-down study of biomarkers in healthy and ill people during long periods of time can be considered of paramount importance. In this regard, the promotion of e-Health philosophy carried out for international organisms has been an important spearhead(1). This approach aims for the almost passive monitoring of people via nontraditional medical inspections (e.g.: Point of care), avoiding unnecessary tests and reducing costs. Furthermore, the data can be collected and stored online to be able to consult it anytime and anywhere by doctors. In addition, the expert clinicians are not extra loaded with routinary assays, being possible to devote their efforts to the most important scenarios. For this reason, the scientific community has been exploring new possibilities to develop efficient alternatives for new point of care (POC) or sensors that allow a useful control of biomarkers(2). Moreover, other features such as portable, cost effective, user friendly, etc. are also pursued. In this sense, one of the most promising tools to develop are electrochemical sensors. Besides the abovementioned characteristics, electrochemical sensors also possess high sensitivity, quick response, and in situ and online measurement possibility, among others. Lastly, the selectivity in these sensors is usually provided by the employment of specific materials such as biological agents (e.g.: enzyme, antibodies) or artificial materials (ionophores, conducting polymers, etc.). Interestingly, wearable glucose sensors are based on electrochemical reactions and are commercial and very popular nowadays. However, the monitoring of other parameters, even the simplest ones has not been equally successfully accomplished. Among the simplest and most useful parameters to monitor, pH and temperature outstand.

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Assessment of pH has been demonstrated to be useful in several health scenarios. Some experts relate pH changes with early stages of sickness such as Alzheimer or cancer where a low pH is a strong symptom of the latter. Besides, blood pH is observed in intensive care unit (ICU) patients to control possible sepsis situations (1,2). On the other hand, temperature has an interesting relevance also in medicine, not only by itself but also in simultaneous determination of several biomarkers. In other words, only temperature is usually assessed to detect fevers or similar process which usually are related to infection processes (e.g.: COVID 19) but this parameter possesses also influence in the measurement of others. This can be easily observed in the Nernst equation where the temperature has influence in the potential reached. This is why a temperature probe is commonly placed in other sensor platforms to improve the accuracy of the sensors by using a correction factor.

In this work, two different new sensors are introduced: i) pH sensor based on PANI layer and ii) temperature probe based on carbon nanotubes paste composite materials. The former possesses an extra novelty due to the electrodeposition employed to grow the conducting polymer, sinusoidal voltages. This not-so-explored technology provides extra features to the polymer layer thanks to the fast and discontinuous growth process (3,4). On the other hand, to the best of our knowledge, the temperature probe exposed here has not been stated before. Additionally, both sensors are built on Sonogel-Carbon electrode transducers aiming for cost effective final devices (i.e., less than 1 € per sensor).

2. Materials and Methods

-Reagents and materials.

All reagents employed were of analytical grade and used as received without further purification. Methyltrimethoxysilane (MTMOS), $CaCl_2$ (98%), $MgCl_2$ (99%), NaCl (99%), KCl (99.5%), D(+)-glucose anhydrous, were purchased from Merck (Darmstadt, Germany). HCl (38%), urea, L(+) ascorbic acid, multiwalled carbon nanotubes (MWCNTs) powder (>95%, 6-9 nm O.D.), bovine serum albumin (fraction IV) and mineral oil were from Sigma Aldrich (Sigma, Steinheim, Germany). Sulfuric acid (95-98%), phosphoric acid (85%), boric acid (99%), glacial acetic acid, sodium hydroxide, $NaHCO_3$, NaH_2PO_4, Na_2HPO_4, were acquired from Panreac (Barcelona, Spain). Aniline was from Honeywell (Charlotte, NC, USA). Graphite powder (99.9999%) was from Alfa Aesar (Johnson Matthey GmbH, Germany). Black silicone was acquired from Visbella (Zhejiang, China). All solutions were prepared with nanopure water with a Wasser lab Ultramatic Plus (type I) system (Navarra, Spain) and used in all experiments (18 MΩ cm). Glass capillary tubes, i.d. 1.15 ± 0.05 mm, were used as the bodies of the electrodes.

-Instrumentation and electrochemical setup.

Sonogel-Carbon electrode material was fabricated by using a high-energy ultrasound generator, Sonicator 4000 MISONIX (MISONIX, Inc. Farmingdale, NY, USA) equipped with a 13-mm-diameter titanium tip, which provides 600 W, as maximum output power. The procedure was published in previous work (5). Electrochemical studies were made using an Autolab PGSTAT 20 potentiostat/galvanostat (Ecochemie, Utrecht, the Netherlands) connected with a personal computer and a 663 Metrohm VA Stand module and a FRA2 module. Processing data was made using GPES (General Purpose Electrochemical System) software and FRA (frequency response analyzer). The measurements concerning for conditioning, characterization and electrodeposition were carried out in a three-electrode electrochemical cell at room temperature, with the following composition: Ag/AgCl/KCl 3 M as reference electrode, platinum wire as counter electrode, and the Sonogel-Carbon-electrodes (geometric area: 1.04×10^{-2} cm^2) as the working electrode. Concerning the calibration curve of pH, potentiometry was employed as follows: two-electrode electrochemical cell at room temperature stablishing the Sonogel-Carbon-Polyaniline (SNGC-PANI) electrode as working electrode and a double junction Ag/AgCl electrode as reference electrode. Regarding the temperature calibration, a digital multimeter, model TRMS T28B/T28C, from Lomvum (Hangzhou, China) was employed to record the resistivity resulting in the MWCNTs composite material placed onto two different SNGC

electrodes bodies-joined by using black silicone. An optical microscope from Ninyoon (Cork, Ireland) was employed to explore the surface of the temperature sensor fabricated.

-Preparation of SNGC-PANI pH sensor.

Firstly, a polarization step was driven in the SNGC electrodes by using cyclic voltammetry: 10 scans, 50 mv/s in HCl 0.5 M. Afterwards, the PANI electrodeposition is performed as follows: a SNGC electrode is immersed in a solution of aniline 0.1 M in 1 M HCl, a fixed potential of 0.45 V with an amplitude of 0.35 V and a frequency of 25 mHz for 10 min is applied by using the FRA manual control (Figure 1a).

-Preparation of SNGC-MWCNTs temperature probe.

In first place, the MWCNTs paste is performed using a similar procedure that can be found in literature (6). Briefly, 12 mg of MWCNTs and 300 mg of mineral oil are mixed in a vortex for 1 min. Once the solution is homogeneous, 0.8 µL are drop-casted onto the surface of two SNGC electrodes joined by pasting their bodies. The solution is dried at room temperature for 1 min. This drop-casting procedure is performed twice. Finally, the electrodes are dried at 4°C for 24 h (Figure 1b).

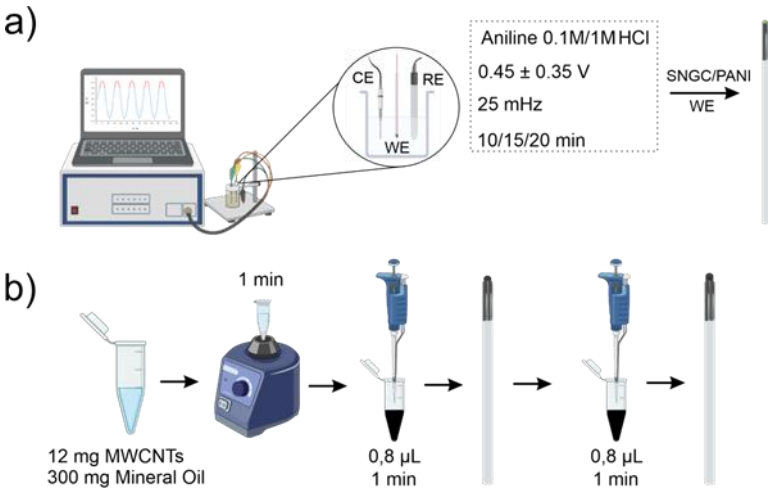

Figure 1. Fabrication procedure scheme of: a) SNGC-PANI pH sensor and b) SNGC-MWCNTs temperature sensor.

3. Results and Discussion

3.1. SNGC-PANI pH sensor characterization and analytical performance.

Firstly, a characterization of the PANI deposited onto the SNGC has been carried out by means of cyclic voltammetry for each deposition time. The results of these studies can be observed in Figure 2a. Two different anodic and cathodic peaks are located around 0.2/0.8V and 0.1/0.6V, respectively. These peaks can be attributed to the redox processes of this conducting polymer. Particularly, according to literature, conversion between leucoemeraldine into emeraldine is ascribed to the first oxidation peak (-0.2/0.6V). Alternatively, transformation between emeraldine and pernigraniline is observed through the peak in the interval 0.6/0.8V (7). Therefore, the presence of polyaniline is confirmed by the results obtained. Even though, the intensity of the peaks is higher with higher deposition time and consequently the polymer growth is major, as expected, the final deposition time was evaluated after assessing the analytical performance of the sensors. Concerning the analytical performance of the proposed pH sensor, simple calibration curve was performed by using Britton-Robinson universal buffer adjusted, by using NaOH, in a pH range from 3 to 8. Potentiometry at zero current was employed as the electroanalytical technique. The changes in the potential due to the conversion of PANI phases can be related with the native pH. Ideally, the slope of the curve of this calibration curve matches with the 59 mV/pH value according to the Nernst equation. However, the slope of the curve found (Figure 2b) was around 66 mV/pH. Other authors have stated previously the higher value of PANI-based sensors ascribing these values to the known super Nernstian behaviour (8). Thus, the presence of PANI is corroborated by super Nernstian behaviour

and the high linearity (R^2>0.999) of the obtained calibration curve. A statistical test was performed to determine if the sensitivity of the sensors was affected by the electrodeposition time. The results (data not shown) demonstrated that the time does not influence the final sensitivity. Thus, for efficiency reasons, 10 min was selected as optimal deposition time. On the other hand, repeatability and reproducibility assays were performed by using a sensor three times in a row and three different sensors once, respectively. The relative standard deviation estimated, taking the slope as studied factor, were 1.1 % and 2.1%, respectively. These values indicate the suitable manufacturing process as well as the robustness of the modified electrodes. The selectivity of the sensor was evaluated by comparison between a calibration curve in buffer media and a matrix of artificial interstitial fluid (see Figure 2c). The later was prepared by using a previously published procedure (9). As it is possible to observe, the curves obtained are almost identical, remarking the excellent selectivity of the sensor in a physiological artificial media, suggesting and acceptable future application in real biomedical samples. Finally, in order to evaluate the possible application of the sensor proposed in continuous monitoring, a reversibility assay was carried out by measuring the potential in 5 different cycles of ascending-descending pH ranges (Figure 2d). The potential recorded during these cycles is almost identical in each cycle proving the adequate application of the sensor in long periods as well as in reversing conditions.

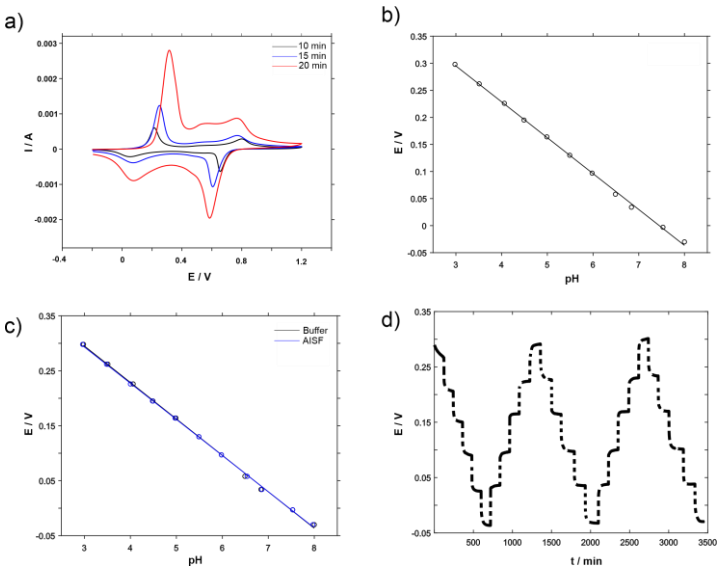

Figure 2. Electrochemical characterization and analytical performance of the SNGC-PANI sensor: a) resulting cyclic voltammetry obtained with different electrodeposition times, ranging from 10 to 20 min, b) calibration curve of the pH sensor SNGC-PANI obtained ranging pH from 3-8, c) performance comparison between buffer and artificial interstitial fluid (AISF) media, d) potentiometry obtained for the reversibility assays ranging pH from 3 to 8.

3.2. SNGC-MWCNTs temperature sensor characterization and analytical performance.

In first place, an optimization study of the volume used to perform the drop-casting procedure was carried out (data not shown). For this purpose, optical microscopy was employed to assess the SNGC-modified surface after each deposition. The selected volume was 0.8 μL, drop-casted twice. This decision follows the reasoning line of maximizing the coverage and also keeping the layer homogenous. An inspection of the resulting surface can be performed observing Figure 3a. In order to ensure the suitable behaviour of the sensor, the deposited layer must cover the junction space between the capillary glasses. MWCNTs paste must be in contact with both SNGC electrodes simultaneously to close the electrical circuit properly. The analytical performance of the temperature probe was assessed by recording the resistivity via a multimeter at different temperatures (10-50°C). The chosen temperature range was selected for the future application of the probe in biomedical samples. The results of the calibration curve are exposed in Figure 3b. As it

was expected, an adequate linearity (R^2>0.999) was obtained. Regarding the sensitivity of the sensor, a value of -0.002kΩ/°C was calculated. This value is similar to other similar CNTs based temperature probes found in literature (10). The negative slope indicates that the obtained sensor can be categorized into a negative temperature coefficient resistance (NTCR) device. To evaluate the repeatability and reproducibility, similar procedure as in the case of SNGC-PANI has been performed. The relative standard deviation results are 2.16% and 2.80 %, respectively, taking the slope as studied factor. Therefore, as in the previous scenario, the analytical performance of the temperature probe obtained can be considered as suitable.

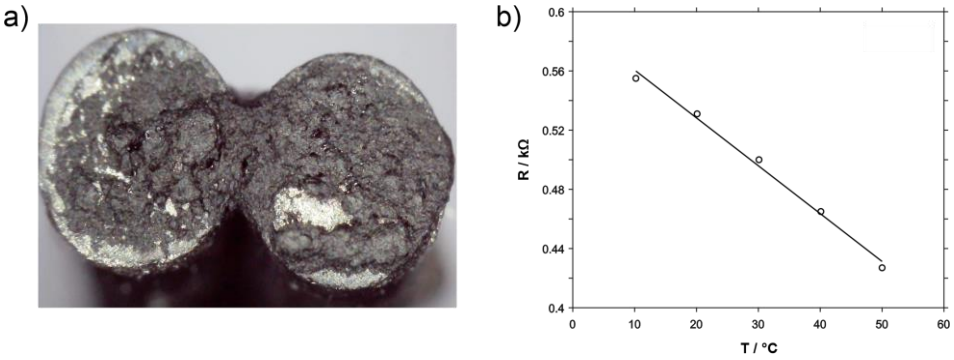

Figure 3. Optical characterization and analytical performance of the temperature based on SNGC-MWCNTs: a) optical microscopy with 1000x magnification factor, b) calibration curve of the temperature sensor SNGC-MWCNTs.

4. Conclusions

The present work proposes two easy-to-prepare and cost-effective pH and temperature sensors. On the one hand, sensors developed are very cost effective. On the other hand, interesting features such as repeatability, reproducibility and selectivity are rather good. Future studies will include the assessment of pH and temperature in real biomedical samples (e.g.: serum or blood). In addition, other conditions for the sinusoidal voltage procedure electrodeposition process and other carbon nanotubes based composite materials are susceptible to be investigated in order to fabricate more robust sensors.

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