




Simple Modifications of Sonogel-Carbon Electrodes to Obtain New pH and T Sensors—Target: Reducing Costs, Not Value [†]

Juan José García-Guzmán, Álvaro Jesús Sainz-Calvo, Ana Pérez-Fernández, Alfonso Sierra-Padilla , Dolores Bellido-Milla, Laura Cubillana-Aguilera *  and José María Palacios-Santander 

Institute of Research on Electron Microscopy and Materials (IMEYMAT), Department of Analytical Chemistry, Faculty of Sciences, Campus de Excelencia Internacional del Mar (CEIMAR), University of Cadiz, Campus Universitario de Puerto Real, Polígono del Río San Pedro S/N, 11510 Puerto Real, Cádiz, Spain; juanjo.garciaguzman@uca.es (J.J.G.-G.); alvarojesus.sainzcalvo@alum.uca.es (Á.J.S.-C.); ana.perezfer@alum.uca.es (A.P.-F.); alfonso.sierra@uca.es (A.S.-P.); dolores.milla@uca.es (D.B.-M.); josem.palacios@uca.es (J.M.P.-S.)

* Correspondence: laura.cubillana@uca.es

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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 an electrodeposited polyaniline (PANI) layer employing sinusoidal voltages and optimizing the deposition time (10–20 min). On the other hand, the temperature probe was designed by taking advantage of the carbon nanotubes' temperature properties. Both sensors were built on sonogel-carbon electrodes, seeking cost effective devices. In both scenarios, the results were satisfactory; the repeatability and reproducibility had values below 5%. Additionally, an excellent pH sensor selectivity 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; multiwalled carbon nanotubes; cost effective sensor



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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 packages of information is critical for early diagnosis and prevention. In order to improve and continue going forward, the deep-down study of biomarkers in healthy and ill people during long periods of time is considered to be of paramount importance. In this regard, the promotion of e-Health philosophy, carried out by international organizations, has been an important spearhead [1]. This approach aims to achieve 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 so it may be consulted at anytime and anywhere by doctors. In addition, expert clinicians are not overloaded with routine assays, making it possible for them 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) sensors that allow for a useful control of biomarkers [2]. Moreover, other features such as portability, cost effectiveness, user friendliness, etc. are also pursued. In this sense, electrochemical sensors are one of the most promising tools to develop. In addition to the abovementioned characteristics, electrochemical sensors also possess high sensitivity, quick response, and in situ and online measurement possibility, among others. Lastly, the selectivity of these sensors is usually provided by the employment

of specific materials such as biological agents (e.g., enzymes, 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 are outstanding. The 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's or cancer, where a low pH is a strong symptom of the latter. In addition, blood pH is observed in intensive care unit (ICU) patients to control possible sepsis situations [3,4]. On the other hand, temperature also has an interesting relevance in medicine, not only by itself but also in the simultaneous determination of several biomarkers. In other words, while temperature alone is usually assessed to detect fevers or similar processes which are usually related to infection processes (e.g., COVID-19), this parameter also possesses influence in the measurement of others. This can be easily observed in the Nernst equation, where the temperature has influence on 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 new different sensors are introduced: (i) a pH sensor based on PANI layer and (ii) a 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 [5,6]. On the other hand, to the best of our knowledge, the temperature probe exposed here has not been established before. Additionally, both sensors are built on sonogel-carbon electrode transducers aiming to produce cost effective final devices (i.e., less than EUR 1 per sensor).

2. Materials and Methods

2.1. Reagents and Materials

All the 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%), and 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 , and Na_2HPO_4 , were acquired from Panreac (Barcelona, Spain). Aniline was acquired from Honeywell (Charlotte, NC, USA). Graphite powder (99.9999%) was acquired from Alfa Aesar (Johnson Matthey GmbH, Germany). Black silicone was acquired from Visbella (Zhejiang, China). All the solutions were prepared with nanopure water with a Wasser lab Ultramatic Plus (type I) system (Navarra, Spain) and used in all experiments (18 M Ω cm). Glass capillary tubes, i.d. 1.15 ± 0.05 mm, were used as the bodies of the electrodes.

2.2. 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 has been published in previous work [7]. Electrochemical studies were conducted using an Autolab PGSTAT 20 potentiostat/galvanostat (Ecochemie, Utrecht, The Netherlands) connected to a personal computer, a 663 Metrohm VA Stand module, and a FRA2 module. Data processing was performed using GPES (General Purpose Electrochemical System) software (VSION 4.9, Eco Chemie B.V., Utrecht, The Netherlands) and FRA (frequency response analyzer). The measurements concerning the 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 the reference electrode, platinum wire as the counter

electrode, and the sonogel-carbon-electrode (geometric area: $1.04 \times 10^{-2} \text{ cm}^2$) as the working electrode. Potentiometry was employed as follows concerning the calibration curve of pH: two-electrode electrochemical cell at room temperature establishing the sonogel-carbon-polyaniline (SNGC-PANI) electrode as the working electrode and a double junction Ag/AgCl electrode as the reference electrode. Regarding the temperature calibration, a digital multimeter, model TRMS T28B/T28C, from Lomvum (Hangzhou, China) was employed to record the resistivity resulting from the MWCNT composite material being placed onto two different SNGC electrode bodies joined by black silicone. An optical microscope from Ninyoon (Cork, Ireland) was employed to explore the surface of the fabricated temperature sensor.

2.3. 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 was performed as follows: a SNGC electrode was immersed in a solution of aniline 0.1 M in 1 M HCl with a fixed potential of 0.45 V, an amplitude of 0.35 V, and a frequency of 25 mHz for 10 min; this was applied by using the FRA manual control (Figure 1a).

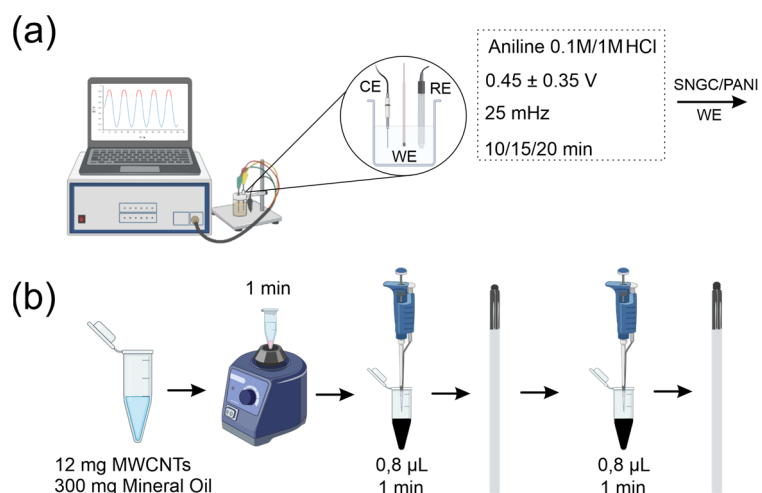


Figure 1. Fabrication procedure scheme of: (a) SNGC-PANI pH sensor and (b) SNGC-MWCNTs temperature sensor.

2.4. Preparation of SNGC-MWCNTs Temperature Probe

In the first instance, the MWCNT paste was produced using a procedure similar to that found in [8]. Briefly, 12 mg of MWCNTs and 300 mg of mineral oil were mixed in a vortex for 1 min. Once the solution was homogeneous, 0.8 µL was drop-casted onto the surface of two SNGC electrodes joined by pasting their bodies. The solution was dried at room temperature for 1 min. This drop-casting procedure was performed twice. Finally, the electrodes were dried at 4 °C for 24 h (Figure 1b).

3. Results and Discussion

3.1. SNGC-PANI pH Sensor Characterization and Analytical Performance

Firstly, a characterization of the PANI deposited onto the SNGC was 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 0.2/0.8 V and 0.1/0.6 V, respectively. These peaks can be attributed to the redox processes of this conducting polymer. In particular, according to the literature, the conversion of leucoemeraldine into emeraldine was ascribed to the first oxidation peak (−0.2/0.6 V). Alternatively, transformation between emeraldine and pernigraniline was observed through the peak in the interval 0.6/0.8 V [9]. Therefore, the presence of polyaniline was confirmed by the results obtained. Even though the intensity of the peaks was higher with higher

deposition time and the polymer growth was consequently 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, a simple calibration curve was performed by using the Britton–Robinson universal buffer adjusted by using NaOH, in a pH range from 3 to 8. The 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 to the native pH. Ideally, the slope of the curve of this calibration curve would match 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 previously stated the higher value of PANI-based sensors, ascribing these values to the known super-Nernstian behaviour [10]. Thus, the presence of PANI was 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 electrodeposition time does not influence the final sensitivity. Thus, for efficiency reasons, 10 min was selected as the 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 deviations estimated, taking the slope as the 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 latter was prepared by using a previously published procedure [11]. As can be seen, the curves obtained are almost identical, remarking the excellent selectivity of the sensor in physiological artificial media, suggesting an 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 five 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.

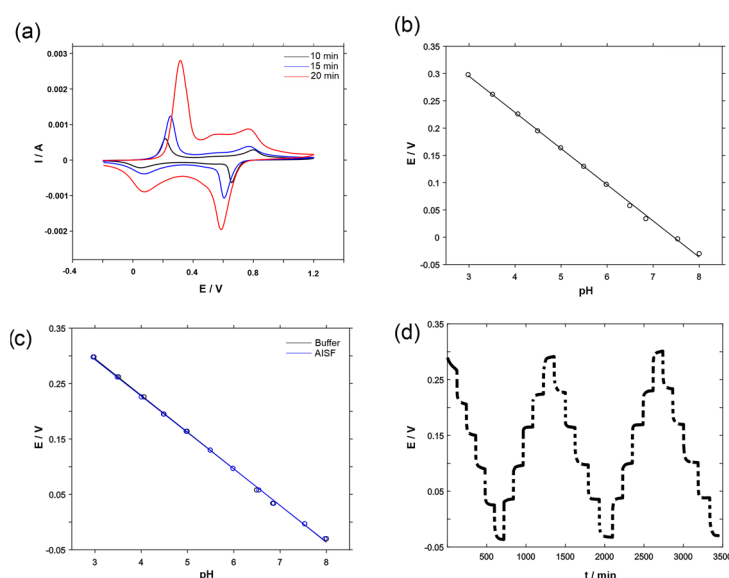


Figure 2. Electrochemical characterization and analytical performance of the SNGC-PANI sensor: (a) resulting cyclic voltammetry obtained with different electrodeposition times, ranging from 10 to 20 min, (b) calibration curve of the pH sensor SNGC-PANI obtained ranging pH from 3 to 8, (c) performance 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 the first instance, 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 seen in Figure 3a. In order to ensure the suitable behaviour of the sensor, the deposited layer must cover the junction space between the capillary glasses. The MWCNT 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 $^{\circ}\text{C}$). The chosen temperature range was selected based on the future application of the probe in biomedical samples. The results of the calibration curve are shown in Figure 3b. As expected, an adequate linearity ($R^2 > 0.999$) was obtained. Regarding the sensitivity of the sensor, a value of $-0.002 \text{ k}\Omega/^{\circ}\text{C}$ was calculated. This value is similar to that of other similar CNT-based temperature probes found in the literature [12]. The negative slope indicates that the obtained sensor can be categorized as a negative temperature coefficient resistance (NTCR) device. To evaluate the repeatability and reproducibility, a similar procedure as in the case of SNGC-PANI was performed. The relative standard deviation results are 2.16% and 2.80%, respectively, taking the slope as the studied factor. Therefore, as in the previous scenario, the obtained analytical performance of the temperature probe is considered as suitable.

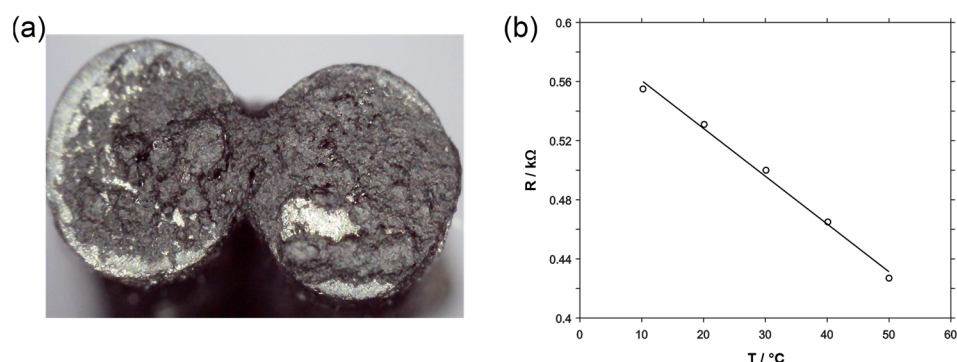


Figure 3. Optical characterization and analytical performance of the temperature based on SNGC-MWCNTs: (a) optical microscopy with 1000 \times magnification factor, (b) calibration curve of the temperature sensor SNGC-MWCNTs.

4. Conclusions

The present work proposes two easy-to-prepare and cost-effective pH and temperature sensors. On the one hand, the sensors developed are very cost effective. On the other hand, interesting features such as the repeatability, reproducibility, and selectivity are rather good. Future studies will include an 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 nanotube-based composite materials may be investigated in order to fabricate more robust sensors.

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