



# Highly activated screen-printed carbon electrodes by electrochemical treatment with hydrogen peroxide

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## ABSTRACT

An easy effective method for the activation of commercial screen-printed carbon electrodes (SPCEs) using H<sub>2</sub>O<sub>2</sub> is presented to enhance sensing performances of carbon ink. Electrochemical activation consists of 25 repetitive voltammetric cycles at 10 mV s<sup>-1</sup> using 10 mM H<sub>2</sub>O<sub>2</sub> in phosphate buffer (pH 7). This treatment allowed us to reach a sensitivity of 0.24 ± 0.01 μA μM<sup>-1</sup> cm<sup>-2</sup> for the electroanalysis of H<sub>2</sub>O<sub>2</sub>, which is 140-fold higher than that of untreated SPCEs and 6-fold more than screen-printed platinum electrodes (SPPtEs). Electrode surface properties were characterized by SEM, EIS and XPS. The results revealed atomic level changes at the electrode surface, with the introduction of new carbon-oxygen groups being responsible for improved electro-transfer properties and sensitivity. Our method was compared with other previously described ones. The methodology is promising for the activation of commercial carbon inks-based electrodes for sensor applications.

## 1. Introduction

Screen printing technology is a relatively modern technique used to produce miniaturized, sensitive portable electrochemical sensors. Given their many advantages over conventional electrodes, screen-printed electrodes (SPEs) have attracted considerable attention in practically all fields of Chemistry, such as clinical tests [1], environmental analysis [2] and food processing [3].

SPEs are composed of working electrodes made of conductive inks based on platinum, gold, silver or carbon, with the latter being the most used material because it is versatile and cheap [4]. Conductive inks from screen-printed carbon electrodes (SPCEs) contain carbon with organic solvents, binding pastes and some additives that provide functional characteristics [5]. The presence of these additional non-conductive materials can lead to sluggish kinetics for heterogeneous electrochemical reactions. To overcome this handicap, pre-treatments can run for activation purposes [6–9]. Some examples are electrochemical treatment [10], heat treatment [11], ultrasonic polishing [12], oxygen plasma treatment [13] or mechanical activation [9]. They all attempt to enhance electro-transfer properties and improve sensitivity to compounds of interest. These improvements may be due to increased hydrophilicity of the surface, an increase in carbon-oxygen functional groups on the surface, and/or removal of surface contaminants [4,14].

Electrochemical treatments allow the *in situ* easy activation of SPCEs. They typically involve holding the electrode at a constant potential for a short time [6,7,10] or potential cycling to extreme anodic potentials [8,15]. In this study, highly activated SPCEs were obtained after an electrochemical pretreatment that consisted of repetitive cyclic voltammetries in diluted H<sub>2</sub>O<sub>2</sub>. H<sub>2</sub>O<sub>2</sub> has been previously used to clean gold electrodes with excellent results [16], but, as far as we know, this is the first time it is used for the electrochemical activation of SPCEs.

## 2. Materials and methods

### 2.1. Chemicals and solutions

H<sub>2</sub>O<sub>2</sub> (35%) NaH<sub>2</sub>PO<sub>4</sub>, Na<sub>4</sub>Fe(CN)<sub>6</sub>, (NH<sub>4</sub>)<sub>2</sub>Fe(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and [Ru(NH<sub>3</sub>)<sub>6</sub>]Cl<sub>3</sub> were purchased from Sigma-Aldrich (Spain). HClO<sub>4</sub> (60%) and NaOH came from Merck. H<sub>2</sub>SO<sub>4</sub> and Na<sub>2</sub>HPO<sub>4</sub> were obtained from Panreac, and KCl from Scharlau. Solutions were freshly prepared with deionized water daily (18.2 MΩ·cm at 25 °C, Millipore, Watford, UK). 0.1 M Sodium phosphate buffer pH 7 (PB) was used as the supporting electrolyte for the electrochemical activation.

### 2.2. Electrochemical measurements

Electrochemical experiments were performed with an AUTOLAB

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PGSTAT128N potentiostat with an electrochemical impedance spectroscopy (EIS) analyzer (Eco Chemie B.V., The Netherlands).

The electroactive areas of SPEs were calculated by performing voltammetric cycles at different scan rates (from 10 to 200  $\text{mV s}^{-1}$ ) using  $\text{N}_2$ -deaerated 10 mM  $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$  in 0.1 M KCl aqueous solutions [17]. EIS was carried out at 0.22 V in 10 mM  $\text{Na}_4\text{Fe}(\text{CN})_6$  (0.1 M KCl). SPCEs were polarized for 30 s. Then sinusoidal amplitude potential perturbation (5 mV *rms*) was imposed between 65 kHz and 10 MHz, with five points per decade.

It is important to note that besides  $\text{H}_2\text{O}_2$  being the reagent used to activate the electrode surface, it was also the analyte to be quantified to check the effectiveness of the activation process. The electroanalytical experiments were performed by successive additions of micromolar amounts of  $\text{H}_2\text{O}_2$  to 10 ml of 0.1 M PB (pH 7) with stirring at 0.7 V and 25 °C. These measurements were checked to not produce any improvement in the electrochemical response of the activated electrodes. To this end, three calibration plots using the same electrode were performed (data not shown).

### 2.3. Electrochemical activation

Screen-printed carbon (DRP-150), platinum (DRP-550) and Prussian Blue/Carbon (DRP-710) electrodes were purchased from DropSens ([www.dropsens.com](http://www.dropsens.com)). Activation of SPCEs consisted of 25 repetitive cyclic voltammeteries at the 10  $\text{mV s}^{-1}$  scan rate between +1.0 and -0.7 V (vs Ag) in 10 mM  $\text{H}_2\text{O}_2$  (in 0.1 M PB, pH 7). After activation, electrodes were rinsed with deionized water and dried in air.

### 2.4. Scanning electron microscopy images (SEM)

SEM images were acquired under a Jeol 6490LV electron microscope (Jeol LTD, Akishima, Japan) equipped with detectors for secondary and backscattered electrons, and operated at an acceleration voltage of 30 kV.

### 2.5. X-ray photoelectronic spectroscopy (XPS)

The XPS experiments were recorded on a K-Alpha Thermo Scientific spectrometer using Al-K $\alpha$  (1486.6 eV) radiation, monochromatized by a twin crystal monochromator to yield a focused X-ray spot with a 400  $\mu\text{m}$  diameter. The alpha hemispherical analyzer was used as an electron energy analyzer, which operated in a fixed analyzer transmission mode, with survey scan pass energy of 200 eV and 40 eV narrow scans. Deconvolution of the XPS spectra was carried out in a Shirley background.

## 3. Results and discussion

### 3.1. Activation of electrodes

Fig. 1A shows the current evolution of a SPCE during 25 repetitive cyclic voltammograms (CV) in 0.1 M PB with 10 mM  $\text{H}_2\text{O}_2$  between +1.0 and -0.7 V at 10  $\text{mV s}^{-1}$ . The charge enclosed under the CV between 0.2 and 1 V increased as cycles progressed, until defining an oxidation peak that centered at 0.73 V in the last cycles. This fact could be related to changes on the electrode surface. Previous reports [18,19] have indicated that oxygen reactive species are able to functionalize carbonaceous surfaces during  $\text{H}_2\text{O}_2$  decomposition.

Fig. 1B shows the current responses at 0.7 V of different SPEs toward  $\text{H}_2\text{O}_2$  additions. Analytical sensitivity was enhanced from  $1.71 \pm 0.09 \times 10^{-3}$  in an untreated SPCE to  $0.24 \pm 0.01 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$  in the activated SPCE (aSPCE). This means that the aSPCE was 140-fold more sensitive than the nonactivated SPCE at this potential. The aSPCE was also compared with other widely used untreated commercial SPEs for  $\text{H}_2\text{O}_2$  detection; e.g., Pt [20,21] and Prussian Blue [22]. The sensitivity obtained for a SPPE was

$0.040 \pm 0.001 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ , which is 6-fold less sensitive than the aSPCE. For Prussian Blue, the sensitivity to the reduction of  $\text{H}_2\text{O}_2$  at -0.1 V was  $0.026 \pm 0.001 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ , which is 9-fold lower than that obtained for the aSPCE (data not shown).

The application of voltage is essential for activation since immersing the SPCE in  $\text{H}_2\text{O}_2$  at an open-circuit voltage for 2.4 h did not improve the amperometric response (data not shown). The activation treatment was effective for SPCEs, but not for SPPEs (Fig. 1B).

### 3.2. Characterization of the electrode surface

Fig. 2 shows the SEM images of a SPCE (A) and an aSPCE (B). Micropores were observed after the electrochemical treatment, which would agree with degradation of graphene by  $\text{H}_2\text{O}_2$  [23]. The electroactive areas calculated from the Randles-Sevcik equation slightly increased from 5.77  $\text{mm}^2$  (SPCE) to 5.95  $\text{mm}^2$  (aSPCE), probably due to the removal of organic binders [24].

Fig. 2C shows the Nyquist plots for a SPCE and an aSPCE. The charge transfer resistance ( $R_{ct}$ ) at the electrode|solution interface was calculated from the width of semicircles. The  $\text{H}_2\text{O}_2$ -mediated activation of SPCEs significantly reduced the charge transfer resistance ( $R_{ct}$ ) values to 11.1  $\Omega \text{cm}^2$  for the aSPCE compared to SPCE (249.0  $\Omega \text{cm}^2$ ), and similarly to the activation of SPPEs by polishing [25]. Therefore, the electrical conductivity of electrodes significantly improved.

CVs of  $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2$  were performed to ascertain possible chemical changes in the activated carbon ink (Fig. 2D). This compound is a redox probe that is very sensitive to some oxygenated groups, particularly carbonyls [9,26]. The electrochemical treatment with  $\text{H}_2\text{O}_2$  completely changed the CV pattern. The aSPCE showed narrower peak-to-peak separation and an increment in the maximum peak current of the Fe(III)/Fe(II) redox process, probably due to the introduction of carbon-oxygen groups on the working electrode, as checked by the XPS analysis.

The XPS analysis showed major changes in the carbon conductive ink (Fig. 3). The high resolution for the analysis of the C 1s and O 1s spectra lowered the surface concentration (at.%) of carbon (obtained from Fig. 3A) from 94.35 to 93.68 and increased oxygen from 5.51 to 14.80 at.% (obtained from Fig. 3B) after the activation process. Moreover, XPS deconvolution of the C 1s spectra demonstrated the presence of energy peaks at 284.6, 285.6, and 286.4 for both SPCE and aSPCE, and an extra peak at 288.7 eV for the aSPCE, which were assigned to graphitic C-C, aliphatic C-C and/or C-H and/or C-N, C-O, and C=O in the carboxyl groups, respectively [27]. The bar chart (Fig. 3C) shows the normalized at.% for SPCE and aSPCE. It was found that the at.% of the C-C graphitic, C-C and/or C-H and/or C-N groups lowered, whereas the at.% of the C-O and C=O groups increased in the aSPCE. The XPS deconvolution of O 1s showed energy peaks at 532.4 and 533.6 eV, assigned to the C-O and C=O groups, respectively. In this case, the C-O to C=O normalized at.% ratio was slightly higher for the aSPCE, which once again demonstrates the existence of C-O linkages in the aSPCE (Fig. 3D). These changes on carbon ink surface promote the diffusion-controlled process of  $\text{H}_2\text{O}_2$  oxidation from ~1.2 V in SPCEs to ~0.7 V in aSPCEs, which was checked by linear voltammetry at different scan rates (data not shown).

### 3.3. Sensor performance

The performance of aSPCEs was compared with that of the SPCEs activated by other methods found in the bibliography [6–8]. Fig. 4 shows the calibration plots of these electrodes toward successive additions of  $\text{H}_2\text{O}_2$ . Maximum sensitivity was obtained with the  $\text{H}_2\text{O}_2$ -activated SPCEs proposed herein ( $0.24 \pm 0.01 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ ). This sensitivity even outdid that of the electrodes activated using a diluted solution of  $\text{H}_2\text{SO}_4$  ( $0.09 \pm 0.01 \mu\text{A} \mu\text{M}^{-1} \text{cm}^{-2}$ ), which is a widely used reagent for this purpose [8]. Although the activation time of this last procedure is still advantageous, the application of too extreme

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