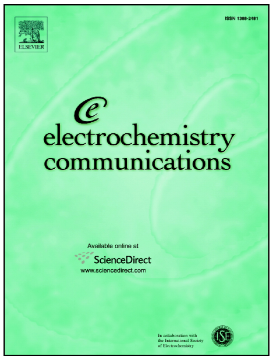

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Highly activated screen-printed carbon electrodes by electrochemical treatment with hydrogen peroxide

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Abstract

An easy effective method for the activation of commercial screen-printed carbon electrodes (SPCEs) using H_2O_2 is presented to enhance sensing performances of carbon ink. Electrochemical activation consists of 25 repetitive voltammetric cycles at 10 mVs^{-1} using 10 mM H_2O_2 in phosphate buffer (pH 7). This treatment allowed us to reach a sensitivity of 0.24±0.01 $\mu A\ \mu M^{-1}cm^{-2}$ for the electroanalysis of H_2O_2, 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.

KEYWORDS: Screen-printed carbon electrodes, hydrogen peroxide, electrochemical activation, sensors.

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_2O_2. H_2O_2 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. Material and Methods

2.1. Chemicals and solutions

H_2O_2 (35%) NaH_2PO_4, $Na_4Fe(CN)_6$, $(NH_4)_2Fe(SO_4)_2\cdot 6H_2O$ and $[Ru(NH_3)_6]Cl_3$ were purchased from Sigma-Aldrich (Spain). $HClO_4$ (60%) and NaOH came from Merck. H_2SO_4 and Na_2HPO_4 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 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 mVs^{-1}) using N_2-deaerated 10 mM $[Ru(NH_3)_6]Cl_3$ in 0.1 M KCl aqueous solutions [17]. EIS was carried out at 0.22 V in 10 mM $Na_4Fe(CN)_6$ (0.1 M KCl). SPCEs were polarized for 30s. 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 H_2O_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 H_2O_2 to 10 ml of 0.1 M PB (pH 7) with stirring at 0.7 V and 25ºC. 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). Activation of SPCEs consisted of 25 repetitive cyclic voltammetries at the 10 mV s^{-1} scan rate between +1.0 and −0.7 V (*vs.* Ag) in 10 mM H_2O_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-Kα (1486.6 eV) radiation, monochromatized by a twin crystal monochromator to yield a focused X-ray spot with a 400 μm 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

Figure 1A shows the current evolution of a SPCE during 25 repetitive cyclic voltammograms (CV) in 0.1 M PB with 10 mM H_2O_2 between +1.0 and −0.7 V at 10 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 H_2O_2 decomposition.

Figure 1B shows the current responses at 0.7 V of different SPEs toward H_2O_2 additions. Analytical sensitivity was enhanced from $1.71\pm0.09 \times 10^{-3}$ in an untreated SPCE to 0.24 ± 0.01 $\mu A \mu M^{-1} cm^{-2}$ 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 H_2O_2 detection; e.g., Pt [20, 21] and Prussian Blue [22]. The sensitivity obtained for a SPPtE was 0.04 ± 0.01 $\mu A \mu M^{-1} cm^{-2}$, which is 6-fold less sensitive than the aSPCE. For Prussian Blue, the sensitivity to the reduction of H_2O_2 at -0.1V was 0.026 ± 0.01 $\mu A \mu M^{-1} cm^{-2}$, 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 H_2O_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 SPPtEs (Figure 1B).

3.2 Characterization of the electrode surface

Figure 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 H_2O_2 [23]. The electroactive areas calculated from the Randles–Sevcik equation slightly increased from 5.77 mm^2 (SPCE) to 5.95 mm^2 (aSPCE), probably due to the removal of organic binders [24].

Figure 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 H_2O_2-mediated activation of SPCEs significantly reduced the charge transfer resistance (R_{ct}) values to 11.1 Ω cm^2 for the aSPCE compared to SPCE (249.0 Ω cm^2), and similarly to the activation of SPPtEs by polishing [25]. Therefore, the electrical conductivity of electrodes significantly improved.

CVs of $(NH_4)_2Fe(SO_4)_2$ were performed to ascertain possible chemical changes in the activated carbon ink (Figure 2D). This compound is a redox probe that is very sensitive to some oxygenated groups, particularly carbonyls [9,26]. The electrochemical treatment with H_2O_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 (Figure 3). The high resolution for the analysis of the C 1s and O 1s spectra lowered the surface concentration (at.%) of carbon (obtained from Figure 3A) from 94.35 to 93.68 and increased oxygen from 5.51 to 14.8 at.% (obtained from Figure 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 (Figure 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 (Figure 3D). These changes on carbon ink surface promote the diffusion-controlled process of H_2O_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]. Figure 4 shows the calibration plots of these electrodes toward successive additions of H_2O_2. Maximum sensitivity was obtained with the H_2O_2-activated SPCEs proposed herein (0.24 ± 0.01 $\mu A \mu M^{-1} cm^{-2}$). This sensitivity even outdid that of the electrodes activated using a diluted solution of H_2SO_4 (0.09 ± 0.01 $\mu A \mu M^{-1} cm^{-2}$), 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 potentials (-2.5 to 2.5V) could be detrimental for controlling surface chemistry. Regarding sensor stability, calibration plots were performed at 0, 4, 6, 8 and 18 days after the activation treatment and the sensitivity obtained was $0.23\pm0.01 \mu A \mu M^{-1} cm^{-2}$ (repeatability 4.74%).

4. Conclusion

A novel electrochemical activation method for SPCEs is presented herein, and consists of 25 repetitive voltammetric cycles between +1 and −0.7 V at 10 mVs^{-1} using 10 mM H_2O_2 in 0.1 M PB, pH 7. This pretreatment substantially improved the electrochemical properties of electrodes, which substantially enhanced H_2O_2 electroanalysis sensitivity. Strikingly, aSPCE sensitivity exceeded that of a SPCE by 140-fold, and even surpassed that of a SPPtE by 6-fold. The enhanced electrochemical properties were attributed mainly to the introduction of oxygenated functional groups during the activation process and, to a lesser extent, to a slight increase in the electroactive area due to the elimination of non-conductive compounds. The proposed method was more effective for the H_2O_2 electroanalysis than other protocols commonly used for activating SPCEs. This simple approach is promising for the activation of commercial carbon inks-based electrodes for sensor applications.

Acknowledgements

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Figure captions

Figure 1. A) 25 repetitive cyclic voltammograms of a SPCE in 10 mM H_2O_2 (10 mVs^{-1}). B) Amperometric response at 0.7V to 10 μM H_2O_2 additions using the indicated electrodes.

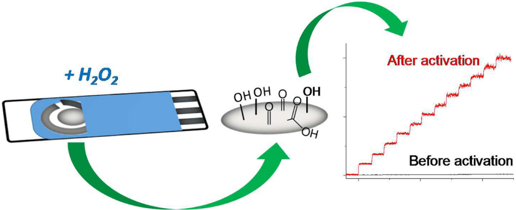
Figure 2. A) SEM image of a SPCE. B) SEM image of an aSPCE. C) Nyquist plots for a SPCE and an aSPCE. The inset in (C) shows the equivalent circuit used and the expanded plot for the aSPCE. D) CV response of 1 mM $(NH_4)_2(FeSO_4)$ in 0.2 M $HClO_4$ for a SPCE and an aSPCE (*vs* external Ag|AgCl|KCl (1M) reference electrode).

Figure 3. XPS C 1s (A) and O 1s (B) spectra for a SPCE and an aSPCE. Normalized surface concentration of functional groups after deconvolution of C 1s (C) and O 1s (D) spectra.

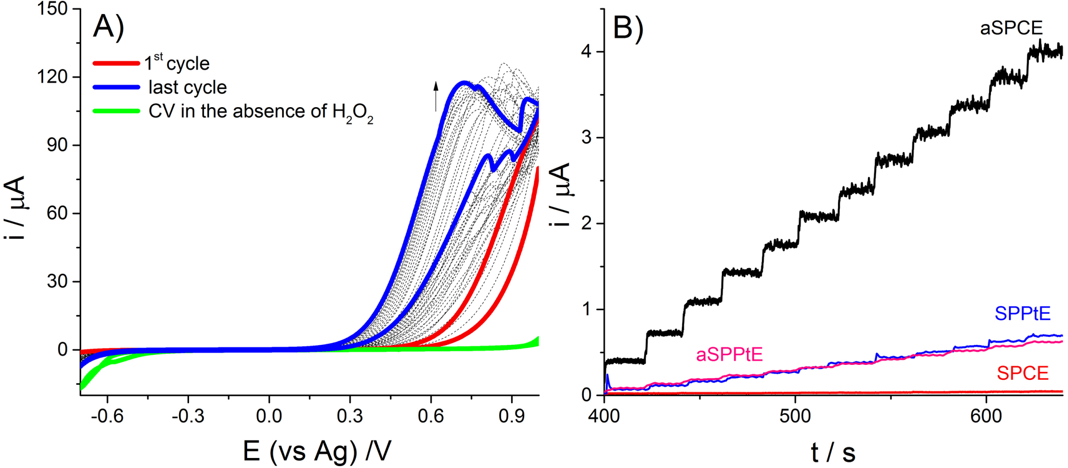
Figure 4. Current density *vs* H_2O_2 concentration of SPCEs activated by different methods at 0.7V (mean ± SD, n = 3). Blue: -1.2 V during 20s in 0.1M NaOH [6], green: 1.7 V during 60s in 0.05M PBS [7], red: one voltammetric cycle between -2.5 and 2.5 V at 100 mVs^{-1} in 0.05M H_2SO_4 [8], black: the proposed method in this work.

HIGHLIGHTS

- Highly activated SPCEs are obtained by an easy treatment with H_2O_2.
- An increase of oxygenated groups on the surface of activated SPCEs was detected.
- Pseudoperoxidase activity of carbonaceous ink has been considerably improved.
- Activated SPCEs showed enhanced sensitivities for the electroanalysis of H_2O_2.
- This pretreatment was more effective than others using H_2SO_4, PBS or NaOH.



Graphics Abstract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0.6
0.9
E (vs Ag) /V
B)
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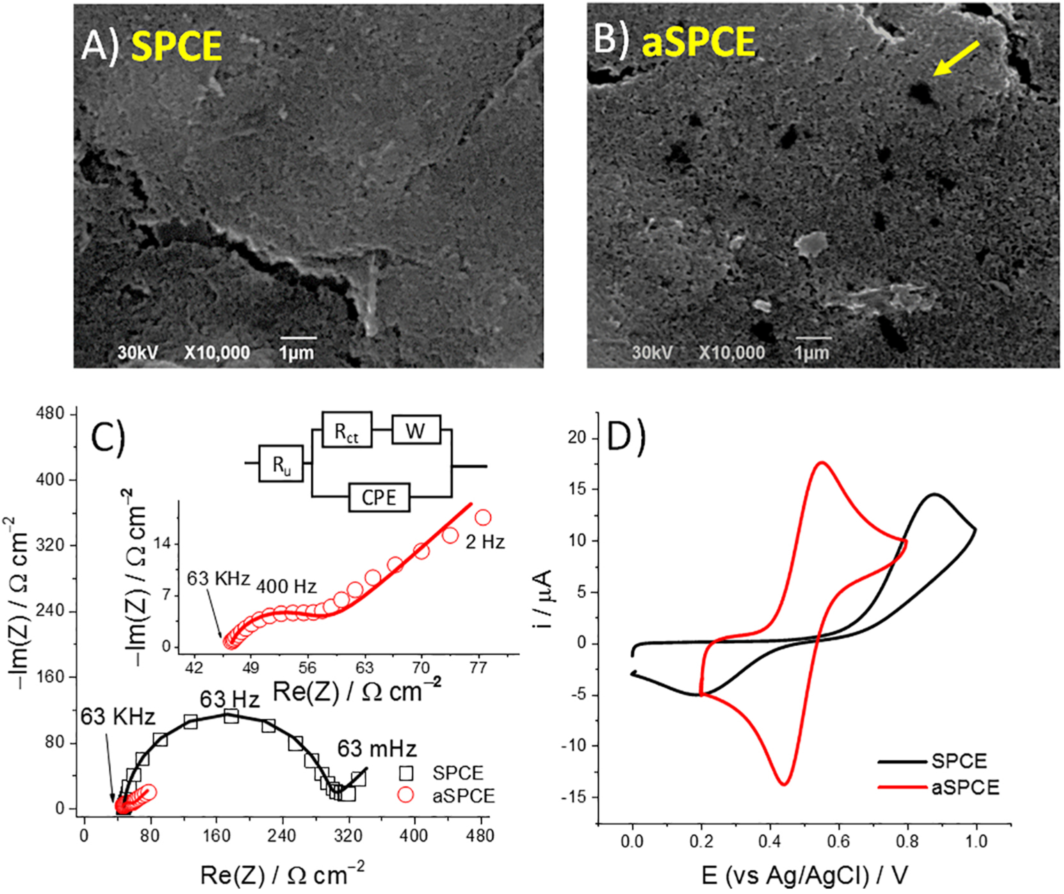
Figure 1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30kV X10,000 1µm
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C)
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2 Hz
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Re(Z) / Ω cm^−2
42 49 56 63 70 77
0 7 14
63 KHz
63 Hz
63 mHz
SPCE
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−Im(Z) / Ω cm^−2
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Figure 2

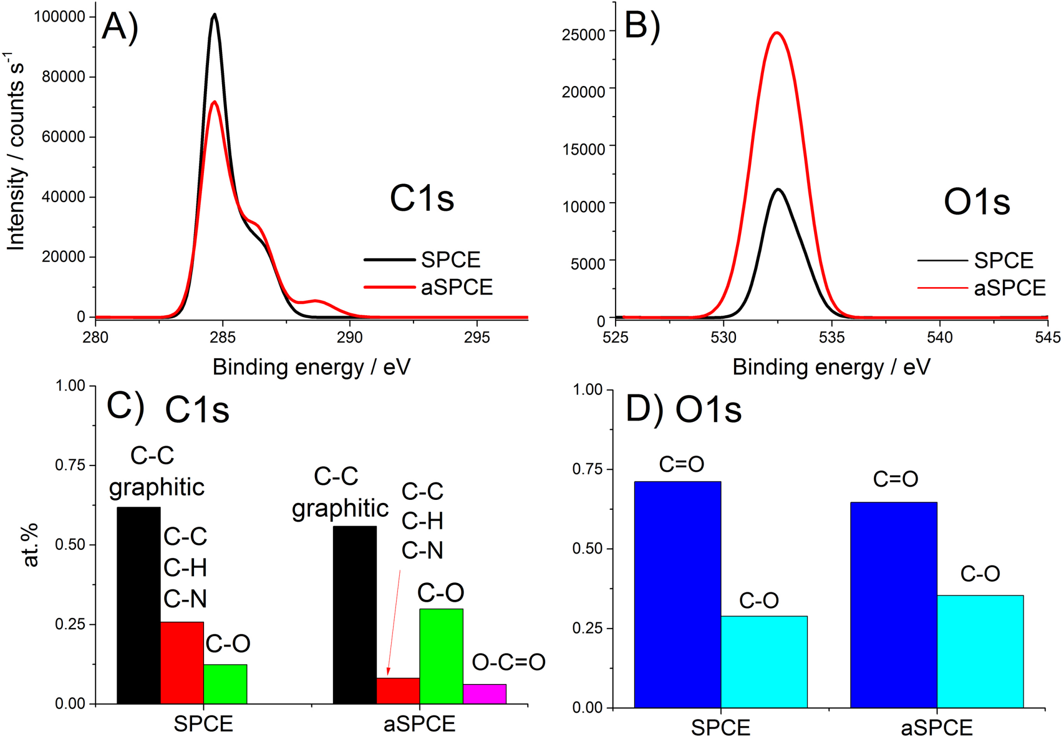
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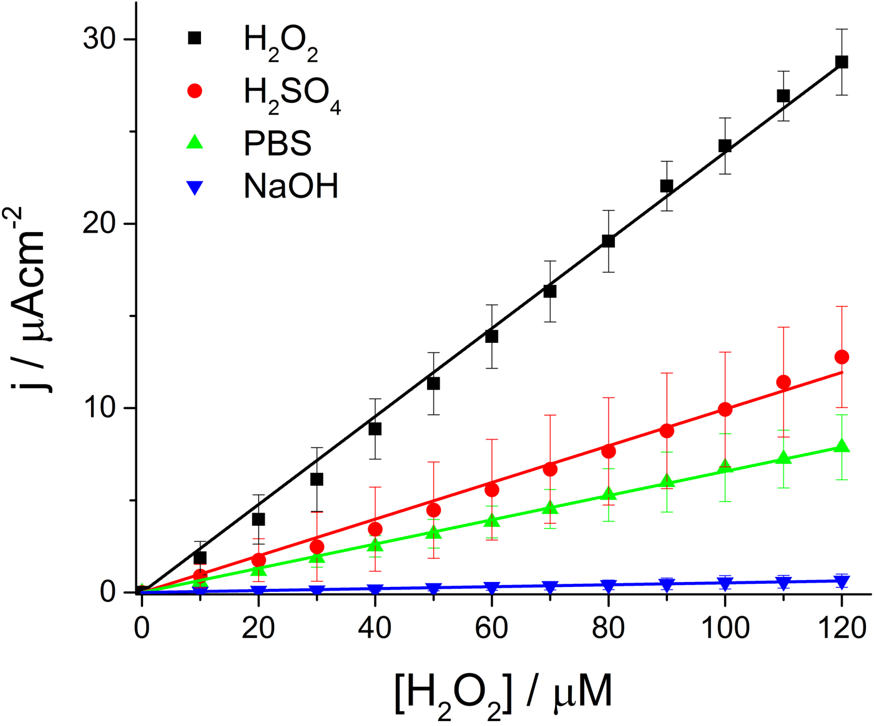
Figure 3



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j / μAcm^{-2}
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30
0
20
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60
80
100
120
[H_2O_2] / μM

Figure 4