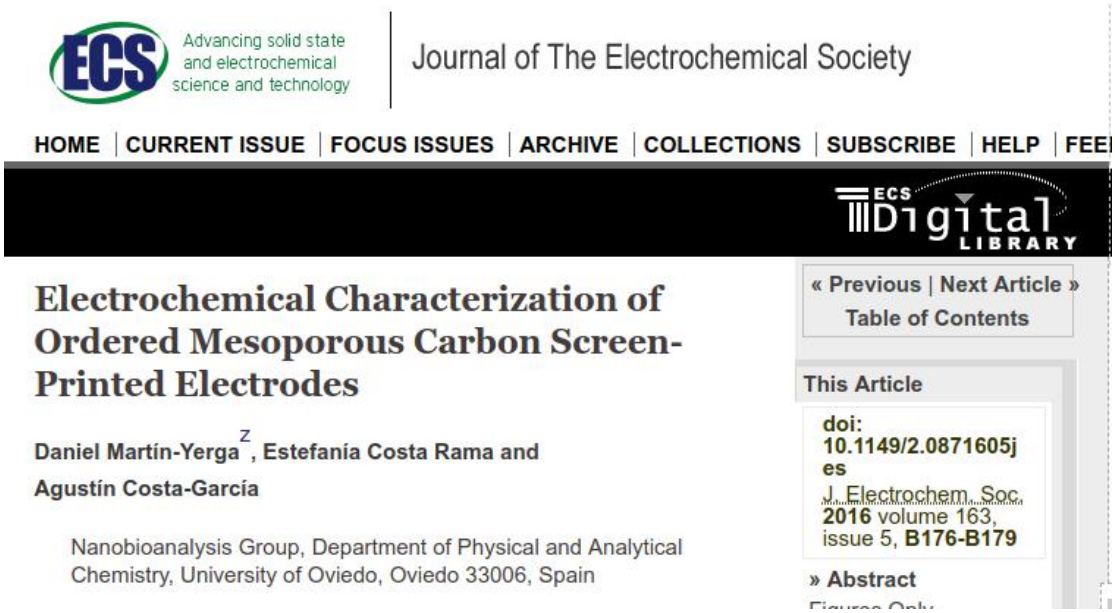

Electrochemical characterization of ordered mesoporous carbon screen-printed electrodes

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ABSTRACT

Screen-printed electrodes have become an essential tool in the development of electrochemical sensors and biosensors. Among the materials used for the fabrication, the most employed are the different forms of carbon. In this work, the electrochemical characterization of ordered mesoporous carbon screen-printed electrodes is carried out. The results show that the surface area is enhanced and the resistance to the electron transfer is highly reduced in comparison to graphite screen-printed electrodes. Although a lower limit of detection is obtained for screen-printed graphite, ordered mesoporous carbon electrodes showed a better voltammetric selectivity.

INTRODUCTION

Carbon materials are widely used in electrochemical applications due to its good electrical properties, low cost, and acceptable chemical inertness. Several kinds of carbon have been used in electrodes such as graphite paste, glassy carbon or highly ordered pyrolytic graphite (HOPG). In recent years, with the rise of the nanotechnology, novel carbon nanomaterials such as carbon nanotubes, carbon black or graphene, have appeared providing different electrode properties. Among the carbon materials employed in electrochemistry is ordered mesoporous carbon (OMC). OMC have a large surface area, ordered mesostructure with well-defined and controlled pore size, chemical inertness and high thermal stability[1]. OMC has been employed as electrode material for electroanalytical applications[2,3], protein immobilization[4], and biosensors[5].

Screen-printed electrodes are a very promising tool for point-of-care (POC) testing[6,7]. They have ideal characteristics such as small size, low cost, ease of use and portability. For these reasons, the use of screen-printed electrodes modified with ordered mesoporous carbon could lead to substantial improvements in the field of (bio)sensing. However, although there are several published studies using conventional electrodes as mentioned previously, the literature using SPEs modified with OMC is scarce. For instance, they have been employed for glucose[5] or norepinephrine[8] detection. The complex modification of the surface with OMC reported in these works is an important disadvantage for the preparation of simple electrochemical sensors. In contrast, the use of commercial readily available electrodes can avoid the tedious steps of the surface modification. Therefore, the characterization of commercial OMC screen-printed electrodes (OMCSPEs) may provide some useful information about their potential as readily available sensing transducers.

In this work, we carried out the electrochemical characterization of ordered mesoporous carbon screen-printed electrodes by cyclic voltammetry using two model species such as ferrocyanide and dopamine, and, also by electrochemical impedance spectroscopy. A critical comparison between the electrochemical properties obtained for OMCSPEs and for screen-printed graphite electrodes is presented. Furthermore, the analytical performance for the dopamine determination and the selectivity towards other species such as uric acid and ascorbic acid were evaluated.

EXPERIMENTAL

Materials and instrumentation.

Potassium ferrocyanide, potassium ferricyanide, dopamine hydrochloride and potassium chloride were purchased from Sigma-Aldrich. Sodium hydroxide and phosphoric acid were purchased from Merck. Ultrapure water obtained with a Millipore Direct Q5 purification system from Merck-Millipore was used throughout this work. Electrochemical measurements were carried out with an Autolab PGSTAT12 (Metrohm) potentiostat/galvanostat interfaced to a computer system and controlled by Autolab GPES 4.9 software for voltammetric measurements and by Autolab FRA 4.9 software for electrochemical impedance spectroscopy (EIS) measurements.

Commercial ordered mesoporous carbon (OMCSPEs) and screen-printed graphite electrodes (SPCEs) were purchased from DropSens (ref. 110OMC and 110, respectively). All indicated potentials are related to the silver quasireference screen-printed electrode. All measurements were performed at room temperature by adding 40 μl of the specific solution to the electrochemical cell. Working solutions of ferrocyanide and dopamine were prepared in KCl 0.1 M. A JEOL 6610LV scanning electron microscope was used to imaging the working electrodes.

Electrochemical measurements

For ferrocyanide, cyclic voltammetry was performed from -0.2 to +0.5 V. For dopamine, cyclic voltammetry was performed from 0 to +0.7 V (+0.9 for SPCEs). Potential step was 4 mV for both cases, and CV was performed at different scan rates such as 10, 25, 50, 75, 100, 250 and 500 mV/s.

Electrochemical impedance spectroscopy (EIS) was performed with a $[Fe(CN_6)]^{3-/4-}$ solution (5 mM) prepared in 0.1 M KCl. A potential of +0.12 V and an AC amplitude of 10 mV were applied. The impedance data was fitted to the Randles equivalent circuit.

Dopamine chronoamperometric measurements were performed by applying a potential of +0.5 V to OMCSPEs and +0.7 V to SPCEs for 50 s.

RESULTS AND DISCUSSION

The microscopic characterization of OMCSPEs was carried out by scanning electron microscopy (SEM) (Figure 1). For comparison, the graphitic surface of SPCEs was also analyzed. For SPCEs, a very rough surface with a continuous-like structure of nanoparticles is observed. This structure is probably due to the graphitic powder and binder used for the fabrication of these electrodes. For OMCSPEs, a different surface is observed with some kind of microtubes (up to 200 nm in diameter) and several layers, which lead to a very porous three-dimensional structure. However, the structure is quite heterogeneous and different surface features can be observed.

The surface of the OMCSPEs was characterized by electrochemical impedance spectroscopy and a comparison was carried out with screen-printed graphite electrodes. Figure 2 shows the impedance spectra in the form of a Nyquist plot, and the equivalent circuit used to fit the EIS data is shown in the inset, where Rs is the solution resistance, Rct is the charge transfer

126 resistance, Cdl is the double-layer capacitance, and W is the Warburg impedance. For SPCEs
127 (circles curve), the impedimetric response observed is characteristic of the equivalent circuit
128 used with a semicircle at high frequencies and a straight line at low frequencies. For
129 OMCSPEs (triangles curve), the behaviour is closer to an ideal conductor, with a semicircle
130 of a very small diameter at high frequencies indicating that the electron transfer in this kind of
131 electrodes is significantly enhanced in comparison to SPCEs. The values obtained after the
132 fitting of the EIS data for Rct were 380 ± 52 and 32 ± 4 Ω for SPCEs and OMCSPEs,
133 respectively. Furthermore, a significant difference was also estimated for Cdl, obtaining
134 values of 1.07 ± 0.02 and 34 ± 5 $\mu F/cm^2$ for SPCEs and OMCSPEs, respectively. These
135 values indicate a much higher capacitance of the electrode surface in OMCSPEs compared to
136 SPCEs, probably due to the three-dimensional structure able to store a higher amount of
137 charge between layers.
138
139 A comparison between the electrochemical response of SPCEs and OMCSPEs using two
140 model analytes (ferrocyanide and dopamine) by cyclic voltammetry was carried out. Cyclic
141 voltammograms at different scan rates of a solution of 0.5 mM of $[Fe(CN)_6]^{4-}$ in 0.1 M KCl
142 were recorded on SPCEs and OMCSPEs. Figure 3A shows the voltammograms for
143 OMCSPEs. The different electrochemical response for both electrodes at 50 mV/s is shown in
144 the Figure 3B. The peak potential difference (ΔEp) was 76 mV for OMCSPEs and 124 mV
145 for SPCEs. The ΔEp value closer to the theoretical reversibility (59 mV) for OMCSPEs
146 indicates an improvement in the electron transfer in good agreement with the EIS data.
147 Although a similar behaviour is found for both electrodes, a study to evaluate the rate-limiting
148 step of the electrochemical reaction was carried out. Peak currents (anodic and cathodic) were
149 plotted against the scan rate and the root of the scan rate. For both cases, a linear plot was
150 obtained, indicating that the rate-limiting control is the diffusion of the species to the

electrode surface, and the Randles-Sevcik equation for a diffusion-controlled process can be applied:

$$i_p = (2.69x10^5)\, n^{3/2}\, A\, C\, D^{1/2}\, v^{1/2}$$

where i_p is the peak current intensity (A), n is the number of electrons transferred in the electrochemical reaction, A is the electrode area (cm^2), C is the bulk concentration of the analyte (mol/cm^3), D is the diffusion coefficient of the analyte ($7.26x10^{-6}$ cm^2/s as found in the literature[9]), and v is the scan rate (V/s).

Using this equation, the electroactive area for both electrodes was calculated, obtaining values of 0.072 ± 0.003 cm^2 and 0.082 ± 0.003 cm^2 for SPCEs and OMCSPEs, respectively. The porous OMC surface result in an increased area compared to SPCEs. However, these values are well below the geometric area of the electrode even with the rough surface of both electrodes. This fact can mainly be due to the binder and other impurities present in the structure preventing the electron transfer.

The standard heterogeneous rate constant, k^o, was estimated using the Nicholson method[10] where the peak separation potential (ΔEp) is correlated to a dimensionless function (ψ) and this function is used to calculate the rate constant using the following equation:

$$\psi = k^0 (D_O/D_R)^{\alpha/2} (RT)^{1/2} (\pi nFDv)^{-1/2}$$

where D_O and D_R are the diffusion coefficient for the redox couple species (cm^2/s), α is the transfer coefficient (0.5), R is the universal gas constant (J/mol K), T is the absolute temperature (K), n is the number of electrons transferred, F is the Faraday constant (C/mol) and v is the scan rate (V/s).

In order to estimate the ψ function, the following equation developed by Swaddle et al.[11] can be employed:

$$\ln \psi = 3.69 - 1.16 \ln(\Delta Ep - 59)$$

Using this methodology, the k^o for $[Fe(CN)_6]^{4-}$ at both electrodes was estimated, obtaining values of 1.5 (± 0.6) $x10^{-3}$ and 3.3 (± 0.6) $x10^{-2}$ for SPCEs and OMCSPEs, respectively. This increment indicates a much faster electron transfer at OMCSPEs, reaching a value very close to the theoretically reversible for one electron transfer. Besides the best features presented by the OMC respect to graphite, the electrode surface seems to be covered with a lower amount of binder, and as previously reported in the literature[12], it could have a great impact on the electron transfer rate.

The electrochemical behaviour on SPCEs and OMCSPEs of a more complex system, dopamine, was also evaluated. Cyclic voltammograms at different scan rates of a solution of 0.5 mM of dopamine in 0.1 M KCl were recorded at SPCEs and OMCSPEs. Figure 3C shows the voltammograms at different scan rates for OMCSPEs and Figure 3D shows the electrochemical response at 100 mV/s for a SPCE and OMCSPE. As in the $[Fe(CN)_6]^{4-}$ case, the ΔEp decreased significantly at OMCSPEs compared to SPCEs. For dopamine, the effect is greater, and the ΔEp decreased from 552 mV at SPCEs to 76 mV at OMCSPEs, indicating a more reversible electrochemical reaction due to an enhanced electron transfer. In this case, a notable increment of the peak current is also observed for cathodic and anodic processes. The study of the rate-limiting step of the electrochemical reaction showed that both processes were diffusion-controlled (peak currents linearly proportional to the square root of the scan rate). Although dopamine appears to undergo adsorption on other carbon materials such as nanotubes[13], it does not seem to occur on OMCSPEs, where only a diffusional process is observed. Therefore, the increment of the peak current is due mainly to the increased surface area involved in the electron transfer and a decreased resistance to charge transfer, and not to any adsorption process.

Using the Nicholson method, the k^o for dopamine at both electrodes was estimated, obtaining values of 1.2 (± 0.8) $x10^{-4}$ and 1.53 (± 0.05) $x10^{-3}$ for SPCEs and OMCSPEs, respectively. A significant increment of the electron transfer rate is also observed for dopamine at OMCSPEs. This fact makes OMCSPEs a good alternative for a diffusion-controlled detection of different species, which undergo adsorption on other advanced carbon materials such as nanotubes or graphene.

In order to evaluate the analytical behaviour of dopamine in these two types of electrodes, chronoamperometric measurements for different concentrations of dopamine were carried out using SPCEs and OMCSPEs. Square-wave or differential-pulse voltammetries seem like most appropriate techniques for dopamine detection, however, the initial results with these techniques showed a lower reproducibility for OMCSPEs than using chronoamperometry. For the chronoamperometric detection for OMCSPEs, a potential of +0.5 V was chosen, while that for SPCEs, +0.7 V was the optimal potential. As expected for the improvement of the electron transfer, a lower detection potential can be used to carry out the oxidation of dopamine, which is positive for the analytical selectivity using such electrodes. In the Figure 4, the calibration plots obtained for both electrodes are presented. For OMCSPEs, a linear range from 50 to 2000 µM was obtained, while that for SPCEs it was from 5 to 2000 µM. These results seem to make clear as the difference in the capacitive current contribution may be responsible for being unable to observe signals at low dopamine concentrations in OMCSPEs, since the background current is much higher, and therefore, the minimum detectable concentration is lower for SPCEs.

The simultaneous detection of several species whose oxidation potential is near the oxidation of dopamine such as ascorbic acid and uric acid is a constant concern, and different types of electrodes have been employed[14,15]. In this case, a proof of concept was conducted to compare the voltammetric response of these species in both SPCEs and OMCSPEs using a 0.1 M pH 7 PBS buffer. Linear sweep voltammograms of different solutions of these species (separately and mixtures of species) at concentrations of 0.4 mM for ascorbic acid, and 0.2 mM for uric acid and dopamine, were recorded. Figure 5 shows the voltammetric response of a solution with the three species. At SPCEs, two broad unresolved peaks are observed, and therefore, the species could not be determined simultaneously. After evaluating the individual responses, it was observed that the dopamine and ascorbic acid appeared at the same potential, while that the uric acid is the species at the more positive potential. For OMCSPEs, a better resolution of the three species is obtained as they appear at different potentials, from most negative to positive potentials: ascorbic acid, uric acid and dopamine. This fact seems to be a very important advantage of OMCSPEs over SPCEs, and it is direct consequence of the improvement in the electron transfer between the ordered mesoporous carbon and the electroactive species.

CONCLUSIONS

Commercial ordered mesoporous carbon screen-printed electrodes have shown interesting electrochemical characteristics such as an enhanced electron transfer even for simple analytes as ferrocyanide and dopamine. The porous structure of OMC leads to an increment of the electrode surface area, enhancing the electrochemical response and may prove useful for modification with biomaterials in biosensing applications. As a drawback, OMC shows large double-layer capacitances, which could hinder small analytical signals, and therefore, they are not the best tool for ultrasensitive determinations. However, the enhanced electron transfer

leads to an improvement in the selectivity compared to graphite electrodes. The results of this work indicate that the OMCSPEs could be useful for some sensing applications where the limit of detection is not the critical aspect. Furthermore, OMCSPEs may prove interesting as solid-contact ion selective electrodes in potentiometric sensors for its high capacitance.

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NOTES

The authors declare no competing financial interest.

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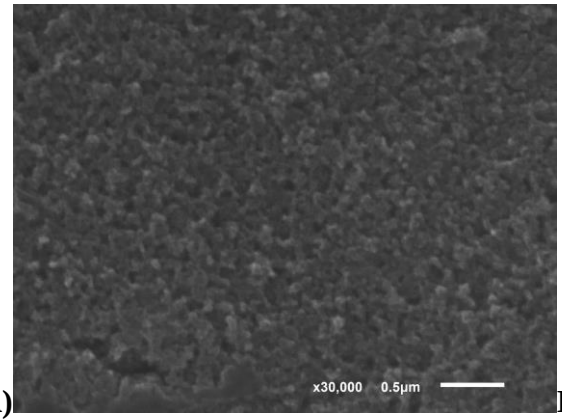
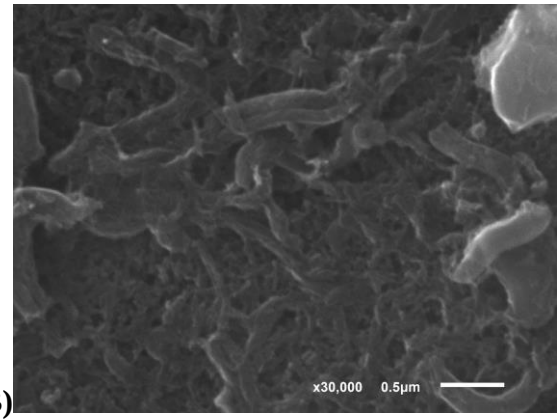
FIGURES

Figure 1. SEM micrograph of a screen-printed graphite electrode (**A**) and of a screen-printed ordered mesoporous carbon electrode (**B**).

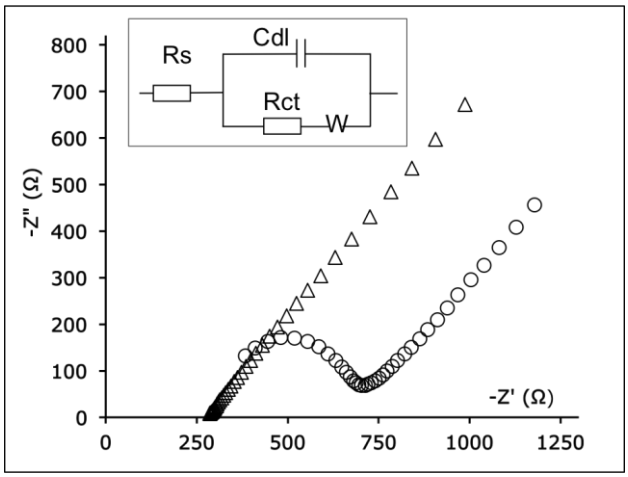
A) 

B) 

290 **Figure 2.** EIS data obtained for a SPCE (circles) and for an OMCSPE (triangles). Inset:

291 Randles equivalent circuit used for fitting the EIS data.

292



293

Figure 3. A) Cyclic voltammograms of 0.5 mM $[Fe(CN)_6]^{4-}$ at an OMCSPE using different scan rates. **B)** Cyclic voltammograms of 0.5 mM $[Fe(CN)_6]^{4-}$ at a SPCE (dashed line) and at an OMCSPE (solid line) using a scan rate of 50 mV/s. **C)** Cyclic voltammograms of 0.5 mM dopamine at an OMCSPE using different scan rates**. D)** Cyclic voltammograms of 0.5 mM dopamine at a SPCE (dashed line) and at an OMCSPE (solid line) using a scan rate of 50 mV/s.

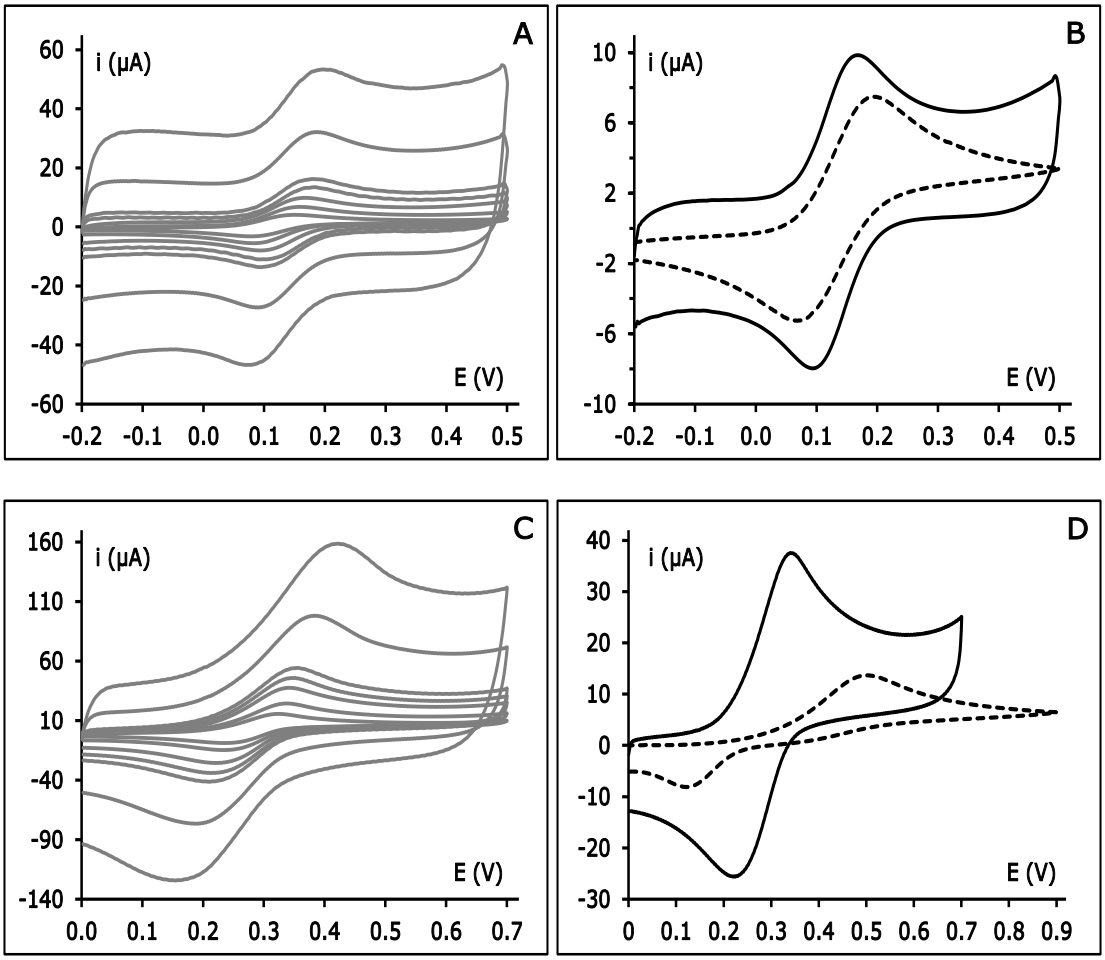
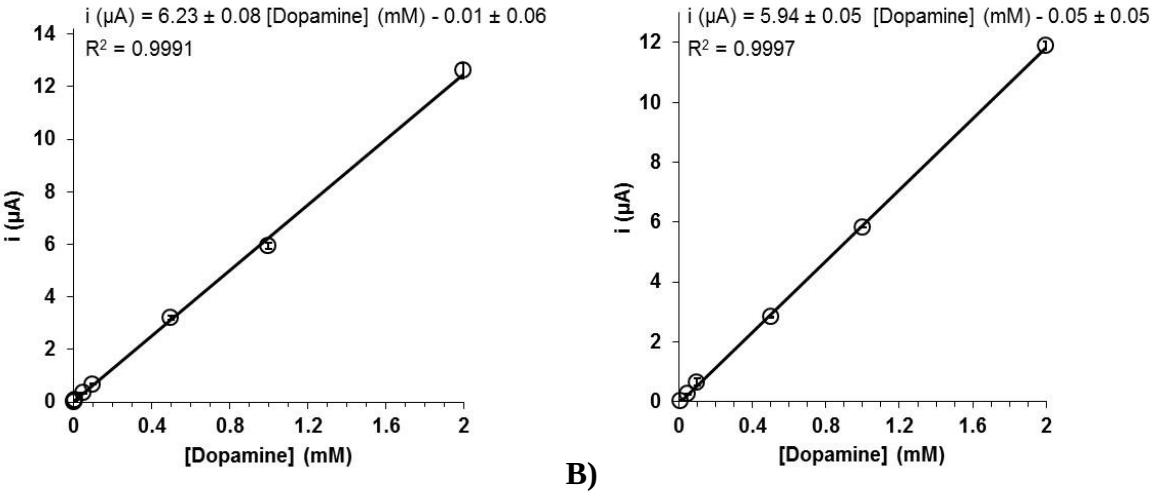


Figure 4. Calibration plots for dopamine using SPCEs (**A**) and OMCSPEs (**B**) by chronoamperometric measurements applying a potential of +0.7 V for SPCEs and +0.5 V for OMCSPEs during 50 s.



A) **B)**

Figure 5. Linear sweep voltammograms for 0.4 mM ascorbic acid (AA) and 0.2 mM dopamine (DA) and uric acid (UA) in 0.1 M PBS pH 7 using a SPCE (dotted line) and a OMCSPE (solid line).