



In situ immobilization of cobalt phthalocyanine on the mesoporous carbon ceramic SiO₂/C prepared by the sol–gel process. Evaluation as an electrochemical sensor for oxalic acid

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ABSTRACT

The mesoporous carbon ceramics SiO₂/20 wt% C ($S_{\text{BET}} = 160 \text{ m}^2 \text{ g}^{-1}$) and SiO₂/50 wt% C ($S_{\text{BET}} = 170 \text{ m}^2 \text{ g}^{-1}$), where C is graphite, were prepared by the sol–gel method. Scanning electron microscopy images and the respective element mapping showed that, within the magnification used, no phase segregation was detectable. The materials containing 20 and 50 wt% of C presented electric conductivities of 9.2×10^{-5} and 0.49 S cm^{-1} , respectively. These materials were used as matrices to support cobalt phthalocyanine (CoPc), prepared in situ on their surfaces, to assure homogeneous dispersion of the electroactive complex in the pores of both matrices. The surface densities of cobalt phthalocyanine on both matrix surfaces were $0.014 \text{ mol cm}^{-2}$ and $0.015 \text{ mol cm}^{-2}$ for materials containing 20 and 50 wt% of C, respectively. Pressed disk electrodes made with SiO₂/50 wt% C/CoPc and SiO₂/20 wt% C/CoPc were tested as sensors for oxalic acid. The electrode was chemically very stable and presented very high sensitivity for this analyte, with a limit of detection, LOD = $5.8 \times 10^{-7} \text{ mol L}^{-1}$.

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1. Introduction

The sol–gel process is a well used procedure to prepare a great variety of porous and amorphous derived silica materials possessing defined compositions and morphologies [1–6]. Single or mixed oxides have been prepared by this method and used to prepare electrochemical sensors [7], with a predominance of those based on carbon paste electrodes (CPEs) [8]. These electrodes have been used to determine a great variety of analytes, such as dissolved oxygen in natural water [9–11], hydrogen peroxide [12], Pb(II) [13], phenolic compounds [14], glucose [15], NADH [16–18] and oxalic acid [19]. Although CPEs have demonstrated good results in general, the mechanical resistance of these electrodes is low, limiting their use over a long period of time. Composite materials based on SiO₂ as support have been used, taking into account its high mechanical, chemical and thermal resistances. To obtain an electrically conducting matrix, finely powdered graphite has been incorporated inside the matrix by the sol–gel method, using HCl or HNO₃ as catalyst. The composites obtained, SiO₂/C, using this procedure show good electrical conductivity, provided by the interconnected graphite particles inside the matrices. These materials have been used to develop electrochemical sensors [20], and the recent literature has reported the determination of NADH [21], BrO₃[−] and IO₃[−] [22], the simultaneous determination of dopamine, ascorbic

and uric acid [23] and bioelectrocatalytic mediatorless reduction of dioxygen [24].

However, using these acids (HCl and HNO₃) as catalysts, sedimentation of a fraction of the graphite particles occurs before the gelation process since the kinetics of pre-hydrolysis of TEOS is very long. To accelerate this reaction, HF has been used as catalyst [25,26], which can contribute to more effective confinement of graphite particles inside the matrix and also to obtain mesoporous materials.

Oxalic acid is important since it can be ingested as dietary constituent or produced as the final product of amino and ascorbic acid metabolism. In the human body metals such as Ca, Fe, Na, Mg or Ca can react with oxalic acid and contribute to formation of kidney stones [27–30]. In the present work we report the preparation of SiO₂/C by the sol–gel method by using both HNO₃ and HF as catalysts in different steps and furthermore, the in situ generation of cobalt(II) phthalocyanine (CoPc) in the pores of the matrix. The material obtained, SiO₂/C/CoPc, pressed in a disk format was used to fabricate an electrode whose potential usefulness was tested by the electrochemical oxidation of oxalic acid.

2. Experimental

2.1. Preparation of materials

2.1.1. SiO₂/C matrix

The SiO₂/C matrix was prepared by the sol–gel processing method with two different SiO₂ and C proportions, according to the

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following procedures: 4 mL of deionized H₂O and 0.1 mL of concentrated HNO₃ (nuclear 70%) were added to 50 mL of a solution of tetraethylorthosilicate (TEOS, Acros 98%) and absolute ethanol (Synth 99.9%) in the proportion 1:1 (v/v) of TEOS/ethanol. The resulting solution was heated to reflux temperature for 3 h under continuous magnetic stirring at the rate of 300 rpm (solution A). Solution A was cooled to room temperature and then under continuous stirring 4.0 mL of deionized water and 20 wt% graphite (Aldrich 99.99%, $S_{\text{BET}} = 9 \text{ m}^2 \text{ g}^{-1}$), calculated from the expected SiO₂ weight were added. To this mixture 0.5 mL of HF (Vetec 48%)¹ was added and then sonicated until gelation of the material, which occurred about 30 min after addition of the HF. The resulting material was stored in the hood for a week at room temperature, just covered with filter paper, for solvent evaporation. In a similar experiment another material was prepared, using 50 wt% of graphite powder based on the expected SiO₂ weight.

The resulting materials from these two preparations were ground in an agate mortar. The powder obtained was immersed in 50 mL of 2.0 mmol L⁻¹ HCl and stirred for 30 min, then filtered and washed with deionized water. Finally the material was washed with absolute ethanol in a Soxhlet extractor for 3 h, and the solvent was eliminated under vacuum (10⁻³ Torr pressure) at 393 K. The materials obtained, nominally containing 20 wt% and 50 wt% graphite, will hereafter be designated as SiO₂/20 wt% C and SiO₂/50 wt% C, respectively.

2.1.2. In situ synthesis of Co(II) phthalocyanine

CoPc was synthesized in situ on the SiO₂/50 wt% C powder matrix as described elsewhere for a similar material [31]. In brief, 1.0 g of SiO₂/C was immersed in 10 mL of 0.01 mol L⁻¹ cobalt acetate, Co(OAc)₂, and the mixture was heated in a water bath at 343 K until complete evaporation of the solvent. The dry solid, now represented as SiO₂/C/Co(II), was mixed with 0.22 g of phthalonitrile and heated in an ampoule at 493 K for 3 h to form the CoPc complex. Cobalt phthalocyanine not confined in the matrix pores and unreacted phthalonitrile were removed from the solid surface in a Soxhlet extractor with absolute ethanol. Then the solid was heated at 398 K under vacuum to evaporate all the solvent.

The amount of the in situ complex formed on SiO₂/C/CoPc was determined as described elsewhere [31] by immersing 10 mg of the SiO₂/C/CoPc in a solution of absolute ethanol, tetrahydrofuran (THF) and pyridine in the ratio of 50:35:15, respectively. The mixture was kept to rest for 15 h to fully extract the CoPc from the SiO₂/C surface. The final volume was adjusted to 25 mL with ethanol and the concentration of CoPc in the solution phase was determined using a spectrophotometric method on a Shimadzu Multispec 1501 UV–vis photodiode array spectrophotometer. The calibration curve was obtained by dissolving CoPc (Aldrich) in a similar ratio of ethanol/THF/pyridine as used for extraction of CoPc from the matrix.

2.2. Characterization

The nitrogen adsorption–desorption isotherms of previously degassed material at 423 K were determined at the liquid nitrogen boiling point on an Autosorb I Quantachrome instrument. The specific surface was determined from the BET (Brunauer, Emmett and Teller) multipoint method [32] and the pore size distribution was obtained using the BJH (Barret, Joyner, and Halenda) method [33].

Scanning electron micrograph (SEM) images were obtained using secondary back scattered electrons on a JEOL JSM 6360LV

microscope operating at 20 kV, equipped with an energy dispersive (EDS) X-ray attachment from NORAN Instruments.

The samples (~1 mg) were fixed onto double-faced carbon tape (3M Electrical Division, Brazil) adhered to an aluminum support and coated with a gold layer using a Bal-Tec MD20 metallizing system.

The electrical resistance (R) of the samples was obtained using the four point probe method on a National Instruments NI PXI-1033 equipment. Measurements were made for a disk of finely powdered SiO₂/C with 0.5 cm diameter and approximately 0.01 cm thickness (w) pressed under a pressure of 4.5 t. The conductivities (σ) were calculated by applying the equation:

$$\sigma = \frac{1}{RwF_2F_4}$$

where R is the electrical resistance, w is the thickness of the disk, and F_2 and F_4 are correction factors taken from the literature as 0.50 and 0.98, respectively [34].

The electronic spectrum of CoPc prepared in situ on the SiO₂/C matrix was obtained using the diffuse reflectance technique on a UV–vis DRS CARY 5G UV/vis spectrophotometer. Barium sulphate was used as the white reference sample. The Kubelka–Munk function was used for the analysis of diffuse reflectance spectrum obtained.

2.3. Electrode preparation and measurements

The working electrodes were prepared by pressing 25 mg of SiO₂/C/CoPc under a pressure of 4 t, at normal atmospheric conditions. The resultant disks (diameter 0.5 cm, thickness ~0.01 cm and geometric area 0.20 cm²) were immersed in pure fused paraffin at 343 K under vacuum (10⁻³ Torr), until all adsorbed gas in the matrix pores was completely eliminated. The resulting self-supported disk was polished with emery paper to remove the paraffin from the disk surface, and then glued with cyanoacrylate ester glue to the end of a glass tube (external area of 0.20 cm² and 15 cm length). A copper wire linked to the disk by graphite powder inserted inside the tube made the electrical contact.

Electrochemical measurements were performed on a PGSTAT-20 (Autolab) potentiostat–galvanostat. The experiments were carried out in a conventional three-electrode system at room temperature. A platinum wire and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The pressed disks of SiO₂/C/CoPc were used as the working electrode. All the measurements were carried out in 1.0 mol L⁻¹ KCl solution, under a nitrogen atmosphere.

3. Results and discussion

3.1. Characteristics of the SiO₂/C matrix

The amount of C used in the preparation of SiO₂/C, based on the number of moles of TEOS, corresponds to 20 and 50 wt% of graphite in the samples.

Fig. 1(A) and (B) shows the adsorption–desorption nitrogen isotherms for samples possessing 20 and 50 wt% of graphite. Both samples exhibit isotherms with hysteresis, typical of mesoporous materials [35,36]. The pore size distributions are shown in the inset of Fig. 1(A) and (B), respectively. The sample containing the lower amount of C, shows a mesopore distribution region with maximum at 19.4 nm diameter while the sample containing 50% of C shows a distribution curve with maximum around 15.8 nm diameter.

The surface area ($S_{\text{BET}}/\text{m}^2 \text{ g}^{-1}$) and pore volume ($p_v, \text{cm}^3 \text{ g}^{-1}$) obtained from the isotherms are: (a) SiO₂/20 wt% C, $S_{\text{BET}} = 160$, $p_v = 1.10$ and (b) SiO₂/50 wt% C, $S_{\text{BET}} = 170$, $p_v = 0.90$.

¹ Safety cautions: used plastic pipette, gloves, safety glass, mask and fume hood.

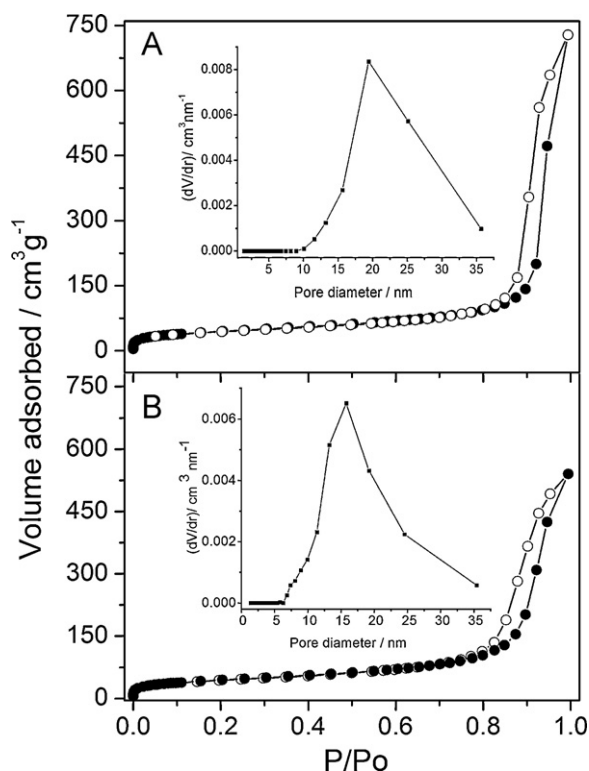


Fig. 1. N₂ adsorption–desorption isotherms: (A) SiO₂/20 wt% C and (B) SiO₂/50 wt% C and pore size distribution curve, respectively. —●—, adsorption —○—, desorption.

Fig. 2 shows the SEM images obtained for SiO₂/20 wt% C (Fig. 2(A)) and SiO₂/50 wt% C (Fig. 2(B)). It can be seen that samples possess particles having granular form. There is a greater compactness of particles in the SiO₂/20 wt% C sample.

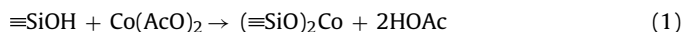
Fig. 3 shows the EDS mapping images for SiO₂/20 wt% C and SiO₂/50 wt% C. Within the magnification used, there is no evidence that Si and C particles have segregated domains, indicating that the Si and C particles appear homogeneously dispersed in the matrix.

The conductivities obtained for SiO₂/20 wt% C and SiO₂/50 wt% C were (in S cm⁻¹) 0.25×10^{-5} and 0.4, respectively. The higher conductivity in the second sample is provided both by the larger amount and by the well dispersed and interconnected graphite particles in the silica network.

3.2. In situ generation of CoPc

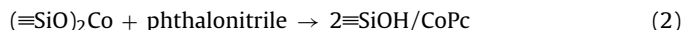
The preparative procedures can be described by two reaction steps. In the first step, Co(II) is adsorbed on the silica surface by a

reaction with formation of a Si–O–Co bond:



where the Bronsted acid $\equiv\text{SiOH}$ represents the silanol groups present on the matrix surface.

In the second step the adsorbed Co(II) served as the template for phthalocyanine complex formation inside the silica pores. The adsorbed Co(II) on the matrix surface, in the presence of phthalonitrile at 473 K, forms CoPc through the reaction described by Eq. (2):



Solid state diffuse reflectance spectrum of the material obtained, SiO₂/C/CoPc, showed two broad bands centered at 618 and 672 nm (figure not shown) that can be assigned as Q bands, for Co(II) under slightly distorted D_{4h} symmetry [37]. The present spectrum when compared with those obtained using a similar procedure of confining pure CoPc on γ -Al₂O₃, SiO₂ or Zeolite-Y, is the same [37,38].

The amounts of CoPc generated on the matrices are: SiO₂/20 wt% C/CoPc = 0.22 mmol g⁻¹ and SiO₂/50 wt% C/CoPc = 0.26 mmol g⁻¹. The surface densities of CoPc on the matrix surface, defined as $\delta = N_f/S_{\text{BET}}$ (in mol cm⁻²), where N_f is the amount of complex species incorporated (in mol g⁻¹), are: $\delta = 1.6 \times 10^{-10}$ and $\delta = 1.5 \times 10^{-10}$ mol cm⁻², respectively, for material containing 20 and 50 wt% of C.

3.3. Electrochemical measurements

Pressed disks of SiO₂/C/CoPc having 20 and 50 wt% C were used to fabricate the electrodes. To test the potential usefulness of the sensor, they were used to oxidize oxalic acid. This acid was chosen because it is well known that CoPc can mediate electrocatalytic oxidation of this acid [39].

Fig. 4 shows cyclic voltammetry experiments of the oxidation of oxalic acid using both electrodes in 1.0 mol L⁻¹ KCl as supporting electrolyte at a scan rate of 20 mV s⁻¹. The acid concentrations changed between 0.0 and 3.84×10^{-4} mol L⁻¹. Fig. 4(A) and (B) shows very clearly the better performance of the electrode made with material containing 50 wt% of C, compared to that of material containing 20 wt% C. The peak current intensities for oxalic acid oxidation are about ten times more intense for the former electrode. Oxidation peak potential is well defined and occurs at about 0.73 V while for electrode with less C it is not so well defined.

Plots of the anodic peak current intensity against the concentration of the acid [H₂C₂O₄] (mol L⁻¹) for the SiO₂/50 wt% C/CoPc electrode showed a linear correlation (figure not shown) represented by the equation: $i_{\text{pa}} (\mu\text{A}) = 13.35 + 1.19 \times 10^6 [\text{H}_2\text{C}_2\text{O}_4] (\text{mol L}^{-1})$, $r = 0.998$ and $n = 10$.

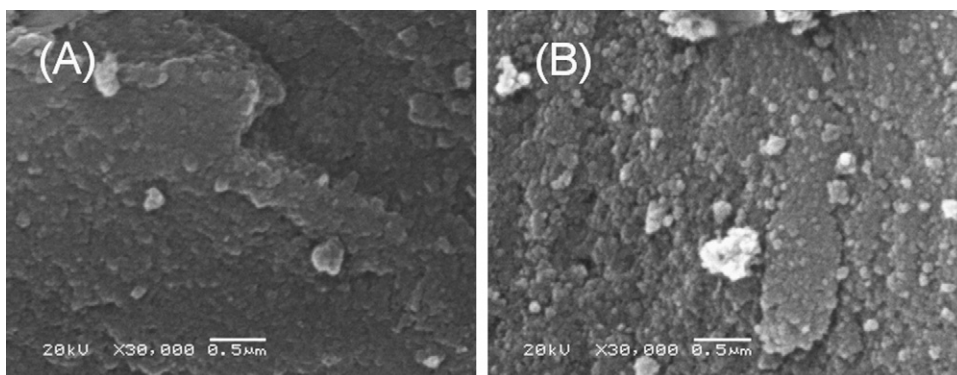


Fig. 2. SEM images for (A) SiO₂/20 wt% C and (B) SiO₂/50 wt% C.

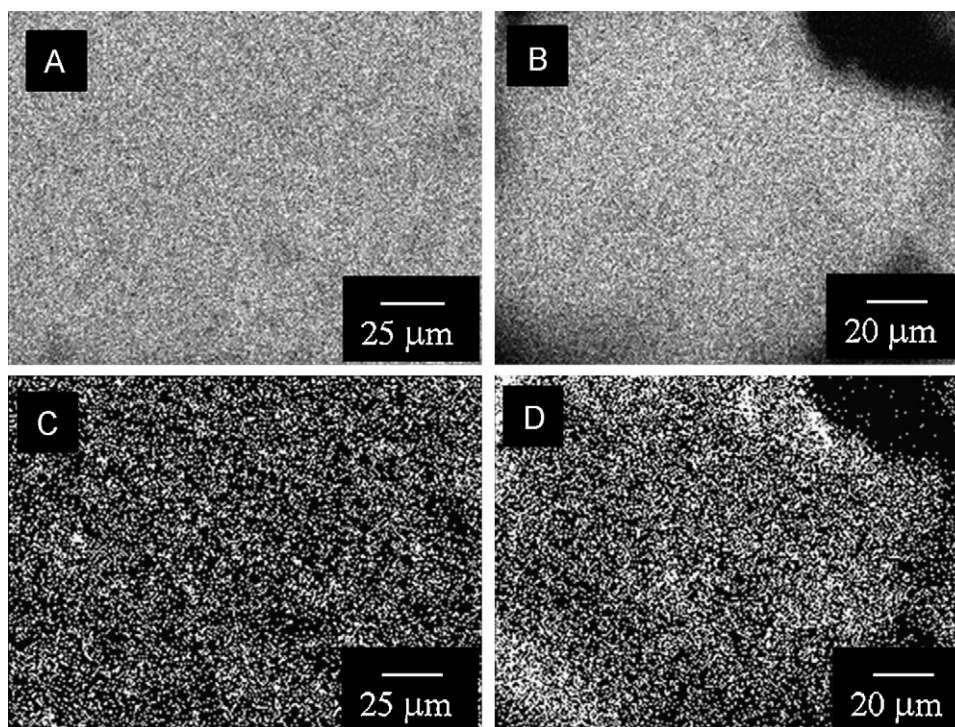
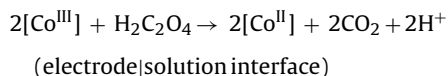
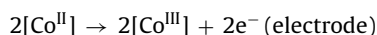


Fig. 3. EDS images: silicon mapping: (A) SiO₂/20 wt% C and (B) SiO₂/50 wt% C; carbon mapping: (C) SiO₂/20 wt% C and (D) SiO₂/50 wt% C.

The electrocatalytic process can be represented by the following equations [40]:



Since CoPc is generated in situ, the following experiment shows how strongly this complex is retained on the matrix surface. The stability of the SiO₂/C/CoPc electrode was checked by successively recording the cyclic voltammograms. After 100 cycles no significant changes of the anodic current intensity i_{pa} were observed in the voltammetric profile of the modified electrode (figure not shown). The i_{pa} intensity remained stable and the voltammograms were reproduced successively with relative standard deviation RSD of 0.12%, showing that CoPc electroactive species release to the solution phase is not detectable.

A plot of the anodic peak current (i_{pa}) against the square root of scan rate ($v^{1/2}$) shows a linear relationship (figure not shown), with equation, $i_{\text{pa}} (\mu\text{A}) = 0.45(\pm 3.04) + 24.03(\pm 0.45)v^{1/2} (\text{mV s}^{-1})^{1/2}$ and

$r = 0.998$, indicating that the oxidation process of oxalic acid is a diffusion controlled process [41]. Since CoPc is strongly confined in the pores of the matrix surface, the analyte must diffuse into the surface–solution interface.

The oxalic acid oxidation process can depend on the solution pH, taking into account that the dissociation constants are $\text{p}K_1 = 1.27$ and $\text{p}K_2 = 4.26$ [42]. However, in the present case, the effect of pH on the electrooxidation response, studied between pH 2 and pH 9 by cyclic voltammetry, was observed to have little effect. Concentration of the oxalic acid solution was fixed at $2.3 \times 10^{-4} \text{ mol L}^{-1}$ and the potential, E , between pH 5 and 9, remained practically invariable with RSD of 4.4% (figure not shown).

In order to test the usefulness of the new electrode as an electrochemical oxalic acid sensor, the chronoamperometric technique was used. Fig. 5 shows the chronoamperometric curves after successive addition of aliquots of oxalic acid solution at a fixed applied potential of 0.73 V, for 100 s. Inset Fig. 5 shows the plot of current intensities against the concentration of oxalic acid, measured at 50 s. It shows a linear relationship, in the concentration range between 3.98×10^{-5} and $4.6 \times 10^{-4} \text{ mol L}^{-1}$ with a linear correlation represented by the equation:

Table 1

Comparison of the limit of detection for oxalic acid between the SiO₂/C/CoPc and other electrodes.

Electrode	Electroactive species	LOD ($\mu\text{mol L}^{-1}$)	References
SiO ₂ /C/CoPc	CoPc, this work	0.58	This work
Glassy carbon	Rh phthalocyanine	1.0	[43]
Glassy carbon	multiwall carbon nanotubes	12.0	[27]
Pyrolytic graphite	–	0.70	[28]
Exfoliated graphite polystyrene composite	–	50.0	[29]
Boron-doped diamond/FIA ^a	–	0.0005	[30]
SiO ₂ /SnO ₂ /CoPc – CPME ^b	CoPc	30.0	[44]
SiO ₂ /SnO ₂ /C/SiPy/CoTsPc ^c	CoTsPc	7.1	[45]
SiO ₂ /CoPc – CPME	CoPc prepared in situ	1000	[31]

^a Flow injection analysis.

^b Carbon paste modified electrode.

^c Cobalt tetrasulphophthalocyanine.

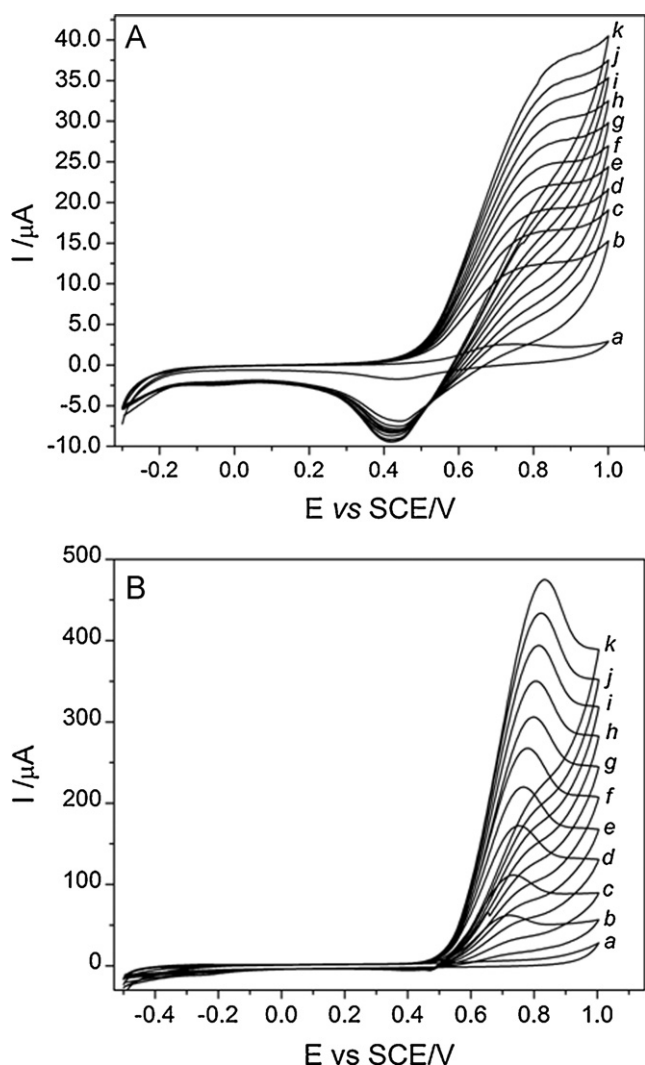


Fig. 4. Cyclic voltammetry curves obtained for different concentration of oxalic acid (in mol L⁻¹): (a) 0.0, (b) 3.98×10^{-5} , (c) 7.94×10^{-5} , (d) 1.19×10^{-4} , (e) 1.57×10^{-4} , (f) 1.96×10^{-4} , (g) 2.34×10^{-4} , (h) 2.72×10^{-4} , (i) 3.1×10^{-4} , (j) 3.47×10^{-4} , (k) 3.84×10^{-4} . Potential scan rate: 20 mV s⁻¹; supporting electrolyte: 1.0 mol L⁻¹ KCl. (A) SiO₂/20 wt% C/CoPc and (B) SiO₂/50 wt% C/CoPc.

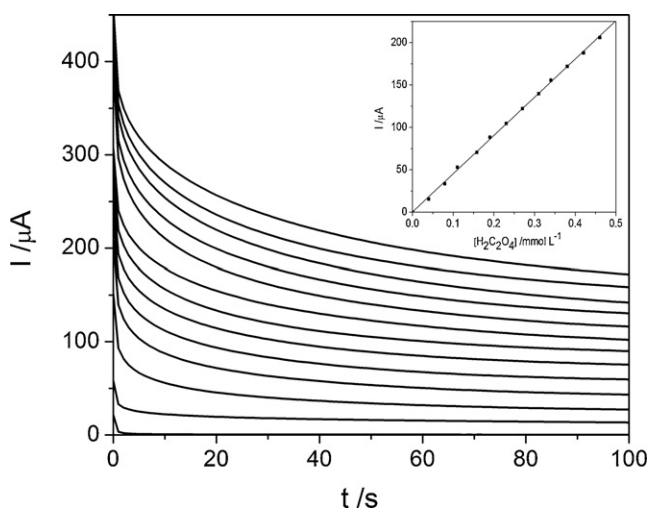


Fig. 5. Chronoamperograms for SiO₂/50 wt% C/CoPc electrode in different concentrations of oxalic acid at fixed potential of 0.73 V. Inset figure is a plot of current intensity against oxalic acid concentration (measured at 50 s).

$i_{pa} (\mu A) = 0.18(\pm 1.04) + 451.18(\pm 3.84)[H_2C_2O_4] (mmol L^{-1})$, $n = 12$, $r = 0.999$. The limit of detection (3 standard deviation of the blank divided by the slope of calibration curve), LOD = $0.58 \mu mol L^{-1}$, was found.

Table 1 summarizes the results obtained to determine oxalic acid by electrochemical process using different types of electrodes [27–31,43–45]. It is clearly observed that a lower detection limit is obtained by using the pressed disk electrode SiO₂/C/CoPc, when compared to the other electrodes, especially when comparing with SiO₂/CoPc-CPE where the LOD obtained was $1 \times 10^{-3} mol L^{-1}$. It is important to note that the surface density of CoPc in the CPE is $\delta = 0.44 \times 10^{-10} mol cm^{-2}$ [31], 3.4 times lower than that observed for SiO₂/50 wt% C/CoPc ($1.5 \times 10^{-10} mol cm^{-2}$).

4. Conclusions

A SiO₂/C/CoPc pressed disk electrode with solid paraffin filled pores, considerably decreased the electrical resistance. Material containing 50 wt% C was chosen and the electrode prepared with this material showed lower LOD when compared with other electrodes based on SiO₂ as the basic substrate to provide structural rigidity and chemical stability. The relatively good electrical conductivity presented by SiO₂/50 wt% C/CoPc makes this a material of great potential in preparing a new electrochemical sensor for oxalic acid and other analytes since many other electroactive species that can be easily confined on this matrix surface. Comparing the dramatic increase of detectivity of SiO₂/50 wt% C/CoPc (LOD = $5.8 \times 10^{-7} mol L^{-1}$) with that shown by SiO₂/CoPc (CPE) (LOD = $1.0 \times 10^{-3} mol L^{-1}$) presented in Table 1, the comparatively better performance of the new electrode is presumably related to the mesoporous nature of the matrix prepared by the sol-gel method. In this process C particles are highly and homogeneously dispersed throughout the bulk matrix phase, improving the connectivity of C particles and then increasing the conductivity of the material.

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References

- [1] M.S.P. Francisco, W.C. Silva, R. Landers, Y.V. Kholin, Y. Gushikem, Langmuir 20 (2004) 8707.
- [2] G. Frenzer, W.F. Maier, Annu. Rev. Mater. Res. 36 (2006) 281.
- [3] B. Samaranch, P.R. de la Piscina, G. Clet, M. Houalla, P. Gelin, N. Homs, Chem. Mater. 19 (2007) 1445.
- [4] A. Aronne, E. Marenga, V. Califano, E. Fanelli, P. Pernice, M. Trifuoggi, A. Vergara, J. Sol-Gel Sci. Technol. 43 (2007) 193.
- [5] Y.C. Wu, W. Hamd, E. Thune, A. Boulle, C. Rochas, R. Guinebreière, J. Non-Cryst. Solids 355 (2009) 951.
- [6] G. Liu, Y. Liu, G. Yang, S. Li, Y. Zu, W. Zhang, M. Jia, J. Phys. Chem. C 113 (2009) 9345.
- [7] A. Walcarius, Electroanalysis 13 (2001), 8, 9, 701.
- [8] I. Švancara, K. Vytřas, K. Kalcher, A. Walcarius, J. Wang, Electroanalysis 21 (2009) 7.
- [9] E.S. Ribeiro, S.L.P. Dias, Y. Gushikem, L.T. Kubota, Electrochim. Acta 49 (2004) 829.
- [10] M.S.P. Francisco, W.S. Cardoso, Y. Gushikem, J. Electroanal. Chem. 574 (2005) 291.
- [11] W.S. Cardoso, M.S.P. Francisco, R. Landers, Y. Gushikem, Electrochim. Acta 50 (2005) 4378.
- [12] J. Li, S.N. Tana, H. Ge, Anal. Chim. Acta 335 (1996) 137.
- [13] M. Ghiaci, B. Rezaei, R.J. Kalbasi, Talanta 73 (2007) 37.
- [14] J. Li, L.S. Chia, N.K. Goh, S.N. Tan, Anal. Chim. Acta 362 (1998) 203.
- [15] R. Liang, J. Jiang, J. Qiu, Anal. Sci. 24 (2008) 1425.
- [16] M.S.P. Francisco, W.S. Cardoso, L.T. Kubota, Y. Gushikem, J. Electroanal. Chem. 602 (2007) 29.
- [17] G. Zaitseva, Y. Gushikem, E.S. Ribeiro, S.S. Rosatto, Electrochim. Acta 47 (2002) 1469.

- [18] A.S. Santos, L. Gorton, L.T. Kubota, *Electroanalysis* 14 (2002) 805.
- [19] A.C. Pereira, D.V. Macedo, A.S. Santos, L.T. Kubota, *Electroanalysis* 18 (2006) 1208.
- [20] M. Tsionsky, G. Gun, V. Giezer, O. Lev, *Anal. Chem.* 66 (1994) 1747.
- [21] C.M. Maroneze, L.T. Arenas, R.C.S. Luz, E.V. Benvenutti, R. Landers, Y. Gushikem, *Electrochim. Acta* 53 (2008) 4167.
- [22] E. Marafon, L.T. Kubota, Y. Gushikem, *J. Solid State Electrochem.* 13 (2009) 377.
- [23] A. Salimi, H.M. Khezri, R. Hallaj, *Talanta* 70 (2006) 823.
- [24] W. Nogala, A. Celebanskaa, K. Szota, G. Wittstockb, M. Opallo, *Electrochim. Acta* 55 (2010) 5719.
- [25] T.N.M. Bernards, M.J. Bommel, J.A.J. Jansen, *J. Sol-Gel Sci. Technol.* 13 (1998) 749.
- [26] H.E. Byrne, W.L. IV Kostedt, J.M. Stokke, D.W. Mazyck, *J. Non-Cryst. Solids* 355 (2009) 525.
- [27] Y. Zheng, C. Yang, W. Pu, J. Zhang, *Food Chem.* 114 (2009) 1523.
- [28] B. Sljukic, R. Baron, R.G. Compton, *Electroanalysis* 19 (2007) 918.
- [29] F. Manea, C. Radovan, I. Corb, A. Pop, G. Burtica, P. Malchev, S. Picken, J. Schoonman, *Sensors* 7 (2007) 615.
- [30] T.A. Ivandini, T.N. Rao, A. Fujishima, Y. Einaga, *Anal. Chem.* 78 (2006) 3467.
- [31] M. Toledo, A.M.S. Lucho, Y. Gushikem, *J. Mater. Sci.* 39 (2004) 6851.
- [32] S. Brunauer, P.H. Emmett, E. Teller, *J. Am. Chem. Soc.* 60 (1938) 309.
- [33] E.P. Barret, L.G. Joyner, P.P. Halenda, *J. Am. Chem. Soc.* 73 (1951) 373.
- [34] E.M. Girotto, I.A. Santos, *Quim. Nova* 25 (2002) 639.
- [35] S.J. Gregg, K.S.W. Sing, *Adsorption Surface Area and Porosity*, 2nd ed., Academic Press, London, 1982.
- [36] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniowska, *Pure Appl. Chem.* 57 (1985) 603.
- [37] S. Ray, S. Vasudevan, *Inorg. Chem.* 42 (2003) 1711.
- [38] D. Wöhrle, U. Hündorf, G. Schulz-Ekloff, E. Ignatzek, *Z. Naturforsch.* 41b (1986) 179.
- [39] J. Wang, P.V.A. Pamidi, C. Parrado, D.S. Park, J. Pingarron, *Electroanalysis* 9 (1997) 908.
- [40] A.M.S. Lucho, E.C. Oliveira, H.O. Pastore, Y. Gushikem, *J. Electroanal. Chem.* 573 (2004) 55.
- [41] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, New York, 2001.
- [42] R.N. Goldberg, N. Kishore, R.M. Lennen, *J. Phys. Chem. Ref. Data* 31 (2002) 231.
- [43] S. Yamazaki, N. Fujiwara, K. Yasuda, *Electrochim. Acta* 55 (2010) 753.
- [44] J. Arguello, H.A. Magosso, R.R. Ramos, T.C. Canevari, R. Landers, V.L. Pimentel, Y. Gushikem, *Electrochim. Acta* 54 (2009) 1948.
- [45] T. Canevari, J. Arguello, M.S.P. Francisco, Y. Gushikem, *J. Electroanal. Chem.* 609 (2007) 61.