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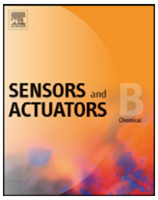

Dissolved O_2 sensor based on cobalt(II) phthalocyanine immobilized *in situ* on electrically conducting carbon ceramic mesoporous SiO_2/C material

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ABSTRACT

This work describes the preparation of mesoporous carbon ceramics SiO_2/50 wt.% C ($S_{BET} = 170\,m^2\,g^{-1}$), where C is graphite, by the sol–gel method. This material was used as a matrix to support cobalt phthalocyanine (CoPc), prepared *in situ* on their surface, to assure homogeneous dispersion of the electrocatalyst complex in the pores of the matrix. Pressed disk electrode made with SiO_2/C/CoPc was used to analyze dissolved oxygen in water by an electrochemical technique in neutral media and dissolved O_2 was reduced at −0.23 V. The linear response range, sensitivity and detection limit obtained were 0.5–6.6 mg L^{-1}, 2.16 μA L mg^{-1} and 0.01 mg L^{-1}, respectively, by chronoamperometry. A mechanism involving two electrons in O_2 reduction was determined by cyclic voltammetry technique. The repeatability of the proposed sensor, evaluated in terms of relative standard deviation was 1.6% for 10 measurements of a solution of 6.5 mg L^{-1} oxygen. The sensor was applied to determine oxygen in pond and tap water samples showing to be a promising tool for this purpose.

1. Introduction

Carbon ceramic electrodes (CCEs), were introduced for the first time by Lev and co-workers, many works have been reported showing the advantages of such kind of electrodes [1–3]. Based on our own experience CCEs offer great prospects for electroanalytical applications due to their physical rigidity, porosity, easy modification and surface renewal [4–7].

The silica-based sol–gel approach has demonstrated some benefits by using a ceramic as binder in the fabrication of carbon–ceramic composite electrodes. For example, the hydrophobicity, polarity and rigidity can be controlled by chemical modification of the gel precursors [8–11]. These advantages make it an attractive choice in the preparation of electrodes with good electrical conductivity, high stability, porosity and surface renewability.

The use of cheaper technology for the development of an electrochemical sensor for dissolved oxygen detection has attracted great interest than those usually employed. Molecular oxygen reduction is an important process in modern electrochemistry, since a number of chemical and biological reactions can be influenced by the amount of dissolved oxygen [12]. In this respect, interest in the development of dissolved oxygen sensor devices is very important in biochemistry, clinical chemistry, environmental control, medical and industrial fields [13,14]. These devices have been applied for oxygen monitoring in water and sewage industries, food production and storage and they are also brewing a clinical tool for blood analysis [15]. However, direct oxygen reduction at solid electrodes is slow and requires a high over potential, which has directed many research groups to study electrocatalytic reactions of oxygen reduction [16]. Several electron transfer mediators have been used to shuttle electrons between electrode surface and the oxygen. Electrodes modified with palladium [17], bilirubin oxidase [18], hemin [19], metallophthalocyanine [20], ruthenium [21], polyoxometalates [22], cobalt(II) porphyrin complexes [23], a self-assembled monolayer (SAM) of mono-(6-deoxy-6-mercapto)-β-cyclodextrin (βCDSH), iron (III) tetra-(N-methyl-4-pyridyl)-porphyrin (FeTMPyP) and cyclodextrin-functionalized gold nanoparticles (CDAuNP) [24], manganese phthalocyanines films [25], nano sized manganese oxide and cobalt octacyano phthalocyanine [26], Au-nano-DNA film [27], glassy carbon electrode modified with different kinds of electroactive species [28–34] and phthalocyanines [35–38] have been used in the study of oxygen reduction.

Among them, the metallophthalocyanines and porphyrins have received considerable interest due to their singular properties, including high thermal stability and catalytic efficiency for a great number of molecules. These complexes belong to a class that makes possible to investigate details of the factors involved in the activation and reduction of molecular oxygen. Effects from axial and peripheral substitution in the macrocyclic ring, the nature of the metallic center and the conjugation degree of the ring can be cited as examples [39].

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In this context, the present work reports the development of an efficient and stable sensor for oxygen determination based on *in situ* synthesis of cobalt phthalocyanine on SiO_2/C substrate.

2. Materials and methods

2.1. Reagents

All the reagents were of analytical grade and used as received. Tetraethyl orthosilicate (TEOS) (Sigma–Aldrich, 99%), HF (Vetec 48%), graphite (Aldrich, 99.99%, $S_{BET} = 9\,m^2\,g^{-1}$), HNO_3 (nuclear 70%), KCl (Vetec, 99%), KOH (F. Maia 85%), ethanol (Synth 99.9%); NaCl (Carlo Erba, 99%), $MgCl_2$ (Merck, 99%), $CaCl_2$ (Carlo Erba, 96%), $Cu(NO_3)_2$ (Ecibra 98.5%), NH_4Cl (Vetec, 99%), $FeCl_3$ (Ecibra 99%), KNO_3 (Merck, 97%), Other used reagents were: K_2SO_4 (Carlo Erba 99.5%), Resorcinol (Acros 98%) and HCl (Synth, 37%).

2.2. Preparation of material

2.2.1. Synthesis of SiO_2/C by sol–gel

The material SiO_2/C was prepared following a procedure described elsewhere [40]. The SiO_2/C 50% composite material was prepared by the sol–gel method: initially, tetraethylorthosilicate (TEOS) was pre-hydrolyzed in an ethanol solution catalyzed by HNO_3 at 70 °C for 3 h. After that, graphite (Aldrich), deionized water and HF (Vetec) catalyst were added to the pre-hydrolyzed TEOS solution. The mixture was sonicated until gelation of the material and then allowed to rest. The xerogel obtained was dried at room temperature and then ground to fine powder and washed thoroughly, initially with deionized water and then with ethanol in soxhlet extractor for 3 h. Finally the product was dried under vacuum at 393 K for 4 h.

2.2.2. In situ synthesis of Co(II) phthalocyanine in the pores of the matrix

CoPc was generated *in situ* on the SiO_2/C powder matrix as described elsewhere for a similar material [40]. In brief, 1.0 g of SiO_2/C was immersed in 10 mL of 0.01 mol L^{-1} cobalt acetate solution and the mixture was heated in a water bath at 343 K until complete evaporation of the solvent. The dry solid SiO_2/C/Co(II), was mixed with 0.22 g of phthalonitrile and heated in sealed ampoule at 493 K for 3 h to form the CoPc complex, followed by soxhlet extractor with ethanol for 2.5 h to remove excess of cobalt phthalocyanine and unreacted phthalonitrile. Then the solid was heated at 398 K under vacuum to evaporate all the solvent resulting in the material SiO_2/C/CoPc.

The amount of the *in situ* complex formed on SiO_2/C/CoPc was determined by immersing 10 mg of the SiO_2/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 SiO_2/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 of the matrix [40].

2.2.3. Fabrication of electrode

The working electrode, a disk with 0.5 cm diameter and an approximately ~0.01 cm thickness, was prepared by pressing 25 mg of SiO_2/C/CoPc under 4 tons of pressure. The disk was immersed in pure fused paraffin at 343 K under vacuum (10^{-3} Torr pressure), 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 to a glass tube with gel glue and was maintained in a vertical position facing downward and allowed to air-dry at room temperature for 24 h. The electrical contact was made by a copper wire inserted inside the glass tube. In order to improve the connection between the wire and the disk surface, pure graphite powder was added to the glass tube.

In a similar way a working electrode, a disk with 0.5 cm diameter and an approximately ~0.01 cm thickness, was prepared by pressing 25 mg of classically mixed (21.25 mg SiO_2/C and 3.75 mg CoPc) under a 4 ton pressure. The remaining processes are the same as described above. The electrode is designated as SiO_2/C/CoPc-classically and used as a working electrode.

2.3. Apparatus

The specific surface area of the SiO_2/C was measured by nitrogen adsorption on a Quantachrome Autosorb Automated Gas Sorption instrument, using the BET method.

Diffuse reflectance spectra (UV–vis DRS) of (SiO_2/C/CoPc), plotted as the Kubelka–Munk function F(R∞), was recorded on a CARY 5 G UV–vis spectrophotometer. Barium sulfate was used as a white reference sample.

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 (3 M Electrical Division, Brazil) adhered to an aluminum support and coated with a gold layer using a Bal-Tec MD20 metallizing system.

Electrochemical measurements were performed using a PGSTAT-20 Autolab potentiostat. All the experiments were carried out in a conventional three-electrode system, which was composed of a working electrode, a platinum wire counter electrode and a saturated calomel reference electrode (SCE). Measurements were carried out in an electrochemical cell containing 25 mL of 1 mol L^{-1} KCl supporting electrolyte solution, at pH 7. Adjustment of the pH of the electrolyte solution was carried out by KOH/HCl solutions.

The different concentrations of O_2 in solution at different pH were adjusted with N_2 and O_2 gas with help of a Digimed DM-4 oxymeter with Clark electrode. All the measurements were carried out at 298 K.

3. Results and discussion

3.1. Characteristics of the matrix

From the N_2 adsorption–desorption isotherm (figure not shown) the specific surface area and pore volume of SiO_2/C was determined as $S_{BET} = 170\,m^2\,g^{-1}$ and $p_v = 0.90\,cm^3\,g^{-1}$ respectively. The material shows a mesopore distribution region (figure not shown) with maximum at 15.8 nm diameter, according to the IUPAC classification [41].

3.2. In situ generation of CoPc

The *in situ* synthesis of CoPc can be described by two reaction steps [40]. In the first step, cobalt acetate reacts with Bronsted acid —OH groups present on the silica surface, making the metal chemically adsorbed on the silica surface by a reaction with formation of a Si—O—Co bond (Fig. 1). 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 in Scheme 1.

The *in situ* reaction allows the adsorption of Co(II) on the surface of the matrix, since it is not possible to adsorbed the metal ion

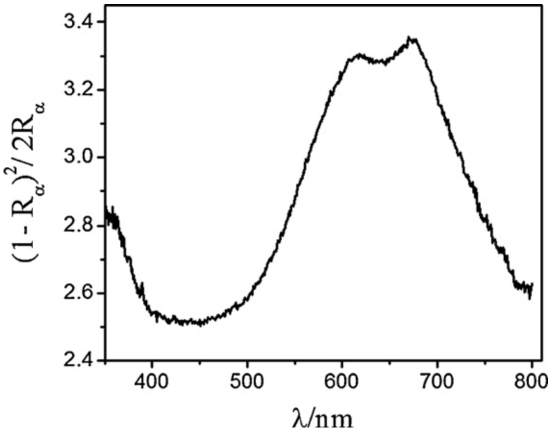
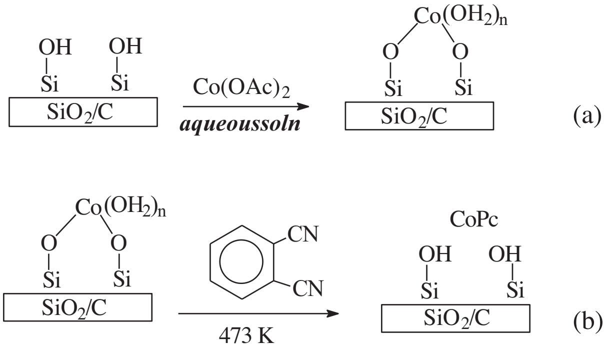


Fig. 1. UV–vis diffuse reflectance spectra of SiO_2/C/CoPc, expressed in Kubelka–Munk units.



Scheme 1. *In situ* generation of cobalt phthalocyanine (CoPc) inside the pores of SiO_2/C: Si—OH Bronsted acid sites in the pores of the matrix: (a) adsorption of Co(II) on the surface through SiO—Co bond formation and (b) generation of CoPc inside the pore.

throughout the bulk phase, as we concluded, when carrying out the electrochemical experiments.

The solid state diffuse reflectance spectrum of the immobilized CoPc on SiO_2/C material shows two broad electronic transition bands observed at 618 and 672 nm (Fig. 1). These two transitions are assigned as Q bands for Co(II) under D_{4h} symmetry, slightly distorted in the confined CoPc in the pores of the matrix [40].

The amount of CoPc generated on the matrix: SiO_2/C/CoPc = 0.26 (±0.01) mmol g^{-1} (1.53(±0.01) wt.%). The surface densities of CoPc on the matrix surface, defined as $\delta = Nf/S_{BET}$ (in mol cm^{-2}), where Nf is the amount of the complex species incorporated (in mol g^{-1}), is: $\delta = 1.5 \times 10^{-10}$ mol cm^{-2} [40].

Table 1
Quantitative results of EDS spectrum.

Element	Weight (%)	Atom (%)
C	13.75	21.20
O	45.27	52.38
Si	39.25	25.87
Co	1.73	0.54

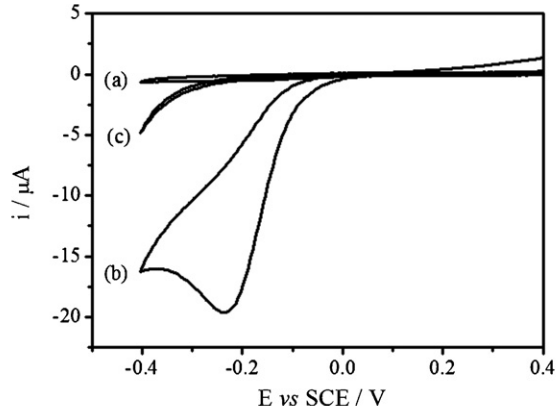


Fig. 3. Cyclic voltammograms for: SiO_2/C/CoPc electrode in the absence (a) and presence of O_2 (b) and voltammogram of SiO_2/C bare electrode in the presence of O_2 (c) in the concentration of 9.1 mg L^{-1} O_2. Experimental conditions: T = 298 K, scan rate υ = 10 mV s^{-1}; 1 mol L^{-1} KCl; pH = 7.

SEM and EDS images are shown in Fig. 1. Within the magnification used we can observe that there are no segregated phases of SiO_2 and graphite particles (Fig. 2a) and the surface EDS image (Fig. 2b) shows within the magnification used, cobalt are homogeneously dispersed throughout the matrix surface. Table 1 also shows the quantitative results obtained of the EDS spectrum and the amount of cobalt (in weight and atom %) are 1.73 and 0.54 respectively, this amount is sufficient for electrocatalysis.

3.3. Electrochemical characterization and sensor performance

Fig. 3 shows the cyclic voltammograms obtained for the SiO_2/C electrode modified with CoPc in the absence (a) and presence (b) of 9.1 mg L^{-1} of oxygen, and the bare SiO_2/C electrode in the presence of oxygen in the same concentration (c) were recorded. As can be seen the material SiO_2/C/CoPc allows a reduction at −0.23 V, a potential closer to zero, suggesting a good electrocatalysis and reduces the influence of the interfering in the measurement signal. The absence of the anodic wave in the voltammograms suggests, this process is controlled by the electron transfer step. To confirm

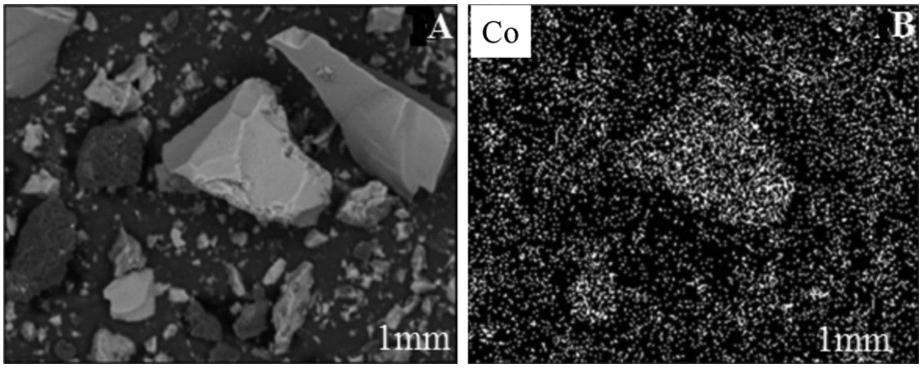


Fig. 2. SEM image (a) and EDS mapping of Co (b) for SiO_2/C/CoPc.

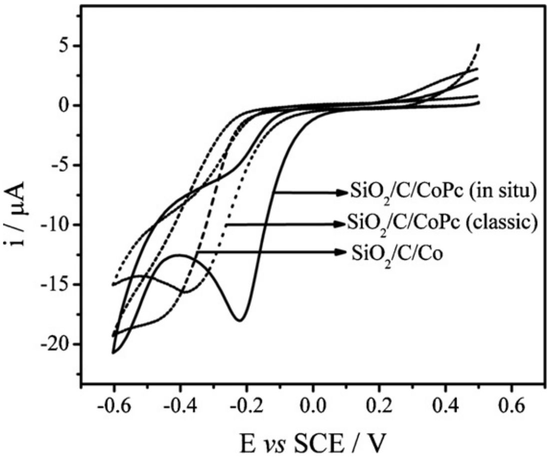


Fig. 4. Cyclic voltammograms obtained for: SiO_2/C/CoPc-*in situ* electrode (solid line), SiO_2/C/CoPc-classically electrode (dotted line) and SiO_2/C/Co electrode (dashed line), all in the presence of 8.2 mg L^{-1} O_2. Experimental conditions: $T = 298$ K, $\upsilon = 10$ mV s^{-1}; 1 mol L^{-1} KCl, pH = 7.

this fact the k_o was calculated using $|E_p - E_{p/2}|$ for a relationship according to Eq. (1) [42].

$$(k_o)_{25\ ^\circ\mathrm{C}} = 1.11\, D_o^{1/2} (E_p - E_{p/2})^{-1/2}\, \upsilon^{1/2} \tag{1}$$

where D_o (cm^2 s^{-1}) is the diffusion coefficient and υ (V s^{-1}) is the scan rate. The $|E_p - E_{p/2}|$ for a scan rate of 10 mV s^{-1} was 84 mV and the electron transfer constant (k_o) was 1.67×10^{-3} cm s^{-1}, characteristics of a quasi-reversible system where the electro transfer is reasonable.

The bare SiO_2/C electrode did not show any redox peak. The presence of carbon in the silica matrix is very important to reduce the electrical resistance and increasing the conductivity of the materials and also the incorporate ion of pure fused paraffin in the electrode eliminates the gas from the matrix pores and reducing the capacitive current.

3.4. Electrocatalytic reduction of oxygen on CoPc modified SiO_2/C electrode and influence of phthalocyanine

Fig. 4 shows the cyclic voltammogram obtained for the oxygen reduction on the SiO_2/C/CoPc *in situ* (solid line), on the SiO_2/C/CoPc classically (dotted line) and SiO_2/C/Co electrode (dashed line). Two important aspects can be verified in this figure, *i.e.* (i) a slightly positive shift of 157 mV for *in situ* immobilized CoPc on SiO_2/C matrix, when compared with classically mixed CoPc with SiO_2/C electrode and (ii) a more pronounced shift of 220 mV for the SiO_2/C/CoPc (*in situ*) electrode, when compared to the SiO_2/C/Co electrode. It is also evident from this figure that phthalocyanine plays an important role in the reduction of oxygen, due to their macrocyclic nature including extended π-systems, phthalocyanines are capable of undergoing fast redox processes, with minimal reorganizational energies and can act as mediators in electron transfer processes involving a great variety of molecules [43].

3.5. Mechanistic studies of the oxygen reduction on SiO_2/C/CoPc

Additional information about the oxygen reduction on SiO_2/C/CoPc was obtained by analyzing the catalytic currents from the cyclic voltammograms. There are two possible mechanisms for oxygen reduction, one involving two electrons, with formation of H_2O_2 (Eq. (1)) and other involving four electrons, with formation of water (Eq. (2)).

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \tag{1}$$

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \tag{2}$$

Study of the mechanism of the electrochemical oxygen reduction can be performed by changing the scan rate in the cyclic voltammetry under a constant oxygen concentration (Fig. 5a). The measurements have showed a linear correlation between current response and the square root of scan rate (Fig. 5b). Since cobalt phthalocyanine is strongly confined in the pores of the matrix, dissolved oxygen must diffuse into the surface–solution interface. Using these results can be possible to perform a mechanistic study of oxygen reduction reaction.

The relationship between cathodic peak current and square root of the scan rate ($\upsilon^{1/2}$) can provide important information about the oxygen reduction reaction. In this case, the numbers of electrons (n) involved in the overall reaction can be calculated from the slope of the curve of Fig. 5b, according to the equation for a totally irreversible process controlled by diffusion [44]:

$$i_p = (2.99 \times 10^5) n [(\alpha) n_a]^{1/2}\, C_o^*\, D_o^{1/2}\, \upsilon^{1/2} A \tag{3}$$

where α is the electron transfer coefficient, n_a represents the number of electrons involved in the rate-determining step, D_o (cm^2 s^{-1}) is the diffusion coefficient, C_o^* (mol cm^{-3}) is the concentration of electroactive species, A (cm^2) is the electrode surface area, n is the total number of electrons, and υ (V s^{-1}) is the scan rate. The measurements were performed in the concentration of oxygen at 9.0 mg L^{-1} and diffusion coefficient for oxygen in aqueous solution considered was 1.9×10^{-5} cm^2 s^{-1} [31].

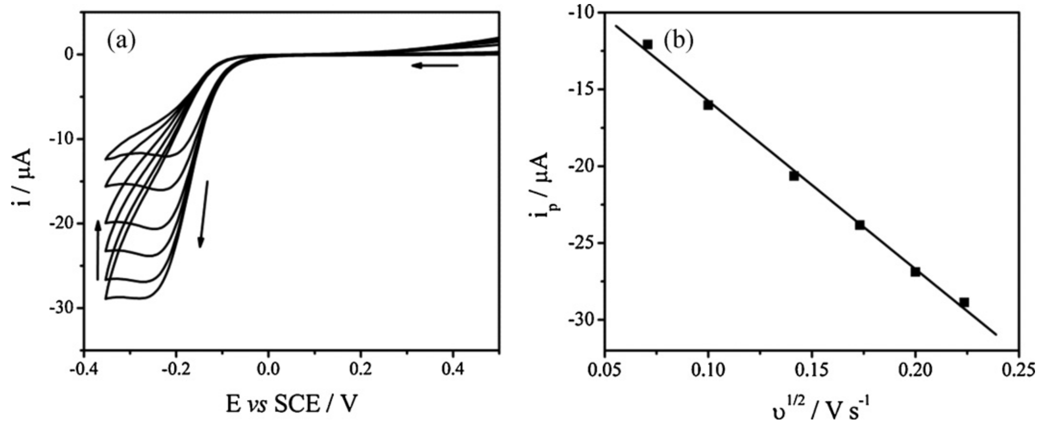


Fig. 5. (a) Cyclic voltammograms of the SiO_2/C/CoPc electrode at different scan rates (mV s^{-1}): from top to bottom: 5, 10, 20, 50, 75, 100, 150, 200. (b) Plot of cathodic peak current against square root of the scan rate ($\upsilon^{1/2}$). Experimental conditions: $T = 298$ K, [O_2] = 9.0 mg L^{-1}; 1 mol L^{-1} KCl; pH = 7.

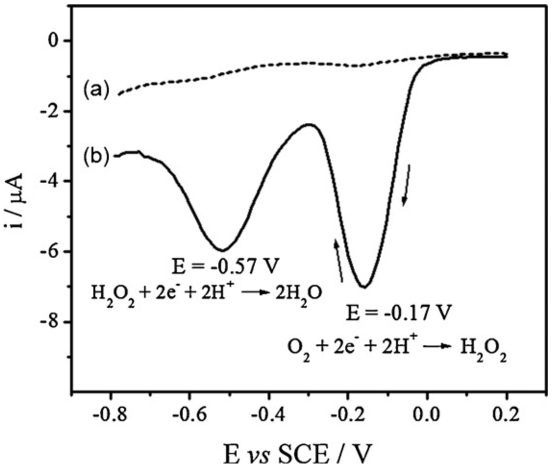


Fig. 6. Differential pulse voltammetry measurement of SiO_2/C/CoPc electrode in the absence (a) and presence (b) of 9.0 mg L^{-1} O_2. Experimental conditions: T = 298 K; 1 mol L^{-1} KCl; pH = 7; υ = 10 mV s^{-1}.

The $(\alpha)n_a$ value can be calculated using a relationship between the peak potential E_p and the potential of the half wave peak $E_{p/2}$, which is described in the equation:

$$(\alpha)n_a = \frac{47.7\ \text{mV}}{E_p - E_{p/2}} \tag{4}$$

The reduction process of the analyte hampered by diffusion in the pores of the material SiO_2/C/CoPc, with increasing scan rate 5–50 mV s^{-1}, obtaining an average value of $|E_p - E_{p/2}|$ equal to 91.35 mV. The value obtained for $(\alpha)n_a$ was equal to 0.52. By using this value and the slope 109.46 $\mu A/(V\,s^{-1})^{1/2}$ of the curve obtained in Fig. 5b, the value of n is equal to 2.07. This means that the proposed mechanism have predominantly with participation of 2 electrons, with formation of H_2O_2. Therefore, a peak must be observed for the peroxide reduction with formation of water. Differential pulse voltammetry was used to demonstrate two peaks (Fig. 6): one at −0.17 V potential, related to the oxygen reduction, and another at −0.57 V, assigned to the peroxide reduction.

For systems with cobalt phthalocyanine, the α value commonly used in the literature is 0.5 [45] and from Eq. (4), was possible to calculate the n_a. The value obtained was 0.96, suggesting that only one electron participate in the determining step. With this information, it is possible to propose a mechanism for the oxygen reduction reaction.

The electrochemical behavior in different solution pH was verified in the range between 4 and 8. The peak potential does not show a great variation, this behavior is characteristic of the system, where metal center of the complex is responsible for the electrocatalytical process. Therefore, to understand a possible mechanism involved in the electrocatalysis of oxygen reduction. The proposed mechanism is described hereafter [45]:

$$\text{Co}^{\text{II}}\text{Pc} + O_2 \rightarrow \text{Co}^{\text{III}}\text{Pc—}{O_2}^{-} \tag{5}$$

$$\text{Co}^{\text{III}}\text{Pc—}{O_2}^{-} + e^{-} + H^{+} \rightarrow \text{Co}^{\text{II}}\text{Pc—}O_2H \tag{6}$$

$$\text{Co}^{\text{II}}\text{Pc—}O_2H + e^{-} + H^{+} \rightarrow \text{Co}^{\text{II}}\text{Pc} + H_2O_2 \tag{7}$$

In the pH 4–8, the small current changes have shown (Fig. 7). There was slight increase in the current at lower pH values. Further measurements were performed at pH equal to 7, since, there was no significant difference in the current as compared to lower pH, while, this is the pH of physiological media. Measurements performed among successive cycles showed a good stability of this material, indicating that the material does not suffers a leaching process.

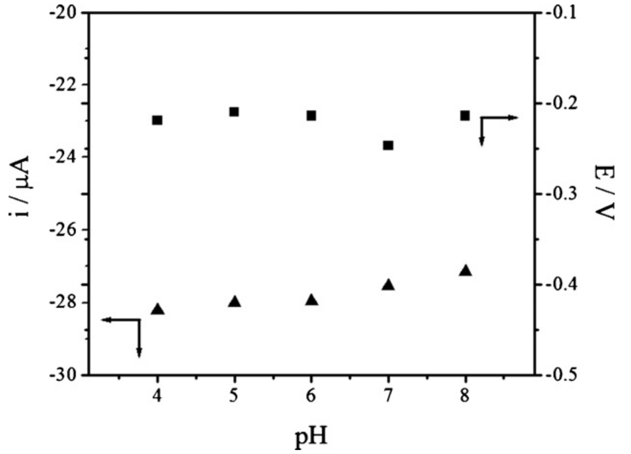


Fig. 7. Values of cathodic peak current and reduction peak potential at a function of the solution pH obtained for the SiO_2/C/CoPc electrode. $[O_2]$ = 9.0 mg L^{-1}; T = 298 K, and υ = 10 mV s^{-1}.

Table 2
Electrode response obtained with different electrode prepared in the same way, containing 6 mg L^{-1} of oxygen.

Electrode	1	2	3	4	5
i (μA)	14.66	14.64	15.02	14.59	16.28
RSD (%)			4.7		

3.6. The sensor characteristics

The sensor characteristics of SiO_2/C/CoPc were verified by amperometry technique. In these measurements, an initial study was performed in order to determine the best potential to be applied in the electrode. The applied potential was chosen based on the measurement of the catalytic current verified at applied potential of –0.23 V *versus* SCE (data not shown). The amperometric curves were recorded at different concentrations of oxygen in solution (Fig. 8a). A linear response range resulted from 0.5 to 6.6 mg L^{-1}, which can be expressed according to the equation: Δi (μA) = −0.84 (±0.27) – 2.16 (±0.07) $[O_2]$ (mg L^{-1}), with a correlation coefficient of 0.996 (for n = 9), was obtained from Fig. 8b. This behavior permits the use of this material as sensor to monitor dissolved oxygen. The sensor presented a sensitivity of 2.16 μA L mg^{-1} and a limit of detection 0.01 mg L^{-1}, in a dynamic range from 0.5 up to 6.6 mg L^{-1} of oxygen.

3.7. Stability of CoPc on the SiO_2/C electrode

The stability of the SiO_2/C/CoPc electrode was checked by recording successive cyclic voltammograms. After 100 cycles no significant changes in the currents response was observed. Furthermore, when the electrode was stored at room temperature no significant change in the response was observed for more than 24 months, just by polishing with emery paper to renew the surface to obtain the same response. This electrode showed good repeatability for oxygen determination. The relative standard deviation of the cathodic peak for ten determinations of 6.5 mg L^{-1} O_2 was 1.6%. Similarly a series of 5 sensors prepared in the same procedure and tested in the same experimental condition containing 6 mg $L^{-1}$of oxygen gave responses with a relative standard deviation of 4.7% shown in Table 2. These experiments indicated that the SiO_2/C/CoPc have good stability (data not shown) and repeatability, probably due to the strong adsorption of CoPc in the SiO_2 matrix.

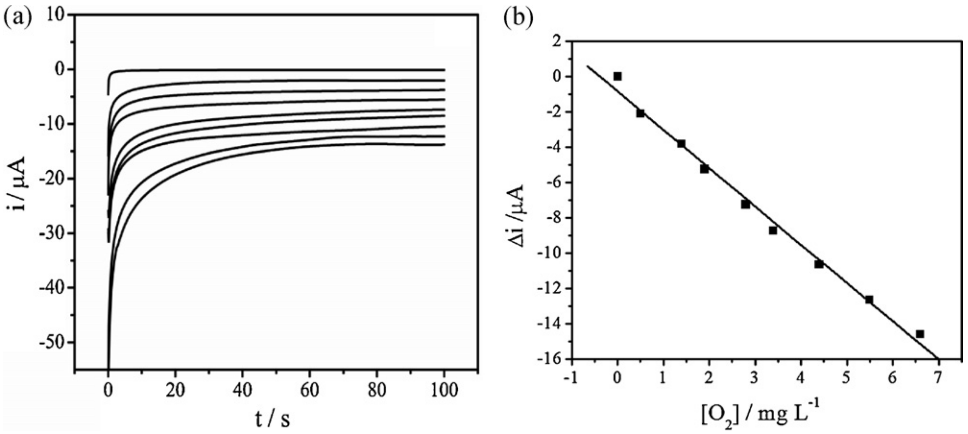


Fig. 8. (a) Amperometry response of the SiO_2/C/CoPc electrode in different oxygen concentrations ($mg\,L^{-1}$): from top to bottom: 0.0, 0.5, 1.4, 1.9, 2.8, 3.4, 4.4, 5.5, 6.6. (b) Plot of cathodic current (Δi_{cp}) *versus* [O_2] (measured at 50 s). Experimental conditions: $T = 298$ K, $E_{appl} = -0.23$ V; 1 $mol\,L^{-1}$ KCl; pH 7.

Table 3
Determination of dissolved oxygen in pond and tap water by the proposed sensor and DO meter (determinations in triplicate).

Dissolvedoxygen ($mg\,L^{-1}$)		
Samples	Proposed method	DO meter
Pond water 1	4.65 (±0.13)	4.60 (±0.10)
Pond water 2	4.74 (±0.15)	4.68 (±0.11)
Tap water 1	4.46 (±0.12)	4.40 (±0.14)
Tap water 2	4.42 (±0.13)	4.37 (±0.11)

$E_{appl} = -0.23$ V *versus* SCE.

Table 4
Interference effects on the detection of dissolved oxygen determination with proposed method in KOH/HCl pH 7 and oxygen concentration of 6 $mg\,L^{-1}$ and interference species concentration = 150 $mg\,L^{-1}$.

Added species	Response change (%)
Na^+	1.02
Ca^{2+}	1.00
$NH_4{}^+$	0.97
Fe^{3+}	0.97
Mg^{2+}	0.99
$NO_3{}^-$	1.02
$SO_4{}^{2-}$	1.03
Cu^{2+}	0.97
Resorcinol	0.90

3.8. Application to the water sample and interference studies

The developed sensor was applied for the determination of dissolved oxygen level in the pond and tap water samples, comparing with the oxygen determined by using a dissolved oxygen meter according to Chen et al. [46]. The results of the determinations are listed in Table 3. The results obtained with the proposed sensor were consistent with those obtained with the dissolved oxygen meter. In addition, applying a paired Student's *t*-test to compare such methods, it was possible to observe that, at 95% confidence level, there was no statistical difference between the comparative and proposed methods.

The effects of foreign species commonly found in water samples on the determination of dissolved oxygen were investigated and the results are listed in Table 4. The sensor response was evaluated in the presence of 150 $mg\,L^{-1}$ Na^+ (NaCl), Mg^{2+} ($MgCl_2$), Ca^{2+} ($CaCl_2$), Cu^{2+} (Cu^{2+} $(NO_3)_2$), $NH^{4\,+}$ (NH_4Cl), Fe^{3+} ($FeCl_3$), NO^{3-} (KNO_3), $SO_4{}^{2-}$ (K_2SO_4) and resorcinol, in a solution of 6 $mg\,L^{-1}$ O_2. As can be verified, the observed influences are all less than 2% on dissolved oxygen response. These results reveal that the developed sensor can tolerate a high concentration of foreign species and, therefore, can be stated as selective over the commonly present species in the samples.

4. Conclusions

A SiO_2/C/CoPc pressed disk electrode with solid paraffin filled pores considerably decreased the electrical resistance and current capacity. 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. Pressed disk electrode is a good alternative when compared with other electrodes based on SiO_2 to provide structural rigidity and chemical stability. The proposed sensor presented a good response for dissolved oxygen at applied potential of −0.23 V. Optimization of the experimental condition yielded detection of O_2 much better than those sensors reported in the literature. This sensor showed good repeatability for both the measurement and electrode preparation, evaluated in term of relative standard deviation, allied with a simple and easy preparation. Thus, the present sensor is a feasible alternative to Clark-type amperometric sensor, since it possesses the advantages of membrane-free, maintenance free, can be miniaturized and present low detection limit.

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