



## Dissolved O<sub>2</sub> sensor based on cobalt(II) phthalocyanine immobilized *in situ* on electrically conducting carbon ceramic mesoporous SiO<sub>2</sub>/C material

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### ARTICLE INFO

#### Article history:

Received 5 July 2012

Received in revised form 12 October 2012

Accepted 23 October 2012

Available online 1 November 2012

#### Keywords:

Carbon ceramic material

Cobalt phthalocyanine

Dissolved oxygen sensor

Sol–gel

### ABSTRACT

This work describes the preparation of mesoporous carbon ceramics SiO<sub>2</sub>/50 wt.% C ( $S_{\text{BET}} = 170 \text{ m}^2 \text{ g}^{-1}$ ), 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<sub>2</sub>/C/CoPc was used to analyze dissolved oxygen in water by an electrochemical technique in neutral media and dissolved O<sub>2</sub> was reduced at  $-0.23 \text{ V}$ . The linear response range, sensitivity and detection limit obtained were  $0.5\text{--}6.6 \text{ mg L}^{-1}$ ,  $2.16 \mu\text{A L mg}^{-1}$  and  $0.01 \text{ mg L}^{-1}$ , respectively, by chronoamperometry. A mechanism involving two electrons in O<sub>2</sub> 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  $6.5 \text{ mg L}^{-1}$  oxygen. The sensor was applied to determine oxygen in pond and tap water samples showing to be a promising tool for this purpose.

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### 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)- $\beta$ -cyclodextrin ( $\beta$ CDSH), 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<sub>2</sub>/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%,  $S_{\text{BET}} = 9 \text{ m}^2 \text{ g}^{-1}$ ), HNO<sub>3</sub> (nuclear 70%), KCl (Vetec, 99%), KOH (F. Maia 85%), ethanol (Synth 99.9%); NaCl (Carlo Erba, 99%), MgCl<sub>2</sub> (Merck, 99%), CaCl<sub>2</sub> (Carlo Erba, 96%), Cu(NO<sub>3</sub>)<sub>2</sub> (Ecibra 98.5%), NH<sub>4</sub>Cl (Vetec, 99%), FeCl<sub>3</sub> (Ecibra 99%), KNO<sub>3</sub> (Merck, 97%), Other used reagents were: K<sub>2</sub>SO<sub>4</sub> (Carlo Erba 99.5%), Resorcinol (Acros 98%) and HCl (Synth, 37%).

### 2.2. Preparation of material

#### 2.2.1. Synthesis of SiO<sub>2</sub>/C by sol–gel

The material SiO<sub>2</sub>/C was prepared following a procedure described elsewhere [40]. The SiO<sub>2</sub>/C 50% composite material was prepared by the sol–gel method: initially, tetraethylorthosilicate (TEOS) was pre-hydrolyzed in an ethanol solution catalyzed by HNO<sub>3</sub> 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<sub>2</sub>/C powder matrix as described elsewhere for a similar material [40]. In brief, 1.0 g of SiO<sub>2</sub>/C was immersed in 10 mL of 0.01 mol L<sup>-1</sup> 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<sub>2</sub>/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<sub>2</sub>/C/CoPc.

The amount of the *in situ* complex formed on SiO<sub>2</sub>/C/CoPc was determined by immersing 10 mg of the SiO<sub>2</sub>/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<sub>2</sub>/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<sub>2</sub>/C/CoPc under 4 tons of pressure. The disk was immersed in pure fused paraffin at 343 K under vacuum (10<sup>-3</sup> 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<sub>2</sub>/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<sub>2</sub>/C/CoPc-classically and used as a working electrode.

### 2.3. Apparatus

The specific surface area of the SiO<sub>2</sub>/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<sub>2</sub>/C/CoPc), plotted as the Kubelka–Munk function  $F(R_{\infty})$ , 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<sup>-1</sup> 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<sub>2</sub> in solution at different pH were adjusted with N<sub>2</sub> and O<sub>2</sub> 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<sub>2</sub> adsorption–desorption isotherm (figure not shown) the specific surface area and pore volume of SiO<sub>2</sub>/C was determined as  $S_{\text{BET}} = 170 \text{ m}^2 \text{ g}^{-1}$  and  $p_v = 0.90 \text{ cm}^3 \text{ g}^{-1}$  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 adsorb the metal ion

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