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Application of manganese (II) phthalocyanine synthesized in situ in the SiO_2/SnO_2 mixed oxide matrix for determination of dissolved oxygen by electrochemical techniques

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ABSTRACT

This work describes the in situ immobilization of Mn(II) phthalocyanine (MnPc) in a porous SiO_2/SnO_2 mixed oxide matrix obtained by the sol gel processing method. The chemically modified matrix SiO_2/SnO_2/MnPc, possessing an estimated amount of 8×10^{-10} mol cm^{-2} of MnPc on the surface, was used to prepare an electrode to analyze dissolved oxygen in water by an electrochemical technique. The electrode was prepared by mixing the material with ultrapure graphite and evaluated using differential pulse voltammetry. Dissolved O_2 was reduced at −0.31 V with a limit of detection (LOD) equal to 7.0×10^{-4} mmol L^{-1}. A mechanism involving four electrons in O_2 reduction was determined by the rotating disk electrode technique.

1. Introduction

Mixed oxides based on silica frameworks, SiO_2/M_xO_y, have been subjects of great interest in recent years and they have been used in different applications, such as HPLC columns [1,2], as adsorbents [3] and in the immobilization of electroactive species for use as electrochemical sensors [4–6]. These mixed oxides present on their surface free Si–OH and M–OH which allow post functionalization of the mixed oxide surface with electroactive species resulting a matrix potentially useful for fabrication of electrochemical sensors [7].

Metallated phthalocyanines belong to a class of compounds that have attracted great interest since the resulting complex MPc (M = transition metal) has as its principal characteristics high chemical stability [8,9]. Associated with this desirable property, a focus of increasing interest on MPc has been its electrochemical properties enhanced by the π electrons of conjugated bonds with which the central metal is involved [10,11]. Therefore, MPc has been used to fabricate electrochemical sensors for determination of several analytes [12–16].

O_2 sensing is very important in several areas because it participates in industrial and environmental processes [17] and in the reaction that occurs in the mitochondria, where oxygen is catalyzed by the enzyme cytochrome C oxidase [18,19]. Other important applications of these sensings are oxygen monitoring in natural water to determinate the degree of pollution [20,21], in the food industry and in clinical analyses [22,23]. The method most used to determine the concentration of dissolved oxygen uses the Clark electrode. With the Clark electrode the reduction occurs at a potential of −0.6 V (vs SCE) [17], so the use of a gas-permeable membrane is necessary. Since changes in membrane permeability can significantly affect the electrode response [24,25] an alternative has been the use of modified electrodes with selective mediators, dispensing with use of the Clark electrode [26].

In this work the in situ generation of Mn(II) phthalocyanine inside the pores of SiO_2/SnO_2 and further use of the material obtained to fabricate an electrochemical sensor for determination of dissolved oxygen in natural water is described. In order to circumvent characteristics associated with low mechanical resistance shown when CPE electrode is used [27,28], a hard pressed disk of the material well mixed with ultra pure carbon, accordingly to recently described procedures [29,30], was prepared. The material obtained SiO_2/SnO_2/MnPc was used to fabricate an electrode presenting as its principal characteristics a high mechanical resistance and chemical stability, associated with a good electrical conductivity.

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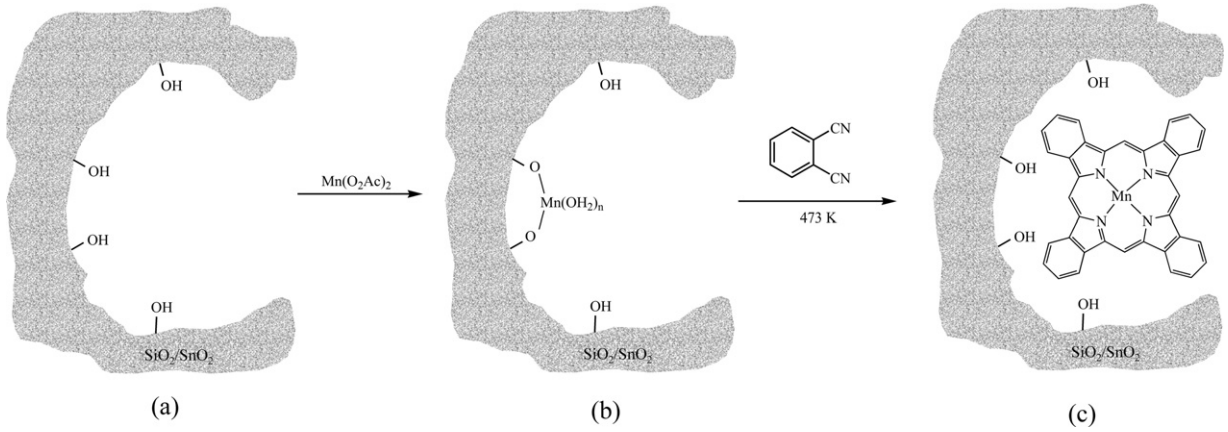

Fig. 1. In situ generation of MnPc inside the pores of SiO_2/SnO_2: a) –OH Brϕnsted acid sites in the pores of the matrix b) adsorption of Mn(II) on the surface through SiO_2/SnO_2/–O–Mn bond formation and c) generation of MnPc inside the pore.

2. Material and methods

2.1. Synthesis and characterization of SiO_2/SnO_2/MnPc

The mixed oxide SiO_2/SnO_2 was prepared by the sol–gel method using tetraethyl orthosilicate (TEOS, 98%, Aldrich) and dibutyl-tin-diacetate (Acros) as precursor reagents. About 12 mL of TEOS (53.4 mmol) was dissolved in 12 mL of pure ethanol (99.9%, Synth) and then 2.0 mL of pure water and 0.2 mL of concentrated HCl (37%, used as catalyst) were added. The solution was stirred at 353 K for 3 h in a reflux system to promote the prehydrolysis of TEOS and then 0.8 mL of dibutyl-tin-diacetate was added. After stirring this resulting solution for 1 h, 3.0 mL more of water and 0.3 mL of HCl were added, the solution was stirred for 3 h more at 333 K and then allowed to stand at this temperature for gelation. The amount of SnO_2 incorporated in the sol gel material SiO_2/SnO_2 obtained was determined by X-ray fluorescence on an EDXRF Spectrace model 5100 X-ray fluorescence spectrometer using standard SiO_2/SnO_2 of known compositon.

The specific surface of the material, previously degassed at 423 K for 6 h, was obtained on a Quantachrome Autosorb Automated Gas Sorption, using the BET method, in a relative pressure range, P/P_0, between 0.05 and 0.25. The pore size distribution was obtained using the BJH method.

Manganese(II) phthalocynine (MnPc) was synthesized in situ inside the pores of the material according to a procedure described elsewhere for CoPc [30]. In the first step, inside the SiO_2/SnO_2 pore and using the Brϕnsted acid sites –OH (Fig. 1a), Mn(II) is adsorbed onto the surface through matrix/–OMn bond formation (Fig. 1b). Then, phthalonitrile is mixed with the modified solid and this is heated at 473 K, generating the complex species MnPc inside the matrix pore, as shown in Fig. 1c [30].

2.1.1. X-ray photoelectron spectra (XPS)

XPS spectra of the powdered samples fixed on a steel holder with double-faced adhesive tape were obtained on a SPECS PHOIBOS150 HSA3500 spectrometer, with nine single channel electron multipliers. The X-ray source with an Al anode (line Ka, $h\nu = 1486.6$ eV) operating at 10 kV and 15 mA and an analyzer pass energy of 40 eV was used.

2.2. Electrode fabrication

The SiO_2/SnO_2/MnPc disk was prepared by mixing a fine powder of the material with pure carbon graphite (99.99%) and then pressed at high pressure into a rigid disk format [31]. The electrochemical measurements were carried out on an Autolab Eco Chemie model PGSTAT30 potentiostat. The three electrode system consisting of a working electrode, Pt as the counter electrode and a saturated calomel electrode (SCE) as the reference was used. The rigid disk electrode (RDE) was used as working electrode.

3. Results and discussion

3.1. Characteristics of the material

From the N_2 adsorption-desorption isotherm (Fig. 2) the specific surface area of SiO_2/SnO_2 was determined as $S_{BET} = 299\ m^2\ g^{-1}$. By applying the BJH method the pore size distribution was obtained (Fig. 2 inset) indicating that the material is microporous [32].

XPS spectrum shows the $Mn2p_{3/2}$ BE peak at 643.1 eV, indicating that only Mn(II) is present on the surface [33]. Integrating the area under this peak, the estimated amount of this metal present on the surface was 0.13 Mn atom % at the depth probed by the technique.

The solid state diffuse reflectance spectrum of the material, the presence of MnPc in the matrix is clearly detected. The Q bands are broader and observed at ~674 and ~731 nm, when compared with those of pure MnPc. This peak broadening in the matrix presumably resulted from the confinement and slight distortion of the complex in the pores of the solid matrix [34,35].

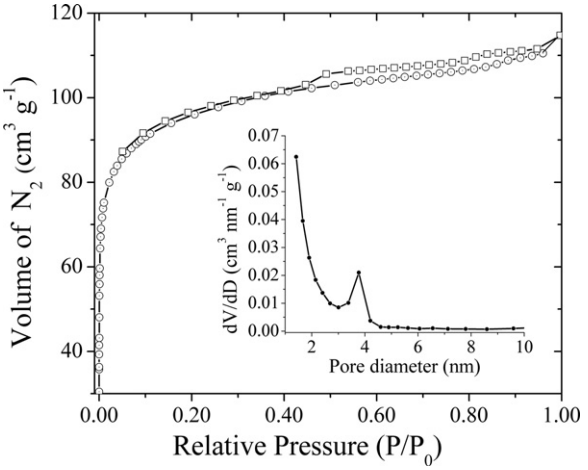

Fig. 2. N_2 adsorption–desorption isotherm for SiO_2/SnO_2 and pore size distribution (Figure inset).

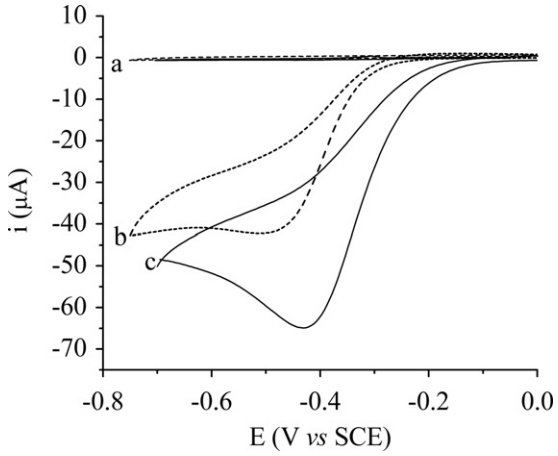

Fig. 3. Cyclic voltammetry curves obtained using the RDE electrodes: a) (---) SiO_2/SnO_2 and (---) SiO_2/SnO_2/MnPc under a nitrogen atmosphere, b) SiO_2/SnO_2 in the presence of dissolved oxygen and c) SiO_2/SnO_2/MnPc in the presence of dissolved oxygen. Experimental conditions: T = 298 K, scan rate υ = 5 mV s^{-1}; 1 mol L^{-1} KCl supporting electrolyte; pH of the solution 6.5; [O_2] = 0.2 75 mmol L^{-1}.

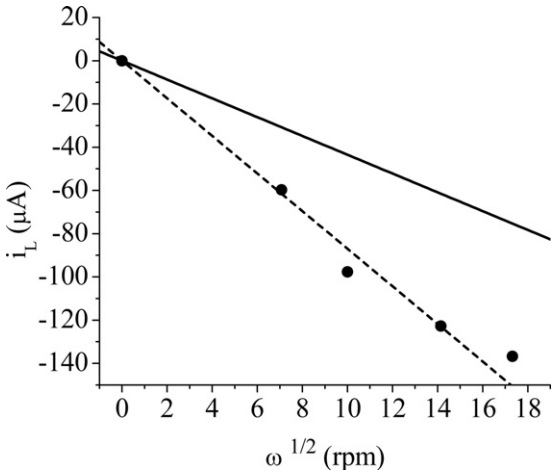

Fig. 5. Plot of limiting current i_L intensity against $\omega^{1/2}$. Calculated ideal plots of reactions involving 2 and 4 electrons: (●) experimental points, (—) 2 electrons and (---) 4 electrons.

3.2. Electrochemical measurements

The surface density of MnPc on the electrode surface was estimated by integrating the area under the peak of the oxidation or reduction process [$Mn^{II}Pc^{2-}$]/[$Mn^{III}Pc^{2-}$] measured by CV in the absence of O_2 [36]. The value found was 1.8×10^{-10} mol cm^{-2}.

Initial tests with the electrodes were made using the chemically modified electrode SiO_2/SnO_2/MnPc and the bare electrode SiO_2/SnO_2 to study the sensitivity towards dissolved oxygen in water. Cyclic voltammetry was used and the results shown in Fig. 3. Fig. 3a shows that no electrode response is observed when the potential is scanned between −0.8 and 0.0 V for both electrodes in the absence of oxygen. In presence of dissolved O_2, with a fixed concentration of 0.275 mmol L^{-1} at 298 K, on the bare electrode surface, the reduction peak is observed at the potential E = −0.50 V (Fig. 3b) and on the modified electrode surface at E = −0.42 V (Fig. 3c). The Current enhancement on the chemically modified electrode, compared to the bare electrode, is clearly observed.

An experiment to test the chemical and mechanical stability of the electrode, keeping the dissolved O_2 concentration constant and measuring the current intensity of the reduction peak maximum, i_{cp}, throughout the measurements, consisted of 100 complete oxidation–reduction cycles at pH 6.5 (Fig. 4). The invariance of i_{cp} observed in this experiment results from two important properties of the supporting substrate: First, the high mechanical stability conferred by the SiO_2 framework and, second, the strong confinement of the electroactive species MnPc in the pores of the rigid support that prevents its release to the solution phase during the experiments. A third important aspect is the invariance of the current intensity, i_{cp}, when the pH of the solution phase is changed between 4.5 and 11, as also shown in Fig. 4.

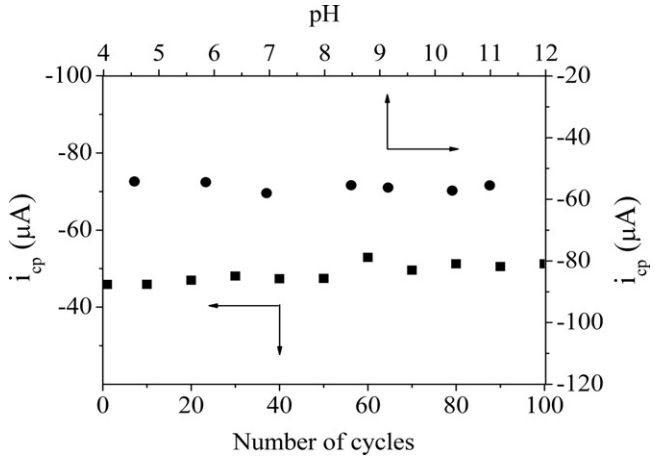

Fig. 4. Values of the i_{cp} current as functions of the numbers of oxidation-reduction cycles and as functions of pH. [O_2] = 0.275 mmol L^{-1}; T = 298 K.

An additional experiment was carried out at pH 6.5 with the dissolved oxygen fixed at 0.275 mmol L^{-1}, changing the scan rates (υ) between 5 and 100 mV s^{-1} (figure not shown). Plotting the peak maxima i_{cp} against $\upsilon^{1/2}$ a linear correlation was obtained indicating that the process is a diffusion controlled process [6]. Since the electroactive species MnPc is confined in the pores of the matrix, it is supposed that the pH of this environment remains constant despite changes in the external solution phase [37]. This hypothesis supports the invariance of i_{cp} when the solution pH is changed, as shown in Fig. 4.

Oxygen reduction can occur by two different mechanisms, one involving two electrons, with the formation of H_2O_2 (Eq. (1)), and other involving four electrons, with the formation of water (Eq. (2)) [19]:

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O_2 \quad (1)$$

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad (2)$$

Estimation of the number of electrons involved in the reduction of O_2 on the electrode surface was obtained by using the rotating disk electrode technique. The values of limiting currents (i_L) were applied to the Levich equation [38]:

$$i_L = (0.620)nFAD^{2/3}\omega^{1/2}\upsilon^{-1/6}C \quad (3)$$

where, n is the number of electrons per molecule oxidized or reduced, F is the Faraday constant, A is the electrode area, D is the diffusion coefficient of the species (5×10^{-6} cm^2 s^{-1}), ω is the rotation rate of the electrode, υ is the kinematic viscosity of the solution (0.01 cm^2 s^{-1}) and C is the O_2 concentration.

A plot of the limiting current i_L vs $\omega^{1/2}$ showed a linear correlation (Fig. 5) that is fitted by a model involving four electrons.

3.3. Determination of dissolved O_2

To determine the concentration of dissolved oxygen in water, differential pulse voltammetry (DPV) was used. As shown in Fig. 6a, oxygen reduction occurs at a potential of −0.3 V. The measurements

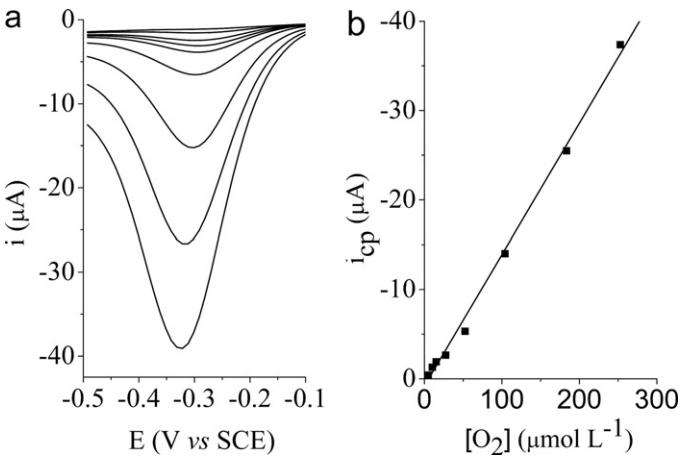

Fig. 6. (a) DPV curves for different concentrations of dissolved O_2 (in μmol L^{-1}): from top to bottom: 0, 5, 10, 15, 28, 53, 104, 183, 253. (b) Plot of i_{cp} vs [O_2] at 298 K.

performed at different concentrations of the dissolved oxygen concentrations (Fig. 6b) showed an analytical curve with linear correlation described by the equation:

$$i(\text{mA}) = 0.806\ (\pm 0.406) - 0.147\ (\pm 3.72 \times 10^{-2})\ [\text{O}_2]\ (\text{mmol L}^{-1}) \quad (4)$$

with $r = 0.995$ ($n = 8$).

The limit of detection (LOD) of this electrode was calculated applying the equation:

$$\text{LOD} = 3\frac{S_b}{S} \quad (5)$$

where S_b is the standard deviation of the blank and S is the slope of the analytical curve [39,40]. The LOD obtained was 7.0×10^{-4} mmol L^{-1} with electrode sensitivity of -0.147 μA L μmol^{-1}. This value is lower than the LOD of other electrodes proposed in the literature using silver nanorods on a gold surface [41] and a sensor using cobalt tetrasulphonated phthalocyanine (CoTSPc) immobilized on a poly-l-lysine (PLL) film [38] with LOD of 1.72×10^{-3} and 2.25×10^{-3} mmol L^{-1}, respectively, and of the same order of magnitude as an electrode using iron tetrasulphonated phthalocyanine with β-cyclodextrin in a modified gold electrode [23], which presented LOD equal to 6.25×10^{-4} mmol L^{-1}.

4. Conclusion

The mixed oxide SiO_2/SnO_2, obtained by the sol–gel processing method and containing 15 wt% of SnO_2, produced a microporous matrix with $S_{BET} = 299\ m^2\ g^{-1}$. The in situ generation of the electroactive species MnPc inside the pores of the matrix resulted in a homogeneous dispersion of the metal complex on the surface. As a consequence, an electrode containing the confined electroactive species in the pores of the matrix, permitted an efficient electrochemical sensor for dissolved oxygen. As the O_2 diffuses into solid–solution interface in the pores of the matrix where the electroactive species are confined, changes of the external solution pH did not affect the reduction potential with current intensity i_{cp} remaining practically invariant the pH between 4 and 11.

Since the material to fabricate the electrode was mixed with ultrapure graphite and pressed at high pressure ($\sim 4 \times 10^3$ kg cm^{-2}) the disk obtained presented high mechanical stability as well as high reproducibility of the measurements with time of use and had easy maintenance. The limit of detection and the sensitivity show that the electrode is potentially useful as a dissolved oxygen sensor.

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