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Electrocatalytic activity of cobalt phthalocyanine stabilized by different matrixes

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Abstract The behavior of cobalt phthalocyanine complexes incorporated inside an hydrotalcite-like clay (HT) or a sonogel–carbon composite has been investigated in order to develop chemically modified electrodes suitable for use as amperometric detectors. The electrocatalytic oxidation process of cysteine at this new electrode has been studied by cyclic voltammetry. For comparison, the oxidation of cysteine catalyzed by the cobalt phthalocyanine complex as a redox mediator, either dissolved in solution or entrapped inside the HT structure, has been followed by polarography. The sonogel–carbon composite electrode is stable and its response is repeatable. Cysteine oxidation is actually induced by the electrogenerated Co(III) complex, and the relevant anodic peak current varies linearly with cysteine concentration within the range 9.0×10^{-4} to 1.0×10^{-2} mol L^{-1}.

Keywords Sonogel–carbon electrode · Hydrotalcite · Cobalt phthalocyanine complexes · Electrocatalysis · Cysteine

Introduction

Metal porphyrins, metal phthalocyanines, and other macrocyclic complexes usually undergo both reversible oxidation and reversible reduction. It has been reported that many reactions are electrocatalyzed by these complexes [1, 2, 3], and if a suitable metal center is present these complexes can be used to reduce simple inorganic species such as carbon dioxide [4], molecular oxygen [5], and nitrite [6, 7].

In particular, cobalt phthalocyanine (CoPc) and its derivatives have electrocatalytic behavior related to both the Co^{III}/Co^{II} and the Co^{II}/Co^{I} redox couples [3, 8, 9]. The possibility of improving the efficiency of such metal complexes in catalytic redox processes by immobilization in close proximity to an electrode surface has been acknowledged for a relatively long time [5, 10]; this way of performing electrocatalyzed redox reactions enhances the stability, lifetime, and selectivity of the catalyst and increases the yield from the catalysis. Among methods suitable for preparing electrodes modified by metal phthalocyanines (MPc–CME) are:

1. mixing of MPc with carbon to give a conductive paste [11, 12, 13];
2. electropolymerization with simultaneous electrodeposition [9, 14, 15, 16]; and
3. adsorption on to the surface of a glassy carbon electrode (GCE) [11, 16, 17].

An important field of research on the electrocatalytic activity of MPc is oxidation of sulfydryl compounds [12, 18] that are oxidized irreversibly at conventional electrodes, thus requiring quite positive potentials. Many electrochemical studies have been devoted to L-cysteine (CysSH) [9, 17], because of the importance of this molecule in living systems. In addition to cystine, oxidation of L-cysteine at platinum, gold or glassy carbon electrodes leads to further oxidation products and is accompanied by adsorption and formation of a surface film, which inactivates the electrode. Consequently, electrochemical detection of cysteine and other thiols has usually been performed at mercury or mercury amalgam electrodes at which the mercury sulfide species formed can be oxidized at comparatively low applied potentials [12], or at electrodes modified with transition metal macrocycles, such as MPc. Although very promising, the use of MPc–CME for the determination of

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CysSH is often poorly effective, because the electrocatalytic activity decreases with time [9, 19]. Such a decrease has been attributed to poisoning of the electrode surface by adsorption of cystine; the drawback is less evident at very low pH, because cystine does not precipitate on to the electrode under these conditions.

In this paper we report results from an investigation performed to develop electrode systems, based on a CoPc compound incorporated either into an hydrotalcite-like clay (HT) or into a sonogel–carbon composite (SCC) [20], with electrocatalytic activity in the oxidation of thiols. The long-term stability of the responses obtained was also of interest. The HT are minerals and synthetic materials with positively charged brucite-type layers of mixed-metal hydroxides which are sometimes known as layered double hydroxides (LDH). Exchangeable anions located in the interlayer spaces compensate for the positive charge of the brucite-type layers. They have general formula $M^{II}_{1-x}M^{III}_{x}(OH)_2[A^{n-}]_{x/n}.yH_2O$, where A^{n-} is the interlayer anion which gives the HT peculiar properties [21, 22]. These materials (hereafter referred to as M^{II}/M^{III}-X) can be successfully used to modify an electrode surface under different critical operating conditions, e.g. high temperatures or strongly oxidizing media [23]. The solgel matrix, on the other hand, is an alternative route for processing materials at low temperature with a large variety of structures and shapes [24].

Combining the two goals outlined, a coating consisting of HT intercalated by cobalt phthalocyanine tetrasulfonate (CoTSPc) and a sonogel–carbon composite including CoPc were investigated as electrode systems for immobilizing the redox active species; cysteine was chosen as a benchmark substrate.

Experimental

Reagents

L-Cysteine, Co(II) phthalocyanine (CoPc), anhydrous acetonitrile (ACN), tetrabutylammonium hexafluorophosphate (TBAHP), tetrahydrofuran (THF), bis-*n*-butyl phthalate (DBP), poly(vinyl chloride) (PVC), HCl, H_2SO_4, Na_2HPO_4, and KH_2PO_4 were of analytical-reagent grade purity from Aldrich. Cobalt(II) 4,4′,4″,4‴-tetrasulfonate phthalocyanine (CoTSPc) and [Mg/Al-CoTSPc] HT were prepared and purified by following methods described in the literature [25]. Glassy carbon rods (GC-20 S from Tokai Carbon, Tokyo, Japan) were used to prepare the glassy carbon electrodes. The graphite powder (spectroscopic grade RBW) was from SGL Carbon (Ringsdorff, Germany). Methyltrimethoxysilane (MTMOS) was from Merck and was used without further purification. Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford, MA, USA).

Apparatus

A Philips model PW 1050/81-PW 1710 diffractometer with CuKα radiation source (λ=1.5418 Å) was used for XRD measurements. FTIR and UV–visible spectra were recorded with Perkin Elmer model 1759 and Varian Cary model 1E spectrophotometers, respectively.

The catalytic oxidation of cysteine was followed by DC polarography performed in solutions saturated with pure oxygen (>99.5%) by passage of the gas both before and during the reaction. The saturation conditions were checked by measuring the height of the polarographic wave arising from O_2 reduction.

Dropping mercury electrode (DME) polarograms were obtained by use of an Amel (Milan, Italy) model 470/WR multipolarograph, the current/potential responses being recorded on an Amel model 863 X/Y recorder. A drop time of 0.5 s was chosen for the polarographic tests.

All electrochemical investigations were performed out with a three-electrode system. Unless otherwise specified the solution in the electrochemical cell was de-aerated by bubbling with pure nitrogen (99.999%). In all experiments a saturated calomel electrode (SCE) and a platinum wire were used as the reference and counter electrodes. All potential values given in this paper are referred to the SCE. pH was measured with a Radiometer (Copenhagen, Denmark) PHM 84 pH meter. Cyclic voltammograms were acquired with an Autolab PGSTAT 20 multimode electrochemical system (EcoChemie, Utrecht, The Netherlands) under the control of appropriate software (GPES, EcoChemie). When the working electrode material was GC (0.075 cm^2 geometric area) the surface was polished to a mirror-finish with 0.3 and 0.05 µm alumina on felt pad, rinsed with de-ionized water and sonicated in Millipore water to remove any traces of trapped alumina. The working electrodes were prepared as described below.

Electrode-modification procedures

GC coated with [Mg/Al-CoTSPc]HT

An HT suspension was prepared by adding ca 30 mg previously milled HT powder to 10 mL carbonate-free de-ionized water. The resulting heterogeneous mixture was sonicated for approximately 30 min and finally stirred overnight. Because all attempts to obtain a colloidal solution failed, it was difficult to form a stable HT film on the electrode. A 10-µL aliquot of the HT suspension was deposited with a micropipet on the clean electrode surface and the resulting clay-modified electrode was stored at room temperature for 24 h up to complete dryness of the coverage. The coarse characteristics of the coating were checked with an optical microscope.

GC coated with [Mg/Al-CoTSPc]HT in PVC film

To obtain electrode coverage of greater mechanical stability and homogeneity a thin film of [Mg/Al-CoTSPc]HT was prepared with PVC as a dispersing material. A solution containing PVC and the DBP plasticizer in THF (both 0.028% w/w, 600 µL) was added to a suspension of 100 mg HT in 500 µL THF; the heterogeneous mixture was stirred and then sonicated to achieve acceptable stability. This PVC/DBP/HT ratio was chosen after trying repeatedly to produce a film as stable as possible. The suspension (5 µL) was deposited on the cleaned GC electrode, which was stored at room temperature for 24 h until complete dryness. The coating appeared homogeneous when observed with an optical microscope and was found to be stable.

Sonogel–carbon composite electrodes containing cobalt phthalocyanine (SCC–CoPc)

For these we used CoPc instead of CoTSPc, because its insolubility in water prevents any leakage from the sonogel composite matrix. To prepare the SCC matrix [20, 26, 27] MTMOS (0.5 mL) and HCl (catalyst) solution (0.2 mol L^{-1}, 0.1 mL) were mixed in a glass vessel and then sonicated for 10 s to initiate hydrolysis. MTMOS was used to obtain hydrophobic electrodes [28], so that only the outer section of the electrode was active. Electrodes of different composition were prepared and studied. In particular, either 1 g graphite powder or 1 g of a powder consisting of graphite and different percentages of CoPc (1.5%, 5%, or 10% w/w) was added to the sonogel mixture. The resulting paste was always homogenized for

1 min. The sticky black pastes (electrodes denoted SCC–CoPc1.5%, SCC–CoPc5%, and SCC–CoPc10%, respectively) were used to fill glass tubes (70 mm length, 1.15 mm diameter) to a height of approximately 3 mm and these were finally left to dry overnight under ambient conditions (25°C). Electrical contact was ensured by means of a 0.5-mm diameter copper wire. The electrodes were first polished with 1200 P grit emery paper (silicon carbide) then gently with weighing paper; they were finally washed with Millipore water.

Results and discussion

Catalytic oxidation of cysteine to cystine by [Mg/Al-CoTSPc] HT

The capability of CoTSPc intercalated into the [Mg/Al]HT to catalyze the oxidation of cysteine was tested by comparing the results obtained for three different kinds of process, when:

1. no metal complex is present in the reaction medium;
2. CoTSPc is dissolved in the solution (homogeneous system); and
3. [Mg/Al-CoTSPc] HT is suspended in the reaction medium (heterogeneous system).

It is well known from the literature that cysteine can be analyzed quantitatively by polarography after the oxidation of mercury to adsorbed mercury cysteinate ($E_{1/2}\approx-0.47$ V, at pH 7.4) [29]. When working in oxygen saturated solutions, however, it is impossible to use the polarographic wave for analytical purposes, because it strongly overlaps the first cathodic process of molecular oxygen, which here has a maximum of the first kind. As a consequence the polarographic wave relative to the reduction of cystine ($E_{1/2}\approx-0.88$ V) was chosen. The wave is cathodic to oxygen reduction, and we were able to check whether the constant oxygen contribution could be reliably subtracted, so that the calculated limiting current was linearly dependent on cystine concentration. The three tests were all performed at pH 7.4, which enabled us to prevent HT dissolution.

Non-catalyzed reaction

The stoichiometry of the oxidation of cysteine by molecular oxygen is expressed by:

$$4\mathrm{RSH} + \mathrm{O}_2 \rightarrow 2\mathrm{RSSR} + 2\mathrm{H}_2\mathrm{O} \quad (1)$$

where RSH=cysteine and RSSR=cystine. This reaction has been performed in 0.02 mol L^{-1} borate buffer solution (pH adjusted to 9.25) [25], the buffer also acting as the supporting electrolyte. Each experiment was performed under an oxygen atmosphere. The saturation conditions were determined by following the growth of the polarographic wave attributable to O_2 reduction in an aqueous solution of cysteine (0.05 mol L^{-1}, 400 μL) was added, under an oxygen atmosphere, to 20 mL of the stirred buffered solution and the oxidation reaction was followed by dc polarography. After ca 6 to 7 h only one fourth of the initial cysteine was converted to cystine.

Homogeneous catalysis

The reaction was performed by following the procedure described above except that 5.14 mg CoTSPc were added to the stirred solution, which was left to equilibrate for 30 min under an oxygen atmosphere before the addition of cysteine. Quantitative oxidation required approximately 1 to 2 h.

Heterogeneous catalysis

In this experiment 3.43 mg [Mg/Al-CoTSPc] HT were added to the stirred solution, saturated with oxygen, before adding cysteine. Between successive polarographic measurements the suspension was stirred continuously to ensure good contact between catalyst and substrate. Approximately 1 to 2 h were required for the quantitative oxidation. Fig. 1 reports the values of the corrected polarographic limiting current for cystine reduction, taken as a measurement of cysteine concentration, as a function of the time elapsed after addition of cysteine.

Each point is an average of three measurements performed on three different solutions of 1 mmol L^{-1} cysteine in borate buffer. The resulting average relative standard deviation was 4.1%. It is evident that in the presence of the CoTSPc catalyst, both free and incorporated inside the HT, the oxidation of cysteine occurs much more efficiently and rapidly than in the presence of oxygen only. The mechanism of oxidation of cysteine by molecular oxygen in the presence of CoTSPc has been studied by many authors (Ref. [9] and references cited therein) and, according to the accepted kinetic law, the reaction rate depends on the concentrations of cysteine, oxygen, and CoTSPc catalyst. Under our reaction conditions we can safely as-

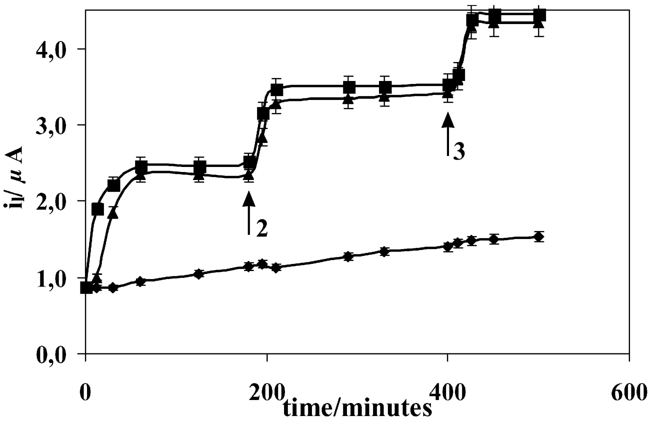


Fig. 1 Plots of limiting current (measured at $E_{1/2}=-0.88$ V) against time for the polarographic reduction of cystine produced under three different conditions: (*diamonds*) no catalyst present; (*squares*) CoTSPc present; (*triangles*) [Mg/Al-CoTSPc] HT present. Experimental conditions: 20 mL oxygen-saturated solution of 1 mmol L^{-1} cysteine in 0.02 mol L^{-1} borate buffer (pH 9.25). Points *2* and *3* indicate the addition of cysteine solution (0.05 mol L^{-1}, 400 μL). Error bars represent one standard deviation (n=3)

sume that the concentrations of both oxygen and CoTSPc are constant at any stage of the reaction and that Eqs. (2), (3), and (4) are valid for the reaction rate in the three different situations:

$$v_1 = k_1\,[O_2]\left[\text{cysteine}\right] = k_1'\left[\text{cysteine}\right] \qquad (2)$$

$$v_2 = k_2\,[O_2]\left[\text{cysteine}\right][\text{CoTSOPc}] = k_2'\left[\text{cysteine}\right] \qquad (3)$$

$$v_3 = k_3\,[O_2]\left[\text{cysteine}\right][\text{CoTSPc}]_{HT} = k_3'\left[\text{cysteine}\right] \qquad (4)$$

where $[\text{CoTSPc}]_{HT}$ represents the 'active' concentration of the cobalt anionic complex in the HT interlayer. By assuming that the oxidation reaction always follows pseudo-first order kinetics approximate relative ratios of 1:10:10 were computed for k_1', k_2', k_3' from the proper kinetic plot. The concentration of cobalt complex used in the heterogeneous catalysis tests is much lower than that used in the homogeneous test (Experimental section). We can therefore conclude that the catalytic activity of CoTSPc not only is preserved when CoTSPc is present in the interlayer of the clay but is even enhanced compared with that of the complex in solution.

For both tests in the presence of catalyst four subsequent additions of substrate were made after reaching the maximum production of cystine, to check the preservation of the catalytic activity by the CoTSPc either when free or incorporated in the hydrotalcite structure (Fig. 1). From these experiments we can conclude that the activity remains essentially unchanged. As an additional indication of the stability of the [Mg/Al-CoTSP] HT it can be also stated that the amount of CoTSPc released by the clay into the buffered solution after immersion for 24 h was less than 4%.

Oxidation of cysteine on [Mg/Al-CoTSPc] HT GC modified electrodes

Because of the difficulty of preparing a colloidal solution, and the consequent poor mechanical stability of the films obtained, we tried to improve the mechanical stability and adhesion to the electrode surface by using PVC as a support system. The electrochemical responses of such electrodes were not very satisfactory, however, because the recorded voltammograms contained no significant signals attributable to the redox couples Co(II)/Co(I) and Co(III)/Co(II) of CoTSPc, and the electrode system had a very high resistance. We therefore chose a different system as a support for the CoPc complex, finally developing an electrode with both the expected catalytic activity and time stability of the response.

Oxidation of cysteine on sonogel–carbon composite electrodes containing cobalt phthalocyanine (SCC–CoPc)

The electrochemical behavior of SCC–CoPc electrodes has been studied in acidic media over the potential range in which oxidation of Co(II) to Co(III) occurs, because at pH<4 [16] autocatalytic oxidation of cysteine to cystine by CoTSPc does not occur. It is known that on CoPc-modified electrodes the electrocatalytic oxidation of cysteine occurs according to the mechanism [9]:

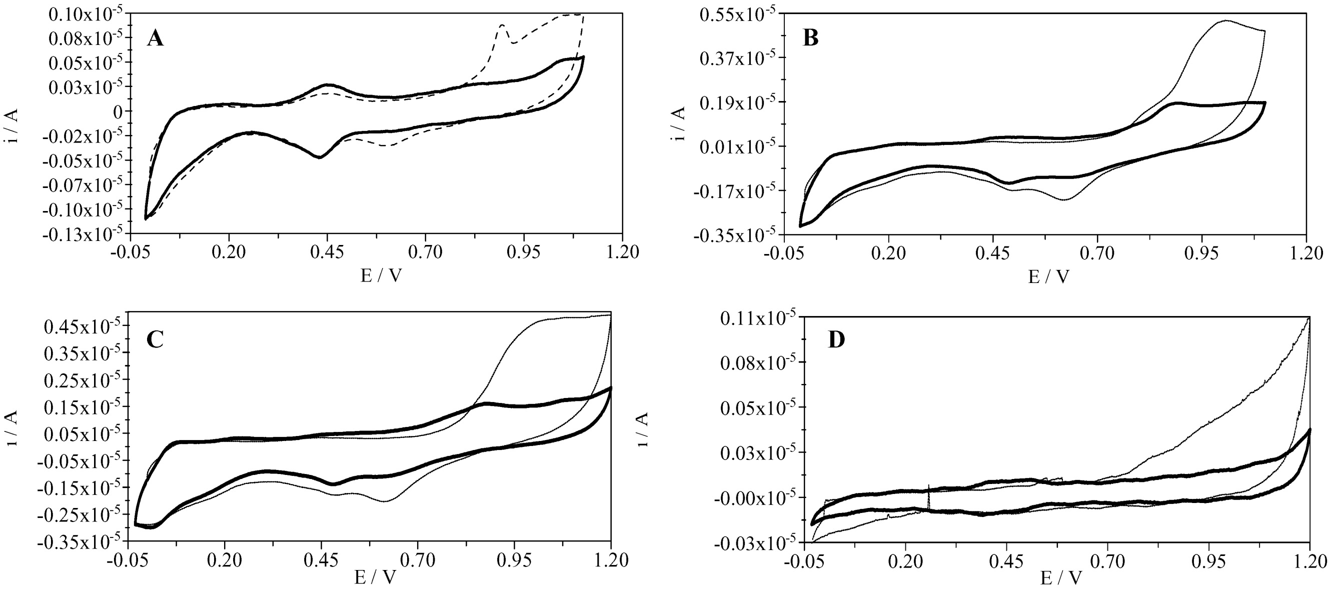
$$\text{Co(II)Pc} \rightarrow \text{Co(III)Pc} + e^- \qquad (5)$$

$$\text{Co(III)Pc} + \text{RSH} \rightarrow \text{Co(II)Pc} + \text{RS}^{+\cdot} + \text{H}^+ \qquad (6)$$

$$2\ \text{RS}^{+\cdot} \rightarrow \text{RSSR} \qquad (7)$$

Figure 2A, B, and C shows the cyclic voltammograms obtained by cycling SCC–CoPc1.5%, SCC–CoPc5%, and SCC–CoPc10% electrodes between 0.00 V and +1.10 or +1.20 V, in 0.05 mol L^{-1} aqueous H_2SO_4 solution (poten-

Fig. 2 Cyclic voltammograms obtained from (**A**) SCC–CoPc1.5%, (**B**) SCC–CoPc5%, (**C**) SCC–CoPc10%, (**D**) SCC electrodes; 1st cycle (*dotted line*), 10th cycle (*full line*). Supporting electrolyte 0.05 mol L^{-1} H_2SO_4; potential scan rate 0.05 V s^{-1}



tial scan rate 0.05 V s^{-1}). The first cycle of all three sets of voltammograms is completely different from the response obtained at steady state (after ca 10 cycles). Let us consider, for example, electrode SCC–CoPc1.5%. The first cycle is characterized by oxidation peaks at +0.46 and +0.90 V, by a large oxidation response centered at ca +1.00 V, and by the reduction peaks at +0.61 and +0.43 V. On repeated cycling of the potential, the broad signal at more positive potentials vanishes and a new oxidation peak centered at +0.86 V gradually arises. This peak is particularly evident in the voltammetric curves obtained with the SCC–CoPc 5% electrode. The signals at higher potentials can be ascribed to the Co(II)/Co(III) redox couple, by comparison with literature reports [12, 30, 31]. The responses obtained at all the electrodes do not decrease further after 10 cycles, when steady state is established. For comparison, the cyclic voltammogram recorded on an unmodified SCC electrode is reported in Fig. 2D; neither anodic nor cathodic signals are present. The change of the responses relative to the Co(II)/Co(III) couple, from the first to the subsequent voltammetric cycles, can be explained as reported by Komorsky-Lovric' (Ref. [30] and references cited therein). During the oxidation of CoPc electrical neutrality is maintained by intercalation of anions from the supporting electrolyte; these are driven out during the reduction process. In cyclic oxidations and reductions gradual loss of the charge-consuming ability of the films occurs, because out-of-plane deformations of the phthalocyanine macrocycles occur, causing irreversible changes to the crystal structure [30].

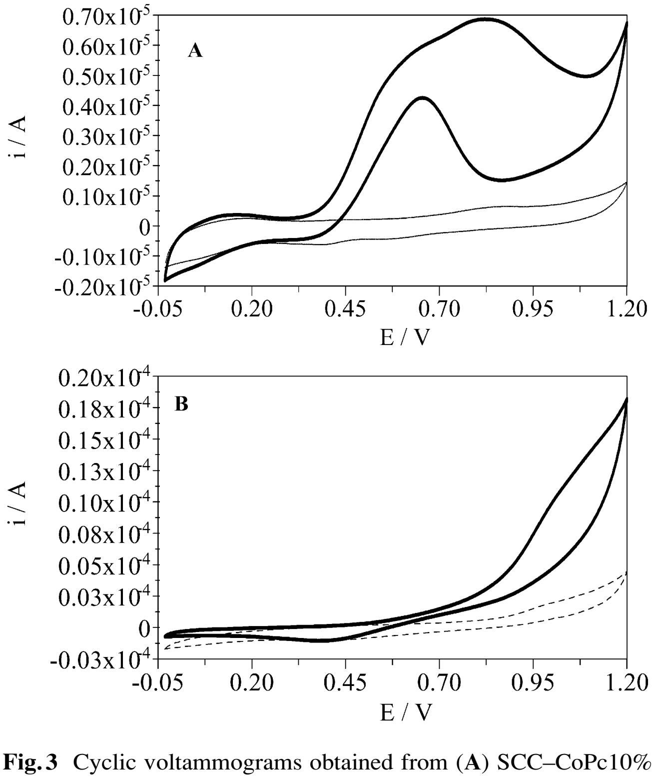


Fig. 3 Cyclic voltammograms obtained from (**A**) SCC–CoPc10% and (**B**) SCC electrodes before (*dotted line*) and after (*full line*) addition of cysteine (1.10×10^{-2} mol L^{-1}). Supporting electrolyte 0.05 mol L^{-1} H_2SO_4; potential scan rate 0.05 V s^{-1}

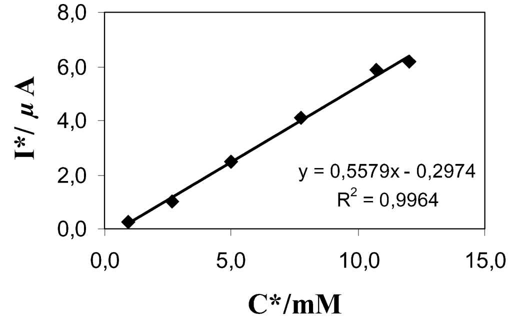


Fig. 4 Calibration plot of I* (μA) against cysteine concentration (C*). I* is the chronoamperometric current measured a fixed, short time after polarization, for each addition of substrate, with the background contribution subtracted; C* is the concentration corrected for dilution

Addition of cysteine to a 0.05 mol L^{-1} H_2SO_4 solution resulted in a marked increase in the current ascribed to the Co(II) to Co(III) oxidation response at SCC–CoPc electrodes, substantially exceeding that observed on an SCC electrode at the same cysteine concentration. As an example, Fig. 3A shows cyclic voltammograms obtained from SCC–CoPc10% before (dotted line) and after (solid line) addition of cysteine at concentrations up to 1.00×10^{-2} mol L^{-1}. Again for comparison, the cyclic voltammogram recorded on the same solution at a simple SCC electrode is reported in Fig. 3B. The catalytic wave centered at +0.86 V increases with cysteine concentration and no cathodic backward response is detectable on the reverse scan within the range of concentrations investigated (9×10^{-4}–1×10^{-2} mol L^{-1}). This is in agreement with the occurrence of a fast catalytic reaction cycle. The features of the voltammetric curves are similar to those reported by Halbert and Baldwin [12], who described the electrocatalytic responses of sulfydryl compounds at electrodes modified with CoPc incorporated into graphite powder. Analogous results were obtained on SCC–CoPc1.5% and SCC–CoPc5% electrodes. To explore the possibility of using the SCC–CoPc electrodes as sensors for quantitative determination of cysteine, chronoamperometric responses were recorded by successive additions of 200 μL of a standard cysteine solution (4.30×10^{-2} mol L^{-1}) to a stirred 10-mL aliquot of 0.05 mol L^{-1} H_2SO_4. On the basis of preliminary tests we selected an applied potential of +0.86 V for these experiments. The response time of the sensor after every addition was very short and the signal was highly repeatable in subsequent tests. As shown in Fig. 4, moreover, by sampling at a fixed time after starting the polarization, linear dependence of chronoamperometric current on concentration was obtained over the entire range investigated.

Conclusions

In the work discussed in this article we studied the behavior of cobalt phthalocyanine complexes incorporated into

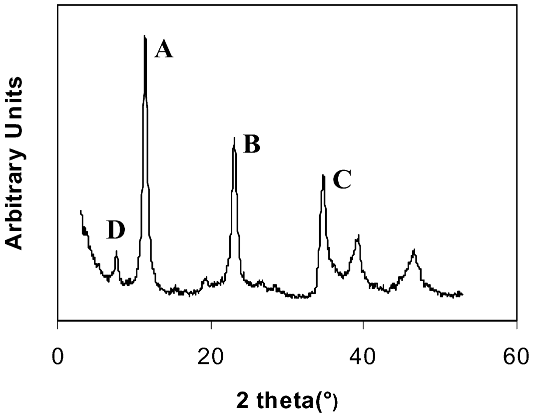


Fig. 5 XRD pattern of the [Mg/Al-CoTSPc] HT

different matrices (hydrotalcite-like clay and a sonogel–carbon composite) with the aim of developing an electrode suitable as an amperometric sensor. The results obtained in this study support the conclusion that the sonogel–carbon composite is an appropriate matrix for immobilization of cobalt phthalocyanine complexes that works well as an electrode and gives repeatable responses. The SCC–CoPc electrodes proved to be suitable for amperometric detection of oxidizable substrates, for example cysteine, mediated by the Co(III)/Co(II) couple. Because of the stability of the matrix and the rapid response, the SCC–CoPc electrode can also be proposed as a detector for use in flow systems.

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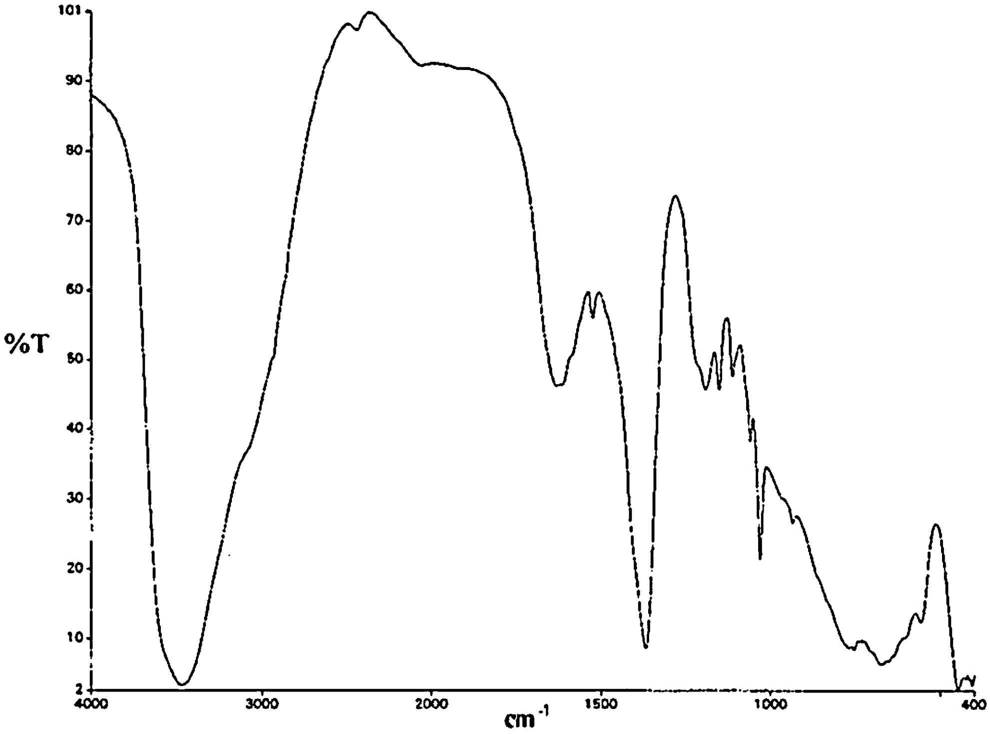
Appendix

Characterization of [Mg/Al-CoTSPc] HT

Figure 5 reports the XRD diffraction pattern obtained from [Mg/Al-CoTSPc] powder. The D reflection is indicative of a basal spacing equal to 23 Å which well agrees with that obtained by Pèrez-Bernal et al. [25] and enables us to conclude that CoTSPc has been intercalated into the anionic clay with the plane of the phthalocyanine ring perpendicular to the brucite sheets in an edge-on similar orientation. At the same time, the presence of A, B, and C reflections, typical of the structure of [Mg/Al-CO_3] HT, suggests that the hydrotalcite was only partially re-constructed. The infrared spectrum of the deep blue powder, reported in Fig. 6, also supports the XRD findings. The typical bands of the $[CoTSPc]^{4-}$ anion intercalated inside the hydrotalcitic phase appear in the regions 1200–1000 cm^{-1} and 800–600 cm^{-1}. They were attributed by comparison with the CoTSPc FTIR spectrum and are in good agreement with the spectra reported for MTSPc in the Aldrich library. The weak band at ca 1368 cm^{-1} due to the ν_3 stretching mode of CO_3^{2-} is also apparent. To evaluate the exact amount of interlayer cobalt anionic complex the synthesized HT was decomposed by 1 mol L^{-1} H_2SO_4 so-

Fig. 6 FTIR spectrum of the [Mg/Al-CoTSPc] HT



lution and the CoTSPc species released was quantified by UV–visible spectrophotometry at the diagnostic peak at λ_{max}=625 nm. The yield is expressed as the ratio between the amount (mol) of the interlayer anion found experimentally and that expected for a quantitative synthetic reaction; the result was approximately 20%. This relatively low value can be related to the persistence of CO_3^{2-} in the clay, as suggested by the IR spectra, both because of to the high affinity of the clay with CO_3^{2-} and the difficulty in intercalating the large CoTSPc anion inside the HT structure. The yield is, however, sufficient high to enable detection of the complex catalytic activity.

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