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In situ preparation of Co phthalocyanine on a porous silica gel surface and the study of the electrochemical oxidation of oxalic acid

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Cobalt phthalocyanine, CoPc, and its derivatives have been studied as catalysts in many electro-oxidation reactions [1]. For such purposes, the electroactive species have been adsorbed or dispersed as electropolymerized thin films onto many kinds of substrate surfaces and used for the oxidation of cysteine [2, 3], nitrite [4], thiols [5] and amitrole (3-amino-1,2,4-triazole) [6]. Procedures to obtain materials presenting high surface densities of the electroactive species have also been studied by their adsorption onto a highly porous substrate surface [7]. In this method the electroactive species is strongly adsorbed inside the matrix pores by an ion exchange reaction process. Furthermore, these materials have been used for oxalic acid and hydrazine oxidation studies [8–10] and oxygen reduction [11]. Other procedures aiming to encapsulate metallated phthalocyanine inside a zeolite cavity [12, 13] or inside the pores of material surfaces presenting high surface areas, such as silica, have been carried out via *in-situ* preparation of the complex [14]. The main objective of this work is to describe a method to obtain CoPc entrapped, by an *in-situ* preparation method, in the pores of highly porous silica gel and its use as a catalyst in an electro-oxidation study of oxalic acid. The interest in using such procedure for preparation is based on the possibility of obtaining highly dispersed electroactive species inside the silica gel matrix pores.

Silica gel presenting a specific surface area of 500 $m^2\ g^{-1}$ and an average pore diameter of 60 Å was immersed in 100 mL of a 0.08 mol L^{-1} cobalt acetate solution. The mixture was allowed to rest for about 8 hrs, with occasional stirring, and the solid was separated by filtration, washed with water and dried at about 373 K. About 10 g of the dry solid, SiO_2/Co(II), was mixed with 5.2 g of phthalonitrile and the mixture was heated in an ampoule at 470 K. The solid was washed with ethanol in a Soxhlet apparatus to remove excess cobalt phthalocyanine and unreacted phthalonitrile.

In order to determine the amount of *in situ* complex formed on the SiO_2 surface, between 25 and 100 mg of the SiO_2/CoPc was immersed in pure ethanol and about 7 mL of pure pyridine was added. The mixture was allowed to rest for 12 hrs to fully extract the CoPc from the SiO_2 surface. The final volume was adjusted to 25 mL and the concentration of the 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 using standard CoPc (Aldrich) in a similar pyridine/ethanol solution.

The carbon paste electrode of the material (working electrode) was prepared by mixing SiO_2/CoPc and graphite in the proportions of 60 and 40 wt%, respectively, and using mineral oil as binder. A system consisting of the working electrode, a SCE electrode as reference and Pt as counter electrode was used. The measurements were carried out on a Autolab PGSTAT 20 apparatus and all the measurements were made in an electrochemical cell at room temperature. The pH of the electrochemical cell solutions was adjusted between 2 and 11 by using HCl or NaOH solutions and measured with a glass electrode connected to a calibrated potentiometer. The differential pulse voltammetry data were obtained by using the carbon paste electrode of SiO_2/CoPc immersed in 1.0 mol L^{-1} KCl supporting electrolyte solution at a scan rate of 20 mV s^{-1}. A pulse amplitude of 10 mV and width of 50 ms were applied. The electrocatalytic behavior of the material for oxalic acid electro-oxidation was studied by using the cyclic voltammetry technique in the potential range between 0.0 and 1.0 V against SCE at a scan rate of 0.02 V s^{-1}.

The preparative procedures can be described by two reaction steps. In the first step, Co(II) is adsorbed on the silica surface by an ion exchange reaction with formation of Si—O—Co bond: $\equiv SiOH + Co(AcO)_2 \rightarrow (\equiv SiO)_2Co + 2HOAc$. In the second step, the adsorbed Co(II) served as the template for phthalocyanine complex formation in the silica pores. The spectrum of the complex extracted from the solid surface, by using pure ethanol mixed with pyridine, is shown in Fig. 1.

The transition bands observed at 600 and 670 nm correspond to the *Q* band of the complex and matches that of pure CoPc complex.

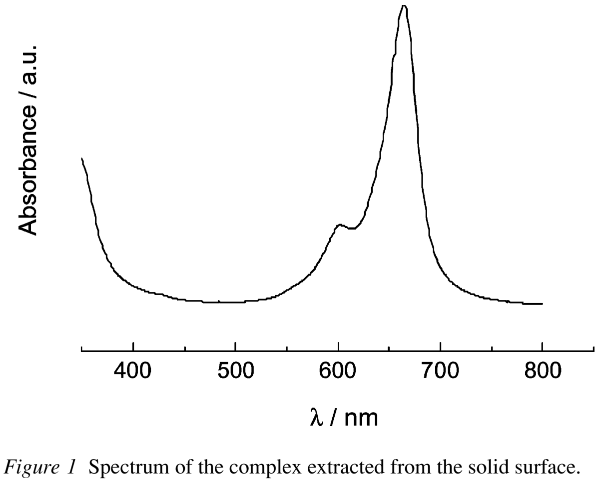

Figure 1 Spectrum of the complex extracted from the solid surface.

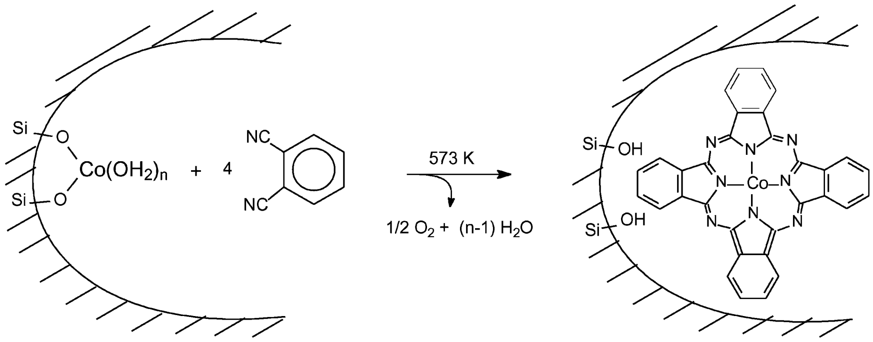

Figure 2 Reaction scheme of Co(II) phthalocyanine complex in the SiO_2 pore.

Chemical analysis showed that 0.22 mmol per gram of CoPc was adsorbed on the SiO_2 surface. An idealized model of how the complex is formed inside the silica pore is illustrated in Fig. 2.

Fig. 3 shows the differential pulse voltammetry for the SiO_2/CoPc electrode. In the anodic scan, Fig. 3a, two peaks, one at 0.19 V and the other one at 0.69 V, are observed. The first peak, of larger magnitude, was attributed to the $Co^{I}Pc/Co^{II}Pc$ oxidation process and the second one to the $Co^{II}Pc/Co^{III}Pc$ oxidation process. In the cathodic scan, Fig. 3b, the peak at 0.66 V was attributed to $Co^{III}Pc/Co^{II}Pc$ reduction process and that at 0.17 V, the peak presenting higher current density, was attributed to the $Co^{II}Pc/Co^{I}Pc$ reversible reduction process [15–17].

In the second step of the experiment, cyclic voltammetry curves after successive additions of oxalic acid into the electrochemical cell, were obtained. In the absence of oxalic acid no current enhancement was observed. Upon the addition of oxalic acid, an anodic current peak at 0.71 V and a redox pair with mid-point potential at ca. 0.5 V (I), were observed. The features of the cyclic voltammogram obtained (Fig. 4) are very similar to those obtained by the linear potential sweeping voltammetric technique. Enhancements of anodic peaks (I) and (II), and the cathodic peak current (III)

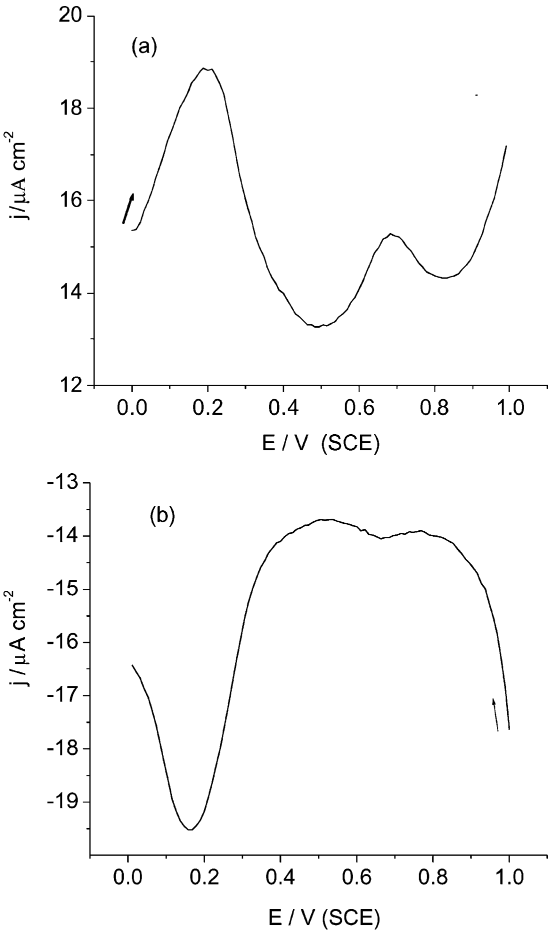

Figure 3 Differential pulse voltammograms of SiO_2/CoPc carbon paste electrode in 1.0 mol L^{-1} KCl, $v = 0.02$ V s^{-1}.

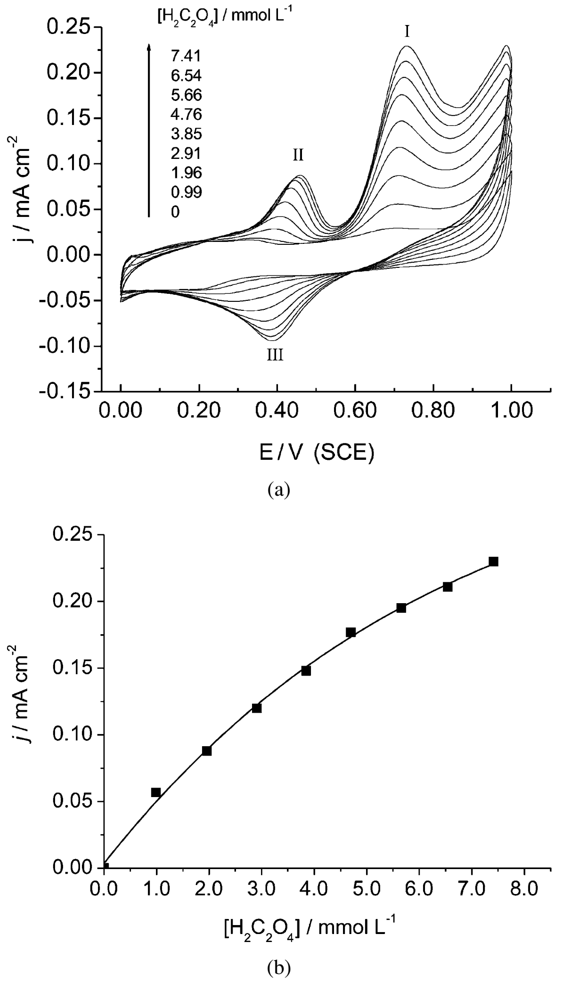

Figure 4 Cyclic voltammetry curves obtained for different concentrations of oxalic acid (in mol L^{-1}): Experimental conditions: scan rate of 0.02 V s^{-1}; supporting electrolyte 1.0 mol L^{-1} KCl (a). Plot of the different concentrations of oxalic acid against the catodic peak current density (b).

by the successive addition of oxalic acid are observed. For the current peak at 0.71 V, its enhancement is due to the presence of more oxalic acid species at the electrode surface, as shown when the current density peak (I) is plotted against the oxalic acid concentration changes. The peaks (II) and (III) are intensified as a consequence of the oxidation process of the oxalic acid, forming more Co(II) complex. Then, the cathodic peak (III) and the anodic peak (II) are enhanced.

In chronoamperometry studies the potential was fixed at 0.71 V and successive additions of known concentrations of oxalic acid were made for a fixed time of 180 s. Fig. 5a shows that the response time is very fast, about 1 s for the current to achieve the maximum value. It means that the charge transfer process is very fast but the slower decrease of the current intensity observed may be attributed to the slow diffusion of oxalic acid into the electrode solid-solution interface. By plotting the charge involved in the oxidation process, Q, against the concentration change of oxalic acid, a linear relationship, described by the equation, Q/mC cm^{-2} $= 1.01 + 5.8$ [oxalic acid]/mmol L^{-1}, with linear correlation $r = 0.997$ and $n = 7$, was obtained. The limit of detection was estimated as 1 mmol L^{-1}.

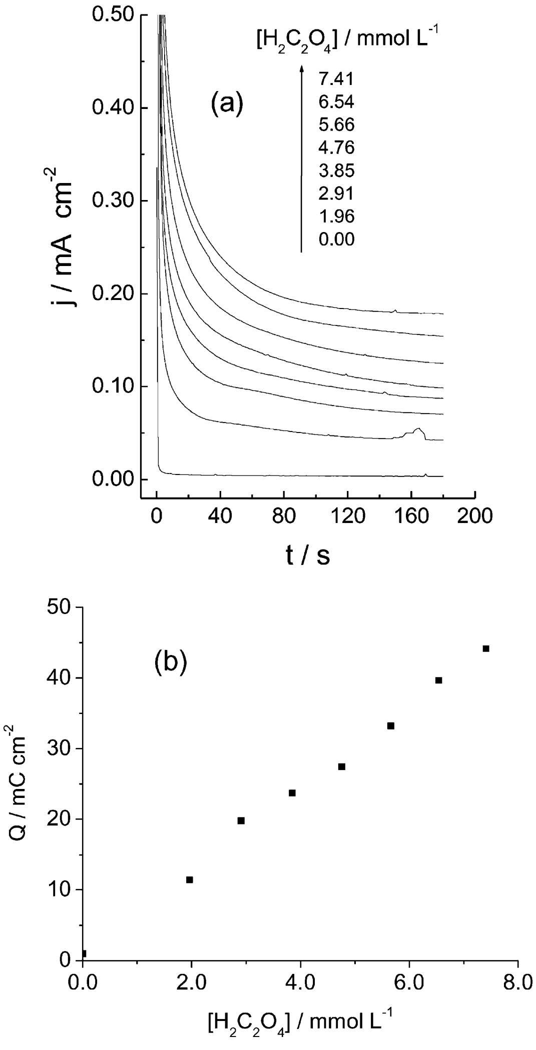

Figure 5 Chronoamperograms for different concentrations of oxalic acid at fixed potential of 0.71 V (a) and plot of charge against oxalic acid concentrations (b).

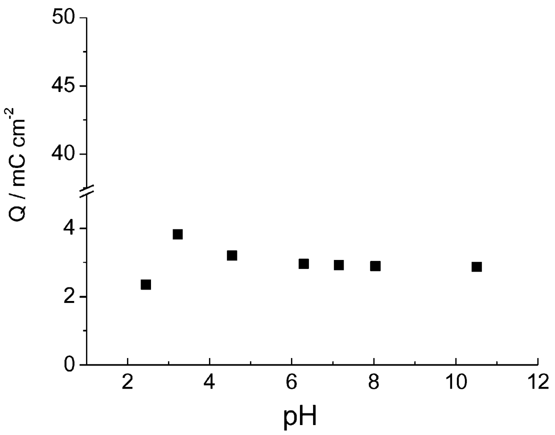

Figure 6 Plot of charge against solution pH change: [$H_2C_2O_4$] = 9.90 × 10^{-4} mol L^{-1} and applied potential of 0.71 V.

The oxalic acid oxidation process can be dependent on the solution pH, taking into account that the dissociation constants are $pK_1 = 1.23$ and $pK_2 = 4.19$. However, in the present case, by plotting the charge involved in the process against solution pH changes, for a fixed concentration of 9.90×10^{-4} mol L^{-1}, the oxidation process within the pH range studied showed a variation of about ±1 mC cm^{-2} (Fig. 6), very small compared to the charge involved, from 10 up to about 45 mC cm^{-2}, as shown in Fig. 5b.

In conclusion, Co(II) adsorbed on a porous SiO_2 surface reacted with phthalonitrile producing well-dispersed CoPc on the matrix surface with a surface density of 0.44×10^{-10} mol cm^{-2}. In the electrochemical studies carried out with the SiO_2/CoPc electrode, very stable current *versus* potential responses were obtained. The electrode response to oxalic acid concentration changes, using cyclic voltammetry and chronoamperometry experiments, showed that the oxidation process of oxalic acid occurred at 0.71 V. The charge involved in the oxidation process was not affected by a change in the external solution pH, presumably because the electroactive species is well protected in the matrix pores from environmental changes. The magnitude of the charge involved in the oxidation process is mainly due to the high surface density of the electroactive species. The linear correlation obtained by plotting Q against [$H_2C_2O_4$] indicated that the material may be useful for preparation of an electrochemical sensor for oxalic acid.

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