

NEW RIGID CONDUCTING COMPOSITES FOR ELECTROCHEMICAL SENSORS

Barbara BALLARIN^{a1,*}, Maria del Mar CORDERO-RANDO^b, Eduardo BLANCO^c,
José Luis HIDALGO-HIDALGO DE CISNEROS^{b1}, Renato SEEBER^d and
Domenica TONELLI^{a2}

^a *Dipartimento di Chimica Fisica e Inorganica, Università di Bologna, V.le Risorgimento 4, 40136 Bologna, Italy; e-mail: ¹ ballarin@ms.fci.unibo.it, ² tonelli@ms.fci.unibo.it*

^b *Departamento de Química Analítica, Facultad de Ciencias, Universidad de Cádiz, Polígono Río San Pedro, Puerto Real, Cádiz, Spain; e-mail: ¹ jluis.hidalgo@uca.es*

^c *Departamento de Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cádiz, Polígono Río San Pedro, Puerto Real, Cádiz, Spain; e-mail: eduardo.blanco@uca.es*

^d *Dipartimento di Chimica, Università di Modena e Reggio Emilia, Via G. Campi 183, 41100 Modena, Italy; e-mail: seeber@unimo.it*

Received December 10, 2002

Accepted February 18, 2003

Dedicated to Professor Sergio Roffia on the occasion of his retirement.

In this work, a novel sonogel-carbon material, obtained *via* a sonocatalytic procedure, is proposed as a matrix for the preparation of composite electrodes. This material combines the electrical properties of graphite with the mechanical resistance of the sonogel network; an electroactive phase is incorporated inside to give a system with peculiar redox properties. Ni/Al-Cl hydrotalcite and cobalt phthalocyanine complex were used to this end. The electrochemical behaviour of the sonogel-carbon-Ni/Al-Cl and of the sonogel-carbon-cobalt phthalocyanine composites is studied by cyclic voltammetry. These electrodes are stable and lead to repeatable responses. The responses have been compared with those of similar electrodes without added graphite. Key points of the electrochemical behaviour have been identified and discussed and the electrocatalytic capabilities have been investigated on oxidisable substrates, on methanol and on cysteine.

Keywords: Composite materials; Sonogel-carbon electrodes; Hydrotalcite-like clay; Amperometric sensors; Cobalt phthalocyanine complexes; Sonocatalysis; Ultrasound; Cyclic voltammetry; Electrochemistry.

The use of composites based on conductive phases dispersed within polymer matrices has led to important advances in analytical electrochemistry, particularly in developing sensor devices. In similar chemically bulk-modified electrodes, two or more materials are combined; though each in-

dividual component retains its original nature, the composite as a whole shows distinctive chemical, mechanical, and physical peculiarities¹. Carbon-based materials are frequently used as conductive phases in composites²; on the other hand, the polymeric insulating phase, acting as a cementing agent, has been widely investigated in the last years with the aim to decrease electrical resistance and to improve the general electrochemical behaviour.

A large number of matrices have been proposed in the literature, such as paraffin oil or Nujol in carbon paste electrodes (CPEs)³, epoxy resin^{4,5}, polyethylene⁶, polystyrene⁷, and modified or unmodified silica matrices in carbon composite electrodes (CCEs)⁸⁻¹¹. In particular, the sol-gel matrix offers an alternative route for processing materials at low temperature into a large variety of structures and shapes¹². Recently, we have developed a novel class of composite electrodes, *i.e.*, the sonogel-carbon composite electrodes, obtained by sonocatalysis¹³. High-energy ultrasound (HEU) was directly applied to precursors in order to promote hydrolysis, in acidic water as a catalyst, in the absence of any additional solvent. The chemical effects of ultrasound arise from acoustic cavitation (formation, growth and implosive collapse of bubbles in a liquid). During cavitation collapse, intensive heating of bubbles and high pressure evolve, realising extreme reaction conditions. HEU allows the sol-gel reaction to occur in a unique environment. The solventless sol-gel processing minimises the volume contraction of the gel due to solvent evaporation during drying and ageing, which leads to the formation of cracks in the resulting solid material. The obtained so-called sonogel¹⁴ exhibits higher density, reduced reticulation, and a more homogeneous structure in comparison with the gels obtained by classic methods¹³. These properties constitute basic conditions for providing high electrical conductivity and reduced capacitive currents in the electrochemical materials¹⁵.

In this paper we present an investigation of the modification of this sonogel-carbon composite by homogeneous addition of a modifier to the bulk of the matrix; this guarantees that a fresh and reproducible surface is obtained after polishing. Two known redox-active systems, *i.e.* Ni/Al-Cl hydrotalcite-like clays (HT)^{16,17} and cobalt phthalocyanine (CoPc)^{18,19} have been used as the redox-active phases. The characterisation and the electrochemical behaviour of the resulting rigid conductive modified composites are reported.

EXPERIMENTAL

Reagents and Materials

L-Cysteine, Co(II) phthalocyanine (CoPc), HCl, H₂SO₄, NaOH were of reagent-grade purity from Aldrich. LiClO₄ was from Fluka. All reagents were of analytical grade and used as received, without further purification. Methyltrimethoxysilane (MTMOS) was from Merck and also used without further purification. Ultrapure water was obtained from a Milli-Q water purification system (Millipore, Bedford (MA), U.S.A.). Graphite powder (spectroscopic grade RBW) was from SGL Carbon (Ringsdorf, Germany). Glass capillary tubes, i.d. 1.15 mm, were used as the bodies of composite electrodes. Ni/Al-Cl HT was prepared as reported in ref.¹⁶ The actual layered structure was confirmed by powder X-ray diffraction and the presence of Ni(II) ions inside the octahedral sites of the HT sheets was tested by UV-VIS-NIR spectroscopy (300–2200 nm).

Instrumentation

A 600-W, 20 kHz ultrasonic processor (Kontes), equipped with a 13 mm titanium tip, was used for the preparation of composite materials. Scanning electron microscopy (SEM) studies were carried out on a JSM 820 instrument (JEOL, Japan) operating at 30 keV and equipped with a Microanalyser AN/10000. Surface morphology was evaluated by optical microscopy (Reichert-Jung MeF3A with a JVC-TK-C1381 colour camera).

All electrochemical investigations were carried out using a three-electrode system. Unless otherwise specified, the solution in the electrochemical cell was de-aerated by bubbling pure nitrogen (99.999%) through the cell. In all experiments a saturated calomel electrode (SCE) and a platinum wire were used as the reference and the auxiliary electrode, respectively. All potentials are referred to SCE. Cyclic voltammograms were performed with an Autolab PGSTAT 20 multimode electrochemical system (EcoChemie, Utrecht, The Netherlands), under control of its own software (GPES, EcoChemie).

The working electrodes were prepared as described in the following.

Sonogel-Carbon Composite Electrodes Containing Ni/Al-Cl HT (SCC-HT)

An amount of 500 μ l MTMOS and 100 μ l of 0.2 M HCl (catalyst) solutions were mixed in a glass vessel and then sonicated for 5 s (energy dose 0.083 kJ ml⁻¹) until hydrolysis started. Subsequently, a fixed amount (1 g) of suitable solid was added and homogeneously dispersed in the sonogel obtained, leading to the different kinds of materials: (i) 1 g of graphite (sonogel-carbon); (ii) 1 g of a powder containing mixed graphite and Ni/Al-Cl HT (50% w/w) (sonogel-carbon-Ni/Al-Cl composite); (iii) pure HT (sonogel-Ni/Al-Cl). The resulting sticky black or green pastes were used to fill ca 3 mm long capillary tubes, and finally allowed to dry overnight under ambient conditions (ca 25 °C) until became hard. Adherence of the developed material and glass was excellent.

Sonogel-Carbon Composite Electrodes Containing Cobalt Phthalocyanine (SCC-CoPc)

CoPc was used owing to the well known catalytic redox ability of the reversible Co(III)/Co(II) couple and its insolubility in water, which prevents any leakage from the sonogel composite matrix. In the preparation of the SCC matrix^{14,15}, 0.5 ml of MTMOS and

0.1 ml of 0.2 M HCl (catalyst) solutions were mixed in a glass vessel, and then sonicated for 10 s until hydrolysis started. MTMOS was used to obtain hydrophobic electrodes²⁰, so that only the outer section of the electrode was active. Electrodes with different composition were prepared and studied. In particular, either 1 g of graphite powder or 1 g of a powder consisting of graphite and different CoPc percentages (1.5, 5, and 10% w/w) were added to the sonogel mixture. In all cases the resulting paste was homogenised for 1 min. The sticky black pastes (electrodes denoted SCC-CoPc1.5%, SCC-CoPc5%, or SCC-CoPc10%) were used to fill glass tubes (70 mm length, 1.15 mm in diameter) up to about 3 mm height and finally allowed to dry overnight under ambient conditions (25 °C). An unmodified sonogel-carbon composite electrode, obtained according to ref.¹⁵, was used for comparison.

The electrical contact in all the working electrodes was assured by a 0.5-mm copper wire. The electrodes were first polished with 1200 P grit emery paper (silicon carbide), then gently with weighing paper, and finally washed with Millipore water.

RESULTS AND DISCUSSION

Surface Morphology

SEM micrographs of the surfaces of a sonogel-carbon-Ni/Al-Cl and of a sonogel-Ni/Al-Cl composite, are reported in Figs 1 and 2, respectively. The 10–20- μm graphite particles, 100–150- μm HT crystals and smaller silica particles that constitute the composite network, can be well distinguished on the polished sonogel-carbon-Ni/Al-Cl composite surface (see Fig. 1). Analogously, the higher proportion of HT crystals, often strictly in contact with one another, can be evaluated in the sonogel-Ni/Al-Cl polished surface (see Fig. 2); this result was confirmed by EDAX analysis.

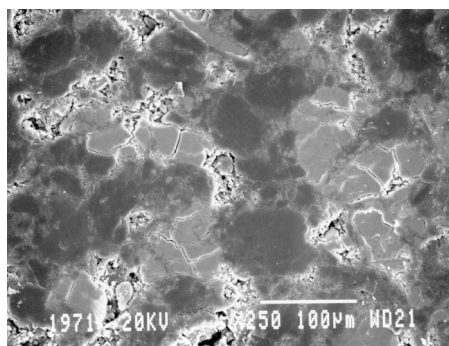


FIG. 1

SEM (30 keV) micrographs of sonogel-carbon-Ni/Al-Cl composite electrode after polishing procedure; magnification 250 \times

Figure 3 reports the optical microscopic image of a SCC-CoPc surface, in which the three different components of the matrix (silica cluster, graphite particles and CoPc powder) are well evident.

Electrochemical Characterisation

Sonogel-Carbon Composite Electrodes Containing Ni/Al-Cl HT (SCC-HT)

Figures 4a–4c show typical voltammetric responses of a sonogel-carbon-Ni/Al-Cl composite electrode (a) and a sonogel-Ni/Al-Cl electrode (b) compared with those recorded on a sonogel-carbon (c) one, obtained in 0.1 M

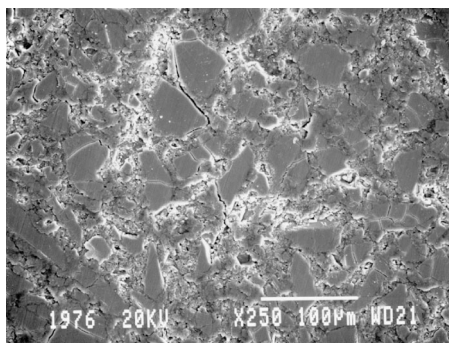


FIG. 2
SEM (30 keV) micrographs of sonogel-Ni/Al-Cl electrode after polishing procedure; 250 \times

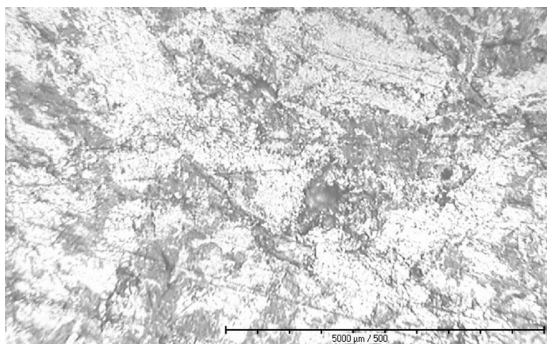


FIG. 3
Optical microscopy image of the sonogel-carbon-CoPc electrode surface; magnification 40 \times

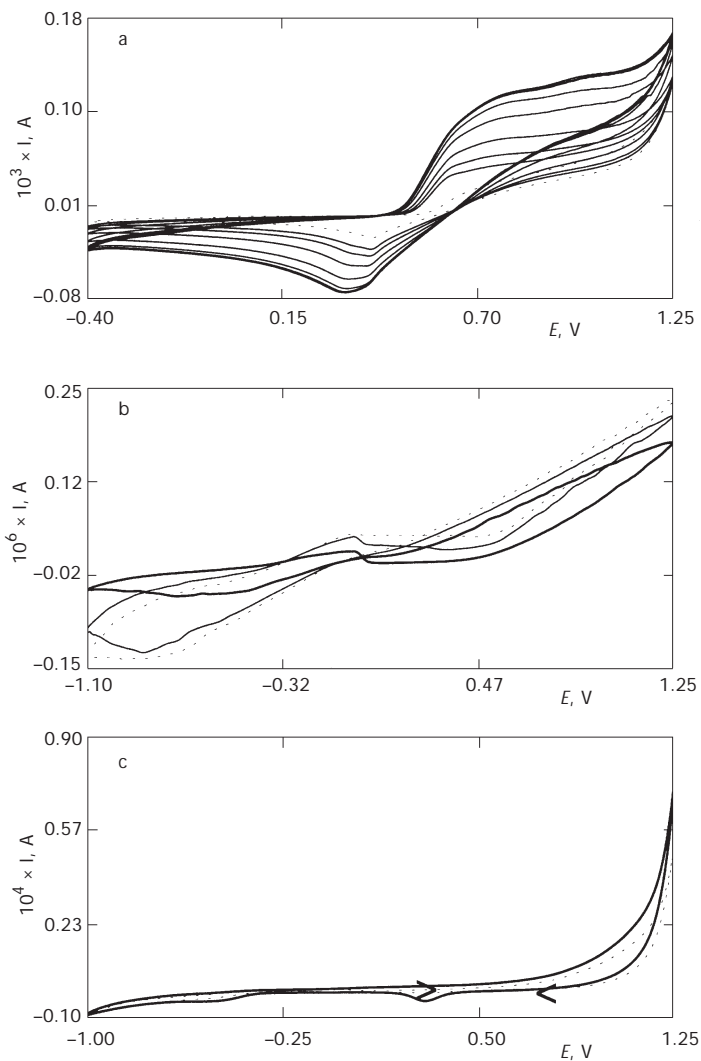


FIG. 4

Repeated cyclic voltammograms on different electrodes in aqueous 0.1 M NaOH; a Sonogel-carbon-Ni/Al-Cl composite: the voltammogram of the first scan (dotted line) and five consecutive scans are shown, the highest trace corresponding to the steady-state voltammogram; b sonogel-Ni/Al-Cl and c sonogel-carbon composites; for b and c the dotted line curve is that of the first scan, the steady-state trace being also shown (lowest curve in b). Potential scan rate 0.050 V s^{-1} . The negative potential limit is different in the three plots in order to cover the whole interesting range

NaOH aqueous solution. A potential scan rate of 0.050 V s^{-1} was used in order to obtain suitable responses for the Ni(III)/Ni(II) redox system inside the HT clay^{16,21}. As can be seen in Fig. 4a, the current in the first voltammogram is initially low, increasing by cycling the potential and reaching steady values only after 20–30 consecutive cycles. The slowness of the conditioning process of similar systems can be explained by the necessity for the HT grains, dispersed inside the solid sonogel-graphite matrix, to establish fast enough exchange of hydroxy groups with the solution. This is a necessary condition for reaching proper equilibrium when passing from the oxidised to the reduced form of the metal centres, and *vice versa*. The quasi-reversible character of the charge transfer involved ($\Delta E_p = 300\text{--}400 \text{ mV}$) allows a rough evaluation of $E_{1/2,r}^{\pi}$ of the Ni(III)/Ni(II) system, taken as the mid of anodic and cathodic peak potentials of the system

The results are comparable with the value found for the pure Ni/Al-Cl HT phase (+0.6 V compared with +0.5 V)²¹. Though the thermodynamics of the Ni(III)/Ni(II) system is hence not considerably altered, the kinetics, apparently, actually is.

On the contrary, the cyclic voltammetric signal exhibited by the sonogel-Ni/Al-Cl HT electrode (Fig. 4b) shows that, in the absence of graphite, the charge percolation mechanism between “adjacent” nickel centres is far from being effective enough to lead to significant currents, so that the current intensities are about five orders of magnitude lower than those recorded on the sonogel-carbon-Ni/Al-Cl composite electrode. Moreover, as a further difference in behaviour, a steady-state signal is obtained through progressive lowering of the current during the first 5–6 potential scans. These results suggest that the presence of graphite inside the composite is very important allowing for charge transfer between two nickel centres which belong to different layers: only adjacent nickel ions within the same layer are close enough so that electron hopping takes place. The resulting *I/E* curves look like those in which a current flows through an almost pure resistance.

The voltammograms reported in Fig. 4c actually constitute the baseline of our signals, *i.e.*, the “background” current trace, relative to the redox processes of the solvent medium on the sol-gel-graphite composite matrix. The baseline for redox systems added to the composite is hence quite satisfactorily low.

In a typical series of tests, five sonogel-carbon-Ni/Al-Cl composite electrodes and five sonogel-Ni/Al-Cl electrodes were prepared and used to test the reproducibility of the responses obtained when employing nominally equal electrodes. As regards the sonogel-Ni/Al-Cl electrodes, on average

only two out of five electrodes showed an electrochemical response at all, similar to the curves in Fig. 4b. For the other three systems, a current flowing through a pure (very high) resistance was recorded. Moreover, for both the sonogel-Ni/Al-Cl electrodes that proved to work, the voltammetric signal was poorly reproducible in subsequent experiments in 0.1 M aqueous NaOH.

On the contrary, each one of the five sonogel-carbon-Ni/Al-Cl composite electrodes showed a peak current intensity ranging from 100–120 μA . Even higher currents were obtained after proper pretreatment consisting in cycling the electrode potential between the limits -0.40 to $+1.29$ V in about 40 consecutive scans, in 0.5 M aqueous NaOH. Figure 5 reports the stationary anodic peak current values recorded on sonogel-carbon-Ni/Al-Cl composite electrodes in 0.1 M NaOH, before and after a pretreatment by repeated potential cycling in 0.5 M NaOH¹⁰ at different times after construction. Renewal of the electrode surface before each repeated-cycle measurement was performed by the polishing procedure described previously. The higher current intensity obtained by the described pretreatment suggests that it actually increases the matrix porosity, favouring the HT-solution intimate contact. In our case, no negative effect on the composite stability was observed; the electrodes worked well for more than one week without significant changes in responses.

The repeatability was tested separately on 10 different electrodes, in 0.1 M NaOH solution, after polishing treatment; the relative standard deviation of

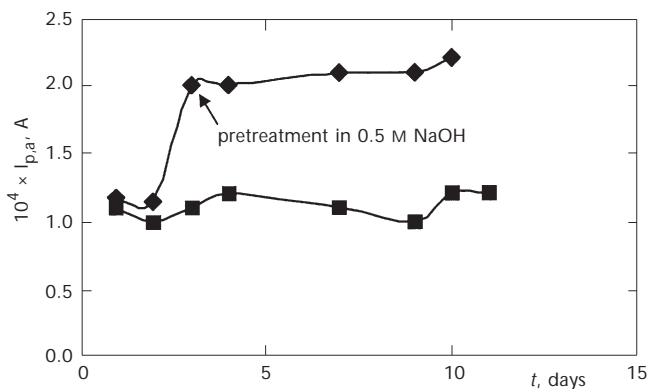


FIG. 5

Stability of sonogel-carbon-Ni/Al-Cl composite electrodes in aqueous 0.1 M NaOH. Effect of pretreatment in 0.5 M NaOH: ■ without any pretreatments; ◆ with pretreatment, performed 2 days after dipping the electrode into the solution, in order to reach proper conditioning

10 measurements of the stationary anodic peak current was in all cases lower than 8%.

The values of the anodic peak currents and peak potentials measured at a fixed scan rate of 0.050 V s^{-1} on sonogel-carbon-Ni/Al-Cl composite electrodes at various pH are reported in Table I. A decrease in pH leads to a shift of the Ni(II) oxidation peak potential towards more positive values and, at the same time, to a significant decrease in the relevant anodic current. The first result can be accounted for by strong interactions between the Ni(III), Ni(IV) oxidised forms of nickel and hydroxide ions²². As a result, the higher the OH^- concentration, the more thermodynamically favoured is the oxidation of Ni(II) and, consequently, the lower is the oxidation potential, in agreement with what was observed in previous studies^{16,21}. Voltammetric tests have also been carried out at different potential scan rates, in solutions at pH 14, 13, 12 and 11. Trends of the logarithmic plot of anodic peak current as a function of the scan rate (not shown) lead to the following conclusions: First, the highest investigated pH value induces the non-optimum stability of the sol-gel matrix^{10,20}. Furthermore, in good agreement with the conclusions drawn from the data in Table I, the Ni(II) oxidation process does not exhibit a diffusive character: a slope of 0.5 is never found in the mentioned log-log plot. A possible equivalent electric circuit accounting for the composite electrode-solution system should be very complex, due to the presence of many interfaces: HT/graphite, HT/solution, graphite/solution. This necessarily implies the formation of capacity effects. It is quite reasonable that the factors opposing the ion mobility inside the composite (the resistances and capacitances inside the multiphase electrode)

TABLE I
Dependence of the $I_{p,a}$ and $E_{p,a}$ of sonogel-carbon-Ni/Al-Cl composite electrodes on NaOH concentration. Potential scan rate 0.050 V s^{-1}

Solution	$E_{p,a}$, V	$I_{p,a}$, mA
1 M NaOH	+0.81	0.76
0.5 M NaOH	+0.77	0.45
0.1 M NaOH	+0.84	0.22
5×10^{-2} M NaOH ^a	+0.86	0.10
1×10^{-2} M NaOH ^a	+0.96	0.07
1×10^{-3} M NaOH ^a	+1.06	0.03

^a KCl is added to the solution to total ionic strength of 0.1 mol l^{-1} .

vary with the increasing rate required for the ions to reach a new equilibrium state imposed by potential change. The internal impedance of the electrode becomes the determining step of the overall process causing a slope lower than 0.5 in the log-log plot.

A 0.1 M NaOH solution was then chosen for all our tests; such a pH assures a good electrochemical signal and, at the same time, does not produce alterations of the sonogel matrix.

Sonogel-Carbon Composite Electrodes Containing Cobalt Phthalocyanine (SCC-CoPc)

The electrochemical behaviour of SCC-CoPc electrodes has been studied in acidic media over the potential range where oxidation of Co(II) to Co(III) occurs.

In Fig. 6a-6c 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 M H₂SO₄ aqueous solution (potential scan rate 0.05 V s⁻¹) are reported. The first cycle of all the three sets of voltammograms is completely different from the response obtained at the steady state, which is reached after *ca* 10 cycles. Let us consider, for example, the SCC-CoPc1.5% electrode. The first cycle is characterised by the oxidation peaks at +0.46 and +0.90 V, by a large oxidation response centred at *ca* +1.00 V and by the reduction peaks at +0.61 and +0.43 V. By cycling repeatedly the potential, the broad signal at more positive potentials vanishes

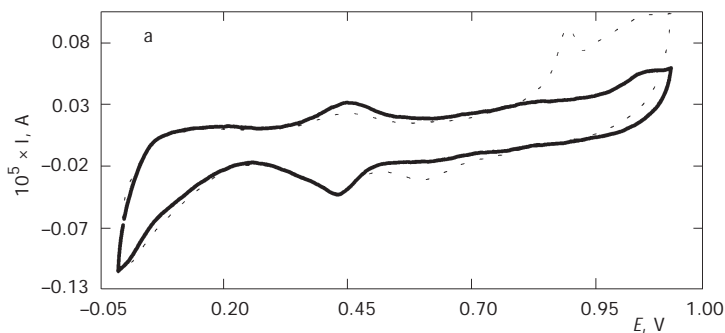


FIG. 6

Cyclic voltammograms of 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 M H₂SO₄; potential scan rate 0.05 V s⁻¹

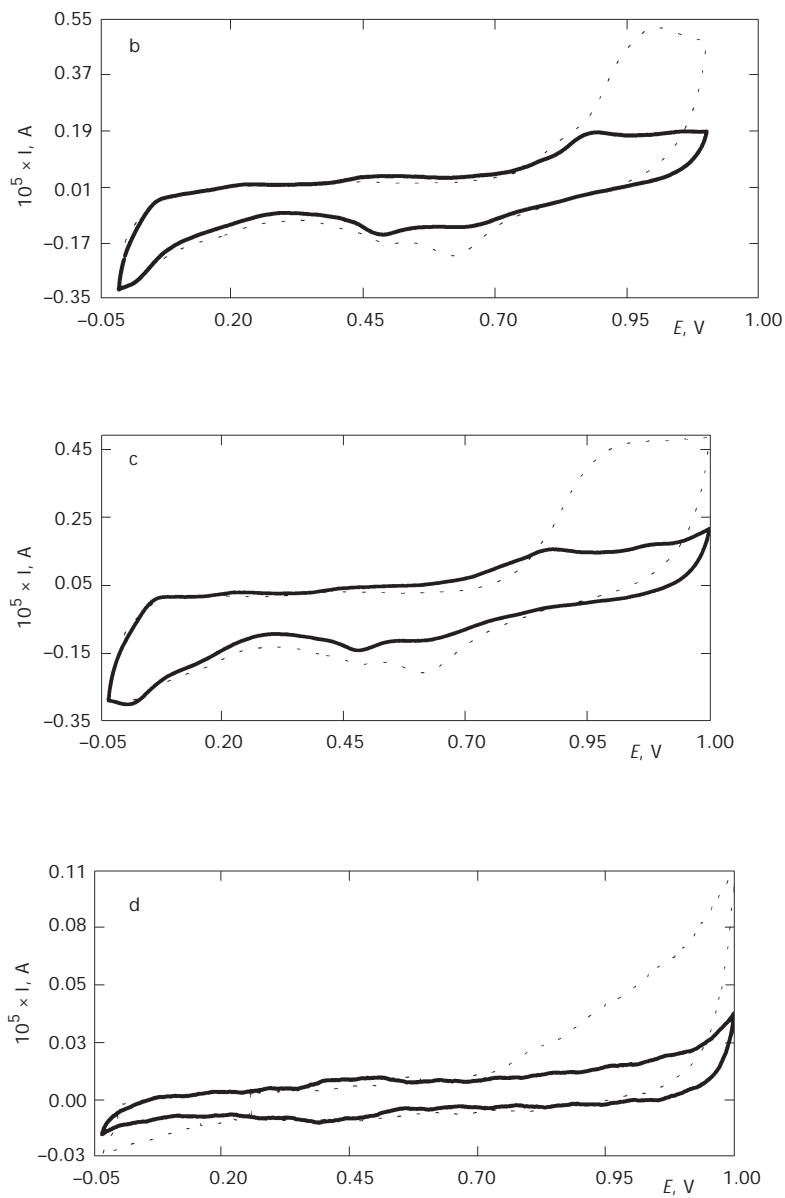


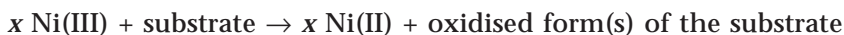
FIG. 6
(Continued)

and a new oxidation peak centred at +0.86 V gradually arises. This peak is particularly evident in the voltammetric curves obtained with the SCC-CoPc5% electrode. The signals at higher potentials can be ascribed to the Co(II)/Co(III) redox couple, by comparison with literature reports²³⁻²⁵. The responses obtained at any of the electrodes do not lower further after 10 cycles, when a steady state is established. As a comparison, the cyclic voltammogram recorded on an unmodified SCC electrode is reported in Fig. 6d, where neither anodic nor cathodic signals are present. The change in 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-Lovrić (ref.²⁴ and references therein). In the oxidation of CoPc, electro-neutrality is maintained by intercalation of anions from the supporting electrolyte, which are displayed during the reduction process. In subsequent cyclic oxidations and reductions, a gradual loss of charge-consuming ability of the films takes place, since out-of-plane deformations of the phthalocyanine macrocycles occur, causing irreversible changes in the crystal structure²⁴.

Electrocatalytic Applications

SCC-HT

In the electrocatalytic reaction, nickel ions act as redox mediators with respect to suitable substrates added to the alkaline solution, according to the following stoichiometry^{16,21}:



The mechanism of the whole process leading to Ni(II) oxidation under the present experimental conditions is even more complex than for the "simple" HT electrode coating. We tested the catalytic capabilities of sonogel-carbon-Ni/Al-Cl composite electrodes in methanolic solutions. Figure 7 reports voltammetric curves recorded in solution containing progressively increasing methanol concentrations. The height of the forward oxidation peak relative to the Ni(II)-to-Ni(III) oxidation increases with increasing substrate concentration and, concomitantly, the backward trace, though leading to negative current values, does not increase in height.

Moreover, the shape of the anodic-cathodic peak system does not change to the sigmoidal shape typical for electrode mechanisms involving catalytic regeneration of the electroactive species in the solution phase^{26,27}. These observations agree with the behaviour observed on neat HT coating under similar experimental conditions^{16,21}. Calibration plots of the peak current values relative to those of Ni(II) oxidation at varying concentrations of alcohol, in 0.1 M NaOH solution, have been drawn using potential sweep rates of 0.050 V s⁻¹ (Fig. 8). The calibration results are quite satisfactorily

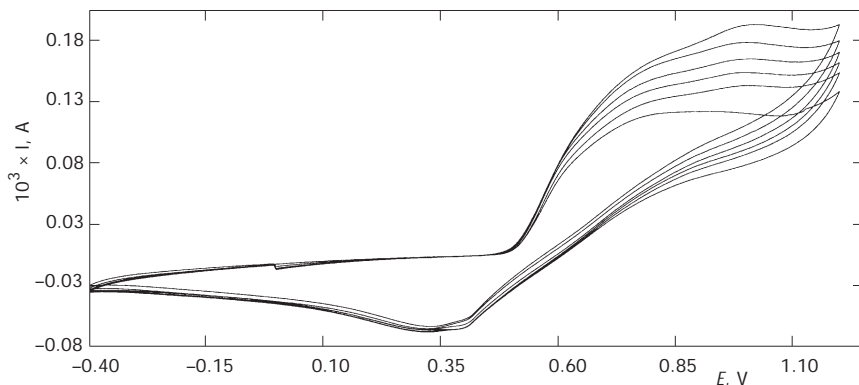


FIG. 7

Cyclic voltammetric curves recorded on a sonogel-carbon-Ni/Al-Cl composite electrode in aqueous 0.1 M NaOH (lower curve), and containing 10.0, 49.5, 98.0, 145.5 or 238.0 ppm MeOH (signals with progressively increasing anodic currents)

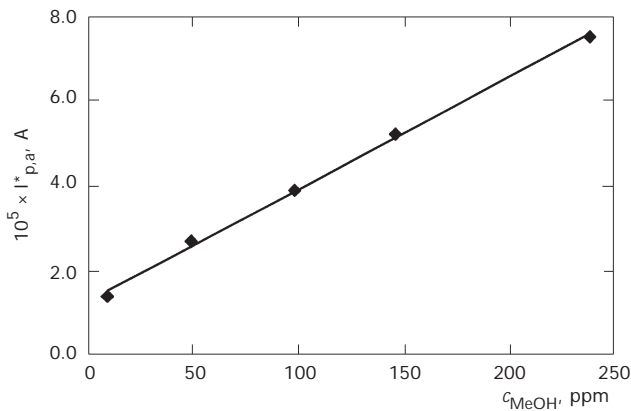


FIG. 8

Calibration straight line for $I_{p,a}^*$ (in μA) vs MeOH concentration (in ppm). $I_{p,a}^*$ is the peak current at $E = +0.95$ V, with the value in absence of substrate subtracted (see Fig. 4). $y = 3\text{E-}07x + 1\text{E-}05$; $R^2 = 0.998$

linear in the range 10–240 ppm, indicating a sensitivity of $0.26 \mu\text{A ppm}^{-1}$ and a detection limit of *ca* 10 ppm.

SCC-CoPc

We tested the catalytic ability of the sonogel-carbon-CoPc composite electrode on cysteine substrate. It is well known that on CoPc modified electrodes the electrocatalytic oxidation of cysteine occurs according to the following mechanism¹⁹:

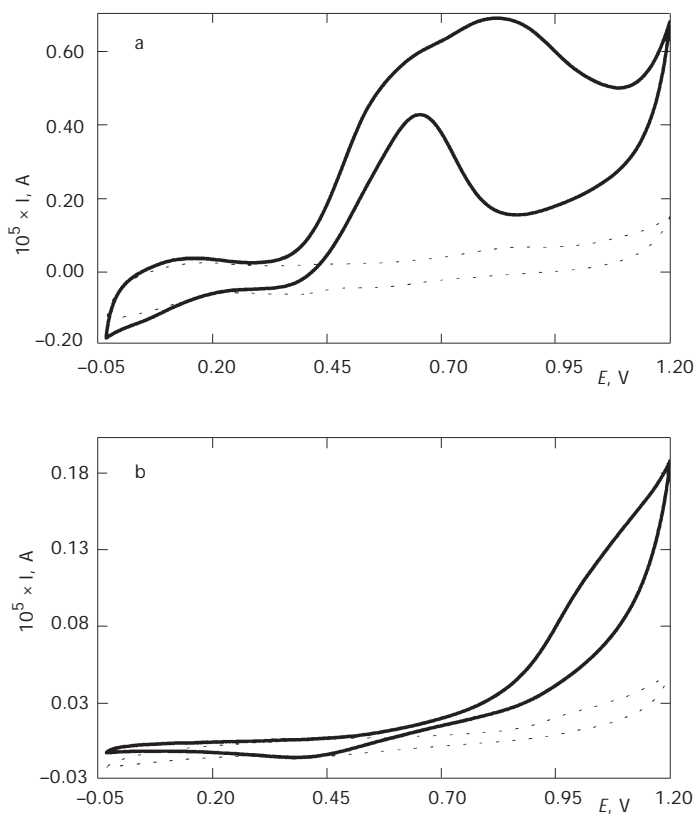
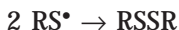
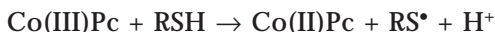


FIG. 9

Cyclic voltammograms of a SCC-CoPc10% and b SCC electrodes recorded before (\cdots) and after ($---$) the addition of 1.10×10^{-2} M cysteine. Supporting electrolyte 0.05 M H_2SO_4 ; potential scan rate 0.05 V s^{-1}



Since at pH values lower than 4, the autocatalytic oxidation of cysteine with CoPc to cystine does not occur²⁷, all tests were carried out under these conditions.

The addition of cysteine to 0.05 M H₂SO₄ solution resulted in a marked increase in the current ascribed to the Co(II)-to-Co(III) oxidation response at SCC-CoPc electrodes, notably exceeding that observed on a SCC electrode at the same cysteine concentration. As an example, in Fig. 9a the cyclic voltammograms obtained on a SCC-CoPc10% before (dotted line) and after (solid line) the addition to a concentration of 1×10^{-2} M cysteine are reported. For comparison, the cyclic voltammogram recorded from the same solution at a simple SCC electrode is reported in Fig. 9b. The catalytic wave increases with the cysteine concentration and no cathodic backward response is detectable on the reverse scan in the investigated range of concentrations (9×10^{-4} – 1×10^{-2} M cysteine). This is in agreement with the occurrence of a fast catalytic reaction cycle. The features of the voltammetric

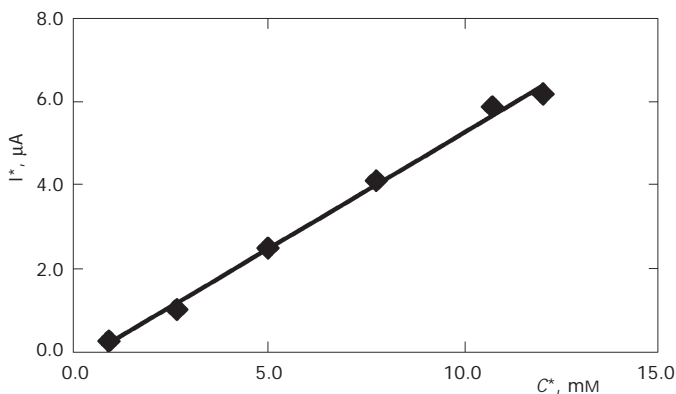


FIG. 10

Calibration line of F^* (in μA) vs cysteine concentration (C^*). F^* is the chronoamperometric current measured at a fixed time (0.5 s) after polarization for each substrate addition; the background contribution was subtracted; C^* is the concentration corrected to dilution. $y = 0.5579x - 0.2974$; $R^2 = 0.9964$

curves are similar to those reported by Halbert and Baldwin²³, who described the electrocatalytic responses of thiol compounds at electrodes modified with CoPc incorporated into graphite powder. Analogous results were obtained on SCC-CoPc1.5% and on SCC-CoPc5% electrodes.

In order 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 standard 4.30×10^{-2} M cysteine solution to a stirred 10 ml aliquot of 0.05 M H_2SO_4 . On the basis of preliminary tests, we selected an applied potential of +0.82 V for these experiments. The sensor displayed a very short response time after every addition and the signal response was well repeatable in subsequent tests. Moreover, as shown in Fig. 10, by sampling the current at a fixed time after starting the polarisation, a linear dependence of the chronoamperometric current on concentration was obtained over the entire investigated range.

CONCLUSIONS

This study evidences the possibility of using a new class of rigid conducting composites, the sonogel-carbon, obtained by sonocatalysis, as a "support" matrix for redox mediators, *i.e.*, HT or CoPc, imparting much higher mechanical and chemical stability to the device, without any significant loss of electrocatalytic properties. These electrodes have proved to be suitable for amperometric detection of oxidisable substrates like methanol, mediated by the Ni(II)/Ni(III) couple, or cysteine, mediated by the Co(III)/Co(II) couple, using SCC-HT and SCC-CoPc electrodes, respectively. The results obtained are comparable with those reached with the pure redox-active phase directly deposited on the electrode surfaces, as in the case of HT, or are even better, in terms of stability, than those reported in the literature, as in the case of CoPc. Due to the stability of the matrix and thanks to the fast response, these electrodes can be proposed also as detectors in flow systems. The use of the sonogel technique hence is an interesting tool for obtaining stable electrodes consisting of composite materials. The study is a starting point for planning future work to seek best conditions for mechanical and chemical stabilisation of different redox-active phases.

Thanks are due to CNR-NATO for supporting B. Ballarin with two Senior Fellowships of two months each (in 1999 and 2000), for stays at the Department of Analytical Chemistry of Cádiz University, which have made possible this collaboration, and to the Ministerio de Ciencia y Tecnología de España for supporting Project BQU2000-0455.

REFERENCES

1. Ruschan G. R., Newnham R. E., Runt J., Smith E.: *Sens. Actuators* **1989**, *20*, 269.
2. Céspedes F., Martínez-Fàbregas E., Algret S.: *Trends Anal. Chem.* **1996**, *15*, 296.
3. Adams R. N.: *Anal. Chem.* **1958**, *30*, 1576.
4. Wang J., Varughese K.: *Anal. Chem.* **1990**, *62*, 318.
5. Wang J., Ozsoz M.: *Electroanalysis* **1990**, *2*, 647.
6. Armentrout D. N., McLem J. D., Long M. W.: *Anal. Chem.* **1979**, *51*, 1039.
7. Creasy K. E., Shaw B. R.: *Anal. Chem.* **1989**, *61*, 1460.
8. Lev O., Tsionsky M., Rabinovich L., Glezer V., Sampath S., Pankratov I., Gun J.: *Anal. Chem.* **1995**, *67*, 22A.
9. Wang J., Pamidi P. V. A., Park D. S.: *Electroanalysis* **1997**, *9*, 52.
10. Li Z., Guadalupe A. R.: *Electroanalysis* **1999**, *11*, 167.
11. Rabinovich L., Lev O.: *Electroanalysis* **2001**, *13*, 265.
12. Binker C. J., Scherer G. W.: *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Chaps 1 and 2. Academic Press, San Diego 1989.
13. Blanco E., Esquivias L., Litrán R., Piñero M., Ramírez del Solar M., de la Rosa Fox N.: *Appl. Organomet. Chem.* **1999**, *13*, 399.
14. Hidalgo-Hidalgo-de-Cisneros J. L., Cordero-Rando M. M., Naranjo-Rodriguez I., Blanco-Ollero E., Esquivias-Fedriani L.: Span P200100556, 2001.
15. Cordero-Rando M. M., Hidalgo-Hidalgo de Cisneros J. L., Blanco-Ollero E., Naranjo-Rodriguez I.: *Anal. Chem.* **2002**, *74*, 2423.
16. Ballarin B., Seeber R., Tonelli D., Zanardi C.: *Electroanalysis* **2000**, *10*, 434.
17. Scavetta E., Berrettoni M., Seeber R., Tonelli D.: *Electrochim. Acta* **2001**, *46*, 2681.
18. Wang Z., Pang D.: *J. Electroanal. Chem.* **1990**, *283*, 349.
19. Maree S., Nyokong T.: *J. Electroanal. Chem.* **2000**, *49*, 120.
20. Gun G., Tsionsky M., Lev O.: *Anal. Chim. Acta* **1994**, *294*, 261.
21. Ballarin B., Seeber R., Tonelli D., Vaccari A.: *J. Electroanal. Chem.* **1999**, *463*, 123.
22. Corrigan D. A., Knight S. L.: *J. Electrochem. Soc.* **1989**, *136*, 613.
23. Halbert M. K., Baldwin R. P.: *Anal. Chem.* **1985**, *57*, 591.
24. Komorsky-Lovrić S.: *J. Electroanal. Chem.* **1995**, *397*, 211.
25. Qi X., Baldwin R. P.: *Electroanalysis* **1994**, *6*, 353.
26. Nicholson R. S., Shain I.: *Anal. Chem.* **1964**, *36*, 706.
27. Murray R. W. in: *Electroanalytical Chemistry* (A. J. Bard, Ed.), Vol. 13, p. 192. Marcel Dekker, Inc., New York 1984.